

## Phase transformation of two-line ferrihydrite: Effects of pH, temperature, and adsorbed arsenate and molybdate

SOUMYA DAS<sup>1\*</sup>, M. JIM HENDRY<sup>1</sup>, JOSEPH ESSILFIE-DUGHAN<sup>1</sup>

<sup>1</sup>University of Saskatchewan, Geological Sciences  
sod671@mail.usask.ca (\* presenting author)  
jim.hendry@usask.ca  
joe377@mail.usask.ca

### Introduction

A dominant control on the mobility and speciation of many toxic elements from mining and milling operations is their adsorption onto the surface of iron oxy-hydroxides, of which two-line ferrihydrite (hereafter called ferrihydrite) is one of the most common and reactive. For example, tailings generated from uranium (U) mining and metallurgical operations are a potential source of As, Mo, Se, and Ra<sup>226</sup> (termed Elements of Concern; EOCs) to the geosphere and biosphere. Generally, these elements are removed from oxic, acidic leach solutions (pH ~1.5) in the U mill via neutralization with lime and co-precipitation with ferric iron. Ferrihydrite starts to precipitate at pH ~3.5-4 during this neutralization process, which ultimately increases the pH to ~9.5 in the tailings prior to discharge. The EOCs subsequently adsorb onto the ferrihydrite, which thus controls their mobility in the pore waters. Because ferrihydrite is metastable and can transform to more structurally ordered oxy-hydroxide phases such as goethite and, under certain geochemical conditions, hematite, this study was conducted to assess the ability of ferrihydrite to act as a long-term sink for As and Mo in U tailings bodies. The results will also be useful in determining the long-term stability of ferrihydrite in other mine environments.

### Materials and Methods

A comprehensive study was carried out to determine the rate of transformation of pure ferrihydrite (i.e., no adsorbed As or Mo) to goethite and hematite as a function of temperature (25, 50, 75, and 100°C) and pH (2, 7, and 10) via batch experiments. Subsequently, the impact of adsorbed arsenate and molybdate on the rate of ferrihydrite transformation was determined based on As/Fe (0.500-0.010) and Mo/Fe (1.000-0.010) molar ratios (to approximate elemental concentrations measured in the tailings) at pH ~10 and 75°C. These rates were extrapolated to the environmental conditions measured in the tailings (i.e., 1°C and pH=10) at Cameco Corporation's Deilmann Tailings Management Facility, Saskatchewan, Canada. Pure and transformed phases were characterized and quantified using XRD, XANES, AFM, SEM, BET, and Raman spectroscopy.

### Results and Discussion

The rate of transformation of pure ferrihydrite to hematite increased with increasing temperature at all pH values considered and followed first order reaction kinetics. In the case of As adsorbed to ferrihydrite, the rate of ferrihydrite transformation decreased by two orders of magnitude as the As/Fe ratio increased from 0.010 to 0.018. No transformation was observed at higher As/Fe ratios (0.050, 0.100, and 0.500). Calculations show that the rate of ferrihydrite transformation under *in situ* conditions (~1°C; pH ~10; As/Fe ratio >0.250) is negligible and thus the ferrihydrite should continue to act as a sink for As for at least 10,000 years. Results of the ferrihydrite-molybdate testing remain to be analyzed.

## Carbon solution and partitioning between metallic and silicate melts in a shallow magma ocean: implications for the origin and distribution of terrestrial carbon

RAJDEEP DASGUPTA<sup>1\*</sup>, HAN CHI<sup>1</sup>, NOBUMICHI SHIMIZU<sup>2</sup>, ANTONIO BUONO<sup>3,4</sup> AND DAVID WALKER<sup>3</sup>

<sup>1</sup>Rice University, Houston, TX, USA, (\*Rajdeep.Dasgupta@rice.edu)  
<sup>2</sup>Woods Hole Oceanographic Institution, Woods Hole, MA, USA  
<sup>3</sup>Columbia University, Palisades, NY, USA  
<sup>4</sup>Massachusetts Institute of Technology, Cambridge, MA, USA

Carbon in the Earth's mantle has critical influence on planetary geodynamics, chemical differentiation, long-term climate, and habitability. But how early did the bulk silicate Earth acquire its current inventory of carbon? Is the mantle carbon mostly recycled or primordial? Answering these questions requires knowledge of the element's fate during magma ocean processes and parameters such as carbon solubility and partitioning between metal and silicate during core formation are key.

Experiments were performed at 2-7 GPa, 2000-2100 °C on mixtures of silicates (tholeiitic basalt/ komatiite/ fertile peridotite) and Fe-Ni-Co-C-S mix contained in graphite or MgO capsules. All the runs produced immiscible Fe-rich metallic and silicate melts at  $f_{O_2}$  between IW-1.0 and IW-2.2. Carbon concentrations of basaltic glasses and non-glassy quenched silicate melts were determined using secondary ionization mass spectrometry (SIMS) and speciation of dissolved C-O-H volatiles in silicate glasses was constrained using Raman spectroscopy. Carbon contents of metallic melts were determined using both electron microprobe and SIMS. Our experiments indicate, that at reduced, core-forming, conditions, carbon in mafic-ultramafic magmas dissolves primarily as a hydrogenated species and its storage capacity remains low. The total C content in our reduced melts at graphite saturation increases with increasing melt depolymerization (NBO/T), consistent with a recent spectroscopic study [1]. Carbon behaves as a metal-loving element during core-mantle separation and  $D_C$  (metallic melt/ silicate melt) varies between ~3500 and  $\geq 100$  and increases with increasing pressure and decreases with increasing melt NBO/T.

Our data suggest that if only a trace amount of carbon (~730 ppm C; [2]) was available to participate in the early differentiation of Earth, most of it was partitioned to the core and no more than ~10-30% of the present-day mantle carbon budget (50-200 ppm CO<sub>2</sub>) can be derived from a magma ocean residual to core formation. With core formation removing most of the carbon initially retained in the terrestrial magma ocean, explanation of the modern Earth carbon inventory requires a later replenishment mechanism. Addition of volatile-rich, late veneer and inefficient core formation both remain viable mechanisms. Alternatively, carbon ingassing by magma ocean-atmosphere interaction, soon after core formation, may also make the Earth's primordial carbon inventory similar to that of the present-day budget.

[1] Mysen et al. (2009) *Geochimica et Cosmochimica Acta* **73**, 1696-1710. [2] McDonough (2003) *Treatise on Geochemistry* **2**, 547-568.