

Carbonatites in a subduction system: The Pleistocene alvikites from Mt. Vulture (southern Italy)

Massimo D'Orazio ^{a,b,*}, Fabrizio Innocenti ^{a,b}, Sonia Tonarini ^b, Carlo Doglioni ^c

^a *Dipartimento di Scienze della Terra, Università di Pisa, Via S.Maria 53, I-56126 Pisa, Italy*

^b *Istituto di Geoscienze e Georisorse, C.N.R., Via Moruzzi 1, I-56124 Pisa, Italy*

^c *Dipartimento di Scienze della Terra, Università "La Sapienza", P.le A. Moro 5, I-00185 Roma, Italy*

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Abstract

We report here, for the first time, on the new finding of extrusive calciocarbonatite (alvikite) rocks from the Pleistocene Mt. Vulture volcano (southern Italy). These volcanic rocks, which represent an outstanding occurrence in the wider scenario of the Italian potassic magmatism, form lavas, pyroclastic deposits, and feeder dikes exposed on the northern slope of the volcano. The petrography, mineralogy and whole-rock chemistry attest the genuine carbonatitic nature of these rocks, that are characterized by high to very high contents of Sr, Ba, U, LREE, Nb, P, F, Th, high Nb/Ta and LREE/HREE ratios, and low contents of Ti, Zr, K, Rb, Na and Cs. The O–C isotope compositions are close to the “primary igneous carbonatite” field and, thus, are compatible with an ultimate mantle origin for these rocks. The Sr–Nd–Pb–B isotope compositions, measured both in the alvikites and in the silicate volcanic rocks, indicate a close genetic relationship between the alvikites and the associated melilitite/nephelinite rocks. Furthermore, these latter products are geochemically distinct from the main foiditic-phonolitic association of Mt. Vulture. We propose a petrogenetic/geodynamic interpretation which has important implications for understanding the relationships between carbonatites and orogenic activity. In particular, we propose that the studied alvikites are generated through liquid unmixing at crustal levels, starting from nephelinitic or melilititic parent liquids. These latter were produced in a hybrid mantle resulting from the interaction through a vertical slab window, between a metasomatized mantle wedge, moving eastward from the Tyrrhenian/Campanian region, and the local Adriatic mantle. The occurrence of carbonatite rocks at Mt. Vulture, that lies on the leading edge of the Southern Apennines accretionary prism, is taken as an evidence for the carbonatation of the mantle sources of this volcano. We speculate that mantle carbonatation is related to the introduction of sedimentary carbon from the Adriatic lithosphere during Tertiary subduction.

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1. Introduction

While it is widely accepted that the parental magmas of most carbonatites ultimately derive from the mantle (Bell et al., 1982; Deines, 1989; Wyllie, 1989), the compositions of these magmas and the processes they underwent during their emplacement into the crust are still debated.

* Corresponding author. Dipartimento di Scienze della Terra, Università di Pisa, Via S.Maria 53, I-56126 Pisa, Italy. Tel.: +39 50 2215700; fax: +39 50 2215800.

E-mail address: dorazio@dst.unipi.it (M. D'Orazio).

Carbonatite melts may be produced directly by partial melting of carbonated mantle peridotites (e.g. Lee et al., 2000) or may stem from CO₂-rich, silica-undersaturated, silicate magmas through liquid immiscibility (Koster van Groos and Wyllie, 1963; Lee and Wyllie, 1998) or crystal fractionation (e.g. Veksler et al., 1998a).

Carbonatites are typically found within stable, intra-plate, continental areas and along continental rifts, more rarely within or in close proximity to orogenic belts and within oceanic plates (Woolley, 1989). This variety of geological settings raised the question of the geodynamic significance of carbonatite magmatism. In turn, this is related to another major problem regarding the genesis of carbonatites, that is, how carbon is supplied to the mantle to sustain the increasing carbonatite magmatism over geological time. There is growing evidence that carbon is largely recycled back into the Earth's mantle through the subduction of crustal carbonate rocks (Barker, 1996; Achterbergh van et al., 2002; Hoernle et al., 2002; Yaxley and Brey, 2004; Ducea et al., 2005).

Over the last fifteen years, a wealth of papers has been addressed to the petrography, geochemistry and petrology of a suite of Pleistocene, volcanic/subvolcanic rocks from the Italian peninsula, sharing a carbonatitic affinity (e.g. Stoppa and Lavecchia, 1992; Stoppa and Lupini, 1993; Stoppa and Cundari, 1995; Stoppa and Woolley, 1997; Bailey and Collier, 2000; Solovova et al., 2005; Stoppa et al., 2005; Bell and Kjarsgaard, 2006). These rocks occur in close association with highly silica-undersaturated volcanic rocks within the central and Southern Apennines (intra-Apennine volcanic rocks, IAV; Peccerillo, 1998) and, though representing a very small proportion of the Neogene to Recent Italian magmatism, they raised a lively debate concerning their nature and tectono-magmatic significance. The authors most concerned in the study of these rocks (e.g. Stoppa and Woolley, 1997) stressed the similarities between the association of carbonatites and melilitite-bearing rocks from Italy and those from the East African Rift, excluding the involvement of subduction-related processes in the petrogenesis of IAV rocks, and suggesting major differences between these latter and the potassic/ultrapotassic, peri-Tyrrhenian, volcanic rocks. Peccerillo (1998), questioned the true carbonatitic nature of these rocks, favouring their origin by shallow-level interaction between silica-undersaturated magmas and barren carbonate materials from the sedimentary basement. Bailey and Collier (2000) listed a series of geological, volcanological, petrological and mineralogical features shared by the Italian and Ugandan

carbonatite-melilitite associations, yet recognizing the drastically different tectonic settings of the two regions (orogenic vs. rifted craton, respectively). According to these authors the generation of melilitite-carbonatite associations requires neither plumes nor subduction processes, but can occur where a thick, ancient lithosphere, under a flux of volatiles from the deep mantle, undergoes low-degree melting during extensional episodes. According to Bell et al. (2004) the Sr–Nd–Pb isotope ratios of the Italian carbonatites and the associated silicate rocks would reveal the occurrence of a plume-related mantle reservoir with moderately high U/Pb and Th/Pb, very high Rb/Sr and low Sm/Nd time-integrated ratios. An opposite view is held by Bianchini et al. (2004), who instead, emphasizing the geochemical and isotopic similarities between the highly silica-undersaturated silicate rocks associated to the central Italy carbonatites and the less extreme potassic rocks from the Tyrrhenian margin of the Italian peninsula, favoured a common source for these magmas, that, according to the most common view, is a mantle extensively metasomatized by crustal materials during Tertiary subduction of the Adriatic lithosphere under the Apennines (e.g. Peccerillo, 2005 and reference therein).

The new finding of a whole sequence of carbonatite lava flows and pyroclastic deposits, described here for the first time, within the volcanic pile of the Pleistocene Mt. Vulture volcano (Basilicata, southern Italy), provides the opportunity to investigate on the nature and petrogenesis of carbonatite magmas in the geodynamic context of a young orogenic belt, the Southern Apennines. In addition, the relatively young extrusive rocks studied in this paper, being only slightly modified by secondary processes, represent good proxies of carbonatite liquid composition, and as such will be useful for understanding some general aspects of carbonatite magmatism.

2. Geological setting

Mt. Vulture is the easternmost occurrence of the whole Quaternary Italian volcanism (Fig. 1a). It is located along the southern border of the ENE-trending Ofanto graben, right on the leading edge of the Southern Apennines accretionary prism. The foreland is composed by the about 100 km thick Adriatic lithosphere, carrying a continental crust of about 30 km with an overlying 6 km thick carbonate platform of Mesozoic age (Calcagnile and Panza, 1981; Scarascia et al., 1994; Scrocca et al., 2005). These rocks plunge under the accretionary prism with a foreland monocline dip of about 6–8°, and constitute the underlying of the volcano. Mt. Vulture is strikingly different from the other major

