Revision 2:

SEM and FIB-TEM analyses on nanoparticulate arsenian pyrite: implications for Au enrichment in the Carlin-type giant Lannigou gold deposit in SW China

Jun Yan¹, Ruizhong Hu¹,²*, Jean S. Cline³, Shanling Fu¹, Shirong Liu¹

¹ State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China
² College of Earth and Planetary Sciences, University of Chinese Academy of Sciences, Beijing 100049, China
³ University of Nevada Las Vegas, Las Vegas, Nevada 89154, USA

*Corresponding author.

Email: huruizhong@vip.gyig.ac.cn (Hu R.Z.)
ABSTRACT

Gold in Carlin-type gold ores is commonly hosted in the arsenian pyrite rim, but the formation of arsenian pyrite and its contribution on Au adsorption are poorly understood. Based on our previous NanoSIMS Au mapping, we conducted SEM and HR-TEM analyses to examine the Au deportment and nano-scale texture of individual auriferous arsenian pyrite grains from the giant Carlin-type Lannigou gold deposit in SW China. The results indicate that the arsenian pyrite rim is composed of numerous nanoparticulate pyrite grains (rather than a single crystal), and gold nanoparticles (Au\(^0\)) occur mainly in sub-rim with the highest Au content, which are porous and lower degree of order. We proposed that nanoparticulate arsenian pyrite attachment and aggregation is the main mechanism for the arsenian pyrite rim growth, and such mechanism is crucial for the Au efficient enrichment for this giant gold deposit.

Keywords: Nanoparticulate arsenian pyrite, nano-pore, FIB-TEM, Au efficient enrichment, Carlin-type gold deposits
INTRODUCTION

The Catlin-type gold deposits (CTGDs) are mainly found in Nevada (USA) (Hofstra and Cline, 2000; Muntean and Cline, 2018) and SW China (Hu et al., 2002, 2017; Su et al., 2018). These deposits host the second largest Au resource on Earth and provide over 9% of the global gold production (Cline et al., 2005; Muntean et al., 2011; Large et al., 2011). Gold in unoxidized CTGDs is hosted exclusively in hydrothermal arsenian pyrite, which usually contains thousands of ppm Au, three orders of magnitude higher than that in typical ore fluid (<10 ppm) (Su et al., 2009; Kusebauch et al., 2019). This implies an effective mechanism to concentration Au into arsenian pyrite to form giant Au CTGDs.

Arsenian pyrite in CTGDs commonly precipitated around earlier gold-barren pyrite cores, forming core-rim texture and/or small individual arsenian pyrite grains (Su et al., 2018; Muntean et al., 2011; Cline, 2011). In addition, gold distribution in arsenian pyrite rim shows micron-scale zoning, which was interpreted to be related to ore-fluid geochemical changes during the pyrite rim growth (Barker et al., 2009; Yan et al., 2018).

Previous works concluded that Au\(^+\) captured in pyrite rims is strongly affected by the pyrite growth rate and mechanism (Fougerouse et al., 2019; Wu et al., 2019) and surface electronegativity (Kusebauch et al., 2019; Rickard and Luther, 2007; Deditius et al., 2014; Xian et al., 2019). Polycrystalline of arsenian pyrite were reported in previous studies, and were interpreted to have formed by Au exsolution, rapid local ore-fluid geochemical changes and/or temperature drop (Palenik et al., 2004; Deditius et al., 2014; Xian et al., 2019).
et al., 2008; Wu et al., 2021). However, the role of nanoparticulate pyrites and As-rich pyrite-rim formation in Au efficient enrichment in CTGDs has not been well understood.

Based on previous works on CTGDs in Nevada, we investigated the Au deportment and nano-scale texture of individual auriferous arsenian pyrites from the giant Carlin-type Lannigou gold deposit in SW China, via a combination of high-resolution transmission electron microscopy (HR-TEM) and secondary electron microscopy (SEM). We proposed that the attachment and aggregation of nanoparticulate arsenian pyrites to form As-/Au-rich rim occur during the fluctuating disequilibrium mineralization process.

