



Milankovitch Forcing and the Timing and Pacing of Devonian Anoxic Events

Jarno J. C. Huygh

University of Liège, Belgium
Faculty of Science
Geology Department
Sedimentology, Cycles, and paleo-Climate (SediCClim) Laboratory
May 2026



Milankovitch Forcing and the Timing and Pacing of Devonian Anoxic Events

Jarno J. C. Huygh

University of Liège, Belgium
Faculty of Science
Geology Department
Sedimentology, Cycles, and paleo-Climate (SediCClim) Laboratory
May 2026

Abstract

Le Dévonien représente une période plus chaude que l'actuelle dans l'histoire de la Terre (419 - 359 millions d'années), caractérisée par une série de perturbations pulsées et exprimées à l'échelle globale – des événements anoxiques associés à des taux d'extinction élevés, des changements climatiques, des perturbations des cycles biogéochimiques, des fluctuations du niveau marin et la déposition de strates riches en matière organique. Malgré des décennies de recherche, aucun consensus n'a émergé quant à leurs mécanismes causaux. Ces dernières années, un nombre croissant d'indices a suggéré que le forçage astronomique pourrait être lié à leur récurrence rythmique, soulevant la possibilité que les cycles de Milankovitch aient structuré le calendrier et le rythme des événements anoxiques dévoniens. Cette thèse intègre la cyclostratigraphie et la géochimie dans un cadre stratigraphique plus large, en appliquant une approche multiproxy à trois archives provenant de deux bassins afin d'évaluer comment le forçage astronomique a façonné la variabilité environnementale dévonienne sur plus de 30 millions d'années. Les astrochronologies flottantes contraignent les durées des événements globaux de Daleje, Choteč, Kačák, *pumilio* et Rhinestreet, de la crise de Kellwasser, ainsi que des événements régionaux de Fir Tree, Hubbard Quarry et Lodi. Leurs positions temporelles relatives aux extrêmes orbitaux révèlent des schémas distincts, indiquant que le forçage astronomique a exercé une influence majeure à la fois sur leur calendrier et leur rythme. Les cycles de modulation astronomique de longue période, sur plusieurs millions d'années, ont fourni l'état de fond régissant les moments où les perturbations environnementales étaient susceptibles de se produire, tandis que le forçage canonique de Milankovitch contrôlait le rythme à court terme et a pu agir comme déclencheur immédiat. Deux modèles conceptuels émergent: un modèle du seuil supérieur, dans lequel les événements surviennent lors des maxima des cycles de modulation à long terme et reflètent des périodes caractérisées par une forte alternance climatique, et un modèle du seuil inférieur, dans lequel les événements apparaissent lors des minima de modulation, reflétant une variabilité climatique comparativement atténuée et une stagnation accrue. Ensemble, ces modèles expliquent les expressions contrastées des événements entre les bassins, la diachronie de l'anoxie et la récurrence sélective des événements globaux par rapport aux perturbations régionales, sans nécessiter d'hypothèses sur des conditions limites particulières du système Terre. Le cadre développé ici fournit une référence pour interpréter les changements environnementaux rythmés par l'astronomie au cours du Phanérozoïque et souligne le rôle central du forçage astronomique dans la structuration des événements anoxiques globaux.

Abstract

The Devonian represents a warmer-than-present period in Earth's history (419 – 359 million years ago), characterized by a series of pulsed, globally expressed perturbations – anoxic events associated with elevated extinction rates, climate changes, disruption of biogeochemical cycles, sea-level fluctuations, and deposition of organic-rich strata. Despite decades of research, no consensus has emerged on their causal mechanisms. In recent years, mounting evidence has suggested that astronomical forcing may be linked to their rhythmic recurrence, raising the possibility that Milankovitch cycles structured the timing and pacing of Devonian anoxic events. This thesis integrates cyclostratigraphy and geochemistry within a broader stratigraphic framework, applying a multi-proxy approach to three records from two basins to evaluate how astronomical forcing shaped Devonian environmental variability across more than 30 million years. Floating astrochronologies constrain the durations of the global Daleje, Choteč, Kačák, *pumilio*, and Rhinestreet events, the Kellwasser Crisis as well as the regional Fir Tree, Hubbard Quarry, and Lodi events. Their temporal positions relative to orbital extrema reveal distinct patterns, indicating that astronomical forcing exerted a major influence on both their timing and pacing. Long-period, multi-million-year astronomical modulation cycles provided the background state that governed when environmental perturbations were likely to occur, while canonical Milankovitch forcing controlled short-period pacing and may have acted as immediate triggers. Two conceptual models emerge: an *Upper-Threshold Model*, in which events occur during maxima in long-term modulation cycles and reflect periods characterized by strong climatic alternation, and a *Lower-Threshold Model*, in which events arise during modulation minima, reflecting comparatively muted climatic variability and enhanced stagnation. Together, these models explain contrasting event expressions across basins, the diachroneity of anoxia, and the selective recurrence of global events versus regional perturbations without requiring assumptions about specific Earth-system boundary conditions. The framework developed here provides a benchmark for interpreting astronomically paced environmental change throughout the Phanerozoic and highlights the central role of astronomical forcing in shaping global anoxic events.

A dissertation submitted to the University of Liège in partial fulfillment of the requirements
for the degree of Doctor of Science

Promotor: Prof. Dr. Anne-Christine da Silva

Co-promotor: Prof. Dr. Michel Crucifix

Acknowledgements

First and foremost, I'd like to thank Anne-Christine and Michel for giving me the opportunity to pursue my PhD research under their supervision. I am forever grateful for your belief in me, your support and advice, your patience, and for the freedom you gave me to carry out my research on my own terms. Thanks for designing such a fantastic WarmAnoxia project. I gratefully acknowledge the support of the Fonds de la Recherche Scientifique – FNRS, whose funding made this research possible.

Many thanks to my office mates Michiel and Dhoha for the interesting discussions and good company over the last four years. Justin Gérard and Loïc Sablon, it has been a great pleasure working with you on the WarmAnoxia project. A big thank you to Frédéric, Joëlle, Mariella, Raphaël, Nicolas, visiting colleagues Hamdi, Valentin, and Damien, and all colleagues from B20 and the entire Department of Geology at ULiège. Thank you, IAS, as well as the cyclostratigraphy and Devonian communities. Special thanks to my PhD Committee Members David, Matthias, and Xavier for their advice and support, and to all my co-authors – this thesis would not have been possible without you. I also thank Philippe, Pim, and Johan for introducing me to the wonderful topic of cyclostratigraphy and guiding me towards my PhD research. A big thank you to Carl, Jeff, and Ian for your excellent company and discussions during my time in the USA, and to Ahmed and Amine for welcoming and guiding our team in Morocco. Chuck, thanks for the nice talks.

Special thanks to you, Sofie, for your love and all your support, and to Scott, who made the last two years even more special. Thanks, Titus the bunny, for all your mischief and cuteness. A big thank you to my parents and family for supporting me all the way through. A big shout-out to all my friends – I love you.

Preface

This thesis investigates the timing, pacing, and expression of Devonian environmental change through complementary sedimentary records. It was carried out in the framework of the 'WarmAnoxia' FNRS research project, which aims at investigating the possible links between astronomical forcing and anoxic events throughout the Devonian by combining numerical climate modeling and evidence emerging from geological records. My contribution to the project focuses on the geological evidence, through the acquisition, analysis, and interpretation of existing and new geochemical, sedimentological, and stratigraphic data. The Introduction outlines scientific background relevant to the overarching research questions but does not include additional content that is also explored in the subsequent chapters, which are written as stand-alone manuscripts. For clarity, the thesis is structured to guide the reader through a coherent progression: from long-term Early to Middle Devonian variability, to high-resolution latest Givetian climate dynamics, and finally to the globally significant anoxic events of the Frasnian-Famennian transition. Each chapter is formatted as an independent manuscript, meaning figure and table numbering restarts in every chapter and with separate supplemental information and reference lists. In-text references follow the numbering as indicated by the table of contents. The thesis concludes with a Synthesis chapter that integrates the results of all four studies, addresses the overarching research questions, and presents a coherent set of conclusions, emerging questions, outlook, and future work.

Table of Contents

1. Introduction	12
1.1. General Introduction	12
1.2. Milankovitch Cycles	16
1.2.1. The Solar System and Earth's Orbital Parameters	16
1.2.2. Cyclostratigraphy	22
1.3. Devonian Events and Anoxia	26
1.3.1. Anoxia or Deoxygenation?	26
1.3.2. Pathways and Causal Mechanisms of Marine Deoxygenation	27
1.3.3. Overview of Devonian Anoxic Events	28
1.3.4. Astronomical Forcing of Devonian anoxic events – A Brief Overview	31
1.4. Introduction to Oued Ferkla, Lansing core and West Valley core Records	33
2. Geochemistry of the Daleje, Choteč, Kačák, and <i>pumilio</i> events (Oued Ferkla, SE Morocco) – in preparation.	42
2.1. Introduction	44
2.2. Geological Setting	47
2.3. Materials and Methods	52
2.3.1. Sampling	52
2.3.2. Portable X-ray Fluorescence	52
2.3.3. Stable Carbon and Oxygen Isotopes	52
2.3.4. Statistical Approaches	53
2.5. Results	58
2.5.1. Elemental Geochemistry	58
2.5.2. Stable Isotopes $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$	58
2.6. Discussion	62
2.6.1. Diagenetic Alteration	62
2.6.2. Detrital Signatures	67
2.6.3. Paleoredox Conditions	73
2.6.4. Carbon and Oxygen Geochemistry	78
2.6.5. Geochemical Expression of the Daleje, Choteč, Kačák, and <i>pumilio</i> events	80
2.7. Conclusions	92
2.8. Supplemental Information	100

3. A Six-Million-Year Astronomical Cycle Pacing Early – Middle Devonian Global Events (Oued Ferkla, SE Morocco) – <i>in preparation</i>	159
3.1. Introduction	161
3.2. Materials and Methods	162
3.3. Results and Discussion	162
3.4. Extended Data	169
3.5. Supplemental Information	175
4. Milankovitch Forcing and Nonlinear Climate Variability during the Late Givetian (Appalachian Basin, New York, USA) – <i>in review in <i>Climate of the Past</i></i>	179
4.1. Introduction	181
4.2. Geological Setting	182
4.3. Material and Methods	186
4.3.1. Gamma-ray Spectrometry	186
4.3.2. Magnetic Susceptibility	186
4.3.3. Statistical Approaches	186
4.4. Results	188
4.4.1. Gamma-ray Spectrometry	188
4.4.2. Magnetic Susceptibility	188
4.5. Cyclostratigraphy	189
4.5.1. Depth-domain Cyclostratigraphy	189
4.5.2. Cyclostratigraphic Age Models	190
4.5.3. Time-domain Cyclostratigraphy	194
4.6. Paleoclimatic and Paleodepositional Response	207
4.7. Conclusions	210
4.8. Supplemental Information	217
5. Astronomical control on marine anoxia during the Kellwasser Crisis and Rhinestreet Event (Appalachian Basin, New York, USA) – <i>published in <i>Global and Planetary Change</i></i>	224
5.1. Introduction	226
5.2. Geological Setting	229
5.3. Materials and Methods	231
5.4. Results	232
5.4.1. Principal Component Analysis of Geochemical Data	232
5.4.2. Depth-domain Cyclostratigraphy	233
5.4.3. Astronomical Age Model	235

5.4.4.	Time-domain Cyclostratigraphy	237
5.5.	Discussion.....	241
5.5.1.	WVC Temporal Framework and Implication for the Kellwasser Crisis	241
5.5.2.	Geochemical Proxy Interpretation.....	242
5.5.3.	Eccentricity Pacing of Marine Anoxia.....	246
5.5.4.	Obliquity Pacing of Sea-level Variations	247
5.5.5.	Controls on the Succession of Events through the middle and late Frasnian	250
5.5.6.	A New Cyclostratigraphic Model for the Kellwasser Crisis	253
5.6.	Conclusions.....	256
5.7.	Supplemental Information.....	265
6.	Milankovitch Forcing and Devonian (Anoxic) Events – A Synthesis.....	275
6.1.	Limitations.....	275
6.1.1.	Available Proxy Records.....	275
6.1.2.	Resolution	276
6.1.3.	Record Duration	277
6.2.	The Duration of Devonian Events.....	278
6.3.	Phase Relationships between Devonian Events and Milankovitch Forcing	280
6.3.1.	Daleje, Choteč, Kačák, and <i>pumilio</i> events (Oued Ferkla)	282
6.3.2.	Fir Tree, Hubbard Quarry, and Lodi events (Lansing core, Sherburne Formation).....	283
6.3.3.	Rhinestreet, Lower Kellwasser, and Upper Kellwasser events (West Valley core)	283
6.4.	Integrated Interpretation of Orbital and Environmental Patterns	284
6.4.1.	Multi-Myr Pacing of Devonian Anoxic Events.....	286
6.4.2.	The Role of Eccentricity and 173 kyr Obliquity on Devonian Anoxic Events	289
6.4.3.	Precession and Obliquity Forcing of Devonian Anoxic Events	290
6.5.	A New Model for the Astronomical Forcing of Devonian Anoxic Events.....	291
6.6.	Causal Mechanisms Linking Astronomical Forcing and Devonian Anoxic Events	296
7.	Conclusions.....	301
8.	Emerging Questions, Outlook, and Future Work.....	304
9.	Supplemental.....	306

1. Introduction

1.1. General Introduction

Earth's history is punctuated by intervals of profound environmental disruption, among which episodes of expanded marine oxygen depletion – often generalized as *anoxia* – exerted major control on biogeochemical cycles (Algeo and Shen, 2024). The geological record preserves numerous manifestations of such anoxic episodes; many coincide with faunal turnovers and, in some cases, mass-extinction pulses (Raup and Sepkoski, 1982; Bambach, 2006). These intervals are commonly recorded as organic-rich facies (black shales) deposited during episodes of enhanced organic-carbon burial. Periods that favored widespread accumulation of organic-rich sediments (without implying complete, global deep-water anoxia) are commonly referred to as ocean anoxic events (OAEs; Arthur and Sageman, 1994) and denote episodes of substantial perturbation to marine redox conditions and carbon cycling (Bond and Grasby, 2017; Algeo and Shen, 2024).

Well-studied examples are the Cretaceous OAEs, such as OAE1a in the Early Aptian and OAE2 at the Cenomanian-Turonian boundary, which are marked by widespread deposition of organic-rich sediments and significant perturbations to the global carbon cycle (Schlanger and Jenkyns, 1976; Jenkyns, 2010). Severe and widespread ocean anoxia has also been implicated in the end-Permian mass extinction, where expanded euxinic (i.e., anoxic and free H₂S) conditions are thought to have contributed to catastrophic marine biodiversity loss (Grice et al., 2005; Clarkson et al., 2015). Episodes of expanded marine anoxia are not restricted to the Mesozoic or Permian; they also feature prominently in the Paleozoic, most notably during the Devonian, which represents an overall warmer-than-present interval characterized by elevated atmospheric CO₂ levels (Joachimski et al., 2009; Foster et al., 2017; Brugger et al., 2019) and the progressive expansion of vascular plants and the eventual rise of forested landscapes profoundly altering weathering, nutrient fluxes, and climate (Algeo et al., 1995; Stein et al., 2012; 2020; Dahl et al., 2022).

In the Phanerozoic marine record, the Devonian stands out as a prolonged interval of elevated extinction intensity (Raup and Sepkoski, 1982) and progressive turnover in dominant taxa (Bambach, 2006). These patterns are commonly associated with pulsed anoxia in many basins (Becker et al., 2020). Rather than a single catastrophic event, the Devonian is characterized by numerous biotic crises (Becker et al., 2016; 2020; Brett et al., 2020), punctuated by mass extinctions during the late Givetian, the late Frasnian Kellwasser Crisis, and late Famennian Hangenberg Event (Bambach, 2006; Kaiser, 2016; Carmichael, 2019; Becker et al., 2020). The Kellwasser Crisis at the Frasnian-Famennian boundary and the Hangenberg Event at the Devonian-Carboniferous boundary together constitute the principal extinction pulses of the Late Devonian mass extinction (Algeo and Shen, 2024), which is historically considered to

represent one of the 'Big Five' Phanerozoic mass extinction intervals (Raup and Sepkoski, 1982). Although these two events represent the most globally recognized extinction pulses, other Devonian biotic crises also contributed to the period's complex extinction record, yet they differ markedly in their scope, duration, and severity across basins (Becker et al., 2020; Brett et al., 2020).

Moreover, these Devonian biotic crises are frequently associated with evidence for expanded marine anoxia, expressed through the deposition of organic-rich sedimentary strata, perturbations to the global carbon cycle, and geochemical indicators of reduced marine redox conditions (Becker et al., 2020). These factors make the Devonian a key interval for investigating the links between marine anoxia, environmental change, and biotic turnover. Understanding the mechanisms that governed Devonian anoxia is also important for evaluating how marine redox systems respond to sustained warming and elevated CO₂ levels, offering insights into the conditions under which future oceans may become increasingly prone to oxygen depletion.

Despite extensive study, the spatial extent, temporal structure, classification, and ultimate drivers of Devonian anoxic events (Walliser, 1996) – and their causal links to extinction pulses – remain contested (e.g., bottom-up vs. top-down anoxia in Carmichael et al., 2019; ultimate vs. proximate causes by Algeo and Shen, 2024). A major challenge in resolving these debates is the differential expression of anoxic intervals across the Devonian record (e.g., Carmichael et al., 2019), combined with limited temporal resolution and inconsistent age control in many successions (Becker et al., 2020). These factors complicate efforts to determine the pacing, synchronicity, and causal relationships among anoxia, carbon-cycle perturbations, and biotic turnover. Further uncertainty concerns the extent to which Devonian anoxic episodes represent globally coherent events versus regionally restricted or basin-specific redox instability (e.g., Hedhli et al., 2023). Mechanistic interpretations are additionally hindered by the fact that the processes invoked to trigger, sustain, or amplify marine anoxia often interact in complex and nonlinear ways rather than operating as isolated drivers. These include, but are not limited to, sea-level fluctuations (e.g., Johnson et al., 1985; Bond and Wignall, 2008), changes in ocean circulation (Pohl et al., 2016; Gérard et al., 2025; 2026), the evolution of land plants and associated enhanced nutrient delivery (e.g., Algeo et al., 1995; Algeo and Scheckler, 1998; 2010; Smart et al., 2023; Zheng et al., 2023), climatic variability (e.g., Joachimski and Buggisch, 2002; Kaiser et al., 2016; Algeo et al., 2026), volcanism (e.g., Racki et al., 2018; Racki, 2020), hydrothermal brine systems linked to sedimentary-exhalative (SedEx) deposits (Emsbo, 2017; De Backer, 2026), and astronomical forcing (e.g., De Vleeschouwer et al., 2013; 2017; Da Silva et al., 2020).

In spite of significant advances (e.g., Kellwasser Crisis; De Vleeschouwer et al., 2017; Da Silva et al., 2020; Ma et al., 2022; Wichern et al., 2024), the role of astronomical forcing in shaping Devonian anoxic and extinction events remains insufficiently resolved and available studies offer somewhat differing interpretations, while broader syntheses often do not recognize astronomical forcing as a potential driving mechanism (cf. Algeo and Shen, 2024). In particular, the mechanisms linking variations in incoming solar radiation (insolation) to the development of marine anoxia remain largely undocumented. It is unclear whether Devonian anoxic episodes were consistently paced by orbital forcing and, if so, how their onset, duration, and recurrence relate to specific components or configurations of the Milankovitch spectrum. Determining the phase relationships between redox instability and orbital extrema is essential for distinguishing externally paced environmental change from internally driven Earth-system dynamics, and for evaluating whether successive anoxic episodes reflect similar forcing conditions or instead arise from distinct astronomical configurations and Earth-system states. A further unresolved aspect is whether astronomical forcing acted primarily as a background modulator that increased the susceptibility of the Devonian Earth system to anoxia following additional perturbations, or whether astronomical forcing itself served as a direct trigger (e.g., tipping point) for the initiation of anoxia. Building on these uncertainties, this thesis addresses the following research questions:

- Are certain Devonian (anoxic) events astronomically paced?
- What are the phase relationships between these events and specific components of the Milankovitch spectrum?
- For intervals with evidence consistent with anoxia, how do onset, duration, and recurrence relate to orbital extrema?
- Do successive Devonian events – despite their differing redox expressions – share similar astronomical forcing relationships, or do they reflect distinct orbital configurations and Earth-system states?
- Did astronomical forcing act as a trigger for Devonian environmental events – particularly those expressed as anoxia – or did it primarily modulate background conditions that made the Earth system prone to redox instability under additional perturbations?

To address these research questions, this thesis integrates high-resolution cyclostratigraphy with multiproxy geochemical and sedimentological analyses to establish astronomically calibrated temporal frameworks for the Oued Ferkla, Lansing core, and West Valley core records (Fig. 1). Cyclostratigraphy provides the means to resolve orbital-scale variability in sedimentary records (Hinnov, 2013; 2018; Sinnesael et al., 2019) and to evaluate the pacing and phase relationships between anoxic intervals and specific components of the Milankovitch spectrum. Complementary geochemical and sedimentological proxies constrain local redox conditions, carbon-cycle dynamics, and depositional environments, allowing the

temporal patterns inferred from orbital forcing to be directly linked to environmental change. Together, these approaches enable a systematic assessment of whether Devonian anoxic events were paced by astronomical forcing, how their timing relates to orbital extrema, and whether successive episodes reflect similar or distinct forcing conditions.

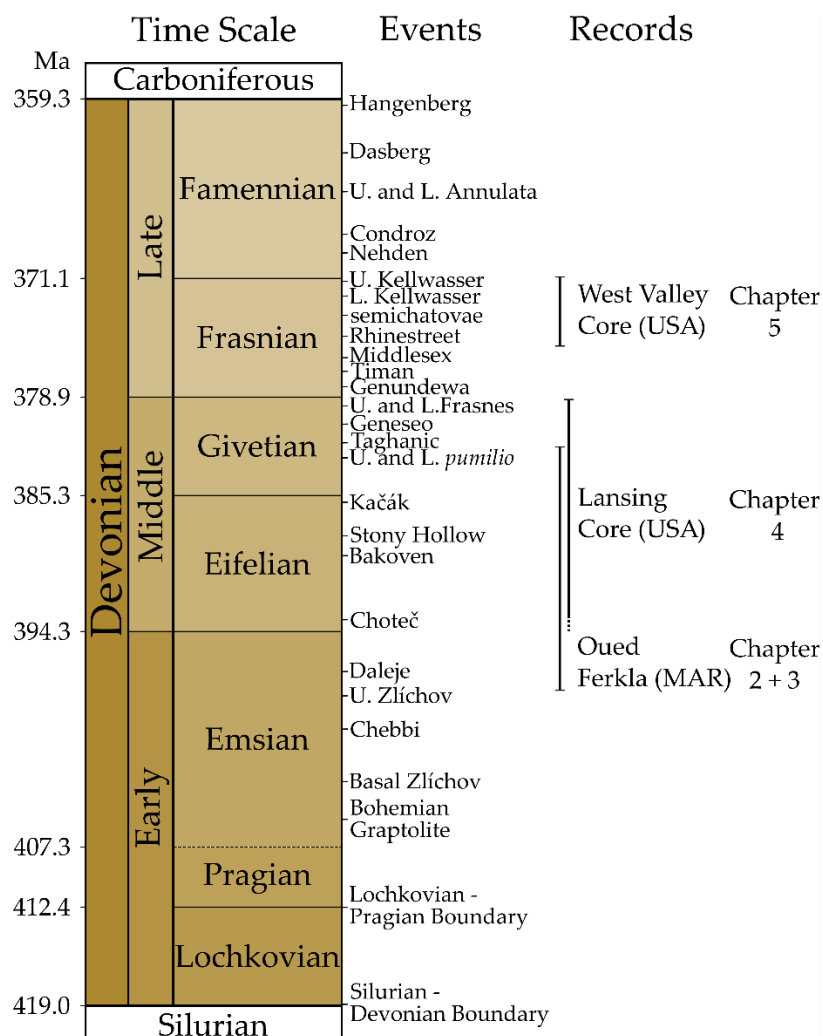


Fig. 1. Devonian time scale, anoxic events, and sections. Devonian time scale (Becker et al., 2020), Devonian anoxic events based on Becker et al. (2016; 2020) and Slavik and Hladil (2020). Oued Ferkla (Morocco), Lansing core (central New York State, USA) and West Valley core (western New York State, USA) are presented in chapters 2+3, 4, and 5, respectively.

1.2. Milankovitch Cycles

1.2.1. The Solar System and Earth's Orbital Parameters

The Solar System can be described as the collection of bodies gravitationally bound to the Sun (Murray and Dermott, 1999). Through their mutual gravitational interactions, the motions of all celestial bodies evolve continuously, producing slow but systematic changes in their orbital parameters. Within this gravitational framework, Earth's motion is shaped not only by gravitational interactions between Earth, the Sun, and the Moon (i.e., luni-solar precession), but also by the cumulative gravitational influence of other celestial bodies, with the major planets exerting the strongest additional perturbations. As a result, the shape of the Earth's orbit around the Sun (eccentricity e), the orientation of that orbit in space (apsidal precession), the tilt of Earth's rotational axis relative to the orbital plane (obliquity ε), and the position of Earth's spin axis itself (axial precession angle) undergo quasi-periodic variations over 10^5 -to- 10^7 -year timescales (Laskar, 2020). The apsidal precession causes perihelion – the point in Earth's orbit where Earth is closest to the Sun – to slowly shift along the orbit with respect to the inertial frame (i.e., longitude of the perihelion ϖ). The axial precession, on the other hand, causes the equinoxes – the two moments in Earth's annual cycle when day and night are equal in length – to shift through time. Together, the apsidal and axial precession determine the timing of perihelion relative to the equinoxes, a combined motion referred to as climatic precession (e.g., Berger, 1973; 1987; 1988; Laskar, 1990). Furthermore, Earth's orbital plane is tilted relative to the Solar System reference plane (inclination) and also precesses – a motion, which is called nodal precession that changes the point where Earth's orbit crosses that reference plane (i.e., longitude of the ascending node; e.g., Murray and Dermott, 1999).

of Earth's climate system – i.e., astronomical forcing (Hayes et al., 1976; Berger, 1988; Zeebe and Lantink, 2024). Often simplified in a geological context as precession, obliquity, and eccentricity, these quasi-periodic variations are referred to as Milankovitch cycles, named after the Serbian astronomer Milutin Milanković, who first quantified how long-term changes in Earth's orbital geometry regulate insolation and thereby pace glacial-interglacial climate variability (Milankovitch, 1941; Berger, 2021).

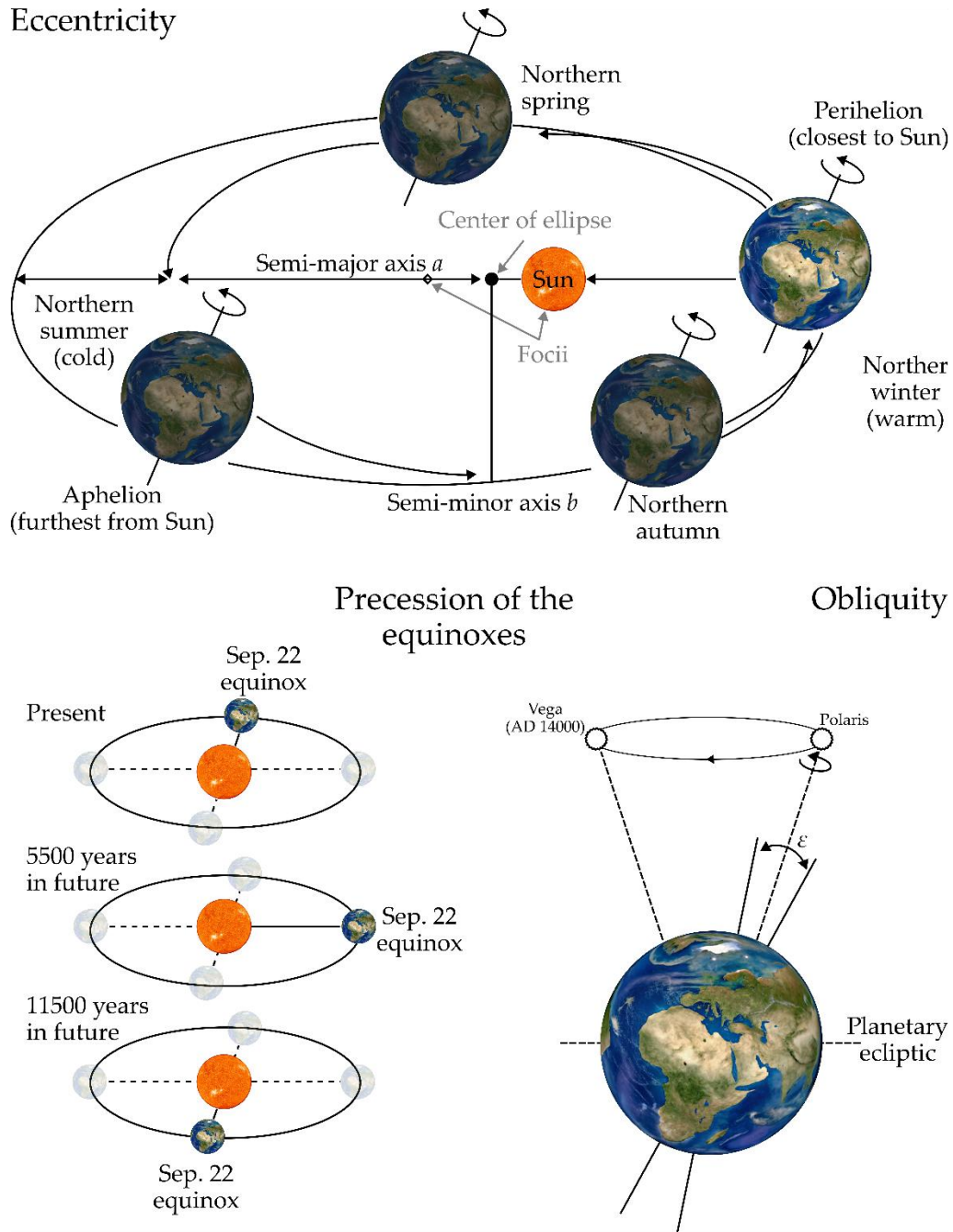


Fig. 3. Orbital motions of Earth. Illustration of the primary orbital parameters: eccentricity, obliquity (ϵ), and precession of the equinoxes. Modified after Pálíke (2005).

To understand how these quasi-periodic variations arise, and how they propagate into the insolation signal, it is necessary to examine the underlying secular frequencies that govern the long-term evolution of Earth's orbit. In the classical theory of celestial mechanics, the precession of a planet's perihelion – modulated by eccentricity – has characteristic fundamental frequencies g_i , while the precession of its orbital plane – modulated by inclination – has characteristic fundamental frequencies s_i (e.g., Bretagnon, 1974; Laskar, 1990). To obtain the quantities relevant for insolation forcing, these orbital variations must be combined with a model of luni-solar precession, which is dominated by a frequency commonly denoted as k . Within this framework, obliquity variations are primarily governed by combinations of s_i and $g_i + k$ terms, climatic precession by the $g_i + k$ terms, and eccentricity by differences among the g_i terms (e.g., Berger and Loutre, 1990; Hinnov, 2013; Laskar, 2020). Although there is no one-to-one relationship between the fundamental frequencies and a single planet, the practice is to order them as such that the i^{th} frequency is close to the free frequency of the i^{th} planet in the gravitational field caused by the other planets, where $i = 1$ for Mercury, etc. (Laskar, 2020; Zeebe and Lantink, 2024). Currently, climatic precession – which can be decomposed into multiple frequencies – covers a range of ~19 to ~24 kyr periods, whereas obliquity has key periods of ~41 kyr as well as two minor periods at ~29 and ~54 kyr (Hinnov, 2013). Key components involving s_i combinations include the ~1200 kyr $s_4 - s_3$ and 173 kyr $s_3 - s_6$ terms, and modulate obliquity on longer timescales (Laskar, 2020). Notable examples of eccentricity are summarized in Table 1.

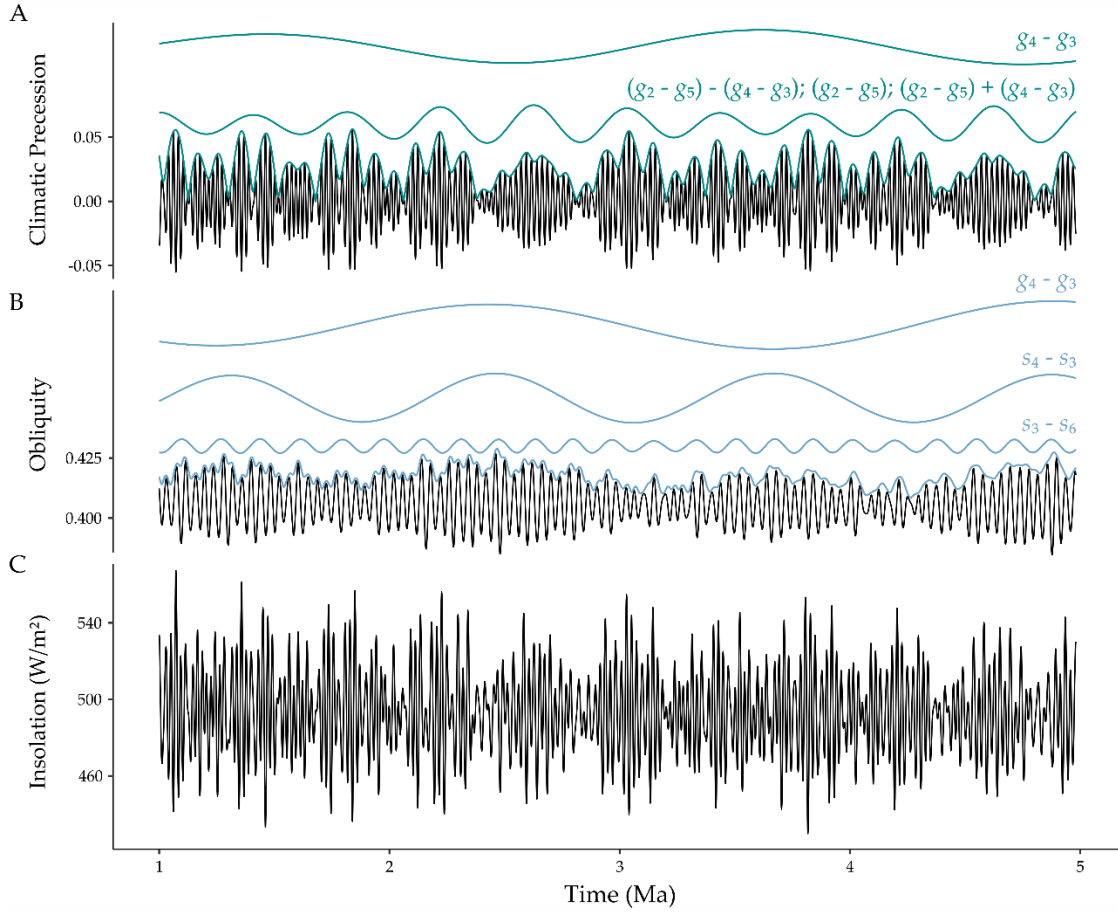


Fig. 4. Climatic precession, obliquity, their main modulators, and insolation for 5 to 1 Ma according to the La04 astronomical solution (Laskar et al., 2004). A) Climatic precession (black), its envelope (cyan) and extracted ~ 405 kyr $g_2 - g_5$ long eccentricity including $(g_2 - g_5) \pm (g_4 - g_3)$ sidebands (cyan), and ~ 2.4 Myr $g_4 - g_3$ Grand eccentricity (cyan). B) Obliquity, its envelope (blue), and extracted 173 kyr $s_3 - s_6$ (blue), ~ 1.2 Myr $s_4 - s_3$ (blue), and ~ 2.4 Myr $g_4 - g_3$ (blue). Insolation at $65^\circ N$ during summer solstice. Extracted $g_4 - g_3$ and $s_4 - s_3$ components have been amplified for visualization purposes.

Variations in climatic precession, obliquity and eccentricity over time can be quantified by computing astronomical solutions (e.g., Laskar, 2004; Zeebe and Lantink, 2024). However, the long-term evolution of the Solar System is extremely sensitive to initial conditions (i.e., Solar System chaos), meaning that uncertainties in planetary (and those of other celestial bodies) positions grow exponentially over time; by a factor of 10 every 10 Myr (Laskar, 1989; 2020). On the other hand, the long-term evolution of the Earth-Moon system is poorly constrained because the histories of tidal dissipation and dynamical ellipticity are not well known (Neron de Surgy and Laskar, 1997; Zeebe and Lourens, 2019; Farhat et al., 2022). Consequently, the phase of precession and obliquity solutions are not well constrained beyond 10 Ma (Sinnesael et al., 2019). As a result of Solar System chaos (Laskar, 1989), astronomical solutions diverge beyond 50 Myr, implying that Solar System reconstruction as well as geological and astrochronological applications are limited (beyond 10^8 years; De Vleeschouwer et al., 2024; Zeebe and Lantink, 2024).

Table 1. Main eccentricity terms. First 6 terms in decreasing amplitude of the frequency decomposition of the Earth’s eccentricity (–15 to +5 Ma; Laskar et al., 2004), adapted from Laskar (2020).

<i>g</i> -terms	Period (kyr)
$g_2 - g_5$	405
$g_4 - g_5$	95
$g_4 - g_2$	124
$g_3 - g_5$	99
$g_3 - g_2$	131
$g_4 - g_3$	2387

Despite these limits, the fundamental frequencies commonly associated with the gas giants (Jupiter: g_5, s_5 ; Saturn: g_6, s_6 ; Uranus: g_7, s_7 , and Neptune: g_8, s_8) exhibit regular behavior and can be considered nearly constant over the age of the solar system (Laskar, 2020). Another fundamental frequency that is comparatively stable is the g_2 and, by extension, the $g_2 - g_5$ term (Laskar, 2020), which generates the long eccentricity metronome (405 kyr; Table 1). Only beyond 1 Ga does the $g_2 - g_5$ term display potential instability, due to a $(g_1 - g_2) + (s_1 - s_2)$ secular resonance encountered in ~40% of the 64 ensemble members of the ZB23 astronomical solutions (Zeebe and Lantink, 2024). The $s_3 - s_6$ term generating the 173 kyr obliquity beat is also fairly stable; it is dubbed the “inclination metronome” (Boulila et al., 2018; Laskar, 2020). Conversely, other cycles, such as the ~2.4 Myr $g_4 - g_3$ cycle, which is present in eccentricity as well as the obliquity envelope, are very unstable prior to 50 Ma due to intermittent changes in resonance regimes and fall within the range of 1.4 to 2.6 Myr (Laskar et al., 2020).

Yet, the quasi-periodic variations in eccentricity, obliquity, and climatic precession described above translate into corresponding variations in the seasonal and latitudinal distribution of insolation, which in turn modulate Earth’s climate system (Fig. 3, 4). Through their influence on temperature, precipitation, ice volume, ocean circulation, biogeochemical cycles (Ruddiman, 2006; Gérard et al., 2025; 2026), Milankovitch cycles generate climate responses that can be transferred into the sedimentary record. The resulting stratigraphic expression of astronomical forcing – recorded as rhythmic variations in, for example, lithology or geochemistry – forms the basis of cyclostratigraphy, which aims at decoding these imprints to primarily reconstruct past climate dynamics and to establish high-resolution geological timescales.

1.2.2. Cyclostratigraphy

Cyclostratigraphy is the subdiscipline of stratigraphy that focuses on identifying, analyzing, and interpreting cyclic variations in the stratigraphic record – particularly those driven by astronomical (Milankovitch) forcing – and on using these cycles to build high-resolution temporal frameworks for sedimentary successions and to understand astronomical climate forcing (Strasser et al., 2006; Sinnesael et al., 2019). The guidelines provided by Sinnesael et al. (2019) form the foundation for the cyclostratigraphic approach applied throughout this thesis – a modified strategy is summarized according to the following key steps:

1. **Constructing an integrated stratigraphic framework**, including – where available – a detailed sedimentological and (litho)stratigraphic description, sequence and event stratigraphy, biostratigraphy (conodont zonation), and geochemical and geophysical proxy records. Biostratigraphy and event stratigraphy provide first-order temporal estimates (i.e., an independent age model) and are complemented by the identification of potential hiatuses or diagenetic overprinting (Sinnesael et al., 2019). Absolute age constraints from high-precision U-Pb geochronology can provide powerful temporal anchors for cyclostratigraphic interpretation; however, such data are not available for the studied sections and are therefore not further considered here.
2. **Stratigraphic-domain cyclostratigraphy**, focusing on objectively documenting cyclicity captured by the proxy record using time series analyses. Prior to analysis, proxy series are typically detrended to some extent – while avoiding removal of meaningful low-frequency signals – and linearly interpolated. Commonly used techniques in this thesis to identify cyclic components include kernel regression, Taner bandpass filtering, and spectral approaches such as the multi-taper method (MTM) power spectrum (Thomson, 1982; Meyers, 2012; 2014), continuous wavelet transform (CWT) scalograms and average wavelet spectrum (Arts, 2023; Arts et al., 2024), evolutive power spectral analysis (EPSA; Meyers, 2014), and evolutive harmonic analysis (EHA; Meyers et al., 2001; Meyers, 2014). MTM, CWT and EPSA are generally used to identify dominant frequency components and evaluate their stability through the record, enabling the calculation of frequency ratios and comparison with expected Milankovitch cycle frequency ratios. In a next step, EHA can be used to track the behavior of a specific cycle, while bandpass filtering isolates selected frequency components. Statistical significance testing may aid in identifying dominant cyclicity, but remains highly debated (Smith, 2020; 2023; Weedon, 2022), and it is used here only as a guide rather than as a strict criterion. These procedures constitute the objective analytical output of cyclostratigraphy and do not involve interpretation.
3. **Cyclostratigraphic interpretation** of the cyclicity recorded in the proxy record(s) within the broader integrated stratigraphic framework. The goal of this step is to formally interpret (some of) the identified frequency components as Milankovitch

cycles. Although, in principle, such an interpretation can be made solely from the revealed frequency components, a more robust approach incorporates first-order temporal estimates to constrain the approximate duration of key frequency components. Inverse modeling approaches, which assume a Milankovitch imprint, used here include TimeOpt and its evolutive variant eTimeOpt (Meyers, 2015; 2019). These methods practically tune (see below) the proxy record by optimizing amplitude-modulation patterns and concentration of spectral power at target frequencies, thereby providing sedimentation-rate estimates. Such analyses offer additional, somewhat semi-objective constraints on the plausibility of the inferred cyclostratigraphic interpretation. Alternative inverse approaches, including (evolutive) average spectral misfit (Meyers et al., 2012) and (evolutive) correlation coefficient (Li et al., 2019), were explored but not applied routinely.

4. **Tuning** the proxy record(s) to construct a cyclostratigraphic age model. Based on the cyclostratigraphic interpretation, sedimentation-rate models are optimized to transform the distance (stratigraphic) domain into the time domain for all available proxies. While multiple definitions of “tuning” exist, tuning as applied here involves correlating and pattern-matching of interpreted cyclicity to a specific astronomical term (Sinnesael et al., 2019). In absence of a stable astronomical solution for the Devonian, the preferred tuning target is the 405 kyr $g_5 - g_2$ long eccentricity metronome (Hinnov, 2013; Zeebe and Lantink, 2024). More specifically, minimal tuning (e.g., Pas et al., 2021) is applied by aligning stratigraphic coordinates (i.e., heights or depths) with local extrema of the eccentricity metronome. This conservative, low-intervention approach preserves Milankovitch frequency ratios, avoids circular reasoning, and typically results in the alignment of other astronomical frequencies as well (Pas et al., 2021). The result of this process is a distance-time matrix that serves as the sedimentation-rate age model for converting all proxy records from the stratigraphic domain into the time domain.
5. **Time-domain cyclostratigraphy** involves applying the aforementioned time-series analysis methods to the tuned proxy records. The goal of this analysis is twofold: first, it provides an independent verification of the cyclostratigraphic age model; second, it enables documentation of proxy relationships, including potential phase offsets, and forms the basis for subsequent paleoenvironmental and paleoclimatic interpretation.

To elaborate on this final step, the evaluation of astronomical imprint and proxy coherence in the time domain relies on several diagnostic criteria. Astronomical frequencies should remain relatively stable, consistent with their predicted stability under astronomical theory. Logically, the observed cycle-frequency ratios should correspond to Milankovitch frequency ratios. Importantly, the amplitudes of individual cycles do not represent a valid criterion for confirming or rejecting the cyclostratigraphic interpretation because a proxy response to

Milankovitch forcing may vary through time due to changes in the depositional conditions, sedimentation dynamics, diagenetic overprinting, or shifts in the sensitivity of the proxy to astronomical forcing (e.g., Hinnov, 2013; Meyers, 2019). However, if a specific stratigraphic interval is interpreted to contain a dominant Milankovitch component (step 3), the interval in the time domain should continue to express that same dominant astronomical cycle after tuning.

Moreover, amplitude- and frequency-modulation patterns – typically assessed using bandpass filtering and Hilbert transforms – should be broadly coherent within a given proxy and, ideally, across proxies, while still allowing for proxy-specific responses to astronomical forcing (Laurin et al., 2016; Zeeden et al., 2019). Modulation patterns can also be visualized through evolutive spectral analysis (e.g., EHA), where frequency modulation produces characteristic bifurcation patterns (Meyers et al., 2001). Intra-proxy coherence can be assessed by examining the phase relationship between a given cycle and the envelope of a hierarchically shorter cycle that it modulates according to astronomical theory. For example, provided short eccentricity and precession are directly imprinted on the proxy signal, the precession envelope (i.e., the precession amplitude modulation derived from the Hilbert transform) should be broadly phase-consistent with the extracted short-eccentricity signal. Phase inversion may occur as a result of this process, most notably during minima in the 2.4 Myr $g_4 - g_3$ eccentricity cycle (i.e., nodes), when minimal modulation of short eccentricity produces a maximum in the extracted long-eccentricity component (see also Fig. 4). This phenomenon has important implications for identifying orbital extrema.

A cyclostratigraphic interpretation can generally be considered robust if (i) cycle frequencies align with expected Milankovitch frequencies, (ii) amplitude modulation patterns are internally consistent, and (iii) there is a relatively strong agreement between the first-order independent age model (step 1) and the floating astrochronology. Although discrepancies among these criteria may weaken the cyclostratigraphic interpretation, they should be evaluated within the broader integrated stratigraphic framework. For example, depending on the sedimentary response to astronomically forced climate changes – often expressed as facies shifts – the proxy phase response to insolation forcing may invert, potentially causing significant distortions in amplitude modulation patterns.

Although lithological cyclicity (visible bedding rhythms) can provide a useful qualitative indication of astronomical forcing, it represents only a single line of evidence and may be influenced by diagenesis or non-orbital processes (e.g., Westphal et al., 2015), particularly when characteristic Milankovitch modulation patterns are unclear or absent. Consequently, robust cyclostratigraphic interpretation relies primarily on quantitative time-series analysis of multiple, preferably independent proxy records, with observed bedding cyclicity serving as complementary support. When comparing the cyclostratigraphic to the independent age

model (e.g., durations derived from integrated conodont biostratigraphy and U-Pb dating; Becker et al., 2020), the robustness of the independent age model must also be critically assessed. Furthermore, the resulting sedimentation-rate history should be geologically reasonable and consistent with the observed facies and depositional processes.

Finally, all cyclostratigraphic age models inherently contain cumulative uncertainty arising from a multitude of errors that occur to some extent during sampling, measurement, as a result of proxy behavior, frequency identification, tuning choices, sedimentation-rate estimation, etc. Unidentified hiatuses or structural faults may further increase error substantially. Numerous approaches exist in literature on how to quantify or express uncertainty – ranging from expert judgement (e.g., De Vleeschouwer et al., 2012; Fang et al., 2015) on how certain the amount of interpreted cycles is – to more statistically robust approaches (e.g., Monte Carlo modelling; Meyers, 2015; 2019). Yet, uncertainty remains a heavily debated topic within the cyclostratigraphic community. Although quantifying uncertainty would be of added value, particularly when constraining the estimated duration of events, it lies beyond the primary objectives of this thesis. Resolving the full scope and quantification of cyclostratigraphic uncertainty is a substantial methodological challenge that could constitute a separate thesis; here, formal uncertainty quantification is applied only in the specific case where two independent floating astrochronologies exist for the same record.

1.3. Devonian Events and Anoxia

1.3.1. Anoxia or Deoxygenation?

Anoxia denotes the near-complete absence of dissolved oxygen in seawater and generally develops when oxygen supply is outpaced by oxygen demand (Tyson and Pearson, 1991). In stratigraphic studies, however, the term *anoxia* is often used more loosely to describe a spectrum of low-oxygen conditions, ranging from dysoxic to anoxic (Wignall, 1994) and, in the most extreme case, euxinia (i.e., anoxic and sulfidic; free H₂S; Canfield, 1994; Meyer and Kump, 2008). Here, *deoxygenation* is used to denote oxygen-depleted conditions of uncertain severity, encompassing both *dysoxia* and *anoxia*. The term *anoxia* is used only when cited employ it or when contextual evidence clearly supports severe oxygen depletion. Anoxia is of broad interest because it is associated with organic-rich sedimentation, perturbations to the global carbon cycle, and several major extinction events (Arthur and Sageman, 1994; e.g., Sageman et al., 2003; Penn et al., 2018). Understanding the mechanisms behind the onset, sustenance, and expansion of anoxia is therefore of high interest to the broader scientific community, especially given the declining oxygen in the global ocean and coastal waters (Breitburg et al., 2018).

One way to unravel causal mechanisms behind ancient anoxia is by investigating the sedimentary record, in which characteristic signatures of deoxygenation can be identified. Because low-oxygen conditions influence biogeochemical cycles, including redox-sensitive geochemical cycles, episodes of marine deoxygenation leave a distinct signature in the sedimentary record. Reduced bioturbation and enhanced preservation of organic matter commonly produces finely laminated, organic-rich sediments such as black shales or bituminous limestones often characterized by elevated total organic carbon (TOC) content (Wignall and Myers, 1988; Arthur and Sageman, 1994; Sageman et al., 2003). Redox-sensitive trace metals such as Mo, U, and V become enriched as they are scavenged from seawater under deoxygenated conditions and therefore represent proxies useful for estimating past oxygenation conditions (Algeo and Lyons, 2006; Tribovillard et al., 2006).

Despite these characteristic expressions, reconstructing past oxygenation levels remains challenging, most notably because of post-depositional alteration (e.g., diagenetic overprinting of redox-sensitive trace metals; Tribovillard et al., 2006). Most sedimentary and geochemical indicators reflect the consequences of low-oxygen conditions rather than dissolved-oxygen concentrations themselves, making it difficult to distinguish confidently among dysoxic, anoxic, and euxinic conditions (Meyer and Kump, 2008; Algeo and Liu, 2020; Bennet and Canfield, 2020). Moreover, some facies traditionally attributed to anoxia – such as finely laminated, organic-rich sediments with little or no bioturbation – can also form under oxygenated bottom waters when sedimentation rates are sufficiently high to outpace benthic

reworking and microbial degradation (Wignall and Myers, 1988; Arthur and Sageman, 1994). Although rapid burial can therefore mimic the sedimentary expression of anoxia, this mechanism appears uncommon in most black shales, which typically accumulated at relatively low sedimentation rates (Wignall, 1994). These caveats highlight the need for a multi-proxy approach and careful interpretation of redox signals within their broader depositional context. Here, past oxygen levels are mostly inferred from geochemical analyses involving redox-sensitive trace elements and TOC content, combined with lithological and sedimentological observations.

1.3.2. Pathways and Causal Mechanisms of Marine Deoxygenation

Marine deoxygenation can arise through several interconnected causal pathways, which can be broadly categorized as (i) enhanced primary productivity (i.e., eutrophication) or productivity-driven anoxia (Tyson and Pearson, 1991; Arthur and Sageman, 1994; Kump and Arthur, 1999), (ii) reduced ocean ventilation or stagnation-driven anoxia (Wignall and Myers, 1988; Jenkyns, 2010), (iii) increased remineralization efficiency (Penn et al., 2018), and (iv) expanded oxygen minimum zones (OMZs) leading to a displacement of the oxycline (Wilde and Berry, 1984; Carmichael et al., 2019). The drivers behind these mechanisms – which do not directly cause deoxygenation but rather may trigger one or more of the pathways listed above – include (LIP) volcanism (Bond and Wignall, 2014; Racki, 2020), continental weathering changes (Jenkyns, 2010; Algeo et al., 2015; Wichern et al., 2026), tectonics (Tyson and Pearson, 1991), climate variations (Penn et al., 2018), and ocean circulation and upwelling changes (Jenkyns, 2010; Gérard et al., 2025; 2026). Milankovitch forcing can modulate several of these drivers through its effect on insolation and climate, influencing, for example, monsoon intensity (affecting weathering and nutrient delivery) or upwelling strength (affecting productivity and OMZs). Hence, Milankovitch forcing is not necessarily a standalone mechanism for anoxia and is generally considered as a pacing mechanism.

Multiple conceptual frameworks exist for interpreting and organizing causes of marine deoxygenation, and the differences among them largely reflect the perspective from which the problem is approached and the particular aspects of the system that researchers aim to emphasize. Algeo and Shen (2024) argue, within the scope of biocrises, that proximate drivers (e.g., CO₂ rise/fall, ocean circulation/stagnation) are themselves initiated by more remote ultimate causes (e.g., bolide impacts, LIP, bioevolutionary events), and that similar proximate climato-environmental changes, such as anoxia, can arise from different ultimate causes. Therefore, they stress that distinguishing between proximate and ultimate causation is essential when attempting to understand mass extinction mechanisms and anoxia. An alternative, process-oriented framework is offered by Carmichael et al. (2019) for the Kellwasser Crisis, who adopt a top-down/bottom-up perspective that focuses directly on the origin and amplification of anoxia itself. Simply put, the bottom-up mechanism of Carmichael

et al. (2019) invokes either (i) migration or expansion of the OMZ through upwelling or transgression, or (ii) upwelling of oxic, nutrient-rich bottom waters that cause eutrophication. The top-down mechanism, by contrast, attributes anoxia to photic-zone eutrophication driven by increased terrestrial nutrient input, changes in plankton communities, the addition of bio-limiting nutrients from volcanic material, or a combination thereof (Carmichael et al., 2019). Although this binary classification is not diagnostic in an ultimate/proximate causal sense (Algeo and Shen, 2024), it remains useful for eliminating implausible pathways in specific depositional settings. For example, in isolated island arc settings only top-down nutrient delivery is deemed possible (Carmichael et al., 2019). This way, the top-down/bottom-up framework retains value when attempting to constrain both ultimate and proximate mechanisms behind anoxic extinction events such as the famous Kellwasser Crisis.

1.3.3. Overview of Devonian Anoxic Events

The Devonian was particularly susceptible to episodes of marine deoxygenation (Becker et al., 2020). Because considerable uncertainties exist regarding Devonian climate (incl. CO₂ levels; Foster et al., 2017; Dahl et al., 2022), continental configuration and bathymetry (Scotese, 2021), determining why this period appears especially prone to deoxygenation – and especially to what extent – remains difficult (see Gérard et al., 2025). Devonian paleogeographic reconstructions vary strongly (cf. Vêrard, 2019; Scotese, 2021), and continental configurations may carry general uncertainties on the order of ~50 % (C. R. Scotese; *pers. comm.*). In combination with unconstrained bathymetry, these factors complicate interpreting ocean circulation, basin restriction, nutrient routing, and ventilation pathways, and so on.

Paleotemperature reconstructions based on conodont apatite $\delta^{18}\text{O}$ data indicate that the Devonian was a warmer-than-present period but characterized by substantial variability in mean temperatures, with the Lochkovian, Pragian, Late Frasnian and Early Famennian characterized by relatively high temperatures (> 25°C), and the Middle Devonian and latest Famennian recording cooler conditions of around ~20°C (Joachimski et al., 2009). A short-lived cooling spike is already reported during the Upper Kellwasser Crisis (Becker et al., 2020; Algeo et al., 2026). The absence of direct evidence for permanent ice sheets, in combination with evidence of relatively elevated temperatures, implies elevated sea levels, which in turn likely have led to extensive shallow epicontinental seas. This view, however, requires nuance; substantial evidence points towards at least partial glaciation during the Early to Middle Devonian (Elrick et al., 2009; Dahl, 2022). Regardless, the occurrence of widespread epicontinental seas and semi-restricted basins which were more sensitive to climatic variability and eustasy (Johnson, 1985; Joachimski et al., 2009; Becker, 2020; Scotese, 2021), facilitated the development of oxygen-minimum zones. In addition, the progressive colonization of the continents by vascular plants during the Silurian-Devonian fundamentally altered Earth-surface processes by affecting weathering and erosion, altering nutrient fluxes

to the marine realm, and modifying CO₂ levels and, by extension, global climate (Algeo et al., 1995; Algeo and Scheckler, 1998; 2010; Berner, 2004; Dahl and Arens, 2020). Tectonic activity (e.g., Acadian Orogeny; Ver Straeten et al., 2023) and volcanism (Racki, 2020) may have further influenced atmospheric CO₂ levels, nutrient delivery, and ocean circulation patterns during the Devonian, adding further complexity to the climatic boundary conditions of the period.

The Devonian is not characterized by long-term anoxia but by punctuated episodes of deoxygenation. While an exhaustive review of these events is beyond the scope of this work – and many details are addressed in Chapters 2 – 5 – a brief reassessment of their global expression and the extent to which they represent anoxic and/or extinction intervals is warranted. Yet, the typical characteristics of the events studied here (Table 2) represent an overgeneralization. As highlighted by Carmichael et al. (2019) for the well-studied first-order Kellwasser Crisis, the expression and signatures are highly variable and, in addition, considerable sampling bias exists. This is especially true for many Early to Middle Devonian events, for which available studies remain limited, particularly with respect to geochemical constraints. As a result, quantitative constraints on oxygenation are lacking, and past oxygenation levels must be inferred primarily from lithological and biostratigraphical observations.

Table 2. Summary of Devonian (anoxic) events. General event expression, evidence for anoxia, biotic severity, carbon cycle perturbations, and estimated duration. The regional Fir Tree, Hubbard Quarry, and Lodi events are of middle to latest Givetian age. The stratigraphic position of the late Emsian to earliest Famennian global events included here can be found in Fig. 1. The severity of the associated bio-event is summarized here based on the nomenclature employed by Becker et al. (2016) and Brett et al. (2020): first-order events represent mass extinctions; second-order events are characterized by complete disappearance of widespread groups and ecosystems at higher taxonomic level (orders and families); third-order events represent global extinction at lower taxonomic levels (genera and species); fourth-order events represent global extinction of fewer but widespread groups; “other” bio-events represent faunal blooms, radiations, and spread rather than extinction – regional bio-events fall outside this framework. References: ¹Becker et al. (2020), ²Baird et al. (2023), ³Carmichael et al. (2019), ⁴Talih et al. (2022), ⁵Brett et al. (2020), ⁶Cramer and Jarvis (2020), ⁷Ellwood et al. (2011), ⁸Kabanov, 2019; 2023, ⁹De Vleeschouwer et al. (2024).

Event	General Event Expression	Evidence for Anoxia	Biotic Severity	Carbon Cycle	Estimated duration
Upper Kellwasser	Variable expression ³ , sudden cooling, typically organic-rich ¹	Lithofacies ¹ , geochemistry ³	1 st order ⁵	Typically, pCIE ^{3,6}	200 to > 400 kyr ⁹
Lower Kellwasser	Variable expression ³ , typically organic-rich ¹	Lithofacies ¹ , geochemistry ³	2 nd order ⁵	Typically, pCIE ^{3,6}	100 to 600 kyr ⁹
Rhinestreet	Black shales in North America, transgressive in Russia, and organic-rich strata in North Africa, possibly transgressive in China ¹	Lithofacies ¹ , geochemistry ⁴	Other ⁵	nCIE ⁶	~2.3 Myr ⁸
Lodi	Transgressive X in North America (Appalachian Basin) ²	N.A.	Regional	N.A.	N.A.
Hubbard Quarry	Highstand dark shales in North America (Appalachian Basin) ²	Lithofacies ²	N.A.	N.A.	N.A.
Fir Tree	Transgressive X in North America (Appalachian Basin) ²	N.A.	Regional	N.A.	N.A.
<i>pumilio</i>	Central Europe and North Africa, North America (Appalachian Basin), China ¹	Eutrophication ¹ lithofacies ⁴	Other (Bloom) ⁵	minor nCIE ⁶	N.A.
Kačák	Polyphased, with a major transgressive pulse ¹	Lithofacies ¹	3 rd order ⁵	pulsed CIE fluctuations ⁶	~200 kyr ⁷
Choteč	Interruption of well-oxygenated outer shelf facies in Europe, North Africa, North America, Siberia, and China ¹	Lithofacies ¹	3 rd order ⁵	minor pCIE ⁶	N.A.
Daleje	Transgressive shales in Europe, North Africa, and China ¹	Lithofacies ¹	3 rd order ⁵	nCIE with superimposed fluctuations ⁶	N.A.

1.3.4. Astronomical Forcing of Devonian anoxic events – A Brief Overview

Despite several decades of research on the mechanisms behind ocean anoxia, no consensus has been reached on the exact pathway(s) (e.g., Carmichael et al., 2019). Moreover, depending on the specific paleoclimatic, paleoenvironmental, and paleodepositional context, different drivers, mechanisms, and pathways may be responsible for deoxygenation. Because a review of all literature related to Devonian anoxic events and their potential triggers would be prohibitively extensive, focus is put here on literature covering Devonian anoxic events that have been linked explicitly to Milankovitch forcing.

Limited evidence from geological records indicates temporal correlations between orbital extrema (Milankovitch cycles) and Devonian events (e.g., De Vleeschouwer et al., 2013; 2017; Da Silva et al., 2020; Ma et al., 2022; Wichern et al., 2024; 2026), suggesting that there might be a link between astronomical forcing and deoxygenation. De Vleeschouwer et al. (2013) documented that the ‘anoxic’ black shales of the Annulata, Dasberg, Kowala, and Hangenberg (events) at Kowala, Poland are separated by 2.2, 1.2, and 1.2 Myr respectively, proposing that 2.4 Myr $g_4 - g_3$ maxima provoked sea-level rise by collapsing small Gondwanan ice sheets, thereby linking astronomically forced transgression and marine anoxia. Wichern et al. (2026) similarly observed 2.3 and 2.4 Myr separating the Upper Annulata, Dasberg and the Hangenberg black shales in the Rhenish Massif, Germany, inferring Myr-Milankovitch pacing of Late Devonian anoxia.

De Vleeschouwer et al. (2017) and Da Silva et al. (2020) focused on the timing, pacing, and duration of the Frasnian-Famennian Kellwasser Crisis. While the former does not emphasize anoxia – largely because their studied records lack black shales – Da Silva et al. (2020) conclude that at Steinbruch-Schmidt, astronomical forcing likely contributed to the expansion of ocean anoxia, particularly through increased continental weathering resulting in eutrophication, subsequent widespread anoxia, and black shale deposition. It should be noted that the focus of De Vleeschouwer et al. (2017) and Da Silva et al. (2020) lies on providing high-precision astrochronologies rather than presenting new redox evidence; instead, the link to anoxia relies on the widely accepted interpretation of the Kellwasser beds as recording deoxygenation. Interestingly, De Vleeschouwer et al. (2017) interpreted a relatively strong obliquity signal to indicate a node in 2.4 Myr eccentricity, which was later supported by Da Silva et al. (2020). This strong resemblance to the timing of the Cretaceous OAE2 in the Umbria-Marche Basin, Italy described by Batenburg et al. (2016) – which links the onset of the event to an increase in eccentricity after a 2.4 Myr minimum (see Batenburg et al., 2016) – gave rise to the eccentricity-minimum hypothesis being invoked for the Kellwasser Crisis (De Vleeschouwer et al., 2017; Da Silva et al., 2020; see also De Vleeschouwer et al., 2024).

Wichern et al. (2024) discusses anoxia during the Kellwasser Crisis in more detail; here, the eccentricity-minimum hypothesis is more firmly associated with anoxia. As explained in Wichern et al. (2024), thick regolith could form during a node due to precession-forced monsoonal activity being dampened. The subsequent precession maximum during the next increase in eccentricity after the node would erode and wash away built-up regolith, leading to nutrient input, eutrophication, anoxia, and black shale deposition (Wichern et al., 2024). After anoxia establishment during precession maximum, P-recycling under reducing conditions is hypothesized to have sustained anoxia in absence of high nutrient input (Wichern et al., 2024, see also Percival et al., 2019; 2020; De Vleeschouwer et al., 2024). The eccentricity-minimum hypothesis relies heavily on the top-down hypothesis (Carmichael et al., 2019) for continental shelf settings (Wichern et al., 2024). Ma et al. (2022) present a hypothesis for the Kellwasser Crisis that contrasts the eccentricity-minimum hypothesis. They propose that, during periods of high obliquity and eccentricity, enhanced seasonality would increase weathering and terrestrial input, resulting in marine eutrophication, causing anoxia that triggered the F-F Kellwasser mass extinction.

All existing literature linking Milankovitch forcing and Devonian anoxic events share commonalities: (i) they focus predominantly on the Late Devonian and, (ii) with the exception of De Vleeschouwer et al. (2013), they invoke primarily a top-down mechanism (Carmichael et al., 2019) for anoxia development irrespective of the specific (interpreted) astronomical configuration(s), and (iii) they emphasize cyclostratigraphy, while associated redox conditions are not critically examined. Together, these commonalities provide a relatively straightforward framework for comparing phase relationships identified in this thesis. However, they also underline the pertinent challenges of Devonian cyclostratigraphy; the true phase relationship to insolation is unknown (i.e., no converging astronomical solution for the Devonian), and therefore underlying mechanisms linking astronomically forced insolation to anoxia remain uncertain to some extent. Because multiple orbital extrema can be reconciled with plausible pathways to deoxygenation, phase alignment alone cannot uniquely establish causality. Nonetheless, some mechanisms are more plausible than others when evaluated against physical constraints, response timescales, and the independent evidence available (Meyer and Kump, 2008; Jenkyns, 2010).

1.4. Introduction to Oued Ferkla, Lansing core and West Valley core Records

In this thesis, three primary records have been investigated: the Late Emsian to Middle Givetian Oued Ferkla section (Anti-Atlas, Morocco), the late Silurian to latest Givetian Lansing core (New York State, USA), and the middle Frasnian to early Famennian West Valley core (New York State, USA; Fig. 5).

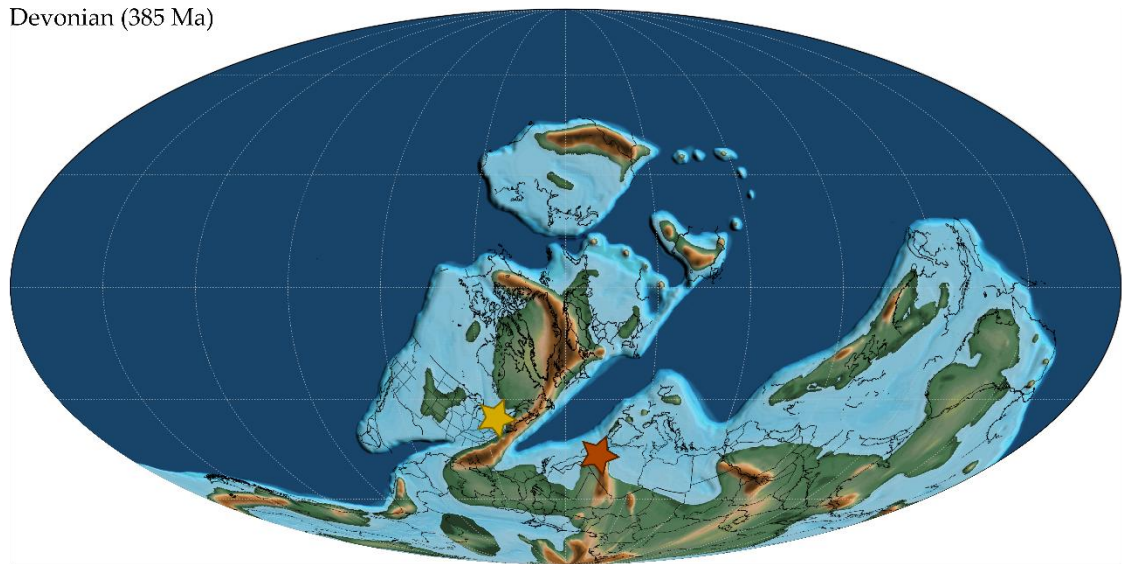


Fig. 5. Paleogeographic reconstruction of the Devonian (385 Ma) by Scotese (2021). The paleodepositional location is marked for Oued Ferkla (Tafilalt Platform, Tisdafine Basin; brown star) and the Lansing and West Valley cores (Appalachian Basin; gold star).

Oued Ferkla is a temporally extensive record that spans approximately 19 Myr and encompasses the global Daleje, Choteč, Kačák, and *pumilio* events (Ward et al., 2013; Becker et al., 2020; Talih et al., 2022). It represents a large, isolated allochthonous glide block derived from the stable Tafilalt carbonate platform and preserves pelagic facies that record environmental conditions on the platform margin and upper slope at $\sim 45^\circ$ S, with facies shifts interpreted to reflect transgression and regression cycles (Ward et al., 2013; Talih et al., 2022). It offers a view on less-investigated Early to Middle Devonian events and their potential link to Milankovitch forcing at precession to multi-Myr timescales. Chapter 2 presents “Geochemical Characterization of the Daleje, Choteč, Kačák, and *pumilio* events at Oued Ferkla (SE Morocco)”, supported by targeted sedimentological assessment to aid interpretation; Chapter 3 “A Six-Million-Year Astronomical Cycle Pacing Early – Middle Devonian Global Events” builds on these geochemical results to develop the cyclostratigraphic framework, focusing on the phase relationships between multi-Myr orbital extrema and the Daleje, Choteč, Kačák, and *pumilio* events.

The Lansing core provides a detailed sedimentary record of the northern Appalachian Basin strata, with investigations focused here on the Emsian to uppermost Givetian interval. Chapter 4 “*Milankovitch forcing and nonlinear climate variability during the Late Givetian*”, submitted to *Climate of the Past*, develops the cyclostratigraphy of the topmost part of the core, the Sherburne Formation, which was deposited in the foredeep of the Appalachian basin at ~30° S paleolatitude. This ~1.2 Myr record encompasses the regional Fir Tree, Hubbard Quarry and Lodi events, offering a view on regional events that lack clear anoxia signatures. Details on the remainder of the Lansing core are provided in the supplementary information (Chapter 9A).

The West Valley core record has been extensively studied by Murphy et al. (2000), Sageman et al. (2003), and Ver Straeten et al. (2011). It spans ~5.7 Myr and encompasses the Rhinestreet, Lower Kellwasser and Upper Kellwasser events as expressed in a distal foreland basin setting deposited at ~30° S paleolatitude. Chapter 5 “*Astronomical control on marine anoxia during the Kellwasser Crisis and Rhinestreet Event*” expands on the already extensive research on this record by developing the cyclostratigraphic framework, assessing the Milankovitch imprint during the Rhinestreet and Kellwasser events, and providing a new cyclostratigraphic model for the Kellwasser Crisis. It is a contribution to a special issue on ‘Oceanic Anoxic Event’ published in *Global and Planetary Change*.

References

- Algeo, T. J. and Liu, J., 2020. A re-assessment of elemental proxies for paleoredox analysis. *Chem. Geol.*; 540, 119549. <https://doi.org/10.1016/j.chemgeo.2020.119549>.
- Algeo, T. J., and Lyons, T. W., 2006. Mo–total organic carbon covariation in modern anoxic marine environments: Implications for analysis of paleoredox and paleohydrographic conditions, *Paleoceanogr.*; 21, PA1016, doi:10.1029/2004PA001112.
- Algeo, T. J. and Scheckler, S. E., 1998. Terrestrial–marine teleconnections in the Devonian: links between the evolution of land plants, weathering processes, and marine anoxic events. *Phil. Trans*; 353, 113–130.
- Algeo, T. J. and Scheckler, S. E., 2010. Land plant evolution and weathering rate changes in the Devonian. *J. Earth Sci.*; 21, 75–78. doi:10.1007/s12583-010-0173-2.
- Algeo, T. J., and Shen, J., 2024. Theory and classification of mass extinction causation. *Natl. Sci. Rev.*, 11, nwad237. doi:10.1093/nsr/nwad237.
- Algeo, T. J., Berner, R. A., Maynard, J. B., Scheckler, S. E., 1995. Late Devonian oceanic anoxic events and biotic crises: “rooted” in the evolution of vascular land plants? *GSA Today*; 5, 3, 45–66.
- Algeo, T. J., Luo, G., Song, H., Y., Lyons, T. W., Canfield, D. E., 2015. Reconstruction of secular variation in seawater sulfate concentrations. *Biogeosc.*; 12, 2131–2151. <https://doi.org/10.5194/bg-12-2131-2015>
- Algeo, T. J., Remírez, M. N., Zhao, H. Schwark, L., Gordon, G., Anbar, A., Bates, S., Lyons, T., Over, D.J., Sageman, B. B., 2026. Transient glacio-eustatic fall and its climato-environmental effects during the Frasnian-Famennian transition. *Glob. Planet. Change*; 256, 105135. <https://doi.org/10.1016/j.gloplacha.2025.105135>
- Arthur M. A., Sageman B. B., 1994. Marine black shales: depositional mechanisms and environments of ancient deposits. *Annu. Rev. Earth Planet. Sci.*; 22:499–551
- Arts, M.C.M., 2023. WaverideR: Extracting Signals from Wavelet Spectra. <https://CRAN.R-project.org/package=WaverideR>
- Arts, M.C.M., Corradini, C., Pondrelli, M., Pas, D., Da Silva, A.-C., 2024. Age and orbital forcing in the upper Silurian Cellon section (Carnic Alps, Austria) uncovered using the WaverideR R package. *Front. Earth Sci.*, 12, <https://doi.org/10.3389/feart.2024.1357751>
- Baird, G. C., Zambito, J. J. VI, Brett, C. E., 2023. Tully Formation and pre-Frasnian Genesee Group succession, 259–378, In: *Devonian of New York, Volume 2: Lower to upper Givetian (Middle Devonian) stage*, Ver Straeten, C. A., Over, D. J., Woodrow, D. (eds.), *Bull. Am. Paleontol.*; 405–406. <https://doi.org/10.32857/bap.2023.405.03>
- Bambach, R. K., 2006. Phanerozoic Biodiversity Mass Extinctions. *Annu. Rev. Earth Planet. Sci.*, 34: 127–55. doi: 10.1146/annurev.earth.33.092203.122654
- Batenburg, S. J., De Vleeschouwer, D., Sprovieri, M., Hilgen, F. J., Gale, A. S., Singer, B. S., Koeberl, C., Cocconi, R., Claeys, P., and Montanari, A., 2016. Orbital control on the timing of oceanic anoxia in the Late Cretaceous. *Clim. Past*, 12, 1995–2009. doi:10.5194/cp-12-1995-2016
- Becker, R. T., Königshof, P., Brett, C. E., 2016. Devonian climate, sea level and evolutionary events: an introduction. In: *Devonian climate, sea level and evolutionary events*, Becker, R. T., Königshof, P., Brett, C. E. (eds.), *Geol. Soc. Lond., Spec. Publ.*, 423, 1–10.
- Becker, R. T., Marshall, J. E. A., Da Silva, A.-C., 2020. The Devonian Period. In: *Gradstein, F. M., Ogg, J. G., Schmitz, M. D. And Ogg, G. (Eds.), The Geologic Time Scale 2020*, chapter 22, 733–810. <https://doi.org/10.1016/B978-0-12-824360-2.00022-X>.
- Bennet, W. W., Canfield, D. E., 2020. Redox-sensitive trace metals as paleoredox proxies: A review and analysis of data from modern sediments. *Earth Sci. Rev.*; 204, 103175. <https://doi.org/10.1016/j.earscirev.2020.103175>.
- Berger, A. L., 1973. La théorie astronomique des paléoclimats, PhD thesis, p315, Université catholique de Louvain. <https://hdl.handle.net/2078.1/233872>

- Berger, A. L., 1987. Long-term variations of caloric insolation resulting from the Earth's orbital elements. *Quat. Res.*; 9, 139-167.
- Berger, A. L., 1988. Milankovitch Theory and Climate. *Rev. Geophys.*; 26, 4, 624-657. <https://doi.org/10.1029/RG026i004p00624>
- Berger, A. L. and Loutre, M. -F., 1990. Origine des fréquences des éléments astronomiques intervenant dans le calcul d'insolation. In: *Bulletin de la Classe des sciences*, 1, 45-106. doi : <https://doi.org/10.3406/barb.1990.38523>
- Berger, A., Loutre, M. -F., Yin, Q., 2010. Total irradiation during any time interval of the year using elliptic integrals. *Quat. Sci. Rev.*; 369, 1, 109660. 10.1016/j.quascirev.2010.05.007
- Berger, A., 2021. Milankovitch, the father of paleoclimate modeling. *Clim. Past.*; 17, 1727-1733. <https://doi.org/10.5194/cp-17-1727-2021>
- Berner, R. A., 2004. *The Phanerozoic Carbon Cycle: CO₂ and O₂*. Oxford University Press, USA.
- Bond, D. P. G. and Grasby, S. E., 2017. On the causes of mass extinctions. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 478, 3-29. <http://dx.doi.org/10.1016/j.palaeo.2016.11.005>
- Bond, D. P. G. and Wignall, P. B., 2008. The role of sea-level change and marine anoxia in the Frasnian-Famennian (Late Devonian) mass extinction. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 263, 107-118. doi:10.1016/j.palaeo.2008.02.015
- Boulila, S., Vahlenkamp, M., De Vleeschouwer, D., Laskar, J., Yamamoto, Y., Pälike, H., Kirtland Turner, S., Sexton, P. F., Westerhold, T., Röhl, U., 2018. Towards a robust and consistent middle Eocene astronomical timescale. *Earth Plan. Sci. Lett.*; 486, 94-107. <https://doi.org/10.1016/j.epsl.2018.01.003>
- Breitburg, D., Levin, L. A., Oschlies, A., Grégoire, M., Chavez, F. P., Conley, D. J., Garçon, V., Gilbert, D., Gutiérrez, D., Isensee, K., Jacinto, G. S., Limburg, K. E., Montes, I., Naqvi, S. W. A., Pitcher, G. C., Rabalais, N. N., Roman, M. R., Rose, K. A., Seibel, B. A., Telszewski, M., Yasuhara, M., Zhang, J., 2018. Declining oxygen in the global ocean and coastal waters. *Science*; 359, 6371. DOI: 10.1126/science.aam7240
- Bretagnon, P., 1974. Termes à longues périodes dans le système solaire, *Astron. Astroph.*, 30, 141-154.
- Brett, C. E., Zambito, J. J. IV, McLaughlin, P. I., Emsbo, P., 2020. Revised perspectives on Devonian biozonation and environmental volatility in the wake of recent time-scale revisions. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 549, 108843. <https://doi.org/10.1016/j.palaeo.2018.06.037>.
- Brugger, J., Hofmann, M., Petri, S., Feulner, G., 2019. On the sensitivity of the Devonian climate to continental configuration, vegetation cover, orbital configuration, CO₂ concentration, and insolation. *Paleoceanogr. Paleoclimatol.*; 34, 1375-1398. <https://doi.org/10.1029/2019PA003562>
- Carmichael, S. K., Waters, J. A., Köningshof, P., Suttner, T. J., Kido, E., 2019. Paleogeography and paleoenvironments of the Late Devonian Kellwasser event: A review of its sedimentological and geochemical expression. *Glob. Planet. Change*; 183, 102984. <https://doi.org/10.1016/j.gloplacha.2019.102984>.
- Clarkson, M. O., Kasemann, S. A., Wood, R., Lenton, T. M., Daines, S. J., Richoz, S., Ohnemüller, F., Meixner, A., Poulton, S. W. and Tipper, E. T., 2015. Ocean acidification and the Permo-Triassic mass extinction. *Science*; 348, 6231, 229-232. <https://doi.org/10.1126/science.aaa0193>
- Cramer, B. D. and Jarvis, I., 2020. Carbon Isotope Stratigraphy. In: Gradstein, F. M., Ogg, J. G., Schmitz, M. D. And Ogg, G. (Eds.), *The Geologic Time Scale 2020*, chapter 11, 309-343. <https://doi.org/10.1016/B978-0-12-824360-2.00011-5>
- Da Silva, A.-C., Sinnesael, M., Claeys, P., Davies, J. H. F. L., de Winter, N. J., Percival, L. M. E., Schaltegger, U., De Vleeschouwer, D., 2020. Anchoring the Late Devonian mass extinction in absolute time by integrating climatic controls and radio-isotopic dating. *Sci. Rep.*; 10, 12940. <https://doi.org/10.1038/s41598-020-69097-6>.
- Dahl, T. W. and Arens, S. K. M., 2020. The impacts of land plant evolution on Earth's climate and oxygenation state – An interdisciplinary review. *Chem. Geol.*; 547, 119665. <https://doi.org/10.1016/j.chemgeo.2020.119665>

- Dahl T. W., Harding, M. A. R., Brugger, J., Feulner, G., Norrman, K., Lomax, B. H., Junium, C. K., 2022. Low atmospheric CO₂ levels before the rise of forested ecosystems. *Nat. Commun.*; 13:7616. <https://doi.org/10.1038/s41467-022-35085-9>
- De Backer T., 2026. Biomonitoring Paleozoic ocean anoxia: how chitinozoan malformations and geochemical anomalies chronicle brine-driven global change. PhD Thesis, Ghent University. Faculty of Sciences. <http://hdl.handle.net/1854/LU-01KFBF76MSG39MA8PG4F3F5YN3>
- De Vleeschouwer, D., Da Silva, A.-C., Boulvain, F., Crucifix, M. & Claeys, P., 2012. Precessional and half-precessional climate forcing of Mid-Devonian monsoon-like dynamics. *Clim. Past.*; 8, 337–351.
- De Vleeschouwer, D., Rakociński, M., Racki, G., Bond, D. P. G., Sobiech, K., Claeys, P., 2013. The astronomical rhythm of Late-Devonian climate change (Kowala section, Holy Cross Mountains, Poland). *Earth Planet. Sci. Lett.*; 365, 25-37. <http://dx.doi.org/10.1016/j.epsl.2013.01.016>.
- De Vleeschouwer, D., Da Silva, A.-C., Sinnesael, M., Chen, D., Day, J. E., Whalen, M. T., Guo, Z., Claeys, P., 2017. Timing and pacing of the Late Devonian mass extinction event regulated by eccentricity and obliquity. *Nat. Comm.*; 8, 2268. doi:10.1038/s41467-017-02407-1.
- De Vleeschouwer, D., Percival, L. M. E., Wichern, N. M. A., Batenburg, S. J., 2024. Pre-Cenozoic cyclostratigraphy and palaeoclimate responses to astronomical forcing. *Nat. Rev. Earth Environ.*; 5, 56-75. <https://doi.org/10.1038/s43017-023-00505-x>.
- Ellwood, B. B., Algeo, T. J., El Hassani, A., Tomkin, J. H., Rowe, H. D., 2011. Defining the timing and duration of the Kačák interval within the Eifelian/Givetian boundary GSSP, Mech Irdane, Morocco, using geochemical and magnetic susceptibility patterns. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 304, 74-78. doi:10.1016/j.palaeo.2010.10.012
- Elrick, M., Berkýová, S., Klapper, G., Sharp, Z., Joachimski, M., Frýda, J., 2009. Stratigraphic and oxygen isotope evidence for My-scale glaciation driving eustasy in the Early-Middle Devonian greenhouse world. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 276, 170-181. doi:10.1016/j.palaeo.2009.03.008
- Emsbo, P., 2017. Sedex brine expulsion to Paleozoic basins may have changed global marine ⁸⁷Sr/⁸⁶Sr values, triggered anoxia, and initiated mass extinctions. *Ore Geol. Rev.*; 86, 474-486. <https://doi.org/10.1016/j.oregeorev.2017.02.031>
- Fang, Q., Wu, H., Hinnov, L. A., Jing, X., Wang, X., Jiang, Q., 2015. Geologic evidence for chaotic behavior of the planets and its constraints on the third-order eustatic sequences at the end of the Late Paleozoic Ice Age. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 440, 848–859. <http://dx.doi.org/10.1016/j.palaeo.2015.10.014>.
- Farhat, M., Laskar, J., Boué, G., 2022. Constraining the Earth's dynamical ellipticity from ice age dynamics. *J. Geophys. Res. Solid Earth*; 127. <https://doi.org/10.1029/2021JB023323>
- Foster, G. L., Royer, D. L., Lunt, D. J., 2015. Future climate forcing potentially without precedent in the last 420 million years. *Nat. Comm.*; 8, 145845. doi: 10.1038/ncomms14845.
- Gérard, J., Sablon, L., Huygh, J. J. C., Da Silva, A.-C., Pohl, A., Vérard, C., Crucifix, M., 2025. Exploring the mechanisms of Devonian oceanic anoxia: impact of ocean dynamics, palaeogeography, and orbital forcing. *Clim. Past*; 21, 239-260. <https://doi.org/10.5194/cp-21-239-2025>.
- Gérard, J., Pohl, A., Sablon, L., Huygh, J. J. C., Da Silva, A.-C., Crucifix, M., 2026. Spatially contrasted response of Devonian anoxia to astronomical forcing. *Clim. Past*; 22, 1003-1021. <https://doi.org/10.5194/cp-22-1003-2026>
- Grice, K., Cao, C., Love, G. D., Böttcher, M. E., Twitchett, R. J., Grosjean, E., Summons, R. E., Turgeon, S. C., Dunning, W., Jin, Y., 2005. Photic zone euxinia during the Permian-Triassic superanoxic event. *Science*; 307, 706-709. 10.1126/science.1104323
- Hays, J. D., Imbrie, J. & Shackleton, N. J., 1976. Variations in the Earth's orbit: pacemaker of the ice ages. *Science* 194, 1121–1132.
- Hedhli, M., Grasby, S. E., Henderson, C. M., Davis, B. J., 2023. Multiple diachronous “Black Seas” mimic global anoxia during the latest Devonian. *Geology*; 51, 973-977. <https://doi.org/10.1130/G51394.1>

- Hinnov, L. A., 2013. Cyclostratigraphy and its revolutionizing applications in the Earth and planetary sciences. *Geol. Soc. Am. Bull.*; 125, 1703–1734.
- Hinnov, L. A., 2018. Cyclostratigraphy and Astrochronology in 2018. *Stratigraphy and Timescales*; 3, 1-64. <https://doi.org/10.1016/bs.sats.2018.08.004>
- Jenkyns, H. C., 2010. Geochemistry of oceanic anoxic events. *Geochem. Geophys. Geosyst.*; 11, Q03004. doi:10.1029/2009GC002788
- Joachimski, M.M. and Buggisch, W., 2002. Conodont apatite $\delta^{18}\text{O}$ signatures indicate climatic cooling as a trigger of the Late Devonian mass extinction. *Geology*; 30: 711-714. [https://doi.org/10.1130/0091-7613\(2002\)030<0711:CAOSIC>2.0.CO;2](https://doi.org/10.1130/0091-7613(2002)030<0711:CAOSIC>2.0.CO;2).
- Joachimski, M. M., Breisig, S., Buggisch, W., Talent, J. A., Mawson, R., Gereke, M., Morrow, J. R., Day, J., Weddige, K., 2009. Devonian climate and reef evolution: Insights from oxygen isotopes in apatite. *Earth Planet. Sci.*; 284, 599-609. doi:10.1016/j.epsl.2009.05.028
- Johnson, J. G., Klapper, G., Sandberg, C. A., 1985. Devonian eustatic fluctuations in Euramerica. *Geol. Soc. Am. Bull.*; 96, 567-587.
- Kabanov, P., 2019. Devonian (c. 388–375 my) Horn River Group of Mackenzie Platform (northwestern Canada) is an open-shelf succession recording oceanic anoxic events. *J. Geol. Soc. Lond.* 176, 29–45.
- Kabanov, P., Hauck, T. E., Gouwy, S. A., Grasby, S. E., van der Boon, A., 2023. Oceanic anoxic events, photic-zone euxinia, and controversy of sea-level fluctuations during the Middle-Late Devonian. *Earth-Sci. Rev.*; 241, 104415. <https://doi.org/10.1016/j.earscirev.2023.104415>
- Kaiser, S. A., Aretz, M., Becker, R. T., 2016. The global Hangenberg Crisis (Devonian-Carboniferous transition): review of a first-order mass extinction. In Becker, R. T., Königshof, P., Brett, C. E., (eds.) *Geol. Soc. London. Spec. Pub.*; 423, 387-437. <http://doi.org/10.1144/SP423.9>
- Kump, L. R., Arthur, M. A., 1999. Interpreting carbon-isotope excursions: carbonates and organic matter. *Chem. Geol.*; 161, 181-198.
- Laskar, J., 1989. A numerical experiment on the chaotic behaviour of the Solar System. *Nature*; 338, 237-238. <https://doi.org/10.1038/338237a0>
- Laskar, J., 1990. The chaotic motion of the solar system: A numerical estimate of the size of the chaotic zones, *Icarus*, 88, 266-291. doi:10.1016/0019-1035(90)90084-m
- Laskar, J., 2020. Astrochronology. In: Gradstein, F. M., Ogg, J. G., Schmitz, M. D. And Ogg, G. (Eds.), *The Geologic Time Scale 2020*, chapter 4, 139-158.
- Laskar, J., Robutel, P., Joutel, F., Gastineau, M., Correia, A. C. M., Levrard, B., 2004. A long-term numerical solution for the insolation quantities of the Earth. *Astron. Astrophys.*; 428, 1, 261-285. <https://doi.org/10.1051/0004-6361:20041335>.
- Laurin, J., Meyers, S. R., Galeotti, S., Lanci, L., 2016. Frequency modulation reveals the phasing of orbital eccentricity during Cretaceous Ocean Anoxic Event II and the Eocene hyperthermals. *Earth Planet. Sci. Lett.*; 442, 143-156. <http://dx.doi.org/10.1016/j.epsl.2016.02.047>
- Li, M., Hinnov, L. A., Kump, L., 2019. Acycle: Time-series analysis software for paleoclimate research and education. *Comput. Geosci.*; 127, 12-22. <https://doi.org/10.1016/j.cageo.2019.02.011>
- Ma, K., Hinnov, L. A., Zhang, X., Gong, Y., 2022. Astronomical climate changes trigger Late Devonian bio- and environmental events in South China. *Glob. Planet. Change*; 215, 103874. <https://doi.org/10.1016/j.gloplacha.2022.103874>.
- Meyer, K. M. and Kump, L. R., 2008. Oceanic euxinia in Earth history: Causes and consequences. *Annu. Rev. Earth Planet Sci.*; 35:251-288. doi: 10.1146/annurev.earth.36.031207.124256
- Meyers, S. R., Sageman, B. B., Hinnov, L. A., 2001. Integrated quantitative stratigraphy of the Cenomanian-Turonian Bridge Creek limestone member using evolutive harmonic analysis and stratigraphic modeling. *J. Sed. Res.*; 71, 4, 628-644. doi:10.1306/012401710628
- Meyers, S. R., 2012. Seeing red in cyclic stratigraphy: Spectral noise estimation for astrochronology. *Paleoc.*; 27, PA3228. doi:10.1029/2012PA002307

- Meyers, S.R., 2014. Astrochron: An R Package for Astrochronology. <https://cran.r-project.org/package=astrochron>
- Meyers, S. R., 2015. The evaluation of eccentricity-related amplitude modulation and bundling in paleoclimate data: An inverse approach for astrochronologic testing and time scale optimization. *Paleoceanogr.*; 30, 12, 1625-1640. <https://doi.org/10.1002/2015PA002850>.
- Meyers, S. R., 2019. Cyclostratigraphy and the problem of astrochronologic testing. *Earth Sci. Rev.*; 190, 190-223. <https://doi.org/10.1016/j.earscirev.2018.11.015>.
- Meyers, S. R., Sageman, B. B., Arthur, M. A., 2012. Obliquity forcing of organic matter accumulation during Oceanic Anoxic Event 2. *Paleoceanogr.*; 27, PA3212. doi:10.1029/2012PA002286.
- Milankovitch, M., 1941. Kanon der Erdbestrahlung und seine Anwendung auf das Eiszeitenproblem, Royal Serbian Academy Special Publication, 133, 1-633
- Murphy, A. E., Sageman, B. B., Hollander, D. J., 2000. Eutrophication by decoupling of the marine biogeochemical cycles of C, N, and P: A mechanism for the Late Devonian mass extinction. *Geology*; 28, 5, 427-430.
- Murray, C. D., Dermott, S. F., 1999. Solar System Dynamics. Cambridge Univ. Press. <https://doi.org/10.1017/CBO9781139174817>
- Neron de Surgy, O., Laskar, J., 1997. On the long term evolution of the spin of the Earth. *Astron. Astrophys.*; 318, 975-989.
- Pälike, H., 2005. Orbital Variation (Including Milankovitch cycles). *Encycl. Geol.*, 410-421. <https://doi.org/10.1016/B0-12-369396-9/00123-4>
- Pas, D., Da Silva, A. -C., Over, D. J., Brett, C. E., Brandt, L., Over, J. -S., Hilgen, F. J., Dekkers, M. J., 2021. Cyclostratigraphic calibration of the Eifelian Stage (Middle Devonian, Appalachian Basin, Western New York, USA). *Geol. Soc. Am. Bull.*; 133, 1/2, 277-286. <https://doi.org/10.1130/B35589.1>.
- Penn, J. L., Deutsch, C., Payne, J. L., Sperling, E. A., 2018. Temperature-dependent hypoxia explains biogeography and severity of end-Permian marine mass extinction. *Science*; 362, 6419. doi: 10.1126/science.aat1327
- Percival, L. M. E., Selby, D., Bond, D. P. G., Rakociński, M., Racki, G., Marynowski, L., Adatte, T., Spangenberg, J. E., Föllmi, K. B., 2019. Pulses of enhanced continental weathering associated with multiple Late Devonian climate perturbations: Evidence from osmium-isotope compositions. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 524, 240-249.
- Percival, L. M. E., Selby, D., Bond, D. P. G., Rakociński, M., Marynowski, L., Hood, A. v. S., Adatte, T., Spangenberg, J. E., Föllmi, K. B., 2020. Phosphorus-cycle disturbances during the Late Devonian anoxic events. *Glob. Planet. Change*; 184, 103070. <https://doi.org/10.1016/j.gloplacha.2019.103070>.
- Pohl, A., Nardin, E., Vandenbroucke, T. R. A., Donnadieu, Y., 2016. High dependence of Ordovician ocean surface circulation on atmospheric CO₂ levels. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 458, 39-51.
- Racki, G., Rakocinski, M., Marynowski, L., Wignall, P. B., 2018. Mercury enrichments and the Frasnian-Famennian biotic crisis: A volcanic trigger proved? *Geology*; 46, 6, 543-546. <https://doi.org/10.1130/G40233.1>
- Racki, G. A., 2020. Volcanic scenario for the Frasnian–Famennian major biotic crisis and other Late Devonian global changes: more answers than questions? *Glob. Planet. Change*; 189, 103174. <https://doi.org/10.1016/j.gloplacha.2020.103174>.
- Raup, D. M. and Sepkoski, J. J., Jr., 1982. Mass extinctions in the marine fossil record. *Science*; 215, 4539, 1501-1503. doi:10.1126/science.215.4539.1501.
- Ruddiman, W. F., 2006. Orbital changes and climate. *Quat. Sci. Rev.*; 25, 23-24, 3092-3112. <https://doi.org/10.1016/j.quascirev.2006.09.001>.
- Sageman, B. B., Murphy, A. E., Werne, J. P., Ver Straeten, C. A., Hollander, D. J., Lyons, T. W., 2003. A tale of shales: the relative roles of production, decomposition, and dilution in the accumulation of organic-

- rich strata, Middle–Upper Devonian, Appalachian basin. *Chem. Geol.*; 195, 229-273. doi:10.1016/S0009-2541(02)00397-2.
- Schlanger, S. O., Jenkyns, H. C., 1976. Cretaceous oceanic anoxic events: causes and consequences. *Geologie en Mijnbouw*; 55, 3-4, 179-184.
- Scotese, C. R., 2021. An atlas of Phanerozoic paleogeographic maps: The seas come in and the seas go out. *Annu. Rev. Earth Planet. Sci.*; 49, 669-718. <https://doi.org/10.1146/annurev-earth-081320-064052>
- Sinnesael, M., De Vleeschouwer, D., Zeeden, C., Batenburg, S. J., Da Silva, A. -C., de Winter, N. J., Dinarès-Turell, J., Drury, A. -J., Gambacorta, G., Hilgen, F. J., Hinnov, L. A., Hudson, A. J. L., Kemp, D. B., Lantink, M. L., Laurin, J., Li, M., Liebrand, D., Ma, C., Meyers, S. R., Monkenbusch, J., Montanari, A., Nohl, T., Pälke, H., Pas, D., Ruhl, M., Thibault, N., Vahlenkamp, M., Valero, L., Wouters, S., Wu, H., Claeys, P., 2019a. The Cyclostratigraphy Intercomparison Project (CIP): consistency, merits and pitfalls. *Earth-Sci. Rev.* 199, 102965. <https://doi.org/10.1016/j.earscirev.2019.102965>
- Slavik, L., Hladil, J., 2020. Early Devonian (Lochkovian – Early Emsian) bioevents and conodont response in the Prague Synform (Czech Republic). *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 549, 109148. <https://doi.org/10.1016/j.palaeo.2019.04.004>
- Smart, M. S., Filippelli, G., Gilhooly, W. P. III, 2023. Enhanced terrestrial nutrient release during the Devonian emergence and expansion of forests: evidence from lacustrine phosphorus and geochemical records. *Geol. Soc. Am. Bull.*; 135: 1879-1898. <https://doi.org/10.1130/B36384.1>.
- Smith D. G., 2020. Misplaced confidence: limits to statistical inference in cyclostratigraphy. *Boletín Geológico y Minero*; 131, 2, 291-307.
- Smith, D. G., 2023. The Orbital Cycle Factory: Sixty cyclostratigraphic spectra in need of re-evaluation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 628, 111744. <https://doi.org/10.1016/j.palaeo.2023.111744>.
- Stein, W. E., Berry, C. M., VanAller Hernick, L., Mannolini, F., 2012. Surprisingly complex community discovered in the mid-Devonian fossil forest at Gilboa. *Nature*; 483, 78-81. doi:10.1038/nature10819
- Stein, W. E., Berry, C. M., Morris, J. L., VanAller Hernick, L., Mannolini, F., Ver Straeten, C., Landing, E., Marshall, J. E. A., Wellman, C. H., Beerling, D. J., Leake, J. R., 2020. Mid-Devonian *Archeopteris* roots signal revolutionary change in earliest fossil forests. *Curr. Biol.*; 30, 1-11. doi:10.1016/j.cub.2019.11.067
- Strasser, A., Hilgen, F. J., Heckel, P. H., 2006. Cyclostratigraphy – concepts, definitions, and applications. *News. Stratigr.*; 42, 2, 75-115. doi: 10.1127/0078-0421/2006/0042-0075
- Talih, A., Aboussalam, S. Z., Becker, R. T., Saadi, M., Benmlih, A., 2022. Stratigraphy and tectono-sedimentary processes of allochthonous and autochthonous Devonian deposits of the Tisdafine Basin, Eastern Anti-Atlas, Morocco. *Bulletin de l'Institut Scientifique, Rabat, Section Sciences de la Terre*; 44, 27-53. e-ISSN : 2458-7184
- Thomson, D. J., 1982. Spectrum estimation and harmonic analysis. *Proc. IEEE*; 70, 9, 1055-1096.
- Tribouillard, N., Algeo, T. J., Lyons, T., Riboulleau, A., 2006. Trace metals as paleoredox and paleoproductivity proxies: An update. *Chem. Geol.*; 232, 12-32. doi:10.1016/j.chemgeo.2006.02.012
- Tyson, R. V., Pearson, T. H., 1991. Modern and ancient continental shelf anoxia: an overview. *Geol. Soc. Lond. Spec. Publ.*; 58, 1-24. <https://doi.org/10.1144/GSL.SP.1991.058.01.01>
- Ver Straeten, C. A., 2023. An introduction to the Devonian Period, and the Devonian in New York State and North America. In: Ver Straeten, C. A., Over, D. J. and Woodrow, D. (Eds.), *Devonian of New York, Volume 1: Introduction and Přídolí to lower Givetian (Upper Silurian to Middle Devonian) stages*. *Bull. Am. Paleontol.*; 403-404. doi:10.32857/bap.2023.403.03.
- Ver Straeten, C. A., Brett, C. E., Sageman, B. B., 2011. Mudrock sequence stratigraphy: A multi-proxy (sedimentological, paleobiological and geochemical) approach, Devonian Appalachian Basin. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 304, 54-73. doi:10.1016/j.palaeo.2010.10.010.
- Vérard, C., 2019. Panalexis: towards global synthetic palaeoceanographies using integration and coupling of manifold models. *Geol. Mag.*; 156, 2, 320-330. <https://doi.org/10.1017/S0016756817001042>

- Walliser, O. H., 1996. Global events and event stratigraphy. ISBN-13: 978-3-642-79636-4. Springer; 225-250. doi:10.1007/978-3-642-79634-0.
- Ward, P. D., Becker, R. T., Aboussalam, S. Z., Rytina, M., Stichling, S., 2013. The Devonian at Oued Ferkla (Tinejdad region, SE Morocco). International Field Symposium "The Devonian and Lower Carboniferous of northern Gondwana, Morocco 2013; 23-30.
- Weedon, G. P., 2022. Problems with the current practice of spectral analysis in cyclostratigraphy: Avoiding false detection of regular cyclicity. *Earth Sci. Rev.*; 235, 104261. <https://doi.org/10.1016/j.earscirev.2022.104261>.
- Westphal, H., Lavi, J., Munnecke, A., 2015. Diagenesis makes the impossible come true: intersecting beds in calcareous turbidites. *Facies*; 61:3, 1-7. doi:10.1007/s10347-015-0427-7
- Wichern, N. M. A., Bialik, O. M., Nohl, T., Percival, L. M. E., Becker, T. R., Kaskes, P., Claeys, P., De Vleeschouwer, D., 2024. Astronomically paced climate and carbon cycle feedbacks in the lead-up to the Late Devonian Kellwasser Crisis. *Clim. Past*; 20, 415-448. <https://doi.org/10.5194/cp-20-415-2024>
- Wichern, N., Becker, R. T., Bialik, O. M., Hartenfels, S., De Vleeschouwer, D., 2026. Cyclostratigraphic calibration of the rhythmically bedded upper Frasnian (upper Devonian) in the Rhenish Massif, Germany. *Newslett. Stratigr.*; DOI: 10.1127/nos/2026/0908
- Wignall, P. B., Myers, K. J., 1988. Interpreting benthic oxygen levels in mudrocks: A new approach. *Geology*; 16, 452-455.
- Wignall, P. B., 1994. *Black Shales*. Clarendon Press Oxford. ISBN 0198540388.
- Wilde, P., Berry, W., 1984. Destabilization of the oceanic density structure and its significance to marine "extinction" events. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 48, 2, 143-162.
- Zeebe, R. E. and Lantink, M. L., 2024. A secular solar system resonance that disrupts the dominant cycle in Earth's orbital eccentricity ($g_2 - g_5$): Implications for astrochronology. *Astron. J.*; 167:204. <https://doi.org/10.3847/1538-3881/ad32cf>.
- Zeebe, R. E., Lourens, L. J., 2019. Solar system chaos and the Paleocene-Eocene boundary age constrained by geology and astronomy. *Science*; 365, 926-929. 10.1126/science.aax0612
- Zeeden, C., Meyers, S., Hilgen, F., Lourens, L., Laskar, J., 2019. Time scale evaluation and the quantification of obliquity forcing. *Quat. Sci. Rev.*; 209, 100-113. <https://doi.org/10.1016/j.quascirev.2019.01.018>.
- Zheng, W., Gilleaudeau, G. J., Algeo, T. J., Zhao, Y., Song, Y., Zhang, Y., Sahoo, S. K., Anbar, A. D., Carmichael, S. K., Xie, S., Liu, C. -Q., Chen, J., 2023. Mercury isotope evidence for recurrent photic-zone euxinia triggered by enhanced terrestrial nutrient inputs during the Late Devonian mass extinction. *Earth Planet. Sci. Lett.*; 613, 118175. <https://doi.org/10.1016/j.epsl.2023.118175>

2. Geochemistry of the Daleje, Choteč, Kačák, and *pumilio* events (Oued Ferkla, SE Morocco) – *in preparation*.

Jarno J.C. Huygh¹, Amine Talih², Hamdi Omar^{1,3,4}, Dhoha Boukhalfa¹, Justin Gérard⁵, Loïc Sablon⁵, Michiel Arts¹, Ahmed El Hassani⁶, Michel Crucifix⁵ and Anne-Christine Da Silva¹

¹ SediCClim Laboratory, Department of Geology, Liège University, Liège, Belgium

² Geo-Biodiversity and Natural Patrimony Laboratory (GEOBIO), Geophysics, Natural Patrimony and Green Chemistry, Research Center (GEOPAC), Scientific Institute, Mohammed V University, Rabat-Agdal, Morocco

³ Department of Atmospheric, Oceanic and Earth Science, George Mason University, Fairfax, USA

⁴ Department of Geology, Ghent University, Ghent, Belgium

⁵ Earth and Life Institute, UCLouvain, Louvain-la-Neuve, Belgium

⁶ Hassan II Academy of Science and Technology, Rabat, Morocco

Corresponding author: Jarno Huygh (jarno.huygh@uliege.be; jarno.huygh@hotmail.com)

Key Points:

- A methodological framework for the geochemical characterization of heterogeneous sedimentary records
- Newly developed Multi-scale Rolling Correlation Analysis producing 2D Pearson-correlation maps for any proxy pair
- Chemozone- and lithology-specific bi- and multivariate analysis of major and trace element concentrations and carbon and oxygen isotope signals
- Characterization of diagenetic, detrital, and redox signatures across the Daleje, Choteč, Kačák, and *pumilio* events

Abstract

The Early to Middle Devonian was punctuated by environmental perturbations, including the global Daleje, Choteč, Kačák, and *pumilio* events. Yet, their stratigraphic expression is highly variable, in part because these events themselves are accompanied by sometimes drastic facies shifts, causing strong heterogeneity in the sections that record them. This study develops an interval-specific, multi-proxy geochemical workflow tailored to such heterogeneous sedimentary records. The approach developed here integrates lithological observations, thin-section petrography, semi-quantitative pXRF, bi- and multivariate analyses of major and trace element concentrations, and carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data. A new Multi-scale Rolling Correlation Analysis generates 2D Pearson correlation maps for any proxy pair, enabling robust, scale-dependent assessment of proxy behavior. Lithology- and chemozone-specific analyses further ensure that geochemical signals are evaluated within internally coherent intervals – so-called chemozones – rather than across facies-driven heterogeneity. Applied to the late Emsian – middle Givetian Oued Ferkla section, this framework enables disentangling diagenetic, detrital, and redox controls and resolves key environmental patterns across the Devonian events. The Daleje interval records increased fine-grained detrital influx and reducing to possibly transient euxinic conditions; the Choteč Event occurs during a period of pulsed increases in fine-grained detrital input, yet is comparatively subdued in comparison and shows no evidence of anoxia; a Mid-Eifelian Oxygenation Event is tentatively identified; the Kačák interval reflects strong pulses of fine-grained detrital material and moderately reducing conditions; and the *pumilio* Event beds record detrital-depleted, productivity-driven reducing conditions likely reflecting eutrophication episodes. The workflow presented here provides a transferable strategy for interpreting complex sedimentary archives while emphasizing the need for record-specific proxy evaluation.

Keywords: Devonian; Elemental Geochemistry; pXRF; Correlation Analysis

2.1. Introduction

The Early to Middle Devonian is characterized by multiple global-scale environmental perturbations, often associated with sea-level variations, faunal turnover, and anoxia (Becker et al., 2020). In comparison to the well-studied mass-extinction episodes such as Kellwasser Crisis and Hangenberg Event, these intervals have received considerably less attention. Moreover, most studies dedicated to Early to Middle Devonian events focus primarily on sedimentology and (conodont) biostratigraphy (e.g., García-Alcalde et al., 1997; Aboussalam et al., 2015; Jamart and Denayer, 2020; Slavík and Hladil, 2020). However, aside from carbon isotope (e.g., Buggisch and Mann, 2004; Buggisch and Joachimski, 2006) and oxygen isotope chemostratigraphy (e.g., Joachimski et al., 2009), few studies investigate their geochemical signatures (e.g., Duchesne et al., 2017). Yet, understanding the geochemical expression of these event intervals is important because many of the environmental processes implicated in the Early to Middle Devonian events leave diagnostic chemical signatures in the sedimentary record, including evidence of changes to detrital influx, paleoproductivity shifts, and redox fluctuations (Tribovillard et al., 2006; Calvert and Pedersen, 2007; Croudace and Rothwell, 2015; Becker et al., 2020). Such signatures provide important constraints that complement sedimentological, lithostratigraphic, and biostratigraphic evidence, thereby refining interpretations of these events.

Reconstructing environmental change across Devonian event intervals using a geochemical approach remains a persistent challenge, particularly in mixed carbonate–siliciclastic successions where proxy signals are strongly influenced by facies shifts, variable detrital input, and, potentially, diagenetic overprinting. Although many studies have documented major Devonian paleoenvironmental events (e.g., Ellwood et al., 2011; Whalen et al., 2015; Kabanov et al., 2023), the interpretation of geochemical datasets from such heterogeneous successions often relies on bulk trends or single-proxy approaches that implicitly assume stable geochemical controls through time – an assumption that is rarely valid. Treating such successions as geochemically uniform obscures these internal structures and can lead to misleading paleoenvironmental interpretations. Moreover, adopting proxy interpretations, such as major and trace element (ratios) following widely used frameworks (e.g., Calvert and Pedersen, 2007; Croudace and Rothwell, 2015) requires explicit validation. In practice, however, such validation is rarely performed, and proxy interpretations are often accepted on the basis of established usage rather than demonstrated behavior within the specific lithological and stratigraphic context. Formation-specific establishment of redox thresholds in paleoredox studies was already emphasized by Algeo and Liu (2020), who also argued against the use of fixed redox thresholds (Bennett and Canfield, 2020). This logic extends beyond redox proxies and applies broadly to any geochemical indicator whose behavior may vary across facies or time.

Semi-quantitative X-ray fluorescence (XRF) techniques (e.g., portable XRF; pXRF) provide a broad suite of potential paleoclimatic and paleodepositional proxies (e.g., Croudace and Rothwell, 2015), yet their application in stratigraphy seldom accounts for internal shifts in geochemical control. A key limitation in many existing studies using such proxies is the lack of interval-specific multivariate evaluation of geochemical behavior (e.g., Ma et al., 2008; 2022 Lash, 2017; He et al., 2022; Liu et al., 2024a, b). In the studies that use multivariate statistical tools such as PCA, these are used across entire or even multiple sections (e.g., Bábek et al., 2016; Duchesne et al., 2017), implicitly assuming static relationships among proxies despite clear evidence that such relationships vary with facies, mineralogy, and diagenetic overprint.

These challenges highlight the need for approaches that explicitly evaluate proxy behavior within internally coherent intervals (e.g., Sageman et al., 2003) rather than across entire heterogeneous successions (e.g., Lash, 2017; Liu et al., 2024a, b). Heterogeneous, mixed successions commonly contain coherent geochemical intervals on smaller scales within which elemental relationships, redox indicators, and detrital fingerprints behave relatively consistently, but which differ markedly from adjacent intervals: chemozones (cf. Ramkumar, 2015). A chemozone-based multivariate statistical analysis provides such a framework by isolating stratigraphic intervals in which geochemical controls remain relatively stable. Within such chemozones, elemental associations, redox indicators, and detrital fingerprints can be interpreted more reliably, while transitions between chemozones capture shifts in environmental, depositional, or diagenetic conditions. Importantly, where chemozones contain multiple lithologies, a lithology-specific approach is required to ensure accurate and robust interpretation of geochemical proxy behavior.

However, even within a chemozone, the dominant controls on geochemical signals may evolve through time. Traditional multivariate tools such as PCA or correlation matrices (e.g., Pearson Correlation Coefficient Matrices; PCCM) provide only static snapshots of proxy relationships and therefore cannot capture well how these relationships shift across stratigraphic space. To address this limitation, we employ a bivariate moving-window Pearson correlation framework (cf. Sageman and Hollander, 1999; Yuan et al., 2016; Oehlert and Swart, 2019), implemented here as Multi-scale Rolling Correlation Analysis (MRCA). MRCA reveals and quantifies changes in elemental and isotopic associations across sliding windows of increasing size. This way, MRCA captures the evolution of processes governing geochemical variability – whether driven by shifts in detrital influx or redox conditions. This dynamic approach offers a complement to interval- and lithology-specific multivariate (PCA, PCCM) by identifying where and when proxy behavior changes, thereby providing a more resolved basis for paleoenvironmental interpretation.

The Oued Ferkla section in the eastern Anti-Atlas of Morocco provides an ideal setting to evaluate this interval- and lithology-specific approach combined with dynamic correlation testing using MRCA. Spanning the late Emsian to middle Givetian, it encompasses a succession of globally significant Devonian events – including the Daleje, Choteč, Kačák and *pumilio* intervals – expressed within a mixed carbonate-siliciclastic system characterized by pronounced facies variability on different scales (Ward et al., 2013; Talih et al., 2022). The section contains thick shale-marl packages, episodic limestone beds, and multiple redox-sensitive intervals, all of which make the interpretation of major and trace element proxy signals challenging. Despite its exceptional quality and temporal span of approximately 19 Myr (Becker et al., 2020, in addition to well-studied microfacies (incl. fossil assemblages) and depositional setting (Talih et al., 2022), Oued Ferkla has received no geochemical attention. Its combination of lithological heterogeneity and multiple global event horizons makes it an excellent test case for assessing how our approach can refine reconstructions of Devonian environmental change, and for developing interpretations and hypotheses that are directly and transparently supported by the structure of the geochemical data. More broadly, this interval-specific, dynamic-correlation framework offers a generalizable methodology for disentangling shifting geochemical controls in any heterogeneous stratigraphic succession, extending well beyond the Devonian or mixed-lithology settings.

2.2. Geological Setting

The Oued Ferkla section is located about 3 km north of Tinejdad (Drâa-Tafilalet region) in the Tisdafine Basin (Eastern Anti-Atlas, Morocco; 31.5369° N, 05.0106° W) and represents approximately 43 m of upper Emsian to middle Givetian strata. It is dominated by limestones which are periodically interrupted or intercalated by marly to shaly facies – often in association with the transgressive Devonian anoxic events (*sensu* Becker et al., 2020, see also Talih et al., 2022). Outcrops are exposed along the northern bank of the seasonal river Oued Ferkla, as well as along the N10 road cut (Fig. 1). The strata are well exposed thanks to the lack of vegetation and are tilted at about 35° to 45°, dipped in the north to northwestern direction.

Deposition occurred at appr. 45° S paleolatitude during a period of tectonic quiescence, prior to the Eovariscan tilted block tectonics during the Famennian-Tournaisian (Talih et al., 2022). Given the strong similarity to the Tafilalt platform, the Oued Ferkla section most likely represents an allochthonous unit (glide block) transported during post-depositional tectonic activity (Talih et al., 2022). Consequently, it is subdivided into ten generic lithostratigraphic units (OF1 to OF10) rather than formalized formations and members. Deposition of Oued Ferkla strata was highly influenced by eustatic sea-level changes, causing a shift from condensed shallow pelagic platform/upper ramp (OF4, OF6, OF7, and OF9), pelagic lower ramp or slope (OF3, OF5, parts of OF6, OF10), and pelagic shelf basin with restricted oxygenation (OF2 and OF8) (Talih et al., 2022).

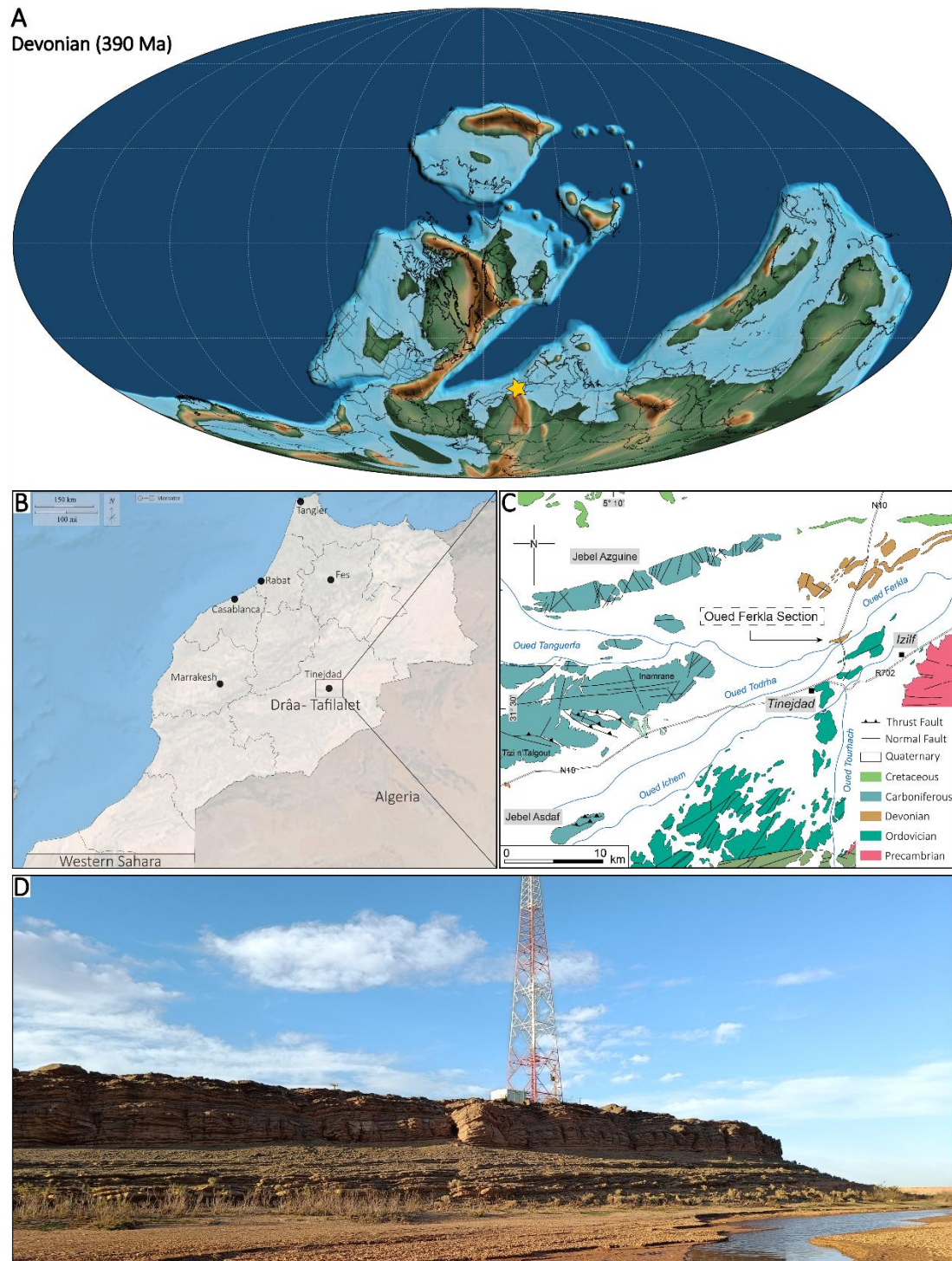


Fig. 1. Geological setting of Oued Ferkla. A) Paleogeographic map of the late Early Devonian (390 Ma) (Scotese, 2021). B) Map of Morocco, adopted from d-maps.com and google.maps.com. C) Local geological map of the Tinejdad region (1/200.000, adapted from Destombes et al., 1988 and Talih et al., 2022). D) Oued Ferkla section.

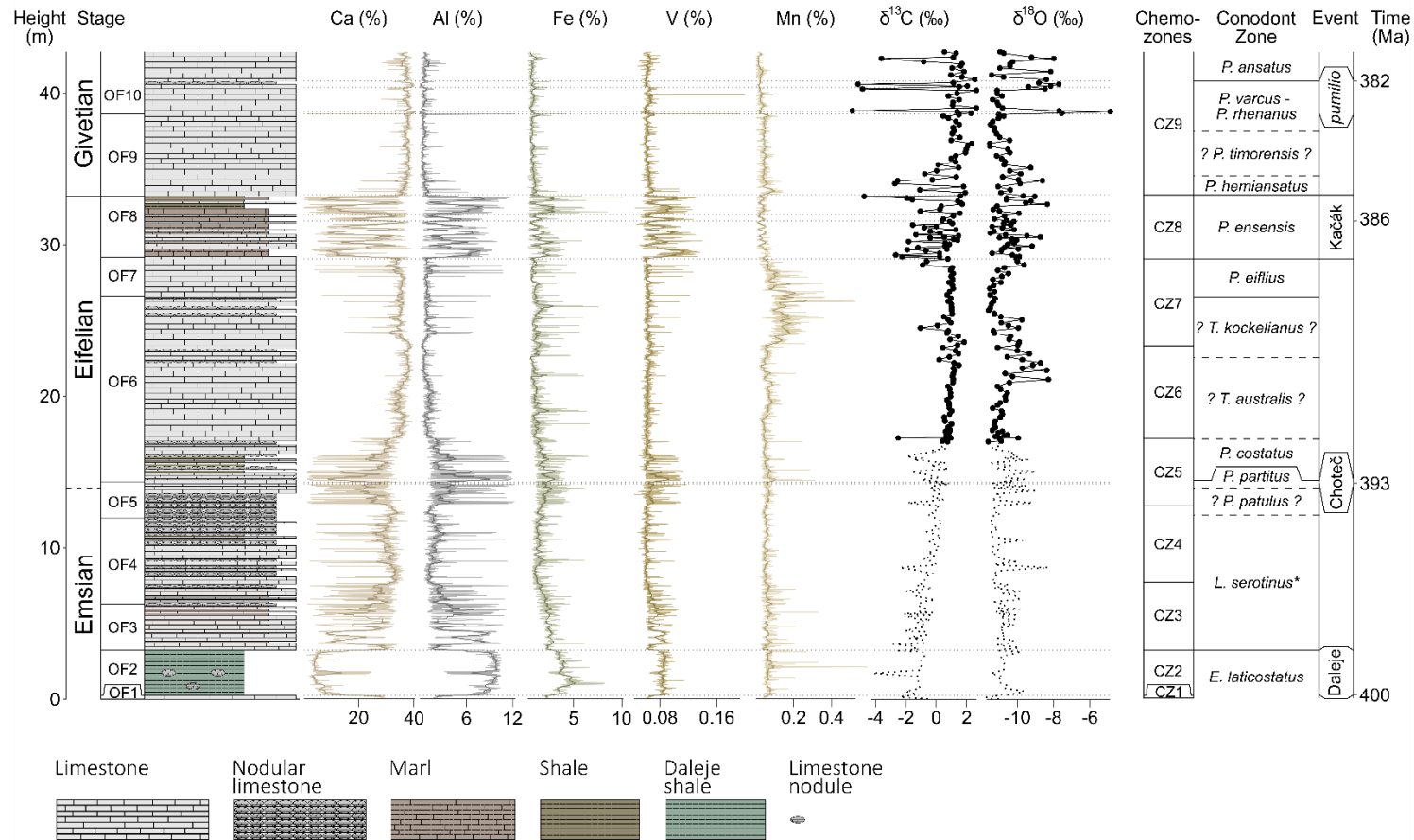


Fig. 2. Integrated stratigraphy of Oued Ferkla. Chronostratigraphy, lithologic column detailing limestone, nodular limestone, marl, shale and greenish shales of the Daleje interval, and limestone nodules, and lithostratigraphic units Oued Ferkla 1 (OF1) to OF10 based on Talih et al. (2022). Element profiles for Ca, Al, Fe, V, Mn, and $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ (dashed lines highlight interval suspected to have diagenetically overprinted isotopic signals). Chemozonation defined in this work (see explanation in text). Conodont zonation biostratigraphy based on Talih et al. (2022), dashed lines indicate uncertain conodont zone boundaries, “?” indicate conodont zones not formally determined at Oued Ferkla based on conodont work by Talih et al. (2022) but inferred based on Becker et al. (2020). * Indicate inferred conodont zonation based on ammonoid zonation (Becker et al., 2020; Talih et al., 2022). Event intervals based on Ward et al. (2013) and Talih et al. (2022). Absolute ages provided are based on Becker et al. (2020) and Talih et al. (2022).

Unit OF1 marks the lowermost documented part of the section and comprises two distinct limestone beds assigned to the middle Emsian (*E. laticostatus* conodont Zone; Becker et al., 2020; Talih et al., 2022). These limestone beds, once level with the edge of the riverbed (e.g. Ward et al., 2013), are now covered by anthropogenic sandy material. However, during excavation of the lowermost OF1 limestone beds, more greenish shales – visually similar to those of unit OF2 (i.e., Daleje interval; cf. Ward et al., 2013; Talih et al., 2022) – were identified just below (see Fig. B1) but were not further investigated to date.

At Oued Ferkla, the Daleje Event is marked by greenish shale facies (OF2) containing early diagenetic pyrite and isolated diagenetic limestone nodules (Talih et al., 2022). These strata represent the local expression of the late Emsian-aged ‘anoxic’ Daleje Event, which is associated with a gradual transgressive phase across the European-North African realms (Becker et al., 2020). First defined in the Barrandian area, the Daleje Event is recognized as a third-order bioevent (Brett et al., 2020) linked to extinction and a major transgressive pulse (House, 1985) that led to the deposition of gray-greenish, sometimes calcareous, Daleje Shale facies (Chlupač and Kukal, 1986; 1988; Ferrová et al., 2012). It is well documented throughout the eastern Anti-Atlas (Becker and House, 1994; Aboussalam et al., 2015). Overlying the Daleje Event shales at Oued Ferkla are alternating limestone, marly-to-shaly, and nodular limestone facies, which dominate units OF3 (*L. serotinus* conodont Zone) and OF4 (*Anarcestes ammonoid* Zone), followed by unit OF5 assigned to the upper part of the *L. serotinus* Zone (Aboussalam et al., 2015; Talih et al., 2022).

