Multiple sulfur isotopes in post-Archean deposits as a potential tracer for fluid mixing processes: An example from an iron oxide–copper–gold (IOCG) deposit in southern Peru

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Abstract
Sulfur has four stable isotopes (32S, 33S, 34S, and 36S), but little research has been conducted to investigate the information that low abundance sulfur isotope ratios (i.e., 32S/33S and 34S/36S) may carry on ore-forming processes in post-Archean deposits. In this study, the Cretaceous Mina Justa iron oxide–copper–gold deposit, was selected to examine the capability of multiple sulfur isotopes to trace ore-forming processes in post-Archean mineral deposits. In situ secondary ion mass spectrometry was applied to the pyrite of the magnetite–pyrite stage in the deposit to characterize the spatial variation of multiple sulfur isotopes at the microscale. This revealed a clear co-variation trend between S/1000 (34S = 1000 × 34S/36S) and Δ34S (= 34S/36S – 1) and Δ36S (= 36S/32S – 1000 × (1 + 34S/36S/1000)0.515 – 1)). Simple modeling suggests that the triple sulfur isotope data recorded is best explained by mixing magmatic and externally derived (e.g., basinal brine) fluids. The contribution of external fluids is also supported by the trace element distribution patterns in pyrite, as revealed by laser ablation–inductively coupled plasma-mass spectrometry. This study is the first attempt to use multiple sulfur isotopes to trace ore-forming processes in post-Archean deposits and demonstrates that multiple sulfur isotopes are a faithful recorder of ore-forming processes at the microscale, especially when multiple fluids mix.

1. Introduction
Sulfur has four stable isotopes (32S, 33S, 34S, and 36S), which have natural abundances of approximately 95.04, 0.75, 4.20, and 0.01%, respectively (Coplen et al., 2002). The ratio of major sulfur isotopes (34S/32S) in sulfide minerals of both magmatic and hydrothermal deposits has been conventionally used to trace the source and evolution of ore-forming fluids as well as identifying how the deposits were formed (Bastrakov et al., 2007; Chang et al., 2008; Ohimoto, 1972; Seal, 2006). Meanwhile, widespread measurement of minor sulfur isotopes (32S and 36S) in terrestrial samples has been catalyzed by the discovery of non-mass-dependent fractionation (NMF) of such isotopes in ancient rocks (>2.3 Ga), which were formed prior to the first Great Oxidation Event (GOE) on Earth (Farquhar et al., 2000). However, interest in measuring more than one isotope ratios in ore deposits has been limited to studies of Archean deposits (Bekker et al., 2009; Chen et al., 2015b; LaFlamme et al., 2018b; Ripley and Li, 2017; Xue et al., 2013). Recent studies have demonstrated that additional information may be preserved by minor sulfur isotope signatures in samples with various ages, which has advanced our understanding of various aspects of sulfur cycling (e.g., Johnston et al., 2005; Wu et al., 2015; Wu et al., 2010). Thus, measuring multiple sulfur isotopes may offer the opportunity to trace contributions from different sulfur reservoirs in post-Archean samples that were formed via moderate- to high-temperature geological processes (e.g., 200–600 °C) (Ono et al., 2007).

Microanalysis can identify variations in isotope composition at the microscale as well as identifying how the deposits were formed. This study is the first attempt to use multiple sulfur isotopes to trace ore-forming processes in post-Archean deposits and demonstrates that multiple sulfur isotopes are a faithful recorder of ore-forming processes at the microscale, especially when multiple fluids mix.

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ion mass spectrometry (SIMS) instruments can analyze $\delta^{34}$S and $\Delta^{33}$S with precisions of approximately 0.4% and 0.10% (2 S.D.), respectively (Li et al., 2018a; Li et al., 2018b), which provides a powerful tool to uncover complex ore-forming processes (Li et al., 2020a; Wu et al., 2019b; Wu et al., 2018).

Fluid mixing, which substantially changes the physical or chemical properties of hydrothermal fluids and dramatically reduces the solubility of metals in ore-forming fluids (Guilbert and Park Jr, 2007; Robb, 2004), is one of the most important ore-forming processes (Audétat et al., 1998; Haynes et al., 1995; Kendrick et al., 2007; Lu et al., 1996; Matthaei et al., 1995; Samson and Russell, 1987; Teagle et al., 1998; Wei et al., 2012; Williams et al., 2001). Fluid mixing is typically identified by analysis of fluid inclusions and/or stable isotopes (Audétat et al., 1998; Lu et al., 1996; Samson and Russell, 1987); however, discriminating between primary and secondary fluid inclusions is often difficult (Bodnar and Samson, 2003; Van den Kerkhof and Hein, 2001), and some fluid inclusions may be too small to analyze effectively (Kelley et al., 1986; Roedder, 1971). At the same time, only measuring one isotopic ratio (e.g., $\delta^{34}$S,$\Delta^{33}$S) may result in ambiguous interpretations (Ono et al., 2007).

Theoretically, mixing of two fluids with different sulfur isotopic compositions would show a mixing trend in a binary diagram of $\delta^{34}$S vs. $\Delta^{33}$S (Ono et al., 2006). Modern seawater is characterized by a $\Delta^{33}$S value of approximately $+0.05\%$ (Wu et al., 2010), although it can be as high as $+0.173\%$ (Johnston et al., 2008). By contrast, a typical magmatic sulfur source is characterized by negative $\Delta^{33}$S values (around $-0.02\%$), but it can be lower than $-0.03\%$ (Labidi et al., 2012; Stefansson et al., 2015). Hence, the difference in $\Delta^{33}$S between magmatic and seawater sulfur is approximately 0.07%, but it can potentially be larger than 0.2%. This difference is equal to or greater than the analytical uncertainty of SIMS analyses, meaning that the relative contributions of magmatic and seawater sulfur in a given ore deposit may be determined via analysis of multiple sulfur isotopes using this technique.

