Seasonal variations recorded in cave monitoring results and a 10 year monthly resolved speleothem $\delta^{18}O$ and $\delta^{13}C$ record from the Han-sur-Lesse cave, Belgium

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Seasonal variations recorded in cave monitoring results

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Abstract

Speleothems provide paleoclimate information on multi-millennial to decadal scales in the Holocene. However seasonal or even monthly resolved records remain scarce. They require fast growing stalagmites and a good understanding of the proxy transfer function on very short time scales. The Proserpine stalagmite from the Han-sur-Less cave (Belgium) displays seasonal layers of 0.5 to 2 mm thickness that reconstruct paleoclimates at a monthly scale. Through a regular cave monitoring, we acquired a good understanding of how $\delta^{18}O$ and $\delta^{13}C$ signals in modern calcite reflect climate variations on sub-seasonal scale. Cave parameters vary seasonally in response to the activity of the vegetation cover and outside air temperature. From December to June, the cave remains in “winter-mode”. Outside temperatures are cold inducing low cave air and water temperatures. Bio-productivity in the soil is limited leading to low $pCO_2$, higher $\delta^{13}C$ composition of the CO$_2$ in the cave air and high discharge due to the inactivity of the plant coverage. From June to December, the cave switches to “summer-mode” and the measured factors display an opposite behavior. The $\delta^{18}O$ and $\delta^{13}C$ signals of fresh calcite precipitated on glass slabs vary seasonally. Lowest $\delta^{18}O$ values occur during the summer-mode when the $\delta^{13}C$ values are high. The $\delta^{18}O$ composition of the calcite is in equilibrium with the drip water $\delta^{18}O$ and display seasonal variations due to changes in the cave air and water temperature. In contrast to the $\delta^{18}O$ signal, $\delta^{13}C$ values of the calcite precipitated on the glass slabs do not reflect equilibrium conditions. Highest $\delta^{13}C$ values occur during summer, when discharge rates are low increasing the evaporation effect on the thin water film covering the stalagmite. This same antithetical behavior of the $\delta^{18}O$ vs. the $\delta^{13}C$ signals is seen in the monthly resolved speleothem record that covers the period between 1976 and 1985 AD. Dark layers are formed during summer, while light layers are formed during winter when calcite deposition occurs fast. The darker the color of a layer, the more compact its calcite structure, the more negative its $\delta^{18}O$ signal and the more positive its $\delta^{13}C$ signal.
1 Introduction

In the past 25 years, speleothem records have provided important information on past climate systems on multi-millennial to decadal scales (Genty et al., 2003; McDermott, 2005; Verheyden et al., 2008b; Wang et al., 2008; Van Rampelbergh et al., 2013). With the increasing number of studies on cave calcite deposition dynamics (Dreybrodt, 1999, 2008; Verheyden et al., 2008a; Lachniet, 2009; Scholz et al., 2009; Ruan and Hu, 2010; Oster et al., 2012) and with the help of modern analytical tools (Fairchild et al., 2006; Spotl and Mattey, 2006; Jochum et al., 2012), speleothems document climate at sub-seasonal and even monthly scales. However, this high resolution is reached in only a few studies due to several limitations (Treble et al., 2003; Mattey et al., 2008).

To study paleoclimate at sub-seasonal scale from stalagmites, their growth rate needs to be significantly high (around 1 mm yr\(^{-1}\)) to deposit thick layers allowing monthly resolved time-series. Speleothem-growth rates vary according to different factors such as drip water rate and calcium ion concentration (Baker et al., 1998; Dreybrodt, 1999) rendering the estimation of an average rate difficult. Generally, stalagmites increase at 10–100 µm yr\(^{-1}\) in cool temperate climates and at 300–500 µm yr\(^{-1}\) in subtropical climates (Fairchild et al., 2006), clearly showing that fast growing (more than 1 mm yr\(^{-1}\)) speleothems are truly exceptional.

A second limitation is that the transfer function of the measured proxies needs to be well understood for the studied cave and time frame. On classical multimillennial and centennial time scales, the transfer functions for the stable isotopes of oxygen and carbon are well established (Fairchild et al., 2006; Baker et al., 2007). However, local cave specific effects affect seasonally or even monthly resolved \(\delta^{18}O\) and \(\delta^{13}C\) signals. For studies at seasonal scales, a detailed study of the cave dynamics is required (Dreybrodt, 1999) in order to understand which factors drive the isotopic signals, and at which intensity. Different cave monitoring systems have been set up all over the world to better understand these seasonal and sub-seasonal processes (Genty and Deflandre, 1998; Mattey et al., 2008; Riechelmann et al., 2011). Only few of them,
provided answers on the isotope fractionation processes occurring between the drip water and recent precipitated calcite (Verheyden et al., 2008a; Tremaine et al., 2011; Riechelmann et al., 2013).

Previous studies of the Han-sur-Lesse karst system show that the cave responds seasonally to external climate factors and that it is well suited for high-resolution speleothem based climate reconstructions (Genty and Quinif, 1996; Verheyden et al., 2006, 2008a). In the Han-sur-Lesse cave, the high growth rate (up to 2.1 mm yr\(^{-1}\)) and clear seasonal banding of the “Proserpine” stalagmite make it possible to reconstruct climate variations at monthly scale (Verheyden et al., 2006). In this study, we report results of a every two-week cave environment monitoring carried out for one year (2013) that shows how oxygen and carbon isotopes signals obtained from the Proserpine banding reflect climate variations at sub-seasonal scale. The results are then compared to high-resolution \(\delta^{18}O\) and \(\delta^{13}C\) signals measured on the 10 thickest layers from the upper 10 cm of the Proserpine, which cover the period from 1976 to 1985 AD. This approach improves the knowledge and accuracy for the use of \(\delta^{18}O\) and \(\delta^{13}C\) signals in speleothems at seasonal scale.

