

1 Revision 1

2 **Transformation of pyrite to pyrrhotite in the presence of Au-Ag alloys at 500°C**

3 GALINA PALYANOVA<sup>1,2\*</sup>, KONSTANTIN KOKH<sup>1,2,3</sup>, YURII SERYOTKIN<sup>1,2</sup>

4 <sup>1</sup>*Sobolev Institute of Geology and Mineralogy, Novosibirsk, Russia*

5 <sup>2</sup>*Novosibirsk State University, Russia*

6 <sup>3</sup>*Tomsk State University, Russia*

7 \*Corresponding author: Galina Palyanova

8 IGM SB RAS, Koptyuga ave., 3, Novosibirsk 630090, Russia, Tel/Fax: +7 383 3066392, E-mail:

9 [palyan@igm.nsc.ru](mailto:palyan@igm.nsc.ru)

10 **Abstract**

11 Dry annealing of Au<sub>x</sub>Ag<sub>1-x</sub> alloys (x=0.19, 0.35, 0.56 or of fineness 300,500,700‰) and pyrite  
12 was used to reveal the solubility of Au (Ag) in FeS<sub>2</sub> and study phase equilibria in the FeS<sub>2</sub> -  
13 Au<sub>x</sub>Ag<sub>1-x</sub> system at 500°C. Pyrrhotite, acanthite and uytenbogaardtite and Au-Ag alloys with  
14 increased fineness were established at the contacts of pyrite blocks with Au-Ag plates. The  
15 obtained results evidence the absence of solubility between FeS<sub>2</sub> and Au (Ag) at 500°C. The Ag  
16 content in alloys influences the stability of pyrite and contributes to its transformation in  
17 pyrrhotite and sulfidation and ennobling of Au-Ag alloys. Au-Ag sulfides and pyrrhotite may be  
18 present in the sulfide ores of metamorphogene deposits as annealing products of Au-Ag-pyrite-  
19 bearing ores.

20

21 **Keywords:** desulfidation, pyrite, pyrrhotite, visible and “invisible” gold (silver), isomorphism,  
22 thermodiffusion, sulfidation, ennobling of Au-Ag alloys, Au-Ag sulfides

23

24 **1. Introduction**

25 Pyrite is the most well-known and widespread mineral of the iron sulfides. It is a common  
26 constituent of many igneous, metamorphic and sedimentary types of rocks and of hydrothermal

27 veins. More important is the fact that pyrite is a collector of gold and silver (Boyle 1979; 1980).  
28 Revealing the forms of occurrence of noble metals in iron sulfides is of fundamental and applied  
29 importance. Pyrite often contains micro inclusions of native gold, Ag-Au chalcogenides and  
30 other minerals of gold and silver that are visible under optical microscope and scanning electron  
31 microscope (Zhou et al. 2004; Palyanova et al. 2015; 2016). It has been established so far that  
32 “invisible” gold occurs as submicron or nano-sized inclusions or solid solution in the structure of  
33 iron sulfides (Vikent’ev 2015 and its reference list). The amount of isomorphous gold  
34 incorporated into pyrite lattice covers a wide range of values as reported by some authors  
35 (Fleischer 1955; Cook and Chryssoulis 1990; Abraitis et al. 2004; Vaughan 2004; Pal’yanova et  
36 al. 2015). Gold and silver concentrations in pyrites range from below one ppm to almost  
37 thousand ppm.

38 To determine the probability of incorporation of gold and silver into pyrite, we conducted  
39 experiments of solid-phase diffusion (Jin 1981), using natural pure pyrite and synthetic Au-Ag  
40 alloys of varying composition. According to this technique, if the plates of two substances A and  
41 B are brought into contact and then kept at temperature when diffusion is probable, their  
42 composition finally becomes homogeneous. If isomorphism between two components is absent,  
43 various compounds stable in the A-B system are formed in the contact zone. This technique is  
44 successfully applied to study many binary and ternary systems and construction of the isothermal  
45 sections of phase diagrams (Kodentsov et al. 2001). However, this technique has restrictions –  
46 melting should be avoided. Data from the phase diagram Fe-S (Kullerud and Yoder 1959;  
47 Arnold 1962; Waldner and Pelton 2005; Wang and Salveson 2005) evidence that pyrite is  
48 unstable at temperatures above 742-745°C and melts incongruently with formation of pyrrhotite  
49 and sulfur. At temperatures between the melting point and 325°C, pyrite coexists with pyrrhotite  
50 of various compositions  $\text{Fe}_{1-y}\text{S}$  ( $0.78 < y < 1$ ) or  $\text{FeS}_x$  ( $1 < x < 1.23$ ). To avoid melting of pyrite, the  
51 specified temperature in the experiments was 500°C. Application of this technique allows  
52 studying phase equilibria in the  $\text{FeS}_2 - \text{Au}_x\text{Ag}_{1-x}$  system. One of the tasks of the investigation was

53 to study the behavior of noble metals in the process of desulfidation of pyrite (Craig and Vokes  
54 1993; Thomas et al. 2011) and sulfidation of native gold (Pal'yanova et al. 2014), which are  
55 typical of natural processes.

56

57

## 2. Experiments and analytical methods

58

### 2.1. Starting compositions

59

In the experiments we used a large natural pyrite single crystal from the Berezovskoe  
60 gold-quartz deposit (Ural, Russia). Microprobe analysis showed that pyrite crystal is  
61 homogeneous and does not contain micro impurities. First, a plate ~5-6 mm thick was cut from  
62 the crystal. After polishing on 1  $\mu\text{m}$  diamond paste, the plate was cut into bars with polished area  
63 ~3x3 mm. Gold-silver alloys of  $\text{Au}_{0.19}\text{Ag}_{0.81}$ ,  $\text{Au}_{0.35}\text{Ag}_{0.65}$  and  $\text{Au}_{0.56}\text{Ag}_{0.44}$  composition (gold  
64 fineness =  $1000 \cdot \text{Au}/(\text{Au}+\text{Ag})$ , by weight, 300, 500 and 700‰, respectively) synthesized from a  
65 stoichiometric mixture of pure metals were rolled out to the thickness of ~200 micron and cut  
66 into plates measuring 3x3 mm. Then metal sheets were placed between polished surfaces of the  
67 pyrite bars, and the resulting column was sealed under  $10^{-3}$  torr in the quartz ampoule. The  
68 samples were slowly heated to 500°C in the isothermal zone of the furnace and kept at this  
69 temperature for 7 days. After annealing, the ampoule was cooled to room temperature in the  
70 switched off furnace.