Iron oxide–copper–gold (IOCG) deposits are magmatic–hydrothermal deposits that contain economic Cu and Au grades, and are characterized by: 1) structurally controlled ores; 2) common presence of pre-sulfide sodic or sodic–calcic alteration; 3) large-scale alteration and/or brecciation zones relative to economic mineralization; 4) abundant, low-Ti iron oxides and/or iron silicates that are intimately associated with, but generally paragenetically older than, Fe–Cu sulfides; 5) light rare earth element (LREE) enrichment and low-S sulfides (i.e., a lack of abundant pyrite); 6) a lack of widespread quartz veins or silicification; and 7) a clear temporal, but not close spatial, relationship to major magmatic intrusions (Groves et al., 2010). Since the IOCG clan was identified and defined, there has been strong debate concerning the sources of fluids, sulfur, and metals that formed them (Barton, 2013; Barton and Johnson, 1996; Groves et al., 2010; Hitzman et al., 1992; Sillitoe, 2003; Williams et al., 2005). Largely based on geological investigations, including fluid inclusion analysis and isotopic geochemistry, some researchers have claimed that ore-forming fluids and metals in these deposits mainly have a magmatic source (de Haller and Fontboté, 2009; Li and Zhou, 2018; Rusk et al., 2010; Sillitoe, 2003), such that evaporite-derived fluids may contribute in some cases, but are not required (Pollard, 2003; Sillitoe, 2003). However, the S-poor nature of hydrothermal fluids in IOCG deposits (Barton, 2013; Richards and Mumin, 2013) indicates that sulfide precipitation is inhibited, and a second sulfur source is required in cases where chalcopyrite elements are abundant (Chen et al., 2010; Haynes et al., 1995; Williams et al., 2005). Whether external fluid is involved and its potential role in the Cu-mineralization stage is critical for understanding the genesis and mineral exploration of IOCG deposits (Barton, 2013; Bastrakov et al., 2007; Chen, 2013; Haynes et al., 1995; Hitzman et al., 1992; Kendrick et al., 2007; Williams et al., 2001). Located in the Central Andes, the Cretaceous Mina Justa Cu deposit has been studied extensively and is classified as a representative IOCG deposit (Chen et al., 2010). Previous research has shown that external fluids may have been involved during the magnetite–pyrite stage (Li et al., 2018a). As mentioned previously, if external fluid is involved in the ore-forming process, a mixing trend should be observed in measured multiple sulfur isotopes. To test this hypothesis and to examine whether multiple sulfur isotopes can be used to identify fluid mixing in post-Archean deposits, we performed in situ SIMS multiple sulfur isotope analysis and laser ablation–inductively coupled plasma-mass spectrometry (LA-ICP-MS) trace element mapping of pyrite from the Mina Justa deposit. Multiple sulfur isotope geochemistry supports an external fluid incursion scenario during the transition from the magnetite–pyrite stage to the Cu mineralization stage at Mina Justa. These results suggest that this technique may be applied to other post-Archean deposits thought to involve magmatic and seawater sulfur, and their relative contribution could be determined as long as the multiple sulfur isotope compositions of the two end members are also determined.

2. Geological background and sampling

The IOCG belt in southern Peru, which contains multiple IOCG deposits (Fig. 1a), is underlain by Paleoproterozoic to Mesoproterozoic high-grade metamorphic rocks of the Arequipa Massif Formation, which includes magnetite, goussis, schist, and meta-granite (Loevey et al., 2004; Wasteneys et al., 1995). Neoproterozoic (San Juan Formation) and Paleoozoic (Marcona Formation) sedimentary covers (Caldas Vidal, 1978; Hawkes, 2002) overlie these units (Fig. 1a–b). The Marcona Formation is overlain by thick Mesozoic meta-sedimentary/volcanic sequences, comprising (from bottom to top) the Rio Grande, Jahuay, Yauca, and Copara Formations (Caldas Vidal, 1978; Hawkes, 2002). The Mina Justa Cu (Ag–Au) deposit is hosted by the upper part of the Rio Grande Formation, which consists mainly of porphyritic andesite and andesitic volcaniclastic units, alongside minor sandstone, conglomerate, and mudstone (Caldas Vidal, 1978; Hawkes, 2002). The Mina Justa deposit, which has an open pit reserve of 346.6 Mt at an average grade of 0.71% Cu, 3.8 g/t Ag, and ~0.03 g/t Au at a cutoff grade of 0.3% Cu, and an inferred resource of 127.9 Mt at 0.6% Cu (Chen et al., 2010), comprises the main orebody and the upper orebody (Fig. 1c). These two lensoidal ore bodies each contain a magnetite–sulfide core surrounded by hydrothermal breccias containing large angular clasts of host rock and a magnetite–sulfide matrix. The hydrothermal breccias are surrounded by extensive stockwork ores. The ore bodies are controlled by NE-trending Mina Justa system faults (Chen et al., 2010) and are displaced by NW-trending Huaca faults and andesitic dikes.

Seven alteration/mineralization stages are recognized at Mina Justa (Chen et al., 2010): stage I – sodic metasomatism; stage II – K–Fe metasomatism; stage III – actinolite–diopside–magnetite alteration; stage IV – hematite alteration; stage V – magnetite–pyrite alteration; stage VI – Cu mineralization; and stage VII – late veins. The minerals that formed during stage V are mainly magnetite, pyrite, actinolite, quartz, and chlorite (Chen et al., 2010; Li et al., 2018a). Stage V magnetite appears as granular or tabular aggregates (Fig. 2a–b) and veins (Fig. S1). Tabular hematite is surrounded by stage V magnetite, indicating that the former was the precursor mineral to the latter (Li et al., 2018a). In most cases, pyrite formed in the presence of magnetite, and the planar crystal boundaries between them, and their coexistence in veins cutting the host rock, indicates that both minerals probably precipitated synchronously (Fig. 2b, S1). Stage VI, which is currently being mined, comprises mainly chalcopyrite, calcite, bornite, chalcocite, and sphalerite (Chen et al., 2010; Li et al., 2018a). The most common Cu-bearing mineral in stage VI is chalcopyrite, which intensely replaces pre-existing stage V and VI pyrite (Fig. 2b–c).

