Fluid source and metal precipitation mechanism of sediment-hosted Chang’an orogenic gold deposit, SW China: constraints from sulfide texture, trace element, S, Pb and He–Ar isotopes and calcite C–O isotopes

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Abstract

The source of fluids and mechanism of metal precipitation in sediment-hosted, disseminated orogenic gold deposits are ambiguous. Pyrite texture, trace element, S, Pb and He–Ar isotope compositions of sulfides and C–O isotope data of calcite from Chang'an orogenic gold deposit in the Ailaoshan orogenic belt, SW China, were studied to provide a new genetic model for the sediment-hosted orogenic gold deposit, and furthering knowledge of the source of fluids and their mechanism of metal precipitation. Orebodies at Chang’an are mainly hosted by Ordovician turbidite with minor in Oligocene syenite. Two stages of mineralization have been identified in the deposit: stage I disseminated quartz–arsenopyrite–pyrite, and stage II veined quartz–calcite–polymetallic sulfides. Five generations of pyrite have been identified in turbidite: pre-ore syn-sedimentary pyrite, py_{I-1} and py_{I-2} in stage I, and py_{II-1} and py_{II-2} in stage II, and an unzoned pyrite population developed in syenite. Py_{I-1} commonly overgrows syn-sedimentary pyrite with irregular boundaries and contains arsenopyrite, galena, chalcopyrite and electrum inclusions along the boundaries. Py_{I-1} is overgrown by thin and inclusion-free py_{I-2}, and crosscut by py_{II-1}, which is rimmed by py_{II-2}.

The syn-sedimentary pyrite is distributed parallel to the sedimentary bedding and contains As (620.8 ppm), Pb (61.6 ppm), Ni (59.8 ppm), Mo (54.4 ppm), Co (23.4 ppm), and Cu (13.0 ppm) with low Au content of 0.06 ppm. This pyrite has δ^{34}S values of −18.1 to +30.4 ‰ and high radiogenic Pb isotope ratios (average $^{206}$Pb/$^{204}$Pb, $^{207}$Pb/$^{204}$Pb and $^{208}$Pb/$^{204}$Pb of 19.05, 15.86 and 39.87, respectively). Py_{I-1} and coexisting arsenopyrite are enriched in invisible Au (up to 227.1 ppm and 353.3 ppm, respectively),
As, Ni, Cu and Pb, while py$_{1-2}$ contain much lower trace element abundances relative to py$_{1-1}$ and arsenopyrite. Partial replacement of syn-sedimentary pyrite by py$_{1-1}$ plus arsenopyrite, galena, chalcopyrite and electrum, and similar Pb isotope ratios between syn-sedimentary pyrite and py$_{1-1}$ indicate that reaction of external deep Au-rich fluids with syn-sedimentary pyrite is responsible for gold precipitation in stage I. Py$_{1-1}$, arsenopyrite and py$_{1-2}$ show a narrower $\delta^{34}$S range of $-3.2$ to $7.1$ ‰ relative to syn-sedimentary pyrite, demonstrating that the fluid-pyrite interaction has homogenized the sulfur. The unzoned pyrite in syenite has similar mineral inclusions (arsenopyrite, galena, etc.), $\delta^{34}$S values (+0.6 to 6.3 ‰) and Pb isotope ratios to py$_{1-1}$, but much lower trace element abundances relative to py$_{1-1}$. It may be attributed to different reactions of similar fluids with different wall-rocks. Py$_{II-1}$ and py$_{II-2}$ in stage II contain elevated As, Pb, Cu, Sb, Zn and Ag with low mean Au content (3.3 ppm) and have $\delta^{34}$S ranges of $-2.8$ to $+1.2$ ‰ and $-6.2$ and $-0.8$ ‰, respectively. Galena in stage II has lower radiogenic Pb isotope ratios than stage I pyrites, indicative of a different Pb source or fluid evolution. The gases released from mixture of py$_{II-1}$-py$_{II-2}$ have R/Ra of 0.38 to 0.98 and $^{40}$Ar*/$^{4}$He of 0.50 to 1.34, falling between the fields of mantle-derived and crustal fluids. Late ore calcites have $\delta^{13}$C$_{PDB}$ of $-8.7$ to $2.7$ ‰ and $\delta^{18}$O$_{PDB}$ of 8.05 to 25.58 ‰, also plotting between sedimentary carbonate and mantle fields. These signatures indicate that ore fluids in stage II are base metal-rich fluids with a small amount contribution from mantle. Different ore assemblages, trace element composition and isotope data between stages I and II at Chang’an suggest that the deposit experienced an evolution from early Au-rich fluids to late base metal-rich ones.
This study highlights that ore metals in sediment-hosted disseminated orogenic gold deposits may be sourced from both deep fluids and local wall-rock, and that fluid-rock interaction behaved as key control on ore precipitation.

Keywords: Pyrite texture, trace element, in situ S–Pb isotopes, sediment-hosted gold deposit, Chang’an, Ailaoshan
Introduction

(Meta)sediment-hosted, disseminated orogenic gold deposits are characterized by wide alteration zones and thick orebodies with low grade but commonly large tonnage (Wilde et al. 2001; Large et al. 2007, 2011; Steadman and Large 2016). Their ore precipitation mechanism and the source of metals, critical subjects for understanding ore-forming process and developing enhanced exploration strategies (Barker et al. 2009; Peterson and Mavrogenes 2014; Velasquez et al. 2014; Tanner et al. 2016; Voute et al. 2019), are poorly understood, thus attracting broad interest. Ore precipitation mechanisms for these orogenic gold deposits are diverse, and include flash boiling of fluids triggered by earthquake-induced fault-valve processes (Sibson and Scott 1998; Weatherley and Henley 2013), fluid-rock reaction (Evans et al. 2006; Li et al. 2019a), and fluid mixing (Bateman and Hagemann 2004). Moreover, the origin for the gold in these orogenic gold deposits has been hotly debated by two contrasting perspectives: locally sourced from metamorphic devolatilization reactions of sedimentary rocks (Large et al. 2007, 2009, 2011; Thomas et al. 2011) and deeply sourced reservoirs, including magmatic (Lawrence et al. 2013; Treloar et al. 2015), mantle (Graupner et al. 2006; Deng et al. 2019a, 2020; Wang et al. 2019), and metamorphic fluids (Pitcairn et al. 2006; Tomkins 2010; Lawrence et al. 2013; Chinnasamy et al. 2015).

Pyrite is the most common ore mineral that forms in different stages of fluid evolution during gold mineralization (e.g., Large et al. 2007; Deditius et al. 2014), which thus allows pyrite composition associated with Au and other metals to be traced by in situ microanalytical techniques throughout the history of formation of a deposit.
(e.g., Large et al. 2007, 2009). Pyrite texture, paragenesis and trace element data have been successfully interpreted to evaluate fluid composition and mechanisms of incorporation or release of Au and other trace metals in different types of gold deposits (Large et al. 2007, 2009, 2011; Thomas et al. 2011; Cook et al. 2013; Steadman and Large 2016; Yang et al. 2016; Li et al. 2019a). Sulfur and lead isotopes in sulfide have been used to determine the fluid source(s), interaction with wall-rocks (including earlier generation of minerals), and fluid mixing processes (Ohmoto and Rye 1979; Chang et al. 2008; Meffre et al. 2008; Woodhead et al. 2009). Noble gases may constrain the fluid source because of their relatively unreactive nature, transportation with the major volatiles, and element and isotope ratios that vary by orders of magnitude between different reservoirs (e.g., Burnard et al. 1999; Mao et al. 2003; Graupner et al. 2006; Li et al. 2010; Goodwin et al. 2017). Synthesizing the methods noted above is an effective approach to understanding ore source, fluid evolution and ore precipitation (e.g., Large et al. 2013; Li et al. 2016).

The Ordovician turbidite-hosted Chang’an gold deposit (with reserves of > 30 tons Au) occurs in the southern segment of the Ailaoshan belt, SW China (Fig. 1a; Yang et al. 2010, 2011; Zhang et al. 2014a). It is one of the rare examples, globally, of an orogenic gold deposit hosted in a Cenozoic orogenic belt (Goldfarb et al. 2001; Deng et al. 2016, 2019b; Li et al. 2019b; Wang et al. 2019, 2020). Although different studies focusing on the fluid source and ore genesis at Chang’an have been carried out, they are still under debated. Characteristics of intermediate to low temperature (200–280 °C) and salinity (8–18 wt% NaCl equiv) from studies of fluid inclusions of quartz and δ34S
values of whole pyrite ($-2.0$ ‰ to $+3.6$ ‰) at Chang’an have been interpreted to be a magmatic source associated with an epithermal gold genesis (Chen et al. 2010; Tian et al. 2014). Based on features of turbidite-hosted disseminated ore, CO$_2$-rich ($-3.8$–$21.2$ ‰) ore fluids and $\delta^{34}$S values of whole pyrite ($+1.1$ ‰ to $+2.9$ ‰), Li et al. (2011) suggested that the Chang’an gold deposit is intermediate between Carlin-type and orogenic gold deposits with magmatic fluids. Based on LA-ICP-MS trace element analysis of pyrite, Zhang et al. (2014a) extrapolated that trace element-poor pyrite in syenite and trace element-rich pyrite in turbidite were formed by magmatic and metamorphic fluids, respectively, and thus considered multiply sourced fluids (metamorphic and magmatic) responsible for the Chang’an gold deposit. In this contribution, based on new observations on the deposit geology, textural and trace element analysis of pyrite, in situ S–Pb isotopes of sulfides, pyrite He–Ar isotopes and carbonate C–O isotopes, we provide systematic evidences for the mechanism of fluid–wall-rock reaction that promoted metal precipitation, and further demonstrate that sediment-hosted disseminated ores at Chang’an may be sourced from both deeply sourced fluids and local wall-rock, in contrast to two popular but contrasting origin: local metamorphic devolatilization or deep source.