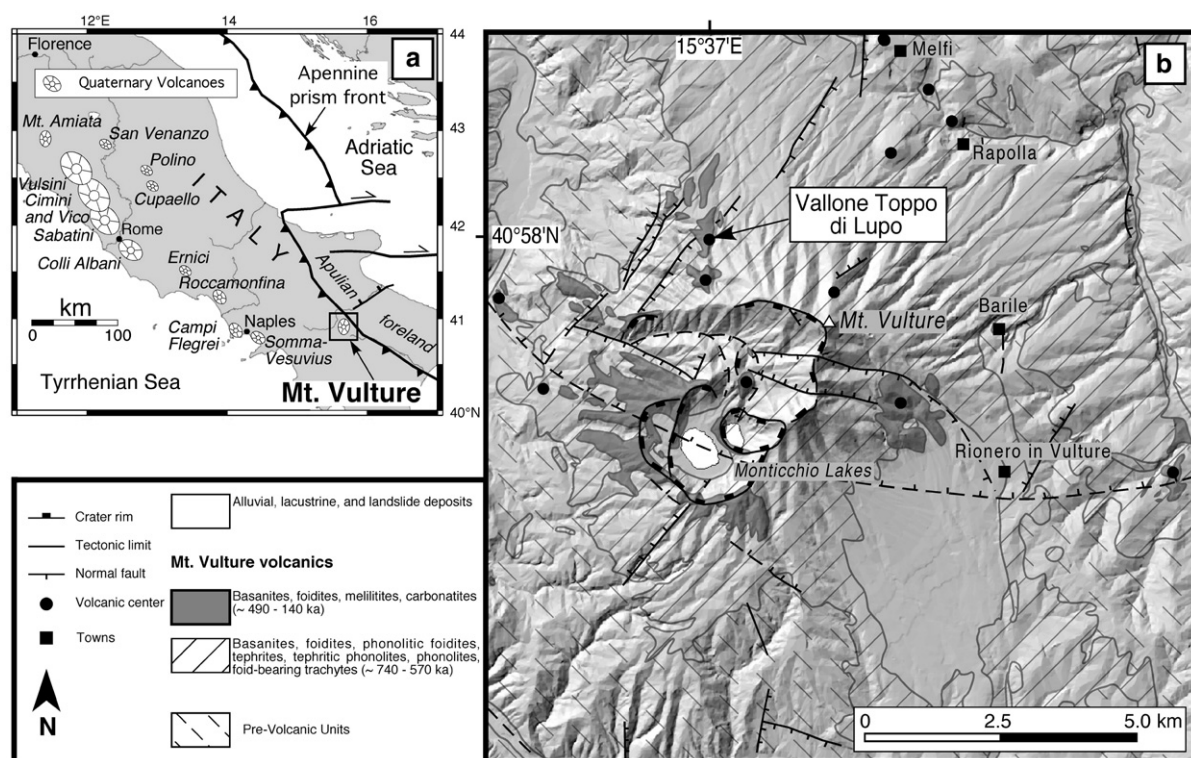


Fig. 1. (a) Sketch map of central-southern Italy with the main occurrences of the Quaternary volcanism cited in the text, and the front of the Apennine prism (Scrocca, 2006). (b) Geotectonic sketch map of the Mt. Vulture area, redrawn and simplified from Giannandrea et al. (2006), overimposed on a digital elevation model image of the area (courtesy of M.T. Pareschi, INGV-Pisa). The arrow points to the position of the carbonatite volcanic center of Vallone Toppo di Lupo.

Quaternary volcanoes of the Italian peninsula, which are aligned along its Tyrrhenian margin, to the west of the Apennines. Like Mt. Etna, it is located at the very front of the orogen, in the external part of the subduction hinge. Therefore, it cannot be sourced directly from the slab which is located further to the west. Unlike most of the Apennine foreland, where subsidence is still active, the foreland in Puglia, to the east of the volcano is uplifting. Indeed, to the north of the study area the foreland is subsiding and the transfer zone between the subsiding and uplifting foreland are E–W-trending right-lateral strike slip faults (Fig. 1a; Doglioni et al., 1994).

Mt. Vulture is a composite volcano (Fig. 1b) consisting of prevailing pyroclastic rocks and subordinate lava flows and domes. The volcanic activity started at ~ 0.75 Ma and continued, interrupted by long-lasting quiescence periods, up to ~ 0.14 Ma (Buettner et al., 2006). The volcanic history of Mt. Vulture (Principe and Giannandrea, 2006) started with the emplacement of a dike swarm followed by a large, caldera-forming, eruption. Thereafter, a series of juxtaposed eruptive centers grew inside the caldera and on its border faults. Successively, the volcanic activity shifted to a central-

type one, and the main body of the volcano was formed. After a long-lasting quiescence interval, a final, very low-volume, volcanic activity resumed along active fault systems. These latter also modified the structure and morphology of the SW sector of the volcano. During this late volcanic phase were produced the two maar craters of the Monticchio Lakes (Fig. 1b).

The erupted products range from foidites (nephelinites, haüynites, leucites) and melilitites (plus minor basanites and tephrites) to phonolitic tephrites, tephritic phonolites, phonolites and trachytes (Melluso et al., 1996; Beccaluva et al., 2002; De Astis et al., 2006). The prevailing primary mineral phases are represented by diopside, haüyne, leucite, alkali feldspar (sanidine and anorthoclase), nepheline, plagioclase, sodalite, melilite, olivine, Ti-magnetite, amphibole and brown mica. Some rock types also contain abundant apatite, melanite garnet and perovskite. In addition to the silicate volcanic rocks, Stoppa and Principe (1998) described carbonatitic tuffs and lapilli in the pyroclastic succession related to the activity of the Monticchio Lakes maars, while Rosatelli et al. (2000) studied intrusive calciocarbonatite ejecta (sövite) found within pyroclastic surge deposits from the

lower portion of the volcanic pile (Rionero Subsynthem, Giannandrea et al., 2006). This latter finding suggests that carbonatite magmatism was not restricted to the final stages of Mt. Vulture activity. Ultramafic xenoliths and megacrysts (both cumulates and lithospheric mantle rocks) are locally abundant, particularly within the carbonatitic-melilititic tuffs from the Monticchio Lakes (Jones et al., 2000; Downes et al., 2002).

3. The carbonatite volcanic center of Vallone Toppo di Lupo

The carbonatite rocks described in this work crop out in the north-western sector of Mt. Vulture ($\sim 40^{\circ}57.7'N$ $15^{\circ}36.7'E$), at an altitude comprised between 780 and 725 m above sea level (Fig. 1). The igneous materials form a sequence of lava flows, dikes and pyroclastic deposits carved by a small, NNE-SSW-trending, valley named Vallone Toppo di Lupo (hereafter VTL; “Carta Tecnica dell’Italia Meridionale alla scala 1:5.000”) (Fig. 2). In this locality, the carbonatitic rocks constitute the uppermost level of the volcanic succession. The inner structure of the VTL eruptive center is partially exposed on the western flank of the valley, whereas it is almost completely covered by colluvial detritus and vegetation on the eastern flank. The upstream side of the section is dominated by a succession of thin layers of pyroclastic rocks with a sub-horizontal or gently dipping (max 15°) layering, that mantles the pre-existing morphology. These pyroclastics deposits have a maximum thickness of 4–5 m, overlie a sequence of matrix-supported volcanic breccia (Giannandrea et al., 2006), and are separated from this latter by a 10–15 cm thick layer of light brown pedogenized tuff (Fig. 2b). The pyroclastic layers are made of alternating carbonatitic lapilli and ash, variably litified by dissolution–reprecipitation of calcite. They carry abundant xenocrysts and lithic fragments, up to decimeter-sized blocks of dark silicate lavas. Towards the central portion of the exposed section, the sub-horizontal pyroclastic layers are cross-cut by a 60–70 cm thick, massive, carbonatite dike trending NW–SE (Fig. 2c). To the north side of the dike is exposed a peculiar, 1–2 m thick layer made of poorly cemented, rounded carbonatite lapilli ranging in size from few millimeters up to 5–6 cm (Fig. 2d). The lapilli are sub-spherical to ovoidal in shape, have a smooth surface and are made of massive carbonatite. Sometimes the largest lapilli have a core of dark silicate lavas, black cumulate clinopyroxenite, or coarse grained, melilitite-bearing mafic/ultramafic rocks. A larger carbonatite dike, trending N–S and dipping $\sim 40^{\circ}$ W, is exposed in the lower central portion of the section (Fig. 2a). This dike

thickens towards its upper end, and was the feeder of a sequence of massive, light grey, lava flows. The two main lava flows are separated by ~ 5 m of pyroclastic material (Fig. 2e). The upper lava is ~ 2.5 m thick and ~ 300 m long, the lower lava is slightly thicker and apparently shorter. The VTL carbonatites have not been dated yet; however, they occur at relatively high elevations on the volcano, at the top of the local volcanic succession, and overlie a volcanic breccia deposit erupted during a late period of activity of Mt. Vulture (Giannandrea et al., 2006). Moreover, they share many petrographical and volcanological features with the carbonatite-melilitite tuffs from the Monticchio Lakes (Stoppa and Principe, 1998). Therefore, it is likely that the VTL carbonatites have been erupted during the final phases of activity of the volcano, possibly at the same time as the maars of the Monticchio Lakes formed.

According to the 1:25.000 scale Geological Map of Mount Vulture (Giannandrea et al., 2004), the rocks studied in this paper are part of the sequence of volcanic products (Imbandina Subsynthem) erupted from a small volcanic center occurring on the northern slope of Mt. Vulture. The authors of the map describe this sequence as formed by massive deposits of ashes and poly lithologic blocks with abundant ultrafemic nodules, subordinate fine-grained ashes with lamination and breccia with travertine at the top over a 8 m-thick lava flow. Our own observation in the field, and the analytical data reported and discussed in the following sections, led us to interpret these deposits as the explosive and effusive products (plus feeder dikes) of a small carbonatite volcanic center distinct from, and younger than, that originating the Imbandina Subsynthem.

