The behaviour of Cu and Zn isotopes during soil development: Controls on the dissolved load of rivers

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33 Highlights

- Light Cu, and unfractionated Zn, isotopes retained in oxic soils.
- Development of anaerobic conditions can lead to loss of this signature.
- Mineral aerosol addition and biological cycling overprint weathering processes.
- Oxic soils contain Cu-Zn isotopes complementary to riverine dissolved pool.
- Mass balance suggests ultimate fate of complementary soil signature in sediments.

39 Abstract

The stable isotopes of copper (Cu) and zinc (Zn) are finding increasing applications in surface Earth 40 geochemistry. An important early observation is that aqueous pools of Cu (rivers and oceans) are 41 isotopically heavier than rocks of the continental crust. For Zn, the global average δ^{66} Zn for rivers 42 is identical to estimates of the upper continental crust, but the oceans are slightly heavier. Here, we 43 study Cu and Zn abundances and isotopes in soils to assess how processes in the weathering 44 environment control isotopic values of rivers, and ultimately the oceans. We investigated a range of 45 soils developed on granitoid (Scotland) and basaltic (Hawaiian Islands) rock substrates, 46 representing soil development times from 0.1 to 400 kyr, mean annual temperatures of 6-16°C, and 47 48 mean annual precipitation (MAP) of 1060-5050mm.

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Soils developed on the island of Maui over 400 kyr and under high rainfall show the clearest 50 chemical weathering signatures. Here, in oxic soils, Cu and Zn are both depleted by 50-90%, with 51 preferential loss of heavy Cu (δ^{65} Cu up to 1.2% lower than parent material), and small shifts in 52 δ^{66} Zn. We attribute this to equilibrium fractionation between aqueous organic species that are 53 removed from the soil versus sorption to residual Fe-oxyhydroxides. In soils that are 0.1-150 kyr 54 old in Scotland and Hawaii, this same pattern is overprinted by biological cycling and the addition 55 of mineral aerosol Cu and Zn with heavier isotope compositions. In reducing soils on Maui, 56 developed under the highest rainfall, Cu and Zn are almost completely stripped from the soil, 57 leaving a very small residual pool with δ^{65} Cu and δ^{66} Zn values that range from those for the oxic 58 59 soils back to and beyond parent material. This removal of the light sorbed Cu seen in oxic soils is attributed to the dissolution of Fe oxides under anaerobic conditions, perhaps microbially mediated, 60 leaving a very small residual isotopically heavier pool. 61

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Overall these data suggest that processes in soils create significant variability in Cu isotopes, with the heavy isotope exported from oxic soils. In contrast, small isotope fractionations of Zn are generated in the soil environment. These observations are consistent with those made previously for Cu and Zn isotopes in rivers. But the maximum amount of Cu and Zn stored by world soils equates to only 30-130 years of the dissolved riverine flux. Soils cannot be the ultimate repository of the residual Cu and Zn required to balance the riverine flux, and this must ultimately reside in the erosive products of soil formation in continental and ocean margin sediments.

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71 Keywords: chemical weathering, geochemistry, metal stable isotopes, soils, rivers.

73 **1. Introduction**

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75 The dissolved pool of the transition metals in rivers and the oceans is almost always isotopically heavy relative to the rocks of the continents. This observation was first made for molybdenum (Mo) 76 77 isotopes in the oceans (e.g. Barling et al., 2001; Nakagawa et al., 2012), and was followed up by the 78 same finding for Mo in world rivers (Archer and Vance, 2008; Neubert et al., 2011; Voegelin et al., 79 2012). Since then the same observation has been made for Cu and Ni isotopes in rivers and 80 seawater (Vance et al., 2008; Cameron and Vance, 2014; Takano et al., 2014; Thompson and Ellwood, 2014). In contrast, a recent survey of Zn isotopes in large and small rivers (Little et al., 81 2014a) finds a global discharge-weighted flux to the oceans that is indistinguishable from estimates 82 of the isotope composition of the upper continental crust. Archer and Vance (2008) discussed two 83 possible causes of the heavy metal isotope composition of rivers: isotope fractionation in soils due 84 to the retention of light isotopes on Fe-Mn oxyhydroxide surfaces in soils, analogous to the process 85 driving the oceans towards heavy Mo isotope compositions (Barling an Anbar, 2004; Wasylenki et 86 al., 2011), or the sorption of light isotopes to oxyhydroxides during transport in rivers themselves. 87 Though these authors favoured the former explanation, a significant problem lies in the size of the 88 89 light reservoir in global soils that is required to balance the dissolved riverine flux of heavy metal isotopes. Vance et al. (2008), in addition to documenting heavy Cu isotope compositions dissolved 90 91 in rivers, also showed that light isotope compositions in the particulate phase in one small river roughly balanced the dissolved pool, and suggested that this Cu isotope separation resulted either 92 93 from partitioning of the heavy isotope into strong organic complexes in the dissolved pool or a postulated preference of Fe-Mn oxyhydroxides for the light isotope, or both acting together. 94

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96 Whether isotope separation of the transition metals predominantly occurs in rivers or not, it almost 97 certainly begins in soils. Our focus here is Cu and Zn isotopes, with their contrasting behaviour in 98 rivers noted above. Studies of Zn isotopes in soils have partly focused on their potential utility as tracers of anthropogenic contamination (e.g. Weiss et al., 2007; John et al., 2007; Chen et al., 2008; 99 Sivry et al., 2008; Thapalia et al., 2010; Juillot et al., 2011), and this may be a confounding factor in 100 any attempt to understand natural processes such as chemical weathering. Viers et al. (2007) 101 conducted a study of Zn isotopes in a "pristine" tropical watershed in Cameroon and found 102 significant isotope variation that was attributed to natural abiotic and biological processes. Cu is 103 probably less prone to anthropogenic effects in environmental samples (e.g. Chen et al., 2014). 104 105 Bigalke et al. (2010a) studied Cu isotopes in soils variably affected by stagnant water, including features such as variations in non-crystalline Fe oxides within the profile. They observed a 106

transition from light isotope enrichment to heavy isotope enrichment as water-logging led to anaerobic conditions. Bigalke et al. (2011) studied oxic Cambisols and Podzols, again documenting significant Cu isotope fractionation, with δ^{65} Cu between -0.57 and +0.44‰.

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Here we present data for soil profiles from Hawaii and Scotland, covering both granitoid and 111 basaltic substrates, incorporating a range of soil development times from 0.1-400 kyr, and a range 112 of mean annual rainfall amounts, from ~1100-5000mm. Our large-scale objective is to assess the 113 extent to which Cu and Zn isotope behaviour in soils are consistent with the riverine data outlined 114 above. In doing so, however, we document the variety of processes in these soils that control Cu 115 116 and Zn and their isotopes: not just the impact of removal by weathering but also the effects of redox 117 transitions on sorption substrates, organic ligands, and atmospheric addition of these metals. Our results confirm the role of both aqueous organic complexes and Fe-Mn oxyhydroxides in 118 119 controlling the isotopic composition of Cu and Zn retained in soil and released to rivers.

120

121 2. Settings and samples

122

Samples for this study derive from two well-studied field locations, representing contrastinglithologies, soil development times, and climate (Figures 1 and 2).

125



126 2.1 Glen Feshie chronosequence, Scotland

Figure 1: Schematic of the Glen Feshie soil profiles studied here, with their ages and soil types at the top. Soil types,
horizons and ages from Bain et al. (1993) and Hodson et al. (1998). Depth scale at left is in cm.

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The *Glen Feshie chronosequence* (Fig. 1) is developed on a generally "granitoid" substrate in Glen
Feshie, Scotland, UK. Glen Feshie is a north-south trending valley (57°02'N, 3°53'W) forming the

¹²⁷

western boundary of the Cairngorm Mountains in the Scottish highlands. The climate is "sub-133 arctic" (Helliwell et al., 1998), with mean monthly temperatures ranging from 1.2°C in February to 134 10.3°C in July, and mean annual precipitation of ~1100mm. The soil chronosequence is developed 135 on four alluvial terraces deposited since the deglaciation of Scotland at ~13 ka. It was identified by 136 Robertson-Rintoul (1986b) who identified 5 different clusters of soils, each corresponding to a 137 terrace formation event. The chronosequence is well characterised for chemistry, mineralogy, 138 weathering rate and texture (Bain et al., 1993; Hodson et al., 1998; Hodson and Langan, 1999; Lee 139 et al., 2008). Maximum durations of soil development on the alluvial terraces have been estimated 140 141 by ¹⁴C dating and soil stratigraphy, and give a range in age for the four studied profiles of 0.1 - 13ka (in radiocarbon years, Bain et al., 1993). The three youngest soils are classified as fluvisols and 142 the oldest as a humo-ferri podzol, according to the FAO classification (Hodson et al., 1998). 143

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The parent material of the chronosequence is predominantly psammitic schist with a small granitic 145 component (10-15%; Roberston-Rintoul, 1986a). Each of the terraces in the chronosequence are 146 considered to share similar parent materials based upon C-horizon chemistry (Bain et al., 1993). As 147 148 the terraces are alluvial in origin the parent material is likely to have undergone weathering during erosion of the original rock and transport of the gravels prior to deposition. The extent of this 149 150 weathering is unknown, but it is expected to have affected the parent material of each chronosequence member to the same extent. Textural evidence suggests minimal weathering of 151 primary biotite occurred during transport of alluvium in Glen Feshie as biotite grains are still clearly 152 visible in river alluvium samples, mica is abundant in the clay fraction, and no vermiculite (the 153 weathering product of biotite), is observed in the youngest soil (0.1 ka; Bain et al., 1993). 154 Vegetation is dominated by dry Calluna moor of Calluna vulgaris, Vaccinium myrtillus and 155 hypnaceous mosses with additional lichen rich Calluna moor, Agrostis-Festuca acid grassland and 156 Betula woodland (Robertson-Rintoul, 1986a). 157

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159 2.2 Chronosequence and climosequences, Hawaiian Islands

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We have analysed a variety of soil profiles from the Hawaiian Islands, all having a basalticsubstrate but varying in soil development times and climate (Fig. 2).



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Figure 2: Schematic of Hawaiian soil profiles studied, representing a range of different ages and mean annual rainfalls,
but all developed on a basaltic substrate (see text for sources of data). The age gradient from 0.3-150 kyr at 2500mm is
part of the LSAG chronosequence (Crews et al., 1995). Note that the top 25 cm of the 1 m profile sampled at
Laupahoehoe consists of a younger less weathered 5 ka ash lying on top of ca 20 ka tephra (Kennedy et al., 1998;
Chadwick et al., 2009). Depth scale at left is in cm. The 0-150 kyr soils are Andisols (Pett-Ridge et al., 2007) while the
400 kyr Maui soils are classified as (Schuur et al., 2001): Inceptisol (Maui 2 and 6) and Andisol (Maui 4).

172

The Long Substrate Age Gradient (LSAG) chronosequence was established by Crews et al. (1995) 173 and well characterized by subsequent studies (Chadwick et al., 1999; Chorover et al., 1999; 174 Hotchkiss et al., 2000; Kennedy et al., 1998; Kurtz et al., 2000; Kurtz et al., 2001; Vitousek, 2004; 175 Monastra et al., 2004; Torn et al., 1997; Pett-Ridge et al., 2007). The chronosequence consists of 176 six sites located on the islands of Hawaii, with substrate soil ages ranging from 0.3 ka to 4.1 Ma. In 177 the present study, Cu and Zn isotope compositions and soil chemistry were examined at three of 178 these soil sites on the island of Hawaii (Fig. 2). The three studied profiles, Ola'a (0.3 ka), 179 Laupahoehoe (~5-20 ka) and Kohala M (~150 ka) formed at similar conditions of ~ 1200m 180 elevation, minimal slope gradient (6%), 2500 mm present-day rainfall and 16°C surface 181 temperatures. The Ola'a soil volcanic substrate is tholeiite, while the Laupahoehoe soil substrate is 182 late-stage alkaline basalts (hawaiite and mugearite). The Kohala M site (150 ka) (Fig. 2) is in a 183 pasture and is similar to, but not the exact Kohala site sampled along the LSAG. The specific 184 185 samples studied here are from the same profiles documented in Pett-Ridge et al. (2007).

The tephra substrates of these soils have ages of 0.3 ka (Ola'a rainforest, Kilauea), 5-20 ka 187 (Laupahoehoe Volcanics, Mauna Kea), and 150 ka (Hawi Volcanics, Kohala M). The uncertainties 188 surrounding the exact ages of the parent material for these sites are discussed in Vitousek (2004). 189 An age of 2.1 ka was originally assigned to the Ola'a site, but a later re examination determined that 190 the soil is developed on a 0.3 ka ash-fall (Keanakakoi Ash) on top of a 2.1 ka substrate (McPhie et 191 al., 1990). Laupahoehoe soils are formed on a tephra deposit that is at least 2-3 m thick and is a 192 cumulic deposit consisting of several buried soils. The top 25 cm of the 1 m profile sampled in this 193 study consists of a younger less weathered 5 ka ash lying on top of ca 20 ka tephra (Kennedy et al., 194 195 1998; Chadwick et al., 2009). The Kohala M site is also part of the rainfall gradient studied by 196 Teutsch et al. (1999) and Chadwick et al. (2003). The profile studied here is described in Chadwick 197 et al (2003).

