ORIGINAL PAPER

Constraints on the source of Cu in a submarine magmatic-hydrothermal system, Brothers volcano, Kermadec island arc

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Abstract

Most magmatic-hydrothermal Cu deposits are genetically linked to arc magmas. However, most continental or oceanic arc magmas are barren, and hence new methods have to be developed to distinguish between barren and mineralised arc systems. Source composition, melting conditions, the timing of S saturation and an initial chalcophile element-enrichment represent important parameters that control the potential of a subduction setting to host an economically valuable deposit. Brothers volcano in the Kermadec island arc is one of the best-studied examples of arc-related submarine magmatic-hydrothermal activity. This study, for the first time, compares the chemical and mineralogical composition of the Brothers seafloor massive sulphides and the associated dacitic to rhyolitic lavas that host the hydrothermal system. Incompatible trace element ratios, such as La/Sm and Ce/Pb, indicate that the basaltic melts from L'Esperance volcano may represent a parental analogue to the more evolved Brothers lavas. Copper-rich magmatic sulphides ($Cu > 2$ wt%) identified in fresh volcanic glass and phenocryst phases, such as clinopyroxene, plagioclase and Fe–Ti oxide suggest that the surrounding lavas that host the Brothers hydrothermal system represent a potential Cu source for the sulphide ores at the seafloor. Thermodynamic calculations reveal that the Brothers melts reached volatile saturation during their evolution. Melt inclusion data and the occurrence of sulphides along vesicle margins indicate that an exsolving volatile phase extracted Cu from the silicate melt and probably contributed it to the overlying hydrothermal system. Hence, the formation of the Cu-rich seafloor massive sulphides (up to 35.6 wt%) is probably due to the contribution of Cu from a bimodal source including wall rock leaching and magmatic degassing, in a mineralisation style that is hybrid between Cyprus-type volcanic-hosted massive sulphide and subaerial epithermal–porphyry deposits.

Communicated by Timothy L. Grove.

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Introduction

Magmatic-hydrothermal systems along convergent plate margins host some of the Earth's most important porphyry Cu–Mo and epithermal Au–Ag–Te deposits (Seedorff et al. 2005; Simmons 2005; Sillitoe 2010). Most of these metals are considered to be derived from fluids of magmatic origin that exsolved from mid- to upper crustal magma chambers (Richards 2011). Recent studies have shown that submarine hydrothermal systems associated with island arc volcanism can be affected by a magmatic volatile component similar to their subaerial counterparts (de Ronde et al. 2005, 2014). Brothers volcano in the Kermadec island arc represents one of the best-studied examples of arc-related submarine magmatic-hydrothermal activity; and fluid and sulphide chemistry suggest a magmatic volatile contribution

(de Ronde et al. 2005, 2011; Keith et al. 2016a). In addition to a magmatic volatile signature, acid-sulphate (advanced argillic) alteration, sulphosalts (e.g., enargite, Cu_3AsS_4) typical for high-sulphidation conditions (Einaudi et al. 2003) and high contents of economically important metals (e.g., Cu and Au) in some submarine arc and back-arc hydrothermal systems imply that they may be comparable to epithermal–porphyry deposits on land, such as the world-class Far Southeast-Lepanto Cu–Au deposits (Philippines; Hedenquist et al. 1998). This includes, for example, the magmatic-hydrothermal systems of Brothers volcano (Kermadec arc; de Ronde et al. 2005; Berkenbosch et al. 2012) and Kolumbo volcano (Hellenic arc; Kilias et al. 2013, 2016), as well as SuSu Knolls in the Manus back-arc basin (Craddock and Bach 2010; Craddock et al. 2010; Yeats et al. 2014; Thal et al. 2016). Hence, arc-hosted hydrothermal systems are characteristically distinct in terms of their chemical and mineralogical composition compared to those along mid-ocean ridges, which were interpreted to be the classic modern analogues of volcanic-hosted massive sulphide (VHMS) deposits mined on land (Hannington et al. 1998, 2011; de Ronde et al. 2014; Keith et al. 2016b).

High bulk ore contents of certain metals and semi-metals, such as Cu (up to 27 wt%), Au (up to 57 ppm), Ag (up to 2010 ppm) and Te (up to 53 ppm) at PACMANUS and SuSu Knolls (Manus Basin; Moss and Scott 2001) have attracted attention for potential future submarine mining operations (Gena 2013). Consequently, it is important to improve our understanding of the ore-forming processes in subduction zone-related magmatic-hydrothermal systems and to identify chemical and mineralogical parameters for exploration and their economic evaluation.

A key process for the formation of a Cu-rich magmatic-hydrothermal ore deposit is the loss of magmatic volatiles prior to the formation of immiscible sulphide liquids. In contrast, early sulphide segregation, i.e., prior to degassing, would extract most chalcophile metals including Cu and Au from the melt leading to a barren arc system (Sun et al. 2004; Jenner et al. 2010; Richards 2011; Park et al. 2015; Fontboté et al. 2017). This idea appears to be supported by previous studies, which suggest that aqueous S- and Cl-bearing magmatic volatiles are the main source and transport medium for Cu in submarine hydrothermal arc systems, such as Brothers volcano (de Ronde et al. 2005; Berkenbosch et al. 2012; Gruen et al. 2014). Therefore, economic mineralisation within an island arc can be controlled by sulphide liquid immiscibility during silicate melt evolution, which is highly sensitive to changes in pressure, temperature, oxygen fugacity (fO_2), the degree of fractional crystallisation and the initial Fe and S contents of the melt (Mavrogenes and O'Neill 1999; Jenner et al. 2010; Yang et al. 2014; Keith et al. 2017). Arc magmas characteristically show higher fO_2 (up to FMQ + 2) and H_2O contents (up to 6–8 wt%) and are enriched in incompatible trace elements and volatiles (e.g., S and Cl) compared to mid-ocean ridge magmas (Wallace 2005; Richards 2011; Kelley and Cottrell 2012; Lee et al. 2012). This discrepancy results in higher S concentrations at sulphide saturation (Fortin et al. 2015), and hence sulphide segregation typically occurs later during magmatic differentiation, perhaps triggered by Fe–Ti oxide fractionation and decreasing fO_2 (Jenner et al. 2010; Keith et al. 2017; Patten et al. 2017). However, distinguishing these different processes and parameters is still challenging and often ambiguous (Hedenquist and Lowenstern 1994) and our knowledge about the interaction between the magmatic and hydrothermal system and its control on the composition of associated ore deposits is limited.

This study combines the chemical and mineralogical composition of magmatic and hydrothermal sulphides with silicate glass and melt inclusion data for the first time to constrain the source characteristics and main enrichment processes of Cu in an island arc-hosted magmatic-hydrothermal system.

Geological setting and sample localities

Island arc systems with a submarine expression have a combined length of about 21,700 km (93% in the Pacific Ocean; de Ronde et al. 2014). Brothers volcano is part of the ~1200 km long Kermadec island arc, northeast of New Zealand (Fig. 1a), which post-dates the earliest phase of Havre Trough back-arc rifting (Wright et al. 1996, 1998). The elongated volcanic edifice of Brothers is 13 km long, 8 km wide and strikes NW–SE at a water depth of 2200 mbsl (de Ronde et al. 2005). The caldera floor (1850 mbsl) has a basal dimension of 3 to 3.5 km and is surrounded by a 350–450 m high caldera wall (Fig. 1b; Wright et al. 1998). The caldera hosts a resurgent dome rising to a water depth of 1300 mbsl at its summit (Fig. 1b; Wright and Gamble 1999; de Ronde et al. 2001). Hence, at least two stages of magmatic activity can be distinguished at Brothers volcano including (1) an effusive incremental caldera-forming eruption (Wright and Gamble 1999) and (2) the subsequent formation of two younger volcanic cones (Embley et al. 2012). The Brothers volcanic rocks range in composition from dacite to rhyolite (Haase et al. 2006). In addition, one basaltic andesite sample was recovered from Brothers Ridge, a young SW-NE striking mafic dyke beneath the Brothers caldera (Wysoczanski et al. 2012).

