Sulfide resorption contributes to porphyry deposit formation in collisional settings

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Abstract
Production of Cu-rich melts via melting of sulfide-bearing lower crustal cumulates is thought to contribute to porphyry Cu formation in the post-collisional Gangdese belt (Tibet). We present new whole rock, including platinum group elements (PGE) data, for ore-causative granites (OCG), ore-related granites (ORG) and barren granites (BG) from the Gangdese belt. The OCG, ORG and BG show indistinguishable Cu, PGE and Cu/Ag behavior during differentiation down to ~2 wt% MgO. During the last decade, there has been a surge of interest regarding the genesis of the Gangdese PCDs (e.g., Hou et al., 2015a; Yang and Cooke, 2019). The exposed Tibetan lower crustal cumulates have been attributed to sulfide accumulation (Hou et al., 2015b). Previous studies have suggested that the ore-related magmas are more Cu-rich than the barren magmas because of melting of sulfides in the lower crust (Hou et al., 2015b) and/or sulfides formed during hydrous metasomatism of the subcontinental lithospheric mantle (SCLM) (Zheng et al., 2019). However, others have argued that magmas that are pre-enriched in economic metals (e.g., Cu and Au) are not a requirement for porphyry Cu mineralization (Halter et al., 2005; Zhang and Audétat, 2017; Du and Audétat, 2020; Hao et al., 2021). Instead, magmatic processes in the upper to middle crust such as: (1) whether the magmas fractionated sulfide before or after volatile exsolution (Jenner et al., 2010; Wilkinson, 2013; Hao et al., 2019; Park et al., 2019); (2) cannibalization of pre-existing magmatic sulfides in upper crustal magmatic systems (Halter et al., 2005; Nadeau et al., 2010); (3) the volume of magma with “normal” Cu concentrations (Cline and Bodnar, 1991); and (4) the timescales of magmatic activity (Chiaradia and Caricchi, 2017; Chelle-Michou et al., 2017; Chelle-Michou and Rottier, 2021), are regarded as contributing factors to the formation of PCDs. Others have emphasized a link between magmatism associated with mineralization in the Miocene Gangdese orogenic belt and periods of post-collisional extension (e.g., Hou et al., 2009).

To further understanding of the processes that contribute to the evolution of post-collisional porphyry ore systems, we selected a series of post-collisional (Miocene: 22–12 Ma) porphyry copper deposits (PCDs) with Cu reserves of over 45 Mt have been discovered in the Gangdese magmatic belt in southern Tibet (Hou et al., 2009; Hou et al., 2015a; Yang and Cooke, 2019). During the last decade, there has been a surge of interest regarding the genesis of the Gangdese PCDs (e.g., Hou et al., 2009; Yang and Cooke, 2019; Wang et al., 2015; Wang et al., 2018; Wang et al., 2021; Zheng et al., 2019). The ore-forming magmas are generally characterized by felsic, high-K calc-alkaline, high-Sr/Y and La/Yb ratios and are regarded as the products of melting of lower crustal sulfide-bearing cumulates or the relative timing of sulfide fractionation. The behavior of chalcophile and siderophile elements during differentiation of the OCG, ORG and BG diverges when melts evolve past 2–3 wt% MgO and exsolve H2O, S and Cl: the BG show a decrease in Cu, whereas the OCG and ORG show highly variable Cu, Au, and PGE trends. Because S degassing causes melts to become sulfur undersaturated and because Cu is highly soluble in Cl-rich fluids, any sulfides in contact with the melt or magmatic fluids following volatile exsolution would dissolve. Continual injection, cooling and ascent of magmas through the Gangdese crust is expected to have resulted in the development of regions of crystal-rich partially molten crust beneath the intrusive granites. We suggest that prior to porphyry mineralization, extension and erosion caused exhumation of these long-lived sulfide-bearing mush zones. This exhumation may have caused a change in magmatism style from volatile exsolution after the melts transited sulfide-bearing mushes (i.e., the OCG), to volatile exsolution during magma transit through sulfide-bearing mushes (i.e., the ORG). We suggest that only the magmas and that exsolved fluids during their ascent through sulfide-bearing mushes were able to assimilate sufficient Cu-rich sulfides to fuel the formation of porphyry Cu deposits in the region.

1. Introduction
A series of post-collisional (Miocene: 22–12 Ma) porphyry copper deposits (PCDs) with Cu reserves of over 45 Mt have been discovered in the Gangdese magmatic belt in southern Tibet (Hou et al., 2009; Hou et al., 2015a; Yang and Cooke, 2019). During the last decade, there has been a surge of interest regarding the genesis of the Gangdese PCDs (e.g., Hou et al., 2009; Yang and Cooke, 2019; Wang et al., 2015; Wang et al., 2018). The exposed Tibetan lower crustal cumulates have higher bulk Cu concentrations (71.3 ppm, Guo et al., 2020) compared to lower continent crust values of 26 ppm (Rudnick and Gao, 2014), which has been attributed to sulfide accumulation (Hou et al., 2015b). Previous studies have suggested that the ore-related magmas are more Cu-rich than the barren magmas because of melting of sulfides in the lower crust (Hou et al., 2015b) and/or sulfides formed during hydrous metasomatism of the subcontinental lithospheric mantle (SCLM) (Zheng et al., 2019). However, others have argued that magmas that are pre-enriched in economic metals (e.g., Cu and Au) are not a requirement for porphyry Cu mineralization (Halter et al., 2005; Zhang and Audétat, 2017; Du and Audétat, 2020; Hao et al., 2021). Instead, magmatic processes in the upper to middle crust such as: (1) whether the magmas fractionated sulfide before or after volatile exsolution (Jenner et al., 2010; Wilkinson, 2013; Hao et al., 2019; Park et al., 2019); (2) cannibalization of pre-existing magmatic sulfides in upper crustal magmatic systems (Halter et al., 2005; Nadeau et al., 2010); (3) the volume of magma with “normal” Cu concentrations (Cline and Bodnar, 1991); and (4) the timescales of magmatic activity (Chiaradia and Caricchi, 2017; Chelle-Michou et al., 2017; Chelle-Michou and Rottier, 2021), are regarded as contributing factors to the formation of PCDs. Others have emphasized a link between magmatism associated with mineralization in the Miocene Gangdese orogenic belt and periods of post-collisional extension (e.g., Hou et al., 2009).
of Gangdese belt post-collisional granitoids (40 samples) from ore-causative (porphyry stocks directly linked to porphyry mineralization), ore-related (precursor pluton or mafic dykes spatially and temporally associated with porphyry stocks) and barren magmatic systems. We use petrology and geochemistry to track the role of magmatic sulfides during ascent, differentiation and degassing of Gangdese magmas. Together with a compilation of 239 published analyses, we show that differences in the initial concentrations of Cu, S, and other economically important elements (Platinum Group Elements, PGE) cannot account for the fertility of some magmatic systems in the Gangdese belt. Additionally, both barren and ore-associated magmas show evidence for sulfide crystallization prior to fluid exsolution. Because the Gangdese magmas typically fractionate sulfides during their ascent through the crust, the partially molten regions of crust beneath the granitic bodies, termed ‘deep crustal hot zones’ or ‘mush zones’ (Annen et al., 2006) likely contain previous generations of sulfides. We suggest that the ore-causative magmas reach volatile saturation during their ascent through these sulfide-bearing mush zones, during which the magmas and associated magmatic fluids assimilate Cu-rich pre-existing sulfides in the mush zone. We further suggest that the transition of the system from degassing during rather than after ascent through the mush zone might be related to post-collisional extension, erosion, and consequent exhumation of the mush zone to lower crustal pressures.

