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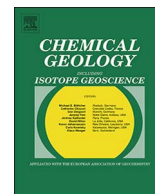
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The influence of weathering and soil organic matter on Zn isotopes in soils



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ABSTRACT

Zinc is an essential micronutrient that is ultimately released during mineral weathering. In soils, organic matter plays a key role in influencing Zn partitioning and therefore on Zn biogeochemical cycling. Soil organic matter is partitioned between carbon that is more readily available for decomposition by microorganisms, and more stable carbon transiently preserved from decomposition. The role of the stable pool of soil organic matter on Zn biogeochemical cycling remains poorly understood. The pool of stable carbon is controlled by combination with mineral constituents or is material that is intrinsically resistant to decomposition. The Zn stable isotopes are fractionated by interactions between Zn and soil mineral and organic constituents. This study reports the Zn isotope composition of five Icelandic soil profiles derived from the same parent basalt and characterized by contrasting degrees of weathering and organic matter content ($\delta^{66}\text{Zn} = +0.10 \pm 0.05$ to $+0.35 \pm 0.02\%$), the distribution of reactive mineral constituents available to form associations with soil organic matter, and the amount of stable organic carbon. Throughout these soils, the $\delta^{66}\text{Zn}$ isotope variations are little influenced by mineral constituents, but rather by soil organic matter content. These data suggest that a combination of organic matter accumulation and Zn loss by leaching is required to explain the observed decrease in Zn concentration in soils and lighter soil $\delta^{66}\text{Zn}$ with increasing organic carbon content. These results suggest that the presence of stable organic carbon in soils provides a pool of light Zn, attributed to the Zn isotope signature of organic matter partially preserved from decomposition. Crucially, this stable organic carbon pool may also contribute to the formation of the light Zn isotope sink reported in organic-rich marine sediments, a key output required to explain the oceanic mass balance of Zn isotopes.

1. Introduction

Zinc is an essential micronutrient involved in key processes such as photosynthesis (Frassinetti et al., 2006), as such there is a growing effort to obtain an accurate understanding of the Zn biogeochemical cycle at the Earth's surface. The current understanding of the oceanic mass balance of Zn isotopes suggests that the main Zn inputs to the ocean are from rivers and dust (Little et al., 2014), and that burial in organic-rich marine sediments acts as a sink in light Zn isotopes (Little et al., 2016). In the oceans, the Zn concentrations in surface water are controlled by biological uptake (e.g., Morel and Price, 2003; Bermin et al., 2006). It has been suggested that Zn association, and burial, with sinking particulate organic matter and potentially Zn sulfide precipitation in buried sediments, could act as a sink for light Zn (Little et al., 2014, 2016).

Soil organic matter (SOM) plays a complex role in Zn partitioning in

soils. Whereas solid organic matter decreases Zn solubility by sorbing Zn on to surface functional groups (Boguta and Sokolowska, 2016), the complexation of Zn with dissolved organic compounds increases Zn solubility and mobility (Weng et al., 2002; Houben and Sonnet, 2012). Soil organic matter turnover is an additional process which can affect Zn solubility as Zn released during litter decomposition may be leached into the soil or become sorbed by the organic matter of the soil surface (Scheid et al., 2009). Moreover, with organic matter transformation, metallic elements such as Zn are progressively incorporated and retained into organo-mineral associations. The progressive decomposition of soil organic carbon (OC) and its reactivity with mineral surfaces in soil aggregates leads to the development of organic molecules characterized by variable mineralization rates depending on their accessibility for enzymatic activity (Lehmann and Kleber, 2015). The SOM is partitioned in a continuum of organic molecules between a “labile” and

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Table 1

Characterization of soils and parent basalt: soil pH, total organic carbon content (OC), stable OC including the mineral protected OC (MP-OC) and the recalcitrant OC (R-OC), Zn concentration and Zn isotopic compositions (‰) (\pm 2SD) in soils and basalt. The $\delta^{66}\text{Zn}$ results are reported relative to the JMC-Lyon-03-0749L. Soil types: Histic Andosol, HA; Histosol, H; Haplic Andosol, BA; Gleyic Andosol, GA; Vitric Andosol, V.

Soil horizon		Depth	pH _{H2O} ^a	Total OC ^a	Stable-OC		Zn	$\delta^{66}\text{Zn}$	2SD
					MP-OC ^b	R-OC ^b			
		cm		%	%	%	$\mu\text{g g}^{-1}$	‰	‰
HA	A1	0–15	5.32	18.52	2.41	1.33	105	+ 0.23	0.04
HA	A2	15–26	4.89	16.94	2.15	0.85	135	+ 0.29	0.03
HA	Bw1	26–40	4.82	14.49	1.26	0.53	131	+ 0.35	0.02
H	O1	0–13	6.18	21.00	2.38	1.59	111	+ 0.22	0.03
H	O2	13–26	5.10	22.94	3.40	3.38	96	+ 0.16	0.06
H	O6	72 +	4.56	30.39	–	–	105	+ 0.10	0.05
BA	A1	0–21	6.35	7.29	0.88	0.14	147	+ 0.19	0.03
BA	A2	21–40	6.40	7.92	1.15	0.13	135	+ 0.16	0.03
GA	A1	0–12	6.22	9.51	1.16	0.19	144	+ 0.32	0.04
GA	A2	12–29	6.30	6.20	0.92	0.13	160	+ 0.28	0.03
GA	Bw2	43–56	6.34	6.76	–	–	169	+ 0.19	0.04
GA	C	56–64	6.57	2.70	–	–	152	+ 0.23	0.02
V	A	0–9	7.77	0.32	0.17	0.04	161	+ 0.26	0.06
V	B/C	9–33	8.20	0.26	0.18	0.05	158	+ 0.19	0.07
V	C	33 +	–	–	–	–	127	+ 0.23	0.06
Parent basalt							132	+ 0.21	0.05

^a Data from Opfergelt et al., 2014

^b STABLE-OC = Mineral protected (MP-OC) + Recalcitrant (R-OC)

