



## **Copper and zinc stable isotopes as tracers of pedogenic evolution: the LSAG chronosequence, Hawaii.**

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Transition metal stable isotopes have great potential for tracing the geochemical evolution and mass transport during soil processes. We explore this potential in a study of the copper and zinc stable isotopic compositions of soil profiles from the classic LSAG chronosequence developed in basaltic rocks on Hawaii<sup>1</sup>. The three studied profiles: Ola'a (0.3 ka); Laupahoehoe (~20 ka) and Kohala (150 ka) formed at similar conditions of ~ 1200m height, 2500 mm present-day rainfall and 16°C surface temperatures. They show a mineralogical progression from dominantly primary crystalline minerals at Ola'a (Oe to C3 horizons) to dominantly metastable non-crystalline Fe-sesquioxides at Laupahoehoe (Oe to Bw3 horizons) and non-crystalline Al-hydroxides at Kohala (Oe to Bw4 horizons). Whole soil samples from each depth profile and sequential chemical extractions representing Fe-oxide bound metals (OX), the organic-associated fraction (ORG) and the residue (RES) consisting of the silicate and amorphous Al-hydroxide located metals were studied for their Cu- and Zn- isotopic composition. Whole soil and sequential extracts from the youngest profile at Ola'a show  $\delta^{65}\text{Cu}$  and  $\delta^{66}\text{Zn}$  values of  $0.05 \pm 0.23 \text{‰}$  and  $0.20 \pm 0.21 \text{‰}$  respectively, and mostly fall in the range of basaltic igneous rocks. The data are consistent with minor mobilization of these metals as a result of incipient pedogenic processes and are consistent with results of other tracers of metallic mobilization such as base metal cations<sup>2</sup>. In contrast, the depth profiles in the two older soils show significant isotopic compositional shifts from basalt values, and correspondingly significant isotopic fractionations among the OX, ORG and RES extracts. Generally, whole soil samples and RES fractions are characterized by marked negative shifts in  $\delta^{65}\text{Cu}$  values and positive shifts in  $\delta^{66}\text{Zn}$ , relative to Ola'a values. Conversely, the OX extracts show higher  $\delta^{65}\text{Cu}$  values and lower  $\delta^{66}\text{Zn}$  values. The isotopic fractionations average at  $\Delta^{65}\text{Cu}(\text{OX-RES}) = 1.1 \pm 0.4 \text{‰}$  and  $\Delta^{66}\text{Zn}(\text{OX-RES}) = -0.3 \pm 0.15 \text{‰}$  and are presumed to represent the partitioning of the metallic isotopes between non-crystalline Fe sesquioxide-bound and Al-hydroxide bound pools. Thus, the Cu and Zn isotopic compositions provide strong evidence for open system leaching of the heavy isotopes of Cu and light isotopes of Zn during the pedogenic processes that lead to breakdown of the original crystalline mineralogy. These shifts appear to be slightly more marked in the Laupahoehoe soil profile, which may suggest that input of atmospheric Cu and Zn, expected to have lithogenic isotopic compositions similar to that of basalts, may be partially buffering the system in the older Kohala soil sequence. The isotopic shifts are compatible with the leaching of isotopically heavy Cu and light Zn associated with iron oxides as a major driving force for the metallic and isotopic mobilization, but it is the mineralogical balance between non-crystalline Fe sesquioxide and Al-hydroxide bound pools that will control the overall isotopic variations. In this weathering system, organically bound metals play a less significant role in the fractionation processes. It is thus clear that metallic isotope systems such as copper and zinc provide a significant insight into critical zone processes.

<sup>1</sup>Chadwick O.A. et al (1999) *Nature*, 397, 491-497

<sup>2</sup>Our data and Vitousek P.M et al. (1998) *GSA Today*, 7, 1-8.