**GEOLOGICAL BACKGROUND**

South China is composed of the Yangtze and Cathaysia blocks in the northwest and southeast, respectively, and is bounded by the North China Craton and Indochina-Simao Block to the north and southwest, respectively. The Youjiang Basin is located in the southwestern Yangtze Block (Fig. 1), and is locally known as the “Golden Triangle” due to the many Carlin-type gold deposits discovered since 1978 (Tu, 1992). The Youjiang Basin is composed of Neoarchean-Neoproterozoic metamorphic rocks and Cambrian-Triassic carbonates and shales (Hu et al., 2002; Peters et al., 2007; Su et al., 2008; Hu and Zhou, 2012; Fig. 1). Indosinian (Triassic) to Yanshanian (Jurassic-Cretaceous) granitic plutons are present only on the margin of the basin, although Triassic-Jurassic intrusions are inferred to be concealed beneath the sedimentary strata according to inherited zircon data of mafic dikes (Hu et al.,
The Lannigou (aka. Jinfeng) gold deposit is a giant CTGD in the Youjiang Basin (Hu et al., 2002; Su et al., 2009, 2018; Fig. 1). The orebodies occur as veins and lenses in the Middle Triassic Xuman and Bianyang formations calcareous siltstone and mudstone, and are mainly controlled along steeply-dipping fault F3 (Yan et al., 2018; Zhang et al., 2003; Fig. 2). The Dachang Formation was identified at depth of Lannigou (Fig. 2A), which is widespread across the Youjiang Basin and has close genetic link to the regional low-temperature mineralization (Liu et al., 2017). Previous fluid inclusion studies on Lannigou suggested medium-low temperature (150-300°C) and low-salinity (<6 wt.% NaCl eqv) ore fluid with no occurrence of boiling (Zhang et al., 2003; Yan et al., 2020). Major alteration styles include decarbonate, pyrite, silicic and argillic alterations (Zhang et al., 2003; Fig. 3A). As one of the largest CTGDs in China, the Lannigou deposit contains total Au reserve of over 109 tones (t) @ 3.83 g/t (Su et al., 2018). Gold at Lannigou is invisible and hosted in arsenian pyrite, which is the dominant sulfide in the auriferous quartz-sulfide veins (Su et al., 2009, 2018; Fig. 3A).

SAMPLES AND METHODS

Sample descriptions

Our samples were collected from a high-grade orebody (~7 g/t Au) at Lannigou. The auriferous pyrites are closely related to silicification with typical core-rim texture (Figs. 3A, B), as confirmed by micro-laser-Raman spectroscopy (Fig. 3C). Fractured
individual auriferous pyrites were prepared for SEM analyses to examine the
micro-nano structures in/between the core and rims. Polished thin sections were
prepared from these samples, which were mapped via the backscattered electron
(BSE), electron probe micro-analysis (EPMA) and nano-scale secondary ion mass
spectrometry (NanoSIMS) techniques (Yan et al., 2018) to select the FIB-TEM
analysis area. EPMA and BSE analyses were performed on a JEOL JSM7800F field
emission scanning electron microscope (FE-SEM). Nano-scale elemental mapping
was conducted on a CAMECA NanoSIMS 50L, with the effective ion beam depth of
< 100 nm (for S-isotope analysis) and < 10 nm (for elemental mapping) (McPhail and
Dowsett, 2009). Foil for TEM observation was conducted across a profile of the
selected area with ~10 μm depth (Fig. 4), and thus the NanoSIMS analysis has no
effect on the TEM observation. Detailed instrument conditions and procedures of
EPMA and NanoSIMS mapping were as described in previous studies (Yan et al.,

Previous NanoSIMS mapping indicated that pyrite growth from Lannigou deposit
can be divided into three stages according to the Au-As contents (Yan et al., 2018;
Figs. 3D, E): Stage I As-Au-poor pyrite core is overgrown by stage II hydrothermal
pyrite rim (As-rich but Au-poor), which is in turn overgrown by stage III auriferous
arsenian pyrite rim. The stage III arsenian pyrite rim also can be divided into several
sub-rims and the 1st sub-rim is usually characterized by highest Au concentration.

