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SPECIAL COLLECTION: NANOMINERALS AND MINERAL NANOPARTICLES

Study on nanophase iron oxyhydroxides in freshwater ferromanganese nodules from Green Bay, Lake Michigan, with implications for the adsorption of As and heavy metals

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Abstract

Nanophase Fe-oxyhydroxides in freshwater ferromanganese nodules (FFN) from Green Bay, Lake Michigan, and adsorbed arsenate have been investigated by X-ray powder diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), Z-contrast imaging, and ab initio calculations using the density functional theory (DFT). The samples from northern Green Bay can be divided into two types: Fe-Mn nodules and Fe-rich nodules. The manganese-bearing phases are todorokite, birnessite, and buserite. The iron-bearing phases are feroxyhyte, nanophase goethite, two-line ferrihydrite, and nanophase FeOOH with guyanaite structure. Z-contrast images of the Fe-oxyhydroxides show ordered FeOOH nano-domains with guyanaite structure intergrown with nanophase goethite. The FeOOH nanophase is a precursor to the goethite. Henceforth, we will refer to it as "proto-goethite." DFT calculations indicate that goethite is more stable than proto-goethite. Our results suggest that ordering between Fe and vacancies in octahedral sites result in the transformation from feroxyhyte to goethite through a proto-goethite intermediate phase. Combining Z-contrast images and TEM-EDS reveals that arsenate (AsO_4^{3-}) tetrahedra are preferentially adsorbed on the proto-goethite (001) surface via tridentate adsorption. Our study directly shows the atomic positions of Fe-oxyhydroxides with associated trace elements. The methods can be applied for identifying structures of nano-phases and adsorbed trace elements and heavy metals.

Keywords: XRD, HRTEM, Z-contrast imaging, ab initio, two-line ferrihydrite, proto-goethite, nanophase goethite, feroxyhyte, ferromanganese nodule, arsenic