

2 **Amphibole perspective to unravel pre-eruptive processes**
3 **and conditions in volcanic plumbing systems beneath intermediate**
4 **arc volcanoes: a case study from Ciomadul volcano**
5 **(SE Carpathians)**

6 **Balázs Kiss · Szabolcs Harangi · Theodoros Ntaflou ·**
7 **Paul R. D. Mason · Elemér Pál-Molnár**

8 Received: 7 June 2013 / Accepted: 10 February 2014
9 © Springer-Verlag Berlin Heidelberg 2014

10 **Abstract** Ciomadul is the youngest volcano in the Car-
11 pathian–Pannonian region produced crystal-rich high-K
12 dacites that contain abundant amphibole phenocrysts. The
13 amphiboles in the studied dacites are characterized by large
14 variety of zoning patterns, textures, and a wide range of
15 compositions (e.g., 6.4–15 wt% Al₂O₃, 79–821 ppm Sr)
16 often in thin-section scale and even in single crystals. Two
17 amphibole populations were observed in the dacite: low-Al
18 hornblendes represent a cold (<800 °C) silicic crystal
19 mush, whereas the high-Al pargasites crystallized in a hot
20 (>900 °C) mafic magma. Amphibole thermobarometry
21 suggests that the silicic crystal mush was stored in an upper
22 crustal storage (~8–12 km). This was also the place where
23 the erupted dacitic magma was formed during the remo-
24 bilization of upper crustal silicic crystal mush body by hot

mafic magma indicated by simple-zoned and composite 25
amphiboles. This includes reheating (by ~200 °C) and 26
partial remelting of different parts of the crystal mush 27
followed by intensive crystallization of the second mineral 28
population (including pargasites). Breakdown textures of 29
amphiboles imply that they were formed by reheating in 30
case of hornblendes, suggesting that pre-eruptive heating 31
and mixing could take place within days or weeks before 32
the eruption. The decompression rim of pargasites suggests 33
around 12 days of magma ascent in the conduit. Several arc 34
volcanoes produce mixed intermediate magmas with sim- 35
ilar bimodal amphibole cargo as the Ciomadul, but in our 36
dacite the two amphibole population can be found even in a 37
single crystal (composite amphiboles). Our study indicates 38
that high-Al pargasites form as a second generation in these 39
magmas after the mafic replenishment into a silicic capture 40
zone; thus, they cannot unambiguously indicate a deeper 41
mafic storage zone beneath these volcanoes. The simple- 42
zoned and composite amphiboles provide direct evidence 43
that significant compositional variations of amphiboles do 44
not necessarily mean variation in the pressure of crystal- 45
lization even if the Al-tschermak substitution can be rec- 46
ognized, suggesting that amphibole barometers that 47
consider only amphibole composition may often yield 48
unrealistic pressure variation. 49

A1 Communicated by T L. Grove.

A2 B. Kiss · S. Harangi · E. Pál-Molnár
A3 MTA-ELTE Volcanology Research Group, Pázmány Péter
A4 sétány 1/C, Budapest 1117, Hungary

A5 B. Kiss · S. Harangi
A6 Department of Petrology and Geochemistry, Eötvös Loránd
A7 University, Pázmány Péter sétány 1/C, Budapest 1117, Hungary

A8 B. Kiss (✉) · E. Pál-Molnár
A9 Vulcano Research Group, Department of Mineralogy,
A10 Geochemistry and Petrology, University of Szeged, Egyetem
A11 utca 2, Szeged 6722, Hungary
A12 e-mail: geobalazs@gmail.com

A13 T. Ntaflou
A14 Department of Lithospheric Research, University of Vienna,
A15 Althanstrasse 14, 1090 Vienna, Austria

A16 P. R. D. Mason
A17 Department of Earth Sciences, Utrecht University, Budapestlaan
A18 4, 3584 CD Utrecht, The Netherlands

Keywords Amphibole perspective · Intermediate 51
magmas · Magma mixing · Volcano plumbing system · 52
Thermobarometry · Amphibole texture and zoning patterns 53

Introduction 54

Eruptions of intermediate (andesitic to dacitic) arc volca- 55
noes are usually preceded by open-system magmatic 56

processes such as magma mixing, cumulate assimilation, and crustal contamination, producing a petrologically complex mixture of minerals and melts (e.g., Humphreys et al. 2006; Reubi and Blundy 2009; Kent et al. 2010). It is essential to understand these processes because they determine the physical state of the erupted magma and as a consequence the style of the volcanic eruption (Ruprecht and Bachmann 2010; Koleszar et al. 2012).

Here, we present the results of a combined textural and chemical (major and trace elements) analyses of amphiboles found in the dacitic rocks of the Ciomadul volcano. The Ciomadul located in the SE Carpathians is the youngest volcano of Carpathian–Pannonian region and referred as a potentially active volcano (Szakács et al. 2002; Harangi 2007; Popa et al. 2012; Szakács and Seghedi 2013). Despite this, very little is known about how the erupted magmas were formed or what triggered their eruptions (Vinkler et al. 2007). Using amphiboles, we could imply the volcanic plumbing system and constrain the pre-eruptive magma chamber processes. Amphibole is a powerful tool as they can record parallel pre-eruptive processes and conditions due to its sensitivity for changing magmatic variables such as temperature, pressure, redox state, H₂O content, melt composition, and co-crystallizing mineral phases (e.g., Johnson and Rutherford 1989a; Rutherford and Hill 1993; Scaillet and Evans 1999; Bachmann and Dungan 2002; Rutherford and Devine 2003; Sato et al. 2005; Humphreys et al. 2006, 2009b; Thornber et al. 2008; Ridolfi et al. 2010; Krawczynski et al. 2012). Consequently, the careful investigation of their crystal growth stratigraphy can provide an “amphibolic” perspective toward understanding the dynamics and processes of dacitic–andesitic volcanoes before eruptions (Thornber et al. 2008) including Ciomadul.

We investigate the implications of our study for using amphibole to constrain the subvolcanic plumbing systems of andesitic to dacitic arc volcanoes in general. Finally, we discuss the origin, conditions, and processes lead to commonly observed bimodal amphibole populations in intermediate mixed magmas erupted at composite arc volcanoes. Our study highlights that different amphibole thermobarometers can produce essentially different results, which may lead to false interpretations on the magma evolution and architecture of the magma storage system without clear textural control and crystal growth stratigraphy. We point out the deficiency of the Ridolfi’s thermobarometric model that yields always the same p–T evolution path for amphiboles along their stability curve.

Geological setting

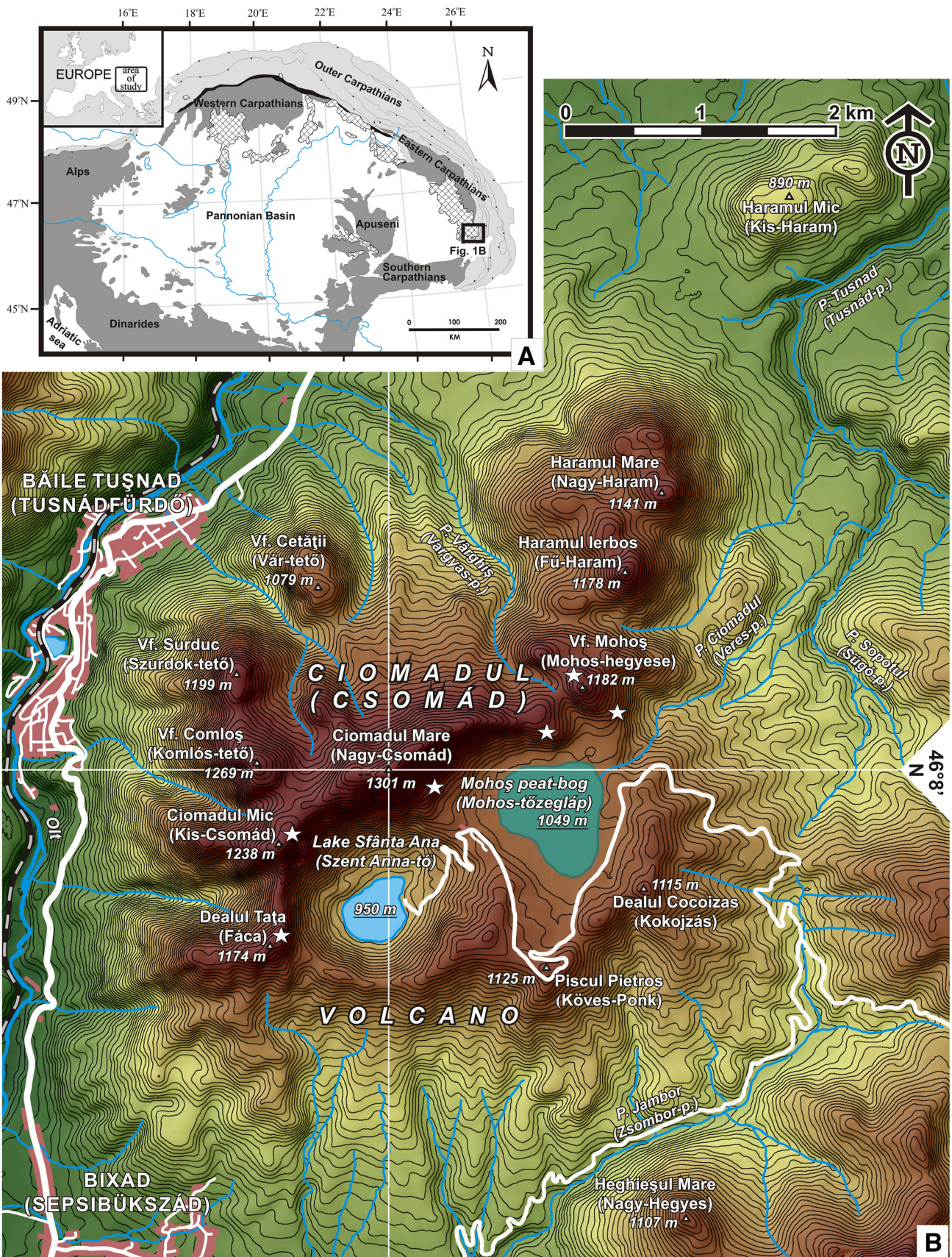
Ciomadul volcano is located at the southeastern edge of the Carpathian–Pannonian region, and this is the youngest

Fig. 1 **a** Geological sketch map of the Carpathian–Pannonian region in Eastern-Central Europe. The cross-hatched areas show the Neogene calc-alkaline volcanic rocks (on the surface). **b** Topographic map of Ciomadul (Csomád) volcano (Karátson et al. 2013). The sample locations are marked by white stars

volcano of this area (Szakács and Seghedi 1995; Szakács et al. 2002; Vinkler et al. 2007; Harangi et al. 2010; Karátson et al. 2013). It is found at the southern termination of the Călimani–Gurghiu–Harghita (CGH) andesitic–dacitic volcanic chain (Fig. 1) that shows a gradually younging volcanism from 11.3 Ma (Peltz et al. 1987; Pécskay et al. 1995). There was a sharp compositional change in the erupted magmas within the Harghita Mountains around 3 Ma that spatially coincides with a major tectonic line (Trotus line; Harangi and Lenkey 2007; Seghedi et al. 2011). The post-3 Ma magmas at the southern Harghita are more potassic and show different trace element compositions compared with the older rocks in the north (Seghedi et al. 1987; Szakács et al. 1993; Mason et al. 1996). Volcanic eruptions in Ciomadul could have started around 200 ka, and the last volcanic event occurred at 31,000 ± 260 cal BP. Initially, the volcanism was mostly effusive and a lava dome complex developed called here “old Ciomadul.” Later, the volcanic activity became more explosive and as a result of successive phreatomagmatic and subplinian eruptions, the edifice of the “old Ciomadul” was partially destroyed and two deep explosive craters were formed (Szakács and Seghedi 1995; Karátson et al. 2013). The erupted magma remained fairly homogeneous through time and shows high-K dacitic composition (Szakács and Seghedi 1986; Vinkler et al. 1997). The geodynamic background of the CGH volcanism and particularly the volcanic activity of southern Harghita and Ciomadul is still highly debated. Roll-back subduction and gradual break off of the subducted slab and/or gravitational instability and lithospheric delamination was invoked to explain the geodynamics of the area (e.g., Seghedi et al. 2011; Mason et al. 1998; Gîrbacea and Frisch 1998; Chalot-Prat and Gîrbacea 2000; Lorinczi and Houseman 2009; Fillerup et al. 2010; Ren et al. 2012). Whatever is the explanation for the origin of the near-vertical slab beneath this area, the active seismicity in the Vrancea zone as well as the gas chemistry and seismicity beneath Ciomadul (Vaselli et al. 2002; Popa et al. 2012) implies that rejuvenation of the volcanism cannot be unambiguously excluded (Szakács et al. 2002; Harangi 2007; Szakács and Seghedi 2013).

Samples and analytical techniques

Samples were collected in Ciomadul during several field campaigns. The fresh lava dome rocks and pumices of the explosive eruptions cover most of eruptive events. During



152 this study, we focused on the lava dome rocks collected at
 153 the northern crater rim of the “old Ciomadul.” They rep-
 154 resent effusive products formed about 100–150 ka and
 155 contain the entire mineral assemblage as well as felsic and
 156 mafic inclusions found in the Ciomadul dacite. Textural
 157 characterization of the mineral phases was performed by
 158 combined investigation with petrographic microscope and
 159 an AMRAY 1830 I/T6 scanning electron microscope at the
 160 Department of Petrology and Geochemistry of the Eötvös
 161 Loránd University. The in situ analyses of the mineral
 162 phases were carried out using a CAMECA SX100 electron
 163 microprobe equipped with four WDS and one EDS at the
 164 University of Vienna, Department of Lithospheric
 165 Research (Austria). The operating conditions were as fol-
 166 lows: 15 kV accelerating voltage, 20 nA beam current,
 167 20 s counting time on peak position, and PAP correction
 168 procedure for data reduction. Amphibole and plagioclase
 169 crystals were measured with defocused beam (3–5 μm).
 170 Calibration was based on the following standards: Amelia
 171 albite (Na, Si, Al), San Carlos olivine (Mg) (Jarosewich
 172 et al. 1980), almandine 112140 (Fe) (McGuire et al. 1992),
 173 microclin (K) (Jarosewich et al. 1980), and the depart-
 174 ment’s own standards wollastonite (Ca), rutile (Ti), spes-
 175 sartine (Mn), synthetic Mg chromite (Cr), and Ni oxide
 176 (Ni).

177 Trace elements in amphibole phenocrysts were mea-
 178 sured by LA-ICP-MS using a 193-nm ArF excimer laser
 179 ablation system (MicroLas GeoLas 200Q) in combination
 180 with quadrupole ICP-MS (Micromass Platform ICP) at
 181 Utrecht University (Mason and Kraan 2002) following the
 182 methodology described by Harangi et al. (2005). Ablation
 183 was performed at a fixed point on the sample with an
 184 irradiance of 0.2 GW cm^{-2} , a laser pulse repetition rate of
 185 10 Hz, and an ablation crater diameter of 40–60 μm . The
 186 signal recorded by the ICP-MS during ablation was care-
 187 fully checked for compositional boundaries to ensure that
 188 only data for the amphiboles were integrated. Quantitative
 189 concentrations were calculated using NIST SRM 612 as a
 190 calibration standard (Pearce et al. 1997) with Ca (previ-
 191 ously determined by electron microprobe analysis) as an
 192 internal standard element. The USGS reference glass BCR-
 193 2 G was continuously measured throughout the analysis of
 194 the amphiboles, and the results were within 5–10 % of
 195 recommended values. Detection limits were typically in the
 196 range 0.01–1 $\mu\text{g g}^{-1}$, and internal precision was <5 %
 197 RSD (1 σ) for concentrations above 1 $\mu\text{g g}^{-1}$ and <15 %
 198 RSD (1 σ) below 1 $\mu\text{g g}^{-1}$.

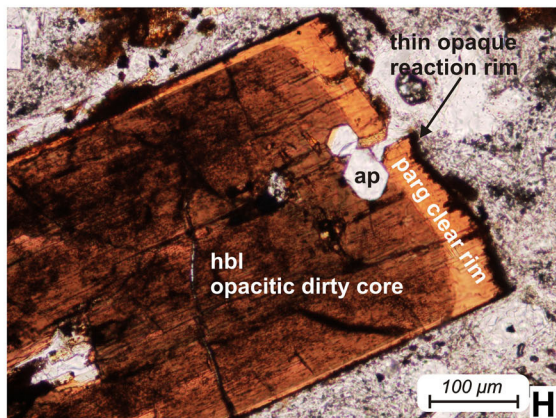
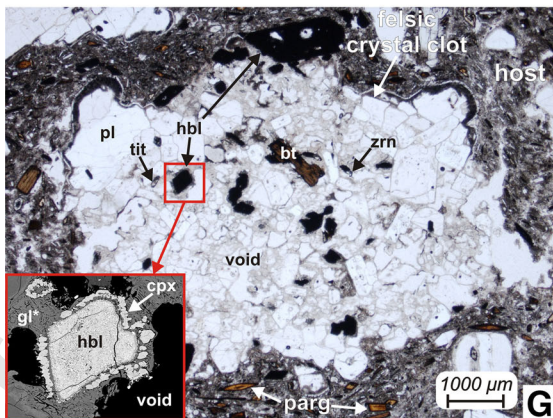
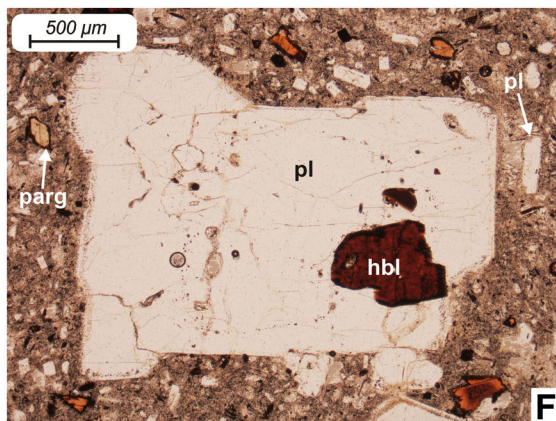
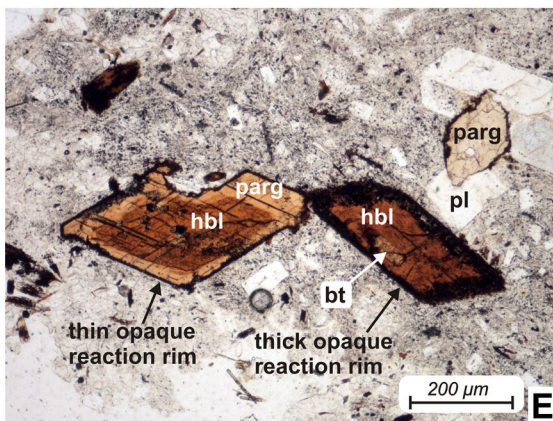
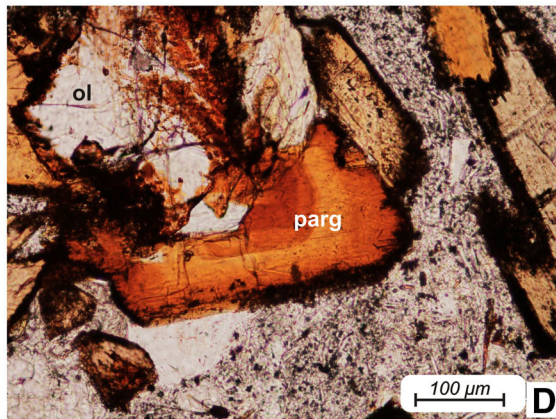
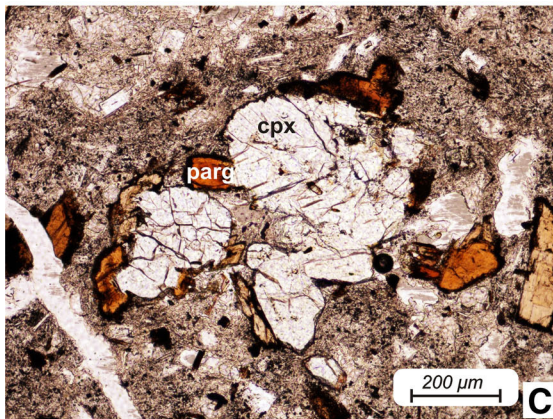
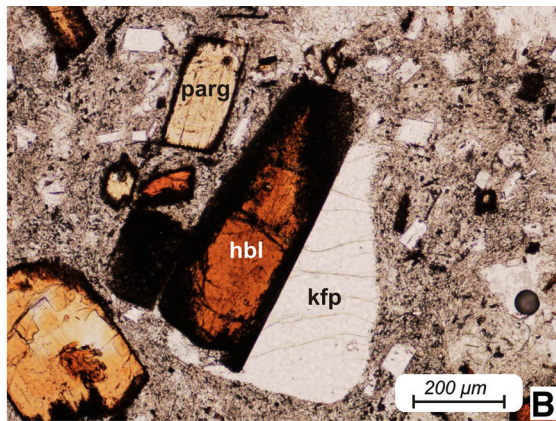
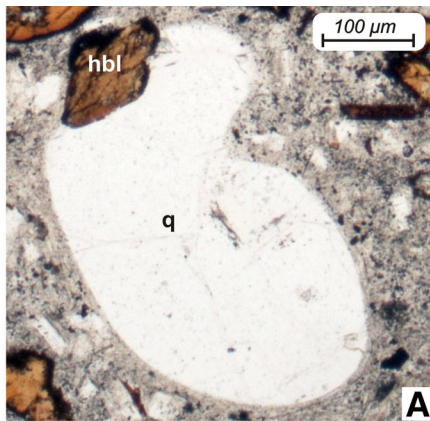
199 Petrology of the dacite

