Abstract

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T-P-fO₂ conditions of sulfide saturation in magmatic enclaves and their host lavas

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ABSTRACT

Physicochemical conditions under which early sulfide saturation occurs and the role of this process in the mineralising potential of magmas in different geodynamic settings have been the subject of interest in many recent studies. Here we present new temperature-pressure-fO₂ data on sulfide-saturated magmatic enclaves and host lavas from volcanic systems in subduction, post-subduction and intraplate geodynamic settings, some of which are associated with porphyry and epithermal deposits. Petrographic investigations coupled with mineral chemistry of sulfide inclusions and their host minerals and with bulk chemistry of amphibole, plagioclase and pyroxene-rich enclaves and their host lavas indicate that sulfide occurrence, abundance, and composition depend on magma evolution. Sulfides are more abundant and have higher Ni/Cu bulk ratios when found in mafic enclaves compared to sulfide inclusions occurring in more evolved lavas. Thermo-oxibarometry estimates indicate that mafic hornblende-rich cumulates (SiO₂ < 45 wt%) occurring at the studied intraplate setting evolve and reach sulfide saturation already in the mantle (61 ± 7 km) at high temperature and pressure conditions (17 kbar and 1135 ± 28 °C) and low ΔNNO (< –1). These cumulates are associated with a greater sulfide abundance (up to 0.23 area %) compared to other types of enclaves and have Cu-poor sulfides (mostly pyrrhotite, with Cu median = 0.16 wt%) with high Ni/Cu values (up to 65). In contrast, more evolved (SiO₂ > 50 wt%) gabbric plutonic enclaves found in arc settings saturate sulfides at shallower crustal levels (~26 ± 10 km, i.e. ≤ 7 kbar) and at lower temperature (1014 ± 28 °C) and higher ΔNNO (> +1), and are characterised by a lower sulfide abundance (down to 0.01 area %), dominated by Cu-rich sulfides (mostly chalcopyrite and bornite with Cu median = 50 wt%). By accounting for the sulfide volume, our results suggest that sulfides can retain significantly higher amounts of metals in the enclaves (Cu = 32–113 ppm) compared to sulfides in the host lavas (Cu < 8 ppm). Considered altogether, our results indicate that alkaline mafic, less oxidised, and barren magmas corresponding to intraplate and back-arc settings saturated in sulfides in the upper mantle. In contrast, calc-alkaline-felsic, oxidised and ore-related magmas corresponding to convergent margins started to be saturated in sulfides at the expected depth of the MASH zone and at shallower crustal levels. This seems to be a consequence of the investigated alkaline systems not forming shallow crustal magma chambers allowing magma differentiation, rather than the fact that late and shallow sulfide saturation is necessary for porphyry formation.

1. Introduction

Sulfide saturation occurring at depth may be responsible for the sequestration of significant amounts of chalcophile elements, thus controlling the metal availability in the later exsolving volatile phase and ultimately affecting the mineralisation potential to produce porphyry-epithermal deposits (Li and Audétat, 2015; Park et al., 2015). However, only a few studies have quantified and modelled the physicochemical conditions under which sulfide saturation takes place and the concentration of metals retained in deep sulfide-rich zones, by investigating sulfide-bearing enclaves (e.g., lower crustal hornblende-rich enclaves, Chang and Audétat, 2018, and deeper pyroxene-rich cumulates, Chen et al., 2020). Results of the above studies suggest that enclaves could represent fertile sources of chalcophile metals in arc settings, by sequestering most of the Cu (and Au) extracted from the mantle. On the other hand, sulfide saturation does not seem to be detrimental for all ore forming systems. This suggests either the possibility of later dissolution and mobilization of metals from the deep sulfide-rich zones (Halter...
et al., 2005) or that metal content is not the primary control on the formation of porphyry deposits and other parameters (magma volumes, amount of fluid) play a more important role (Chelle-Michou et al., 2017; Chiaradia and Caricchi, 2017; Du and Audet, 2020; Lee and Tang, 2020). This is also indirectly supported by studies of sulfides in the host rocks and in enclaves (Chang and Audet, 2018; Du et al., 2014; Georgatou et al., 2018; Georgatou and Chiaradia, 2020; Rottier et al., 2019, 2020), showing that many systems, irrespective of whether they are associated with mineralisation or not, saturate sulfides during most of their evolution. Lastly, it has been suggested that sulfide saturation is a multi-stage process starting with early crystallising Fe- and Ni-rich sulfides hosted by early crystallising mineral phases (olivine), switching to Ni-poor, Cu-rich sulfides (pyroxene, amphibole, plagioclase and magnetite) and finally to late Cu-rich sulfides hosted by magnetite (Du et al., 2014; Georgatou and Chiaradia, 2020; Keith et al., 2017). The latter Cu-rich sulfide type has been observed to occur only in the lavas and it appears to form at a late stage (Georgatou and Chiaradia, 2020).

In this study we aim to constrain the pressure (P)-temperature (T) range of the different stages of sulfide saturation, a process considered to be one of the most important steps leading to the formation of porphyry Cu deposits (e.g., Wilkinson, 2013), and to gain insights into the suggested process of mobilization/dissolution of the early sulfides. In order to achieve this we investigate the petrography and mineral chemistry of compositionally different magmatic enclaves and their host lavas. We focus our study on sulfide-bearing enclaves occurring in the host lavas of previously investigated areas, including volcanoes located in Western Turkey and two volcanoes of the Ecuadorian volcanic arc, where sulfide saturation has already been described (Georgatou et al., 2018; Georgatou and Chiaradia, 2020). Correlating a specific P-T range with sulfide occurrence and composition for diverse geodynamic settings in both mineralised and barren systems allows us to assess the effect of multistage sulfide saturation on the mineralising potential of magmas.

2. Geodynamic setting and mineralisation

We studied enclaves belonging to volcanic areas in subduction, post-subduction and intraplate geodynamic settings, some of which are associated spatially and/or temporally with porphyry Cu-(Au) and epithermal deposits. The volcanic areas associated with a subduction geodynamic setting include Pichincha and El Reventador volcanoes, located in the Quaternary Ecuadorian volcanic frontal and back arcs, respectively. Although there are no known examples of Quaternary mineralisation proximal to these study areas, there are world class Late Miocene Cu-Mo-(Au) porphyry deposits in the frontal arc, like the Llurimagua/Junín Cu-Mo porphyry deposit (Schütte et al., 2012). Previous petrographic investigations have shown that volcanic rocks coeval to mineralisation are affected by a strong overprint by hydrothermal fluids which renders impossible the study of magmatic sulfides in these rocks (Georgatou et al., 2018; Schütte et al., 2012). Therefore, only unaltered Quaternary volcanic rocks were studied which, based on their geochemical signatures (e.g., high Sr/Y values; Loucks, 2014), can be used as a proxy for a potentially fertile syn-subduction magnetic environment (Georgatou and Chiaradia, 2020). The investigated areas characterised by a post-subduction setting (Rabayrol and Hart, 2019a) include the mid-Miocene to Pliocene volcanic-plutonic complex of Konya (Temel, 2001 and references therein) and the Miocene Beydağı volcano in the Usak province (Karaoğlu et al., 2010), in Western Turkey. Both areas contain significant economic deposits with Konya hosting the Doganbey Cu-Mo-W porphyry (Hall et al., 2007; Rabayrol and Hart, 2020) and the İncelu Au-epithermal deposit (Zürcher et al., 2015), and Beydağı hosting the Kisladag Au-porphyry deposit (Baker et al., 2016). Finally, we studied the Kula Plio-Quaternary volcano in the Usak basin, which is also hosted in Turkey, which is characterised by an intraplate setting with OIB-signatures (Agostini et al., 2007) and which is not associated with any type of mineralisation.

3. Methods

3.1. Samples and petrography

The samples were selected and prepared with a special focus on amphibole and/or plagioclase and/or pyroxene-rich sulfide-bearing enclaves found in host lavas. The latter may also contain sulfide-bearing phenocrysts. This was done in an effort to include all stages of sulfide saturation, with sulfides in the enclaves representing the early and deeper stage and those in the lavas representing the late and shallower stage. Hereafter, the term ‘enclave’ will be used as a generic term for all types of cognate magmatic rock inclusions within a host lava. A preliminary petrographic study was undertaken on 67 thin sections from which 25 were studied in detail (5 for Kula, 6 for Beydağı, 4 for Konya, 6 for Pichincha and 4 for El Reventador). High-resolution images of thin sections, including both the enclave and the host lava, were obtained in transmitted and reflected light with an automated stage scanning petrographic microscope (JEOL-Olympus BX61; Figs. 1–14 in Electronic appendix A). In an effort to apply multiple methods and include all volcanic areas we have only investigated a small number (2–5) of samples carrying enclaves for each area accounting for a total number of 18 thin sections on which we conducted SEM and electron probe microanalyser (EPMA) mineral analysis and applied the chosen thermobarometers. The selection of these specific samples (N = 18) was aimed at including as many enclaves as possible, characterised by variable lithologies, origin (cumulate versus plutonic enclaves: see details in Electronic appendix A), and sulfide abundance in order to sample the entire progress of magmatic sulfide evolution from depth to surface. These 18 thin sections hosted the following number and type of enclaves: 3 hornblendites, 2 hornblende-rich diorites, 4 diorites, 1 basalt, and 6 gabbros, as well as 2 amphibole/clinoxyroxene-aggregates, 1 amphibole-megacryst, and 1 amphibole-core. Out of these, 5 thin sections were analysed by Qemscan® corresponding to 4 samples from Kula and 1 from Pichincha. Based on these limitations, it is important to note that the results of this study cannot be representative of a full spectrum of conditions and a possible bias caused by insufficient sampling has to be considered.

