

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

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18 **Highlights**

- 19 • Soil  $\delta^{66}\text{Zn}$  more influenced by soil organic matter than by mineral constituents
- 20 • Zn loss by acidification and with dissolved organic carbon yields light soil  $\delta^{66}\text{Zn}$
- 21 • A pool of stable soil organic carbon may store a sink of light Zn isotopes in soils
- 22 • Stable organic carbon  $\delta^{66}\text{Zn}$  may record a Zn contribution of undecomposed organic C

26 *Abstract*

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

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47 **Keywords:** volcanic soil, Zn isotopes, soil organic matter, weathering, basalt, stable carbon

## 48           1. Introduction

49 Zinc is an essential micronutrient involved in key processes such as photosynthesis (Frassinetti et al  
50 2006), as such there is a growing effort to obtain an accurate understanding of the Zn biogeochemical  
51 cycle at the Earth's surface. The current understanding of the oceanic mass balance of Zn isotopes  
52 suggests that the main Zn inputs to the ocean are from rivers and dust (Little et al., 2014), and that burial  
53 in organic-rich marine sediments acts as a sink in light Zn isotopes (Little et al., 2016). In the oceans,  
54 the Zn concentrations in surface water are controlled by biological uptake (e.g., Morel and Price, 2003;  
55 Bermin et al., 2006). It has been suggested that Zn association, and burial, with sinking particulate  
56 organic matter and potentially Zn sulfide precipitation in buried sediments, could act as a sink for light  
57 Zn (Little et al., 2014, 2016).

58 Soil organic matter (SOM) plays a complex role in Zn partitioning in soils. Whereas solid organic matter  
59 decreases Zn solubility by sorbing Zn on to surface functional groups (Boguta and Sokolowska, 2016),  
60 the complexation of Zn with dissolved organic compounds increases Zn solubility and mobility (Weng  
61 et al., 2002; Houben and Sonnet, 2012). Soil organic matter turnover is an additional process which can  
62 affect Zn solubility as Zn released during litter decomposition may be leached into the soil or become  
63 sorbed by the organic matter of the soil surface (Scheid et al., 2009). Moreover, with organic matter  
64 transformation, metallic elements such as Zn are progressively incorporated and retained into organo-  
65 mineral associations. The progressive decomposition of soil organic carbon (OC) and its reactivity with  
66 mineral surfaces in soil aggregates leads to the development of organic molecules characterized by  
67 variable mineralization rates depending on their accessibility for enzymatic activity (Lehmann and  
68 Kleber, 2015). The SOM is partitioned in a continuum of organic molecules between a "labile" and  
69 "stable" pool. The "labile" carbon is more readily available for decomposition by microorganisms  
70 (Schmidt et al., 2011), while the "stable" carbon is briefly preserved from decomposition in a mineral-  
71 protected organic carbon (MP-OC) pool, i.e., a combination of organic matter associated with mineral  
72 constituents, and/or recalcitrant organic carbon (R-OC), i.e., intrinsically resistant to decomposition  
73 (Chenu and Plante, 2006; Mikutta et al., 2006). The presence of reactive mineral constituents that form  
74 MP-OC is controlled by the soil weathering degree (e.g., Mikutta et al., 2009; Lawrence et al., 2015;  
75 Kleber et al., 2015). The pool of Zn associated with stable soil OC potentially constitutes a sink of Zn  
76 preserved in soils, which might also exist in organic-rich sediments. To date, most studies investigating  
77 the impact of SOM on Zn biogeochemical cycling have predominantly focused on the relative  
78 contribution of dissolved organic matter and bulk soil organic matter on Zn mobility (Sauvé et al., 2000;  
79 Fan et al., 2016; Boguta and Sokolowska, 2016). By contrast, the specific role of the stable pool of SOM  
80 on Zn biogeochemical cycling remains poorly understood.

81 The stable isotopes of Zn provide the potential to better understand interactions between Zn and soil  
82 constituents, including metal oxides (Juillot et al., 2008; Balistrieri et al., 2008; Bryan et al., 2015;  
83 Pokrovsky et al., 2005), phyllosilicates (Guinoiseau et al., 2016), and organic matter (Jouvin et al., 2009;

84 Gélabert et al., 2006 ; Kafantaris et al., 2014; John and Conway, 2014). Heavy Zn isotopes are  
85 preferentially adsorbed on to the surface of Mn-oxides (birnessite; Bryan et al., 2015) and Fe-oxides,  
86 with a higher fractionation factor for poorly crystalline Fe-oxides (ferrihydrite) than for crystalline Fe-  
87 oxides (goethite) (Juillot et al., 2008; Balistrieri et al., 2008). Heavy Zn isotopes are also preferentially  
88 retained by sorption onto kaolinite (Guinoiseau et al., 2016). With organic matter, there is a preferential  
89 retention of heavy Zn isotopes on phenolic sites of purified humic acids (Jouvin et al., 2009), which is  
90 also confirmed for surface complexation onto the organic coating of diatom cell walls (Gélabert et al.,  
91 2006) or bacteria (Kafantaris et al., 2014). Zinc mobilization by plant roots or root exudates  
92 preferentially releases heavy Zn isotopes (Smolders et al., 2013; Houben et al., 2014). Within the plant,  
93 heavy Zn isotopes sorb onto the root surface, and light Zn isotopes are preferentially transported into  
94 aerial plant parts (Arnold et al., 2010; Aucour et al., 2011; Jouvin et al., 2012; Moynier et al., 2009;  
95 Weiss et al., 2005; Viers et al., 2007, 2015; Couder et al., 2015; Tang et al., 2016; Caldelas and Weiss,  
96 2017). Plant litter at the soil surface is therefore generally isotopically lighter, and organic matter  
97 decomposition is considered to lead to the retention of heavier Zn isotopes by humification (Viers et al.,  
98 2015).

99 Zinc isotope compositions of soils are anticipated to be offset from the composition of the parent  
100 material by the removal or addition of significant pools of fractionated Zn, driven by mineral or organic  
101 constituents (Vance et al., 2016; Moynier et al., 2017). In soils in which OC is included in a stable OC  
102 pool, organic carbon is briefly preserved from decomposition (Chenu and Plante, 2006; Mikutta et al.,  
103 2006). Such work suggests that the presence of a stable OC pool in soils provides the potential to  
104 preserve a pool of Zn with an isotope signature of organic matter partially preserved from  
105 decomposition: this pool of Zn is currently not considered in the understanding of Zn isotope behaviour  
106 in soils (Moynier et al., 2017). This study investigates Zn isotope variations in a suite of five Icelandic  
107 soil profiles derived from the same parent basalt and characterized by contrasting degrees of weathering  
108 and organic matter content. The distribution of reactive mineral constituents (available to form an  
109 association with SOM) controlled by the soil weathering degree, and the amount of stable OC within  
110 the total OC have been assessed by chemical and mineralogical analysis and selective extractions of Fe,  
111 Al, Si, and C. These data provide a framework to investigate the influence of weathering and soil organic  
112 matter on Zn isotope fractionation in soils, and more specifically, the role of the stable pool of SOM on  
113 Zn biogeochemical cycling.