198

Ola'a, Laupahoehoe and Kohala M all receive approximately 2500 mm yr⁻¹ of orographic rainfall, 199 200 dominantly associated with northeasterly trade winds. Soil sites older than 20 ka have been subject to cooler and drier conditions than present due to changes in the elevation of the inversion layer and 201 202 island subsidence (Hotschkiss et al., 2000). Based on data published for the climosequence on Maui by Schuur et al. (2001) (see Chadwick and Chorover, 2001; Pett-Ridge et al., 2007), Eh conditions 203 204 in the present-day soils are estimated at ~ 400 ± 100 mV. Soil mottling suggests that, though the 205 soils are well aerated most of the time, they are subjected to occasional declines in Eh values during and after high rainfall events. The Ola'a and Laupahoehoe sites were sampled in intact rainforest 206 composed of a dominant canopy tree, O'hia (Metrosideros polymorpha), whereas the Kohala soil 207 was sampled in a pasture site whose forest had been cleared about 100 years ago. 208

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Though the Hawaiian Islands are remote from potential dust sources, previous mineralogical, 210 chemical and isotopic studies have documented significant additions of trace elements in Hawaiian 211 soils due to long-range atmospheric transport and deposition of Asian dust (e.g. Kennedy et al., 212 1998; Teutsch et al., 1999; Kurtz et al., 2001; Stewart et al., 2001; Huh et al., 2004; Monastra et al., 213 2004; Scribner et al., 2006; Pett-Ridge et al., 2007; Chadwick et al., 2009; Mikutta et al., 2009). 214 215 These studies show that atmosphere-transported metal input may account for a large, or even dominant, portion of the overall metal budget in 150 kyr soils. For example, the Laupahoehoe and 216 217 Kohala M soils have up to 15% and 40% quartz, respectively, with smaller amounts of mica and Kfeldspar, accumulated from eolian sources (Kurtz et al., 2001). 218

219

220 In addition to the profiles described in detail above, we have also studied a low rainfall site

(1060mm), also 150 kyr in age, at Kohala (Kohala H) (Chadwick et al., 2003). This soil profile is
developed on the same alkali basalt substrate as Kohala M, and over the same length of time (150 kyr), thus creating a two-point climosequence at this age for comparison with a wetter
climosequence on Maui.

225

The Maui climosequence consists of soil profiles developed on the 410 kyr shield-building Kula 226 Volcanic Series on the northwest slope of Haleakala, is described in detail by Miller et al. (2001), 227 Schuur et al (2001a,b), Scribner et al. (2006), and has previously been the subject of iron and 228 229 molybdenum isotope studies (Thompson et al., 2007; Siebert et al., 2015). Soil elevation is 230 ~1300mm and <5% slopes lead to low erosion rates and timescales of pedogenesis similar to the age of the underlying basalt. Mean annual temperatures are ~16°C. Three of the 8 sites across the 231 full rainfall gradient are studied here: Site 2 (mean annual precipitation = 2450mm), Site 4 232 (3350mm) and Site 6 (5050mm). These precipitation levels, as well as differences between sites, 233 234 have probably persisted throughout the Holocene (Hotchkiss et al., 2000; Chadwick et al., 2003). The sites have undisturbed native forest dominated by the same single tree species as for the LSAG 235 236 chronosequence, Metrosideros polymorpha.

237

238 A particular feature of the Maui sequence (see Fig. 2) is a well-characterized redox gradient and its impact on the fate of oxidized Fe minerals (Schuur et al., 2001; Thompson et al., 2011). At the 239 lowest rainfall Site 2, the relatively well-drained soils contain abundant Fe(III) minerals. At rainfall 240 levels around 3000mm a redox threshold is crossed leading to waterlogged soils, so that sites 4 and 241 6 are characterized by periods of suboxic conditions leading to mobilization of the oxidized Fe via 242 reductive dissolution of Fe oxyhydroxides (Chadwick and Chorover, 2001; Miller et al., 2001). Soil 243 organic matter content increases across this redox gradient, as degradation is suppressed in 244 anaerobic conditions, from about 15% carbon at Site 2 to about 25% at Site 6 (Schuur et al., 2001). 245 Addition of material via mineral aerosol dust is also a potential complication for these old soils. 246 Profiles of quartz (absent from basaltic parent rock) concentrations show a sharp maximum in 247 quartz concentrations (22 wt%) at 10 cm at Site 2, but very low concentrations elsewhere in this 248 249 profile. At the wetter sites this peak is less pronounced (about 18% at Site 4 and about 13% at Site 6) but significant concentrations of quartz persist further down the profile (50cm at Site 4 and 80 250 251 cm at Site 6).

252

253 **3. Methods**

Glen Feshie soils were sampled (~1 kg) from each soil horizon at the same locations as in Bain et 255 al. (1993). Soil samples were dried at 60°C for 48 hours and sieved at 2mm. A representative 256 257 sample of the fine fraction (10-15g) was taken and powdered in an agate mill. River alluvium 258 samples were collected from the river bed using a clean trowel, and rock samples from outcrop on 259 the valley floor. The alluvium was collected at Glen Feshie because it will be closer to the parent material of the soils, which are developed on alluvial terraces. Rock and alluvium samples were 260 crushed to sub-mm size in a jaw crusher. A representative (10-15g) aliquot of all samples was then 261 taken and powdered in an agate mill. Plant samples (Heather (*Calluna vulgaris*) and common grass) 262 263 were also collected from the 1 and 13 kyr sites. Plant samples were separated into root, stem and 264 leaf fractions for Cu and Zn isotope analysis, cleaned with 18.2Mohm MQ water and dried at 60°C 265 for three days. Finally, samples of the River Feshie were collected for dissolved load analysis, in low-density poly-ethylene bottles. Water samples were immediately filtered at 0.2 µm and acidified 266 to pH 2 prior to storage. Hawaiian soil samples, 6-8 samples per profile, come from pits down to 267 bedrock or 1m, were sieved at 0.2mm, and dried at 105°C for 48 hours (Pett-Ridge et al., 2007; 268 269 Scribner et al. 2006).

270 Soil, river alluvium and rock samples were digested on a hotplate with a 4:1 mixture of 271 concentrated HF and HNO₃. Plant samples were also dry-ashed at 500°C, before digestion using 272 HNO₃, H₂O₂ and HCl. River Feshie water samples were evaporated to dryness and the residue re-273 dissolved in concentrated nitric acid to oxidise organic matter. Procedures for the major and trace element analysis of rocks, soils and waters in our laboratory, as well as those for the isotopic 274 analysis of Cu and Zn, have been thoroughly documented in previous publications (e.g. Archer and 275 Vance, 2004; Vance et al., 2008; Little et al., 2014a). Only a brief summary is given here. An 276 aliquot of each sample was taken for major and trace element concentration analysis, on a Thermo-277 Fisher Element XR sector-field inductively-coupled-plasma mass spectrometer at ETH Zürich. 278 279 Measured intensities were converted to concentrations using a single-point calibration relative to an 280 in-house primary standard, using indium-doping for internal standardisation. Accuracy and precision were assessed using two secondary multi-element standards: National Research Council 281 282 of Canada river standard SLRS5, and USGS shale standard SGR1. The concentrations obtained 283 matched certified values to within 5-10% for most of the elements of interest here. For Pb we obtain a value for SLRS5 (but not SGR1) that is 20% lower than the certified value (c.f. some but not all 284 285 laboratories in the Yeghicheyan et al., 2013 compilation). Two sigma uncertainties for repeat 286 analyses of these standards during the period when the samples studied here were run (n = 14 for 287 both standards) were less than 7%, except for Nb (11-15%).

Following concentration analysis an aliquot of the remaining solution was doped with a ⁶⁴Zn-⁶⁷Zn 288 double spike (Bermin et al. 2006; Zhao et al., 2014), and Cu and Zn purified using a two-stage 289 anion-exchange via the Bio-Rad AG MP-1M resin, using procedures described in detail previously 290 291 (Archer and Vance, 2004; Vance et al., 2008; Little et al., 2014a), and including data for standard reference materials. Isotopic analyses were performed using a ThermoFinnigan Neptune multi-292 293 collector inductively-coupled-plasma mass spectrometer (MC-ICP-MS) at the University of Bristol. Cu was introduced to the mass spectrometer using a glass spray-chamber (Stable Introduction 294 System, Elemental Scientific Inc, Omaha, NE, USA) and instrumental mass discrimination was 295 296 corrected using standard-sample bracketing (Archer and Vance, 2004; Vance et al., 2008; Little et 297 al., 2014a). Zinc isotopes were introduced using an Aridus, and mass discrimination corrected using the double spike (Bermin et al. 2006; Zhao et al. 2014). All Cu and Zn isotopic compositions are 298 299 given in standard notation as follows relative to the NIST SRM976 and JMC Lyon Zn standards 300 respectively:

301
$$\delta^{65} \text{Cu} = 1000 \left[\frac{({}^{65} \text{Cu}/{}^{63} \text{Cu})_{\text{sample}}}{({}^{65} \text{Cu}/{}^{63} \text{Cu})_{\text{SRM976}}} - 1 \right]$$

302
$$\delta^{66} Zn = 1000 \left[\frac{\left({}^{66} Zn / {}^{64} Zn \right)_{\text{sample}}}{\left({}^{66} Zn / {}^{64} Zn \right)_{\text{Lyon JMC}}} - 1 \right]$$

303 Long-term reproducibility of isotopic analyses were $\leq 0.09\%$ and $\leq 0.07\%$ for Cu and Zn respectively. This was assessed for Cu based on repeat measurements of a secondary standard 304 (standard AM, measured at Bristol, Jerusalem and Zurich and with $\delta^{65}Cu = +0.11$). Zn 305 reproducibility was assessed through repeat analyses of spiked JMC Lyon standards (mean δ^{66} Zn = 306 $0.01\% \pm 0.07$ ($\pm 2\sigma$; n=57)). In addition, during the course of this study we performed duplicate 307 analyses of 11 various soil samples for Cu and Zn isotopes (completely separate digestion and 308 309 analysis), though 9 of these were sequential extractions with the attendant variability associated with the leaching process. Despite this the average reproducibility was ± 0.11 for both δ^{65} Cu and 310 δ^{66} Zn. Internal errors obtained from the mass spectrometric analysis were always substantially 311 lower than long-term reproducibility, and it is the latter that is given as the uncertainty in the 312 footnotes to the tables in this paper. Procedural blanks for sample digestion and Cu and Zn 313 314 separation were <1ng and 2ng respectively, with mean isotopic compositions of 0.0% and +0.3% 315 respectively. These blanks would lead to insignificant corrections to sample isotopic compositions 316 and none were applied.

In order to quantify net loss or gain of an element relative to the parent material, in a procedure that eliminates the impact of density changes during soil development, we use the tau parameter (τ) of Chadwick et al. (1990). This is defined as the fraction of an element of interest (*i*) lost from, or added to, a soil horizon relative to an immobile index element (*j*):

321
$$\tau_{ij} = \left[\frac{(C_i/C_j)_h}{(C_i/C_j)_p} - 1\right]$$

where C is concentration, subscript h refers to the soil horizon under consideration and subscript p 322 to the concentration in the unweathered parent material. Tau values greater than zero denote 323 addition of the element of interest relative to the immobile element and values less than zero loss. 324 Integrated tau values for the entire soil profile can identify net additions - or loss - from the soil 325 profile as a whole. In our calculation of integrated tau we include the O horizon because plant 326 growth should not add Cu or Zn to the soil, merely relocate them. A detailed study of Hawaiian 327 soils (Kurtz et al., 2000) identified niobium (Nb) as the least mobile element, so we use it here for 328 both Hawaii and Scotland. This approach assumes that a good estimate of the chemistry of the 329 330 parent material is available. In the case of the Glen Feshie soils studied here, the fact that they probably underwent an earlier cycle of erosion and weathering before the material was deposited on 331 the current river terraces suggests that local rocks may not be an appropriate reference. Thus, we 332 choose here to reference to samples of river alluvium collected from the river draining the valley 333 where the soils occur. For the Hawaiian samples, parent rock major elements and Nb values come 334 from previous soil studies. - Ziegler et al. (2005) for LSAG, Scribner et al. (2006) for Maui. Cu, Zn, 335 Mn and Pb concentrations derive from analyses of tholeiitic and alkali basalts in the literature, as 336 detailed later in the appropriate tables. 337

Sample	Horizon	Depth (cm)	τ _{Na} ¹	τai	τ _{Fe}	τ _{Mn}	τρ	τрь	[Cu] ppm	τ _{Cu}	δ ⁶⁵ Cu ³	[Zn] ppm	τzn	δ ⁶⁶ Zr
0. 1 kvr							-					•		
641	Ah	2.5	-0.23	-0 17	0.01	0.32	0.23	0.00	36	0.15	-0.26	24	0.03	0.25
642	BC	6.5	-0.32	-0.28	-0.10	0.14	0.34	-0.19	2.4	-0.15	-0.37	17	-0.19	0.26
643	C	25	-0.19	-0.13	0.06	0.17	0.30	-0.14	3.4	-0.10	-0.34	27	-0.05	0.27
Integrated			-0.20	-0.14	0.05	0.19	0.30	-0.12		-0.07	-0.33		-0.04	0.27
1 kvr														
659	АН	5	-0.57	-0.53	-0.30	-0.36	0.07	-0.16	53	-0.06	0.03	24	-0 41	0.30
660	B(s)	15.5	-0.12	-0.17	0.02	-0.11	0.27	-0.10	4.8	0.35	-0.33	23	-0.12	0.30
661	C	45	0.01	-0.04	0.10	-0.03	0.29	-0.10	4.4	0.26	-0.26	25	-0.05	0.35
Integrated			-0.07	-0.12	0.04	-0.08	0.26	-0.11		0.24	-0.23		-0.10	0.34
2 (hum			0.07	0.12	0.01	0.00	0.20	0011			0.20		0110	0.0
5.0 Kyr		2.5	0.27	0.17	0.51	0.50	5.24	5 50	5.0	5.01	0.24	11	1.00	0.12
644	Н	5.5	-0.27	-0.1/	-0.51	-0.50	5.54	5.50	5.0	5.91	-0.24	11	1.00	0.13
045	AE D(a)	13	-0.51	-0.24	0.25	0.49	0.77	-0.13	4.1	0.20	-0.37	1/	-0.28	0.12
040	B(S)	30 57	-0.13	-0.10	0.15	-0.30	0.33	-0.14	5.9	0.09	-0.33	30	0.12	0.30
64 /	C	57	-0.10	-0.13	0.08	-0.13	0.24	-0.15	4.0	0.13	-0.36	27	0.04	0.32
Integrated			-0.14	-0.14	0.08	-0.11	0.62	-0.14		0.14	-0.35		0.01	0.29
13 kvr														
653	Н	3	-0.47	-0.36	0.00	-0.54	1.81	3.01	2.8	0.74	-0.15	14	0.16	0.07
654	AEh	13	-0.47	-0.23	0.23	-0.57	0.80	0.22	3.0	0.17	-0.06	18	-0.06	0.21
655	Bhs	25	-0.42	-0.23	-0.02	-0.61	0.05	-0.16	2.6	-0.16	-0.37	18	-0.22	0.17
656	Bs	45	-0.31	-0.03	0.50	-0.49	-0.12	-0.24	4.1	0.16	-0.26	27	0.01	0.22
657	BC	75	0.04	0.05	0.24	-0.28	-0.54	-0.05	4.9	0.69	-0.22	20	-0.07	0.33
658	С	102	-0.03	-0.05	0.12	-0.32	-0.54	-0.05	5.4	0.68	-0.26	21	-0.13	0.25
Integrated			-0.19	-0.07	0.23	-0.42	-0.18	-0.12		0.50	-0.25		-0.07	0.24
River Alluvi	im average								3.4		-0.23	25		0.22
2SD(n=3)	ann avoiago								1.5		0.12	5		0.08
Rocks average	ge		-0.14	-0.21	0.16	0.65	0.15	-0.39	4.2	-0.19		27	-0.16	0.21
2SD(n=4)	-		0.27	0.11	0.20	0.24	0.60	0.18	1.3	0.15		13	0.22	0.04

Table 1: Mass balance (t) calculations. Cu and Zn concentration and isotope data, for the Glen Feshie chronosequence, Scotland.

