1   *Revision 1*

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3   **Characterization of ferric arsenate-sulfate compounds: Implications for**

4   **arsenic control in refractory gold processing residues**

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ABSTRACT

A combination of techniques, including powder X-ray diffraction (XRD), electron microprobe analysis (EPMA), transmission electron microscopy (TEM) and X-ray absorption spectroscopy (XAFS), is used to characterize the common ferric-arsenate-sulfate compounds which could result from the pressure oxidation of refractory gold ores at elevated temperatures. Three general types of precipitate are identified; namely, arsenate-bearing basic ferric sulfate ($FeSO_4(OH)$ and designated as BFS), ferric arsenate-sulfate (an extensive solid solution $Fe(AsO_4)_{0.2-0.7}(SO_4)_{0.7-0.2}(OH)_{0.7-0.2}$ and designated as FAS) and hydrated ferric orthoarsenate ($FeAsO_4 \cdot 0.75H_2O$). The crystal structure of FAS is solved by precession electron-diffraction experiments. The structures of BFS and FAS are constructed from octahedral Fe^{3+} chains which are cross-linked by sulfate and arsenate tetrahedra. Extensive substitution of arsenate for sulfate occurs in both types of compound with charge neutrality being maintained of variations in the (OH) content. The XAFS spectra indicate that the local structures of both BFS and FAS are made of corner-linked single chains of FeO_6 octahedra where the chains are linked by AsO_4 or SO_4 tetrahedra forming alternating layers of FeO_6 octahedra and AsO_4 or SO_4 tetrahedra. Preliminary Toxicity Characteristics Leaching Procedure (TCLP) testing of the precipitates indicates that FAS with a molar ratio As/(As+S) ratio of ≤ 0.5 could be an acceptable material for disposal in a tailings impoundment whereas more As-rich FAS and BFS may require further treatment. The results for the laboratory-prepared precipitates are compared with those obtained on three residues from the processing of refractory gold ores. The major As-carrier in one of the residues is FAS, whereas As-bearing goethite and hematite are the dominant As-carriers in the other two residues. Thus, the mineralogical characteristics of the residues dictate the appropriate arsenic management and disposal options in the processing of refractory gold ores.

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INTRODUCTION

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64   In refractory gold ores, gold occurs as submicroscopic particles or in solid solution in

65   arsenopyrite and pyrite at ppb to ppm levels; these occurrences are often referred to as

66   "invisible gold". Pyrite in refractory gold-sulfide deposits is often rich in As, and As

67   contents as high as 20 wt % have been reported (Abraitis et al. 2004; Paktunc et al. 2006).

68   Therefore, like the less abundant arsenopyrite, pyrite can be an important primary source

69   of As in refractory gold processing circuits. Gold extraction from refractory gold ores

70   requires a pre-treatment process such as roasting, pressure oxidation or bacterial

71   oxidation to destroy the host sulfide so that the gold is liberated and made available for

72   cyanide leaching. Roasting and pressure oxidation are the most commonly used pre-

73   treatment technologies. In addition to its technical advantages, such as improved

74   liberation of gold, pressure oxidation is preferred over roasting because of environmental

75   concerns associated with the generation of gaseous emissions with SO_2 and As_2O_3 in the

76   roasting process (Fleming 2010). Pressure oxidation is performed in large autoclaves

77   commonly operating in acidic media at relatively high temperatures (i.e., 190-230 °C) to

78   achieve complete oxidization of the sulfide minerals within a few hours. With the

79   destruction of arsenopyrite and pyrite, significant amounts of As can be incorporated in

80   the residues along with sulfate and ferric iron.

81   Swash and Monhemius (1994) were among the first to examine the Fe^{+3}-AsO_4-SO_4

82   system at elevated temperatures under hydrothermal conditions. They synthesized a series

83   of compounds including scorodite ($FeAsO_4 \cdot 2H_2O$), basic ferric sulfate ($Fe(SO_4)(OH)$)

84   and two unknown ferric arsenate and ferric arsenate-sulfate compounds, designated as

85   Type-1 and Type-2 (Table 1). Scorodite formed at temperatures below 175 °C whereas

86   the other compounds formed at higher temperatures which were dependent on the starting

87   solution composition. Despite the compositional differences, the X-ray diffraction (XRD)

88   pattern of Type-1 is similar to the ferric orthoarsenate hydrate ($FeAsO_4 \cdot 0.75H_2O$)

89   reported by Jakeman et al. (1991). Type-2 has a composition defined as

90    $Fe_4(AsO_4)_3(SO_4)_y(OH)_x$ (where $x+2y=3$). Similarly, Dutrizac and Jambor (2007)

91   performed synthesis experiments in the same system to determine the compositions of the

92   precipitates that may be analogous to those generated in industrial autoclaves. In addition

93   to scorodite, $Fe(SO_4)(OH)$ and two unknown compounds labelled as Phase 3 and Phase 4

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94   formed. Among these, Phase 4 is a ferric arsenate with a composition of
95   $Fe_{0.96}(AsO_4)_{0.99}(SO_4)_{0.01}(H_2O)_{0.54}$. Like Type-1, Phase 4 is similar to the ferric
96   orthoarsenate hydrate of Jakeman et al. (1991). Phase 3 has a wider compositional range
97   between $Fe_{0.8-1.1}(AsO_4)_{0.25}(SO_4)_{0.75}(OH)_{0.75}$ and $Fe_{0.8-1.1}(AsO_4)_{0.54}(SO_4)_{0.46}(OH)_{0.46}$. Based
98   on our experimental work conducted at CANMET and earlier studies conducted at
99   Imperial College (Ugarte and Monhemius 1992; Swash and Monhemius 1994), it is
100 anticipated that As and S released during the oxidation of arsenopyrite and pyrite under
101 industrial autoclave conditions would likely precipitate predominantly as a ferric
102 arsenate-sulfate phase (FAS). Despite their likelihood as the most abundant arsenic
103 compounds in autoclave residues, the characteristics and crystal structures of Phase 3 and
104 Type-2 remained unknown.

105 The objectives of this study are to characterize the common arsenical compounds
106 which would result from the pressure oxidation of refractory gold ores and to assess their
107 solubilities. In addition, three residue samples from industrial gold processing operations
108 and two samples of bukovskýite ($Fe_2(AsO_4)(SO_4)(OH)\cdot 9H_2O$ (Majzlan et al. 2012a))
109 were characterized to provide a basis for comparison. Mineralogical characteristics and
110 the stability of the As species in the residues will dictate the development of appropriate
111 arsenic management and disposal options at mine sites.

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113   **METHODOLOGY**

114 In order to determine the As-bearing compounds that are typically present in pressure
115 oxidation residues, a series of experiments was performed in the ferric iron, arsenate and
116 sulfate system using solutions containing reagent grade $Fe(SO_4)_{1.5}$, As_2O_5, H_2SO_4 and
117 $Fe(NO_3)_3$. Synthesis work was performed in Parr 2-L autoclaves under hydrothermal
118 conditions at temperatures greater than ~100 °C with retention times varying from 1 to 5
119 hours. These experiments produced various ferric arsenate-sulfates, scorodite, ferric
120 orthoarsenate, ferric sulfate and jarosite; some of compounds were previously described
121 as Phase 3 and Phase 4 by Dutrizac and Jambor (2007). In addition, pressure oxidation
122 residue samples from three commercial gold operations, designated as POX-2, POX-9,
123 POX-14, were obtained to provide a basis for comparison with the synthesized samples.

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124   The samples were characterized by a combination of techniques including powder X-

125   diffraction (XRD), electron microprobe analysis (EPMA), transmission electron

126   microscopy (TEM) and X-ray absorption spectroscopy (XAFS).

127   Powder XRD analyses were performed using a RIGAKU D/MAX 2500 rotating-

128   anode powder diffractometer with CuKα radiation (1.5406 Å) at 50 kV, 260 mA, a step-

129   scan of 0.02°, and a scan rate of 1° per minute in 2θ from 5 to 70°. The samples were

130   finely ground in a mortar and pestle, and packed either on Teflon covered aluminum

131   sample holders or on zero-background plates for the XRD analyses. Powder XRD

132   patterns were also collected at the bending-magnet beamline PDIFF at the synchrotron

133   light source ANKA (Angströmquelle Karlsruhe, Germany). X-rays of wavelength of

134   0.82694(1) Å were selected by a double crystal Si(111) monochromator. The wavelength

135   and the zero angle of the diffractometer were determined with silicon powder (NIST

136   standard reference material 640). The sample was loaded into a 1.0 mm glass capillary

137   which was rotated about its axis during data collection. The intensity of the incoming

138   beam was monitored during data collection by an ion chamber and the measured

139   intensities of the diffracted beam were corrected for the decay and fluctuations of the

140   primary beam. The XRD patterns were collected at room temperature, over an angular

141   range of 4 to 40º in 2θ, with a step of 0.005º and counting time of 1 s per point. The

142   diffraction data were treated with a full-profile Rietveld refinement with the GSAS

143   (General Structure Analysis System) program of Larson and von Dreele (1994).