200 The studied lava dome rocks are calc-alkaline, high-K
 201 dacites ($\text{SiO}_2 = 62\text{--}68 \text{ wt}\%$; $\text{K}_2\text{O} = 3.0\text{--}3.6 \text{ wt}\%$)

Fig. 2 Photomicrographs of amphiboles in the Ciomadul dacite. **a** Hornblende (hbl) and adjacent embayed quartz (q). **b** Hornblende with thick opaque rim and touched pair of K-feldspar (kfp); a small pargasite (parg) microphenocryst with thin opaque rim. **c, d** Pargasite crystal overgrowth on clinopyroxene (cpx) and olivine (ol) crystals, respectively. **e** Hornblende with thick opaque reaction rim with biotite inclusion (bt) next to simple-zoned amphibole with thin reaction rim; a plagioclase (pl)–pargasite microphenocryst pair. **f** Hornblende inclusion in a large plagioclase phenocryst; pargasite microphenocrysts and plagioclase laths in the matrix. **g** Black opacitized hornblendes in a felsic crystal clot (microdioritic microinclusion) that also contain plagioclase, titanite (tit), zircon (zrn), and interstitial glass; pargasite phenocrysts in the host are also indicated; enlargement (BSE image) of the hornblende in the framed area: close view of the microdioritic inclusion, the hornblende inside is surrounded by clinopyroxene corona set in vesiculated glass gl*. **h** Simple-zoned amphibole with a “dirty” opacitic core (hornblende), a clear pargasitic rim and a thin opaque reaction rim; apatite (ap) inclusions are present in the core

202 according to the classification of Gill (1981) and Miyashiro
 203 (1974). The erupted dacites are poorly vesicular and por-
 204 phyritic (phenocrysts content is 30–40 vol%), crystal-rich
 205 rocks. They contain abundant glomerocrystic aggregates
 206 and crystal clots, and the groundmass is totally crystalline.
 207 Thus, the texture of the dacite is glomeroporphyritic holo-
 208 crystalline. The term “phenocryst” is used here for crystals
 209 exceeding 300 μm , whereas “microphenocrysts” are in the
 210 size range of $\sim 300\text{--}50 \mu\text{m}$. “Microlites” are smaller than
 211 50 μm . The phenocrysts are (in the order of relative
 212 occurrence) plagioclase, amphibole, biotite, clinopyroxene,
 213 quartz, K-feldspar, and olivine. The Ciomadul dacite is rich
 214 in accessories such as apatite, titanite, and zircon. Allanite
 215 is observed occasionally. The groundmass is composed of
 216 plagioclase laths, pyroxene microlites, Fe–Ti oxides, and
 217 SiO_2 patches, probably tridymite.

218 Plagioclase is the most common phenocrystic phase.
 219 Two major types were observed: they occur in large
 220 glomerocrystic aggregates and as euhedral micro-
 221 phenocrysts (Fig. 2f). The compositional range of the
 222 phenocrysts and microphenocrysts overlaps but the An
 223 contents of the phenocrysts’ cores are lower (An:
 224 $34 \pm 8 \text{ mol}\%$) than those of the cores of microphenocrysts
 225 (An: $52 \pm 4 \text{ mol}\%$). Amphibole phenocrysts are the most
 226 common mafic minerals. Detailed descriptions of amphi-
 227 boles are presented in the following sections. Biotite
 228 phenocrysts are euhedral or subhedral, often rounded and
 229 always have a reaction rim. Common inclusions in biotite
 230 are apatite, zircon, and glass. Quartz phenocrysts (<5 vol%
 231 of the phenocrysts) are always rounded and embayed
 232 (Fig. 2a), and occasionally, there are a clinopyroxene-rich
 233 rim around them. They are found mostly in the samples
 234 with higher proportions of mafic crystal clots, clinopyrox-
 235 ene, and olivine phenocrysts. K-feldspar phenocrysts
 236 (<5 vol% of the phenocrysts) are also embayed and
 237 rounded (Fig. 2b). Some of them are large ($\sim 5 \text{ mm}$ sized)



238 crystals enclosing amphibole, biotite, apatite, titanite, plagioclase, and quartz. Rare olivine crystals are anhedral and usually strongly reacted (Fig. 2d). They are surrounded by fine-grained reaction products (pyroxenes and oxides) and overgrown by amphibole crystals. Tiny euhedral and homogenous Cr-spinel inclusions often occur in the olivines. Clinopyroxenes usually form crystal clots but they also appears as single crystals. They have euhedral or subhedral habit and show various internal zoning. It is often observed that clinopyroxene crystals have rounded edges and they are overgrown by amphibole crystals (Fig. 2c).

250 The dacites contain various crystal clots. Two larger groups were recognized according to their mineralogy: felsic and mafic clots. Felsic clots are ~1-cm-sized inclusions consisting dominantly of felsic minerals such as plagioclase ± K-feldspar ± quartz. The most common type of the felsic clots is microdioritic (Fig. 2g) composed of plagioclase, amphibole, biotite, titanite, zircon, and apatite. They are texturally similar to adcumulate plutonic rocks but 10–15 vol% interstitial vesiculated glass is always present. These felsic inclusions could represent a highly crystalline magmatic body in the magma chamber (i.e., crystal mush). Mafic clots contain clinopyroxene or olivine or both with minor amount of plagioclase laths. They are occasionally overgrown by amphibole crystals. (Fig. 2c, d).

264 Amphibole texture and chemistry

265 All of the studied rocks contain two major amphibole types according to their general optical appearances. Amphiboles that are “dirty” and have dark brown-reddish brown pleochroism are termed here “hornblendes” (Fig. 2e). They usually occur as euhedral or subhedral single phenocrysts with no optical zoning and often coexist with K-feldspar, glomerocrystic plagioclase, and quartz (Fig. 2a, b, f) where hornblende is found as intergrowth or inclusions. Amphiboles in the microdioritic inclusions are also hornblendes. These amphiboles contain biotite, apatite, rhyolitic glass, and rarely titanite and plagioclase inclusions (Fig. 2e, h). Hornblendes show various breakdown textures. The second type of amphiboles is “clear” with light brown-yellow pleochroism and will be called “pargasite.” They occur as single phenocrysts with optical zoning, but are often found also as overgrowth rim on hornblende, clinopyroxene, and olivine crystals (Fig. 2b–d, h). Amphiboles in the mafic clots are also pargasites. They contain small clinopyroxene, apatite, and sulfide inclusions (Fig. 2d). Pargasites also show breakdown texture, which is described in the following section in more detail. Amphiboles often coexist with plagioclase. The hornblendes typically occur with glomerocrystic plagioclase and pargasites with euhedral plagioclase microphenocrysts (Fig. 2e, f).

Amphibole breakdown textures

290 Amphibole phenocrysts show different breakdown textures: reaction rims, internal breakdown patches, and clinopyroxene-rich zones or coronas (Fig. 2, 3). Optically, the reaction rims and internal breakdown patches are optically. These various textures can be observed in single thin sections and even in single crystals (Fig. 2e, h). The two amphibole groups show marked differences in their breakdown textures. Hornblendes are characterized by a higher degree of breakdown. They are surrounded by a thick, coarse-grained rim consisting of pyroxene, Fe–Ti oxide, feldspar, and glass. Additionally, similar breakdown products also appear within the crystals as patches or along cleavages (internal breakdown patches; Fig. 3). The reaction rim is often present also where the hornblende is in solid–solid contact with other phenocryst (Fig. 3d). The average rim thickness is ~15 μm (Fig. 3e) but in some samples, the hornblendes are almost totally replaced by the reaction products (Fig. 2g). Clinopyroxene-rich corona was also observed around some hornblendes, partly in crystal clots (Fig. 2g). Around the pargasite crystals, the reaction rim is finer-grained compared to the breakdown products of hornblendes (Fig. 3c). These rims consist of pyroxenes, Fe–Ti oxides, and some feldspar. The reaction rim can be seen only where the pargasite is in direct contact to the matrix.

315 Some amphiboles show multiple breakdown textures. The core of these crystals is characterized by internal breakdown patches similar as it was observed in the hornblendes, but their outer reaction rim is thin and fine-grained as it was observed around pargasites (Fig. 3a, b). Additionally, thin clinopyroxene-rich zone is occasionally observed at the core–rim boundary.

Amphibole major and trace element chemistry, classification

324 Amphiboles show large intercrystalline compositional variation in major (e.g., Al₂O₃ = 6.4–15 wt%, MgO = 9.3–17.6 wt%) and trace elements (e.g., Ba = 20–500 ppm, Sr = 100–800 ppm) (Table 1, 2, 3). In spite of the diversity of their textural appearance and variable zoning patterns, the amphiboles can be divided into two separate compositional groups, which correspond to the petrographically determined groups. Hornblendes show low-Al and Ba, Sr, Zr contents, and they are characterized by high SiO₂ and MnO, and low TiO₂ and Na₂O contents (Fig. 4, 5) compared with the pargasites. Their low Al/Si (0.19 ± 0.02) ratio, low Ba, Sr, Zr concentrations, and the negative Eu anomaly in the normalized trace element patterns (Fig. 5) suggest that they originated from an evolved, fractionated silicic magma. Pargasite crystals are rich in Al as well as Ba, Sr, Zr, and they have high

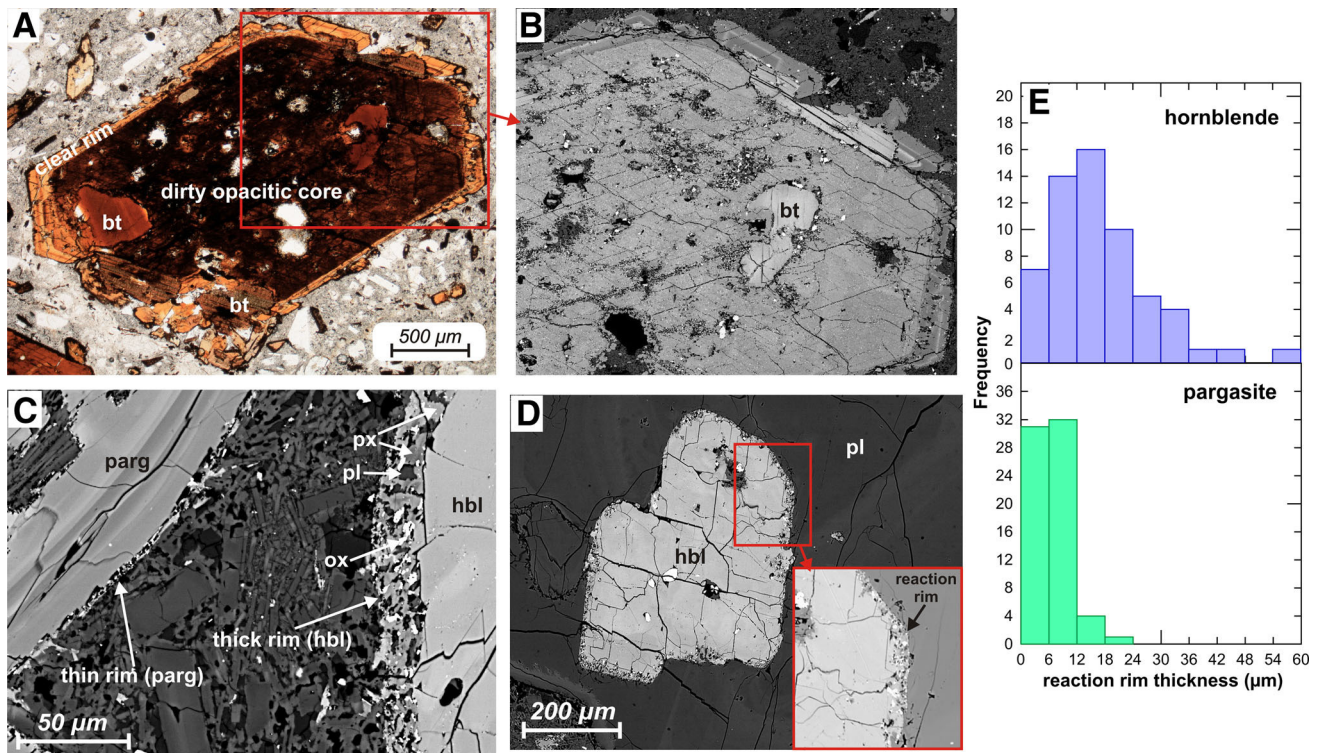


Fig. 3 Pictures of amphibole breakdown textures and histograms of reaction rim thicknesses. **a** Photomicrograph of an amphibole phenocryst with dirty opacitic core and clear rim (plane-polarized light). **b** Close-up (BSE image) of the area shown by the rectangle in picture **a** showing that the internal breakdown patches of the core

contain fine-grained reaction products. **c** Close view of the fine-grained thin reaction rim of pargasite and the coarser-grained thick reaction rim of hornblende. **d** Hornblende inclusion in plagioclase: the hornblende is surrounded by a reaction rim. **e** Histogram of the reaction rim thicknesses of the studied amphiboles

Table 1 Representative major element compositions of Ciomadul amphibole crystals

sample	NCS2-30a	Tc-30a	kcs17-100			kcs17-100			kcs17-30	Mo2-30b
	<i>Hornblende:</i>					<i>Pargasite:</i>				
crystal	NCS2 am7 felsic clot	Tc30a_am4 felsic clot	am_2 phcr	am_19_1 phcr	am_19_2 phcr	am_15 phcr	am_17 phcr	am_13 mafic clot	38_am4 mafic clot	mo2 am4 mpher
SiO ₂	46.02	44.98	46.75	45.88	46.43	43.07	41.33	42.65	43.08	43.23
TiO ₂	1.02	1.32	0.97	1.21	1.13	2.18	2.14	2.18	2.35	2.35
Al ₂ O ₃	7.66	8.57	7.35	8.46	7.70	11.92	13.73	13.30	11.91	11.2
FeO	14.54	15.33	14.57	14.38	14.05	9.15	9.68	7.30	7.67	10.2
MnO	0.39	0.42	0.47	0.39	0.38	0.12	0.09	0.11	0.09	0.14
MgO	12.98	12.19	13.50	13.20	13.40	15.92	14.46	16.56	16.55	15.11
CaO	11.79	11.86	11.81	11.74	11.88	11.69	11.60	11.80	11.96	11.57
Na ₂ O	1.46	1.48	1.27	1.53	1.32	2.30	2.40	2.44	2.48	2.34
K ₂ O	0.80	0.94	0.68	0.84	0.77	0.93	0.98	1.16	0.97	0.75
BaO	n.a.	n.a.	0.07	0.07	0.09	0.11	0.09	0.09	n.a.	n.a.
Total	96.67	97.09	97.43	97.69	97.14	97.38	96.50	97.57	97.06	96.94

FeO, total amount of iron

phcr phenocryst, mpher microphenocryst, n.a. not analyzed

339 TiO₂ and Na₂O, and low SiO₂ and MnO contents (Fig. 4, 5).
 340 The lack of negative Eu anomaly, along with the high Al/Si
 341 ratio (0.33 ± 0.03), suggests that these amphiboles crystal-
 342 lized from a more primitive, presumably mafic magma. The

CaO content is similar in both groups and show minor vari-
 343 ations. The MgO concentration of the two groups overlaps but
 344 the low-Al amphiboles cluster at lower MgO than the high-Al
 345 amphiboles. The compositional variation can be also large
 346

Table 2 Representative trace element compositions of Ciomadul amphibole crystals

sample	kcs17-100				MO2	kcs17-100			Mo2	Ncs2
	<i>Hornblende:</i>					<i>Pargasite:</i>				
crystal	am_2 phcr	am_19_1 phcr	am_19_2 phcr	am_6 S-Z core	MO2-7 phcr	am_15 phcr	am_17 phcr	am_13 mafic clot	MO2-1 phcr	NCS2-4 phcr
V	332.17	323.88	296.97	319.30	315.27	352.49	421.31	479.17	426.33	444.71
Cr	84.56	179.22	114.45	135.51	114.98	79.13	18.61	405.56	33.27	90.2
Ni	50.84	45.31	37.65	39.04	56.18	47.23	53.61	56.48	28.91	22.76
Rb	5.53	2.66	2.45	15.21	3.49	3.83	8.08	5.53	4.58	3.94
Sr	73.92	132.21	109.02	168.27	84.44	749.01	822.30	585.64	652.25	745.93
Y	45.84	31.06	27.87	33.50	36.22	20.85	22.76	19.04	25.64	20.53
Zr	28.93	35.53	31.27	34.14	25.75	60.20	68.39	58.71	77.56	56.27
Nb	18.29	18.51	16.27	16.17	19.09	15.74	10.53	19.25	14.29	14.57
Ba	74.77	119.66	104.02	115.83	65.24	347.92	401.52	294.31	331.53	366.85
La	15.53	23.51	16.70	18.29	12.98	14.15	15.21	11.81	15.71	11.38
Ce	54.25	77.01	61.27	60.10	48.76	46.91	50.42	38.50	47.35	37.01
Pr	9.04	12.34	9.15	9.47	8.18	8.08	8.51	6.59	7.75	6.38
Nd	40.52	48.18	39.35	41.16	36.65	35.74	39.78	28.08	37.64	30.53
Sm	10.74	9.89	7.66	9.31	8.35	9.04	10.00	7.71	8.84	7.45
Eu	2.55	2.45	2.02	2.34	1.85	3.08	3.30	2.23	2.73	2.55
Gd	9.79	9.57	8.40	8.83	7.42	7.34	7.76	6.07	7.59	6.6
Dy	10.90	8.35	6.86	8.62	8.18	6.49	7.55	5.90	6.82	6.12
Er	6.38	4.41	3.88	5.21	4.53	3.08	3.83	3.19	3.44	3.19
Yb	5.37	3.88	3.51	4.41	4.42	2.71	2.98	2.50	2.78	2.13
Lu	0.74	0.53	0.43	0.64	0.65	0.32	0.43	0.32	0.44	0.32
Hf	2.45	2.13	2.02	2.34	2.29	3.19	3.19	2.87	3.27	2.87
Ta	0.74	0.43	0.53	0.53	0.55	0.96	0.64	1.17	0.98	0.74
Pb	3.08	1.70	2.23	2.02	2.07	2.45	4.68	1.49	1.42	1.28
Th	0.53	0.19	0.19	0.43	0.1	0.43	0.53	0.24	0.44	0.32
U	0.14	0.04	0.05	0.12	0.04	0.09	0.22	0.04	0.15	0.05

Phcr phenocryst, *S-Z core* core of simple-zoned amphibole

347 within a single crystal; it can be equal to the whole variation of
348 the phenocrysts (Fig. 4).