4. Methods

Major- and trace-element analyses were performed at Pisa University’s Dipartimento di Scienze della Terra. Silica, TiO_2 , Al_2O_3 , total iron as Fe_2O_3 , MnO, MgO, CaO, Na_2O , K_2O and P_2O_5 were determined by X-ray fluorescence (XRF) on a ARL 9400 XP+ spectrometer, using $Li_2B_4O_7/LiBO_2$ glass disks. Estimated precision (relative standard deviation, RSD) is $\sim 1\%$ for CaO and $\sim 2\%$ for the other major element except for low concentrations ($\sim <0.50$ wt.%) for which the absolute standard deviation is about $\pm 0.01\%$. Loss on ignition (LOI) was determined by gravimetry at $1000^{\circ}C$ after preheating at $110^{\circ}C$. Total C, reported as CO_2 , and F were determined by LECO (SC-144DRPC analyser) and fluoride selective electrode, respectively, at CRPG-CNRS (Vandoeuvre-lès-Nancy, France). Precision is better than 2% RSD for CO_2 , and better than 5% RSD for F.



Fig. 2. Photographs of the carbonatite eruptive center of Vallone Toppo di Lupo. a) Panoramic view of the western flank of the Vallone Toppo di Lupo valley, showing the two main carbonatite lava flows (right side), the sub-horizontal carbonatite pyroclastic deposits (top left side) and the main feeder dike (center-left). Arrows point to the sites magnified in the following photographs. b) Contact between the sub-horizontal, carbonatite lapilli and ash tuffs and the light-brown pedogenized tuff (notebook scale is 22 cm). c) Small carbonatite dike cross-cutting the sub-horizontal layers of carbonatite lapilli and ash tuffs. d) Layer of ovoidal, massive, carbonatite lapilli. e) Contact between the upper carbonatite lava flow and the underlying carbonatite lapilli.

The concentrations of Li, Be, Sc, V, Cr, Co, Ni, Cu, Rb, Sr, Y, Nb, Cs, Ba, rare earth elements (REE), Ta, Pb, Th and U were determined by inductively coupled plasma — mass spectrometry (VG PQII Plus). Analyses were performed by external calibration using international geochemical reference samples. The correction procedure includes (i) blank subtraction; (ii) instrumental drift correction using internal standardization and repeated analysis of a drift monitor; (iii) oxide-hydroxide interference correction. For the analyte concentration levels in the studied samples, the analytical precision is better than 5% RSD, except for Sc, Cr, Co, Ni, Cu which are determined with a precision of 10–15% RSD.

The concentrations of Zr were determined by XRF (estimated precision ~5% RSD) on pressed powder pellets accurately correcting for the significant spectral interference of the Sr $K\beta$ line on the Zr $K\alpha$ analytical line.

The isotope compositions of Sr, Nd and Pb were measured with a Finnigan MAT 262V multicollector mass spectrometer at the CNR Istituto di Geoscienze e Georisorse in Pisa. Conventional ion exchange methods were used for Sr, Nd and Pb separations. Measured

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios were normalized to $^{86}\text{Sr}/^{88}\text{Sr}=0.1194$; $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were normalized to $^{146}\text{Nd}/^{144}\text{Nd}=0.7219$. During the collection of isotopic data for this study, replicate measurements of NIST SRM 987 (SrCO_3) and JNdi-1 (Tanaka et al., 2000) standards gave values of 0.710243 ± 13 (2s, $N=20$) for $^{87}\text{Sr}/^{86}\text{Sr}$, and 0.512100 ± 10 (2s, $N=25$) for $^{143}\text{Nd}/^{144}\text{Nd}$. Lead was loaded on Re filaments with tetraethyl orthosilicate as activator. Replicate analyses ($N=50$) of NIST SRM 981 (natural lead) indicate that Pb isotope ratios are measured with a precision within 0.03% (2s) per mass unit. Mass fractionation was corrected for applying a factor of $0.14 \pm 0.01\%$ per mass unit (NIST SRM 981 certified values after Todt et al., 1996).

The isotopic composition of B was measured with a VG 54 E mass spectrometer at the CNR Istituto di Geoscienze e Georisorse in Pisa. Boron was extracted fluxing the samples with K_2CO_3 , (flux to sample ratio = 5:1) followed by ion-exchange purification. Data are reported in the conventional $\delta^{11}\text{B}$ notation as ‰ deviation from the accepted composition of NIST SRM 951 (certified $^{11}\text{B}/^{10}\text{B}=4.04362$; Catanzaro et al., 1970). The

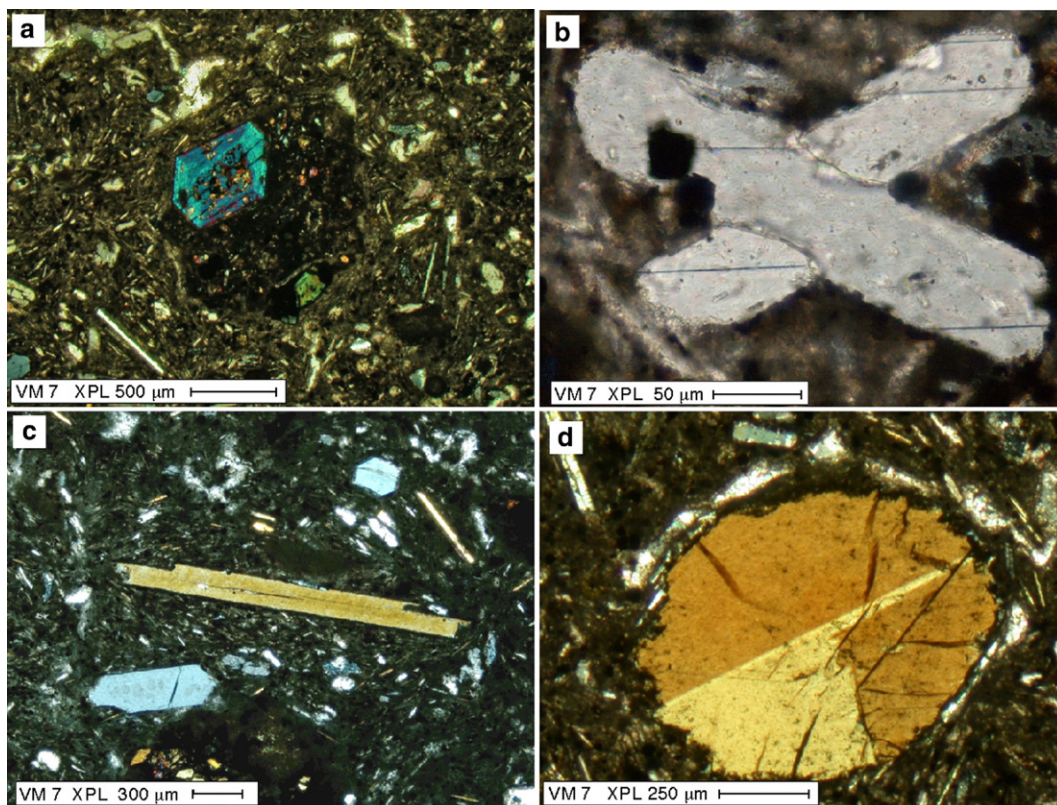


Fig. 3. Optical microscope views (transmitted light) of thin sections of the Vallone Toppo di Lupo alvikites. a) Fragment of porphyritic silicate lava entrained by the alvikite magma. b) Microphenocryst of calcite tabular on {0001} and twinned on (0112). c) Euhedral phenocrysts of apatite (grey) and melilite (orange). d) Twinned amphibole (Mg-hastingsite) xenocryst. XPL, crossed polars.

Table 1
Representative EMP and SEM-EDS mineral analyses (wt.%) of the VTL alvikites

