Petrology of some amphibole-bearing volcanics of the pre-Ellittico period (102-80 ka), Mt. Etna

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Abstract. — We present here petrological and geochemical data on volcanics cropping out in southern and northeastern walls of the Valle del Bove (Mt. Etna), belonging to the Rocche, Serra Giannicola Grande and Canalone della Montagnola Units. These units constitute the remnants of several volcanoes that were active in the time span 102-80 ka, i.e. before the growth of the Ellittico-Mongibello strato-volcano. Their products, range in composition from hawaiites to benmoreites. Amphibole (kaersutite) is present as phenocryst in all the studied rocks, and commonly shows breakdown coronas of rhönite ± clinopyroxene and plagioclase formed during magma ascent. Nevertheless, in mafic rocks, amphibole occurs as an early liquidus phase enclosed in a Ca-rich plagioclase (up to An_{87}). We propose that early cotectic crystallization of amphibole and Ca-plagioclase may reflect H_2O-rich melts. Variations in major and trace elements among lavas erupted from coeval centres, suggest that fractional crystallization was the principal evolutionary process but at the same time magmas feeding the various volcanoes belonging to the Rocche Unit were more heterogeneous with respect to the younger Units studied here.

Key Words: *Etna, Valle del Bove, alkaline magmatism, kaersutite, rhönite.*

Riassunto. — Sono riportati alcuni dati petrologici riguardanti le vulcaniti affioranti nelle pareti meridionale e settentrionale della Valle del Bove (Etna), appartenenti alle Unità Rocche, Serra Giannicola Grande e Canalone della Montagnola. Esse rappresentano l'attività sviluppatasi nell'intervallo temporale 102-80 ka, che ha preceduto la formazione dello strato vulcano Ellittico-Mongibello.

I prodotti studiati variano composizionalmente da hawaiiti a benmoreiti e sono caratterizzati dalla presenza di fenocristalli d'anfibolo (kaersutite). L'anfibolo è caratterizzato da frequenti corone di decomposizione in rhönite±clinopirosseno, formatesi durante la risalita magmatica. Nelle rocce più mafiche l'anfibolo cristallizza precocemente, talora co-precipitando con un plagioclasio ricco in Ca (An_{87}). La cristallizzazione cotettica di Ca-plagioclasio ed anfibolo potrebbe indicare magmi relativamente ricchi in acqua.

Le variazioni negli elementi maggiori ed in tracce suggeriscono che la cristallizzazione frazionata è stato il principale processo evolutivo, ma al tempo stesso i magmi emessi dai centri riconducibili all'Unità Rocche sono caratterizzati da maggiore eterogeneità rispetto alle altre due unità studiate.

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Introduction

Within the Etna volcanic succession a tendency of decreasing alkalinity occurred at around 100 ka, when volcanic activity changed from fissural to centered and early central volcanic edifices

started to grow (Branca *et al.*, 2004; De Beni *et al.*, 2005). This shift from alkaline silica-undersaturated (ne-normative) to sub-alkaline (silica saturated) magmatism, although poorly documented by limited sampling, was ascribed to a changing source from the typical within plate to a slab-influenced one (Beccaluva *et al.*, 1982). This hypothesis was also partly supported by relevant change of eruptive style that progressively became more explosive (Branca *et al.*, 2004).

We present here new petrological data of Etna successions in the age interval 102-80 ka,

with the main goal to place tighter petrological, mineralogical and lithostratigraphic constraints on the magmatic evolution of this key period of Etna volcanic history. We focused on three volcanic units which crop out in the NE and SW walls of the Valle del Bove (VdB) volcano-tectonic depression (Fig. 1), from bottom to top: Rocche (RC), Serra Giannicola Grande (SGG) and Canalone della Montagnola Units (CM). These units are younger than the "Timpe" stage, (which ended at 142 ka, Gillot *et al.*, 1994), and older than the Ellittico stratovolcano, (age 80–15 ka; Branca *et al.* 2004).
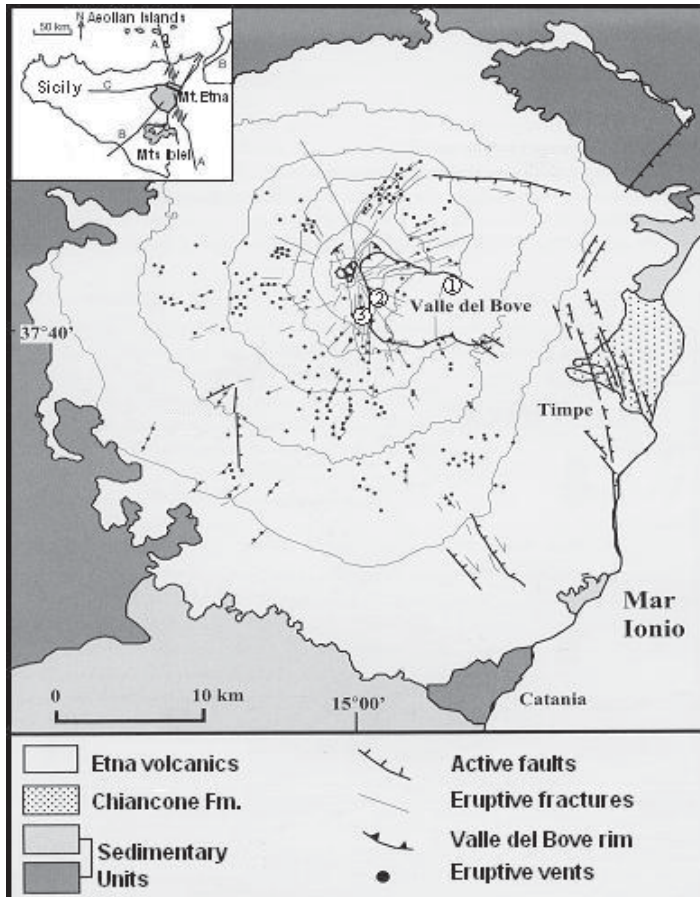

Fig. 1 – Location of Mt. Etna (inset) and Valle del Bove studied Units: (1) Rocche, (2) Serra Giannicola Grande, (3) Canalone della Montagnola. In the inset are shown three major regional faults intersecting in the Etna area (AA: Tindari-Letojanni; BB: Comiso-Messina; CC: Kumeta-Alcantara).