144   Electron microprobe analyses were performed by wavelength-dispersive spectrometry

145   (WDS) on carbon-coated polished sections using JEOL JXA 8900 (CANMET) and JEOL

146   8230 (Earth Sciences, University of Ottawa) microanalyzers, operated at 15 kV using a

147   probe current of 10 to 30 nA, counting times of 10 seconds and a ZAF correction. The

148   following X-ray lines and standards were used: Fe$K\alpha$ (marcasite), S$K\alpha$ (marcasite) and

149   As$L\alpha$ (synthetic GaAs).

150   Transmission electron microscopy (TEM) examination of the samples, including

151   structural determinations, was conducted on a Philips CM120 microscope with a LaB$_6$

152   cathode operating at 120 kV. The microscope is equipped with a DigiStar (NanoMegas)

153   precession device for application of the precession electron diffraction (PED) and with a

154   CCD Camera Olympus SIS Veleta with a 14-bit dynamical range. Precession electron

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155   diffraction was used to suppress the dynamical diffraction effects to as large an extent as

156   possible. Small, homogeneous crystals were selected for the diffraction experiment. The

157   crystals were not oriented along a special zone axis prior to the data collection but were

158   intentionally left in a random orientation. During the data collection the crystal was tilted

159   in steps of 1° around the main tilt axis of the sample holder, and at each tilt a diffraction

160   pattern was recorded. This experimental method dubbed "electron diffraction

161   tomography" and pioneered by Kolb and coworkers (Mugnaioli et al., 2009) allows a

162   collection of 3-dimensional electron diffraction data set and subsequent *ab initio* solution

163   of crystal structures from electron diffraction data. The data were processed using the

164   computer programs PETS (Palatinus, 2011) and Jana2006 (Petříček et al., 2006), to yield

165   the unit cell parameters and integrated reflection intensities. The crystal structures were

166   solved *ab initio* using the computer program Superflip (Palatinus and Chapuis, 2007),

167   and refined with Jana2006 (Petříček et al., 2006).

168   XAFS spectroscopy measurements were made at the Pacific Northwest Consortium's

169   (PNC-CAT) bending magnet beam line of the Advanced Photon Source. Samples were

170   packed in Teflon sample holders after mixing with boron nitride to achieve a sample

171   thickness of about one absorption length. Each sample was scanned 5 to 8 times at room

172   temperature in both the transmission and fluorescence modes. Data reduction and

173   analysis were accomplished by ATHENA and ARTEMIS (Ravel and Newville 2005)

174   with data analysis considering the theoretical phase and amplitude functions generated in

175   FEFF6 (Zabinsky et al. 1993).

176   The samples were subjected to the Toxicity Characteristics Leaching Procedure

177   (TCLP) test (USEPA 1992). Due to the homogenous and fine-grained nature of the

178   precipitates, only 5 g samples of the precipitates were contacted for 20 hours at room

179   temperature by 100 mL of deionised water buffered at pH 5. Prior to the tests, the

180   samples were water-washed to remove any possible remaining soluble secondary salts

181   and dried at 100°C. The residue materials following the TCLP tests were filtered through

182   0.1 μm filters and the solutions were analysed for As, Fe and S by ICP-AES (Varian,

183   Vista RL) and ICP-MS (Thermo Scientific X-series 2) techniques.

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RESULTS AND DISCUSSION

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Long-range structures and chemical compositions

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188   The chemical composition of the precipitates formed from solutions with initial Fe/As

189   molar ratios ≥ 1.6 is highly variable from 29.0 to 33.3 wt % Fe, 0.1 to 43.2 wt % AsO_4

190   and 15.6 to 56.6 wt % SO_4. In terms of the Fe, AsO_4 and SO_4 molar contents, the

191   variation is essentially continuous as illustrated in Figure 1. The composition of the

192   samples projects from the point with a Fe:SO_4 ratio of 1 to $Fe(AsO_4)_{0.5}(SO_4)_{0.5}$, but

193   deviates towards $Fe_{1.5}AsO_4$ as the AsO_4 content increases and the SO_4 content decreases.

194   This trend requires that OH initially decreases from 1 to 0.5 in unison with the decrease

195   in SO_4, and this substitution can be written as $SO_4^{2-} + OH^- = AsO_4^{3-}$. In this case, the

196   change in the formula would be from $Fe(SO_4)(OH)$ to $Fe(AsO_4)_{0.5}(SO_4)_{0.5}(OH)_{0.5}$. For the

197   compositions in which AsO_4 dominates over SO_4, the formulae change between

198     $Fe(AsO_4)_{0.5}(SO_4)_{0.5}(OH)_{0.5}$ and $Fe_{1.5}AsO_4(OH)_{1.5}$. This substitution can be formally

199   written as $SO_4^{2-} = Fe^{3+} + AsO_4^{3-} + 2OH^-$. Based on the powder XRD patterns (Fig. 2),

200   the precipitates were grouped as Type-2, Phase 3 and Phase 5. In the following text, we

201   describe the structures of all the identified phases and the variations thereof with the

202   observed AsO_4-SO_4 substitutions. We begin with the sulfur-rich phases and proceed

203   toward the most arsenic-rich one, as shown in Figure 1.

204   **Jarosite.** Jarosite, nominally $KFe_3(SO_4)_2(OH)_6$, has a dense heteropolyhedral

205   structure with octahedral kagomé sheets, sulfate tetrahedra, and monovalent cations (K^+,

206   but several other ions including H_3O^+) in twelve-fold coordination (Fig. 3a). Because of

207   its relatively dense atomic arrangement, the AsO_4-SO_4 substitution is limited and the

208   maximum was reported to be 17 % $AsO_4/(AsO_4+SO_4)$ (Paktunc and Dutrizac 2003).

209   These authors investigated the incorporation of As^{5+} in the jarosite structure in detail and

210   their analyses and conclusions will not be repeated here.

211   **Basic ferric sulfate (BFS).** Another nominally arsenic-free phase with limited AsO_4-

212   SO_4 substitution is $Fe(SO_4)(OH)$, hereafter referred to as basic ferric sulfate (BFS). The

213   structure of this phase was solved by Johansson (1962) and was shown to be in the

214   orthorhombic space group *Pnma*. Ventruti et al. (2005) investigated the order-disorder

215   nature of the structure of BFS and showed that the orthorhombic phase of Johansson

216   (1962) is one of two maximum-degree-of-order (MDO) phases. The other MDO

217    $Fe(SO_4)(OH)$ phase is monoclinic, space group $P2_1/c$. Small changes in the stacking

218   order between the two MDO phases results in small modifications in the powder XRD

219   patterns. These changes, especially visible in the intensities of selected peaks, can be

220   qualitatively traced in our XRD data. Structures of both MDO $Fe(SO_4)(OH)$ phases are

221   heteropolyhedral frameworks. In contrast to jarosite, the Fe^{3+} octahedra in $Fe(SO_4)(OH)$

222   are arranged in chains and cross-linked by the tetrahedral units (Fig. 3b). A peculiar

223   change in lattice parameters upon substitution of AsO_4 for SO_4 can be observed (Fig. 4).

224   With the addition of a small amount of AsO_4, the unit-cell volume initially decreases

225   despite the fact that the AsO_4 tetrahedron is significantly larger than the SO_4 tetrahedron.

226   Only upon further insertion of AsO_4 into the structure does the unit-cell volume begin to

227   expand. A closer inspection of the lattice parameters (in the orthorhombic phase setting

228    $Pnma$) reveals the non-linear change of a and near linear expansion of b and c (Fig. 4b).

