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How to cite

GEORGATOU, Ariadni Afroditi, CHIARADIA, Massimo, KLAVER, M. Deep to Shallow Sulfide Saturation at Nisyros Active Volcano. In: Geochemistry, geophysics, geosystems, 2022, vol. 23, n° 2, p. e2021GC010161. doi: 10.1029/2021GC010161

This publication URL: <https://archive-ouverte.unige.ch/unige:159090>

Publication DOI: [10.1029/2021GC010161](https://doi.org/10.1029/2021GC010161)

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Geochemistry, Geophysics, Geosystems®



RESEARCH ARTICLE

10.1029/2021GC010161

Deep to Shallow Sulfide Saturation at Nisyros Active Volcano

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Key Points:

- Magmatic sulfide saturation is triggered at the base of the crust due to the replacement of clinopyroxene by amphibole
- Magmatic sulfide abundance and composition vary according to magma evolution and the *T-P*-depth of magma differentiation
- Increased mafic input followed by magma mingling and enclave disaggregation lead to sulfide dissolution and Cu-enrichment of the magmas

Supporting Information:

Supporting Information may be found in the online version of this article.

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Citation:

Georgatou, A., Chiaradia, M., & Klaver, M. (2022). Deep to shallow sulfide saturation at Nisyros active volcano. *Geochemistry, Geophysics, Geosystems*, 23, e2021GC010161. <https://doi.org/10.1029/2021GC010161>

Received 24 SEP 2021

Accepted 24 DEC 2021

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Abstract We report new petrographic and geochemical observations on magmatic sulfides occurring in different enclave types, including hornblende and/or clinopyroxene-rich cumulates, and in the host lavas, in Nisyros (South Aegean volcanic arc). We discuss our findings in the context of pre-existing petrological and thermobarometry studies. Our results indicate that sulfides become less abundant and Cu-richer (Cu_{median} values) with magma differentiation at progressively lower pressure/*P*-temperature/*T*-depth conditions. Starting with high *T-P* sulfide-free pillow lavas and wehrlitic cumulates still representing a sulfide undersaturated system, passing to high *T* and lower *P*, deep-forming sulfide-rich and hornblende-rich gabbroic enclaves (SiO₂ = 53–55 wt.%, 4–5 × 10^{−5} area %, Cu = 260 μg/g) at the base of the crust (~25–30 km), then to clinopyroxene-rich gabbroic micro-cumulates (2–3 × 10^{−5} area %, Cu = 570 μg/g) forming in shallower crustal levels (~10 km), then to more evolved sulfide-poor hybrid enclaves (SiO₂ = 56–70 wt.%, 1 × 10^{−5} area %, Cu = 602 μg/g), and finally to even more sulfide-poor rhyodacitic host lavas (SiO₂ = 66–76 wt.%, <0.5 × 10^{−5} area %, Cu = 6.4 wt.%) differentiating at even shallower crustal levels (~7 km). Sulfide-free quenched basaltic andesitic enclaves differentiating near surface levels, carry no textural evidence of pre-existing magmatic sulfides suggesting that the system returned to a sulfide-undersaturated state. Finally, we point out two important processes for sulfide evolution, a reaction replacement of clinopyroxene by amphibole observed in the deep-forming hornblende-rich gabbroic enclaves triggering the onset of sulfide saturation, and an increased mafic input followed by magma mingling and enclave disaggregation leading to sulfide dissolution and Cu-enrichment of the magmas.

Plain Language Summary In this study we investigate the occurrence and chemistry of magmatic sulfide minerals found within volcanic lavas, and within smaller rock inclusions (-enclaves), of Nisyros active volcano, located in the Aegean arc. Sulfides are the main repositories of Cu and other precious metals and thus determine their availability in the residual ascending melt which in turn affects the potential of a system to produce an economic ore deposit. Meanwhile, enclaves offer a unique possibility to “access” different parts of a plumbing system, as they preserve the information corresponding to a specific depth range. Our results are discussed in the context of previous studies which have extensively studied the plumbing system of Nisyros. Understanding what triggers the formation of these sulfides, as well as how do they evolve from the roots to the surface of a well-studied plumbing system can help to further constrain metal transport and concentration through the crust. Our results suggest that sulfides: (a) form at the base of the crust with the first occurrence of amphibole, (b) become less abundant and Cu-richer with magma evolution at progressively lower crustal depths, and (c) dissolve, thus causing the release of metals back in the system.

1. Introduction

Recent studies have shown that magmatic sulfide phases are present in a variety of rocks corresponding to diverse geodynamic settings, lithologies, and magma compositions (Z. Chen et al., 2021; Costa et al., 2021; Georgatou & Chiaradia, 2020; Mandon et al., 2021; Rottier et al., 2020). It thus appears that many magmatic systems have the potential to reach sulfide saturation at some point during their lifespan. Even though, sulfide saturation at depth, does not seem to have a direct negative impact on the potential to produce magmatic-related deposits like porphyry deposits (e.g., Du & Audétat, 2020), not all systems that appear to have the necessary prerequisites eventually form an economic deposit (e.g., Richards, 2003). In fact, specific factors like the nature and amount of sulfides saturated, as well as the timing of sulfide saturation relative to volatile saturation, can still play a crucial role (e.g., Park et al., 2021). Meanwhile, it has been suggested that assimilation of sulfide-rich cumulates at shallow crustal levels could result in partial sulfide-dissolution making metals available to the magma and its exsolving fluids (e.g., Bai et al., 2020; Nadeau et al., 2010; Park et al., 2019; Wilkinson, 2013). Because of the strong

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affinity of chalcophile and siderophile element (e.g., Cu and Au) for sulfide melt compared to the silicate melt, sulfide-bearing deep-forming enclaves/cumulates are expected to be Cu-rich, explaining the compatible behavior of Cu in arc settings (Chiaradia, 2014; Cox et al., 2019; Lee et al., 2012). Although, such sulfide-bearing enclaves and cumulates have been reported in a number of settings such as convergent margin (Santa Rita and Cerillos, USA-Chang & Audétat, 2018, Camp Creek and Sullivan Buttes, Arizona-K. Chen et al., 2020, Tongling, China-Du & Audétat, 2020, and El Reventador, Ecuador-Georgatou et al., 2021) and within-plate volcanoes (Kula, Western Turkey-Georgatou et al., 2021) the above-mentioned dissolution scenario is still debated. Constraining what triggers the formation of magmatic sulfides in such enclaves, as well as how do they evolve from the roots to the surface of a well-studied plumbing system can help to further constrain metal transport and concentration through the crust.

To date, the most reliable study material for the investigation of deep magmatic processes such as, the one mentioned above, are magmatic enclaves occurring in volcanic products of arc magmas (Annen et al., 2006; Erdman et al., 2016; Melekhova et al., 2017). Enclaves can provide a vertical understanding of the evolution of sulfide-saturated magmas within the plumbing system. More specifically, quantitative modeling studies have pointed out that mafic hornblende/clinopyroxene-rich enclaves/cumulates can be Cu-rich (up to 1,000 $\mu\text{g/g}$ Cu bulk; K. Chen et al., 2020) and contain significant amounts of sulfides and thus of metals (up to 1–2 wt.% of Cu stored in sulfides; Du & Audétat, 2020). Thermobarometry results on sulfide-bearing enclaves and cumulates indicate that, in evolved magmas in convergent settings, sulfide saturation usually occurs in the middle crust and extends to shallower levels (e.g., Chang & Audétat, 2018; Du & Audétat, 2020; Georgatou et al., 2021), whereas for more mafic systems related to back-arc and intraplate volcanism, sulfide saturation appears to start already in the mantle and lower-crust and terminate earlier, at mid-crustal level (e.g., Z. Chen et al., 2021; Georgatou et al., 2021). Considering that most porphyry economic deposits are related to felsic rocks and convergent settings (e.g., Richards, 2009; Sillitoe, 2010), this may indicate that the depth of the onset of sulfide saturation may still play a role in the potential of the system to recycle sulfide-saturated magma batches stored at depth.

The primary aim of this study is to investigate the progress of magmatic sulfide saturation from the upper mantle/lower crust to near surface levels through the study of magmatic sulfides in lavas and enclaves of Nisyros volcano (Aegean arc, Greece). Among the factors that make this study area unique are: (a) the wide compositional range of Nisyros volcanic products (basaltic andesites-rhyolites), (b) the variable enclave lithologies, including hornblende and/or clinopyroxene-rich enclaves and cumulates, and (c) the petrological and geochemical evidence for magma mingling between basaltic andesitic and rhyolitic end-members and enclave disaggregation (e.g., Braschi et al., 2014; Francalanci et al., 1995; Klaver et al., 2018; Wyers & Barton, 1989; Zouzias & St. Seymour, 2014). An additional important argument that makes this geological area special is that Nisyros is a well-constrained volcanic system (Dietrich, 2018; Dietrich & Popa, 2018 and references therein) which appears to be barren, with no known associated mineralization. In fact, the backbone of this study is based on previous studies of Braschi et al. (2012, 2014) and recent results by Klaver et al. (2017, 2018) who have extensively investigated the plumbing system of Nisyros and conducted detailed petrographic and geochemical studies. These studies also provided thermobarometry estimates of diverse enclave and cumulate types and of their host lavas. Characterizing sulfide abundances and compositions in Nisyros volcanic products will allow us to assess the possibility that recycling sulfide-rich enclaves and cumulates can make chalcophile elements available to later exsolving fluids, which would in turn control the potential of such a magmatic-hydrothermal system to form an economic deposit.

2. Geology and Volcanism

Nisyros is a hydrothermally active stratovolcano with an 8 km diameter and a 3.6 km wide caldera, located in the easternmost part of the Aegean volcanic arc, 20 km south of the island of Kos, in Greece (Figure 1). The volcanic activity of the region is a result of the northward subduction of the African plate underneath the Anatolian-Aegean microplate (Pe-Piper & Piper, 2005). The volcano is situated on thinned continental crust with the Moho located at an approximate depth of 27 km (Makris et al., 2018). Nisyros is part of the Kos-Nisyros-Yali volcanic system with volcanism starting at 2.7–0.5 Ma with the emplacement of dacitic-rhyolitic domes on Kos Island and continuing with the eruption and deposition of the Kos Plateau Tuff (KPT) at 161 ± 1 ka (Bachmann et al., 2007; Di Paola, 1974; Pe-Piper & Moulton, 2008; Smith et al., 1996). Four major volcanic stages are recognized in Nisyros starting with submarine basaltic to andesitic volcanism including pillow lavas and hyaloclastites (Basal volcanic complex stage, Keller, 1971; Zellmer & Turner, 2007). These were followed by subaerial stratocone

