

## Study on Nanophase Minerals and Their Associated Trace Elements in Freshwater Ferromanganese Nodules From Green Bay, Lake Michigan

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Freshwater ferromanganese nodules (FFN) from Green Bay, Lake Michigan have been investigated by X-ray powder diffraction (XRD), micro X-ray fluorescence (XRF), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and aberration-corrected scanning transmission electron microscopy (STEM). The samples can be divided into three types: Mn-rich nodules, Fe-Mn nodules, and Fe-rich nodules. The manganese-bearing phases are todorokite, birnessite, and busserite [1]. The iron-bearing phases are ferrihydrite, goethite, 2-line ferrihydrite, and proto-goethite (intermediate phase between ferrihydrite and goethite) [2].

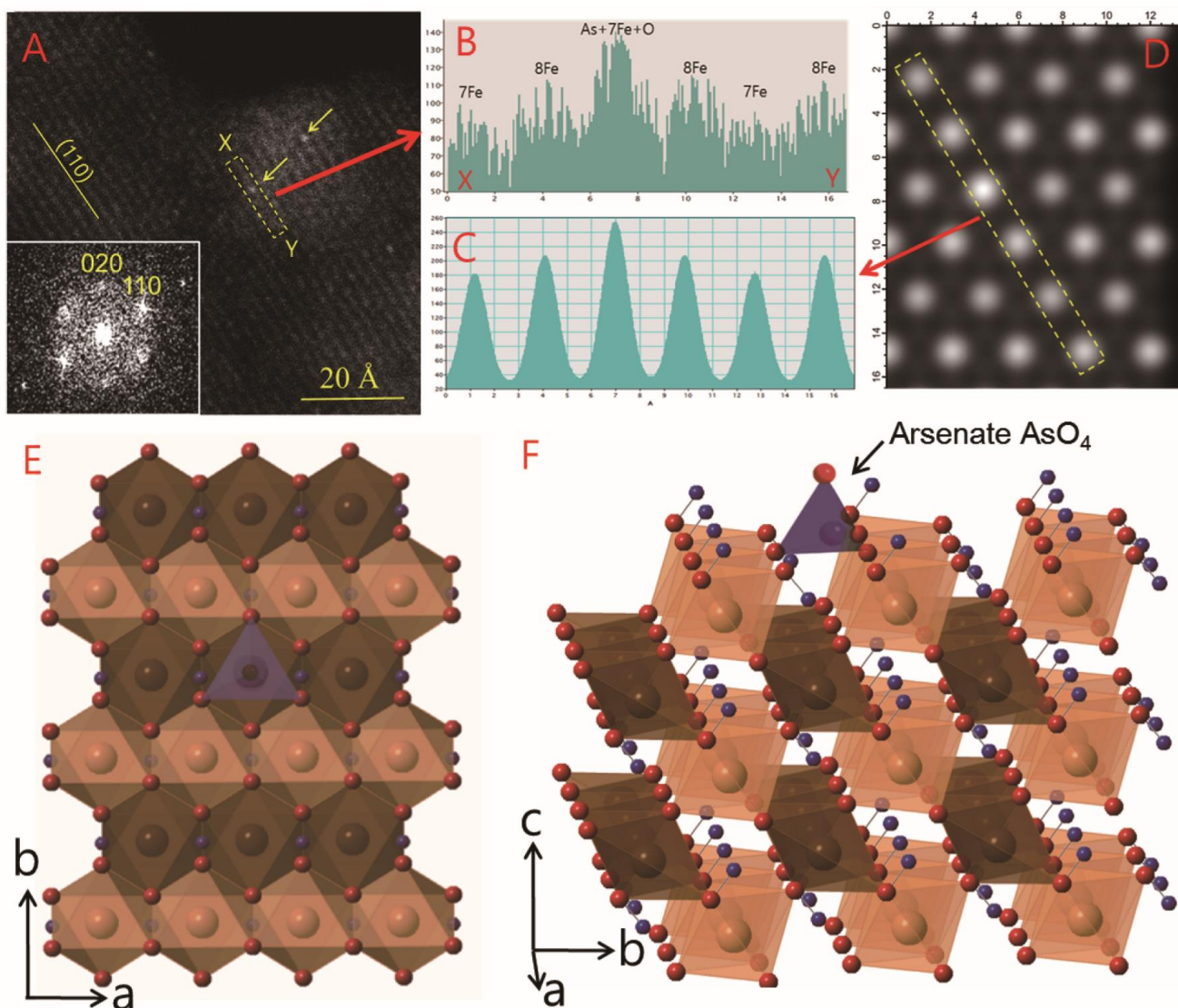
XRD patterns from a cross section of nodule suggest the transformation of birnessite to todorokite for Mn-rich nodule. TEM-EDS spectra show that todorokite is associated with Ba, Co, Ni, and Zn, birnessite with Ca and Na, and busserite with Ca. The todorokite has an average chemical formula of  $\text{Ba}^{2+}_{0.28}(\text{Zn}^{2+}_{0.14}\text{Co}^{3+}_{0.05}\text{Ni}^{2+}_{0.02})(\text{Mn}^{4+}_{4.99}\text{Mn}^{3+}_{0.82}\text{Fe}^{3+}_{0.12}\text{Co}^{3+}_{0.05}\text{Ni}^{2+}_{0.02})\text{O}_{12}\cdot n\text{H}_2\text{O}$ . Barium is the main cation in the structure tunnels of the todorokite. The average chemical formula of birnessite and busserite are  $\text{Na}^{+}_{0.14}\text{Ca}^{2+}_{0.19}(\text{Mn}^{4+}_{1.48}\text{Mn}^{3+}_{0.52})\text{O}_4\cdot n\text{H}_2\text{O}$ , and  $\text{Ca}^{2+}_{0.27}(\text{Mn}^{4+}_{1.46}\text{Mn}^{3+}_{0.54})\text{O}_4\cdot n\text{H}_2\text{O}$ , respectively.

For Fe-rich nodule, 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 ferrihydrite to goethite through a proto-goethite intermediate phase. Combining Z-contrast images and TEM-EDS reveals that arsenate ( $\text{AsO}_4^{3-}$ ) tetrahedra are preferentially adsorbed on the proto-goethite (001) surface via tridentate adsorption (Fig.1).

Most of the nodules have a concretionary structure of alternating Fe/Mn layers, commonly with a core of reddish feldspar containing hematite micro-crystals. Other cores are goethite, cristobalite, tridymite, hercynite, hematite-bearing quartz, coal, and chlorite-bearing rock fragments. The hexagonal or hexagonal-like structures of hematite micro-crystals and clay minerals in the cores may serve as heterogeneous nucleation sites for the Mn-oxides and Fe-oxyhydroxides. The alternating Fe/Mn layers of the FFN might be caused by oscillatory changes of redox conditions at the sediment-water interface due to water level changes [3].

### References:

- [1] Lee, S and Xu, H *Clays and Clay Minerals*, **64**, (2016), 488.
- [2] Lee *et al*, *American Mineralogist*, **101**, (2016) 1986.
- [3] The authors acknowledge funding from the NSF, US DOE, and NASA Astrobiology Institute.



**Figure 1.** (A) a [001]-zone-axis Z-contrast image of proto-goethite, bright spots are positions of Fe atom columns. Very bright spots are As atoms on the surface right above Fe; (B) the intensity profile of an outlined area from X to Y; (C) the intensity profile of simulated Z-contrast image; (D) a simulated Z-contrast image; (E-F) Polyhedral models showing arsenate adsorption on (001) surface of the proto-goethite.