229   This observation is interesting because the octahedral chains extend in the direction of the

230   a axis. Tetrahedra are bridging FeO octahedra along the chains and the shared oxygen

231   atoms are perfectly aligned with the oxygen atoms linking the octahedra; therefore,

232   substitution of smaller sulfate by the larger arsenate (e.g. S-O=1.47 Å vs. As-O=1.68 Å)

233   would translate to the largest increases along the a axis. Three adjacent octahedral chains

234   are cross-linked or anchored by the tetrahedra; therefore, expansions along the b and c

235   axes would be restricted. It seems that with a small amount of AsO_4, the chains are

236   allowed to relax and actually contract. The expansion of the unit cell (i.e., the octahedral

237   chains) begins only with higher amounts of AsO_4, at 2 % $AsO_4/(AsO_4+SO_4)$. It appears

238   that BFS is able to accommodate up to about 10 wt % AsO_4, which corresponds to the

239   X_{As} mole fraction of 0.12. Interestingly, this is similar to the limit of AsO_4-SO_4

240   substitution in jarosite (Paktunc and Dutrizac 2003).

241   Our powder XRD data suggest that the BFS samples contain a minor amount of

242   hydronium jarosite. In addition, the BFS samples with the highest As content contain

243   Phase 3, which is chemically and structurally related to BFS and is described in detail

244   below.

245   **Ferric arsenate sulfate (FAS).** Phase 3 which spans most of the mixed SO_4-AsO_4

246   compositions (Fig. 1) is a ferric arsenate-sulfate (FAS). Structure of this phase was not

247   known previously, but the powder XRD data bear a remarkable similarity to the

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248   monoclinic $Fe(SO_4)(OH)$. Despite this similarity, the structure solution of FAS turned out

249   to be a difficult problem.

250   Early attempts to index the synchrotron powder XRD data failed because of the small

251   amount of impurities in the samples. TEM examinations indicated that FAS is the major

252   phase and occurs as isometric or blocky crystals, often twinned (Fig. 5). Energy-

253   dispersive X-ray microanalyses indicate that the crystals have a variable S:As ratio in the

254   range of 0.7-1. The electron diffraction tomography data were collected on a small crystal

255   with dimensions 130x180 nanometres. In total, 118 diffraction patterns with exposure

256   time 2 s were collected. The data analysis revealed that the FAS is triclinic (pseudo-

257   orthorhombic), with approximate lattice parameters a=5.42 Å, b=5.44 Å, c=13.58 Å, and

258   α=89.21º, β=89.68º, γ=87.89º, space group I-1. Just as BFS, the structure of FAS is

259   constructed from octahedral Fe^{3+} chains which are cross-linked by sulfate and arsenate

260   tetrahedra (Fig. 6). The atomic positions of the structure as refined against the electron

261   diffraction data are given in Table 2. It should be emphasized that this structure is only

262   approximate, as the refinement does not take into account the dynamical scattering

263   effects. However, the experience with the refinement from precession electron diffraction

264   data shows that the errors in the refined atomic positions often range around 0.1-0.2 Å,

265   and very rarely exceed 0.5 Å (Gorelik *et al.* 2011).

266   The lattice parameters refined from the X-ray powder diffraction data are a=5.1663,

267   b=5.1892, c=12.917 Å and α=89.000º, β=89.645º, γ=87.868º. These refined parameters

268   agree well with those determined from electron diffraction data supporting the triclinic

269   symmetry with the exception of an overall scaling factor of ~1.05, resulting from

270   imperfect calibration of the electron diffraction patterns.

271   The FAS phase precipitates from solutions with initial Fe/As molar concentrations

272   ≥1.5 at temperatures between 180 and 220 °C. It is the most abundant precipitate with X_{As}

273   mole fractions varying from 0.26 to 0.63. The lower end of this range seems to

274   correspond to higher synthesis temperatures.

275   Profile fitting of the in-house and synchrotron powder XRD data obtained from the

276   samples with variable X_{As} mole fractions shows an intriguing trend (Fig. 4, Table 3). As

277   was the situation for the BFS, the unit-cell volume does not change linearly with

278   increasing amounts of AsO_4 in the structure. Within the scatter of the data, the unit-cell

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279   volume increases linearly up to X_{As} ~0.55, but then levels off for the most As-rich

280   compositions. These changes are most likely related to the capability of the octahedra

281   within the chains to rotate and adjust for the attachment of the sulfate or arsenate

282   tetrahedra.

283   Type-2 synthesized by Swash and Monhemius (1994) with the X_{As} mole fraction of

284   0.75 has an XRD pattern similar to that of FAS, and this indicates that they are essentially

285   the same compound (Fig. 2). Electron microprobe analyses of the material synthesized by

286   Swash and Monhemius (1994) revealed that Type-2 is not homogeneous. The grains

287   showing hedge-hog type morphology display zoning with respect to As and S (Fig. 7a).

288   Some of the grains have margins with increased As and decreased S contents. In addition,

289   the X-ray maps show sulfur-deficient rosettes within the grains indicating a ferric

290   arsenate phase exsolved from the compound (Fig. 7b). Electron microprobe analyses

291   indicate that the exsolved phase has X_{As} mole fractions varying from 0.77 to 0.96 with an

292   average value of 0.90±0.05; however, it is possible that this exsolved phase is nearly

293   sulfate-free. Furthermore, because of the small size, it is likely that some of the S counts

294   in the microanalyses originate from the host phase. The X_{As} mole fraction of the main

295   phase is 0.69±0.05. The structural formula of the dominant phase is determined to be

296    $Fe_{1.1-1.3}(As_{0.6-0.8}S_{0.2-0.4}O_4)(OH)_{0.2-0.4}$. It appears that this composition represents an end-

297   member of FAS with the highest X_{As} fraction in the structure. The structural formula of

298   the exsolved phase is $Fe_{1.1-1.5}(As_{0.8-1.0}S_{0.0-0.2}O_4)(OH)_{0.0-0.2}$. In summary, the composition of

299   FAS can be defined as $Fe(AsO_4)_{0.2-0.7}(SO_4)_{0.7-0.2}(OH)_{0.7-0.2}$ where $AsO_4+SO_4=1$.

300   **Scorodite.** Scorodite, nominally $FeAsO_4 \cdot 2H_2O$, is another heteropolyhedral network

301   among the studied phases. The structure consists of monomers of $FeO_4(H_2O)_6$ polyhedra

302   which attach via the oxygen ligands to the four neighboring AsO_4 tetrahedra (Fig.3c).

303   Little SO_4 can be incorporated into the scorodite structure and from the limited data

304   acquired herein, it seems that the unit cell contracts monotonically with increasing SO_4

305   substitution (Table 3).

306   **Ferric orthoarsenate hydrate.** In our synthesis experiments, $FeAsO_4 \cdot 0.75H_2O$ is the

307   phase with the least amount of SO_4. The structure of this phase was reported by Jakeman

308   et al. (1991). The structure is built by kinked tetramers of edge-sharing of $Fe(O,H_2O)_6$

309   octahedra (Fig.3d). The tetramers are interlinked by the AsO_4 tetrahedra in a tightly

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310   knitted heteropolyhedral framework which probably does not leave much room for the

311   substitution of the smaller SO_4 group. This phase forms when the Fe/As molar ratio of the

312   initial solution is low (i.e., near 1) and at synthesis temperatures of 180ºC and greater. At

313   lower temperatures, between 150 and 175 ºC, the precipitate is scorodite.

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315   **Short-range structures**

316   The k^3-weighted As K-edge spectra of BFS and FAS samples are broadly similar

317   (Fig. 8a). The k^3-weighted Fe K-edge XAFS spectra also display similarities (Fig. 8b).

318   The changes in the spectra point to the progressive variation of the X_{As} mole fractions in

319   the precipitates. This indicates that the local structures around the As and Fe atoms in

320   BFS and FAS are similar, and this confirms the continuity in the long-range structures

321   discussed earlier. The gradual changes in the oscillation features of the Fe K-edge XAFS

322   spectra reflect the differences in the number of As and S atoms surrounding the central Fe

323   atoms. For instance, the gradual development of humps on the low k sides of the

324   oscillation features at ~4, 6 and 8 Å^{-1} in samples with X_{As} mole fractions ≤0.35 suggests

325   the influence of S. The changes in the As K-edge XAFS spectra are not as apparent

326   suggesting that the local As environment is not significantly affected by the changes in

327   the X_{As} mole fraction. Instead, it appears that Fe is the closest neighbour surrounding the

328   AsO_4 tetrahedra in both compounds. Considering these similarities and the gradual

329   changes in the spectral features, the XAFS fitting was intended to test the similarity of the

330   compounds to the $Fe(SO_4)(OH)$ structure in terms of local structures around the As and

331   Fe atoms. In the $Fe(SO_4)(OH)$ structure, a central Fe atom is surrounded by four S atoms

332   at 3.31 Å and two Fe atoms at 3.67 Å, whereas a central S atom, which is assumed to be

333   substituted by As in this case, is surrounded by four Fe atoms at 3.31 Å and four S atoms

334   at 4.09 Å.