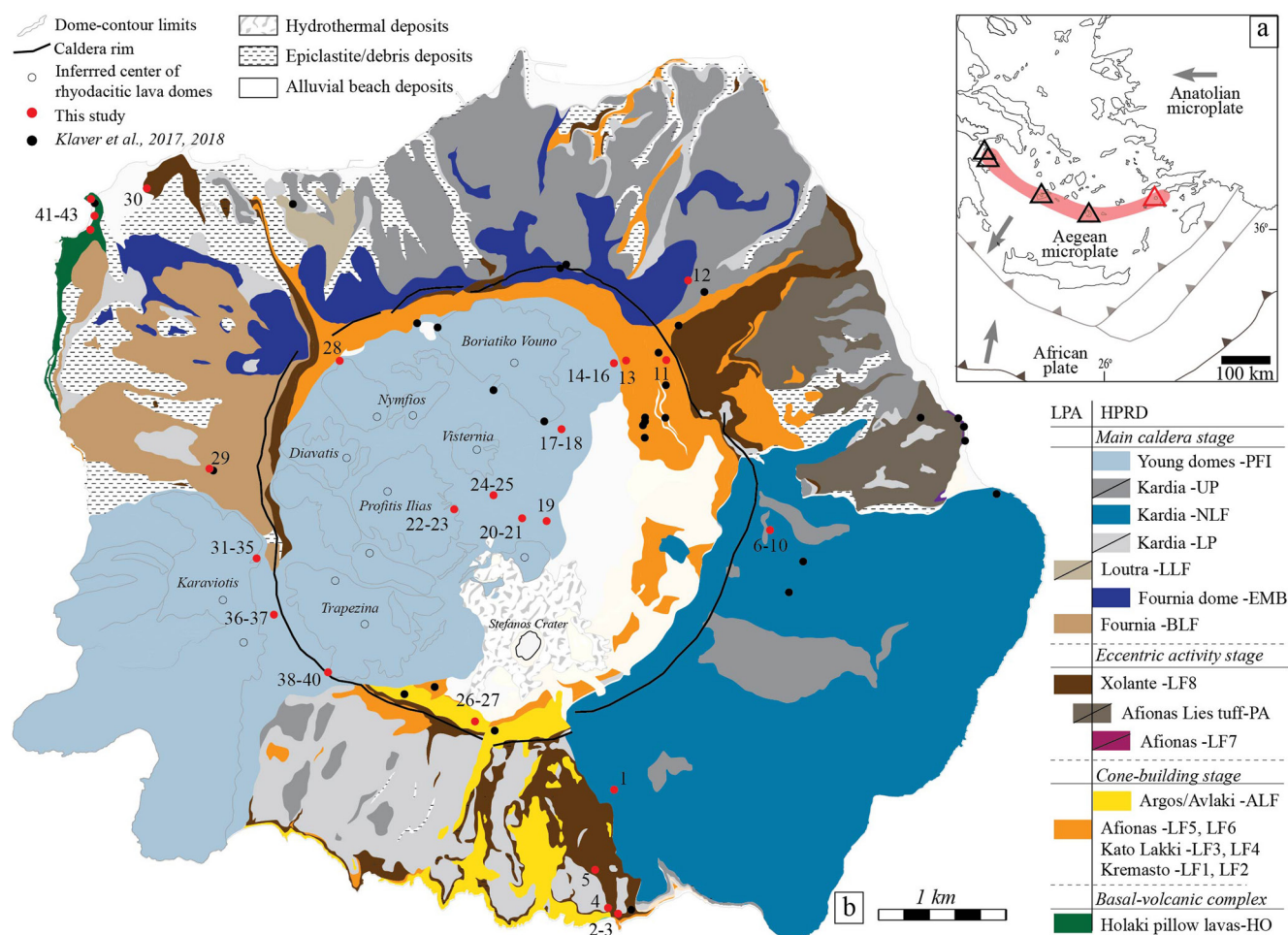


Figure 1. Simplified maps of (a) the present day geodynamism and relative location of Nisyros in the modern Aegean volcanic arc and (b) the geology in Nisyros showing the sampling locations, modified after GEOWARN (2003) and Vougioukalakis (2003). The geological units are presented after Volentik et al. (2005) with the division into an LPA and HPRD suite following Klaver et al. (2017, 2018) in two suites LPA and HPRD. Crossed-out units (LF7, PA, LLF, LP, and UP) were not sampled during this study.

volcanism post-dating the KPT, comprising lava flows, domes and pyroclastic deposits ranging from basaltic-andesites to dacites, now exposed in the caldera walls (Early cone-building stage, Francalanci et al., 1995; Volentik et al., 2005). The continuous alternation of effusive and explosive events during the eccentric activity stage associated with multiple caldera collapses lead to the formation of a complex strato-cone volcano of which the main caldera formed in two main phases. The first phase includes a lower pumice unit and rhyolitic lava flow while the second phase formed an upper pumice unit and lead to extrusion of post-caldera domes and lava flows marking the last magmatic activity recorded at ca. 10 ka (Main caldera formation stage, St. Seymour & Vlasopoulos, 1989, 1992; Volentik et al., 2002). The latter domes occur inside and along the rim of the caldera, and on the NW-volcanic flank and are characterized by mingling processes between evolved magmas indicated also by abundant magmatic mafic enclaves, including cumulates and quenched enclaves (Braschi et al., 2012, 2014; Klaver et al., 2017, 2018; Zouzias & St. Seymour, 2014).

The volcanic products of Nisyros consist of lava flows, domes and pyroclastic deposits that range in composition from basaltic andesite to rhyolite, belonging to a typical calc-alkaline island trend. Based on the crystallinity index, macroscopic mingling-textures and chemistry, the volcanic products of Nisyros have been previously divided in two suites (Klaver et al., 2017). A low porphyritic basaltic-andesitic suite (Figure 2; LPA, phenocrysts <10 vol.%) and a high porphyritic rhyodacitic suite (Figure 3; HPRD, phenocrysts = 20–40 vol.%). The LPA

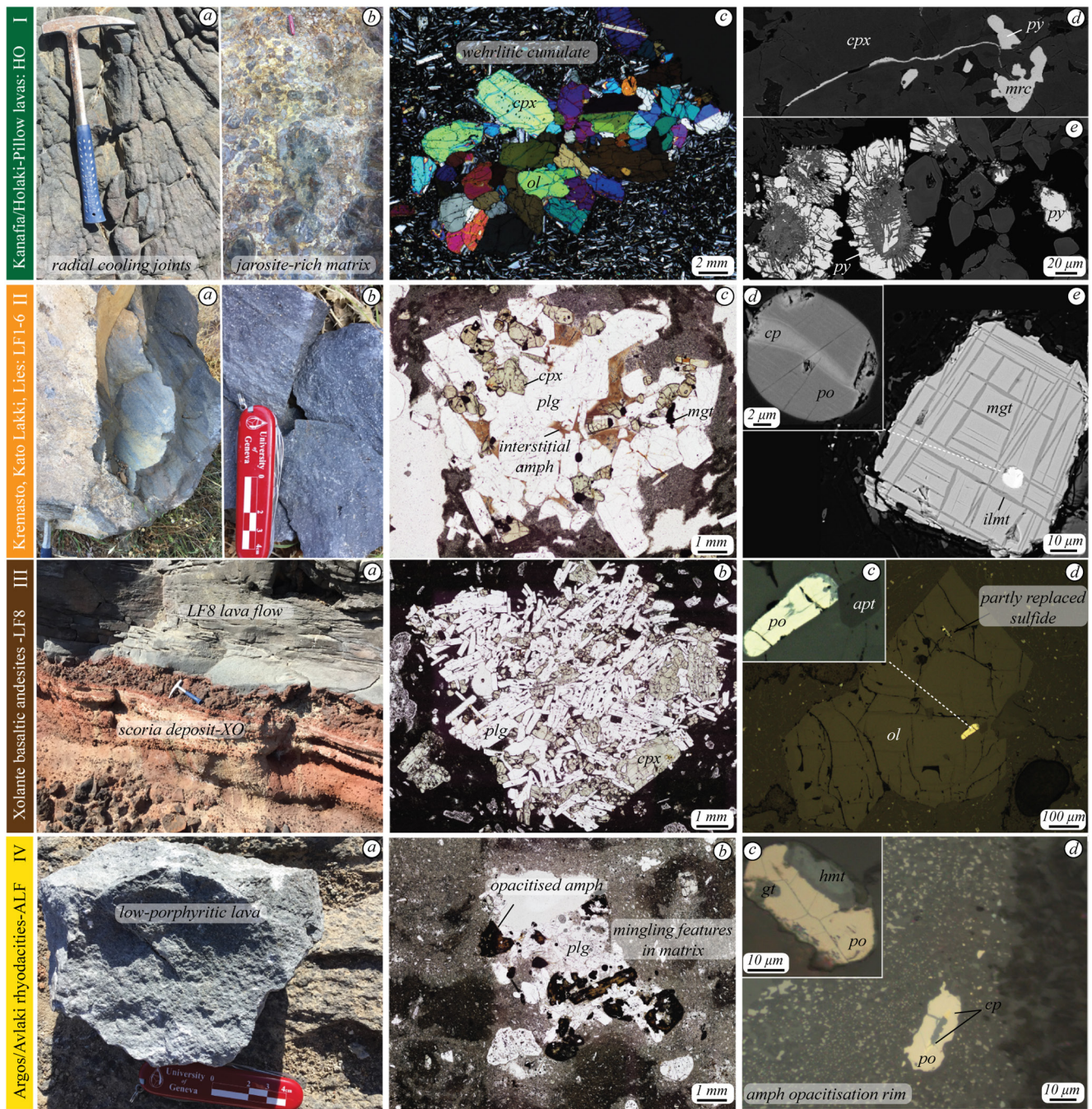


Figure 2. Macro- and micro-photographs of the geology and petrography of the LPA series and of the ALF unit. A representative example of different sulfide-bearing cumulate types present in each unit (I–IVa–b) is shown: Ic-wehrlitic clinopyroxene-rich cumulate, IIc-plagioclase-clinopyroxene-magnetite and interstitial-amphibole cumulate, IIb-clinopyroxene-plagioclase cumulate, and IIb-plagioclase-amphibole-clinopyroxene-magnetite cumulate. Hydrothermal sulfides in the radial pillow lavas (Ia) and cemented jarosite-rich hyaloclastites (Ib) are characterized by space filling radial or vein-like sulfide textures while they are composed of mostly pyrite and marcasite (Id and Ie). In contrast, all other units (II–IV) show only magmatic sulfides, occurring within oxides and silicate phases, composed of mostly pyrrhotite $\pm$ chalcopyrite which often have been partly replaced by goethite (II–IVc–e). Note, the rims of the chalcopyrite band showing a diffusive contact with the pyrrhotite (IIId) and the resorbed textures of sulfides hosted within the amphibole breakdown-rim (IVd).

series includes the Holaki basal-volcanic complex of pillow basaltic-andesitic lavas and hyaloclastites (HO-unit names from Volentik et al. [2005]), the Kremasto, Kato Lakki, and Afionas basaltic andesitic to andesitic lava flows (LF1-LF6), and the basaltic flows of Xolante (LF8), Fournia (BLF), and finally Loutra (LLF). In contrast,