Several hydrothermal fields were distinguished including hydrothermal venting of evolved seawater derived fluids with limited magmatic contribution at the NW caldera wall and magmatic volatile-dominated systems at the Brothers cone complex (Fig. 1b; de Ronde et al. 2005, 2011; Baker et al. 2012; Caratori Tontini et al. 2012). Hydrodynamic
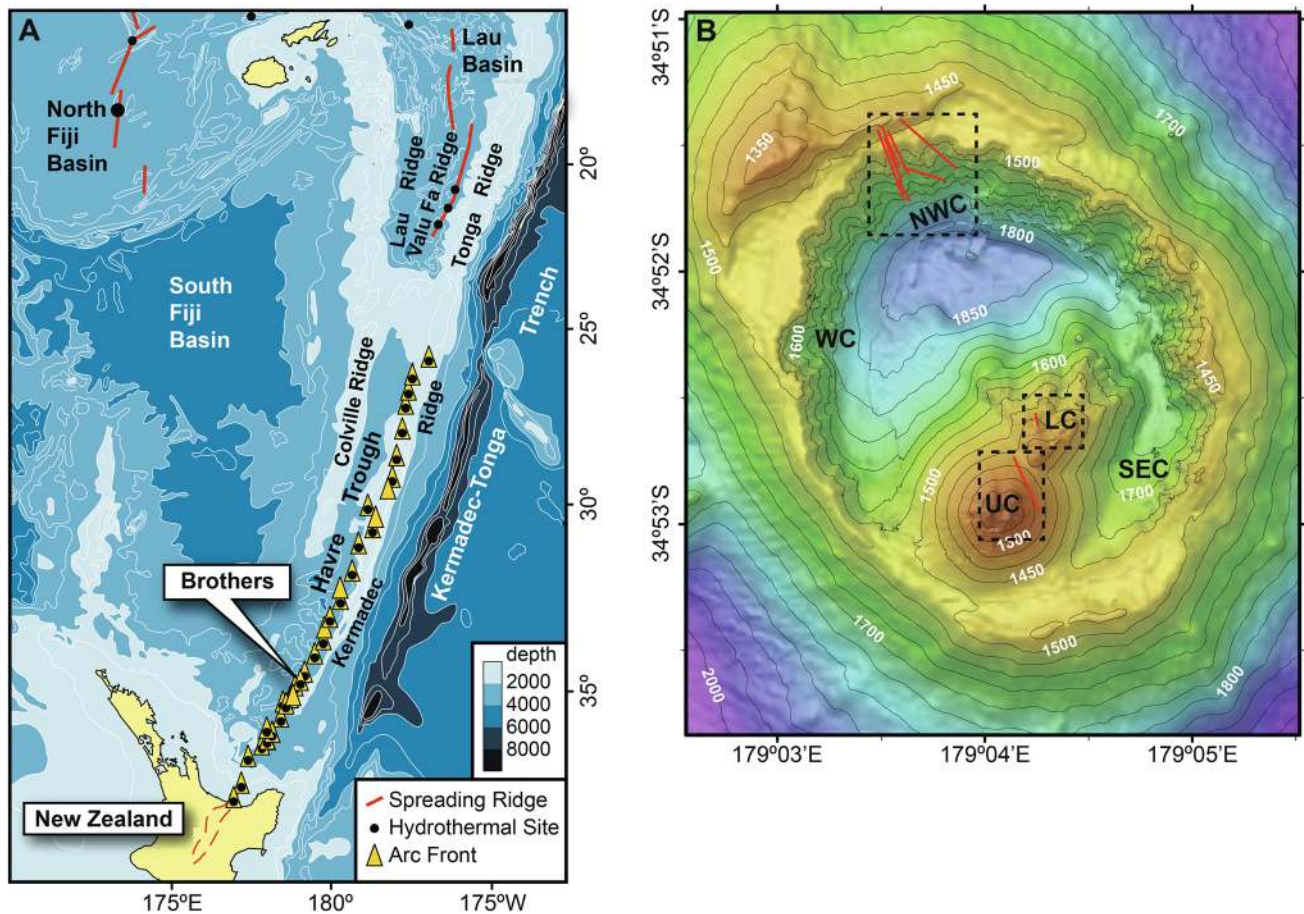
Fig. 1 a Map of the Kermadec island arc showing the location of Brothers volcano, modified after de Ronde et al. (2011). **b** Detailed bathymetric map of Brothers volcano with the dredge locations (dashed boxes) of research cruise SO135 (Stoffers et al. 1998) for the samples investigated in this study from the NW caldera and the lower and upper cone complex. Map modified after Baker et al. (2012). *LC* lower cone, *NWC* NW caldera, *SEC* SE caldera, *UC* upper cone, *WC* western caldera (figures in colour can be found in the web version of the article)

modelling calculations by Gruen et al. (2014) suggest that a 3×2 km² sized magma chamber at ~2.5 km depth below the seafloor may represent the heat source for the Brothers magmatic-hydrothermal system. In 1996 the R/V Tangaroa dredged the first massive sulphide-bearing samples suggesting that Brothers volcano hosts a magmatic-hydrothermal system (Wright et al. 1998). This finding lead to the discovery of an active black smoker field at the caldera floor in 1998 during R/V Sonne cruise SO135 (Stoffers et al. 1998). Two types of massive sulphide mineralisation were distinguished including (1) high temperature (> 300 °C) chalcopyrite-dominated Cu–Fe-rich samples with up to 35.6 wt% Cu and (2) low temperature (< 120 °C) Zn–Fe-rich samples with abundant sphalerite reaching Zn concentrations of up to 18.8 wt% in the bulk ore (Wright et al. 1998; de Ronde et al. 2011; Berkenbosch et al. 2012). The samples presented in this study were dredged from Brothers volcano during R/V Sonne cruise SO135 (Table 1; Stoffers et al. 1998) and include volcanic rocks that are representative for the

caldera-forming event ($n = 19$) and the formation of the cone complex ($n = 6$, Fig. 1b).

Methods

Electron probe microanalysis

In a previous study, volcanic glass fragments ($n = 25$) from Brothers volcano were analysed for their major element composition (Haase et al. 2006). The same samples were used in this study to investigate the chemistry of melt inclusions ($n = 157$), plagioclase crystals ($n = 36$), Fe–Ti oxides ($n = 241$) and magmatic sulphides ($n = 134$) by electron probe microanalysis using a JEOL JXA-8200 Superprobe at the GeoZentrum Nordbayern.

For the quantitative analyses of melt inclusions and their plagioclase host crystals an acceleration voltage of 15 kV and a beam current of 15 nA were used. A defocused beam

Table 1 List of the samples investigated in this study including the dredge locations at Brothers volcano during cruise SO135 (Stoffers et al. 1998)

Dredge #	Sample #	n	Location	Start		Depth (mbsl)	End		Depth (mbsl)
				Latitude	Longitude		Latitude	Longitude	
52DR	− 1 to − 4, − 6	5	NW Caldera wall	34°51.685′S	179°03.584′E	1605	34°51.461′S	179°03.336′E	1462
56DR	− 1, − 2, − 4	3	NW Caldera wall	34°51.662′S	179°03.476′E	1567	34°51.397′S	179°03.439′E	1400
58DR	− 1, − 2, − 4, − 13	4	NW Caldera wall	34°51.596′S	179°03.793′E	1612	34°51.339′S	179°03.523′E	1415
59DR	− 1, − 3, − 4	3	NW Caldera wall	34°51.665′S	179°03.561′E	1623	34°51.471′S	179°03.462′E	1447
60DR	− 10	1	NW Caldera wall	34°51.794′S	179°03.548′E	1745	34°51.691′S	179°03.439′E	1576
67DR	− 1, − 2	2	NW Caldera wall	34°51.657′S	179°03.734′E	1645	34°51.755′S	179°03.337′E	1577
68DR	− 7	1	NW Caldera wall	34°51.665′S	179°03.522′E	1611	34°51.421′S	179°03.512′E	1445
65DR	− 1 to − 4	4	Lower cone	34°52.553′S	179°04.268′E	1439	34°52.799′S	179°04.303′E	1402
66DR	− 1, − 2	2	Upper cone	34°52.784′S	179°04.243′E	1371	34°53.049′S	179°04.027′E	1313

of 10 and 3 μm, respectively, has been applied for these measurements to minimise the Na loss.

The natural glass standards VG-2 (basalt glass), VG-A99 (basalt glass) and VG-568 (rhyolite glass) of the Smithsonian Institution were analysed as secondary standards to monitor the precision an accuracy of the electron microprobe set up for the melt inclusion analyses (electronic supplement, Table A1). The same measurement conditions were used with the exception of a focused beam for the Fe–Ti oxide analyses. The FeO and Fe_2O_3 contents in Fe–Ti oxide were calculated based on the method presented by Lepage (2003). The analysed elements and the assigned standards are listed in Table A2 (electronic supplement). Different measurement conditions were applied for the analyses of the magmatic sulphides. Due to high concentrations of chalcophile elements, such as Cu and Ni with atomic numbers > 26 (Fe) a focused beam, an acceleration voltage of 20 kV and a beam current of 20 nA was used. The electron microprobe was calibrated by the following standards: FeS_2 (S), Fe_2O_3 (Fe), $CuFeS_2$ (Cu), NiO (Ni), Co (Co) and $CaSi_2O_6$ (Si). The count times were set to 20 and 10 s for the peak and background measurements, respectively.