**Regional Geology**

The NW-trending Ailaoshan belt is a Paleo-Tethyan suture zone separating the South China block from Indochina block (Wang et al. 2014; Deng et al. 2014; Yang et al. 2018; Fig. 1a). During the Neoproterozoic, the South China block went through oceanic
subduction, which triggered formation of a series of magmatic arcs along the western margin of the block (Cai et al. 2014). From Cambrian to Devonian, the South China block was situated along the margin of Gondwana and comprised passive continental margin sedimentary sequences (YNGMR 1990; Wang et al. 2014). As a result of opening of the Paleo-Tethys during the Silurian to Devonian, the Ailaoshan Paleo-Tethyan Ocean developed between the South China and Indochina blocks and the clastic rock sequences were deposited along the western margin of the South China block and the eastern margin of the Indochina block (YNGMR 1990; Yang et al. 2018). Southwest-directed (current direction as reference) subduction of the Ailaoshan Paleo-Tethyan oceanic crust and subsequent collision of South China and Indochina blocks determined the NW-trending structural framework (e.g., fold and thrust system, Faure et al. 2016) and formed the arc, syn- and post-collisional magmatic rocks mainly distributed in the eastern margin of the Indochina block (Liu et al. 2015a; Yang et al. 2018).

In the early stage of the continent-continent collision between India and Asia (Yin and Harrison 2000; Chung et al. 2005), the Ailaoshan belt evolved to be a metamorphic core complex belt comprising high-grade metamorphic core constrained by the Ailaoshan and Red River faults (Fig. 1b) and low-grade metamorphic or unmetamorphosed cover (Schärer et al. 1994; Jolivet et al. 2001; Anczkiewicz et al. 2007; Searle et al. 2010). The metamorphic core complex contains high-grade metavolcanic and metasedimentary rocks, including gneiss, amphibolite, and schist with predominantly Proterozoic protoliths and also some igneous protoliths of Triassic
The rocks experienced peak amphibolite-granulite facies metamorphism associated with crustal anatexis at 44–36 Ma and post-peak near-isothermal decompression occurred at 32–25 Ma, which was followed by late retrograde metamorphism at 25–14 Ma (Liu et al. 2013, 2015a). The low-grade metamorphic or unmetamorphosed cover is further subdivided into a Paleo-Tethyan arc magmatic belt in the Indochina block and the Jinping terrane in the South China block (Fig. 1b; Wang et al. 2014). Alkali-rich porphyry and lamprophyre dykes formed between ca. 36 and ca. 30 Ma as a result of melting of lower crust and enriched mantle, respectively, in the Ailaoshan belt (Wang et al. 2001; Deng et al. 2015). Major ductile shearing with a large sinistral displacement occurred between ca. 30 and ca. 22 Ma, as indicated by U–Pb zircon ages of pre-, syn-, and post-tectonic leucogranites (Chung et al. 1997; Cao et al. 2012; Liu et al. 2015b). The Ailaoshan belt has developed two-stage rapid exhumation cooling at ca. 27–17 Ma and ca. 14–13 Ma (zircon U-Th-He and apatite fission track; Wang et al. 2016). The metamorphic core complex was extruded upward along pre-existing NW-trending thrusts during in a transpressional setting and exposed by regional exhumation (Burchfiel et al. 2008).

The Chang’an gold deposit is located in the low-grade Jinping terrane, which is bound by the Ailaoshan fault to the east and Tengtiaohe fault to the west (Fig. 1b). Strata exposed in the terrane are mostly Ordovician to Triassic and Quaternary (Fig. 1b). The Ordovician and Silurian strata are composed of turbidite packages and carbonate, respectively (YNGMR 1990). Magmatic rocks occurring in the easternmost
part of the Jinping terrane are Neoproterozoic intrusions that form the basement to Phanerozoic successions (Fig. 1b). Lamprophyre dikes (Chen et al. 2014) and alkali-rich porphyries associated with porphyry/skarn mineralization (Zhu et al. 2009; Zhang et al. 2014b) were widely intruded in the Jinping area (Fig. 1b). The timing of mineralization in the Chang’an gold deposit has not been constrained precisely. Some researchers considered that the Chang’an gold deposit shares a similar age with the Tongchang porphyry deposit with age of ca. 34 Ma (molybdenite Re-Os dating; Wang et al. 2005) due to their close proximity (< 1.5 km). Based on a paleomagnetic study, Gao et al. (2018) interpreted gold mineralization at Chang’an to post-date large-scale sinistral shearing along the Ailaoshan shear zone (ca. 30–22 Ma; Liu et al. 2015b).

Deposit Geology

Lithologic units

The sedimentary units mainly consist of an Ordovician turbidite package and Silurian dolostone (Fig. 2a, b). The Ordovician sequence trends NE to EW with northwest to northerly dip and is exposed in the eastern and western parts of the mining area (Figs. 3, 4a). The Silurian rocks trend EW and are exposed in the middle part of the mining district (Fig. 2a). The Ordovician turbidite packages include a thick sequence of sandstone with minor thin layers of carbonaceous and calcareous sandstone, siltstone, mudstone and conglomerate (YNGMR 1990). The Silurian sequence, dominated by dolostone, unconformably overlies the Ordovician rocks (Fig. 3). The Palaeozoic sedimentary rocks are cut by both NE- to E-trending lamprophyre dikes (35.16 ± 0.16
Ma; biotite Ar-Ar plateau age; Wang, 2008), and NE- to E-trending and NW-trending syenite dikes (ca. 34−35 Ma; zircon U-Pb dating; Zhang et al. 2017) (Figs. 2a, 3, 4b).

The syenite dikes cut the lamprophyre dikes (Fig. 4b). The Ordovician turbidite, especially the sandstone, is the main host for orebodies with minor occurrences in the syenite (Fig. 2a, b).

**Structural setting and orebody occurrence**

The Chang’an fault, which dips at ~75° towards ~070° in the vicinity of the Chang’an gold deposit (Figs. 3, 4c), is a splay of the regional-scale Ganhe fault (Figs. 2a). The Chang’an fault is developed mainly within the Silurian dolostone and locally along the unconformity boundary between Ordovician turbidite and Silurian dolostone (Fig. 2a). The fault zone is 150–200 m wide and consists of a 10–30 m wide core central to a 60–80 m wide zone of cataclastic deformation in the Silurian dolostone and 80–100 m wide zone of cataclastic deformation in the Ordovician sandstone (Figs. 2a, b, 3). The lamprophyre and syenite dikes in the fault zone have also been deformed to cataclastic rocks (Figs. 3, 4b). Sinistral-reverse displacement on the Chang’an fault is inferred from the striations and steps on the fault planes and the secondary faults (Fig. 4c, d).

Orebodies occur within the Chang’an fault zone and are distributed in the hanging wall cataclastic sandstone zone (Fig. 2a, b). The orebodies, occurring as lenticular, stratiform-like and podiform in shape, show a NW trend with a dip of 70~80° to NE, and taper out towards the east (Fig. 2a, b). They are discontinuous over 1.8 km along strike and 20 to 253 m down dip with average thickness of 16 m and average grade of
4.54 g/t (Zhang et al. 2014). Ore shoots are mainly distributed around the intersection between secondary faults and the contact between Ordovician turbidites and intrusions (syenite and lamprophyre) (Fig. 3).

Alteration

The alteration types at Chang’an include silicification, sericitization, sulfidation, and carbonation (Fig. 5a-f), which are found in the Ordovician turbidite, Silurian dolostone, lamprophyre and syenite in the hanging wall of the Chang’an fault with no obvious zonation (Fig. 2a, b). In the turbidite (dominated by sandstone), the silicification and sericitization show a pervasive distribution along microfractures (Fig. 5a, b). The quartz and sericite arising from alteration are commonly distributed in pressure shadows at crystal terminations of pyrite (Fig. 5a). In the lamprophyre and syenite, the sericite and quartz together with pyrite, ankerite, apatite and rutile were preferentially developed along the biotite cleavage and grain boundaries (Fig. 5c, d). Sulfidation (sulfides; e.g. pyrite, arsenopyrite, etc.) mainly occur in the sandstone-hosted cataclastic zone (Fig. 5a, b, e, f). Two stages of carbonation including phases of calcite and ankerite may be identified in all rock types, i.e., intergrowth with sulfidation (Fig. 5e) and cross-cutting sulfidation (Fig. 5f).
Samples and Analytical Techniques

Sample preparation

Forty-three samples of pre-ore and different hydrothermal stages were collected for this study (Fig. 3). Thirty-five thin sections and nineteen polished mounts from different spatial locations were prepared for mineralogical and textural studies. Nine polished mounts from orebodies (CA20, CA33, CA36, CA38 and CA39) and weakly mineralized turbidite sequence (CA21 and CA25) and syenite (CA1 and CA29) (Fig. 3) were further selected for analyses of trace elements and S–Pb isotopes of sulfides (pyrite and arsenopyrite). Trace element and Pb isotope of sulfides were analyzed by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), and S isotopes in sulfides were analyzed using sensitive high-resolution ion microprobe (SHRIMP). Four pyrite samples from hydrothermal stage II (CA17, CA31, CA34 and CA35) were separated by hand-picking (60–80 mesh size; 99% purity) for He–Ar isotope analysis. Four calcite samples from stage II (CA22B, CA24B, CA27B and CA37B) and six from stage III (CA22N, CA24N, CA27N, CA33N, CA37N and CA38N) (Fig. 3) were hand-picked under a binocular microscope with the purity of 99% for C–O isotope analysis.

Morphology and composition analysis of sulfides

Polished thin sections and mounted blocks of ore samples were examined under optical microscope to study the morphological and paragenetic features of the sulfides. The samples were further examined using a scanning electron microscope (SEM) to
identify compositional zoning and micro-textures. The SEM analysis was carried out at the Key Laboratory of Deep-Earth Dynamics, Institute of Geology, Chinese Academy of Geological Sciences, using the FEI Nova NanoSEM 450. The back scattered electron (BSE) images were taken under operating voltage of 15-20 KV and the working distance of 13.5 mm.

