Development of arsenic and iron biogeochemical gradient within constructed aggregate upon redox fluctuation

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Reduction of As(V) and Fe(III) are ubiquitous processes controlling the fate and transport of As in soils and sediments. However, the coupling of biological, chemical and physical processes that ultimately control As transport in soils is remains poorly understood. Soils consist of aggregates which provide a multitude of pore-domains that result in varying degrees of advective and diffusive solute transport. As a result, As and Fe redox processes likely vary on micron-scales. To resolve the role of soil physical structure on As migration in soils, we examined As elution in simulated preferential flow paths resulting from constructed aggregates. Spherical artificial aggregates were made with As(V)-bearing ferrihydrite-coated sand inoculated with *Shewanella* sp. ANA-3; anoxic or aerated solute flow around the aggregate (simulating preferential flow) was then induced within a flow cell. Our results show that extensive Fe(III) reduction accelerated As desorption from the exterior of aggregates under the anoxic condition. In contrast, As desorption declined under aerated flow as As(III) and rapidly oxidizing Fe(II) coprecipitated along the aggregate exteriors; a "protective barrier" formed along the advective (preferential) flow boundary limiting As transport despite anoxia within diffusively constrained aggregate interiors. However, the accumulation of As on aggregate exterior proximal to preferential flow paths under aerated conditions can lead to a pulse of arsenic release upon transition to anaerobic conditions through the soil system. Our study illustrates the duration of anoxic condition ultimately controls the extent of arsenic release; however, anaerobiosis within aggregate interiors under aerated flow can promote As transport by accumulating As along the transport front.

Temperature-pressure-volume equations of state of Au and Pt

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Temperature-pressure-volume (T-P-V) equations of state (EOSs) of standard materials, such as NaCl, MgO, Au, and Pt, are generally used to measure the pressure of the system concerned. However, there are large discrepancies between proposed pressure scales, especially at high temperatures and high pressures. For example, errors between Au, Pt, and MgO pressure scales reach more than 20 percent at 120 GPa and 2000 K. The aim of this study is to develop reliable pressure scales for both Au and Pt without relying on any pressure scale. Here we derive T-P-V EOSs of the two metals based on the combined use of the observed data from shock compression, volume thermal expansion at 0 GPa, and high temperature elasticity at 0 GPa from ultrasonic measurements.

The lattice thermal pressures at high temperatures have been estimated based on the Mie-Grüneisen relation with the Debye thermal model and the Vinet isothermal EOS. The electronic thermal pressure at high T's, previously estimated from first-principles electronic structure calculations using density functional theory by [1], have also been included in the present analysis. The Grüneisen constant γ is assumed to be independent of temperature, and its volume dependence is taken as $\gamma = \gamma_0 (V/V_0)^q$, in which q is a fitting constant.

Using the measured data described above, the EOS parameters are successfully optimized to be K_{0T} = 273 GPa, K'_{0T} = 5.2, γ_0 = 2.7, and q = 1.1 for Pt [2], and K'_{0T} = 6.0 and q = 1.6 with fixed K_{0T} = 167 GPa, γ_0 = 2.97 for Au. The agreement between the observed and calculated T-P-V data was very satisfactory over wide T and P ranges for both Au and Pt. We find, for each Au and Pt, the 300 K isotherm developed here agrees very well with the measured data by [3] based on the recalibrated ruby pressure scale in [3].

Based on simultaneous volume measurements of Au and MgO, and Pt and MgO, previously reported by [2, 4, 5], we find the present Au and Pt EOSs are both consistent with the MgO scale developed by MD simulation [6] over wide T and P ranges more than 2000 K and 100 GPa

[1] Tsuchiya & Kawamura (2002) *Phys. Rev*. B**66**, 094115. [2] Matsui *et al*. (2009) *J. Appl. Phys.* **105**, 013505. [3] Dewaele *et al.* (2004) *Phys. Rev*. B**70**, 094112. [4] Hirose et al. (2008) *Phys. Earth Planet. Inter.* **167**, 149. [5] Zha *et al*. (2008) *J. Appl. Phys.* **103**, 054908. [6] Matsui *et al*. (2000) *Am. Mineral*. **85**, 312.