The presented dataset was supplemented by previously published magmatic sulphide data from Brothers volcano ($n = 128$; Keith et al. 2017) and from mid-ocean ridges of the Atlantic (Kanehira et al. 1973; MacLean 1977; Mathez 1980; Petersen 1984; Patten et al. 2012, 2013; Marchesi et al. 2013), Pacific (Mathez and Yeats 1976; Foder et al. 1980; Distler et al. 1983; Schrader and Stow 1983; Francis 1990; Ackermand et al. 2007; Patten et al. 2012) and Indian Ocean (Francis 1990; Yang et al. 2014).

Laser Ablation ICP-MS

The Laser Ablation ICP-MS study was carried out at the GeoZentrum Nordbayern to determine the trace element composition of the volcanic glass fragments from Brothers volcano that have previously been studied by Haase et al. (2006) for their major element composition. For this purpose a UP193FX (New Wave Research) laser attached to an Agilent 7500i ICP-MS was used. The Laser operated with a frequency of 20 Hz, an irradiance of 0.52 GW/cm^2 and a fluence of 2.5 J/cm^2. The total analysis time for each spot was 50 s, including 20 s for gas blank analysis. The beam diameter was typically set to 50 μm and on occasion due to high amounts of phenocryst phases to 25 μm. The glass reference material NIST SRM 612 (Pearce et al. 1997) was used for the external calibration of Cu, Mo, La, Ce, Sm and Pb. Analytical precision and accuracy was monitored based on the repeated analyses of BCR-2 g and NIST SRM 614, as secondary standards, yielding < 4.2% RSD for all elements (electronic supplement, Table A3). To monitor the instrument drift the silicate standards were analysed several times during an analytical day. The trace element concentrations were calculated with Glitter (van Achterbergh et al. 2000) using Si as internal standard, determined by electron probe microanalyses as reported in Haase et al. (2006). Based on a single spot ablation pattern each glass sample was analysed at least 3 times for homogenous laser signals and up to 6 times for more heterogeneous compositions. Mean concentrations and standard deviations were calculated for each element based on multiple analyses in the different glass samples (electronic supplement, Table A4).

Results

Petrography

The petrographic observations reveal that globules of magmatic sulphides in the Brothers arc lavas are common but highly variable in size (< 10–300 μm). The round shape of most globules (Fig. 2), that are hosted in volcanic glass from the seafloor, suggest that they were not affected by metal

Fig. 2 Photomicrographs of samples from Brothers volcano in reflected light: **a** magmatic sulphide inclusion in plagioclase (SO135-66DR-01), **b** matrix- and clinopyroxene-hosted magmatic sulphides (SO135-59DR-01), **c** magmatic sulphides associated with Fe–Ti oxide (SO135-59DR-01; Keith et al. 2017), **d** Fe–Ti oxide phase acting as nucleation site during magmatic sulphide segregation (SO135-52DR-01), **e** ilmenite and ulvöspinel in textural equilibrium (SO135-52DR-01), **f** sulphides along a vesicle margin (SO135-66DR-01). *cpx* clinopyroxene, *ilm* ilmenite, *plag* plagioclase (figures in colour can be found in the web version of the article)
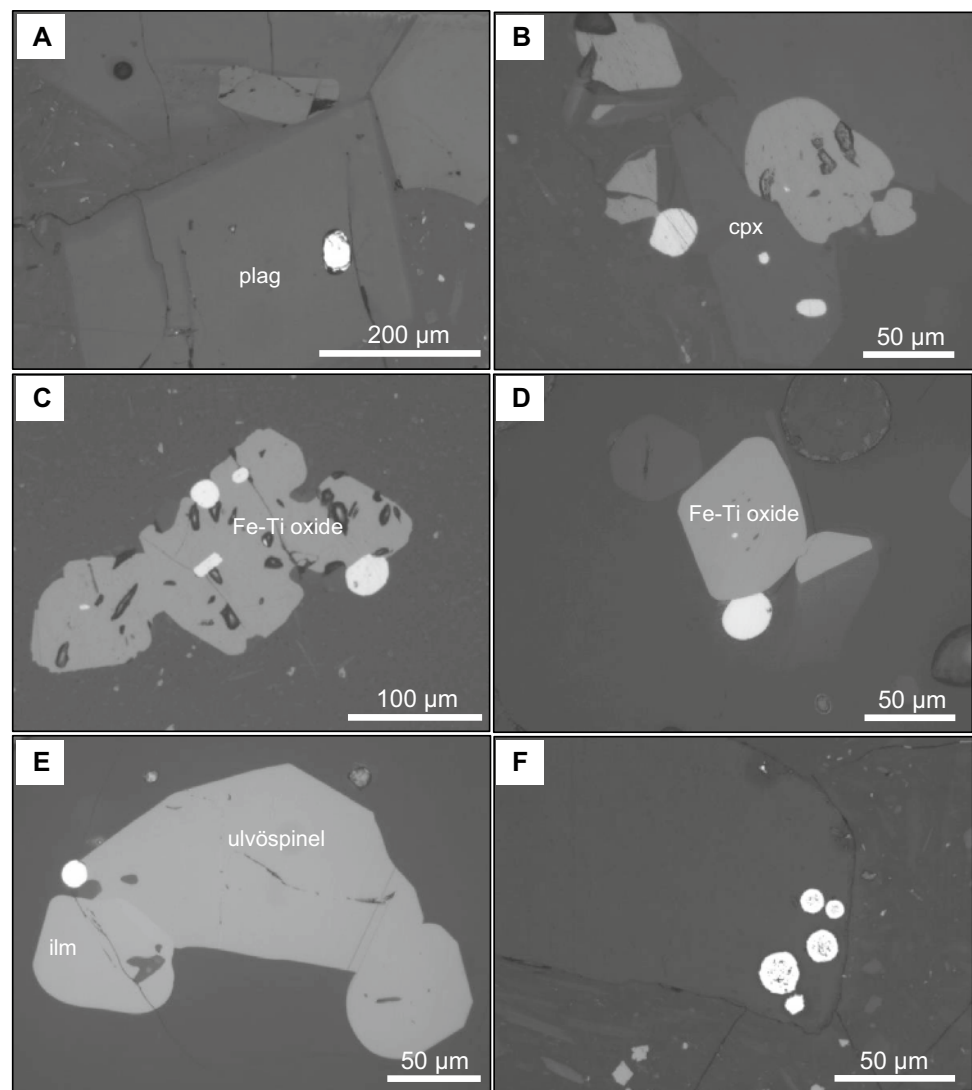
leaching or fluid alteration to significant amounts indicating that they preserve the original composition of the former sulphide liquid (Mathez 1980). Sulphide globules are typically hosted in volcanic glass and occur in association with different silicate and oxide phases (Fig. 2). For instance, magmatic sulphide inclusions were observed in plagioclase (Fig. 2a) and clinopyroxene phenocrysts (Fig. 2b). However, they are most abundant in association with Fe–Ti oxides, which either host the globules (Fig. 2c, d) or served as nucleation sites during sulphide segregation indicated by a flat surface in contact to the oxide phase (Fig. 2c–e). Two types of Fe–Ti oxides were distinguished in reflected light: ilmenite and magnetite/ulvöspinel solid solutions; the two phases commonly show textural equilibrium (Fig. 2e).

Pyrrhotite has been identified as the most abundant phase in the sulphide segregates from Brothers volcano (Fig. 2). Copper-rich sulphides (e.g., cubanite and chalcopyrite) were less common and Ni-rich phases are absent or must be sub-microscopic in size. This finding is in agreement with previous results showing that Ni-rich phases, such as pentlandite are rare or absent in island arc magmatic systems (Keith et al. 2017). Hence, most globules show a homogenous texture exclusively composed of pyrrhotite ($n = 67$), whereas heterogeneous globules ($n = 19$) and zoned segregates, in which distinct phases can be distinguished ($n = 9$) are rare. In addition, sulphides have been identified along vesicle margins (Fig. 2f), as described in previous studies from other localities (Francis 1990; Ackermand et al. 2007). Systematic mineralogical variations in sulphide globule occurrence between samples from the NW caldera and the cone complex of Brothers volcano were not observed.

Plagioclase and Fe–Ti oxide mineral chemistry

Anorthite contents in plagioclase vary over a small compositional range ($An_{49–56}$, electronic supplement, Table A5)

between andesine and labradorite. Differences between plagioclase cores (An$_{49-55}$) and rims (An$_{49-56}$) were not observed. Iron and Ti contents in the oxide phases vary between ilmenite (FeTiO$_3$) and magnetite (Fe$_3$O$_4$). Oxides with compositions between these two potential endmembers can be classified as ulvöspinel (TiFe$_2$O$_4$, electronic supplement, Table A6).

