

## Tungsten isotopic investigation of Eoarchean terrestrial rocks with implications for mantle evolution

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Young terrestrial rock samples exhibit a  $\epsilon^{182}\text{W}$  that is  $\sim 2\epsilon$  higher than that of chondrites. The  $^{182}\text{W}$  excess has been used to infer the timing of core-separation, by assuming that the  $\epsilon^{182}\text{W}$  for the samples are representative of those for the bulk silicate Earth at the time of core formation. However, this assumption may not be valid for the following two reasons. (i) Mixing of core material back into the mantle could change  $\epsilon^{182}\text{W}$  of the mantle with geological time. Indeed, a grain-boundary diffusion study [1] indicates that W mobility is high enough to allow significant core-mantle interaction, especially if material diffused into the lowermost mantle is swept into the mantle convection. (ii) The superchondritic  $^{142}\text{Nd}/^{144}\text{Nd}$  ratios for all terrestrial rocks analyzed so far suggest the presence of an early-formed enriched reservoir (EER) that has never participated in surface volcanism. If the hidden EER was formed during the lifetime of  $^{182}\text{Hf}$  (in the first  $\sim 60$  Myr of the solar system) as proposed by the  $^{142}\text{Nd}$ - $^{143}\text{Nd}$  isotope systematics [2], the EER will have lower  $\epsilon^{182}\text{W}$  relative to the known terrestrial rocks due to the high incompatibility of W relative to Hf during mantle melting.

To constrain W isotopic evolution of the Earth's mantle, we studied Eoarchean meta-igneous rocks from the Isua greenstone belt (3.8–3.7 Ga) and Acasta Gneiss Complex (4.0–3.6 Ga). The Isua rocks display a  $^{142}\text{Nd}$  excess of 11 ppm relative to modern upper mantle composition [3], suggesting the heterogeneity of the  $^{142}\text{Nd}/^{144}\text{Nd}$  within the early depleted reservoir (EDR) that is complementary to the EER. Our data reveal that  $\epsilon^{182}\text{W}$  in the analyzed samples are uniform within analytical uncertainties ( $\pm 0.3\epsilon$ ), and indistinguishable from the modern mantle signatures, suggesting that the  $\epsilon^{182}\text{W}$  of the upper mantle has not changed from the Eoarchean to the present. These results imply that the lowermost mantle involving W from the core has isolated from the mantle convective cycling and that a silicate fractionation causing the  $^{142}\text{Nd}/^{144}\text{Nd}$  heterogeneity within the EDR occurred after  $^{182}\text{Hf}$  became extinct.

[1] Hayden & Watson (2007) *Nature* **450**, 709–711. [2] Boyet & Carlson (2005) *Science* **309**, 576–581. [3] Caro *et al.* (2006) *GCA* **70**, 164–191.

## Controls on antimony and arsenic speciation via sorption and redox chemistry at the clay mineral – water interface

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Antimony (Sb) and arsenic (As), both toxic metalloids, pose a potential threat to aquatic systems and water quality throughout the world. The mobility of these metalloids is controlled to a large extent by adsorption and redox reactions at mineral surfaces, including Fe, Al and Mn oxides, and clay minerals, that find widespread occurrence in low-temperature settings. The extent of As and Sb adsorption depends on a number of variables including, oxidation state (+5/+3), physicochemical conditions, type of surface moieties available for reaction, and presence or absence of effective electron donor/acceptor species. Our primary motive in this study is to investigate the potential for heterogeneous redox in clay dominated systems with variable composition and at variable redox potential.

Batch measurements of the rate and extent of arsenic and antimony sorption to iron-rich nontronite clay (NAu-1) were coupled with spectroscopic analysis of the sorption products using X-ray absorption spectroscopy (XAS). Reduced and oxidized forms of nontronite clay were equilibrated with As(III/V), and Sb(III/V) solutions under anoxic conditions, with UV light excluded. Additional measurements were performed in the presence of soluble Fe(II). Synthetic hydrous Al oxide with As(III/V), Sb(III/V) adsorbed were examined as non-redox control samples. The extent of adsorption, speciation and local bonding environment of arsenic and antimony on iron rich nontronite clay will be discussed along with the significance for the environmental cycling of As and Sb.