The ‘basal’ Choteč Event (House, 1985; Chlupač and Kukal, 1986; 1988; Walliser, 1996; Brocke et al., 2016) is recognized at the top of unit OF5 by a thin dark microcrystalline limestone overlain by marl (uppermost *P. partitus* conodont Zone; Talih et al., 2022). This early Eifelian event is a 3rd-order bioevent (Brett et al., 2020), associated with faunal turnover/extinction (*jugleri* Event; Walliser 1985; 1996), regression followed by rapid transgression (eustatic sea-level rise; Koptíková, 2011), onset of dysoxia to anoxia, and a moderate pCIE (Buggisch and Mann, 2004; Brocke et al., 2016; Becker et al., 2020; Kabanov et al., 2023). To date, no conodont assemblages indicative of the *P. patulus* conodont Zone (Becker et al., 2020) have been recovered, meaning the *P. patulus* to *P. partitus* conodont Zone transition – which marks the Emsian-Eifelian boundary – remains to be precisely identified at Oued Ferkla (Talih et al., 2022). Importantly, however, no field evidence for a hiatus or unconformity within unit OF5 was observed. The lower to upper Eifelian-aged strata of Oued Ferkla are dominated by limestone and nodular limestone facies of unit OF6 (*P. costatus* conodont Zone) and well-oxygenated pelagic limestones of unit OF7 (*Cabrieroceras* to *Agoniatites* ammonoid zones, *T. kockelianus* to *P. eiflii* conodont zones) that mark the immediate pre-Kačák Event interval (Talih et al., 2022).

Strongly alternating dark gray laminated limestone and fissile, shaly-marly beds indicate the Kačák Event interval (*P. ensensis* conodont Zone; Talih et al., 2022). Eutrophic conditions persisted during this interval, witnessed by extensive laminations of black marl and shale facies indicating faunal blooms, anoxia and transgression (Talih et al., 2022; Fig. B2). Like the preceding Daleje and Choteč events, the Kačák Event interval (House, 1985) is generally associated with faunal turnover (extinction followed by rapid radiation), transgression, and associated anoxia (Chlupač and Kukal, 1986; 1988; Jamart and Denayer, 2020). As emphasized by Walliser (1996), the ‘broader’ Kačák Event (*sensu* House, 1985) is subdivided into two distinct extinction intervals: the *otomari* or Lower Kačák Event and the Upper Kačák Event (i.e., Kačák Event *sensu strictu*; Walliser, 1996). Although visually similar, the Lower and Upper Kačák Event intervals can be distinguished at Oued Ferkla (Ward et al., 2013; Talih et al., 2022). The Eifelian-Givetian boundary (*P. ensensis* to *P. hemiansatus* conodont Zone transition; Becker et al., 2020) coincides with the upper boundary of the Upper Kačák Event (Walliser, 1996), which is marked by the transition of shaly facies (top of OF8) to a ~30 cm-thick limestone bed at the base of OF9 assigned to the *P. hemiansatus* conodont Zone (Talih et al., 2022).

The Givetian-aged strata of units OF9 and OF10 are dominated by massive and nodular limestones, occasionally intercalated by very thin (1-2 cm-thick) marly to shaly layers. The uppermost strata of unit OF9 are assigned to the *P. rhenanus-varcus* conodont Zone (Talih et al., 2022), indicating lower middle Givetian strata (Becker et al., 2020). This interval encompasses the *pumilio* events, which are minor bioevents (Brett et al., 2020) not typically associated with extinction (Walliser, 1996). The Lower *pumilio* Event marks the transition from OF9 to OF10 (upper *P. rhenanus-varcus* conodont Zone; Talih et al., 2022). Similar to their expression at the neighboring Bou Tchrafine section (Lottmann, 1990b), at Oued Ferkla, the Lower *pumilio* Event is expressed as a massive dark limestone, while the Upper *pumilio* Event appears as two distinct *pumilio* dark limestone beds interrupted by shaly facies. These middle Givetian events represent small-scale global bio-events, named after the sudden bloom of brachiopods (e.g. *Ense pumilio*) (Roemer, 1855; Denckmann, 1892; Lottmann, 1990a; Brett et al., 2020; Becker et al., 2020).

The uppermost documented strata of the section fall within the *P. ansatus* conodont Zone (Talih et al., 2022). Although overlying strata are accessible, these were not further investigated as their overall quality is very poor. However, given that Frasnian-aged strata were recognized 50 m to the north (Talih et al., 2022), it is very likely that these low-quality strata represent the onset of the Taghanic transgression, which incidentally occurs within the *P. ansatus* conodont Zone, which directly overlies the *P. rhenanus-varcus* conodont Zone (Becker et al., 2020). More detailed description of lithology, sedimentary structures and microfacies of the entire Oued Ferkla section can be found in Talih et al. (2022).

2.3. Materials and Methods

2.3.1. Sampling

Sampling was carried out using a generator-powered circular saw, hammer and chisel. All samples (ranging from small sub-cm-thick pieces of shale to 30-cm-thick limestone slabs), representing a continuous record of the entire Oued Ferkla section, were cleaned and polished prior to sub-sampling and measurements. Further sub-sampling was carried out on cleaned samples for thin-section petrography (Suppl. C).

2.3.2. Portable X-ray Fluorescence

Major and trace element concentrations (Mg, Al, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Zr, Ba) were measured ($n = 5601$) at the SediCClim laboratory, Liège University, Belgium using a Bruker Tracer 5 g portable X-ray Fluorescence (pXRF) spectrometer, equipped with a Rh X-ray source (4 W, 200 μ A, 50 kV) and a silicon drift detector (20 mm²) with a 1 μ m graphene window and a spectral resolution under 140 eV at 250000 cps (on the Mn K α spectral line) (Da Silva et al., 2023). Elemental concentrations (expressed in weight per cent; wt%; Suppl. D) were obtained through calibration and validation using in-house standard reference materials (Da Silva et al., 2023). For selected elements (Mg, Mn, Cu, Zn, Rb, Sr, Zr), an additional slope bias correction, derived through linear regression after validation using in-house standard reference materials, was applied to refine semi-quantitative estimates. Despite extensive in-house calibration and validation efforts, pXRF-derived concentrations are considered semi-quantitative. Therefore, relative variations in elemental abundances and element ratio proxies are interpreted rather than absolute threshold values. Moreover, P appears depleted in limestones, which can most likely be attributed to analytical limitations rather than to a real geochemical signature and is therefore interpreted cautiously. After manual removal of outliers – mostly due to a poor sample surface quality – 5318 datapoints were retained for further analysis. The average sampling resolution of the elemental dataset is 0.8 cm.

2.3.3. Stable Carbon and Oxygen Isotopes

Powders for carbon and oxygen isotope measurements ($n = 282$) were collected using a drill (limestones) or pestle and mortar (marls and shales) from cleaned samples. Carbonate carbon $\delta^{13}\text{C}_{\text{carb}}$ and oxygen $\delta^{18}\text{O}_{\text{carb}}$ isotopic composition were measured at Erlangen University, under the following protocol: Carbonate powders were reacted with 100% phosphoric acid at 70 °C using a Gasbench II connected to a ThermoFisher Delta V Plus mass spectrometer. All values are reported per mil relative to V-PDB. Reproducibility and accuracy was monitored by replicate analysis of laboratory standards calibrated by assigning a $\delta^{13}\text{C}$ of +1.95‰ to NBS19 and -47.3‰ to IAEA CO9 and a $\delta^{18}\text{O}$ of -2.20‰ to NBS19 and -23.2‰ to NBS18. The sampling

resolution of the stable isotope record is variable (< 1 to 20 cm), with highest resolution around event intervals.

2.3.4. Statistical Approaches

All statistical analysis was carried out in R Studio 2025.05.0 Build 496. Principal component analysis (PCA) was carried out on z-scored, log-transformed proxy series to reduce dimensionality. Because a full-section PCA (Fig. E1) mixes geochemical regimes across several major facies transitions, PCA is carried out on the two most abundant (groups of) lithologies per distinct geochemical interval (hereafter referred to as ‘chemozones’, numbered CZ1 to CZ10; Fig. 2, 3). This way, it provides a lithology-specific geochemical fingerprint allowing for interval and lithology-specific analysis. To aid interpretation of PCA loading patterns, Pearson correlation coefficient matrices (PCCM; Suppl. F) were computed to highlight statistically significant linear relationships between geochemical proxies, which are visualized using element cross-plots.

Multi-scale rolling correlation analysis (MRCA) was developed to detect statistically significant localized Pearson correlation coefficients (PCC) between two proxy series across multiple scales (Suppl. G). This approach applies a moving-window PCC framework (cf., Sageman and Hollander, 1999; Yuan et al., 2016; Oehlert and Swart, 2019) with incrementally increasing window sizes, creating a two-dimensional correlation map. Prior to MRCA, all proxy series were linearly interpolated to equal sample spacing (0.8 cm), log-transformed to reduce skewness and stabilize variance, and z-scored to center and scale the data. These preprocessing steps were implemented to ensure comparability across proxies and facies. Detrending was not applied, specifically to preserve large-scale variation and non-stationary behavior (cf. Oehlert and Swart, 2019). This approach enables objective comparison of the relationship between two proxies and is particularly effective for identifying transitions or coupling zones across the entire stratigraphic record.

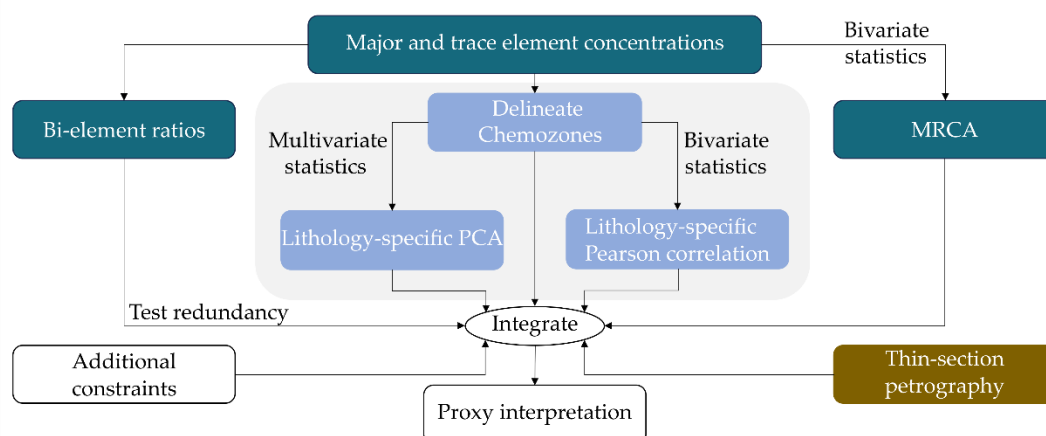


Fig. 3. Methodological Framework. Colors represent different scales: major and trace element concentrations, relevant bi-element ratios (tested for redundancy; see also Van der Weijden, 2002) and Multi-scale Rolling Correlation Analysis (MRCA) are carried out at the full-record-scale (cyan); chemozone-specific multivariate statistics (lithology-specific PCA) and bivariate statistics (lithology-specific) analyses are carried out at the chemozone-scale (blue); thin-section petrography applies to cm-scale observations in this study (brown).

A workflow was developed that delineates a methodological framework that can be applied for any multi-proxy study on heterogeneous records (Fig. 3). Full-record-scale analyses encompass assessment of major and trace element concentrations complemented with MRCA bi-variate statistics and identification of non-redundant¹ bi-element ratios (Van der Weijden, 2002). The delineation of chemozones is highly record- and context-dependent. At Oued Ferkla, lithological units OF1 to OF10, combined with the recognized event intervals, serve as a first-order indication of the chemozones. Litho- and event-stratigraphic subdivision is then re-adjusted to adhere to geochemically distinct intervals (Table 1). To accommodate the event-specific scope of this study, each chemozone is given a descriptive, event stratigraphy-based name which is further situated in an event-scale framework. For example, CZ1 represents the pre-Daleje interval of the Daleje interval, and CZ2 represents the Daleje Event interval of the Daleje interval (Table 1). Such a hierarchy is required to preserve an intuitive structure. Together with thin-section petrography and additional constraints such as literature study, complementary proxies and other relevant information, the full-record-scale and chemozone-specific analyses are integrated into a proxy interpretation. In heterogeneous records, proxy interpretation may be strongly chemozone and lithology specific.

¹ While informative to some extent, bi-element ratios strongly dominated by either numerator or denominator are considered redundant; they are solely informative in the sense that one element dominates variability captured by it.

Table 1. Delineation of chemozones at Oued Ferkla. Lithostratigraphic units and event stratigraphy by Talih et al. (2022).

Chemozone	Lithostratigraphic Unit	Event Stratigraphy	Geochemical Observations	Name	Interval
CZ1	OF1		Elevated Ca-values	pre-Daleje interval	Daleje Interval
CZ2	OF2	Daleje Event	Low Ca-values	Daleje Event interval	
CZ3	OF3 + l. OF4		Strongly fluctuating Ca	post-Daleje interval	
CZ4	u. OF4 + l. OF5		Fluctuating Ca	pre-Choteč interval	Choteč Interval
CZ5	u. OF5 + l. OF6	Choteč Event	Strongly fluctuating Ca	Choteč Event interval	
CZ6	m. OF6		Elevated Ca-values	post-Choteč interval	
CZ7	u. OF6 + OF7		Mn-enrichment	pre- Kačák interval	Kačák Interval
CZ8	OF8	Kačák Event	Strongly fluctuating Ca	Kačák Event interval	
CZ9	OF9 + OF10	<i>pumilio</i> Event	Elevated Ca-values	<i>pumilio</i> interval	<i>pumilio</i> Interval

2.4. Elemental Behavior and Interpretative Framework

Geochemical proxies may behave differently depending on the local paleodepositional and post-depositional conditions (i.e., diagenesis) governing deposition and alteration of sedimentary strata. To avoid misrepresenting paleoenvironmental and paleoclimatic signals, proxies should be interpreted within the specific context of the studied section (e.g., Algeo and Liu, 2020). To support such lithology-specific interpretation, we outline some fundamental geochemical characteristics of the elements included in this study.

Generally, Al, Ti, Zr, Rb and K represent a detrital signature that may indicate changes in the total amount, composition, and/or provenance of detrital input. Si may similarly represent such a signal, although a potential contribution from biogenic Si needs to be considered (Sageman and Lyons, 2004; Croudace and Rothwell, 2015). Some elements, such as K (and Rb, which may substitute into K-bearing minerals) may be depleted as a result of increased chemical weathering (e.g., Wichern et al., 2024) but may also exhibit increased mobility during diagenesis (Wintsch and Kvale, 1994). Commonly, while Ti and Zr generally reflect coarse grain sizes, Al is often associated with the fine-grained clay fraction and Si may reflect either coarse (quartz) or fine (aluminosilicates) detrital influx (Croudace and Rothwell, 2015). Cr and Fe may represent a detrital signature, but both elements are, to a variable degree, susceptible to changes in redox-chemistry (Tribouillard et al., 2006; Bruggmann et al., 2023) and should also be interpreted within a broader paleoredox and diagenetic context. Other redox-sensitive

elements included in this study are Mn, V, Ni, Cu, Zn and S. Redox cycling of Fe and Mn exerts strong control on the distribution of many trace metals in marine sedimentary systems (Tribovillard et al., 2006). Under oxidizing conditions, Fe-Mn-oxyhydroxides precipitate and act as highly efficient scavengers for elements such as Ni, Cu, Zn, V and Cr. When conditions shift toward reducing, these oxyhydroxides dissolve and may release the adsorbed trace metals, which in turn may be sequestered in, for example, sulfides, and leads to a net enrichment in sediments. A key distinction exists between Fe and Mn under reducing conditions, however. Fe is efficiently sequestered through iron-sulfide precipitation, resulting in substantial Fe draw down under anoxic or euxinic conditions. Conversely, Mn is not readily captured by sulfide phases and is typically depleted under reducing conditions while being enriched in oxic environments (Banner, 1995; Tribovillard et al., 2006; Bruggmann et al., 2023). Both Ni and Cu are associated with organic matter and may have merit as paleoproductivity indicators, provided that reactive Fe does not limit pyritization – a precondition for sequestering these trace metals into the sediment (Tribovillard, 2021; Bruggmann et al., 2024). However, because Ni enrichment may occur under both oxic (in association with Mn-oxides) as well under reducing conditions (Bruggmann et al., 2024), it requires assessment in a broad geochemical framework, including Mn and other paleoredox indicators. A final group of elements included in this work are those generally associated with carbonates: Ca, Sr, Mg, Ba. It should be noted however that, depending on the paleodepositional context, these elements may equally be associated with the detrital fraction (e.g., Ba; Swart, 2015), primarily through processes of weathering and erosion (e.g., Ott et al., 2023).

Multiple elements, including Ca, Sr, Mg, Ba, Mn, Fe, Zn, and Cu, are well known to be diagenesis-sensitive and require assessment within a broader litho- and chemostratigraphic framework (Brand and Veizer, 1980; Veizer, 1983; Banner and Hanson, 1990; Banner, 1995; Machel, 2004). Within the scope of this study, and given that the Oued Ferkla section is composed predominantly of limestone facies, the focus is placed here mainly on carbonate diagenesis. Post-depositional alteration of carbonates occurs mostly through recrystallization (replacement involving no changes in mineralogy), dissolution-precipitation (mineralogical transformation) and cementation (growth of diagenetic carbonate minerals) (Banner, 1995). Typically, facies-dependent meteoric or diagenetic recrystallization leads to a depletion of certain elements (e.g., Sr, Ba, Pb) and enrichment of others (e.g., Mn, Fe, Zn, Cu, Ni) (Brand and Veizer, 1980; Veizer, 1983; Banner, 1995; Swart, 2015). Depending on the original carbonate phase (e.g., low-Mg versus high-Mg), Mg may be enriched or depleted following recrystallization (Brand and Veizer, 1980; Veizer, 1983). During cementation, enrichment of specific elements (e.g., Sr) may occur if the cementing fluids are Sr-rich, whereas dissolution-precipitation can variably increase or decrease element concentrations depending on fluid chemistry and water-rock ratios (Banner, 1995). Redox-sensitive elements (e.g., Fe) that are

prone to diagenetic remobilization may also become enriched under reducing diagenetic conditions (Banner, 1995).

Diagenetic dolomitization can further modify the geochemical fingerprint. Dolomitization typically enriches Mg and may increase Sr or decrease Mn depending on the composition of the flux of the dolomitizing fluid flow (Machel, 2004), often resulting in variable and sometimes ambiguous Mn-Sr signatures. In this context, elements such as Mn, Fe, Sr, and Mg are used as indicators of diagenetic alteration in limestone facies. Although Mn and Fe enrichment combined with Sr depletion commonly suggests points to diagenetically altered carbonates (e.g., Hu et al., 2023), different alteration signatures may arise depending on the dominant diagenetic mechanism and pathway. Also, the effect of detrital input and redox variations on Ni, Cu, Zn, Mn and Fe is typically stronger than enrichment through dolomitization (Swart, 2015). Note that this diagenesis-screening framework based on PCA and Sr, Mn, Mg and Fe as outlined above is specific to carbonate lithologies; it cannot be applied to marls and shales because their mineral hosts and bulk-geochemical behavior differ fundamentally from those of carbonates.

Use of bi-element ratios as a proxy for paleoenvironmental and paleoclimatic reconstructions is common practice and is especially useful for normalizing to the detrital background to account for detrital dilution in mixed siliciclastic-carbonate systems or for distinguishing detrital signals. Bi-element ratios such as K/Ti, Ti/Rb, Zr/Rb and Ti/Al are primarily controlled by mineralogy and sediment provenance, but they can also reflect grain-size variations because the associated minerals respond differently to hydrodynamic sorting (Croudace & Rothwell, 2015). Consequently, their interpretation needs to be derived within a facies-specific context. Even within such a context, interpretation of such ratios requires caution because uncorrelated variables may acquire spurious correlations when normalized (Van der Weijden, 2002). In this work, redundancy of bi-element ratios was tested to exclude some that are entirely dominated by either numerator or denominator.

2.5. Results

2.5.1. Elemental Geochemistry

Elemental concentrations vary systematically across the succession and appear strongly tied to facies shifts. The predominantly carbonate-dominated Oued Ferkla section is characterized by generally elevated Ca concentrations, specifically in units OF1, lower OF5, upper OF6, OF7, OF9 and OF10 (Fig. 2). Strong, short-lived fluctuations towards lower Ca values occur in units OF3, OF4, upper OF5, and lower OF6, marking intervals dominated by marly and shaly intercalations (Fig. 2). Units OF2 and OF8 have overall low Ca concentrations throughout, which are occasionally interrupted by relative increases associated with limestone nodules (OF2) or distinct carbonate beds (OF8; Fig. 2). Detrital elements (Al, K, Si, Ti, Zr, Rb) closely mirror variations in Ca (Fig. 2; Fig. D1). Although other elements such as Fe and V (Fig. 2) as well as Cr, Mg, Zn, Cu and Ba (Fig. D1, D2) show variability broadly similar to the detrital suite and remain closely tied with lithological changes, they each exhibit distinct baseline shifts and short-lived spikes of differing amplitudes such as the more gradual decrease of Fe (and Cr) through OF3 (Fig. 2; Fig. D2). Mn has a distinct pattern, with irregular co-variation relative to the detrital suite and substantially elevated values from middle OF6 to upper OF7 (Fig. 2).

2.5.2. Stable Isotopes $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$

Carbonate $\delta^{13}\text{C}_{\text{carb}}$ values range from -5.52 ‰ to 2.65 ‰, while $\delta^{18}\text{O}_{\text{carb}}$ values vary between -11.72 ‰ and -4.87 ‰. The carbon isotope signal is characterized by a steadily increasing baseline from OF1 to OF6, with minor superimposed negative excursions. From OF6 onwards, the baseline $\delta^{13}\text{C}_{\text{carb}}$ signal stabilizes, although higher-amplitude negative excursions occur more frequently in OF8 to OF10, most prominently in the Kačák and *pumilio* Event intervals (Fig. 2). In contrast, baseline $\delta^{18}\text{O}_{\text{carb}}$ values remain relatively constant throughout the studied interval but are punctuated by short-lived positive excursions as well as longer intervals of elevated values, most notably in the middle OF6 and in the Kačák and *pumilio* Event intervals (Fig. 2).

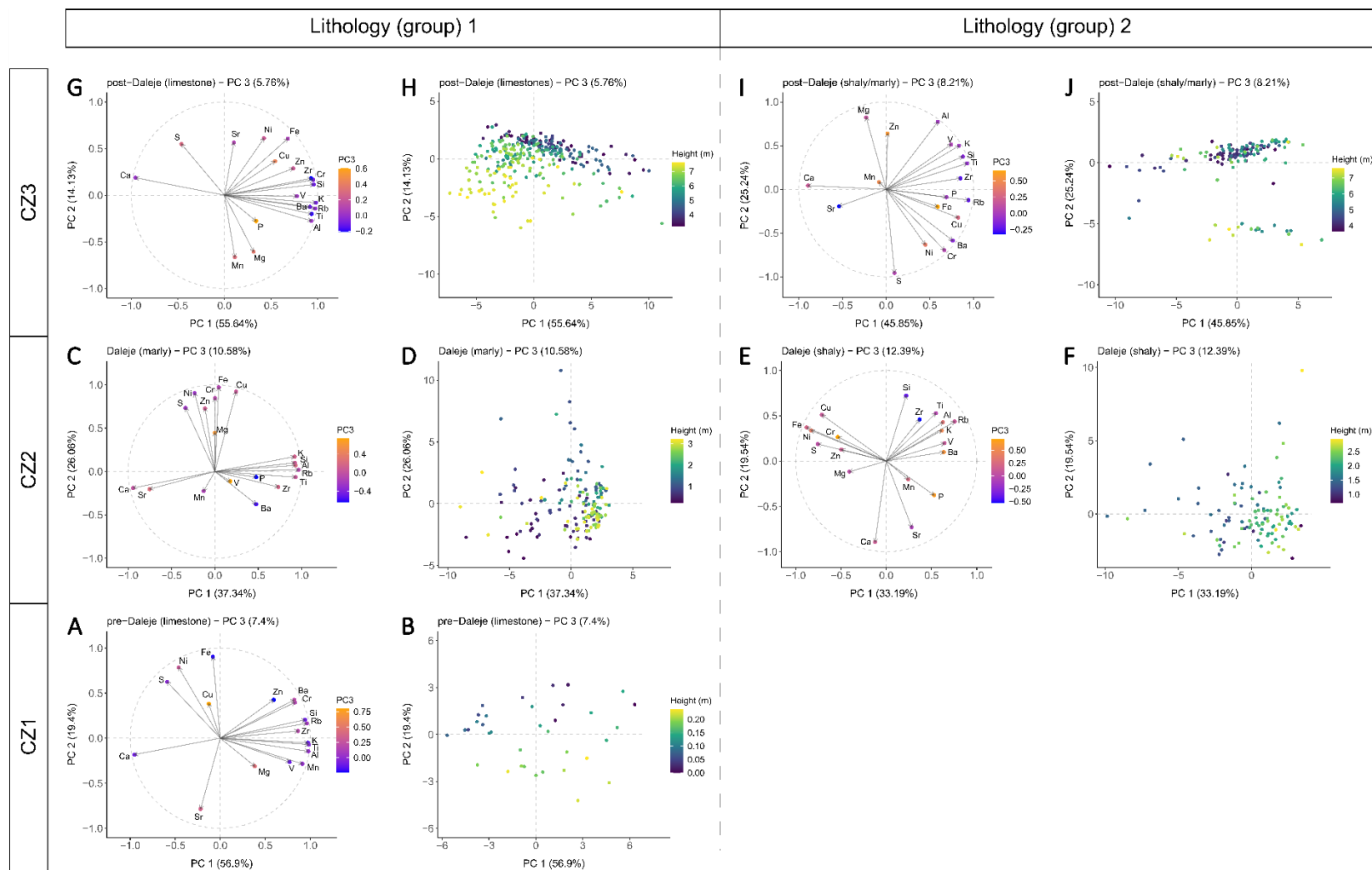


Fig. 4. Principal component analysis of the Daleje Interval. Panels A, C, E, G, I: loading plots along PC1-PC2 and PC3 (colored). Panels B, D, F, H, J: score plots along PC1-PC2 resolved in function of stratigraphic height (m; colored).

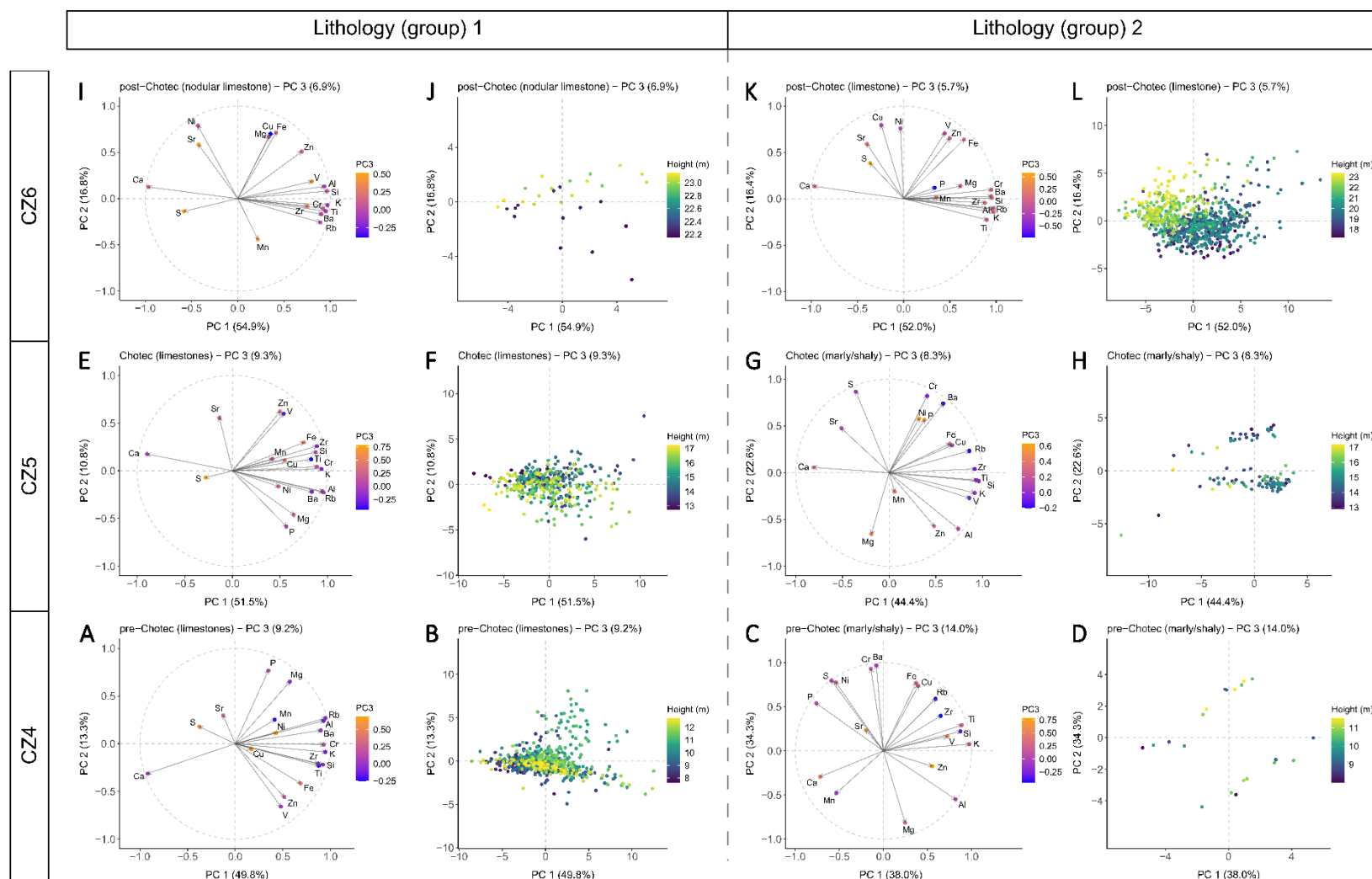


Fig. 5. Principal component analysis of the Chotec Interval. Panels A, C, E, G, I, K: loading plots along PC1-PC2 and PC3 (colored). Panels B, D, F, H, J, L: score plots along PC1-PC2 resolved in function of stratigraphic height (m; colored).

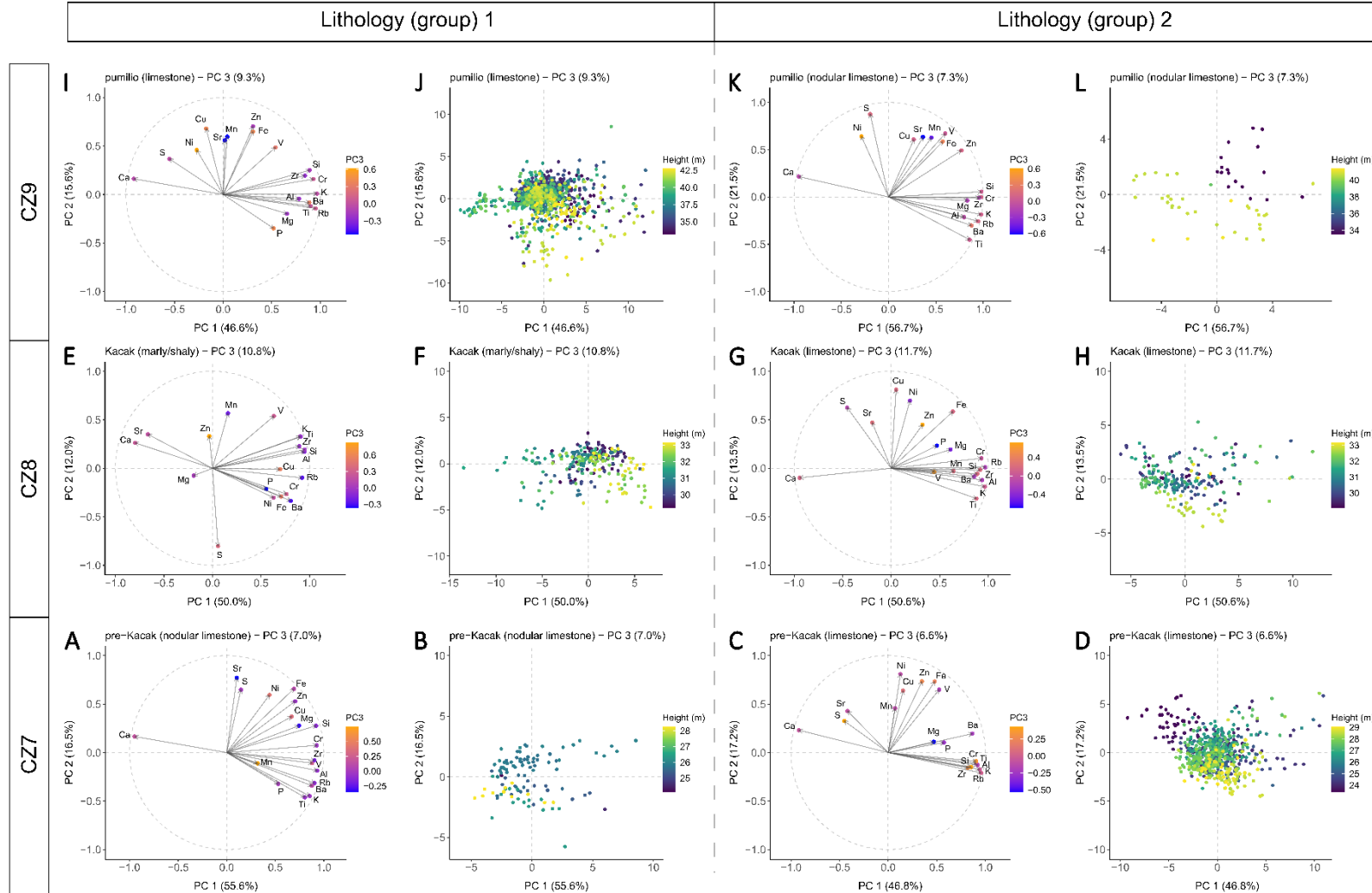


Fig. 6. Principal component analysis of the Kačák and *pumilio* intervals. Panels A, C, E, G, I, K: loading plots along PC1-PC2 and PC3 (colored). Panels B, D, F, H, J, L: score plots along PC1-PC2 resolved in function of stratigraphic height (m; colored).

2.6. Discussion

Here, focus is put on interpreting post-depositional diagenetic alteration, detrital indicators and paleoredox conditions. Reconstructions of paleotemperature (e.g., Mg/Ca; Nürnberg, 1996), paleosalinity (Sr/Ca, Ba/Ca; e.g., Dissard et al., 2021) or paleohydrology (e.g., Mo/TOC; Algeo and Lyons, 2006) are not possible due to the limited set of elemental proxies and sensitivity of Mg and Sr to diagenesis in bulk, mixed siliciclastic-carbonate rocks. In addition, $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ and are evaluated within a global framework (Becker et al., 2020; Cramer and Jarvis., 2020) whilst considering the potential for diagenetic overprinting of the primary isotopic signals. Elemental geochemistry is discussed for four intervals bracketing the Daleje, Choteč, Kačák and *pumilio* events, which are in turn subdivided into chemozones (Table 1).

2.6.1. Diagenetic Alteration

Diagenesis may obscure primary paleoenvironmental signals and is assessed here for carbonates through qualitative interpretation of PCA loadings (Fig. 4-6) and PCCM (Suppl. F). Clustering of diagenesis-sensitive elements (e.g., Fe, Mn, Sr, Mg; Brand and Veizer, 1980; Veizer, 1983; Banner and Hanson, 1990; Banner, 1995; Machel, 2004) is interpreted as indicative of a diagenetic contribution to the geochemical fingerprint. To further elucidate potential diagenetic signals on an interval- and lithology-specific basis, element cross-plots of the following element pairs are investigated: Mg-Sr (cementation, dolomitization, recrystallization), Mn-Sr (cementation, recrystallization), Fe-Mn (reducing dissolution-precipitation) and Fe-Sr (cementation, recrystallization) (Brand and Veizer, 1980; Veizer, 1983; Banner and Hanson, 1990; Banner, 1995; Machel, 2004; Hu et al., 2023), complemented by Sr-Ti, Mg-Ti, Fe-Ti and Mn-Ti cross-plots to test for facies dependencies (Suppl. H, I). Where available, geochemical interpretations are complemented by thin section petrography (Suppl. C).

2.6.1.1. Daleje Interval – Diagenetic Imprint

The limestones of the pre-Daleje interval (OF1, CZ1; Fig. 2) show a coherent grouping of S, Ni, Fe, and Cu along PC1-PC2 (Fig. 3A), reflecting a typical authigenic sulfide association. This “sulfide-group” corresponds to elevated PC2-values and contrasts with Sr – and to a lesser extent Mg – which load negatively along PC2 and plot along PC3 (Fig. 4A), consistent with their control by carbonate diagenesis rather than sulfidic mineralization. Ca and Sr load separately from all other elements, whereas the remaining elements cluster along positive PC1 values, reflecting their shared detrital affinity. The PCA score plot (Fig. 4B) shows a clear stratigraphic gradient: lower samples plot toward higher PC2 values (sulfide association), whereas higher samples trend toward the detrital cluster. This shift reflects a change in the relative influence of sulfidic conditions versus detrital input across the interval. The strong

positive Fe-Sr correlation ($r = 0.7$, $p < 0.05$) together with Fe-Ti ($r = -0.13$, $p > 0.05$) and Sr-Ti ($r = -0.16$, $p > 0.05$) indicates both elements primarily respond to porewater chemistry (Fig. I1). The pronounced negative Mn-Ti ($r = -0.91$, $p < 0.05$) coupled with the weak Fe-Mn ($r = -0.33$, $p = 0.06$) suggests Mn-mobilization under reducing conditions and detrital dilution while Fe is fixed as sulfide or other Fe-rich diagenetic phases (see also PCA; Fig. 4A; Fig. I1). Together with weak or absent correlations between Mg-Sr, Fe-Mn, Fe-Sr, and Sr-Ti (Fig. H1; H2; I1), such patterns are consistent with diagenetic modification (recrystallization and/or cementation) of the carbonate phase. This interpretation is corroborated by thin-section petrography, which shows strongly recrystallized carbonates (Fig. C1A). Overall, the pre-Daleje limestones record a moderate diagenetic imprint, and redox interpretations therefore require care. The geochemical patterns primarily reflect reducing to locally sulfidic porewater conditions, and the elements used in this study cannot be reliably applied to reconstruct bottom-water redox conditions in such diagenetically altered interval.

The Daleje Event interval is dominated by greenish shaly to marly facies with interspersed limestone nodules (Fig. 2), which commonly carry a substantial diagenetic imprint. Here, data from one limestone nodule is analyzed, despite the low number of datapoints which affects statistical significance testing. Nevertheless, it represents an opportunity to apply this geochemical diagenetic screening approach to samples that were most probably formed through post-depositional processes². The observed negative Fe-Mn relationship ($r = -0.36$), together with positive Mn-Ti ($r = 0.54$) and near-zero Fe-Ti ($r = -0.02$), indicates that Mn variability is partly linked to detrital input, whereas Fe is fully decoupled from detrital phases and instead reflects diagenetic redox conditions, suggesting sulfate-reducing conditions which mobilize Mn but precipitate Fe-sulfides during nodule formation (Fig. H1; H2; I3). In this setting, the combined Mn-Sr ($r = -0.42$), Mn-Ti ($r = 0.54$), and Sr-Ti ($r = -0.88$) relationships (Fig. I2) are best interpreted as reflecting partitioning between clay-rich matrix and carbonate nodules rather than Sr loss. The weak, positive Fe-Sr correlation ($r = 0.28$) likewise reflects preferential enrichment of both Fe and Sr in the carbonate nodule relative to the surrounding clay-rich matrix during diagenetic nodule formation. The limestone nodule analyzed here was sampled from a shale matrix, where the inverse Fe-Ti trend ($r = -0.29$) is consistent with Fe being concentrated in the nodule and correspondingly depleted in the adjacent clay-rich host (Fig. I5).

The post-Daleje interval limestones (CZ3; Fig. 2) appear geochemically different from the pre-Daleje limestones: while Ni, Fe, and Cu still group toward higher values along PC2, they cluster closer to the other detrital elements along PC1 (Fig. 3G). This broader spread does partly reflect the fact that several limestone lithologies are represented in chemozone, which

² Thin-section petrography would need to be carried out to further complement the geochemical analysis to fully support this assumption but is currently unavailable.

are grouped together in the PCA. Thus, lithology-specific element correlations are required to disentangle diagenetic from detrital, carbonate and potential redox controls within this chemozone. Because a description of the diagenetic imprint on limestone, nodular limestone and limestone nodule facies would be excessive, only the most relevant evidence is summarized here. In the massive limestones, aside from Mn-Sr ($r = -0.38$, $p < 0.05$; Fig. I1) suggesting minor carbonate diagenesis (e.g., Sr-loss or Mn-enrichment), there is no indication of significant post-depositional alteration (see also Fig. H1; H2). The nodular limestones show a significant Fe-Sr correlation ($r = 0.4$, $p < 0.05$), which is consistent with lithology-dependent carbonate recrystallization rather than redox control, and may also be partly linked to detrital mixing (Fig. I2). Similarly, the limestone nodules recovered from CZ3 differ markedly from those of the Daleje Event interval (CZ2); they show no unequivocal evidence for considerable (reducing) diagenesis, and their geochemical variability appears closely tied to changes in the detrital fraction (Fig. I3). Although CZ3 does present different limestone facies, the lithology-specific correlations confirm that the post-Daleje interval limestones lack strong characteristics of sulfidic porewater conditions (PCA; Fig. 4). Instead, trace-metal variability is primarily governed by detrital mixing, and diagenetic overprinting is minor compared to the pre-Daleje and Daleje Event intervals.

2.6.1.2. Choteč Interval – Diagenetic Imprint

This interval is, compared to the underlying Daleje interval, characterized by a more uniform geochemical fingerprint (Fig. 5), consistent with less drastic facies shifts and only a minor diagenetic imprint. In the pre-Choteč interval (CZ4; Fig. 2), correlation patterns in both massive and nodular limestones indicate only limited carbonate diagenesis; at most, negative Sr-Mn relationships point to limited Sr redistribution (Fig. H3; I6, I7). The Choteč Event interval (CZ5; Fig. 2) presents slightly stronger correlations than the underlying interval (Fig. H3; H4; I6, I7). In massive limestones, a negative Mg-Sr relationship ($r = -0.22$, $p < 0.05$) suggests minor dolomitization, while other correlations remain weak and consistent with subtle recrystallization (Fig. I6, I7). Thin-section petrography shows minor traces of brown dolomite and localized recrystallization (Fig. C1B), supporting the interpretation of only limited diagenetic modification. In the post-Choteč interval, nodular limestones show grouping of Sr-Ni and Mg-Cu-Fe in PC1-PC2 space (Fig. 5), which could indicate a diagenetic overprint, although the Mg-Sr relationship ($r = 0.32$, $p > 0.05$; Fig. I7), which may indicate minor dolomitization, it is statistically not significant. In massive limestones, Sr, Cu, Ni, and S also group along PC1-PC2, but because this cluster plots relatively close to Ca and is clearly separated from the V-Zn-Fe cluster, it is interpreted to reflect a primary or productivity-related carbonate signature rather than a diagenetic overprint. This interpretation is supported by element cross-plots, which show only limited Sr redistribution consistent with mild recrystallization (Mn-Sr; $r = -0.17$, $p < 0.05$; Fig. I6). Similarly to the Choteč interval, thin-section petrography reveals minor recrystallization or patchy dolomitization, often restricted

to detrital-rich seams or stylolites that were avoided during pXRF measurements (Fig. C1C, D). Overall, the Choteč interval shows only minor diagenetic modification compared to the underlying Daleje interval, and its trace-element patterns largely preserve primary depositional signals.

2.6.1.3. Kačák Interval – Diagenetic Imprint

In the pre-Kačák massive limestones, PCA reveals a typical pattern where Ca opposes the detrital cluster along PC1 and redox-sensitive elements cluster along positive values of PC1 and PC2 (Fig. 6C), a configuration that is not indicative of a single, pervasive diagenetic imprint. Although Mn loads together with Ni, Cu, Zn, Fe, and V, forming a broader transition-metal association, the very low positive Mn-Sr ($r = 0.13$, $p < 0.05$) and Fe-Mn ($r = 0.19$, $p < 0.05$) correlations reflect only minor Mn-Sr co-variation consistent with subtle recrystallization (Fig. I11). Evidence for pervasive dolomitization is lacking (Mg-Sr; Fig. H5; I11). Thin-section petrography supports these geochemical interpretations, evidencing recrystallization and dolomitization of a relatively low, yet variable degree (C1E, F). Thus, the anomalous Mn enrichment (Fig. 2) does not appear to be diagenetically driven in the massive limestones.

In contrast, for nodular limestones, all elements except Ca plot more diffusely along PC2 and lack a clear diagnostic elemental grouping (Fig. 6A). While a positive Mg-Sr correlation ($r = 0.42$, $p < 0.05$) may be indicative of dolomitization through a Sr-rich fluid, the poor correlation between Fe-Mn ($r = 0.17$, $p > 0.05$), Mn-Sr ($r = -0.11$, $p > 0.05$), and the moderately strong correlation between Mg-Ti ($r = 0.48$, $p < 0.05$) does not point towards pervasive dolomitization or a unified diagenetic overprint (Fig. H5; H6; I12). Instead, these relationships suggest that Mg, Fe, and Mn variability in the nodular limestone beds is partly controlled by detrital input (as supported by the significant Fe-Ti and Mn-Ti correlations; Fig. H6; I12). Although a minor diagenetic contribution cannot be fully excluded, the very high concentrations of Mn coinciding with very low concentrations of redox-sensitive elements (Fig. 6; Fig. D2, D3) likely reflects a primary paleoredox imprint instead.

The Kačák Event interval is characterized by thick marly/shaly packages interrupted by thinner, massive limestone beds. The PCA loading plot of these limestones (Fig. 6G) looks very similar to that of the underlying pre-Kačák interval limestones (Fig. 6C), with the only notable difference being that Mn and V now plot with the detrital cluster along positive PC2 values. This shift of Mn and V from a paleoredox-linked association in the pre-Kačák interval to a detrital association in the Kačák limestones suggests a dominant facies control rather than a diagenetic or redox signal, likewise, indicating that the carbonate beds likely did not suffer substantial post-depositional alteration at the scale captured by geochemical analyses. Bi-element cross-plots fully support this interpretation, with Mg-Sr ($r = -0.04$, $p > 0.05$), Mn-Sr ($r = 0.04$, $p > 0.05$), Fe-Sr ($r = -0.01$, $p > 0.05$) showing no meaningful co-variation, while Mn-Ti (r

= 0.54, $p < 0.05$) and Fe-Ti ($r = 0.34$, $p < 0.05$) indicate a strong detrital control (Fig. H6; I11). Yet, thin-section petrography reveals significant dolomitization in some parts of the limestone beds. A similar observation was made by Talih et al. (2022), who noted that dark micritic envelopes surrounding some crinoids and dacryoconarids indicate diagenetic mineralization. Such a discrepancy between thin-section petrography and geochemical screening highlights limitations of geochemical diagenesis screening but also the sometimes-patchy nature of diagenesis in this interval: whereas some samples show little dolomite, often restricted to clay-rich seams or stylolites that were avoided during pXRF measurement, others are almost completely dolomitized (Fig. C2A, B) but do not contribute sufficiently to produce a diagnostic geochemical imprint.

2.6.1.4. *pumilio* Interval – Diagenetic Imprint

The Givetian-aged part of the section (CZ9) is dominated by massive limestone and nodular limestone beds and includes the two *pumilio* Event horizons (Fig. 2). The massive limestones display a distinct geochemical fingerprint compared to the underlying Eifelian-aged units. In the PCA loading plot (Fig. 6I), S, Ni and Cu cluster in the upper left quadrant near Ca, while Sr and Mn form a separate cluster expressed strongly by negative PC3 values (Fig. 6I). The latter indicates that diagenesis is present, but not dominant. Mg plots with common detrital indicators (Fig. 6I), suggesting it largely reflects a detrital signal rather than diagenetic. The distribution of redox-sensitive elements – association of S, Ni, Cu with Ca, and clustering of Zn, Fe and V near the detrital group – indicates a limited redox influence and does not suggest diagenetic overprinting. The PCA loading of the nodular limestones is broadly similar (Fig. 6K).

In contrast with the underlying intervals, lithology-specific cross-plots including Sr, Mn, Mg and Fe are evaluated here by separating background limestones from the Lower and Upper *pumilio* Event beds, rather than by stratigraphic sub-intervals. This approach is preferred here to resolve the anomalous event horizons, which geochemically contrast with an otherwise more homogenous background. The massive limestones of the background interval do not carry strong geochemical indications of diagenetic overprinting, aside from a moderate, positive Mn-Sr correlation ($r = 0.38$, $p < 0.05$) that may be indicative of minor recrystallization (Fig. H7; H8; I15). In contrast, the background nodular limestones are characterized by strong correlations between Mn-Sr ($r = 0.77$, $p < 0.05$), Mg-Sr ($r = 0.72$, $p < 0.05$), and Fe-Sr ($r = 0.38$, $p > 0.05$) and Fe-Mn ($r = 0.39$, $p > 0.05$), which are consistent with either recrystallization and/or dissolution-precipitation in addition to dolomitization or Mg-rich recrystallization (Fig. I16).

The Lower *pumilio* Event bed consists of limestones show considerable geochemical differences compared to the background interval, which require careful interpretation given it is largely depleted of detrital material. The low detrital content may amplify apparent

diagenetic signatures relative to intervals containing more siliciclastic material. Correlation between Mg-Sr ($r = -0.41$, $p < 0.05$), Fe-Mn ($r = -0.79$, $p < 0.05$), Mn-Sr ($r = 0.48$, $p < 0.05$), and Fe-Sr ($r = -0.39$, $p < 0.05$) in combination with Sr-Ti ($r = -0.67$, $p < 0.05$), Fe-Ti ($r = 0.59$, $p < 0.05$), Mg-Ti ($r = 0.6$, $p < 0.05$), and Mn-Ti ($r = -0.46$, $p < 0.05$) suggest a partitioning into two element groups: Mg and Fe associated with the minor detrital fraction, opposing Mn and Sr (Fig. H7; H8; I15). This pattern is consistent with subtle recrystallization and/or cementation, as also revealed by thin-section petrography (Fig. C2C).

The Upper *pumilio* Event bed contains both massive and nodular limestones (Fig. 2). Correlations between Mg, Mn, Sr, and Fe suggest weaker diagenetic overprinting compared to the Lower *pumilio* bed, with only Mn-Sr being statistically significant ($r = 0.55$, $p < 0.05$; Fig. I15) and suggesting potential recrystallization and/or dissolution-precipitation that redistributed Mn and Sr in tandem. Although their geochemical fingerprint differs, the nodular limestones appear only weakly diagenetically altered, with only Fe-Mn ($r = 0.32$, $p > 0.05$) and Mn-Sr ($r = 0.34$, $p > 0.05$) correlating poorly (Fig. I16). Thin-section petrography of the Upper *pumilio* bed similarly supports the interpretation that diagenetic overprinting was limited in this interval (Fig. C2D).

2.6.2. Detrital Signatures

Elements commonly associated with the detrital fraction (Al, Si, K, Ti, Rb, Zr) correlate positively and cluster strongly along PC1 in all PCA loading plots (Fig. 4-6), even across distinct facies transitions, confirming their shared detrital signal and facies-dependent variability in their concentrations. Thus, PC1 represents a proxy for total detrital input, with positive values indicating elevated detrital influx (and vice-versa). Interestingly, the upper part of PC1 that covers the Kačák-*pumilio* intervals closely resembles the magnetic susceptibility (MS) curve by Ellwood et al. (2011) from the neighboring Mech Irdane GSSP section. This similarity arises because MS in mixed siliciclastic-carbonate successions is typically dominated by detrital influx (Da Silva et al., 2009; 2013). Ellwood et al. (2011) proposed that MS variations reflect transgressive-regressive (T/R) cycles. However, MS variations do not uniquely record T/R cycles, nor do they constitute an eustatic sea-level curve. MS is driven primarily by the concentration and type of magnetic minerals and therefore reflects changes in total detrital input, mineralogy, grain-size distribution, weathering intensity, etc. – assuming the primary signal is preserved (Da Silva et al., 2009; 2013). Because these processes are not uniquely tied to sea level, MS cannot be used as a standalone proxy for T/R cycles. Thus, we refrain from interpreting PC1 as a eustatic sea-level curve.

In order to identify shifts in provenance, mineralogy, as well hydrodynamic sorting (i.e., grain size), selected bi-element ratios are assessed: Ti/Al, K/Ti, Ti/Rb, Zr/Rb, Ti/Zr, Rb/K, K/Al, Si/Al and Si/Ti (Fig. 7). Provided mineralogy and provenance remain relatively stable, Ti/Al, K/Ti,

Ti/Rb and Zr/Rb may serve as grain-size indicators. Variations within the coarse-grained and fine-grained fractions can be tracked using Ti/Zr and Rb/K, and K/Al, respectively. Lastly, Si/Al and Si/Ti aid in disentangling the contribution of clay (aluminosilicates) or sand (quartz) to the Si-budget. While most of these proxies are investigated on an interval-specific basis, K/Ti, Ti/Al and Zr/Rb are considered for the entire section to establish the dominant controls behind variations in the elemental composition of detrital influx.

MRCA of K/Ti and Zr/Rb (Fig. 7) indicates strongly varying correlation on different scales, meaning these ratios do not strictly represent grain-size proxies. Fundamentally, provenance and mineralogy are the first-order controls on the chemical composition of detrital material, whereas hydrodynamic and aeolian sorting act only as secondary modulators through their influence on, amongst others, grain size distributions, weathering state and erosion processes. The parts of the section characterized by a negative correlation most likely reflect periods during which hydrodynamic/aeolian sorting dominated detrital variability through grain-size variations, while provenance and/or mineralogy likely remained stable. Several parts of the section are characterized by absence of correlation between K/Ti and Zr/Rb (parts of CZ4, CZ6, CZ7) at smaller scales (< 5 m) or even positive correlation (CZ6, parts of CZ8 and CZ9) at variable scales (Fig. 7), which indicates that either changes in mineralogy, provenance and/or chemical weathering and erosion processes dominated variability within the detrital fraction instead. These interpretations are supported by Ti/Al and Zr/Rb, which display, as expected, reversed correlations (Fig. J1).

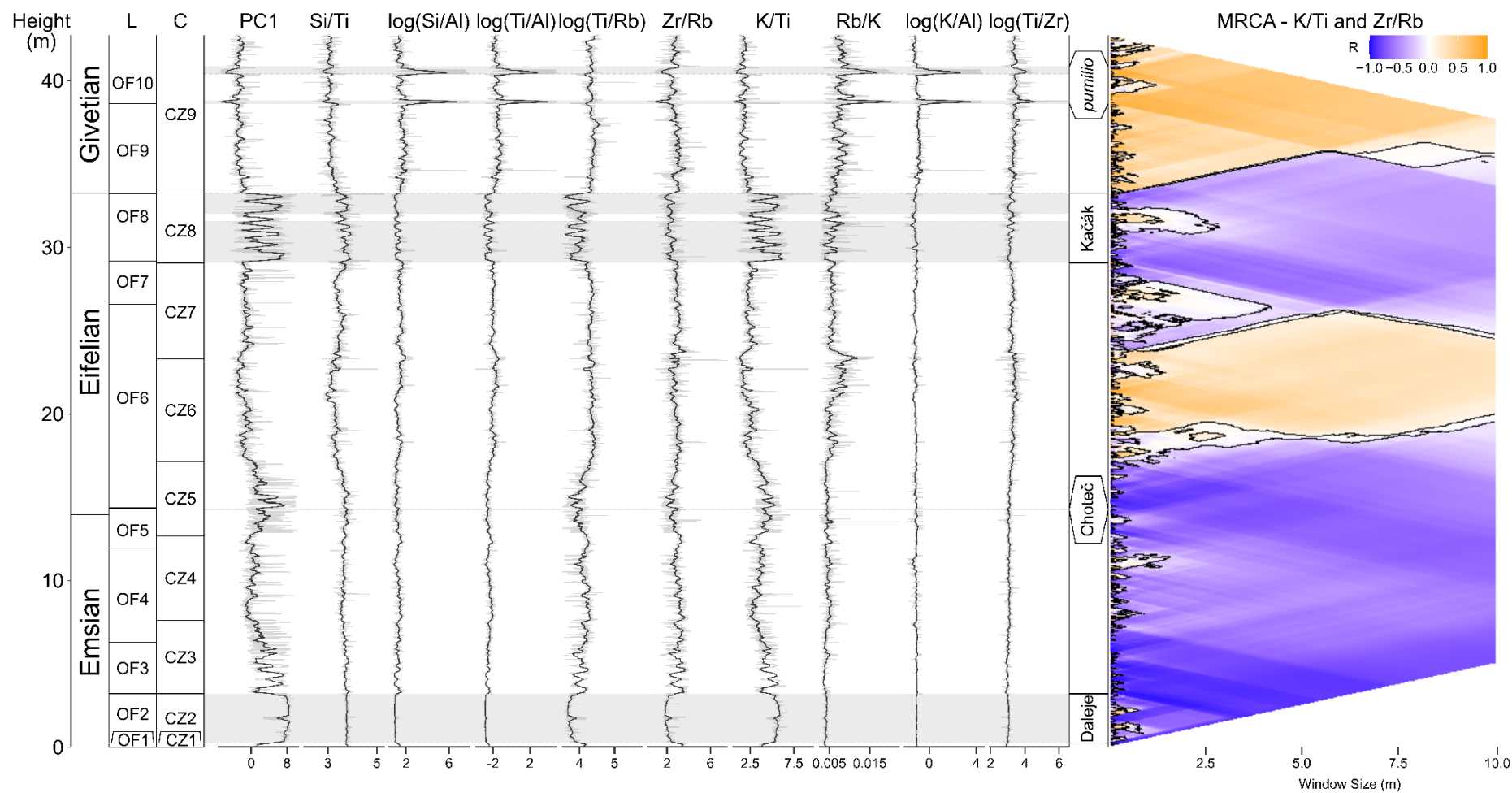


Fig. 7. Detrital signals and Multi-scale Rolling Correlation Analysis (MRCA) of K/Ti and Zr/Rb. Lithological units (L) and chemozonation (C). Detrital signals PC1, Si/Ti, log(Si/Al), log(Ti/Al), log(Ti/Rb), Zr/Rb, K/Ti, Rb/K, log(K/Al), log(Ti/Zr) (light gray) and 21-point running averages (dark gray). Multi-scale rolling correlation analysis (MRCA) of K/Ti and Zr/Rb, significant positive (orange) or negative (blue) Pearson correlation (95% confidence interval) is demarcated by black lines.

2.6.2.1. Daleje Interval – Detrital Input and Composition

The Daleje interval is characterized by drastic facies shifts, which is reflected by stark variations in total detrital input (PC1) and also variability within the detrital fraction (e.g., Ti/Al, Ti/Rb, Zr/Rb; Fig. 7, D4). These proxies consistently track facies-dependent grain-size variations, whereas ratios that track variability within the fine-grained (Rb/K, K/Al) and coarse-grained (Ti/Zr) show weaker facies control. The latter likely reflect more subtle changes in provenance, mineralogy, and weathering-erosion dynamics linked to variations in sediment supply

The pre-Daleje interval is characterized by low concentrations of detrital elements, indicating reduced detrital influx during limestone deposition (PC1; Fig. 7, D4). Elevated Ti/Al, Ti/Rb, and Zr/Rb suggest dominance of coarse-grained detrital material, consistent with significant aeolian input relative to clay under dry climatic conditions (see clay mineralogy in Talih et al., 2022). The transition towards the Daleje Event interval is characterized by a drastic increase in total detrital input, which appears finer grained compared to the underlying limestones (e.g., Ti/Al; Fig. D4). This is with Si/Ti and Si/Al variability; while Si/Al tracks the shift in grain size variation, Si/Ti baseline remains relatively stable – signaling a relative increase in aluminosilicate input. Note that a minor contribution of biogenic Si cannot be excluded based on the available data. While Ti/Zr signals a shift in coarse-grained mineralogy during the Daleje Event, Rb/K and K/Al remain relatively consistent from 0 to ~4 m compared to overlying strata, indicating clay assemblages remained somewhat consistent in interval bracketing the Daleje Event. Such detrital fingerprints support the lithostratigraphic interpretation that the Daleje Event represents a shift toward increased accommodation, most likely driven by a relative sea-level rise during a period characterized by wetter paleoclimatic conditions (Talih et al., 2022).

The post-Daleje interval (CZ3) has a bipartite character, with the lower part displaying thick alternations of carbonate and shaly/marly facies, and the upper part (from ~5.5 m onwards) showing thinner alternations indicative of more rapid facies shifts (Fig. 2, 7, D4). Within the limestones, however, a clear stratigraphic gradient toward increasingly carbonate-dominated compositions is evident in the PCA score plot (Fig. 4H), indicating that the decrease in detrital material occurred gradually. Negative correlation between K/Ti and Zr/Rb is strongest in this interval (MRCA; Fig. 7), which is interpreted to reflect dominant control of hydrodynamic sorting. In addition to grain-size variations (e.g., Ti/Al), there is also stronger variability within the fine-grained fraction (Rb/K, K/Al) and coarse-grained fraction (Ti/Zr) (Fig. 7, D4). Together with stark facies shifts, these patterns are consistent with sea-level fluctuations (Talih et al., 2022). This suggests that the post-Daleje depositional setting lay near a hydrodynamically sensitive threshold, where paleoclimatic shifts – potentially even minor ones – produced amplified sedimentary responses.

2.6.2.2. Choteč Interval – Detrital Input and Composition

The Choteč sub-intervals are characterized by distinct detrital signatures. While the pre-Choteč interval is marked by short-term increases in detrital input, the Choteč Event interval shows the strongest detrital pulses and an overall slightly elevated baseline. In both intervals, Ti/Al, Ti/Rb, Zr/Rb and K/Ti predominantly track grain-size variations of detrital influx (MRCA, Fig. 7), indicating considerable influence of hydrodynamic sorting. Transient negative spikes in Ti/Rb and Zr/Rb coinciding with pulses of increased detrital input (PC1) indicate that these pulses in CZ4 and CZ5 are characterized by finer grain sizes. Variations in K/Ti, which peak in the Choteč Event interval (Fig. D5), equally suggest increased K-rich fine-grained input. Likely, sea-level variations (Talih et al., 2022) exerted facies-control, and the combination of increased total detrital input, finer-grained material and marl/shale deposition is consistent with a transgressive trend (and vice-versa).

In contrast, the post-Choteč interval, characterized by massive limestone beds often lacking marl/shale intercalations, lacks strong detrital spikes. This interval represents a phase of progressively decreasing detrital input up-section (Fig. D5), as shown also by the PCA score plot (Fig. 5L) which exhibits a shift towards more negative PC1 loadings that represent a stronger affinity with the carbonate fraction. Compared to the underlying strata, MRCA of K/Ti and Zr/Rb (Fig. 7) suggests that variability within detrital influx the post-Choteč interval (CZ6) was dominated by changes in provenance and/or mineralogy rather than hydrodynamic sorting. While baseline Si/Al remains relatively stable, PC1 and Si/Ti values decrease in the post-Choteč interval, equally suggesting changes in the provenance and mineralogy of the detrital fraction. Together, these patterns suggest drier climatic conditions, characterized by a shift in sediment provenance, possibly tied to a relative increase aeolian input (Talih et al., 2022).

2.6.2.3. Kačák Interval – Detrital Input and Composition

The pre-Kačák interval is characterized by generally low detrital input, with short-lived increases corresponding to marly/shaly intercalations that interrupt the thick limestone beds (PC1, Fig. 6). The PCA score plot of massive limestones shows a smaller spread in function of stratigraphy (Fig. 6C, D), indicating increasing compositional uniformity for younger samples. Although some variability in detrital indicators can be observed, these likely represent only minor changes in the composition of detrital input. For example, a gradual rise in Si/Ti from ~28 m onwards towards the base of the Lower Kačák Event may reflect a minor shift in mineralogy (Ti-depletion; note stable Si/Al in this interval) (Fig. D6).

The Kačák Event marks an abrupt shift toward thick, alternating shaly/marly facies and comparatively thinner limestone beds, a pattern clearly captured by PC1 (Fig. 7). It contains

~7 strong, prolonged pulses of elevated detrital input, expressed as geochemically homogeneous marl/shale beds at the current sampling resolution. The response of grain-size indicators varies strongly here. On larger scales, K/Ti and Zr/Rb correlate negatively in the Lower and Upper Kačák Event beds, whereas they correlate positively in the inter-Event interval (MRCA, Fig. 7). In the event intervals, on the smallest scale (< 1m), loss of correlation between K/Ti and Zr/Rb at low PC1 values indicates that hydrodynamic sorting was suppressed. Conversely, intervals with elevated PC1 values are characterized by a negative correlation between K/Ti and Zr/Rb, meaning marly/shaly intervals were deposited under a depositional setting where hydrodynamic sorting dominated. Yet, Rb/K, K/Al as well as Ti/Zr indicate a co-occurring, facies-dependent shift in mineralogy and/or provenance of variable magnitude throughout the entire event interval.

2.6.2.4. *pumilio* Interval – Detrital Input and Composition

The Givetian-aged limestones (OF9 and OF10; Fig. 2) contain the lowest amounts of detrital material in the section (CZ9; Fig. 7), consistent with the near-absence of shaly/marly intercalations. Baseline concentrations of detrital elements remain constant, with only minor fluctuations (Fig. D7). Two clear exceptions are the Lower and Upper *pumilio* Event intervals, which stand out in the PCA score plot by their strongly negative PC1 values (Fig. 6J). These values reflect the highest affinity with the carbonate fraction (Ca; Fig. 6I) and correspond to pronounced decreases in detrital input (PC1; Fig. D7). In the Upper *pumilio* Event bed, this decrease is briefly interrupted by a characteristic, thin shaly/marly interval (Lottman, 1990a; b). In this interval, provenance and/or mineralogy exert primary control over K/Ti, Zr/Rb and Ti/Al (Fig. 7, J1), meaning we refrain from interpreting these as grain-size proxies.

One exception to this are the Lower and Upper *pumilio* Event beds, which are both characterized by a highly unique detrital signature. For both events, there is an almost complete depletion of most elements associated with the fine-grained fraction (Al, K), with exception of Rb (Fig. 7, D7). Moreover, elevated Rb/K, Ti/Zr and low Zr/Rb points towards the depletion of Zr-containing minerals. In addition to elevated Si/Al and Ti/Al, likely due to the depletion of Al-species, this suggests increased quartz- and Ti-bearing phases and supports depletion of aluminosilicate-rich fine-grained material. Such a drastic mineralogy shift is very compatible with dry, low-runoff conditions, although a change in provenance and/or intense winnowing cannot be excluded.

2.6.3. Paleoredox Conditions

Interpretation of paleoredox conditions requires integrating the geochemical patterns with the diagenetic and detrital constraints established in the preceding chapters within each chemozone. This is crucial because the degree of redox influence on most proxies can vary strongly even within a single record (Algeo and Liu, 2020), for example due to lithological transitions. Here, Fe, V, Ni, Cu, Zn, Cr, Mn, and S are evaluated within such a context by complementing interval-specific PCA (Fig. 4-6) with raw element signals (Fig. 8, D8-11). Avoiding enrichment factors and fixed redox-thresholds is preferred because normalization schemes (particularly to Al) introduce artifacts when detrital flux varies or when the normalizing element is not strictly conservative (Van der Weijden, 2002; Tribouvillard et al., 2006; Algeo and Liu, 2020). Moreover, enrichment factors may reflect lithological changes (e.g., dilution effects) rather than true redox behavior. Given the semi-quantitative nature of pXRF data and the absence of classical quantitative redox proxies (e.g., Fe-speciation, TOC, Mo, U; Algeo and Liu, 2020), redox conditions are therefore assessed qualitatively.

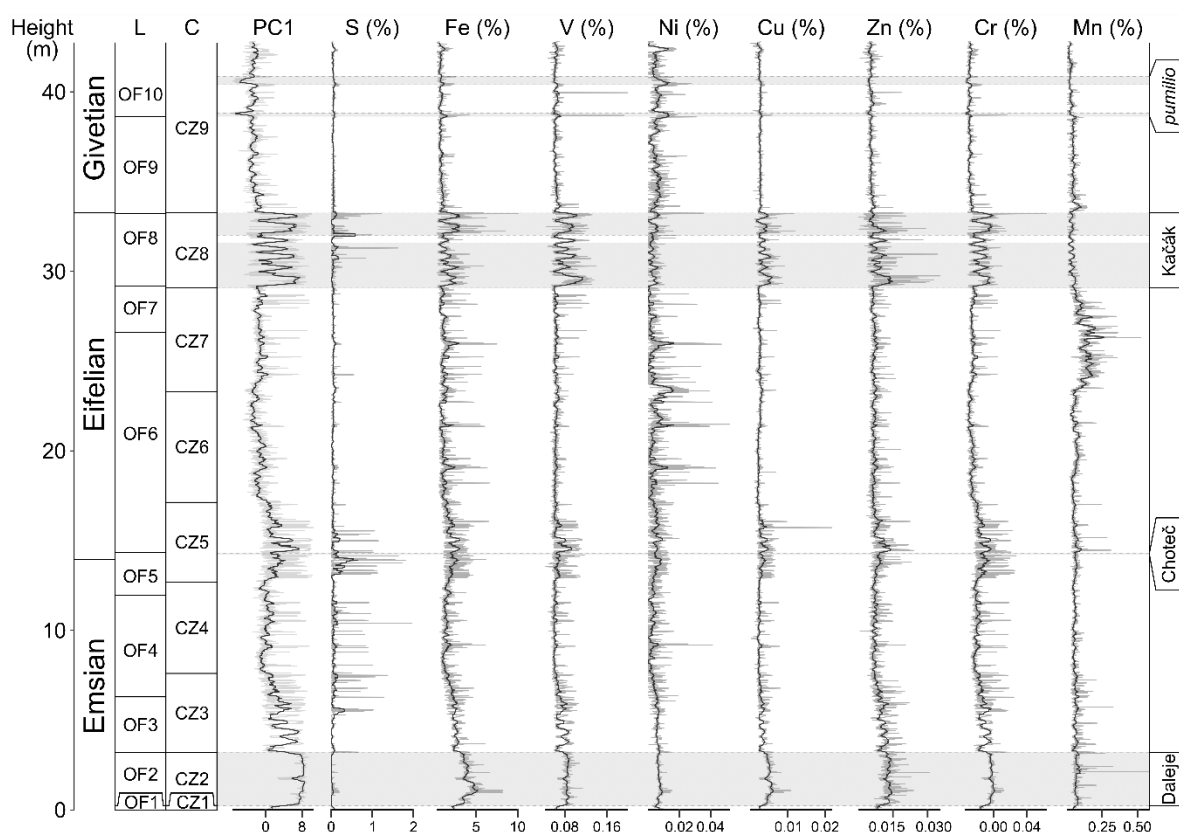


Fig. 8. Oued Ferkla redox signals. Lithological units (L) and chemozonation (C). Detrital signals PC1, S, Fe, V, Ni, Cu, Zn, Cr, and Mn in weight per cent (%; light gray) and 21-point running averages (dark gray).

2.6.3.1. Daleje Interval – Redox Signatures

The limestones of the pre-Daleje interval (OF1, CZ1) are characterized by overall low concentrations of detrital (PC1) and redox-sensitive trace elements (incl. V, Cu, Zn, Cr; Fig. 8). The clustering of S, Ni, Cu, and Fe in PC1-PC2 space (Fig. 4A), together with the diagenetic relationships documented in the previous chapter indicates minor authigenic sulfide formation during diagenesis (see also Fig. I1). Importantly, other redox-sensitive elements such as V, Cr, and Zn do not cluster with this group but instead plot with detrital indicators (Fig. 4A), further demonstrating that S-Ni-Cu-Fe association is diagenetic rather than environmental. Furthermore, the stratigraphic gradient observed in the PCA score plot (Fig. 4B), with lower samples plotting closer to the sulfide-associated group and higher samples shifting away, reflects a diminishing diagenetic overprint upward rather than a primary redox gradient.

The greenish shales and marls of the Daleje Event interval display a clear shift toward more reducing conditions. This interval is characterized by enrichment in multiple redox-sensitive trace elements (Fig. 8, D8) and by a geochemical fingerprint typical of primary redox control: in both marls and shales, S, Ni, Zn, Cr, Fe, and Cu form a coherent cluster in PC1-PC2 space (Fig. 4C, E). Moreover, comparison with detrital indicators (e.g., PC1; Fig. 8, D8) shows that the elevated concentrations of Fe, V, Cu, Zn, and Cr in the Daleje interval are only partly facies-controlled, indicating that their higher abundances reflect genuine redox enrichment rather than solely increased detrital influx. MRCA further reveals that, particularly on sub-1.5-m scales, Ti exhibits no significant correlation with Cu (Fig. J2) or Fe (Fig. J3), supporting the interpretation that short-scale variability in these elements is not controlled by detrital input. No clear stratigraphic trend is observed in PC1-PC2 space (PCA score plots; Fig. 4D, F) across the Daleje Event interval, suggesting broadly similar paleodepositional conditions throughout. One notable exception is a distinct interval characterized by elevated Fe, Ni, and Cu concentrations, accompanied by the appearance of S above the detrital baseline (from 0.8 to 1.7 m; Fig. 8, D8). This interval is tentatively interpreted to reflect transient euxinic conditions.

In the post-Daleje interval, redox-sensitive elements such as Ni, Fe, Cu, Zn and Cr toward the detrital cluster (e.g., Zr, Ti), indicating a waning of reducing conditions and an increasing influence of detrital input (Fig. 4G, I). This pattern is most clearly expressed in the post-Daleje limestones (Fig. 4H), where younger (i.e., stratigraphically higher) samples plot progressively farther from the redox-associated cluster, reflecting a return to less reducing depositional conditions. Although the marls and shales exhibit a somewhat different geochemical structure, their loading patterns (Fig. 4I) similarly point to diminished redox control and stronger detrital influence in the post-event interval. Notably, Ni concentrations remain relatively elevated immediately after the Daleje Event, whereas other redox-sensitive and

detrital elements decline more rapidly (Fig. 8, D8). This decoupling suggests that Ni enrichment in the immediate aftermath of the event is not primarily detrital or redox-driven, but instead reflects lingering post-depositional authigenic processes (Bruggmann et al., 2024).

2.6.3.2. Choteč Interval – Redox Signatures

Overall, redox conditions appear largely comparable in the pre-Choteč (CZ4) and Choteč Event (CZ5) intervals (Fig. 8). Element clustering – most notably grouping of several redox-sensitive elements (e.g., V, Zn, Fe, Mn, Ni) close to the detrital group in PC1-PC2 space – indicates an absence of pervasive reducing conditions during deposition of limestones, marls, and shales (Fig. 5A, C). This interpretation is further supported by significant positive correlations between these elements and detrital indicators, especially in limestones (e.g., Ti; see PCCM Fig. F7, F9). Although several redox-sensitive elements (e.g., S, Cu, Fe, Ni, Zn) load positively on PC3 in pre-Choteč and Choteč limestones (Fig. 5A, E), this component explains only ~9% of total variance and therefore does not provide strong evidence for reducing conditions. Enrichment of most redox-sensitive elements appears either facies-dependent or related to minor diagenetic processes. The absence of stratigraphic trends or clustering in the limestone PCA suggests overall geochemical stability.

In contrast, limestones of the post-Choteč interval (CZ6; Fig. 8) display clearer structure in PCA space, with clustering of several redox-sensitive elements (Fig. 5K) and a gradient along PC2 in the score plot (Fig. 5L), indicating a response to changing depositional and diagenetic conditions. A Mn enrichment pulse (23.3 to 28.3 m; Fig. 8, D9), superimposed on a decreasing detrital background, together with the grouping of P and Mn separated from a cluster containing S, Sr, Cu, Ni, V, Zn, and Fe (Fig. 5K), likely reflects diagenetic remobilization of Mn rather than a clear bottom-water oxygenation signal, especially given the relatively low concentrations of other redox-sensitive elements (e.g., Ni, Cu, Fe, Cr; Fig. 8, D9). Toward the top of the post-Choteč interval, a shift toward more reducing conditions in PC1-PC2 space (Fig. 5L), accompanied by increases in V, Fe, Cu, and Ni (Fig. 8, D9), may indicate a subtle strengthening of slightly reducing conditions and modest increases in productivity, although such an interpretation requires caution given the likely diagenetic overprint in this interval.

2.6.3.3. Kačák Interval – Redox Signatures

The pre-Kačák interval (CZ6; Fig. 2, 8) is characterized by overall low concentrations of Fe and other redox-sensitive trace elements (V, Ni, Cu, Zn, Cr; Fig. D10), which are typically enriched under reducing conditions. In contrast, this interval displays the highest Mn concentrations in the section (Fig. 2, 8). Combined with the association of Mn with other redox-sensitive elements (PCA; Fig. 6C), this pattern strongly suggests redox control and well-oxygenated conditions (Tribovillard et al., 2006, Bruggmann et al., 2024), consistent with vertical

chemocline displacement or an oxygenation event. A brief enrichment of Fe and Ni around ~26 m, decoupled from the detrital signal (Fig. 8, D10), is interpreted as reflecting a short-lived chemocline fluctuation (Tribovillard et al., 2006; Bruggmann et al., 2024). Moderately strong Ni-Fe correlation and moderate Ni-Mn correlation (PCCM; Fig. F13, F14) suggests efficient Ni sorption onto Mn-Fe-oxyhydroxides (Tribovillard et al., 2006; Bruggmann et al., 2024). A gradual shift toward slightly more detrital-rich (PC1) and less reducing (PC2) conditions in the PCA score plot (Fig. 6D) suggests that the transition to well-oxygenated conditions was progressive. Although nodular limestones show somewhat stronger diagenesis, their scarcity prevents them from affecting the broader geochemical signal.

The Kačák Event interval (CZ7; Fig. 2, 8) contrasts sharply with the underlying strata, with thick marly-shaly packages interrupted by relatively thin limestone beds (Fig. 2). This is reflected by the co-variation of most redox-sensitive trace elements and PC1 (Fig. 8, D10). Although their geochemical fingerprint broadly resembles that of the underlying limestones, the grouping of Mn and V with detrital elements indicates stronger facies-control (Fig. 6G). In contrast, Cu-Ni-Zn-Fe cluster separately from the detrital group, suggesting only moderate redox control (Fig. 6G). The absence of Cr and V from this association reflects their strong detrital control (Cr; Tribovillard et al., 2006), with their variability driven mainly by pulses of siliciclastic input (Fig. 8, D10). Thus, the Kačák Event limestones record only limited traces of reducing conditions, and any anoxia or euxinia was probably absent or, at most, short-lived.

A thorough redox assessment of the Kačák Event marls-shales is complicated by several factors. Importantly, mm-thick laminations – including thin black layers – are present throughout the interval (Fig. B1B) but are not resolved at the current 8 mm resolution. While these blackish laminae could reflect fluctuating redox conditions, this cannot be directly supported by the geochemical data. Consequently, the element loadings likely represent an averaged signal (PCA; Fig. 6E, F), which explains why they appear not entirely diagnostic. Opposing Ca-Sr and K-Ti-Zr-Si-Al reflect carbonate-detrital dichotomy, whereas redox-sensitive elements are dispersed across multiple groups (Fig. 6E). Although detrital input exerts a major influence on bulk geochemistry, the dispersed behavior of redox-sensitive elements indicates that the signal cannot be attributed to detrital dilution alone. Some degree of diagenetic redistribution is also likely, as suggested by the independent behavior of S, Zn and Mg (Fig. 6E), further contributing to the mixed geochemical pattern. In combination with fine black laminations, we interpret this pattern cautiously as evidence for intermittent reducing conditions, rather than sustained or pervasive anoxia.

2.6.3.4. *pumilio* Interval – Redox Signatures

The Givetian-aged limestones of the *pumilio* interval (CZ9; Fig. 2) are characterized by overall very low concentrations in redox-sensitive elements (Fe, V, Cu, Zn, Cr, Fig. 8). S, Ni, Cu, Sr, Mn, Zn, Fe, and V are spread across PC1 and load positively across PC2, clearly separated from the detrital cluster, which also includes Cr (Fig. 6I). Notably, Ni and Cu group relatively close to Ca compared to all other intervals, which suggests they may reflect paleoproductivity rather than a strict paleoredox signal (cf. Tribovillard, 2021). This is further supported by the absence of correlation between Ni and Mn (see PCCM; Fig. F17, F18), indicating Ni-enrichment is likely not due to Mn-oxyhydroxide sequestration (Tribovillard et al., 2006; Tribovillard, 2021; Bruggmann et al., 2024). Instead, this reflects an interplay of paleoproductivity signals and authigenic enrichment, consistent with the low detrital background and the limited diagenetic overprint in these facies. Given the considerable diagenetic imprint on nodular limestones, which may significantly alter concentrations and signatures of many redox-sensitive elements, these are not further interpreted within a paleoredox context.

From a redox-geochemistry point of view, the Lower and Upper *pumilio* Event beds share considerable similarities. They appear to initiate immediately after a rise in redox-sensitive elements (S, Fe, V, Ni, Cu, Cr) relative to detrital input (Fig. 8, Fig. D11). This is most clearly expressed by increasing Fe/Ti, V/Ti, Cr/Ti and Ni/Ti values prior to the events (Fig. D12). Such a signature is tentatively interpreted to reflect a brief shift toward mildly reducing conditions, potentially accompanied by a modest increase in paleoproductivity during an anomalously low detrital background. For the entire Lower *pumilio* Event V/Ti and Ni/Ti values remain elevated (Fig. D12). An increase in V decoupled from the detrital signal is indicative of slightly reducing conditions (e.g., Algeo and Maynard, 2004; Tribovillard et al., 2006). The Ni enrichment could in principle reflect redox or paleoproductivity changes (Tribovillard et al., 2006; Tribovillard, 2021), or lingering authigenic processes (Bruggmann et al., 2024) similar to those inferred for the post-Daleje interval. However, the parallel Cu enrichment (Fig. 8, D11), which is expected for a classic paleoproductivity signal (Tribovillard, 2021), is consistent with Ni and Cu jointly reflecting elevated paleoproductivity and prolonged, likely mildly, reducing conditions throughout the event. The Upper *pumilio* Event bed appears largely similar, whereas enrichment of V and Ni appears two-phased, consistent with its bi-phased expression, but declines more rapidly within the event interval (V/Ti, Ni/Ti; Fig. D12). This suggests that the event recorded two short-lived pulses of elevated paleoproductivity and mildly reducing conditions, with the brief interruption – marked by the increased detrital input – likely contributing to the rapid attenuation of trace-metal enrichment (Fig. 2, 8, D11, D12).

2.6.4. Carbon and Oxygen Geochemistry

Bulk carbonate isotopic composition is easily affected by post-depositional alteration, most notably $\delta^{18}\text{O}_{\text{carb}}$ (Grossman and Joachimski, 2020). Therefore, significant correlation between $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$ is usually interpreted to reflect extensive diagenetic overprinting of the carbon isotopic composition, although such covariance can also arise from primary environmental processes (Oehlert and Swart, 2018). At Oued Ferkla, there is only a weak negative correlation between $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$ ($r = -0.14$, $p < 0.05$) across the entire record (Fig. K3A) and for limestones ($r = -0.14$, $p < 0.05$; Fig. K3B). There is no significant correlation between both isotopic signals in marls and shales (Fig. K3C, D). As such, this commonly applied criterion requires caution in vertically heterogeneous, extensive records.

MRCA of $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ (Fig. 9B) illustrates this complexity: on sub-meter scales, the record alternates between positive and negative PCC values, whereas larger windows (~4 m) reveals intervals of positive correlation (e.g., OF2-OF3 or Daleje and post-Daleje intervals, middle OF6 or post-Chotec interval, and OF8 or Kačák interval) interspersed with intervals dominated by predominantly negative $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ correlation (Fig. 9B). These scale-dependent shifts demonstrate that $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ relationships at Oued Ferkla are not uniform and require further evaluation in relation to lithology and stratigraphy. In limestones, positive correlations between $\delta^{13}\text{C}_{\text{carb}}$ and CaCO_3 ($r = 0.47$, $p < 0.05$) and between $\delta^{18}\text{O}_{\text{carb}}$ and CaCO_3 ($r = 0.33$, $p < 0.05$) indicate substantial facies control on carbonate carbon and oxygen isotopic composition (Fig. K1B, K2B). Marls and shales do not show such relationship (Fig. K1C, D, K2C, D). These observations show that $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ values are strongly modulated by lithostratigraphic context and have not been uniformly diagenetically reset.

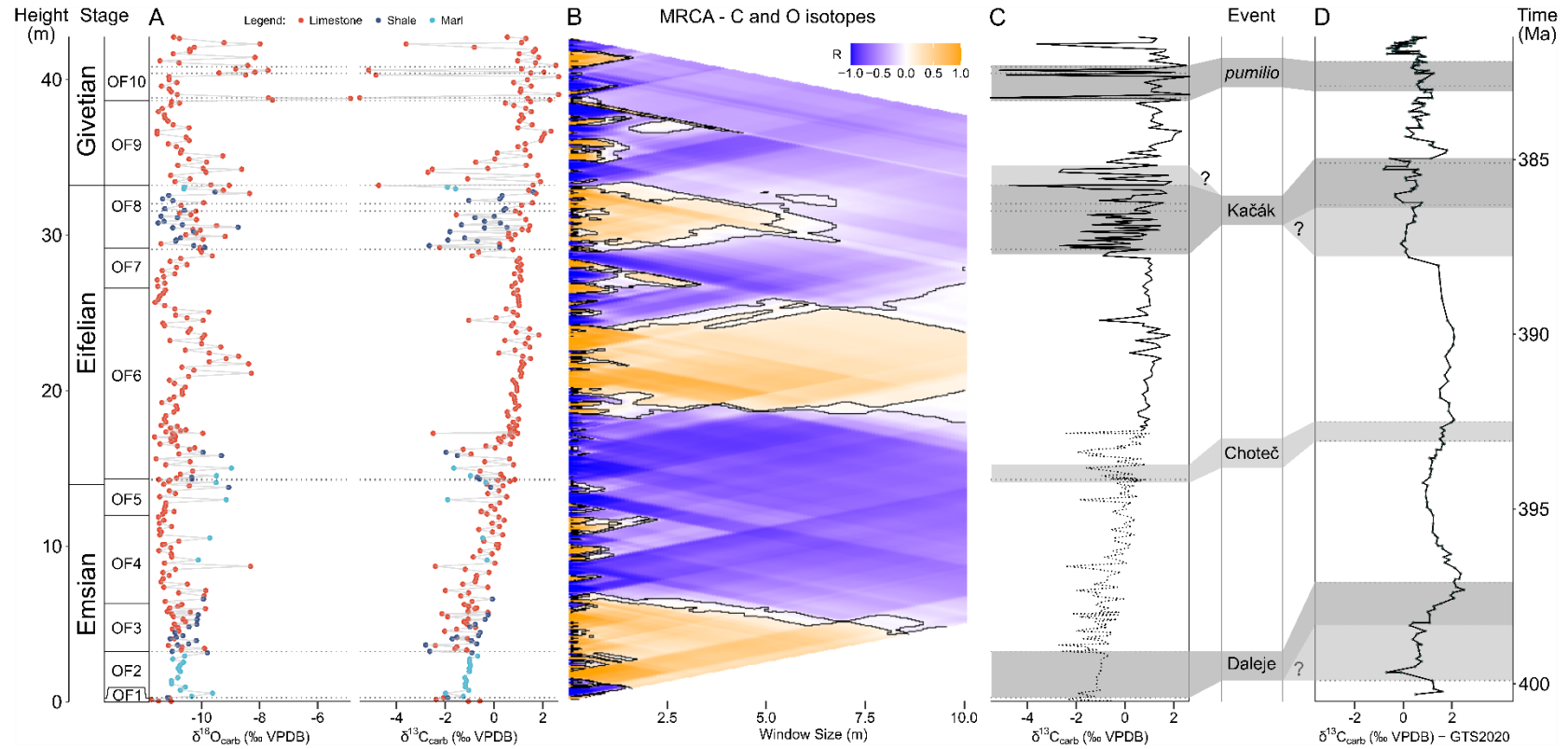


Fig. 9. Carbon and oxygen isotope stratigraphy of Oued Ferkla. A) Oued Ferkla $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ (‰ VPDB) in function of lithology (limestone: red, shale: dark blue, marl: light blue). B) Multi-scale Rolling Correlation Analysis of $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$, significant positive (orange) or negative (blue) Pearson correlation (95% confidence interval) is demarcated by black lines. C) Oued Ferkla $\delta^{13}\text{C}_{\text{carb}}$ profile, dotted part indicates interval likely affected more strongly by diagenesis. D) Carbon isotope curve from the Geological Timescale by Cramer and Jarvis (2020), absolute ages based on Becker et al. (2020). Dark gray bands indicate event-stratigraphy-guided correlation of local $\delta^{13}\text{C}_{\text{carb}}$ inflection points, light gray bands indicate alternative correlations guided by similar $\delta^{13}\text{C}_{\text{carb}}$ excursions and are equally marked by a '?'.

Comparison of absolute $\delta^{13}\text{C}_{\text{carb}}$ ‰ VPDB-values from Oued Ferkla with the Devonian carbon isotope curve (Cramer and Jarvis, 2020) highlights that the lower part (up to ~17 m) of the $\delta^{13}\text{C}_{\text{carb}}$ signal is shifted towards more negative values (up to ~-2 ‰ VPDB), consistent with diagenetic overprinting. Yet, comparison with source material (e.g., figure 13 in Buggisch and Mann, 2004; van Hengstum and Gröcke, 2008) underscores that a gradual increase towards more positive baseline $\delta^{13}\text{C}_{\text{carb}}$ values is expected for the interval ranging from the Daleje up to Kačák events. Because diagenetic alteration is unlikely to have lowered $\delta^{13}\text{C}_{\text{carb}}$ uniformly through the section (see MRCA; Fig. 9B), the superimposed fluctuations cannot simply be corrected by a constant offset. Consequently, this part of the $\delta^{13}\text{C}_{\text{carb}}$ signal is tentatively correlated to the Devonian carbon isotope curve (Cramer and Jarvis, 2020), guided by event-stratigraphy (Fig. 9), but is not discussed further. Due to large differences in resolution, carbon isotope chemostratigraphic correlation of the Kačák Event is likewise tentative and primarily guided by event stratigraphy. In contrast, in the upper part of the section, $\delta^{13}\text{C}_{\text{carb}}$ excursions, including those associated with the *pumilio* events, closely resembles the Devonian carbon isotope curve (Cramer and Jarvis, 2020). Integrating carbon-isotope chemostratigraphy with the event stratigraphy of Talih et al. (2020) places the Oued Ferkla section more firmly within a global framework.

2.6.5. Geochemical Expression of the Daleje, Choteč, Kačák, and *pumilio* events

Here, the proxy-level interpretations of detrital input and paleoredox conditions are integrated into a higher-order environmental synthesis for Oued Ferkla. Given the moderate confidence in the carbon isotope chemostratigraphy and the patchy but generally minor to moderate diagenetic overprint, no further section-wide interpretation is carried out regarding carbon-cycle perturbations or post-depositional alteration.

Lithological observations and interpreted depositional environments from thin-section petrography (Talih et al., 2022) are integrated here with total detrital input, the composition of the detrital fraction, and paleoredox conditions. Total detrital input reflects variability in the major detrital elements (e.g., Al, Ti, K, Zr, Rb, Si; Fig. D1) and is best represented by PC1 across all intervals and lithologies (Fig. 4-6, Fig. E1). Elevated detrital input characterizes the intervals bracketing the Daleje, Choteč and Kačák events, whereas the *pumilio* event beds represent anomalous intervals marked by a near-complete depletion of detrital material (Fig. 10). Superimposed on these secular trends, detrital input fluctuates throughout the record with variable amplitudes.

Inferring grain-size variations from elemental signals is limited by the extent to which hydrodynamic sorting exerted dominant control on the detrital composition. In chemozones CZ6, CZ7, CZ8 (inter-Kačák interval only), and CZ9 (excluding the *pumilio* Event beds), the geochemical fingerprint does not indicate sorting as the dominant control; instead, changes in

provenance and/or mineralogy are likely more important (Fig. 7, 10; Fig. J1). Although hydrodynamic sorting may still contribute to detrital variability in these intervals, we refrain from inferring grain-size changes there (gray boxes in Fig. 10), as resolving such variations would require targeted petrographic analysis beyond the methodological scope of this geochemical study. For intervals characterized by a dominant imprint of hydrodynamic sorting, however, grain-size variability can be estimated based on geochemical fingerprints. A coherent picture emerges when comparing total detrital input and grain-size variations; detrital-rich intervals are characterized by relatively elevated amounts of fine-grained material (and vice versa; Fig. 10). These patterns suggest that variations in detrital input and grain-size tendencies are likely to reflect changes in relative sea level in addition to variations in hydrological conditions, provenance and mineralogy. These relationships are consistent with the interpretation of Talih et al. (2022), who inferred that deposition at Oued Ferkla was modulated by relative sea-level variations.

Redox-sensitive proxies and facies shifts indicate substantial variability in bottom-water oxygenation across the section, in-line with interpretations of Talih et al. (2022). The Daleje and Kačák events record (fluctuating) reducing conditions with brief, possibly euxinic episodes, consistent with deposition in a pelagic shelf basin prone to restricted oxygenation. Aside from the *pumilio* beds, which are discussed in detail below, stronger reducing conditions coincide with elevated, fine-grained detrital input (Fig. 10).

Two fundamentally different environmental configurations can be distinguished at Oued Ferkla. Firstly, intervals marked by a combined increase in fine-grained detrital input and the onset of more reducing bottom-water conditions correspond to shifts from condensed shallow pelagic ramp/platform settings into a pelagic shelf basin with restricted oxygenation (Talih et al., 2022), as documented for both the Daleje and Kačák events. This facies transition is best explained by an increase in accommodation, which would have deepened the water column, displaced the chemocline upward, and promoted oxygen restriction in the lower part of the basin. At the same time, deepening would have enhanced the trapping of fine siliciclastics, as indicated by the grain-size proxies. An invigorated hydrological cycle during wetter intervals may have further amplified detrital delivery, reinforcing the apparent transgressive signals and contributing to the observed coupling between fine-grained siliciclastic input and reducing conditions during these events.

Secondly, intervals characterized by extremely low, coarse-grained detrital input, combined with slightly reducing conditions and indications of elevated paleoproductivity, reflect a contrasting environmental configuration. These intervals correspond to the Lower and Upper *pumilio* Event beds, which occur around the transition from condensed shallow pelagic platform/upper ramp settings into the pelagic lower ramp or slope (Talih et al., 2022; Fig. 10). Although situated within a generally condensed facies context, the dark, 'organic-rich' *pumilio*

beds (Talih et al., 2022) display a unique geochemical signature marked by near-complete detrital depletion and mild oxygen deficiency. Under such conditions, water-column stratification or stagnation could have developed, leading to the 'hypoxic' *pumilio* limestones *sensu* House (1996), driven by enhanced organic-matter production and reduced ventilation.

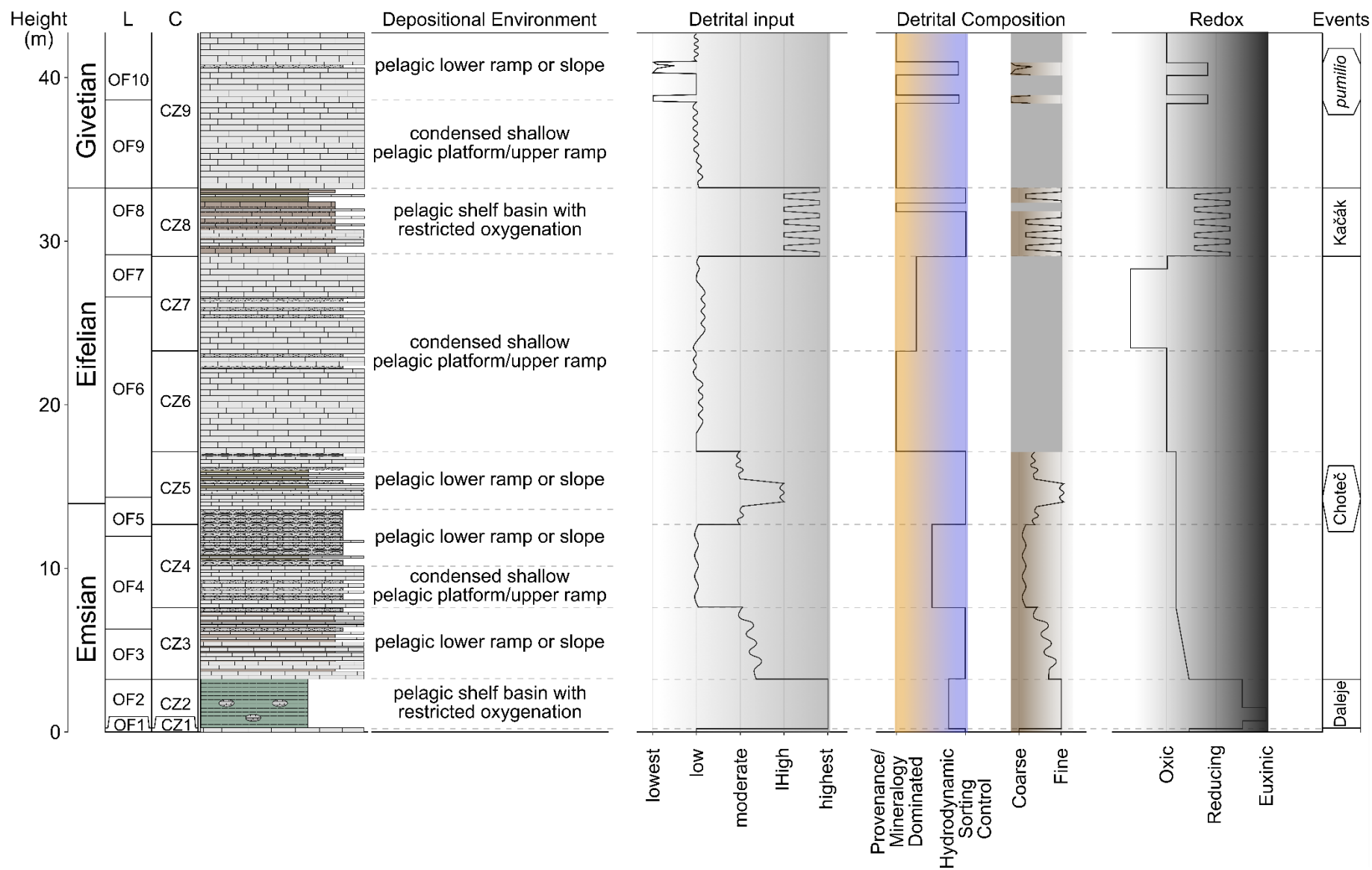


Fig. 10. Synthesis of stratigraphy, depositional setting, and environmental controls at Oued Ferkla. Chronostratigraphy and lithostratigraphic units OF1-OF10 based on Talih et al. (2022). Lithologic column detailing limestone, nodular limestone, marl, shale and greenish shales of the Daleje interval, and limestone nodules (see Fig.2 for legend). Chemozones CZ1 to CZ9 (this work). Interpreted depositional environments are based on thin-section petrography (Talih et al., 2022). Qualitative interpretations include total detrital input (primarily from principal component 1), the dominant regime controlling the composition of detrital material (hydrodynamic sorting vs. provenance/mineralogy), and, where possible, grain-size tendencies inferred from detrital element ratios. Gray boxes mark intervals where hydrodynamic sorting is not dominant and grain-size cannot be inferred. Qualitative paleoredox conditions are inferred from redox-sensitive trace elements and lithological observations. Event stratigraphy is refined from Talih et al. (2022).

2.6.5.1. Daleje Event

At Oued Ferkla, the ‘transgressive’ Daleje Event (Becker et al., 2020) is marked by a sudden shift from limestones to greenish shales. Its geochemical signatures indicate a substantial influx of fine-grained detrital material and onset of reducing to transiently euxinic bottom-waters. This combination of facies change, increased ‘clayey’ detrital input, and more reducing conditions strongly suggests a deepening pulse, consistent with reports of an *anoxic*, transgressive Daleje Event at both local and global scales (House 1985; Chlupač and Kukal, 1986; 1988; Tonarová et al., 2017; Becker et al., 2020; Talih et al., 2022).

The visual similarity between pre-OF1 greenish shales (Fig. B1), which were not formally analyzed here, and Daleje shales raises the possibility that OF1 represents a short-lived interruption within the transgressive anoxic Daleje Event instead. If so, both the pre-OF1 greenish shales and OF1-limestones may belong to the Daleje Event, although targeted characterization would be required to confirm this. Comparable short interruptions of clastic-rich deposition by relatively thin limestone beds also occur in the younger Kačák-interval (Fig. 2), suggesting that pulsed or episodic sedimentation may be characteristic of these anoxic transgressive phases. Alternatively, these strata may mark the termination of the Upper Zlíchov Event – a transgressive-regressive episode well-described in the Prague Basin (Chlupač and Kukal, 1986; 1988). This event is characterized by an upper Zlíchovian regression just prior to the Daleje transgression in the *N. cancellata* Dacryoconarid Zone (Tonarová et al., 2017), which overlaps with the *E. laticostatus* conodont Zone and OF1 limestones (Becker et al., 2020; Talih et al. 2022).

Termination of the Daleje Event appears gradually and pulsed in terms of fine-grained detrital input (Fig. 13), likely linked to a pulsed decrease in relative sea-level. Likewise, reducing conditions appear to gradually decrease although caution is warranted given the potential for a diagenetic contribution, especially concerning the latent Ni-enrichment that may be authigenic (Bruggmann et al., 2024).

2.6.5.2. Choteč Event

The Choteč Event can be recognized at Oued Ferkla by a thin, dark microcrystalline limestone followed by marls (Talih et al., 2022) but does not bear a characteristic geochemical fingerprint. It occurs in an interval characterized by a relative increase in detrital input and relatively strong pulses of elevated fine-grained input, likely indicative of sea-level fluctuations (Fig. 10) that characterize the event in the Prague Basin (Chlupáč and Kukal, 1986, 1988; Vodrážková et al., 2013). Possibly, sea-level fluctuations only amplified the effect of global climate on the organic production, which exerted primary control according to Bábek et al. (2018). While Vodrážková et al. (2013) hypothesize that enhanced nutrient influx during (maximum) flooding triggered oxygen depletion, this can only be partially supported by our results. A similar expression of the Choteč Event is reported from Spain, where it is inferred to have been deposited under warm, humid climatic conditions with greatly enhanced primary productivity (Bond et al., 2024), increased rainfall and terrestrial runoff during maximum transgression (Lopes et al., 2025). While such detrital signatures are consistent with those of the Choteč Event interval at Oued Ferkla, evidence is lacking to support increased paleoproductivity and prevailing reducing conditions. This may be in part due to a relatively weak geochemical redox-imprint in combination with the Choteč Event bed being relatively thin (~35 cm), in addition to possible diagenetic overprinting. Alternatively, differences in the paleodepositional setting may have caused a weaker expression or lack of preservation of reducing conditions, for example if the redox chemocline was located deeper than the point of deposition on the pelagic ramp or slope at Oued Ferkla. (Fig. 10; see also Talih et al., 2022). Readers are referred to Vodrážková et al. (2013), Brocke et al. (2016), Bábek et al. (2018), and Becker et al. (2020) for a more extensive comparison and discussion of the global 'basal' Choteč Event.

2.6.5.3. Mid-Eifelian Oxygenation Event?

The interval preceding the Kačák Event (pre-Kačák interval, CZ7; Fig. 2) is characterized by anomalously high, broadly Gaussian-shaped Mn concentrations, which may reflect either increased oxygenation (Calvert and Pedersen, 1986; Planavsky et al., 2014) or enrichment through diagenesis (Brand and Veizer, 1980; Johnson et al., 2016). This enrichment is stratigraphically and temporally extensive, covering the *T. australis*, *T. kockelianus* to *P. eiflii* conodont zones (Becker et al., 2020; Talih et al., 2022). In sedimentary carbonates, Mn enrichment is generally attributed to diagenetic alteration, resulting from concentration in pore waters following Mn-(oxy)hydroxide reduction and dissolution (Calvert and Pedersen, 1996; Van Cappellen et al., 1998; Tribovillard et al., 2006; Johnson et al., 2016). However, multi-proxy (Mn, Sr, Fe, Mg) diagenetic screening of both limestones and nodular limestones (Fig. I11; Fig. 9) does not reveal typical, long-lasting diagenesis signatures. Although diagenetic remobilization of Mn-oxides may occur independently of changes in Sr, Fe or Mg (Brand and Veizer, 1980; Wittkop et al., 2020), several lines of evidence instead point toward well-oxygenated bottom waters, implying that the substantial Mn enrichment reflects a predominantly primary signal in CZ7.

Firstly, low to moderate diagenetic overprinting in the pre-Kačák interval, identified through thin section petrography, does not consistently correspond to Mn variability; diagenetic overprinting appears moderate and patchy at most. Secondly, the Mn enrichment extends over several meters, potentially representing > 2 Myr of deposition (interpolation based on Becker et al., 2020; Talih et al., 2022). Thirdly, this interval is temporally equivalent (notably the *T. kockelianus* conodont Zone) to a period of increased oxygenation in the North American realm, marked by highest $\delta^{238}\text{U}$ -values of the entire Devonian, as reported by Elrick et al. (2022). Moreover, facies-control over Mn is also excluded as it is not associated with the detrital fraction (Fig. 6A, C; Fig. I11, I12). The meters-thick, stratigraphically continuous Mn spike combined with the depletion of elements that normally are enriched under reducing diagenesis (e.g., Fe), combined with only minor post-depositional diagenetic alteration (thin-section petrography), favors a depositional origin (oxygenation and/or ventilation) rather than localized diagenetic Mn remobilization and enrichment (Banner and Hanson, 1990; Banner, 1995; Tribovillard et al., 2006). While additional analyses are warranted to support this hypothesis, we suggest – based on the arguments outlined above – that the pre-Kačák interval (CZ7) represents an oxygenation pulse or event that preludes the Kačák Event and extends across much of the middle Eifelian. In this condensed shallow-pelagic platform to upper-ramp setting (Talih et al., 2022), intervals characterized by elevated Mn concentrations and more positive $\delta^{238}\text{U}$ (Elrick et al., 2022) values may indicate enhanced bottom-water oxygenation. In this depositional context, such oxygenation pulses are most plausibly linked to relative sea-level fall and associated shoaling of the oxycline and increased water-mass ventilation (cf. Talih et al., 2022).

2.6.5.4. Kačák Event

The Kačák interval is marked by thick shaly-marly successions interbedded with thinner limestone series, representing the regional expression of the global Kačák Event at Oued Ferkla. The ‘broader’ Kačák Event (*sensu* House, 1985) is typically subdivided into two distinct extinction intervals: the *otomari* or Lower Kačák Event and, the Upper Kačák Event or Kačák Event *sensu strictu* (Walliser, 1996; Jamart and Denayer, 2020). A similar distinction was made at Oued Ferkla by Ward et al. (2013) and Talih et al. (2022). The lower ‘transgressive’ event includes “*mass occurrences of dacryoconarids in association with small crinoid ossicles*”, interpreted to reflect “*maximum eutrophication and plankton blooms during a prolonged phase of maximum flooding*” (Ward et al., 2013). Although the Upper Kačák Event is described as being “*slightly regressive*” and “*not distinctive*” at Oued Ferkla (Ward et al., 2013), both Ward et al. (2013) and Talih et al. (2022) emphasize that it is present, albeit with only approximate stratigraphic localization. In this study, the absence of *Tentaculites* was used during logging to identify the inter-Kačák interval, thereby distinguishing the Lower and Upper Kačák Events. This interpretation is supported by MRCA of K/Ti and Zr/Rb (Fig. 7) and Ti/Al and Zr/Rb (Fig. J1), which show a distinct shift in correlation between the event and inter-event intervals that coincides with the lithologically defined boundaries. Although the Kačák Event is widely regarded as polyphased (House, 1996; Becker et al., 2020), the polyphased expression at Oued Ferkla relates specifically to the sedimentological record, where ~7 discrete detrital pulses can be identified.

The onset of the Kačák event signals the shift from preceding stable, dry, well-oxygenated conditions toward more dynamic paleoclimatic conditions, likely linked to an intensification of the hydrological cycle (i.e., wetter paleoclimate) and associated increased fine-grained detrital influx, probably in conjunction with elevated relative sea level (Ward et al., 2013; Talih et al., 2022). The shift in correlation between grain-size proxies (Fig. 7, J1) across the inter-Kačák interval indicates that hydrodynamic sorting is no longer the dominant driver of variability within the detrital fraction. Combined with the strong similarity in lithology with the Lower and Upper Kačák events, the inter-Kačák interval is interpreted as reflecting a sustained highstand phase. Under such deep, stable conditions, hydrodynamic sorting would no longer be the primary control; instead, geochemical variability within the detrital fraction is dominated by the composition and provenance of detrital input. In contrast, while still generally characterized by elevated relative sea-level, the onset of the Upper Kačák Event is interpreted to reflect the beginning of decreasing long-term sea levels – consistent with its regressive character (Ward et al., 2013). As relative sea level decreased, hydrodynamic sorting regained a stronger influence on detrital variability (i.e., correlation between K/Ti, Zr/Rb, and Ti/Al; Fig. 7, J1).

Elemental and lithological evidence indicates that redox conditions also became more variable during the Kačák event, with short-lived, facies-dependent episodes of reduced oxygenation – particularly within the shaly/marly intervals. In contrast, the thin intercalated limestone beds, although locally affected by diagenesis, appear to record brief returns to drier and less reducing conditions. This pattern is consistent with relative sea-level variations and/or wet-dry cycles governing local sedimentation patterns. Given the limited number and qualitative nature of the available redox proxies in addition to the mm-thick black laminations that are not captured in this study, these patterns are best interpreted as strong indications of oxygenation fluctuations. A more detailed reconstruction of redox evolution during the Kačák Event at Oued Ferkla would require μm -resolution sampling using a broader suite of redox-sensitive proxies.

The Kačák Event interval is characterized by overall more negative $\delta^{13}\text{C}_{\text{carb}}$ values with sharp, superimposed fluctuations that are largely, though not entirely, facies-controlled (Fig. K1, K2). Correlation between $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ is highly unstable at sub-meter resolution but is mostly positively throughout (Fig. 9), which may hint at diagenetic overprinting (Oehlert and Swart, 2018). However, comparison with the Devonian carbon-isotope curve (Cramer and Jarvis, 2020), based on $\delta^{13}\text{C}_{\text{carb}}$ values from Canada (van Hengstum and Gröcke, 2008), reveals striking similarities in the timing, magnitude ($\sim 4\text{‰}$), and direction of characteristic negative and positive CIE's (Fig. 9C). This suggests that first-order variations in the $\delta^{13}\text{C}_{\text{carb}}$ signal likely still reflect primary carbon-cycle fluctuations, indicating that carbon-cycle perturbations were strongly pulsed during the Kačák Event at Oued Ferkla.

These lithological, elemental and isotopic signatures are consistent with reports from the neighboring Mech Irdane section, where the Kačák event is characterized by more reducing conditions, greater organic carbon burial, and an increased influx of fine-grained detrital material (Ellwood et al., 2011). Similar signatures are described in the Appalachian Basin, where the Lower Kačák Event extinction coincides with the onset of dysoxic flooding and the Upper Kačák Event is associated with sea-level fall (Bartholomew and Schramm, 2014). Additional global comparisons are provided in Becker et al. (2020) and Kabanov et al. (2023).

2.6.5.5. *pumilio* Event

At Oued Ferkla, the *pumilio* Event limestone beds represent two short-lived pulses of environmental change expressed under exceptionally detrital-poor, carbonate dominated conditions. Both events show extreme depletion of aluminosilicates, indicating very low runoff and minimal siliciclastic input, consistent with increased aridity, in combination with increased paleoproductivity and mildly reducing conditions. While their expression is largely comparable, a brief detrital pulse in the upper event bed introduces a distinctly two-phased expression that sets it apart from the more sustained signal observed in the Lower *pumilio* Event.

Both *pumilio* Event beds display intricate $\delta^{13}\text{C}_{\text{carb}}$ as well as $\delta^{18}\text{O}_{\text{carb}}$ variability, which are discussed in tandem here owing to their unique combination of strongly shifted ‰ VPDB-values and stratigraphically offset carbon and oxygen isotope extrema. At a lower resolution, both events are marked by a minor pCIE (~1‰), showing highest values of the entire record – consistent with earlier reports (Buggisch and Joachimski, 2006) – together with persistently elevated $\delta^{18}\text{O}_{\text{carb}}$ values (Fig. 9). However, the uniphased Lower *pumilio* Event contains a major negative $\delta^{13}\text{C}_{\text{carb}}$ spike interrupting the positive excursion, whereas the biphased Upper *pumilio* Event is characterized by two such negative $\delta^{13}\text{C}_{\text{carb}}$ spikes. In the Lower *pumilio* Event bed, the negative $\delta^{13}\text{C}_{\text{carb}}$ spike is preceded by a pronounced positive $\delta^{18}\text{O}_{\text{carb}}$ spike (Fig. 12). This pattern is inconsistent with typical diagenetic control and instead likely signals a substantial shift in water mass or temperature (e.g., cooling pulse, evaporation; Grossman and Joachimski, 2020) closely followed by carbon-cycle perturbation.

The *pumilio* events remain perhaps some of the most enigmatic events of the entire Devonian (Kabanov et al., 2023). Initially, these event beds were interpreted as tsunami deposits (Lottmann, 1990b). However, work by Brett and Baird (1997) and House (2002) suggests these reflect transgressive pulses. This view is contrasted by Buggisch and Joachimski (2006), who interpreted the mass accumulation of brachiopod shells to represent distal tempestites that were deposited during a lower sea level (i.e., regression). Later work framed both *pumilio* Events as interruptions within a regressive succession (Aboussalam and Becker, 2011), formed under elevated primary productivity (eutrophication) and reduced detrital influx during maximum flooding (Ellwood et al., 2011; Becker et al., 2020). At Oued Ferkla, the *pumilio* beds record pulses of enhanced productivity and mild oxygen depletion formed under extreme detrital starvation, consistent with the reduced siliciclastic input and eutrophication emphasized by Aboussalam and Becker (2011) and Ellwood et al. (2011). While very low runoff and relative increase in coarse-grained detrital material are consistent with arid conditions, winnowing, as suggested by Buggisch and Joachimski (2006) cannot be excluded as an alternative mechanism for the detrital signature. Our data do not allow sea-level to be inferred confidently; detrital geochemical signatures and thin section petrography (Fig. C2C,

D; Talih et al., 2022) are not sufficiently diagnostic to distinguish between the regressive context proposed by Buggisch and Joachimski (2006) and the minor deepening pulse as suggested by Brett and Baird (1997) and Aboussalam and Becker (2011). Regardless of the precise mechanism, the isotope patterns – elevated $\delta^{18}\text{O}_{\text{carb}}$ values together with superimposed negative $\delta^{13}\text{C}_{\text{carb}}$ excursions – point to a transient shift in water mass or temperature as well as a minor carbon cycle perturbation (cf. Buggisch and Joachimski, 2006).

2.7. Conclusions

This study demonstrates a multi-proxy, interval-specific geochemical framework that integrates lithological observations with semi-quantitative pXRF, multivariate statistics (PCA, PCCM), bi-element cross-plots, and the newly developed Multi-scale Rolling Correlation Analysis (MRCA). Applied to the late Emsian to middle Givetian succession at Oued Ferkla, this approach enables high-resolution paleoclimatic and paleoenvironmental reconstruction across multiple Devonian events.

The methodology developed here emphasizes interval-specific analysis carried out on geochemically homogeneous intervals (chemozones), allowing proxy behavior to be evaluated within internally consistent intervals rather than across heterogeneous successions. This is essential for correctly interpreting geochemical signals across major facies shifts. By combining lithological context, thin-section petrography, elemental detrital fingerprinting, paleoredox proxies, and carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data within a qualitative interpretive framework, this approach also provides a robust means of distinguishing primary environmental signals from diagenetic overprinting. Although carbon and oxygen isotope signals show evidence of diagenetic modification, key excursions in the Kačák-*pumilio* intervals still provide constraints on carbon-cycle variability and transient hydrographic or temperature shifts when compared to established Devonian reference curves. MRCA, applied on both elemental and isotopic signals, plays a pivotal role in tracking shifting geochemical controls across stratigraphic space and, hence, time.

This integrated strategy allows reconstruction of paleoclimatic and paleoenvironmental conditions of key events as expressed at Oued Ferkla:

- The Daleje Event, characterized locally by greenish shales, is marked by increased fine-grained detrital influx, reducing to transiently euxinic conditions and signatures consistent with increased accommodation, likely reflecting relative sea-level rise.
- The Choteč Event occurs within an interval showing pulses of increased fine-grained detrital input but is comparatively less pronounced at Oued Ferkla; evidence for anoxia is lacking.
- A Mid-Eifelian Oxygenation Event is tentatively identified in the *T. australis* - *T. kockelianus* - *P. eiflii* conodont zones, indicating locally long-lasting, elevated oxygenation. Post-dating the Emsian-Eifelian boundary oxygenation event, it is interpreted to reflect well-oxygenated global baseline conditions persisting throughout the middle to upper Devonian.
- The Kačák Event interval encompasses the visually similar Lower and Upper Kačák events, identified here through mass occurrences of *Tentaculites* in addition to geochemical shifts revealed by MRCA. This interval is marked by thick laminated marl

and (black) shale packages rich in fine-grained detrital material and recording reducing conditions, interrupted by relatively thin limestones beds – a pattern that is consistent with pulsed sea-level variations and/or alternating wet-dry conditions, accompanied by rapid carbon cycle fluctuations.

- The *pumilio* Event interval encompasses the Lower and Upper *pumilio* Event beds, both characterized by brachiopod-rich (*Ense pumilio*) black crystalline limestones almost entirely depleted in detrital material. Although the Upper event differs from the Lower by its biphasic expression, both events are characterized by increases in paleoproductivity and reducing conditions, accommodation changes and carbon-cycle perturbations.

The methodological workflow outlined here provides a general framework for disentangling diagenetic, detrital, and redox signals in extensive and heterogeneous sedimentary records. While the workflow itself is broadly transferable, the specific choice of elements, ratios, and correlation structures must be adapted to the lithological, stratigraphic, and geochemical characteristics of each record. Thus, our approach offers a methodological benchmark rather than a fixed, universally applicable recipe. It equally underscores the need for record-specific proxy interpretation – grounded in complementary geochemical and petrographic analyses – rather than the uncritical application of proxy behavior derived from other basins or records.

While the framework developed here already resolves the major environmental patterns in a coherent and internally consistent manner, future work may further enrich this approach by incorporating quantitative elemental analyses (e.g., ICP-MS), TOC and $\delta^{13}\text{C}_{\text{org}}$ measurements, Fe-speciation, and additional isotopic systems capable of refining paleoredox (e.g., $\delta^{238}\text{U}$; Elrick et al., 2022) and paleotemperature reconstructions (e.g., clumped Δ_{47} isotopes). These additions would not replace the present workflow, but would extend its resolution and robustness, offering an even more detailed and complete view of the environmental dynamics associated with Devonian event intervals.

Acknowledgements

This is a contribution to the "Projet de Recherche" funded by the Belgian National Fund of Scientific Research (FNRS), contract T.0037.22 "WarmAnoxia". Michael M. Joachimski from the GeoZentrum Nordbayern, Friedrich-Alexander Universität of Erlangen-Nürnberg, Erlangen, Germany is warmly thanked for the carbonate carbon and oxygen isotope measurements and the insightful discussion on their interpretation. Raphaël Deville is greatly acknowledged for providing excellent thin sections.

References

- Aboussalam, S. Z., Becker, R. T., 2011. The global Taghanic Biocrisis (Givetian) in the eastern Anti-Atlas, Morocco. *Palaeogeogr., Palaeoclimatol., Palaeoecol.*; 304, 163-164. doi:10.1016/j.palaeo.2010.10.015
- Aboussalam, S. Z., Becker, R. T., Bultynck, P., 2015. Emsian (Lower Devonian) conodont stratigraphy and correlation of the Anti-Atlas (Southern Morocco). *Bull. Geosci.*; 90, 4, 893-980. doi:10.3140/bull.geosci.1534
- Algeo, T. J. and Liu, J., 2020. A re-assessment of elemental proxies for paleoredox analysis. *Chem. Geol.*; 540, 119549. <https://doi.org/10.1016/j.chemgeo.2020.119549>.
- Algeo, T. J., Maynard, B. J., 2004. Trace-element behavior and redox facies in core shales of Upper Pennsylvanian Kansas-type cyclothems. *Chem. Geol.*; 206, 289-318. doi:10.1016/j.chemgeo.2003.12.009
- Algeo, T. J., and Lyons, T. W., 2006. Mo–total organic carbon covariation in modern anoxic marine environments: Implications for analysis of paleoredox and paleohydrographic conditions, *Paleoceanogr.*; 21, PA1016, doi:10.1029/2004PA001112.
- Bábek, O., Kumpan, T., Kalvoda, J., Grygar, T. M., 2016. Devonian/Carboniferous boundary glacioeustatic fluctuations in a platform-to-basin direction: A geochemical approach of sequence stratigraphy in pelagic settings. *Sediment. Geol.*; 337, 81-99. <http://dx.doi.org/10.1016/j.sedgeo.2016.03.009>
- Bábek, O., Faměra, M., Šimíček, D., Weinerová, H., Hladil, J., 2018. Sea-level changes vs. Organic productivity as controls on Early and Middle Devonian bioevents; Facies- and gamma-ray based sequence-stratigraphic correlation of the Prague Basin, Czech Republic. *Glob. Planet. Change*; 160, 75-95. <https://doi.org/10.1016/j.gloplacha.2017.11.009>
- Banner, J. L., 1995. Application of the trace element and isotope geochemistry of strontium to studies of carbonate diagenesis. *Sedimentol.*; 42, 802-824.
- Banner, J. L., Hanson, G. N., 1990. Calculation of simultaneous isotopic and trace element variations during water-rock interaction with applications to carbonate diagenesis. *Geochim. Cosmochim. Acta*; 54, 3123-3137.
- Bartholomew, A. J., Schramm, T. J., 2013. The nature and timing of the Middle Devonian Kačák bioevents in the Marcellus subgroup of the Appalachian Basin. *Palaaios*; 28, 825-823. <http://dx.doi.org/10.2110/palo.2014.021>
- Becker, R. T., Marshall, J. E. A., Da Silva, A.-C., 2020. The Devonian Period. In: Gradstein, F. M., Ogg, J. G., Schmitz, M. D. And Ogg, G. (Eds.), *The Geologic Time Scale 2020*, chapter 22, 733-810. <https://doi.org/10.1016/B978-0-12-824360-2.00022-X>.
- Becker, R. T., House, M. R., 1994. International Devonian goniatite zonation, Emsian to Givetian, with new records from Morocco. *CFS*; 169, 79-135.
- Bennet, W. W., Canfield, D. E., 2020. Redox-sensitive trace metals as paleoredox proxies: A review and analysis of data from modern sediments. *Earth Sci. Rev.*; 204, 103175. <https://doi.org/10.1016/j.earscirev.2020.103175>.
- Bond, D., Blanco-Ferrera, S., Grasby, S., Greene, S., Hilton, J., Lopes, G., Lu, J., Marshall, J., Sanz-López, J., Wellman, C., and Yin, L., 2024. The early Middle Devonian Choteč Event in northern Spain: a brief anoxic pulse driven by enhanced weathering and eutrophication, EGU General Assembly 2024, Vienna, Austria, 14–19 Apr 2024, EGU24-21645, <https://doi.org/10.5194/egusphere-egu24-21645>.
- Brand, U., Veizer, J., 1980. Chemical diagenesis of a multicomponent carbonate system – 1: Trace elements. *J. Sediment. Petrol.*; 50, 4, 1219-1236.
- Brett, C. E., Baird, G. C., 1997. *Paleontological Events: Stratigraphic, Ecological, and Evolutionary Implications*. Columbia University Press, New York. ISBN: 9780231082501
- Brett, C. E., Zambito, J. J. IV, McLaughlin, P. I., Emsbo, P., 2020. Revised perspectives on Devonian biozonation and environmental volatility in the wake of recent time-scale revisions. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 549, 108843. <https://doi.org/10.1016/j.palaeo.2018.06.037>.