LA-ICP-MS trace element analyses

The trace element compositions of pyrite and arsenopyrite were analyzed at the LA-ICP-MS facility at the University of Tasmania using a 213-nm solid-state laser microprobe (UP213, NewWave Research) coupled to an Agilent 7500a quadruple mass spectrometer. The LA-ICP-MS spot and mapping data may be used to characterize spatial and temporal variations in the trace element composition of the sulfides (Large et al. 2009).

Because of the range of grain sizes, the beam size for spot analyses of pyrite and arsenopyrite was kept as 29 μm and 19 μm, respectively. Laser repetition rate was typically 5 Hz and laser beam energy at the sample was maintained at 2.7 J/cm². The analysis time for each spot was 90 s, comprising a 30-s measurement of background (laser off) and a 60-s analysis of the sample (laser on). The analyses were carried out in an atmosphere of pure He, which was introduced into the cell at a rate of 0.8 l/min. To improve aerosol transport, 0.85 l/min of Ar was mixed with the He carrier gas. Calibration standards STDGL3, GSD-1G and PeruPy (Belousov et al. 2015) were analyzed twice between every 31 unknown analyses and between each sample change.
Geometric mean of detection limit for Co$^{59}$, Ni$^{60}$, Cu$^{65}$, Zn$^{66}$, As$^{75}$, Se$^{77}$, Mo$^{95}$, Ag$^{109}$, Sb$^{121}$, Te$^{125}$, Au$^{197}$, Tl$^{205}$, Pb$^{208}$ and Bi$^{209}$ selected for following discussion are 0.01 ppm, 0.01 ppm, 0.76 ppm, 0.42 ppm, 3.58 ppm, 6.75 ppm, 0.004 ppm, 0.01 ppm, 0.05 ppm, 0.21 ppm, 0.007 ppm, 0.01 ppm, 0.03 ppm and 0.002 ppm, respectively.

Line and image analyses were performed under similar conditions except that a 11-µm spot size and 10-Hz pulse rate were used. Instead of individual spot locations, a series of parallel lines were ablated at a speed of 11 µm/s. The detailed process for creating a trace element map may be found in Steadman et al. (2013).

**SHRIMP S isotope**

*In situ* SHRIMP S-isotopic analysis of pyrite and arsenopyrite was undertaken at the Research School of Earth Sciences, Australian National University. A 25 µm spot size and ~1 µm beam depth were used for all samples, regardless of grain size. The Ruttan pyrite, with a $\delta^{34}$S$_{V\text{-}CDT}$ (Vienna-Canyon Diablo Troilite) values of +1.2 ‰ (Crowe and Vaughan 1996), was used as a primary standard to normalized all analyses. Errors for each sulfur isotope ratio are reported at the 2σ confidence level. The analytical errors (2σ) of Ruttan pyrite were ±0.35 ‰ (n=12), and the internal precisions are better than ±0.08 ‰ (Ireland et al. 2014). Data are expressed in delta notation such that ratios are expressed as per mil (‰) deviations from a reference value, e.g.

$$\delta^{34}\text{S} =\left(\frac{^{34}\text{S}/^{32}\text{S}}{}\right)\text{measured} / \left(\frac{^{34}\text{S}/^{32}\text{S}}{}\right)\text{reference} - 1\right] \times 1000$$

where $\left(\frac{^{34}\text{S}/^{32}\text{S}}{}\right)\text{measured}$ is the measured $^{34}\text{S}/^{32}\text{S}$ ratio, $\left(\frac{^{34}\text{S}/^{32}\text{S}}{}\right)\text{reference}$ is the reference value of that ratio used for normalization, and $\delta^{34}\text{S}$ is expressed in per mil (‰) deviation.
The detailed analytical procedures are described by Ireland et al. (2014).

**LA-ICP-MS Pb isotope**

*In situ* Pb isotope analyses of different generations of pyrites and galena in the Chang’an deposit were analyzed at the University of Tasmania, using a 213-nm solid-state laser microprobe (UP213, NewWave Research) coupled to an Agilent 7500a quadruple mass spectrometer. Laser spot sizes for analyses of pyrite and galena are 74 µm and 29 µm, respectively, and the laser operated at 10 Hz, using fluence at the sample of 2.9 J/cm². Analytical processes and conditions of the analyses are similar to those described in Woodhead et al. (2009). The NIST610 and STDGL3 glasses (Belousov et al. a. 2015), and Chatree and Jaguar pyrites (Woodhead et a. 2009) were used as calibration standard for pyrite, whereas the MtMurch and BH galena together with STDGL3 glass (Belousov et a. 2015) were used as calibration standard for galena.

**He–Ar isotopes**

Measurements of He and Ar isotopes were conducted at the Institute of Geology and Geophysics, Chinese Academy of Sciences in Beijing, using the Noblesse mass spectrometer. The Noblesse instrument with >700 mass resolution is sufficient to allow complete separation of $^3$He and HD. The operating and data processing procedures were similar to those described by He et al. (2011).

Post-mineralization structural overlap cannot be found in veinlet-hosted mineralization in hydrothermal stage II, thus fluid inclusions from pyrite (pyII-1 and pyII-
in stage II may characterize the He–Ar isotopic composition of this stage. The veinlets were separated from wall-rocks and then crushed and sieved to pass the 80–100 mesh fractions. Fresh pyrite crystals were picked by hand and washed with acetone in an ultra-sonic bath for 10 min. The grains were then rinsed in the ultra-sonic bath several times with distilled water and dried. Approximately 1 g of sample was loaded into the in vacuum crusher. Samples were transferred to an oven and roasted under conditions of 130 °C in the purification system for two or three days to remove the atmosphere attached to the surface of the samples. The mineral grains were crushed by a one-step or multistep process in a vacuum crusher at about 1500 psi to extract the noble gases. The Ar in the noble gas mixtures was trapped in a cold finger with charcoal at the temperature of liquid nitrogen. Helium was trapped in another cold finger at about 10 K and released at 35 K.

C–O isotopes

The δ¹³C and δ¹⁸O compositions of calcites formed in stages II and III were measured by GasBench coupled with Thermo Finnigan Delta V Advantage at Oxy-Anion Stable Isotope Consortium (OASIC) at Louisiana State University. About 0.20 mg samples were loaded into 12 mL Labco Exetainer vials and sealed with Labco septa were flushed with 99.999% Helium and automatically acidified at 70 °C. The carbon dioxide analyte gas was isolated via gas chromatography, and water was removed using a Nafion trap. Isotopic results are expressed in the delta notation as per mil (‰) deviations from the V-PDB standard. Precisions for δ¹³C and δ¹⁸O are routinely better than 0.06 ‰ and 0.09 ‰, respectively.
Paragenesis and Pyrite Generations

Pre-ore pyrite, termed as pyₜ, is composed of layered or banded concentrations of porous pyrite or pyrite nodules parallel to the bedding of the Ordovician sequence (Fig. 4a; Table 1). The pyrite nodules are formed by dense aggregates of 5–200 µm euhedral to subhedral crystals (Fig. 6a). The porous Pyₜ occur as subhedral pyrite varying from 20 to 1000 µm across (Fig. 6b, c, d).

Based on the mineral paragenesis and cross-cutting relationships, three distinct hydrothermal stages are recognized, namely: stage I quartz–arsenopyrite–pyrite, stage II quartz–calcite–polymetallic sulfides and stage III quartz–calcite. Hydrothermal stage I is represented by disseminated distribution of quartz–arsenopyrite–pyrite, and three generations of pyrite have been identified in stage I: py₁-1 and py₁-2 in turbidite (especially sandstone), and py₁-Sy in the syenite (Figs. 3, 6b-d; Table 1). Py₁-1 has a pervasive distribution in the sandstone and is composed of euhedral-subhedral crystals ranging from 20 to 200 µm across. Py₁-1 commonly develops oscillatory zoning structure and overgrows pyₜ with irregular contact boundaries (Figs. 6c, 7b). It shows fine-grained porous texture that is commonly filled with anhedral quartz, arsenopyrite, galena, chalcopyrite and electrum inclusions (Fig. 6a-d). Py₁-Sy is euhedral-subhedral, unzoned pyrite with 20 to 150 µm across and contains similar mineral inclusions (such as fine-grained quartz, arsenopyrite and galena) to py₁-1 (Fig. 7a). Py₁-2 with 20 to 50 µm across occurring in the sandstone generally overgrows py₁-1 as thin rim to produce euhedral grains, and rarely contains base-metal mineral inclusions (Fig. 6d; Table 1).
Hydrothermal stage II occurs as quartz–calcite–polymetallic veinlets controlled by the NW-, NE- and EW-trending faults (Fig. 4e, f), which crosscut the syenite and lamprophyre (Fig. 4b). Two generations of pyrite, named pyII-1 and pyII-2, may be identified in stage II (Fig. 7b, c) and crosscut pyI-1 and pyI-2 (Fig. 7b). PyII-1 is subhedral crystal with 20 to 150 µm across and generally has porous textures with abundant inclusions of galena, sphalerite, and tetrahedrite (Fig. 7b, c). PyII-2 is euhedral with 30 to 200 µm across and commonly overgrows pyII-1 (Fig. 7b, c). PyII-2 is cogenetic with euhedral galena, chalcopyrite, sphalerite, tetrahedrite and proustite (Fig. 7c, d).

Hydrothermal stage III is dominated by NW-trending quartz and calcite veinlets with only minor sulfides (Figs. 3, 4g). The mineral paragenesis during pre-mineralization and different hydrothermal stages are summarized in Fig. 8 and Table 1.