114

## 115 **2. Materials and methods**

### 116 *2.1 Environmental setting*

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

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

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

## 140 *2.2 Characterization of reactive soil mineral constituents*

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

144 Iron was selectively extracted from different soil aliquots using dithionite-citrate-bicarbonate (DCB)  
145 (Fe<sub>d</sub>; Mehra and Jackson, 1960), ammonium oxalate (Fe<sub>o</sub>; Blakemore et al., 1981), and Na-  
146 pyrophosphate (Fe<sub>p</sub>; Bascomb, 1968) and measured by ICP-AES. The DCB-extractable Fe provides an  
147 estimate of the content of free iron oxides in soils, i.e., poorly crystalline and crystalline Fe-oxides. The  
148 oxalate-extractable Fe is used as an indicator of poorly crystalline Fe-oxides. The pyrophosphate-  
149 extractable Fe is used as an indicator of organo-Fe complexes, and is used together with pyrophosphate-  
150 extractable Al (Al<sub>p</sub>) to estimate metal complexed with organic ligands. These extractions are, however,  
151 to be considered with caution. Magnetite can be partly dissolved by oxalate and contribute to Fe<sub>o</sub> (e.g.,  
152 Walker et al., 1983). The dithionite extraction is usually considered to not dissolve magnetite, but some  
153 studies report magnetite dissolution with DCB (e.g., Kostka and Luther, 1994; Henkel et al., 2016).

154 Pyrophosphate is a dispersing agent and  $Fe_p$  may include the contribution of Fe-oxide nanoparticulates  
155 in addition to the organically-bound Fe (Jeanroy and Guillet, 1981), even if this contribution is reduced  
156 by the centrifugation and filtration of the extract. These selective extractions are not fully quantitative,  
157 but can, nevertheless, be used as indicators of the relative evolution of the mineral phases during the soil  
158 development under identical soil parent material. The  $Fe_o/Fe_d$  ratio is used as a reflection of the relative  
159 proportion of short-range ordered Fe oxyhydroxides (ferrihydrite) in the global pool of Fe-oxides.  
160 Within the total iron content ( $Fe_t$ ) in soils, the  $Fe_d/Fe_t$  ratio reflects the relative proportion of Fe-oxides  
161 in the total Fe pool in soil.

162 The organic carbon released after dispersion by the pyrophosphate ( $C_p$ ) was quantified by combustion  
163 (Shimadzu Total OC analyzer, detection limit  $< 2 \text{ mg.l}^{-1}$ ) and provides an indication of the amount of  
164 OC associated with organo-metallic complexes (Cornu and Clozel, 2000; Cornu et al., 2008).

165 The oxalate-extractable Si ( $Si_o$ ) was determined by ICP-AES to estimate the quantity of Si associated  
166 with poorly crystalline aluminosilicates (allophane) as an indicator of the evolution of the mineral phases  
167 in soils with weathering. The  $Si_o$  is, however, to be considered with caution because volcanic glass might  
168 also be partly dissolved using this protocol, particularly at pH values below 6 (Oelkers and Gislason,  
169 2001; Arnalds and Gislason, 2002; Wolff-Boenisch et al., 2004).

### 170 *2.3 Characterization of soil organic carbon distribution*

171 The content of total OC was quantified in the soil samples (Opfergelt et al., 2014; Table 1). Within the  
172 total OC, the stable OC is here defined as the pool of NaOCl-resistant OC (Siregar et al., 2005). The  
173 oxidizing NaOCl attack (pH 8) is reported to be one of the most efficient and reliable method to isolate  
174 a stable OC (NaOCl-resistant OC), without dissolving pedogenic oxides (Mikutta et al., 2005; Siregar  
175 et al., 2005; von Lützow et al., 2007). We quantified the stable OC by mixing 3 g of air dried soil with  
176 30 ml of 6 wt % NaOCl (adjusted to pH 8). The NaOCl-treated soil was then washed (shaken and  
177 centrifuged) with de-ionized water until the solution was chloride free (i.e. no reaction with  $AgNO_3$   
178 occurred). The samples were then dried at  $105^\circ\text{C}$  and homogenized before collecting a subsample for  
179 total OC measurement by flash dry combustion.

180 Within the stable OC pool, the amount of mineral-protected (MP-OC) and recalcitrant (R-OC) organic  
181 carbon was distinguished. The R-OC is here defined as the OC pool resistant against NaOCl and  
182 insoluble in HF (Mikutta et al. 2006) and the MP-OC pool can be estimated by the difference between  
183 the stable OC and the R-OC. The NaOCl-treated samples were subsequently extracted with HF in order  
184 to dissolve mineral constituents and associated OC. Two grams of dried soil sample were transferred  
185 into pre-weighed centrifuge bottles and treated four times with 20 ml 10% HF. The samples were shaken  
186 for 2h, centrifuged (4000 rpm; 15 min) and the supernatant discarded. The residues were washed five  
187 times with 20 ml deionized water, dried at  $105^\circ\text{C}$ , and the weights recorded. The OC content was  
188 measured on ground subsamples of the HF-treated soil by flash dry combustion. After HF treatment, the

189 absolute amount of OC was calculated using the OC content measured in the sample residuum, and the  
190 weights of the initial and residual sample. The MP-OC/Stable-OC and R-OC/Stable-OC ratios are used  
191 to reflect the proportion of MP-OC and R-OC in the stable organic carbon pool.

#### 192 2.4 Measurements of Zn concentration and Zn isotope compositions in soils

193 Zinc isotope analyses were carried out on the parent basalt and the soil horizons (Table 1). Zinc  
194 concentrations in these samples were measured by ICP-MS (Open University, UK) after soil digestion  
195 in concentrated HF:HNO<sub>3</sub> 4:1 volume ratio, and recovery in 2% HNO<sub>3</sub>. The accuracy was assessed  
196 using the reference materials BHVO-2 and SLRS-4 (Yeghicheyan et al., 2001). The analytical precision  
197 was ± 6%, with a detection limit < 0.01 μM.

198 Sample preparation for Zn isotope measurement involves dissolution and Zn purification. Crushed soil  
199 samples (~ 2 mg) were dry-ashed for 24 hours at 450°C to remove organic matter (Couder et al., 2015).  
200 The dry-ashed samples were dissolved by applying the tri-acid digestion technique (with concentrated  
201 14 M HNO<sub>3</sub> 24 M HF and re-dissolution in 6 M HCl) in a Teflon Savillex® beaker placed on a hot plate  
202 (120°C) for evaporation until dryness (Couder et al., 2015). The Zn was then purified by a novel  
203 chromatographic separation technique on micro-columns loaded with 0.2 ml AG1-X8 resin. This  
204 method involves successive additions of acids: 6N HCl (for column conditioning and sample loading),  
205 1N HCl (for matrix rinsing) and 1N HNO<sub>3</sub> /HBr (for zinc fraction elution) (Couder et al., 2015). Upon  
206 separation the eluate was dried down and digested with 100 μL concentrated HNO<sub>3</sub> to dissolve potential  
207 co-eluted organics. The Zn yield values were higher than 98% and procedural blanks were ≤ 2 ng of Zn.