335   Local structural parameters determined by As and Fe XAFS fitting for the BFS and

336   FAS compounds are given in Tables 4 and 5, and the fits are shown in Figure 8. By

337   limiting the number of variables through constraining the coordination numbers from the

338   crystal structure, it was possible to include up to 4 coordination shells in fitting. This

339   allowed an independent assessment of the interatomic distances around As and Fe atoms

340   and the changes due to arsenate-for-sulfate substitution. The As-O radial distances are

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341   relatively uniform at 1.68±0.01 and 1.69±0.01 Å. Beyond the oxygen shell, spectral

342   features at 3.36±0.02 (3.34-3.39), 3.73±0.02 (3.70-3.76) and 4.03±0.03 (3.99-4.07) Å

343   correspond to Fe, S and As atoms, respectively. As expected, the variations in the As-Fe,

344   As-S and As-As distances do not appear to be influenced by the changes in the X_{As} mole

345   fraction in the structures. The As-S radial distances are shorter than those of the As-As

346   due to smaller size of the sulfate tetrahedra. Fit quality was improved with the inclusion

347   of the multiple scattering paths, As–O1–O2, As–O1–As–O2 and As–O1–As–O1 derived

348   from FEFF calculations (Ankudinov et al. 1998) based on the crystal structure of

349   scorodite from Kitahama et al. (1975).

350   Fitting of the Fe K-edge XAFS spectrum of the BFS samples resulted in Fe-O

351   distances of 1.99±0.01 - 2.00±0.01 Å in octahedral coordination and Fe-S distances of

352   3.34±0.03 – 3.38±0.03 Å (Table 5). In contrast, the FAS samples have slightly shorter

353   Fe-O distances at 1.96±0.01 and 1.97±0.01 Å. Because of the similarity of the Fe-As and

354   Fe-S interatomic distances, simulations of the second shell were performed with As for

355   the FAS samples which resulted in Fe-As distances of 3.31±0.02 – 3.34±0.02 Å. These

356   are comparable to the As-Fe distances of 3.34±0.02 - 3.39±0.03 Å from the As-XAFS

357   and the nominal FAS distances varying from 3.25 to 3.38 Å (3.33±0.05 Å). Constraining

358   the coordination numbers to their structural values made it possible to include two Fe

359   shells in the simulations. The first Fe shell with a coordination number of 2 is at

360   3.69±0.03 - 3.71±0.05 Å for the BFS and 3.62±0.10 – 3.68±0.04 Å for the FAS samples,

361   representing corner-linked FeO_6 octahedra along the octahedral chains. The second Fe

362   shell with a coordination number of 8 is at 5.10±0.03 – 5.12±0.02 Å for the BFS and

363   5.14±0.04 – 5.18±0.04 Å for the FAS samples representing corner-linked FeO_6 dimers in

364   the four adjacent octahedral chains. These Fe-Fe radial distances are comparable to the

365   Fe-Fe distances of 3.67 and 5.14 Å of the $Fe(SO_4)(OH)$ structure (Johansson 1962), and

366   3.76 and 5.17 Å of the FAS structure (this study). The increased Fe-Fe2 distances of the

367   FAS samples indicate that the arsenate-for-sulfate substitution causes increases in

368   distance between the octahedral chains which reflect the increases along *a* and *b*.

369   In summary, the XAFS-derived interatomic distances are comparable to their

370   counterparts from the crystal structures of FAS and BFS. The average S-O distances of

371   1.457 Å in $Fe(SO_4)(OH)$ and 1.473 Å in sulfate minerals (Hawthorne et al. 2000) are

12

372 shorter by about 0.22 Å from the measured As-O distance of 1.68 Å. It is possible that the

373 observed differences between the As-As and As-S distances, ranging from 0.29±0.06 to

374 0.32±0.07 Å, are reflecting this difference. In addition, substitution of sulfate ions by the

375 larger arsenate ions would cause the Fe-Fe distance to become greater, lengthening the

376 iron chains and widening the distance between the octahedral chains. This would explain

377 the gradual shifts to lower 2θ or wider d-spacings and the enlargement of the unit-cell

378 volume with increased arsenate substitution.

379

380 **Leachability**

381   TCLP testing was used to make a preliminary assessment of the environmental

382 stability of the BFS and FAS precipitates. Materials that produce effluents with As

383 concentrations exceeding the Canadian metal-mine effluents limit of 0.5 mg/L

384 (Government of Canada 2002) could be considered unacceptable for safe disposal in the

385 environment, and even materials which pass this short-term test often require testing for

386 longer times at various pH values and under a range of oxidation/reduction conditions.

387 TCLP testing of the BFS with an X_{As} mole fraction of 0.08 resulted in an As

388 concentration of 16.2 mg/L in the leachate. The FAS samples produced As concentrations

389 that varied between 0.06 and 0.88 mg/L. The upper end of this range is represented by the

390 sample with the highest X_{As} molar fraction (i.e., 0.62). Swash and Monhemius (1994)

391 reported that Type-2 with an X_{As} mole fraction of 0.75 produced a similar As

392 concentration (i.e., 0.8 mg/L) in the TCLP leachate at pH 5. Some of the FAS samples

393 contain trace to minor amounts of BFS, as evidenced by the presence of overlapping

394 peaks at 2θ values of ~26.5º and 27.5º which appear as asymmetric and broadened peaks.

395 The BFS samples containing minor amounts of FAS have leachate As concentrations

396 between 0.46 and 2.26 mg/L. Arsenic concentrations in the leachates of the FAS samples

397 increase exponentially with a decrease in the leachate Fe concentration (Fig. 9), although

398 all the As concentrations are less than 1 mg/L. This is with the exception of the samples

399 containing minor amounts of BFS. In contrast, the As and Fe concentrations in the

400 leachates of BFS and those containing both compounds display a positive correlation.

401 Leachate S concentrations are variable from 55.6 to 252.7 mg/L in the samples containing

402 BFS and less than 1 to 39.6 mg/L in the FAS samples, forming a trend of increasing Fe

13

403 and S concentrations from both types of precipitates (Fig. 9). The highest releases of As,

404 Fe and S are from BFS. Leachate Fe concentrations of 13 to 259 mg/L released from BFS

405 and the FAS samples containing BFS are unusually high for solutions at the TCLP test

406 value of pH 4.5.

407   The FAS samples with X_{As} mole fractions of 0.40, 0.42 and 0.52 gave the lowest As

408 concentrations in the leachates (i.e., 0.063-0.069 mg/L) and also yielded molar Fe/As

409 ratios that are greater than 20. These samples contain trace amounts of BFS. For

410 precipitates with molar Fe/As+S ratios between 0.002 and 0.572, the releases of Fe, As

411 and S from both the FAS and BFS precipitates are non-stoichiometric. The highest ratio

412 is from a BFS sample indicating that dissolution of BFS releases about twice as much As

413 and S as Fe. With the exception of the samples containing minor to trace BFS, the molar

414 Fe/As+S ratios of the TCLP extracts of the FAS samples are less than 0.008 indicating

415 that very little iron is released in comparison to the combined As and S releases from the

416 dissolution of FAS. In consideration of the crystal structure of BFS, the non-

417 stoichiometric dissolution behaviour can be explained by the precipitation of a ferric

418 oxyhydroxide phase or by the preferential release of SO_4 leaving behind chains of FeO_6

419 octahedra.

