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Abstract: Copper and Zn are trace metal micronutrients whose stable isotope systematics are receiving increasing attention as possible paleoenvironmental tracers. However, to realise this potential, their behaviour during chemical weathering must be better constrained. We present coupled Cu and Zn isotope data for a well-characterised Indian laterite weathering profile, which includes a full suite of samples from unaltered greywacke bedrock to indurated lateritic duricrust. This sample set provides an exceptional opportunity to interrogate Cu and Zn isotope compositions during an extreme example of chemical weathering. Despite their occurrence in different host phases within the parent greywacke, Cu and Zn isotopes behave coherently during weathering. We observe preferential loss of heavy isotopes at increasing degrees of alteration, with 0.6‰ total variability in δ^{66}Zn and 0.9‰ in δ^{65}Cu. Given the absence of evidence for CuS or ZnS phases in the parent lithology, we attribute the liberation of heavy isotopes to organic complexation in the aqueous phase and/or incorporation of light isotopes in secondary aluminous Fe-oxides. Strong enrichment of both metals is also associated with a peak in Mn at a previously identified paleo-water table horizon. This dataset confirms that weathering under oxygenated conditions releases isotopically heavy Cu, regardless of the host phase. Meanwhile, Zn isotopes are only fractionated to any significant extent at the most extreme degrees of chemical weathering reached during lateritization. We conclude that the isotopic composition of the weathering-derived input of Zn to rivers should be largely insensitive to climate change on geological timescales.

Cu and Zn isotope fractionation during extreme chemical weathering

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Abstract

Copper and Zn are trace metal micronutrients whose stable isotope systematics are receiving increasing attention as possible paleoenvironmental tracers. However, to realise this potential, their behaviour during chemical weathering must be better constrained. We present coupled Cu and Zn isotope data for a well-characterised Indian laterite weathering profile, which includes a full suite of samples from unaltered greywacke bedrock to indurated lateritic duricrust. This sample set provides an exceptional opportunity to interrogate Cu and Zn isotope compositions during an extreme example of chemical weathering. Despite their occurrence in different host phases within the parent greywacke, Cu and Zn isotopes behave coherently during weathering. We observe preferential loss of heavy isotopes at increasing degrees of alteration, with 0.6‰ total variability in δ^{66}Zn and 0.9‰ in δ^{65}Cu. Given the absence of evidence for CuS or ZnS phases in the parent lithology, we attribute the liberation of heavy isotopes to organic complexation in the aqueous phase and/or incorporation of light isotopes in secondary aluminous Fe-oxides. Strong enrichment of both metals is also associated with a peak in Mn at a previously identified paleo-water table horizon. This dataset confirms that weathering under oxygenated conditions releases isotopically heavy Cu, regardless of the host phase. Meanwhile, Zn isotopes are only fractionated to any significant extent at the most extreme degrees of chemical weathering reached during lateritization. We conclude that the isotopic composition of the weathering-derived input of Zn to rivers should be largely insensitive to climate change on geological timescales.

Keywords: Cu, Zn, Isotopes, Laterite, Weathering, Organic complexation, Fe oxides

2

1.0 Introduction

Variations in the stable isotope ratios of the bioessential transition metals Zn and Cu are increasingly being utilised as tracers of past Earth surface processes, particularly in the ocean (e.g., Kunzmann et al., 2013; Pons et al., 2013; Chi Fru et al., 2016; John et al., 2017; Isson et al., 2018). However, while isotopic shifts in sedimentary records of both Zn and Cu are undoubtedly present during periods of global change (e.g., Snowball Earth events in the Neoproterozoic), and often tantalisingly systematic (e.g., Kunzmann et al., 2013; John et al., 2017), their underlying controls remain difficult to elucidate.

Paleoceanographic interpretations of observed Zn and Cu isotope variations can be divided into one or more of three main causal categories. (1) Invoking a change in biological productivity (or other related process) in the ocean itself (Kunzmann et al., 2013; Isson et al., 2018). (2) Suggesting a change in the balance of the removal fluxes to different oceanic sinks, for example, due to a change in ocean redox state (Chi Fru et al., 2016; John et al., 2017). (3) Interpretations that require a change in the magnitude or isotopic composition of a *source* of the element to the ocean, for example, a change in the weathering-derived flux due to tectonic or climate change (Kunzmann et al., 2013; Pons et al., 2013; Chi Fru et al., 2016).

Weathering of the continents supplies solutes to rivers, which constitute a key input of Zn and Cu to the modern ocean (Little et al., 2014b). The Zn and Cu isotope composition of rivers will thus reflect that supplied by weathering, though biogeochemical processes in rivers may subsequently modify this primary signature (e.g., Borrok et al., 2008; Coutaud et al., 2014; Szynkiewicz and Borrok, 2016; Coutaud et al., 2018). The aim of this study is to investigate Zn and Cu isotope fractionation during extreme chemical weathering. This approach provides an end-member constraint on the degree of isotope fractionation possible in the weathering environment. It is a starting point from which to evaluate the leverage of chemical weathering in modifying the isotopic composition of rivers through time, and hence its possible influence on the wider marine inventory.

33

34   A study of the dissolved phase in rivers found a discharge-weighted Zn isotope

35   composition unfractionated from continental rocks (Little et al., 2014b). The absence

36   of systematic Zn isotope fractionation in rivers implies little or no Zn isotope

37   fractionation during weathering, a hypothesis partially supported by studies of Zn

38   isotopes in soils (Bigalke et al., 2010a; Vance et al., 2016; Opfergelt et al., 2017; Suhr

39   et al., 2018). However, studies carried out in extreme, (sub-) tropical weathering

40   regimes have observed preferential release of heavy Zn isotopes (Viers et al., 2007;

41   Lv et al., 2016; Guinoiseau et al., 2017; Suhr et al., 2018). This observation has been

42   explained by various processes, including release of isotopically heavy Zn during

43   oxidative weathering of sulphides (Fernandez and Borrok, 2009; Lv et al., 2016);

44   organic complexation of the heavy isotope in the dissolved pool (Guinoiseau et al.,

45   2017); incorporation or adsorption of isotopically light Zn in/on clays (Viers et al.,

46   2007; Guinoiseau et al., 2017) or Fe oxides (Viers et al., 2007; Suhr et al., 2018); or

47   release of isotopically light Zn from refractory mineral phases and subsequent re-

48   precipitation with Fe oxide phases (Suhr et al., 2018).

49

50   In contrast to Zn, Cu in the riverine dissolved pool is isotopically heavy relative to

51   rocks (Vance et al., 2008); this behaviour is similar to observations for Mo (Archer

52   and Vance, 2008; Neubert et al., 2011), Li (Huh et al., 1998), Ni (Cameron and

53   Vance, 2014), and Cr isotopes (Frei et al., 2014). Accordingly, there are two proposed

54   explanations for the heavy Cu isotope composition in rivers: (1) An equilibrium

55   isotope fractionation in rivers (Vance et al., 2008) and/or in soils (Vance et al., 2016)

56   between an isotopically heavy, organic ligand bound, dissolved pool and an

57   isotopically light pool sorbed to particulates; (2) Redox-driven release of isotopically

58   heavy Cu during oxidative weathering of sulphides in black shales or supergene

59   systems (Mathur et al., 2005; Mathur et al., 2012; Mathur and Fantle, 2015; Lv et al.,

60   2016).

61

62   The present study investigates the Zn and Cu isotope systematics of a well-

63   characterised Indian lateritic weathering profile. The term laterite is not always used

64   ubiquitously or consistently. We follow the definition in the widely cited

65   *Encyclopaedia of Geomorphology* (Goudie, 2004; Widdowson, 2004), which states

66   that: 'Laterite is an iron-rich, sub-aerial, weathering product, commonly believed to

67 evolve as a result of intense, *in situ* substrate alteration under tropical or sub-tropical

68 climatic conditions.' A lateritic weathering profile therefore constitutes a chemical

69 residuum resulting from the relative enrichment of relatively immobile elements

70 (notably Fe and Al), as described initially by Newbold (1844), and more recently by

71 many other authorities (e.g., McFarlane, 1976; McFarlane, 1983; Schellman, 1983;

72 Aleva, 1984; Widdowson, 2004, 2007; Babechuk et al., 2014). This definition

73 emphasises the relative enrichment of Fe (and Al) through desilication processes

74 involved in the development of a laterite profile; this enrichment/depletion may be

75 modified through hydromorphism associated with oscillating redox conditions in the

76 developing weathering profile and typically driven by pluvial seasonality and

77 associated water-table recharge.

78

79 Laterites typically form on parent lithologies with inherently high iron contents (such

80 as mafic and ultramafic igneous rocks and chemically immature sediments) and on

81 stable continental landmasses subject to high mean annual temperatures, high

82 humidity and seasonal, high annual rainfall (Widdowson, 2007). These climatic

83 conditions promote intense *in situ* chemical weathering and mineral alteration,

84 making laterites an ideal natural laboratory to study the weathering process *in*

85 *extremis*. Today, laterites and associated weathering products account for

86 approximately 30% of Earth surface cover, and almost 50% of continental drainage

87 flows over these terrains (Tardy, 1997).

88

89 To date, two studies have reported Zn isotope data from lateritic weathering profiles,

90 one developed on granodiorite in Cameroon (Viers et al., 2007) and the other for the

91 Bidar laterite developed on Deccan basalt in central India (Suhr et al., 2018). Both

92 studies observe preferential retention of light Zn isotopes in the laterite residues. To

93 the best of our knowledge, no Cu isotope data for laterites has yet been reported.

94

95 **2.0 Geological setting and background**

96

97 **2.1 Geological setting**

98

99   The coastal lowlands of western peninsular India between ~8° and ~19°N comprise

100   dissected, laterite-capped 'tablelands' with maximum altitudes of ~150–200m in the

101   east systematically descending to less than 50–100m at the coastline (Widdowson,

102   2009). These tablelands are remnants of a once extensive laterite belt that extended

103   along the length of western peninsular India (Widdowson, 2009), developed upon a

104   variety of lithologies. This belt provides evidence of an important phase of Cenozoic

105   lateritization that affected western India during the latest Eocene to the Miocene

106   (Schmidt et al., 1983; Bonnet et al., 2014), when climatic conditions were optimal for

107   deep weathering (Tardy et al., 1991).

108

109   The site of the investigated profile lies in the small coastal state of Goa. Metamorphic

110   rocks of varying grade and composition dominate the geology of Goa (Pascoe, 1950)

111   and include weakly metamorphosed Dharwar sediments of the Dharwar craton,

112   including abundant Late Archaean greywackes (Argast and Donnelly, 1986; Devaraju

113   et al., 2010; Dessai, 2011). The samples in this study (hereafter referred to as 'SQ')

114   are from a quarried laterite profile developed upon meta-greywackes of the

115   Sanvordem Fm (of the Proterozoic age Dharwar Supergroup; > 2.5 Ga) at Merces

116   village, near Panjim Goa (15°28'44"N, 73°52'35"E; Fig. 1).

117

118   The parent greywacke consists of a detrital assemblage of quartz, feldspar and

119   volcanic rock fragments (Srinivasan et al., 1989) and geochemical analysis suggests

120   that the bulk sediment was derived from submarine weathering of a felsic volcanic

121   source (Devaraju et al., 2010). Sparse biotite has developed in response to low-grade

122   thermal metamorphism of unknown age. The SQ laterite profile itself is of probable

123   Oligocene-Miocene age (c. 35 – 20 Ma; Schmidt et al., 1983; Bonnet et al., 2014),

124   and developed upon the low-lying coastal (Konkan) plain, subsequent to erosion (i.e.

125   removal of c.1 – 1.5km thickness) across the Indian continental margin (Widdowson,

126   1997; Widdowson and Gunnell, 1999).

127

128   **2.2 Sample description**

129

130   The lithology and mineralogy of the 34 m thick laterite profile has previously been

131   reported in Wimpenny et al. (2007) as the SQ samples series, and comprehensively in

132   Hibbert (2017) as an independent MQ sample series. A schematic diagram of the SQ

profile is shown in Figure 2 (mineralogy and major element data from Wimpenny et al., 2007). Samples SQ2 – SQ14 were sampled from increasingly shallow depths and represent a greywacke parent that has undergone increasing degrees of alteration (Table S1; Figs. 2, 3). Sample SQ1 was taken from a small mafic dyke, which cuts unaltered greywacke near the base of the profile. All samples have previously been analyzed for major element (Table S2) and high-precision trace element concentrations (Table S3) (Howarth et al., 2018; Wimpenny et al., 2007).

Deep lateritic weathering profiles such as the one described here have considerable antiquity and affect the substratum far below that of modern pedogenetic processes. The degree of alteration progresses upward from unaltered 'parent' material, through saprock to saprolite, through a 'mottled zone', and ultimately to the topmost Fe-rich laterite duricrust (i.e. 'carapace' and then indurated 'cuirasse' in the francophone terminology).

Saprock (from the Greek '*sapros*' meaning 'rotten') is the first stage of weathering: It consists of partially weathered minerals and as yet unweathered minerals (e.g., feldspars have begun to alter to clay minerals and/or olivine to iddingsite). Saprock maintains all the fabrics and features of the fresh rock, and is distinguished from the more advanced stage of saprolite by retaining much of its original physical strength, and some primary mineralogy. Saprolite is more altered than saprock but, like saprock, there has been little or no change in bulk volume, and the distribution of resistant minerals remain more or less in position as they occurred in the parent. Weatherable minerals in saprolite are typically wholly pseudomorphed by clays and/or oxides and oxyhydroxides, whilst the original rock fabric remains largely preserved (Taylor and Eggleton, 2001). In the zone of alternating reduction and oxidation due to repeated wetting and drying, segregation of iron occurs, forming 'mottles'. The uppermost laterite duricrust hardens irreversibly due to complete drying and oxic conditions, and consists predominantly of crystallised Fe and Al oxide and oxyhydroxides.

The SQ profile can be divided into four zones of alteration (Figs. 2, 3), as defined by Wimpenney et al. (2007):

166　Zone I, at 34 – 15m depth (samples SQ2 – SQ6), exhibits no alteration (parent rock)

167　or low degrees of alteration while retaining the primary texture and fabric of the

168　bedrock (saprock);

169　Zone II, at 15 – 8.5m depth (samples SQ7 – SQ9), consists of altered saprolite in

170　which most weatherable primary minerals are destroyed, then passing into a 'mottled'

171　region, in which secondary minerals and Fe-Al-rich accretions (i.e. mottles) form;

172　Zone III, at 8.5 – 7m depth (samples SQ10 and SQ11), is a narrow zone thought to be

173　influenced by a paleo-water table (Wimpenny et al., 2007);

174　Zone IV, at 7m – surface (samples SQ12 – SQ14), is the Fe-rich cap in which

175　secondary minerals are removed and the Fe-Al-rich accretions fuse to form a resistant,

176　indurated laterite duricrust.