349 According to the classification of IMA (Leake et al.
350 1997), both amphibole groups belong to the Ca amphi-
351 boles. The low-Al amphiboles are dominantly Mg hornblende
352 and some of them are edenites. The high-Al
353 amphiboles are dominantly pargasites but Mg hastingsites
354 also occur.

355 Zoning types and amphibole profiles

356 *Patchy zoning*

357 Two types of patchy zoning were distinguished in the dacite
358 (based on BSE images). Type A1 patchy zoning was
359 observed in the backscattered electron images of hornblende
360 phenocrysts. These crystals consist of a core of irregular-

361 shaped bright and dark patches and oscillatory-zoned rims.
362 In the dark patches, melt inclusion with euhedral apatite and
363 mineral inclusions of biotite and apatite are present (Fig. 6).
364 Where it is appreciable, the bright patch looks as a spongy
365 framework with strongly dissolved margin. Brighter por-
366 tions are richer in Al, Ti, and (Na + K)^A and have lower Mg
367 number than the dark regions (Fig. 8). Oscillatory-zoned
368 rims are characterized by Al spikes along with increase in Fe,
369 Ti, and (Na + K)^A, and a decrease in Mg and Si that follows
370 the dissolution surface (Fig. 7). The other type (type A2) of
371 patchy-zoned amphiboles has rounded patchy-spongy cel-
372 lular core and dark rim (Fig. 6) and can be observed less
373 frequently. The patches have sharper boundary, and an
374 abrupt shift was observed in their composition. Brighter
375 patches have lower Al, Ti, (Na + K)^A, and Mg contents
376 compared to the dark ones (Fig. 8). The dark patches have
377 similar compositions as the rim that contains pyroxene

Table 3 Representative major element compositions of zoned amphibole crystals

Zoning-type crystal	Simple-zoned (Type C)		Patchy-zoned (Type A1)		Patchy-zoned (Type A2)		Oscillatory-zoned (Type B1)		Oscillatory-zoned (Type B2)		Composite crystal (Type D)								
	core	rim	dark patch	light patch	core	rim	bright band	dark band	core	rim	core	rim							
	kcs17 amf sz3	am5	am5	am5	kcs_17_amf_1_4	am8	am8	am12	am12	am12	am12	kcs17 amf x							
SiO ₂	47.19	43.91	46.44	44.07	45.86	43.14	43.56	44.10	48.67	44.03	38.80	42.91	48.02	44.76	43.05	38.89	44.64	41.08	43.75
TiO ₂	0.83	1.99	1.20	1.43	0.83	2.07	2.17	1.50	0.85	2.05	2.89	2.30	0.84	1.32	2.18	2.06	2.18	2.37	2.20
Al ₂ O ₃	7.19	11.74	7.84	9.41	7.78	11.52	11.28	9.14	6.09	11.76	14.43	12.18	6.46	8.72	12.17	14.48	10.87	13.33	11.86
FeO	14.27	8.76	14.42	15.48	14.58	8.23	6.86	15.42	13.29	7.14	14.19	8.58	13.63	15.31	9.70	16.87	7.01	12.71	8.67
MnO	0.46	0.12	0.43	0.38	0.43	0.09	0.09	0.41	0.44	0.11	0.17	0.13	0.40	0.41	0.12	0.20	0.05	0.15	0.15
MgO	13.39	15.82	13.18	11.92	13.44	16.75	17.56	11.90	14.27	17.48	11.19	15.62	14.20	12.51	15.02	9.31	17.26	12.53	15.62
CaO	11.91	11.88	11.68	11.74	11.75	11.87	11.81	11.67	11.95	11.23	11.73	12.17	11.72	11.82	11.80	11.69	11.91	11.83	11.94
Na ₂ O	1.23	2.12	1.26	1.58	1.52	2.35	2.24	1.49	1.05	2.48	2.40	2.28	1.51	1.70	2.29	2.20	2.16	2.22	2.26
K ₂ O	0.74	0.88	0.74	0.97	0.84	0.97	0.97	1.00	0.51	0.96	1.10	1.03	0.64	0.93	0.94	1.10	1.00	1.04	0.98
BaO	n.a.	n.a.	0.02	0.07	0.75	0.25	0.41	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	97.22	97.23	97.25	97.04	97.77	97.28	96.96	96.63	97.17	97.23	96.90	97.26	97.436	97.488	97.251	96.786	97.064	97.265	97.443

FeO, total amount of iron
n.a. not analyzed

inclusion. The bright patches fall into the compositional field of hornblendes, while the compositions of the dark patches and the rim belong to the pargasite field.

Cyclic zoning

Cyclic zoning (type B) is a commonly observed zoning pattern in Ciomadul amphiboles, and it occurs in two subtypes, i.e., type B1 and type B2 (Fig. 6). The subtypes can be distinguished by their Al^{tot} content and the compositional pattern of the growth zones. Type B1 zoning is typical in the hornblende crystals, and these crystals show compositional variation at the low-Al level. Type B1 cyclic zoning is characterized by internal asymmetric growth zones and Al spikes at their rim. Each growth zone contains a dark Mg- and Si-rich band and a brighter Al-, Fe-, Ti-, (Na + K)^A-rich band. The growth zones are bounded by resorption surfaces (Fig. 7, line 2). Each zone begins with Al-rich and Mg-poor composition but Al gradually decreases and Mg increases toward the end of the zone. Al spikes are thin, symmetrical Al-, Fe-, Ti-, and (Na + K)^A-rich zones.

Type B2 zoning was observed in pargasite crystals. This zoning type is present in single phenocrysts or in overgrowth rim on hornblende and olivine crystals. Composition of Type B2 crystals varies at the high-Al range. This zoning type is built up by asymmetric growth zones that have resorbed boundaries (Fig. 6). In these crystals, the bright zones show often rounded edges suggesting dissolution. The bright zones enriched in Al, Fe, and (Na + K)^A, whereas the dark zones are Mg- and Si-rich (Fig. 7, line 3, 4). Each growth zone begins with Mg-rich and Al-poor composition, and they show gradual change (increasing Al, decreasing Mg) toward the end of the growth zone.

Simple zoning

Simple-zoned (Type C) amphiboles are frequent in the dacite and show revers geochemical variation toward the crystal rims (Fig. 6). The most important features are the presence of major resorption surfaces with an abrupt shift in Al, Ti, (Na + K)^A, and Mg at the core-rim boundary (example shown in Fig. 7, line 5). The bright cores are typically rounded and often spongy cellular, and the cavities are filled by fine-grained reaction products of pyroxene, magnetite, and glass. In extreme cases, the core is totally replaced by these reaction products. The resorbed cores are overgrown by dark amphibole rims enriched in Al, Ti, (Na + K)^A, and Mg. The composition of the cores overlaps the hornblende field, while the rims have composition akin to pargasites (Fig. 4).

Composite crystals (Type D) are special types of simple-zoned amphiboles. They (Fig. 6) consist of the same

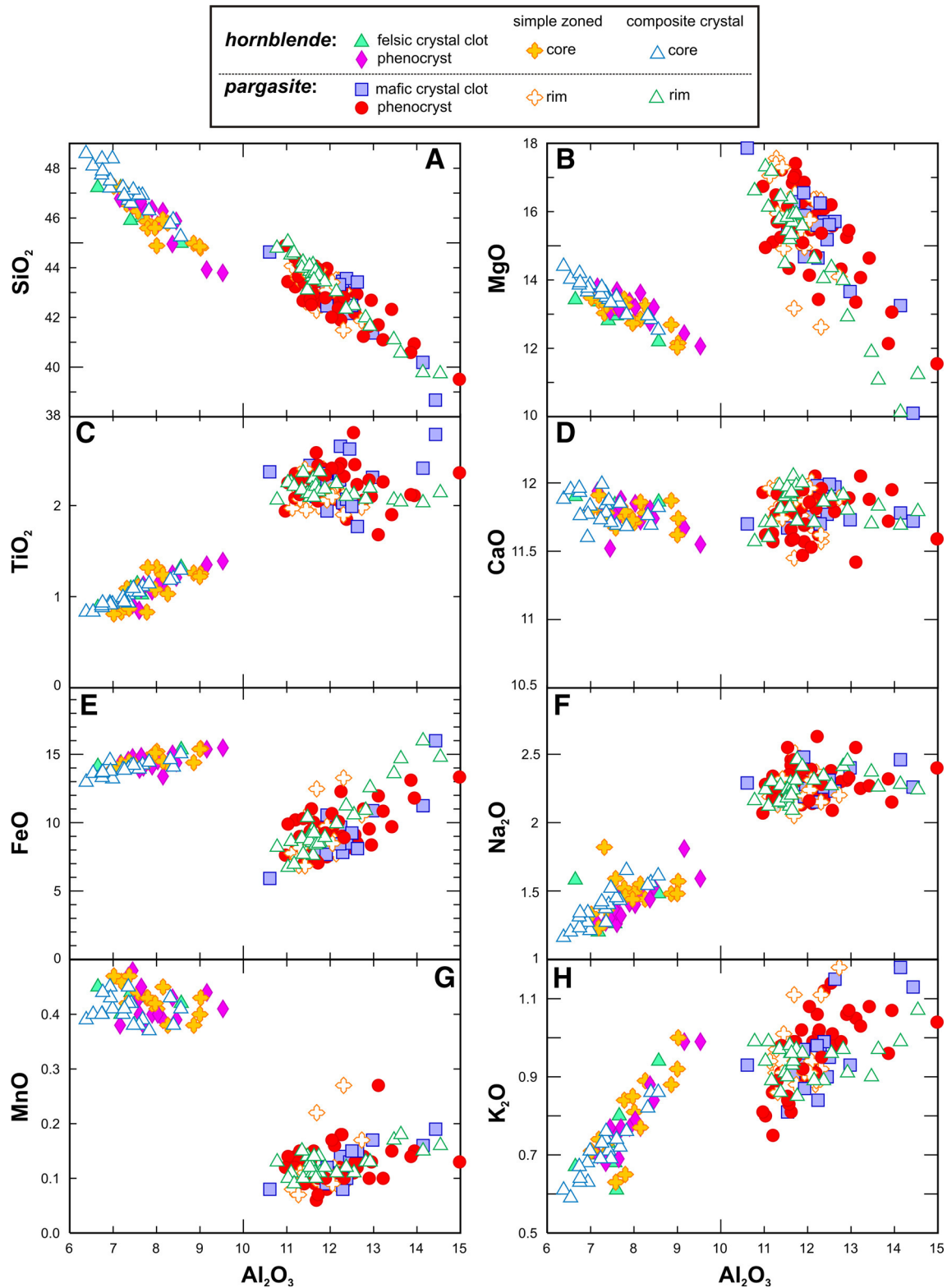


Fig. 4 Major element variation diagrams for the studied amphiboles of the Ciomadul dacite: Al₂O₃ versus SiO₂ (a), MgO (b), TiO₂ (c), CaO (d), FeO (e), Na₂O (f), MnO (g), and K₂O (h) contents. All oxides are in wt%

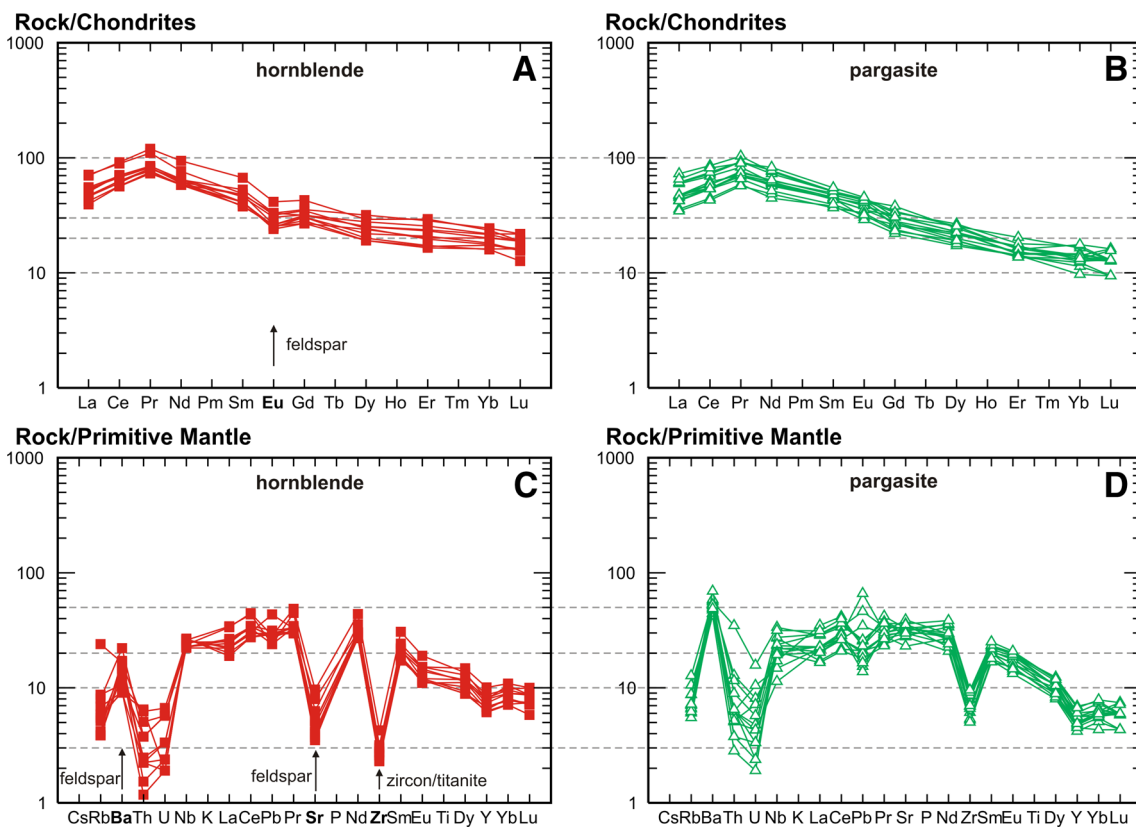


Fig. 5 Chondrite-normalized (Nakamura 1974) REE variation diagrams (a, b) and primitive mantle-normalized (Sun and McDonough 1989) trace element variation diagrams (c, d) of the studied amphiboles from the Ciomadul dacite

427 compositions that are seen in the two main amphibole
 428 populations with the full range of compositional variation
 429 seen even in a single crystal. These crystals are 2–3 mm
 430 sized, usually much larger than the other phenocrysts. The
 431 crystals can be divided into three parts: a rounded, reacted
 432 core, which is surrounded by a thin zone of clinopyroxene
 433 and an oscillatory-zoned amphibole rim (Fig. 7, line 6).
 434 The crystal core contains mineral inclusion (biotite, apatite,
 435 titanite) and compositionally is indistinguishable from
 436 hornblende phenocrysts. The rim shows the same type of
 437 oscillatory zoning as Type B2 pargasites. The composi-
 438 tional variation in these crystals is particularly remarkable,
 439 since it overlaps the whole chemical variability of the
 440 amphibole phenocrysts (Fig. 4). Despite the relatively rare
 441 occurrence of the composite crystals, they have a great
 442 significance concerning the condition of the magma
 443 reservoir.

444 Al^{IV}–Mg# systematics and substitutions in the zoned
 445 amphibole phenocrysts

446 Three intracrystalline compositional trends can be distin-
 447 guished in the Al^{IV}–Mg# diagram (Fig. 8a). Trend 1 is a
 448 continuous low-slope negative trend that is observed in the

hornblende group including type A1 patchy and type B1
 oscillatory-zoned crystals. Trend 2 is also a continuous
 negative trend, but its slope is much steeper and it is typical
 for the pargasite group (type B2 and rim of type D). The
 composition of these crystals is controlled by the Ti-
 tschermak [Si^{IV} + Mg^{VI} = Al^{IV} + Ti^{VI}] and edenite sub-
 stitution [Si^{IV} + (□)^A = Al^{IV} + (Na + K)^A]. Some role
 of the Al-tschermak substitution [Si^{IV} + Mg^{VI} = -
 Al^{IV} + Al^{VI}] can be inferred in the Type B2 crystals. The
 third intracrystalline compositional variation of amphiboles
 is the covariation of Al^{IV} and Mg# characterizing core-to-
 rim variation of Type C and Type A2 crystals. It is rep-
 resented by the positive, non-continuous trend 3 that
 associates with increasing Ti, Al^{VI}, and (Na + K)^A from
 core to rim suggests the role of edenite and tschermak
 substitutions.

Amphibole thermobarometry

Empirical and experimental studies indicate that amphibole
 composition can be effectively used to quantify the pre-
 eruptive p–T conditions during crystallization (e.g., Ham-
 marstrom and Zen 1986; Johnson and Rutherford 1989a;

Author Proof

470 Blundy and Holland 1990; Anderson and Smith 1995;
471 Ernst and Liu 1998; Bachmann and Dungan 2002; Ridolfi
472 et al. 2010). For the estimation of the pre-eruptive condi-
473 tions, the following strategy was applied: first, we com-
474 pared the composition of the Ciomadul amphiboles with
475 experimental results that was followed by the application
476 of different thermobarometric techniques. The experimen-
477 tal data set was filtered as suggested by Ridolfi et al. (2010)
478 to avoid inconsistent amphiboles. This comparison could
479 be used as a first approximation of the pre-eruptive
480 parameters.

481 The composition of the Ciomadul amphiboles and the
482 coexisting minerals is such that several different thermo-
483 barometric methods can be applied. The Ridolfi et al.
484 (2010) amphibole thermobarometer called here R2010, and
485 its later extension (Ridolfi and Renzulli 2012, called here
486 as R2012) is calibrated for a wide range of conditions and
487 can thus be applied for both amphibole groups in the
488 Ciomadul dacite. The other advantage of this thermobar-
489 ometer is that it does not require other minerals to be in
490 equilibrium, and therefore, the intensive parameters can be
491 calculated even along zoning profiles in single amphiboles.
492 Petrographic observations and trace element data indicate
493 that low-Al hornblendes could crystallized along with the
494 mineral assemblage that is required for the amphibole
495 thermobarometric calculation developed by Anderson et al.
496 (2008) (called here as A2008) (RiM69_Ch04_hbld_-
497 plag_thermo-jla.xls spreadsheet). This thermobarometry
498 comprises the Al^{tot} in amphibole barometry ($P_{Al-in-am}$)
499 (Schmidt 1992; Anderson and Smith 1995) and the
500 amphibole–plagioclase thermometry (Blundy and Holland
501 1990; Holland and Blundy 1994). Hornblendes often
502 coexist with glomerocrystic plagioclases (Fig. 2f), and they
503 can be considered as cocrystallized phases. On the other
504 hand, pargasites were observed with plagioclase micro-
505 phenocrysts as touched pairs (Fig. 2e) and were used in the
506 Anderson's calculation in spite of the lack of the necessary
507 mineral phases. The hygro-barometer of Krawczynski et al.
508 (2012) (K2012) was used to estimate the crystallization
509 pressure of pargasites. The results of thermobarometric
510 calculations are summarized in Fig. 9.