3.2. Bulk rock and mineral chemistry

Automated mineral analysis and textural imaging of 5 thin sections, including enclaves and host lavas, were performed using an FEI Qemscan® Quanta 650F facility at the Department of Earth Sciences, University of Geneva, Switzerland. The system is equipped with two Bruker QUANTAX light-element energy dispersive X-ray spectrometer (EDS) detectors. Analyses were conducted under high vacuum, with accelerating voltage of 25 kV, and a beam current of 10 nA on carbon-coated polished thin sections. FieldImage operating mode (Pirrie et al., 2004) was used for analyses. In total 221 individual fields were measured per sample, with 1500 μm² per field, and point spacing of 10 μm. The standard 1000 counts per point were acquired, yielding a limit of detection of approximately 2 wt% per element for mineral classifications. Measurements were performed using iMeasure v5.3.2 software and data processing using iDiscover® v5.3.2 software package. Final results consist of: i) high-quality spatially resolved and fully quantified mineralogical maps; ii) BSE images with identical resolution to the mineralogical maps; iii) X-ray element distribution maps.

Due to the small size of the enclaves (diameter < 4 cm), conventional whole rock methods (e.g., X-ray fluorescence-XRF and laser ablation-inductively coupled plasma mass spectrometry-LA-ICP-MS) could not be used to obtain the bulk enclave chemical composition. For this reason, bulk enclave chemistry was calculated by combining modal mineral abundances (in area %), resulting from Qemscan® analysis, with elemental concentrations of the main mineral phases (in wt%) resulting from EPMA. Representative examples of mineral compositions used as input for the bulk composition calculations are included in...
Feldspar feldspars belonging to the matrix varied in composition from K-feldspar (Orthoclase) to Na-feldspar (Albite), in between compositions are named below as 'Alkali representative composition to the partially recrystallised matrix textures and aphanitic matrix, the biggest challenge was to assign a tion. Since most of the studied samples are characterised by porphyritic few phases lacking an EPMA concentration were given a hypothetical -Values followed by an ‘*’ correspond to the initial modal area % of before the break-down of amphibole. Italic mineral names stand for sub-mineral groups. Micro-feldspars belonging to the matrix varied in composition from K-feldspar (Orthoclase) to Na-feldspar (Albite), in between compositions are named below as ‘Alkali Feldspars’.

Table 1 of Electronic Appendix B. Minor mineral phases (< 1 area %) or few phases lacking an EPMA concentration were given a hypothetical concentration based on the expected theoretical elemental concentra- Since most of the studied samples are characterised by porphyritic textures and aphanitic matrix, the biggest challenge was to assign a representative composition to the partially recrystallised matrix composed of microlites (often <10 μm) which matched the detected Qemscan® mineralogy (point spacing of 10 μm). For this reason, in order to obtain a representative elemental composition for the matrix of the host lavas, 10–20 areas for each lava and representative enclave were analysed with a JEOL JSM7001F digital SEM at the University of Geneva, Switzerland. The accuracy and reproducibility of this indirect method to calculate bulk enclave chemistry has been evaluated by comparing the results calculated as described above to the known whole rock chemistry obtained by direct methods (XRF and LA-ICP-MS, see analytical conditions in Georgatou and Chiaradia, 2020) for the host lava (Figs. A.20–21, Table B.2). This was also applied for a gabbroic enclave (E05015-Pichincha), large enough to apply both methods. In addition, to further investigate the sensitivity of Qemscan® to accurately quantify the mineral composition of the matrix, Qemscan® ana- lyses of the same sample (LP56-Kula) were acquired with different point spacing (5, 10, 20 and 50 μm) and compared (Table B.3). Lastly, LP56 hornblenditic cumulate was processed also by point counting using the Jeol JXA-8200 Superprobe EPMA at the University of Geneva, Switzerland. Major and minor element concentrations (N = number of measurements) were acquired for amphibole (N = 273), pyroxene (N = 168), plagioclase (N = 68), olivine (N = 10), sulfide (N = 205),apatite (N = 138), and oxides (N = 107). Silicates were analysed for Si, Fe, Ti, Al, Mg, Mn, Na, Ca, K; Cr; phosphates were analysed for Si, S, P, F, Cl, Ca, Na, Mg; K; oxides were analysed for Fe, Mg, Ti, Al, Ni, Si, ±Cr, ±V and sulfides were analysed for S, Fe, Cu, Ni, As, Zn, Se, Ag, and Au. Details on the standards, analytical conditions used for calibration, peak and background time as well as detection limits as well as the complete EPMA dataset are included for each mineral group analysed in Tables 1–8 of Electronic Appendix C. Analytical conditions of SEM analysis were 15 kV accelerating voltage and 2 nA absorbed current, whereas the size of the ana- lyzed area was around 0.01 μm². The results are presented in Table C.9.

3.3. Thermo–oxibarometry

In order to estimate the P-T-fO₂ ranges at which sulfide saturation occurred in the different areas, we applied the following thermobarometers depending on the mineral assemblage of the enclave and the host lavas: (i) one mineral-only methods including amphibole only for T-P with Ridolfi and Renzulli (2012), for fO₂ with Ridolfi et al. (2010) and for T with Putirka (2016) and clinopyroxene-only for P with Putirka (2008); (ii) mineral pair methods including amphibole and plagioclase for T-P with Holland and Blundy (1994), clinopyroxene and
orthopyroxene for T-P with Putirka (2008) and magnetite-ilmenite for T-

Concentrations are given in wt%, ‘dl’ stand for the detection limit and not analysed, respectively.

### 4. Results

#### 4.1. Petrography of investigated lavas and enclaves

The studied samples include fresh lava flows with porphyritic textures which host comagmatic amphibole- and/or pyroxene-rich enclaves with sizes that exceed 4 cm in maximum dimension. Amphibole, pyroxene and plagioclase crystals are observed as phenocrysts in lavas and within the enclaves. Most amphibole phenocrysts are characterised by euhedral to subhedral crystal shapes, and often show partial to full opacification, optical zonation and occasionally contain magnetite (± ilmenite), plagioclase and biotite mineral inclusions. The majority of pyroxenes observed are clinopyroxenes with optical zoning. Clinopyroxene is the most abundant phenocrystic mineral and can be found in all study areas with different degrees of sieve textures, optical zonation and often containing glass and apatite inclusions. Representative examples of sulfide occurrence in diverse enclaves are shown in Fig. 1. Detailed petrographic observations of the lavas and the enclaves for each studied area are included in Electronic Appendix A. For modal mineralogy, including vesicle proportions, see Table 1.

#### 4.2. Sulfide occurrence, texture and composition

Multiphase sulfide inclusions are found in phenocrysts of both lavas and enclaves with a significantly greater abundance and grain size in the enclaves compared to the lavas (e.g. Table 1, Fig. 1). Sulfide mineral host distribution in the enclaves seems to be controlled by the main mineral phase of the specific enclave, with amphibole (+ magnetite) as a main host in hornblendeititic enclaves, plagioclase (+ amphibole) in dioritic enclaves, and pyroxene (+ plagioclase) in gabbroric enclaves. Most sulfide inclusions are characterised by globular to ellipsoidal shapes and usually have average size <20 μm. Sulfide occurrence, texture and composition will be presented below for every study area with emphasis on the enclaves. Absolute and relative sulfide abundances for lavas and enclaves are indicated with the number of sulfides (N) observed in the samples for each study area and wherever possible with the sulfide abundance (area %) obtained by Qemscan®, respectively. Textural and morphological details on the sulfides observed in phenocrysts from the lavas of Ecuador and of Western Anatolia can be found in Georgatou et al. (2018) and Georgatou and Chiaradia (2020), respectively.

