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## The Occurrence Mechanism of Gold in Pyrite from the Qiucun Gold Deposit in Fujian Province, China

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### 1 Introduction

Precipitation and enrichment of gold is an important subject in the study of gold deposits. As the most common sulphide in gold deposits, pyrite is not only a good indicator of the evolution of mineralizing fluids, but also the important gold-bearing mineral. In this paper, we have focused on the occurrence form of invisible gold in pyrite, which has a great significance in understanding mineralogy and geochemical behavior of gold and choosing the technology to extract gold ores.

Scientists hold different views in the enrichment and the occurrence form of gold in pyrite. Palenik et al. (2004) considered gold nanoparticles form by exsolution from pyrite as the temperature decreases. Reich et al. (2005) indicated that the relationship of gold and arsenic in pyrite ( $C_{Au}=0.02C_{As}+4\times 10^{-5}$ ) puts an upper limit on the solubility of gold in pyrite; above the limit, gold nanoparticles would occur, while gold would form the solid solution in pyrite below the limit. The above two views are closely related to gold solubility in pyrite. Fougere et al. (2016) considered that the occurrence of gold nanoparticles may result from the combined effect of crystal growth rate and gold ion diffusion; the slow growth favors ion diffusion on the surface and formation of nanoparticles. Prokhorov and Lu (1971) considered that arsenic can change semiconducting properties of pyrite and promote the adsorption of gold on the surface of pyrite (Prokhorov and Lu, 1971; Mironov et al., 1981; Maddox et al., 1998; Mikhlin et al. 2007).

The substitutions of Au for Fe and As for S will inevitably result into changes of the lattice because gold and arsenic own larger effective ion radii than iron and sulfur. Moreover, the faster the crystal grows, the denser the defects are. Invisible gold is probably accommodated

at these defects. By studying the variation characteristics of pyrite lattice, we have acquired a preliminary understanding of occurrence form of gold in pyrite.

### 2 Geologic Setting

The Qiucun Gold Deposit is located in Dehua County, Fujian Province. The ore deposit outcropped in the diorite porphyrite, sandstone, and belongs to the volcanic and subvolcanic type gold deposit. The pyrites behave as fine euhedral and subhedral grains. The crystal forms are mainly cube and pentagonal dodecahedron. It can be seen that early pyrites are replaced by chalcopyrite, sphalerite and galena. Electrum and silver minerals such as polybasite and fahlore filled in the fissures and pores of pyrite. The mineralization stage can be divided into a quartz-pyrite stage, a quartz-sulphide stage and a quartz-carbonation stage.

### 3 Methods and Results

The samples were collected from the Qiucun Gold Deposit and analysed by Field emission scanning electron microscopy (FESEM), electron-microprobe analysis (EMPA), Laser ablation plasma mass spectrometer (LA-ICP-MS) and Laser Raman microprobe (Raman).

FESEM results show pyrite owns the arsenic-rich rim, which indicates higher arsenic fugacity in the later fluid. EMPA results show the arsenic content is up to 8wt% in pyrite and S/Fe ratios decrease from the inside outwards indicating the mineralizing fluid evolved towards As-rich and S-poor. LA-ICP-MS results show pyrite contains 36ppm Au, 64ppm Ag, 39ppm Sb averagely, and abnormal values of Au-Te-Sb indicate presence of Au-Te-Sb inclusions. Raman results for pyrite reveal the As-rich rims own lower wavenumbers, weaker Fe-[S<sub>2</sub>] bending vibration intensity than As-poor kernels, while

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there are no obvious changes in intensities of Fe-[S<sub>2</sub>] stretching vibration and S-S stretching vibration. HRTEM results show dislocations and small angle grain boundaries in pyrite; TEM-EDS shows Au and As are unevenly distributed in pyrite and As-rich parts are relatively enriched in Au; no gold nanoparticles have been found by HAADF-STEM. In the [001] crystal diffraction pattern, the degree of widening of the interplanar spacing gradually decreases from the plane (022), then to the plane (111), finally to the plane (200).

#### 4 Discussion and Conclusion

The decreased sulfur fugacity favors the introduction of arsenic and gold into the pyrite lattice as solid solutions. Previous studies have shown As<sup>-1</sup> enters the crystal lattice by substituting sulfur (Deditius et al., 2008; Fleet and Mumin, 1997) while As<sup>+3</sup> enters the crystal lattice by substituting iron (Deditius et al., 2008). There is a good inverse correlation of As and S ( $R^2 = 0.90$ ) as well as no correlation of As and Fe ( $R^2 = 0.15$ ), indicating arsenic is in the form of As<sup>-1</sup>.

It is generally believed that the smaller bond energy and the greater relative atomic mass result into the decreased Raman shift. Arsenic owns the greater relative atomic mass and the smaller effective ion radius than sulphur, which cause Fe<sup>2+</sup>-[AsS]<sup>3-</sup> owns smaller bond energy than Fe<sup>2+</sup>-[S<sub>2</sub>]<sup>2-</sup>. The change of the bond energy causes the shift of Raman vibration.

As is well known, the Raman intensity is up to polarization that is related to the symmetry, composition and bond properties of the analyzed mineral (Yang and Wu, 2008). [AsS]<sup>3-</sup> substituting [S<sub>2</sub>]<sup>2-</sup> will result into the lowering symmetry of the lattice which causes greater polarization and then stronger Raman intensity. However, it has been found Fe-[S<sub>2</sub>] bending vibration intensity weakens, which can be attributed to the greater polarity of As-S than S-S and the dipole moments generated by the two groups that constrain the movement of the electronic cloud, and then cause weaker Fe-[S<sub>2</sub>] bending vibration intensity.

There is an obvious positive correlation between As and Au ( $R^2 = 0.85$ ) and LA-ICP-MS datas have been plotted below the limit (Reich et al., 2005), indicating Au forms the solid solution in pyrite. Au and Cu ( $R^2 = 0.31$ ) as well as Au and S ( $R^2 = 0.36$ ) behave as moderate correlations, while no correlation can be seen between Au and Fe. Barrie et al. (2009) indicated As tends to be absorbed to the crystal plane (111) and (110) and promotes the growth in the crystal orientation of <111> and <110>. The increased interplanar spacings of {111} and {110} are probably resulted from the substitution of

As for S and promote Au with the large radius enters the crystal lattice. The relationship between Au and Fe suggests parts of Au would not substitute Fe into the lattice. The lattice defects such as the low-angle grain boundary and dislocations probably accommodate gold in pyrite.

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