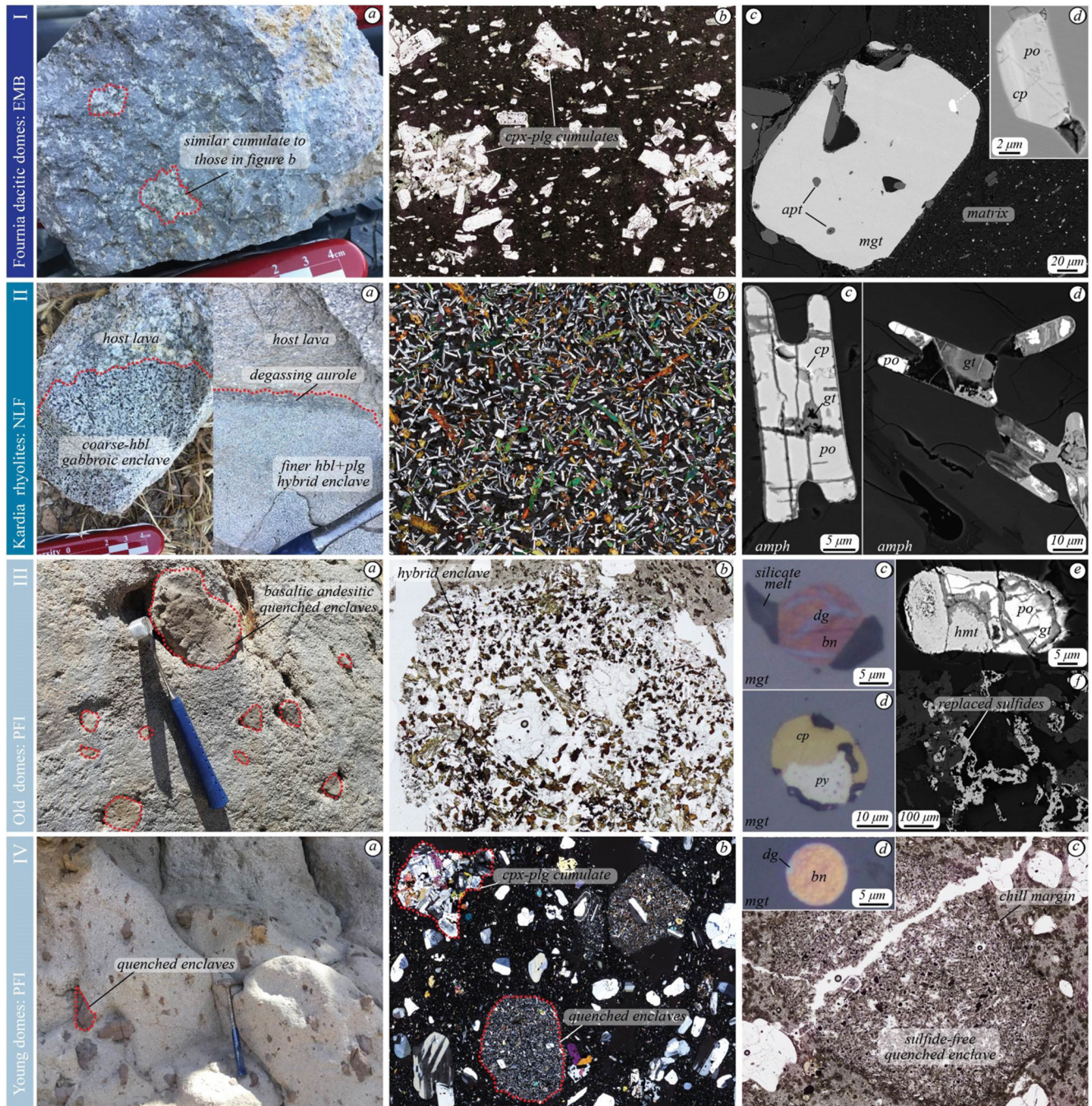


Figure 3. Macro- and micro-photographs of the geology and petrography of the HPRD series. Graphs-b are scans of entire thin sections (5 cm long for scale) showing a representative example of diverse sulfide-bearing cumulate types and sulfide-poor/free quenched enclaves present in each unit (I–Iva): Ib plagioclase-clinopyroxene-magnetite microcumulate, Iib Type-II hornblende-rich gabbroic enclave, IIIb Type-III hybrid enclave showing plagioclase exchange with host lava, and Ivb-c quenched Type-I basaltic andesitic enclave and clinopyroxene-plagioclase cumulate (Ivb). Some enclaves may exhibit hilled margins which reach up to 5 cm in size (hybrid enclave in Iia-right image). Magmatic sulfides in the cumulate enclave of EMB dome hosted by magnetite and composed of pyrrhotite + chalcopyrite (Ic and Id); gabbroic enclave of NLF hosted by amphibole and plagioclase, composed of mostly pyrrhotite ($\pm$ minor chalcopyrite) and showing H-like elongated shapes; hybrid enclave of PFI occurring interstitially are composed of mostly pyrrhotite and are partly or completely replaced by goethite (IIIe and IIIf). While no sulfides have been noted in the quenched enclaves of PFI unit (Ivc) rare Cu-rich sulfides were observed in magnetites of the lavas hosting the hybrid (IIIc and IIId) and the quenched enclaves (IVd).

the HPRD-suite includes, the Afionas dacitic lava flow (LF7), the Fournia/Emporio dacitic domes (EMB), the Nikia rhyolitic lava flow (NLF), which occurs between the Lower and Upper Pumice (LP-UP), and finally the youngest rhyodacitic dome lavas of Profitis Ilias (PFI). In terms of bulk chemistry, the LPA-suite corresponds to mostly medium-K basaltic andesites and andesites, whereas the HPRD series spans from medium- to high-K and from dacitic to rhyolitic compositions. Lastly, an additional unit called the Argos/Avlaki rhyodacitic lava flow (ALF) is grouped in the HPRD suite based on its high-K rhyolitic composition although, in terms of petrography, it fits the LPA suite. Previous studies have reported a significant difference between the two suites concerning the enclave abundance and occurrence with the HPRD suite showing significantly more enclaves compared to the LPA-suite (Braschi et al., 2012; Klaver et al., 2017; Zouzias & St. Seymour, 2014). In this study, we focus only on lava flows and lava domes (excluding pumices and scoria), and on diverse types of enclaves hosted within the lavas, belonging to both LPA and HPRD series. Hereafter, the term “enclave” will be used as a generic term for all types of cognate magmatic rock inclusions within a host lava. These include cumulates (i.e., formation due to settling and accumulation of early phenocrysts; Wager & Brown, 1967) and quenched melts (i.e., a portion of a co-mingled magma indicating magma hybridization and causing internal cooling of the hotter mafic magma portion within a colder more felsic host rock; Didier, 1987). Xenoliths (i.e., enclaves foreign to the magmatic system) have not been included in this study.

3. Materials and Methods

During sampling, a special interest was shown to enclave-bearing units and amphibole/clinopyroxene-rich cumulates and enclaves, due to their usual higher sulfide abundance relative to the host lavas (Georgatou et al., 2021). We focused on the Profitis Ilias domes (PFI) and the Nikia lava flow (NLF), where there was a higher probability of finding such enclaves and micro-cumulates, respectively, based on previous literature on the area (e.g., Braschi et al., 2012; Gansecki, 1991; Lodise, 1987). A total of 43 samples were collected, most of which corresponds to lava flows with a few examples of scoria, pumice and pillow lavas. Sampling locations of this study and of previous sampling expeditions of Klaver et al. (2017, 2018) are indicated on the map of Figure 1. Out of these 43 samples, 27 samples correspond to host lavas carrying enclaves of variable sizes and lithologies whereas 16 samples correspond to hand-size enclaves. Sample description (including enclave types/lithologies) and location (including GPS coordinates and geological units sampled) are reported in Table S1 of Supporting Information S2. A total of 44 thin sections were made, some of which correspond to different parts of the same sample including different types of enclaves. High-resolution images of all sections were obtained in transmitted and reflected light with an automated stage scanning petrographic microscope (JEOL-Olympus BX61) at the University of Geneva (see Figures S1–S16 in Supporting Information S1). An initial petrographic study on all thin sections revealed that 25 of them carried sulfides. Image analysis software (ImageJ® 1.38 software) was used to obtain modal abundances in Table S2 of Supporting Information S2. Bulk major and trace element analysis of 20 host lava samples and nine enclaves was conducted with X-ray fluorescence-XRF (PANalytical Axiom AX spectrometer) and laser ablation-inductively coupled plasma mass spectrometer (LA-ICP-MS; Agilent 7700) on fused glass beads at the University of Lausanne (see Georgatou & Chiaradia, 2020). For trace element measurements by LA-ICP-MS, 70 s of background measurement was followed by three cycles of ~50 s of sample measurement, on different parts of the sample, with 15 s of wash-out in between. After every four samples the SRM 612 standard was measured, with 70 s of background followed by two cycles of ~50 and 15 s of wash out. Three measurements have been done on each of the 29 samples, and the results presented are the mean of those three measurements. Raw data were reduced off-line using the software LAMTRACE (Jackson, 2008). Internal standardization was based on the CaO content measured by X-ray fluorescence analysis (XRF) whose accuracy was based on repeated measurements of the BHVO, SY-2, NIM-G and NIM-N reference standards. Major and trace element whole rock analysis are reported in Table S3 of Supporting Information S2. Eight thin sections were selected for sulfide backscatter imaging-BSE and sulfide chemical mapping by Scanning Electron Microscope-SEM at 15 kv and 1 nA (JEOL JSM7001F digital) while 10 thin sections were chosen for in situ sulfide chemical analysis by a JEOL 8200 probe microanalyser-EPMA at 20 kv, 20 nA and beam size <1 µm (summary in Table 1, for complete data set see Table S4 of Supporting Information S2). Both analytical methods were performed at the University of Geneva, Switzerland. For details on the analytical and operating conditions used during EPMA see Text S1 in Supporting Information S1.

Table 1
Summary of Sulfide Chemistry in Host Lavas and Enclaves Based on EPMA Analysis (N: Number of Analysis)

			Cu (wt%)	Ni (wt%)	Fe (wt%)	S (wt%)
LF1-6	Host lavas (Sample: 11; N = 45)	Min	0.01	0.02	32.7	33.5
		Max	31.8	0.36	61.7	41.5
		Mean	3.70	0.12	57.0	37.8
		Med	0.33	0.12	60.0	38.1
	Cpx-micro cumulates (Sample: 11; N = 6)	Min	0.02	0.14	59.2	35.6
		Max	0.32	0.18	60.7	38.5
		Mean	0.13	0.16	59.8	37.8
		Med	0.08	0.15	59.7	38.2
EMB	Host lavas (Sample: 12; N = 18)	Min	0.01	0.05	55.5	36.8
		Max	5.13	0.20	61.6	39.1
		Mean	1.15	0.12	59.6	38.1
		Med	0.13	0.11	60.3	38.3
	Cpx-micro cumulates (Sample: 12; N = 9)	Min	0.02	0.05	47.6	36.5
		Max	12.0	0.15	60.4	38.8
		Mean	2.05	0.13	57.9	38.1
		Med	0.06	0.13	60.1	38.3
NLF	Host lavas (Samples: 1, 10; N = 12)	Min	0.004	0.02	53.2	33.1
		Max	8.95	0.38	61.0	39.8
		Mean	0.95	0.23	59.2	38.2
		Med	0.04	0.31	59.4	38.8
	Type-II hbl-gabbroic enclaves (Samples: 8A, 8B, 9, N = 107)	Min	0.01	0.01	40.0	36.0
		Max	20.7	0.74	61.0	40.6
		Mean	0.39	0.08	59.0	38.6
		Med	0.02	0.05	59.4	38.7
	Type-III hybrid enclaves. (Samples: 1,10, N = 10)	Min	0.01	0.09	53.8	37.8
		Max	3.96	1.1	69.0	40.5
		Mean	0.59	0.55	58.2	39.1
		Med	0.03	0.55	58.6	39.2
PFI	Host lavas (Sample: 38, N = 4)	Min	0.04	0.01	45.2	35.8
		Max	13.3	0.31	57.8	38.9
		Mean	6.54	0.12	52.0	37.5
		Med	6.40	0.09	52.5	37.7
	Type-III hybrid enclave (Sample: 38, N = 19)	Min	0.01	0.37	48.4	35.7
		Max	10.1	3.28	58.1	39.0
		Mean	0.65	1.34	56.5	37.9
		Med	0.06	1.14	57.3	38.1

Note. Only measurements with totals higher than 98 wt.% are reported. For full data set including trace elements and analysis of hydrothermal sulfides occurring in Holaki pillow lavas unit of the LPA-suite see Table S4 in Supporting Information [S2](#).

4. Results

4.1. Sample Petrography and Sulfide Occurrence

All volcanic products have a plagioclase-rich matrix with rocks from the LPA suite showing plagioclase,

clinopyroxene, olivine, magnetite and rare orthopyroxene phenocrysts whereas rocks from the HPRD suite show plagioclase, orthopyroxene, magnetite ($\pm$ ilmenite), and rare clinopyroxene phenocrysts. While in both LPA and HPRD-suites polycrystal-aggregates and micro-clots are present, in the LPA suite enclaves are rare, with average sizes <1 cm, and consist mostly of clinopyroxene-rich cumulates/aggregates and wehrlite cumulates (Figures S1, S2, S10, and S14 in Supporting Information S1). In contrast, in the HPRD suite enclaves are more abundant with average size of 10 cm (but up to 80 cm) and include enclaves (some of which show quenching textures) and clinopyroxene-rich micro-cumulates (Figures S3–S9 and S11–S13 in Supporting Information S1). A summary of the key petrographic features for the units sampled in this study belonging to both LPA and HPRD suites will be reported below with a main focus on the petrography of magmatic sulfides occurring in the lavas and in the diverse enclave types. Sulfide abundances in area % are summarized for each unit (host lavas and enclaves) in Table S2 of Supporting Information S2. Detailed information on transmitted light petrography and silicate mineral and melt chemistry of the Nisyros complete volcanic sequence, including pumices, scoria and tuffs, can be found in Dietrich (2018) and Dietrich and Popa (2018) and reference therein.

