Magmatic and metasomatic effects of magma-carbonate interaction recorded in calc-silicate xenoliths from Merapi volcano (Indonesia)

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25 **ABSTRACT**

26 Magma-carbonate interaction is an increasingly recognised process occurring at active volcanoes

27 worldwide, with implications for the magmatic evolution of the host volcanic systems, their eruptive

28 behaviour, volcanic CO_2 budgets, and economic mineralisation. Abundant calc-silicate skarn xenoliths are

29 found at Merapi volcano, Indonesia. We identify two distinct xenolith types: magmatic skarn xenoliths,

30 which contain evidence of formation within the magma, and exoskarn xenoliths, which more likely

31 represent fragments of crystalline metamorphosed wall-rocks. The magmatic skarn xenoliths comprise

32 distinct compositional and mineralogical zones with abundant Ca-enriched glass (up to 10 wt% relative to

33 lava groundmass), mineralogically dominated by clinopyroxene ($En_{15-43}Fs_{14-36}Wo_{41-51}$) + plagioclase

34 (An_{37-100}) ± magnetite in the outer zones towards the lava contact and by wollastonite ± clinopyroxene

35 ($En_{17-38}Fs_{8-34}Wo_{49-59}$) ± plagioclase ($An_{46-100}$) ± garnet ($Grs_{0-65}Adr_{24-75}Sch_{0-76}$) ± quartz in the xenolith

36 cores. These zones are controlled by Ca transfer from the limestone protolith to the magma and by

37 transfer of magma-derived elements in the opposite direction. In contrast, the exoskarn xenoliths are

38 unzoned and essentially glass-free, representing equilibration at sub-solidus conditions. The major

39 mineral assemblage in the exoskarn xenoliths is wollastonite + garnet ($Grs_{73-97}Adr_{3-24}$) + Ca-Al-rich

40 clinopyroxene ($CaTs_{0-38}$) + anorthite ± quartz, with variable amounts of either quartz or melilite (Geh_{42-91})

41 + spinel. Thermobarometric calculations, fluid inclusion microthermometry and newly calibrated

42 oxybarometry based on $Fe^{3+}/\Sigma Fe$ in clinopyroxene indicate magmatic skarn xenolith formation conditions

43 of ~850 ± 45°C, < 100 MPa and at an oxygen fugacity between the NNO and HM buffer. The exoskarn

44 xenoliths, in turn, formed at 510-910°C under oxygen fugacity conditions between NNO and air. These

45 high oxygen fugacities are likely imposed by the large volumes of CO_2 liberated from the carbonate.

46 Halogen and sulphur-rich mineral phases in the xenoliths testify to the infiltration by a magmatic brine. In

47 some xenoliths this is associated with the precipitation of copper-bearing mineral phases by sulphur

48 dissociation into sulphide and sulphate, indicating potential mineralisation in the skarn system below

49 Merapi. Compositions of many xenolith clinopyroxene and plagioclase crystals overlap with that of

50 magmatic minerals, suggesting that the crystal cargo in Merapi magmas may contain a larger proportion

51 of skarn-derived xenocrysts than previously recognised. Assessment of xenolith formation timescales

52 demonstrates that magma-carbonate interaction and associated CO_2 release could affect eruption intensity,

53 as recently suggested for Merapi and similar carbonate-hosted volcanoes elsewhere.

54 Key words: Merapi; magma-carbonate interaction; skarn; xenolith; carbonate assimilation; oxybarometry

55

INTRODUCTION

Calc-silicate (skarn) xenoliths are found within the deposits of many hazardous arc volcanoes worldwide, including Popocatépetl (e.g. Goff *et al.*, 2001), Vesuvius (e.g. Fulignati *et al.*, 2001), Merapi (e.g. Chadwick *et al.*, 2007), Colli Albani (e.g. Di Rocco *et al.*, 2012) and Nisyros (Spandler *et al.*, 2012). Formed as a result of interaction between crustal carbonate and the host magmatic system, these xenoliths preserve evidence of complex reaction processes that can have profound impact on the host magmatic system, including altering magmatic differentiation paths (e.g. Iacono-Marziano *et al.*, 2008), influencing eruptive dynamics (e.g. Freda *et al.*, 2011; Troll *et al.*, 2012; Carr *et al.*, 2018), and liberating large volumes of crustal CO_2 into the atmosphere (e.g. Mason *et al.*, 2017).

Much of the knowledge about crustal magma-carbonate interaction processes has been derived from diverse approaches. Isotope mass balance calculations (e.g. Troll *et al.*, 2012, 2013; Jolis *et al.*, 2015) have shown that large volumes of crustal carbonate, up to 30%, are incorporated into some volcanic systems, and *in situ* stable isotopes have demonstrated decarbonation is highly efficient in magmatic systems (Whitley *et al.*, 2019). Experimental magma-carbonate studies (e.g. Iacono-Marziano *et al.*, 2008; Deegan *et al.*, 2010; Jolis *et al.*, 2013; Blythe *et al.*, 2015; Carter and Dasgupta, 2016) have further demonstrated how magmatic melt differentiation paths are modified towards silica undersaturation in mafic melts, and that magma-carbonate interaction may be extremely rapid (syn-magmatic), operating on the order of minutes to hours. Moreover, detailed petrographical and geochemical studies of the individual xenoliths have provided insights into the architecture of subvolcanic skarn contact aureoles (Matthews *et al.*, 1996; Fulignati *et al.*, 2004), the depth of magma-carbonate interaction from fluid inclusions (Clocchiatti *et al.*, 1982), xenocryst incorporation into the magma and skarn recycling (Chadwick *et al.*, 2007; Jolis *et al.*, 2015), changes in magmatic redox conditions and phase equilibria (Wenzel *et al.*, 2002), and the economic metallogenic potential of magmatic fluids that interact with the country rock (Fulignati *et al.*, 2013).

In this study, we present a detailed analysis of the petrography, mineralogy and geochemistry of calc-silicate xenoliths from the 1994-2010 eruptions of Merapi volcano, Indonesia. We demonstrate that these xenoliths represent fragments of either complete replacement of carbonate wall rock to calc-silicate mineral assemblages around the magma reservoir margins, or are transient fragments of entrained carbonate which are caught in the process of being metamorphosed within the magma itself. The xenoliths record evidence of interaction with a magmatic-derived halogen-bearing fluid that produced exotic halogen-bearing mineral phases, whilst enriching the xenoliths in economically important metals such as copper and iron, and by analogy the more extensive skarn system below Merapi. We also show

89 that traditional mineral-melt thermobarometry and fluid inclusion analysis can be applied to some of the
90 xenoliths, and we present a new calibration of a single clinopyroxene crystal oxybarometer to determine
91 intensive variables (T, P, fO$_2$) during xenolith formation.

GEOLOGICAL BACKGROUND

93 Merapi is the most active of Indonesia's volcanoes, and is considered one of the Sunda arc's most
94 dangerous (e.g. Voight *et al.*, 2000; Gertisser *et al.*, 2011, 2012; Surono *et al.*, 2012). Activity is near
95 continuous, with periods of dome growth frequently interrupted by gravitational dome collapse and
96 associated pyroclastic density currents (e.g. Andreastuti *et al.*, 2000; Camus *et al.*, 2000; Newhall *et al.*,
97 2000; Voight *et al.*, 2000; Gertisser *et al.*, 2012). Larger explosive Vulcanian and sub-Plinian eruptions
98 occur at longer ~100 year time-scales, such as the 2010 VEI 4 eruption which killed close to 400 people
99 (Surono *et al.*, 2012; Komorowski *et al.*, 2013). Compositionally, the erupted material is medium to high-
100 K basalt to basaltic andesite with a restricted range of ~49 to 58 wt% SiO$_2$ (Gertisser and Keller, 2003a,
101 2003b). Early work at Merapi suggested a subducted sediment contamination component to the Merapi
102 magmas (Gertisser and Keller, 2003b), while subsequent work also highlighted a significant influence
103 from crustal carbonate on magma genesis (e.g. Chadwick *et al.*, 2007; Troll *et al.*, 2013; Aiuppa *et al.*,
104 2017). Merapi overlies an upper crust of 8 to 11 km thick sediments of the Kendeng basin, where
105 Cretaceous to Cenozoic volcaniclastic sediments are overlain by shallow marine limestones and marls, all
106 of which overlie inferred Cretaceous arc and ophiolite basement rocks (van Bemmelen, 1949; Smyth *et*
107 *al.*, 2005). Fragments of the sedimentary basement are frequently found as thermally metamorphosed
108 xenoliths within the eruptive deposits (Brouwer, 1928; Clocchiatti *et al.*, 1982; Camus *et al.*, 2000;
109 Gertisser and Keller, 2003b; Chadwick *et al.*, 2007; Troll *et al.*, 2012, 2013). These xenoliths testify to
110 prevalent magma-carbonate interaction (Chadwick *et al.*, 2007; Troll *et al.*, 2013; Whitley *et al.*, 2019), a
111 process that is ongoing and occurs at rapid timescales (Deegan *et al.*, 2010, 2011; Troll *et al.*, 2012;
112 Reagan *et al.*, 2017). Radiogenic (^{87}Sr/^{86}Sr) and stable (δ^{13}C, δ^{18}O) isotope analysis of bulk xenoliths and
113 mineral separates of calc-silicate mineral phases (wollastonite, diopside, calcite), have been used to
114 demonstrate up to 30% crustal carbonate assimilation during the genesis of Merapi magmas (Chadwick *et*
115 *al.*, 2007; Troll *et al.*, 2013; Whitley *et al.*, 2019). Liberation of large volumes of crustal CO$_2$ during syn-
116 magmatic activity has additionally been linked to enhancing eruptive explosivity at Merapi (e.g. Troll *et*
117 *al.*, 2012, 2013; Borisova *et al.*, 2013; Carr *et al.*, 2018). The available evidence thus indicates that
118 magma-carbonate interaction at Merapi may have wide-ranging implications for the magmatic evolution
119 and volcanic hazard potential at Merapi.

METHODS

Scanning electron microscopy was undertaken at Keele University, UK using a Hitachi TM3000 scanning electron microscope. A rare unknown mineral found in sample MX1, compositionally similar to wadalite, was analysed with Raman spectroscopy at Keele University using a confocal Thermo Scientific DXR Raman spectrometer with a 532 nm laser, a 50x objective, and a standard 30 μm uncovered polished thin section.

Microthermometry was carried out at Keele University using a Linkam THMS600 freezing-heating stage. Thermocouples were calibrated at –56.6°C, 0.0°C and +374.1°C using synthetic fluid inclusions provided by Linkam. The precision of temperature measurements at -56.6°C is ±0.1°C, and ±2°C at 374.1°C. Measurements were made on ~100 μm thick double polished wafer fragments.

Major element concentrations in minerals, and major element, chlorine and sulphur concentrations in groundmass glasses and melt inclusions were determined with a JXA 8900R Electron Probe Microanalyser at the University of Kiel, Germany. Silicate and oxide minerals were analysed with a 15 kV accelerating voltage, a 15 nA beam current and a 2 μm beam diameter. Calcite was measured with a 7 μm beam diameter at 15 kV accelerating voltage and a 10 nA beam current. Glasses were measured with a 5 μm beam at 15 kV accelerating voltage and a 12 nA beam current. Measurement times were 15 s at the peak and 7 s on the background, excluding S, Cl, P which were measured for 30 s at the peak and 10s on the background. Extended counting times of 30 s peak and 10 s background for Fe, Mg and Mn, and 60 s peak and 30 s background for Ba and Sr were applied during calcite analyses. Na was measured first to minimise alkali migration. Natural mineral standards were used for calibration and Smithsonian basaltic glass A-99, forsterite 83 USNM2566, plagioclase USNM115900, garnet RV2 USNM 87375, and obsidian ASTIMEX Block SPGLASS7 were used as secondary within run standards to assess accuracy and precision, presented in the supplementary material.

All Mg# values were calculated assuming all Fe as Fe^{2+} using $Mg\# = 100 \frac{Mg}{Mg+Fe_{total}}$. Ternary clinopyroxene components are calculated assuming all Fe as Fe^{2+} e.g. $Fs = 100 \frac{Fe_{total}}{Mg+Fe_{total}+Ca}$. Fe^{3+} was estimated for clinopyroxene from stoichiometry using Droop (1987). Al^{IV} was calculated as 2-Si, and any remaining Al was allocated as Al^{VI}. Components for clinopyroxene thermobarometry were calculated using Putirka et al. (1996). Garnet end member mole fractions and Fe^{3+} were estimated using the Arai (2010) R script implementation of the Muhling and Griffin (1991) calculation scheme, which provides a more accurate Fe^{3+} estimate for garnet than Droop (1987). Melilite mole fractions were calculated considering 4 end members by firstly allocating Na to the Na-melilite end member, and then the remaining cations, minus the Al required for Na-melilite, were allocated between gehlenite, åkermanite and Fe-åkermanite. These mole fractions were calculated as follows (abbreviations as in Table 1):

$$153 \qquad \text{Na-Mel} = \frac{Na}{Na + Ca - 1}$$

$$154 \qquad \text{Geh} = (1 - \text{Na-Mel}) \cdot \frac{\frac{Al - 2Na}{2}}{\frac{Al - 2Na}{2} + Fe + Mg}$$

$$155 \qquad \text{Ak} = (1 - \text{Na-Mel}) \cdot \frac{Mg}{\frac{Al - 2Na}{2} + Fe + Mg}$$

$$156 \qquad \text{Fe-Ak} = (1 - \text{Na-Mel}) \cdot \frac{Fe}{\frac{Al - 2Na}{2} + Fe + Mg}$$

157 Due to the small size of most xenoliths (typically < 5 cm) combined with the textural and mineralogical
158 uniqueness of each sample, whole-rock compositions for six representative xenoliths were determined by
159 point counting (1000-2000 points) combined with averaged mineral and glass chemistry. Each zone was
160 counted individually, then the respective areas of the zones were combined to calculate a whole-rock
161 composition. The zone and whole-rock compositions were corrected for varying mineral densities using
162 mineral densities from Deer *et al.* (1997) and the bulk compositions were obtained using the Rock-Maker
163 spreadsheet (Büttner, 2012), which generates bulk compositions from mineral volumes. All calculated
164 compositions are presented in the supplementary material.

165 All data produced in this study are found as supplementary material, including the collated published
166 datasets used to produce the figures.

167 Thermodynamic modelling of the exoskarn samples MX99-5s and MX99-3s was undertaken using the
168 Theriak-Domino software (built date 3-1-2012, de Capitani and Petrakakis, 2010), using calculated
169 whole-rock compositions (see above) in the system Si-Al-Fe-Mg-Ca-C. The database used (Holland and
170 Powell, 1998, version 5.5) lacks solid solution models that include the CaTs component in clinopyroxene,
171 and mixing between gehlenite and åkermanite. Therefore, ideal mixing was assumed for these two solid
172 solutions (Charlu *et al.*, 1981; Povoden *et al.*, 2002). Implementing a CaTs-Di-Hd ideal mixing model for
173 clinopyroxene over the default database model however has little effect on the calculated phase
174 boundaries of the system. For example, this clinopyroxene model produces only a ~20°C variation in
175 melilite-garnet phase boundaries, which is relevant to the xenoliths.

176

PETROGRAPHY

178 Calc-silicate xenoliths (*n=33*) collected from the 1994 to 2010 eruption deposits at Merapi can be
179 subdivided into three distinct groups (magmatic skarn *n=25*, exoskarn *n=5* and buchite *n=3*) on the basis

180   of their dominant mineralogy, modal zonation, and the presence of glass. Twelve xenoliths that best
181   represent the three groups, and which highlight the mineralogical and textural variety of the xenoliths
182   were chosen for detailed study. The xenoliths are generally centimetre to tens of centimetre in size, and
183   texturally complex variations in mineralogy and zonation can be seen at hand specimen scale.
184   Volcaniclastic and metasedimentary xenoliths are additionally present at Merapi but not discussed in this
185   paper (see Chadwick *et al.*, 2007). A summary of the mineral phases identified in this study and their
186   formulas are presented in Table 1.

Magmatic Skarn xenoliths

188   The most abundant calc-silicate xenolith type (*n*=25) is the one we term 'magmatic skarn' (*c.f.* Fulignati
189   *et al.*, 2004) based on the abundance of Ca-enriched magmatic glass, melt inclusions in the newly formed
190   calc-silicate skarn minerals, and pronounced reaction zones at contacts with the host lava. Attempting to
191   explain the variety of xenoliths in this group, the magmatic skarn xenoliths are subdivided into a series of
192   idealised mineralogical/textural zones, such as a series of reaction zones and a core zone (Figs. 1, 2). The
193   lava contact (R1) is represented by a zone of coarse (100-300 μm), pale green clinopyroxene and a
194   concentration of magnetite (Fig. 2A). This is followed by a finer grained (up to 100 μm) zone (R2) of
195   plagioclase + clinopyroxene ± glass (Fig. 2A), with rare amphibole also present in sample MX1. This
196   zone grades into a zone of coarse dark green/yellow pleochroic clinopyroxene (R3) separating R2 from a
197   zone of vesicular glass (R4) (Fig. 2A-B). The glass zone typically contains strongly irregularly Fe-Mg
198   zoned (see mineral chemistry), colourless to deep green/yellow pleochroic diopsidic clinopyroxene
199   crystals (Fig. 2B). These clinopyroxene crystals are similar to those of zone R3, and often appear to be
200   incorporated from zone R3. Plagioclase and wollastonite microlites are additionally present within the
201   glass. Sample MX5 has comparatively large quartz and plagioclase crystals (~100 μm) within the glass
202   zone, and sample MX3 shows this zone to be almost fully crystallised to quartz and plagioclase, with
203   scarce melt inclusions within the quartz crystals. The xenolith core (Fig. 2C) has a sharp contact to
204   decussate wollastonite, but occasionally the core is a mixture of wollastonite, clinopyroxene, and
205   accessory garnet. Additionally, glass is often present within the core of these xenoliths. At glass-
206   wollastonite contacts, a thin rim of semi-dendritic ferrobustamite often forms. The samples have a
207   vesicular texture across all zones.

208   The described zonation is idealised, and variations naturally occur. Samples MX1 and M13-10, for
209   instance, show no glass zone (R4) separating the wollastonite-dominant core from R3 and R2. In this
210   case, a pale yellow clinopyroxene and garnet zone formed instead of the coarse clinopyroxene of zone R3,
211   which we call R3b (Figs. 1, 2D). This clinopyroxene is optically and chemically distinct (CaTs:
212    $CaAlAlSiO_6$ rich, see section Mineral Chemistry) from any others in the Merapi magmatic skarn
213   xenoliths. In sample MX1, one half of the xenolith shows the common zonation (with glass zone R4

present), whilst the other half has no glass and instead has the zone R3b CaTs clinopyroxene and garnet zone (Fig. 1). Rare patches of garnet are found interstitial to wollastonite in the MX1 core, and also together with wollastonite and CaTs clinopyroxene in sample CS16.

Accessory phases are generally restricted to the xenolith cores, and include calcite, titanite, chromite, gehlenite, a wadalite-like Si-Al-Fe-Ca-O-Cl mineral, perovskite, a Ca-Zr-Ti-O mineral, cotunnite, sulphates (anhydrite and baryte) and sulphides (pyrrhotite and cubanite) (Table 1). Titanite is also present within the glass in zone R4 and ilmenite is exclusively found in sample MX3 in zone R2. Calcite is present as four distinct textural types: 1) globular crystals within the glass R4 zone, 2) interstitial to wollastonite in the cores, 3) inclusions in wollastonite and garnet, and 4) a melt-like infiltrative texture containing rare Cl-F rich phases such as fluorite, cuspidine and the wadalite-like mineral within regions where the calcite pools (Fig. 3A-B). These calcites are discussed in detail in Whitley *et al.* (2019).

Many crystals contain significant quantities of melt inclusions (Fig. 3C-G), exceeding 80 in a single 600 μm long wollastonite crystal. Melt inclusions are also present in clinopyroxene of zones R3-4, plagioclase in zone R4 and titanite within the xenolith cores. The inclusions are most commonly glassy and have a single shrinkage bubble but, in rare cases, they can contain daughter crystals and multiple bubbles. The daughter crystals are found either in the glass or in the bubble, and are most commonly Fe-bearing phases (pyrrhotite, cubanite, magnetite) and occasionally apatite. Vapour-rich CO_2 fluid inclusions are also common in wollastonite.

Exoskarn Xenoliths

Exoskarn xenoliths are distinct from the magmatic skarn xenoliths by having a different mineralogy, lacking mineralogical zonation, and by almost entirely lacking glass. On the basis of their mineral assemblages resembling typical high temperature skarns worldwide (e.g. Meinert, 1992), and the lack of glass, which indicates formation by subsolidus reactions, we classify these xenoliths as exoskarns (*c.f.* Fulignati *et al.*, 2004, see also discussion). These xenoliths comprise two distinct skarn mineral assemblages (A and B), often with a rim of clinopyroxene and plagioclase at the host lava contact. The most common assemblage (A) is wollastonite + garnet + plagioclase ± CaTs clinopyroxene ± quartz ± calcite with a granoblastic texture (Fig. 4A). Some clinopyroxenes and garnets exhibit weak patchy zonation. Accessory S, Cl, and F-bearing phases such as cuspidine, ellestadite, anhydrite and pyrrhotite are additionally present, and also unidentified Ca-Al-Si-Cl-F minerals that are distinct from the wadalite-like mineral in the magmatic skarn xenoliths. No hydrous phases that can often occur in skarns, such as epidote and vesuvianite (*c.f.* Meinert, 1992), have been identified in this study, although epidote and prehnite have been identified in earlier descriptions of Merapi xenoliths (Kerinec, 1982; Camus *et al.*, 2000). Garnet often contains inclusions of plagioclase and wollastonite. Calcite is present as either rare inclusions within garnet crystals or as large mm-sized crystals, surrounded by complex reaction rims that

248   contain larnite, spurrite, and Ca-Si-rich S-Cl-F-bearing phases including fluorite, cuspidine, ellestadite,

249   anhydrite, and many additional unidentified phases (Ca-Si-O, Ca-Al-Si-O, Ca-Al-Si-P-O Table 8, Fig.

250   4B). Xenotime and monazite form accessory inclusions within these calcites.

251   The second assemblage (B), only found in one sample (MX99-3s), comprises gehlenite + grossular garnet

252   + CaTs clinopyroxene + spinel + wollastonite + plagioclase, with trace amounts of ellestadite (Fig. 4C).

253   This sample shows evidence for disequilibrium, such as patchy compositional zoning of garnets, and

254   spinel with rims of gehlenite followed by an outer rim of CaTs clinopyroxene. Patches of localised

255   equilibrium are shown by granular ~120° triple junctions in the gehlenite-dominant areas of the sample.