The Rocche Unit (RC) (ca. 100 ka) encompasses part of the "Ancient Alkaline Centers" of Romano (1982), while the Canalone della Montagnola Unit corresponds to the "Trifoglietto II" Unit of Romano (1982) (see Branca *et al.*, 2004, for a complete stratigraphic comparison among various Authors).

GEOLOGICAL AND PETROLOGICAL BACKGROUND

Etna magmatism is characterized by an (i) early tholeiitic stage (500-700 ka), during which submarine to subaerial magmas were erupted close to Acicastello and Adrano-Paternò areas, (ii) a transitional stage ("Timpe", age≈130 ka), and a (iii) late Na-alkaline magmatism, when the focus of magmatism shifted westwards (age < 120 ka) from its initial position. The Valle del Bove depression, on the eastern flank of Mt. Etna, offers excellent exposures of the volcanic edifices and related successions that were built in the period immediately following the "Timpe" stage and before the stratovolcano stage (Ellittico-Mongibello). Strangely, among the numerous petrological papers focused on the Etna magmatism, only minor attention has been devoted to the volcanic sequences cropping out along the Valle del Bove walls (Cristofolini and Lo Giudice, 1969; Klerkx, 1968; Kieffer, 1969; Lo Giudice *et al.*, 1974; McGuire, 1982; D'Orazio *et al.*,1997). Most of these papers were focused on recognising compositional variations within the succession in order to track the evolution of magma chambers. In addition, some Authors recognised some "compositional signature" useful to discriminate products of different volcanoes. McGuire (1982) studying the volcanics cropping out in the southern wall of the Valle del Bove ("Trifoglietto II" edifice), observed an anomalous trend low in TiO_2 (0.7-1.5%), which was considered due to fractionation of kaersutite, extensively occurring in these volcanics. Similarly, Cristofolini (1971) made a distinction between older Units ("Rocche" centers), higher in Ti, and younger volcanics ("Cuvigghiuni" center) which instead are Ti-poorer.

Several Authors recognized in etnean products of the last decades a progressive tendency to the enrichment in K and large-ion lithophile elements (LILE). LILE and volatile-enriched primitive magmas have also been erupted explosively (sub-plinian eruption) 3930±60 BP (Coltelli *et al.*, 2005). Geochemical characters of these magmas have been ascribed to a progressive increasing influence of fluid-rich melts (Tonarini *et al.*, 2001; Schiano *et al.*, 2001) in a plume-related intraplate source. These processes have been related to progressive south-eastward retreat of the young Aeolian subduction front and associated to the southward rollback of the Ionian slab (Doglioni *et al.*, 2001). In fact, Mt. Etna lies near the boundary between the Aeolian subduction zone magmatism with the alkaline/subalkaline magmatism of the Etna-Iblei system.

However, both present-day activity and older picritic eruption as well, represent only a short period in the Mt. Etna history and produced only a small fraction of the magma erupted by the volcano in the last 700 ka. Conversely, we expect that large scale geodynamic processes as the rollback of the Ionian lithosphere, related slab windows, and migration of K-rich slab derived fluid in the Etna source would have produced large anomalies in magma compositions, as a result of large significant changes in production rates, in geometry of source and feeding system and in eruptive style as well.

ANALYTICAL METHODS

Mineral analyses have been obtained using a (i) LEO™440 scanning electron microscope coupled to an Oxford-Link EDS (hosted at Dept. CFTA, University of Palermo; operating conditions: 20 kV accelerating voltage, 600 pA beam current), and by a (ii) JEOL-JXA 8600 electron microprobe (hosted at CNR-IGG of Florence; operating conditions: 15 kV accelerating voltage and 20 nA beam current). In both cases quantitative analyses (adopting the ZAF correction procedures) were calibrated using natural mineral and glass standards.

Major and trace element whole-rock analyses were performed on 14 samples by X-ray fluorescence following the analytical procedures of Franzini *et al.* (1975), AAS (Na and Mg), titration (FeO) and LOI at Istituto Nazionale di Geofisica e Vulcanologia (Catania).

Petrography and mineral chemistry

The Rocche (RC), Serra Giannicola Grande (SGG) and Canalone della Montagnola (CM) Units consist essentially of porphyritic lava flows, except a sample (VBN 6) from the Rocche Unit, which is a pyroclastic flow. Phenocrysts (crystals > 500 μm in length) are set in a mainly intersertal groundmass, subordinately hyalopilitic and pilotaxitic (Table 1). Phenocrysts consist of euhedral plagioclase and, in order of decreasing abundance, subhedral clinopyroxene, anhedral olivine, amphibole and Fe-Ti oxides. Among Fe-Ti oxides, magnetite is the most abundant, ilmenite is scarce since has been found only in SGG samples. Magnetite is the principal groundmass mineral but frequently occurs also as larger (up to 0.8 mm) subhedral phenocrysts.

As a general rule, plagioclase becomes more abundant in more evolved rocks (benmoreites, see below), principally at the expense of olivine.

Among accessory phases, rhönite is often found in amphibole coronas; apatite is frequently enclosed in plagioclase and amphibole. Iddingsite alteration affects frequently olivine phenocrysts. Microlites (<50 μm in length) are commonly represented by the same phases found as phenocrysts.

Plagioclase

In the whole set of studied rocks, plagioclase abundance is in the range 40-78 vol % (proportion on the total phenocryst content), increasing in mugearites and benmoreiites respect to hawaiites. Plagioclase composition varies from bytownitic to labradoritic (Table 2). Normal zoning is dominant in the RC and SGG Units while the CM Unit shows dominant reverse and patchy zoning. The An content of phenocryst rims in the RC Unit is the highest among the studied Units: An_{83-66} with Ca-rich cores up to An_{87}, while microlites are in the range An_{58-51}. In the SGG Unit vary from An_{64-46}

TABLE 1 – *Petrographic features of studied lava samples. (1) CM = Canalone della Montagnola, SGG = Serra Giannicola Grande, RC = Rocche. (2) P.I. % = porphyritic index (vol. %). (3) pl = plagioclase, cpx = clinopyroxene, ol = olivine, mt = Ti-magnetite, amph = amphibole, tr = trace amounts (<1%). (4) GDM = groundmass (crypt = cryptocrystalline; hyal = hyalopilitic, hyp = hypocrystalline, int = intersertal, pil = pilotaxitic). Modal data from SGI (2006).*