4.1.1. Low Porphyritic Series – LPA

The stratigraphically lowest LPA series volcanic unit cropping out in Nisyros is the Holaki basal complex (HO). It consists of pillow lavas and pillow breccias which are often cemented by a yellow-orange hyaloclastitic matrix rich in cryptocrystalline Fe-hydroxide and jarosite (St. Seymour et al., 1993, Figures 2Ia and 2Ib). Two enclave types are seen in this unit: the most common type comprises clinopyroxene and olivine-rich wehrlitic cumulates characterized by holocrystalline and granulitic textures (Figure 2Ic and Figure S14 in Supporting Information S1) and the second type are rare angular altered clinopyroxenitic enclaves hosted in the pillow pebbles/blocks (Figure S15 in Supporting Information S1, see also Spandler et al. [2012]). In contrast to all younger volcanic units, magmatic sulfides are not present in Holaki basal complex in neither lavas nor cumulates. Instead, hydrothermal pyrite ($\pm$ marcasite) was observed as sub rounded inclusions and within mineral fractures in clinopyroxene and olivine phenocrysts of the lava (Figure 2Id, Figures S15d and S15e in Supporting Information S1), and as open-space filling radial and angular marcasite clusters found within the clinopyroxenitic-altered enclaves (Figure 2Ie and Figure S15h in Supporting Information S1) and in the groundmass of the lavas. The latter case was only observed in the samples associated with sulfuric alteration where later hydrothermal activity had occurred. This is also confirmed by the presence of hydrothermal oxides (goethite) and quartz found often in contact with pyrite or cut by pyrite veinlets (Figures S15d and S15e in Supporting Information S1).

The next unit comprises basaltic-andesitic to dacitic lava flows from the Kremasto, Kato Lakki and Afionas systems, which are characterized by sub- to euhedral plagioclase phenocrysts in a fine-grained dark glassy groundmass (Figures 2IIa and 2IIb). The most common enclave type is a clinopyroxene + plagioclase + magnetite ($\pm$ interstitial hornblende) cumulate (Figure 2IIc). Sulfides are rare in the lavas compared to the cumulates, 0.03×10^{-4} and 0.28×10^{-4} area %, respectively. In the lavas, they are found mostly within clinopyroxene and magnetite and to a lesser degree in plagioclase, whereas sulfides are hosted mainly by plagioclase and magnetite-ilmenite in the cumulates (Figures 2IId and 2IIe). In terms of composition, sulfides mostly consist of pyrrhotite plus minor chalcopyrite, but when hosted by magnetite the chalcopyrite proportion is higher (Figure 2IId).

Rocks from the following two units, belonging to Xolante-LF8 and Fournia-BLF lava flows, are dense, heavy and dark-green in color, compared to any other unit of the LPA suite (Figure 2IIIa). In Xolante, clinopyroxene-plagioclase-magnetite cumulates are present, similar to the LF1-LF6 units but without interstitial amphibole (Figure 2IIb). Sulfides in the lavas are hosted by magnetite, plagioclase and pyroxene as well as by an olivine megacryst (~ 2 mm) where sulfides (mostly pyrrhotite) are as large as 100 μ m, reaching up to 0.017×10^{-4} area % (Figures 2IIc and 2IIId). In contrast, sulfides in the cumulates are rare (0.002×10^{-4} area %) and appear to be composed mostly of chalcopyrite. Only one sample was recovered from the andesitic Fournia lava flow which was enclave-free. In the lavas no sulfides were observed.

Finally, the Argos/Avlaki lava flow have similar low crystallinity to the other LPA units, however, these lavas differ by being lighter in color resembling dacites (Figure 2IVa). A characteristic feature is the more evident occurrence of amphibole, both in the lavas as phenocrysts and in hornblende-plagioclase-clinopyroxene-magnetite cumulates, which often shows opacitised rims (Figure 2IVb). Magmatic sulfides are rare and are mostly found in plagioclase and magnetite and to a lesser degree in pyroxene phenocrysts and in amphibole and between plagioclases in the cumulates (Figures 2IVc and 2IVd) reaching up to 0.02×10^{-4} and 0.18×10^{-4} area %, respectively.

Sulfides are composed mostly of pyrrhotite with rare chalcopyrite and often show goethite-replacement textures (Figure 2IIId).

4.1.2. High Porphyritic Series -HPRD

The Fournia/Emporio lava domes have larger plagioclase phenocrysts and a lighter-colored fine-grained matrix compared to most of the LPA series (Figure 3Ia). These lavas are the freshest volcanic products of the HPRD suite and have abundant clinopyroxene-plagioclase-olivine-magnetite cumulates which are visible to the naked eye (Figure 3Ib). Sulfides are present both in the lava and in the clinopyroxene-rich cumulates and crystal clots making up for 0.04×10^{-4} and 0.16×10^{-4} area %, respectively. In the host lava, sulfides are hosted by magnetite, plagioclase and amphibole and in the cumulates by plagioclase and magnetite. Like in LF1-LF6 of the LPA suite, sulfides hosted by magnetite consist of pyrrhotite and more abundant Cu-rich sulfide phase (cubanite-chalcopyrite) than sulfides hosted by silicate phases (Figure 3Ic).

The following unit of the HPRD suite is the Kardia unit consisting of the Nikia lava flow (NLF). The lavas contain a high proportion of euhedral plagioclase (up to 40 vol.%) and orthopyroxene phenocrysts, and minor magnetite. Besides the occasional clinopyroxene-rich micro-cumulate, there are three types of enclaves present in these rocks: Type-I is small enclaves (1 mm) consisting of spherulitic amphibole, plagioclase and abundant resorbed magnetite crystals ($\pm$ ilmenite exsolution), Type-II is a rounded hornblende-rich gabbroic enclave with distinctive acicular hornblende and plagioclase plus minor clinopyroxene and interstitial glass, forming diktytaxitic textures (Figure 3IIa, Figures S7–S9 in Supporting Information S1), and Type-III is a finer grained hornblende-plagioclase-clinopyroxene-magnetite enclave which can reach up to 40 cm and which often is surrounded by a degassing aureole-chilled margin. As previously noted by Klaver et al. (2017), the type-ii gabbroic enclaves have been infiltrated in a later stage by rhyolitic melts and as result the rims of the amphibole and plagioclase phenocrysts are in chemical disequilibrium with the interstitial matrix. Type-III enclaves are found in two samples of the NLF unit (AGN01, –10) and show extensive interaction with the host lava and evidence for phenocryst exchange (e.g., plagioclase phenocrysts and clinopyroxene-clots, also reported by Zouzias and St. Seymour [2014] and Braschi et al. [2014]). In this study we consider this to be a hybrid enclave, also observed in the following unit (PFI-Figure 3IIb). In both Type-II and -III enclaves amphibole is observed replacing clinopyroxene (Klaver et al., 2017). Sulfide abundance and occurrence varies as follows: 0.02×10^{-4} area % hosted by magnetite and plagioclase in the lavas, and 0.45×10^{-4} area % hosted mostly by plagioclase and to a smaller extend by amphibole in Type-II enclaves, and 0.014×10^{-4} area % hosted mostly by plagioclase in Type-III enclaves. Sulfides were not found in Type-I quenched enclaves nor in the clinopyroxene cores (surrounded by replacing amphibole) in Type-II and -III enclaves. Noteworthy is the sulfide texture in the Type-II enclaves with the majority of sulfides ($N \sim 500$ out of 900 sulfide inclusions included in silicate minerals) characterized by an unusual, elongated shape resembling the letter “H” which often are oriented according to the cleavage of the host mineral in growth zones (Figures S7d and S8j in Supporting Information S1), and have average size 20–30 μm and up to 70 μm (Figures 3IIc and 3IIId; Figures S7 and S8d–S8k in Supporting Information S1). Generally, these sulfides are composed of pyrrhotite ($\pm$ chalcopyrite) and often show fracturing associated with oxide (goethite and magnetite)-replacement textures (e.g., Larocque et al., 2000). Sulfides in Type-III hybrid enclaves occur mostly interstitially and show partial to full oxide replacement (Figures 3IIIf and 3IIIf).

Lastly, the youngest unit of the HPRD suite comprises the domes of Profitis Ilias (PFI). Although most PFI lavas show severe weathering and oxidation, they are easily distinguishable from all other units by the abundant occurrence of type-i basaltic andesitic sub rounded quenched and, in many cases, oxidized enclaves (Figure 3IVa). Even though there are no type-ii gabbroic enclaves, some samples (AGN16, –38, –40) present type-iii hybrid enclaves and other clinopyroxene-plagioclase micro-cumulates common to all volcanic rocks of Nisyros (Figure 3IVb). Sulfides in the lavas of these domes are very rare (0.01×10^{-4} area %) and they are mostly hosted in plagioclase. Rare Cu-rich (bornite-digenite and pyrite-chalcopyrite) magnetite-hosted sulfides are also present (Figures 3IIIf and 3IIId). Like in the NLF-unit Type-I quenched enclaves are sulfide-free while type-iii hybrid enclaves are characterized by at least 0.01×10^{-4} area % sulfides. Specifically concerning the younger dome (Boriatiiko-Figure 1), most sulfides occurring in hybrid enclaves (e.g., AGN16) are composed of solely Cu-rich (chalcopyrite-bornite) sulfide phases hosted by mostly plagioclase and to a lesser degree by magnetite (Figure 3IVd). Lastly, sulfides were not observed in the common clinopyroxene-hornblende micro-cumulates.

4.2. Bulk Chemistry

In agreement with previous studies (e.g., Francalanci et al., 1995; Klaver et al., 2017, 2018; Popa et al., 2019; Spandler et al., 2012; Zellmer & Turner, 2007), considered all together, the studied rocks range from medium- to high- K calc-alkaline ($K_2O = 0.5\text{--}3.6$ wt.%) and from basaltic andesites to rhyolites ($SiO_2 = 54\text{--}70$ wt.% and $MgO = 0.8\text{--}5.5$ wt.%) with the data splitting into two groups, the more mafic LPA suite and the more evolved-felsic HPRD (Figures 4a and 4b). Type-II hornblende-rich gabbroic enclaves and Type-III hybrid enclave in the Nikia lava flow have generally higher Fe_2O_3 (8.0–8.1 wt.%) and lower SiO_2 (53–55 wt.%) and Sr/Y (33–35) compared to type-I quenched enclaves of the Profitis Ilias domes ($Fe_2O_3 = 5.5\text{--}6.3$ wt.%, $SiO_2 = 54\text{--}58$ wt.% and Sr/Y = 53–62; Figures 4c–4f). Both lavas and enclaves show typical Nb-Ta depletion indicative of subduction-related magmas with enclaves presenting lower LILE contents compared to the lavas (Table S2 in Supporting Information S2).

In addition, there is a general gradual decrease of Cu from 70 to 2.5 $\mu\text{g/g}$ in the host lavas with the increase of SiO_2 , indicating a compatible behavior which can also be seen within the individual petrogenetic series and stages of formation of the volcano (Figures 4g and 5ai–5bi). Starting with Cu med = 50 $\mu\text{g/g}$ for the Basal volcanic complex (-HO) followed by the Cone-building stage with Cu med = 34.5 $\mu\text{g/g}$ (LF1-LF6) and 7.5 $\mu\text{g/g}$ (-ALF), then by the Eccentric activity stage with Cu med = 32.6 $\mu\text{g/g}$ (-LF8), 26 $\mu\text{g/g}$ (-BLF) and 28 $\mu\text{g/g}$ (-LLF) and finally by the Main caldera stage with Cu med = 8.9 $\mu\text{g/g}$ (-LF7, EMB), 5 $\mu\text{g/g}$ (-NFL) and 12.55 $\mu\text{g/g}$ (PFI domes). Figures 5aii and 5bii show the Cu- SiO_2 systematics of the enclaves and lavas within the individual domes of the PFI group, starting with the oldest Profitis Ilias (-PFI), Visterna (-VIS) and Trapezina (-TRA) domes followed by the intermediate Nymfios (-NYM) dome and finally the youngest Karaviotis (-KAR) and Boriatiko (-BOR) domes. Meanwhile, sulfide abundances in cumulates, enclaves and host lavas decrease with magma evolution (Figure 5ci) and for the same sample distribution with Cu bulk increase (Figure 5cii).

4.3. Sulfide Composition

The results of 230 measurements (with totals ≥ 98 wt.%) on magmatic sulfide inclusions occurring in the enclaves ($N = 152$) and the host lavas ($N = 78$) of Nisyros are shown in Figure 6 and summarized in Table 1 (for the complete data set of 267 sulfide analysis with totals >96 wt.% including trace element contents see Table S4 in Supporting Information S2). Chemical mapping (SEM) of a partly dissolved sulfide (remnant pyrrhotite core) hosted by amphibole in the hornblende-rich gabbroic enclaves is shown in Figure 7.

