

Iron isotope fractionations under different diagenetic environments in lake sediments

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Elucidating Fe isotope fractionations during early diagenesis in modern sediments is important for our better understanding of iron isotope variations in ancient sedimentary rocks [1, 2]. Iron isotope compositions of sediments and porewaters sampled from Aha Lake (a high mineralized water system) and Hongfeng Lake (a mesotrophic water system) were primarily investigated to study iron isotope fractionations under different diagenetic environments.

Fe isotope compositions were performed on Nu HR MC-ICP-MS. Sediments collected from Aha Lake displayed significant negative $\delta^{56}\text{Fe}$ values relative to IRMM-014. From 1cm to 10cm depth, Fe isotope compositions of sediments became gradually lighter, ranging from -0.59‰ to -1.75‰. Porewaters varied in an opposite trend, increasing from -2.03‰ to 0.12‰. In case of Hongfeng Lake, $\delta^{56}\text{Fe}$ values of sediments are relatively constant with depth, being similar to the average of igneous rocks. The corresponding porewaters have lower $\delta^{56}\text{Fe}$ values, ranging from -0.57‰ to -0.31‰.

Dissimilatory Fe reduction and pyrite formation are reported to be important for Fe isotope fractionations during early diagenesis [1, 3]. There are abundant inputs of reactive iron in Aha Lake and the sulfate concentration is high. Dissimilatory Fe reduction bacteria were detected through the sediment core and the concentrations of pyrite and AVS were also high, Fe isotope fractionations here are considered to be dominated by similar Fe recycling processes. Besides, adsorption may also play an important role in decreasing $\delta^{56}\text{Fe}$ value of porewaters near the surface sediments [4, 5]. In Hongfeng Lake, phytoplankton die-offs are thought to be important contributions for sediments. The results imply that there is a big difference on mechanisms and pathways of Fe isotope fractionations under different diagenetic environments.

[1] Severmann *et al.* (2006) *GCA* **70**, 2006–2022. [2] Rouxel *et al.* (2005) *GCA* **68**, 2295–2311. [3] Fehr *et al.* (2008) *GCA* **72**, 807–826. [4] Teutsch *et al.* (2005) *GCA* **69**, 4175–4185. [5] Rouxel *et al.* (2008) *GCA* **72**, 3413–3430.

Structural study of aluminous goethite nano/micro particles

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Goethite is one of the most common Fe (III) (hydr)oxide minerals in soils. In many natural goethite samples, up to 33 mol% of the Fe appears to be replaced by Al substitution [1]. Maurice *et al.* demonstrated that increasing Al substitution (up to 8.8 mol%) not only reduces goethite unit cell dimensions but also results in decreasing mean particle length and aspect ratio, fewer domains, increasing structural order (determined by XRD) and increasing dissolution by aerobic *Pseudomonas mendocina var. bacteria* [2]. However, the exact nature of Al substitution and the effect of Al substitution on goethite crystal structure have not been determined. Specific questions include, for example, whether Al is uniformly distributed within the structure as substitutional defects, whether there are Al (hydr)oxide domains, and/or whether Al poisons growth by adsorbing to specific sites on the goethite surface as a particle grows.

In this study, Fe K edge extended x-ray absorption fine structure (EXAFS) spectroscopy and x-ray diffuse scattering with pair distribution function (PDF) analysis were conducted on well characterized aluminous goethite nano/micro particle samples with 0, 1.9, 4.2 and 8.8 mol% Al, respectively. Both EXAFS and PDF indicate that: (1) Al uniformly incorporated into the goethite crystal structure in all samples, with no separate Al (hydr)oxide phase observed; (2) the lattice parameter decreases with increasing Al incorporation, which is consistent with smaller Al atoms replacing Fe. EXAFS data demonstrate Al incorporation does not change the coordination environment of the three nearest O shells around Fe. The more distant Fe shells are significantly affected, however, consistent with the change in bond lengths around individual incorporated Al atoms. X-ray photoelectron spectroscopy (XPS) measurements are underway to examine whether the surface composition is different from the bulk in terms of Al content.

[1] Schwertmann U. (1984) *Clay Miner.* **19**, 9–19. [2] Maurice P.A. Lee Y.-T. & Hersman L.E. (2000) *Geochim. Cosmochim. Acta* **64**, 1363–1374.