



Short communication

External fluid incursion during Cu-mineralization stage of Mina Justa iron oxide copper-gold (IOCG) deposit: Evidence from triple sulfur isotope geochemistry of chalcopyrite

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ABSTRACT

IOCG deposits are major host for Cu, rare earth elements (REEs), U and other metals, and whose source(s) of ore-forming fluids are highly debated. Particularly, whether or not external fluid was involved during Cu-mineralization stage is of great interest and intense debate. In this contribution, we investigate this topic using triple sulfur isotope geochemistry of Cu-mineralization stage sulfides in the Mina Justa deposit. The results show that the chalcopyrite that intensely replaced early-stage pyrite has similar triple sulfur isotopic composition to early-stage pyrite, which largely in the range of magmatic sulfur ($\Delta^{33}\text{S} = 0 \pm 0.05\text{‰}$, $\Delta^{33}\text{S} = \delta^{33}\text{S} - 1000 \times [(1 + \delta^{34}\text{S}/1000)^{0.515} - 1]$). However, chalcopyrite that occurs alone or with only minimal replacement of coexisting pyrite shows triple isotope ($\Delta^{33}\text{S} = 0.05$ to 0.20‰) that deviates from magmatic sulfur. This indicates that the sulfur of chalcopyrite with intense replacement of early-stage pyrite mainly inherits sulfur from early-stage pyrite, while the sulfur of chalcopyrite that exist alone or with minimal replacement of pyrite obtained their sulfur from a non-magmatic source. Collectively, the triple sulfur isotope data indicates that external fluid is present in the Cu-mineralization stage.

1. Introduction

IOCG deposits are magmatic-hydrothermal deposits that contain economic Cu and Au grades. The sensu stricto IOCG deposits 1) are structurally controlled; 2) commonly contain significant volumes of breccia; 3) are commonly associated with pre-sulfide sodic or sodic-calcic alteration; 4) have abundant low Ti iron oxides and/or iron silicates that are intimately associated with, but generally paragenetically older than, Fe-Cu sulfides; 5) have LREE enrichment and low S sulfides (lack of abundant pyrite) and lack widespread quartz veins or silicification; 6) show a clear temporal, but not close spatial, relationship to major magmatic intrusions (Groves et al., 2010). Largely based on fluid inclusion analysis and isotope geochemistry investigation, some researchers suggest that ore-forming fluids and metals in these deposits are largely sourced from magmatic fluid (Sillitoe, 2003; de Haller et al., 2009; Li and Zhou, 2018), and external fluid may contribute in some cases, but are not required (Sillitoe, 2003). However, sulfide precipitation would be inhibited in the S-poor nature of the IOCG hydrothermal system (Barton, 2013; Richards and Mumin, 2013), and researchers have suggested that a second sulfur source is required in cases where

chalcophile elements are abundant (Haynes et al., 1995; Williams et al., 2005; Chen, 2013; Li et al., 2021).

Most IOCG deposits are Precambrian in age (Groves et al., 2010), and their original hydrothermal characteristics are commonly variably masked by post-mineralization deformation and alteration. Therefore, young and unmetamorphosed IOCG deposits are good research targets to resolve aforementioned metallogenic problems. Located in the South American Coastal Cordillera, the Mesozoic Central Andean IOCG province is one of the world's youngest continental arc-related IOCG belts (Sillitoe, 2003). In this IOCG province, the Mina Justa deposit was formed in the Cretaceous and classified as a representative IOCG deposit (Chen et al., 2010; Rodriguez-Mustafa et al., 2022).

Researchers has applied detailed research on the Mina Justa deposit (Chen et al., 2010; Li et al., 2018; Hu et al., 2020; Rodriguez-Mustafa et al., 2022). Preliminary sulfur isotope geochemistry investigation has suggested that the source of sulfur of the magnetite-pyrite stage are mainly magmatic with a small number of elevated sulfur isotopic data sourced from minor external fluids incursion (Li et al., 2018). This conclusion is supported by new Fe isotope and O isotope data, which also suggests a major magmatic fluid for magnetite-pyrite stage

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(Rodríguez-Mustafa et al., 2022). Modeling results suggested that the sulfur isotopic composition ($\delta^{34}\text{S}$) of the ore-forming fluids responsible for the Cu-mineralization stage is around +10 ‰ (Li et al., 2021), which possibly resulted from interaction of basinal brine and andesite wall rocks (Li et al., 2018). However, this conclusion is challenged by new Cu isotope data ($\delta^{65}\text{Cu}$ around 0 ‰), which suggests no significant input of basinal brines (Rodríguez-Mustafa et al., 2022). Whether external fluid is involved and its potential role in the Cu-mineralization stage is critical for understanding the genesis and ore prospecting for IOCG deposits (Hitzman et al., 1992; Haynes et al., 1995; Williams et al., 2001; Bas-trakov et al., 2007; Barton, 2013; Chen, 2013), which should be further addressed using other geochemistry tool.