2. Geological setting

The Gangdese belt in southern Tibet (Fig. 1) preserves a continuous magmatic record from the Late Triassic to the middle Miocene, which includes Neo-Tethyan oceanic slab subduction from 210 to 60 Ma and the India-Asia collision from 60 to 55 Ma (Zhu et al., 2011, 2015; van Hinsbergen et al., 2012; Wang et al., 2018). The Miocene post-collisional extension-related magmatism is characterized by predominantly potassic-ultrapotassic (trachytic) volcanism west of ~89°E and by granitoids with high-Hf/Y ratios (also named high-Sr/Y granitoids) east of ~89°E (Wang et al., 2018). There are also sparse Oligocene high-Sr/Y granitoids at Zedang and Miocene diorite porphyries at Xigaze and in the ore fields (Fig. 1). Many of the Oligocene to Miocene granitic intrusions contain mafic magmatic enclaves (MME), which have been attributed to mixing between the high-Sr/Y granitic magmas and more mafic mantle-derived ultra-potassic magmas (Zheng et al., 2012a; Lu et al., 2015). Others attribute the occurrence of MME at other settings (e.g., Nisyros volcano, Aegean arc, Greece) to entrainment of clasts of mafic material (e.g., sulfide-bearing cumulates) from the lower crustal magmatic mush zones that lie beneath the intrusions and volcanoes (e.g., hot crustal mush zones, see Annen et al., 2006) by melts that are filtering upwards through the mush zones (Georgatou et al., 2022 and references therein). Indeed, the MME associated with the Gangdese Miocene Qulong porphyry magmas (Yang, 2008) show a range in Cu from 130 to 1287 ppm, which are consistent with the high Cu concentrations expected for sulfide-bearing mushes (e.g., Chen et al., 2020; Guo et al., 2020). Additionally, mineral barometry has been used to argue for crystallization of Gangdese magmas over a large range in pressures (Wang et al., 2014a; Lu et al., 2015; Yang et al., 2015), which is consistent with the presence of mush zones in the plumbing systems beneath the Miocene granitic intrusions.

Most of the porphyry Cu-Mo deposits in the Gangdese belt, including two giant deposits (Qulong, 2200 Mt @ 0.5 % Cu; Jiama, 1055 Mt @ 0.44 % Cu; Yang and Cooke, 2019) and several smaller deposits, were formed in the Miocene, in response to rapid uplift and erosion of the Gangdese arc batholiths (Yang et al., 2009). These porphyry Cu-Mo systems are centered around granitic porphyritic stocks which intruded into and/or through composite precursor batholiths. The ore-causative stocks and other ore-bearing pre-mineralization and post-mineralization intrusions are commonly high-Sr/Y granitoids emplaced at 30–12 Ma. At some deposits the ore-causative stocks are associated with post-mineralization high-Mg diorites or lamprophyre dykes (Yang and Cooke, 2019; Wang et al., 2021). This study focuses on: (1) the ore-causative granitoids (OCG); (2) pre- and post-mineralization high-Sr/Y ore-related granitoids (ORG); and (3) high and low Sr/Y granitoids that are unrelated to any deposits, which are referred to here as barren granitoids (BG). Details of the samples selected for this study are presented in Table 1.

A range of geochemical and experimental techniques have been used to place constraints on the origin of high-Sr/Y granitoids: models invoking melting of the Gangdese lower crust are widely accepted (Hou et al., 2004; Wang et al., 2015; Wang et al., 2019). The high-Sr/Y (Sr/Y >50) granitoids are characterized by high K2O contents (~2.5 wt%). They inherit many of the Gangdese arc root compositions, such as LILE enrichments, HFS depletions, a wide range of εNd(t) values from ~8.1 to ~3 and relative low 87Sr/86Sr ratios from 0.70765 to 0.70672 (Hou et al., 2004; Wang et al., 2018). Other aspects to the chemistry of the high-Sr/Y granitoids, such as their high K2O (3.0–3.8 wt%) and variable radiogenic isotope compositions (187Os/187Os = 0.7057–0.7072 and εNd(t) values (-6.5 to –3.4)), cannot be achieved by melting of Gangdese
Summary of the age and petrography of investigated samples from the Gangdese belt, Tibet.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Sample group</th>
<th>Location</th>
<th>Lithology</th>
<th>Age (Ma)</th>
<th>Alteration</th>
<th>Mineralogy</th>
<th>sulfide type</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZK001-360H</td>
<td>OCG</td>
<td>Qulong</td>
<td>monzogranite porphyry</td>
<td>17.6±0.7</td>
<td>minor sericitization</td>
<td>Phenocrysts:Pl (15 %), Qtz (5-7 %), Kf (3-5 %), Bt (3 %)</td>
<td></td>
</tr>
<tr>
<td>ZK1615-743M</td>
<td>OCG</td>
<td>Jiru</td>
<td>monzogranite porphyry</td>
<td>16.2±0.2</td>
<td>K-feldspar + qtz vein</td>
<td>Phenocrysts:Pl (17 %), Kf (8 %), Qtz (6 %), Bt (3 %)</td>
<td></td>
</tr>
<tr>
<td>ZK1624-H103-206M</td>
<td>OCG</td>
<td>Jiama</td>
<td>monzogranite porphyry</td>
<td>14.9±0.2</td>
<td>serious sericitization</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>18QL-9</td>
<td>OCG</td>
<td>Qulong</td>
<td>monzogranite porphyry</td>
<td>17.6±0.7</td>
<td>minor disseminated</td>
<td>Phenocrysts:Pl (20 %), Kfs (15 %), Qtz (10 %), Bt (3 %)</td>
<td></td>
</tr>
<tr>
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<td>Qulong</td>
<td>monzogranite porphyry</td>
<td>17.6±0.7</td>
<td>minor disseminated</td>
<td>Phenocrysts:Pl (20 %), Kfs (15 %), Qtz (10 %), Bt (3 %)</td>
<td></td>
</tr>
<tr>
<td>ZK001-360H</td>
<td>OCG</td>
<td>Qulong</td>
<td>monzogranite porphyry</td>
<td>17.6±0.7</td>
<td>minor disseminated</td>
<td>Phenocrysts:Pl (20 %), Kfs (15 %), Qtz (10 %), Bt (3 %)</td>
<td></td>
</tr>
<tr>
<td>JR-2</td>
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<td>Jiru</td>
<td>monzogranite porphyry</td>
<td>16.2±0.2</td>
<td>minor sericitization</td>
<td>Phenocrysts:Pl (15 %), Qtz (10 %), Amp (10 %), Bt (3 %)</td>
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<tr>
<td>ZK1613-498M</td>
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<td>Jiama</td>
<td>monzogranite porphyry</td>
<td>16.2±0.2</td>
<td>fresh</td>
<td>Phenocrysts:Pl (15 %), Kf (8 %), Qtz (8 %), Bt (3 %)</td>
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</tr>
<tr>
<td>ZK1621-H451-844M</td>
<td>OCG</td>
<td>Jiama</td>
<td>monzogranite porphyry</td>
<td>15.7±0.3</td>
<td>fresh</td>
<td>Cu-rich sulfide (most Cu ≥ 50 wt %)</td>
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</tr>
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<td>BP-5</td>
<td>OCG</td>
<td>Bangpu</td>
<td>Granodiorite</td>
<td>14.6±0.3</td>
<td>fresh</td>
<td>Phenocrysts:Pl (15 %), Qtz (15 %), Kf (10 %)</td>
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</tr>
<tr>
<td>CB-4</td>
<td>OCG</td>
<td>Chengba</td>
<td>Granodiorite</td>
<td>27.2±0.3</td>
<td>fresh</td>
<td>Phenocrysts:Pl (18 %), Qtz (8 %), Amp (10 %), Bt (5 %)</td>
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<tr>
<td>601-203</td>
<td>OCG</td>
<td>Qulong</td>
<td>aplite</td>
<td>17.7±0.3</td>
<td>fresh</td>
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<td></td>
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<tr>
<td>601-312</td>
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<td>Qulong</td>
<td>aplite</td>
<td>17.7±0.3</td>
<td>fresh</td>
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<td>Qulong</td>
<td>Granodiorite</td>
<td>19.5±0.4</td>
<td>epidote + py</td>
<td>Pl (35 %), Kf (25 %), Qtz (20 %), Bt (15 %), Amp (5 %)</td>
<td></td>
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<tr>
<td>BP-7</td>
<td>ORG</td>
<td>Bangpu</td>
<td>Dioritic porphyry</td>
<td>13.2±0.04</td>
<td>sericitization</td>
<td>Phenocrysts: Amp (10 %), Pl (5 %), Qtz (5 %), Bt (2 %)</td>
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<td>Jiama</td>
<td>Granodiorite</td>
<td>15.2±0.2</td>
<td>K-feldspar + qtz vein</td>
<td>*</td>
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<tr>
<td>ZK1218-H187-359M</td>
<td>ORG</td>
<td>Jiama</td>
<td>Quarz-monzonite dioritic porphyry</td>
<td>15.1±0.4</td>
<td>sericitization + py vein</td>
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<tr>
<td>ZK2409-293M</td>
<td>ORG</td>
<td>Jiama</td>
<td>Quarz-monzonite dioritic porphyry</td>
<td>15.1±0.4</td>
<td>sericitization + py vein</td>
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<tr>
<td>18QL-25</td>
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<td>Qulong</td>
<td>dioritic porphyry</td>
<td>15.7±0.2</td>
<td>fresh</td>
<td>Phenocrysts: Pl (5 %), Qtz (5 %), Amp (3 %), Cpx (2 %), Bt (2 %)</td>
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<td>WR-1</td>
<td>ORG</td>
<td>Qulong</td>
<td>Mafic magmatic enclaves</td>
<td>22.2±0.5</td>
<td>fresh</td>
<td>Pl (45 %), Amp (25 %), Kfs (15 %), Bt (10 %), Qtz (5 %)</td>
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<td>Qulong</td>
<td>Mafic magmatic enclaves</td>
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<td>fresh</td>
<td>Pl (45 %), Amp (25 %), Kfs (15 %), Bt (10 %), Qtz (5 %)</td>
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<td>JR-5</td>
<td>ORG</td>
<td>Jiru</td>
<td>Dioritic porphyry</td>
<td>15.5±0.3</td>
<td>fresh</td>
<td>Phenocrysts: Pl (10 %), Amp (8 %), Bt (2 %)</td>
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<td>MZ-3</td>
<td>ORG</td>
<td>Mingze</td>
<td>Granodiorite</td>
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<td>fresh</td>
<td>Pl (35 %), Kf (30 %), Amp (15 %), Bt (10 %), Qtz (10 %)</td>
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<td>fresh</td>
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<td>fresh</td>
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<td>Qulong</td>
<td>Granodiorite</td>
<td>19.5±0.4</td>
<td>fresh</td>
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<td>Granodiorite</td>
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<td>fresh</td>
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<td>Granodiorite</td>
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<td>fresh</td>
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<td>Granodiorite</td>
<td>19.5±0.4</td>
<td>fresh</td>
<td>*</td>
<td></td>
</tr>
</tbody>
</table>