 ¹ Raw data for tau calculations tabulated in electronic appendix, including alluvium values used.
 ² Tau values also calculated for analysed rocks relative to alluvium to illustrate impact of choice of rock versus alluvium as "parent" material.
 ³ 2 sigma uncertainties for δ⁶⁵Cu and δ⁶⁶Zn are 0.09 and 0.07 respectively, based on long-term reproducibility of standards.

342 **4. Results**

343 4.1 Glen Feshie chronosequence: soils, alluvium, plants and water samples

Cu and Zn concentrations and isotope data for the Glen Feshie soil chronosequence, as well as relevant tau data, are given in Table 1. Table 1 also presents data for averages of 3-4 analyses each of river alluvium and rock samples. The full major and trace element data required for the tau calculations in Table 1 can be found in the electronic appendix.

348

Selected tau values as well as Cu and Zn isotope data for the four analysed soil profiles from Glen 349 350 Feshie are displayed in Figure 3. As noted previously, we use river alluvium as a reference parent 351 material. Tau calculation for rocks (Table 1) relative to river alluvium yield data that are generally within ± 0.2 of zero, suggesting that for many elements this choice is not critical. The exceptions are 352 Mn, where river alluvium is about 65% depleted over Nb relative to the rocks analysed, and Pb, 353 where river alluvium is about 40% depleted over Nb relative to rocks. Our choice of river alluvium 354 355 to calculate tau values is also justified by the fact that calculated taus for Na, Al, Fe and Mn are close to zero for the C horizons in the younger soil profiles. 356

357

The fact that these young soils, developed on a granitoid substrate in a cold climate, display only 358 359 incipient weathering is demonstrated by the tau values for base cations like Na (contrast with older 360 soils developed on more rapidly weathering basaltic substrates in Figures 4-6) which are generally only slightly less than zero in the upper soil horizons, and approach zero in the C horizons. Al and 361 Fe are relatively depleted in the upper horizons of the 1-13 kyr soil profiles, and variably enriched 362 in the B horizons, suggesting translocation downwards, perhaps in association with organic acids 363 (e.g. Bigalke et al., 2011). Mn is slightly enriched relative to Nb throughout the youngest profile but 364 is depleted throughout all other soil profiles except the B horizon in the 3.6 kyr soil. Absolute Mn 365 enrichments or depletions depend critically, however, on whether river alluvium or rock 366 concentration values are used as a reference. Phosphorous concentrations (Fig. 3) show an evolution 367 through the chronosequence. This element is only depleted in the deepest horizons of the oldest soil 368 profile. In the two youngest soils it is depleted in the upper horizons whereas it is strongly enriched 369 370 at the top of the two oldest profiles. A final feature is a strong enrichment in Pb (Table 1, not figured) in the H horizons of the two oldest profiles. 371



Figure 3: Tau parameters for selected elements (left), τ (black) and isotope (red) data for Cu (centre) and Zn (right) in Glen Feshie soils. The y axis in all plots is drawn at $\tau = 0$ to highlight gain or loss of each element. The red dashed lines in the panels at centre and right show the isotope composition of river alluvium (Table 1) to highlight shifts in isotope composition of the soil relative to this reference. Horizontal dashed lines show horizon boundaries.

Cu is nearly always enriched in these soils, relative to the starting material. Though this could again be an artefact of the initial concentrations used to calculate taus, the data in Table 1 suggest that this picture would also emerge if local rocks were used as a reference. Zn, in contrast, is almost always

depleted. The tau profiles do, however, suggest significant translocation of Cu and Zn during 382 incipient weathering. The most fully developed soil profiles (3.6 and 13 kyr) show enrichments in 383 Cu and Zn near the top, correlated with those in phosphorous (Fig. 3), while AE and B horizons are 384 usually depleted relative to horizons above and below. These features of Cu and Zn distribution 385 within the soils are reminiscent of those previously found for cambisols and podzols by Bigalke et 386 al. (2011). Incipient weathering, and the translocations of Cu and Zn within the soil profiles, is 387 associated with barely significant shifts in Cu and Zn isotopes (Fig. 3). Overall, Cu isotopes are 388 very slightly heavier (0.07-0.26‰ heavier than the profile average, and in the case of the 13 kyr soil 389 390 heavier than the starting material) at the top of each profile and very slightly light (up to 0.12%) lighter than the profile average) lower down. If anything there is a subtle change downwards in Zn 391 isotopes towards slightly heavier (e.g. by 0.26‰ in the 13 kyr soil) isotope compositions. 392

393

395

			[Cu]		[Zn]	
Sample	Туре	Soil age (kyr)	ррт	δ ⁶⁵ Cu ¹	ppm	δ ⁶⁶ Zn
GFP1	Heather - leaves	1	4.0	-0.84	0.59	-0.40
GFP2	Heather - roots	1	2.1	-1.02	0.36	0.00
GFP3	Heather - leaves	13	6.6	-0.35	0.73	-0.45
GFP4	Heather - stems	13	2.0	-0.79	0.21	-0.30
GFP5	Heather - roots	13	2.1	-0.80	0.46	-0.17
GFP6	Grass	13	4.7	-0.22	1.39	0.01
			[Cu]		[Zn]	
			nM	δ ⁶⁵ Cu	nM	δ ⁶⁶ Zn
GFWn1	River water		2.7	0.01	17	0.50
GFWn4	River water		4.0	-0.04	12	0.48
GFWn6	River water		1.9	0.13	14	0.55
GFWn7	River water		3.8	0.11	19	0.53
GFWn8	River water		5.0	-0.07	22	0.40

Table 2: Cu and Zn concentration and isotope data for river water and plants from Glen Feshie.

396 ¹ 2 sigma uncertainties for δ^{65} Cu and δ^{66} Zn are 0.09 and 0.07 respectively, based on long-term reproducibility of standards.

398

Cu and Zn abundance and isotope data for plants and river water collected in Glen Feshie are presented in Table 2. Concentrations of Cu in the River Feshie are low, ranging from 1.9 to 5.0 nM and consistent with the low concentrations seen in other relatively undisturbed catchments like the Kalix (northern Sweden) and the Amazon (Vance et al., 2008). Zn concentrations range from 12-22 nM, again within the range of values for the Kalix and Amazon (Little et al., 2014a). δ^{65} Cu in the River Feshie samples are -0.07 to +0.13‰, compared to a wide range of +0.02 to +1.45 in global rivers (Vance et al., 2008). In common with these previous data, the Feshie is about 0.2-0.3‰ heavier than the soils it drains and the river alluvium it carries (Vance et al., 2008). δ^{66} Zn is +0.40 to +0.55‰, also heavier than the solid material the river carries (at +0.22‰).

408

The plant samples are all isotopically lighter for Cu and Zn than the soils on which they grow, with 409 δ^{65} Cu ranging from -0.22 to -1.02 and δ^{66} Zn from +0.01 to -0.45‰. Plant samples contain 2.0-6.6 410 ppm Cu, in the same range as previously observed (e.g. Weinstein et al., 2011). Zn contents in the 411 plants are 1-2 orders of magnitude lower than previously observed (Weiss et al., 2005; Viers et al., 412 413 2007; Arnold et al., 2010), at 0.2-1.4 ppm Zn. Our purpose in presenting the plant data is to facilitate a later discussion of their impact on soil development. It is not to present a detailed 414 415 discussion of the mechanisms of Cu and Zn uptake by plants, which has recently been reviewed (Moynier et al., 2016). All plants yet studied have a bulk Cu isotopic composition lighter than the 416 external pool (e.g. Weinstein et al., 2011) while for Zn bulk plants can be both heavier and lighter 417 than this pool, depending on whether free or complexed Zn is taken up (e.g. Weiss et al., 2005; 418 Arnold et al., 2010). 419

Table 3: Mass balance (τ) calculations, Cu and Zn concentration and isotope data, for Hawaiian soils.