#### 4.2.1. Kula

In lavas of Kula, sulfide inclusions are abundant (0.005–0.03%, N = 30–60 in host) and larger in size (around 10–50 μm) than in any other study area. In the lava, sulfide inclusions occur mostly in amphibole and pyroxene, but rarely plagioclase, olivine and magnetite have also been noted as a host. Sulfides have also been observed in the lava matrix, mostly associated with oxide phases forming aggregates and reaching up to 600 μm in size. The most sulfide-abundant enclave is LP56B followed by LP06 with approximately 0.23% (N ~ 400) and 0.15% (N ~ 150) sulfides, respectively (Figs. 1A-a, B-a). In enclaves LP17 and LP56B, sulfides dominantly occur in the amphibole breakdown corona (Fig. 1A-b) or in the outer rim of the clinopyroxene (Fig. 1A-c), whereas in enclaves LP06 and LP19 sulfides are hosted by amphibole and plagioclase crystals and are often found in contact with apatite inclusions (Figs. 1B-b, c-iii). In LP19 sulfides also occur interstitially and are partly replaced by oxide phases (e.g. goethite; Fig. 1B-cii, ciii). The average size for sulfide inclusions found in the enclaves ranges from 20 to 100 μm, while interstitial sulfides are usually around 200 μm but can reach up to 500 μm. Only Cu-poor sulfides composed of pyrrhotite (± pentlandite) and minor chalcopyrite (± cubanite) are observed in enclaves and host lavas of Kula.
4.2.2. Konya

There is significant variability between the sulfide abundance of the samples from Konya, with BP07 being the most sulfide abundant sample and BP37 the least sulfide abundant, with \( N \sim 150 \) and \( N < 10 \), respectively. Sulfides occur, both in the lavas and in the enclaves, only in amphibole (Fig. 1D-b), magnetite and plagioclase phenocrysts, and never in the groundmass or interstitially. Sulfide size in the lava ranges, depending on the sample, from less than 5 up to 10 \( \mu m \) with a few examples reaching up to 15 \( \mu m \) for BP37, 25 \( \mu m \) for BP65 and BP25, and 45 \( \mu m \) for BP07. Only a few cases of enclave-hosted sulfides were observed (\( N < 10 \)) which is likely to result from the small enclave size and the fact that only part of the enclaves was still present (e.g. Fig. 1D-a). For those cases, sulfide size ranges between 5 and 10 \( \mu m \), with one exception — up to 20 \( \mu m \) (BP07). In BP07, BP25 and BP65 sulfide...
incisions in both lavas and enclaves are generally Cu-poor, composed of pyrrhotite and minor chalcopyrite (e.g. Fig. 1D-cii), whereas in sample BP37 sulfide incisions composed of chalcopyrite and bornite (± digenite) were only found in magnetite phenocrysts of the lava, (Fig. 1D-ciii, civ).

4.2.3. Beydagi

In lavas of Beydagi mafic sulfides are rare ($N = 30–40$) and generally small ($< 30 \mu m$). Depending on the sample, sulfides in the lavas are mostly hosted by amphibole (LP36- Fig. 1C-a), plagioclase (LP49B), magnetite (LP52B2) and pyroxene (LP54A). Rarely sulfides are found in pyroxene and very often they are seen in the groundmass. The latter are irregular and, in most cases, associated with oxide phases (mainly magnetite). In sample LP52 and LP54 both hydrothermal and magmatic sulfides were observed in the groundmass of the lava due to overprinting of hydrothermal mineralisation (see Fig. A.13 and for petrographic criteria distinguishing hydrothermal from magmatic sulphides please see Georgatou and Chiaradia, 2020). In enclaves, sulfides are also rare ($N = 15–30$) and the average size is between 20 and 25 $\mu m$, with a few examples reaching up to 50 $\mu m$ in LP49B and 80 $\mu m$ in LP36. More specifically, in enclave LP36 amphibole, (Fig. 1C-ci, cii), plagioclase and, in rare cases, magnetite are the main sulfide hosts, whereas in enclave LP49B sulfides occur in plagioclase and occasionally in pyroxene. For enclave LP52B1, sulfides were found in plagioclase and magnetite whereas for LP52B2 and LP54 pyroxene is the main sulfide host. For LP52B2 greater numbers of sulfides also occur interstitially (>40%) and in the amphibole xenocrysts, which carry sulfides hosted by and associated with magnetite (e.g. Fig. 1D-ci, cii). Where hosted by opacitised amphibole, sulfides show replacement textures, irregular shapes and partly dissolved cores (Fig. 1C-ci). Sulfides in the phenocrysts of the lavas of Beydagi, in particular those hosted by magnetite, are composed of chalcopyrite (± pyrite) compared to the sulfides found in the enclaves which are mostly pyrrhotite and minor chalcopyrite.

4.2.4. Ecuador (Pichincha and El Reventador)

Sulfides in sample E05015 of Pichincha are more abundant in the gabbroic enclaves than in the host lavas. No sulfides were found in the pyroxene enclave. In the lava sulfide inclusions are rare (0.001%, $N = 5$) and small (5–10 $\mu m$), occurring in magnetite, clinof- orthopyroxene aggregates, whereas in the gabbroic enclave sulfides (0.01%, $N = 20$) are usually around 10–15 $\mu m$ with one example reaching 25 $\mu m$ (Fig. 1D-iii), and are hosted by pyroxene, followed by plagioclase and, to lesser degree, by magnetite. In addition, sulfides in the lava are composed mostly of chalcopyrite whereas in the gabbroic enclave they consist of chalcopyrite and bornite (± digenite) (Fig. 1D-ciii, civ). Previous observations of Georgatou et al. (2018) on the additional samples considered in this study (El Reventador- AG14013/15A/15B, Pichincha-AG14050) indicate that enclaves carried more sulfides than their host lavas ($< 0.02$ and $< 0.001\%$, respectively) and that sulfides in the enclaves (with the exception of the AG14050 gabbroic enclave-and now also E05015) were Cu-poor compared to the ones found in the lavas.

4.3. Mineral chemistry

Sulfide inclusions, their host minerals (silicates and oxides) and accessory phosphate mineral phases were analysed for major and minor element composition with EPMA. Although priority was given to crystals hosting sulfides, a smaller number of sulfide-free crystals was also analysed in order to investigate any chemical trends. Key points from four of the important mineral groups are mentioned below whereas all the results, including also other mineral groups and petrographic observations (e.g., whether sulfides were observed in a specific crystal zone of the host mineral), can be found in Tables C.2–8.

4.3.1. Sulfides

Results of 180 measurements (with totals $\geq 96$ wt%) on sulfide inclusions found in the enclaves of Kula (LP06, LP17, LP18, LP19, LP56B), Konya (BP07, Beydagi (LP36, LP49B, 52B2), Reventador (AG14015A) and Pichincha (E05015) are shown in Fig. 2. The full dataset, including results obtained from previous studies, on sulfides in enclaves and host lavas (Georgatou et al., 2018; Georgatou and Chiaradia, 2020) is reported in Table C.2. Median Cu and Ni values (in wt%) for the different study areas and number of measurements ($N$) are 0.21 and 0.43 for Kula ($N = 90$), 0.46 and 0.01 for Konya ($N = 1$), 0.74 and 0.17 for Beydagi ($N = 36$), 0.3 and 0.21 for El Reventador ($N = 45$), and 47 and 0.01 for Pichincha ($N = 20$). Sulfides in the enclaves of Kula present the lowest Cu and highest Ni values compared to the other areas. Sulfides from two enclaves of Beydagi volcano, LP36A and especially LP52B2, differ from the rest by yielding pyrite compositions. Considered altogether and according to the enclave mineralogy, the Cu mean values are: 0.86 wt% for the dioritic enclaves (LP06, LP18, LP19, LP49B, LP56A), 11 wt% for the amphibolite enclaves (LP17, LP56B, AG14015A) and 26 wt% for the gabbroic enclaves (E05015, LP52B2, AG14050).

