

## Iron isotope variations in Icelandic soil profiles and fractionation of Fe isotopes during weathering

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Iron stable isotopes have considerable potential as a new geochemical tool that can be used to address the bioavailability and biogeochemical cycling of Fe in soils and the behaviour of Fe during weathering processes. The degree to which Fe isotopes may be fractionated during pedogenic and weathering processes is, however, controversial [e.g. 1-4]. This study investigates the distribution of Fe stable isotopes in four typical Icelandic soil profiles from a basaltic catchment (Borgarfjörður): Histic Andosol (HA), Histosol (H), Gleyic Andosol (GA), Brown andosol (BA). Among the soil profiles, the weathering degree increases following the sequence BA<GA<H<HA, as supported by a decreasing Total Reserve in Bases (TRB, the total content in Ca+Na+Mg+K) or an increasing content in crystalline Fe-oxides with increasing weathering. These soil profiles are all derived from the same parental basalt and hence provide an ideal opportunity to investigate the response of Fe stable isotopes to pedogenic and weathering processes. Bulk soil samples, pore waters, oxalate extracts (Fe<sub>o</sub>, specific for short range ordered Fe-oxide and humus-bound Fe) and dithionite-citrate-bicarbonate extracts (Fe<sub>d</sub>, including Fe<sub>o</sub> and crystalline Fe oxides, thus excluding Fe bound in silicates) were analysed for their Fe isotope compositions by MC-ICP-MS (Thermo Neptune) at Durham University using standard Fe purification and mass spectrometry procedures (long-term reproducibility: 0.03‰/amu 2 S.D.; blanks < 1ng Fe) [5]. Bulk soil Fe isotope compositions (δ<sup>57</sup>Fe, relative to the IRMM014 Fe standard) are correlated with the TRB weathering index: the most weathered soil profiles (e.g. HA) display isotopically light and variable Fe isotope compositions (-0.55 ± 0.08‰ to 0.20 ± 0.04‰ 2 S. D.) relative to the parental Icelandic basalt (0.07 ± 0.08‰), providing direct evidence for the fractionation of Fe isotopes during weathering to progressively lighter values. In contrast, poorly weathered soils (e.g. BA) display relatively invariant Fe isotope compositions (0.01 ± 0.07‰ to 0.20 ± 0.06‰) within error of the δ<sup>57</sup>Fe value of the parental basalt. In these poorly weathered soil profiles, pore waters, Fe<sub>o</sub> and Fe<sub>d</sub> also show minimal deviations in δ<sup>57</sup>Fe value with respect to the parental basalt, whereas in the highly weathered HA soil profile the Fe isotope compositions of pore waters, Fe<sub>o</sub> and Fe<sub>d</sub> are highly fractionated. In HA, the Fe isotope compositions of Fe<sub>d</sub> are extremely similar to those of the bulk soils, reflecting the large proportion of crystalline Fe oxides in this soil profile. In contrast, Fe<sub>o</sub> from the near-surface horizons in HA (0.34 ± 0.08‰ to 0.66 ± 0.06‰) are heavier than the bulk soil and become increasingly lighter than the bulk soil with depth. This pattern is also displayed by the soil pore waters, which suggests that the crystallinity of Fe-oxides in soils partly controls the fractionation of Fe isotopes in dissolved Fe in pore waters.

[1] Guelke et al., (2010) *Chemical Geology*, 277, 3–4, pp 269-280; [2] Poitrasson et al., (2008) *Chemical Geology*, 253, 1–2, pp 54-63; [3] Emmanuel et al., (2005) *Chemical Geology*, 222, 1–2, pp 23-34; [4] Wiederhold et al., (2007) *GCA*, 73, 23, pp 5821-5833; [5] Williams et al., (2012) *EPSL*, in press

## Accounting for post-depositional effects of a neo-Tethyan Permian-Triassic Section in the Himalayan Mountains.

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The Permian-Triassic Boundary (PTB) extinction is considered the largest extinction in earth's history. However interpreting paleo-environmental conditions from sedimentary records may prove difficult due to the occurrence and preservation of PTB sections. The PTB sediments of the Spiti Valley (Himachal Pradesh, Himalaya, India) have been subjected to diagenesis and low-grade metamorphism. These two processes potentially alter the original geochemical signatures. In Spiti Valley, PTB sections consist of Permian Gungri Formation (Kuling Group) black shale unconformably overlain by an iron-rich pebbly layer ("ferruginous layer") which marks the PTB. Overlying the ferruginous layer is the Triassic Mikin Formation, a limestone inter-bedded with calcareous and black shales. In this study we assessed the post-depositional overprint on the geochemistry of Spiti Valley Muth PTB section using methods geochemical and chemometric approaches to identify original signatures preserved in this section. The results show that the section does preserve original signatures useable for paleoenvironmental reconstruction. More importantly we show evidence of depositional events preceding the Neo-Tethyan main regression associated with the timing of the extinction.