256   # Buchite

257   These rare xenoliths (samples M13-04C, CS14, CS10) contain abundant (> 70 vol%) quartz (or SiO_2

258   polymorphs) with interstitial glass around the crystal borders, and minor small interstitial clinopyroxene,

259   plagioclase and wollastonite (Supplementary Fig. S1). Patches of clinopyroxene-rich glass are present,

260   similar to zone R4 of the magmatic skarn xenoliths. We have classified these samples as buchites

261   (pyrometamorphic glass-rich rocks), following the classification by Matthews *et al.* (1996) of texturally

262   similar xenoliths at Lascar volcano, Chile. Similar quartz-rich, partially melted xenoliths have also been

263   described from the Aeolian islands (e.g. Frezzotti *et al.*, 2004; Zanon and Nikogosian, 2004; Del Moro *et*

264   *al.*, 2011), Etna (Mollo *et al.*, 2017) and the Central Apennines (Melluso *et al.,* 2003). Although the

265   quartz-rich assemblage could be derived from a volcaniclastic protolith, the presence of wollastonite

266   suggests a carbonate or marl component. The rounded shape of the quartz crystals, separated by

267   interstitial glass, indicates that partial melting has occurred. The dissolution of quartz xenocrysts in arc

268   magmas was observed in products of the 1991 Pinatubo eruption, where highly silicic glass (~80-85 wt.%

269   SiO_2) formed in reaction zones around the xenocrysts, pointing to possible compositional modifications of

270   the melt, at least on a micrometre scale (Borisova *et al.,* 2014). However, although the Merapi buchite

271   xenoliths are briefly mentioned here for completeness, details of their occurrence and potential

272   ramifications for melt chemistry at Merapi are beyond the scope of the current study and will not be

273   discussed further.

274   # RESULTS

275   # Whole-Rock Major Element Chemistry

276   Calculated major element compositions of individual zones in magmatic xenoliths are compared for two

277   selected samples to evaluate chemical changes (Fig. 5). There are distinct differences between the zones

278   and some systematic variations from the lava contact towards the xenolith cores point to a progressive

279   change from magmatic to calcic compositions (Fig. 5A; Supplementary Figs. S2, S3) (*c.f.* Troll *et al.*,

280   2012). CaO contents are lowest in the lavas and highest in the xenolith cores, whereas Al_2O_3 contents

281   show exactly the opposite behaviour. One xenolith (sample MX1) shows a systematic increase in CaO

282   from the contact towards the core, except for glass zone R4 that creates a distinct anomaly in the element

283   profiles, having higher SiO_2 and lower CaO than the adjacent zones. FeO is relatively enriched in zone

284   R1, decreasing towards the core, whereas SiO_2 is lowest in this zone. MgO shows only limited variation

285   and has the lowest contents in the innermost zone (R4) and in the core.

286   In terms of whole rock major element composition (Fig. 5B), magmatic skarn xenoliths fall within the

287   range of xenoliths analysed by Chadwick *et al.* (2007), which we believe classify as magmatic skarn

288   xenoliths in our grouping), forming diverging trends from basaltic-andesite compositions. Magmatic

289   skarn xenoliths have lower Al_2O_3 contents than lavas (< 16 wt%), while exoskarn xenoliths display Al_2O_3

290   contents comparable to lava values (18 to 25 wt%), although at a much lower SiO_2 content (33 to 45

291   wt%). All xenoliths have much higher CaO than the lavas, up to 36 wt%, but lower TiO_2 and K_2O

292   contents. FeO and MgO span the range of lava values, with FeO up to 10.0 wt%, and MgO up to 6.6 wt%.

293   Exoskarn xenoliths generally plot distinct from magmatic skarn xenoliths when considered with the

294   Chadwick *et al.* (2007) data (Fig. 5B). For instance, the exoskarn xenoliths have low SiO_2, TiO_2 and FeO,

295   relative to the magmatic skarn xenoliths, but form a linear trend of decreasing TiO_2 and FeO with

296   increasing SiO_2.

Mineral Chemistry

Feldspar

299   Feldspar compositions in the Merapi calc-silicate xenoliths are entirely plagioclase, but spanning a wide

300   compositional range (An_{46-100}) (Table 2). In magmatic skarn xenoliths, anorthite content progressively

301   increases towards the xenolith cores (Fig. 6A). Zoning is relatively insignificant compared to the

302   differences between zones. Magmatic skarn xenolith plagioclase comprises both microlites (An_{46-59})

303   within the interstitial glass in zone R4, and interstitial plagioclase in the high-An cores (An_{73-100}). Where

304   analyses of the host lava attached to the xenolith were possible (An_{29-81}), plagioclase in zones R2 and R4

305   overlap magmatic plagioclase compositions, including the previously published data (Gertisser, 2001;

306   Preece, 2014; Erdmann *et al.*, 2016). In An-FeO space, xenolith core plagioclase compositions generally

307   fall within and extend the high FeO-An compositional ellipse of Merapi xenolith plagioclase from

308   Chadwick *et al.* (2007) (Fig. 6B). Plagioclase microlites within the zone R4 glass have strong FeO

309   enrichment (up to 1.7 wt% FeO), as is observed with the strong FeO enrichment of both clinopyroxene

310   and ferrobustamite overgrowths on wollastonite within this glass zone (see below). Exoskarn plagioclase

311   is essentially pure anorthite, with lower anorthite contents restricted to the lava contact (Table 2). FeO

312   concentrations in exoskarn anorthite are characteristically lower than those of magmatic plagioclase and

313   the majority of the magmatic skarn plagioclase data.

Clinopyroxene

Clinopyroxene compositions range from quadrilateral diopside-hedenbergite (Di-Hd) (Morimoto, 1988) to high-Al diopside (Table 3). These high Al clinopyroxenes are enriched both in esseneite ($CaFe^{3+}AlSiO_6$) and Calcium-Tschermak's (CaTs: $CaAlAlSiO_6$) components, demonstrated by the strong correlation between Fe^{3+} and Al^{IV} (R^2=0.88, Fig. 7A), and Al^{IV} with Al^{VI} (R^2=0.81, not shown) across all analysed crystals. Incorporation of Al^{IV} is accommodated by a strong reduction of Si in the tetrahedral site. These clinopyroxenes are commonly generalised as fassaite [$Ca(Mg,Fe^{3+},Al)(Si,Al)_2O_6$] where Al^{IV} > 0.25; Deer *et al.* (1997)]. As this is not a formal name (Morimoto, 1988) and the clinopyroxenes show an enrichment in the CaTs component, we refer to these clinopyroxenes as CaTs-clinopyroxene in this manuscript.

In magmatic skarn xenoliths, the clinopyroxene compositions are generally comparable to Merapi magmatic clinopyroxenes in zone R1 (Fig. 7A-C), and progressively become more Ca/wollastonite-rich until sitting along the diopside-hedenbergite (Di-Hd) join (Wo_{50}) in zones R3, R4 and in the core (Fig. 7C). There is a sharp compositional change at zone R4 and within the core, where the clinopyroxenes closely follow the Di-Hd join and progressively become more Hd-rich (Fig. 7C). Xenolith core clinopyroxenes can also be enriched in Al_2O_3 (up to 11.57 wt%, corresponding to 18 mol% CaTs), bringing compositions above the DiHd join in the traditional clinopyroxene composition ternary diagrams, although this is uncommon and only observed in sample CS16. These Al-rich clinopyroxenes are strongly zoned, from this Al-rich core to weakly oscillatory Di-Hd zoned mantle and rim zones (Fig. 7E). Commonly however, magmatic skarn xenolith clinopyroxene zonation is restricted to the Di-Hd join (Fig. 7C), with patchy, highly irregular resorption surfaces (Fig. 7F). Titanium is correlated well with Al^{IV} across the magmatic skarn xenolith zones, excluding zone 3b, where CaTs-rich clinopyroxenes form with low Ti, comparable to the compositionally distinct exoskarn xenolith clinopyroxene (Fig. 7B).

Exoskarn clinopyroxenes are highly Al enriched (Fig. 7A, B, D; Table 3), containing up to 22.3 wt% Al_2O_3, approaching the highest natural terrestrial values known to the authors (24.0 wt% in gehlenite-rich skarns from the Carpathians, Romania; Pascal *et al.*, 2005). $Fe^{3+}/\sum Fe$ (calculated following Droop, 1987) approaches unity (Fig. 7A). Clinopyroxene compositions at the exoskarn xenolith rim overlap magmatic compositions, but then immediately jump to highly Al-rich compositions, usually lacking the gradual progression observed in the magmatic skarn xenoliths (Fig. 7A-C).

Pyroxenoids

Wollastonite, present in all xenoliths, ranges from essentially pure $CaSiO_3$ to 5 mol% $FeSiO_3$ with < 1.5 mol% $MnSiO_3$ (Fig. 8A; Table 3). Wollastonite compositions from 17 to 21 mol% $FeSiO_3$ are attributed to the ferrobustamite member of the wollastonite group rather than iron-rich wollastonite, as bustamite is the stable crystal structure above ~12 mol% FeSiO3 (Rutstein, 1971; Rutstein and White, 1971). The

348 ferrobustamite crystals are found as overgrowth crystals on wollastonite in the glass-bearing magmatic

349 skarn xenoliths, in rare inclusions in wollastonite in magmatic skarn xenoliths, and in accessory phases in

350 the calcite reaction rims in large calcite-bearing exoskarn xenoliths.

Garnet

352 Garnet is found predominantly in the exoskarn xenoliths as a main rock forming mineral, with magmatic

353 skarn xenolith garnet restricted to small interstitial patches in the cores or in zone R3b (Figs. 1, 2B).

354 Garnet compositions across all xenolith types closely follow the grossular ($Ca_3Al_2Si_3O_{12}$)–andradite

355 ($Ca_3Fe^{3+}_2Si_3O_{12}$) join, with only schorlomite ($Ca_3Ti_2SiFe^{3+}_2O_{12}$) being a notable additional component

356 (Fig. 8B; Table 4), increasing with andradite content (Sch_{0-76}). Pyrope ($Mg_3Al_2Si_3O_{12}$) and almandine

357 ($Fe_3Al_2Si_3O_{12}$) end members combined are < 6 mol%.

358 Magmatic skarn xenolith garnets exhibit a wide compositional range ($Grs_{0-66}Adr_{24-75}Sch_{0-76}$). In zone R3b,

359 these garnets are compositionally distinct ($Grs_{60-66}Adr_{31-37}Sch_{1-2}$) from interstitial garnets within the

360 wollastonite core ($Grs_{0-66}Adr_{24-75}Sch_{1-76}$). The interstitial garnets, in close spatial association with calcite,

361 cuspidine, gehlenite and a wadalite-like phase (see below), have inclusions of this wadalite-like phase,

362 possibly a result of similarities between the crystal structure between hydrogarnet and wadalite-mayenite

363 (e.g. Glasser, 1995; Grew *et al.*, 2013). Garnets with 76 mol% schorlomite

364 [$Ca_{3.0}(Ti_{1.5}Fe^{2+}_{0.1}Fe^{3+}_{0.2}Mg_{0.1})(Si_{1.8}Al_{0.6}Fe^{3+}_{0.6})O_{12}$] are found as rims around titanite, in close association

365 with perovskite. Ti gradients are found across rare wadalite-like phase-bearing garnet crystals (Sch_{3-21}).

366 Exoskarn xenolith garnets have a more restricted compositional range (Table 4), limited to higher

367 grossular contents ($Grs_{73-97}Adr_{3-24}Sch_{0-2}$). The highest grossular contents, up to Grs_{97} are found

368 exclusively within exoskarn A type xenoliths, around residual calcite crystals and their spurrite ± larnite-

369 rich reaction rims.

Melilite

371 Melilite is only found in non-trace quantities in exoskarn assemblage B xenoliths. Melilite compositions

372 are gehlenite-rich, closely following the gehlenite-åkermanite join, with < 8 mol% Na-melilite and < 10

373 mol% Fe-åkermanite ($Gh_{43-91}Ak_{2-45}Na\text{-}Mel_{0-8}$) (Fig. 8C; Table 5). In exoskarn type B xenoliths, melilite

374 has three textural forms: surrounding spinel, intergrown with CaTs-clinopyroxene, and locally texturally

375 equilibrated with 120° grain boundaries (Fig. 4C). Melilite in association with spinel is richer in gehlenite

376 (Gh_{68-83}) than the clinopyroxene intergrowths (Gh_{57-58}) and well equilibrated types (Gh_{47-50}).

Sulphur and Halogen-bearing Phases

378 Pyrrhotite is found in both magmatic and exoskarn xenoliths, often touching or rimmed by anhydrite. In

379 magmatic skarn xenoliths, pyrrhotite is found in zone R2, as accessory inclusions in wollastonite and

380   CaTs-clinopyroxene, and as rare inclusions in melt inclusions in the core. Fe/S ranges from 83 to 85%,

381   and Cu concentrations range from 0.06 to 0.59 wt%. Pyrrhotite is sometimes found with near

382   stoichiometric cubanite (Table 6). The associated anhydrite is pure, with < 0.04 wt% BaO and < 0.1 wt%

383   SrO.

384   Cuspidine is found as crystals within calcite (magmatic skarn xenoliths) or forming within the reaction

385   rim around calcite (exoskarn xenoliths) associated with stoichiometric spurrite $\pm$ larnite and an

386   unidentified Ca-Si-Al-O phase. Fluorine a.p.f.u. approach the ideal 2 (1.937-2.035) indicating negligible

387   OH. Fluorite is a fine grained (< 20 μm) accessory phase replacing calcite in both xenolith types, and

388   evidently nucleated at crystal borders or forming fine halos around vesicles in calcite.

389   Apatite is found in magmatic skarn xenolith zone R4, and contains 0.7 to 0.8 wt% Cl and no detectable

390   SO_3. Ellestadite is found as an accessory phase in exoskarn xenoliths with 7.2 to 10.0 wt% SO_3 and 0.7 to

391   1.2 wt% Cl. F was not analysed with EMPA, however ~2 wt% F was identified using SEM-EDS,

392   indicating that OH is minimal. Stoichiometric ellestadite (undetectable P_2O_5) with ~1.9 wt% Cl was

393   determined with SEM-EDS coexisting with anhydrite in sample M13-02, within the reaction rim around

394   large remnant calcite crystals.

395   Qualitative EDS analyses have identified trace quantities of small (< 5 μm) baryte crystals in both

396   magmatic and exoskarn xenoliths, and additionally a crystal of cotunnite ($PbCl_2$) is present in the

397   magmatic skarn xenoliths.

398   There are unidentified Cl-bearing minerals, which may possibly be new minerals. Skarn xenoliths, such

399   as those from the Upper Chegem caldera, Russia, can be host to numerous new minerals (e.g. Galuskin *et*

400   *al.*, 2013), and this may additionally be the case at Merapi. A wadalite-like Ca-Al-Fe-Si-Cl mineral

401   compositionally similar to the wadalite-eltyubyuite mayenite solid solution (when normalised to 26

402   cations) is found in association with calcite, cuspidine, garnet and gehlenite in magmatic skarn xenolith

403   MX1 (Table 7). These crystals however have compositions with Si a.p.f.u. 4.6-5.5, higher than the ideal

404   Si 4, and lack sufficient Mg to balance this increase in Si in wadalite (*c.f.* Galuskin *et al.*, 2015). Raman

405   spectra of this phase are included as supplementary Fig. S4.

406   A Ca-Al-Si-Cl-F mineral is found in exoskarn xenoliths CS11 and M-XCS in the rim around areas where

407   larnite and spurrite have replaced calcite. Concentrations of Cl and F in this mineral have only been

408   determined by SEM-EDS, and as it contains 10 wt% more CaO than the wadalite-like mineral, and lower

409   volatile contents (~7 wt%) we believe it to be a different mineral.

Oxides, Other Silicates, and Accessory Minerals

411   The dominant Fe-Ti oxide in the magmatic skarn xenoliths is magnetite, with 0.3 to 11.5 wt% TiO_2.

412   Magnetite within the xenolith cores is distinct (< 0.3 wt% TiO_2) from magnetite in the other zones (8.9-

413   11.5 wt% TiO_2). Ilmenite is present in zone R2 of one xenolith. Qualitative EDS analysis has identified

414   micrometre sized chromite in the xenolith cores. Hematite is the dominant oxide found in the exoskarn

415   xenoliths, with rare magnetite present as well. Perovskite is found as a 50 μm vermicular cluster

416   intergrown with wollastonite and plagioclase in one magmatic skarn xenolith (sample MX1) and is

417   essentially stoichiometric $CaTiO_3$. A Ca-Zr-Ti-O mineral (calzirtite?) is found in the same magmatic

418   skarn xenolith. Titanite across all xenolith types contains 1.04 to 2.51 wt% Al_2O_3 and 0.73 to 2.86 wt%

419   FeO. An unidentified Ca-Al-Si-P mineral is found in exoskarn A samples CS11 and MXCS,

420   approximating the formula $Si_{3.1}Ti_{0.1}Al_{2.9}Ca_{3.0}P_{0.9}O_{16}$ when assuming 16 oxygens. Xenotime and monazite

421   are very rare calcite inclusions in exoskarn A xenoliths. Spinel ($Sp_{83-89}Her_{11-17}$) is found exclusively in the

422   gehlenite-garnet-CaTs clinopyroxene-spinel exoskarn B xenolith (MX99-3s). These mineral analyses are

423   given in Table 8.

Glass Chemistry

425   Melt inclusions and interstitial glass are almost entirely restricted to magmatic skarn xenoliths, with melt

426   inclusions and glass only found in the exoskarn xenoliths within the clinopyroxene-rich reaction rim at

427   the host lava contact. Xenolith interstitial (zones R1, R2, R4 and core) and melt inclusion (zones R1, R3,

428   R4 and core) glass compositions show strong deviation from lava groundmass glass and melt inclusion

429   compositions, and also show compositional differences between zones (Fig. 9; Table 9). Melt inclusions

430   are compositionally more diverse than the interstitial glass. CaO concentrations in interstitial glass and

431   melt inclusions from zone R1 and some R2 analyses overlap lava glass CaO values (0.2 to 3.8 wt%). CaO

432   concentrations in the interstitial glass (0.9-6.5 wt%) and in melt inclusions (0.5-11.3 wt%) within the

433   xenolith zones R3, R4 and the core are elevated by up to ~4 wt% in the interstitial glasses in relation to

434   magmatic values and by up to 10 wt% in the melt inclusions. These glasses, especially the melt

435   inclusions, are also characterised by low Al_2O_3 and K_2O relative to lava glasses (Fig. 9), and smaller

436   variations from the lavas are observed in all other major and minor elements. Al_2O_3 concentrations are up

437   to 5 wt% lower than in the lavas, and up to 2 wt% lower in K_2O. Xenolith glass volatile concentrations

438   are broadly comparable to the lava glasses, with only a few analyses exceeding that of the lavas. Sulphur

439   exceeds lava groundmass concentrations in some zone R1 and zone R4 analyses, containing up to 510

440   ppm sulphur. Chlorine is typically within lava groundmass glass concentrations, and only exceeds lava

441   glass values in plagioclase-hosted melt inclusions in sample CS16 and interstitial glasses in MX99-4s.

442   The few analyses for F (< 1110 ppm) show that concentrations are within the wider range of lava values

443   (< 2637 ppm). Although the melt inclusion analyses for MX1 show negligible F, localised patches of

444   cuspidine and fluorite have been observed.

Fluid Inclusions

Fluid inclusions in the magmatic skarn xenoliths ($n=28$) are two phase vapour-rich inclusions in wollastonite. The dominant fluid composition is CO_2, confirmed by instantaneous melting at -57.3 to -56.1°C. The slight deviation from ideal melting at -56.6°C indicates the presence of a small percentage other dissolved gases such as SO_2, N_2, which are not thought to have a significant effect on pressure estimates (Frezzotti *et al.*, 2002). No H_2O is observed either as ice or clathrate. Homogenisation is to the vapour phase at 12.9 to 29.9°C. These temperatures correspond to densities of 0.15 to 0.35 g/cm^3, indicating trapping pressures of 33 to 92 MPa, when assuming a formation temperature of 850°C (see discussion), utilising the Hansteen and Klügel (2008) spreadsheet implementation of Sterner and Pitzer (1994) and Span and Wagner (1996) density and equation of state models. An extreme temperature estimate increase to 1200°C only increases pressure estimates by ~30 MPa. No inclusions for barometry with resolvable homogenisation were found in the exoskarn xenoliths, but CO_2 melting was observed in some inclusions.

DISCUSSION

In this section we discuss the processes during formation of the xenoliths, and the pressure, temperature and fO_2 conditions that can be determined from the recorded mineral assemblages. We also discuss the implications for the magmatic system at Merapi, such as magmatic contamination by xenolith phases, metal transport and the CO_2 output by decarbonation reactions. Accurate determination of temperature in the magmatic skarn xenoliths requires accurate estimates of the melt composition during xenolith formation; therefore we first discuss the implications for any modification of melt inclusion compositions.

Post-entrapment Modification of Melt Inclusions

The abundance of melt inclusions in the magmatic skarn xenoliths allows for constraining the original composition of the melt present during xenolith formation, and, potentially, application of thermobarometric models (discussed below). Post-entrapment modification of melt inclusion compositions however is a well-documented phenomenon, occurring via diffusive exchange of elements, crystallisation of a host mineral boundary layer, or from crystallisation of daughter crystals (e.g. Nakamura and Shimakita, 1998; Danyushevsky *et al.*, 2000; Nielsen, 2011). Therefore, assessment of these effects is required before interpreting the inclusion compositions. Melt inclusions are found within clinopyroxene, plagioclase and wollastonite hosts in the magmatic skarn xenoliths, all of which have no universally accepted way to back-calculate the original composition. The interstitial glass within the xenoliths provides a first order constraint on the original melt composition, showing that it is strongly elevated in CaO compared to lava glass compositions (Fig. 9). We have not attempted correction of our

477   melt inclusions, and consider the wollastonite-hosted melt inclusions to be the best estimates of melt CaO

478   concentrations for the following reasons.

479   Examples of correcting for inclusion modification in clinopyroxene hosts include adding the host

480   clinopyroxene to the inclusion (e.g. Hartley *et al.*, 2018) until Fe-Mg partitioning between the inclusion

481   and clinopyroxene (KD_{Fe-Mg}^{cpx-MI}) approaches the widely accepted equilibrium value of 0.28 ± 0.08 (Putirka,

482   2008), and adding calculated equilibrium clinopyroxene back to the melt inclusion until the calculated

483   clinopyroxene has the same Mg# as the host (e.g. Preece *et al.*, 2014). A compilation of magma-carbonate

484   (both limestone and dolomite) interaction experimental data shows that $KD_{Fe-Mg}^{cpx-melt}$ in carbonate-

485   contaminated systems may strongly diverge from the magmatic-derived 0.28 ± 0.08 (Putirka, 2008) (Fig.

486   10A), suggesting that $KD_{Fe-Mg}^{cpx-melt}$ is redox-sensitive (see oxybarometry discussion below) and an Fe-Mg

487   partitioning equilibrium-based correction is not appropriate.

