Magmatic degassing controlled the metal budget of the Axi epithermal gold deposit

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ABSTRACT

From integrated textural and compositional studies of auriferous and barren pyrite/marcasite in the epithermal Axi gold deposit, China, we have identified a relationship between multiple gold mineralizing events, mafic magma recharge and fluid-rock reactions. Three generations of pyrite (Py1–3) and four generations of marcasite (Mar1–4) record episodic gold mineralizing events, followed by silver-copper-lead-zinc-cadmium enrichment. The gold mineralizing events were recorded by high concentrations of sub-nanometer sized gold in Py1, Py3, and Mar3 (max. = 147, 129 and 34 ppm, med. = 39, 34 and 12 ppm). Based on previous Re-Os ages determinations of pyrite and U-Pb zircon ages of the andesitic wallrock, these gold events slightly postdated pulsed mafic magma recharge, and represent the incursion of Au-As-S-rich magmatic volatiles into circulating meteoric water. Silver-Cu-Pb-Zn-Cd enrichment in Py2, Mar2 and Mar4 are consistent with quiescent degassing and gradual Ag-Cu-Pb-Zn-Cd enrichment in an evolved felsic magma. Barren Mar1 records the dominance of meteoric water, and a limited magmatic fluid contribution. High Co-Ni-V-Cr-Ti contents in porous cores of Py1 and Mar2 are attributed to wall rock alteration and dissolution-reprecipitation. The results provide convincing evidence that the metal budget (especially for Au, Ag, Cu, Pb, Zn, Sb) of the hydrothermal fluids and sulfides in epithermal systems is controlled by the influx of magmatic fluids and associated magma, whereas the enrichment of certain
fluid-immobile elements, such as Co, Ni, V, Cr and Ti, is caused in part by fluid-rock interaction.

**Keywords**: Mafic recharge; magma degassing; metal budget; fluid-rock interaction; epithermal deposit; Axi; Central Asian Orogenic Belt

**INTRODUCTION**

Andesites play an important role in the formation and evolution of continental crust at convergent margins (Rudnick, 1995). They can be produced through fractional crystallization of basalt and crustal assimilation, slab melting, hydrous melting of peridotite, or magma mixing between mafic and felsic magmas (Carmichael, 2002; Defant and Drummond, 1990; Laumonier et al., 2014; Lee and Bachmann, 2014; Reubi and Blundy, 2009). In the last of these mechanisms, the replenishment of a shallower, felsic and partially solidified magma reservoir by mafic magma yields evolved (andesitic to dacitic), volatile-rich magmas that are of sufficiently low density to erupt (Kent et al., 2010).

Epithermal deposits are commonly associated with volcanic rocks in magmatic arcs (Simmons et al., 2005). Notwithstanding the debate concerning the nature of the magmatic contribution to the epithermal mineralization, it has been proposed that the characteristics of epithermal ore-forming systems, as well as those of analogous geothermal systems, are mainly determined by the nature of the associated magmatism (Giggenbach, 1995; Sillitoe and Hedenquist, 2003; Simmons and Brown,
Considering that mafic melt is intrinsically rich in gold and sulfur (Hattori and Keith, 2001; Nadeau et al., 2016), the question arises: Does mafic magma replenishment and the mixing of mafic magma with felsic magma at mid-crustal levels affect the upper-crustal epithermal mineralization?

We selected the Axi epithermal gold deposit (>70 t Au; Chen et al., 2012), NW China (Fig. 1), to provide the context in which to answer this question because it has been clearly shown that the host andesitic rocks were the products of episodic mafic magma injection and mixing with shallower felsic magmas (Zhang, 2020). Moreover, detailed geochronologic studies demonstrate that precipitation of auriferous pyrite (at ca. 355 Ma and 332 Ma, Re-Os isochron, Liu et al., 2020; Li et al., 2022) slightly postdated mafic magma injection (351–357 Ma and 340 Ma, zircon U-Pb age, Li et al., 2022), indicating a potential link between mafic magma replenishment and gold mineralization.

In this paper, we report the results of combined textural and \textit{in situ} trace-element studies of auriferous and barren pyrite/marcasite. These results reveal how mafic magma intrusion, magma mixing, and fluid-rock interaction affect metal budgets in epithermal systems.

