

1 Research Highlight: Study on nanophase iron oxyhydroxides in freshwater ferromanganese
2 nodules from Green Bay, Lake Michigan by Seungyeol Lee, Zhizhang Shen, and Huifang Xu

3

4 Michael Schindler

5 Department of Earth Sciences

6 Laurentian University

7 Sudbury, ON, Canada

8 e-mail: mschindler@laurentian.ca

9

10 The study of Lee et al. (2016) examined the adsorption of arsenate on various Fe-hydroxides
11 with a combination of classical techniques (optical microscopy, Scanning Electron Microscopy),
12 High-resolution Transmission Electron microscopy (HR-TEM) and chemical modelling. The
13 results of their study may have an impact on future environmental studies as their applied
14 techniques allows the characterization of selective adsorption of contaminants on mineral
15 surfaces composed of multiple phases.

16 Iron-(hydr)oxide minerals are one of the most prominent groups of minerals in soils,
17 sediments and anthropogenic environments such as tailings and slag piles (Cornell and
18 Schwertmann 1996). Their large surface area and reactivity makes them effective sorbents for
19 many contaminants in the environment. This is especially the case with respect to the retention
20 of Arsenic by Fe-(hydr)oxides. Arsenic is highly toxic and its occurrence in sulfide bearing soils,
21 sediments and tailings results in environmental and health problems on the global scale
22 (Vaughan, 2006). The oxy-anion $(\text{AsO}_4)^{3-}$ has a high affinity to sorb on Fe-O surface
23 terminations and its mobility in soils, sediments and tailings is thus often controlled by the
24 presence of Fe-(hydr)oxides (e.g. Morin and Calas 1996). Not surprisingly, there has been
25 many studies on the adsorption behavior of $(\text{AsO}_4)^{3-}$ on Fe-(hydr)oxide surfaces in different
26 environments and under different pH and Eh settings. The most common analytical tools to

27 study the distribution and crystal-chemical environments of adsorbed Arsenate species on Fe-
28 (hydr)oxides have been synchrotron-based methods such as X-ray absorption spectroscopy, X-
29 ray fluorescence spectroscopy and X-ray diffraction. These methods allow the characterization
30 of the distribution and speciation of Arsenic on Fe-hydroxide surfaces at the lower to upper
31 micrometer scale (e.g. Singer et al. 2013). Rather than following this more or less conventional
32 approach, Lee et al. (2016) studied the adsorption of arsenate ions on complex Fe-rich nodules
33 with HR-TEM and chemical modelling. The results of their study are ground breaking in terms
34 how we study adsorption and transformation processes involving mineral surfaces and
35 contaminants in aqueous solution. The authors could show that areas composed of Fe-
36 hydroxides are not simply composed of the common phases ferrihydrite and goethite but are
37 rather a mixture of multiple low-crystalline nano-size Fe-hydroxide phases. Their detailed study
38 on the occurrence, chemical composition and intergrowth of Fe-(hydr)oxide phases in the
39 nodules enabled them to (a) develop a model for their transformation pathway and (b) resolve
40 the spatial relationship between their abundance and the chemical distribution of arsenate.
41 Impressive modified High-resolution TEM images (so called Z-contrast images) in combination
42 with chemical modelling allowed additionally the development of an atomic model for the
43 adsorption of the arsenate ion on one of Fe-hydroxide modifications. Although the visualization
44 of adsorbed ions on solid surfaces with HR-TEM is not new (e.g. Wang et al. 2004), it has been
45 never shown for contaminants adsorbed on mineral surfaces in the environment.

46 To conclude, the study by Lee et al. (2016) shows that a combination of HR-TEM with
47 chemical modelling allows (a) the identification of nano-size phases on the surface of minerals,
48 rocks and low-T precipitates, (b) the visualization of the distribution of contaminants on mineral
49 surfaces and (c) the identification of adsorption complexes between contaminants and mineral
50 surfaces. The results of their study may have an impact in the field of environmental sciences as
51 their approach will open new gateways to examine adsorption processes on surfaces composed

52 of multiple previously unknown nano-size phases with different surface structures and
53 adsorption properties.

54

55 **REFERENCES CITED**

56 Cornell, R.M.; Schwertmann, U. (1996) The iron oxides. Structure, properties, reactions,
57 occurrence and uses. VCH Verlagsgesellschaft mbH, D-69451: Weinheim, Germany.

58 Lee, S., Shen, Z. and Xu, H. (2016) Study on nanophase iron oxyhydroxides in freshwater
59 ferromanganese nodules from Green Bay, Lake Michigan. American Mineralogist.

60 Morin, G. and Calas, G (1996) Arsenic in Soils, Mine Tailings, and Former Industrial Sites.
61 Elements 2, 97-101.

62 Singer D.M., Fox P.M., Guo H., Marcu M.A. and Davis J.A. (2013) Sorption and redox reactions
63 of As(III) and As(V) within secondary mineral coatings on aquifer sediment grains.
64 Environmental Science & Technology 47, 11569-11576.

65 Vaughan, D.J. (1996) Arsenic. Elements 2, 71-75.

66 Wang, S., Borisevich, A.Y. Rashkeev, S.N. Glazoff, M.V Sohlberg, K, Pennycook, S.J and
67 Pantelides, S.T (2004) Dopants adsorbed as single atoms prevent degradation of
68 catalysts *Nature Materials* 3, 143-146.