488   The difference between observed and predicted clinopyroxene diopside-hedenbergite (DiHd) components

489   (ΔDiHd: Putirka, 1999, 2008; Mollo *et al.*, 2013; Neave and Putirka, 2017) is more accurate at predicting

490   equilibrium (Fig. 10B), with 68% of magma-carbonate experimental equilibrium clinopyroxene-melt

491   pairs predicted to fall within model error ($\pm$ 0.07; Mollo *et al.*, 2013). Applied to the Merapi xenoliths,

492   clinopyroxene-hosted melt inclusions within zones R3 and R4 have irregular embayed forms, suggesting

493   some sidewall crystal growth, and ΔDiHd values > 0.07, indicating some potential modification of

494   trapped melt compositions. Melt inclusion-clinopyroxene pairs from zones R1 and R2 have ΔDiHd values

495   from 0 to 0.14, with an average of 0.05, indicating some may represent unmodified melt values. These

496   compositions overlap lava glass compositions, consistent with their proximity to the lava contact,

497   indicating a magmatic character.

498   An example of plagioclase-hosted melt inclusion correction is regressing the magmatic liquid line of

499   descent in TiO_2-Al_2O_3 space, and adding plagioclase back until the inclusions lie on the liquid line of

500   descent (Hartley *et al.*, 2018). This cannot be applied here as our measured xenolith melt inclusion

501   compositions, evidenced by elevated CaO in xenolith interstitial glass compositions, are contaminated and

502   are not closed system magmatic values (see below), and therefore cannot be assumed to lie on a

503   regression line through the magmatic liquid line of descent. Moreover, a micron thick rim of Ab-rich

504   plagioclase is observed around the inclusion walls (Fig. 3E, G) and suggests some modification of

505   plagioclase inclusion compositions occurred as well.

506   Wollastonite-hosted melt inclusions are generally well formed and equant with a single shrinkage bubble,

507   and lack textural evidence of sidewall crystallisation and modification (Fig. 3D). Although Fe and Mn are

508   weakly compatible in wollastonite, traverses from inclusion contact to 20 μm into the crystal do not show

509   any resolvable chemical gradients that would indicate diffusion and melt inclusion alteration. Therefore,
510   wollastonite-hosted inclusions are likely the best inclusions to represent original compositions.

511   The effect of post-entrapment crystallisation of a melt inclusion can be tested graphically. Fractionation
512   vectors in Fig. 9 show the effect of 10% subtraction (crystallisation) of clinopyroxene, plagioclase and
513   wollastonite on glass compositions. Taking the fractionation vectors for the CaO vs SiO$_2$ plot, Fig. 9
514   shows that that any post-entrapment crystallisation of the respective host phase would lower the CaO
515   concentration of the trapped melt, therefore our analyses must reflect minimum original CaO estimates,
516   regardless of inclusion sidewall crystallisation. Melt inclusion compositions instead follow the vector for
517   addition of calcite to the published melt compositions. As the current methods of correcting for post
518   entrapment crystallisation are not suitable for these compositions, no attempt has been made to account
519   for the effects of melt inclusion modification. Additionally, these compositions overlap the compositions
520   of Ca-contaminated interstitial glasses, and high CaO is present regardless of the host mineral phase. This
521   shows that although post-entrapment modification may have occurred, the very high CaO values may
522   reasonably represent minimum estimates of original melt compositions.

Intensive Variables

### *Magmatic Skarn Xenolith Thermobarometry*

525   The abundance of glass and common mineral phases (clinopyroxene, plagioclase) allows for the
526   application of thermobarometric models to the xenoliths (Fig. 11). On the basis of the uncertainty in
527   mineral-melt equilibrium testing, and the results of testing thermobarometric models with experimental
528   carbonate assimilation data (see supplementary material), application of the glass-only equation 34 of
529   Putirka (2008) to the clinopyroxene-saturated interstitial glasses of the magmatic skarn xenoliths with
530   water contents estimated by difference from 100 wt% (Anderson, 1973, 1974; Devine *et al.*, 1995),
531   provides a temperature of 829 $\pm$ 45°C (*n*=89). Melt inclusions, in turn, reflect a slightly higher
532   temperature of 876 $\pm$ 49°C (*n*=88). These temperatures are consistent with the presence of ferrobustamite
533   overgrowths on the coexisting wollastonite, which is thought to be stable between ~800-880°C (Rutstein,
534   1971). A pressure of 50 MPa was assumed for thermometry, consistent with the results of fluid inclusion
535   barometry (our results: 34-92 MPa, and those of Clocchiatti *et al.* (1982): 67-109 MPa). Temperature
536   estimates are lowered by a negligible 5°C per 100 MPa. Temperatures estimated for glasses within any
537   lava attached to the xenolith, and lava interstitial glasses from the literature (with an assumed pressure of
538   200 MPa; *c.f.* Preece *et al.*, 2014; Erdmann *et al.*, 2016) are higher than that of the xenolith glasses, at 937
539    $\pm$ 43°C. Phase equilibria estimates of pre-eruptive temperatures for Merapi are 925-950°C (Erdmann *et*
540   *al.*, 2016), which supports the higher lava glass temperature from our glass thermometry.

541   Additional constraints can be gained from comparison with experimental phase equilibria. The small
542   interstitial patches of garnet, plagioclase and wollastonite in sample MX1 are stable between ~510-890°C,

543   with an $XCO_2 < 0.6$ at 100 to 200 MPa (Gordon and Greenwood, 1971; Tracy and Frost, 1991), consistent

544   with temperatures from the glass thermometry. The R3b zone in sample MX1, comprising coexisting

545   grossular-andradite garnet ($Adr_{0.3}$) and CaTs-clinopyroxene ($CaTs_{0.23}$) indicates temperatures of 900-

546   950°C based on experimental phase equilibria (Huckenholz *et al.*, 1974; Gustafson, 1974).

547   *Exoskarn T-XCO₂*

548   Although the exoskarn xenoliths lack glass, many phases and assemblages in the exoskarn xenoliths can

549   help constrain temperatures by comparison with experimental data and thermodynamic modelling.

550   Spurrite + cuspidine ± larnite-bearing reaction rims between calcite and wollastonite + grossular +

551   anorthite in samples CS11 and MXCS-0 allow temperature constraints, while additionally demonstrating

552   the progressive interaction along a $CaO-SiO_2-CO_2$ system (e.g. Zharikov, 1969). The presence of spurrite

553   and absence of evidence for lower temperature tilleyite-forming reactions indicate spurrite formation by

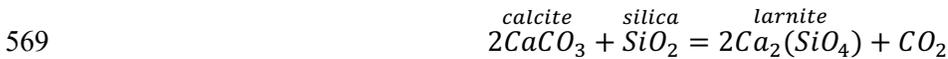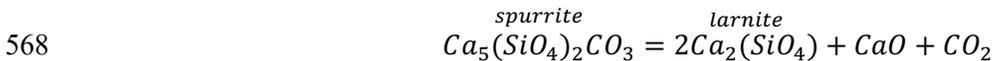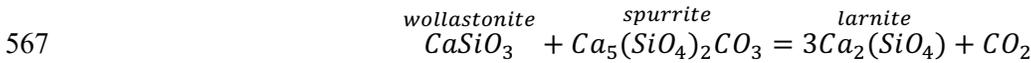554   either interaction between wollastonite and calcite

555
$$\overset{calcite}{3CaCO_3} + \overset{wollastonite}{2CaSiO_3} = \overset{spurrite}{Ca_5(SiO_4)_2CO_3} + 2CO_2$$
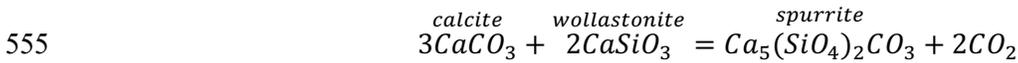
556   or calcite directly with SiO_2

557
$$\overset{calcite}{5CaCO_3} + \overset{silica}{2SiO_2} = \overset{spurrite}{Ca_5(SiO_4)_2CO_3} + 4CO_2$$

558   The former reaction indicates temperatures of ~700-1000°C (Tuttle and Harker, 1957). Spurrite is stable

559   as low as 430°C at low CO_2 partial pressure (Henmi and Henmi, 1978), but the proximity of tens of

560   microns to a decarbonating calcite crystal and a significant proportion of voids suggests a high CO_2

561   partial pressure. The latter reaction occurs at 910°C at 1 atm when in the presence of chlorine or fluorine

562   (Bolio-Arceo and Glasser, 1990). Cuspidine and fluorite are found within tens of microns of the spurrite,

563   confirming a reaction occurred with a fluorine-bearing fluid.

564   Larnite forms further from the calcite near the wollastonite contact (Deegan *et al.*, 2010 Fig. 10b) in

565   sample MXCS-0, indicating temperatures of > 850°C (Wyllie and Haas Jr, 1965; Joesten, 1974; Treiman

566   and Essene, 1983), following the potential reactions:

567
$$\overset{wollastonite}{CaSiO_3} + \overset{spurrite}{Ca_5(SiO_4)_2CO_3} = \overset{larnite}{3Ca_2(SiO_4)} + CO_2$$

568
$$\overset{spurrite}{Ca_5(SiO_4)_2CO_3} = \overset{larnite}{2Ca_2(SiO_4)} + CaO + CO_2$$

569
$$\overset{calcite}{2CaCO_3} + \overset{silica}{SiO_2} = \overset{larnite}{2Ca_2(SiO_4)} + CO_2$$

570   The dominant mineral assemblage in these large calcite-bearing xenoliths can be described in the SiO_2-
571   Al_2O_3-CaO system, comprising grossular garnet (Grs$_{78-96}$), wollastonite and anorthite. This assemblage is
572   stable between ~510-890°C at 50-200 MPa, with an increasingly restricted XCO_2 with pressure, varying
573   from > ~0.2 to 1 at 50 MPa, and from ~0.2 to 0.4 at 200 MPa (Gordon and Greenwood, 1971; Tracy and
574   Frost, 1991). Grossular with inclusions of calcite, wollastonite and anorthite is additionally found in the
575   CaTs-clinopyroxene bearing xenoliths, suggesting the following reaction has occurred:

576
$$\underset{calcite}{CaCO_3} + \underset{wollastonite}{CaSiO_3} + \underset{anorthite}{CaAl_2Si_2O_8} = \underset{grossular}{Ca_3Al_2Si_3O_{12}} + CO_2$$

577   The equilibration temperature of CaTs-clinopyroxene and grossular-andradite-bearing exoskarn xenoliths
578   is estimated as 900-950°C based on experimental data (Huckenholz *et al.*, 1974). Reactions involving
579   these phases were further investigated using Theriak-Domino software (build date 3-1-2012, de Capitani
580   and Petrakakis, 2010) using calculated whole-rock compositions in the system Si-Al-Fe-Mg-Ca-C. An
581   upper limit of temperature for the exoskarn xenoliths is ~910°C at 100 MPa, which represents the limit of
582   garnet stability (Fig. 12). Garnet reacts out just after melilite becomes stable at ~900°C. Exoskarn type A
583   xenoliths contain abundant garnet and trace amounts of gehlenite, constraining the temperature to this
584   narrow field between 900 and 910°C. The calculated high (30 mol%) CaTs contents at the melilite-in
585   boundary are in agreement with the high (up to 38 mol%) CaTs contents observed in these xenoliths, as
586   are modelled gehlenite contents (> 70 mol%) compared to the observed ones (74-94 mol%). The mineral
587   assemblage of the exoskarn type B xenolith is constrained by a slightly lower maximum temperature as
588   garnet becomes unstable at 860°C (Fig. (12). A minimum temperature estimate is given as ~780°C from
589   high clinopyroxene CaTs component (22-39 mol%). Conditions are further constrained to $a_{CO2} < 0.5$ for
590   both xenolith types by the absence of meionite and calcite. The results closely match the temperatures
591   from previously cited experimental studies. These temperature estimates are similar to those estimated for
592   the magmatic skarn xenoliths by thermobarometry.

593   In summary, the comparison with experimental studies and results from modelling indicate exoskarn
594   formation temperatures up to ~910°C, with a lower limit at around 780°C for xenoliths with CaTs
595   clinopyroxene and 510°C for xenoliths without CaTs clinopyroxene. There is no evidence for low
596   temperature retrograde overprint, and these temperatures overlap the temperatures estimates for the
597   magmatic skarn xenoliths (~850°C). These temperature estimates extending to as low as 510°C,
598   combined with the petrological differences described above, indicate a metasomatic origin for the
599   exoskarn xenoliths instead of petrogenesis via magmatic crystallisation for the magmatic skarn/endoskarn
600   xenoliths.

Oxygen Fugacity

Estimates of oxygen fugacity (fO_2) are difficult due to the lack of mineral assemblages commonly used to determine this variable. A first order estimate is obtained from the presence of magnetite in magmatic skarn xenoliths compared to hematite in the exoskarn xenoliths, indicating more oxidising conditions in the latter. Two single crystal clinopyroxene oxybarometers exist that use Fe^{3+} concentrations in clinopyroxene to estimate oxygen fugacity (Cortés *et al.*, 2006; Simakin *et al.*, 2012). Although Fe^{3+} concentrations in clinopyroxenes calculated by stoichiometry (e.g. Lindsley, 1983; Droop, 1987) have been shown in some studies to have a weak correlation to measured clinopyroxene Fe^{3+} concentrations (e.g. Sobolev *et al.*, 1999), a positive correlation between clinopyroxene Fe^{3+}/Fe^{total} and fO_2 has been demonstrated from experimental data by Cortés *et al.* (2006) and Simakin *et al.* (2012). When taking a much larger dataset (the Library of Experimental Phase Relations, Hirschmann *et al.*, 2008), with high fO_2 experiments such as those from Mollo and Vona (2014) and Sugawara (2001) and normalise the data to the NNO (nickel-nickel oxide) buffer (*c.f.* Cortés *et al.* 2006) using buffer equations from Frost (1991), then a broad positive correlation is still observed, although with a large scatter ($R^2 = 0.44$). Fe^{3+}/Fe_{total} falls short of unity at an fO_2 of air, and all Fe is Fe^{2+} at $\sim\Delta NNO-2$. When applied to this large experimental dataset, the oxybarometer of Cortés *et al.* (2006) strongly overestimates fO_2 conditions, whilst Simakin *et al.* (2012) fails to recover experiments performed in air (Fig. 13).

We use a selection of data from experiments that span a wide fO_2 range to calibrate a new oxybarometer that recovers high fO_2 conditions more accurately. We use the datasets of Whitaker *et al.* (2007), Freise *et al.* (2009), Feig *et al.* (2006), Feig *et al.* (2010), and Mollo and Vona (2014) (excluding Mollo and Vona's relatively high Fe^{3+}/Fe_{total} NNO experiments). This calibration dataset spans a fO_2 between $\Delta NNO-5$ to air, temperatures between 900 to 1280°C, 0 to 5 wt% H_2O, and 50-68 wt% SiO_2 and has a high coefficient of determination ($R^2 = 0.80$). Although the dataset of Sugawara (2001) spans the widest fO_2 range known to the authors ($\sim$13 log units), calculated Fe^3/Fe_{total} values have larger scatter than those from other datasets, therefore we exclude these from the regression. Additionally, although Al^{IV} increases in clinopyroxene with increasing fO_2 (e.g. Mollo and Vona, 2014), adding Al^{IV} to the models shows no significant improvement on the model, therefore we only use Fe^3/Fe_{total} for prediction. There is also no significant improvement in R^2 or the standard error when using a polynomial fit over a linear model, however we use a polynomial fit to marginally improve the estimates at low fO_2, as was shown by Simakin *et al.* (2012). We additionally considered constructing a similar oxybarometer based on Fe^{3+} in garnet as Fe^{3+} can be estimated accurately for garnet (Arai, 2010), however there is an insufficient range of oxygen fugacity controlled experiments in the Library of Experimental Phase Relations (LEPR; Hirschmann *et al.,* 2008) database to attempt building a similar single crystal oxybarometer for garnet.

For testing, we filtered the entire experimental database to clinopyroxenes equilibrated < 1 GPa, with Si a.p.f.u. < 2, Ca > 0.5 a.p.f.u., cation totals between 3.98 and 4.1, and Na_2O < 1 wt%. Our models recover

636 the calibration dataset with a residual standard error of 1.5 log units, the global database and additional

637 experimental data to 1.8 log units, compared to 2.1 for Cortés *et al.* (2006) and Simakin *et al.* (2012). The

638 improvements in the error are small, in part due to a lack of high fO_2 experiments and potential variable

639 data quality of the individual experiments in the LEPR database. However, the accuracy at high fO_2 is

640 improved, which is most relevant to our Merapi xenoliths. We obtain the following equation:

641
$$\Delta NNO = 22.705(\frac{Fe^{3+}}{\sum Fe})^3 - 32.400(\frac{Fe^{3+}}{\sum Fe})^2 + 21.799(\frac{Fe^{3+}}{\sum Fe}) - 3.066$$

642 where Fe^{3+} and $\sum Fe$ are Fe a.p.f.u. estimated from stoichiometry (e.g. Lindsley, 1983; Droop, 1987),

643 and ΔNNO is the deviation from the nickel - nickel oxide oxygen fugacity buffer in log units.

644 Application of our oxybarometric model shows a wide spread of fO_2 values for the xenoliths (Fig. 14A).

645 Magmatic skarn xenolith clinopyroxenes at the lava contact zone R1 and in zones R2, R3 and R4, have

646 values similar to the magmatic values both predicted by our model and published estimates (ΔNNO-0.2 to

647 +1.6 Gertisser, 2001; Erdmann *et al.*, 2014). Touching pyrrhotite and anhydrite crystals in zone R2 in a

648 small subset of magmatic skarn xenolith samples additionally indicate a near-magmatic fO_2 range

649 between ΔNNO+0.5 to +2.5 (Luhr, 2008; Parat *et al.*, 2011), consistent with other estimates. The R3b

650 zone in sample MX1 records higher oxygen fugacity conditions than the CaTs clinopyroxene + garnet

651 absent samples, at ΔNNO > +5. Xenolith core clinopyroxenes are formed through a large range of oxygen

652 fugacity conditions. The higher values come from the CaTs-rich clinopyroxene cores of sample CS16

653 (Fig. 14B). Anhydrite crystals within these clinopyroxene cores (stable at > ΔNNO+1 Carroll and

654 Rutherford, 1987) provide further evidence for a relatively high fO_2 during early clinopyroxene

655 formation. Exoskarn xenolith clinopyroxene indicates formation under higher fO_2 than magmatic skarn

656 xenoliths, approaching that of air (~ΔNNO + 8). While exoskarn type A xenoliths record a large range

657 from NNO -1 to +8, the exoskarn type B xenolith uniquely records conditions of exclusively > ΔNNO +

658 5. The high fO_2 conditions recorded in the exoskarns are similar to that recorded in zone R3b of magmatic

659 skarn xenolith MX1.

660 High fO_2 in skarn systems is a result of CO_2 release from carbonate, and this CO_2 can impose a fO_2 equal

661 to or greater than the HM buffer (e.g. Nicholls, 1971; Wenzel *et al.*, 2002). The magnitude of fO_2 increase

662 is proportional to the freedom CO_2 has to leave the system. An open system continuous flux of CO_2

663 increases fO_2 higher than that of a closed system (Ganino *et al.*, 2008). The generally higher fO_2 observed

664 in the exoskarn xenoliths may thus be a result of prolonged open system flux of CO_2, whereas the syn-

665 magmatic magmatic skarn xenoliths were rapidly processed within the magma. Magmatic skarn xenolith

666 zone R3b however records a high fO_2, comparable to the exoskarns, and additionally mineral phases in

667 there, such as clinopyroxene, compositionally overlap exoskarn mineral compositions (Fig. 7). These

668 compositions may be in part due to a lack of melt in this region of the magmatic skarn xenolith, restricting

669 SiO$_2$ availability, and producing as a result silica-undersaturated mineral compositions such as CaTs
670 clinopyroxene.

Xenolith Petrogenesis

Protolith

673 An absence of Mg-rich skarn minerals within the xenoliths (olivine, periclase, merwenite, åkermanite)
674 and the abundance of wollastonite instead suggests a calcite-limestone protolith for the xenoliths. The
675 Merapi xenoliths do not match any mineral assemblages produced during magma-dolomite interaction
676 experiments, instead they closely resemble the results of magma-limestone experiments (e.g. Zarayskiy *et*
677 *al.*, 1987: wollastonite, clinopyroxene, garnet). Electron microprobe analyses of calcites (Whitley *et al.*,
678 2019) are pure calcites with < 0.2 wt% MgO + FeO + SrO, which additionally indicates a pure limestone
679 protolith in the absence of Mg-rich skarn minerals. Furthermore, local carbonate sampled from
680 Parangtritis (50 km south of Merapi) is limestone. The progressive chemical zonation within the xenoliths
681 from "magmatic" to calcic compositions (Fig. 5) shows that the Mg-Fe-Al-bearing phases source these
682 elements from the host magma, not from a dolomite or marl.

Magmatic Skarn Xenoliths

684 The abundance of Ca-rich melt inclusions and Ca-rich groundmass glass (Fig. 3) indicate crystallisation
685 of the main skarn mineralogy of clinopyroxene, plagioclase and wollastonite from a Ca-contaminated
686 magmatic melt, produced from dissolution of the carbonate protolith (Fig. 9) (*c.f.* Deegan *et al.*, 2010).
687 Calcic melt inclusions and matrix glasses were also described from volcanic products of the 2010
688 eruption of Merapi (Borisova *et al.,* 2013). Thermodynamic modelling suggests formation of Ca-rich
689 melts via a peritectic reaction of grossular-bearing calc-silicate material with the magma (Borisova *et al.,*
690 2016). The Ca-rich melt inclusions are spread randomly throughout their host crystals, or less commonly,
691 along crystal growth zones, showing a primary origin (Roedder, 1984; Goldstein, 2003). Clinopyroxene
692 compositions in these xenoliths are compositionally distinct from those in the exoskarn xenoliths, most
693 notably those from the glass zone R4 (Fig. 7), supporting formation from the Ca-rich melt instead of an
694 origin as incorporated xenocrysts from partially melted exoskarns. Fe-rich ferro-bustamite growths on
695 some wollastonite crystals is also consistent with crystallisation from this melt, as the glass and core
696 zones are characterised by FeO-enrichment (Figs. 6, 7). Melt inclusions in wollastonite are not
697 exclusively comprising CaO and SiO$_2$, but also contain other major element oxides such as K$_2$O, which
698 can only be derived from the magmatic melt as there no K-bearing phases found in any of the xenoliths
699 studied. The composition of these melt inclusions cannot be explained by dissolution of wollastonite but
700 supports the idea that wollastonite crystallized from a Ca-enriched melt. Experimental work at Merapi has
701 shown the contaminated melt takes up Sr and B from the carbonate protolith (Deegan *et al.*, 2010; 2016a),
702 which supports the idea of dynamic element exchange between carbonate and the surrounding melt. The

arrows in Fig. 9 show the addition of 10% CaO to the melt, indicating that the melt inclusions record crystallisation from a melt with up to 20% CaO added. The groundmass glasses retain evidence for up to 10% added CaO, after crystallisation of wollastonite and other minerals. Although whole-rock compositions at Merapi are basaltic to basaltic-andesite, the lava groundmass glasses, the melt compositions in contact with the carbonate, and xenolith glasses, are distinctly more felsic (60-76 wt% SiO_2). The melt inclusion CaO concentrations observed in our study (Fig. 9) far exceed (up to 11.3 wt% CaO) those observed in glasses from calcite-saturated dacite-carbonate experiments of Carter and Dasgupta (2016) (< 4.3 wt%), confirming their hypothesis that natural systems may be able to assimilate more carbonate than their closed system experiments indicated.

