

4.3.P12

Effect of desferrioxamine, ferrichrome and rhodotorulic acid on Pb(II) desorption from goethite

E.L. ANDER¹ AND W.E. DUBBIN²

¹ British Geological Survey, Keyworth, Nottingham NG12 5GG, UK

² Department of Mineralogy, The Natural History Museum, London SW7 5BD, UK (B.Dubbin@nhm.ac.uk)

Siderophores are low molecular weight organic molecules secreted by plants and micro-organisms in response to iron stress [1]. With stability constants commonly exceeding 10^{30} , siderophores are considered to have higher affinities for Fe(III) than for any other major or trace element dissolved in soil solution [2]. However, several siderophores have affinities for trace metals that approach those for Fe(III), and certain actinides form siderophore complexes of surprisingly high stability [3]. The purpose of this study was to examine the role of hydroxamate siderophores in controlling Pb sorption to an Fe(III) oxide adsorbent.

Goethite [α -FeOOH], prepared by standard methods and identified by X-ray diffraction, gave a specific surface of $36 \text{ m}^2 \text{ g}^{-1}$ as determined by nitrogen multipoint BET analysis. Adsorption experiments were performed aseptically using a batch method with a goethite concentration of 1.0 g l^{-1} and an ionic strength of 0.01 M NaClO_4 . Soluble Pb and Fe were measured between pH 3 and 8 by first adding Pb ($10 \text{ }\mu\text{M}$) and then siderophore (10 , 20 , or $40 \text{ }\mu\text{M}$) to the goethite suspension. Three hydroxamate siderophores were employed: desferrioxamine B (DFB), ferrichrome (FC), and rhodotorulic acid (RA). Following 20 hr reaction, Pb and Fe in solution were measured by ICP-MS and ICP-AES, respectively.

The efficacy of siderophore-mediated Pb desorption varied with siderophore type and generally increased with pH and siderophore/Pb molar ratio. Desferrioxamine B, at pH 6.5 and a DFB/Pb molar ratio of 4, solubilised nearly 25% of the total sorbed Pb. In the presence of $10 \text{ }\mu\text{M}$ FC, Pb adsorption largely mimicked that for the siderophore-free system, whereas significant amounts of Pb were desorbed with $20 \text{ }\mu\text{M}$ FC at pH > 5.5 . The dihydroxamate siderophore, RA, was the least effective Pb chelator, requiring $20 \text{ }\mu\text{M}$ to desorb detectable amounts of Pb.

References

- [1] Cheah S.F., Kraemer S.M., Cervini-Silva J, and Sposito G. (2003) *Chem. Geol.* **198**, 63-75.
- [2] Coccozza C., Tsao C.G., Cheah S.F., Kraemer S.M., Raymond K.N., Miano T.M., and Sposito G. (2002) *Geochim. Cosmochim. Acta* **66**, 431-438.
- [3] Kraemer S.M., Xu J., Raymond K.N., and Sposito G. (2002) *Environ. Sci. Technol.* **36**, 1287-1291.

4.3.P13

Controls on $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ of peat pore-water sulfate

M. NOVAK¹ AND M. A. VILE²

¹ Czech Geological Survey, Geologická 6, 152 00 Prague 5, Czech Republic

² Department of Ecology, Princeton University, NJ, USA

High atmospheric sulfur deposition minimizes the impact of climatic warming by decreasing the rates of methanogenesis in wetlands [1]. We have shown at a number of peatlands on the Northern Hemisphere that anaerobic carbon flow through sulfate reduction is greater than through methanogenesis [2]. Anaerobic bacterial sulfate reduction is known to discriminate against the heavy isotopes ^{18}O and ^{34}S . Therefore, an estimation of the net carbon mineralization flux via bacterial sulfate reduction could be based on a comparison between S and O isotope systematics of sulfate in wetland inputs and outputs. We have determined $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values in rainfall, surface bog water, 40-cm deep bog pore water and stream discharge at six Sphagnum peatlands in Ireland, Scotland, England and the Czech Republic. We hypothesized that at greater peat depths advancing dissimilatory bacterial reduction would leave residual sulfate progressively enriched in the heavy isotopes ^{18}O and ^{34}S . However, we found that the in residual sulfate was simultaneously enriched in ^{18}O and ^{34}S only in about 50 % of the observations ($n=45$). At some sites and times of the year, we found low- ^{18}O and low- ^{34}S sulfate. We suggest that two other enzymatically controlled processes in peat porewater can alter the isotope composition of sulfate: Upon depletion of the free sulfate pool, hydrolysis of low- ^{34}S ester sulfate (isotopically corresponding to rainfall) may occur, pushing down $\delta^{34}\text{S}$ value of porewater sulfate. The $\delta^{18}\text{O}$ values of porewater sulfate may be pushed down by an isotope exchange between low- ^{18}O water and sulfate. Such process is slow in abiotic environments, but can proceed rapidly during bacterial sulfate reduction [3]. Because ester cleavage and enzymatic O-isotope exchange between water and sulfate operate independently, the resulting $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values of porewater sulfate are not always positively correlated. Each step in the bacterial sulfate reduction pathway is reversible, so perhaps, water rapidly exchanges O with sulfite, which is then partly reoxidized. This mechanism, if confirmed, could provide a tool for the estimation of the amount of reoxidized S in wetlands and improve the calculation of anaerobic C mineralization via bacterial sulfate reduction.

References

- [1] Dise N.B., Verry E.S. (2001) *Biogeochem.*, **53**, 143-160.
- [2] Vile M.A., Bridgman S.D., Wieder R.K., Novak M. (2003) *Global Biogeochem. Cycles*, **17**, 1058.
- [3] Fritz P. et al. (1989) *Chem. Geol.* **79**, 99-105.