Results

Trace element compositions

Data analyzed by 77 spots and 2 lines (one crosscuts pyI-1 and pyS in sample CA20 and the other crosscuts pyII-2 and pyII-1 in sample CA38; Fig. S1) include 14 analyses of pyS, 23 of pyI-1, 17 of pyI-Sy, 4 of pyI-2, 14 of pyII-1, 9 of pyII-2 and 13 of arsenopyrite. Results of LA-ICP-MS spot and line analyses are given in Table S1 and selected trace element compositions of different generation of pyrites and arsenopyrite are illustrated in Table 2. PyS contains a wide range of trace elements, the most abundant of which are As (geometric mean 620.8 ppm), Pb (61.6 ppm), Ni (59.8 ppm), Mo (54.4 ppm), Co (23.4 ppm), Cu (13.0 ppm), Se (8.3 ppm), Sb (4.8 ppm), Tl (4.1 ppm), Zn (4.1 ppm),
Te (3.3 ppm), Bi (0.7 ppm) and Ag (0.4 ppm) with geometric mean Au/Ag of 0.1 (Table 2). Notably, py_s contains low Au content ranging from below detection limit to 0.46 ppm (geometric mean of 0.06 ppm; standard deviation (S.D.) of 0.2) and highly variable As (2.3–10371 ppm; S.D.=3569.2) (Table 2). Py_{t-1} has significantly elevated trace elements, except Mo, Te and Tl, compared to py_s (Fig. 9; Figs. S1-3). The Au content in py_{t-1} ranges from 0.6 to 227.1 ppm (geometric mean=8.9 ppm; S.D.=63.2) (Table 2).

Other elevated trace elements include As (geometric mean 8931 ppm), Ni (248.1 ppm), Cu (139.9 ppm), Pb (120.0 ppm), Co (79.8 ppm), Sb (26.2 ppm), Zn (8.4 ppm) and Ag (8.2 ppm) with geometric mean Au/Ag of 1.2 (Table 2).

Arsenopyrite contains As (geometric mean 474554 ppm) and much higher Pb (347.2 ppm), Au (268.8 ppm; S.D.=155.6), Cu (239.1 ppm) and Sb (73.1 ppm) with Au/Ag of 22.6, but lower Ni (113.9 ppm) and Co (26.1 ppm) than py_{t-1} (Table 2). In sharp contrast, py_{t-sy} has much lower trace element contents relative to py_{t-1} and arsenopyrite (Fig. 10; Fig. S4), such as As (geometric mean 1131 ppm), Ni (63.0 ppm), Co (62.7 ppm) and Pb (8.6 ppm) with mean Au/Ag of 0.3 (Table 2). The Au content in py_{t-sy} ranges from below detection limit to 2.3 ppm with a geometric mean value of 0.4 ppm. Similarly, py_{t-2} has lower Au (0.5 to 2.4 ppm; geometric mean 0.4 ppm; S.D.=0.7) and other trace elements, such as As (2183 ppm), Ni (44.8 ppm), Co (21.7 ppm) and Pb (27.7 ppm) (Table 2), which is similar to those of py_{t-sy} but lower than those of py_{t-1} and arsenopyrite (Fig. 10). LA-ICP-MS images of pyrite from stage I also reveal spectacular compositional zoning patterns (Fig. 9; Figs. S2-3), which correspond to distinct generations of pyrite revealed by BSE petrographic observation. Figure 9 highlights
three generations of a selected pyrite grain: the core (py$_s$) has low Au, As, Sb, Pb, Cu but high Co, Ni, Bi and Te, whereas the inner rim (py$_{I-1}$) enriches in Au, As, Ag, Co, Ni, Sb, Pb, Cu and Bi, and the thin outer rim (py$_{I-2}$) contains much lower trace elements compare to py$_{I-Sy}$.

Py$_{II-1}$ contains higher As (geometric mean 11325 ppm), Pb (1061 ppm), Cu (558 ppm), Sb (241.7 ppm), Zn (63.4 ppm) and Ag (58 ppm), but lower Au (1.0 to 34.8 ppm with a geometric mean value of 4.1 ppm; S.D.=9.7) and Au/Ag (geometric mean=0.1) relative to py$_{I-1}$ (Table 2). Py$_{II-2}$ contains As (geometric mean 6311 ppm), Pb (98.5 ppm), Ni (26.6 ppm), Cu (19.5 ppm), Sb (16.8 ppm), Ag (11.7 ppm), Co (8.0 ppm), Zn (6.8 ppm) and Au (geometric mean 2.3 ppm; S.D.=4.6), all much lower than values of py$_{II-1}$ (Table 2). The spot and line analysis results for py$_{II-1}$ to py$_{II-2}$ are consistent with their LA-ICP-MS spectra (Fig. 10). Figure 10 shows a porous core (py$_{II-1}$) with galena and Au-bearing polybasite inclusions enriched in As, Pb, Cu, Sb, Ag and Zn, and a rim (py$_{II-2}$) contains lower contents of these elements compared with py$_{II-2}$. Plots based on Au-As relationship of aforementioned arsenian pyrites of different generations at Chang’an fall below the gold saturation line of Reich et al. (2005) (Fig. 11a), indicating that the gold is most probably held within the structure of the arsenian pyrite and arsenopyrite.

The pattern of the As-Au data in Figure 11a for py$_{I-1}$, strongly suggests that the gold saturation line for the Chang’an deposit is about an order of magnitude lower in Au than for Carlin-type deposits as defined by Reich et al (2005). This difference in the position of the gold saturation line has been noticed by Large and Maslennikov (in press) for several other orogenic gold deposits.
**In situ S-isotope analyses**

The SHRIMP S-isotopic data for arsenopyrite and the different generations of pyrite are shown in Table S2 and plotted in Figure 12. The $\delta^{34}S$ values of thirteen analyses of py$_{S}$ show a fairly wide range of $\sim 18.1$ to $+30.4 \text{%}$ with mean value of $+1.9 \text{%}$ (n=20), respectively. In hydrothermal stage I, twelve analyses of py$_{I1}$ grains yielded a relatively restricted $\delta^{34}S$ range of $\sim 3.2$ to $+3.3 \text{%}$ with a mean of $+0.6 \text{%}$ and seven analyses on py$_{I1-Sy}$ grains gave a $\delta^{34}S$ range of $+0.6$ to $6.3 \text{%}$ (mean = 3.4 \%). The six $\delta^{34}S$ values of arsenopyrite range from $+3.0$ to $+7.1 \text{%}$ (mean = $+4.6 \text{%}$; Table S2). The $\delta^{34}S$ values of three analyses of py$_{I2}$ range from $-2.8$ to $+0.2 \text{%}$ (mean = $-1.1 \text{%}$). In hydrothermal stage II, $\delta^{34}S$ values of py$_{II1}$ range from $-2.8$ to $+1.2 \text{%}$ (mean = $-1.2 \text{%}$, n=8), which are slightly higher than those of py$_{II2}$ with a range from $-6.2$ and $-0.8 \text{%}$ (mean = $-3.6 \text{%}$, n=10) (Table S2; Fig. 12).

**In situ Pb isotope**

**In situ** Pb isotopes of different generations of pyrites and galena in the Chang’an deposit are shown in Table S3 and Figure 13. Py$_{S}$ have $^{206}\text{Pb}/^{204}\text{Pb}$ of 18.88–19.19 (average 19.05), $^{207}\text{Pb}/^{204}\text{Pb}$ = 15.76–16.01 (average 15.86), and $^{208}\text{Pb}/^{204}\text{Pb}$ = 38.55–40.20 (average 39.87, n=5; Table S3). In hydrothermal stage I, Pb isotope ratios of py$_{I1}$ are 18.98–19.31 (average 19.15) for $^{206}\text{Pb}/^{204}\text{Pb}$, 15.85–15.90 (average 15.87) for $^{207}\text{Pb}/^{204}\text{Pb}$ and 38.37–39.91 (average 39.64, n=2), which have overlapped ranges of those of py$_{I1-Sy}$ but slight lower average values than those of py$_{I1-Sy}$ (Table S3; Fig. 13). Pb isotope ratios of galena in hydrothermal stage II fall in a limited range as follows: $^{206}\text{Pb}/^{204}\text{Pb}$ = 18.75–18.89 (average 18.84), $^{207}\text{Pb}/^{204}\text{Pb}$ = 15.63–15.71 (average 15.67),
and $^{208}\text{Pb}/^{204}\text{Pb} = 38.01–39.41$ (average 39.25, n=12; Table S3), which have generally lower average Pb isotope ratios compared to those of py$_{s}$, py$_{1-1}$ and py$_{1-Sy}$ (Fig. 13).

**He–Ar isotopes**

Results of pyrite He–Ar isotopes in stage II are shown in Table S4. The corresponding R/Ra are 0.38 to 0.98 (average = 0.73). The $^{40}\text{Ar}/^{36}\text{Ar}$ and $^{40}\text{Ar}^{*}/^{4}\text{He}$ ratios show ranges of 353.9 to 959.4 (average = 606.93) and 0.50 to 1.34 (average = 0.89), respectively (Fig. 14a), where $^{40}\text{Ar}^{*}$ represents the $^{40}\text{Ar}$ content corrected for atmospheric contribution.

**C–O isotopes**

Carbon and oxygen isotopic compositions for calcites from stages II and III are listed in Table S5 and plotted in Fig. 14b. The $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{PDB}}$ of calcites in stage II are –8.7 to -4.4 ‰ and 9.0 to 18.4 ‰, respectively, whereas those in stage III separately range from –4.7 ‰ to 2.7 ‰ and from 8.1 to 25.6 ‰ (Table S5). It is shown that the $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{PDB}}$ of most calcites in stage III are slightly higher than those in stage II (Fig. 14b).