\textbf{THE AXI VOLCANICS AND GOLD MINERALIZATION}

The Axi district is located in the Chinese Western Tianshan in an area of long-lived, subduction-related arc magmatism (Yu et al., 2018; Ye et al., 2020). The deposit is hosted by volcanic-sedimentary rocks of the Late Paleozoic Dahalajunshan...
Formation (Fig. 1). Volcanism began at ca. 410 Ma and focused in the vicinity of the Axi deposit from 361 to 340 Ma (Li et al., 2022 and references therein). The volcanics exposed in the deposit consist of crystal-rich (30−50%) andesitic to dacitic rocks in which plagioclase, clinopyroxene, amphibole and quartz phenocrysts are embedded in a microcrystalline groundmass of plagioclase, magnetite and ilmenite. A wealth of petrological and geochemical evidence shows that magma mixing played an important role in the petrogenesis of the Axi volcanics, including the development of disequilibrium textures (e.g., inverse zoning, patchy zoning, sieve textures) involving plagioclase phenocrysts, the resorption of quartz phenocrysts, the entrapment of quenched mafic and felsic silicate melt inclusions by quartz phenocrysts and the changes in bulk rock chemistry that led to simple linear trends on bivariate plots of major oxide components (Zhang, 2020).

Nearly 90% of the gold (ca. 60 tonnes, with an average grade of 5.6 g/t) were mined from the No. 1 orebody (Rui et al., 2002; Chen et al., 2012). As details of the alteration and mineralization have been reported by Zhai et al. (2009), An and Zhu (2018); Liu et al. (2018, 2020), and Zhang et al. (2018), only a brief summary of these features is presented below.

The hydrothermally altered rock contains quartz, chalcedony, calcite, sericite and adularia (Bao et al., 2002; Zhai et al., 2009), an assemblage typical of low sulfidation epithermal deposits (White and Hedenqueist, 1990, 1995; Simmons et al., 2005). A zonal distribution of alteration is observed, from an inner silicification zone outwards.
through adularia-sericite to propylitic alteration zones. Silicification is most closely associated with gold mineralization. The adjacent adularia-sericite alteration zone comprises sericite, quartz, adularia, plus minor illite and carbonate (Zhai et al., 2009; An and Zhu, 2018; Liu et al., 2020). The peripheral propylitic alteration is characterized by the mineral assemblage chlorite, carbonate, and epidote. Native gold, electrum, pyrite, marcasite, sphalerite, chalcopyrite, tetrahedrite and galena are the main ore minerals (Liu et al., 2018; Zhang et al., 2018).

**SAMPLING AND ANALYSIS TECHNIQUES**

### Sampling

Over 500 samples from outcrop and eight drill holes (ZK2404, ZK2405, ZK4811, ZK3605, ZK3507, ZK4002, ZK4004, ZK4007) were examined petrographically in order to identify key minerals and textures. Twelve representative pyrite and marcasite samples from drill holes ZK2404 and ZK2405 were selected for further study.

### SEM-BSE imaging

Thin sections were prepared and examined using transmitted and reflected light microscopy to characterize the morphology, textures and paragenesis of pyrite and marcasite. This was followed by SEM-BSE imaging using a FEI Quanta 650 FEG scanning electron microscope (SEM) at the Key Laboratory of Orogenic Belts and Crustal Evolution, Peking University. The SEM is equipped with an energy dispersive spectrometer (EDS), which allows combined backscattered electron (BSE) imaging of...
mineral morphology and compositional analysis. The applied voltage was 10 to 20 kV, with a spot-size of 4.0 to 5.0 μm, and a dwell time of 20 to 30 μs.

**LA-ICPMS trace element analyses**

The trace element composition of the sulfide minerals was analyzed using laser-ablation inductively coupled plasma mass spectrometry (LA-ICPMS) at the Aarhus Geochemistry and Isotope Research platform (AGiR), Department of Geoscience, Aarhus University, Denmark. A 193 nm ArF Excimer laser from Resonetics attached to an Agilent 7900 ICPMS was used for this purpose. The ablation rate was 8 Hz and the laser energy was 70 mJ. Helium was used as the carrier gas, which was mixed with Ar before it entered the ICP. A total of 245 single-spot analyses were performed using a laser beam that varied from 6 to 60 μm, depending on the size of the crystals. All the data were collected in time-resolved mode. The analysis time was 55 seconds, including an initial 25 seconds of background measurement and 30 seconds of ablation. Data for a set of 20 elements were reported for the spot analyses (Hg, Au, Sb, Ag, Mo, Se, As, Zn, Cu, Co, Mn, Cr, V, Cs, Tl, Pb, Sc, Ti, Ni and Al). Bismuth, Sn, In, Cd, Pt and U were also analyzed, but their concentrations were typically very low (<1 ppm) and in many cases below the limit of detection.