71

72

### 2.2. Analytical techniques

73

Optical microscopy, scanning electron microscopy (SEM), electron microprobe analysis  
74 (EPMA) and X-ray powder diffraction methods were applied to study the samples. A polished  
75 section was prepared from the synthesized phases for microscopy analyses. Studies on the  
76 chemical composition of the synthesized substances were carried out using MIRA 3 LMU SEM  
77 (TESCAN Ltd.) combined with the microanalysis system INCA Energy 450+ on the basis of the  
78 high sensitive silicon drift detector XMax-80, and WDS INCA Wave 500 (Oxford Instruments

79 Ltd.). The analyses were conducted at 20 kV accelerating voltage, 1.5 nA probe current. Most  
80 analyses of Au-Ag sulfides were performed using SEM-EDS at 15–20 s live acquisition time of  
81 spectrum. Acquisition of spectra was performed in the raster mode with the scanning area from  
82  $0.5 \times 0.5 \mu\text{m}^2$  for fine phases, and to  $2 \times 2 \mu\text{m}^2$  for larger phases with a slightly defocused  
83 electron beam. While a bulk composition of decay structures was obtained with the scanning  
84 area from  $5 \times 5 \mu\text{m}^2$  to  $10 \times 10 \mu\text{m}^2$ . The analyses were made with a slightly defocused electron  
85 beam, to reduce the destructive effects of the electron beam on unstable Au-Ag sulfides. For  
86 analysis we used the characteristic X-ray S K-series and L-series of Ag and Au. Under these  
87 conditions the random error of measurement caused by the counting statistic for Au-Ag sulfide,  
88 corresponding to uytenbogaardtite was 0.17, 0.37, and 0.98 wt.% for S, Ag, and Au,  
89 respectively. Detailed measurement techniques have been worked out for the natural Au-Ag  
90 sulfides and described in (Pal'yanova et al. 2014). Pure silver and gold, PbS and CuFeS<sub>2</sub> were  
91 used as standards for Ag, Au, S, and Fe, respectively.

92 X-ray powder diffraction study of the synthesized phases was performed on a Stoe IPDS-  
93 2T diffractometer (MoK $\alpha$  radiation, graphite monochromator) using Gandolfi mode. Two-  
94 dimensional X-ray patterns were radially integrated using the XArea software package. The  
95 diffraction profiles were treated by using the WinXPow (Stoe) program packages. For the phase  
96 analysis, the database of PDF-4 Minerals (The Powder Diffraction File PDF-4 +, 2006) was  
97 used.

98

99

### 3. Results

100 The data on solid phase products of experiments are given in Table 1. The reaction zones  
101 between pyrite blocks and Au-Ag alloys contained pyrrhotite, acanthite- and uytenbogaardtite  
102 phases and Au-Ag alloys of fineness higher than the initial fineness, but lower than 830‰  
103 (Figs.1, 2). It was established that pyrrhotite in all three zones had an identical and stable  
104 composition very close to Fe<sub>7</sub>S<sub>8</sub>. Analysis of Au-Ag alloys shows up to 1.6 weight % of sulfur,

105 which may be explained by micro inclusions of Au-Ag sulfides. The fineness of alloys was  
106 calculated without account of sulfur. Acanthite and uytenbogaardtite form the structures of solid  
107 solution decay. SEM photos made at high magnification (Fig. 3a-c) show two phases of Au-Ag  
108 sulfides well discriminated by color - acanthite (light grey) and uytenbogaardtite (grey). It is  
109 supposed that this aggregate reflects the possible composition of the Au-A sulfide solid solution  
110 stable at 500°C.

111 The amount of acanthite phase prevails in all experiments. According to EPM analysis,  
112 the mole ratios of metals to sulfur (Ag+Au)/S in the acanthite and uytenbogaardtite phases vary  
113 from 1.5 to 1.6, which is considerably lower compared to their ideal compositions. This may be  
114 described by the visually observed partial decomposition of the phases under ion beam. The  
115 features of phases and chemical compositions of each reaction zone are described below:

116 **Pyrite + Ag-Au alloy (300‰):** In the reaction zone with initial low-fineness alloy we  
117 established alloys with the fineness from 830 near the pyrite to 740‰ in the middle part of the  
118 alloy plate (Figs. 1a, 2a, 4a, Table 1). Uytenbogaardtite forms parallel thin veinlets (less than 1-3  
119 micron wide) in acanthite (Fig. 3a). The maximal content of gold reaches 29.4 wt.% in  
120 uytenbogaardtite ( $\text{Ag}_{2.98}\text{Au}_{0.84}\text{S}_2$ ). Acanthite was analyzed as  $\text{Ag}_{>1.61-1.54}\text{S}$ . The possible bulk  
121 composition of the Au-Ag sulfide solid solution existing at 500°C corresponds to the formula  
122  $\text{Ag}_{1.60}\text{Au}_{0.26}\text{S}$ .

123 **Pyrite + Ag-Au alloy (500‰):** In the reaction zone with the initial alloy of medium  
124 fineness we have established alloys of fineness from 520 to 830‰ (Fig. 1b, 2b, Table 1). In  
125 contrast to previous sample, the fineness of alloy has varied more slightly remaining almost  
126 unchanged in the center (Fig. 4b). Gold content does not exceed 8 wt.% in Au-Ag sulfides. Au-  
127 Ag sulfides are presented by two phases (Fig. 3b) – acanthite ( $\text{Ag}_{1.60}\text{Au}_{0.05}\text{S}$ ) and  
128 uytenbogaardtite ( $\text{Ag}_{3.26}\text{Au}_{0.50}\text{S}$ ). The possible composition of Au-Ag sulfide solid solution  
129 stable at 500°C is equal to  $\text{Ag}_{1.62}\text{Au}_{0.06}\text{S}$  (Table 1).

130           **Pyrite + Ag-Au alloy (700‰):** The alloy of a high-fineness appeared to be most stable.  
131   The reaction zone in this experiment (Figs.1c, 2c) is narrower than those with alloys of fineness  
132   300 (Figs.1a, 2a) and 500‰ (Figs.1b, 2b). Purely unreacted areas of the alloy were found in the  
133   central parts. The maximum fineness of the reacted alloy, again, does not exceed 830‰. The  
134   fineness of alloys insignificantly increased from the center of the Au-Ag plate toward the contact  
135   with pyrite (Fig.2c, 4c). In Au-Ag sulfides, gold concentration varies from 1.1 to 8.2 wt.%. Two  
136   phases of Au-Ag sulfides were found - acanthite ( $\text{Ag}_{1.50}\text{Au}_{0.01}\text{S}$ ) and uytenbogaardtite  
137   ( $\text{Ag}_{3.12}\text{Au}_{0.17}\text{S}_2$ ). The possible bulk composition of the Au-Ag sulfide stable at 500°C is equal to  
138    $\text{Ag}_{1.55}\text{Au}_{0.03}\text{S}$  (Table 1).

139           Figure 4 shows the variations of Fe, S, Au and Ag concentrations along the reaction  
140   zones and new phases found between pyrite and Au-Ag alloys in each experiment. The same  
141   pattern of variations in Fe and S concentrations was established in all samples. The concentration  
142   of sulfur decreases in transition from pyrite to pyrrhotite and further to Au-Ag sulfides. Finally,  
143   its content becomes almost zero in Au-Ag alloys. Iron has the same behavior; its concentration  
144   falls to zero in Au-Ag alloys and Au-Ag sulfides. The alloy plates have considerable variation of  
145   Au/Ag ratio and the most constant composition was found in the sample with initial 300 ‰  
146   fineness. A similar pattern of noble metals redistribution was found in each experiment (Fig.4a-  
147   c). Au content close to the contact with pyrite is maximal and appears to be higher than that in  
148   the initial alloy. While silver concentration is lower than in initial alloy and it gradually increases  
149   towards the center of alloy plate.

150           The estimations of the composition of sulfide solid solution at 500°C showed that the  
151   maximum content of Au belongs to the sample with 300‰ plate. Impurities of noble metals were  
152   not found in pyrite and pyrrhotite or their content was lower than the detection limit of EPMA.

