1   *Revision 3*

2   **X-ray spectroscopy study of the chemical state of "invisible" Au in synthetic minerals in**

3   **the Fe-As-S system**

4

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1

Abstract

Minerals of the Fe-As-S system are the main components of Au ores in many

hydrothermal deposits, including Carlin-type Au deposits, volcanogenic massive sulfide

deposits, epithermal, mesothermal, sedimentary-hosted systems, and Archean Au lodes. The

"invisible" (or refractory) form of Au is present in all types of hydrothermal ores and often

predominates. Knowledge of the chemical state of "invisible" Au (local atomic

environment/structural position, electronic structure, and oxidation state) is crucial for

understanding the conditions of ore formation and necessary for the physical-chemical modeling

of hydrothermal Au mineralization. In addition, it will help to improve the technologies of ore

processing and Au extraction. Here we report an investigation of the chemical state of "invisible"

Au in synthetic analogues of natural minerals (As-free pyrite FeS_2, arsenopyrite FeAsS, and

löllingite $FeAs_2$). The compounds were synthesized by means of hydrothermal (pyrite) and salt

flux techniques (in each case) and studied by X-ray absorption fine structure (XAFS)

spectroscopy in a high energy resolution fluorescence detection (HERFD) mode in combination

with first-principles quantum chemical calculations. The content of "invisible" Au in the

synthesized löllingite (800±300 ppm) was much higher than that in arsenopyrite (23±14 ppm).

The lowest Au content was observed in zonal pyrite crystals synthesized in a salt flux. High

"invisible" Au contents were observed in hydrothermal pyrite (40-90 ppm), which implies that

this mineral can efficiently scavenge Au even in As-free systems. The Au content of the

hydrothermal pyrite is independent of sulfur fugacity and probably corresponds to the maximum

Au solubility at the experimental P/T parameters (450 °C, 1 kbar). It is shown that Au replaces

Fe in the structures of löllingite, arsenopyrite, and hydrothermal pyrite. The Au-ligand distance

increases by 0.14 Å (pyrite), 0.16 Å (löllingite), and 0.23 Å (As), 0.13 Å (S) (arsenopyrite)

relative to the Fe-ligand distance in pure compounds. Distortions of the atomic structures are

localized around Au atoms and disappear at $R > \sim 4$ Å. Chemically bound Au occurs only in

58   hydrothermal pyrite, whereas pyrite synthesized without hydrothermal fluid contains only Au°.

59   The heating (metamorphism) of hydrothermal pyrite results in the decomposition of chemically

60   bound Au and formation of Au° nuggets, which coarsen with increasing temperature. Depending

61   on the chemical composition of the host mineral, Au can play a role of either a cation or an

62   anion: the Bader atomic partial charge of Au decreases in the order pyrite (+0.4 e) > arsenopyrite

63   (0) > löllingite (-0.4 e). Our results suggest that other noble metals (platinum group elements,

64   Ag) can form a chemically bound refractory admixture in base metal sulfides/chalcogenides. The

65   content of chemically bound noble metals can vary depending on the composition of the host

66   mineral and ore history.

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Introduction

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69   Minerals of the Fe-As-S system (pyrite FeS_2, arsenopyrite FeAsS, and löllingite $FeAs_2$)

70   are ubiquitous in sulfide ores in many geologic environments and Au-bearing ore deposits,

71   including Carlin-type Au deposits (for example, Palenik et al., 2004, and reference therein),

72   volcanogenic massive sulfide (VMS) deposits (e.g. Mercier–Langevin et al., 2011; Vikentyev,

73   2015a), mesothermal (Genkin et al., 1998), epithermal (e.g. Cook et al., 2009), sedimentary-

74   hosted systems (Large et al., 2007), and Archean Au lodes (Goldfarb et al., 2005). These

75   occurrences are an important source of Au, and many of them belong to world-class gold

76   deposits (>100 t Au, c.f., Genkin et al., 1998; Mercier–Langevin et al., 2011). In these ores Au

77   exists (i) as discrete minerals – compounds with chalcogens (S, Se, Te), semimetals (As, Sb, Bi),

78   or intermetallic compounds with Cu, Ag, Hg, etc., and (ii) in an "invisible" (or refractory) state.

79   "Invisible" Au includes nanoscale particles and Au solid solutions. Neither form can be

80   identified by conventional optical or scanning electron microscopy. Visible nuggets of Au and

81   Au-alloys can be extracted from the ore using, for example, cyanide leaching, whereas

82   "invisible" Au cannot be extracted by conventional ore processing methods. In many deposits

83   the proportion of "invisible" Au can be very high. For example, it reaches 85% at the Uchaly

84   VMS deposit in the South Urals, Russia. The estimated total loss of Au from all VMS deposits of

85   the South Urals region is 10-15 t per year (Vikentyev, 2015a).

86   In hydrothermal ores, pyrite often shows the maximal concentrations of "invisible" Au.

87   In many cases, there is a positive correlation between Au and As in pyrite (e.g., Reich et al.,

88   2005; Deditius et al., 2014), although deposits with Au-rich and As-poor pyrite are also known.

89   For example, colloform pyrite bands and veinlets in the large Agua Rica Cu (Mo–Au) deposit

90   (Argentina) are As-poor (<30 ppm) but contain up to 6.7 ppm Au (Franchini et al., 2015). A

91   number of studies of Au-bearing deposits of the Urals (Russia), including VMS deposits

92   (Vikentyev, 2015a, 2015b), Novogodnee-Monto Fe-Au-skarn deposit (Ivanova et al., 2015), and

93   Svetlinsk Au-Te deposit (Vikent'eva and Bortnikov, 2015), did not reveal any significant

94   correlation between Au and As in pyrite. Hence, depending on the deposit type and ore

95   formation conditions, both As-rich and As-poor pyrites can bear economic Au content, although

96   the highest Au contents were documented in arsenian pyrites.

97   The understanding of the chemical state of "invisible" Au in sulfide ores is necessary for

98   the physical-chemical modeling of hydrothermal Au mineralization and has important

99   implications for the mineral processing industry. The chemical state of "invisible" Au, including

100   its local atomic environment, position in the host mineral structure in the case of solid solution,

101   and valence state can be reliably determined only by spectroscopic methods. Previously, Au-

102   bearing sulfides were studied by X-ray photoelectron (XPS, see Widler and Seward, 2002 and

103   reference therein; Laptev and Rozov, 2006), Mössbauer (Cardile et al., 1993; Genkin et al.,

104   1998; Kozerenko et al., 2001), and X-ray absorption near edge structure (XANES) spectroscopy

105   (Simon et al., 1999; Cabri et al., 2000). Our study aims at determining the chemical state of

106   "invisible" Au in pyrite, arsenopyrite, and löllingite (FeAs$_2$) by X-ray absorption spectroscopy

107   (XAS) in a high energy resolution fluorescence detection mode (HERFD), with emphasis on Au

108   solid solution. To estimate the conditions favoring formation of this form of "invisible" Au, we

109   synthesized Au-bearing chalcogenides using different methods (hydrothermal and salt flux) at

110   contrasting T/f(S$_2$) conditions, characterized the amount and distribution of Au, and determined

111   the local environment of Au using XAS. An *in situ* heating experiment was performed to

112   estimate the effect of metamorphism on chemically bound Au in pyrite. The experimental data

113   were combined with first-principles quantum chemical calculations and Bader charge analysis in

114   order to reveal the local atomic environment and oxidation state of Au in pyrite, arsenopyrite,

115   and löllingite.

