Incorporation mechanism of structurally bound gold in pyrite: Insights from an integrated chemical and atomic-scale microstructural study

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Abstract

Pyrite is one of the most important carriers for Au in hydrothermal deposits, but the incorporation mechanism of structurally bound Au has long been a matter of
debate due to poor understanding of chemical state and atomic-scale structure of Au in the pyrite lattice. Arsenian pyrite is the dominant Au-hosting mineral from the Shanggong Au deposit (130t Au) in the southern margin of the North China Craton. New EPMA and LA-ICP-MS results show that the arsenian pyrite has remarkably high Au (0.05-0.78 wt%) and As (0.39-4.60 wt%). Au is negatively correlated with Fe but positively correlated with As. Z-contrast HAADF-STEM imaging reveals that Au atoms sit at the Fe atom sites in the lattice of the arsenian pyrite. Our μ-XANES results and previously reported data suggest that Au and As in arsenian pyrite are predominant of chemically bound Au$^+$ and As$^-$, respectively. We thus propose that Au$^+$ and As$^-$ are both structurally bound and sit at the Fe and S atom sites of pyrite, respectively. As may not be necessary but favorable for the incorporation of structurally bound Au in pyrite. Our study has significant implications for understanding the enrichment mechanism of Au from ore-forming fluids with low Au and As concentrations into arsenian pyrite and for exploring the role of As in Au mineralization of hydrothermal deposits.

**Keywords:** arsenian pyrite, μ-XANES spectroscopy, Z-contrast HAADF-STEM image, Au incorporation mechanism

**Introduction**

Pyrite, the most common sulfide in the Earth’s crust, has long been considered to be economically significant because it hosts large amounts of Au and many other trace elements, such as As, Tl, Te, Sb, and Se (Reich et al. 2005; Deditius et al. 2014). A positive correlation between Au and As in pyrite has been well recognized and is
taken to indicate the control of As on Au enrichment (Reich et al. 2005; Deditius et al. 2014; Kusebauch et al. 2019; Xing et al. 2019). Arsenian pyrite is also a common mineral in hydrothermal ore deposits such as Carlin, epithermal, and orogenic Au deposits (Fleet and Mumin 1997; Cline 2001; Reich et al. 2005; Deditius et al. 2014 and references therein). Invisible Au accounts for the majority of Au in arsenian pyrite, and occurs as structurally bound Au and/or Au-bearing nanoparticles (Reich et al. 2005; Deditius et al. 2014; Filimonova et al. 2020 and references therein).

Although the incorporation mechanism of structurally bound Au in arsenian pyrite has been extensively investigated (Arehart et al. 1993; Fleet and Mumin 1997; Simon et al. 1999a, 1999b; Palenik et al. 2004; Chouinard et al. 2005; Reich et al. 2005; Deditius et al. 2008), it remains a matter of debate. Precise chemical state and atomic-scale structural features of Au in the pyrite lattice are still poorly understood.

The state of Au in pyrite has attracted many studies in the past three decades (Arehart et al. 1993; Simon et al. 1999a; Palenik et al. 2004; Deditius et al. 2008; and references therein), but is still not absolutely convincing confirmed. It was traditionally considered that structurally bound Au is likely present as Au$^+$ (Simon et al. 1999a; Reich et al. 2005; Deditius et al. 2014) or Au$^{3+}$ (Arehart et al. 1993; Chouinard et al. 2005) in the lattice of arsenian pyrite, but Au$^{3+}$ has not been confirmed by spectroscopic data. Au$^0$ and ionic Au$^+$ in Au-bearing arsenian pyrite were identified by X-ray absorption near edge structure spectroscopy (XANES) with a broad-beam of 15×1 mm (Simon et al. 1999a). However, the broad beam can potentially produce mixed spectra of different states of Au. In addition, the coupled
occurrence of Au and As makes it more difficult to identify the exact chemical state and local structure of Au in arsenian pyrite because Au XANES spectra can be partly obscured by that of As (Merkulova et al. 2019). Such issues were further addressed by using recently developed high energy-resolution X-ray absorption spectroscopy (HERFD-XAS) (Trigub et al. 2017; Merkulova et al. 2019; Pokrovski et al. 2019; Filimonova et al., 2020). Trigub et al. (2017) reported that chemically bound Au replaces Fe in the synthesized As-free hydrothermal pyrite structure. Inversely, Pokrovski et al. (2019) proposed that chemically bound Au$^+$ in As-poor pyrite mainly occurs in Au$_2$S clusters. Merkulova et al. (2019) reported that chemically bound Au$^+$ also replaces Fe$^{2+}$ in the arsenian pyrite structure. Filimonova et al. (2020) demonstrated that chemically bound Au$^+$ in As-free and/or arsenian pyrite is present as both structural Au$^+$ that substitutes for Fe$^{2+}$ in the pyrite lattice and Au$_2$S-like inclusions. Given these results, understanding of the chemical state of structurally bound Au in pyrite remains elusive due to the diversity of natural samples (depending on the deposit type and ore formation conditions), low concentrations and heterogeneous distribution of Au in arsenian pyrite, and even controversial interpretations of the XAS results (Cabri et al. 2000; Pokrovski et al. 2014; Filimonova et al. 2020).