## 2 Study area and hydrological setting

The Han-sur-Lesse cave is located within Givetian limestones of the Dinant syclinorium and is the largest and best-developed karst system in Belgium (Delvaux De Fenffe, 1985). The Lesse River carves the cave within a hill called the “Massif de Boine” entering the karst system at the “Gouffre de Belvaux” and exiting approximately 24 h later through the “Trou de Han” (Fig. 1). The cave is exploited since the mid 19th century as a touristic attraction and is characterized by large chambers and well developed speleothem formations. The cave monitoring and speleothem sampling for this study is carried out in the "Salle-Du-Dôme" chamber. This 150 m wide and 60 m high chamber formed by collapse and is the largest of the whole cave system. The Proserpine stalagmite is easily reachable following the tourist path into the cave for approximately
700 m from the cave’s exit at the “Trou de Han” (Fig. 1). It has a large tabular shape with a relatively horizontal slightly undulating surface of about 1.5 m\(^2\) and is fed by a continuous high drip water flow. The epikarst thickness above the stalagmite is estimated to be 40 m (Quinif, 1988). Based on a study comparing the isotopic signals of rainwater and drip water in the Pere Noel cave, formed in the same karst system as the Han-sur-Lesse cave, the residence time of the water in the epikarst is approximately 5 to 6 months (Verheyden et al., 2008a). After a heavy in rainfall, the drip rate above the stalagmite reacts within 24 h suggesting a piston flow system above the studied stalagmite. Two passages connect the “Salle-Du-Dôme” to the neighboring chambers and allow air circulation in the chamber. The Lesse River flows at the bottom of the chamber enhancing air circulation and causing the chamber to remain well ventilated throughout the year.

The mean annual precipitation at the nearest meteorological station of Han-sur-Lesse is 844 mmyr\(^{-1}\) and the mean annual air temperature 10.3°C (Royal Meteorological Institute Belgium). While the temperature displays a well-marked seasonality with cool summers and mild winters, the rainfall is spread all over the entire year. For the studied period lasting between November 2012 and January 2014, air temperature was at its lowest between December and March and highest between July and September. The coldest temperature of \(-4.2°C\) was reached on 15 March 2013. The plant coverage above the cave consists of C3-type vegetation with oaks, beech and hazel trees. The soil is approximately 40 cm thick and consists of silty stony soil with more than 50% limestone fragments (Belgian Geological Survey map). The area above the cave is part of a protected natural reserve, preserved from direct human influence for more than 50 years.

3 Methods

Between October 2012 and January 2014, the cave was visited every two weeks to record environmental parameters. Cave air and water temperature were measured with
a HANNA HI95501 thermometer with a precision of 0.2 °C. Air temperature was taken directly above the stalagmite. The drip water temperature and pH were determined in a small pool on the stalagmite’s surface. The pH of the drip water was measured with a HANNA HI991300 sensor (precision of 0.01 pH). The concentration of CO₂ in the cave air was obtained using an ACCURO 640000 manual Dräger pump with a standard deviation of 10 to 15 %. Three times per visit, pCO₂ values were measured and reported as an average of the three values. The drip water discharge (volumetric flow rate, here given in volume (mL) of water reaching the speleothem surface per minute) above the Proserpine stalagmite was measured in a graded cylinder after collecting the drip water during 10 min in an inflatable soft plastic swimming pool that was placed on the stalagmite’s surface and that covered a slightly larger area (1.77 m²). Drip water samples for δ¹⁸O and δD measurements were collected in fully filled glass bottles and stored in a cool and dark environment. Rainwater samples for δ¹⁸O and δD measurements were collected in a garden close to the cave using a thermos bottle and sampled every 15 days between November 2012 and January 2014. To avoid evaporation processes, the rainwater was collected using a funnel with a raised edge connected to a tube reaching the bottom of the thermos bottle. The funnel was attached to the bottle trough a hermetic cap. Glass bottles were fully filled with the collected rainwater and stored in a dark fridge until being analyzed.

The δ¹⁸O and δD composition of the waters were measured using a PICARRO L2130-c Cavity Ring down Spectrometer at the Vrije Universiteit Brussel (VUB). For every sample, 1.4 mL of water was used for the measurements. Every sample was injected and analyzed 10 consecutive times. The measured values were then corrected using a three point correction method with three home made standards with isotopic composition ranging between 6.8 ‰ and −22.3 ‰ for δ¹⁸O and 32.5 ‰ and −127.3 ‰ for δD. All water samples were analyzed two times in different order. The reported values are the average of the two measurement rounds. Analytical uncertainties (2σ) equal 0.07 ‰ for the δ¹⁸O values and 0.5 ‰ for the δD values.
The isotopic composition of the cave air CO$_2$ was measured from samples collected by filling vacuum 2 L glass containers. To avoid “human” contamination, these samples were taken at the beginning of every cave visit. The CO$_2$ was extracted from the container using a manual extraction line at the VUB. The extracted CO$_2$ was then analyzed for its isotopic composition on a Thermo Delta plus XL mass spectrometer in dual inlet mode. To test the reproducibility of the method, samples for the analyses of the $\delta^{13}$C composition of the dissolved inorganic carbon (DIC) in the water were collected following two different methods. The first method consisted of sampling the drip water by filling 12 mL gastight glass tubes all the way to the top to avoid air CO$_2$ contamination. A drop of HgCl$_2$ was immediately added and the bottle hermetically closed and stored in a dark and cool environment until being analyzed. The day before the analysis, a headspace was created in the bottle by taking out 3 mL of water, while bubbling He trough the septum. Once the headspace was formed, H$_3$PO$_4$ was added and the sample shaken overnight to convert all DIC species into CO$_2$. The CO$_2$ gas was then extracted from the bottle and measured for its $\delta^{13}$C composition. Samples were duplicated and measured immediately after sampling and 1 month later to test if evaporation processes affect the DIC composition.

The second method is based on that described by Mattey et al. (2008). Gastight 12 mL glass vials were first flushed with He in the lab. In the cave, 1 mL of drip water was injected in these vials trough the septum. Back in the lab, samples were acidified with H$_3$PO$_4$ and equilibrated for at least 2 h before being analyzed. Using this method, samples must be analyzed within 2 days to avoid possible evaporation of the CO$_2$ trough the pierced septum. For both sampling methods, the $\delta^{13}$C composition of the DIC was measured on a Flash EA 1112 device connected to a Delta V plus mass spectrometer, with an analytical uncertainty of 0.4 ‰ (2σ).

Every visits, 3 glass slabs were placed on the surface of the stalagmite to test current calcite deposition conditions within the cave. The slabs were collected during the next visit. The freshly precipitated calcite was then scraped off the glass and 5 samples per
slab were measured for their $\delta^{18}$O and $\delta^{13}$C composition. The reported value per cave visit is the average of the results of the three slabs collected during each visit.

