Utilizing µXRF and EXAFS to map arsenic speciation and distribution in fine-grained mine wastes: implications for arsenic bioaccessibility

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The legacy of the 19th-20th century California gold rush has left numerous abandoned mining areas enriched with arsenic (As), a known carcinogen. Recent studies have focused on the bioaccessibility and bulk As speciation of mine wastes [1]; however, there has been less focus on mechanism(s) that control arsenic bioaccessibility over time, including physical weathering. In addition, micro-X-ray fluorescence maps have been used to determine As oxidation state localization in many organic systems including soil [2] and rice roots [3], but few have mapped the distribution of arsenic species in mine waste particles.

µXRF maps were collected on 30 µm thin sections of size-fractionated mine wastes from the Empire Mine (Grass Valley, CA, USA); extended X-ray absorption fine structure (EXAFS) spectra of the dry mine waste samples were measured to determine their initial arsenic speciation. Combining principal component analysis, linear combination fitting (LCF), and XANES fitting, arsenic speciation maps frequently identified encapsulated arsenopyrite microprecipitates and homogenously distributed As(V) species sorbed on iron (hydr)oxide-rich particle surfaces.

To simulate physical weathering, mine waste samples were pulverized in a mechanical shatterbox fitted with an alumina ceramic ring and puck. *In vitro* simulated gastric fluid extraction (SGF) was performed on triplicate sets of each sample, unground and ground, the arsenic concentration of the supernatant was measured using ICP-OES and EXAFS were collected for the exposed samples. EXAFS analysis shows a decrease in arsenopyrite and an increase in sorbed As(V) species. The magnitude of speciation change becomes amplified proportional to the initial particle size as the mine waste particles are grounded indicating the increased dissolution of arsenopyrite and resorption of As(V).

[1] Kim *et al.* (2014) Aeolian Research **14**, 85-96. [2] Masue-Slowey *et al.* (2011) Environ. Sci. Technol. **45**, 582-588. [3] Seyfferth *et al.* (2010) Environ. Sci. Technol. **44**, 8108-8113