420

421 **Implications for the disposal of gold processing residues**

422   Fine grained residue samples from three autoclaves treating refractory gold ores were

423 obtained. In terms of bulk chemical compositions, the sample designated as POX-2

424 analyzed 22.7% Fe, 5.42% As and 3.90% SO_4. The POX-9 sample analyzed 12.9% Fe,

425 2.39% As and 1.40% SO_4; the analysis of the POX-14 sample was 20.0% Fe, 4.01% As

426 and 3.50% SO_4. Electron microprobe analyses of the heterogeneous oxidation residues

427 indicate that the arsenic carrier in the POX-2 sample is a FAS compound (Fig. 10). The

428 POX-9 sample has jarosite, hematite and goethite as the main As carriers. The jarosite

429 has significant amount of Al and contains between 0.5 and 8.6 wt % As_2O_5. Hematite has

430 3.6 to 6.1 wt % As_2O_5 whereas goethite contains much higher As concentrations, in the

431 7.9 to 23.5 wt % range. Goethite, with As_2O_5 concentrations in the 0.1 to 14.9 wt %

432 range, is the dominant As carrier in the POX-14 sample. The compositional similarity of

433 the POX-2 residues to the As-rich members of Phase 3 or Type-2 is apparent on the Fe-

14

434   AsO_4-SO_4 plot (Fig. 10). Spherical ferric arsenate-sulfate grains from the Red Lake

435   autoclave (McCredie et al. 1998) have a similar composition. The POX-14 data cluster

436   near the Fe^{3+} corner along the Fe-AsO_4 join in agreement with the compositions of As-

437   adsorbed goethite and hematite. The arsenic carriers in the POX-9 residue plot with those

438   of POX-14 and are close to the Fe^{3+} corner and near the mid point along the Fe-SO_4 join

439   close to the theoretical jarosite composition. In terms of contained As, these residues are

440   similar to the synthetic arsenical jarosites reported by Paktunc and Dutrizac (2003).

441   In agreement with their chemical compositions, analysis of the As-XAFS spectra of

442   the POX-2 and POX-14 residue sample (Fig. 11) yielded local structural parameters that

443   are similar to those of FAS and goethite, respectively (Table 6). POX-9 has an optimized

444   iron coordination number of 2 but the As-Fe radial distance is rather long at 3.40±0.10 Å

445   in comparison to the 3.24-3.32 Å distances for goethite (Foster et al. 1998; Sherman and

446   Randall 2003; Paktunc et al. 2004; 2008), 3.25-3.26 Å for jarosite (Paktunc and Dutrizac

447   2003), and 3.24-3.35 Å for hematite (Sherman and Randall 2003). However, considering

448   the large uncertainty associated with the measured As-Fe distance for POX-9 and the

449   number of As carriers in the sample, the calculated "average" As-Fe distance is not

450   unreasonable.

451   Minerals in the Fe-AsO_4-SO_4 system are also shown on the Fe-AsO_4-SO_4 plot (Fig.

452   10). The minerals are essentially restricted to near Fe/anion ratios of 1 and 1.5.

453   Kaatialaite with a Fe/As molar ratio of 1/3 is the exception but this is a very rare mineral

454   found only in extremely acidic environments. Other than scorodite, jarosite, hematite and

455   goethite, the compounds that form during pressure oxidation do not have natural analogs.

456   There are three ferric arsenate-sulfate minerals, bukovskýite

457   ($Fe(AsO_4)_{0.5}(SO_4)_{0.5}(OH)_{0.5}\cdot4.5H_2O$), sarmientite ($Fe(AsO_4)_{0.5}(SO_4)_{0.5}(OH)_{0.5}\cdot2.5H_2O$)

458   and zykaite ($Fe_4(AsO_4)_3(SO_4)(OH)\cdot15H_2O$). The exsolved ferric arsenate phase present in

459   the FAS sample with the highest As content is similar to ferrisymplesite

460   ($Fe_3(AsO_4)_2(OH)_3\cdot5H_2O$) in terms of the Fe/As ratio. Ferrisymplesite is an amorphous

461   ferric arsenate supposedly resulting from the oxidation of symplesite, but little is known

462   about this compound and its existence as a valid mineral species may be questionable.

463   Bukovskýite and sarmientite could be considered as hydrated natural analogs of FAS

464   with equal numbers of AsO_4 and SO_4 molecules in the structure. Along with zykaite and

15

465   kaatialaite, these are uncommon arsenate minerals, occurring as alteration products of

466   scorodite and arsenopyrite in several mine waste sites. The As-XAFS spectra of two

467   bukovskýite specimens from Kutná Hora (Czech Republic) and the Ketza River mine in

468   Yukon (Canada) display similarities to those of FAS (Fig. 11). Local structural

469   parameters of bukovskýite determined by As-XAFS are four O at 1.69±0.01 Å, four Fe at

470   3.33±0.03 Å and two As at 3.97±0.07 Å (Table 6). Fitting of the Fe-XAFS spectra (Fig.

471   11b) resulted in six O at 1.99±0.01 Å, two As at 3.35±0.02 Å and one Fe at 3.61±0.03 Å

472   and one Fe at 5.09±0.05 Å (Table 7). These independently determined local structures are

473   reasonable in consideration of the crystal structure of bukovskýite (Majzlan et al. 2012a)

474   and they are broadly similar to the local structures of FAS, indicating that bukovskýite

475   and FAS have similar local structures around As and Fe in the sense that arsenate

476   tetrahedra link octahedral "chains" which are only dimers in bukovskýite.

477   Most of the FAS samples have TCLP As concentrations that are less than the

478   Canadian metal-mine effluent limit of 0.5 mg/L (Government of Canada 2002)

479   suggesting that FAS could meet the current regulatory guideline for mine effluents at pH

480   5. The precipitates having X_{As} mole fractions between 0.4 and 0.5 could even meet

481   stricter mine effluent limit of 0.2 mg/L imposed by the Provincial Government of Québec

482   for new operations (Gouvernement du Québec 2005). In contrast, the BFS with an X_{As}

483   mole fraction of 0.08 yields 16.2 mg/L As in the TCLP leachate. This is only a

484   preliminary assessment, however, as these short-term tests may not represent the

485   solubility or near equilibrium conditions. Type-2 which has the highest As content and an

486   exsolved ferric arsenate compound, has As leachate values of less <0.5 to 7.3 mg/L,

487   determined at pH values of 3, 5, 7 and 10 by Swash and Monhemius (1994). This

488   suggests that As control by FAS precipitation would be acceptable only over the limited

489   pH range from 3 to 5. Nevertheless, these preliminary assessment results for FAS are

490   promising in that they are comparable to the solubility levels of scorodite (Krause and

491   Ettel 1989; Paktunc and Bruggeman 2010; Majzlan et al. 2012b).

492   Limited leaching tests indicate that the basic orthoarsenate hydrate (i.e., Phase 4 of

493   Dutrizac and Jambor 2007 and the Type-1 compounds of Swash and Monhemius 1994)

494   would not be suitable for disposal. Similarly, BFS would be an unwanted compound

495   because of its high solubility which would result in the release of much of the contained

16

496   As. In addition to environmental concerns, the formation of $Fe(SO_4)(OH)$ can cause

497   problems during subsequent cyanidation and impact on the economics of the process by

498   causing excessive lime consumption during cyanidation and potentially exposing the

499   plant workers to hazardous HCN gas as pointed out by Fleming (2010). According to

500   Fleming et al. (2008), the autoclave temperatures should be around 190°C for the

501   optimum recovery of gold from the refractory Kittila ore. Higher temperatures, around

502   210-230°C, promote the formation of $Fe(SO_4)(OH)$. Accordingly, As control practices at

503   mine sites could aim to optimize the conditions for the formation of FAS at the lower end

504   of the temperature range (185-225°C) during pressure oxidation, without compromising

505   gold recoveries.

506

507   **ACKNOWLEDGEMENTS**

523

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632

633   **FIGURE CAPTIONS**

634   **FIGURE 1**. Compositions of Phase 3, Phase 4, Phase 5 and Type-2 in terms of molar

635   Fe^{3+}, AsO_4 and SO_4 contents. Note that only the upper half of the plot is shown as Fe-

636    $0.5AsO_4$-$0.5SO_4$. Type-2 plots are based on electron microprobe analyses. Cores are

637   represented by blue stars and exsolution-like features by purple stars (Type-2 exs).

638   Synthetic jarosite data from Paktunc and Dutrizac (2003) and scorodite from Dutrizac

639   and Jambor (1970).

640   **FIGURE 2**. XRD patterns of Phase 3, Phase 5 and Type-2. Numbers next to the patterns

641   are X_{As} mole fractions of the samples.

642   **FIGURE 3**. Polyhedral representation of the crystal structures of (a) jarosite, (b) BFS, (c)

643   scorodite, (d) $FeAsO_4 \cdot 0.75H_2O$. Fe: brown; As: purple; S: yellow; K: green.