Sulfur has four stable isotopes (^{32}S , ^{33}S , ^{34}S , and ^{36}S), which have natural abundances of approximately 95.04, 0.75, 4.20, and 0.01 %, respectively (Coplen et al., 2002). Major sulfur isotopes (i.e., $^{34}\text{S}/^{32}\text{S}$) have been frequently used to trace the source and evolution of ore-forming fluids, but minor sulfur isotopes (e.g., ^{33}S , ^{36}S) may also carry important information of the ore-forming fluids. Magmatic sulfur tends to have near zero $\Delta^{33}\text{S}$ values (0 ± 0.05 ‰) (Labidi et al., 2013; Magalhães et al., 2019), while sedimentary sourced sulfur (e.g., sedimentary pyrite, pore water sulfate) tend to have larger $\Delta^{33}\text{S}$ range (e.g., -0.15 to $+0.35$ ‰) (Johnston et al., 2008; Johnston, 2011). Since magmatic and sedimentary sulfur have distinct triple sulfur isotopic characteristics, it could be used to constrain potential contribution of these two reservoirs. For example, Magalhães et al. (2019) detected elevated $\Delta^{33}\text{S}$ values (average at 0.113 ‰) in one of the platinum group element deposit of the Bushveld Complex, and conclude that there are contamination of the causative magma with a surface-derived component. In light of previous studies which demonstrated the advantage of multiple sulfur isotopes, we applied triple sulfur isotope analysis on the Cu-mineralization stage chalcopyrite and coexisting pyrite to constrain the characteristics and potential source(s) of the Cu-mineralization stage fluids. Our new data allow us to conclude that external fluid (i.e., basinal brine) was significantly involved during the Cu-mineralization stage at Mina Justa.

2. Regional and deposit geology

The regional and deposit geology has been described intensively previously (Chen et al., 2010; Li et al., 2018; Hu et al., 2020; Rodríguez-Mustafa et al., 2022) and was summarized briefly as follows.

The IOCG belt in Perú is underlain by Paleoproterozoic to Mesoproterozoic Arequipa Massif Formation high-grade metamorphic rocks, which include migmatite, gneiss, schist and meta-granite (Wasteneys et al., 1995; Loewy et al., 2004). Overlying this formation are the Neoproterozoic (San Juan Formation) and Paleozoic (Marcona Formation) sedimentary cover sequences (Caldas Vidal, 1978; Hawkes, 2002). The Marcona Formation is 1500 m thick and is overlain by thick Mesozoic meta-sedimentary/volcanic sequences, which is comprised by (from bottom to top) the Río Grande, Jahuay, Yauca and Copara formations (Caldas Vidal, 1978). The Mina Justa deposit is hosted by the upper part of the Río Grande Formation, which consists mainly of porphyritic andesite and andesitic volcanoclastic rocks with minor sandstone, conglomerate and mudstone (Caldas Vidal, 1978; Hawkes, 2002).

During the Cretaceous, the Peruvian coastal margin had likely undergone oblique subduction, which led to widespread arc plutonism and formation of five volcanosedimentary basins in the Western Peruvian Trough (WPT) (Polliand et al., 2005). The Huarmey (400 km long, 80 km wide) and Cañete (300 km long, 100 km wide) are the two major volcanosedimentary basins in the western WPT (Cobbing, 1978). The Mina Justa deposit lies on the margin of the Cañete basin. Deposition of the Cañete basin likely commenced in the Tithonian (152–145 Ma) and ceased in the Albian (113–100.5 Ma), with a total lifespan of >32 My (up to 51.5 My) (Cobbing, 1978). The Mina Justa deposit (magnetite-pyrite stage: 104–101 Ma; Cu-mineralization stage, Stage VI: 99–95 Ma; Chen et al., 2010) was formed during late stage of the Cañete basin

development. The Cañete basin is comprised of, from bottom to top, shale (~1500 m), limestone (~1000 m) and marine volcanoclastic andesite (~4000 m) (Cobbing, 1978).