Sample Phase	VM 8 Cal (S)	VM 8 Cal (P)	VM 8 Cal (P)	VM 8 Mel core	VM 8 Mel rim	VM 9 Mel	VM 9 Mel	VM 8 Mag core	VM 8 Mag rim	VM 8 Mtc core	VM 8 Mtc rim	VM 9 Mtc core	VM 8 Mtc rim	VM 8 Cpx xeno core	VM 8 Cpx xeno rim	VM 9 Cpx xeno core	VM 8 amp xeno	VM 8 amp xeno	VM 8 Phl xeno	VM 8 Phl xeno	VM 8 Phl xeno
Method	1	1	1	1	1	2	2	1	1	2	2	2	2	1	1	2	1	1	1	1	1
SiO ₂	<d.l.	<d.l.	<d.l.	40.4	40.6	40.0	40.3	0.04	<d.l.	36.6	37.4	36.3	38.1	43.2	39.7	45.0	38.7	37.7	34.0	35.0	34.1
TiO ₂	–	–	–	–	–	–	–	2.40	1.48	–	–	–	–	2.50	2.35	1.97	2.37	2.59	0.17	0.16	0.19
Al ₂ O ₃	<d.l.	0.09	0.26	13.8	12.8	14.0	14.2	6.84	4.78	–	–	–	–	10.6	13.9	8.93	15.9	15.4	20.0	18.8	20.4
FeOtot	0.13	<d.l.	0.08	3.53	3.71	3.17	3.08	83.4	86.3	7.32	1.55	7.37	1.40	7.68	11.8	8.76	9.33	9.41	10.4	7.96	10.1
MnO	–	–	–	0.16	0.11	–	–	1.77	1.99	4.44	3.07	4.76	2.88	0.05	0.25	0.45	0.14	0.17	0.47	0.71	0.51
MgO	0.08	<d.l.	<d.l.	5.07	5.24	4.69	4.83	2.62	2.31	17.9	20.3	16.0	23.1	11.4	8.34	11.1	15.1	15.1	19.0	20.7	18.6
CaO	56.3	51.9	51.9	33.3	33.6	34.1	33.8	0.01	0.02	33.7	37.7	35.6	34.6	24.3	24.4	23.3	13.0	12.8	0.09	0.09	0.02
SrO	<d.l.	1.61	1.37	0.50	0.68	–	–	–	–	–	–	–	–	–	–	–	0.14	0.16	0.09	0.03	0.19
BaO	<d.l.	1.63	1.90	0.05	<d.l.	–	–	–	–	–	–	–	–	–	–	–	0.19	0.09	2.84	3.48	2.85
Na ₂ O	0.11	0.22	0.08	4.04	4.22	3.89	3.82	–	–	–	–	–	–	0.26	0.19	0.48	2.10	1.97	0.24	0.16	0.26
K ₂ O	0.01	0.04	0.02	0.15	0.16	–	–	–	–	–	–	–	–	–	–	–	1.92	1.93	9.13	8.82	8.98
Total	56.6	55.5	55.6	101.0	101.1	100.0	100.0	97.1	96.9	100.0	100.0	100.0	100.0	100.0	100.9	100.0	98.9	97.3	96.4	95.9	96.2
O	3	3	3	7	7	7	7	4	4	4	4	4	4	6	6	6	23	23	23	23	23
Si				1.81	1.83	1.81	1.81			1.00	1.00	1.00	1.01	1.61	1.49	1.68	5.61	5.55	5.04	5.17	5.06
Ti								0.06	0.04					0.07	0.07	0.06	0.26	0.29	0.02	0.02	0.02
Al			0.01	0.73	0.68	0.75	0.76	0.28	0.20					0.46	0.61	0.39	2.72	2.67	3.50	3.27	3.56
Fe ³⁺								1.59	1.72					0.20	0.30	0.17	0.59	0.72			
Fe ²⁺				0.13	0.14	0.12	0.12	0.87	0.86	0.17	0.03	0.17	0.03	0.04	0.07	0.10	0.54	0.44	1.29	0.98	1.25
Mn				0.01				0.05	0.06	0.10	0.07	0.11	0.06		0.01	0.01	0.02	0.02	0.06	0.09	0.06
Mg				0.34	0.35	0.32	0.32	0.14	0.12	0.73	0.81	0.66	0.91	0.63	0.47	0.62	3.26	3.31	4.20	4.56	4.11
Ca	1.01	0.93	0.93	1.60	1.62	1.65	1.63			0.99	1.08	1.05	0.98	0.97	0.98	0.93	2.02	2.02	0.01	0.01	
Sr		0.02	0.01	0.01	0.02														0.01		0.02
Ba		0.01	0.01																0.16	0.20	0.17
Na		0.01		0.35	0.37	0.34	0.33							0.02	0.01	0.03	0.59	0.56	0.07	0.05	0.07
K				0.01	0.01												0.36	0.36	1.73	1.66	1.70

Mineral abbreviations: Cal, calcite (S, secondary; P, primary); Mel, melilite; Mag, magnetite; Mtc, monticellite; Cpx, Ca-rich clinopyroxene; Amp, amphibole; Phl, phlogopite.

Method: 1, electron microprobe; 2, scanning electron microscope — energy-dispersive spectrometry. <d.l., below detection limit; –, not determined; xeno, xenocryst.

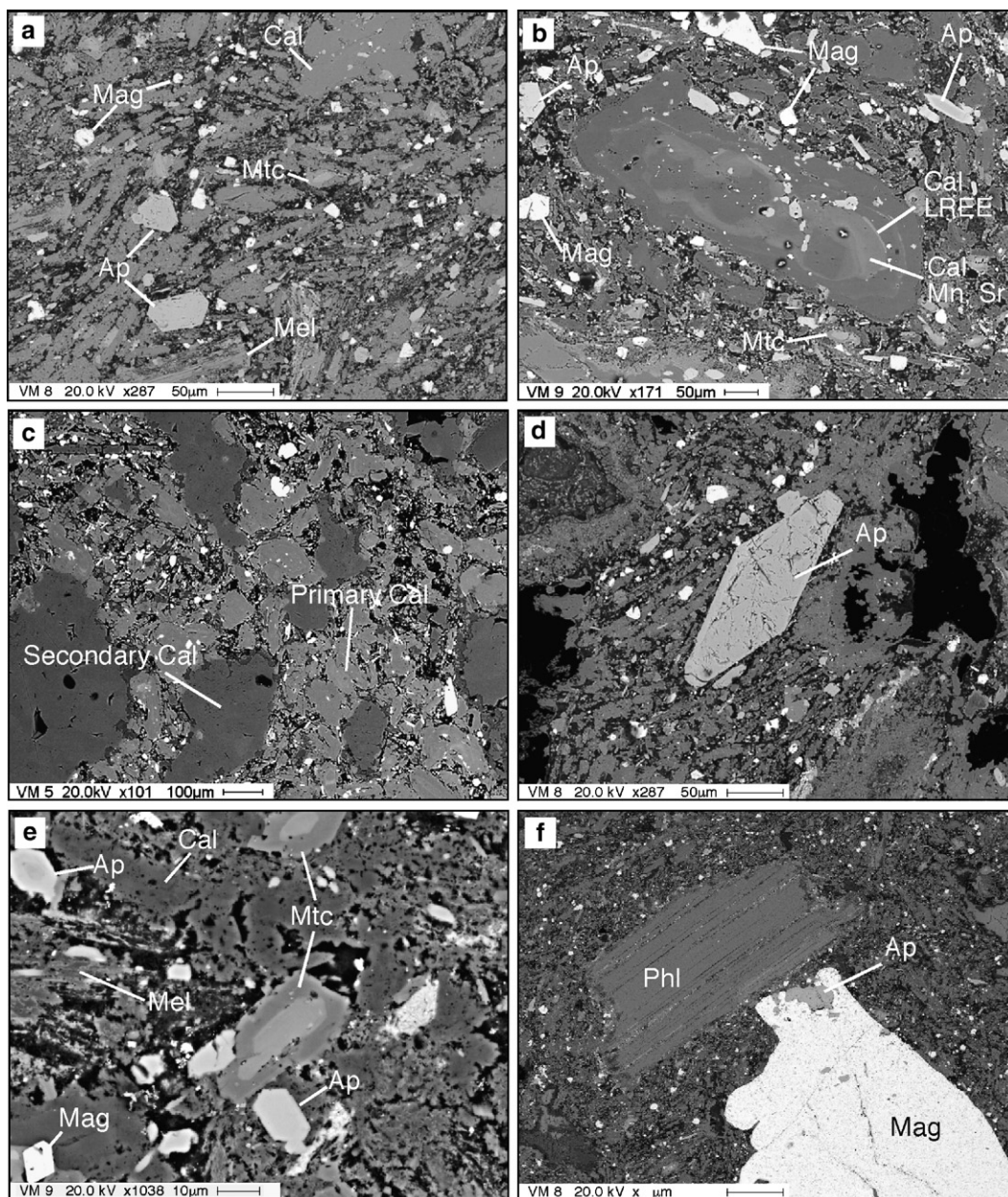


Fig. 4. Back-scattered electron images from thin sections of the Vallone Toppo di Lupo alvikites. a) Detail of the groundmass of the upper lava sample showing oriented microcrystals of tabular calcite (medium grey), Fe–Ti and Ca–Fe–Ti–Nb oxides (white) and apatite (light grey). b) Euhedral calcite phenocryst, tabular on {0001}, showing a complex compositional zoning. Light grey zones are enriched in LREE, whereas medium grey zones are enriched in Sr and Mn. c) Detail of a carbonatite tuff showing primary (light grey) and secondary (dark grey) calcite. d) Large euhedral phenocryst of apatite. e) Highly zoned, euhedral crystal of monticellite embedded in the groundmass of a lava sample. f) Anhedral phenocryst of Ti-magnetite with apatite inclusions, and resorbed, and partially altered xenocryst of phlogopite. Mineral abbreviations: Ap, apatite; Cal, calcite; Mag, magnetite; Mel, melilite; Mtc, monticellite; Phl, phlogopite.

reproducibility for isotopically homogeneous samples is approximately $\pm 0.5\%$ and replicate analysis of samples agree within this limit. Boron concentration was determined by isotope dilution/thermal ionization mass spec-

trometry; analytical uncertainty is estimated to be $\sim 5\%$ RSD on the basis of replicate analyses. This conservative error is ascribed almost entirely to the alkaline fluxing procedure of the sample before adding the spike solution.