The NIST 610 synthetic glass and MASS 1 pressed sulfide reference materials were used as external calibration standards. The reproducibility and accuracy of MASS-1 for different analytical sessions are given in Table A1. The relative standard
deviation for the different elements is between 2 – 10% (Table A1). The standards were analyzed after roughly every 10th pyrite analysis. For the quantification of the data, the Fe concentration obtained by electron microprobe analysis (Zhang et al., 2018) was used as the internal standard. The data processing and quantification were done using Iolite software (Paton et al., 2011).

In order to develop a chemical profile across selected pyrite grains, two LA-ICPMS line scans were conducted. The sample was moved under the laser along a line, crossing the mineral grain at a scanning speed of 8 μm/s with a spot size of 8 μm. The elements mentioned above were chosen for these analyses. The profiles varied between 300 to 400 μm in length.

RESULTS

Types of pyrite/marcasite

Previous studies have documented many features of the pyrite at Axi, including their textures, paragenetic relationships and composition (Zhang et al., 2018; Liu et al., 2015, 2018). These studies reveal that pyrite hosts nearly half of the total gold reserve, and that there are three generations of pyrite. In this study, we couple detailed SEM/EDS imaging of pyrite and marcasite with specific textures/minerals, including crustiform banding, hydrothermal breccias, adularia, platy calcite/quartz and replacement textures, and use them to refine previous textural and mineralogic interpretations.
The earliest pyrite, Py1 (50 – 1500 µm in diameter, Fig. 2, 3) is associated with quartz and sericite. It comprises a corroded, porous core (Py1a), a compact, inclusion-free mantle (Py1b), an oscillatory-zoned rim (Py1c), and an arsenopyrite overgrowth (these features are not present in all the crystals). The anhedral Py1a replaced clinopyroxene phenocrysts as pseudomorphs (Fig. 3B) or is concentrated close to the fluid-rock reaction front (Fig. 3C). Subhedral to euhedral Py1b and Py1c are more common in quartz-dominated cements or veinlets and away from the fluid-rock reaction front (Fig. 3C). Anhedral Py2 (50 – 1000 µm in diameter) coexists with chalcopyrite, sphalerite, tetrahedrite, quartz, calcite and chlorite (Fig. 2B, 3D). Tiny Py3 crystals (10 – 50 µm in diameter) are euhedral to subhedral, and oscillatory-zoned (Fig. 2C). They are surrounded by chalcedony ± calcite, and cement Py1 and/or Py2 clasts in breccias (Fig. 3F).

In addition to pyrite, we identified four generations of marcasite (Figs. 2-4) at shallower depth (< 280 m) than pyrite (that is present to 720 m). The blade-shaped Mar1 (50 – 600 µm in length) coexists with fine- to coarse-grained quartz, chalcedony and/or calcite. It may crosscut Py1 (Fig. 3A) and Py2 and hence crystallized later than them. This marcasite occurs in crustiform layers with a rhythmic alternation of quartz, chalcedony, Py3 and Mar1 (Fig. 4). Since Py3 occurs more commonly in the outer layers, and Mar1 in the inner layers, we propose that Mar1 crystallized contemporaneously with or slightly later than Py3. The second marcasite generation, Mar2, forms radial or fan-shaped aggregates (100 – 2000 µm in length) and has an
inclusion-rich, porous core (Mar2a) that is surrounded by a homogeneous marcasite overgrowth (Mar2b) and arsenopyrite (Fig. 2D). It cements hydrothermal breccia fragments together with fine-grained quartz, chalcedony and minor calcite. This generation of marcasite was followed by Mar3 (100 – 1500 μm in length) in calcite±chalcedony veins/cements. Commonly, Mar3 crosscuts anhedral Py2 (Fig. 3E), or cements breccia clasts containing earlier pyrite and marcasite generations. Locally, Mar3-calcite veins crosscut lattice structures and adularia, and calcite may fill the lattice interstices (Fig. 3I). The latest marcasite generation (Mar4) forms acicular crystals/aggregates (50 –1000 μm in length) and is hosted by calcite veins, in which the calcite is euhedral to subhedral and occurs as rhombs with alternating clear and “dusted” zones due to sub-microscopic inclusions. These veins crosscut calcite-chalcedony-Mar3 veins (Fig. 3H), indicating that Mar4 was later than Mar3.

On a modal basis, Py1, Py3, Mar2 and Mar3 are the most abundant pyrite and marcasite phases, followed by minor Py2, and traces of Mar4 and Mar1.

The trace element record of episodic mineralization

The trace element data for pyrite and marcasite are summarized in Table 1 and listed in Appendix A2. In the following text, the maximum (max.) values are reported for gold hosted by Py1b, Py3 and Mar3, and median (med.) values are reported for all other elements/samples (see also Fig. 5).