208 Zinc isotope ratios were measured on a Nu plasma I MC-ICP-MS in wet plasma mode (ULB, Belgium).  
209 Zn (and Cu, for the doping technique) isotopic compositions were measured by static multi-collection.  
210 Nickel contributions were systematically corrected by monitoring mass 62 (<sup>62</sup>Ni). Mass discrimination  
211 effects were corrected by using simultaneous external normalization (Cu-doping method) and standard-  
212 sample bracketing with a in-house Zn-Cu standard solution (previously calibrated against the JMC-  
213 Lyon-03-0749L Zn and NIST SRM 976 Cu reference standard solutions) (Mattielli et al. 2009; Petit et  
214 al. 2008). Every sample was analysed at least in triplicate; the Zn isotopic composition is expressed in  
215 ‰ in δ<sup>66</sup>Zn relative to a standard solution following Eq. 1, where  $R_{Zn}$  is the <sup>66</sup>Zn/<sup>64</sup>Zn isotopic ratio of  
216 the sample (*sample*) and of the bracketing standards (*std1* and *std2*):

$$217 \quad \delta^{66}\text{Zn}_{\text{sample}} = 1000 \times \left[ \left\{ \frac{(R_{Zn})_{\text{sample}}}{0.5(R_{Zn})_{\text{std1}} + 0.5(R_{Zn})_{\text{std2}}} \right\} - 1 \right] \quad \text{Eq. 1}$$

218  
219 During data acquisition, repeated measurements of the in-house Zn and Cu standard solution gave an  
220 average δ<sup>66</sup>Zn value of 0.00±0.03‰ (2SD) (n~200). Repeated measurements of the Zn standard solution  
221 JMC-Lyon-03-0749L gave δ<sup>66</sup>Zn = +0.11± 0.03‰ (2SD) (n = 17) relative to our in-house standard  
222 solution. The δ<sup>66</sup>Zn values of the samples measured relative to our in-house standards were converted

223 to the JMC-Lyon-03-0749L Zn standard using the conventional conversion equation (Hoefs, 2008). All  
224 Zn isotope compositions are reported relative to the JMC-Lyon-03-0749L. Measurements of a basaltic  
225 reference material BCR-1 at  $0.18 \pm 0.07\text{‰}$  (2SD) ( $n = 3$ ), are consistent with the  $\delta^{66}\text{Zn}$  composition of  
226 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;  
227  $0.32 \pm 0.13\text{‰}$ , Cloquet et al., 2006;  $0.29 \pm 0.12\text{‰}$ , Chapman et al., 2006;  $0.20 \pm 0.09\text{‰}$ , Archer and  
228 Vance, 2004 ;  $0.26 \pm 0.04\text{‰}$ , Sivry et al., 2008). The bulk soil sample HA A1 was fully replicated  
229 (including column chemistry) and yielded undistinguishable  $\delta^{66}\text{Zn}$  values:  $0.23 \pm 0.01\text{‰}$  ( $n = 2$ ) and  
230  $0.23 \pm 0.04\text{‰}$  ( $n = 2$ ).

231

### 232 3. Results

#### 233 3.1 Distribution of soil mineral constituents and stable organic carbon

234 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  
235 1). The five soils can be subdivided in two groups for the OC stabilization as a function of the soil  
236 weathering degree. In V-BA-GA, the least weathered soils, stable soil OC is mainly found as MP-OC  
237 (MP-OC/Stable-OC from 0.77 to 0.90; Table 1). This MP-OC is largely associated with amorphous and  
238 poorly crystalline minerals, as indicated by a higher MP-OC/Stable-OC ratio with an increased  
239 proportion of poorly crystalline Fe-oxides (higher  $\text{Fe}_o/\text{Fe}_d$  ratio; Figure 1a), and to a lesser extent with a  
240 higher proportion of poorly crystalline aluminosilicates, such as allophane (Figure 1b).

241 The HA-H soils, more weathered and poorly drained, are characterized by a lower MP-OC/Stable-OC  
242 ratio (from 0.50 to 0.72; Table 1), and a lower contribution from poorly crystalline Fe-oxides (lower  
243  $\text{Fe}_o/\text{Fe}_d$  ratio; Figure 1a), to stabilize OC. Instead, the proportion of organically complexed Fe and Al  
244 are higher in these soils. This is indicated by a higher proportion of pyrophosphate-extractable Fe and  
245 Al (higher  $\text{Fe}_p/\text{Fe}_t$  and  $\text{Al}_p/\text{Al}_t$ ) in HA-H soils than in V-BA-GA soils (Figure 2a and 2b). These  
246 components contribute, as insolubilizing agents, to the stabilization of OC partly quantified in the pool  
247 of R-OC.

#### 248 3.2 Zinc concentrations and Zn isotope variations in soils

249 Zinc concentrations in Icelandic soils range from 96 to  $169 \mu\text{g.g}^{-1}$  (Table 1), and decrease with increasing  
250 total organic carbon content in soils (Figure 3). The Zn isotope composition ( $\delta^{66}\text{Zn}$ ) of the basalt is  $+0.21$   
251  $\pm 0.05\text{‰}$  (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  
252  $\delta^{66}\text{Zn}$  isotope compositions of soils are similar or heavier than the basalt at soil pH above 6, whereas  
253 below pH 6, the  $\delta^{66}\text{Zn}$  of soils are both heavier (HA) and lighter (H) than the basalt (Figure 4a).  
254 Importantly, the lighter  $\delta^{66}\text{Zn}$  of soils are found in those with a higher amount of organic carbon (Figure  
255 4b).

256

## 257 4. Discussion

### 258 4.1 Influence of mineral constituents on Zn isotope variations in soils

259 The parent basalt has a  $\delta^{66}\text{Zn}$  isotope composition ( $+0.21 \pm 0.05$  ‰; Table 1) well in agreement with the  
260 distribution reported for igneous rocks (excluding ultramafic rocks;  $+0.31 \pm 0.12$  ‰,  $n = 77$ ; Moynier  
261 et al., 2017). The  $\delta^{66}\text{Zn}$  isotope composition of the Icelandic soils (from  $+0.10 \pm 0.05$  to  $+0.35 \pm 0.02$   
262 ‰; Table 1), derived from basalt and aged  $\sim 10$  kyr old (Arnalds, 2008), is close to the range of  $\delta^{66}\text{Zn}$   
263 reported for volcanic soils derived from basalt with a similar age in Hawaii ( $+0.24$  to  $+0.41$  ‰ for soils  
264 of 0.3 and 20 kyr; Vance et al., 2016). More generally  $\delta^{66}\text{Zn}$  in Icelandic soils are within the range of  
265  $\delta^{66}\text{Zn}$  reported for soils in the literature ( $-0.2$  to  $+1.7$  ‰; Bigalke et al., 2013; Weiss et al., 2007; Viers  
266 et al., 2007; Aranda et al., 2012; Juillot et al., 2011; Aucour et al., 2015; Tang et al., 2012).