								[Cu]			[Zn]		
Horizon	Depth (cm)	$\tau_{Ca}{}^1$	$ au_{Al}$	τ _{Fe}	τ_{Mn}	τp	$ au_{Pb}$	ррт	τ _{Cu}	$\delta^{65}Cu^2$	ррт	τ_{Zn}	δ ⁶⁶ Zn
ea, 0.3 kyr, 25	00 mm	0.10	0.00	0.01	0.10	0.04	1 40	07	0.04	0.05	100	0.15	0.00
Oe+Oa	0-8	-0.10	0.02	-0.01	-0.13	0.04	1.40	97	-0.04	0.05	108	0.15	0.30
Oa	8-13	-0.17	-0.02	-0.03	-0.19	0.01	1.48	84	-0.22	0.01	104	0.03	0.26
A	13-21	-0.12	-0.08	-0.02	-0.24	-0.17	0.35	94	-0.16	0.07	117	0.10	0.31
$\mathbf{B}\mathbf{w}$	21-27	-0.08	-0.05	0.03	-0.21	-0.31	-0.11	113	-0.02	0.09	100	-0.07	0.34
C1	27-38	-0.05	-0.07	0.02	-0.20	-0.31	-0.14	117	0.03	0.12	106	-0.01	0.32
C2	38-49	0.03	0.05	0.00	-0.23	-0.29	0.36	114	0.00	0.00	109	0.02	0.38
C3	49-73	0.05	0.03	0.01	-0.21	-0.31	0.29	117	0.02	0.14	115	0.07	0.33
		-0.01	0.00	0.01	-0.21	-0.27	0.28		-0.01	0.10		0.04	0.33
e, Mauna Ke	a, 20 kyr, 2500 mm												
Oe	0-5	-0.99	-0.18	-0.12	-0.76	-0.32	0.55	32	0.45	0.25	39	-0.80	0.32
Oa	5-12	-0.99	-0.56	-0.52	-0.80	-0.54	-0.20	27	-0.32	0.30	80	-0.77	0.38
А	12-20	-0.99	-0.85	-0.51	-0.92	-0.56	0.13	23	0.13	-0.35	49	-0.73	0.38
А	20-27	-1.00	-0.91	-0.44	-0.90	-0.84	-0.24	14	-0.79	-0.60	104	-0.82	0.24
Bw1	27-39	-0.99	-0.81	-0.22	-0.88	-0.75	0.03	16	-0.64	-0.48	73	-0.82	0.31
Bw2	39-52	-0.99	-0.64	-0.50	-0.82	-0.68	-0.43	10	-0.76	0.04	91	-0.77	0.39
Bw3	52-71	-1.00	-0.76	-0.35	-0.86	-0.73	-0.20	13	-0.73	-0.19	91	-0.78	0.41
Bw3+Bw4	71-94	-0.98	0.03	-0.24	-0.68	-0.33	-0.18	20	0.04	-0.04	46	-0.74	0.27
Bw4	94-103	-0.98	-0.14	-0.32	-0.72	-0.42	-0.11	26	0.22	0.05	51	-0.73	0.36
		-0.99	-0.43	-0.34	-0.79	-0.55	-0.16		-0.29	-0.08		-0.76	0.35
vi, 150 kyr, 25	500 mm												
Oe+A1	0-12	-0.98	-0.72	-0.08	0.25	-0.52	2.74	38	0.92	-0.07	138	-0.33	0.46
A1+A2	12-21	-0.99	-0.73	0.15	-0.07	-0.69	2.60	15	-0.41	0.00	99	-0.63	0.30
A2+2Bw1	21-27	-0.96	-0.59	0.58	0.05	-0.77	1.82	12	-0.49	0.15	95	-0.61	0.34
3Bw2	27-39	-0.99	-0.40	0.49	-0.09	-0.73	2.42	15	-0.22	0.18	73	-0.63	0.44
3Bw3	39-51	-0.99	-0.26	0.23	0.03	-0.73	1.52	21	-0.01	0.38	88	-0.60	0.40
3Bw3	51+	-0.99	-0.25	-0.01	0.16	-0.58	0.88	22	-0.19	0.26	91	-0.68	0.81
		-0.98	-0.45	0.22	0.04	-0.67	1.94		-0.09	0.13		-0.60	0.43
	Horizon ea, 0.3 kyr, 25 Oe+Oa Oa A Bw C1 C2 C3 e, Mauna Ken Oe Oa A A Bw1 Bw2 Bw3 Bw3 Bw3+Bw4 Bw4 wi, 150 kyr, 25 Oe+A1 A1+A2 A2+2Bw1 3Bw2 3Bw3 3Bw3 3Bw3	HorizonDepth (cm) $ea, 0.3 kyr, 2500 mm$ Oe+Oa0-8 OaOa8-13 AA13-21 BwBw21-27 C1C127-38 C2C238-49 C3C349-73	HorizonDepth (cm) τ_{Ca}^1 ea, 0.3 kyr, 2500 mm0e+Oa0-8-0.10Oa8-13-0.17A13-21-0.12Bw21-27-0.08C127-38-0.05C238-490.03C349-730.05-0.01pe, Mauna Kea, 20 kyr, 2500 mmOe0-5-0.99Oa5-12-0.99A12-20-0.99A20-27-1.00Bw127-39-0.99Bw239-52-0.99Bw352-71-1.00Bw3+Bw471-94-0.98Bw494-103-0.98Mu494-103-0.98A1+A212-21-0.99A2+2Bw121-27-0.963Bw227-39-0.993Bw339-51-0.993Bw351+-0.99	HorizonDepth (cm) τ_{Ca}^{1} τ_{Al} ea, 0.3 kyr, 2500 mm $Oe+Oa$ 0.8 -0.10 0.02 Oa $8-13$ -0.17 -0.02 A $13-21$ -0.12 -0.08 Bw $21-27$ -0.08 -0.05 C1 $27-38$ -0.05 -0.07 C2 38.49 0.03 0.05 C3 $49-73$ 0.05 0.03 -0.01 0.00 o.05 -0.01 o.05 -0.01 Oe $0-5$ -0.99 -0.18 Oa $5-12$ -0.99 -0.56 A $12-20$ -0.99 -0.56 A $20-27$ -1.00 -0.91 Bw1 $27-39$ -0.99 -0.64 Bw2 $39-52$ -0.99 -0.64 Bw3 $52-71$ -1.00 -0.76 Bw3+Bw4 $71-94$ -0.98 0.03 Bw4 $94-103$ -0.98 -0.14 o.e+A1 $0-12$ -0.98 -0.72 A1+A2 $12-27$ -0.96 -0.72 A1+A2 $12-27$ -0.96 -0.59 $3Bw3$ $39-51$ -0.99 -0.40 $3Bw3$ $39-51$ -0.99 -0.26 $3Bw3$ $51+$ -0.99 -0.25	HorizonDepth (cm) τ_{Ca}^{-1} τ_{Al} τ_{Fe} ea, 0.3 kyr, 2500 mm 0.8 -0.10 0.02 -0.01 Oa $8-13$ -0.17 -0.02 -0.03 A $13-21$ -0.12 -0.08 -0.02 Bw $21-27$ -0.08 -0.05 0.03 C1 $27-38$ -0.05 -0.07 0.02 C2 $38-49$ 0.03 0.05 0.00 C3 $49-73$ 0.05 0.03 0.01 -0.01 0.00 0.01 Pe, Mauna Kea, 20 kyr, 2500 mmOe $0-5$ -0.99 -0.18 -0.12 Oa $5-12$ -0.99 -0.18 -0.12 Oa $5-12$ -0.99 -0.85 -0.51 A $20-27$ -1.00 -0.91 -0.44 Bw1 $27-39$ -0.99 -0.64 -0.50 Bw3 $52-71$ -1.00 -0.76 -0.35 Bw3+Bw4 $71-94$ -0.98 0.03 -0.24 Bw4 $94-103$ -0.98 -0.14 -0.32 -0.99 -0.43 -0.99 -0.43 A1+A2 $12-21$ -0.99 -0.72 -0.08 A1+A2 $12-21$ -0.99 -0.73 0.15 A2+2Bw1 $21-27$ -0.96 -0.59 0.58 $3Bw2$ $27-39$ -0.99 -0.45 0.23 $3Bw3$ $51+$ -0.99 -0.25 -0.01	HorizonDepth (cm) $\tau_{Ca}{}^1$ τ_{Al} τ_{Fe} τ_{Mn} $ea, 0.3 kyr, 2500 mm$ Oa0.8-0.100.02-0.01-0.13Oa8-13-0.17-0.02-0.03-0.19A13-21-0.12-0.08-0.02-0.24Bw21-27-0.08-0.050.03-0.21C127-38-0.05-0.070.02-0.20C238-490.030.050.00-0.23C349-730.050.030.01-0.21-0.010.000.01-0.010.000.01-0.21-0.010.000.01-0.21-0.010.000.01-0.21-0.010.000.01-0.21-0.010.000.01-0.21-0.010.000.01-0.21-0.010.000.01-0.21-0.010.000.01-0.21-0.010.000.01-0.21-0.010.000.01-0.21-0.010.00-0.01-0.21-0.02-0.99-0.18-0.12-0.76Oa5-12-0.99-0.64-0.50-0.82Bw352-71-1.00 <td>HorizonDepth (cm)$\tau_{Ca}^{1}$$\tau_{Al}$$\tau_{Fe}$$\tau_{Mn}$$\tau_P$ea, 0.3 kyr, 2500 mmOe+Oa0-8-0.100.02-0.01-0.130.04Oa8-13-0.17-0.02-0.03-0.190.01A13-21-0.12-0.08-0.02-0.24-0.17Bw21-27-0.08-0.050.03-0.21-0.31C127-38-0.05-0.070.02-0.20-0.31C238-490.030.050.00-0.23-0.29C349-730.050.030.01-0.21-0.31-0.010.000.01-0.21-0.31-0.010.000.01-0.21-0.31-0.010.000.01-0.21-0.31-0.010.000.01-0.21-0.31-0.010.000.01-0.21-0.31-0.010.000.01-0.21-0.31-0.010.000.01-0.21-0.31-0.010.000.01-0.21-0.31-0.010.000.01-0.21-0.31-0.010.000.01-0.21-0.31-0.010.000.01-0.21-0.32Oa5-12-0.99-0.18-0.12-0.76-0.32Oa5-12-0.99-0.85-0.51<</td> <td>Horizon Depth (cm) τ_{Ca}^{1} τ_{Al} τ_{Fc} τ_{Mn} τ_{P} τ_{Pb} ea, 0.3 kyr, 2500 mm Oc+Oa 0-8 -0.10 0.02 -0.01 -0.13 0.04 1.40 Oa 8-13 -0.17 -0.02 -0.03 -0.19 0.01 1.48 A 13-21 -0.12 -0.08 -0.02 -0.24 -0.31 -0.11 C1 27-38 -0.05 0.03 -0.21 -0.31 -0.11 C2 38-49 0.03 0.05 0.00 -0.23 -0.29 0.36 C3 49-73 0.05 0.03 0.01 -0.21 -0.31 0.29 e. Mauna Kea, 20 kyr, 2500 mm </td> <td>Horizon Depth (cm) τ_{Ca}^{-1} τ_{Al} τ_{Fe} τ_{Mn} τ_{P} τ_{Pb} ppm ea, 0.3 kyr, 2500 mm 0.8 -0.10 0.02 -0.01 -0.13 0.04 1.40 97 0a 8-13 -0.17 -0.02 -0.03 -0.19 0.01 1.48 84 A 13-21 -0.12 -0.08 -0.02 -0.24 -0.17 0.35 94 Bw 21-27 -0.08 -0.02 -0.24 -0.11 113 C1 27-38 -0.05 0.03 -0.21 -0.31 -0.11 113 C1 27-38 -0.05 0.03 0.01 -0.21 -0.31 0.29 117 C2 38-49 0.03 0.05 0.00 -0.21 -0.27 0.28 ve, Mauna Kea, 20 kyr, 2500 mm - - - 0.99 -0.18 -0.12 -0.56 0.32 0.55 32 Oa 5-12 -0.99</td> <td>Horizon Depth (cm) τ_{cs}^{1} τ_{Al} τ_{Fe} τ_{Mh} τ_{F} τ_{Fb} ppm τ_{cu} ea, 0.3 kyr, 2500 mm 0.4 0.8 -0.10 0.02 -0.01 -0.13 0.04 1.40 97 -0.04 Oa 8-13 -0.17 -0.02 -0.03 -0.19 0.01 1.48 84 -0.22 A 13-21 -0.12 -0.08 -0.02 -0.24 -0.11 0.13 -0.01 1.14 0.00 C1 27.38 -0.05 -0.07 0.02 -0.20 -0.31 -0.14 117 0.03 C2 38.49 0.03 0.05 0.00 -0.21 -0.27 0.28 -0.01 me, Mauna Kea, 20 kyr, 2500 mm - - -0.01 0.00 0.01 -0.21 -0.27 0.28 -0.01 Mauna Kea, 20 kyr, 2500 mm - - - 0.99 -0.56 -0.52 -0.80 -0.54 -0.20 <t< td=""><td>Horizon Depth (cm) τ_{c_a} τ_{Al} τ_{Fe} τ_{Ba} τ_{Fb} ppm τ_{c_a} $\delta^{65}Cu^2$ ea, 0.3 kyr, 2500 mm 0.02 -0.01 -0.13 0.04 1.40 97 -0.04 0.05 Oc +Oa 0.8 -0.17 -0.02 -0.03 -0.19 0.01 1.48 84 -0.22 0.01 A 13-21 -0.12 -0.08 -0.02 -0.24 -0.17 0.35 94 -0.16 0.07 Bw 21-27 -0.08 -0.05 0.03 -0.21 -0.31 -0.11 113 -0.02 0.09 C2 38-49 0.03 0.05 0.00 -0.23 -0.29 0.36 114 0.00 0.00 C3 49-73 0.05 0.03 0.01 -0.21 -0.27 0.28 -0.01 0.10 me, Mauna Kea, 20 kyr, 2500 mm -0.01 -0.02 -0.32 0.55 32 0.45 0.25</td><td>Horizon Depth (cm) τ_{C_a} τ_{H_c} τ_{M_a} τ_P τ_{H_b} ppm τ_{C_a} $\delta^{45}Cu^2$ ppm ea, 0.3 kyr, 2500 mm 0.08 -0.10 0.02 -0.01 -0.13 0.04 97 -0.04 0.05 108 Oe+Oa 0.8 -1.17 -0.02 -0.03 -0.19 0.01 1.48 84 -0.22 0.01 104 A 13-21 -0.12 -0.08 -0.02 -0.21 -0.31 -0.11 113 -0.02 0.09 100 C1 27.38 -0.05 -0.07 0.02 -0.20 -0.31 -0.14 117 0.03 0.12 106 C2 38.49 0.03 0.05 0.00 -0.21 -0.31 0.29 117 0.02 0.14 115 -0.01 0.00 0.01 -0.27 0.28 -0.01 0.10 0.01 0.03 0.02 1.7 0.32 0.35 39</td><td>Horizon Depth (cm) τ_{Ca} τ_{NL} τ_{NL} τ_{PL} τ_{PL} ppm τ_{Ca} $\delta^{es}Cu^2$ ppm τ_{Za} <i>ca, 0.3 kyr, 2500 mm</i> 0 0 0.0 0.02 -0.01 0.13 0.04 1.40 97 -0.04 0.05 108 0.15 Oa 8-13 -0.17 -0.02 -0.03 -0.19 0.01 1.48 84 -0.22 0.01 104 0.03 A 13-21 -0.12 -0.08 -0.02 -0.31 -0.11 113 -0.02 0.09 100 -0.07 C1 27-38 -0.05 0.07 0.02 -0.21 -0.31 0.29 117 0.02 0.14 115 0.00 0.02 -0.21 -0.31 0.29 117 0.02 0.14 115 0.07 0.02 -0.41 100 0.00 0.01 0.02 0.36 114 0.00 0.01 0.04 0.92 0.56</td></t<></td>	HorizonDepth (cm) τ_{Ca}^{1} τ_{Al} τ_{Fe} τ_{Mn} τ_P ea, 0.3 kyr, 2500 mmOe+Oa0-8-0.100.02-0.01-0.130.04Oa8-13-0.17-0.02-0.03-0.190.01A13-21-0.12-0.08-0.02-0.24-0.17Bw21-27-0.08-0.050.03-0.21-0.31C127-38-0.05-0.070.02-0.20-0.31C238-490.030.050.00-0.23-0.29C349-730.050.030.01-0.21-0.31-0.010.000.01-0.21-0.31-0.010.000.01-0.21-0.31-0.010.000.01-0.21-0.31-0.010.000.01-0.21-0.31-0.010.000.01-0.21-0.31-0.010.000.01-0.21-0.31-0.010.000.01-0.21-0.31-0.010.000.01-0.21-0.31-0.010.000.01-0.21-0.31-0.010.000.01-0.21-0.31-0.010.000.01-0.21-0.32Oa5-12-0.99-0.18-0.12-0.76-0.32Oa5-12-0.99-0.85-0.51<	Horizon Depth (cm) τ_{Ca}^{1} τ_{Al} τ_{Fc} τ_{Mn} τ_{P} τ_{Pb} ea, 0.3 kyr, 2500 mm Oc+Oa 0-8 -0.10 0.02 -0.01 -0.13 0.04 1.40 Oa 8-13 -0.17 -0.02 -0.03 -0.19 0.01 1.48 A 13-21 -0.12 -0.08 -0.02 -0.24 -0.31 -0.11 C1 27-38 -0.05 0.03 -0.21 -0.31 -0.11 C2 38-49 0.03 0.05 0.00 -0.23 -0.29 0.36 C3 49-73 0.05 0.03 0.01 -0.21 -0.31 0.29 e. Mauna Kea, 20 kyr, 2500 mm	Horizon Depth (cm) τ_{Ca}^{-1} τ_{Al} τ_{Fe} τ_{Mn} τ_{P} τ_{Pb} ppm ea, 0.3 kyr, 2500 mm 0.8 -0.10 0.02 -0.01 -0.13 0.04 1.40 97 0a 8-13 -0.17 -0.02 -0.03 -0.19 0.01 1.48 84 A 13-21 -0.12 -0.08 -0.02 -0.24 -0.17 0.35 94 Bw 21-27 -0.08 -0.02 -0.24 -0.11 113 C1 27-38 -0.05 0.03 -0.21 -0.31 -0.11 113 C1 27-38 -0.05 0.03 0.01 -0.21 -0.31 0.29 117 C2 38-49 0.03 0.05 0.00 -0.21 -0.27 0.28 ve, Mauna Kea, 20 kyr, 2500 mm - - - 0.99 -0.18 -0.12 -0.56 0.32 0.55 32 Oa 5-12 -0.99	Horizon Depth (cm) τ_{cs}^{1} τ_{Al} τ_{Fe} τ_{Mh} τ_{F} τ_{Fb} ppm τ_{cu} ea, 0.3 kyr, 2500 mm 0.4 0.8 -0.10 0.02 -0.01 -0.13 0.04 1.40 97 -0.04 Oa 8-13 -0.17 -0.02 -0.03 -0.19 0.01 1.48 84 -0.22 A 13-21 -0.12 -0.08 -0.02 -0.24 -0.11 0.13 -0.01 1.14 0.00 C1 27.38 -0.05 -0.07 0.02 -0.20 -0.31 -0.14 117 0.03 C2 38.49 0.03 0.05 0.00 -0.21 -0.27 0.28 -0.01 me, Mauna Kea, 20 kyr, 2500 mm - - -0.01 0.00 0.01 -0.21 -0.27 0.28 -0.01 Mauna Kea, 20 kyr, 2500 mm - - - 0.99 -0.56 -0.52 -0.80 -0.54 -0.20 <t< td=""><td>Horizon Depth (cm) τ_{c_a} τ_{Al} τ_{Fe} τ_{Ba} τ_{Fb} ppm τ_{c_a} $\delta^{65}Cu^2$ ea, 0.3 kyr, 2500 mm 0.02 -0.01 -0.13 0.04 1.40 97 -0.04 0.05 Oc +Oa 0.8 -0.17 -0.02 -0.03 -0.19 0.01 1.48 84 -0.22 0.01 A 13-21 -0.12 -0.08 -0.02 -0.24 -0.17 0.35 94 -0.16 0.07 Bw 21-27 -0.08 -0.05 0.03 -0.21 -0.31 -0.11 113 -0.02 0.09 C2 38-49 0.03 0.05 0.00 -0.23 -0.29 0.36 114 0.00 0.00 C3 49-73 0.05 0.03 0.01 -0.21 -0.27 0.28 -0.01 0.10 me, Mauna Kea, 20 kyr, 2500 mm -0.01 -0.02 -0.32 0.55 32 0.45 0.25</td><td>Horizon Depth (cm) τ_{C_a} τ_{H_c} τ_{M_a} τ_P τ_{H_b} ppm τ_{C_a} $\delta^{45}Cu^2$ ppm ea, 0.3 kyr, 2500 mm 0.08 -0.10 0.02 -0.01 -0.13 0.04 97 -0.04 0.05 108 Oe+Oa 0.8 -1.17 -0.02 -0.03 -0.19 0.01 1.48 84 -0.22 0.01 104 A 13-21 -0.12 -0.08 -0.02 -0.21 -0.31 -0.11 113 -0.02 0.09 100 C1 27.38 -0.05 -0.07 0.02 -0.20 -0.31 -0.14 117 0.03 0.12 106 C2 38.49 0.03 0.05 0.00 -0.21 -0.31 0.29 117 0.02 0.14 115 -0.01 0.00 0.01 -0.27 0.28 -0.01 0.10 0.01 0.03 0.02 1.7 0.32 0.35 39</td><td>Horizon Depth (cm) τ_{Ca} τ_{NL} τ_{NL} τ_{PL} τ_{PL} ppm τ_{Ca} $\delta^{es}Cu^2$ ppm τ_{Za} <i>ca, 0.3 kyr, 2500 mm</i> 0 0 0.0 0.02 -0.01 0.13 0.04 1.40 97 -0.04 0.05 108 0.15 Oa 8-13 -0.17 -0.02 -0.03 -0.19 0.01 1.48 84 -0.22 0.01 104 0.03 A 13-21 -0.12 -0.08 -0.02 -0.31 -0.11 113 -0.02 0.09 100 -0.07 C1 27-38 -0.05 0.07 0.02 -0.21 -0.31 0.29 117 0.02 0.14 115 0.00 0.02 -0.21 -0.31 0.29 117 0.02 0.14 115 0.07 0.02 -0.41 100 0.00 0.01 0.02 0.36 114 0.00 0.01 0.04 0.92 0.56</td></t<>	Horizon Depth (cm) τ_{c_a} τ_{Al} τ_{Fe} τ_{Ba} τ_{Fb} ppm τ_{c_a} $\delta^{65}Cu^2$ ea, 0.3 kyr, 2500 mm 0.02 -0.01 -0.13 0.04 1.40 97 -0.04 0.05 Oc +Oa 0.8 -0.17 -0.02 -0.03 -0.19 0.01 1.48 84 -0.22 0.01 A 13-21 -0.12 -0.08 -0.02 -0.24 -0.17 0.35 94 -0.16 0.07 Bw 21-27 -0.08 -0.05 0.03 -0.21 -0.31 -0.11 113 -0.02 0.09 C2 38-49 0.03 0.05 0.00 -0.23 -0.29 0.36 114 0.00 0.00 C3 49-73 0.05 0.03 0.01 -0.21 -0.27 0.28 -0.01 0.10 me, Mauna Kea, 20 kyr, 2500 mm -0.01 -0.02 -0.32 0.55 32 0.45 0.25	Horizon Depth (cm) τ_{C_a} τ_{H_c} τ_{M_a} τ_P τ_{H_b} ppm τ_{C_a} $\delta^{45}Cu^2$ ppm ea, 0.3 kyr, 2500 mm 0.08 -0.10 0.02 -0.01 -0.13 0.04 97 -0.04 0.05 108 Oe+Oa 0.8 -1.17 -0.02 -0.03 -0.19 0.01 1.48 84 -0.22 0.01 104 A 13-21 -0.12 -0.08 -0.02 -0.21 -0.31 -0.11 113 -0.02 0.09 100 C1 27.38 -0.05 -0.07 0.02 -0.20 -0.31 -0.14 117 0.03 0.12 106 C2 38.49 0.03 0.05 0.00 -0.21 -0.31 0.29 117 0.02 0.14 115 -0.01 0.00 0.01 -0.27 0.28 -0.01 0.10 0.01 0.03 0.02 1.7 0.32 0.35 39	Horizon Depth (cm) τ_{Ca} τ_{NL} τ_{NL} τ_{PL} τ_{PL} ppm τ_{Ca} $\delta^{es}Cu^2$ ppm τ_{Za} <i>ca, 0.3 kyr, 2500 mm</i> 0 0 0.0 0.02 -0.01 0.13 0.04 1.40 97 -0.04 0.05 108 0.15 Oa 8-13 -0.17 -0.02 -0.03 -0.19 0.01 1.48 84 -0.22 0.01 104 0.03 A 13-21 -0.12 -0.08 -0.02 -0.31 -0.11 113 -0.02 0.09 100 -0.07 C1 27-38 -0.05 0.07 0.02 -0.21 -0.31 0.29 117 0.02 0.14 115 0.00 0.02 -0.21 -0.31 0.29 117 0.02 0.14 115 0.07 0.02 -0.41 100 0.00 0.01 0.02 0.36 114 0.00 0.01 0.04 0.92 0.56