Table 2

Bulk chemistry data for the VTL (Mt. Vulture) alvikites plus one sample from the Polino (Umbria) alvikite

Sample	VM 5	VM 6	VM 7	VM 8	VM 9	SVK 116
Locality	VTL	VTL	VTL	VTL	VTL	Polino
Type	Lapilli tuff	Ash tuff	Rounded lapilli	Upper lava flow	Feeder dike	Massive alvikite
<i>Major elements (wt.%)</i>						
SiO ₂	12.9	12.8	18.0	16.3	17.2	18.7
TiO ₂	0.23	0.32	0.50	0.46	0.47	0.51
Al ₂ O ₃	4.61	4.45	6.10	5.41	5.57	4.78
Fe ₂ O ₃ tot	2.91	5.84	6.59	6.51	6.73	4.55
MnO	0.22	0.38	0.35	0.35	0.36	0.07
MgO	1.70	2.53	2.77	2.96	3.06	10.9
CaO	40.4	39.0	36.6	40.2	39.5	36.2
SrO	1.16	1.31	0.87	1.24	0.84	0.18
BaO	0.45	0.95	0.80	0.72	0.73	0.10
Na ₂ O	0.39	0.33	0.71	0.47	0.47	0.55
K ₂ O	0.69	0.44	0.39	0.17	0.19	0.72
P ₂ O ₅	1.24	2.36	2.21	2.18	2.23	0.42
LOI	32.2	29.1	24.5	22.4	21.9	22.94
Total	99.1	99.8	100.4	99.4	99.3	100.6
CO ₂	28.9	25.5	20.8	17.4	18.3	16.9
F	0.10	0.32	0.16	0.43	0.37	–
<i>Trace elements (ppm)</i>						
B	–	–	7	32	–	–
Li	64	59	46	54	33	–
Be	5.3	10.1	8.7	9.8	9.6	12.0
Sc	7	5	7	7	8	11
V	151	303	373	316	393	48
Cr	12	7	7	7	10	542
Co	13	17	19	19	20	36
Ni	26	19	20	22	21	351
Cu	19	28	43	40	39	–
Rb	92	33	11.1	21.2	8.2	42
Y	47	99	91	87	86	30
Zr	187	169	175	210	175	334
Nb	207	389	320	332	337	13.2
Cs	6.8	4.8	1.38	5.3	1.07	14.3
La	373	697	619	604	621	94
Ce	592	1203	1051	1027	1054	211
Pr	56	113	100	98.9	102	25.6
Nd	168	357	318	313	319	102
Sm	21.6	47	43	42	43	18.6
Eu	4.6	10.0	9.2	9.2	9.1	3.3
Gd	14.1	30.5	28.3	28.2	28.9	12.1
Tb	1.72	3.7	3.5	3.4	3.4	1.44
Dy	8.6	17.9	16.5	16.1	16.6	6.4
Ho	1.43	3.01	2.80	2.88	2.76	0.97
Er	3.4	7.0	6.6	6.8	6.7	2.13
Tm	0.50	1.02	0.96	1.03	0.98	0.26
Yb	2.89	6.0	5.4	5.6	5.6	1.39
Lu	0.39	0.77	0.72	0.76	0.76	0.20
Ta	5.3	11.2	9.7	10.2	10.2	0.56
Pb	47	88	72	70	71	21
Th	36	92	85	85	91	39
U	27.3	63	43	56	56	8.8

–, not determined.

Further analytical details about the determination of boron isotope composition and concentration are given in Tonarini et al. (2003).

The C and O isotope composition of the whole carbonate fraction of three samples was determined by conventional methods at the Geochron Laboratories (Cambridge, Massachusetts, USA).

Mineral compositions were determined with a JEOL electron microprobe (EMP) fitted with four wavelength dispersive spectrometers at the CNR Istituto di Geoscienze e Georisorse in Florence. Running conditions were 20 kV accelerating voltage, 20 nA beam current and 1 μ m nominal beam spot. Energy-dispersive-spectrometry (EDS) semi-quantitative analyses, mainly used for detecting REE-bearing phases, and back-scattered electron (BSE) images were also obtained with a Philips XL30 scanning electron microscope (SEM) at Pisa University's Dipartimento di Scienze della Terra. The volumetric proportions of various components (primary and secondary calcite, xenocrysts and microxenoliths, groundmass, etc.) were estimated by point-counting on thin sections (more than 2000 points counted for each sample using a 0.5 mm $\times$ 0.5 mm grid).

5. Results

5.1. Petrography, mineral chemistry, and classification

The VTL carbonatites are made of a prevailing juvenile fraction and of subordinate amounts of extraneous material and secondary minerals. The extraneous material is represented by fragments of sedimentary rocks (e.g. limestones, clays) and silicate lavas (Fig. 3a), or by fragmented xenocrysts of diopside, melilite, amphibole and phlogopite. The sizes of these fragments range from few tens of μ m to the pluridecimeteric blocks found within the lapilli-tuff. In the pyroclastic rock samples (VM 5 and VM 6) the fraction of extraneous material is higher ($\sim$ 15–20 vol.%), whereas in the dikes, lavas and massive rounded lapilli it is between 7 and 10 vol.%. Selected EMP and SEM-EDS analyses of the main mineral phases of the VTL rocks are reported in Table 1.

The juvenile fraction of the VTL dikes and lavas shows a sub-aphyric texture with sparse (<5 vol.%) phenocrysts of calcite, melilite, apatite and Ti-magnetite set in a groundmass made of the same phases plus monticellite and Ca–Fe–Ti–Nb–LREE oxides (Fig. 4a).

The clear phenocrysts of calcite are tabular on {0001}, as observed for the carbonatites from Kaiserstuhl (Keller, 1989), and show lath-like sections with rounded edges due to the development of the

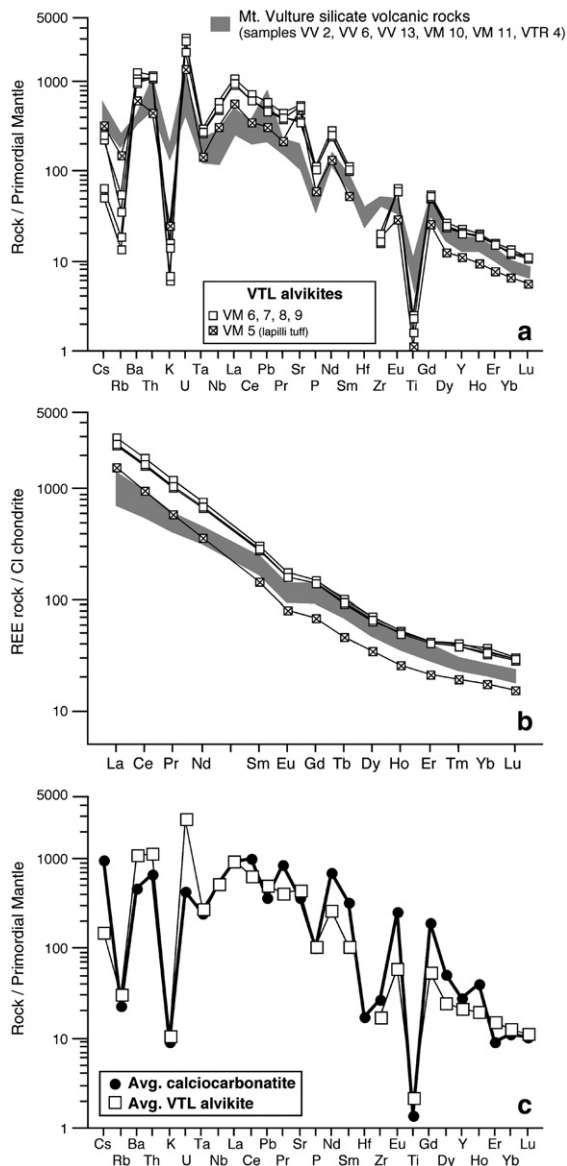


Fig. 5. Incompatible-element distributions of Vallone Toppo di Lupo alvikites and selected silicate rocks from Mt. Vulture. a) Incompatible-element concentrations normalized to the estimated composition of the Primordial Mantle. b) Rare earth element concentrations normalized to the CI chondrite. c) Average compositions of calciocarbonatites (Woolley and Kempe, 1989; Chakhmouradian, 2006) and Vallone Toppo di Lupo alvikites normalized to Primordial Mantle. Primordial Mantle and CI chondrite composition from McDonough and Sun (1995).

rhombohedral crystal faces. In addition, calcite phenocrysts may be twinned on (01 $\bar{1}$ 2) (Fig. 3b), and may show a complex zoning with portions variably enriched in Sr, Ba, Mn and LREE (Fig. 4b).

Calcite of secondary origin, as that filling the voids in the lapilli-tuff (Fig. 4c), can be easily identified by its

nearly pure end-member CaCO_3 composition and the absence of inclusions. In addition, primary calcite has a higher reflectivity in BSE images, due to its high content of LREE, Sr, Ba and Mn.