Overall, sulfides are generally Cu-poor corresponding to monosulfide solid solution (mss) compositions, plotting either around the compositional field of pyrrhotite or between the pyrrhotite and cubanite compositions, with only two sulfides hosted in magnetite phenocrysts of the lavas showing higher Cu contents with Cu max = 32 wt.% (~chalcopyrite). Rare sulfides composed of only Cu-rich mineral phases (chalcopyrite, bornite and digenite) were too small to analyze by EPMA but SEM indicates Cu = 35–75 wt.% and Fe/S = 0.3–0.85 (Figure 6c), corresponding to intermediate solid solution-iss and bornite solid solution-bnss. Sulfides occurring in the enclaves show higher Ni (Ni med = 0.06 wt.%) and lower Cu (Cu med = 0.03 wt.%) compared to sulfides occurring in the lavas (Ni med and Cu med = 0.12 wt.% and 0.18 wt.%, respectively; Figure 6). Most sulfide analysis had Zn median contents below 0.02 wt.% and As and Se below 0.04 and 0.03 wt.%, respectively. Only some (N) measurements resulted in detectable trace element contents by EPMA analysis and vary as follows: $N = 74$ for Ag up to 1,750 $\mu\text{g/g}$, $N = 91$ for Au up to 1,270 $\mu\text{g/g}$, $N = 16$ for Pd up to 4580 $\mu\text{g/g}$, $N = 14$ for Pt up to 1,100 $\mu\text{g/g}$ and $N = 13$ for Ir up to 820 $\mu\text{g/g}$. These unusually high values of noble metals are most likely caused by clustering and nugget effects of sub-micron sized (<1 μm) metals observed also in previous studies and need to be considered with caution (e.g., Holwell et al., 2015; Mandon et al., 2021; Savelyev et al., 2018). Results from 15 measurements on hydrothermal sulfides (Figures 2ld and 2le) occurring within fractures of pyroxenes and in the matrix of pillow lavas, correspond to pyrite composition with minor Cu and Ni (Cu max and Ni max = 0.1 and 0.02 wt.%, respectively) and higher Ag med (911 $\mu\text{g/g}$) contents compared to magmatic sulfides in enclaves (Ag = 290 $\mu\text{g/g}$) and in lavas (Ag = 210 $\mu\text{g/g}$), respectively (Figure 6).

When considering the individual units within the LPA and HPRD suites, sulfides in the host lavas are characterized by Cu and Ni/Cu median values of 3,300 $\mu\text{g/g}$ and 0.49 for Afionas lava flows (LF1-LF6), 1,300 $\mu\text{g/g}$ and 1.2 for Fournia/Emborio dome (EMB), 380 $\mu\text{g/g}$ and 10 for Nikia lava flow (NFL) and 6.4 wt.% and 0.011 for

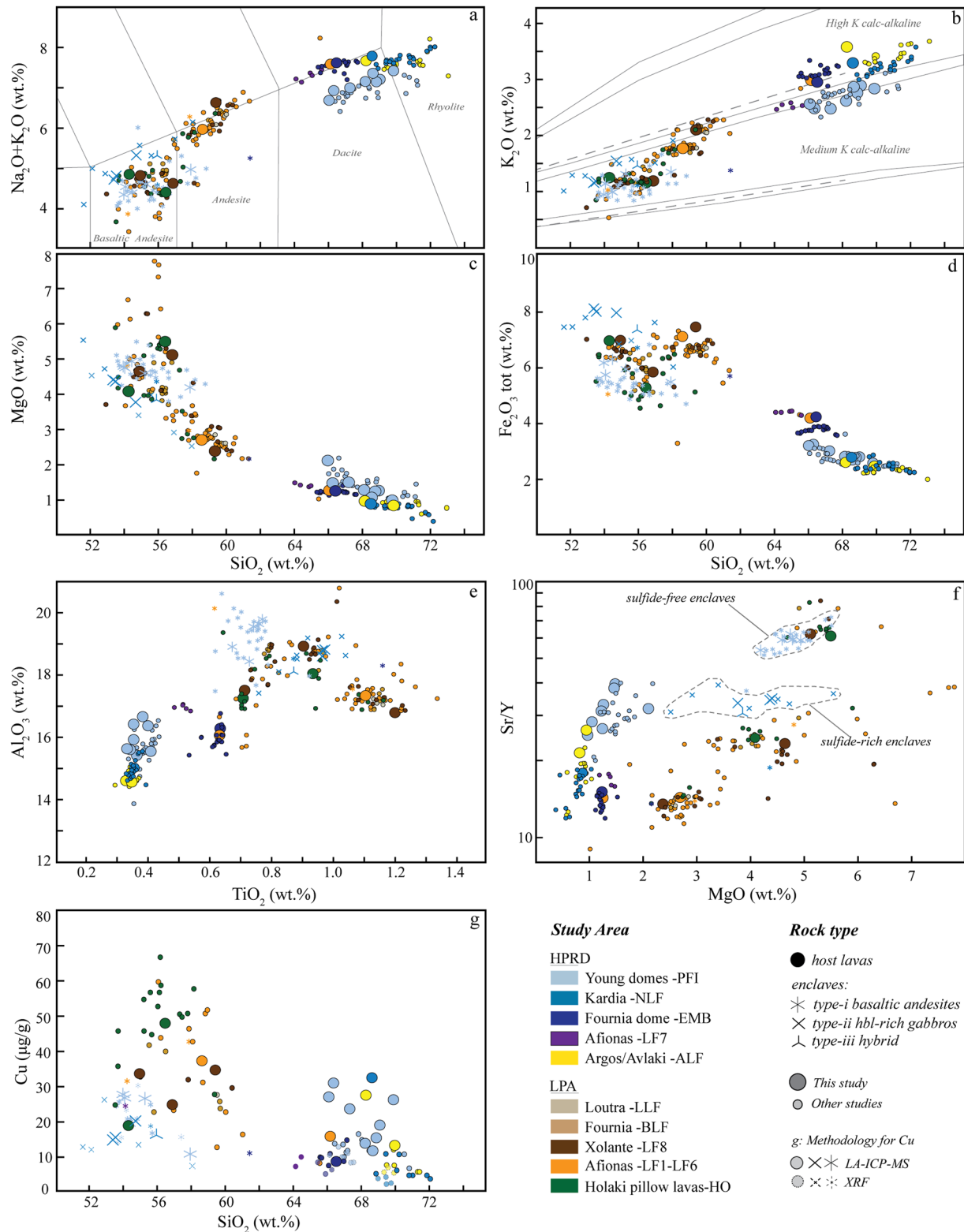


Figure 4. Bulk chemistry of whole-rock host lavas and enclaves. The volcanic products have been divided in the two suites (LPA & HPRD) following Klaver et al. (2017). Note that in graph-g the lowest Cu values correspond to XRF analysis (Popa et al., 2019).

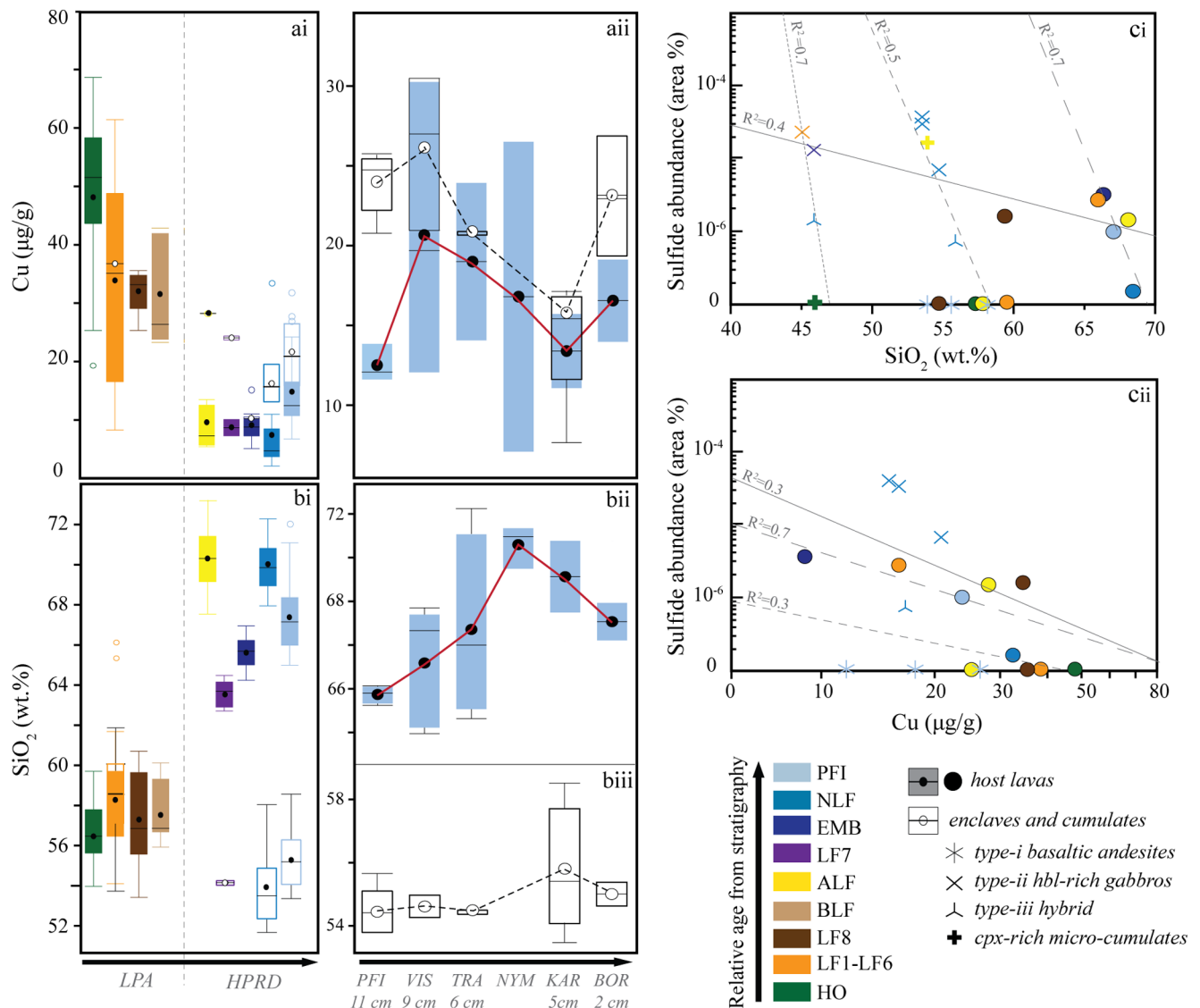


Figure 5. Cu bulk and sulfide abundance trends with magmatic evolution in lavas, hornblende-rich gabbroic enclaves of NLF and basaltic andesitic quenched enclaves of PFI. Boxplots in Graphs-ai and bi depict the Cu and SiO₂ data distribution of all units while in Graphs-aii, bii, and biii only samples from the different domes of the PFI unit are presented (box: 50% of data, dot: mean, and line: median). Note the decreasing enclave average size from the oldest to the youngest dome (values are from Braschi et al. [2012]). In all boxplot graphs the units/domes have been arranged from left to right based on the relative age inferred from the stratigraphy. In Graphs-c the regression lines show the decreasing trend of sulfide abundance with SiO₂ and Cu-bulk increase. Note that sulfide free samples (0 area %) occur throughout magma evolution. In graph ci for samples where bulk composition could not be obtained due to the small size of the enclaves (e.g., cross symbol-micro cumulates), based on mineralogy and enclave type, values have been taken from Klaver et al. (2017).

sulfides in the lavas belonging to Profitis Ilias domes (PFI), respectively (Figures 6a–6c). In contrast, sulfides in the enclaves have Cu and Ni/Cu median values of 840 µg/g and 2.24 for clinopyroxene-rich cumulate in Afionas (Figure 2IIc), 570 µg/g and 2.7 for clinopyroxene-rich cumulate in Emborio (Figures 3Ib–3Id), 260 µg/g and 2.3 for type-ii hornblende-rich gabbroic enclaves in Nikia (Figures 3IIb–3IIId) and 610 µg/g and 14 for Type-III hornblende-rich hybrid enclave in Profitis Ilias (Figures 3IIIb, 3IIIe, and 3IIIf). Lastly, Au contents are higher in sulfides belonging to the Profitis Ilias domes lavas (893 µg/g) and hybrid enclave (877 µg/g) compared to all other areas (<266 µg/g).