In January 2011, the Proserpine was sampled by drilling a 1 m long core in the middle of the large stalagmite. A slab was cut from the middle of the core and polished with Al$_2$O$_3$ powder. Layer counting established the age model of the upper 16 mm of the core knowing that one dark and one light layer are deposited every year (Verheyden et al., 2006). Samples to test the evolution of the isotopic composition of the individual layers were milled in 9 consecutive layer couplets where the dark and white layers were the largest. Samples were drilled every 40 µm over a length of 4 mm with a Merchantic MicroMill giving a temporal resolution of approximately 1 sample a month. The glass slab and speleothem calcite powders were measured for their $\delta^{18}$O and $\delta^{13}$C composition using a Kiel-III-device coupled on a Thermo Delta plus XL. Analytical uncertainties ($2\sigma$) were $\leq 0.12$ ‰ for $\delta^{13}$C and $\leq 0.16$ ‰ for $\delta^{18}$O.

### 4 Results

Figure 2 presents the results of the cave monitoring campaign from November 2012 to January 2014 (15 months) together with precipitation amounts and air temperatures at the RMI station of Han-sur-Lesse (Fig. 2a and b respectively) for the same period. The cave air temperature (Fig. 2c) in the Salle-Du-Dôme varies seasonally over a range of ca. 4 °C with highest values reaching up to 14 °C during the summer months of June, July and August (JJA). After a slow decrease through autumn the cave air temperature remains relatively constant around 11 °C, which is slightly higher than the yearly outside air temperature average of 10.3 °C (Fig. 2b). Drip water temperatures (Fig. 2d) follow a similar trend as the cave air temperature (Fig. 2c) but are on average 0.5 °C colder. The water flow above the Proserpine stalagmite (Fig. 2e) is continuous and averages 161 mL min$^{-1}$. It sharply increases during early winter (December) to an average value above 200 mL min$^{-1}$) to remain high throughout winter and spring until early summer (June), when it decreases again to around 100 mL min$^{-1}$. Just be-
before this “early summer” decrease, the discharge record shows a short maximum to 280 mL min$^{-1}$. In early June, most probably related to the heavy rainfall period at the end of May 2013 (Fig. 2a). An increase in drip water flow above the Proserpine is observed within 24 h following a heavy rainfall event. The drip water pH (Fig. 2f) varies between 8.4 and 7.9, decreasing in spring (sharply in May) and gradually increasing back at the end of summer and throughout autumn (from September through January). The heavy rainfall period at the end of May 2013 (Fig. 2a) seems to correspond with a pH decrease below 8.0. The $p$CO$_2$ values (Fig. 2g) remain relatively stable around 500 ppm throughout much of the year except for a marked increase in the summer, reaching 1000 ppm in July and August. The $\delta^{13}$C signature (Fig. 2h) of the cave air varies around an average of $-19.5\%$ displaying an opposite trend to that of the $p$CO$_2$ concentrations. During the high discharge event at the end of May, the $\delta^{13}$C values of cave air fall to $-20.7\%$, and remain around $-20.0\%$ or below during summer (JJA). The $\delta^{13}$C composition of the DIC (Fig. 2i) stay constant throughout the year at an average of $-11.8\pm0.3\%$. The $\delta^{13}$C compositions of the DIC measured using the new sampling method and preparation developed in this study (Table 1a) are the same as those obtained using the approach established by Mattey et al. (2008) (Table 1b). No meaningful differences were found between both methods as can be seen in Table 1b.

Rainwater $\delta^{18}$O values (Fig. 3c) average $-8.18\pm0.07\%$ and the $\deltaD$ values (Fig. 3d) $-55.52\pm0.5\%$. Both the $\delta^{18}$O and $\deltaD$ signals increase by 3% and 30% respectively during the summer months, presumably due to temperature effect. Both $\delta$ values also display 6 small drops (blue clouds and numbered 1 trough 6 in Fig. 3c and d) of approximately 2% for the $\delta^{18}$O and 20% for the $\deltaD$. They occur in November 2012, December 2012, May 2013, July 2013, December 2013 and January 2014. They appear to correspond to periods of higher rainfall recorded in the site (Fig. 3b). One larger drop (red arrow in Fig. 3c and d) of 9% for the $\delta^{18}$O and of 90% for the $\deltaD$ signal occurs at the beginning of March and seems to correlate with unusually cold air temperatures of $-6.3\,^\circ$C (Fig. 3a), measured at the RMI station of Han-sur-Lesse.
The drip water $\delta^{18}O$ and $\delta D$ values (Fig. 3e and f) weakly vary around an average of $-7.65 \pm 0.07 \%$ and $-50.1 \pm 0.5 \%$, respectively. These values appear slightly higher compared to the yearly average $\delta^{18}O$ and $\delta D$ values of the rainwater. The drip water isotopic records of oxygen and hydrogen are well correlated and remain stable throughout the year with the exception of one small but meaningful negative excursion in July and August of 0.06\% for $\delta^{18}O$ and of 0.5\% for $\delta D$ (red arrow in Fig. 3e and f). The range of these shifts is of the order of the analytical uncertainties (0.07\% for $\delta^{18}O$ and 0.5\% for $\delta D$), but they are recorded by at least four consecutive measurements, suggesting that they are significant.

The $\delta^{18}O$ signal of the calcite recovered from glass slabs placed on top of the stalagmite (Fig. 2l) remains stable at $-6.5 \pm 0.16 \%$ most of the year, but decreases to more negative values of $-7.1 \pm 0.16 \%$ during summer (JJA) (red arrow in Fig. 2l). The slabs’ calcite $\delta^{13}C$ signal (Fig. 2m) remains relatively constant except for a bulge from August through January, with a maximal $\delta^{13}C$ values of $-8.8 \pm 0.12 \%$ at the end of October (blue arrow in Fig. 2m). The two isotopic signatures are decoupled suggesting that different forcing factors affect these signals.

