

OCCURRENCE AND MICRO-DISTRIBUTION OF ARSENIC IN PYRITE

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Redox reactions involving pyrite or iron oxyhydroxides derived from pyrite oxidation, are important sources and sinks of arsenic in the environment. This paper reports on the abundance and micro-scale distribution of arsenic in selected arsenic-rich pyrite samples. The overall compositional range for arsenic is about 0 to 10 weight percent, based on the highest concentrations obtained in individual electron microprobe spot analyses and selected results from the literature. The grain-scale compositional range for sedimentary pyrites is similar to that of pyrite in hydrothermal ore deposits (Fig. 1). The range for sedimentary pyrite includes the following new determinations: 1) the Mississippian Marshall Sandstone of southeastern Michigan (0 to 8.5 wt.% As); 2) arsenic-rich coal of the Warrior Basin, Alabama (0 to 4.9 wt. %); and 3) pyrite in about 10 other U.S. coals, none of which exceed the range for the Warrior Basin (Kolker and Koeppen, 1998, Kolker et al., 1998, Kolker et al., 1999). Arsenic enrichment in Warrior Basin coals, and other highly metal-enriched coals, is likely the result of hydrothermal processes (Goldhaber et al., this meeting; Ding et al., 1999), but these pyrites are considered “sedimentary” for purposes of this comparison. The compositional range for hydrothermal pyrites is based on a selected compilation of results from the literature. The most arsenic-rich determination for hydrothermal pyrite is a sample in the Bulldog Mountain vein system of the Creede Mining District, Colorado, having arsenic contents ranging from 1.3 to 9.97 weight (Plumlee, 1989). Co-existing marcasite is also arsenic-rich (0.48 to 1.19 wt. % As).

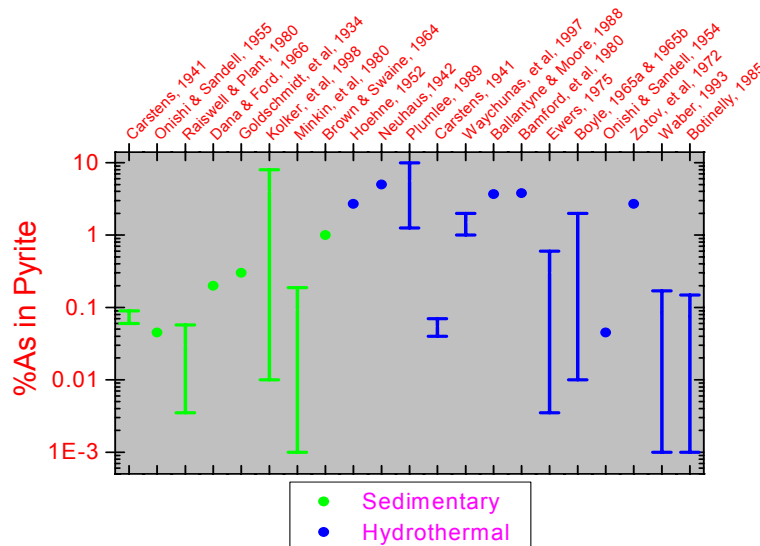


Figure 1. Plot of arsenic compositional range in pyrite (in weight percent) for selected sedimentary and hydrothermal pyrites, based on literature compilation (Nordstrom, in prep.).

Microanalysis confirms that arsenic-rich pyrite does not contain inclusions of arsenopyrite (FeAsS). The micro-scale compositional range for arsenic in pyrite exceeds the maximum arsenic contents (about 5 wt. % As) reported in earlier compilations for pyrite separates (Fleischer, 1955). Similar compositional ranges for sedimentary and hydrothermal pyrite suggest a limit at about 10 weight percent, to the extent that arsenic solid solution can occur. Chalcophile elements such as Ni, Cu, Zn, Co, and Pb also substitute in pyrite. High concentrations of these elements do not necessarily correspond to areas with the highest arsenic contents, as arsenic substitutes for sulfur, whereas Co and Ni substitute for iron (Table 1).

Table 1. Representative electron microprobe analyses of pyrite in southeastern Michigan samples of Marshall Sandstone (1-4, 6-8) and Michigan Formation (5).