177　The 'line of seepage', at ~15m depth, divides little altered greywacke (zone I) from

178　the zones of increasing alteration above, and is so-called because it marks a

179　significant increase in porosity and permeability (Wimpenny et al., 2007).

180

181　The mineralogical changes that occur upwards in the profile (Table S1, Fig. 3) are

182　reflected in variations in major element concentrations (Table S2, Fig. 2),

183　characterized by a general decrease in Si and concomitant enrichment in Fe and Al

184　(Wimpenny et al., 2007; Widdowson, 2009). In the low alteration zone I, the range of

185　major element concentration variations are somewhat limited (Table S2, Fig. 2) and

186　are likely related to lithological heterogeneity in the parent greywacke (Widdowson,

187　2009). Above the line of seepage, in zones II and IV, there is an increasing degree of

188　depletion of more mobile elements (e.g., Si, Mg, Ca, Na, K), due to the formation and

189　then breakdown and removal of secondary clay minerals, generating the observed

190　enrichment of less mobile elements (e.g., Fe, Al and Ti) in the residue (Widdowson,

191　2009). Notably, this broad pattern is interrupted at ~7 – 8.5m depth (zone III; samples

192　SQ10 and 11) by significantly elevated concentrations of Fe and Mn and depletion of

193　Al; previously interpreted as the depth of a paleo-water table (Fig. 2; Wimpenny et

194　al., 2007).

195

196　Trace element concentrations exhibit similar coherent trends as the rock becomes

197　increasingly altered in zones II-IV (Wimpenny et al., 2007; Howarth et al., 2018).

198　Some fluid-mobile elements (e.g., Li, Rb, Ba, Cu, Zn) show a general decrease in

199　concentration towards the surface but a pronounced peak at the paleo-water table (Fig.

S1A). Other fluid mobile elements, particularly the REE and PGEs, show enrichment
at the paleo-water table and in zone IV (Fig. S1B), this is attributed to mobilization in
low pH, high Eh conditions below, followed by scavenging from solution and
incorporation in the oxide phases that precipitate above (Wimpenny et al., 2007). By
contrast, relatively immobile elements (e.g., Zr, Ti, Nb) display a general increase in
concentration towards the surface and a pronounced concentration decrease at the
paleo-water table (Fig. S1C).

3.0 Analytical Methods

3.1 Sulphur analyses

Sulphur concentrations were measured on an aliquot of solution previously digested
for high precision trace element analysis (see Howarth et al., 2018, for details on
digestion techniques). Analyses were conducted on an Agilent triple quadrupole ICP-
MS (ICP-QQQ) at the Open University. For conventional ICP-MS systems measuring
sulphur concentrations has been challenging, owing to the high background
contribution (from O_2). The ICP-QQQ has an octopole reaction system (ORS) that
separates two quadrupole mass filters, allowing for targeted interference removal. For
S we use O_2 as the reactive gas, forming SO^+ as the product in the ORS, and measure
the mass shifted oxide ion (i.e. at mass 50 for ^{34}S). This effectively reduces the
background from ~1.1 x 10^4 cps to ~2 x 10^2 cps. Detection limits are 0.2 ng/g in the
solutions (equivalent to 0.2 µg/g in the rock – samples are diluted 1000 fold prior to
analysis). Analyses were standardised against a suite of five reference materials
(BIR-1, W-2, BHVO-2, AGV-1, BE-N) measured at the start of each analytical
session. An internal standard solution was also bled in online throughout the
analytical session, and used to monitor and correct for instrument drift. In addition, a
monitor block, consisting of BHVO-2 (digested at Imperial College with the
unknowns and not used in the calibration) BE-N and 2% HNO_3 was run every 4 – 5
unknowns to further monitor drift, and to monitor precision and accuracy of
measurements.

233   The reference materials used in the calibration have only information values listed in

234   the GEOREM database (and where uncertainties are quoted these are also large, e.g

235   BHVO-2 = 164 ± 25 µg/g). However, for the majority of materials we find that using

236   these information values yields a calibration line with an R^2 value of 0.9995. We also

237   find that rock reference materials behave very similarly to the samples during

238   ionisation in the plasma, and therefore find this a more robust method of calibrating

239   rather than having to apply an ionisation correction to a suite of synthetic calibration

240   materials. The one outlier from our calibration line is BIR-1. Further investigation by

241   standard addition methods indicate that the concentration of S is 4.5 µg/g in three

242   further BIR-1 digests from our powder aliquot (rather than 70 µg/g as quoted from

243   GEOREM) and, when this is taken into account, the BIR-1 measurements again sit on

244   the calibration line as described above, and do not alter the R^2 value of the line. We

245   find that our repeat measurements of the BHVO-2 standard digested at Imperial

246   College show both a precision and accuracy of <4 % (RSD) compared to the

247   information values given. Whilst some caution must be exercised in using these

248   information values, we remain confident in the relative concentration variations

249   within our sample suite.

250

251   **3.2 Zn and Cu isotope analyses**

252

253   All isotopic analytical work was carried out in the MAGIC clean laboratories at

254   Imperial College London using deionized 18.2 MΩ water (MQ), Teflon-distilled acids

255   (HF, HNO_3 and HCl), Suprapur H_2O_2, and acid-cleaned Savillex PFA labware. 20 mg

256   of each sample was digested in a ~3:1 $HF:HNO_3$ mix at 140°C for ~48 hours. After

257   drying down to a gel-like consistency, samples were treated three times with

258   concentrated HNO_3 to drive off fluoride salts. Previously published high precision

259   trace element data for the same sample powders (Howarth et al., 2018) were used to

260   estimate the appropriate volume of a ^{64}Zn-^{67}Zn double spike required to obtain a Zn

261   spike:sample ratio of approximately 1.2 (Arnold et al., 2010; Bridgestock et al.,

262   2014). After spike equilibration, conversion to chloride, and re-dissolution in 7M HCl

263   + trace H_2O_2, Cu and Zn fractions were purified from the same digest solutions via

264   anion exchange using AG MP-1M resin (BioRad), as detailed previously (Maréchal et

265   al., 1999; Archer and Vance, 2004; Little et al., 2014b). Due to the highly refractory

266   nature of the samples (i.e. high concentrations of potentially interfering elements such

267   as Ti and Fe), three column passes were performed for both the Cu and Zn fractions.

268   The final Zn column was smaller in volume, following Bridgestock et al. (2014).

269

270   Prior to analysis, purified Cu fractions were refluxed overnight in $HNO_3 + H_2O_2$ and

271   purified Zn fractions were treated twice with ~100 µL HNO_3, with the intention of

272   eliminating residual resin-derived organics, before final re-dissolution in 1 mL 2%

273   HNO_3. Aliquots of these solutions were diluted to final concentrations of ~100ppb

274   total Zn (i.e. spike + sample Zn) and ~100ppb Cu for analysis. For both Cu and Zn,

275   the USGS rock standards BHVO-2, BIR-1A, BCR-2 and Nod-P1 were processed

276   using the same procedures and analysed to assess accuracy. Table 3 compares our

277   data with previously published $\delta^{66}Zn$ and $\delta^{65}Cu$ values.

278

279   Zinc isotope analyses followed protocols described previously (Arnold et al., 2010;

280   Bridgestock et al., 2014). Briefly, measurements were made on a Nu Plasma HR MC-

281   ICP-MS equipped with an ARIDUS II (CETAC Technologies) desolvating system

282   and nominal 100 µL/min MicroMist glass nebulizer, in low resolution mode.

283   Instrumental sensitivities were >100 V/ppm Zn. Data collection (3×20 5s

284   integrations) was preceded by an analysis (15 5s integrations) of the 2% HNO_3 used

285   to dilute solutions, with subtraction of these "on-peak zeroes" from sample signals.

286   Instrumental mass bias was corrected via the double spike technique described in

287   Arnold et al. (2010) and Bridgestock et al., (2014). Data reduction was carried out

288   offline following Siebert et al. (2001), with corrections for spectral interferences from

289   ^{64}Ni (via monitoring ^{62}Ni) and Ba^{2+} ions (via monitoring at mass 68.5). Interference

290   corrections were negligible, however, with $^{64}Ni^+/^{64}Zn^+$ and $^{134}Ba^{2+}/^{67}Zn^+$ levels at less

291   than 1×10^{-5} in all cases. The Zn isotope ratios of samples were determined relative

292   to matching (spike:natural Zn ratio and total Zn) standard solutions of IRMM-3702:

293   Eqn. 1: $\delta^{66}Zn = [(R_{Sample}/R_{Standard}) - 1] \times 1{,}000$

294   Final values are reported normalised to JMC Lyon by applying a correction of

295   +0.30‰, as recommended in the recent review by Moynier et al. (2017). Over the

296   course of this study the long-term reproducibility of a secondary standard, the in-

297   house 'London Zn', was $\delta^{66}Zn_{JMC\text{-}Lyon} = +0.08 \pm 0.07‰$ (n = 99, 2 SD), compared

298   with $+0.08 \pm 0.04‰$ (n = 10, 2 SD) reported by Arnold et al. (2010) and $+0.12 \pm$

299      $0.04‰$ (n = 6, 2 SD) by Larner and Rehkämper (2012). Total procedural blanks for

300   Zn were 3.6 ± 2.6 ng (n = 8, 1 SD), less than 1% of the Zn content of the smallest

301   sample. Yields were 104 ± 10% (1 SD).

302

303   Copper isotope analyses employed a Nu Plasma II HR MC-ICP-MS at Imperial

304   College London. Measurements were made in low resolution mode, with introduction

305   via a Peltier cooled (to 5°C) glass spray chamber coupled to a ~100 µL/min glass

306   nebulizer. Instrumental mass bias was corrected via doping with Ni following e.g.,

307   Ehrlich et al. (2004) and Larner et al., (2011). Nickel was chosen ahead of Zn for this

308   study because it has a first ionization potential (7.64 eV) close to that of Cu (7.72 eV)

309   and it is less sensitive to contamination. All samples and standards were doped to

310   achieve a Ni:Cu ratio of 3 to 4, matched to within ± 5%. Tests at variable Ni/Cu ratios

311   (2 to 5) suggested that neither accuracy nor precision is sensitive to the selected Ni:Cu

312   ratio. Analyses were carried out in static mode using Faraday cups to monitor masses

313   60, 61, 62 (for Ni), and 63, 65 (for Cu).

314

315   Data collection consisted of 60 x 5s integrations preceded by an analysis (15 x 5s

316   integrations) of the 2% HNO_3 solution, with the latter subtracted from sample signals.

317   Sensitivity for Cu was typically ~25 V/ppm. The exponential law was used to mass

318   bias correct measured $^{65}Cu/^{63}Cu$ ratios relative to $^{62}Ni/^{60}Ni$. $\delta^{65}Cu$ values were then

319   calculated as the deviation of the mass bias corrected $^{65}Cu/^{63}Cu$ ratio of the sample

320   relative to two bracketing standards (ERM-AE633):

321   Eqn. 2: $\delta^{65}Cu = [(R_{Sample}/R_{ERM-AE633}) - 1] \times 1,000$

322   This combination of external element doping and standard-sample bracketing has

323   previously been described for e.g., Tl with Pb (Nielsen et al., 2004) and for Cu with

324   Ni (Larner et al., 2011).

325

326   Finally, the minor reported offset of -0.01‰ between AE633 and the international

327   standard NIST SRM 976 was applied, such that data are reported normalised to SRM

328   976 (Moeller et al., 2012). The long-term reproducibility of a secondary Romil Cu

329   solution standard was $\delta^{65}Cu_{SRM-976} = +0.23 \pm 0.07‰$ (n = 22, 2 SD), comparable to

330   the +0.20 ± 0.08‰ (n = 5, 2 SD) reported by Larner et al. (2011). Total procedural

331   blanks for Cu were 4.9 ± 1.7 ng (n = 4, 1 SD), less than 1% of the Cu content of the

332   smallest sample. Yields, estimated by comparison of Cu concentration data from the

333   OU (Howarth et al., 2018) with concentrations from the isotopic analysis (obtained by

334   a less precise beam matching approach), were 93 ± 9% (1 SD). Complete yields are

335   essential for Cu isotope analyses due to the potential for isotopic fractionation during

336   anion exchange (Maréchal and Albarède, 2002); no relationship is observed between

337   sample isotopic composition and calculated yield, corroborating the accuracy of the

338   Cu isotope data presented here.

339

340   **3.3 Calculating CIA, IOL and τ –values**

341

342   Two useful measures of the degree of weathering are presented. First, the Chemical

343   Index of Alteration (CIA) is calculated following Nesbitt and Young (1982). CIA

344   utilises the molar mass of key indicator elements:

345   Eqn. 3: CIA = $[Al_2O_3/(Al_2O_3 + CaO^* + Na_2O + K_2O)] \times 100$

346   [Where each compound is expressed as its molar mass]

347   CaO* is the amount of CaO incorporated in the silicate fraction of the rock. Since

348   CaO contents of the SQ samples are low (<1 wt%), and because inherent carbonate

349   phases were absent, no correction for the sample carbonate content was deemed

350   necessary. CIA effectively tracks feldspar dissolution and the concomitant release of

351   Ca, Na, and K relative to Al, since the latter is typically retained within resulting

352   clays. Most igneous rocks of varying composition will plot between a CIA value of 35

353   and 55, with mafic rocks occupying the lower values. Unaltered granites and

354   granodiorites, which may be representative of the greywacke protolith of the SQ

355   profile, have CIA values of between 45 and 55. By comparison, sample SQ2 has a

356   CIA value of 57 (Table 2; Fig. 2).

357

358   Second, Babechuk et al., (2014) suggest an alternative means to chemically

359   characterise the stages of extreme weathering at which the CIA becomes ineffective,

360   the Index of Lateritisation (IOL; Table 2, Fig. 2):

361   Eqn. 4: IOL = $100 \times [(Al_2O_3 + Fe_2O_{3(T)}) / (SiO_2 + Al_2O_3 + Fe_2O_{3(T)})]$

362

363   Enrichment or depletion of an element can be quantified by comparison to an

364   immobile reference element. For this purpose, we calculate the tau (τ) parameter

365   (after Chadwick et al., 1990):

366   Eqn. 5: $\tau_{i/j} = \left[\dfrac{(\frac{C_i}{C_j})_h}{(\frac{C_i}{C_j})_p} \right] - 1$

367   Where C is the measured concentration, i is the element of interest (e.g.. Zn, Cu), j is

368   an immobile reference element (Nb, Ti or Zr), h is the weathering product, and p the

369   unaltered parent lithology. A value greater than zero indicates net gain of an element

370   relative to the parent material at that horizon within the weathering profile, while a

371   value less than zero indicates loss.