In this study, we investigated the in-situ chemical and textural features of pyrite from the Shanggong Au deposit in the southern margin of the North China Craton by using high-resolution spectroscopic techniques. The Shanggong deposit is an epizonal orogenic Au deposit, containing 130t Au at an average ore grade of 2-7g/t (No.1

Arsenian pyrite is the foremost Au carrier in the deposit. Chemical compositions of Au-rich arsenian pyrite were obtained by using electron probe microanalysis (EPMA), and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). Atomic-scale microstructural data were obtained by aberration-corrected scanning transmission electron microscopy (ACSTEM). Furthermore, \textit{in-situ} micro-X-ray absorption near edge structure (\textit{\mu}-XANES) was utilized to determine the chemical speciation of Au and As in the arsenian pyrite. The new dataset allows us to comprehensively constrain the chemical state and incorporation mechanism of Au in the arsenian pyrite.

**Geology of the Shanggong gold deposit**

The Shanggong deposit is located in the Xiong’er terrane, southern margin of the North China Craton (Gao and Zhao 2017; Zhao et al. 2018; Fig. 1a). The Xiong’er terrane contains numerous Au deposits hosted in Neoarchean high-grade metamorphic rocks and/or late Paleoproterozoic volcanic rocks (Fig. 1b). Detailed geology and metallogeny of the terrane are available in previous studies (Mao et al. 2002; Chen et al. 2006; Zhao et al. 2018). The Shanggong deposit, the largest Au deposit in the Xiong’er terrane, is located in the northern part of the Kangshan-Qiliping fault (Fig. 1c), and contains more than 30 orebodies that are controlled by the NE-NNE-trending faults (Fig. 1c). The ore-hosting rocks include metamorphic rocks of the Neoarchean-Paleoproterozoic Taihua Complex and the overlying volcanic rocks of the Paleoproterozoic Xiong’er Group. The majority of ore-hosting alteration belts in this
deposit strike northeast and broadly dip 58°-63° NW. Besides, the belts are 700-2200 m long and extend for a few hundred meters down plunge (Chen et al. 2006).

Three stages of mineralization and alteration in this deposit are identified: pre-ore quartz-ankerite alteration (S1), gold-pyritized-phyllite alteration (S2), and late quartz-calcite alteration (S3). The mineral assemblage of the S1 stage comprises quartz, ankerite, and minor epidote and pyrite, and was sheared, mylonitized, and brecciated (Fig. 2a-b), suggesting that the deformation of this assemblage formed under compressional conditions. The S2 stage, the main Au mineralizing stage, is characterized by sericitization, pyritization, and silicification (Fig. 2c-d). Two main types of ores were formed during this stage, including breccia and altered rock-type ores. Pyrite (>5 vol.%, Fig. 2c) is the predominant ore mineral and the most important Au-carrier mineral. Apart from pyrite, the ore minerals also include minor galena and sphalerite (0.1-5 vol.%) and trace chalcopyrite, magnetite, hematite, chalocite, tetrahedrite, argentite, bornite, pyrrhotite, siderite, electrum, tellurides, and native elements (Au, Ag) (<0.1 vol. %). Commonly, pyrite is crosscut or enclosed by later sphalerite, galena, and trace hessite and electrum (Fig. 2e-h). Gangue minerals are mainly quartz, sericite, and chlorite (Fig. 2c-d), with minor epidote and ankerite. The S3 stage is dominated by quartz-carbonate veinlets, locally containing chlorite, sericite, fluorite, and barite. These veinlets crosscut both mineralized fracture zones and country rocks.

