The role of aluminum in ferrihydrite preservation

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The poorly crystalline Fe(III) (hydr)oxide ferrihydrite is considered one of the most important sinks for (in)organic contaminants within the environment. In sedimentary environments, the oxidation of carbon and hydrogen is constrained by microbial reduction of Fe(III) (hydr)oxides, of which ferrihydrite is considered the most biologically available. Yet, pure ferrihydrite ripens rapidly to more crystalline Fe phases, such as goethite, leading to diminished sorption capacities and bioavailability. This ripening is accelerated by surface reactions between ferrihydrite and aqueous Fe(II) and can also lead to ferrihydrite conversion to magnetite at higher Fe(II) levels. While ferrihydrite within most natural systems contains high levels of adsorbed or co-precipitated cations, particularly aluminum (Al), little is known regarding the impact of these cations on the capacity for ferrihydrite to ripen to more stable Fe(III) phases or serve as an effective electron acceptor. Accordingly, we explored the impact of adsorbed and substituted Al on the microbial reduction and abiotic Fe(II)-induced secondary mineralization of ferrihydrite over a wide range of Al levels.

Here, we show that Al substituted within (6-24 mole %) or adsorbed on (0.1 to 27% Γ_{max}) ferrihydrite results in diminished microbial reduction and abiotic Fe(II)-induced secondary mineralization resulting, in both cases, in the preservation of ferrihydrite even at low Al levels. The preservation of ferrihydrite increases linearly with the amount of Al adsorbed on or co-precipitated within ferrihydrite. In fact at Al substitution levels exceeding 17 mole %, the rate of microbial Fe(III) reduction is lower for ferrihydrite than for the more crystalline (and hence considered less bioavailable) phase goethite. Furthermore, formation of magnetite is completely inhibited at Al substitution levels greater than 17 mole %, levels that are frequently observed within natural ferrihydrites. Interestingly, the secondary minerals formed upon reaction with different Fe(II) levels (0.2 and 2.0 mM) varies not only with the concentration of Al, but also the mode of Al incorporation (adsorption versus co-precipitation). These findings provide insight into the mechanisms that may be responsible for ferrihydrite preservation and low levels of secondary magnetite typically found in sedimentary environments. The findings also have large implications for constraints on carbon oxidation in sedimentary systems containing compromised ferrihydrites.

Lithium isotope perspective on the Iceland mantle plume

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The Iceland mantle plume represents a quest of searching for the individual mantle end members as well as other components that may have contributed to the observed elemental and isotope variability. Here we present Li contents and isotope compositions in samples from two distinct volcanic centres in Iceland, Krafla and Theistarykir, that show a considerable range in Li and δ^7Li extending that reported previously [1–3]. Pristine Theistareykir basalts (MgO>7%) have consistently low Li contents and range in δ^7Li (+4.2 to +8.1‰) that mimics "depleted" lavas of [1], thought to be variously contributed by an old altered oceanic crust that underwent prior extraction of Li-rich arc magmas at convergent boundaries. Chemically evolved rocks from Krafla (MgO<2%) have similarly invariant δ^7Li pattern coupled with high Li enrichments as reported in [2]; this suggests that magmatic differentiation does not impart resolved Li isotope fractionation in juvenile crust derived from plume basalts. The radiogenic Sr–Nd isotope data appear to follow bi-modal distribution akin to [1] and no influence of magmatic evolution on either Sr or Nd in Li-rich rhyolitic and dacitic magmas which may mean a rapid formation of silicic rocks from parental basalts. The new and published data show a strong negative correlation between Li and Mg which shows a significant coupled data density gap between 2 and 5% MgO and 10 and 20 ppm Li, respectively, suggesting a lack of andesitic lavas between basalts and chemically evolved dacites and rhyolites. This may have petrogenetic consequences for formation of new crustal material through magmatic differentiation of rising plume magmas.

[1] Magna *et al.* (2011) *GCA* **75**, 922-936; [2] Schuessler *et al.* (2009) *EPSL* **258**, 78-91; [3] Ryan & Kyle (2004) *Chem Geol* **212**, 125-142