(continued on next page)
lower crust. Instead, these signatures are attributed to mixing of crustal melts with mantle-derived ultrapotassic magmas (Yang et al., 2015; Wang et al., 2016; Wang et al., 2018).

The OCG samples were collected from Qulong, Jiama, Bangpu, Jiru and Chengba porphyry Cu-(Mo) deposits and the ORG samples were collected from Qulong, Jiama, Bangpu, Jiru and Mingze deposits (Fig. 1). Previously published literature data for OCG and ORG intrusions were only compiled for the two giant deposits, Qulong and Jiama, because these deposits are most representative of porphyry-Cu-Mo deposits in the Gangdese belt (Yang et al., 2009; Hou et al., 2013; Hu et al., 2015). BG samples were collected from Quxu, Sangri, Xueba and Bumeicun (Fig. 1). Samples were collected outside of the porphyry alteration zone to minimize the effects of hydrothermal alteration and supergene weathering.

Detailed petrography for the selected samples is reported by other authors (e.g., Hou et al., 2004; Yang et al., 2009; Yang et al., 2015; Wang et al., 2014a, b; Zhao et al., 2015; Zheng et al., 2016) and the phenocryst assemblages are given in Table 1. In summary, the OCG samples have porphyritic textures, and range in composition from monzogranite porphyry to granite porphyry. Phenocrysts are mainly plagioclase, quartz, K-feldspar, with minor biotite and amphibole (Hou et al., 2004; Yang et al., 2009; Yang et al., 2016a; Zhao et al., 2015). The OCG magmas, which commonly intrude as stocks or dikes, are derived through extensive cooling and fractionation of ORG-type magmas (Yang et al., 2009, 2016a; Lu et al., 2015). Some OCG dikes show direct textural evidence for fluid exsolution, such as miarolitic cavities and/or quartz unidirectional solidification textures (USTs), which indicate that these dikes directly fuel porphyry Cu-(Mo) mineralization (Yang et al., 2009; Yang and Cooke, 2019). OCG samples include granodiorite, monzogranite, high-Mg diorite porphyries and MME hosted in precursor granitoids. ORG samples from precursor batholiths (e.g., granodiorite and monzogranite) are comparable to the OCG samples with equigranular or hypidiomorphic-granular texture, but some of the ORG samples have more amphibole than the OCG samples (Yang et al., 2009; Yang et al., 2016b; Hu et al., 2015). MME and high-Mg diorite porphyries consist mainly of plagioclase, biotite and some of the high-Mg dikes contain broken-down clinopyroxene grains (Yang et al., 2009; Yang et al., 2015; Zheng et al., 2012a; Sun et al., 2018). BG samples have both porphyritic and equigranular textures, they range in compositions from granite, monzogranite, granodiorite, granite porphyry and include MME. The dominant mineral phases are plagioclase, K-feldspar, and quartz. Amphibole phenocrysts are notably rare in BG granitoids (Zheng et al., 2012b, Hou et al., 2013; Yu, 2015).

### 3. Analytical techniques

A total of 40 samples were analysed for whole rock PGE, Au, and S concentrations. The whole rock major and trace element concentrations were measured for 22 samples, and the rest of data were taken from Yang (2008) and Sun et al. (2022). Silver concentration were measured on 18 samples. New data and compiled data for the 40 samples that were analyzed of this study are presented in Supplementary Table 1 and 2. Whole rock major and trace element concentrations of the 22 samples were analyzed at the Institute of Geochemistry, Chinese Academy of Sciences (IGCAS), Guiyang. Major element and sulfur concentration of were determined using a Philips PW2400 X-ray fluorescence (XRF) spectrometer on fused glass disks following techniques outlined in Stix et al. (1996). The analytical precision is better than 1 % (RSD) for elements with higher concentrations than 1 wt% and better than 5 % (RSD) for S and elements with lower concentrations than 1 wt%.

Whole rock trace element analyses, including Ag, were determined using a PerkinElmer DRCE-ICP-MS and following the techniques reported by Qi et al. (2000) and Gao et al. (2003). The analytical accuracy is generally better than 5 % (Supplementary Table 1). Whole rock PGE and Au concentrations, including two duplicate analyses, were undertaken using isotope-dilution ICP-MS (ID-ICP-MS) at IGCAS, Guiyang. A mixed ion exchange resin of Dowex 50 W-X8 cation exchange and P507 extraction chromatograph resin were used to remove Cu, Ni, Zr, and Hf to minimize interference on. Details of sample preparation and analytical protocols are described in Qi et al. (2013). The procedural blanks were lower than 0.002 ppb for Os, 0.002 ppb for Ir, 0.003 ppb for Rh, 0.002 ppb for Ru, 0.020 ppb for Pt, and 0.012 ppb for Pd, respectively. Standard reference materials NRCAN UMT-1 (mill tailings) and WPR-1 were analyzed at the same time as our samples to monitor PGE data accuracy. Analytical precision is better than 15 % according to the analysis of standard reference materials. Whole rock analyses of samples and reference materials are given in Supplementary data 1. Duplicate analyses of Pd, Ru and Au for a BG sample (XB-12-6n9) and an ORG sample (CB-4) lie outside of analytical uncertainty, which is indicative of sample heterogeneity for these elements, whereas Pt and Ir for CB-4 are within the analytical error (Supplementary data 1).

Analysis of seven rare sulfide inclusions (Supplementary data 1) were undertaken using Zeiss Supra 55 field emission scanning electron microscope (FESEM) under 20 kV accelerating voltage with a working distance of ~15 mm at China University of Geosciences (Beijing). Backscattered electron (BSE) images of sulfides were obtained using an AEs detector. In situ chemical analysis of micrometer-sized spots were carried out using Oxford energy-dispersive X-ray spectrometer (EDS) connected to the FESEM.