**Sampling and analytical methods**

The arsenian pyrite grains used for analyses are those closely associated with
stage 2 sericite, quartz, galena, sphalerite, chalcopyrite, chlorite, and ankerite (Fig. 2c-h). In this study, samples were collected in the Exploration Tunnels, and thus are representative ores forming in the main mineralization stage (stage 2). The sampling locations are shown in Electronic Appendix Table A1.

Petrological features and major element compositions of sulfides were determined by scanning electron microscopes (SEM) and EPMA, respectively. Trace element analysis of arsenian pyrite was performed using LA-ICP-MS and Nano secondary ion mass spectroscopy (NanoSIMS). Atomic-scale structural data of arsenian pyrite were obtained by ACSTEM. Furthermore, μ-XANES was utilized to determine the chemical speciation of Au and As in the arsenian pyrite. Detailed descriptions of all the analytical methods are provided in Electronic Appendix.

Results

Textures and compositions of pyrite

According to backscattered electron (BSE) images and EPMA results, three different growth zones of pyrite (Py1, Py2, and Py3) in the S2 stage were identified (Fig. 2c-h). Py1 generally occurs in the core of pyrite grains and rimmed by Py2 (Fig. 2e-f). Py2 is further rimmed by Py3. Py1 contains abundant mineral inclusions and pores (Fig. 2e-f). In some cases, Py2 also contains pores and inclusions of rutile, sphalerite, sericite, quartz, galena, and clay minerals, but in many cases, the mineral inclusions or pores are absent (Fig. 2g-h). Generally, Py3 is almost homogenous and free of any mineral inclusions or pores (Fig. 2e-h). Notably, the zoning of Py2 is parallel to the growing boundary of pyrite (Figs. 2e-h and 4f-g). The contacts between
Py2 and Py3 are sharp and the reaction front is planar and/or curvilinear, which suggests that Py2 was replaced by the ore-forming fluids from which Py3 was deposited.

Py1, Py2, and Py3 formed in stage 2 have different compositions (Figs. 2e-h and 3a). Py2 is richer in Au and As than Py1 and Py3 and has the highest concentrations of Au (up to 0.78 wt%) and As (up to 4.60 wt%) (Table 1). The Au-rich (verified with EPMA) Py2 was selected for LA-ICP-MS analyses and the results confirm that Py2 is rich in As (10291 - 34679 ppm) and Au (1390 - 4823 ppm) (Table 2). Generally, concentrations of other trace metals in Py2 are evidently lower than that of Au and As, such as Zn (<2.71 - 57 ppm), Mo (0.28 - 0.51 ppm), Ag (67 - 320 ppm), Cd (0 - 1.40 ppm), Tl (1.12 - 7.75 ppm), Sb (7.58 - 88 ppm), and Pb (28 - 210 ppm) (Table 2). Furthermore, concentrations of Se, Sn, Hg, and Bi in Py2 are close to or below the detection limit of LA-ICP-MS.

Based on EMPA BSE and X-ray elemental images (Figs. 2e-f and 4a-c), the Py2 zones are generally 1 to 20 μm in width, As- and Au-rich, and occur as an overgrowth on Py1. Notably, some Py1 domains are also rich in As and Au (Fig. 4b-c), which might be due to overprints of the ore-forming fluids from which have precipitated Py2 (Figs. 2f and 4a-c). The elemental mapping shows that Au concentrations vary inversely with Fe and S and increase with As in Py2 (Fig. 4b-e). Additionally, EMPA results of Py2 show apparent negative correlations of As with S ($R^2=0.93$) (Fig. 3b) and Au with Fe ($R^2=0.82$) (Fig. 3c), whereas a positive correlation between As and Au in Py2 ($R^2=0.81$) is evident (Fig. 3d).
EMPA results show that Py1 has limited variations in Au (bdl-0.03 wt%) and As (bdl-0.94 wt%) contents (Table 1). Py3 has similar contents of Au (bdl-0.02 wt%) and As (bdl-0.38 wt%) with Py1. The concentrations of other trace elements in both Py1 and Py3 almost overlap and are broadly similar to those of Py2.