The individual layers of the Proserpine stalagmite also display contrasting behavior of the oxygen and carbon isotopic signals. The $\delta^{18}O$ composition oscillates around an average $-6.5 \pm 0.16 \%$ over a range of 0.9\%. The $\delta^{13}C$ varies around an average $-8.4 \pm 0.12 \%$ and over a range of 2.4\%. Both oxygen and carbon isotopic signals measured in the stalagmite correspond to the values measured on the glass slabs. At the end of a dark layer (dotted lines in Fig. 5) $\delta^{18}O$ values reach their minimum while the $\delta^{13}C$ values reach their maximum, illustrating the opposite trend between the $\delta^{18}O$ and $\delta^{13}C$ values at seasonal level.
5 Discussion

5.1 Forcing of the rain and drip water variations

Rainwater $\delta^{18}$O values at a specific location vary due to temperature changes, variation in the amount of rainfall, fluctuations in the source of the rainwater or cloud track (Rozanski et al., 1992). The rainwater $\delta^{18}$O signal increases by a few per mille during the summer months, when air temperature is high (Fig. 3a and c). Six small drops are recorded in November 2012, December 2012, May 2013, July 2013, December 2013 and January 2014 and are numbered 1 through 6 in Fig. 3. These drops not correspond with air temperature decreases measured in the Han-sur-Lesse weather station. They however, systematically occur after a period marked by heavy rainfall (blue clouds in Fig. 3b). Therefore, the amount effect likely causes the smaller negative excursions in $\delta^{18}$O values recorded in the rainwater. Negative $\delta^{18}$O excursions appearing shortly after an increase in precipitation amount may be due to the bi-monthly collection of rainwater, which may explain a time lag of up to 15 days. A single larger drop in drip water $\delta^{18}$O occurs in March 2013 and is indicated by a red arrow in Fig. 3. This large drop does not correspond with a temperature drop or an increase in rainfall. A modification in rainwater source could be a plausible explanation, but is not supported by changes in wind direction during that month based on RMI data. However, in March 2013, an unusually late snow layer covered the area for several weeks (RMI data). The observed decrease in $\delta^{18}$O is then most probably related to the low $\delta^{18}$O signal of the incorporate snow in the sampling bottle.

The $\delta^{18}$O and $\delta$D compositions of the drip water display almost no variations throughout the year indicating that the epikarst-storage reservoir is relatively large and that the water residence time is sufficiently long to homogenize the isotopic composition of the drip water (Fig. 2j). In July and August, a small negative excursion in the drip water $\delta^{18}$O of hardly 0.1 ‰ occurs. Although it is only of the size of the analytical uncertainty, we consider it meaningful because it is supported by two consecutives points as well as by trends of several points before and after. Since, meteoric water is by far the
major source of vadose/epikarst water and consequently of the drip water, the small negative $\delta^{18}O$ excursion in the drip water record is the subdued result of the $\delta^{18}O$ drop of several $\%$ found in the meteoric water, as a result of snowfall in March 2013. The intense mixing of the percolating vadose water in the epikarst, deduced from the generally constant $\delta^{18}O$ in drip water record, would then reduce a $\delta^{18}O$ shift of about 8 $\%$ in the meteoric to a hardly detectable one of about 0.1 $\%$ in the drip water. This would also mean that the average residence time of the water in the epikarst must be estimated around five to six months (from March till August–September). Such a residence time is similar to that observed in the nearby Pere Noel cave, which formed in the same karst system as the Han-sur-Lesse cave, and where summer rainwaters only reach the cave in winter (Verheyden et al., 2008a). With an increase in drip rate within 24 h following a heavy rainfall event and a residence time of the water in the epikarst of 5 to 6 months, the epikarst hydrological system appears to act like a piston flow system with a delay of the order of half a year, long enough for the epikarst water to be well mixed before entering the cave.

5.2 Cave dynamics seasonal variations

Based on our observations, the temperatures of cave air, of drip water, and of outside air all follow the same seasonal evolution. However, the temperature range, which is around 20°C outside the cave, is reduced to about 3°C inside the cave with the drip water being about 1°C colder than the cave air, an observation that is made in many caves (McDermott, 2004; Fairchild et al., 2006).

The Lesse River, which flows through the chamber, most probably causes the cave air to mix with that from neighboring chambers, including those openly connected to the outside. Compared to other Belgian caves where values up to 15 000 vppm are measured for cave air $CO_2$ (Verheyden, 2001), the $CO_2$ content in the Salle-du-Dôme chamber is very low, indicating that exchanges between cave air and external air must be relatively important. In the Salle-du-Dôme, $CO_2$ values fall close to outside air $pCO_2$, and values of 400 vppm are measured during much of the year (Fig. 2g). Only during
summer, higher $p\text{CO}_2$ values, up to 1000 vppm are measured in the chamber. During spring and summer, soil $p\text{CO}_2$ increases due to stronger bio-production and bacterial activity. A more negative $\delta^{13}\text{C}$ signature of the CO$_2$ air is measured in the Salle-du-Dôme, suggesting enhanced input of soil CO$_2$ into the cave atmosphere. The $\delta^{13}\text{C}$ values of the cave air $p\text{CO}_2$ fall to $-21.9\%$ in summer (Fig. 2 h), indicating the higher contribution of C3-plant derived CO$_2$ to the cave atmosphere.

Seasonal variations are also seen in the flow rates above the stalagmite, with less water dripping on the stalagmite during spring and summer (Fig. 2e). This seasonal variation in discharge is mostly related to seasonal variations in evapo-transpiration ie. evaporation from the surface combined with transpiration from the plant coverage. This lowers the quantity of water feeding the epikarst during summer reducing the amount of water that can reach the cave. In winter, the situation reverses: the activity of the vegetation cover diminishes, air temperatures lowers, reducing evaporation, all of which allows more water to enter the soil, and the epikarst. The pressure on the piston flow system is raised and more water is pushed into the cave increasing the discharge above the stalagmite.

The seasonally varying recharge of the epikarst is also visible in the evolution of the drip water pH. Since recharge is lower in summer, the weaker pressure on the piston flow will cause the water to stay for a longer time in the epikarst. Moreover, in summer the soil $p\text{CO}_2$ concentration is also higher due to the bio-production and bacterial activity, further lowering the pH of the water. As a result, water in the epikarst is more acidic in summer and also has more time to dissolve the carbonate bedrock, resulting in a pH increase of the drip water. Consequently, although a high yearly mixing of the water in the epikarst, results show that summer water is preferentially reaching the cave in winter (because of the half a year delay due to the average residence time in the epikarst). Winter drip water has consequently a higher pH value and contains more dissolved ions. This seasonal difference in ion concentration also affects the calcite precipitation rate, which accelerates during winter when the ion rich summer water reaches the stalagmite. On top of this general seasonal variation, on shorter time scales, heavy
rainfalls also affect the pH values of the drip water. In a piston-flow system, when high amounts of fresh water, – such as during a rainstorm –, are added to an epikarst that functions as a piston system, the total Ca\(^{2+}\)-ion concentration of the water diminishes and the water becomes more acid. This effect is illustrated during the very wet event of 30 May 2013 (“May wet event” in black box in the precipitation curve in Fig. 2a), where the discharge peaks to high values and where the pH (Fig. 2f) drops from 8.2 to 7.9 in one month (3 successive points), after a 2 month period of increase, during a much drier period.

