Speciation of Arsenic in Pyrite by Micro-X-ray Absorption Fine-Structure Spectroscopy (XAFS)

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INTRODUCTION

Pyrite (FeS2) often contains variable levels of arsenic, regardless of the environment of formation. Arsenian pyrite has been reported in coals, sediments and ore deposits. Arsenian pyrite having As concentrations of up to 10 wt % in sedimentary rocks (Kolker et al. 1997), about 10 wt% in gold deposits (Fleet et al. 1993), 12 wt % in a refractory gold ore (Paktunc et al. 2006) and 20 wt % in a Carlin-type gold deposit in Nevada (Reich et al. 2005) have been reported. Arsenian pyrite is the carrier of gold in hydrothermal Carlin-type gold deposits, and gold concentrations of up to 0.9 wt % have been reported (Reich et al. 2005; Paktunc et al. 2006). In general, high Au concentrations correlate with As-rich zones in pyrite (Paktunc et al. 2006).

Pyrite often ends up in mining and metallurgical wastes as an unwanted mineral and consititutes one of the primary sources of As in the wastes. Arsenic can be readily released to the environment due to rapid oxidative dissolution of host pyrite under atmospheric conditions. Pyrite is also the primary source of arsenic in emissions and dust resulting from combustion of bituminous coals.

Despite the importance of arsenian pyrite as a primary source of anthropogenic arsenic in the environment and its economic significance as the primary carrier of gold in Carlin-type gold deposits, our understanding of the nature of arsenic in pyrite is limited. There are few papers dealing with the mode of occurrence of arsenic by bulk XAFS in a limited number of pyrite-bearing samples. The present study documents the analysis of pyrite particles displaying different morphologies and a range of arsenic and gold concentrations to determine the nature and speciation of arsenic.

METHODOLOGY

Micro-XAFS analyses were performed at the PNC-CAT's undulator beamline (20-ID) of the Advanced Photon Source (APS), Argonne, IL, USA. A Si (111) monochromator was used and the harmonics rejection was achieved by the Kirkpatrick-Baez mirrors. The beam was focused to 7 µm vertical and 6 µm horizontal on the sample with the help of the Kirkpatrick-Baez mirrors. The mineral grains that are greater than 50 µm in polished sections were located under the beam using a binocular microscope. Inclusion-rich samples were placed under the beam by scanning the area at 5 to 6 µm steps and producing As and Fe fluorescence maps of the area. Four scans were collected on each grain in fluorescence mode using a diode detector and a multi-element Ge detector. XANES (X-ray Absorption Near-Edge Structure) spectra were collected at 0.2 to 0.7 eV steps from 11847 to 11897 eV and EXAFS (Extended XAFS) spectra at 1.1 to 5.7 eV steps from 11897 to 12719 eV.

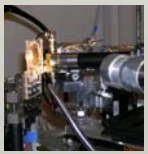


Table 1. Description and chemical composition of pyrite grains analysed by micro-XAFS

SNo	Morphological features	As (wt %) avg±sd	n	range
109	semi-massive	0.92±0.54	6	0.22-1.73
110	framboidal	0.12±0.26	6	<0.64
111	inclusion-rich	4.40±0.28	6	3.92-4.69
113	inclusion-rich	0.23±0.26	6	0.02-0.64
114	semi-massive	1.05±2.44	6	0.01-6.03
119	semi-massive	0.85±0.59	7	0.03-1.46
121	semi-massive	1.54±1.78	6	<4.04
207	inclusion-rich	0.60±0.27	7	0.16-1.01
209	semi-massive	0.31±0.28	6	<0.73
212	massive	nd	8	<0.01
213	semi-massive	0.04±0.05	7	<0.12
214	inclusion-rich	0.27±0.04	6	0.23-0.32
215	massive	0.51±0.28	7	0.24-0.99
217	semi-massive	0.03±0.03	7	<0.08
218	massive	1.63±0.28	7	1.06-1.85

avg: average; sd: standard deviation; n: number of anayses; nd: analysed but not detected (i.e. below the electron microprobe detection limit of 0.01 wt%).

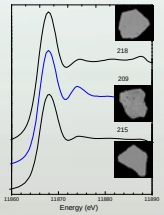
Micro-XANES

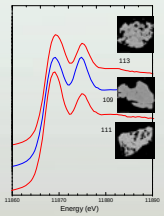
With the exception of spectra from pyrite grains 215 and 218, the results indicate the presence of two As species. The prominent peak occurring at about 11868 eV is close to the As K-edge position in arsenopyrite and suggests a valence state of -1. The second peak occurring at about 11874 eV indicates a valence state of +5. Judging from the peak heights, the amount of As^{5+} species in pyrite is highly variable.

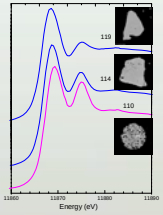
Massive pyrite grains (i.e. 215 and 218) appear to be devoid of the higher energy peak at 11874 eV. Massive pyrite grain 212, however, has a significant proportion of As^{5+} species in addition to As^{1-}. This massive pyrite grain is different from the other two (i.e. 215, 218) in terms of As concentrations. Whereas massive pyrite grains 215 and 218 contain average As concentrations of 0.51 and 1.63 wt%, the one (i.e. 212) possessing high As^{5+} has less than 0.01 wt% As.