Melilite forms euhedral prisms tabular on {001} (Fig. 3c). It is compositionally homogeneous and rich both in the gehlenite and soda-melilite components. The SrO content (~ 0.6 wt.%) is reasonably high. Interestingly, melilite crystals are stable in the massive rounded lapilli, whereas show resorbed rims in the lava and the dike samples. Among the melilites from the silicate rocks from Mt. Vulture, those found within the mela-foidite lava from S. Caterina (northeastern sector of the volcano) are similar to the VTL melilites (Melluso et al., 1996). The melilite of the Prete della Scimmia melilitite dike (about 1 km north of Lago Piccolo, Monticchio Lakes) is significantly enriched in the åkermanite component, whereas that from the Melfi foidite is enriched in Na, Fe and Sr and depleted in Al (it is peralkaline; Melluso et al., 1996).

Apatite occurs as well-formed euhedral prisms both in the groundmass and as microphenocrysts (Fig. 3c, 4d). The EMP analyses revealed high contents of SiO_2 (~ 3.6 wt.%), F (~ 0.6 wt.%) and SrO (~ 0.4), whereas the Cl concentration is low (~ 0.05 wt.%). Semi-quantitative SEM-EDS analyses show that the VTL apatites also contain high amounts of LREE (in the order of 1–2 wt.% total LREE).

Oxide primary minerals occur in the VTL carbonatites as abundant Ti-magnetite and rare Ca–Ti–Nb–Fe–LREE perovskite-type phases. Titanomagnetite forms microphenocryst-sized anhedral crystals or, more commonly, tiny octahedra in the groundmass (Fig. 4a). Its composition is depleted in the ulvöspinel component ($\text{Ülv} = 6\text{--}18$ mol%) and reasonably enriched in Al_2O_3 (4.8–12.3 wt.%) and MgO (2.6–6.9 wt.%). The perovskite-type oxides occur as very small (<30 μm) cubic or octahedral crystals in the groundmass or within calcite crystals. They have been identified by SEM-EDS for their high concentrations of Ca, Nb and LREE.

Monticellite occurs as very small (up to ~ 60 μm) zoned prismatic crystals enclosed in calcite or scattered in the groundmass (Fig. 4e). The rims of the monticellite crystals have compositions close to the Mg end-member, whereas the cores are enriched in the kirschsteinite component (CaFeSiO_4) and in MnO (up to 4.5 wt.%).

Fragmented xenocrysts of clinopyroxene are the most abundant extraneous material entrained in the VTL carbonatites; usually, they are highly zoned with a pale green core and a thick deep-green, pleochroic rim. They are aluminian diopsides very rich in Al_2O_3 (up to 15 wt.% in the deep-green rims).

Table 3

Bulk chemistry data for selected, highly silica-undersaturated, silicate rocks from Mt. Vulture

Sample	VM 10	VM 11	VV 2	VTR 4	VV 6	VV 13	VU 621 ^a
Locality	Prete della Scimmia	Prete della Scimmia	Melfi	Melfi	Foggiano	Mt. Vulture summit area	S. Caterina
Classification	Melilitite	Melilitite	Foidite	Foidite	Ph-foidite	Foidite	Mela-foidite
<i>Major elements (wt.%)</i>							
SiO ₂	37.8	38.6	39.5	40.4	45.9	42.5	38.4
TiO ₂	2.05	2.06	0.92	0.97	1.47	1.17	1.66
Al ₂ O ₃	13.8	13.8	18.1	18.0	15.0	16.8	18.0
Fe ₂ O ₃ tot	11.6	11.8	8.30	8.69	8.54	9.45	10.3
MnO	0.22	0.21	0.22	0.23	0.13	0.19	0.24
MgO	3.81	3.42	2.79	3.05	6.75	4.69	4.03
CaO	17.3	17.1	11.1	12.5	12.2	12.7	16.5
SrO	0.30	0.29	0.44	0.50	0.24	0.30	0.30
BaO	0.25	0.26	0.29	0.26	0.25	0.31	0.18
Na ₂ O	3.33	2.85	7.36	6.15	3.26	4.00	4.40
K ₂ O	5.28	5.30	5.39	3.79	4.29	5.08	2.04
P ₂ O ₅	1.06	1.10	0.75	0.69	1.08	1.13	1.12
LOI	4.85	3.54	2.32	3.75	1.05	1.39	1.29
Total	101.6	100.3	97.5	99.0	100.2	99.7	98.5
CO ₂	0.44	0.30	–	–	–	–	0.66
<i>Trace elements (ppm)</i>							
B	–	17	–	45	11	49	–
Li	34	25.5	–	–	–	–	–
Be	9.7	9.7	10.0	10.3	5.5	7.7	–
Sc	13	13	8	5	24	15	10
V	293	302	251	249	212	271	274
Cr	5	6	3	5	105	7	3
Co	30	30	22	21	30	30	48
Ni	13	13	10	11	38	20	15
Cu	72	62	58	57	52	61	–
Rb	111	107	133	117	133	153	65
Y	78	77	59	58	55	69	49
Zr	545	539	495	466	433	478	406
Nb	136	134	179	176	80	112	76
Cs	7.7	7.6	12.0	12.2	6.9	10.3	2.32
La	218	217	322	323	166	277	173
Ce	437	445	582	554	330	512	318
Pr	48	48	56	54	38	55	–
Nd	189	190	191	188	143	199	123
Sm	35	35	28.6	28.2	24.9	34	25.4
Eu	7.6	7.6	6.2	6.4	5.3	7.3	5.7
Gd	26.8	27.3	20.3	18.5	18.2	23.8	–
Tb	3.6	3.6	2.57	2.44	2.42	3.15	2.1
Dy	16.5	16.3	12.3	12.0	11.2	14.8	–
Ho	2.70	2.64	2.00	1.97	1.88	2.39	–
Er	5.9	5.9	4.8	4.7	4.4	5.4	–
Tm	0.76	0.72	0.63	0.63	0.56	0.65	–
Yb	4.3	4.2	3.8	3.7	3.27	3.8	4.4
Lu	0.58	0.56	0.51	0.49	0.45	0.53	0.57
Ta	6.6	6.6	8.6	8.4	4.6	5.8	5.4
Pb	44	40	106	120	31	67	–
Th	56	51	85	82	38	72	40
U	13.1	13.0	16.7	23.4	8.5	18.7	11.2

Ph-foidite, phonolitic foidite; –, not determined.

^a From De Fino et al. (1986) and De Astis et al. (2006).

Amphibole xenocrysts are anhedral, pleochroic from dark to light brown and frequently twinned (Fig. 3d). They occur also as centimeter-sized black megacrysts. The amphibole composition falls in the Mg-hastingsite field and is very similar to other amphiboles found, though not frequently, within Mt. Vulture volcanics (Melluso et al., 1996; Stoppa and Principe, 1998).

The phlogopite xenocrysts found in the studied rock are variably resorbed and partially altered (Fig. 4f). They are rich in the eastonite component and in BaO (1.5–3.5 wt.%) as observed for the other phlogopites from Mt. Vulture (Melluso et al., 1996; Stoppa and Principe, 1998).

Besides calcite, other secondary phases include Ca (K, Na, Ba)-zeolites, more abundant in the feeder dike sample, and iron hydroxides.

The VTL carbonatites are medium- to fine-grained and contain calcite (>50 vol.%) as the unique carbonate phase; accordingly, they are classified as alvikite (Le Maitre, 2002).

5.2. Bulk chemistry

The bulk-rock major- and trace-element analyses of the studied rocks are reported in Table 2, which also includes, for comparative purposes, one analysis of the Polino (Umbria) alvikite.

The dominant chemical components (sum > 86 wt.%) are: CaO (36.6–40.4 wt.%), CO₂ (17.4–28.9 wt.%), SiO₂ (12.8–18.0 wt.%), Al₂O₃ (4.4–6.1 wt.%) and Fe₂O₃tot (2.9–6.7 wt.%). All samples have CaO/(CaO + MgO + FeOtot + MnO) ratios (wt.%) > 0.8 in accordance with their classification as alvikite. The VTL rocks show quite high concentrations of P₂O₅, SrO, BaO (SrO/BaO = 1.1–2.6), MnO and F, and low to very low contents of Na₂O, K₂O and TiO₂, as typically found in calciocarbonatites (Woolley and Kempe, 1989). Sample VM 5 (lapilli tuff) is chemically different from the other samples being depleted, with respect to these latter, in TiO₂, Fe₂O₃tot, MnO, MgO, BaO and P₂O₅, and enriched in K₂O. This is due to the higher abundance

Table 4
Sr–Nd–Pb–O–C–B isotope data

Sample	VM 7	VM 8	VM 9	VM 11	VTR 4	VV 6	VV 13	SVK 116	B7IAEA
Locality	VTL (Vulture)	VTL (Vulture)	VTL (Vulture)	Prete della Scimmia (Vulture)	Melfi (Vulture)	Foggiano (Vulture)	Mt. Vulture summit (Vulture)	Polino	Maiella Massif
Classification	Alvikite	Alvikite	Alvikite	Melilitite	Foidite	Ph-foidite	Foidite	Alvikite	Calcareneite
⁸⁷ Sr/ ⁸⁶ Sr — WR	0.706159	0.706147		0.706432	0.705791	0.705227	0.705918		0.708325
⁸⁷ Sr/ ⁸⁶ Sr — leach		0.706151							
⁸⁷ Sr/ ⁸⁶ Sr — sil. ph.		0.706138							
¹⁴³ Nd/ ¹⁴⁴ Nd — WR	0.512586	0.512579		0.512593	0.512699	0.512712	0.512709		0.511440
¹⁴³ Nd/ ¹⁴⁴ Nd — leach		0.512569							
¹⁴³ Nd/ ¹⁴⁴ Nd — sil. ph.		0.512572							
²⁰⁶ Pb/ ²⁰⁴ Pb — WR	19.231	19.231		19.553	19.290	19.389	19.280		
²⁰⁷ Pb/ ²⁰⁴ Pb — WR	15.669	15.667		15.714	15.707	15.693	15.718		
²⁰⁸ Pb/ ²⁰⁴ Pb — WR	39.181	39.174		39.500	39.289	39.389	39.351		
δ ¹⁸ O — carbonates	+12.7	+10.2	+12.4					+22.6	
δ ¹³ C — carbonates	−9.2	−6.9	−6.7					−11.9	
δ ¹¹ B — WR		−5.9		−7.3	−5.6	−9.6	−8.1		+5.7 ^a

WR, whole-rock; leach, 5% acetic acid leach; sil. ph., separated silicate phenocrysts.

