Fe electron transfer and atom exchange at mineral/water interfaces

M. SCHERER*[1], D. LATTA[2], T. PASAKARNIS[1], A. NEUMANN[1], M. BARGER[1], K. ROSSO[3], AND C. JOHNSON[4]

[1]Civil and Environmental Engineering, University of Iowa, Iowa City, IA 52242(*correspondence: michelle-scherer@uiowa.edu)
[2] Molecular Environmental Science Group, Biosciences Division, Argonne National Laboratory, Argonne, IL 60439, USA
[3]Chemical and Materials Science Division, Pacific Northwest National Laboratory, Richland, Washington 99352
[4]Dept. of Geoscience, University of Wisconsin-Madison, Madison WI 53706

Electron and ion exchange reactions at mineral/water interfaces influence the composition of natural waters, the biogeochemical availability of nutrients, and the environmental fate of heavy metals and contaminants. A new conceptual model is emerging to describe the reaction of aqueous Fe(II) at the mineral/water interface that couples oxidation and reduction reactions between spatially separated surface sites connected through the bulk mineral via either electrical conduction, atom diffusion, both, or some other yet unknown mechanism [1, 2]. We are collaborating to combine ^{57}Fe Mössbauer spectroscopy, Fe isotope tracer experiments, and molecular modeling to investigate Fe electron transfer at mineral surfaces and the rates and mechanism of Fe atom exchange.

We are exploring these processes in commonly occurring Fe oxides and Fe-containing clay minerals over a range of environmentally relevant conditions. Here we provide a summary of what we have learned so far, as well as present new findings investigating whether cation substitution influences the rate of atom exchange, and whether similar reactions will occur in clay minerals, as well as between aqueous Fe(III) and Fe(II) containing minerals.

[1] Gorski and Scherer (2011) *Aquatic Redox Chemistry* **1071**, 315-343.
[2] Yanina and Rosso (2008) *Science* **320**, 218-222.

Effect of Ce(III) oxidation by Mn(IV) on its use as a paleo-redox proxy

JOHAN SCHIJF[1*] AND KATHLEEN S. MARSHALL[2]

[1]University of Maryland Center for Environmental Science, Chesapeake Biological Laboratory, Solomons, MD, USA, schijf@cbl.umces.edu (* presenting author)
[2]University of Maryland Center for Environmental Science, Chesapeake Biological Laboratory, Solomons, MD, USA, marshall@cbl.umces.edu

Research outline

Marine sedimentary cerium (Ce) anomalies are due to enhanced Ce sorption with respect to the strictly trivalent REEs as it is oxidized from Ce(III) to more reactive Ce(IV). They are often interpreted as indicative of oxidizing conditions, specifically the presence of free oxygen, in the bottom water of ancient ocean basins at the time of sediment deposition. Such an interpretation could be complicated if Ce(III) were oxidized in the absence of free oxygen, as has been shown to occur on the surface of manganese oxides. We performed sorption experiments under anaerobic conditions with yttrium and the REEs in 0.5 M NaCl on pure synthetic Fe(III) and Mn(IV) oxides, plus three synthetic ferromanganese oxides containing 25, 50, and 90 mol% Mn. All precipitates were found to be X-ray amorphous and to contain Mn(IV) only.

REE sorption on the pure Fe and Mn oxides is well described with a non-electrostatic surface complexation model (SCM) that accounts for the higher acidity of hydroxyl groups on the Mn oxide, for monodentate and bidentate binding of the REEs by these groups, and for the binding of REE–hydroxide complexes at elevated pH [1,2]. REE sorption on ferromanganese oxides is moreover adequately described with a linear combination of the pure Fe and Mn oxide SCMs that reflects the proportion of each phase in the mixture. A clear presence, respectively absence, of Ce anomalies indicates that Ce(III) is oxidized on Mn oxide at all experimental pH values (4–8), but never on Fe oxide. The extent of oxidation on ferromanganese oxides is similar to that on pure Mn oxide, even at the lowest Mn content.

Below pH ~ 5.5 the Ce anomaly in pure Mn oxides is independent of pH, suggesting that the oxidation reaction involves direct transfer of an electron from Ce(III) to Mn(IV). Above pH ~ 5.5 the Ce anomaly has a linear pH dependence and the oxidation reaction may involve the species $CeOH^{2+}$, or otherwise require the presence of H_2O or OH^-.

Conclusions

Laboratory experiments of REE sorption on pure Fe and Mn oxides and on ferromanganese oxides with a wide range of Mn contents, in 0.5 M NaCl at T = 25°C, demonstrate that Ce(III) is oxidized under anaerobic conditions at the Mn oxide surface and thus probably by Mn in ferromanganese oxides, not by Fe. Hence, marine sedimentary Ce anomalies are not a reliable proxy of the presence of free oxygen in the deep paleo-ocean wherever Mn oxides abound in the watercolumn or on the seafloor. At the very least, such records should be interpreted with appropriate caution.

[1] Schijf & Marshall (2011) *Marine Chemistry* **123**, 32-43.
[2] Marshall & Schijf (2012) *Chemical Geology*, in review.