Evidence for syngenetic micro-inclusions of As$^{3+}$- and As$^{5+}$-containing Cu sulfides in hydrothermal pyrite

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ABSTRACT

Most frequently arsenic is nominally monovalent (As$^+$) in pyrite (FeS$_2$) and substituted for S. Nominally trivalent arsenic (As$^{3+}$) has been reported previously in hydrothermal Peruvian pyrite and was considered to be substituted for Fe based on the negative correlation between the concentrations of the two elements. Here, we provide the first observation of the incorporation of As$^{3+}$ in goldfieldite [Cu$_6$,(As,Sb,Bi)$_2$Te$_2$S$_8$] and As$^{5+}$ in colusite [Cu$_{26}$V$_2$(As,Sb)$_4$Sn$_2$S$_{32}$] inclusions in As$^+$-pyrite from high-sulfidation deposits in Peru. This information was obtained by combining spatially resolved electron probe (EPMA), synchrotron-based X-ray fluorescence (SXRF), and absorption spectroscopy (micro-XANES and micro-EXAFS) with new high energy-resolution XANES spectroscopy (HR-XANES). The two Cu sulfide inclusions range from several to one hundred micrometers in size, and the As$^{3+}$/As$^{5+}$ concentration varies from a few parts per million (ppm) to a maximum of 17.33 wt% compared to a maximum of 50 ppm As$^+$ in pyrite. They also contain variable amounts of Sn (18.47 wt% max), Te (15.91 wt% max), Sb (8.54 wt% max), Bi (5.53 wt% max), and V (3.25 wt% max). The occurrence of As$^{3+}$/As$^{5+}$-containing sulfosalts in As$^+$-containing pyrite grains indicates that oxidizing hydrothermal conditions prevailed during the late stage of the mineralization process in the ore deposits from Peru. From an environmental perspective, high concentrations of potentially toxic As, contained in what appear to be non-As-bearing pyrite, may pose a heretofore unrecognized threat to ecosystems in acidic mine drainage settings. More generally, the combination of techniques used in this study offers a new perspective on the mineralogy and crystal chemistry of hazardous elements in pyrite, such as highly toxic and little studied thallium.

Keywords: Pyrite, goldfieldite, colusite, arsenic, high-sulfidation deposits

INTRODUCTION

In sulfide ore deposits, arsenic occurs commonly as realgar (As$_4$S$_4$), orpiment (As$_2$S$_3$), and arsenopyrite (FeAsS), and less commonly as enargite (Cu$_3$AsS$_4$), tennantite (Cu$_{12}$As$_4$S$_{13}$), and luzonite (Cu$_4$As$_2$S$_4$) (Fleet and Mumin 1997; Baumgartner et al. 2008; Bendezú and Fontboté 2009). Even more frequently, however, As occupies substitutional position, as in pyrite (FeS$_2$) and in complex sulfosalts minerals, such as colusite (Spry et al. 1994). Arsenian pyrite is of particular interest because it can contain as much as ~20 wt% As in hydrothermal Au deposits (Reich et al. 2005), and the release of As in acid mine drainage poses a threat to ecosystems and humans.

Arsenic is nominally trivalent (As$^{3+}$) in tennantite (Moëlo et al. 2008) and five-valent (As$^{5+}$) in enargite (Kouzmanov et al. 2004), colusite (Frank-Kamenetskaya et al. 2002), and luzonite (Moëlo et al. 2008). It can occur in three oxidation states in arsenian pyrite. The usual type is As$^{3+}$. As$^{5+}$-pyrite is abundant in Carlin-type and low-sulfidation epithermal and hydrothermal gold deposits (e.g., Simon et al. 1999; Savage et al. 2000; Paktunc 2008; Deditius et al. 2014). The nominal 1– oxidation state was informed by XANES spectroscopy (e.g., Simon et al. 1999; Paktunc 2008), and on the basis of EXAFS spectroscopy As substitutes for S (Savage et al. 2000). Indirect structural evidence for this substitution is provided by the negative correlation between S and As concentrations (Fleet et al. 1989; Deditius et al. 2014).

A second type, As$^{3+}$-pyrite, has been described in high-sulfidation epithermal deposits from Peru and Japan and is considered to be formed under oxidizing conditions (Deditius et al. 2008; Tanimizu et al. 2009). The 3+ oxidation state was established by XPS and XANES, and Deditius et al. (2008) suggested that As$^{3+}$ substitutes for Fe based on the negative correlation between the two elements measured by EPMA. Chouinard et al. (2005) had suggested earlier that one As$^{3+}$ and one Ag$^+$ substitute for two Fe$^{2+}$, effectively balancing the total charge.

A third type, As$^{5+}$-pyrite, has been reported from hydrothermal synthesis with As$_2$O$_3$ and Na$_2$HAsO$_4$·7H$_2$O (Qian et al. 2013). A nominal oxidation state of 2+ was derived from the comparison with the XANES spectrum of realgar (As$_4$S$_4$) and by XPS. Incorporation of As$^{2+}$/$3+$ at the Fe site in synthetic pyrite has been demonstrated by EXAFS supplemented with density functional theory (DFT) (Le Pape et al. 2017). Despite this progress in the identification and characterization of the oxidized forms of As in pyrite, their structural chemistry is as yet unknown in natural...