The presence of variable proportions of As^{5+} species in pyrite is attributed to oxidation of arsenic exposed on the surfaces of pyrite. This is in part supported by the finding that coarse-grained massive pyrite type having the smallest surface area per unit is essentially composed of As^{1-} species.

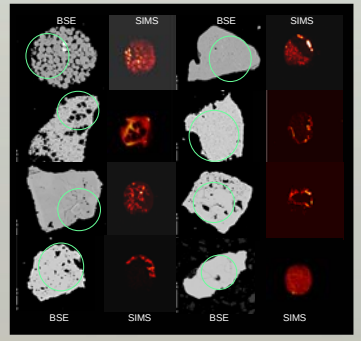
Although the presence of the oxidizied As species complicates XAFS analysis and interpretations, based on XANES spectra and preliminary examination of EXAFS, there do not appear to be significant differences in the As speciation among pyrite grains possessing different morphologies and As concentrations.

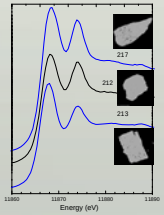


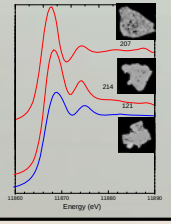




Backscattered electron (BSE) images of pyrite particles with corresponding Secondary Ion Mass Spectrometry (SIMS) ion images (^{75}As). Circles are 20 µm in diameter and outline the areas from which the SIMS images are obtained

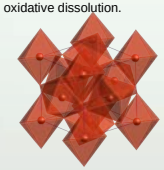


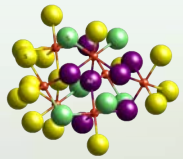




Micro-EXAFS

EXAFS analysis of the massive pyrite grain, 218, indicated that As-Fe interatomic distances are 2.33 Å and 3.50 Å and the central As atom is surrounded by 3 As atoms at 3.24 Å, suggesting that As substitutes for S in the crystal structure. EXAFS-derived Fe-As interatomic distances of 2.33 Å and 3.50 Å are slightly longer than the nominal S-Fe distances of 2.26 and 3.48 Å of pyrite. In pyrite structure, there are 6 S atoms at 3.08 Å and 6 S atoms at 3.32 Å around a central S atom that occur in pairs having S-S distances of 2.135 Å. In contrast, EXAFS fitting indicated a coordination number of 2.3 for the shell of S atoms at 3.34 Å. Arsenic coordination number of about 3 appears to be high in consideration of the As concentration of the pyrite grain. Including the absorber, it appears that As occupies about 30 % of the S positions in the structure which is in sharp contrast to the electron microprobe analyses indicating only 1.5 mol % As in the structure (i.e. $FeAs_{0.03}S_{1.97}$). The EXAFS-derived high As coordination numbers can be explained by the clustering of As atoms in the pyrite structure. This is similar to the interpretation of Savage et al. (2000) implying that the clustering of As atoms in the structure causes about 2.6 % expansion of the unit cell, making pyrite more susceptible to oxidative dissolution.





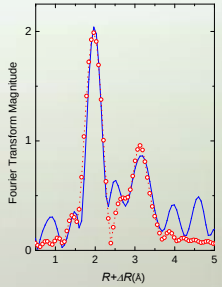
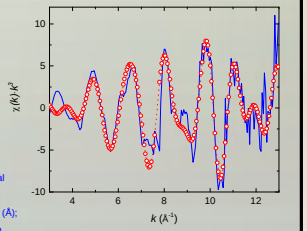


Table 2. Arsenic local structure from EXAFS fitting (within 3-13 Å^{-1})

		218 [a]	Clio-2 [b]	As-py [c]	FeS_2 [d]
As-Fe	*N*	3*	3*	3*	3 [e]
	R(Å)	2.33	2.32	2.32	2.26 [e]
	σ^2	0.0052	0.0018	0.0110	
As-As	*N*	2.99	3*	3*	6 [f]
	R(Å)	3.24	3.17	3.17	3.08 [f]
	σ^2	0.0047	0.0036	0.0040	
As-S	*N*	2.26	4*		6 [f]
	R(Å)	3.34	3.10		3.32 [f]
	σ^2	0.0132	0.0089		
As-Fe	*N*	4*	4*		4 [e]
	R(Å)	3.50	3.50		3.48 [e]
	σ^2	0.0094	0.0022		
E_0(eV)		8.6			
S_0^2		0.9*			
wt *F* factor		0.4761			

[a] this study; [b] Savage et al.(2000); [c] Bostick and Fendorf (2003); [d] nominal values from pyrite crystal structure; [e] S-Fe parameters; [f] S-S parameters; fixed value during fitting; *N*: coordination number; *R*: interatomic distance (Å); σ^2: Debye-Waller parameter; E_0 : energy offset; S_0^2 : amplitude reduction factor



ACKNOWLEDGEMENTS

The XAFS experiments were carried out at the Pacific Northwest Consortium - Collaborative Access Team's (PNC/XOR) beamline at the Advanced Photon Source (APS) under the user agreement to the author and through a major facilities access grant by the Natural Sciences and Engineering Research Council of Canada. Research at the PNC/XOR beamline is supported by US DOE under contracts W-31-109-Eng-38 (APS) and DE-FG03-97ER45628. Steve Heald helped with the experiments.

Natural Sciences and Engineering Research Council of Canada — Advanced Photon Source, Argonne National Laboratory — PNC CAT