372

373   Two approaches were used to investigate uncertainty in τ –values. First, we compared

374   τ-values calculated assuming p is represented by the deepest sample in the section

375   (SQ2) with those calculated by taking an average of all samples from the little altered

376   zone I (SQ2 – SQ6). Second, Babechuk et al. (2014) advocate the use of Nb as the

377   most appropriate immobile reference element (j) for lateritic sample suites. In

378   addition, and for comparison, we compare τ-values calculated using Nb with those

379   determined using immobile elements Ti and Zr. Importantly, we find no significant

380   difference in absolute values or patterns of elemental enrichment or loss independent

381   of the choice of p or j (Fig. S2, Fig. 4).

382

383

384   **4.0 Results**

385

386   **4.1 Zn and Cu concentrations and enrichment-depletion patterns (τ-values)**

387

388   Copper concentrations exhibit limited absolute variability up-section (31 – 66 µg/g)

389   compared to larger variations in Zn (21 – 146 µg/g) (Table 2, Fig. 4A). Both Cu and

390   Zn concentrations decrease in stepwise fashion across the line of seepage, which

391   represents the transition from zone I to zone II at ~15m depth (Fig. 4A). Elevated

392   concentrations of both elements are observed at 7.5m (zone III, sample SQ11), the

393   uppermost depth of the paleo-water table (Wimpenny et al., 2007). The surface-most

394   sample (SQ14) has distinctly higher Cu and Zn concentrations compared to the other

395   two samples beneath; together these three samples make up the Fe-rich duricrust

396   (zone IV).

397   Both τ_{Zn} and τ_{Cu} become increasingly negative up section, with up to ~90% Zn and

398   ~70% Cu depletion relative to the protolith composition (Fig. 4B). The pattern of

399   enrichment and depletion of both elements above the line of seepage (at ~15m) is

400   similar, with marked depletion immediately above this transition, interrupted by a

401   sharp peak of enrichment at the paleo-water table, followed by more moderate

402   enrichment in the uppermost sampling horizon (SQ14, particularly evident for τ_{Cu}).

403   τ_{Zn} exhibits a very strong correlation with τ_{Li} throughout the laterite profile, while τ_{Cu}

404   is decoupled from both τ_{Li} and τ_{Zn} in zone I, at 15m and below (Fig. 4B).

405

406   **4.2 Zn and Cu isotope systematics**

407

408   The unaltered greywacke protolith, represented by sample SQ2 at 34 m, has a Zn

409   isotope composition of +0.50 ± 0.04‰ (n = 2, 2SD). This value is isotopically heavy

410   compared to typical lithogenic Zn in clastic sediments, at +0.28 ± 0.13‰ (n = 105,

411   Moynier et al., 2017). For Cu, sample SQ2 has a Cu isotope value of +0.03 ± 0.05‰

412   (n = 2, 2SD), which is within the typical range for Cu in clastic sediments at +0.08 ±

413   0.20‰ (n = 42, Moynier et al., 2017).

414

415   In the low alteration zone I, below the line of seepage (samples SQ2 to SQ6, 34 to 15

416   m), Zn isotope ratios do not vary outside of analytical uncertainty ($\delta^{66}Zn$ = +0.47 ±

417   0.09‰, n = 5, 2SD). Copper isotope ratios show a resolvable shift from ~0‰ at the

418   base of the profile to lower values at 22.5m (SQ5, -0.28‰) and 15m (SQ6, -0.23‰)

419   (Fig. 5A).

420

421   Above the line of seepage in zones II–IV (15 m – surface), samples SQ7 to SQ14

422   show considerably more marked, correlated shifts in Zn and Cu isotope compositions.

423   This is manifest as a general trend towards lower $\delta^{66}Zn$ and $\delta^{65}Cu$ upwards in the

424   weathering profile (Fig. 5). Again, the paleo-water table interrupts this trend in $\delta^{65}Cu$,

425   with a marked offset towards a higher Cu isotope ratio (at -0.30‰) compared to the

426   samples directly above and below (at -0.86‰ and -0.65‰ respectively). The surface-

427   most sample (SQ14) is isotopically lightest for both Cu (at -0.87‰) and Zn (at -

428   0.02‰). In summary, the total variability up section in $\delta^{65}Cu$ is 0.91‰, which is

429   greater than that observed for $\delta^{66}Zn$, at 0.55‰.

430

431

5.0 Discussion

433

5.1 Zone I: Host phases and lithological heterogeneity in the low alteration zone (parent – saprock)

436

437 Wimpenny et al. (2007) described the mineralogical variations through the SQ

438 sequence, which we briefly recount here. The deepest greywacke sample (SQ2, 34 m)

439 comprises 75% quartz, 15% biotite, 5% plagioclase, 2% opaques and 3% other

440 minerals (Wimpenny et al., 2007). Up-section in zone I (SQ2 – SQ6 at 34 – 15m),

441 lithological variability is observed (Fig. 3). For example, biotite contents vary

442 between 8 and 20%, plagioclase from 2 – 8% and quartz from 74 – 80%. Secondary

443 clay minerals (e.g., kaolinite) are not observed in zone I (Fig. 3), confirming the

444 limited extent of chemical weathering at these depths. CIA values are consistent with

445 this inference, and remain essentially unchanged between the base of the profile (CIA

446 = 57 at 34m) to the top of zone I (CIA = 59 at 15m; Fig. 2)

447

448 Lithological variability is reflected in the major and trace element geochemistry of the

449 zone I samples. Al_2O_3, Fe_2O_3, MgO, Li and many other trace element concentrations

450 positively co-vary with biotite crystal content in this zone (Table S1, S3; Fig. S3).

451 SiO_2 concentrations show the opposite trend (Fig. S4). These observations are

452 consistent with known minor lateral variation in the quarry (Hibbert, 2017) and are

453 likely linked to a grain size control on mineralogy and geochemistry, as previously

454 recognised in sedimentary settings (e.g., Vdović et al., 1991; Roser et al., 1996;

455 Lupker et al., 2011). Accordingly, Al_2O_3 and SiO_2 contents generally correlate and

456 anti-correlate with grain size respectively, due to the predominance of aluminium-rich

457 phyllosilicates (like biotite) in the fine grain size fraction.

458

459 Zinc concentrations in zone I samples correlate with biotite content (Fig. S3B), as

460 well as with several trace elements and major oxides that are commonly hosted in

461 biotite, including Li, Co, Rb, Cs and Tl, MnO, MgO and K_2O (Fig. 6A, C, data from

462 Howarth et al., 2018). Potassium and Mg are both key structural components in

16

463   biotite ($K_2(Mg,Fe^{2+})_{6-4}(Fe^{3+},Al,Ti)_{0-2}[Si_{6-5}Al_{2-3}O_{20}](OH,F)_4$) (Deer et al., 1992).

464   Manganese and Li are commonly substituted into biotite octahedral sites, and Cs, Rb

465   and Tl commonly replace K in interlayer sites (Deer et al., 1992; Gomez-Gonzalez et

466   al., 2015). These observations suggest that the Zn present in the parent greywacke is

467   principally hosted within biotite.

468

469   Both Zn and Cu are chalcophile and, if sulphide phases were present, would be

470   expected to strongly partition into these phases. However, measured S concentrations

471   in the SQ profile are low (<0.1 wt%, Fig. 6, Table 2) and, while there is a positive

472   correlation between Zn and S concentrations in zone I samples (Fig. 6G), a negative

473   correlation is observed between Cu and S concentrations (Fig. 6H). This observation

474   appears to rule out the presence of CuS phases in the parent lithology. Furthermore,

475   Banks (1973) reports $116 - 316$ µg/g S in biotite, suggesting that biotite-hosted S

476   provides a satisfactory explanation for the correlation of Zn with S (Fig. 6G).

477

478   In contrast to Zn, Cu shows negative correlations with almost all elements in zone I

479   except SiO_2 and Na_2O (Fig. 6). As discussed, higher SiO_2/Al_2O_3 ratios likely reflect a

480   coarser grain size. Higher Na_2O contents in sandstone versus siltstone have been

481   hypothesised to reflect a greater abundance of detrital plagioclase (Roser et al., 1996),

482   but no correlation is observed between Na_2O and plagioclase abundance in the SQ

483   sample set. Plagioclase contains only scarce quantities of trace elements (Deer et al.,

484   1992), in any case, making this an unlikely Cu host. We conclude that identification

485   of the Cu host phase(s) requires detailed micro-analytical work that is beyond the

486   scope of this study. Nevertheless, we suggest that Cu is present in one or more detrital

487   phase(s), the abundance of which is greater in the coarser grained beds of the

488   greywacke.

489

490   To summarise, the τ_{Zn} and τ_{Cu} values in zone I samples similarly reflect primary

491   lithological heterogeneity of the greywacke, rather than recording any elemental mass

492   transfer. Thus, in order to take account of this heterogeneity in calculating τ-values,

493   we use an average of all samples in zone I as the best estimate of the parent material

494   ('p' in Eqn. 5). This approach, rather than simply selecting the least altered sample

495   SQ2, leads to a greater coherence of the calculated τ-profiles for different elements

496 (e.g., Zn cf. Li) and for the same element using different immobile reference elements

497 (e.g., Ti, Zr, 'j' in Eqn. 5; Fig. S2).

498

499 Isotopically, the greywacke δ^{65}Cu lies within the range of typical clastic sediments, at

500 about 0‰ (Moynier et al., 2017). For δ^{66}Zn, however, it is isotopically heavy (e.g.,

501 sample SQ2 at +0.50‰) relative to lithogenic Zn (at about +0.3‰; Moynier et al.,

502 2017). Similarly isotopically heavy Zn has been observed in biotite-granites from the

503 Kaapvaal craton, South Africa (Doucet et al., 2018), from Taiwanese andesite,

504 sandstones and suspended river sediment (Bentahila et al., 2008), and in granitoids

505 from the Nyong Basin, Cameroon (Viers et al., 2007) and the Lachlan Fold Belt,

506 Australia and Black Hills, South Dakota, USA (Telus et al., 2012).

507

508 At 22.5m (sample SQ5), a small shift (of about –0.3‰) towards a lower δ^{65}Cu value

509 is observed (Fig. 5). This shift may either be a primary lithological signature, or

510 indicate the earliest detectable onset of oxic chemical weathering. Sample SQ5 has

511 the highest phyllosilicate abundance (sum of biotite, muscovite and chlorite, 23%;

512 Table S1, Fig. 3) and a slightly elevated CIA value (of 63; Table 2, Fig. 2) compared

513 to the other samples in zone I (at 12–15% and 57–59 respectively). The high

514 abundance of easily weatherable, fine fraction phyllosilicates increases the

515 susceptibility of this sample to alteration (Goldich, 1938).

516

517 Overall, elemental variations in the low alteration zone I can primarily be explained

518 by lithological heterogeneity in the parent greywacke. Copper and Zn isotopes in this

519 zone exhibit small shifts, either reflecting this lithological heterogeneity and/or early

520 stage chemical alteration. A greater spatial resolution of sampling in the quarry would

521 improve constraints on the importance of lateral variability and lithological

522 heterogeneity.

523

524

525 **5.2 Zones II and IV: the Mottled and Laterite Zones**

526

527 Above the line of seepage, the mottled and laterite zones (II and IV) are characterised

528 by depletion of Cu and Zn (observed in negative τ_{Cu} and τ_{Zn}) and isotopically light

529 δ^{65}Cu and δ^{66}Zn values (Figs. 4, 5). This pattern could reflect either (i) preferential

530 release of heavy isotopes during mobilization from (i.e. dissolution of) the host phase,

531 or (ii) isotope fractionation in the aqueous phase and/or during precipitation of

532 secondary Fe oxide phases.

533

534 *5.2.1 Isotope fractionation during host mineral dissolution*

535

536 Mineral dissolution may be accompanied by isotope fractionation. For example,

537 isotopically light Zn and Cu in weathered black shales from China and the USA have

538 been interpreted to result from preferential release of heavy Cu and Zn isotopes

539 during oxidative weathering of sulphide minerals (Mathur et al., 2005; Fernandez and

540 Borrok, 2009; Kimball et al., 2009; Mathur et al., 2012; Lv et al., 2016). However, the

541 greywacke lithology of the SQ laterite is sulphide-poor, and neither Cu nor Zn

542 appears to be dominantly hosted in a sulphide phase (Section 5.1).

543

544 The alternation of wet and dry seasons results in oscillating reducing and oxic

545 conditions in the developing weathering profile. Under water-saturated conditions, Fe

546 (as ferrous Fe^{2+}) is mobile, while during drier periods this Fe precipitates as ferric Fe

547 oxides, forming the Fe-rich mottles of zone II. Hence, redox changes play an

548 important role in mineral breakdown, the removal of mobile elements, and the

549 formation of secondary minerals enriched in Fe_2O_3 and Al_2O_3. Zinc is not redox

550 active, but mobilization of Cu via Cu(II) reduction has been hypothesised for

551 waterlogged soils and wetland systems (Bigalke et al., 2010c; Bigalke et al., 2013;

552 Babcsányi et al., 2014). However, Cu(II) to Cu(I) reduction is associated with release

553 of the light isotope of Cu (Bigalke et al., 2010c; Bigalke et al., 2013; Babcsányi et al.,

554 2014). The preferential release of light Cu isotopes from host mineral phases via

555 Cu(II) reduction is inconsistent with the isotopically light solid residue observed in

556 the SQ laterite. Hence, though oscillating redox is an important process in

557 lateritization, alone it cannot explain the observed Zn and Cu isotope variations.

558

559 In abiotic, proton-promoted dissolution experiments investigating the release of Fe

560 from hornblende, a small light isotope fractionation is observed (Brantley et al.,

561 2001). Similar light isotope fractionation of Fe and Zn is observed during dissolution

562 of granite with HCl (Chapman et al., 2009; Weiss et al., 2014). This preferential

563 release of light isotopes during proton-promoted dissolution likely reflects a kinetic

564   isotope fractionation. Again, preferential mobilization of light isotopes is inconsistent

565   with the isotopically light residue observed in the SQ weathering profile.