116

117   **Methods**

5

Mineral synthesis and analytical methods

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119   Synthesis experiments were performed using hydrothermal (450 °C, 1 kbar) and salt flux

120   (520 – 650 °C) methods. Saturation with respect to $Au_{(cr)}$ was achieved in all experiments by

121   placing a piece of Au foil or wire in the autoclave or silica glass ampoule together with initial

122   reagents. The hydrothermal method was used for pyrite synthesis only; the salt flux method was

123   employed to obtain crystals of Au-bearing pyrite, arsenopyrite, and löllingite. The chemical

124   composition of the synthesized phases was determined by electron microprobe analysis (EPMA)

125   and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The chemical

126   composition of hydrothermal pyrite was determined by wet chemistry. Details of the synthesis

127   procedures and analytical methods are given in Supplementary Methods.

128

X-ray absorption spectroscopy (XAS)

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130   XAS spectra of Au-bearing pyrite, arsenopyrite, löllingite, and other substances (Au foil

131   and synthetic Au_2S, $AuSb_2$ and Au_2Bi) were collected at high-brilliance X-ray absorption and X-

132   ray emission spectroscopy undulator beamline ID26 (Gauthier et al., 1999) of the European

133   Synchrotron Radiation Facility (ESRF) at Grenoble. The incident energy was selected using the

134   <111> reflection from a double Si crystal monochromator. The rejection of higher harmonics

135   was achieved by three Cr/Pd mirrors positioned at an angle of 2.5 mrad relative to the incident

136   beam. The flux of the incident X-ray beam was approximately $2 \cdot 10^{13}$ photon s^{-1} on the sample

137   position. XANES spectra were simultaneously measured in the total fluorescence yield (TFY)

138   mode using a photodiode and in the high energy resolution fluorescence detection (HERFD)

139   mode using an X-ray emission spectrometer (Glatzel and Bergmann, 2005; Kvashnina and

140   Scheinost, 2016). The sample, analyzer crystal, and photon detector (silicon drift diode) were

141   arranged in a vertical Rowland geometry. The Au XANES/EXAFS HERFD spectra at the L_3

142   edge were obtained by recording the intensity of the Au $L\alpha_1$ emission line (9713 eV) as a

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143 function of the incident energy. The emission energy was selected using the <660> reflection of

144 four spherically bent Ge crystal analyzers (1 m curvature radius) aligned at 80° Bragg angle. A

145 combined (incident convoluted with emitted) energy resolution of 1.2 eV was determined by

146 measuring the elastic peak. The intensity was normalized to the incident flux.

147 For the heating experiment, a powder of hydrothermal pyrite was loaded into a silica

148 glass capillary (Polymicro Technologies^{TM}, 350 μm OD, 200 μm ID, 20 mm length) together

149 with a small amount of sulfur, which prevented sample oxidation and fixed sulfur fugacity $f(S_2)$

150 during the experiment. The capillary was evacuated and hermetically sealed. This simple

151 experimental technique was developed by Chou et al. (2008, 2012) and Ding (2010) for the

152 Raman spectroscopy of solids and liquids, and we adopted it for the synchrotron experiment. For

153 *in situ* XAS measurements, the capillaries were placed into a microtomography furnace (Bellet et

154 al., 2003). Temperature was measured by a K-type thermocouple in contact with the capillary at

155 an accuracy of ±5 °C.

156

157 **Density Functional Theory (DFT) calculations**

158 The QUANTUM ESPRESSO software package (Giannozzi et al., 2009) was used for

159 quantum chemical DFT calculations. We employed a projector-augmented wave (PAW) all-

160 electron description of electron-ion-core interactions (Blöhl, 1994; Kresse, 1999) and the

161 Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. For the electronic structure

162 calculations, the self-consistent field (SCF) method was applied with a 100 Ry kinetic energy

163 cutoff for the plane waves, a 1500 Ry charge density cutoff, and an SCF tolerance better than 10^{-9}.

164 ^{9}. The relaxation of atomic positions and cell parameters was performed in a supercell containing

165 2×2×2 unit cells for the pyrite and arsenopyrite, and 2×2×3 unit cells for the löllingite.The

166 crystal structure and supercell parameters were optimized using the BFGS algorithm for atomic

167 coordinates with a convergence threshold of 10^{-3} Ry/au for forces and 10^{-4} Ry for energy.

7

168   Topological atomic charges were determined from the quantum theory of atoms in molecules

169   (QTAIM). The local atomic charges were calculated by integrating the charge density within

170   Bader volumes around the atoms (Otero-de-la-Roza et al., 2009, 2014).

171

172   **EXAFS spectra analysis**

173   The analysis of EXAFS spectra provided insight into the Au local atomic environment.

174   The EXAFS data ($\chi_{exp}(k)$) were analyzed using the IFEFFIT software package (Ravel and

175   Newville, 2005). After the standard procedures of pre-edge subtraction and spline background

176   removal, interatomic distances (R_i), coordination numbers (N_i), and Debye–Waller factors (σ^2)

177   were determined by the non-linear fitting of experimental data with the theoretical spectrum

178   described by the equation

179    $$\chi(k) = S_0^2 \sum_{i=1}^{n} \frac{N_i F_i(k)}{R_i^2 k} e^{\frac{-2R_i}{\lambda(k)}} e^{-2\sigma_i^2 k^2} \sin(2kR_i + \varphi_i(k)) \qquad . \qquad (1)$$

180   The parameters necessary for the simulation of the theoretical spectra (photoelectron mean free

181   path $\lambda(k)$, amplitude $F_i(k)$, phase shift $\varphi_i(k)$) were calculated *ab initio* using the FEFF6 program

182   (Zabinsky et al., 1995). The statistical uncertainty of the calculation method is 0.01–0.02 Å for

183   refined R_i in the first coordination shell.

184

185   **XANES spectra simulation**

186   Theoretical calculations of Au L_3 edge XANES spectra were performed using two

187   approaches: finite difference method (FDM) and full multiple scattering (FMS). The FDM is

188   implemented in the FDMNES code (Joly, 2001; Guda et al., 2015). Relativistic self-consistent

189   field FDMNES calculations were carried out with the exchange-correlation part of the potential

190   in a local density approximation (Hedin and Lundqvist, 1971). The final electronic states were

191   calculated in a full core hole screening. Atomic clusters inside the spheres with radii of 8 Å and 7

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192   Å were chosen for self-consistent calculations and FDM XANES calculations, respectively. To

193   account for many body effects and core hole lifetime broadening, the arctangent convolution was

194   applied (Bunău and Joly, 2009). Although the FDMNES procedure is computationally

195   expensive, it is best for systems with non-spherical charge distribution.

