

Reduction of Cu(II) adsorbed to bacterial cells: A role for Fe(II)?

CHRISTOPHER J. DAUGHNEY^{1*}, PETER J. SWEDLUND²,
MAGALI MOREAU-FOURNIER³, SARAH L. HARMER⁴,
BERNT JOHANNESSEN⁵, RACHEL FRANZBLAU⁶
AND CHRISTOPHER G. WEISNER⁶

¹GNS Science, Lower Hutt, New Zealand (*correspondence:
c.daughney@gns.cri.nz)

²University of Auckland, Auckland, New Zealand,
(p.swedlund@auckland.ac.nz)

³GNS Science, Wairakei, New Zealand (m.moreau-
fournier@gns.cri.nz)

⁴Flinders University, Bedford Park, Australia,
(sarah.harmer@flinders.edu.au)

⁵Australian Synchrotron, Clayton, Australia,
(bernt.johannessen@synchrotron.org.au)

⁶University of Windsor, Windsor, Canada
(franzbl@uwindsor.ca, weisener@uwindsor.ca)

Laboratory experiments were performed to track the fate of dissolved Cu(II) and Fe at a fixed pH of 5.2 during the gradual, incremental oxidation of dissolved Fe(II) and precipitation of iron oxide in the presence of *Anoxybacillus flavithermus* cells. X-ray absorption spectra of wet pastes were collected at the Cu K-edge and the Fe K-edge at the Australian Synchrotron and at the Australian National Beamline Facility in Japan. The samples consisted of 3 ppm Cu(II) that had been allowed to equilibrate with the bacteria alone, abiotic iron oxide without bacteria, or the bacteria-iron oxide composites. Standards included aqueous solutions of Cu(II) perchlorate, Cu(II) formate and Cu(II) nitrile(tris)methylphosphonic acid, and powdered Cu₂O. Fe standards included aqueous solutions of Fe(II), Fe(II) citrate and Fe(II) phosphate, and powdered lepidocrocite and ferrihydrite. The EXAFS data for the bacteria-iron oxide composites showed that under the experimental conditions Cu in the solid phase was associated predominantly with carboxyl structures on the bacterial cell walls, not with bacterial phosphoryl structures or with binding sites on the iron oxide. These results are consistent with previous studies. The XANES data indicated that the solid phase Cu existed partially as Cu(I), with a ratio of Cu(I) to Cu(II) that was proportional to the concentration of solid phase Fe(II). Tests revealed that beam damage was negligible under the conditions employed. Hence, the occurrence of Cu(I) was not an artefact, and so we hypothesise that reduction to Cu(I) was facilitated by oxidation of Fe(II) that was co-adsorbed to the bacterial cells. This type of reaction that has direct relevance to natural environments, where bacteria and Fe(II) often coexist, and may play an important role in the transport of many different types of redox-sensitive contaminants. The immobilization of metal cations in bacteria-bearing settings should not be examined independently of progressive oxidation, hydrolysis and precipitation of iron.

MC-ICPMS and NRIXS: A Stereo View of Iron Isotopic Fractionation in Silicic Magmas

N. DAUPHAS¹, M. ROSKOSZ², M. TELUS³, M.Y. HU⁴, E.E. ALP⁴, F. MOYNIER⁵, C.K. SIO¹, F.L.H. TISSOT¹, F.Z. TENG⁶, D. NEUVILLE⁷, P.I. NABELEK⁸, P. CRADDOCK⁹,
L.A. GROAT¹⁰ AND J. ZHAO⁴

¹Origins Laboratory, The University of Chicago

²Université de Lille 1, France

³University of Hawaii at Manoa

⁴Argonne National Laboratory

⁵Washington University in St. Louis

⁶Dept. of Earth & Space Sciences, University of Washington

⁷Institut de Physique du Globe de Paris

⁸University of Missouri

⁹Schlumberger-Doll Research Center

¹⁰University of British Columbia

Silicic rocks show trends of increasing $\delta^{56}\text{Fe}$ values with increasing SiO₂ content [*e.g.*, 1-3]. These trends have been ascribed to Soret effect, fluid exsolution, and magmatic differentiation. To understand the cause of Fe isotopic variations in silicic magmas, we measured the Mg, Fe, Zn, and U isotopic compositions of a range of migmatites, granites, and pegmatites with well-characterized petrologic and geochemical contexts [3]. No clear positive correlation is found between the isotopic compositions of Mg, U and Fe, which rules out the process of Soret diffusion. Zinc can easily be mobilized by aqueous fluids as chloride complexes. Pegmatites and some granitic rocks with high $\delta^{56}\text{Fe}$ values also have high $\delta^{66}\text{Zn}$ values. However, some granites with high $\delta^{56}\text{Fe}$ values have unfractionated $\delta^{66}\text{Zn}$ values and were presumably poor in fluids (A-type granitoids). For these samples, iron isotopic fractionation during magma differentiation is the most likely interpretation. We used the technique of Nuclear Resonant Inelastic X-ray Spectroscopy at the Advanced Photon Source to measure the mean force constant of Fe in basalt, andesite, dacite, and rhyolite glasses. We find a sudden increase in the force constant of Fe²⁺ from dacite to rhyolite. The β -factors derived from these force constants [4,5] were used in a model of magma differentiation using Rhyolite-MELTS. The correlation between $\delta^{56}\text{Fe}$ and SiO₂ is well explained by magmatic differentiation.

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