- Brocke, R., Fatka, O., Lindemann, R. H., Schindler, E., Ver Straeten, C. A., 2016. Palynology, dacroconarids and the lower Eifelian (Middle Devonian) Basal Choteč Event: case studies from the Prague and Appalachian basins. In: Devonian Climate, Sea Level and Evolutionary Events, Becker, R. T., Königshof, P., Brett, C. E., (eds.). Geol. Soc. Lond., Spec. Publ.; 423. <http://doi.org/10.1144/SP423.8>
- Bruggmann, S., Severmann, S., McManus, J., 2023. Geochemical conditions regulating chromium preservation in marine sediments. *Geochim. Cosmochim. Acta*; 348, 239-257. <https://doi.org/10.1016/j.gca.2023.03.003>
- Bruggmann, S., McManus, J., Archer, C., Vance, D., Severmann, S., 2024. Nickel's behaviour in marine sediments under aerobic to anaerobic diagenetic conditions. *Chem. Geol.*; 662, 122234. <https://doi.org/10.1016/j.chemgeo.2024.122234>
- Buggisch, W., Joachimski, M. M., 2006. Carbon isotope stratigraphy of the Devonian of Central and Southern Europe. *Palaeogeogr., Palaeoclimatol., Palaeoecol.*; 240, 68-88. doi:10.1016/j.palaeo.2006.03.046
- Buggisch, W., Mann, U., 2004. Carbon isotope stratigraphy of Lochkovian to Eifelian limestones from the Devonian of central and southern Europe. *Int. J. Earth Sci.*; 91, 521-541. DOI 10.1007/s00531-004-0407-6
- Calvert, S. E. and Pedersen, T. F., 1996. Sedimentary geochemistry of manganese; implications for the environment of formation of manganiferous black shales. *Econ. Geol.*; 91, 1, 36-47. <https://doi.org/10.2113/gsecongeo.91.1.36>
- Calvert, S. E. and Pedersen, T. F., 2007. Elemental proxies for palaeoclimatic and palaeoceanographic variability in marine sediments: interpretation and application. In: Hillaire-Marcel, C. and De Vernal, A. (Eds.), *Proxies in late Cenozoic Paleocyanography*, chapter 14, Dev. In Mar. Geol.; 1, 567-643. ISSN 1572-5480, doi:10.1016/S1572-5480(07)01019-6.
- Chlupáč, I., Kukal, Z., 1986. Reflection of possible global Devonian events in the Barrandian area, C.S.S.R. In: *Lecture Notes in Earth Sciences*, Vol., Walliser, O. (ed.). Springer-Verlag, Berlin.
- Chlupáč, I., Kukal, Z., 1988. Possible global events and the stratigraphy of the Palaeozoic of the Barrandian (Cambrian-Middle Devonian, Czechoslovakia). *Sbor. Geol. Ved.*; 43, 83-146. ISSN 0581-9172.
- Cramer, B. D. and Jarvis, I., 2020. Carbon Isotope Stratigraphy. In: Gradstein, F. M., Ogg, J. G., Schmitz, M. D. And Ogg, G. (Eds.), *The Geologic Time Scale 2020*, chapter 11, 309-343. <https://doi.org/10.1016/B978-0-12-824360-2.00011-5>
- Croudace, I. W. and Rothwell, R. G., 2015. Micro-XRF studies of sediment cores, Applications of a non-destructive tool for the environmental sciences. In: Smol, J. P. (Ed.), *Dev. in Paleoenv. Res.*; 17, ISSN 1571-5299.
- Da Silva, A. -C., Triantafyllou, A., Delmelle, N., 2023. Portable x-ray fluorescence calibrations: Workflow and guidelines for optimizing the analysis of geological samples. *Chem. Geol.*; 623, 121395. <https://doi.org/10.1016/j.chemgeo.2023.121395>
- Denckmann, A. 1892. Schwarze Goniatiten-Kalke im Mitteldevon des Kellerwaldgebirges, *Jb. kgl. preuß. geol. L.-A. f.*; 13, 12-15.
- Destombes, J., Hollard, H., Willefert, S., 1985. Lower Paleozoic rocks of Morocco. In: *Lower Paleozoic rocks of North-Western and West-Central Africa*, Holland, C. H. (ed.). John Wiley, Chichester; 91-336.
- Dissard, D., Reichart, G. J., Menkes, C., Mangeas, M., Frickenhaus, S., Bijma, J., 2021. Mg/Ca, Sr/Ca and stable isotopes from the planktonic foraminifera *T. sacculifer*: testing a multi-proxy approach for inferring paleotemperature and paleosalinity. *Biogeosciences*; 18, 423-439. <https://doi.org/10.5194/bg-18-423-2021>
- Duchesne, J. -C., Meus, P., Boulvain, F., 2017. Geochemistry of Lower Devonian terrigenous sedimentary rocks from the Belgian Ardenne: Source proxy and paleogeographic reconstruction. *Sediment. Geol.*; 375, 157-171. doi: 10.1016/j.sedgeo.2017.11.008
- Ellwood, B. B., Algeo, T. J., El Hassani, A., Tomkin, J. H., Rowe, H. D., 2011. Defining the timing and duration of the Kačák interval within the Eifelian/Givetian boundary GSSP, Mech Irdane, Morocco, using

- geochemical and magnetic susceptibility patterns. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 304, 74-78. doi:10.1016/j.palaeo.2010.10.012
- Elrick, M., Gilleaudeau, G., Romaniello, S. J., Algeo, T. J., Morford, J. L., Sabbatino, M., Goepfert, T. J., Cleal, C., Cascales-Miñana, B., Chernyavkiy, P., 2023. Major Early-Middle Devonian oceanic oxygenation linked to early land plant evolution detected using high-resolution U isotopes of marine limestones. *Earth Planet. Sci. Lett.*; 581, 117410. <https://doi.org/10.1016/j.epsl.2022.117410>
- Ferrová, L., Frýda, J., Lukeš, P., 2012. High-resolution tentaculite biostratigraphy and facies development across the Early Devonian Daleje Event in the Barrandian (Bohemia): implications for global Emsian stratigraphy. *Bull. Geosc.*; 87, 3, 587-624. doi: 10.3140/bull.geosci.1336
- García-Alcalde, J. L., 1997. North Gondwanan Emsian Events. *Episodes*; 20, 4, 241-246.
- Grossman, E. L., Joachimski, M. M., 2020. Oxygen Isotope Stratigraphy. *The Geologic Time Scale 2020*, chapter 10, 279-307. <https://doi.org/10.1016/B978-0-12-824360-2.00010-3>
- He, R., Elrick, M., Day, J., Lu, W., Lu, Z., 2022. Devonian upper ocean redox trends across Laurussia: Testing potential influences of marine carbonate lithology on bulk rock I/Ca signals. *Front. Mar. Sci.*; 9, 874759. doi: 10.3389/fmars.2022.874759
- House, M. R., 1985. Correlation of mid-Palaeozoic ammonoid evolutionary events with global sedimentary perturbations. *Nature*; 313, 3, 17-22.
- House, M. R., 1996. Juvenile, goniatite survival strategies following Devonian extinction events. In: *Biotic recovery from Mass Extinction Events*, Hart, M. B. (ed). *Geol. Soc., Spec. Publ.*; 102, 163-185.
- House, M. R., 2002. Strength, timing, setting and cause of mid-Palaeozoic extinctions. *Palaeogeogr., Palaeoclimatol., Palaeoecol.*, 181, 5-25.
- Hu, D., Li, D., Zhou, L., Sun, L., Xu, Y., 2023. Diagenetic effects on strontium isotope ($^{87}\text{Sr}/^{86}\text{Sr}$) and elemental (Sr, Mn, and Fe) signatures of Late Ordovician carbonates. *JUSTC*; 53, 5, 0503. DOI: 10.52396/JUSTC-2022-0160
- Jamart, V., Denayer, J., 2020. The Kačák event (late Eifelian, Middle Devonian) on the Belgian shelf and its effects on rugose coral palaeobiodiversity. *Bull. Geosc.*; 95, 3, 279-311. DOI 10.3140/bull.geosci.1788
- Joachimski, M. M., Breisig, S., Buggisch, W., Talent, J. A., Mawson, R., Gereke, M., Morrow, J. R., Day, J., Weddige, K., 2009. Devonian climate and reef evolution: Insights from oxygen isotopes in apatite. *Earth Planet. Sci.*; 284, 599-609. doi:10.1016/j.epsl.2009.05.028
- Johnson, E., Webb, S. M., Ma, C., Fischer, W. W., 2016. Manganese mineralogy and diagenesis in the sedimentary rock record. *Geochim. Cosmochim. Acta*; 173, 210-231. 10.1016/j.gca.2015.10.027
- Kabanov, P., Hauck, T. E., Gouwy, S. A., Grasby, S. E., van der Boon, A., 2023. Oceanic anoxic events, photic-zone euxinia, and controversy of sea-level fluctuations during the Middle-Late Devonian. *Earth-Sci. Rev.*; 241, 104415. <https://doi.org/10.1016/j.earscirev.2023.104415>
- Koptíková, L., 2011. Precise position of the Basal Chotec event and evolution of sedimentary environments near the Lower-Middle Devonian boundary: The magnetic susceptibility, gamma-ray spectrometric lithological, and geochemical record of the Prague Synform (Czech Republic). *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 304, 96-112. doi:10.1016/j.palaeo.2010.10.011
- Lash, G. G., 2017. A multiproxy analysis of the Frasnian-Famennian transition in western New York State, USA. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 473, 108-122. <http://dx.doi.org/10.1016/j.palaeo.2017.02.032>
- Liu, Y., Shi, W., Hu, Q., Yuan, K., Xu, X., Zhang, X., Wang, R., Chen, X., Bai, L., Gingras, M. K., Konhauser, K. O., 2024a. The mechanism of organic matter accumulation in the archipelago marine sediments: Insights from the Middle Devonian Givetian mudstone with low TOC in the Youjiang Basin, South China. *Mar. Pet. Geol.*; 160, 106626. <https://doi.org/10.1016/j.marpetgeo.2023.106626>
- Liu, Y., Shi, W., Yuan, K., Wang, R., Xu, X., Zhang, X., Bai, L., Feng, Q., Konhauser, K. O., 2024. Petrographic and geochemical characteristics of the Middle Devonian Eifelian Nabiao Formation in the Youjiang Basin, South China: implications for paleoenvironment and organic matter accumulation mechanism. *Geoenergy Sci. Eng.*; 232, 212419. <https://doi.org/10.1016/j.geoen.2023.212419>

- Lopes, G., Blanco-Ferrera, S., Bond, D. P. G., Greene, S. E., Hilton, J., Marshall, J. E. A., Sanz-López, J., Wellman, C. H., 2025. A palynological investigation of the Early-Middle Devonian transition and associated Choteč Event in Northern Spain. *Rev. Palaeobot. Palynol.*; 332, 105222. <https://doi.org/10.1016/j.revpalbo.2024.105222>
- Lottmann, J., 1990a. The middle Givetian pumilio-events A tool for high time resolution and event-stratigraphical correlation. In: Kaufmann, B., Walliser, O. H. (eds.), *Extinction Events in Earth History*, 30: 145–149.
- Lottmann, J., 1990b. Die pumilio-Events (Mittel-Devon). *Göttinger Arbeiten zur Geologie und Paläontologie*; 44, 1-98.
- Ma, X. -P., Wang, C. -Y., Racki, G., Racka, M., 2008. Facies and geochemistry across the Early–Middle Frasnian transition (Late Devonian) on South China carbonate shelf: Comparison with the Polish reference succession. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 269, 130-151. doi:10.1016/j.palaeo.2008.04.034
- Ma, K., Hinnov, L. A., Zhang, X., Gong, Y., 2022. Astronomical climate changes trigger Late Devonian bio- and environmental events in South China. *Glob. Planet. Change*; 215, 103874. <https://doi.org/10.1016/j.gloplacha.2022.103874>.
- Machel, H. G., 2004. Concepts and models of dolomitization: a critical reappraisal. *Geol. Soc. Lond., Spec. Publ.*; 235, 7-63. doi: 10.1144/GSL.SP.2004.235.01.02
- Nürnberg, D., Bijma, J., Hemleben, C., 1996. Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures. *Geochim. Cosmochim. Acta*; 60, 5, 803-814. 10.1016/0016-7037(95)00446-7
- Oehlert, A. M., Swart, P. K., 2019. Rolling window regression of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in carbonate sediments: Implications for source and diagenesis. *Depos. Rec.*; 5, 3, 613-630. <https://doi.org/10.1002/dep2.88>
- Ott, R., Gallen, S. F., Helman, D., 2023. Erosion and weathering in carbonate regions reveal climatic and tectonic drivers of carbonate landscape evolution. *Earth Surf. Dynam.*; 11, 2, 247-257. <https://doi.org/10.5194/esurf-11-247-2023>
- Planavsky, N., J., Asael, D., Hofmann, A., Reinhard, C. T., Lalonde, S. V., Knudsen, A., Wang, X., Ossa, F. O., Pecoits, E., Smith, A. J. B., Beukes, N. J., Bekker, A., Johnson, T. M., Konhauser, K. O., Lyons, T. W., Rouxel, O. J., 2014. Evidence for oxygenic photosynthesis half a billion years before the Great Oxidation Event. *Nat. Geosci.*; 7, 283-286. DOI: 10.1038/NNGEO2122
- Ramkumar, M., 2015. Toward standardization of terminologies and recognition of chemostratigraphy as a formal stratigraphic method. *Chemostratigraphy*, Chapter 1; 1-21. <https://doi.org/10.1016/B978-0-12-419968-2.00001-7>
- Roemer, 1855. Beiträge zur geologischen Kenntnis des nordwestlichen Harzgebirges. III. - *Palaeontographica* 5: 1-46.
- Sageman, B. B., Hollander, D. J., 1999. Cross correlation of paleoecological and geochemical proxies: A holistic approach to the study of past global change. In: *Evolution of the Cretaceous Ocean-Climate System*: Boulder, Colorado; *Geol. Soc. Am., Spec. Pap.*; 332, 365-384.
- Sageman, B. B., Lyons, T. W., 2004. Geochemistry of Fine-grained sediments and sedimentary rocks. *Treatise on Geochemistry*; 7, 115-158. ISBN: 0-08-043751-6.
- Sageman, B. B., Murphy, A. E., Werne, J. P., Ver Straeten, C. A., Hollander, D. J., Lyons, T. W., 2003. A tale of shales: the relative roles of production, decomposition, and dilution in the accumulation of organic-rich strata, Middle–Upper Devonian, Appalachian basin. *Chem. Geol.*; 195, 229-273. doi:10.1016/S0009-2541(02)00397-2.
- Scotese, C. R., 2021. An atlas of Phanerozoic paleogeographic maps: The seas come in and the seas go out. *Annu. Rev. Earth Planet. Sci.*; 49, 669-718. <https://doi.org/10.1146/annurev-earth-081320-064052>
- Slavik, L., Hladil, J., 2020. Early Devonian (Lochkovian – Early Emsian) bioevents and conodont response in the Prague Synform (Czech Republic). *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 549, 109148. <https://doi.org/10.1016/j.palaeo.2019.04.004>

- Swart, P., 2015. The geochemistry of Carbonate Diagenesis: The Past, Present and Future. *Sedimentology*; 62, 5, 1233-1304. <https://doi.org/10.1111/sed.12205>
- Talih, A., Aboussalam, S. Z., Becker, R. T., Saadi, M., Benmlih, A., 2022. Stratigraphy and tectono-sedimentary processes of allochthonous and autochthonous Devonian deposits of the Tisdafine Basin, Eastern Anti-Atlas, Morocco. *Bulletin de l'Institut Scientifique, Rabat, Section Sciences de la Terre*; 44, 27-53. e-ISSN : 2458-7184
- Tribovillard, N., Algeo, T. J., Lyons, T., Riboulleau, A., 2006. Trace metals as paleoredox and paleoproductivity proxies: An update. *Chem. Geol.*; 232, 12-32. doi:10.1016/j.chemgeo.2006.02.012
- Tribovillard, N., 2021. Re-assessing copper and nickel enrichments as paleoproductivity proxies. *Earth Sci. Bull.*; 192, 54. <https://doi.org/10.1051/bsgf/2021047>.
- Van Cappellen, P., Viollier, E., Roychoudhury, A., Clark, L., Ingali, E., Lowe, K., Dichistrina, T., 1998. Cycling of iron and manganese in surface sediments; a general theory for the coupled transport and reaction of carbon, oxygen, nitrogen, sulfur, iron, and manganese. *Environ. Sci. Technol.*; 32, 2931-2939.
- Van der Weijden, C. H., 2002. Pitfalls of normalization of marine geochemical data using a common divisor. *Mar. Geol.*; 184, 167-187.
- van Hengstum, P. J., Gröcke, D. R., 2008. Stable isotope record of the Eifelian-Givetian boundary Kačak-otomari Event (Middle Devonian) from Hungry Hollow, Ontario, Canada. *Can. J. Earth Sci.*; 45, 353-366. doi:10.1139/E08-005
- Veizer, J., 1983. Chemical diagenesis of carbonates: Theory and application of trace element technique. *Ottawa-Carleton Centre for Geoscience Studies*; 06-82.
- Vodrážková, S., Frýda, J., Suttner, T. J., Koptíková, L., Tonarová, P., 2013. Environmental changes close to the Lower-Middle Devonian boundary: the Basal Choteč Event in the Prague Basin (Czech Republic). *Facies*; 59, 425-449. DOI 10.1007/s10347-012-0300-x
- Walliser, O. H., 1985. Natural boundaries and commission boundaries in the Devonian. *Courier Forschungsinstitut Senckenberg*; 75, 401-408.
- Walliser, O. H., 1996. *Global events and event stratigraphy*. ISBN-13: 978-3-642-79636-4. Springer; 225-250. doi:10.1007/978-3-642-79634-0.
- Ward, P. D., Becker, R. T., Aboussalam, S. Z., Rytina, M., Stichling, S., 2013. The Devonian at Oued Ferkla (Tinejdad region, SE Morocco). *International Field Symposium "The Devonian and Lower Carboniferous of northern Gondwana, Morocco 2013"*; 23-30.
- Whalen, M. T., Śliwiński, M. G., Payne, J. H., Day, J. E., Chen, D., Da Silva, A. -C., 2015. Chemostratigraphy and magnetic susceptibility of the Late Devonian Frasnian-Famennian transition in western Canada and southern China: implications for carbon and nutrient cycling and mass extinction. In: *Magnetic Susceptibility Application: A Window onto Ancient Environments and Climatic Variations*, Da Silva, A. -C., Whalen, M. T., Hladil, J., Chadimova, L., Chen, D., Spassov, S., Boulvain, F., Devleeschouwer, X. (eds.). *Geol. Soc. Lond., Spec. Publ.*; 414, 37-72. <http://doi.org/10.1144/SP414.8>
- Wichern, N. M. A., Bialik, O. M., Nohl, T., Percival, L. M. E., Becker, T. R., Kaskes, P., Claeys, P., De Vleeschouwer, D., 2024. Astronomically paced climate and carbon cycle feedbacks in the lead-up to the Late Devonian Kellwasser Crisis. *Clim. Past*; 20, 415-448. <https://doi.org/10.5194/cp-20-415-2024>
- Wintsch, R. P., Kvale, C. M., 1994. Differential mobility of elements in burial diagenesis of siliciclastic rocks. *J. Sediment. Res.*; A64, 2, 349-361.
- Wittkop, C., Swanner, E. D., Grengs, A., Lambrecht, N., Fakhraee, M., Myrbo, A., Bray, A. W., Poulton, S. W., Katsev, S., 2020. Evaluating a primary carbonate pathway for manganese enrichments in reducing environments. *Earth Planet. Sci. Lett.*; 538, 116201. <https://doi.org/10.1016/j.epsl.2020.116201>
- Yuan, N., Xoplaki, E., Zhu, C., Luterbacher, J., 2016. A novel way to detect correlations on multi-time scales, with temporal evolution and for multi-variables. *Sci. Rep.*; 6, 27707. DOI: 10.1038/srep27707

2.8. Supplemental Information

A. R code and Raw Data

All data and R-code can be found via <https://doi.org/10.5281/zenodo.20305371>.

B. Photos of Oued Ferkla

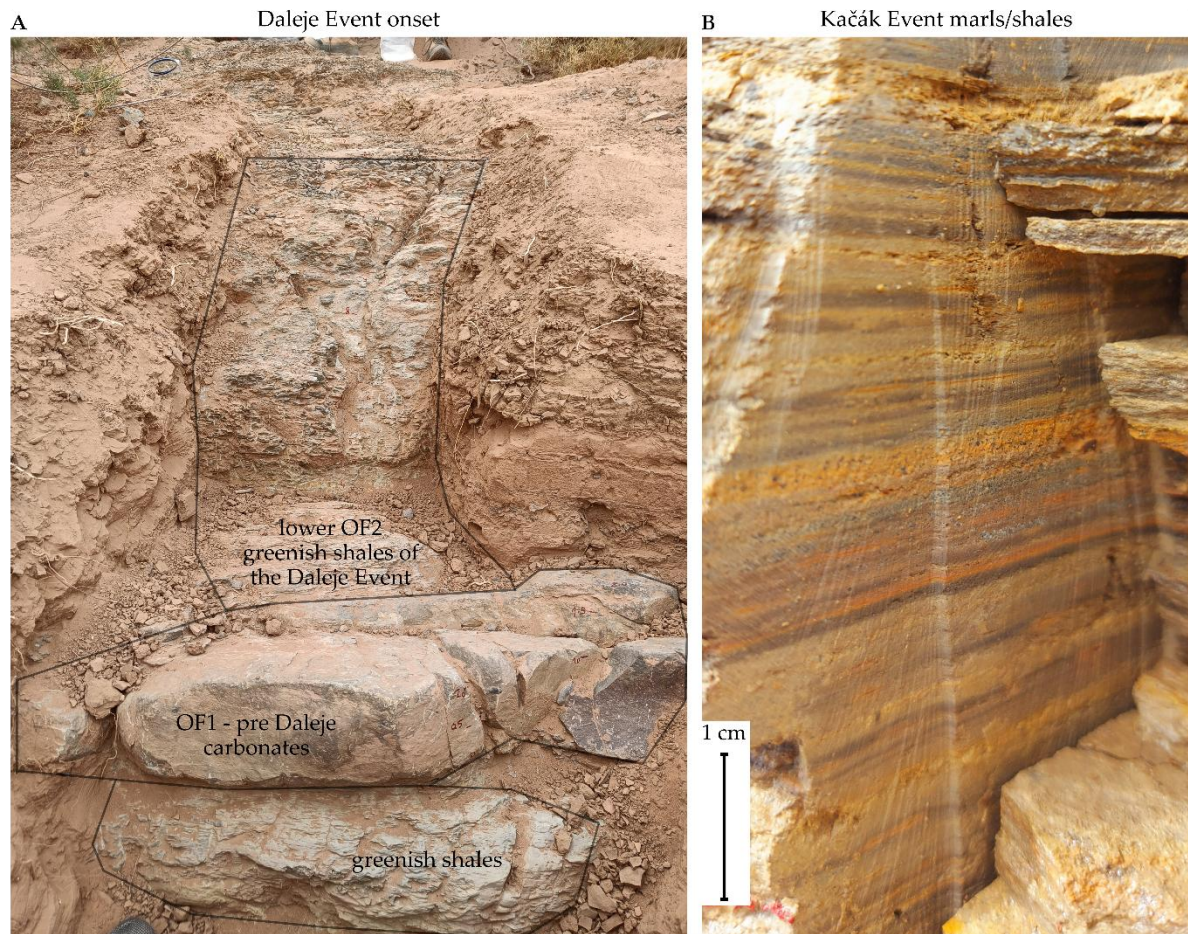


Fig. B. Photos of the Daleje and Kačák events. A) The greenish shales below the pre-Daleje limestones (OF1) are visually strikingly similar to the greenish shales of the Daleje Event (OF2). B) Kačák marls and shales; zoom-in on mm-thin black laminations – scale bar at 1 cm.

C. Thin-section Petrography

Thin sections were produced for a limited amount of limestone samples ($n = 30$) to complement petrography carried out by Talih et al., (2022) as a support when interpreting geochemical signals, focusing on traces of diagenetic alteration and Event intervals. Thin section petrography was done using an Olympus BH2-UMA at 10×5 magnification. Selected photos of thin sections are displayed here, including the OF1 limestones, but also OF1 limestones, dolomitized and not dolomitized Kačák limestones as well as recrystallization and/or dolomitization in *pumilio* interval.

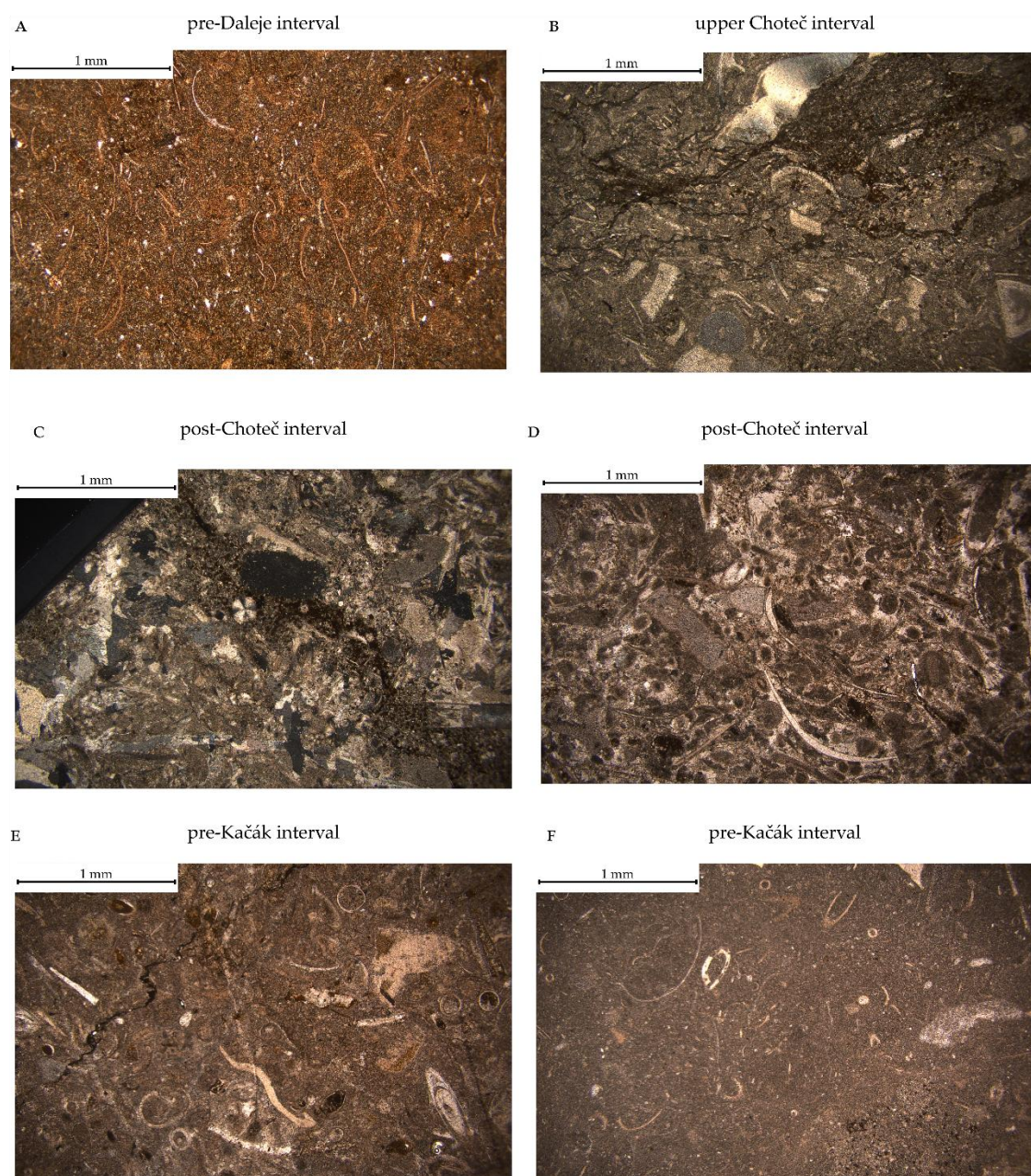


Fig. C1. Thin-section petrography of Oued Ferkla (1). A) pre-Daleje mud-to-wackestones showing traces of recrystallization (sample OF-Z-2.5), B) Wacke-packstones of the upper Choteč interval with minor recrystallization and brown dolomite (sample OF-2.0), C) Packstones and grainstones of the post-Choteč interval with brown dolomite in stylolite (sample OF-41), D) Bioturbated grainstones of the post-Choteč interval (sample OF-49.5), more heavily altered, E) Relatively unaltered wacke-packstones of the pre- Kačák interval (sample OF-60) with minor dolomite and clays in fossils, F) Moderately altered mud-to-wackestones of the pre-Kačák interval showing dolomitization and recrystallization. (sample OF-79.5).

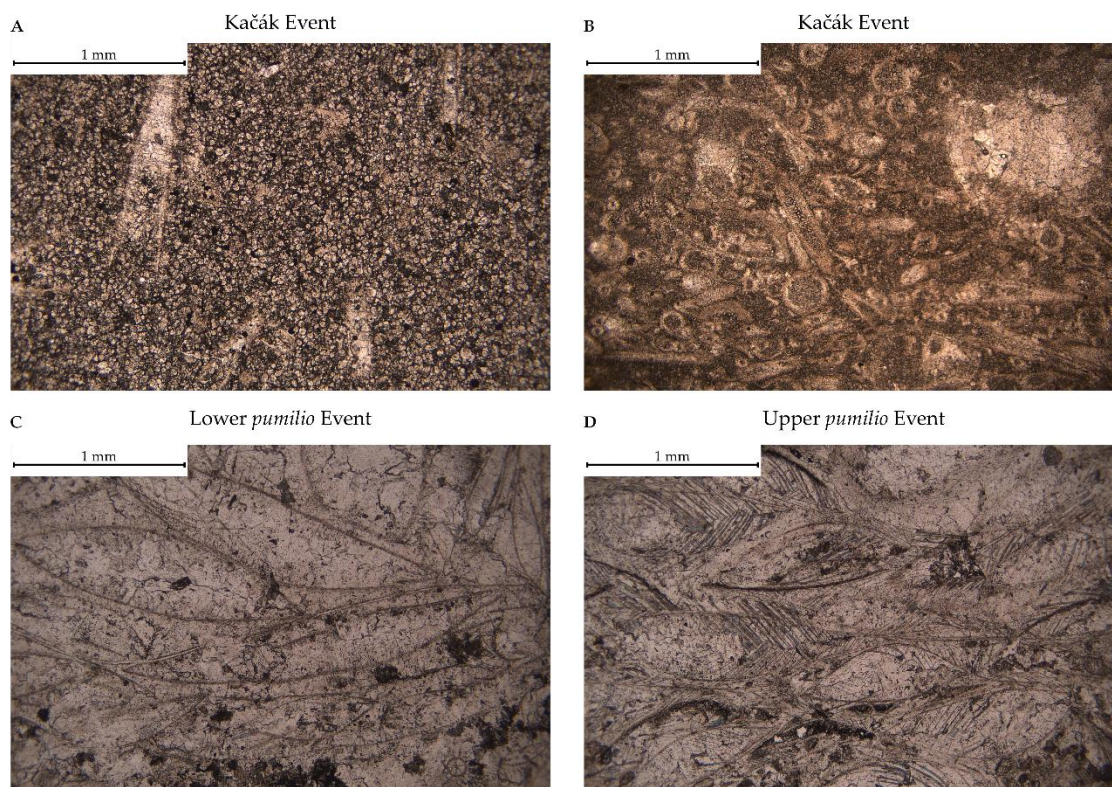


Fig. C2. Thin-section petrography of Oued Ferkla (2). A) Completely dolomitized carbonates of the Kačák Event containing *Tentaculites* (sample OF-150a), B) Packstones of the Kačák Event carbonates low degree of dolomitization and recrystallization (sample OF-150b), C) Grainstones of the Lower *pumilio* Event (OF-225.0) showing minor recrystallization only, D) Grainstones of the Upper *pumilio* Event (OF-243.0) showing minor recrystallization only.

D. Element Profiles (pXRF)

All element concentrations, measured using portable X-ray fluorescence (pXRF), included in this study are provided on the stratigraphic plots below. Element profiles are color-coded into three main groups; detrital indicators (gray), diagenesis- and redox-sensitive elements (brown), and carbonate-fraction elements (beige) and are based on the full-section PCA (Suppl. E). These element concentrations are to be interpreted semi-quantitatively only.

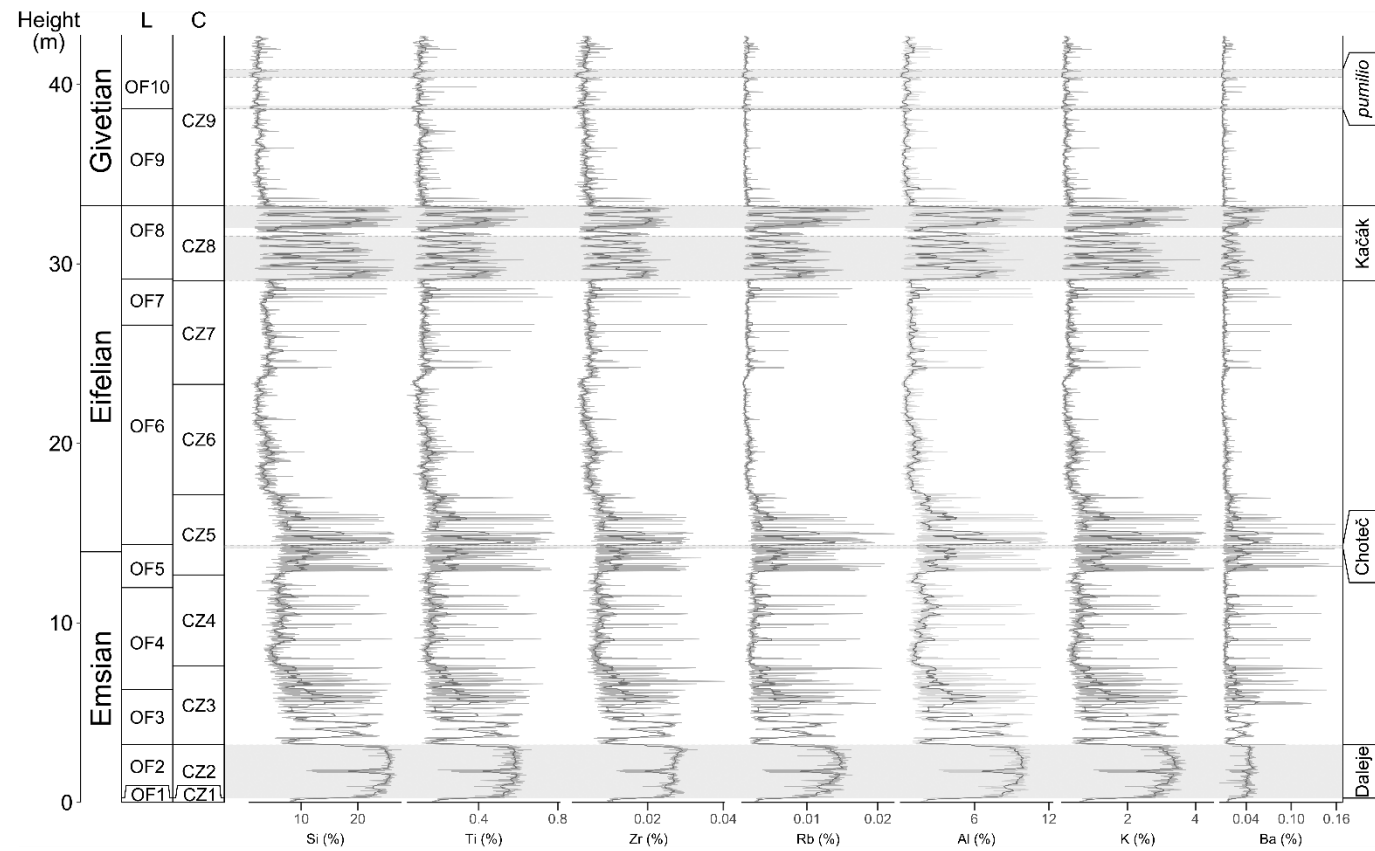


Fig. D1. Oued Ferkla elemental composition (1). Chronostratigraphy, lithostratigraphic units Oued Ferkla 1 (OF1) to OF10 based on Talih et al. (2022). Element profiles for Si, Ti, Zr, Rb, Al, K, and Ba in weight per cent (%). Chemozonation defined in this work (see explanation in text). Event stratigraphy; Daleje, Choteč, Kačák, and *pumilio* events demarcated by gray boxes.

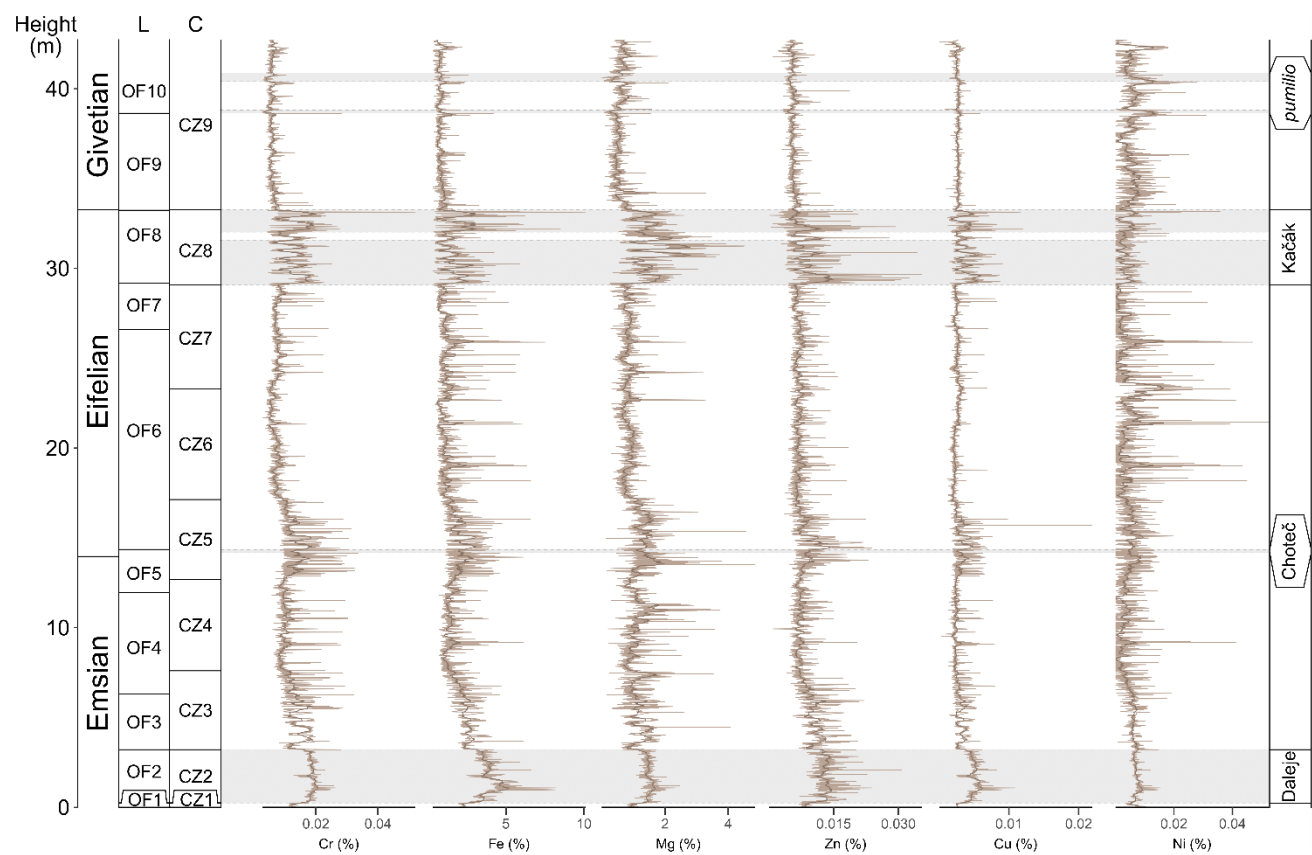


Fig. D2. Oued Ferkla elemental composition (2). Chronostratigraphy, lithostratigraphic units Oued Ferkla 1 (OF1) to OF10 based on Talih et al. (2022). Element profiles for Cr, Fe, Mg, Zn, Cu, and Ni in weight per cent (%). Chemozonation defined in this work (see explanation in text). Event stratigraphy; Daleje, Choteč, Kačák, and *pumilio* events demarcated by gray boxes.

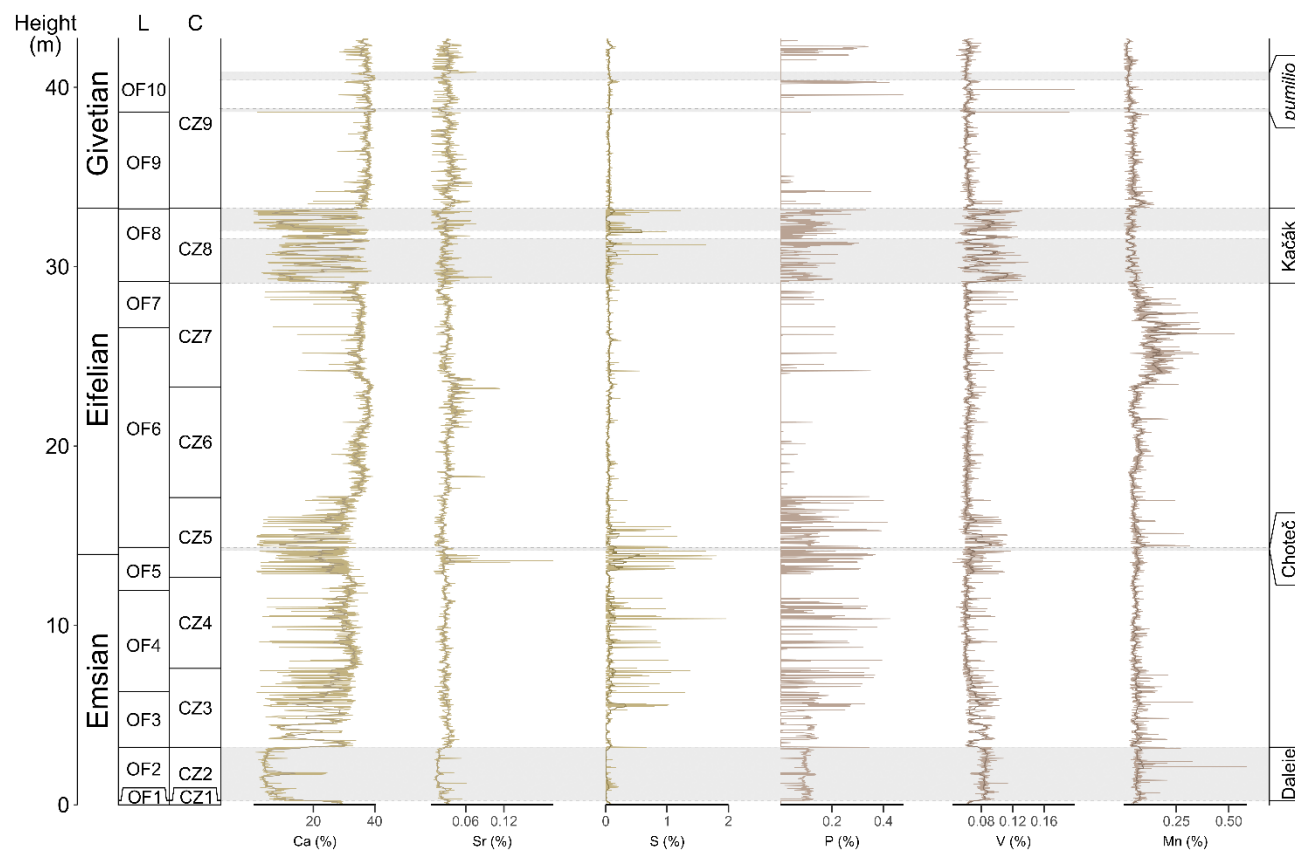


Fig. D3. Oued Ferkla elemental composition (3). Chronostratigraphy, lithostratigraphic units Oued Ferkla 1 (OF1) to OF10 based on Talih et al. (2022). Element profiles for Ca, Sr, S, P, V, and Mn in weight per cent (%). Chemozonation defined in this work (see explanation in text). Event stratigraphy; Daleje, Choteč, Kačák, and *pumilio* events demarcated by gray boxes.

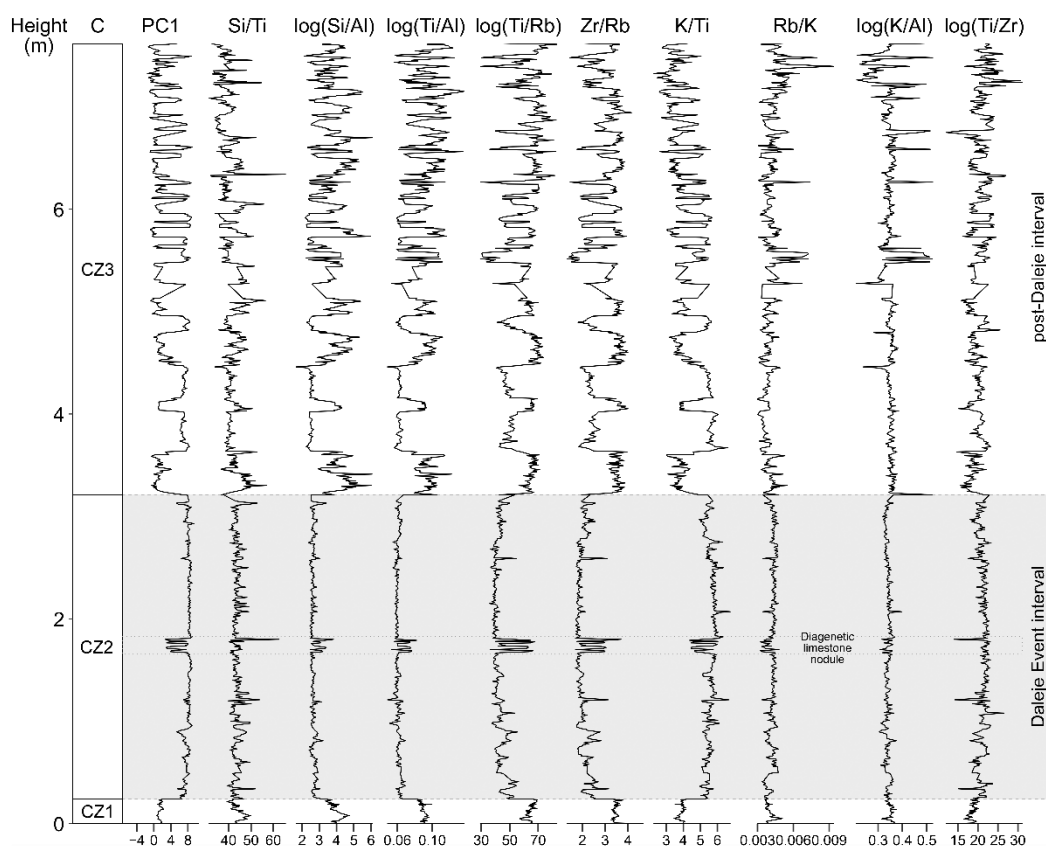


Fig. D4. Detrital indicators of the Daleje interval. From left to right: chemozonation, principal component 1 (PC1) as indicator of total detrital input, Si/Ti, log(Si/Al), log(Ti/Al), log(Ti/Rb), Zr/Rb, K/Ti, Rb/K, log(K/Al), log(Ti/Zr). Interval corresponding to a diagenetic limestone nodule marked by dashed lines. Daleje Event marked in gray.

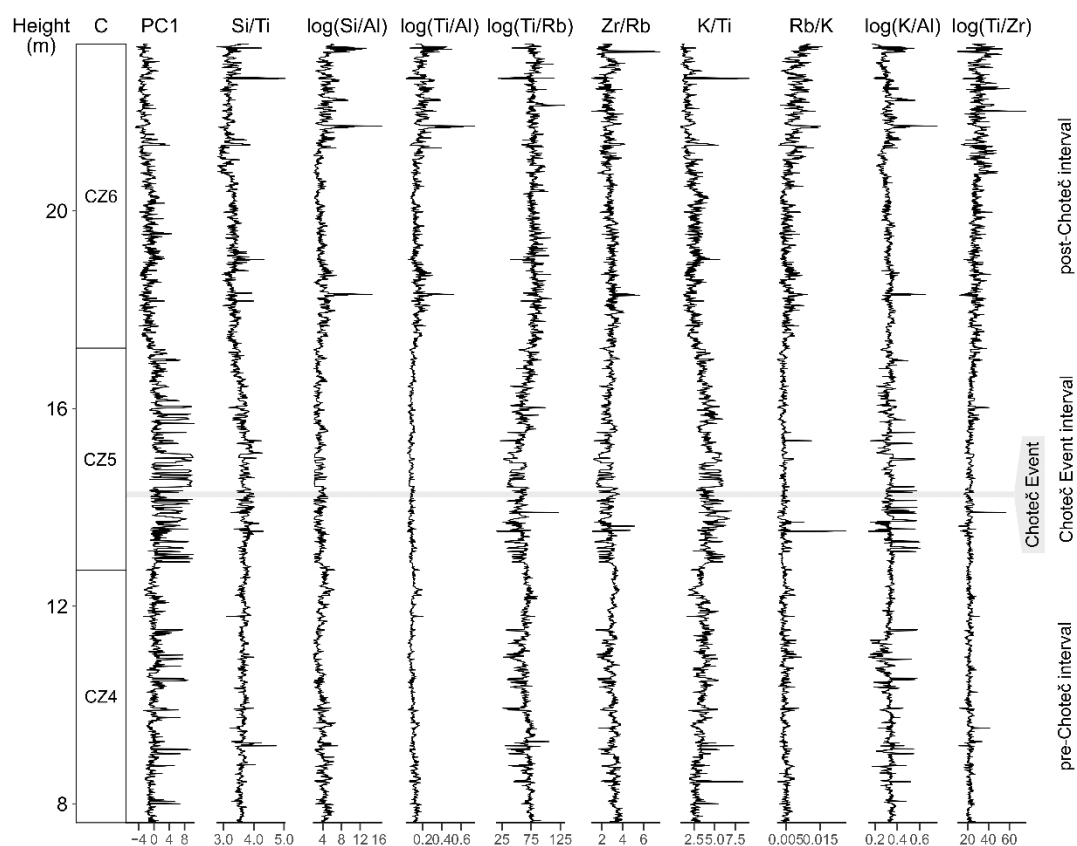


Fig. D5. Detrital signals of the Choteč interval. From left to right: chemozonation, principal component 1 (PC1) as indicator of total detrital input, Si/Ti, log(Si/Al), log(Ti/Al), log(Ti/Rb), Zr/Rb, K/Ti, Rb/K, log(K/Al), log(Ti/Zr). Choteč Event marked in gray.

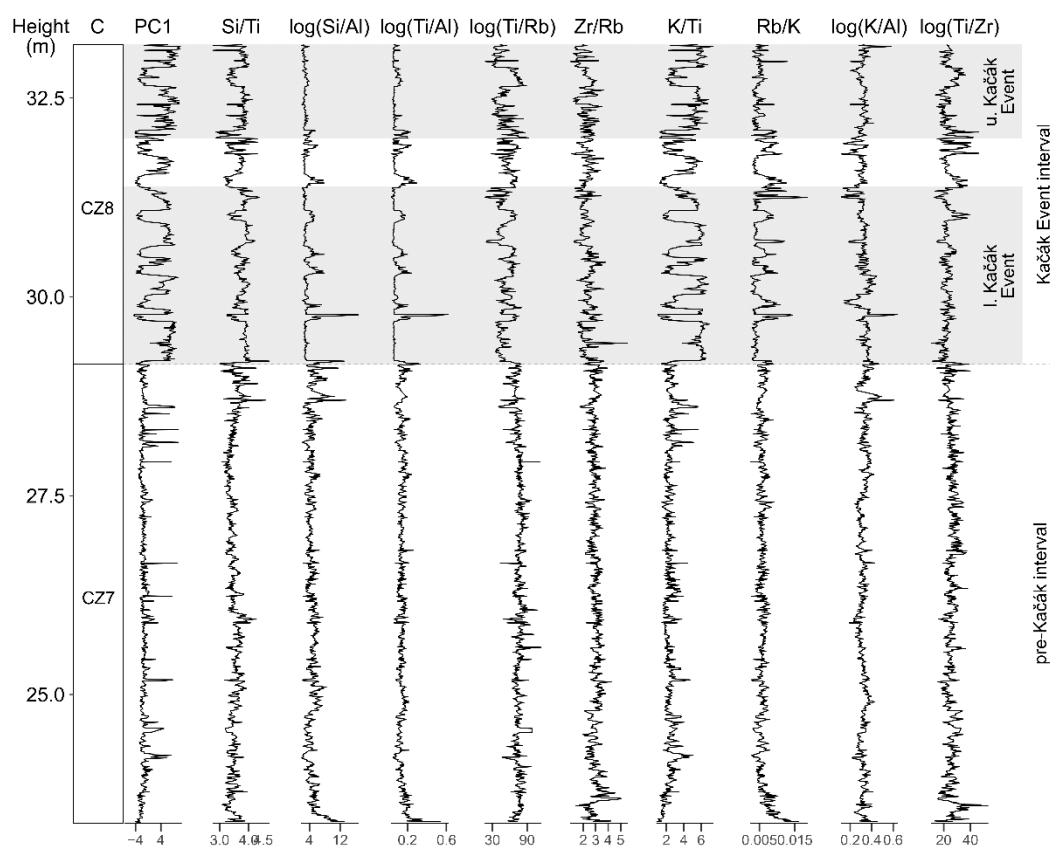


Fig. D6. Detrital signals of the Kačák interval. From left to right: chemozonation, principal component 1 (PC1) as indicator of total detrital input, Si/Ti, log(Si/Al), log(Ti/Al), log(Ti/Rb), Zr/Rb, K/Ti, Rb/K, log(K/Al), log(Ti/Zr). L. and U. Kačák events marked in gray.

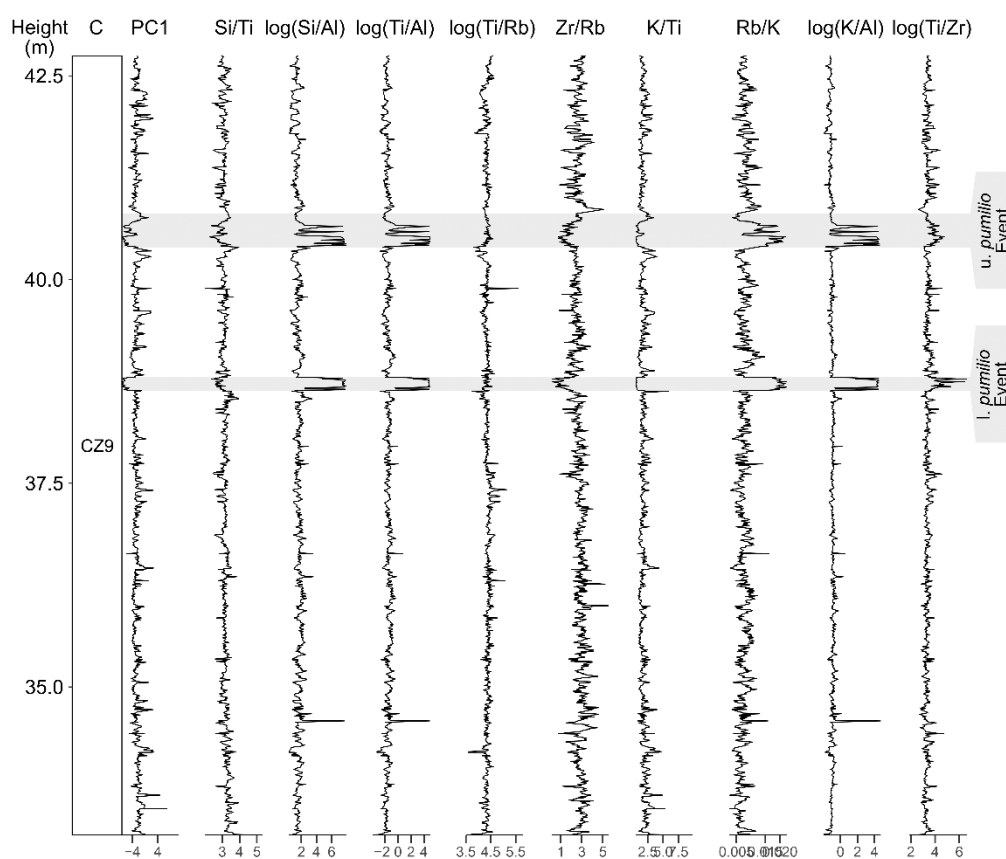


Fig. D7. Detrital signals of the *pumilio* interval. From left to right: chemozonation, principal component 1 (PC1) as indicator of total detrital input, Si/Ti, log(Si/Al), log(Ti/Al), log(Ti/Rb), Zr/Rb, K/Ti, Rb/K, log(K/Al), log(Ti/Zr). Lower and Upper *pumilio* events marked in gray.

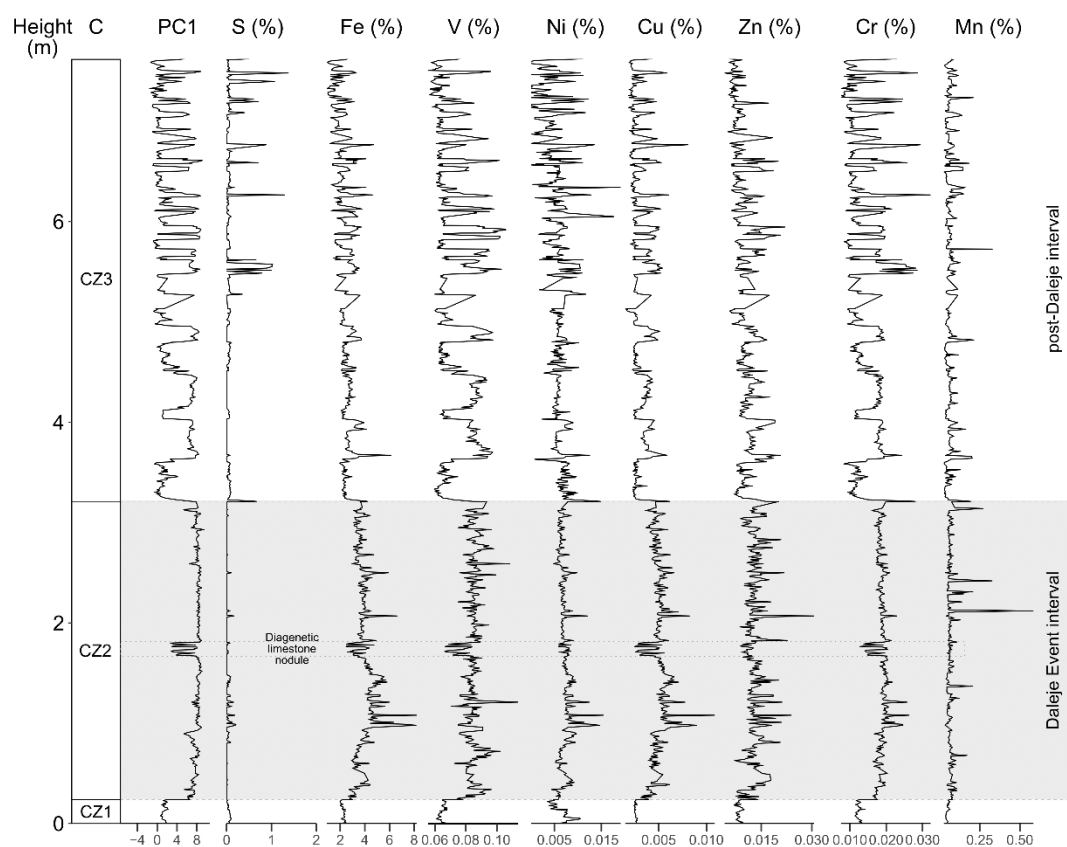


Fig. D8. Redox indicators of the Daleje interval. From left to right: chemozonation, principal component 1 (PC1) as indicator for total detrital input, S, Fe, V, Ni, Cu, Zn, Cr, Mn in weight per cent (%). Interval corresponding to a diagenetic limestone nodule marked by dashed lines. Daleje Event marked in gray.

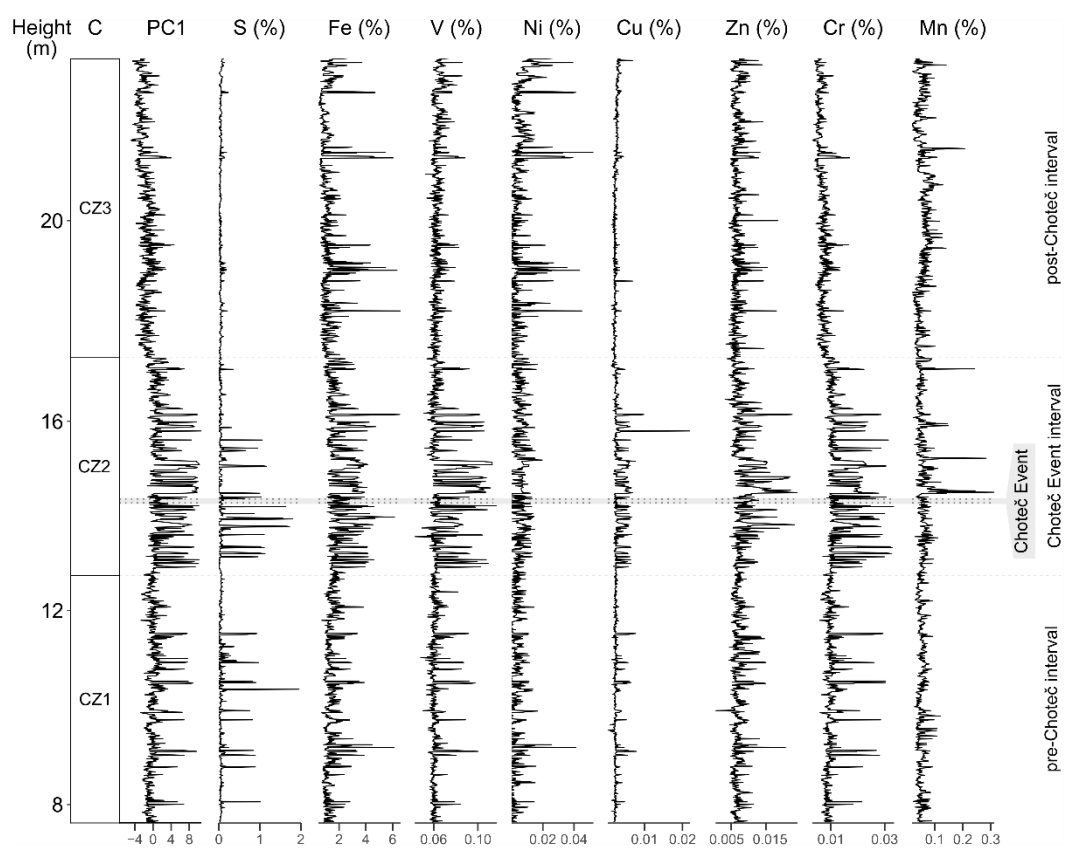


Fig. D9. Redox indicators of the Choteč interval. From left to right: chemozonation, principal component 1 (PC1) as indicator for total detrital input, S, Fe, V, Ni, Cu, Zn, Cr, Mn in weight per cent (%). Choteč Event marked in gray.

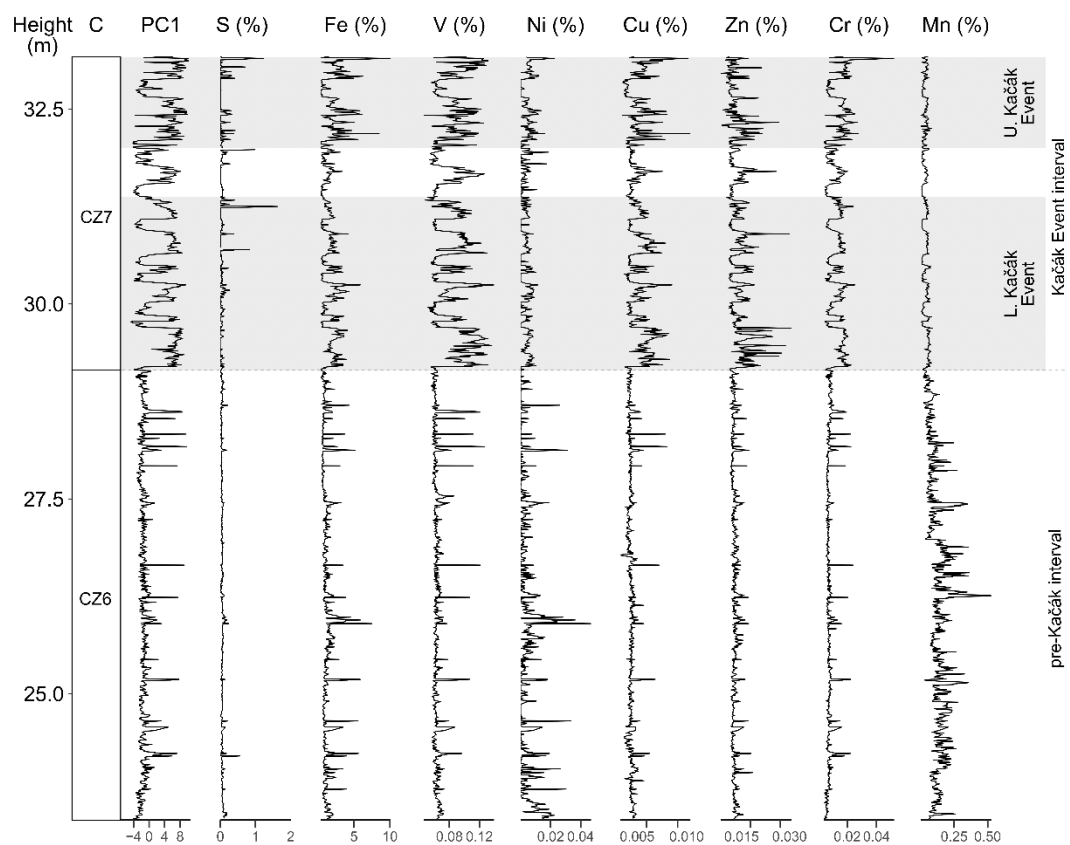


Fig. D10. Redox indicators of the Kačák interval. From left to right: chemozonation, principal component 1 (PC1) as indicator for total detrital input, S, Fe, V, Ni, Cu, Zn, Cr, Mn in weight per cent (%). Lower and Upper Kačák events marked in gray.

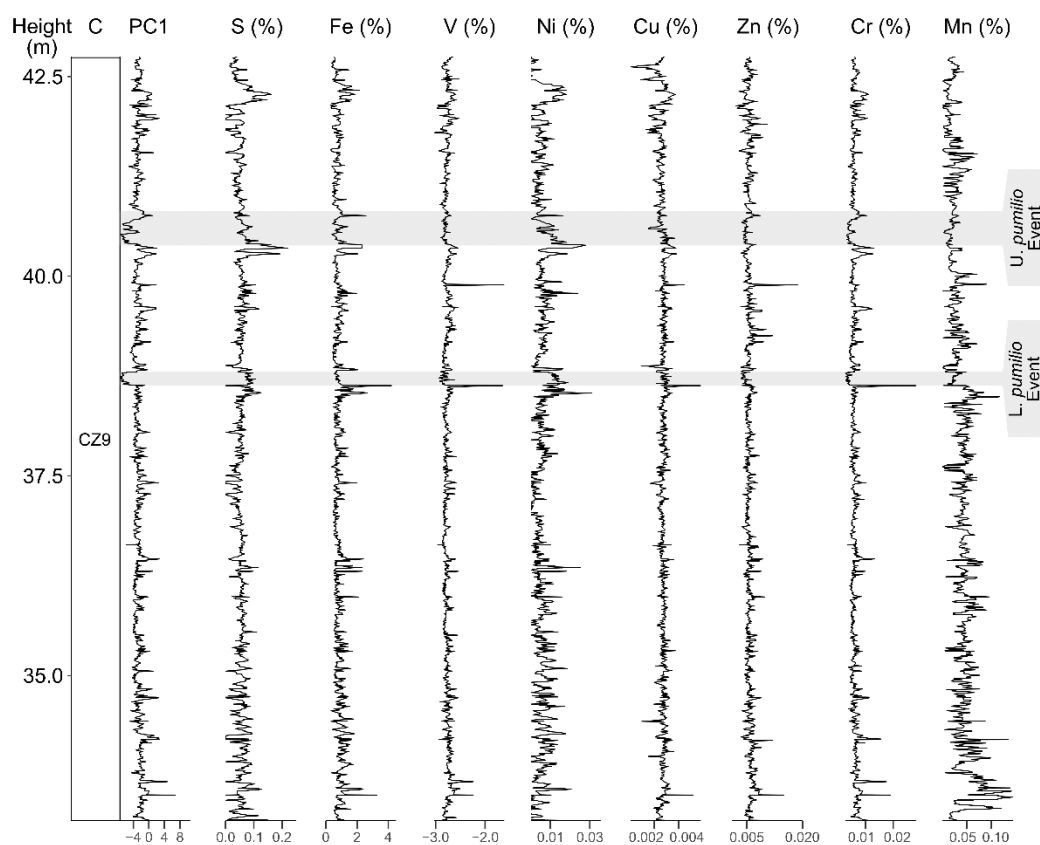


Fig. D11. Redox indicators of the *pumilio* interval (1). From left to right: chemozonation, principal component 1 (PC1) as indicator for total detrital input, S, Fe, V, Ni, Cu, Zn, Cr, Mn in weight per cent (%). Lower and Upper *pumilio* events marked in gray.

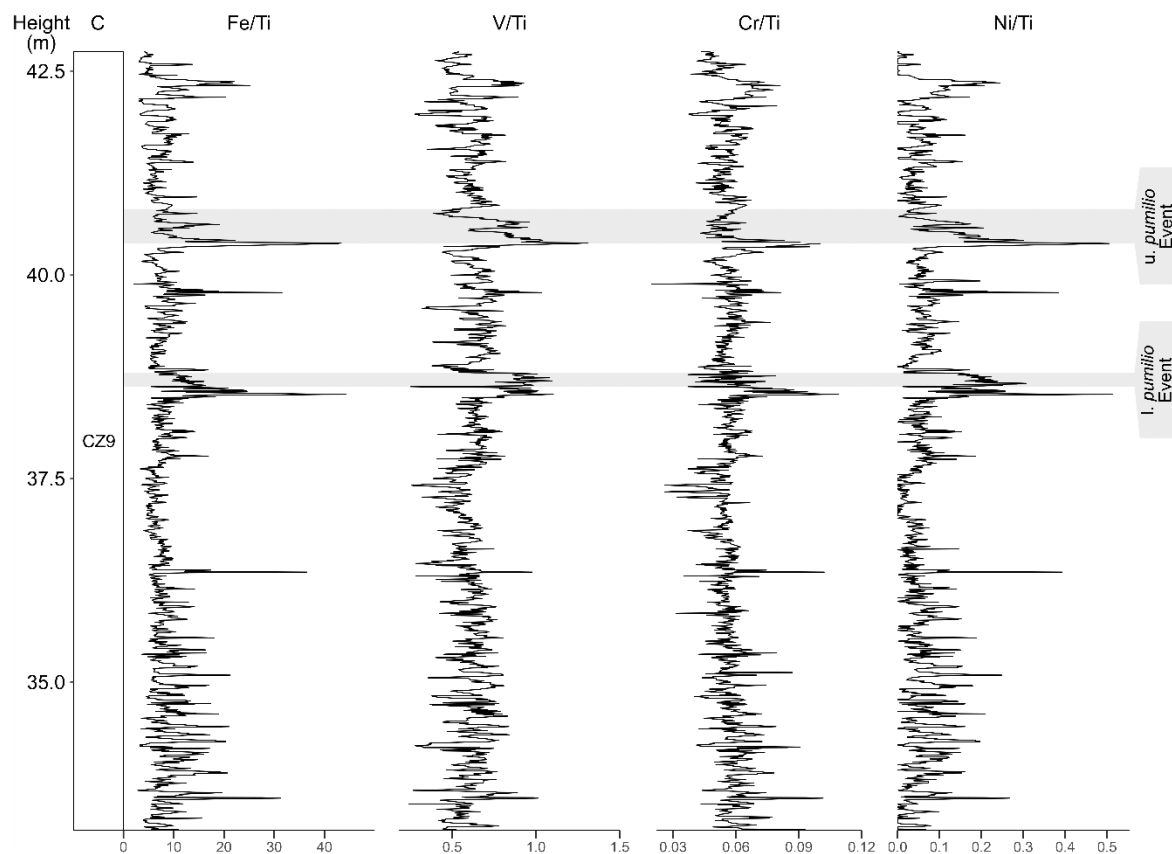


Fig. D12. Redox indicators of the *pumilio* interval (2). From left to right: chemozonation, Fe/Ti, V/Ti, Cr/Ti and Ni/Ti. Lower and Upper *pumilio* events are marked in gray.

E. Principal Component Analysis of Oued Ferkla

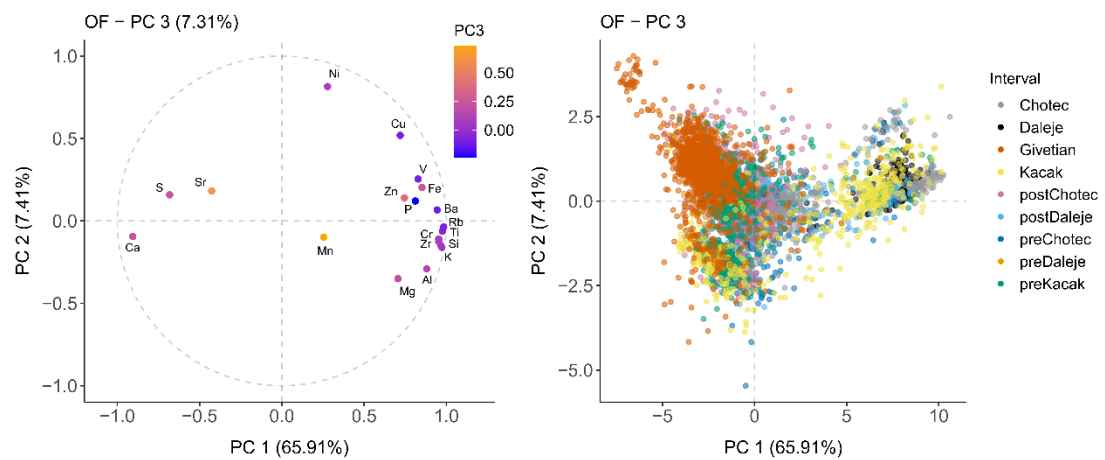


Fig. E1. Full-section PCA. A) Loading plot along principal component 1 (PC1), PC2 and PC3 (color). B) Score plot for each interval (chemozones CZ1 to CZ9; color) along PC1-PC2.

F. Pearson Correlation Coefficient Matrices (PCCM)

To support the interpretation of interval-specific PCA of the two (groups) of lithologies, hierarchically clustered Pearson correlation coefficient matrices are provided. This approach allows the quantification of correlation between two elements. Moreover, hierarchical clustering offers a complementary view to the groupings that can be observed on PCA loading plots. Note that 'limestone' refers to limestone only, while 'limestones' refer to multiple types of limestones, which may also include nodular limestone, limestone nodules or undulating limestones. All elements provided below have been measured using pXRF.

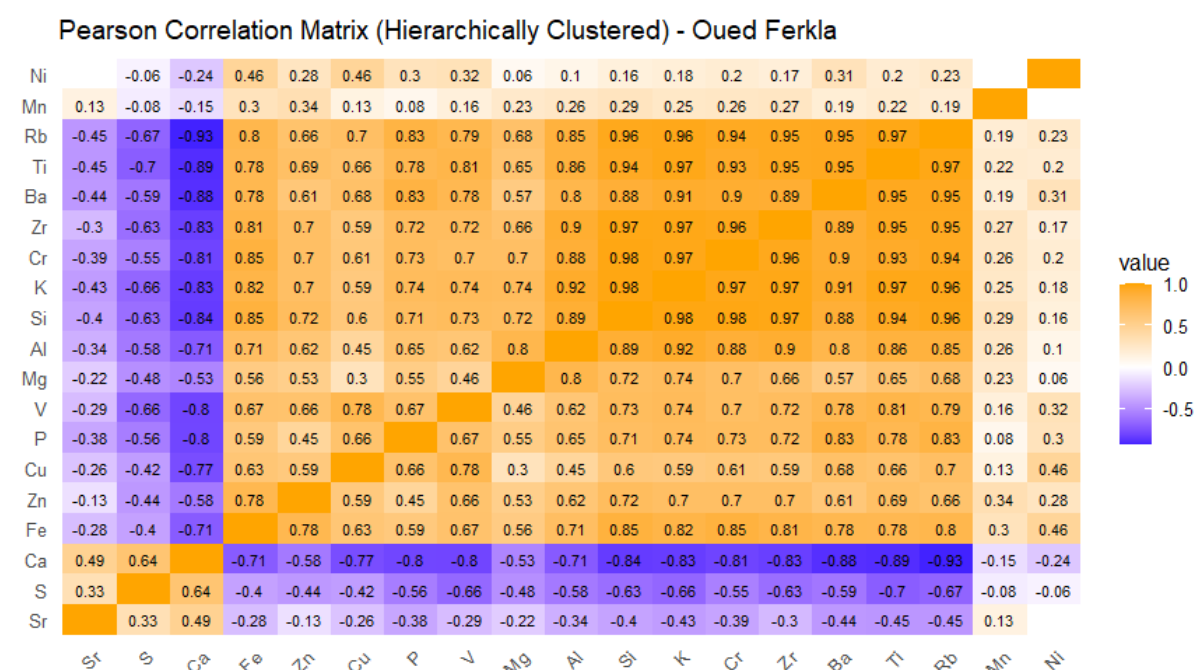


Fig. F1. Hierarchically Clustered Pearson Correlation Coefficient Matrix for Oued Ferkla. Positive (orange) and negative (blue) Pearson correlation coefficients at the 95 % confidence level interval. Blank boxes indicate statistically insignificant correlation.

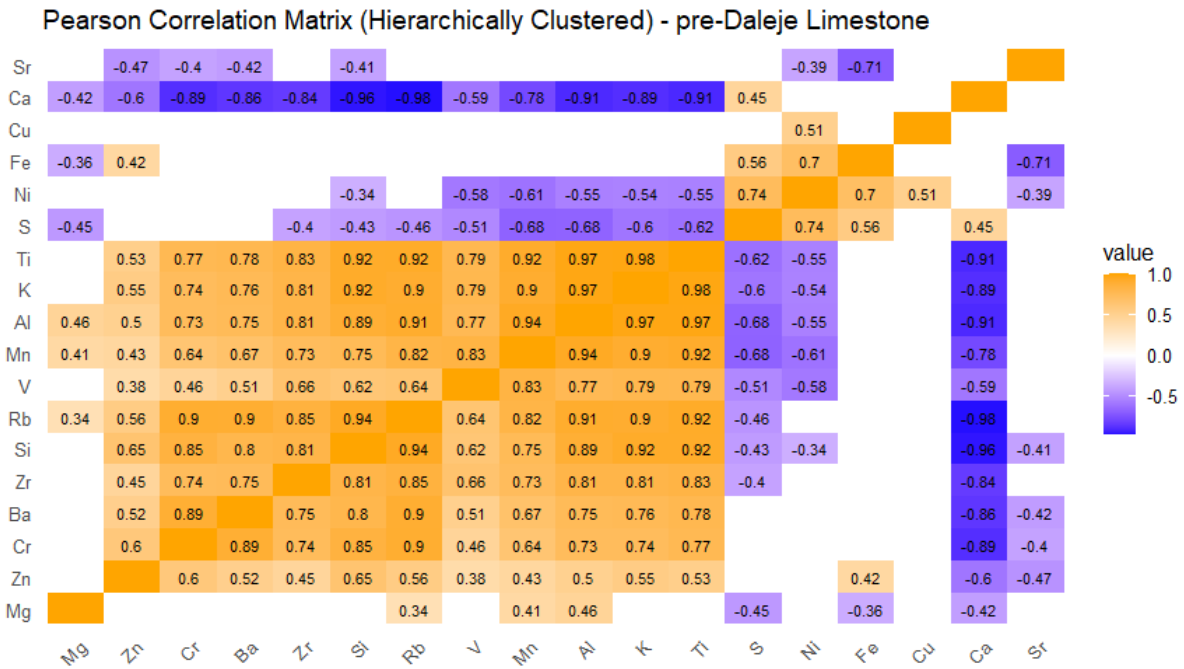


Fig. F2. Hierarchically Clustered Pearson Correlation Coefficient Matrix for the pre-Daleje interval limestones. Positive (orange) and negative (blue) Pearson correlation coefficients at the 95 % confidence level interval. Blank boxes indicate statistically insignificant correlation.

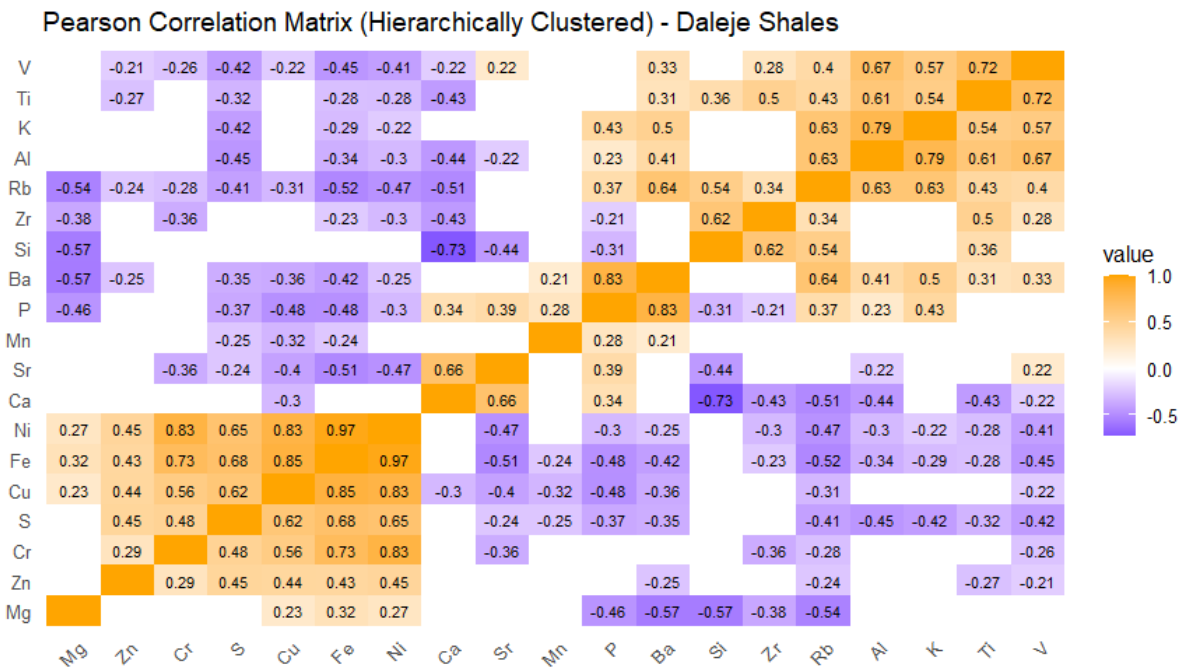


Fig. F3. Hierarchically Clustered Pearson Correlation Coefficient Matrix for the Daleje Event interval shales. Positive (orange) and negative (blue) Pearson correlation coefficients at the 95 % confidence level interval. Blank boxes indicate statistically insignificant correlation.

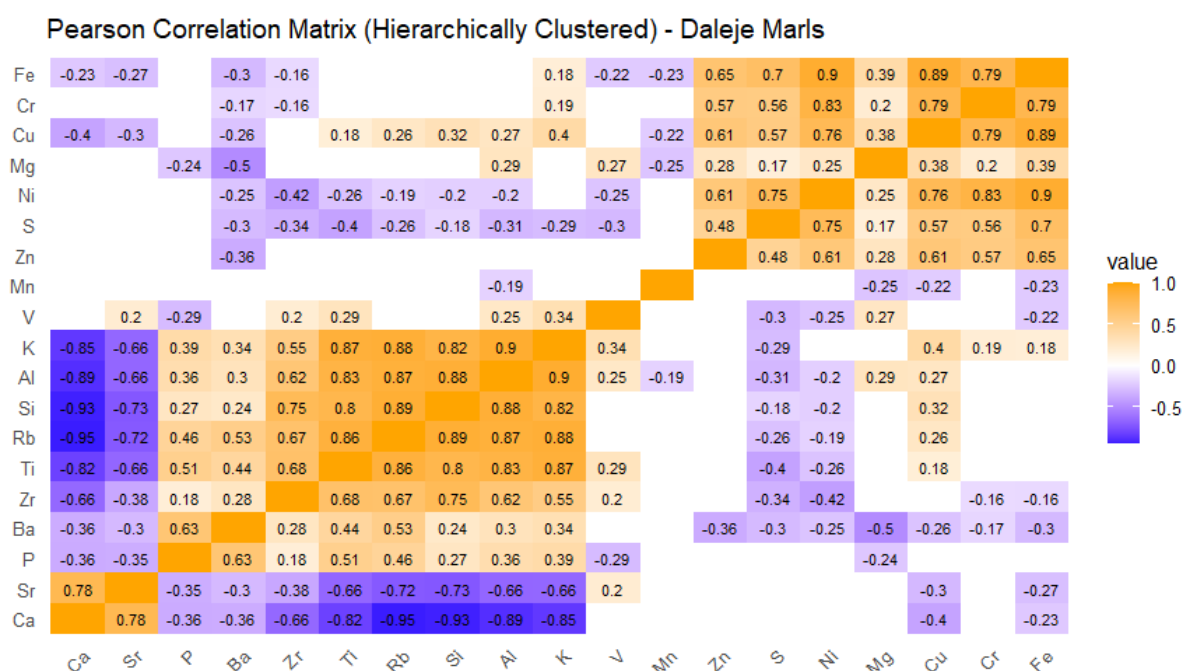


Fig. F4. Hierarchically Clustered Pearson Correlation Coefficient Matrix for the Daleje Event interval marls. Positive (orange) and negative (blue) Pearson correlation coefficients at the 95 % confidence level interval. Blank boxes indicate statistically insignificant correlation.

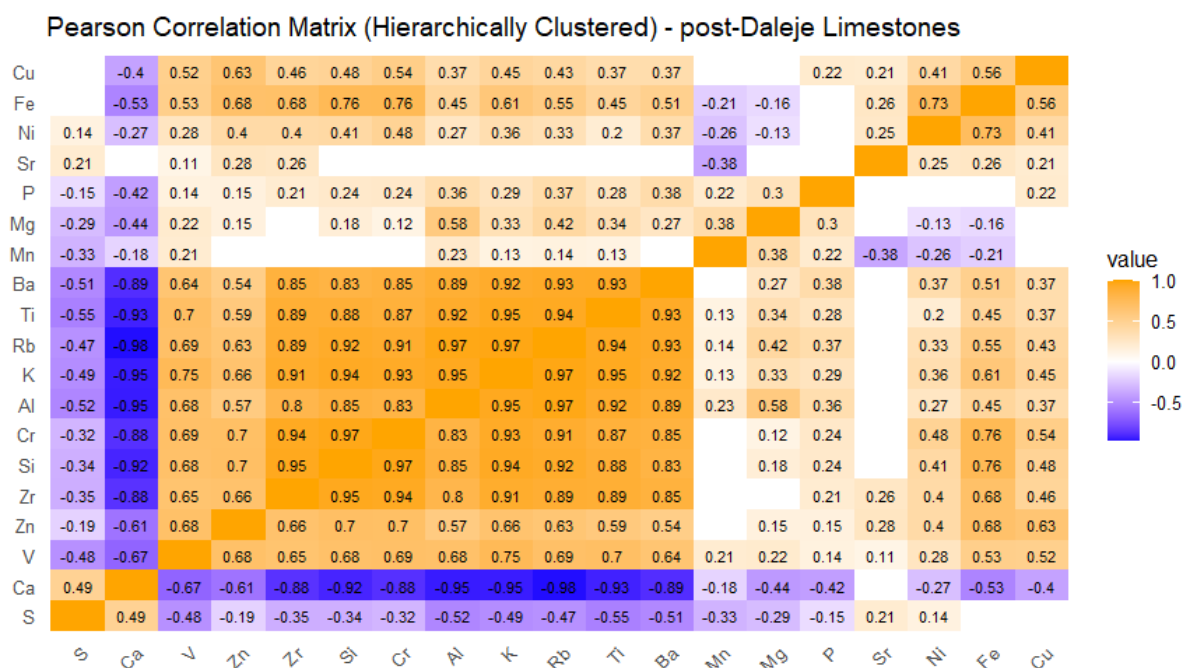


Fig. F5. Hierarchically Clustered Pearson Correlation Coefficient Matrix for the post-Daleje interval limestones. Positive (orange) and negative (blue) Pearson correlation coefficients at the 95 % confidence level interval. Blank boxes indicate statistically insignificant correlation.

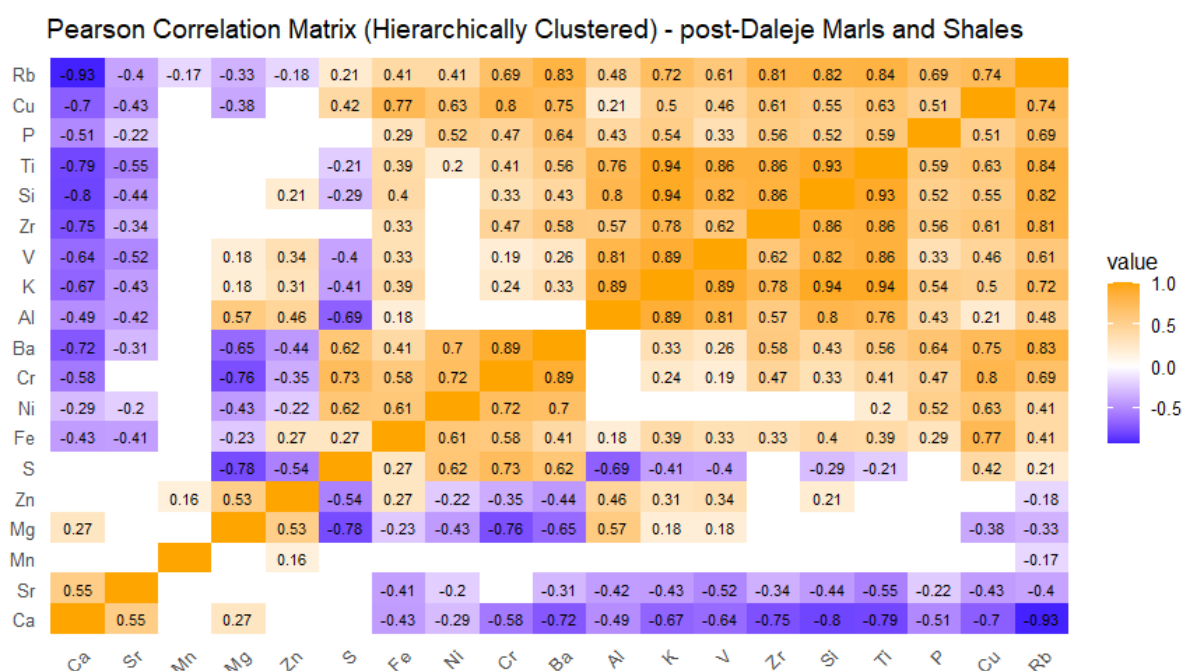


Fig. F6. Hierarchically Clustered Pearson Correlation Coefficient Matrix for the post-Daleje interval marls and shales. Positive (orange) and negative (blue) Pearson correlation coefficients at the 95 % confidence level interval. Blank boxes indicate statistically insignificant correlation.

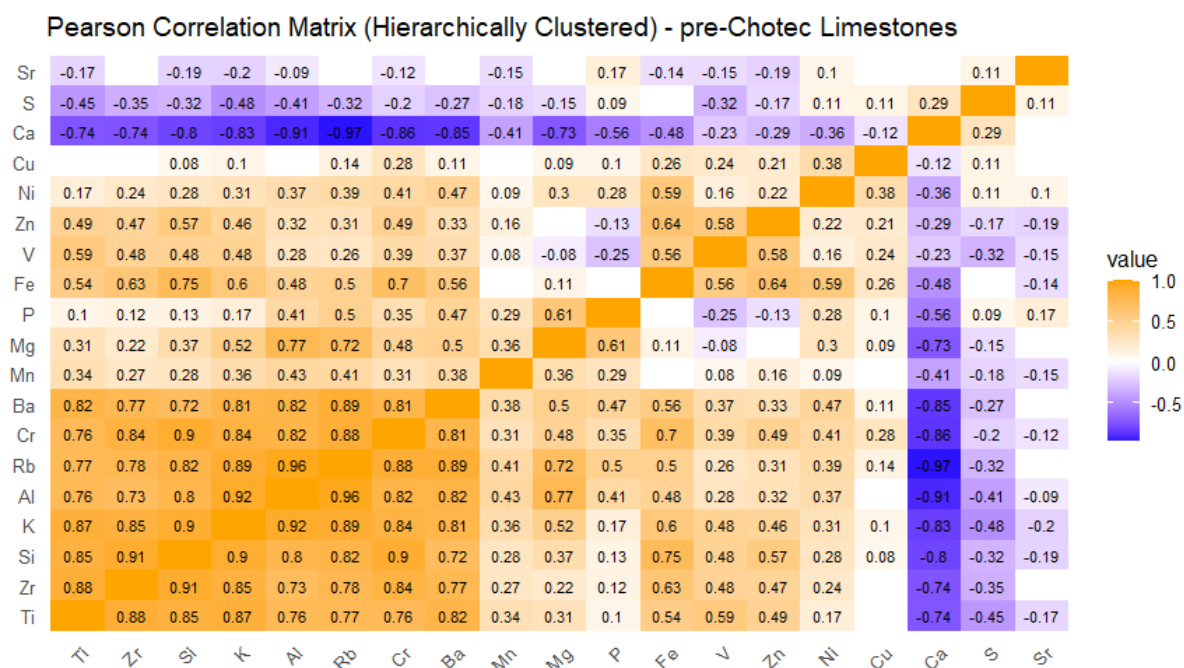


Fig. F7. Hierarchically Clustered Pearson Correlation Coefficient Matrix for the pre-Chotec interval limestones. Positive (orange) and negative (blue) Pearson correlation coefficients at the 95 % confidence level interval. Blank boxes indicate statistically insignificant correlation.

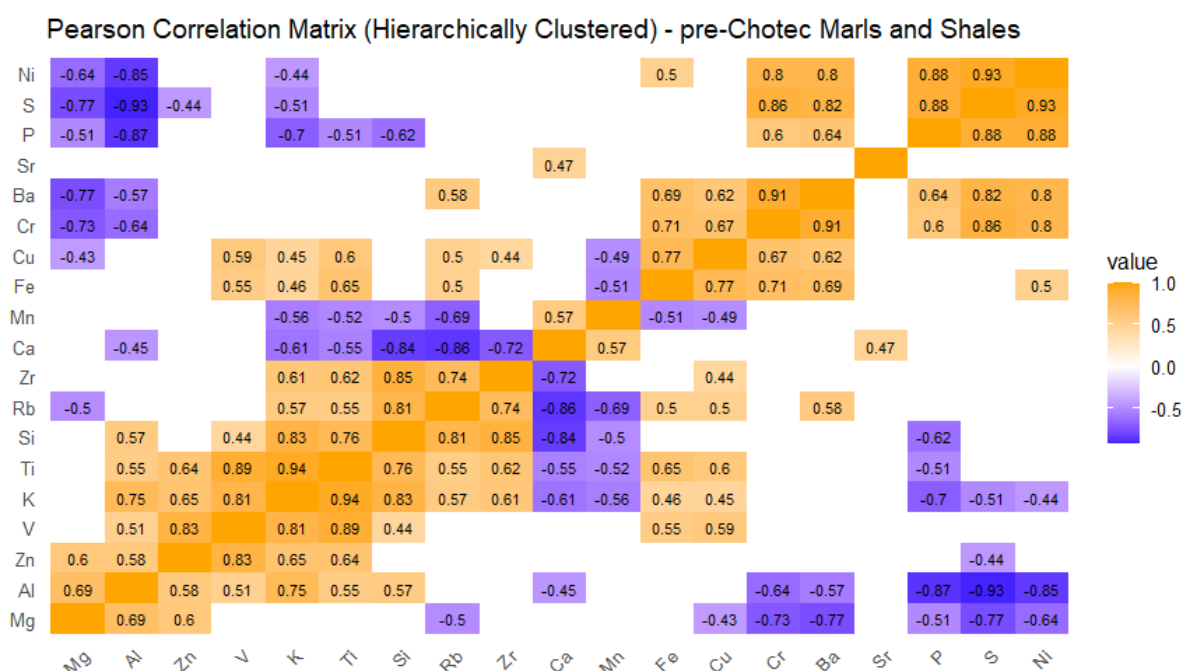


Fig. F8. Hierarchically Clustered Pearson Correlation Coefficient Matrix for the pre-Chotec interval marls and shales. Positive (orange) and negative (blue) Pearson correlation coefficients at the 95 % confidence level interval. Blank boxes indicate statistically insignificant correlation.

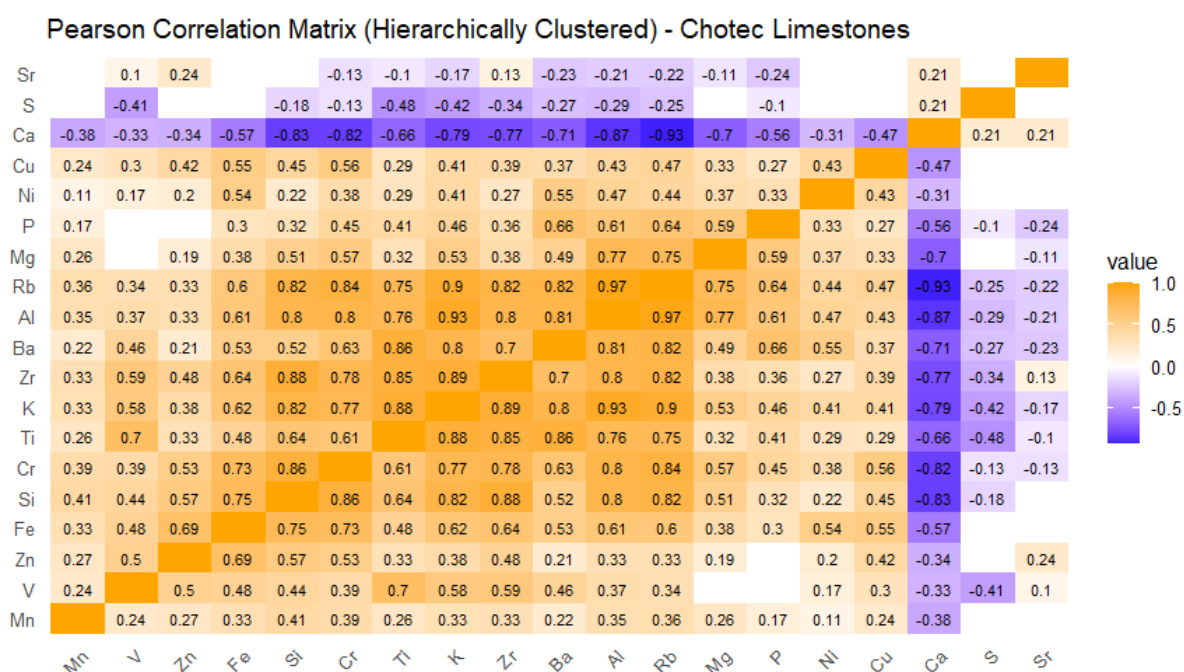


Fig. F9. Hierarchically Clustered Pearson Correlation Coefficient Matrix for the Chotec Event interval limestones. Positive (orange) and negative (blue) Pearson correlation coefficients at the 95 % confidence level interval. Blank boxes indicate statistically insignificant correlation.

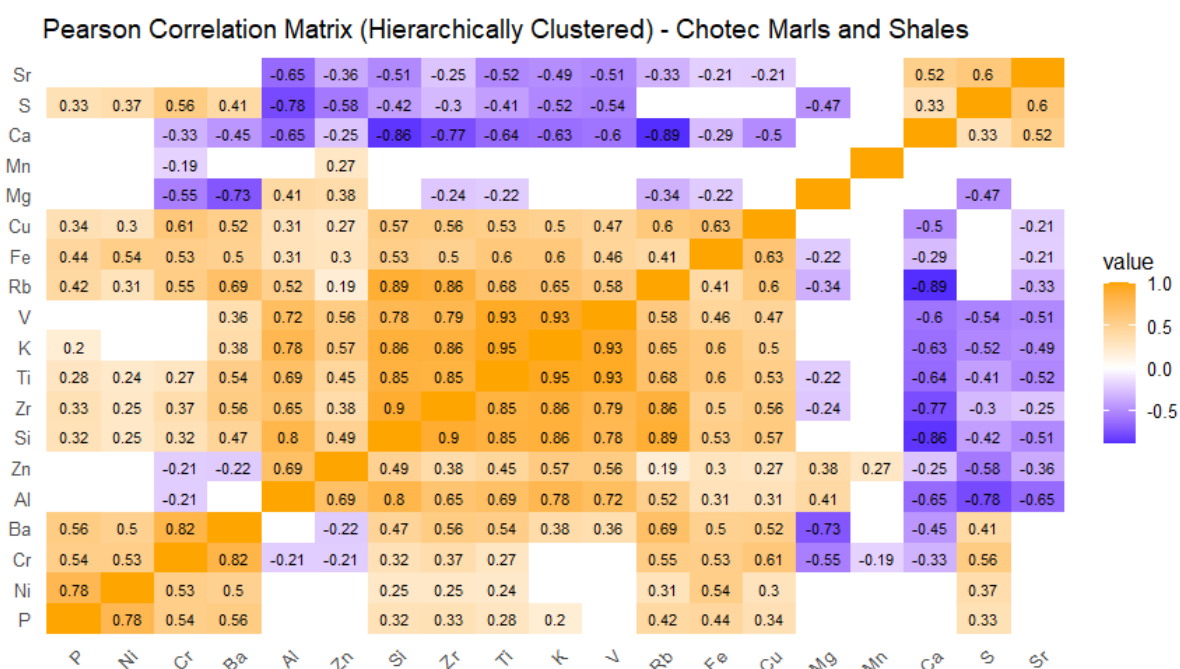


Fig. F10. Hierarchically Clustered Pearson Correlation Coefficient Matrix for the Choteč Event interval marls and shales. Positive (orange) and negative (blue) Pearson correlation coefficients at the 95 % confidence level interval. Blank boxes indicate statistically insignificant correlation.

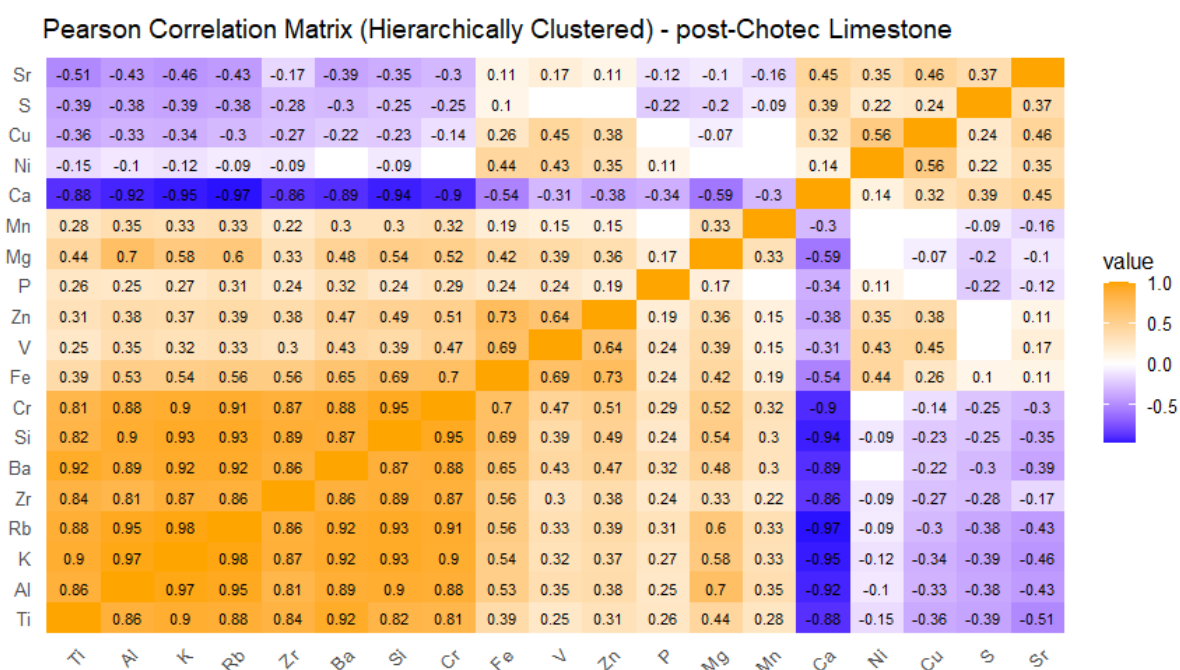


Fig. F11. Hierarchically Clustered Pearson Correlation Coefficient Matrix for the post-Choteč interval limestone. Positive (orange) and negative (blue) Pearson correlation coefficients at the 95 % confidence level interval. Blank boxes indicate statistically insignificant correlation.

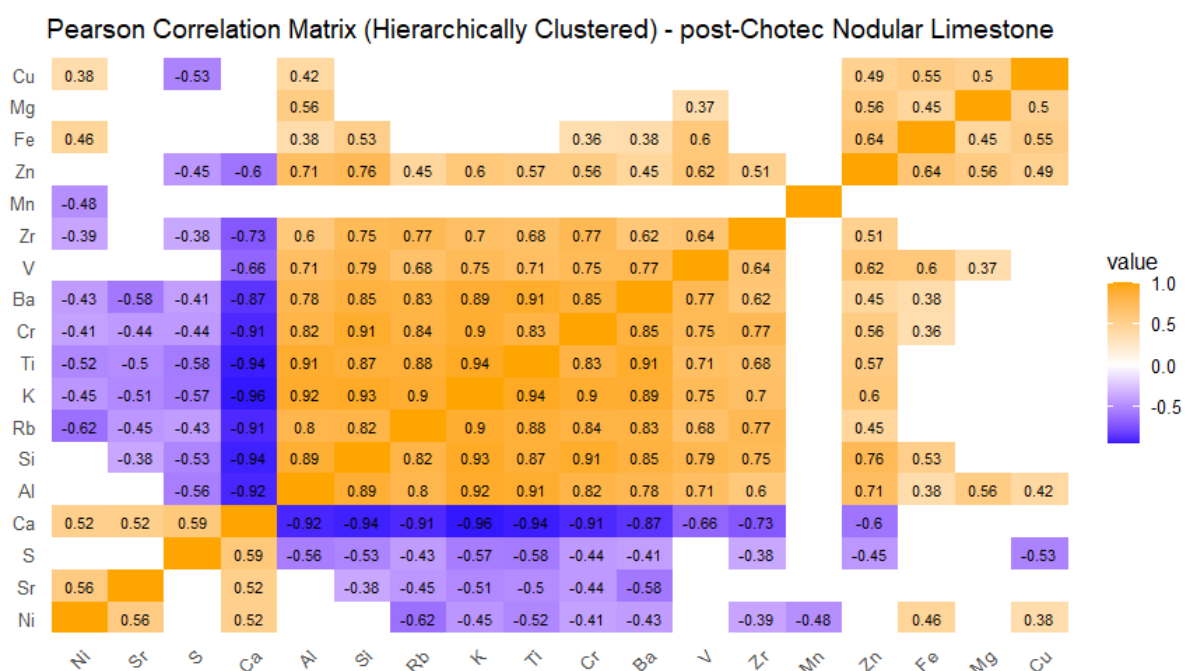


Fig. F12. Hierarchically Clustered Pearson Correlation Coefficient Matrix for the post-Chotec interval nodular limestone. Positive (orange) and negative (blue) Pearson correlation coefficients at the 95 % confidence level interval. Blank boxes indicate statistically insignificant correlation.

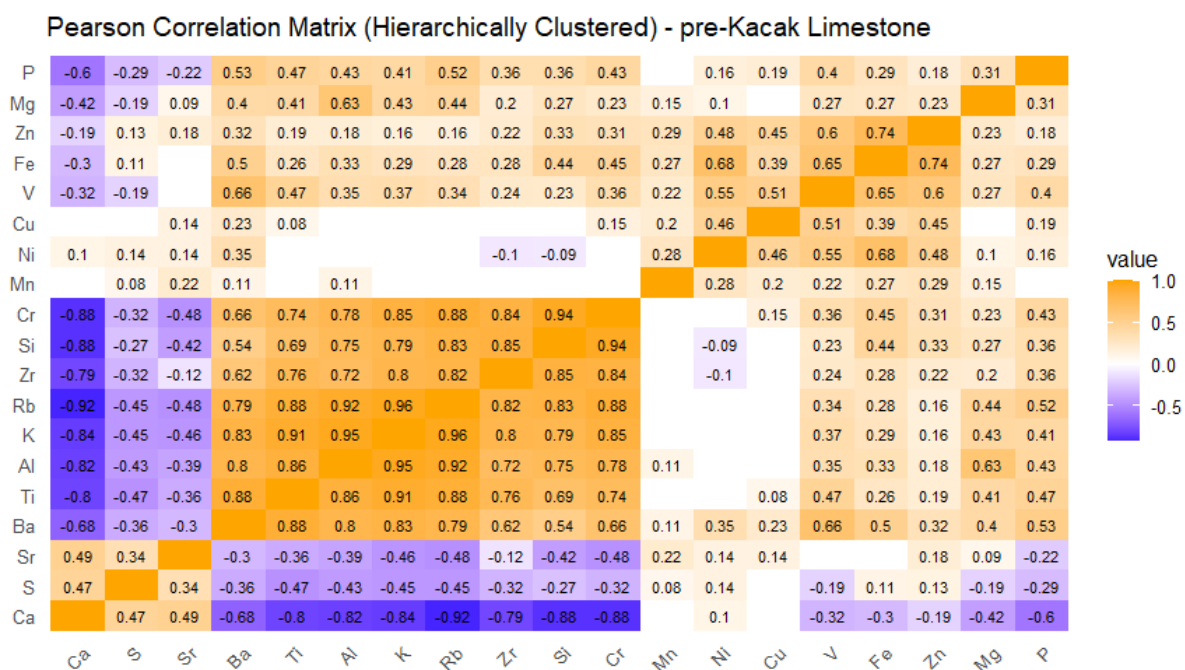


Fig. F13. Hierarchically Clustered Pearson Correlation Coefficient Matrix for the pre-Kačák interval limestone. Positive (orange) and negative (blue) Pearson correlation coefficients at the 95 % confidence level interval. Blank boxes indicate statistically insignificant correlation.

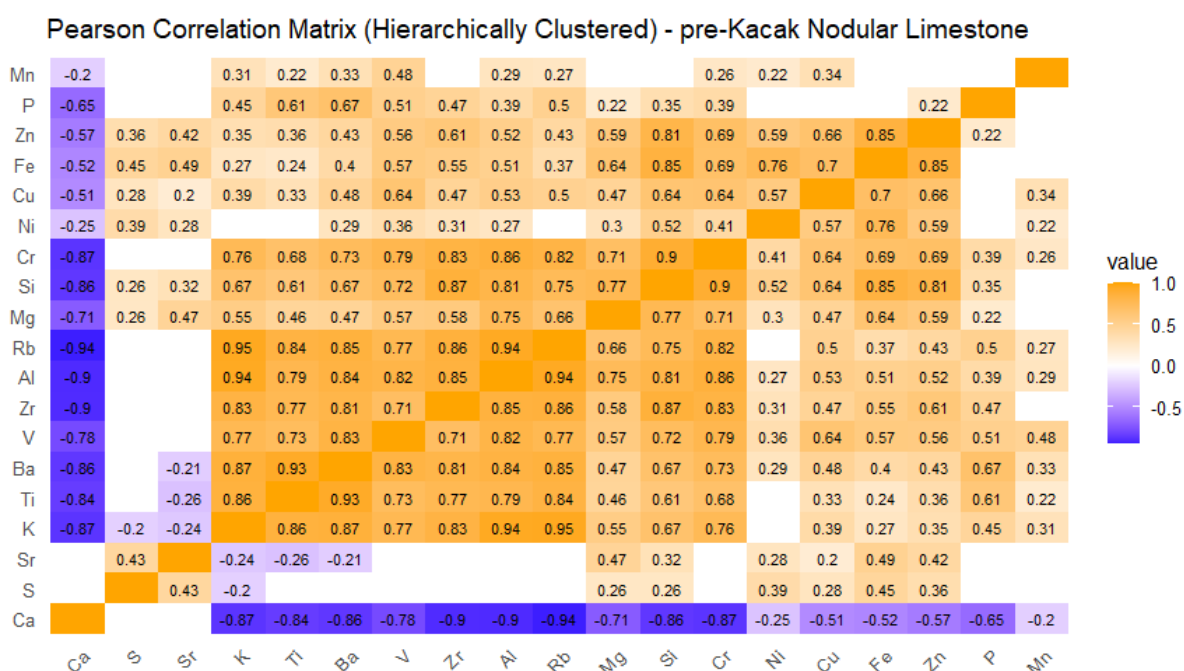


Fig. F14. Hierarchically Clustered Pearson Correlation Coefficient Matrix for the pre-Kačák interval nodular limestone. Positive (orange) and negative (blue) Pearson correlation coefficients at the 95 % confidence level interval. Blank boxes indicate statistically insignificant correlation.

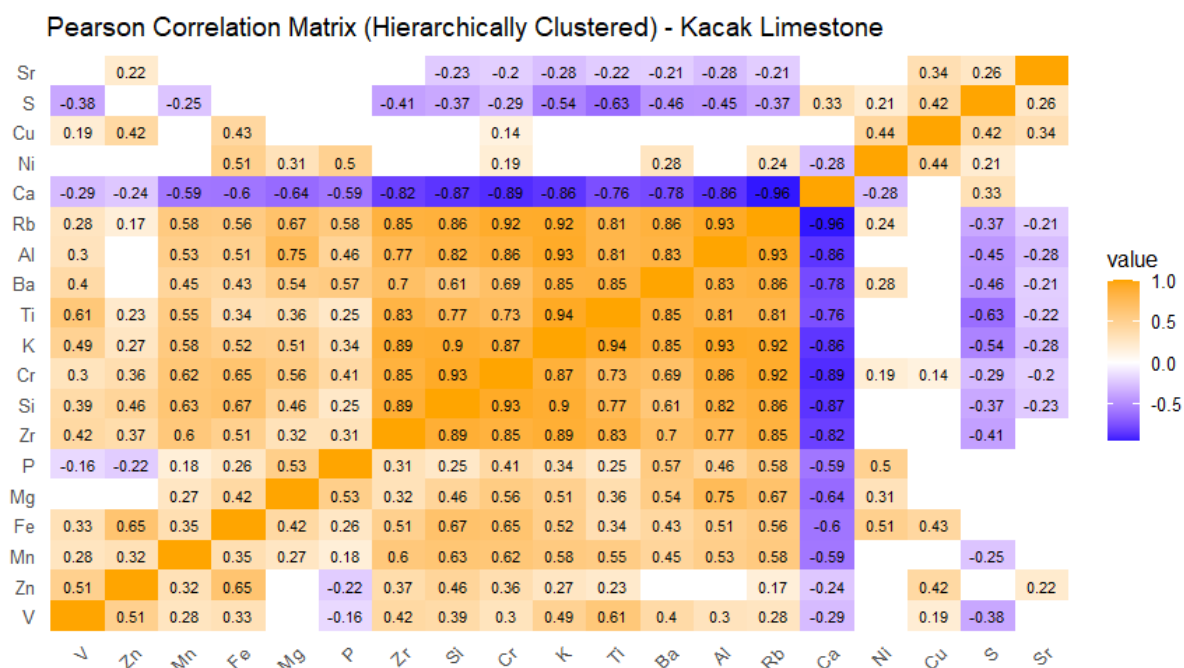


Fig. F15. Hierarchically Clustered Pearson Correlation Coefficient Matrix for the Kačák Event interval limestone. Positive (orange) and negative (blue) Pearson correlation coefficients at the 95 % confidence level interval. Blank boxes indicate statistically insignificant correlation.

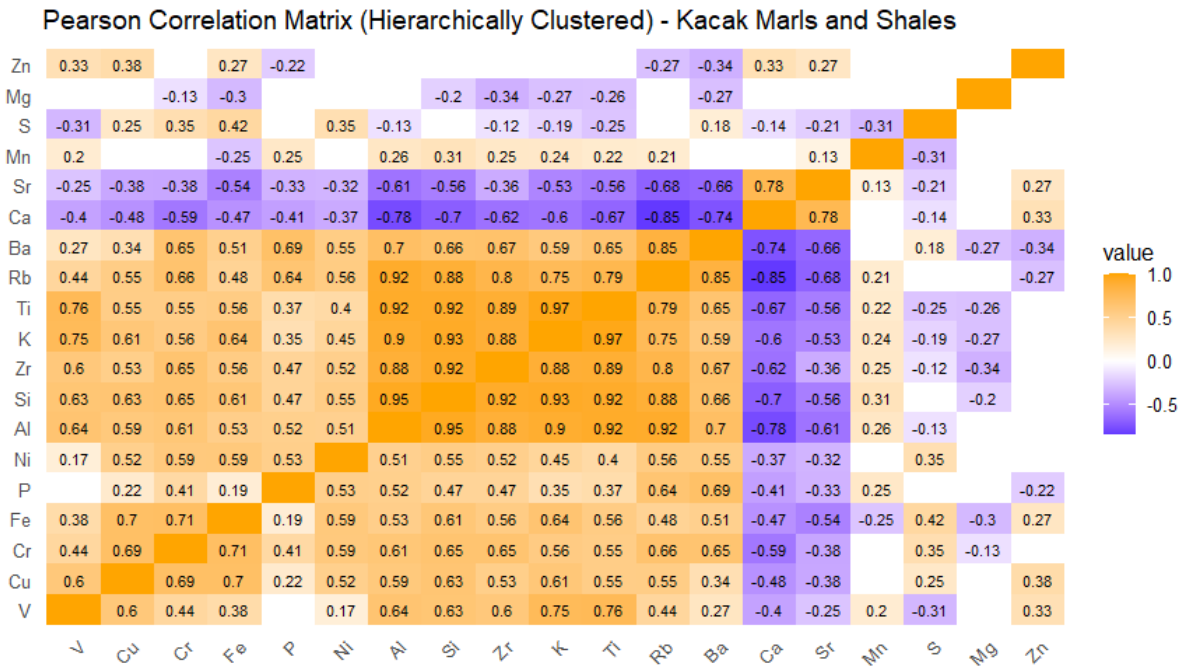


Fig. F16. Hierarchically Clustered Pearson Correlation Coefficient Matrix for the Kačák Event interval marls and shales. Positive (orange) and negative (blue) Pearson correlation coefficients at the 95 % confidence level interval. Blank boxes indicate statistically insignificant correlation.

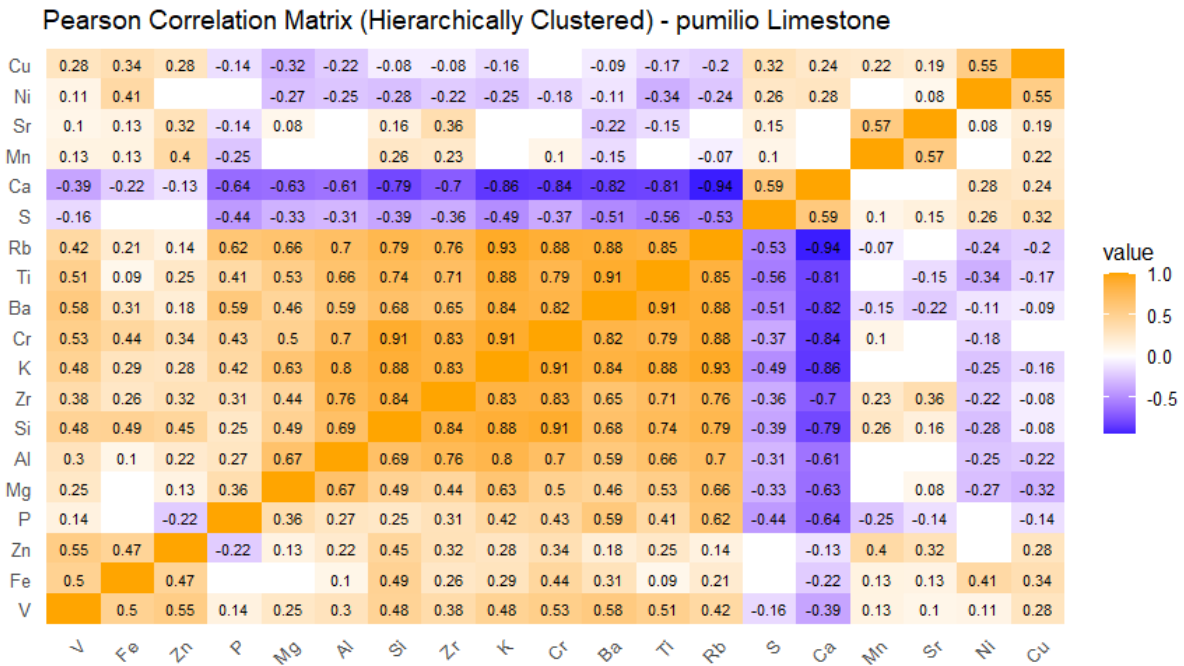


Fig. F17. Hierarchically Clustered Pearson Correlation Coefficient Matrix for the pumilio interval limestone. Positive (orange) and negative (blue) Pearson correlation coefficients at the 95 % confidence level interval. Blank boxes indicate statistically insignificant correlation.

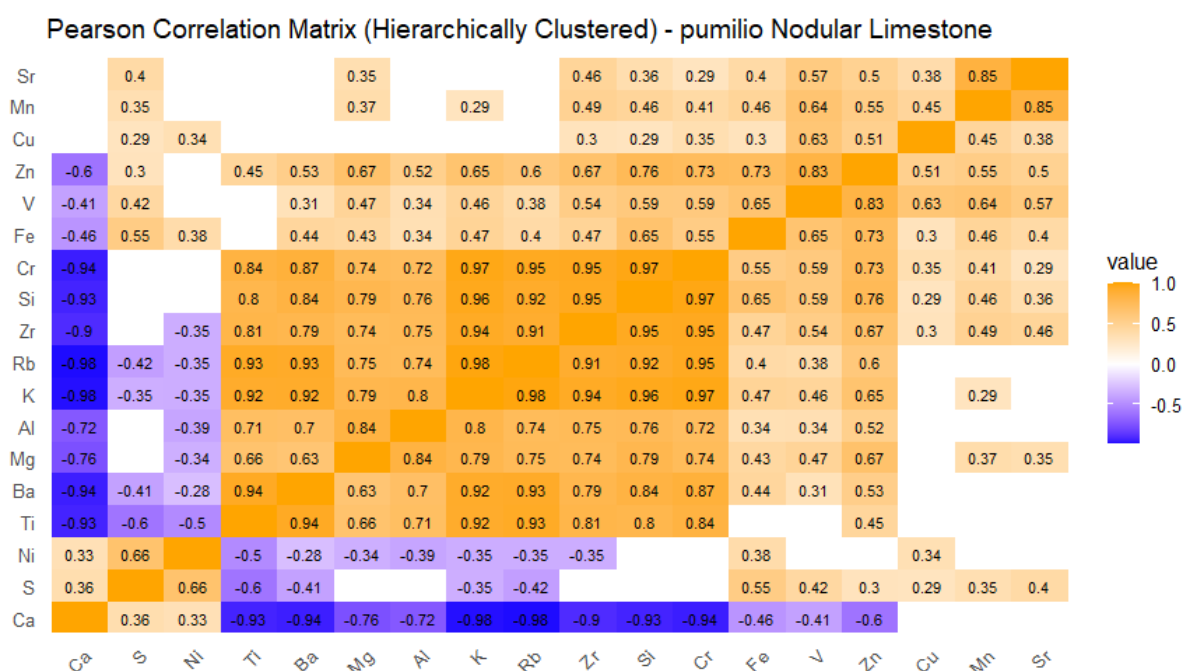


Fig. F18. Hierarchically Clustered Pearson Correlation Coefficient Matrix for the *pumilio* interval nodular limestone. Positive (orange) and negative (blue) Pearson correlation coefficients at the 95 % confidence level interval. Blank boxes indicate statistically insignificant correlation.

G. Multi-scale Rolling Correlation Analysis (MRCA)

Here, the multi-scale rolling correlation analysis (MRCA), inspired by the cross correlation of paleoecological and geochemical proxies by Sageman and Hollander (1999), is introduced to visualize the statistically significant Pearson correlation coefficient between two proxy signals. This approach is broadly similar to the rolling window regression used in Oehlert and Swart (2019) but assesses the Pearson correlation for multiple window sizes, effectively creating a two-dimensional correlation map. While it is also conceptually related to the temporal evolution of detrended cross-correlation analysis and temporal evolution of detrended partial-cross-correlation analysis proposed by Yuan et al. (2016), the main difference is that MRCA does not mathematically remove polynomial trends at each scale, meaning it is – intentionally – sensitive to non-stationarity. This method preserves long-term shifts, potentially driven by lithological transitions, and baseline changes that are intrinsic to stratigraphic proxy records. As such, correlation patterns can be interpreted directly in the context of evolving depositional, diagenetic and paleoenvironmental regimes. MRCA captures full co-evolution of two signals across both short- and long-term scales, making it particularly suited for exploratory analysis of proxy behavior over multi-Myr intervals.

While a windowed correlation analysis is conceptually straightforward, for completeness we briefly outline the mathematical background of MRCA. For each window size w , a centered window is defined around each valid height (or time) h according to:

$$Window(h, w) = \left\{ i : h_i \in \left[h - \frac{w}{2}, h + \frac{w}{2} \right] \right\}$$

Next, for two proxies x and y , their values are extracted for each window:

$$x^{(h,w)} = \{x_i : i \in Window(h, w)\}, y^{(h,w)} = \{y_i : i \in Window(h, w)\}$$

This step implies that both proxy series share a common depth/time axis and the same number of datapoints. Next, the Pearson correlation coefficient $r(h, w)$ is calculated inside each window, using values $x(h, w)$ and $y(h, w)$, following:

$$r(h, w) = \frac{\sum_{i \in Window(h, w)} (x_i - \hat{x}^{(h, w)})(y_i - \hat{y}^{(h, w)})}{\sqrt{\sum_{i \in Window(h, w)} (x_i - \hat{x}^{(h, w)})^2 \sum_{i \in Window(h, w)} (y_i - \hat{y}^{(h, w)})^2}}$$

where $\hat{x}^{(h, w)}$ and $\hat{y}^{(h, w)}$ are the means of $x^{(h, w)}$ and $y^{(h, w)}$, respectively.

For each $Window(h, w)$, a hypothesis test is performed where the Null hypothesis $H_0: r(h, w) = 0$, and the alternative hypothesis $H_1: r(h, w) \neq 0$ according to:

$$t(h, w) = r(h, w) \sqrt{\frac{n(h, w) - 2}{1 - r(h, w)^2}}$$

where $n(h, w)$ is the number of data points in $Window(h, w)$ and the corresponding two-tailed p-value is:

$$p(h, w) = 2[1 - F_{t(n(h, w) - 2)}(|t(h, w)|)]$$

where $F_{t(k)}$ is the cumulative distribution function of the Student's t-distribution with k degrees of freedom. Here, a correlation is considered statistically significant at the 95 % confidence level when:

$$p(h, w) < 0.05$$

MRCA is illustrated using two synthetic signals characterized by fixed intervals of correlation (Fig. G1); positive correlation (segment S1), negative correlation (S2), and no correlation (S3).

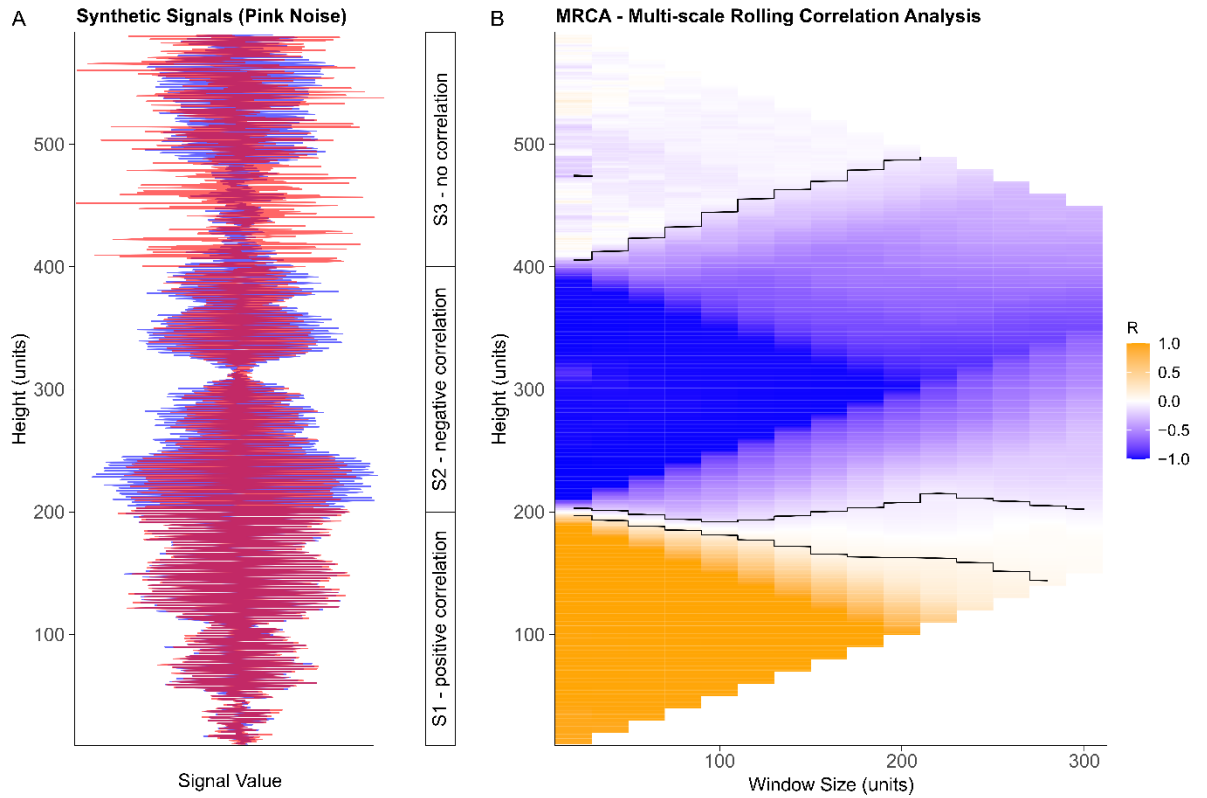


Fig. G1. Illustration of Multi-scale Rolling Correlation Analysis (MRCA) using synthetic signals. A) Synthetic pink noise signals (blue and red) characterized by positive correlation in segment 1 (S1), negative correlation (S2) and, no correlation (S3). B) MRCA of the pink noise signals, indicating significant positive (orange) and negative (blue) Pearson correlation and the 95 % confidence level (demarcated by black lines).