The compositional data reveal episodic gold mineralizing events. Each of these events was followed by a period of silver and base metal enrichment. The first gold
mineralizing event is recorded by Py1b that has the highest concentrations of Au (max. = 147 ppm, med. = 39 ppm) and As (67500 ppm). The precursor Py1a, by contrast, is characterized by higher Co (209 ppm), Ni (510 ppm), V (14 ppm), Cr (12 ppm) and Ti (3300 ppm) contents than Py1b (Co = 25 ppm, Ni = 35 ppm, V = 0.83 ppm, Cr = 3.5 ppm, Ti = 12 ppm). The compositional variation of different parts of Py1 crystals is clearly illustrated by the laser ablation traverses across a Py1 grain (Fig. 6). The subsequent Py1c is relatively deficient in most trace elements in comparison to Py1a and Py1b, especially As (15000 ppm), Zn (1.1 ppm), Cu (96 ppm), Co (11 ppm), V (0.67 ppm), Cr (1.0 ppm) and Ti (7.7 ppm). Gold mineralization was followed by the introduction of Cu, Pb, Zn and Sb, which is recorded in Py2 (Cu = 928 ppm, Pb = 124 ppm, Zn = 96 ppm, Sb = 884 ppm). This pyrite type has the highest concentration of Ag among all the samples (max. = 305 ppm, med. = 157 ppm) but is depleted in Au (6.0 ppm).

The second gold mineralizing event is documented by the composition of Py3 (max. = 129 ppm, med. = 34 ppm Au). Later Mar1, however, is depleted in most trace elements. A second period of Ag-Zn enrichment is recorded by Mar2 (containing 243 ppm Ag and 69 ppm Zn in the core, and 60 ppm Ag and 27 ppm Zn in the rim). Its porous core (Mar2a) has higher Co (298 ppm), Ni (697 ppm), V (9.7 ppm), Cr (8.0 ppm) and Ti (32 ppm) contents than the compact Mar2b overgrowth (Co = 58 ppm, Ni = 195 ppm, V = 7.0 ppm, Cr = 3.8 ppm, Ti = 13 ppm), mimicking the compositional difference between Py1a and Py1b (Fig. 5).
A weak gold mineralizing event may be indicated by the composition of Mar3, although its Au content is much lower (max. = 34 ppm, med. = 12 ppm) than those of Py1b (39 ppm) and Py3 (34 ppm). It also has relatively high Ag (146 ppm), Pb (169 ppm), Zn (29 ppm) and Sb (872 ppm) contents. The youngest marcasite variety, Mar4, is characterized by extremely low contents of Au (0.11 ppm), Ag (13 ppm) and As (3115 ppm), but moderately high Pb (1027 ppm), Zn (104 ppm) and Sb (417 ppm) contents.

INTERPRETATION AND DISCUSSION

In a previous study, we showed that the Axi andesites accumulated incrementally through injections of mafic magma into a shallow, felsic magma reservoir (Li et al., 2022). We documented the injection events by the textural features of zircon in which an anhedral, antecrystic core is resorbed and embayed by a thin, irregular zone (<5 μm) prior to overgrowth by an oscillatory-zoned autocrystic rim (Li et al., 2022). Using the ages of the core and rim of the zircon, the main period of injections is interpreted to have been between 351 and 357 Ma, contemporaneous with the crystallization of Py1b (357 ± 18 Ma, 353 ± 6 Ma, Re-Os isochron, Liu et al., 2020; Li et al., 2022). This chronology, in combination with our new sulfide trace element data, provides compelling evidence for a link between magma injection and gold mineralization. We propose that fluid exsolution associated with mafic magma injections and interspersed periods of magma quiescence exerted a first-order control on the metal budget of the ores (Fig. 7). We further propose that enrichment of certain
fluid-immobile elements, such as Co, Ni, V, Cr and Ti, was caused, in part, by fluid-rock interaction. A detailed discussion is provided below.

The earliest pyrite, anhedral Py1a, is interpreted to have formed as a result of fluid-mediated sulfidation, or coupled dissolution-reprecipitation reactions (Putnis, 2009), based on the observation that it replaced clinopyroxene phenocrysts as pseudomorphs, or is concentrated close to the sharp fluid-rock reaction front (Fig. 3C). Intense alteration led to the breakdown of clinopyroxene, amphibole, plagioclase, magnetite-ilmenite and other constituents of the andesite host. Consequently, elements that were once compatible in these phases (such Co, Ni, V, Cr and Ti) were released into the circulating fluids (Mustard et al., 2006; Jenner et al., 2010), and were scavenged by the alteration products. Thus, it was the alteration of the parent mineral, coupled in space and time with the precipitation of daughter minerals and co-generation of porosity, that led to the development of porous, Co-Ni-V-Cr-Ti-rich Py1a.