**Micro-laser Raman spectroscopy**
To constrain the pyrite phase of the pyrite core and rim, we performed micro-Laser
Raman spectroscopic analysis using Renishaw RM 2000 and inVia Plus micro-Raman
spectrometers, equipped with a CCD detector at the Institute of Geochemistry, Chinese Academy of Sciences. The laser (532 nm) energy is 50 mW, and the acquisition time for each spectrum is 30 s. Silicon (520 cm⁻¹ Raman shift) was used as the standard.

**Scanning electron microscope (SEM) imaging**

The analysis was performed at the State Key Laboratory of Ore Deposit Geochemistry (Guiyang), Chinese Academy of Sciences. Selected pyrite grains were cracked to expose the fracture surface, and the fragments were placed on the copper stump by conductive tapes and carbon coated. Secondary electron (SE) images were collected with a JEOL JSM7800F SEM, under the operation conditions of 10 kV accelerating voltage and 10 mm working distance.

**In situ lift-out TEM foil by Focused Ion Beam (FIB)**

Based on previous NanoSIMS Au mapping (Figs. 3D-E and 5A-B; Yan et al., 2018), in-situ lift-out foils for TEM analysis from same pyrites were prepared with an FEI Dual Beam Focused Ion Beam/Scanning Electron Microscope (FIB/SEM) system, at the Center for Lunar and Planetary Sciences, Institute of Geochemistry, Chinese Academy of Sciences (Fig. 4). Polished thin sections were carbon coated and the selected areas were protected by platinum coating. The foils are about 15 μm ×7 μm ×70 nm in size. The areas with “curtain structures” on pyrite foils are usually caused by the ion beam effect (Fig. 4D), which are avoided for the TEM analysis. The vitrification of pyrite crystal may occur in the foils due to the ion beam affect, but this lattice transformation can easily be observed and avoided under the bright field TEM.
Detailed analysis procedures follow those of Wirth (2009) (Figs. 4, 5), and are summarized below:

(1) Positioning and Pt coating: the final thickness of the Pt layer is 2 μm, Ga\(^+\) beam current is 50 pA for real-time observation and 300 pA for Pt coating (30 kV).

(2) Initial digging for pyrite lamella: 15 nA for rough digging and 3nA for milling (30 kV), pyrite lamella thickness is ~1 μm (Fig. 4A).

(3) Additional milling and partial cut of the pyrite lamella, 1 nA (30 kV).

(4) Final cut-off of pyrite lamella from the sample, 1 nA (30 kV).

(5) Lift out and attach to the copper grid with Pt coating, 50 pA (30 kV) (Figs. 4B-C).

(6) Final milling to <100nm thickness pyrite foil, 1 nA, 500 pA and 300 pA (30 kV) (Fig. 4D).

(7) Polishing of foil, 48 pA (5 kV) and 43 pA (2 kV).

**TEM observation**

Transmission electron microscopy (TEM) was conducted using an FEI field emission (FE) gun microscope Tecnai G2 F20 S-TWIN with an energy dispersive X-ray spectrometer (EDS), at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Science. Point-to-point resolution is 0.24 nm, and can reach 0.19 nm in the STEM mode. The EDS detection limit is ~1 w.t.% and the analysis area for single spot is about 40 nm in diameter. The Fe-S-As peaks reflect the arsenian pyrite matrix, whilst Cu peak is mainly caused by the Cu-grid.

**RESULTS**

**Gold deportment**
Typical of auriferous pyrite in CTGDs, oscillatory-zoned pyrite rim (hundreds of nm wide) was also observed in foils by bright field TEM (BFTEM) and TEM-EDS (Figs. 6A-B). Based on the positive correlation between band brightness (under BFTEM) and As-Au contents, NanoSIMS Au mapping in horizontal plane of arsenian pyrite (Yan et al., 2018; Figs. 5B, 6C) was used to indicate Au distribution in the vertical arsenian pyrite foil for TEM (Fig. 6D). Two areas in stage III pyrite rim (with different Au content) were selected to examine the quantity and occurrence of gold nanoparticles.