H. Bi-element Cross-plots

The bi-element cross-plots are provided here to complement PCA and PCCM and provide lithology-specific Pearson correlation coefficients at the 95 % confidence level for each of the Daleje, Choteč, Kačák, and *pumilio* intervals.

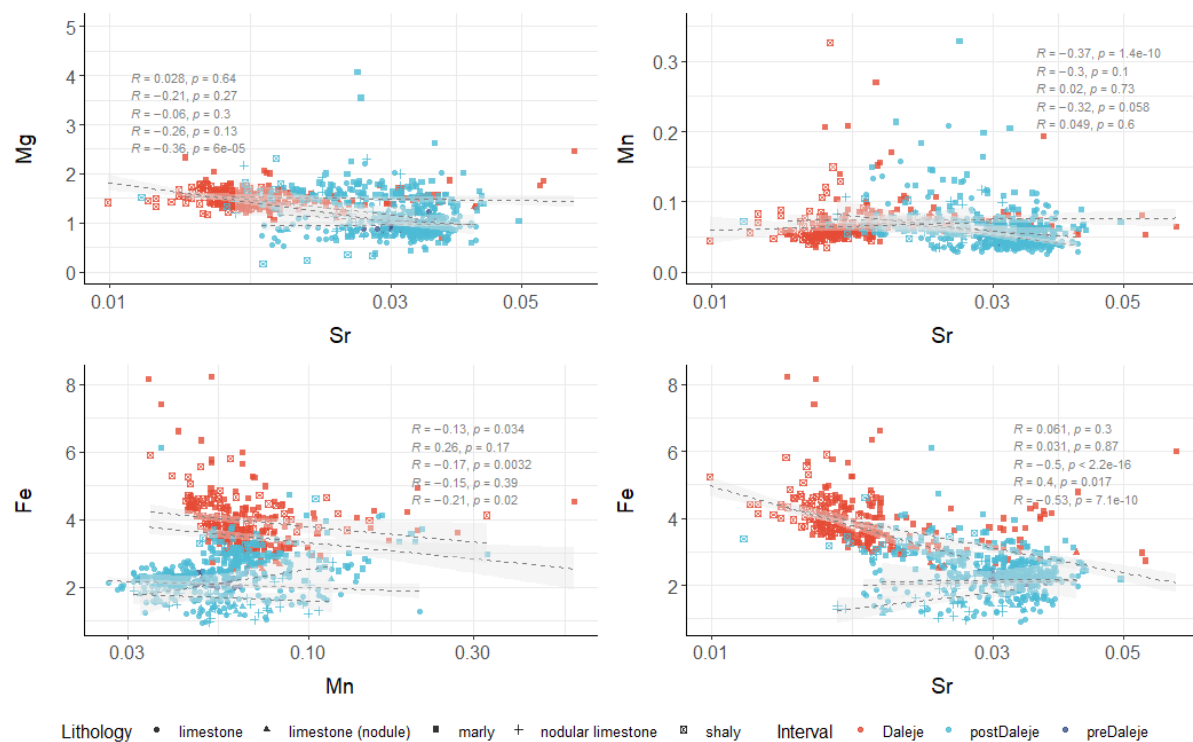


Fig. H1. Daleje Interval diagenesis element cross-plots. Mg-Sr, Mn-Sr, Fe-Mn and Sr-Fe. Symbols indicate lithology, and colors indicate sub-interval (dark blue: pre-Daleje interval, red: Daleje Event interval, light blue: post-Daleje interval). Linear regression (dashed black line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

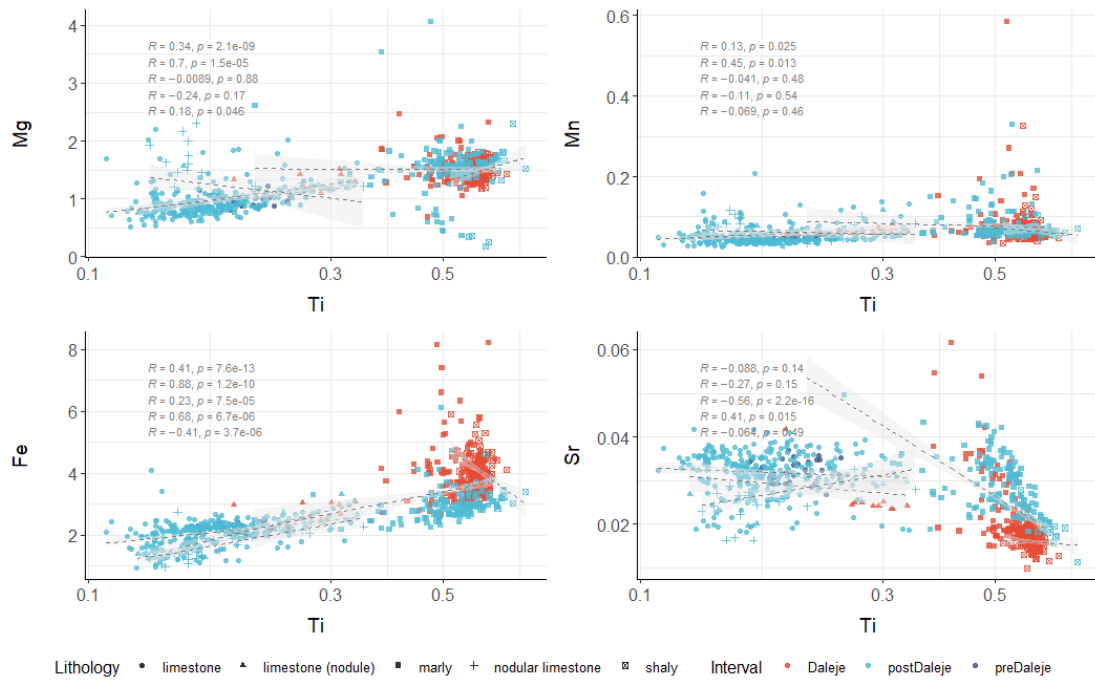


Fig. H2. Daleje Interval diagenesis element cross-plots. Mg-Ti, Mn-Ti, Fe-Ti, and Sr-Ti. Symbols indicate lithology, and colors indicate sub-interval (dark blue: pre-Daleje interval, red: Daleje Event interval, light blue: post-Daleje interval). Linear regression (dashed black line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

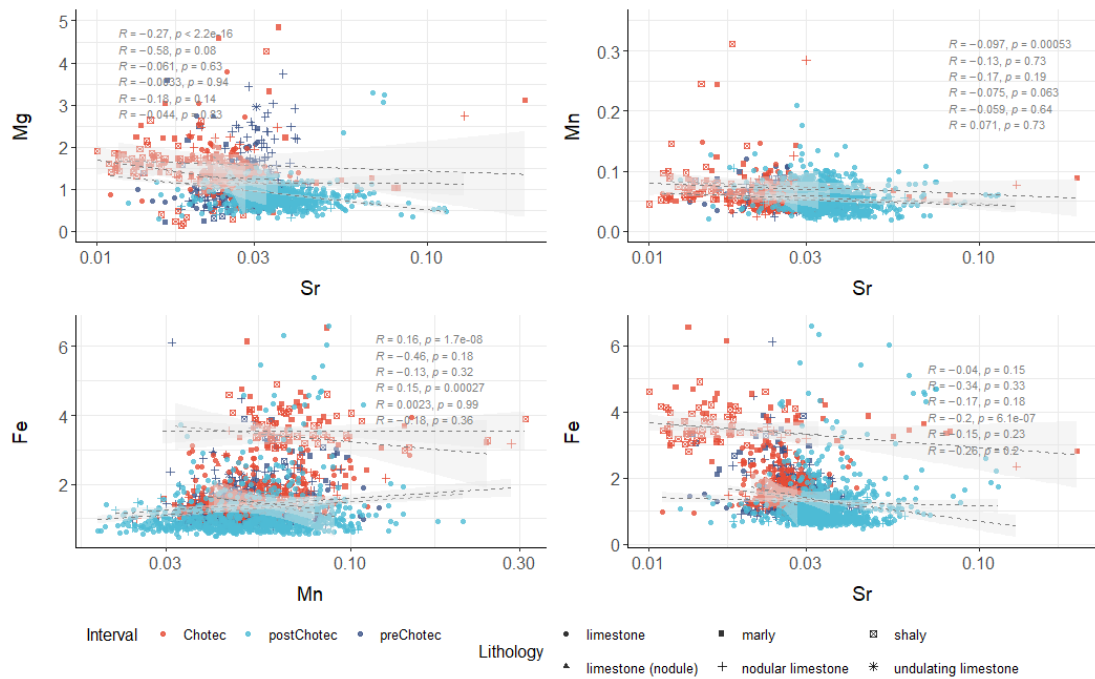


Fig. H3. Chotec Interval diagenesis element cross-plots. Mg-Sr, Mn-Sr, Fe-Mn, and Sr-Fe. Symbols indicate lithology, and colors indicate sub-interval (dark blue: pre-Chotec interval, red: Chotec Event interval, light blue: post-Chotec interval). Linear regression (dashed black line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

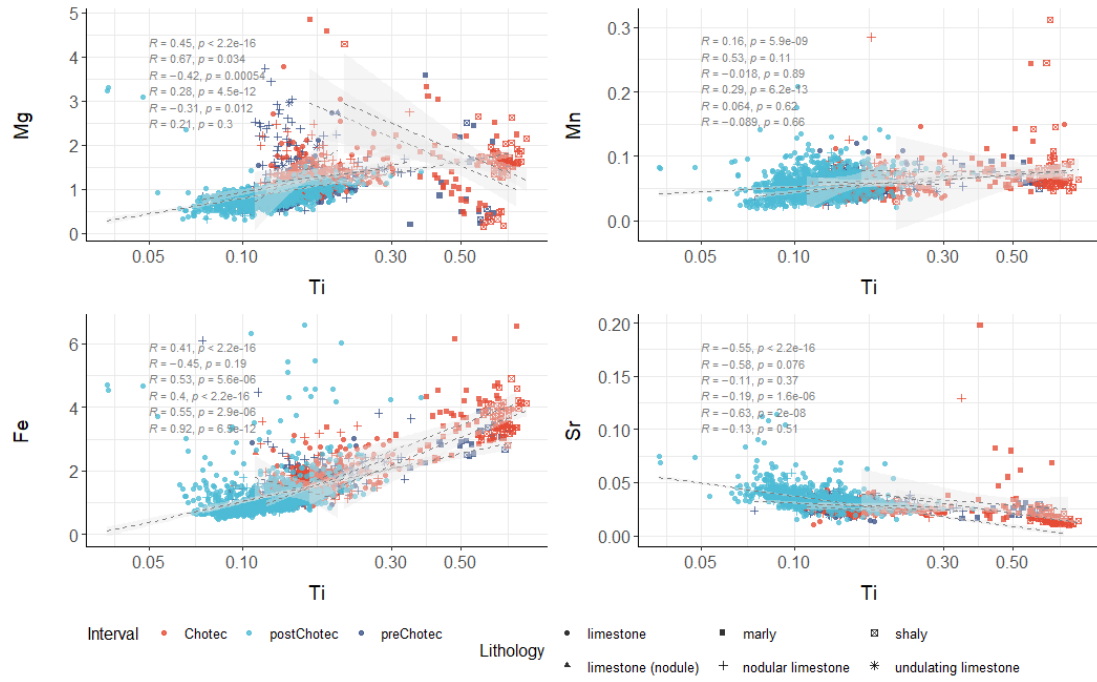


Fig. H4. Choteč Interval diagenesis element cross-plots. Mg-Ti, Mn-Ti, Fe-Ti, and Sr-Ti. Symbols indicate lithology, and colors indicate sub-interval (dark blue: pre-Chotec interval, red: Chotec Event interval, light blue: post-Chotec interval). Linear regression (dashed black line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

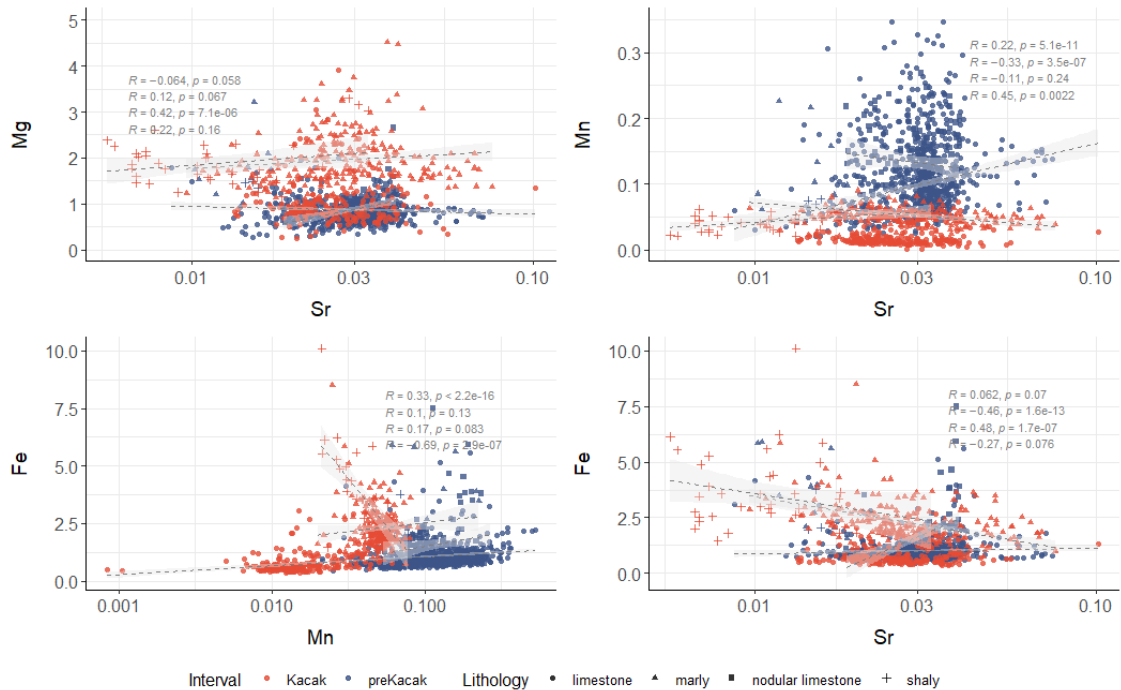


Fig. H5. Kačák Interval diagenesis element cross-plots. Mg-Sr, Mn-Sr, Fe-Mn, and Sr-Fe. Symbols indicate lithology, and colors indicate sub-interval (dark blue: pre-Kačák interval, red: Kačák Event interval). Linear regression (dashed black line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

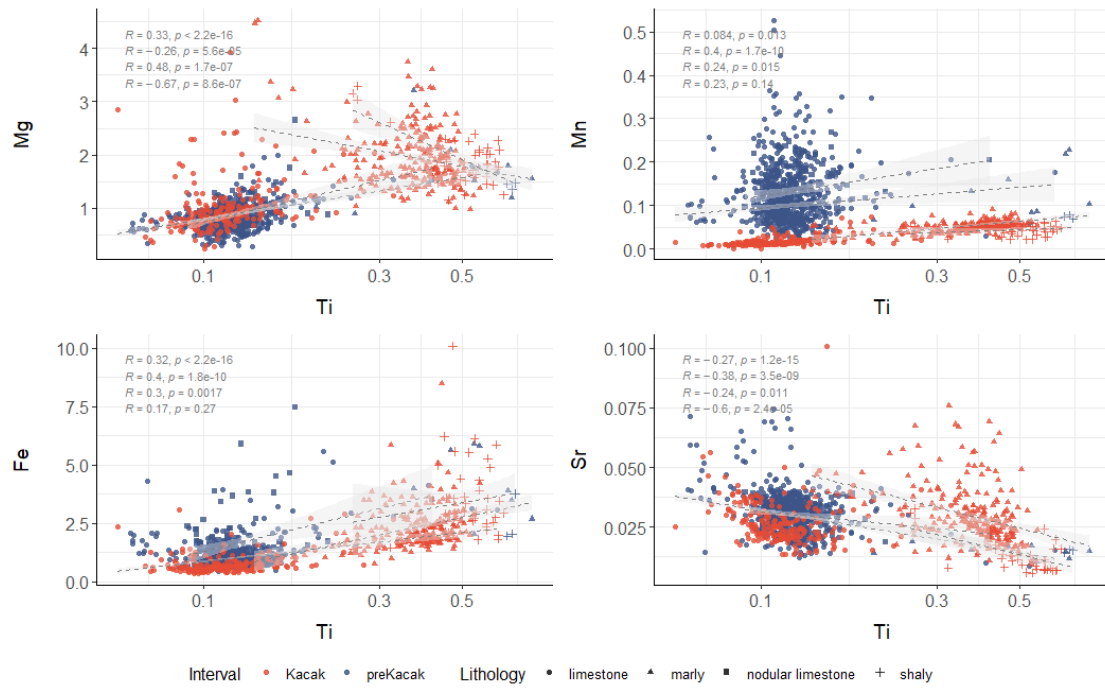


Fig. H6. Kačák Interval diagenesis element cross-plots. Mg-Ti, Mn-Ti, Fe-Ti, and Sr-Ti. Symbols indicate lithology, and colors indicate sub-interval (dark blue: pre-Kačák interval, red: Kačák Event interval). Linear regression (dashed black line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

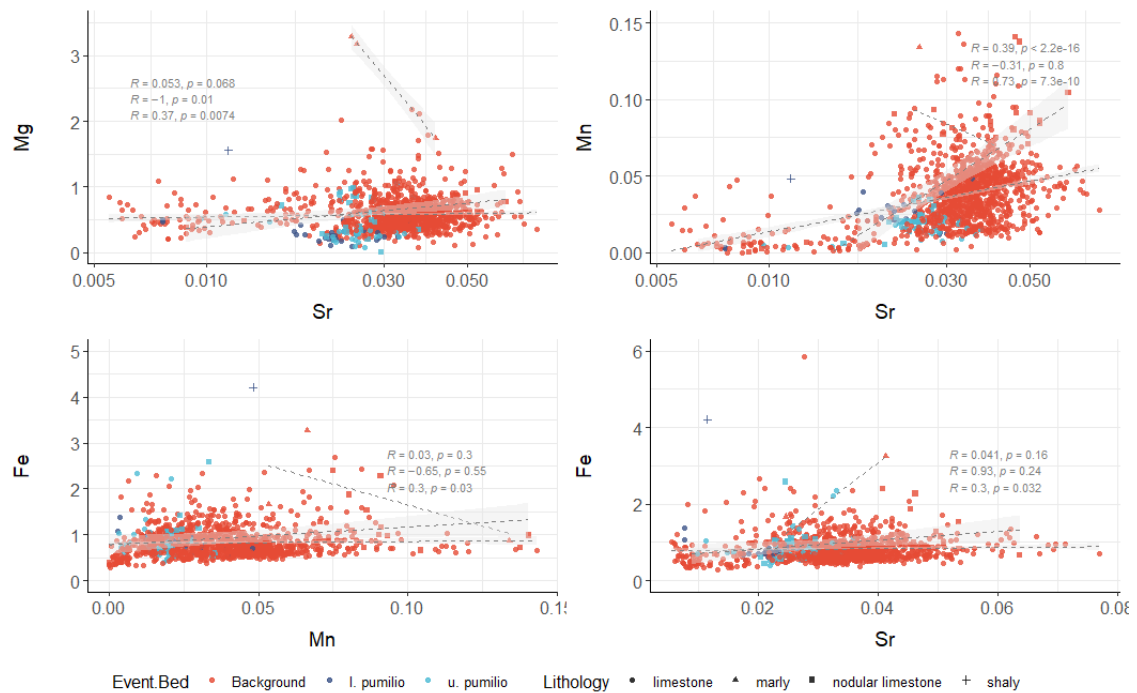


Fig. H7. *pumilio* Interval diagenesis element cross-plots. Mg-Sr, Mn-Sr, Fe-Mn, and Sr-Fe. Symbols indicate lithology, and colors indicate sub-interval (red: background, dark blue: Lower *pumilio* Event, light blue: Upper *pumilio* Event). Linear regression (dashed black line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

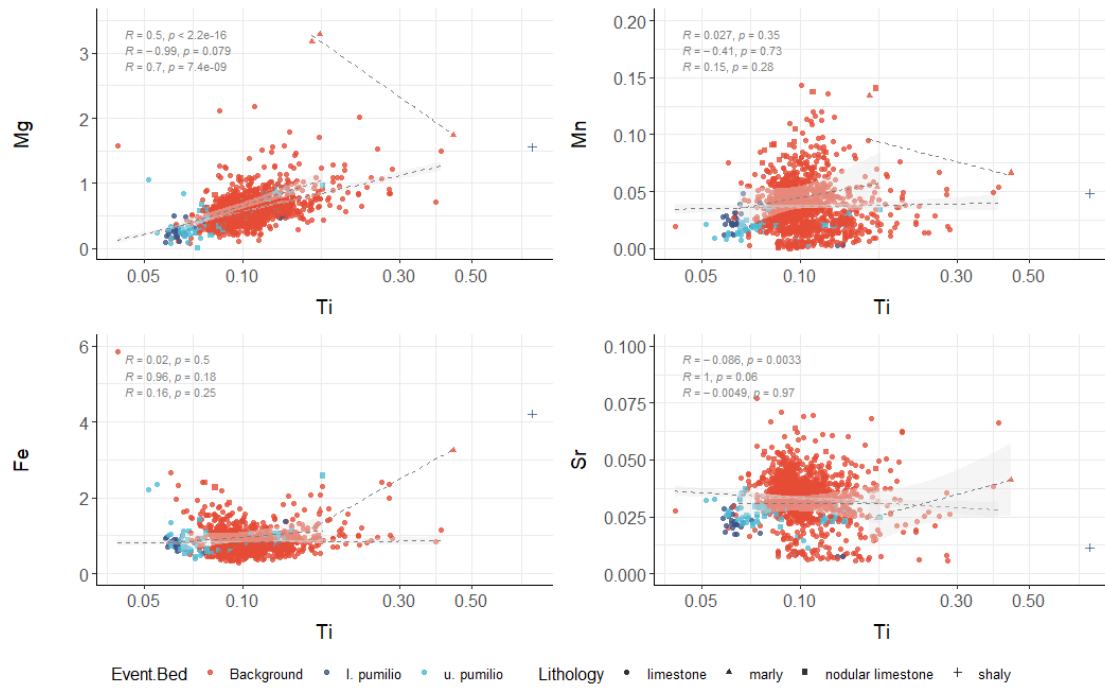


Fig. H8. *pumilio* Interval diagenesis element cross-plots. Mg-Ti, Mn-Ti, Fe-Ti, and Sr-Ti. Symbols indicate lithology, and colors indicate sub-interval (red: background, dark blue: Lower *pumilio* Event, light blue: Upper *pumilio* Event). Linear regression (dashed black line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

I. Lithology-specific Bi-element Cross-plots

Throughout the main text of the manuscript, statistical analyses using PCA, PCCM and bi-element cross-plots are often applied on the two most dominant (groups of) lithologies to limit the figure count. However, this may lead to amalgamation where, for example, marls and shales are grouped together (PCA, Fig. 4-6) but likely have contrasting geochemical imprints that are obscured when treated as a single unit. This risks masking lithology-specific trends, diluting environmental signals, and potentially generating misleading correlations driven by mixed sediment sources rather than true geochemical relationships. Thus, to aid in the interpretation, lithology-specific cross-plots for the Daleje, Choteč, Kačák and *pumilio* intervals are presented here. While all values below are provided as weight per cent (%), these are intentionally not added here because these concentrations should be interpreted semi-quantitatively.

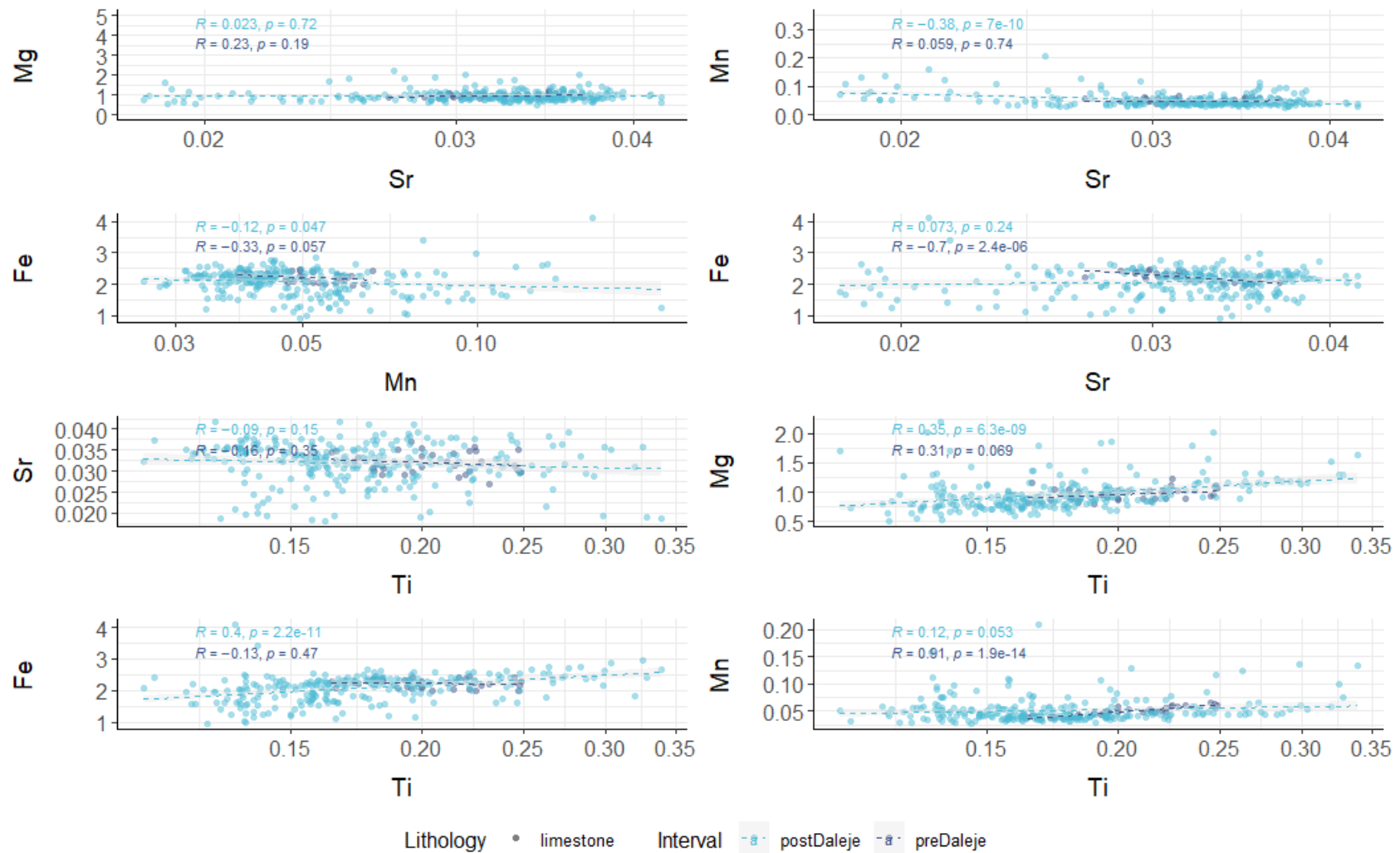


Fig. 11. Daleje interval limestone facies cross-plots. Mg-Sr, Mn-Sr, Fe-Mn, Fe-Sr, Sr-Ti, Mg-Ti, Fe-Ti, and Mn-Ti for the pre-Daleje (dark blue) and post-Daleje interval (light blue). Linear regression (dashed line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

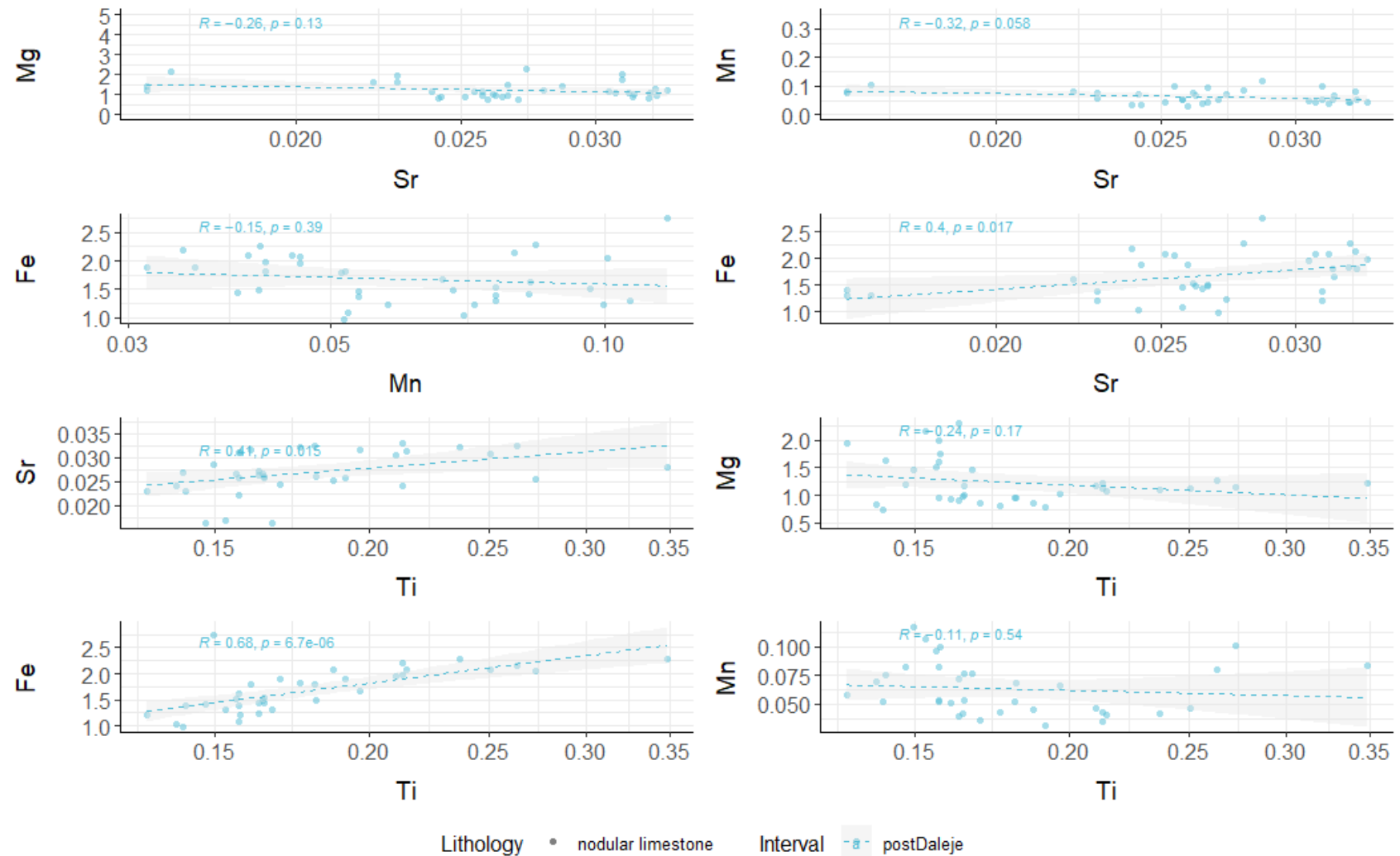


Fig. I2. Daleje interval nodular limestone facies cross-plots. Mg-Sr, Mn-Sr, Fe-Mn, Fe-Sr, Sr-Ti, Mg-Ti, Fe-Ti, and Mn-Ti for the post-Daleje interval (light blue). Linear regression (dashed line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

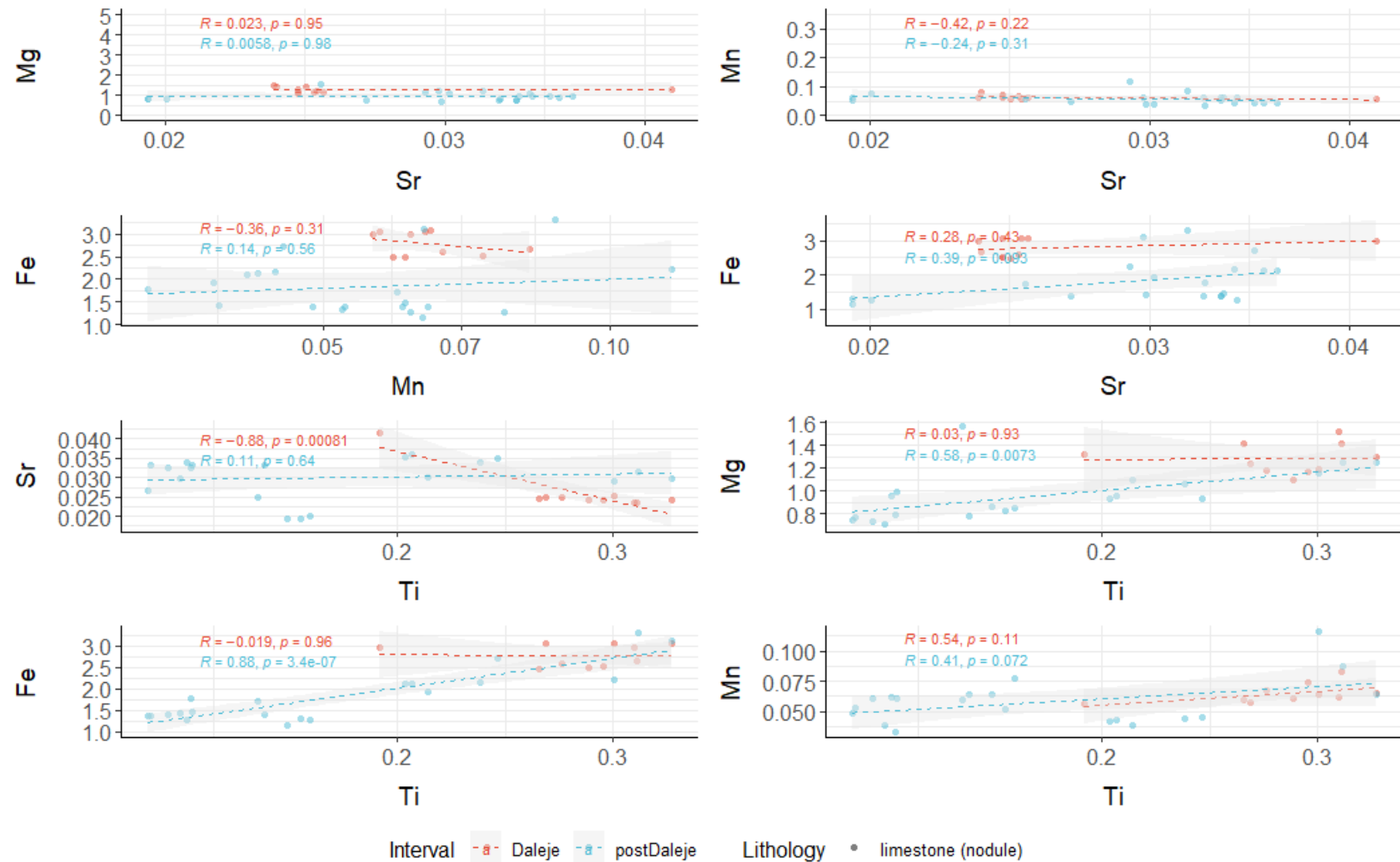


Fig. I3. Daleje interval limestone nodule facies cross-plots. Mg-Sr, Mn-Sr, Fe-Mn, Fe-Sr, Sr-Ti, Mg-Ti, Fe-Ti, and Mn-Ti for the Daleje Event (red) and post-Daleje interval (light blue). Linear regression (dashed line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

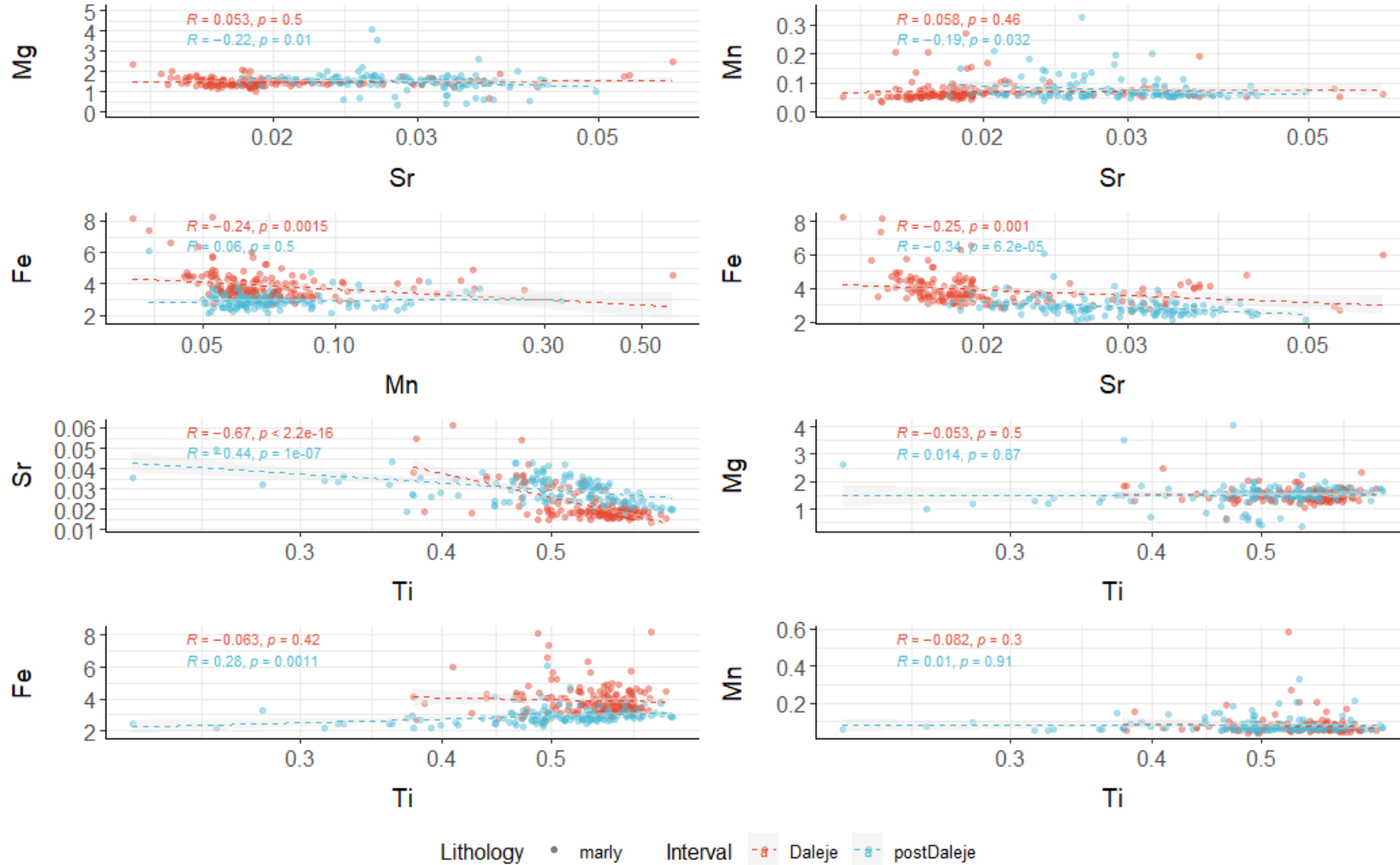


Fig. 14. Daleje interval marly facies cross-plots. Mg-Sr, Mn-Sr, Fe-Mn, Fe-Sr, Sr-Ti, Mg-Ti, Fe-Ti, and Mn-Ti for the Daleje Event (red) and post-Daleje interval (light blue). Linear regression (dashed line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

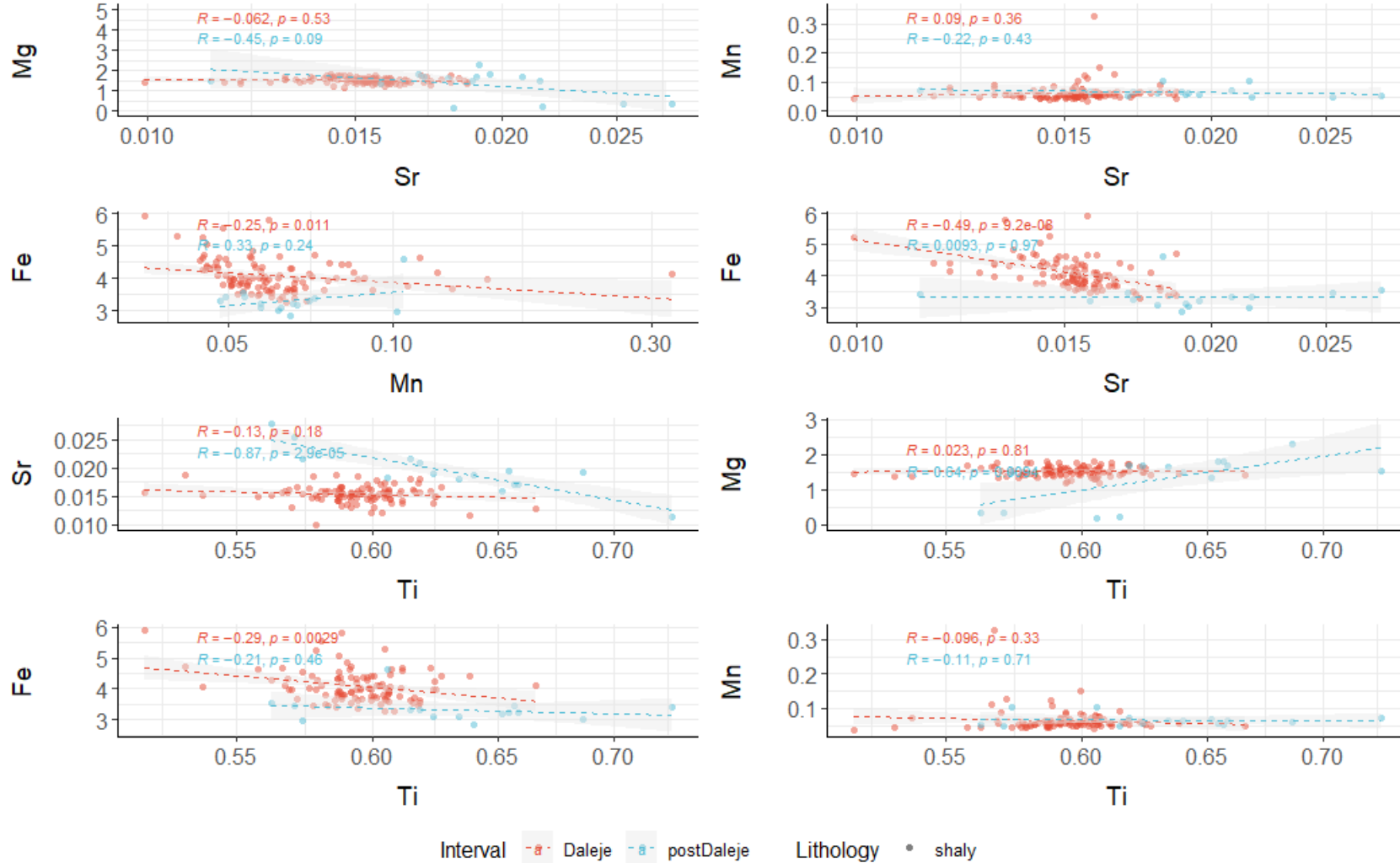


Fig. I5. Daleje interval shaly facies cross-plots. Mg-Sr, Mn-Sr, Fe-Mn, Fe-Sr, Sr-Ti, Mg-Ti, Fe-Ti, and Mn-Ti for the Daleje Event (red) and post-Daleje interval (light blue). Linear regression (dashed line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

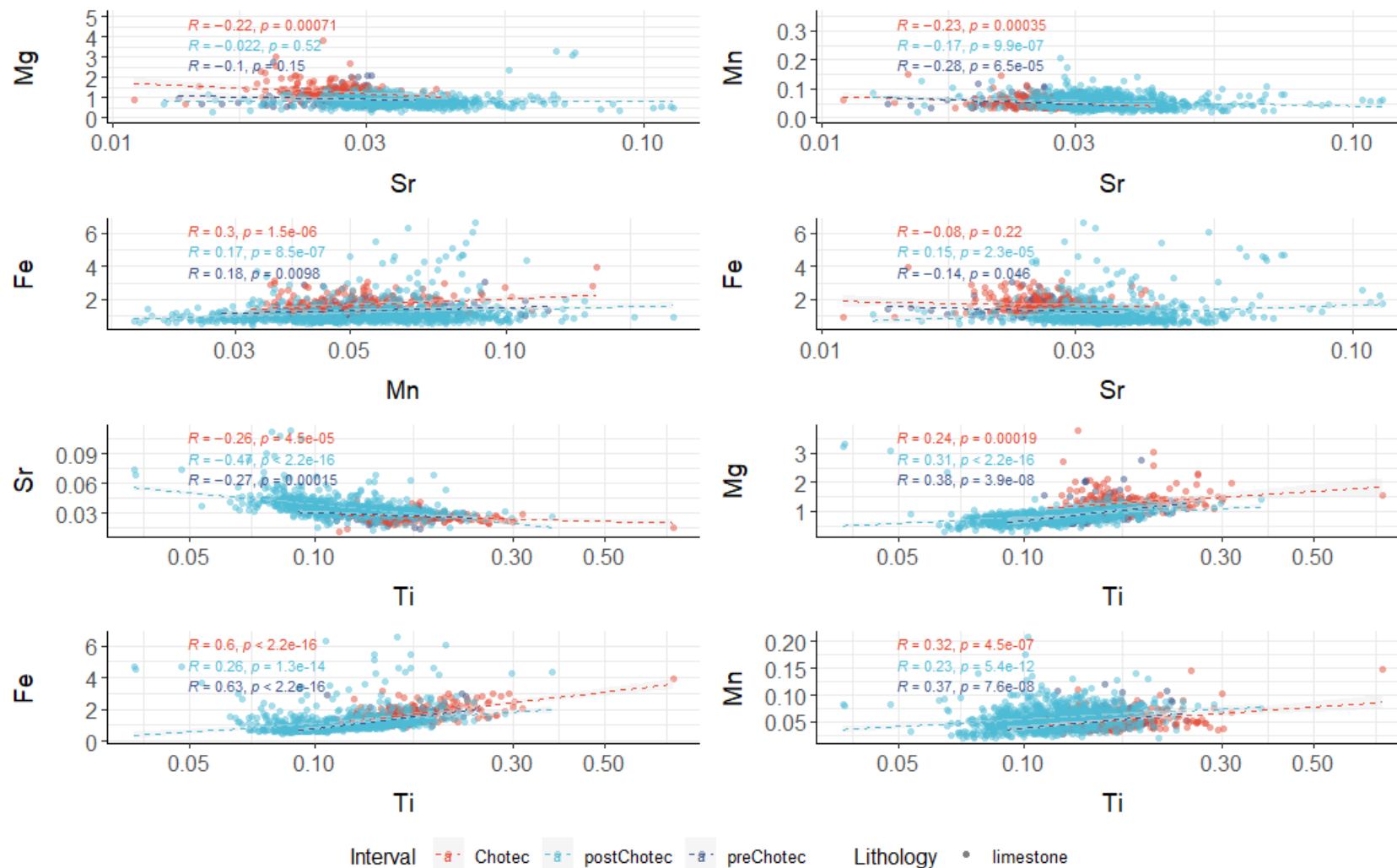


Fig. I6. Choteč interval limestone facies cross-plots. Mg-Sr, Mn-Sr, Fe-Mn, Fe-Sr, Sr-Ti, Mg-Ti, Fe-Ti, and Mn-Ti for the pre-Choteč (dark blue), Choteč Event (red) and post-Choteč (light blue) interval. Linear regression (dashed line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

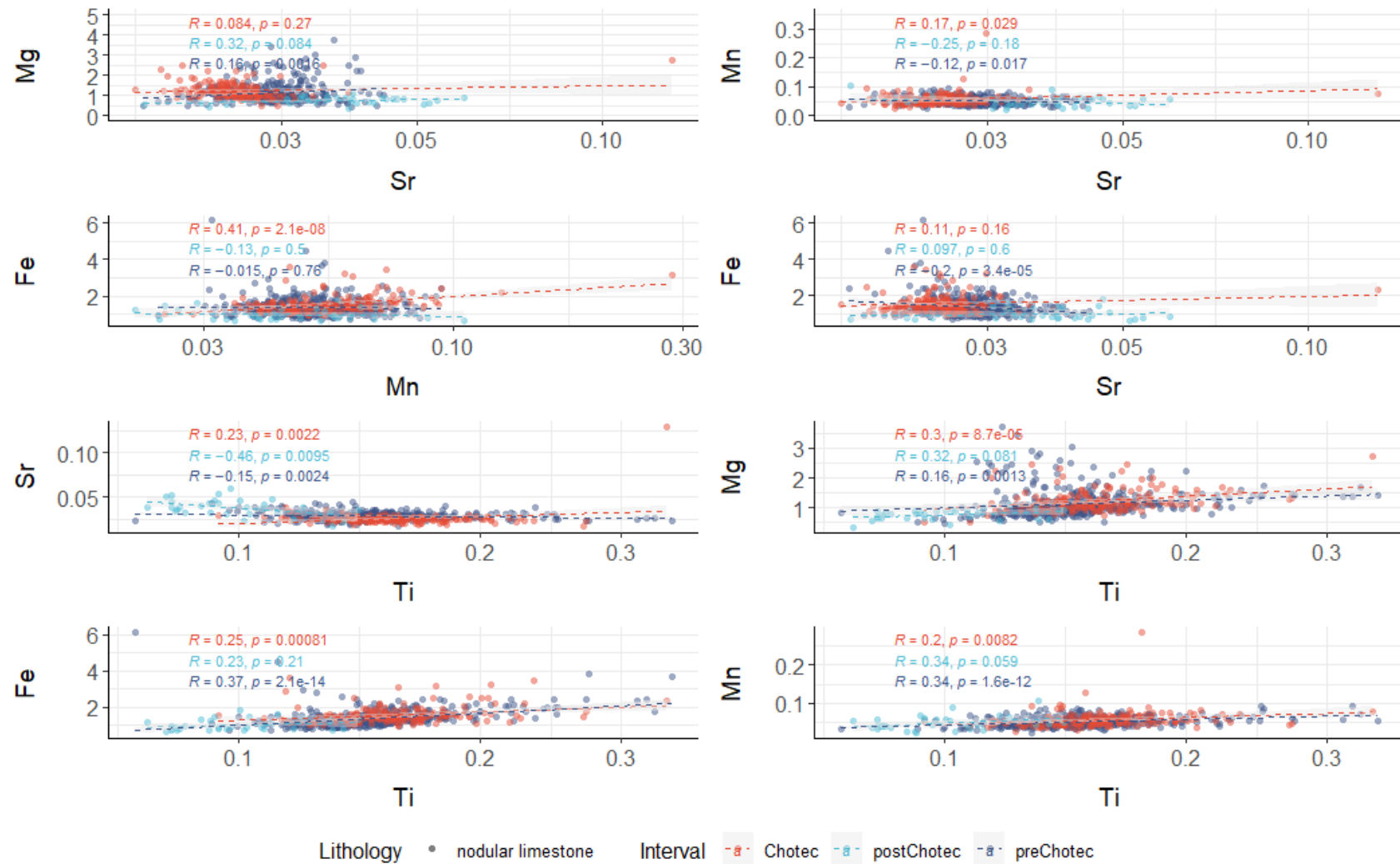


Fig. 17. Chotec interval nodular limestone facies cross-plots. Mg-Sr, Mn-Sr, Fe-Mn, Fe-Sr, Sr-Ti, Mg-Ti, Fe-Ti, and Mn-Ti for the pre-Chotec (dark blue), Chotec Event (red) and post-Chotec (light blue) interval. Linear regression (dashed line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

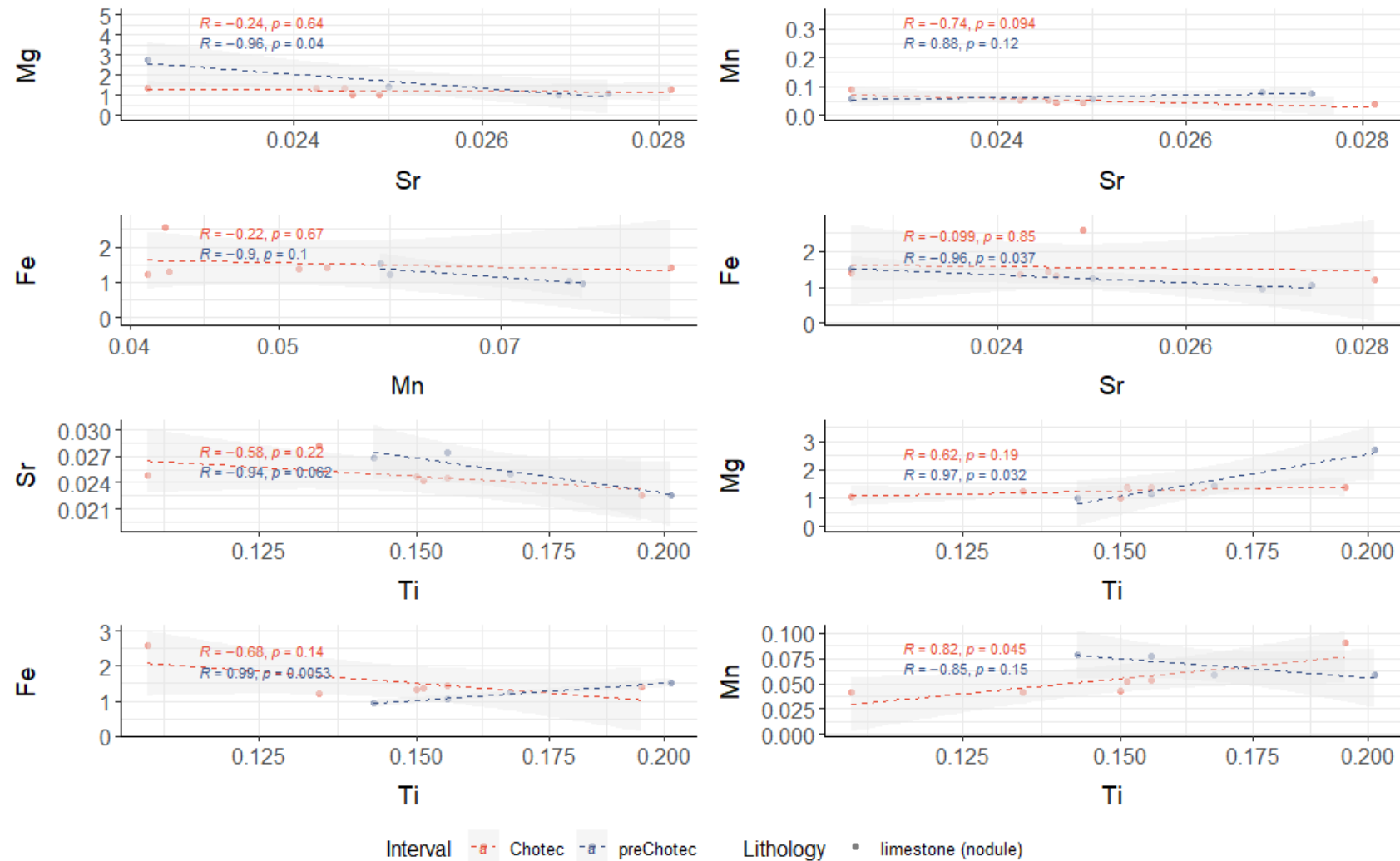


Fig. 18. Choteč interval limestone nodule facies cross-plots. Mg-Sr, Mn-Sr, Fe-Mn, Fe-Sr, Sr-Ti, Mg-Ti, Fe-Ti, and Mn-Ti for the pre-Choteč (dark blue) and Choteč Event (red) interval. Linear regression (dashed line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

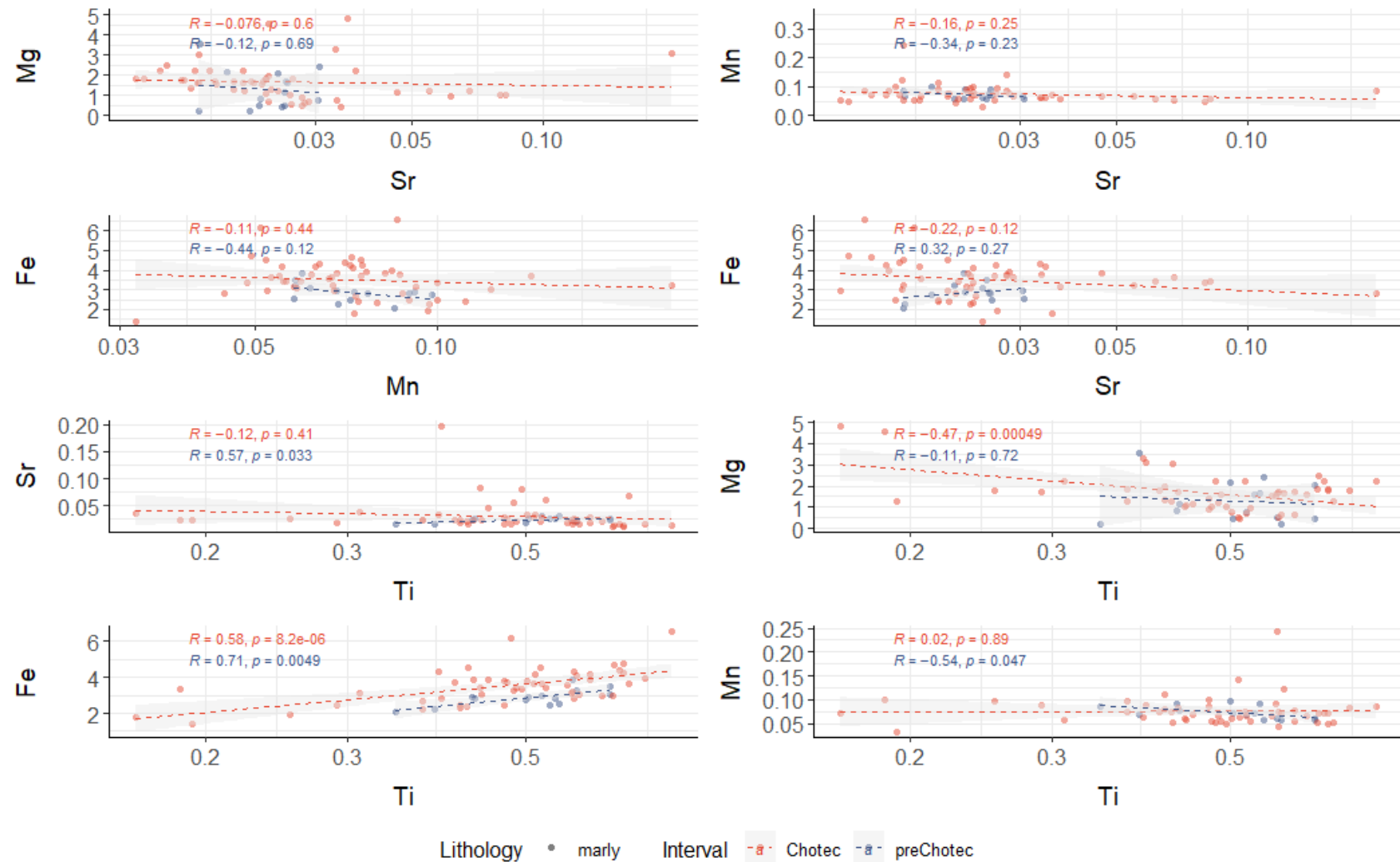


Fig. 19. Choteč interval marly facies cross-plots. Mg-Sr, Mn-Sr, Fe-Mn, Fe-Sr, Sr-Ti, Mg-Ti, Fe-Ti, and Mn-Ti for the pre-Choteč (dark blue) and Choteč Event (red) interval. Linear regression (dashed line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

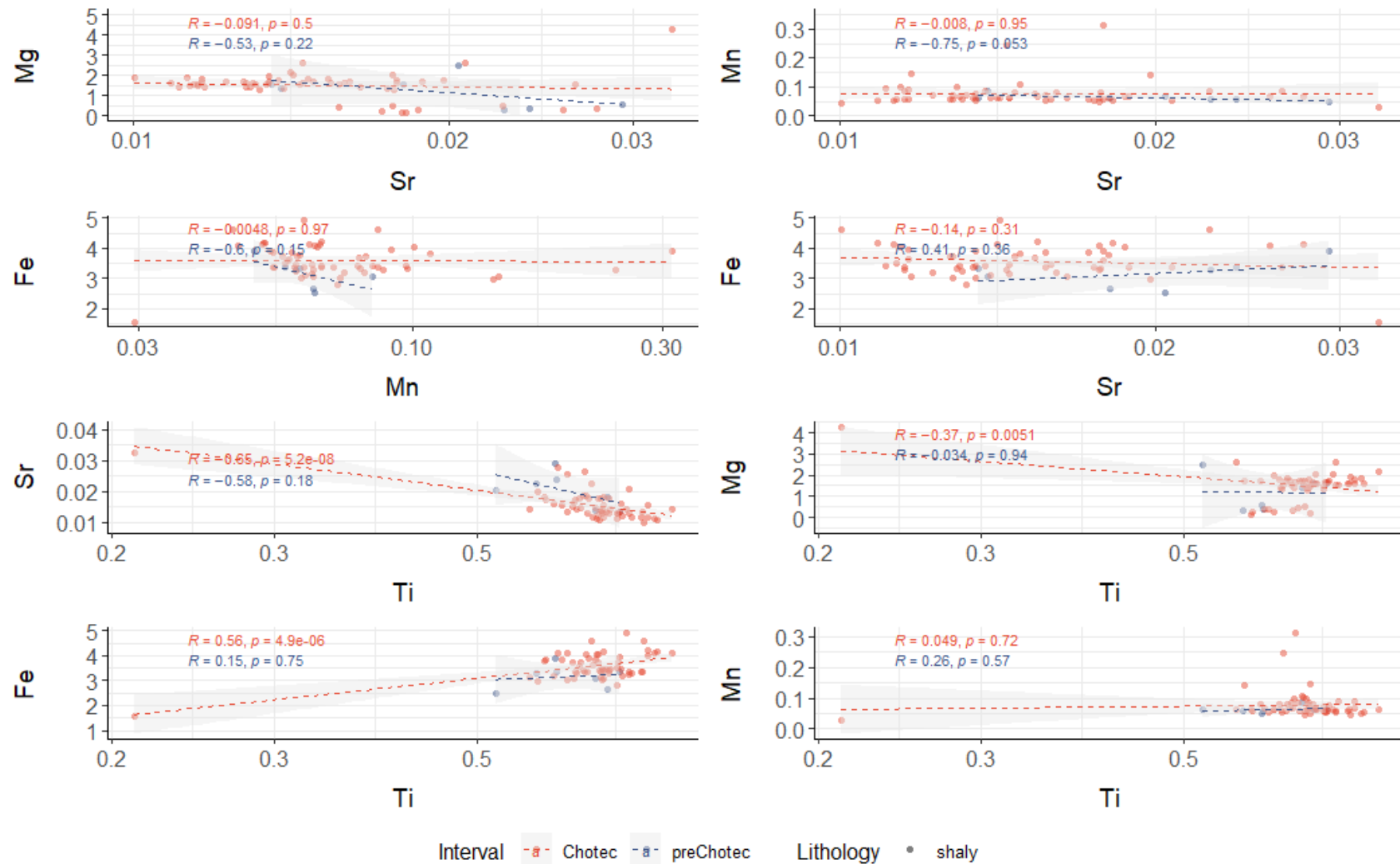


Fig. I10. Choteč interval shaly facies cross-plots. Mg-Sr, Mn-Sr, Fe-Mn, Fe-Sr, Sr-Ti, Mg-Ti, Fe-Ti, and Mn-Ti for the pre-Choteč (dark blue) and Choteč Event (red) interval. Linear regression (dashed line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

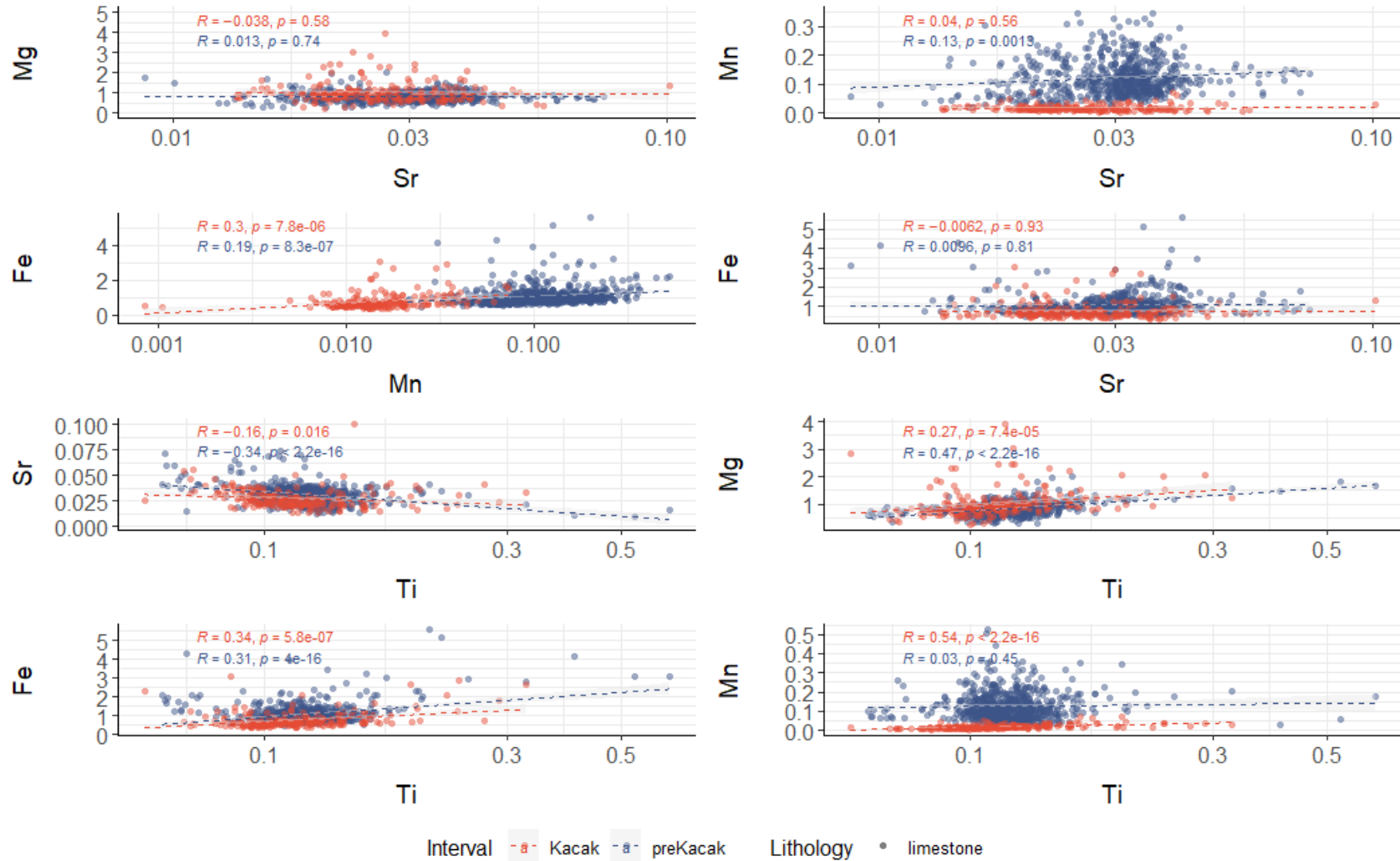


Fig. I11. Kačák interval limestone facies cross-plots. Mg-Sr, Mn-Sr, Fe-Mn, Fe-Sr, Sr-Ti, Mg-Ti, Fe-Ti, and Mn-Ti for the pre-Kačák (dark blue) and Kačák Event (red) interval. Linear regression (dashed line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

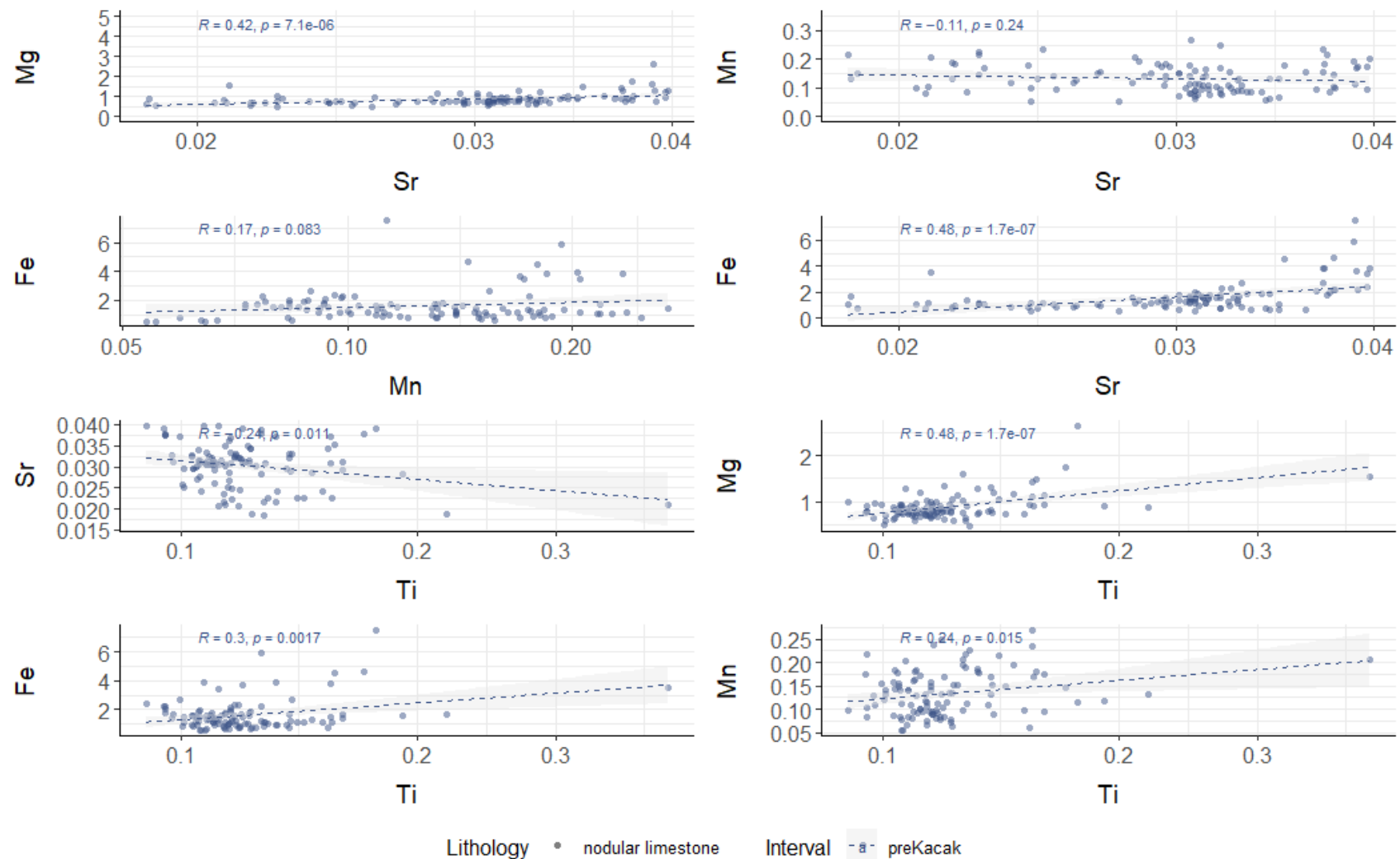


Fig. I12. Kačák interval nodular limestone facies cross-plots. Mg-Sr, Mn-Sr, Fe-Mn, Fe-Sr, Sr-Ti, Mg-Ti, Fe-Ti, and Mn-Ti for the pre-Kačák (dark blue) interval. Linear regression (dashed line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

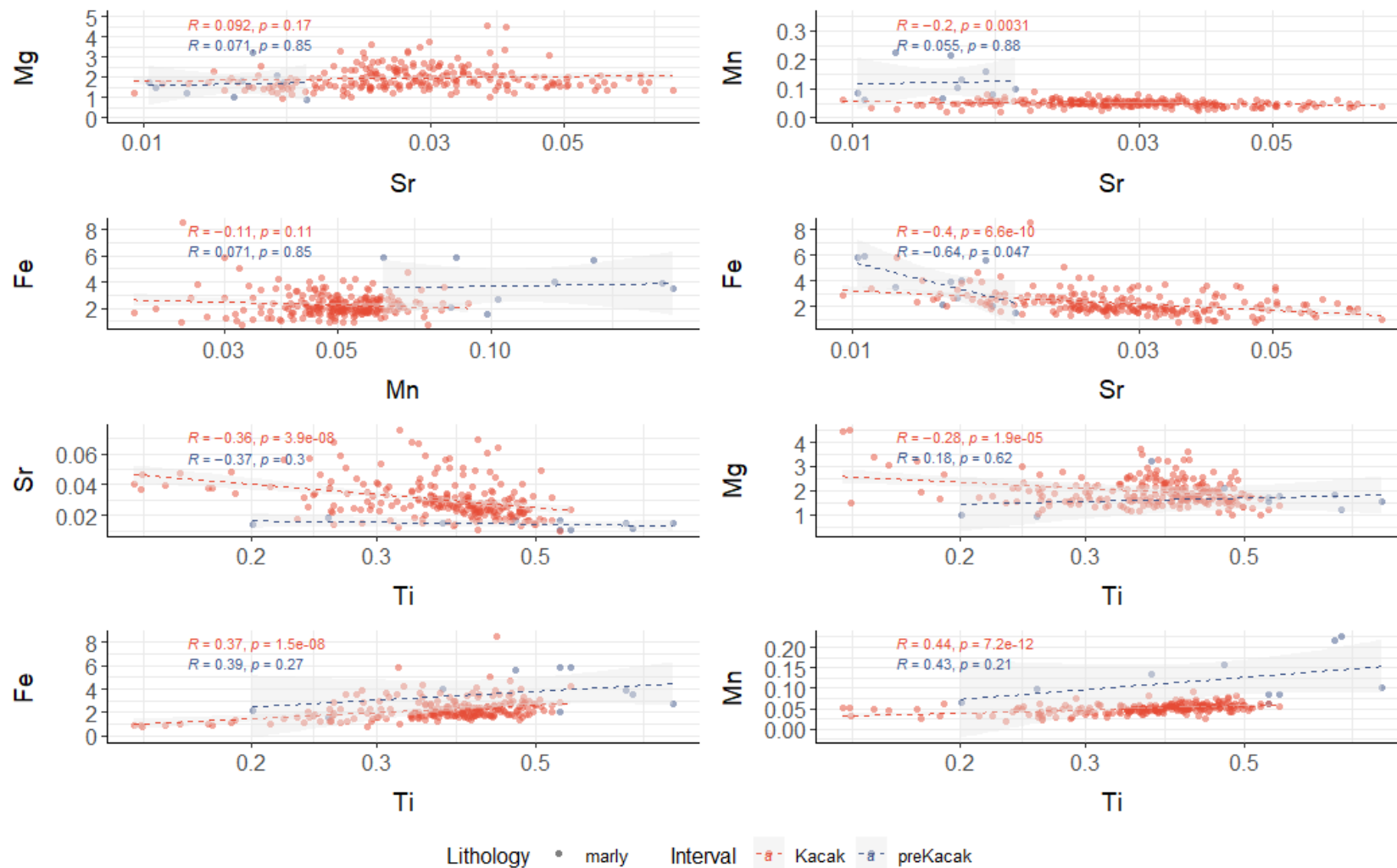


Fig. I13. Kačák interval marly facies cross-plots. Mg-Sr, Mn-Sr, Fe-Mn, Fe-Sr, Sr-Ti, Mg-Ti, Fe-Ti, and Mn-Ti for the pre- Kačák (dark blue) and Kačák Event (red) interval. Linear regression (dashed line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

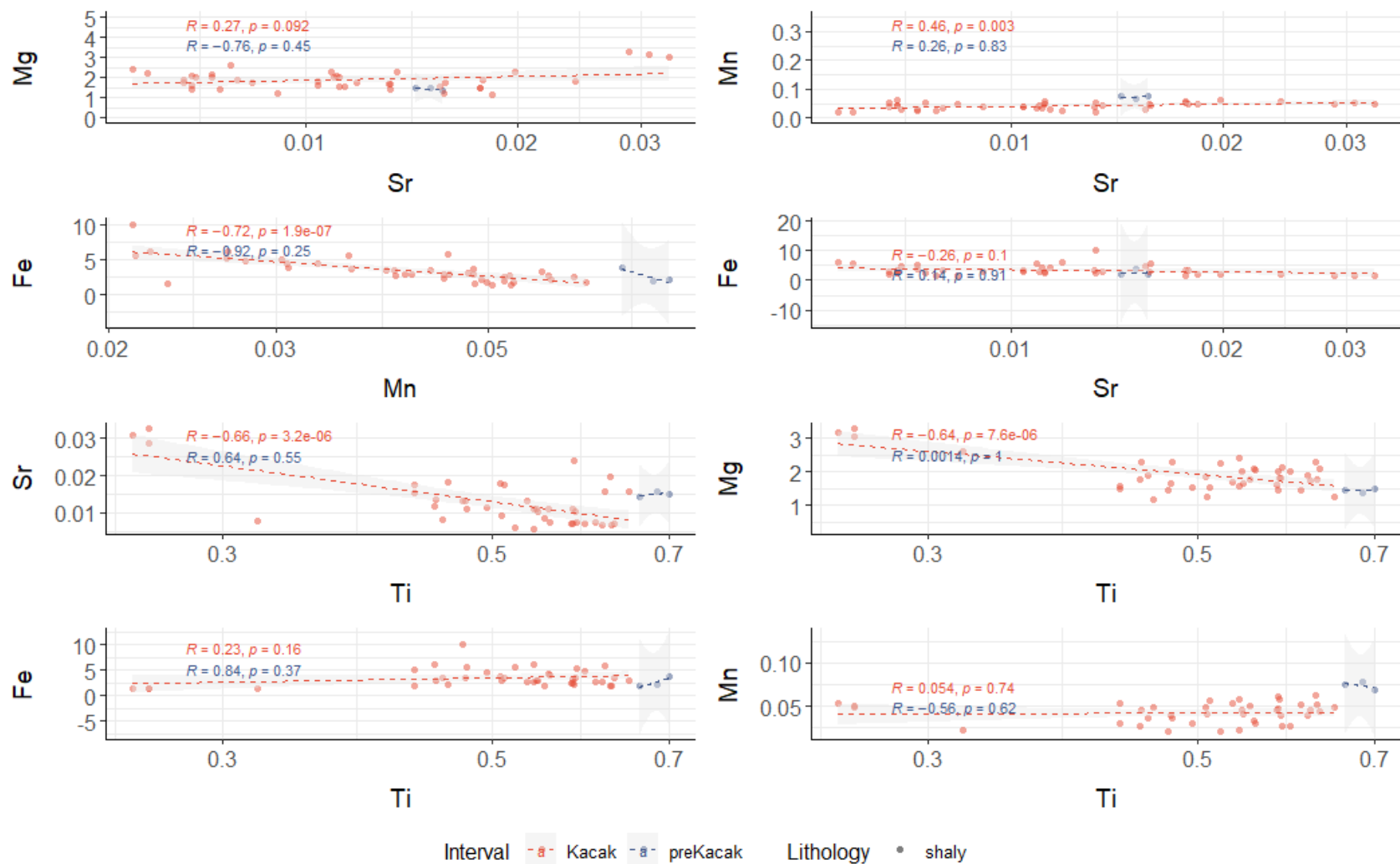


Fig. I14. Kačák interval shaly facies cross-plots. Mg-Sr, Mn-Sr, Fe-Mn, Fe-Sr, Sr-Ti, Mg-Ti, Fe-Ti, and Mn-Ti for the pre-Kačák (dark blue) and Kačák Event (red) interval. Linear regression (dashed line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

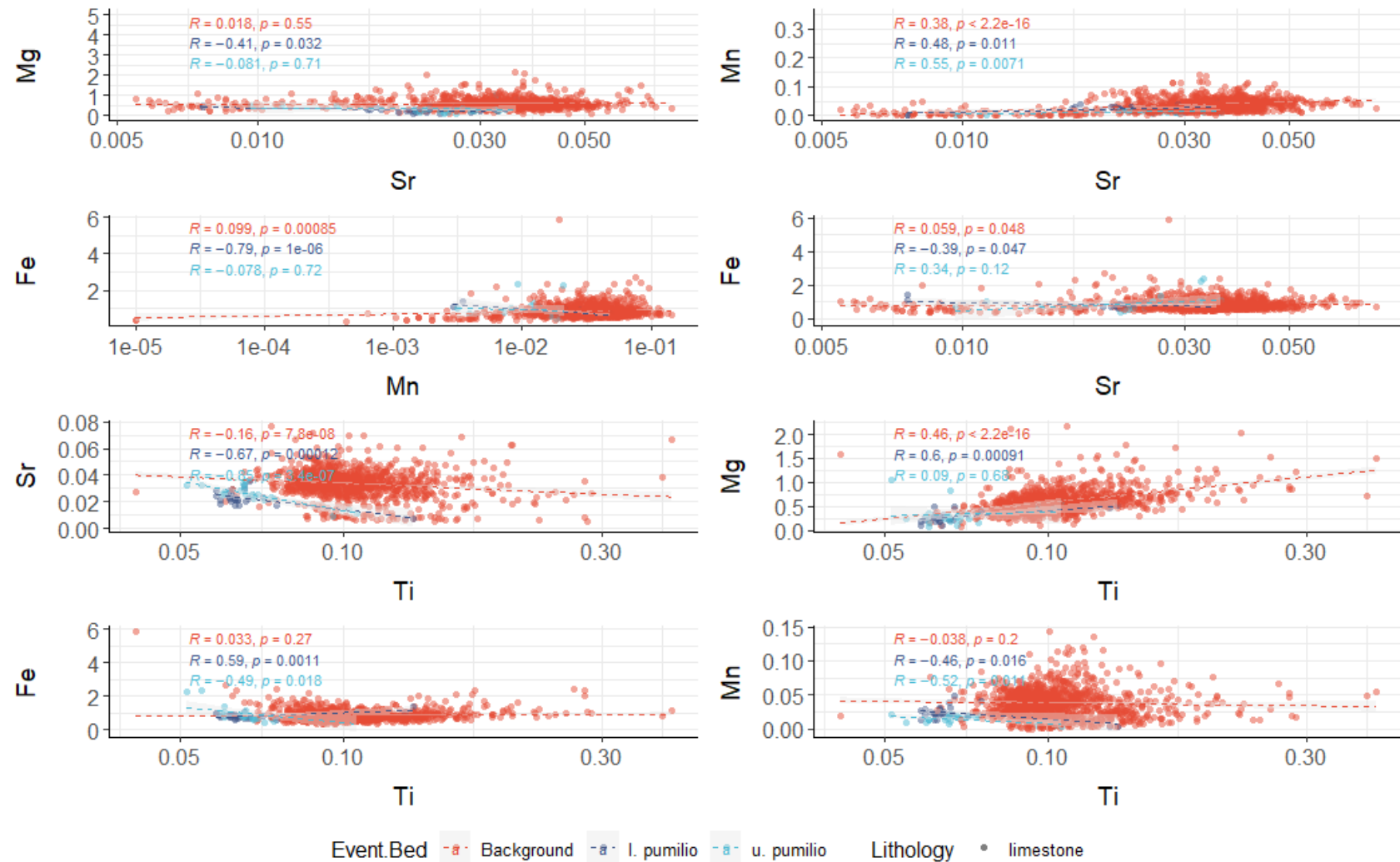


Fig. I15. *pumilio* interval limestone facies cross-plots. Mg-Sr, Mn-Sr, Fe-Mn, Fe-Sr, Sr-Ti, Mg-Ti, Fe-Ti, and Mn-Ti for the background interval (red), Lower *pumilio* (dark blue) and Upper *pumilio* Event bed (light blue). Linear regression (dashed line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

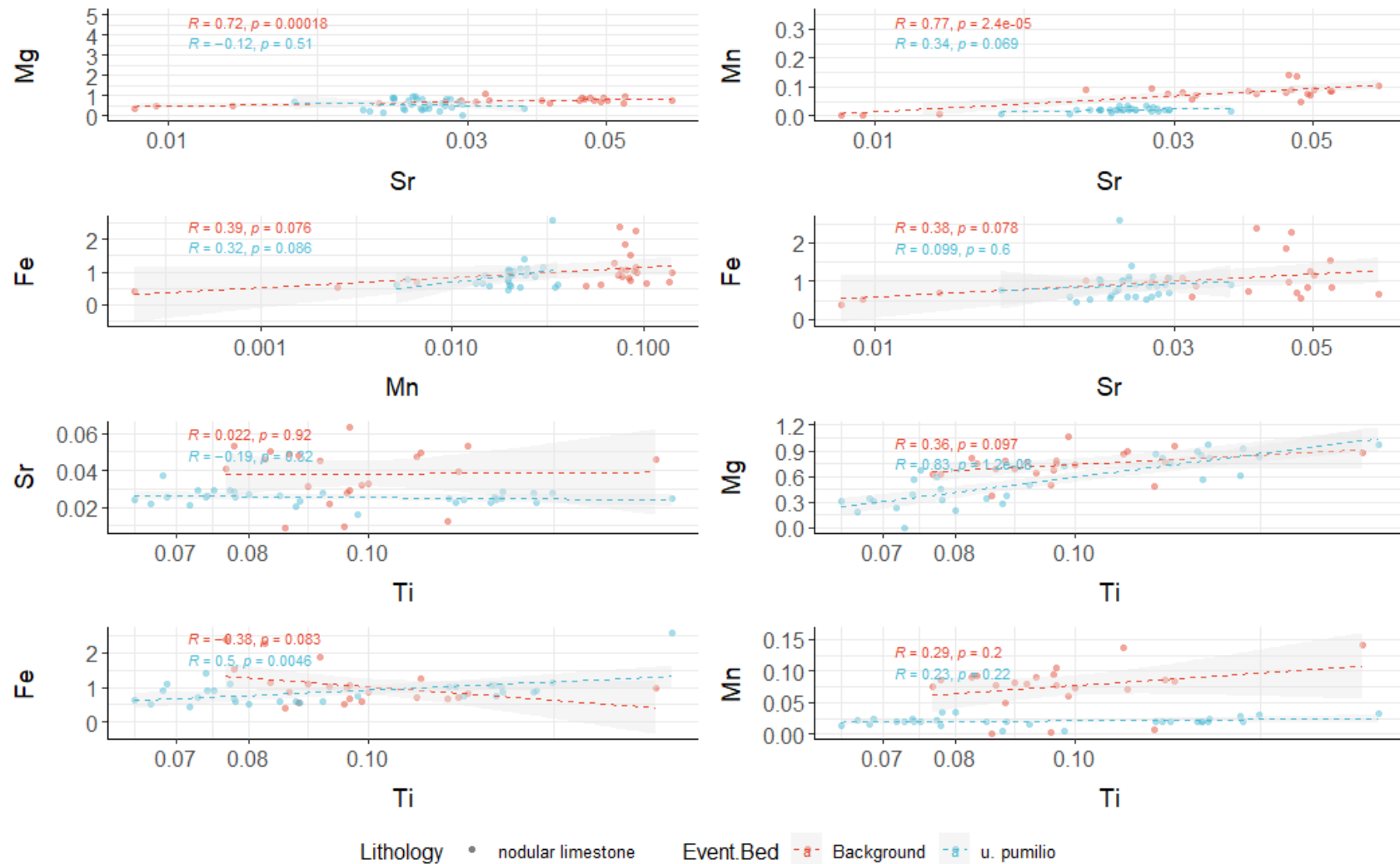


Fig. I16. *pumilio* interval nodular limestone facies cross-plots. Mg-Sr, Mn-Sr, Fe-Mn, Fe-Sr, Sr-Ti, Mg-Ti, Fe-Ti, and Mn-Ti for the background interval (red) and Upper *pumilio* Event bed (light blue). Linear regression (dashed line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

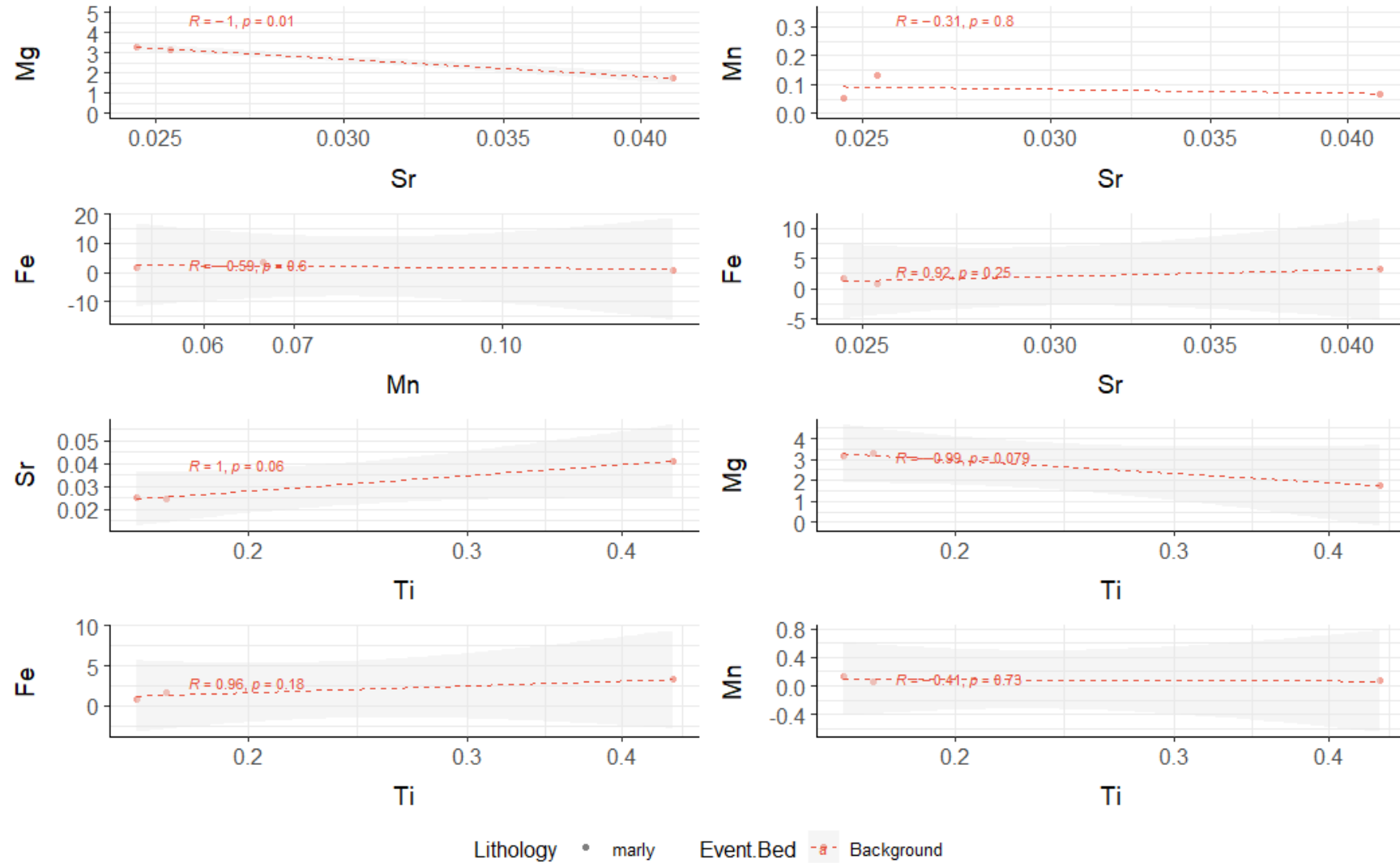


Fig. I17. *pumilio* interval marly facies cross-plots. Mg-Sr, Mn-Sr, Fe-Mn, Fe-Sr, Sr-Ti, Mg-Ti, Fe-Ti, and Mn-Ti for the background interval (red). Linear regression (dashed line) and 95% confidence level interval (light gray). Pearson correlation coefficient and p-value at the 95% confidence level interval are provided per lithology across the entire interval.

J. MRCA of Detrital and Redox Indicators

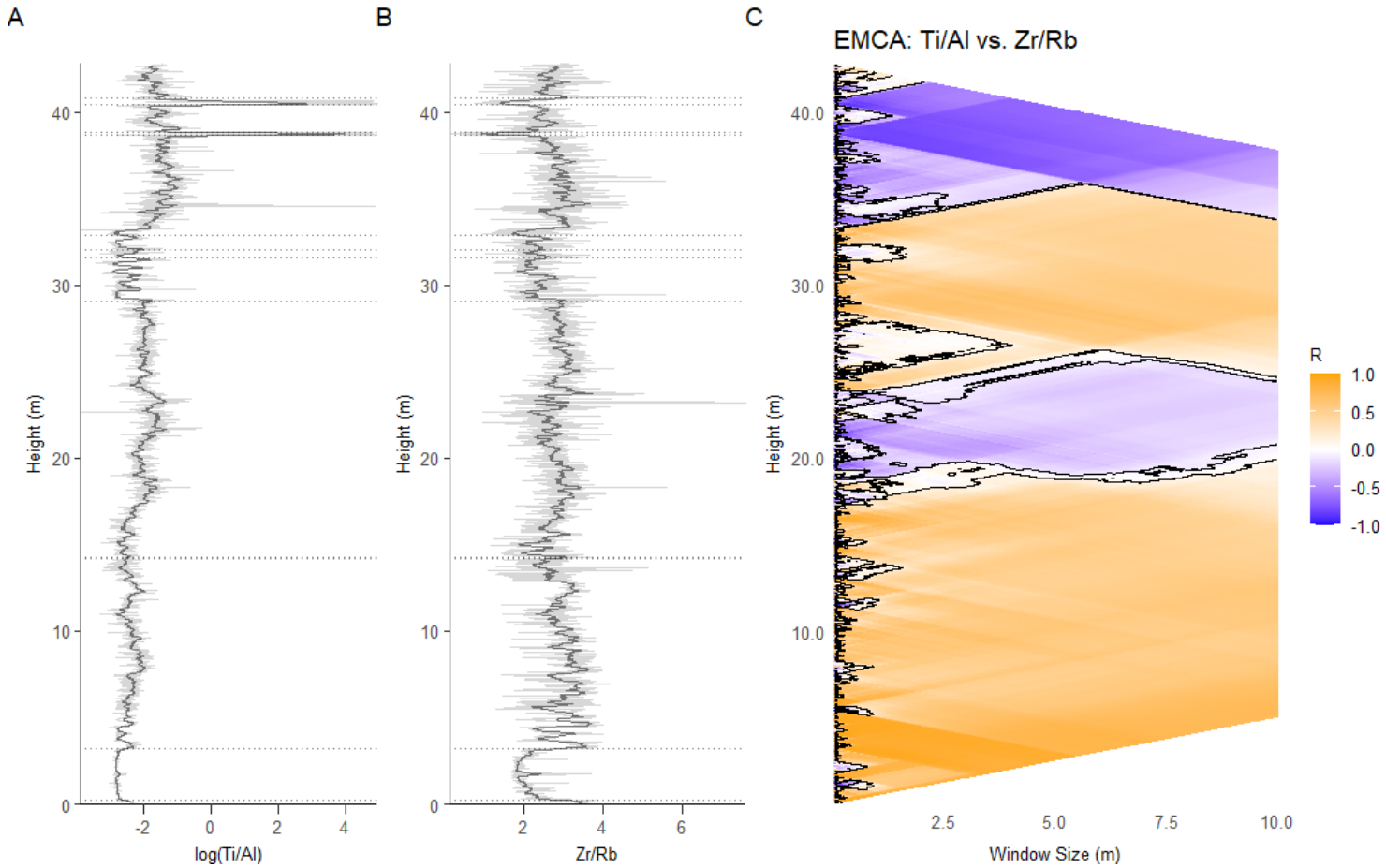


Fig. J1. Multi-scale Rolling Correlation Analysis of Ti/Al and Zr/Rb. A) log(Ti/Al) (light gray) and 21-point running average (dark gray). B) Zr/Rb (light gray) and 21-point running average (dark gray). C) Multi-scale Rolling Correlation Analysis (MRCA) of Ti/Al versus Zr/Rb, significant positive (orange) or negative (blue) Pearson correlation (95% confidence interval) is demarcated by black lines. Horizontal dashed lines indicate, from bottom to top, the Daleje, Choteč, Lower Kačák, Upper Kačák, Lower *pumilio* and Upper *pumilio* events.

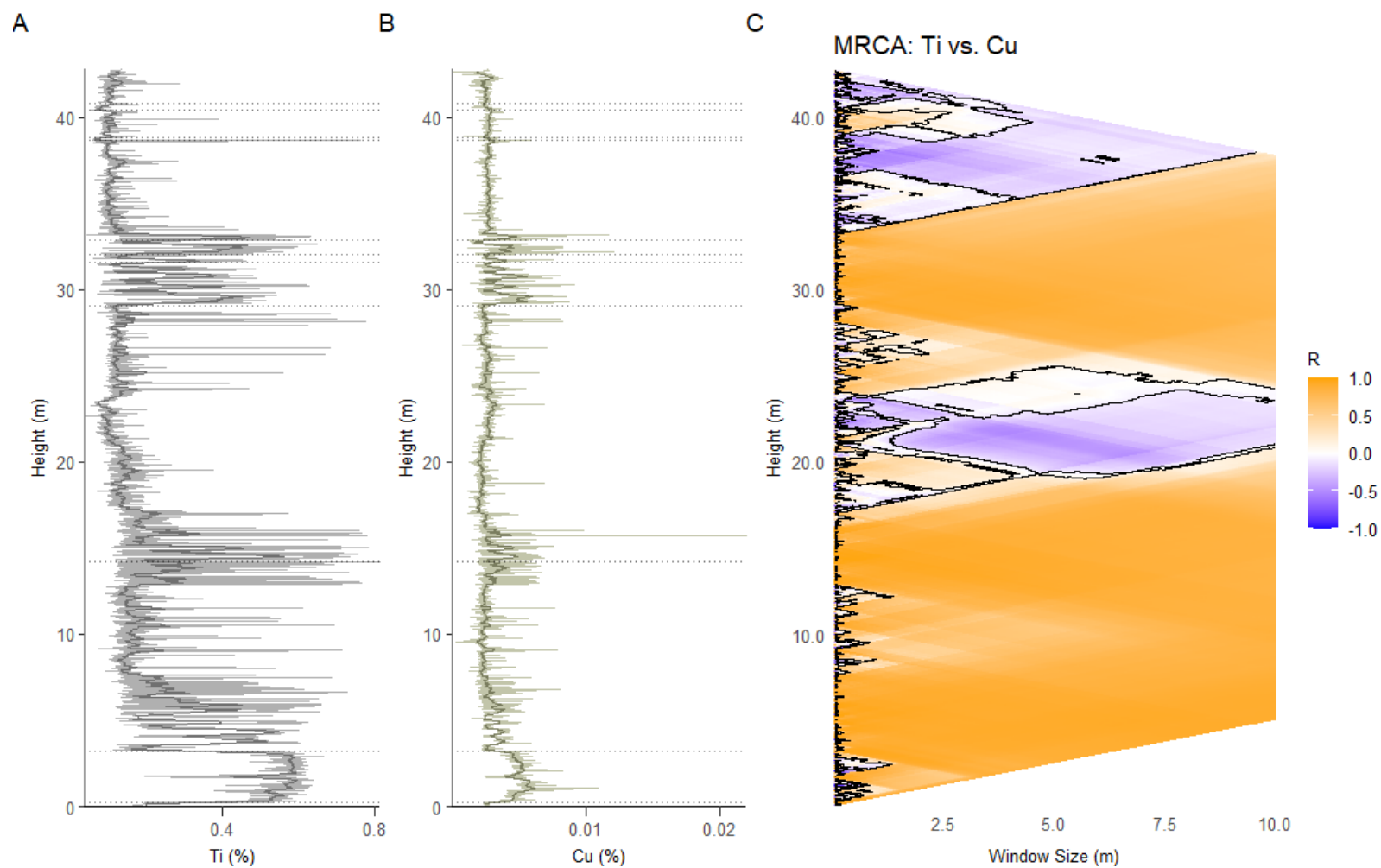


Fig. J2. Multi-scale Rolling Correlation Analysis of Ti and Cu. A) Ti (weight per cent, %; light gray) and 21-point running average (dark gray). B) Cu (weight per cent, %; light green) and 21-point running average (dark green). C) Multi-scale Rolling Correlation Analysis (MRCA) of Ti versus Cu, significant positive (orange) or negative (blue) Pearson correlation (95% confidence interval) is demarcated by black lines. Horizontal dashed lines indicate, from bottom to top, the Daleje, Choteč, Lower Kačák, Upper Kačák, Lower *pumilio* and Upper *pumilio* events.

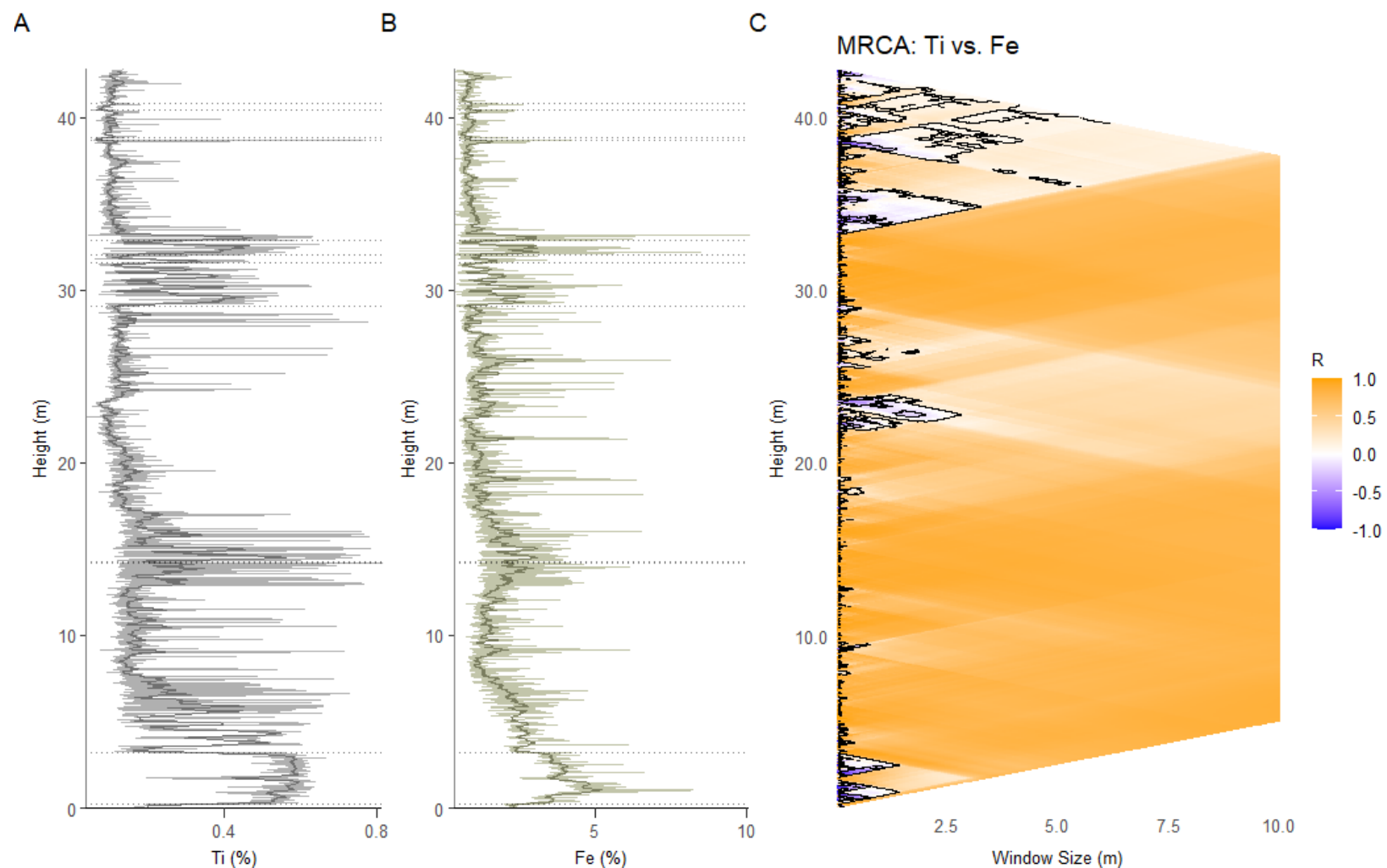


Fig. J3. Multi-scale Rolling Correlation Analysis of Ti and Fe. A) Ti (weight per cent, %; light gray) and 21-point running average (dark gray). B) Fe (weight per cent, %; light green) and 21-point running average (dark green). C) Multi-scale Rolling Correlation Analysis (MRCA) of Ti versus Fe, significant positive (orange) or negative (blue) Pearson correlation (95% confidence interval) is demarcated by black lines. Horizontal dashed lines indicate, from bottom to top, the Daleje, Choteč, Lower Kačák, Upper Kačák, Lower *pumilio* and Upper *pumilio* events.

K. Carbon and Oxygen Isotopes and Ca Cross-plots

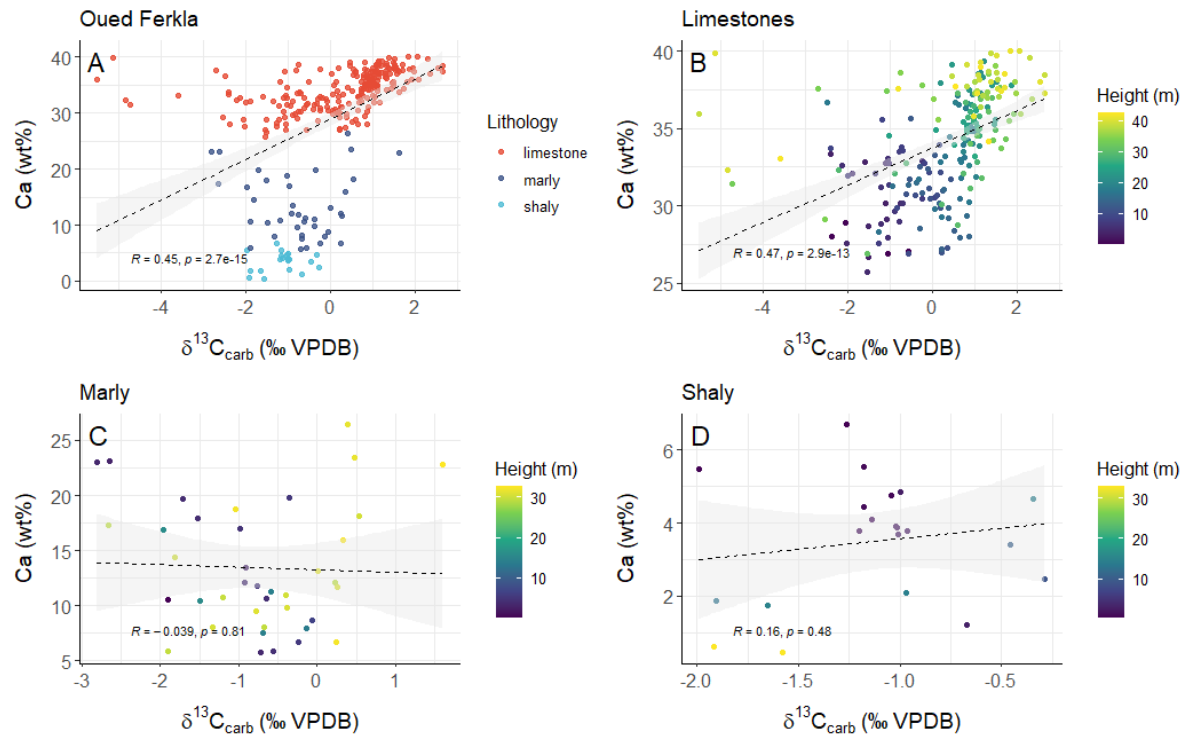


Fig. K1. Cross-plots of Ca and $\delta^{13}\text{C}_{\text{carb}}$. A) lithology-resolved cross-plot: limestone (red), marls (dark blue), and shales (light blue). B) Height-resolved cross-plot for limestones. C) Height-resolved cross-plot for limestones. D) Height-resolved cross-plot for limestones.

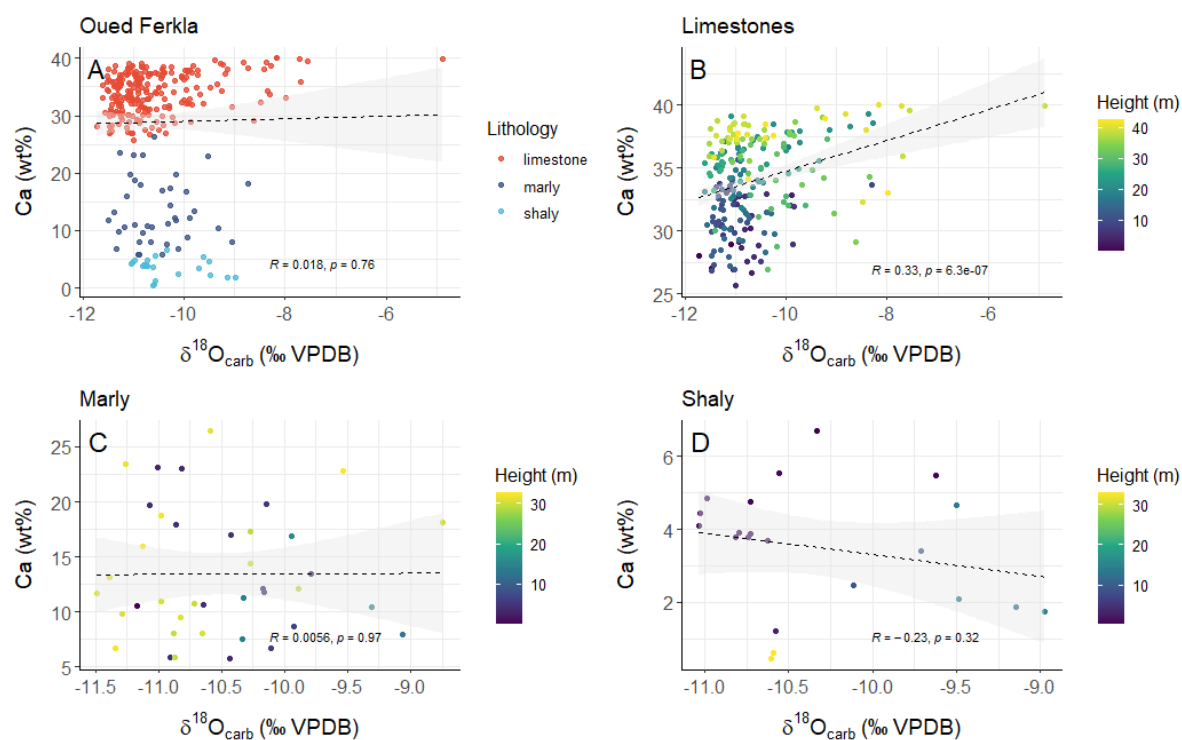


Fig. K2. Cross-plots of Ca and $\delta^{18}\text{O}_{\text{carb}}$. A) lithology-resolved cross-plot: limestone (red), marls (dark blue), and shales (light blue). B) Height-resolved cross-plot for limestones. C) Height-resolved cross-plot for limestones. D) Height-resolved cross-plot for limestones.

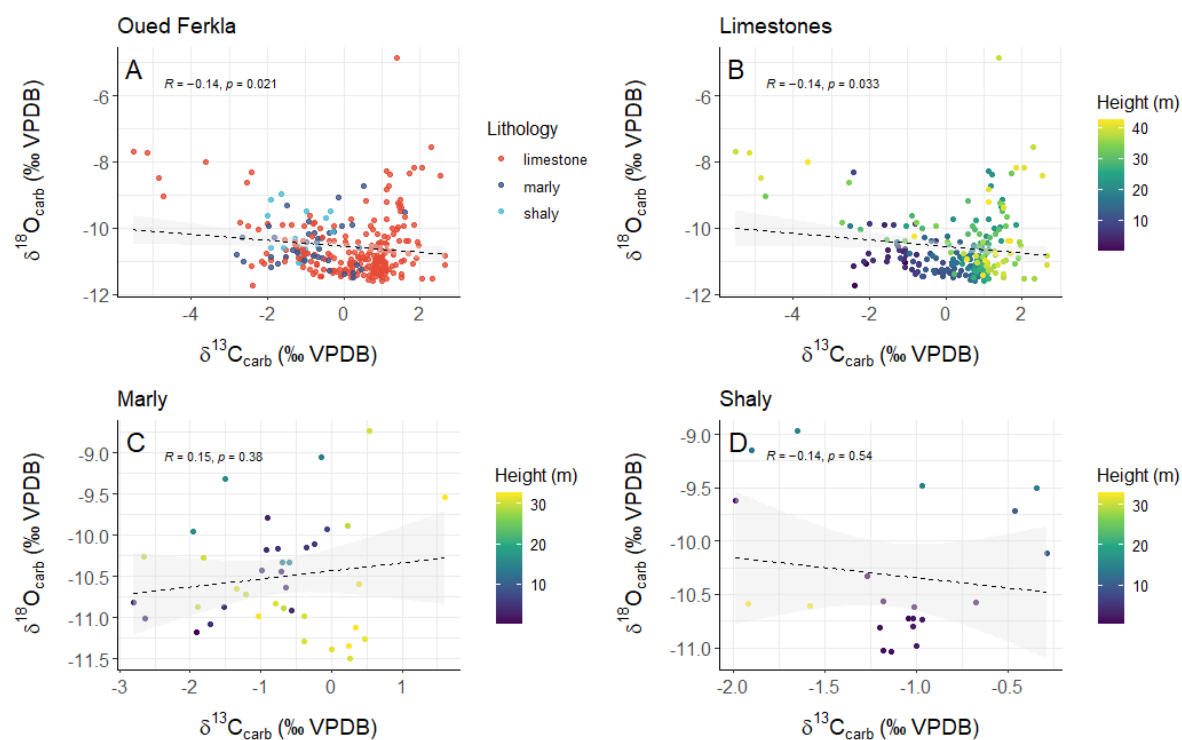


Fig. K3. Cross-plots of $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$. A) lithology-resolved cross-plot: limestone (red), marls (dark blue), and shales (light blue). B) Height-resolved cross-plot for limestones. C) Height-resolved cross-plot for marls. D) Height-resolved cross-plot for shales.

Supplemental References

- Oehlert, A. M., Swart, P. K., 2019. Rolling window regression of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in carbonate sediments: Implications for source and diagenesis. *Depos. Rec.*; 5, 3, 613-630. <https://doi.org/10.1002/dep2.88>
- Sageman, B. B., Hollander, D. J., 1999. Cross correlation of paleoecological and geochemical proxies: A holistic approach to the study of past global change. In: *Evolution of the Cretaceous Ocean-Climate System*: Boulder, Colorado; Geol. Soc. Am., Spec. Pap.; 332, 365-384.
- Talih, A., Aboussalam, S. Z., Becker, R. T., Saadi, M., Benmlih, A., 2022. Stratigraphy and tectono-sedimentary processes of allochthonous and autochthonous Devonian deposits of the Tisdafine Basin, Eastern Anti-Atlas, Morocco. *Bulletin de l'Institut Scientifique, Rabat, Section Sciences de la Terre*; 44, 27-53. e-ISSN: 2458-7184
- Yuan, N., Xoplaki, E., Zhu, C., Luterbacher, J., 2016. A novel way to detect correlations on multi-time scales, with temporal evolution and for multi-variables. *Sci. Rep.*; 6, 27707. DOI: 10.1038/srep27707

3. A Six-Million-Year Astronomical Cycle Pacing Early – Middle Devonian Global Events (Oued Ferkla, SE Morocco) – *in preparation*.

Jarno J.C. Huygh¹, Amine Talih², Hamdi Omar^{1,3,4}, Dhoha Boukhalifa¹, Justin Gérard⁵, Loïc Sablon⁵, Michiel Arts¹, Ahmed El Hassani⁶, Michel Crucifix⁵ and Anne-Christine Da Silva¹

¹ SediCClim Laboratory, Department of Geology, Liège University, Liège, Belgium

² Geo-Biodiversity and Natural Patrimony Laboratory (GEOBIO), Geophysics, Natural Patrimony and Green Chemistry, Research Center (GEOPAC), Scientific Institute, Mohammed V University, Rabat-Agdal, Morocco

³ Department of Atmospheric, Oceanic and Earth Science, George Mason University, Fairfax, USA

⁴ Department of Geology, Ghent University, Ghent, Belgium

⁵ Earth and Life Institute, UCLouvain, Louvain-la-Neuve, Belgium

⁶ Hassan II Academy of Science and Technology, Rabat, Morocco

Corresponding author: Jarno Huygh (jarno.huygh@uliege.be; jarno.huygh@hotmail.com)

Abstract

The Early to Middle Devonian is punctuated by global episodes of environmental perturbation, characterized by elevated extinction rates, paleoredox fluctuations, and marine anoxia. However, their quasi-periodic recurrence remains poorly understood, and their driving mechanisms ill-constrained. Astronomical insolation forcing has, through its potential to induce major climatic and environmental change, been linked to anoxic events at 10^4 -to- 10^5 -year timescales, yet the role of long-period modulation of Milankovitch cycles in pacing major Paleozoic events remains underexplored. Here we present an extensive ~19 Myr, sub-centimeter-resolution geochemical record from the Oued Ferkla section (Anti-Atlas, Morocco), spanning the uppermost Emsian to middle Givetian, encompassing the global Daleje, Choteč, Kačák, and *pumilio* events. A pervasive Milankovitch imprint is recovered from proxies tracking detrital-input variability, and a floating astrochronology was developed by tuning to the 405 kyr long-eccentricity metronome. Spectral and time-domain analyses consistently reveal multi-Myr components in addition to canonical Milankovitch frequencies, including the 2.4 Myr eccentricity cycle and a previously unrecognized ~6 Myr component. Comparison with the ZB23 astronomical solutions shows that a comparable ~6 Myr cycle emerges as a modulator of eccentricity during this time interval, supporting its plausibility as a feature of Devonian Solar System dynamics. Local extrema of the 2.4 and ~6 Myr cycles align with the timing of the Daleje, Choteč, Kačák, and *pumilio* events, indicating that Early-Middle Devonian environmental perturbations were paced by long-period astronomical forcing. We propose that this ~6 Myr modulation amplified climatic sensitivity by modulating precession- and obliquity-driven insolation variability, creating ‘windows of opportunity’ during which shorter-period astronomical or external triggers could generate globally expressed anoxia and biotic turnover. The ~6 Myr cycle identified here represents the first Paleozoic expression of such long-period astronomical pacing of anoxic events.

3.1. Introduction

Secular gravitational interactions among the planets generate million-year modulations of Earth's orbital parameters (Laskar, 2020; Zeebe and Lantink, 2024), adding long-period variability beyond the classical Milankovitch bands. These modulations arise from secular resonances among the planetary eigenfrequencies, such as the ~ 1.2 Myr $s_4 - s_3$ inclination (nodal) precession beat and the ~ 2.4 Myr $g_4 - g_3$ apsidal (perihelion) precession beat (~ 2.4 Myr; Laskar, 2020). Such long-period astronomical cycles modulate the amplitude and structure of shorter-period insolation forcing, potentially altering the climatic sensitivity to climatic precession- and obliquity-driven variability. Yet, the expression of such long-period cycles in Paleozoic sedimentary archives and their potential to pace global environmental change, however, remain largely unconstrained.

The late Early to Middle Devonian was marked by a series of globally recognized anoxic events – including the Daleje, Choteč, Kačák, *pumilio*, and Taghanic events (House, 1985; Becker et al., 2020). Each episode is associated with widespread marine redox instability and faunal turnover, contributing to incrementally increasing environmental stress and elevated extinction rates during the Middle Devonian (House, 1985; Raup and Sepkoski, 1982; Bambach, 2006; Becker et al., 2020). Despite their global significance and recurrence on multi-Myr timescales, no mechanism has been demonstrated to explain their pacing or to link them to long-period astronomical forcing.

Here, we analyze a ~ 19 Myr sedimentary record from the Oued Ferkla section (Anti-Atlas, Morocco), spanning the uppermost Emsian to middle Givetian (Ward et al., 2013; Talih et al., 2022). Deposited at appr. 45° S, it represents a large, isolated glide block derived from the western continuation of the Tafilalt Platform preserving pelagic facies that record environmental conditions on the platform margin and upper slope (Talih et al., 2022). A detrital influx indicator proxy (Chapter 2) was tuned to the 405 kyr $g_2 - g_5$ eccentricity metronome (Laskar, 2020). Although recent developments suggest that a secular Solar System resonance may disrupt this metronome, it remains a reliable tuning target for the Devonian (Zeebe and Lantink, 2024). At Oued Ferkla, both classical Milankovitch variability and longer-period modulations are preserved, allowing evaluation of multi-Myr components predicted by the 64-member ZB23 astronomical ensemble (Zeebe and Lantink, 2024). We identify a coherent ~ 6 Myr astronomical modulation expressed in the sedimentary record and independently present in multiple ZB23 ensemble members. This ~ 6 Myr astronomical modulation aligns with the timing of the Daleje, Choteč, Kačák, *pumilio* events at Oued Ferkla, demonstrating that a multi-Myr astronomical cycle paced middle Devonian global environmental change.

3.2. Materials and Methods

Oued Ferkla was sampled continuously, enabling the reconstruction of the entire record at a sub-cm-scale resolution. A high-resolution major and trace element dataset ($n = 5601$) was generated, measured at 0.8 cm resolution using portable X-ray fluorescence (pXRF; Da Silva et al., 2023; see also Chapter 2), covering ~43 m (Extended Data Fig. 1). All statistical analysis was carried out in R Studio 2026.01.0 Build 392. Time series and spectral analyses used “Astrochron” (Meyers, 2014) and “WaverideR” (Arts, 2023).

Principal component analysis isolates a dominant detrital-carbonate mixing signal (PC1; Extended Data Fig. 2), which captures lithological variability associated with carbonate-shale facies shifts (Chapter 2). The stable 405 kyr $g_2 - g_5$ eccentricity metronome was used as a tuning target, considering sedimentation rate changes identified through depth-domain cyclostratigraphy (Extended Fig. 3). An astronomically calibrated age model was constructed based on PC1 that resolves Milankovitch-scale periodicities across the section (Fig. 1A).

3.3. Results and Discussion

Spectral analysis of PC1, TiO_2 and CaO reveals a pervasive Milankovitch imprint across the entire record, recovering precession, obliquity, ~100 kyr short eccentricity, 405 kyr $g_2 - g_5$ long eccentricity, as well as frequencies associated with ~980 kyr $g_1 - g_5$ and ~2.4 Myr $g_4 - g_3$ eccentricity (Fig. 1; Extended Figures 4-6). Recovery of the $g_4 - g_3$ component demonstrates that the record captures long-period, cyclic variability suitable for extracting secular components. Notably, a component with a mean period of ~6.2 Myr appears consistently and is recovered both directly from these proxies and from their eccentricity envelopes (Extended Data Figures 4-6).

The canonical ~2.4 Myr $g_4 - g_3$ ‘grand’ eccentricity cycle is robustly expressed throughout the record, and several of its extrema coincide with the Daleje, Choteč, Kačák, and *pumilio* events, consistent with patterns observed in the Late Devonian (De Vleeschouwer et al., 2013; Huygh et al., 2026; Wichern et al., 2026). However, at Oued Ferkla, not every 2.4 Myr extremum corresponds to a distinct environmental event, and the spacing between the Daleje, Choteč, Kačák, and *pumilio* events far exceeds a strict 2.4 Myr pacing. This contrasts with the Late Devonian, where the *Annulata*, Dasberg, and Hangenberg event more closely track successive 2.4 Myr extrema (De Vleeschouwer et al., 2013; Wichern et al., 2026). Maxima in the $g_4 - g_3$ cycle generally correspond to intervals when climatic precession and/or obliquity are most strongly modulated, amplifying seasonal contrasts and intensifying climate-system responses (e.g., Hays et al., 1976; Laskar et al., 2004; Ma et al., 2022). At Oued Ferkla, a similar mechanism is interpreted to have driven the alternation between thick, massive carbonate beds and

thinner carbonate beds intercalated with marls and shales, reflected by variability in PC1 (Fig. 1).

The ~6 Myr modulation recovered from PC1, TiO₂, and CaO, together with the consistent results from time-domain cyclostratigraphic analyses (Extended Figures 4-6), demonstrates that this long-period signal is robust across proxies. Unlike tectonic forcing – which is inherently irregular and spatially heterogeneous – there is no evidence for tectonically driven facies shifts at Oued Ferkla (Talih et al., 2022). Instead, the period progradation-retrogradation phases of the platform are interpreted as responses to climate-controlled sea-level variations (Talih et al., 2022). Local extrema of the ~6 Myr component align closely with the timing of the Daleje, Choteč, Kačák, and *pumilio* events (Fig. 1), marking a distinct difference from the Late Devonian pattern (cf., De Vleeschouwer et al., 2013; Wichern et al., 2026).

The Daleje, Choteč, and Kačák event intervals coincide broadly with successive maxima of the ~6 Myr component, corresponding to stark increases in PC1 (Fig. 1), consistent with elevated fine-grained detrital input (Extended Data Figure 7) and interpreted as a strengthened hydrological cycle and intensified runoff under high-amplitude eccentricity forcing (De Vleeschouwer et al., 2024). In contrast, the *pumilio* events interval occurs near a pronounced minimum and is characterized by minimal, predominantly coarse-grained detrital input (Fig. 1; Extended Data Figure 7), representing the opposite expression of the same long-period pacing. This alternating pattern of maxima- and minima-aligned events indicates that the recurrence of Middle Devonian environmental perturbations follows the phase structure of the ~6 Myr cycle. Although the precise climatic mechanisms and link to sea-level variations remain to be solved, the phase-consistent alternation of these expressions indicates a climatic-sediment response to eccentricity-modulated precession at 10⁵-to-10⁶-year timescales.