The gold mineralization event recorded by Py1b is interpreted to have been associated with mafic magma intrusion into the shallow, felsic magma reservoir referred to above. Although the sulfur and gold contents of igneous rocks in the Axi area have not been analyzed, mafic magma is generally considered to have high sulfur (more than several thousand ppm; Nadeau et al., 2016) and Au contents (Keith et al., 1997; Hattori and Keith, 2001; Halter et al., 2005; Stern et al., 2007; Zajacz et al., 2012; Guo and Audetat, 2017), and thus, is likely to have been the source of sulfur.
and gold. Injections of mafic magma would have induced a sudden over-saturation in volatiles (Kent et al., 2010; Nadeau et al., 2016), with sulfur partitioning preferentially into the exsolving supercritical fluid (a $D_S^{\text{fluid/melt}}$ value of 20 has been proposed based on hydrothermal S partitioning experiments, Webster and Botcharnikov, 2011). Elements such as Au, As and Hg are readily transported by aqueous vapor, as shown by the compositions of volcanic gases and their sublimates (Williams-Jones and Heinrich, 2005). This reflects the high volatility of Hg and As (Williams-Jones et al., 2002); and Au prefers reduced sulfur, which also partitions preferentially into the vapor (Hurtig and Williams-Jones, 2014; Williams-Jones and Migdisov, 2014). In contrast, elements such as Pb and Zn are likely to have low volatility because of the very strong bonds that they form with chloride ions in aqueous liquids. On rising above the depth of exsolution, the supercritical fluid, which would have been liquid-like because of the high temperature of the mafic magma, would have condensed a small proportion of brine and Au-As-S would have been transported upwards dominantly by the more buoyant vapor. Incursion of this Au-As-S-rich vapor thus would have greatly increased the gold content of the circulating meteoric fluids and decreased their pH (Zhai et al. 2009), leading to gold mineralization and associated quartz-sericite-pyrite (Py1b) alteration. Later Py1c is interpreted to have precipitated from fluids with lesser inputs of magmatic components, and thus less Au and As.
The Ag and base metal-rich Py2 postdated Py1 (Liu et al., 2020; Zhang et al., 2018) and the related mafic magma injection. It possibly accompanied a period of magma quiescence, during which there was a gradual enrichment of Ag, Cu, Pb, Zn and Sb in the evolved magma and exsolved fluids (Nadeau et al., 2016). In the absence of mafic magma injection, the supercritical fluid would have been liquid-like because of its lower temperature, and would have separated to produce a small proportion of vapor leaving a brine more enriched in Cl (Giggenbach, 1997; Zajacz et al., 2008). This, in turn, would have enhanced the transportation of Cl-complexed elements (such as Ag, Cu, Pb, Zn and Sb, Wood and Samson, 1998; Seward et al., 2014) into shallow meteoric water. As a representative of the second gold mineralizing event, Py3 incorporated comparable amounts of Au and As to Py1b, indicating a similar source, i.e., mafic magma. The concentrations of Ag, Cu, Pb, Zn and Sb in Py3, however, are slightly higher than those of Py1b. Invoking a contribution from the felsic magma would reconcile this issue, by providing an additional metal reservoir for Ag, Cu, Pb, Zn and Sb. The deposition of Py3 is attributed to fluid boiling, as shown by: (1) the development of hydrothermal breccias (with Py3 ± chalcedony as the cement); and (2) the occurrence of adularia and bladed calcite (pseudomorphed by quartz) (Fig. 3I). Boiling not only caused precipitation of gold, bladed calcite and adularia (Simmons et al., 2005), but fractured the surrounding rocks, accelerating mixing with meteoric fluids. Marcasite has been shown to form from aqueous solutions with a pH < 5, at temperatures of 80 – 240 °C, in the presence
of H$_2$S$_2$ (aq) (Murowchick, 1992), whereas Py3 is interpreted to have deposited at 325 – 385 °C, as determined by the arsenopyrite geothermometer (Zhang et al., 2018).

The occurrence of Py3 and Mar1 in alternating crustiform layers (Fig. 4) may have been the result of fluid mixing, with the high temperature, Au-rich Py3 recording a greater magmatic fluid contribution and the low temperature, trace-element-poor Mar1 recording the predominance of meteoric water and a minor magmatic fluid component.