Sulphide composition

Copper varies significantly in the Brothers magmatic sulphides from trace amounts in pyrrhotite to 24.1 wt% in cubanite. However, most sulphide segregates are characterised by Cu concentrations < 2 wt% (n = 225) and only a small proportion shows Cu contents > 2 wt% (n = 37, Fig. 3). Similarly, Ni-rich sulphides were not identified in lavas from Brothers volcano suggesting that pentlandite is at best a trace component in the sulphide globules (Fig. 3). Hence, the sulphide segregates from Brothers volcano are depleted in Ni compared to those hosted in basalts from mid-ocean ridges (Fig. 3). These results confirm the textural classification based on the petrographic observations. The dominance of compositions near stoichiometric pyrrhotite or cubanite is indicative for homogenous (consisting of one single phase) or zoned globules. Systematic variations in magmatic sulphide chemistry with respect to the host phase were not observed. Compositions between two stoichiometric endmembers, such as cubanite and pyrrhotite, are rare implying that fine-grained heterogeneously textured sulphides, where single phases cannot be analysed due to an
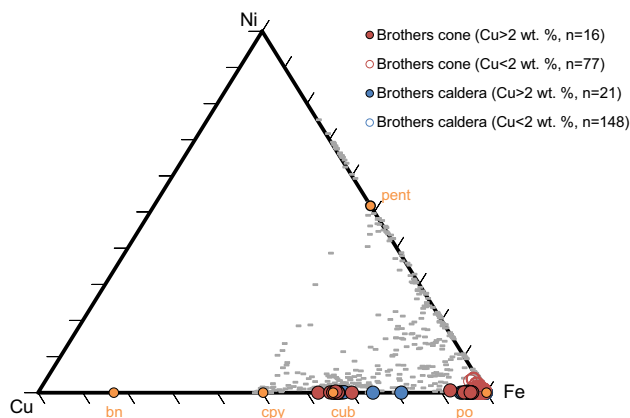

Fig. 3 Composition of magmatic sulphides from Brothers volcano in the Cu–Fe–Ni system, concentrations in at%. Orange symbols show the stoichiometric composition of bornite (bn), chalcopyrite (cpy), cubanite (cub), pentlandite (pent) and pyrrhotite (po). The Brothers data set includes the published analyses by Keith et al. (2017). Grey symbols represent literature data from mid-ocean ridges, as described in the text (cf. "Methods"). New data presented in this figure can be found in the electronic supplement (Table A7) (figures in colour can be found in the web version of the article)

overlapping electron beam (Keith et al. 2017), are uncommon at Brothers volcano.

Most sulphides (n = 40) that are attached to vesicle margins in glass samples from Brothers volcano were classified as pyrite based on their chemical composition. Only one analyses showed high Cu contents (22.8 wt%) in the range of cubanite (electronic supplement, Table A8).

Lava composition

The composition of volcanic glass samples revealed that the Brothers lavas vary in terms of their SiO$_2$ contents over a small range from 66.3 to 72.4 wt%, i. e. from dacites to rhyolites. The glass samples from the volcanic cone are slightly more evolved than those from the caldera (Fig. 4; Haase et al. 2006). Published whole rock data shows SiO$_2$ concentrations between 62.2 and 66.2 wt% (Wright and Gamble 1999; Smith et al. 2003; Timm et al. 2012), which are slightly lower than those of the volcanic glass samples (Fig. 4). Only one mafic glass sample of basaltic andesitic composition (SiO$_2$ = 55.0 wt%, Fig. 4) was recovered from Brothers Ridge, which was interpreted as a young dyke-like structure beneath Brothers caldera (Wysoczanski et al. 2012).

Due to the limited compositional range of the Brothers lavas the dataset was supplemented by melt inclusion, volcanic glass and whole rock data from other subduction zone-related magmatic systems to investigate the evolution of island arc magmas. This includes data from the L'Esperance (Ewart et al. 1994, 1998; Turner et al. 1997) and the Rumble III and IV (Wysoczanski et al. 2006, 2012) island arc volcanoes, as well as from the Valu Fa Ridge (Davis et al. 1990; Vallier et al. 1991; Peate et al. 2001; Haase et al. 2002; Fretzdorff et al. 2006; Jenner et al. 2015) and the Pual Ridge (Kamenetsky et al. 2001; Moss and Scott 2001; Yang and Scott 2002, 2005; Sun et al. 2004; Jenner et al. 2010, 2012), as examples for back-arc volcanism. Three groups of major elements can be distinguished based on their behaviour during magma evolution, i.e., with increasing SiO$_2$, including elements with an (1) incompatible (K$_2$O, Na$_2$O), (2) compatible (MgO, Al$_2$O$_3$, CaO) and (3) an initially incompatible and later compatible (TiO$_2$, FeO^T) character (Fig. 4).

Volatile elements, such as Cl and S, show distinct variations in the Brothers melts (Fig. 5). Sulphur varies between trace and minor element levels from about 10 to 420 ppm possibly with a tendency to lower concentrations in the most evolved samples (Haase et al. 2006). In contrast, Cl is consistently high in all Brothers volcano glass samples with concentrations from 4370 to 6570 ppm. The S and Cl contents of plagioclase-hosted melt inclusions tend to be higher compared to those in the glass samples (Fig. 5).

Incompatible trace element ratios, such as La/Sm and Ce/Pb in the Brothers lavas (2.7 and 4.1, respectively) are

similar to other island arc and back-arc systems showing average values of about 2.3 and 4.6, respectively. Only the Valu Fa Ridge data set (grey field) differs significantly due to lower La/Sm (av. 1.3) and higher Ce/Pb ratios (av. 9.0, Fig. 6).

The transition metals Cu and Mo represent trace elements in the samples investigated in this study (Fig. 7). Copper either represents a compatible element (Valu Fa Ridge; Francis 1990) or shows a strong incompatible behaviour during the early stages of magma evolution ($SiO_2 < 60$ wt%) followed by a sudden drop in Cu at about 60 wt% SiO_2 and a slightly compatible behaviour in the more evolved melts ($SiO_2 > 60$ wt%, Fig. 7a). In contrast, Mo contents increase with increasing SiO_2 (Kamenetsky and Eggins 2012), however, variations in the slope of the linear trends with respect to the tectonic setting suggest that Mo is more incompatible in island arc than in back-arc magmas (Fig. 7b).

Discussion

Parental mafic analogue to the Brothers dacites

Ratios of incompatible trace elements with similar solid–liquid distribution coefficients show no variation during magmatic differentiation, and can therefore, be used to identify the source or mafic parental magma composition of a more evolved melt (Miller et al. 1994; Haase et al. 2006). The La/Sm and Ce/Pb ratios in samples from Brothers Ridge, L'Esperance, Rumble III and IV and Pual Ridge are similar to those from Brothers volcano indicating that mafic compositions from these localities may act as a parental magma analogue (Fig. 6). This conclusion is supported by Haase et al. (2006) showing that the basaltic L'Esperance and Rumble III lavas can be used as parental magmas to the evolved Brothers melts based on similar Ba/La as well as comparable Sr and Nd isotope ratios. Moreover, the L'Esperance, Rumble III and Brothers volcanoes are part of the same segment of the Kermadec arc (Ewart and Hawkesworth 1987; Haase et al. 2006). In contrast, the Valu Fa Ridge lavas vary in terms of their incompatible trace element ratios probably due to a different source or parental melt composition. Miller et al. (1994) and Beaudoin et al. (2007) have shown that the Ce/Pb ratio can be used to track the fluid contribution from the subducted slab to the mantle wedge, the source region for arc (and back-arc) magmas. Subduction zone fluids are enriched in Pb leading to low Ce/Pb ratios in systems with a strong subduction influence (e.g., Brothers volcano) compared to those, which are less affected by a subduction component (Valu Fa Ridge, Fig. 6b).