“stable” pool. The “labile” carbon is more readily available for decomposition by microorganisms (Schmidt et al., 2011), while the “stable” carbon is briefly preserved from decomposition in a mineral-protected organic carbon (MP-OC) pool, i.e., a combination of organic matter associated with mineral constituents, and/or recalcitrant organic carbon (R-OC), i.e., intrinsically resistant to decomposition (Chenu and Plante, 2006; Mikutta et al., 2006). The presence of reactive mineral constituents that form MP-OC is controlled by the soil weathering degree (e.g., Mikutta et al., 2009; Lawrence et al., 2015; Kleber et al., 2015). The pool of Zn associated with stable soil OC potentially constitutes a sink of Zn preserved in soils, which might also exist in organic-rich sediments. To date, most studies investigating the impact of SOM on Zn biogeochemical cycling have predominantly focused on the relative contribution of dissolved organic matter and bulk soil organic matter on Zn mobility (Sauvé et al., 2000; Fan et al., 2016; Boguta and Sokolowska, 2016). By contrast, the specific role of the stable pool of SOM on Zn biogeochemical cycling remains poorly understood.

The stable isotopes of Zn provide the potential to better understand interactions between Zn and soil constituents, including metal oxides (Juillot et al., 2008; Balistrieri et al., 2008; Bryan et al., 2015; Pokrovsky et al., 2005), phyllosilicates (Guinoiseau et al., 2016), and organic matter (Jouvin et al., 2009; Gélabert et al., 2006; Kafantaris and Borrok, 2014; John and Conway, 2014). Heavy Zn isotopes are preferentially adsorbed on to the surface of Mn-oxides (birnessite; Bryan et al., 2015) and Fe-oxides, with a higher fractionation factor for poorly crystalline Fe-oxides (ferrihydrite) than for crystalline Fe-oxides (goethite) (Juillot et al., 2008; Balistrieri et al., 2008). Heavy Zn isotopes are also preferentially retained by sorption onto kaolinite (Guinoiseau et al., 2016). With organic matter, there is a preferential retention of heavy Zn isotopes on phenolic sites of purified humic acids (Jouvin et al., 2009), which is also confirmed for surface complexation onto the organic coating of diatom cell walls (Gélabert et al., 2006) or bacteria (Kafantaris and Borrok, 2014). Zinc mobilization by plant roots or root exudates preferentially releases heavy Zn isotopes (Smolders et al., 2013; Houben et al., 2014). Within the plant, heavy Zn isotopes sorb onto the root surface, and light Zn isotopes are preferentially

transported into aerial plant parts (Arnold et al., 2010; Aucour et al., 2011; Jouvin et al., 2012; Moynier et al., 2009; Weiss et al., 2005; Viers et al., 2007, 2015; Couder et al., 2015; Tang et al., 2016; Caldelas and Weiss, 2017). Plant litter at the soil surface is therefore generally isotopically lighter, and organic matter decomposition is considered to lead to the retention of heavier Zn isotopes by humification (Viers et al., 2015).

Zinc isotope compositions of soils are anticipated to be offset from the composition of the parent material by the removal or addition of significant pools of fractionated Zn, driven by mineral or organic constituents (Vance et al., 2016; Moynier et al., 2017). In soils in which OC is included in a stable OC pool, organic carbon is briefly preserved from decomposition (Chenu and Plante, 2006; Mikutta et al., 2006). Such work suggests that the presence of a stable OC pool in soils provides the potential to preserve a pool of Zn with an isotope signature of organic matter partially preserved from decomposition: this pool of Zn is currently not considered in the understanding of Zn isotope behaviour in soils (Moynier et al., 2017). This study investigates Zn isotope variations in a suite of five Icelandic soil profiles derived from the same parent basalt and characterized by contrasting degrees of weathering and organic matter content. The distribution of reactive mineral constituents (available to form an association with SOM) controlled by the soil weathering degree, and the amount of stable OC within the total OC have been assessed by chemical and mineralogical analysis and selective extractions of Fe, Al, Si, and C. These data provide a framework to investigate the influence of weathering and soil organic matter on Zn isotope fractionation in soils, and more specifically, the role of the stable pool of SOM on Zn biogeochemical cycling.

2. Materials and methods

2.1. Environmental setting

Five typical Icelandic soil types (Histic Andosol, HA; Histosol, H; Haplic Andosol, BA; Gleyic Andosol, GA; Vitric Andosol V; IUSS, 2014) under grassland were selected for this study (Electronic Annex 1). The

soil profiles were described following the World Reference Base for Soil Resources (IUSS, 2014; Electronic Annex 2) and sampled by horizon. The climate in the area is temperate, with a mean annual precipitation (MAP) of 1017 mm year⁻¹ and a mean annual temperature (MAT) of 4.6 °C. Soils are characterized by seasonal freeze-thaw cycles (Orradottir et al., 2008). The underlying lithology is basaltic. The soil profiles have been characterized previously for their Mg and Mo isotope compositions (Opfergelt et al., 2014; Siebert et al., 2015).

The five soil profiles can be divided into two groups as a function of drainage: the freely drained soils V-BA-GA and the poorly drained soils HA-H. Profiles V, BA, and GA are characterized by a neutral pH and a low organic carbon content (pH 6.7 ± 0.7; 5.4 ± 2.9% C; Table 1), in contrast to profiles HA and H which are acidic and organic rich soils (pH 4.8 ± 0.6; 21 ± 9% C; Table 1; Opfergelt et al., 2014). The primary minerals present in these soils, i.e., augite, Ca-rich plagioclase, magnetite, and volcanic glass directly reflects the mineralogy of the tholeiitic basalt, typical of the Tertiary basalts of West Iceland (Hardarson et al., 2008; Moulton et al., 2000). In volcanic soils, short-range ordered or poorly crystalline phases (i.e., aluminosilicates and Fe-oxides) are formed first (e.g., Thompson et al., 2011; Delmelle et al., 2015): with increasing time for soil development, the poorly crystalline phases transform to more crystalline minerals. Among the five soil profiles, the weathering degree increases in the following order: Basalt < V < BA < GA < H < HA (Opfergelt et al., 2014), with an increasing clay content (fraction < 2 μm) from the first group of soils V-BA-GA to the second group of soils HA-H (Opfergelt et al., 2014). The samples selected for the present study comprise at least the top 40 cm of each soil profile to integrate a range a soil weathering degree and a range of soil organic carbon content, and assess the influence on the Zn isotope fractionation in soils.