The Mina Justa deposit contains two orebodies, i.e., the Main and the Upper orebodies, which are controlled by the NE-trending Mina Justa fault system (Fig. 1). The two orebodies are both comprised by a magnetite-sulfide core and surrounding hydrothermal breccias, which contain large (5–50 mm) angular host-rock clasts and magnetite-sulfide cement. The hydrothermal breccias are surrounded by extensive Cu-bearing stockwork ore. Seven alteration/mineralization stages were identified at Mina Justa (Chen et al., 2010; Li et al., 2018): Stage I (sodic metasomatism) is represented by widespread albite which replaced plagioclase in the andesitic lavas and volcanoclastic host rocks. Stage II (K-Fe metasomatism) mainly consists of K-feldspar and magnetite but without sulfide. Massive aggregates of diopside, actinolite and minor magnetite were formed in Stage III (Ca metasomatism). Stage IV is dominated by calcite and specular hematite, with the latter being almost entirely replaced by Stage V magnetite. Stage V (magnetite-pyrite stage) mostly consists of magnetite, pyrite, quartz and chlorite and Stage VI (Cu-mineralization stage) is dominated by calcite, chalcocite, bornite and chalcocite. Stage VII hematite locally developed in the upper part of the orebodies.

3. Sampling and analytical technique

3.1. Sampling

Two types of chalcopyrite samples were selected for this study: chalcopyrite with no/minor replacement of coexisting pyrite (Fig. 2a and b) and those that intensely replaced Stage V pyrite (Fig. 2c and d). For the first type of samples, only chalcopyrite was analyzed and for the samples in which chalcopyrite intensely replaced Stage V pyrite, both pyrite and chalcopyrite were analyzed.

3.2. Secondary ion mass spectrometry (SIMS)

The analysis was conducted at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIGCAS) with a CAMECA IMS 1280-HR instrument. Analytical parameters were similar to those described in Li et al. (2019), and are briefly summarized here: A primary $^{133}\text{Cs}^+$ ion beam (~2 nA current and 20 keV total impact energy) was focused on the sample surface. A raster of $10 \times 10 \mu\text{m}^2$ was used in this study. A 20 s pre-sputtering was applied to remove the Au coating, and a normal-incidence electron gun was used for charge compensation. An NMR field sensor was applied to stabilize the magnetic field. ^{32}S , ^{33}S and ^{34}S were measured simultaneously using three Faraday cups (L2, L1 and H1, respectively). The mass resolving power was set at ~5000 to avoid isobaric interference of $^1\text{H}^{32}\text{S}$ to ^{33}S . The amplifier gains were automatically calibrated before the whole session started. Total analysis time for each spot was ~3.5 min. The calibration reference materials used for IMF correction were PPP-1 (Gilbert et al., 2014) for pyrite and CPY-1 (inhouse standard) for chalcopyrite. Data reduction was the same as that described in Li et al. (2019), and is briefly summarized here:

Instrumental bias correction factors for $\delta^{33}\text{S}$ were determined by $\delta^{33}\text{S}_{\text{raw}}$ of the standards as follows:

$$\alpha_{(\text{SIMS})} = \left(\frac{{}^{33}\text{S}/{}^{32}\text{S}}{\text{standard raw}} \right) / \left(\frac{{}^{33}\text{S}/{}^{32}\text{S}}{\text{standard recommend}} \right)$$

$$\left(\frac{{}^{33}\text{S}/{}^{32}\text{S}}{\text{sample}} \right) = \left(\frac{{}^{33}\text{S}/{}^{32}\text{S}}{\text{measured}} \right) / \alpha_{(\text{SIMS})}$$

where $\times = 3, 4$.

Corrected $^{33}\text{S}/^{32}\text{S}$ ratios was normalized to the Vienna Canyon Diablo Troilite (V-CDT) ($^{34}\text{S}/^{32}\text{S} = 1/22.6436$, $^{33}\text{S}/^{32}\text{S} = 1/126.948$) (Ding et al., 2001), according to the following equation and taken as true δ -value ($\delta^{33}\text{S}$).