4.3.2. Amphibole

A total of 273 amphibole measurements corresponding to samples from Konya (BP25, BP65), Kula (LP06, LP17, LP56B), Beydagi (LP36) and Reventador (AG14015) are reported in Table C.3 and plotted in Fig. 3a-d. Amphiboles are calcic, characterised by ($Na + K > 0.5$, ($Ca + Na > 2$, $Al^{iv} > Fe^{III}$, $Al_{tot}$ ranging from 1.1 to 2.8 and are Mg-rich (Mg/ ($Mg + Fe^{III}$) > 0.5 with a Mg# between 0.48 and 0.79. Most amphiboles correspond to paragisitic (NaCa$_2$(MgAl)(Si$_2$Al$_2$O$_{22}$(OH))$_2$) paragisitic amphiboles of Kula are Ti-rich and can be further classified as kaersutite (NaCa$_2$(MgAlTi) (Al$_2$Si$_6$O$_{24}$O$_2$)) amphiboles. Amphiboles found in the Beydagi enclave (LP36) classify as edenite, ferro-edenite paragisite and ferro-paragisite and show the lowest range of Mg# (amphibolite) = 0.48–0.53 compared to all other samples, but also compared to the lava of LP36 with Mg# (median-enclave) = 0.52 and Mg# (median-lava) = 0.72, respectively. In Kula, amphiboles in hornblendeic enclaves (LP17, LP56B) show overlapping Mg# (median) ranging from 0.64 to 0.76 for enclaves and lavas, respectively, while amphiboles in the dioritic enclave (LP06) show lower Mg# (median) (0.60) compared to the values corresponding to amphiboles of the lava (0.71). Konya samples show generally similar Mg# between paragisitic amphiboles occurring in enclaves (Mg# (median-enclave) = 0.67 for gabbrodioritic-BP25 and hbl core-BP65) and in lavas (Mg# (median-lava) = 0.64). All amphiboles show a positive correlation between Al$^{iv}$ and Al$^{vi}$ and between Ti and Al$^{iv}$ indicating pressure and temperature driven substitutions of Al$^{iv}$ and Ti by Al$^{vi}$, respectively. Compared to the other study areas amphiboles from Kula show the highest Al$^{vi}$, Ca and K contents and the strongest core to rim variability in Mg#.

4.3.3. Pyroxene

A total of 155 pyroxene analyses obtained from samples of Konya (BP25), Kula (LP01, LP06, LP17, LP19, LP56B) and Pichincha (E05015) are reported in Table C.4 and shown in Fig. 3e-f. According to their Ca, Mg and Fe content clinopyroxenes classify mostly as diopside (En$_{22–48}$Wo$_{03–53}$Fs$_{77–28}$) for Kula and augite (En$_{34–49}$Wo$_{42–46}$Fs$_{10–19}$) for Konya and Pichincha, with Mg# ranging from 0.68 to 0.80 and from 0.66 to 0.99, respectively. In general, pyroxene crystals in enclaves have similar compositions to those found in the lavas. Pichincha is the only case presenting both clino- and ortho-pyroxene in the lavas and enclaves with orthopyroxenes ($N = 30$) plotting in the enstatite field, covering a large compositional range (En$_{57–78}$ Wo$_{1–5.3}$ Fs$_{17–41}$) and with Mg# ranging from 0.58 to 0.82.

4.3.4. Plagioclase

A total of 68 plagioclase measurements on samples from Konya (BP07, BP25), Kula (LP06, LP19) and Pichincha (E05015) are reported in Table C.5 and are depicted in Fig. 3g-h. According to their An-Ab
content, plagioclase crystals vary in composition from andesine to labradorite and bytownite. Plagioclase phenocrysts from the lavas and the enclaves have similar An content, ranging from An$^{32}$ to An$^{71}$, with only Konya yielding plagioclase crystals with An content up to 82%. Plagioclase belonging to the enclaves of Kula contains the highest Sr content (0.2–0.4 wt%) compared to plagioclase found in the lavas and enclaves of Pichincha (<0.2 wt%). Compared to Kula, plagioclases in Pichincha lava and enclave show evident Ca and Si zoning.

4.4. Bulk rock chemistry and elemental maps

Lava flows are mostly andesitic to dacitic in composition for Pichincha, El Reventador and Konya, showing medium (Pichincha) and high-K calc-alkaline affinity (El Reventador and Konya). Beydagi is characterised by rocks with andesitic to trachyandesitic composition and high-K calc-alkaline to shoshonitic affinity while Kula is characterised by the most mafic and alkaline rocks, of tephritic to phonetephritic composition (see Georgatou and Chiaradia, 2020).

Modal mineralogy results from Qemscan® analyses of five enclave samples from Kula (LP-06, -17, -19, -56B) and Ecuador (Pichincha-E05015) were combined with corresponding mineral analysis obtained by EPMA, thus allowing calculation of the bulk composition of the enclaves (Tables 1, 2). All studied enclaves have more mafic compositions compared to their host lavas. Hornbleniditic enclaves and diorites of Kula are characterised by lower SiO$_2$ (40.6–45.8 wt%) and higher K$_2$O + Na$_2$O and TiO$_2$ ranges of 7.68–9.77 and 1.5–3.85 wt%, respectively, compared to the gabbroic enclave of Pichincha with SiO$_2$ of 53.4 wt%, K$_2$O + Na$_2$O of 6.46 wt% and TiO$_2$ of 0.73 wt%. All mineral and elemental mapping results are included in Figs. A.15–26, while in Figs. 4 and 5 results from two examples belonging to Kula (LP56) and Pichincha (E05015) are displayed. Note that Pichincha is characterised by a significant abundance of quartz in the gabbroic enclave as well as an
Fig. 3. Chemical variation of silicates used for thermobarometry occurring in lavas (circle) and enclaves (stars); a-d) amphibole, e-f) pyroxene and g-h) plagioclase. In graph (a) classification is according to Leake et al. (1997) based on Mg# (\(= \frac{Mg}{Mg + Fe^{2+}}\)) and Si with most amphiboles plotting in the pargasitic field and in (b, d) the T-P regression lines show the T-P sensitivity behaviour based on substitution and variation of total Al (vi) and Ti by Al (iv), respectively. In ternary graphs, (f) the pyroxene classification graph is according to Morimoto et al. (1988) based on the Wollastonite (Ca) - Enstatite (Mg) - Forsterite (Fe) ternary system and most pyroxenes have diopside composition with only Pichincha showing orthopyroxene crystals in gabbroic enclave and in lavas and in (h) the plagioclase classification is according to Deer et al. (1966) and is based on the Anorthite (Ca) - Albite (Na) content with most plagioclase crystals corresponding to andesine to labradorite compositions.
obvious chemical zonation of Si and Ca detected in plagioclase crystals occurring in lava and enclave, whereas reverse zoning-mixing features with orthopyroxene cores replaced by olivine and clinopyroxene rims are seen in the lavas (Fig. 4a).

4.4.1. Sulfide abundance and bulk metal contents

Sulfide modal abundance (area %, Table 1) shows a negative correlation with SiO$_2$ and positive correlation with MgO, TiO$_2$, Cu and Ni whole rock concentrations of enclaves and lavas (Fig. 6a-c). In contrast, the sulfide abundance appears to correlate negatively with the metal content in the sulfides, decreasing with the decrease of Cu and/or Ni median sulfide contents (Fig. 6d). These results suggest that with magmatic evolution sulfides decrease in number but present higher Cu values. The latter, however, do not correspond to the bulk Cu content of the sulfide but rather to the in situ EPMA analysis of the multiphase sulfide inclusion.

In order to assess the total bulk Cu and Ni content sequestered by sulfides we combined the Cu and Ni median weighted concentrations obtained by EPMA (based on the proportions of Cu-rich and Cu-poor mineral phases composing the sulfide inclusion, respectively) with the total modal sulfide abundance (area %) converted in volume (assuming a spherical shape of the sulfide inclusions). Details on the methodology are included in Table A.1. Our results show that sulfides in enclaves sequester 4.8–32 ppm of Cu and 0.19–5.6 ppm of Ni in deep mafic cumulates and 13–113 ppm of Cu and 0.53–1.5 ppb of Ni in late gabbroic enclaves. In contrast, sulfides in the host lavas present lower metal contents, 1.2–8 ppm of Cu and 0.01–0.15 ppm of Ni in mafic lavas and 0.74 ppm of Cu and 0.003 ppb of Ni in felsic lavas, respectively. As a

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Fig. 4. Qemscan® mineral and elemental maps (Si, Fe, Mg and Ca) of two thin section examples corresponding to andesitic lavas and gabbroic plutonic enclave of Pichincha (a) and to phonetephritic lavas and amphibole-cumulate enclave of Kula (b). Thin section microphotographs acquired with an automated stage under transmitted light are shown in figures a-ii and b-ii in which the scale bar corresponds to 1 mm. Note the increased porosity in Kula compared to the host lava of Pichincha.
result, the Ni/Cu ratio decreases with the increase of SiO$_2$ with the highest Ni/Cu recorded in sulfides occurring in the most mafic (MgO = 10–8.6 wt%) hornblenditic enclaves (Fig. 6 e-f).

4.5. Crystallisation conditions

The complete dataset of all T-P-fO$_2$ estimates resulting from the composition of amphibole only (N of measurements = 275), amphibole-liquid (N = 106), clinopyroxene-only (N = 125), clinopyroxene-liquid (N = 58), amphibole-plagioclase (N = 22), orthopyroxene-clinopyroxene (N = 16), olivine-liquid (N = 16) and magnetite-ilmenite (N = 9) pairs are shown in Tables D.1-6, whereas a summary of the results is reported in Table 3 and presented in Figs. 7 and 8. In addition to the samples described in this study, T-P-fO$_2$ were also obtained for samples previously studied by Georgatou et al. (2018), including samples from Ecuador containing gabbroic (Pichincha-AG14050) and hornblenditic (El Reventador-AG14013/15A/B) mafic enclaves.