The thermodynamic modelling software Rhyolite-MELTS (Gualda et al. 2012) was used to calculate a liquid line of descent for the evolved Brothers lavas based on the assumption that the L'Esperance island basalts represent the parental magma of the Brothers dacites and rhyolites (Fig. 4). The MELTS modelling was conducted based on the most primitive lava composition ($SiO_2 = 51.6$ wt%; Turner et al. 1997) from L'Esperance volcano assuming a uniform magma chamber pressure governed by a water depth of 1500 mbsl (~0.15 kbar) and a crustal depth of 2500 mbsf (~0.71 kbar; Gruen et al. 2014) yielding a total pressure of ~0.86 kbar. Variable redox conditions (FMQ −1, FMQ, FMQ +1) and H_2O contents (0.5, 1.5 wt%) were applied for the calculations. The results are based on 10 °C temperature increments (Fig. 4). Fractionated phases include plagioclase (46–47%), clinopyroxene (33–44%), spinel (~7%) and apatite (~0.01%) matching the observed phenocrysts in the examined Brothers volcano samples (Fig. 2; Gamble and Wright 1995; Haase et al. 2002, 2006; de Ronde et al. 2005). The modelling curves resemble the observed chemical trends of the Brothers volcano dacites and rhyolites (Fig. 4), which confirms that the L'Esperance basalts can be used as a mafic parental melt to the Brothers lavas. Furthermore, the composition of the cone and the caldera lavas can be simulated by the same parental magma composition, which coincides with the identical incompatible trace element ratios and isotope compositions (Fig. 6; Haase et al. 2006). This is also in agreement with the similar chemical and mineralogical composition of the magmatic sulphides from the cone and the caldera of Brothers volcano (Fig. 3).

Thermodynamic investigations on the Brothers magmatic systems

Previous studies have shown that it is important to define the physicochemical conditions (T, p, $f\mathrm{O}_2$, H_2O) in a fractionating magma because they control the S solubility limit in a silicate melt and therefore the behaviour of chalcophile metals and the composition of potential immiscible sulphide liquids (Distler et al. 1983; Mavrogenes and O'Neill 1999; Ackermand et al. 2007; Yang et al. 2014).

To determine the temperature and $f\mathrm{O}_2$ of the Brothers melts the magnetite-ulvöspinel geo-thermometer and oxygen barometer by Anderson and Lindsley (1985), integrated in the ILMAT spreadsheet (Lepage 2003) was used (electronic supplement, Table A6). The petrographic observations imply that the Fe–Ti oxides crystallised under equilibrium conditions (Fig. 2e). The calculated temperatures vary from 871 to 988 °C with an average value of 913 ± 14 °C ($n = 248$). Temperature variations between samples from the caldera (879–985 °C, $n = 99$) and the cone (871–988 °C, $n = 149$) of Brothers volcano were not observed. Similarly, the $f\mathrm{O}_2$ calculations revealed no systematic differences between these two sites, which show an overall variation from −10.1 to −11.9 log $f\mathrm{O}_2$ units, approximately FMQ −0.6 to +1.5 at 913 °C and ~0.86 kbar total pressure (Frost 1991). The $f\mathrm{O}_2$
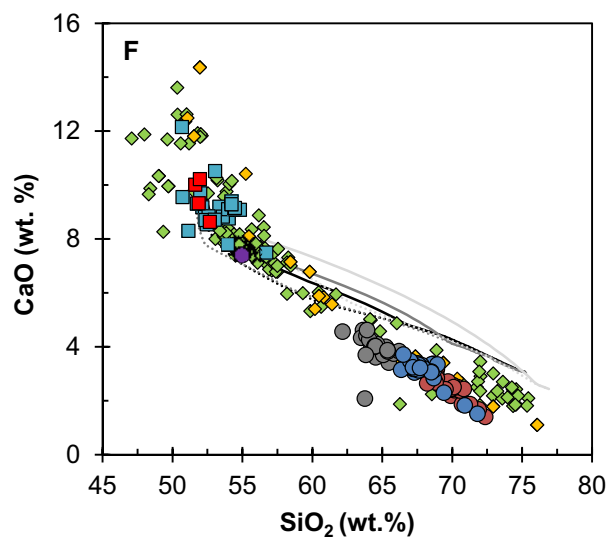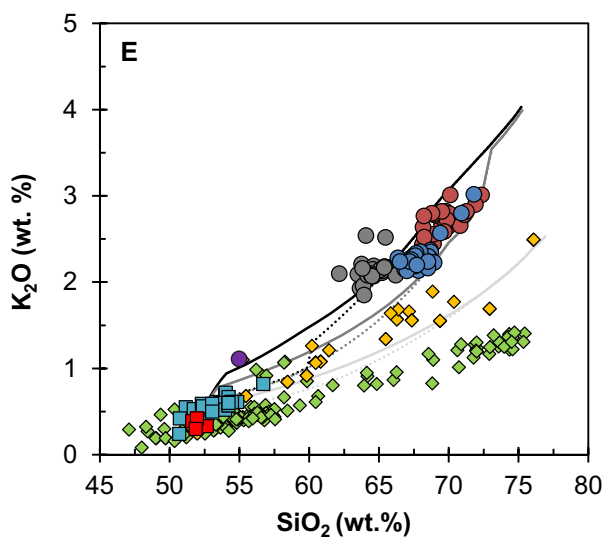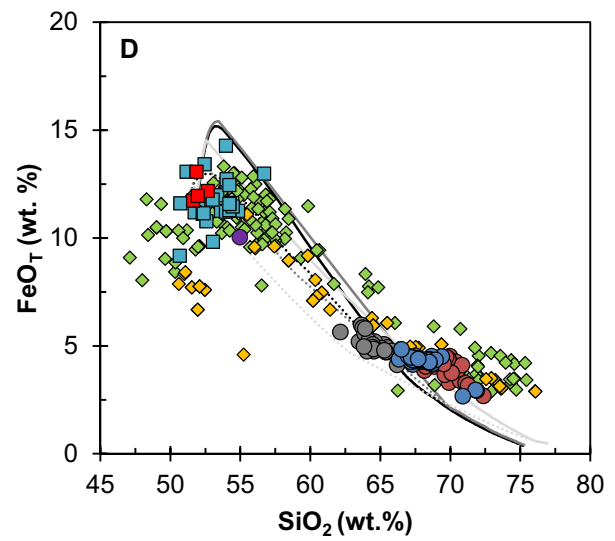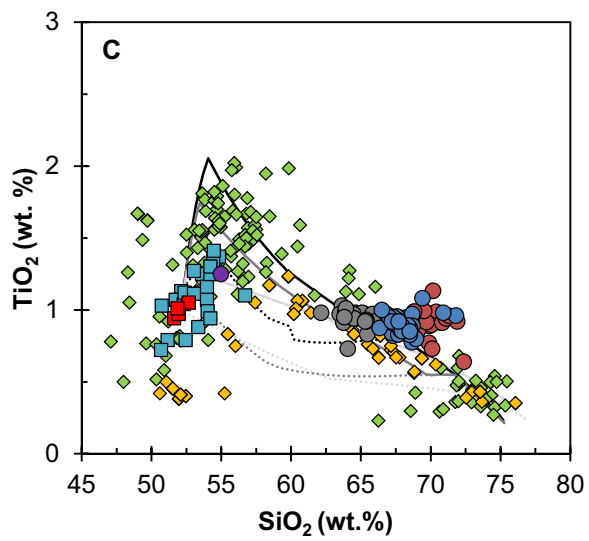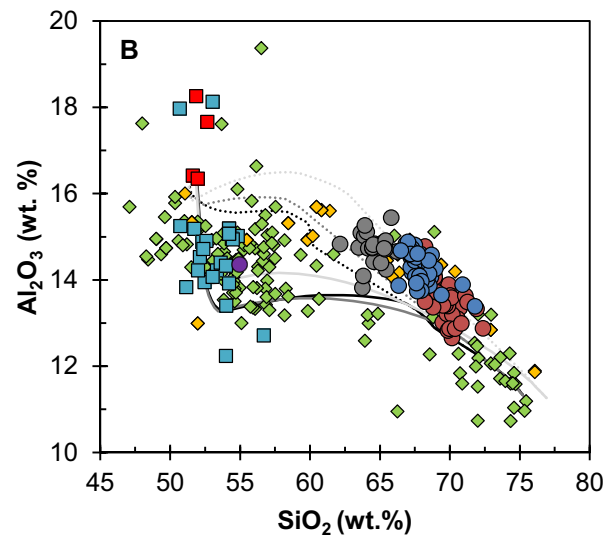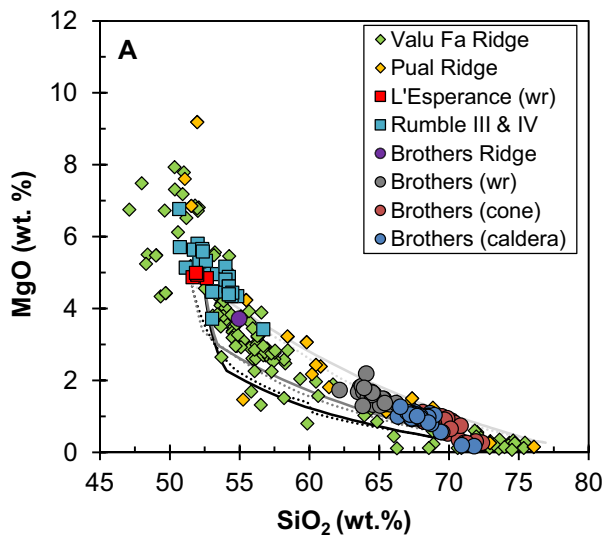
◀**Fig. 4** Major element variation diagrams of arc and back-arc lavas. **a** MgO, **b** Al_2O_3, **c** TiO_2, **d** FeO^T, **e** K_2O and **f** CaO vs. SiO_2. The most primitive lava composition ($SiO_2 = 51.6$ wt%; Turner et al. 1997) from L'Esperance volcano was used to perform the MELTS simulations. The different lines represent the isobaric (~ 0.71 kbar) MELTS simulations based on different starting parameters: solid ($H_2O = 0.5$ wt%), dashed ($H_2O = 1.5$ wt%), black (FMQ −1), dark grey (FMQ), light grey (FMQ +1). Data taken from literature as specified in the text (cf. Results, Lava composition). All analyses represent glass data if not specified otherwise. *wr* whole rock (figures in colour can be found in the web version of the article)