511 Pre-eruptive temperature estimation

512 Comparison of the Ciomadul amphiboles with experimental
513 amphibole compositions indicates that the two amphibole
514 groups could crystallize over two distinct temperature ranges
515 (Fig. 10), and this is corroborated by the thermometric cal-
516 culations. Low-Al hornblendes coexist and probably co-
517 crystallized with a mineral assemblage of biotite, K-feldspar,
518 quartz, plagioclase, titanite, apatite, zircon, allanite, and
519 rhyolitic melt. Experimental studies on similar dacitic rock
520 composition and mineral assemblage (e.g., Fish Canyon tuff

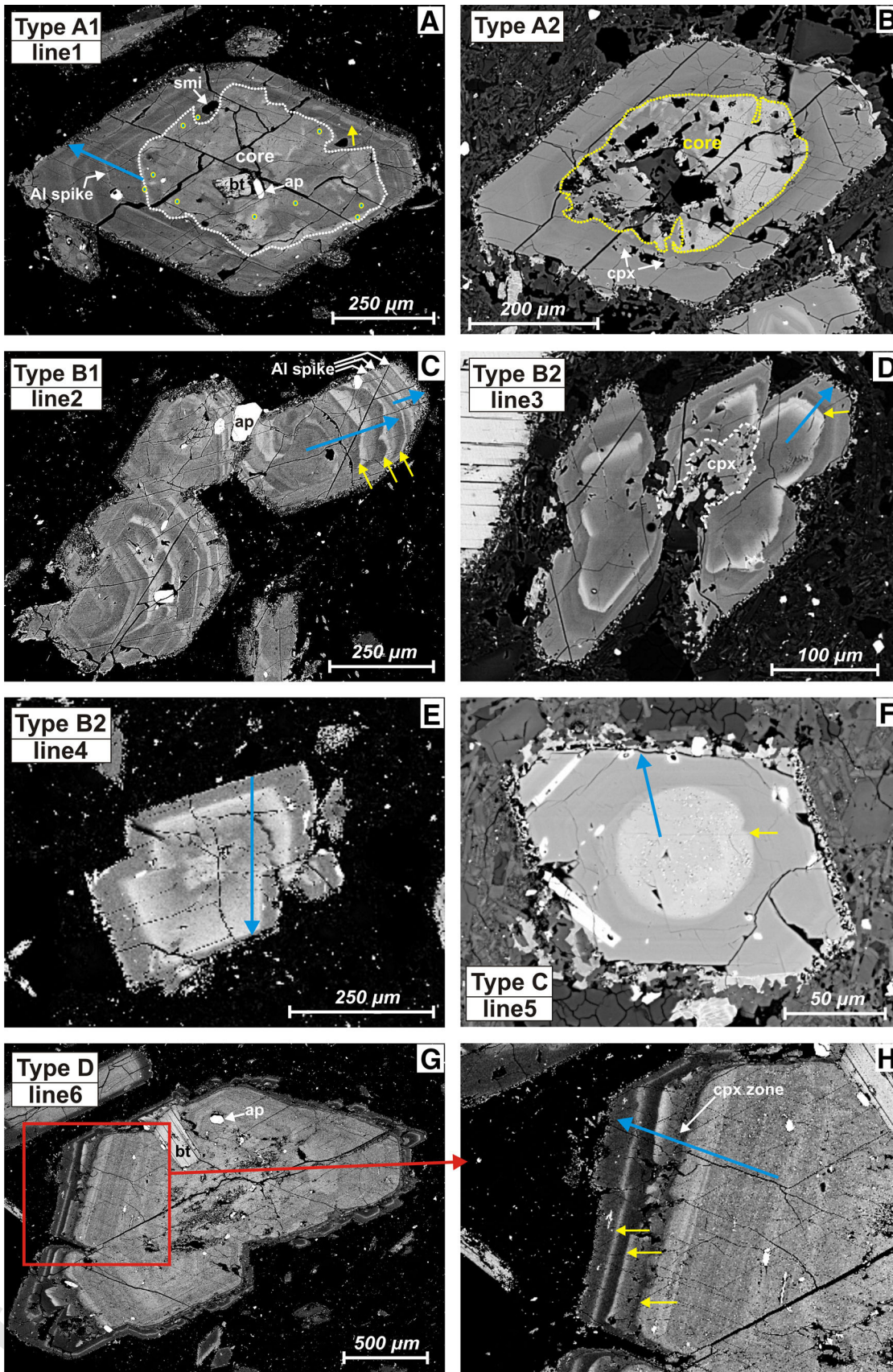
Fig. 6 BSE images showing the zoning patterns and textures of
amphiboles in the Ciomadul dacite. *Smallest arrows* show dissolution
surfaces. Compositional profiles of amphiboles are indicated by *large
thick arrows* in Fig. 7. **a** Type A1 patchy-zoned amphibole; the *points*
indicate the places of chemical measurements from the patchy core.
b Type A2 patchy zoning with spongy core in amphibole. Irregular
dotted lines indicate the outlines of the patchy cores. **c** Type B1 cyclic-
zoned amphiboles (hornblende). **d** Type B2 cyclic zoning in amphiboles
(pargasite). **e** Type B2 cyclic-zoned amphibole (pargasite). **f** Type C
simple zoning in amphibole. **g** Type D composite amphibole crystal with
internal breakdown patches in its core. **h** Enlargement of the area
indicated by the rectangle in picture **g** displaying the dissolution
surfaces as well as the clinopyroxene zone. *Bt* biotite, *ap* apatite, *smi* silicate melt
inclusion, *cpx* clinopyroxene

dacite, Johnson and Rutherford 1989b) reproduced amphi- 521
boles with similar composition at near-solidus temperatures 522
($<800\text{ }^{\circ}\text{C}$). The amphibole–plagioclase thermometry yields 523
 $T_{am-plag} = 732 \pm 27\text{ }^{\circ}\text{C}$ for mineral pairs, which are in 524
contact with each other and $T_{am-plag} = 730 \pm 15\text{ }^{\circ}\text{C}$ for the 525
hornblende composition combined with mean plagioclase 526
glomerocrystal core composition. For the same amphibole 527
crystals, the R2010 thermometer gives an average tempera- 528
ture $T_{R2010} = 821 \pm 20\text{ }^{\circ}\text{C}$, which is almost $100\text{ }^{\circ}\text{C}$ higher 529
then the previous values. The R2012 calibration provides a 530
little bit lower temperature ($T_{R2012} = 776 \pm 21\text{ }^{\circ}\text{C}$) than the 531
R2010, and this is close to the $T_{amp-plag}$ within error. 532

The high-Al pargasites fall into the experimental com- 533
position field of amphiboles that was produced at much 534
higher temperatures, i.e., $>900\text{ }^{\circ}\text{C}$. Thermometric calcu- 535
lations give high crystallization temperature values 536
($T_{R2010} = 972 \pm 20\text{ }^{\circ}\text{C}$, $T_{R2012} = 944 \pm 20$). The amphi- 537
bole–plagioclase thermometry indicates lower temperature 538
 $T_{am-plag} = 837 \pm 20\text{ }^{\circ}\text{C}$ for the analyzed pargasite–pla- 539
gioclase pairs and $T_{am-plag} = 840 \pm 11\text{ }^{\circ}\text{C}$ for the 540
pargasite composition combined with mean the core com- 541
position of plagioclase microphenocrysts. 542

Estimated depth of the magma storage 543

Pressure of the amphibole crystallization, i.e., the depth of 544
the magma storage, was also calculated using the same 545
strategy outlined in the previous section. Comparison of 546
our data and the experimental data set suggests amphibole 547
crystallization in the mid- to lower-crust beneath the 548
Ciomadul volcano ($P < 400\text{ MPa}$, $D < 15\text{ km}$). Horn- 549
blendes crystallized between 200 and 300 MPa and parga- 550
sites between 50 and 400 MPa according to the 551
experimental data set. The so-called Ridolfi barometers 552
(R2010, R2012) indicate that low-T hornblendes crystal- 553
lized in a shallow magma chamber ($P_{R2010} = 130 \pm 24\text{ -}$ 554
MPa, $D = 5 \pm 1\text{ km}$ depth) while the high-T pargasites 555
could evolve in a significantly deeper level 556
($P_{R2010} = 395 \pm 104\text{ MPa}$, $D = 15 \pm 4\text{ km}$) (Fig. 9). 557
The two barometers give fairly similar pressure range for 558



559 the two distinct amphibole group, respectively; the only
560 difference is the occasional large pressure values (up two
561 $\sim 1,500$ MPa) yielded by the R2012 technique.

562 On the other hand, the Al^{tot} in amphibole barometry (P_{Al} -
563 $in-am$) indicates that the two amphibole group crystallized at
564 the same depth interval. For the low-temperature *hornblen-*
565 *des*, this calculation indicates deeper storage (262 ± 40 MPa,
566 $D 10 \pm 2$ km) than the R(2010) and R2012 barometry. In the
567 case of the high-T pargasites, the calculated pressure is lower
568 (290 ± 48 MPa, $D 11 \pm 2$ km) than the values that were
569 calculated by the R2010 and R2012 equations. The Kra-
570 wczynski et al. (2012) barometry yields similar pressure for
571 pargasites (306 ± 124 MPa)—using the oxygen fugacity
572 values calculated by the R2012—that is partially overlapping
573 with the results of Al^{tot} in amphibole barometry while
574 yielding larger pressure range.

575 Amphibole p–T–H₂O–fO₂ profiles

576 The R2010 and R2012 equations require only the composition
577 of amphibole and thus enable p–T–H₂O–fO₂ profiles to be
578 calculated in zoned amphiboles. We selected representative
579 crystals having the typical zoning patterns of the Ciomadul
580 amphiboles to check the intracrystalline variation of the
581 intensive parameters. The R2010 profiles show significant
582 variations in temperature and pressure. In the oscillatory-zoned
583 amphiboles, the temperature variation is about 60–80 °C,
584 while the pressure varies by 100–400 MPa in single amphi-
585 boles. The H₂O and fO₂ profiles also show fluctuations
586 principally in the amphiboles having type B2 oscillatory zon-
587 ing. The fluctuations in the intensive parameters clearly mirror
588 the Al^{tot} and Mg-number variations along the profiles (Fig. 11,
589 lines 2 and 3). In the simple-zoned amphiboles, a strong and
590 sharp increase in temperature (by ~ 150 °C) and pressure (by
591 more than 200 MPa) was observed in the rim, but H₂O and
592 fO₂ remain constant. The R2012 equations also show fluctu-
593 ations in the estimated parameters but the interpretation of
594 these changes is often controversial (e.g., high fO₂ in the low
595 Mg-number zone). Hence, these profiles were not used during
596 the interpretation. The composite crystals show the largest
597 intracrystalline variation in the calculated parameters. The p–T
598 values of a single composite crystal cover the whole range that
599 was calculated for the Ciomadul amphibole phenocrysts
600 (Fig. 11, line 6).

601 Discussion

602 The significance of Al^{IV} versus Mg# interrelation

603 The large compositional variation in the Ciomadul
604 amphiboles covers the range typical for intermediate
605 magmas. However, unusually in our case, this large

Fig. 7 Compositional profiles— $(Na + K)^A$, Al^{VI} , Ti, Mg, and Al^{IV} —of the studied amphiboles, which are shown in Fig. 6. Lines 2, 3, 5, and 6 are core-to-rim profiles, and line 4 is a rim-to-rim traverse. *Line1* the compositions of the patches in the core (Fig. 6a) are plotted as separate points, and the compositions of the Al^{IV} -richest and Al^{IV} -poorest points are connected with dotted vertical lines. *Dashed vertical lines* indicate dissolution surfaces. *Line5* the zone boundary of the simple-zoned amphibole (Fig. 6f) is affected by diffusion (d.z.). The typical error is indicated by the *symbol size*

606 variability can be detected even in a single crystal (com-
607 posite amphiboles; Fig. 12). Large chemical variation of
608 amphiboles is often difficult to interpret (De Angelis et al.
609 2013), because the amphibole composition responds sensi-
610 tively to changes in many thermodynamic parameters,
611 such as melt composition, pressure, temperature, redox
612 state, and volatile content of the magma and the co-crys-
613 tallizing mineral phases (e.g., Johnson and Rutherford
614 1989a; Schmidt 1992; Anderson and Smith 1995; Ernst and
615 Liu 1998; Scaillet and Evans 1999; Bachmann and Dungan
616 2002; Pichavant et al. 2002; Rutherford and Devine 2003;
617 Sato et al. 2005; Krawczynski et al. 2012). Consequently,
618 the measured compositional variation is a net result of the
619 combination of these parameters. Thus, it is important to
620 determine which parameters are responsible for the
621 observed inter- and intracrystalline compositional varia-
622 tions to avoid misinterpretations of the thermobarometric
623 results (Shane and Smith 2013). The substitution analysis
624 (i.e., studying the correlation of Al^{IV} and Ti, $A^{(Na+K)}$, Al^{VI} ,
625 Ca, etc.) is the most common way to determine the main
626 (intensive) parameters that could control the amphibole
627 crystallization (e.g., Bachmann et al. 2002, Humphreys
628 et al. 2006, De Angelis 2013). Our findings indicate that
629 although this step should not be ignored, a better inter-
630 pretation can be achieved, when it is completed by the
631 analyses of Al^{IV} versus Mg# interrelation and the varia-
632 tions of trace element contents.

633 The changes in the conditions during the magma evolution
634 are reflected principally in the variation in the tetrahedral
635 alumina (Al^{IV}) value and the Mg number of amphiboles (e.g.,
636 Bachmann and Dungan 2002; Rutherford and Devine 2008;
637 Krawczynski et al. 2012), suggesting that these two variables
638 can be useful to recognize and distinguish the main processes
639 that control the growing amphibole composition. The
640 amphiboles of the Ciomadul dacite define two main contin-
641 uous compositional trends in the Al^{IV} versus Mg-number
642 diagram (Fig. 8a). The inverse variation of Al^{IV} and Mg
643 number can be interpreted as coupled substitutions according
644 to the substitution equations that were presented for amphi-
645 boles by Vyhnał et al. (1991) and Almeev et al. (2002). These
646 negative compositional trends as well as the positive corre-
647 lation between Al^{IV} and Ti, $(Na + K)^A$, Al^{VI} indicate the role
648 of edenite [$Si^{IV} + ()^A = Al^{IV} + (Na + K)^A$], Ti-tschermak
649 [$Si^{IV} + Mg^{VI} = Al^{IV} + Ti^{VI}$], and Al-tschermak [$Si^{IV} +$