153           Figure 5 demonstrates redistribution of elements throughout the reaction zone formed at  
154   the contact of the 500‰-fineness alloy and pyrite. Compared to gold (Fig. 5b), the silver (Fig.  
155   5a) is more intensively transferred from Au-Ag alloys to react with sulfur, which appeared as a

156 result of pyrite desulfidation. The final products of reaction at 500°C are Au-Ag sulfide solid  
157 solution, which decomposes at room temperature, and pyrrhotite Fe<sub>7</sub>S<sub>8</sub> substituting pyrite (Fig.  
158 5c).

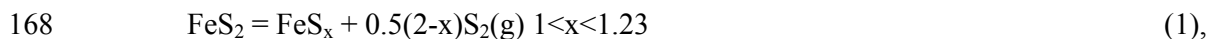
159 X-ray powder diffraction results show that pyrite, pyrrhotite, acanthite, uytenbogaardtite,  
160 and Au-Ag alloys are present in each reaction zone (Fig. 6). In all samples the peaks intensities  
161 of uytenbogaardtite phase are considerably lower than those of acanthite phase, which is  
162 confirmed by EPMA analyses (Fig.3a-c).

163

164

#### 4. Discussion

165 Data from Lambert et al. (1998) evidence that thermal decomposition of pyrite in the  
166 temperature range of 347-700°C in vacuum proceeds with the formation of pyrrhotite and a gas  
167 phase that mainly consists of S<sub>2</sub>:

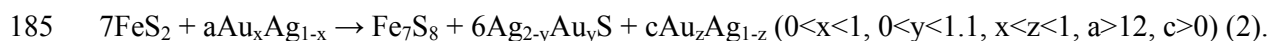


169 And pyrrhotite composition is determined by the equation:  $x = 1.45 \cdot 10^{-4} \cdot T(\text{K}) + 1.0354$ . The  
170 composition of pyrrhotite calculated by this equation is 1.147, which is in good agreement with  
171 the data of microprobe analysis of pyrrhotite from the reaction zones (Fe<sub>7</sub>S<sub>8</sub>~FeS<sub>1.14</sub>).

172 According to data of electrum-tarnish method (Barton and Toulmin 1964), at 500°C in  
173 the presence of pyrite-pyrrhotite buffer the alloys of fineness lower 780‰ must be sulfidated and  
174 become black. In our experiments all three alloys have turned black due to sulfidation which  
175 agrees with the previous data. In addition, we have found newly formed uytenbogaardtite and  
176 Au-enriched noble alloys. Francis (1971) investigated the kinetics and mechanism of electrum  
177 tarnish by sulfur. One of his results was a decrease of silver in Au-Ag alloys put in contact with  
178 silver sulfide.

179 Since pyrite blocks and Au-Ag plates were placed into one ampoule, the value of sulfur  
180 pressure was identical for all samples and was mainly determined by the pyrite-pyrrhotite buffer  
181 at 500°C, and probably by some average activity of gold and silver in alloy plates.

182 Pyrite desulfidation is accompanied by a sulfidation reaction of Au-Ag alloys. According  
183 to the solid state products found in the reaction zones, the following quazi-reaction is assumed to  
184 take place between pyrite and Au-Ag alloys (in general mode):



186 The ternary  $\text{Ag}_{2-y}\text{Au}_y\text{S}$  sulfides lie from  $\text{Ag}_2\text{S}$  to slightly beyond  $\text{AgAuS}$  (Barton 1980). From eq.  
187 (2) it is possible to estimate the compositions of Au-Ag sulfide solid solution. Table 1 contains  
188 the calculated variations in the solid solution according to the measured range of Au-Ag alloys in  
189 each sample. It may be concluded that the sample with 300‰ alloy is mostly close to the  
190 equilibrium since the EPMA data of Au-Ag sulfide solid solution decay structures have shown  
191 the highest content of gold. Also, the fineness of resulting alloy has the shortest range 740-830  
192 ‰ compared to 510-830 and 700-830 ‰ intervals found in the experiments with 500 and 700 ‰  
193 initial alloys, respectively.

194 Au-Ag sulfide solid solution is unstable at room temperature and therefore it decomposes  
195 to form a mixture of acanthite and uytenbogaardtite or uytenbogaardtite and petrovskaitite,  
196 according to  $\text{Ag}_2\text{S} - \text{Au}_2\text{S}$  phase diagram (Folmer et al. 1976; Barton 1980; Osadchii and Rappo  
197 2004; Palyanova et al. 2011). When studying the system Fe-Au-S, it was impossible to  
198 synthesize  $\text{Au}_2\text{S}$  by a similar reaction with gold even at high temperatures and longer period of  
199 time (Barton and Toulmin 1964; Toulmin and Barton 1964). In the system Fe-Ag-Au-S we  
200 obtained Ag-Au sulfides of various compositions through melt crystallization:  $\text{Ag}_2\text{S}$ ,  $\text{Ag}_3\text{AuS}_2$ ,  
201  $\text{AgAuS}$  and solid solutions  $(\text{Ag},\text{Au})_2\text{S}$  together with pyrite and pyrrhotite (Palyanova et al.  
202 2012).

203 The sulfidation reactions of native gold with participation of  $\text{S}_2$  gas were considered in a  
204 few papers (Barton et al. 1978; Barton 1980; Gurevich et al. 2011; Palyanova et al. 2014). These  
205 reactions may provide one or two phases of Au-Ag sulfides and ennobled alloys up to pure gold  
206 (Palyanova et al. 2014). The results of this work also evidence that sulfidation of Au-Ag alloys



207 proceeds through a quazi-equilibria resulting in the formation of alloy with a higher fineness  
208 according to reaction (2).

209 The pyrite, close to or at a distance from the reaction zone, and the newly formed  
210 pyrrhotite contain no traces of gold and silver. It is worth noting that pyrite which was not at the  
211 contact with Au-Ag plates did not undergo any changes. These data suggest that gold and silver  
212 do not dissolve in pyrite and are not incorporated isomorphously into its structure.

213 It was established before that pyrite stability is controlled partly by temperature and  
214 pressure, and partly by the amount of H<sub>2</sub>O (Tomkins 2010). Our results suggest that in a dry  
215 system the presence of silver in the initial alloys seems to promote the reactions of desulfidation  
216 of pyrite and sulfidation of Ag-Au alloys. Interestingly that the lower the fineness of initial  
217 alloys, the higher is the rate of desulfidation reaction of pyrite and parallel sulfidation reaction of  
218 Au-Ag alloys. In natural processes, pyrite containing micro inclusions of native gold on heating  
219 will react with them to form pyrrhotite Fe<sub>7</sub>S<sub>8</sub> and Au-Ag sulfides (acanthite, uytenbogaardtite  
220 and petrovskaitite) and higher fineness Au-Ag alloys. The presence of native gold inclusions,  
221 especially low fineness, in pyrite will promote pyrrhotite formation.

222

223

## 5. Implications

224 A great number of gold deposits are characterized by the presence of visible inclusions of  
225 native gold in pyrite and in the intergrain space of pyrite (Zhou et al. 2004). We predict the  
226 presence of Au-Ag sulfides with pyrrhotite for metamorphogene deposits with native silver,  
227 kustelite, electrum and pyrite. Au-rich native gold is stable and less disposed to sulfidation in  
228 comparison to the Ag-rich alloys. Sulfidation reactions of native gold with the appearance of Au-  
229 Ag sulfides - acanthite, uytenbogaardtite, petrovskaitite, or their mixtures (such as acanthite with  
230 uytenbogaardtite or uytenbogaardtite with petrovskaitite) are typical of some gold deposits  
231 (Palyanova et al. 2014; 2016). Au-Ag sulfides in association with pyrite and Fe-sphalerite were  
232 found in several mines: Konechnoe Au-quartz occurrence (Taimyr, Russia) (Proskurnin et al.