estimations for Brothers volcano are comparable to other island arc systems that typically range from FMQ 0 to FMQ +2 (Parkinson and Arculus 1999; Lee et al. 2012; Wysoczanski et al. 2012). The fO_2 of the Brothers magmas is also comparable to the Lau back-arc (Nilson and Peach 1993) explaining similar fractionation processes in the magmas (Fig. 4). At FMQ −1 to FMQ 0 the dominant S species is S^{2-}, whereas at FMQ above +1 most S exists as S^{6+} and between FMQ 0 and FMQ +1 both S^{2-} and S^{6+} are stable (Jugo et al. 2010). This indicates that in the Brothers melts S most likely exists as S^{2-} and S^{6+}. The high concentrations of S in the Brothers melts (up to 740 ppm) reaching the sulphide saturation limit (Fig. 5a) explain the high abundance of magmatic sulphides in the Brothers volcano samples (Fig. 2), which also coincides with the existence of S^{2-}. The melt inclusions tend to plot above the calculated sulphide saturation limit (Fig. 5a), which may be due to the analyses of melt inclusion-hosted invisible sulphide segregates by the defocused beam (10 μm) of the electron microprobe.

The H_2O contents of the Brothers volcano melts were estimated based on the plagioclase-melt hygro-thermometer (electronic supplement, Table A5) by Putirka (2008) and Lange et al. (2009). Crystallisation temperatures varied between 987 and 1034 °C with an average error of ± 38 °C (Putirka 2008). Lower temperatures were generally observed for plagioclase rims (987–993 °C) compared to the corresponding cores (1021–1034 °C), which are also above the temperatures determined by magnetite-ulvöspinel geothermometer (871–988 °C). This is in agreement with the onset of the plagioclase crystallisation prior to Fe–Ti oxides in tholeiitic magmatic systems (Fig. 4; Haase et al. 2006). Estimated H_2O contents varied between 2.3 and 4.1 wt%, which is comparable to previous suggestions ($H_2O = 2$–3 wt%) for the Brothers dacites (Haase et al. 2006). Calculations based on the composition of plagioclase rims generally yielded higher H_2O contents (3.4 to 4.1 wt%) compared to the cores of the same crystal (2.3–2.8 wt%) reflecting the typical incompatible behaviour of H_2O during fractional crystallisation (Schmitt 2001).

The H_2O saturation limit of the Brothers melts was calculated in an isobaric system (0.86 kbar) using the empirical model of Moore et al. (1998). Compositional variations

with respect to the lava chemistry of Brothers volcano ($SiO2 = 66.5$–72.4 wt%) had no effect on the saturation limit. However, temperature changes significantly influenced the H_2O saturation limit. Based on the temperature estimations the H_2O solubility limit was calculated between 850 and 1050 °C yielding a maximum H_2O content of 3.7 and 3.2 wt%, respectively. This suggests that the Brothers melts reached the H_2O saturation limit during crystallisation (between 66.4 and 77.4 wt% SiO_2) and storage at 0.86 kbar (electronic supplement, Fig. A1). Importantly, the temperature, fO_2 and H_2O estimations between the thermodynamic calculations and the MELTS simulations are comparable, which confirms that the presented results are in a reliable range (electronic supplement, Fig. A1).

Formation of magmatic sulphides and their potential role as a Cu source

The petrographic results imply that sulphide–silicate melt immiscibility represents a continuous or multistage process in the Brothers volcanic system (cf. Keith et al. 2017). This conclusion is based on the sulphide–silicate mineral relationships indicating that sulphide segregation occurs during different stages of magmatic differentiation in association with plagioclase, clinopyroxene and in particular Fe–Ti oxide fractionation (Fig. 2). The S concentration at sulphide saturation in silicate melts is controlled by temperature, pressure, fO_2, the degree of fractional crystallisation and the initial S and Fe contents of the magma (Mathez and Yeats 1976; Distler et al. 1983; Mavrogenes and O'Neill 1999; Ackermand et al. 2007; Yang et al. 2014). However, fO_2 seems to be by far the most important parameter controlling the solubility of S (Jenner et al. 2010; Jugo et al. 2010; Keith et al. 2017). Magmatic sulphides that post-date the Fe–Ti oxides (Fig. 2c–e) and the occurrence of S^{2-} and S^{6+} in the Brothers melts suggest that the formation of these late stage sulphides may be related to the proposed "magnetite crisis", the reduction of S^{6+} to S^{2-} caused by fO_2 changes in the Fe–Ti oxide fractionating magma (Jenner et al. 2010).

Recent studies have shown that magmatic sulphides represent an important source of chalcophile metals in hydrothermal fluids and associated sulphide precipitates (Patten et al. 2016a, b). Arc-hosted hydrothermal systems are known to be economically important due to their high Cu contents (Sillitoe 2010; Richards 2011). Copper is highly compatible in immiscible sulphide liquids as indicated by high sulphide liquid-silicate melt partition coefficients between 600 and 1500 (Peach et al. 1990; Lynton et al. 1993; Gaetani and Grove 1997; Ripley et al. 2002; Li and Audétat 2012; Patten et al. 2013; Li 2014). Hence, Cu will strongly partition into a segregating sulphide phase leaving behind a Cu depleted silicate melt. This coincides with the observed Cu depletion in the Brothers melts (Fig. 4) and the Cu enrichment (up to 24.1
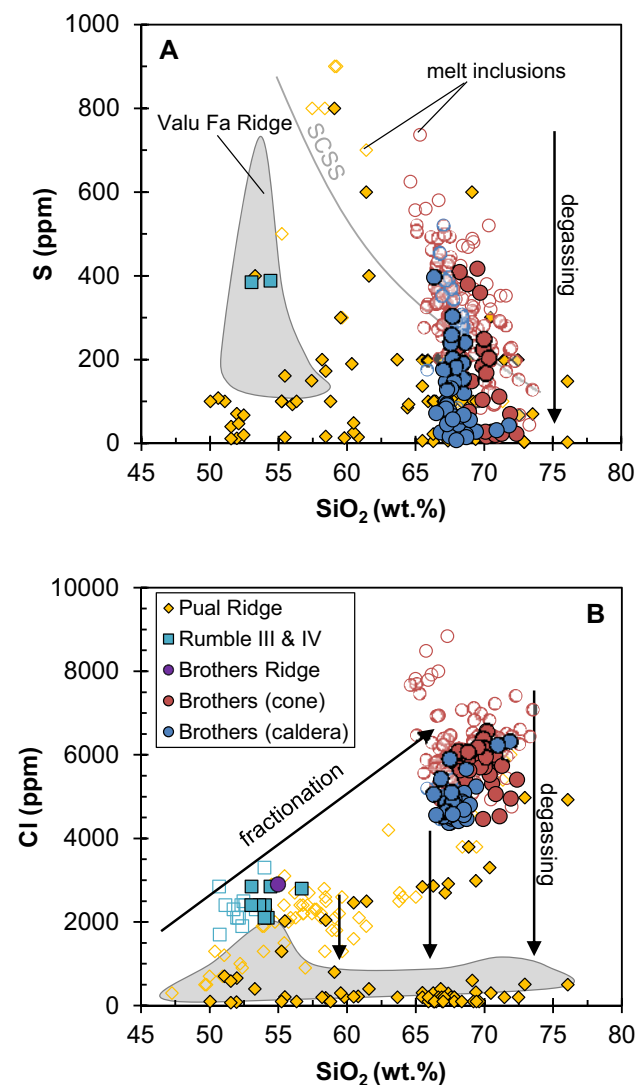
Fig. 5 Variation diagrams of **a** S and **b** Cl vs. SiO$_2$. Sulphur and Cl variations at a given SiO$_2$ concentration are interpreted to be due to magma degassing. Open symbols generally represent melt inclusion data of the glass and whole rock samples with the same colour coding. The grey field represents the glass composition of the Valu Fa Ridge lavas. The grey solid line displays the S concentration at sulphide saturation (SCSS) calculated based on the method presented by Smyth et al. (2017). Input parameters include the composition of the Brothers volcano sulphide droplets and the corresponding glass samples, as well as physical values, such temperature and pressure, as specified in the text. Data taken from literature as specified in the text (cf. "Results", Lava composition). New data presented in this figure can be found in the electronic supplement (Table A9) (figures in colour can be found in the web version of the article)