Skarn minerals that contain melt inclusions and show evidence for crystallisation from a carbonate contaminated magmatic melt, instead of through metasomatic transfer, are a rare but increasingly recognised phenomenon (e.g. Fulignati *et al.*, 2001; Bin and Jin-song, 2016). Homogenisation temperatures of these melt inclusions in the literature (Fulignati *et al.*, 2001; Bin and Jin-song, 2016) indicate temperatures of 860-1200°C, which are in excess of those typically experienced during metasomatic skarn formation in contact metamorphic aureoles (< c. 800°C; Meinert, 1992), indicating direct interaction between a magmatic melt and carbonate. Trapping of melt inclusions in skarn minerals precipitated from a calcite contaminated quartz diorite melt has been experimentally confirmed (Bin and Jin-song, 2016), and dacite-carbonate interaction experiments (Carter and Dasgupta, 2016) have been shown to crystallise wollastonite, in contrast to producing dominantly Ca-rich melt in experiments with mafic melt compositions (Deegan *et al.*, 2010; Carter and Dasgupta, 2015).

As well as this rare and unique evidence for skarn mineral formation from carbonate contaminated melts, and therefore exoskarn formation by this process, the magmatic skarn xenoliths also provide insights into the morphology and cumulate-forming processes at the wall-rock contact at Merapi. Carbonate assimilation has been shown to form and/or influence the mineralogy of cumulate assemblages; for example, changes to the mineral chemistry of dunites at the Ioko-Dovyren Intrusion, Russia (Wenzel *et al.*, 2002), formation of clinopyroxenite xenoliths at Nisyros, Greece (Spandler *et al.*, 2012), and olivine+clinopyroxene+spinel cumulate xenoliths at Colli Albani (Gaeta *et al.*, 2009; Di Rocco *et al.*, 2012). Reaction between carbonate and magmatic melt increases the stability of clinopyroxene and in more evolved melts, plagioclase also (e.g. Mollo *et al.*, 2010). This results in a wallrock grading from a cumulate zone adjacent to the magma body (endoskarn), to skarn assemblages at the limestone contact (exoskarn). Skarn-derived Ca-rich melts are inferred (Wenzel *et al.*, 2002; Gaeta *et al.*, 2009) to be the main source of carbonate components contaminating the magmatic melt. Our magmatic skarn xenoliths are perfect examples of these processes. Zones R1 to R3 comprise the cumulate zone formed under the influence of carbonate assimilation. Similar to cumulates at Ioko-Dovyren (Wenzel *et al.*, 2002) and Colli Albani (Gaeta *et al.*, 2009), clinopyroxenes and plagioclase in these zones only show relatively subtle

738   variations in mineral chemistry from magmatic-derived mineral compositions that reveal their carbonate

739   contamination origin. The CaO-enriched glass-rich zone R4 captures the carbonate process of the

740   magmatic melt contamination, and the xenolith cores in some samples preserve very rare instances of the

741   actual calcite carbonate melt (see Whitley *et al.*, 2019). This carbonate melt has since only been inferred

742   to occur during other instances of carbonate assimilation (Wenzel *et al.*, 2002; Barnes *et al.*, 2005; Gaeta

743   *et al.*, 2009), whilst the magmatic skarns at Merapi preserve and demonstrate direct evidence for its

744   existence.

745   A syn-magmatic origin for these xenoliths, i.e. formation by direct magma-carbonate contact during

746   magmatic events such as eruptive periods, is consistent with the presence of glass and additionally the

747   low pressures of 37-93 MPa (corresponding to < 3.5 km) estimated from fluid inclusion barometry. These

748   pressures are similar to some pressure estimates derived from re-equilibrated melt inclusions in magmatic

749   clinopyroxenes at Merapi (Nadeau *et al.*, 2013b; Preece *et al.*, 2014), and they are lower than pressures

750   estimated for the main pre-eruptive magma chamber or reservoir at Merapi (100-400 MPa, corresponding

751   to depths of ~4-15 km; Commer *et al.*, 2006; Chadwick *et al.*, 2013; Costa *et al.*, 2013; Preece *et al.*,

752   2014; Erdmann *et al.*, 2016; Deegan *et al.*, 2016b). This indicates that the fluid inclusions have re-

753   equilibrated during ascent, or have been formed at very shallow crustal pressures. The lack of a 're-

754   equilibration tail' (Hansteen and Klügel 2008) and no evidence for pressures > 100 MPa in our fluid

755   inclusion dataset suggest re-equilibration is unlikely, and instead is indicative of fluid inclusion formation

756   in small ephemeral pre-eruptive reservoirs or during magmatic ascent during eruptive periods.

757   Patchy zoned clinopyroxenes with prominent irregular resorption surfaces (Fig. 7) show that this syn-

758   magmatic carbonate interaction is a dynamic process, under temporarily variable imposed oxygen

759   fugacity conditions caused by rapid CO_2 release (Fig. 14) (*c.f.* Mollo *et al.*, 2010). Variations in the ability

760   of this CO_2 to migrate from the reaction site (Ganino *et al.*, 2008; Blythe *et al.*, 2015) may cause the

761   variation in oxygen fugacity across texturally similar samples, and even within xenolith zones. Al, Fe^{3+}-

762   rich clinopyroxene cores and andraditic-rich garnet indicate high initial oxygen fugacity conditions (Figs.

763   7, 14; Meinert, 2005; Mollo and Vona, 2014), whilst diopside-rich cores indicate high initial carbonate-

764   derived Ca activity in the melt (Zarayskiy *et al.*, 1987). Increasing CO_2 release causes clinopyroxene Fe-

765   enrichment in the mantle and rims (Zarayskiy *et al.*, 1987) to higher than observed in magmatic

766   clinopyroxenes in later stages of xenolith formation (Fig. 7). Fe is additionally concentrated in plagioclase

767   as An concentrations decrease (Fig. 6).

768   Although we propose that the magmatic skarn xenoliths reflect crystallisation from a Ca-contaminated

769   melt, it is interesting to note that their mineralogical zonation still bears strong resemblance to contact

770   metamorphic zoned bimetasomatic skarns and experimental reconstructions of these, such as produced

771   during granodiorite-calcite interaction experiments (Zarayskiy *et al.*, 1987). Magmatic skarn xenolith

772 samples with a garnet + CaTs clinopyroxene zone (zone R3b in Fig. 1) represent the exo/endoskarn
773 transition in natural skarns, where carbonate-derived elements are transferred to the magmatic system
774 (clinopyroxene + plagioclase endoskarns, zones R1-R3). In turn, certain magma-derived elements are
775 transferred to the carbonate protolith forming garnet + wollastonite + Di-Hd/CaTs clinopyroxene
776 exoskarns (zone R3b and the xenolith cores), reflected also in the chemistry of the individual zones (Fig.
777 5).

778 Dissolution of carbonate in high temperature mafic magmatic melts has been experimentally confirmed to
779 operate on the order of hours (Deegan *et al.*, 2010; Jolis *et al.*, 2013), but mineral equilibration is slower
780 (*c.f.* Carter and Dasgupta, 2016). First order constraints on the timescales of carbonate interaction at
781 Merapi can be tentatively placed using the growth rate of xenolith mineral phases such as clinopyroxenes.
782 Experimental and measured growth rates for euhedral clinopyroxenes in basaltic to andesitic magmatic
783 systems are on the order of 10^9 to 10^7 cm/s (e.g. Kouchi *et al.*, 1983; Simakin *et al.*, 2003; Orlando *et al.*,
784 2008; Kilgour *et al.*, 2014). Assuming similar growth rates for the clinopyroxenes in the xenoliths, a
785 typical 300 μm clinopyroxene in zone R4, which has an entirely different composition to the Merapi
786 magmatic clinopyroxenes (Fig. 7) and therefore formed uniquely during magma-carbonate interaction,
787 could have formed in 3.5 to 347 days. Measurements of the growth rate of skarn formation between
788 granodiorite and calcite, and quartz and brucite marble, in experiments of Zarayskiy *et al.* (1987) indicate
789 similar timescales. Although clinopyroxene growth rates are poorly constrained, especially in magma-
790 carbonate systems, it is conceivable that the xenoliths could have formed on shorter timescales, e.g. in the
791 lead up to and during eruptive periods. The associated CO_2 release may then be able to influence eruption
792 dynamics (*c.f.* Troll *et al.*, 2012). Future work utilising diffusive timescales would potentially increase the
793 accuracy of these timescale estimates and aid hazard assessment at Merapi.

794 In summary, we propose that the magmatic skarn xenoliths are syn-magmatic in origin, forming as a
795 result of limestone dissolution into a magmatic melt, from which skarn minerals precipitate (Fig. 15).
796 Localised changes in oxygen fugacity caused by the CO_2 released to the fluid phase influenced the
797 composition of the minerals formed. Variable transfer of Ca from limestone, and magma-derived
798 elements, form zonations similar to those observed in metasomatic skarns, but at above solidus
799 temperatures. The composition of the zones is controlled by element transfer between magma and
800 limestone and the stability and abundance of the major minerals that form in the respective zones. Our
801 evidence of syn-magmatic magma-carbonate interaction is in agreement with previous studies on Merapi
802 magma-carbonate interaction (Deegan *et al.*, 2010, 2016a; Troll *et al.*, 2012), at Vesuvius (Blythe *et al.*,
803 2015; Jolis *et al.*, 2015) and at Colli Albani (Iacono-Marziano *et al.*, 2007; Freda *et al.*, 2011), which all
804 note the likely very rapid, syn-eruptive timescales of carbonate dissolution and CO_2 liberation. If correct,
805 this process has the potential to enhance eruption explosivity due to external CO_2 additions.

Exoskarn Xenoliths

806

807 Exoskarn xenoliths contain dominantly Al+Si+Ca-bearing phases, and < 10 wt% FeO+MgO based on
808 calculated whole rock compositions. Although the high Al could be indicative of a marl protolith, we
809 believe these samples come from a calcite-bearing protolith with input from magmatically derived
810 elements, on the basis of calcite oxygen isotopes showing evidence of interaction with magmatic fluids
811 (Whitley *et al.*, 2019), and the presence of F-Cl-S-rich phases most likely derived from magmatic
812 volatiles.

813 The exoskarn xenoliths lack the interstitial glass, melt inclusions and mineralogical zonation of the
814 magmatic skarn xenoliths, with only a clinopyroxene ± plagioclase reaction rim at the lava contact. Melt
815 inclusion compositions within these rim clinopyroxenes are indistinguishable from the lava groundmass
816 glasses (Fig. 9). The core assemblage (garnet + CaTs clinopyroxene + wollastonite + anorthite ±
817 gehlenite) is distinct from the magmatic skarn xenoliths (wollastonite ± glass ± DiHd clinopyroxene ±
818 garnet ± anorthite). The much higher fO_2 conditions recorded in the clinopyroxenes (Fig. 14) indicate that
819 these xenoliths experienced a longer period of CO_2 flushing than the magmatic skarn xenoliths (*c.f.*
820 Ganino *et al.*, 2008). This, coupled with the distinct mineralogy, a lack of glass and a lack of
821 mineralogical zonation, suggests that the exoskarn xenoliths originate from a contact metamorphic
822 aureole (exoskarn) around the upper crustal Merapi magma reservoir system (Fig. 15). The dominance of
823 high temperature anhydrous mineral assemblages indicates that they are sourced proximal to the magma
824 reservoir. Contact metamorphic aureoles can be extensive in size (Aarnes *et al.*, 2010), therefore we
825 expect low-temperature distal skarn assemblages to be present at Merapi, but these may not have been
826 frequently sampled during this study, possibly because of the high temperature 'skarn shell' (*c.f.* Fulignati
827 *et al.*, 2001; Jolis *et al.*, 2015) being overrepresented in our dataset.

828 The presence of spinel, as observed in one of our samples (MX99-3s), has been noted in several case
829 studies on magma-carbonate interaction (e.g. Wenzel *et al.,* 2002; Gaeta *et al.*, 2009; Spandler *et al.*,
830 2012). For instance, hercynitic spinel is widespread in skarns from the Italian volcanic provinces. Skarns
831 from the Colli Albani Volcanic District (Italy) contain Al-rich spinel in textural equilibrium with glass,
832 which was interpreted to reflect melting of calcite and mixing of this melt with the host magma (Gaeta *et*
833 *al.*, 2009). Metasomatic development through leaching was invoked to explain the occurrence of banded
834 forsterite-spinel skarns in ejecta from the 1631 Vesuvius eruption (Pascal *et al.,* 2009). Experimental
835 work on magma-carbonate interaction with andesitic (Carter and Dasgupta, 2016) and basanitic (Conte *et*
836 *al.,* 2009) magmas also produced aluminous spinel. Clearly, the presence of aluminous spinel is a
837 common characteristic of carbonate assimilation. None of these studies, however, shows the unique
838 texture and association with gehlenite as in sample MX99-3s, and we classify this sample as exoskarn
839 (type B) based on the lack of glass and the mineralogical differences to the more common magmatic
840 skarns at Merapi.

Volatiles and Metal Transport

The numerous F-Cl-S phases identified in the xenoliths record evidence of interaction with a magmatic-derived volatile phase (MVP; *c.f.* Nadeau *et al.*, 2010; Preece *et al.*, 2014) during formation of the xenoliths. Although F-Cl-S-bearing phases indicate the presence of an aqueous fluid, there is no clear evidence of the role of H_2O during xenolith formation. Silicate magma has a limited capacity to dissolve the excess liberated crustal-derived CO_2 and any increase in melt CO_2 would strongly reduce the solubility of H_2O (e.g. Tamic *et al.,* 2001), increasing the free H_2O available during magma-carbonate interaction. The xenoliths however contain anhydrous mineral assemblages, and fluid inclusions are two phase liquid CO_2 + vapour CO_2 with only very rare small fluid inclusions containing unidentified daughter crystals. Excess CO_2 in the magma causes the typical wollastonite-forming reaction SiO_2 + $CaCO_3 \rightarrow CaSiO_3 + CO_2$ to favour the reactants and promote skarn mineral formation.

F-Cl-S-bearing phases are found within both magmatic and exoskarn xenoliths, however they are not found in every magmatic skarn xenolith sample. In the magmatic skarn xenoliths, they are found in zone R2 (anhydrite surrounding pyrrhotite ± cubanite), zone R3b (ellestadite) and as interstitial patches the wollastonite-dominant cores. These patches contain cuspidine, fluorite and the wadalite-like mineral, whilst anhydrite, apatite, and cotunnite ($PbCl_2$) are found as accessory phases elsewhere in the cores. Pyrrhotite, cubanite, Fe-oxides and apatite are sometimes found as daughter crystals in melt inclusions. The presence of fluorine-bearing phases in sample MX1 is closely related to calcite with a melt-like texture, consistent with fluorine lowering the melting temperature of calcite (Jago and Gittins, 1991; Gorzkowska *et al.*, 1988a, 1988b; see Whitley *et al.*, 2019 for more detail). Chlorine and limited data for F in the Ca-rich xenolith core interstitial glass and melt inclusions do not show elevated concentrations compared to the lavas. This suggests that the volatile-rich minerals are unlikely to have precipitated directly from the melt, like the wollastonite, clinopyroxene and plagioclase, but are instead the result of interaction with this magmatic-derived volatile phase. In sample MX1, the melt-like calcite is in places replaced by the wadalite-like mineral, which retains the calcite texture (Fig. 3). Instances where garnet is replaced by this wadalite-like phase may be from reaction with magmatic HCl (e.g. Fujita *et al.*, 2001). Calcite additionally reacts with fluorine to form fluorite as distinct crystal phases, and as radial growths around a vesicle touching calcite (Fig. 3A-B), suggesting fluorine is an important component of the volatile phase.

The exoskarn xenoliths additionally contain phases enriched in magmatic-derived volatiles. For instance, ellestadite is found throughout the xenoliths, and rare pyrrhotite and anhydrite are present in some samples, but the majority of volatile-rich phases (cuspidine, anhydrite, ellestadite, fluorite, spurrite) are concentrated in the reaction rims around residual large calcite crystals. A magmatic fluid source for these

875 mineral phases is evidenced by calcite oxygen isotopic shifts towards magmatic values (Whitley *et al.*,
876 2019) and elevated trace element LREE/HREE in these calcites compared to marine limestone
877 (Supplementary Fig. S5; Supplementary Table S1).

878 The presence of the magmatic-derived volatile phase within the xenoliths indicates potential for economic
879 metal mineralisation beneath Merapi and similar carbonate-hosted arc volcanoes in the region. Oxidised
880 silicic calc-alkaline arc intrusions are frequently associated with porphyry Cu, Zn, Pb and Fe deposits
881 (Meinert, 2005). Ubiquitous calc-silicate xenoliths at Merapi provide evidence for skarn formation, and
882 garnet and clinopyroxene compositions in these xenoliths overlap those characteristic of Cu, Zn and Fe
883 skarns (Meinert, 1992). Although these economic metals are rare in our studied xenoliths, our data
884 suggest that ongoing mineralisation may occur at depth beneath Merapi within the upper part of the
885 plumbing system, during the later stages of magmatic evolution at Merapi.

886 Sulphur-bearing arc magmas are important sources of Cu, and Cu transport has been noted across the
887 Sunda arc (Nadeau *et al.*, 2010; Agangi and Reddy, 2016). Globules of Cu-rich sulphide melt are found in
888 the Merapi lavas recording evidence of Cu-rich sulphide melts exsolving from primitive magma, which
889 are later dissolved in the magmatic-derived volatile phase and distributed through more evolved magmas,
890 and potentially into the host-rock system (Nadeau *et al.*, 2010, 2013a). As previously discussed, the
891 xenoliths are evidence of interaction between this Cu-S-enriched fluid phase and carbonate. In the
892 magmatic skarn xenoliths, Cu is found as cubanite and as a minor constituent in pyrrhotite in zone R2,
893 which are generally surrounded by anhydrite. Disproportionation of SO_2 into sulphide and sulphate is a
894 potential mineralisation process in carbonate and calcium-bearing rocks, and can occur in the timescale of
895 hours (Mavrogenes and Blundy, 2017), and may have formed the coexisting pyrrhotite + cubanite +
896 anhydrite in the xenoliths. Within the magmatic skarn xenolith cores, Cu is rare, only found as a cubanite
897 inclusion in a plagioclase hosted melt inclusion, and as a minor constituent in pyrrhotite inclusions within
898 CaTs-rich clinopyroxene cores. The relative abundance of Cu in zone R2 compared to the core (and
899 exoskarn xenoliths) shows limited transfer of the magmatic-derived volatile phase into the xenolith cores,
900 and/or conditions unfavourable for Cu deposition. Oxygen fugacity is estimated to be similar to typical
901 oxidised arc magma conditions in zone R2 (~ΔNNO + 1), producing favourable conditions for sulphur
902 transport and deposition (e.g. Hattori, 2018). The higher oxygen fugacity estimated in some xenolith cores
903 by the presence of anhydrite and CaTs clinopyroxene cores ($\leq \Delta$NNO + 4) is potentially too high for Cu
904 transfer, as an upper limit to mineralisation at the hematite-magnetite (~ΔNNO + 4) buffer may exist for
905 porphyry copper deposition (Sun *et al.*, 2013). The large volumes of CO_2 released during decarbonation
906 of the original carbonate which causes this fO$_2$ increase, combined with magmatic CO_2, strongly reduces
907 Cu solubility in the fluid phase (van Hinsberg *et al.*, 2016; Kokh *et al.*, 2017). Vesicles are found within
908 zones proximal to the host lava and the core, suggesting that a high XCO_2 in zone R2 may promote the
909 deposition of Cu before it can be transferred fully into the xenolith core. Xenolith formation temperatures

910 are additionally higher than those estimated for the bulk of Cu and Au deposition in copper porphyry
911 systems (starting < 700°C and dominantly < 400°C) where fluid immiscibility produces coexisting
912 vapour-rich and saline fluid inclusions (Sillitoe, 2010), which are not observed in the xenoliths studied
913 here.

914 Our model, where carbonate is assimilated into a melt from which skarn minerals precipitate (magmatic
915 skarns), has been discussed as a process occurring in many Chinese Cu-Fe-Au-deposits (e.g. Bin and Jin-
916 song, 2016). The xenoliths of this study demonstrate that Cu-Fe sulphides can be formed during this
917 process, and may be capable, at least in part, of producing metal sulphide deposits. Magnetite, hematite
918 and Fe-enrichment in some silicate phases may additionally indicate iron oxide ore potential. Whilst we
919 only have xenoliths that show Cu deposition proximal to the Merapi magma reservoir (no low
920 temperature hydrous skarn phases observed), Cu deposition may occur at greater distances into the
921 contact aureole. Percolation of a Cu-bearing magmatic volatile phase through the carbonate over a longer
922 period of time, on cooling when large amounts of magmatic fluids are released, has potential to promote
923 sulphide and Fe-oxide deposition, enhancing ore forming potential such as observed in copper porphyry
924 systems (e.g. Landtwing *et al.*, 2005; Sillitoe, 2010).

Implications of Carbonate Interaction for the Merapi Magmatic System

Xenocryst Cargo

928 Calc-silicate xenoliths are ubiquitous in Merapi eruptive deposits, showing that magma-carbonate
929 interaction is an on-going process at Merapi. The amount of interaction is debated in the literature, with
930 estimates of mixing up to 40% recorded in some samples on the basis of isotopic modelling (Troll *et al.*,
931 2013, Borisova *et al.*, 2013, 2016). Although our study cannot elaborate on estimating the volume of
932 carbonate that interacts with Merapi magmas, our data suggests that calc-silicate derived crystals
933 (xenocrysts) may be more difficult to recognise in erupted magmatic deposits than previously appreciated,
934 as we discuss below.

