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

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ABSTRACT

Dry annealing of AuAg1-x alloys (x = 0.19, 0.35, 0.56 or of fineness 300, 500, 700‰) and pyrite was used to reveal the solubility of Au (Ag) in FeS2 and study phase equilibria in the FeS2-AuAg1-x system at 500 °C. Pyrrhotite, acanthite, and yutnoboagardite and Au-Ag alloys with increased fineness were established at the contacts of pyrite blocks with Au-Ag plates. The obtained results evidence the absence of solubility between FeS2 and Au (Ag) at 500 °C. The Ag content in alloys influences the stability of pyrite and contributes to its transformation in pyrrhotite and sulfidation and ennobling of Au-Ag alloys. Au-Ag sulfides and pyrrhotite may be present in the sulfide ores of metamorphogene deposits as annealing products of Au-Ag-pyrite-bearing ores.

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

INTRODUCTION

Pyrite is the most well-known and widespread mineral of the iron sulfides. It is a common constituent of many igneous, metamorphic, and sedimentary types of rocks and of hydrothermal veins. More important is the fact that pyrite is a collector of gold and silver (Boyle 1968, 1979). Revealing the forms of occurrence of noble metals in iron sulfides is of fundamental and applied importance. Pyrite often contains micro inclusions of native gold, Ag-Au chalcogenides and other minerals of gold and silver that are visible under optical microscope and scanning electron microscope (Zhou et al. 2004; Palyanova et al. 2015a, 2016). It has been established so far that “invisible” gold occurs as submicrometer or nano-sized inclusions or solid solution in the structure of iron sulfides (Vikentyev 2015 and its reference list). The amount of isomorphous gold incorporated into pyrite lattice covers a wide range of values as reported by some authors (Fleischer 1955; Cook and Chryssoulis 1990; Abraitis et al. 2004; Vaughan 2004; Palyanova et al. 2015b). Gold and silver concentrations in pyrites range from below one parts per million to almost thousand parts per million.

To determine the probability of incorporation of gold and silver into pyrite, we conducted experiments of solid-phase diffusion (Jin 1981), using natural pure pyrite and synthetic Au-Ag alloys of varying composition. According to this technique, if the plates of two substances A and B are brought into contact and then kept at temperature when diffusion is probable, their composition finally becomes homogeneous. If isomorphism between two components is absent, various compounds stable in the A-B system are formed in the contact zone. This technique is successfully applied to study many binary and ternary systems and construction of the isothermal sections of phase diagrams (Kodentsov et al. 2001). However, this technique has restrictions; melting should be avoided. Data from the phase diagram Fe-S (Kullerud and Yoder 1959; Arnold 1962; Waldner and Pelton 2005; Wang and Salveson 2005) evidence that pyrite is unstable at temperatures above 742–745 °C and melts incongruently with formation of pyrrhotite and sulfur. At temperatures between the melting point and 325 °C, pyrite coexists with pyrrhotite of various compositions Fe1–yS (0.78 < y < 1) or FeS (1 < x < 1.23). To avoid melting of pyrite, the specified temperature in the experiments was 500 °C. Application of this technique allows studying phase equilibria in the FeS2-AuAg1-x system. One of the tasks of the investigation was to study the behavior of noble metals in the process of desulfidation of pyrite (Craig and Vokes 1993; Thomas et al. 2011) and sulfidation of native gold (Palyanova et al. 2014), which are typical of natural processes.

EXPERIMENTS AND ANALYTICAL METHODS

Starting compositions

In the experiments we used a large natural pyrite single crystal from the Beresovskoe gold-quartz deposit (Ural, Russia). Microprobe analysis showed that pyrite crystal is homogenous and does not contain micro impurities. First, a plate ~5–6 mm thick was cut from the crystal. After polishing on 1 μm diamond paste, the plate was cut into bars with polished area ~3 × 3 mm. Gold-silver alloys of AuAg0.19, AuAg0.35, AuAg0.56, and AuAg0.65 composition [gold fineness = 1000×Au/(Au+Ag), by weight, 300, 500, and 700‰, respectively] synthesized from a stoichiometric mixture of pure metals were rolled out to the thickness of ~200 μm and cut into plates measuring 3 × 3 mm. Then metal sheets were placed between polished surfaces of the pyrite bars, and the resulting column was sealed under 10−3 torr in the quartz ampoule. The samples were slowly heated to 500 °C in the isothermal zone of the furnace and kept at this temperature for 7 days. After annealing, the ampoule was cooled to room temperature in the switched off furnace.

Analytical techniques

Optical microscopy, scanning electron microscopy (SEM), electron microprobe analysis (EPMA), and X-ray powder diffraction methods were applied to study the samples. A polished section was prepared from the synthesized phases for microscopy analyses. Studies on the chemical composition of the synthesized substances were carried out using MIRA 3 LMU SEM (TESCAN Ltd.) combined with the microanalysis systems INCA Energy 450+ on the basis of the high-sensitivity silicon