Looking beyond the sampled interval, the quality of the outcrop decreases toward the top and the uppermost part was not sampled. Nevertheless, we hypothesize that the Taghanic Crisis (Chapter 2) occurs near the next predicted maximum of the ~6 Myr cycle, consistent with its temporal position and its globally coherent expression, which broadly resembles the Daleje, Choteč, and Kačák events at preceding maxima (Becker et al., 2020).

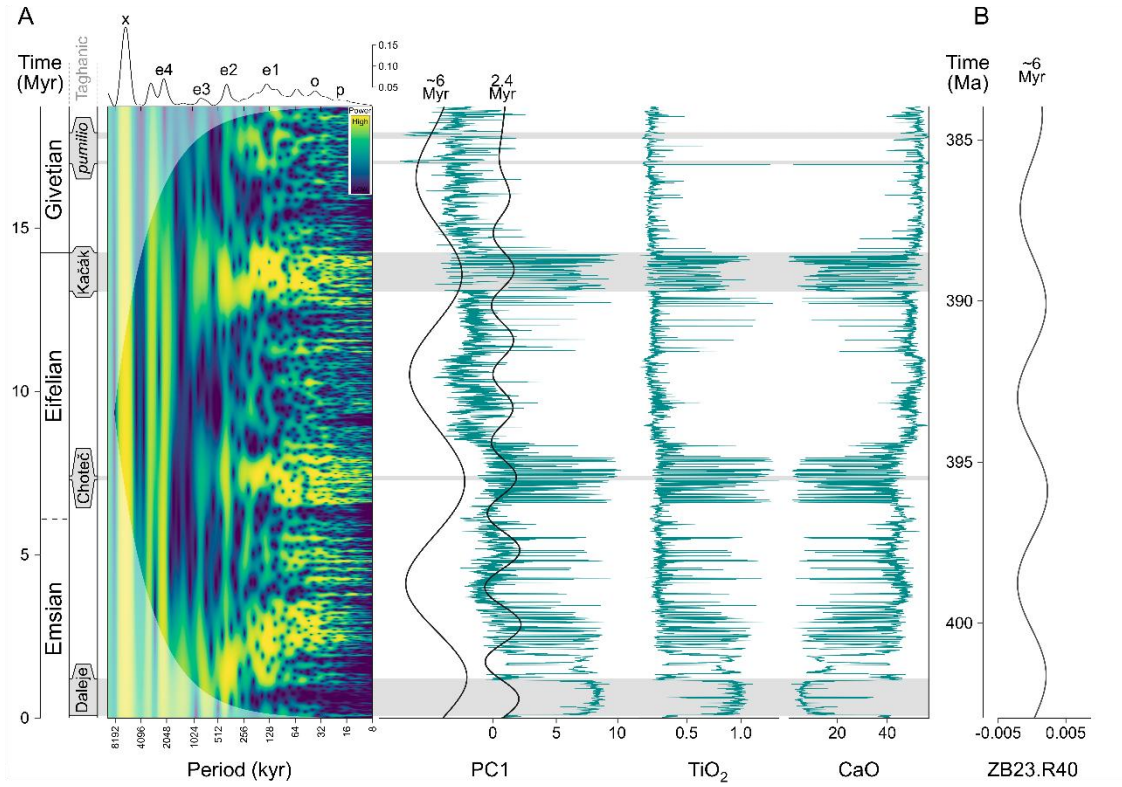


Fig. 1. Cyclostratigraphy of Oued Ferkla and a ~6 Myr astronomical cycle. A) Chronostratigraphy, event stratigraphy (estimated temporal location of the Taghanic Event included in gray), continuous wavelet scalogram (x = ~6 Myr component; $e_4 = g_4 - g_3$ ~2.4 Myr eccentricity; $e_3 = \sim 980$ kyr $g_1 - g_5$; $e_2 = 405$ kyr $g_2 - g_5$ long eccentricity; $e_1 = \sim 100$ kyr short eccentricity; o = obliquity; p = precession), average wavelet power spectrum, extracted 2.4 Myr $g_4 - g_3$ and 6.2 Myr cycles (black), principal component 1 (PC1), TiO_2 , and CaO (cyan). Anti-phasing of TiO_2 and CaO reflects detrital input versus carbonate productivity/dilution. Global Daleje, Choteč, Kačák, and *pumilio* event intervals are highlighted in gray. B) Extracted ~6 Myr cycle (black) from the ensemble member ZB23.R40 (Zeebe and Lantink, 2024).

Long-period astronomical cycles have been reported only from a limited number of younger records, including an ~8 Myr cycle during the Triassic to Jurassic (Ikeda and Tada, 2013), a ~9 Myr eccentricity modulation cycle in Cenozoic $\delta^{13}C$ (Boulila et al., 2012) and Mesozoic (Jurassic to Early Cretaceous) $\delta^{13}C$ (Martinez and Dera, 2015), and an even longer ~10 Myr cycle pacing Mesozoic monsoon dynamics (Ikeda et al., 2020). While these multi-Myr cycles are linked to eccentricity amplitude modulation in each of these cases, the secular frequencies involved remain unconstrained and their exact origin therefore unknown. We hypothesize that the ~6 Myr component identified here may reflect a similar underlying mechanism, with its differing period arising from the chaotic divergence of secular frequencies over geological timescales (Zeebe and Lantink, 2024).

Interestingly, a ~9.5 Myr component is recovered from the decomposition of obliquity: $k + s_6 + g_5 - g_6$ (Laskar et al., 2004). Despite the stability of the g_5 , g_6 , and s_6 terms (Laskar, 2020), this component is not strictly quasi-periodic because of the presence of the dissipative term k in

the evolution of the precession frequency (Laskar et al., 2004). Moreover, its amplitude is relatively small compared to the current-day ~ 41 kyr $k + s_3$ obliquity component (Laskar et al., 2004). Therefore, it is unlikely that this term is behind the reported 8-10 Myr cyclicity during the Mesozoic (Boulila et al., 2012; Ikeda and Tada, 2013; Martinez and Dera, 2015; Ikeda et al., 2020). We propose further investigation into resonances including the very stable g_5 , g_6 , and s_6 terms – which are involved in a long-period obliquity component – that may be behind the modulation of specific Milankovitch cycles on multi-Myr timescales.

Analysis of the 64-member ZB23 astronomical ensemble (Zeebe and Lantink, 2024) reveals that a ~ 6 Myr eccentricity modulation emerges in the envelope of (405 kyr) eccentricity for a subset of solutions (Fig. 2). For each ensemble member, we estimated the MTM spectral peak closest to 6.2 Myr (Fig. 2A) and quantified its expression using a Gaussian-weighted score centered on this target period (Fig. 2B). This approach identifies at least ten solutions that exhibit a well-expressed ~ 6 Myr component (Fig. 2C), demonstrating that such modulation arises in multiple dynamically consistent astronomical configurations. Of these, ZB23.R40 represents the most suitable candidate for further comparison, and the ~ 6 Myr component was extracted for direct alignment with Oued Ferkla (Fig. 1B). The occurrence of a comparable ~ 6 Myr component in both the astronomical ensemble and the Oued Ferkla record indicates that this periodicity reflects a plausible feature of Solar System dynamics rather than a pattern unique to the sedimentary data.

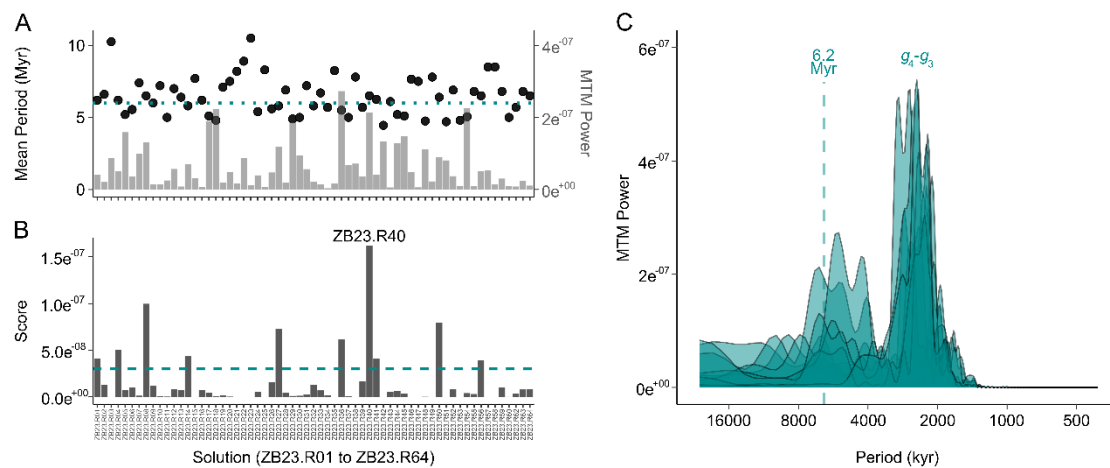


Fig. 2. Analysis of the envelope of the 405 kyr long eccentricity in the ZB23 ensemble (Zeebe and Lantink, 2024) from 410 to 380 Ma. A) Mean period (Myr) of the astronomical cycle (black dots) closest to 6.2 Myr (cyan dotted line) in the envelope of the 405 kyr long eccentricity, and corresponding MTM power (gray bars). B) Gaussian distance-weighted score combining mean periods and MTM power (see panel A). The cyan dashed line marks the ten ensemble members with the highest scores (see panel C). C) MTM power spectra of the ten ensemble members with highest score (see panel B).

Through combination of integrated stratigraphy and statistical analyses of astronomical solutions (ZB23; Zeebe and Lantink, 2024), it has been revealed that Early to Middle Devonian

environmental perturbations associated with redox instability and extinction (Raup and Sepkoski, 1982; Bambach, 2006; Becker et al., 2024) are paced by long-term astronomical cycles modulating Milankovitch forcing on multi-Myr timescales. The identified ~6 Myr component provides the first Paleozoic expression of such long-period astronomical pacing and offers a testable target for future astronomical solutions. Its first-order influence on the timing and pacing of the Daleje, Choteč, Kačák, *pumilio* – and potentially, Taghanic – events suggests that multi-Myr astronomical modulation shapes intervals of climatic extremes that alter the climatic and environmental baseline, essentially creating a window of opportunity during which shorter-period astronomical or external triggers can generate pronounced environmental perturbations, including global marine anoxia and biotic turnover.

Acknowledgements

This is a contribution to the "Projet de Recherche" funded by the Belgian National Fund of Scientific Research (FNRS), contract T.0037.22 "WarmAnoxia". Richard E. Zeebe and Jacques Laskar are gratefully acknowledged for their insightful discussions on the nature and origin of a ~6 Myr astronomical cycle.

Data Availability

All data and R-code can be found via <https://doi.org/10.5281/zenodo.20305637>.

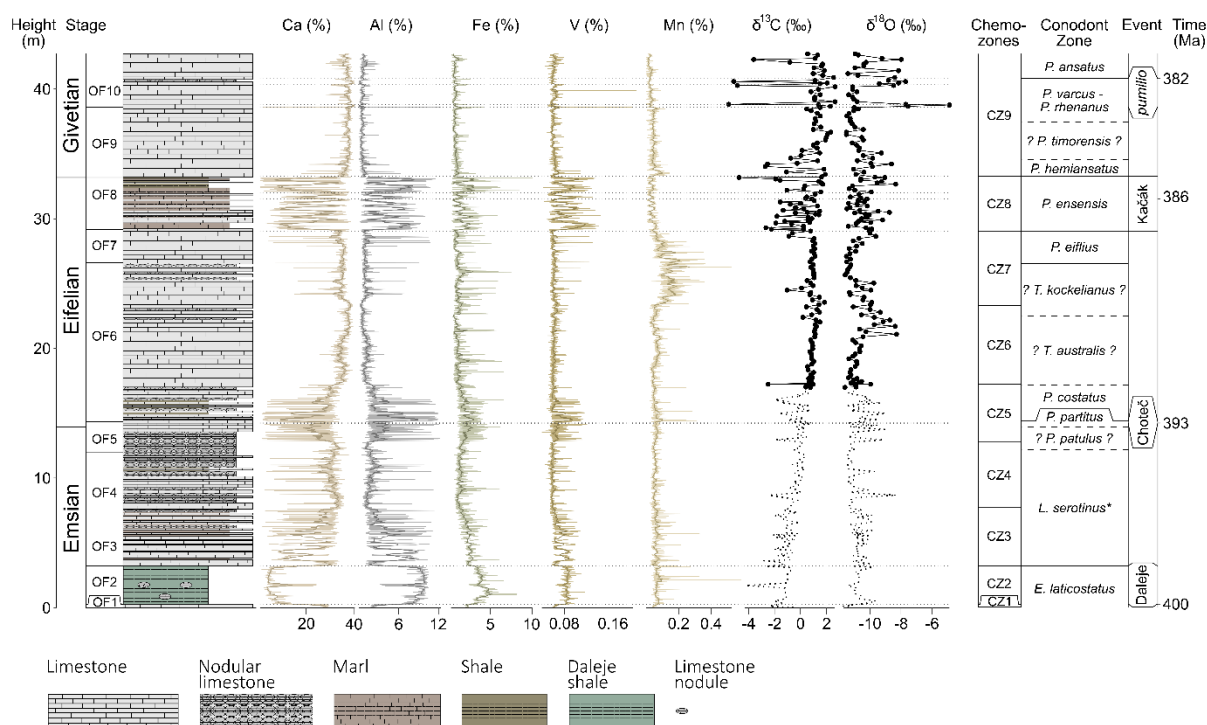
References

- Bambach, R. K., 2006. Phanerozoic Biodiversity Mass Extinctions. *Annu. Rev. Earth Planet. Sci.*, 34: 127-55. doi: 10.1146/annurev.earth.33.092203.122654
- Becker, R. T., Marshall, J. E. A., Da Silva, A.-C., 2020. The Devonian Period. In: Gradstein, F. M., Ogg, J. G., Schmitz, M. D. And Ogg, G. (Eds.), *The Geologic Time Scale 2020*, chapter 22, 733-810. <https://doi.org/10.1016/B978-0-12-824360-2.00022-X>.
- Boulila, S., Galbrun, B., Laskar, J., Pälike, H., 2012. A ~9 Myr cycle in Cenozoic $\delta^{13}\text{C}$ record and long-term orbital eccentricity modulation: Is there a link? *Earth Planet. Sci. Lett.*; 317-318, 273-281. doi:10.1016/j.epsl.2011.11.017
- Da Silva, A. -C., Triantafyllou, A., Delmelle, N., 2023. Portable x-ray fluorescence calibrations: Workflow and guidelines for optimizing the analysis of geological samples. *Chem. Geol.*; 623, 121395. <https://doi.org/10.1016/j.chemgeo.2023.121395>
- De Vleeschouwer, D., Rakociński, M., Racki, G., Bond, D. P. G., Sobieć, K., Claey, P., 2013. The astronomical rhythm of Late-Devonian climate change (Kowala section, Holy Cross Mountains, Poland). *Earth Planet. Sci. Lett.*; 365, 25-37. <http://dx.doi.org/10.1016/j.epsl.2013.01.016>.
- De Vleeschouwer, D., Percival, L. M. E., Wichern, N. M. A., Batenburg, S. J., 2024. Pre-Cenozoic cyclostratigraphy and palaeoclimate responses to astronomical forcing. *Nat. Rev. Earth Environ.*; 5, 56-75. <https://doi.org/10.1038/s43017-023-00505-x>.
- Hays, J. D., Imbrie, J. & Shackleton, N. J., 1976. Variations in the Earth's orbit: pacemaker of the ice ages. *Science* 194, 1121-1132.
- House, M. R., 1985. Correlation of mid-Palaeozoic ammonoid evolutionary events with global sedimentary perturbations. *Nature*; 313, 3, 17-22.
- Huygh, J. J. C., Algeo, T. J., Sageman, B. B., Arts, M., Ver Straeten, C. A., Over, D. J., Gérard, J., Sablon, L., Crucifix, M., Da Silva, A. -C., 2026. Astronomical control on marine anoxia during the Kellwasser Crisis and Rhinestreet Event (Appalachian Basin, New York, USA). *Glob. Planet. Change*; 257, 105216. <https://doi.org/10.1016/j.gloplacha.2025.105216>
- Huygh, J. J. C., Talih, A., Omar, H., Boukhalfa, D., Gérard, J., Sablon, L., Arts, M., El Hassani, A., Crucifix, M., Da Silva, A. -C., *in prep.* Geochemical characterization of the Daleje, Choteč, Kačák, and pumilio events at Oued Ferkla (SE Morocco).
- Ikeda, M., Tada, R., 2013. Long period astronomical cycles for the Triassic to Jurassic bedded chert sequence (Inuyama, Japan); Geological evidences for the chaotic behavior of solar planets. *Earth Planets Space*; 65, 351-360. doi:10.5047/eps.2012.09.004
- Ikeda, M., Ozaki, K., Legrand, J., 2020. Impact of 10-Myr scale monsoon dynamics on Mesozoic climate and ecosystems. *Sci. Rep.*; 10, 11984. <https://doi.org/10.1038/s41598-020-68542-w>

- Laskar, J., Robutel, P., Joutel, F., Gastineau, M., Correia, A. C. M., Levrard, B., 2004. A long-term numerical solution for the insolation quantities of the Earth. *Astron. Astrophys.*; 428, 1, 261-285. <https://doi.org/10.1051/0004-6361:20041335>.
- Laskar, J., 2020. Astrochronology. In: Gradstein, F. M., Ogg, J. G., Schmitz, M. D. And Ogg, G. (Eds.), *The Geologic Time Scale 2020*, chapter 4, 139-158.
- Ma, K., Hinnov, L. A., Zhang, X., Gong, Y., 2022. Astronomical climate changes trigger Late Devonian bio- and environmental events in South China. *Glob. Planet. Change*; 215, 103874. <https://doi.org/10.1016/j.gloplacha.2022.103874>.
- Martinez, M., Dera, G., 2015. Orbital pacing of carbon fluxes by a ~9 My eccentricity cycle during the Mesozoic. *PNAS*; 112, 41, 12604-12609
- Raup, D. M. and Sepkoski, J. J., Jr., 1982. Mass extinctions in the marine fossil record. *Science*; 215, 4539, 1501-1503. doi:10.1126/science.215.4539.1501. www.pnas.org/cgi/doi/10.1073/pnas.1419946112
- Talih, A., Aboussalam, S. Z., Becker, R. T., Saadi, M., Benmlih, A., 2022. Stratigraphy and tectono-sedimentary processes of allochthonous and autochthonous Devonian deposits of the Tisdafine Basin, Eastern Anti-Atlas, Morocco. *Bulletin de l'Institut Scientifique, Rabat, Section Sciences de la Terre*; 44, 27-53. e-ISSN : 2458-7184
- Ward, P. D., Becker, R. T., Aboussalam, S. Z., Rytina, M., Stichling, S., 2013. The Devonian at Oued Ferkla (Tinejdad region, SE Morocco). *International Field Symposium "The Devonian and Lower Carboniferous of northern Gondwana, Morocco 2013"*; 23-30.
- Wichern, N., Becker, R. T., Bialik, O. M., Hartenfels, S., De Vleeschouwer, D., 2026. Cyclostratigraphic calibration of the rhythmically bedded upper Frasnian (upper Devonian) in the Rhenish Massif, Germany. *Newslett. Stratigr.*; DOI: 10.1127/nos/2026/0908
- Zeebe, R. E. and Lantink, M. L., 2024. A secular solar system resonance that disrupts the dominant cycle in Earth's orbital eccentricity ($g_2 - g_5$): Implications for astrochronology. *Astron. J.*; 167:204. <https://doi.org/10.3847/1538-3881/ad32cf>.

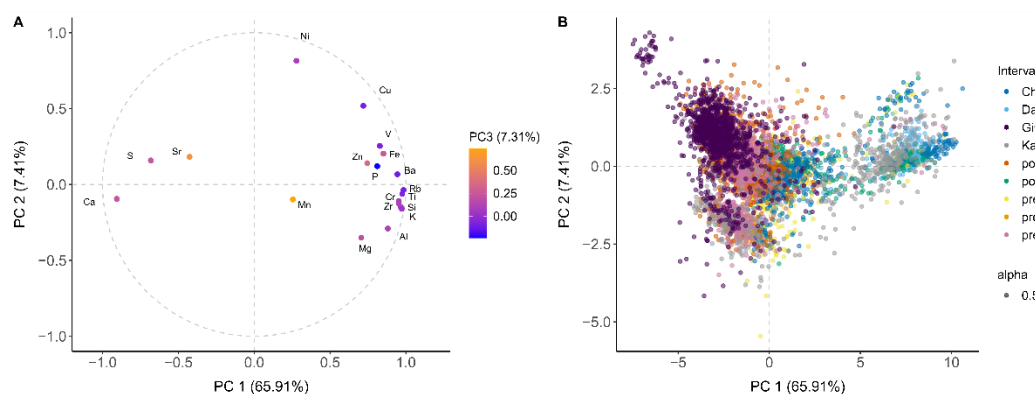
3.4. Extended Data

A. Integrated Stratigraphy of Oued Ferkla



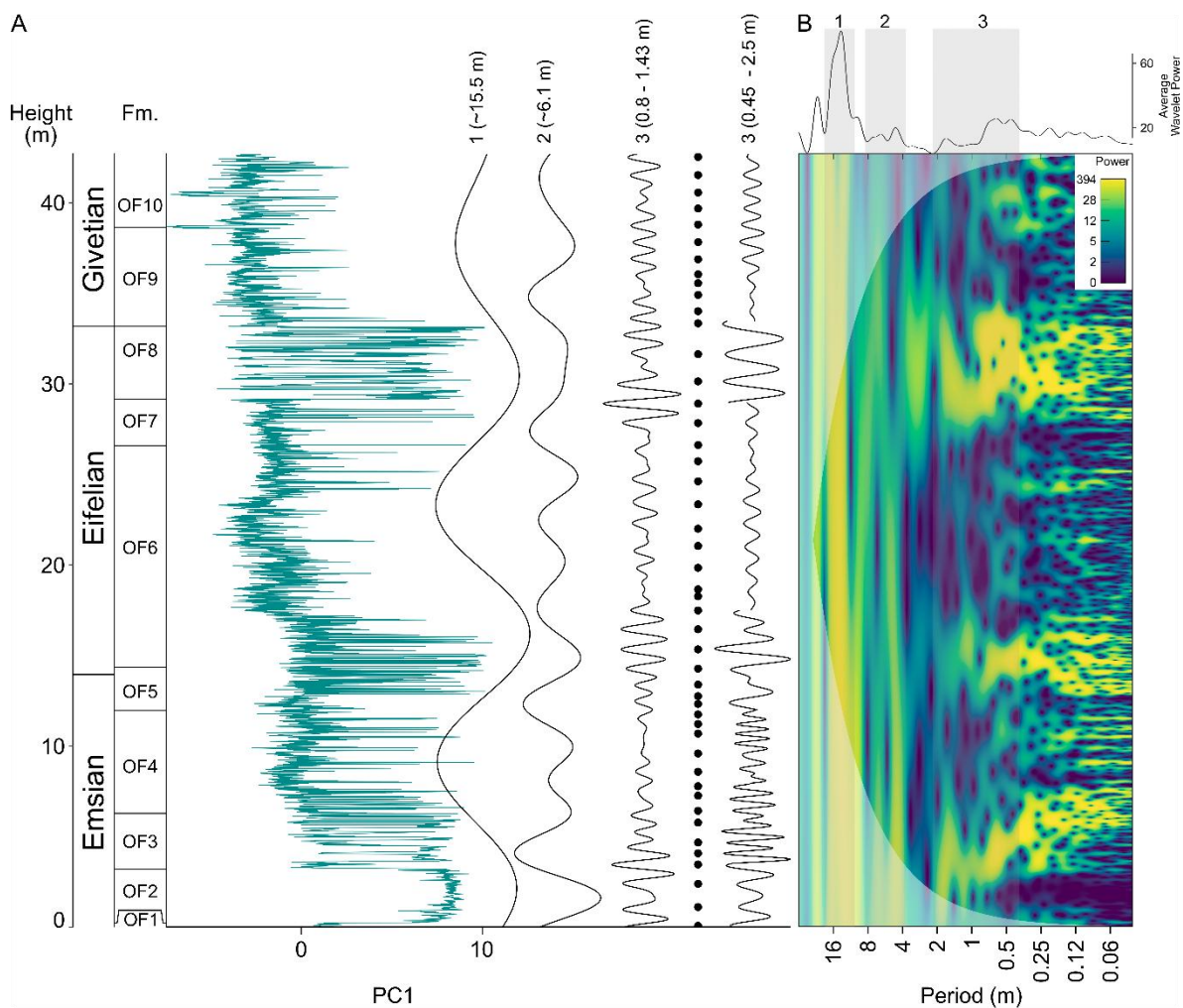
Extended Fig. 1. Integrated stratigraphy of Oued Ferkla. Chronostratigraphy, lithostratigraphy; Oued Ferkla represents an allochthonous glide block and thus has no formal formation names and instead has units Oued Ferkla 1 (OF1) to OF10 (Talib et al., 2022), lithological column, key major and trace element profiles incl. Ca, Al, Fe, V, and Mn in weight per cent (%), $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ (dashed lines indicate likely diagenetic overprinted isotopic composition), chemozonation, tentative conodont zonation (Talib et al., 2022), event stratigraphy and absolute time estimates (Becker et al., 2020). Chemozones (CZ) 1 to 9 (Chapter 2).

B. Principal Component Analysis



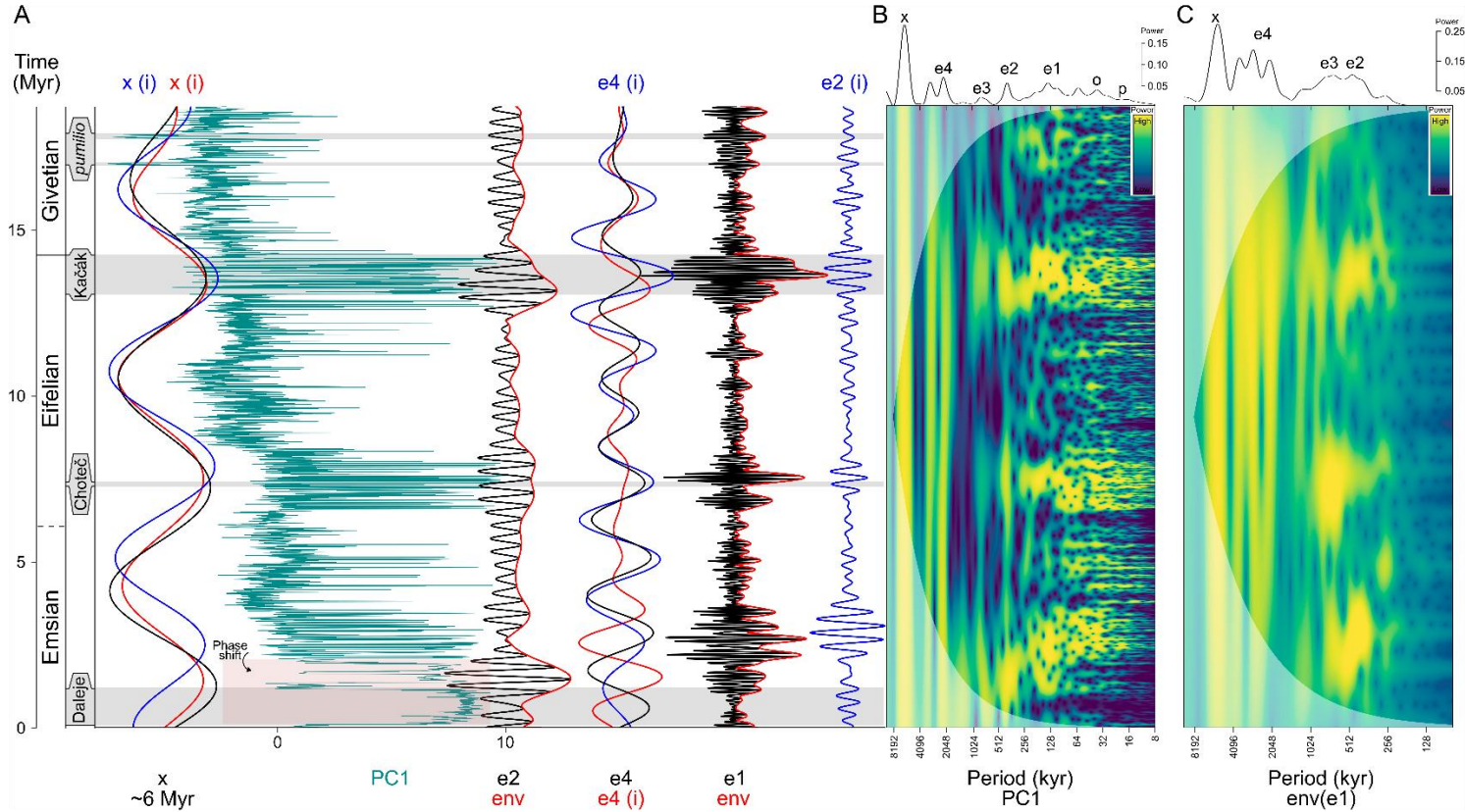
Extended Fig. 2. Principal component analysis (PCA). A) Loading plot along principal component 1 (PC1) to PC3. B) Score plot in function of chemozone (CZ) intervals (see Extended Figure 1); pre-Daleje (CZ1), Daleje (CZ2), post-Daleje (CZ3), pre-Choteč (CZ4), Choteč (CZ5), post-Choteč (CZ6), pre-Kačák (CZ7), Kačák (CZ7), Givetian (CZ9).

C. Depth-domain Cyclostratigraphy (PC1)



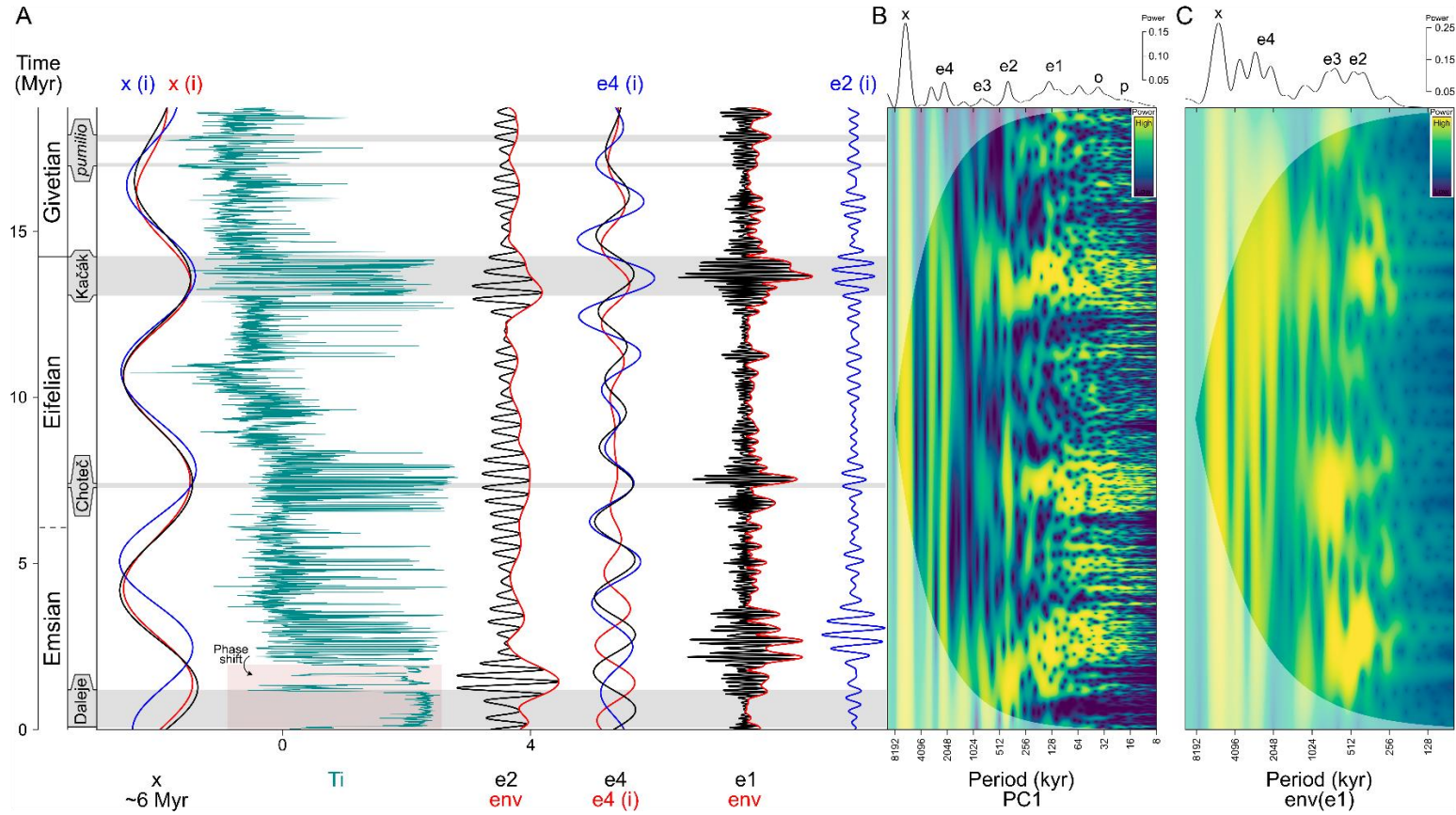
Extended Fig. 3. Depth domain cyclostratigraphy of PC1. A) Chronostratigraphy, lithostratigraphy; Oued Ferkla represents an allochthonous glide block and thus has no formal formation names and instead has units Oued Ferkla 1 (OF1) to OF10 (Talih et al., 2022), principal component 1 (PC1; cyan), filtered components and mean periods (m); 1 (~15.5 m), 2 (~6.1 m), 3 (0.8 to 1.43 m; across entire record), 3 (0.45 to 2.5 m; segmented to accommodate for sedimentation rate changes). Black dots indicate depth tie-points anchored to interpreted 405 kyr local minima, guided by bandpass filters. B) Continuous Wavelet Transform (CWT) scalogram, average wavelet spectrum and highlighted components 1-3 highlighted in gray.

D. Time-domain Cyclostratigraphy (PC1)



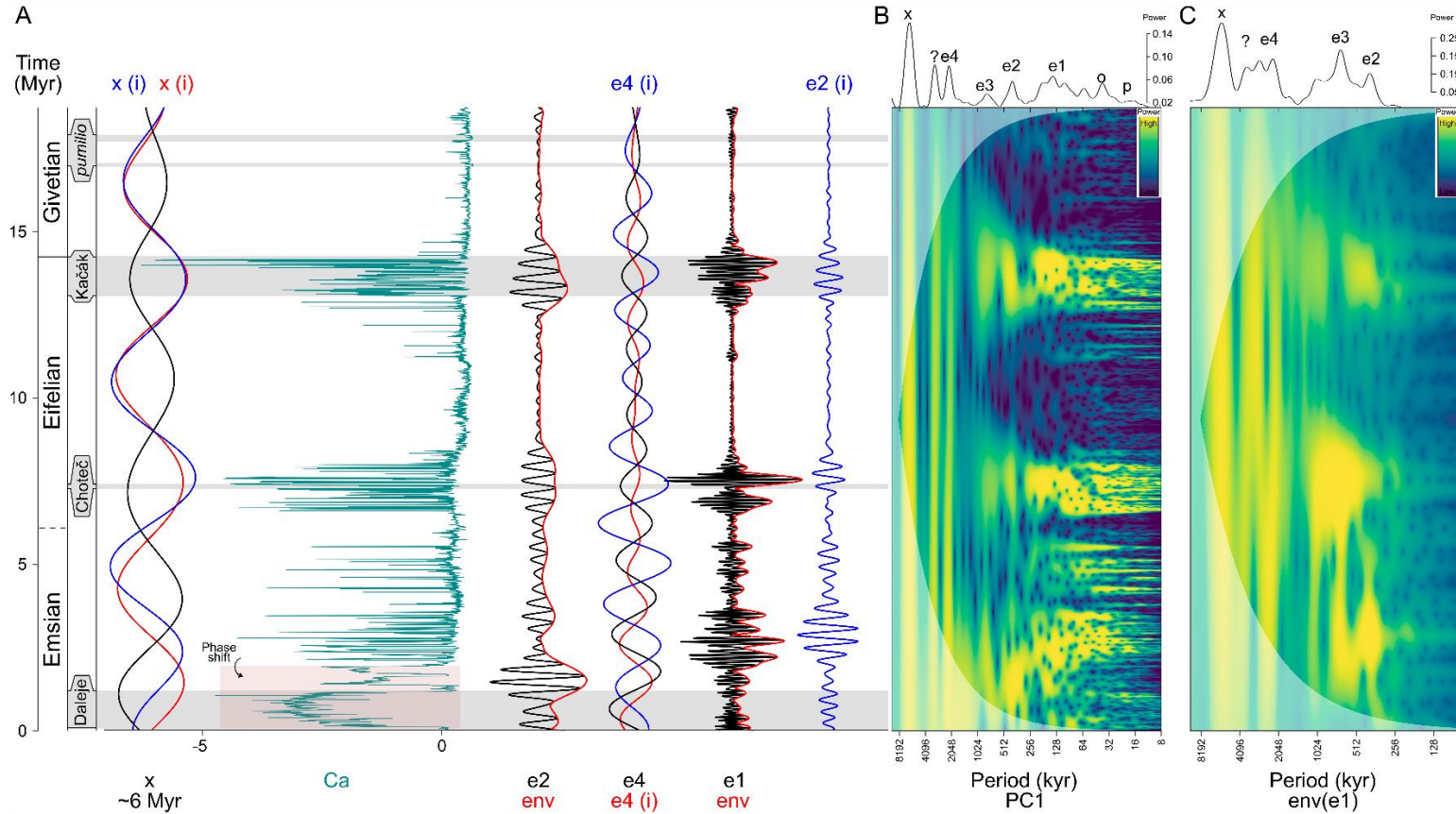
Extended Fig. 4. Time domain cyclostratigraphy of PC1. A) Chronostratigraphy, event stratigraphy, PC1 (cyan), bandpass filtered signals. The ~6 Myr component (x) extracted from PC1 (black), from the envelope of short eccentricity ($e1(i)$; blue), and from the envelope of long eccentricity ($e2(i)$; red); $g_2 - g_5$ 405 kyr long eccentricity ($e2$; black) and its envelope (red); ~2.4 Myr $g_4 - g_3$ extracted from PC1 (black), from the envelope of short eccentricity ($e1(i)$; blue), and from the envelope of long eccentricity ($e2(i)$; red), 100 kyr short eccentricity ($e1$; black) and its envelope (red), long eccentricity extracted from the envelope of short eccentricity ($e2(i)$; blue). Red box indicates a phase shift influencing longer-term cycles due to a facies shift. B) Continuous Wavelet Transform scalogram of PC1, including identified ~6 Myr component (x), ~2.4 Myr $g_4 - g_3$ ($e4$), ~980 kyr $g_1 - g_5$ ($e3$), 405 kyr $g_2 - g_5$ ($e2$), ~100 kyr short eccentricity ($e1$), obliquity (o), and precession (p). C) Continuous Wavelet Transform scalogram of the envelope of short eccentricity extracted from PC1, including identified ~6 Myr component (x), ~2.4 Myr $g_4 - g_3$ ($e4$), ~980 kyr $g_1 - g_5$ ($e3$), 405 kyr $g_2 - g_5$ ($e2$).

E. Time-domain Cyclostratigraphy (Ti)



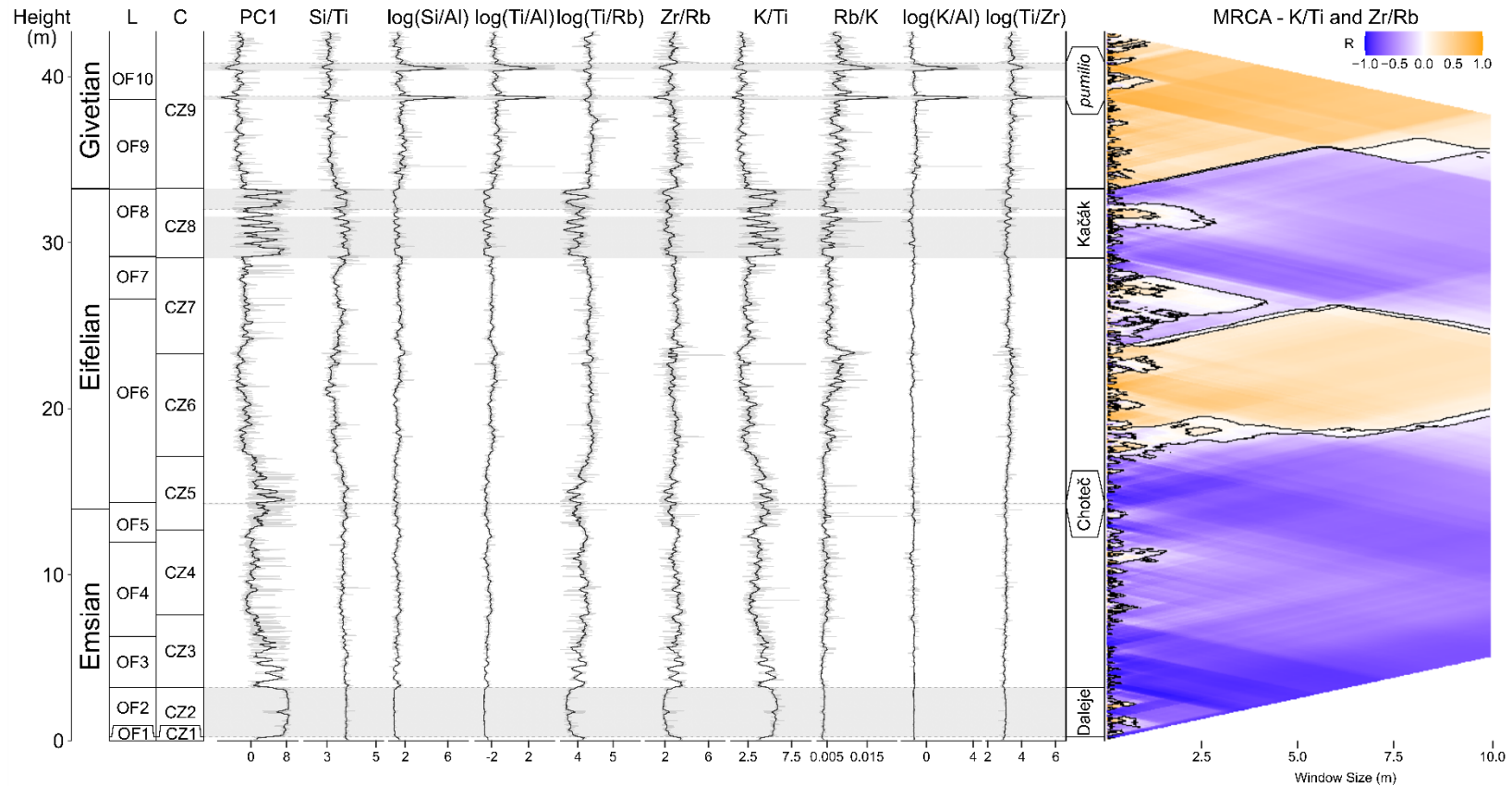
Extended Fig. 5. Time domain cyclostratigraphy of Ti. A) Chronostratigraphy, event stratigraphy, log-transformed, z-scored Ti (cyan), bandpass filtered signals. The ~6 Myr component (x) extracted from Ti (black), from the envelope of short eccentricity (e1(i); blue), and from the envelope of $g_2 - g_5$ long eccentricity (e2(i); red); 405 kyr long eccentricity (e2; black) and its envelope (red); ~2.4 Myr $g_4 - g_3$ extracted from Ti (black), from the envelope of short eccentricity (e1(i); blue), and from the envelope of long eccentricity (e2(i); red), 100 kyr short eccentricity (e1; black) and its envelope (red), long eccentricity extracted from the envelope of short eccentricity (e2(i); blue). Red box indicates a phase shift influencing longer-term cycles due to a facies shift. B) Continuous Wavelet Transform scalogram of Ti, including identified ~6 Myr component (x), ~2.4 Myr $g_4 - g_3$ (e4), ~980 kyr $g_1 - g_5$ (e3), 405 kyr $g_2 - g_5$ (e2), ~100 kyr short eccentricity (e1), obliquity (o), and precession (p). C) Continuous Wavelet Transform scalogram of the envelope of short eccentricity extracted from Ti, including identified ~6 Myr component (x), ~2.4 Myr $g_4 - g_3$ (e4), ~980 kyr $g_1 - g_5$ (e3), 405 kyr $g_2 - g_5$ (e2).

F. Time-domain Cyclostratigraphy (Ca)



Extended Fig. 6. Time domain cyclostratigraphy of Ca. A) Chronostratigraphy, event stratigraphy, log-transformed, z-scored Ca (cyan), bandpass filtered signals. The ~6 Myr component (x) extracted from Ca (black), from the envelope of short eccentricity (e1(i); blue), and from the envelope of $g_2 - g_5$ long eccentricity (e2(i); red); 405 kyr long eccentricity (e2; black) and its envelope (red); ~2.4 Myr $g_4 - g_3$ extracted from Ca (black), from the envelope of short eccentricity (e1(i); blue), and from the envelope of long eccentricity (e2(i); red), 100 kyr short eccentricity (e1; black) and its envelope (red), long eccentricity extracted from the envelope of short eccentricity (e2(i); blue). Red box indicates a phase shift influencing longer-term cycles due to a facies shift. B) Continuous Wavelet Transform scalogram of Ca, including identified ~6 Myr component (x), ~2.4 Myr $g_4 - g_3$ (e4), ~980 kyr $g_1 - g_5$ (e3), 405 kyr $g_2 - g_5$ (e2), ~100 kyr short eccentricity (e1), obliquity (o), and precession (p). C) Continuous Wavelet Transform scalogram of the envelope of short eccentricity extracted from Ca, including identified ~6 Myr component (x), ~2.4 Myr $g_4 - g_3$ (e4), ~980 kyr $g_1 - g_5$ (e3), 405 kyr $g_2 - g_5$ (e2).

G. Detrital Proxies and Multi-scale Rolling Correlation Analysis (MRCA)



Extended Fig. 7. Detrital signals and Multi-scale Rolling Correlation Analysis (MRCA) of K/Ti and Zr/Rb. Lithological units (L) and chemozonation (C). Detrital signals PC1, Si/Ti, log(Si/Al), log(Ti/Al), log(Ti/Rb), Zr/Rb, K/Ti, Rb/K, log(K/Al), log(Ti/Zr) (light gray) and 21-point running averages (dark gray). Multi-scale rolling correlation analysis (MRCA) of K/Ti and Zr/Rb, significant positive (orange) or negative (blue) Pearson correlation (95% confidence interval) is demarcated by black lines. A negative indication indicates K/Ti and Zr/Rb indicates both ratios can be interpreted as grain-size indicators, suggesting hydrodynamic control exerted primary influence on their variability. Positive or absent correlation indicates K/Ti and Zr/Rb do not represent grain size proxies, and that mineralogy and/or provenance exerted primary control on their variability.

3.5. Supplemental Information

A. Time-Domain Cyclostratigraphy

Below, zoom-in figures are provided that allow observing the phase relationship between the Daleje, Choteč, Kačák, and *pumilio* events relative to short-period (< Myr) orbital extrema. While these figures are not discussed in the main text of this chapter, they are included here as supplementary material because they further support the underlying analyses and are referenced in the synthesis chapter.

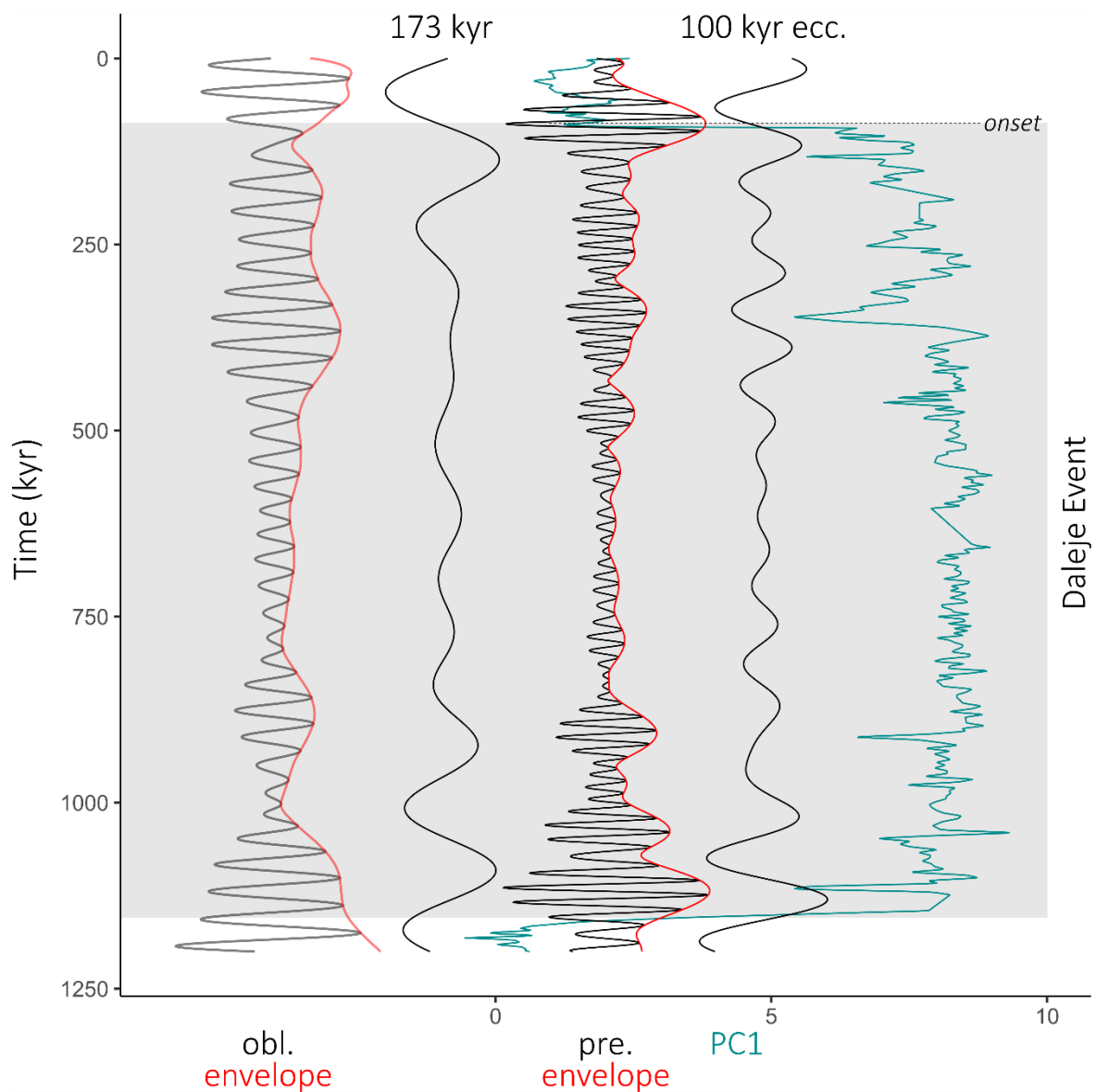


Fig. A1. Daleje Event Cyclostratigraphy. Principal component 1 (PC1; cyan), extracted obliquity (obl.; black), precession (pre.; black) and their envelopes (red), ~100 kyr short eccentricity and 173 kyr obliquity (black). Daleje Event is marked in gray.

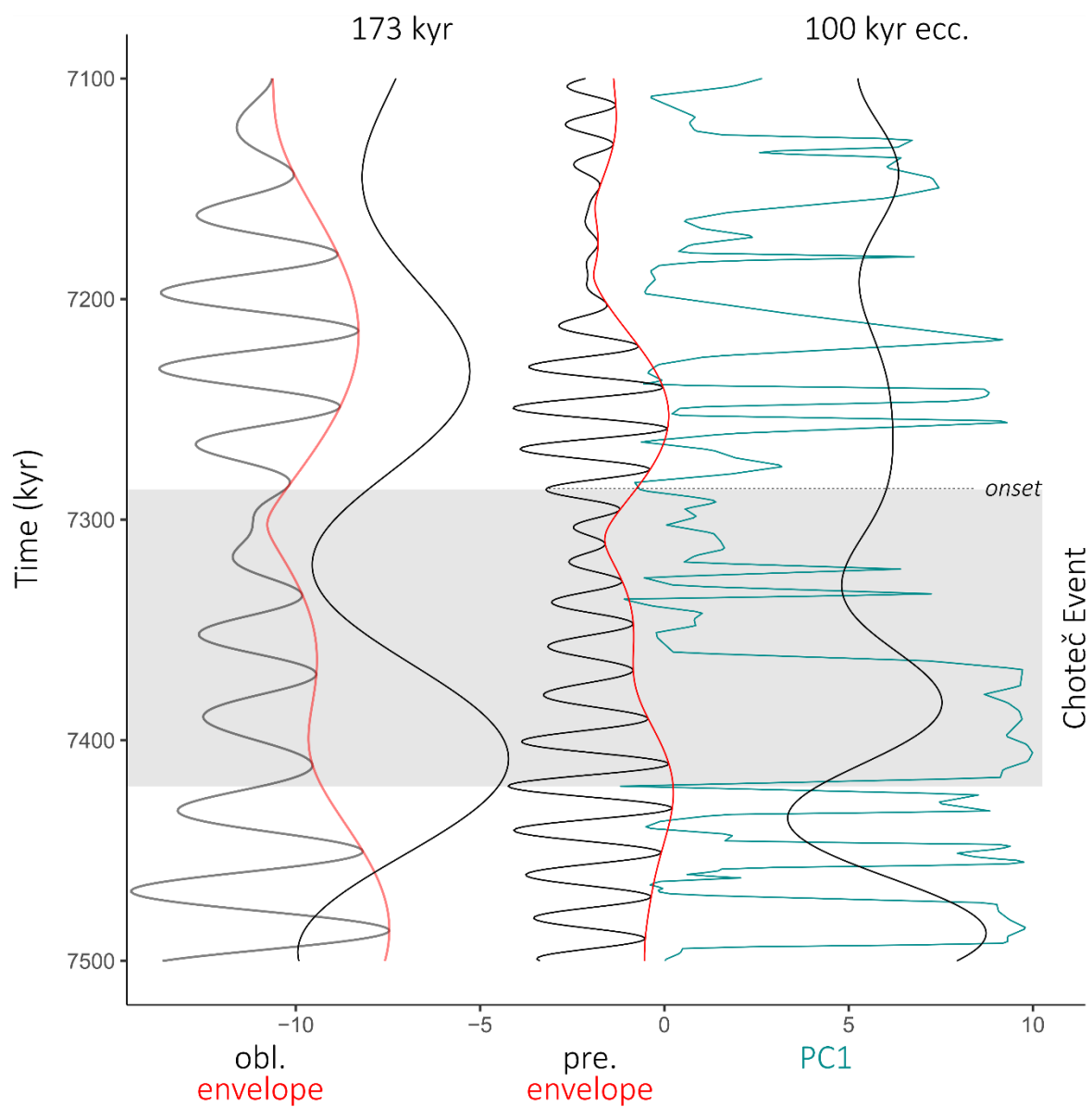


Fig. A2. Choteč Event Cyclostratigraphy. Principal component 1 (PC1; cyan), extracted obliquity (obl.; black), precession (pre.; black) and their envelopes (red), ~100 kyr short eccentricity and 173 kyr obliquity (black). Choteč Event is marked in gray.

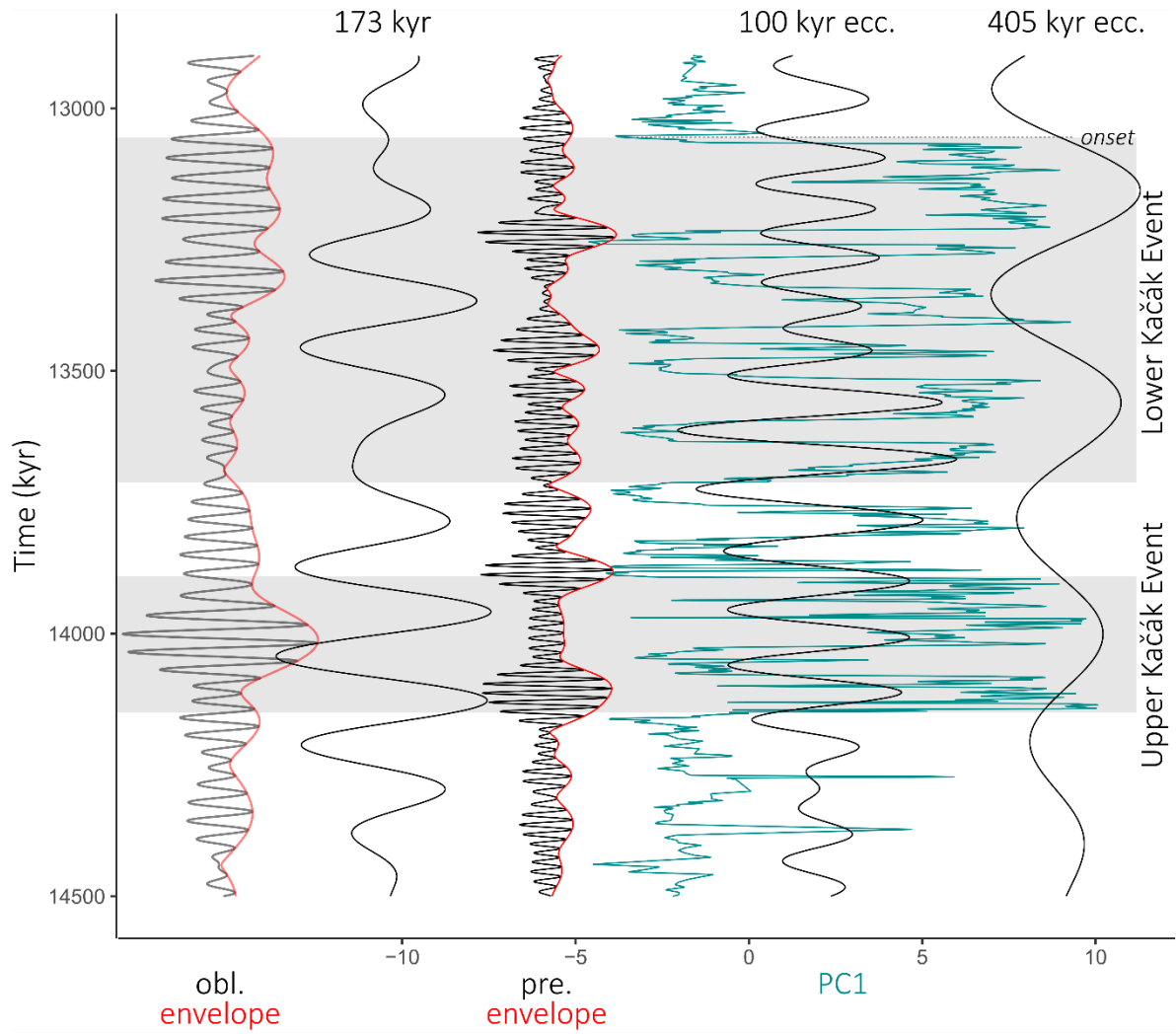


Fig. A3. Kačák Event Cyclostratigraphy. Principal component 1 (PC1; cyan), extracted obliquity (obl.; black), precession (pre.; black) and their envelopes (red), ~100 kyr short eccentricity, 173 kyr obliquity, and 405 kyr long eccentricity (black). Lower and Upper Kačák events are marked in gray.

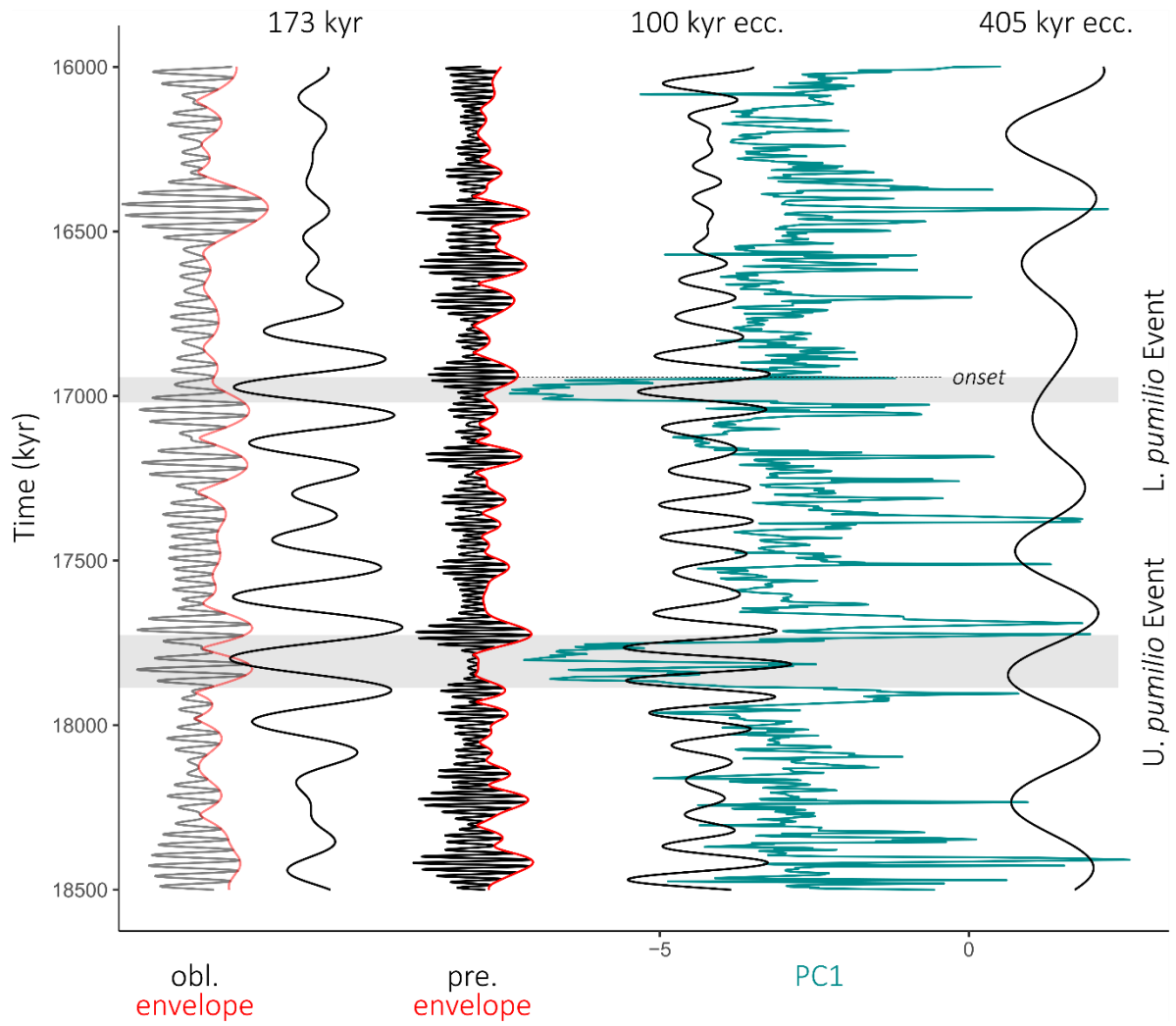


Fig. A4. *pumilio* Event Cyclostratigraphy. Principal component 1 (PC1; cyan), extracted obliquity (obl.; black), precession (pre.; black) and their envelopes (red), ~100 kyr short eccentricity, 173 kyr obliquity, and 405 kyr long eccentricity (black). Lower and Upper *pumilio* events are marked in gray.

4. **Milankovitch Forcing and Nonlinear Climate Variability during the Late Givetian (Appalachian Basin, New York, USA)** – in review in *Climate of the Past*

Jarno J.C. Huygh¹, Carlton E. Brett², James J. Zambito IV³, Ian J. Forsythe², Loïc Sablon⁴, Justin Gérard⁴, Michel Crucifix⁴ and Anne-Christine Da Silva¹

¹ SediCClim Laboratory, Department of Geology, Liège University, Liège, Belgium

² Department of Geosciences, University of Cincinnati, Ohio, United States of America

³ Department of Geology, Beloit College, Wisconsin, United States of America

⁴ Earth and Life Institute, UCLouvain, Louvain-la-Neuve, Belgium

Correspondance to: Jarno Huygh (jarno.huygh@uliege.be; jarno.huygh@hotmail.com)

Key Points:

- High- and low-latitude climatic and hydrological teleconnections shaped Late Givetian climate variability
- Linear and nonlinear (half)precession-obliquity interactions governed climate-sediment responses in the pantropical belt
- Astronomical forcing paced regional events and the timing of the Frasnian Crisis in the Appalachian Basin

Abstract

Astronomical forcing is a major driver of Earth's climate variability, yet the linear and nonlinear climate responses to this forcing under warmer-than-present conditions remain poorly constrained. We use cyclostratigraphy of the Sherburne Formation, a Givetian record from the Appalachian Basin, to characterize Milankovitch cyclicity and evaluate the complex climatic behavior inferred from the sedimentary record. A new cyclostratigraphic age model refines the timing of the regional Fir Tree, Hubbard Quarry and Lodi events and places the onset of the global Frasnian Crisis (represented by the regional Lodi Event) into an astronomically calibrated framework. Our results reveal precession-eccentricity-paced detrital influx, obliquity amplification, precession-obliquity interference patterns, half-precessional cyclicity, and nonlinear climate-sediment dynamics. These findings show how pantropical late Givetian climate variability is shaped by high- and low-latitude climatic and hydrologic teleconnections and highlight the sensitivity of Devonian climate to orbital variability.

Keywords: Cyclostratigraphy; Devonian; Orbital Forcing; Nonlinear; Half Precession

Plain Language Summary

Earth's climate is influenced by predictable changes in its orbit around the Sun and variations in its rotational axis. These are known as Milankovitch cycles (precession, obliquity and eccentricity) and shape climate patterns over tens of thousands to millions of years. We studied rocks from the Sherburne Formation in the Appalachian Basin (New York State, USA) to see how these orbital cycles affected climate during the late Givetian, about 380 million years ago, when Earth's climate was in a warmer-than-present state. We show that the late Givetian climate responded strongly to changes in the Earth's orbit. The rocks recorded clear signals of precession, obliquity, and eccentricity, including complex interactions and amplified responses that point to nonlinear climate behavior. Using these patterns, we built a new timeline for several important events during the investigated interval. Overall, our results reveal that the late Givetian climate was highly sensitive to orbital variations, and that these astronomical rhythms played a key role in shaping environmental change and biological turnover.

4.1. Introduction

Earth's climate system is fundamentally shaped by interactions among astronomical forcing, large-scale atmospheric and oceanic circulation, the hydrological cycle, and internal feedbacks (e.g., Saltzman, 2002). Astronomical forcing refers to the modulation of incoming solar radiation (insolation) caused by quasi-periodic variations in Earth's orbital parameters – precession, obliquity, and eccentricity (Milankovitch 1941). These 'predictable' Milankovitch cycles alter both the amount and latitudinal distribution of insolation (Berger, 1987; 1988; Laskar et al., 2004), strongly influencing seasonality and long-term climate patterns, and they form a cornerstone of our understanding of past climate change (e.g., Hays et al., 1976). However, the climatic expression of astronomical forcing is rarely a simple linear response to insolation changes (Rial et al., 2004). Complex Earth-system dynamics can modulate, amplify or reshape orbital signals across a wide range of timescales (e.g., Imbrie and Imbrie, 1980; Paillard, 1998). Such relationships are increasingly well understood in more recent Cenozoic records (e.g., Lourens et al., 2005; Sullivan et al., 2023) but less so in the Paleozoic (De Vleeschouwer et al., 2024). Recent work has documented the influence of orbitally forced climatic cycles on Devonian paleoenvironmental patterns (e.g., De Vleeschouwer et al., 2012; 2014; Da Silva et al., 2020; Wichern et al., 2024; Gérard et al., 2025; 2026; Huygh et al., 2026), but with a focus on major anoxic or extinction intervals (e.g., the Kellwasser Crisis). Typically, cyclostratigraphic studies apply linear time-series analysis and spectral tools, such as bandpass filtering and continuous wavelet transforms (e.g., De Vleeschouwer et al., 2012; Laurin et al., 2015; Arts et al., 2024; Spiering et al., 2024), to detect Milankovitch pacing of sedimentary cyclicity. Such approaches, however, are not designed to resolve the nonlinear feedbacks which may be responsible for the observed variability. Consequently, their influence on the expression of orbital forcing in Paleozoic climate records remains poorly constrained.

In this work, we investigate how astronomical forcing shaped late Givetian paleoclimate using an approach that allows us to detect both linear and potential nonlinear expressions of Milankovitch cyclicity preserved within the Sherburne Formation (lower Genesee Group) of central New York State (Baird et al., 2023). The Sherburne Formation represents a well-preserved archive of late the Givetian subtropical Appalachian Basin, making it well suited for evaluating the expression of orbital forcing outside major extinction intervals. Within this framework, we employ high-resolution proxies for detrital input, to analyze the character and frequency structure sedimentary cycles observed within the Sherburne Formation and develop two complementary floating astrochronologies. In addition, we put the regional Fir Tree, Hubbard Quarry and Lodi eustatic and hypoxic events into an integrated sequence- and cyclostratigraphic framework and assess phase relationships between astronomical forcing and paleoclimatic response. Together, these analyses illustrate a workflow that may be

broadly applicable to Paleozoic climate archives and show how astronomical forcing and internal Earth-system dynamics interacted to shape the late Givetian paleoclimate.

4.2. Geological Setting

The Cargill Salt Company Test Core #17 (hereafter Cargill #17 Core) was drilled in 1977 near Lansing, Tomkins County, southern Cayuga Lake area in central New York State, USA (42°31'22.9" N, 76°30'17.5" W) and spans ~847 m of strata, providing a detailed sedimentary record through the upper Silurian to Middle Devonian strata of the northern Appalachian Basin. Deposition of the Sherburne Formation (uppermost Givetian) occurred in a foredeep setting of this foreland basin, which developed during early Tectophase 4 of the Acadian Orogeny and lay within an expanded subtropical zone at approximately 30° S paleolatitude (Fig. 1; Ver Straeten, 2010; Baird et al., 2023; Ver Straeten et al., 2023).

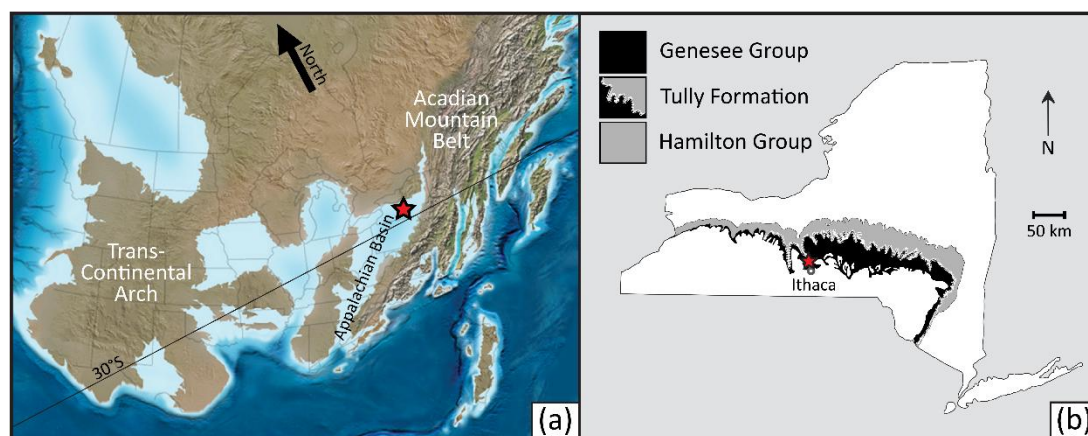


Fig. 1. Geological setting of the Cargill #17 Core. a) Middle Devonian paleogeographic map adapted from Blakey, 2014 (~380 Ma). b) Outcrop belt for the Genesee, Tully and Hamilton in the Appalachian Basin of New York State. Location of the Cargill #17 Core, just north of Ithaca, is indicated by a red star. Figure adapted from Zambito et al. (2016).

The depositional setting of the Sherburne has been interpreted in various ways, traditionally characterized as part of the northern Appalachian Basin Portage Magnafacies that formed on the distal shelf, slope, and proximal basin through turbiditic processes (Rickard, 1975; deWitt and Colton, 1978; see summary in Baird et al., 2023). However, recent work by Wilson and Schieber (2014; 2015; 2017) has interpreted the turbidites of the Sherburne Formation in the Cargill #17 core to more specifically represent fluvial-discharge events deposited in a storm-dominated proximal shale setting through hyperpycnal processes with a high sedimentation rate. Importantly for this study, hyperpycnites are dependent on flood frequency and magnitude, and therefore climate (Mulder et al., 2003).

The uppermost part of the Cargill #17 Core covers ~41.3 m of the Upper Givetian Sherburne Formation, attributed to the upper portion of the third-order sequence Giv-5 (Brett et al., 2011).

Lithostratigraphic correlations and conodont biostratigraphy date the Sherburne Formation from 379.2 to 380.0 Ma (*K. disparilis* to *S. norrisi* zones) (Kirchgasser, 1994; Brett et al., 2011; Becker et al., 2020). Stratigraphically, the Sherburne Formation in the southern Cayuga Lake area comprises the Fir Tree, Hubbard Quarry, and Lodi members, as well as an upper, unnamed Penn Yan Formation-equivalent that is not present in the Cargill #17 Core (Fig. 2; Zambito et al., 2009; Baird et al., 2023). The Sherburne Formation is a time transgressive unit, the base of which generally gets older to the east and south along the outcrop belt in the northern Appalachian Basin and replaces the basinal shale of the Penn Yan Formation through progradation (Baird et al., 2023). The Fir Tree Member (lower *K. disparilis* conodont Zone) in this core consists of medium gray calcareous siltstones to laminated silt and dark shales, marking the onset of subsequence Giv-5D and representing a 3rd order late highstand systems tract (LHST) (previously designated as Giv-5C Brett et al., 2011; but elevated to Giv-5D in Baird et al., 2023). The base of the Fir Tree (subsequence Giv-5D boundary; Fig. 2) is a widely recognized erosion surface marked in cratonic successions by deep incision, for example at the base of the Coralville Formation of the Cedar Valley Group in Iowa (Witzke et al., 1988; Witzke and Bunker, 1996, 1997). The Fir Tree Event therefore represents a regionally recognized event in at least eastern North America, however this event is poorly characterized and not recognized in most recent tabulations of Devonian events (e.g., Becker et al., 2016, 2020; Baird et al., 2023) and may have been conflated with the Genesee Event of the Taghanic Crisis in studies outside of the Appalachian basin (the Genesee Event is now understood to have been earlier in the *S. hermanni* Zone). However, some workers have noted the beginnings of decline of reefal organisms associated with widespread anoxia toward the end of the *K. disparilis* or *P. dengleri* Zone, with reefal collapse noted at the end of the Givetian (Copper and Scotese, 2003); it also marks the end of most trilobites in the Appalachian Basin, notably *Dipleura* (Zambito et al., 2015; Baird et al., 2023).

The contact between the Fir Tree and the overlying Hubbard Quarry Member (at 38.3 m depth; Fig. 2) marks a maximum starvation surface (MSS) and minor discontinuity (Brett et al., 2011; Baird et al., 2023); using the sequence stratigraphic model proposed by Zambito et al. (2009) for these strata, the transgression continues through to the base of the middle Hubbard Quarry, which is identified as the maximum flooding surface (MFS) at 28.3 m depth (Fig. 2). While in more distal settings within the Appalachian Basin the deepest, most anoxic conditions of the Hubbard Quarry occur at or near the contact with the Fir Tree, progradation into the study location means the environmental expression of the Hubbard Quarry occurs closer to the MFS (Fig. 2). The Fir Tree – Hubbard Quarry Member succession (*K. disparilis* to *P. dengleri sagitta* conodont zones) therefore represents a 3rd order transgressive to highstand to falling stage systems tracts (TST-HST-FSST) (Brett et al., 2011; Baird et al., 2023). It comprises: (i) lower Hubbard Quarry dark gray shales with light gray silty stringers, (ii) a middle subunit composed of alternating dark and lighter gray shales containing crinoids and,

(iii) upper Hubbard Quarry gray calcareous siltstones. From 17.7 m upwards, thin traces of cross-lamination are visible, suggesting a higher-energy environment, interpreted as storm-influenced hyperpycnites by Wilson and Schieber (2014;2015;2017). After an initial deepening (lower Hubbard Quarry through lowest middle Hubbard Quarry Member), the middle-upper Hubbard Quarry Member displays a significant regressive phase of sediment aggradation (Fig. 2; Baird et al., 2023).

The Lodi Member (10.8 m to 0.8 m depth, *P. dengleri dengleri* to *S. norrisi* conodont zones) consists of medium light gray, slightly bioturbated, calcareous siltstone with abundant *Aulopora* and represents a 3rd order transgressive systems tract (TST) (Brett et al., 2011). The onset of the Frasnian Crisis (Becker et al., 2020) coincides with the base of the Lodi Member and is marked by the regional Lodi Event, which represents another major lowstand sequence boundary. Indeed, a major incised erosion surface of up to 18 meters is observed at the base Lithograph City Formation (middle Cedar Valley Group) in Iowa (Witzke et al., 1988; Witzke and Bunker, 1996, 1997). The uppermost Lodi Member (*S. norrisi* conodont Zone, uppermost Givetian) is absent in the Cargill #17 Core, so the Givetian-Frasnian boundary is most likely not recorded. The uppermost ~3.8 m of the core are fragmented, with multiple missing intervals.

The Frasnian Crisis was multi-phased with three pulses of extinction, each associated with a transgression and widespread dysoxic-anoxic events. The first phase occurred at the later *P. dengleri* to *S. norrisi* zone, the age of the Lodi Member and just prior to the Givetian-Frasnian boundary. The largest phase is associated with black shales of the early Frasnian MN-1 zone and a final event in the lower MN-2 zone (see e.g., Klapper, 1989 regarding Montagne Noire (MN) conodont zonation). The early phase, which is regionally called the Lodi Event, includes major ammonoid extinction and termination of reef growth in many areas (Becker et al., 2016, 2020).

The Sherburne Formation records environmental characteristics of the late Givetian. This interval is broadly regarded as a warm-temperate greenhouse world (Becker et al., 2020), although recent work by Dahl et al. (2022) challenges this view: CO₂ reconstructions and climate-sensitivity modeling suggests that the Givetian climate may have been cooler and more variable than previously thought. The Givetian was marked by the expansion of tree-like terrestrial vegetation (e.g., *Archaeopteris*; Stein et al., 2020), and considerable faunal turnover that shaped evolutionary steps in the marine realm (Raup and Sepkoski, 1982; House 2002; Brett et al., 2020; Becker et al., 2020; Ver Straeten et al., 2023). Regionally, the Sherburne Formation captures environmental variability following the major, second-order Taghanic Crisis and leading into the onset of the second-order Frasnian Crisis (Brett et al., 2011; 2020; Zambito et al., 2012, 2016; Becker et al., 2016, 2020; Baird et al., 2023). These broader climatic

and biotic conditions provide the environmental backdrop against which the Sherburne Formation's cyclicity is evaluated.

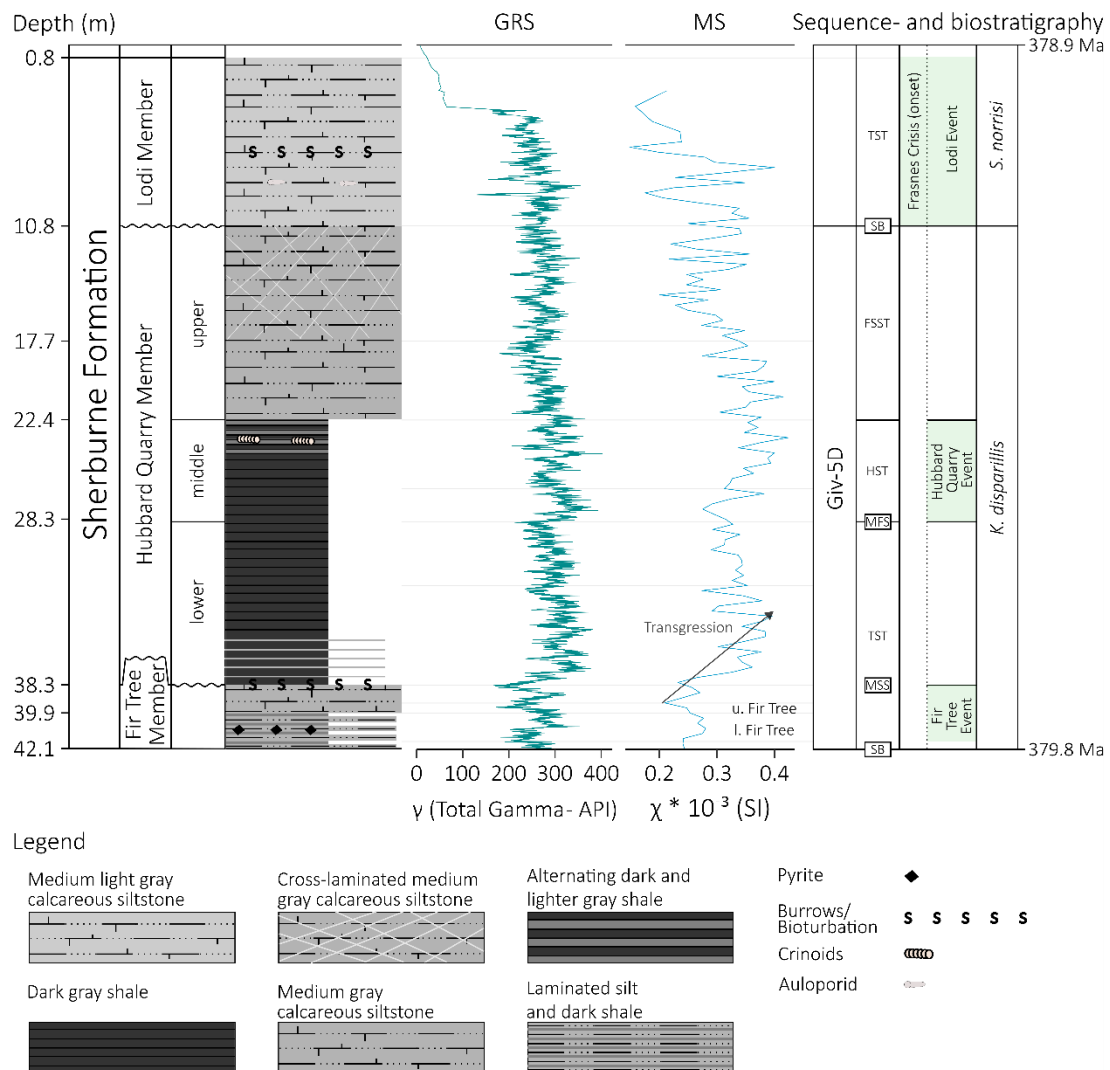


Fig. 2. Integrated stratigraphy of the Sherburne Formation in the Cargill #17 Core. Stratigraphy, lithological column, gamma ray spectrometry (GRS, total gamma – API), magnetic susceptibility (MS, SI – Kappa * 10⁻³), sequence stratigraphy; subsequence Giv-5D, sequence boundary (SB), maximum starvation surface (MSS), highstand systems tract (HST), falling stage systems tract (FSST), transgressive systems tract (TST) from Brett et al. (2011) and Baird et al. (2023), event stratigraphy, conodont zonation (Kirchgasser, 1994), and numerical ages based on the conodont zonation (Becker et al., 2020).

4.3. Material and Methods

4.3.1. Gamma-ray Spectrometry

High-resolution gamma ray spectrometry (GRS) total gamma ' γ ' (API units) was acquired at ± 0.013 m spacing using a Core Lab Instruments Gamma Logger at the Department of Geosciences at the University of Cincinnati (Ohio, USA). The γ -signal is proportional to the naturally occurring γ -radiation of the sample and integrates contributions primarily from ^{40}K , ^{232}Th and ^{238}U (Killeen, 2015). It represents an amalgamated signal dominated by ^{40}K (and to a lesser extent by ^{232}Th), typically associated with clay-rich, detrital material, and by ^{238}U , which is often enriched in organic-rich intervals. Across most of the Sherburne Formation, the γ -signal is a reliable proxy for detrital input, with minor organic contributions restricted mostly to dark gray shales of the lower and middle Hubbard Quarry members.

4.3.2. Magnetic Susceptibility

Magnetic susceptibility (MS; ' χ ' in SI-units Kappa 10^{-3}) was measured at ± 0.3 m spacing using Beloit College's handheld Terraplus KT-10R v2 meter while the core was on loan at the University of Cincinnati. The χ -signal represents the degree of magnetization of a material in response to an applied external magnetic field, which is commonly dominated by paramagnetic and ferromagnetic minerals which are typically enriched in detrital fractions of sedimentary rocks (Ellwood et al., 2000). When primary, the χ -signal also serves as a proxy for detrital input (Da Silva et al., 2009; 2012; De Vleeschouwer et al., 2012).

4.3.3. Statistical Approaches

Data treatment and statistical testing were performed in R Studio (version 2025.05.0+496). Time series and spectral analyses used "Astrochron" (Meyers, 2014) and "WaverideR" (Arts, 2023). GRS γ - and MS χ -signals were linearly interpolated and detrended using the `detrend()` or `noLow()` functions. Power spectral density was estimated via the multi-taper method (MTM; Thomson, 1982; Meyers, 2012). Significance testing employed AR(1) models with a Bonferroni correction at the 90 %, 95 %, and 99 % confidence levels, assuming an AR(1) process as the null hypothesis. Evolutive spectral analysis was carried out primarily using continuous wavelet transforms (CWT; Arts, 2023; Arts et al., 2024), suited for capturing both frequency and depth/time localization in non-stationary signals, across a range of cyclicities, though with limited frequency resolution. Normalized evolutive harmonic analysis (EHA) and evolutive power spectral analysis (EPSA) ('*eha*' function, Meyers et al., 2001) tracked spectral features through time, highlighting oscillation magnitude and frequency strength. Taner bandpass filters isolated components of interest. Hilbert transforms were applied to filtered signals to assess envelopes, allowing for assessment of amplitude modulation patterns. Focus was placed on amplitude modulation patterns of precession, obliquity and short eccentricity cycles

by extracting higher-order cycles from the envelope of hierarchically shorter cycles. To avoid convoluted phrases, for example, SE(i) is used to denote the '100 kyr short eccentricity cycle, recovered indirectly (i.e., 'i') from the envelope of precession'.

TimeOpt, an inverse modeling approach designed primarily for the evaluation of eccentricity-related amplitude modulation and bundling, was used to estimate sedimentation rates. This method enables astronomical tuning by identifying an optimal sedimentation rate that simultaneously optimizes (i) amplitude modulation of precession (or short eccentricity) by eccentricity, and (ii) concentration of spectral power at target orbital frequencies (Meyers, 2015). An average climatic precession target frequency of 0.0525 kyr^{-1} ($\sim 19.1 \text{ kyr}$) was calculated based on estimates by Waltham (2015) at 380 Ma.

Nonlinear interactions were assessed using bicoherence analysis, a high-order spectral method capable of identifying quadratic phase coupling (Hasselmann et al., 1963; Kim and Powers, 1979; Hinich, 1982; Choudhury et al., 2008; Sullivan et al., 2023). This approach detects a third, new frequency that arises from Milankovitch combination tones; sum ($f_3 = f_1 + f_2$) and difference ($f_3 = f_1 - f_2$) tones (e.g., Hagelberg et al., 1991; von Döbenek and Schmieder, 1999; Da Silva et al., 2018; Sullivan et al., 2023).

4.4. Results

4.4.1. Gamma-ray Spectrometry

The γ -values fluctuate between 200-350 API across the Sherburne Formation, except in the fragmented upper Lodi Member, which is excluded from further analysis. The lowest values occur in the laminated siltstones to shales and calcareous siltstones of the Fir Tree Member, oscillating strongly around a ~250 API baseline. A pronounced shift to higher γ -values marks the base of the overlying Hubbard Quarry Member at 38.3 m, followed by fluctuations around a slightly declining ~300 API baseline. The transition from the lower to middle Hubbard Quarry Member (28.3 m) is marked by the highest γ -values, reaching approximately 400 API (MSS; Fig. 2), after which values progressively decrease through the upper Hubbard Quarry Member. In the Lodi Member, γ -values fluctuate around 250-300 API (Fig. 2). Superimposed on these larger-scale trends are prominent 0.5-1.5 m bundles, in turn grouped into meter- to decameter-scale rhythmic packages.

4.4.2. Magnetic Susceptibility

The Fir Tree Member shows consistently low χ -values (~0.25 SI). A pronounced increase marks the transition to the overlying lower Hubbard Quarry Member, followed by a gradual decline toward the middle Hubbard Quarry Member (28.3 m; Fig. 2). χ -values rise again to ~0.40 SI near the base of the upper Hubbard Quarry Member, then decrease to ~0.20 SI in its middle portion. From the middle of the upper Hubbard Quarry Member into the overlying Lodi Member, χ -values display strongest variability, ranging from 0.2 to 0.4 SI in the middle part of the Lodi Member (Fig. 2). Similar to the γ -signal, meter- to decameter-scale rhythmicity is superimposed on these larger-scale trends in the χ -signal.

4.5. Cyclostratigraphy

4.5.1. Depth-domain Cyclostratigraphy

A CWT applied to the detrended γ -signal (Fig. 3a) reveals about six significant components exhibiting elevated wavelet power that appear significant versus 90 % AR(1) confidence level (MTM in Fig. A1). Although spectral power varies locally, mean periods remain relatively stable throughout the Sherburne Formation (Fig. 3b). Taner bandpass filtering extracted five components from the detrended γ -signal: 1 (~12 m), 2 (~6.5 m), 3 (~3.0 m), 4 (~1.0 m) and 5 (~0.6 m) (Fig. 3a). To account for minor mean frequency shift of components 4 and 5, filtering was applied separately to each member, centering the window around intervals of highest spectral power. At the Fir Tree-Hubbard Quarry and Hubbard Quarry-Lodi contacts, a discrepancy in these components (Fig. 3) is interpreted as the expression of the minor discontinuities present (Baird et al., 2023).

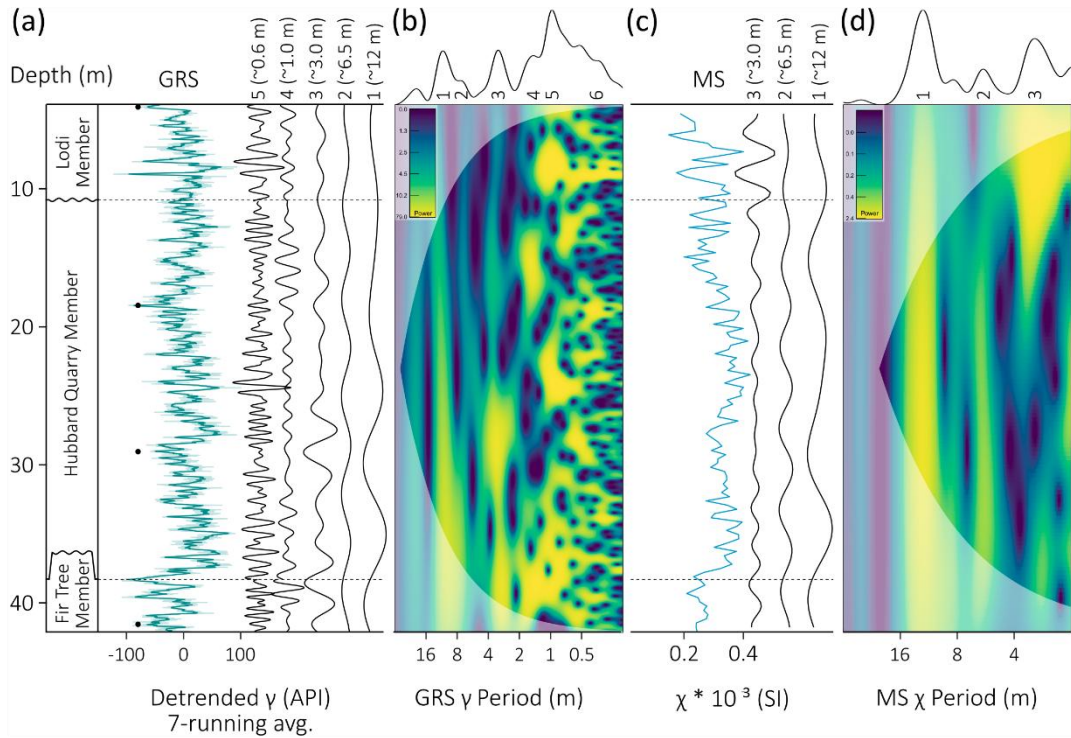


Fig. 3. Depth-domain cyclostratigraphy of the Sherburne Formation. a) Stratigraphy, detrended GRS γ -signal (light cyan) and 7-running average γ -signal (cyan), and bandpass filter output of key components 1 to 5 (black) and their corresponding mean periodicities (m). Components 3 to 5 were extracted separately for each member. Black dots indicate interpreted local minima in long-term cyclicity. b) GRS γ continuous wavelet transform and average wavelet power spectrum. c) MS χ -signal (blue) and bandpass filter output of key components 1 to 3 (black) and their corresponding mean periodicities (m). d) MS χ continuous wavelet transform and average wavelet power spectrum.

A similar approach applied to the MS χ -signal (Fig. 3d) identified three key components with mean periodicities of ~12, ~6.5, ~3.0, and ~1 m. Of these, component 1 is statistically significant

(90 % AR(1); Fig. A1). A fourth ~1.0-m component was also detected (Fig. A1) but excluded from interpretation due to low signal resolution. Taner bandpass filtering was used to extract three key signals (Fig. 3c).

4.5.2. Cyclostratigraphic Age Models

Milankovitch cycles are essential for constructing astronomical age models, and a key characteristic is their well-defined hierarchical structure, expressed through time-dependent frequency ratios. For the late Givetian (~380 Ma), average durations are: 405 kyr long eccentricity, 173 kyr long obliquity, ~100 kyr short eccentricity, 34.3 kyr obliquity, and ~19.1 kyr precession, yielding ratios of 1.0:1.8:5.2:9.1:21.2 that reflect their hierarchical structure. Components 1 to 5 in the γ -signal (Fig. 3b) exhibit ratios of 1.0:1.7:5.0:10.0:20.0, strongly suggesting the imprint of Milankovitch cyclicity. Similar periodicities in components 1 to 3 of the χ -signal further support this interpretation. Accordingly, the Sherburne Formation spans ~1.2 Myr at an average sedimentation rate of ~3 cm/kyr.

TimeOpt (0.2 to 4.0 cm/kyr; Meyers, 2015) was applied to test for amplitude modulation of precession by eccentricity and of short eccentricity by long eccentricity. For the γ -signal, average sedimentation rates of 3.29 and 3.39 cm/kyr were obtained, respectively (r^2_{opt} ; Fig. B1 and B2). In complement, TimeOpt testing for amplitude modulation of short eccentricity by long eccentricity, applied to the χ -signal, yielded an average sedimentation rate of 3.71 cm/kyr (r^2_{opt} ; Fig. B3). These estimates agree closely with the frequency-ratio estimates, strengthening the cyclostratigraphic interpretation. Conodont biostratigraphy (*K. disparilis* and *S. norrisi*; ~900 kyr; Becker et al., 2020) suggest comparable rates, well within the same order of magnitude (Fig. 2).

For the Late Givetian, the 405 kyr eccentricity ‘metronome’ remains the most stable and reliable Milankovitch cycle, even when considering the possibility that it could have been temporarily disrupted (Zeebe and Lantink, 2024). Accordingly, minimal tuning to the 405 kyr eccentricity was applied to the γ -signal (see black dots on Fig. 3a), guided by four local minima in the bandpass filter output of component 1 (Fig. 3b), interpreted to reflect 405 kyr long eccentricity. In the absence of an astronomical solution due to solar system chaos (Laskar, 2020), this approach provides the most reliable duration estimate. Using only four depth-time tie-points minimizes manipulation of the original γ -signal and preserves frequency modulation (e.g., precession frequency modulation by eccentricity). This age model (hereafter AM1) yields a floating astrochronology ~1238 kyr and is ideal for investigating longer-term processes (~ 10^5 yr).

Recovery of all identified Milankovitch cycles (Fig. 3) from the time-domain γ -signal (Fig. 4) enabled a second, complementary tuning approach based on precession. Guided by the

bandpass filter output of component 5 (Fig. 3a) and assuming a fixed 19.1 kyr precession period, a second age model (hereafter AM2) was constructed. The resulting floating astrochronology spans ~1267 kyr. Although the use of 67 depth-tie points at fixed 19.1 kyr intervals sacrifices information on the different frequency components of precession, this approach corrects more effectively for small-scale sedimentation rate variations. This is most crucial when investigating processes on sub-Milankovitch timescales, for which such a high-resolution age model is most ideal.

Finally, the estimated duration of the Cargill #17 Core Sherburne Formation is calculated by averaging AM1 and AM2, yielding 1252 ± 29 kyr (Fig. C1). The uncertainty associated with this estimate reflects the difference in relative time between AM1 and AM2 and is a realistic error margin equivalent to nearly two precession cycles. Both γ - and χ -signals were tuned using both AM1 and AM2 prior to subsequent cyclostratigraphic analysis.

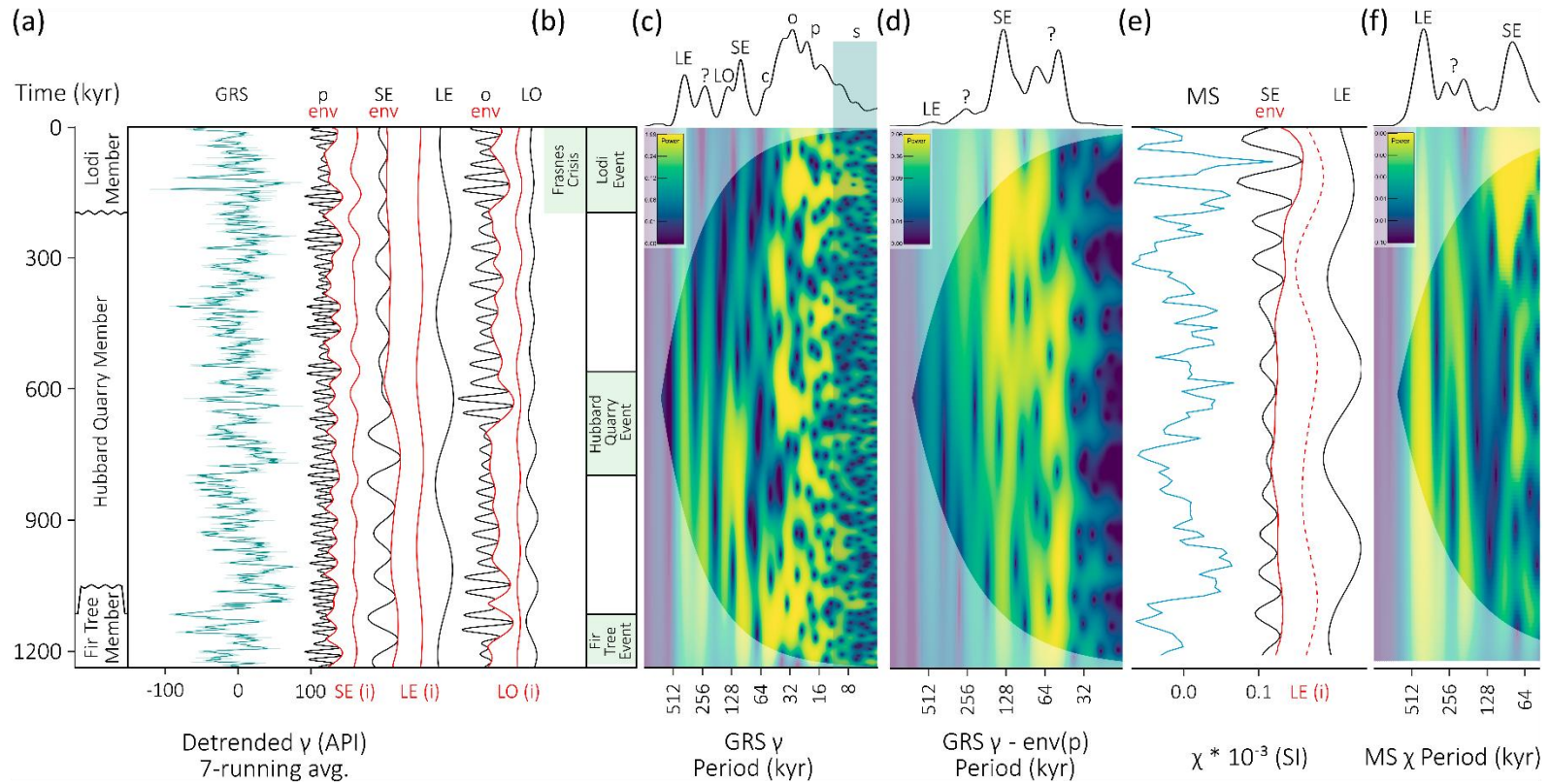


Fig. 4. Time-domain (AM1) cyclostratigraphy of the Sherburne Formation. a) Stratigraphy, detrended GRS γ -signal (light cyan) and 7-running average γ -signal (cyan), and bandpass filter output of precession (p; black) and its envelope (red), short eccentricity (SE; black) and its envelope (red), long eccentricity (LE; black) and its envelope (red), obliquity (o; black) and its envelope (red), long obliquity (LO; black). b) Bio-event stratigraphy. c) GRS γ CWT and average wavelet power spectrum, combination tones (c), and sub-Milankovitch cyclicity (s) highlighted in light blue. d) GRS γ CWT of the envelope of precession and average wavelet power spectrum. e) MS χ -signal (blue) and bandpass filter output of short eccentricity (SE; black) and its envelope (red), long eccentricity (LE; black) and its envelope (red), long obliquity (LO; black). f) MS χ CWT and average wavelet power spectrum.

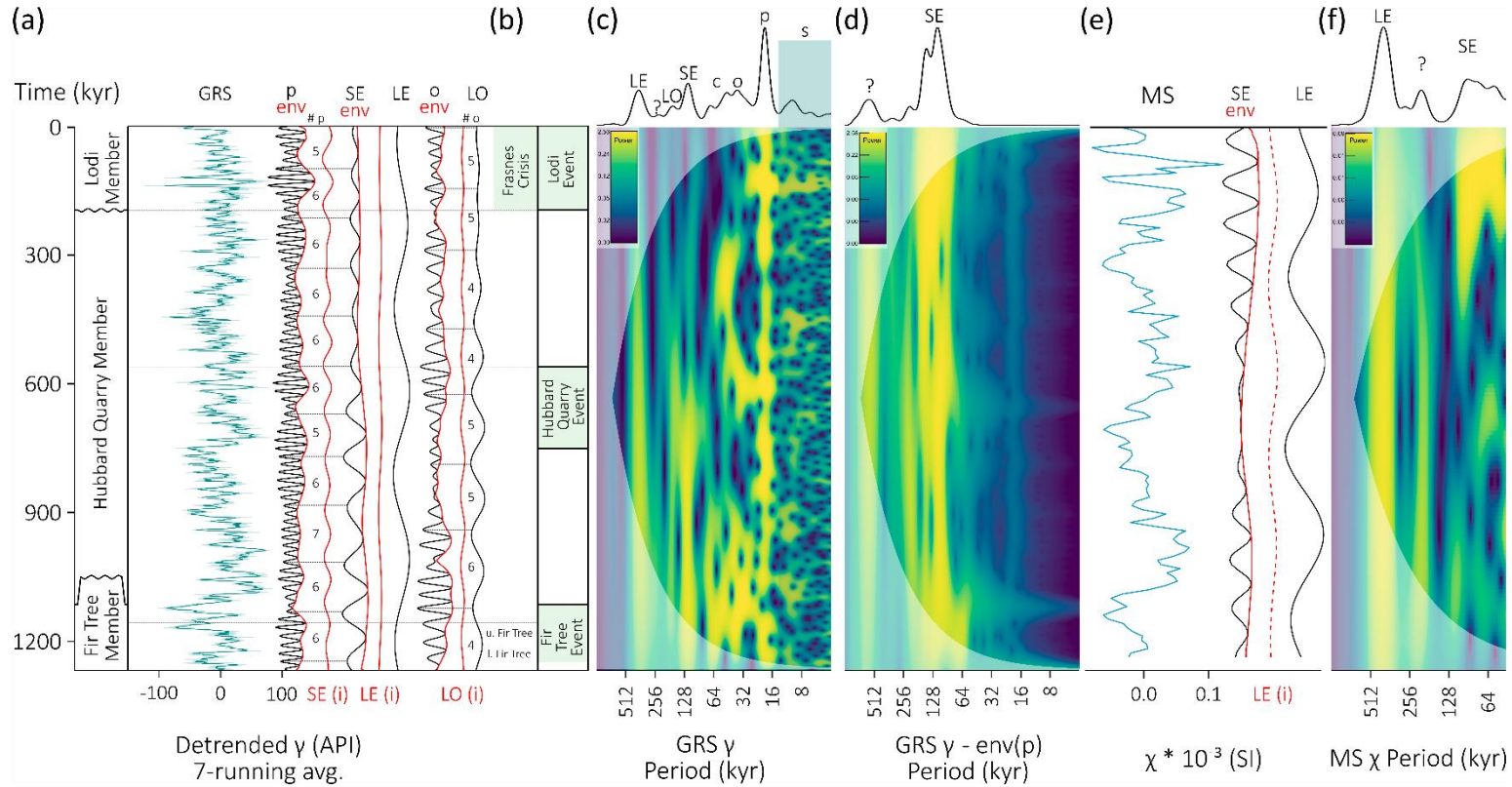


Fig. 5. Time-domain (AM2) cyclostratigraphy of the Sherburne Formation. a) Stratigraphy, detrended GRS γ -signal (light cyan) and 7-running average γ -signal (cyan), and bandpass filter output of precession (p; black) and its envelope (red), short eccentricity (SE; black) extracted from the envelope of precession (SE(i); red), short eccentricity (SE; black) and its envelope (red), long eccentricity extracted from the envelope of short eccentricity (LE(i); red), long eccentricity (LE; black), obliquity (o; black) and its envelope (red), long obliquity extracted from the envelope of obliquity (LO(i); red), long obliquity (LO; black). Numbers indicate counted precession (# p) cycles per interpreted SE cycle and obliquity (# o) per interpreted LO cycle. b) Bio-event stratigraphy. c) GRS γ CWT and average wavelet power spectrum, sub-Milankovitch cyclicity (s) highlighted in light blue. d) GRS γ CWT of the envelope of precession and average wavelet power spectrum. e) MS χ -signal (blue) and bandpass filter output of short eccentricity (SE; black) and its envelope (red), long eccentricity extracted from the short eccentricity envelope (LE(i); dashed red), long eccentricity (black). f) MS χ CWT and average wavelet power spectrum.

4.5.3. Time-domain Cyclostratigraphy

The Devonian lies beyond the interval for which astronomical solutions remain reliable, as chaotic divergence limits the precision of deep-time orbital calculations (Laskar, 2020; Zeebe and Lantink, 2024). We therefore assess the Milankovitch imprint through time-series and spectral analyses of the GRS γ - and MS χ -signals, tuned using two complementary age models: AM1 (405 kyr eccentricity) and AM2 (19.1 kyr precession). Both age models offer specific advantages and limitations that complement one another. Due to the long-term stability of the 405 kyr LE cycle, AM1 provides the most accurate temporal estimation and preserves frequency modulation, but it performs poorly in correcting for high-frequency sedimentation rate changes. In contrast, AM2 offers the highest temporal resolution and effectively accounts for sedimentation rate changes – thereby also more faithfully capturing amplitude modulation patterns – though it sacrifices precession frequency modulation. Consequently, while analyses targeting the linear Milankovitch imprint should yield comparable results across both models, higher-order spectral methods (e.g., bicoherence analysis) may produce divergent outputs, as they are more sensitive to phase structure and nonlinear interactions, whose detection can be affected by the tuning.

4.5.3.1. Long Eccentricity-based Age Model (AM1)

CWT analysis of the γ -signal tuned to AM1 reveals imprints of 405 kyr long eccentricity (LE), as well as 173 kyr long obliquity (LO), ~100 kyr short eccentricity (SE), obliquity and precession cycles (Fig. 4c). These Milankovitch components were filtered, and their amplitude modulation (i.e., envelope) was obtained via Hilbert transform. About 5 to 7 precession cycles occur per short eccentricity cycle (Fig. 4a), matching predictions for the late Givetian (~380 Ma; Waltham, 2015). The amplitude modulation patterns of precession align satisfactorily with SE extrema. A second CWT of the precession envelope (Fig. 4d) shows dominant SE power, with only minor LE power, as expected for such a relatively short record (~3 LE cycles). Sub-Milankovitch spectral power (s ; Fig. 4c) suggests half-precession cycles and/or high-frequency combination tones (i.e., millennial-scale variability), statistically significant at the 90 % AR1 level (MTM; Fig 6a, Fig. A1c, d). Additional wavelet power appears between 35-65 kyr periods (Fig. 4c), which is also present in the envelope of precession (Fig. 4d) and half-precession, as shown later. These may reflect localized sedimentation rate changes, linear Milankovitch interferences (affecting the envelope of precession) or nonlinear interactions. To explore the origin of cyclic components that deviate from canonical Milankovitch frequencies, bicoherence analysis was performed, with a focus on nonlinear interactions between precession and obliquity (Fig. 6c). In several regions of the spectrum, quadratic coupling between precession and obliquity is evident, producing sum tones (10.3 to 13.9 kyr) and/or difference tones (~36 to 128 kyr). Additional coupling occurs between sub-Milankovitch components and precession and obliquity components (Fig. 6c).

4.5.3.2. Precession-based Age Model (AM2)

Spectral analyses similar to those described in the previous section confirm LE, LO, SE and obliquity in addition to the precession cyclicity in the γ -signal that was tuned according to AM2 (i.e., precession-based; Fig. 5). This equally serves as a cross-check of the proposed cyclostratigraphic interpretation. Precession counts consistently yield 5-7 cycles per SE cycle (Fig. 5a). Similarly, obliquity counts reveal 4-6 cycles per LO cycle (Fig. 5a), equally in-line with astronomical predictions (~150 to 177 kyr in the ZB23 solutions; Zeebe and Lantink, 2024). These counts suggest the Fir Tree-Hubbard Quarry discontinuity represents only a minor hiatus, most likely shorter than one obliquity cycle. Similarly, the sequence boundary (SB) at the base of the Lodi Member also appears to represent only a minor hiatus of about the same duration. From this SB onwards, the precession envelope shifts slightly out of phase with the extracted SE cycle, possibly reflecting either the influence of the hiatus, edge effects introduced by bandpass filtering and subsequent Hilbert transform, or a change in the paleoclimatic response. A similar but weaker effect occurs in the lower Fir Tree Member. Conversely, the envelope of obliquity and LO does exhibit a consistent anti-phased relationship, which may in part be due to the tendency of bandpass filtering and the Hilbert transform to impose smoother, more regular phase behavior when signal amplitudes are low (Fig. 4a, Fig. 5a).

Tuning to 19.1 kyr precession enhances sub-Milankovitch power (Fig. 5c), suggesting half-precession and/or nonlinear interactions. Bicoherence analysis reveals strong diagonal coupling at 19.1 kyr (Fig. 6d), consistent with (mathematical) harmonic generation producing a ~9.55 kyr component. Quadratic coupling between precession and this component in turn yields a ~6.37 kyr component, suggesting involvement of a harmonic cascade. Tuning to precession can generate a harmonic cascade as an artefact, because it forces variations in the sedimentation rate that effectively result in frequency modulation of the signal. However, we observe that a ~9.55 kyr component is recovered through spectral analysis (Fig. 4) and it also appears on the bicoherence spectrum of the γ -signal tuned according to AM1 (Fig. 6c), where it couples with precession and obliquity components. This strongly suggests that the detected sub-Milankovitch cyclicity (incl. the ~9.55 kyr component) is not only a tuning artifact (Fig. 8).

4.5.3.3. Magnetic Susceptibility

Spectral and time series analyses of the χ -signal tuned to AM1 and AM2 yield highly similar results and are therefore treated together. CWT analysis shows increased wavelet power at LE and SE periodicities (Fig. 4), which are extracted using Taner bandpass filtering (Fig. 4) to facilitate comparison of phase relationship between γ and χ . Crucially, the extracted SE and LE components appear broadly in-phase with those recovered from the γ -signal (Fig. 4, 5),

indicating that both proxies exhibit a similar response to astronomically forced insolation changes. This reinforces their interpretation as reflecting detrital input variations.

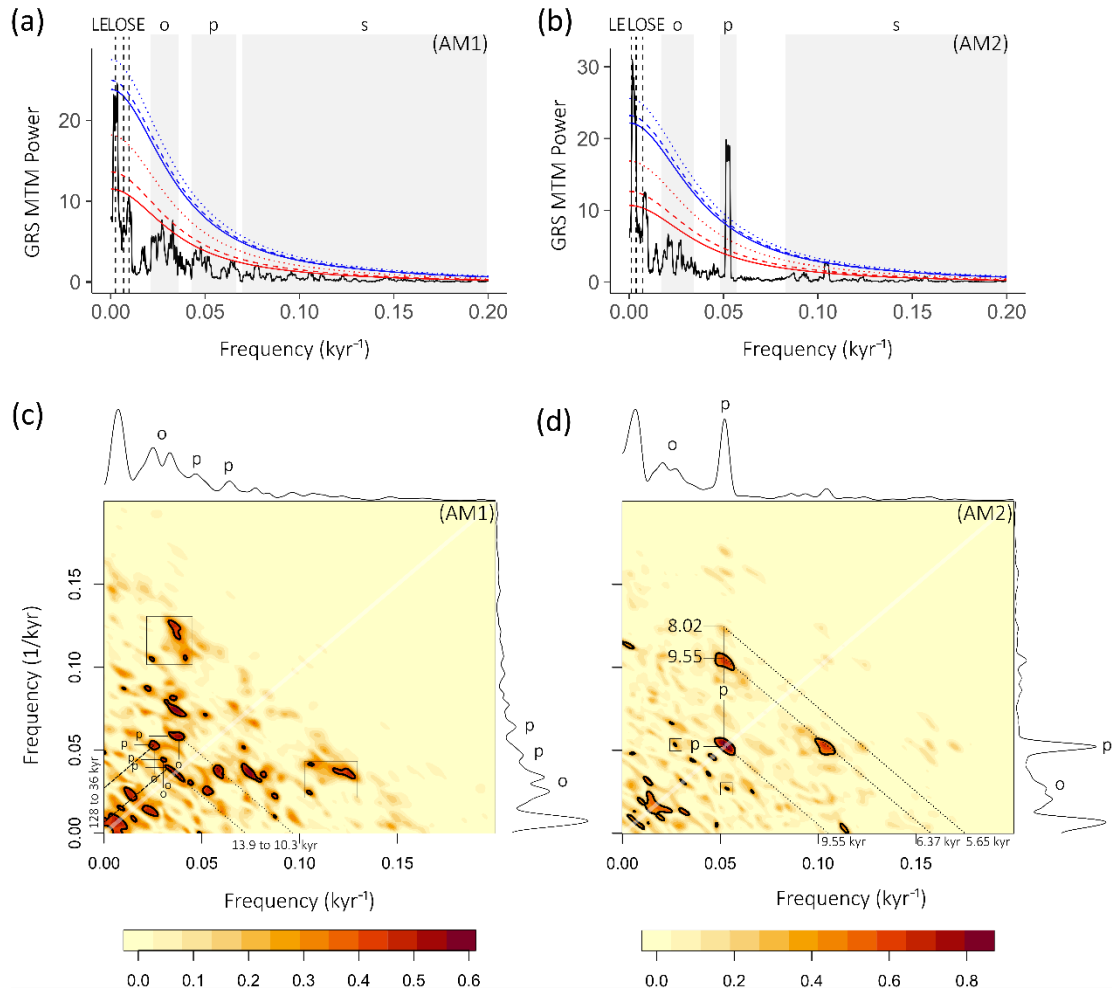


Fig. 6. Bicoherence analysis of the tuned GRS γ -signal. a) Time-domain γ (AM1) MTM spectrum. b) Time-domain γ (AM2) MTM spectrum. Classical significance testing at 90, 95 and 99 % confidence levels using an autoregressive model of order 1 (AR(1)) is included for each spectrum (red full, dashed and dotted red lines, respectively) and Bonferroni corrections (blue). c) Weighted overlap segment averaging (WOSA) power spectrum and bicoherence spectrum of γ (AM1). Obliquity and precession marked by 'o' and 'p', respectively. Increased bicoherence indicates quadratic coupling, revealing nonlinear Milankovitch combination (dotted diagonals) and difference (dashed diagonals) tones. Black squares indicate quadratic coupling of 9.55 kyr and sub-Milankovitch components. d) WOSA and bicoherence spectra of γ (AM2), black squares indicate regions of precession-obliquity coupling. Obliquity and precession marked by 'o' and 'p', respectively. Nonlinear Milankovitch combination tones (dotted diagonals). Key sub-Milankovitch durations highlighted on the bicoherence spectrum in kyr.

4.5.3.4. Phase Relationship of Proxies to Astronomical Forcing

Interpretation of proxy dynamics and their phase relationships with astronomical forcing is critical for understanding proxy responses and assessing the timing of regional events relative to Milankovitch cycle extrema. Cyclostratigraphy of γ - and χ -signals demonstrates that deposition of the Sherburne Formation strata within the Appalachian Basin was strongly influenced by astronomically paced changes in detrital input. Because both proxies represent an amalgamated signal (e.g., Da Silva et al., 2009; 2012; Killeen, 2015), it remains uncertain whether these variations represent changes in the total amount of detrital input or its composition. The dominant driver is most plausibly the hydrological cycle, influencing detrital delivery through variations in weathering, erosion, runoff, and/or astronomically paced eustatic sea-level fluctuations (Da Silva et al., 2009; 2012; Zhang et al., 2022). This is in agreement with the interpretation of the Sherburne Formation strata as hyperpycnites (Wilson and Schieber, 2014; 2015; 2017).

Intervals characterized by stronger γ precession-scale amplitude variation are interpreted to correspond to maxima in SE (Fig. 4, 5). The in-phase relationship between eccentricity signals extracted from both γ and χ indicates that both proxies respond synchronously to changes in insolation forcing. This is reinforced by the in-phase relationship between SE and SE(i) extracted from the γ -signal, suggesting maximal precession amplitude modulation during SE maxima (Fig. 4, 5). Accordingly, high γ - and χ -values are interpreted to reflect periods of strong climatic precession at the paleodepositional site. Similarities in proxy responses suggest that shared processes influenced χ in the same way, although its lower resolution limits detailed analysis. Although a 405 kyr LE imprint is recognizable in both proxy signals, its expression is less clear in the precession envelopes (Fig. 4, 5). This is attributed primarily to the presence of obliquity, combination tones (Fig. 6) and interferences involving precession and obliquity (Fig. 7), which affect the amplitude of the γ -signal and may hamper indirect recovery of eccentricity cycles from the envelopes of hierarchically shorter cycles.

4.5.3.5. Duration of Regional Events and their Phase Relationship to Astronomical Forcing

The durations of the Fir Tree, Hubbard Quarry, and Lodi events can be estimated with age model AM1, tuned to the stable 405 kyr eccentricity metronome. The Fir Tree Event lasted 108 ± 29 kyr, broadly equivalent to the duration of one short eccentricity cycle. The error margin of 29 kyr is estimated based on the difference between AM1 and AM2. The succeeding Hubbard Quarry Event, representing highstand conditions and associated low oxygen conditions inferred from the black shale facies (Fig. 2), is more protracted; its duration is 214 ± 29 kyr, equivalent to two SE cycles. Finally, the Lodi Event, which also marks the onset of the Frasnian Crisis, has an estimated duration of at least 200 ± 29 kyr.

The Fir Tree, Hubbard Quarry and Lodi events share a notable similarity: their onset occurs near a minimum in precession and short eccentricity (Fig. 5). Although this pattern is not explicitly diagnostic of the underlying causal mechanisms, it does indicate that astronomical forcing exerted a strong control on the timing of their initiation. Based on the 405 kyr long eccentricity cycle extracted directly from the γ - and χ -signals, the temporal position of these events can be placed within the broader long-eccentricity framework. Both the Fir Tree and Hubbard Quarry events appear to occur shortly after a minimum in 405 kyr eccentricity, initiating on the rising limb of the long-eccentricity cycle. Conversely, the Lodi Event appears to occur shortly after a maximum in 405 kyr eccentricity and unfolds on the decreasing limb of the long-eccentricity cycle.

Yet, while the Lodi and Fir Tree events are both interpreted to occur during a TST after a SB, the hypoxic Hubbard Quarry Event develops during a HST (Fig. 2). These differences – closely tied to eustatic sea-level variations – cannot be entirely reconciled with the eccentricity-paced forcing identified above. Although the timing of these events appears dictated by precession-eccentricity minima, their expression and relationship to sea-level variations likely involved additional controls. Given that the three events occur over slightly more than 1.2 Myr, we hypothesize that the $s_4 - s_3$ 1.2 Myr obliquity cycle (Laskar, 2020) may represent the additional pacing mechanism required to explain their differing sea-level contexts. Astronomically controlled sea-level variability on such timescales was already reported by Huygh et al. (2026) for the Appalachian Basin during the Frasnian. Although the Sherburne Formation record is too short to resolve the $s_4 - s_3$ cycle directly, the spacing of the Fir Tree, Hubbard Quarry and Lodi events is consistent with their development near successive extrema of this long-period obliquity modulation.

Whether the Fir Tree and Lodi event occur during a $s_4 - s_3$ minimum or maximum – and, conversely, whether the Hubbard quarry corresponds to the opposite extremum – cannot be inferred from the available data. This uncertainty arises because the phase relationship

between obliquity and sea-level change is mechanism-dependent: glacio-eustasy and limno/aquifer-eustasy respond in opposite phase to obliquity forcing (Lourens and Hilgen, 1997; Li et al., 2018), and the dominant mechanism depends on the prevailing climatic regime. Although the presence of substantial (continental) ice during the cooler Givetian (Becker et al., 2020) remains debated, integrated stratigraphy and oxygen-isotope evidence does suggest that glacio-eustatic processes may have operated on < 1.7 Myr timescales (Elrick et al., 2009). Hence, we propose that glacio-eustasy may have contributed to the observed eustatic sea-level variations. As noted above, the Fir Tree and Lodi events correspond with substantial incision of up to 18 meters in Iowa that is difficult to explain without glacio-eustasy, which could be substantial under relatively cool and variable climate conditions (cf. Dahl et al., 2022). Taken together, we hypothesize that obliquity-scale climate variability modulated the sea-level context in which the Fir Tree, Hubbard Quarry and Lodi events unfolded, superimposed on their precession-eccentricity-paced timing.

4.5.3.6. Milankovitch Interference Patterns and Nonlinearities

Insolation at a given latitude depends, among other factors (e.g., solar cycles), on climatic precession and obliquity (e.g., Milankovitch, 1941; Berger et al., 2006). Because different paleodepositional settings and proxies can respond to these orbital cycles through distinct mechanisms, their interplay may be recorded in multiple ways. Within the scope of this study, two types of interactions between astronomical frequencies are therefore relevant for understanding climate responses to insolation forcing.

The first involves linear interference between carrier frequencies such as precession and obliquity, which does not generate new frequencies in the underlying forcing (Fig. 8a, c; Laskar et al., 2004). Because precession and obliquity are not phase-locked, their extrema may coincide regularly but not periodically, and their combined linear effect generates time-dependent interference patterns manifested as amplitude modulation and beating patterns (Fig. 8b, d). The resulting amplitude envelope – extractable using a Hilbert transform (Fig. 8a, c) – contains frequency variability associated with the modulation itself (i.e., new frequencies; Fig. 8b, d). Depending on the sensitivity of the proxy system, a purely linear response may therefore record either the carrier frequencies and/or the amplitude envelope produced by their interference (Imbrie and Imbrie, 1980; Meyers and Hinnov, 2010). For completeness, certain processes, such as bioturbation, may mimic an envelope-type response (Meyers, 2014).

A second class of interactions involves nonlinear responses to astronomical forcing, leading the Earth system to generate new frequencies that are not present in the original insolation signal. Such behavior can occur in a range of contexts, including threshold-controlled climate-sediment interactions such as runoff-driven erosion and sediment accumulation (Tucker and Slingerland, 1997) as well as nonlinear sediment-transport dynamics (Jerolmack and Paola,

2010). This is conceptually illustrated in Fig. 8e, where a hyperbolic tangent $f(x) = \tanh[2(x-1)]$ acts as a nonlinear operator that produces mixed frequencies ($f_3 = f_1 \pm f_2$), such as ~50 kyr components (see Fig. 8f, g). Note that processes that appear to track the amplitude envelopes of higher-frequency carriers may also be nonlinear in their underlying dynamics (e.g., Huybers and Wunsch, 2004). Quantifying the linear proxy response to the envelope of the carrier frequencies (e.g., to total insolation variability) and a nonlinear proxy response in inherently noisy sedimentary proxy series is challenging, especially because neither amplitudes nor frequencies are entirely diagnostic.

The framework presented above clarifies how new frequency components – such as those observed in the Sherburne Formation γ -signal – may arise and provides the basis for a qualitative interpretation of their origin. For example, a ~50 kyr component is present in obliquity (Laskar et al., 2004), but it is relatively weak and is not expected to contribute substantially (Spiering et al., 2024). Alternatively, such a component (Fig. 4-6) can result either from a linear response to the amplitude envelope of higher-frequency insolation components (Fig. 8d) or from nonlinear interactions involving, for example, precession and obliquity (Fig. 8g). A third possibility is that these components represent harmonics of the ~100 kyr short-eccentricity cycle. However, this pathway is readily evaluated: in the Sherburne Formation γ -signal, the extracted short-eccentricity component shows no stable phase relationship with the 40-60 kyr variability (Fig. D1), making a harmonic origin unlikely (Spiering et al., 2024). Moreover, this framework also highlights the limitations of time-series and spectral analysis in elucidating a proxy response to climatic variability as a result of insolation forcing. Although new frequency components arising from a response to the insolation envelope may exhibit higher amplitudes than those generated through nonlinear interactions (Fig. 8d, f), the amplitudes preserved in sedimentary proxy series may be muted, amplified, or overprinted by noise and other non-cyclic contributions (Mudelsee, 2010; Meyers, 2014), complicating their interpretation.