SAMPLE	SYNTHEM	UNIT (1)	UTM coordin.	ALTITUDE (m a.s.l.)	P.I.% (2)	PHENOCRYST ABUND. % (3)	GDM (4)
VBS 98	Girolamo	CM	(E) 501180 (N) 4175400	2380	19	pl (10), cpx (5), ol (2), mt (1), amph (1)	cryp
VBS 67	Girolamo	CM	(E) 501440 (N) 4175000	2310	32	pl (25), cpx (5), ol (1), mt (1)	int
VBS 65	Girolamo	CM	(E) 501090 (N) 4174440	2430	< 35	pl > cpx > ol > mt	int
VBS 61	Girolamo	CM	(E) 501980 (N) 4174610	2450	< 5	cpx > pl > amph > ol	pil
VBS 49	Girolamo	CM	(E) 501210 (N) 4174870	2310	28	pl (15), cpx (10), ol (2), mt (1)	int
VBS 20	Girolamo	CM	(E) 501360 (N) 4174380	2370	18	pl (10), cpx (5), ol (1), mt (2)	pil
VBS 18	Girolamo	CM	(E) 501220 (N) 4174950	2240	19	pl (10), cpx (2), ol (5), mt (2)	int
VBS 15	Girolamo	CM	(E) 501090 (N) 4175050	2400	28	pl (20), cpx (5), ol (2), mt (1)	int
VBS 133	Zappini	SGG	(E) 501800 (N) 4176190	2350	27	pl (15), cpx (5), ol (5), mt (2)	int
VBS 132	Zappini	SGG	(E) 501800 (N) 4176200	2350	< 5	pl (1), cpx (tr) ol (tr), mt (tr)	pil
VBS 28	Zappini	SGG	(E) 502390 (N) 4175920	1960	< 35	pl > cpx > ol > amph > mt	int
VBS 24	Zappini	SGG	(E) 502210 (N) 4175760	2090	< 35	pl > cpx > ol > mt	int
VBS 199	Zappini	SGG	(E) 502080 (N) 4176058	2050	> 35	pl > cpx > ol > amph > mt	int
VBN 88	Acireale	RC	(E) 507820 (N) 4176880	1150	28	pl (20), cpx (5), ol (2), mt (1)	int
VBN 6	Acireale	RC	(E) 506000 (N) 4177590	1400	< 5	pl (2), ol (tr), mt (1), amph (1)	hyal
VBN 7	Acireale	RC	(E) 506100 (N) 4177418	1420	40	pl (25), cpx (10), ol (2), mt (2)	int
VBN 10	Acireale	RC	(E) 504900 (N) 4177828	1410	37	pl (20), cpx (15), mt (2)	hyal
VBN 5	Acireale	RC	(E) 506100 (N) 4177570	1350	15	pl (10), cpx (2), ol (1), mt (2)	hyp

TABLE 2 – *Selected analyses of plagioclases (analyses by EPMA-WDS) from the Rocche (RC), Serra Giannicola Grande (SGG) and Canalone della Montagnola (CM) Units of the Valle del Bove volcanic rocks. Core Ph = core phenocrysts, rim Ph = rim phenocrysts; m= microlites (n = number of analyses).*

Sample	RC Unit			SGG Unit			CM Unit		
	VBN 88	VBN 88	VBN 88	VBS 134	VBS 134	VBS 134	VBS 65	VBS 65	VBS 65
	core Ph	rim Ph	m	core Ph	rim Ph	m	core Ph	rim Ph	m
(n=)	5	5	5	5	5	5	5	5	5
SiO_2	47.70	50.40	52.18	50.37	51.36	54.33	56.56	52.18	55.80
Al_2O_3	32.90	31.11	29.78	30.89	30.01	27.77	27.07	29.76	27.24
FeO tot	0.64	0.70	0.76	0.73	0.88	0.91	0.46	0.75	0.77
CaO	15.91	13.80	12.13	13.42	12.95	10.23	8.58	12.08	9.11
Na_2O	2.72	3.81	4.66	3.98	4.25	5.50	6.09	4.69	5.93
K_2O	0.05	0.13	0.34	0.30	0.39	0.86	1.17	0.36	1.01
Total	99.93	99.96	99.86	99.69	99.83	99.61	99.93	99.83	99.85
An	76	66	58	64	61	48	41	57	43
Ab	24	33	40	34	36	47	52	41	51
Or	0	1	2	2	2	5	7	2	6

for phenocrysts to An_{48-40} for microlites. In the CM Unit the range is An_{66-41} for phenocrysts to An_{54-43} for microlites. It is worth of note that An-rich portions of patchy-zoned phenocrysts of the latter Unit, encloses frequently anhedral amphiboles (Fig. 2).

Pyroxene

Clinopyroxenes is the second by abundance phenocryst phase (11–36 vol %) and range in composition from diopside to augite (following IMA classification reported in Morimoto, 1989; Table 3). Clinopyroxene is rather homogeneous throughout all the units: RC phenocrysts $Wo_{48}En_{39}Fs_{13}$ and microlites $Wo_{45}En_{35}Fs_{19}$; SGG ($Wo_{46}En_{40}Fs_{14}$) and ($Wo_{46}En_{38}Fs_{15}$); CM ($Wo_{46}En_{40}Fs_{12}$) and ($Wo_{47}En_{38}Fs_{14}$), phenocrysts and microlites respectively.

They have generally variable Al_2O_3 contents (2.2-9.3 wt. %) and the average content of TiO_2 is 1.5 wt. %. Clinopyroxene phenocrysts, do not exhibit evident zoning and show an homogeneous composition, without significant variations among various Units.

Olivine

Olivine phenocrysts abundance is in the range 3-26 vol %. The range of phenocryst-microlite compositions for all analysed samples does not vary greatly in forsterite (Fo) content, which ranges from 72 to 69 mole % for phenocrysts and 72 to 62 mole % for microlites (Table 4). Rare, extensively crystallized melt inclusions, are hosted in olivine phenocrysts.

Fe-Ti oxides

Magnetite abundance is in the range 3-10 vol %; its composition is variably enriched in TiO_2 (i.e. ulvöspinel, usp, component): Usp_{50-64} is the variation range for the RC Unit, Usp_{50-63} of the SGG Unit, while the CM Unit exhibits a smaller range, Usp_{60-64}.