### 4. Petrology and geochemical results

Photomicrographs of two porphyry samples (OCG samples ZK1612-438.2 and 18QL-13), three granitoid samples (ORG sample ZK1517-1, 18QL-26 and BG sample WR12-4), two high-Mg ORG diorite porphyry samples (18-QL-25 and JR-4), and a mafic magmatic enclave sample
Commonly observed mineral phases in the Gangdese samples are embayed in shape, and commonly have resorption textures (Fig. 2D). High-Mg ORG diorite porphyry samples were collected from ore deposits and occur as dikes. They have porphyritic textures and consist of a fine matrix with ~10 vol% phenocrysts of amphibole, plagioclase, quartz, and biotite (Fig. 2D and E). Quartz phenocrysts are subhedral and embayed in shape, and commonly have resorption textures (Fig. 2D).

Composed of amphibole, K-feldspar, biotite, and quartz. (Fig. 2A–I).

A few exposed magmatic sulfides are present as small (10–15 μm) and rare (2–5 per thin section) mineral inclusions in magnetite and amphibole in samples CB-4 (OCG), WR-1 (ORG), XB-125n7 and SR-2 (BG, Fig. J-O). Hence, magmatic sulfides are present as inclusions in each of our three groups of samples (i.e., OCG, ORG, and BG samples). Analyses of the sulfide inclusions in BG sample SR-2 (Fig. 2J, M) show that the major sulfide phase has high Ni concentrations (Ni = 0.64 wt%) and low Cu concentrations (Cu ≤ 0.28 wt%), indicative of monosulfide solid solution (MSS). The MSS phase is in contact with minor chalcopyrite with Cu = 26.6 wt% and Ni = 0.14 wt% (Supplementary data 1). The rounded shaped sulfide inclusion that is hosted by magnetite in BG sample XB-125n7 (Fig. 2K, N) is chalcopyrite with Cu = 33.2–33.6 wt% and Ni < 0.05 wt% (Supplementary data 1). In sample XB-12-5n7 the sphalerite phase in contact with chalcopyrite has high Zn concentrations (Zn = 58.2–61.2 wt%) and low Cu concentrations (Fig. 2K and N, 2.59–0.63 wt%, Supplementary data 1). The Cu-rich chalcopyrite in BG sample XB-125n7 is in contact with voids (Fig. 2K and N). Sulfide inclusions in OCG sample CB-4 (Fig. 2L and O) are mainly hosted by magnetite and consist of chalcopyrite blades within bornite and digenite. The major element concentrations of sulfide inclusions in CB-4 are as follows: Cu = 73.9–49.8 wt%, Ni ≤ 0.84 wt%, Fe = 4.31–21.5 wt% (Supplementary data 1). Sulfide and anhydrite inclusions were observed in anapatite phenocryst from Qulong OCG (Fig. 3), which were too small to analyze. It is likely that the irregular shaped voids around the sulfide inclusions that are present in other samples (e.g., Fig. 2K) were filled by anhydrite or possibly fluids prior to dissolution during polishing (Georgatou and Chiaradia, 2020).

Although our sample collection avoided the alteration zone, a few samples show minor evidence for hydrothermal alteration. Our identification of alteration is based on our examination of thin sections under the microscope and detailed petrographic observations given by other authors (Yang, 2008; Yang et al., 2009; Hou et al., 2013; Zheng et al., 2019). A total of eight OCG samples and six ORG samples are classified as potentially altered and are plotted as open symbols on each of our plots (e.g., Fig. 4). Of these samples, five OCG and three ORG samples show selective replacement of primary magmatic minerals (e.g., amphibole, biotite, and plagioclase) by low-temperature hydrothermal alteration assemblages (e.g., epidote, chlorite, and sericite). The remainder of the potentially altered samples show disseminated pyrite and chalcopyrite in the groundmass, which might be of high-temperature magmatic origin or low-temperature hydrothermal origin. We distinguish the samples with disseminated sulfides using crosses on each of our plots (e.g., Fig. 4). We note that a few of these samples (e.g., 18QL-9, 18QL-13 and 18QL-26) show no evidence for replacement of primary magmatic minerals by low-temperature replacement and therefore, the sulfide phases could be magmatic in origin. For example, Tian et al. (2022) used correlations between Li isotopes and Cu concentrations to suggest that such sulfides likely precipitated from magmatic fluids that exsolved from deep magma chambers that underly the granitic systems.

On Fig. 4 we compare the data presented in this study with our compilation of previously published analyses (references for data provided in Supplementary data 2) of OCG and ORG from Qulong and Jiama, and BG samples, together with the representative field for the compositions of the ultrapotassic volcanic rocks (Fig. 4A and B), which are thought to represent the mantle-derived end-member component to Miocene magmatism in the region. On the total alkalis (Na2O + K2O) versus silica (TAS) diagram (Fig. 4A), the Gangdese samples show a range in compositions from monzodiorite to granodiorite and granite, with SiO2 concentrations ranging from 50.2 wt% to 75.5 wt%. The OCG samples span to higher SiO2 concentrations than the ORG and BG samples (Fig. 4A), whereas the BG samples span to lower SiO2 concentrations compared to the other samples. Each of the suites show a decrease in FeO in decreasing MgO (Fig. 4B) and the rate of FeO decrease becomes greater at ~3 wt% MgO. The least fractionated (highest MgO) ORG samples are offset to lower FeO at a given MgO compared to the BG samples and mostly plot within the field of ultrapotassic volcanic rocks. The BG samples have FeO at a given MgO that are more comparable to volcanic rocks from Chile than the ORG. However, all three groups of samples (OCG, ORG, BG) with ~2 wt% MgO show an overlapping range in FeO. Collectively, the Gangdese samples show a peak in P2O5 concentrations at ~3 wt% MgO and a sharp decrease in P2O5 with decreasing MgO in samples with <3 wt% MgO (Fig. 4C).

The literature and the majority of our ORG sample analyses appear to show an initial increase in Sr with decreasing MgO and an inflection in the trend at ~2 wt% MgO, which is marked by a strong decrease in Sr with further decreases in MgO (Fig. 4D). The decrease in Sr takes place at a lower MgO compared to the decrease in P2O5 (Fig. 4C). The OCG samples show a decrease in Sr with decreasing MgO that is indistinguishable from the trend defined by the evolved (low MgO) ORG samples (Fig. 4D). The BG samples analyzed for this study show a trend of decreasing Sr with decreasing MgO that is distinct from the trend defined by the OCG samples, most of the ORG samples and most literature BG data (Fig. 4D). The majority of the OCG and ORG samples show a decrease in Y with decreasing MgO, whereas the BG samples show approximately constant Y with decreasing MgO (Fig. 4E). Literature data for ORG and OCG samples appear to show an increase and then a decrease in Sr/Y with decreasing MgO, with an inflection in the trend at ~2 wt% MgO (Fig. 4F) that coincides with the decrease in Sr (Fig. 4D). Our new analyses of BG samples show significantly lower Sr/Y compared to the majority of literature data for other BG suites and a subtle decrease in Sr/Y with decreasing MgO (Fig. 4F). Samples that are labelled as ‘altered’ on Fig. 4 show an overlapping range in concentrations to samples that show no evidence for alteration.

Scandium, Y, and Cr decrease with decreasing MgO in all suites (Fig. 5A–C) and there is an inflection in the trend for Y and Cr at ~3.5 wt% MgO and ~4.5 wt% MgO, respectively. Nickel concentrations of the ORG appear to initially increase with decreasing MgO until ~5.5 wt% MgO, then decreases with further decreases in MgO (Fig. 5D). On Bulk Silicate Earth (BSE) normalized plots, all samples are enriched in light rare earth elements (LREE) relative to the heavy rare earth elements (HREE, Fig. 6A) and are enriched in the large-ion lithophile elements (LILE) relative to the high field strength elements (HFSE, Fig. 6B). The OCG samples show a large range in HREE concentrations and a span to lower HREE concentrations compared to the ORG and BG samples (Fig. 6A).