Our samples were collected at elevations between 260 m and 526 m above sea level (a.s.l.) from the main orebody, which itself lies at an elevation of 250–550 m a.s.l. Thirteen samples belonging to the magnetite–pyrite stage (stage V) were selected for this study (Table 1). Based on petrological observations (Fig. 2a–e), stage V pyrite is divided into early (Py-E) and late (Py-L) forms. Py-E is characterized by planar crystal boundaries with magnetite and has no actinolite and/or chalcopyrite.
Fig. 1. (a) Locations of Cu-rich iron-ore–copper–gold (IOCG) deposits in Peru and Chile (modified after Chen et al., 2010). (b) Geology of the area surrounding the Mina Justa prospect. (c) Geological map of the Mina Justa IOCG deposit. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
3. Methods

3.1. In situ SIMS triple sulfur isotope analysis

SIMS analysis was conducted on a Cameca IMS1280-HR at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIG-CAS), China. The analytical parameters are summarized below.

Selected sulfide samples were mounted onto 25 mm diameter epoxy and polished. A primary $^{133}$Cs$^+$ ion beam (~2.0 nA current and 20 keV total impact energy) with a spot diameter of 10 μm was focused on the sample surface. Twenty seconds of pre-sputtering was applied to remove the Au coating, and a normal-incidence electron gun was used for charge compensation. The mass-resolving power was set to ~5000 to avoid isobaric interference. An NMR field sensor was used to stabilize the magnetic field. $^{32}$S, $^{33}$S, $^{34}$S, and $^{36}$S were measured simultaneously using the multi-collection system, and the total analysis time for one spot was approximately 5 min. Data reduction was performed according to the methods described by Li et al. (2020b), and the standards used in this study were UWPy-1 (Ushikubo et al., 2014), PPP-1 (Gilbert et al., 2014) and Py-1 (Maier et al., 2016). When PPP-1 was used as the primary standard, Py-1 or UWPy-1 were used as quality control standards, and when UWPy-1 was used as the primary standard, PPP-1 was used as the quality control standard. The isotope ratios were expressed relative to the Vienna Canyon Diablo Troilite (V-CDT) standard: $\delta^{34}$S (‰) = 1000 × ($^{34}$S/$^{32}$S)sample/($^{34}$S/$^{32}$S)V-CDT − 1). $\Delta^{33}$S (‰) = $\delta^{33}$S − 1000 × ([1 + $^{34}$S/$^{32}$S]V-CDT/0.515 − 1), and $\Delta^{36}$S (‰) = $\delta^{36}$S − 1000 × [(1 + $^{34}$S/$^{32}$S)/1000]$^{1.91}$ − 1) (Farquhar et al., 2000; Seal, 2006). At the Cameca IMS 1280-HR laboratory at GIG-CAS, we adopted a protocol in which reproducibility was calculated as two standard deviations (2 S.D.) of all analyses of the working standard over the course of an analytical session. The two reproducibility determinations were as follows: 2 S.D. = 2√(1/n) $\sum_{i=1}^{N} (X_i - \bar{X})^2$, where N is the number of analyzed spots, $X_i$ is the $\delta^{34}$S value, and $\bar{X}$ is the average $\delta^{34}$S value of the working standard.

Quadrapole sulfur isotope results obtained for UWPy-1 in this study are +8.01 ± 0.51‰ for $\delta^{33}$S, +15.61 ± 0.96‰ for $\delta^{34}$S, and +29.55 ± 0.73‰ (2 S.D., n = 23) for $\delta^{36}$S. The results for PPP-1 are +2.75 ± 0.20‰ for $\delta^{33}$S, +5.33 ± 0.34‰ for $\delta^{34}$S, and +10.24 ± 1.25‰ (2 S.D., n = 76) for $\delta^{36}$S, and those for Py-1 are +0.01 ± 0.57‰ for $\delta^{33}$S, and −0.01 ± 1.08‰ for $\delta^{34}$S (2 S.D., n = 17). The recommended values for UWPy-1 were +8.23 ± 0.09‰ for $\delta^{33}$S, +16.04 ± 0.18‰ for $\delta^{34}$S, and +30.53 ± 0.34‰ for $\delta^{36}$S. The recommended $\delta^{34}$S values for PPP-1 and Py-1 were +5.3 ± 0.20‰ (2 S.D.) and −0.6 ± 1.12‰ (2 S.D.), respectively. The results reported here are thus consistent with the recommended values. For all six sessions, the $\Delta^{35}$S values for UWPy-1, PPP-1, and Py-1 were 0.00 ± 0.08‰, +0.01 ± 0.08‰, and +0.06 ± 0.06‰ (2 S.D.), respectively. The $\Delta^{36}$S values for UWPy-1 and PPP-1 were −0.51 ± 0.80‰ and −0.05 ± 0.73‰ (2 S.D.), respectively. These results suggest that none of the standards used here have NMF-S signals, consistent with their post-Archean age. More details about the standards are provided in Table S1. To summarize, the analytical uncertainty for $\delta^{33}$S, $\Delta^{33}$S, and $\Delta^{36}$S using this technique is better than 0.50, 0.08, and 0.79‰ (2 S.D.), respectively.