Ilmenite is rare and occurs as discrete crystal in the groundmass of the SGG Unit. Its composition is variably enriched in hematite component (ilm=
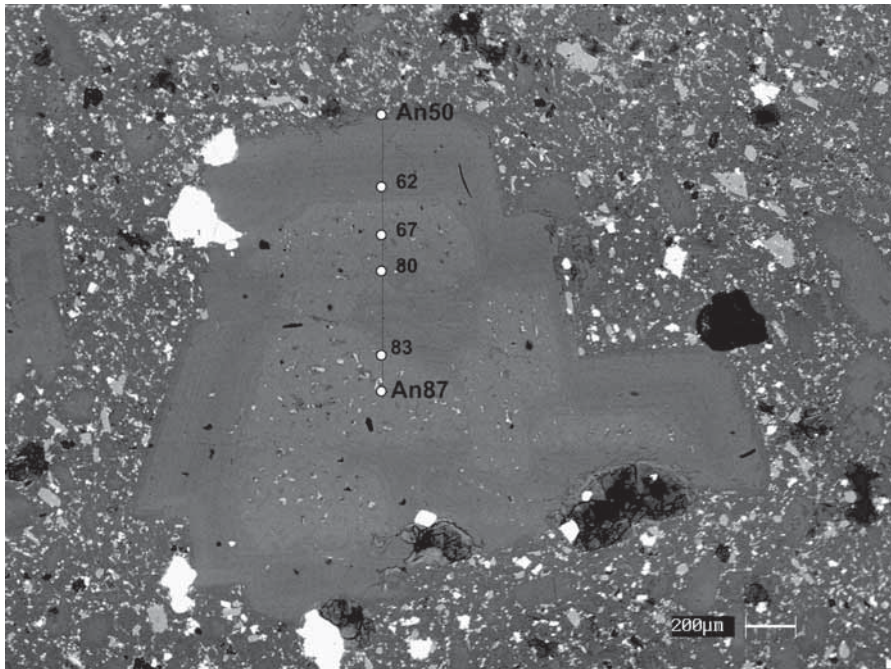
Fig. 2 – Back-scattered electron image of patchy zoning in plagioclase phenocrysts. Numbers represent the anorthite (%) content of plagioclase, along a 50-point traverse. Note the tiny amphibole inclusions (whitish spots) in plagioclase (sample VBS 18, Canalone della Montagnola Unit).

TABLE 3 – *Selected analyses of clinopyroxenes (Analyses by EPMA-WDS). Symbols as in Table 2.*

	RC Unit			SGG Unit			CM Unit		
Sample	VBN 88	VBN 88	VBN 88	VBS 134	VBS 134	VBS 134	VBS 65	VBS 65	VBS 65
	core Ph	rim Ph	m	core Ph	rim Ph	m	core Ph	rim Ph	m
(n=)	3	3	5	5	5	5	5	5	5
SiO_2 (wt%)	49.00	48.85	49.67	48.23	47.75	47.37	49.24	48.77	47.54
TiO_2	1.36	1.58	1.48	1.57	1.82	2.35	1.18	1.48	1.94
Al_2O_3	4.72	4.45	3.23	5.53	5.73	4.88	4.60	4.77	3.95
FeO tot	7.98	8.37	9.20	7.93	8.61	9.99	7.88	8.18	8.34
MnO	0.19	0.18	0.34	0.15	0.14	0.16	0.25	0.15	0.26
MgO	13.51	13.38	13.44	13.34	12.89	12.16	13.93	13.56	12.63
CaO	22.40	22.65	21.83	22.62	22.37	22.03	22.11	22.19	22.68
Na_2O	0.70	0.52	0.76	0.68	0.76	0.83	0.76	0.78	1.13
Total	99.85	99.97	99.93	100.06	100.09	99.80	99.97	99.93	98.60
Wo	47	47	46	48	48	47	46	47	48
En	40	39	39	39	38	36	41	40	38
Fs	13	14	15	13	14	17	13	13	14

TABLE 4 – *Selected analyses of olivines (analyses by SEM-EDS). Symbols as in Table 2.*

Sample	RC Unit			SGG Unit			CM Unit		
	VBN 88	VBN 88	VBN 88	VBS 134	VBS 134	VBS 134	VBS 65	VBS 65	VBS 65
	core Ph	rim Ph	m	core Ph	rim Ph	m	core Ph	rim Ph	m
(n=)	3	2	5	5	5	5	5	5	5
SiO_2	36.92	37.41	35.85	37.33	37.60	37.23	37.76	37.19	37.08
FeO tot	25.92	24.63	32.23	24.33	24.38	25.15	22.50	25.60	24.79
MnO	0.59	0.60	1.02	0.50	0.53	0.54	0.43	0.78	0.85
MgO	35.66	36.58	29.38	37.16	36.51	35.54	38.29	35.50	35.81
CaO	0.30	0.23	0.61	0.32	0.34	0.55	0.22	0.27	0.45
Cr_2O_3	0.12	0.00	0.00	0.03	0.00	0.00	0.03	0.04	0.03
NiO	0.07	0.00	0.18	0.02	0.07	0.08	0.11	0.13	0.11
Tot.	99.57	99.45	99.27	99.70	99.43	99.09	99.34	99.52	99.13
Fo %	71	73	62	73	73	72	75	71	72

61-85); more rarely ilmenite occurs as exsolved lamellae within magnetite, most likely developed during the post-emplacement cooling.

Amphibole

Brown amphibole is common in all the analyzed samples (abundance ≤ 7 vol %), it occurs as:

– phenocrysts, ranging from pargasite to Mg-hastingsite (Leake *et al.*, 1997; Table 5) with a rather high halogen content: Cl=0.10-0.13 wt. %, F=0.39-2.07 wt. %. Phenocrysts are characterized by a variably thick breakdown corona composed of clinopyroxene, Fe-Ti oxides, plagioclase and rhönite. The TiO_2 content ranges from 2.4 to 5.1 wt. % in the SGG Unit, a different trend of Ti vs. Al_{tot} (not shown) is depicted with respect to amphiboles of 2001 and 2003 eruptions (Clocchiatti *et al.*, 2004, Corsaro *et al.*, 2006, Viccaro *et al.*, 2006).

– Amphibole anhedral relics, enclosed in Ca-rich (up to An_{87}) plagioclase cores. The TiO_2 content is in the same range of amphiboles of the previous type, but whilst TiO_2 is rather constant in the RC Unit (2.1-2.6 wt.%), in the CM Unit is instead more variable (3.5 – 5.8%).