**As and Au distribution in arsenian pyrite (Py2)**

EPMA mapping with a beam diameter of 1μm shows that the pyrite bears a systematic zoning pattern for As and Au (Fig. 4b-c). To confirm the occurrence of Au and As in arsenian pyrite, high-resolution NanoSIMS mapping with a beam diameter of 250 nm was carried out at the location outlined by the red rectangle in Fig. 4a. The NanoSIMS images reveal that the distributions of Au and As are approximately uniform in Py2 (Fig. 4f-g), suggesting the absence of nanoparticles of Au and/or As-bearing phases in Py2. Furthermore, the LA-ICP-MS time-resolved spectra of Au and As are smooth with only minor and weak spikes (Fig. 5), also indicating that these elements preferably occur as structurally bound phases rather than nanoparticles in Py2 (Large et al. 2007; Cabri and Jackson, 2011).

**TEM data of arsenian pyrite (Py2)**

The Z-contrast HAADF-STEM images of Au-rich arsenian pyrite show that higher contrasts were detected at the Fe sites as indexed by red arrows (Fig. 6a-b), which is further confirmed by the line profile analysis with evident peaks (Fig. 6d-6e). Its corresponding fast Fourier transformation (FFT) pattern shows a higher degree of crystallinity (Fig. 6c). Besides Fe and S, the TEM energy dispersive X-ray spectrometry (EDS) analyses show that As and Au are the only detected elements in
As K-edge and Au LIII-edge micro-XANES spectra of arsenian pyrite (Py2)

As K-edge XANES spectra of arsenian pyrite and As-bearing reference materials are shown in Fig. 7. The spectra for different arsenian pyrite grains have analogous characteristics (Fig. 7a), suggesting that the local structure around As is almost the same. A sharp white line peak at 11868 eV is found in the curve of 44J-P5, which is a typical XANES curve of As in arsenian pyrite (Simon et al., 1999a; Cabri et al., 2000). Its energy position is very close to that of FeAsS as As$^-$ reference material (Fig. 7b), but far from those of As$_2$O$_3$ as As$^{3+}$ reference material and Na$_2$HAsO$_4$·7H$_2$O as As$^{5+}$ reference material, which are at 11870 eV and 11874 eV, respectively. This indicates that As in arsenian pyrite bonds as As$^-$ instead of As$^{3+}$ or As$^{5+}$.

Au LIII-edge XANES spectra of arsenian pyrite and Au-bearing reference materials, and their first derivative curves are shown in Fig. 8. The XANES spectra analyses on different grains of arsenian pyrite all have analogous characteristics (Fig. 8a), suggesting that the local structure around Au is almost the same. The XANES curve of 44J-P3 (Fig. 8b), which is Au in electrum (Fig. 2h), is similar to that of Au foil, indicating Au in electrum occurs as Au$^0$. However, for all XANES spectra of arsenian pyrite, the two broad peaks observed at 11946 eV and 11969 eV in the XANES curves of Au foil and electrum (Fig. 8b), are not found. The energy positions of the absorption edge of Au foil, representative arsenian pyrite (44J-P5), Au$_2$S, AuCl, and AuCl$_3$, usually defined as the maximum of the first derivative curve are observed at 11919.0 eV, 11919.5 eV, 11919.4 eV, 11919.6 eV, and 11918.7 eV, respectively (Fig. 8b).
Discussion

Incorporation mechanism of As in arsenian pyrite

Although As was traditionally considered to be present as As\(^{-}\) in arsenian pyrite (Simon et al. 1999a; Deditius et al. 2014), cationic As\(^{3+}\) (Deditius et al. 2008) and As\(^{2+}\) (Qian et al. 2013) also have been documented. Our \(\mu\)-XANES results suggest that the chemical speciation of As is predominantly present as As\(^{-}\) in the crystal structure of arsenian pyrite (Py2) from the Shanggong deposit. In addition, \(\mu\)-XANES spectra of different grains of arsenian pyrite are very consistent with each other (Fig. 7a), implying the chemical state of As in all arsenian pyrite crystals is univalent anion.