3.2. EPMA and LA-ICP-MS trace element analyses

Backscattered electron imaging (BSE) and elemental mapping using wavelength-dispersive X-ray spectroscopy were applied to reveal the internal texture of the pyrite grains. All analyses were performed using an SXFiveFE electron microprobe at GIG-CAS, with an accelerating voltage of 15 kV, probe current of 50 nA, and beam size of 4 μm. The standard used for Co was natural pentlandite. The step size was 4 μm and the dwell time was set to 100 ms for each point.

Elemental mapping by LA-ICP-MS was conducted at the Tuoyan in situ analysis lab, Guangzhou, China, using a 193 nm ArF excimer laser.

Fig. 2. Photographs and microphotographs of the Mina Justa iron oxide-Cu (Ag–Au) ores: (a)–(b) typical Py-E sample in the magnetite–pyrite stage (stage V), showing a planar grain boundary between magnetite and pyrite. (c)–(d) Py-E sample in the magnetite–pyrite stage (stage V), with pyrite replaced by stage VI chalcopyrite. The pyrite in (a) to (c) has no actinolite and/or chalcopyrite inclusions. (e)–(f) Typical Py-L sample in which the magnetite is a minor component and the pyrite has abundant actinolite inclusions. Note the chalcopyrite–actinolite–sphalerite assemblage in this sample. Panels (b) and (d) are adapted from Li et al. (2018a). Abbreviations: Mt.: magnetite; Cpy: chalcopyrite; Py: pyrite; Act: actinolite; Sph: sphalerite.
Table 1
Sulfur isotope results of pyrite in this study (‰).

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<th>Pyrite substage</th>
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(continued on next page)
ablation system (NWR 193) coupled with a Thermal Fisher iCAP RQ and a dual concentric injector (DCI) plasma torch integrated with a two-volume ablation cell for LA-ICP-MS mapping. The laser frequency, laser scan speed, scan speed, and laser spot size were set to 100 Hz, 6 μm/s, 5.64 μm/s, and 6 μm, respectively. The ICP-MS was set to a time-resolved method and automatically triggered by the laser; the elements 59Co, 62Ni, 75As, and 79Se were collected at each duty cycle, with a dwell time of 6 ms for each element. Mass bias and instrument drift were carefully corrected by routine analysis of NIST 612, which was used as the primary standard. The raw data were calibrated using the internal standard of the average Fe value of the whole map. The detailed analytical procedures and data reduction process utilized were similar to those described by Li et al. (2020a).

Table 1 (continued)

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<th>2SD</th>
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*: no data.

Stage V: magnetite-pyrite stage.
Py-E: early magnetite-pyrite stage.
Py-L: late magnetite-pyrite stage.
The sample names with superscript “a” and “b” indicates the samples that are assumed to be formed directed from the two deduced fluid ends in our fluid mixing model (Fig. 5a).

Fig. 3. Photograph, backscattered electron (BSE) image, and elemental mapping of selected Py-L samples. (a) BSE image; (b) Co mapping by electron probe microanalysis (EPMA), used to identify Py-L core and Py-L mantle domains; (c)–(f) Co–Ni–As–Se mapping determined by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). The red spots and numbers in (a) indicate locations and δ34S values of secondary ion mass spectrometry (SIMS) results reproduced from Li et al. (2018a). The yellow spots and numbers in (b) indicate locations of triple sulfur isotope analyses acquired in this study. The outmost Co- and As-rich and Ni-poor rim formed from post-break reworking by the Cu-bearing stage ore-forming fluid. Abbreviations: Mt.: magnetite; Cpy: chalcopyrite; Py: pyrite. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
activity (cf. section 5.2) and is not a result of continuous growth onto the Py-L mantle. The internal texture of pyrite in Fig. 4 cannot be revealed by BSE imaging (Fig. 4a), but is evident from trace element mapping (Fig. 4b–c), similar to examples reported from high-sulfidation epithermal systems (Deditius et al., 2009). In this sample, the Py-L core is Co- and As-poor but Se-rich, the Py-L mantle is Co- and As-rich but Se-poor, and the Py-L rim is poor in Co, As, and Se relative to both the Py-L core and the Py-L mantle (Fig. 4b–c). Nickel has a low concentration in both the Py-L core and Py-L mantle but is enriched in the Py-L rim (Fig. 4c). The cores of both samples are Co- and As-poor but Se-rich, and the mantles are Co- and As-rich but Se-poor. The absolute concentrations of Co, Ni, As, and Se in both samples were similar to each other (Figs. 3–4); the main difference between them is that there is no “Py-L rim” in the sample in Fig. 3.

4.2. In situ SIMS multiple sulfur isotopes

Multiple sulfur isotopes (δ34S and Δ33S, yellow spots in Figs. 3–4) were analyzed from both the Py-E and Py-L samples of the magnetite–pyrite stage (stage V). Areas near the cracks and rims of the pyrite crystals were intentionally avoided to minimize the effect of the sample topography (Kita et al., 2009). The red spots with only δ34S determination are reported in Li et al. (2018a) and are presented in Figs. 3–4 for comparison.

For the sample shown in Fig. 3, the Py-L core has δ34S of +1.3‰, the Py-L mantle has δ34S values from +4.8 to +7.4‰, and a minimal decrease is observed from the Py-L mantle to the outermost thin rim (+6.4‰, Fig. 3a) (see section 5.2 for details). The increase in δ34S from the Py-L core to the Py-L mantle is abrupt. Along with δ34S, Δ33S values also increased outwards from +0.04‰ (Py-L core) to +0.15‰ (Py-L mantle) (Fig. 3b).

