Mixed mineralogical and biogeochemical controls on arsenic fate in diffusively controlled and physically complex media

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Manganese (Mn) and iron (Fe) oxides are ubiquitous minerals that occur under similar redox conditions in terrestrial systems and have high sorptive capacities for many trace metals, including arsenic (As). Although numerous studies have characterized the effects of As adsorption onto Fe and Mn oxides individually, the fate of arsenic within mixed systems representative of natural environments is unresolved. Here, we examine competitive retention of As on goethite and birnessite using a Donnan reactor, where each oxide is isolated by a semi-permeable membrane through which arsenic can migrate. To initiate the Donnan reactor experiments, As(III) is simultaneously added to both chambers. As(III) injected into the birnessite chamber is rapidly oxidized to As(V) and then slowly redistributes across both chambers, while that added to the goethite chamber undergoes rapid adsorption; oxidation of As(III) on goethite is then controlled by desorption and diffusion into the birnessite chamber. With increased reaction time, As(V) is generated and preferentially partitioned onto goethite at low As concentrations. To further explore the role of Fe and Mn oxides in controlling the fate and transport of arsenic, we investigate arsenic dynamics in an aerobic aggregate composed of ferrihydrite and birnessite coated quartz sand fused by an agarose polymer. Mn and Fe oxide coated sands, having pre-adsorbed As(V), are cast into cohesive spheres and inoculated with Shewanella sp. ANA-3, a bacterial strain capable of reducing As(V) and Mn and Fe oxides. Arsenic(III) produced by bacterial reduction of As(V) diffuses into the aggregate exterior (proximal to advecting, aerated solutes), where it is re-oxidized to As(V) by Mn-oxides; following oxidation, As(V) is repartitioned onto the Fe oxides. These results illustrate the dynamic interplay or biogeochemical transformation, physical heterogeneity of natural systems, and mixed sorbents on the fate of arsenic.

Distribution of Hf and W between metal and olivine phase in pallasites

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Hafnium-tungsten isotope systematics has been widely used to estimated the timing of metal/silicate segregation in the planetesimals (e.g. Lee and Halliday, 1996; Lee *et al.*, 2002; Kleine *et al.*, 2005). Despite the obvious success in obtaining the precise chronological information, cosmochemical meaning of the resulting Hf-W age is still unclear. To define the reliable Hf-W age data from the samples, great care must be given to minimize the contribution of secondary redistribution of W, because it is recognised that the distribution coefficient of W among the minerals is seriously dependent upon various conditions such as oxygen fugacity (f_{O2}), pressure, or matrix component (nbo). To achieve this, we have developed a new analytical technique utilizing a Ti:S femtosecond laser ablation-ICP-mass spectrometer. Laser ablation with the high energy irradiance achieved by the shorter pulse duration results in better ablation efficiency and higher ionization efficiency of analytes even in the metallic samples.

In this study, Hf and W abundances in olivine and metallic phases of two main group pallasite (Brenham and Esquel) have been measured. The resulting distribution coefficients of W ($D_W^{met/sil}$) for both the pallasite samples were unity, and this is consistent with the experimentally determined values by Jones and Drake (1998). These data suggested that the W was very weakly-siderophile element within the pallasite parent body. More importantly, Hf abundance in olivine was significantly lower than those for chondrites. This suggests that the Hf-W age would indicate the timing of depletion of Hf through a fractional crystallization process, rather than the timing of metal/silicate segregation. To unveil the Hf-W ages of multiple cosmochemical stages, *in situ* Hf and W abundance data among the minerals is highly desired. The number of meteorite analyses is increased, and the data such as the mineral boundaries will be expanded in the future.

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