233 2011); Au–Ag deposits - Broken Hills adularia-sericite (Hauraki Goldfield, New Zealand)  
234 (Cocker et al. 2012) and Dzhulietta (northeastern Russia) (Palyanova et al. 2016). The number  
235 of deposits with uytenbogaardtite with petrovskaites is increasing every year  
236 (<http://www.mindat.org/min-4127.html>).

237 Along with a hypogene origin and crystallization from hydrothermal solutions,  
238 volcanic gases or sulfide melts (Cocker et al. 2012; Palyanova et al. 2011; 2012; Savva et al.  
239 2012), these Au-Ag sulfides could be formed due to sulfidation of Au-Ag alloys in  
240 metamorphic processes. According to the relationship between the fineness of alloy and the  
241 rate of pyrite/alloy reaction, the amount of resulting acanthite should prevail that of  
242 uytenbogaardtite and petrovskaites.

243 In the annealing products of Au-Ag-pyrite-bearing ores the presence of Au-Ag sulfides and  
244 pyrrhotite is also probable. The higher mobility of silver compared to gold during  
245 thermomigration at the contact of Au-Ag alloys with pyrite is one of the probable mechanisms of  
246 the increase in gold fineness and genesis of Au-Ag sulfides in nature. The presence of fine-  
247 grained micro inclusions of Au-Ag sulfides, which are hard to diagnose in pyrite-bearing ores,  
248 can be one of the reasons for the low extracting ability of noble metals.

249

250

#### **Acknowledgments**

251 This work is supported by the Russian Foundation for Basic Research, grant N 14-05-00504a.  
252 The authors thank Dr. Khokhryakov A.F. which gave us a pyrite crystal for research. We thank  
253 Dr. N.S. Karmanov (Institute of Geology and Mineralogy SB RAS) for the electron microprobe  
254 studies of polished sections and Dr. V.V. Bakakin (Institute of Inorganic Chemistry SB RAS) for  
255 advice. We are sincerely thankful to the Editor Prof. Foustoukos and anonymous reviewer for  
256 their comments and constructive suggestions which improved this manuscript.

257

258

#### **References cited:**

- 259 Abraitis, P.K., Pattrick, R.A.D., and Vaughan, D.J. (2004) Variations in the compositional,  
260 textural and electrical properties of natural pyrite: a review. *International Journal of Mineral*  
261 *Processing*, 74, 41–59.
- 262 Arnold, R.G. (1962) Equilibrium relations between pyrrhotite and pyrite from 325° to 741°C.  
263 *Economic Geology*, 57, 72–90.
- 264 Barton, M.D. (1980) The Ag-Au-S system. *Economic Geology*, 75, 303–316.
- 265 Barton, P.B. Jr., and Toulmin, P. (1964) The electrom-tarnish method for the determination of  
266 the fugacity of sulfur in laboratory sulfide systems. *Geochimica et Cosmochimica Acta*, 28,  
267 619–640.
- 268 Boyle, R.W. (1968) The geochemistry of silver and its deposits. Geological Survey of Canada,  
269 Ottawa.
- 270 Boyle, R.W. (1979) The Geochemistry of Gold and Its Deposits. Geological Survey of Canada,  
271 Ottawa.
- 272 Chareev, D.A., and Osadchii, E.G. (2006) Thermodynamic studies of pyrrhotite–pyrite equilibria  
273 in the Ag–Fe–S system by solid-state galvanic cell technique at 518–723 K and total  
274 pressure of 1 atm. *Geochimica et Cosmochimica Acta*, 70, 5617–5633.
- 275 Cocker, H.A., Mauk, J.L., Rabone, S.D.C., 2013. The origin of Ag–Au–S–Se minerals in  
276 adularia-sericite epithermal deposits: constraints from the Broken Hills deposit, Hauraki  
277 Goldfield, New Zealand. *Miner. Deposita* 48 (2), 249–266.
- 278 Cook, N.J., and Chryssoulis, S.L., (1990) Concentrations of “invisible gold” in the common  
279 sulfides. *Canadian Mineralogist*, 28, 1–16.
- 280 Craig, J. R., and Vokes, F.M. (1993) The metamorphism of pyrite and pyritic ores: an overview.  
281 *Mineralogical Magazine*, 57, 3–18.
- 282 Fleischer, M. (1955) Minor elements in some sulphide minerals. *Economic Geology 50th Anniv.*  
283 *V.*, 970–1024.

- 284 Folmer, J.C.W., Hofman, P., and Wieggers, G.A. (1976) Order-disorder transitions in the system  
285  $\text{Ag}_{2-x}\text{Au}_x\text{S}$  ( $0 < x < 1$ ). J. Less-Common Metals, 48, 251–268.
- 286 Francis, D.M. (1971) Electrum-tarnish by sulfur: a study of an irreversible processes. A thesis of  
287 Degree Master of Science. The University of British Columbia. 58p.
- 288 Jin, Z. (1981) A Study of the Range of Stability of Phase in Some Ternary Systems.  
289 Scandinavian Journal of Metallurgy, 10, 279–287.
- 290 Kodentsov, A.A., Bastin, G.F., and Loo, van F.J.J. (2001) The diffusion couple technique in  
291 phase diagram determination. Journal of Alloys and Compounds, 320, 207–217.
- 292 Kullerud, G., Yoder, H.S. (1959) Pyrite stability relations in the Fe-S system. Economic  
293 Geology, 54, 533–572.
- 294 Lambert, J.M., Simkovich, J.R., and Walker, P.L. (1998) The kinetics and mechanism of the  
295 pyrite-to-pyrrhotite transformation. Metallurgical and Materials Transactions B, 29B, 385–  
296 396.
- 297 Pal'yanova, G.A., Kravtsova, R.G., Zhuravkova, T.V. (2015)  $\text{Ag}_2(\text{S},\text{Se})$  solid solutions in the  
298 ores of the Rogovik gold-silver deposit (northeastern Russia). Russian Geology and  
299 Geophysics, 56, 1738–1748.
- 300 Pal'yanova, G., Mikhlin, Yu., Kokh, K., Karmanov, N., and Seryotkin, Yu. (2015) Experimental  
301 constraints on gold and silver solubility in iron sulfides. Journal of Alloys and Compounds,  
302 649, 67-75.
- 303 Palyanova, G., Karmanov, N., and Savva, N. (2014) Sulfidation of native gold. American  
304 Mineralogist, 99, 1095-1103.
- 305 Palyanova, G.A., Kokh, K.A., and Seryotkin, Yu.V. (2012) Formation of gold-silver sulfides and  
306 native gold in Fe-Ag-Au-S system. Russian Geology and Geophysics, 53, 321-329.
- 307 Palyanova G.A., Savva N.E., Zhuravkova T.V., E.E. Kolova. (2016) Gold and silver minerals in  
308 low-sulfide ores of the Dzhulietta deposit (*northeastern Russia*) // Russian Geology and  
309 Geophysics, 57, 1171–1190.