Rhönite

In the etnean lavas, the occurrence of *rhönite* (an aenigmatite group mineral, Johnston, 1985;

Bonaccorsi *et al.*, 1990) is uncommon, having been reported by D'Orazio (1994), Clocchiatti *et al.* (2004) and Corsaro *et al.* (2006). Recently, it has been also found in amphibole breakdown products in alkaline lavas from Ustica Island (Alletti *et al.*, 2005). In the studied lavas rhönite (Table 5) forms at the expense of amphibole and forms variably thick coronas (Fig. 3). If compared with amphibole-related rhönites from mafic alkaline magmas at Ustica (Alletti *et al.*, 2005), Etna rhönites are higher in their TiO_2 and MgO contents.

WHOLE-ROCK GEOCHEMISTRY

Lavas belonging to the RC and SGG units show a rather wide compositional variation (hawaiite to benmoreite), whilst lavas from CM unit are all mugearites (Fig. 4; Table 6). All analysed samples are rather low in MgO content (<6 wt. %) and the Mg_v ratio (=[$MgO/MgO+FeO_{tot}$]×100 molar) is generally lower than 57. TiO_2, MgO, FeO_{tot}, CaO and P_2O_5 decrease with increasing silica, while K_2O and Na_2O increase.

Hawaiitic rocks of RC and SGG Units are relatively high in TiO_2 (up to 2.1%), while the CM Unit volcanics are distinctly lower in TiO_2 (1.1 - 1.5 wt.%). The TiO_2 content decreases with magma

Table 5 – *Selected analyses of amphiboles and rhonite (analyses by EPMA-WDS). Symbols as in Table 2.*

|	RC Unit	SGG Unit						CM Unit		CM Unit
Sample	VBN5	VBS199	VBS199	VBS199	VBS199	VBS199	VBS199	VBS18	VBS18	VBS35
(n=)	2	2	4	5	6	7	8	1	3	rhonite
	m	ph	ph	ph	ph	ph	ph	m	m	(n=3)
SiO_2 (wt%)	45.32	39.62	41.92	41.18	41.25	41.56	39.32	45.66	39.02	24.93
TiO_2	2.59	3.36	5.09	5.04	4.26	5.06	4.76	3.52	5.84	6.97
Al_2O_3	14.84	15.49	11.67	11.68	11.89	11.68	11.43	6.00	5.75	16.87
FeO tot	9.37	10.88	11.11	11.31	10.87	11.21	18.63	12.06	23.03	21.69
MnO	0.26	0.13	0.11	0.22	0.21	0.24	0.24	0.29	0.57	0.20
MgO	5.18	13.81	13.70	13.31	14.49	13.56	13.58	9.44	8.87	14.99
CaO	15.55	12.24	11.62	11.62	11.80	11.57	10.82	20.95	11.95	10.93
Na_2O	3.57	2.11	2.86	3.16	2.84	3.04	3.07	1.08	2.19	1,63
K_2O	0.67	1.11	1.03	0.90	0.91	0.94	0.81	0.03	0.74	0.02
Total	97.35	98.76	99.11	98.46	98.52	98.88	102.66	99.06	97.96	98.32
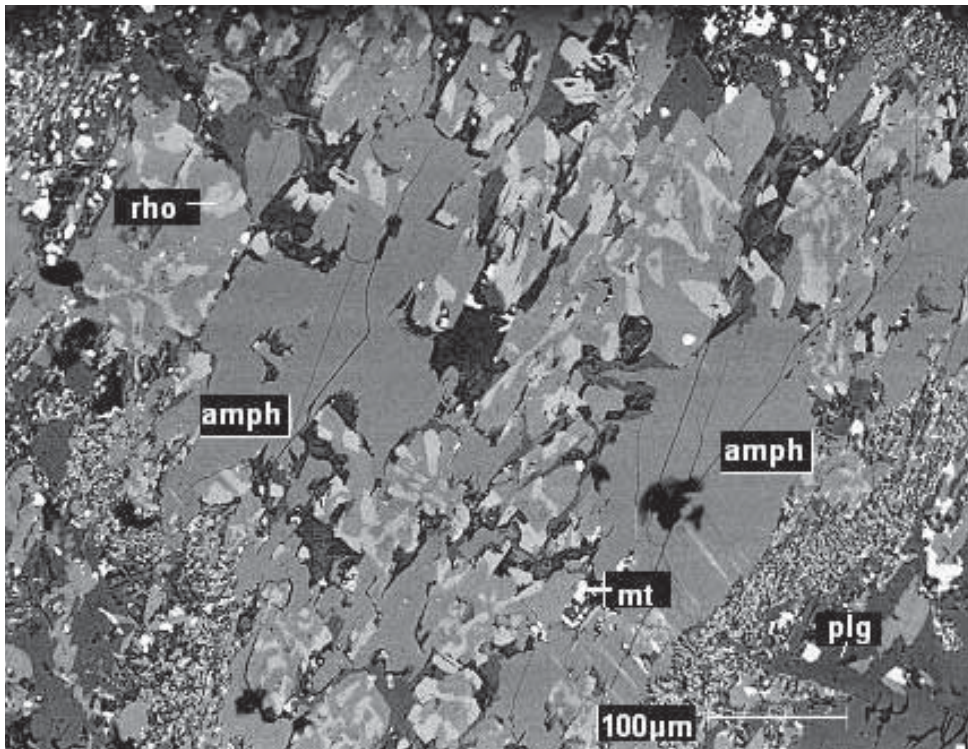
Fig. 3 – Back-scattered electron image of amphibole phenocrysts and their breakdown products consisting of rhönite (light grey) and plagioclase (dark grey).
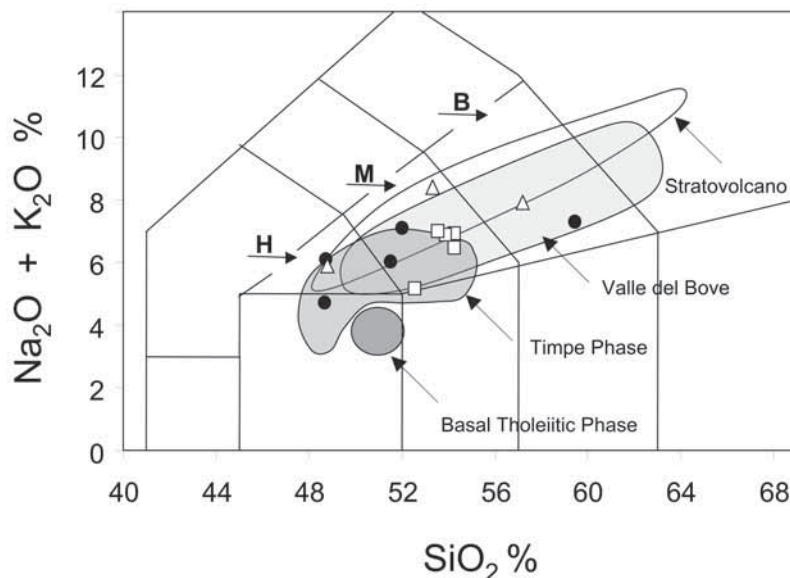
Fig. 4 – Total alkali vs. silica (TAS, Le Maitre *et al.*, 1989) diagram for Valle del Bove volcanic rocks. Filled circles: Rocche Unit (RC); Triangles: S. Giannicola Grande Unit (SGG); open squares; Canalone della Montagnola Unit (CM). H=hawaiite; M=Mugearite; B=Benmoreiite. Fields labeled: Tholeiitic, Timpe, Valle del Bove and Stratovolcano, are taken from Corsaro and Pompilio (2004).