566

567   In natural aqueous solutions both Zn and Cu are dominantly complexed to strong

568   organic ligands (McBride, 1981; Coale and Bruland, 1988; e.g., Bruland, 1989; Xue

569   et al., 1995; Moffett and Brand, 1996; Wells et al., 1998; Shank et al., 2004; Grybos

570   et al., 2007; Hoffmann et al., 2007; Vance et al., 2008). It is well documented that

571   mineral dissolution rates are enhanced above proton-promoted rates by the presence

572   of organic ligands, via a ligand-promoted dissolution mechanism (e.g., Berthelin and

573   Munier-Lamy, 1983; Amrhein and Suarez, 1988; Bennett, 1991; Welch and Ullman,

574   1993; 1996; 2000). For example, release of Cu from Columbia River Basalt was

575   elevated in a batch experiment containing an organic ligand (citrate) compared to the

576   inorganic control (Neaman et al., 2005b). At equilibrium, organic complexation is

577   associated with preferential chelation of heavy isotopes (Dideriksen et al., 2008;

578   Jouvin et al., 2009; Bigalke et al., 2010b; Morgan et al., 2010; Fujii and Albarede,

579   2012; Fujii et al., 2013; Sherman, 2013; Fujii et al., 2014; Ryan et al., 2014; Marković

580   et al., 2017). Therefore, at equilibrium, ligand-mediated dissolution should be

581   associated with release of isotopically heavy Zn and Cu, consistent with the observed

582   isotopically light laterite residue.

583

584   We model this scenario as a simple open-system Rayleigh distillation process in

585   Figure 7. In this model, we envisage that the isotopically heavy, organically

586   complexed pool is continuously removed from the profile under a constant

587   fractionation factor. For Zn, the Rayleigh model isotope fractionation factor that best

588   fits the data is of the order α = 1.0002, i.e. $\Delta^{66}Zn_{aqueous\text{-}solid} \approx$ +0.2‰ (Fig. 7A). For

589   Cu, the required fractionation factor is larger, at about α = 1.001 or $\Delta^{65}Cu_{aqueous\text{-}solid} \approx$

590   +1.0‰ (Fig. 7B). The fractionation factors derived from the Rayleigh approach can

591   only be confidently ascribed meaning for a single-step process, e.g., mobilization

592   from the host mineral phase. Several processes are operating and, likely, fractionating

593   Zn and Cu isotopes during lateritization. Nevertheless, the Rayleigh model produces

594   an acceptable fit to the data in spite of its simplicity (Fig. 7), and we proceed to

595   compare our model-derived fractionation factors to those for organic complexation of

596   Zn and Cu in the literature.

597

The magnitude of Zn and Cu isotope fractionation on organic complexation is a
function of the stability constant of complex formation (Ryan et al., 2014; Marković
et al., 2017). Organic ligands in freshwater solutions fall into two categories: low
molecular weight organic acids (or 'L1-type' ligands, e.g., polyphenols, hydroxamate
siderophores), and soluble humic/fulvic acids (Harter and Naidu, 1995). While
humic/fulvic acids generally have relatively weak stability constants (at around $\sim 10^7$ –
10^9), L1-type ligands can be much stronger (up to $\sim 10^{25}$). Copper has a particular
affinity for strong organic ligands (as compared to, e.g., Zn and Cd; Benedetti et al.,
1995; Xue et al., 1995; McBride et al., 1997). Relatedly, the magnitude of isotope
fractionation for organic complexation is also larger for Cu compared to Zn
(Marković et al., 2017; cf. Ryan et al., 2014).

609

A fractionation factor $\Delta^{66}Zn_{aqueous\text{-}solid} \approx +0.2$‰ (Fig. 7A) is consistent with an
experimental estimate of isotope fractionation for Zn complexation with purified
humic acid ($\Delta^{66}Zn_{humic\text{-}aquo} = +0.24 \pm 0.06$‰; Jouvin et al., 2009). By comparison, the
larger fractionation factor for Cu ($\Delta^{65}Cu_{aqueous\text{-}solid} \approx +1.0$‰; Fig. 7B) implies
complexation by complexes stronger than humic acids, which have a reported range
in $\Delta^{65}Cu_{humic\text{-}aquo}$ of +0.24 to + 0.55‰ (Bigalke et al., 2010b; Sherman, 2013; Ryan et
al., 2014). Sherman (2013) predicts a fractionation factor for a L1 ligand model
complex (Cu acetohydroxamate) of $\Delta^{65}Cu_{hydroxamate\text{-}aquo} = +1.1$‰, while Ryan et al.
(2014) measured fractionation factors of up to +0.84‰ for strong synthetic L1-type
ligands. Both of these estimates would be consistent with the Rayleigh model
prediction.

621

In practice, it is unclear if chemical equilibrium between the rock and aqueous phase
(or something approaching it) can be obtained during weathering. Contrary to the
predicted release of heavy isotopes during ligand-promoted dissolution, dissolution of
granite in the laboratory in the presence of oxalic acid resulted in release of
isotopically *light* Zn (Weiss et al., 2014). Similarly, Brantley et al. (2004) and
Wiederhold et al. (2006) observed release of isotopically light Fe in ligand-mediated
leaching experiments with hornblende and goethite, respectively. However, these
leaching experiments were not at equilibrium, and the observed light isotope
fractionation may reflect a kinetic control. By contrast, long duration experiments of

631   Wiederhold et al. (2006) did exhibit the predicted reverse trend, with isotopically

632   heavy Fe in solution. It remains to be determined whether these longer duration

633   experiments more closely reflect processes operating in more advanced (i.e., lateritic)

634   weathering environments.

635

636   Mineral dissolution rates in the lab are typically one to three orders of magnitude

637   faster than in the field (e.g., Swoboda-Colberg and Drever, 1993; Kump et al., 2000;

638   Brantley, 2003). In the lab, dissolution rates are thought to be interface-limited, i.e.

639   the rate of reaction is determined by the dissolution rate of the mineral (Brantley,

640   2003). By contrast, mineral dissolution rates in a transport-limited scenario are

641   controlled by the rate of diffusion or advection in solution (Brantley, 2003). Mineral

642   dissolution is likely predominantly interface-limited in the field (see discussion in

643   Kump et al., 2000), but it can be transport-limited at low water-rock flushing rates

644   (Schnoor, 1990; Kump et al., 2000). This difference may partially explain the offset in

645   lab and field-derived mineral dissolution rates, with transport-limited dissolution

646   operating more slowly than interface-limited dissolution (Kump et al., 2000).

647

648   Lateritic weathering is likely to occur in a transport-limited (also called "supply

649   limited"; West et al., 2005) weathering regime, with low denudation rates coupled to

650   high weathering intensity (White and Buss, 2014). Weathering fluxes in this scenario

651   reflect thermodynamic constraints, with chemical weathering reactions occurring

652   close to equilibrium (White and Buss, 2014). Indeed, this regime is sometimes

653   referred to as 'local-equilibrium' (Lebedeva et al., 2010; Brantley and Lebedeva,

654   2011). Hence, we suggest that transport-limited mineral dissolution may be associated

655   with equilibrium isotope fractionation, while interface-limited mineral dissolution will

656   typically be kinetically controlled (e.g., Brantley et al., 2004; Wiederhold et al., 2006;

657   Weiss et al., 2014). If this hypothesis were correct, ligand-mediated mineral

658   dissolution at equilibrium would promote release of heavy Zn and Cu isotopes,

659   consistent with observations in the SQ laterite (see also section 5.2.2). The corollary

660   of this hypothesis, however, would predict kinetic isotope fractionation (i.e.

661   mobilization of light isotopes) in kinetic-limited (or 'weathering-limited') regimes, in

662   which the physical removal of eroded material is faster than its breakdown by

663   chemical weathering. There is limited evidence for this prediction in Zn and Cu

664   isotope weathering studies to date. We return to this topic in section 5.4.1.

665

To summarise, the isotopically light compositions observed in the SQ laterite residue

may reflect ligand-mediated dissolution of their host phases, if dissolution is

occurring close to equilibrium in a transport-limited regime. By contrast, mobilization

via either a kinetic or reductive (in the case of Cu) mechanism would be associated

with preferential release of isotopically light Zn and Cu. In this case, the salient

isotope fractionation during lateritic weathering must occur after Zn and Cu

mobilization, in pore waters and/or during precipitation of secondary minerals.

673

674   *5.2.2 Isotope fractionation in the aqueous phase*

675

As discussed, Zn and Cu will be dominantly complexed by organic ligands in the

aqueous phase (e.g., McBride, 1981; Xue et al., 1995; Grybos et al., 2007; Hoffmann

et al., 2007), and organic complexation is associated with chelation of heavy Zn and

Cu isotopes (Jouvin et al., 2009; Bigalke et al., 2010b; Fujii and Albarede, 2012; Fujii

et al., 2013; Sherman, 2013; Fujii et al., 2014; Ryan et al., 2014; Marković et al.,

2017). By comparison, the free or weakly complexed pool of Zn or Cu will be

isotopically light. Taking Cu as an example, free Cu^{2+} and organically complexed Cu

and are isotopically offset by up to −1.1‰ (Sherman, 2013). In a closed system at

isotopic equilibrium, the Cu isotope composition of organically complexed Cu (δ_{org})

is constrained by this fractionation factor ($\Delta_{free-org}$) and the ratio of organically

complexed Cu to free Cu (N_{org}/N_{free}), as described by equation 6 (modified after

Stevenson et al., 2017):

688   Eqn 6: $\delta_{org} = \delta_{system} - \dfrac{\Delta_{free-org}}{1 + \dfrac{N_{org}}{N_{free}}}$

In nature, N_{org}/N_{free} for Cu is always very high – i.e. Cu is almost quantitatively

organically complexed. Thus, mass balance constraints dictate that organically

complexed Cu in solution will closely reflect the isotopic composition of the Cu that

is mobilized during weathering, while the free Cu species will be fractionated by as

much as −1.1‰. Consequently, in a scenario in which Zn and Cu are organically

complexed in pore waters, secondary mineral phases may simply scavenge the

isotopically light uncomplexed (or weakly-complexed) pool of Zn and Cu (as

proposed by Vance et al., 2016).

697

5.2.3 Isotope fractionation during coprecipitation with aluminous Fe oxide

699

700 An alternative mechanism to explain the light isotopic composition of the laterite

701 residue is light Zn and Cu isotope fractionation associated with precipitating Fe oxide

702 phases. For example, Viers et al. (2007) observed isotopically light Zn in laterite

703 samples from Cameroon, which they attributed to 'ferrugination', a term which

704 implies preferential incorporation or sorption of light isotopes in or on precipitating

705 Fe oxide phases. Suhr et al. (2018) suggested a similar process to explain isotopically

706 light Zn in the residue of a basaltic laterite from Bidar, India. We observe negative

707 correlations of δ^{66}Zn and δ^{65}Cu with Fe_2O_3 (Fig. 8), indicating that Fe oxide

708 formation may well play a role in the very light isotopic compositions of Cu and Zn in

709 zone II and IV samples.

710

711 Can ferrugination alone lead to isotopically light Zn and Cu in the laterite residue?

712 Most experimental studies have focussed upon inorganic *sorption* of Zn and Cu on Fe

713 oxide (or other mineral) surfaces, with the prevailing paradigm that such sorption is

714 typically associated with preferential accumulation of heavy isotopes on the mineral

715 surface (Pokrovsky et al., 2005; Balistrieri et al., 2008; Juillot et al., 2008; Pokrovsky

716 et al., 2008; Bryan et al., 2015; Guinoiseau et al., 2016). Preferential sorption of

717 heavy isotopes on precipitating oxide surfaces would be contrary to the observed light

718 isotopic compositions of laterite samples in zones II and IV.

719

720 The dominant Fe oxide phases present in the SQ samples are aluminous goethite and

721 aluminous haematite (Table S1; Wimpenny et al., 2007). Both phases can also

722 *incorporate* Zn^{2+} and Cu^{2+} into their structures, via substitution for Fe^{3+} on octahedral

723 (VI-fold coordinated) sites (e.g., Cornell and Giovanoli, 1988; Gerth, 1990; Manceau

724 et al., 2000; Cornell and Schwertmann, 2003). Incorporation of significant Zn (19.9

725 µg/g) and Cu (31 µg/g) in goethite and haematite, comparable to the concentrations

726 observed in the indurated SQ duricrust (Zn: 25 – 31 µg/g, Cu: 39 – 61 µg/g), has been

727 suggested for lateritic samples from Western Australia (Anand and Gilkes, 1987;

728 Singh and Gilkes, 1992). Preferential incorporation of isotopically light Zn and Cu

729 into precipitating aluminous Fe oxides could thus provide a mechanism to drive the

730 laterite residue isotopically light.

731

732   The trajectory of the dashed arrow in Figure 9A implies a maximum effective isotopic

733   fractionation factor on incorporation of Zn into Fe oxides of $\Delta^{66}Zn_{Fe\ oxide-aqueous} \approx -$

734   0.7‰ (Fig 9A). A conference abstract indicates that Zn incorporation in goethite may

735   indeed be associated with a preference for the light Zn isotope, though the magnitude

736   of associated isotope fractionation is not reported (Becker et al., 2014). In the case of

737   Cu, the equivalent maximum effective isotope fractionation factor described by the

738   trajectory of the dashed arrow in Figure 9B is about –1.3‰. Experiments measuring

739   isotope fractionation on incorporation of trace metals in Fe (and other, e.g., Al) oxides

740   are an important avenue for future research.

741

742   To conclude, we postulate that a combination of strong complexation by organic

743   ligands in association with the retention of light isotopes in or on secondary

744   aluminous Fe oxide phases can explain the residual light Zn and Cu isotope signatures

745   of the zone II and IV laterite samples. If ferrugination alone is driving the light

746   isotopic composition of the laterite residue, Zn and Cu must be incorporated in (rather

747   than sorbed on) Fe oxide phases. Micro-analytical techniques, such as EXAFS, may

748   allow identification of the phase association and crystal chemistry of Zn and Cu in

749   laterite samples.

750

751   *5.2.4 Upper horizon: a role for organic matter?*

752

753   Surface organic-rich layers of soils are often enriched in light Zn and Cu isotopes,

754   which has been related to the uptake and recycling of plants (e.g., Bigalke et al., 2011,

755   2010a; Liu et al., 2014; Vance et al., 2016; Weiss et al., 2007). Therefore, the

756   presence of isotopically light solid organic matter in the uppermost sample of the SQ

757   weathering profile is plausible, given that the surface of the lateritic mesa into which

758   the quarry has been excavated is characterized by well-developed sub-tropical scrub

759   vegetation, predominantly acacia. The uppermost sample (SQ14) is slightly enriched

760   in Cu and Zn relative to the other two indurated laterite duricrust samples (SQ12 and

761   SQ13), and is indeed the isotopically lightest sample in the whole section ($\delta^{66}Zn = -$

762   0.02‰ and $\delta^{65}Cu = -0.89$‰; Figs. 3 and 4). Unfortunately, we lack sufficient

763   sampling resolution to evaluate in detail the role of recent biological activity and

764   modern soil formation in the uppermost meters of the weathering profile.