The EPMA results have shown a distinct negative correlation between As and S (Fig. 3b), and fairly constant (\(S + As = 1.9997\) (apfu)) content approaching stoichiometry with a variance of \(\sigma=0.0004\) in Py2 (Electronic Appendix Table A4). These features indicate a substitution of S by As in the arsenian pyrite structure. Similarly, a strong negative correlation between S and As has been reported in pyrite from Carlin Au, porphyry Cu–Au, and epithermal Au, orogenic Au, volcanogenic massive sulfide (VHMS), iron-oxide Cu–Au (IOCG) and Witwatersrand modified paleoplacer Au deposits (Deditius et al. 2014; Pokrovski et al. 2014 and references therein). Moreover, the ratios of the decrease of S atoms to the increase of As atoms per formula unit (\(N_{2:S}/N_{As}\)) range from 1.00 to 1.03 with an average value of 1.01 and variance of \(\sigma=0.01\) (Electronic Appendix Table A4), which further indicates that one As substituted one S in the pyrite lattice. It is also well shown in the \(\mu\)-XANES
spectra that the chemical speciation of As in arsenian pyrite is dominant As\(^-\). We thus conclude that As was incorporated into Py2 structure through a substitution of S by As\(^-\) in the S\(_{2-2}\) unit to form (S\(_{2-x}\), As\(_x\))\(_{2-2}\), this mechanism is commonly documented in previous studies (Cook and Chryssoulis 1990; Simon et al. 1999a, 1999b; Savage et al. 2000; Pals et al. 2003; Liang et al. 2013).

**Occurrence of Au in arsenian pyrite**

Elemental mapping by EPMA and NanoSIMS and LA-ICP-MS time-resolved spectra discussed above show that both Au and As are broadly homogenously distributed in Au-rich arsenian pyrite (Fig. 4b-c), suggesting that the two elements are mainly bonded in the structure of arsenian pyrite from the Shanggong deposit.

The Z-contrast HAADF-STEM image is a powerful method to identify not only the atomic arrangement but also trace elemental substitution within crystal lattice in sub-angstrom resolution with an ACSTEM (Lee et al. 2016; Liao et al. 2019), thus useful for exploring the Au occurrence in arsenian pyrite at the atomic-scale. ACSTEM observations show higher contrasts at the Fe sites of the arsenian pyrite (Fig. 6a-b), which is further confirmed by the line profile analysis with evident peaks (Fig. 6d-e). In theory, the intensity of HAADF-STEM images is roughly proportional to the square of the atomic number and number of atoms along the beam direction in Z-contrast images (Liao et al. 2019). This means that the brighter spots in Fig. 6a-b indicate substitution of Fe by some heavy elements in the pyrite lattice. Indeed, the TEM-EDS spectrum suggests the existence of Au and As in the arsenian pyrite crystal (Fig. 6f), and the EPMA and LA-ICP-MS results confirm that the arsenian pyrite...
grains are relatively rich in Au but depleted in other metals (e.g. Zn, Ni, Co, Ag, Te, Cu, Sb, and Pb; Tables 1 and 2). This allows us to propose that the heavy elements preferably are Au, as the atomic number of Au (Z=79) is much larger than those of Fe (Z=26), As (Z=33), and S (Z=16).

Chemical state of Au in arsenian pyrite

XANES spectrum is very sensitive to the state of elements (Simon et al. 1999a; Filimonova et al., 2020, and references therein). However, the low concentration and the heterogeneity of Au in arsenian pyrite make it very difficult to obtain high-quality Au L_{III}-edge XANES spectra (Merkulova et al. 2019; Pokrovski et al. 2019; Filimonova et al. 2020). Such a situation is further enlarged by the presence of As because the As Kα line is seriously overlapped with the Au Lα line. Given these facts, we carried out μ-XANES analyses on the arsenian pyrite that is relatively rich in Au. Moreover, these studied arsenian pyrites are depleted in other elements (e.g. Zn, Ni, Co, Ag, Cu, and Pb, Tables 1 and 2), in particular, Sb, Te, and Bi are possible coordinated with Au. The XANES spectra for Au in arsenian pyrite show a white line peak at ~11922 eV and the absence of the two broad peaks at 11946 eV and 11969 eV (Fig. 8a), implying that the Au speciation is not metal state but chemically bound Au. Besides, the XANES spectra for Au in arsenian pyrite are consistent with each other and the absorption edge of the representative μ-XANES spectrum is very close to that of Au\(_2\)S and AuCl but relatively far from that of AuCl\(_3\) (44J-P5, Fig. 8c), suggesting that Au in arsenian pyrite probably mainly occurs as Au\(^+\). Our work is consistent with recent studies of high-quality XANES using the HERFD-XAS technique (Merkulova...
Incorporation mechanism of Au in arsenian pyrite

