

## The influence of Aluminum on the partitioning of water between clinopyroxene and basaltic melt

J.A. O'LEARY<sup>1</sup>, G.A. GAETANI<sup>2</sup> AND E.H. HAURI<sup>1</sup>

<sup>1</sup>Department of Terrestrial Magnetism, Carnegie Institution of Washington, Washington DC, 20015 USA  
(oleary@dtm.ciw.edu, hauri@dtm.ciw.edu)

<sup>2</sup>Department of Geology & Geophysics, Woods Hole Oceanographic Institution, Woods Hole MA 02543 USA  
(ggaetani@whoi.edu)

The distribution of water between basaltic melt and nominally anhydrous minerals has implications for the transport and storage of water during peridotite melting. Although there is evidence that mineral-melt partitioning is effected by the aluminum content of the crystals [1, 2], experimental data are only available for a limited range of bulk compositions. To isolate the effect of clinopyroxene aluminum content on partitioning behavior we conducted high temperature hydrous melting experiments in aluminum-free and aluminum-bearing systems. Our results indicate that the capacity of clinopyroxene to incorporate hydroxyl through a substitution involving Mg vacancies is limited to ~300 ppm. For the same concentration of water dissolved in the melt, the water content of aluminum-bearing clinopyroxene is ~500 ppm. This indicates that approximately 40% of the hydroxyl is charge balanced by aluminum.

Experiments were carried out in a piston-cylinder device at 1.5 GPa, 1275 °C, with oxygen fugacity controlled at Ni-NiO using a solid buffer. Starting compositions consisted of either a natural basalt or a synthetic, aluminum-free basalt. Experiments were carried out with up to ~6 wt% H<sub>2</sub>O dissolved in the melt. The volatile content of each phase present in the experiments was determined *in situ* by SIMS.

Our experimental results suggest that the mechanism for incorporation of OH into pyroxene is strongly effected by the presence of aluminum. Al-bearing experiments have partition coefficients  $D_{\text{melt/cpx}} = .019-.036$ , in agreement with previous reports [1, 2]. Partition coefficients for Al-free composition experiments are much lower,  $D_{\text{melt/cpx}} = .006-.012$ . The water content of pyroxene in all Al-free composition experiments is the same within error,  $315 \pm 12$  ppm H<sub>2</sub>O, and is similar to water saturated Al-free pyroxene [3].

[1] Aubaud *et al.* (2004) *GRL*, V. 31, L20611, doi, 10.1029/2004GL021341. [2] Hauri *t al.* (2006) *EPSL* **248**, 715-734. [3] Rauch & Keppller (2002) *CMP* **143**, 525-536.

## Interactions of U(VI) with secondary mineralization products from the bioreduction of Fe(III) oxides

E.J. O'LOUGHLIN<sup>1\*</sup>, S.D. KELLY<sup>1</sup>, M.I. BOYANOV<sup>2</sup>  
AND K.M. KEMNER<sup>1</sup>

<sup>1</sup>Biosciences Division, Argonne National Laboratory, Argonne, IL, 60439, USA

(\*correspondence: oloughlin@anl.gov)  
(skelly@anl.gov, kemner@anl.gov)

<sup>2</sup>Faculty of Physics, University of Sofia, Sofia, 1000, Bulgaria  
(mboyanov@nd.edu)

### Introduction

Biogenic Fe(II) phases (magnetite, green rust, siderite, vivianite, etc.) provide a reservoir of reducing capacity in the subsurface that may contribute to the reduction of contaminants such as U(VI). In this study we examined the potential for reduction of U(VI) in the presence of biogenic green rust, (BioGR) biogenic magnetite (BioMAG), and biogenic siderite (BioSID) resulting from the bioreduction of Fe(III) oxides (lepidocrocite and ferrihydrite) by *Shewanella putrefaciens* CN32.

### Experimental Methodology

Suspensions of biogenic Fe(II) phases were pasteurized (70°C for 1 h) to eliminate the potential for microbial reduction of U(VI) and washed repeatedly to remove any soluble reductants. The resulting suspensions had initial total Fe(II) concentrations of 60 mM, 42 mM and 66 mM for BioGR, BioMAG, and BioSID, respectively. The suspensions were then spiked with a stock solution of uranyl chloride to achieve an initial U(VI) concentration of 500 µM.

### Discussion of Results

Within 48 h, the total solution-phase U(VI) concentrations decreased from 500 µM to 1.5 µM in the U-bioGR system, to 392 µM in the U-bioMAG system, and to 472 µM in the U-bioSID system, as determined by ICP-OES. Analysis of the samples by U L<sub>III</sub> X-ray absorption fine structure spectroscopy (XAFS) indicated that despite a stoichiometric excess of Fe(II), no more than 6% of U(VI) was reduced in the U-BioSID system, and no more than 22% of U(VI) was reduced in the U-BioMAG system. For comparison, in the U-BioGR system, no less than 80% of U(VI) was reduced to U(IV). Thus, differences in the reactivity of the different biogenic Fe(II) phases with respect to the reduction of U(VI) were substantial, with BioGR >> BioMAG > BioSID.