Schwertmannite formation in acid mine drainage in NE Viet Nam

RETO GIERÉ[1*], THI BICH HOÀNG-HÒA[1], RAUL E. MARTINEZ[1], AND RICHARD WIRTH[2]

[1] Universität Freiburg, Geowissenschaften, 79104 Freiburg, Germany (giere@uni-freiburg.de)

[2] GeoForschungsZentrum Potsdam, Section 4.1, Telegrafenberg C120, 14473 Potsdam, Germany

The province of Quang Ninh in northeastern Viet Nam is one of the largest coal mining districts of the country, hosting reserves estimated at 10 Gt. The coal is mostly anthracite and is mined both in open pits and underground. This study focuses on acid mine drainage from the Coc Sau open-pit mine near the town of Cam Pha. The mine is approximately 3 km in diameter and has an orange-colored lake in the center, which drains through a tunnel into a creek. After flowing for ~4 km through the densely populated town, the acid mine waters discharge into the ocean.

The drainage waters have a pH of 2.4±0.4, a temperature of 30.3 ºC, and an Eh of 0.63±0.02 V under normal conditions, but after major rain storms the pH may be as high as 7.2±0.1, with an associated Eh of 0.29±0.05 V. The low-pH water contains the following major components (in mg/L): Fe = 46±18, SO_4^{2-} = 850±100, Al = 7±2, Mg = 76±3, and Ca = 66±18.

The creek bed and the contained pebbles are covered by a bright orange crust. This crust consists primarily of schwertmannite, quartz and sheet silicates (mostly kaolinite and illite) in the outer, highly porous part, whereas the inner part, directly on the substrate, consists of mostly ferrihydrite and sheet silicates. Scanning electron microscopy revealed the typical appearance of schwertmannite, i.e. small (usually <1µm across), spherical to ellipsoidal aggregates resembling sea urchins, and further suggested that schwertmannite also forms crusts on, and is intergrown with, sheet silicates. This suggestion was corroborated by transmission electron microscopy, which has shown that the schwertmannite aggregates in many cases contain a core of sheet silicate. Selected area electron diffraction allowed for unequivocal identification of schwertmannite, but the typical needle-like features (~200 nm long) are in many cases amorphous and therefore not whiskers.

In order to construct an Eh-pH diagram showing the stability fields for schwertmannite and ferrihydrite, we calculated the activity of the major chemical components using the extended Debye-Hückel equation. The ionic strength of the system (I = 0.016 M) was computed from the water conductivity [1]. Based on the available thermodynamic data, including a logK_{sp} value of 1.2±0.5 for schwertmannite with the ideal formula $FeO(OH)_{3/4}(SO_4)_{1/8}$ [2], a plot of Eh *vs*. pH was generated showing a schwertmannite field that is consistent with the observed conditions of our low-pH water samples. The diagram also coincides with an Eh-pH diagram constructed with a logK_{sp} of 0.88±0.01 for schwertmannite with the formula corresponding to $FeO(OH)_{0.738}(SO_4)_{0.131}$ [3].

At present, we do not understand yet, why the innermost part of the crust, directly on the substrate, consists mostly of ferrihydrite.

[1] Dittrich *et al.* (2004) *Geomicrobiol J* **21**, 45-53, 2004. [2] Majzlan *et al.* (2004) *Geochim Cosmochim Acta* **68**, 1049-1059. [3] Kawano and Tomita (2001) *Am Mineral* **86**, 1156-1165.

Structural and chemical studies of the pyrite (001) surface

B. GILBERT[1,*], P. J. ENG[2], D. SINGER[1], J. F. BANFIELD[3] AND G. A. WAYCHUNAS[1]

[1]Lawrence Berkeley National Laboratory, Earth Sciences Division, Berkeley, USA, bgilbert@lbl.gov, gawaychunas@lbl.gov. (* presenting author)

[2]University of Chicago, Chicago, USA, eng@cars.uchicago.edu

[3]University of California – Berkeley, Dept. Earth & Planetary Science, Berkeley, USA, jbanfield@berkeley.edu.

Pyrite, FeS_2, is a widespread and important sulfide mineral. Pyrite is thermodynamically stable under reducing conditions and in saturated sediments provides surfaces for the adsorption of aqueous species. When exposed to oxidizing environments, for example through mining activities, pyrite oxidation leads to the generation of low pH solutions termed acid mine drainage (AMD). The impact of AMD on environmental health is a global concern.

Detailed understanding of the reactivity of pyrite surfaces requires knowledge of their atomic structure under relevant conditions. Many groups have studied the surface chemistry of pristine and oxidized pyrite surfaces but the structure of a hydrated surface has never been experimentally determined. We have employed the crystal truncation rod (CTR) method and complementary surface-sensitive techniques in order to determine the structure of the water—pyrite (001) interface and to establish how adsorbates interact with this surface.

We developed an anaerobic chemical–mechanical polishing method that creates low-roughness pyrite (001) surfaces shown by atomic force microscopy (AFM) to be dominated by irregularly shaped (001) terraces. We studied the structure of the hydrated pyrite (001) surface using the CTR method, obtaining reproducible results from three crystals. Optimal fitting of the CTR data requires the incorporation of two structurally distinct termination surfaces that differ in the coverage, and likely the chemical speciation, of surface sulfur atoms. In each case, surface iron atoms and disulfur groups are significantly displaced from bulk positions.

The adsorption of aqueous metal ions provides a complementary approach for assessing the chemical speciation of sites on the (001) surface. We observed modulation in the CTR scattering patterns following exposure to Fe^{3+} and Pb^{2+} ions, confirming that the termination surface is accessible and chemically reactive. Grazing incidence extended X-ray absorption fine structure (EXAFS) studies of surface-adsorbed Pb^{2+} revealed at least two near-neighbor distances consistent with a fraction of lead atoms adsorbing via inner-shell interactions with surface sulfur sites.