On the basis of elemental correlations, available chemical state, and nanoscale structure of Au, several incorporation mechanisms of structurally bound Au in pyrite have been proposed. Some studies suggested that Au is adsorbed on the As-rich, Fe-deficient surface of arsenian pyrite, and such a process is able to be enhanced by As incorporation (Sha 1993; Fleet and Mumin 1997; Simon et al. 1999b; Pals et al. 2003). In contrast, most studies argued that the structurally bound Au should be incorporated into arsenian pyrite by coupled substitution of cationic Fe in distorted arsenian pyrite due to the substitution of S by anionic As in the mineral (Arehart et al. 1993; Chouinard et al. 2005; Deditius et al. 2008). Arehart et al. (1993) suggested that Au was probably incorporated into arsenian pyrite as $Au^{3+}$ at the Fe site through coupled substitution with $As^-$ at the S site by the model of $(Au_x^{3+}, Fe_{1-x}^{2+}), ([AsS^{3-}]_x, [S^{2-}_{2}]_{1-x})$. Other possible substitution models for Au and As in pyrite were also proposed, including $Au^{3+} + Cu^+ \leftrightarrow 2Fe^{2+}$ (Chouinard et al. 2005), $As^{3+} + yAu^{+} + (1 - y)\square \leftrightarrow 2Fe^{2+}$ and $As^{3+} + Au^{3+} + \square \leftrightarrow 3Fe^{2+}$ (Deditius et al. 2008).

In this study, our new results of EPMA and NanoSIMS mapping (Fig. 4b-g) and LA-ICP-MS time-resolved spectrum (Fig. 4h) indicate that Py2 is relatively rich in Au and As (Table 1) but depleted in other elements (Tables 1 and 2), and that Au and As occur as chemically bound phases in their carrier. As discussed in the previous section, Au occurs overwhelmingly as chemically bound $Au^+$ in arsenian pyrite (Py2).
Considering the large ionic size of Au\(^+\) (0.137 nm), earlier studies proposed that Au is incorporated into the arsenian pyrite structure in vacancy or defect positions rather than directly substituting for Fe\(^{2+}\) (0.061 nm) (Cook and Chryssoulis 1990; Fleet and Mumin 1997). Moreover, Pokrovski et al. (2019) proposed that chemically bound Au\(^+\) mainly occurs in sulfide clusters composed of Au\(_2\)S linear units rather than Fe or S atom sites in the structure of As-free pyrite. In contrast, recent spectroscopy studies of Au in pyrite using HERFD-XAS suggest that chemically bound Au\(^+\) occupies the Fe site (Trigub et al. 2017; Merkulova et al. 2019; Filimonova et al. 2020). Moreover, our new results of the [100] zone axis Z-contrast images of Au-rich arsenian pyrite suggest that Au atoms probably occupy the Fe atom sites (Fig. 6a-b), further confirming that Au atoms might directly substitute Fe atoms in the studied arsenian pyrite.

The local atomic environment of Au is the key factor to investigate Au incorporation in pyrite. Generally, the formal oxidation states of Fe and S in pyrite are traditionally regarded as +2 and -1, respectively. Considering the conservation law of charge, the amount of Au\(^+\) in arsenian pyrite of the Shanggong deposit is not high enough to balance the deficit of positive charge connected with a substitution of Au\(^+\) for Fe\(^{2+}\). As such, the charge imbalance may be compensated by anionic vacancies with a coupled substitution:

\[
\text{Au}^+ + \Box \leftrightarrow \text{Fe}^{2+} + S^-/[\text{As}^-] \quad (1)
\]