Under BFTEM images, abundant Au nanoparticles (diameter: 10-40 nm) were observed. Previous NanoSIMS study on the same sample has shown that the first sub-rim has the highest Au content (No. 1 rim in Fig. 6C; Yan et al., 2018), and the Au nanoparticles occur also mainly in this sub-rim (Fig. 6E). In contrast, there are only a few Au nanoparticles in the other sub-rims, with slightly lower Au content (Fig. 6F). Most of the observed gold nanoparticles is isolated from each other in pyrite rim and/or closed to nanoparticulate pyrites which have different lattice fringes from Au nanoparticles (Fig. 7A). A few of gold nanoparticles are distributed linearly within nano-fractures in arsenian pyrite (Fig. 7B).

Polycrystallinity of arsenian pyrite rim

The micro-/nano-particulate pyrites were observed by secondary electron imaging (SEI) of SEM in fractured individual auriferous pyrite (Fig. 8). Different from the crystalline core with conchoidal fractures (orange circle in Fig. 8B), nanoparticulate pyrites closed to the pyrite core show tetrahedron/irregular polyhedron shape or...
spherule aggregates (diameter 100-500 nm) (Figs. 8B-D), whilst micro-particulate pyrites in the outer shell (equal to arsenian pyrite rim) show typical pyritohedron shape (diameter 10-30 μm) (Fig. 8E).

The selected area electron diffraction (SAED) and fast Fourier transformation (FFT) pattern is the primary method to evaluate pyrite crystallization. The SAED or FFT patterns of monocrystalline pyrite shows dot arrays. However, patterns of polycrystalline pyrite show disorganized scatters (Deditius et al., 2008). Crystallinity features of the stage II and III arsenian pyrite sub-rims were examined from the inner to outer of pyrite rim by BFTEM image (Figs. 5C-E, 9B-E). Different from the SAED feature of pyrite core (inset in Fig. 9A), SAED patterns of pyrite rim (insets in Figs. 9B-E) show disorderly feature with systematic change from inner to outer of arsenian pyrite rim. Highly disorder (inset in Fig. 9D) and porous features were observed in early-stage III pyrite sub-rim (equal to the 1st sub-rim of arsenian pyrite in Fig.6C), which contains the highest Au content (Fig. 3E; Yan et al., 2018) and amount of Au nanoparticles (Fig. 6E). Nanoparticulate pyritohedron pyrites (diameter: 10 nm (Fig. 7A) to 200 nm (Fig. 9F)) were observed under highly-magnified BFTEM. The nanoparticulate pyrites have different lattice fringes, and the matrix between them is composed of smaller nanoparticulate or colloidal pyrite grains (Fig. 7A).

DISCUSSION

Gold deportment in arsenian pyrite

Determining the invisible gold speciation and distribution in arsenian pyrite is essential in understanding the Au deposition in CTGDs (Deditius et al., 2014;
Pokrovski et al., 2019). It is widely accepted that Au in the pyrite occurs as structural-bound $Au^+$ and minor submicron $Au^0$ particles (Muntean et al., 2011; Deditius et al., 2014; Palenik et al., 2004; Simon et al., 1999). Based on the decoupling between isolated distribution of gold nanoparticles and continuous variation of Au concentration revealed by the high-resolution (100 nm) NanoSIMS Au mapping (Yan et al., 2018; Figs. 3E, 5B), we confirm that there is significantly more structural-bound $Au^+$ and/or $Au^0$ atoms in the auriferous rim. Combining the absence of fluid boiling in the Lannigou deposit and ore-fluid Au content of typical Carlin-type gold deposits in SW China (<10 ppm) (Zhang et al., 2003; Su et al., 2009; Su et al., 2009; Yan et al., 2020), we suggest that Au was mainly absorbed from Au-undersaturated fluid as ionic state and/or atom clusters, rather than deposited as nanoparticles from Au-supersaturated fluid.

Gold nanoparticles could be formed by multiple mechanisms: Previous experimental studies suggested that as Au-HS complexes were adsorbed onto the pyrite surface. Some $S^{2-}$ ions in the complexes may be oxidized to $S^{-1}$, and form more pyrite and reduce $Au^+$ to $Au^0$ (Kusebauch et al., 2019; Scaini et al., 1998). Exsolution of $Au^0$ in arsenian pyrite could be caused by Au oversaturation as solid solution state in pyrite (Palenik et al., 2004; Reich et al., 2005; Deditius et al., 2014). Gold atom-scale clusters could also be generated by slower pyrite crystal growth (Fougerouse et al., 2016). Temperature rise or recrystallization of metastable arsenian pyrite would also trigger Au nanoparticle formation, as $Au^0$-$Au^0$ bonds are more
energetically favorable than bonds between \( \text{Au}^0 \) and pyrite matrix (Becker et al., 2001; Mikhlin et al., 2006).