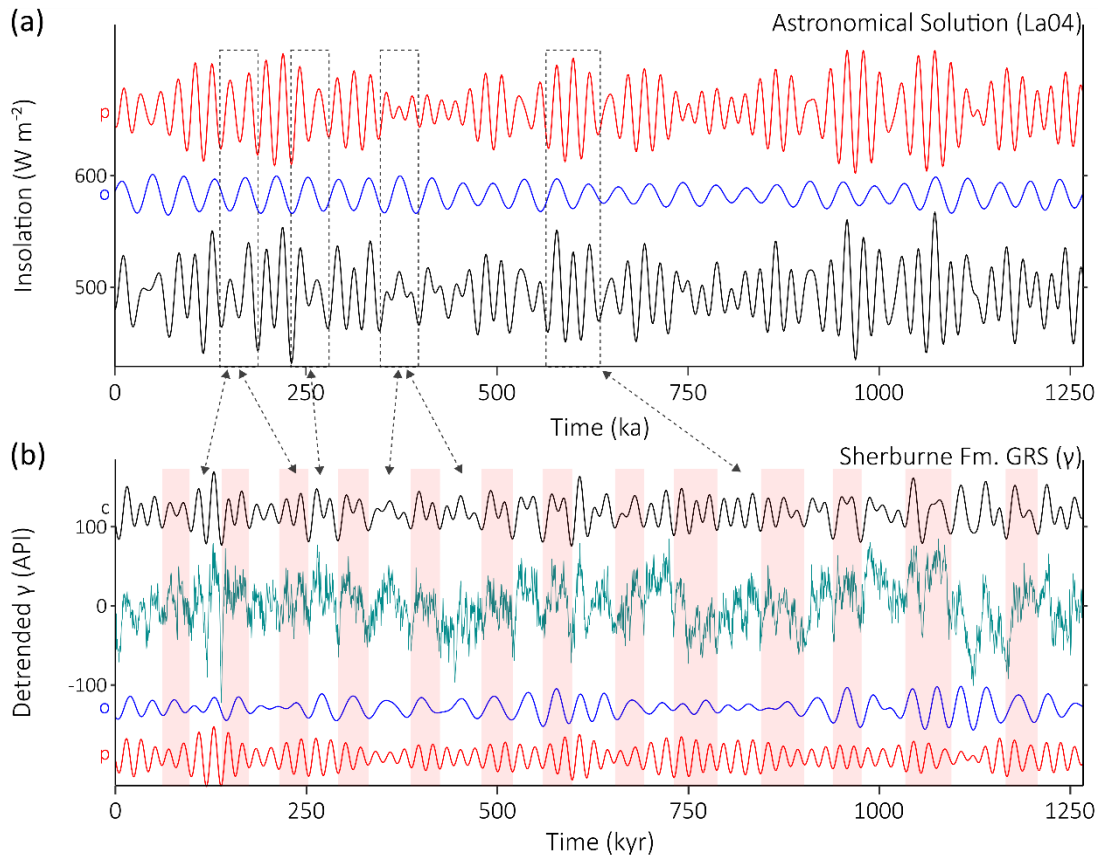


Fig. 7. Milankovitch interference patterns in the Sherburne Formation γ -signal. a) Insolation series (La04 at 65° N; Laskar et al., 2004) from 0 to 1267 ka (black), filtered precession (p; red) and obliquity (o; blue). Red bands and black dashed arrows highlight and indicate similar precession-obliquity interference patterns – not correlation. b) Detrended γ -signal (cyan) tuned according to AM2 and bandpass filter output of precession (p; red), obliquity (o; blue) and a linear superposition (i.e., sum) of the precession and obliquity filter output (c; black). Vertical red bars highlight interference patterns between precession and obliquity. Black dashed boxes and arrows indicate similar interference patterns.

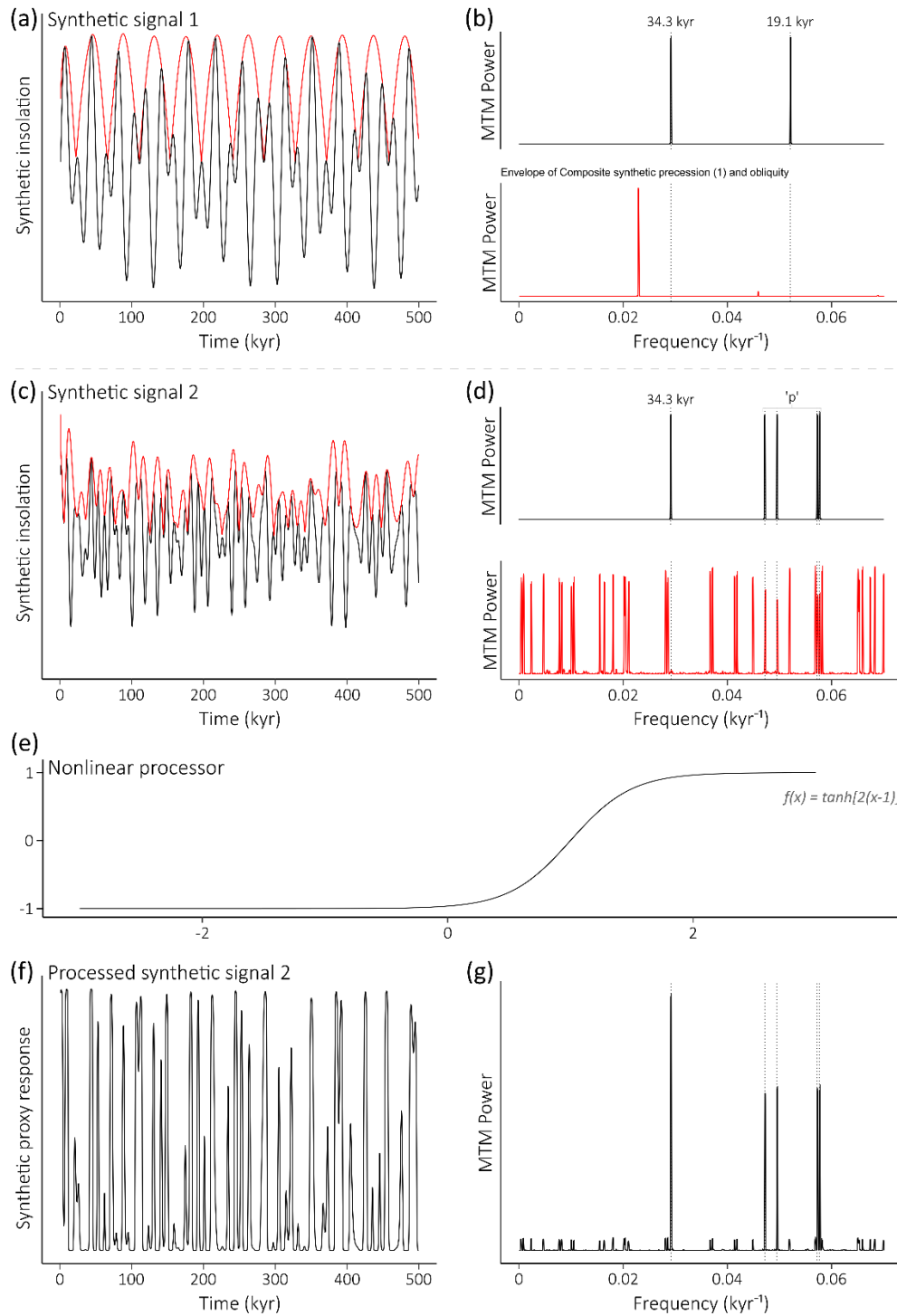


Fig. 8. Conceptual illustration of synthetic insolation forcing, proxy responses, and their MTM spectra. a) Synthetic insolation of linearly superimposed 19.1 and 34.3 kyr signals (black) and Hilbert-derived envelope (red), zoom-in on 0-500 kyr. b) MTM power spectra of the signals in a); upper: synthetic insolation (black), lower: its envelope (red). c) Synthetic insolation of linearly superimposed 17.34, 17.47, 20.2, 21.2 and 34.3 kyr signals (black) and Hilbert-derived envelope (red), zoom-in on 0-500 kyr. b) MTM power spectra of the signals in d); upper: synthetic insolation (black), lower: its envelope (red). e) nonlinear processor $f(x) = \tanh[2(x-1)]$. f) Synthetic proxy response after nonlinear processing using $f(x) = \tanh[2(x-1)]$ of the time series plotted in panel e. g) MTM power spectrum of the synthetic proxy response (f). Note that the prominence of envelope-derived or nonlinear frequency components is sensitive to the chosen input parameters of the conceptual experiment.

Building on this framework, the cyclicity observed in the Sherburne Formation γ -signal is interpreted here as reflecting a nonlinear proxy response to climatic variability with substantial contributions from a linear response to insolation and its envelope. Integration of bandpass filtering (Fig. 3, 4, 5, 7) with CWT (Fig. 4, 5) and bicoherence analysis (Fig. 6) supports this dual-mechanism interpretation. Apparent interference patterns, resulting from linear superposition of precession and obliquity appear to dominate the γ -signal (Fig. 7) and reflect a response to changes in total insolation (Laskar et al., 2004). The similarity between these precession-obliquity interference patterns and the La04 solution (Fig. 7a) is highly suggestive of a dominant contribution by a linear proxy response to insolation variability. Because no unique astronomical solution exists for the Givetian, these interference patterns are compared with the La04 insolation series for illustration purposes (from 0 to 1267 ka; Laskar et al., 2004; Fig. 7). Note that direct comparison may be somewhat limited due to the shorter Givetian precession and obliquity durations (Laskar et al., 2004; Waltham, 2015; Laskar, 2020).

In addition to these interference patterns, the Sherburne Formation γ -signal also exhibits features that cannot be produced by linear superposition alone; significant bicoherence between astronomical components (Fig. 6) demonstrates that the climate-sediment system introduces nonlinear interactions, generating new frequencies through quadratic phase coupling (Sullivan et al., 2023) and likely further modifying the amplitude structure of the proxy response. Such nonlinear interactions may give rise to both lower-frequency (i.e., sum tones) and higher-frequency (i.e., difference tones) components (Hagelberg et al., 1991; von Döbeneck and Schmieder, 1999). Although nonlinear interactions can generate similar frequencies, for example, in the 40-60 kyr band (Fig. 6), climate-sediment nonlinearities are typically state-dependent and not expected to generate persistent, well-defined patterns (Tucker and Slingerland, 1997; Jerolmack and Paola, 2010) such as those arising from a response to total insolation variability (Fig. 7a, b). While bicoherence analysis does not allow discrimination between sum and difference tones, our integrated spectral (Fig. 4-7) and conceptual (Fig. 8) results indicate that both types of nonlinear products were likely captured by the γ -signal. Although additional cyclicity is evident at eccentricity timescales (Fig. 4-6), the summed precession-obliquity signal appears to account for the majority of variability observed in the γ -signal (Fig. 7), while non-cyclic contributions and sedimentary noise likely also contributed. The considerations outlined above are equally relevant for interpreting variability in the sub-Milankovitch band, where both half-precession and nonlinear frequency generation can produce similar spectral expressions, which is addressed in the next section.

4.5.3.7. Half-precession Cycles

In the intertropical belt, in particular at the equator, the Sun culminates at the zenith of both equinoxes (Berger et al., 2006). If climate responds predominantly to the largest of these twice-annual insolation maxima (Berger and Loutre, 1997), then the precessional modulation of equinox intensity produces two insolation peaks per precession cycle, giving rise to variability at approximately half the precession period (i.e., mean ~9.5 kyr for the Givettian). Thus, half-precession does not represent a harmonic of precession; rather, it is a geometric consequence of how equatorial insolation responds to climatic precession (Berger and Loutre, 1997; Berger et al., 2006; Wu et al., 2025). However, distinguishing half-precession is not straightforward, because nonlinear interactions between precession and obliquity (Fig. 6; Table E1) or a proxy response to the total-insolation envelope (Fig. 8d) can generate frequencies that fall within the same band, complicating the elucidation of a true half-precessional signal.

The γ -signal consistently shows splitting of precession-scale cycles (Fig. 9a), suggesting a half-precession-like imprint. In addition, the γ CWT spectra reveal prominent power centered around a ~9.5 kyr period (Fig. 4, 5). MTM and EPSA analyses (Fig. F1) show that this band comprises multiple components (7.8 to 12.3 kyr) across the Sherburne Formation (see MTM spectrum, Fig. A1). Moreover, elevated bicoherence (Fig. 6) suggests the presence of similar frequencies resulting from nonlinearities and their involvement in quadratic coupling.

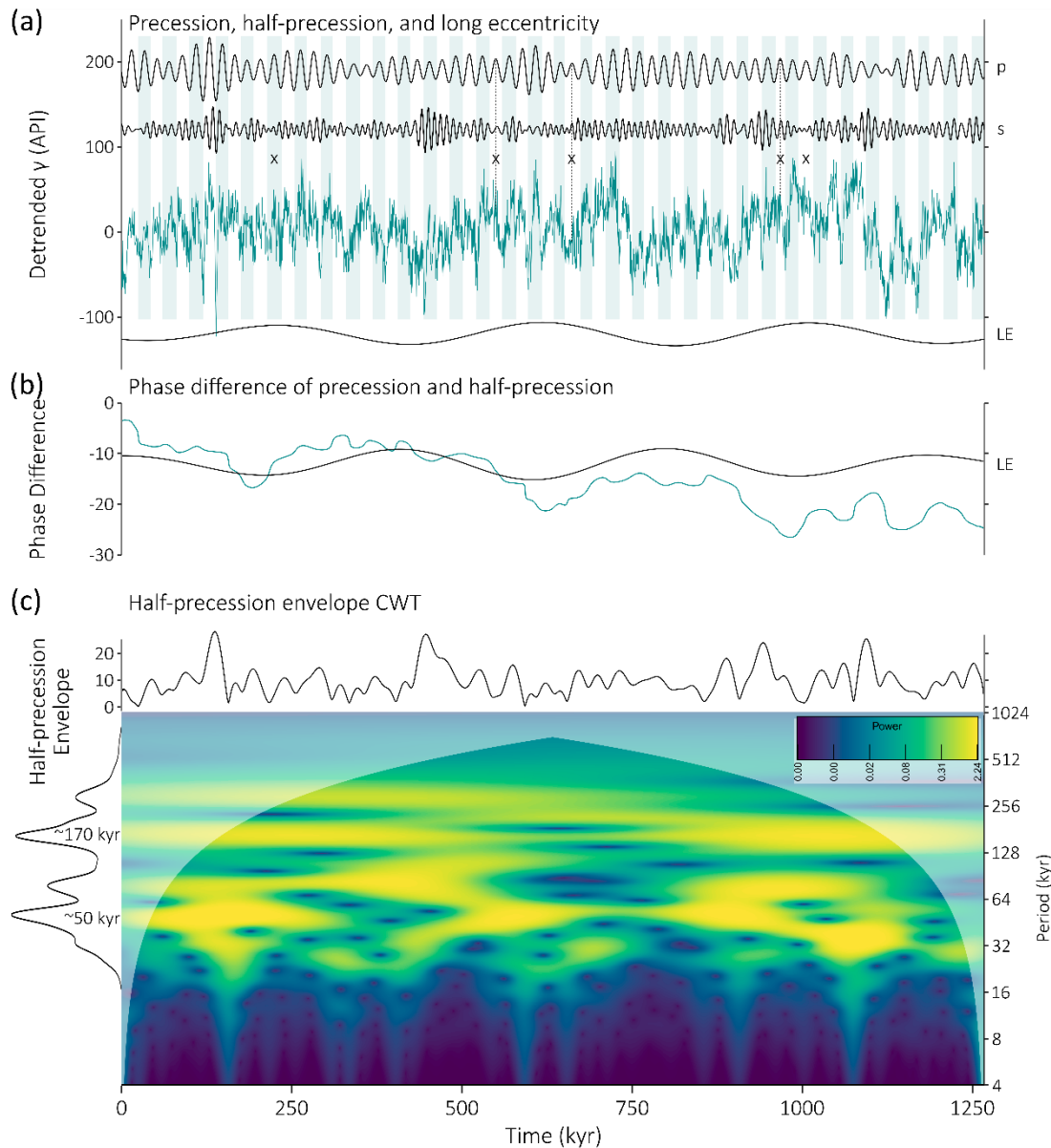


Fig. 9. Half-precession cyclicity in the Sherburne Formation γ -signal. a) Detrended γ -signal (cyan) tuned according to AM2 and bandpass filter output of ~ 9.5 kyr sub-Milankovitch ‘half-precession’ cycles (s; black), precession (p; black) and 405 kyr long eccentricity (LE; black). Intervals where a 2:1 s:p-structure breaks down are marked using ‘x’, for which dashed vertical lines demarcate the temporal location of interpreted half-precession cycles. b) The phase difference between extracted precession and half-precession cycles (cyan) and filtered 405 kyr component (LE; black). c) Half-precession envelope (black) and continuous wavelet spectrum of the half-precession envelope revealing pronounced ~ 50 kyr and ~ 170 kyr cyclicity.

Using Taner bandpass filters, precession and the ~ 9.5 kyr sub-Milankovitch components were isolated from the γ -signal (AM2), enabling direct comparison of bundling patterns and phase coherency (Fig. 9). The robustness of the ~ 9.5 kyr bandpass filter was verified to exclude artefacts arising from filter-window parameters. Throughout the formation, two ~ 9.5 kyr cycles consistently occur per precession cycle (Fig. 9a). Only four intervals ($\sim 6\%$) deviate from this 1:2 ratio, which may reflect localized sub-precession sedimentation-rate changes,

sedimentary noise (e.g., traditional slope-derived turbidites) or, more likely, interference from combination tones (Fig. 6). Such tones are absent from the insolation spectrum (e.g., Laskar et al., 2004) and instead reflect state-dependent climate-sediment feedbacks (Hagelberg et al., 1991; Tucker and Slingerland, 1997; Jerolmack and Paola, 2010), rather than a consistent half-precession response. The persistent ~9.5 kyr frequencies (Fig. 6; Fig. F1) and repeated two-per-precession bundling (Fig. 9a) strongly suggest half-precession cyclicity as the dominant source of sub-Milankovitch variability, with secondary contributions from nonlinear interactions. Therefore, while the identified ~9.5 kyr components cannot be interpreted as reflecting half-precession alone, we consider half-precession to be the dominant contributor and use this term as shorthand for this frequency band in the following discussion. Sub-7-kyr cyclicity is attributed to either Milankovitch combination tones or harmonics of (half-) precession (Fig. 6; Fig. F1). To further assess the relative contributions of half-precession and nonlinear sub-Milankovitch imprints, we examine the phase and amplitude modulation patterns of half-precession.

Visual inspection of the extracted precession and half-precession shows that their local extrema do not align, suggesting that the two signals are not phase locked. Such behavior is expected given the identified presence of nonlinearities (Fig. 6). To test this visual observation, the 1:2 phase-locking signal at a given time index (t) was calculated (Fig. 9b) using the instantaneous phases (using a Hilbert transform) of filtered precession and half-precession, according to:

$$\Delta\phi(t) = 2\phi_{pre}(t) - \phi_{hpre}(t) \quad (1)$$

where $\Delta\phi(t)$ represents the phase difference between the instantaneous phase of precession $\phi_{pre}(t)$ and 'half-precession' $\phi_{hpre}(t)$ (Rosenblum et al., 1996). The phase locking value (PLV) was calculated to quantify the consistency of the phase difference over (t), with values of 0 indicating random phase difference (i.e., no locking) and 1 indicating perfect phase locking:

$$PLV = \left| \frac{1}{N} \sum_{t=1}^N e^{i\Delta\phi(t)} \right| \quad (2)$$

where N represents the number of datapoints and the $ei\Delta\phi(t)$ term expresses the phase difference as a unit-length complex vector (Lachaux et al., 1999). A PLV of ~0.28 indicates that the phase difference between precession and half-precession is not entirely random, but highly unstable. This behavior is illustrated in Fig. 9b, which shows a steadily decreasing baseline in $\Delta\phi(t)$ with a superimposed ~405 kyr fluctuation that strongly resembles long eccentricity and is consistently anti-phased to the 405 kyr LE extracted from the γ -signal (Fig. 9). From this, we infer that eccentricity influenced the phase evolution of precession and half-precession.

To further investigate the origin of sub-Milankovitch cyclicity, the envelope of the extracted half-precession, obtained through a Hilbert transform, was examined to assess the longer-period amplitude modulation of this band. A CWT shows that the resulting envelope is dominated by ~50 kyr and ~170 kyr variability. At first glance, this appears unexpected, because eccentricity modulates precession and one might therefore anticipate ~100 kyr (short eccentricity) and ~405 kyr (long eccentricity) modulation in the envelope of the half-precession signal. Such a ~170 kyr component is intriguing given it broadly corresponds to the $s_3 - s_6$ “metronome” (Laskar, 2020), which has a periodicity of 150 to 177 kyr (Zeebe and Lantink, 2024) but, given that the 173 kyr component extracted from the γ -signal is relatively weak (Fig. 4, 5), we refrain from attempting to further interpret this feature.

4.6. Paleoclimatic and Paleodepositional Response

We now set insights obtained through cyclostratigraphic analysis of the Sherburne Formation γ - and χ -signals into a broader paleoclimatic perspective, providing new constraints on how astronomical forcing shaped the late Givetian paleoclimate and depositional processes in the Appalachian Basin. The cyclic variability points to a complex interplay among precession, obliquity, and eccentricity, reflecting a climate system responding to changes in total insolation, for example through precession-obliquity interferences, in combination with nonlinear climate-sediment interactions.

An obliquity imprint is – at first glance – somewhat surprising at a ~30° S paleolatitude because the direct effect of obliquity on insolation is strongest at high latitudes and is less pronounced near the equator (Milankovitch 1941, Berger et al., 1993, 2006; Laskar et al., 2004). Indeed, focusing on a Belgian record, De Vleeschouwer et al. (2012) suggested that the influence of high-latitude climate variability was very limited (or absent) at ~7° S paleolatitude during the Middle Devonian. Yet, the detected combination tones involving obliquity (Fig. 6) and the clear precession-obliquity interference patterns in the γ -signal (Fig. 7A) unmistakably reaffirm the imprint of obliquity on the Sherburne Formation γ -signal, identified through spectral analysis (Fig. 4, 5). This suggests that obliquity was also transmitted into the subtropics through climate-system pathways – rather than direct insolation forcing alone – consistent with a dynamically coupled tropical-subtropical climate system. Dynamic variations of, for example, the Intertropical Convergence Zone (ITCZ) net precipitation (De Vleeschouwer et al., 2012) are expected to respond to both precession and obliquity, which modulate seasonal and annual-mean temperature gradients, respectively (Schneider et al., 2014). This interplay between tropical hydrology and higher-latitude forcing is consistent with modeling results of Tuenter et al. (2003), who demonstrated – for the modern African summer monsoon – that obliquity-driven high-latitude climate variability can be transmitted into the tropics and subtropics through large-scale atmospheric circulation. Moreover, Zhang et al. (2022) reported combined precession and obliquity forced ITCZ migration at 5-20° N during

the Early Cambrian as a result of interhemispheric pressure contrasts, thereby influencing the lower-latitude hydrological cycle.

Recovery of a relatively strong obliquity imprint could suggest climatic teleconnections from high latitudes (e.g., Meyers, 2012; Zeeden et al., 2019) involving changes in ice volume (cf. De Vleeschouwer et al., 2014). Although direct evidence of continental ice during the Middle Devonian is absent, the potential presence of continental ice during this cooler interval (Becker et al., 2020) has long been pondered (Elrick et al., 2009; Dahl et al., 2022) and on eustatic sea-level fluctuations. Although a glacio-eustatic regime could strongly contribute to the amplification of obliquity, it should be stated that a relatively strong obliquity imprint does not per se reflect the presence of continental ice (Gérard et al., 2026). Moreover, Bosmans et al. (2015) reported that “*obliquity-induced changes in tropical climate can occur without high-latitude ice sheet fluctuations*” and that tropical circulation changes (in their climate model) are consistent with obliquity-induced changes in the cross-equatorial insolation gradient. The effect of changes in insolation on high-latitude productivity in combination with ocean circulation changes influenced by obliquity at higher latitudes (i.e., thermohaline circulation) offer alternative or additional explanations for the translation and amplification of obliquity at lower latitudes (Gérard et al., 2025; 2026). As currently reconstructed (Fig. 1), the paleogeography of the northern Appalachian Basin is restricted and therefore prone to ocean circulation changes (see Zambito et al., 2012, for discussion of circulation changes in the Sherburne-preceding Tully Formation). Ultimately, the Sherburne Formation record underscores that subtropical climate during the Middle Devonian was not isolated from high-latitude forcing, but dynamically linked via a combination of teleconnection, circulation dynamics and, potentially, ice-volume variability.

Half-precession is generally considered unique to equatorial insolation forcing (Berger and Loutre, 1997; Berger et al., 2006). Recovery of such frequencies from detrital influx at relatively high latitudes ($\sim 30^\circ$ S) therefore suggests considerable interactions with tropical climate variability, likely mediated through the hydrological cycle (cf., western equatorial Pacific; Wu et al., 2025). During the Middle Devonian, one of the most potent drivers of hydrological cycle variability was the precession-forced monsoonal circulation over the Euramerican continent within the pantropical belt (De Vleeschouwer et al., 2012). Migration of the intertropical convergence zone (ITCZ) modulated monsoonal activity, producing wet-dry cycles that governed detrital input and composition (De Vleeschouwer et al., 2012; 2014; Zhang et al., 2022; Wichern et al., 2024). Yet, the Sherburne Formation was deposited at an estimated paleolatitude of $\sim 30^\circ$ S – potentially beyond the latitudinal range typically reached by the ITCZ. Although De Vleeschouwer et al. (2014) inferred a substantial southward ITCZ displacement toward the Appalachian Basin during the Late Devonian SH summer (see also Wichern et al., 2024), such migration was likely part of a broader dynamical framework. In particular, ITCZ position should be viewed in conjunction with Hadley-cell behavior, which

governs the large-scale redistribution of heat and moisture across the tropics and subtropics (e.g., Bian et al., 2025). Given the sensitivity of the hydrological cycle to astronomical forcing, it is hypothesized that similar mechanisms contributed to amplification of half-precession at higher latitudes, alongside ocean-circulation-driven teleconnections (Wu et al., 2025). Fundamentally, climatic precession and half-precession cycles are both driven by eccentricity-modulated precession (Berger and Loutre, 1997; Berger et al., 2006). Even though two half-precession cycles occur per precession cycle (Berger et al., 2006), their insolation expression in terms of amplitude and phase may differ depending on latitude and geometry (e.g., Wu et al., 2025). This would, in addition to high-frequency sedimentation rate changes, and the presence of combination tones as a result of nonlinearities in the climate-sediment system, explain why the extracted half-precession cycles are not phase-locked with precession (Fig. 9). Additionally, climate simulations show that the presence of ice sheets can further modulate the amplitude and phase of half-precession responses by altering the background climate state (Wu et al., 2025). Together, these mechanisms offer an explanation that accounts for the modulated, non-phase-locked half-precession signal recovered from the Sherburne Formation.

4.7. Conclusions

The cyclostratigraphic framework developed for the Sherburne Formation, guided by the 405 kyr long-eccentricity metronome, reveals substantial astronomical forcing of detrital influx in the late Givetian Appalachian Basin at $\sim 30^\circ$ S. Our results support a precession-dominated hydrological regime with a distinct obliquity imprint and persistent half-precession cycles. Based on the recognized Milankovitch imprint, the new cyclostratigraphic age model constrains the duration of the Sherburne Formation in the Cargill #17 core to 1252 ± 29 kyr, and constrains the durations of the regional Fir Tree, Hubbard Quarry, and Lodi events to 108 ± 29 kyr, 214 ± 29 kyr, and at least 200 ± 29 kyr, respectively – consistent with one to two short eccentricity cycles. The onset of the global Frasnian Crisis unfolds during a 405 kyr long eccentricity maximum and, possibly, during an extremum of the 1.2 Myr $s_4 - s_3$ obliquity-modulation cycle governing eustatic sea-level variations.

The recovery of half-precession and obliquity in the pantropical belt highlights a complex interplay of equatorial and high-latitude dynamics, shaping changing climatic conditions. Nonlinear climate-sediment dynamics further influenced how these astronomical rhythms were transmitted into the basin, affecting their expression in the detrital record. This interplay can be understood in terms of the broader climatic mechanisms at work: climatic teleconnections, monsoonal dynamics, ITCZ and Hadley-cell migration, ocean-circulation changes, and possibly glacio-eustasy, collectively exerted considerable control over the paleodepositional environment. Together, these mechanisms exerted strong control over sediment supply to the Appalachian Basin, underscoring the strong and complex influence of astronomical forcing on the late Givetian climate.

Conflict of Interest

The authors declare there are no conflicts of interest in this manuscript.

Acknowledgements

This is a contribution to the "Projet de Recherche" funded by the Belgian National Fund of Scientific Research (FNRS), contract T.0037.22 "WarmAnoxia". Thomas J. Algeo is acknowledged for supervising the GRS measurements of the Cargill #17 Core at the University of Cincinnati, Ohio (USA) by Kyleigh Hope, A.J. Kmetz, and Thomas Gott. Magnetic susceptibility data collection was undertaken by Beloit College undergraduates May Willison and Olivia Farbarik; this work was supported by the donors of ACS Petroleum Research Fund under Undergraduate Research Grant 60525-UR2 to J. Zambito.

Author contributions

Jarno J.C. Huygh: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft. Carlton E. Brett: Funding acquisition, Investigation, Project administration, Resources, Supervision, Validation, Writing – review & editing. James J. Zambito IV: Funding acquisition, Investigation, Project administration, Resources, Validation, Writing – review & editing. Loïc Sablon: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft. Justin Gérard: Conceptualization, Investigation, Validation, Writing – review & editing. Ian J. Forsythe: Data curation, Investigation, Supervision, Validation, Writing – review & editing. Michel Crucifix: Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Writing – review & editing. Anne-Christine Da Silva: Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Writing – review & editing.

Data and Code Availability Statement

All data and R-code can be found via <https://doi.org/10.5281/zenodo.19483389>.

References

- Arts, M. C. M., 2023. WaverideR: Extracting Signals from Wavelet Spectra. <https://CRAN.R-project.org/package=WaverideR>
- Arts, M. C. M., Corradini, C., Pondrelli, M., Pas, D., Da Silva, A.-C., 2024. Age and orbital forcing in the upper Silurian Cellon section (Carnic Alps, Austria) uncovered using the WaverideRR package. *Front. Earth Sci.*; 12, <https://doi.org/10.3389/feart.2024.1357751>
- Baird, G. C., Zambito, J. J. VI, Brett, C. E., 2023. Tully Formation and pre-Frasnian Genesee Group succession, 259-378, In: *Devonian of New York, Volume 2: Lower to upper Givetian (Middle Devonian) stage*, Ver Straeten, C. A., Over, D. J., Woodrow, D. (eds.), *Bull. Am. Paleontol.*; 405-406. <https://doi.org/10.32857/bap.2023.405.03>
- Becker, R. T., Königshof, P., Brett, C. E., 2016. Devonian climate, sea level and evolutionary events: an introduction. In: *Devonian climate, sea level and evolutionary events*, Becker, R. T., Königshof, P., Brett, C. E. (eds.), *Geol. Soc. Lond., Spec. Publ.*, 423, 1-10.
- Becker, R. T., Marshall, J. E. A., Da Silva, A.-C., 2020. The Devonian Period. In: *Gradstein, F. M., Ogg, J. G., Schmitz, M. D. And Ogg, G. (eds.), The Geologic Time Scale 2020; chapter 22*, 733-810. <https://doi.org/10.1016/B978-0-12-824360-2.00022-X>
- Berger, A. L., 1987. Long-term variations of caloric insolation resulting from the Earth's orbital elements. *Quat. Res.*; 9, 139-167.
- Berger, A. L., 1988. Milankovitch Theory and Climate. *Rev. Geophys.*; 26, 4, 624-657. <https://doi.org/10.1029/RG026i004p00624>
- Berger, A., and Loutre, M.F., 1997. Intertropical latitudes and precessional and half-precessional cycles. *Science*; 278, 1476-1478.
- Berger, A., Loutre, M.F., Mélice, J.L., 2006. Equatorial insolation: from precession harmonics to eccentricity frequencies. *Clim. Past*; 2, 131-136
- Bian, J., Räisänen, J., and Seppä, H., 2025. Mid-Holocene Intertropical Convergence Zone migration: connection with Hadley cell dynamics and impacts on terrestrial hydroclimate. *Clim. Past*; 21, 7, 1209-1233. <https://doi.org/10.5194/cp-21-1209-2025>
- Bosmans, J. H. C., Hilgen, F. J., Tüenter, E., Lourens, L. J., 2015. Obliquity forcing of low-latitude climate. *Clim. Past*; 11, 1335-1346. doi:10.5194/cp-11-1335-2015
- Brett, C. E., Baird, G. C., Bartholomew, A. J., DeSantis, M. K., Ver Straeten, C. A., 2011. Sequence stratigraphy and a revised sea-level curve for the Middle Devonian of eastern North America. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 304, 21-53. doi:10.1016/j.palaeo.2010.10.009
- Brett, C. E., Zambito, J. J. IV, McLaughlin, P. I., Emsbo, P., 2020. Revised perspectives on Devonian biozonation and environmental volatility in the wake of recent time-scale revisions. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 549, 108843. <https://doi.org/10.1016/j.palaeo.2018.06.037>.
- Choudhury, S., Shah, S., Thornhill, N., 2008. Diagnosis of process nonlinearities and valve stiction: Data driven approaches, Chapter 3, 29-41. Springer, ISBN: 978-3-540-79223-9. doi:10.1007/978-3-540-79224-6
- Copper, P., and Scotese, C. R., 2002. Megareefs in Middle Devonian supergreenhouse climates, In: Chan, M. A., and Archer, A. W. (eds.), *Extreme depositional environments: Mega end members in geologic time*: Boulder, Colorado, *Geol. Soc. America Spec. Pap.*, 370, 209-230.
- Da Silva, A.-C., Potma, K., Weissenberger, J. A. W., Whalen, M. T., Humblet, M., Mabilie, C., Boulvain, F., 2009. Magnetic susceptibility evolution and sedimentary environments on carbonate platform sediments and atolls, comparison of the Frasnian from Belgium and Alberta, Canada. *Sed. Geol.*; 2014, 3-18. doi:10.1016/j.sedgeo.2008.01.010
- Da Silva, A.-C., Dekkers, M. J., Mabilie, C., Boulvain, F., 2012. Magnetic susceptibility and its relationship with paleoenvironments, diagenesis and remagnetization: examples from the Devonian carbonates of Belgium. *Stud. Geophys. Geod.*; 56, 677-704. doi:10.1007/s11200-011-9005-9

- Da Silva, A.-C., Dekkers, M. J., De Vleeschouwer, D., Hladil, J., Chadimova, L., Slavík, L., Hilgen, F. J., 2018. Millennial-scale climate changes manifest Milankovitch combination tones and Hallstatt solar cycles in the Devonian greenhouse world. *Geology*; 47, 19-22. <https://doi.org/10.1130/G45511.1>
- Da Silva, A.-C., Sinnesael, M., Claeys, P., Davies, J. H. F. L., de Winter, N. J., Percival, L. M. E., Schaltegger, U., De Vleeschouwer, D., 2020. Anchoring the Late Devonian mass extinction in absolute time by integrating climatic controls and radio-isotopic dating. *Sci. Rep.*; 10, 12940. <https://doi.org/10.1038/s41598-020-69097-6>.
- De Vleeschouwer, D., Da Silva, A.-C., Boulvain, F., Crucifix, M. & Claeys, P., 2012. Precessional and half-precessional climate forcing of Mid-Devonian monsoon-like dynamics. *Clim. Past.*; 8, 337–351.
- De Vleeschouwer, D., Crucifix, M., Bounceur, N. & Claeys, P., 2014. The impact of astronomical forcing in the Late Devonian greenhouse climate. *Glob. Planet. Change*; 120, 65–80.
- De Vleeschouwer, D., Da Silva, A.-C., Sinnesael, M., Chen, D., Day, J. E., Whalen, M. T., Guo, Z., Claeys, P., 2017. Timing and pacing of the Late Devonian mass extinction event regulated by eccentricity and obliquity. *Nat. Comm.*; 8, 2268. doi:10.1038/s41467-017-02407-1.
- De Vleeschouwer, D., Percival, L. M. E., Wichern, N. M. A., Batenburg, S. J., 2024. Pre-Cenozoic cyclostratigraphy and palaeoclimate responses to astronomical forcing. *Nat. Rev. Earth Environ.*; 5, 56-75. <https://doi.org/10.1038/s43017-023-00505-x>.
- de Witt, Jr., W., and Colton, G. W., 1978. Stratigraphy and conodonts of the Genesee Formation (Devonian) in western and central New York. U. S. Geological Survey Professional Paper, 1032-A, 22 pp., 7 pl.
- Ellwood, B. B., Crick, R. E., El Hassani, A., Benoist, S. L., Young, R. H., 2000. Magnetosusceptibility event and cyclostratigraphy method applied to marine rocks: Detrital input versus carbonate productivity. *Geology*; 28, 12, 1135-1138. [https://doi.org/10.1130/0091-7613\(2000\)028<1135:MEACMA>2.3.CO;2](https://doi.org/10.1130/0091-7613(2000)028<1135:MEACMA>2.3.CO;2)
- Gérard, J., Pohl, A., Sablon, L., Huygh, J. J. C., Da Silva, A.-C., Crucifix, M., 2026. Spatially contrasted response of Devonian anoxia to astronomical forcing. *EGUsphere*, 2025-4238 (preprint). <https://doi.org/10.5194/egusphere-2025-4238>
- Gérard, J., Sablon, L., Huygh, J. J. C., Da Silva, A.-C., Pohl, A., Vérard, C., Crucifix, M., 2025. Exploring the mechanisms of Devonian oceanic anoxia: impact of ocean dynamics, palaeogeography, and orbital forcing. *Clim. Past*; 21, 239-260. <https://doi.org/10.5194/cp-21-239-2025>.
- Hagelberg, T., Pisias, N., Elgar, S., 1991. Linear and nonlinear couplings between orbital forcing and the marine $\delta^{18}\text{O}$ record during the late Neogene. *Paleoceanogr.*; 6, 6, 729-746.
- Hasselmann, K., Munk, W., MacDonald, G., 1963. Bispectra of Ocean Waves, Chapter 8 In: *Proceedings of the Symposium on Time Series Analysis held at Brown University, June 11-14, 1962*, Rosenblatt, M. (ed.). John Wiley & Sons, Inc.; 125-139
- Hays, J. D., Imbrie, J. & Shackleton, N. J., 1976. Variations in the Earth's orbit: pacemaker of the ice ages. *Science* 194, 1121–1132.
- Hinich, M.J., 1982. Testing for Gaussianity and linearity of a stationary time series. *J. Time Ser. Anal.*; 3, 3, 169-176.
- Huybers, P. J. and Wunsch, C., 2004. A depth-derived Pleistocene age-model: Uncertainty estimates, sedimentation variability, and nonlinear climate change. *Paleoceanogr.*; 19, PA1028, 1-24. doi:10.1029/2002PA000857
- Huygh, J. J. C., Algeo, T. J., Sageman, B. B., Arts, M. C. M., Ver Straeten, C. A., Over, D. J., Gérard, J., Sablon, L., Crucifix, M., Da Silva, A.-C., 2026. *Glob. Plan. Change*; 257:105216. <https://doi.org/10.1016/j.gloplacha.2025.105216>
- Imbrie, J. and Imbrie, J. Z., 1979. Modeling the climatic response to orbital variations. *Science*; 207, 29, 943-953.
- Jerolmack, D. J. and Paola, C., 2010. Shredding of environmental signals by sediment transport. *Geophys. Res. Lett.*; 37, 19, L19401. doi:10.1029/2010gl044638

- Kirchgasser, W. T., 1994. Early morphotypes of *Ancyrodella rotundiloba* at the Middle/Upper Devonian boundary. In: *Studies in Stratigraphy and Paleontology in honor of D. W. Fisher, E. Landing* (ed.), New York State Museum Bulletin, 481, 117-134.
- Klapper, G. (1989). The Montagne Noire Frasnian (Upper Devonian) conodont succession. In: McMillan, J.N., Embry, A.F., Glass, D. J. (eds.), *Devonian of the World*, CSPG Memoir, 14, 3, 449-468.
- Lachaux, J.-P., Rodriguez, E., Martinerie, J., Varela, F.J., 1999. Measuring phase synchrony in brain signals. *Hum. Brain Mapping*; 8, 194-208.
- Laurin, J., Meyers, S. R., Uličný, D., Jarvis, I., Sageman, B. B., 2015. Axial obliquity control on the greenhouse carbon budget through middle- to high-latitude reservoirs. *Paleoceanogr.*; 30, 2, 133-149. <https://doi.org/10.1002/2014PA002736>
- Laskar, J., 2020. Astrochronology. In: Gradstein, F. M., Ogg, J. G., Schmitz, M. D. And Ogg, G. (eds.), *The Geologic Time Scale 2020*, chapter 4, 139-158.
- Laskar, J., Robutel, P., Joutel, F., Gastineau, M., Correia, A. C. M., Levrard, B., 2004. A long-term numerical solution for the insolation quantities of the Earth. *Astron. Astrophys.*; 428, 1, 261-285. <https://doi.org/10.1051/0004-6361:20041335>.
- Lourens, L. J., Sluijs, A., Kroon, D., Zachos, J. C., Thomas, E., Röhl, U., Bowles, J., Raffi, I., 2005. Astronomical pacing of late Paleocene to early Eocene global warming events. *Nature*; 435, 1083-1087. doi:10.1038/nature03814
- Meyers, S. R., 2012. Seeing red in cyclic stratigraphy: Spectral noise estimation for astrochronology. *Paleoc.*; 27, PA3228. doi:10.1029/2012PA002307
- Meyers, S. R., 2014. Astrochron: An R Package for Astrochronology. <https://cran.r-project.org/package=astrochron>
- Meyers, S. R., 2015. The evaluation of eccentricity-related amplitude modulation and bundling in paleoclimate data: An inverse approach for astrochronologic testing and time scale optimization. *Paleoceanogr.*; 30, 12, 1625-1640. <https://doi.org/10.1002/2015PA002850>.
- Meyers, S. R. and Hinnov, L. A., 2010. Northern hemisphere glaciation and the evolution of Plio-Pleistocene climate noise. *Paleoceanogr.*; 25, PA3207, 1-11. <https://doi.org/10.1029/2009PA001834>
- Meyers, S. R., Sageman, B. B., Hinnov, L. A., 2001. Integrated quantitative stratigraphy of the Cenomanian-Turonian Bridge Creek limestone member using evolutive harmonic analysis and stratigraphic modeling. *J. Sed. Res.*; 71, 4, 628-644. doi:10.1306/012401710628
- Milankovitch, M., 1941. *Kanon der Erdbestrahlung und seine Anwendung auf das Eiszeitenproblem*, Royal Serbian Academy Special Publication, 133, 1-633
- Mudelsee, M., 2010. *Climate time series analysis: Classical statistical and bootstrap methods*. Springer. ISBN 978-90-481-9481-0. Doi:10.1007/978-90-481-9482-7
- Mulder, T., Syvitski, J. P. M., Migeon, S., Faugères, J.-C., Savoye, B., 2003. Marine hyperpycnal flows: initiation, behavior and related deposits. A Review. *Mar. Pet. Geol.*, 20, 861-882. doi:10.1016/j.marpetgeo.2003.01.003
- Paillard, D., 1998. The timing of Pleistocene glaciations from a simple multiple-state climate model. *Nature*; 391, 378-381.
- Raup, D. M. and Sepkoski, J. J., Jr., 1982. Mass extinctions in the marine fossil record. *Science*; 215, 4539, 1501-1503. doi:10.1126/science.215.4539.1501.
- Rial, J. A., Pielke, R. A. Sr., Beniston, M., Claussen, M., Canadell, J., Cox, P., Held, H., De Noblet-Ducoudré, N., Prinn, R., Reynolds, J. F., Salas, J. D., 2004. Nonlinearities, feedbacks and critical thresholds within the Earth's climate system. *Clim. Change*; 65, 11-38.
- Rickard, L. V. 1975. *Correlation of the Silurian and Devonian Rocks in New York State*. New York State Museum and Science Service, Map and Chart Series, 24, 16 pp. and 4 pl.
- Rosenblum, M. G., Pikovsky, A. S., Kurths, J., 1996. Phase synchronization of chaotic oscillators. *Phys. Rev. Lett.*; 76, 11, 1804-1807.

- Saltzman, B. (2002). *Dynamical Paleoclimatology: Generalized Theory of Global Climate Change*. Academic Press, San Diego, 354 pp, ISBN 0-12-617331-1.
- Schneider, T., Bischoff, T., Haug, G.H., 2014. Migrations and dynamics of the intertropical convergence zone. *Nature*; 513, 45-53. doi:10.1038/nature13636
- Scotese, C. R., 2021. An atlas of Phanerozoic paleogeographic maps: The seas come in and the seas go out. *Annu. Rev. Earth Planet. Sci.*; 49, 669-718. <https://doi.org/10.1146/annurev-earth-081320-064052>
- Stein, W. E., Berry, C. M., Morris, J. L., VanAller Hernick, L., Mannolini, F., Ver Straeten, C., Landing, E., Marshall, J. E. A., Wellman, C. H., Beerling, D. J., Leake, J. R., 2020. Mid-Devonian *Archeopteris* roots signal revolutionary change in earliest fossil forests. *Curr. Biol.*; 30, 1-11. doi:10.1016/j.cub.2019.11.067
- Sullivan, N. B., Meyers, S. R., Levy, R. H., McKay, R. M., Golledge, N. R., Cortese, G., 2023. Millennial-scale variability of the Antarctic ice sheet during the early Miocene. *Earth Atmos. Planet. Sci.*; 120, 39, 1-8, e2304152120. <https://doi.org/10.1073/pnas.2304152120>
- Thomson, D. J., 1982. Spectrum estimation and harmonic analysis. *Proc. IEEE*; 70, 9, 1055-1096.
- Tucker, G. E., and Slingerland, R., 1997. Drainage basin responses to climate change. *Water Resour. Res.*; 33, 8, 2031-2047. doi:10.1029/97wr00409
- Tuenter, E., Weber, S. L., Hilgen, F. J., Lourens, L. J., 2003. The response of the African summer monsoon to remote and local forcing due to precession and obliquity. *Glob. Plan. Change*; 36, 219-235. doi:10.1016/S0921-8181(02)00196-0
- Ver Straeten, C. A., 2010, Lessons from the foreland basin: Northern Appalachian basin perspectives on the Acadian orogeny. In: Tollo, R. P., Bartholomew, M. J., Hibbard, J. P., and Karabinos, P. M., (eds.), *From Rodinia to Pangea: The Lithotectonic Record of the Appalachian Region*: Geological Society of America Memoir 206, 251–282, doi: 10.1130/2010.1206(12).
- Ver Straeten, C. A., Over, D. J., & Woodrow, D. L. (eds.). 2023. *Devonian of New York, Volume 2: Lower to Upper Givetian (Middle Devonian) Stage*. Paleontol. Res. Inst., Bull. Am. Paleontol.
- Ver Straeten, C. A., 2023. An introduction to the Devonian Period, and the Devonian in New York State and North America. In: Ver Straeten, C. A., Over, D. J. and Woodrow, D. (eds.), *Devonian of New York, Volume 1: Introduction and Pridoli to lower Givetian (Upper Silurian to Middle Devonian) stages*. Bull. Am. Paleontol.; 403-404. doi:10.32857/bap.2023.403.03
- von Döbenek, T., and Schmieder, F., 1999. Using rock magnetic proxy records for orbital tuning and extended time series analysis into the super- and sub-Milankovitch bands. In: *Use of proxies in paleoceanography: Examples from the South Atlantic*, Fischer, G., Wefer, G., (eds.), Springer-Verlag Berlin Heidelberg, 601-603.
- Waltham, D., 2015. Milankovitch period uncertainties and their impact on cyclostratigraphy. *J. Sed. Res.*; 85, 990-998. <https://doi.org/10.2110/jsr.2015.66>
- Wichern, N. M. A., Bialik, O. M., Nohl, T., Percival, L. M. E., Becker, T. R., Kaskes, P., Claeys, P., De Vleeschouwer, D., 2024. Astronomically paced climate and carbon cycle feedbacks in the lead-up to the Late Devonian Kellwasser Crisis. *Clim. Past*; 20, 415-448. <https://doi.org/10.5194/cp-20-415-2024>
- Wilson, R. D. and Schieber, J., 2014. Muddy prodeltaic hyperpynites in the lower Genesee Group of Central New York, USA: Implications for mud transport in epicontinental seas. *J. Sediment. Res.*, 84, 866-874. <http://dx.doi.org/10.2110/jsr.2014.70>
- Wilson, R. D. and Schieber, J., 2015. Sedimentary facies and depositional environment of the Middle Devonian Genesee Formation of New York, USA. *J. Sediment. Res.*, 85, 1393-1415. <http://dx.doi.org/10.2110/jsr.2015.88>
- Wilson, R. D. and Schieber, J., 2017. Association between wave- and current-aided hyperpynites and flooding surfaces in shelfal mudstones: An integrated sedimentological, sequence stratigraphic, and geochemical approach. *J. Sediment. Res.*, 87, 1143-115. <http://dx.doi.org/10.2110/jsr.2017.62>
- Witzke, B. J., Bunker, B. J., and Rogers, F. S., 1988. Eifelian through lower Frasnian stratigraphy and deposition in the Iowa area, Midcontinent, U.S.A., In: McMillan, N. J., Embry, A. F., and Glass, D. J., (eds.),

Devonian of the World; proceedings of the 2nd international symposium on the Devonian System; Volume I, Regional synthesis: CSPG Memoir, 14, 221-250.

- Witzke, B. J., Bunker, B. J., 1996. Relative sea-level changes during the Middle Ordovician through Mississippian deposition in the Iowa area, North American Craton. In: *Paleozoic Sequence Stratigraphy*, Witzke, B. J., Ludvigson, G. A., Day, J. (eds.). GSA Spec. Pap. ISBN 9780813723068. <https://doi.org/10.1130/0-8137-2306-X.307>
- Witzke, B. J., Bunker, B. J., 1997. Sedimentation and stratigraphic architecture of a Middle Devonian (late Givetian) transgressive-regressive carbonate-evaporite cycle, Coralville Formation, Iowa area. In: *Paleozoic sequence stratigraphy, biostratigraphy, and biogeography*, Klapper, G., Murphy, M. A., Talen, J. A. (eds.). GSA Spec. Pap. ISBN 9780813723211. <https://doi.org/10.1130/SPE321>
- Wu, Z., Yin, Q., Berger, A., Guo, Z., 2025. Forcing mechanisms of the half-precession cycle in the western equatorial Pacific temperature. *Nat. Commun.*; 16, 1841. <https://doi.org/10.1038/s41467-025-57076-2>
- Zambito, J., Baird, G., Brett, C., and Bartholomew, A., 2009. Depositional sequences and paleontology of the Middle – Upper Devonian transition (Genesee Group) at Ithaca, New York: a revised lithostratigraphy for the Northern Appalachian Basin, In: *Studies in Devonian Stratigraphy*, Over, D. J. (ed.). *Paleontogr. Am.*; 63, 49-69.
- Zambito, J.J. IV, Brett, C. E., Baird, G. C., 2012. The late Middle Devonian (Givetian) global Taghanic biocrisis in its type area (northern Appalachian Basin): Geologically rapid faunal transitions driven by global and local environmental changes. In: *Earth and Life, International Year of Planet Earth*, Talent, J. A. (ed.), 677-703. doi:10.1007/978-90-481-3428-1_22
- Zambito, J. J. IV, Day, J. E., and Narkiewicz, K., 2015. New insights in the trilobite and conodont biostratigraphy of the Middle-Upper Devonian Genesee Group in eastern New York State. P. 154, In: *IGCP 596–SDS Symposium: Climate Change and Biodiversity Patterns in the Mid-Palaeozoic*, Mottequin, B., Denayer, J., Königshof, P., Prestianni, C., and Olive, S. (eds.), STRATA, série 1: Communications, 16.
- Zambito, J.J. IV, Joachimski, M. M., Brett, C. E., Baird, G. C., Aboussalam, Z. S., 2016. A carbonate isotope record for the late Givetian (Middle Devonian) global Taghanic biocrisis in the type region (northern Appalachian Basin). In: *Devonian Climate, Sea Level and Evolutionary Events*, Becker, R. T., Königshof, P., and Brett, C. E. (eds.), Geological Society, London, Special Publications, 423, 223-233. <http://doi.org/10.1144/SP423.7>
- Zeebe, R. E. and Lantink, M. L., 2024. A secular solar system resonance that disrupts the dominant cycle in Earth's orbital eccentricity ($g_2 - g_5$): Implications for astrochronology. *Astron. J.*; 167:204. <https://doi.org/10.3847/1538-3881/ad32cf>.
- Zeeden, C., Meyers, S., Hilgen, F., Lourens, L., Laskar, J., 2019. Time scale evaluation and the quantification of obliquity forcing. *Quat. Sci. Rev.*; 209, 100-113. <https://doi.org/10.1016/j.quascirev.2019.01.018>.
- Zhang, T., Li, Y., Fan, T., Da Silva, A.-C., Kuang, M., Liu, W., Ma, C., Gao, Q., Shi, J., Gao, Z., & Li, M., 2022. Orbital forcing of tropical climate dynamics in the Early Cambrian. *Glob. Planet. Change*; 219, 103985. <https://doi.org/10.1016/j.gloplacha.2022.103985>

4.8. Supplemental Information

A. MTM Power Spectra of γ (GRS) and χ (MS)

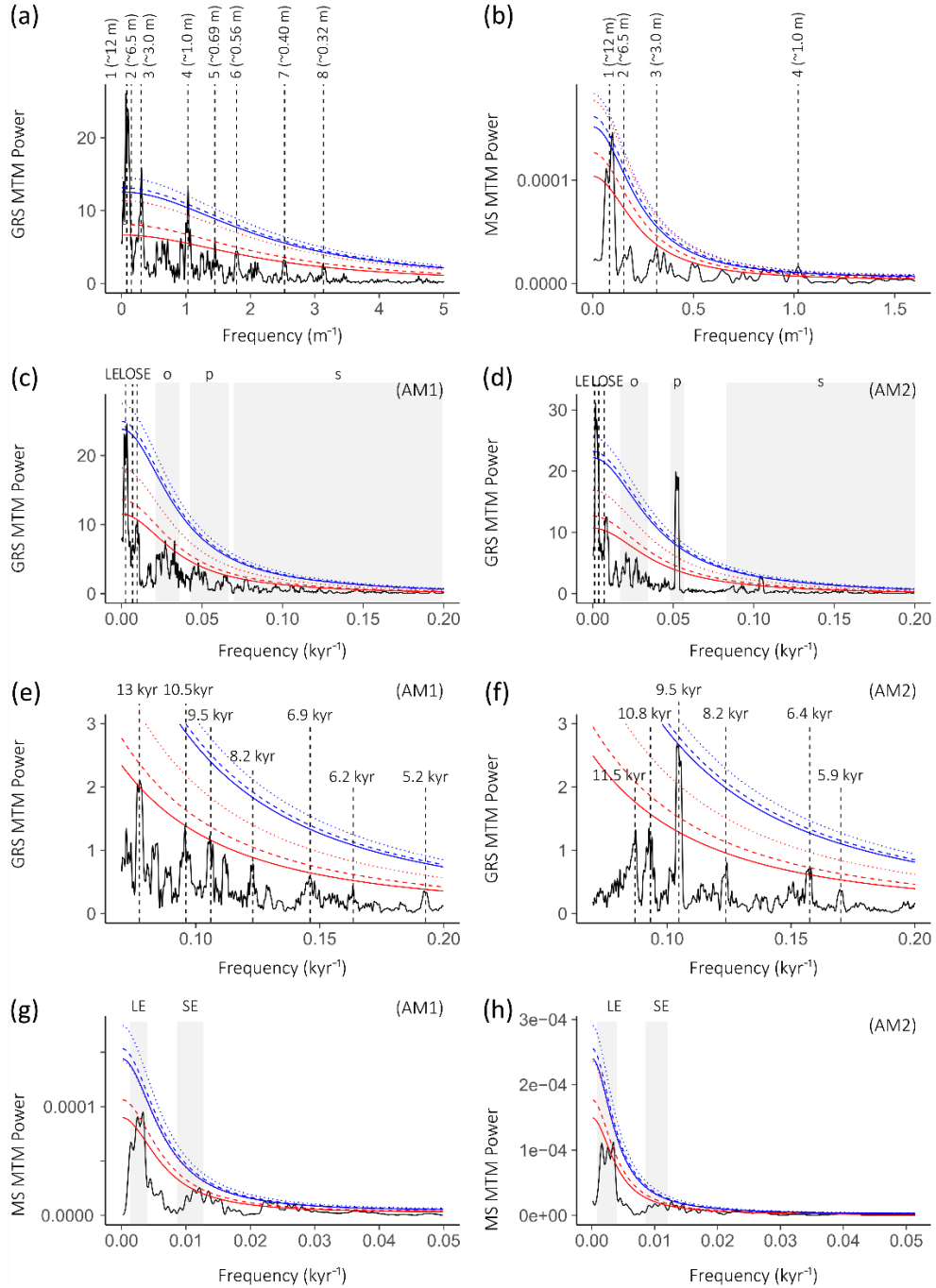


Fig. A1. MTM power spectra of γ and χ . a) MTM spectrum of γ with key components and corresponding periods numbered 1-8, b) MTM spectrum of χ with key components and corresponding periods numbered 1-4, c) MTM spectrum of γ tuned according to AM1, d) MTM of γ tuned according to AM2, e) zoom-in of panel c, f) zoom-in of panel d, g) MTM spectrum of tuned χ according to AM1, h) MTM spectrum of tuned χ according to AM2. Classical significance testing at 90, 95 and 99 % confidence levels using an autoregressive model of order 1 (AR(1)) is included for each spectrum (red full, dashed and dotted red lines, respectively), including Bonferroni corrections (blue). Gray boxes indicate spectral bands of 405 kyr long eccentricity (LE), 173 kyr long obliquity (LO), 100 kyr short eccentricity (LE), obliquity (o), precession (p) as well as sub-Milankovitch cyclicity (s).

B. Average Sedimentation Rate Estimation using TimeOpt

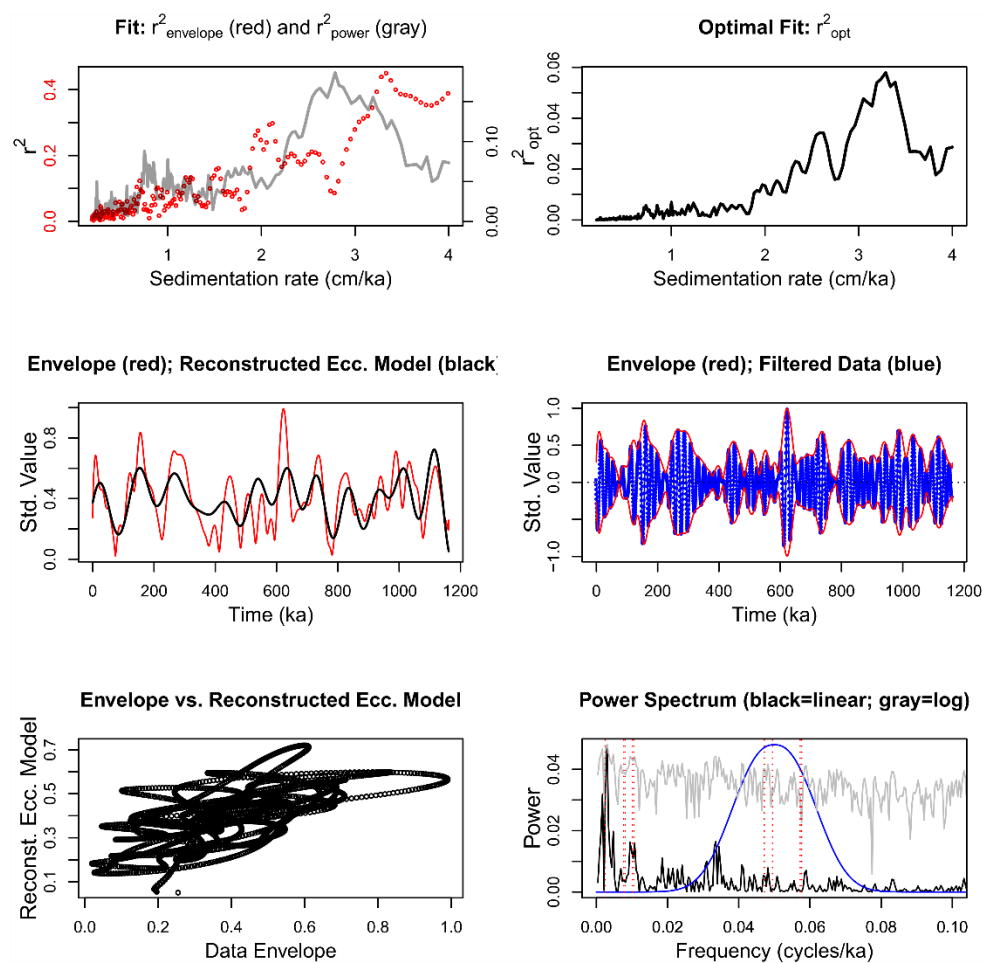


Fig. B1. TimeOpt evaluation of GRS γ , precession modulation by eccentricity. Maximum spectral power r^2 at an average sedimentation rate of 2.79 cm/kyr, maximum envelope r^2 at an average sedimentation rate of 3.34 cm/kyr, r^2_{opt} at an average sedimentation rate of 3.29 cm/kyr. Sedimentation rates tested range from 0.2 to 4.0 cm/kyr.

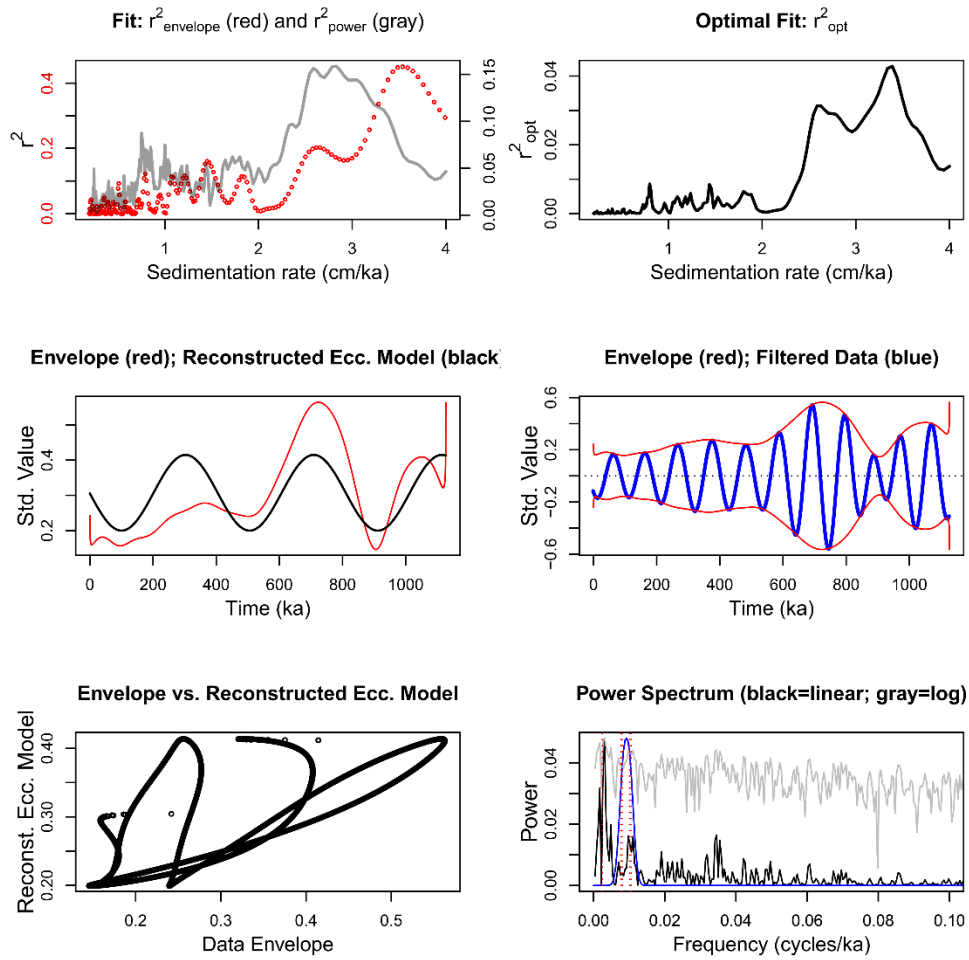


Fig. B2. TimeOpt evaluation of GRS γ , short eccentricity modulation by long eccentricity. Maximum spectral power r^2 at an average sedimentation rate of 2.83 cm/kyr, maximum envelope r^2 at an average sedimentation rate of 3.55 cm/kyr, r^2_{opt} at an average sedimentation rate of 3.39 cm/kyr. Sedimentation rates tested range from 0.2 to 4.0 cm/kyr.

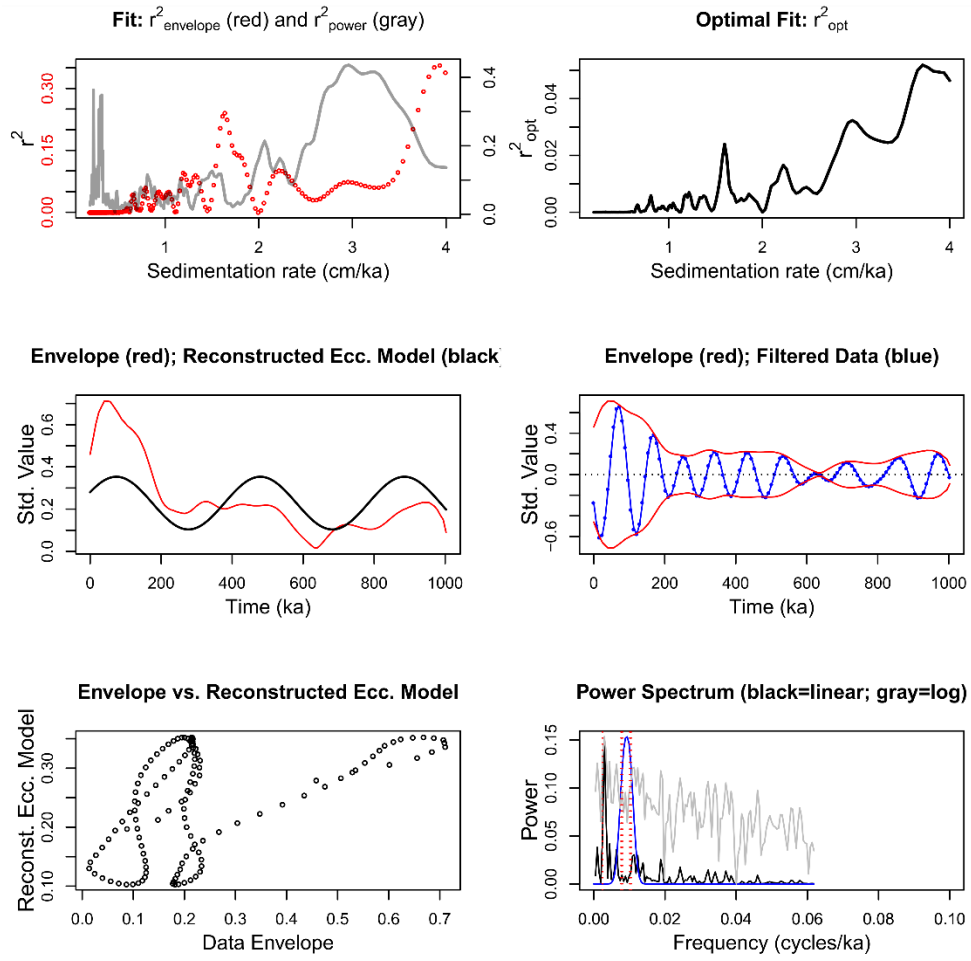


Fig. B3. TimeOpt evaluation of MS χ , short eccentricity modulation by long eccentricity. Maximum spectral power r^2 at an average sedimentation rate of 2.96 cm/kyr, maximum envelope r^2 at an average sedimentation rate of 3.94 cm/kyr, r^2_{opt} at an average sedimentation rate of 3.71 cm/kyr. Sedimentation rates tested range from 0.2 to 4.0 cm/kyr.

C. Cyclostratigraphic Age Model of the Sherburne Formation – Comparison

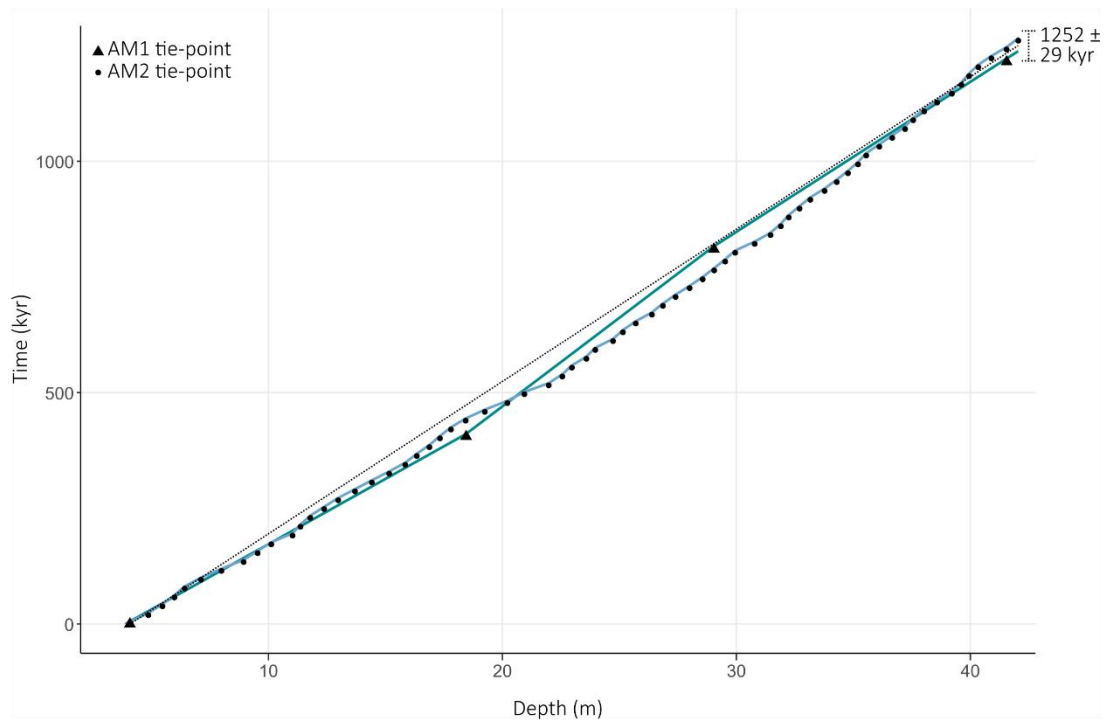


Fig. C1. Sherburne Formation sedimentation rate curves. AM1 (cyan; 405 kyr LE) depth-time tie-points indicated by black triangles, AM2 (blue; precession) depth-time tie-points indicated by black dots. Dotted line represents the average sedimentation rate according to an average estimated duration of 1252 ± 29 kyr.

D. Testing Short-eccentricity Harmonics

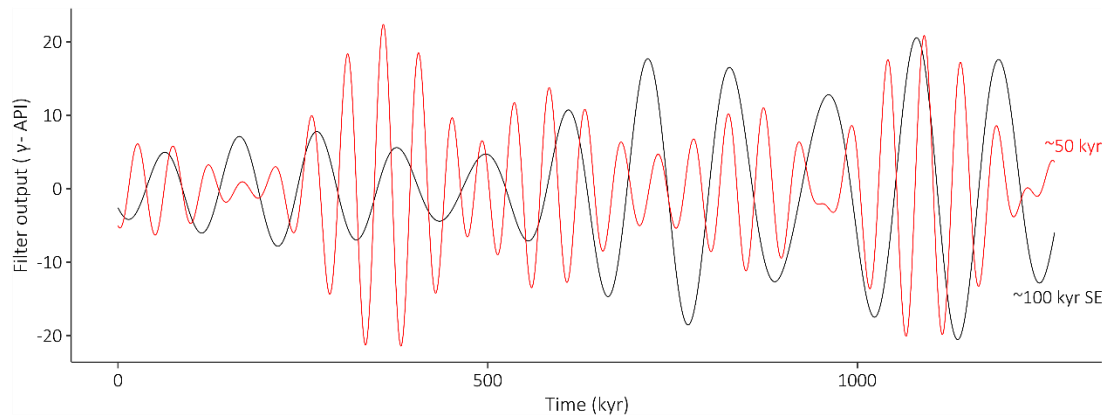


Fig. D1. Extracted short eccentricity and ~50 kyr band. 100-kyr short eccentricity (SE; black) and ~50 kyr band (red). The lack of stable phase and amplitude relationships indicates this ~50 kyr band is most probably not a harmonic of short eccentricity.

E. Precession-obliquity Combination Tones

Table E1. Precession-obliquity combination tones. Upper-right quadrant represents sum tones, lower-left quadrant difference tones. Bold numbers indicate combinations tones close to the conspicuous ~50 kyr duration.

Period (kyr)	34.3	21.2	20.2	17.47	17.34
34.3		13.1	12.7	11.6	11.5
21.2	55.5		10.3	9.6	9.5
20.2	49.1	428.2		9.4	9.3
17.47	35.6	99.3	129.3		8.7
17.34	35.1	95.2	122.5	2330.2	

F. MTM and EPSA of Tuned γ (GRS)

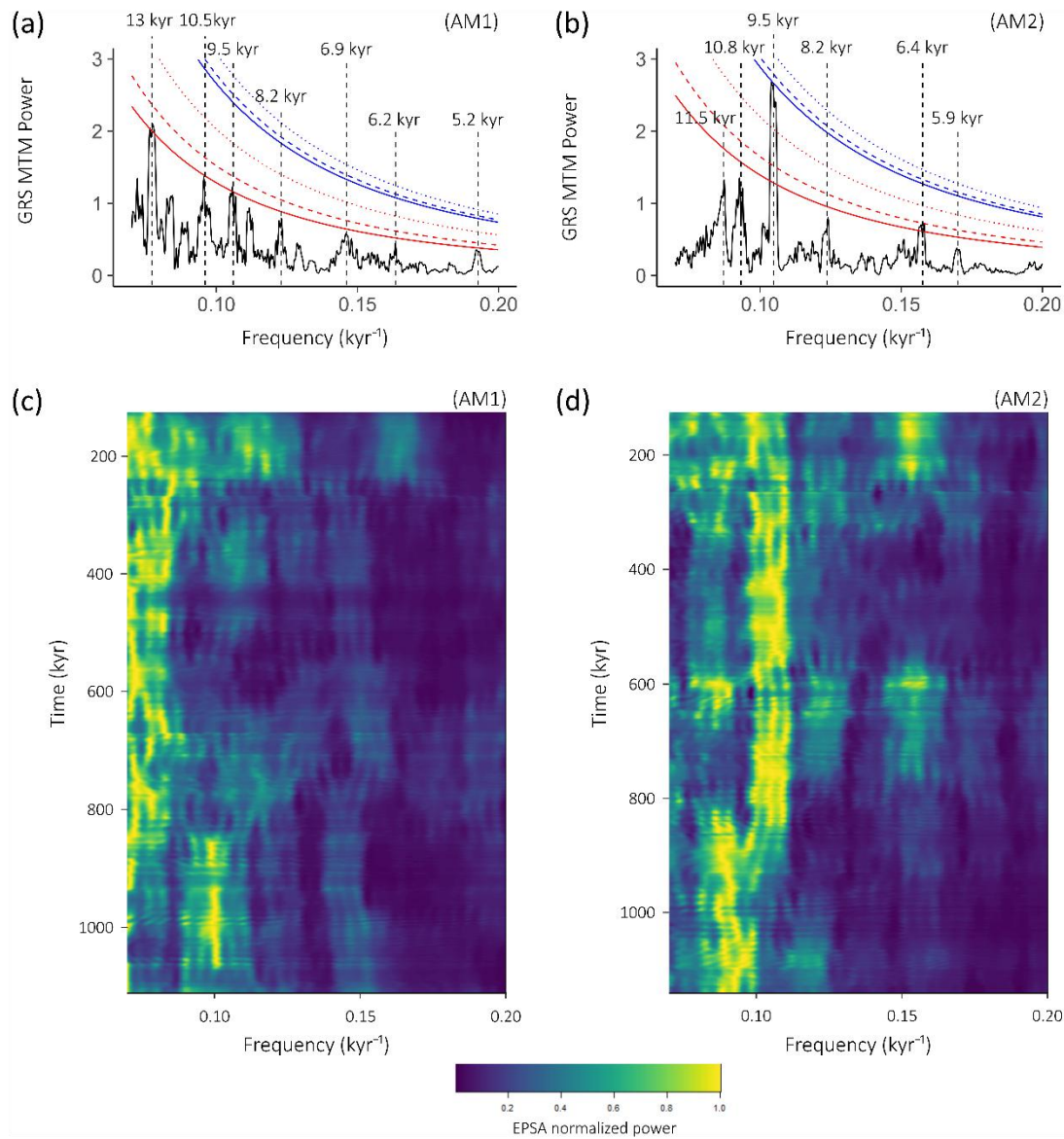


Fig. F1. Spectral analysis of Sherburne Formation sub-Milankovitch cyclicity. a) and b) MTM power spectrum of tuned γ according to AM1 and AM2, respectively, including classical significance testing at 90, 95 and 99 % confidence levels using an autoregressive model of order 1 (AR(1); red full, dashed and dotted red lines, respectively) and Bonferroni corrections (blue), c) and d) evolutive power spectrum analysis (EPSA) normalized power of tuned γ according to AM1 and AM2, respectively

5. Astronomical control on marine anoxia during the Kellwasser Crisis and Rhinestreet Event (Appalachian Basin, New York, USA) – published in *Global and Planetary Change*

Jarno J.C. Huygh¹, Thomas J. Algeo^{2,3,4}, Bradley B. Sageman⁵, Michiel Arts¹, Charles A. Ver Straeten⁶, D. Jeffrey Over⁷, Justin Gérard⁸, Loïc Sablon⁸, Michel Crucifix⁸ and Anne-Christine Da Silva¹

¹ SediCClim Laboratory, Department of Geology, Liège University, Liège, Belgium

² Department of Geosciences, University of Cincinnati, Cincinnati, OH, USA

³ State Key Laboratory of Geomicrobiology and Environmental Changes (GMEC), China University of Geosciences, Wuhan, China

⁴ State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Institute of Sedimentary Geology, Chengdu University of Technology, Chengdu, China

⁵ Department of Earth, Environmental and Planetary Sciences, Northwestern University, Evanston, IL, USA

⁶ New York State Museum, Albany, NY, USA

⁷ Department of Geological, Environmental, and Planetary Sciences, SUNY Geneseo, Geneseo, NY, USA

⁸ Earth and Life Institute, UCLouvain, Louvain-la-Neuve, Belgium

Corresponding author: Jarno Huygh (jarno.huygh@uliege.be; jarno.huygh@hotmail.com)

Abstract

The Kellwasser Crisis near the Frasnian-Famennian boundary (~372 Ma) is linked to one of the major Phanerozoic biodiversity crises. It is associated with sea-level changes, carbon-cycle perturbations, and pulsed oceanic anoxia, that led to black shale deposition characterized by positive carbon isotope excursions, akin to the Kellwasser horizons in Germany. Despite growing evidence of astronomically forced climatic stresses influencing Devonian marine systems, the trigger mechanism(s) of the Kellwasser Event remain debated. The West Valley core (WVC) comprises middle Frasnian to lower Famennian strata, including the Rhinestreet and Kellwasser events, characterized by black shales, elevated total organic carbon (TOC) content, and a positive $\delta^{13}\text{C}_{\text{org}}$ carbon isotope excursion in the Kellwasser Crisis interval. In this work, we performed cyclostratigraphic analysis of Ti, Ti/Al and TOC, which reveals a strong astronomical imprint, particularly eccentricity amplitude modulation patterns. The TOC record was tuned to the stable 405 kyr eccentricity period, yielding a 5.67-Myr-long floating astrochronology, with event durations for the Rhinestreet and Kellwasser intervals consistent with previous reports. Subsequent analysis confirmed an equally strong eccentricity imprint on the titanium content, strongly implying a link between organic matter preservation, detrital sediment supply and astronomical forcing. Additionally, a dominant imprint of the 1.2 Myr and 2.4 Myr obliquity cycles on sea-level variation supports astronomical control on the Kellwasser Crisis. Finally, new insights into the phase relationship between the Rhinestreet and Kellwasser events and astronomically forced climate changes are globally contextualized within a new cyclostratigraphic model, emphasizing the role of eccentricity and obliquity in pacing marine anoxia.

Keywords: Cyclostratigraphy; Devonian; Frasnian-Famennian boundary; West Valley core; Black Shale; Orbital Forcing

5.1. Introduction

The Kellwasser Crisis interval is one of the “big five” mass extinction events in Earth’s history (Raup and Sepkoski, 1982; Schindler, 1990; 1993). It was a period of increased climate instability, marine biodiversity loss and pulses of marine anoxia, culminating during the Lower Kellwasser (LKW) Event and Upper Kellwasser (UKW) Event at the Frasnian-Famennian (F-F) boundary (Walliser, 1996; Carmichael et al., 2019; Becker et al., 2020; Brett et al., 2020). The Kellwasser Crisis is associated with positive carbon isotope excursions (pCIE), eustatic sea-level change (e.g., transgressive-regressive pulses), and deposition of organic-rich strata (Becker et al., 2020). Yet Carmichael et al. (2019) highlighted that, despite a considerable sampling bias, the expression of the Kellwasser Crisis in the geological record is highly dependent on paleoenvironment and paleogeography. In addition to the severe Kellwasser Crisis, the Rhinestreet (RS) Event, named after black shale deposits in New York, USA (Lash and Blood, 2006) was a minor bio-event of low severity (Brett et al., 2020) that nonetheless represents a global event associated with transgression, marine anoxia and deposition of organic-rich facies (Sageman et al., 2003; Lash and Blood, 2006; Becker et al., 2020; Kabanov et al., 2023).

Marine anoxia is often attributed to water-column stratification caused by stagnation of the ocean circulation, or to enhanced productivity in upwelling zones or epeiric seas, which leads to eutrophication, and ultimately results in anoxia (Murphy et al., 2000; Carmichael et al., 2019; Kabanov et al., 2023; Algeo and Shen, 2024). Alternative explanations also point to vertical chemocline displacement, particularly during transgression (see reviews in Carmichael et al., 2019; Kabanov et al., 2023). These mechanisms represent the environmental response (i.e., proximal causes) to changes in redox chemistry and temperature, which are, in turn, related to a perturbation of the (global) carbon cycle (Algeo and Shen, 2024). Biocrises linked to organic carbon burial (i.e., pCIE), atmospheric CO₂ drawdown, and climatic cooling are typically driven by weathering and productivity changes, whereas those linked to carbon release (i.e., negative CIE), atmospheric CO₂ rise, and climatic warming are generally temperature-driven (Algeo and Shen, 2024).

The ultimate causes behind the most severe mass extinctions include bolide impacts, large igneous province (LIP) volcanism, tectono-oceanic events, or bioevolutionary events (Kabanov et al., 2023; Algeo and Shen, 2024). Even though ongoing orogeny (e.g., Averbuch et al., 2005) or LIP volcanism (e.g., Pisarzowska and Racki, 2020; Racki, 2020) have been proposed as the triggering mechanism behind the Kellwasser Crisis (see also Carmichael et al., 2019; Kabanov et al., 2023), its ecological scope, protracted multistage nature and characteristic positive carbon cycle response – indicating net carbon burial and associated cooling – points to a bioevolutionary trigger as the ultimate cause (Algeo and Shen, 2024). In addition, the conspicuous temporal link with the expansion of land plants (Algeo and

Scheckler, 1998, 2010) further substantiates a connection between the mass extinction, associated anoxia, and land-plant-mediated changes in carbon burial and continental weathering ('land-plant weathering' hypothesis; Algeo et al., 1995).

Recent work on Devonian cyclostratigraphy suggests that astronomical forcing, in interplay with other factors, played a key role in the timing and pacing of the Kellwasser marine anoxia episodes (De Vleeschouwer et al., 2017; Da Silva et al., 2020; Lu et al., 2021; Ma et al., 2022; Wichern et al., 2024). Moreover, recent modelling efforts using an Earth system model of intermediate complexity (cGENIE) revealed that astronomical forcing, primarily obliquity variation, is able to drive changes in ocean oxygenation and impact marine anoxia by altering both circulation and oxygen solubility (Gérard et al., 2025). Astronomical forcing refers to changes in the amount and distribution of insolation caused by variations in Earth's orbital parameters and obliquity, driven by gravitational interactions with other celestial bodies, including luni-solar precession. In the classical theory of planetary motion, the precession of the planet's perihelion in the reference frame, modulated by eccentricity, has characteristic frequencies g_i , and the precession of the orbital plane around the reference frame, modulated by inclination, has characteristic frequencies s_i (e.g., Bretagnon 1974, Laskar, 1990). The key factors controlling the distribution of insolation are the obliquity of the equator with respect to the orbital plane, and the eccentricity-modulated precession of the perihelion with respect to Earth's position at the vernal equinox. To obtain these two quantities, one must combine the orbital model with a model of luni-solar precession, largely described by a movement of frequency k . Obliquity is mainly dominated by the s_i+k terms, climatic precession by the g_i+k terms, and eccentricity – the envelope of climatic precession – by differences in the g_i terms (Berger, 1973). These are commonly referred to as the Milankovitch cycles, which affect Earth's insolation and climate and, if amplified and preserved, can be found imprinted in the sedimentary record (Hinnov, 2000).

Cyclostratigraphy leverages the recognized imprint of Milankovitch cycles, enabling the construction of high-resolution (floating) astrochronologies. This way, the duration of the WVC Rhinestreet Event, as well as the Kellwasser Crisis interval LKW and UKW events can be estimated. Additionally, the temporal location of these events relative to extrema in astronomical cycles can be investigated and documented. To date, two models have been proposed that describe the link between Milankovitch cycles and the LKW and UKW events. The eccentricity-minimum hypothesis proposes the presence of a 2.4 Myr minimum in eccentricity (i.e., 'node') before the UKW Event (De Vleeschouwer et al., 2017, Da Silva et al., 2020; Wichern et al., 2024). Such a minimum, characterized by limited modulation of precession by eccentricity, could favor stable climatic conditions allowing for the buildup of nutrients on the continent (nutrient-gun hypothesis; De Vleeschouwer et al., 2024), facilitated by the evolution and colonization of land plants (Algeo and Scheckler, 1998). After the node, the increase in eccentricity-modulated precession would intensify nutrient runoff and cause

subsequent eutrophication and anoxia (De Vleeschouwer et al., 2024). Alternatively, Ma et al. (2022) proposed that both LKW and UKW were associated with an orbital configuration of high obliquity and eccentricity. Accordingly, significantly increased seasonality would, in turn, lead to enhanced nutrient input and sea-level rise, leading to eutrophication and anoxia (Ma et al., 2022). Regardless, both models suggest that the anoxia onset is climate-driven (proximate cause; Algeo and Shen, 2024). These models are complementary with the ‘weak version’ of the land-plant weathering hypothesis (Algeo and Shen, 2024); land-plant bioevolutionary events inducing considerable environmental stress, bringing the Earth system closer to a tipping point towards marine anoxia, with Milankovitch forcing providing the final contribution towards episodic marine anoxia and extinction (De Vleeschouwer et al., 2024). The impact of eustatic sea-level oscillations and ocean circulation changes on anoxia development during the Kellwasser Crisis have not yet been formulated within a cyclostratigraphic context.

Still, due to diverging cyclostratigraphic interpretations (e.g., De Vleeschouwer et al., 2017; Ma et al., 2022), the temporal history of the Kellwasser Crisis interval and its relationship with astronomically forced paleoclimatic and paleoenvironmental change remain debated. Additional sections containing the Kellwasser Crisis interval need to be investigated to provide new temporal estimates of the crisis interval and to test current models for astronomically forced marine anoxia. Building upon a long history of research on the Devonian of the Appalachian Basin, this work presents a cyclostratigraphic interpretation of cyclicity observed in the West Valley core (WVC), further refining work carried out by Murphy et al. (2000), Sageman et al. (2003) and Ver Straeten et al. (2011). In complement, a re-assessment of the geochemical data is carried out to establish the paleoclimatic and paleodepositional conditions of WVC strata within a cyclostratigraphic framework.

Even though the cyclicity captured by this record has been explicitly described within a sequence stratigraphic framework (e.g., Ver Straeten et al., 2011), no temporal framework based on Milankovitch cyclicity has been reported to date. First, the presence of an astronomical imprint in geochemical proxy series is leveraged for the construction of an astronomical age model. This way, the time encompassed by the WVC strata, as well as the Rhinestreet, LKW and UKW event beds is estimated. Next, the mechanisms (i.e., paleoclimatic and paleoenvironmental response) translating astronomically forced insolation changes into the WVC strata are put into a cyclostratigraphic context. Finally, the phase relationship between recovered Milankovitch cycles and the Rhinestreet, LKW, and UKW event beds is documented, formalized into a new model, and compared to current hypotheses.

5.2. Geological Setting

The 260-m-thick western New York Nuclear Fuel Service core #1 or West Valley core NX-1 was drilled by the Western New York Nuclear Fuel Service near the town of Ashford (42.35306 °N, 78.67383 °W) in Cattaraugus County, New York State (USA) (Fig. 1A). It comprises middle Frasnian to lower Famennian distal foreland basin strata deposited in an expanded subtropical zone at appr. 30° S paleolatitude (Ver Straeten et al., 2020), as the Catskill Delta prograded westward into the Appalachian foreland basin as a result of the Acadian Orogeny (Ver Straeten, 2009;2010; Smith and Jacobi, 2023). During deposition of WVC strata, alongside eustatic sea-level variations, tectonic processes related to the ongoing orogeny (Tectophase 4 of Ver Straeten, 2023) exerted additional influence on relative sea-level through flexural adjustments, subsidence, and rebound (Ver Straeten, 2009; 2010; 2023).

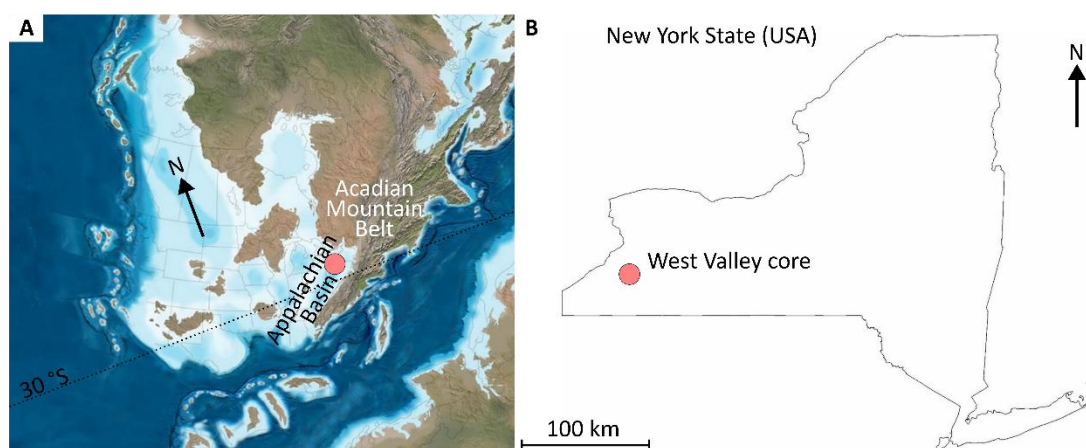


Fig. 1. Geological setting of the WVC. A) Late Devonian paleogeographic map (Blakey, 2023; 373 Ma). B) New York State (USA) modified from d-maps.com. WVC locality is indicated by a red dot.

From base to top, the WVC contains the black shales of the Rhinestreet Formation, mudstones intercalated with black shale of the Angola Formation, the mudstone to sandstones of the Gardeau and West Hill formations, the black shales of the Pipe Creek Formation, mudstones intercalated with black shale of the Hanover Formation, black shales and mudstones of the Dunkirk Formation and, the shales and mudstones of the South Wales Formation (Gowanda Formation in Ver Straeten et al., 2011) (Fig. 2). The contact between the Rhinestreet Formation and the underlying Cashaqua Formation is missing, indicating that the lowermost Rhinestreet Formation is absent in the WVC (Sageman et al., 2003; Ver Straeten et al., 2011). Identification of the LKW (Pipe Creek Formation) and UKW (Point Gratiot Bed-equivalent) events in western New York was based on conodont biostratigraphy (Over, 1997; Over et al., 2023), increased total organic carbon and a positive carbon isotope excursion (Murphy et al., 2000).

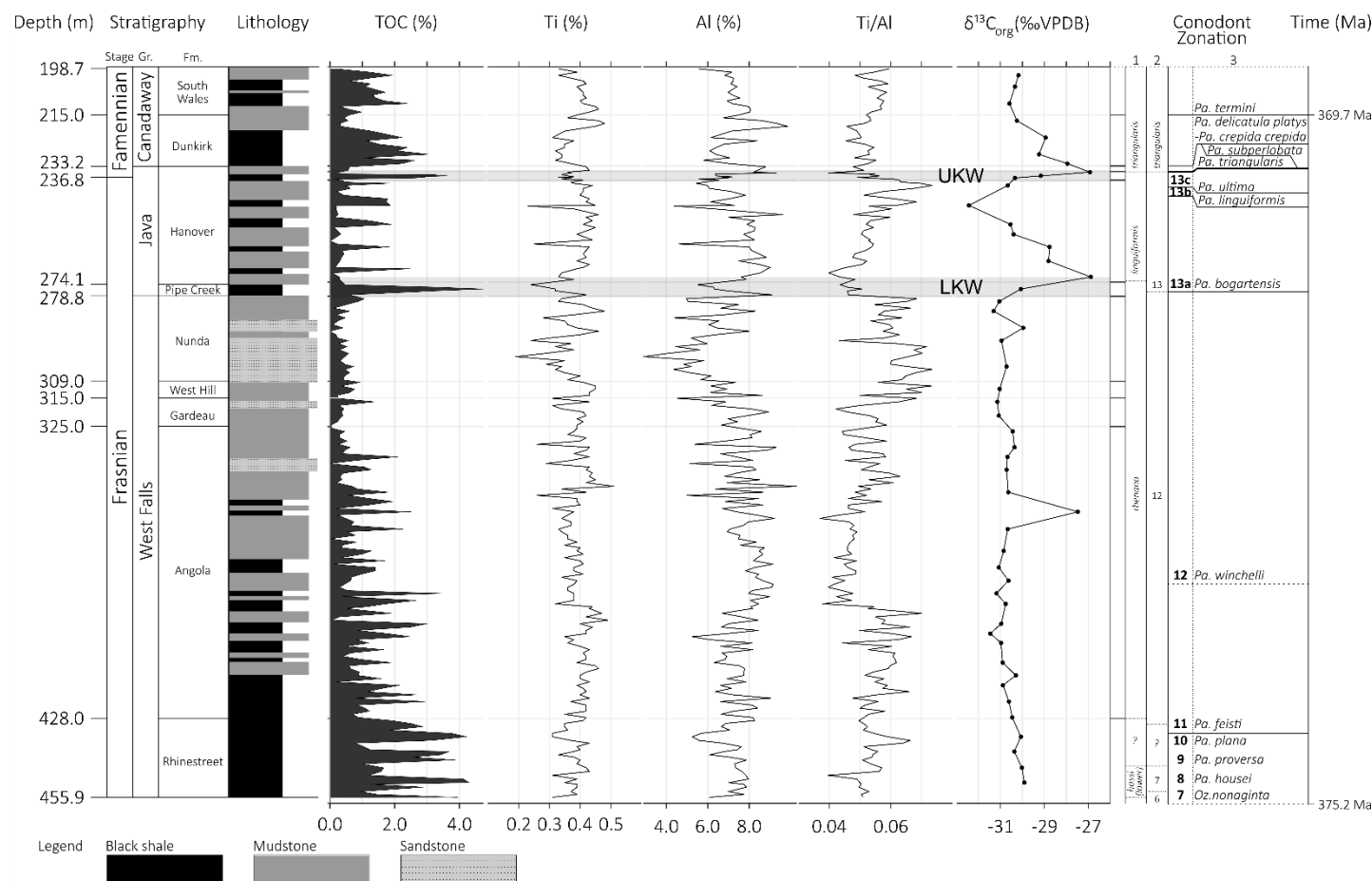


Fig. 2. WVC stratigraphy, lithological column, selected geochemical proxy signals and conodont zonation. Stratigraphy and lithological column modified after Ver Straeten et al. (2011). Geochemical proxy signals TOC, Ti, Al, Ti/Al and $\delta^{13}C_{org}$ from Sageman et al. (2003). Conodont zonation correlation based on Sageman et al. (2003) (1), Ver Straeten et al. (2011) (2) and Klapper and Kirchgasser (2016) and Over et al. (2023) (3). Numerical ages estimated based on correlation to conodont zonation by Becker et al. (2020).

5.3. Materials and Methods

Geochemical proxy records used for cyclostratigraphy in the present study were published in Murphy et al. (2000) and Sageman et al. (2003), as was also the methodology for the acquisition of these. Here, emphasis is put on a specific set of proxies, primarily selected based on principal component analysis (PCA; Fig. 3.); total organic carbon (TOC; preserved organic matter), Ti (coarse-grained detrital influx; Croudace and Rothwell, 2015), Ti/Al (sea-level; Sageman et al., 2003) and stable carbon isotopes of organic matter ($\delta^{13}\text{C}_{\text{org}}$), as well as redox-sensitive proxies Ni enrichment factor (Ni_{EF}), Mo/Al, V/Al (Algeo and Liu, 2020), P (Murphy et al., 2000; Sageman et al., 2003; Percival et al., 2020) and Mo/TOC (Algeo and Lyons, 2006). Enrichment of Ni was calculated as: $\text{Ni}_{\text{EF}} = [(\text{Ni}/\text{Al})_{\text{sample}}/(\text{Ni}/\text{Al})_{\text{upper crust}}]$ according to McLennan (2001) using $\text{Al}_{\text{crust}} = 8.04\%$ and $\text{Ni}_{\text{crust}} = 44 \text{ ppm}$.

Furthermore, the lag-1 autocorrelation coefficient (q_1), a measure for sedimentary noise, is included as a proxy for sea-level change (Meyers and Hinnov, 2010). Lower relative sea-level would induce increased sedimentary noise (see Mudelsee, 2010), which is reflected by a decrease in q_1 -values (and vice-versa) (Li et al., 2018). Here, sedimentary noise recorded by TOC and Ti/Al is estimated by $q_{1, \text{TOC}}$ and $q_{1, \text{Ti/Al}}$, respectively (see R script in Suppl. A). These proxies are utilized, either as time series for cyclostratigraphic analysis and/or as a complement for synthesizing a paleoclimatic interpretation.

Statistical treatment and analyses were carried out in RStudio (2024.12.1, Build 563). Cyclostratigraphic analyses were carried out in RStudio using the Astrochron v1.4 package (Meyers, 2014). Additional analysis using continuous wavelet transform with a Morlet wavelet ($\omega = 6$) was carried out using the WaverideR package (Arts, 2023; Arts et al., 2024). The Nadaraya–Watson kernel regression estimate was calculated via the ‘ksmooth’ function. Proxy time series were detrended, either by subtracting a linear trend using the ‘detrend’ function or by fitting and removing a ‘lowess’ smoother using the ‘noLow’ function (Meyers, 2014). All proxy time series were linearly interpolated (0.25 m sampling rate) prior to carrying out any cyclostratigraphic analysis. TimeOpt and eTimeOpt (Astrochron; Meyers, 2015; 2019) were utilized to estimate the average and evolutive apparent sedimentation rate (ASR), respectively. Estimation of sedimentation rate is carried out by simultaneously optimizing (i) the modulation of the short-eccentricity cycle by the long-eccentricity cycle, and (ii) the concentration of spectral power at the periods of short-eccentricity (appr. 95, 99, 125, and 131 kyr) and long-eccentricity (405 kyr) (i.e., estimating r^2_{opt} ; Meyers, 2015; 2019). The formulated cyclostratigraphic hypothesis and proposed astrochronology is subsequently tested by applying time series and spectral analyses on time-domain geochemical proxy signals. Specific focus is put on amplitude modulation patterns of eccentricity and obliquity cycles by extracting higher-order cycles from the envelope of hierarchically shorter cycles. To avoid convoluted phrases, LE(i) is used to denote the ‘405 kyr long eccentricity cycle, recovered

indirectly (i) from the envelope of the 100 kyr short eccentricity (SE) cycle'. Similarly, GE(i) and GO(i) are used for the indirectly recovered 2.4 Myr grand eccentricity and 1.2 Myr grand obliquity cycles, recovered from the envelopes of LE and 173 kyr long obliquity (LO), respectively. All R-code is available in the Supplementary Materials (Suppl. A).

5.4. Results

5.4.1. Principal Component Analysis of Geochemical Data

While the geochemical framework of the WVC has been previously characterized by Murphy et al. (2000), Sageman et al. (2003), Ver Straeten et al. (2011), and briefly by Percival et al. (2020), a re-evaluation of the dataset using PCA is warranted to refine proxy selection and interpretation – particularly in light of recent advances in redox-proxy evaluation (Algeo and Liu, 2020). While principal component 1 (PC1) accounts for 30.4% of variance, PC2 and PC3 account for 18.8% and 14.2% of variance, respectively (Fig. 3). Most elements are grouped off-axis in PC1-PC2 space, with four distinct clusters of elements each occupying one of the quadrants: Ca, P and Mn (upper left), Fe, Al, Cr, K and Ti (upper right), V, Cu, Ni, Mo and TOC (lower right) and, Co, Si, Zr (lower left) (Fig. 3A). As such, PC1 and PC2 primarily reflect changes in detrital input and redox conditions, respectively (Fig. 3A). Grouping of elements such as Si, Zr and Ti (coarse-grained particles), Fe, Al, Cr, K, V and Co (finer, clay-rich sedimentation), and associations between TOC, Mn, Mo, Cu and Ni (redox-sensitive organic-rich facies) along PC3 (Fig. 3A) suggests clustering as a function of grain size or sedimentological differences (Tribovillard et al., 2006; Croudace and Rothwell, 2015; Algeo and Liu, 2020; Tribovillard, 2021). Consequently, only a minority of the datapoints can be associated with the carbonate-containing fraction (i.e., Ca; blue data points on Fig. 3B) – consistent with the predominant mudstone, shale and sandstone facies of the WVC.

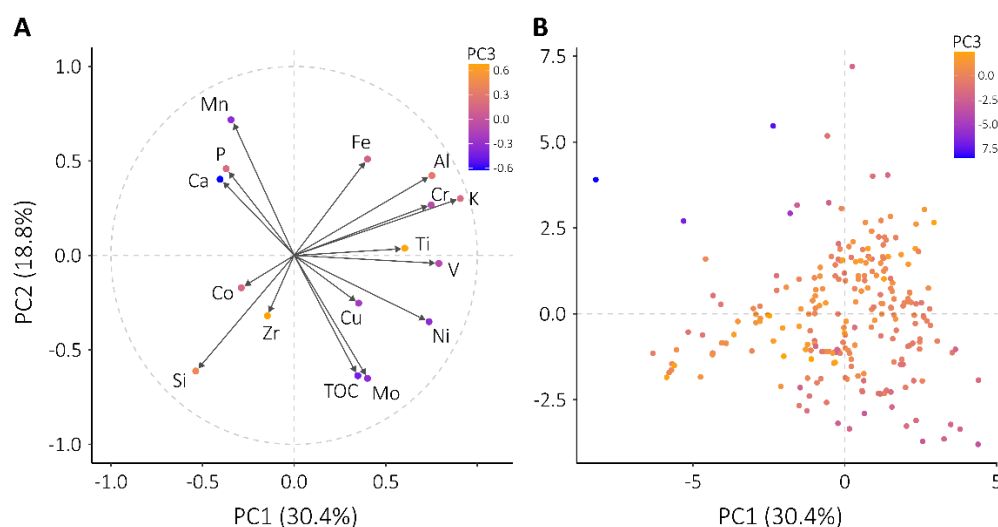


Fig. 3. Principal component analysis. A) Loading plot of selected elements along PC1, PC2 and PC3 (color scale). B) Score plot along PC1, PC2 and PC3 (color scale). PC3 accounts for 14.2% of variance.

5.4.2. Depth-domain Cyclostratigraphy

Throughout the WVC, TOC spikes appear rhythmically, superimposed on a fluctuating baseline (Fig. 2). These are visually most striking within the Kellwasser Crisis interval (appr. 236 to 283 m), but also Rhinestreet, Angola, Dunkirk and South Wales formations. Time series analysis using a Nadaraya–Watson kernel regression estimate fit reveals apparent rhythmicity in the TOC baseline (Fig. 4A). Similarly, rhythmicity can also be observed in the Ti baseline (Fig. 4C).

In order to identify the presence of Milankovitch cyclicity imprinted on the TOC and Ti, spectral analysis was applied using a continuous wavelet transform (Arts, 2023; Arts et al., 2024). Increased wavelet power can be observed for two components with periodicities ranging from 4 to 8 m and 15 to 30 m, respectively (black dotted lines, Fig. 4B, D). Slight shifts in periodicity can be identified on the wavelet spectra (Fig. 4B, D) for both identified components, which may reflect changes in the ASR.

A Taner bandpass filter (window size of $1/30$ to $1/15 \text{ m}^{-1}$) was used to extract the low-frequency component, identified in the wavelet spectra, from the TOC and Ti signals. In both cases, the bandpass filtered signals match the Nadaraya–Watson kernel regression estimates (Fig. 4A, C), confirming that the rhythmic changes in the TOC and Ti baselines are cyclic. Moreover, the low-frequency components extracted from TOC and Ti appear anti-phased. Secondly, the 4 to 8 m component is extracted using a bandpass filter. It fits with the sharp TOC (and Ti) spikes that can be observed most clearly in the Kellwasser Crisis interval (230 to 280 m, Fig. 2, 4).

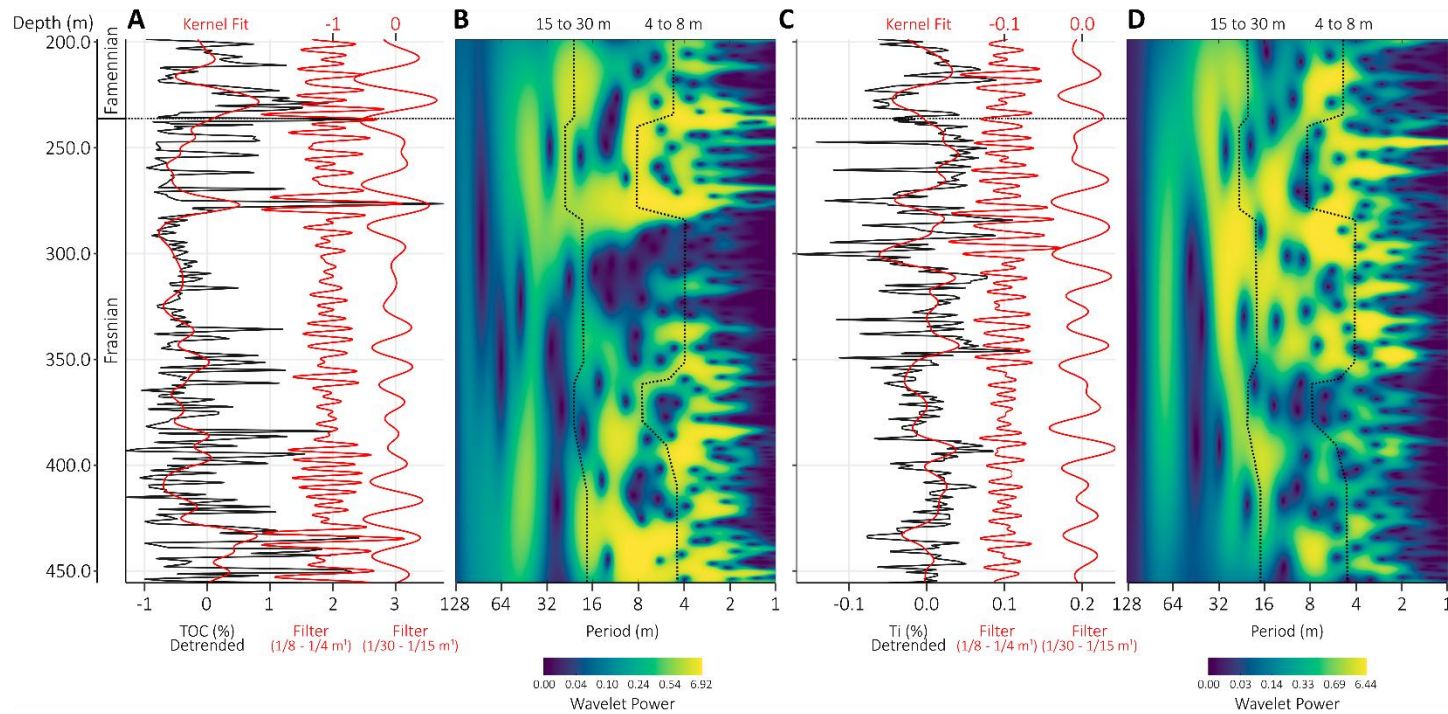


Fig. 4. WVC TOC and Ti, depth-domain time series and spectral analysis. A) Detrended TOC (%; black), Nadaraya–Watson kernel regression estimate (red) and bandpass filtered output (1/30 to 1/15 m⁻¹ and 1/8 to 1/4 m⁻¹; red). B) TOC wavelet power with indicated periodicities from 15 to 30 m and 4 to 8 m, interpreted to correspond to the long- and short-eccentricity cycles, respectively. C) Detrended Ti (%; black), Nadaraya–Watson kernel regression estimate (red) and bandpass filtered output (1/30 to 1/15 m⁻¹ and 1/8 to 1/4 m⁻¹; red). D) Ti wavelet power with indicated periodicities from 15 to 30 m and 4 to 8 m, interpreted to correspond to the long- and short-eccentricity cycles, respectively. The cone of influence was removed from the wavelet periodograms for visual clarity (see Suppl. A).

5.4.3. Astronomical Age Model

Published conodont zonation biostratigraphy offers an independent age model for the WVC (Fig. 2; see also Sageman et al., 2003; Ver Straeten et al., 2011; Becker et al., 2020). Based on tentative correlations to generalized conodont zonation (Klapper and Kirchgasser, 2016; Becker et al., 2020; Over et al., 2023), the approximate amount of time encompassed by the WVC strata is roughly 5.5 Myr (Klapper and Kirchgasser, 2016; Becker et al., 2020) and accordingly, the ASR for the WVC is about 4.7 cm/kyr. At this rate, the 405 kyr long-eccentricity (LE) cycle would span on average 18.9 m. This suggests that the long-term periodic 15 to 30 m component that was identified in both TOC and Ti (Fig. 4) corresponds to the LE cycle. Similarly, the short-term periodic 4 to 8 m component most likely corresponds to the ~100 kyr SE cycle. The periods of these components also exhibit a 1:4 ratio akin to that between the long- and short-eccentricity cycles.

TimeOpt analysis (testing ASRs from 1 to 7 cm/kyr) estimates an average ASR of 4.75 cm/kyr ($r^2_{\text{opt TOC}}$) and 3.86 cm/kyr ($r^2_{\text{opt Ti}}$), well in line with biostratigraphic estimates (e.g., Becker et al., 2020). Furthermore, eTimeOpt (from 1 to 7 cm/kyr) is applied to TOC and Ti in order to assess potential changes in ASR as suggested by the continuous wavelet transform (Fig. 4). In both cases, eTimeOpt confirms previously estimated ASRs as well as the stratigraphic location of main shifts in ASR (r^2_{opt}) (see Fig. S1).

Integration of biostratigraphy and cyclostratigraphy strongly suggests an imprint of the short- and long-eccentricity cycles on TOC and Ti. Because TOC reflects the clearest apparent Milankovitch imprint (in terms of bundling and pacing of sharp spikes superimposed on the fluctuating baseline), this signal is used to construct an astronomical age model. Using the extracted long-eccentricity signal (Fig. 4A) as a guide, 14 local extrema in the TOC signal are visually identified and utilized to construct a floating astrochronology (i.e., minimal tuning on the LE cycle), encompassing 5.67 Myr at an average ASR of 4.53 cm/kyr (as illustrated in Fig. 5).

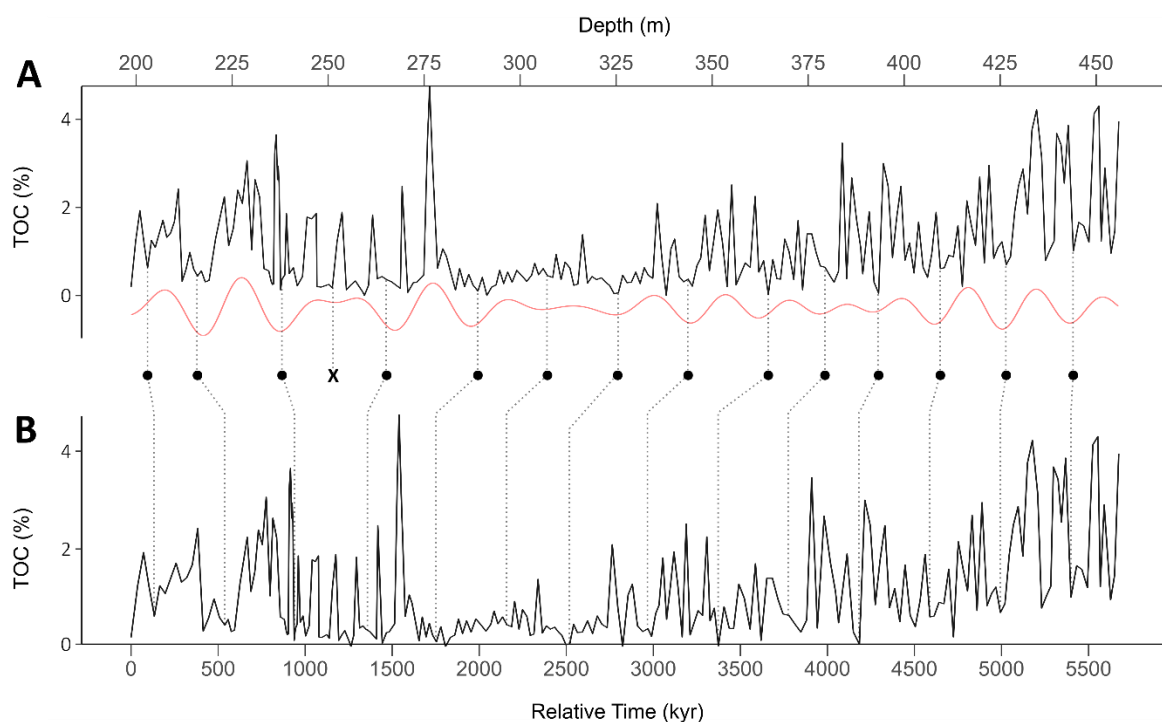


Fig. 5. Tuning of TOC using the 405 kyr LE cycle. A) Depth-domain TOC and bandpass filter output (1/30 to 1/15 m^{-1}) interpreted to reflect 405 kyr LE. B) Tuned, relative time-domain TOC. Dots reflect interpreted extrema in LE and are depth-time tie-points utilized to construct the age model. X reflects a potential additional extremum in LE which, after investigation, was not added for constructing the age model (see Suppl. Fig. S2).

Based on the interpreted imprint of eccentricity on TOC, the astronomical age model is used to transform all available geochemical proxies from the depth domain to the time domain. Note that at these estimated ASRs, recovery of precession (and short obliquity) is impeded by the limited resolution of the available geochemical dataset. So, the paleoclimatic response to astronomical forcing on short 10^4 -yr timescales cannot be further investigated. Because statistical significance testing remains a debated subject within the cyclostratigraphy community (e.g., Weedon, 2022; Smith, 2023), a different approach is followed here by leveraging specific frequency ratios and amplitude modulation patterns that can be expected from longer-term (105-yr timescales) obliquity and eccentricity cycles. Note that both 1.2 Myr ($s_4 - s_3$) and 2.4 Myr ($g_4 - g_3$) cycles are unstable (Laskar, 2020) and that frequency ratios related to these cycles may diverge accordingly. In addition, the astronomical age model is tested by assessing the imprint of Milankovitch cycles on other proxies (that were tuned using the TOC age model).

5.4.4. Time-domain Cyclostratigraphy

5.4.4.1. Organic Matter (TOC)

In a first step, the imprint of Milankovitch cycles on the tuned TOC signal (Fig. 6A) is verified and documented. Continuous wavelet transform analysis reveals increased spectral power corresponding to LE and also at periodicities corresponding to SE, GE, LO, and GO (Fig. 6B). Notably, decreased SE spectral power can be observed around appr. 2.00 Myr (Nunda Formation) and 4.50 Myr (base of the Angola Formation) (Fig. 6), tentatively indicating the presence of a node (i.e., 2.4 Myr GE cycle minimum), during which the amplitude of SE is expected to be minimal (Laskar, 2020). Spectral power associated with GE remains moderate throughout the record, as expected given its low amplitude in Earth's eccentricity (Laskar, 2020). Spectral power associated with LO is strongly localized; primarily in the Rhinestreet Formation (appr. 5.00 to 5.67 Myr) but also in the LKW Event interval (appr. 1.40 to 1.80 Myr; Fig. 6B). As expected, increased GO spectral power is equally documented for the Rhinestreet Formation and, to a smaller extent, the overlying black shales of the lower Angola Formation (up to appr. 3.80 Myr; Fig. 6B).

In a second step, Taner bandpass filtering and Hilbert transforms are utilized to extract identified Milankovitch cycles and to assess their amplitude modulation patterns, respectively (Fig. 6A). Overall, bundles of 4 SE cycles can be counted per LE cycle, illustrating the expected 4:1 frequency ratio. A consistent in-phase relationship is documented between SE amplitude modulation patterns (and LE(i) on Fig. 6A) and the extracted LE cycle. An alternative age model, including an additional 405 kyr LE cycle in the Kellwasser interval, was discarded after displaying clear discrepancies in amplitude modulation patterns and cycle counting (see Fig. S2). Similar to SE and LE, the imprint of the GE cycle on TOC is investigated and documented. Extraction of the 2.4 Myr GE cycle is somewhat challenging due to the relatively short duration of the record (5.67 Myr), minor amplitude modulation observed for the recovered LE cycles (see GE(i), Fig. 6A), and the low amplitude and unstable nature of the $g_4 - g_3$ term (Laskar, 2020). In this case, definite recovery of the exact temporal location of GE cycle extrema based on 1 proxy remains uncertain. Lastly, the fluctuating power of LO and GO (Fig. 6B) is visualized using bandpass filtering. Even though, overall, a frequency ratio of 7:1 LO to GO cycles is respected, a mismatch can be observed between GO(i) and GO (Fig. 6A). This is attributed to the weak imprint of obliquity on TOC in the Gardeau, West Hill, and Nunda formations, causing discrepancies in phasing. To conclude, a pronounced imprint of eccentricity on TOC has been documented. Conversely, strong evidence for obliquity control on TOC is lacking, except for the Rhinestreet Formation (Fig. 6). A highly similar analysis of Ti as described for TOC, corroborates the proposed astronomical interpretation (Fig. S3).

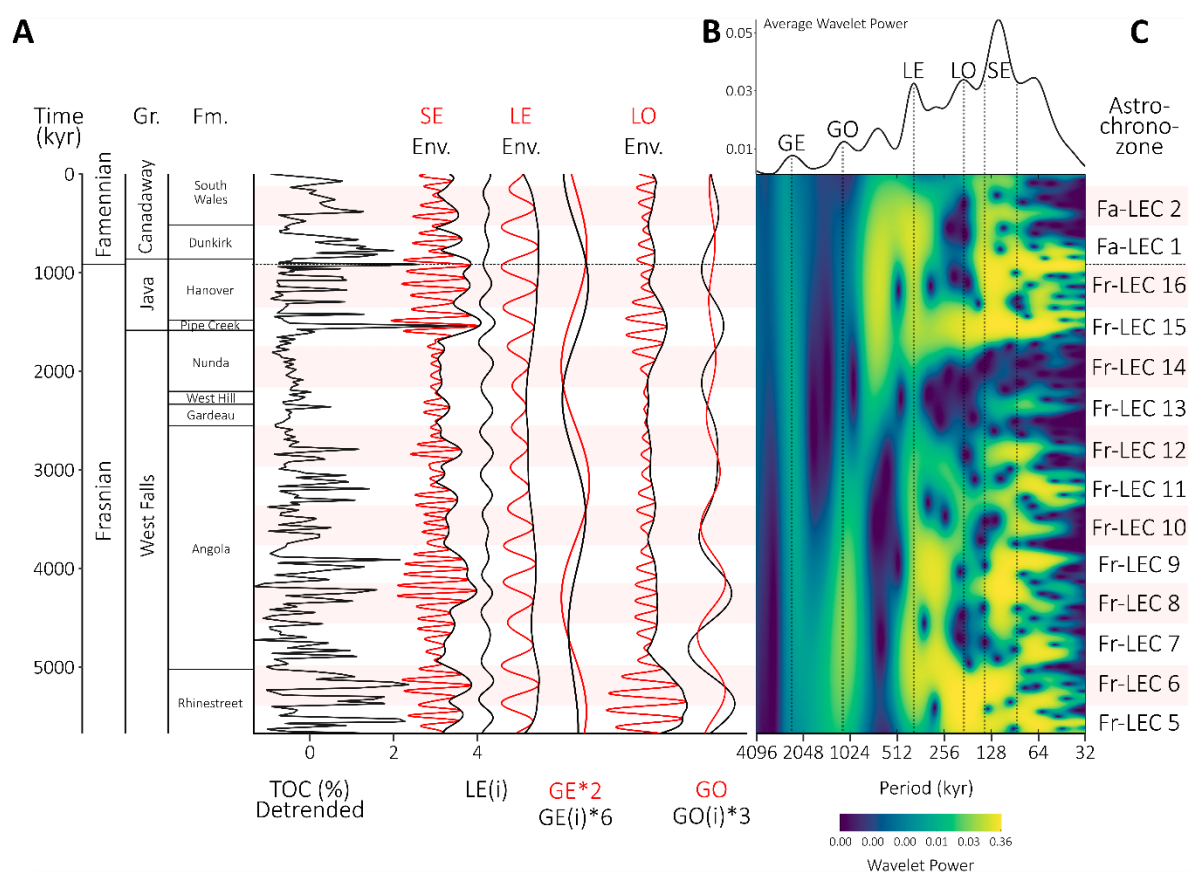


Fig. 6. Time-domain cyclostratigraphic analysis of TOC. A) WVC Stratigraphy: Stage, Group (Gr.) and Formation (Fm.), detrended TOC and bandpass filters corresponding to ~100 kyr SE (red; $1/150$ to $1/80$ kyr $^{-1}$), its envelope (black), 405 kyr LE extracted from the envelope of SE (black; $1/505$ to $1/305$ kyr $^{-1}$), its envelope (black), 2.4 Myr GE extracted from the envelope of GE (black; $1/2900$ to 1900 kyr $^{-1}$), 2.4 Myr GE (red; $1/2900$ to 1900 kyr $^{-1}$), 173 kyr LO (red; $1/203$ to $1/143$ kyr $^{-1}$), its envelope (black), 1.2 Myr GO extracted from the envelope of LO (black; $1/1500$ to $1/900$ kyr $^{-1}$) and 1.2 Myr LO (red; $1/1500$ to $1/900$ kyr $^{-1}$), respectively. B) Average and evolutive wavelet periodogram. Target periodicities (kyr) indicated by dashed vertical lines for GE (2.4 Myr), GO (1.2 Myr), LE (405 kyr), LO (173 kyr) and SE (95 and 131 kyr, respectively). C) Assigned astrochronozones (De Vleeschouwer et al., 2017; Whalen et al., 2017). The cone of influence was removed from the wavelet periodogram for visual clarity (see Suppl. A). Note relative time based on floating astrochronology.

5.4.4.2. Sea Level (Ti/Al, $q_{1, \text{TOC}}$ and $q_{1, \text{Ti/Al}}$)

Analogous to previous analyses, the imprint of Milankovitch cycles on proxies representing sea-level changes (Ti/Al, $q_{1, \text{TOC}}$ and $q_{1, \text{Ti/Al}}$) (Sageman et al., 2003; Li et al., 2018) were investigated and documented. Continuous wavelet transform analysis of Ti/Al reveals an apparent absence (or weak imprint) of LE. Even though increased power for SE appears to be present, this cannot be further tested due to the limited resolution of the dataset (i.e., absence of precession). In lack of unambiguous, conclusive evidence for LE modulating SE, these components are not interpreted to reflect eccentricity per se and are not further discussed. Conversely, a conspicuous ~ 2.4 Myr ($g_4 - g_3$) cycle is recognized on Ti/Al (Fig. 7).

A moderate-to-weak imprint of LO can be observed (Fig. 7B), which is extracted using a Taner bandpass filter with a broad frequency window ($1/203$ to $1/143 \text{ kyr}^{-1}$) (Zeeden et al., 2019). As expected from frequency ratio calculations, roughly 7 LO cycles can be counted per GO cycle. Moreover, assessment of the envelope of LO and comparison of GO(i) and GO indicate excellent amplitude modulation patterns and phasing (Fig. 7A). Conversely, the $g_4 - g_3$ cycle appears weak overall (Fig. 7C, D).