where [As\(^-\)] and (\(\Box\)) represent an As atom occupying at the S atom site and an anionic vacancy, respectively. However, recent spectroscopic results indicate that
structurally bound Au is covalently bonded with 6 S (Merkulova et al. 2019; Filimonova et al. 2020), suggesting that anionic vacancies are less likely to be formed in the nearest shell around Au atoms in pyrite structure. Moreover, the Fe-S bonds in pyrite structure possess both ionic and covalent character and the S-S bonds show strong covalent peculiarity (Schmøkel et al. 2014). In other words, pyrite is a mineral with highly covalent chemical bonds. This suggests that the above deficit of positive charge may be compensated by the partial electron transfers of atoms, rather than the formation of anionic vacancies on the S atom sites in pyrite structure (Schmøkel et al. 2014; Trigub et al. 2017). In summary, chemically bound Au$^+$ was incorporated into arsenian pyrite via a substitution of Au for Fe in the structure of the mineral. Nevertheless, the accurate coordination of Au in arsenian pyrite of this study needs to be further studied using HERFD-XAS and crystal structure determinations.

The role of As on the enrichment of Au in arsenian pyrite remains unclear. The positive correlation between the structurally bound Au and As in pyrite from different types of ore deposits has been widely reported (Pals et al. 2003; McClenaghan and Lentz 2004; Reich et al. 2005; Deditius et al. 2008; Muntean et al. 2011; Agangi et al. 2013; Deditius et al. 2014 and this study (Fig. 3d)), implying that the distribution and incorporation of Au in arsenian pyrite are closely related to As. Recent experimental studies demonstrated that Au incorporation in pyrite is largely dependent on As enrichment and a prolonged fluid-rock interaction rather than an anomalously Au-rich ore-forming fluid (Kusebauch et al. 2019; Xing et al. 2019). As a result, we propose that the pyrite with higher As tends to have higher Au, in other words, the
incorporation of As in pyrite could provide a favorable structural environment for the incorporation of Au. However, some other studies found that Au and As do not have a pronounced correlation and thus proposed that incorporation of the structurally bound Au in their studied pyrite is independent of As (Trigub et al. 2017; Merkulova et al. 2019; Filimonova et al. 2020 and references therein). Rather, the Au on the Fe site is only coordinated with S atoms (Filimonova et al. 2020). Moreover, these authors proposed that the correlation between Au and As should be related to the occurrence of the Au-bearing arsenopyrite or löllingite-like clusters/inclusions in pyrite, and/or the simultaneously increasing As and Au dissolved in the ore-forming fluids (Trigub et al. 2017; Filimonova et al. 2020). Pokrovski et al. (2019) proposed that Au incorporation is independent of As content in As-poor pyrite but facilitated by increasing As content in As-rich pyrite. These results imply that As might be beneficial rather than necessary for the incorporation of chemically bound Au in pyrite. In view of the diversity of natural samples, more comprehensive studies are necessary to reveal the role of As on the incorporation of Au in arsenian pyrite.

**Implication**

Arsenian pyrite is one of the most common structurally bound Au-hosting minerals in hydrothermal ore deposits. The incorporation mechanism of structurally bound Au in pyrite has been extensively investigated, but the accurate mechanism remains poorly understood. Combining a comprehensive chemical and atomic-scale structural study on Au-bearing arsenian pyrite, we propose that the chemically bound Au\(^+\) was incorporated into arsenian pyrite of this study via a substitution of Au\(^+\) for
Fe$^{2+}$ in the lattice of the mineral. Moreover, our study suggests that As could be a favorable rather than necessary condition for the incorporation of structurally bound Au in pyrite. Notably, our findings have important significance for exploring the process by which Au was enriched from ore-forming fluids with low Au and As concentrations into arsenian pyrite of hydrothermal ore deposits such as Carlin, epithermal, and orogenic Au deposits. Additionally, this study can serve as a reference for investigating the occurrence, chemical state, and incorporation mechanism of structurally bound other scatter and noble metals (e.g. PGE, Ag, Co) in their host sulfides.

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Figure captions

Fig. 1 (a) Major Tectonic outlines of China and (b) Geological map showing major deposits in the Xiong’er terrane, the southern margin of the North China Craton (modified after Zhao et al. 2018); (c) Geological map of the Shanggong deposit (modified from a 1:10,000-scale geologic map).