644   **FIGURE 4**. (a) changes in unit-cell volume as a function of substitution of AsO_4 for SO_4

645   in BFS and FAS, (b) changes in the *a*, *b* and *c* lattice parameters of BFS (normalized to

646   XAs0 parameters) as a function of the AsO_4 fraction.

21

647   **FIGURE 5**. TEM photomicrographs of the FAS precipitates. The acicular crystal marked

648   04 is ferric orthoarsenate hydrate which occurs in trace amounts in the sample. The other

649   labels indicate the spots where microanalysis of the FAS crystals was performed.

650   **FIGURE 6**. Crystal structure of FAS as visualized projected along a (a) and along the

651   FeO_6 octahedral chains (b). A comparative visualization of the crystal structures of FAS

652   (c) and BFS (d), showing the rotation of the FeO_6 octahedra and AsO_4/SO_4 tetrahedra in

653   FAS. Fe: brown; As: purple; S: yellow.

654   **FIGURE 7**. (a) Backscattered electron (BSE) image and (b) X-ray maps of As and S

655   showing depletion of As along the outer margin of Type-2 grains and its enrichment in

656   exsolution-like small spotty areas or circular zones in the interior. Note that the changes

657   in S are inversely related to those of As. Scale bar of X-ray maps is 100 μm.

658   **FIGURE 8**. (a) k^3-weighted As XAFS spectra and (b) k^3-weighted Fe XAFS spectra of

659   BFS and FAS. Numbers next to the curves are As mole fractions: $100 \times AsO_4/(AsO_4+SO_4)$

660   with 0 to 12 being BFS and 34 to 75 being FAS. Experimental curves indicated by solid

661   lines and fitted spectra by circles.

662   **FIGURE 9**. (a) As and Fe concentrations (mg/L) and (b) Fe and S concentrations (mg/L)

663   in the leachates resulting from TCLP testing.

664   **FIGURE 10**. Fe^{3+}-AsO_4-SO_4 plot showing the compositions of the pressure-oxidation

665   (POX) residues from three gold mining operations. POX-RL represents ferric arsenate-

666   sulfate grains from the Red Lake autoclave. Also shown for comparative purposes are the

667   representative mineral compositions and the synthesized compounds.

668   **FIGURE 11**. (a) k^3-weighted As-XAFS spectra of the pressure oxidation residues from

669   the three gold mining operations and of bukovskýite. (b) k^3-weighted Fe-XAFS spectra of

670   bukovskýite. Experimental spectra shown by solid curves and fitted spectra by circles.

671   Bukovskýite specimens from Kutna Hora (bukKH) and the Ketza River mine (bukKe).

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674 **TABLE 1**. Compositions of precipitates synthesized in the Fe-AsO$_4$-SO$_4$ system
675

Compound	Formula	Temperature (ºC)	Ref.	Structure*
Type-1	Fe$_2$(HAsO$_4$)$_3$·zH$_2$O (z<4)	125-225	1	
Ferric orthoarsenate hydrate	FeAsO$_4$·¾H$_2$O	700-800	2	
Phase 4	Fe$_{0.96}$(AsO$_4$)$_{0.99}$(SO$_4$)$_{0.01}$(H$_2$O)$_{0.54}$	205-215	3	
Type-2	Fe$_4$(AsO$_4$)$_3$(SO$_4$)$_y$(OH)$_x$ (x+2y=3)	175-225	1	FAS
Phase 3	Fe$_{0.8-1.1}$(AsO$_4$)$_{0.25-0.54}$(SO$_4$)$_{0.46-0.75}$(OH)$_{0.46-0.75}$	185-225	3,4	FAS
Basic iron sulfate	Fe(SO$_4$)(OH)	200	5	BFS
Basic iron sulfate	Fe(SO$_4$)(OH)	>175	1	BFS
Phase 5	Fe(SO$_4$)(OH)	205-215	3,4	BFS
Scorodite	FeAsO$_4$·2H$_2$O	<175	1,2,6	
Jarosite	KFe$_3$(SO$_4$)$_2$(OH)$_6$	98	7	

676 1: Swash and Monhemius (1994); 2: Jakeman et al. (1991); 3: Dutrizac and Jambor (2007); 4: present study;
677 5: Johansson (1962); 6: Paktunc et al. (2008); 7: Paktunc and Dutrizac (2003); Structure*: in reference to the
678 abbreviations used in text.
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682 **TABLE 2**. Lattice parameters, space group and atomic coordinates of ferric
683 arsenate sulfate (FAS), as refined from the electron diffraction data.
684
685 Space group I-1
686 Lattice parameters: a = 5.1639 Å, b = 5.1863 Å, c = 12.9457 Å, α = 89.209º, β = 89.675º, γ = 87.892º,
687 V = 346.433 Å^3

atom	x	y	z	U_{iso}
As/S*	0.7474(14)	0.018(2)	0.1227(6)	0.0038(18)
Fe1	0.25	-0.25	0.25	0.038(4)
Fe2	0	0.5	0	0.024(3)
O1	0.782(5)	-0.190(6)	0.0442(18)	0.026(6)
O2	0.746(5)	0.309(6)	0.083(2)	0.028(6)
O3	0.471(4)	0.014(6)	0.1906(17)	0.023(5)
O4	0.949(9)	-0.001(10)	0.208(3)	0.069(10)
OH	0.241(7)	-0.449(9)	0.123(3)	0.065(10)

688 * occupancy 50 % As, 50 % S
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693   **TABLE 3**. Lattice parameters of basic ferric sulfate (BFS) and ferric arsenate-
694   sulfate (FAS)

	a	*b*	*c*	*α*	*β*	*γ*	*V* (Å³)
BFS							
XAs0	7.3434(4)	6.4133(4)	7.1330(4)				335.93(3)
XAs1	7.3353(4)	6.4143(3)	7.1377(4)				335.84(3)
XAs2	7.3357(4)	6.4145(4)	7.1359(4)				335.78(3)
XAs4	7.3431(4)	6.4178(4)	7.1393(4)				336.45(3)
XAs8	7.3565(6)	6.4215(5)	7.1407(6)				337.33(5)
XAs12	7.3936(7)	6.4261(6)	7.1414(6)				339.30(5)
Nominal(OR)	7.33	6.42	7.14				336.00
Nominal(MO)	7.33	7.14	7.39		119.7		295.27
FAS							
XAs26	5.1744(3)	5.1644(3)	12.9929(9)	89.641(5)	89.910(5)	87.852(4)	346.95(4)
XAs30	5.1841(5)	5.1599(5)	13.0179(12)	89.518(6)	90.022(7)	87.939(5)	347.98(5)
XAs32	5.1852(4)	5.1653(4)	13.0624(11)	89.437(4)	89.796(6)	87.837(4)	349.59(5)
XAs33	5.1801(4)	5.1674(4)	13.0483(10)	89.503(5)	89.851(5)	87.873(4)	349.02(4)
XAs34	5.1908(4)	5.1807(4)	13.0265(9)	89.599(4)	89.506(4)	87.692(4)	350.01(4)
XAs35	5.1932(3)	5.1834(4)	12.9906(11)	89.530(6)	89.460(5)	87.633(4)	349.36(4)
XAs36	5.1990(3)	5.1836(3)	12.9697(9)	89.581(4)	89.226(4)	87.590(3)	349.18(4)
XAs37.1	5.2018(6)	5.1744(6)	13.091(2)	89.321(6)	90.15(1)	88.044(7)	352.14(7)
XAs37.3	5.1835(3)	5.1739(3)	13.0515(8)	89.415(4)	89.818(4)	87.830(3)	349.76(3)
XAs38	5.2082(6)	5.1721(6)	13.095(2)	89.409(6)	89.920(9)	87.999(7)	352.50(7)
XAs40	5.1985(3)	5.1764(3)	13.1062(8)	89.427(4)	89.775(4)	87.870(3)	352.42(4)
XAs42	5.1939(4)	5.1649(4)	13.1357(13)	89.267(5)	89.679(6)	87.771(5)	352.07(5)
XAs44	5.2131(3)	5.2051(3)	13.0583(9)	89.556(4)	89.208(4)	87.544(3)	353.97(4)
XAs45	5.2042(3)	5.1815(3)	13.0774(8)	89.600(4)	89.911(4)	87.996(3)	352.41(4)
XAs46	5.2068(4)	5.1854(4)	13.0626(10)	89.615(5)	89.913(5)	88.023(5)	352.46(5)
XAs46.6	5.2147(3)	5.1934(3)	13.0690(8)	89.621(4)	89.909(4)	88.129(4)	353.74(4)
XAs47	5.2192(3)	5.1956(4)	13.1330(10)	89.366(4)	89.755(4)	87.861(4)	355.85(4)
XAs48	5.2264(5)	5.1979(4)	13.1119(12)	89.550(6)	89.924(6)	88.040(5)	355.98(5)
XAs51.3	5.2341(3)	5.2140(4)	13.0527(9)	89.564(5)	90.048(4)	88.340(4)	356.05(4)
XAs51.6	5.2293(4)	5.1974(4)	13.1172(12)	89.487(5)	89.929(6)	88.122(5)	356.31(5)
XAs51.8	5.2319(4)	5.2142(4)	13.0881(10)	89.731(6)	89.952(6)	88.186(4)	356.86(5)
XAs52.0	5.2124(3)	5.1960(4)	13.1187(9)	89.464(5)	89.621(5)	87.835(5)	355.03(4)
XAs52.1	5.2059(5)	5.1849(4)	13.1244(11)	89.381(5)	89.679(6)	87.760(5)	353.96(5)
XAs52.2	5.2219(3)	5.1946(4)	13.1404(9)	89.408(4)	89.809(4)	87.930(4)	356.19(4)
XAs52.3	5.2118(5)	5.1898(5)	13.1267(12)	89.386(6)	89.721(6)	87.788(5)	354.77(6)
XAs59	5.2187(4)	5.2397(4)	13.0298(11)	89.578(6)	88.938(5)	87.888(5)	355.98(5)
XAs62	5.2173(4)	5.2506(3)	13.0150(10)	89.558(5)	88.900(5)	88.168(5)	356.28(4)
XAs63	5.2225(3)	5.20014(33)	13.1390(8)	89.435(4)	89.779(4)	87.854(4)	356.55(4)
XAs75	5.2134(4)	5.2415(4)	13.0156(12)	89.519(6)	88.837(5)	87.781(5)	355.31(5)
Scorodite							