Author Proof

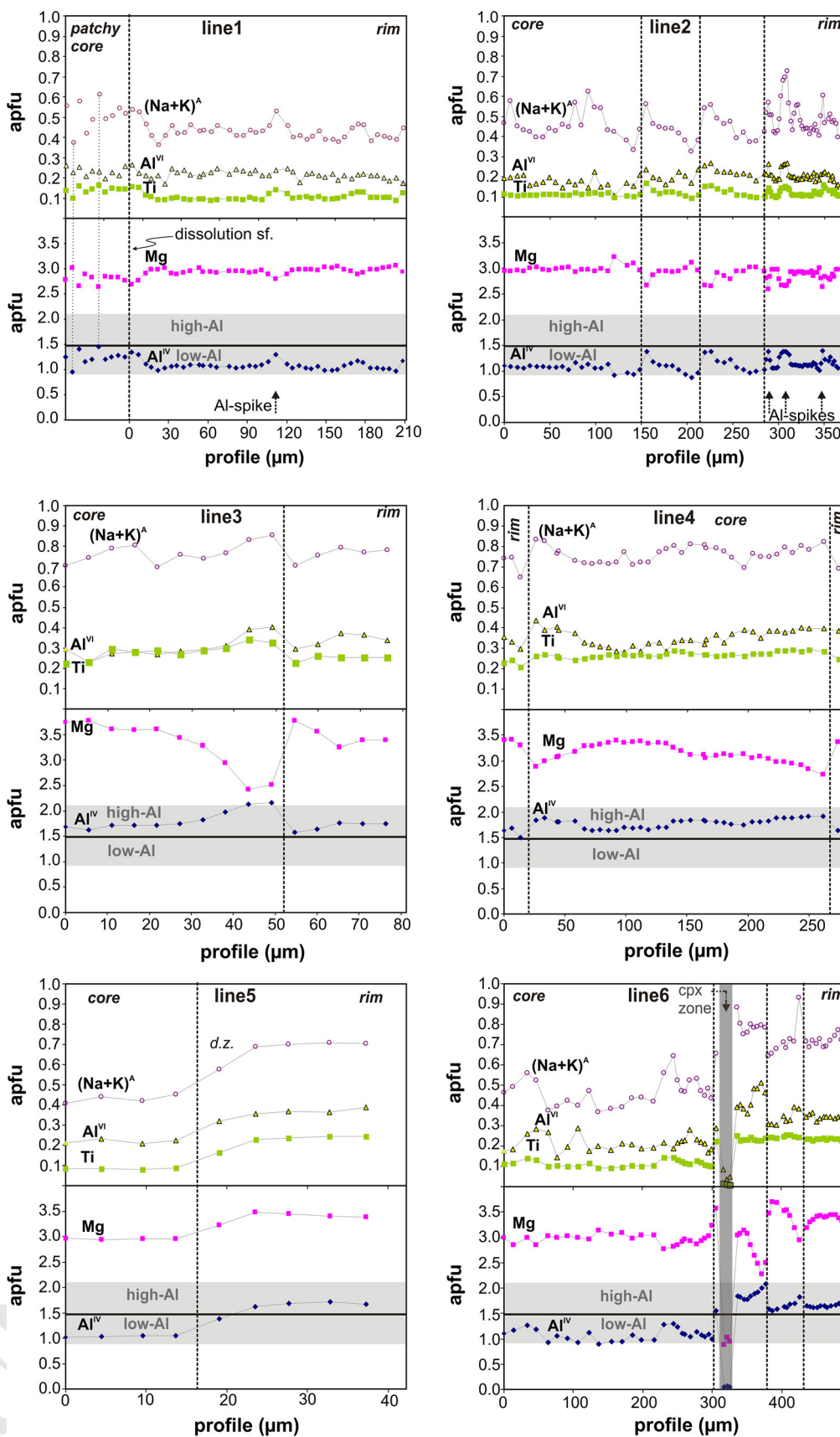
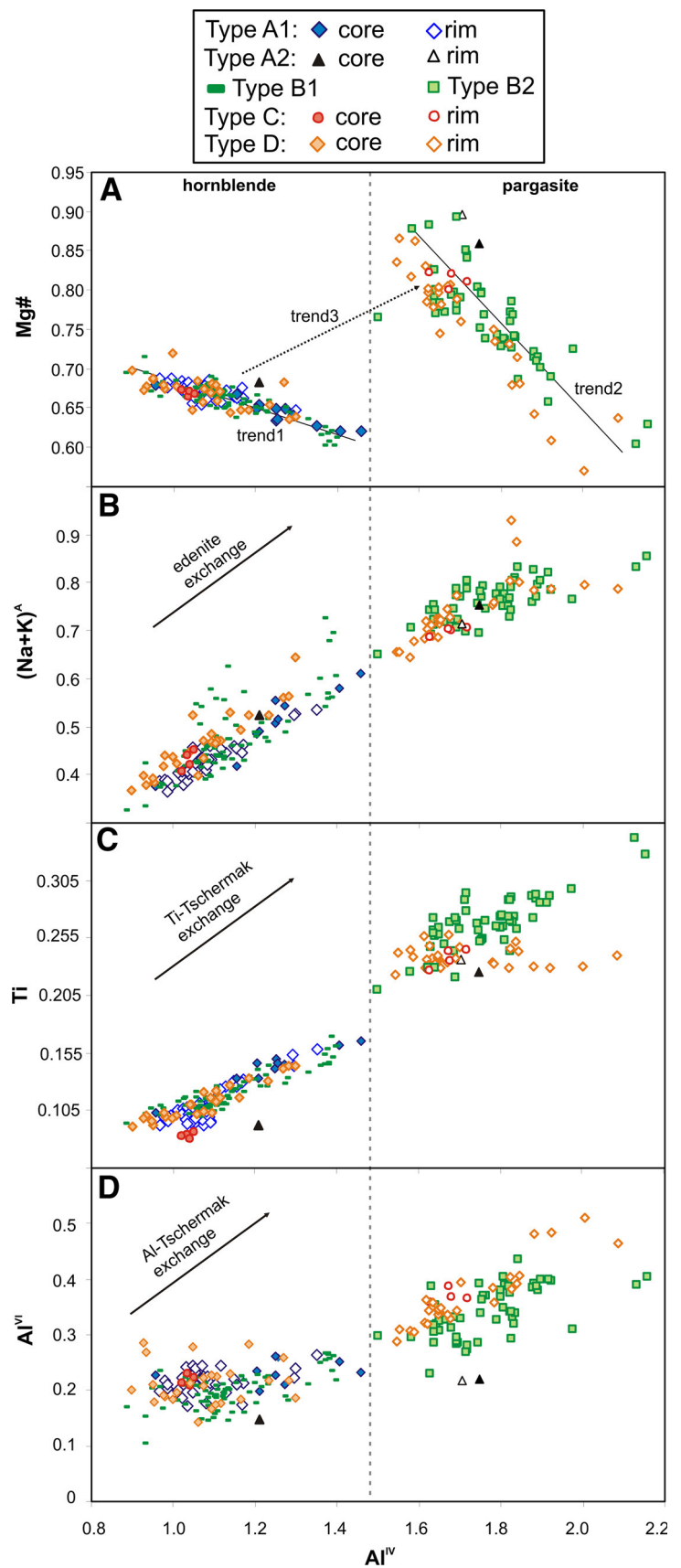
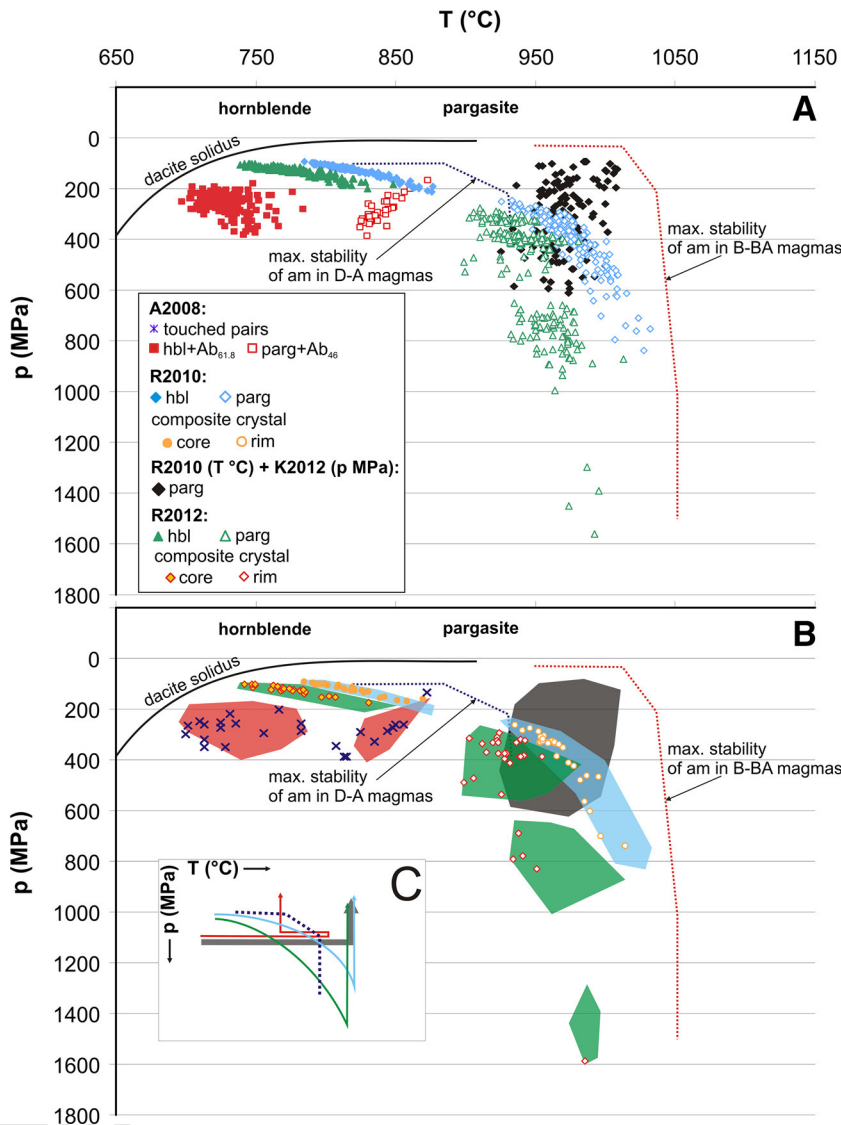


Fig. 8 Plots of Al^{IV} versus $Mg\#$ ($Mg/(Mg + Fe^{2+})$) (**a**), $(Na + K)^A$ (**b**), Ti (**c**), and Al^{VI} (**d**) illustrating the substitution mechanisms in the Ciomadul amphiboles. The *exchange vectors* are indicated in the **b**, **c**, and **d** diagrams. **a** Trends 1, 2, 3 show intracrystalline Al^{IV} - $Mg\#$ systematics of zoned amphiboles. All plotted values are in apfu



Author Proof

Fig. 9 Temperature–pressure plots (a, b) of the Ciomadul amphiboles that summarizes the results of amphibole thermobarometry. *Inset* in b shows various p–T paths according to the thermobarometry and crystallization history of amphiboles, the colored arrows are identical for the different thermobarometers used in determination of the p–T paths. The gray arrow shows our preferred p–T path (see details in the text). Dacite solidus is according to Holtz et al. (2001). The maximum stability of amphiboles in dacite and andesite was determined using the experimental results of Rutherford and Devine (1988); Johnson and Rutherford (1989a, b); Schmidt (1992); Martel et al. (1999); Sato et al. (1999); Scaillot and Evans (1999); Rutherford and Devine (2003); Costa et al. (2004); Holtz et al. (2005); Sato et al. (2005); Larsen (2006); Rutherford and Devine (2008); Simakin et al. (2009). Maximum stability of amphiboles in primitive magmas (basalt, basaltic andesite, Mg andesite) is based on the experiments of Pichavant et al. (2002); Grove et al. (2003); Barclay and Carmichael (2004); Adam et al. (2007); Krawczynski et al. (2012); Simakin et al. (2012). See text for details



650 Mg^{VI} = Al^{IV} + Al^{VI}] substitutions (Fig. 8) as it has been
 651 described also in other localities (e.g., Bachmann and Dungan
 652 2002; Rutherford and Devine 2003; Sato et al. 2005; Rutherford
 653 and Devine 2008; Humphreys et al. 2009a, b). These
 654 substitutions are sensitive primarily to the crystallization
 655 temperature and pressure (e.g., Johnson and Rutherford
 656 1989a; Blundy and Holland 1990; Rutherford and Devine
 657 2003). The clear separation of the two trends (indicated by
 658 “trend 3”) suggests that the crystallization of amphiboles
 659 may have occurred in two different magmas. According to the
 660 experimental data, the Al/Si ratio of amphibole depends on
 661 the Al/Si ratio of the melt (Sisson and Grove 1993; Pichavant
 662 et al. 2002). Increasing silica activity in the melt increases the
 663 silica content of the coexisting amphibole following the
 664 equation pargasite + 4SiO₂ = hornblende + albite (Blundy
 665 and Holland 1990). As a consequence, the alumina content
 666 in the tetrahedral site decreases and therefore the Al^{IV} content
 667 of the amphiboles could be viewed as a relative

differentiation index too (Ridolfi et al. 2010). This can be
 668 refined by plotting experimentally produced amphibole
 669 compositions on the Al^{IV} versus Mg diagram. Figure 10
 670 shows that low-T amphiboles crystallized from dacitic
 671 magmas have low-Al^{IV} and a low-Mg number (blue field). In
 672 contrast, amphiboles formed from more mafic magmas at
 673 high temperature tend to have higher Al^{IV} and higher Mg
 674 numbers. As the silica content of the parent magma decreases,
 675 the Al^{IV} values of the amphiboles increase (yellow field in
 676 Fig. 10). Mafic magma replenishment into a silicic reservoir
 677 could cause abrupt decrease in silica activity in the mixed
 678 magma. Moreover, mafic input will also increase the Mg/
 679 (Mg + Fe) ratio in the mixed magma; thus, concomitant
 680 increase in Al^{IV} and Mg# of amphibole will be expected due
 681 to magma replenishment. The trace element composition of
 682 the studied amphiboles appears to support the mixing model
 683 since the low-Al hornblendes have much lower Sr, Ba, Eu,
 684 and Zr contents than the high-Al pargasites. As the trace
 685

Author Proof

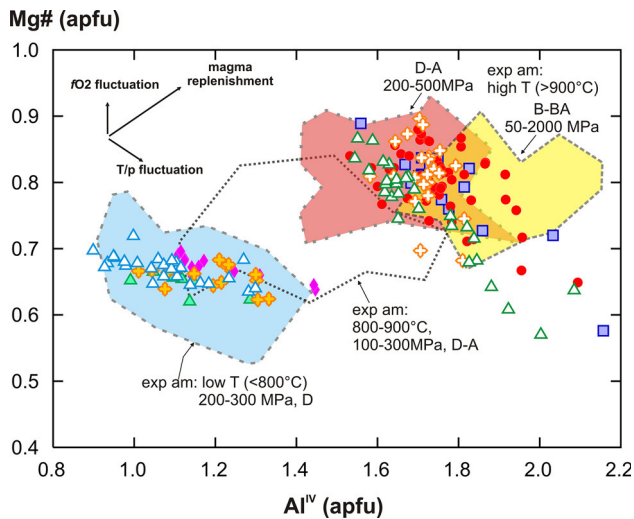


Fig. 10 Plot of Al^{IV} versus $Mg\#$ showing the Al^{IV} – $Mg\#$ systematics of Ciomadul and experimental amphiboles. Symbols (for Ciomadul amphiboles) as in Fig. 4. The black arrows at the upper left edge indicate the interpretation of Al^{IV} – $Mg\#$ systematics of amphiboles (for details, see text). Experimental results were filtered by the method of Ridolfi et al. (2010). High- and low-temperature experimental amphiboles can be separated in the plot. The starting materials used in the experiments are also indicated (D: dacite, A: andesite, BA: basaltic andesite, B: basalt). Results of the following experiments are plotted: Rutherford and Devine (1988); Johnson and Rutherford (1989a, b); Schmidt (1992); Martel et al. (1999); Sato et al. (1999); Scaillet and Evans (1999); Pichavant et al. (2002); Grove et al. (2003); Rutherford and Devine (2003); Barclay and Carmichael (2004); Costa et al. (2004); Holtz et al. (2005); Sato et al. (2005); Larsen (2006); Adam et al. (2007); Rutherford and Devine (2008); Simakin et al. (2009); Krawczynski et al. (2012); Simakin et al. (2012)

686 element content is primarily influenced by the composition of
 687 the coexisting melt, the observed differences indicate that the
 688 two amphibole populations in the Ciomadul dacites were
 689 formed in different magmas. Similarly, positive Al^{IV} – $Mg\#$
 690 trends in amphiboles were reported at other volcanoes (e.g.,
 691 Soufriere Hills, Humphreys et al. 2009a; Unzen, Sato et al.
 692 2005) where compositional mixing was detected (Nakamura
 693 1995; Murphy et al. 2000).

694 Interpretation of amphibole thermobarometry

695 Application of various amphibole thermometers indicates
 696 that the hornblendes in the Ciomadul dacite crystallized at
 697 much lower temperature than the pargasites, but they yield
 698 different temperature ranges for each population. According
 699 to the amphibole–plagioclase thermometry, the hornblendes
 700 crystallized at almost 100 °C lower temperature than it is
 701 indicated by the R2010 thermometer. This difference is
 702 notable even if we consider the relatively large error of the
 703 thermometers ($T_{am-plag}$ error = 40 °C according to Holland
 704 and Blundy (1994), and T_{R2010} error = 22 °C according to
 705 Ridolfi et al. (2010)). Experimental works on the dacitic rocks

of the Fish Canyon Tuff resulted in amphiboles and coexist- 706
 ing mineral assemblage similar to the Ciomadul rocks at low 707
 temperatures (~740 °C; Johnson and Rutherford 1989b). 708
 Thus, the R2010 thermometry appears to overestimate the 709
 crystallization temperature of the Ciomadul hornblendes but 710
 the R2012 yields more appropriate results. Consequently, the 711
 hornblendes crystallized below 800 °C may be at ~730 °C 712
 as indicated by amphibole–plagioclase thermometry. For the 713
 high- Al amphiboles (pargasites), the amphibole–plagioclase 714
 thermometer gives consistently lower crystallization tem- 715
 perature than the R2010 and R2012. This is corroborated by 716
 the comparison with the experimental data set (Fig. 10) and is 717
 in agreement with the suggestion of Blundy and Cashman 718
 (2008) who claimed that this thermometry is not so accurate 719
 for amphiboles with such high- Mg number as shown by the 720
 Ciomadul pargasites. On the other hand, the results of the 721
 R2010 and R2012 thermometers are in agreement with the 722
 experimental data and most likely indicate the crystallization 723
 temperature (940–980 °C) of the pargasites. Thus, careful 724
 evaluation of the thermometric results indicates that the 725
 crystallization of the hornblendes and pargasites in the 726
 Ciomadul magma could occur at significantly different 727
 (about $\Delta T = 200$ °C) temperatures. Additionally, the Ridolfi 728
 et al. (2010) thermometer likely overestimates the crystalli- 729
 zation temperature of low- Al (cold) amphiboles. 730

The barometric calculations can be used to infer the pre- 731
 eruptive magma chamber architecture beneath the Ciomadul 732
 volcano. Both the R2010 and R2012 barometry imply 733
 a vertically extended magma plumbing system in which the 734
 two amphibole populations could crystallize at two separated 735
 magma storage levels. According to these barometers, the 736
 hornblendes were crystallized at shallow depth 737
 (~5 km), whereas the pargasites were formed at much 738
 greater depth, in the middle crust (~15 km). The Al^{IV} 739
 versus Al^{VI} correlation in the two amphibole populations 740
 indicates the role of the pressure-sensitive Al -tschermak 741
 substitution during their crystallization and seemingly 742
 support these barometric results. However, the crystal 743
 growth stratigraphy and the inferred growth history indicate 744
 that the crystallization of the high- Al pargasites could 745
 not occur deeper than the low- Al hornblendes. Namely, the 746
 calculated pressure profiles of simple-zoned and composite 747
 amphiboles using the R2010 and R2012 barometer indicate 748
 an abrupt increase in the crystallization pressure at the 749
 core–rim boundary. This would mean that the rim of these 750
 amphiboles would crystallize about 8–10 km deeper than 751
 the cores, and therefore, the low- Al hornblendes should 752
 sink many kms in the magma reservoir not long before the 753
 eruption. A similar model (i.e., circulating crystals) was 754
 suggested for the origin of the cyclically zoned amphiboles 755
 in the Mt. St. Helens dacites, where a vertically elongated, 756
 large magma chamber is hypothesized (Pallister et al. 757
 2008). However, no such simple-zoned and composite 758

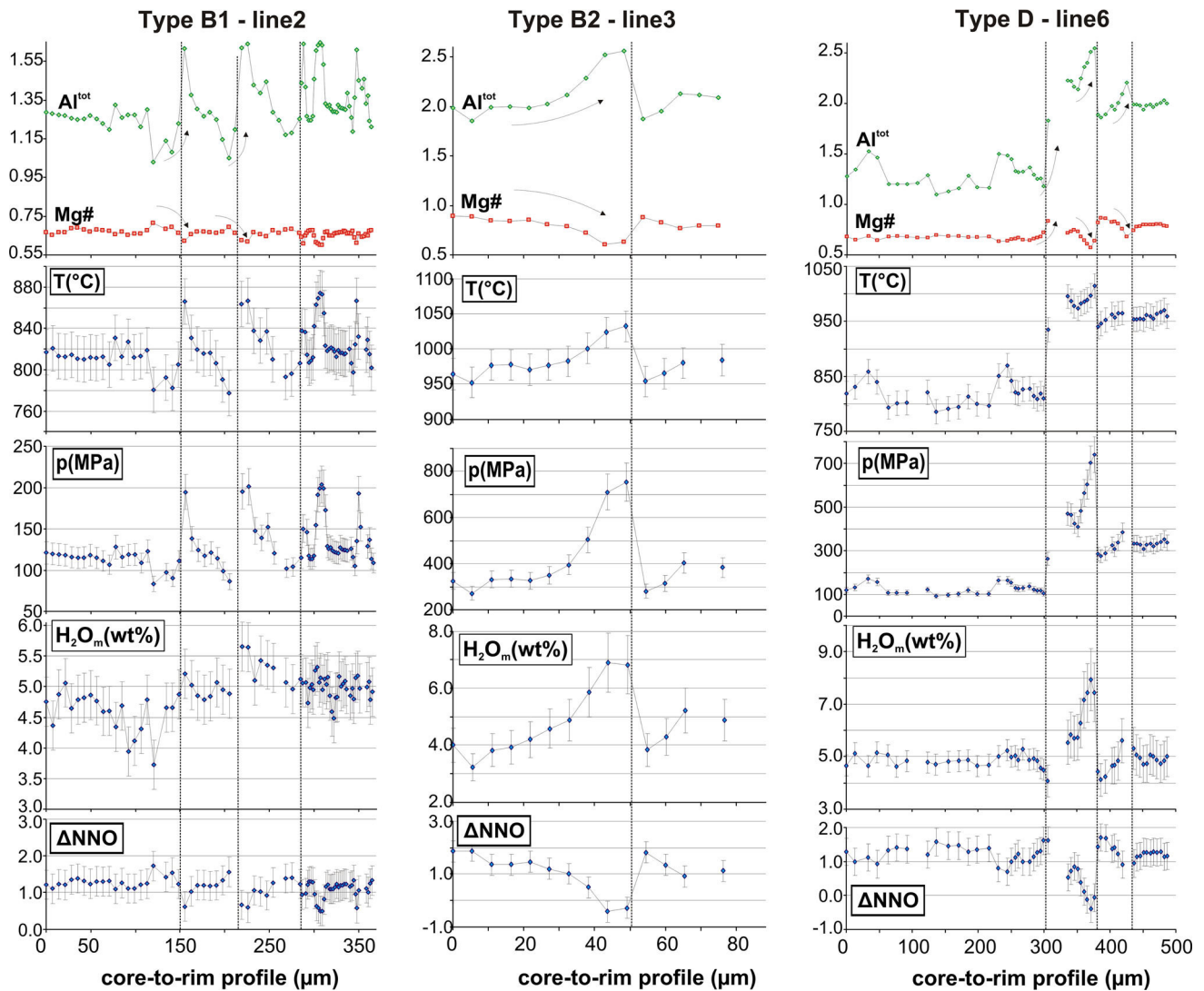


Fig. 11 Temperature (T), pressure (p), melt H_2O content (H_{2O_m}), oxygen fugacity (fO_2), and compositional (Al^{tot} , $Mg\#$ [apfu]) profiles of three selected amphiboles shown in Fig. 6c, d and h, respectively.