2.2. Characterization of reactive soil mineral constituents

The mineral phases playing a key role in SOM stabilization in soils (Fe-oxyhydroxides such as ferrihydrite and goethite, and poorly crystalline aluminosilicates such as allophane) have been quantified through selective extractions of Fe, Al, and Si.

Iron was selectively extracted from different soil aliquots using dithionite-citrate-bicarbonate (DCB) (Fe_d; Mehra and Jackson, 1960), ammonium oxalate (Fe_o; Blakemore et al., 1981), and Na-pyrophosphate (Fe_p; Bascomb, 1968) and measured by ICP-AES. The DCB-extractable Fe provides an estimate of the content of free iron oxides in soils, i.e., poorly crystalline and crystalline Fe-oxides. The oxalate-extractable Fe is used as an indicator of poorly crystalline Fe-oxides. The pyrophosphate-extractable Fe is used as an indicator of organo-Fe complexes, and is used together with pyrophosphate-extractable Al (Al_p) to estimate metal complexed with organic ligands. These extractions are, however, to be considered with caution. Magnetite can be partly dissolved by oxalate and contribute to Fe_o (e.g., Walker, 1983). The dithionite extraction is usually considered to not dissolve magnetite, but some studies report magnetite dissolution with DCB (e.g., Kostka and Luther, 1994; Henkel et al., 2016). Pyrophosphate is a dispersing agent and Fe_p may include the contribution of Fe-oxide nanoparticles in addition to the organically-bound Fe (Jeanroy and Guillet, 1981), even if this contribution is reduced by the centrifugation and filtration of the extract. These selective extractions are not fully quantitative, but can, nevertheless, be used as indicators of the relative evolution of the mineral phases during the soil development under identical soil parent material. The Fe_o/Fe_d ratio is used as a reflection of the relative proportion of short-range ordered Fe oxyhydroxides (ferrihydrite) in the global pool of Fe-oxides. Within the total iron content (Fe_t) in soils, the Fe_d/Fe_t ratio reflects the relative proportion of Fe-oxides in the total Fe pool in soil.

The organic carbon released after dispersion by the pyrophosphate (C_p) was quantified by combustion (Shimadzu Total OC analyzer, detection limit < 2 mg l⁻¹) and provides an indication of the amount of

OC associated with organo-metallic complexes (Cornu and Clozel, 2000; Cornu et al., 2008).

The oxalate-extractable Si (Si_o) was determined by ICP-AES to estimate the quantity of Si associated with poorly crystalline aluminosilicates (allophane) as an indicator of the evolution of the mineral phases in soils with weathering. The Si_o is, however, to be considered with caution because volcanic glass might also be partly dissolved using this protocol, particularly at pH values below 6 (Oelkers and Gíslason, 2001; Arnalds and Gíslason, 2002; Wolff-Boenisch et al., 2004).

2.3. Characterization of soil organic carbon distribution

The content of total OC was quantified in the soil samples (Opfergelt et al., 2014; Table 1). Within the total OC, the stable OC is here defined as the pool of NaOCl-resistant OC (Siregar et al., 2005). The oxidizing NaOCl attack (pH 8) is reported to be one of the most efficient and reliable method to isolate a stable OC (NaOCl-resistant OC), without dissolving pedogenic oxides (Mikutta et al., 2005; Siregar et al., 2005; von Lützow et al., 2007). We quantified the stable OC by mixing 3 g of air dried soil with 30 ml of 6 wt% NaOCl (adjusted to pH 8). The NaOCl-treated soil was then washed (shaken and centrifuged) with deionized water until the solution was chloride free (i.e. no reaction with AgNO₃ occurred). The samples were then dried at 105 °C and homogenized before collecting a subsample for total OC measurement by flash dry combustion.

Within the stable OC pool, the amount of mineral-protected (MP-OC) and recalcitrant (R-OC) organic carbon was distinguished. The R-OC is here defined as the OC pool resistant against NaOCl and insoluble in HF (Mikutta et al., 2006) and the MP-OC pool can be estimated by the difference between the stable OC and the R-OC. The NaOCl-treated samples were subsequently extracted with HF in order to dissolve mineral constituents and associated OC. Two grams of dried soil sample were transferred into pre-weighed centrifuge bottles and treated four times with 20 ml 10% HF. The samples were shaken for 2 h, centrifuged (4000 rpm; 15 min) and the supernatant discarded. The residues were washed five times with 20 ml deionized water, dried at 105 °C, and the weights recorded. The OC content was measured on ground subsamples of the HF-treated soil by flash dry combustion. After HF treatment, the absolute amount of OC was calculated using the OC content measured in the sample residuum, and the weights of the initial and residual sample. The MP-OC/Stable-OC and R-OC/Stable-OC ratios are used to reflect the proportion of MP-OC and R-OC in the stable organic carbon pool.

2.4. Measurements of Zn concentration and Zn isotope compositions in soils

Zinc isotope analyses were carried out on the parent basalt and the soil horizons (Table 1). Zinc concentrations in these samples were measured by ICP-MS (Open University, UK) after soil digestion in concentrated HF:HNO₃ 4:1 volume ratio, and recovery in 2% HNO₃. The accuracy was assessed using the reference materials BHVO-2 and SLRS-4 (Yeghicheyan et al., 2001). The analytical precision was ± 6%, with a detection limit < 0.01 μM.