196   The FMS spectra modeling was performed using the FEFF9.6 revision 4 code (Rehr et

197   al., 2010), which is based on the self-consistent muffin-tin potentials. The Dirac-Hara exchange-

198   correlation potentials were used. The parameter for the imaginary potential was set to -2 to

199   account for the reduced broadening of HERFD-XANES spectra. Self-consistent calculations

200   were refined with a radius of 6 Å around the central Au atom, whereas a radius of 7 Å was

201   chosen for FMS calculations. The RPA core hole approximation was applied to simulate the

202   central excited atom.

203
204   **Results**

205   **Au content and distribution in synthesized minerals**

206   **Pyrite FeS$_2$.** The contents of Au in the hydrothermal pyrites and coexisting aqueous fluid

207   (450 °C, 1 kbar) are presented in Supplementary Table S1. The hydrothermal pyrite is a fine-

208   grained aggregate of particles <10 µm in size (Fig. 1a). The powder is free of metallic Au and,

209   therefore, the total Au content determined by the dissolution of the pyrite samples corresponds to

210   "invisible" Au. We note here that the synthesis of pyrite free of metallic Au inclusions was

211   possible only in acidic solutions with a low concentration of dissolved Au. Our attempts to

212   increase the content of "invisible" Au in pyrite using weakly alkaline solutions with high

213   aqueous Au concentrations (up to 0.1 mol·kg H$_2$O^{-1}, or 2·10^5 ppm) yielded a mixture of pyrite

214   and Au metal (Fig. S1). The content of Au in pure FeS$_2$ grains obtained in these experiments was

215   close to the EPMA detection limit of 100 ppm.

216   Sulfur fugacity was buffered in the hydrothermal experiments owing to elemental sulfur

217   dissolution and hydrolysis reactions (see Supplementary Methods). The concentration of Au in

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218   aqueous fluid increases with increasing $f(S_2)$ (Fig. 1b). The slope of the linear fit of the

219   experimental Au solubility vs. $f(S_{2(g)})$ is $S = 0.67$ in the logarithmic scale. This means that

220    $AuHS^\circ_{(aq)}$ dominates aqueous Au speciation. For this complex $S = 0.5$, which is consistent with

221   the reaction

222         $$Au_{(cr)} + \mathbf{0.5}\ S_{2(g)} + 0.5\ H_{2(g)} = AuHS^\circ_{(aq)} \qquad , \qquad\qquad (2)$$
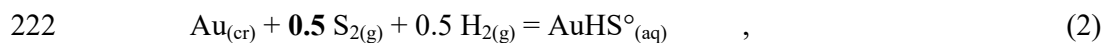
223   because $f(H_{2(g)})$ is the same for all experimental points (except for the S + H_2SO_4 experiment).

224   The observed increase of the slope could be caused by the presence of $Au(HS)_2^-$ and/or

225   uncertainty of the calculated $f(S_{2(g)})$ values.

226   The effect of $f(S_{2(g)})$ on the content (solubility) of Au in solid sulfide determines the

227   stoichiometry of the solubility reaction (number of S_2 molecules interacting with Au to form Au-

228   bearing sulfide)

229    $$Au_{(cr)} + n/2\ S_{2(g)} = AuS_{n(sulfide)} \qquad\qquad\qquad (3)$$

230   and, therefore, the Au/S ratio and the formal oxidation state of Au in the sulfide. In contrast to

231   the Au solubility in aqueous fluid, the content of Au in hydrothermal pyrite is weakly sensitive to

232    $f(S_2)$ and oxidation potential and always falls within the 40 – 90 ppm range (Table S1). We

233   consider a value of ~100 ppm as an upper Au concentration limit for the T/P conditions of the

234   synthesis experiments. Formally, the slope $S \sim 0$ may indicate that Au does not interact with

235   dissolved sulfur and, therefore, the Au oxidation state in the sulfide remains unchanged.

236   However, the real structural position and valence state of Au distributed in the sulfide mineral

237   matrix could be determined only by spectroscopic experiments described in the following

238   section.

239   Grains of high-temperature pyrite synthesized at 620 °C using the salt flux method show

240   zonal Au distribution with $C(Au)$ ranging from the LA-ICP-MS detection limit to several

241   hundred ppm (Table S2). The smooth character of the Au time-resolved LA-ICP-MS spectra

242   (Fig. S2) suggests that microscopic and submicroscopic inclusions of Au are absent. It is

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243   interesting that, in addition to Au, this pyrite sample contains several ppm Pt, which was

244   accidentally introduced into the charge.

245   **Arsenopyrite FeAsS and löllingite FeAs$_2$.** Examples of arsenopyrite and löllingite

246   crystals are shown in Supplementary Figs. S3 and S4, respectively. Two types of LA-ICP-MS

247   spectra were obtained for the arsenopyrite. The first type shows Au-rich (hundreds of ppm) and

248   Au-poor (up to 30 ppm) zones (top of Fig. S5), and the second type corresponds to

249   homogeneously distributed Au at C(Au) ~10 ÷ 30 ppm (Fig. S5, bottom). In the löllingite Au is

250   distributed homogeneously at C(Au) = 800 ± 300 ppm (Fig. S6).

251

252   **XANES spectroscopy**

253   **Ambient temperature experiment.** The HERFD-XANES spectroscopic technique could

254   be used to acquire Au L$_3$ edge spectra not only for pyrite but also for arsenopyrite and löllingite,

255   in which the signal from the trace amount of "invisible" Au is masked by the As K edge in the

256   TFY mode (Fig. 2). Another advantage of this technique is that the weak features of Au(I)

257   spectra are considerably enhanced compared with TFY spectra, which facilitates interpretation

258   and modeling. Figure 3a shows Au L$_3$ edge HERFD-XANES spectra of Au-bearing pyrite

259   (hydrothermal), arsenopyrite, and löllingite together with spectra of model substances. All these

260   minerals contain Au in the chemically bound state that is different from both Au$_{(cr)}$ and Au$_2$S.

261   The positions of the edge jump (e.j.) and the first intense feature (white line, WL) are given in

262   Table 1. We observed a significant positive energy shift of the e.j. position increasing in the

263   order pyrite < arsenopyrite < löllingite. A positive e.j. shift usually indicates an increase in the

264   positive charge of the excited atom. However, we will show below that this is not the case for the

265   Fe-As-S system.

266   The Au L$_3$ edge absorption is related to $2p$-$5d$ dipole-allowed transitions: $2p_{3/2} \rightarrow$

267    $5d_{5/2}/5d_{3/2}$. Therefore, the WL intensity reflects the number of empty states in the $5d_{5/2}$ and $5d_{3/2}$

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268   orbitals above the Fermi level. The WL intensity for arsenopyrite and löllingite is much greater

269   than that for pyrite (Fig. 3a), indicating a higher number of holes in the $5d$ electronic shell of As-

270   bearing minerals. Another important characteristic of the Au L_3 edge HERFD-XANES spectra of

271   these minerals is the negative correlation between the intensity of the second feature at ~11929

272   eV and As content. This can be clearly seen in the spectra of Au-bearing pyrite, the arsenopyrite

273   spectra contain only traces of the feature, and it is absent in the löllingite spectra.