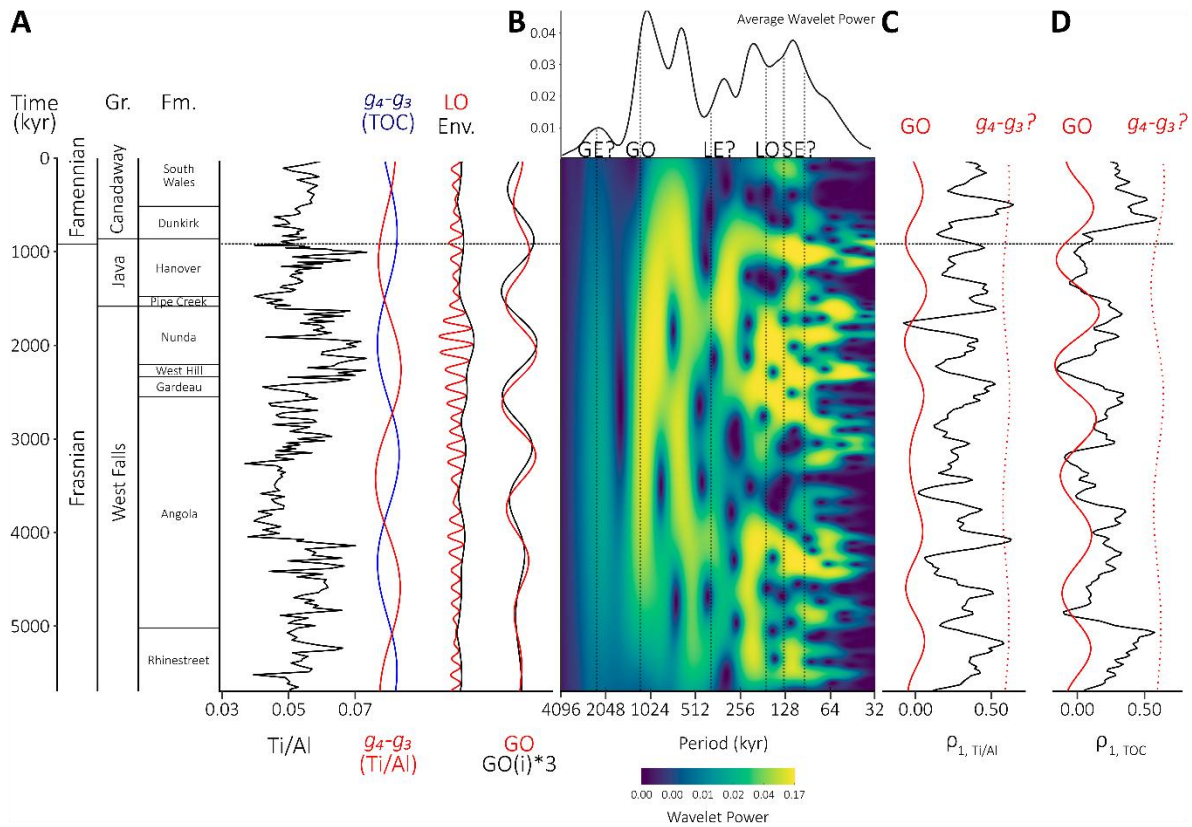


Fig. 7. Time-domain cyclostratigraphic analysis of sea-level change proxies. A) WVC stratigraphy: Stage, Group (Gr.) and Formation (Fm.), Ti/Al and bandpass filters corresponding to $g_4 - g_3$ (Ti/Al, red; TOC GE, blue; 1/2900 to 1/1900 kyr⁻¹), 173 kyr LO (red; 1/203 to 1/143 kyr⁻¹), its envelope (black), 1.2 Myr GO extracted from the envelope of LO (black; 1/1500 to 1/900 kyr⁻¹) and 1.2 Myr GO (red; 1/1500 to 1/900 kyr⁻¹), respectively. Bandpass filter output corresponding to $g_4 - g_3$ (TOC, Fig. 6) is added for comparison (blue). B) Average and evolutive wavelet periodogram of Ti/Al. Target periodicities (kyr) indicated by dashed vertical lines for GE (2.4 Myr), GO (1.2 Myr), LE (405 kyr), LO (173 kyr) and SE (95 and 131 kyr, respectively). C) $Q_{1, Ti/Al}$ (black) and bandpass filter corresponding to 1.2 Myr GO (red) and $g_4 - g_3$ (dotted red). D) $Q_{1, TOC}$ (black) and bandpass filter corresponding to 1.2 Myr GO (red) and $g_4 - g_3$ (dotted red). The cone of influence was removed from the wavelet periodogram for visual clarity (see Suppl. A). Note relative time based on floating astrochronology.

5.5. Discussion

5.5.1. WVC Temporal Framework and Implication for the Kellwasser Crisis

The recognized, unambiguous imprint of Milankovitch cycles in multiple proxies enables the construction of a high-resolution (i.e., 0.1 Myr) floating astrochronology spanning 5.67 Myr for the WVC (Fig. S4). Because radiometric ages for the WVC are unavailable, the astrochronology is not anchored in this work. Temporal constraints can be provided on the duration of the WVC Rhinestreet, LKW, and UKW events and the Kellwasser Crisis interval (Table 1). Note that the duration of an Event is strongly tied to the criteria (e.g., (litho)stratigraphic unit, biostratigraphy, carbon isotope chemostratigraphy) used for its definition (Whalen et al., 2017; De Vleeschouwer et al., 2024). In the narrowest sense (i.e., (litho)stratigraphy), the LKW and UKW Event represent the black shales of the Pipe Creek Formation and the Point Gratiot Bed equivalent in the upper Hanover Formation, respectively, as expressed in the WVC strata (Fig. 2). Accordingly, the Kellwasser Crisis is estimated to encompass appr. 760 kyr. The durations of the LKW and UKW events are 84 kyr and 123 kyr, respectively. These estimated durations are close to those reported by Da Silva et al. (2020), 90 kyr and 130 kyr, respectively, and are in the order of magnitude of one short-eccentricity cycle. Moreover, based on lithostratigraphy, appr. 580 kyr separates the top of the Pipe Creek Formation (LKW) and the F-F boundary, perfectly consistent with the radiometric estimates provided by Percival et al. (2018). Finally, the duration of the Rhinestreet Event, as expressed in the WVC, is appr. 650 kyr according to the developed floating astrochronology. Given the absence of the lowermost Rhinestreet Formation in the WVC, this estimate represents a minimum constraint, suggesting that the actual duration could be longer (see also Kabanov et al., 2023).

Table 1. Astrochronologies for the Kellwasser Crisis. Table modified after De Vleeschouwer et al. (2024). All durations are based on $\delta^{13}\text{C}$ signatures.

Reference	Location	Kellwasser Crisis		LKW	UKW
		Onset-to-onset	Peak-to-peak		
Da Silva et al. (2020)	Germany	670 kyr	600-700 kyr	300 kyr	>400 kyr
De Vleeschouwer et al. (2017)	Global	600-700 kyr	800 kyr	100-300 kyr	>400 kyr
Ma et al. (2022)	South China	1300 kyr	1600 kyr	600 kyr	>405 kyr
Whalen et al. (2017)	Canada	500 kyr	650 kyr	200-250 kyr	>405 kyr

Wichern et al. (2024)	Germany	900 kyr	800 kyr	350 kyr	>405 kyr
This work	New York, USA	630 kyr	580 kyr	470 kyr	610 kyr

All temporal estimates provided here should be interpreted as ‘order-of-magnitude’ only as they were obtained by interpolating the 0.1-Myr-resolution floating astrochronology. Minor shifts in sedimentation rate (e.g., on precession-timescales) or small hiatuses that could not be captured may slightly impact the estimated durations. This is especially critical for the low resolution $\delta^{13}\text{C}_{\text{org}}$ chemostratigraphy.

Building on work by De Vleeschouwer et al. (2012; 2017) and Whalen et al. (2017), the WVC is put into the Frasnian astrochronologic framework (i.e., defining astrochronozones; Hilgen et al., 2020). According to their work, the Frasnian counts appr. 16.5 LE cycles (Fr-LEC). Thus, the last LE cycle is appointed Fr-LEC-16 (Fig. 6C). Similar to De Vleeschouwer et al. (2017), the WVC F-F boundary appears to occur slightly after the 405 kyr eccentricity minimum in Fa-LEC 1 (equivalent to Fr-LEC 17).

5.5.2. Geochemical Proxy Interpretation

The cyclostratigraphic framework of the WVC was established primarily using TOC as a proxy for preserved organic matter. This is complemented by additional insight into the Milankovitch imprint on sedimentation, captured through variations in Ti (coarse-grained detrital input), Ti/Al and, $Q_{\text{I, TOC}}$ and $Q_{\text{I, Ti/Al}}$ (sea-level variations) (Fig. 4, 6, 7, S2). While these proxies provide a robust foundation for constructing an astronomical age model, a broader paleoenvironmental and paleodepositional interpretation requires a more comprehensive assessment of the geochemical dataset.

More recently, somewhat contrasting views on establishing oxygenation levels, derived from paleoredox proxies, emerged; while Bennett and Canfield (2020) proposed (the use of) threshold values, Algeo and Liu (2020) caution against their use altogether. Following the recommendation by Algeo and Liu (2020), we refrain from applying fixed threshold values to redox-sensitive trace metal proxies, which should be established on formation-specific basis through internal cross-calibration of multiple redox proxies – something entirely out of scope for this work. Instead, qualitative paleoredox, -productivity and -hydrography conditions are discussed within a cyclostratigraphic framework to explore the influence of astronomical forcing on marine anoxia.

The clustering of TOC and typical redox-sensitive elements (Mo, Cu, Ni and V) along PC1 to PC3 (PCA; Fig. 3) is interpreted to primarily reflect a coupling between organic matter preservation and oxygen-depleted (suboxic to anoxic-euxinic) paleodepositional conditions (Tribovillard et al., 2006; Algeo and Liu, 2020). V undergoes a two-step reduction process that is strongly dependent on the intensity of reducing conditions (Tribovillard et al., 2006). Accordingly, V/Al is used to qualitatively distinguish between suboxic and anoxic-euxinic conditions.

In the absence of clear evidence for post-depositional diagenetic alteration, both Cu and Ni may serve as dual paleo-redox and -productivity proxies (Tribovillard et al., 2006; Tribovillard, 2021). Enrichment of Ni – particularly when associated with other paleoredox indicators such as V and Mo, and elevated TOC-values – suggests a coupling between enhanced paleoproductivity and anoxic conditions (Tribovillard et al., 2006, Tribovillard, 2021). Accordingly, an increase in Ni_{EF} is interpreted as indicative of elevated paleoproductivity and, when accompanied by enrichment in other redox-sensitive elements, a decline in bottom-water oxygenation. Due to its moderate-to-weak loading in the PC1-PC2 space (Fig. 3), Cu is not further considered within a cyclostratigraphic context.

Sedimentary Mo is typically enriched in organic-rich marine facies deposited under anoxic conditions and is widely used as a proxy for benthic redox potential, particularly in association with other paleoredox proxies such as V (Algeo and Lyons, 2006; Tribovillard et al., 2006). In restricted marine environments, Mo burial generally peaks in weakly sulfidic paleoenvironments and tends to be lower under strongly sulfidic conditions (see Algeo and Lyons, 2006). Thus, lowered Mo-values during an anoxic interval may signal more intensely reducing (sulfidic) conditions. However, Mo is highly sensitive to reservoir effects in anoxic silled basins (Algeo and Lyons, 2006) – conditions that likely prevailed intermittently in the Late Devonian Appalachian Basin (Algeo et al., 2026). Consequently, the Mo/Al ratio is not only reflective of redox conditions but is also linked to hydrographic restriction of the deep-water mass, making it an amalgamated signal. Short-scale punctuated increases in Mo/Al are interpreted as enrichment due to marine anoxia, whereas long-term (secular) Mo/Al changes are indicative of variations in water-mass restriction, serving as a paleohydrography proxy (Algeo and Lyons, 2006). This interpretation is complemented by Mo/TOC, which decreases under increasing restriction (Algeo and Lyons, 2006). Specifically, secular increases in Mo/Al and Mo/TOC suggest reduced restriction (e.g., transgression (Ti/Al) in the middle Angola Fm. renewing the Mo-budget, causing highest Mo/Al and Mo/TOC spikes; Fig. 8), while declines imply enhanced restriction. The latter can be observed on the largest scale as relative sea-level decreases from the Rhinestreet Fm. onwards (Sageman et al., 2003), leading to decreasing Mo/Al up to the base of the Pipe Creek Fm. (Fig. 8). In all cases, normalization to Al did not introduce spurious correlations (Van der Weijden, 2002).

The recycling of phosphorus (P), a limiting nutrient for primary production, has been thoroughly highlighted for the Kellwasser Crisis (WVC) by Murphy et al. (2000) and Percival et al. (2020). Indeed, the clustering of P and Mn, opposing the TOC-cluster (Fig. 3), indicates that the paleoredox conditions exerted dominant control on P availability (Algeo and Scheckler, 1998; Murphy et al., 2000; Percival et al., 2020; Sageman et al., 2003). Specifically, the anti-phasing of TOC and P peaks strongly suggests a coupling between bottom-water oxygenation, benthic phosphorus retention, and marine primary productivity (Van Cappellen and Ingall, 1994), and is interpreted here as a signal of marine anoxia.

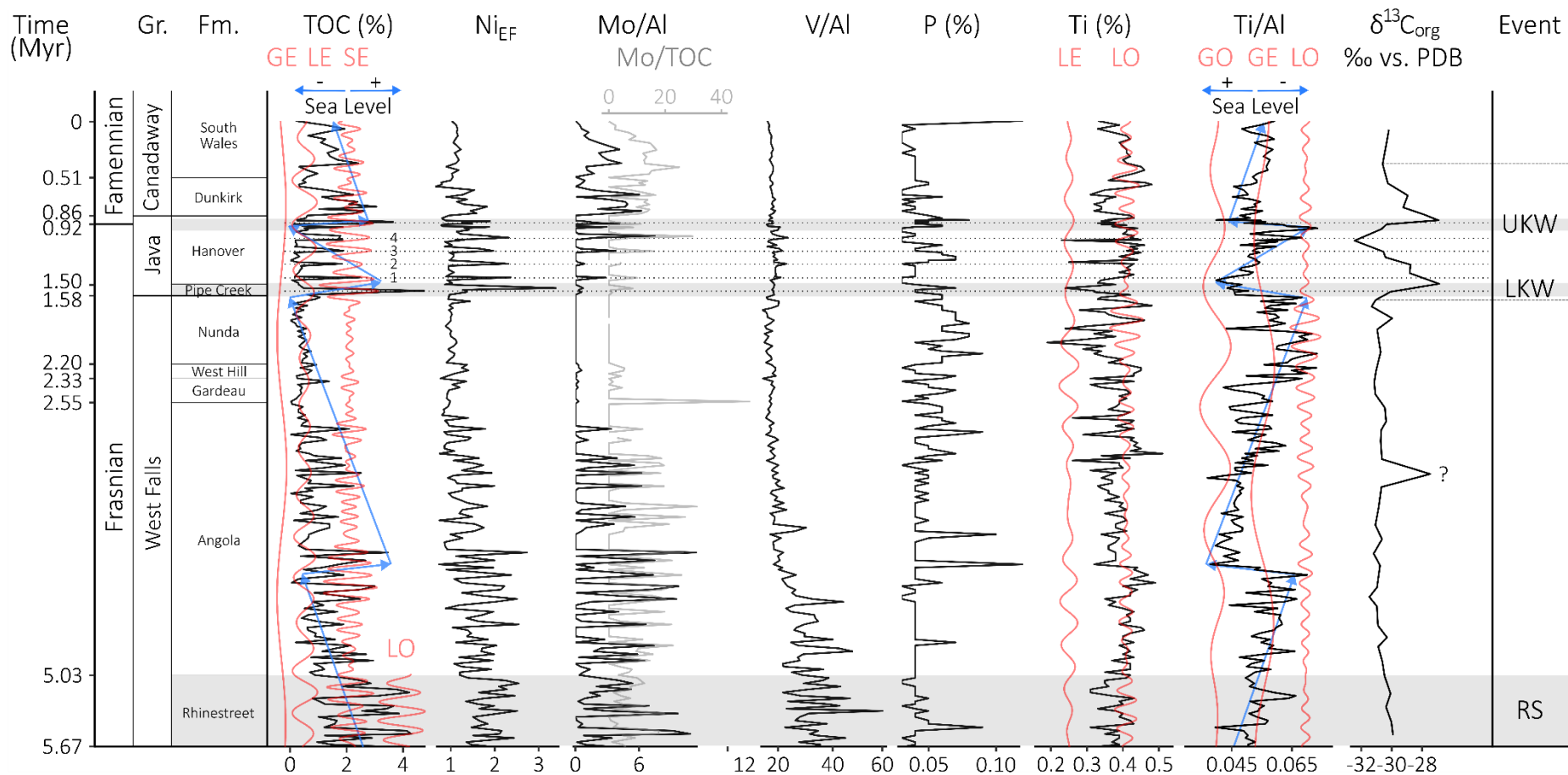


Fig. 8. WVC geochemical profiles in relative time. From left to right; WVC stratigraphy: Stage, Group (Gr.) and Formation (Fm.); TOC (%) incl. ~100 kyr SE, 173 kyr LO (RS), 405 kyr LE and 2.4 Myr GE bandpass filter output; Ni_{EF} ; Mo/Al; Mo/TOC; V/Al; P(%); Ti (%) incl. 173 kyr LO and 405 kyr LE bandpass filter output; Ti/Al incl. 173 kyr LO, 1.2 Myr GO and 2.4 Myr GE bandpass filter output, blue arrows indicate major transgression/regression trends, based on Ti/Al (Sageman et al., 2003); $\delta^{13}C_{org}$; Anoxic event intervals of the Rhinestreet (RS), Lower Kellwasser (LKW) and Upper Kellwasser (UKW) are indicated in light gray; dotted lines in the Kellwasser Crisis interval indicate maxima in ~100 kyr SE. Dashed gray lines indicate lower and upper boundaries of the Kellwasser Crisis based on CIE trends. See Fig. 6, 7 and Suppl. A for details on used bandpass filter windows. Note relative time based on floating astrochronology.

5.5.3. Eccentricity Pacing of Marine Anoxia

The strong imprint of eccentricity on TOC (Fig. 6), redox conditions (Ni_{EF} , Mo/Al , V/Al ; Fig. 8; Fig. S5), and on variations in coarse-grained detrital input (Ti; Fig. 8, S2) demonstrates a significant influence of astronomical forcing on sedimentary and organic matter deposition in the Late Devonian Appalachian Basin. Peak OM accumulation and preservation (TOC) coincides with SE maxima throughout the record, most strikingly in the Kellwasser Crisis interval, but also in the Rhinestreet Formation, and is strongly indicative of eccentricity pacing of marine oxygen depletion. Conversely, an increase in coarse-grained material (Ti; Calvert and Pedersen, 2007; Croudace and Rothwell, 2015) during eccentricity minima is interpreted to reflect a relative increase in mechanical erosion, suggesting increased aridity and a relative weakening of monsoonal activity (e.g., Wichern et al., 2024). Under such a scenario, fewer nutrients would reach the basin, leading to reduced primary productivity (Ni_{EF} , Fig. 8; Jaminski et al., 1998; Sageman et al., 2003; Liu et al., 2019).

Given the quasi-absence of eccentricity in the power spectrum of insolation (Berger, 1988), its strong imprint on OM accumulation and preservation suggests a non-linear mechanism, such as amplification of positive (or negative) extremes, which effectively demodulate the forcing (Hays et al., 1976; Wigley, 1976). During eccentricity maxima, precession modulation is strongest, amplifying climatic extremes. Because precession commonly drives monsoonal variability in warm climates such as the Devonian (De Vleeschouwer et al., 2014; Wichern et al., 2024), maximum eccentricity configuration may enhance nutrient influx and cause eutrophication (De Vleeschouwer et al., 2024), leading to black shale deposition.

For the Late Devonian, previous work (De Vleeschouwer et al., 2017; Whalen et al., 2017; Da Silva et al., 2020; Ma et al., 2022; Wichern et al., 2024) already documented the relationship between Milankovitch cycles and the (Upper) Kellwasser Event(s), highlighting the contribution of astronomical forcing as (a part of) a pacing mechanism of anoxic events. Most recently, Wichern et al. (2024) demonstrated precession-sensitive monsoonal climate during the Kellwasser Crisis interval in Germany. However, direct evidence linking marine anoxia (i.e., paleoredox conditions and OM enrichment) to precession-controlled monsoonal climate is still lacking. To further investigate whether such mechanisms could explain the strong imprint of eccentricity (modulating precession), new high-resolution geochemical data of Kellwasser Crisis sections is required. In addition, (geo)physical climate modelling may equally play a crucial role in advancing our understanding the role of astronomical forcing on marine anoxia. Whilst the aforementioned studies primarily focused on the relationship between Milankovitch cycle extrema, event timing and carbon isotopic shifts, no explicit evidence was brought forth documenting the astronomical pacing of marine anoxia (De Vleeschouwer et al., 2017; Whalen et al., 2017; Da Silva et al., 2020; Ma et al., 2022; Wichern et al., 2024). This study demonstrates, for the first time, that short-eccentricity cycle maxima

controlled the pacing of OM enrichment and paleoredox conditions during the Kellwasser Crisis, highlighting astronomical forcing as a key driver of marine anoxia in the Frasnian Appalachian Basin.

Eccentricity control on OM is consistent with a climate-driven mechanism for anoxia development, likely involving changes in weathering profiles, nutrient runoff and/or productivity (Carmichael et al., 2019; Percival et al., 2019; Algeo and Shen, 2024; De Vleeschouwer et al., 2024; Fig. 8). Even though a volcanic trigger (or contribution) cannot be excluded, cyclic variations in weathering, productivity, and carbon burial, as well as an increase in $\delta^{13}\text{C}_{\text{org}}$ are consistent with an astronomically-forced, productivity-driven biocrisis (Carmichael et al., 2019; Algeo and Shen, 2024; De Vleeschouwer et al., 2024). Bio-evolutionary events driving land-plant colonization, weathering (Algeo and Scheckler, 1998), and CO_2 -drawdown (Algeo et al., 2001) could at least have created environmental stress bringing the Earth system close to the tipping point for biocrisis (Smart et al., 2023; Algeo and Shen, 2024). Whereas volcanism may have further contributed to additional environmental stress (e.g., Piszarska and Racki, 2020), for the Appalachian Basin, it does not appear to have been the (sole) trigger mechanism. The consistent ~ 100 kyr pacing of pulses of anoxia during the Kellwasser Crisis interval strongly suggests that astronomically forced insolation change may have ultimately triggered and paced the onset of anoxia.

5.5.4. Obliquity Pacing of Sea-level Variations

In contrast to the dominant control of eccentricity on OM, coarse-grained detrital input and redox conditions, a strong imprint of obliquity has been recovered from proxies for sea-level change (Ti/Al , q_1 , TOC and q_1 , Ti/Al ; Fig. 7), indicating strong astronomical control on third-order sea-level fluctuations through 1.2 Myr GO cyclicity. The GO cycles recovered from q_1 , TOC and q_1 , Ti/Al are anti-phased to the 1.2 Myr GO cycle extracted from Ti/Al which is expected as minima in Ti/Al indicate maxima in relative sea level, while maxima in q_1 indicate minima in sedimentary noise and, thus, maxima in relative sea level (Li et al., 2018). The recovered LO imprint from Ti/Al provides additional insight into fourth-order cycles despite its moderate-to-weak amplitude, which is primarily interpreted to reflect a decreased sensitivity to obliquity changes on the 173 kyr timescale. Fluctuation of LO-associated power may also be due to the overall weaker amplitude of the $s_3 - s_6$ term (Laskar, 2020) and instability beyond 50 Ma (Zeebe and Lantink, 2024).

Recovery of a ~ 2.4 Myr cycle imprint on Ti/Al variations (interpreted to reflect sea-level changes), is surprising at first glance. Indeed, the ~ 2.4 Myr $g_4 - g_3$ cycle is classically associated with the modulation of eccentricity terms, while the Ti/Al signal displays an unclear imprint of SE and LE (Fig. 7). Both SE and LE are expected to be stronger in amplitude than GE (Laskar, 2020) and were found to dominate TOC (Fig. 6). Instead, this 2.4 Myr cycle is interpreted to

originate from a strong obliquity imprint. In fact, the $g_4 - g_3$ term influences not only the modulation of precession (and eccentricity) but also the modulation of obliquity (i.e., the envelope of obliquity contains the 2.4 Myr $g_4 - g_3$ cycle; see figure. 4.15 in Laskar, 2020 and table 4 and figure 6 in Zeebe and Kocken, 2025). Recovery of the anti-phasing $g_4 - g_3$ cycles in eccentricity and obliquity hints at the $s_4 - s_3 = 2(g_4 - g_3)$ resonance being active (e.g., Laskar, 2020) during the Late Devonian. This also indicates that, also on a Myr-timescale, baseline TOC increases as relative sea-level increases (and Ti/Al decreases). Such a scenario is consistent with interpreted deepening and black shale deposition (e.g., Sageman et al., 2003). In addition, the consistent anti-phasing between the $g_4 - g_3$ (TOC) and $g_4 - g_3$ (Ti/Al) (Fig. 7) further validates the proposed astronomical age model.

Typically, two dominant mechanisms are invoked to explain sea-level fluctuations within a cyclostratigraphic framework, depending on the prevailing climatic regime (Li et al., 2018). During cooler intervals (e.g., the Quaternary) with significant ice sheets, sea level is primarily regulated through ‘glacio-eustasy’ (continental volume ice changes) (Lourens and Hilgen, 1997). In contrast, during globally warmer intervals without major ice sheets, sea level is largely influenced by ‘aquifer-eustasy’ or ‘limno-eustasy’ (variations in groundwater and lake volume) and thermal expansion (Miller et al., 2005; Li et al., 2018; see also references in Kabanov et al., 2023). Higher sea levels can be interpreted differently depending on the governing mechanism. Under a ‘limno-eustasy’ eustatic regime, higher sea level would correspond to lower obliquity, as reduced seasonality causes the lake and groundwater system to release water in the ocean (Li et al., 2018). Conversely in a ‘glacio-eustatic’ regime, higher sea level would correspond to higher obliquity, which enhances summer melting and reduces ice volume (e.g., Lourens and Hilgen, 1997). During a greenhouse period such as the Late Devonian, limno-eustasy represents a more probable dominant mechanism (with a contribution by thermal expansion) controlling minor sea-level variations (Kabanov et al., 2023).

The observed anti-phasing between the $g_4 - g_3$ extracted from TOC and the $g_4 - g_3$ extracted from Ti/Al (Fig. 7) is leveraged to shed light on which mechanism predominantly controls sea-level fluctuations. Assessment of an astronomical solution (La04, from 0 to 20 Ma during which the $s_4 - s_3 = 2(g_4 - g_3)$ resonance is active; Laskar et al., 2004) illustrates that anti-phasing of the $g_4 - g_3$ cycle can be expected depending on whether it is extracted from eccentricity or from the envelope of obliquity (Fig. 9) – coherent with what can be observed for the $g_4 - g_3$ cycle extracted from TOC and Ti/Al, respectively (Fig. 7). Analogous to such a scenario, for the WVC, high eccentricity reflects high TOC and, accordingly, high obliquity reflects high Ti/Al (or low sea-level). This scenario aligns with ‘limno-eustasy’, most clearly paced by obliquity at 1.2 Myr and 2.4 Myr timescales. Nevertheless, glacio-eustatic sea-level variations operating on different timescales – such as those potentially linked to the cooling pulses

associated with the Kellwasser events (Joachimski and Buggisch, 2002; Huang et al., 2018; Algeo and Shen, 2024) – cannot be entirely ruled out (Algeo et al., 2026).

Although uncertainty regarding the amplitude of sea-level changes during the Devonian remains (Kabanov et al., 2023), even smaller (~5 m) amplitude-variations of third-order cycles could have played a major role in the deposition of Devonian black shales in the semi-restricted Appalachian Basin (Algeo et al., 2026). This is exemplified most clearly by the coinciding transgression and OM enrichment during the LKW and UKW and relative highstand during the deposition of the black shales of the Rhinestreet Formation (Fig. 8). As such, changes in eustatic sea-level are unequivocally associated with anoxic (extinction) events in the Appalachian Basin. This provides strong evidence that obliquity played a role in Frasnian marine anoxia, either through the upwelling of nutrients or the intrusion of anoxic water-masses, particularly during the Rhinestreet, LKW, and UKW events.

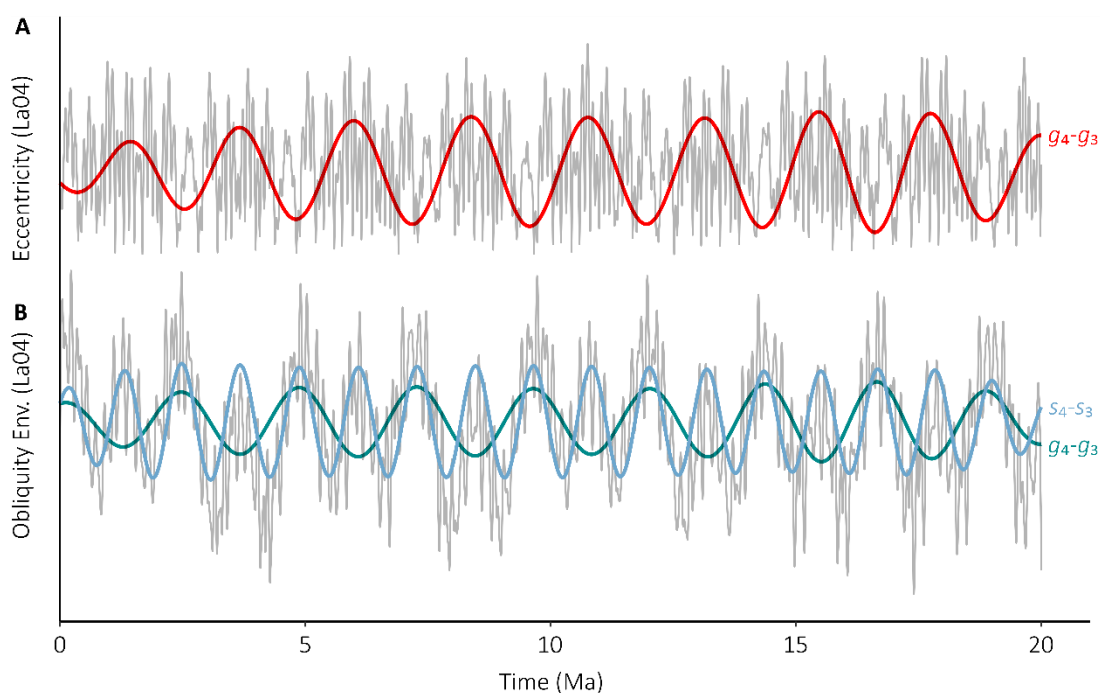


Fig. 9. Eccentricity and obliquity for the last 20 Myr (La04). A) La04 solution for eccentricity (0-20 Ma; Laskar et al., 2004) (gray) and extracted $g_4 - g_3$ cycle (red). B) Envelope of the La04 solution for obliquity (0-20 Ma; Laskar et al., 2004) obtained via a Hilbert transform (gray), subsequently extracted $g_4 - g_3$ (cyan) and $s_4 - s_3$ (blue).

5.5.5. Controls on the Succession of Events through the middle and late Frasnian

5.5.5.1. Rhinestreet Event

The global Rhinestreet (RS) anoxic event (Becker et al., 2020) represents a period of prolonged, significant marine anoxia, as is exemplified by its large thickness and protracted duration (estimated 650 kyr in this work; compared to > 600 kyr in Becker et al., 2020; > 1 Myr in Kabanov et al., 2023). The black shales of the Rhinestreet Formation are interpreted to have recorded progradational/retrogradational cycles (Lash and Blood, 2006). Flexural adjustments, subsidence, and rebound resulting from the ongoing Acadian Orogeny would have lesser influence (especially during mid to late portions of tectophases) (Ver Straeten, 2009; 2010; 2023), superimposed onto astronomically forced eustatic sea-level variations. In the WVC, the Rhinestreet Event is characterized by high TOC values (up to 4%), enrichment of paleoredox elements (e.g., Ni_{EF} , Mo/Al, V/Al; see Fig. 8) indicating increased paleoproductivity and oscillating anoxic to euxinic conditions. Elevated Mo/Al and Mo/TOC values in the Rhinestreet (and lower Angola) Formation (Fig. 8), indicate minimal restriction in the Appalachian Basin (cf. Algeo and Lyons, 2006), an interpretation that is consistent with high eustatic sea-levels associated with the RS Event (Sageman et al., 2003; Becker et al., 2020).

Here, the Rhinestreet Formation stands apart from the overlying strata by an equally strong eccentricity and 173 kyr obliquity imprint on OM accumulation and preservation (Fig. 8). TOC peaks during ~100 kyr eccentricity maxima (modulated by LE), indicating climatically-induced forcing of marine anoxia. Yet, the relative amplitude of peaks in TOC appears dictated by 173 kyr variations (see Fig. 8), suggesting a strong contribution to anoxia development by obliquity. Based on the correlation of known global marine transgressions and co-eval gray/black shale intervals, Lash and Blood (2006) suggested that (fourth-order) eustatic oscillations played a role in the deposition of black shales, which would be consistent with 173 kyr obliquity forcing (considering the extensive role of obliquity forcing on sea level). Such a pronounced obliquity imprint may be due to the highest relative sea level in the Appalachian Basin during the deposition of the Rhinestreet Formation (Mo/Al, Mo/TOC Fig. 8; see also Sageman et al., 2003; Ver Straeten et al., 2011).

5.5.5.2. Kellwasser Crisis

In the Appalachian Basin, the pre-Kellwasser interval is characterized by the sandstones of the Nunda Formation, predominantly deposited during periods of strong obliquity modulation (maxima in $s_4 - s_3$ and $g_4 - g_3$ for obliquity, akin to Fig. 9) and associated lowstand conditions (Fig. 8, 10). Note that maximal $g_4 - g_3$ for obliquity corresponds to minimal $g_4 - g_3$ for eccentricity (Fig. 9). Consequently, the deposition of this interval is interpreted to have occurred during a 2.4 Myr eccentricity cycle minimum (i.e., node), suggesting a period

characterized by the avoidance of climatic extremes and potentially a weakened monsoonal climate (Wichern et al., 2024). Furthermore, low levels of TOC and paleoredox proxies (Ni_{EF} , Mo/Al and V/Al, Fig. 8) indicate well-oxygenated bottom waters, while high Ti indicates increased coarse-grained detrital input (Fig. 8). As eccentricity increased and strong obliquity modulation diminished, sandstone deposition ceased in the run-up to the LKW Event.

The LKW Event (Pipe Creek Formation) occurs after a node in eccentricity (Nunda Formation), strongly reminiscent of the UKW ‘nutrient-gun’ hypothesis (De Vleeschouwer et al., 2024), and culminates appr. 200 kyr later (half LE cycle). The onset of the LKW Event appears rapid (≤ 100 kyr timescales), OM accumulation and preservation is paced by eccentricity, and the associated transgression appears paced by 173 kyr obliquity. However, the amplitude of the excursion in Ti/Al does not reflect the amplitude in 173 kyr obliquity, most probably indicating that processes driving flooding on yet shorter timescales should be investigated. Peak TOC values are recorded in the subsequent 173 kyr LO and 1.2 Myr GO minima (i.e., maximum flooding) and coincide with SE and LE maxima (Fig. 8, 10D). The low-obliquity, high-eccentricity configuration would lead to relatively elevated sea levels and increased clay and nutrient inputs (decreased Ti), respectively (Fig. 10D). This would consequently amplify eutrophication through increased nutrient influx and productivity (see Ni_{EF} , Fig. 8) and upwelling of either nutrient-rich or oxygen-depleted bottom-waters (Carmichael et al., 2019) through ocean circulation invigoration (Algeo and Shen, 2024). Although anoxic (*sensu stricto*) conditions appear to have been mostly absent (based on Mo/Al, V/Al; Fig. 8) in this interval of the WVC, productivity and OM burial were maximal, displaying highest TOC and Ni_{EF} values for the entire record. The anti-phased response of P relative to TOC may indicate P-recycling under reducing conditions (Murphy et al., 2000; Percival et al., 2020), contributing to sustained oxygen depletion (increased Mo/Al and V/Al) and prolonged black shale deposition (TOC) during the associated transgression (thereby potentially renewing the Mo-budget) (Fig. 8).

The inter-Kellwasser interval (lower to middle Hanover Formation) displays strong ~ 100 kyr short-eccentricity pacing of deoxygenation (Ni_{EF} , Mo/Al, V/Al; Fig. 8) and OM preservation (TOC spikes 1 to 4 on Fig. 8). This contrasts with other sections (e.g., Kowala, Poland) that display a period of non-response to orbital forcing in this interval (De Vleeschouwer et al., 2013) and was, based on increased obliquity power, interpreted to represent a node in eccentricity by De Vleeschouwer et al. (2017) and Da Silva et al. (2020). Such contrast may, in part, be attributed to the large variety in how the Kellwasser Crisis is expressed (Carmichael et al., 2019) and may thus reflect regional influences. This may also reflect the spatially heterogeneous transfer of astronomical forcing into the ocean’s biogeochemical response (Gérard et al., 2025), with local circulation exerting a key control on the distribution of these patterns.

Nevertheless, in the Appalachian Basin, this interval experiences oscillating dysoxic to anoxic conditions and increased paleoproductivity (Ni_{EF}). Spikes in Mo/Al are interpreted to represent increasing dysoxic to anoxic conditions and Mo-burial (Algeo and Lyons, 2006). Renewal of the Mo budget is attributed to the preceding LKW transgression. Yet, it should be mentioned that a steady regression coincides with this interval (Ti/Al; Fig. 8). Most striking is that TOC spike 4 (Fig. 8) appears protracted compared to previous pulses and paleoredox proxies point towards anoxic to slightly euxinic conditions (Fig. 8), indicating strong paleoenvironmental stress on the biosphere. This spike (4) coincides with a 173 kyr minimum, which may also explain elevated Mo/Al and Mo/TOC (i.e., reduced restriction; Fig. 8) and why it appears more protracted and more anoxic to euxinic. Similar to the LKW Event, P appears anti-phased to TOC, indicating that P-recycling is possibly contributing to sustained oxygen depletion and recurring black shale deposition.

The UKW represents the major, 1st-order extinction pulse at the F-F boundary (Raup and Sepkoski, 1982; Brett et al., 2020; Algeo and Shen, 2024) in the upper Hanover Formation (Over, 1997). In the WVC, it is characterized by one minor TOC spike, followed by a second major peak in TOC marking the culmination of the UKW OM burial during a ~100 kyr eccentricity maximum and during the decreasing limb of 173 kyr obliquity (i.e., transgression) (Fig. 8; n.b. see Algeo et al., 2026, for higher-resolution chemostratigraphic records of this interval). Although coinciding TOC, Ni_{EF} and Mo/Al spikes (Fig. 8) indicate oxygen depletion, V/Al remains relatively low, suggesting that dysoxic conditions prevailed. Increases in Ni_{EF} and Mo/Al hence may have been associated with increased paleoproductivity and decreased restriction as a result of the UKW transgression (Mo/TOC, Ti/Al; Fig. 8). The amount of time separating these peaks appears considerably shorter than 100 kyr, strongly suggesting that the first minor TOC peak is paced by short obliquity or precession (note that this part of the dataset has higher resolution, allowing for such a statement). In contrast to the LKW Event, the UKW Event peak TOC values occur after a LE minimum (Fig. 8). Such a scenario similarly reminds of the ‘nutrient-gun’ hypothesis (De Vleeschouwer et al., 2024), albeit following a minimum in LE instead of GE. The final peak in TOC at the F-F boundary marks the culmination of a series of ~100 kyr SE-paced anoxia pulses, probably causing the strongest environmental stress. What further differentiates the UKW from the prior anoxia pulses and OM burial episodes is the orbital configuration associated with the rapid transgression; relative sea level gradually declined in the inter-KW interval, culminating during a maximum in 173 kyr and 1.2 Myr obliquity near the F-F boundary ($s_4 - s_3$ and $s_3 - s_6$, respectively) (Fig. 8). This is in stark contrast with the minimum in 1.2 Myr obliquity (i.e., higher relative sea level) associated with the LKW Event through the WVC.

The post-Kellwasser interval is represented by the lower Dunkirk Formation (earliest Famennian) in the Appalachian Basin. Even though it still exhibits considerable OM enrichment (TOC), paleoproductivity (Ni_{EF}) further decreases (Fig. 8). A relative increase in

Mo/Al is interpreted to result primarily from a rising relative sea level on 1.2 Myr timescales (GO, Ti/Al; Fig. 8), renewing the Mo-budget. As baseline relative sea-level would continue to decrease (on > 1.2 Myr timescales, attributed mostly to progradation of synorogenic sediments of the Catskill Delta complex eroded from the Acadian Orogen (Ver Straeten, 2009; 2010; Smith and Jacobi, 2023), it becomes apparent that the influence of obliquity on OM enrichment and black shale deposition diminishes. OM burial appears to be paced dominantly by both SE and LE, which is exemplified by TOC peaks coinciding with ~100 kyr SE maxima (and lower TOC-values during the GO maximum).

5.5.6. A New Cyclostratigraphic Model for the Kellwasser Crisis

An interplay between eccentricity and obliquity forcing (over a range of timescales) dominated the Frasnian Appalachian Basin and, more specifically, the Kellwasser Crisis interval. Even though 1.2 Myr obliquity forcing appears to dominate the WVC record, both LKW and UKW are clearly associated with shorter-term (173 kyr or short obliquity?) eustatic sea-level variations (Fig. 7, 8). Short (~100 kyr) eccentricity maxima pace TOC throughout the record, most strikingly in the Kellwasser Crisis interval (Fig. 6, 8). These observations provide the foundation for formalizing a new model for astronomical forcing during the Kellwasser Crisis in restricted basins such as the Appalachian Basin. Here, a low-eccentricity configuration at ~100 kyr is associated with increased coarse-grained detrital influx (Ti), potentially indicating a weakened monsoonal system and lower nutrient-availability (Fig. 10A, B). Even though 173 kyr obliquity forcing (also affecting seasonal contrast) may modulate the amount of clay and nutrient influx (cf. Jaminski et al., 1998; Liu et al., 2019), the low-eccentricity scenario appears not conducive for anoxia and black shale deposition – regardless of relative sea-level changes.

Conversely, a high-eccentricity configuration at ~100 kyr would amplify seasonality, by intensifying monsoonal systems on precession timescales (De Vleeschouwer et al., 2014; Wichern et al., 2024), and intensify nutrient runoff, causing eutrophication and anoxia development (Fig. 10C, D), as suggested in the astronomical scenarios by Ma et al. (2022) and De Vleeschouwer et al. (2024). Clay and nutrient input would be maximized under a high-eccentricity, high-obliquity configuration (i.e., strongest seasonality; similar to the model proposed by Ma et al., 2022 – yet, on shorter timescales in this scenario). Even though under a high-eccentricity, low-obliquity orbital configuration (Fig. 10D), clay and nutrient influx would no longer be maximal, the oceanic invigoration and co-occurring transgression would enforce oxygen depletion and reducing conditions (Carmichael et al., 2019; Kabanov et al., 2023; Algeo and Shen, 2024), maximizing black shale deposition. Even though OM enrichment appears to occur regardless of relative sea-level, obliquity-forced transgression (Fig. 10D) appears to exacerbate anoxia and trigger maximal stress on the biosphere (i.e., mass extinction/depletion; Carmichael et al., 2019; Brett et al., 2020). Yet, it remains unclear whether

the transgressions associated with the deposition of black shales during the LKW and UKW represent a primary or secondary contribution. Resolving short obliquity would be required to shed light on this by investigating the succession of events on even shorter (10^4 -yr) timescales. Regardless of whether the associated transgressions were entirely astronomically forced, their potential for contributing to anoxia (Carmichael et al., 2019; Kabanov et al., 2023) remains unchanged. Phosphorus influx and recycling under reducing conditions (Percival et al., 2019, 2020) may provide a pathway to sustaining eutrophication. However, this mechanism remains debated (Reershemius and Planavsky, 2021) and recent simulations (Gérard et al., 2025) suggest that the variations of phosphate, induced by astronomical forcing, may be either too gradual or too limited in amplitude to trigger or maintain an anoxic state over extended timescales. Nevertheless, coinciding decreases in P and increases in TOC, Ni_{EF} , Mo/Al and V/Al underscore transient reducing paleoenvironmental conditions (Van Cappellen and Ingall, 1994; Tribovillard et al., 2006), especially in the Kellwasser Crisis interval.

Even though existing cyclostratigraphic interpretations ('eccentricity-minimum' hypothesis; De Vleeschouwer et al., 2017; 2024; Da Silva et al., 2020; Wichern et al., 2024 and 'maximum obliquity and eccentricity' hypothesis; Ma et al., 2022) differ to some extent, they both rely on climatically-induced anoxia, induced by increased nutrient-runoff causing eutrophication (Ma et al., 2022; De Vleeschouwer et al., 2024). Interestingly, despite the often-clear association between transgression and the Kellwasser events, as well as the observed Myr-obliquity imprint (see Ma et al., 2022), the role of eustatic sea-level variations in contributing to anoxia has not yet been considered within an astronomical framework. Here, the interplay between eccentricity- and obliquity-forced anoxia is recognized. In accordance with existing models by Da Silva et al. (2020), De Vleeschouwer et al. (2017; 2024) Ma et al. (2022) and Wichern et al. (2024), deposition and preservation of anoxic facies (e.g., black shales) were maximal during periods of maximum (short) eccentricity (i.e., maximal modulation of precession). Such a scenario is consistent with climate-driven anoxia (Jaminski et al., 1998; Liu et al., 2019; De Vleeschouwer et al., 2024). In complement, obliquity-forced sea-level variations equally contributed to marine anoxia. Whilst influx of nutrient-rich bottom waters could contribute to eutrophication, recent work by Gérard et al. (2025) suggests that, on the other hand, obliquity-forced ocean circulation and oxygen solubility changes may have caused upwelling of anoxic bottom waters.

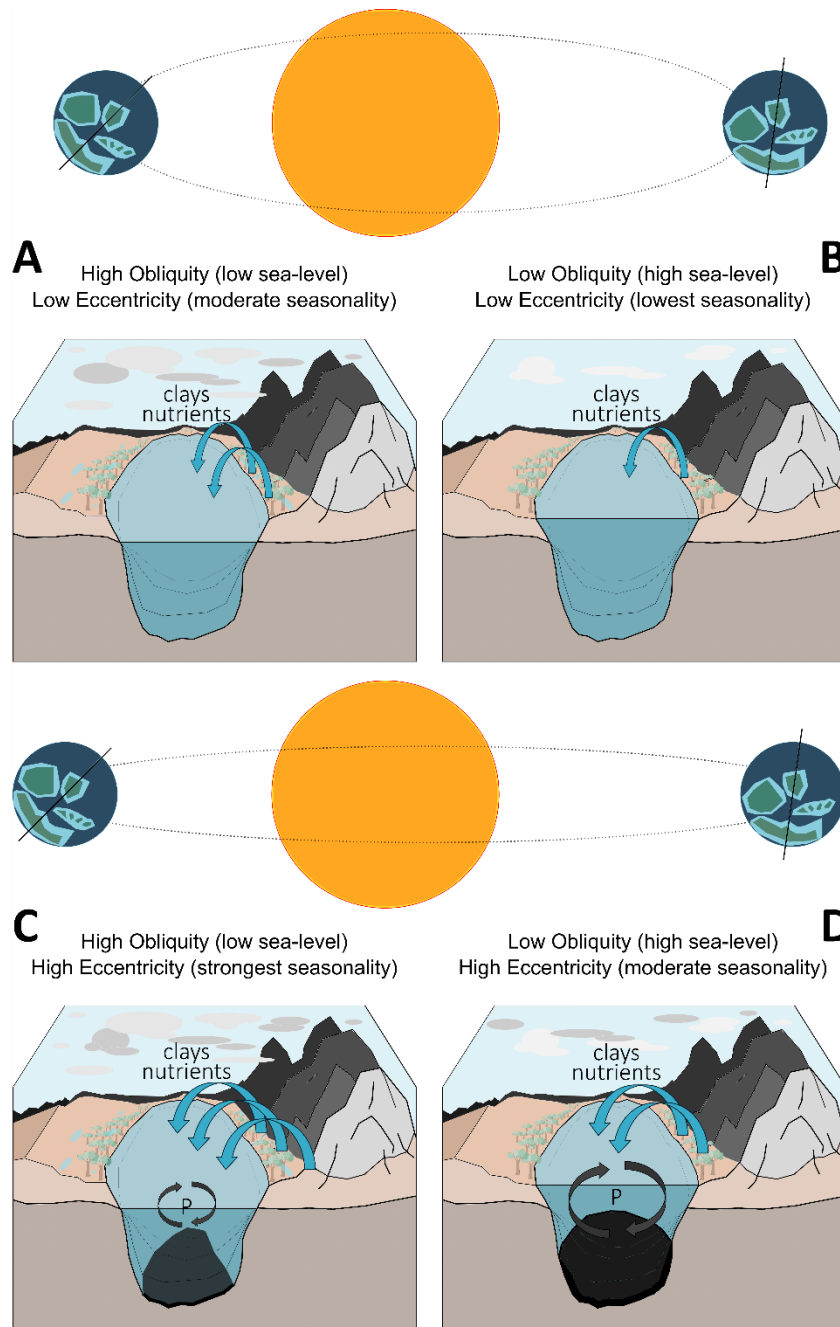


Fig. 10. Cyclostratigraphic model for the Kellwasser Crisis in a restricted (Appalachian) basin. A) High-obliquity, low-eccentricity orbital configuration corresponding to relatively low eustatic sea level and moderate seasonality resulting in moderately low influx of clays and nutrients from land. B) Low-obliquity, low-eccentricity orbital configuration corresponding to relatively high eustatic sea level and low seasonality resulting in a low influx of clays and nutrients from land. C) High-obliquity, high-eccentricity orbital configuration corresponding to relatively low eustatic sea level and strongest seasonality, resulting in the largest influx of clays and nutrients from land, increased P-recycling under oxygen-depleted conditions and OM deposition. D) Low-obliquity, high-eccentricity orbital configuration corresponding to relatively high eustatic sea level and strong seasonality, resulting in large influx of clays and nutrients from land, maximally increased P-recycling under oxygen-depleted conditions and maximal OM deposition. Blue arrows indicate influx of clays and nutrients (based on lower coarse-grained input; Ti), black arrows indicate phosphorus recycling and, hence, benthic anoxic (reducing) conditions.

Lastly, it should be mentioned that the proposed orbital configuration of maximal ~100 kyr eccentricity and obliquity-driven transgression (Fig. 10D) associated with the LKW and UKW events is not unique. Such an astronomical configuration would have occurred frequently, whereas marine anoxia appears to have been less common, indicating that other factors should be considered to explain marine anoxia development.

Even though many trigger mechanisms may be invoked that could cause regional-to-global climate perturbations and make the Earth system prone to anoxia, evidence from the WVC record hints, again, at a combined effect of seasonal contrast and sea-level variations. During the deposition of the pre-KW Crisis sandstones of the Nunda Formation, lowstand (1.2 Myr GO maximum as well as decreased subsidence; Lash and Blood, 2006; Smith and Jacobi, 2023) coincided with a node in eccentricity, during which there is a strong avoidance of seasonal contrast during a period of 405 kyr (De Vleeschouwer et al., 2024). Potentially, the termination of such long-term climatic stability during the deposition of the upper Nunda Formation may have induced rapid bio-evolutionary events (i.e., ‘strong version’ of the land-plant weathering hypothesis, Algeo et al., 1995; Algeo and Shen, 2024). This way, the Earth system may have been sufficiently stressed and brought close to the tipping point towards marine anoxia and extinction (Algeo and Shen, 2024).

5.6. Conclusions

A strong astronomical imprint on the WVC strata is recognized in multiple geochemical proxies. Short-eccentricity maxima paced enrichment and preservation of OM (TOC), oxygen depletion suggesting transient anoxia (Ni_{EF} , Mo/Al, V/Al) and influx of coarse-grained detrital material (Ti) indicating reduced monsoonal activity. A strong imprint of obliquity on Ti/Al, Q_1 , TOC and Q_1 , Ti/Al – most clearly paced by 1.2 Myr and 2.4 Myr cycles – strongly highlights astronomical control on eustatic sea-level fluctuations, predominantly through limno-eustasy. Coinciding orbitally-forced transgression and pacing of oxygen depletion implies strong orbital control on the Kellwasser Crisis interval and, most strikingly, on the LKW and UKW events. In the Appalachian Basin, the Kellwasser events are separated by four sharp peaks in TOC, paced by short eccentricity maxima. OM enrichment during the Rhinestreet Event appears paced by both 173 kyr obliquity and short- and long-eccentricity cycles, interpreted to be mediated through relative eustatic highstand.

Based on the recovered imprint of Milankovitch cycles on the WVC strata, a new model for astronomical control on the Kellwasser events in the Appalachian Basin is proposed. It reconciles existing cyclostratigraphic models for the Kellwasser Crisis (Da Silva et al., 2020; De Vleeschouwer et al., 2017; 2024; Ma et al., 2022; Wichern et al., 2024) in terms of causal mechanisms, with high eccentricity driving increased nutrient runoff, eutrophication and marine anoxia as well as the influence of obliquity on eustatic sea-level variations. Yet, it

provides a novel, more detailed synthesis of the orbital configuration commonalities of the LKW and UKW Event; an interplay of obliquity-forced transgression and eccentricity-forced increased monsoonal activity. Accordingly, an interplay of eccentricity- and obliquity-forced mechanisms for anoxia development have governed OM accumulation and preservation in the Appalachian Basin. However, since the orbital configurations associated with the Kellwasser events are not unique, it is highly probable that astronomical forcing was not the sole causal mechanism. The LKW Event appears to have occurred after a 405 kyr-period of prolonged avoidance of seasonal extrema (i.e., a node in 2.4 Myr grand eccentricity) and marks the onset of the Crisis interval. The UKW Event appears to have occurred on the rising limb of short eccentricity right after a long-eccentricity minimum, culminating during a short-eccentricity maximum at the F-F boundary.

An astronomical age model encompassing 5.67-Myr is constructed based on the recovered eccentricity imprint on TOC. The floating astrochronology provides new estimates for the duration of the Rhinestreet, LKW, and UKW events as well as the Kellwasser Crisis interval. These align with current estimates from coeval, globally distributed sections. Finally, the floating astrochronology is put into the Frasnian astrochronozonal framework of Whalen et al. (2017) and De Vleeschouwer et al. (2017), further putting the WVC record into a global and astronomical context. Future work may further refine the proposed astrochronology by increasing data resolution, thereby allowing resolving precession and short obliquity. In addition, this approach would enable an investigation into the extent to which eccentricity-modulated precession controls anoxia development, as well as whether short-obliquity forcing contributed to the stark transgressions associated with the Kellwasser events. Nevertheless, other potential mechanisms should also be considered to fully capture the complexity of these sea-level fluctuations during this key interval.

This cyclostratigraphic investigation of the Upper Devonian WVC highlights the intricate interplay of Milankovitch cycles and their effect on the Rhinestreet and Kellwasser events. By integrating existing models of anoxia, sea-level change and astronomical forcing, this study advances our understanding of the causal mechanisms that shaped these key intervals in Earth's history.

Acknowledgements

Carlton E. Brett, David De Vleeschouwer and Damien Pas are acknowledged for insightful discussions on the Devonian of New York State (USA), Devonian anoxic events and cyclostratigraphy.

Funding Sources

This is a contribution to the "Projet de Recherche" funded by the Belgian National Fund of Scientific Research (FNRS), contract T.0037.22 "WarmAnoxia". Michiel Arts is financially supported by the FNRS-PDR T.0051.19 grant "SiluCarb". FNRS had no involvement in the study design, analysis and interpretation of data, writing of the manuscript or decision to submit this study for publication.

Author contributions

Jarno J.C. Huygh: Conceptualization, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft. Thomas J. Algeo: Conceptualization, Data curation, Methodology, Project administration, Resources, Supervision, Writing – review and editing. Bradley B. Sageman: Conceptualization, Data curation, Project administration, Resources, Supervision, Writing – review and editing. Michiel Arts: Conceptualization, Formal Analysis, Investigation, Methodology, Writing – review and editing. Charles A. Ver Straeten: Data curation, Formal analysis, Investigation, Writing – review and editing. D. Jeffrey Over: Formal analysis, Investigation, Visualization, Writing – review and editing. Justin Gérard: Conceptualization, Writing – review and editing. Loïc Sablon: Conceptualization, Writing – review and editing. Michel Crucifix: Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing – review and editing. Anne-Christine Da Silva: Conceptualization, Formal Analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Writing – review and editing.

References

- Algeo, T. J. and Liu, J., 2020. A re-assessment of elemental proxies for paleoredox analysis. *Chem. Geol.*; 540, 119549. <https://doi.org/10.1016/j.chemgeo.2020.119549>.
- Algeo, T. J., and Lyons, T. W., 2006. Mo–total organic carbon covariation in modern anoxic marine environments: Implications for analysis of paleoredox and paleohydrographic conditions, *Paleoceanogr.*; 21, PA1016, doi:10.1029/2004PA001112.
- Algeo, T. J. and Scheckler, S. E., 1998. Terrestrial–marine teleconnections in the Devonian: links between the evolution of land plants, weathering processes, and marine anoxic events. *Phil. Trans*; 353, 113–130.
- Algeo, T. J. and Scheckler, S. E., 2010. Land plant evolution and weathering rate changes in the Devonian. *J. Earth Sci.*; 21, 75–78. doi:10.1007/s12583-010-0173-2.
- Algeo, T. J., and Shen, J., 2024. Theory and classification of mass extinction causation. *Natl. Sci. Rev.*, 11, nwad237. doi:10.1093/nsr/nwad237.
- Algeo, T. J., Berner, R. A., Maynard, J. B., Scheckler, S. E., 1995. Late Devonian oceanic anoxic events and biotic crises: “rooted” in the evolution of vascular land plants? *GSA Today* 5, 3, 45–66.
- Algeo, T. J., Maynard, J. B., Scheckler, S. E., 2001. Effects of the Middle to Late Devonian spread of vascular land plants on weathering regimes, marine biotas, and global climate. In: Gensel, P. G., Edwards, D. (Eds.), *Plants Invade the Land*, chapter 12, 213–236. doi:10.7312/gens11160-013
- Algeo, T. J., Remírez, M. N., Zhao, H., Schwark, L., Gordon, G., Anbar, A., Bates, S., Lyons, T., Over, D.J., , Sageman, B. B., 2026. Transient glacio-eustatic fall and its climato-environmental effects during the Frasnian-Famennian transition. *Glob. Planet. Change*; 256, 105135. <https://doi.org/10.1016/j.gloplacha.2025.105135>
- Alvarez, L. W., Alvarez, W., Asaro, F., Michel, H. V., 1980. Extraterrestrial Cause for the Cretaceous-Tertiary Extinction. *Science*; 208, 4448, 1095–1108. doi: 10.1126/science.208.4448.1095.
- Arts, M.C.M., 2023. WaverideR: Extracting Signals from Wavelet Spectra. <https://CRAN.R-project.org/package=WaverideR>
- Arts, M.C.M., Corradini, C., Pondrelli, M., Pas, D., Da Silva, A.-C., 2024. Age and orbital forcing in the upper Silurian Cellon section (Carnic Alps, Austria) uncovered using the WaverideR R package. *Front. Earth Sci.*, 12, <https://doi.org/10.3389/feart.2024.1357751>
- Averbuch, O., Tribouillard, N., Devleeschouwer, X., Riquier, L., Mistiaen, B., Van Vliet-Lanoe, B., 2005. Mountain building-enhanced continental weathering and organic carbon burial as major causes for climatic cooling at the Frasnian–Famennian boundary (c. 376 Ma)? *Terra Nova*; 17; 1, 25–34. doi:10.1111/j.1365-3121.2004.00580.x
- Becker, R. T., Marshall, J. E. A., Da Silva, A.-C., 2020. The Devonian Period. In: Gradstein, F. M., Ogg, J. G., Schmitz, M. D. And Ogg, G. (Eds.), *The Geologic Time Scale 2020*, chapter 22, 733–810. <https://doi.org/10.1016/B978-0-12-824360-2.00022-X>.
- Bennet, W. W., Canfield, D. E., 2020. Redox-sensitive trace metals as paleoredox proxies: A review and analysis of data from modern sediments. *Earth Sci. Rev.*; 204, 103175. <https://doi.org/10.1016/j.earscirev.2020.103175>.
- Berger, A. L., 1973. La théorie astronomique des paléoclimats, PhD thesis, p315, Université catholique de Louvain. <https://hdl.handle.net/2078.1/233872>
- Berger, A. L., 1987. Long-term variations of caloric insolation resulting from the Earth’s orbital elements. *Quat. Res.*; 9, 139–167.
- Berger, A. L., 1988. Milankovitch Theory and Climate. *Rev. Geophys.*; 26, 4, 624–657. <https://doi.org/10.1029/RG026i004p00624>
- Bretagnon, P., 1974. Termes à longues périodes dans le système solaire, *Astron. Astroph.*, 30, 141–154.

- Brett, C. E., Zambito, J. J. IV, McLaughlin, P. I., Emsbo, P., 2020. Revised perspectives on Devonian biozonation and environmental volatility in the wake of recent time-scale revisions. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 549, 108843. <https://doi.org/10.1016/j.palaeo.2018.06.037>.
- Calvert, S. E. and Pedersen, T. F., 2007. Elemental proxies for palaeoclimatic and palaeoceanographic variability in marine sediments: interpretation and application. In: Hillaire-Marcel, C. and De Vernal, A. (Eds.), *Proxies in late Cenozoic Paleocanography*, chapter 14, Dev. In Mar. Geol.; 1, 567-643. ISSN 1572-5480, doi:10.1016/S1572-5480(07)01019-6.
- Carmichael, S. K., Waters, J. A., Köningshof, P., Suttner, T. J., Kido, E., 2019. Paleogeography and paleoenvironments of the Late Devonian Kellwasser event: A review of its sedimentological and geochemical expression. *Glob. Planet. Change*; 183, 102984. <https://doi.org/10.1016/j.gloplacha.2019.102984>.
- Croudace, I. W. and Rothwell, R. G., 2015. Micro-XRF studies of sediment cores, Applications of a non-destructive tool for the environmental sciences. In: Smol, J. P. (Ed.), *Dev. in Paleoenv. Res.*; 17, ISSN 1571-5299.
- Da Silva, A.-C., Sinnesael, M., Claeys, P., Davies, J. H. F. L., de Winter, N. J., Percival, L. M. E., Schaltegger, U., De Vleeschouwer, D., 2020. Anchoring the Late Devonian mass extinction in absolute time by integrating climatic controls and radio-isotopic dating. *Sci. Rep.*; 10, 12940. <https://doi.org/10.1038/s41598-020-69097-6>.
- De Vleeschouwer, D., Da Silva, A.-C., Boulvain, F., Crucifix, M. & Claeys, P., 2012. Precessional and half-precessional climate forcing of Mid-Devonian monsoon-like dynamics. *Clim. Past*; 8, 337–351.
- De Vleeschouwer, D., Rakociński, M., Racki, G., Bond, D. P. G., Sobieć, K., Claeys, P., 2013. The astronomical rhythm of Late-Devonian climate change (Kowala section, Holy Cross Mountains, Poland). *Earth Planet. Sci. Lett.*; 365, 25-37. <http://dx.doi.org/10.1016/j.epsl.2013.01.016>.
- De Vleeschouwer, D., Crucifix, M., Bounceur, N. & Claeys, P., 2014. The impact of astronomical forcing in the Late Devonian greenhouse climate. *Glob. Planet. Change*; 120, 65–80.
- De Vleeschouwer, D., Da Silva, A.-C., Sinnesael, M., Chen, D., Day, J. E., Whalen, M. T., Guo, Z., Claeys, P., 2017. Timing and pacing of the Late Devonian mass extinction event regulated by eccentricity and obliquity. *Nat. Comm.*; 8, 2268. doi:10.1038/s41467-017-02407-1.
- De Vleeschouwer, D., Percival, L. M. E., Wichern, N. M. A., Batenburg, S. J., 2024. Pre-Cenozoic cyclostratigraphy and palaeoclimate responses to astronomical forcing. *Nat. Rev. Earth Environ.*; 5, 56-75. <https://doi.org/10.1038/s43017-023-00505-x>.
- d-maps.com, State of New York map. Last accessed via: https://d-maps.com/pays.php?num_pay=379&num_pag=1&lang=en on April 7th, 2025.
- Gérard, J., Sablon, L., Huygh, J. J. C., Da Silva, A.-C., Pohl, A., Vérard, C., Crucifix, M., 2025. Exploring the mechanisms of Devonian oceanic anoxia: impact of ocean dynamics, palaeogeography, and orbital forcing. *Clim. Past*; 21, 239-260. <https://doi.org/10.5194/cp-21-239-2025>.
- Gérard, J., Pohl, A., Sablon, L., Huygh, J. J. C., Da Silva, A.-C., Crucifix, M., 2026. Spatially contrasted response of Devonian anoxia to astronomical forcing. *Clim. Past*; 22, 1003-1021. <https://doi.org/10.5194/cp-22-1003-2026>.
- Hays, J. D., Imbrie, J. & Shackleton, N. J., 1976. Variations in the Earth's orbit: pacemaker of the ice ages. *Science* 194, 1121–1132.
- Hilgen, F., Lourens, L., and Pälike, H., 2020. Should unit-stratotypes and astrochronozones be formally defined? A dual proposal (including postscriptum). *News. Stratigr.*; 53, 19.
- Hinnov, L. A., 2000. New perspectives on orbitally forced stratigraphy. *Annu. Rev. Earth Planet. Sci.*, 28, 419-475. doi:10.1146/annurev.earth.28.1.419
- Hinnov, L. A., 2013. Cyclostratigraphy and its revolutionizing applications in the Earth and planetary sciences. *Geol. Soc. Am. Bull.*; 125, 1703–1734.

- Huang, C., Joachimski, M. M., Gong, Y., 2018. Did climate changes trigger the Late Devonian Kellwasser Crisis? Evidence from high-resolution conodont $\delta^{18}\text{OPO}_4$ record from South China. *Earth Planet. Sci. Lett.*; 495, 174-184. <https://doi.org/10.1016/j.epsl.2018.05.016>.
- Jaminski, J., Algeo, T.J., Maynard, J.B., Hower, J.C., 1998. Climatic origin of dm-scale compositional cyclicity in the Cleveland Member of the Ohio Shale (Upper Devonian), Central Appalachian Basin, USA. In: Schieber, J., et al. (eds.), *Shales and Mudstones*, vol. 1, Schweizerbart'sche, Stuttgart, Germany, 217-242.
- Joachimski, M.M. and Buggisch, W., 2002. Conodont apatite $\delta^{18}\text{O}$ signatures indicate climatic cooling as a trigger of the Late Devonian mass extinction. *Geology*; 30: 711-714. [https://doi.org/10.1130/0091-7613\(2002\)030<0711:CAOSIC>2.0.CO;2](https://doi.org/10.1130/0091-7613(2002)030<0711:CAOSIC>2.0.CO;2).
- Kabanov, P., Hauck, T. E., Gouwy, S. A., Grasby, S. E., van der Boon, A., 2023. Oceanic anoxic events, photic-zone euxinia, and controversy of sea-level fluctuations during the Middle-Late Devonian. *Earth Sci. Rev.*; 241, 104415. <https://doi.org/10.1016/j.earscirev.2023.104415>.
- Lash, G. G. and Blood, D. R., 2006. The Upper Devonian Rhinestreet black shale of western New York State – evolution of a hydrocarbon system. In: 78th Meeting, New York State Geological Association, Sunday B1 field trip, p. 223-289.
- Laskar, J., 1990. The chaotic motion of the solar system: A numerical estimate of the size of the chaotic zones, *Icarus*, 88, 266-291. doi:10.1016/0019-1035(90)90084-m
- Laskar, J., 2020. Astrochronology. In: Gradstein, F. M., Ogg, J. G., Schmitz, M. D. And Ogg, G. (Eds.), *The Geologic Time Scale 2020*, chapter 4, 139-158.
- Laskar, J., Robutel, P., Joutel, F., Gastineau, M., Correia, A. C. M., Levrard, B., 2004. A long-term numerical solution for the insolation quantities of the Earth. *Astron. Astrophys.*; 428, 1, 261-285. <https://doi.org/10.1051/0004-6361:20041335>.
- Li, M., Hinnov, L. A., Huang, C., Ogg, J. G., 2018. Sedimentary noise and sea levels linked to land–ocean water exchange and obliquity forcing. *Nat. Comm.*; 9, 1004. doi:10.1038/s41467-018-03454-y.
- Liu, J.S., Algeo, T.J., Jaminski, J., Kuhn, T., Joachimski, M.M., 2019. Evaluation of high-frequency paleoenvironmental variation using an optimized cyclostratigraphic framework: Example for CS-Fe analysis of Devonian-Mississippian black shales (Central Appalachian Basin, USA). *Chem. Geol.*, 525, 303-320.
- Lourens, L. J., Hilgen, F. J., 1997. Long-periodic variations in the Earth's obliquity and their relation to third-order eustatic cycles and late Neogene glaciations. *Quat. Int.*; 40, 43-52.
- Lu, M., Lu, Y., Ikejiri, T., Sun, D., Carroll, R., Blair, E.H., Algeo, T.J. and Sun, Y., 2021. Periodic oceanic euxinia and terrestrial fluxes linked to astronomical forcing during the Late Devonian Frasnian–Famennian mass extinction. *Earth and Planetary Science Letters*, 562, 116839.
- Ma, K., Hinnov, L. A., Zhang, X., Gong, Y., 2022. Astronomical climate changes trigger Late Devonian bio- and environmental events in South China. *Glob. Planet. Change*; 215, 103874. <https://doi.org/10.1016/j.gloplacha.2022.103874>.
- McLennan, S. M., 2001. Relationships between the trace element composition of sedimentary rocks and upper continental crust. *Geochem. Geophys. Geosyst.*; 2, 2000GC000109. <https://doi.org/10.1029/2000GC000109>.
- Meyers, S.R., 2014. Astrochron: An R Package for Astrochronology. <https://cran.r-project.org/package=astrochron>
- Meyers, S. R., 2015. The evaluation of eccentricity-related amplitude modulation and bundling in paleoclimate data: An inverse approach for astrochronologic testing and time scale optimization. *Paleoceanogr.*; 30, 12, 1625-1640. <https://doi.org/10.1002/2015PA002850>.
- Meyers, S. R., 2019. Cyclostratigraphy and the problem of astrochronologic testing. *Earth Sci. Rev.*; 190, 190-223. <https://doi.org/10.1016/j.earscirev.2018.11.015>.
- Meyers, S. R. and Hinnov, L. A., 2010. Northern Hemisphere glaciation and the evolution of Plio-Pleistocene climate noise. *Paleoceanogr.*; 25, PA3207. doi:10.1029/2009PA001834.

- Miller, K. G., Kominz, M. A., Browning, J. V., Wright, J. D., Mountain, G. S., Katz, M. E., Sugarman, P. J., Cramer, B. S., Cristie-Blick, N., Pekar, S. F., 2005. The Phanerozoic Record of Global Sea-Level Change. *Science*; 310, 1293-1298. doi: 10.1126/science.1116412.
- Mudelsee, M., 2010. *Climate Time Series Analysis, Classical statistical and bootstrap methods*. ISSN 1383-9601.
- Murphy, A. E., Sageman, B. B., Hollander, D. J., 2000. Eutrophication by decoupling of the marine biogeochemical cycles of C, N, and P: A mechanism for the Late Devonian mass extinction. *Geology*; 28, 5, 427-430.
- Over, D. J., 1997. Conodont biostratigraphy of the Java Formation (Upper Devonian) and the Frasnian-Famennian boundary in western New York State. *GSA Spec. Pap.*; 321.
- Over, D. J., Baird, G. C., Kirchgasser, W. T., 2023. The Frasnian Strata - Lower Upper Devonian – of New York State. Chapter 1 in: Ver Straeten, C.A., Over D. J., and Woodrow, D. (Eds.), *Devonian of New York, Volume 3: Frasnian to Famennian (Upper Devonian) stages and the Devonian terrestrial system in New York*, , *Bull. Am. Paleontol.*; 1-28. doi:10.32857/bap.2023.407.01.
- Percival, L.M.E., Davies, J. H. F. L., Schaltegger, U., De Vleeschouwer, D., Da Silva, A.-C., Föllmi, K. B., 2018. Precisely dating the Frasnian-Famennian boundary: implications for the cause of the Late Devonian mass extinction. *Sci. Rep.*; 8, 9578. doi:10.1038/s41598-018-27847-7.
- Percival, L. M. E., Selby, D., Bond, D. P. G., Rakociński, M., Racki, G., Marynowski, L., Adatte, T., Spangenberg, J. E., Föllmi, K. B., 2019. Pulses of enhanced continental weathering associated with multiple Late Devonian climate perturbations: Evidence from osmium-isotope compositions. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 524, 240-249.
- Percival, L. M. E., Selby, D., Bond, D. P. G., Rakociński, M., Marynowski, L., Hood, A. v. S., Adatte, T., Spangenberg, J. E., Föllmi, K. B., 2020. Phosphorus-cycle disturbances during the Late Devonian anoxic events. *Glob. Planet. Change*; 184, 103070. <https://doi.org/10.1016/j.gloplacha.2019.103070>.
- Pisarzowska, A. and Racki, G., 2020. Comparative carbon isotope chemostratigraphy of major Late Devonian biotic crises, chapter 8. *Stratigr. Timescales*; 5, 387-466.
- Racki, G. A., 2020. Volcanic scenario for the Frasnian–Famennian major biotic crisis and other Late Devonian global changes: more answers than questions? *Glob. Planet. Change*; 189, 103174. <https://doi.org/10.1016/j.gloplacha.2020.103174>.
- Raup, D. M. and Sepkoski, J. J., Jr., 1982. Mass extinctions in the marine fossil record. *Science*; 215, 4539, 1501-1503. doi:10.1126/science.215.4539.1501.
- Reershemius, T. and Planavsky, N. J., 2021. What controls the duration and intensity of ocean anoxic events in the Paleozoic and Mesozoic? *Earth Sci. Rev.*; 221; 103787. <https://doi.org/10.1016/j.earscirev.2021.103787>.
- Sageman, B. B., Murphy, A. E., Werne, J. P., Ver Straeten, C. A., Hollander, D. J., Lyons, T. W., 2003. A tale of shales: the relative roles of production, decomposition, and dilution in the accumulation of organic-rich strata, Middle–Upper Devonian, Appalachian basin. *Chem. Geol.*; 195, 229-273. doi:10.1016/S0009-2541(02)00397-2.
- Schindler, E., 1990. The late Frasnian (Upper Devonian) Kellwasser Crisis. In: Kauffman, E.G., Walliser, O.H. (Eds.), *Extinction Events in Earth History: Proceedings of the Project 216: Global Biological Events in Earth History*; 151–159. <https://doi.org/10.1007/BFb0011143>.
- Schindler, E., 1993. Event-stratigraphic markers within the Kellwasser Crisis near the Frasnian/Famennian boundary (Upper Devonian) in Germany. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 104, 1, 115–125.
- Smart, M. S., Filippelli, G., Gilhooly, W. P. III, 2023. Enhanced terrestrial nutrient release during the Devonian emergence and expansion of forests: evidence from lacustrine phosphorus and geochemical records. *Geol. Soc. Am. Bull.*; 135: 1879-1898. <https://doi.org/10.1130/B36384.1>.
- Smith, D. G., 2023. The Orbital Cycle Factory: Sixty cyclostratigraphic spectra in need of re-evaluation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 628, 111744. <https://doi.org/10.1016/j.palaeo.2023.111744>.
- Smith, G. J. and Jacobi, R. D., 2023. Upper Frasnian and Famennian stratigraphy in western New York State. Chapter 3 in: Ver Straeten, C.A., Over D. J., and Woodrow, D. (Eds.), *Devonian of New York, Volume*

- 3: Frasnian to Famennian (Upper Devonian) stages and the Devonian terrestrial system in New York, *Bull. Am. Paleontol.*; 47-111. doi:10.32857/bap.2023.407.03.
- Tribovillard, N., 2021. Re-assessing copper and nickel enrichments as paleoproductivity proxies. *Earth Sci. Bull.*; 192, 54. <https://doi.org/10.1051/bsgf/2021047>.
- Tribovillard, N., Algeo, T. J., Lyons, T. W., Riboulleau, A., 2006. Trace metals as paleoredox and paleoproductivity proxies: An update. *Chem. Geol.*; 232, 12-32. doi:10.1016/j.chemgeo.2006.02.012.
- Van Cappellen, P. and Ingall, E. D., 1994. Benthic phosphorus regeneration, net primary production, and ocean anoxia: A model of the coupled marine biogeochemical cycles of carbon and phosphorus. *Paleoceanography*, 9, 5, 677-692. <https://doi.org/10.1029/94PA01455>
- Van der Weijden, C. H., 2002. Pitfalls of normalization of marine geochemical data using a common divisor. *Mar. Geol.*; 184, 167-187.
- Ver Straeten, C. A., 2009. The classic Devonian of the Catskill Front: A foreland basin record of Acadian Orogenesis. In: Vollmer, F. (Ed), *New York State Geological Association, 81st Annual Meeting Guidebook*; 7, 1-54.
- Ver Straeten, C. A., 2010. Lessons from the foreland basin: Appalachian basin perspectives on the Acadian orogeny. In: Tollo, R.P., Bartholomew, M.J., Hibbard, J.P. and Paul M. Karabinos, P.M. (Eds.), *From Rodinia to Pangea: The Lithotectonic Record of the Appalachian Region*, *Geol. Soc. Am.*, 206, 251-282.
- Ver Straeten, C. A., 2023. An introduction to the Devonian Period, and the Devonian in New York State and North America. In: Ver Straeten, C. A., Over, D. J. and Woodrow, D. (Eds.), *Devonian of New York, Volume 1: Introduction and Pridoli to lower Givetian (Upper Silurian to Middle Devonian) stages*. *Bull. Am. Paleontol.*; 403-404. doi:10.32857/bap.2023.403.03.
- Ver Straeten, C. A., Brett, C. E., Sageman, B. B., 2011. Mudrock sequence stratigraphy: A multi-proxy (sedimentological, paleobiological and geochemical) approach, Devonian Appalachian Basin. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 304, 54-73. doi:10.1016/j.palaeo.2010.10.010.
- Ver Straeten, C. A., Over, D. J., Baird, G. C., 2020. Arc-to-craton: Devonian air-fall tephra in the eastern United States. In: Avari, K. L., Hasson, K. O. and Diecchio, R. J. (Eds.), *The Appalachian Geology of John M. Dennison: Rocks, People, and a Few Good Restaurants along the Way*. *Geol. Soc. Am. Spec. Pap.*; 545, 35-53. [https://doi.org/10.1130/2020.2545\(03\)](https://doi.org/10.1130/2020.2545(03)).
- Walliser, O. H., 1996. *Global events and event stratigraphy*. ISBN-13: 978-3-642-79636-4. Springer; 225-250. doi:10.1007/978-3-642-79634-0.
- Wang, X., Liu, S.-A., Wang, Z., Chen, D., Zhang, L., 2018. Zinc and strontium isotope evidence for climate cooling and constraints on the Frasnian-Famennian (~372 Ma) mass extinction. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 498, 68-82. <https://doi.org/10.1016/j.palaeo.2018.03.002>.
- Weedon, G. P., 2022. Problems with the current practice of spectral analysis in cyclostratigraphy: Avoiding false detection of regular cyclicity. *Earth Sci. Rev.*; 235, 104261. <https://doi.org/10.1016/j.earscirev.2022.104261>.
- Whalen, M. T., De Vleeschouwer, D., Payne, J. H., Day, J. E., Over, D. J., Claeys, P., 2017. Pattern and timing of the Late Devonian biotic crisis in western Canada: Insights from carbon isotopes and astronomical calibration of magnetic susceptibility data. In: Playton, T. E., Kerans, C., Weissenberger, J. A. W. (Eds.), *New advances in Devonian carbonates: Outcrop analogs, reservoirs and chronostratigraphy*, *SEPM*; 107, 185-201. ISBN 978-1-56576-344-9. <https://doi.org/10.2110/sepm.107>
- Wichern, N. M. A., Bialik, O. M., Nohl, T., Percival, L. M. E., Becker, T. R., Kaskes, P., Claeys, P., De Vleeschouwer, D., 2024. Astronomically paced climate and carbon cycle feedbacks in the lead-up to the Late Devonian Kellwasser Crisis. *Clim. Past*; 20, 415-448. <https://doi.org/10.5194/cp-20-415-2024>
- Wigley, T. M. L., 1976, Spectral analysis and the astronomical theory of climatic change, *Nature*, 264, 629–631, doi:10.1038/264629a0
- Zeebe, R. E. and Lantink, M. L., 2024. A secular solar system resonance that disrupts the dominant cycle in Earth's orbital eccentricity (g₂ – g₅): Implications for astrochronology. *Astron. J.*; 167:204. <https://doi.org/10.3847/1538-3881/ad32cf>.

- Zeebe, R. E. and Kocken, I. J., 2025. Applying astronomical solutions and Milanković forcing in the Earth sciences. *Earth Sci. Rev.*; 261, 104959. <https://doi.org/10.1016/j.earscirev.2024.104959>
- Zeeden, C., Meyers, S., Hilgen, F., Lourens, L., Laskar, J., 2019. Time scale evaluation and the quantification of obliquity forcing. *Quat. Sci. Rev.*; 209, 100-113. <https://doi.org/10.1016/j.quascirev.2019.01.018>.

5.7. Supplemental Information

A. R-script and Research Data

The R-script and research data can be accessed via <https://doi.org/10.5281/zenodo.17295523>.

B. Proxies

Total Organic Carbon – Total organic carbon (TOC), a proxy for the flux, accumulation and preservation of OM (Sageman et al., 2003; Ver Straeten et al., 2011), varies from 0.00 to 4.75 % throughout the record. The highest values are recorded in the black shales of the basal Rhinestreet Formation as well as the Pipe Creek Formation (LKW) and Hanover Formation (incl. UKW) (Fig. 2). Petrographic studies indicate that the majority of OM in Appalachian Basin Devonian black shales originated from the marine realm (Jaminski et al., 1998; Sageman et al., 2003). As a prime indicator for marine anoxic events in semi-restricted basins (Carmichael et al., 2019), the TOC proxy signal is the primary target for cyclostratigraphy, with the goal of determining whether these events and their pacing are astronomically forced (cf. Liu et al., 2025).

Detrital Input (Ti) – Titanium is a conservative, redox-insensitive, diagenetically resistant element that is associated with the coarse-grained, detrital fraction of the sedimentary record and is commonly transported from the continent into the ocean (Calvert and Pedersen, 2007; Croudace and Rothwell, 2015). For the Appalachian foreland Basin, the majority of Ti originated from dense, silt-to-sand-sized grains from the surrounding Euramerican continent and is interpreted to reflect increased influx of coarse-grained material due to reduced monsoonal activity during periods of increased aridity (Jaminski et al., 1998; Liu et al., 2019; Wichern et al., 2024). Most likely, the prograding Catskill Delta complex as a result of the Acadian Orogeny further contributed to the Ti-budget (Ver Straeten, 2009; Smith and Jacobi, 2023).

Sea Level (Ti/Al) – Often, elemental proxy concentrations are normalized versus immobile elements such as Al to account for facies changes, dilution, etc. (Calvert and Pedersen, 2007; Croudace and Rothwell, 2015), which has proven useful for interpreting geochemical element profiles (Van der Weijden, 2002). Moreover, normalization to Al is also utilized for the calculation of trace-metal enrichment factors (Algeo and Liu, 2020; McLennan, 2001; Tribouvillard, 2021). Here, both Ti and Al can be attributed to the detrital fraction of the sediment. Generally, Ti/Al is interpreted as a sedimentary grain-size proxy (Calvert and Pedersen, 2007). Grain-size variations may be the result of a wide range of paleoclimatic and paleoenvironmental changes, such as a shift in climatic conditions (e.g. wet/dry cycles) causing a shift in eolian versus fluvial influx (Croudace and Rothwell, 2015; Lourens et al., 2001) or eustatic sea-level variations (Calvert and Pedersen, 2007; Chen et al., 2013).

Specifically for the West Valley core, the Ti/Al ratio is interpreted – based on geochemical and petrographic data – to reflect relative sea-level changes and related aggradation/progradation (Sageman et al., 2003). Thus, an increase Ti/Al is interpreted to primarily reflect progradation and relative sea-level fall (and vice-versa). In addition, trends in Ti/Al match well with regional stratigraphic trends (Sageman et al., 2003), further justifying its use as a proxy for sea-level change. Yet, a minor eolian contribution to variations in the Ti/Al signal is not excluded by Sageman et al. (2003). Therefore, it is highly likely that Ti/Al represents an amalgamated signal, containing long-term global signals (e.g. sea level changes) with superimposed shorter-term regional-to-global changes in the composition of terrigenous influx (e.g. due to increased aeolian supply).

Trace Metal Proxies – A plethora of trace metal paleoredox proxies are readily available from the geochemical dataset by Sageman et al. (2003). In this study, three proxies are included that provide insight on paleoredox conditions, as well as paleoproduction and -hydrography.

Ni_{EF} is an efficacious proxy across the redox-spectrum and can be strongly enriched under sulfate-reducing conditions (Algeo and Liu, 2020). This enrichment factor was calculated as: $Ni_{EF} = [(Ni/Al)_{sample}/(Ni/Al)_{upper\ crust}]$ according to McLennan (2001) using Al_{crust} = 8.04% and Ni_{crust} = 44 ppm. In addition, re-assessment of the geochemical database of Algeo and Liu (2020) by Tribovillard (2021) highlights that Ni_{EF} equally has merit as a paleoproductivity proxy. Enrichment of Ni in association with other paleoredox proxies (e.g., V, Mo) and elevated TOC-values indicate paleoproductivity and anoxia were intertwined (Tribovillard et al., 2006). Conversely, absence of Ni in otherwise anoxic sediment may be explained by restricted water-mass renewal or stagnation (Tribovillard et al., 2006). Thus, an increase in Ni_{EF} is interpreted to reflect increased paleoproductivity and, if accompanied by an increase of other paleoredox proxies, a decrease in bottom water oxygenation. The Pearson's correlation indicates positive correlation between Ni_{EF} and TOC ($r = +0.67$, $p < 2.2e^{-16}$).

Sedimentary Mo is generally enriched in organic-rich marine facies deposited under anoxic conditions and is classically used as a benthic redox potential proxy, especially in association with other paleoredox proxies such as V (i.e., paleoredox proxy; Algeo and Lyons, 2006; Tribovillard et al., 2006). Typically, Mo burial peaks in weakly sulfidic paleoenvironments and is lower under strongly sulfidic conditions (see Algeo and Lyons, 2006). Hence, lower Mo-values during an anoxic interval may be indicative of stronger reducing (sulfidic) conditions. However, this proxy is highly susceptible to reservoir effects in anoxic silled basins (Algeo and Lyons, 2006), as was most likely – at least intermittently – the case for the Late Devonian Appalachian Basin (Algeo et al., 2025). As such, Mo/Al is also linked to hydrographic restriction of the deep-water mass and is therefore interpreted as an amalgamated signal. This interpretation is complemented by Mo/TOC (Algeo and Lyons, 2006). The Pearson's product-moment correlation indicates correlation between Mo/Al and TOC ($r = 0.7342$, $p < 2.2e^{-16}$).

V is considered a redox proxy with minimal detrital influence (Tribovillard et al., 2006), undergoing a two-step reduction process that is strongly dependent on the intensity of reducing conditions (Tribovillard et al., 2006). Through comparison of its covariation with other paleoredox proxies (e.g., Ni, Mo) and TOC, it enables distinguishing anoxic and euxinic paleoconditions (Tribovillard et al., 2006). The Pearson's product-moment correlation indicates moderate correlation between V/Al and TOC ($r = 0.3838$, $p < 1.25e^{-09}$).

Stable Carbon Isotopes – Carbon cycle perturbations are tracked using $\delta^{13}\text{C}_{\text{org}}$ (from Murphy et al., 2000; Sageman et al., 2003). A positive carbon isotope excursion (pCIE) is interpreted to reflect reservoir shifts (e.g., net atmospheric CO_2 drawdown and carbon burial) and can be associated with climatic cooling (and vice-versa) (Murphy et al., 2000; Algeo and Shen, 2024). Two pCIE's, reaching peak values of -26.88‰ and -26.92‰ ($\delta^{13}\text{C}_{\text{org}} \text{‰}$ vs. PDB) characterize the LKW and UKW, respectively (Sageman et al., 2003).

Phosphorus – The key role of phosphorus (P) during the Kellwasser Crisis as a limiting nutrient for primary production and, consequently, as a proxy for nutrient flux, has been thoroughly highlighted by Percival et al. (2020) for the WVC. Land-plant-mediated nutrient influx, combined with ocean circulation changes and upwelling as well as P-recycling in reducing sediment offer multiple mechanisms via which the global phosphorus cycle may have contributed to marine anoxia development and sustenance (Algeo and Scheckler, 1998; Murphy et al., 2000; Percival et al., 2020; Sageman et al., 2003).

C. eTimeOpt Analyses (TOC, Ti)

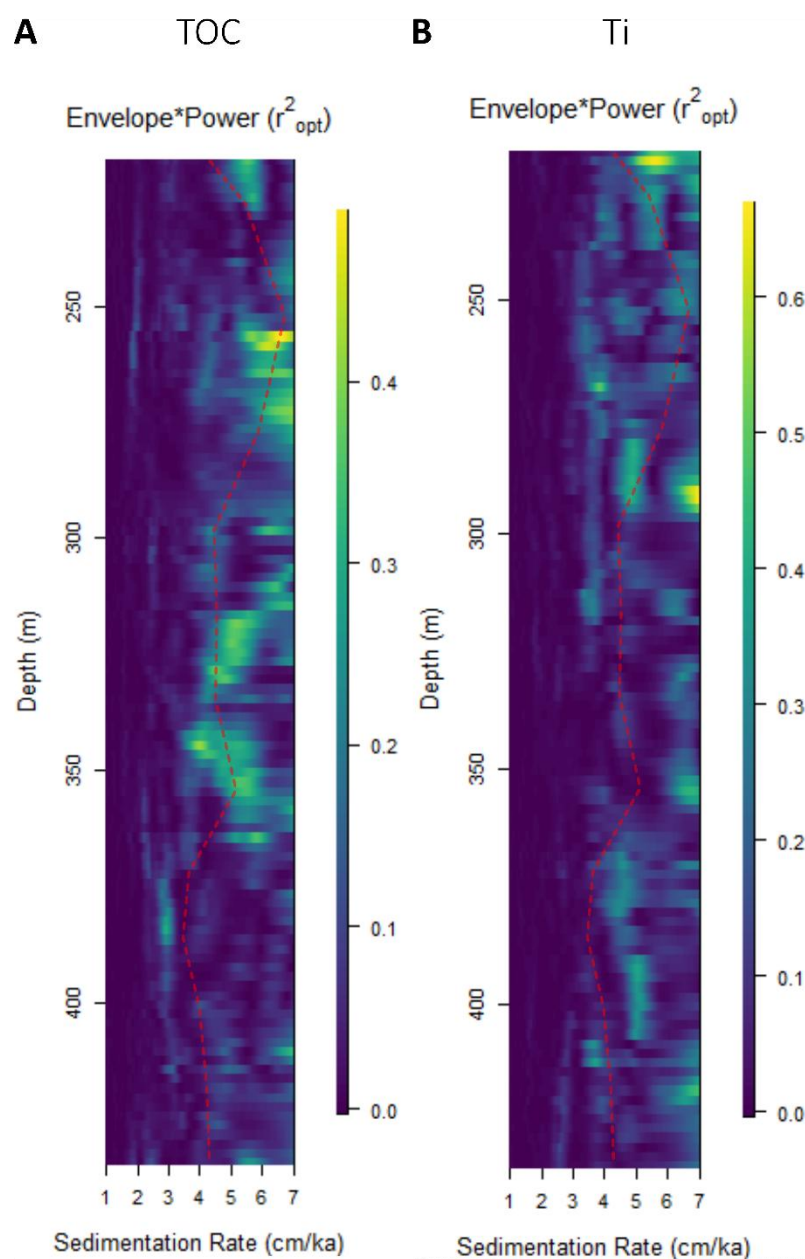


Fig. S1. eTimeOpt analysis of TOC and Ti. The ASR curve of the astronomical TOC age model is superimposed (dashed red).

D. Alternative Age Model (TOC)

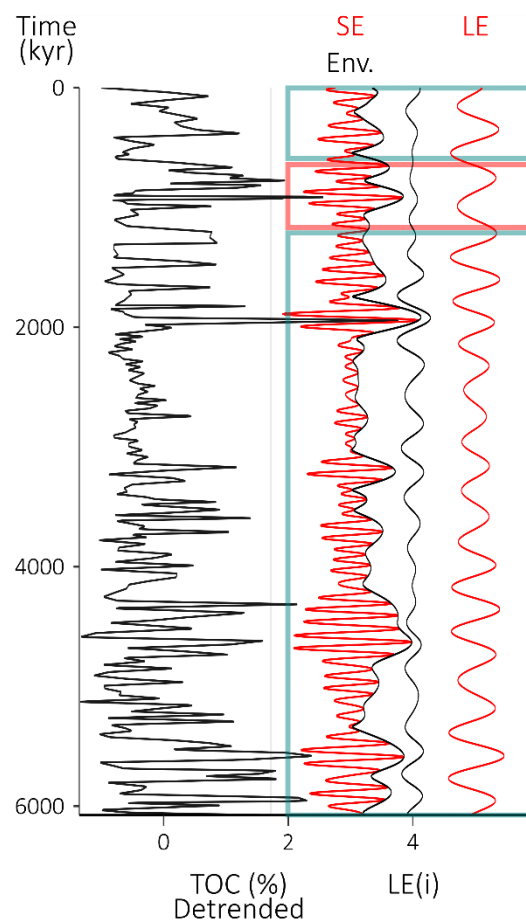


Fig. S2. Tuned TOC and eccentricity bandpass filter output. Detrended TOC (%), black), bandpass filters corresponding to 100 kyr SE (red), its envelope (black), 405 kyr LE(i) extracted from the envelope of SE (black), 405 kyr LE (red). Green boxes indicate a consistent phase relationship; the red box indicates an inconsistent phase relationship between the envelope of SE (LE(i)) and LE. Note relative time based on floating astrochronology.

E. Time-domain Cyclostratigraphy (Ti)

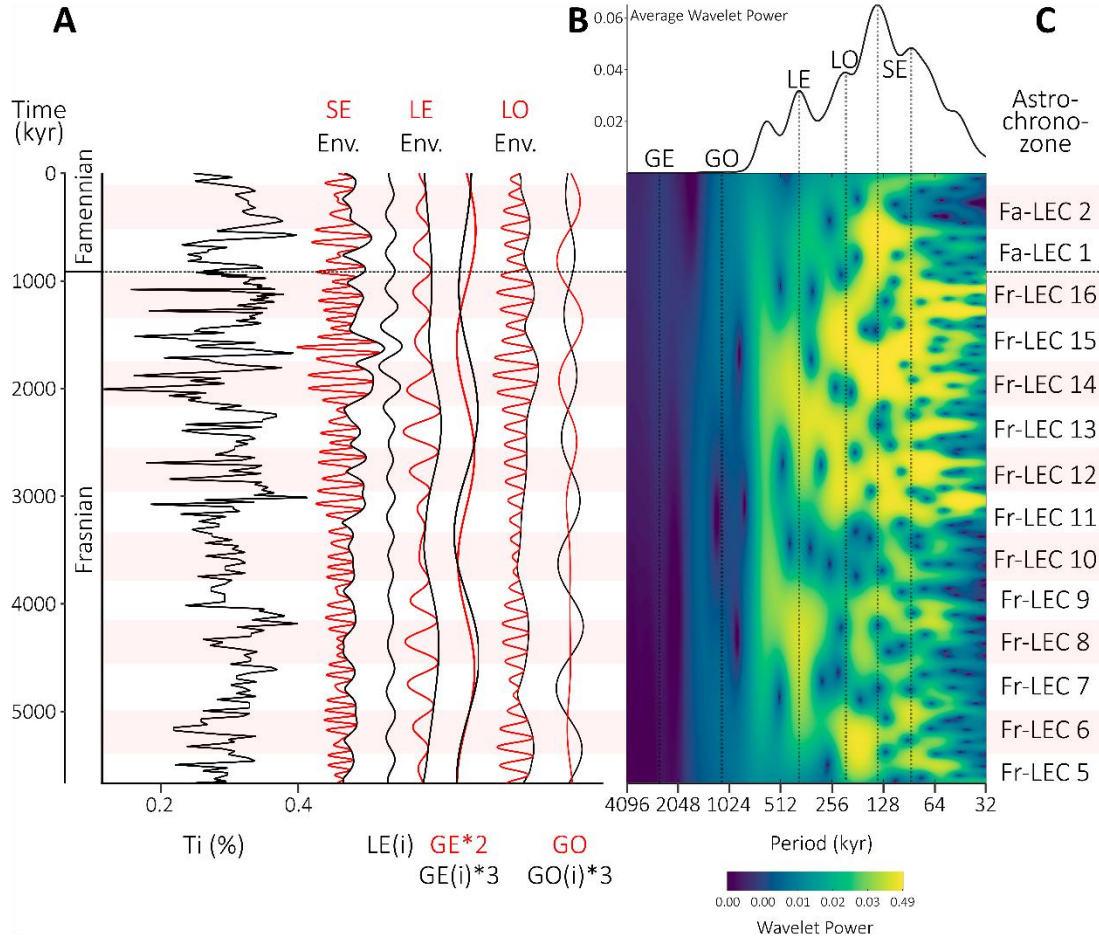


Fig. S3. Time-domain cyclostratigraphic analysis of Ti. A) Detrended Ti and bandpass filters corresponding to 100 kyr SE (red; $1/150$ to $1/80 \text{ kyr}^{-1}$), its envelope (black), 405 kyr LE extracted from the envelope of SE (black; $1/505$ to $1/305 \text{ kyr}^{-1}$), 405 kyr LE (red; $1/505$ to $1/305 \text{ kyr}^{-1}$), its envelope (black), 2.4 Myr GE extracted from the envelope of GE (GE(i), black, scaled by factor 3; $1/2900$ to $1/1900 \text{ kyr}^{-1}$), 2.4 Myr GE (red, scaled by factor 2; $1/2900$ to $1/1900 \text{ kyr}^{-1}$), 173 kyr LO (red; $1/213$ to $1/133 \text{ kyr}^{-1}$), its envelope (black), 1.2 Myr GO extracted from the envelope of LO (GO(i), black, scaled by factor 3; $1/1500$ to $1/900 \text{ kyr}^{-1}$) and 1.2 Myr GO (red; $1/1500$ to $1/900 \text{ kyr}^{-1}$), respectively. B) Average and evolute wavelet periodogram. Target periodicities (kyr) indicated by dashed vertical lines for GE (2.4 Myr), GO (1.2 Myr), LE (405 kyr), LO (173 kyr) and SE (131 and 95 kyr, respectively). Note that both average and evolute power spectra were calculated on detrended Ti to highlight higher frequency components (see R-script in Suppl. A for details). C) Assigned astrochronozones (Whalen et al., 2017; De Vleeschouwer et al., 2017). The cone of influence was removed from the wavelet periodogram for visual clarity (see Suppl. A). Note relative time based on floating astrochronology.

F. WVC Age-Depth Model

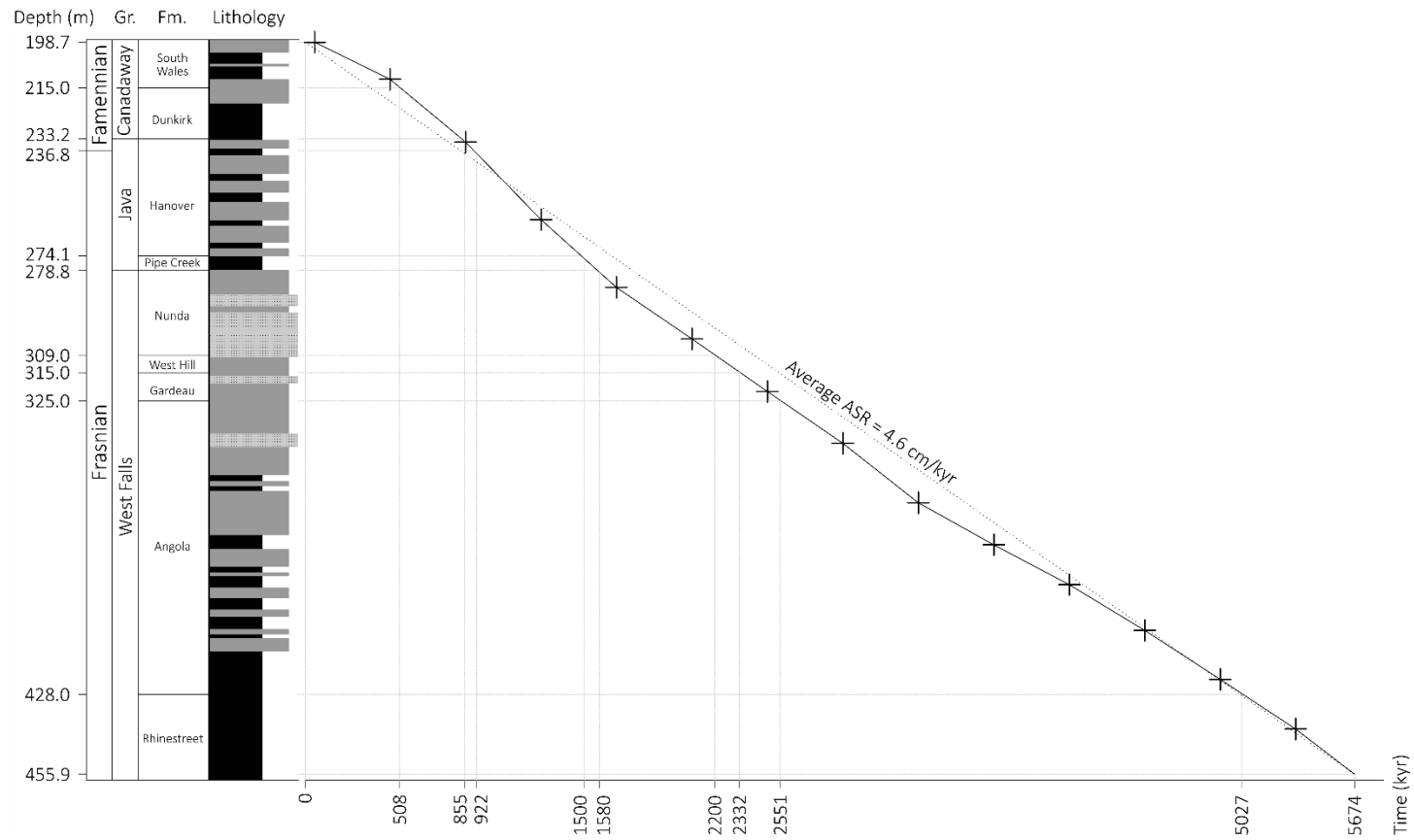


Fig. S4. Stratigraphy, lithostratigraphy and sedimentation rate curve. Note relative time based on floating astrochronology.

G. MTM Spectra of Redox-sensitive Proxies

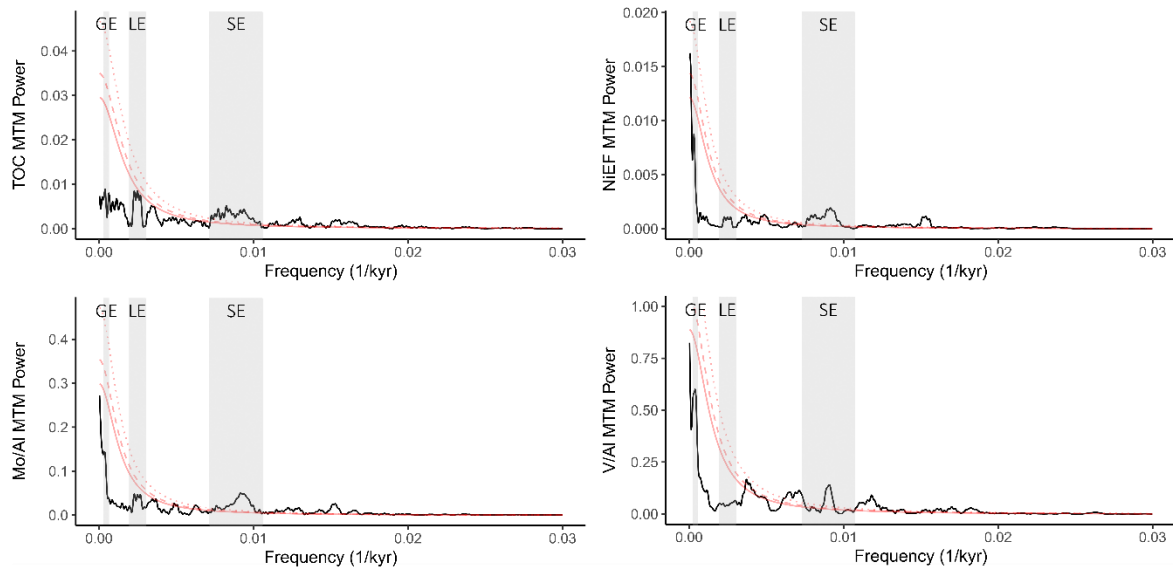


Fig. S5. Multitaper method (MTM) power spectra of TOC, Ni_{EF}, Mo/Al and V/Al. ~100 kyr short eccentricity (SE), 405 kyr long eccentricity (LE) and ~2.4 Myr Grand eccentricity (GE) marked by gray vertical lines. Full, dashed and dotted lines indicate AR1 90%, 95% and 99% confidence intervals, for indicative purposes only.

Supplemental References

- Algeo, T. J. and Liu, J., 2020. A re-assessment of elemental proxies for paleoredox analysis. *Chem. Geol.*; 540, 119549. <https://doi.org/10.1016/j.chemgeo.2020.119549>.
- Algeo, T. J., and Lyons, T. W., 2006. Mo–total organic carbon covariation in modern anoxic marine environments: Implications for analysis of paleoredox and paleohydrographic conditions, *Paleoceanogr.*; 21, PA1016, doi:10.1029/2004PA001112.
- Algeo, T. J. and Scheckler, S. E., 1998. Terrestrial–marine teleconnections in the Devonian: links between the evolution of land plants, weathering processes, and marine anoxic events. *Phil. Trans*; 353, 113–130.
- Algeo, T. J., and Shen, J., 2024. Theory and classification of mass extinction causation. *Natl. Sci. Rev.*, 11, nwad237. doi:10.1093/nsr/nwad237.
- Algeo, T. J., Remírez, M. N., Zhao, H. Schwark, L., Gordon, G., Anbar, A., Bates, S., Lyons, T., Over, D.J., Sageman, B. B., 2025. Transient glacio-eustatic fall and its climato-environmental effects during the Frasnian-Famennian transition. *Glob. Planet. Change* – this issue.
- Bennet, W. W., Canfield, D. E., 2020. Redox-sensitive trace metals as paleoredox proxies: A review and analysis of data from modern sediments. *Earth Sci. Rev.*; 204, 103175. <https://doi.org/10.1016/j.earscirev.2020.103175>.
- Calvert, S. E. and Pedersen, T. F., 2007. Elemental proxies for palaeoclimatic and palaeoceanographic variability in marine sediments: interpretation and application. In: Hillaire-Marcel, C. and De Vernal, A. (Eds.) *Proxies in late Cenozoic Paleooceanography*, chapter 14, *Dev. In Mar. Geol.*; 1, 567-643. ISSN 1572-5480, doi:10.1016/S1572-5480(07)01019-6.
- Carmichael, S. K., Waters, J. A., Köningshof, P., Suttner, T. J., Kido, E., 2019. Paleogeography and paleoenvironments of the Late Devonian Kellwasser event: A review of its sedimentological and geochemical expression. *Glob. Planet. Change*; 183, 102984. <https://doi.org/10.1016/j.gloplacha.2019.102984>.
- Chen, D., Wang, J., Racki, G., Li, H., Wang, C., Ma, X., Whalen, M. T., 2013. Large sulphur isotopic perturbations and oceanic changes during the Frasnian–Famennian transition of the Late Devonian. *J. Geol. Soc.*; 170, 465-476. <https://doi.org/10.1144/jgs2012-037>.
- Chen, J., Lu, Y., Sun, Y., Hogancamp, N., Lu, M., 2024. Oceanic euxinia and seafloor oxygenation caused by continental weathering and influxes during the Late Devonian Frasnian-Famennian bio-crisis and Annulata bioevents. *Chem. Geol.*; 662, 122213. <https://doi.org/10.1016/j.chemgeo.2024.122213>.
- Croudace, I. W. and Rothwell, R. G., 2015. Micro-XRF studies of sediment cores, Applications of a non-destructive tool for the environmental sciences. In: Smol, J. P. (Ed.), *Dev. in Paleoenv. Res.*; 17, ISSN 1571-5299.
- De Vleeschouwer, D., Da Silva, A.-C., Sinnesael, M., Chen, D., Day, J. E., Whalen, M. T., Guo, Z., Claeys, P., 2017. Timing and pacing of the Late Devonian mass extinction event regulated by eccentricity and obliquity. *Nat. Comm.*; 8, 2268. doi:10.1038/s41467-017-02407-1.
- Jaminski, J., Algeo, T.J., Maynard, J.B., Hower, J.C., 1998. Climatic origin of dm-scale compositional cyclicity in the Cleveland Member of the Ohio Shale (Upper Devonian), Central Appalachian Basin, USA. In: Schieber, J., et al. (eds.), *Shales and Mudstones*, vol. 1, Schweizerbart'sche, Stuttgart, Germany, 217-242.
- Klapper, G. and Kirchgasser, W. T., 2016. Frasnian Late Devonian conodont biostratigraphy in New York: graphic correlation and taxonomy. *J. Paleontol.*; 90, 3, 525-55. doi: 10.1017/jpa.2015.70.
- Liu, J.S., Algeo, T.J., Jaminski, J., Kuhn, T., Joachimski, M.M., 2019. Evaluation of high-frequency paleoenvironmental variation using an optimized cyclostratigraphic framework: Example for CS-Fe analysis of Devonian-Mississippian black shales (Central Appalachian Basin, USA). *Chem. Geol.*, 525, 303-320.
- Liu, J., Algeo, T.J., Hinnov, L.A., 2025. Identifying and quantifying stratigraphic disconformities in shale: An example from the Upper Devonian of the Appalachian Basin. *Geol. Soc. Am. Bull.*, 137, 20.

- Lourens, L. J., Wehausen, R., Brumsack, H. J., 2001. Geological constraints on tidal dissipation and dynamical ellipticity of the Earth over the past three million years. *Nature*; 409, 1029-1033. <https://doi.org/10.1038/35059062>.
- McLennan, S. M., 2001. Relationships between the trace element composition of sedimentary rocks and upper continental crust. *Geochem. Geophys. Geosyst.*; 2, 2000GC000109. <https://doi.org/10.1029/2000GC000109>.
- Murphy, A. E., Sageman, B. B., Hollander, D. J., 2000. Eutrophication by decoupling of the marine biogeochemical cycles of C, N, and P: A mechanism for the Late Devonian mass extinction. *Geology*; 28, 5, 427-430.
- Percival, L. M. E., Selby, D., Bond, D. P. G., Rakociński, M., Marynowski, L., Hood, A. v. S., Addate, T., Spangenberg, J. E., Föllmi, K. B., 2020. Phosphorus-cycle disturbances during the Late Devonian anoxic events. *Glob. Planet. Change*; 184, 103070. <https://doi.org/10.1016/j.gloplacha.2019.103070>.
- Sageman, B. B., Murphy, A. E., Werne, J. P., Ver Straeten, C. A., Hollander, D. J., Lyons, T. W., 2003. A tale of shales: the relative roles of production, decomposition, and dilution in the accumulation of organic-rich strata, Middle–Upper Devonian, Appalachian basin. *Chem. Geol.*; 195, 229-273. doi:10.1016/S0009-2541(02)00397-2.
- Smith, G. J. and Jacobi, R. D., 2023. Upper Frasnian and Famennian stratigraphy in western New York State. Chapter 3 in: *Devonian of New York, Volume 3: Frasnian to Famennian (Upper Devonian) stages and the Devonian terrestrial system in New York*, Ver Straeten, C.A., Over D. J., and Woodrow, D. (Eds.), *Bull. Am. Paleontol.*; 47-111. doi:10.32857/bap.2023.407.03.
- Tribouvillard, N., 2021. Re-assessing copper and nickel enrichments as paleoproductivity proxies. *Earth Sci. Bull.*; 192, 54. <https://doi.org/10.1051/bsgf/2021047>.
- Tribouvillard, N., Algeo, T. J., Lyons, T. W., Riboulleau, A., 2006. Trace metals as paleoredox and paleoproductivity proxies: An update. *Chem. Geol.*; 232, 12-32. doi:10.1016/j.chemgeo.2006.02.012.
- Van der Weijden, C. H., 2002. Pitfalls of normalization of marine geochemical data using a common divisor. *Mar. Geol.*; 184, 167-187.
- Ver Straeten, C. A., 2009. The classic Devonian of the Catskill Front: A foreland basin record of Acadian Orogenesis. In: Vollmer, F. (Ed), *New York State Geological Association, 81st Annual Meeting Guidebook*; 7, 1-54.
- Ver Straeten, C. A., Brett, C. E., Sageman, B. B., 2011. Mudrock sequence stratigraphy: A multi-proxy (sedimentological, paleobiological and geochemical) approach, Devonian Appalachian Basin. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 304, 54-73. doi:10.1016/j.palaeo.2010.10.010.
- Whalen, M. T., De Vleeschouwer, D., Payne, J. H., Day, J. E., Over, D. J., Claeys, P., 2017. Pattern and timing of the Late Devonian biotic crisis in western Canada: Insights from carbon isotopes and astronomical calibration of magnetic susceptibility data. In: Playton, T. E., Kerans, C., Weissenberger, J. A. W. (Eds.). *New advances in Devonian carbonates: Outcrop analogs, reservoirs and chronostratigraphy*, SEPM; 107, 185-201. ISBN 978-1-56576-344-9. <https://doi.org/10.2110/sepm.107>
- Wichern, N. M. A., Bialik, O. M., Nohl, T., Percival, L. M. E., Becker, T. R., Kaskes, P., Claeys, P., De Vleeschouwer, D., 2024. Astronomically paced climate and carbon cycle feedbacks in the lead-up to the Late Devonian Kellwasser Crisis. *Clim. Past*; 20, 415-448. <https://doi.org/10.5194/cp-20-415-2024>

6. Milankovitch Forcing and Devonian (Anoxic) Events – A Synthesis

In this chapter, a synthesis is provided of the timing, pacing, and phase relationships of the Daleje, Choteč, Kačák, *pumilio*, Fir Tree, Hubbard Quarry, Lodi (onset of the Frasnian Crisis), Rhinestreet, Lower Kellwasser, and Upper Kellwasser events relative to orbital extrema. However, a comprehensive comparison and synthesis of these events is challenged by differences in duration, resolution, and available proxies of the Oued Ferkla, Sherburne Formation and West Valley core records. These aspects are briefly discussed below and form the basis for assessing to what extent, and at which timescales, these events can be characterized and their relationship to astronomically forced insolation variations constrained. They also limit how confidently each event can be interpreted as anoxic, therefore also limiting the assessment of the phase relationship between anoxia and orbital extrema.

6.1. Limitations

6.1.1. Available Proxy Records

Differences in proxy availability limit the extent to which different records and events can be investigated and compared, because each proxy may capture different environmental processes and may also require distinct or more cautious interpretation. This is especially relevant here, as the records investigated here each have a unique set of geochemical and geophysical proxy data (Table 1).

Table 1. Available proxy records. Major and trace elements measured using portable X-ray fluorescence (pXRF) or inductively coupled plasma mass spectrometry (ICP-MS; Sageman et al., 2003), total gamma measured using gamma-ray spectrometry (GRS), magnetic susceptibility (MS), total organic carbon (TOC) and carbonate carbon isotopes ($\delta^{13}\text{C}_{\text{carb}}$; Murphy et al., 2000; Sageman et al., 2003).

Record	Available proxies
Oued Ferkla	Major and trace elements (pXRF) and $\delta^{13}\text{C}_{\text{carb}}$
Sherburne Fm.	Total gamma (GRS) and MS
West Valley core	Major and trace elements (ICP-MS), TOC, and $\delta^{13}\text{C}_{\text{carb}}$

Proxy interpretations should be carried out on a record- and lithology-specific basis (cf., Algeo and Liu, 2020). Because pXRF major and trace elemental concentration data are at best semi-quantitative, major and trace element variations should be interpreted qualitatively, avoiding the use of enrichment factors or fixed threshold values altogether. In contrast, ICP-MS derived

concentrations allow for a more quantitative interpretation. An additional limitation of pXRF data is the restricted suite of measurable/quantifiable elements; key redox-sensitive trace metals such as Mo, Co, and U are not available for Oued Ferkla, which substantially limits the strength of any redox interpretation.

For the Sherburne Formation, redox-sensitive geochemical proxies are currently unavailable, meaning it cannot be determined whether the regional Fir Tree, Hubbard Quarry, and Lodi events were associated with deoxygenation. At best, this can only be inferred indirectly from lithological characteristics. In addition, carbon isotope data are likewise absent, preventing interpretation of carbon cycle perturbations and not allowing correlation of these intervals to regional or global $\delta^{13}\text{C}_{\text{carb}}$ excursions.

6.1.2. Resolution

The resolution of a time series refers to the spacing between successive samples – in the time domain this is the temporal sampling interval, and in the stratigraphical (i.e., depth or height) domain it corresponds to the physical spacing between samples in the rock. The temporal sampling interval itself depends on the physical sample spacing (or measurement spacing) and the associated apparent sedimentation rate, and it directly determines the shortest cycle that can be resolved. Classically, this is expressed through the Nyquist frequency f_{Nyquist} , which represents the highest frequency that can be resolved without aliasing:

$$f_{\text{Nyquist}} = \frac{1}{2\Delta t}$$

where Δt is the temporal sampling interval (Weedon, 2003). However, in practice, at least four – preferably ten – datapoints per oscillation are recommended (Weedon, 2003; Martinez et al., 2016). Consequently, for any cyclostratigraphic study, the sampling or measurement spacing determines the shortest cycle that can be resolved.

For example, the West Valley core proxy data were collected at a relatively low resolution of ~1 m on average, in part because it was originally not sampled for cyclostratigraphic purposes. At an average sedimentation rate of 4.53 cm/kyr ($\Delta t \sim 22$ kyr), ~20 kyr precession and ~34 kyr obliquity (Waltham, 2015) remain unresolved. This not only makes the cyclostratigraphic analysis more challenging (e.g., fewer frequency components and amplitude-modulation patterns to test and support any interpretation) but also limits the assessment of phase relationships relative to precession and obliquity. Thus, for the Rhinestreet, Lower Kellwasser, and Upper Kellwasser events, their temporal positions relative to such short-period Milankovitch cycles cannot be evaluated here.

For similar reasons, the condensed Oued Ferkla section (~0.23 cm/kyr average sedimentation rate) was sampled continuously and pXRF measurements were carried out at 0.8 cm-

resolution (i.e., $\Delta t \sim 3.5$ kyr). This way, precession can generally be resolved confidently, allowing evaluation the temporal positions of the Daleje, Choteč, Kačák, and *pumilio* events across a broad range of Milankovitch timescales. The Sherburne Formation (Lansing core) total gamma (GRS) record is substantially less condensed (~ 3.05 cm/kyr average sedimentation rate) and was measured at a superior resolution of 1.27 cm (i.e., $\Delta t \sim 0.4$ kyr), enabling the resolution of sub-Milankovitch cyclicity and assessment of the temporal positions of the Fir Tree, Hubbard Quarry, and Lodi events at precession scale.

6.1.3. Record Duration

The duration of a sedimentary record (i.e., the amount of time it is interpreted to encompass) puts a limit on the longest (Milankovitch) cycle that can be recovered. Evidently, it thereby equally constrains how many repetitions of each recovered cycle are present, which also has direct implications for statistical significance testing. Additional implications include frequency resolution during spectral analysis (e.g., short records generally produce broad spectral peaks) and the ability to confidently detect longer-period amplitude modulation patterns (Weedon, 2003).

For the three records studied, the interpreted durations are: West Valley core ~ 5.67 Myr, Sherburne Formation (Lansing core) $\sim 1252 \pm 29$ kyr, and Oued Ferkla ~ 18.72 Myr. For example, longer-term cycles such as the ~ 1.2 Myr $s_4 - s_3$ and ~ 2.4 Myr $g_4 - g_3$ (for the period 0 – 60 Ma; Laskar, 2020) cannot be recovered from the Sherburne Formation record and can only be hypothesized based on the sequence stratigraphic framework. While the ~ 2.4 Myr $g_4 - g_3$ cycle has been recovered from the West Valley core, only ~ 2 repetitions are present, meaning that identifying its local extrema is done with lower confidence. In contrast, although only ~ 3 repetitions of a ~ 6 Myr cycle were recovered from Oued Ferkla, its strong expression across multiple proxies allows for a more confident recovery.

The largest implications of differing record durations arise during synthesis. The temporal positions of the Fir Tree, Hubbard Quarry, and Lodi events (Sherburne Formation) relative to extrema in ~ 1.2 Myr $s_4 - s_3$ and ~ 2.4 Myr $g_4 - g_3$, or a potential ~ 6 Myr component cannot be assessed. Likewise, for the West Valley core, the relationship between the (onset of) the Rhinestreet, Lower Kellwasser, and Upper Kellwasser events and extrema in precession, (short) obliquity, as well as a potential ~ 6 Myr cycle remain unresolved. Together, these differences in record duration place fundamental limits on how astronomical forcing can be compared across the late Emsian to earliest Famennian as represented by these three successions.

6.2. The Duration of Devonian Events

Here, a brief summary is provided of the durations of the Daleje, Choteč, Kačák, *pumilio*, Fir Tree, Hubbard Quarry, Lodi, Rhinestreet, and Kellwasser events as constrained and discussed in Chapters 2 – 5. Because the duration of an event is highly dependent on the proxy used, it should always be reported together with the method by which it was determined (e.g., De Vleeschouwer et al., 2024). For example, for the Kellwasser Crisis (West Valley core), the duration differs depending on how the event boundaries are defined: ~630 kyr when using $\delta^{13}\text{C}$ excursions, but ~760 kyr when using lithology and TOC (Huygh et al., 2026; Chapter 5). Once the stratigraphical onset and termination of an event are constrained, its duration can be estimated using an age model based on a cyclostratigraphic interpretation. Table 2. below summarizes the duration (and associated uncertainty – if determined) of the Daleje, Choteč, Kačák, *pumilio*, Fir Tree, Hubbard Quarry, Lodi, Rhinestreet, and Kellwasser events. For all events, approximate stratigraphical locations were determined using integrated stratigraphic approach, combining sequence stratigraphy and event stratigraphy, biostratigraphy, and lithostratigraphy. The exact lower (onset) and upper (termination) boundaries were further refined using either geochemical or geophysical proxies. The estimated duration of each event assumes relatively stable sedimentation rates and relies on linear interpolation.

Table 2. Event Durations. All durations are based on (floating) astrochronologies tuned to the 405 kyr eccentricity metronome. For Oued Ferkla (OF) and West Valley core (WVC), no uncertainty was estimated for the cyclostratigraphic age model, for the Sherburne Formation (Lansing core; LC), the uncertainty was estimated by integrating a second, precession-based age model (see chapter 4). The proxy column shows which proxy was used for constructing the cyclostratigraphic age model and how it was interpreted.

Event	Record	Proxy	Event Indicators	Duration (kyr)
Daleje	OF	PC1 (detrital input)	Greenish shales, elevated PC1	1082
Choteč	OF	PC1 (detrital input)	Dark limestone-marl couplet, PC1	138
L. Kačák	OF	PC1 (detrital input)	Marl-limestone alternations, PC1	646
U. Kačák	OF	PC1 (detrital input)	Marl-limestone alternations, PC1	260
Kačák	OF	PC1 (detrital input)	Marl-limestone alternations, PC1	1088
L. <i>pumilio</i>	OF	PC1 (detrital input)	Dark limestones, minimal PC1	64
U. <i>pumilio</i>	OF	PC1 (detrital input)	Dark limestones, minimal PC1	124
Fir Tree	LC	GRS (detrital input)	Sequence stratigraphy, GRS	108 ± 29
Hubbard Quarry	LC	GRS (detrital input)	Sequence stratigraphy, GRS	214 ± 29
Lodi	LC	GRS (detrital input)	Sequence stratigraphy, GRS	> 200 ± 29
Rhinestreet	WVC	TOC (organic matter)	Black shales, elevated TOC	> 650
L. Kellwasser	WVC	TOC (organic matter)	Black shales, elevated TOC	84
U. Kellwasser	WVC	TOC (organic matter)	Black shales, elevated TOC	123
Kellwasser	WVC	TOC (organic matter)	Black shales, elevated TOC	760

Temporal estimates of the Daleje Event are sparse, but it may have represented a protracted event approaching ~1 Myr (Becker et al., 2020). At Oued Ferkla, its duration is estimated at 1082 kyr, very close – likely coincidentally – to the projection in Becker et al. (2020). However, the lower portion of the Daleje Event may be missing from the currently accessible interval (Chapter 2), in which case the estimate presented here is probably an underestimation. The Choteč Event represents a short environmental perturbation at Oued Ferkla, lasting approximately 138 kyr, broadly one short eccentricity cycle (Table 2) – in agreement with the qualitative estimates in Becker et al. (2020) and Kabanov et al. (2023). This estimate provides the first cyclostratigraphic age constraint on the global Choteč Event. The entire Kačák Event interval is interpreted to span 1088 kyr at Oued Ferkla (Chapter 3), considerably longer than the 200 ± 10 kyr estimate by Ellwood et al. (2011) for the neighboring Mech Irdane section. Their shorter duration corresponds broadly to the Upper Kačák Event at Oued Ferkla, which represents the Kačák Event *sensu strictu* (Walliser, 1996). If their preliminary, MS-based cyclostratigraphy is indeed robust, Ellwood et al. (2011) may have identified only this upper horizon. The total duration of the Kačák Event is highly similar to the Daleje Event at Oued Ferkla (Table 2; see also Chapter 3), although – for reasons described above – this similarity should be viewed cautiously. If correct, however, the comparable durations suggest very similar astronomical controls despite a substantial difference in their expression (Chapter 2), likely due to a shift in paleodepositional conditions. The Lower and Upper *pumilio* events represent short environmental perturbations (Table 2). The evidence at Oued Ferkla does not support instantaneous deposition as tsunami deposits, as originally proposed by Lottman (1990). Thin-section petrography shows relatively well-layered *pumilio* shells (Chapter 2, Fig. C2), and geochemical indicators suggest an increase in paleoproductivity just before their onset combined with slightly reducing conditions (Chapter 2, Fig. D12). Together with the cyclostratigraphic patterns described here (see also Chapter 3, Fig. A4), these observations indicate sustained deposition rather than instantaneous emplacement, likely mediated through astronomical forcing of sea-level variations (Brett and Baird, 1997; House 2002; Buggisch and Joachimski; 2006; Ellwood et al., 2011; Aboussalam and Becker, 2011) and/or eutrophication (Becker et al., 2020; Talih et al., 2022).

First temporal estimates are provided for the regional Fir Tree, Hubbard Quarry, and Lodi events (Chapter 4). Although these do not strictly represent anoxic events, they share several characteristics with globally recognized Devonian perturbations and have comparable durations as the Choteč, Upper Kačák, Upper *pumilio*, and Upper Kellwasser events (Table 2) – typically one to two short-eccentricity cycles. This correspondence, in combination with the recognized Milankovitch pacing, suggests similar underlying causal mechanisms.

The Rhinestreet event in the West Valley core is estimated to span at least 650 kyr (Huygh et al., 2026), substantially shorter than the ~2.3 Myr duration proposed by Kabanov (2019) (see also Kabanov et al., 2023). Two factors explain this discrepancy; (i) the lower part of the

Rhinestreet Event is likely absent in the West Valley core, and (ii) the estimate by Kabanov (2019) as reported in Kabanov et al. (2023) is poorly constrained, relying solely on conodont biostratigraphy and correlates to the Middlesex and Rhinestreet events in Eastern-Central North America. Finally, the reader is referred to Chapter 5 for a comparison of the estimated duration of the Kellwasser Crisis (Huygh et al., 2026).