Table 3 (continued): Mass balance (τ) calculations, Cu and Zn concentration and isotope data, for Hawaiian soils

									[Cu]			[Zn]		
Sample	Horizon	Depth (cm)	${\tau_{Ca}}^1$	$ au_{Al}$	τ _{Fe}	τ_{Mn}	τρ	$ au_{Pb}$	ppm	$ au_{Cu}$	$\delta^{65}Cu^2$	ppm	τ_{Zn}	δ ⁶⁶ Zn
Kohala H,	Hawi, 150kyr,	1060 mm												
KOH-1	Ap	0-22	-0.73	0.16	0.06	5.03	-0.27	1.65	28	1.05	-0.18	135	-0.05	0.43
KOH-2	Bw1	22-31	-0.83	-0.01	-0.11	2.55	-0.66	0.79	14	-0.27	-0.03	113	-0.44	0.28
KOH-3	Bw1+Bw2	31-41	-0.82	0.06	0.01	2.47	-0.62	0.51	10	-0.48	0.56	107	-0.47	0.24
KOH-4	Bw2	41-51	-0.76	0.03	0.03	2.59	-0.33	0.14	5.2	-0.73	0.36	102	-0.49	0.29
KOH-5	Bw2+Bw3	51-59	-0.79	0.02	0.04	2.08	-0.49	0.13	5.8	-0.68	0.92	107	-0.43	0.33
KOH-6	Bw3	59+	-0.79	0.01	0.05	1.86	-0.48	0.11	4.9	-0.73	0.89	84	-0.56	0.49
Integrated			-0.78	0.07	0.02	3.14	-0.44	0.74		-0.08	0.06		-0.35	0.36
	G1	2 (001 2 (50												
Maui Clime	osequence, Site	e 2, 400kyr, 2450 n	nm	0.07	0.25	0.70	0.70	0.00	20	0.51	0.40	114	0.54	0.27
2A1	A	0-5	-0.98	-0.8/	-0.35	-0.70	-0./9	0.90	30	-0.51	-0.40	114	-0.54	0.37
2A2	Ag	5-12	-0.99	-0.88	-0.33	-0.//	-0.8/	0.79	33	-0.63	-0.61	128	-0.64	0.32
2A3	BWI	12-24	-1.00	-0.8/	-0.21	-0.86	-0.92	1.12	15	-0.85	-0.42	70	-0.82	0.33
2A4	BW2	24-34	-1.00	-0.83	-0.21	-0.89	-0.91	0.82	10	-0.90	-0.56	54	-0.8/	0.27
2A5	Bg	34-55	-1.00	-0.81	-0.44	-0.86	-0.93	1.16	18	-0.83	-0.49	84	-0.81	0.33
2A6	Bw3	55-69	-1.00	-0.82	-0.42	-0.89	-0.92	0.8/	17	-0.85	-1.09	83	-0.82	0.28
2A7	Bw4	69-100	-1.00	-0.70	-0.28	-0.87	-0.84	0.60	13	-0.85	-0.80	66	-0.80	0.29
Integrated			-1.00	-0.81	-0.33	-0.86	-0.89	0.90		-0.82	-0.67		-0.79	0.31
Maui Clim	ocamanaa Cit	a A ADDIDU 2250 w	14 144											
	$\Delta \gamma$	2-10	-1.00	-0.84	-0.79	-0.96	-0.74	0.87	6.0	-0.95	-0.01	37	-0.92	0.40
4/12	Ra	10-17	-1.00	-0.87	-0.75	-0.96	-0.74	2.02	8.8	-0.93	-0.01	41	-0.92	0.40
4A3	Dg Bw1	17 21	-1.00	-0.87	-0.85	-0.90	-0.70	0.01	5.8	-0.93	-0.02	41	-0.92	0.30
445	Bw1 Bw2	21_34	-1.00	-0.89	-0.85	-0.97	-0.92	0.91	5.8	-0.97	-0.10	51	-0.94	0.39
116	Bw2	21-54	-1.00	-0.00	-0.85	-0.97	-0.94	0.90	5.0	-0.97	-0.20	20	-0.94	0.50
4A0	DW3 Dw4	51 75	-1.00	-0.09	-0.03	-0.90	-0.94	0.07	5.5 5.1	-0.97	-0.24	24	-0.94	0.40
4A /	DW4	51-75	-1.00	-0.00	-0.85	-0.9/	-0.79	0.38	3.1	-0.90	0.10	34	-0.93	0.39
Integrated			-1.00	-0.78	-0.84	-0.97	-0.86	0.75		-0.96	-0.06		-0.93	0.38

Table 3 (continued): Mass balance (τ) calculations, Cu and Zn concentration and isotope data, for Hawaiian soils