δ¹⁸O, δ¹³C and δ¹¹B are expressed as ‰ deviation from the SMOW, PDB and NIST SRM 951 isotopic standards, respectively.

^a From Tonarini et al. (2003).

(~23 vol.%) of sedimentary xenoliths and igneous xenocrysts (mainly phlogopite) plus secondary calcite (~23 vol.%) occurring in this sample.

The trace-element distribution of the VTL alvikites (Fig. 5) is characterized by: 1) very high contents of LREE (La=370–690 ppm, Ce=590–1200 ppm); 2) high LREE/HREE fractionation ($[La/Yb]_N=73–88$); 3) negative Eu anomalies ($Eu/Eu^*=0.79–0.81$); 4) high Nb concentrations (207–389 ppm) and high Nb/Ta ratios; 5) low Zr/Nb ratios (0.4–0.9); 6) high to very high concentrations of Th (36–92 ppm), U (27–63 ppm) and Pb (47–88 ppm); 7) relatively low concentrations of the alkaline trace elements Cs (1.1–6.8 ppm) and Rb (8–92 ppm); 8) low levels of the 3d transition elements Sc, Cr, Co, Ni and Cu; 9) quite high V concentration (150–390 ppm). Again, the lapilli tuff sample can be separated from the others by virtue of its lower content of incompatible trace elements, with the exception the alkaline elements Li, Rb and Cs (Fig. 5a).

Taken collectively, the trace-element features of the VTL alvikites are those typically observed for calcio-carbonatites world-wide (Woolley and Kempe, 1989; Chakhmouradian, 2006; Fig. 5c).

The boron contents are 32 and 7 ppm, for the lava and the rounded massive lapilli, respectively. The low value measured for the latter could be ascribed to a depletion of this element due to an efficient degassing during the explosive activity and/or a higher degree of alteration of this material.

In Tables 3 and 4 are presented the bulk chemical analyses and the Sr–Nd–Pb–B isotope compositions, respectively, of some silicate volcanic rocks from Mt. Vulture, selected for their high silica undersaturation and high incompatible elements contents. In particular, the melilitite dike of Prete della Scimmia, the foidite lava from Melfi and the mela-foidite lava from S. Caterina contain variable amounts of melilite associated with clinopyroxene, haüyne/sodalite, leucite, nepheline and accessory phases. All these silicate rocks, though characterized by high incompatible elements concentrations, are less enriched than the VTL alvikites in Ba, Th, U, Ta, Nb, Sr, P and REE (Fig. 5). This is in strikingly contrast to the other carbonatite occurrences of central Italy, where the carbonatite rocks are depleted in incompatible elements with respect to the associated silicate volcanic rocks (e.g. Stoppa and Woolley, 1997).

5.3. Isotope data

5.3.1. Oxygen and carbon isotopes

The $\delta^{18}O_{SMOW}$ and $\delta^{13}C_{PDB}$ values of the carbonate fraction from the VTL upper lava flow (sample VM 8), the

main feeder dike (VM 9) and the rounded lapilli (VM 7) range from +10.2‰ to +12.7‰ and from –9.2‰ to –6.7‰, respectively (Table 4, Fig. 6). These samples were chosen for their lower content of secondary calcite (4.0–6.5 vol.%). The O and C isotope composition of the VTL samples is close to that measured for the sövite from Mt. Vulture (Rosatelli et al., 2000), that, however, is characterized by higher $\delta^{13}C$ values. The carbonates of the carbonatitic-melilititic tuffs from the Monticchio Lakes, and from other occurrences of Quaternary, carbonate-rich, igneous rocks from central Italy (San Venanzo, Cupaello and Polino) are characterized by much higher $\delta^{18}O$ values ($\delta^{18}O > +21‰$) and $\delta^{13}C$ comparable to, or much lower (Polino alvikite, San Venanzo carbonatitic tuff) than the VTL alvikites (Turi, 1969; Stoppa and Woolley, 1997; Fig. 6).

The $\delta^{18}O$ and $\delta^{13}C$ of the VTL alvikites and the sövite sample lie in proximity of the field of the “primary igneous carbonatites” (PIC box in Fig. 6; Taylor et al., 1967; Keller and Zaitsev, 2006), enclosing carbonatite rocks in O and C equilibrium with mantle silicates. However, as clearly shown by the review study of Deines (1989), volcanic (tuffs and lavas) and subvolcanic carbonatites show much more variable and higher $\delta^{18}O$ with respect to the intrusive carbonatites. Though less clearly, volcanic carbonatites seem to be also depleted in ^{13}C (Deines, 1989). The larger O and C isotopic variability of extrusive carbonatites has been attributed to secondary isotopic exchange processes with magmatic/hydrothermal fluids and/or meteoric water that affect more extensively the “less massive” extrusive carbonatites rather than the intrusive types.

In summary, the C and O isotope data suggest that: 1) the O and, to a lesser extent, C isotope compositions of the VTL alvikites have been modified to variable extent by secondary exchange processes that probably moved their pristine $\delta^{18}O$ and $\delta^{13}C$ value outside the “primary igneous carbonatite” field; 2) the $\delta^{18}O$ and $\delta^{13}C$ values of the VTL alvikites are strikingly different from those typically measured in Phanerozoic sedimentary marine limestones, characterized by $\delta^{18}O$ in excess of +25‰ and $\delta^{13}C \approx 0‰$ (Faure, 1986; Fig. 6).

To the authors' knowledge, just one $\delta^{18}O$ value for silicate volcanic rocks from Mt. Vulture has been to date published ($\delta^{18}O = +6.72‰$, Melfi foidite; Turi et al., 1991); in addition, Matthey et al. (1997) reported $\delta^{18}O$ values around +5.6‰ for coexisting olivine and pyroxene in spinel-lherzolite xenoliths found in the carbonatite-melilitite tuffs from the Monticchio Lakes.

5.3.2. Strontium, neodymium, lead and boron isotopes

The Sr isotope composition of two whole-rock samples ($^{87}Sr/^{86}Sr = 0.70615, 0.70616$) fall well within

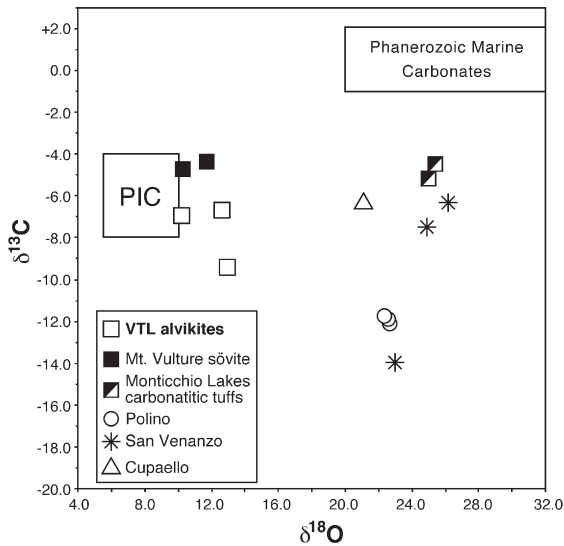


Fig. 6. Plot of $\delta^{13}\text{C}$ (PDB) vs. $\delta^{18}\text{O}$ (SMOW) (in ‰) for the Vallone Toppo di Lupo alvikites and other Quaternary Italian carbonatites. Data sources: this work, Turi (1969), Stoppa and Woolley (1997), Rosatelli et al. (2000). The Primary Igneous Carbonatite field (PIC box) combines the fields as defined by Taylor et al. (1967) and Keller and Zaitsev (2006). The O and C isotope compositions of Phanerozoic marine carbonate rocks are also plotted (Faure, 1986).

