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Environmentally important, poorly crystalline Fe/Mn hydrous oxides: Ferrihydrite and a possibly new vernadite-like mineral from the Clark Fork River Superfund Complex

MICHAEL F. HOCHELLA, JR.,[1,*] TAKESHI KASAMA,[2,†] ANDREW PUTNIS,[2] CHRISTINE V. PUTNIS,[2] AND JOHNNIE N. MOORE[3]

[1]Nanogeoscience and Technology Lab, Department of Geosciences, Virginia Tech, Blacksburg, Virginia 24061-0420, U.S.A.
[2]Institüt für Mineralogie and Interdisciplinary Centre for Electron Microscopy and Microanalysis, Universität Münster, Corrensstrasse 24, D-48149 Münster, Germany
[3]Department of Geology, University of Montana, Missoula, Montana 59812, U.S.A.

ABSTRACT

Ferrihydrite and a vernadite-like mineral, in samples collected from the riverbeds and floodplains of the river draining the largest mining-contaminated site in the United States (the Clark Fork River Superfund Complex), have been studied with transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) analysis. These poorly crystalline minerals are environmentally important in this system because contaminant heavy metals (As, Cu, Pb, and/or Zn) are always associated with them. Both two- and six-line ferrihydrite have been identified with selected-area electron diffraction. For the vernadite-like mineral, the two *d* values observed are approximately between 0.1 and 0.2 Å larger than those reported for vernadite, the Mn hydrous oxide that is thought to have a birnessite-like structure, but which is disordered in the layer stacking direction. In several field specimens, the ferrihydrite and vernadite-like minerals are intimately mixed on the nanoscale, but they also occur separately. It is suggested that the vernadite-like mineral, found separately, is produced biogenically by Mn-oxidizing bacteria, whereas the same mineral associated with ferrihydrite is produced abiotically via the heterogeneous oxidation of Mn^{2+}_{aq} initially on ferrihydrite surfaces. Evidence from this study demonstrates that the vernadite-like mineral sorbs considerably more toxic metals than does ferrihydrite, demonstrating that it may be a good candidate for application to heavy-metal sorption in permeable reactive barriers.