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

278 Zinc isotopes in soils may be fractionated by adsorption onto Fe-oxides (Juillot et al., 2008; Balistrieri  
279 et al., 2008; Pokrovsky et al., 2005), with heavy Zn isotopes being preferentially adsorbed at the surface  
280 of Fe-oxides. However, in Icelandic soils, there is no correlation between the  $\delta^{66}\text{Zn}$  of the soils and the  
281 Fe oxide content estimated from the  $\text{Fe}_d/\text{Fe}_t$  ratio ( $R^2 = 0.03$ ). There is no correlation either between the  
282  $\delta^{66}\text{Zn}$  of soils and the proportion of poorly crystalline Fe-oxides estimated from the  $\text{Fe}_o/\text{Fe}_d$  ratio ( $R^2 =$   
283  $0.02$ ), despite the fact that a higher fractionation factor is reported for poorly crystalline Fe-oxides than  
284 for crystalline Fe-oxides (Juillot et al., 2008; Balistrieri et al., 2008). Therefore, interaction between Zn  
285 and Fe-oxides appears not to be a major controlling factor on the Zn isotope variations in these soils.

286 Zinc isotopes in soils may also be fractionated by adsorption onto kaolinite (Guinoiseau et al., 2016).  
287 However, the clay fraction in these volcanic soils is dominated by poorly crystalline aluminosilicates  
288 such as allophane. Crystalline clay minerals such as smectite and kaolinite are only found in trace  
289 amounts in the HA (Opfergelt et al., 2014), and Zn adsorption onto kaolinite is likely limited in acidic  
290 soil conditions (Gu and Evans, 2008) such as in HA soil (pH 4.8 to 5.3; Table 1). Therefore, interaction  
291 between Zn and kaolinite is unlikely to be the main controlling factor on the Zn isotope variations in

292 these soils. Even if the fractionation factor has not been determined, Zn adsorption likely also occurs  
293 onto allophane. However, there is no correlation between the  $\delta^{66}\text{Zn}$  of soils and the  $\text{Si}_0$  content used as  
294 an indicator of the presence of allophane ( $R^2 = 0.04$ ). Therefore, interaction between Zn and allophane  
295 is not likely to control Zn isotope variations in soils.

296 The Zn isotope compositions of soils may also be affected by atmospheric contribution of Zn to the soil,  
297 either anthropogenic and/or natural. There is no local contamination from industry or urban areas in the  
298 vicinity of our site, indicating that Zn isotope fractionation in these soils is unlikely to be associated with  
299 polluted Zn sources (Borrok et al., 2009; Cloquet et al., 2006, 2008; Juillot et al., 2011; Sivry et al.,  
300 2008; Chen et al., 2008, 2009; Bigalke et al., 2010; Fekiacova et al., 2015). Atmospheric dust input on  
301 Icelandic soils is dominated by volcanic material mainly basaltic from volcanic ash deposition during  
302 eruption or resuspended volcanic material (Sigfusson et al., 2008; Arnalds et al., 2001; Wittmann et al.,  
303 2017). Volcanic ash input contributes to soil forming processes in Icelandic soils (Arnalds, 2008) and is  
304 characterized by a  $\delta^{66}\text{Zn}$  isotope composition similar to the one of the soil parent material. Atmospheric  
305 Zn input from rainfall and sea spray may also contribute to the soils. The Zn concentration in rain in  
306 Iceland can be considered as low (based on a Zn concentration of 5.7 ppb in Langjökull ice from the  
307 West Iceland glacier the closest to the site (Electronic Annex 1); it is the same order of magnitude as the  
308 Zn concentration in Greenland ice at 2.7 ppb) relative to the rain in Paris which contains between 11 and  
309 115 ppb Zn, most likely due to anthropogenic contamination (Chen et al., 2008). The Zn concentration  
310 in seawater producing sea spray is even lower (e.g., from 0.007 to 0.6 ppb; Bermin et al., 2006) with a  
311  $\delta^{66}\text{Zn}$  of 0.5 ‰ (e.g., Little et al., 2014). Relative to the total soil Zn reservoir (51 to 144 kg ha<sup>-1</sup>)  
312 calculated from the total Zn concentration in soil (96 to 169  $\mu\text{g}\cdot\text{g}^{-1}$ ; Table 1) and the bulk density of the  
313 soil (0.22 to 0.78 g cm<sup>-3</sup>; Opfergelt et al., 2014), a Zn contribution from rainfall and sea spray is  
314 considered as negligible and is not expected to affect the bulk soil  $\delta^{66}\text{Zn}$ .

#### 315 *4.2 Influence of vegetation uptake on Zn isotope variations in soils*

316 Light Zn isotopes are preferentially transported into aerial plant parts, therefore, the biological uptake  
317 of Zn by vegetation is a factor that may influence the  $\delta^{66}\text{Zn}$  in soils (Jouvin et al., 2012; Moynier et al.,  
318 2009; Weiss et al., 2005; Viers et al., 2007, 2015; Smolders et al., 2013; Couder et al., 2015; Tang et al.,  
319 2016; Caldelas and Weiss, 2017). The Zn concentration in Icelandic grass reported in the literature  
320 ranges from 14 to 85  $\mu\text{g}\cdot\text{g}^{-1}$  (e.g., Johannesson et al., 2007; Gudmundsson and Thorsteinsson, 1980).  
321 Considering a high Zn concentration in vegetation (i.e., 104  $\mu\text{g}\cdot\text{g}^{-1}$  for HA A1 as the topsoil litter; Table  
322 1), the yearly Zn uptake by vegetation ranges from 208 to 520 g Zn ha<sup>-1</sup> yr<sup>-1</sup>, taking into account the  
323 vegetation biomass produced (from 2 to 5 T ha<sup>-1</sup> yr<sup>-1</sup> for hay-making; Opfergelt et al., 2014; Arnalds et  
324 al., 2016). Relative to the total soil Zn reservoir (51 to 144 kg ha<sup>-1</sup>; as calculated in section 4.1), the Zn  
325 uptake in vegetation only represents 0.1% to 0.7% of the soil Zn reservoir, which indicates that the  
326 amount of Zn exported by harvested vegetation is not expected to affect the bulk soil  $\delta^{66}\text{Zn}$ .

327 *4.3 Contribution from organic matter to the Zn isotope variations in soils*

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

332 The part of the vegetation that returns to the soil and forms the litter contributes to the accumulation of  
333 organic matter in soils, and provides a source of light Zn isotopes from plant aerial parts. Considering a  
334 Zn concentration in the litter such as measured in the HA A1 litter ( $105 \mu\text{g}\cdot\text{g}^{-1}$ ; Table 1) and a maximum  
335 content in organic carbon of 30 % (higher organic carbon content in H O6; Table 1), if the total organic  
336 carbon content is considered as litter, then the Zn concentration in the organic carbon pool is estimated  
337 to be  $\sim 31 \mu\text{g}\cdot\text{g}^{-1}$ . This calculation suggests that in organic-rich soils, one third of the total soil Zn  
338 concentration ( $96$  to  $169 \mu\text{g}\cdot\text{g}^{-1}$ ; Table 1) may originate from the soil organic carbon pool accumulated  
339 from the litter. Therefore, organic matter accumulation is likely to contribute to the observed lighter Zn  
340 isotope composition in soils with increasing organic carbon content in HA-H soils (Figure 4b).