935 Incorporation of skarn-derived minerals into the Merapi magmatic system has been shown previously
936 (Chadwick *et al.* 2007; Deegan *et al.*, 2010; Borisova *et al.*, 2016; Deegan *et al.*, 2016b). Chadwick *et al.*
937 (2007) suggested that 6 to 12 % of crystalline material at Merapi may be crustal derived based on elevated
938 $^{87}Sr/^{86}Sr$ plagioclase compositions and distinct major element plagioclase chemistry. Similarly,
939 thermodynamic-geochemical models for the 2010 Merapi eruption are consistent with the incorporation
940 of 18% of crustal calc-silicate material (Borisova *et al.*, 2016). Based on a detailed oxygen isotope study,
941 Borisova *et al.* (2016) were even able to distinguish two stages of magma-crust interaction, resulting in
942 distinct xenocryst plagioclase $\delta^{18}O$ values related to either high-T altered crustal rocks depleted in ^{18}O or
943 ^{18}O-enriched assimilated carbonate material. . Our data show that both plagioclase and clinopyroxene

944 compositions are produced during magma carbonate interaction in zones R1 and R2 that completely
945 overlap magmatic compositions in respect to major elements (Figs. 6, 7). These minerals are formed as a
946 result of Ca transfer from carbonate to the melt, such as occurs within endoskarns. Increased stability of
947 clinopyroxene and plagioclase in carbonate contaminated melts has been experimentally confirmed across
948 a range of magmatic compositions (e.g. Iacono-Marziano *et al.*, 2007; Mollo *et al.*, 2010; Carter and
949 Dasgupta, 2016), and with rhyoliteMELTS (version 1.2; Gualda *et al.*, 2012; Ghiorso, 2016) which
950 successfully reproduced Ca-contaminated xenolith glass and basaltic andesite compositions. Mineral
951 compositions that are distinct from those found in the magma occur from zone R3 to the xenolith core,
952 but to our knowledge, no highly CaTs-enriched, skarn derived clinopyroxenes have yet been detected in
953 the magmatic products. Although Al-rich clinopyroxenes (up to 8 wt%) are discussed in Costa *et al.*
954 (2013), and were attributed to higher pressure magmatic crystallisation, we have found none in our
955 literature data synthesis that compositionally match our specific skarn clinopyroxenes. Clinopyroxene
956 compositions matching zones R3 and R4, which lie on the DiHd join and are volumetrically more
957 abundant, are also exceedingly rare in the lavas, with only 3 out of 431 analyses reported in Preece (2014)
958 overlapping these compositions. A lack of these compositions may be due to a combination of a
959 volumetrically smaller amount of 'exotic' compositions in the xenolith cores compared to magmatic-type
960 compositions in the xenolith endoskarn rims. Alternatively, dissolution into the magma, and/or re-
961 equilibration with the magma might also be an option. Indeed, Carter and Dasgupta (2016) showed that in
962 carbonate assimilation experiments, within 48 hours, initially compositionally variable clinopyroxenes
963 had equilibrated to a diopsidic composition. Some crystals that are a result of magma-carbonate
964 interaction may therefore be 'cryptic' and distinguishable from magmatic crystals only on the basis of
965 their isotope or trace element chemistry (e.g. Chadwick *et al.*, 2007; Borisova *et al.*, 2016). Another
966 consequence of this finding is that clinopyroxene thermobarometry may include carbonate-interaction
967 pressures and temperatures in their output. Although *in situ* oxygen isotope evidence for magma-
968 carbonate interaction in Merapi clinopyroxene shows limited crustal additions to the bulk of the crystals
969 (Deegan *et al.*, 2016b), a small number of the clinopyroxenes analysed by Deegan *et al.* (2016b) have
970 anomalously high oxygen isotope ratios ($\delta^{18}O$ values of up to c. 7 ‰), which may be a result of magma-
971 carbonate interaction. Furthermore, studies utilising *in situ* isotope analysis of other mineral phases such
972 as plagioclase for Sr (Chadwick *et al.*, 2007) and oxygen (Borisova *et al.*, 2016) have demonstrated the
973 presence of xenocrysts and contaminated mineral zones, consistent with the usually shallow
974 crystallisation of intermediate plagioclase (e.g. Chadwick *et al.*, 2013). Whilst our plagioclase data for the
975 glass-rich zone R4 have high-FeO that overlaps some literature values for plagioclase in lavas, and
976 therefore may suggest that high-FeO plagioclase in lavas might be xenocrystic, this is more likely to be a
977 result of disequilibria due to quenching of the xenolith glass. For example, FeO in plagioclase increases
978 with cooling rate, producing plagioclase with up to 2.33 wt% FeO in 15°C/min experiments (Mollo *et al.*,
979 2011). The zone R4 plagioclase crystals contain up to 1.7 wt% FeO, and similarly wollastonite crystals in

980   zone R4 have thin Fe-rich ferro-bustamite overgrowths, indicating that cooling rate may have the more

981   pronounced impact on Fe-rich mineral rims in the xenoliths.

Magma Composition

983   Much of the experimental work on magma-carbonate interaction focuses on reproducing the highly

984   potassic, silica-undersaturated compositions erupted at volcanoes such as Vesuvius and Colli Albani

985   (e.g. Iacono-Marziano *et al.*, 2007; Mollo *et al.*, 2010; Jolis *et al.*, 2013). Strong silica-undersaturation

986   from carbonate assimilation in Italian volcanoes is a result of the increased stability of clinopyroxene

987   taking up SiO_2, coupled with the redissolution of olivine, which drives melts towards silica

988   undersaturation (e.g. Mollo *et al.*, 2010). Recent Merapi lava whole rock compositions range from ~50 to

989   68 wt% SiO_2, and the interstitial glasses within these record pre-eruptive melts with 60-75 wt% SiO_2 (Fig.

990   9). These would not be driven to silica-undersaturation by an increase in clinopyroxene or plagioclase

991   precipitation due to these minerals containing lower SiO_2 concentrations. Whole-rock compositions

992   instead traverse a differentiation vector defined by that of the typical arc magma plagioclase and

993   clinopyroxene differentiation assemblage (Fig. 9; *c.f.* Handley *et al.*, 2014), although at a slightly elevated

994   CaO. It is interesting to note however, that while the overall major element chemistry at Merapi is not

995   dominated by a carbonate assimilation signature, very rare, highly localised phonolitic leucite-bearing

996   silica-undersaturated melts have been identified in some Merapi calc-silicate xenoliths by Brouwer (1928,

997   1945). These demonstrate that these exotic compositions can be formed at Merapi during very localised

998   periods of extremely high levels of carbonate interaction, but the quantities of melt generated are

999   volumetrically negligible.

1000   In addition to the effects of crystal fractionation on the major element chemistry, lower temperature, high-

1001 SiO_2 melts such as those represented by the groundmass lava glass compositions at Merapi have a lower

1002   capacity to assimilate material than hotter mafic melts (e.g. Wenzel *et al.*, 2002; Barnes *et al.*, 2005;

1003   Gaeta *et al.*, 2009; Jolis *et al.*, 2015), and instead favour formation of skarn minerals (e.g. wollastonite)

1004   that cause only small apparent changes to melt compositions (Spandler *et al.*, 2012; Carter and Dasgupta,

1005   2016). These minerals may become trapped as a cumulate or exoskarn layer (see above, e.g. Gaeta *et al.*,

1006   2009; Di Rocco *et al.*, 2012) at the wall rock contact, and only have a small impact on the melt

1007   composition during skarn recycling and xenocryst incorporation (e.g. Di Rocco *et al.*, 2012; Jolis *et al.*,

1008   2015). A discrepancy between limited whole-rock major element evidence for magma-carbonate

1009   interaction (*c.f.* Costa *et al.*, 2013; Handley *et al.*, 2014) and high levels of interaction recorded in

1010   multiple isotope systems (Chadwick *et al.*, 2007; Troll *et al.*, 2013; Borisova *et al.*, 2013, 2016), may thus

1011   be due a combination of the lower capacity of the magmatic melt to incorporate carbonate material, and a

1012   relatively limited mobility of Ca in these relatively low temperature, high SiO_2 Merapi pre-eruptive melts

1013   compared to the higher mobilities usually displayed by isotopes of trace elements (e.g. Sr, B). This

1014   decoupling has been observed in high temperature (1200°C) carbonate interaction experiments (Deegan *et*

1015   *al.*, 2010, 2016a; Blythe *et al.*, 2015). Moreover, quantitative modelling of magma-carbonate interaction

1016   demonstrated that low-to-moderate amounts of carbonate assimilation cause only limited changes to the

1017   major element chemistry of the magma (Spandler *et al.*, 2012). Whereas there is no doubt that magma-

1018   carbonate interaction is an important petrogenetic process at Merapi, the degree of major element

1019   compositional change may not be prominent enough to distinguish the modified magma from the overall

1020   spectrum of Merapi magmas (*c.f.* Spandler *et al.*, 2012).

Merapi Volatile Budget

1022   Carbonate assimilation at Merapi has been shown to have a strong impact on the composition of the gases

1023   released to the atmosphere. Release of crustal derived CO_2 has been proposed by identification of

1024   elevated $\delta^{13}C$ and He isotopes in fumarole gases (Troll *et al.*, 2012, 2013 and references therein). An

1025   increase in these isotopic tracers has additionally been observed during eruptive periods, attributed to a

1026   positive feedback loop of wall rock fracturing during eruption, and increased CO_2 liberation from magma-

1027   carbonate interaction on this increased surface area (Deegan *et al.*, 2011; Troll *et al.*, 2012; Carr *et al.*,

1028   2018). Our work shows that the magmatic skarn xenoliths may represent snapshots of this syn-magmatic

1029   carbonate interaction, and therefore eruptive flare-ups could potentially be influenced by temporal

1030   increases in carbonate interaction (*c.f.* Troll *et al.*, 2012; Carr *et al.*, 2018). The 2010 eruption was

1031   preceded by an influx of hotter volatile-rich magma that exceeded the capacity of the shallow storage

1032   system (Costa *et al.*, 2013; Preece *et al.*, 2016; Carr *et al.*, 2020). This increased heat and volume would

1033   have caused both increased thermal decarbonation and fracturing, which could penetrate deeper into the

1034   bedrock. A positive feedback would then occur, where increased decarbonation promotes a decrease in

1035   water solubility, producing bubbles and more explosive behaviour, promoting more fracturing, resulting

1036   in temporal increases in carbonate interaction (Deegan *et al.,* 2011; Troll *et al.*, 2012; Carr *et al.*, 2018;

1037   2020). Dome instability from weakened fractured/altered wall-rock could also contribute to magmatic

1038   overpressure through increasing fracturing, and a resulting larger surface area of the carbonate available

1039   to react (Mollo *et al.,* 2012). In the magmatic skarn xenoliths, residual calcite is only present in trace

1040   quantities, and the $\delta^{13}C$ composition of these calcites are exceptionally negative (down to -29 ‰),

1041   demonstrating extremely efficient decarbonation in the magmatic skarn xenoliths (Whitley *et al.*, 2019). It

1042   is unlikely that this is exclusive to Merapi, and indeed, temporal increases in carbonate assimilation

1043   increasing explosivity has been proposed elsewhere e.g. at Colli Albani (Freda *et al.*, 2011) and Vesuvius

1044   (Jolis *et al.*, 2015). CO_2 release is not restricted to just syn-magmatic carbonate interaction, and

1045   decarbonation reactions in the exoskarn additionally add to the CO_2 budget. The current CO_2 output at

1046   Merapi compared to estimated contact metamorphic aureole volumes around a Merapi reservoir

1047   demonstrate that this CO_2 release is rapid, on the timescales of just thousands of years (Whitley *et al.*,

1048   2019). When considering volcanoes that interacted with crustal carbonate, at present and in the geological

1049 past (*c.f.* Mason *et al.*, 2017; Carter and Dasgupta, 2018), CO_2 release such as evidenced at Merapi may

1050 have the potential to modify long term climatic trends.

CONCLUSIONS

A detailed mineralogical, petrological and geochemical study of a range of calc-silicate (skarn-type) xenoliths from Merapi volcano shows that two distinct types of xenoliths are present; magmatic skarn xenoliths that record syn-magmatic magma-carbonate interaction that preserves abundant CaO-rich glass, and fragments of the metasomatic exoskarn aureole around the Merapi magma reservoir, respectively. Thermobarometry indicates that the CaO-rich glass-bearing magmatic skarn xenoliths formed at ~850°C. Fluid inclusions record shallow pressures of < 100 MPa, corresponding to depths < 3.7 km. These xenoliths are the physical representation of carbonate entrained during eruptive events, which we interpret to increase eruption intensity during rapid decarbonation. The disaggregated nature of some of these xenoliths, and the similarity in the geochemistry of lava and some xenolith minerals, indicate that skarn-derived xenocrysts may be difficult to recognise at Merapi. Experimental comparisons and thermodynamic modelling indicate formation temperatures of 510 to 910°C for the range of mineralogies shown in the metasomatic exoskarn xenoliths. A newly developed oxybarometric model indicates a wide range of f_{O_2} conditions during xenolith formation. Magmatic skarn xenoliths are predominantly formed around the NNO buffer, similar to magmatic values, whilst the cores of these xenoliths can reach values above the HM buffer in the presence of an increased amount of newly released CO_2. Protracted periods of CO_2 flushing caused conditions predominantly above the NNO buffer during exoskarn formation, covering the full range between NNO and air. High f_{O_2} in both xenolith types promoted formation of andradite garnet and highly aluminous clinopyroxene compositions. A magmatic volatile phase present at Merapi reacts with the xenoliths to form rare Ca-Al-Si-F-Cl phases such as cuspidine, ellestadite and wadalite-like phases. Evidence of xenolith formation during eruptive timescales demonstrates that magma-carbonate interaction and subsequent CO_2 release could affect eruption intensity, as recently suggested for Merapi and similar carbonate-hosted volcanoes elsewhere. In addition, copper and occasionally Fe (and likely other associated elements of economic value such as Zn) are carried within this fluid and are found concentrated in the outer shells of some of the xenoliths, indicating potential for ongoing skarn-type mineralisation at depth beneath Merapi and similar volcanoes within carbonate basement worldwide.

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1506

1507 **FIGURES**

1508

1509 *Fig. 1: Zoning in sample MX1 (thin section) and idealised diagram for zoning patterns in the magmatic*

1510 *skarn xenoliths. Highlighted zones (a) and (d) correspond to the respective panels in Fig. 2. See Table 1*

1511 *for all mineral abbreviations used. Gls: interstitial Ca-rich glass.*

1512

1513 *Fig. 2: Examples of the respective zones in magmatic skarn xenoliths. A) Host lava contact and zones R1*

1514 *to R4. Note the progressive darkening of the clinopyroxene colour due to changing composition to iron*

1515 *enrichment. Sample MX1. B) Normally zoned diopside-hedenbergite clinopyroxene within glass dominant*

1516 *zone R4. Also present are plagioclase microlites and wollastonite. Sample CS2. C) Wollastonite-dominant*

1517 *xenolith core with vesicles and accessory calcite. Sample MX5. D) Zone R3b, showing garnet + CaTs*

1518 *clinopyroxene formation where there is no glass zone R4 between the core and zone R2. Sample MX1. See*

1519 *Table 1 for mineral abbreviations. Gls: interstitial Ca-rich glass.*

1520

1521 *Fig. 3: Magmatic skarn accessory minerals and melt inclusions. All images are from sample MX1, apart*

1522 *from panels E and G, which are from sample CS16. A-B) Accessory gehlenite, fluorite, calcite and the*

1523 *wadalite-like mineral in the xenolith core. C-G) Examples of wollastonite, clinopyroxene and*

1524 *plagioclase-hosted melt inclusions, showing variable abundance and textural forms. Mineral*

1525 *abbreviations as in Table 1. Gls: interstitial Ca-rich glass.*

1526

1527 *Fig. 4: Typical textures in exoskarn xenoliths. A) CaTs-cpx + Wo + An + Grs in exoskarn type A xenolith*

1528 *MX99-5s. B) Large residual calcite crystals in exoskarn type A xenolith CS11. Expanded image shows the*

1529 *complex decarbonation textures and reactions occurring influenced by a F-rich fluid. A Ca-Si-O phase is*

1530 *present with low analytical totals (~65 wt%). C) Exoskarn B xenolith MX99-3s shows a unique*

1531 *assemblage of spinel, gehlenite, CaTs-cpx, grossular, with accessory wollastonite and anorthite. Spinel is*

1532 *rimmed by gehlenite followed by CaTs-cpx. For mineral abbreviations, see Table 1.*

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Fig. 5: Xenolith whole-rock geochemistry (calculated from mineral modes and mineral chemistry, corrected for mineral densities using data from Deer et al. (1997) and the Rock-Maker spreadsheet (Büttner, 2012)). A) Profiles through the distinct zones of two magmatic xenoliths. B) Calculated whole-rock compositions of bulk xenoliths compared to published lava and xenolith data. Published volcanic whole-rock data are from Nadeau et al. (2013b), Borisova et al. (2013), Costa et al. (2013), Innocenti et al. (2013) and the GEOROC database (http://georoc.mpch-mainz.gwdg.de/georoc/, accessed 03/2019). Published Merapi calc-silicate xenoliths from Chadwick et al. (2007).

Fig. 6: Merapi xenolith and magmatic feldspar compositions. A) Anorthite content histograms showing (left) published data from Merapi lavas (grey), enclaves (dark blue) and plutonic xenoliths (green) for comparison with xenolith and host lava feldspar data (right, key below). B) An vs FeO plot showing the different xenolith plagioclase compositions compared to Merapi lava plagioclase. Ellipse of xenolith and xenocryst plagioclase compositions from Chadwick et al. (2007). Notably, plagioclase from zones R1 and R2 overlaps with the lava compositions, although they are formed from magma-carbonate interaction. Published lava feldspar data from Gertisser (2001), Preece (2014) and Erdmann et al. (2016). Enclave and plutonic xenolith data from Chadwick et al. (2013).

Fig. 7: Clinopyroxene compositions. A) Fe^{3+}/Fe_{total} versus Al^{IV} plot showing a good correlation ($R^2=0.88$). The fassaitic boundary ($Al^{IV} \geq 0.25$) is from Deer et al. (1997). B) Ti versus Al^{IV} plot. Exoskarn clinopyroxene plot distinct from magmatic skarn clinopyroxenes. Zone 3b plots with the exoskarn data, showing a metamorphic character to this zone. C) Ternary Wo-En-Fs components for magmatic skarn clinopyroxene. Two partial ternary diagrams shown for clarity, with ternary location shown on inset figure. Clinopyroxenes in zones 1 to 3 progressively become more Wo-rich, diverging from magmatic compositions. The remaining zones follow the Di-Hd join or plot above due to the large amount of Al. D) Partial ternary Wo-En-Fs components for exoskarn clinopyroxenes. E) Al and Mg# traverse along a magmatic skarn clinopyroxene (sample CS16). Al and Mg-rich cores progressively grade to low Al-high Fe compositions. F) Al and Mg# traverse in magmatic skarn clinopyroxene from sample CS2. These crystals do not have an Al-rich core, and compositions instead follow the Di-Hd join. Published data sources as in Fig. 6 and additionally Deegan et al. (2016b).

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1565

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1567 *Melilite. Note the different ternary scales for each plot. Arrows indicate truncated scales. Mineral*
1568 *abbreviations as in Table 1.*

1569

1570 *Fig. 9: Interstitial and melt inclusion glass compositions. All values are normalised to 100 wt% volatile*
1571 *free. Published data for whole rock, glass and melt inclusions at Merapi are shown for comparison.*
1572 *Published data from Nadeau et al. (2013b), Borisova et al. (2013), Costa et al. (2013), Innocenti et al.*
1573 *(2013) and the GEOROC database (accessed 03/2019). Arrows show the effect of adding 10% calcite,*
1574 *and subtracting 10% clinopyroxene, wollastonite or plagioclase. Mineral abbreviations as in Table 1.*

1575

1576 *Fig. 10: A) Box plots of $KD_{Fe-Mg}^{cpx-melt}$ values from carbonate assimilation experiments. Black circles*
1577 *represent outliers calculated as 1.5 x interquartile range from the third quartile. Experiments with*
1578 *carbonate added have a general increase in $KD_{Fe-Mg}^{cpx-melt}$ values. Experiments by Carter and Dasgupta*
1579 *(2016) and Carter and Dasgupta (2018) use more evolved andesite and dacite compositions, compared to*
1580 *the remaining basaltic experiments, which were less affected by carbonate interaction. The extremely*
1581 *high values from Mollo and Vona (2014) are likely the result of very high experimental fO_2 conditions (up*
1582 *to air), which would strongly affect Fe^{2+}/Fe^{3+} partitioning between clinopyroxene and melt. B)*
1583 *Comparison between measured clinopyroxene Diopside-Hedenbergite (DiHd) components and predicted*
1584 *ones, using the iterative approach of Neave and Putirka (2017). Light grey data are calculated from*
1585 *clinopyroxenes in the Library of Experimental Phase Relations (LEPR, Hirschmann et al., 2008)*
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1587

1588 *Fig. 11: Stacked histogram results of thermometry estimates for the magmatic skarn xenoliths and host*
1589 *lava glasses using equation 34 of Putirka (2008). Xenolith glasses produce temperatures of 829 $\pm$ 45°C*
1590 *(n=89). Melt inclusions have a slightly higher temperature of 876 $\pm$ 49°C (n=89). These temperatures*
1591 *are slightly below the thermometry estimates for published lava glass analyses, at 937 $\pm$ 43°C. Published*
1592 *glass data are from Preece et al. (2014) and Erdmann et al. (2016).*

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1596 *Fig. 12: Theriak-Domino (de Capitani and Petrakakis, 2010) T-XCO$_2$ modelling of exoskarn xenoliths.*

1597 *Isobaric sections at 100 MPa. Green contours show the gehlenite mole fraction. Red contours show the*

1598 *CaTs mole fractions. The exoskarn A xenolith (MX99-5s) formed in a narrow temperature range between*

1599 *~900 to 910°C, and XCO$_2$ < 0.5. The exoskarn B xenolith (MX99-3s) mineral assemblage records*

1600 *temperatures between 680 and 860°C at a XCO$_2$ < ~0.5. Abbreviations as in Table 1. Additional*

1601 *abbreviations: Grt - garnet (andradite-grossular), Me - meionite, Ol – olivine.*

1602

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1604 *calibration of the new oxybarometer are highlighted (Feig et al., 2006, 2010; Berndt et al., 2005;*

1605 *Whitaker et al., 2007; Mollo and Vona, 2014). Sugawara (2001)'s experiments which cover 13 log units,*

1606 *and the results of applying the oxybarometers to the filtered Library of Experimental Phase Relations*

1607 *(LEPR Hirschmann et al., 2008) are also shown. A) Results of the Cortés et al. (2006) oxybarometer*

1608 *applied to the experimental clinopyroxenes. B) Results of the Simakin et al. (2012) oxybarometer applied*

1609 *to the experimental clinopyroxenes. C) Results of the model calibrated in this study applied to the*

1610 *experimental clinopyroxenes. The model error is shown in the top left.*

1611

1612 *Fig. 14: fO$_2$ estimates from clinopyroxenes across all zones and traverses. A) Violin density plots of*

1613 *oxygen fugacity estimates for xenolith clinopyroxenes. The model error has been applied as the*

1614 *smoothing bandwidth. The light grey field shows published estimates of Merapi magma fO$_2$ from other*

1615 *independent methods (ΔNNO -0.2 to 1.6. Gertisser, 2001; Erdmann et al., 2014). Application of our*

1616 *model to the literature clinopyroxene dataset detailed in Fig. 7 is shown for comparison to past literature*

1617 *estimates. The solid dashed line is the magnetite-hematite oxygen fugacity buffer. The results show*

1618 *xenolith rims (zones R1-3) formed in fO$_2$ similar to magmatic conditions, whilst the cores and exoskarn*

1619 *xenoliths formed at much higher fO$_2$, up to that of air. B) Results of application of the oxybarometer to*

1620 *the core to rim traverse of the same clinopyroxene from sample CS16 as shown in Fig. 7E. The results*

1621 *show an initial period of high fO$_2$ during initial clinopyroxene formation and vigorous carbonate-magma*

1622 *interaction, then a progressive decline as the carbonate-contaminated melt precipitates mineral phases*

1623 *and CO$_2$ migrates from the reaction zone.*

1624

Fig. 15: Summary of the processes occurring during magma carbonate interaction at Merapi. Carbonate

1626 is rapidly digested forming a Ca-rich contaminated melt, from which wollastonite and other phases

1627 precipitate, forming the magmatic skarn xenoliths. Proximal to the magmatic melt, clinopyroxene and

1628 plagioclase form from Ca transfer to the melt from the carbonate. The abundance of melt in the xenoliths

1629 allows disaggregation and disperses xenolith crystals into the magma (e.g. Deegan et al., 2010). The

1630 magmatic volatile phase (MVP c.f. Nadeau et al., 2010; Preece et al., 2014) infiltrates the xenoliths

1631 forming rare halogen and sulphur-bearing minerals. At the wall-rock contact, abundant clinopyroxene

1632 forms, partially insulating the carbonate and skarn. Magma-derived elements are transferred to the wall-

1633 rock, influenced by the increasing oxygen fugacity caused by CO_2 flushing, forming the exoskarn

1634 mineralogy. Regions of main magma crystallisation from Chadwick et al. (2013), Preece et al. (2014) and

1635 Erdmann et al. (2016). Moho depth from Wölbern and Rümpker (2016). Description of the lower crust

1636 from van Bemmelen (1949).