**Discussion**

**Genetic classification**

The geological and geochemical features of mineralization in the Chang’an gold
deposit include: (1) proximity to the major lithospheric-scale Ailaoshan shear zone (Fig. 1) but hosted by second- or third-order structures (e.g., the Chang’an fault; Fig. 2a); (2) ore bodies thicken in the fault bend where the fault dip becomes more gentle; (3) gold-related alteration dominated by silicification, sericitization, sulfidation and carbonation (Fig. 5a-f); (4) lack of lateral metal zoning; and (5) trace element association of Au–As with low Ag, Cu, Zn and Pb contents (Fig. 10). These characteristics are inconsistent with the epithermal (e.g., cryptocrystalline silicification and clayization alteration with featured minerals of adularia/alunite/kaolinite; Sillitoe 1997; Hedenquist et al. 2000) and Carlin-type (e.g., decarbonation and argillation alteration and fuzzy gold-pyrite rim; Cline et al. 2005; Wang and Grove 2018) gold deposits, but consistent with those of orogenic gold deposit as summarized by Groves et al. (1998, 2003), Kerrich et al. (2000), and Goldfarb et al. (2005). These features, together with the moderate to low (200–280 °C) mineralization temperature and depths of ~3 km (Chen et al. 2010), suggest a sediment-hosted epizonal orogenic gold affiliation for this deposit.

Pre-ore pyrite formation

Distribution of py, parallel to the bedding of Ordovician strata indicates a syn-sedimentary origin for py. The Ordovician global ocean anoxic events (Strauss 2006), were favorable for trace elements (As, Pb, Ni, Mo, Co, Cu, Se, Sb, Tl, Zn and Te; in decreasing order) to be preferentially partitioned into arsenian pyrites (e.g., Large et al. 2014). δ34S values of py show a wide range of −18.1 to +30.4 ‰ (Table S2; Fig. 12), which is consistent with syn-sedimentary pyrites with large δ34S range (e.g., Large et
The highest $\delta^{34}S$ values of $\sim$30 ‰ is compared with that of Ordovician global seawater sulfate (Chang et al. 2008). Such large $\delta^{34}S$ range and occurrence of negative $\delta^{34}S$ values can be explained as bacterial sulfate reduction in a marine sedimentary environment (Canfield and Thamdrup 1994; Habicht and Canfield 1997; Canfield 2001). Py$_5$ has relatively high radiogenic Pb isotope ratios plotting above the upper crust curve of Zartman and Doe (1981) (Fig. 13), which may be attributed to the radioactive decay of U and Th of the organic matter in the Ordovician strata.

**Texture and chemical evolution of pyrite**

Based on textural observation and LA-ICP-MS data of pyrite, the textural evolution of pyrite at Chang’an, from py$_{I-1}$ to py$_{II-2}$, correlates to the systematic changes in gold and other trace metal concentrations in pyrite, indicating two pulses of metal enrichment. During the early fluid pulse (i.e., hydrothermal stage I), oscillatory-zoned py$_{I-1}$ (Figs. 6c, 7b), accompanied by quartz grains with pressure shadow structures (Fig. 5a), was precipitated. LA-ICP-MS data shows an Au, As, Cu and Sb oscillatory zoning (Fig. 9), and Au shows a positive relationship with As, Cu and Sb (Fig. 11a, b, d). The LA-ICP-MS element maps in Figure 9 show that whereas the As and Sb are uniformly distributed through py$_{I-1}$, the maximum gold band (10 – 70 ppm Au) is much thinner and concentrated on the outer part of the py$_{I-1}$ As-Sb growth zone. Py$_{I-1}$ is enriched in As, Ni, Cu, Pb, Co, Sb, Au, Zn and Ag (in decreasing order; Table 2; Fig. 9) and contains cogenetic arsenopyrite, galena and electrum inclusions (Figs. 6a-d, 9b, d), indicating
that the ore-forming fluid carried these elements noted above. The ubiquitous presence
of the Au-As–rich hydrothermal pyrite (py$_{1-1}$) overgrowths on detrital pyrites (py$_s$) (Fig.
6a-d) and their uniform trace element composition across all samples studied indicate a
uniform deposit-scale As-Au-rich hydrothermal event. The element zoning in py$_{1-1}$ may
be explained by two possible scenarios: fluid pressure fluctuation (Sibson and Scott
1998; Peterson and Mavrogenes 2014) and crystallographic incorporation of trace
elements controlled by growth rate (Barker and Cox 2011; Fougerouse et al. 2016; Wu
et al. 2019). Although pressure shadow structure of quartz that intergrown with py$_{1-1}$
indicates a possible relationship between structural pressure and formation of py$_{1-1}$ and
quartz, lack of direct evidence for pressure fluctuation from fluid inclusion study makes
the former not confirm. Similarly, the later cannot be confirmed or excluded at the
current scale of observation. Although py$_{1-Sy}$ in the syenite has much lower As, Ni, Co,
Pb and Au relative to py$_{1-1}$ (Table 2; Fig. 11), their similar mineral inclusions of fine-
grained quartz, arsenopyrite and galena (Figs. 6, 7a), and undistinguishable S and Pb
isotope compositions (Figs. 12, 13) indicate that they may be produced by the same ore
fluids. Differences in trace element compositions and sulfide texture may be attributed
to different wall-rock composition (py$_{1-1}$ in turbidite and py$_{1-Sy}$ in syenite) in which
sulfides precipitated (see “Mineralization mechanism” for further discussion). The thin
py$_{1-2}$, occurring as py$_{1-1}$ rim in the sandstone (Fig. 6d), contains much lower trace
elements (Fig. 9), indicative of a fluid waning of the early hydrothermal pulse.
The late hydrothermal pulse is represented by the formation of veinlet-hosted py$_{II-1}$
and py$_{II-2}$ in hydrothermal stage II. Py$_{II-1}$ contains galena, chalcopyrite, tetrahedrite,
sphalerite and Au-bearing polybasite inclusions (Figs. 7b, c, 10) and is enriched in As, Pb, Cu, Sb, Zn and Ag (in decreasing order) with minor Au (geometric mean 4.1 ppm; Table 2; Fig. 10). Although the trace elements in pyII-2 is lower than those in pyII-1 (Table 2; Fig. 10), pyII-2 is cogenetic with abundant euhedral galena, chalcopyrite, tetrahedrite and sphalerite (Fig. 7d). The signatures indicate that the late hydrothermal fluids are As- and base metal-rich but Au-poor. The LA-ICP-MS element images of pyII-1 show that Ag, Pb, Cu and Sb have a similar distribution (Fig. 10), and appear to be concentrated in cracks, indicating that the elevated base-metal elements are related to micro-inclusions of base-metal sulfides, particularly galena and tetrahedrite in cracks in pyII-1 (Fig. 10). Two mechanisms may explain the base-metal elements related to galena and tetrahedrite in the cracks: Ag enters into the crystal lattice of galena together with Sb (or Bi) by substitution for Pb as illustrated in the formula Ag$^+ + (\text{Sb, Bi})^{3+} = 2\text{Pb}^{2+}$ (Li et al. 2016); Ag incorporates into tetrahedrite to form argentiferous tetrahedrite via an Ag–Cu solid-state exchange reaction (Sack et al. 2003). The LA-ICP-MS element images and positive correlations between Pb and Ag, Ag and Sb, and Ag and Cu (Figs. 10d, g, h, i, 11f) support the two interpretations.

**Mineralization mechanism**

A series of lines of key evidences, including (1) partial replacement textures of py$_s$ and irregular contact boundaries between py$_s$ and py$_{II-1}$; and (2) existence of hydrothermal minerals (arsenopyrite, galena, electrum, quartz, calcite, etc.) along the contact boundaries or in the porous py$_s$ and py$_{II-1}$, support an interaction of ore fluids with sedimentary pyrite. The interaction of sedimentary pyrite and ore fluids, and
formation of hydrothermal pyrites plus minor inclusions (Apy, Gn, Ccp and Ele) can be described by:

$$\text{Py}_s + \text{Au-bearing ore fluids} \rightarrow \text{remnant py}_s + \text{py}_{1-1} \text{ (enriched in Au, As, Ni, Cu, Pb, etc)}$$

+ Apy + Gn + Ccp + Ele

There may be an intermediate step required in the above reaction, i.e., after the initiation of the reaction, a meta-stable pyrite first formed with Au, As, Pb, and Cu dissolved in the structure before it broke down to py$_{1-1}$ and arsenopyrite, galena, chalcopyrite and electrum (e.g., Stepanov 2019). This step is unequivocally supported by the fact that arsenopyrite, galena, chalcopyrite and electrum are very fine-grained (micro-inclusions) crowded in py$_{1-1}$ (Fig. 6a-d). The cogenetic gold-bearing arsenian pyrite and arsenopyrite, and hydrothermal calcite (Fig. 5b, e) and rutile in the sandstone (Fig. 9a, Fig. S3) suggest that the ore fluids have also reacted with the Fe carbonate and Fe-Ti oxides in the sandstone. Similarly, unzoned py$_{1-Sy}$ may be produced by the reaction of ore fluids with biotite in the syenite as evidenced by the replacement of biotite by pyrite and ankerite (Fig. 5d). Different reactors (py$_s$ in the sandstone and biotite in the syenite) may be responsible for differences in trace element compositions and sulfide texture between py$_{1-1}$ and py$_{1-Sy}$, such as zoned py$_{1-1}$ and unzoned py$_{1-Sy}$ that contains much lower trace elements and finer cogenetic mineral inclusions than py$_{1-1}$ (Figs. 6, 7a, 11).

These reactions indicate that the host rocks could provide part of ore materials in low-grade metamorphic rocks through fluid–wall-rock/mineral interaction rather than metamorphic devolatilization reaction.
Sources of early fluid pulse

Sulfur isotope. The Au is hosted by the sulfides, like pyrite and arsenopyrite, implying that ore fluids were enriched in reduced S and that Au was principally transported as an Au-HS complex (e.g., Seward 1991; Stefánsson and Seward 2004; William-Jones et al. 2009). The S isotope ratios thus provide insights into potential Au and ore fluid sources. The S isotope fractionation between pyrite and a reduced hydrothermal fluid is less than 2 ‰ at a temperature of ~250 °C (Ohmoto 1972), consistent with ore-forming temperature of the Chang’an gold deposit (Chen et al. 2010). Thus, the δ³⁴S values of ore sulfides should broadly mimic those of the ore-forming fluids.