274   A comparison of the spectra of arsenopyrite and löllingite with those of synthetic $AuSb_2$

275   and Au_2Bi revealed a significant positive shift of the e.j. position increasing in the order $Au_2Bi <$

276    $AuSb_2 <$ Au in arsenopyrite < Au in löllingite (Fig. 3b, Table 1). This order corresponds to a

277   decrease in the number of the chemical element in the 15th group of the periodic system and

278   implies that Au is chemically bound to As in the arsenopyrite and löllingite matrices.

279   **Pyrite heating experiment.** This experiment (Fig. 4) was aimed at modeling the

280   behavior of chemically bound "invisible" Au during hydrothermal ore metamorphism. The

281   spectra collected at ambient temperature indicate different chemical states of Au in hydrothermal

282   and salt flux pyrites. Chemically bound "invisible" Au exists only in the hydrothermal pyrite.

283   Well-crystallized large pyrite grains formed in the eutectic anhydrous chloride mixture contain

284   mostly metallic Au°. Heating of the hydrothermal pyrite to 460 °C results in the decomposition

285   of the Au-bearing phase and precipitation of Au°. Note that this process takes place even in the

286   presence of $S_{(liq)}$, which should promote the formation of an Au-bearing solid solution (Eq. 3).

287   Further heating to 630 °C results in a dramatic drop of the XAFS signal; the spectrum collected

288   at this temperature indicates traces of chemically bound Au. This can be explained by the

289   coalescence of Au nanoparticles. These data are consistent with the analyses of natural Au-

290   bearing arsenopyrite reported by Wagner et al. (2007), which showed that metamorphism caused

291   Au depletion in arsenopyrite. The irreversible coarsening of Au nanoparticle during arsenian

292   pyrite heating was observed by means of in situ transmission electron microscopy (Reich et al.,

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293   2006). Our results demonstrate that the heating (metamorphism) of Au-bearing pyrite results in

294   the decomposition of chemically bound "invisible" Au incorporated into the hydrothermal pyrite

295   matrix during ore formation.

296

297   **EXAFS analysis**

298   The EXAFS spectra of pyrite and löllingite are shown in Fig. 5. Contamination with

299   metallic Au° hampered the collection of good quality EXAFS spectra for arsenopyrite; therefore,

300   only the XANES region was used to characterize the chemical state of Au in this mineral. The

301   EXAFS spectra of pyrite and löllingite (Fig. 5, top) are different: the maxima of the EXAFS

302   function of the latter are clearly shifted to higher k values. The main peak in the Fourier

303   transforms (FTs) of the löllingite EXAFS function (Fig. 5, bottom) lies at higher R values,

304   reflecting a larger Au-L distance in the first coordination shell. The results of the least-squares fit

305   of the FTs are shown by thick red lines in Fig. 5, and the calculated model parameters are given

306   in Table 2. For both minerals, the best fit of the experimental spectra is achieved for Au

307   occupying the position of Fe in the mineral structure. In these minerals (see Supplementary

308   Structures), the metal atom is octahedrally coordinated. In the structure of pyrite, the first

309   neighbors of Au are 6 S atoms at 2.40 Å distance; in the structure of löllingite, 6 As atoms at

310   2.52 Å. Due to the large Au ionic radius, the Au-L distances increase by 0.14 Å and 0.16 Å

311   relative to the crystal structures of pure pyrite and löllingite. Fitting of the first coordination shell

312   of Au yielded $N = 5.9\pm1.5$ and 5.3 ± 0.8 for pyrite and löllingite, respectively, confirming the

313   octahedral coordination of Au in these minerals. The distortion of the local environment around

314   Au in pyrite decreases to $0.06 - 0.08$ Å for S atoms in the second coordination shell, and the Au-

315   Fe distance for the nearest Fe atoms at ~3.8 Å remains almost unchanged (within 0.04 Å).

316   Similar relations are observed for löllingite: the distortion of the crystalline structure decreases

317   for distant coordination shells and disappears at $R > 4.2$ Å.

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318

DFT calculations

320   Interatomic distances optimized by the DFT method for pyrite and löllingite are given in

321   Table 2. In the case of löllingite, good agreement is observed between the simulated structure

322   and the results of the EXAFS spectra fitting for the first and second neighbors (±0.02 Å for the

323   first coordination shell at 2.5 Å and ±0.03 Å for the second shell at 3 Å). Similar results were

324   obtained in our recent study of Au-bearing covellite CuS, the EXAFS model of which was

325   adequately reproduced by DFT simulation at distances up to 4 Å (agreement between DFT

326   calculations and EXAFS fitting was within 0.01 – 0.04 Å depending on the distance) (Tagirov et

327   al., 2016). Based on these results, we can suggest that our method of DFT calculation reproduces

328   the atomic coordinates of Au-bearing chalcogenides within ±0.02 and 0.04 Å, at least for the first

329   two coordination shells located at distances up to 3 Å.

330   In the case of pyrite, the agreement between the DFT simulation and EXAFS fit is poor:

331   the difference is 0.055 Å for the first neighbors around Au atom. This fact can be explained by

332   the thermodynamic instability of Au-bearing pyrite, the structure of which cannot be accurately

333   reproduced by equilibrium structure relaxation methods. This inference is consistent with the

334   results of the pyrite heating experiment, in which chemically bound Au was decomposed at high

335   temperature and escaped from the FeS_2 matrix. This is opposite to the general rule that an

336   increase in temperature tends to stabilize solid solutions.

337   Table 3 reports the results of the DFT simulation of the local atomic environment of Au-

338   bearing arsenopyrite. The distances Au-S and Au-As in the first coordination shell increase by

339   0.13 Å and 0.23 Å, respectively. The Au-Fe distance for the nearest two Fe atoms increases by

340   0.25 Å relative to pure arsenopyrite. This model was checked by the results of Au L_3 edge

341   HERFD-XANES spectra simulation, which is described below.

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343   **XANES spectra simulation**

344   The results of Au L_3 edge HERFD-XANES spectra modeling are shown in Fig. 6a-c. The

345   FDMNES simulation of Au in pyrite spectrum (Fig. 6a) overestimates the WL intensity and

346   shifts the second feature by ~-2 eV relative to the experimental spectrum. This disagreement

347   probably stems from the metastable nature of "invisible" Au in pyrite, which leads to

348   discrepancies in FDM SCF-based spectra modeling. The spectrum calculated using the FEFF9

349   computer code is given for comparison. The agreement between the experimental and simulated

350   spectra is good, with the exception of the third diffuse feature with a centroid at ~11945 eV,

351   which is absent in the calculated spectrum.