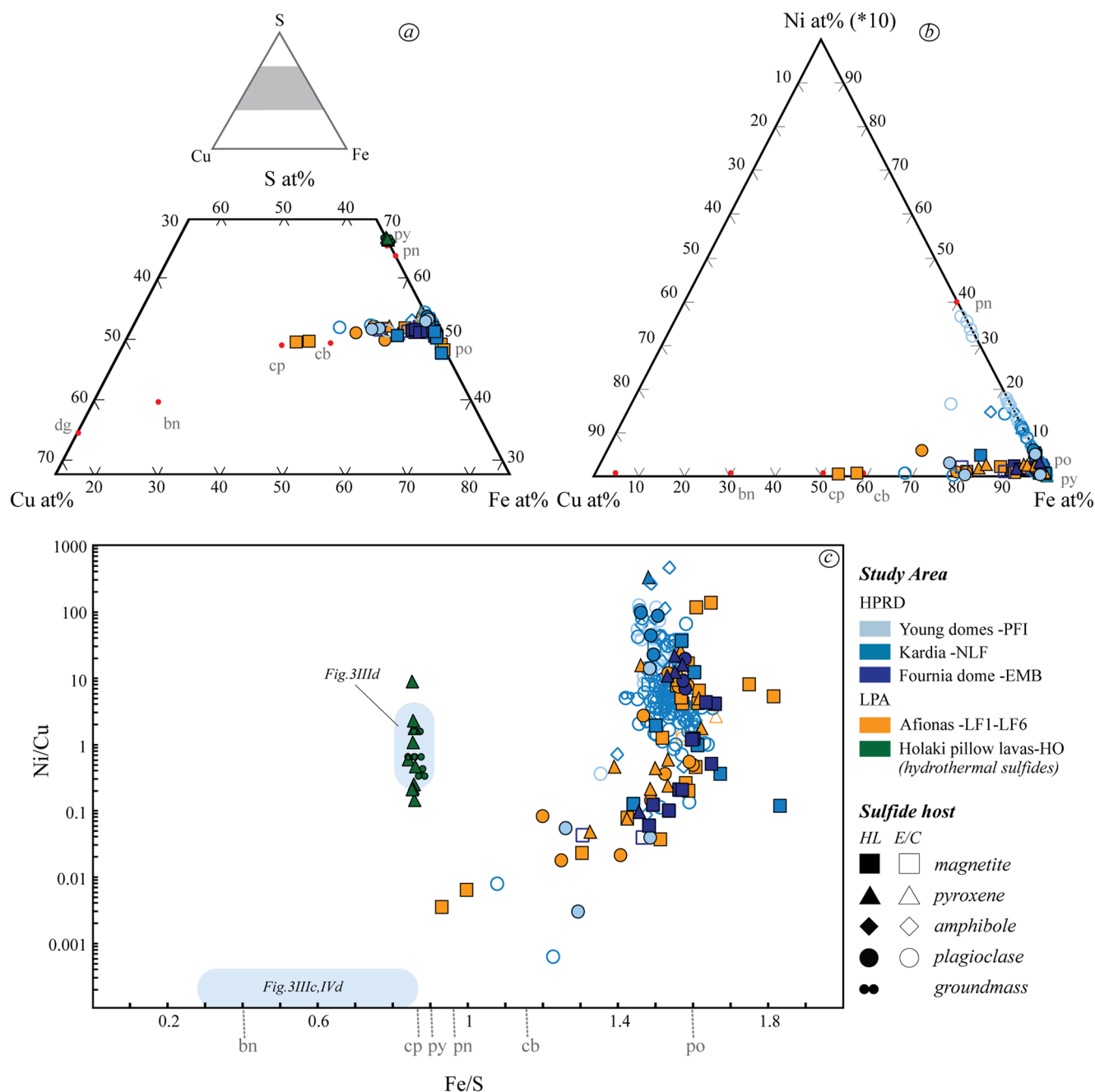


Figure 6. EPMA analyses on sulfides hosted by different host minerals and occurring within lavas (HL, full symbols), Type-II hornblende-rich gabbroic enclaves (NLF) and Type-III hybrid enclaves (PFI) (E/C, open symbols). The abbreviations mss and iss stand for monosulfide solid solution and intermediate solid solution, respectively. All analysis correspond to magmatic sulfides besides, the composition of hydrothermal pyrite found in the wehrilitic cumulates (HO, Figures 21c and 21d). Blue background fields in graph c represent the semiquantitative compositional range measured by SEM of magmatic sulfides found in the dome lavas, composed of chalcopyrite-pyrite (PFI, Figure 311ld) and bornite-digenite (PFI, Figures 311lc and 31Vd).

5. Discussion

5.1. Sulfide Evolution From Bottom to Top

According to a number of previous studies based on isotope and bulk rock geochemistry coupled with detailed petrography and mineral chemistry, the youngest rhyodacitic domes of Profitis Ilias (PFI) are hybrid magmas resulting from progressive mingling between an older rhyolitic crystal-rich magma body, represented by the Upper

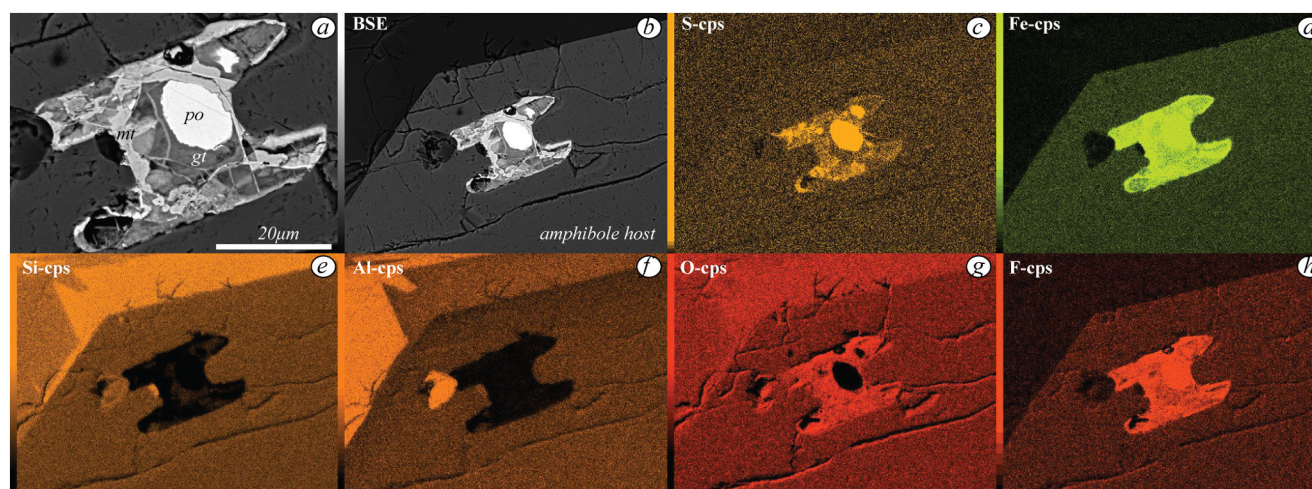


Figure 7. Chemical SEM mapping of an amphibole-hosted sulfide in the hornblende-rich gabbroic enclaves of Nikia lava flow (NLF). The sulfide inclusion is composed of pyrrhotite (po) and is being replaced by goethite (gt) and magnetite (mt). The presence of fluorine (h) possibly indicates that the fluids were F-rich (F has been corrected for the interference with high-Fe contents, thus the difference in Fe and F intensities in maps d and h, respectively). The map was acquired with dead time of 1 msec and a total analysis time of 1 hr resulting into a total of 12 sweep counts.

Pumice magma, and a refilling mafic magma, represented by the basaltic andesitic quenched enclaves found in the PFI (e.g., Braschi et al., 2012; Francalanci et al., 1995; St. Seymour & Vlassopoulos, 1989, 1992; Wyers & Barton, 1989; Zouzias & St. Seymour, 2014). A gradual increase in enclave abundance has been reported from the lower pumice (LP), to the Nikia lava flows (NLF), then to the Upper Pumice (UP) and finally to the PFI domes (Figure 1, Gansecki, 1991; Lodise, 1987). In particular, Braschi et al. (2012) noted that the chemical and petrographic variation between the enclaves of the PFI domes, is correlated with the domes eruptive sequence, suggesting a compositional variation of the refilling mafic magma with enclaves decreasing in the average size and increasing in abundance from the oldest domes (11–6 cm and 5–8 vol.% for Profitis Ilias, Visterna and Trapezina) to the youngest domes (2–5 cm and 8–13 vol.% for Karaviotis and Boriatico; Figures 3III, 3IV, 5bii, 5cii, and 5iii). Noteworthy is the fact that, Karaviotis and Boriatico domes include sub-enclaves of the previous mafic inputs (that formed the enclaves of the previous domes), confirming that they are a product of at least one mafic refilling episode (Braschi et al., 2012).

Regarding magma differentiation in Nisyros, Klaver et al. (2017, 2018) proposed that the LPA and HPRD series have two distinct petrogenetic paths, with no evident hybridization between the two series. The LPA suite is a result of fractional crystallization at shallow crustal levels, and the HPRD of cumulate-melt reactions in the lower crust, followed by, mixing and shallow crystallization (Klaver et al., 2017, 2018). More specifically, previous thermobarometry estimates of Klaver et al. (2017) based on petrographic observation and comparison with experimental petrology results from other studies (e.g., Blatter et al., 2013; Melekhova et al., 2015; Nandedkar et al., 2014) indicated that hydrous ($\text{H}_2\text{O} > 3$ wt.%) primitive melts delivered to the base of the crust (Nisyros crustal thickness = 25–27 km, Makris et al., 2018) evolve and differentiate through the following two distinct paths. While the basaltic andesites of the LPA series crystallized at a shallow mid-upper crustal reservoir (0.2–0.4 GPa, ~7–14 km and 1030–1090°C), the HPRD suite magmas differentiate to rhyodacitic compositions through peritectic amphibole crystallization in the lower crust (0.5–0.8 GPa, ~18–29 km and 1050–1150°C). Upon extraction from this deep crustal hot zone, HPRD magmas stall at shallower crustal levels to form crystal-rich magma (0.2–0.4 GPa, ~7–14 km and 925°C). In particular, concerning the enclaves and cumulates of the HPRD series, wehrlitic cumulates show the highest T range (1050–1150°C) followed by the hornblende-rich gabbroic enclaves of the NLF (920–1044°C), both showing similar P ranges (0.7–1 GPa, ~18–34 km; Klaver et al., 2017). These P - T ranges are also confirmed by Dietrich and Popa (2018) who give approximately 0.9 GPa (~32 km) and 1040°C as a starting point for amphibole crystallization belonging to the hornblende-rich gabbroic enclaves of NLF. In contrast, clinopyroxene-rich cumulates of the LPA suite represent lower T - P ranges typical of shallower crustal levels (~10 km), while basaltic andesitic quenched enclaves of the PFI domes (HPRD suite) crystallized even shallower (≤ 7 km; Klaver et al., 2017). Finally, studies based on the caldera size (~3.6 km diameter) report that the expected depth of the shallow magma reservoir may be as shallow as 3–7 km while

geothermal wells show evidence for the presence of a high-T brine at around 1.8 km (Dietrich & Popa, 2018 and references therein).

All these studies provide a well-constrained picture on the evolution of the plumbing and magmatic system in Nisyros allowing us to track sulfide saturation in detail from the upper mantle/lower crust to near surface-levels.