In our samples, the isolated Au nanoparticles (Fig. 7A) could be formed by accumulation of reduced Au atoms/clusters during the arsenian pyrite rim formation. In contrast, the linear distributed Au nanoparticles (Fig. 7B) were likely formed by later exsolution and accumulation, possibly led by temperature rise and/or auriferous pyrite recrystallization. Compared with the Au-poor area (Fig. 6F), there are more Au nanoparticles in 1st sub-rim of stage III, which has the highest Au content (Fig. 6E).

**Growth of arsenian pyrite rim and Au adsorption**

Gold-rich arsenian pyrite is commonly formed through the reaction of Au-HS complexes (e.g., \( \text{Au}^{(HS)^0} \), \( \text{Au}^{(HS)_{2^-}} \)) in the As\(^-\)/H\(_2\)S\(^-\) bearing fluid with reactive iron in Fe-bearing carbonate minerals and occupies the vacancy of dissolved carbonate in the wall-rock (Hofstra and Cline, 2000; Muntean and Cline, 2018; Su et al., 2009; Kusebauch et al., 2019). Previous works revealed the occurrence of nanoparticulate pyrites in arsenian pyrites, which were interpreted as the phase transition of metastable arsenian pyrite, caused possibly by Au exsolution or rapid pyrite precipitation (Palenik et al., 2004; Deditius et al., 2008; Wu et al., 2021).

In our SEI and TEM analyses, the quantity and shapes of nanoparticulate pyrites in arsenian pyrite rim (Figs. 7A, 8-9) suggest that these nanoparticulate pyrites were formed from rapid disequilibrium precipitation, instead of phase transition of metastable arsenian pyrites. The different directions of nanoparticulate pyrites’ lattice fringe under TEM analyses and (Fig. 7A) and multiple shapes (Fig. 8D) of
nanoparticulate pyrites under SEM observation suggest that the pyrite rim grew by
attachment and aggregation, rather than by single crystal or epitaxial growing (Wu et
al., 2021). The highly disorder and porous feature of pyrite rims in early stage III (Fig.
9D) could be generated by a more fluctuating fluid conditions, and formed the first
sub-rim with the highest Au concentration (No. 1 sub-rim; Fig. 6C). Previous in-situ
NanoSIMS S-isotope and As/Au mapping supported such fluctuating fluid conditions
(Yan et al., 2018; Figs. 3E, 5C). The occurrence of nanoparticulate (~10 nm) and
colloidal (<10 nm) pyrites (Fig. 7A) suggested that the observed nano-scale zoning
(Figs. 6A-B) may also be caused by fluid fluctuation or diffusion-limited
self-organization process (Wu et al., 2019).

Previous studies suggested that, under such fluctuating fluid conditions, FeS$_2$ could
be supersaturated and nucleation rate of pyrite is likely much higher than growth rate,
and amount of pyrite nuclei were formed (Wu et al., 2021; Hu et al., 2019). Benefit
from the nano-scale size and the Brownian movement, these pyrite nuclei may not
have precipitated immediately from the fluid, but keep growing into nanoparticulate
pyrite (Banfield et al., 2000). Due to crystallographic parameters preference (Tan et
al., 2015), these nanoparticulate pyrites would preferentially attach and aggregate
onto the surface of pre-existing pyrite, forming the core-rim texture observed (Fig. 3),
as well as some auriferous arsenian pyrite clusters (Figs. 5A-B). The micro-particulate
pyrites (Fig. 8E) could be formed by recrystallization of nanoparticulate pyrites which
is similar to the transformation process from pyrite framboids to euhedral pyrite
(Sawlowicz, 1993).
Gold adsorption could be affected by many factors. Experimental studies have demonstrated that Au can be efficiently chemisorbed by arsenian pyrite as $\text{Au(HS)}^0$ and $\text{Au(HS)}_2^-$ complexes (Fleet et al., 1997; Widler and Seward, 2002; Palenik et al., 2004; Xing et al., 2019). Previous studies showed that incorporation of arsenic and complex crystal shape could decrease the surface electronegativity of pyrite and promote Au-HS chemisorption (Deditzius et al., 2008, 2014; Kusebauch et al., 2019; Xian et al., 2019). Compared with monocrystalline pyrite (diameter $\sim$100 $\mu$m), the surface area of pyrite nanoparticles (diameter $\sim$10 nm) is tens of thousand times higher (Langmuir, 1916) and more beneficial for Au chemisorption. The porosity of arsenic pyrite rim (Figs. 9D, F) could allow continuous chemisorption of Au by the precipitated nanoparticulate pyrites until they are solidified and isolated from the ore fluid.