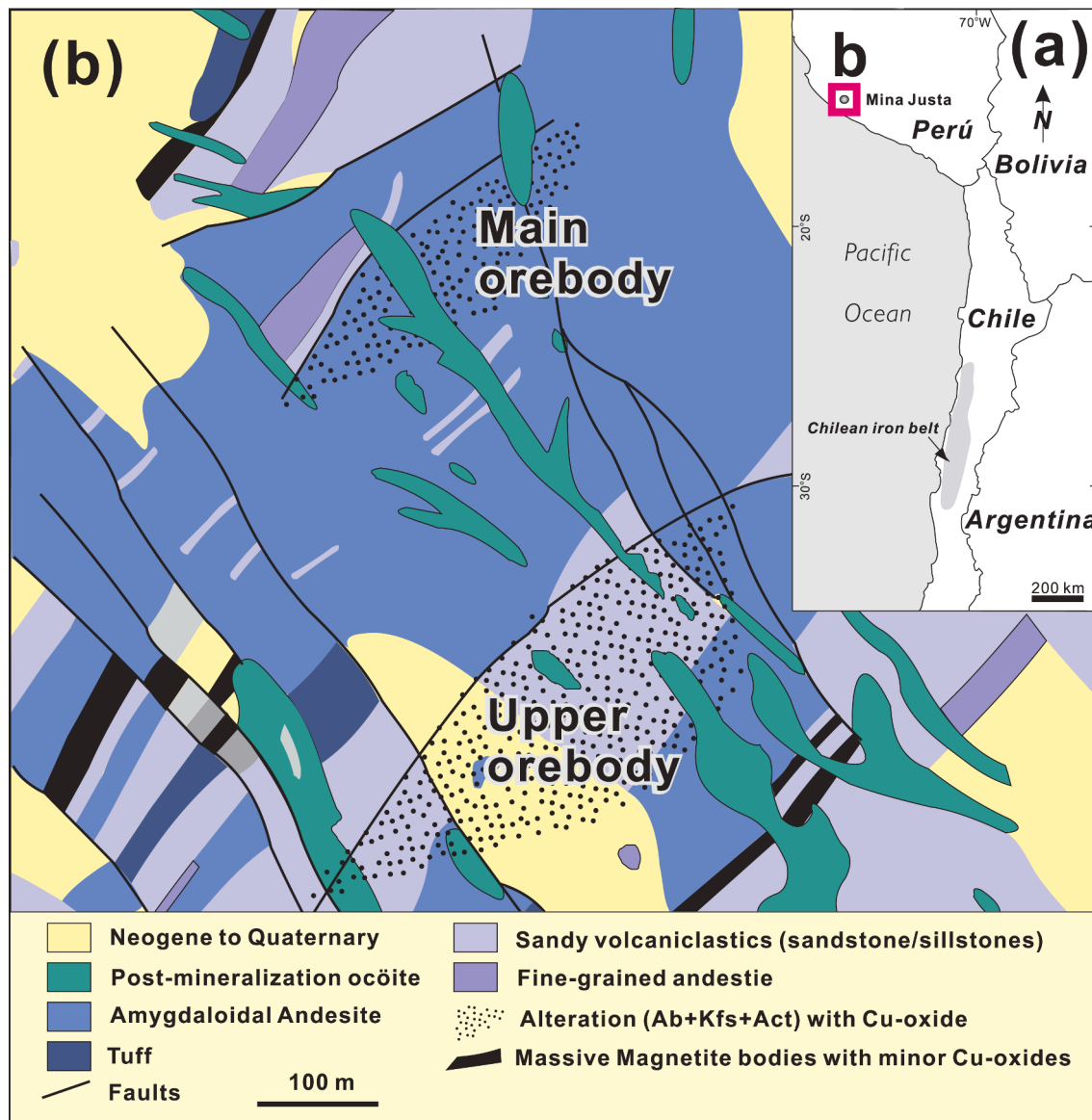


Fig. 1. Deposit geologic map of Mina Justa, modified from Chen et al. (2010).

$$\delta^{34}\text{S}_{\text{sample}} = \left[\left(\frac{{}^{34}\text{S}}{{}^{32}\text{S}} \right)_{\text{sample}} / \left(\frac{{}^{34}\text{S}}{{}^{32}\text{S}} \right)_{\text{V-CDT}} - 1 \right] \times 1000$$

$\Delta^{33}\text{S}$ was calculated using the equation below: $\Delta^{33}\text{S} = \delta^{33}\text{S} - 1000 \times [(1 + \delta^{34}\text{S}/1000)^{0.515} - 1]$.

The analytical uncertainty, estimated by reproducibility of the bracketing standards, were 0.2–0.5 ‰ for $\delta^{34}\text{S}$ and 0.07–0.13 ‰ for $\Delta^{33}\text{S}$.

4. Results

All the results were presented in Fig. 3a and Table 1. The $\delta^{34}\text{S}$ of all analyzed sulfides were in the range of ~ -2 to $+5$ ‰, and the $\Delta^{33}\text{S}$ in the range of -0.10 to $+0.20$ ‰. An outstanding characteristic is that the chalcopyrite which intensely replaced Stage V pyrite tend to have similar triple sulfur isotopic composition to Stage V pyrite, whose $\Delta^{33}\text{S}$ generally in the range of magmatic sulfur (0 ± 0.05 ‰) (Fig. 3a). The chalcopyrite occurs alone or with minimal replacement of coexisting pyrite tends to have elevated $\Delta^{33}\text{S}$ values ($+0.12 \pm 0.10$ ‰) (Fig. 3a).

5. Discussion

5.1. Potential source for the sulfur of chalcopyrite in the Cu-mineralization stage

The chalcopyrite that intensely replaced Stage V pyrite tends to have similar triple sulfur isotopic composition to the pyrite they replaced. This means that this type of chalcopyrite might have inherited sulfur from the pyrite they replaced, indicating that they are not ideal proxy of the Cu-mineralization ore-forming fluid. The best proxy for the Cu-mineralization ore-forming fluid is the chalcopyrite occurs alone or with only minimal replacement of coexisting pyrite.