- 310 Proskurnin, V.F., Palyanova, G.A., Karmanov, N.S., Bagaeva, A.A., Gavrish, A.V., 2011. The  
311 first discovery of uytzebogardite in Taimyr (Konechnoe occurrence). Dokl. Earth Sci. 441  
312 (2), 1661–1665.
- 313 Taylor, L.A. (1970) The system Ag-Fe-S: phase equilibria and mineral assemblages. Mineral.  
314 Deposita, 5, 41–58.
- 315 The Powder Diffraction File PDF-4+, International Centre for Diffraction Data (ICDD), Release,  
316 2006.
- 317 Thomas, H.V., Large, R.R., Bull, S.W., Maslennikov, V.V., Berry, R.F., Fraser, R., Froud, S.,  
318 and Moye, R. (2011) Pyrite and Pyrrhotite textures and composition in sediments, laminated  
319 quartz veins, and reefs at Bendigo Gold Mine, Australia: Insights for ore genesis. Economic  
320 Geology, 106, 1-31.
- 321 Tomkins, A.G. (2010) Windows of metamorphic sulfur liberation in the crust: Implications for  
322 gold deposit genesis. Geochimica et Cosmochimica Acta, 74, 3246–3259.
- 323 Toulmin, P., and Barton, P.B. Jr. (1964) A thermodynamic study of pyrite and pyrrhotite.  
324 Geochimica et Cosmochimica Acta, 28, 641–671.
- 325 Vaughan, J.P. (2004) The process mineralogy of gold: the classification of ore types. Journal of  
326 metals, 56, 46–48.
- 327 Vikentyev, I.V. (2015) Invisible and microscopic gold in pyrite: methods and new data for  
328 massive sulfide ores of the Urals. Geology of Ore Deposits, 57, 237–265.
- 329 Waldner, P., and Pelton, A.D. (2005) Thermodynamic modeling of the Fe-S system. Journal of  
330 Phase Equilibria and Diffusion, 26, 23-38.
- 331 Wang, H., and Salveson, I. (2005) A review on the mineral chemistry of the non-stoichiometric  
332 iron sulphide,  $\text{Fe}_{1-x}\text{S}$  ( $0 \leq x \leq 0.125$ ): polymorphs, phase relations and transitions, electronic  
333 and magnetic structures. Phase Transitions, 78, 547–567.
- 334 White, J.L., Orr, R.L., and Hultgren, R. (1957) Thermodynamic properties of silver–gold alloys.  
335 Acta Metallurgica, 5, 747–760.

336 Zhou, J., Jago, B., and Martin, C. (2004-03) Establishing the process mineralogy of gold ores.  
337 SGS Miner. Tech. Bull., 1–16.  
338 <http://www.mindat.org/min-4127.html>

339

#### 340 **Figure captions**

341 **Figure 1.** Photo (in reflected light) of polished sections: phases in the reaction zone formed at  
342 the contact of pyrite and Au-Ag alloys of fineness 300 (a), 500 (b) and 700 ‰ (c). Symbols of  
343 the phases: Py – pyrite, Po – pyrrhotite, Ac – acanthite, Uy – uytenbogaardtite,  $N_{Au}$  – fineness of  
344 Au-Ag alloys, ‰.

345 **Figure 2.** SEM photo of phases in the reaction zone formed at the contact of pyrite and Au-Ag  
346 alloys of fineness 300 (a), 500 (b) and 700 ‰ (c).

347 **Figure 3.** SEM photo of Au-Ag sulfides (acanthite and uytenbogaardtite phases) formed at the  
348 contact of pyrite and Au-Ag alloys of fineness 300 (a), 500 (b) and 700 ‰ (c) as well as their  
349 relationships and compositions.

350 **Figure 4.** Cross-section showing the content of elements (in wt.%) and phases along the  
351 "reaction zones" between pyrite and Au-Ag alloys of fineness 300 (a), 500 (b) and 700 ‰(c).

352 **Figure 5.** Distribution of elements Ag (a), Au (b), Fe (c) and S (d) in characteristic radiations  
353 ( $AgL\alpha_1$ ,  $AuM\alpha_1$ ,  $FeK\alpha_1$ ,  $SK\alpha_1$ , respectively) over the scanning area of reaction zone formed at  
354 the contact of pyrite and alloy of fineness 500‰.

355 **Figure 6.** X-ray powder diffraction pattern of sample with 700‰ initial alloy. Vertical lines  
356 under graph represents the peaks position of (from top to bottom): experimental pattern, gold,  
357 uytenbogaardtite  $Ag_3AuS_2$ , pyrite  $FeS_2$ , pyrrhotite  $Fe_7S_8$  and acanthite  $Ag_2S$ .

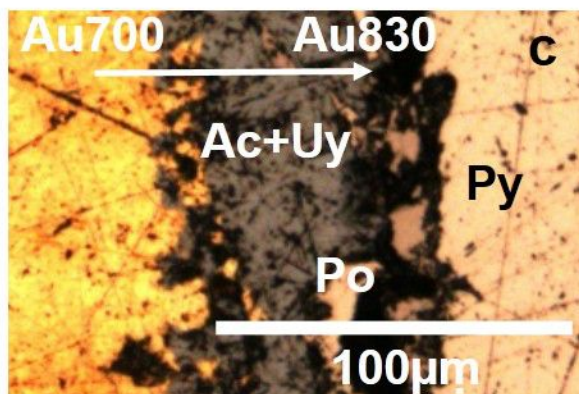
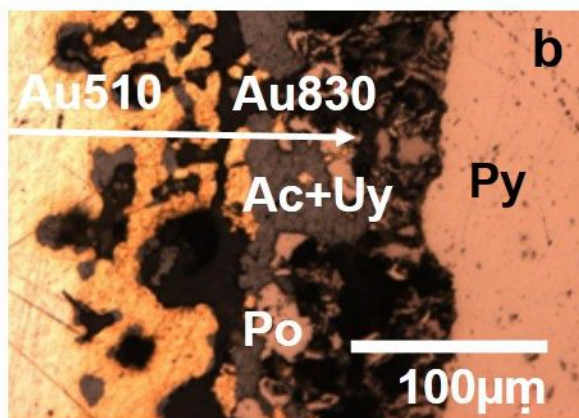
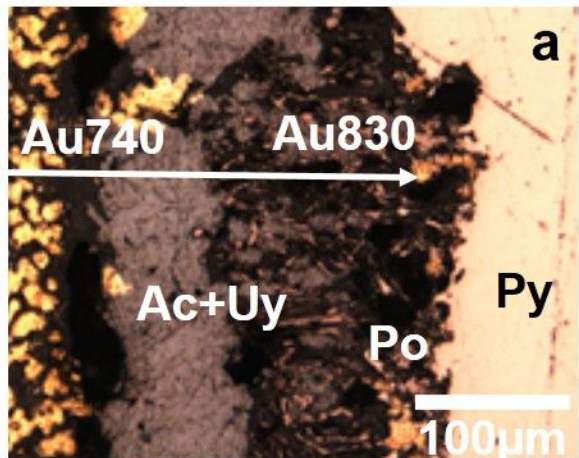
358

**Table 1.** Initial fineness ( $N_{Au}$ ) and compositions of Au-Ag alloys and compositions of new phases formed at the contact Au-Ag alloys and pyrite at 500°C.