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

352 *4.4 Influence of the presence of stable organic carbon on Zn isotope variations in soils*

353 A key observation in each soil profile (HA, H, BA, GA, V) is that the higher the proportion of stable  
354 OC in the total organic carbon content, the lighter the Zn isotope composition in the soil (Figure 4c).  
355 The stable OC pool comprises organic matter associated with mineral constituents (mineral-protected  
356 organic carbon, MP-OC), and/or organic carbon intrinsically resistant to decomposition (recalcitrant  
357 organic carbon, R-OC) (Chenu and Plante, 2006; Mikutta et al., 2006). Previous work (Viers et al., 2015)  
358 suggests that the humification of litter (which mainly results in a pool of stable organic carbon  
359 intrinsically resistant to decomposition, R-OC; Berg and McLaugherty, 2008; Mikutta et al., 2005,  
360 2006) leads to release of the lighter Zn isotopes in solution and thus preserves the heavy Zn isotopes in  
361 the humification products such as aromatic structures. These findings are consistent with studies

362 showing that Zn adsorption and complexation with organic compounds or biological surfaces favour the  
363 heavy Zn isotopes (Jouvin et al., 2009, Gélabert et al., 2006; Wanty et al., 2013; Kafantaris et al., 2014).  
364 Accordingly, an increasing amount of stable OC, if driven by humification, should result in enrichment  
365 in heavy Zn isotopes in soils.

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

#### 378 *4.5 Implications*

379 This study suggests that the presence of stable OC in soils dominated by mineral-protected organic  
380 carbon is likely to favour the preservation of the Zn isotope signature of partially decomposed organic  
381 matter, and thereby contributes to form a sink of light Zn isotopes in soils. This suggests that the Zn  
382 isotope composition of the stable soil OC pool could be considered as an archive of an original organic  
383 matter Zn contribution to the soil, and may be preserved in erosive products of soils (Vance et al., 2016).  
384 Considering that organic carbon is also stabilized in other environments than soils such as lake or marine  
385 sediments, for example by association with mineral phases (e.g., Lalonde et al., 2012), and that light Zn  
386 isotopes may be delivered to sediments via uptake of light Zn by phytoplankton and settling particles  
387 (John et al., 2007; Peel et al., 2009), this study supports the finding that organic-rich sediments may well  
388 constitute a sink of light Zn isotopes (Little et al., 2016), and further suggests that this is likely to be  
389 partly due to a Zn pool associated with stable organic carbon, although direct field verification of this  
390 hypothesis requires further study of lake or marine sediments.

#### 391 **5. Conclusion**

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

397 organic carbon content.

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

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

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417

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701 **Figure captions**

702 **Figure 1.** Evolution of the proportion of mineral-protected organic carbon (MP-OC) in the stable organic  
703 carbon (Stable-OC) as a function of: (a) the proportion of oxalate-extractable Fe ( $Fe_o$ ) in the DCB-  
704 extractable Fe ( $Fe_d$ ), data in V soil not presented due to a potential contribution from magnetite  
705 dissolution to  $Fe_o$  (see methods section 2.2;  $Fe_o/Fe_d > 1$  in V); (b) the proportion of oxalate-extractable  
706 Si ( $Si_o$ ) in the total Si content in soils ( $Si_t$ ). Soil types: Histic Andosol, HA; Histosol, H; Haplic Andosol,  
707 BA; Gleyic Andosol, GA; Vitric Andosol, V.

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

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

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

718 **Table 1.** Characterization of soils and parent basalt: soil pH, total organic carbon content (OC), stable  
 719 OC including the mineral protected OC (MP-OC) and the recalcitrant OC (R-OC), Zn concentration and  
 720 Zn isotopic compositions (‰) ( $\pm$  2SD) in soils and basalt. The  $\delta^{66}\text{Zn}$  results are reported relative to the  
 721 JMC-Lyon-03-0749L. Soil types: Histic Andosol, HA; Histosol, H; Haplic Andosol, BA; Gleyic  
 722 Andosol, GA; Vitric Andosol, V.

Soil horizon	Depth	pH <sub>H<sub>2</sub>O</sub> <sup>a</sup>	Total OC <sup>a</sup>	Stable-OC		Zn	$\delta^{66}\text{Zn}$	2SD
				MP-OC <sup>b</sup>	R-OC <sup>b</sup>			
	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

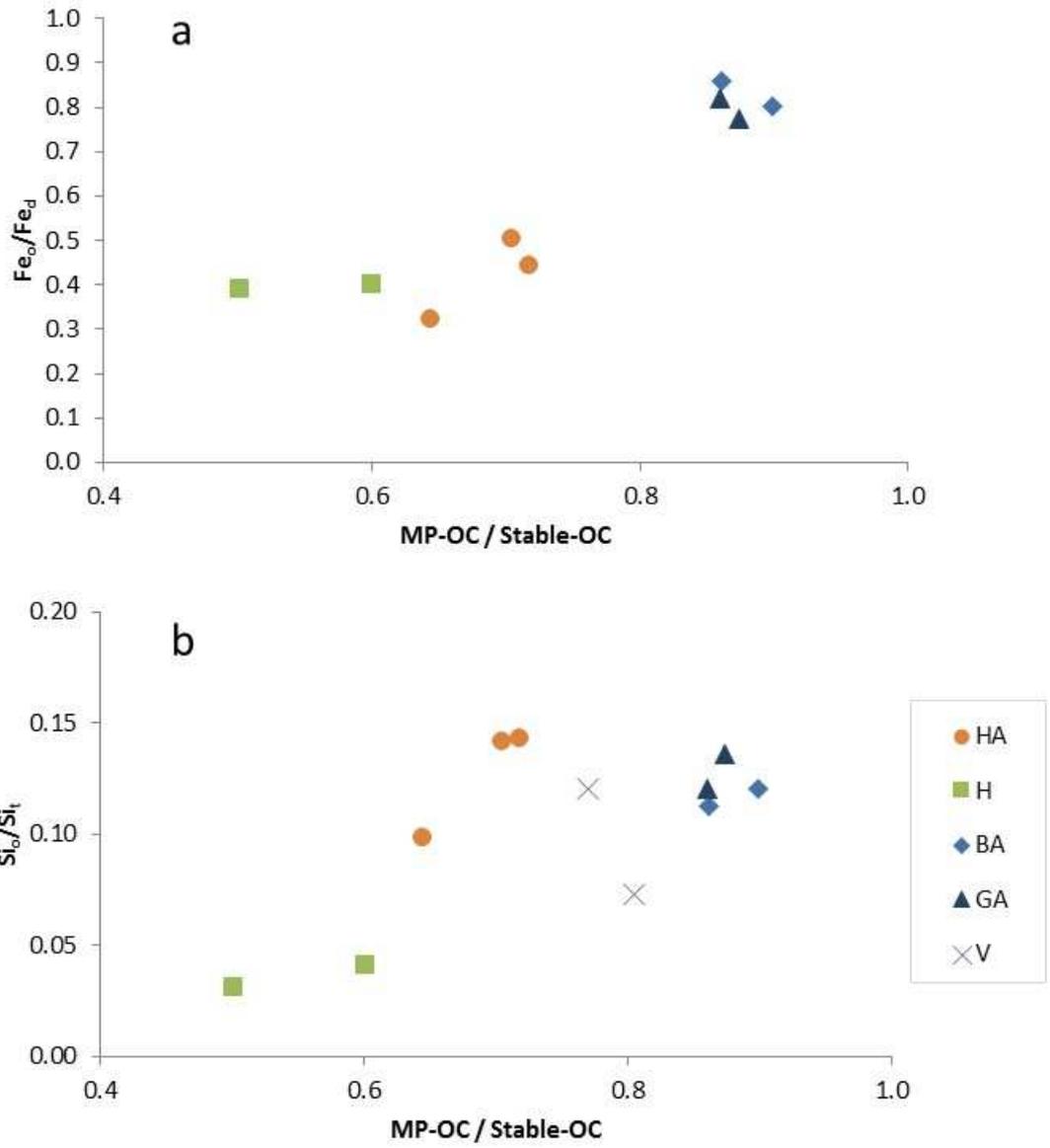
<sup>a</sup> data from Opfergelt et al., 2014