Sample preparation for Zn isotope measurement involves dissolution and Zn purification. Crushed soil samples (~2 mg) were dry-ashed for 24 h at 450 °C to remove organic matter (Couder et al., 2015). The dry-ashed samples were dissolved by applying the tri-acid digestion technique (with concentrated 14 M HNO₃ 24 M HF and re-dissolution in 6 M HCl) in a Teflon Savillex® beaker placed on a hot plate (120 °C) for evaporation until dryness (Couder et al., 2015). The Zn was then purified by a novel chromatographic separation technique on micro-columns loaded with 0.2 ml AG1-× 8 resin. This method involves successive additions of acids: 6N HCl (for column conditioning and sample loading), 1 N HCl (for matrix rinsing) and 1N HNO₃/HBr (for zinc fraction elution) (Couder et al., 2015). Upon separation the eluate was dried down and digested with 100 μl concentrated HNO₃ to dissolve

potential co-eluted organics. The Zn yield values were higher than 98% and procedural blanks were ≤ 2 ng of Zn.

Zinc isotope ratios were measured on a Nu plasma I MC-ICP-MS in wet plasma mode (ULB, Belgium). Zn (and Cu, for the doping technique) isotopic compositions were measured by static multi-collection. Nickel contributions were systematically corrected by monitoring mass 62 (^{62}Ni). Mass discrimination effects were corrected by using simultaneous external normalization (Cu-doping method) and standard-sample bracketing with a in-house Zn-Cu standard solution (previously calibrated against the JMC-Lyon-03-0749L Zn and NIST SRM 976 Cu reference standard solutions) (Mattielli et al., 2009; Petit et al., 2008). Every sample was analysed at least in triplicate; the Zn isotopic composition is expressed in ‰ in $\delta^{66}\text{Zn}$ relative to a standard solution following Eq. (1), where R_{Zn} is the $^{66}\text{Zn}/^{64}\text{Zn}$ isotopic ratio of the sample (*sample*) and of the bracketing standards (*std1* and *std2*):

$$\delta^{66}\text{Zn}_{\text{sample}} = 1000 \times \left[\left\{ \frac{(R_{\text{Zn}})_{\text{sample}}}{0.5(R_{\text{Zn}})_{\text{std1}} + 0.5(R_{\text{Zn}})_{\text{std2}}} \right\} - 1 \right] \quad (1)$$

During data acquisition, repeated measurements of the in-house Zn and Cu standard solution gave an average $\delta^{66}\text{Zn}$ value of $0.00 \pm 0.03\text{‰}$ (2SD) ($n \sim 200$). Repeated measurements of the Zn standard solution JMC-Lyon-03-0749L gave $\delta^{66}\text{Zn} = +0.11 \pm 0.03\text{‰}$ (2SD) ($n = 17$) relative to our in-house standard solution. The $\delta^{66}\text{Zn}$ values of the samples measured relative to our in-house standards were converted to the JMC-Lyon-03-0749L Zn standard using the conventional conversion equation (Hoefs, 2008). All Zn isotope compositions are reported relative to the JMC-Lyon-03-0749L. Measurements of a basaltic reference material BCR-1 at $0.18 \pm 0.07\text{‰}$ (2SD) ($n = 3$), are consistent with the $\delta^{66}\text{Zn}$ composition of BCR-1 reported in the literature (e.g., $0.20 \pm 0.07\text{‰}$, Viers et al., 2015; $0.26 \pm 0.05\text{‰}$, Viers et al., 2007; $0.32 \pm 0.13\text{‰}$, Cloquet et al., 2006; $0.29 \pm 0.12\text{‰}$, Chapman et al., 2006; $0.20 \pm 0.09\text{‰}$, Archer and Vance, 2004; $0.26 \pm 0.04\text{‰}$, Sivry et al., 2008). The bulk soil sample HA A1 was fully replicated (including column chemistry) and yielded undistinguishable $\delta^{66}\text{Zn}$ values: $0.23 \pm 0.01\text{‰}$ ($n = 2$) and $0.23 \pm 0.04\text{‰}$ ($n = 2$).

3. Results

3.1. Distribution of soil mineral constituents and stable organic carbon

The stable-OC content ranges from $0.9 \pm 0.5\%$ in V-BA-GA soils to $3.9 \pm 1.8\%$ in HA-H soils (Table 1). The five soils can be subdivided in two groups for the OC stabilization as a function of the soil weathering degree. In V-BA-GA, the least weathered soils, stable soil OC is mainly found as MP-OC (MP-OC/Stable-OC from 0.77 to 0.90; Table 1). This MP-OC is largely associated with amorphous and poorly crystalline minerals, as indicated by a higher MP-OC/Stable-OC ratio with an increased proportion of poorly crystalline Fe-oxides (higher Fe_o/Fe_d ratio; Fig. 1a), and to a lesser extent with a higher proportion of poorly crystalline aluminosilicates, such as allophane (Fig. 1b).

The HA-H soils, more weathered and poorly drained, are characterized by a lower MP-OC/Stable-OC ratio (from 0.50 to 0.72; Table 1), and a lower contribution from poorly crystalline Fe-oxides (lower Fe_o/Fe_d ratio; Fig. 1a), to stabilize OC. Instead, the proportion of organically complexed Fe and Al are higher in these soils. This is indicated by a higher proportion of pyrophosphate-extractable Fe and Al (higher Fe_p/Fe_t and Al_p/Al_t) in HA-H soils than in V-BA-GA soils (Fig. 2a and b). These components contribute, as insolubilizing agents, to the stabilization of OC partly quantified in the pool of R-OC.