Petrographic and geochemical observations indicate that sulfide abundance (s.a.) and composition (e.g., Cu content) vary according to magma differentiation as well as the temperature and depth of differentiation. With decreasing pressure, we find sulfide-undersaturated pillow lavas ($\text{SiO}_2 = 54\text{--}57$ wt.%) and wehrlitic clinopyroxene-rich cumulates therein ($\text{SiO}_2 = 45\text{--}46$ wt.%) forming in the upper mantle/base of the crust, followed by also deep forming but lower-T sulfide-rich type-ii gabbroic enclaves found only at the NLF ($\text{SiO}_2 = 53\text{--}55$ wt.%, s.a. = $4\text{--}5 \times 10^{-5}$ area %, Cu med = 260 $\mu\text{g/g}$) representing the onset of sulfide saturation, then to clinopyroxene-rich gabbroic micro-cumulates found in the LPA series and EMB dome (s.a. = $2\text{--}3 \times 10^{-5}$ area %, Cu med = 570 $\mu\text{g/g}$) differentiating in shallower crustal levels, and finally to more evolved sulfide-poor Type-III hybrid enclaves of NLF and PFI ($\text{SiO}_2 = 56$ wt.%, s.a. $<1 \times 10^{-5}$ area %, Cu med = 602 $\mu\text{g/g}$) and rhyodacitic host lavas of PFI ($\text{SiO}_2 = 66\text{--}76$ wt.%, s.a. $<0.5 \times 10^{-5}$ area %, Cu med = 6.4 wt.%) pointing to a system that is close to sulfide undersaturation. At even shallower levels quenched Type-I enclaves of the PFI domes corresponding to basaltic andesitic composition ($\text{SiO}_2 = 66\text{--}76$ wt.%) are sulfide-free. Lastly, our results suggest that although there is no major difference in terms of sulfide texture and occurrence between the two series, (LPA and HPRD) the lavas LF1–LF6 of the LPA series are generally sulfide-poor, but sulfides are Cu-rich, and are comparable only to the sulfide composition of the lavas of the PFI domes, both of which are expected to have crystallized at shallow crustal levels ($\sim 14\text{--}7$ km).

The above-mentioned, gradual decrease in sulfide abundance is associated to an increase in the measured Cu/Ni sulfide content with magma evolution, indicating an increase of Cu content in the mss with magma differentiation followed by the presence of rare Cu-rich iss and bnss sulfides in more differentiate rocks. This is consistent with results from other studies (e.g., Georgatou et al., 2021; Keith et al., 2017). This counterbalance of sulfide abundance and sulfide metal contents results in the concomitant decrease in whole rock Cu content as expected due to the compatible behavior of Cu with magma evolution (e.g., Chiaradia, 2014). As a result, the Cu-rich basaltic to basaltic andesitic magmas of the LPA series, with the most primitive samples having 30–60 $\mu\text{g/g}$ Cu, (i.e., closer to values of typical arc magmas), are either still sulfide undersaturated (pillow lavas) or show low sulfide abundance (LF1–6, LF8), while the most felsic sample ($N = 13$; $\text{SiO}_2 = 66$ wt.%) corresponds to the highest sulfide abundance (0.03 area %). The sudden drop of Cu characterizing this series (LPA, Figures 4g and 5ai), suggests deep metal sequestration by cumulates, which is confirmed here by the presence of sulfides in the clinopyroxene-rich gabbroic micro-cumulates (Figure 2Ic). In contrast, the Cu-poor (5–20 $\mu\text{g/g}$) dacitic to rhyolitic lavas of the HPRD-series, already lost most of their Cu as confirmed by the higher sulfide abundance seen in the mafic hornblende-rich gabbroic enclaves of the NLF (Figures 3IIb, 4g, 5ai, 5ci, and 5cii). Therefore, within the same petrogenetic suite, sulfide abundance is decreasing with magma evolution while, as discussed further down the Cu bulk corresponding to the same samples is increasing (Figures 5ci and 5cii).

All the above data and observations provide petrographic and geochemical evidence that sulfides become less abundant and Cu-richer/Ni-poorer at progressively lower P-T conditions (and likely $\text{H}_2\text{O}/\text{fO}_2$ increase). Future, detailed hydro- and oximetry based on mineral chemistry of sulfide-bearing phenocrysts (e.g., amphiboles) can help to further narrow the physicochemical conditions upon sulfide saturation in Nisyros.

5.2. Cu Enrichment Through Mingling and Enclave Disaggregation

The rhyodacitic PFI domes have lower sulfide abundances (<0.01 area %) and slightly higher whole rock Cu contents even though they have similar SiO_2 contents compared to the other HPRD units (Figures 5a and 5b). This Cu enrichment of the host lavas, could be explained by the previously noted magma mingling and enclave disaggregation characterizing the PFI unit (e.g., Braschi et al., 2012). More specifically, these are the likely processes causing the above-mentioned Cu enrichment of the PFI lavas.

The first process includes dissolution of sulfides present in the PFI hybrid enclaves. These hybrids show petrographic evidence for sulfide-partial or complete dissolution and oxide-replacement (Figures 3IIe and 3IIIf). While weathering and hydrothermal alteration can cause such sulfide dissolution, magmatic processes like, progressive sulfur degassing, magma oxidation and pressure decrease, may also lead to dissolution, resorption

and oxidation of sulfides (e.g., Berlo et al., 2014; Z. Chen et al., 2021; Edmonds & Mather, 2017; Larocque et al., 2000). Whatever the exact causes of sulfide dissolution in Nisyros are, decomposition of pyrrhotite (+minor chalcopyrite) would result in the release of most of their chalcophile element cargo back into the melt and the later exsolving magmatic-hydrothermal fluids (Berlo et al., 2014; Z. Chen et al., 2021). A study from Zhang and Audétat (2017) comparing the metal contents of fresh versus altered sulfides in latites confirm that such sulfide decomposition leads to major loss (in $\mu\text{g/g}$) of S (1,000), Cu (500), Se (50), Te (10), and Au (0.5) from the sulfides.

The second process, implying an additional Cu source, is magma mingling with a Cu-richer (Cu med = 21 $\mu\text{g/g}$) and more mafic ($\text{SiO}_2 = 53\text{--}59$ wt.%, $\text{MgO} = 3.8\text{--}5.5$ wt.%) pulse, represented by the PFI quenched basaltic andesitic enclaves (Type-I), resulting in higher Cu med and lower SiO_2 med contents in the PFI lavas (12.5 $\mu\text{g/g}$, 68 wt.%) compared to the host lavas of the other HPRD units ($\sim 5\text{--}10$ $\mu\text{g/g}$ Cu). An increase of mafic input and more efficient magma mingling combined to gradual enclave disaggregation of these PFI Cu-rich basaltic andesitic quenched enclaves would result in the previously noted decrease in enclave size and increase in enclave abundance from the oldest to the youngest domes (e.g., Braschi et al., 2012) but also in a further progressive Cu enrichment of the domes lavas (Figure 5a_{ii}). Interestingly, all oxidized basaltic andesitic quenched enclaves of PFI domes are sulfide-free, indicating that either the system had already saturated with water which would result in sulfur and metals partitioning into the fluid phase, or that any existing sulfides have already been consumed by hydrothermal fluids and replaced by oxides. There is no textural evidence to indicate that sulfides were originally present in the latter basaltic andesitic quenched enclaves. Such evidence would include sulfide-replacement by oxides as seen in the hybrid enclaves, or even remnant sulfide inclusion shapes in phenocrysts. In addition, no mineral fracturing and secondary filling textures are observed to support the presence of hydrothermal fluids, while the increased vascularity of these enclaves compared to any other enclave type confirms the more likely scenario of an already water saturated system. Moreover, the system must have been more oxidized at the time of undercooling of this basaltic andesitic magma pockets since magnetite phenocrysts, still showing ilmenite exsolution, have been replaced by hematite and all fine and prismatic amphibole crystals show opacitization (Figure S6e in Supporting Information S1). Such magma oxidation would inhibit sulfide saturation from occurring. Thus, disaggregation of the above-mentioned basaltic andesitic quenched enclaves and of their exsolved Cu-rich fluids would lead in a further Cu-enrichment of the youngest PFI host lavas (Figure 5a_i).

5.3. Amphibole Crystallization as a Trigger for Sulfide Saturation

In general amphibole phenocrysts are rare in lava flows of Nisyros, which could explain why sulfides are mostly hosted by plagioclase, magnetite, and pyroxene phenocrysts and not by amphibole (as previously noted in other study areas; e.g., Chang & Audétat, 2018; Georgatou et al., 2021). For the rare cases where amphibole is present in the rocks, extensive opacitization, decompression rim textures and progressive resorption result in the low preservation of sulfides (Figures 2IIb–2IIId). However, this does not appear to be the case for deep forming Type-II hornblende-rich gabbroic enclaves of the Nikia lava flow (NLF) unit where sulfides are found also in amphibole (Figures 3IIc and 3IIId). Klaver et al. (2017) proposed that these hornblende-rich enclaves found in the NLF are a product of maturation of the primitive wehrilitic clinopyroxene-rich cumulates by a reaction replacement of clinopyroxene by amphibole producing dacitic melts, confirmed by remnant clinopyroxene cores surrounded by newly formed amphibole (cf., Smith, 2014). This peritectic reaction was also reported in sulfide-bearing hornblende-rich cumulates of Santa Rita and Cerillos, New Mexico (Chang & Audétat, 2018). Interestingly, in both the clinopyroxene-rich wehrilitic cumulates found in the pillow lavas (-HO) and the clinopyroxene cores of hornblende-rich gabbroic enclaves (-NLF), sulfides are not observed in clinopyroxene while hornblende and plagioclase are the most sulfide abundant hosts.

The above suggest that the onset of sulfide saturation in Nisyros is marked by amphibole crystallization at upper mantle/lower crustal levels (25–32 km). Such peritectic reactions of clinopyroxene by amphibole, occurring in the Type-II NLF gabbroic enclaves is triggered by a H_2O increase. Although, magmas with larger concentrations of magmatic H_2O are able to dissolve a larger amount of sulfur before reaching sulfide saturation and thus inhibiting sulfide formation (e.g., Fortin et al., 2015), amphibole fractionation would cause a decrease of the total Fe of the melt, like in the case of magnetite fractionation, converting soluble sulfate (S^{6+}) into less soluble sulfide (S^{2-}) and thus promoting sulfide saturation (Carroll & Rutherford, 1988). In fact, a recent study has shown that extensive amphibole fractionation in andesitic rocks at temperatures below 1050°C, which is also the case here with the

type-ii gabbroic enclaves of the NLF corresponding to a temperature range of 920–1044°C (Klaver et al., 2017), would substantially decrease the melt FeO_{tot} content and thus also the sulfur content at sulfide saturation (Barber et al., 2021). Considered altogether deep forming “amphibole sponges” appear to be an important sink for sulfur and chalcophile elements in the continental crust.

Lastly, it is important to note that sulfides hosted within magnetite in the lavas of the PFI domes corresponding to shallower crustal levels are composed of Cu-richer phases (pyrrhotite + chalcopyrite or bornite + digenite, Figures 3IIIc and 3IIId) compared to Cu-poor sulfides (pyrrhotite $\pm$ chalcopyrite) found in the deep forming hornblende-rich gabbroic enclaves. On one hand, this confirms once again the crucial role of magnetite for sulfide saturation (e.g., Jenner et al., 2010) and especially of Cu-rich sulfides which has been previously seen in other study areas at convergent geodynamic settings (Georgatou & Chiaradia, 2020). On the other hand, this implies that there can be multiple triggers for sulfide saturation from deep to shallow crustal levels and that fractionation of certain host minerals (e.g., amphibole vs. magnetite) may also reflect the nature of the sulfides saturating at the time. Such sulfide compositional variation along T-P- $f\text{O}_2$ was previously reported (Georgatou et al., 2021) for sulfides in hornblende-rich mafic cumulates compared to sulfides occurring in more evolved lavas of other study areas, the results of which will be discussed below.