Vertical lines indicate dissolution surfaces. The intensive parameters were estimated based on the Ridolfi et al. (2010) formulation

759 amphibole crystals were described in the Mt. St. Helens
 760 rocks as we found here in the Ciomadul dacite. Moreover,
 761 in our system, the R2010 and R2012 barometry would
 762 indicate two separated magma chamber for the bimodal
 763 amphiboles, at least 5 km vertical transportations of crystals
 764 seems to be highly unrealistic scenario and rather
 765 implies that these barometers significantly overestimate the
 766 crystallization pressure of the high-Al pargasites and/or
 767 underestimate the crystallization pressure of low-Al
 768 hornblendes. Interestingly, the Al-in-amphibole barometry
 769 (Schmidt 1992; Anderson and Smith 1995) yields appropriate
 770 results (i.e., overlapping pressure values for both
 771 hornblendes and pargasites) in spite of the lack of the
 772 required coexisting mineral assemblage in the case of the
 773 pargasites. Additionally, Grove et al. (2003) and Krawczynski
 774 et al. (2012) proposed that the $Mg\#$ of the

primitive (i.e., near liquidus) amphiboles is related to the
 775 P_{H_2O} , and therefore, their hygro-barometer can be used for
 776 the pargasites. Although we do not have direct evidence of
 777 H_2O saturation in the Ciomadul magmas, the lack of negative
 778 Eu anomaly in the pargasites probably suggests that they are
 779 originated from a melt that was too H_2O -rich to crystallize
 780 plagioclase. Nevertheless, the overlapping result of the
 781 $P_{Al-in-am}$ calculations and the Krawczynski's barometry is
 782 notable and likely informative and is in agreement with the
 783 crystal growth stratigraphy. All of these suggests that the
 784 depth of the main (eruption feeder) magma storage is indicated
 785 by the range of the overlapping barometric results of hornblendes
 786 and pargasites that is approximately 200–300 MPa, 8–12 km.
 787 An important point is that the simple-zoned and composite
 788 crystals provide direct evidence that the significant variation in
 789 Al
 790

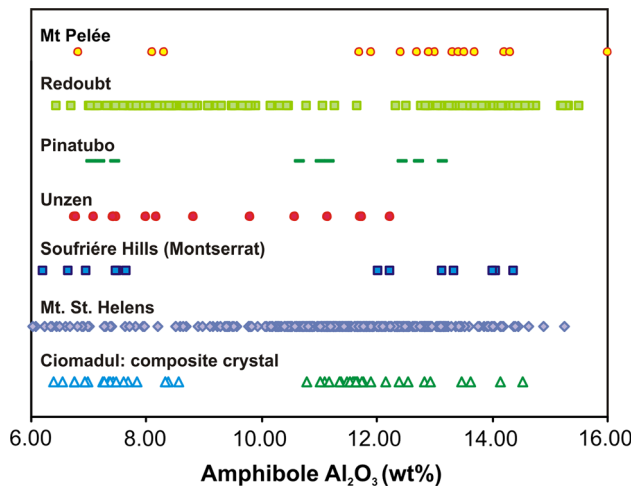


Fig. 12 Compositional variation of amphiboles from selected volcanoes. It is important to note that a single composite crystal of the Ciomadul dacite overlaps almost the entire Al_2O_3 range of the other volcanoes. Amphibole compositions are from the following references: Mt. St. Helens, Thornber et al. (2008); Mt. Pinatubo, Pallister et al. (1996); Soufrière Hills (SHV), Murphy et al. (2000); Redoubt, Coombs et al. (2012); Unzen, Sato et al. (2005); Mt Pelée, Pichavant et al. (2002) Ciomadul, this study

791 content in amphiboles cannot be always explained by
792 crystallization at different pressures/depths even if the Al-
793 tschermak substitution can be recognized. Furthermore, the
794 low-Al hornblendes—crystallized well inside their stability
795 field—of the Ciomadul dacite also demonstrate that
796 amphiboles do not necessarily crystallize along their stability
797 curve in a narrow stability field as indicated by the
798 thermobarometric formula of Ridolfi et al. (2010). Thus, it
799 can yield unrealistic estimations for the crystallization
800 conditions of crystal mush-derived amphiboles and high-Al
801 amphiboles derived from mafic hybrid magmas.

802 The origin of amphiboles in the Ciomadul dacites

803 Despite the observed diversity in zoning types and the petro-
804 graphic occurrences of the amphiboles, they can be divided
805 into two coherent compositional groups (Fig. 10). The origin
806 of the two amphibole populations is constrained based on
807 their major and trace element compositions, the coexisting
808 mineral phases, and the thermobarometric results.

809 Hornblendes in the Ciomadul dacites are characterized
810 typically by low- Al^{IV} and low-crystallization temperature,
811 suggesting that they are derived from a cold silicic magma.
812 This is supported by the petrographic observations, because
813 hornblendes are coexistent with a mineral assemblage
814 involving quartz, biotite, K-feldspar, plagioclase, titanite,
815 apatite, and zircon common to silicic magmas. Inter-
816 growths with these minerals (Fig. 2a) unambiguously
817 indicate their common origin. The trace element content of
818 hornblendes shows depletion in Ba, Sr, Zr, and Eu (Fig. 5).

819 These trace elements behave nearly compatible in amphi-
820 boles (Viccaro et al. 2007 and references therein); thus,
821 their relative depletion can be explained by co-crystalliza-
822 tion of minerals such as plagioclase, K-feldspar, titanite,
823 and zircon. The observed mineral assemblage is often form
824 felsic crystal clots in the studied dacites with up to a few
825 cm size. The texture of these felsic clots resembles plutonic
826 rock textures, suggesting that they could be derived from a
827 highly crystalline silicic magma body, where the consti-
828 tuting minerals are usually joined by solid–solid contacts.
829 Nevertheless, occurrence of thin interstitial rhyolitic glass
830 implies that this magma body still contained some melt
831 portions, i.e., it could have been a hornblende-bearing
832 crystal mush/sponge residing at shallow depth
833 ($\sim 8\text{--}12$ km) as shown by the geobarometric calculations.

834 The high-Al pargasites is characterized by high- Al^{IV}
835 content and high crystallization temperature (>900 °C),
836 suggesting that they could crystallize in a hotter, more
837 mafic magma. This is corroborated by the petrographic
838 observations, since pargasites often coexist with Fo-rich
839 olivine and Mg-rich clinopyroxenes (Fig. 2c, d). Further-
840 more, they have a distinct trace element content with no
841 depletion in the components (Ba, Sr, Zr, Eu) seen in the
842 hornblendes and resemble the trace element composition of
843 the amphiboles found in the mafic volcanic products of
844 Etna (Viccaro et al. 2007). The origin of such high-Al
845 amphiboles is often interpreted as forming in a deep mafic
846 source (e.g., Grove et al. 2003, 2005; Ridolfi et al. 2010;
847 Krawczynsky et al. 2012) and is then transferred and
848 incorporated into a more differentiated magma via mafic
849 replenishment, partly by disaggregation of the mafic
850 enclaves (Humphreys et al. 2009a). This commonly cited
851 scenario, however, does not work for the Ciomadul dacite
852 as it was discussed in the former section. In fact, there are
853 a few studies, which suggest that high-Al amphiboles can
854 crystallize also at low pressures in upper crustal magma
855 storage or even in the conduit (Sato et al. 1999; Coombs
856 et al. 2013) and this condition could be valid for the origin
857 of the Ciomadul amphiboles, as well. The low-pressure
858 formation of the Ciomadul pargasite is supported by further
859 petrographic observation, such as their occurrence around
860 reacted Mg-rich olivine crystals. Coombs and Gardner
861 (2004) showed that a reaction rim is formed around mag-
862 nesian olivine in contact with silicic magmas. Pargasites
863 are grown on this reaction rim implying that the olivines
864 were already in the silicic magma and pargasites crystal-
865 lized from a hybrid melt after the mixing of mafic and
866 silicic magmas. Although experimental studies produced
867 high-Al amphiboles such as our pargasites at low pressure
868 (e.g., Sato et al. 1999, Browne 2005, Barclay and Carmi-
869 chael 2004), direct evidence for low-pressure crystalliza-
870 tion of high-Al amphiboles is rarely presented in natural
871 rock samples (Sato et al. 2005).

872 Magma chamber processes

873 *Formation of simple zoning and the composite amphiboles*

874 Thermometric calculation of the simple-zoned and composite amphiboles from the Ciomadul dacite implies a rim
875 ward temperature rise at least with 150 °C, but it could be
876 as high as 200 °C if the results of the Holland and Blundy
877 (1994) amphibole–plagioclase thermometry are used for
878 the low-Al hornblendes (Fig. 11, line 6). This is consistent
879 with the experimental data shown in Fig. 10. Such a
880 major increase in temperature can be explained only by
881 intrusion of basaltic magma into the shallow, cold, silicic
882 magma chamber. The strong reheating is reflected also in
883 the complex zoned, composite amphiboles (Fig. 6e, f). At
884 the core–rim boundary, a narrow zone composed of
885 clinopyroxenes is observed that is interpreted as the
886 remnant of the reaction rim around the low-Al amphibole
887 formed due to thermal breakdown. This could mean that
888 the low-Al amphiboles came out of the stability field due
889 to the reheating of the silicic crystal mush body. Experimental data on amphibole stability suggest that amphiboles in dacitic magmas are stable up to about 910 °C (e.g., Rutherford and Devine 2008) that is approximately 150 °C higher than the calculated crystallization temperature of the hornblendes. This abrupt temperature increase as well as change in the Mg number toward the rim is consistent with the injection of fresh mafic magma before eruption. Isobaric reheating experiments of Browne (2005) on dacitic magma produced a breakdown rim around amphiboles with minor pargasite overgrowth. However, the extensive crystallization of the high-Al pargasites in the dacitic magma of Ciomadul needs additional mafic components during reheating. This suggests that mafic magma not only reheated the silicic resident magma but hybridization could have also occurred (e.g., Costa and Singer 2002; Rutherford and Devine 2003). A hybridization zone at the boundary of silicic and mafic magmas is also likely due to the observation that pargasites are present around hornblendes from the silicic magma and also around olivine crystals transported by the intruded mafic magma. Another explanation of this compositional shift could be a concordant increase in fO_2 and temperature, since experiments on dacitic magmas indicate that this change in redox state positively influences the amphibole Mg number and temperature also positively influences the Al^{tot} content (e.g., Scaillet and Evans 1999; Costa et al. 2004). According to Scaillet and Evans (1999), a temperature increase from 780 to 900 °C induces an increase of ~ 0.4 apfu in Al^{tot} at isobaric conditions. However, in the Ciomadul amphiboles, this variation in Al^{tot} is almost the double (~ 0.78) from core to rim, thus this cannot be produced only by a temperature

increase. Furthermore, Costa et al. (2004) reported that high T and low fO_2 promote high-Al content in the experimentally produced amphiboles instead of high T and high fO_2 that needs to increase both Al^{tot} and the Mg number. Thus, it is not likely that the observed core-to-rim compositional variation can be produced without the involvement of mafic magma replenishment and magma mixing. According to the experimental results of Kravczynski et al. (2012), the high- Al^{tot} content in pargasites suggests that the mafic magma could be hot and also water-rich. The mafic replenishment is also supported by the presence of magnesian olivine and clinopyroxene crystals in the erupted dacitic magma.

893 *Origin of the cyclic zoning in amphiboles*

894 The Ciomadul dacite contains two types of oscillatory-zoned amphiboles: type B1 and type B2. Both types show a negative trend on the Al^{IV} –Mg number diagram (Figs. 8a, 10) indicating that their crystallization was influenced by the fluctuation in intensive thermodynamic parameters. The variation in the Al content in both zoning types is primarily controlled by the temperature-sensitive edenite and Tschermak substitutions. Temperature profiles of the oscillatory-zoned amphiboles suggest 60–80 °C variation (Fig. 11, line 2, 3). This temperature change could be explained by convective motion of the magma in the magma chamber due to the temperature contrast (Couch et al. 2001). Oscillatory-zoned amphiboles, which experience convection, may also show Al-tschermak substitution as was demonstrated by Rutherford and Devine (2008). However, in our case, only type B2 crystals show Al-tschermak substitution, suggesting that type B1 crystals require another explanation. Input/degassing of volatiles could be an alternative model for the formation of oscillatory zoning as was indicated by Humphreys et al. (2009b) and Sato et al. (2005). Experimental data on the Pinatubo dacite show that the H_2O content of the melt can affect the Al^{tot} content of the amphibole (Scaillet and Evans 1999). Furthermore, fluid input/degassing may also affect the redox state of the magma, which influences the amphibole composition as well. Hence, changes in the volatile budget can indeed be reflected in the amphibole composition. Calculation of H_2O_{melt} and fO_2 values along profiles in cyclic-zoned amphibole crystals was performed using Ridolfi et al.'s (2010) equations. These variables show minor fluctuations and change at the dissolution surfaces, suggesting that volatiles might play a role in addition to the temperature change in the formation of type B1 oscillatory zoning (Fig. 11, line 2). Heat can be transferred by volatiles; thus, input of hot fluids into the magma reservoir may be responsible for the temperature variation and dissolution of the growth zones.

974 *Origin of patchy zoning in amphibole*

975 Patchy zoning can form due to open-system processes or
 976 diffusional chemical re-equilibration of a zoned crystal
 977 (Streck 2008). In the former case, disequilibrium condi-
 978 tions initiate a spongy-like dissolution of the mineral and
 979 parallel or after this, crystallization can occur with a
 980 composition reflecting changing conditions. This type of
 981 patchy zoning is commonly observed in plagioclase,
 982 clinopyroxene, or amphibole (Streck 2008). The most
 983 important feature that could help us to identify this texture
 984 is the sharpness of the compositional transition between
 985 patches and the enclosed mineral or melt inclusions at the
 986 boundary of the patches due to rapid re-growth. According
 987 to these criteria, both types of the patchy-zoned amphiboles
 988 in the Ciomadul dacite could be formed during open-sys-
 989 tem processes. Type A1 crystals show similar chemical
 990 features as the type B1 oscillatory-zoned amphiboles.
 991 Additionally, this type of patchy-zoned amphibole often
 992 has a type B1 oscillatory rim. Hence, these two zoning
 993 types might have been formed due to the same petrogenetic
 994 processes. Type A2 patchy-zoned amphiboles show similar
 995 chemical variability as the simple-zoned amphiboles sug-
 996 gesting their common origin. Based on these similarities,
 997 we can conclude that similar processes, i.e., mafic magma
 998 replenishment, could lead to the formation of the (Type
 999 A2) patchy zoning.

1000 *Processes and rates of amphibole breakdown*

1001 The amphiboles in the Ciomadul dacite show diverse
 1002 breakdown textures, suggesting that they were caused by a
 1003 combination of processes. Similar diversity of amphibole
 1004 breakdown textures was also found in the Soufrière Hills
 1005 andesite, where decompression, heating, and late stage
 1006 oxidation were all referred to as potential mechanisms
 1007 leading to amphibole breakdown (Rutherford and Devine
 1008 2003).

1009 Hornblendes with opacitic breakdown textures in the
 1010 Ciomadul dacite are often surrounded by high-temperature
 1011 pargasitic rims (Fig. 2h). Additionally, coarse-grained
 1012 clinopyroxene rims around hornblendes were also observed
 1013 (Fig. 2g) providing important evidence of reheating (Ruth-
 1014 erford and Devine 2003). The breakdown rim of high-Al
 1015 pargasites is only developed where these crystals are in direct
 1016 contact with the matrix, i.e., it should have formed by crystal-
 1017 melt reaction (Fig. 2e), suggesting that they were formed due
 1018 to decompression and degassing during magma ascent to the
 1019 surface (Rutherford and Hill 1993).

1020 Experimental works indicate that the extent of amphi-
 1021 bole breakdown is a function of the time that the amphibole
 1022 spends outside its stability field (Rutherford and Hill
 1023 1993), although it depends also on the ambient conditions

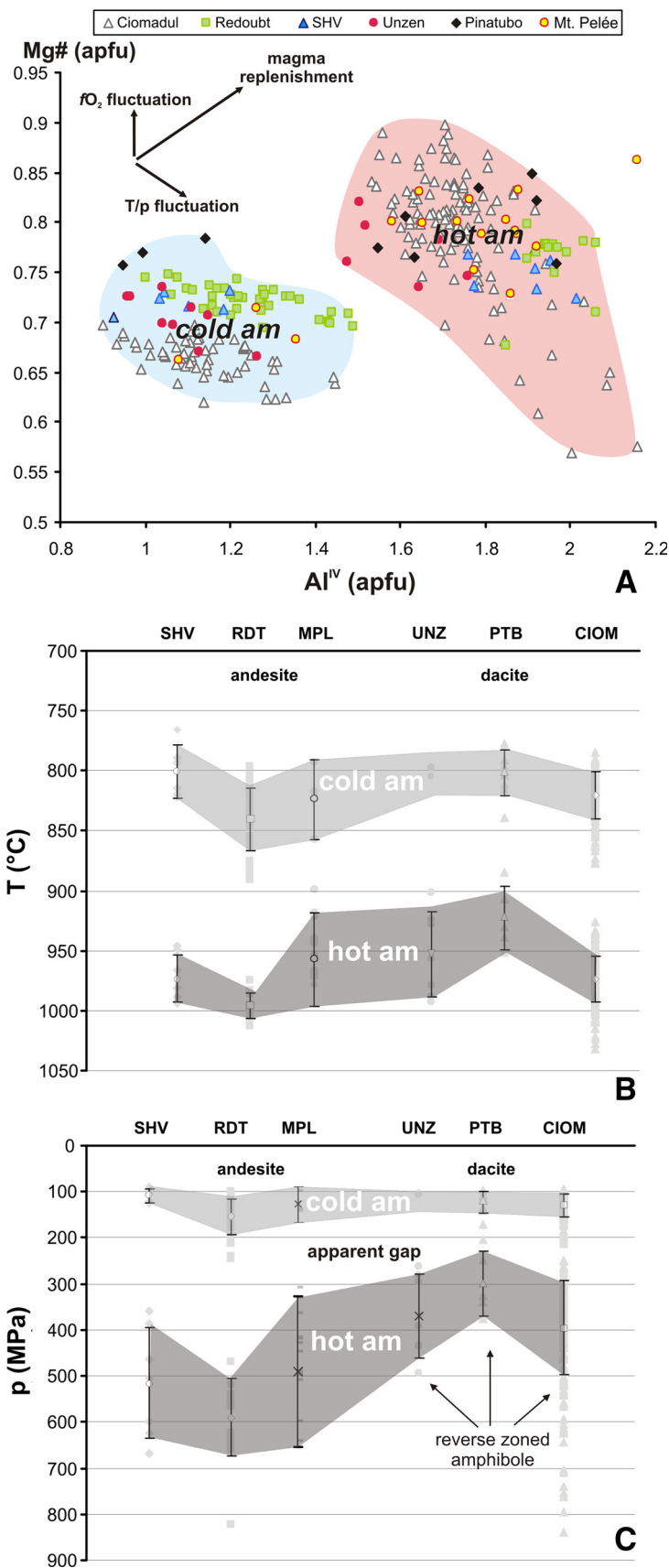
(Rutherford and Devine 2003; Browne and Gardner 2006).
 We used the rim thickness data to estimate the time of
 heating and ascent. According to the different calibrations
 of the rim formation rate, the pargasites spent a maximum
 of approximately 12 days outside their stability field. As
 the rim of pargasites most probably formed via decom-
 pression, this estimate may correspond to the magma
 ascent rate from the magma chamber. The dacites con-
 taining hornblendes with the thinnest rims (~15 µm) may
 suggest the timescale of pre-eruption heating and magma
 mixing. Unfortunately, very little experimental data exist
 about the rate of thermal breakdown of amphiboles. The
 available amphibole breakdown rates were calibrated for
 decompression and suggesting ~6–22 days for hornblende
 breakdown. As the thermal breakdown rate could be much
 faster Browne (2005), the reaction rim of the Ciomadul
 hornblendes might have been formed only within a few
 days, suggesting that the magma chamber was reheated just
 before the eruption.