evolution reaching the lowest value (0.8-0.9 wt.%) in benmoreites of the RC and SGG Units.

Rocche Unit (RC) volcanics (hawaiites to benmoreites) are characterized by a wide variation in silica saturation, from nepheline (*ne*-norm=2-4%) to quartz normative (*q*-norm=7%). Major elements are also very variable: SiO_2 = 48.6-58.0 wt.%; TiO_2 = 0.9-2.0 wt.%; MgO= 1.9-4.0 wt.%, with an Mg_v in the range from 35 to 48.4. Rather high Sr values (1277-1363 ppm) are coupled to variable amounts in other trace elements Rb (27-40 ppm), Zr (138-158 ppm) and Ba (717 ppm).

Serra Giannicola Grande Unit (SGG) rocks are hawaiitic to benmoreitic in composition (SiO_2=48.6-56.7%), mainly *ne*-normative (*ne*-norm=5-3%), with Mg_v varying from 30.5 to 49.5. Trace elements are rather contrasting: values of Cr (9-39 ppm), Zr as well (197-320 ppm) but Ni is very low (3-24 ppm) and both Nb (67-101 ppm) and La (93-119 ppm) are very variable.

Canalone della Montagnola Unit (CM) is composed of *hy*-normative mugearites with Mg_v in the range 40.8-56.2. Major elements show

limited variability: SiO_2 (52.0-53.9 wt.%), TiO_2 (1.1-1.5 wt.%), Al_2O_3 (16.9-20.1 wt.%). Trace elements are characterized by limited variability and intermediate values: Cr (13-120 ppm), Ni (10-51ppm), Rb (34-49 ppm), Nb (48-82 ppm), Sr (849-1401 ppm) and Ba (570-930 ppm).

DISCUSSION

Geothermobarometric constraints

T and fO_2 calculations were performed using coexisting magnetite-ilmenite discrete grains (i.e. not exsolved lamellae) in mugearite from SGG, using the calibration of Spencer and Lindsley (1981). Even if fulfilling the criteria for chemical equilibrium stated by Bacon and Hirschmann (1988), results are likely to reflect late stage of crystallisation or some sub-solidus re-equilibration: T= 900-973 °C, log fO_2 = -11 (ΔQFM=+1.5).

An attempt to constrain pre-eruptive temperatures and pressures using the single-pyroxene calibration

Table 6 – *Whole-rock analyses: major element composition (wt%), selected CIPW normative minerals and trace elements. (*) FeO recalculated according to $Fe_2O_3/FeO=0.40$ (Middlemost, 1989) (LOI= Loss on ignition, Mg_v = molar $[MgO/MgO+FeO_{tot}] \times 100$). CIPW norms were calculated recasting the Fe_2O_3/FeO ratio following Middlemost (1989). B.d.l.= below detection limit; n.d.= not determined.*

	Acireale					Zappini			Girolamo				
Synthem													
UNIT	RC	RC	RC	RC	RC	SGG	SGG	SGG	CM	CM	CM	CM	CM
SAMPLE	VBN 5	VBN 6	VBN 7	VBN 10	VBN 88	VBS 132	VBS 133	VBS 199	VBS 15	VBS 18	VBS 20	VBS 49	VBS 67
Rock-type	Haw	Benm	Haw	Mug	Mug	Mug	Haw	Mug	Mug	Mug	Mug	Mug	Mug
SiO₂ (wt%)	48.64	58.00	48.73	52.32	51.46	52.98	48.64	56.70	53.90	52.73	53.46	52.04	53.38
TiO₂	2.01	0.92	1.84	1.66	1.55	1.65	2.06	0.89	1.12	1.11	1.16	1.47	1.14
Al₂O₃	19.06	17.66	18.97	18.53	19.65	18.22	18.43	18.83	18.78	18.19	19.64	16.89	20.08
Fe₂O₃	1.85	*1.69	2.56	3.23	2.23	3.29	2.45	*1.57	3.01	4.97	6.41	2.68	3.53
FeO	7.35	4.25	6.91	5.99	5.70	4.84	7.30	3.94	4.21	2.41	1.25	5.68	3.52
MnO	0.15	0.16	0.17	0.15	0.14	0.17	0.17	0.11	0.15	0.14	0.15	0.16	0.14
MgO	3.61	1.97	4.45	2.55	4.03	2.63	4.60	2.33	3.46	3.72	2.71	5.78	2.84
CaO	9.27	4.96	9.42	7.81	7.96	6.01	8.68	6.14	6.88	6.89	6.85	8.06	7.04
Na₂O	4.25	4.86	3.95	4.41	4.53	5.76	4.03	5.35	4.85	4.15	4.78	3.54	4.91
K₂O	1.82	2.24	1.29	2.05	1.46	2.59	1.84	2.50	2.00	2.13	2.04	1.55	2.06
P₂O₅	1.07	0.33	0.62	0.84	0.60	0.72	0.75	0.35	0.54	0.53	0.64	0.56	0.67
L.O.I.	0.94	2.86	1.03	0.53	0.68	1.15	1.06	0.85	1.10	3.02	0.91	1.59	0.68
Total	100.02	99.90	99.94	100.07	99.99	100.01	100.01	99.56	100.00	99.99	100.00	100.00	99.99
Mg_v	41.9	37.8	46.3	35.0	48.4	37.7	46.5	43.7	47.3	49.2	40.8	56.2	43.2
q (CIPW)		7											
or	11	14	8	12	9	16	11	15	12	13	12	9	12
ab	29	42	30	38	39	41	29	46	42	36	41	30	42
an	28	20	31	25	29	16	27	20	24	26	26	26	27
ne	4		2			5	3						
di	10	2	10	7	5	7	9	7	6	5	3	9	3
hy		9		6	1			7	6	14	7	18	2
ol	9		11	3	10	7	12		5		4		7
Nb (ppm)	47	68	51	53	67	101	67	66	71	62	82	48	76
Zr	138	235	116	187	158	320	197	253	223	239	250	182	242
Y	31	24	30	29	20	27	22	19	20	17	20	18	20
Sr	1277	888	1195	1239	1363	1040	1138	953	1054	1158	1395	849	1401
Rb	40	59	26	45	27	49	32	68	47	49	44	34	47
Ce	n.d.	126	n.d.	n.d.	151	196	158	129	146	141	175	107	167
Ba	n.d.	792	n.d.	n.d.	717	1072	852	927	753	802	930	570	902
La	n.d.	74	n.d.	n.d.	89	119	93	80	89	87	108	56	101
Ni	n.d.	b.d.l.	n.d.	n.d.	14	3	24	b.d.l.	14	18	10	51	12
Cr	n.d.	b.d.l.	n.d.	n.d.	17	9	39	25	18	17	16	120	13
V	n.d.	77	n.d.	n.d.	211	143	252	129	156	171	168	184	172
Co	n.d.	11	n.d.	n.d.	28	25	37	16	26	27	26	33	25