The chalcopyrite that intensely replaced Stage V pyrite has $\Delta^{33}\text{S}$ around 0 ‰ (Fig. 3a), similar to the range of magmatic sulfur, which usually has $\Delta^{33}\text{S}$ around 0 ‰ (0 ± 0.05 ‰) (Bekker et al., 2009; Labidi et al., 2012; Labidi et al., 2013). This indicates that the sulfur in the chalcopyrite and the pyrite they replaced is largely magmatic. This conclusion is consistent with modelling results which suggest that magmatic sulfur is the dominant source of sulfur in the magnetite-pyrite stage (Stage V) (e.g., Li et al., 2018). Additional evidence from O and Fe isotope of this stage also agrees with this conclusion (Rodríguez-Mustafa

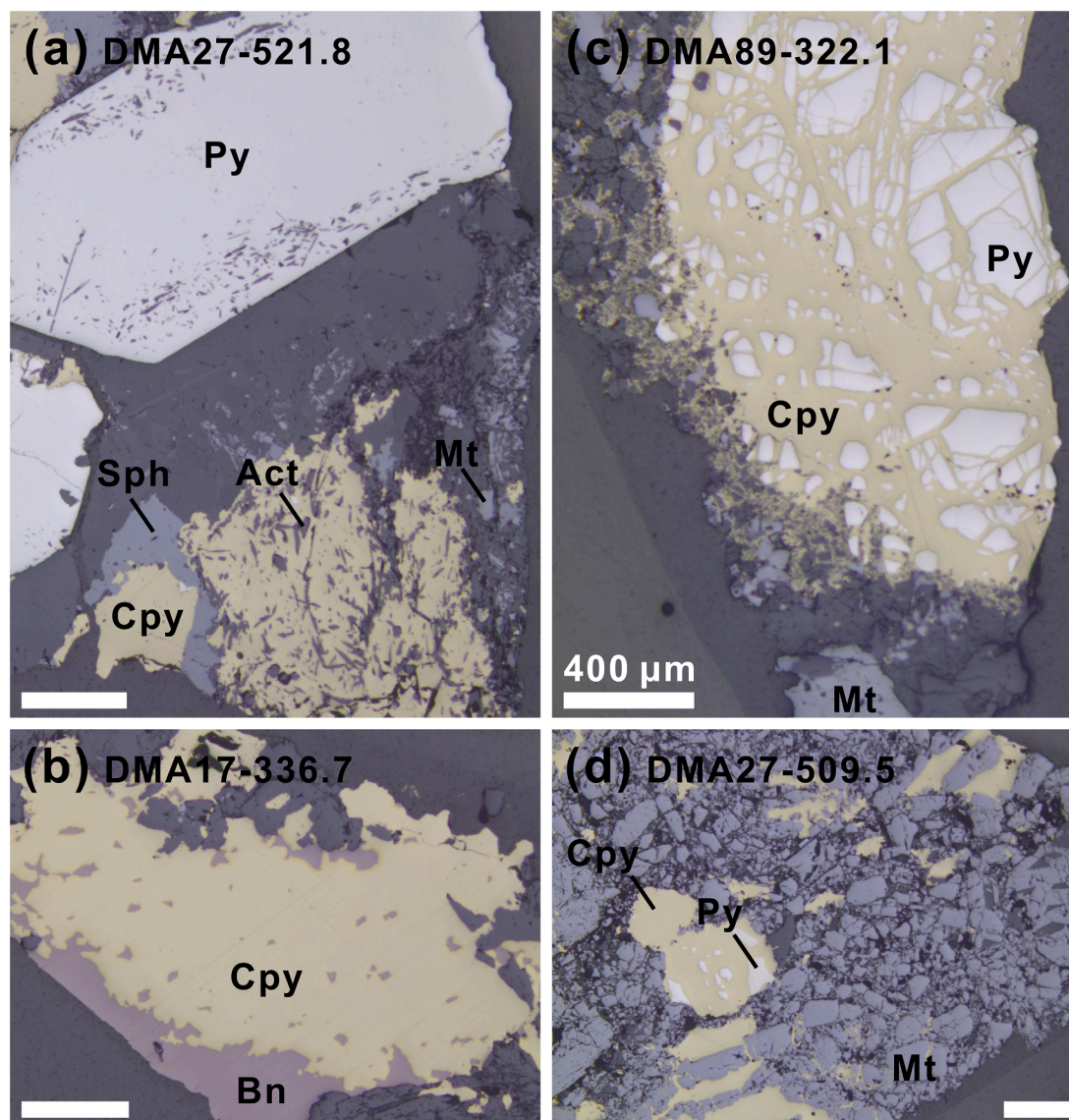


Fig. 2. Photomicrographs of Cu-mineralization stage samples. (a)-(b) Chalcopyrite samples that occur alone or with only minimal replacement of pyrite. (c)-(d) Chalcopyrite samples that intensely replaced Stage V pyrite.

et al., 2022).