The marcasite variety, Mar2a, shares textural (porous) and compositional (Co-Ni-V-Cr-Ti-rich) characteristics similar to Py1a. The compact overgrowth contains proportions of Ag, Pb, Zn and Sb overlapping with or slightly lower than those of Py2, suggesting a similar metal control by quiescent degassing. Thus, the conditions of formation of Mar2a and Mar2b were comparable to those of Py1a and Py1b, with the exception that the invading fluid was Pb-Zn-Sb-rich instead of Au-As-S-rich. Crystallization of Mar2 was followed by that of Mar3, which contains slightly less Au and As than Py1b and Py3 and may record a small injection of mafic magma that was not identified by zircon age dating. The elevated Ag, Sb and Zn contents suggest a hybrid input involving a contribution from the evolved felsic magma. In the final variety of marcasite, Mar4, the fingerprint of the mafic magma is absent, and only that of the felsic magma (high Pb, Zn and Sb) is recorded.

**CONCLUSION AND IMPLICATION**
The present work provides convincing evidence for a linkage between mafic recharge, andesite formation and epithermal gold mineralization. It suggests that the bulk metal budget (especially for Au, Ag, Cu, Pb, Zn, Sb) of an epithermal system is controlled primarily by the composition of the fluids, which, in turn, is controlled by the nature of the magma in a shallow magma chamber (Keith et al., 2018; Martin et al., 2020). The episodic gold mineralizing events are attributed to repeated mafic magma injections into a shallow, felsic magma chamber and associated magma degassing. Silver-Cu-Pb-Zn-Sb enrichment, by contrast, is related to quiescent degassing of the felsic magma. It also acknowledges that fluid-rock interaction would have involved coupled dissolution and reprecipitation and facilitated immobile element enrichment such as Co, Ni, V, Cr and Ti. Considering that mafic magma replenishment and its mixing with felsic magma play an important role in the formation of andesite (Anderson, 1976; Eichelberger, 1978; Reubi et al., 2009; Kent et al., 2010), the metal budget reported for Axi may also apply to similar cases in convergent margins.

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FIGURE CAPTIONS

FIGURE 1. A simplified geological map of the Axi epithermal deposit (modified after Zhang et al., 2018).

FIGURE 2. Representative SEM images, showing textures of different types of pyrite and marcasite.

A: Py1 characterized by a porous core (Py1a), a compact mantle (Py1b) and an oscillatory-zoned rim (Py1c). Near it is bladed Mar1 with an arsenopyrite overgrowth. Also shown is a laser ablation traverse across the crystal; B: Py2 accompanied by coeval chalcopyrite and tetrahedrite; C: tiny, oscillatory-zoned Py3; D. Mar2 with a laminated relict “core” (Mar2a), clear “rim” (Mar2b) and an arsenopyrite overgrowth; E. fan-shaped Mar3 (with an arsenopyrite overgrowth) coexisting with chalcedony and calcite; F. Homogeneous Mar4 characterized by the absence of an arsenopyrite overgrowth and coexistence with zoned calcite.

Abbreviations: Asp-arsenopyrite; Cc-calcite; Ccp-chalcopyrite; Mar-marcasite; Py-pyrite; Qz-quartz; Td-tetrahedrite.
FIGURE 3. Photomicrographs showing paragenetic relationship among different types of pyrite and marcasite.

A: Py1 crosscut by Mar1; B: pseudomorphic replacement of clinopyroxene by Py1; C: a breccia clast containing Py1 cemented by Py1+quartz; Py1 crystals at the reaction front or in the clast are morphologically irregular (Py1a), whereas those away from the front or in the cement are subhedral to euhedral Py1b or Py1c; D: Py1 included in or surrounded by Py2; E: Py2 crosscut by Mar3; F: Py1-bearing clast cemented by Py3+chalcedony; G: a clast containing Py1, Py3 and Mar1 cemented by Mar2; H: a calcite-Mar4 vein crosscutting a calcite-chalcedony-Mar3 vein; I: a lattice texture composed of platy quartz (pseudomorphs after calcite) and adularia, which was crosscut or infilled by later calcite. The yellow lines illustrate the inner textural boundary (A), and the white lines outline the phenocryst (B), breccia (C, F, G), or veinlet (H).

Mineral abbreviation: Adl-adularia; Apy-arsenopyrite; Cc-calcite; Cln-chalcedony; Mar-marcasite; Py-pyrite; Qz-quartz.

FIGURE 4. Crustiform banding characterized by the rhythmic alternation of quartz, chalcedony, Py3 and Mar1.

The crustiform bands comprise eight thin layers (numbered 1 to 8); Mar1 either forms thin laminae (layer 7 in Fig. C)) alternating with aggregates of Py3 and
chalcedony (layer 1), or coexist with Py3 and arsenopyrite in a single band, indicating nearly contemporaneous precipitation of Mar1 and Py3.

Mineral abbreviation: Apy-arsenopyrite; Mar-marcasite; Py-pyrite.