Many of the Gangdese samples show a decrease in Cu concentrations with decreasing MgO (Fig. 7A), from 361 ppm Cu in the most MgO-rich sample, down to 15.2 ppm Cu in the most MgO-poor sample. The ORG and BG samples show an overlapping range in Cu until ~2 wt% MgO. Our data and the literature data for samples with ~2 wt% MgO show a huge range in Cu from 6660 ppm to 1.64 ppm that span to considerably lower and higher Cu than samples with ~2 wt% MgO. The increase in Cu variability at ~2 wt% MgO coincides with the inflection in the trend of Sr and Sr/Y versus MgO (Fig. 7A). The ORG samples show a decrease in Cu with decreasing MgO (Fig. 7A). The majority of the ORG and BG samples show a decrease in Cu with decreasing MgO (Fig. 7A). The majority of the OCG and ORG samples show a decrease in Ca with decreasing MgO (Fig. 7A), from 857 ppm Ca in the most MgO-rich sample, down to 30 ppm Ca in the most MgO-poor sample. The ORG and BG samples show an overlapping range in Ca until ~2 wt% MgO. Our data and the literature data for samples with ~2 wt% MgO show a huge range in Ca from 857 ppm to 0.63 ppm that span to considerably lower and higher Ca than samples with ~2 wt% MgO.
Fig. 2. Selected photomicrographs and backscattered electron (BSE) images of high-Sr/Y granitoids and their magmatic sulfide inclusions. Abbreviations: Amp = amphibole; Bn = bornite; Bt = Biotite; Cp = chalcopyrite; Dg = digenite; Ep = Epidote; Kf = K-feldspar; Mt = magnetite; Plag = plagioclase; Po = pyrrhotite; Qtz = quartz.; Sph = sphalerite. (A) Granite porphyry (OGG sample ZK1612-438.2) with plagioclase and quartz phenocrysts from Jiama deposit drill hole; cross-polarized light. (B) Monzogranite porphyry (OCG sample 18QL-13) with plagioclase, K-feldspar, and quartz phenocrysts from Jiama deposit; cross-polarized light. (C) Monzogranite (ORG sample 18QL-26) with quartz, amphibole, biotite and plagioclase phenocrysts from Qulong; cross-polarized light. (D) High-Mg diorite porphyry (ORG sample 18-QL-25) with quartz, amphibole, biotite and plagioclase phenocrysts from Qulong; cross-polarized light. (E) Diorite porphyry (ORG sample JR-5) with plagioclase and amphibole phenocrysts from Jiama; cross-polarized light. (F) Granodiorite (ORG sample ZK1517-1) with biotite, K-feldspar, and plagioclase. Epidote has partially infilled cracks in the K-feldspar; cross-polarized light. This sample was collected from the Qulong deposit. (G) Dioritic enclaves (ORG sample WR-4) with euhedral amphibole and subhedral plagioclase from Qulong; cross-polarized light. (H) Dioritic enclaves (ORG sample WR-4) with euhedral amphibole and subhedral plagioclase from Qulong; cross-polarized light. (I) Granite porphyry (ORG sample ZK2409-293 M); cross-polarized light. Plagioclase and K-feldspar were partially replaced by sericite and kaolinite owing to hydrothermal alteration. (J) Two exposed polygonal shape MSS inclusions in amphibole from sample SR-2 (BG) from Sangri. (K) A rounded sulfide inclusion which in turn is hosted by a magnetite in amphibole phenocrysts from XB to 125n7 (BG) from Xueba. (L) An exposed Cu-rich sulfide inclusion in magnetite in sample CB-4 (OCG) from Chengba. (M) BSE image of one of the MSS inclusions shown in panel J. (N) BSE image of the sulfide grain shown in panel K, showing unmixing of the Cp and Sph. (O) BSE image of the sulfide grain shown in panel L, consisting of bornite and a chalcopyrite blade within digenite.
literature BG analyses, there is an apparent inflection in the trend at \( \sim 2 \) wt% MgO to extremely low Cu concentrations (Fig. 7A). Similarly, large compilations of data (Chiaradia, 2014, Barber et al., 2021) show that convergent margin samples with \(< 2 \) wt% MgO typically have \(< 50 \) ppm Cu and therefore, concentrations that are similar to those of the BG samples, but significantly lower than most of the OCG and ORG samples (Fig. 7A). If we compare the compositions of the Gangdese samples to whole rock analyses of volcanoclastic rocks from Chile (volcanic samples where Ag data are available) that erupt through thick crust (\( \geq 70 \) km) and thin crust (\( \leq 40 \) km), it is notable that the few high MgO Gangdese samples have significantly higher Cu at a given MgO (Fig. 7A). These differences are not apparent when comparing the compositions of Gangdese and Chilean samples with 3–5 wt% MgO. The highest MgO ORG sample has Cu/Ag that is comparable to the most primitive samples from Chile and the global MORB array (Fig. 7B). Most samples from the Gangdese show a decrease in Cu/Ag with decreasing MgO, including those that show no visual evidence for alteration (Fig. 9). The overlapping compositions make it unclear if the low-temperature hydrothermal alteration that caused primary magmatic minerals (e.g., amphibole, biotite and plagioclase) to be replaced by alteration assemblages (e.g., epidote, chlorite and sericite) in a few of our low MgO samples are responsible for a proportion of the variability in the chalcophile and siderophile element compositions of the Gangdese samples with \(< 2 \) wt% MgO, or whether the variability existed prior to alteration. Indeed, the overlapping range in compositions for most elements (e.g., Cu) in the altered and least altered samples, together with the clear differentiation trends shown on Figs. 4 and 5, indicate that much of the variability in compositions is likely magmatic in origin.

Tian et al (2022) suggested that the high Cu concentrations of granite porphyry samples from Qulong (OCG samples in this study) might be linked to Cu enrichment by magmatic fluids that were exsolved from underlying deep magma chambers and resulted in the precipitation of Cu-rich sulfides from the magmatic fluids. Hence, a similar conclusion could account for the large range in chalcophile and siderophile element concentrations that are displayed by the samples that were analyzed for this study. The increase in variability in the concentrations of Cu, Ag, Au and the PGE coincides with a decrease in Sr and Sr/Y of the Gangdese samples. The increase in variability could therefore be linked to a specific stage during the crystallization of the magmas, rather than subsequent low-temperature hydrothermal alteration. Hence, excluding these samples from discussion might prevent us from documenting an important stage to the evolution of porphyry systems. In the following discussion we therefore debate whether the variability in compositions between the ORG, OCG and BG samples might be attributable to high-temperature processes, such as exsolution of chalcophile element rich fluids from evolving magmas.

Various studies have used the concentrations of Cu, Ag, Au and the PGEs and proxies such as Cu/Ag to place constraints on the behavior of the economically important elements during differentiation (Jenner et al., 2010, Jenner, 2017; Hao et al., 2019; Park et al., 2019; Nekrylov et al., 2022). We now use these findings to assess the role of sulfide on the fertility of the magmatic systems in the Gangdese belt. Literature data and our analyses of samples from the Gangdese belt with \( \geq 2 \) wt% MgO show an overlapping range in Cu concentrations (Fig. 7A). These Cu trends are defined by Gangdese samples from a range of different localities, but mostly from Qulong (Fig. 7A, Table 1). With the exception...
for Pt, the other chalcophile and siderophile element concentrations of ORG samples with >2 wt% MgO are also indistinguishable from the BG samples (Fig. 8, Supplementary Table 1). Hence, the propensity for Gangdese magmas to fuel the formation of ore-deposits in the region appears to be unrelated to the initial Cu of the parental melt or the initial behavior of Cu during magma differentiation down to ~2 wt% MgO. Hence, melting of lower-crustal sulfide-bearing cumulates (Hou et al., 2015b; Zheng et al., 2019) as a model to explain why only some of the magmas are ore-causative appears to be inconsistent with the chalcophile elements systematics of the Gangdese samples.

