

The Role of Iron in the Reduced Bioavailability of Arsenic in Soil

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ABSTRACT

Arsenic (As) is a naturally occurring element in soil and often the key chemical of concern at former mines in the California Mother Lode Region. Risk based screening levels are often below the naturally occurring background concentrations of As in soil. These screening levels assume 100% bioavailability, which can be greatly affected by the association of As with other elements. Iron(Fe)-bearing minerals are known to bind As and reduce its bioavailability; however the mechanism is not completely understood. The soils in the Mother Lode Region are relatively high in Fe, ranging from 2-10%. Total As in soils collected from the Empire Mine State Historic Park ranged from 16 to 9,700 mg/kg. Bulk soil samples were sieved to <250µm, the fraction that adheres to skin and is most likely to be ingested by humans. The mass of the <250µm fraction averaged 17.4% of the bulk sample (pre-sieved <6mm). *In vitro* bioaccessible As (IVBA As), a surrogate for *in vivo* bioavailable As, in the <250µm fraction ranged from 1-44%. The spatial association between As and Fe was visualized utilizing QEMSCAN that provides quantitative chemical and mineralogical data at the 2.5µm pixel scale. Polished sections of mine waste rock analyzed by QEMSCAN demonstrated variable As content in hydrous Fe-oxide rims on weathered sulfide minerals. Further analysis, using a variety of synchrotron-based x-ray techniques, mapped the various oxidation states of As and Fe in these samples. Similar analysis of the <250µm fraction soil samples should provide useful information on the effect of Fe content and speciation on bioavailability of As in mining environments.



Figure 1: Sample Collection: A) Field activities were performed by DTSC in conjunction with USGS at the Empire Mine State Historic Park in Nevada County, California. B) Samples were field sieved to reduce the volume of soil collected. Sample locations were chosen based on total and IVBA arsenic results from a previous sampling event. C) Twenty-five individual soil samples, totaling 2593 pounds, were collected.

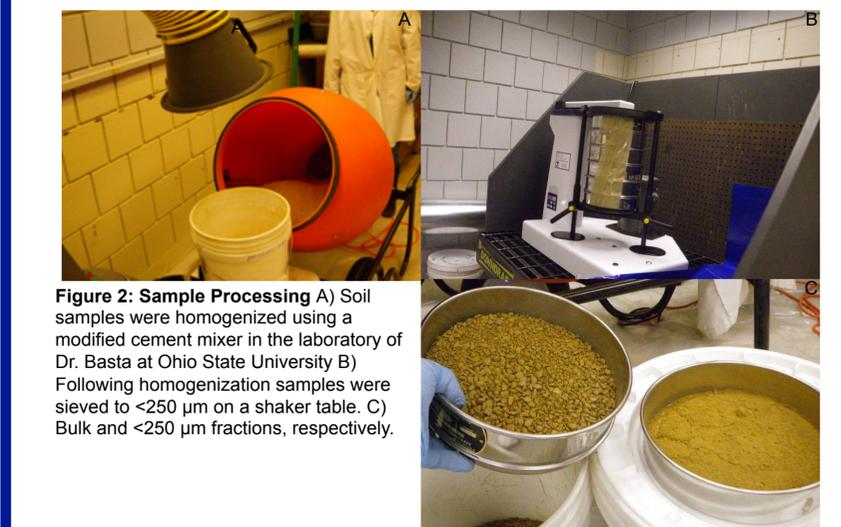
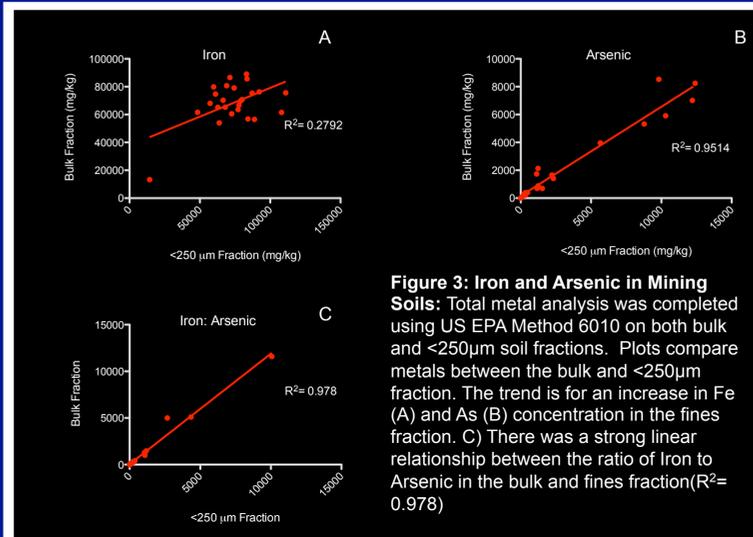


Figure 2: Sample Processing A) Soil samples were homogenized using a modified cement mixer in the laboratory of Dr. Basta at Ohio State University B) Following homogenization samples were sieved to <250 µm on a shaker table. C) Bulk and <250 µm fractions, respectively.