of Nimis (1996) gave exceedingly high temperatures (1268 – 1356 °C) at pressures in the range 0.4 – 0.7 GPa, the higher values were obtained for the rocks of the older RC Unit.

Plagioclase–liquid equilibria are demonstrated to be very sensitive to H_2O-melt content, which is reflected in the Ca-Na exchange coefficient (Sisson and Grove, 1993). In fact the $K_D^{plg-liq}(Ca-Na)$ increases in the range 1-5, i.e. plagioclase becomes Ca-richer, with increasing H_2O-melt [$K_D^{plg-liq}(Ca-Na)= (Ca/Na_{plg})/(Ca/Na)_{melt}$]. Among the studied rocks the highest values of $K_D^{plg-liq}(Ca-Na)$ (assuming whole rock analyses as representative of the melt) characterize the RC Unit although with a significant spread (K_D= 1.6 - 4.8; mean = 2.9), the lower values are for the SGG Unit (K_D= 0.7-1.6) while CM Unit is in an intermediate range (K_D= 1.1-1.8) (Fig. 5).

As regards to the amphibole occurrence, it is worth to remind here that amphibole is common in Etnean lavas, particularly in the Ellittico period. In the products younger than 15 ka amphibole is a rather rare occurrence: e.g. the 122 B.C. and the 1886 A.D. eruptions (Branca and Del Carlo, 2004) and the recent 2001 and 2003 eruptions (Clocchiatti *et al.*, 2004; Corsaro *et al.*, 2006). Experimental works on basaltic compositions (Barclay and Carmichael, 2004; Pompilio and Rutherford, 2002) clearly show that amphibole is a late-liquidus phase and can form only at temperature lower than 1000 °C and pressure > 75 MPa. Thus the occurrence of this mineral can be considered as accidental or xenocrystic in basalts or in hawaiites since amphibole forms into the relatively cold part of a crystallising basaltic magma body (i.e. walls, roof) like in 2001-2003 A.D eruption (Pompilio *et al.*, 2002). On the contrary in mugearites or benmoreites, that derive from liquids produced by protracted crystallisation at low temperature of a parent basaltic magma, the amphibole can be an equilibrium phase. In this framework, the anhedral amphibole enclosed in anorthitic plagioclase, would record an early crystallisation stage from a poorly evolved liquid (basaltic-hawaiitic), while
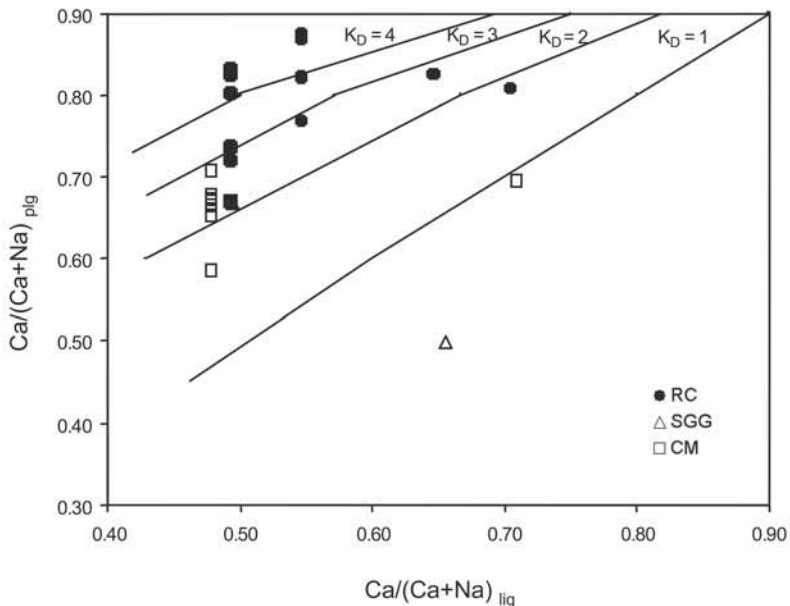

Fig. 5 – Plagioclase-liquid equilibria: Ca/(Ca+Na) atomic ratio in plagioclase phenocrysts versus Ca/(Ca+Na) in the melt (assumed equal to whole-rock analyses). K_d = (Ca/Na)$_{plg}$ / (Ca/Na)$_{melt}$. Filled circles: Rocche Unit (RC); Triangles: S. Giannicola Grande Unit (SGG); open squares: Canalone della Montagnola Unit (CM). The high K_D shown by plagioclase -liquid pairs from the RC Unit may suggest higher H_2O content in the melt.

idiomorphic amphiboles must have co-precipitated with an Na-rich feldspar from evolved mugearitic–benmoreitic liquids. Whatever was the stage of the evolution of magma chamber (fully developed, cold and evolved or initial, hot and pristine) the occurrence of the amphibole puts a strong constraint on the pressure/depth conditions of emplacement of these magma chambers. In order to crystallise amphibole, these magmas are needed to reside, cool and evolve at $P = P_{H2O} \geq 75$ MPa, corresponding to a depth of 1.8 km b.s.l. (according to the crustal density profile proposed by Corsaro and Pompilio, 2004b). The occurrence of rhönite in amphibole breakdown coronas, is related to the amphibole instability (Kunzmann, 1989) due to H_2O loss during the magma ascent.