№	Initial Au-Ag alloys ( $N_{Au}$ )	Compositions of new phases				
		Au-Ag alloys ( $N_{Au}\%$ )	Au-Ag sulfides 25°C	Au-Ag sulfide ss 500°C <sup>1</sup>	Au-Ag sulfide ss (reaction 2) <sup>2</sup>	Iron sulfide
1	Au <sub>0.19</sub> Ag <sub>0.81</sub> (300)	Au <sub>0.61</sub> Ag <sub>0.39</sub> (740) Au <sub>0.72</sub> Ag <sub>0.28</sub> (830)	Ac (Ag <sub>&gt;1.54-1.61</sub> S) Uy (Ag <sub>2.98</sub> Au <sub>0.84</sub> S <sub>2</sub> )	Ag <sub>1.60</sub> Au <sub>0.26</sub> S	Ag <sub>1.69</sub> Au <sub>0.31</sub> S Ag <sub>1.71</sub> Au <sub>0.29</sub> S	Fe <sub>0.875</sub> S
2	Au <sub>0.35</sub> Ag <sub>0.65</sub> (500)	Au <sub>0.36</sub> Ag <sub>0.64</sub> (510) Au <sub>0.73</sub> Ag <sub>0.27</sub> (830)	Ac (Ag <sub>1.60</sub> Au <sub>0.05</sub> S) Uy (Ag <sub>3.26</sub> Au <sub>0.50</sub> S <sub>2</sub> )	Ag <sub>1.62</sub> Au <sub>0.06</sub> S	Ag <sub>1.30</sub> Au <sub>0.70</sub> S Ag <sub>1.36</sub> Au <sub>0.64</sub> S	Fe <sub>0.875</sub> S
3	Au <sub>0.56</sub> Ag <sub>0.44</sub> (700)	Au <sub>0.56</sub> Ag <sub>0.44</sub> (700) Au <sub>0.73</sub> Ag <sub>0.27</sub> (830)	Ac (Ag <sub>1.50</sub> Au <sub>0.01</sub> S) Uy (Ag <sub>3.12</sub> Au <sub>0.17</sub> S <sub>2</sub> )	Ag <sub>1.55</sub> Au <sub>0.03</sub> S	- Ag <sub>1.28</sub> Au <sub>0.72</sub> S	Fe <sub>0.875</sub> S

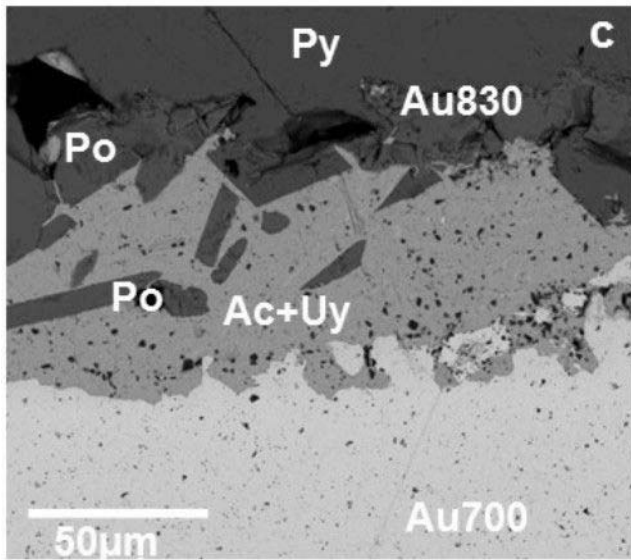
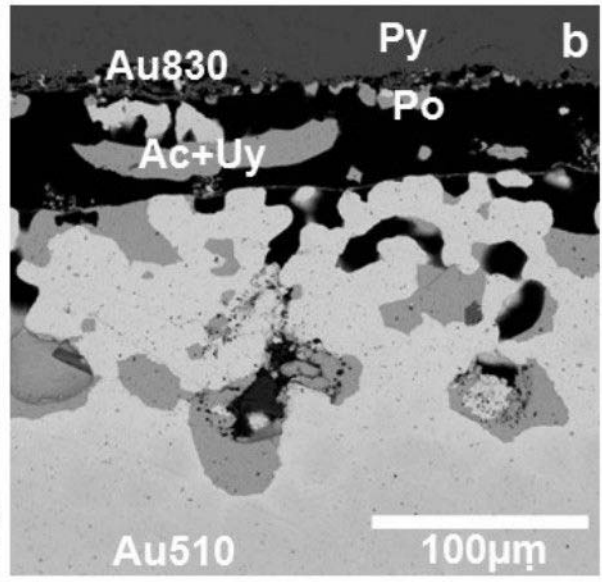
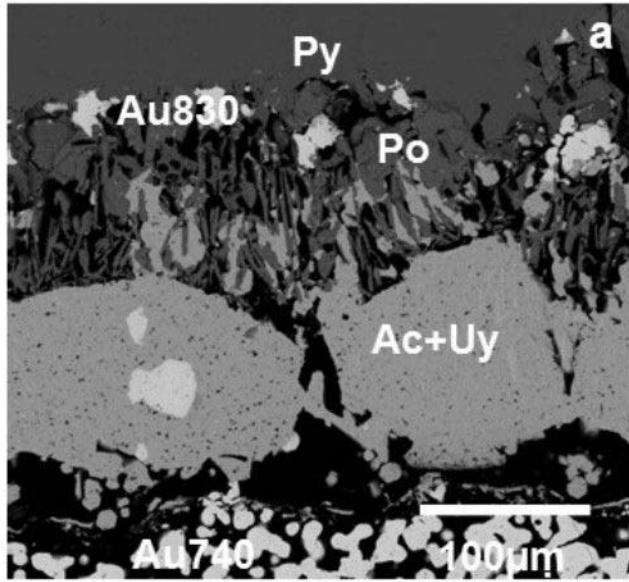
<sup>1</sup> compositions of acanthite-uytenbogaardtite mixture, obtained with the scanning extended area with a slightly defocused electron beam at EPMA;

<sup>2</sup> calculated compositions of the solid sulfide solutions on reaction 2 for a=13 and c=1 according to the measured range of Au-Ag alloys in each sample (column 3 left)