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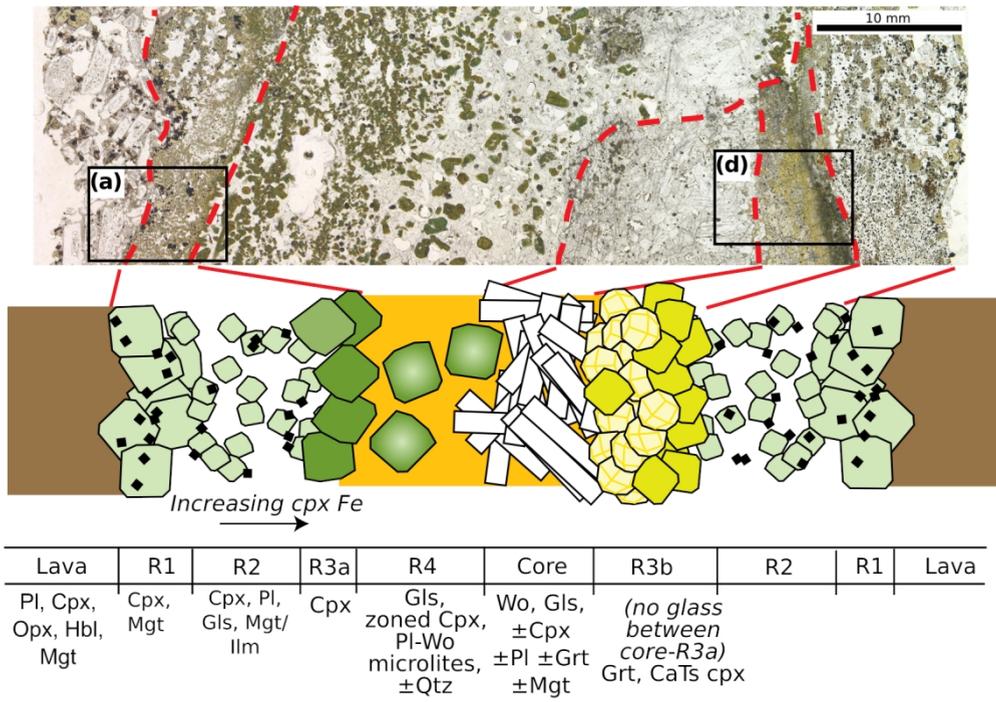
Lava	R1	R2	R3a	R4	Core	R3b	R2	R1	Lava
Pl, Cpx, Opx, Hbl, Mgt	Cpx, Mgt	Cpx, Pl, Gls, Mgt/ Ilm	Cpx	Gls, zoned Cpx, Pl-Wo microlites, ±Qtz	Wo, Gls, ±Cpx ±Pl ±Grt ±Mgt	*(no glass between core-R3a)* Grt, CaTs cpx			

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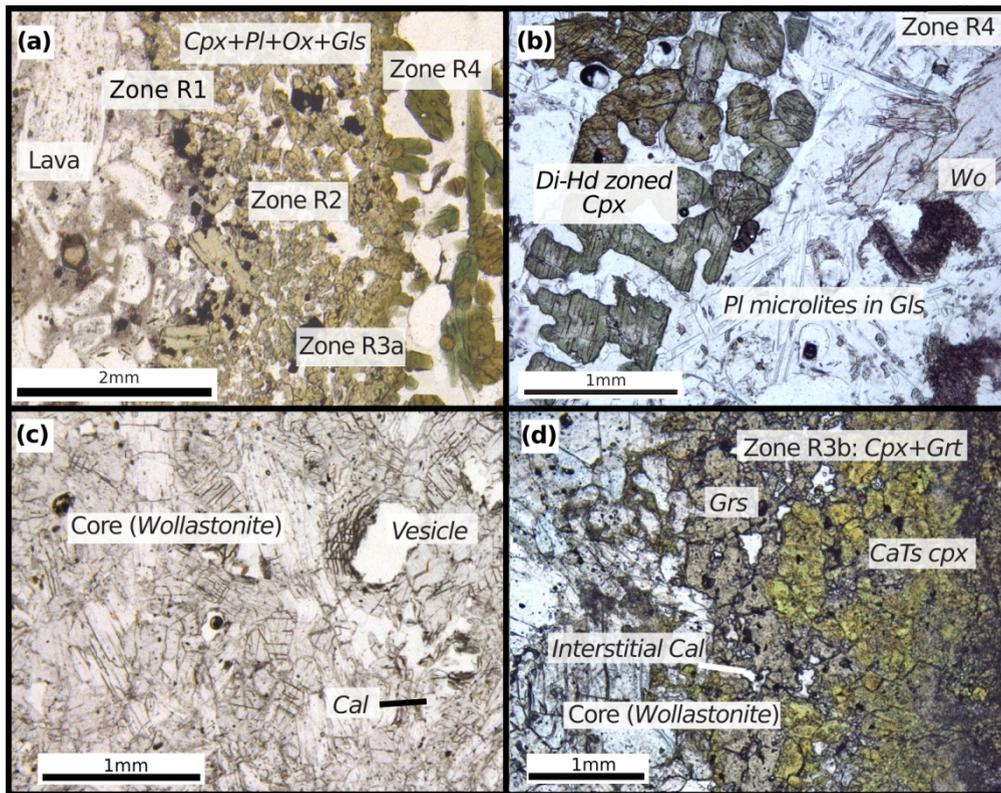
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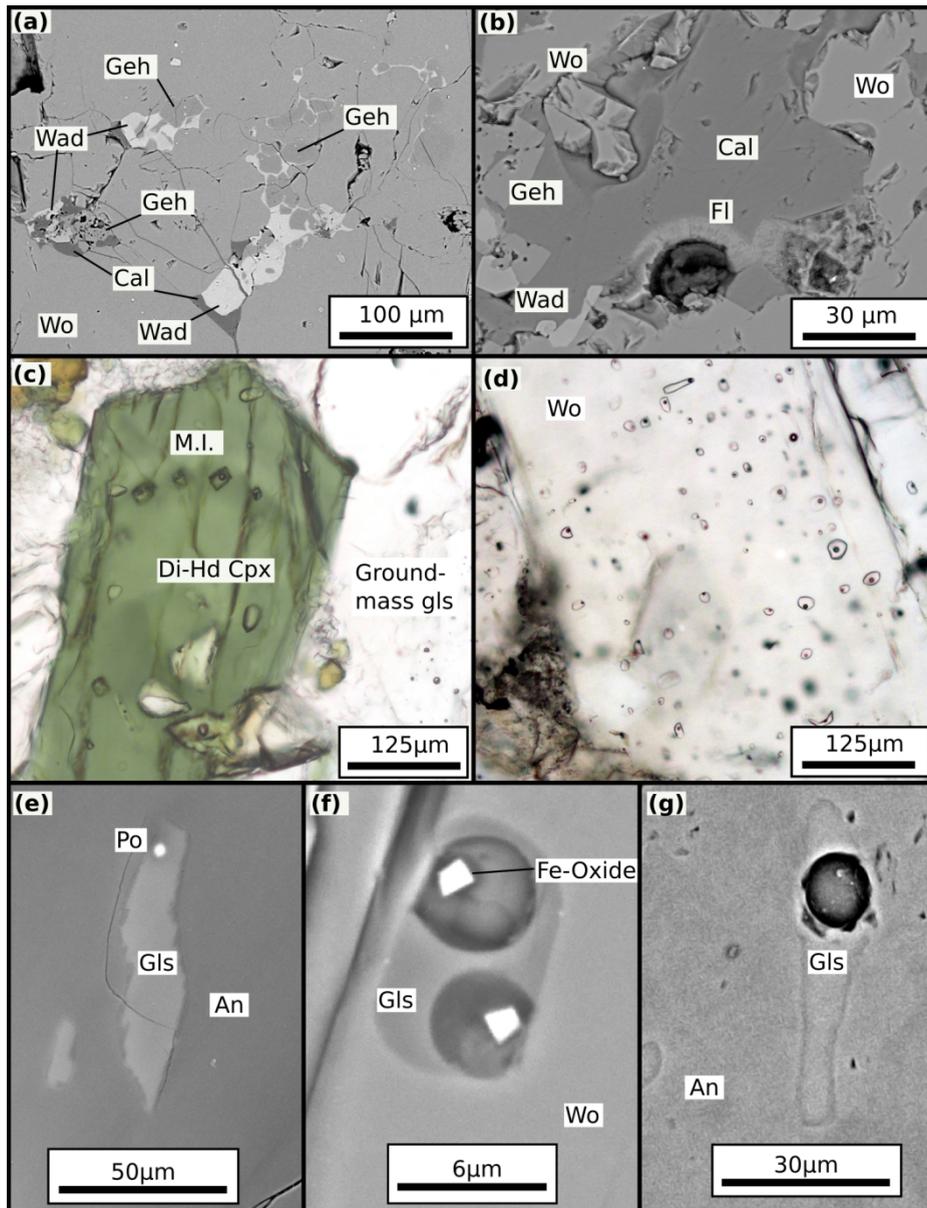
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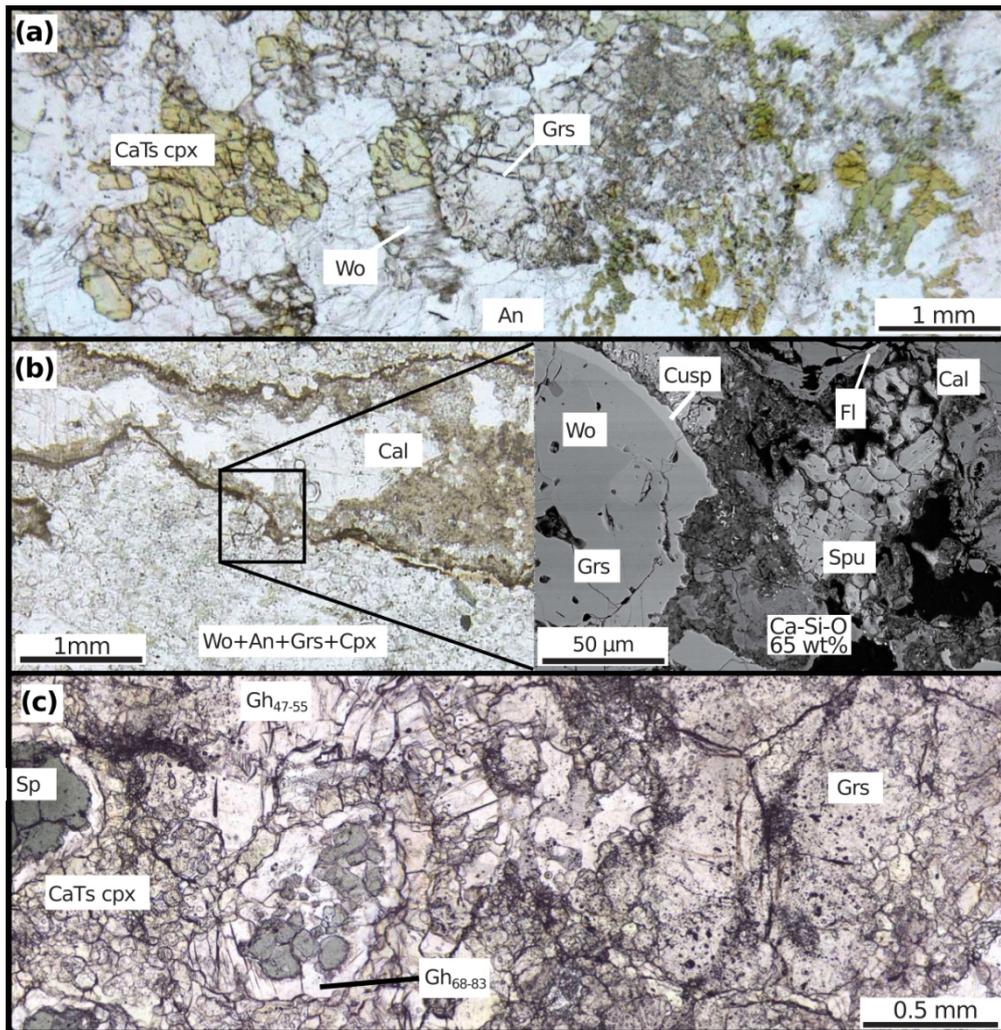
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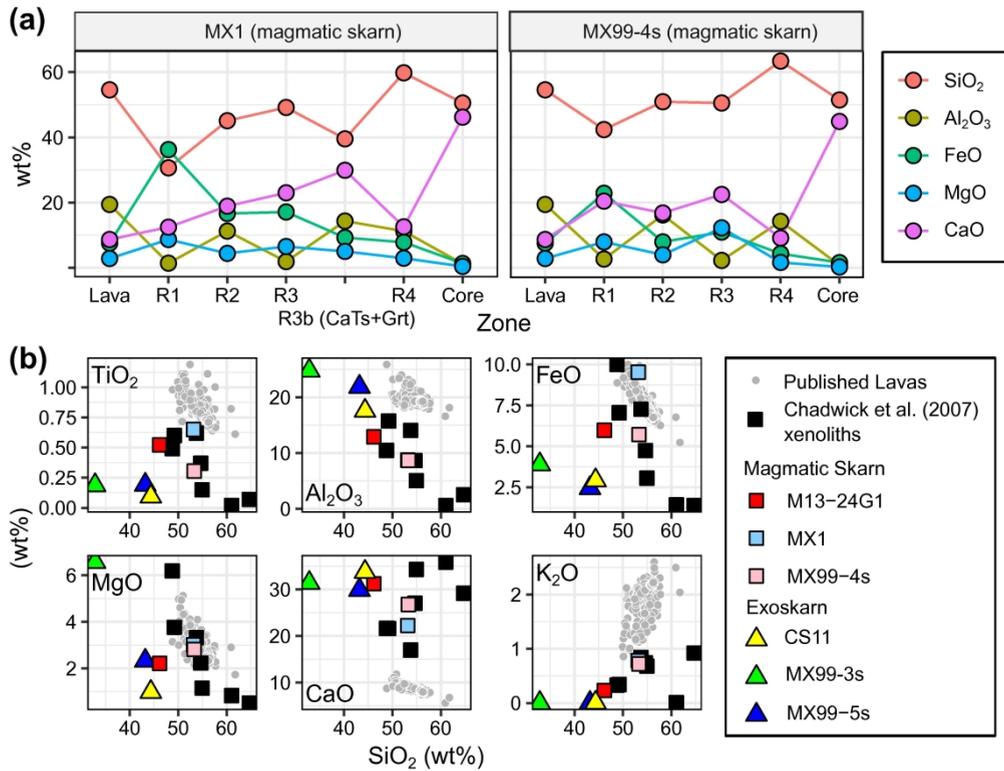
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139x139mm (600 x 600 DPI)

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199x292mm (600 x 600 DPI)