Sample	Horizon	Denth (cm)	$\tau_{C_2}^1$	TAI	τe	τm	τp	Трь	[Cu] ppm	τcu	δ ⁶⁵ Cu ²	[Zn] ppm	T7n	δ ⁶⁶ Zn
~~~~		_ <b>_ _ _ _ _ _ _ _ _ _</b>	veu	•11	vite	• 1011		*15	FF	veu			•2h	
Maui Climo	Maui Climosequence, Site 6, 400kyr, 5050 mm													
6A1	Agl	0-14	-0.87	-0.78	-0.88	-0.84	0.00	5.03	5.2	-0.36	-0.01	23	-0.30	0.59
6A2	Ag2	14-26	-1.00	-0.88	-0.97	-0.97	-0.90	2.06	5.3	-0.96	-0.56	20	-0.96	0.63
6A3	Bg1	26-38	-1.00	-0.84	-0.97	-0.97	-0.90	2.08	11	-0.88	-0.63	16	-0.96	0.56
6A4	Bg2	38-49	-1.00	-0.92	-0.98	-0.96	-0.97	0.88	4.7	-0.98	-0.13	26	-0.98	0.42
6A5	Bg3	49-67	-1.00	-0.94	-0.98	-0.97	-0.98	0.71	2.8	-0.99	-0.09	30	-0.98	0.46
6A6	Bg4	67-93	-1.00	-0.76	-0.97	-0.97	-0.86	-0.01	2.6	-0.98	-0.01	26	-0.96	0.26
Integrated			-0.98	-0.86	-0.96	-0.95	-0.81	1.51		-0.89	-0.32		-0.88	0.45

#### 

¹ Raw data for tau calculations tabulated in electronic appendix, including parent rock values used. ² 2 sigma uncertainties for  $\delta^{65}$ Cu and  $\delta^{66}$ Zn are 0.09 and 0.07 respectively, based on long-term reproducibility of standards. 

#### 433 4.2 Basaltic Soil Development, Hawaiian Islands

Cu and Zn concentrations and isotope data for all the Hawaiian soils, as well as relevant tau data,
are given in Table 3. The full major and trace element data required for the tau calculations in Table
3, including data used to represent parent material, can be found in the electronic appendix.

437

438 Selected tau values as well as Cu and Zn isotope data for the three analysed soil profiles from the 439 LSAG chronosequence are displayed in Figure 4. As expected, chemical and isotopic features 440 associated with weathering processes are clearer in these data than at Glen Feshie, in older soils, 441 developed on more rapidly weathering basaltic substrates, in a setting with significantly higher 442 annual rainfall. However, there are also complications introduced by mineral aerosol addition that 443 become evident at the older end of the chronosequence.

444

In the youngest soil profile at Ola'a Kilauea (0.3 kyr, Fig. 4) only Mn and P are substantially 445 446 depleted relative to Nb. The 20 kyr profile at Laupahoehoe, Mauna Kea, in contrast, shows near total depletion of base cations (e.g. Ca, Fig. 4) and moderate depletion of Fe, while ~90% of the 447 448 original Mn has been lost from the profile. Aluminium and phosphate show similar patterns to each other, with marked depletions in most of the B horizon and only slight depletions in the O horizons 449 450 and the lowest part of the profile studied. At the 150 kyr site the maximum enrichment in Fe at 20-451 30 cm correlates with a peak in quartz+mica abundances (Kurtz et al., 2001). Moreover, Pb enrichment throughout this profile (Table 3, not figured) has previously been attributed to aeolian 452 dust deposition on the basis of its isotopic composition (Monastra et al., 2004). It seems likely that 453 the lack of Mn depletion compared to the younger Laupahoehoe profile is also attributable to dust 454 deposition. 455

456

The 300 year old, Ola'a soil exhibits only small shifts in abundance or isotopic patterns compared 457 to parent rock values. The slight depletion in the A and upper B horizons develops into a more 458 pronounced feature with soil age in the Laupahoehoe and Kohala M profiles. At Laupahoehoe this 459 Cu depletion is associated with an isotopic fractionation, such that the most depleted upper B 460 horizon has a  $\delta^{65}$ Cu about 0.7 ‰ lighter than the starting material. The minimum in  $\delta^{65}$ Cu and the 461 maximum Cu depletion occurs around the break in the profile noted earlier (see dashed blue line in 462 Fig. 4). The lower B horizon is identical to the starting material while the O horizon is about 0.2 ‰ 463 heavier. In contrast, Zn becomes uniformly depleted throughout the Laupahoehoe profile, with 75-464 80% of the original inventory lost from the soil. Moreover, this loss is associated with barely 465

significant isotopic effects. Cu and Zn in the older Kohala M profile are again more complicated, perhaps also due to dust deposition. Depletions in Cu and Zn are less intense than at Laupahoehoe, and there has been net addition of Cu to the top of the profile. Cu isotopes shifts from the parent material (at about +0.2 ‰ relative to parent material) are only significant at the bottom of the profile, where Zn is also heavy (+0.5‰ relative to starting material).





473 Figure 4: Tau parameters for selected elements (left),  $\tau$  (black) and isotope (red) data for Cu (centre) and Zn (right) in 474 LSAG soils, island of Hawaii. The y axis in all plots is drawn at  $\tau = 0$  to highlight gain or loss of each element. The horizontal dashed blue line in the Laupahoehoe panels marks the break in this profile between the 5 kyr ash on top and 475 476 the 20kyr tephra below. The red dashed lines in the panels at centre and right show the isotope composition of parent basalt to highlight shifts in isotope composition of the soil relative to this reference. The reference value for Cu is the 477 average for all ocean island basalts in Liu et al. (2015), for which  $\delta^{65}$ Cu = +0.09±0.07 (1SD). That for Zn is the average 478 for Kilauean basalts in Chen et al. (2013), for which  $\delta^{66}Zn = +0.29\pm0.03$  (1SD). Horizontal dashed lines show horizon 479 480 boundaries.

There are some striking differences between the two 150 kyr sites at Kohala that receive different 481 annual rainfall – as well as some intriguing similarities. The lower rainfall site (Kohala H, 1060 482 mm), shows pronounced Mn enrichment that peaks in the upper part of the profile (Fig. 5). Base 483 cations (e.g. Ca in Fig. 5) and P show lesser depletion than at Kohala M, while Fe and Al are barely 484 depleted at all. In contrast to the rather different mass balance behaviours for these major elements, 485 Cu and Zn show rather similar patterns at the two sites, both in their mass balance and isotopic 486 compositions. Thus both sites show large enrichments of Cu at the top of the profile, in the case of 487 488 the Kohala H profile closely co-incident with the peak in Mn enrichment. Both profiles show a change in  $\delta^{65}$ Cu from values around 0.2-0.3 % lighter than parent material at the top, to values 489 490 distinctly heavier at the bottom, though this is much more pronounced at Kohala H. Zn is about 70-80% depleted throughout both profiles, with the exception of the upper horizon where depletions 491 are distinctly lower, again especially at Kohala H. Zn isotopes also show the same pattern, with 492 493 values very close to parent material in the upper B horizon contrasting with significantly heavier values above and below, in this case more pronounced at Kohala M. 494



496 497

**498** Figure 5: Tau parameters for selected elements (left),  $\tau$  (black) and isotope (red) data for Cu (centre) and Zn (right) in 499 Kohala soils, island of Hawaii. The y axis in all plots is drawn at  $\tau = 0$  to highlight gain or loss of each element. Note 500 the different scale on the tau plot for Kohala H. The red dashed lines in the panels at centre and right show the isotope 501 composition of parent basalt (electronic appendix) to highlight shifts in isotope composition of the soil relative to this 502 reference. Reference isotope values from same source as in Fig. 4.

#### 504 4.3 Maui rainfall gradient: influence of climate on Cu and Zn Distributions

505 Selected tau values as well as Cu and Zn isotope data for the three analysed soil profiles from the 506 Maui rainfall gradient are displayed in Figure 6. Base cations and aluminium are all very strongly 507 depleted in these soils, and the main feature visible in the tau data on Fig. 6 is the drop in Fe 508 concentrations between annual rainfall values of 2500mm and 3350 mm (sites 2 and 4 on Fig. 6) as 509 a result of the change in redox state that has been noted in previous publications (Schuur et al., 510 2001; Chadwick and Chorover, 2001; Miller et al., 2001; Scribner et al. 2006), caused by a 511 transition from well-drained to water-logged soils as rainfall increases.

512



513 514

**Figure 6:** Tau parameters for selected elements (left),  $\tau$  (black) and isotope (red) data for Cu (centre) and Zn (right) in Maui soils. The y axis in all plots is drawn at  $\tau = 0$  to highlight gain or loss of each element. The red dashed lines in the panels at centre and right show the isotope composition of parent basalt (electronic appendix) to highlight shifts in isotope composition of the soil relative to this reference.

The disappearance of Fe oxides along the rainfall gradient is associated with changes in the 520 behaviour of Cu and Zn and their isotopes (Fig. 6). The 2500mm site, which retains some Fe in 521 secondary oxyhydroxide phases (Schuur et al., 2001; Chadwick and Chorover, 2001; Miller et al., 522 2001; Scribner et al. 2006) has the lightest Cu isotopes measured in this study, with  $\delta^{65}$ Cu up to 1.2 523 % lighter than parent material. This profile also retains the most Cu of the three Maui sites, with  $\tau_{Cu}$ 524 values suggesting loss of 50-90% of the initial inventory. In contrast, Cu loss at the other two sites 525 is nearly complete, except in the Oe horizon of Site 6 (5050mm rainfall). Moreover, though the 526 intermediate depths of the two wetter profiles retain the light Cu isotope signature, with  $\delta^{65}$ Cu at 527 0.3-0.7% lighter than parent material, this is bracketed by much heavier isotope compositions 528 (<0.1‰ lighter than the parent isotope composition) at top and bottom.  $\tau_{Zn}$  shows patterns at these 529 three sites that are very similar to  $\tau_{Cu}$ : strong depletion throughout but less strong at Site 2 and 530 moderate at the top of Site 6. Zn isotopes again show rather subtle shifts from parent material 531 values: no shift at all at site 2 and increasing shifts across the rainfall/redox gradient, culminating in 532  $\delta^{66}$ Zn ~0.35‰ heavier than parent material in the O horizon of the wettest Site 6. 533

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#### 536 5. Discussion

538 Our overall objective in this contribution is to assess the extent to which processes in soils can explain the characteristics of Cu and Zn isotopes in the dissolved phase of rivers. Though Cu 539 540 isotope compositions in the incipient weathering environment of Glen Feshie document a dissolved riverine pool that is only marginally heavier than alluvium and soils (-0.07 to +0.11‰ versus -541 542 0.23‰), Vance et al. (2008) found that large rivers globally were universally heavier than continental crust, at  $\delta^{65}$ Cu = +0.02 to +1.45‰ with a discharge weighted average of +0.68‰, much 543 heavier than the bulk continental crust at around 0 to +0.2%. The same study found that particulate-544 545 associated Cu in one small river was 1.2±0.4‰ lighter than the dissolved phase. Zn isotopes in large and small rivers (Little et al., 2014a), though likely more severely impacted by anthropogenic 546 activities (e.g. Chen et al., 2008), display much more subtle variations and the global dissolved 547 riverine flux to the oceans is identical to the upper continental crust at +0.33‰ (Little et al., 2014a). 548

In pursuing this objective, however, complications arise due to a suite of pedological processes that overprint the impact of chemical weathering, such as variability in redox conditions, addition of mineral aerosol, and biological redistribution of elements. In the following we attempt to pick apart the datasets presented here to try to understand the impact of each of these processes individually before concluding with an assessment of the degree to which soils lose heavy or light Cu and Zn isotopes during the weathering process. We acknowledge that this approach, of isolating a single dominant controlling process in each profile, simplifies somewhat. Given the multiplicity and complexity of soil processes, however, it is a more instructive analytical approach than an attempt to consider all the contributing processes in each soil profile.



## 558 5.1 Cu-Zn loss and redox processes in the Maui rainfall sequence

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560 Figure 7:  $\tau_{Cu}$ ,  $\tau_{Zn}$  and Cu and Zn isotope compositions in Maui soils. Cu and Zn are clearly lost from the parent 561 material of these soils in proportions very closely related to their original concentrations. In the 2500mm, oxic, soil this is associated with the loss of the heavy isotope of Cu, and a very subtle fractionation of Zn in the same direction (blue 562 563 arrows), probably controlled by partitioning of isotopes between aqueous organic complexes and Fe oxides retained in 564 the soil. In the wetter, reducing, soils, however, the dominant process involves a move to heavy isotope compositions and the near total depletion of Cu and Zn. We suggest that this is due to the well-known loss of the Fe oxide pool in 565 these anaerobic, water-logged soils (e.g. Schuur et al., 2001; Scribner et al., 2006; Thompson et al., 2011), leaving a 566 567 residual pool of Cu that is close to the original rock composition (red dashed lines in (b) and (c)) and of Zn that is 568 significantly heavier than the original parent material.

569 In many ways the Maui rainfall sequence presents the clearest set of processes seen in this study.

This is emphasized by the data presented in Figure 7, which plots  $\tau_{Cu}$  versus  $\tau_{Zn}$ ,  $\delta^{65}$ Cu and  $\delta^{66}$ Zn for this set of soils. The data in Figure 7a demonstrate that Zn and Cu behave remarkably coherently in these soil samples, being lost in precise proportion to their original concentrations in parent material, as illustrated by the line fitted to all the data but effectively defined by data from Site 2. Soil samples from the two more reduced sites plot at the lower left end of the array, having lost almost all their Cu and Zn, with the exception of the topmost sample from Site 6. Cu-Zn data from these sites show no relationship with quartz contents, which peak at 18-22 wt % in the upper ⁵⁷⁷ levels of Sites 2 and 4 (Scribner et al., 2006), but it nevertheless seems likely that the higher Cu and ⁵⁷⁸ Zn concentrations at the uppermost horizon of Site 6 is due to some kind of addition at the surface. ⁵⁷⁹ Though there is no overall correlation between  $\tau_{Pb}$  and Cu and Zn abundances in these soils,  $\tau_{Pb}$  is ⁵⁸⁰ higher in this sample than any other (at 5.03, Table 3), and it is possible that the added Cu and Zn is ⁵⁸¹ anthropogenic in origin as opposed to mineral aerosol.

Aside from this sample, data for Cu and Zn isotopes also behave in a relatively straightforward way 582 at these sites (Fig. 7b, c). At Site 2 progressive Cu depletion is clearly associated with preferential 583 loss of isotopically heavy Cu, or retention of light Cu, such that the most Cu-depleted soils in the B 584 horizon at Site 2 (85-90% loss) have  $\delta^{65}$ Cu as low as -1.09‰. At the other two sites where, aside 585 from the exceptional sample at the top of Site 6 mentioned above, Cu loss becomes extreme (up to 586 99%) and the isotopic composition of this small residual pool shifts back towards the isotopic 587 composition of the parent material (red dashed line in Fig. 7b). The pattern for Zn isotopes is 588 similar except that the shift to light isotopes upon Zn loss is very subtle while the shift to heavier 589 isotopes at Sites 4 and 6 takes the residual Zn beyond the initial parent material to  $\delta^{66}$ Zn that is up 590 to 0.35% heavier. 591