To summarize: the cave system is subdivided into a “winter-mode” lasting from December to June and a “summer-mode” from June to December (Fig. 2). During the winter mode, cave air and drip water temperature are low. The plant coverage above the cave is inactive leading to a higher water discharge, low \(pCO_2\) and high \(\delta^{13}C\) values of the cave air CO\(_2\). Drip water pH is more basic due to the longer residence time of the summer rainwater in the epikarst. During the “summer-mode”, cave air and drip water temperatures increase. The plant coverage reactivates leading to lower discharge, higher \(pCO_2\) and lower \(\delta^{13}C\) values of the cave air CO\(_2\). The drip water pH is more acid due to its shorter residence time in the epikarst.

5.3 \(\delta^{18}O\) composition of the precipitated calcite reflects temperature variations

The \(\delta^{18}O\) composition of calcite deposited on the glass slabs varies seasonally with more negative values during summer (Fig. 2l). If the calcite is deposited in isotopic equilibrium with its drip water, these variations can be caused by changes in the \(\delta^{18}O\) composition of the drip water and/or by changes in temperature that affect the fractionation factor between the drip water and the precipitating calcite (Lachniet, 2009). If not deposited in equilibrium, the seasonal \(\delta^{18}O\) variations on the glass slabs are due to kinetic effects that require further investigation.

A first step in understanding the \(\delta^{18}O\) transfer-function of the Salle-du-Dôme demands to determine whether the calcite is deposited in equilibrium or not. In speleothems, this is traditionally done by applying the Hendy-test (Hendy, 1971) that
compares the $\delta^{18}$O and $\delta^{13}$C values in the center of the stalagmite with those on the sides within a single growth layer. However, since we work on a drill core taken “in the middle” of a 1 to 2 m wide speleothem, the Hendy-test cannot be applied. As an alternative, we calculated equilibrium conditions of the deposited calcite using the calcite-water fractionation factor. Different authors have proposed fractionation factors based on three approaches.

The first approach, using in-lab experiments, has been tested in different studies each giving another value for the water-calcite fractionation factor. The most used in-lab established fractionation factors remain the ones by O’Neil et al. (1969) later modified by Friedman and O’Neil (1977), the relationship of Kim and O’Neil (1997) later modified by Kim et al. (2007), the results of Tarutani et al. (1969) and Jimenez-Lopez et al. (2001) (Table 2). A second category of fractionation factors is established by using theoretical models as the ones from Horita and Clayton (2007) and Chacko and Deines (2008). A third approach consists of using cave-monitoring data to make an average of the in-cave observed fractionation factors. Tremaine et al. (2011) established such a “cave calcite” relationship by doing a best fit through the data on a large number of modern caves at different latitudes, altitudes and temperatures.

Applying the different fractionation factors to our data shows that the measured $\delta^{18}$O signals in the glass slabs calcite correspond within 1 ‰ with the calculated values suggesting that it is deposited close to equilibrium with the drip water (Table 3). However, variations occur between the results derived from different methods. Of the in-lab established relationships, that of O’Neil et al. (1969) modified by Friedmann and O’Neil (1977), corresponds best to our observations. This is also confirmed in other studies where this experimental fractionation factor is considered to give the best approximation for in-cave observations (McDermott et al., 2005; Riechelmann et al., 2013). The theoretical values (Horita and Clayton, 2007; Chacko and Deines, 2008) suggest a more negative $\delta^{18}$O composition for the deposited calcites. This also confirms other studies where theoretical results seem to overestimate the fractionation factor (Tremaine et al., 2011). The optimal results are given by the Tremaine et al. (2011)
fractionation factor, which is not surprising since the latter is based on experimental studies on calcite formed in caves.

The matching results indicate that the deposition of calcite occurs in oxygen isotopic equilibrium in the Salle-du-Dôme. Seasonal variations of δ¹⁸O observed in calcite are likely caused by variations in the drip water δ¹⁸O composition and/or in the temperature dependent fractionation factor (Fairchild et al., 2006). However, the δ¹⁸O composition of the drip water, within analytical uncertainty, remains constant throughout the year. Consequently, variations in the fractionation factor due to temperature changes in the cave air likely explain the seasonal pattern seen in the δ¹⁸O composition of the glass slab. If the most commonly accepted temperature dependence of the water-calcite fractionation factor for the oxygen isotopes of 0.247 ‰/1°C (O’Neil et al., 1969) is used, our measured net difference in fresh calcite δ¹⁸O composition (i.e. δ¹⁸O range of the fresh calcite minus the δ¹⁸O range of the drip water) of 0.58 ‰ would result from a 2.3°C variation in the drip water temperature. This temperature corresponds well with the 2 to 2.5°C temperature range measured in the drip waters. This correspondence constitutes a strong confirmation of both the isotopic equilibrium and the temperature dependence of the calcite δ¹⁸O.

To summarize, the δ¹⁸O composition of the fresh calcite (Fig. 2l) is deposited in equilibrium with its drip water. Seasonal variations in δ¹⁸O composition of the glass slabs are caused by the seasonal temperature variation of the cave air and drip water (Fig. 2c and d). A temperature increase of 1°C corresponds with a decrease of 0.20 ‰ in isotopic composition of the deposited calcite. The warmer the cave air, the more negative the δ¹⁸O composition of the formed calcite. No disequilibrium processes, are active, as they would shift the isotopic composition to heavier values with increasing temperature.

5.4 Discharge drives the δ¹³C calcite composition

The δ¹³C composition of the deposited glass slab calcite varies around −10‰ reflecting the C3 type vegetation growing above the cave (Fig. 2m). No correlation can be
established between the $\delta^{18}$O (Fig. 2l) and $\delta^{13}$C (Fig. 2m) values of the glass slab calcite ($R^2 = 0.008$, on a 99% confidence level) indicating that both proxies evolve independently under the influence of different factors. The $\delta^{13}$C composition of calcite deposited in equilibrium with its drip water depends on (i) the $\delta^{13}$C composition of the Dissolved Inorganic Carbon (DIC) in the drip water and (ii) the fractionation factor between the DIC and the deposited calcite.