An increase in δ34S was also observed in the sample shown in Fig. 4. The Py-L core has δ34S values between +2.2 and +2.6‰, Py-L mantle has values between +3.1 and +3.9‰, and Py-L rim has values of +4.0 to +4.9‰ (Fig. 4a–b). Like the sample shown in Fig. 3, the Δ33S values increase outwards from −0.02‰ (Py-L core) to +0.19‰ (Py-L rim) (Fig. 4b). The increases in δ34S and Δ33S values in both samples (Fig. 5a) are coupled with apparent changes in trace element concentrations (e.g., a consistent decrease in Se) (Figs. 3c–f, 4c). While all the multiple sulfur isotope results are taken together, two linear trends appear in the binary diagram of δ34S vs. Δ33S (Fig. 5a). In addition, in the binary diagram of Δ33S vs. Δ34S, our data mostly cluster around the origin (i.e., with values close to 0 for both variables) (Fig. 5b).

5. Discussion

5.1. Incursion of external fluids

Pyrite cores in Figs. 3–4 reveal low δ34S values and high Se concentrations, which is best interpreted by these grains having formed from a magmatic fluid (Huston et al., 1995). The cores have δ34S values ranging from +1.3 to +2.6‰ (Figs. 3–4); thus, given the formation temperature of 540–600 °C (Chen et al., 2011) and the presence of magnetite, the ore-forming fluid should have had a δ34S value of approximately +4.6‰ (Fig. 5a). An interpreted δ34S value of approximately +4.6‰ for the magmatic fluid assumes that the fluid and pyrite had reached equilibrium. Experimental studies of multiple sulfur isotopes have shown that SO4 and H2S at a temperature of around 300 °C reach equilibrium in about 60 h (Fig. 5 in Syverson et al., 2015), which is negligible when compared to geological time. This implies that equilibrium was likely attained in Mina Justa. To make the figure more concise, H2S is omitted, and only pyrite is shown in Fig. 6d, which considers the alternative equation: Δ34S = δ34S(SO4)pyrite − δ34S(SO4)H2S = Δ34S(SO4)H2S − Δ34S(SO4)pyrite. The fractionation between SO4 and H2S (Δ34S(SO4)H2S) and pyrite and H2S (Δ34S(SO4)pyrite) was determined using the equations given by Ohmoto and Goldhaber (1997). A recent
experimental study by Syverson et al. (2015) indicated that $\Delta^{34}S_{\text{pyrite-H}_2S}$ is different from that adopted from Ohmoto and Goldhaber (1997) (i.e., $-1.9\%$ vs. $+1\%$ at 350 °C). However, using the equation above, we found that there was no significant difference in the $\Delta^{34}S_{\text{SO}_4\text{-pyrite}}$ value (i.e., $19.4\%$ in Syverson et al., 2015, and $+19.1\%$ in Ohmoto and Goldhaber, 1997) at 350 °C. Therefore, while the value of $\Delta^{34}S_{\text{pyrite-H}_2S}$ may need to be revised, as suggested by Syverson et al. (2015), the value of $\Delta^{34}S_{\text{SO}_4\text{-pyrite}}$ adopted from Ohmoto and Goldhaber (1997) is considered reliable. In addition, the temperature range investigated by Syverson et al. (2015) is limited (300–350 °C), and hence cannot cover the temperature range considered here. Therefore, the fractionation factor between $\text{SO}_2$ and pyrite used in this study was obtained from Ohmoto and Goldhaber (1997). Once $\Delta^{34}S_{\text{SO}_4\text{-pyrite}}$ was determined, the slope of the pyrite evolution line in Eq. 6d was calculated (i.e., slope = tan($\alpha$) = $\Delta_{\delta^{34}S_{\text{SO}_4\text{-pyrite}}}$/$\Delta_{\delta^{34}S_{\text{SO}_4\text{-pyrite}}}$. Combined with the estimated oxygen fugacity, as constrained by the coexistence of magnetite and pyrite (Fig. 2), and the $\delta^{34}S$ value of pyrite (Table 1), $\delta^{34}S_{\text{Cu}}$ could be determined ($\delta^{34}S_{\text{Cu}}$).

Values of $\delta^{34}S$ increased from core to rim, with the most significant increase being $6.1\%$ in DMA14–394 (Py-L, Fig. 3a) (Li et al., 2018a) and 3.0% in DMA27–526 (Py-L, Fig. 4b). Four possible mechanisms may account for this increase of $\delta^{34}S$: 1) an increase in ore-forming temperature; 2) Rayleigh fractionation; 3) decrease in $fO_2$; and 4) increase in the $\delta^{34}S$ of the ore-forming fluid. An increase in ore-forming temperature cannot account for the $\delta^{34}S$ increase in this study because this requires a new pulse of magma intrusion, for which there is no evidence in the deposit (Chen et al., 2010). Further, the variation in pyrite $\delta^{34}S$ resulting from temperature fluctuation within the range 540–600 °C (Chen et al., 2011) should not exceed 1% (Fig. 6a). Rayleigh fractionation is also unlikely for two reasons: 1) driving the $\delta^{34}S$ value from $+1.3$ to $-7.4\%$ would consume approximately 80% of the sulfur in the magmatic fluid (Fig. 6b), which implies a relatively long crystallization history; and 2) Rayleigh fractionation produces a gradually increasing trend in $\delta^{34}S$ value, a monotonous increase or decrease trend in trace element concentration from core to rim (Fitzpatrick, 2008), and most of the data should lie in the low $\delta^{34}S$ side in a single grain (Guo et al., 2020; Ohmoto, 1972; Seal, 2006). None of these features were observed in our samples (Figs. 3–4). To account for the increase of 6.1% in $\delta^{34}S$ (+1.3 to $-7.4\%$), a decrease in $fO_2$ would cause $\delta^{34}S$ to decrease commensurately by approximately 56% (Fig. 6c). As documented by Li et al. (2018a), stage V magnetite replaced stage IV hematite. This indicates the coexistence of stage V (magnetite–pyrite stage) fluid and stage IV hematite, and the $fO_2$ of the stage V fluid would be buffered by the stage IV hematite. Hence, an abrupt decrease in $fO_2$ during the magnetite–pyrite stage is not likely, given the presence of hematite (Bastrakov et al., 2007).

