

Sorption of iron from siderophore complexes by Mn oxides

O.W. DUCKWORTH^{1*}, J.R. BARGAR² AND G. SPOSITO³

¹Department of Soil Science, North Carolina State University, Raleigh, NC 27695-7619,

(*correspondence: owen_duckworth@ncsu.edu)

²Stanford Synchrotron Radiation Laboratory, 2575 Sand Hill Rd, Bldg 137, MS 69, Menlo Park, CA 94025 (bargar@slac.stanford.edu)

³Division of Ecosystem Science, University of California, Berkeley, CA 94720-3114 (gsposito@nature.berkeley.edu)

Siderophores are chelating agents produced by terrestrial and marine biota to increase the bioavailability of ferric iron [1]. Recent work has suggested that both aqueous and solid-phase Mn(III) may affect siderophore-mediated iron transport [2, 3], but little is known about the effects of manganese(III,IV) oxides. To probe the effects of layer type manganese oxides, which are a reactive component of soils and the oligotrophic marine water column [4], on the stability of aqueous Fe-siderophore complexes, the sorption of ferrioxamine B [Fe(III)HDFOB⁺, an Fe(III) chelate of the trihydroxamate siderophore desferrioxamine B (DFOB)] to two synthetic birnessites [layer type Mn(III,IV) oxides] and a biogenic birnessite produced by *Pseudomonas putida* was examined. The Mn(III,IV) oxides greatly reduced the aqueous concentration of Fe(III)HDFOB⁺ at pH 8. Fe K-edge EXAFS spectra suggest that the dominant fraction of Fe(III) associated with the Mn(IV) oxides is specifically adsorbed to the mineral structure at multiple sites, thus indicating that the Mn(IV) oxides displaced Fe(III) from the siderophore complex. These results indicate manganese oxides, including biominerals, may sequester iron from soluble ferric complexes, and thus we conclude that the sorption of iron-siderophore complexes may play a significant role in the bioavailability and biogeochemical cycling of iron in marine and terrestrial environments.

[1] Winkelmann, G. (1991) G. Winkelmann, Editor. CRC Press, Boca Raton. [2] Duckworth, O.W. and Sposito, G. (2005) *Environ. Sci. Technol.* **39**, 6037-6044. [3] Duckworth, O.W. and Sposito, G. *Environ. Sci. Technol.* **39**, 6045-6051. [4] Tebo, B.M. *et al.* (2004) *Ann. Rev. Earth Planet. Sci.* **32**, 287-328.

High-pressure phases in the MgO-FeO-Al₂O₃-SiO₂ system: Implications for the deep mantle

T.S. DUFFY^{1*}, A. KUBO², S. SHIEH³, S. DORFMAN¹ AND V. PRAKAPENKA²

¹Dept. of Geosciences, Princeton University, Princeton, NJ 08544, USA (*correspondence: duffy@princeton.edu)

²GSECARS, University of Chicago, Chicago, IL 60610, USA

³Dept. of Earth Sciences, U. Western Ontario, London, N6A 5B7 Canada

The discovery of the transition of MgSiO₃ from the perovskite (Pv) phase to the CaIrO₃-type (post-perovskite, pPv) structure is a key for understanding the Earth's deep mantle. FeO and Al₂O₃ are important components of the lower mantle and they can affect phase boundaries, equations of state, and other key properties. Using synchrotron x-ray diffraction techniques, we have examined perovskites and post-perovskites for selected compositions in the MgO-FeO-Al₂O₃-SiO₂ system over a wide pressure-temperature range.

For the MgO-Al₂O₃-SiO₂ system, powdered glasses with the bulk composition of X mol% MgSiO₃ and (1-X) mol% Al₂O₃ (X = 100, 95, 90, and 85) were used. *In situ* x-ray diffraction experiments at high pressures and temperatures were conducted at GSECARS, Advanced Photon Source. Our results demonstrate that Al₂O₃ incorporation into the pPv phase increases the transition pressure, transition width, unit cell volume, and decreases density, bulk modulus, and bulk sound velocity. The pPv phase transition in En95 composition, which is relevant to pyrolytic bulk composition, occurs at ~125 GPa at 2500 K, which corresponds to the condition at the top of D'' layer. The pressure interval for the pPv phase transition in En95 bulk composition is ~7 GPa corresponding to a thickness of ~120 km, which is inconsistent with seismic observation of sharp D'' discontinuity.

A series of experiments have also been carried out in the pyrope(Pyr)-almandine(Alm) system for compositions corresponding to Alm38, Alm54, Alm73, and Alm100. We synthesized perovskites in all compositions at 70-90 GPa and ~2000 K, including Alm100 for the first time. We also show that Alm38, Alm54, and Alm73 transform to the post-perovskite phase above 140 GPa. Our results show that perovskites and post-perovskites with a wide range of Al₂O₃ and FeO compositions could exist under deep Earth conditions.