The average $\delta^{13}$C composition of the DIC in the Han-sur-Lesse drip water (Fig. 2i) equals $-11.8\pm0.9$‰ and does not show seasonal variations, presumably because the water residence time in the epikarst is long enough for the DIC to mix well enough to homogenize the $\delta^{13}$C signal. The seasonal variation seen in the $\delta^{13}$C composition of the glass slabs (Fig. 2m) is not related to changes in the DIC isotopic composition. The fractionation factor between the DIC and the deposited calcite is estimated to be 1.001 for temperatures between 10 and 40°C (Romanek et al., 1992). Mook (2000) suggests a temperature dependence for this fractionation factor of $\varepsilon = (-4232/T) + 15.1$ (with $T$ in K). With an average water temperature of 11.4°C, the equation of Mook (2000) leads to a very limited effect of $\varepsilon = 0.2$‰ due to fractionation. The measured differences of the $\delta^{13}$C values between the DIC and the calcite average 2.0 ± 0.9‰, which is much higher than the temperature effect of the fractionation factors mentioned above. This implies that the carbon isotopes are deposited out of isotopic equilibrium with the DIC in the drip water. However, the carbon isotopes vary seasonally suggesting that the equilibrium conditions change on a seasonal base. During the cave “winter-mode” (December to June), the $\delta^{13}$C values of the calcite is only 1.4 ± 0.5‰ higher compared to the $\delta^{13}$C DIC values, suggesting deposition closer to equilibrium during winter than during the cave “summer-mode” when the differences reach 3.2 ± 0.5‰.

Different factors can induce this out of equilibrium deposition of the calcite. A first possible factor leading to higher $\delta^{13}$C of the deposited calcite in summer can be variations in the $p$CO$_2$ of the cave air (Mühlinghaus et al., 2007, 2009; Scholz et al., 2009). A large difference between the cave air $p$CO$_2$ and the drip water $p$CO$_2$ causes the fast degassing of the drip water and consequently an enrichment in the $\delta^{13}$C value of the
formed calcite. Monitoring of a Gibraltar cave clearly showed this effect on the \( \delta^{13}C \) composition of the calcite (Mattey et al., 2008). Also in the Grotta di Ernesto (Italy, Frisia et al., 2011), the \( \delta^{13}C \) variations are linked to \( pCO_2 \) variations. The Salle-du-Dôme chamber displays small seasonality in its \( pCO_2 \) concentration with a variation range of only 500 ppm between the low winter and the high summer values. This range is too small to have a significant effect on the calcite deposition kinetics and consequently is unlikely to cause variations in the \( \delta^{13}C \) composition of the calcite. Cave monitoring confirms this observation by showing no link between the cave air \( pCO_2 \) and calcite \( \delta^{13}C \) composition (Fig. 2g and m). Furthermore, for stalagmites growing under continuous drip flows, which is the case of the Proserpine stalagmite, the effect of the \( pCO_2 \) is negligible (Mühlinghaus et al., 2009).

A second factor causing higher \( \delta^{13}C \) values in the calcite can be variations in the air temperature (Mühlinghaus et al., 2007, 2009; Scholz et al., 2009). As for the \( pCO_2 \), the temperature variations (\( \sim 3^\circ C \)) in the Salle-Du-Dôme are too small to significantly influence the carbon fractionation factor. The temperature dependence of the carbon fractionation factor between the DIC and the forming calcite is indeed very small (see above).

A third factor influencing the \( \delta^{13}C \) composition of the calcite may be the drip interval (Mühlinghaus et al., 2007, 2009). With a slow drip rate (and long intervals between drips), the residence time of the water film on the stalagmite’s surface is longer and \( CO_2 \)–degassing is more important. The DIC in the water film gets enriched in in \( ^{13}C \), leading to more positive \( \delta^{13}C \) values in the formed calcite.

For the Proserpine stalagmite, we consider that the drip rate determines the variations in \( \delta^{13}C \) in the deposited calcite. The drip water flow on the Proserpine stalagmite is continuous and relatively important, but higher in winter than in summer (Fig. 2e). In winter, with a higher discharge, kinetic evaporation of \( CO_2 \) from the water film on the stalagmite top is lower. Calcite deposition and C fractionation take place relatively close to equilibrium. In summer, with higher temperatures, lower discharge, dryer cave air, a thinner water film, all resulting effects are reversed from the winter situation, and
the calcite is formed further out of equilibrium, leading to less negative $\delta^{13}$C values. The inverse relationship between drip flow and $\delta^{13}$C values of the glass slab calcite is clearly demonstrated in the cave monitoring results (Fig. 2e and m). The established relationship between the drip rate and the $\delta^{13}$C values of the calcite has also been showed in other cave monitoring programs (Riechelmann et al., 2011) in laboratory experiments (Polag et al., 2010) and using numerical models (Mühlinghaus et al., 2007, 2009; Scholz et al., 2009; Deininger et al., 2012). We find an additional illustration for this relation in the short excursion (1 single point in early May) to less negative $\delta^{13}$C values of the cave air (arrow in Fig. 2 h), which falls at the beginning of the “May wet event” and during the sharp decrease of pH-values in the drip water. It is however not visible in the $\delta^{13}$C record of the DIC (Fig. 2i), which is at its lowest value then.

The C isotopic composition of the calcite formed on top of the Proserpine stalagmite is thus deposited out of equilibrium and affected by kinetic effects. Heavier values occur during the cave “summer mode” when the drip rate decreases and more water evaporate from the water film covering the stalagmite, and while also more CO$_2$ escapes from it into gas phase.

5.5 Variations in the $\delta^{18}$O and $\delta^{13}$C of the stalagmite reflect seasonal variations

The Proserpine stalagmite displays clear lamination formed by alternating dark, compact layers with elongated crystals and white more porous layers with small crystals (Fig. 4). The seasonal character of the layering in the Proserpine stalagmite, with one dark and one white layer deposited every year, was already demonstrated by Verheyden et al. (2006). However, these authors were not able to determine the correspondence between layer type and season. In our studied core, 10 additional layer couplets (= dark + white layer) can be counted, compared to the Proserpine core of Verheyden et al. (2006) drilled in 2001. The 10 additional layer couplets, counted over a period of 10 years, confirm that one layer couplet is deposited every year. Layer couplets establish the age model of the laminated part of the stalagmite. Twenty-six layer couplets
are counted from the top of the stalagmite to the start of the isotope sampling indicating that the youngest analyzed layer formed in 1985 AD. The isotopic measurements were conducted on 9 consecutive layer couplets and consequently run from 1985 to 1976 AD.