While there may be a number of potential explanations for the patterns in Fig. 7, they are consistent 592 593 with some observations that have been made before in soils (e.g. Bigalke et al., 2010a, 2011), and are also consistent with a dual set of processes that are both controlled by the redox switch in the 594 middle of this rainfall sequence (Schuur et al., 2001). Though none of the Maui soils are podzols 595 596 (van Breemen and Buurman, 2004), there has clearly been translocation of Fe and Al through and out of the soil (Fig. 6). The aqueous organic species that complex Fe also complex Cu and Zn (e.g. 597 Grybos et al., 2007; Bigalke et al., 2010b; Ryan et al., 2014) and move them through and out of the 598 soil as well (e.g. Keller and Domergue, 1996; Bigalke et al., 2010a,b, 2011). In contrast, sorption of 599 both Cu and Zn to Fe-Mn oxyhdyroxides tends to retain both elements in soils, and the trace metal 600 characteristics of soils have been described in terms of the dual controls of mobile aqueous organic 601 species and oxyhydroxide surfaces (e.g. Grybos et al., 2007). We suggest that it is these two 602 competing processes that determine the patterns in Fig. 7, with heavy Cu and slightly heavy Zn 603 604 moved out of the soil complexed to aqueous organic species. The light Cu, and very slightly light Zn, retained in the dry soil at Site 2, we suggest, is sorbed to Fe oxide phases (blue arrows on Fig. 605 606 7). At the high rainfall end of the gradient, Fe-oxides are lost by reduction and with them the light Cu and Zn, leaving a very small residual pool that is isotopically similar to the parent material for 607 608 Cu, and distinctly heavier for Zn (green arrows in Fig. 7). We note that though conditions are

reducing enough in the two wetter soils to mobilise Fe as Fe(II), there is no evidence that they are 609 reducing enough to form sulphide. The measured Eh at Site 4 where the Fe oxides first disappear is 610 about +300 mV, at Site 6 it is around zero (Schuur et al., 2001). It is possible that wet periods and 611 occasional water-logging could cause Eh to descend transiently from the above measured values, 612 closer to that for sulphate reduction. However, even in water-logged floodplain soils that can 613 become anoxic enough to encounter sulphate reduction, trace metal mobility is controlled by release 614 from Fe oxyhydroxides, organic matter or mobilisation of colloidal metal forms (e.g. Grybos et al., 615 2007; Weber et al. 2009, 2010). 616

617

618 There is experimental and theoretical support for this scenario (reviewed in detail in Moynier et al., 2016), and natural Cu-Zn isotopic data for rivers and the oceans (Vance et al., 2008; Little et al., 619 620 2014a,b) suggest that these controls are ubiquitous in controlling partitioning of Cu and Zn isotopes between aqueous and particulate phases at the Earth's surface. As summarised in a recent review 621 622 (Moynier et al., 2016), experimental studies of the sorption of Cu and Zn isotopes to Fe-Mn oxyhydroxides suggest a range of behaviours. Thus, Pokrovsky et al. (2005) document small 623 624 (<0.2‰) Zn isotope fractionations, in both positive and negative directions depending on the mineral phase, between inorganic aqueous species and sorption to oxides - in both directions 625 626 depending on identity of oxide and never more than  $\pm 0.2$  per mil. Juillot et al. (2008) observed 627 preferential sorption of heavy Zn isotopes to ferrihydrite and goethite by 0.3-0.5‰ and Balistrieri et al. (2008) found sorption of heavy Cu and Zn onto Fe oxyhydroxides, by 0.7 and 0.5% 628 respectively. Some of this variability might be rationalised by the recent study of Bryan et al. 629 (2015), who found that sorption to Mn-oxide (birnessite) involved no significant fractionation at 630 low ionic strengths, whereas at ionic strengths equivalent to seawater sorption to birnessite strongly 631 632 favours the heavy isotope.

633

Sorption of residual metal to the solid, however, is only half the story. All the above experiments 634 were performed with reference to an aqueous phase in which the Cu and Zn were in simple 635 inorganic species. But these two metals are ubiquitously complexed to aqueous organic ligands in 636 637 natural solutions. These organic species have a strong preference for heavy metal isotopes due to stiffer bonds (e.g. Fujii et al., 2014; see review in Moynier et al., 2016), and this often appears to 638 639 govern the distribution of their isotopes in nature (e.g. Little et al., 2014b). Experimentally, Jouvin 640 et al. (2009) and Bigalke et al. (2010b) document heavy isotopes of Zn and Cu associated with 641 humic acids, heavier than free aqueous ion by 0.25% in both cases. Most recently Ryan et al. (2014) used a Donnan dialysis technique to show that ⁶⁵Cu is enriched over ⁶³Cu by +0.14 to 642

+0.84‰ in a range of soluble organic ligands relative to inorganic aqueous species, and that the size 643 of the fractionation was correlated with the stability constants of the complexes. We emphasise that 644 645 the organic species we invoke as important here transport Cu and Zn as organically-complexed species in the aqueous phase. In our view this pool is removed from the soil, and will not be found 646 647 in residual organically-bound Cu and Zn that remains behind in soils and that is targeted through sequential extractions studies (e.g. Kusonwiriyawong et al., 2016). This residual organic fraction 648 may be isotopically light if dominated by metabolic Cu and Zn from plants, or heavy if it has 649 undergone fractionation associated with solid-phase organic material such as humic acids. 650

We suggest that it is the mobilization of Cu and Zn into soil solutions that causes the extreme 651 depletion of Cu, and its heavy isotope, in the oxic site 2 soil profile at Maui, with residual light Cu 652 sorbed onto Fe oxyhydroxide surfaces. Cu isotope ratios in this profile are up to 1.1‰ lighter than 653 the parent material, however, either suggesting an organic complex with an even stronger 654 preference for the heavy isotope of Cu than documented by Ryan et al. (2014) or, perhaps more 655 656 likely, multiple cycles of Cu mobilization and re-adsorption to a smaller residual pool of Fe oxide in a Rayleigh type process. In contrast to Cu, isotope effects during Zn depletion at Maui Site 2 are 657 very small (Fig. 7). This is consistent with the conclusion from the experimental data that Zn 658 isotopic partitioning between aqueous organic complexes and Fe-Mn oxyhydroxide surfaces must 659 be very small indeed. In this scenario, the shift towards heavy isotopes at the higher rainfall sites 660 would be explained by the removal of the isotopically light Fe oxide pool at the low redox 661 potentials observed (e.g. Schuur et al., 2001; Thompson et al., 2007). The fact that the residual pool 662 of Zn is heavier than the parent material may be attributable either to mineral aerosol addition (see 663 664 section 5.2 below), or it may imply that the extremely small residual pool itself records another translocation process and associated Zn isotope fractionation. 665

While we recognize that we cannot rule out a role for other soil sorption sites, our interpretation of 666 the Maui data emphasizes the role of Fe-Mn oxyhydroxides in retaining Cu and Zn in the oxic soils. 667 This emphasis derives from previous work on these samples (e.g. Schuur et al., 2001; Thompson et 668 al., 2007) that documents a sudden loss of the soil Fe oxide pool as well as a prominent shift in Fe 669 isotopes at the point in the rainfall gradient where residual light Cu is seen here to be lost. The 670 scenario described above may also apply to Cu and Zn isotope features of oxic and water-logged 671 soils described previously. In the context of this study we postulate that light isotopes of Cu at 20-672 30 cm in the Laupahoehoe profile might be explained in terms of mobilization of heavy Cu into 673 aqueous organic complexes in soil solutions and retention of light Fe on residual Fe oxides. Bigalke 674 675 et al. (2010a) studied a Skeleti-Stagnic Luvisol, with variations in non-crystalline oxides with depth

within the profile related to drained versus water-logged conditions. They also observe a transition 676 from light isotopes of Cu at the surface to heavier isotopes at depth, coupled to an associated drop 677 in Cu concentrations. Bigalke et al. (2010a) attributed this to redox cycling, without settling on a 678 precise explanation. Viers et al. (2007) found similar features to those seen in Maui soils for Zn, in 679 680 a soil-plant system in a pristine tropical watershed in Cameroon: strong Zn depletion with enrichment in light Zn isotopes (but by up to 0.6% in their case) in "ferruginous" horizons, that 681 contrasted with a water-logged "swamp zone" that had Zn isotopes very similar to the bedrock. We 682 also note that this potentially important process controlling Cu, Zn and their isotopes in soils is 683 analogous to that proposed for Fe isotope behaviour in Podzols, where heavy Fe is mobilised into 684 685 aqueous solutions by organic-ligand-promoted dissolution and complexation, while illuvial B horizons are enriched in the light isotopes by 0.6‰ (Wiederhold et al., 2007). 686

687

#### 5.2 The impact of mineral aerosol dust: the example of the Kohala 150 kyr soil profiles

689 The Hawaiian island soil sites were specifically chosen for their remoteness from sources of anthropogenic and natural contamination via the atmosphere. Though the surfaces of many soils 690 691 studied here, in both Hawaii and Scotland, often show very significant enrichment in Pb (Tables 1,3), there is no overall relationship between  $\tau_{Pb}$  and  $\tau_{Cu}$ ,  $\tau_{Zn}$  or Cu-Zn isotopes, suggesting that 692 anthropogenic impacts on Cu, Zn and their isotopes are not significant in these soils. A recent study 693 of Mo and its isotopes (King et al., 2016) has documented the significance of atmospheric Mo 694 695 sourced in volcanic fog (vog), but too little is known about the Cu-Zn content of this material to be 696 more precise about its relevance to our study. Many previous studies, however, using tracers such as quartz and mica content (not present in parent basalt but present throughout Hawaiian soils, even 697 698 at depth within soil profiles, e.g. Kurtz et al., 2001) as well as an array of isotopic and trace element approaches, have documented the importance of Asian dust to the Hawaiian soils (e.g. Kennedy et 699 700 al., 1998; Teutsch et al., 1999; Kurtz et al., 2001; Stewart et al., 2001; Huh et al., 2004; Monastra et 701 al., 2004; Scribner et al., 2006; Pett-Ridge et al., 2007; Chadwick et al., 2009; Mikutta et al., 2009). 702 Examination of the detailed systematics of the soils studied here reveal the impact of a similar 703 complication for these metals (Fig. 8). The blue and green arrows on the tau-tau plots on Fig. 8 704 recap the findings for Maui soils described in section 5.1, but also show data for the other Hawaiian 705 soils studied. Clearly, the soils from Laupahohoe and Kohala in particular show deviations from the simple removal trajectories for Cu, Zn and heavy Cu isotopes seen in Maui Site 2 (blue arrows in 706 707 Fig. 8). The russet arrows on panels (a), (c) and (d) in Fig. 8 illustrate the trajectory that would be observed for a variable supply of Asian dust, using the constraints on its chemistry derived from the 708

study of North Pacific deep sea sediments (Kyte et al., 1993) in a fashion analogous to the approach
taken by Pett-Ridge et al. (2007) for uranium.



711

712 **Figure 8:** Relationships between  $\tau_{Mn}$ ,  $\tau_{Cu}$ ,  $\tau_{Zn}$  and Cu isotope compositions Maui Site 2 and all other Hawaiian soils studied here. Site 2 at Maui is shown to illustrate the important process identified there involving coupled loss of Cu 713 714 and Zn in proportion to their occurrence in parent material, and preferential loss of the light isotope of Cu (blue arrows). 715 Note that Cu isotopic composition in (b) is plotted as a  $\Delta$  value from parent material. The green arrow on this figure 716 shows schematically the trajectory seen in Sites 4 and 6 at Maui, involving loss of the light Fe-oxide pool of Cu. A trajectory similar to the blue arrow explains a lot of the data from other soils. The prominent exceptions are soils from 717 Kohala, and to a lesser extent Laupahoehoe. The russet arrows on the tau diagrams (a) and (c) and show the trajectory 718 expected through addition of Asian dust (Kyte et al., 1993; Pett-Ridge et al., 2007). The exact trajectory created by such 719 720 addition on (b) is difficult to estimate, and depends on how much Cu is left in the soil when the dust is added - e.g. if 721 Cu is completely removed from the soil before dust Cu is added the trajectory could be near vertical, whereas the slope 722 will be gentler if the dust is added when there is still significant parent Cu remaining in the soil.

The slope of the arrows on Fig. 8 are obtained by calculating a "tau" value for Asian dust relative to 723 the parent material from which the soils derive and then a ratio, e.g. of  $\tau_{Cu}$  to  $\tau_{Zn}$  in panel (a). Thus 724 725 the trajectories illustrate how the chemistry of a soil that had not been chemically weathered at all would respond to dust addition. If two elements plotted on one of these panels are removed by 726 chemical weathering in the proportions they are found in parent material before dust addition, the 727 russet arrows accurately indicate the impact of dust. This is apparently the case for Cu vs. Zn at 728 Maui site 2 (section 5.1), and the blue arrow drawn on Fig. 8c also suggests that it is the case for Zn 729 vs. Mn. As can be seen, the trajectories for dust addition match data arrays well. These dust 730 trajectories are relatively flat on both the  $\tau_{Cu}$ -  $\tau_{Zn}$  and  $\tau_{Mn}$ - $\tau_{Zn}$  plots because Hawaiian soils are very 731 depleted in Cu and Mn relative to Asian dust, while Zn concentrations are similar. In other words, 732 the flat trajectory on the Mn-Zn plot results from the very high Mn/Zn ratio of Asian dust relative to 733

Hawaiian soils. Though the Mn addition to the Kohala H soil appears extreme, we note that Kraepiel et al. (2015) document soil  $\tau_{Mn}$  values up to 6 times higher, which they also attribute to atmospheric addition, possibly in combination with biolifting by plants and the fact that oxidizing conditions lead to retention of dust-derived Mn near the top of the soil. Given the mean annual precipitation of 1060mm at the Kohala H site, and the well-established relationship between MAP and redox, we expect Eh to be well in excess of +500 mV and that Mn should remain in oxidized form.