MINING SOILS

Metals in Bulk and <250µm Soil Fractions



Arsenic *in vitro* Bioaccessibility

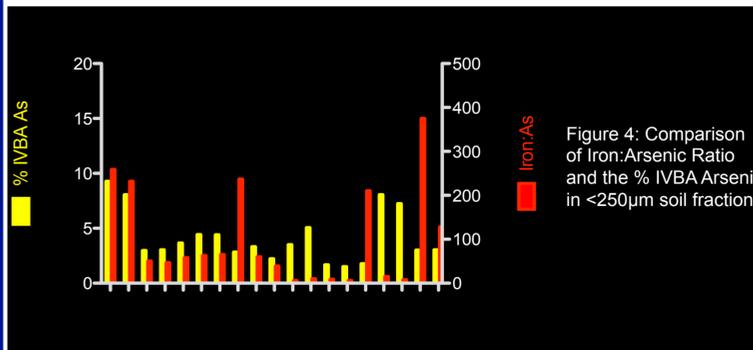
In vitro Gastrointestinal Method:

Gastric Phase

- 0.1M NaCl, 1% Pepsin
- 1:150 soil:solution ratio
- Manual adjustment with HCl to pH 1.8 with constant stirring for 1 hr.

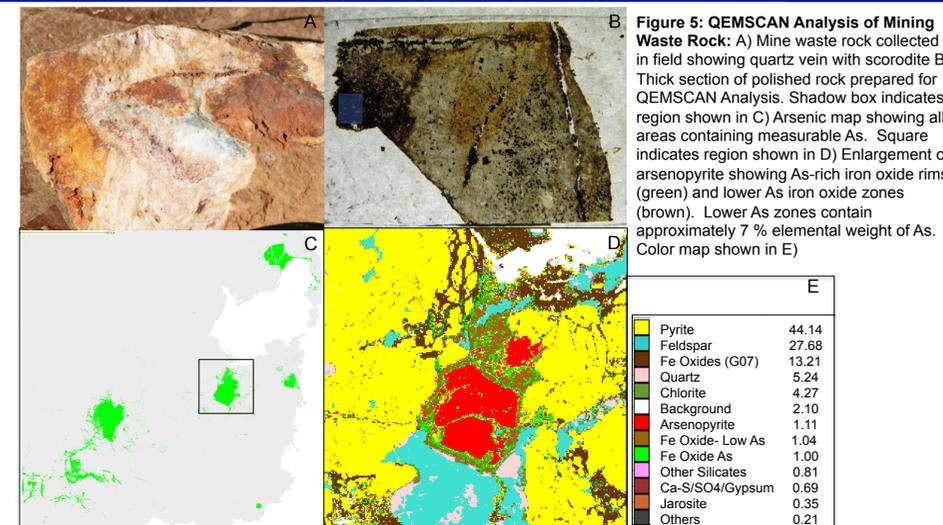
Intestinal Phase

- 0.563 g Bile, Pancreatin added
- Manual adjustment with Na_2CO_3 to pH 6.1 with constant stirring for 2 hrs.



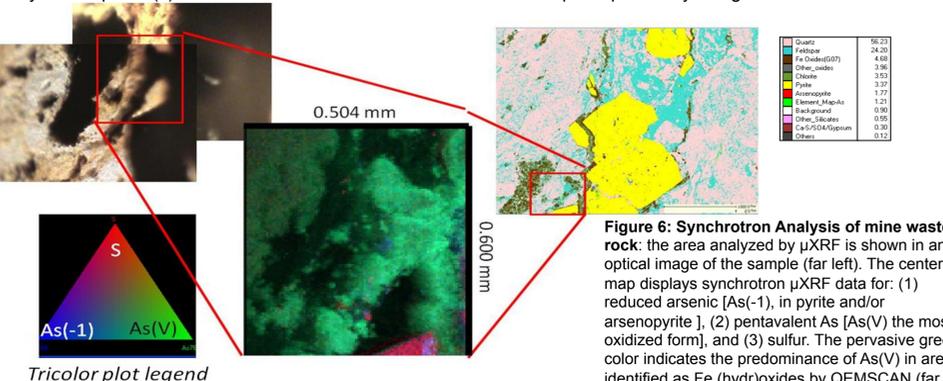
MINING WASTE ROCK

QEMSCAN Analysis



Synchrotron Analysis

Dr. Foster with USGS analyzed the polished sections using micro x-ray fluorescence (μXRF) and micro x-ray absorption spectroscopy (μXAS) at the Stanford Synchrotron Radiation Lightsource (SSRL). SSRL operates at a voltage of 3.0 GeV and 200-100 mAmp $\mu\text{-XRF}$ is used to map the distribution of multiple elements and/or multiple oxidation states of a single element; this information can be displayed in single element maps or as multiple element overlays, in which each element is represented by a color. $\mu\text{-XAS}$ is used to determine more specific chemical information about a single volume of the sample that is defined by the current beam size and penetration depth (this volume is represented by a point on the 2-d maps). Usually the identity of the mineral(s) or poorly-crystalline phase(s) in which arsenic is hosted can be determined quite specifically using this information.



SUMMARY

Arsenic-Bearing Minerals in Empire Mine Waste Rock

Primary Mineral	Wt. % Arsenic	Secondary Mineral	Wt. % Arsenic
Arsenopyrite FeAsS	37-44%	Scorodite $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$	32.5% (stoichiometric)
Arsenian Pyrite Fe(S,As)_2	<0.05 to 3.5%	Kaňkite $\text{FeAsO}_4 \cdot 3.5\text{H}_2\text{O}$	29.1% (stoichiometric)
		Goethite FeOOH	~10 to ~25%
		Ferrihydrite $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$	~2 to ~11%

What's Next?

Relative Bioavailability *in vivo* Studies
Scheduled to begin in May 2011



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