FIGURE 5. Boxplots of selected trace element concentrations in pyrite and marcasite, illustrating the episodic nature of the gold mineralizing events (Au1, Au2, Au3) and Ag-Pb-Zn-Sb enrichment (BM1, BM2, BM3).

FIGURE 6. Two laser ablation traverses across a Py1 grain illustrating the elevated Au and As contents of Py1b. There are numerous inclusions (e.g., rutile and galena) in the core (Py1a).

FIGURE 7. A schematic model showing the relationship between mafic magma replenishment, magmatic degassing, sulfide precipitation and mineralization. Fig. A shows intense magmatic degassing associated with the intrusion of mafic magma into a shallow, felsic magma reservoir, where the degassed, supercritical volatile is enriched in Au, As and S. Fig. B illustrates a period of magma quiescence, during which the magma and exsolved supercritical fluids are gradually enriched in Ag, Cu, Pb, Zn and Sb. During intrusion of the mafic magma, the supercritical fluid is vapor-like and condenses brine, with S, Au and As transported dominantly by the vapor before injection into circulating meteoric water, whereas during magma
quiescence the temperature is lower, the supercritical fluid is liquid-like and Cl, Cu, Ag, Pb, Zn are transported by the brine.

Fig. C illustrates the association between magma degassing and precipitation of FeS$_2$.

The formation of porous, Co-Ni-V-Cr-Ti-rich Py1a and Mar2a was caused by coupled dissolution-reprecipitation of the host andesite (here represented by the clinopyroxene, i.e. Cpx). The incursion of Au-As-S-rich volatile induced precipitation of Py1b, Py3 and Mar3, while the Ag-Cu-Pb-Zn-Cd-rich volatile favored formation of Py2, Mar2b and Mar4. Interlayered Mar1 with Py3 in crustiform banding resulted from mixing with (or diluted by) meteoric water.

TABLE CAPTIONS

Table 1 Summary of compositions of pyrite and marcasite from the Axi gold deposit (ppm).

Appendix

Appendix A1. Composition and reproducibility of the standard MASS-1.