Fig. 2 (a) Typical orebody. Quartz (ankerite) vein was cross-cut by quartz-sericite-pyrite vein. (b) Representative brecciated ore, in which the quartz (ankerite) breccias are surrounded by quartz-sericite-pyrite vein. (c-d) Alteration of quartz-sericite-pyrite. (e-h) BSE images show the paragenesis of pyrite. Py1 generally occurs as core overgrown by Py2. The Py2 is further overgrown by Py3. The Py1 contains abundant mineral inclusions and pores and was locally corroded or replaced Py2. In some cases, the Py2 zones also contain pores and inclusions of rutile, sericite, quartz, galena, and others, but in many cases, they are absent of the mineral inclusions or pores. Generally, Py3 is homogenous and free of any pores or mineral inclusions. (f) An altered Py1 shown by a white arrow might be replaced by a later ore-fluid forming Py2 (Fig. 2e). (g-h) Fractures in Py1-3 are filled by sphalerite (Sph), galena (Gn), and trace hessite (Hes) and electrum (Elc). The area marked by the red rectangle in Fig. 2g.
is the sampling location (T5) for TEM analyses. Abbreviations: Q-quartz, Ank-ankerite, Ser-sericite, Py-pyrite, Py1-euhedral Au, As-poor pyrite, Py2- Au-rich arsenian pyrite, Py3-Au, As-poor pyrite.

Fig. 3 EPMA analyses of Py1-3 (in at.% ) from the Shanggong deposit (Electronic Appendix Table A3). (a) Ternary Fe-S-As diagram for Py1-3 (b). S vs. As diagram for Py2. (c) Fe vs. Au diagram for Py2; (d) As vs. Au diagram for Py2.

Fig. 4 (a-e) Back-scattered electron image associated with X-ray element mappings of As_Lα, Au_Mα, Fe_Kα and S_Kα obtained by EPMA. (f-g) NanoSIMS mapping images of ^75 As ^32 S and ^197 Au for the area labeled with the red rectangle shown in Fig. 4a. The intensity of color was enhanced to show the inverse relationship between As and S and Au and Fe and does not represent actual concentrations of the analyzed elements.

Fig. 5 LA-ICP-MS time-resolved spectra of spot analyses for the Au-rich arsenian pyrite (Py2). Note: The stable Fe time-resolved spectrum becomes sharp outside the red dashed rectangular box (Figs. 5a, 5e, and 5f), which might be caused by micro-inclusions in the Py2 or its fractures. Additionally, the Fe signal intensity starts to drop rapidly outside the box (Fig. 5b-d), suggesting that the Py2 was punctured. Thus, we chose the spectra marked by the box as the research object to explore the occurrence of Au and As in Py2.
Fig. 6 TEM analyses. (a) A large area [100] zone axis Z-contrast micrograph of Py2, its location (T5) is shown in Fig. 2g. (b) A Z-contrast image with the pyrite atomic model in the upper left. The red and yellow balls represent Fe and S atom, respectively. The Z-contrast image demonstrates an Au substitution at the Fe atom site with atomic resolution as significant from a brighter contrast. (c) The associated FFT pattern image. (d-e) The intensity profiles of the marked lines in Fig. 6a. The labeled stronger peaks are associated with Fe columns with substituted heavy atoms of Au. (f) The corresponded EDS spectrum for the arsenian pyrite of Fig. 6a.

Fig. 7 XANES spectrum for As in arsenian pyrite, and standard compounds of FeAsS (As$^-$), As$_2$O$_3$ (As$^{3+}$), and Na$_2$HAsO$_4$·7H$_2$O (As$^{5+}$).

Fig. 8 (a-b) XANES spectrum for Au in arsenian pyrite (Py2), electrum (44J-P3), and standard compounds of Au foil (Au$^0$, this study), Au$_2$S (Au$^+$, Pokrovski et al. 2019), AuCl (Au$^+$, Huergo et al. 2019) and AuCl$_3$ (Au$^{3+}$, Huergo et al. 2019). (c) The first derivative of Au L$_{III}$-edge XANES for Au foil, 44J-P5, AuCl, Au$_2$S and AuCl$_3$. 

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Note: (1) bdl denotes below detection limit; (2) Hg, Pb, Bi, Se, close to or below detection limit; (3) The whole dataset is listed in Electronic Appendix Table A2. (4) The reported mean concentrations for elements were calculated as half of the detection limit.
Table 2 LA-ICP-MS data for Py2 (in ppm)

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Fig. 8

(a) Relative Intensity vs. Energy (eV)

(b) Normalized Absorption vs. Energy (eV)

(c) The first derivative vs. Energy (eV)