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XAs84	8.9365(3)	10.2617(4)	10.0553(4)	922.11(6)
XAs92±3	8.9394(6)	10.2871(6)	10.0435(6)	923.61(9)
XAs93	8.9335(8)	10.2610(8)	10.0484(8)	921.1(1)
XAs99	8.9514(9)	10.3254(10)	10.0369(9)	927.7(1)
Nominal*	8.937(1)	10.278(2)	9.996(2)	918.2(3)

695 Nominal $FeOHSO_4$ lattice parameters (OR) from Johannson (1962) and (MO) from Ventruti et al. (2005);
696 Nominal scorodite is based on Hawthorne (1976); Numbers in sample labels next to XAs refer to
697 $100 \times AsO_4/(AsO_4+SO_4)$; *a, b and c* in Å; α, β and γ in degrees; numbers in bracket are uncertainty values.
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706 **TABLE 4**. Arsenic XAFS fitting results

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Sample		N	R	σ^2	$E0$	rf	Ni/Nv
XAs8	O	4*	1.68±0.01	0.0008	-0.9	0.033	1.7
	Fe	4*	3.34±0.02	0.0074			
	S	3.5*	3.72±0.02	0.0047			
	MS2-1	12*	3.08±0.12	0.0085			
XAs12	O	4*	1.68±0.01	0.0009	0.4	0.029	1.7
	Fe	4*	3.35±0.02	0.0087			
	S	3.5*	3.73±0.02	0.0046			
	MS2-1	12*	3.07±0.09	0.0044			
XAs34	O	4*	1.68±0.01	0.0020	0.5	0.017	1.5
	Fe	4*	3.34±0.02	0.0111			
	S	2.6*	3.72±0.03	0.0064			
	As	1.4*	4.01±0.05	0.0085			
	MS2-1	12*	3.14±0.08	0.0127			
XAs35	O	4*	1.69±0.01	0.0012	2.0	0.012	1.5
	Fe	4*	3.38±0.02	0.0108			
	S	2.6*	3.76±0.02	0.0028			
	As	1.4*	4.06±0.02	0.0043			
	MS2-1	12*	3.11±0.07	0.0040			
XAs37	O	4*	1.68±0.01	0.0010	-0.2	0.016	1.5
	Fe	4*	3.35±0.02	0.0091			
	S	2.5*	3.73±0.03	0.0038			
	As	1.5*	4.02±0.04	0.0064			
	MS2-1	12*	3.11±0.11	0.0079			
XAs47	O	4*	1.69±0.01	0.0014	1.4	0.009	1.5
	Fe	4*	3.39±0.03	0.0123			
	S	2*	3.76±0.03	0.0024			
	As	2*	4.07±0.04	0.0084			
	MS2-1	12*	3.12±0.09	0.0060			
XAs59	O	4*	1.68±0.01	0.0012	-0.5	0.015	1.5
	Fe	4*	3.35±0.02	0.0103			
	S	1.6*	3.70±0.03	0.0011			
	As	2.4*	4.02±0.06	0.0115			
	MS2-1	12*	3.15±0.18	0.0017			
XAs63	O	4*	1.68±0.01	0.0013	1.4	0.011	1.5
	Fe	4*	3.38±0.03	0.0045			
	S	1.5*	3.74±0.02	0.0015			
	As	2.5*	4.05±0.03	0.0089			
	MS2-1	12*	3.10±0.07	0.0045			
XAs75	O	4*	1.68±0.01	0.0014	-0.4	0.015	1.7
	Fe	4*	3.38±0.03	0.0151			
	As	3*	3.99±0.07	0.0155			
	MS2-1	12*	3.10±0.08	0.0039			

708 Fit performed in k-space (3-13 Å^{-1}); amplitude reduction factor (S_0^2) is constrained to 0.9 following its
709 optimization; N: coordination number; R: interatomic distance (Å); σ^2: Debye–Waller parameter (Å^2); $E0$:
710 energy offset (eV); rf: r-factor as goodness-of-fit; Ni/Nv: number of independent points/number of variables;
711 * Fixed value; Multiple scattering paths, MS2-1, MS3-1 and MS3-2 refer to As–O1–O2, As–O1–As–O2 and
712 As–O1–As–O1, respectively (Manceau et al. 2007); N and R values of MS3-1 and MS3-2 were fixed to their
713 crystallographic values (i.e. 12 at 3.34 Å and 4 at 3.34 Å, respectively) and their Debye-Waller parameters
714 were constrained to be identical with that of MS2-1; Numbers in sample labels next to XAs refer to
715 $100×AsO_4/(AsO_4+SO_4)$.

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718 **TABLE 5**. Iron XAFS fitting results

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Sample		N	R	σ^2	$E0$	rf
XAs0	O	6*	2.00±0.01	0.0054	-.03	0.017
	S	4*	3.38±0.02	0.0111		
	Fe1	2*	3.69±0.03	0.0122		
	Fe2	8*	5.12±0.02	0.0122[a]		
XAs8	O	6*	1.99±0.01	0.0062	-2.3	0.025
	S	3.7*	3.38±0.03	0.0147		
	Fe1	2*	3.69±0.03	0.0132		
	Fe2	8*	5.12±0.02	0.0132[a]		
XAs12	O	6*	1.99±0.01	0.0076	-3.6	0.039
	S	3.5*	3.34±0.03	0.0174		
	Fe1	2*	3.71±0.05	0.0163		
	Fe2	8*	5.10±0.03	0.0163[a]		
XAs34	O	6*	1.97±0.01	0.0094	0.6	0.027
	As	1.4*	3.32±0.06	0.0145		
	Fe1	2*	3.68±0.04	0.0193		
	Fe2	8*	5.14±0.04	0.0193[a]		
XAs35	O	6*	1.97±0.01	0.0093	0.8	0.026
	As	1.4*	3.32±0.04	0.0155		
	Fe1	2*	3.67±0.06	0.0200		
	Fe2	8*	5.14±0.04	0.0200[a]		
XAs47	O	6*	1.96±0.01	0.0106	0.9	0.027
	As	2*	3.31±0.02	0.0117		
	Fe1	2*	3.62±0.06	0.0201		
	Fe2	8*	5.18±0.04	0.0201[a]		
XAs62	O	6*	1.96±0.01	0.0111	0.8	0.031
	As	2.5*	3.32±0.02	0.0112		
	Fe1	2*	3.62±0.10	0.0241		
	Fe2	8*	5.17±0.06	0.0241[a]		
XAs75	O	6*	1.97±0.01	0.0110	2.6	0.029
	As	3*	3.34±0.02	0.0140		
	Fe1	2*	3.65±0.08	0.0213		
	Fe2	8*	5.17±0.04	0.0213[a]		

720 Fit performed in k-space (2.5-12 Å^{-1}); amplitude reduction factor (S_0^2) is constrained to 0.9 following its
721 optimization; N: coordination number; R: interatomic distance (Å); σ^2: Debye–Waller parameter (Å^2); $E0$:
722 energy offset (eV); rf: r-factor as goodness-of-fit; number of independent points/number of variables=2 for
723 all; * Fixed value optimized to crystallographic value; [a]: constrained to be identical with preceding Debye–
724 Waller parameter. Numbers in sample labels next to XAs refer to $100 \times AsO_4/(AsO_4+SO_4)$.

