

Multisite Surface-Complexation of Zn and Cu on Goethite

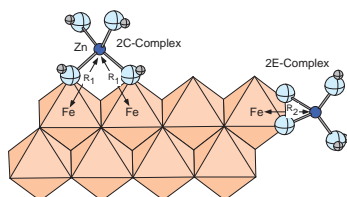
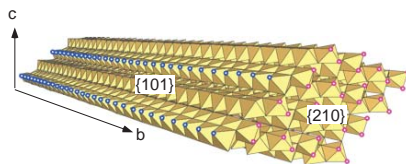
DAVID M SHERMAN*¹, DAVID MOORE

³School of Earth Sciences, University of Bristol, Bristol, BS8 1RJ,
UK dave.sherman@bris.ac.uk (* presenting author)

Goethite (α -FeOOH) is the paradigm mineral for the scavenging of metals in terrestrial environments. The structure of goethite is based on edge-sharing FeO₆ octahedra which form double chains along the **b**-direction (using space-group setting Pnma); the double chains are linked to each other via corner-sharing in the **a**- and **c**-directions. At the nano-scale, goethite forms long needles along the **b**-direction with the {101} surfaces being dominant (Fig 1). The {101} surfaces

have singly coordinated surface oxygens which can

complex to metals via the formation of a bidentate double corner-sharing (2C) complex. However, the goethite needles are terminated by a {210} surface; on this surface, Zn and Cu could bind by forming an edge-sharing 2E complex (Fig. 2). The {210} surfaces comprise only a few per-cent of the surface area of goethite but we can infer that the {210} surfaces would be much more reactive than the {101} surfaces. We hypothesise that sorption of metals such as Zn and Cu to goethite will first take place on the more reactive {210} surface. However, since this surface only comprises a few percent of the total surface area the sorption capacity of the {210} surface will be limited to ~0.01wt % Cu or Zn.



We have measured the sorption of Cu and Zn to goethite as a function of surface loading (0.008 to 0.8 wt. %). We find that our sorption edges can only be simultaneously modelled if we invoke several different surface

complexes. For both Cu and Zn, the strong edge-sharing 2E complex on the {210} surface dominates at loadings < 0.01 wt. %. The weaker double corner-sharing 2C complex on the {101} surface dominates at loadings near 0.1 wt. %. Above 0.1 wt. %, both Cu and Zn form polynuclear complexes. Previous EXAFS studies of Cu [1] and Zn [2], at surface loadings > 0.1 wt %, only resolved 2C and polynuclear complexes of Zn or Cu on the {101} surface. However, at more environmentally relevant surface loadings, the 2E complexes on the {210} surface should be dominant. More powerful synchrotron sources (e.g., I20 at Diamond) will enable us to confirm the existence of the 2E complexes, at least for Zn.

[1] Peacock, L., & Sherman, D. M. (2004). *Geochimica et Cosmochimica Acta*, 68(12), 2623-2637. [2] Trivedi, P., Axe, L., & Tyson, T. A. (2001). *Journal of Colloid and Interface Science*, 244(2), 230-238.

Mercury in precipitation, sediments, and largemouth bass in FL: Insights using mercury stable isotopes

LAURA S. SHERMAN^{1*} AND JOEL D. BLUM²

¹University of Michigan, Earth and Environmental Sciences, Ann Arbor, MI, USA, lsaylors@umich.edu (*presenting author)

²(Same as 1), jdblum@umich.edu

Mercury (Hg) concentrations in precipitation and fish are elevated across Florida (FL), U.S.A.[1] However, it is difficult to determine the specific biogeochemical pathways by which fish acquire Hg. Recent studies suggest that newly deposited Hg can be more bioavailable than Hg in sediments and that this Hg can rapidly enter aquatic food webs.[2] To gain insight into the sources of Hg to fish in FL, we analyzed Hg stable isotope ratios in precipitation, lake sediments, and largemouth bass collected across central FL.

We sampled surface sediments from freshwater lakes in central FL that are impacted by a mixture of local and regional Hg sources. These surface sediments displayed a wide range of $\delta^{202}\text{Hg}$ values from -1.19 to -0.46‰ (mean = -0.72‰, 1 s.d. = 0.24‰, n = 18) and did not display significant mass-independent fractionation (MIF). Largemouth bass collected from a subset of these lakes displayed a range of $\delta^{202}\text{Hg}$ values and significant positive MIF ($\Delta^{199}\text{Hg}$ up to 4.43‰). We suggest that this MIF is due to photochemical degradation of methylmercury[3] prior to uptake into the food web. By using an experimentally derived fractionation relationship[3], we estimated $\delta^{202}\text{Hg}$ values of the fish methylmercury prior to photochemical processing and uptake. These $\delta^{202}\text{Hg}$ values were consistently offset from those of the corresponding sediments by 0.50‰ (1 s.d. = 0.14‰, n = 8). In addition, $\delta^{202}\text{Hg}$ values in the sediments were found to be correlated with the calculated $\delta^{202}\text{Hg}$ values for the fish methylmercury ($r^2 = 0.47$). These data suggest that methylmercury in the fish originates in large part from Hg in the sediments, which represents a mixture of historic Hg and modern atmospheric Hg. Prior to uptake by fish, non-photochemical processes[4, 5] cause an increase in $\delta^{202}\text{Hg}$ of ~0.50‰ and photochemical demethylation causes further increases in $\delta^{202}\text{Hg}$ values as well as large increases in $\Delta^{199}\text{Hg}$ values.

To examine the impact of a single, isolated source of Hg deposition on these relationships, we collected precipitation samples, lake sediments, and largemouth bass near a large coal-fired power plant in Crystal River, FL. These precipitation samples were uniquely characterized by large negative $\delta^{202}\text{Hg}$ values (mean = -2.56‰, 1 s.d. = 1.10‰, n = 28).[6] However, we did not observe similarly negative $\delta^{202}\text{Hg}$ values in sediments or fish collected in the area. Instead, $\delta^{202}\text{Hg}$ values of sediments and fish from the Crystal River area were comparable to those of the other lakes and were similarly offset and correlated. If emissions from the power plant have been isotopically consistent through time, this suggests that these emissions are not more rapidly bioavailable and are instead mixed with Hg in sediments prior to uptake by largemouth bass.

[1] Hand and Friedemann (1990) Florida Department of Environmental Regulation Report, 57pp. [2] Harris et al. (2007) *PNAS* 104, 16586-16591. [3] Bergquist and Blum (2007) *Science* 318, 417-420. [4] Rodríguez-González et al. (2009) *Environ. Sci. Technol.* 43, 9183-9188. [5] Kritee et al. (2009) *Geo. Cosmo. Acta* 73, 1285-1296. [6] Sherman et al (2012) *Environ. Sci. Technol* 46, 382-390.