352   The simulated spectrum of löllingite is in good agreement with the experimental one (Fig.

353   6b). The only difference is the overestimated width of WL. The intensity and positions of the

354   spectral features for Au-bearing arsenopyrite are correctly reproduced by the FDMNES

355   calculation (Fig. 6c), which supports our results of DFT calculation for this mineral.

356   Theoretical FDMNES calculations showed that the second feature in the spectra of Au

357   bearing pyrite and arsenopyrite (at ~11929 eV) originates mostly from the mixing of hybridized

358   Au p,d and S p orbitals. At this energy, the contribution of As p empty valence states to chemical

359   bond formation is weak for arsenopyrite and negligible for löllingite. This is why the second

360   feature is intense in the spectra of Au-bearing pyrite and absent in the löllingite spectra.

361   Despite the fact that both the FDMNES and FEFF programs calculate charge states using

362   the muffin-tin approximation, the FEFF code is known to be more efficient for systems with

363   isotropic potential compared with systems with anisotropic potential, whereas the FDMNES

364   program successfully reproduces charge states and spectral features in systems of both types.

365   The fact that the theoretical spectra of Au-bearing pyrite obtained by the FEFF code are in close

366   agreement with the experimental Au L_3 edge XANES is indicative of a highly symmetric

367   environment (octahedral) of Au in pyrite, rather than a linear coordination like that in Au_2S.

15

368

369   **The valence state of "invisible" Au**

370   The results of the Bader analysis of electron density performed using QTAIM for the

371   pure and Au-bearing minerals are summarized in Table 4. The partial atomic charge of S in

372   pyrite is more negative than that of As in löllingite (-0.7 e for disulfide group in pyrite vs. -0.08 e

373   for As in löllingite). The topological charge of As in arsenopyrite is +0.18 e, whereas S is

374   negatively charged (-0.6 e). These atomic partial charges reflect the distribution of delocalized

375   electrons and are in line with Pauling electronegativity: $\chi(S) = 2.58 >> \chi(As) = 2.18$ (Huheey et

376   al., 2000). In the Au-bearing minerals discussed here, the atomic charge of Au increases in the

377   order löllingite < arsenopyrite < pyrite. Au is positively charged in the pyrite, nearly neutral in

378   the arsenopyrite, and negatively charged in the löllingite. Note that the charge of Au in the

379   löllingite is much more negative than that of As. This is explained by the fact that Au is the most

380   electronegative metal ($\chi(Au) = 2.54$) whose electron affinity is higher than that of semi-metals.

381

382   **Discussion and implications**

383   The results of our study demonstrate that Au substitutes for Fe in the crystal structures of

384   pyrite, arsenopyrite, and löllingite. However, the chemical nature of "invisible" Au in these

385   minerals is different. In pyrite, chemically bound Au is formed only in the presence of

386   hydrothermal solution. This is consistent with the results of Widler and Seward (2002) on Au

387   adsorption by pyrite. They found that Au can be efficiently scavenged by natural and synthetic

388   pyrites from acidic aqueous solutions in which $AuHS^{\circ}_{(aq)}$ is the dominant Au complex. Similar

389   Au adsorption isotherms were observed for As_2S_3 and Sb_2S_3 by Renders and Seward (1989). In

390   view of these results, our observation of independence of Au concentration in pyrite on $f(S_2)$

391   (and, consequently, on $AuHS^{\circ}_{(aq)}$ concentration) can be attributed to the attainment of the

392   maximum pyrite sorption capacity with respect to Au. In contrast, pyrite grains synthesized in a

16

393   dry salt melt contain only Au°. Furthermore, heating of hydrothermal pyrite in a dry system

394   results in the decomposition of chemically bound Au.

395   The XPS measurements by Widler and Seward (2002) on Au-bearing pyrites showed that

396   the chemical state of Au in pyrite is different from Au°. The Au $4f_{7/2}$ electron binding energy

397   (BE) is 84.8 eV for Au in pyrite, whereas BE = 84.0 eV for metallic Au. A similar value of BE =

398   85.1 eV was obtained for Au-bearing pyrite synthesized at 200 °C (Laptev and Rozov, 2006).

399   This value is higher than Au $4f_{7/2}$ BE in Au_2S, where Au is linearly coordinated with two S atoms

400   (BE_{Au/Au_2S} ~84 eV, Tagirov et al., 2014) implying different local environments of Au in pyrite

401   and Au_2S. However, the core level XPS technique is less sensitive to local atomic environment

402   geometry and chemical bonding compared to XAFS spectroscopy, which is appropriate for

403   reliable determination of the chemical state of Au.

404   The present study and experimental investigations of Au-bearing As-free pyrites (Fadeev

405   and Kozerenko, 1999; Kozerenko et al., 2001; Widler and Seward, 2002; Laptev and Rozov,

406   2006) combined with data on Au contents in sulfide ores from different geologic environments,

407   suggest that pyrite can efficiently uptake Au even in As-poor systems, if large amounts of

408   hydrothermal ore are rapidly formed. Such a process may occur, for example, in hydrothermal

409   black smoker systems where fine-grained sulfides are formed owing to the mixing of

410   hydrothermal solutions with cold oxidized seawater (Bortnikov et al., 2003; Grichuk, 2012). The

411   content of chemically bound "invisible" Au in As-free pyrite determined in the present study for

412   450 ° (tens of ppm) is somewhat lower than the maximum values of ~100 ppm measured in

413   pyrite synthesized at 200 °C (Laptev and Rozov, 2006) and ~100 - 300 ppm in the ambient-

414   temperature sorption experiments of Widler and Seward (2002). Neglecting differences in

415   surface area or grain size, which is usually within 1÷n×10 μm for fine-grained pyrite, the

416   maximum content of chemically bound Au in As-free hydrothermal pyrite formed at 25-450 °C

417   can be estimated as 30 ppm < C(Au) < 300 ppm. A temperature increase tends to reduce the Au

17

418   content, which is partly compensated by the stabilization and enrichment of AuHS°$_{(aq)}$ in high-

419   temperature solution/fluid (Stefánsson and Seward, 2004). The maximum content of chemically

420   bound "invisible" Au in hydrothermal pyrite can be roughly estimated as 100-300 ppm at 25 °C,

421   ~150 ppm at 100 °C, ~100 ppm at 200 °C, and 100-50 ppm at 300-500 °C; a retrograde behavior

422   is thus evident. One should expect that excess Au will be present in the metallic state. This

423   behavior of "invisible" Au in synthetic pyrite is consistent with published data on natural

424   minerals (e.g. Fig 9a in Deditius et al., 2014).

425   In contrast to pyrite, Au can form an isomorphous solid solution in arsenopyrite and

426   löllingite even at high temperatures (> 500°C) in the absence of aqueous fluid. This suggests a

427   thermodynamic stability of this form of chemically bound Au in these minerals. The maximum

428   content of chemically bound "invisible" Au is tens ppm for arsenopyrite and hundreds ppm for

429   löllingite. Our data are consistent with natural observations, which show that As stabilizes Au-

430   bearing sulfides and leads to an increase in Au content (c.f., Reich et al., 2005; Deditius et al.,

431   2014). Further insight into the speciation of chemically bound Au can be drawn from the fact

432   that As substitutes for S in pyrite with formation of an isomorphous solid solution showing

433   significant clustering of As atoms (Zotov et al., 1972, Savage et al., 2000; Reich and Becker,

434   2006). However, more spectroscopic data are necessary to determine unambiguously the

435   chemical state of As and Au in arsenian pyrite.

