

The effect of redox cycles on the partitioning of Fe, C, and P within soil systems

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Developing a quantitative understanding of the coupled cycling of Fe, C, and P in soil systems can lead to better land management practices for both agriculture and forestry systems. The biogeochemical cycles of C and P are known to be coupled through sorption and co-precipitation of iron-oxide minerals, and through valence-state transitions of C and Fe. The reduction of iron-oxides to aqueous Fe (II) can lead to the release of sorbed phosphate and organic compounds which can then migrate to different reservoirs within the soil system. Re-oxidation of aqueous Fe (II) to insoluble iron-oxides may result in further repartitioning of the soil system as phosphate and organic carbon sorb onto the newly formed minerals. Thus, oscillating redox conditions promote dynamic redistribution of Fe, C, and P within the soil.

To quantify the importance of redox oscillation on Fe, C and P distribution, retention and – in the case of iron oxide – reactivity in soils, we have constructed controlled atmospheric chambers (CAC) that allow precise dynamic manipulation of soil redox conditions. These chambers are situated within a larger anoxic chamber allowing for the sample extraction under strict anoxic conditions. We exposed soils from a lowland site within the Luquillo National Forest, Puerto Rico, to redox oscillations of two frequencies for several months. We will present results from sequential extractions targeting different Fe, P and C pools, XRD and Mossbauer mineral composition data, and a preliminary model quantitatively describing reductive and oxidative iron cycling.

Chalcophile elements in peridotites as a proxy for sulfide mineralization during serpentinization

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Petrographic observations in serpentinized abyssal peridotites [1] show evidence for sulfide mobilization / recrystallization during hydrothermal alteration, while thermodynamic modelling suggests that sulfide, Fe-Ni-O-S, systematics may be a useful indicator of T, fO_2 , fS_2 for hydrothermal systems [2]. Chalcophile element concentrations (e.g. Cu, Zn, Pb) in peridotites may then reflect the processes of sulfide precipitation / desulfurization during serpentinization. We present preliminary trace element data on bulk-rock serpentinized abyssal peridotite and fresh Hawaiian peridotites with a focus on chalcophile elements, to investigate the effects of sulfide precipitation in the mantle. Our results show that Cu concentrations in abyssal peridotites are extremely variable ($\times 10$), and extend to significantly higher concentrations than the Hawaiian peridotites. Copper, and to a lesser extent Zn, are entirely decoupled from any lithophile element (Ti, Zr, REE), indicators of melt depletion and refertilization in both the serpentinized and fresh peridotites. Petrographic and EPMA investigation showed a much greater modal abundance of sulfides in the abyssal vs. Hawaiian peridotites, with abyssal sulfides being dominantly petlandites with often Cu-rich lamellae. We suggest that the high Cu contents in abyssal peridotites likely result from sulfide precipitation during serpentinization, and bulk rock Cu contents may be a proxy for the abundance of chalcopyrite ($CuFeS_2$) in peridotites.

[1] Lugué *et al.* (2003) *GCA* **67**, 11553–1570. [2] Klein & Bach (2009) *J Pet.* **50**, 37–59.