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

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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 Mn4+ 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.

INTRODUCTION

Environmental aspects of mineralogy encompass extraordinarily diverse subjects that are vitally important in several Earth sustainability issues (see, e.g., Banfield and Nealson 1997; Buseck et al. 2000; Hochella 2002). One such issue is the short- and long-term effects of mine wastes on the environment. Certainly, metals gained from the world’s mining industries are vital to all of us, but not without incurring an environmental price. Present and former mining sites, numbering in the hundreds of thousands the world over, release acid and metals into the surrounding environment when sulfides are involved (Moore and Luoma 1990). Metal release can occur and propagate as much as hundreds of kilometers down hydrologic gradient from the mining and mine-waste sites for months, years, or even decades to centuries. In the United States alone, 20,000 km of streams and rivers have been adversely affected by mining operations (DaRosa and Lyons 1997). Understanding these systems has become an important part of environmental mineralogy and geochemistry (e.g., Jambor and Blowes 1994; Alpers and Blowes 1994; Jambor et al. 2003).

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The mineralogy, water chemistry, and microbiology of mining and smelter wastes dictate the attenuation or release of toxic metals from any particular site, whether the wastes are in a tailings impoundment at the mine site or as river sediment hundreds of kilometers away. Within this construct, toxic metal association/transport and bioavailability then becomes the central issue. In terms of mineralogy, it is common in many mining waste scenarios for the formation of secondary minerals to be influenced by high solute concentrations of iron at low pH from the dissolution of pyrite and other Fe-containing sulfides. Mixing with oxygenated surface waters results in the formation of iron oxyhydroxides and hydrous oxides, such as goethite, lepidocrocite, and ferrihydrite, as well as hydroxysulfates such as schwertmannite and jarosite (e.g., Alpers et al. 1994; Schwertmann et al. 1995; Jambor and Blowes 1998). Although manganese is usually much less abundant, various manganese (hydr)oxides and hydrous oxides have also been observed (e.g., Lind and Hem 1993; Davis et al. 1993; Hudson-Edwards et al. 1996; Holmström and Öhlander 2001).

This article is part of a larger study in which we have assessed, using principally transmission electron microscopy (TEM) and electron diffraction, coupled with energy dispersive X-ray (EDX) analysis, the distribution and bioavailability of toxic heavy metals from mining-contaminated floodplains and riverbeds in and along Silver Bow Creek and the Clark Fork River, Montana, USA (Fig. 1).