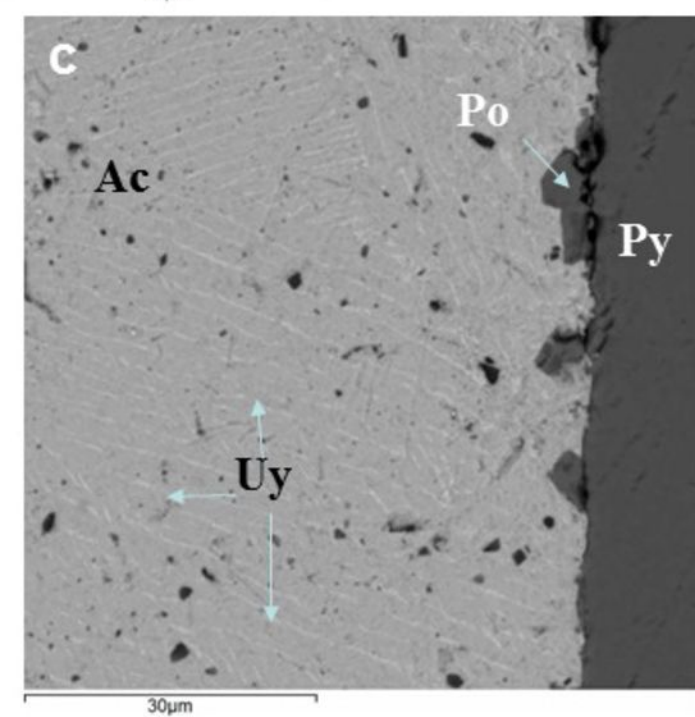
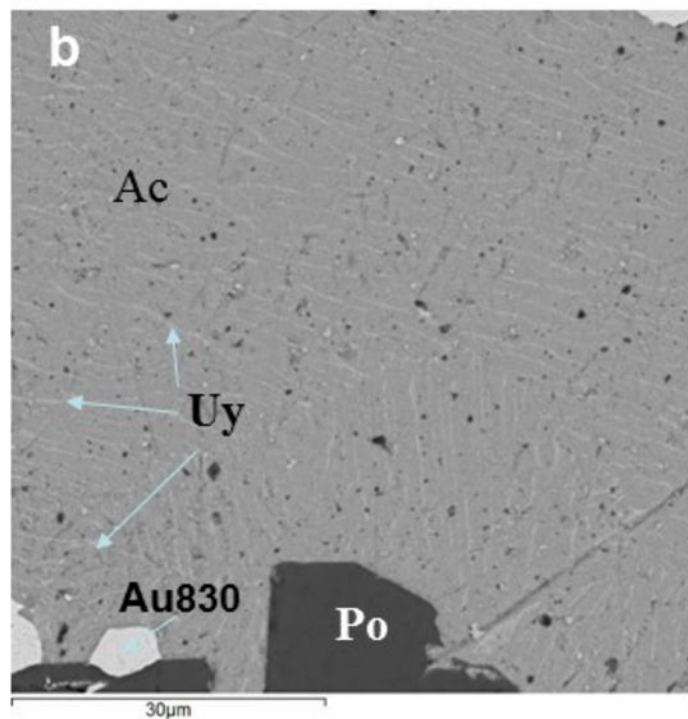
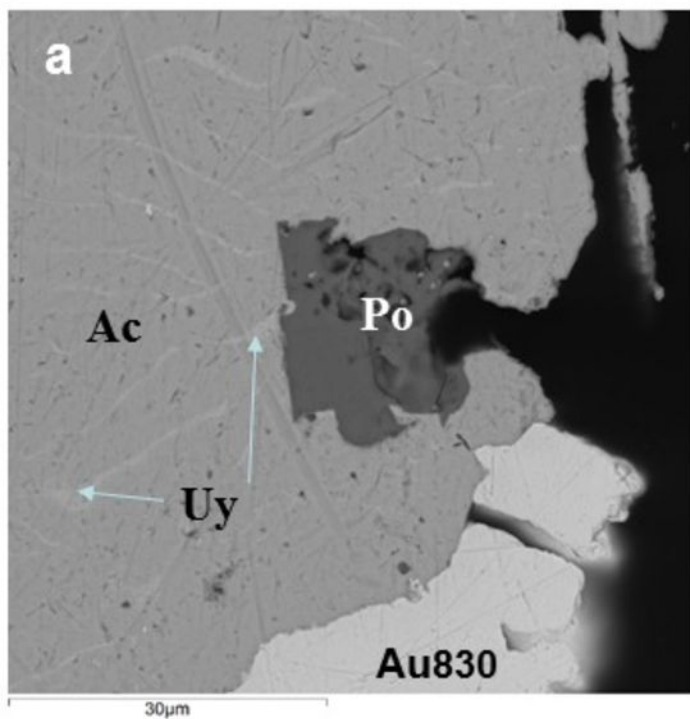