<sup>b</sup> Stable-OC = Mineral protected (MP-OC) + Recalcitrant (R-OC)

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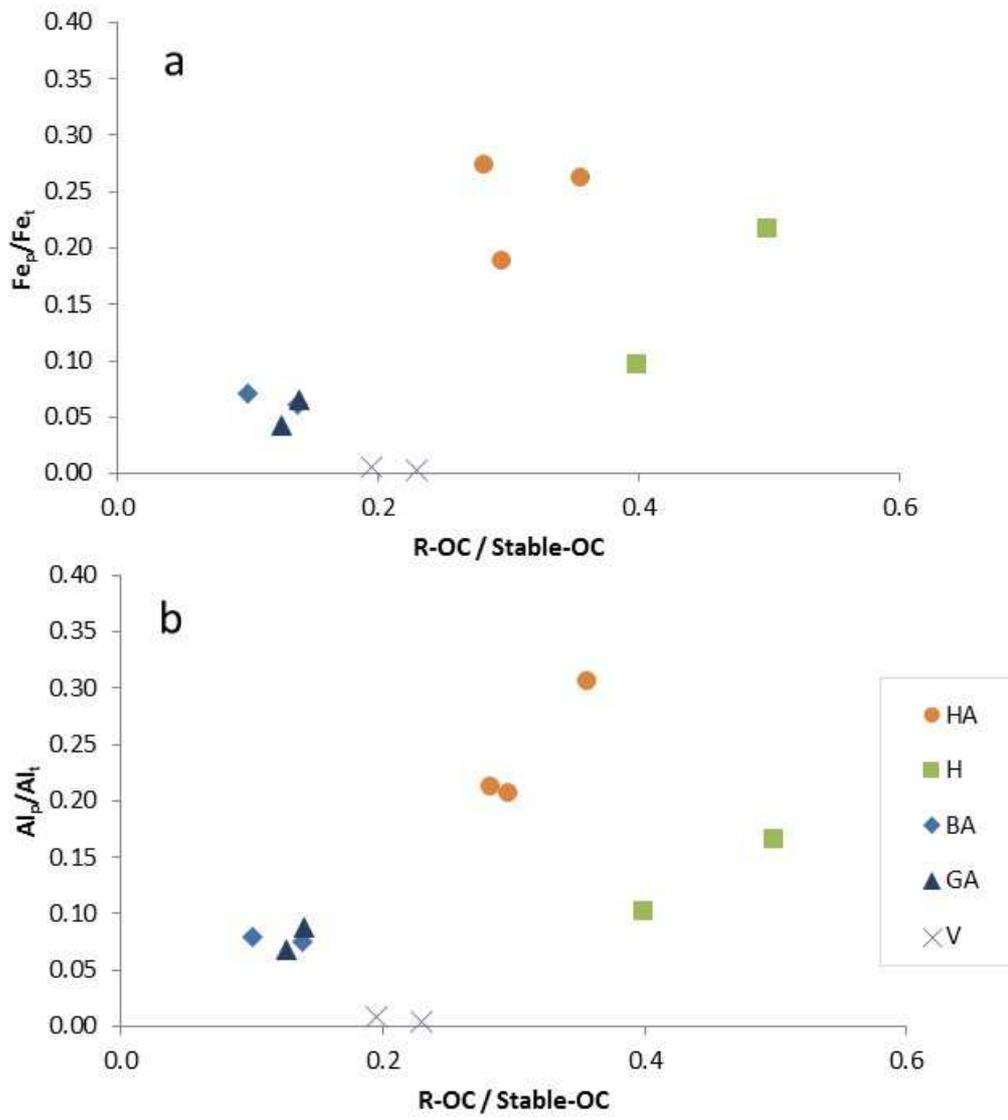
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728 Figure 1

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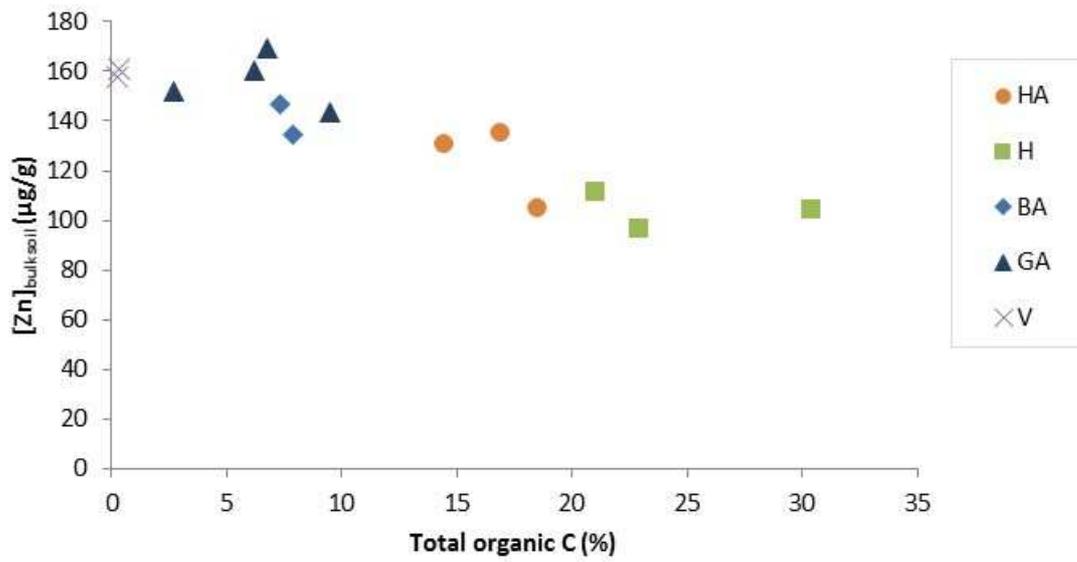