Insights on magma evolution

The low content of MgO and the low concentrations of Ni and Cr in all studied rocks imply a not strictly primitive magma. The whole compositional range from hawaiite to benmoreite (for RC and SGG rocks) can be obtained removing about 30 wt. % of solid phases (plg 15%, cpx 7%, ol 5%, mt 3%).

The plot FeO_{tot}/MgO vs. CaO/Al_2O_3 (Fig. 6) shows that a major role in the liquid line of descent is played by clinopyroxene, olivine and subordinately by amphibole. In detail, two main trends are evident: the first, formed by CM, most of SGG rocks and younger samples of Rocche Unit, is consistent with a dominant process of
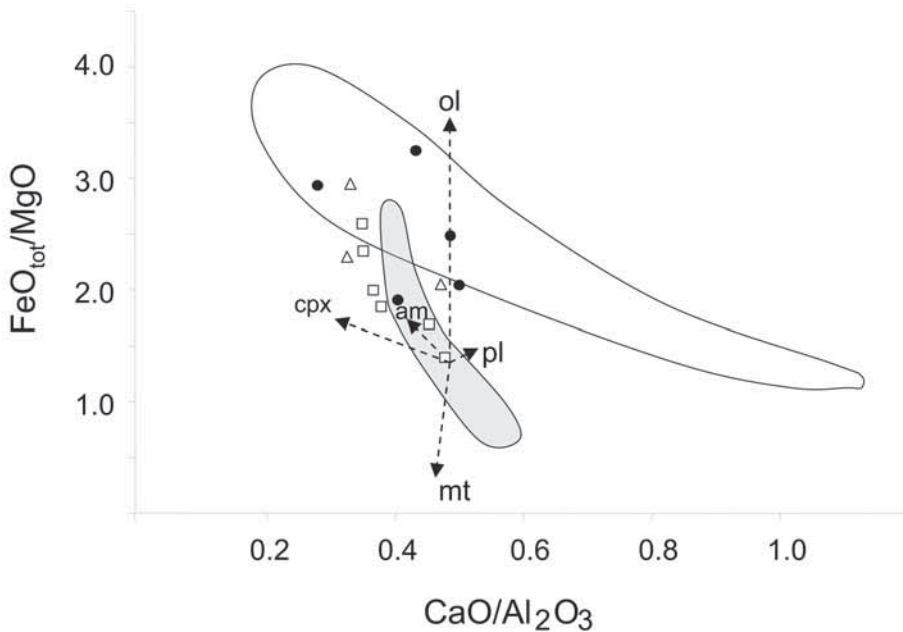
Fig. 6 – Whole-rock FeO_{tot}/MgO vs. CaO/Al_2O_3 ratios. Filled circles: Rocche Unit (RC); Triangles: S. Giannicola Grande Unit (SGG); open squares; Canalone della Montagnola Unit (CM). Am: amphibole; cpx:clinopyroxene; mt: magnetite; Ol: olivine; pl: plagioclase. The unpatterned area refers to the Stratovolcano phase; the grey area to the Timpe phase (data from Corsaro and Pompilio (2004). Vectors represent the melt modification after 10 wt % removal of the given mineral phase.

Mineral compositions were calculated from VBS 49 whole rock analysis assuming a $K_d^{xtal-liq}(Fe/Mg) = (Fe/Mg)_{xtal} / (Fe/Mg)_{melt} =$ 0.30 for olivine (i.e. Fo_{81}) and 0.26 for clinopyroxene (i.e. $Wo_{41}En_{49}Fs_{10}$) and a $K_d^{xtal-liq}(Fe/Mg) = 2$ (i.e. An_{72}); amphibole and spinel compositions were those analyzed in the VBS 49 sample. The array depicted by natural samples suggests that the liquid line of descent is mainly controlled by clinopyroxene and olivine.

fractional crystallisation of clinopyroxene, olivine and amphibole starting from an hawaiitic parent magma. The second trend involves mainly rocks of Rocche unit and is compatible with fractionation of olivine and subordinate plagioclase.

Under the assumption of a common parental magma, the above separate trends reflect different fractionating assemblage and imply diverse conditions of crystallisation and degassing in distinct magma reservoirs. Thus CM and SGG magmas should have resided in one or more reservoirs under comparable and almost constant P_{H2O} and temperature. Conversely RC products, showing a large scatter, must have evolved in a more complex and probably extended plumbing system in which olivine was an early crystallising phase. On the whole liquid lines of descent defined by the studied rocks are different from those observed in older Timpe products or in younger Ellittico-Mongibello products, denoting again important changes in conditions of ascent, residence and evolution of magmas during the volcano history.

Conclusive remarks

The principal results of this research can be summarized as follows:

– none of the studied rocks (all of them Na-alkaline in serial affinity) is strictly primitive (MgO < 6%). They display a wide compositional range from hawaiites to benmoreites. This is in contrast with the recent products of Etna (< 4 ka), which are instead more homogeneous and less evolved in composition (mostly trachybasalts). This consideration may be taken as evidence of a feeding system characterized by magma accumulation zones where crystal fractionation processes were taking place extensively with removal of phenocryst phases (pl, cpx, ol, amph). The large abundance of plagioclase and the occurrence of amphibole suggest a protracted crystallisation of hydrous magma. Major element trends in the three Units show small but significant variations, suggesting a feeding system characterized by different reservoirs. Evidence (e.g. reverse zoning patterns in phenocrysts) of repetitive refilling by more primitive magma is lacking.

– The occurrence of Ca-rich plagioclase cores, co-precipitated with an early liquidus amphibole,

suggest that magmas from the Rocche period (age: 102-100 ka) were H_2O-rich. This is supported also by the plagioclase-liquid Ca-Na distribution that suggest that magmas of this period might have equilibrated at deeper and more hydrated conditions with respect to the two younger units examined here. Finally, the ascent of H_2O-exsolving magma destabilized amphibole producing at low-pressure the rhönite and clinopyroxene coronas.

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