**IMPLICATIONS**

**Pyrite growth model for Au efficient enrichment**

Gold nanoparticles and nanoparticulate pyrites were revealed by FIB-TEM at the stage II and III of auriferous pyrite rim in the giant Lannigou gold deposit, SW China. Based on our results, published studies of arsenian pyrite and aggregation-based crystal growth model of natural iron oxyhydroxide (Banfield et al., 2000), we proposed that auriferous pyrite growth based on attachment and aggregation is essential for Au enrichment in this giant CTGD, as explained below in detail (Fig. 10).

1. High-As and low-Au pyrite rim composed by nanoparticulate arsenian pyrites
was formed (Figs. 10A-B) by the initial high-As and low-Au fluid pulse and pH buffer effect caused by fluid-rock interaction, in which substantial H₂S is consumed to produce the H⁺ needed \([\text{H}_2\text{S} \rightarrow \text{H}^+ + \text{HS}^-]\) for Fe-bearing carbonate dissolution \([\text{Ca(Fe)CO}_3 + 2\text{H}^+ \rightarrow \text{Ca(Fe)}^{2+} + \text{H}_2\text{O} + \text{CO}_2]\), which is a key factor for pyrite formation in CTGDs (Cline et al., 2005; Muntean et al., 2018; Hu et al., 2002).

Increased HS⁻ would hamper Au chemisorption via \(\text{Fe(S, As)}_2^+ \cdot \text{Au(HS)}_2^- \rightarrow \text{Fe(S, As)}_2^+ \cdot \text{Au(HS)}^0 + \text{HS}^-\) (Simon et al., 1999; Bowers, 1991).

2. Alternatively, with more high-As-Au ore fluid recharge and extensive neutralization of acidic ore fluid, the arsenian nanoparticulate pyrites would adsorb substantial amount of Au from the ore fluid, even though the fluid was Au-undersaturated (Fig. 10B). Meanwhile, these auriferous arsenian nanoparticulate pyrites attached on the earlier-formed low-Au pyrite would form high-Au arsenian pyrite rims (Fig. 10C).

3. Due to temperature dropping and recrystallization of nanoparticulate pyrite, native gold nanoparticles were formed by exsolution and accumulation of structural-bound Au⁰ grains and aggregates (Fig. 10D).

**Economic geology implications**

Pyrite is the most common sulfide in hydrothermal gold deposits, including orogenic, porphyry, epithermal and volcanic-hosted massive sulfide (VHMS) types. The ubiquitous zoning in pyrite from these deposits suggests that the ore fluids have undergone fluctuation and disequilibrium processes (Cline et al., 2005; Deditius et al., 2011, 2014; Goldfarb et al., 2005; Large et al., 2007, 2009; Reich et al., 2013; Sung et
al., 2009; Thomas et al., 2011). In epithermal and VHMS deposits, colloform and
316 nanoscale pyrites occur widely in growth or sector zoning of pyrite, with high
concentrations of Au, As and Cu (Deditius et al., 2008, 2009; Barrie et al., 2009;
Masslennikov et al., 2009). This suggests that nanoparticulate pyrite precipitation may
be common and important for Au efficient enrichment in these hydrothermal gold
deposits.

In addition, the occurrence of nano-gold may also have an impact on the Au
recovery in refractory ores from these gold deposits. Currently, refractory gold ores
are oxidized firstly for Au chemical leach (La Brooy et al., 1994; Eldorado Gold Corp.
Ltd., 2011). A better understanding of the forming mechanism of nano-gold, including
redox process of $\text{Au}^{+}$ and temperature behavior of $\text{Au}_0^0$, may lead to more
cost-effective methods for Au recovery.