3.2. Zinc concentrations and Zn isotope variations in soils

Zinc concentrations in Icelandic soils range from 96 to $169 \mu\text{g g}^{-1}$ (Table 1), and decrease with increasing total organic carbon content in

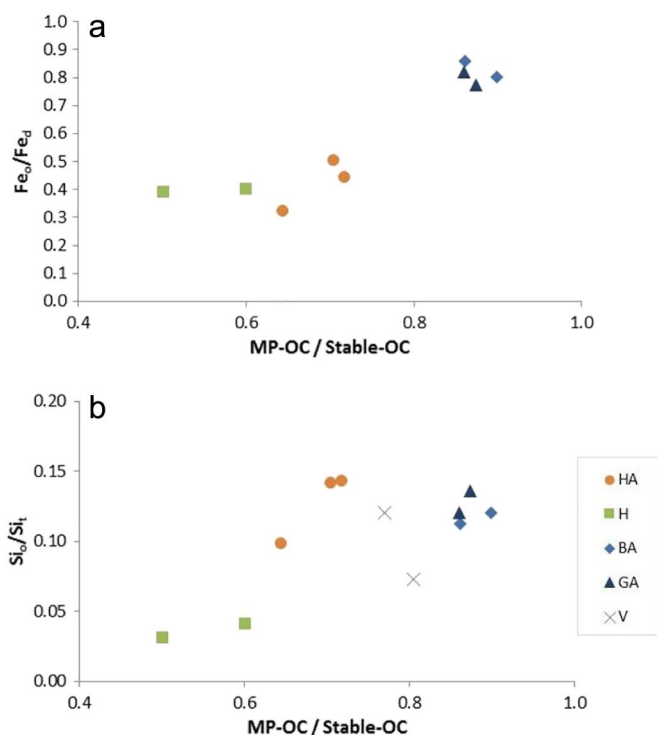


Fig. 1. Evolution of the proportion of mineral-protected organic carbon (MP-OC) in the stable organic carbon (Stable-OC) as a function of: (a) the proportion of oxalate-extractable Fe (Fe_o) in the DCB-extractable Fe (Fe_d), data in V soil not presented due to a potential contribution from magnetite dissolution to Fe_o (see methods Section 2.2; $\text{Fe}_o/\text{Fe}_d > 1$ in V); (b) the proportion of oxalate-extractable Si (Si_o) in the total Si content in soils (Si_t). Soil types: Histic Andosol, HA; Histosol, H; Haplic Andosol, BA; Gleyic Andosol, GA; Vitric Andosol, V.

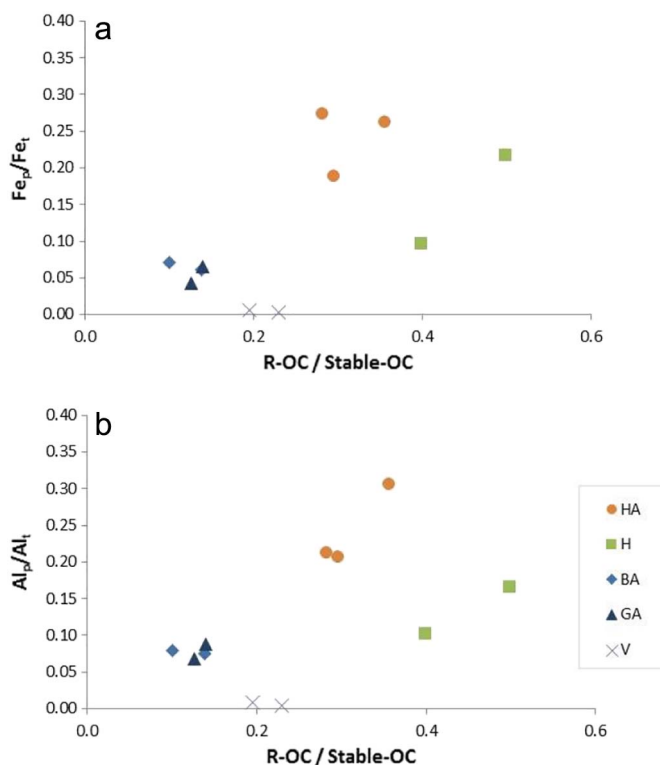


Fig. 2. Evolution of the proportion of recalcitrant organic carbon (R-OC) in the stable organic carbon (Stable-OC) as a function of: (a) the proportion of pyrophosphate-extractable Fe (Fe_p) in the total Fe content in soils (Fe_t); (b) the proportion of pyrophosphate-extractable Al (Al_p) in the total Al content in soils (Al_t). Soil acronyms as in Fig. 1.

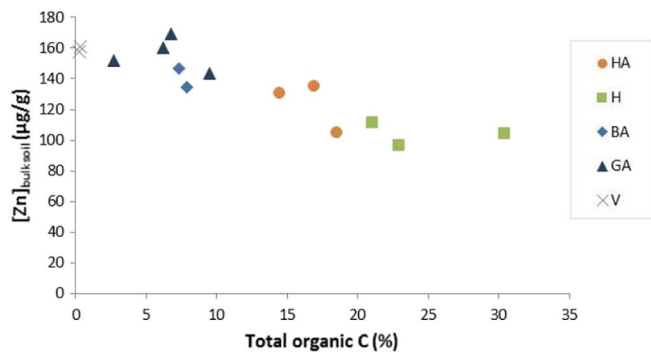


Fig. 3. Evolution of the bulk soil Zn concentration ($\mu\text{g/g}$) as a function of the total organic carbon content (%) in soil. Error bars are included in the symbols. Soil acronyms as in Fig. 1.