An important finding of this study is that samples from the Gangdese belt with <2 wt% MgO, together with literature data for <2 wt% MgO
samples (Figs. 7 and 8) show an extremely large range in chalcophile and siderophile element concentrations compared to samples with >2 wt% MgO. However, it is also important to emphasize that our BG data and literature BG data do not show the trend to extremely high Cu concentrations that are displayed by the ORG and OCG and neither do most subduction-related suites, such as volcanic samples from Chile. During magma differentiation, silicate melts fractionate sulfides and/or sulfates when the sulfur content of the melt exceeds the sulfur content at sulfide or sulfate saturation (Fortin et al., 2015; Smythe et al., 2017; Zajacz and Tsay, 2019). Because Cu is highly compatible in sulfide, melts that fractionate sulfides show a decrease in Cu with decreasing MgO, such as global MORB magmas (Jenner, 2017), whereas melts that are sulfide undersaturated show an increase in Cu with decreasing MgO (Jenner et al., 2010; Lee et al., 2012; Chiaradia, 2014; Jenner, 2017; Cox et al., 2019, 2020). Because Cu is not compatible in anhydrite (Chowdhury et al., 2022), any decrease in Cu concentrations during melt evolution cannot be attributed to anhydrite fractionation. The presence of sulfides and anhydrite as inclusions in minerals (Fig. 3), demonstrates
that the evolving melts were sulfur saturated by at least 6 wt% MgO during differentiation. The decrease in Cu in turn indicates that the sulfides that partitioned the Cu likely remained in the underlying lower crustal hot zone rather than being entrained by the ascending melt (Fig. 7A). Additionally, the MME analyzed by Yang (2008) from Qulong show an increase in Cu with decreasing MgO, which might indicate that the upper portions of the mush zones beneath the Gangdese plutons are more sulfide-rich than the lower portions of the mush zones. The presence of sulfides as inclusions in apatite and magnetite in an evolved sample (e.g., CB-4), demonstrates that the sulfur saturated state of the magma persisted to relatively evolved melt compositions.

Jenner et al. (2010) identified that during fractionation of sulfides from mid-ocean ridge basaltic (MORB) magmas, the evolving melts show decreasing Cu with decreasing MgO, but constant Cu/Ag with decreasing MgO (Fig. 7). In contrast, during fractionation of the magmas from convergent settings, samples often show a decrease in both Cu and Cu/Ag with decreasing MgO. These different Cu/Ag systematics were attributed to fractionation of sulfide melt from MORB magmas and monosulfide-solid-solution (MSS) from convergent margin magmas (Jenner et al., 2010; Jenner et al., 2015; Jenner et al., 2012; Cox et al., 2019; Chen et al., 2020). Subsequent experimental studies confirmed that MSS favors Cu over Ag which leads to the decreasing Cu/Ag trends during differentiation of convergent margin magmas (Li and Audetat, 2012; Li et al., 2021b). Hence, the overall decrease in Cu/Ag with decreasing MgO that is displayed by most of the Gangdese samples, together with the presence of MSS as an inclusion phase (Fig. 2J), is attributable to fractionation of high Cu/Ag MSS.

The overlapping range in Cu and Cu/Ag of the BG samples and most of the ORG and OCG samples implies that the primitive Gangdese magmas that are associated with mineralization or are barren both fractionate similar proportions of similar sulfide assemblages (including MSS to drive the decrease in Cu/Ag) during ascent and cooling (Fig. 7). Hence, neither the initial composition of the parental melts (e.g., FeO_T or Cu) nor the compositions of the fractionating sulfides appear to determine whether a given batch of magma can fuel the formation of a porphyry Cu deposit in the Gangdese. Our results show that the BG samples and many of the ORG, and OCG samples have Cu/Ag versus MgO that are similar to those of magmas ascending through thick (>70 km) rather than thinner (<40 km) Andean continental crust (Fig. 7). The lower Cu/Ag of Chilean samples that erupt through thicker crust has been attributed to a higher proportion of sulfides fractionating from the magmas that transit thicker crust (Cox et al., 2019; Cox et al., 2020) and/or the greater proportion of MSS (Li et al., 2021b). Hence, it is likely that the mush zones beneath the Gangdese porphyries were significantly enriched in Cu relative to Ag.

The extremely high Cu at a given MgO of many of the <2 wt% MgO ORG and OCG (from Jiama, JM, and Qulong, QL) samples compared to the slightly higher MgO samples, together with the slightly higher Cu/Ag of a few of the <3 wt% MgO samples, might indicate that some of the ore-causative and ore-related magmas were sulfur-undersaturated during differentiation. Consequently, the concentrations of Cu of the melt might have increased with decreasing MgO, whereas Cu/Ag remained unfractoned. However, this interpretation is inconsistent with the occurrence of sulfides and anhydrite as inclusions in many of the samples (Fig. 3A and B). The sulfide inclusion discovered in the evolved OCG sample from Chengba porphyry with 1.4 wt% MgO (CB-4 on Fig. 7B) also suggests that the ore causative Gangdese magmas were sulfur saturated during most of their differentiation history and thus, should have evolved to decreasing Cu and Cu/Ag with decreasing MgO. We conclude that the incredibly large range in Cu concentrations of the most evolved Gangdese samples is unrelated to whether the primary magma was originally sulfur saturated or sulfur undersaturated.

Because Pt, Ir and Ru can be partitioned by sulfides, alloys and chromites (Park et al., 2013), unravelling the differentiation history of magmatic systems using these elements is challenging. Hence, from the highly variable PGE trends that are shown on Fig. 8, it is difficult to establish which systematics are linked to sulfide fractionation and/or a change in the nature of the fractionating sulfide phase. Of note, Cr and Ni show an inflection in the trend at ~4 – 5 wt% MgO (Fig. 5C and D) that is likely linked to the fractionation of chrome or Cr-spinel from the melt. Hence, the inflection in the trend of Ir and Ru at a similar MgO that is displayed by the ORG might be unrelated to sulfide fractionation (Fig. 8D – F). We therefore conclude that the most robust evidence that can be used to argue that Gangdese magmas are typically sulfide saturated during most of their differentiation history is the presence of sulfides in ORG, OCG and BG samples, together with the decrease in Cu and Cu/Ag with decreasing MgO of samples with >2 wt% MgO (Fig. 7) and the high Cu concentrations (130 to 1287 ppm) of MME associated with the Gangdese Miocene Qulong porphyry magmas (Yang, 2008). The propensity of a given batch of magmas to fractionate sulfides appears to be unrelated to the propensity of a given batch of magma to be associated with economic porphyry copper mineralization. Consequently, we now investigate the potential role of late-stage volatile exsolution in creating the extreme variability in chalcophile and siderophile elements concentrations of the <2 wt% MgO Gangdese magmas.
5.2. Decompression-related fluid exsolution

Although the >2 wt% BG and ORG samples show very similar Cu and Cu/Ag systematics with decreasing MgO (Figs. 7 and 8), this is not the case for other elements, such as Fe, Sr and Y (Fig. 4). We now investigate the cause of these differences to assess whether they can account for the variability in chalcophile and siderophile elements in the <2 wt% MgO BG, ORG and OCG samples. The BG magmas have higher FeO_T at a given MgO compared to the ORG samples (Fig. 4B). Sulfur solubility increases with increasing melt FeO_T (O’Neill and Mavrogenes, 2002), and therefore the BG magmas potentially required more S to reach sulfur saturation than the ORG samples. However, the occurrence of sulfides as inclusions in both BG and OCG samples, together with the similar Cu and Cu/Ag trends of the >2 wt% MgO ORG and BG samples (Fig. 7A and B) indicates that both types of Gangdese magmas had sufficient S to achieve sulfide saturation at relatively early stages of differentiation, regardless of their initial FeO_T. Hence, it is likely that there was the ubiquitous occurrence of sulfides in the mush zones that filtered the Miocene
Gangdese magmas, which accounts for their inclusion as phases in mafic minerals such as amphibole, and the high Cu concentrations (140–1287 ppm Cu) of MME that are hosted by the Qulong porphyry magmas. Despite the initial variability in FeO of the most primitive samples, the OCG, BG and ORG samples with <2 wt% MgO have indistinguishable FeO at a given MgO (Fig. 4B). Global datasets for subduction-related magmas show a similar decrease in variability of FeO and other major elements with decreasing MgO, which has been attributed to the buffering effect of the increasing number of minerals that are at saturation during filtering of evolved melts through crustal mush zones (Blatter et al., 2017, Blundy, 2022). Hence, it is likely that the Gangdese magmas with <2 wt% MgO were multiply saturated in clinopyroxene-hornblende-orthopyroxes-magnetite-plagioclase-ilmenite (CHOMPI) plus melt and H2O-CO2-rich fluid, which is consistent with the observed mineralogy.