Au-rich py₁₋₁ and arsenopyrite and Au-poor py₁₋₁,₃₋₄ have δ³⁴S range of −3.2 to +7.1 ‰ (Fig. 12), which falls within the normal range between about −15 ‰ and +15 ‰ for sediment-hosted orogenic gold deposits (Chang et al. 2008 and references therein). A homogeneous sulfur isotope composition may only be shifted with few per mil via changes in redox and other thermo-chemical parameters (Goldfarb and Groves 2015; Zhao et al. 2018). Such sulfur isotope composition and range (10.3 ‰) of δ³⁴S values is inconsistent with a single homogeneous sulfur reservoir, such as magmatic (0 ± 5 ‰) and mantle sulfur (0 ± 3 ‰; Ohmoto and Rye 1979), and is more compatible with, but not diagnostic of, a (meta)sedimentary sulfur source or mixed sulfur source. A comparison between the sulfur isotope data for Chang’an and sea-water sulfate plus global sediment-hosted orogenic gold deposits through time (Fig. 12) shows that the sulfur isotope composition of sulfides in stage I at Chang’an is inconsistent with those
in the underlying strata of the Ordovician hosting sequence. Several lines of evidence support that py has provided part of trace metals for this stage, as follows: (1) py contains a suite of As, Pb, Cu, Sb, etc. (Figs. 9, 11); (2) arsenopyrite, galena, chalcopyrite and electrum in stage I are intergrown with py-1 and occur as fine-grained micro-inclusions along contact between py and py-1 (Fig. 6a-d); (3) py has been partly dissolved by ore fluids, resulting in irregular boundaries (Fig. 6a-d). However, py has very low Au content (mean 0.06 ppm), suggesting that external deep Au-bearing fluid is certainly required for gold mineralization in hydrothermal stage I. Therefore, we infer that ore fluids in hydrothermal stage I were sourced from mixing external deep Au-bearing fluids and pre-ore py. There are two preferred explanations about the external Au-bearing fluids: one is deep metamorphic fluids if the Chang’an gold mineralization was coeval to regional exhumation and cooling of hot metamorphic core complex (720 °C to 760 °C; Liu et al. 2013), which could trigger metamorphic devolatilization of contacted rocks, and the other is metasomatic lithospheric mantle-sourced fluids if the Chang’an gold mineralization is later than regional exhumation and cooling. Paleomagnetic study indicates that gold mineralization at Chang’an postdated large-scale sinistral shearing along the Ailaoshan shear zone (Gao et al. 2018). If this age is valid, the external Au-bearing fluids would be sourced from metasomatic lithospheric mantle as interpreted by Wang et al. (2019). The hydrothermal sulfides in stage I show a narrower δ34S range (−3.2 to 7.1 ‰) relative to syn-sedimentary pyrite (−18.1 to +30.4 ‰; Fig. 12), demonstrating that the fluid-pyrite interaction has gradually homogenized the sulfur. The homogenization of early sulfur driven by fluid-rock
interaction and metamorphism has been reported by Chang et al. (2008).

**Lead isotopes.** Lead isotope ratios for py$_{I-1}$ and py$_{I-Sy}$ in hydrothermal stage I plot above the upper crust curve of Zartman and Doe (1981). As shown in Figure 13, py$_{I-1}$ and py$_{I-Sy}$ display higher $^{206}\text{Pb}/^{204}\text{Pb}$ ratios than those of Proterozoic volcanics and alkali-rich porphyry in the Ailaoshan belt and mafic rocks in the vicinity of Chang’an deposit (Zhou et al. 1998; Zhang and Scharer 1999; Lu et al. 2013; Fig. 13). Such Pb isotopic signature rules out the main contribution of metal from these reservoirs. Ranges of Pb isotope ratios of hydrothermal py$_{I-1}$ and py$_{I-Sy}$ at Chang’an are undistinguishable from those of py$_{S}$ (Fig. 13), indicating that the Pb metal may be sourced from the Ordovician turbidite sequence, which supports the above inference that the Ordovician sequence provided part of metals.

**Sources of late fluid pulse**

**S isotope.** Sulfur isotopic composition ($\delta^{34}\text{S} = -2.8$ to $+1.2 \permil$ with a mean of $-1.2 \permil$) of py$_{II-1}$ formed in stage II can result from a metamorphic, magmatic (0 $\pm$ 5 \permil; Ohmoto and Rye 1979), or mantle S (0 $\pm$ 3 \permil; Ohmoto and Rye 1979) source. Relative negative $\delta^{34}\text{S}$ values of $-6.2$ to $-0.8 \permil$ in py$_{II-2}$ (Fig. 12) can be attributed to the fluid oxidation since the ratio of H$_2\text{S}/\text{SO}_4^{2-}$ will decrease in the oxidized fluids, resulting in more $^{34}\text{S}$ to concentrate in $\text{SO}_4^{2-}$ and thus more negative $\delta^{34}\text{S}$ values in sulfides (e.g., Duuring et al. 2009; Kamvong and Zaw 2009).

**Pb isotope.** Lead isotope ratios for galena in hydrothermal stage II plot near the orogen and upper crust curves of Zartman and Doe (1981) (Fig. 13), indicative of a
crustal-derived lead source. The $^{207}$Pb/$^{204}$Pb and $^{206}$Pb/$^{204}$Pb ratios of galena is lower than those of py$_{1-1}$, py$_{1-Sy}$ and py$_{s}$ (Fig. 13), indicating that ore-forming fluids in stage II have less radiogenic Pb than pre-ore py$_{s}$ and those in stage I. Higher $^{206}$Pb/$^{204}$Pb ratios of galena relative to Proterozoic volcanics (Fig. 13; Zhou et al. 1998) rule out the main contribution of Pb metal from Proterozoic volcanics. In contrast, lead isotope ratios for galena partly overlaps those of Ailaoshan leucogranite, alkali-rich porphyry and mafic rocks in Western Yunnan (Fig. 13; Zhang and Scharer 1999; Lu et al. 2013), suggesting that the Pb metal in stage II possibly share similar source region with these rocks.

**He–Ar isotopes.** The 0.38 – 0.98 range (average = 0.73) in R/Ra ratios of pyrite (mixture of py$_{II-1}$ and py$_{II-2}$) at Chang’an are intermediate between the crust R/Ra ratio (0.01 to 0.05 Ra; Tolstikhin 1978) and the sub-continental lithospheric mantle (5 – 6 Ra; Dunai and Baur 1995) (Fig. 14a). The He–Ar isotopic composition at Chang’an is different from that in the Macraes gold deposits with crust-dominant helium source (Goodwin et al. 2017) and that in the Dongping gold deposit with mantle-dominant helium source (Mao et al. 2003), but consistent with those in the Murantau, Daping and Zhenyuan gold deposits with a mixed crust-mantle helium source (Burnard et al. 1999; Graupner et al. 2006; Sun et al. 2009). This signature could be explained by two possible scenarios: a mixed crust-mantle source, or mantle source with wall-rock contamination. The R/Ra ratios have been used to estimate the proportion of mantle and crustal components in fluids (Li et al. 2010). Using 5.5 Ra and 0.03 Ra as representative of mantle and typical crustal He respectively, a proportion of mantle He between 6 % and 17 % is estimated.
C–O isotopes. The $\delta^{13}C_{\text{PDB}}$ of calcites in hydrothermal stages II and III range from $-8.7$ to $+2.7 \%$ (Fig. 14b), which are consistent with those for most orogenic gold deposits ($-23$ to $+2 \%$; Ridley and Diamond 2000 and reference therein). The calcite $\delta^{13}C_{\text{PDB}}$ values at Chang’an are lower (except one value of $+2.7 \%$) than those of seawater ($0 \%$; Ohmoto and Rye 1979), much higher than those of reduced carbon in sedimentary or metamorphic rocks ($-25 \%$; Hoefs 1997), and close to but slightly higher than those of magmatic fluids and mantle ($-7$ to $-2 \%$; Deines et al. 1991; Cartigny et al. 1998). Figure 14b shows that the $\delta^{13}C_{\text{PDB}}$ and $\delta^{18}O_{\text{PDB}}$ values are intermediate between the fields of sedimentary carbonates and mantle carbonates. Sulfur isotopes of py$_{\text{II-1}}$, He–Ar isotopes of fluid inclusions released from pyrite (mixture of py$_{\text{II-1}}$ and py$_{\text{II-2}}$) and C–O isotopes of calcites suggest that the ore-forming materials in hydrothermal stage II have mantle contributions.