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**Figure captions**

**Fig. 1** Regional geology of the Youjiang Basin, showing the location of Lannigou Au deposit (modified after Su et al., 2018).

**Fig. 2** Geological map (A) and profile (B) of the Lannigou gold deposit (after Yan et al., 2020).

**Fig. 3** Core-rim texture of auriferous pyrite revealed by reflected-light, BSE and NanoSIMS: A, B: Reflected-light photos showing the auriferous pyrite coexists with quartz and clay minerals; C: micro laser-Raman spectra of pyrite core and rim, compared with standard pyrite. Standard pyrite data are from the RRUFF project database (https://rruff.info). Raman shift peaks of core and rim mimic those of standard pyrite at 341 cm\(^{-1}\) and 375 cm\(^{-1}\); D, E: BSE and NanoSIMS Au maps of selected pyrite, showing the three pyrite growth stages (after Yan et al., 2018).

**Fig. 4** Schematic diagram showing the procedure of in-situ lift-out TEM foils prepared by focused ion beam (FIB) technique: A: initial digging; B: lifting out; C: attachment to the copper grid using Pt deposition; D: final milling to <100 nm thickness and polishing. White box in D shows the “curtain” structure caused by FIB ion beam effect.

**Fig. 5** Locations of the TEM foils shown in Figures 6, 7, 9: White boxes denote the TEM foil profile locations. A, B: BSE and NanoSIMS Au maps of selected pyrite shown in Figures 6-7. C: BSE image of selected pyrite shown in Figure 9. Red dots show NanoSIMS \(\delta^{34}S\) values, and orange dots show EPMA arsenic content (data from Yan et al., 2018). D, E: TEM foils shown in Figure 9.

**Fig. 6** Occurrence of gold nanoparticles. A, B: Arsenic oscillatory zoning revealed by
bright field TEM image. C: NanoSIMS Au map to indicate Au content for TEM observation in B. Line a-b denotes the TEM foil profile location. Numbers 1-5 represents the 1st to 5th Au-rich sub-rims, and the color legend is as in Figure 5. D: bright field TEM image of the foil. E, F: Gold nanoparticles in bright field TEM image of the Au-rich sub-rims (E) and Au-poor part (F).

Fig. 7 Separated and linear distributed gold nanoparticles. A: HRTEM image of a gold nanoparticle and nano-phase pyrites with different lattice fringes; B: bright field TEM image showing linear distribution of gold nanoparticles; C, D: Representative TEM-EDS of pyrite matrix and gold nanoparticles. Nano-Au = Au nanoparticles. Py NPs = pyrite nanoparticles.

Fig. 8 Nano-phase pyrites from fractured auriferous pyrite: A: SEI image of the cracked pyrite grain. The majority of this grain is gold-barren core with bits of stage II pyrite rim; B, C: magnified SEI image of selected area; D: Nano-pores and nanoparticulate pyrites (distinct from broken pyrite fragments in Figure 8B) with irregular or spherical shape; E: microparticulate pyrites in stripy stage II and III pyrite rim.

Fig. 9 Nano-phase pyrites revealed by FIB-TEM. A-E: bright field TEM images showing the core and inner to outer rim, and their respective SAED patterns are shown in the insets. White-dashed circles in A-E shown the SAED locations; F: bright field TEM image of nanoparticulate arsenian pyrites (50-100 nm diameter) (white-dashed polygon). Nano-Py = nanoparticulate pyrite.

Fig. 10 Schematic diagram for the auriferous arsenian pyrite rims growth and Au
adsorption. Black dots and spots denote the dissolved Au (Au$^+$ and Au$^0$) and Au nanoparticles, respectively.
Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 5
Fig. 6
Fig. 7

A

Py NPs

Nano-Au

10 nm

B

Nano-Au

Nano-fracture or nano-particulate Py boundary

100 nm

C

Fe S Fe Cu As

Energy (keV)

D

S Cu Au As

Energy (keV)

Fig. 7
Fig. 8
Fig. 9
Fig. 10