The literature and our data show that the Sr concentrations and Sr/Y of most of the ORG samples initially increases with decreasing MgO until ~2 wt% MgO, and with further decreases in MgO show a decrease in Sr and Sr/Y (Fig. 4D and F). The OCG samples and the literature data for BG samples show similar Sr and Sr/Y versus MgO trends as the ORG samples (Fig. 4D and F). In contrast, our analyses of BG samples show a decrease in Sr and Sr/Y with decreasing MgO (Fig. 4D and F). These systematics indicate that our low Sr/Y BG samples fractionated plagioclase during most of their differentiation history, whereas the majority of Gangdese samples only reached plagioclase saturation at ~2 wt% MgO. Plagioclase saturation is sensitive to the H2O concentration of evolving magmas (Waters et al., 2015). Hence, the simplest explanation for these trends is that the parental magmas of our BG samples were less hydrous than the parental magmas of the OCG and ORG samples and literature BG analyses. This conclusion is consistent with those of previous studies (Wang et al., 2014a, 2014b, 2018), and previous estimates of >10 wt% H2O for ore-causative high Sr/Y granitoids from the Gangdese (Lu et al., 2015). At such hydrous melt conditions, plagioclase fractionation is expected to be suppressed (Naney, 1983).

Because amphibole stability requires high (>4 wt%) melt H2O concentrations (Naney, 1983; Ridolfi et al., 2010; Blatter et al., 2017) and amphibole is an important host of Y (Müntener et al., 2001; Davidson et al., 2007; Rooney et al., 2011), similar conclusions regarding initial

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**Fig. 9.** Plots of MgO, FeO, Cu and Pd vs. S for samples from the Gangdese belt compared to Chilean volcanic rocks (Cox et al., 2019, 2020) and MORB data (Jenner and O'Neill, 2012). (A-B) The Gangdese samples are significantly enriched in S compared to volcanic rocks from Chile. (C-D) Sulfur shows a scattered positive correlation with Cu, whereas S shows no correlation with Pd. Notably, the altered and least altered OCG show an overlapping range in S, which indicates that low-temperature alteration alone cannot account for the chalcophile element systematics of the Gangdese samples.
H$_2$O melt variability can also be gleaned from the differences in Y versus MgO trends between the OCG and ORG samples compared to our low Sr/ Y BG samples (Fig. 4E). The decrease in Y with decreasing MgO of the OCG and the ORG samples is consistent with the occurrence of significant amphibole-producing reactions during magma cooling (e.g., orthopyroxene or clinopyroxene + melt = hornblende), whereas the relatively constant Y with decreasing MgO of our low Sr/ Y BG samples is indicative of only minor amphibole-forming reactions during magma cooling (Fig. 4E). In support of this conclusion, amphibole was found to be extremely scarce in our BG samples, but a common mineral in the ORG and OCG samples. Importantly, despite the differences in the timing and proportions of saturating phases (i.e., timing of plagioclase crystallization and proportion of amphibole-forming reactions), which are consistent with differences in the H$_2$O of the evolving OCG and ORG magmas compared to our low Sr/ Y BG magmas, our analyses show that the barren, ore-related and ore-causative magmas have overlapping Cu concentrations at a given MgO. Hence, differences in initial melt H$_2$O appears to have little effect on the proportion of sulfides in the mush zone and the resulting partitioning of Cu into sulfides during cooling of the Miocene Gangdese magmas down to ~2 wt% MgO.

The suppression of plagioclase saturation during cooling of most of the Gangdese magmas only proceeds until ~2 wt% MgO, where subsequent plagioclase crystallization drives a decrease in Sr and Sr/Y with further decreases in MgO (Fig. 4D and F). A comparable example of the inflection in the behavior of Sr during late-stage evolution of hydrous magmas has been made using the compositions of Mount St. Helens volcanic rocks and melt inclusions (Blundy and Cashman, 2001; Blundy et al., 2008; Blundy, 2022): as the Mount St. Helens magmas ascend from their launch point (top of the mush zone) and the system reaches volatile saturation, the decrease in H$_2$O drives significant plagioclase fractionation and a decrease in Sr. Hence, the similar trends exhibited by the <2 wt% MgO OCG and ORG samples, together with the literature data for BG samples, are consistent with the effects of ascent, decompression crystallization and volatile exsolution.

Our conclusions regarding the link between volatile saturation and plagioclase fractionation are supported by previous analyses ofapatite grains from Miocene Gangdese magmas. Apatite is a common accessory mineral in hydrous magmas and partitions all the major magmatic volatiles (OH, C, Cl, F, S) into its crystal structure (Stock et al., 2018). Analyses ofapatite grains from both fertile and non-fertile Gangdese Miocene intrusions (Li et al., 2021a) show evidence for a transition from volatile-underated differentiation to volatile-underated differentiation, together with partitioning of Cl into exsolving fluids. Apatite grains from both fertile and non-fertile systems show S-rich cores and S-poor rims, which were attributed to crystallization of sulfate and presumably sulfide minerals from vapor under-saturated magmas, followed by partitioning of S into exsolving fluids from vapor-saturated magmas. These interpretations are in agreement with our identification of both anhydrite and sulfide inclusions in an apatite grain from Qulong (Fig. 3A and B). Other studies of the Qulong deposit have also noted the presence of magmatic anhydrite as inclusions in plagioclase and apatite (Xiao et al., 2012). Importantly, previous studies have demonstrated that the compositions of the OCG samples can be derived through extensive cooling of ORG-type magmas (Yang et al., 2009; Lu et al., 2015). The inflection in the trend between P$_2$O$_5$ and Sr versus MgO (Fig. 4C and D) for OCG, ORG and literature data for BG samples indicates that apatite saturation occurred at a slightly higher MgO (~3 – 4 wt%) than plagioclase fractionation (~2 wt% MgO). We therefore conclude that the timing of volatile exsolution during differentiation of most of the Miocene magmas was likely between ~3 – 4 (i.e., following the onset of apatite saturation) and ~2 wt% MgO (i.e., immediately prior to the onset of decompression-related plagioclase crystallization).

Like our whole rock analyses, which show that the >2 wt% MgO ORG, OCG and BG have similar Cu concentrations at a given MgO, the cores ofapatite grains from barren and mineralized systems have similar SO$_3$ concentrations (Li et al., 2021a). Furthermore, apatites from both barren and mineralized systems show evidence for partitioning of Cl into the exsolving fluid phase (Li et al., 2021a). Notably, Cl partitioning into exsolving fluids is required to promote significant partitioning of Cu into exsolving fluids (Candela and Holland, 1984; Migdisov et al., 2014). In summary, neither: 1) differences in initial H$_2$O, S and Cl abundances; 2) differences in the behavior of S and Cu during differentiation and sulfide fractionation; 3) differences in the timing of volatile exsolution, nor 4) differences in the composition of the exsolving fluid (i.e., Cl concentration) appear to be able to account for why some Miocene Gangdese magmas are ore-causative whereas others are barren.

5.3. Sulfide dissolution triggered by fluid exsolution

The chalcophile and siderophile element systematics of the Gangdese magmas, together with the occurrences of sulfides as inclusions in amphibole, apatite and magnetite, can be used to infer that the trans-crustal mush zones that filtered both the barren and ore-causative magmas contained sulfides. The increase in Cu with decreasing MgO of the MME analyzed by Yang (2008) hint that the concentration of Cu and therefore, the proportion of sulfides, increases from the base to the top of the mush zone, although detailed barometry would be required to confirm this suggestion. It therefore appears that successive batches of magmas that were filtered through the mush zone created a region of the crust that was enriched in Cu. Thus, a mechanism to transport the mush-zone hosted Cu to higher crustal levels appears to be needed to produce Cu-rich portions of crust at higher crustal levels (i.e., shallow porphyry Cu deposits).

The onset of volatile-exsolution-driven plagioclase fractionation at ~2 wt% MgO (Fig. 4D) is concomitant with an increase in Cu variability of the OCG and ORG (Fig. 7A), together with an increase in variability of Cu/Au (Fig. 7B), Au, Pt and the PGE (Fig. 8). It is also at this stage of magma differentiation that the BG samples (both our data and literature data) show a steep decrease in Cu with further decreases in MgO (Fig. 7A). Hence, following release of volatiles from the evolving magmas appears to be the stage when the Cu behavior of the barren compared to the ore-related and ore-causative systems start to diverge. Previous studies have also argued that sulfide fractionation is a ubiquitous process prior to expulsion of hydrothermal fluids and the generation of porphyry deposits (Rottier et al., 2019; Hao et al., 2019; Park et al., 2019, 2021).