Although a decrease in $fO_2$ cannot be totally excluded, we find that an increase in the $\delta^{34}S$ of the ore-forming fluid is the most likely mechanism for the observed abrupt increase in $\delta^{34}S$ in pyrite samples. Two main points of evidence support the introduction of a new pulse of ore-forming fluid. First, the abrupt $\delta^{34}S$ increase is coupled with a dramatic change in trace element concentrations (Figs. 3–4). Several factors have been invoked to explain chemical zonation in minerals, including changes in temperature, pressure, and the composition of bulk fluids (Shore and Fowler, 1996). However, a recent novel study using nanoscale secondary ion mass spectrometry (NanoSIMS) and atom probe tomography revealed that chemically distinct, micron-scale concentric areas show MDF as redefined in LaFlamme et al. (2018a). Both samples DMA14–394 and DMA27–521 are considered as Py-L. The pyrite evolution trend denotes that pyrite formed (from core to rim) in response to an incursion of basinal fluid. (b) Binary plot of $\Delta^{34}S$ vs. $\Delta^{32}S$. MDF: mass-dependent fractionation (Ono et al., 2006); ARA: Archean Reference Array (Ono, 2017).
bearing stage fluid—as evidenced by the intimate relationship between its Co- and As-rich rim and chalcopyrite (Fig. 12 in Li et al., 2018a). Nonetheless, the exact timing of formation of the Co- and As-rich rim of this crystal could not be determined and may belong to the magnetite–pyrite stage (stage V) or the Cu-bearing stage (stage VI). Therefore, it is not appropriate to consider it as a representative of the Cu-bearing stage fluid, and it is excluded from the discussion below.

The Py-L rim in Fig. 4 is interpreted to be a representative of the Cu-bearing stage (stage VI) fluid based on several points of evidence. First, the Py-L rim is rich in actinolite, which formed synchronously with chalcopyrite (Fig. 2 e–f). Chalcopyrite (white inclusions in the BSE image, Fig. 4 a) is also present in the Py-L rim, which suggests simultaneous formation of actinolite, chalcopyrite, and Py-L rim. Second, pyrite influenced by a Cu-bearing fluid should be Co- and As-rich (Fig. 3 a and Fig. 12 in Li et al., 2018a), although this is not the case for the Py-L rim. Third, the width of a pyrite grain influenced by a Cu-bearing fluid is generally <50 μm (Fig. 3 a and Fig. 12 in Li et al., 2018a), but the width of the Py-L rim in this study is approximately 200 μm, which is much wider than those observed in samples that were influenced by Cu-bearing fluids. Based on these arguments, we interpret that the Py-L rim was not formed by reworking of earlier pyrite, but it was formed at the transition from the magnetite–pyrite stage (stage V) to the Cu-bearing stage (stage VI), and hence serves as a good proxy for the Cu-bearing stage fluid.

Because the Py-L rim is representative of the ore-forming fluid responsible for the Cu-bearing stage at Mina Justa, the mineral assemblage (chalcopyrite, bornite, and sphalerite, which indicate a relatively low \( f_{O_2} \), Fig. 2 ) and the temperature determined by the study of fluid inclusions (~220 °C (Chen et al., 2011)) can be combined to determine that the ore-forming fluid of the Cu-bearing stage had a \( \delta^{34}S \) value of around +10.6‰ (Fig. 6d). The most plausible Cu-bearing fluid with such a \( \delta^{34}S \) value is a basin-derived fluid, which may have formed by the reaction of basin fluid with pre-existing volcano-sedimentary rocks in the basin (Li et al., 2018a).

5.3. Feasibility of using triple sulfur isotope to trace fluid mixing processes

A simple binary mixing model readily explains the triple sulfur isotope data presented in this study (Fig. 5). Because Py-L cores have the lowest \( \delta^{34}S \) values and highest Se concentrations (Figs. 3–4), they most resemble the magmatic fluid end member. The Py-L rim, which formed coevaly with its chalcopyrite inclusions (Figs. 2c, 4a), has the highest \( \delta^{34}S \) value and lowest Se concentration, and thus resembles the externally derived Cu-bearing fluid end member. Because this model describes the transitional conditions from the magnetite–pyrite stage to the Cu-bearing stage, the temperatures of the two ore-forming fluid end members in our model were set to 540 and 220 °C (Chen et al., 2011), respectively. The two pyrite spots that correspond to both fluid end