436   A comparison of the Au L$_3$ edge HERFD-XANES spectra shows that edge energy (e.j.)

437   increases when As replaces S in the order pyrite < arsenopyrite < löllingite (Table 1, Fig. 3a).

438   Usually, the atomic charge increases in the same order, becoming more positive at higher e.j.

439   (higher energy is necessary to excite the core level electron). However, the data in Table 4 show

440   that the opposite is true: the Au charge is positive in pyrite and negative in löllingite. Such an e.j.

441   behavior cannot be explained by the effect of the atomic charge alone and needs further

442   examination.

18

443   The WL position and intensity indicate that the number of Au $5d$ unoccupied electronic

444   states increases in As-bearing phases relative to pyrite, despite the fact that Au is more

445   electronegative than As. This peculiarity can be explained by the charge compensation model

446   describing the charge flow in Au alloys (Watson et al., 1971). In this model, the Au d-charge loss

447   upon alloying is overcompensated by conduction (mainly s-p) charge gain from the second alloy

448   component. As a result, Au gains an overall negative charge (see Kuhn and Sham, 1994;

449   Bzowski et al., 1995, and reference therein).

450   The fact that the valence state of Au can vary depending on the host mineral composition

451   (Table 4) demonstrates that coupled charge-compensation substitution is not necessary for the

452   formation of isomorphous solid solutions in crystals with highly covalent chemical bonds.

453   Along with Au, other noble metals (platinum group elements, Ag) often occur as an

454   "invisible" admixture in sulfide ore (c.f., Filimonova et al., 2015, and reference therein).

455   Considering their chemical state in sulfide minerals from the point of view of our study, we

456   suggest that these metals can also form a chemically bound refractory admixture. The chemical

457   state and the concentration of this form of noble metals can vary with the local atomic

458   environment/structural position and valence state depending on the composition of host sulfide

459   and ore origin (e.g., hydrothermal, magmatic, or metamorphic). Further spectroscopic studies,

460   including in situ X-ray absorption/emission spectroscopy at high T/P parameters, will help to

461   determine the chemical state of noble metals and mechanisms of ore-forming processes.

462

19

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638

639   **Table 1.** Position of edge jump (e.j.) and white line (WL) of

640   Au L_3 edge HERFD-XANES spectra. Uncertainty is ± 0.2 eV.

Sample/Standard	Feature	Position, eV
Löllingite $FeAs_2$	e.j. WL	11920.1 11922.0
Arsenopyrite FeAsS	e.j. WL	11919.7 11921.5
Hydrothermal pyrite FeS_2	e.j. WL	11918.6 11920.3
$AuSb_2$	e.j. WL	11919.4 11920.0
Au_2Bi	e.j. WL	11918.6 11921.2
Au_2S	e.j. WL	11919.0 11921.3
Au metal	e.j. WL	11918.1 11921.1

641

642

643 **Table 2.** Au local atomic structure in pyrite and löllingite determined by EXAFS fitting and

644 DFT calculations. The last column shows interatomic distances for the unrelaxed structure of

645 pure minerals. Uncertainties are calculated by the Artemis code.

646

Bond	EXAFS					Quantum Espresso R, Å	Crystal structure[1]
	N	R, Å	σ^2, Å^{-2}	E^0, eV	Fit quality, R-factor		
Au in pyrite							
Au-S	6	2.40±0.028	0.014±0.0014			2.455	2.264
Au-S	6	3.51±0.16	0.027±0.024	6.4± 3.5	0.005	3.499	3.445
Au-S	2	3.69±0.11	0.008±0.018			3.854	3.613
Au-Fe	12	3.79±0.19	0.034±0.023			3.577	3.830
Au in löllingite							
Au-As	6	2.52±0.007	0.005±0.00003			2.536	2.361
Au-Fe	2	3.00±0.025	0.006±0.002			2.973	2.882
Au-As	4	3.88±0.032	0.006±0.004			3.739	3.726
Au-As	6	4.06±0.056	0.006±0.004	1.2± 1.9	0.011	3.984	3.927
Au-Fe	8	4.23±0.032	0.008±0.007			4.261	4.249
Au-As	4	4.67±0.054	0.004±0.010			4.737	4.723
Au-As	6	4.82±0.058	0.004±0.010			4.869	4.871

[1] unrelaxed structures: Bayliss (1977) for pyrite and Lutz et al. (1987) for löllingite.

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28

648 **Table 3.** Au local atomic structure in arsenopyrite determined by DFT
649 calculations compared to the unrelaxed structure of pure arsenopyrite.
650

Bond	N	Quantum Espresso R, Å	Crystal structure[1] R, Å
Au-S	3	2.466	2.231
Au-As	3	2.530	2.397
Au-Fe	2	2.984;3.655	2.734;3.741
Au-S	4	3.719;3.739;3.779; 3.781	3.681;3.725;3.762;3.762
Au-As	4	3.791;3.811;3.913;3.919	3.693;3.3.755;3.755;3.798

[1] unrelaxed structure from Bindi et al. (2012).

651
652 **Table 4.** Calculated Bader atomic partial charges for pure
653 and Au-bearing pyrite, löllingite, arsenopyrite, and for
654 $Au_2S_{(cr)}$. Literature data (Tagirov et al., 2016) on charges
655 of atoms in covellite CuS are given for comparison.
656

Au	Fe	As	S
FeAs$_2$			
	+0.16	-0.08	
FeAsS			
	+0.42	+0.18	-0.6
FeS$_2$			
	+0.70		-0.35
Au in FeAs$_2$ (nearest atoms to Au)			
-0.37	+0.18	-0.08; -0.01	
Au in FeAsS (nearest atoms to Au)			
-0.01	+0.43	+0.30	-0.56
Au in FeS$_2$ (nearest atoms to Au)			
+0.42	+0.72		-0.36
Au in Au$_2$S[1]			
+0.21			-0.42
Au	**Cu**		**S**
CuS			
	+0.56, +0.50		-0.84, -0.82(S$_2$)
Au in CuS (nearest atoms to Au)			
+0.19	+0.56, +0.48		-0.69, -0.80(S$_2$)

[1] calculated for the Au$_2$S structure relaxed by DFT
method, optimized lattice constant a = 5.35 Å, Au-S
distance R = 2.32 Å.

657

29

Figure Captions

Figure 1. Results of the pyrite hydrothermal synthesis experiment, t = 450 °C, P = 1 kbar. **A -** BSE image of the fine-grained aggregate of the synthetic pyrite; **b -** the concentration of Au in pyrite and coexisting aqueous fluid as a function of sulfur fugacity. Filled symbols – sulfur was used to control $f(S_2)$; empty symbols correspond to the S + H_2SO_4 system (last row in Table S1), where $f(S_2)$ value has to be corrected.