5. Discussion

5.1. Statistical significance and limitations

The main aim of this study is an exploratory investigation of the P-T-fO$_2$ conditions of sulfide saturation in cognate magmatic enclaves and their host lavas from different geodynamic settings, that are both
representative (syn-subduction, post-subduction) and not (intraplate volcanism) of potential porphyry Cu deposit environments. We have chosen for this purpose five selected areas representative of these different settings. It is important to note that the current investigated study area associated with intraplate volcanism (Kula) is characterised by mafic alkaline magmas in an extensional setting where asthenospheric upwelling has been noted (e.g., Agostini et al., 2007; Rabayrol et al., 2019b). Therefore, it should not be considered as a classical example of intraplate volcanism and generalisation on intraplate settings cannot be made based on the present study. Although we are aware that the results of this study concern a limited number of areas and samples, we believe that they can serve as a roadmap to guide future studies in this field. To assess the representativeness of our results, wherever possible we report T-P estimates of previous studies in the same geological areas and compare our estimates to previously studied sulfide-hosting enclaves with similar lithologies (e.g. Table D.7).

Fig. 6. Binary graphs depicting the correlation between the sulfide modal abundance (area %) deriving from Qemscan® analysis and the bulk composition of the lavas and the enclaves (a-c) and the metal content of the sulfide inclusions (d-f). In graphs a-c, bulk composition of lavas (circles) correspond to XRF analyses while of enclaves corresponds to the calculated composition derived from EPMA and Qemscan®, with the exception of bulk Cu in enclave of Pichincha (260 ppm) corresponding to LA-ICP-MS analysis. In graph d the Cu median values are based on the proportions of Cu-poor and of Cu-rich sulfide mineral phases while in graphs e-f the bulk Cu median and Ni/Cu median accounts for the bulk sulfide composition based on the sulfide area % (and therefore sulfide volume) resulting from Qemscan® analysis. Graphs a-d include in grey symbols other samples belonging to volcanoes of the Ecuadorian arc for which previous estimates obtained by manual calculation of sulfide area in both lavas and enclaves were available (see data and method in Georgatou et al., 2018). In graph e the gabbroic enclave AG1450-Pichincha for which no whole rock chemistry was obtained, has been plotted with an assumed SiO₂ = 50 ± 2 wt% uncertainty.
| Area      | Sample | Methods                      | Amphibole-only | Amphibole-liquid | Clinopyroxene-liquid | Clinopyroxene-only |
|-----------|--------|------------------------------|---------------|------------------|----------------------|--------------------|
|           |        | Reference                    | Ridolfi et al., 2010 | Ridolfi and Renzulli, 2012 | Putirka, 2016 | Neave and Putirka, 2017 | Putirka, 2008 |
| Rock type | N      | T (°C)/30                    | P (kbar)/3,6   | T (°C)/30         | P (kbar)/2,7        | T (°C)/33          |
| Kula      | LP16006| Host Phonotephrite           | 27 (-1.24)(-0.11) | 991-1068          | 9.5-13              | 1011-1090          |
|           |        | Enclave Hb-diortite C        | 28 (-1.0)(-0.11) | 988-1056          | 6.1-12              | 982-1083           |
|           |        | LP16017 Host Phonotephrite   | 9 (-0.59)(-0.44) | 1029-1093         | 9.3-12              | 1056-1089          |
|           |        | Enclave Hornblendeite C      | 15 (-0.38)(-0.21) | 1042-1074         | 9.7-11              | 1068-1093          |
|           |        | LP16056B Host Phonotephrite  | 7 (-0.49)       | 1025-1065         | 9.3-12              | 1056-1092          |
|           |        | Enclave Hornblendeite C      | 34 (-0.65)(-0.47) | 1007-1062         | 7.8-11              | 1049-1092          |
|           |        | Enclave Hb-diortite C        | -               | -                 | ne                  | ne                 |
|           |        | LP16031 Host Phonotephrite   | 7 (-0.14)       | 1040              | 9.3                 | 1069               |
|           |        | Enclave Px-aggregates        | -               | -                 | ne                  | ne                 |
|           |        | LP16001 Host Phonotephrite   | -               | -                 | -                  | -                 |
|           |        | Enclave Hb-diortite C        | -               | -                 | -                  | -                 |
| Konya     | BP16025| Host Andesite                | 9 (-0.09)(-0.72) | 771-945           | 2.7-8.7             | 803-966            |
|           |        | Enclave Gabbro P             | 19 (+0.05)(-0.78) | 884-943           | 5.9-9.3             | 909-962           |
|           |        | BP16007 Host Andesite        | 6 (+0.91)(+1.42) | 877-962           | 3.6-3.9             | 848-934           |
|           |        | BP16065 Host Andesite        | 17 (+1.17)(-1.41) | 822-1001         | 0.4-8.5             | 814-965          |
|           |        | Beydagı LP16036 Host Andesite | 11 (+0.79)    | 841-1015          | 6.4-11              | 951-992          |
|           |        | Enclave Hb core              | 22 (+0.71)(-1.13) | 810-944            | 0.4-7.4             | 839-955          |
|           |        | El AG14015A Host Andesite    | 8 (+0.29)(-0.4)  | 762-871           | 0.3-3.6             | 784-861          |
|           |        | Reventador AG14015A Host Andesite | (+0.41)(+1.0) | 947-974         | 4.8-10              | 929-976          |
|           |        | Pichincha AG14050 Host Andesite | (+0.96)(-1.16) | 894-944           | 3.2-5.4             | 917-933          |
|           |        | E05015 Host Andesite         | 3 (+0.52)      | 845-959           | 7.3                 | 849-950          |
|           |        | Pyroxinite X                 | -               | -                 | -                  | -                 |

| Area      | Sample | Methods                      | Reference                  | Ortho and Clinopyroxene | Magnetite-Irmenite | Olivine-liquid | Summary                  |
|-----------|--------|------------------------------|----------------------------|-------------------------|-------------------|----------------|--------------------------|
|           |        |                              | Holland and Blundy, 1994  | Putirka, 2008           | Ghiorso and Evans, 2008 | Putirka, 2008 |                         |
| Rock type | N      | T (°C)/40                    | P (kbar)/2,3               | T (°C)/45               | P (kbar)/3,2       | T (°C)/25 | log(Dz)                  |

### Table 3
Summary of T-P(Depth)-ΔNNO estimates derived from different thermo-oxibarometers applied on sulfide hosting silicate minerals occurring in lavas and enclaves.

| Area      | Sample | Methods                      | Value/±                  |
|-----------|--------|------------------------------|--------------------------|
| Kula      | LP16006| Host Phonotephrite           | ΔNNO/0.22                |
|           |        |                              | T (°C)/23.5              | P (kbar)/2.7            |
|           |        |                              | T (°C)/33                | T (°C)/30               | P (kbar)/3.6       |

(continued on next page)
Table 3 (continued)