6.3. Phase Relationships between Devonian Events and Milankovitch Forcing

Constraining the phase relationship between orbital extrema and events provides direct insight into the timing and pacing of the events, thereby allowing evaluation of potential causal relationships and helping to identify plausible causal mechanisms within a broader paleoclimatic and paleoenvironmental framework. To this end, the synthesis proceeds by outlining the degree to which the event, and potentially associated anoxia, can be identified in each record and by summarizing the Milankovitch timescales that can be resolved (Table 3). For Oued Ferkla and the West Valley core, only a limited number of redox-sensitive proxies are available and thus anoxia is estimated qualitatively and semi-quantitatively, respectively. For the Sherburne Formation, no redox proxies are available, meaning anoxia can only be inferred from lithological observations. Assessing the temporal position of Devonian events – and specifically their onset – relative to orbital extrema requires evaluating phase relationships on multiple timescales, especially because different Milankovitch bands are associated with different climatic mechanisms and response times (Berger, 1973; 1987; Zachos, 2001).

Table 3. Summary of Anoxia interpretability and resolvable Milankovitch timescales.

Record	Anoxia	Milankovitch Timescales
Oued Ferkla	Qualitatively	Precession to ~6 Myr
Sherburne Fm.	N.A.	Sub-Milankovitch to 405 kyr $g_2 - g_5$
West Valley core	Semi-quantitatively	Short eccentricity to ~2.4 Myr $g_4 - g_3$

To constrain the phase relationship between orbital extrema (i.e., insolation extrema) and a single-phased event, the temporal position of the event needs to be established first, for which three proxy-dependent temporal markers are useful: its onset, apex, and termination (Fig. 1). However, there is often a considerable offset between these markers for different proxies, e.g., carbon cycle perturbations ($\delta^{13}\text{C}$) and lithologic or biotic expressions of the same event; during the Kellwasser Crisis, multiple records show that positive $\delta^{13}\text{C}$ excursions and organic-rich

shale deposition are not strictly synchronous and can be separated by tens to several hundred thousand years in many sections (e.g., De Vleeschouwer et al., 2017; 2024; Huygh et al., 2026). This discrepancy can be attributed to multiple factors that are inherently challenging to constrain, including but not limited to, different system component response times (e.g., MS versus $\delta^{13}\text{C}$; De Vleeschouwer et al., 2017), facies-dependent proxy expression (e.g., preservation of organic matter; Carmichael et al., 2019), diagenetic overprinting and reworking, and proxy record resolution and correlation.

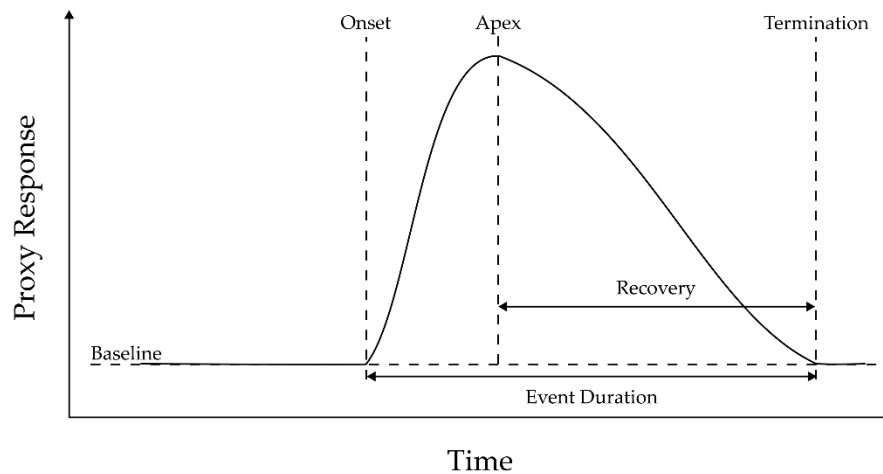


Fig. 1. The temporal markers of an event. The onset marks the departure from baseline conditions, peak event expression and maximal departure from baseline conditions occur during its apex, the recovery represents an often gradual return to baseline conditions, which marks the termination of the event.

A second, more challenging aspect of linking orbital extrema to events is constraining the phase relationship between insolation forcing and proxy response. Ideally, bandpass-filtered proxy records from anchored astrochronologies should be compared with insolation curves, provided a reliable astronomical solution is available. However, because of uncertainties in the Earth-Moon system and Solar System chaos (Laskar, 1989; 1990 see also Chapter 1), no unique deterministic solution can be extended reliably through the Mesozoic and Paleozoic (Laskar, 2020), which complicates direct comparison between proxy records and insolation curves.

In absence of an insolation curve (astronomical solution), indirect estimation of insolation-proxy phase relationships can be attempted, provided (i) sufficient proxy records are available and, (ii) a coherent paleoenvironmental interpretation supports the inferred phasing. If two proxies exhibit anti-phased short-period carriers but their amplitude-modulation (envelopes) are in phase, this indicates that the long-period forcing modulates both records similarly, while the short-period carrier in one proxy is inverted relative to the other. This pattern is potentially indicative of one proxy exhibiting an anti-phased response to insolation. By extracting the hierarchical components – the short-period carrier, its amplitude envelope, and the long-period modulation – and comparing their phases, one can determine which proxy's

carrier is inverted relative to the long-period forcing, and therefore which proxy is likely responding in anti-phase to insolation (Chapter 3, Extended Fig. 5, 6). At Oued Ferkla, Ti and Ca (and their 405 kyr carriers) are anti-phased, yet the ~6 Myr cycle extracted from the envelope of eccentricity (Ca; Chapter 3, Extended Fig. 6) is in-phase with the extracted ~6 Myr cycle extracted from Ti (Chapter 3, Extended Fig. 5). Moreover, the ~6 Myr cycle extracted directly from Ti as well as from the envelope of long eccentricity extracted from Ti are in phase (Chapter 3, Extended Fig. 5). Conversely, the ~6 Myr cycle extracted directly from Ca is anti-phasing with both the ~6 Myr cycle extracted from the envelope of long eccentricity (Ca; Chapter 3, Extended Fig. 6) and ~6 Myr cycle(s) extracted from Ti (Chapter 3, Extended Fig. 5). Thus, at Oued Ferkla, it can be inferred that Ti likely responds in phase with insolation forcing, whereas Ca responds in anti-phase. This inference is further supported by a paleoenvironmental and paleoclimatic interpretation; during insolation maxima, an invigorated hydrological cycle leads to increased runoff and potentially relative sea-level increase (Talib et al., 2022), thereby interrupting carbonate deposition and favoring marl/shale deposition. This interpretation is also consistent with minima in 405 kyr long eccentricity being expressed as thick limestone beds lacking marl/shale intercalations.

Although the phase relationships between each event and the relevant orbital extrema are discussed in detail in Chapters 2 – 5, a concise summary is provided below. Where possible, explicit links to anoxia are highlighted.

6.3.1. Daleje, Choteč, Kačák, and *pumilio* events (Oued Ferkla)

At Oued Ferkla, redox conditions during the Daleje, Choteč, Kačák, and *pumilio* events differ markedly. The transgressive greenish shales of the Daleje Event record anoxic to transiently euxinic bottom-waters. Assuming the onset of the Daleje Event is captured at Oued Ferkla, it appears to coincide with precession and obliquity minima, with anoxic conditions developing during the first precession, obliquity, and short-eccentricity maxima. Yet, considerable uncertainty remains regarding the phase behavior of the detrital proxy used here to delineate the temporal extent of the Daleje Event and orbital extrema due to an apparent phase inversion. The shift from limestones to anoxic green shales coincides with a rising limb of 405 kyr $g_2 - g_5$ long eccentricity. On longest timescales, the event is interpreted to unfold during a 2.4 Myr $g_4 - g_3$ maximum and on the rising limb or maximum of a ~6 Myr cycle.

The thin, dark microcrystalline limestones of the Choteč Event however, bear no evidence of anoxia. The event begins during a minimum in precession on what appears a decreasing limb of short eccentricity and 173 kyr long obliquity. The onset coincides with a 405 kyr $g_2 - g_5$ long eccentricity minimum and unfolds on its rising limb. On longer timescales, the Choteč Event coincides with 2.4 Myr $g_4 - g_3$ and ~6 Myr maxima. In contrast, the poly-phased Kačák Event interval contains thick marl/shale packages that are characterized by mm-thick black laminae

suggestive of anoxia (not captured at current resolution using geochemical proxies). The first pulse of the Kačák Event begins during precession and obliquity minima on the rising limb of 100 kyr short and 405 kyr long eccentricity, with the first apex coinciding with the first precession maximum – similar to the Daleje Event. A similar phase relationship can be observed on precession- to obliquity-timescales for all subsequent pulses, while their pacing appears controlled by 100 kyr short eccentricity and 173 kyr obliquity cycles. The entire event unfolds during a 2.4 Myr $g_4 - g_3$ and ~6 Myr maximum.

Finally, the two *pumilio* beds show geochemical signatures consistent with increased paleoproductivity and mild oxygen depletion (Chapter 2). Their onsets coincide with maxima in precession and short eccentricity and the events unfold during a long-eccentricity maximum, further hinting at their astronomical pacing on short-timescales. During their apex, however, precession power is notably weak and, especially during the bi-phased Upper *pumilio* Event, obliquity appears to dominate, although the proxy phase response to obliquity remains ambiguous – especially on 1.2 Myr timescales. On even longer timescales, the events occur around a minimum in 2.4 Myr $g_4 - g_3$ as well as ~6 Myr cyclicity.

6.3.2. Fir Tree, Hubbard Quarry, and Lodi events (Lansing core, Sherburne Formation)

The regional Fir Tree, Hubbard Quarry and Lodi events stand out because they lack evidence for pervasive anoxia, with only the Hubbard Quarry interval containing darker shale. Despite this, their stratigraphic signatures – including sea-level variability and limited biotic turnover – closely resemble those of globally recognized Devonian anoxic events. Nevertheless, this makes them informative intervals, highlighting cases where the environmental framework typical of major anoxic episodes was present to some extent, yet (widespread) oxygen depletion did not develop. The onset of all three events occur near minima in precession, and short eccentricity, suggesting astronomical control on the timing of their initiation. Their relationship to short-term obliquity appears less consistent and is not further interpreted here. Whereas the oxic Fir Tree and Lodi events appear to develop during transgression and begin during 173 kyr maxima, the dysoxic Hubbard Quarry interval corresponds to highstand, with its onset coinciding with 173 kyr minima. Possibly, their rhythmic occurrence and expression reflect longer-period 1.2 Myr $s_4 - s_3$ modulation of sea-level variability.

6.3.3. Rhinestreet, Lower Kellwasser, and Upper Kellwasser events (West Valley core)

Across the Kellwasser and Rhinestreet intervals, anoxia consistently aligns with short-eccentricity maxima, with the Rhinestreet Event also showing a 173 kyr pacing. Both intervals occur during relatively strong 2.4 Myr eccentricity modulation. Anoxia remains weak during eccentricity minima across all intervals, regardless of Myr-obliquity paced sea-level variations, whereas anoxia is strongest during eccentricity maxima and appears exacerbated

by elevated sea levels. Although the timing of these major anoxic intervals aligns with astronomical pacing at 100 kyr to 2.4 Myr timescales, the limitations outlined above prevent evaluation of event onsets at precession- and obliquity-scale resolution and, thus, preclude identification of specific trigger mechanisms.

6.4. Integrated Interpretation of Orbital and Environmental Patterns

Investigating multiple (anoxic) events across two basins over ~30 Myr provides the basis for identifying how astronomical forcing structured environmental perturbations during the Devonian. The forcing itself exhibits a triadic character, influencing the timing of event onsets, the pacing of their subsequent evolution, as well as the recurrence of later events. This triadic structure arises because each tier of astronomical forcing – precession/obliquity, short to long eccentricity, and multi-Myr cycles – govern a distinct mode of system behavior: short-term pacing, intermediate modulation, and long-term state control, respectively. Thus, the astronomical forcing relevant to Devonian environmental variability is conceptualized here in three tiers. Precession and obliquity, which have a predominant influence on insolation, provide strongest direct control of the timing and internal evolution of events on shortest timescales. The short-eccentricity to long-eccentricity band (incl. 173 kyr obliquity) provides the modulation envelopes that shapes the amplitudes and, in many cases, duration of the events. Multi-Myr cycles, ranging from 1.2 Myr $s_4 - s_3$ to 2.4 Myr $g_4 - g_3$ and even longer ~6 Myr determine the long-term climatic state that conditions when events can occur and how their recurrence is organized.

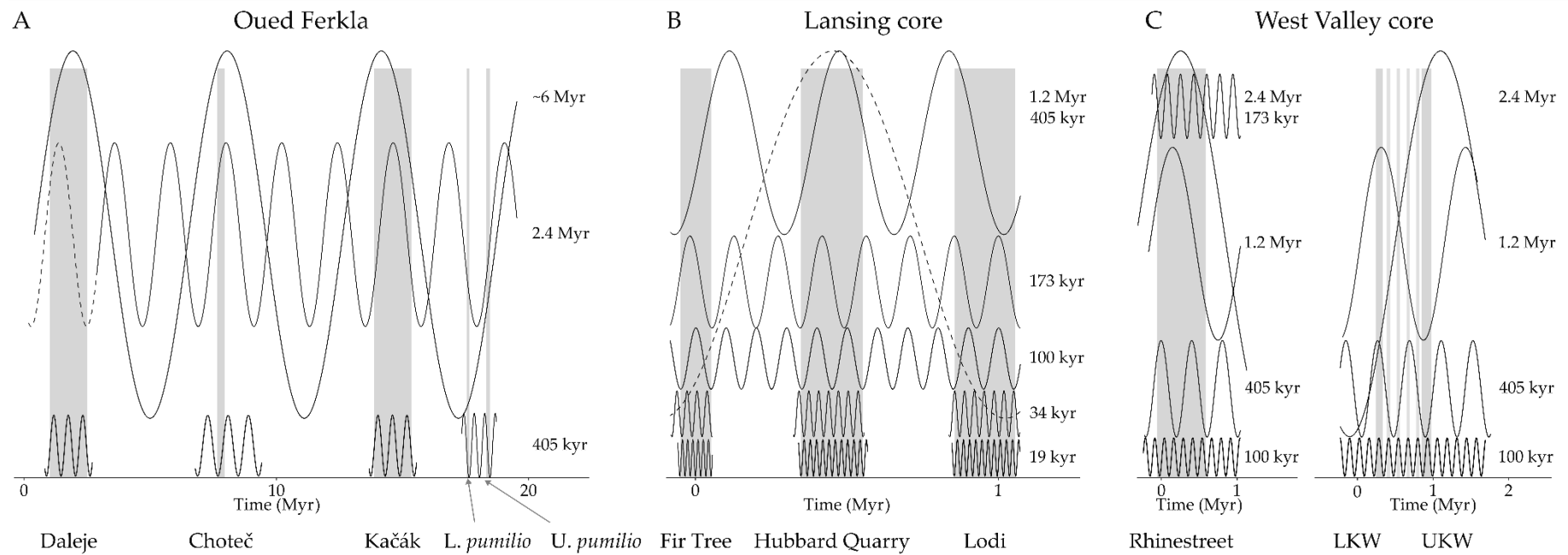


Fig. 2. Summary of Devonian events and their phase relationships to orbital extrema. A) Oued Ferkla Daleje, Choteč, Kačák, and *pumilio* events (gray) and 405 kyr $g_2 - g_5$, 2.4 Myr $g_4 - g_3$, and ~6 Myr cycles. B) Lansing core Sherburne Formation Fir Tree, Hubbard Quarry, and Lodi events (gray) and ~19 kyr precession, ~34 kyr obliquity, ~100 kyr short-eccentricity, 173 kyr $s_3 - s_6$, 405 kyr $g_2 - g_5$, and 1.2 Myr $s_4 - s_3$ (dashed) cycles. C) West Valley core Rhinstreet and Kellwasser events (gray) and ~100 kyr short eccentricity, 405 kyr $g_2 - g_5$, 1.2 Myr $s_4 - s_3$, and 2.4 Myr $g_4 - g_3$ cycles. Sea level of Oued Ferkla according to (Talib et al., 2022); transgressive (T), regressive (R); severity based on (Brett et al., 2020).

6.4.1. Multi-Myr Pacing of Devonian Anoxic Events

Multi-Myr cycles exert first-order control on the Earth system, setting the astronomical boundary conditions within which shorter-period orbital forcing operates. This hypothesis is based primarily on the pacing of the Daleje, Choteč, Kačák, *pumilio*, Rhinestreet, and Kellwasser events by the 2.4 Myr $g_4 - g_3$, complemented by the observed pacing of the *Annulata*, Dasberg, Kowala, and Hangenberg events by this component (De Vleeschouwer et al., 2013; Wichern et al., 2026). It is the interaction between these long-term cycles – essentially shaping astronomical boundary conditions – and the internal, regional-to-global Earth-system boundary conditions. In this context, ‘Earth-system boundary conditions’ refers to the combined state of the major, interconnected components of the Earth system that regulate how, amongst others, the climate and ocean respond to astronomical forcing. These include, but are not limited to, continental configuration; climatic state (temperature, pCO₂, pO₂, continental ice); sea level, ocean circulation, and the degree of water-mass stratification; nutrient delivery and geochemical cycling; and the extent and nature of terrestrial vegetation.

These conditions ultimately determine whether environmental perturbation occurs, how it is expressed, and how long it persists. This hierarchy is conceptualized on Fig. 3A, where Earth-system boundary conditions are assumed to be constant. Within this framework, whenever long-term astronomical boundary conditions cross the Earth-system boundary conditions, environmental perturbation will occur. In reality, a range of drivers or external triggers – including tectonics and LIP volcanism – can shift the Earth-system boundary conditions substantially. Such shifts may push the system across critical thresholds, enabling environmental perturbations (including anoxia and faunal turnover) to develop irrespective of the prevailing astronomical configuration (Fig. 3B). Under these heightened-sensitivity states, astronomical boundary conditions can exert a far more pronounced influence than would otherwise be possible during that specific time interval. This mechanism may operate under either extreme; both maximal and minimal modulation of the astronomical boundary conditions can produce a threshold-like response.

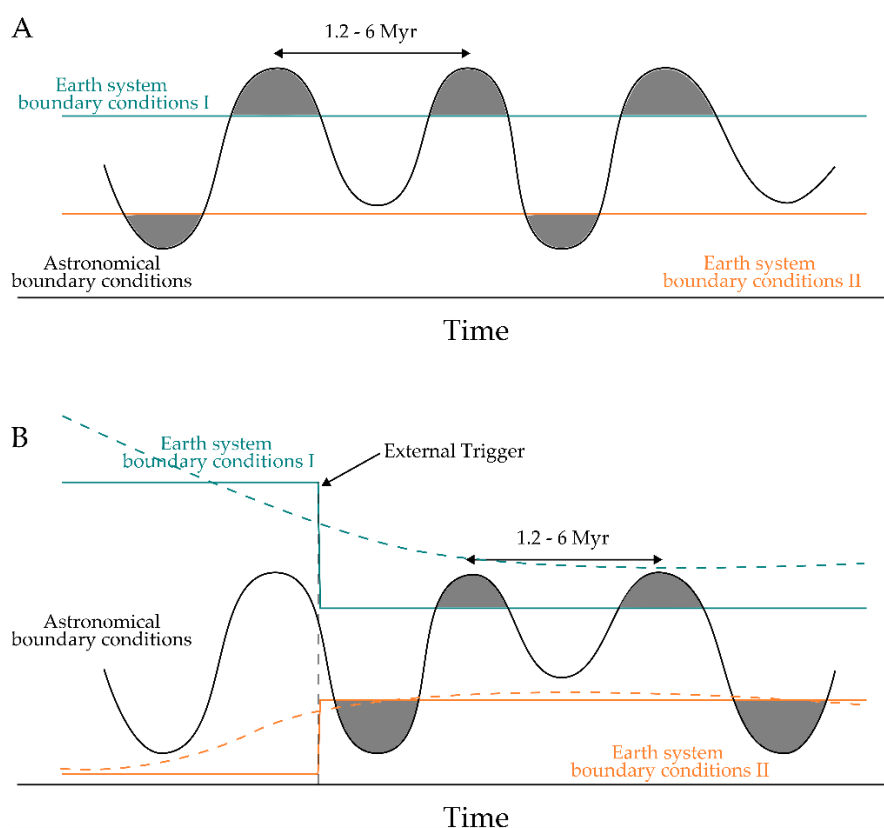


Fig. 3. Conceptual representation of Earth-system and astronomical boundary conditions and their threshold-like interplay on multi-Myr timescales. Boundary conditions (I) interact with maximal modulation by astronomical boundary conditions (cyan), boundary conditions (II) interact with minimal modulation by astronomical boundary conditions (orange). A) Under stable Earth-system boundary conditions, long-term astronomical modulation cycles allow for a threshold to be surpassed, leading to environmental perturbations (gray). B) A shift in Earth-system boundary conditions as a result of an external trigger (solid lines) or long-term changes (dashed lines) allow for a threshold to be surpassed by long-term astronomical modulation cycles, equally leading to environmental perturbations such as anoxia, faunal turnover, sea-level variations (gray). To some extent, this framework can potentially be extended to shorter timescales.

Long-term, multi-Myr astronomical modulation cycles – such as the 2.4 Myr $g_4 - g_3$, are ever-present, yet they exert only a minor direct influence on insolation itself, operating in a manner analogous to short- and long-eccentricity forcing (see Fig. 2, Chapter 1). Their climatic significance arises primarily through their modulation of, for example, precession-driven insolation variability. However, the expression of these modulated signals depends critically on the prevailing Earth-system boundary conditions and the system's subsequent response. The Daleje, Choteč, Kačák, Rhinestreet, and Kellwasser Events are interpreted to unfold during 2.4 Myr $g_4 - g_3$ maxima (Chapters 3, 5), suggesting that these events occurred under a scenario where astronomical forcing crossed an upper threshold corresponding to Earth-system boundary conditions I (Fig. 3). While this pattern is not diagnostic of a specific causal mechanism, it does highlight that these events occurred during intervals characterized by more extreme seasonality and, likely, enhanced climate-ocean dynamics. Conversely, the

pumilio events coincide broadly with a 2.4 and ~6 Myr minimum, which aligns with an alternative scenario during which astronomical forcing crossed a lower threshold corresponding to Earth-system boundary conditions II (Fig. 3). This suggests that they occurred during periods characterized by long-term stability and muted seasonality.

The recurrence of the late Early to Middle Devonian Daleje, Choteč, Kačák events appears paced by a ~6 Myr cycle, whereas the *Annulata*, Dasberg and Hangenberg (De Vleeschouwer et al., 2013; Wichern et al., 2026) events align with a 2.4 Myr cycle. Between the Rhinestreet and Kellwasser events, one 2.4 Myr maxima remains unassigned to any event at the West Valley core³. In addition, the Bakoven and Stony Hollow events – most clearly expressed in North America (DeSantis and Brett, 2011) – are not recognized at Oued Ferkla. These ‘unrecognized events’ likely reflect intervals in which (i) the prevailing regional Earth-system boundary conditions were not sufficiently susceptible to the long-term astronomical modulation cycles, and/or (ii) the events themselves were not astronomically paced but instead driven by regional or non-astronomical processes.

Taken together, those observations suggest that ~6 Myr modulation dominated the recurrence of late Early to Middle Devonian events, and that the Earth system may have transitioned into a state in which sensitivity to the 2.4 Myr cycle became increasingly important. Alternatively, the 2.4 Myr cycle may represent the primary astronomical modulation pacing Devonian events altogether, with regional differences in the prevailing Earth-system boundary conditions allowing only those events coinciding with extrema in longer-period ~6 Myr cycles to be expressed. The latter hypothesis does imply a coherent phase relationship between 2.4 Myr and 6 Myr maxima, for which evidence is sparse (Zeebe and Lantink, 2024). Nevertheless, the available data do not allow constraining either interpretation with confidence, and both remain viable within the conceptual framework outlined here.

Lastly, the direct influence of long-term obliquity modulation – most notably the 1.2 Myr $s_4 - s_3$ cycle – remains somewhat ambiguous. Especially because its relationship with the 2.4 Myr $g_4 - g_3$ cycle through chaotic transitions in the $2(g_4 - g_3) - (s_4 - s_3)$ secular resonance (Laskar, 2020) remains poorly constrained for the Devonian (Zeebe and Lantink, 2024). If the resonance is active – as is inferred to be the case during the Eifelian to Middle Givetian (Chapter 3) and the Frasnian (Chapter 5) – it may further amplify the Earth system response to 1.2 and 2.4 Myr forcing through co-operating climatically-induced processes. In the West Valley core, such long-term obliquity forcing paced sea-level variations that, at variable timescales, appeared to exacerbate anoxia that developed during maximum eccentricity configuration. At Kowala, Poland, the Dasberg, regional Kowala, and Hangenberg events are separated by 1.2 Myr (De

³ Alternatively, the *semichatovae* Event – not recognized in the West Valley core – may coincide with this maximum, although this remains entirely speculative.

Vleeschouwer et al., 2013) – a duration that reminds strongly of the $s_4 - s_3$ cycle. Potentially, the regional Kowala event is the result of a regional environmental perturbation associated with the $s_4 - s_3$ cycle surpassing an Earth-system threshold (Fig. 3). The long-term modulation of obliquity likely contributed to varying degrees, to shaping (regional) environmental variability, regardless of the driving mechanisms.

Finally, based on the framework outlined above, the Fir Tree, Hubbard Quarry, and Lodi events are hypothesized to occur outside of extrema in the 2.4 Myr (and/or longer-term) cycles. This inference is not only temporally plausible (Becker et al., 2020) but would also explain the absence of pervasive anoxia and their regional nature. Instead, as touched upon in Chapter 4, they may have been shaped by 1.2 Myr obliquity-paced sea-level variability.

6.4.2. The Role of Eccentricity and 173 kyr Obliquity on Devonian Anoxic Events

The conceptual framework outlined above (Fig. 3) may also apply on shorter timescales, relevant to short eccentricity, 173 kyr $s_3 - s_6$ obliquity, and the $g_2 - g_5$ long eccentricity (Fig. 4). These shorter-period astronomical components operate within, and are themselves modulated by, the longer multi-Myr cycles, producing a superimposed hierarchy of forcing that shapes the expression and magnitude of environmental variability on shorter timescales. For nearly all events covered here, these cycles appear decisive in determining the duration of the environmental perturbations with the protracted Daleje, Kačák, and Rhinestreet events representing notable exceptions. For these events – especially the Kačák and Rhinestreet events – the short eccentricity and 173 kyr obliquity cycles appear dominant in pacing anoxic pulses, a pattern attributed to Earth system being near-threshold for an extended interval (> 1 Myr), such that amplitude modulation by these cycles repeatedly pushed the system into and out of (stronger) anoxic conditions. Shorter events can be conceptualized in a similar fashion, but they typically manifest as (i) single-pulsed (e.g., Lower *pumilio* Event), (ii) ‘protracted-pulsed’ (e.g., Hubbard Quarry Event), or (iii) double-pulsed (e.g., Upper *pumilio* Event) – see Fig. 4. On short eccentricity timescales, a protracted-pulsed event occurs when astronomical boundary conditions remain above the relevant environmental threshold for two or more consecutive short eccentricity cycles. The Upper *pumilio* Event shows two distinct pulses, likely separated by a phase of relatively strong short-term obliquity (Chapter 3, Fig. A4) that counteracted the eccentricity-modulated precessional forcing, giving rise to its double-pulsed structure. These patterns are exemplified conceptually assuming stable Earth-system boundary conditions I on Fig. 4, although an inverse mechanism similar to Fig. 3 (Earth-system boundary conditions II) may be equally applicable. Moreover, this conceptual framework can be extended to poly-phased events such as the Kačák Event.

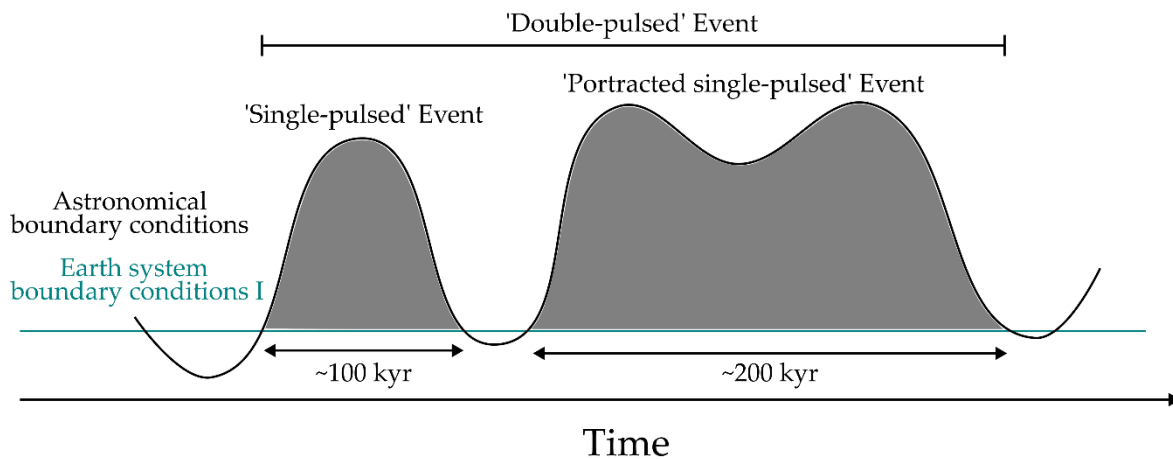


Fig. 4. Conceptual representation of Earth-system and astronomical boundary conditions (I) and their threshold-like interplay on short eccentricity to long eccentricity timescales. Boundary conditions (I) interact with maximal modulation by astronomical boundary conditions (cyan). Under stable Earth-system boundary conditions, short eccentricity, long obliquity to long eccentricity cycles allow for a threshold to be surpassed by modulating precession and obliquity, leading to environmental perturbations (gray) – illustrated here using the ~100 kyr short eccentricity cycle. These modulations are in turn governed by longer-term cycles. Examples of a single-pulse on short-eccentricity timescales include the Choteč, Lower *pumilio*, Fir Tree, and Upper Kellwasser events, whereas examples of a ‘protracted’ pulse on short-eccentricity timescales (i.e., a response to two subsequent cycles) include the Hubbard Quarry and Lodi events. The Upper *pumilio* Event is an example of a double-pulsed event. This framework can operate analogously to Fig. 3 under Earth system boundary conditions II (not illustrated here).

Most events investigated here share a similar pattern: their onset coincides with increasing short eccentricity forcing (i.e. on the rising limb), and maximal short eccentricity coincides broadly with the (first) maximal expression or apex of the event. Notable exceptions include the *pumilio* events, which begin during short eccentricity maxima and culminate during subsequent minima. This opposite phasing becomes clearer when the role of precession is also considered and is therefore elaborated further in the next subchapter.

6.4.3. Precession and Obliquity Forcing of Devonian Anoxic Events

Precession and obliquity contribute most strongly to the insolation spectrum and operate on somewhat comparable timescales. Yet, their influence on insolation differs fundamentally (see 1.2.1) and, consequently, if both signals are recorded, they can be expected to imprint distinct expression in the sedimentary record because they act through different Earth-system processes. The phase relationship between precession and the investigated events is highly similar to that described for short eccentricity, which is expected given that precession is amplitude-modulated by short eccentricity (i.e., climatic precession). Consequently, the timing of the event onset and peak expression follows the same directional ramping: the Daleje, Choteč, Kačák, Fir Tree, Hubbard Quarry, and Lodi events begin near precession minima – interpreted here as perihelion during austral winter – and reach their (first) apex

during precession maxima, corresponding to perihelion during austral summer. This pattern suggests that these events reflect conditions in which increasing precession-driven insolation and seasonality – during long-term modulation maxima – gradually pushed the system toward an upper environmental threshold associated with anoxia development. This interpretation is consistent with the paleogeographic setting, as both Oued Ferkla and the Sherburne Formation were deposited on the Southern Hemisphere. In contrast, the *pumilio* events begin near precession maxima and culminate during precession minima – highlighting that these events differ markedly from the others investigated here, even on short Milankovitch timescales. The inferred increase in paleoproductivity and slightly reducing conditions (Chapter 2) are consistent with precession maxima (austral summer) under a scenario of increased runoff and nutrient delivery that could have promoted eutrophication – consistent with sedimentological evidence by Talih et al. (2022). At the precession and short eccentricity maxima, an Earth-system boundary likely was crossed, potentially causing stagnation, leading to stratification and reduced bottom-water ventilation.

Obliquity, on the other hand, shows a less straightforward connection to the onset and immediate development of events. Across all records examined here, no consistent or recurring configuration of obliquity extrema relative to precession or event extrema can be identified. Despite the strong similarity in event characteristics, the phase of obliquity relative to precession varies from case to case, indicating that obliquity does not provide a uniquely diagnostic signal for deciphering the mechanisms underlying these events. Although its imprint is evident and its effects can be substantial (e.g., during the Upper *pumilio* Event), obliquity does not show a clear association with event onset in the successions investigated here. Instead, it likely acts independently of precession – as would be expected from astronomical theory⁴ – and likely modulates the climatic and paleoenvironmental background states, thereby shaping the broader environmental context in which astronomical forcing operates.

6.5. A New Model for the Astronomical Forcing of Devonian Anoxic Events

Two distinct modes emerge from the cyclostratigraphic interpretations outline above, each reflecting a different relationship between astronomical configuration at multiple timescales and the development of Devonian anoxic events. These two modes correspond to (i) events governed by crossing an upper environmental threshold, and (ii) *pumilio*-type events governed by crossing a lower threshold (see also Fig. 3; Fig. 4). These modes can be formalized into two conceptual models that capture how specific combinations of long-term background state and climatic precession-scale forcing governed the timing, pacing, recurrence, and

⁴ Precession and obliquity are not phase-locked, and therefore, a coherent relationship between them is not anticipated. This is mainly due to precession terms being mostly combinations of $k + g_i$, and obliquity terms of $k + s_i$ (e.g., Hinnov, 2013).

expression of the events (Fig. 5). Practically, the interaction between astronomical forcing and the Earth-system background state is interpreted here as a threshold-governed climate system. Indeed, environmental perturbations represent extreme states in Earth's history and are therefore expected to arise as a result of extreme drivers. Furthermore, through this work, our cyclostratigraphic analysis reveals a consistent association between event onset and apex on the one hand, and orbital extrema on the other.

The modes operate independently of the specific timescales involved and are defined solely by whether an Earth-system threshold is crossed. Astronomical boundary conditions, however, determine how strongly and how frequently the system is pushed toward such thresholds over time. The conceptual models presented here therefore describe threshold-governed behavior without requiring nonlinear climate dynamics, even though such dynamics could further amplify (or mute) the climatic impact of long-term modulation cycles. For clarity, the models are illustrated here using climatic precession and its modulation on multi-Myr timescales (Fig. 5). Depending on the prevailing boundary conditions and the system's sensitivity, obliquity and its modulation may also contribute and should be considered as additional or alternative influences to a precession-based scenario.

The crossing of an Earth-system threshold on multi-Myr timescales does not represent a linear insolation-threshold crossing. Instead, it reflects the system exceeding a threshold in the *strength of climatic modulation* itself. In this sense, maxima in long modulation cycles such as the $g_4 - g_3$ cycle represent intervals of 'maximum modulation power', and vice-versa. On shorter timescales, environmental perturbations such as anoxic events may arise through two distinct processes: (i) a linear insolation-threshold crossing, or (ii) the succession of either extreme alternations between maximal and minimal climatic states or the prolonged absence of such alternations. Which of these processes dominates is likely context-dependent, but the relatively consistent spacing of Devonian anoxic events suggests that the degree of climatic alternation – strong during modulation maxima and weak during modulation minima – may have been the prevailing mechanism, even though linear insolation-threshold crossings remain conceptually possible. The latter would explain the occurrence of events that do not coincide with extrema in multi-Myr cycles, although this interpretation carries a conceptual caveat for one of the models that is addressed later in this section.

Within this framework of extreme environmental states shaped by orbital forcing, we propose two conceptual models: the *Upper-Threshold Model* and the *Lower-Threshold Model*. The *Upper-Threshold Model* (Fig. 5A) corresponds to a system in which global events are triggered when an upper threshold is crossed. This model applies to the Daleje, Choteč, Kačák, Rhinestreet,

and Kellwasser⁵ events as expressed at Oued Ferkla and the West Valley core, respectively. In this interpretation, their global nature reflects the fact that they occur during maxima in long-term multi-Myr astronomical modulation cycles. Data from the Sherburne Formation (Lansing core) indicate that the Fir Tree, Hubbard Quarry, and Lodi events also largely follow this model, but with one key difference: they correspond with short eccentricity, but they are hypothesized not to coincide with maxima in these > 2.4 Myr-long modulation cycles, which may explain their regional rather than global extent. The Lodi Event may be an exception, representing the regional expression of the onset of the global Frasnian Crisis. Further constraints on specific Earth-system boundary conditions would be required to refine these interpretations.

⁵ At the time of writing, contrasting interpretations exist regarding the 2.4 Myr orbital configuration relative to the Kellwasser Crisis exist, which are discussed in briefly in Huygh et al. (2026; Chapter 5). Because the West Valley core record is long enough to extract this 2.4 Myr component rather than having to infer its orbital extrema indirectly, the interpretation outlined in Huygh et al. (2026) is adopted here.

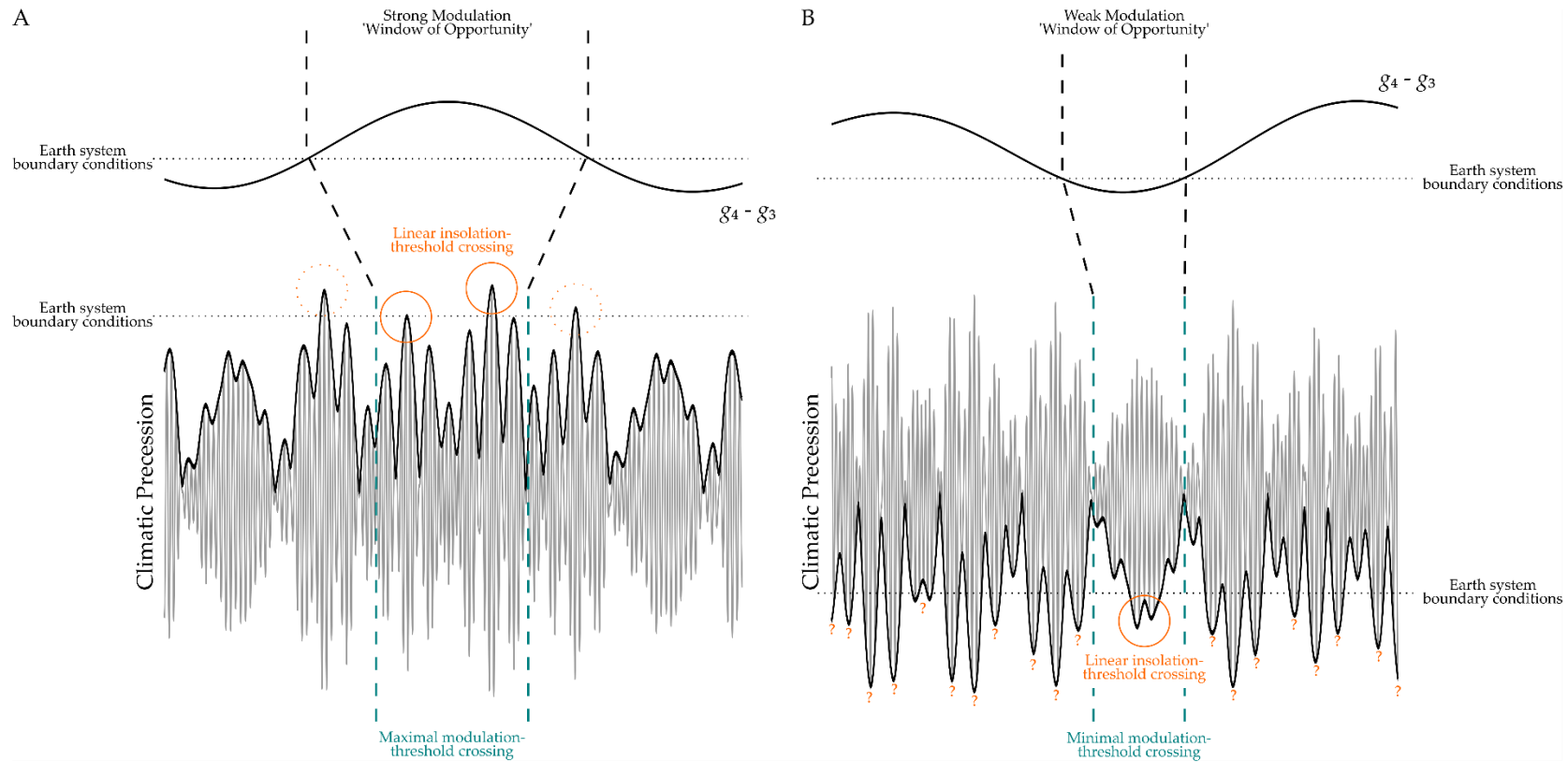


Fig. 5. Conceptual Model for the timing, pacing, and triggering of Devonian (anoxic) events. A) Upper-Threshold Model. B) Lower-threshold Model. Dashed vertical lines indicate periods characterized by either strong or weak modulation of precession – illustrated here using the $g_4 - g_3$ cycle. Dotted horizontal lines indicate the Earth-system boundary conditions. Linear insolation-threshold crossing is marked by orange circles (dashed circles indicate a crossing outside the modulation window), question marks indicate expected linear insolation-threshold crossing outside the modulation window but are empirically unlikely. Climatic precession from sampled from ~5 to ~2 Ma (La04; Laskar et al., 2004).

The *Lower-Threshold Model* (Fig. 5B) corresponds to a contrasting scenario in which global events are triggered when a lower threshold is crossed. As alluded to earlier, a linear insolation-threshold crossing within this scenario would only be possible during intervals of weak modulation; otherwise, numerous perturbations would be expected under comparable Earth-system boundary conditions (see ‘?’ on Fig. 5B). Of all investigated Devonian events here, only the *pumilio* events appear to follow this model. They occur during a period of low astronomical modulation on multi-Myr timescales and culminate during precession and short eccentricity minima. This contrasting behavior also explains their unique expression in terms of sedimentology and geochemical signatures compared to the other events at Oued Ferkla (Chapter 2). This approach reconciles the differing expressions of the same event across different paleodepositional environments, while also explaining the diachroneity observed among Devonian anoxic events (cf. Hangenberg Event; Hedhli et al., 2023). Differences in Earth-system boundary conditions determine how close a basin is to its relevant threshold; as a result, basins may cross that threshold at different times under the same long-term astronomical forcing, producing temporal offsets in event expression that can extend to multi-Myr scales. Such observations are consistent with the proposed models, in which global astronomical forcing ultimately interacts with basin-specific boundary conditions, the latter exerting a dominant control on when anoxia occur, as is evidence for the Hangenberg Event (Hedhli et al., 2023).

Astronomical configurations are independent of Earth-system boundary conditions⁶. At any given time in a given hemisphere, a unique combination of orbital parameters (precession, obliquity, and eccentricity) determines the incoming insolation, whose seasonal and latitudinal distribution is governed primarily by precession and obliquity (see 1.2.1.). Yet, the recovered imprint of separate astronomical components can vary strongly between paleogeographic settings for a given orbital configuration, and in ways that deviate from what would be expected based solely on insolation patterns (Gérard et al., 2026). Here, this variability is interpreted in the same way: primarily as a consequence of differences in local Earth-system boundary conditions, rather than as a simple function of paleolatitude. Although insolation distribution does vary with latitude, the interconnected nature of the Earth system suggests that this effect is generally secondary. This interpretation is supported by the unexpectedly strong expression of half-precession and obliquity in the Appalachian Basin at ~30° S (Chapter 4), as well as numerous cyclostratigraphic studies reporting surprisingly robust obliquity signals at low paleolatitudes (e.g., Bosmans et al., 2015; Laurin et al., 2015).

⁶ This statement requires nuance: for example, the Earth’s dynamical ellipticity – reflecting departures of its mass distribution from perfect spherical symmetry – affects precession and other rotational modes, and uncertainties in its past evolution introduce uncertainties in astronomical solutions (Farhat et al., 2022). For the purposes of this study, these effects are assumed to be negligible.

6.6. Causal Mechanisms Linking Astronomical Forcing and Devonian Anoxic Events

This section examines how Earth-system boundary conditions, the processes that drive their variability, and astronomically forced changes in insolation may have interacted to produce the observed Devonian anoxic events. Broadly put, the *Earth-system boundary conditions* as conceptually utilized here represent the integrated state of key, interconnected components of the Earth system. These include, but are not limited to, continental configuration; climatic state (incl. temperature, $p\text{CO}_2$, $p\text{O}_2$, continental ice); sea level, ocean circulation, and degree of water-mass stratification; nutrient delivery and geochemical cycling; and the extent and nature of terrestrial vegetation cover. Strictly speaking, these major Earth-system boundary conditions cannot be constrained independently at the temporal resolution and confidence needed to disentangle their separate contributions. Therefore, the causal mechanisms underlying Devonian anoxic events cannot be uniquely determined here. This represents an asymptotic, ongoing effort of the broader scientific community – one that will likely continue to evolve over the coming decades to centuries. The aim here is therefore not to identify a single definitive cause – an inference that the available proxies simply do not permit – but to outline mechanistic scenarios that are consistent with the threshold framework developed above and with the combined sedimentological, geochemical, and cyclostratigraphic evidence.

According to the *Upper-Threshold Model* (Fig. 5A), substantial environmental perturbation occurs during intervals characterized by prolonged strong alternation of climatic extremes. Combining evidence from Oued Ferkla, the Sherburne Formation, and the West Valley core highlights the most plausible causal mechanisms for events occurring during such intervals. These events likely involved a combination of (i) intensified monsoonal activity leading to enhanced nutrient runoff, eutrophication, and subsequent ‘top-down’ anoxia development (Tyson and Pearson, 1991; Arthur and Sageman, 1994; Kump and Arthur, 1999; De Vleeschouwer et al., 2012; Carmichael et al. 2019; Wichern et al., 2024), and (ii) atmospheric and oceanic invigoration that strengthened circulation and potentially promoted upwelling of anoxic waters or nutrients, or vertical chemocline displacement, resulting in ‘bottom-up’ anoxia development (Arthur and Sageman, 1994; Carmichael et al., 2019 and references therein). Both mechanisms allow for pulsed anoxia, arising either from progressively increasing environmental stress during intervals of strong climatic alternation or from the eventual crossing of a final insolation threshold that tips the local-to-regional Earth system into an anoxic state. Such mechanisms explain the expression of the global Daleje, Choteč, Kačák, Rhinestreet, and Kellwasser events (Chapter 2, 3, 5) as well as the regional Fir Tree, Hubbard Quarry, and Lodi events (Chapter 4).

Conversely, the *Lower-Threshold Model* (Fig. 5B) aligns with stagnation-driven anoxia, in which nutrient supply is potentially more continuous, atmospheric and ocean circulation are more muted, and semi-restricted silled basins or epicontinental seas characteristic of the Devonian become increasingly prone to eutrophication-driven anoxia. In addition, enhanced remineralization efficiency (Penn et al., 2018) could promote ‘bottom-up’ anoxia development through intensified oxygen consumption at depth and subsequent shoaling of the chemocline, potentially leading to an expansion of the OMZ (Wilde and Berry, 1984; Carmichael et al., 2019). Such a scenario is broadly consistent with the global expression of the *pumilio* event, studied here at Oued Ferkla (Becker et al., 2020; Talih et al., 2022; Chapter 2).

While climatic precession generally exerts the strongest imprint, evidence for obliquity amplification (Chapter 4) and 173 kyr obliquity pulses primarily during the Kačák (Chapter 2, 3) and Rhinestreet (Chapter 5) events demonstrates that both components have the capacity to contribute substantially to anoxia. Although the timing of those events appears dictated by climatic precession, obliquity-paced processes likely played a major role in shaping the development of anoxia, for example through their inferred influence on long-term sea-level variations during the Rhinestreet and Kellwasser events (Chapter 5). Any further discrimination between these astronomical components – and the specific mechanisms through which they act – would be speculative given the existing data. The cyclostratigraphic framework proposed here also highlights a limitation of the top-down/bottom-up model as outlined by Carmichael et al. (2019) for the Kellwasser Crisis. While conceptually useful, it is diagnostically weak; both pathways can produce the same sedimentological and geochemical signatures and can both be reconciled with an astronomically driven scenario. In addition, it also does not allow discriminating ultimate and proximate causality (Algeo and Shen, 2024).

Regardless of which model – *Upper-Threshold* or *Lower-Threshold* – is appropriate, astronomical forcing may act as the immediate trigger either way. Under the first scenario, either strong or increasingly amplified climatic alternation can push the system across an upper environmental limit, leading to widespread anoxia. In the *Lower Threshold Model*, by contrast, persistently weak climatic alternation of climatic states or crossing of an insolation-threshold crossing may act as the immediate trigger. As already mentioned before, a multitude of other triggers that act on the Earth-system boundary conditions baseline may be equally responsible – these are not the focus of this study and are not further considered. However, given the clear pacing by Devonian anoxic events on 2.4 Myr timescales, it is highly probable that, at least on multi-Myr timescales, the astronomical background state plays a crucial role in enabling environmental perturbation for these events. In addition, the consistent phase relationship between climatic precession and the evolution of events – from their onset to apex – suggests that Milankovitch forcing also determined the timing of events on shorter timescales. This highlights the often-unrecognized potency of astronomical forcing to play a major role in global anoxic and extinction events (cf. Algeo and Shen, 2024).

References

- Aboussalam, S. Z., Becker, R. T., 2011. The global Taghanic Biocrisis (Givetian) in the eastern Anti-Atlas, Morocco. *Palaeogeogr., Palaeoclimatol., Palaeoecol.*; 304, 163-164. doi:10.1016/j.palaeo.2010.10.015
- Algeo, T. J. and Liu, J., 2020. A re-assessment of elemental proxies for paleoredox analysis. *Chem. Geol.*; 540, 119549. <https://doi.org/10.1016/j.chemgeo.2020.119549>.
- Algeo, T. J., and Shen, J., 2024. Theory and classification of mass extinction causation. *Natl. Sci. Rev.*; 11, nwad237. doi:10.1093/nsr/nwad237.
- Arthur M. A., Sageman B. B., 1994. Marine black shales: depositional mechanisms and environments of ancient deposits. *Annu. Rev. Earth Planet. Sci.*; 22:499–551
- Becker, R. T., Marshall, J. E. A., Da Silva, A.-C., 2020. The Devonian Period. In: Gradstein, F. M., Ogg, J. G., Schmitz, M. D. And Ogg, G. (Eds.), *The Geologic Time Scale 2020*, chapter 22, 733-810. <https://doi.org/10.1016/B978-0-12-824360-2.00022-X>.
- Berger, A. L., 1973. La théorie astronomique des paléoclimats, PhD thesis, p315, Université catholique de Louvain. <https://hdl.handle.net/2078.1/233872>
- Berger, A. L., 1987. Long-term variations of caloric insolation resulting from the Earth's orbital elements. *Quat. Res.*; 9, 139-167.
- Bosmans, J. H. C., Hilgen, F. J., Tüenter, E., Lourens, L. J., 2015. Obliquity forcing of low-latitude climate. *Clim. Past*; 11, 1335-1346. doi:10.5194/cp-11-1335-2015
- Brett, C. E. and Baird, G. C., 1997. Epiboles, outages, and ecological evolutionary bioevents: taphonomic, ecological, and evolutionary factors. In: Brett, C. E., and Baird, G. C., (eds.), *Paleontological Events: Stratigraphic, Ecological, and Evolutionary Implications*, 249–285.
- Buggisch, W., Joachimski, M. M., 2006. Carbon isotope stratigraphy of the Devonian of Central and Southern Europe. *Palaeogeogr., Palaeoclimatol., Palaeoecol.*; 240, 68-88. doi:10.1016/j.palaeo.2006.03.046
- Carmichael, S. K., Waters, J. A., Köningshof, P., Suttner, T. J., Kido, E., 2019. Paleogeography and paleoenvironments of the Late Devonian Kellwasser event: A review of its sedimentological and geochemical expression. *Glob. Planet. Change*; 183, 102984. <https://doi.org/10.1016/j.gloplacha.2019.102984>.
- De Vleeschouwer, D., Da Silva, A.-C., Boulvain, F., Crucifix, M. & Claeys, P., 2012. Precessional and half-precessional climate forcing of Mid-Devonian monsoon-like dynamics. *Clim. Past.*; 8, 337–351.
- De Vleeschouwer, D., Rakociński, M., Racki, G., Bond, D. P. G., Sobieć, K., Claeys, P., 2013. The astronomical rhythm of Late-Devonian climate change (Kowala section, Holy Cross Mountains, Poland). *Earth Planet. Sci. Lett.*; 365, 25-37. <http://dx.doi.org/10.1016/j.epsl.2013.01.016>.
- De Vleeschouwer, D., Da Silva, A.-C., Sinnesael, M., Chen, D., Day, J. E., Whalen, M. T., Guo, Z., Claeys, P., 2017. Timing and pacing of the Late Devonian mass extinction event regulated by eccentricity and obliquity. *Nat. Comm.*; 8, 2268. doi:10.1038/s41467-017-02407-1.
- De Vleeschouwer, D., Percival, L. M. E., Wichern, N. M. A., Batenburg, S. J., 2024. Pre-Cenozoic cyclostratigraphy and palaeoclimate responses to astronomical forcing. *Nat. Rev. Earth Environ.*; 5, 56-75. <https://doi.org/10.1038/s43017-023-00505-x>.
- DeSantis M. K., Brett, C. E., 2011. Late Eifelian (Middle Devonian) biocrises: Timing and signature of the pre-Kačák Bakoven and Stony Hollow Events in eastern North America. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 304, 113-135. doi:10.1016/j.palaeo.2010.10.013
- Ellwood, B. B., Algeo, T. J., El Hassani, A., Tomkin, J. H., Rowe, H. D., 2011. Defining the timing and duration of the Kačák interval within the Eifelian/Givetian boundary GSSP, Mech Irdane, Morocco, using geochemical and magnetic susceptibility patterns. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 304, 74-78. doi:10.1016/j.palaeo.2010.10.012

- Gérard, J., Pohl, A., Sablon, L., Huygh, J. J. C., Da Silva, A.-C., Crucifix, M., 2026. Spatially contrasted response of Devonian anoxia to astronomical forcing. *Clim. Past*; 22, 1003-1021. <https://doi.org/10.5194/cp-22-1003-2026>
- Hedhli, M., Grasby, S. E., Henderson, C. M., Davis, B. J., 2023. Multiple diachronous “Black Seas” mimic global anoxia during the latest Devonian. *Geology*; 51, 973-977. <https://doi.org/10.1130/G51394.1>
- House, M. R., 2002. Strength, timing, setting and cause of mid-Palaeozoic extinctions. *Palaeogeogr., Palaeoclimatol., Palaeoecol.*, 181, 5-25.
- Huygh, J. J. C., Algeo, T. J., Sageman, B. B., Arts, M., Ver Straeten, C. A., Over, D. J., Gérard, J., Sablon, L., Crucifix, M., Da Silva, A. -C., 2026. Astronomical control on marine anoxia during the Kellwasser Crisis and Rhinestreet Event (Appalachian Basin, New York, USA). *Glob. Planet. Change*; 257, 105216. <https://doi.org/10.1016/j.gloplacha.2025.105216>
- Kabanov, P., 2019. Devonian (c. 388–375 my) Horn River Group of Mackenzie Platform (northwestern Canada) is an open-shelf succession recording oceanic anoxic events. *J. Geol. Soc. Lond.* 176, 29–45.
- Kabanov, P., Hauck, T. E., Gouwy, S. A., Grasby, S. E., van der Boon, A., 2023. Oceanic anoxic events, photic-zone euxinia, and controversy of sea-level fluctuations during the Middle-Late Devonian. *Earth-Sci. Rev.*; 241, 104415. <https://doi.org/10.1016/j.earscirev.2023.104415>
- Kump, L. R., Arthur, M. A., 1999. Interpreting carbon-isotope excursions: carbonates and organic matter. *Chem. Geol.*; 161, 181-198.
- Laskar, J., 1989. A numerical experiment on the chaotic behaviour of the Solar System. *Nature*; 338, 237-238. <https://doi.org/10.1038/338237a0>
- Laskar, J., 1990. The chaotic motion of the solar system: A numerical estimate of the size of the chaotic zones, *Icarus*, 88, 266-291. doi:10.1016/0019-1035(90)90084-m
- Laskar, J., 2020. Astrochronology. In: Gradstein, F. M., Ogg, J. G., Schmitz, M. D. And Ogg, G. (Eds.), *The Geologic Time Scale 2020*, chapter 4, 139-158.
- Laskar, J., Robutel, P., Joutel, F., Gastineau, M., Correia, A. C. M., Levrard, B., 2004. A long-term numerical solution for the insolation quantities of the Earth. *Astron. Astrophys.*; 428, 1, 261-285. <https://doi.org/10.1051/0004-6361:20041335>.
- Laurin, J., Meyers, S. R., Uličný, D., Jarvis, I., Sageman, B. B., 2015. Axial obliquity control on the greenhouse carbon budget through middle- to high-latitude reservoirs. *Paleoceanogr.*; 30, 2, 133-149. <https://doi.org/10.1002/2014PA002736>
- Lottmann, J., 1990. The middle Givetian pumilio-events A tool for high time resolution and event-stratigraphical correlation. In: Kaufmann, B., Walliser, O. H. (eds.), *Extinction Events in Earth History*, 30: 145–149.
- Martinez, M., Kotov, S., De Vleeschouwer, D., Pas, D., Pälike, H., 2016. Testing the impact of stratigraphic uncertainty on spectral analyses of sedimentary series. *Clim. Past*; 12, 1765-1783. doi:10.5194/cp-12-1765-2016
- Penn, J. L., Deutsch, C., Payne, J. L., Sperling, E. A., 2018. Temperature-dependent hypoxia explains biogeography and severity of end-Permian marine mass extinction. *Science*; 362, 6419. doi: 10.1126/science.aat1327
- Sageman, B. B., Murphy, A. E., Werne, J. P., Ver Straeten, C. A., Hollander, D. J., Lyons, T. W., 2003. A tale of shales: the relative roles of production, decomposition, and dilution in the accumulation of organic-rich strata, Middle–Upper Devonian, Appalachian basin. *Chem. Geol.*; 195, 229-273. doi:10.1016/S0009-2541(02)00397-2.
- Talih, A., Aboussalam, S. Z., Becker, R. T., Saadi, M., Benmlih, A., 2022. Stratigraphy and tectono-sedimentary processes of allochthonous and autochthonous Devonian deposits of the Tisdafine Basin, Eastern Anti-Atlas, Morocco. *Bulletin de l'Institut Scientifique, Rabat, Section Sciences de la Terre*; 44, 27-53. e-ISSN : 2458-7184
- Tyson, R. V., Pearson, T. H., 1991. Modern and ancient continental shelf anoxia: an overview. *Geol. Soc. Lond. Spec. Publ.*; 58, 1-24. <https://doi.org/10.1144/GSL.SP.1991.058.01.01>

- Walliser, O. H., 1996. *Global Events and Event Stratigraphy*. Springer, Berlin. ISBN-13: 978-3-642-79636-4.
- Waltham, D., 2015. Milankovitch Period Uncertainties and Their Impact on Cyclostratigraphy. *J. Sediment. Res.*; 85, 8, 990-998. <https://doi.org/10.2110/jsr.2015.66>
- Weedon, G., 2003. *Time Series Analysis and Cyclostratigraphy*. Cambridge University Press, ISBN-13: 978-0-511-06809-6.
- Wichern, N., Becker, R. T., Bialik, O. M., Hartenfels, S., De Vleeschouwer, D., 2026. Cyclostratigraphic calibration of the rhythmically bedded upper Frasnian (upper Devonian) in the Rhenish Massif, Germany. *Newslett. Stratigr.*; DOI: 10.1127/nos/2026/0908
- Wilde, P., Berry, W., 1984. Destabilization of the oceanic density structure and its significance to marine “extinction” events. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*; 48, 2, 143–162.
- Zachos, J., Pagani, M., Sloan, L., Thomas, E., Billups, K., 2001. Trends, Rhythms, and Aberrations in Global Climate 65 Ma to present. *Science*; 292, 686-692.
- Zeebe, R. E. and Lantink, M. L., 2024. A secular solar system resonance that disrupts the dominant cycle in Earth’s orbital eccentricity ($g_2 - g_5$): Implications for astrochronology. *Astron. J.*; 167:204. <https://doi.org/10.3847/1538-3881/ad32cf>.

7. Conclusions

Global Devonian anoxic events are astronomically paced. While an association with Milankovitch cycles is somewhat expected – insolation variability is ever-present – it is the specific pacing by canonical Milankovitch cycles together with long-period, multi-Myr modulation cycles that demonstrates this astronomical control. This does not imply, however, that astronomical forcing acted alone; multiple additional drivers – rooted in complex Earth-system processes – must also be considered.

The phase relationship between these events and orbital extrema need to be assessed across different timescales. At Oued Ferkla, the Daleje, Choteč, and Kačák events, and in the West Valley core, the Rhinestreet Event and Kellwasser Crisis, all unfold during intervals of increased astronomical modulation of insolation – specifically during 2.4 Myr to ~6 Myr maxima. On shorter, Milankovitch timescales, these events are most clearly paced by climatic precession and/or eccentricity; they initiate generally near minima, develop on the rising limb, and reach their apex during maxima. In contrast, the *pumilio* events, as expressed at Oued Ferkla, represent clear anomalies: they broadly coincide with 2.4 Myr and ~6 Myr minima and initiate during precession and short eccentricity maxima, developing along the declining limb and reaching their apex during minima. Notably, they unfold during long-eccentricity maxima, suggesting that they reflect a linear lower-threshold response, triggered under extreme minima in precession-forced insolation. The phasing relative to obliquity is less pronounced, yet broadly similar, with most events aligning with obliquity minima and developing toward subsequent maxima.

Successive Devonian events share broadly similar, though not identical, relationships to orbital extrema. Strong similarities are evident on multi-Myr timescales and often at the precession scale. Their differing expressions, however, primarily reflect variations in Earth-system state – including climatic conditions and paleodepositional setting – and only secondarily the differences in phasing relative to, for example, obliquity extrema. Nonetheless, distinct differences in relative phasing between successive events and specific orbital extrema (e.g., Lower versus Upper Kellwasser Event) indicate that, from an astronomical perspective, the immediate causal pathways were not uniform across all events.

Astronomical forcing primarily modulates background conditions that make Earth system prone to redox instability, notably on multi-Myr timescales. However, the development of anoxia does not appear to be tied to any single, specific orbital configuration. Instead, Earth-system boundary conditions – including paleodepositional setting and basin restriction – exert dominant control on whether insolation-driven variability translates into deoxygenation. These boundary conditions therefore determine whether astronomical forcing functions merely as a background modulator or becomes an effective trigger for anoxia. At precession

to short eccentricity timescales, Milankovitch forcing can thus act as the immediate trigger when the system is sufficiently close to its threshold, a situation more likely during long-term Milankovitch modulation extrema.

The importance of sea-level variations in the development, sustenance, and intensification of marine anoxia is underscored, likely through their influence on ocean circulation and the vertical displacement of the oxycline⁷. While eccentricity strongly modulates the hydrological cycle, obliquity-driven seasonal contrast may be equally potent, particularly given its role in driving sea-level change – whether through aquifer/limno-eustasy or glacio-eustasy. The combined influence of climatic precession and obliquity forcing, potentially acting together, points to an interplay between top-down and bottom-up anoxia. This suggests that these conceptual models – although useful in certain scenarios – are not diagnostic in isolation but represent end-members within a continuum of mechanisms capable of producing deoxygenation.

High-resolution cyclostratigraphy of the Sherburne Formation (Lansing core, 30° S) highlights the potency of half-precessional forcing at relatively higher latitudes as well as obliquity forcing at relatively lower latitudes, likely mediated through atmospheric teleconnections involving ITCZ and Hadley cell migration in combination with changes in circulation changes. The interplay of precession and obliquity in the pantropical belt produces complex climate-sediment responses involving nonlinear pathways.

The *Upper-Threshold – Lower-Threshold* Models integrate the astronomical interpretations within a conceptual threshold framework that incorporates direct (linear) insolation variability as well as modulation on short eccentricity to multi-Myr timescales. This framework is able to explain the timing, pacing, and recurrence of Devonian anoxic events whose expression varies widely depending on local-to-regional paleodepositional conditions. It also accounts for the occurrence of regional events and does not require invoking external trigger mechanisms – while neither excluding nor underestimating their potential influence. Importantly, it does not rely on assumptions about specific Earth-system boundary conditions such as continental configuration; climatic state (incl. temperature, pCO₂, pO₂, continental ice); sea level, ocean circulation, and degree of water-mass stratification; nutrient delivery and geochemical cycling; and the extent and nature of terrestrial vegetation cover.

⁷ The oxycline refers to the depth interval in the water column where dissolved oxygen concentration decline sharply from oxygenated surface waters to oxygen-poor deeper waters.

The models developed here also provide a transferable framework that can be applied to other stratigraphic intervals across the entire Phanerozoic, across basins, and regardless of the specific event expression – provided a cyclostratigraphic framework exists. This way, the present work not only contributes a small but coherent piece to the broader Devonian puzzle, but also offers a consistent basis for comparison in future studies. As such, this work provides a foundation on which future Devonian and deep-time paleoenvironmental studies can build, test, and refine increasingly integrated models of Earth-system behavior.

To conclude, a distinct combination of long-term astronomical forcing and regional-to-global Earth-system boundary conditions – including climatic state and paleodepositional setting - governs the occurrence of environmental perturbations. On shorter timescales, the degree to which the Earth system is positioned near a tipping point – that is, the proximity to a threshold, whether linear or modulation-controlled – determines how climatic precession and obliquity shape the regional expression of an event. Within such a framework astronomical forcing may act as the final trigger that pushes an already stressed Earth system into anoxia. However, external factors that contribute to the prevailing Earth-system boundary conditions can equally serve as the ultimate trigger mechanism.

8. Emerging Questions, Outlook, and Future Work

Do similar relationships between orbital extrema and (Devonian) (anoxic) events exist across basins and throughout geological time? The patterns documented at Oued Ferkla, the Sherburne Formation (Lansing core), and the West Valley core provide the basis for the *Upper-Threshold Model* and *Lower Threshold Model*, which now serve as a benchmark for evaluating additional evidence. Addressing this question requires investigating further sections across a wide range of paleodepositional environments that preserve a robust Milankovitch imprint and long-term, multi-Myr cyclicity during the Devonian and, by extension, the Phanerozoic. For anoxic events specifically, such work should follow a dual strategy: (i) establishing robust cyclostratigraphy and (ii) characterizing paleoredox conditions using a broad suite of geochemical proxies. Although substantial data already exist, these records must be consolidated, compared, and evaluated systematically. The models developed here provide a consistent, cyclostratigraphy-based framework that is diagnostic for the questions they aim to address and can guide such comparative efforts.

What are the causal mechanisms behind marine anoxia during the Devonian? The exact processes that translate astronomical insolation forcing into a sedimentary response – the underlying transfer functions governed by Earth-system boundary conditions – require extensive research beyond the scope of cyclostratigraphy. Although this work provides evidence for a crucial role of astronomical forcing in shaping marine anoxia during the Devonian, it can only infer or hypothesize the mechanisms linking insolation variability and sedimentary response. Cyclostratigraphy is a powerful tool for constraining event duration and relative phasing to orbital extrema, but it cannot directly resolve the causal pathways that generate marine anoxia or extinction events. Addressing these mechanisms demands an integrated approach that combines high-resolution proxy records with numerical modelling. Only through such multi-disciplinary work, supported by comparison with suitable modern analogues, can a robust ‘most-plausible scenario’ for Devonian anoxic events be established. Yet, integration of geological evidence and numerical modelling output is challenging, as the spatial scales and process representations rarely align. Therefore, future interdisciplinary efforts should continue to integrate both, with a strong focus on the integration itself – developing approaches that explicitly bridge the gap between stratigraphic observations and the outputs of Earth-system models.

The field of cyclostratigraphy continues to evolve rapidly, with new approaches, statistical tools, and astronomical solutions expanding its potential. For the Devonian, the development of a complete astrochronozonation – a standardized, astronomically calibrated temporal framework – represents a major but increasingly feasible challenge. Such a zonation would enable high-resolution correlation across basins and provide a unified reference for integrating both legacy and newly generated datasets. In combination with the threshold-

based models proposed in this thesis, an astrochronozonation would offer a robust structure for synthesizing diverse cyclostratigraphic records and evaluating the pacing of (anoxic) events at the regional to global scales. Achieving this, however, requires coordinated efforts to expand extensive and high-quality Devonian records, refine astronomical solution for deep time, and strengthen the integration of multi-disciplinary research outputs. Together, these advances would bring the Devonian one step closer to a fully astronomically calibrated Earth history – a framework capable of revealing the rhythms that shaped ancient climates, environments, and the evolving biosphere.

9. Supplemental

A. Lansing core

a. Preface and Introduction

The Lansing core covers about 847 m of strata, of which the upper ~460 m have been meticulously investigated together with Jay Zambito and Carl Brett. From bottom to top, this interval of the Lansing core contains the Onondaga, Union Springs, Oatka Creek, Skaneateles, Ludlowville, Moscow, Tully, Geneseo, and Sherburne formations. Even though it is considered to be the most complete Middle Devonian core from the Appalachian Basin, some unconformities at the base of the Skaneateles and Oatka Creek Fm.'s (minor) and Tully Fm. (major) are most probably present. For a more detailed (draft) description of the stratigraphy, lithology, and inferred sequence -and biostratigraphy.

Low resolution (avg. sampling rate around 0.3 m) magnetic susceptibility (MS) data has been made available by Jay Zambito. In addition, during the summer of 2023, high resolution (avg. 0.013 m) core scanner gamma ray spectrometry (GRS) measurements were carried out at the Geology Department of the University of Cincinnati, Ohio (USA) – See Fig. 1. However, during measurement, gaps due to missing pieces of core were closed by pushing the two parts of the core back-to-back in order to have GRS response (i.e., not measuring an air gap). Unfortunately, the exact position where such corrections were carried out were not recorded, due to which, bit by bit, a massive artificial condensation of 30' or 9 m was introduced into the 2023 GRS dataset. Using 300+ photos, the 35760-lines GRS dataset was manually corrected by comparing to the original low-resolution 1977 GRS dataset and the recently measured low-resolution MS dataset. Averaged values from the data surrounding the gaps was used to fill the missing data points manually. Still, when comparing the lithology on the Member or Sub-member scale, discrepancies appear to remain. Especially near the lowest part of the core (Eifelian), it can be expected that the accumulation of error amounts to considerable uncertainty. Because the Eifelian is highly condensed in the Lansing core, the impact of the uncertainty is especially impactful. The resolution of the 1977 GRS dataset is too low to be used to further correct the 2023 GRS dataset, meaning that some depth-domain uncertainty will remain. Lastly, the K, Th and U detectors of the core scanner had not been calibrated. As such, only the Total Gamma (API) (hereafter γ) and MS signals are available for interpretation and (cyclostratigraphic) analysis. While these factors limit documenting phase relationships between specific events and orbital extrema, the dataset offers many other advantages that can be leveraged, most notably its high resolution (see Chapter 4).

To facilitate the cyclostratigraphic analysis of the 460 m record, known to contain some unconformities and drastic condensation near its base, the Lansing core GRS record was subdivided largely into its separate formations. This approach was selected because the formations of the upper Eifelian to Givetian Hamilton Group are based indirectly upon a type of allostratigraphy (i.e., they are not strictly lithostratigraphic units; Brett et al., 2011), likely making them internally consistent in terms of paleodepositional setting, paleoclimatic response and, potentially, sedimentation rate. The following subchapters contain a very brief description of the current cyclostratigraphic working hypotheses for each of the Lansing core subdivisions.

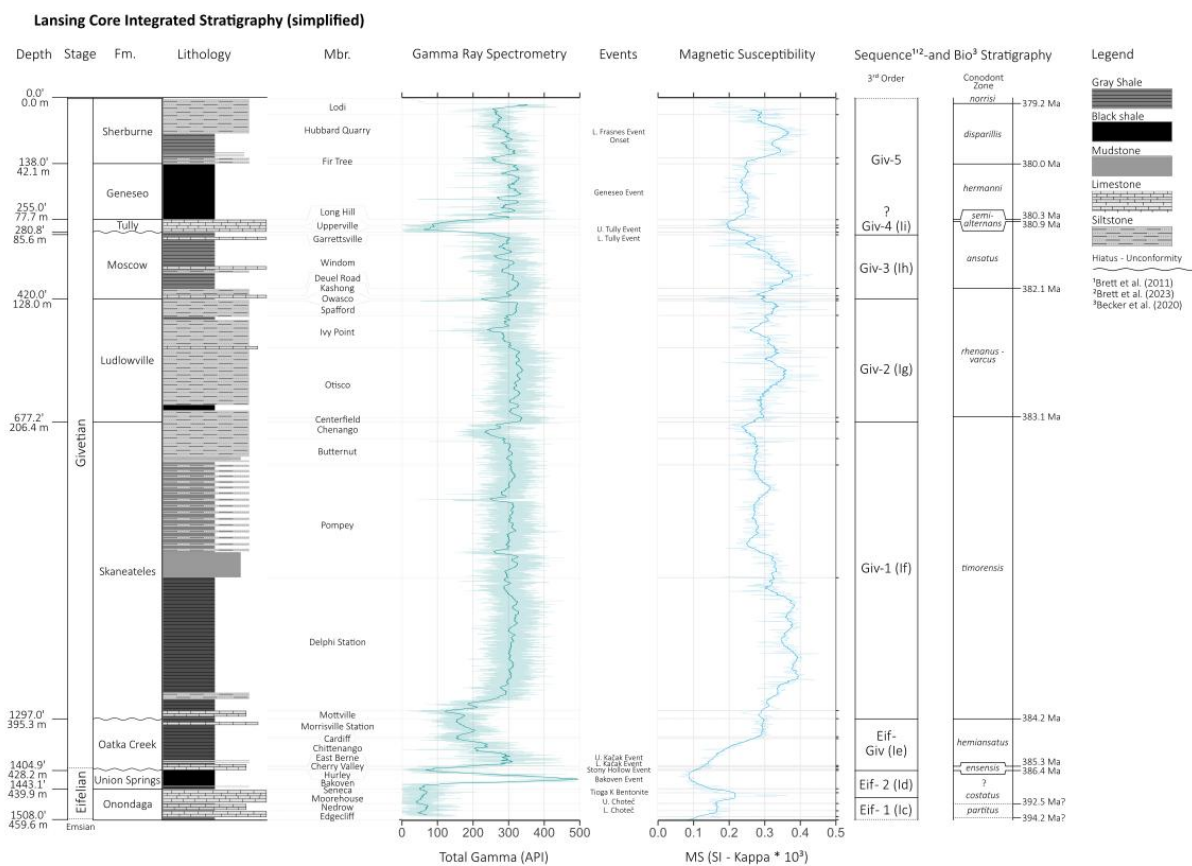


Fig. 1. Lansing core integrated stratigraphic framework. Stratigraphy, lithological column, high-resolution GRS total gamma (API) signal, low-resolution magnetic susceptibility (SI), sequence stratigraphy (Brett et al., 2011) and conodont Zone biostratigraphy (ages from Becker et al., 2020).

b. Onandaga, Union Springs, and Oatka Creek formations

Given the strong condensation (and errors introduced during the GRS measurement) in the lower part of the Lansing core, it is expected that the cyclostratigraphic analysis will be more complicated than for the upper part. For this reason, focus has been put primarily on the majority of the Givetian-aged part of the core.

c. Cyclostratigraphy of the Skaneateles Formation

The thick Skaneateles Formation is assigned to the lower-to-middle *timorensis* conodont Zone (Fig. 1; duration of 1100 kyr; Becker et al., 2020), however, it is suspected that its duration may be substantially longer than indicated by biostratigraphy (Carlton E. Brett, *pers. comm.*). Based on preliminary analyses (not documented here), an age model based on 20 short eccentricity cycles, recognized in the GRS signal (Fig. 2), is proposed. The obtained floating astrochronology encompasses 2200 kyr – which is indeed considerably long compared to biostratigraphy. Spectral analysis of the tuned γ -signal reveals the presence of multiple components with frequencies similar to those of expected astronomical cycles (Fig. 3). Extraction of the short and long eccentricity cycles (rescaled on Fig. 2 for visibility) reveals an anti-phased relationship between the γ -signal and astronomically forced climate/insolation. While the cyclostratigraphic age model of the Skaneateles Formation requires refining, it constrains its tentative duration to approximately 2200 kyr – roughly five 405 kyr cycles.

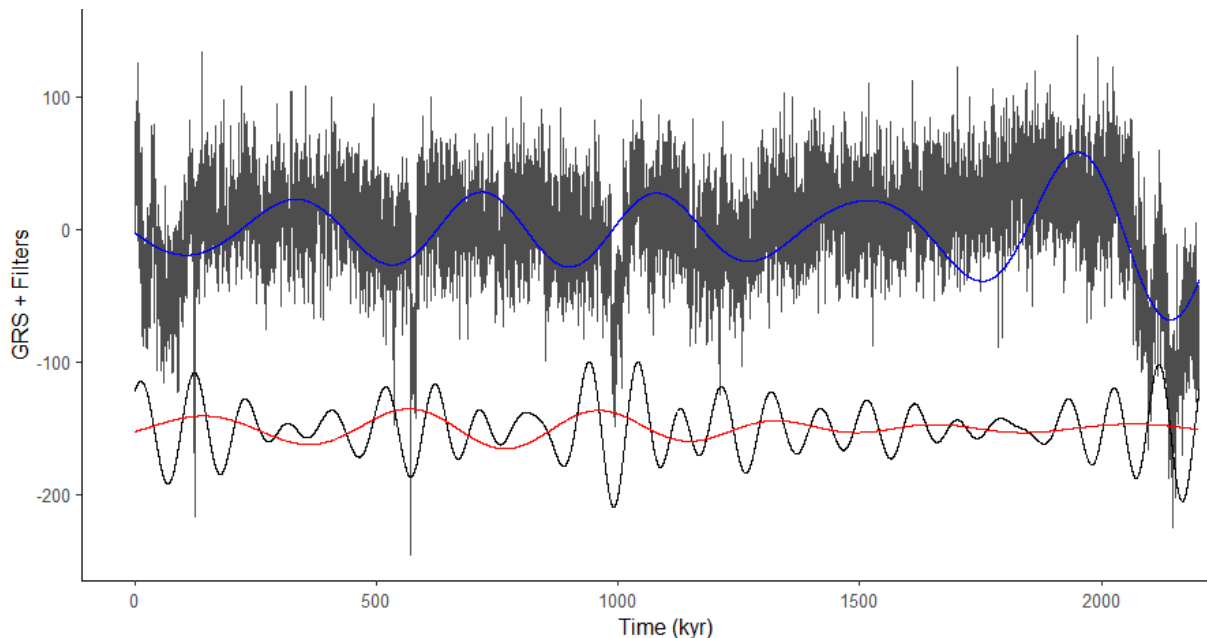


Fig. 2. Skaneateles Fm. tuned γ -signal and bandpass filtered short and long eccentricity cycles. Short eccentricity (black), long eccentricity extracted from the envelope of short eccentricity (red) and long eccentricity directly extracted from the γ -signal (blue).

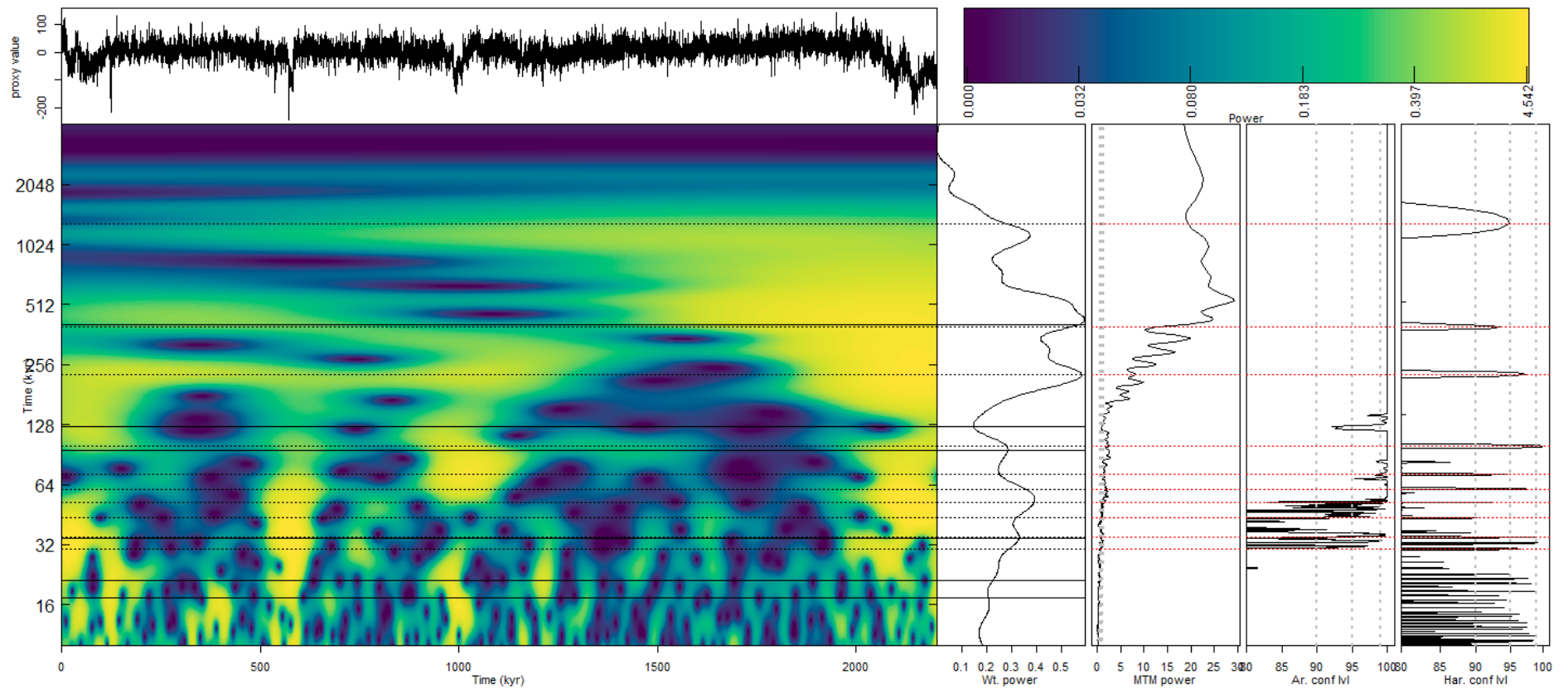


Fig. 3. Skaneateles Formation time-domain γ CWT analysis. Dotted horizontal lines indicate significant components versus 90% CL. Full horizontal lines indicate periods corresponding to 405 kyr, 125 kyr, 95 kyr, 34.4 kyr, 21.2 kyr, and 17.4 kyr

d. Cyclostratigraphy of the Ludlowville Formation

The majority of the Ludlowville Formation is assigned to the lower-to-middle *rhenanus-varcus* conodont Zone (1000 kyr duration; Becker et al., 2020), whereas the lowermost Centerfield Member is assigned to the upper *timorensis* conodont Zone (Fig. 1). Overall, γ -values remain high throughout the Ludlowville Fm., averaging around 300 API (Fig. 4). Wavelet analysis reveals a strong component with a varying periodicity of 6 m to 9 m (Fig. 5), which is interpreted to reflect ~100 kyr short eccentricity.

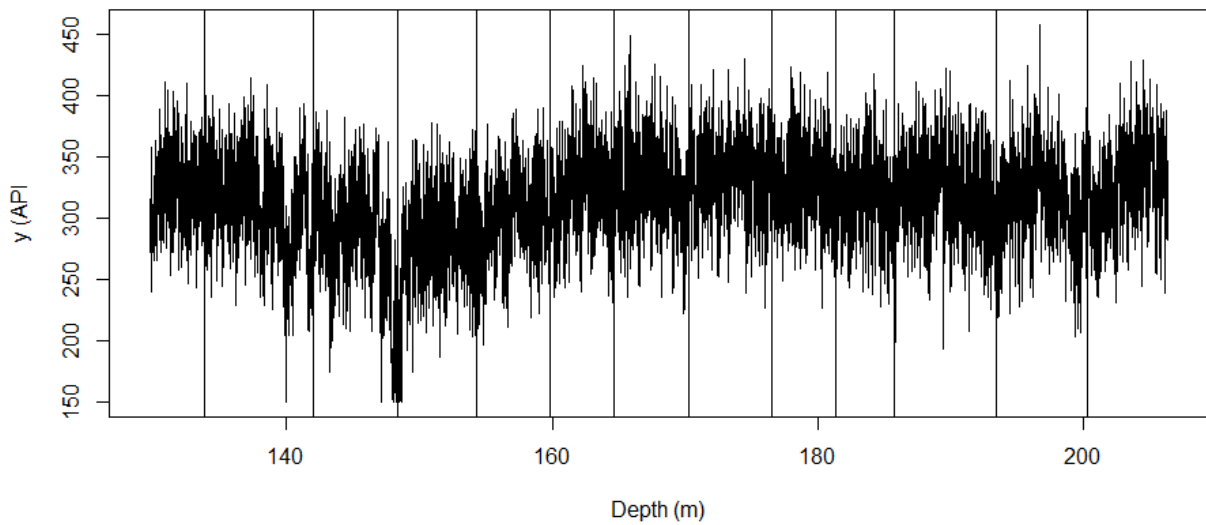


Fig. 4. Ludlowville Fm. γ -signal and indicated depth-time tie-points (black vertical lines).

Minimal tuning was carried out based on the assigned local minima in γ – assuming to correspond to local extrema of short eccentricity cycles (see black vertical lines on Fig. 4). According to this age model, the Ludlowville Formation has an estimated duration of 1240 kyr – consistent with the estimated duration provided by conodont biostratigraphy (Fig. 1).

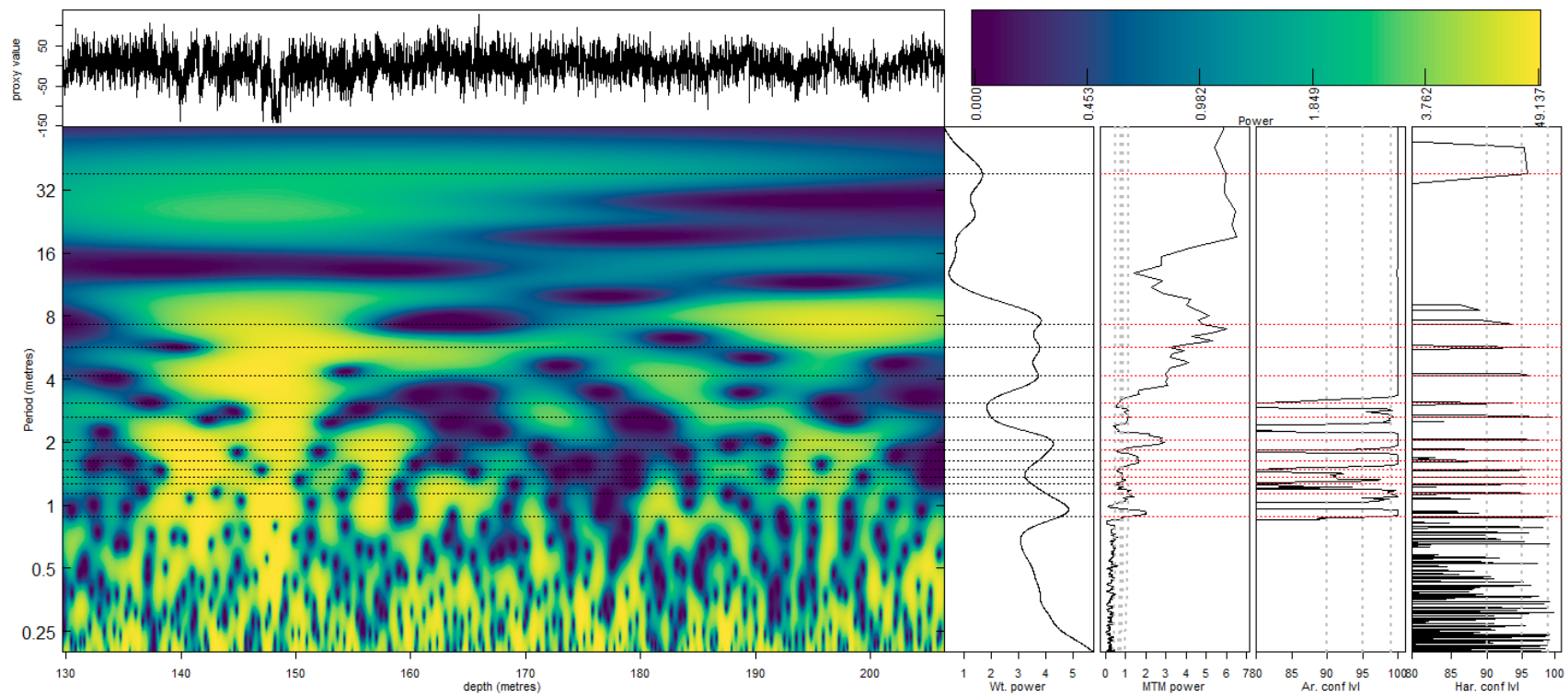


Fig. 5. Ludlowville Fm. depth domain γ CWT analysis. Dotted horizontal lines indicate significant components versus 90% CL.

Spectral analysis (MTM) of the tuned γ -signal reveals multiple components that correspond to expected astronomical frequencies (Fig. 6). Subsequent assessment of the amplitude modulation of precession by short eccentricity reveals a complex phase relationship between the extracted short eccentricity cycles (Fig. 7); going from anti-phased to in-phased, back to anti-phased and again to in-phased. This either indicates that the current age model is to be refined, re-interpreted or that the paleoenvironment responded differently throughout the deposition of the Ludlowville Formation.

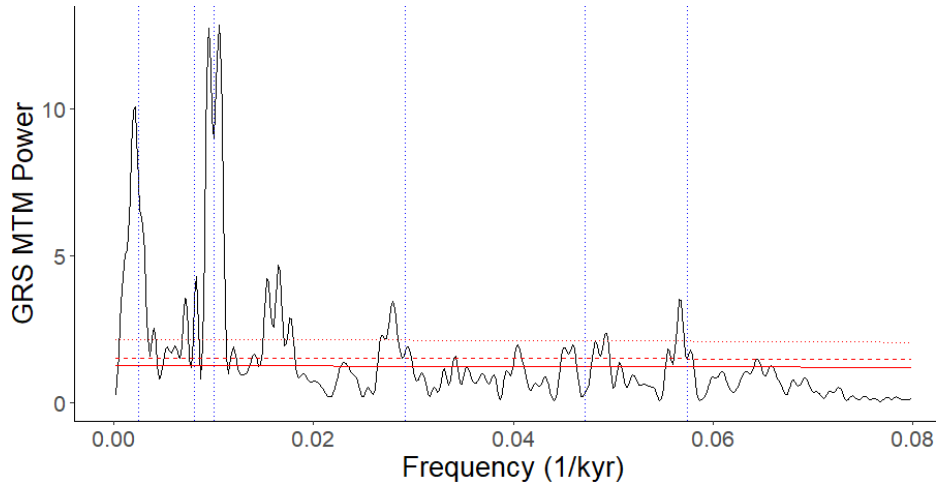


Fig. 6. MTM power spectrum of tuned γ -signal. 90%, 95% and 99% AR1 confidence levels indicated by solid, striped and dotted red lines. Blue dotted horizontal lines represent frequencies corresponding to 405 kyr, 125 kyr, 100 kyr, 34.3 kyr, 21.2 kyr and 17.4 kyr.

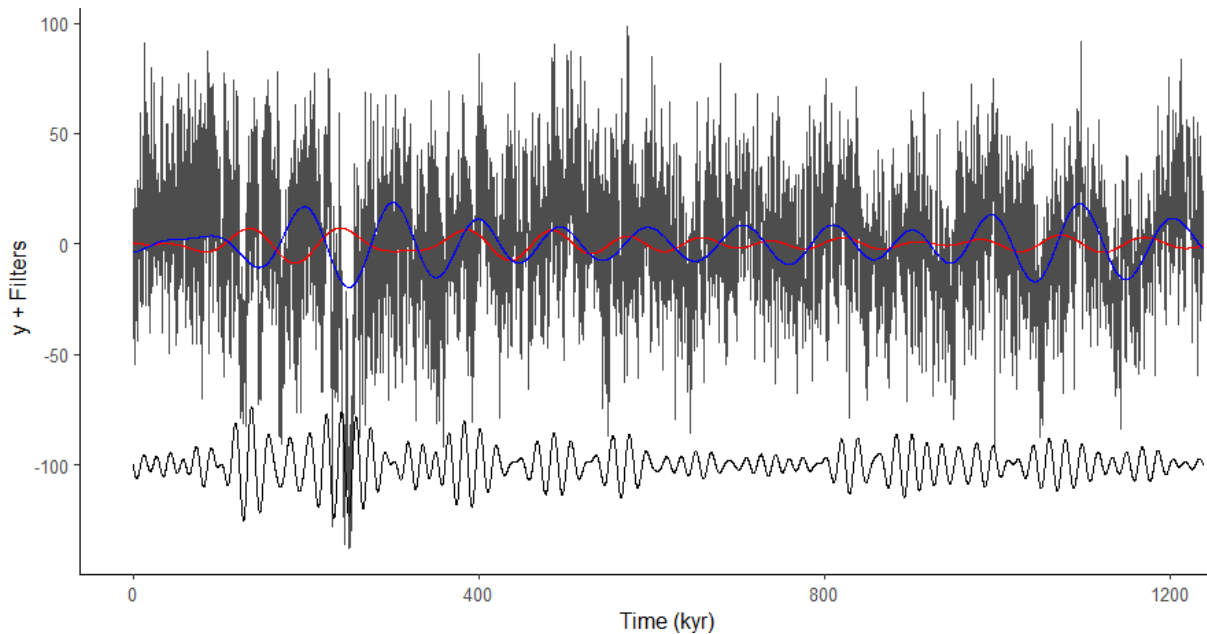


Fig. 7. Tuned γ -signal and bandpass filtered precession and short eccentricity cycles. Precession (black), short eccentricity extracted from the envelope of precession (red) and short eccentricity directly extracted from the γ -signal (blue).

e. Cyclostratigraphy of the Moscow Formation

The Moscow Formation is believed to be unaffected by the sub-Tully/Taghanic unconformity and is considered to be complete in the Lansing core. The majority of the Moscow Formation (as well as the overlying, incomplete Tully Fm.) is assigned to the *ansatus* conodont Zone. Because it is not precisely known how much of the *ansatus* Zone is missing, however, biostratigraphic age constraints are rather poor. The lower part, the Portland Point sub-formation, is believed to be highly condensed (based on sequence stratigraphy, Brett et al., 2011) and is assigned to the upper part of *rhenanus-varcus* conodont Zone. CWT analysis of the γ -signal reveals multiple significant components (versus 90% CL) around 8 m and 2 m, which are tentatively assigned to long and short eccentricity cycles, respectively. This way, 5 long eccentricity cycles can be assigned to the Moscow Formation, with the last cycle assigned to the condensed Portland Point (Fig. 8). This is motivated by a potential decrease in sedimentation rate; on the CWT, it can be observed that the dominant 8-meter component shifts towards a period of 3 meter at approximately 122 meter depth.

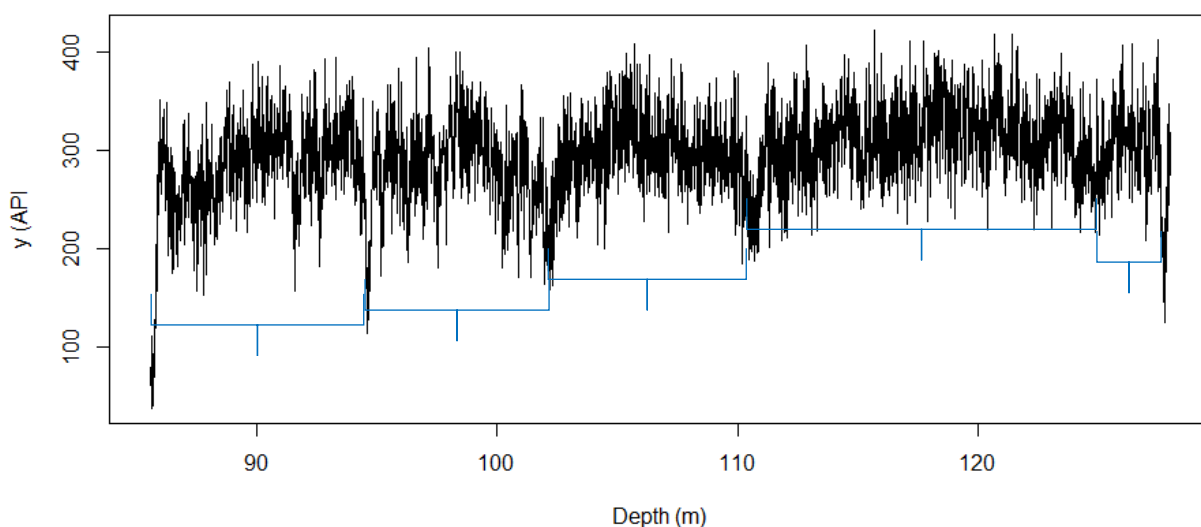


Fig. 8. Moscow Formation depth-domain cyclostratigraphic interpretation. Interpreted 405 kyr long eccentricity cycles marked by blue accolades.

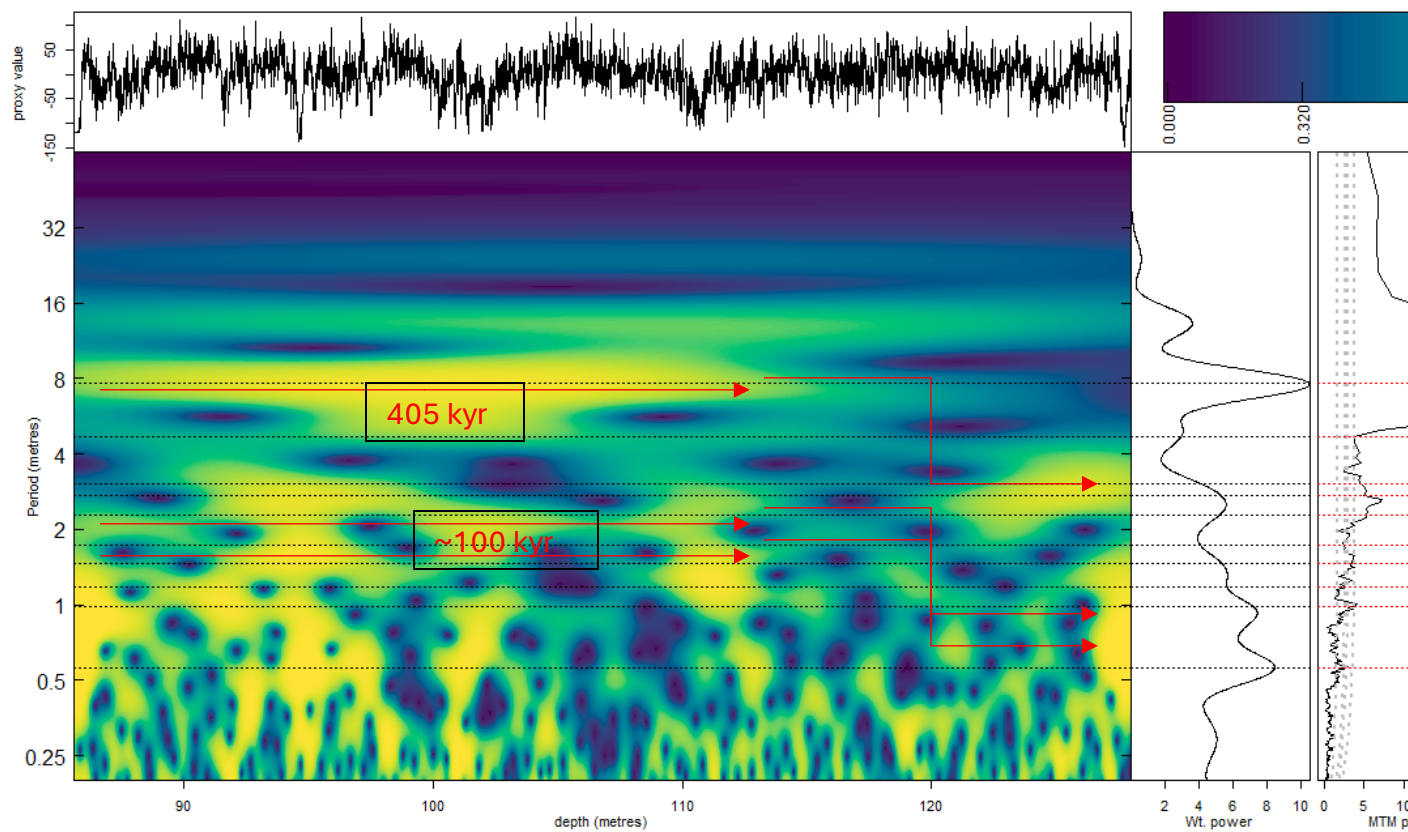


Fig. 9. Moscow Formation depth-domain γ CWT analysis. Dotted horizontal lines indicate significant components versus 90% CL. Red arrows indicate hypothesized shift in sedimentation rate near the Portland Point sub-formation. Interpreted ~100 kyr and 405 kyr eccentricity cycles marked in red.

Minimal tuning of the γ -signal was carried out based on the hypothesized 405 kyr long eccentricity cycle imprint. The obtained floating astrochronology encompasses 2238 kyr. Spectral analysis (MTM, Fig. 10; CWT, Fig. 12) reveals the presence of components corresponding to long and short eccentricity, obliquity and precession cycles. However, bandpass filtering of the long eccentricity cycles (Fig. 11) reveals inconsistent phase relationships between them, possibly indicating the current age model is to be refined or, alternatively, a shift in paleodepositional response.

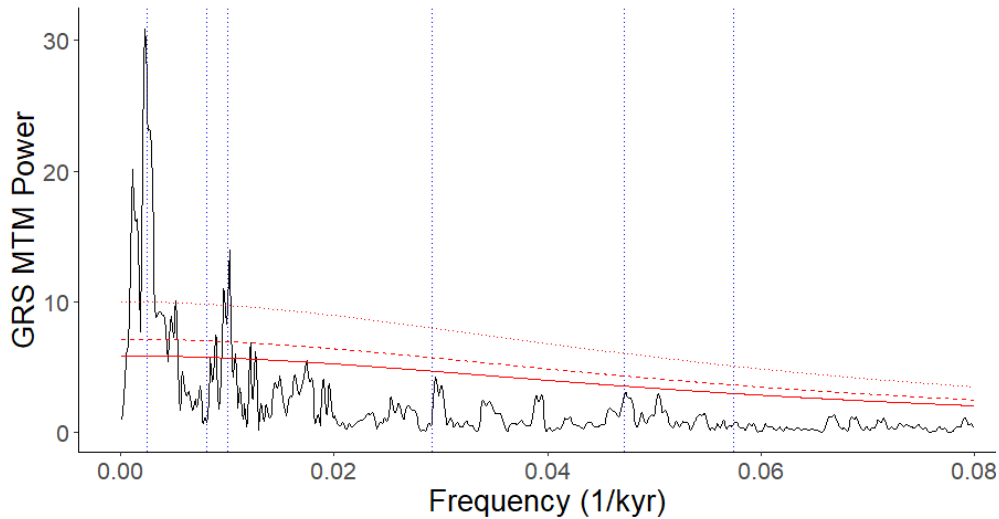


Fig. 10. MTM power spectrum of tuned γ -signal. 90%, 95% and 99% AR1 confidence levels (solid, striped and dotted red lines). 405 kyr, 125 kyr, 100 kyr, 34.3 kyr, 21.2 kyr and 17.4 kyr periods (blue dotted vertical lines).

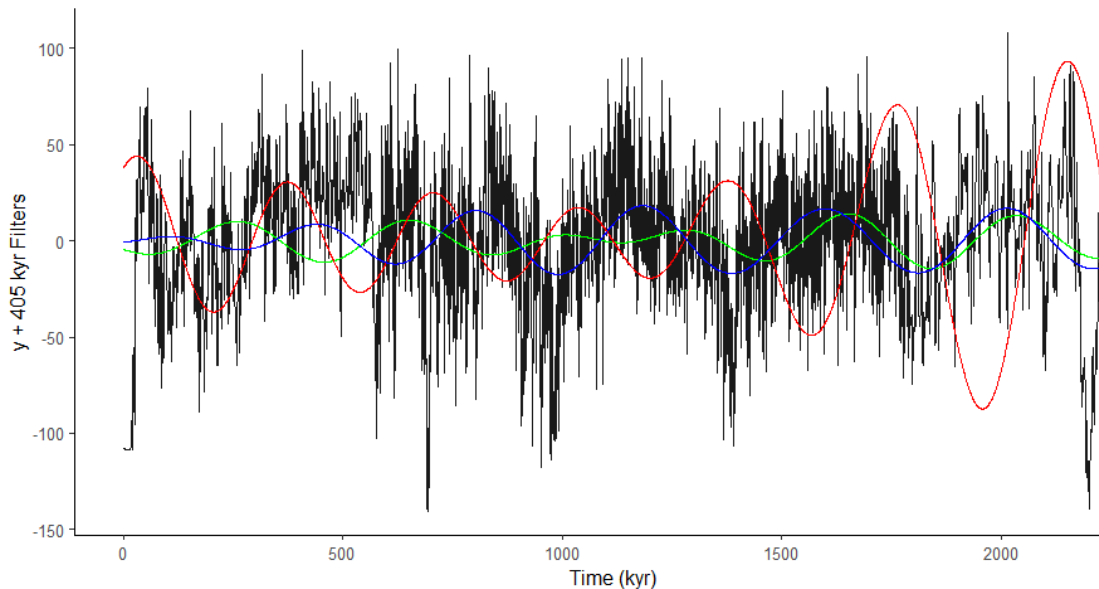


Fig. 11. Tuned γ -signal and bandpass filtered long eccentricity cycles. The long eccentricity cycle was filtered directly out of the γ -signal (blue), out of the envelope of the filtered short eccentricity (red), and out of the envelope of the filtered short eccentricity, extracted from the envelope of filtered precession (green).

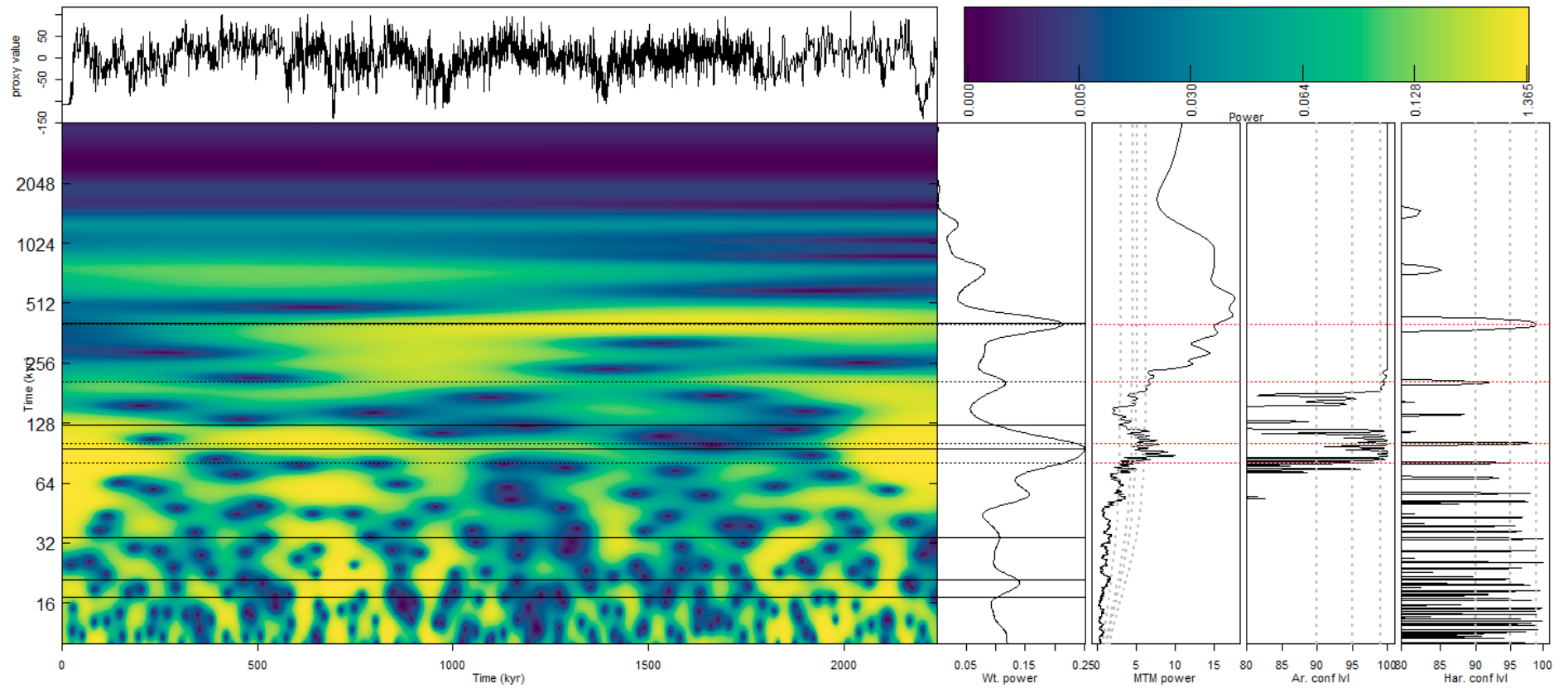


Fig. 12. Time domain γ CWT analysis. Dotted horizontal lines indicate significant components versus 90% CL. Full horizontal indicate periods corresponding to 405 kyr, 125 kyr, 95 kyr, 34.4 kyr, 21.2 and 17.4 kyr.

f. Cyclostratigraphy of the Tully Formation

The Tully limestone Formation of the Lansing core is incomplete, with a large unconformity believed to be present near the contact of the underlying Moscow Formation. Biostratigraphic constraints are similarly very limited; the uppermost Filmore Glen submember (77.7 m to 81.3 m) is assigned to the *semialternans* conodont Zone, which has a duration of appr. 600 kyr (Becker et al., 2020). Throughout the Filmore Glen, the γ -signal gradually decreases from 250 to 50 API. The remainder of the Tully Fm. is assigned to the *ansatus alveoliposticus* conodont sub-zone. No clear Milankovitch imprint can be recovered from the Tully Formation. This can likely be attributed to the magnitude of the GRS amplitudes, which are on the order of ~50 to ~100 API for the majority of the Tully Formation, which is comparable to the expected noise level. Thus, additional measurements such as pXRF should be carried out on the Tully Formation.

g. Cyclostratigraphy of the Genesee Formation

The black shales of the Genesee Formation represents the Genesee Event interval (*hermanni* conodont Zone; ~300 kyr; Becker et al., 2020). The γ -signal is characterized by bundled fluctuations: from 50 to 57 m and from 57 to 65 m, 6 to 8 groups of small-scale bundles can be observed per larger bundle, which are interpreted to reflect primarily eccentricity-modulated precession (Fig. 13). Outside this interval, visual identification of the Milankovitch imprint is less straightforward. An preliminary age model was constructed using eCOCO (Acycle; Li et al., 2019 – not illustrated here) that constrains the duration of the Genesee Formation to approximately 738 kyr, which contrasts with the estimated 300 kyr based on conodont biostratigraphy.

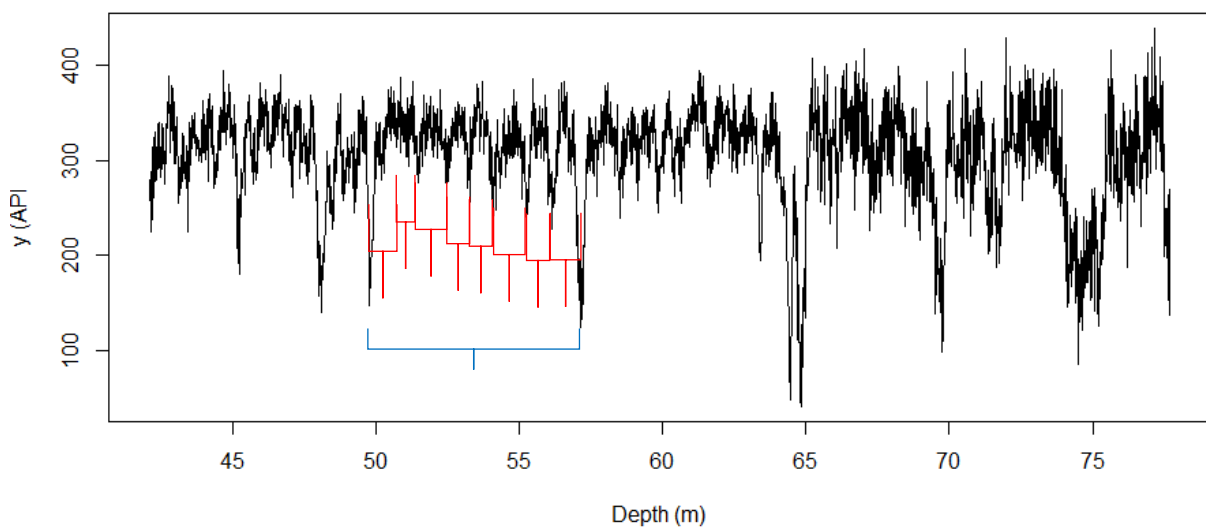


Fig. 13. Depth-domain cyclostratigraphic interpretation. Interpreted precession (red) and short eccentricity cycle (blue).

Subsequent time-domain cyclostratigraphy reveals components corresponding to precession, obliquity, and short eccentricity. In addition, bandpass filtering reveals amplitude modulation patterns of precession by short eccentricity cycles, which anti-phases the short eccentricity cycle extracted directly from the γ signal (Fig. 14). The CWT scalogram reveals significant (95% CL) components corresponding to precession and short eccentricity (Fig. 15). Increased power around the obliquity period can also be observed towards the upper and lower parts of the Geneseo Formation, albeit less significant.

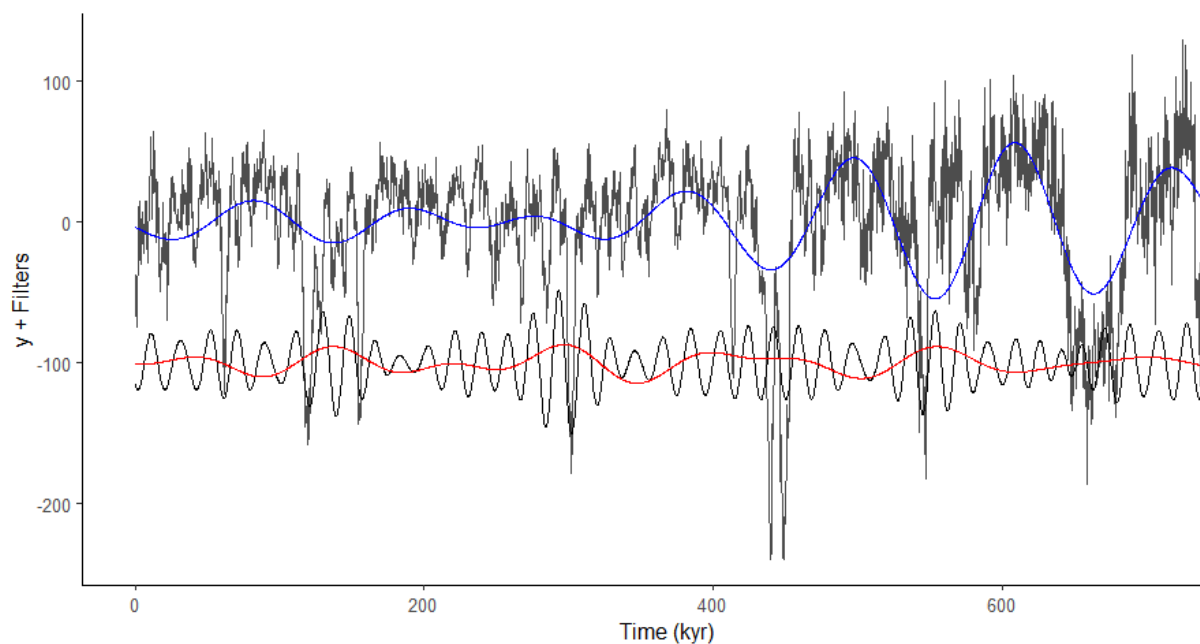


Fig. 15. Tuned γ -signal and bandpass filtered precession and short eccentricity cycles. Precession (black), short eccentricity extracted from the envelope of precession (red), and short eccentricity directly extracted from the γ -signal (blue).

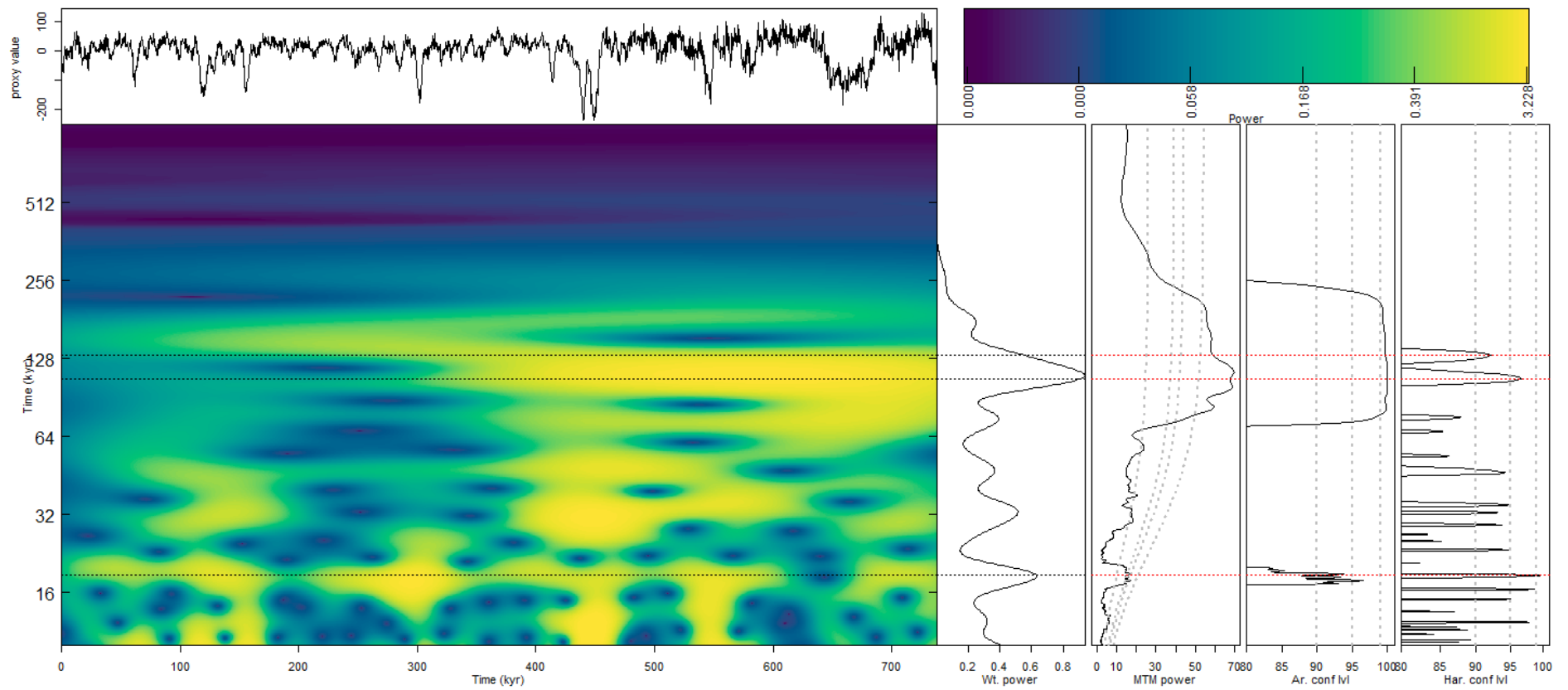


Fig. 16. Tuned γ CWT analysis. Dotted horizontal lines indicate significant components versus 90% CL.

Curriculum Vitae

Jarno J. C. Huygh

Institutional Address: Pétrologie sédimentaire B20, Allée du Six Août, 12, Quartier Agora, Université de Liège, 4000 Liège, Belgium

Institution Contact: Jarno.Huygh@uliege.be

Personal Contact: Jarno.Huygh@hotmail.com

Languages: Dutch (Native), English (Fluent), French (Proficient), German (Basic)

Education:

2022-2026: PhD Candidate, SediCClim Laboratory, Department of Geology, University of Liège, Belgium. PhD thesis title: “Milankovitch Forcing and the Timing and Pacing of Devonian Anoxic Events”. Promotor: Prof. Dr. Anne-Christine da Silva, co-promotor: Prof. Dr. Michel Crucifix.

2021: M.Sc. Chem., Department of Analytical, Environmental and Geo-Chemistry, Vrije Universiteit Brussel, Belgium (*summa cum laude*). Master thesis title: “A new independent age model for type-Maastrichtian chalk near Hallembaye (Gulpen Formation, Upper Cretaceous) using a cyclostratigraphic approach based on X-ray fluorescence data” (*summa cum laude*). Thesis supervisor: Prof. Dr. Philippe Claeys, co-supervisors: Prof. Dr. Johan Vellekoop, Dr. Pim Kaskes, Prof. Dr. Matthias Sinnesael.

2020: Bridging program M.Sc. Chem., Department of Analytical, Environmental and Geo-Chemistry, Vrije Universiteit Brussel, Belgium (*cum laude*). Bachelor thesis title: “Geochemical study on Maastrichtian chalk: Stable isotopes ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) and elemental analysis” (*magna cum laude*). Thesis supervisor: Prof. Dr. Philippe Claeys, co-supervisors: Prof. Dr. Johan Vellekoop, Dr. Pim Kaskes, Prof. Dr. Matthias Sinnesael.

2014: Teacher’s Degree, PCVO Het Perspectief Gent, Belgium (*cum laude*)

2012: Pr.B.Sc. Chem., KAHOSint-Lieven Gent, Belgium (*cum laude*). Internship at Procter & Gamble, Strombeek-Bever, Belgium.

Publications:

- Vellekoop, J., Kaskes, P., Sinnesael, M., Huygh, J., Déhais, T., Jagt, J. W. M., Speijer, R. P., Claey, P., 2022. A new age model and chemostratigraphic framework for the Maastrichtian type area (southeastern Netherlands, northeastern Belgium). *Newslett. Stratigr.*; 55, 4, 479-501. doi: 10.1127/nos/2022/0703.
- Huygh, J. J. C., Sinnesael, M., Kaskes, P., Vellekoop, J., Van der Geest, H., Jagt, J. W. M., Claey, P., 2025. Flint formation and astronomical pacing in the Maastrichtian chalk of northwestern Europe. *Palaeogeogr., Palaeoclimatol., Palaeoecol.*; 675, 113095. <https://doi.org/10.1016/j.palaeo.2025.113095>
- Gérard, J., Sablon, L., Huygh, J. J. C., Da Silva, A. -C., Pohl, A., Vêrard, C., Crucifix, M., 2025. Exploring the mechanisms of Devonian oceanic anoxia: impact of ocean dynamics, palaeogeography, and orbital forcing. *Clim. Past*; 21, 239-260. <https://doi.org/10.5194/cp-21-239-2025>
- Sablon, L., Maffre, P., Goddêris, Y., Valdes, P. J., Gérard, J., Huygh, J. J. C., Da Silva, A. -C., Crucifix, M., 2025. An emulator-based modelling framework for studying astronomical controls on ocean anoxia with an application on the Devonian. *Geosci. Model Dev.*; 18, 10095-10117. <https://doi.org/10.5194/gmd-18-10095-2025>
- Huygh, J. J. C., Algeo, T. J., Sageman, B. B., Arts, M., Ver Straeten, C. A., Over, D. J., Gérard, J., Sablon, L., Crucifix, M., Da Silva, A. -C., 2026. Astronomical control on marine anoxia during the Kellwasser Crisis and Rhinestreet Event (Appalachian Basin, New York, USA). *Glob. Planet. Change*; 257, 105216. <https://doi.org/10.1016/j.gloplacha.2025.105216>
- Gérard, J., Pohl, A., Sablon, L., Huygh, J. J. C., Da Silva, A. -C., Crucifix, M., 2026. Spatially contrasted response of Devonian anoxia to astronomical forcing. *Clim. Past*; 22, 5, 1003-1021. <https://doi.org/10.5194/cp-22-1003-2026>
- Pas, D., Sinnesael, M., Mghazli, K., Jamart, V., Geyer, G., Landing, E., Youbi, N., Ounar, J., Omar, H., Boumehdi, M. A., Arts, M., Huygh, J. J. C., Da Silva, A. -C., Daley, A. C., 2026. A new chronostratigraphic anchor for the early Cambrian: Integrating $\delta^{13}\text{C}$ chemostratigraphy and Bayesian astrochronology in West Gondwana (Anti-Atlas, Morocco). *Earth Sci. Rev.*, *accepted*
- El Hassani, A., Tabără, D., Slimani, H., Talih, A., Huygh, J. J. C., Da Silva, A. -C. Early Carboniferous palynofloral record from the Oued Bou Regreg Valley (NW Moroccan Meseta): New insights into biostratigraphy, palaeoenvironment, and palaeoclimate. *Rev. Palaeobot. Palynol.*; *in review*
- Huygh, J. J. C., Brett, C. E., Zambito, J. J. IV, Forsythe, I. J., Sablon, L., Gérard, J., Crucifix, M., Da Silva, A. -C. Milankovitch forcing and nonlinear climate variability during the Late Givetian (Appalachian Basin, New York, USA). *Clim. Past*; *in review*

Work Experience:

Sep, 2021 – May, 2022: Research Technician Liquid Chromatography and Internship Mentor, Analytical Science Department, ExxonMobil Chemical, European Technology Center, Machelen, Belgium. Key responsibilities and achievements: Liquid Chromatography – Photo Diode Array, measurements method development; internship mentor; design of experiment; solvent extractions; contribution to general good lab practices as well as site safety and operation integrity aspects.

2016 – Sep, 2019: Lab Technician Nuclear Magnetic Resonance Spectroscopy, Advanced Characterization Department, ExxonMobil Chemical, European Technology Center, Machelen, Belgium. Key responsibilities and achievements: Nuclear Magnetic Resonance spectroscopy; measurements, analysis and reporting; analytical characterization consultant; ad-hoc method developments; equipment maintenance and troubleshooting; inter -and intra-departmental cooperation and global support for troubleshooting and problem solving; emergency response team member; contribution to general good lab practices as well as site safety and operation integrity aspects.

May, 2014 – 2016: Junior Lab Technician, Heterogenous Catalysis Department, ExxonMobil Chemical, European Technology Center, Machelen, Belgium. Key responsibilities and achievements: Bench-scale pilot unit design assistance, operation, troubleshooting and improvements; Gas Chromatography measurements, analyses and reporting, method development and equipment maintenance; contribution to general good lab practices as well as site safety and operation integrity aspects.

Patents: Trujillo, R., Bodet, J. -F., Boutique, J. -P., Bianchetti, G. O., Maes, J., Huygh, J. J. C., 2014. Pouch comprising a liquid detergent composition (publication number 20140323383), The Procter & Gamble Company.