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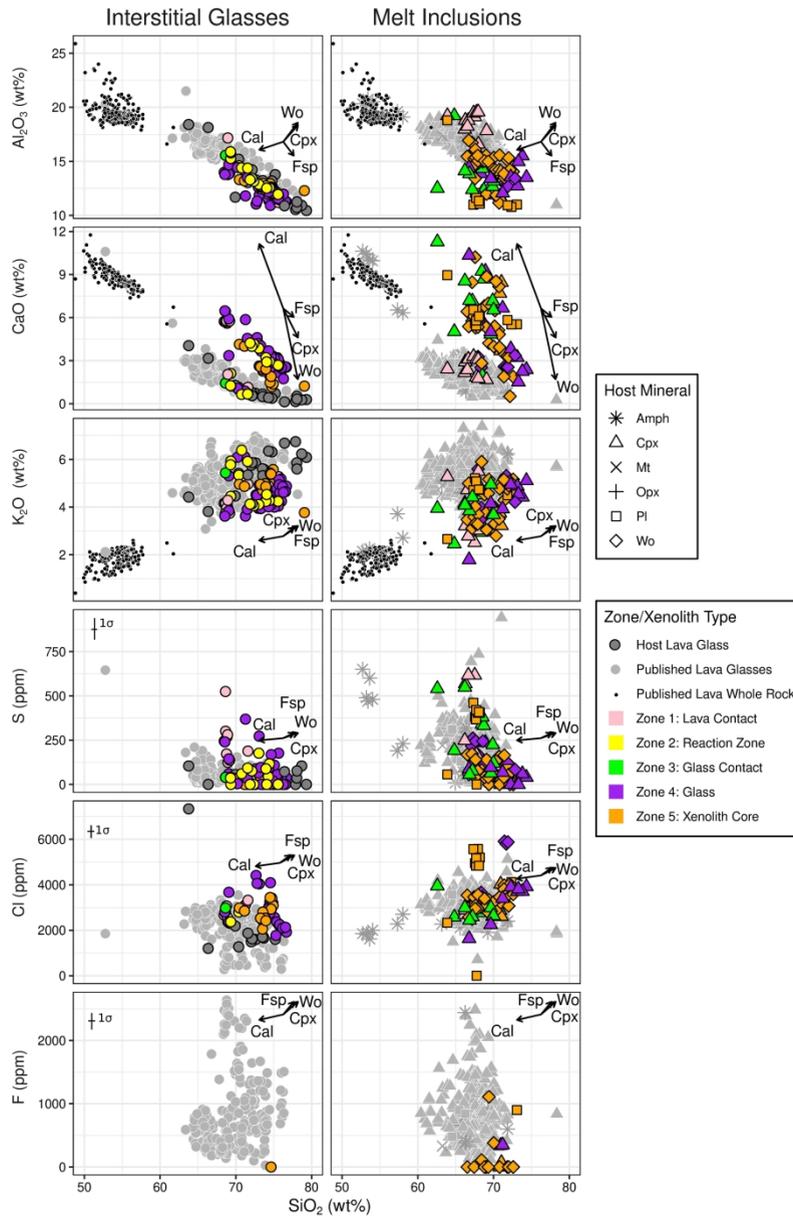
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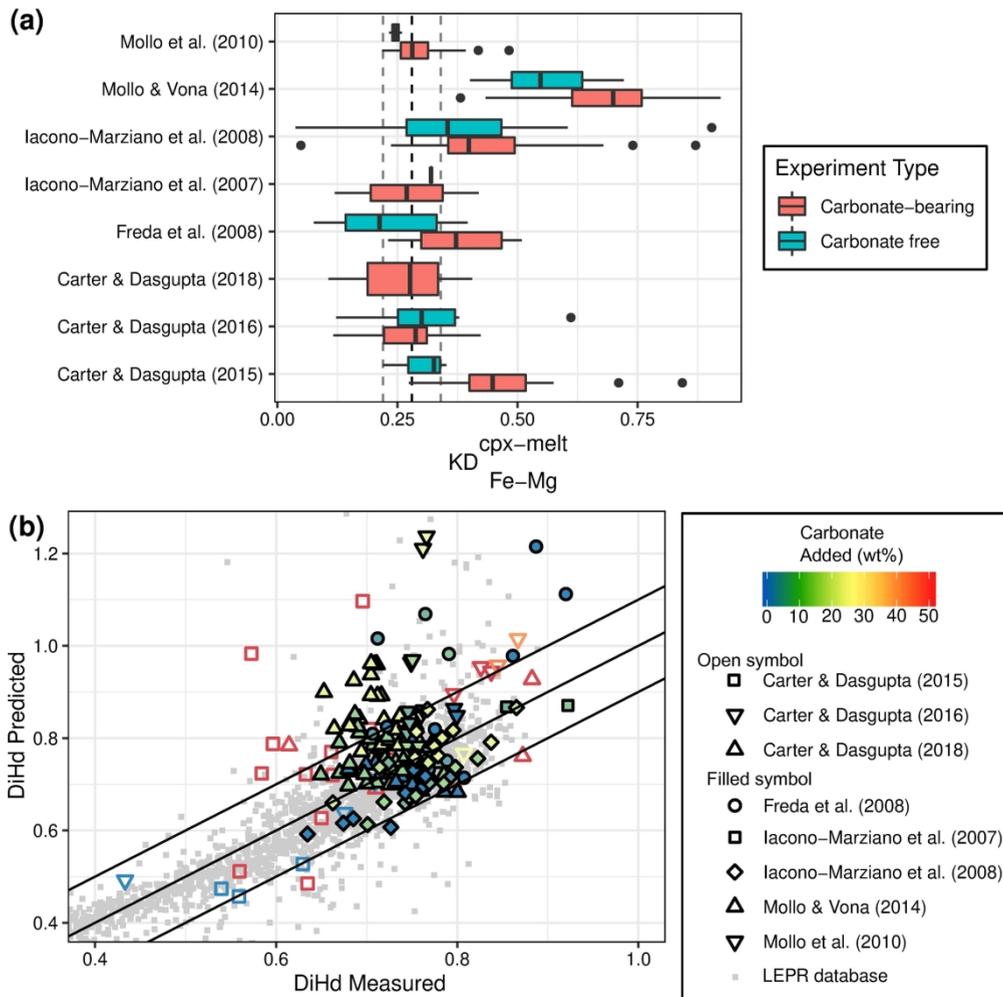
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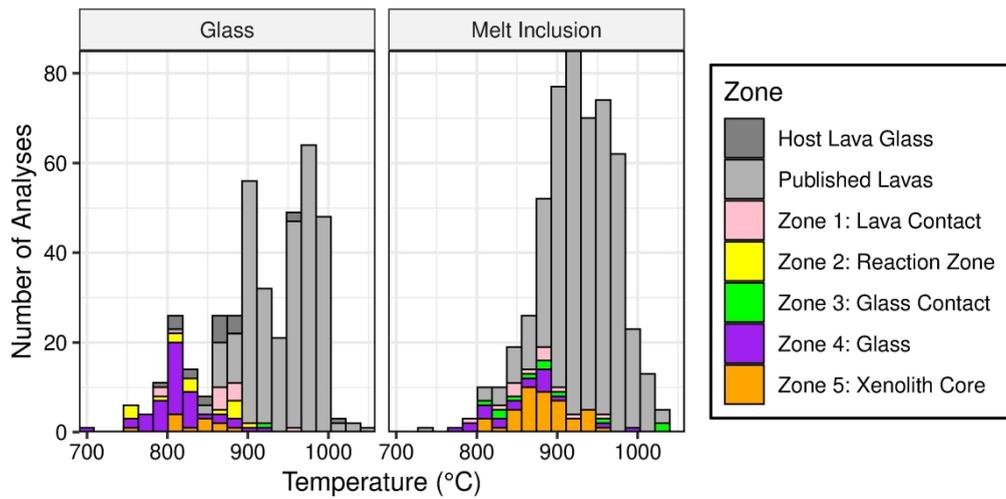
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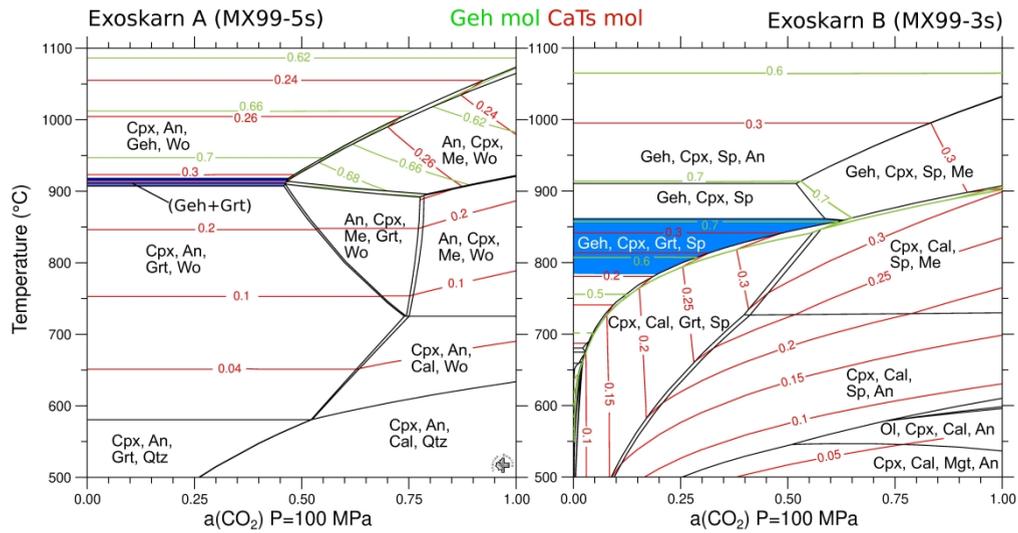
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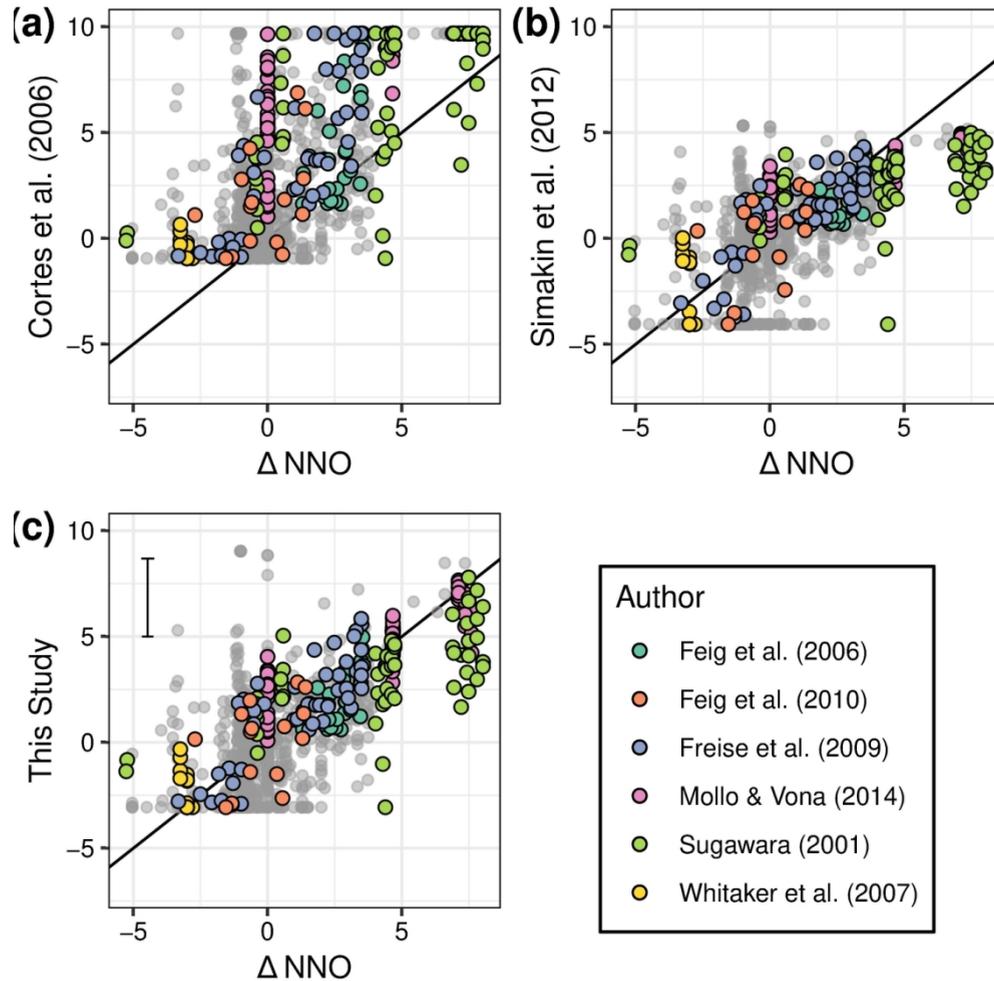
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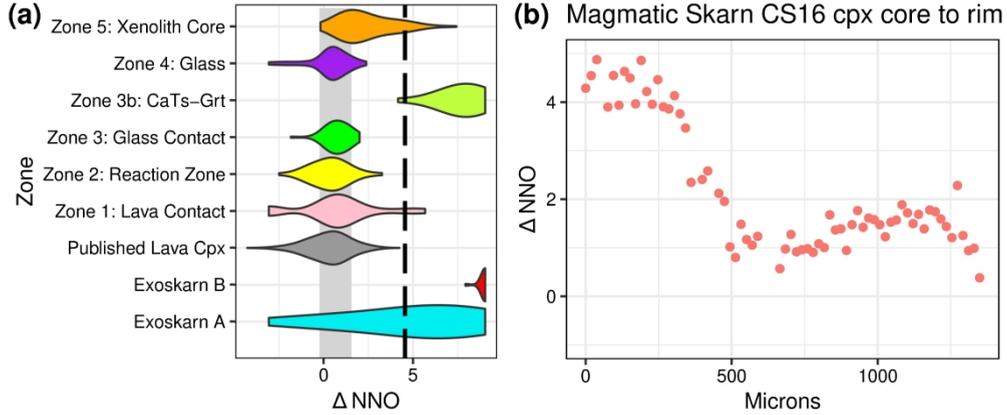
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177x76mm (600 x 600 DPI)
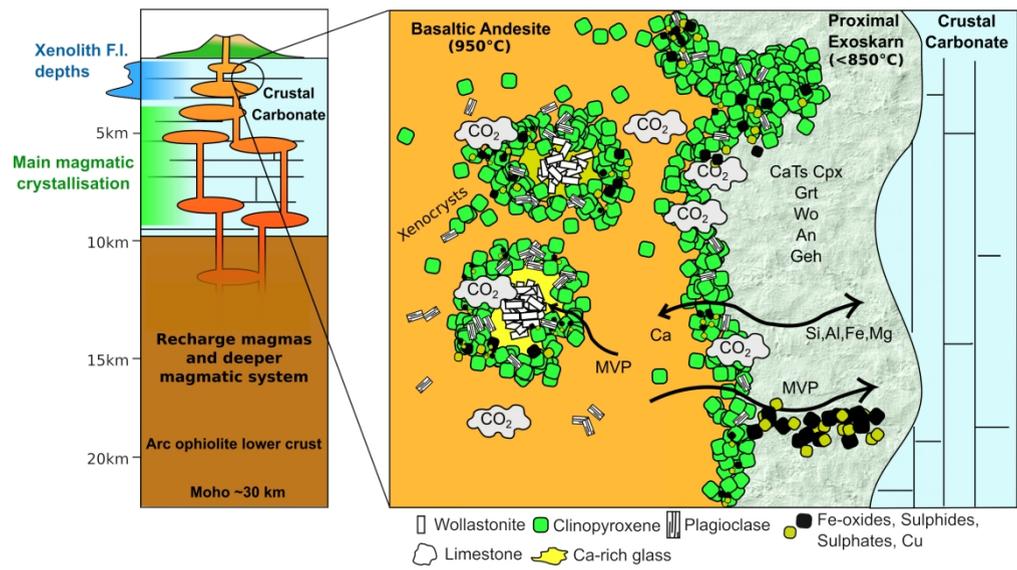
Fig. 15: Summary of the processes occurring during magma carbonate interaction at Merapi. Carbonate is rapidly digested forming a Ca-rich contaminated melt, from which wollastonite and other phases precipitate, forming the magmatic skarn xenoliths. Proximal to the magmatic melt, clinopyroxene and plagioclase form from Ca transfer to the melt from the carbonate. The abundance of melt in the xenoliths allows disaggregation and disperses xenolith crystals into the magma (e.g. Deegan et al., 2010). The magmatic volatile phase (MVP c.f. Nadeau et al., 2010; Preece et al., 2014) infiltrates the xenoliths forming rare halogen and sulphur-bearing minerals. At the wall-rock contact, abundant clinopyroxene forms, partially insulating the carbonate and skarn. Magma-derived elements are transferred to the wall-rock, influenced by the increasing oxygen fugacity caused by CO2 flushing, forming the exoskarn mineralogy. Regions of main magma crystallisation from Chadwick et al. (2013), Preece et al. (2014) and Erdmann et al. (2016). Moho from Wölbern and Rümpker (2016). Description of the lower crust from van Bemmelen (1949).

Line numbers: 1, 2, 3

Table 1: Mineral phases identified within the Merapi calc-silicate xenoliths in this study, and abbreviations used throughout the text. The minerals are grouped alphabetically within three general groupings.

Mineral	Abbreviation	Formula	Mag	Exo A	Exo B
Rock-forming and their endmembers					
Clinopyroxene	Cpx	$Ca(Fe,Mg)Si_2O_6$	M		
–Calcium Tschermak's Pyroxene	CaTs	$CaAlAlSiO_6$	m	M	M
–Esseneite (Clinopyroxene)	Ess	$CaFe^{3+}AlSiO_6$	m	M	M
Garnet	Grt	$Ca_3(Fe^{3+},Al,Ti)_2Si_3O_{12}$	m	M	M
–Andradite	Adr	$Ca_3Fe^{3+}_2Si_3O_{12}$	m	M	m
–Grossular	Grs	$Ca_3Al_2Si_3O_{12}$	m	M	M
–Schorlomite	Sch	$Ca_3Ti_2Si_3O_{12}$	m		
Melilite					
–Åkermanite	Åk	$Ca_2MgSi_2O_7$	m	m	M
–Fe-Åkermanite	Fe-Åk	$Ca_2FeSi_2O_7$	m	m	M
–Gehlenite	Gh	$Ca_2Al_2SiO_7$	m	m	M
–Na-Melilite	Na-Mel	$CaNaAl_2SiO_7$			
Plagioclase	Pl	$(Ca,Na)(Al,Si)_4O_8$	M	M	m
–Anorthite	An	$CaAl_2Si_2O_8$	M	M	m
Wollastonite	Wo	$CaSiO_3$	M	M	m
–Ferrobustamite	Bst	$Ca(Fe^{2+},Ca,Mn^{2+})Si_2O_6$	m	m	
Sulphur and Halogen-bearing					
Anhydrite	Anh	$CaSO_4$	m	m	
Apatite	Ap	$Ca_5(PO_4)_3(OH,F,Cl)$	m		
Baryte	Ba	$BaSO_4$	m		
Cotunnite*	Cot	$PbCl_2$	m		
Cubanite	Cu	$CuFe_2S_3$	m		
Cuspidine	Cusp	$Ca_4Si_2O_7(F,OH)_2$	m	m	
Ellestadite	El	$Ca_5(SiO_4,PO_4,SO_4)_3(F,OH,Cl)$		m	m
Fluorite	Fl	CaF_2	m		
Larnite	Lrn	Ca_2SiO_4		m	
Pyrrhotite	Po	$Fe_{1-x}S$ (x=0-0.2)	m	m	
Spurrite	Spu	$Ca_5Si_2O_8CO_3$		m	
Wadalite†	Wad	$Ca_{12}Al_{10}Si_4O_{32}Cl_6$	m		
Oxides, Other Silicates, and Accessory Minerals					
Calcite	Cal	$CaCO_3$	m	M	
Ca-Zr-Ti oxide*	CaZrTi	Ca-Zr-Ti	m		
Cebollite†	Ce	$Ca_5Al_2(SiO_4)_3(OH)_4$		m	
Chromite*	Chr	$FeCr_2O_4$	m		
Hematite	Hm	Fe_2O_3		m	
Ilmenite	Ilm	$FeTiO_3$	m		
Magnetite	Mgt	$Fe^{2+}Fe^{3+}_2O_4$	M	m	
Quartz	Qtz	SiO_2	M	m	
Monazite*	Mo	$(Ce,La)PO_4$		m	
Perovskite	Psk	$CaTiO_3$	m		
Titanite	Ttn	$CaTiSiO_4$	m	m	
Spinel	Sp	$(Fe,Mg)Al_2O_4$			M
Xenotime*	Xe	YPO_4		m	

* Identified with SEM only   † Uncertain identification

Mag Magmatic skarn xenoliths, Exo A: Exoskarn type A xenoliths, Exo B: Exoskarn type B xenoliths

M: Major rock forming mineral, m: Minor to accessory (<1 vol%) mineral

4

1　*Table 2: Average plagioclase compositions for the zones in the magmatic skarn xenoliths, and in the*
2　*exoskarn xenoliths. All analyses normalised to 8 oxygens. Lava analyses are where the xenolith section*
3　*had a small rind of lava still attached. Analyses are reported as the mean with one standard deviation in*
4　*brackets. Plagioclase components: An = anorthite, Ab = albite, Or = orthoclase.*

Type	Magmatic Skarn								Exoskarn			
Zone	Host Lava		R2		R4		Core		Exoskarn A		Exoskarn B	
n	8		49		27		76		63		7	
SiO_2	53.61	(4.03)	48.91	(4.42)	52.91	(4.28)	45.21	(2.80)	44.43	(3.50)	42.51	(0.51)
Al_2O_3	28.10	(2.94)	31.73	(3.31)	28.68	(3.00)	33.98	(2.03)	34.90	(2.48)	36.55	(0.37)
FeO	0.72	(0.34)	0.58	(0.16)	0.94	(0.33)	0.65	(0.22)	0.33	(0.33)	0.24	(0.02)
MgO	0.06	(0.07)	0.02	(0.02)	0.02	(0.03)	0.01	(0.02)	0.02	(0.02)		
CaO	11.12	(3.28)	15.05	(3.72)	12.25	(2.99)	17.82	(2.18)	19.09	(2.63)	20.17	(0.26)
Na_2O	5.06	(1.70)	3.01	(2.12)	4.25	(1.65)	1.34	(1.23)	0.78	(1.45)	0.08	(0.03)
K_2O	0.68	(0.52)	0.23	(0.20)	0.53	(0.44)	0.10	(0.14)	0.07	(0.17)	0.02	(0.01)
Total	99.47	(0.64)	99.56	(0.87)	99.76	(1.20)	99.12	(1.09)	99.75	(1.01)	99.56	(1.06)
Cations based on 8 oxygens												
Si	2.449	(0.166)	2.252	(0.188)	2.416	(0.168)	2.108	(0.113)	2.063	(0.138)	1.983	(0.009)
Al	1.515	(0.168)	1.724	(0.191)	1.546	(0.178)	1.869	(0.118)	1.912	(0.146)	2.009	(0.009)
Fe	0.028	(0.013)	0.022	(0.006)	0.036	(0.013)	0.025	(0.009)	0.013	(0.013)	0.009	(0.001)
Mg	0.004	(0.005)	0.001	(0.001)	0.001	(0.002)	0.000	(0.001)	0.001	(0.001)	0.000	(0.000)
Ca	0.546	(0.165)	0.744	(0.189)	0.601	(0.154)	0.891	(0.114)	0.951	(0.135)	1.008	(0.006)
Na	0.448	(0.147)	0.267	(0.188)	0.375	(0.143)	0.120	(0.109)	0.069	(0.126)	0.007	(0.003)
K	0.039	(0.030)	0.013	(0.012)	0.030	(0.025)	0.006	(0.008)	0.004	(0.010)	0.001	(0.000)
∑Cations	5.032	(0.009)	5.025	(0.011)	5.011	(0.020)	5.020	(0.007)	5.017	(0.018)	5.017	(0.006)
An	52.9	(16.2)	72.8	(19.1)	59.8	(15.5)	87.6	(11.1)	92.9	(13.1)	99.2	(0.3)
Ab	43.3	(14.0)	25.9	(18.1)	37.2	(14.1)	11.8	(10.7)	6.7	(12.2)	0.7	(0.3)
Or	3.8	(2.9)	1.3	(1.1)	3.1	(2.7)	0.6	(0.8)	0.4	(0.9)	0.1	(0.0)

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1 *Table 3: Average clinopyroxene (cpx), wollastonite (wo), and ferrobustamite (bst) compositions for each zone in the magmatic skarn xenoliths, exoskarns,*
2 *and across all samples for wollastonite and ferrobustamite as there is very little compositional variability for the pyroxenoids. Fe^{3+} calculated using*
3 *Droop (1987). Analyses are reported as the mean with one standard deviation in brackets. Clinopyroxene components: Wo = wollastonite, En = enstatite,*
4 *Fs = ferrosilite. All Fe assumed as Fe^{2+} for ternary component calculation.*