| Area   | Sample | Methods | Amphibole-Plagioclase | Ortho and Clino-pyroxene | Magnetite-Irmenite | Olivine-liquid | Summary |
|--------|--------|---------|------------------------|--------------------------|-------------------|---------------|---------|
|        |        | Reference | Value/± T (C)/40 P (kbar)/2,3 | T (C)/45 P (kbar)/3,2 | T (C)/25 logO2 | T (C)/25 | Sulfide saturation onset |
|        |        |          | N |        | N |        | N | Depth max (km) | T max (°C) |
|        |        | Enclave | Hbl-diorite C | 14 | 867-925 | 0,8-4,1 | – | – | – | – | 44 ± 13 | 1063 ± 33 |
|        |        | Host    | Phonolite | – | – | – | – | – | – | – | – | – | – |
|        |        |          | Enclave | Hornblende C | – | – | – | – | – | – | – | – | – |
|        |        |          | Enclave | Hornblende C | – | – | – | – | – | – | – | – | – |
|        |        |          | Enclave | Hornblende C | – | – | – | – | – | – | – | – | – |
|        |        |          | Enclave | Hornblende C | – | – | – | – | – | – | – | – | – |
| Konya  | BP16025| Host    | Andesite | 2 | 728-737 | 3-3,1 | – | – | – | – | 31 ± 10 | 966 ± 33 |
|        |        | Enclave | Gabbro P | – | – | – | – | – | – | – | – | – | – |
|        |        | BP16007| Host    | Andesite | – | – | – | – | – | – | – | – | – | – |
|        |        |          | Enclave | Hbl core | – | – | – | – | – | – | – | – | – |
| Beydagi| LP16036| Host    | Trachyandesite | – | – | – | – | – | – | – | – | – | – |
|        |        |          | Enclave | Diorite C-P | – | – | – | – | – | – | – | – | – |
| El Reventador | AG14015A | Host | Andesite | – | – | – | – | – | – | – | – | – | – |
|        |        |          | Enclave | Hbl-megacryst C | – | – | – | – | – | – | – | – | – |
|        |        |          | AG14015B | Host | Andesite | – | – | – | – | – | – | – | – | – |
|        |        |          | AG14013 | Host | Andesite | – | – | – | – | – | – | – | – | – |
|        |        |          | AG14050 | Host | Andesite | 8 | 833-899 | 0,6-3,4 | – | – | – | – | 19 ± 10 | 944 ± 23 |
|        |        |          | Enclave | Gabbro C-P | 1 | 869 | 2,4 | – | – | – | – | 26 ± 10 | 959 ± 23 |
|        |        | E05015 | Host | Andesite | – | – | – | 2, | 887-899, | 5,2-5,5, | – | – | – | – | 26 ± 10 | 899 ± 45, |
|        |        |          | Enclave | Gabbro P | – | – | 2* | 901-911* | 5,9-6,1* | – | – | – | – | 26 ± 11 | 1009 ± 28* |
|        |        |          | Pyroxenite X | 6 | 855-921 | 4,4-6,3 | – | – | – | – | 26 ± 7 | 921 ± 45, |
|        |        |          |          | – | – | – | – | – | – | – | – | – | – | 1048 ± 28* |

The letters C, P and X after the rock type description of enclaves, correspond to Cumulate, Plutonic or Xenolith and indicate the enclave’s origin (see Electronic Appendix A). Values followed by an (*) correspond to crystals that showed apparent textural equilibrium and for which the predicted composition of the crystals based on the T-P models was correct but that fall outside of the strict Kd equilibrium values and are characterised 0.41 < Kd < 0.5 for amph-liq, 0.31 < Kd < 0.4 for cpx-liq, 0.24 < Kd < 0.27 for oliv-liq and 0.4 and 0.9 < Kd < 0.5 and 1 for opx-cpx (depicted in Figs. 7 and 8 by more transparent symbols). Where ne is indicated, it corresponds to compositions not in equilibrium. For the complete dataset see Electronic Appendix D.
Fig. 7. Thermobarometry results of host lavas and enclaves for the different study areas; a-d) pressure-temperature-$\Delta$NNO graphs based on amphibole-only composition, e) pressure-temperature graph based on amphibole-liquid, f) amphibole-only and amphibole-liquid pressure correlation and g-h) clinopyroxene-only temperature correlation to clinopyroxene-only and -liquid pressure. The T-P-$f_2O_2$ meters applied and the equations are indicated in the bottom left corner of the graph whereas the uncertainties are included in the axis names and indicated as a cross in the top right part of the graph. Note that for graphs (e-f) and (h) all measurements pass the condition of apparent textural equilibrium and for which the predicted composition of the crystals based on the T-P models was correct, see precise KD values on graphs. T from graph b and P from Putirka, 2008 using clinopyroxene-only plus the $H_2O$ content of the liquid (here equal to 6 wt%).
5.2. The effect of magma composition on sulfide saturation

Our results suggest that sulfide abundance (expressed as area %, based on the Qemscan® analysis) depends on the composition of the enclaves and lavas (Fig. 6a-b). Sulfides are more abundant (0.01–0.23%) and generally larger (up to 100 μm) in enclaves compared to sulfides found in the more evolved host lavas (0.001–0.03% and up to 50 μm, respectively). Additionally, sulfides are more abundant in mafic cumulate-enclaves (SiO₂ < 46 wt%) and lavas (SiO₂ ~ 47 wt%) compared to more evolved-felsic enclaves and lavas (SiO₂ > 55 wt%) (Fig. 6a). These observations agree with previous petrographic studies on sulfide size and abundance, using point counting techniques (Chang and Audétat, 2018; Collins et al., 2012; DeWaal and Clark, 1975; Dromgoole and Pasteris, 1987; Guo et al., 1999; MacRae, 1979; Shaw, 1997; Zajacz and Szabó, 2003). In contrast, studies of sulfide inclusions found in MORB lavas (Czamanske and Moore, 1977) indicate average sizes of 55 μm (but up to 220 μm) and abundance of 0.004% while in more evolved lavas of arc settings (Georgatou et al., 2018; Stavast et al., 2006) sulfides have smaller size (20–50 μm) and abundance between 0.001 and 0.002%. Although the lower preservation of sulfides in the lava matrix is due to higher oxidation and water contents of the system before and during eruption (e.g. Chen et al., 2021; Stavast et al., 2006), the presence of multiple sulfide inclusions hosted by phenocrysts occurring in the enclaves compared to the usually singular occurrence of a sulfide in a phenocryst of the lava, indicates that the conditions under which the phenocrysts of the lava crystallise are less favourable to...
sulfide saturation processes. This observation, coupled with the fact that lavas are more evolved and felsic relative to the enclaves (Table 3, Fig. 5d-e), suggests a lower degree of sulfide saturation with magmatic evolution, both in lavas and enclaves (Fig. 6a).

In addition to sulfide abundance sulfide composition also seems to depend on magmatic evolution (Fig. 6d-f). Cu-poor/Ni-rich sulfides (up to 22 wt% Cu and 17 wt% Ni) occur in mafic hornblendites/hornblende-rich cumulates (SiO$_2$ < 46 wt%) whereas Cu-rich sulfides (up to 72 wt% Cu and 9 wt% Ni) occur only in evolved andesitic-dacitic lavas (SiO$_2$ > 58 wt%) and enclaves (SiO$_2$ > 50 wt%; maximum of 65 wt% Cu and of 1.2 wt% Ni) (Fig. 2c, Fig. 6d). However, we have found gabbroic enclaves from Pichincha (E05015) and Beydagi (LP52B2) with sulfides reaching up to 65 wt% of Cu in the enclaves and 33 wt% in the lavas. Results from other studies reporting EPMA and LA-ICP-MS sulfide analyses correspond to similar lithologies confirm our findings (e.g., Georgatou and Chiaradia, 2020; del Campo et al., 2019; Tang et al., 2018). Nonetheless, it is important to keep in mind that, although sulfides show higher Cu contents, sulfide abundances in more evolved rocks are lower compared to more primitive rocks. As a result, the bulk Cu, Ni and Ni/Cu sulfide contents decrease with magmatic evolution (Fig. 6f). This also explains why sulfides hosted in MORB glass of the FAMOUS region decrease in bulk Ni + Cu content with the increase of TiO$_2$ and FeO content in the glasses, passing from bulk Ni + Cu of 20–26 wt% in more primitive glasses to <10 wt% in more differentiated glasses (Czamanske and Moore, 1977).

Sulfides occurring within enclaves are hosted by the main mineral phase of the enclave (e.g., amphibole for hornblendeitic cumulates, plagioclase for dioritic cumulates, pyroxene and magnetite for gabbroic enclaves) suggesting that sulfide saturation occurs under broad compositional P-T-fo$_2$ ranges of fractionating magmas. Nevertheless, a greater sulfide abundance is noted in hornblendeitic cumulates and in enclaves carrying amphibole and magnetite. This is likely linked to the crystallisation effect of those minerals on sulfide saturation which is also observed in the lavas with most sulfides being either hosted by or associated with amphibole crystals followed by magnetite, plagioclase and pyroxene (Fig. 2c). These observations confirm the known effect of magnetite crystallisation on sulfide saturation (e.g., Jenner et al., 2010) and possibly indicate a similar, if not even more significant, role of amphibole crystallisation which could be compared to the effect of garnet fractionation on early sulfide saturation (Chen et al., 2020; Cox et al., 2019; Tang et al., 2018) and should be the object of further investigation. Additionally, similar sulfide textures are observed for similar types of enclaves with the two examples of preserved sulfide globules within phenocrysts and interstitial and/or intergranular sulfides within glass and between other minerals. The first sulfide texture is mostly seen in more evolved enclaves (e.g., dioresites) while the latter texture (interstitial/intergranular) is seen in mafic cumulates (also observed by Collins et al., 2012). This latter texture confirms the early timing of entrapment of sulfide melt in deep cumulates.

Our results suggest that even though there is obvious variability in the compositions of all the enclave-bearing rocks, sulfide abundance, composition, occurrence and texture are similar for enclaves characterised by similar lithology, composition and origin, indicating therefore the existence of distinct processes controlling sulfide saturation.