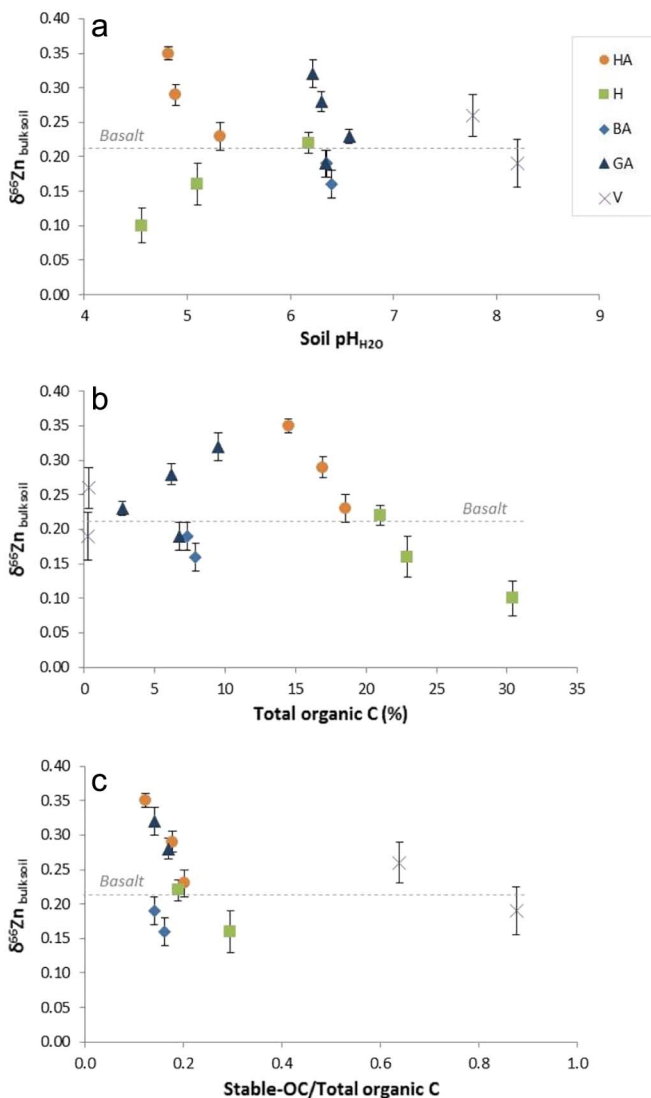


Fig. 4. Evolution of the bulk soil Zn isotope composition ($\delta^{66}\text{Zn}$ in ‰, $\pm 2\text{SD}$) as a function of: (a) the soil pH measured in water ($\text{pH}_{\text{H}_2\text{O}}$); (b) the total organic carbon content (%); (c) the proportion of stable OC (stable OC/total OC). The horizontal dashed line represents the $\delta^{66}\text{Zn}$ value of the basaltic parent material of the soil. Soil acronyms as in Fig. 1.

soils (Fig. 3). The Zn isotope composition ($\delta^{66}\text{Zn}$) of the basalt is $+0.21 \pm 0.05\text{‰}$ (Table 1). The $\delta^{66}\text{Zn}$ values of soils range from $+0.10 \pm 0.05$ to $+0.35 \pm 0.02\text{‰}$ (Table 1). The $\delta^{66}\text{Zn}$ isotope compositions of soils are similar or heavier than the basalt at soil pH

above 6, whereas below pH 6, the $\delta^{66}\text{Zn}$ of soils are both heavier (HA) and lighter (H) than the basalt (Fig. 4a). Importantly, the lighter $\delta^{66}\text{Zn}$ of soils are found in those with a higher amount of organic carbon (Fig. 4b).

4. Discussion

4.1. Influence of mineral constituents on Zn isotope variations in soils

The parent basalt has a $\delta^{66}\text{Zn}$ isotope composition ($+0.21 \pm 0.05\text{‰}$; Table 1) well in agreement with the distribution reported for igneous rocks (excluding ultramafic rocks; $+0.31 \pm 0.12\text{‰}$, $n = 77$; Moynier et al., 2017). The $\delta^{66}\text{Zn}$ isotope composition of the Icelandic soils (from $+0.10 \pm 0.05$ to $+0.35 \pm 0.02\text{‰}$; Table 1), derived from basalt and aged ~ 10 kyear old (Arnalds, 2008), is close to the range of $\delta^{66}\text{Zn}$ reported for volcanic soils derived from basalt with a similar age in Hawaii ($+0.24$ to $+0.41\text{‰}$ for soils of 0.3 and 20 kyear; Vance et al., 2016). More generally $\delta^{66}\text{Zn}$ in Icelandic soils are within the range of $\delta^{66}\text{Zn}$ reported for soils in the literature (-0.2 to $+1.7\text{‰}$; Bigalke et al., 2013; Weiss et al., 2007; Viers et al., 2007; Aranda et al., 2012; Juillot et al., 2011; Aucour et al., 2015; Tang et al., 2012).

With increasing soil development, silicate weathering and precipitation of secondary minerals are known to largely influence element mobility and retention in soils. Silicate mineral dissolution preferentially releases light Zn isotopes in the aqueous phase in the early stage of dissolution (with 30–40% of the Zn pool released, both with proton or ligand promoted dissolution; Weiss et al., 2014) then moves back to release the initial mineral $\delta^{66}\text{Zn}$ composition. Zinc isotope fractionation in early stage silicate mineral dissolution may occur in soils, but the impact on the bulk soil $\delta^{66}\text{Zn}$ composition is likely limited with bulk mineral dissolution. Isotope fractionation accompanying weathering has also been reported for black shales that contain sulfides (e.g., Fernandez and Borrok, 2009; Lv et al., 2016). However, there is no evidence for the presence of sulfides in the studied soils, and no volcanic hydrothermal system in the vicinity of the site, so any contribution from Zn isotope fractionation associated with sulfides (e.g., Fujii et al., 2011; Chen et al., 2014) is considered unlikely.

Zinc isotopes in soils may be fractionated by adsorption onto Fe-oxides (Juillot et al., 2008; Balistrieri et al., 2008; Pokrovsky et al., 2005), with heavy Zn isotopes being preferentially adsorbed at the surface of Fe-oxides. However, in Icelandic soils, there is no correlation between the $\delta^{66}\text{Zn}$ of the soils and the Fe oxide content estimated from the Fe_d/Fe_t ratio ($R^2 = 0.03$). There is no correlation either between the $\delta^{66}\text{Zn}$ of soils and the proportion of poorly crystalline Fe-oxides estimated from the Fe_o/Fe_d ratio ($R^2 = 0.02$), despite the fact that a higher fractionation factor is reported for poorly crystalline Fe-oxides than for crystalline Fe-oxides (Juillot et al., 2008; Balistrieri et al., 2008). Therefore, interaction between Zn and Fe-oxides appears not to be a major controlling factor on the Zn isotope variations in these soils.