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732 Figure 2

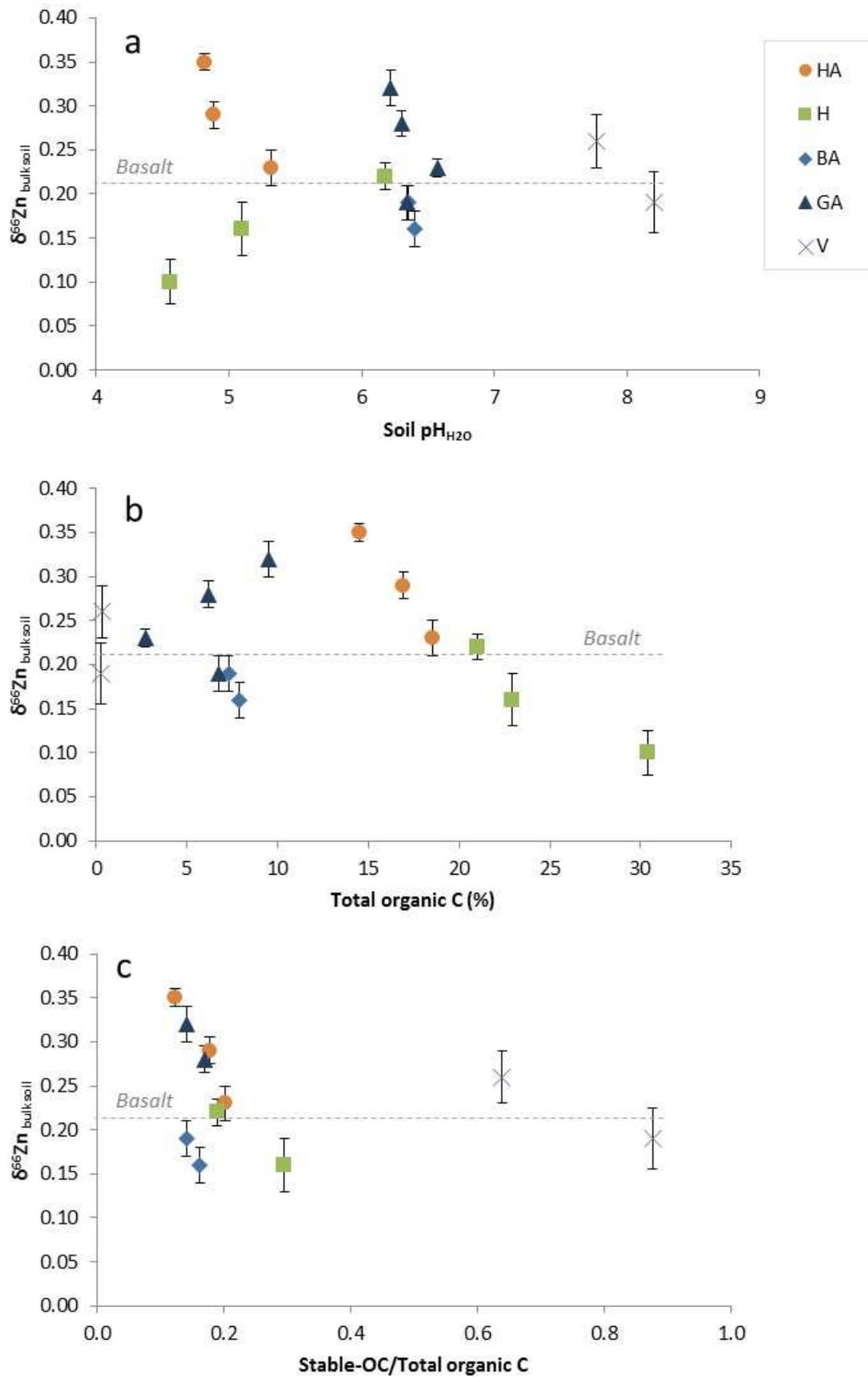
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736 Figure 3