765

5.3 Zone III: the Paleo-water Table

Previous studies have noted considerable major and trace element and isotope variability associated with the paleo-water table zone III (at $7 - 8.5$ m depth, samples SQ10 and SQ11; Howarth et al., 2018; Wimpenny et al., 2007; Widdowson, 2009), which represents a transition from sub-oxic to fully oxidising conditions (Wimpenny et al., 2007). There are two ways of interpreting this zone of alteration. To date, it has been suggested to be at the top of a 'classic' groundwater level that was abandoned during uplift (Wimpenny et al., 2007). As such, it is considered to have developed through a combination of open system, allochthonous input of trace elements from circulating groundwaters, and the precipitation of Fe and Mn-oxides, which act as effective scavengers of other elements (Howarth et al., 2018; Wimpenny et al., 2007; Widdowson, 2009).

An alternative interpretation suggests that zone III was at the base of an ancient, episodic stagnant water body (i.e. seasonally present between the surface and ~8 m depth). In this case, water would have accumulated at a depth with reduced water permeability at the base of zone III during the rainy season, and zones III and IV could be considered together as a single lateritized package that subsequently underwent uplift, drying and hardening to form the present duricrust. In this scenario, the Fe-rich mottles in zone II (i.e. at depths below ~8 m) would reflect a second phase of waterlogging and lateritization, with seasonal stagnant water pooling close to the present day line of seepage (at ~15 m depth). This idea, of two repeating packages of lateritic alteration, could plausibly explain the τ_{Zn}, τ_{Cu} and Zn and Cu isotope data (Figs. 4B, 5A). However, we would expect to observe Fe enrichment at the line of seepage, equivalent to that observed in zone III (Fig. 4C), and no such Fe (or Mn) enrichment is observed. Further sampling at higher resolution, and laterally within the quarry, would help reconcile these two scenarios. For the purpose of this study, we consider that the distinct geochemistry of the samples in zone III deserve separate treatment to the more predictable upwardly progressing alteration characteristics of the remainder of the profile.

Evidence for the allochthonous input of elements to zone III is demonstrated through the behaviour of τ_{Fe} and τ_{Mn} values (Fig. 4C, Table 2). Both τ_{Fe} (18.9) and τ_{Mn} (5.5)

800   show extreme enrichment at 7.5m (SQ11), while τ_{Fe} (4.6) is also considerably

801   enriched at 8.5m (SQ10). The allochthonous input of elements to the profile can be

802   quantified by calculating integrated τ-values, weighting taus for each horizon (h) by

803   density (ρ) and thickness (z), following Vance et al. (2016):

804   Eqn. 6: $\tau_i^{int} = \frac{\sum_{h=0}^{n}(\tau_h \rho_h z_h)}{\sum_{h=0}^{n}(\rho_h z_h)}$

805   where i refers to the element of interest (Zn or Cu). This approach assumes negligible

806   denudation (physical erosion) of the weathering profile during development.

807

808   Positive integrated τ_{Fe}^{int} (1.5) and, marginally, τ_{Mn}^{int} (0.02) values (Table 2), suggest that

809   the zone III enrichments in τ_{Fe} and τ_{Mn} cannot simply be explained by redistribution

810   of these elements vertically (from zone II or IV, depending on the location of the

811   water body) in the weathering profile. If we assume allochthonous input of Fe and Mn

812   at the paleo-water table depths and exclude these zone III samples from the integrated

813   τ calculations (giving $\tau_i^{int\text{-}III}$ values), we find a negative integrated $\tau_{Mn}^{int\text{-}III}$ (–0.21) value,

814   consistent with that calculated for $\tau_{Li}^{int\text{-}III}$ (–0.21) and $\tau_{Zn}^{int\text{-}III}$ (–0.22). $\tau_{Fe}^{int\text{-}III}$ remains

815   positive, however, at 0.36, suggesting 30 to 40% Fe addition to the weathering profile

816   during alteration.

817

818   Both Cu (52 µg/g) and Zn (97 µg/g) show enrichment in zone III, with τ_{Cu} = 0.8 and

819   τ_{Zn} = 0.5 at 7.5m (SQ11, Fig. 4B). Integrated τ_{Zn}^{int} and τ_{Cu}^{int} values are negative,

820   however, both including (τ_{Zn}^{int} = –0.23, τ_{Cu}^{int} = –0.07) and excluding ($\tau_{Zn}^{int\text{-}III}$ = –0.22,

821     $\tau_{Cu}^{int\text{-}III}$ = –0.06) the zone III samples (Table 2). Therefore, the enrichments of Zn and

822   Cu in zone III do not *require* an allochthonous source of these two elements, though

823   such a source is not excluded.

824

825   The enrichments in Cu and Zn in zone III are restricted to a narrow depth range,

826   sampled at SQ11 only (7.5m, Fig. 4B). This pattern is similar to the narrow band of

827   enrichment observed for Mn (Fig. 4C) and contrasts with that of Fe, which is

828   significantly elevated across both SQ10 and SQ11 (8.5 – 7.5m; Fig. 4C). Manganese

829   oxide develops large areas of negative charge under the pH conditions of natural

830   waters, as a consequence of its low pH point of zero charge and relatively high

831   specific surface area (Catts and Langmuir, 1986). These characteristics make it a very

832   effective sorbent for other trace metals (e.g., Aplin and Cronan, 1985; Balistrieri and

833   Murray, 1986; Koschinsky and Hein, 2003; Peacock and Sherman, 2007; Tessier et

834   al., 1996). Accordingly, we suggest that Cu and Zn are scavenged by a precipitating

835   Mn oxide phase at the paleo-water table, rather than by the abundant Fe oxide phases

836   (as suggested for the zone II and IV samples; section 5.2). Sequential leaching

837   experiments would be required to further test this hypothesis.

838

839   Sample SQ11 is marked by an excursion towards isotopically heavier Cu compared to

840   the samples below and above, indicating scavenging of heavy Cu (Figs. 5, 7). In the

841   case of Zn, there is no resolvable shift in δ^{66}Zn (at +0.14‰) compared to the samples

842   above and below. In both cases sample SQ11 is distinct from the coherent τ−δ trends

843   observed throughout the rest of the profile, which are reasonably well described by a

844   simple Rayleigh model (as described in Section 5.2.1; Fig. 7). There are two possible

845   explanations for the enrichment and distinct isotopic composition of SQ11: first, a

846   source with an isotopically heavy Cu isotope composition, or second, a source

847   combined with *in situ* isotope fractionation on sorption to the postulated Mn-oxide

848   phase.

849

850   Aerosols are one possible external source of trace metals to weathering profiles, and

851   are typically approximately lithogenic in Zn and Cu isotope composition (δ^{66}Zn

852   ~0.3‰ and δ^{65}Cu ~0‰; Dong et al., 2013; Little et al., 2014b). Based on the data in

853   this study, a locally derived lateritic aerosol source would be very isotopically light,

854   however, inconsistent with the shift toward heavier Cu isotope compositions at the

855   depth of the paleo-water table. Further, assuming an atmospheric route for aerosol

856   deposition, any aerosol addition should also be apparent as enrichment at the surface-

857   most depths of the laterite profile; such behaviour is not observed for the SQ profile.

858

859   Solute-laden groundwater has previously been suggested as providing an external

860   source of Re, Os, and Tl, to the SQ laterite, possible due to its low-lying topographic

861   position (Howarth et al., 2018; Wimpenny et al., 2007). Relatively few constraints

862   exist on the isotopic composition of Zn and Cu in groundwater, however. An

863   isotopically heavy groundwater source of Cu is certainly plausible, given observations

864   of isotopically heavy Cu in the dissolved phase in rivers (+0.02 to +1.45‰, discharge-

865   weighted average of +0.68‰; Vance et al., 2008). A groundwater-borne source of Zn

866   at about +0.2‰ is also possible, given the range of dissolved δ^{66}Zn in global rivers (–

867   0.12 to +0.88‰, discharge-weighted average of +0.33‰; Little et al., 2014b) and

868   mountain streams (+0.02 to +0.46‰, Borrok et al., 2008). Future isotope studies

869   should target groundwater in conjunction with surface-flowing water bodies.

870

871   Isotope fractionation may occur on sorption to the postulated Mn oxide phase. Bryan

872   et al. (2015) investigated Zn isotope fractionation on inorganic sorption to synthetic

873   birnessite (δ-MnO$_2$), a phyllomanganate phase common in terrestrial environments

874   (e.g., Taylor et al., 1964; Ross et al., 1976; Tokashiki et al., 1986; Uzochukwu and

875   Dixon, 1986; Post, 1999). At low ionic strength (applicable to freshwater

876   environments) they observe negligible Zn isotope fractionation, which is attributed to

877   the formation of octahedral surface complexes (Manceau et al., 2002); i.e. there is no

878   marked change in coordination environment on sorption compared to the hydrated

879      $Zn(H_2O)_6^{2+}$ ion present in solution (Bryan et al., 2015). Sorption of ~V-fold

880   coordinated hydrated Cu^{2+} on δ-MnO$_2$ is predicted to be associated with an

881   enrichment in heavy isotopes, due to the formation of tetrahedral surface complexes

882   (Manceau et al., 2002; Sherman and Peacock, 2010; Little et al., 2014a), though an

883   experimental study observed the opposite: preferential sorption of light Cu isotopes

884   on δ-MnO$_2$ (Δ^{65}Cu$_{MnO2-aqueous}$ = –0.45 ± 0.18‰, n=12; Ijichi et al., 2018).

885

886   As described, the paleo-water table sample SQ11 is unusual in that it is unfractionated

887   in δ^{66}Zn and isotopically heavy in δ^{65}Cu compared to the samples above and below,

888   thus partly consistent with these inorganic predictions for sorption of hydrated Zn^{2+}

889   and Cu^{2+} on δ-MnO$_2$. However, the system is underconstrained: we lack information

890   about the isotopic composition of the contemporaneous fluid. Speciation in the natural

891   environment is more complex compared to these inorganic experimental and

892   theoretical considerations. In future, more realistic models and experiments should be

893   designed that incorporate mixtures of organic and inorganic ligands and analogue

894   mineral surfaces.

895

896   To summarise, the distinctive Fe and Mn enrichment of the paleo-water table samples

897   supports the suggestion of open system behaviour in this zone (Wimpenny et al.,

898   2007). The observed Zn and Cu enrichment could be explained by mobilisation from

899   zones II or IV of the weathering profile or an additional groundwater-borne source,

900   with scavenging on precipitating oxide phases. Specifically, we suggest that Cu and

901   Zn are primarily scavenged by a Mn oxide phase at 7.5m depth, consistent with

902   previously published Tl isotope evidence (Howarth et al., 2018).

903

904

905   **5.4 Synthesis: Cu and Zn isotopes in the weathering environment**

906

907   *5.4.1 Integrated weathering profiles and isotope fractionation during weathering*

908

909   To draw broader conclusions regarding the behaviour of Cu and Zn during

910   lateritization, and weathering in general, we compare integrated τ-values and isotopic

911   compositions from weathering and soil profiles from diverse localities. To facilitate

912   this comparison, we normalise weathered delta values to the presumed parent material

913   (where, e.g., $\Delta^{66}Zn = \delta^{66}Zn_{parent} - \delta^{66}Zn_{sample}$) and calculate integrated $\Delta^{66}Zn_{int}$ and

914    $\Delta^{65}Cu_{int}$ values (Table 2) for the entire weathering profile in the same fashion as used

915   to calculate integrated τ-values (Eqn. 6).

916

917   The SQ laterite profile shows an integrated loss of Zn of –23%, with an integrated

918    $\Delta^{66}Zn_{int}$ of –0.14‰ (Table 2). These SQ τ–Δ data are plotted alongside data from the

919   literature in Figure 9, updating the compilation in Moynier et al. (2017, their Fig. 11).

920   Overall, Zn-depleted (negative τ_{Zn}) weathering profiles and soils show limited isotope

921   fractionation from the parent lithology. However, at the highest degrees of chemical

922   weathering, above ~70% Zn depletion compared to the protolith, significant

923   preferential loss of heavy Zn isotopes in three different lateritic weathering profiles is

924   observed (from India: Suhr et al., 2018 and this study; from Cameroon: Viers et al.,

925   2007).

926

927   For Cu, a smaller integrated loss of –7% from the SQ profile is calculated, with a

928   more negative $\Delta^{65}Cu_{int}$ of –0.32‰ (Table 2). There is considerably more scatter in the

929    $\tau_{Cu} - \Delta^{65}Cu$ plot (Fig. 9B) – likely due to the multiple potential processes influencing

930   Cu isotopes and to more heterogeneous protolith Cu concentrations. However, nearly

931   all Cu-depleted profiles show negative $\Delta^{65}Cu_{int}$ values (plotting in the lower left

932 quadrant of Fig. 9B), indicating consistent loss of isotopically heavy Cu during

933 weathering.

934

935 Two plausible explanations for the release of isotopically heavy Zn and Cu during

936 lateritic weathering have been discussed: (1) incorporation of light isotopes in

937 aluminous Fe oxide phases (ferrugination) or (2) organic complexation of heavy

938 isotopes in the dissolved phase. In section 5.2.1, we suggested that organic

939 complexation might lead to mobilization of heavy isotopes if mineral dissolution

940 approaches chemical equilibrium, and that this scenario would be plausible in a

941 transport-limited weathering regime. However, Figure 9 does not provide evidence

942 for the converse prediction – of mobilization of light Cu (or Zn) isotopes in

943 kinetically controlled, weathering-limited regimes (Fig. 9). Alternatively, in section

944 5.2.2, we suggested that organic complexation retains heavy isotopes in the aqueous

945 phase *after* mobilization of Cu and Zn from their host mineral phases, with sorption of

946 the complementary light pool on secondary Fe oxide minerals (section 5.2.2).

947

948 It is notable that Cu isotope data from weathering profiles developed on different

949 lithologies fall on a similar fractionation trend (Fig. 9B, dashed arrow). Mathur et al.

950 (2012) and Lv et al. (2016) favour oxidative weathering of Cu sulphides to explain

951 residual isotopically light Cu signatures observed in weathered black shales. Given

952 the absence of Cu-hosting sulphide phases in the SQ laterite, we propose that a

953 combination of organic complexation in the aqueous phase and retention of light

954 isotopes by secondary precipitating Fe oxide phases is the most likely explanation for

955 the release of heavy Cu (and Zn) isotopes during lateritization. At greater degrees of

956 Cu loss (>80%), Vance et al. (2016) observe a return towards protolith Cu isotope

957 compositions in a sequence of increasingly waterlogged basaltic soils in Hawaii (Fig.

958 9B, dotted arrow), which they attribute to reduction of Fe oxides and return of the

959 associated isotopically light Cu to the aqueous phase.