Implications for the volcanic plumbing systems beneath
 intermediate arc volcanoes

Petrological mapping of the magmatic plumbing system
 beneath active and dormant volcanoes provides constraints
 on eruption style and aids interpretation of geophysical
 signals. This information is an essential component of
 volcanic hazard assessment. The composition, especially
 the alumina content of amphibole phenocrysts, often shows
 large variation in the erupted intermediate magmas even in
 the thin-section scale, and this is commonly interpreted as
 the result of amphibole crystallization at different pressures
 and temperatures (e.g., Pichavant et al. 2002; Thornber
 et al. 2008; Ridolfi et al. 2010; Chambefort et al. 2013;
 Walker et al. 2013; Costa et al. 2013; and Turner et al.
 2013). Results of such studies imply that these volcanoes
 are underlined by a vertically extended magma storage
 zone, where the different amphibole populations crystallize
 at different depths. This zone may consist of separated
 magma chambers (e.g., Soufriere Hills and Bezymianny,
 Turner et al. 2013) or a larger, vertically extended magma
 reservoir (e.g., Mt. Pelée, Pichavant et al. 2002; Santiagu-
 ito, Scott et al. 2012; Mt. St. Helens, Pallister et al. 2008).
 However, in the Ciomadul, dacite single composite crystals
 show almost the same variation in the Al content as the
 amphibole crystals in the entirety of other volcanic systems
 (Fig. 12). Such crystals have a major importance as they
 verify that if the composition of amphiboles is controlled
 by temperature and magma composition at constant pres-
 sure (as in our rock samples), the variation in the crystal-
 lization pressure/depth detected with amphiboles can be
 only apparent. This finding highlights that amphibole
 barometers that consider only amphibole composition such

Fig. 13 a Comparison of amphibole populations of mixed intermediate magmas from different volcanic arcs defines two separate groups: 1. cold amphiboles (cold am) derive from a silicic crystal mush, and hot amphiboles (hot am) originate from a hybrid melt that was formed due to fresh mafic intrusion into the mush and mixing of the mafic and silicic magmas, thus they are mafic recharge-related amphiboles. **b** Crystallization conditions of cold and hot amphiboles according to the Ridolfi et al. (2010) thermobarometer. Data of Mt. Pinatubo (PTB): Pallister et al. (1996); Soufrière Hills (SHV): Murphy et al. (2000); Redoubt (RDT): Coombs et al. (2012); Unzen (UNZ): Sato et al. (2005); Mt Pelée (MPL): Pichavant et al. (2002); Ciomadul (CIOM): this study

Author Proof



Magma chamber architecture and petrogenesis of mixed intermediate magmas:

1. based on the Ridolfi thermobarometry

2. based on our study

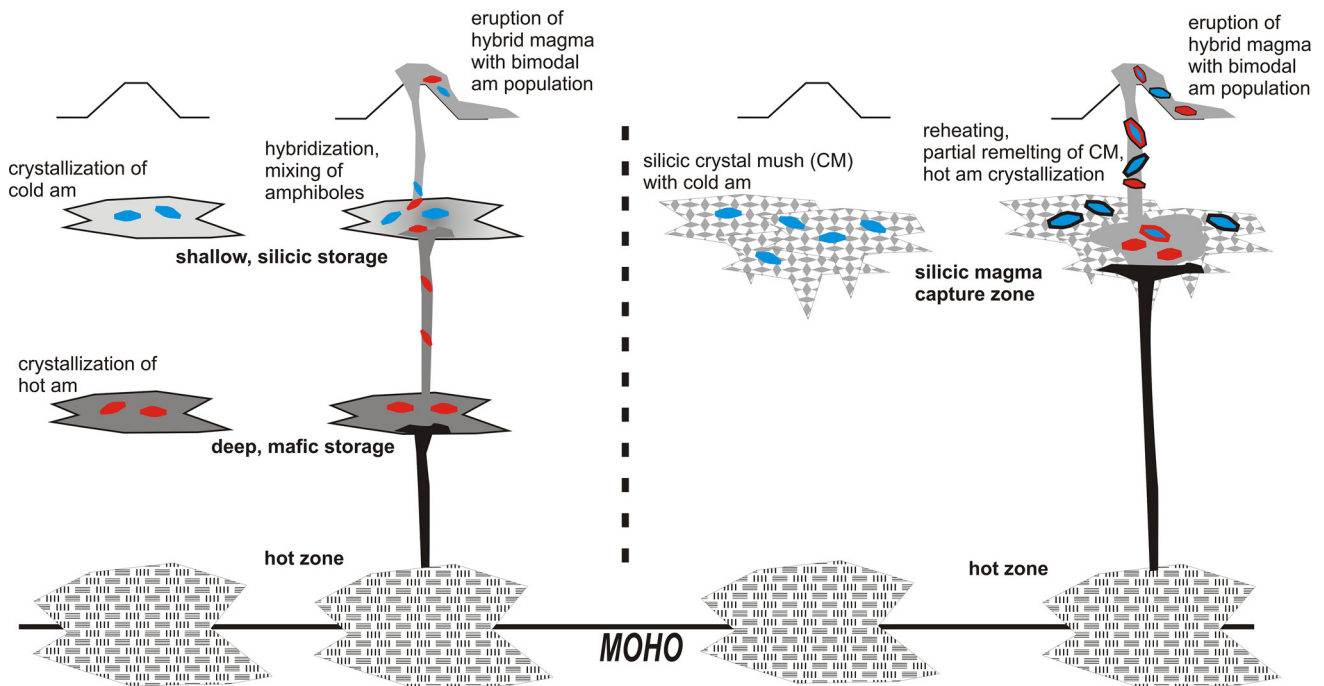


Fig. 14 Schematic cartoon that shows two different models for the inferred magma storage system and petrogenesis of mixed intermediate magmas based on bimodal amphibole populations. As it is

shown, only the second model provides realistic interpretation for the formation of simple-zoned and composite amphiboles. For further details, see the discussion. The figures are not to scale

1075 as Ridolfi et al. (2010) may often yield unrealistic pressure
1076 variation and magma chamber architecture (Fig. 13).

1077 *Processes and conditions of magma mixing beneath*
1078 *andesite–dacite composite volcanoes—the amphibole*
1079 *perspective*

1080 Intermediate mixed magmas of volcanic arcs often host
1081 almost the same bimodal amphibole cargo as it was
1082 observed in the Ciomadul dacites. Bimodal amphiboles
1083 characterize the erupted products of, e.g., Mt. Pinatubo
1084 (Pallister et al. 1996), Unzen (Sato et al. 1999, 2005),
1085 Soufrière Hills (Humphreys et al. 2009a), Redoubt (Wolf
1086 and Eichelberger 1997; Coombs et al. 2012), Mt. Pelée
1087 (Pichavant et al. 2002), and the Central Volcanic Zone
1088 dacites in Chile (Nakada 1991). Although the similar
1089 amphibole cargo may suggest similar processes and con-
1090 ditions beneath these volcanoes, several models have been
1091 established to explain the origin of the bimodal amphiboles
1092 (e.g., Pichavant et al. 2002; Coombs et al. 2012; Ridolfi
1093 et al. 2010; Sato et al. 1999; Koleszar and Kent 2011). Our
1094 amphibole perspective investigation indicates that bimodal
1095 amphibole populations cannot unambiguously mean crys-
1096 tallization at different depths as it is commonly indicated

(Pichavant et al. 2002; Ridolfi et al. 2010; Koleszar and
1097 Kent 2011; Chambefort et al. 2013), but an alternative
1098 model could be the remobilization of a long-lived, near-
1099 solidus crystal mush by hot mafic magma intrusion (Na-
1100 kamura 1995; Pallister et al. 1996; Murphy et al. 2000).
1101 This suggests that these volcanoes can be underlain by a
1102 shallow (100–300 MPa) storage zone where cold, silicic
1103 magmas are captured and low-Al amphiboles are formed.
1104 High-Al amphiboles can crystallize at shallow depth during
1105 reactivation and remobilization of this crystal mush due to
1106 mafic magma intrusion followed by hybridization of the
1107 different magmas (Fig. 14). The amphibole thermobarom-
1108 etry of Ridolfi et al. (2010) and Ridolfi and Renzulli (2012)
1109 seems to be useful in the case of mixed magmas in which
1110 equilibrium mineral phases are difficult to find as well as
1111 experiments are limited due to their mixed character.
1112 However, these equations lead to the same p–T evolution
1113 path for all amphiboles along their stability curve; at the
1114 same time, bimodal amphiboles in mixed intermediate
1115 magmas usually not follow this trend, as it is demonstrated
1116 in this study. Thus, these formulations are unable to
1117 reproduce the conditions and p–T path of mafic magma
1118 replenishment into shallow eruption feeder magma storage
1119 filled with cold silicic crystal mush, that is, however, a
1120

1121 commonly observed process in arc volcanoes (Nakamura
1122 1995; Pallister et al. 1996; Murphy et al. 2000; Eichel-
1123 berger et al. 2000).

1124 Conclusion

1125 The amphibole perspective of the studied Ciomadul's dacite
1126 suggesting that eruptions of the volcano were pre-
1127 ceded by complex magma chamber processes. An
1128 important implication is that the erupted dacitic magma
1129 was formed in an upper crustal magma storage zone where
1130 reheating and partial remelting of silicic crystal mush
1131 occurred due to mafic magma replenishment days or weeks
1132 before the eruption. Our model is in contrast to the former
1133 view that suggested lower crustal conditions for the dacite
1134 genesis including continuous melting of the lower crust by
1135 mafic under plating and mixing—hybridization of mantle-
1136 and crustal-derived magmas (Vinkler et al. 2007).

1137 Our study highlights that without the knowledge of the
1138 processes that is responsible for the compositional varia-
1139 tion of amphiboles, thermobarometers based on solely their
1140 chemistry can lead misleading conclusions on magma
1141 chamber architecture and conditions of the magma
1142 evolution.

1143 **Acknowledgments** This research has been supported by the Hun-
1144 garian Scientific Research Fund (OTKA No. 68587). Kiss Balázs in
1145 this research was supported by the European Union and the State of
1146 Hungary, co-financed by the European Social Fund in the framework
1147 of TÁMOP-4.2.4.A/2-11/1-2012-0001 'National Excellence Pro-
1148 gram'. Ioan Seghedi, Csaba János, and Alex Szakács provided
1149 invaluable help during the field trip campaigns. Fruitful discussions
1150 with Malcolm Rutherford, Filippo Ridolfi, Gerhard Wörner, Jon
1151 Blundy, and Olivier Bachmann at different stages of this study have
1152 helped to refine our model and clarify our ideas on amphibole for-
1153 mation and on the nature of the magma storage zone beneath inter-
1154 mediate volcanoes. M. Éva Jankovics are thanked for improvements
1155 in English and figures. Tamás Sági, Zsolt Bendő, and Franz Kraly are
1156 acknowledged for help during SEM and EMPA analyses. Construc-
1157 tive comments provided by Olivier Bachmann and Michael J. Kra-
1158 wczynski and the editor Timothy L. Grove helped us to refine
1159 significantly the original manuscript.

1160 References

1161 Adam J, Oberti R, Camara F, Green TH (2007) An Electron
1162 microprobe, LAM-ICP-MS and single-crystal X-ray structure
1163 refinement study of the effects of pressure, melt-H₂O concen-
1164 tration and fO₂ on experimentally produced basaltic amphiboles.
1165 *Eur J Mineral* 19(5):641–655
1166 Almeev RR, Ariskin AA, Ozerov AY, Kononkova NN (2002)
1167 Problems of the stoichiometry and thermobarometry of mag-
1168 matic amphiboles: an example of hornblende from the andesites
1169 of Bezymyanni volcano, Eastern Kamchatka. *Geochem Int*
1170 40(8):723–738
1171 Anderson JL, Smith DR (1995) The effects of temperature and fO₂ on
1172 the Al-in-hornblende barometer. *Am Mineral* 80:549–559

Anderson JL, Barth AP, Wooden JL, Mazdab F (2008) Thermometers
1173 and thermobarometers in granitic systems. *Rev Mineral Geo-*
1174 *chem* 69(1):121–142
1175
1176 Bachmann O, Dungan MA (2002) Temperature-induced Al-zoning in
1177 hornblendes of the Fish Canyon magma, Colorado. *Am Mineral*
1178 87(8–9):1062–1076
1179
1180 Barclay J, Carmichael ISE (2004) A hornblende basalt from Western
1181 Mexico: water-saturated phase relations constrain a pressure-
1182 temperature window of eruptibility. *J Petrol* 45(3):485–506
1183
1184 Blundy J, Cashman K (2008) Petrologic reconstruction of magmatic
1185 system variables and processes. *Rev Mineral Geochem*
1186 69(1):179–239
1187
1188 Blundy JD, Holland TJB (1990) Calcic amphibole equilibria and a
1189 new amphibole-plagioclase geothermometer. *Contrib Mineral*
1190 *Petrol* 104(2):208–224
1191
1192 Browne BL (2005) Petrologic and experimental constraints on magma
1193 mixing and ascent: examples from Japan and Alaska. Ph.D.
1194 Thesis, University of Alaska Fairbanks
1195
1196 Browne BL, Gardner JE (2006) The influence of magma ascent path
1197 on the texture, mineralogy, and formation of hornblende reaction
1198 rims. *Earth and Planetary Science Letters* 246(3–4):161–176
1199
1200 Chalot-Prat F, Gîrbacea R (2000) Partial delamination of continental
1201 mantle lithosphere, uplift-related crust-mantle decoupling, vol-
1202 canism and basin formation: a new model for the Pliocene-
1203 Quaternary evolution of the southern East-Carpathians, Roma-
1204 nia. *Tectonophysics* 327:83–107
1205
1206 Chambeftort I, Dilles JH, Longo AA (2013) Amphibole geochemistry
1207 of the yanacocha volcanics, peru: evidence for diverse sources of
1208 magmatic volatiles related to gold ores. *J Petrol*
1209 54(5):1017–1046
1210
1211 Coombs ML, Gardner JE (2004) Reaction rim growth on olivine in
1212 silicic melts: implications for magma mixing. *Am Mineral*
1213 89(5–6):748–758
1214
1215 Coombs ML, Sisson TW, Bleick HA, Henton SM, Nye CJ, Payne AL,
1216 Cameron CE, Larsen JF, Wallace KL, Bull KF (2013) Andesites
1217 of the 2009 eruption of Redoubt Volcano, Alaska. *J Volcanol*
1218 *Geoth Res* 259:349–372
1219
1220 Costa F, Singer B (2002) Evolution of holocene dacite and
1221 compositionally zoned magma, volcán San Pedro, Southern
1222 Volcanic Zone, Chile. *J Petrol* 43(8):1571–1593
1223
1224 Costa F, Scaillet B, Pichavant M (2004) Petrological and experimen-
1225 tal constraints on the pre-eruption conditions of holocene dacite
1226 from Volcán San Pedro (36°S, Chilean Andes) and the impor-
1227 tance of sulphur in silicic subduction-related magmas. *J Petrol*
1228 45(4):855–881
1229
1230 Costa F, Andreastuti S, Bouvet de Maisonneuve C, Pallister JS (2013)
1231 Petrological insights into the storage conditions, and magmatic
1232 processes that yielded the centennial 2010 Merapi explosive
1233 eruption. *J Volcanol Geotherm Res* 261:209–235
1234
1235 Couch S, Sparks RSJ, Carroll MR (2001) Mineral disequilibrium in
1236 lavas explained by convective self-mixing in open magma
1237 chambers. *Nature* 411:1037–1039
1238
1239 De Angelis SH, Larsen J, Coombs M (2013) Pre-eruptive magmatic
1240 conditions at Augustine volcano, Alaska, 2006: evidence from
1241 amphibole geochemistry and texture. *J Petrol* 0(0):1–23
1242
1243 Eichelberger JC, Chertkoff DG, Dreher ST, Nye CJ (2000) Magmas
1244 in collision: rethinking chemical zonation in silicic magmas.
1245 *Geology* 28:603–606
1246
1247 Ernst WG, Liu J (1998) Experimental phase-equilibrium study of Al-
1248 and Ti-contents of calcic amphibole in MORB—a semiquanti-
1249 tative thermobarometer. *Am Mineral* 83:952–969
1250
1251 Fillerup MA, Knapp JH, Knapp CC, Raileanu V (2010) Mantle
1252 earthquakes in the absence of subduction? Continental delam-
1253 ination in the Romanian Carpathians. *Lithosphere* 2(5):333–340
1254
1255 Gill JB (1981) Orogenic andesites and plate tectonics. Springer,
1256 Berlin 1237
1257 1238