Figure 2. Difference between the TFY and HERFD spectra for the löllingite sample, C(Au) =800 ppm. In TFY mode, the Au features are completely masked by the As K edge. The HERFD mode makes it possible to record the Au L_3 edge spectra.

Figure 3. The Au L_3 edge HERFD-XANES spectra of the Au-bearing pyrite (hydrothermal synthesis, sample 6-16), arsenopyrite, löllingite (salt flux synthesis), and model substances. **A -** comparison with $Au_{(cr)}$ and $Au_2S_{(cr)}$; **b -** enlarged energy scale, a comparison of arsenopyrite and löllingite with $AuSb_2$ and Au_2Bi. Note that the spectra of all the samples of hydrothermal pyrites shown in Fig. 1 were similar to the spectra of sample 6-16 shown in this figure.

Figure 4. The Au L_3 edge HERFD-XANES spectra of pyrites synthesized using the hydrothermal (sample 6-16, C(Au) = 36 ppm) and salt flux techniques (CD-624, C(Au) ~60 ppm, measured concentrations of Au in this sample are listed in Table S2). The heating of hydrothermal pyrite resulted in a decomposition of the chemically bound Au and a decrease in signal intensity. At 630 °C, the spectra corresponded to the traces of the chemically bound Au whose concentration continuously decreased with time during the experiment (see text for explanation). Vertical lines indicate the position of the 3 main features of $Au_{(cr)}$.

Figure 5. EXAFS spectra of Au-bearung pyrite (*left pannel*, hydrothermal synthesis) and löllingite (*right pannel*, salt flux synthesis). *Top* – background subtracted EXAFS spectra, k^2 weighted; *bottom* – Fourier transforms of the k^2 weighted EXAFS spectra, not corrected for phase shift. Paths are indicated near the FT features. Thin black lines – experiment, thick red lines – fit results.