Two fluid pulses from distinct systems or an evolving fluid system

The field, textural, compositional and isotopic data support that the two fluid pluses in stages I and II at Chang’an may have been derived from both two distinct fluid systems and from a single, evolving hydrothermal system. These signatures are listed as follows: (1) Au-rich py$_{\text{I-1}}$ in stage I is characterized by pervasive disseminated distribution (Fig. 2b) and oscillatory zoning (Figs. 6c, 7b), whereas mineralization in stage II is hosted in veinlets (Fig. 4e, f), which cuts across the mineralization in stage I (Fig. 7c); (2) the ore assemblage in stage I is dominated by pyrite and arsenopyrite (Fig. 6a–d), which are enriched in Au, As, Ni, Cu and Pb (Fig. 10) with geometric mean
Au/Ag of 3.6 (involving py1-1 and arsenopyrite; Table 2), and contain few galena and chalcopyrite inclusions (Fig. 6a-d), whereas ore assemblage in stage II comprises pyrite containing much higher As, Pb, Cu, Sb, Zn and Ag (Fig. 11) with geometric mean Au/Ag of 0.1 (Table 2) and abundant base-metal minerals (Fig. 7c, d); and (3) sulfides in stage I have high radiogenic Pb isotope ratios and wide δ34S range, whereas those in stage II have lower radiogenic Pb isotope ratios and more concentrated δ34S range relative to those in stage I (Figs. 12, 13). Differences in ore assemblages (Fig. 8), trace element composition (Figs. 9-11) and S-Pb isotope data (Fig. 12) between two fluid pluses may be easily explained by two distinct fluid systems, which have been extrapolated as metamorphic and magmatic fluids by Zhang et al. (2014a) based on LA-ICP-MS trace element analysis of pyrite. However, any alteration overlap related to the fluid pluses at Chang’an is not identified by this work or previous studies in the literature (Li et al. 2011; Zhang et al. 2014). The differences noted above may also be attributed to various mineralization mechanism and changing mineralization conditions from stage I to stage II. For example, the high radiogenic Pb isotope ratios of pyrite in stage I relative to those of galena were more likely caused by the interaction of fluid and rock (or sedimentary pyrite). The more negative δ34S values in sulfides in stage II may be triggered by fluid oxidation due to fracture-controlled veinlets in this stage (Fig. 7b-d; Duuring et al. 2009; Kamvong and Zaw 2009). Further deposit-scale documentation and robust geochronological studies are required to better constrain the two fluid pluses in the deposit.
Implications

Two distinct metal-enrichment stages with distinct mineral assemblages and trace element compositions were identified in the Chang’an gold deposit. Early quartz–arsenopyrite–pyrite stage is dominated by Au mineralization with low base metals, whereas veinlet-hosted quartz–calcite–polymetallic sulfide stage is characterized by base metal mineralization with low gold. Mineral assemblages and trace elements of pyrite indicate that ore fluids in stage I are enriched in Au, As, Ni, Cu and Pb, whereas those in stage II contain As, Pb, Cu, Sb, Zn and Ag with low Au content. Replacement of syn-sedimentary pyrite with low Au content by inclusion- and Au-rich pyrite in stage I, $\delta^{34}$S value range (10.3‰) of pyrite in stage I, and similar Pb isotope ratios between pyrite in stage I and syn-sedimentary pyrite indicate that reaction of external deep Au-rich fluids and syn-sedimentary pyrite is responsible for gold precipitation. Sulfur and He–Ar isotopes of sulfides and C–O isotopes of calcite in stage II indicate that ore fluids have 6–17% mantle contribution. This study highlights that ore metals in sediment-hosted disseminated orogenic gold deposits can be sourced from both deep fluids and local wall-rock, and that fluid-pyrite interaction behaved as key control on ore precipitation.

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Figure Captions

Figure 1. (a) Generalized map showing major tectonic structures developed during the collision between India and Eurasia and the geographic location of the Ailaoshan orogenic belt (revised from Tapponnier et al. (1990)). Red dashed line represents part of current China National boundary. (b) Geological map of the Ailaoshan gold belt showing the distribution of high- and low-grade metamorphic belts. The location of the Chang’an gold deposit in the low-grade Jinping terrane is indicated (revised from Wang et al. (2014)).

Figure 2. (a) Geological map of the Chang’an gold deposit, showing the major lithologic units, widespread wall-rock alteration halo and gold orebodies (revised from Yunnan Gold Mining Co. Ltd, unpublished report, 2015). (b) Cross-section of the Chang’an gold deposit, showing lithologic units, wall-rock alteration, and geometry of ore bodies. Modified from the unpublished internal geological map of Yunnan Gold Mining Co. Ltd. Two colors in a legend (turbidite, dolostone, syenite or lamprophyre) represent unaltered (to the left) and altered (to the right) rock.

Figure 3. Photograph of open mining pit, showing distribution of lithologic units, structures, and sample locations as well as contour map of Au grade at 1580 m level.

Figure 4. Photographs of structural features, crosscutting relationship and mineralization styles. (a) Sedimentary pyrites (py; outlined by dashed ellipses) in the...
Ordovician strata. (b) A syenite dike cutting an earlier lamprophyre. (c) Core of the Chang’an fault composed of several secondary faults in the northern part of the open pit. (d) Striations and steps in the fault planes of the Chang’an fault, showing a sense of sinistral-reverse movement. (e) An EW-trending quartz-calcite-polymetallic sulfide veinlet in the Ordovician sandstone. (f) A NS-trending quartz-calcite-polymetallic sulfide veinlet in the syenite. (g) NW-trending quartz-calcite veinlets in the Ordovician sandstone.

Figure 5. Photomicrographs (cross-polarized light: a-c and e; BSE: d; plane-polarized light: f) of different rocks showing the alteration characteristics in the Chang’an gold deposit. (a) Quartz-, sericite-, and pyrite (py$_s$ and py$_{1-1}$)-altered sandstone. (b) Quartz-, sericite-, pyrite (py$_{1-1}$)- and arsenopyrite-altered sandstone. (c) Quartz-, sericite-, and pyrite (py$_{1-Sy}$)-altered syenite. (d) Quartz-, and ankerite-, and sphalerite-altered syenite. The ankerite and sphalerite, together with theapatite and rutile, are distributed along the cleavage of biotite. White dashed lines mark outlines of biotite. (e) Calcite- and pyrite (py$_{II-1}$)-altered sandstone, showing a cogenetic calcite and py$_{II-1}$. (f) Quartz-, sericite-, pyrite (py$_s$ and py$_{1-1}$)- and calcite-altered sandstone. The calcite cuts the quartz, sericite and pyrite (py$_s$ and py$_{1-1}$). Abbreviation: Ank=ankerite, Ap=apatite, Apy=arsenopyrite, Bt=biotite, Cal=calcite, Py=pyrite (py$_s$, py$_{1-1}$, py$_{1-Sy}$ and py$_{II-1}$ represent different generations of pyrite), Qtz=quartz, Rut=rutile, Ser=sericite, Sp=sphalerite.

Figure 6. BSE images showing the mineralogy, pyrite texture and paragenesis in pre-
ore and hydrothermal stage I. Also shown are the locations of representative spot analyses for sulfur isotopes (red) and Au concentration (pink) results of selected sulfide grains. (a) Subhedral py$_s$ overlapped by py$_{I-1}$ containing inclusions of arsenopyrite. (b) Subhedral py$_s$ overgrown by py$_{I-1}$ with galena inclusions. Apertures in py$_s$ are filled by quartz and calcite. (c) Subhedral py$_s$ overgrown by oscillatory zoning py$_{I-1}$ with arsenopyrite inclusions along the contact between py$_s$ and py$_{I-1}$. (d) Corrosive py$_s$ with irregular contact boundary overgrown by py$_{I-1}$, which in turn is rimmed by py$_{I-2}$.

Abbreviation: Apy= arsenopyrite, Cal=calcite, Py=pyrite (py$_s$, py$_{I-1}$ and py$_{I-2}$ represent different generations of pyrite), Qtz=quartz.

**Figure 7.** BSE images showing the mineralogy, pyrite texture and paragenesis of hydrothermal stages I and II. Also shown are the locations of representative spot analyses for sulfur isotopes (red) and Au concentration (pink) results of selected sulfide grains. (a) Unzoned py$_{I-Sy}$ with porous texture filled by quartz, galena and arsenopyrite in stage I in the syenite. (b) Py$_{I-1}$ with oscillatory zoning overgrown by py$_{I-2}$ in stage I, which is cut by subhedral to anhedral py$_{II-1}$ (with porous texture filled by galena) overgrown by euhedral py$_{II-2}$ in stage II. (c) Subhedral to euhedral py$_{II-1}$ overgrown by py$_{II-2}$ with cogenetic Ga in stage II. (d) A cogenetic mineral assemblage of py$_{II-2}$, galena and arsenopyrite, chalcopyrite, tetrahedrite, proustite, sphalerite in stage II.

Abbreviation: Apy= arsenopyrite, Ccp=chalcopyrite, Ga=galena, Pr=proustite, Py=pyrite (py$_{I-1}$, py$_{I-Sy}$, py$_{I-2}$, py$_{II-1}$ and py$_{II-2}$ represent different generations of pyrite), Qtz=quartz, Sp=sphalerite, Tet=tetrahedrite.
Figure 8. Interpreted paragenetic sequence of pre-ore and ore-related minerals in the Chang’an gold deposit. Small yellow cycles indicate the phase contains invisible gold.

Figure 9. LA-ICP-MS images of trace elements (ppm) in pyrite from sample CA33. The pyrite core (py₅) contains minor electrum inclusions and contains up to ~1 wt% Co and Ni in solid solution. The pyrite inner zone (py₁₁) has higher Au, As, Ag, Co, Ni, Pb, Sb and Cu concentrations relative to py₅ and the rimming pyrite (py₁₂), which has low As, Co, Ni, Pb and Au contents. See text for more explanation of pyrite generations and their compositions.

Figure 10. LA-ICP-MS images of trace elements (ppm) in pyrite from sample CA38. Pyrite inner zone (py₁₁) is enriched in Au, As, Ag, Co, Ni, Pb, Sb and Cu. Py₁₁ contains Au-Ag-Sb-Cu inclusions, possible suggestive of Au-bearing polybasite. Pyrite outer zone (py₁₂) shows As-Co-Ni enrichment and zonation but depletion in Au. See text for more explanation of pyrite generations and their compositions. Red lines represent inferred cracks in pyrite.

Figure 11. Interelement correlations for pyrites of different generations and arsenopyrite from samples CA01, CA20, CA25, CA29, CA33, CA36 and CA38. (a) Au-As. Black solid line in Figure a is Au saturation line defined by Reich et al. (2005) and red dashed line is preferred Au saturation line of arsenian pyrite from the Chang’an
gold deposit. (b) Au-Cu. (c) Au-Ag. (d) Au-Sb. (e) Co-Ni. (f) Pb-Ag.