However, the $\Delta^{33}\text{S}$ value (average at $+0.12 \pm 0.10$ ‰, 2SD) of chalcopyrite with no or only minimal replacement of coexisting pyrite deviated significantly from what was expected for magmatic sulfur, meaning that the elevated $\Delta^{33}\text{S}$ need a second source. The only known source of sulfur with elevated $\Delta^{33}\text{S}$ value in nature is sedimentary sulfur, which may include sedimentary sulfides (Ono et al., 2006; Ono et al., 2007; Johnston, 2011; Magalhães et al., 2019) and seawater sulfate (Johnston et al., 2008). Sedimentary sulfides could generate positive $\Delta^{33}\text{S}$ values (up to $+0.35$ ‰) through bacterial sulfate reduction (BSR) (Ono et al., 2006; Ono et al., 2007; Johnston, 2011). Meanwhile, seawater sulfate could also has elevated $\Delta^{33}\text{S}$ (up to $+0.17$ ‰) (Johnston et al., 2008). These are the two possible sources for the elevated $\Delta^{33}\text{S}$ in the chalcopyrite at Mina Justa.

Additional evidence for the presence of external fluid comes from oxygen isotope data. Calcite in Cu-mineralization stage has $\delta^{18}\text{O}$ around $+13.5$ ‰ ($n = 8$) (Chen et al., 2011). Considering that the temperature of the ore-forming fluid is around 140 °C (constrained by fluid inclusion study), the calculated $\delta^{18}\text{O}$ for the ore-forming fluid should be around $+0.1$ ‰ (Chen et al., 2011). This result is very close to the value of seawater/basin brine. We did a simple modelling on the sulfur isotopic

composition of the ore-forming fluid for the Cu-mineralization stage. The temperature (constrained by fluid inclusion study) is taken from Chen et al. (2011) and the fractionation factor is taken from Eldridge et al. (2016). Since there are ubiquitous magnetite, the oxygen fugacity of the ore-forming fluid would be buffered by magnetite and be moderately reduced (Bastrakov et al., 2007). Given that the $\delta^{34}\text{S}$ of chalcopyrite with no or only minimal replacement of coexisting pyrite are in the range of $+1$ to $+3$ ‰, the $\delta^{34}\text{S}$ of the Cu-mineralization stage should be around $+9.5$ ‰ (Fig. 3b). Combining the oxygen and sulfur isotope data, we propose that interacting of basin brine (residual seawater) with the andesitic wall rocks in the Cañete basin possibly offers the sulfur in the ore-forming fluid during Cu-mineralization.

5.2. Disagreement between triple sulfur and Cu isotope geochemistry

Recently, Rodriguez-Mustafa et al. (2022) reported bulk Cu isotope data of Cu sulfide samples, and $\delta^{65}\text{Cu}$ ranges from -0.32 to -0.09 ‰, by which the authors suggest that the ore-forming fluid is largely magmatic and meteoric water/basinal brines are not required. What is important here and overlooked by Rodriguez-Mustafa et al. (2022) may be the Cu concentration in magmatic fluid and external fluid. The Cu