Figure 6. Results of a theoretical calculation of Au L_3 edge HERFD-XANES spectra for Au-bearing pyrite (**a**), löllingite (**b**), and arsenopyrite (**c**). Experimental spectra are shown for comparison (*Pyrite*: sample 6-16, hydrothermal, C(Au) = 36 ppm; *Löllingite*: sample 5333, salt flux synthesis, C(Au) = 800±300 ppm; *Arsenopyrite*: sample 5140, salt flux synthesis, C(Au) = 23±14 ppm). For pyrite, the EXAFS structure was built by setting the first-neighbour Au-S distances in accordance with the EXAFS model (Table 2), whereas all the other distances were adopted from the unrelaxed structure of pure pyrite.
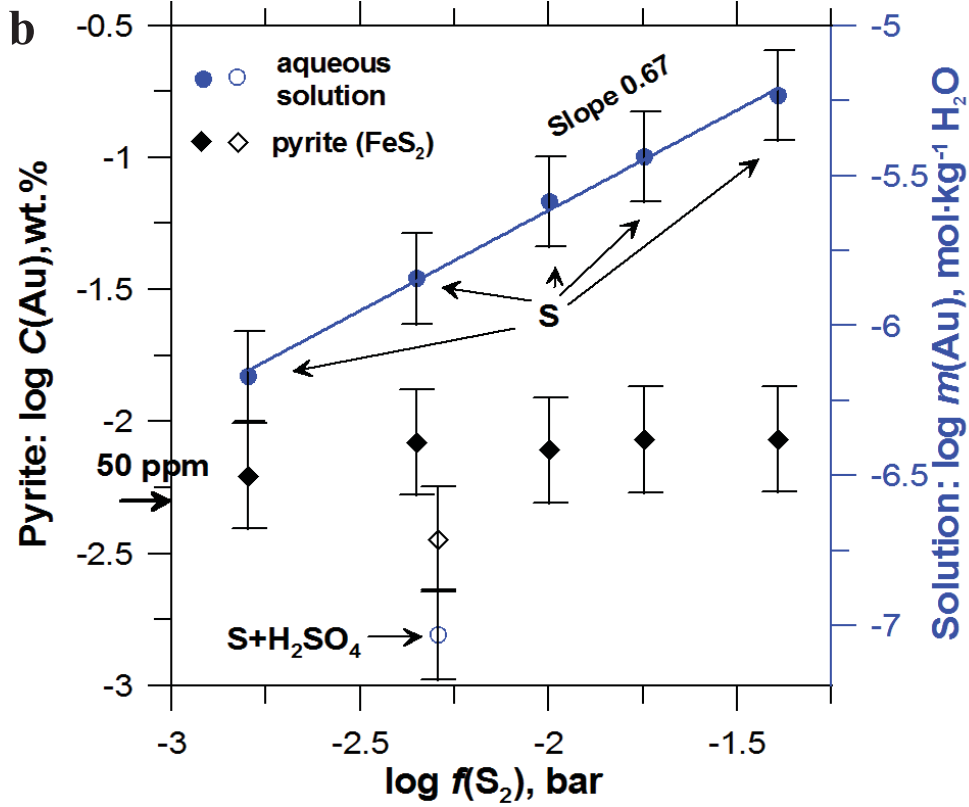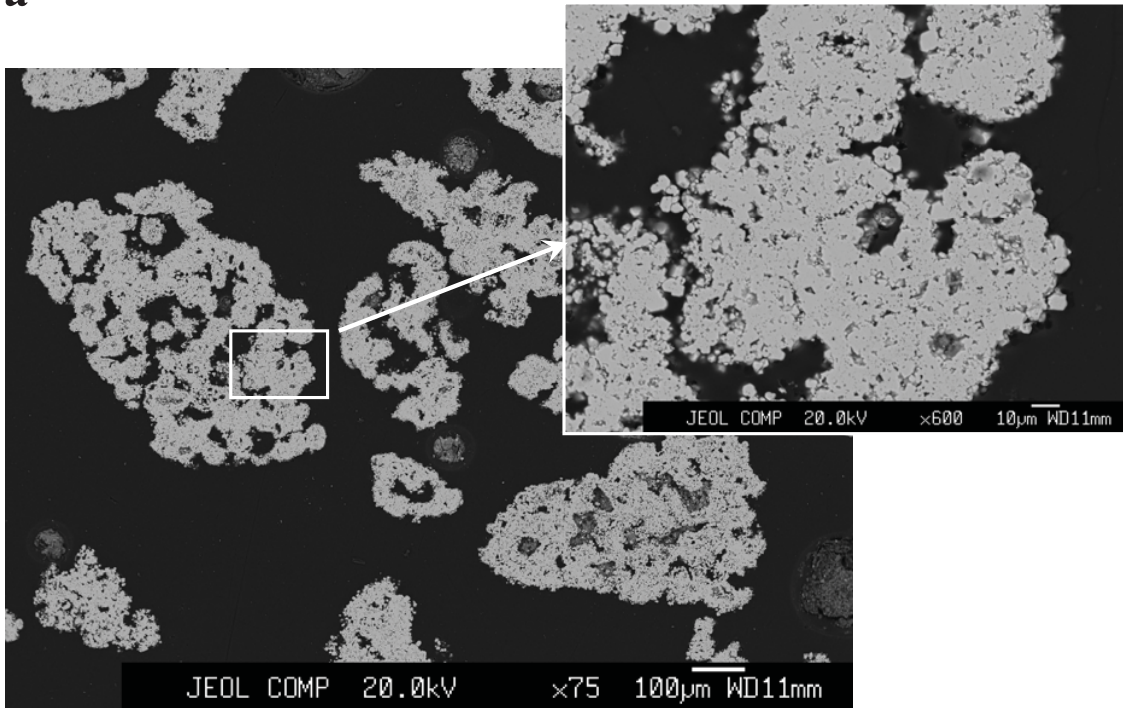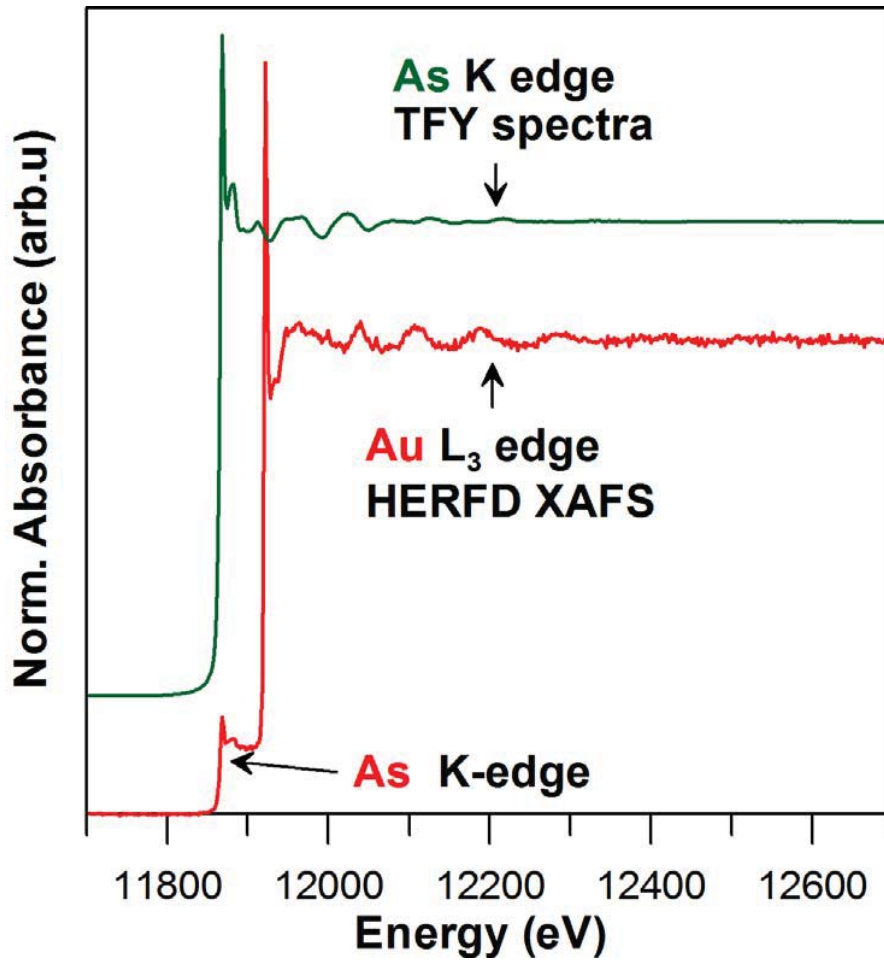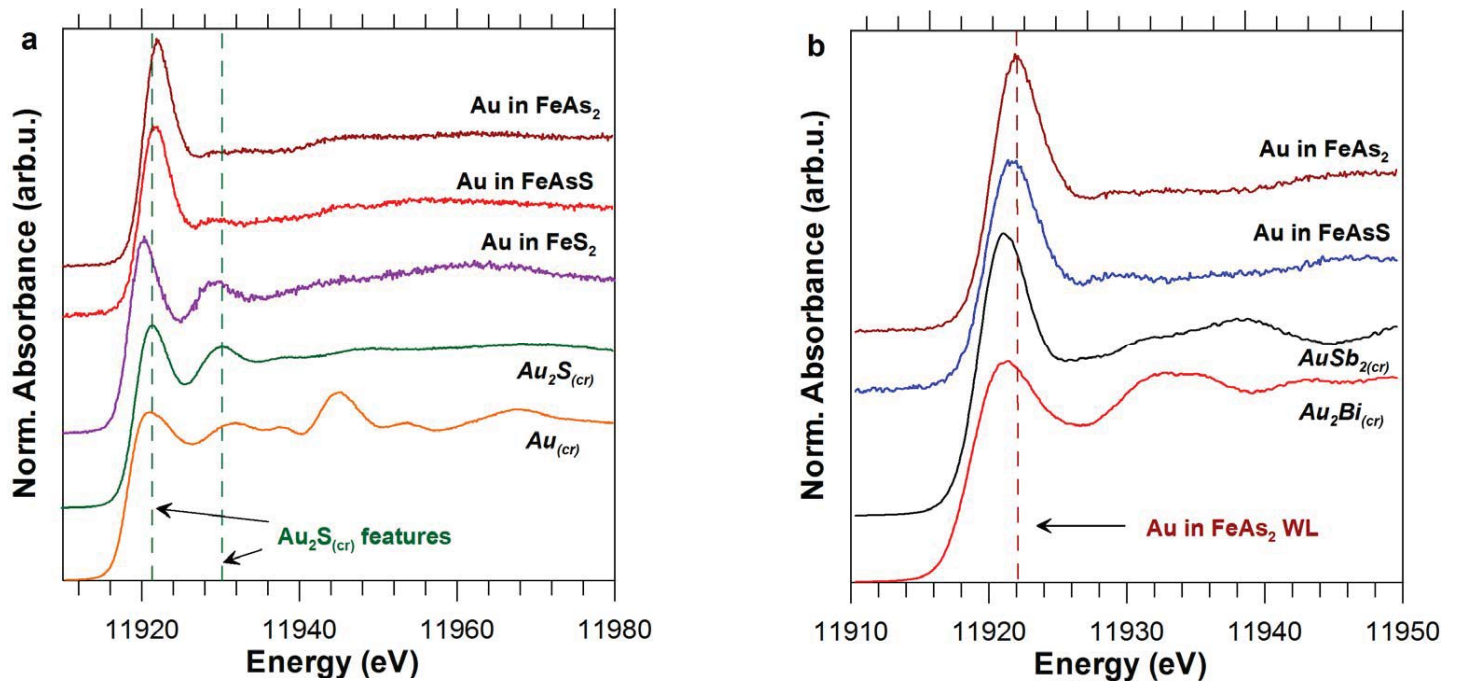
a

b

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4

Fig. 5

Fig. 6