5.3. Temperature-depth-fo$_2$ variation at the onset of sulfide saturation

The use of one oxybarometer (amphibole-only) and at least two thermobaroimeters (amphibole-only and/or -liquid), crosschecked with additional methods wherever possible (e.g. clinopyroxene-liquid, clinopyroxene-only, amphibole-plagioclase), indicates that T-P-fo$_2$ (ΔNNO) conditions upon sulfide saturation in lavas and enclaves vary between the different study areas with differences greater than the uncertainty of the methods (Figs. 7, 8, Table 3). More specifically, estimates derived from mineral analysis of sulfide-hosting silicates in the lavas indicate the following T$_{max}$ /P-/depth$_{max}$ -ΔNNO$_{min}$ transition (Fig. 8a), starting with the phono-tephritic lavas of Kula (T = 1174 °C, P = 18 kbar/65 ± 5 km, ΔNNO = (−1.24)), passing to the andesitic lavas of El Reventador (T = 1019 °C, P = 13 kbar/47 ± 10 km, ΔNNO = 0.25), and then to basaltic-andesitic lavas of Konya (T = 1001 °C, P = 8.7 kbar/39 ± 10 km, ΔNNO = (−0.1)), and finally to the andesitic lavas of Beydagi (T = 956 °C, P = 7.4 kbar/27 ± 10 km, ΔNNO = 0.71), and andesitic-dacitic lavas of Pichincha (T = 1009 °C, P = 7.2 kbar/26 ± 10 km, ΔNNO = 0.96). A similar variation is also noted in the T-P-ΔNNO values corresponding to sulfide-hosting silicates occurring in enclaves (Fig. 8b) with values varying between enclaves of the same study area depending on the lithology (Table 3). Hornblendeitic cumulates (LP-17, LP56B-Kula and AG14015B-El Reventador) show the highest T-P values, while gabbroic (E05015, AG14050-Pichincha) and dioritic (LP36-Beydagi) enclaves present the lowest T-P values. These estimates suggest that sulfide saturation occurred already in the upper mantle at Kula and in the lower and upper-crust at El Reventador, Konya, Beydagi and Pichincha.

Considering the minimum pressure/depth values inferred from sili cate phenocrysts hosting sulfides and occurring in lavas and enclaves (Table 3), based on the exact occurrence of sulfides within a crystal (core to rim, Electronic Appendix D), it is noteworthy that Kula and El Reventador indicate a lack of shallow sulfide saturation below 4.6 kbar (~17 km) and 4.8 kbar (~17 km), respectively.

Although previous T-P estimates on the same study areas reported for El Reventador and Kula volcanoes agree with our results (Gutzner et al., 2013; Ridolfi et al., 2008), T-P$_{max}$ estimates from past studies on sulfide-bearing host lavas and enclaves belonging to other study areas may vary even between similar lithologies (Du et al., 2014, Chang and Audétat, 2018, Upton et al., 2000, Rottier et al., 2020; see summary of these results in Table D.7). Some of the parameters that could explain the variability in the depth at which sulfide saturation occurs and the evolution of sulfide saturated magmas for the different study areas, may include geodynamic setting and magma composition.

There is no obvious difference in the maximum depth of sulfide saturation between areas characterised by subduction and post-subduction setting, varying from 26 to 47 ± 10 km and 1014–1019 °C (Fig. 9a-b). In contrast, the onset of sulfide saturation in the Kula volcanic province (intraplate volcanism) occurs deeper than in any other area, at 65 ± 5 km depth and 1174 °C (Fig. 9c). Among the possible factors that could account for this difference between intraplate and subduction/post-subduction settings are variability in crustal thickness, preservation, and magma composition. Studies including areas with variable crustal thickness show that thicker continental crust is likely to promote early sulfide saturation due to higher average pressures of magma evolution (Cox et al., 2019). The deeper magma evolution in the thick crust may promote early sulfide saturation due to the effect of pressure on sulfide stabilisation even under relatively oxidised conditions (Majuschkin et al., 2016) and therefore at low Cu contents of mafic rocks compared to those associated with thin arcs (Chiaradia, 2014). However, in this study the sulfide saturation depth difference cannot be related to crustal thickness variation, since all investigated areas are characterised by a crust thicker than 30 km (Kula and Beydagi ~30 km, Konya ~38 km, 2 km for Kula and El Reventador up to ~50 km: Guillier et al., 2001, Araujo, 2016, Mutlu and Karabulut, 2011). A more likely explanation is that areas characterised by rapid magma ascent (like in intraplate volcanism) are expected to better preserve sulfide-bearing mineral phases and thus also maintain the record of higher P-T conditions during sulfide saturation.

More importantly, our results indicate a clear correlation between the magma composition of enclaves and lavas and the maximum T-P-depth-fo$_2$ of sulfide saturation. In fact, alkaline mafic and less oxidised
magmas of Kula became saturated in sulfides in the upper mantle (Figs. 8c, 9c) while calc-alkaline more evolved and oxidised-felsic magmas of the other study areas became saturated in sulfides starting at the expected depth of the MASH zone and upwards in the crustal column (Figs. 8c, 9a-b). Rezeau and Jagoutz (2020) have shown that the predominant factors controlling the timing of sulfide saturation are the liquid lines of descent in thin arcs (<25 km) and the pressure of differentiation in thicker arcs (>25 km) compared to the crustal thickness and fO2 of the melt. Our findings do not exclude the potential of all magmas to start to saturate in the mantle, however only magmas that ascend rapidly without having the time to stall at shallower crustal levels may be able to retain this information, possibly due to the increasing solubility of sulfide with decreasing pressure (Matjuschkin et al., 2016). This may likely be the case for Kula, where asthenospheric upwelling, due to the formation of a tear-related slab window has been reported (Rabayrol et al., 2019b) resulting in minimum magma ascent rate of about 4–11 days from the Moho to the surface (Grutzner et al., 2013). Lastly, it is worth mentioning that other parameters, like the dip and rate of slab subduction, may also play a role. However such considerations are beyond the scope of the present study.

5.4. Sulfide metal retention and implications for metal enrichment

Sulfides are found in a wide compositional range of lavas (SiO2 = 47–63 wt%) and enclaves (SiO2 = 41–55 wt%) formed at variable depths, from the upper mantle (63 ± 5 km) to the upper crust (<1 km), suggesting that sulfide saturation may occur over a large range of magma compositions and T-P conditions (Fig. 8). Based on the above observations, we expect to find higher amounts of Cu-poor sulfides in magmas differentiating at depth (high T-P/low fO2) compared to lower amounts of Cu-rich sulfides occurring at shallower crustal levels (low T-P/high fO2). The Ni/Cu values of sulfides increase with decreasing fO2 (ΔNNO) and increasing T and P (Fig. 8d-f). In contrast, the sulfide abundance decreases with magmatic evolution and, thus, the bulk Ni/Cu and of sulfides decreases gradually as the magma differentiates at shallow crustal levels coeval with a Cu (and Ni) depletion of the bulk
Despite being sulfide-rich (0.23 sulfide area %), hornblende-rich cumulates of Kula formed at upper-mantle levels have no detectable whole rock Cu contents based on reconstructed (from Qemscan® and EPMA analysis) and not directly measured composition. We have calculated that this corresponds to up to 32 ppm of Cu$_{med}$ and 5.6 ppm of Ni$_{med}$ in sulfides compared to sulfides occurring in the host lavas that account for 0.005 sulfide area % sequestrating 1.9 ppm of Cu$_{med}$ and 7.2 ppm of Ni$_{med}$ (Figs. 6, 9c, Table A.1). In contrast, the mid-crustal Pichinchina gabbroic enclave contains 256 ppm whole rock Cu (measured) and 99 ppm (calculated based on Qemscan®). This enclave has 0.01 sulfide area %, sequestrating up to 113 ppm Cu$_{med}$ and 1.5 ppm of Ni$_{med}$ in sulfides compared to the host lava that only has 40 ppm Cu and 0.001 sulfide area % containing 0.74 ppm of Cu$_{med}$ and 0.003 ppm of Ni$_{med}$ (Figs. 6, 9a, Table A.1). Based on the above volumetric calculations of metal retainment in sulfides, it is important to mention that there is more than 100 ppm of Cu difference between the measured (256 ppm) and the calculated (113 ppm) Cu content for the unusually Cu-rich gabbroic enclave-E05015. Since Cu has no textural indication of sulfide dissolution or oxide-replacement (where sulfides may have been consumed by later hydrothermal fluids) our calculations (113 ppm) should not be far off. Such a difference between the calculated/reconstructed and measured Cu contents that sulfides sequestrate, have been reported before (Borrok et al., 1999). This could be a result of not accounting for the Cu content, of sub-micron size tiny sulfide inclusions or even other mineral phases, like silicates or melt inclusions (e.g. amphibole >200 ppm, plg = 400–500 ppm, Pilavó frontal-arc volcano proximal to Pichinchina in Ecuador, Chiariadía et al., 2012). Nevertheless, it has to be noted that such methodology may not be the best way to calculate bulk Cu contents.