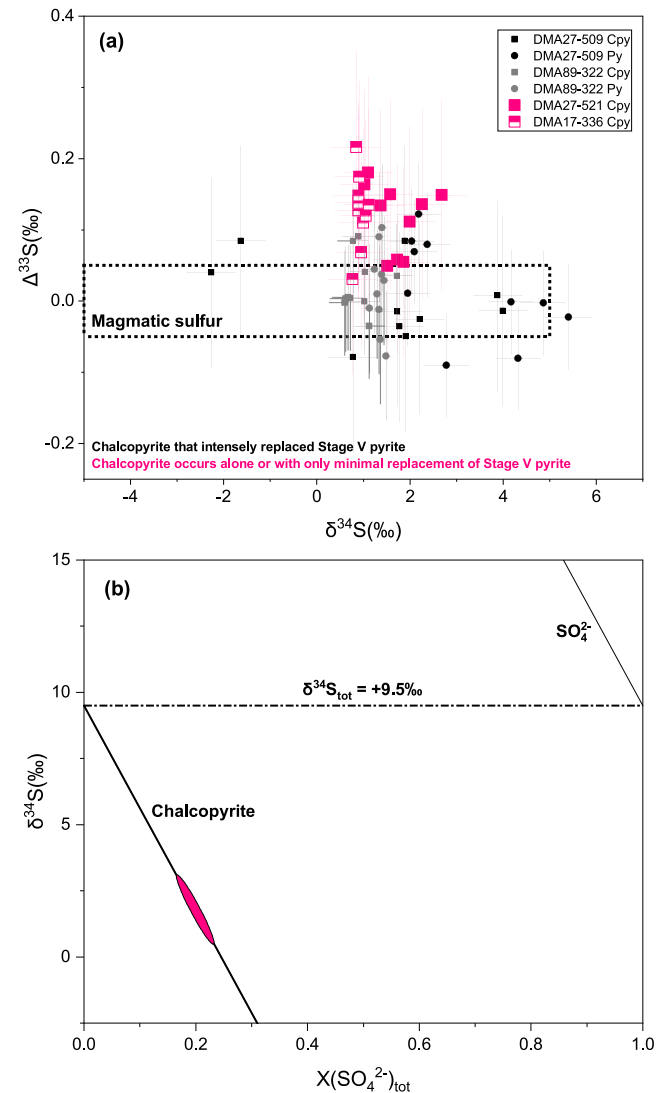


Fig. 3. Triple sulfur isotope data (a) and modelling results (b) of the sulfides at Mina Justa.

concentration in andesite is around 400–1000 ppm (Oppenheimer et al., 2003), which is orders of magnitude higher than that in seawater (0.2 ppb, Bruland, 1980). This means that, even when basinal brine is dominant (e.g., >90 %), most of the Cu would still be sourced from andesite and $\delta^{65}\text{Cu}$ would be around 0 ‰. According to modeling results, the $\delta^{34}\text{S}$ of the ore-forming fluid responsible for Cu-mineralization is around +9.5 ‰. Assuming the $\delta^{34}\text{S}$ of magmatic sulfur is 0 ‰ (Seal, 2006) and seawater sulfate at 99 Ma is +17.4 ‰ (Wu et al., 2010), and S concentration in andesite and seawater are 400–1000 ppm (Oppenheimer et al., 2003) and ~900 ppm (28 mM/kg) respectively, this would result in equal mass of magmatic fluid (~50 %) and seawater (~50 %) in the ore-forming fluid. Assuming magmatic fluid has $\delta^{65}\text{Cu}$ around 0 ‰ and seawater around +1 ‰ (Moynier et al., 2017), mixing equal amount of magmatic fluid and basinal brine (residual seawater in the Cañete basin) would result in an ore-forming fluid with $\delta^{65}\text{Cu}$ around 0.0001 ‰ [$\delta^{65}\text{Cu}_{\text{mix}} = (C_{\text{magmatic}} \cdot \delta^{65}\text{Cu}_{\text{magmatic}} \cdot f_{\text{magmatic}} + C_{\text{seawater}} \cdot \delta^{65}\text{Cu}_{\text{seawater}} \cdot f_{\text{seawater}}) / (f_{\text{magmatic}} + f_{\text{seawater}})$, where C and f are the copper concentration and mass fraction of copper in the reservoir, respectively], identical to what is expected for magmatic copper. The above calculation indicates that Cu isotope data are not a useful tool to assess relative contribution of different sulfur reservoirs.

Table 1
Triple sulfur isotopic composition of sulfides at Mina Justa.

Sample ID	Chalcopyrite type	$\delta^{34}\text{S}$ (‰)	2SD (‰)	$\Delta^{33}\text{S}$ (‰)	2SD (‰)
DMA27-509 Cpy@01	Samples in which chalcopyrite intensely replaced Stage V pyrite.	1.73	0.53	−0.01	0.13
DMA27-509 Cpy@2		1.91	0.53	−0.05	0.13
DMA27-509 Cpy@3		−2.26	0.53	0.04	0.13
DMA27-509 Cpy@4		−1.63	0.53	0.08	0.13
DMA27-509 Cpy@5		0.77	0.53	−0.08	0.13
DMA27-509 Cpy@6		4.00	0.53	−0.01	0.13
DMA27-509 Cpy@7		2.21	0.53	−0.03	0.13
DMA27-509 Cpy@8		1.77	0.53	−0.04	0.13
DMA27-509 Cpy@9		1.89	0.53	0.08	0.13
DMA27-509 Cpy@10		3.88	0.53	0.01	0.13
DMA89-322 Cpy@01	Chalcopyrite occurs alone or with only minimal replacement of Stage V pyrite	1.12	0.34	−0.04	0.07
DMA89-322 Cpy@2		1.03	0.34	0.00	0.07
DMA89-322 Cpy@3		0.62	0.34	0.00	0.07
DMA89-322 Cpy@4		0.60	0.34	0.00	0.07
DMA89-322 Cpy@5		1.72	0.34	0.04	0.07
DMA89-322 Cpy@6		0.90	0.34	0.09	0.07
DMA89-322 Cpy@7		1.03	0.34	0.04	0.07
DMA89-322 Cpy@8		0.72	0.34	0.00	0.07
DMA89-322 Cpy@9		0.67	0.34	0.01	0.07
DMA89-322 Cpy@10		0.78	0.34	0.08	0.07
DMA27-509 Py@01	Pyrite	4.86	0.49	0.00	0.07
DMA27-509 Py@02		4.32	0.49	−0.08	0.07
DMA27-509 Py@03		2.10	0.49	0.07	0.07
DMA27-509 Py@04		2.19	0.49	0.12	0.07
		2.04	0.49	0.08	0.07