Type	Magmatic Skarn							Exoskarn		All	All
Zone	Host Lava	R1	R2	R3	R3b	R4	Core	Exoskarn A	Exoskarn B		
Mineral	Cpx	Cpx	Cpx	Cpx	Cpx	Cpx	Cpx	Cpx	Cpx	Wo	Bst
n	7	19	43	44	18	71	112	40	18	94	16
SiO_2	51.13 (0.72)	50.11 (1.54)	50.37 (0.94)	49.89 (1.41)	40.89 (0.46)	49.83 (1.70)	46.26 (1.94)	43.24 (2.67)	40.52 (1.87)	50.70 (0.69)	49.81 (0.52)
TiO_2	0.5 (0.11)	0.49 (0.10)	0.45 (0.16)	0.42 (0.10)	0.57 (0.10)	0.37 (0.23)	0.67 (0.27)	0.53 (0.36)	0.36 (0.27)	0.04 (0.05)	0.06 (0.04)
Al_2O_3	2.63 (0.43)	2.71 (1.56)	2.09 (0.64)	2.37 (0.59)	14.64 (0.40)	2.08 (0.96)	5.76 (2.89)	13.93 (5.95)	18.19 (1.97)	0.07 (0.08)	0.02 (0.02)
Cr_2O_3	0 (0.01)	0.02 (0.02)	0.02 (0.02)	0.02 (0.02)	0.01 (0.01)	0.01 (0.02)	0.02 (0.02)	0.01 (0.01)	0.02 (0.02)	0.01 (0.01)	0.01 (0.01)
FeO	8.85 (0.12)	12.38 (5.99)	10.62 (1.85)	12.58 (2.84)	8.58 (0.47)	13.46 (4.14)	11.26 (3.03)	7.96 (6.72)	5.65 (1.15)	1.31 (0.80)	10.81 (0.97)
MnO	0.56 (0.11)	0.57 (0.19)	0.55 (0.11)	0.48 (0.10)	0.32 (0.02)	0.5 (0.16)	0.21 (0.10)	0.24 (0.32)	0.08 (0.03)	0.37 (0.16)	1.13 (0.19)
MgO	14.43 (0.43)	11.38 (4.68)	11.74 (1.77)	10.82 (2.83)	9.07 (0.52)	9.45 (2.73)	9.66 (1.41)	8.59 (2.25)	9.57 (1.12)	0.22 (0.08)	0.70 (0.22)
CaO	21.2 (0.66)	22.06 (1.27)	22.62 (0.68)	22.72 (1.12)	25.18 (0.17)	23.9 (0.77)	23.76 (0.70)	25.04 (0.84)	25.88 (0.47)	47.09 (0.92)	38.08 (1.48)
Na_2O	0.43 (0.04)	0.34 (0.12)	0.41 (0.08)	0.38 (0.07)	0.02 (0.02)	0.29 (0.14)	0.33 (0.15)	0.07 (0.07)	0.04 (0.02)	0.02 (0.02)	0.04 (0.03)
Total	99.75 (0.50)	100.08 (0.81)	98.87 (0.71)	99.67 (0.82)	99.28 (0.64)	99.93 (0.60)	97.92 (0.70)	99.62 (1.24)	100.31 (0.81)	99.93 (0.88)	100.8 (1.40)
Cations based on 6 oxygens, 4 cations											
Si	1.901 (0.021)	1.895 (0.059)	1.918 (0.028)	1.898 (0.024)	1.535 (0.013)	1.906 (0.040)	1.786 (0.086)	1.624 (0.136)	1.485 (0.065)	1.967 (0.025)	1.956 (0.038)
Ti	0.014 (0.003)	0.014 (0.003)	0.013 (0.005)	0.012 (0.003)	0.016 (0.003)	0.011 (0.006)	0.019 (0.008)	0.015 (0.011)	0.010 (0.008)	0.001 (0.001)	0.002 (0.001)
Al^{IV}	0.099 (0.021)	0.105 (0.059)	0.082 (0.028)	0.102 (0.024)	0.465 (0.013)	0.094 (0.040)	0.214 (0.086)	0.376 (0.136)	0.515 (0.065)	0.033 (0.025)	0.044 (0.038)
Al^{VI}	0.018 (0.013)	0.018 (0.021)	0.013 (0.009)	0.006 (0.008)	0.183 (0.013)	0.007 (0.018)	0.047 (0.047)	0.238 (0.117)	0.271 (0.036)	0.000 (0.000)	0.000 (0.000)
Cr	0.000 (0.000)	0.000 (0.001)	0.001 (0.001)	0.000 (0.001)	0.000 (0.000)	0.000 (0.001)	0.000 (0.001)	0.000 (0.000)	0.000 (0.001)	0.000 (0.000)	0.000 (0.000)
Fe^{2+}	0.190 (0.032)	0.309 (0.241)	0.264 (0.071)	0.300 (0.087)	0.019 (0.022)	0.339 (0.122)	0.212 (0.106)	0.138 (0.230)	0.000 (0.002)	0.010 (0.018)	0.269 (0.076)
Fe^{3+}	0.086 (0.033)	0.088 (0.060)	0.075 (0.031)	0.102 (0.024)	0.251 (0.014)	0.094 (0.041)	0.153 (0.038)	0.117 (0.051)	0.173 (0.037)	0.033 (0.023)	0.086 (0.075)
Mn	0.017 (0.004)	0.018 (0.007)	0.018 (0.004)	0.015 (0.003)	0.010 (0.001)	0.016 (0.005)	0.007 (0.003)	0.008 (0.011)	0.002 (0.001)	0.012 (0.005)	0.038 (0.006)
Mg	0.800 (0.021)	0.635 (0.255)	0.665 (0.092)	0.611 (0.148)	0.507 (0.027)	0.536 (0.143)	0.555 (0.072)	0.478 (0.118)	0.523 (0.058)	0.013 (0.005)	0.041 (0.013)
Ca	0.844 (0.028)	0.895 (0.064)	0.923 (0.037)	0.927 (0.060)	1.013 (0.006)	0.980 (0.022)	0.982 (0.014)	1.006 (0.016)	1.017 (0.008)	1.957 (0.033)	1.601 (0.043)
Na	0.031 (0.003)	0.024 (0.009)	0.030 (0.006)	0.028 (0.005)	0.002 (0.001)	0.022 (0.010)	0.025 (0.012)	0.005 (0.005)	0.003 (0.001)	0.002 (0.001)	0.003 (0.002)
#Mg	74.4 (0.6)	60.6 (22.7)	66.1 (7.3)	59.8 (11.3)	65.3 (2.5)	55.3 (14.2)	60.7 (9.9)	68.3 (21.5)	75 (5.8)	27.5 (14.1)	10.4 (3.0)
Wo	43.6 (1.2)	46 (3.3)	47.5 (1.9)	47.4 (3.0)	56.3 (0.6)	49.8 (0.8)	51.5 (1.7)	57.9 (3.9)	59.3 (1.3)	96.7 (1.5)	78.7 (1.5)
En	41.3 (1.1)	32.7 (13.1)	34.2 (4.7)	31.3 (7.6)	28.2 (1.4)	27.3 (7.1)	29.1 (4.1)	27.8 (7.8)	30.4 (2.9)	0.6 (0.2)	2.0 (0.6)
Fs	15.1 (0.3)	21.3 (10.8)	18.3 (3.2)	21.3 (4.8)	15.5 (0.9)	22.9 (7.1)	19.4 (5.3)	14.3 (11.4)	10.3 (2.3)	2.7 (1.4)	19.3 (1.5)

5

1 *Table 4: Average garnet compositions for the zones in the magmatic skarn xenoliths, and in the exoskarn*
2 *xenoliths. Abbreviations as in Table 1. Additional garnet abbreviations: Prp - pyrope, Alm - almandine,*
3 *Sp - spessartite, Uv - uvarovite. See Methods section for end-member calculation details. Fe^{3+} calculated*
4 *using Arai (2010). Analyses are reported as the mean with one standard deviation in brackets.*

Xenolith Type	Magmatic Skarn				Exoskarn			
Zone	R3b		Core		Exoskarn A		Exoskarn B	
n	10		65		47		10	
SiO_2	38.27	(0.23)	35.01	(2.93)	39.27	(0.55)	38.94	(0.30)
TiO_2	0.76	(0.24)	3.45	(3.73)	0.23	(0.20)	0.29	(0.19)
Al_2O_3	14.24	(0.50)	9.64	(3.16)	20.37	(1.68)	18.88	(1.02)
Cr_2O_3			0.02	(0.03)	0.01	(0.02)	0.01	(0.02)
FeO	10.14	(0.49)	15.25	(3.60)	3.26	(1.88)	4.66	(1.11)
MnO	0.47	(0.05)	0.26	(0.09)	0.72	(0.68)	0.15	(0.03)
MgO	0.57	(0.04)	0.49	(0.19)	0.42	(0.17)	0.74	(0.10)
CaO	35.13	(0.26)	33.75	(0.78)	35.86	(0.78)	36.68	(0.54)
Total	99.59	(0.29)	97.86	(0.98)	100.23	(0.92)	100.35	(0.65)
Cations based on 12 oxygens, 8 cations								
Si	2.972	(0.013)	2.831	(0.196)	2.966	(0.026)	2.944	(0.032)
Ti	0.044	(0.014)	0.214	(0.243)	0.013	(0.012)	0.016	(0.011)
Al	1.304	(0.043)	0.913	(0.281)	1.813	(0.139)	1.681	(0.077)
Cr	0.000	(0.000)	0.001	(0.002)	0.000	(0.001)	0.001	(0.001)
Fe^{2+}	0.007	(0.017)	0.042	(0.042)	0.013	(0.024)	0.000	(0.000)
Fe^{3+}	0.652	(0.038)	0.995	(0.247)	0.194	(0.120)	0.295	(0.073)
Mn	0.031	(0.003)	0.018	(0.007)	0.046	(0.043)	0.010	(0.002)
Mg	0.066	(0.004)	0.059	(0.023)	0.047	(0.019)	0.083	(0.011)
Ca	2.923	(0.023)	2.926	(0.039)	2.902	(0.064)	2.970	(0.024)
Grs	64.3	(1.6)	37.5	(17.2)	87.7	(6.6)	83.9	(4.0)
Adr	33.5	(1.9)	52.0	(14.4)	9.6	(6.4)	15.1	(3.7)
Sch	1.4	(0.6)	9.3	(12.7)	0.4	(0.4)	0.7	(0.4)
Alm	0.0	(0.2)	0.2	(0.5)	0.4	(0.7)	0.0	(0.0)
Prp	0.7	(0.8)	0.8	(0.9)	0.7	(0.8)	0.3	(0.6)
Sp	0.1	(0.4)	0.1	(0.3)	1.2	(1.7)	0.0	(0.0)
Uv	0.0	(0.0)	0.0	(0.1)	0.0	(0.0)	0.0	(0.0)

5

Table 5: Average melilite compositions for the magmatic skarn xenolith core, and in the exoskarn
xenoliths. All analyses are normalised to 7 oxygens. Abbreviations as in Table 1. See Methods section for
details about the calculation of mole fractions of end-member compositions. Analyses are reported as the
mean with one standard deviation in brackets.

Xenolith Type	Magmatic Skarn		Exoskarn			
Zone	Core		Exoskarn A		Exoskarn B	
n	4		7		26	
SiO$_2$	24.72	(0.43)	25.29	(1.80)	29.06	(3.01)
TiO$_2$	0.01	(0.02)	0.01	(0.02)	0.01	(0.02)
Al$_2$O$_3$	29.87	(0.47)	28.92	(2.03)	25.09	(4.37)
Cr$_2$O$_3$	0.02	(0.01)	0.02	(0.01)	0.01	(0.01)
FeO	2.66	(0.07)	1.87	(0.97)	0.93	(0.18)
MnO	0.10	(0.02)	0.35	(0.24)	0.05	(0.03)
MgO	0.69	(0.03)	1.22	(1.05)	3.74	(1.43)
CaO	39.56	(0.16)	40.60	(0.43)	40.56	(0.95)
Na$_2$O	0.54	(0.10)	0.13	(0.12)	0.52	(0.21)
Total	98.17	(0.88)	98.55	(0.93)	99.99	(1.09)

Cations based on 7 oxygens

Si	1.165	(0.013)	1.186	(0.074)	1.331	(0.136)
Ti	0.000	(0.001)	0.000	(0.001)	0.000	(0.001)
Al	1.659	(0.012)	1.600	(0.120)	1.354	(0.237)
Cr	0.001	(0.000)	0.001	(0.001)	0.000	(0.000)
Fe	0.105	(0.002)	0.074	(0.038)	0.036	(0.007)
Mn	0.004	(0.001)	0.014	(0.010)	0.002	(0.001)
Mg	0.048	(0.002)	0.085	(0.072)	0.255	(0.097)
Ca	1.998	(0.021)	2.042	(0.032)	1.990	(0.036)
Na	0.049	(0.009)	0.012	(0.011)	0.046	(0.018)
∑Cations	5.029	(0.013)	5.018	(0.012)	5.015	(0.017)

Gh	79.7	0.7	82.3	7.1	65.2	12.5
Ak	4.9	0.2	8.9	7.6	26.6	10.5
Fe-Ak	10.7	0.2	7.7	3.9	3.7	0.7
Na-Mel	4.7	0.8	1.1	1.1	4.5	1.8

1 *Table 6: Cu-bearing mineral compositions. Cubanite has only been found in magmatic skarn xenoliths,*
2 *whilst pyrrhotite is found across all xenolith types, with little chemical variation between xenolith types.*
3 *Analyses are reported as the mean with one standard deviation in brackets*

	Po		Cub	
n	10		5	
Fe	58.44	(0.49)	38.7	(1.12)
S	39.83	(0.24)	35.08	(0.67)
Co	0.20	(0.02)	0.12	(0.03)
Ni	0.48	(0.11)	0.06	(0.05)
Cu	0.30	(0.17)	24.26	(1.51)
Zn	0.03	(0.02)	0.09	(0.05)
Total	99.28	(0.60)	98.3	(0.57)
Sulphurs	1		3	
Fe	0.842	(0.007)	1.899	(0.036)
Co	0.003	(0.003)	0.005	(0.001)
Ni	0.007	(0.002)	0.003	(0.002)
Cu	0.004	(0.002)	1.048	(0.082)
Zn	0.005	(0.003)	0.004	(0.002)
Total	0.856	(0.007)	2.959	(0.072)
Fe/S	0.84	(0.01)		

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1 *Table 7: Selected analyses of halogen and sulphur-bearing minerals. Wad-1, Wad-2 are the wadalite-like*
2 *phase, found in sample MX1. Unk1 and Unk2 are unknown volatile-bearing minerals in samples CS11*
3 *and MXCS-b respectively. SEM-EDS analysis shows the presence of Cl and F in these latter two*
4 *minerals. Normalisation cations for the unknown volatile-bearing minerals are chosen to produce*
5 *plausible formula units, and are not to represent any currently known minerals. Analyses are reported as*
6 *the mean with one standard deviation in brackets*

Sample	Multiple		Multiple		MX1		MX1		CS11		M-XCS-1	
Mineral	Cusp		El		Wad-1		Wad-2		Unk1		Unk2	
Type	Magmatic Skarn		Magmatic Skarn		Magmatic Skarn		Magmatic Skarn		Exoskarn A		Exoskarn B	
n	5		4		11		2		2		2	
SiO_2	32.70	(0.42)	8.37	(1.27)	17.63	(0.41)	24.98	(1.99)	26.70	(0.05)	23.33	(0.44)
TiO_2	0.19	(0.15)	0.02	(0.03)	0.38	(0.17)	0.56	(0.29)	0.00	(0.00)	0.01	(0.02)
Al_2O_3	0.02	(0.01)	0.03	(0.02)	23.85	(1.05)	19.59	(0.98)	14.47	(0.42)	12.98	(0.02)
Cr_2O_3	0.02	(0.02)	0.00	(0.00)	0.01	(0.02)	0.00	(0.01)	0.00	(0.00)	0.00	(0.00)
FeO	0.14	(0.08)	0.08	(0.03)	5.63	(1.21)	6.26	(2.60)	1.52	(0.37)	0.71	(0.15)
MnO	0.08	(0.02)	0.03	(0.01)	0.18	(0.05)	0.24	(0.15)	0.26	(0.10)	0.07	(0.06)
MgO	0.07	(0.07)	0.05	(0.02)	0.60	(0.08)	0.43	(0.09)	0.24	(0.01)	0.01	(0.01)
CaO	60.20	(0.24)	54.16	(1.19)	40.18	(0.43)	39.67	(3.09)	52.48	(0.13)	56.23	(0.26)
Na_2O	0.02	(0.02)	0.01	(0.02)	0.17	(0.16)	0.09	(0.04)	0.00	(0.00)	0.01	(0.02)
K_2O	0.01	(0.01)	0.00	(0.00)	0.00	(0.01)	0.02	(0.00)	0.00	(0.00)	0.01	(0.01)
P_2O_5	0.00	(0.00)	24.03	(3.25)	0.13	(0.13)	0.13	(0.18)			0.04	(0.02)
SO_3	0.00	(0.00)	8.12	(1.42)	0.01	(0.01)	0.00	(0.00)			0.02	(0.01)
Cl	0.01	(0.00)	1.04	(0.22)	12.91	(0.17)	8.87	(2.74)			2.12	(0.00)
F	10.26	(0.14)			0.02	(0.02)	0.00				4.90	(0.00)
Total	103.70	(0.40)	95.94	(0.81)	101.69	(0.56)	100.85	(2.08)	95.67	(0.12)	100.61	(0.10)
$O=(F_2,Cl_2)$	-4.32	(0.06)	-0.23	(0.05)	-2.92	(0.04)	-2.00	(0.62)	0.00	(0.00)	-2.54	(0.00)
Total.1	99.38	(0.44)	95.71	(0.78)	98.77	(0.53)	98.85	(1.46)	95.67	(0.12)	98.07	(0.10)
Cations based on x cations	6		8		26		26		9		16	
Si	2.002	(0.009)	0.701	(0.106)	4.753	(0.092)	6.168	(0.277)	2.337	(0.006)	4.042	(0.058)
Ti	0.009	(0.007)	0.002	(0.002)	0.078	(0.034)	0.103	(0.051)	0.000	(0.000)	0.001	(0.002)
Al	0.001	(0.001)	0.003	(0.002)	7.578	(0.297)	5.713	(0.484)	1.493	(0.037)	2.649	(0.009)
Cr	0.001	(0.001)	0.000	(0.000)	0.003	(0.003)	0.001	(0.001)	0.000	(0.000)	0.000	(0.000)
Fe	0.007	(0.004)	0.006	(0.002)	1.270	(0.277)	1.285	(0.493)	0.112	(0.028)	0.103	(0.022)
Mn	0.004	(0.001)	0.002	(0.001)	0.042	(0.012)	0.050	(0.030)	0.019	(0.008)	0.011	(0.008)
Mg	0.007	(0.006)	0.007	(0.003)	0.240	(0.032)	0.159	(0.039)	0.031	(0.001)	0.002	(0.002)
Ca	3.949	(0.026)	4.858	(0.102)	11.610	(0.160)	10.524	(1.187)	4.923	(0.008)	10.436	(0.096)
Na	0.002	(0.002)	0.001	(0.003)	0.087	(0.083)	0.045	(0.022)	0.000	(0.000)	0.004	(0.005)
K	0.001	(0.001)	0.000	(0.000)	0.002	(0.003)	0.007	(0.000)	0.000	(0.000)	0.002	(0.002)
P	0.000	(0.000)	1.704	(0.230)	0.031	(0.029)	0.027	(0.038)	0.000	(0.000)	0.006	(0.003)
S	0.000	(0.000)	0.510	(0.089)	0.001	(0.003)	0.000	(0.000)	0.000	(0.000)	0.002	(0.001)
Cl	0.001	(0.000)	0.147	(0.031)	5.903	(0.087)	3.735	(1.277)	0.000	(0.000)	0.622	(0.003)
F	1.986	(0.044)	0.000	(0.000)	0.006	(0.011)	0.000	(0.000)	0.000	(0.000)	2.684	(0.012)

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Table 8: Average analyses of oxides and other silicate minerals found in the Merapi xenoliths. Analyses are reported as the mean with one standard deviation in brackets

Xenolith Type	Magmatic skarn									Exoskarn A	Exoskarn B	
Mineral	Mgt		Ilm	Hem		Psk		Ttn		CaSiAlP	Sp	
n	27		1	4		3		8		1	8	
SiO_2	0.14	(0.10)	5.92	0.31	(0.15)	1.13	(0.83)	30.91	(1.13)	33.30	0.01	(0.01)
TiO_2	9.91	(5.16)	43.22	0.15	(0.20)	54.75	(0.63)	36.28	(2.33)	1.19	0.01	(0.01)
Al_2O_3	2.66	(1.15)	1.10	0.59	(1.14)	0.43	(0.16)	1.70	(0.51)	26.28	66.59	(0.58)
Cr_2O_3	0.18	(0.20)	0.19	0.02	(0.02)	0.01	(0.01)	0.03	(0.03)	0.00	0.10	(0.07)
FeO	78.73	(4.81)	42.16	86.61	(2.79)	0.80	(0.15)	1.31	(0.70)	0.28	8.48	(1.41)
MnO	0.89	(0.30)	0.87	0.13	(0.14)	0.04	(0.03)	0.08	(0.07)	0.00	0.38	(0.08)
MgO	1.78	(0.55)	1.54	0.35	(0.58)	0.01	(0.01)	0.12	(0.29)	0.00	22.69	(0.77)
CaO	0.17	(0.21)	1.74	0.47	(0.19)	40.71	(0.47)	28.13	(1.04)	29.53	0.01	(0.00)
Na_2O	0.05	(0.05)	0.40	0.06	(0.04)	0.02	(0.02)	0.02	(0.01)	0.46	0.00	(0.00)
Total	94.51	(1.37)	97.37	88.70	(1.67)	97.92	(0.45)	98.66	(2.18)	102.40	98.27	(0.68)
Cations based on oxygens	4		3	3		3		5		16	4	
Si	0.005	(0.004)	0.146	0.006	(0.005)	0.026	(0.019)	1.010	(0.034)	3.098	0.000	(0.000)
Ti	0.280	(0.153)	0.802	0.001	(0.001)	0.944	(0.008)	0.892	(0.053)	0.084	0.000	(0.000)
Al	0.117	(0.048)	0.032	0.001	(0.001)	0.012	(0.004)	0.065	(0.019)	2.880	1.965	(0.012)
Cr	0.005	(0.006)	0.004	0.000	(0.000)	0.000	(0.000)	0.001	(0.001)	0.000	0.002	(0.001)
Fe^{2+}	1.145	(0.181)	0.774	0.000	(0.000)	0.000	(0.000)	0.002	(0.007)	0.000	0.145	(0.023)
Fe^{3+}	1.311	(0.288)	0.095	1.478	(0.985)	0.015	(0.003)	0.033	(0.022)	0.022	0.033	(0.013)
Mn	0.028	(0.009)	0.018	0.001	(0.001)	0.001	(0.000)	0.002	(0.002)	0.000	0.008	(0.002)
Mg	0.098	(0.029)	0.057	0.002	(0.002)	0.000	(0.000)	0.006	(0.014)	0.000	0.847	(0.024)
Ca	0.006	(0.008)	0.046	0.009	(0.007)	1.000	(0.014)	0.985	(0.033)	2.942	0.000	(0.000)
Na	0.003	(0.004)	0.019	0.003	(0.002)	0.001	(0.001)	0.001	(0.001)	0.082	0.000	(0.000)

1 *Table 9: Average interstitial glass and melt inclusion compositions for the zones in the magmatic skarn xenoliths. Analyses are reported as the mean with*
2 *one standard deviation in brackets*

Glass Type	Interstitial Glasses										Melt Inclusions			
Zone	Host Lava		R1		R2		R4		Core		R1		R4 and Core	
n	15		11		15		48		12		12		70	
SiO_2	70.45	(3.36)	69.02	(2.54)	71.07	(2.76)	73.23	(2.21)	73.32	(1.78)	63.99	(3.03)	67.38	(3.72)
TiO_2	0.42	(0.11)	0.37	(0.10)	0.31	(0.14)	0.35	(0.13)	0.32	(0.09)	0.44	(0.05)	0.40	(0.19)
Al_2O_3	13.75	(1.83)	13.29	(0.95)	13.47	(1.17)	12.00	(0.88)	12.6	(0.38)	17.55	(0.82)	13.33	(1.97)
Cr_2O_3	0.01	(0.01)	0.01	(0.01)	0.01	(0.01)	0.01	(0.01)	0	(0.01)	0.02	(0.02)	0.01	(0.01)
FeO	2.59	(0.79)	3.03	(0.15)	2.52	(0.28)	2.22	(0.46)	2.22	(0.56)	2.55	(0.56)	2.84	(1.31)
MnO	0.12	(0.08)	0.13	(0.05)	0.10	(0.04)	0.07	(0.03)	0.05	(0.03)	0.13	(0.04)	0.09	(0.06)
MgO	0.40	(0.57)	0.12	(0.09)	0.12	(0.12)	0.06	(0.06)	0.07	(0.04)	0.33	(0.22)	0.35	(0.90)
CaO	1.05	(1.04)	4.71	(1.79)	2.49	(1.29)	3.04	(1.15)	2.26	(0.97)	2.44	(0.52)	5.87	(3.47)
Na_2O	3.89	(1.15)	3.41	(0.46)	3.59	(0.46)	3.22	(0.37)	3.32	(0.53)	4.01	(0.90)	3.43	(0.74)
K_2O	5.28	(0.72)	4.20	(0.52)	4.71	(0.80)	4.51	(0.56)	4.92	(0.50)	3.82	(1.03)	4.00	(0.99)
P_2O_5	0.12	(0.12)	0.08	(0.05)	0.07	(0.08)	0.09	(0.36)	0.04	(0.02)	0.23	(0.08)	0.08	(0.04)
SO_3	0.01	(0.01)	0.06	(0.03)	0.01	(0.01)	0.02	(0.02)	0.00	(0.01)	0.11	(0.05)	0.03	(0.03)
Cl	0.21	(0.16)	0.27	(0.03)	0.26	(0.03)	0.29	(0.07)	0.28	(0.04)	0.29	(0.02)	0.34	(0.11)
F (ppm)									0;00	(0.00)			184	(326)
Total	98.26	(1.38)	98.63	(0.83)	98.73	(1.56)	99.09	(0.92)	99.39	(1.12)	95.53	(3.48)	98.14	(1.97)

3