Any attempt to subtract the impact of dust on the Cu and Zn isotopic compositions of the soils it 741 affects is rendered difficult by two issues, as illustrated in the  $\tau_{Cu}$ - $\delta^{65}$ Cu panel (b) of Fig. 8. On this 742 diagram the trajectories that would be defined by samples that have seen dust added are variable 743 because the impact on Cu isotopes depends on the Cu concentration of the soil - how much 744 depletion by chemical weathering it had undergone - when the dust is added. The other problem is 745 746 that if the isotopic data at Kohala are to be explained by dust addition then that dust must sometimes have a minimum  $\delta^{65}$ Cu +0.9‰ (Fig. 8b) and a minimum  $\delta^{66}$ Zn of +0.8‰ (not figured, 747 Table 3). We expect the copper isotope composition of an Asian dust source to approximate that of 748 the continental crust and sediments. This is close to zero in  $\delta^{65}$ Cu, and measured values for Chinese 749 Loess as well as Atlantic marine aerosols range from -0.2 to +0.3% (Li et al, 2009; Little et al., 750 2014a).  $\delta^{65}$ Cu values = 0.03±0.12 and 0.20± 0.16‰ and  $\delta^{66}$ Zn values = 0.20±0.05 and 0.28±0.08 751 ‰ have been reported for the <4µm fractions of dust samples from Taklamakan Desert, China, 752 753 considered to be a major source of the Asian dust plume (Dong et al., 2013). This study also found variations of up to 0.5‰ among the different size fractions, with some samples of the >63µm 754 755 fraction notably giving isotopic values 0.37-0.48‰. Copper and zinc in atmospheric dust is likely to 756 be present in metal-rich coatings (desert varnish) on the surfaces of quartz. It is possible that these 757 oxide coatings could have heavy Cu and Zn due to adsorption fractionation, as suggested for iron 758 isotopes on desert varnishes by Busigny and Dauphas (2007). Supergene enriched copper minerals tend to have heavier Cu-isotopic compositions than primary copper minerals (Mathur et al, 2005, 759 2009; Markl et al., 2006; Matthews unpublished data) with values as high as 9.5‰ and their 760 exposure in the surface could bias the dust record. 761

### 762 5.3 Impact of biological cycling on surface horizons of young Glen Feshie soils

The surface horizons of Glen Feshie soils are variably enriched in Cu and Zn. Cu isotopes are
generally slightly heavier, while Zn isotopes are subtly lighter than horizons immediately beneath. *A priori* these features could be caused either by deposition of Cu and Zn from the atmosphere onto

the surface, of either mineral dust or anthropogenic particulates, or with translocation of Cu and Zn
upwards through the soil due to plant activity at the surface. Bigalke et al. (2010a, 2011) discuss
both these possibilities with regard to enrichments of Cu in the surface horizons of soils.

769 The field site at Glen Feshie is situated away from major industrial centres. The most likely source 770 of anthropogenic Cu and Zn would therefore be long-range transfer of ash or dust from smelters and refineries. Some deposition at Glen Feshie is possible given the transport distances previously 771 observed for anthropogenic Zn (Candelone et al. 1995; Planchon et al. 2002). The isotopic 772 773 composition of anthropogenic Cu in ash or dust is highly dependent upon that of the ores being smelted (Mattielli et al. 2009), which can be highly variable (Mathur et al. 2009). Conversely, Zn 774 in ash or dust is light due to evaporation during the smelting process (Mattielli et al. 2009), and is 775 fractionated during atmospheric transport, leading to increasingly light compositions with 776 increasing transport distances (Sonke et al. 2008). Anthropogenic Zn deposited at Glen Feshie 777 would therefore be expected to be isotopically light, as is observed. 778

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780 Major deposition of anthropogenic Cu and Zn from smelting has occurred since ~1900 (Thapalia et al. 2010). It follows, therefore, that if significant anthropogenic deposition had occurred at Glen 781 Feshie, all the soils older than ~100 years would be affected to the same extent. This is clearly not 782 the case.  $\tau_{Cu}$  and  $\tau_{Zn}$  at Glen Feshie (Fig. 3) show accumulation of both metals at the surface. This 783 could indicate addition of the metals via dust or ash but, since accumulation increases with age and 784 is not the same for all soils older than ~100 years, an anthropogenic origin does not seem likely. 785 Furthermore, the trend towards lighter isotopic compositions of Zn at Glen Feshie is progressive 786 787 with age rather than a step change between the 0.1ka and older soils (Fig. 3).

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Additional Cu and Zn could also be derived from mineral aerosols. But Nd data for Glen Feshie 789 (Keech 2011) suggest no significant accumulation of mineral aerosols. This is supported by simple 790 estimates of dust input to Glen Feshie. Modelling by Mahowald (2006) suggests a present-day rate 791 of dust deposition over Scotland of  $0.75\pm0.25$  g/m²/yr. Using this rate and assuming concentrations 792 of Cu and Zn in dust equal to their concentrations in the upper continental crust (25 and 71 ppm 793 respectively; Taylor and McClennan, 1995), then the total masses of Cu and Zn deposited on the 794 Glen Feshie soils over 13 ka are 0.24 and 0.69  $g/m^2$  respectively. These values are equivalent to 795 about 5% and 2% of the total amount of Cu and Zn in the uppermost metre of the 13 ka soil 796 797 (assuming a density of 1000  $g/m^3$ ). These estimates confirm that mineral aerosols must constitute, 798 at most, a minor input of Cu and Zn to these soils and, combined with an apparent lack of anthropogenic input, we propose that vegetation and weathering are the dominant controls uponcycling of Cu and Zn in organic-rich shallow soils horizons at Glen Feshie.



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**Figure 9:** Relationships between  $\tau_P \tau_{Cu}$ ,  $\tau_{Zn}$  and Cu-Zn isotope compositions for the upper organic-rich levels of Glen Feshie soils., showing coupled enrichment of phosphorous and Cu (top left) and Zn (bottom left). Such biological concentration of Cu and Zn in surface horizons may come with lighter Zn isotopes (bottom right), but data for Cu isotopes does not indicate any particular trend.

Schulz et al. (2010) observed the effect of biolifting on the distribution and composition of Fe in a 807 soil chronosequence from Santa Cruz, California. Biolifting is the process by which plant roots and 808 symbiotic fungi (mycorrhizae) transport an element from deep in the regolith to the shallow soil. 809 The  $\tau_{Cu}$  and  $\tau_{Zn}$  and  $\tau_P$  (Fig. 3) profiles observed at Glen Feshie are indicative of biolifting.  $\tau_{Zn}$ 810 increases with soil age in the uppermost soil horizons but decreases at depth, suggesting movement 811 of Zn upwards with increasing soil development. Moreover,  $\tau_{Cu}$  and  $\tau_{Zn}$  are correlated with  $\tau_P$ , as 812 demonstrated in Fig. 9. Calluna vulgaris is strongly mycorrhizal, and therefore biolifting provides a 813 likely explanation for the distribution of Zn observed at Glen Feshie. Enrichment of Cu is also seen 814 at the surface of the Glen Feshie soils. Biolifting and fractionation by vegetation can also explain 815 some aspects of soil  $\delta^{66}$ Zn and  $\delta^{65}$ Cu at Glen Feshie. Plant samples from Glen Feshie demonstrate 816 a preference for light Cu and Zn (Table 2). This is broadly in keeping with the observations of 817 previous studies, but also with some important differences as discussed earlier in section 4.1 The 818 general trend towards lighter Zn with  $\tau_P$  (Fig. 9) may reflect the preferential movement of light Zn 819 upwards through the soil profile facilitated by mycorrhizae. Additional light Zn at the surface could 820 come from leaf litter and the decay of dead plant matter enriched in the light isotopes. Conversely 821 however, one might expect plant uptake of the light isotopes to leave soils enriched in heavy Zn. 822

This type of process could explain the trend towards heavier  $\delta^{65}$ Cu values at the surface of the soil profiles (Fig. 3). The relative impact of these processes is unknown, as total biomass per unit soil has not been measured for the Glen Feshie soils, but their dual control could explain the absence of a relationship between  $\tau_P$  and Cu isotopes seen in Fig. 9. Overall, a more definitive identification of the process of bio-lifting for Cu and Zn and their isotopes must await more targeted studies than possible here.

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## 830 6. Concluding remarks: Integrated soil Cu-Zn isotopes and the isotopic composition of rivers

In this concluding section we return to our larger-scale objective in this paper, to investigate the extent to which processes in soils can explain observations of heavy Cu isotopes relative to rocks, in contrast with relatively unfractionated Zn isotopes, in the dissolved phase of rivers. To do so we calculate values of tau for elements of interest, integrated for entire soil profiles, weighting taus for individual horizons for density ( $\rho$ ) (where data are available) and thickness (z) as follows:

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$$\tau_{i}^{int} = \sum \frac{\left(\tau_{h} \rho_{h} z_{h}\right)}{\left(\rho_{t} z_{t}\right)}$$

837 where *h* refers to each individual horizon and *t* to the values for the entire profile. Unfortunately, 838 density data are not available for the Glen Feshie or Kohala H samples, and we are forced to 839 calculated integrated taus without weighting for the density of each horizon. Figure 10 plots these 840 data versus integrated soil  $\Delta^{65}$ Cu_{parent material-soil} and  $\delta^{66}$ Zn _{parent material-soil}. On these diagrams the lower 841 left quadrant denotes loss of heavy isotopes from soils while the upper left quadrant denotes loss of 842 light isotopes.

We have discussed an array of fundamental soil geochemistry processes that determine the fate of 843 844 Cu and Zn in coarse- and fine-grained granitic and basaltic soils, respectively. Isotopically light Cu is retained on Fe oxyhydroxides in the least reduced Maui soil profile, while reduction of Fe oxides 845 at the wetter sites strips out this residual light Cu under anaerobic conditions. Though there has 846 presumably been addition of mineral aerosol to the Maui soils, Cu-Zn isotopes appear to be 847 848 dominated by depletion processes. At Kohala in particular, on the other hand, these chemical weathering processes are overprinted by the addition of mineral aerosol dust. In the young Scottish 849 soils, bio-lifting of Cu and Zn to surface horizons is an important process. Nevertheless, and despite 850 these complexities, it is clear from Fig. 10 that, overall, isotopically heavy Cu is lost from soils, 851 while integrated isotopic compositions of Zn in soils do not depart significantly from those of 852

parent material. The trajectories for addition of Asian dust illustrated in Fig. 8 could, in principle, allow us to remove this overprint from the older Hawaiian soils. Unfortunately, however, quantitative correction is precluded by the lack of constraint on the Cu isotopic composition of the added mineral aerosol. What can be concluded for sure, however, is that the Cu added by mineral aerosol is isotopically heavy, so that the degree to which weathering and other processes cause enrichment of light Cu in soils, and the export of heavy isotopes, is under-emphasised in Fig. 10.





Figure 10: Integrated (whole-profile) taus and isotopic compositions for the soils studied here, with Zn isotopes plotted on the same scale as Cu to illustrate the relative subtlety of Zn isotope variation in soils. The blue and green arrows indicate the weathering processes identified in the Maui rainfall sequence identified earlier: retention of light residual Cu isotopes on Fe oxides in oxic soils (blue), loss of this pool in water-logged soils (green). Weathering loss of light isotopes of Cu, however, is obscured in other locations due to addition of heavy dust-derived Cu (Kohala, Hawaii), while the Scottish soils also appear to have accumulated Cu. All soils have lost Zn but with insignificant isotope fractionation.

We suggest, however, that the weathering process identified in the oxic soils of Maui, involving the 868 partitioning of stable isotopes between aqueous organic complexes and particulate oxyhydroxide 869 surfaces, is likely to be a key factor in the behaviour of metal isotopes in soils and elsewhere at the 870 surface of the Earth. In low ionic strength aqueous solutions, experiments suggest subdued isotopic 871 fractionation via sorption from an inorganic Zn pool (Bryan et al., 2015), which may be negated or 872 873 reversed if the aqueous Zn pool is complexed by organic ligands (Jouvin et al., 2009), as seen here for soils and for rivers in Little et al. (2014a). The more pronounced preference of these organic 874 complexes for heavy isotopes (Ryan et al., 2014) probably causes the larger fractionations seen for 875 Cu in oxic soils (this study), and in the dissolved versus particulate pool of rivers (Vance et al., 876 2008). The higher ionic strength of the oceans, on the other hand, coupled to organic speciation of 877 both Cu and Zn in the aqueous phase, produces smaller fractionations for Cu (e.g. Vance et al., 878 879 2008; Little et al. 2014a,b) and significantly heavy Zn isotopes sorbed on oxyhydroxides relative to

the dissolved pool (e.g. Marechal et al., 2000; Vance et al., 2008; Zhao et al., 2014; Conway and
John, 2014; Little et al., 2014a,b; Bryan et al., 2015).

So it is clear that the isotopic characteristics of the dissolved pool of rivers (Vance et al., 2008; 882 Little et al., 2014a) can be rationalised by processes that at least start in soils. Nevertheless, there is 883 a mass balance issue to be considered. Neubert et al. (2011) pointed out that soils cannot be the 884 ultimate long-term storage reservoir for the isotopically light particulate-bound Mo that is required 885 886 to balance the isotopically heavy riverine Mo flux. The same is true for Cu and Zn, as illustrated by 887 a simple order of magnitude calculation. If we use the Maui Cu and Zn concentrations and soil densities, and if we calculate the Cu and Zn inventories in 1m of soil spread over the entire extra-888 Antarctic continental area, we find that soils could store only about 30 years worth of the riverine 889 flux of Cu, and about 125 years worth of the riverine flux of Zn. These figures are almost certainly 890 maxima: soils cannot be the ultimate storage reservoirs of the light Cu required to balance rivers. At 891 Glen Feshie, and in the small river studied in detail by Vance et al. (2008), riverine particulates are 892 also isotopically light. The ultimate storage reservoir is likely, then, to be fluvial and continental 893 margin sediments. The fate of the oxyhydroxide-associated Cu that might be stored in these 894 settings, against diagenetic processes that potentially re-mobilise it into the oceanic dissolved pool 895 (e.g. Shaw et al. 1990), will be important for oceanic mass and isotopic balances (e.g. Little et al., 896 2014a,b), and a target for future work. 897

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