Zinc isotopes in soils may also be fractionated by adsorption onto kaolinite (Guinoiseau et al., 2016). However, the clay fraction in these volcanic soils is dominated by poorly crystalline aluminosilicates such as allophane. Crystalline clay minerals such as smectite and kaolinite are only found in trace amounts in the HA (Opfergelt et al., 2014), and Zn adsorption onto kaolinite is likely limited in acidic soil conditions (Gu and Evans, 2008) such as in HA soil (pH 4.8 to 5.3; Table 1). Therefore, interaction between Zn and kaolinite is unlikely to be the main controlling factor on the Zn isotope variations in these soils. Even if the fractionation factor has not been determined, Zn adsorption likely also occurs onto allophane. However, there is no correlation between the $\delta^{66}\text{Zn}$ of soils and the Si_o content used as an indicator of the presence of allophane ($R^2 = 0.04$). Therefore, interaction between Zn and allophane is not likely to control Zn isotope variations in soils.

The Zn isotope compositions of soils may also be affected by atmospheric contribution of Zn to the soil, either anthropogenic and/or

natural. There is no local contamination from industry or urban areas in the vicinity of our site, indicating that Zn isotope fractionation in these soils is unlikely to be associated with polluted Zn sources (Borrok et al., 2009; Cloquet et al., 2006, 2008; Juillot et al., 2011; Sivry et al., 2008; Chen et al., 2008, 2009; Bigalke et al., 2010; Fekiacova et al., 2015). Atmospheric dust input on Icelandic soils is dominated by volcanic material mainly basaltic from volcanic ash deposition during eruption or resuspended volcanic material (Sigfusson et al., 2008; Arnalds et al., 2001; Wittmann et al., 2017). Volcanic ash input contributes to soil forming processes in Icelandic soils (Arnalds, 2008) and is characterized by a $\delta^{66}\text{Zn}$ isotope composition similar to the one of the soil parent material. Atmospheric Zn input from rainfall and sea spray may also contribute to the soils. The Zn concentration in rain in Iceland can be considered as low (based on a Zn concentration of 5.7 ppb in Langjökull ice from the West Iceland glacier the closest to the site (Electronic Annex 1); it is the same order of magnitude as the Zn concentration in Greenland ice at 2.7 ppb) relative to the rain in Paris which contains between 11 and 115 ppb Zn, most likely due to anthropogenic contamination (Chen et al., 2008). The Zn concentration in seawater producing sea spray is even lower (e.g., from 0.007 to 0.6 ppb; Bermin et al., 2006) with a $\delta^{66}\text{Zn}$ of 0.5‰ (e.g., Little et al., 2014). Relative to the total soil Zn reservoir (51 to 144 kg ha⁻¹) calculated from the total Zn concentration in soil (96 to 169 $\mu\text{g g}^{-1}$; Table 1) and the bulk density of the soil (0.22 to 0.78 g cm⁻³; Opfergelt et al., 2014), a Zn contribution from rainfall and sea spray is considered as negligible and is not expected to affect the bulk soil $\delta^{66}\text{Zn}$.

4.2. Influence of vegetation uptake on Zn isotope variations in soils

Light Zn isotopes are preferentially transported into aerial plant parts, therefore, the biological uptake of Zn by vegetation is a factor that may influence the $\delta^{66}\text{Zn}$ in soils (Jouvin et al., 2012; Moynier et al., 2009; Weiss et al., 2005; Viers et al., 2007, 2015; Smolders et al., 2013; Couder et al., 2015; Tang et al., 2016; Caldelas and Weiss, 2017). The Zn concentration in Icelandic grass reported in the literature ranges from 14 to 85 $\mu\text{g g}^{-1}$ (e.g., Johannesson et al., 2007; Gudmundsson and Thorsteinsson, 1980). Considering a high Zn concentration in vegetation (i.e., 104 $\mu\text{g g}^{-1}$ for HA A1 as the topsoil litter; Table 1), the yearly Zn uptake by vegetation ranges from 208 to 520 g Zn ha⁻¹ year⁻¹, taking into account the vegetation biomass produced (from 2 to 5 T ha⁻¹ year⁻¹ for hay-making; Opfergelt et al., 2014; Arnalds et al., 2016). Relative to the total soil Zn reservoir (51 to 144 kg ha⁻¹), as calculated in Section 4.1, the Zn uptake in vegetation only represents 0.1% to 0.7% of the soil Zn reservoir, which indicates that the amount of Zn exported by harvested vegetation is not expected to affect the bulk soil $\delta^{66}\text{Zn}$.

4.3. Contribution from organic matter to the Zn isotope variations in soils

The Zn concentrations in soils are lower in HA-H (114 ± 16 $\mu\text{g g}^{-1}$) than in V-BA-GA (150 ± 14 $\mu\text{g g}^{-1}$; Table 1). This may result from a combination of (i) the dilution of the Zn pool associated with the mineral constituents by an increasing organic matter content in the HA-H soils (Fig. 3), and/or (ii) a process favouring Zn loss from the HA-H soils relative to the V-BA-GA soils.

The part of the vegetation that returns to the soil and forms the litter contributes to the accumulation of organic matter in soils, and provides a source of light Zn isotopes from plant aerial parts. Considering a Zn concentration in the litter such as measured in the HA A1 litter (105 $\mu\text{g g}^{-1}$; Table 1) and a maximum content in organic carbon of 30% (higher organic carbon content in H O6; Table 1), if the total organic carbon content is considered as litter, then the Zn concentration in the organic carbon pool is estimated to be ~31 $\mu\text{g g}^{-1}$. This calculation suggests that in organic-rich soils, one third of the total soil Zn concentration (96 to 169 $\mu\text{g g}^{-1}$; Table 1) may originate from the soil organic carbon pool accumulated from the litter. Therefore, organic

matter accumulation is likely to contribute to the observed lighter Zn isotope composition in soils with increasing organic carbon content in HA-H soils (Fig. 4b).