A first conclusion from the isotopic analyses of the individual layers is that the $\delta^{13}C$ and $\delta^{18}O$ signals display opposite behavior within one layer (Fig. 5). When the $\delta^{13}C$ signal reaches its maximum value at the end of a dark layer, the $\delta^{18}O$ value arrives at its minimum value. This antithetical behavior is also seen in the cave monitoring results where more positive $\delta^{13}C$ and more negative $\delta^{18}O$ signals form during summer when drip rates are lower and drip water temperatures are higher. Consequently, dark layers displaying more positive $\delta^{13}C$ and more negative $\delta^{18}O$ signals form in summer. The crystal structure of dark layers is compact and formed by elongated crystals while the white layers consist of more porous calcite formed by smaller crystals (Verheyden et al., 2006). The slower the calcite growth rate, the longer time available to form nice compact and elongated crystals and thus the darker bands. One of the factors affecting the growth rate of speleothems is the concentration of dissolved ions in the water. The higher the concentration of carbonate dissolved ions in the water, the faster the calcite deposition (as also suggested by Genty and Deflandre, 1998). Due to its longer residence time in the epikarst, summer water preferentially reaching the cave in winter is more concentrated in ions compared to winter water entering the epikarst. During winter, calcite deposition from this supersaturated summer water occurs faster, leading to more porous and thus whiter calcite.

Another factor also affecting the growth rate of speleothems is the amount of water feeding the stalagmite. Higher discharge occurs during winter leading to an increase in growth rate of the calcite deposited in winter. Both factors, the supersaturation of the water and drip rate, confirm what the isotopes suggest: white layers are deposited in winter when calcite deposition rates are high. The whiter and thus the more porous the layer, the faster it is deposited, the lower its $\delta^{13}C$ and the higher its $\delta^{18}O$. This is also clearly visible in the variation range of the $\delta^{13}C$ and $\delta^{18}O$ signals in the layers around
1977 AD compared to the layers around 1985 AD. In 1977 AD (Fig. 5), the color contrast between dark and white layers is stronger corresponding to stronger differences in the isotopic composition of two consecutive layers. More compact layers with large crystals have more negative $\delta^{18}$O and more positive $\delta^{13}$C values. Data from the Pere Noel cave, located in the same karst system as the Han-sur-Lesse cave, also show that during periods of lower drip rate, the conductivity of the drip water is lower leading to slower calcite deposition and thus darker layers (Genty and Deflandre, 1998). The observations gained from combined monitoring observation and stable isotopic analyses answer the remaining question in Verheyden et al. (2006). Darker layers are formed during the summer months when calcite precipitation is slower.

6 Conclusion

Coupling a biweekly monitoring of the cave with a high resolution stable isotopic record of a recent finely laminated part of a growing speleothem documents the seasonal variation of the cave environment, and how these parameters are recorded in the speleothem proxies.

1. Cave air temperatures follow the seasonal variation of the outside air temperature, but in a subdued way. The temperature of the cave drip water follows closely the cave air temperature but is $\sim 0.5^{\circ}$C colder. This suggests that the meteoric water percolating though the epikarst to form the drip water is the major factor controlling the cave air temperature. The $\delta^{18}$O and $\delta$D composition of the rainwater increases smoothly with a few $\%$ during the summer months and is related to the increasing air temperature (temperature-effect). The 6 smaller drops seen in the $\delta^{18}$O and $\delta$D records of the rainwater are linked with increased rainfall periods and consequently reflect the amount effect. The large drop in $\delta^{18}$O and $\delta$D composition of the rainwater seen in March 2013 corresponds with a heavy snowfall event. The $\delta^{18}$O and $\delta$D composition of the drip water remains constant
at values slightly more positive than the average \( \delta^{18}O \) and \( \delta D \) composition of the rainwater indicating a well-mixed aquifer. A drop in isotopic composition of the drip water is seen 5 months after the March 2013 snowfall event indicating that the residence time of the water in the epikarst is 5 to 6 months. The drip water flow in the monitored Salle-du-Dôme reacts within 24 h on a heavy rainfall event indicating the piston flow character of the epikarst.

2. The records of the different measured factors in and outside the cave suggest that the physico-chemical behavior of the Han-sur-Lesse cave closely responds to the seasonally varying external climate. The cave interior climatology varies between a “summer-mode” lasting from June to December and a “winter-mode” from December to June. During the summer mode, the cave air and drip water temperatures are higher and the cave air \( pCO_2 \) increases due to an active vegetation cover above the cave. More negative plant derived \( CO_2 \) with a C3-signature is brought into the cave with the drip water decreasing the \( \delta^{13}C \) signature of the cave air in summer. The drip flow decreases due to higher evaporation at the surface and because of higher water uptake by the vegetation. During the “winter-mode” the temperature cools down and the vegetation cover becomes less active leading to an opposite behavior of the measured factors compared to the “summer-mode”.

3. Calcite precipitated on glass slabs placed on top of the stalagmite and sampled throughout the year has more negative \( \delta^{18}O \) and less negative \( \delta^{13}C \) values when formed during summer. The opposite is observed in winter. After modeling of all possible mechanisms influencing these stable isotopic signals, we conclude that more negative \( \delta^{18}O \) values of precipitated calcite in late summer are due to a temperature increase of the cave air and drip water. The less negative \( \delta^{13}C \) values in summer are due to a decrease in water discharge.

4. The studied part of the Proserpine stalagmite displays seasonal layering with one dark and one white layer deposited every year. The opposite seasonal behavior
of the $\delta^{18}$O and the $\delta^{13}$C signals on the glass slabs is also visible in the isotopic signals of the individual layers in the stalagmite. Dark layers have low $\delta^{18}$O and high $\delta^{13}$C values while white layers have high $\delta^{18}$O and low $\delta^{13}$C values. Dark layers are formed during the cave “summer-mode” with lower drip rate and lower calcite super-saturation of the drip water. They consist of compact elongated crystals that are formed slowly. White layers are formed by fast growing calcite during the cave’s “winter-mode”. The drip water is more supersaturated increasing the deposition rate of the precipitated calcite. Smaller crystals are deposited forming the porous white layers visible in the stalagmite. The clearer the lamination, the larger the amplitude of the variations in the isotopic composition, the stronger the difference between summer cave conditions and winter cave conditions.

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Seasonal variations recorded in cave monitoring results

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Seasonal variations recorded in cave monitoring results

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Table 1. (a) Comparison between samples measured immediately after sampling and samples measured one month after sampling to test the reproducibility of the “new” method used in this study to measure the $\delta^{13}$C composition of the DIC in the drip water. Results show no difference with the samples measured one month after sampling. (b) A comparison of the “new” method used in this study for sampling and sample preparation for delta C analyses of DIC in waters with the method of Mattey et al. (2008). Both methods deliver similar results confirming that the new method used in this study delivers reproducible results.

