Early-stage phase transformation and growth of iron oxyhydroxides during neutralization of simulated acid mine drainage

MENGQIANG ZHU[1*], BENJAMIN LEGG [2], HENGZHONG ZHANG[2], BENJAMIN GILBERT[1], YANG REN[3], JILLIAN F. BANFIELD[1,2] AND GLENN A. WAYCHUNAS[1]

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

[2]University of California, Earth and Planetary Science, Berkeley, CA, USA, jbanfield@berkeley.edu;

[3]Argonne National Laboratory, Advanced Photon Source, Argonne, IL, USA, ren@aps.anl.gov

Metal and coal mines produce iron-rich sulfuric acid solutions that contain a broad range of toxic elements [1]. These solutions, referred to as acid mine drainage (AMD), adversely affect environmental quality. When AMD mixes with neutral water bodies, such as in rivers or during wetland treatment, interacts with rock surfaces, or reacts with lime during remediation, neutralization occurs. As a result, ferric iron (Fe^{3+}) hydrolyzes and precipitates as Fe oxyhydroxide nanoparticles, such as ferrihydrite and schwertmannite. However, the formation pathways of these nanoparticles are relatively unknown largely due to their rapid formation rates and low abundances of initially-formed species. In this study, we used *in situ* time-resolved synchrotron radiation X-ray diffraction (XRD), quick-scanning extended X-ray absorption fine structure (QEXAFs) and UV-Vis spectroscopic techniques to study the products formed initially ($2 < t < 60$ minutes) when ferric iron sulfate solutions ($[Fe^{3+}] = 0.2$ M) are partially neutralized ($[HCO_3^-]/[Fe^{3+}] < 3$) by addition of $NaHCO_3$.

When $[HCO_3^-]/[Fe^{3+}] = 0.6$ (initial pH ~ 2.2), the only particles formed were ferrihydrite-like clusters that were stable throughout the duration of the experiment. When $[HCO_3^-]/[Fe^{3+}] = 1$ (initial pH ~ 2.5), the ferrihydrite-like molecular clusters formed initially but mostly disappeared and were replaced by schwertmannite. Schwertmannite and larger ferrihydrite particles formed immediately when $[HCO_3^-]/[Fe^{3+}] = 2$ (initial pH ~ 2.7), but the ferrihydrite particles completely disappeared and were replaced by schwertmannite. The schwertmannite particle size increased with reaction time, and extensive particle aggregation occurred.

The ferrihydrite-like cluster is very intriguing and its structure deserves further characterization. The data are consistent with Fe_{13} having Baker-Figgis δ-keggin structure, i.e., the motif in the ferrihydrite structure proposed by Michel et al. [2]. The existence of the cluster may result from sulfate binding on its surface, preventing the cluster from growing into larger ferrihydrite particles.

In conclusion, the results suggest that particular molecular clusters and small nanoparticles may be important, early-formed components of natural acidic solutions.

[1] Evangelou & Zhang (1995) *Crit. Rev. Environ. Sci. Technol.* **25**, 141-199.
[2] Michel et al. (2007) *Science* **316**, 1726-1728.

XPS study of bioleached arsenopyrite by *Acidithiobacillus ferrooxidans*

TINGTING ZHU[1*], XIANCAI LU[1], RUCHENG WANG[1], AND JIANJUN LU[1]

[1]School of Earth Sciences and Engineering, Nanjing University, Nanjing, China, ttzhu.nju@gmail.com (* presenting author)

Arsenopyrite (FeAsS) is a commonly discarded sulfide mineral in mining wastes. The arsenic release from it due to oxidation can cause serious environment contamination in mines. It has been well proved previously that microorganisms can remarkably accelerate the oxidation of arsenopyrite. However, the detailed oxidation mechanism is still unclear. This study on surface chemistry of bioleached arsenopyrite may cast insights into it.

In our experiments, the arsenopyrite obtained from a W-Sn deposit and a strain of *Acidithiobacillus ferrooxidans* isolated from the acid mine drainage in Tongling, eastern China, were used. The sterilized 9K culture with an adjusted Fe^{2+} concentration of 16 mM was poured into 6 flasks and then divided into two groups. Three flasks were inoculated with *Acidithiobacillus ferrooxidans* and the other three were only abiotic. Arsenopyrite particles were dropped into flasks simultaneously, and then extracted after 4 days, 7 days and 10 days, respectively. The reacted samples were freeze-dried in vacuum and ready for SEM observation and XPS analysis.

Several types of secondary mineral, such as elemental sulfur and scorodite, can be observed on the surface of 4 days-biooxidized arsenopyrite. However, native sulfur diminished gradually as bio-oxidation continuing and finally disappeared on the 10 days-biooxidized surface. The XPS depth profiles show that the altered layer of biooxidized arsenopyrite is much thicker than that of abiotic case. In addition, the contents of Fe(III), As(V) and sulfate in surface layer of bio-oxidized arsenopyrite are all higher than those of abiotically oxidized sample. The oxidation progress varies with the elements in both experimental systems. In the biotic system, the oxidized sequence is in the order of As, S, and then Fe, whereas in the abiotic system Fe is preferentially oxidized than As and S. In the depth profile of altered layer of each systems, a transition depth can be identified, where the contents of As, S and Fe change sharply. This depth of bio-oxidized arsenopyrite is about 450 nm, and that of abiotically oxidized one is around 30 nm. The change of Fe speciation in depth profile reveals that *A. ferrooxidans* initially breaks Fe(II)-AsS to form Fe(III)-AsS and a small quantity of Fe(III)-OH, and at a very late stage a trace fraction transform into Fe(III)-SO. For As-oxide, As(III)-O dominates on the bio-oxidized surface while As(I)-O prevails on the abiotically oxidized one. The contents of S^0 and S_n^{2-} of abioticaly oxidized surface keep stable as depth increase, while those of bio-oxidized surface show a significant increase from 500 nm to 1000 nm, which is consistent to the observed emergence and dis-appearance of native sulfur. It is proposed that native sulfur is only an intermediate product during microbial oxidation.

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