Fig. 6 Trace element ratios of **a** La/Sm and **b** Ce/Pb vs. SiO$_2$. The grey field represents the glass composition of the Valu Fa Ridge lavas. Note the similar trace element ratios between Brothers volcano, Pual Ridge and the other island arc volcanoes suggesting a similar parental magma composition. Data taken from literature as specified in the text (cf. "Results", Lava composition). New data presented in this figure can be found in the electronic supplement (Table A4) (figures in colour can be found in the web version of the article)

wt%, Fig. 3) in the magmatic sulphides hosted in the Brothers lavas. This can likely be explained by the proposed "magnetite crisis" (Jenner et al. 2010) causing sulphide saturation in association Fe–Ti-oxide fractionation (Fig. 2c–e). The occurrence of Cu-rich sulphides (Fig. 3) further imply that wall rock leaching in the reaction and fluid upflow zone represents a
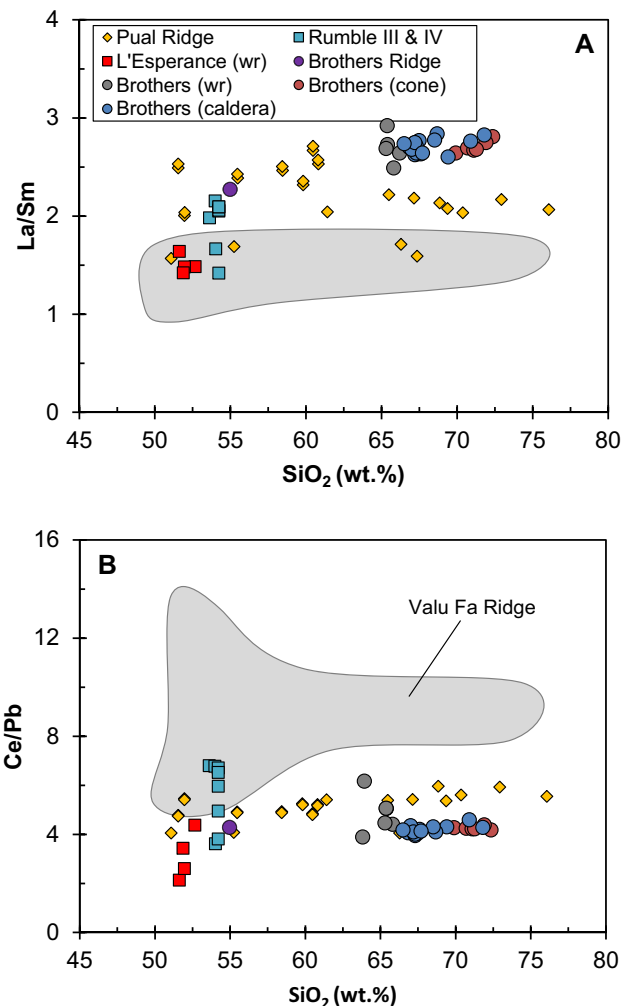
likely process that can explain the high Cu concentrations (up to 35.6 wt%) in the seafloor massive sulphide ores (de Ronde et al. 2011). However, previous studies also suggested that Cu and other chalcophile metals are contributed to the Brothers hydrothermal system by exsolving magmatic volatiles from the underlying magma chamber (de Ronde et al. 2011; Keith et al. 2016a), possibly suggesting a bimodal Cu source.

Evidence for Cu degassing in the Brothers magmatic system

Arc magmas commonly reach volatile saturation during differentiation in the upper crust (Wallace 2005). Vapour
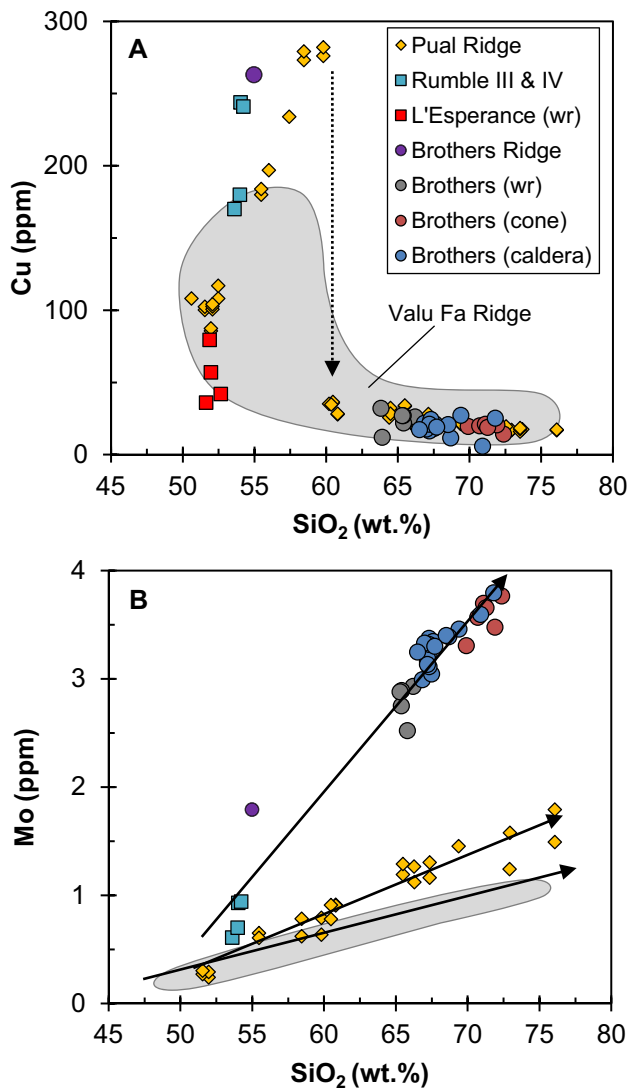
Fig. 7 Variation diagrams of **a** Cu and **b** Mo vs. SiO$_2$. The grey field represents the glass composition of the Valu Fa Ridge lavas. The black arrows represent the best fit regression of the, island arc (upper line), Pual Ridge (middle line) and Valu Fa Ridge (lower line) data set. The antithetic behaviour of Cu and Mo with proceeding magmatic differentiation lead to low Cu and high Mo contents in the evolved Brothers melts. Note the higher incompatibility of Mo in island arc compared to back-arc systems. Data taken from literature as specified in the text (cf. "Results", Lava composition). New data presented in this figure can be found in the electronic supplement (Table A4) (figures in colour can be found in the web version of the article)

bubbles in plagioclase-hosted melt inclusions from Brothers volcano (electronic supplement, Fig. A2) indicate that the magma was saturated with volatiles in the magma chamber suggesting pre-eruptive degassing of an immiscible fluid phase (Yang and Scott 1996, 2002). Those melt inclusions are enriched in S (and Cl) compared to the corresponding glass matrix (Fig. 5; electronic supplement, Fig. A3). The presented thermodynamic calculations suggest that the

Brothers volcano melts reached H$_2$O saturation between 3.2 and 3.7 wt% H$_2$O during their evolution and that both S^{2-} and S^{6+} were present. Hence, an aqueous S- and Cl-rich magmatic volatile phase with variable proportions of SO$_2$ and H$_2$S probably exsolved from the Brothers volcano melts. Copper can form stable complexes with reduced S but also shows a strong affinity to Cl in magmatic volatiles (Williams-Jones and Heinrich 2005; Pokrovski et al. 2008; Zajacz and Halter 2009; Zajacz et al. 2011; Blundy et al. 2015). Although high Cu solubility in a magmatic aqueous vapour phase is under discussion (Lerchbaumer and Audétat 2012), experimental studies have shown that mixed ligand complexes including S and Cl are the most stable Cu complexes (e.g., CuCl(HS)$^-$) representing the most efficient form to transport Cu in magmatic volatiles (Simon et al. 2006; Mei et al. 2013). Such a magmatic volatile phase can contribute Cu and other chalcophile metals to an overlying hydrothermal system, which can result in high concentrations of these metals in the seafloor massive sulphides (de Ronde et al. 2005; Berkenbosch et al. 2012; Gruen et al. 2014).