960

961 *5.4.2 Implications for the weathering-derived flux of Zn and Cu to rivers on*

962 *geological timescales*

963

964 The sensitivity of the global cycles of Zn and Cu to a change in the riverine flux

965 depends on the magnitude and timescale of the change compared to the residence time

966   of the element in the ocean. In the modern ocean, both Zn and Cu have relatively

967   short residence times of a few thousand years (Hayes et al., 2018 and references

968   therein). Thus, there is scope to influence the global ocean budgets of Zn and Cu via a

969   change in the riverine input. There are two possible ways to influence the isotopic

970   composition of the weathering-derived input of Zn and Cu to rivers: (1) change the

971   isotopic composition of the predominant weathered lithology and (2) change the

972   intensity of weathering and any associated isotope fractionation. The former is

973   unlikely to be a major control, because clastic sediments and igneous rocks have

974   restricted Zn and Cu isotope compositions (Moynier et al., 2017) and because there is

975   no consistent relationship between riverine δ^{66}Zn or δ^{65}Cu and catchment lithology in

976   modern dissolved phase river data (Vance et al., 2008; Little et al., 2014b). In this

977   contribution, we set out to address the latter, i.e. what is the maximum leverage of

978   chemical weathering on the isotopic composition of Zn and Cu supplied to rivers?

979

980   Figure 9A illustrates that significant weathering-derived Zn isotope fractionation only

981   occurs during extreme chemical weathering (lateritization). Lateritization was

982   promoted during Greenhouse climate periods of Earth history (e.g., the mid Miocene

983   Climatic Optimum), with the mid Tertiary to mid Quaternary considered to be a

984   period of particularly intensive chemical weathering (e.g., Dalvi et al., 2004; Thorne

985   et al., 2012; Widdowson, 2009). Could such a shift in weathering style have an impact

986   on the riverine δ^{66}Zn signature? While our data indicate that the Zn isotope

987   composition of the instantaneous flux to rivers from lateritic terrains can change, we

988   suggest that even widespread lateritization is unlikely to have had a major impact on

989   global average riverine δ^{66}Zn. At the very high degrees of Zn mobility observed

990   during lateritic weathering, the isotopic composition of the cumulative aqueous phase

991   will approach that of the protolith by mass balance. Thus, the average Zn isotope

992   composition of the source of Zn to rivers should be rather insensitive to climate-

993   driven change on geological timescales. Nevertheless, the scope for an instantaneous

994   change in the riverine flux should be considered on short timescales and at local and

995   regional spatial scales.

996

997   The small but growing dataset for Cu isotopes during weathering indicates release of

998   isotopically heavy Cu in all oxygenated environments (Fig. 9B), consistent with the

999   observed isotopically heavy Cu in the dissolved phase of modern rivers (Vance et al.,

2008). In contrast, weathering in modern reducing environments appears to re-release isotopically light Cu associated with Fe-Mn oxides (Fig. 9B; Vance et al., 2016). Periodic flooding may also lead to reduction of Cu(II) to Cu(I), with release of isotopically light Cu(I) to the aqueous phase (Bigalke et al., 2010c; Bigalke et al., 2013; Babcsányi et al., 2014). Generally, however, Cu mobility during chemical weathering is likely to be significantly reduced under anoxic conditions (e.g., Neaman et al., 2005a, 2005b). Copper and Cu isotopes may therefore be an interesting marker for the presence or absence of oxygen during the development of paleosols.

Finally, release of isotopically heavy Cu during weathering is consistent with the scenario outlined by Chi Fru et al. (2016) for an observed shift from relatively low to higher $\delta^{65}Cu$ values in marine sediments across the great oxidation event (GOE). This shift was interpreted to reflect release of isotopically heavy Cu from the continents on the establishment of oxidative weathering (Chi Fru et al., 2016). These authors favoured oxidative weathering of sulphides as the primary mechanism responsible for releasing heavy Cu, while our study emphasizes that weathering in an oxygenated environment promotes retention of light Cu and release of heavy Cu, regardless of the primary host phase.

6.0 Conclusions

We have presented evidence of systematic and correlated Zn and Cu isotope fractionation during lateritization, observing retention of light isotopes in the associated weathering profile. Zinc and Cu in the residue are likely incorporated in secondary aluminous Fe oxide phases in the laterite, a process of 'ferrugination' that may itself be accompanied by isotope fractionation. Alternatively, the precipitating Fe oxide phases may passively scavenge light isotopes due to preferential organic complexation of heavy isotopes in the aqueous phase. The relative roles of organic complexation versus incorporation in Fe oxide phases, and their interaction with the multitude of other controls on metal speciation in the weathering environment (e.g., presence of inorganic ligands, pH, redox, solid organic matter) are an important target for future experimental and theoretical work.

1033 Our study, taken together with those previously published, illustrates that Zn isotope

1034 fractionation during weathering is limited, except at very extreme degrees of Zn

1035 removal. Therefore, mass balance constraints limit the impact of isotopic fractionation

1036 at high degrees of chemical weathering on the δ^{66}Zn of the riverine flux. This

1037 inference is consistent with the modern measured average δ^{66}Zn in rivers, which is

1038 unfractionated from the lithogenic δ^{66}Zn value.

1039

1040 In contrast, weathering of all lithologies studied to date appears to be associated with

1041 preferential retention of isotopically light Cu, consistent with isotopically heavy Cu in

1042 the dissolved pool of rivers. Weathering alone cannot account for the isotopically

1043 heavy riverine flux on long timescales, however, due to the relatively small pool of

1044 light Cu stored in terrestrial reservoirs like soils (Vance et al., 2016). Likely, the

1045 processes responsible for the liberation of heavy Cu during weathering (or,

1046 conversely, the retention of light Cu) continue to operate in some form downstream,

1047 with partitioning between the dissolved and particulate phase maintained in rivers and

1048 the oceans.

1049

1050

1062

Figure Captions

1064

1065 **Figure 1**. **Left**: The location of Goa state (red) on the Indian Dharwar Craton

1066 (adapted from Paton et al., 2007). In the northeastern corner of the state, Deccan Trap

1067 flood basalts overlie the Dharwar metasediments. **Right**: The geology of Goa state

1068 (adapted from Widdowson, 2009; Devaraju et al., 2010). The black dashed line

1069 represents the state boundary. The Merces Quarry (SQ) laterite profile (labelled) is

1070 located at 15°28'44"N, 73°52'35"E. It is developed on Dharwar Late Archaean

1071 biotite-bearing greywacke.

1072

1073 **Figure 2.** Left: Schematic illustrating the depth distribution of samples in the laterite

1074 profile in relation to characteristic zones of alteration (Wimpenny et al., 2007;

1075 Widdowson, 2009). Graphs from left to right: Major element concentration variations

1076 (SiO_2, Al_2O_3, Fe_2O_3; Widdowson, 2009), MnO concentration variations (Widdowson,

1077 2009), and indices of alteration (Chemical Index of Alteration, CIA; Index of

1078 Lateritization, IOL; see text for further details). Grey shading highlights zone III, the

1079 paleo-water table. Samples showing only limited alteration, from below the dotted

1080 line of seepage (zone I), are paler in colour.

1081

1082 **Figure 3.** The crystal abundances of major mineral phases in the SQ laterite

1083 weathering profile compared to the four identified zones of alteration (Fig. 2;

1084 Wimpenney et al., 2007).

1085

1086 **Figure 4. A.** Concentration profiles and **B.** τ enrichment-depletion profiles (see text

1087 for details) of Li (grey triangles), Zn (red squares) and Cu (blue diamonds) in the SQ

1088 profile. C. τ enrichment-depletion profiles for Fe and Mn. Open symbols: little

1089 altered samples in zone I, below line of seepage (dotted line). Filled symbols: altered

1090 samples in zones II-IV, above line of seepage. Grey shaded zone III has been

1091 influenced by the paleo-water table.

1092

1093 **Figure 5. A.** Depth profiles of $\delta^{66}Zn$ (red squares) and $\delta^{65}Cu$ (blue diamonds). Open

1094 symbols: unaltered-little altered samples in zone I, below line of seepage (dotted line).

1095 Filled symbols: very increasingly altered zone II-IV mottled and lateritic samples.

1096 Shaded grey rectangle: zone III, influenced by the paleo-water table. **B.** Positive

1097 correlation between $\delta^{66}Zn$ and $\delta^{65}Cu$ in the SQ profile. Linear regression (arrow)

1098 indicates coupled loss of heavy Cu and Zn isotopes during lateritization and a

1099 resultant shift towards residual isotopically light values. Error bars represent long-

1100 term external 2SD reproducibility.

1101

1102 **Figure 6**. Covariation of Zn and Cu with selected major (A-D) and trace elements (E-

1103 H) in samples from zone I (unaltered − little altered) of the SQ laterite profile.

1104 Positive correlations of Zn with elements commonly hosted in biotite (Mg, K, Li, Co

1105 and Rb) suggest that Zn is primarily hosted in biotite in the parent greywacke (see

1106 also Fig. S3). Copper shows negative correlations with most other major and trace

1107 elements, with the exception of SiO_2 and Na_2O (Panel D), suggesting an association

1108 with a detrital phase.

1109

1110 **Figure 7.** Rayleigh fractionation modelling of **A**. Zn and **B.** Cu isotopes assuming

1111 preferential mobilization of heavy isotopes to the dissolved phase, assuming $R = R_0 \cdot f$

1112 $^{\alpha-1}$ (where R_0 is the isotope ratio of the protolith (larger open symbols), f the fraction

1113 removed and α the fractionation factor. For Zn: $\alpha = 1.0002$, for Cu: $\alpha = 1.001$).

1114 Dashed line: residual isotopic composition of the solid. Dash-dotted line: cumulative

1115 isotopic composition of the fluid removed from the system. Dotted line: instantaneous

1116 fluid isotopic composition. Symbols as in Figures 4 and 6. Error bars represent long-

1117 term external 2SD reproducibility. Paleo-water table sample SQ11 labelled.

1118

1119 **Figure 8.** Negative correlations of $\delta^{66}Zn$ (red squares) and $\delta^{65}Cu$ (blue diamonds)

1120 with Fe_2O_3 in the SQ profile. Paleo-water table sample SQ11 circled, other symbols

1121 as in Figure 4. Regressions are shown excluding (solid lines) and including (dashed

1122 lines) SQ11. Error bars represent long-term external 2SD reproducibility.

1123

1124 **Figure 9.** Integrated τ and integrated isotopic compositions for global weathering

1125 profiles **A**. Zn and **B**. Cu. Note, data are only included for studies where τ values are

1126 reported or can be calculated (Viers et al., 2007; Mathur et al., 2012; Liu et al., 2014;

1127 Lv et al., 2016; Vance et al., 2016). In order to include as much data as possible, but

1128 where an integrated τ-value cannot be calculated because horizon depths are not

1129 reported, either the full profile (for the central China black shale; Lv et al., 2016) or

1130 the mean and 1SD for each published profile (for the Cameroon laterite profiles; Viers

1131 et al., 2007) is shown. The SQ laterite dataset is shown as a full profile and as an

1132 integrated signature (larger symbol). Recently published full profile Zn isotope data is

1133 also included for the Bidar laterite, developed on Deccan basalt, for comparison (Zn

1134 only: Suhr et al., 2018). Literature data: [1] Viers et al. (2007), [2] Suhr et al. (2018),

1135 [3] Vance et al. (2016), [4] Lv et al. (2016), [5] Liu et al. (2014), [6] Mathur et al.

1136 (2012).

1137

1138

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1628

Table 1

Table 1. Isotope data for USGS rock standards (mean and 2SD) analysed in this study (in grey) versus recommended (Moynier et al., 2017) or published values.

	$\delta^{66}Zn_{JMC\text{-}Lyon}$ (‰)	2SD	n	$\delta^{65}Cu_{SRM976}$ (‰)	2SD	n
BHVO-2	0.39	0.07	6	0.07	0.05	6
Recommended	*0.28*			*0.12*		
Published Range	*0.21 to 0.48*		*7*	*0.10 to 0.15*		*5*
BIR-1	0.27	0.04	3	-0.02	0.05	3
Recommended	*0.26*			*0.02*		
Published Range	*0.20 to 0.36*		*5*	*-0.02 to 0.08*		*3*
Nod P1	0.86	0.06	3	0.28	0.09	3
Published Range	*0.78 to 0.87*		*3*	*0.29 to 0.46*		*3*
BCR-2	0.33	0.06	3	nd		
Recommended*	*0.25*			*0.17*		
Published Range*	*0.20 to 0.33*		*12*	*0.07 to 0.22*		*6*

* Combined BCR1/2

'n' refers to the number of complete duplicates analysed in this study, or the number of studies compiled in the given published range.

Table 2

Table 2. Data table, including calculated CIA and IOL values (see text for details), S concentrations, calculated τ values (where j = Nb, and p = SQ2-6 mean: see Eqn. 5 and text for details), measured Zn and Cu isotope values, and calculated Δ isotope values (where $\Delta = \delta_{sample} - \delta_{SQ2}$). Fe_2O_3 and MnO concentrations from Wimpenny et al. (2007). Li, Zn and Cu concentrations from Howarth et al. (2018).