**Figure 1.**



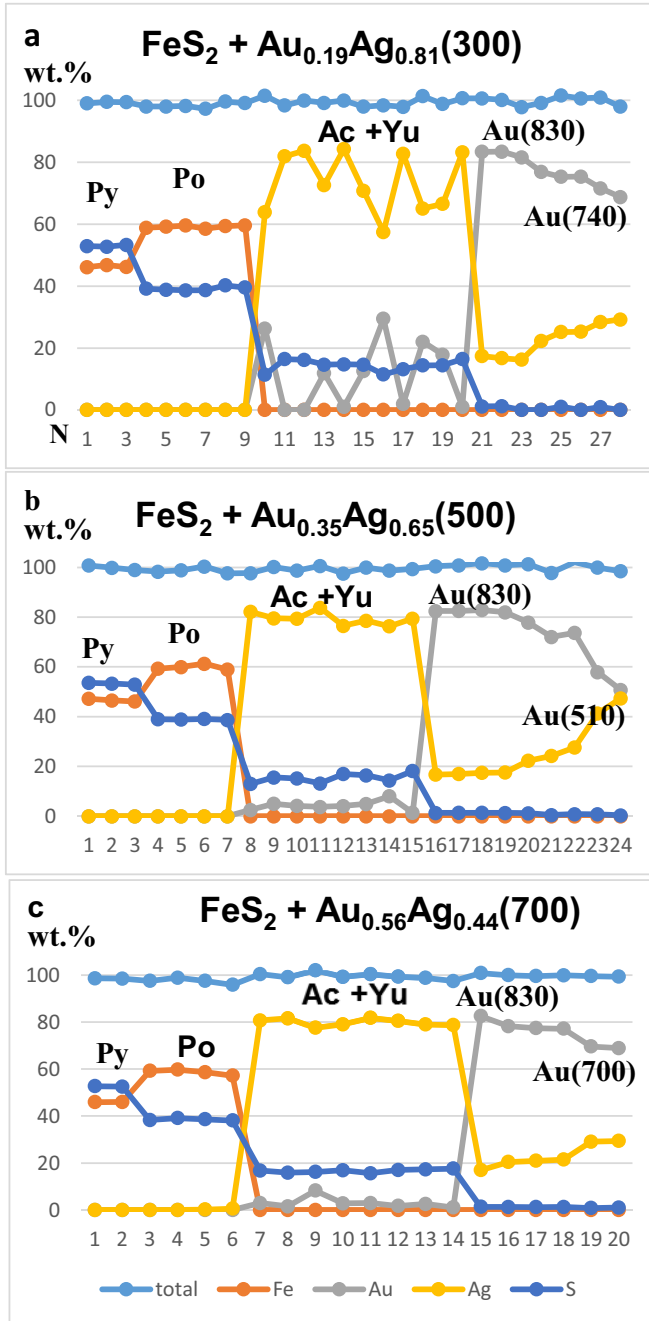


**Figure 2.**



**Figure 3.**

Figure.4



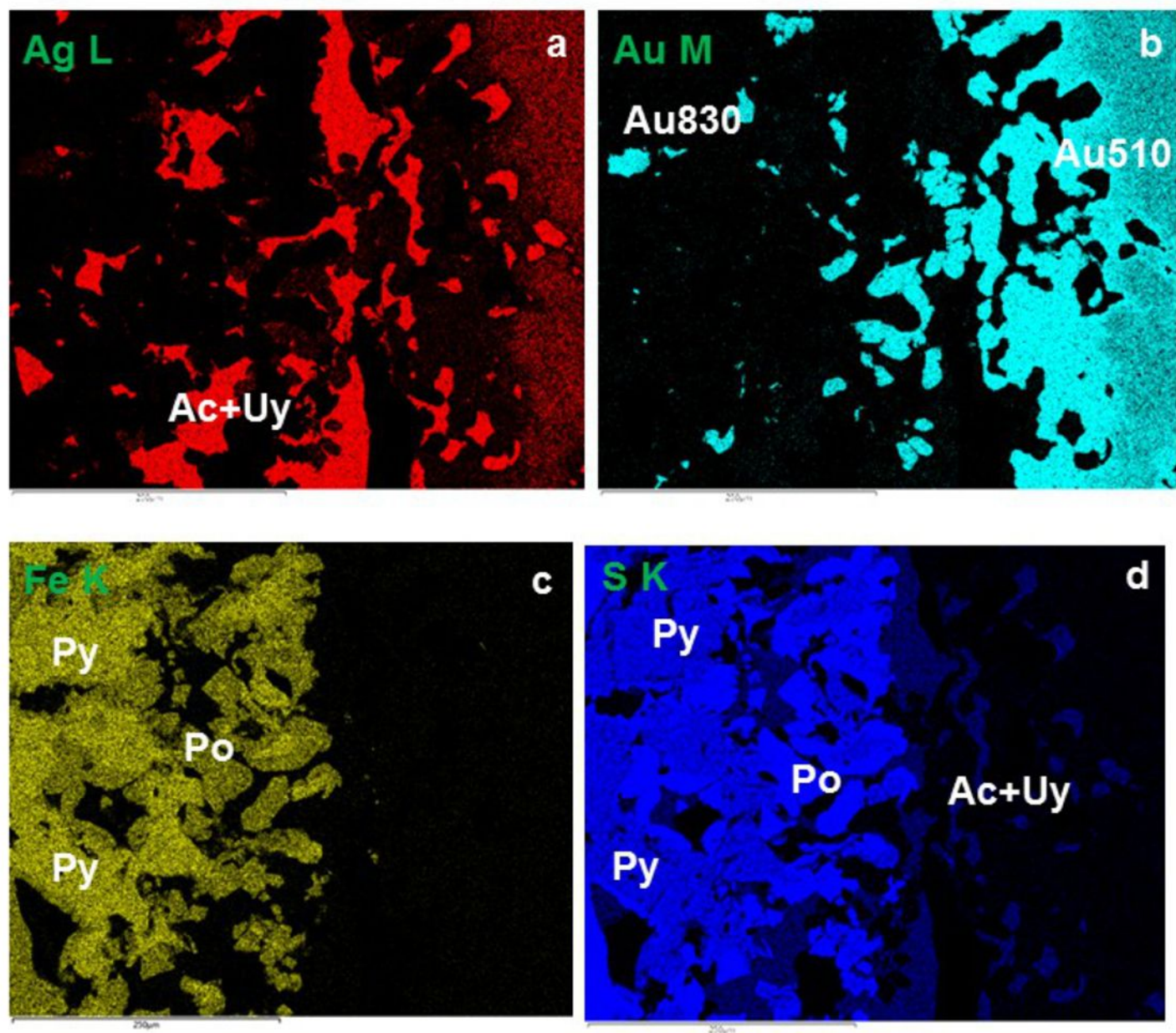
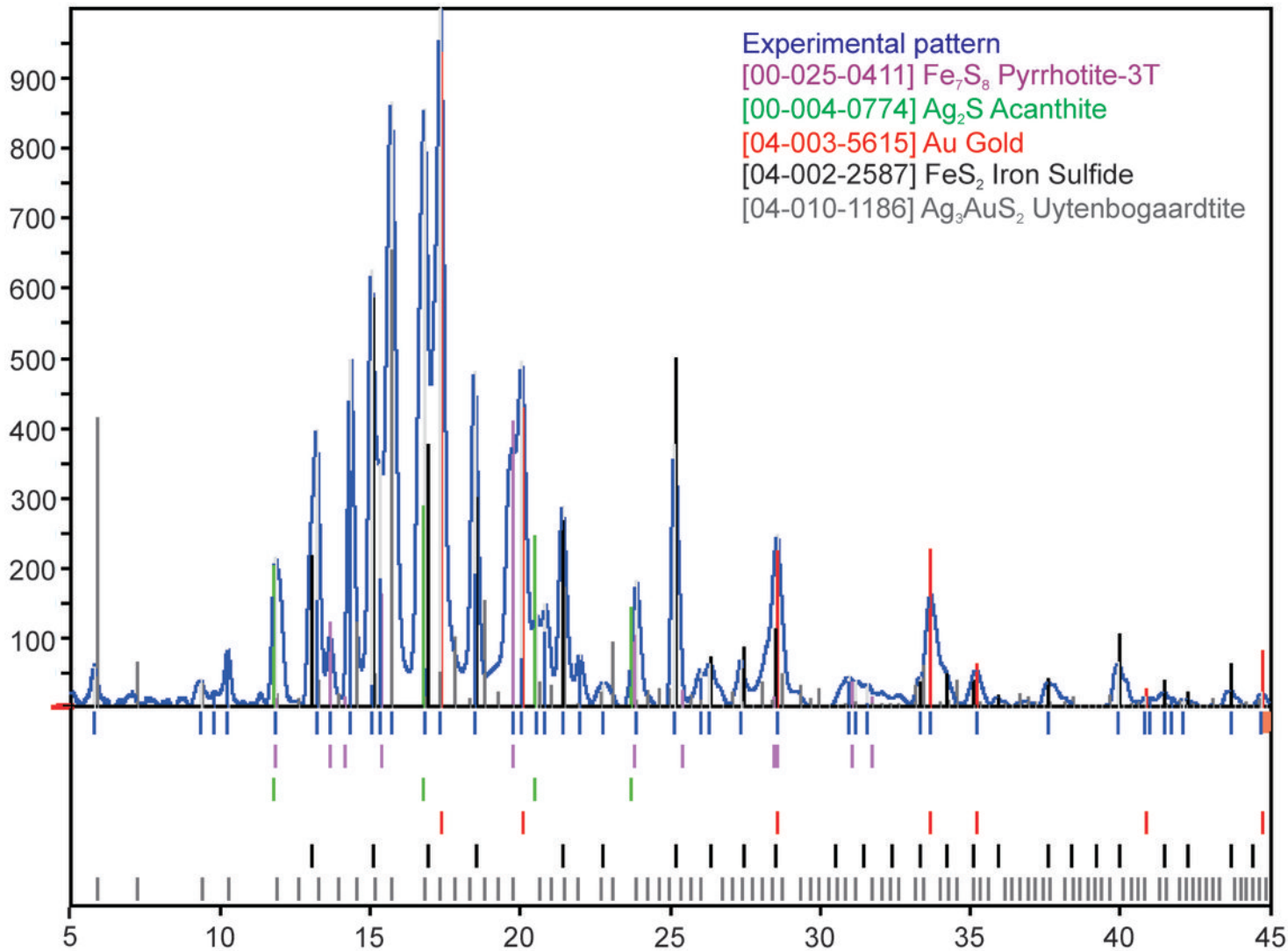


Figure 5



Intensity, counts



Experimental pattern  
[00-025-0411] Fe<sub>7</sub>S<sub>8</sub> Pyrrhotite-3T  
[00-004-0774] Ag<sub>2</sub>S Acanthite  
[04-003-5615] Au Gold  
[04-002-2587] FeS<sub>2</sub> Iron Sulfide  
[04-010-1186] Ag<sub>3</sub>AuS<sub>2</sub> Uyttenbogaardite

Diffraction angle, °2θ