Element	1	2	3	4	5	6	7	8
	<u>Weight Percent</u>							
S	47.26	50.94	50.67	52.04	51.48	49.20	51.66	50.07
Fe	44.52	45.99	34.06	47.53	46.63	45.56	46.27	46.28
Co	0.04	0.25	2.99	d.l.	d.l.	0.03	0.11	0.01
Ni	0.06	0.12	9.57	d.l.	d.l.	d.l.	0.36	d.l.
Cu	0.01	0.01	0.33	d.l.	0.01	0.03	0.09	d.l.
Zn	d.l.	0.01	d.l.	d.l.	d.l.	0.02	0.01	d.l.
As	7.08	2.00	1.68	0.02	2.12	5.96	1.31	4.43
Se	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.
Cd	0.02	0.01	d.l.	0.02	d.l.	d.l.	d.l.	d.l.
Pb	0.02	d.l.	0.57	d.l.	d.l.	n.d.	n.d.	n.d.
Total	99.02	99.33	99.87	99.61	100.24	100.80	99.81	100.80

1 - 2 = Core samples, Lapeer County LP-1 test well, 266.5' depth.

3 - 5 = Core samples, Huron County H15-D test well, 237.5', 153.0', 69.0', respectively.

6 - 8 = Well cuttings, Tuscola County BC 97C well, 230-235', 235-240', 230-235', respectively.

d.l = below detection limit (0.04 wt. % for Co, 0.01 wt. % for other elements; results for Co are background-subtracted); n.d = not determined.

Elemental mapping of pyrite grains by wavelength-dispersive spectroscopy, using an electron microprobe, delineates arsenic-rich and arsenic-poor internal domains, and provides textural information on arsenic uptake during diagenesis and hydrothermal alteration. These textures also allow us to better understand pyrite behavior in the environment. In southeastern Michigan, arsenic contents up to about 300 µg/L are present in various wells, primarily those completed in the Marshall Sandstone, which locally contains authigenic pyrite cement. Arsenic-rich pyrite occurs as overgrowths on arsenic-poor framboids that have in turn been incorporated into an arsenic-poor (≤ 0.1 wt. % As) pyrite host (Fig. 2). Arsenic is also present (up to 0.80 wt. %) in iron-oxyhydroxides in till fragments derived from Marshall Sandstone bedrock. Together, these provide two widespread natural sources of arsenic that may allow it to be incorporated into ground water during oxidation of bedrock aquifers, reduction of glacial aquifers, and progressive weathering of un-oxidized material in tills.

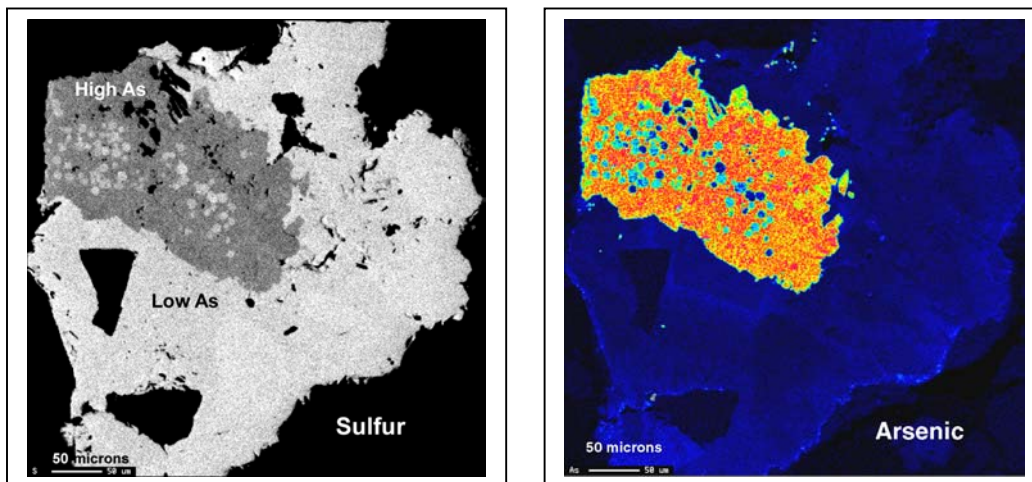


Figure 2. Wavelength dispersive spectrometric elemental maps for sulfur (left) and arsenic (right) in authigenic pyrite cement, Marshall Sandstone, southeastern Michigan. Maps show 3 generations of pyrite: 1) early-formed arsenic-poor framboids contained in arsenic-rich zone; 2) zone of arsenic-rich pyrite (6 to 7 wt. % As), and; 3) arsenic-poor host of pyrite 1) and 2).

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