| Zone	Sample	Depth m	ρ gcm^{-3}	CIA	IOL	S µg/g	Fe_2O_3 wt%	MnO wt%	Li µg/g	Zn µg/g	Cu µg/g	$\tau_{Fe,Nb}$	$\tau_{Mn,Nb}$	$\tau_{Li,Nb}$	$\tau_{Zn,Nb}$	$\tau_{Cu,Nb}$	$\delta^{66}Zn$ ‰	2 SD	$\Delta^{66}Zn$ ‰	$\delta^{65}Cu$ ‰	2 SD	$\Delta^{65}Cu$ ‰
	SQ14	0	1.45	97	86	350	48.5	0.04	8.8	31	61	2.7	-0.89	-0.88	-0.87	-0.52	-0.02	0.07	-0.51	-0.87	0.07	-0.89
IV	SQ13	2.5	1.57	97	82	418	45.0	0.04	9.5	25	50	2.9	-0.87	-0.85	-0.89	-0.56	nd	nd	na	-0.70	0.07	-0.73
	SQ12	3.5	1.64	98	80	274	36.4	0.06	7.1	25	39	1.6	-0.85	-0.91	-0.90	-0.71	0.07	0.07	-0.42	-0.69	0.07	-0.67
	SQ12dup																nd			-0.61	0.07	
III	SQ11	7.5	1.25	95	84	203	68.3	0.57	4.2	97	52	18.9	5.5	-0.78	0.51	0.54	0.14	0.07	-0.34	-0.30	0.07	-0.32
	SQ10	8.5	1.80	96	82	408	49.6	0.02	4.5	21	31	4.6	-0.91	-0.91	-0.87	-0.64	0.15	0.07	-0.33	-0.86	0.07	-0.89
	SQ9	12	1.29	92	31	205	10.8	0.02	8.7	23	34	0.59	-0.91	-0.77	-0.82	-0.49	0.28	0.07	-0.20	-0.60	0.07	-0.63
II	SQ8	13.5	1.37	92	31	227	10.3	0.02	9.7	38	38	0.37	-0.87	-0.77	-0.73	-0.48	0.02	0.07	-0.46	-0.45	0.07	-0.47
	SQ7	14	1.25	90	27	192	7.6	0.06	13.8	38	42	0.07	-0.64	-0.66	-0.72	-0.40	0.38	0.07	-0.11	-0.03	0.07	-0.06
	SQ6	15	2.20	59	18	630	3.4	0.05	20.2	66	53	-0.26	-0.46	-0.22	-0.23	0.19	0.42	0.07	-0.06	-0.23	0.07	-0.25
	SQ5	22.5	1.99	63	27	861	7.6	0.17	45.0	146	37	0.44	0.59	0.51	0.47	-0.29	0.53	0.07	0.05	-0.28	0.07	-0.31
I	SQ4	25.5	2.23	57	15	343	2.4	0.07	12.5	33	66	-0.20	0.01	-0.27	-0.43	1.24	0.43	0.07	-0.05	-0.05	0.07	-0.08
	SQ3	30	2.68	58	22	818	5.6	0.11	32.4	115	40	-0.12	-0.22	-0.10	-0.04	-0.36	0.47	0.07	-0.01	0.04	0.07	0.02
	SQ2	34	2.75	57	23	725	6.1	0.13	31.6	112	50	0.04	0.06	-0.04	0.02	-0.12	0.51	0.07	na	0.01	0.07	na
	SQ2dup																0.48	0.07		0.04	0.07	
Dyke	SQ1	-	3.11	-	-	1634	-	-	7.4	127	122			na	na	na	0.35	0.07	na	0.08	0.07	na
											Integrated (all):	**1.5**	**0.02**	**-0.28**	**-0.23**	**-0.07**			**-0.14**			**-0.32**
											Integrated (excl. zone III):	**0.36**	**-0.21**	**-0.21**	**-0.22**	**-0.06**			**-0.11**			**-0.28**

nd – not done
na – not applicable
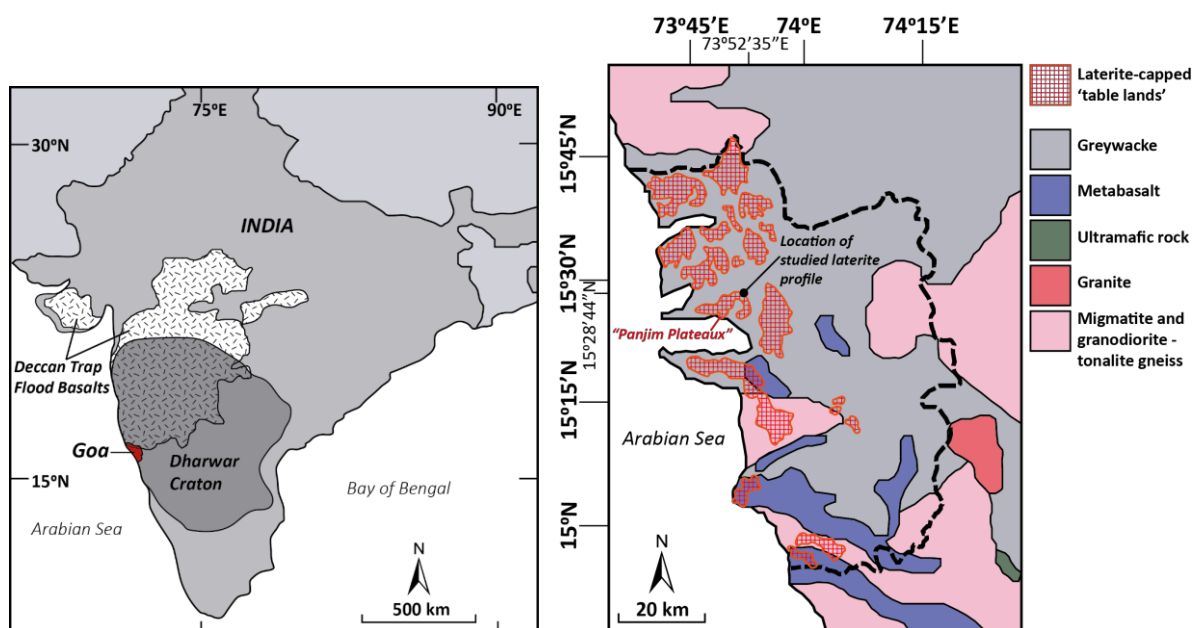
Figure 1. **Left**: The location of Goa state (red) on the Indian Dharwar Craton (adapted from Paton et al., 2007). In the northeastern corner of the state, Deccan Trap flood basalts overlie the Dharwar metasediments. **Right**: The geology of Goa state (adapted from Devaraju et al., 2010 and Widdowson, 2009). The black dashed line represents the state boundary. The Merces Quarry (SQ) laterite profile (labelled) is located at 15°28'44"N, 73°52'35"E. It is developed on Dharwar Late Archaean biotite-bearing greywacke.
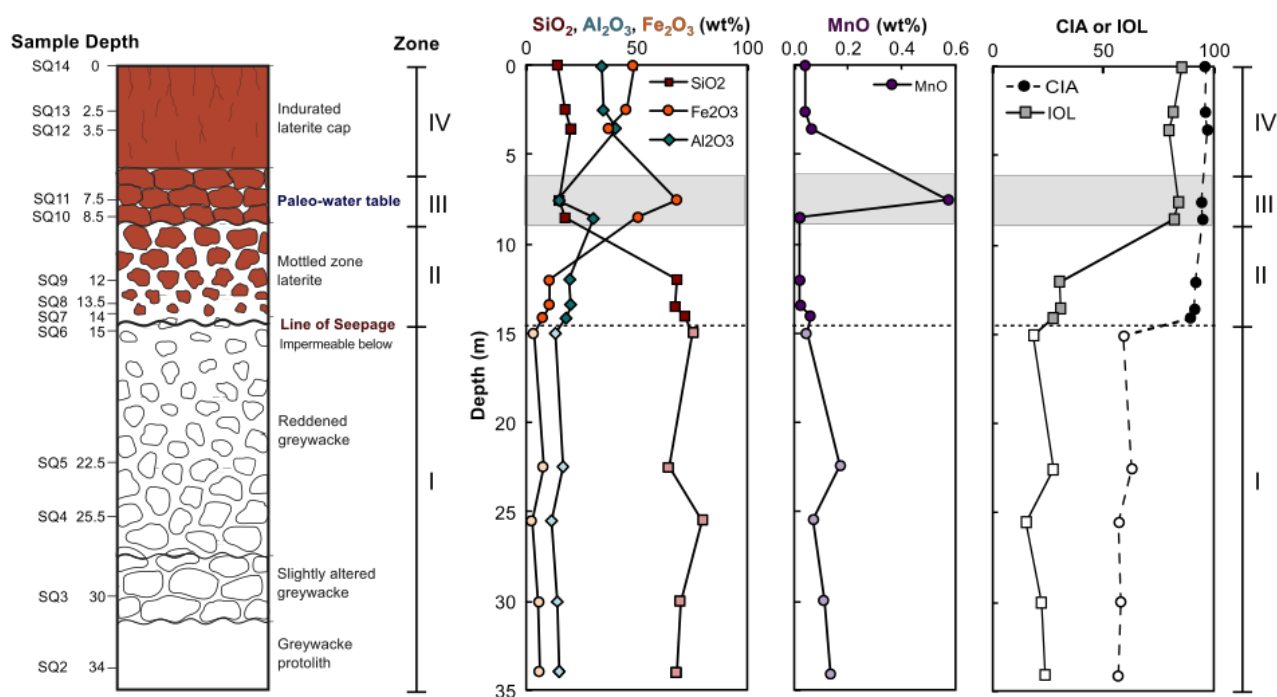
Figure 2. Left: Schematic illustrating the depth distribution of samples in the laterite profile in relation to characteristic zones of alteration (Wimpenny et al., 2007; Widdowson, 2009). Graphs from left to right: Major element concentration variations (SiO_2, Al_2O_3, Fe_2O_3; Widdowson, 2009), MnO concentration variations (Widdowson, 2009), and indices of alteration (Chemical Index of Alteration, CIA; Index of Lateritization, IOL; see text for further details). Grey shading highlights zone III, the paleo-water table. Samples showing only limited alteration, from below the dotted line of seepage (zone I), are paler in colour.
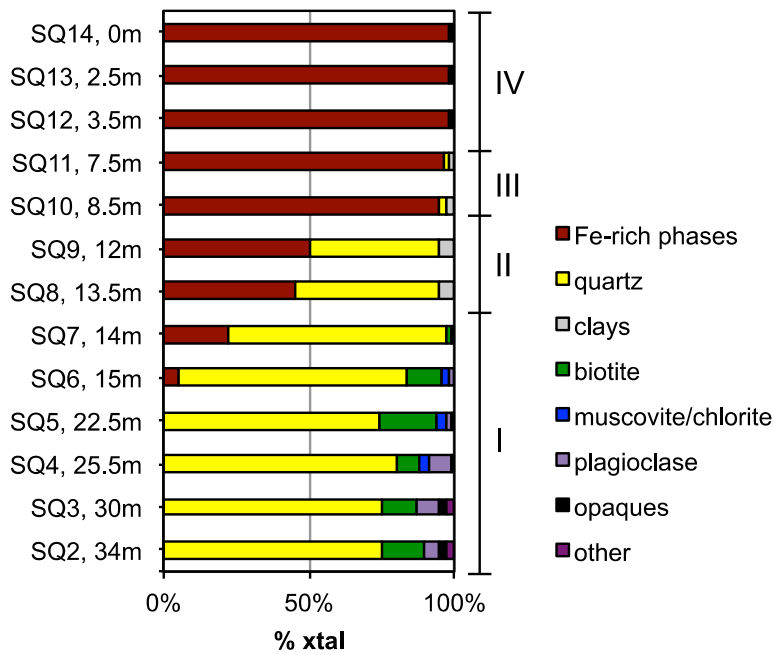
Figure 3. The crystal abundances of major mineral phases in the SQ laterite weathering profile compared to the four identified zones of alteration (see also Fig. 2; after Wimpenney et al., 2007).
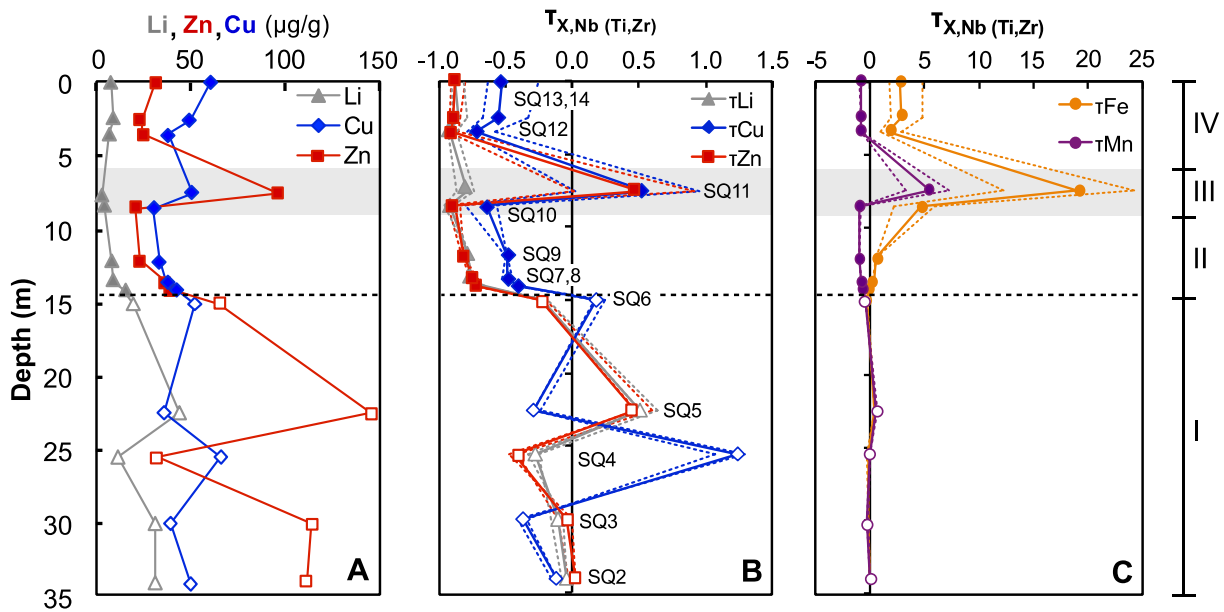