(a) New method used in this study

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<th>Sample 1</th>
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<td>–11.32</td>
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<tr>
<td></td>
<td>c</td>
<td>–11.20</td>
<td>–11.24</td>
<td></td>
<td></td>
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<td>d</td>
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<td>–11.05</td>
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</table>

(b) New method used in this study

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<th>Sample 2</th>
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<th>–11.77</th>
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<td>–11.82</td>
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<tr>
<td></td>
<td>d</td>
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<td></td>
<td>–11.82</td>
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</tr>
<tr>
<td></td>
<td>e</td>
<td></td>
<td></td>
<td>–11.84</td>
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</table>
Table 2. A selection of the most commonly used water-calcite oxygen fractionation factors. Laboratory and theoretical approaches differ from the relationships found in cave settings.

<table>
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<tr>
<th>Author</th>
<th>Method</th>
<th>$1000 \times \ln \alpha$</th>
<th>$d\alpha/dT$ ($%$°C$^{-1}$)</th>
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<tr>
<td>O'Neil et al. (1969) modified by Friedman and O'Neil (1977)</td>
<td>Laboratory</td>
<td>$2.78(10^6T^{-2}) - 3.39$</td>
<td>$-0.247$</td>
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<tr>
<td>Kim and O'Neil (1997) modified by Kim et al. (2007)</td>
<td>Laboratory</td>
<td>$18.03(10^6T^{-2}) - 2.89$</td>
<td>$-0.221$</td>
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<tr>
<td>Chacko and Deines (2008) constructed relation by Tremaine et al. (2011)</td>
<td>Theoretical calculation</td>
<td>$2.573(10^6T^{-2}) - 0.869$</td>
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<tr>
<td>Horita and Clayton (2007)</td>
<td>Calculations compared with experimental results</td>
<td>$0.952(10^6T^{-2}) + 11.59(10^3T^{-1}) - 21.56$</td>
<td></td>
</tr>
<tr>
<td>Tremaine et al. (2011)</td>
<td>Linear best-fit trough large number of cave studies</td>
<td>$(16.01 \pm 0.65) \times (10^3T^{-1}) - (24.6 \pm 2.2)$</td>
<td>$-0.177$</td>
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<td>Demeny et al. (2010)</td>
<td>Cave monitoring results Hungarian cave</td>
<td>$17500 \times T^{-1} - 29.89$</td>
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Table 3. Calculated $\delta^{18}O$ values for calcite deposited in equilibrium its drip water for different authors. Values were calculated using the average drip water composition of $-7.65\,^{\circ}\text{o}$ for the lowest, highest and average measured temperatures at the Salle-du-Dôme. The second part of the table shows the difference between the calculated $\delta^{18}O$ values and the $\delta^{18}O$ values measured on the glass slabs. Best results are given by the “in-cave”-relationship of Tremaine et al. (2011).

<table>
<thead>
<tr>
<th>Author</th>
<th>$T_{\text{min}}$</th>
<th>$T_{\text{mid}}$</th>
<th>$T_{\text{max}}$</th>
<th>$d^{18}O_{\text{min}}$</th>
<th>$d^{18}O_{\text{mid}}$</th>
<th>$d^{18}O_{\text{max}}$</th>
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<td>O’Neil et. al (1969)</td>
<td>-6.44</td>
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<td>-6.04</td>
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<td>-0.51</td>
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<td>Horita and Clayton (2007)</td>
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<td>-7.85</td>
<td>0.71</td>
<td>0.75</td>
<td>0.87</td>
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<td>-7.32</td>
<td>-7.86</td>
<td>0.73</td>
<td>0.77</td>
<td>0.88</td>
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<tr>
<td>Demeny et al. (2010)</td>
<td>-6.30</td>
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<td>0.05</td>
<td>0.07</td>
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<td>Tremaine et al. (2011)</td>
<td>$-6.26 \pm 0.09$</td>
<td>$-6.55 \pm 0.08$</td>
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<td>$0 \pm 0.08$</td>
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</table>
Fig. 1. The Han-sur-Lesse karst system with the Han-sur-Lesse cave being the northern cave system and the Pere Noel cave being the southern cave system. The Lesse-river enters the cave system at the “Gouffre de Belvaux” and exits 24 h later at the “Trou de Han”. The studied speleothem is located in the “Salle-du-Dôme” and grows on a pile of debris. Figure adapted after Quinif (1988).
Fig. 2. Cave monitoring results show that the cave conditions vary seasonally between a “summer-mode” lasting from June to December and a “winter-mode” lasting from December to June. The δ\textsuperscript{18}O signal of the glass slabs (l) is deposited in equilibrium with the drip water and reflects the seasonally varying cave temperatures (c). The δ\textsuperscript{13}C composition of the glass slabs (m) is not deposited in equilibrium and variations are affected by the seasonally varying discharge amounts (e).
Fig. 3. The $\delta^{18}O$ composition of the drip water averages the annual mean composition of the rainwater $\delta^{18}O$. 6 small drops occur in the rainwater composition in November 2012, December 2012, May 2013, July 2013, December 2013 and January 2014 (indicated in light blue) and correspond with increased rainfall periods. At the end of March a cold temperature peak and prolonged snowfall cause the rainwater $\delta^{18}O$ to display a large drop. A similar negative drop is seen in the drip water $\delta^{18}O$ composition in August indicating that this drop in $\delta^{18}O$ values in the rainwater can be used as spike and shows that the residence time of the water in the epikarst is 4 to 5 months.
Fig. 4. Detail of the upper 16 mm of the Proserpine core drilled in 2011. 10 additional dark layers are counted compared to the core of Verheyden et al. (2006) confirming the seasonal character of the layering. Ages are based on layer counting with one dark and one white layer deposited every year. The frame indicates the location of the monthly resolved $\delta^{18}$O and $\delta^{13}$C signal.
Fig. 5. The $\delta^{18}$O and $\delta^{13}$C signals from the Proserpine stalagmite anticorrelate at monthly scale. At the end of a dark layer (dotted lines), the $\delta^{18}$O values reach their minimum values while the $\delta^{13}$C values reach their maximum. Dark layers are formed during summer when cave temperatures are high (leading the low $\delta^{18}$O) and discharge rates are low (leading to high $\delta^{13}$C). The clearer the lamination, the large the amplitude of the variations in the isotopic composition.