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728 **TABLE 6**. Arsenic XAFS fitting of pressure oxidation residues and bukovskýite

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		N	R	σ^2	$E0$	rf	Ni/Nv
POX-2	O	4*	1.68±0.01	0.0013	6.2	0.013	1.5
	Fe	4*	3.38±0.03	0.0129			
	S	2*	3.72±0.04	0.0055			
	As	2*	4.05±0.05	0.0097			
	MS2-1	12*	3.11±0.09	0.0081			
POX-9	O	4*	1.70±0.01	0.0019	7.8	0.032	1.6
	Fe	2*	3.43±0.04	0.0086			
	MS2-1	12*	3.13±0.07	0.0009			
POX-14	O	4*	1.69±0.01	0.0016	5.8	0.020	1.6
	Fe	2*	3.35±0.05	0.0133			
	MS2-1	12*	3.11±0.06	0.0010			
bukKH	O	4*	1.69±0.01	0.0014	5.8	0.011	1.7
	Fe	4*	3.36±0.02	0.0092			
	As	2*	3.95±0.06	0.0113			
	MS2-1	12*	3.10±0.07	0.0034			
bukKe	O	4*	1.69±0.01	0.0011	6.3	0.011	1.7
	Fe	4*	3.35±0.01	0.0077			
	As	2*	3.95±0.05	0.0113			
	MS2-1	12*	3.13±0.07	0.0045			

730 Fit performed in k-space (3-13 Å^{-1}); amplitude reduction factor (S_0^2) is constrained to 0.9 following its
731 optimization; N: coordination number; R: interatomic distance (Å); σ^2: Debye–Waller parameter (Å^2); $E0$:
732 energy offset (eV); rf: r-factor as goodness-of-fit; Multiple scattering paths, MS2-1, MS3-1 and MS3-2 refer to
733 As–O1–O2, As–O1–As–O2 and As–O1–As–O1, respectively (Manceau et al. 2007); * Fixed value; N and R
734 values of MS3-1 and MS3-2 were fixed to their crystallographic values (i.e. 12 at 3.34 Å and 4 at 3.34 Å,
735 respectively) and their Debye-Waller parameters were constrained to be identical with MS2-1; bukKH:
736 bukovskýite from Kutna Hora, Czech Republic; bukKe: bukovskýite from Ketza River Mine, Yukon, Canada;
737 POX-2, -9, -14 pressure oxidation residues from gold processing operations.

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741 **TABLE 7**. Fe-XAFS fitting of bukovskýite

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		N	R	σ^2	rf	$E0$
bukKH	O	6*	1.99±0.01	0.0084	0.029	-3.5
	As	2*	3.35±0.01	0.0076		
	Fe1	1*	3.62±0.02	0.0064		
	Fe2	1*	5.08±0.04	0.0064[a]		
bukKe	O	6*	1.99±0.01	0.0079	0.033	-4.4
	As	2*	3.34±0.01	0.0057		
	Fe1	1*	3.60±0.02	0.0058		
	Fe2	1*	5.09±0.04	0.0058[a]		

743 Fit performed in k-space (3-13 Å^{-1}); amplitude reduction factor (S_0^2) is constrained to 0.9 following its
744 optimization; N: coordination number; R: interatomic distance (Å); σ^2: Debye–Waller parameter (Å^2); $E0$:
745 energy offset (eV); rf: r-factor as goodness-of-fit; number of independent points/number of variables=2;
746 *:Fixed value optimized to crystallographic value; [a]: constrained to be identical with preceding Debye–Waller
747 parameter. bukKH: bukovskýite from Kutna Hora, Czech Republic; bukKe: bukovskýite from Ketza River
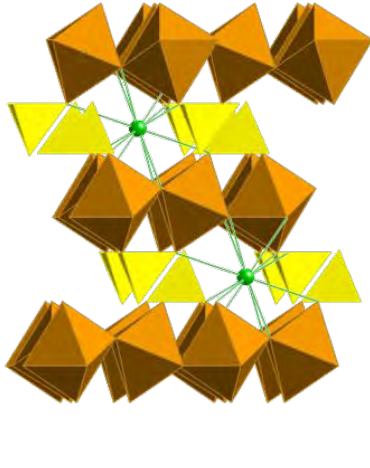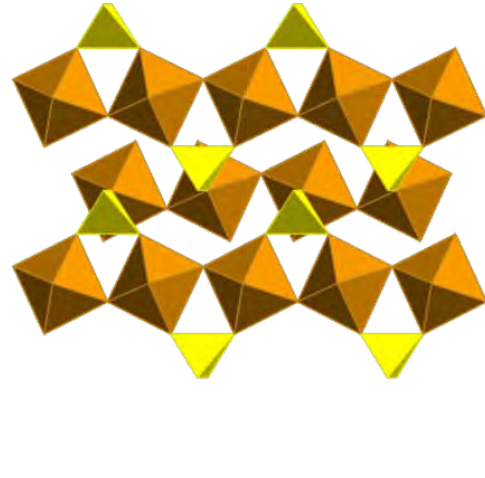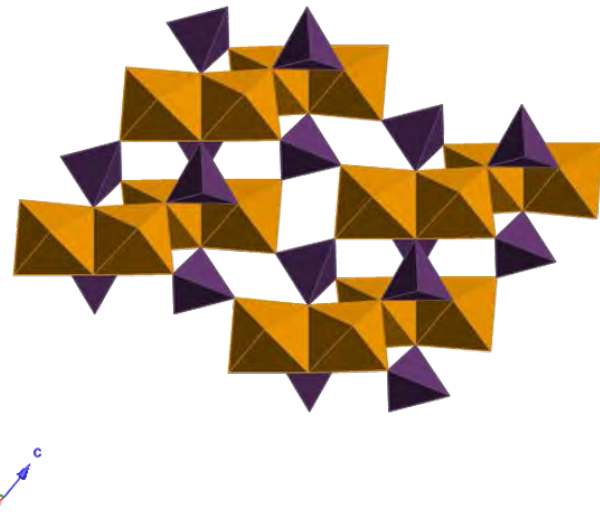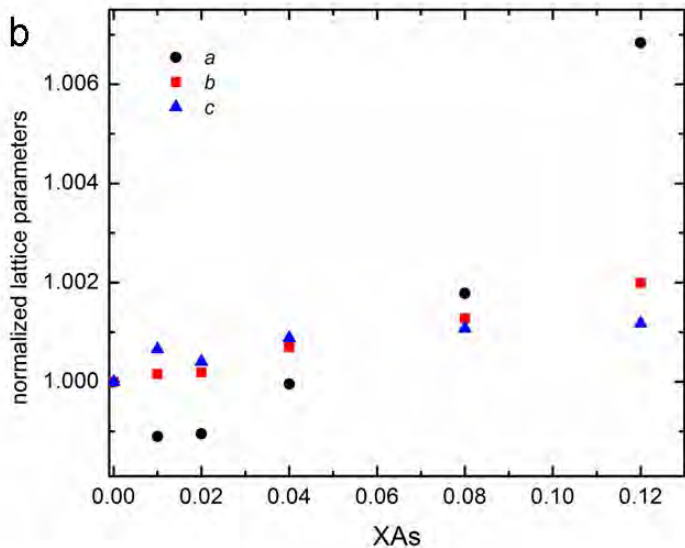748 Mine, Yukon, Canada.

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