It is likely that this model is applicable for the Brothers volcano magmatic-hydrothermal system. For example, negative S isotope values to −4.7‰ in hydrothermal sulphides from the Brothers vents were interpreted to be the result of an isotopically light magmatic volatile phase, which was added to the hydrothermal system by sulphur disproportionation (de Ronde et al. 2011). The plagioclase-hosted melt inclusions from Brothers volcano show Cu concentrations of up to 69 ppm, whereas Cu in the corresponding glass matrix is generally below 21 ppm indicating Cu loss (electronic supplement, Fig. A4; de Ronde et al. 2011). Importantly, the Cu enrichment in the melt inclusions cannot be explained by Cu diffusion from the host mineral, since Cu is highly incompatible in plagioclase and other silicates (Jenner et al. 2010; de Ronde et al. 2011). Sulphide occurrences along vesicle margins (Fig. 2F) emphasise that a S-rich volatile phase exsolved from the magma (Francis 1990; Ackermand et al. 2007; Blundy et al. 2015). Alternatively, they could represent sulphide compounds transported by floatation of sulphide melt on vapour bubbles (Mungall et al. 2015), which could also explain the proposed occurrence of melt inclusion-hosted sulphide droplets (Fig. 5a). These sulphides almost exclusively consists of pyrite (n = 40), only one Cu-rich phase with a composition close to cubanite was identified (electronic supplement, Table A8). Iron diffusion from the melt to the vesicle margin where it reacted with S-bearing volatiles possibly explains the precipitation of pyrite (Ackermand et al. 2007). In contrast, the low Cu contents in the Brothers volcano melts (Fig. 7a) suggest that diffusion cannot explain the occurrence of cubanite. Hence, it is more likely that Cu was transported in an exsolving volatile phase together with S and possibly Cl (Fig. 5;

Francis 1990; Blundy et al. 2015). The rare occurrence of Cu-sulphides along the vesicle margins may imply that most of the degassed Cu did not precipitate but rather was transported in the volatile phase to shallower crustal levels where it interacted with the circulating hydrothermal fluids. Therefore, it is likely that a Cu-bearing magmatic volatile phase exsolved from the Brothers melts, which added Cu to the overlying hydrothermal system in addition to the common leaching process of Cu from the wall rock-hosted magmatic sulphides (Fig. 3).

The Brothers magmatic-hydrothermal system: A submarine analogue for subaerial epithermal–porphyry deposits?

It was shown that H_2O-rich arc magmas in the upper crust have the potential to exsolve magmatic volatiles that can carry significant amounts of chalcophile metals to form a magmatic-hydrothermal deposit (e.g., Richards 2011). Advanced argillic alteration assemblages, enargite-bearing veins and elemental S occur at Brothers volcano indicating high-sulphidation conditions similar to subaerial epithermal–porphyry systems (de Ronde et al. 2005). The dacites and rhyolites that host the Brothers volcano magmatic-hydrothermal system are highly depleted in Cu (Fig. 7a) suggesting that Cu was extracted from the silicate melt during the segregation of an immiscible sulphide liquid preserved as wall rock-hosted magmatic sulphides representing a potential Cu source for hydrothermal fluids. In addition, the results presented here suggest that a Cu-rich volatile phase exsolved from the Brothers melts, which also contributed Cu to the overlying hydrothermal system resulting in the precipitation of Cu-rich massive sulphides at the seafloor (up to 35.6 wt%; de Ronde et al. 2011).

Copper and Mo show a compatible and incompatible behaviour during magmatic differentiation leading to low Cu and high Mo contents (Fig. 7), as well as low Cu/Mo ratios in the evolved Brothers melts (Fig. 8). Importantly, Cu has the stronger affinity to partition into an exsolving magmatic volatile phase as shown by volatile-silicate melt partition coefficients between 10 and 100 (Candela and Holland 1984; Zajacz et al. 2008; Guo and Audétat 2017). In contrast, the volatile-silicate melt partition coefficients for Mo is between 0.1 and 4 (Candela and Holland 1984; Guo and Audétat 2017). Consequently, associated magmatic volatiles will characteristically be enriched in Cu compared to Mo. leading to a high Cu/Mo ratio. This chemical signature may be preserved in associated sulphide precipitates from hydrothermal systems that are affected by a magmatic volatile component (Fig. 8).

Data from high-sulphidation epithermal and porphyry Cu deposits (grey and white field) were compared with the Brothers magmatic-hydrothermal system to test this
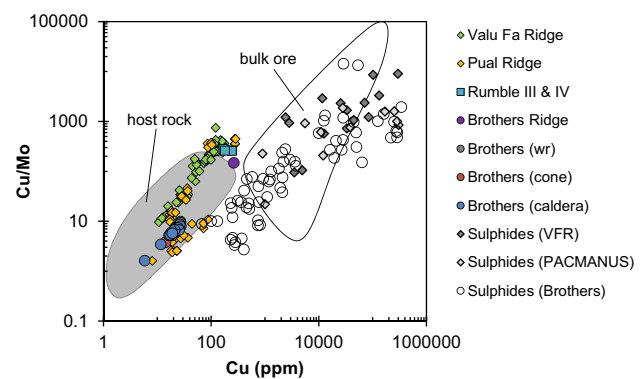
Fig. 8 Diagram of Cu/Mo vs. Cu. Symbols in grey scale generally represent the bulk ore composition of the submarine massive sulphides, whereas coloured symbols show the composition of the associated magmatic host rocks. Data from subaerial high-sulphidation epithermal–porphyry system were added for reference including the bulk ores (white field) and the least altered host rock compositions of these systems (grey field). Ore samples from the selected arcs generally show higher Cu and Cu/Mo ratios than there associated host rocks, which are interpreted to be the result of a Cu-rich and Mo-poor magmatic volatile phase added to the hydrothermal system. Data for the submarine systems taken from literature as specified in the text (cf. "Results", Lava composition). The OSNACA data base (http://www.cet.edu.au/) and the references listed in the electronic supplement (A1) have been used as the data source for the subaerial systems. New data presented in this figure can be found in the electronic supplement (Table A4). All analyses from the submarine systems represent glass data if not specified otherwise. *VFR* Valu Fa Ridge, *wr* whole rock (figures in colour can be found in the web version of the article)

hypothesis (Fig. 8). Magmatic volatiles are the main source and transport medium for Cu in these subaerial systems and their Cu concentrations and Cu/Mo ratios in the bulk ores and in least altered host rock samples match those from Brothers volcano remarkably well (Fig. 8). This implies for Brothers volcano that Cu was also added to the hydrothermal system by magmatic volatiles and this signature is preserved in the seafloor sulphide precipitates. Importantly, this seems to be no local feature because similar Cu concentrations and Cu/Mo ratios in magmatic rocks and bulk ore samples were observed for other island arc and back-arc systems (Fig. 8). Therefore, we conclude that magmatic volatiles represent an important source for Cu in addition to wall rock leaching in the reaction and fluid upflow zone of submarine magmatic-hydrothermal arc and back-arc systems.

Summary and conclusions

The results presented here imply that a bimodal Cu contribution to the Brothers volcano magmatic-hydrothermal system can best explain the occurrence of the Cu-rich seafloor massive sulphide ores (up to 35.6 wt%). High Cu contents

(up to 24.1 wt%) in the magmatic sulphides from Brothers volcano suggest that wall rock leaching of such sulphides in the reaction and fluid upflow zone represents a likely source of Cu for the hydrothermal system and its precipitates. In addition, the combined use of chemical, mineralogical and thermodynamic investigations revealed that the Brothers melts reached volatile saturation during their evolution. Hence, an aqueous S- and Cl-rich magmatic volatile phase extracted some of the Cu from the silicate melt. This Cu-rich volatile phase ascended to shallower crustal levels where it contributed Cu to the hydrothermal fluids from which the Cu-rich seafloor massive sulphides formed.

High Cu/Mo ratios as suggested for the magmatic volatiles are preserved in the seafloor sulphide precipitates, which are probably due to the distinct behaviour of Cu and Mo during magmatic differentiation and volatile exsolution. Similar Cu/Mo ratios were observed in subaerial high-sulphidation epithermal–porphyry systems, where magmatic volatiles represent the main source for Cu. Therefore, we conclude that shallow marine arc (and back-arc) magmatic-hydrothermal-systems share mineralogical and chemical features with epithermal–porphyry deposits on land suggesting that these active systems represent a new hybrid seafloor analogue between those subaerial systems and classic Cyprus-type VHMS deposits. Importantly, our results further suggest that this is no local feature since similar Cu/Mo ratios in magmatic rocks and bulk ore samples were observed for other island arc and back-arc systems. Hence, future investigations have to focus on the source characteristics and the enrichment processes of other chalcophile and economically critical trace metals (e.g., Au and Te) to identify new sites and to assess the potential of such locations for submarine mining operations.

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