Atom exchange between aqueous Fe(II) and Fe oxides: Fate of As(V)

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Human exposure to arsenic in groundwater is a global concern, and arsenic mobility in groundwater is often controlled by iron minerals. Recently, it has been shown that electron transfer and atom exchange between aqueous Fe(II) and iron oxides can enable structural incorporation of trace elements into iron oxides [1]. The structural incorporation of As(V) into magnetite has been observed during magnetite precipitation [2], and during the reductive transformation of lepidocrocite [2] and 2-line ferrihydrite [3] to magnetite. As(V) does not appear, however, to be incorporated into goethite and hematite in the presence of aqueous Fe(II) [4]. To better understand the controls on As(V) incorporation into iron oxides, we investigate whether the presence of As(V) inhibits atom exchange between aqueous Fe(II) and goethite or magnetite, and whether As(V) is incorporated into goethite, magnetite, and ferrihydrite in the presence of Fe(II).

Enriched Fe isotope experiments were used to investigate the extent of Fe atom exchange between aqueous Fe(II) and goethite in the presence of varying concentrations of As(V). Near-complete atom exchange between aqueous Fe(II) and goethite was observed at 1 mg/L As(V), whereas exchange was severely inhibited at the exceedingly high concentration of 20 mg/L As(V). Surface-adsorbed As was determined by phosphate extraction, and the remaining As was recovered by complete dissolution of the solid. As(V) remained adsorbed to the surface of the goethite rather than being incorporated, with 96% of the As(V) recoverable by a phosphate extraction on the time frame of near-complete atom exchange.

Additional experiments are underway to explore the fate of As(V) during Fe atom exchange between aqueous Fe(II) and magnetite and ferrihydrite. We hypothesize that atom exchange between aqueous Fe(II) and magnetite will occur in the presence of As(V) and that that As(V) may be incorporated into the magnetite structure, since As incorporation into magnetite has been observed in other systems [2,3].

[1] Frierdich *et al.* (2011) *Geology* **39**, 1083-1086. [2] Wang *et al.* (2011) *Environ. Sci. Technol.* **45**, 7258-7266. [3] Coker *et al.* (2006) *Environ. Sci. Technol.* **40**, 7745-7750. [4] Catalano *et al.* (2011) *Environ. Sci. Technol.* **45**, 8826-8833.

Tungsten isotopic evolution of the earliest terrestrial mantle

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Introduction

Recently, two reports of ε^{182}W>0 in Archean samples [1-2] challenge previous conceptions of a homogeneous W isotopic composition of the mantle. The removal of these positive anomalies by late accretion of a chondritic veneer [1] can be quickly refuted by comparison with lunar breccia siderophile element abundances which contain too low an accreted meteoritic component to affect a mantle-wide change in W isotope composition. Here, we present two sets of alternative models to interpret this incredible finding.

Results and Conclusions

Post core-formation mantle: Because D(metal-silicate) for W diminishes with increasing depth [3], the deep mantle has a higher W abundance, and a lower Hf/W ratio and consequently evolves a negative anomaly in ε^{182}W while the upper mantle evolves a positive ε^{182}W. Subsequent solid-state convection (4.55-2.8 Ga) mixes away the complementary ε^{182}W anomalies. This set of models predicts that the complementary negative anomalies in ε^{182}W should eventually be discovered in ancient magmatic rocks.

Hadean melting models: Tungsten is significantly more incompatible (like U, Th and Ba) than Hf, the latter being similar in compatibility to Nd and Sm. Our results show that extraction of low-degree partial melts (<2%) leaving a Hadean depleted mantle that can have Sm/Nd~20% higher than chondrites [4] also creates a $f_{Hf/W}$~2-3, sufficient to generate the anomalies observed [1,2] in the first 100 Ma of Earth history. These models increase Hf/W and Sm/Nd ratios in a correlated fashion explaining the tendency of positive anomalies of ε^{182}W to occur in rocks with positive ε^{142}Nd. Recycling of the complementary Hadean crust would result in negative anomalies, while partitioning of W into an enriched "hidden reservoir" [5] would not. Evidence from Hadean zircons indicates crust was preserved from 4.4 Ga onwards [6], too late to constrain ε^{182}W anomalies which are more challenging to create after the first 100 Ma. ^{142}Nd anomalies indicate a melting event around 35-75 Ma after solar system formation [4], the upper end of which is consistent with our models of Hf/W fractionation that also yield a depleted mantle composition consistent with DMM [7]. The presence of ε^{182}W anomalies in the Hadean mantle complicates the search for W isotopic evidence of core-mantle interaction, now predicted to be ε^{182}W~ -0.1 [8].

[1] Willbold et al. (2011) *Nature* **477**, 195-198. [2] Touboul et al. (2011) *Min. Mag.* **75**, 2026. [3] Righter (2011) *EPSL* **304**, 158-167. [4] Bennett et al. (2007) *Science* **318**, 1907-1910. [5] Boyet and Carlson (2005) *Science* **309**, 576-581. [6] Wilde et al. (2001) *Nature* **409**, 175-178. [7] Salters and Stracke (2004) *G-cubed* **5**, Q05004, doi:10.1029/2003GC000597. [8] Humayun (2011) *G-cubed* **12**, Q03007, doi:10.1029/2010GC003281.