Appendix A2. Compositions of selected pyrite and marcasite crystals from the Axi gold deposit (ppm).
<p>| Table 1. Summary of compositions of pyrite and marcasite from the Axi gold deposit (ppm) |
|---------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| No.   | Hg   | Au    | Sb    | Ag    | Mo    | Sc    | As    | Zn    | Cu    | Co    | Mn    | Cr    | V     | Cs    | Ti    | Pb    | Sc    | Ti    | Ni    | Al    |
|-------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| <strong>Py1a</strong> |      |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| Min.  | 0.08 | 1.3  | 47    | 6.3  | 0.04  | 4.4  | 9400  | 0.60  | 258   | 6.8   | 5.4   | 0.93  | 1.5   | 0.83  | 7.3   | 108   | 2.9   | 306   | 63    | 117   |       |       |       |       |
| Max.  | 6.2  | 129   | 1160  | 95   | 27    | 17000 | 66300 | 37    | 2070  | 690   | 336   | 32    | 820   | 50    | 244   | 2550  | 50    | 38700 | 1400  | 17900 |       |       |       |       |
| Med.  | 1.5  | 23    | 168   | 27   | 0.77  | 70    | 44000 | 9.6   | 459   | 209   | 28    | 12    | 14    | 10    | 43    | 381   | 11    | 3300  | 510   | 3860  |       |       |       |       |
| Std.  | 2.2  | 35    | 276   | 22   | 7.6   | 4198  | 15257 | 9.3   | 370   | 159   | 83    | 8.0   | 168   | 11    | 67    | 627   | 13    | 7279  | 376   | 4537  |       |       |       |       |
| <strong>Py1b</strong> |      |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| Min.  | 0.32 | 1.0  | 44    | 6.2  | 0.26  | 15    | 18900 | 0.20  | 56    | 0.61  | 0.80  | 0.24  | 0.37  | 0.32  | 0.16  | 2.3   | 0.09  | 8.3   | 3.9   | 2.5   |       |       |       |       |
| Max.  | 4.4  | 147   | 2070  | 70   | 14    | 44000 | 168000 | 23   | 790   | 326   | 1600  | 34    | 1630  | 88    | 570   | 1090  | 36    | 18300 | 500   | 11200 |       |       |       |       |
| Med.  | 1.2  | 39    | 107   | 23   | 1.5   | 195   | 67500 | 1.8   | 265   | 25    | 7.3   | 3.5   | 0.83  | 1.3   | 1.8   | 25    | 0.22  | 12    | 35    | 175   |       |       |       |       |
| Std.  | 1.6  | 58    | 682   | 20   | 4.5   | 19149 | 48377 | 7.5   | 244   | 101   | 521   | 10    | 511   | 30    | 182   | 335   | 13    | 5745  | 148   | 4491  |       |       |       |       |
| <strong>Py1c</strong> |      |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| Min.  | 0.03 | 1.0  | 11    | 1.5  | 0.02  | 1.10  | 3010  | 0.25  | 0.75  | 0.05  | 0.19  | 0.25  | 0.04  | 0.01  | 0.47  | 0.06  | 0.01  | 4.1   | 0.05  | 1.0   |       |       |       |       |       |
| Max.  | 2.8  | 137   | 702   | 253  | 276   | 104   | 84300 | 2330  | 1710  | 570   | 202   | 266   | 164   | 5.7   | 125   | 3190  | 37    | 27000 | 936   | 32000 |       |       |       |       |
| Med.  | 0.20 | 13    | 119   | 27   | 2.7   | 11    | 15000 | 1.1   | 96    | 11.0  | 4.9   | 1.0   | 0.67  | 1.0   | 8.0   | 30    | 0.16  | 7.7   | 40    | 153   |       |       |       |       |
| Std.  | 0.57 | 35    | 138   | 44   | 43    | 18    | 17816 | 356   | 416   | 100   | 31    | 45    | 26    | 1.3   | 22    | 506   | 7.1   | 4453  | 206   | 5241  |       |       |       |       |
| <strong>Py2</strong> |      |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| Min.  | 0.10 | 1.0  | 156   | 53   | 0.02  | 0.3   | 1890  | 0.20  | 296   | 0.74  | 0.42  | 0.18  | 0.04  | 0.02  | 6.2   | 6.3   | 0.01  | 4.2   | 5.3   | 0.40  |       |       |       |       |       |
| Max.  | 0.45 | 15    | 2700  | 305  | 1.4   | 27    | 9600  | 1620  | 10200 | 221   | 11    | 6.8   | 6.3   | 2.1   | 39    | 521   | 0.17  | 270   | 242   | 1160  |       |       |       |       |
| Med.  | 0.25 | 6.0   | 884   | 157  | 0.28  | 5.2   | 4610  | 96    | 928   | 38    | 2.4   | 0.64  | 0.59  | 0.53  | 18    | 124   | 0.07  | 5.3   | 66    | 341   |       |       |       |       |
| Std.  | 0.08 | 3.3   | 596   | 86   | 0.38  | 6.1   | 1582  | 402   | 2388 | 51    | 2.4   | 1.5   | 1.6   | 0.59  | 9.8   | 117   | 0.05  | 77    | 69    | 326   |       |       |       |       |
| <strong>Py3</strong> |      |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| Min.  | 0.20 | 0.17 | 10    | 0.04 | 0.02  | 6.0   | 5340  | 1.5   | 5.2   | 0.21  | 1.0   | 0.80  | 0.30  | 0.64  | 0.40  | 1.3   | 0.10  | 1.30  | 7.3   | 4.5   |       |       |       |       |       |
| Max.  | 6.2  | 129   | 1590  | 330  | 10    | 650   | 142000 | 73   | 729   | 715   | 590   | 205   | 232   | 15    | 134   | 3300  | 75    | 95000 | 1660  | 62000 |       |       |       |       |       |</p>
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Fig. 1

- Quaternary
- Clastic sediment
- Aqialehe Fm.
- Dahalajunshan Fm.
- Breccia and lava
- Subvolcanic rocks
- Volcanic breccia
- Agglomerate
- Lava
- Tuff
- Plagiogranite
- Unconformity
- Fault
- Au orebody
- Sample location

0.5 km
Fig. 2
Fig. 3
Fig. 4
Fig. 5

Au1, BM1, Au2, BM2, Au3, BM3, Au1, BM1, Au2, BM2, Au3, BM3

Au (ppm)

Ag (ppm)

As (ppm)

Sb (ppm)

Cu (ppm)

Zn (ppm)

Pb (ppm)

- Outlier
- Max
- Q3
- Median
- Q1
- Min

Py1a

Py1b

Py1c

Py2

Py3

Mar1

Mar2a

Mar2b

Mar3

Mar4
Gold mineralization

incursion of Au-As-S-rich vapor

Mar1

mixing with (diluted by) meteoric water

Mar2b

stable crystallization

Py1b

Ag+base metal mineralization

incursion of Ag-Cu-Pb-Zn-Cd-rich liquid

Mar3

Py3

Py1a

Mar2a

coupled dissolution - reprecipitation

Co-Ni-V-Cr-Ti-rich

Cpx