Figure 4. A. Concentration profiles and **B.** τ enrichment-depletion profiles (see text for details) of Li (grey triangles), Zn (red squares) and Cu (blue diamonds) in the SQ profile. **C.** τ enrichment-depletion profiles for Fe and Mn. Open symbols: little altered samples in zone I, below line of seepage (dotted line). Filled symbols: altered samples in zones II-IV, above line of seepage. Grey shaded zone III has been influenced by the paleo-water table.
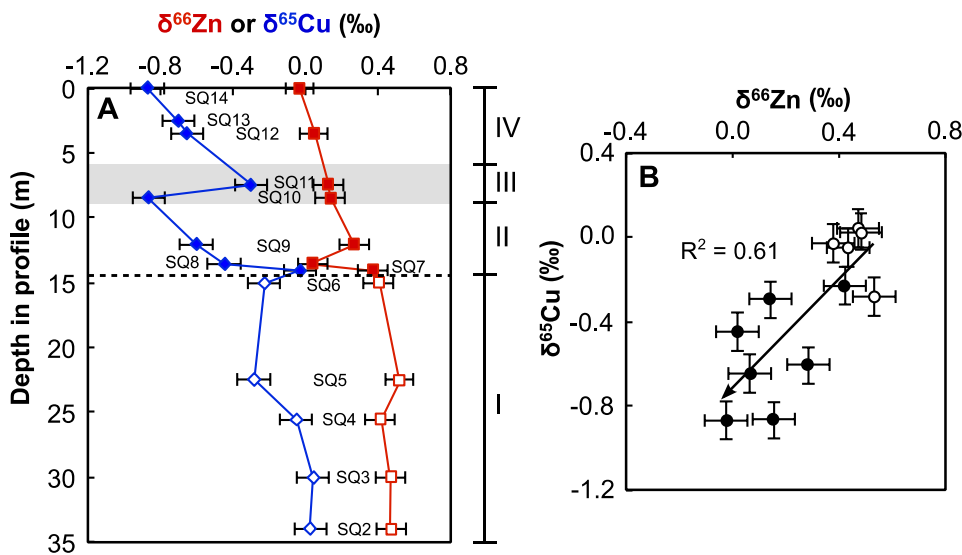
Figure 5. A. Depth profiles of $\delta^{66}Zn$ (red squares) and $\delta^{65}Cu$ (blue diamonds). Open symbols: unaltered-little altered samples in zone I, below line of seepage (dotted line). Filled symbols: increasingly altered zone II-IV mottled and lateritic samples. Shaded grey rectangle: zone III, influenced by the paleo-water table. **B**. Positive correlation between $\delta^{66}Zn$ and $\delta^{65}Cu$ in the SQ profile. Linear regression (arrow) indicates coupled loss of heavy Cu and Zn isotopes during lateritization and a resultant shift towards residual isotopically light values. Error bars represent long-term external 2SD reproducibility.
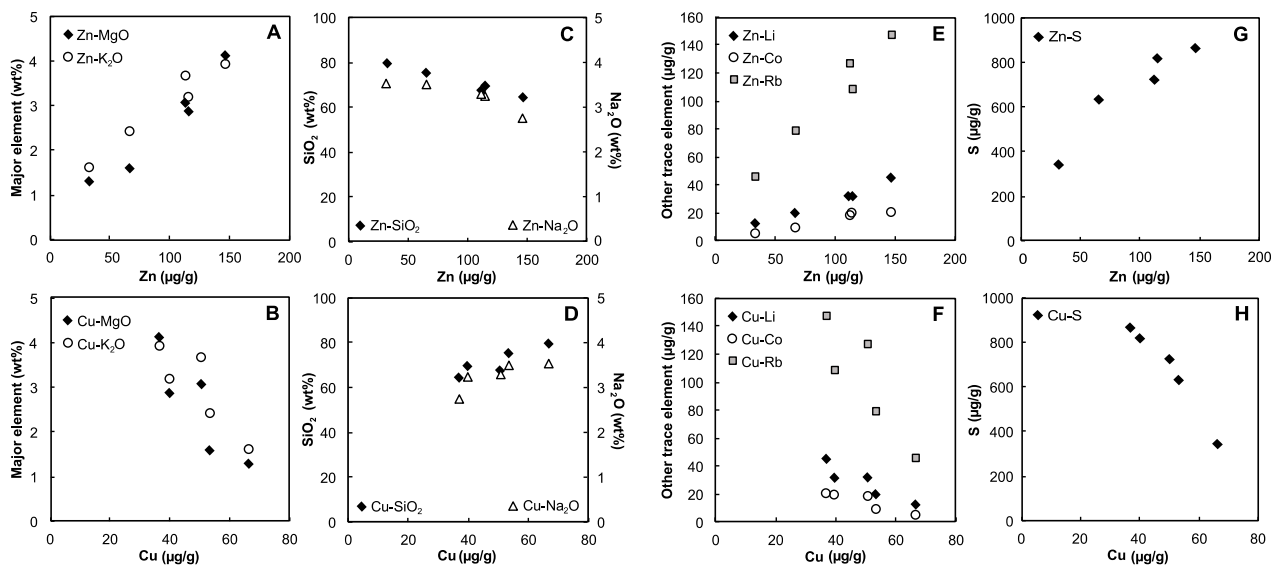

Figure 6. Covariation of Zn and Cu with selected major (A-D) and trace elements (E-H) in samples from zone I (unaltered – little altered) of the SQ laterite profile. Positive correlations of Zn with elements commonly hosted in biotite (Mg, K, Li, Co and Rb) suggest that Zn is primarily hosted in biotite in the parent greywacke (see also Fig. S3). Copper shows negative correlations with most other major and trace elements, with the exception of SiO_2 and Na_2O (Panel D), suggesting an association with a detrital phase.
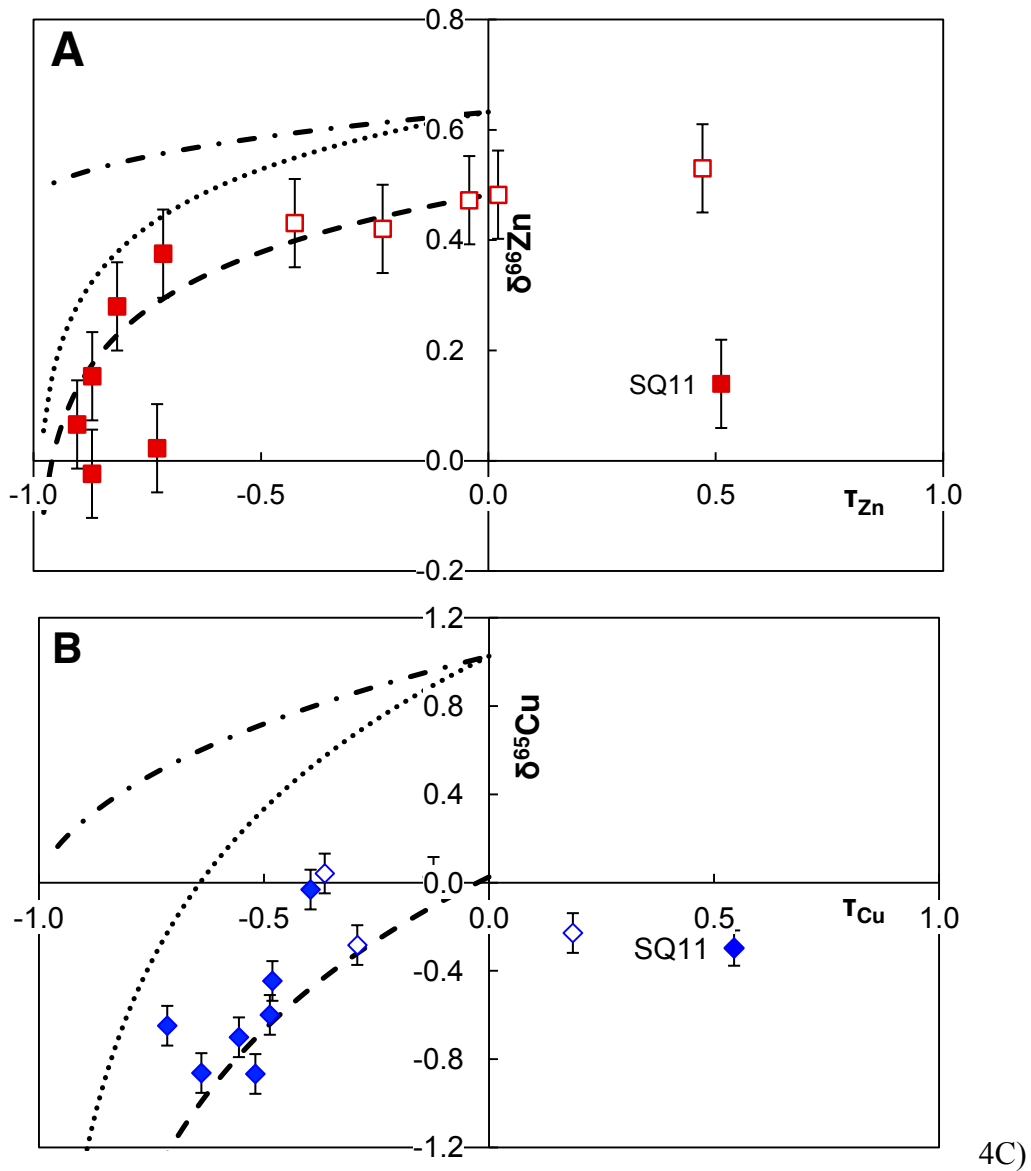
Figure 7. Rayleigh fractionation modelling of **A**. Zn and **B**. Cu isotopes assuming preferential mobilization of heavy isotopes to the dissolved phase, assuming $R = R_0 \cdot f^{\alpha-1}$ (where R_0 is the isotope ratio of the protolith (larger open symbols), f the fraction removed and α the fractionation factor. For Zn: $\alpha = 1.00015$, for Cu: $\alpha = 1.001$). Dashed line: residual isotopic composition of the solid. Dash-dotted line: cumulative isotopic composition of the fluid removed from the system. Dotted line: instantaneous fluid isotopic composition. Symbols as in Figures 4 and 5. Error bars represent long-term external 2SD reproducibility. Paleo-water table sample SQ11 labelled.
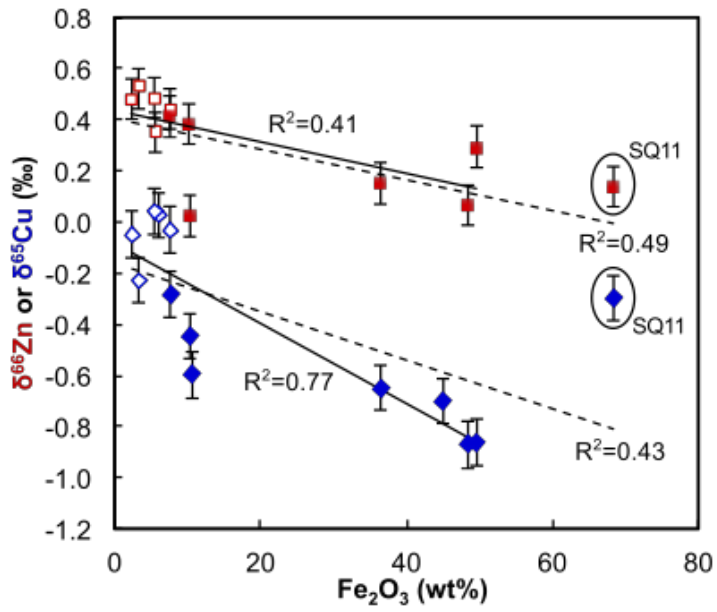
Figure 8. Negative correlations of $\delta^{66}Zn$ (red squares) and $\delta^{65}Cu$ (blue diamonds) with Fe_2O_3 in the SQ profile. Paleo-water table sample SQ11 is circled, other symbols as in Figure 5. Regressions are shown excluding (solid lines) and including (dashed lines) SQ11. Error bars represent long-term external 2SD reproducibility.
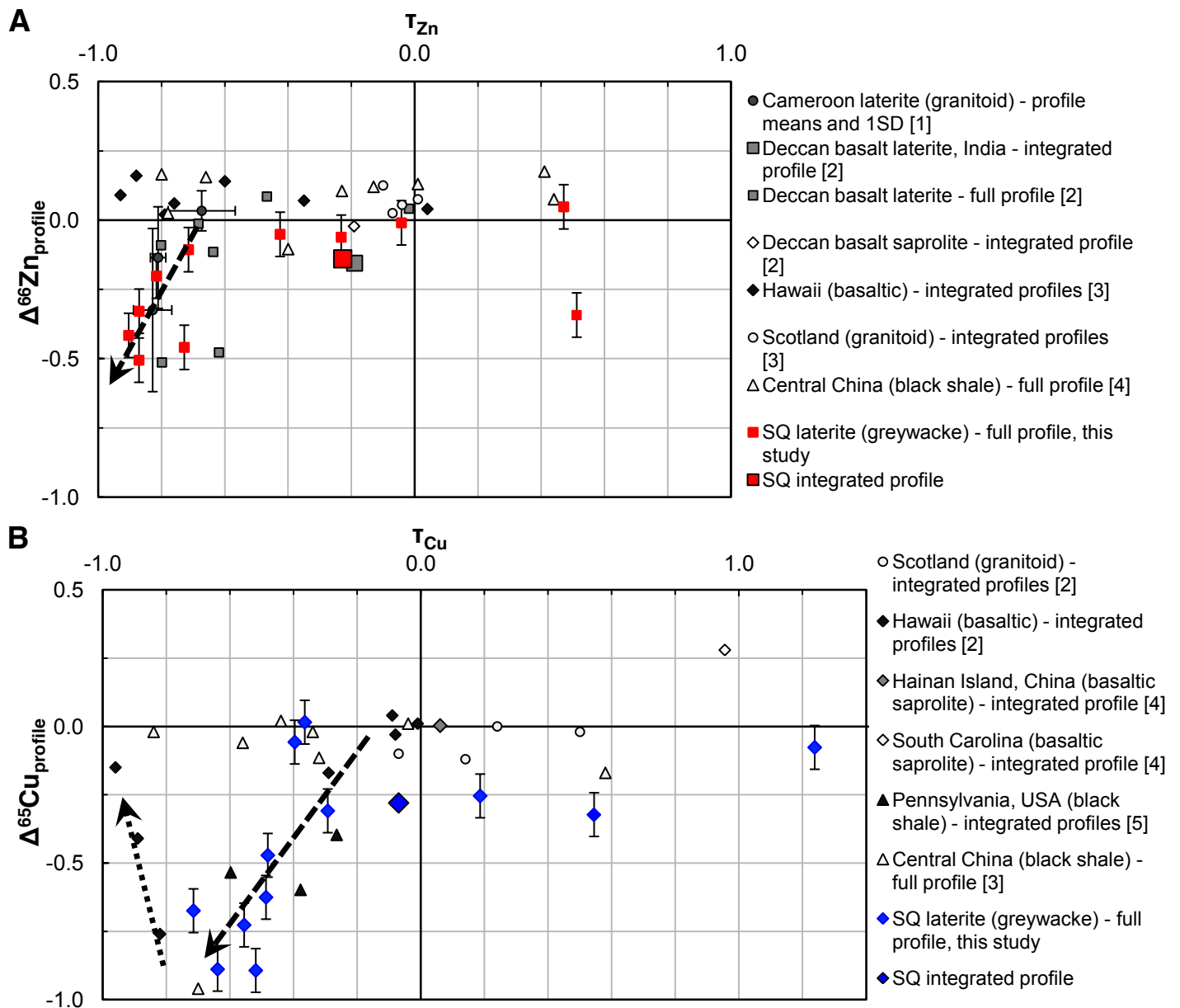
Figure 9. Integrated τ and integrated isotopic compositions for global soils **A**. Zn and **B**. Cu. Note, data are only included for studies where τ values are reported or can be calculated (Viers et al., 2007; Mathur et al., 2012; Liu et al., 2014; Lv et al., 2016; Vance et al., 2016). In order to include as much data as possible, but where an integrated τ-value cannot be calculated because horizon depths are not reported, either the full soil profile (for the central China black shale; Lv et al., 2016) or the mean and 1SD for each published profile (for the Cameroon laterite profiles; Viers et al., 2007) is shown. The SQ laterite dataset is shown as a full profile and as an integrated signature (larger symbol). Recently published full profile Zn isotope data is also included for the Bidar laterite, developed on Deccan basalt, for comparison (Zn only: Suhr et al., 2018). Literature data: [1] Viers et al. (2007), [2] Suhr et al. (2018) [3] Vance et al. (2016), [4] Lv et al. (2016), [5] Liu et al. (2014), [6] Mathur et al. (2012).

Electronic Annex

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