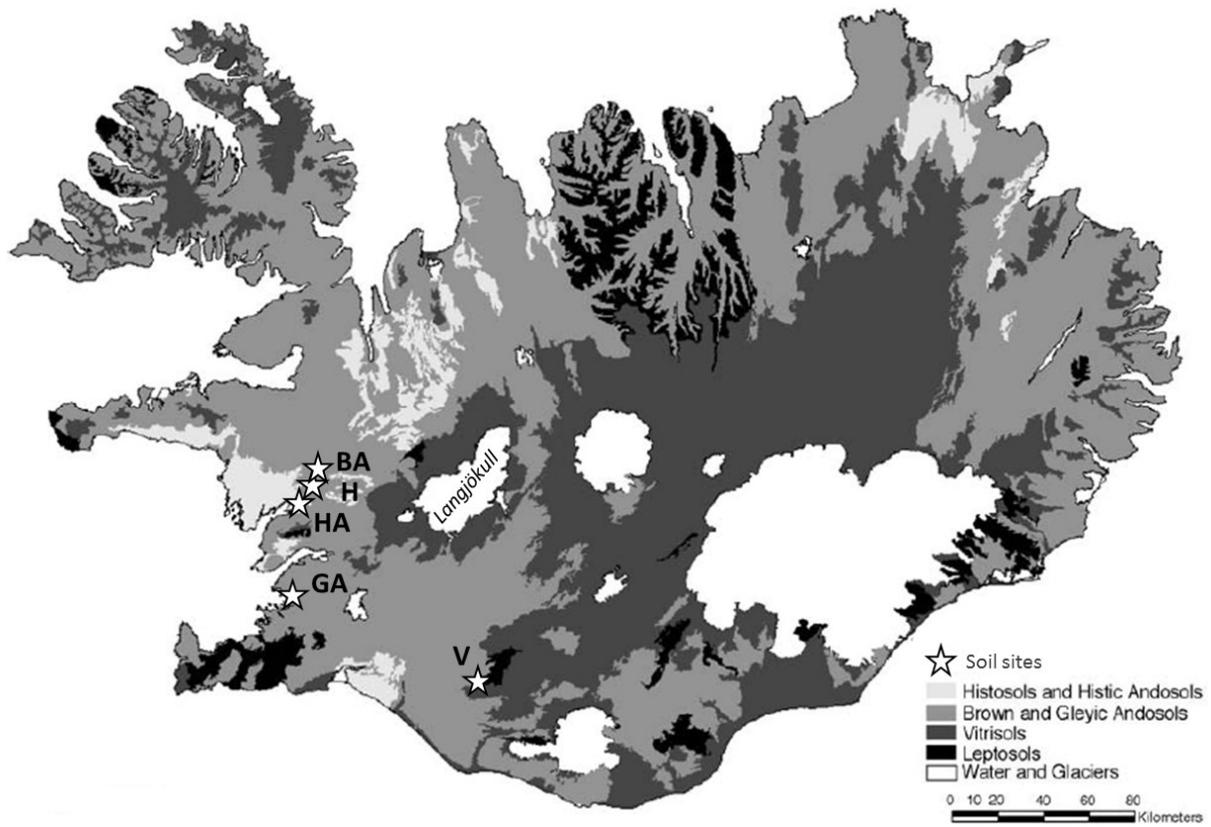


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738 Figure 4

739 **Electronic Annex 1.**

740 Location map of the soil sites (HA, H, BA, GA, V) in Iceland. Histic Andosol, HA; Histosol,  
741 H; Haplic Andosol, BA; Gleyic Andosol, GA; Vitric Andosol, V. Soil types are given according  
742 World Reference Base for Soil Resources (IUSS, 2014). The soil map is based on Arnalds  
743 (2004) and Arnalds and Gretarsson (2001).

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748 **Electronic Annex 2.**

749 Soil profiles description according to the World Reference Base for Soil Resources (IUSS, 2014). Histic  
 750 Andosol, HA; Histosol, H; Haplic Andosol, BA; Gleyic Andosol, GA; Vitric Andosol, V.

751

Soil ID	Horizon	Depth (cm)	Color (Munsell)	Texture	Structure	Limit with below horizon
HA	A1	0-15	7.5YR 3/4	silt loam	-	gradual and regular
	A2	15-26	7.5YR 4/4	silt loam	-	gradual and regular
	Bw1	26-40	7.5YR 3/3	silt loam	-	gradual and regular
H	O1	0-13	7.5YR 3/2	-	-	gradual and regular
	O2	13-26	7.5YR 3/2	-	platy structure	gradual and regular
	O6	72+	10YR 2/2	-	-	
BA	A1	0-21	7.5YR 3/3	silt	granular	gradual and regular
	A2	21-40	10YR 3/6	silt loam	granular/sub-angular blocky	gradual and regular
GA	A1	0-12	7.5YR 3/3	sandy loam	granular	gradual
	A2	12-29	7.5YR 2.5/3	silt loam	subangular/granular	abrupt and regular
	Bw2	43-56	10YR 4/3	sandy loam	fine to medium subangular blocky	abrupt and wavy
	C	56-64	5YR 3/4	-	fine to medium subangular blocky	abrupt and wavy
V	A	0-9	7.5YR 2.5/1	sand	-	gradual
	B/C	9-33	7.5YR 4/4 and 7.5YR 3/2	silt loam	-	abrupt
	C	33+	GLE2 2.5/10B	gravel	no structure	

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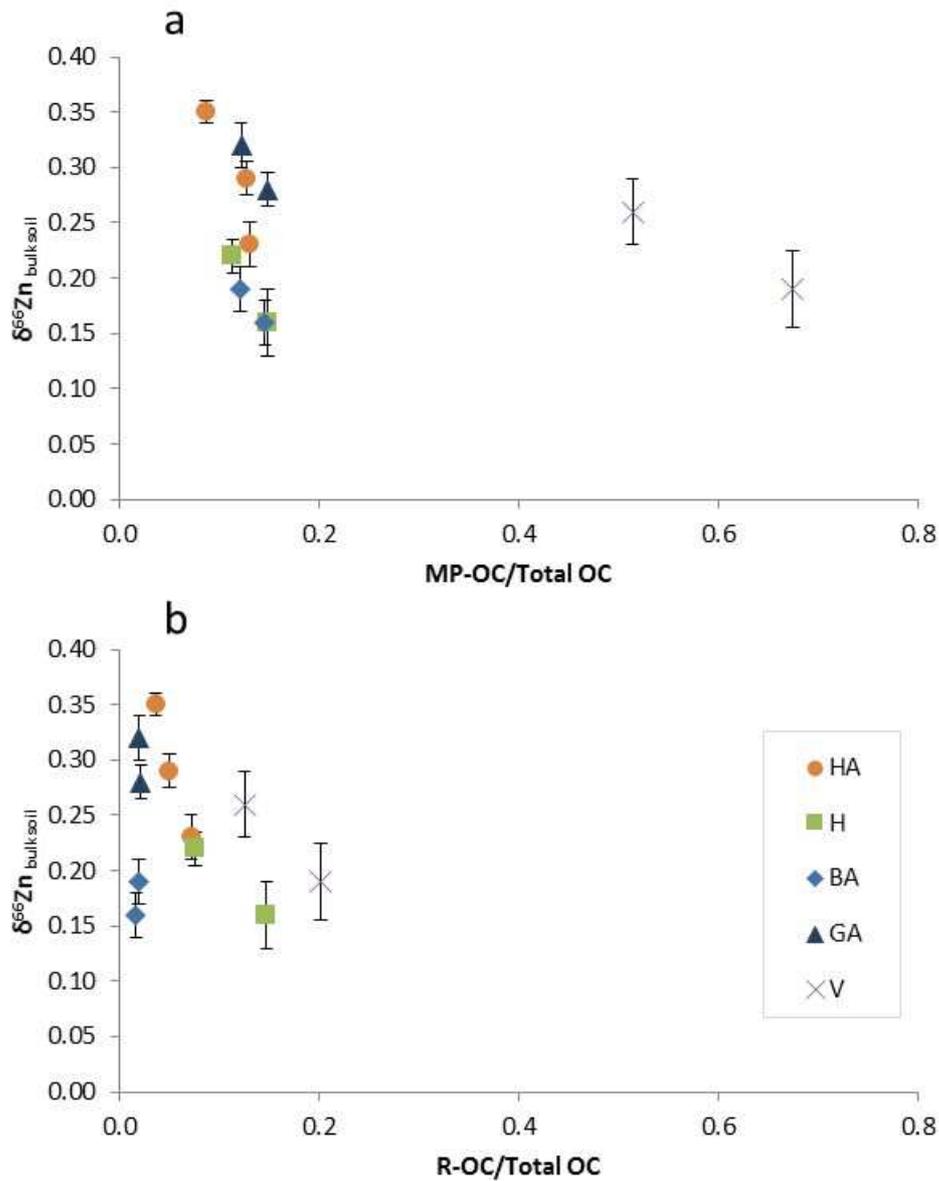
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756 **Electronic Annex 3.**

757 Evolution of the bulk soil Zn isotopic composition ( $\delta^{66}\text{Zn}$  in ‰,  $\pm 2\text{SD}$ ) as a function of: (a) the  
758 proportion of mineral protected organic carbon (MP-OC) in the total organic carbon pool; (b) the  
759 proportion of recalcitrant organic carbon (R-OC) in the total organic carbon pool. No data available for  
760 MP-OC and R-OC for H O6, GA Bw2, GA C. Soil acronyms as in Electronic Annex 1.

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