![Fig. 6. Modeled conditions that may account for the \( \delta^{34}S \) variation recorded at the Mina Justa iron–copper–gold (IOCG) deposit: (a) a changing temperature scenario; (b) a Rayleigh fractionation scenario; (c) a changing \( f_{O_2} \) scenario; and (d) an external fluid incursion scenario. The parameters used for modeling were adopted from Ohmoto and Goldhaber (1997). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
members of our mixing model are listed in Table 1. Their $\delta^{34}\text{S}$ values were +1.36 and +4.26‰, and their $\Delta^{32}\text{S}$ values were −0.05 and +0.19‰, respectively. The $\Delta^{32}\text{S}$ value we selected for the magmatic fluid end member is −0.05‰, which is consistent with the reported value for mid-ocean ridge basalt (MORB, −0.03 to +0‰) (Labidi et al., 2012). The $\delta^{34}\text{S}$ values of both fluid end members were +4.6 and +10.6‰, respectively, as determined from Fig. 6. The $X(\text{SO}_2^2-\text{H}_2\text{S})$ values for both end members were taken from Fig. 6 (i.e., 0.3 and 0.22, respectively). The fractionation factors (SO22→H2S and pyrite-H2S) at different temperatures were taken from Omoto and Goldhaber (1997). Two-mass-mixing calculation were carried out following Ono et al. (2006), using the equations $\Delta^{34}\text{S}_\text{fluid} = f \times \Delta^{34}\text{Smagmatic} + (1 - f) \times \Delta^{34}\text{Sbasinal}$ and $\Delta^{33}\text{S}_\text{fluid} = f \times \Delta^{33}\text{Smagmatic} + (1 - f) \times \Delta^{33}\text{Sbasinal}$, where $f$ is the fraction of magmatic fluid within the total fluid. It is important to note that this relationship will theoretically form a curving trend on a $\delta^{34}\text{S}$ vs. $\Delta^{32}\text{S}$ plot for any binary end member mixing process. However, in reality, curvature will only be visible—assuming a sufficiently high analytical uncertainty—when the difference in $\delta^{34}\text{S}$ values between both end members is large (e.g., >4‰, Fig. S2) (Ono et al., 2006). The mixing line may be regarded as linear when this difference is small (e.g., <1‰), which is similar to the situation in this study (Figs. 5a, S2).

Despite having large associated errors, the triple sulfur isotope data from the Mina Justa deposit fit our model well. Mixing of magmatic fluid and Cu-bearing fluid can readily explain the triple sulfur isotope trend observed in our samples (Fig. 5a). Further, as discussed, variation in sulfur isotope composition being coupled with variation in trace element concentration (Figs. 3–4) may indicate the involvement of a new pulse of ore-forming fluid (Wu et al., 2019b), which is also compatible with the external fluid incursion hypothesis. Both triple isotope and trace element geochemical evidence support the scenario of incursion of basin fluid into a magmatic fluid. At the same time, the sample in Fig. 3 and some of the Py-E samples form a mixing trend that lies between the ore-forming fluid mixing line and the pyrite growth evolution line. This may have resulted from the complexity of the actual ore-forming process, during which local variations in temperature, sulfur isotope composition, and oxygen fugacity of the ore-forming fluid could have occurred. Some data points are slightly discrepant to our modeled results (Fig. 5a), which could be due to analytical uncertainty and/or the deviation of selected parameters from their “true/ideal values” during the modeling processes. Theoretically, modeling results can be affected by local fluctuations in temperature, sulfur isotope composition and oxygen fugacity of the ore-forming fluids, analytical uncertainty of the measured sulfur isotope composition of pyrite, and uncertainty in the sulfur isotope fractionation factor between pyrite and the ore-forming fluids. Unfortunately, while none of these factors can be precisely constrained, most of our data fit this model well; thus, a small deviation of some data points from the modeled results is considered acceptable.

### 5.4. Does basin-derived fluid contain NMF$-\Delta^{32}\text{S}$?

The most positive $\Delta^{33}\text{S}$ value obtained in this study is +0.19‰ (Fig. 5a), which approaches the traditional limit of mass-dependent fractionation of sulfur (MDF$-\Delta^{32}\text{S} = 0 \pm 0.2%$) (Farquhar and Wing, 2003). In addition, according to an updated interpretation of the MDF-S threshold by LaFlamme et al. (2018a), the data presented here with $\Delta^{32}\text{S} < +0.1%$ are well above the MDF-S threshold (dotted area in Fig. 5a). This raises the question of whether the positive $\Delta^{32}\text{S}$ values (> +0.1‰) indicate the presence of NMF$-\Delta^{32}\text{S}$.

The equilibrium reaction is generally characterized by a $33\lambda = 0.515$ (Hulsink and Thode, 1965) ($33\lambda = \ln([\text{SO}_2^2-]/[\text{H}_2\text{S}])$, where $\lambda$ is the fractionation factor), while kinetic reactions (i.e., microbial or thermochloric sulfate reduction) can be characterized by a $33\lambda$ ranging from 0.508 to 0.519 (Farquhar and Wing, 2003; Johnstone, 2011; Leavitt et al., 2013; Oduro et al., 2011; Ono et al., 2007). Because $33\lambda = 0.515$ was used to calculate $\Delta^{32}\text{S}$ (Farquhar et al., 2013; Ono, 2017), a small deviation of $33\lambda$ from the reference value (0.515) would result in small non-zero $\Delta^{32}\text{S}$ values (Ono et al., 2007; Ono et al., 2006). LaFlamme et al. (2018a) used the reported $33\lambda$ values (0.508 < $33\lambda$ < 0.519) to redefine the theoretical threshold of MDF-S (dotted area in Figs. 5a and 7), and hence any data that lie outside the MDF area should be treated as NMF$-\Delta^{32}\text{S}$.

We collected examples of reported data for sulfide and sulfate proposed to have formed from the MDF process (Johnstone et al., 2008; Ono et al., 2007; Ono et al., 2006). This indicates that most samples lie within the MDF area defined in LaFlamme et al. (2018a), but there are several samples that lie outside the MDF area (Fig. 7). Johnstone et al. (2008) showed that two seawater sulfate samples representing typical modern marine environments and modern marine tidal flat environments, which could not have any contribution of NMF$-\Delta^{32}\text{S}$, have $\Delta^{33}\text{S}$ values of +0.170 and +0.173‰, respectively, and are plotted well outside the MDF area. Ono et al. (2007) showed that modern seafloor hydrothermal vent sulfide samples have contributions from both magmatic and seawater sulfur and have $\Delta^{33}\text{S}$ values of approximately +0.050‰ ($\delta^{34}\text{S}$ of 0 to +5‰), but do not fall within the MDF area on Fig. 7. Sedimentary sulfate minerals of the Noerozic age reported by Ono et al. (2006) are characterized by $\Delta^{34}\text{S} > +0.20%$, and therefore also lie outside the MDF area, and are expected to have formed due to Rayleigh distillation. None of the samples in these studies need any contribution from NMF$-\Delta^{32}\text{S}$; thus, data with $\Delta^{33}\text{S}$ values that deviate slightly away from those defining the MDF area do not necessarily indicate NMF$-\Delta^{32}\text{S}$.