(continued on next page)

Table 1 (continued)

Sample ID	Chalcopyrite type	$\delta^{34}\text{S}$ (‰)	2SD (‰)	$\Delta^{33}\text{S}$ (‰)	2SD (‰)
DMA27-509 Py@05	Samples in which chalcopyrite occurs alone or with only minimal replacement of Stage V pyrite.	1.95	0.49	0.01	0.07
DMA27-509 Py@06		2.37	0.49	0.08	0.07
DMA27-509 Py@07		5.40	0.49	-0.02	0.07
DMA27-509 Py@08		4.17	0.49	0.00	0.07
DMA27-509 Py@09		2.79	0.49	-0.09	0.07
DMA27-509 Py@10		1.13	0.19	-0.01	0.09
DMA89-322 Py@01		1.40	0.19	0.10	0.09
DMA89-322 Py@02		1.23	0.19	0.04	0.09
DMA89-322 Py@03		1.33	0.19	0.09	0.09
DMA89-322 Py@04		1.33	0.19	-0.01	0.09
DMA89-322 Py@05		1.40	0.19	0.04	0.09
DMA89-322 Py@06		1.29	0.19	0.01	0.09
DMA89-322 Py@07		1.36	0.19	-0.05	0.09
DMA89-322 Py@08		1.44	0.19	0.03	0.09
DMA89-322 Py@09		1.49	0.19	-0.08	0.09
DMA89-322 Py@10		2.26	0.53	0.14	0.13
DMA27-521 Cpy@01		1.99	0.53	0.11	0.13
DMA27-521 Cpy@2		1.02	0.53	0.16	0.13
DMA27-521 Cpy@3		1.10	0.53	0.18	0.13
DMA27-521 Cpy@4		2.68	0.53	0.15	0.13
DMA27-521 Cpy@5		1.57	0.53	0.15	0.13
DMA27-521 Cpy@6		1.86	0.53	0.05	0.13
DMA27-521 Cpy@7		1.37	0.53	0.13	0.13
DMA27-521 Cpy@8		1.52	0.53	0.05	0.13
DMA27-521 Cpy@9					

Table 1 (continued)

Sample ID	Chalcopyrite type	$\delta^{34}\text{S}$ (‰)	2SD (‰)	$\Delta^{33}\text{S}$ (‰)	2SD (‰)
DMA27-521 Cpy@10		1.73	0.53	0.06	0.13
DMA17-336 Cpy@01		0.90	0.53	0.13	0.13
DMA17-336 Cpy@2		1.00	0.53	0.11	0.13
DMA17-336 Cpy@3		0.77	0.53	0.03	0.13
DMA17-336 Cpy@4		0.90	0.53	0.14	0.13
DMA17-336 Cpy@5		0.89	0.53	0.15	0.13
DMA17-336 Cpy@6		0.91	0.53	0.17	0.13
DMA17-336 Cpy@7		0.85	0.53	0.22	0.13
DMA17-336 Cpy@8		1.12	0.53	0.14	0.13
DMA17-336 Cpy@9		1.06	0.53	0.12	0.13
DMA17-336 Cpy@10		0.95	0.53	0.07	0.13

Cpy: chalcopyrite; Py: pyrite.

6. Conclusions

In-situ triple sulfur isotope analysis was applied on two types of chalcopyrite-bearing samples, i.e., chalcopyrite that occurs alone or with only minimal replacement of coexisting pyrite and chalcopyrite that intensely replaced early-stage pyrite. The chalcopyrite that intensely replaced pyrite tends to have similar triple sulfur isotopic composition to the pyrite ($\Delta^{33}\text{S}$ around 0 ‰), indicating that it has inherited sulfur from the replaced pyrite. The chalcopyrite occurring alone or with minimal replacement of coexisting pyrite tends to have elevated $\Delta^{33}\text{S}$ values (+0.05 to +0.2 ‰, average at $+0.12 \pm 0.10$ ‰, 2SD), which are significantly deviated from what was expected for magmatic sulfur, indicating that there must be external fluid incursion during Cu-mineralization stage.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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