Most importantly, the above results suggest that sulfide-rich cumulates at depth can retain significantly more Cu and Ni compared to sulfides in their host lavas, resulting in an early and continuous Cu depletion which justifies the depletion in Cu seen in the bulk lavas due to the compatible behaviour of Cu (Chiariadía, 2014, Fig. 9). Noteworthy are the gabbroic Cu-rich enclaves of Pichinchina, formed at shallower crustal levels, which retain an even higher Cu amount in the sulfides compared to mafic cumulates, thus reaching unusually high Cu whole rock contents (E05015–256 ppm) compared to the whole rock content of the host lavas in which the enclave was found (40 ppm). A similar Cu enrichment is observed for Cu-rich pyroxene-cumulates reflecting the Cu-poor nature of arc magmas (Chen et al., 2020).

Interestingly, these gabbroic plutonic enclaves, found in Pichinchina (E05015, AG14050) and Beydagi (LP36, LP52B), show petrographic and chemical evidence of mixing (e.g., orthopyroxene reverse zoning and macroscopic mingling features, Electronic Appendix A) with Cu-rich sulfides not only hosted by amphibole but even other mineral phases, like silicates or melt inclusions (e.g., amphibole >200 ppm, plg = 400–500 ppm, Pilavó frontal-arc volcano proximal to Pichinchina in Ecuador, Chiariadía et al., 2012). Nevertheless, this is late sulfide saturation of Cu-rich sulfides which may have been caused by magma mixing with Cu-rich magmas at shallow crustal levels.

It is worth mentioning that lavas from Kula and El Reventador, that saturated in sulfides at deep levels in the upper mantle and lower crust (65 ± 5 and 47 ± 10 km, respectively), are not associated with any known mineralisation (Fig. 9a, c). This agrees with the general understanding of the metal-barren character of areas characterised by intra-plate volcanism (like for the case of Kula). A recent study (Chen et al., 2021) on sulfide-bearing basaltic andesites from a barren back-arc basin in the southern Okinawa Trough (crustal thickness ~ 11 km) indicates that the onset of sulfide saturation occurred at the base of the crust at 1042 ± 10°C and 3.2 ± 0.7 kbar (11.4 ± 2.7 km). Although, the depth at which sulfide saturation occurs in Reventador (47 ± 10 km) is significantly deeper, it is noteworthy that in both areas sulfide saturation started in the MASH zone. In contrast, magmas from the Konya volcanic province, associated with Cu-porphry (Doganbey) and Au-epithermal (Inlice) deposits, and from Beydagi, associated with the large porphyry Au deposit of Kisiladag, record sulfide saturation at mid-crustal levels (32 ± 10 km and 27 ± 10 km, respectively). Pichinchina Quaternary volcano is only spatially and not temporarily associated with economic deposits and therefore it can only be used as proxy for older mineralisation in the area (late Miocene Llurimagua/Junín Cu-Mo porphyry deposit); yet magmas in Pichinchina record sulfide saturation at similar crustal depths (27 ± 5 km) as in Konya and Beydagi. The latter agree with previous studies on volcanic systems associated spatially and temporally with porphyry Cu (± Au) deposits where sulfide saturation occurs at depth max < 29 ± 5–13 km (Cerillos and Santa Rita, New Mexico; Chang and Audétat, 2018; Stiavnica, Slovakia: Rottier et al., 2020; Tongling, China: Du et al., 2014, Du and Audétat, 2020).

The fact that lavas from Kula and El Reventador lack any significant record of shallow level crystallisation (< ~17 km) is consistent with those magmas ascending rapidly from depth without forming crustal reservoirs at shallow levels of 5–10 km (the expected depth of parental magma reservoirs associated with porphyry mineralisation, Burnham, 1979). As a result, this prevents magma differentiation and H$_2$O saturation, both required to form porphyry deposits, usually at depths <5–6 km. This implies that the depth at which sulfide saturation ends plays an equally important role as the depth marking the onset of sulfide saturation, because it will determine whether metals are available to fluids before the magma reaches water saturation.

Overall, the findings of this study indicate that sulfide saturation in convergent margins occurs from deep to shallow crustal levels, recording both early and late sulfide saturation stages. In contrast, back-arc and intraplate settings, start to saturate in sulfides deep/early with no record of shallow/late saturating sulfides. Previous models studying sulfide saturation by bulk PGE systematics have proposed that late sulfide saturation is beneficial for ore formation (e.g., Park et al., 2015). However, the correlation of late sulfide saturation occurring at shallow crustal levels and porphyry deposit formation, seems to be more a consequence of the fact that no shallow magma chamber is built up in such geodynamic settings rather than that there is no sulfide saturation. Thus, sulfide saturation seems to follow the evolution of the magma. Most importantly, when magma differentiation occurs, sulfides are formed throughout the life of the magmatic system from deep to shallow suggesting that porphyry deposits can form even with the low residual amounts of chalcopybite metals not captured by sulfides. In order to investigate further the impact of the depth of the onset of sulfide saturation and of the corresponding bulk metal contents sequestered by deep cumulates on magma fertility, more thermobarometry results coupled with sulfide and bulk trace element geochemistry are needed on magmas from different geodynamic settings (including intraplate settings).

6. Conclusions

We carried out detailed petrography combined with mineral and bulk rock chemistry and with thermo-oxibarometry of sulfide-hosting silicates in amphibole-, plagioclase- and pyroxene-rich enclaves and in
their host lavas in areas characterised by diverse geodynamic settings and magma compositions. The results suggest that sulfide abundance, occurrence, and composition depend on magma composition and P-T-O\textsubscript{2} conditions of magma differentiation. Sulfides are 2 to 3 orders of magnitude more abundant in mafic enclaves (up to 0.23 area %) than in more evolved-felsic enclaves (up to 0.01 area %) and host lavas (up to 0.001 area %). Overall, sulfide saturation occurs at variable depths both in the upper mantle and within the crust. In the upper mantle (61–7 km) sulfides have been identified in mafic hornblende-rich cumulates (SiO\textsubscript{2} < 45 wt%) from an intraplate alkaline volcanic system, recording high temperature and pressure conditions (17 kbar and 1160 °C) and low ΔNNO (< −1). In contrast, in the crust of syn- and post-subduction settings sulfides occur in many enclave types, including dioritic and gabbroic enclaves (≥ 55 wt% SiO\textsubscript{2}), which record variable crustal depths (< 7.3 kbar ± 26 ± 10 kbar), lower temperatures (< 950 °C), and higher P-T-O\textsubscript{2} conditions (ΔNNO > +1). Deep sulfide-rich cumulates are characterised mostly by high sulfide abundance (up to 0.23% area) of Cu-poor sulfides (pyrrhotite with Cu median 0.01 wt% and Ni/Cu values ≤0.65) compared to shallower enclaves which are characterised by a lower sulfide abundance (0.001% area) of Cu-rich sulfides (chalcopyrite to bornite with Cu median = 50 wt% and Ni/Cu content <25).

Based on their volumetric proportions, mass balance calculations suggest that sulfides can retain 4.8–32 ppm of Cu and 0.19–5.6 ppm of Ni in deep magmatic cumulates, 1.2–8 ppm of Cu and 0.01–0.15 ppm of Ni in their host mafic lavas, 13–113 ppm of Cu and 0.53–1.5 ppb of Ni in late gabbroic enclaves, and 0.74 ppm of Cu and 0.003 ppb of Ni in their host felsic lavas. Thus, this indicates that the bulk Ni/Cu median ratio of the sulfides decreases with sulfide abundance and with magmatic evolution. Considered altogether, while magmas in convergent margin settings associated with porphyry deposits become saturated in sulfides from deep to shallow crustal levels, the investigated intraplate and back-arc barren magmas display a record only of deep (upper mantle to lower crust) sulfide saturation. This seems to derive from the fact that no shallow sulfide saturation is built up in the latter geodynamic setting, which suggests that sulfide saturation follows the evolution of the magma. Finally, these findings indicate that although sulfides are formed throughout the life of the magmatic system, porphyry deposits can form even with the low residual amounts of chalcophile metals in the residual melt.

Author contribution

AAG and MC designed the project and the methodology. MC carried out petrographic investigation and mineral and bulk analysis on sample E05015. KK carried out all Qemscan\textsuperscript{a} analysis and generated all mineral and elemental maps. AAG carried out petrographic investigation and all other EPMA mineral analysis and bulk chemical analysis. AAG wrote the manuscript with contributions from MC and KK.

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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Appendix A. Supplementary data

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