Sulfur is known to partition strongly into magmatic fluids at crustal pressures for H$_2$O-rich relatively evolved magmas (see Edmonds and Woods, 2018). Partitioning of both Cl and S into the exsolving fluid phase, as indicated by the core to rim decrease in Cl and S in apatite (Li et al., 2021a), likely caused the melts to become sulfur undersaturated and consequently, caused any sulfides and sulfates that were in contact with the melt to dissolve (e.g., Halter et al., 2005; Nadeau, 2010; Reekie et al., 2019; Wieser et al., 2020; Xu et al., 2022). Indeed, sulfide dissolution can account for the lack of sulfides in the matrix of most of the BG, the ORG and the OCG samples, with the exception of the samples that contain disseminated pyrite and chalcopyrite, which likely precipitated from magmatic fluids (see Tian et al., 2022). A growing number of studies (Nadeau et al., 2010; Wieser et al., 2021; Reekie et al., 2019; Georgatou et al., 2022) have noted the absence of sulfides as minerals in the matrix of volcanic rocks, over-enrichments in elements such as Cu in the melt, and other evidence to suggest that the sulfide grains that were not hosted by minerals may have dissolved and/or were replaced by oxides and minor pyrite during ascent and degassing of S. Hence, the presence of pyrite and chalcopyrite in some of our samples might instead reflect incomplete dissolution of magmatic sulfides.

Comparisons between the compositional and textural differences of pristine versus decomposing sulfides have shown that the decomposing sulfides have lower Cu, S, Se, Te and Au (loss to the melt), higher Mn, Zn, Ph, Mo, As, Bi and TI (retained by the sulfide), but comparable Pt, Pd, Cd, Ag, Ni and Fe (Zhang and Audétat, 2017). Hence, progressive sulfide dissolution will first result in the enrichment of the neighboring melt in elements such as...
Cu and S, followed by elements such as the PGE. Preferential release of some sulfide-hosted elements (e.g., Cu and S) before others (e.g., Pt and Pd) we consider is one explanation for why the most Cu rich ORG and ORG samples that we analysed do not consistently have the highest Pt, Pd and other PGE concentration (Figs. 8 and 9). Other studies have also concluded that partial (e.g., leaving minor pyrite) and complete sulfide dissolution and oxide replacement is thought to release sulfide-hosted elements back into the melt (Nadeau et al., 2010; Wieser et al., 2021, Reekie et al., 2019, Georgatou et al., 2022). Others have suggested that volatile-element-rich bubbles are likely to nucleate on sulfide particles, which allows for S and Cu transport from the sulfide directly to the fluid (Heinrich and Connolly, 2022). In this scenario, the melts are unlikely to evolve to high Cu and S during sulfide decomposition, because the Cu and S partitions directly into the fluid. Hence, variable partitioning of Cu and S into either the melt and subsequently, the exsolving fluid, or directly into the exsolving fluid likely contributed the extreme variability in Cu and S concentrations of the Gangdese samples with <2 wt% MgO. However, because the ORG, the OCG and the BG samples show evidence for both sulfide fractionation (i.e., sulfides as inclusions in minerals) and subsequent exsolution of volatiles, sulfide dissolution alone cannot account for why some magmatism in the region is linked to the formation of porphyry Cu deposits, whereas the BG are not.

The similarities in Cu and Cu/Ag versus MgO trends of the BG and ORG prior to degassing-driven plagioclase fractionation indicates that the sulfides that caused the Cu depletions remained in the underlying mush zone, with the exception of those that occur as inclusions in minerals. Hence, we infer that the proportion of Cu in the melt and proportion of sulfides in contact with the melt at the onset of fluid exsolution during evolution of the BG magmas was insufficient to produce melts and fluids that were sufficiently Cu-rich to promote economic mineralization. From the similar Cu concentrations of the >2 – 3 wt% MgO ORG compared to the BG, it is likely that a similar conclusion applies to the evolving ORG and OCG. Indeed, Tian et al. (2022) conclude that even if the melts remained sulfide undersaturated during differentiation, fractional crystallization alone cannot account for the span to extremely high Cu concentrations of samples from Qulong porphyry. Hence, the question remains as to where the excess Cu was derived from to cause the span to extremely high Cu concentrations that are displayed by the <2 wt% MgO ORG and OCG.

Studies of the thermal and tectonic evolution of the Qulong porphyry Cu deposit have argued that the ore-causative stocks intruded into or above (i.e., to higher crustal levels) composite precursor batholiths that evolved through numerous pulses of magmatism that took place over several millions of years (Zhao et al., 2016, and references therein). Hence, it is likely that both the ore-related and ore-causative magmas transited through composite precursor sulfide-bearing mush zones. Importantly, the Miocene magmatism that led to mineralization took place during post-collisional extension and rapid exhumation (Yang et al., 2009; Zhao et al., 2016; Yang and Cooke, 2019). Because the drop in pressure associated with uplift and extension likely also resulted in uplift of the underlying sulfide-bearing mush zone, we suggest that the OCG and the ORG magmas may have achieved volatile saturation while they transited the pre-existing sulfide-bearing mush zone and therefore, the sulfur undersaturated magmas and the cosogenic CI-rich magmatic fluids were able to assimilate previous generations of sulfides. The slightly higher Cu/Ag of some of the ORG and OCG compared to the overall trend supports this interpretation. In contrast, we suggest that the BG magmas achieved volatile saturation after launching from the sulfide-bearing mush zone and thus, were only able to cannibalize their cosogenic cargo of sulfides, rather than previous generations of mush-zone hosted sulfides. In summary, we suggest that assimilation of mush-zone-hosted sulfides by ascending magmas and exsolving CI-rich magmatic fluids likely contributes to the trend to extremely high Cu (up to 6660 ppm) over a narrow range in MgO of some of the ORG and OCG samples, following the onset of volatile exsolution, rather than the variability being exclusively linked to late-stage alteration, which is only exhibited by some of our samples and appears to have had minimal impact on the bulk rock chemistry of the samples.

6. Concluding remarks

Previous studies have linked the evolution of porphyry Cu deposits to the cannibalization of pre-existing magmatic sulfides (Halter et al., 2005; Nadeau et al., 2010). In support of these conclusions, we attribute the span to high and variable Cu of the ORG and OCG to sulfide assimilation following degassing, which permitted the magmas and exsolving CI-rich fluids to assimilate previous generations of sulfides that were hosted in crustal mush zones beneath the granitic intrusions. We link the differences in Cu systematics of the <2 wt% MgO Gangdese BG and OCG to a drop in pressure of the magmatic system in response to rapid uplift and erosion and consequently, the BG magmas reached volatile saturation after launching from the underlying sulfide-bearing mush zone, whereas the OCG achieved sulfide saturation while still transiting the sulfide-bearing mush zone. The evolution of ore-causative magmas has been attributed by some to the long-timescales of magmatic activity (Chiaradia and Caricchi, 2017; Chelle-Michou et al., 2017; Chelle-Michou and Rottier, 2021). Hence, the lack of mineralization associated with some BG samples, such as much of the literature data which show similar Sr/Y trends to the OCG and ORG samples, may simply reflect the lack of persistent magmatism at these locations and consequently, the lack of sufficient sulfides in the mush that were available for assimilation.

Models invoking addition of Cu via melting of lower crustal cumulates has long prevailed as the vital ingredient for forming porphyry deposits (Hou et al., 2015a; Hou et al., 2015b). In support of this model, the most primitive sample from Qulong has significantly higher Cu (361 ppm Cu) compared to primitive MORB, which have ~115 ppm Cu (Jenner, 2017). However, the similarities in Cu between the most primitive ORG, OCG and BG samples shows that high Cu concentrations alone are not sufficient and that other later-stage processes determine whether a given batch of magma is likely to fuel formation of a related mineral deposit. Various studies have linked porphyry Cu deposit formation to release of unusually large volumes of hydrothermal fluids from evolving melts (Chiaradia and Caricchi, 2017; Chelle-Michou and Rottier, 2021). We suggest that significant volatile release, together with dissolution of pre-existing sulfides that were located in the pre-existing mush zone, both contribute to the formation of porphyry copper deposits.

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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