Fractionation of Cu, Zn and Fe within the plant-soil environment

J.B. CHAPMAN[1], K. PEEL[1], T. ARNOLD[1], J.J. WILKINSON[1,2], B.J. COLES[1,2] AND D.J. WEISS[1,2]

[1] Dept. of Earth Science and Engineering, Imperial College London, South Kensington, London SW7 2AZ, UK ; d.weiss@imperial.ac.uk

[2] Dept. of Mineralogy, The Natural History Museum, Cromwell Road, London SW7 5PD, UK

The isotope systematics of transition elements offer exiting possibilities to study nutrient cycling in ecosystems and various biogeochemcial processes such as plant uptake. Also possible applications such as screening rice genotypes or tracing of pollutant sources are of great interest. However, a thorough quantitative and qualitative understanding of the various mechanisms that lead to fractionation in the low temperature environment is needed beforehand. Equally key is the development of analytical methods for accurate and high precision isotope ratio measurements in a wide variety of sample types, but particularly for organic samples.

We improved the quality of isotopic measurements of Fe, Cu and Zn in a wide variety of challenging matrixes including plants and silicates using a combination of wet and dry ashing, acid digestion and anion exchange chromatography. We obtain clean Fe, Zn and Cu fractions from both matrix types and achieved precisions for $\delta^{66}Zn$, $\delta^{65}Cu$ and $\delta^{56}Fe$ below ±0.1‰ in all matrixes using standard-sample bracketing and an IsoProbe MC-ICP-MS.

We investigated isotopic fractionation of Fe and Cu during congruent and incongruent dissolution of granites and carbonates using well constrained batch experiments. We leached malachite ($Cu_2(OH)_2CO_3$) and commercially available reference granites (G-2 and GS-N) with aqueous solutions and variable pH. The results for malachite show negligible isotopic fractionation of Cu ($\Delta^{65}Cu(Cu(II)_{(aq)}\text{-}Cu_{malachite}$) = -0.03±0.12 (1s, n=16) during congruent dissolution and in absence of organic ligands. Temparature changes between 4 and 50˚C had no effect. In contrast, significant fractionation of Fe was observed in leached granite with $\delta^{56}Fe$ values up to 0.35‰ lighter in solution. This has important implications for the definition of the 'bulk earth baseline' (BEB) and for labile Fe in soil (pedogensis vs. plant uptake).

Preliminary studies of Fe isotope ratios measured in different grass species showed different $\delta^{56}Fe_{IRMM\text{-}014}$ values (-0.365 and -0.095‰, respecitively) and are also significantly fractionated relative to the BEB. This could be, in light of the experimental findings of the leaching experiments, due to weathered labile Fe in the soil solution and/or the plant uptake itself.