By definition, NMF$-\Delta^{32}\text{S}$ denotes the fractionation of $33\lambda$ and $36\lambda$ deviates from the mass-dependent fractionation relationship with $34\lambda$. Before the GOE occurred at about 2.45–2.33 Ga, an NMF$-\Delta^{32}\text{S}$ signature could be generated through photodissociation of sulfur-bearing gases by short wavelength ultraviolet rays in the oxygen-poor Archean atmosphere ($\text{pO}_2 < 10^{-5}$ present-day atmospheric level: PAL) (Farquhar et al., 2000; Farquhar and Wing, 2003; Johnstone, 2011; Pavlov and Kasting, 2002; Philipps et al., 2018). The NMF-S signature disappeared after the GOE (Farquhar et al., 2000; Ono, 2017). The Mina Justa deposit formed at approximately 142–95 Ma (Chen et al., 2010). At this time, atmospheric $\text{pO}_2$ (Berner and Canfield, 1989) had evolved to a level much higher than the threshold required to generate NMF$-\Delta^{32}\text{S}$, and the basin-derived fluid in this study is therefore unlikely to acquire NMF$-\Delta^{32}\text{S}$ signals in an oxygen-rich atmosphere.

Because the $\Delta^{33}\text{S}$ values in this study generally fall into the traditional limit of MDF-S (Farquhar and Wing, 2003), and our data clusters around zero in the plot of $\Delta^{32}\text{S}$ vs. $\Delta^{33}\text{S}$ ($\Delta^{33}\text{S} = 0 \pm 1.0%$, $\Delta^{32}\text{S} = 0 \pm 0.2%$) (Fig. 5b), we interpret the data in our study to be mass-dependent (Kokh et al., 2020). This interpretation is consistent with previous works.
that have suggested that small $\Delta^{33}S$ and $\Delta^{36}S$ variations in inorganic sulfur-bearing fluid–mineral (pyrite) systems result from the MDF process in terms of reaction kinetics and mixing of different sulfur reservoirs (Koh et al., 2020; McDermott et al., 2015; Ono et al., 2007; Ono et al., 2006; Stefansson et al., 2015; Syverson et al., 2015).

To the best of our knowledge, the significantly elevated $\Delta^{33}S$ values reported for modern seawater are $+0.170$ and $+0.173\%$, and their $\delta^{33}S$ values are $+23.53$ and $+24.43\%$ (Johnston et al., 2008). Their $\delta^{36}S$ values are similar to the widely accepted value for modern seawater ($-21\%$) (Seal, 2006). The mechanism by which local seawater produces such elevated $\Delta^{36}S$ values is not clear, but the study by Johnston et al. (2008) indicated that locally high values of $\Delta^{36}S$ could be produced—and possibly preserved—even when local seawater was well mixed with open seawater, as shown by their nearly identical $\delta^{33}S$ values. As described in our model discussed in Section 5.2, we assume that the elevated $\Delta^{36}S$ values in this study are inherited from the basin-derived fluid. Nonetheless, how the external fluid at Mina Justa acquired a $\Delta^{36}S$ value as high as $+0.19\%$ is still unclear, although the processes that affected the samples analyzed by Johnston et al. (2008) may have also occurred in the Cañete Basin. Several possibilities can be invoked. First, the sulfide minerals in modern marine conditions are frequently reported to have $\Delta^{33}S$ values as high as $+0.16\%$ (Johnston et al., 2008; Lin et al., 2017; McDermott et al., 2015; Peters et al., 2010), such that recycling (e.g., oxidizing) of such sulfide back into the water column would significantly increase the $\Delta^{33}S$ value of the basal sulfate. Second, the Mina Justa deposit formed during the terminal stage of basin evolution (i.e., basin inversion) (Chen et al., 2010), and thus when the basinal sulfate could not exchange sulfate with the open ocean, Rayleigh fractionation could have increased the $\Delta^{33}S$ value of the basinal sulfate (Ono et al., 2006). Alternatively, some combination of these two scenarios may have taken place.

Although we have listed several points of evidence to argue that an MDF-S scenario is more reasonable for our data, the NMF-S scenario cannot be excluded. For example, while unlikely, an intense explosive volcanic eruption during the late stage of basin evolution could release volcanic $SO_2$ into the stratosphere, where it could have experienced photodissociation, thus generating products with NMF-S (Whitehill et al., 2020; Martin and Bindeman, 2009). This question could be resolved by performing high-precision, bulk-SF$_6$ fluorination quadruple sulfur isotope analysis of sedimentary sulfides in the Cañete Basin.

6. Conclusion

Early (Py-E) and late (Py-L) substages of pyrite were identified from the magnetite–pyrite stage (stage V) samples at Mina Justa. Coupled in situ sulfur isotope and trace element analyses confirmed the incursion of a basin fluid during the formation of Py-L. A linear trend on a binary plot of $\delta^{33}S$ vs. $\Delta^{36}S$ for representative samples indicates the feasibility of using the triple sulfur isotope as a reliable tracer for fluid mixing processes at Mina Justa. High-precision in situ multiple sulfur isotope analysis holds great potential for gaining new insights into ore-forming processes at the macroscale. This approach could be extended to other deposits and ore-forming systems that may involve both magmatic and seawater-basin-derived sulfur.

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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.

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