



# Kinetics of Inorganic Arsenic Contamination

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The rate of release of aqueous arsenic from common primary source minerals in rocks and soils has been quantified experimentally, yielding rate equations that can be used in computer modeling of arsenic contamination in surface and subsurface waters. Arsenopyrite, rather than pyrite, has been found to release aqueous arsenic the most rapidly.

## **Project Summary**

Pyrite and arsenopyrite are the most abundant arsenic (As)-bearing minerals in the crust, making them important natural primary sources of As release to waters and soils. Although the kinetics of aqueous pyrite oxidation are well known, those of arsenopyrite are not. Determining the kinetic rate laws for arsenopyrite will allow their use in computer models to predict the release rates of As from rocks and soils, and to model the downstream migration of As in surface and subsurface waters, particularly those waters impacted by mine tailings.

A high flow-rate batch reactor was used to measure rates of inorganic arsenopyrite oxidation in 0.01 M NaCl aqueous solutions as a function of pH, oxidant concentration and temperature. Natural arsenopyrite crystals were ground, sieved, and cleaned ultrasonically and chemically to produce fresh, bulk grain surfaces free of fine mineral powder for the rate measurements. The initial rate method was used to determine reaction rate order dependencies on pH (from 2-5) and oxidant concentrations ( $O_{2(aq)}$ ,  $Fe^{3+}$ ). B.E.T surface area measurements of the grains were used to calculate specific rate constants, and temperature dependence of the rates were measured over the range 10-40°C.

For systems in which ferric ion is initially absent, the specific rate law at 25°C is:

$$R_{sp} = -k (O_2)^{0.33} (H^+)^{0.27}$$

where dissolved oxygen and proton concentrations are expressed in molar units, the specific rate in units of moles arsenopyrite  $m^{-2} s^{-1}$ , and the rate constant is  $10^{6.11} \text{ moles}^{0.5} L^{0.5} m^{-2} s^{-1}$ .

Arsenopyrite oxidation by aqueous ferric iron is significantly faster and shows a first-order dependence

on  $Fe^{3+}$  concentration. Arsenopyrite oxidation by aqueous  $O_2$  and  $Fe^{3+}$  under these conditions is nearly three orders of magnitude faster than pyrite oxidation, indicating that arsenopyrite will release As even faster in rocks with high pyrite/arsenopyrite ratios.

In the absence of initial ferric iron, the release of As into solution is non-stoichiometric, with about half of it apparently remaining behind with sulfur on mineral surfaces. The presence of initial ferric iron or pH values above 4.5 cause As release to become stoichiometric. This behavior suggests that ferric iron either inhibits As retention on arsenopyrite surfaces or rapidly oxidizes As to a more mobile aqueous species.

## **Publications**

McKibben, M.A., Tallant, B.A., and Del Angel Jozi K., Kinetics of aqueous arsenic release from sulfide minerals, Geological Society of America Abstracts with Programs, Vol. 37, No. 7, Oct. 2005, 1 (abstract)

Tallant, B.A. and McKibben, M.A., Arsenic Mineral Kinetics: Arsenopyrite Oxidation, Geochimica et Cosmochimica Acta, Volume 69, Issue 10, Supplement 1, p. 820., May 2005, 1 (abstract)

Tallant, B.A., Kinetic Rate of Arsenopyrite Dissolution by Oxygen in Low Temperature, Low pH Solutions, M.Sc Thesis, June 2005, U C Riverside, 204 pp.

## **Professional Presentations**

McKibben, Michael A., Tallant, Bryan A., and Del Angel Jozi K., Kinetics of aqueous arsenic release from sulfide minerals, Geological Society of America Annual Meeting, Salt Lake City, UT, Oct. 2005

Tallant, B.A. and McKibben, M.A., Arsenic Mineral Kinetics: Arsenopyrite Oxidation, Goldschmidt Geochemistry Conference, Moscow, ID, May 2005