Zinc leaching from soils may contribute to a Zn loss from the poorly drained organic-rich HA-H soils relative to the well-drained V-BA-GA soils. HA-H soils are acidic (pH 4.8 ± 0.6; Table 1) relative to V-BA-GA soils (pH 6.7 ± 0.7; Table 1), and previous studies have reported that the low pH of peatlands may be responsible for a high Zn release from these soils, resulting in a progressive depletion of the soil metal pool (e.g., Tipping et al., 2003). Additionally, the release of dissolved organic compounds, especially in rewetting periods (Fenner et al., 2001), was also found to favour the leaching of Zn through the formation of soluble metal-organic complexes (Kalbitz and Wennrich, 1998; Houben et al., 2013). Soil acidification and complexation with organic ligands mobilize preferentially heavy Zn isotopes (Houben et al., 2014; Balistreri et al., 2008; Markovic et al., 2017; Fujii et al., 2014; Moynier et al., 2017). As a result, Zn leaching likely contributes to the Zn loss from HA-H soils and to the relative enrichment in light Zn isotopes in these organic-rich soils (Fig. 4b).

4.4. Influence of the presence of stable organic carbon on Zn isotope variations in soils

A key observation in each soil profile (HA, H, BA, GA, V) is that the higher the proportion of stable OC in the total organic carbon content, the lighter the Zn isotope composition in the soil (Fig. 4c). The stable OC pool comprises organic matter associated with mineral constituents (mineral-protected organic carbon, MP-OC), and/or organic carbon intrinsically resistant to decomposition (recalcitrant organic carbon, R-OC) (Chenu and Plante, 2006; Mikutta et al., 2006). Previous work (Viers et al., 2015) suggests that the humification of litter (which mainly results in a pool of stable organic carbon intrinsically resistant to decomposition, R-OC; Berg and McClaugherty, 2008; Mikutta et al., 2005, 2006) leads to release of the lighter Zn isotopes in solution and thus preserves the heavy Zn isotopes in the humification products such as aromatic structures. These findings are consistent with studies showing that Zn adsorption and complexation with organic compounds or biological surfaces favour the heavy Zn isotopes (Jouvin et al., 2009; Gélabert et al., 2006; Wanty et al., 2013; Kafantaris and Borrok, 2014). Accordingly, an increasing amount of stable OC, if driven by humification, should result in enrichment in heavy Zn isotopes in soils.

This contrasts with our observations of lighter Zn isotope composition in the soils with increasing proportion of stable OC (Fig. 4c). This apparent inconsistency is likely explained by the lower contribution of R-OC to the stable OC pool relative to the MP-OC pool in Icelandic soils (Table 1; Electronic Annex 3). The pool of stable OC is mainly dominated by MP-OC, which is thought to comprise organic materials protected against biological attack (Baldock and Skjemstad, 2000). Therefore, the enrichment in light Zn isotopes with an increasing proportion of stable OC likely results from the stabilization of plant-derived Zn-organic compounds, which are usually relatively enriched in light Zn isotopes (Jouvin et al., 2012; Moynier et al., 2009; Weiss et al., 2005; Viers et al., 2007, 2015; Couder et al., 2015; Tang et al., 2016; Caldelas and Weiss, 2017), through association with the soil mineral matrix. This interpretation is in line with previous studies that report plant-derived Zn being mainly found in organo-metallic complexes associated with the clay fraction which are relatively resistant to biodegradation (Quenea et al., 2009).

4.5. Implications

This study suggests that the presence of stable OC in soils dominated by mineral-protected organic carbon is likely to favour the preservation of the Zn isotope signature of partially decomposed organic matter, and thereby contributes to form a sink of light Zn isotopes in soils. This suggests that the Zn isotope composition of the stable soil OC pool could

be considered as an archive of an original organic matter Zn contribution to the soil, and may be preserved in erosive products of soils (Vance et al., 2016). Considering that organic carbon is also stabilized in other environments than soils such as lake or marine sediments, for example by association with mineral phases (e.g., Lalonde et al., 2012), and that light Zn isotopes may be delivered to sediments via uptake of light Zn by phytoplankton and settling particles (John et al., 2007; Peel et al., 2009), this study supports the finding that organic-rich sediments may well constitute a sink of light Zn isotopes (Little et al., 2016), and further suggests that this is likely to be partly due to a Zn pool associated with stable organic carbon, although direct field verification of this hypothesis requires further study of lake or marine sediments.

5. Conclusion

The influence of weathering and organic matter on Zn isotope fractionation in soils has been investigated in five Icelandic soil profiles derived from the same parent basalt and covering contrasting degrees of weathering and organic matter content. The role of the stable pool of soil organic matter on Zn isotope fractionation was specifically investigated by quantifying the reactive mineral constituents available to form association with soil organic matter, and the amount of stable organic carbon within the total organic carbon content.

Throughout the range of soil weathering degree covered in this study, the influence of mineral constituents such as secondary clay minerals, Fe-oxides or sulfides or atmospheric deposition on $\delta^{66}\text{Zn}$ variations in soils appears to be limited. In contrast, the influence of soil organic matter on $\delta^{66}\text{Zn}$ variations in soils appears to be more important. The data suggest that the decrease in Zn concentrations and lighter $\delta^{66}\text{Zn}$ in soils with increasing organic carbon content can be explained by a combination of (i) litter contribution to the soil and organic matter accumulation, thereby diluting the Zn soil content from the mineral constituents and providing a source of light Zn isotopes from the aerial part of the vegetation, and (ii) Zn leaching due to acidic conditions and to complexation by dissolved organic compounds decreasing the Zn concentration in soils and favouring the loss of heavy Zn isotopes, and hence leaving soils with a lighter $\delta^{66}\text{Zn}$.

More specifically, the data indicate that the presence of stable organic carbon in soils provides a pool of Zn with an isotope signature attributed to the $\delta^{66}\text{Zn}$ of organic matter partially preserved from decomposition. The observations suggest that this pool of light Zn occurs when the stable organic carbon is dominated by mineral-protected organic carbon. The pool of Zn associated with the stable organic carbon is likely to contribute to a sink of light Zn isotopes in soils, and should be considered in the future in order to understand the fractionation of Zn isotopes in soils. A similar pool of Zn is likely to contribute to the light sink of Zn isotopes reported in organic-rich marine sediments (Little et al., 2016), which provides a perspective for further investigation beyond that of soil alone.

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