**Figure 12.** Sulfur isotope composition of different generations of pyrites and arsenopyrites in the Chang’an gold deposit. Variation curves of $\delta^{34}$S values of pyrites in the sedimentary rock-hosted orogenic gold deposits and sulfate seawater through time are based on Chang et al. (2008). Dashed line marks the $\delta^{34}$S value of $0$ ‰ and yellow shadow area represents the $\delta^{34}$S range of sulfides in hydrothermal stages I and II.

**Figure 13.** In situ Pb isotope of different generations of pyrite and galena in the Chang’an gold deposit. The field for western Yunnan volcanics is from Zhou et al. (1998). The field for western Yunnan potassic mafic rocks is from Lu et al. (20013). The field for leucogranite within the Ailao Shan-Red River shear zone (ASRR) in western Yunnan is from Zhang and Schärer (1999).

**Figure 14.** (a) R/Ra vs. $^{40}$Ar*/$^{4}$He diagram of fluid inclusions in composites of pyII-1-pyII-2 in the Chang’an gold deposit, in comparison to typical crustal and mantle reservoirs (Ballentine et al. 2002; Ozima and Podosek 2002) as well as those in the Murantau, Macreas, Zhenyuan, Daping and Dongping gold deposits (Burnard et al. 1999; Mao et al. 2003; Graupner et al. 2006; Sun et al. 2009; Goodwin et al. 2017). The $^{40}$Ar* is the $^{40}$Ar content corrected for atmospheric contribution. (b) $\delta^{13}$C_PDB–$\delta^{18}$O_PDB diagram of calcites in hydrothermal stages II and III. Fields for sedimentary carbonate
and sedimentary organic carbon are from Hoefs (2009) and field for mantle is from Ray et al. (1999).

Supplementary Materials

Table S1. Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) analyses of pyrite and arsenopyrite from the Chang'an gold deposit.

Table S2. In situ sulfur isotope composition of different sulfide types from the Chang'an gold deposit.

Table S3. In situ Pb isotopic composition of pyrite and galena from Chang'an gold deposit.

Table S4. He-Ar isotopic composition of composites of PyII-1-PyII-2 in hydrothermal stage II in the Chang'an gold deposit.

Table S5. C-O isotopic composition of calcites in hydrothermal stages II and III in the Chang'an gold deposit

Figure S1. LA-ICP-MS count outputs for a composite of (a) pyS-pyI-1 from sample CA20 and (b) pyII-1-pyII-2 from sample CA38. Insets show the analyzed pyrites and paths of the laser analysis (arrows indicate the direction of ablation). Note that the pyS
is lower Au, As and Pb contents, compared to the surrounding py_{I-1}, which is enriched in Au and As compared to py_{II-1} and py_{II-2}. The pattern of analyzed py_{II-1} and py_{II-2} indicates micro-inclusions of galena and free gold.

**Figure S2.** LA-ICP-MS images of trace elements (ppm) in pyrite from sample CA20. Core of the pyrite (py_{s}) contains Au, As, Ag, Co, Ni, Pb, Sb and Cu. Rim of the pyrite (py_{I-1}) is more enriched in these elements. See text for more explanation of pyrite generations and their compositions.

**Figure S3.** LA-ICP-MS images of trace elements (ppm) in pyrite from sample CA25. Pyrite core (py_{s}) has higher Co, Ni and Pb concentrations than the rimming pyrite (py_{I-1}), which has higher Au, As, Ag, Co, Ni, Pb, Sb and Cu contents. See text for more explanation of pyrite generations and their compositions.

**Figure S4.** LA-ICP-MS images of trace elements (ppm) in pyrite (py_{I-sy}) from sample CA29. Py_{I-sy} has high As, Ni and Co contents with inclusions of chalcopyrite, galena and sphalerite.
<table>
<thead>
<tr>
<th>Pyrite</th>
<th>Timing</th>
<th>Host rock</th>
<th>Texture</th>
<th>Co-genetic minerals</th>
<th>Evidence for timing</th>
</tr>
</thead>
<tbody>
<tr>
<td>PyS</td>
<td>Synsedimentary/diagenetic</td>
<td>Turbidite</td>
<td>Bedding-parallel nodule; corroded structure</td>
<td>Detrital quartz, Fe-dolomite, apatite</td>
<td>Bedding parallel; nodal texture (Fig. 4a); overgrown by py$_{I-1}$ (Fig. 6a-d)</td>
</tr>
<tr>
<td>Py$_{I-1}$</td>
<td>Hydrothermal stage I</td>
<td>Turbidite</td>
<td>Euhedral-subhedral; oscillatory zoning structure; inclusion-rich</td>
<td>Fine-grained quartz, arsenopyrite, galena, chalcopyrite and electrum</td>
<td>Overgrow py$<em>S$ and overgrown by py$</em>{I-2}$ (Fig. 6a-d); crosscut by py$<em>{II-1}$ and py$</em>{II-2}$ (Fig. 7b)</td>
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<tr>
<td>Py$_{I-2}$</td>
<td>Hydrothermal stage I</td>
<td>Turbidite</td>
<td>Euhedral to subhedral; outer thin rim; inclusion-free</td>
<td>No or rarely</td>
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<tr>
<td>Py$_{I-Sy}$</td>
<td>Hydrothermal stage I</td>
<td>Syenite</td>
<td>Euhedral to subhedral; disseminated</td>
<td>Fine-grained quartz, arsenopyrite, galena</td>
<td></td>
</tr>
<tr>
<td>Py$_{II-1}$</td>
<td>Hydrothermal stage II</td>
<td>Turbidite</td>
<td>Subhedral; porous textures; inclusion-rich</td>
<td>Abundant fine-grained inclusions of galena, sphalerite, and tetrahedrite</td>
<td>Crosscut py$<em>{I-1}$ and py$</em>{I-2}$ (Fig. 7b)</td>
</tr>
<tr>
<td>Py$_{II-2}$</td>
<td>Hydrothermal stage II</td>
<td>Turbidite</td>
<td>Euhedral</td>
<td>Euhedral galena, chalcopyrite, sphalerite, tetrahedrite and proustite</td>
<td>Crosscut or overgrow py$_{II-1}$ (Fig. 7b, c)</td>
</tr>
</tbody>
</table>

Explanation of nomenclatures: “Py” represents pyrite; “S” and “Sy” represent sedimentary rock and syenite, respectively; “I” and “II” donate hydrothermal stages I and II, respectively; “-1” and “-2” represent the first and second generations of pyrite. For example, py$_S$ represent sedimentary pyrite, py$_{I-1}$ donates the first generation of pyrite formed in hydrothermal stage I, and py$_{I-Sy}$ represent stage-I pyrite in syenite.

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Table 2. Summarized Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) analyses of pyrite and arsenopyrite from the Chang'an gold deposit

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<th>Ni</th>
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<th>Zn</th>
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<th>Se</th>
<th>Mo</th>
<th>Ag</th>
<th>Sb</th>
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<th>Tl</th>
<th>Pb</th>
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<tr>
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| **Min**  | 0.0           | 1.2             | 7.0             | 0.4             | 1965         | 5.7             | b.d.l           | 1.5            | 2.1       | b.d.l           | 0.4             | b.d.l           | 14.0            | b.d.l           | 0.0             |
| **Max**  | 987.0         | 1152.3          | 99.4            | 70774.0         | 16968        | 19.6            | 0.5             | 731.8          | 1077.1    | 2.0             | 11.1            | 0.3             | 49622           | 1.1             | 7.4             |
| **Mean** | 8.0           | 26.6            | 19.5            | 6.8             | 6311.3       | 9.3             | 0.0             | 11.7           | 16.8      | 0.5             | 2.3             | 0.1             | 98.5            | 0.1             | 0.2             |
| **S.D.** | 326.0         | 376.4           | 30.2            | 23589           | 4839         | 7.6             | 0.3             | 6.9            | 354.8     | 0.7             | 4.6             | 0.1             | 16519           | 0.4             | 2.4             |

| **Min**  | 15.6          | 80.2            | 113.1           | 0.5             | 446274       | b.d.l           | b.d.l           | 4.6            | 60.2      | b.d.l           | 110.5           | 0.3             | 206.9           | 7.3             | 8.9             |
| **Max**  | 82.6          | 233.1           | 555.5           | 63.1            | 516615       | 12.4            | 1.7             | 18.6           | 111.9     | 8.3             | 353.3           | 4.3             | 558.4           | 12.9            | 34.9            |
| **Mean** | 26.1          | 113.9           | 239.1           | 2.5             | 474555       | 9.8             | 0.1             | 11.9           | 73.1      | 1.6             | 268.8           | 1.9             | 347.2           | 9.2             | 22.6            |
| **S.D.** | 216.3         | 239.4           | 160.8           | 15442           | 235796       | 3.9             | 0.5             | 5.1            | 221.1     | 2.0             | 155.6           | 1.3             | 10527           | 4.7             | 12.8            |

b.d.l = below detection limit, S.D.=standard deviation, — =not suitable for calculation.
Figure 2

(a) 

(b) 

Legend:
- Quaternary alluvium
- Silurian dolostone
- Ordovician turbidite
- Oligocene syenite
- Oligocene lamprophyre
- Alteration halo
- Bedding
- Unconformity boundary
- Fault
- Orebody
- Drill hole

North-south section and east-west section along AA'.
Figure 3

Au grade (ppm)
- 0-0.5
- 0.5-1
- 1-2
- 2-4
- 4-6
- 6-8.3

Cataclastic turbidite zone
/Cataclastic dolostone zone/
Fault core

Syenite Lamprophyre Fault Fault breccia Bedding Sample and number Dip

Unconformity boundary
Ordovician
Silurian
Chang'an fault zone

202° 278° 0 20 m

Dip angle
Figure 4
Figure 6
Figure 7
## Figure 8

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Figure 11
Figure 12
Figure 13

[Diagram showing isotopic lead ages for various geological samples, including Proterozoic volcanics, Ailaoshan alkali-rich porphyry, Ailaoshan leucogranite, and Mafic rocks in western Yunnan. The diagram also includes data points for mantle, orogeny, and upper crust.]