5.4. Comparison Between Nisyros and Previously Studied Areas

Sulfide-bearing volcanic rocks of Nisyros span from basaltic andesites to andesites of medium K calc-alkaline compositions and dacites to rhyolites of high-K calc-alkaline compositions comparable to Ecuador (subduction setting) and, to a lesser degree, to Konya (post-subduction setting), which were areas in convergent settings previously studied by Georgatou and Chiaradia (2020) (Figures 8a–8c). In general, Nisyros lavas are characterized by low sulfide abundance ($<0.04 \times 10^{-4}$ area %), of Cu and Ni-poor sulfides (no Ni-rich sulfide phase-pentlandite was found). In contrast, lavas from Ecuadorian volcanoes are characterized by sulfide abundance in the host lavas (up to 7×10^{-4} area %, Cu ≤ 60 –70 wt.% and Ni/Cu < 0.01 ; Georgatou et al., 2018; Figure 8d). The exception to this rule is magmatic sulfides in hybrid enclaves from Boriatico dome and in a few lavas of the other PFI youngest domes which carry rare Cu-rich sulfides (bornite) in magnetite (Figures 3IVd and 6c). A generally low sulfide abundance is recorded even for the most sulfide-rich samples corresponding to the type-ii hornblende-rich gabbroic enclaves of the NLF (0.45×10^{-4} or 1×10^{-4} area % including oxide-replaced sulfides), compared to other hornblende-rich cumulates of Ecuador and Kula, Western Turkey (Intraplate mafic alkaline volcano) reaching up to 2.4×10^{-4} and 0.23 area %, respectively (Georgatou et al., 2018, 2021).

Nevertheless, there are significant similarities in terms of petrography and chemistry of sulfides and their hosts between the Type-II hornblende-rich gabbroic enclaves of Nisyros and hornblende-plagioclase cumulates of Kula. Even though cumulates from Kula are more mafic ($\text{SiO}_2 = 44$ wt.% and $\text{TiO}_2 = 2.4$ wt.%) compared to gabbroic enclaves from Nisyros ($\text{SiO}_2 = 53$ –55 wt.% and $\text{TiO}_2 \leq 1$ wt.%, which is likely the result of the interstitial rhyolitic matrix; Klaver et al., 2017), they both have similar Fe_2O_3 (8–9 wt.%), Al_2O_3 (17–19 wt.%) contents with both enclave types presenting similar acicular amphibole with decomposing/breakdown rims consisting of clino- and ortho-pyroxene and oxides (magnetite-ilmenite; Georgatou et al., 2021). Studies on mineral chemistry on the above-mentioned hornblende-rich gabbroic enclaves record, for Nisyros, high Al_2O_3 (12–15 wt.%) and Mg# (70–80) for amphiboles-pargasites, An = 50–80 for plagioclase and high Al_2O_3 (7–9 wt.%) and Mg# (75–80) for clinopyroxenes (Klaver et al., 2017), and for Kula high Al_2O_3 (13–15 wt.%) and Mg# (55–75) for amphiboles-pargasites, An = 45–60 for plagioclase and Al_2O_3 (7–8 wt.%) and Mg# (75–90) for clinopyroxene (Georgatou et al., 2021). In addition, both enclave types are characterized by large (average size $>20 \mu\text{m}$) and Cu-poor sulfides (Cu med = 0.21 wt.%-Kula and 0.03 wt.%-Nisyros) often occurring interstitially. However, based on thermobarometry (and mineral chemistry) hornblende-plagioclase cumulates in Kula represent higher T-P conditions (up to 1165–1150°C and 1.1–1.6 GPa) compared to Nisyros (950–1044°C and 0.5–0.9 GPa, Dietrich & Popa, 2018; Georgatou et al., 2021; Klaver et al., 2017).

Worth mentioning is the unique occurrence of the “H” shapes sulfides in the hornblende-rich gabbroic enclaves found in the NLF. To date, the only other similar examples of such oxide-replaced “H” shaped sulfides have been reported to occur in clinopyroxene phenocrysts in the basaltic andesitic magma from the Yaeyama Central Graben (YCG) in the southern Okinawa Trough (Z. Chen et al., 2021). Interestingly, the latter study gave similar T ($1042 \pm 10^\circ\text{C}$) but generally lower P (0.3 ± 0.07 GPa) estimates for the basaltic andesitic magmas of YCG compared to the Type-II gabbroic enclaves of Nisyros ($T = 950$ –1044°C, $P = 0.5$ –0.9 GPa). This suggests that such

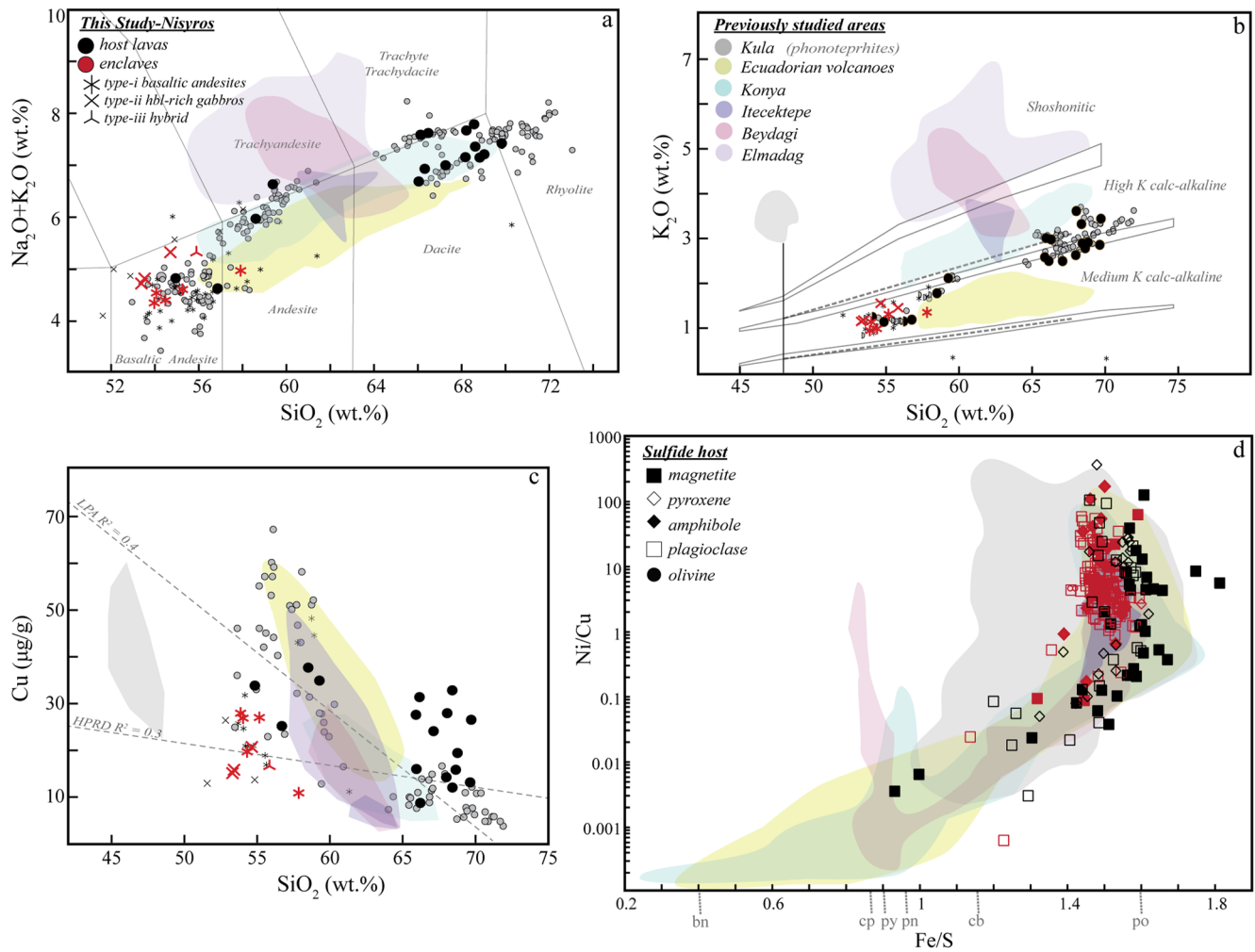


Figure 8. Whole rock and sulfide chemistry comparison graphs between Nisyros data set and other geological areas, illustrated here by shaded data fields, where sulfide saturation has been already studied (Georgatou & Chiaradia, 2020; Georgatou et al., 2018, 2021). The previously studied areas are characterized by diverse geodynamic settings and magma composition; Kula, Western Turkey-Intraplate volcanism, Ecuador-Subduction, Konya volcanic belt and Itecektepe, Beydagi, and Elmadag volcanoes belonging to the Usak basin, in Western Turkey. All symbols belong to Nisyros, black and red symbols correspond to host lavas and to enclaves, respectively and represent the data set presented in this study while gray symbols belong to previous studies (Klaver et al., 2017, 2018; Popa et al., 2019). In Graph-c the two regression lines correspond to the Cu trend with magma evolution for the two series, HPRD and LPA.

sulfides are not unique to deep-forming enclaves. More importantly, the fact that H-shaped sulfides often follow the host mineral's growth zones, would suggest that in the time of entrapment the sulfides may have been still partially molten. Although, *P-T* ranges in Nisyros are not direct values based on thermobarometry, and therefore we cannot be certain on the absolute associated error, the above hypothesis is consistent with previous experimental studies constraining the nature of the sulfide in similar *T-P* ranges representative of the upper mantle (Zhang & Hirschmann, 2016), with the “H” shaped sulfides falling either between the mss-liquidus and mss-solidus or -for the same pressures and lower temperatures- right on and slightly below the mss-solidus.

Finally, considered altogether the depth of onset of sulfide saturation in Nisyros is noted in the upper most part of the mantle or in the lower crust comparable to other study areas in convergent settings, taking place in the lower crust (e.g., Du & Audétat, 2020; Georgatou et al., 2021; Rottier et al., 2020). Moreover, while for the most part Nisyros sulfide-bearing volcanic rocks show similarities to previously studied barren volcanics which are characterized by mafic to andesitic and less oxidized magmas and which are not associated to economic mineralization (Itecektepe, Elmadag, and Kula), the youngest rhyodacitic PFI dome lavas are more similar to subduction-related areas associated with more evolved and more oxidized magmas which may be used as a fertile-proxy of porphyry Cu deposits (e.g., Ecuador; Georgatou et al., 2021). However, it is important to keep in mind that Nisyros is an

open/active magmatic-hydrothermal system with a shallow water saturated reservoir and thus it is likely that even if the system had enough metals to form a mineralization most chalcophile and siderophile elements would have already partitioned into the exsolving volatile phase, rendering the residual magma barren. Even so, magmatic processes controlling metal evolution in such active magmatic arc systems are similar to those characterizing magmas associated to porphyry Cu systems and can thus provide essential information on the early stages of ore genesis (Costa et al., 2021). Further detailed studies of magmatic sulfides, in similarly well constrained and magmatic-hydrothermal systems can help investigate the potential of using such petrographic and geochemical evidence as tools for distinguishing barren from fertile or potentially fertile geological areas.

6. Conclusions

The results of this study indicate that sulfide abundance and composition vary according to magma evolution and the T - P -depth of magma differentiation. More specifically, sulfides become less abundant and Cu-richer at progressively lower T - P -depth conditions; starting with high T - P sulfide-free pillow lavas and wehrlitic cumulates representing still a sulfide undersaturated system, passing to high T and lower P , deep-forming sulfide-rich hornblende-rich gabbroic enclaves forming at the base of the crust (~25–30 km), then to clinopyroxene-rich gabbroic micro-cumulates forming in shallower crustal levels (~10 km), and then to more evolved sulfide-poor hybrid enclaves, and rhyodacitic host lavas differentiating at even shallower crustal levels (~7 km). The system returned to a sulfide under saturated state with sulfide-free basaltic andesitic enclaves differentiating at surface levels. An increasing mafic input followed by magma mingling and enclave disaggregation lead to sulfide dissolution and Cu-enrichment of the magmas. Finally, sulfide saturation in Nisyros is triggered through amphibole fractionation via a reaction replacement of clinopyroxene, confirming that “amphibole sponges” may be an important sink for sulfur and chalcophile elements in the continental crust.

Data Availability Statement

The data set used for this study is available from the figshare repository (<https://doi.org/10.6084/m9.figshare.16575212.v1>; Georgatou et al., 2022).

Acknowledgments

The authors acknowledge the Swiss National Science Foundation for funding this work under the Grant No. 200021_169032 as well as Editor Marie Edmonds and two anonymous reviewers for their prompt and valuable revision of this study which improved the original manuscript. Georgatou Ariadni thanks Dr. Andreas Audétat for his valuable input on an earlier version of this manuscript.

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