- 1239 Gîrbacea R, Frisch W (1998) Slab in the wrong place: lower
1240 lithospheric mantle delamination in the last stage of the Eastern
1241 Carpathian subduction retreat. *Geology* 26(7):611–614
- 1242 Grove T, Elkins-Tanton L, Parman S, Chatterjee N, Müntener O,
1243 Gaetani G (2003) Fractional crystallization and mantle-melting
1244 controls on calc-alkaline differentiation trends. *Contrib Mineral
1245 Petrol* 145(5):515–533
- 1246 Grove T, Baker M, Price R, Parman S, Elkins-Tanton L, Chatterjee N,
1247 Müntener O (2005) Magnesian andesite and dacite lavas from
1248 Mt. Shasta, northern California: products of fractional crystal-
1249 lization of H₂O-rich mantle melts. *Contrib Mineral Petrol*
1250 148(5):542–565
- 1251 **AQS** Hammarstrom JM, Zen E (1986) Aluminum in hornblende; an
1252 empirical igneous geobarometer. *Am Mineral*
1253 71(11–12):1297–1313
- 1254 Harangi S (2007) A Kárpát-Pannon térség legutolsó vulkáni kitöré-
1255 sei—lesz-e még folytatás? (The last volcanic eruptions in the
1256 Carpathian-Pannonian Region—to be continued?). *Földrajzi
1257 Közlemények* 131(4):271–288
- 1258 Harangi S, Lenkey L (2007) Genesis of the Neogene to Quaternary
1259 volcanism in the Carpathian–Pannonian region: role of subduc-
1260 tion, extension, and mantle plume. *Geol Soc Am Spec Pap*
1261 418:67–92
- 1262 **AQS** Harangi S, Mason PRD, Lukács R (2005) Correlation and petrogen-
1263 esis of silicic pyroclastic rocks in the Northern Pannonian Basin,
1264 Eastern-Central Europe: in situ trace element data of glass shards
1265 and mineral chemical constraints. *Journal of Volcanology and
1266 Geothermal Research* 143(237–257)
- 1267 Harangi S, Molnár M, Vinkler AP, Kiss B, Jull ATJ, Leonard AG
1268 (2010) Radiocarbon dating of the last volcanic eruptions of
1269 Ciomadul Volcano, Southeast Carpathians, Eastern-Central
1270 Europe. *Radiocarbon* 52(3):1498–1507
- 1271 Holland T, Blundy J (1994) Non-ideal interactions in calcic
1272 amphiboles and their bearing on amphibole-plagioclase ther-
1273 mometry. *Contrib Mineral Petrol* 116:433–447
- 1274 Holtz F, Johannes W, Tamic N, Behrens H (2001) Maximum and
1275 minimum water contents of granitic melts generated in the crust:
1276 a re-evaluation and implications. *Lithos* 56:1–14
- 1277 Holtz F, Sato H, Lewis J, Behrens H, Nakada S (2005) Experimental
1278 petrology of the 1991–1995 Unzen dacite, Japan. Part I: phase
1279 relations, phase composition and pre-eruptive conditions. *J Petrol*
1280 46(2):319–337
- 1281 Humphreys MCS, Blundy JD, Sparks RSJ (2006) Magma evolution
1282 and open-system processes at Shiveluch volcano: insights from
1283 phenocryst zoning. *J Petrol* 47(12):2303–2334
- 1284 Humphreys M, Christopher T, Hards V (2009a) Microlite transfer by
1285 disaggregation of mafic inclusions following magma mixing at
1286 Soufriere Hills volcano, Montserrat. *Contrib Mineral Petrol*
1287 157(5):609–624
- 1288 Humphreys MCS, Edmonds M, Christopher T, Hards V (2009b)
1289 Chlorine variations in the magma of Soufrière Hills volcano,
1290 Montserrat: insights from Cl in hornblende and melt inclusions.
1291 *Geochim Cosmochim Acta* 73(19):5693–5708
- 1292 Jarosewich E, Nelen JA, Norberg JA (1980) Reference samples for
1293 electron microprobe analysis. *Geostand Newsl* 4:43–47
- 1294 Johnson MC, Rutherford MJ (1989a) Experimental calibration of the
1295 aluminum-in-hornblende geobarometer with application to Long
1296 Valley caldera (California) volcanic rocks. *Geology*
1297 17(9):837–841
- 1298 Johnson MC, Rutherford MJ (1989b) Experimentally determined
1299 conditions in the Fish Canyon Tuff, Colorado, magma chamber.
1300 *J Petrol* 30(3):711–737
- 1301 Karátson D, Telbisz T, Harangi S, Magyar E, Dunkl I, Kiss B, Jánosi
1302 C, Veres D, Braun M, Fodor E, Biró T, Kósik S, von Eynatten H,
1303 Lin D (2013) Morphometrical and geochronological constraints
1304 on the youngest eruptive activity in East-Central Europe at the
1305 Ciomadul (Csomád) lava dome complex, East Carpathians. *J
1306 Volcanol Geotherm Res* 255:43–56
- 1307 Kent AJR, Darr C, Koleszar AM, Salisbury MJ, Cooper KM (2010)
1308 Preferential eruption of andesitic magmas through recharge
1309 filtering. *Nat Geosci* 3(9):631–636
- 1310 Koleszar AM, Kent AJR (2011) Compositional diversity and
1311 plumbing systems: evidence from amphiboles from Mount
1312 Hood, Oregon. *AGU abstract #V52A-01*
- 1313 Koleszar AM, Kent AJR, Wallace PJ, Scott WE (2012) Controls on
1314 long-term low explosivity at andesitic volcanoes: insights from
1315 Mount Hood, Oregon. *J Volcanol Geotherm Res* 219–220:1–14
- 1316 Krawczynski M, Grove T, Behrens H (2012) Amphibole stability in
1317 primitive arc magmas: effects of temperature, H₂O content, and
1318 oxygen fugacity. *Contrib Mineral Petrol* 164(2):317–339
- 1319 Larsen J (2006) Rhyodacite magma storage conditions prior to the
1320 3430 yBP caldera-forming eruption of Aniakchak volcano,
1321 Alaska. *Contrib Mineral Petrol* 152(4):523–540
- 1322 Leake BE, Woolley AR, Arps CES, Birch WD, Gilbert MC, Grice JD,
1323 Hawthorne FC, Kato A, Kisch HJ, Krivovichev VG, Linthout K,
1324 Laird J, Mandarino JA, Maresch WV, Nickel EH, Rock NMS,
1325 Schumacher JC, Smith DC, Stephenson NCN, Ungaretti L,
1326 Whittaker EJC, Youzhi G (1997) Nomenclature of amphiboles:
1327 report of the subcommittee on amphiboles of the International
1328 Mineralogical Association, commission on new minerals and
1329 mineral names. *Can Mineral* 35:219–246
- 1330 Pécskay Z, Lexa J, A. S, Balogh K, Seghedi I, Konecny V, Kovács M,
1331 Márton E, Kaliciak M, Széky-Fux V, Póka T, Gyarmati P,
1332 Edelstein O, Rosu E, Zec B (1995) Space and time distribution
1333 of Neogene-Quaternary volcanism in the Carpatho-Pannonian
1334 Region. In: Downes H, Vaselli O (eds) *Neogene and Related
1335 Magmatism in the Carpatho-Pannonian Region*, vol 7. pp 15–28
- 1336 Lorinczi P, Houseman GA (2009) Lithospheric gravitational insta-
1337 bility beneath the Southeast Carpathians. *Tectonophysics*
1338 474(1–2):322–336
- 1339 Martel C, Pichavant M, Holtz F, Scaillet B, Bourdier J-L, Traineau H
1340 (1999) Effects of fO₂ and H₂O on andesite phase relations
1341 between 2 and 4 kbar. *J Geophys Res Solid Earth*
1342 104(B12):29453–29470
- 1343 Mason PRD, Kraan WJ (2002) Attenuation of spectral interferences
1344 during laser ablation inductively coupled plasma mass spec-
1345 trometry (LA-ICP MS) using an rf only collision and reaction
1346 cell. *J Anal At Spectrom* 17:858–867
- 1347 Mason PRD, Downes H, Thirlwall M, Seghedi I, Szakács A, Lowry
1348 D, Matthey D (1996) Crustal assimilation as a major petrogenetic
1349 process in the East Carpathian Neogene and Quaternary
1350 continental margin arc, Romania. *J Petrol* 37(4):927–959
- 1351 Mason PRD, Seghedi I, Szakács A, Downes H (1998) Magmatic
1352 constraints on geodynamic models of subduction in the East
1353 Carpathians, Romania. *Tectonophysics* 297:157–176
- 1354 McGuire AV, Francis CA, Dyar Darby M (1992) Mineral standards
1355 for electron microprobe analysis of oxygen. *Am Mineral*
1356 77:1087–1091
- 1357 Miyashiro A (1974) Volcanic rock series in island arcs and active
1358 continental margins. *Am J Sci* 274:321–355
- 1359 Murphy MD, Sparks RSJ, Barclay J, Carroll MR, Brewer TS (2000)
1360 Remobilization of Andesite Magma by Intrusion of Mafic
1361 Magma at the Soufriere Hills Volcano, Montserrat, West Indies.
1362 *J Petrol* 41(1):21–42
- 1363 Nakada S (1991) Magmatic processes in titanite-bearing dacites, Central
1364 Andes of Chile and Bolivia. *Am Mineral* 76(3–4):548–560
- 1365 Nakamura N (1974) Determination of REE, Ba, Fe, Mg, Na and K in
1366 carbonaceous and ordinary chondrites. *Geochim Cosmochim
1367 Acta* 38(5):757–775
- 1368 Nakamura M (1995) Continuous mixing of crystal mush and
1369 replenished magma in the ongoing Unzen eruption. *Geology*
1370 23(9):807–810

- 1371 **AQ7** Pallister JS, Hoblitt RP, Meeker GP, Knight RJ, Siems DF (1996) Magma mixing at Mount Pinatubo: petrographic and chemical evidence from the 1991 deposits. In: Newhall CG, Punongbayan RS (eds) *Fire and Mud: Eruptions and Lahars of Mount Pinatubo, Philippines*. Seattle and London, pp 687–731
- 1376 Pallister JS, Thornber CR, Cashman KV, Clynne MA, Lowers HA, Mandeville CW, Brownfield IK, Meeker GP (2008) Petrology of the 2004–2006 Mount St. Helens lava dome—implications for magmatic plumbing and eruption triggering. In: Sherrod DR, Scott WE, Stauffer PH (eds) *A volcano rekindled: the renewed eruption of mount St. Helens, 2004–2006*, vol 1750. pp 674–702
- 1382 Pearce NJG, Perkins WT, Westgate JA, Gorton MP, Jackson SE, Neal CR, Chenery SP (1997) A compilation of new and published major and trace element data for NIST SRM 610 and NIST SRM 612 glass reference materials. *Geostand Newsl* 21:115–144
- 1386 Peltz S, Vajdea E, Balogh K, Pécskay Z (1987) Contributions to the geochronological study of the volcanic processes in the Calimani and Harghita Mountains (East Carpathians, Romania). *Dari de Seama ale Sedintelor Institutul de Geologie si Geofizica* 72–73:323–338
- 1391 Pichavant M, Martel C, Bourdier J-L, Scaillet B (2002) Physical conditions, structure, and dynamics of a zoned magma chamber: mount Pelée (Martinique, Lesser Antilles Arc). *J Geophys Res* 107(B5):1–28
- 1395 Popa M, Radulian M, Szakács A, Seghedi I, Zaharia B (2012) New seismic and tomography data in the southern part of the Harghita mountains (Romania, Southeastern Carpathians): connection with recent volcanic activity. *Pure appl Geophys* 169(9):1557–1573
- 1400 Ren Y, Stuart GW, Houseman GA, Dando B, Ionescu C, Hegedüs E, Radovanović S, Shen Y (2012) Upper mantle structures beneath the Carpathian–Pannonian region: implications for the geodynamics of continental collision. *Earth Planet Sci Lett* 349–350:139–152
- 1405 Reubi O, Blundy J (2009) A dearth of intermediate melts at subduction zone volcanoes and the petrogenesis of arc andesites. *Nature* 461:1269–1273
- 1408 Ridolfi F, Renzulli A (2012) Calcic amphiboles in calc-alkaline and alkaline magmas: thermobarometric and chemometric empirical equations valid up to 1,130°C and 2.2 GPa. *Contrib Mineral Petrol* 163(5):877–895
- 1412 Ridolfi F, Renzulli A, Puerini M (2010) Stability and chemical equilibrium of amphibole in calc-alkaline magmas: an overview, new thermobarometric formulations and application to subduction-related volcanoes. *Contrib Mineral Petrol* 160(1):45–66
- 1416 Ruprecht P, Bachmann O (2010) Pre-eruptive reheating during magma mixing at Quizapu volcano and the implications for the explosiveness of silicic arc volcanoes. *Geology* 38:919–922
- 1419 Rutherford MJ, Devine JD (1988) The May 18, 1980, eruption of Mount St. Helens Stability and chemistry of amphiboles in the magma chamber. *J Geophys Res* 93(B10):11949–11959
- 1422 Rutherford MJ, Devine JD (2003) Magmatic conditions and magma ascent as indicated by hornblende phase equilibria and reactions in the 1995–2002 Soufrière hills magma. *J Petrol* 44(8):1433–1453
- 1426 **AQ8** Rutherford MJ, Devine JD (2008) Magmatic conditions and processes in the storage zone of the 2004–2006 Mount St. Helens Dacite. In: Sherrod DR, Scott WE, Stauffer PH (eds) *A volcano rekindled: the renewed eruption of Mount St. Helens, 2004–2006*, vol 1750. pp 703–725
- 1431 Rutherford MJ, Hill PM (1993) Magma ascent rates from amphibole breakdown: an experimental study applied to the 1980–1986 Mount St. Helens eruptions. *J Geophys Res* 98(B11):19667–19685
- 1435 Sato H, Nakada S, Fujii T, Nakamura M, Suzuki-Kamata K (1999) Groundmassargasite in the 1991–1995 dacite of Unzen volcano: phase stability experiments and volcanological implications. *J Volcanol Geotherm Res* 89(1–4):197–212
- 1438 Sato H, Holtz F, Behrens H, Botcharnikov R, Nakada S (2005) Experimental petrology of the 1991–1995 Unzen dacite, Japan. Part II: cI/OH partitioning between hornblende and melt and its implications for the origin of oscillatory zoning of hornblende phenocrysts. *J Petrol* 46(2):339–354
- 1442 Scaillet B, Evans BW (1999) The 15 June 1991 eruption of Mount Pinatubo. I. phase equilibria and pre-eruption P–T–fO₂–fH₂O conditions of the dacite magma. *J Petrol* 40(3):381–411
- 1446 Schmidt MW (1992) Amphibole composition in tonalite as a function of pressure: an experimental calibration of the Al-in-hornblende barometer. *Contrib Mineral Petrol* 110(2–3):304–310
- 1449 Scott JAJ, Mather TA, Pyle DM, Rose WI, Chigna G (2012) The magmatic plumbing system beneath Santiaguito volcano, Guatemala. *J Volcanol Geotherm Res* 237–238:54–68
- 1452 Seghedi I, Szakács A, Udrescu C, Stoian M, Grabari G (1987) Trace element geochemistry of the South Harghita volcanics (East Carpathians): calc-alkaline and shoshonitic association. *Dari de Seama ale Sedintelor Institutul de Geologie si Geofizica* 72–73:381–397
- 1457 Seghedi I, Maţenco L, Downes H, Mason PRD, Szakács A, Pécskay Z (2011) Tectonic significance of changes in post-subduction Pliocene–Quaternary magmatism in the south east part of the Carpathian–Pannonian Region. *Tectonophysics* 502(1–2):146–157
- 1462 Shane P, Smith VC (2013) Using amphibole crystals to reconstruct magma storage temperatures and pressures for the post-caldera collapse volcanism at Okataina volcano. *Lithos* 156–159:159–170
- 1466 Simakin AG, Salova TP, Babansky AD (2009) Amphibole crystallization from a water-saturated andesite melt: experimental data at P = 2 kbar. *Petrology* 17(6):591–605
- 1469 Simakin A, Zakrevskaya O, Salova T (2012) Novel Amphibole Geobarometer with Application to Mafic Xenoliths. *Earth Sci Res* 1(2):82–97
- 1472 Sisson TW, Grove TL (1993) Experimental investigations of the role of H₂O in calc-alkaline differentiation and subduction zone magmatism. *Contrib Mineral Petrol* 113(2):143–166
- 1475 Streck MJ (2008) Mineral Textures and Zoning as Evidence for Open System Processes. In: Putirka KD, Tepley III FJ (eds) *Reviews in Mineralogy and Geochemistry*, vol 69. Mineralogical Society of America & Geochemical Society, pp 595–622
- 1479 Sun S-s, McDonough WF (1989) Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. *Geol Soc Lond Spec Publ* 42(1):313–345
- 1482 Szakács A, Seghedi I (1986) Chemical diagnosis of the volcanics from the southeastermost part of the Harghita Mountains—proposal for a new nomenclature. *Revue Roumaine de Géologie* 30:41–48
- 1486 Szakács A, Seghedi I (1995) The Călimani-Gurghiu-Harghita volcanic chain, East Carpathians, Romania: volcanological features. *Acta Vulcanol* 7(2):145–153
- 1489 Szakács A, Seghedi I (2013) The relevance of volcanic hazard in Romania: is there any? *Environ Eng Manag J* 12:125–135
- 1491 Szakács A, Seghedi I, Pécskay Z (1993) Peculiarities of South Harghita Mts. as the terminal segment of the Carpathian Neogene to Quaternary volcanic chain. *Revue Roumaine de Géologie Géophysique et Géographie*, *Géologie* 37:21–37
- 1495 Szakács A, Seghedi I, Pécskay Z (2002) The most recent volcanism in the Carpathian–Pannonian Region. Is there any volcanic hazard? In: *The XVIIth Congress of Carpathian-Balkan Geological Association*, vol 53. Geologica Carpathica, Bratislava, Slovakia, pp 193–194
- 1500 Thornber CR, Pallister JS, Lowers HA, Rowe MC, Mandeville CW, Meeker GP (2008) Chemistry, mineralogy, and petrology of

- 1503 amphibole in Mount St. Helens 2004–2006 dacite. In: Sherrod
1504 DR, Scott WE, Stauffer PH (eds) *A Volcano rekindled: the*
1505 *renewed eruption of Mount St. Helens, 2004–2006*, vol 1750.
1506 pp 727–754
- 1507 Turner SJ, Izbekov P, Langmuir C (2013) The magma plumbing
1508 system of Bezymianny Volcano: insights from a 54 year time
1509 series of trace element whole-rock geochemistry and amphibole
1510 compositions. *J Volcanol Geotherm Res* 263:108–121
- 1511 Vaselli O, Minissale A, Tassi F, Magro G, Seghedi I, Ioane D,
1512 Szakács A (2002) A geochemical traverse across the Eastern
1513 Carpathians (Romania): constraints on the origin and evolution
1514 of the mineral water and gas discharges. *Chem Geol*
1515 182(2–4):637–654
- 1516 Viccaro M, Ferlito C, Cristofolini R (2007) Amphibole crystallization
1517 in the Etnean feeding system: mineral chemistry and trace
1518 element partitioning between Mg-hastingsite and alkali basaltic
1519 melt. *Eur J Mineral* 19(4):499–511
- 1520 Vinkler AP, Harangi S, Ntaflou T, Szakács A (2007) A Csomád
1521 vulkán (Keleti-Kárpátok) horzszaköveinek közzetani és geokémiai
vizsgálata—petrogenetikai következtetések (Petrology and geo-
chemistry of pumices from the Ciomadul volcano (Eastern
Carpathians)—implications for petrogenetic processes). *Földtani*
Közlöny (Bull. Hung. Geol. Soc.) 137(1):103–128
- Vyhnal CR, McSween HY, Speer JA (1991) Hornblende chemistry in
southern Appalachian granitoids: implications for aluminum
hornblende thermobarometry and magmatic epidote stability.
Am Mineral 76:176–188
- Walker B Jr, Klemetti E, Grunder A, Dilles J, Tepley F, Giles D
(2013) Crystal reaming during the assembly, maturation, and
waning of an eleven-million-year crustal magma cycle: ther-
mobarometry of the Aucanquilcha Volcanic Cluster. *Contrib*
Mineral Petrol 165(4):663–682
- Wolf KJ, Eichelberger JC (1997) Syneruptive mixing, degassing, and
crystallization at Redoubt Volcano, eruption of December, 1989
to May 1990. *J Volcanol Geoth Res* 75(1–2):19–37

Journal : 410
Article : 986

Author Query Form

Please ensure you fill out your response to the queries raised below and return this form along with your corrections

Dear Author

During the process of typesetting your article, the following queries have arisen. Please check your typeset proof carefully against the queries listed below and mark the necessary changes either directly on the proof/online grid or in the 'Author's response' area provided below

Query	Details Required	Author's Response
AQ1	References Vinkler et al. (1997), Bachmann et al. (2002), Angelis (2013), Krawczinsky et al. (2012) and Coombs et al. (2012) are cited in text but not provided in the reference list. Please provide references in the list or delete these citations.	
AQ2	Please check the layout of Tables 1, 2 and 3, and correct if necessary.	
AQ3	Shane and Smith (2012) has been changed to Shane and Smith (2013) so that this citation matches the list.	
AQ4	Please check and confirm the inserted citation of Fig. 13 is correct. If not, please suggest an alternative citation. Please note that figures and tables should be cited in sequential order in the text.	
AQ5	Please check and confirm the author names and initials are correct in the references Hammarstrom and Zen (1986).	
AQ6	Please provide page range for reference Harangi et al. (2005).	
AQ7	Please provide complete details for reference Pallister et al. (1996, 2008), Pécskay et al. (1995) and Thornber et al. (2008).	
AQ8	Please provide publisher name and location for reference Rutherford and Devine (2008).	
AQ9	Please provide publisher location for reference Streck (2008).	
AQ10	Please provide editor names for reference Szakacs et al. (2002).	