the range observed for Mt. Vulture volcanics ($^{87}\text{Sr}/^{86}\text{Sr}=0.70523\text{--}0.70705$; Beccaluva et al., 2002; De Astis et al., 2006 and this work; Fig. 7). More interestingly, the Nd isotope composition of the whole rocks ($^{143}\text{Nd}/^{144}\text{Nd}=0.51258, 0.51259$) is among the

least radiogenic ever measured for Mt. Vulture ($^{143}\text{Nd}/^{144}\text{Nd}=0.51256\text{--}0.51271$; De Astis et al., 2006 and this work; Fig. 7). The $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ of the mixed xenocryst/phenocrysts (clinopyroxene + amphibole + melilite + phlogopite + apatite) separated from sample VM 8 (0.70614 and 0.51257) and the 5% acetic acid leachate of the same sample (0.70615 and 0.51257) are indistinguishable, within the analytical error, from the whole-rock values (0.70615 and 0.51258). The sövite has a lower $^{87}\text{Sr}/^{86}\text{Sr}$ (0.70598) and higher $^{143}\text{Nd}/^{144}\text{Nd}$ (0.51265; Rosatelli et al., 2000). Downes et al. (2002) studied a collection of ultramafic mantle xenoliths (spinel-lherzolite, harzburgite and wehrlite) found within the volcanic succession of Mt. Vulture. The Sr and Nd isotope compositions of these mantle rocks, originated in the subcontinental lithospheric mantle beneath Mt. Vulture, are characterized by lower $^{87}\text{Sr}/^{86}\text{Sr}$ values at a given $^{143}\text{Nd}/^{144}\text{Nd}$ with respect to the volcanic rocks, and by a much wider range of $^{143}\text{Nd}/^{144}\text{Nd}$ values (Fig. 7). The Sr–Nd isotope compositions of the carbonatites and the carbonate-rich igneous rocks from central Italy (San Venanzo, Polino and Cupaello) are extremely different from those of the VTL alvikites. Indeed, the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ values measured on whole rocks, mineral separates, acid leaches and residues range from 0.70919 to 0.71537 and from 0.51188 to 0.51219, respectively (Castorina et al., 2000).

The $^{206}\text{Pb}/^{204}\text{Pb}$ (19.23), $^{207}\text{Pb}/^{204}\text{Pb}$ (15.67) and $^{208}\text{Pb}/^{204}\text{Pb}$ (39.17–39.18) ratios measured in two VTL alvikites are indistinguishable within the analytical

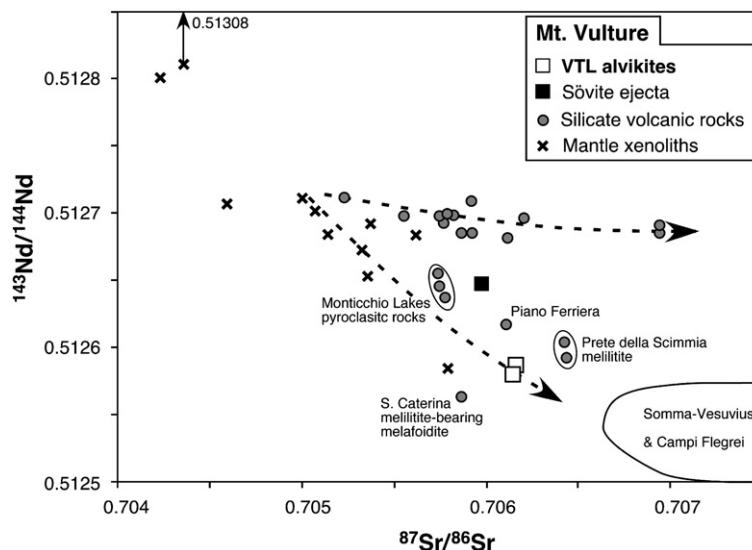


Fig. 7. Plot of $^{143}\text{Nd}/^{144}\text{Nd}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$ for volcanic rocks and mantle xenoliths from Mt. Vulture. Data sources: Vallone Toppo di Lupo alvikites, this work; sövite ejecta, Rosatelli et al. (2000); silicate volcanic rocks, De Astis et al. (2006) and this work; mantle xenoliths, Downes et al. (2002). The partial field for Somma-Vesuvius and Campi Flegrei is also shown for comparison (data from Peccerillo, 2006 and reference therein).

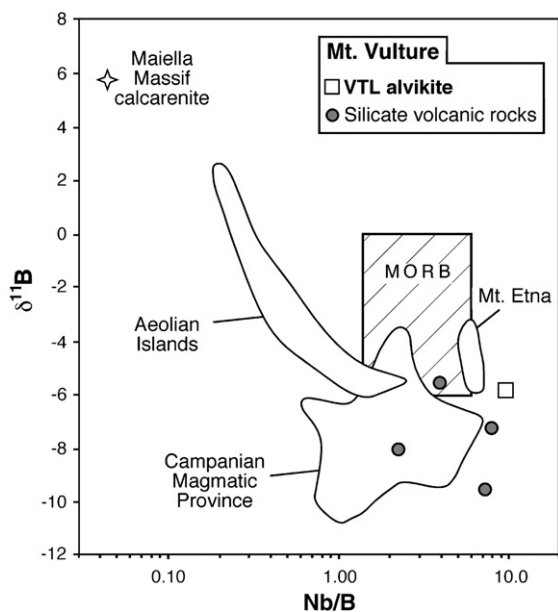


Fig. 8. Plot of $\delta^{11}\text{B}$ (in ‰) vs. Nb/B ratio for the Vallone Toppo di Lupo alvikite lava (VM 8) and other silicate rocks from Mt. Vulture. Data for the volcanic rocks from the Campanian Magmatic Province (Somma-Vesuvius, Campi Flegrei, Ischia and Procida; D'Antonio et al., 2007), Aeolian Islands (Tonarini et al., 2001a) and Mt. Etna (Tonarini et al., 2001b) are also plotted for comparison. The box for the MOR basalts is from Leeman and Sisson (1996).

uncertainty, and fall in proximity of the least radiogenic extremes of the trends formed by the Pb isotope ratios of Mt. Vulture volcanics (not shown; De Astis et al., 2006 and this work).

The B isotope composition was determined for the alvikite lava (VM 8) and four silicate volcanic rocks

from Mt. Vulture (Table 4). In Table 4 is also reported the $\delta^{11}\text{B}$ values measured in a Miocene bioclastic calcarenite from the Maiella Massif (Abruzzo, central Italy; Tonarini et al., 2003).

The $\delta^{11}\text{B}$ of the alvikite lava is -5.9‰ , while the silicate rocks from Mt. Vulture have $\delta^{11}\text{B}$ between -9.6 and -5.6‰ . These values are comparable to, or lower than, those typically measured for MORB (Leeman and Sisson, 1996), and markedly lower than the sedimentary carbonate rocks from the Maiella Massif ($+5.7\text{‰}$).

6. Discussion

6.1. The VTL alvikites in the frame of Mt. Vulture magmatism

The genesis and evolution of Mt. Vulture magmatism have been the object of several recent studies (Melluso et al., 1996; Stoppa and Principe, 1998; Beccaluva et al., 2002; Downes et al., 2002; De Astis et al., 2006). In referring to Mt. Vulture, some of these authors used the adjectives “anomalous” or “hybrid” to underline that the products of this volcano, as well as its geological setting, are different from those of the other Quaternary alkaline volcanoes from the Italian peninsula. In particular, though still characterized by negative anomalies of Nb, Ta, P and Ti, as typically observed for magmas derived from orogenic sources, Mt. Vulture rocks show an attenuation of these anomalies, and, in addition, they are characterized by high relative contents of Th, U, Pb and LREE and negative anomalies of Rb and K (Fig. 5a). Taken as a whole, the Sr–Nd–Pb isotope compositions

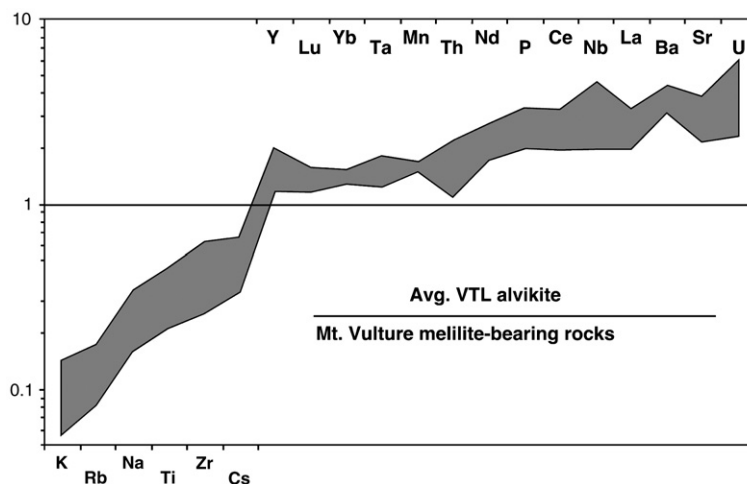


Fig. 9. Enrichment factor for selected elements of the average Vallone Toppo di Lupo alvikite (average composition of samples VM 6, 7, 8, 9) with respect to three melilite-bearing silicate rocks from Mt. Vulture (Melfi foidite, sample VTR 4, Prete della Scimmia melilitite, sample VM 11 and S. Caterina mela-foidite, sample VU 621).

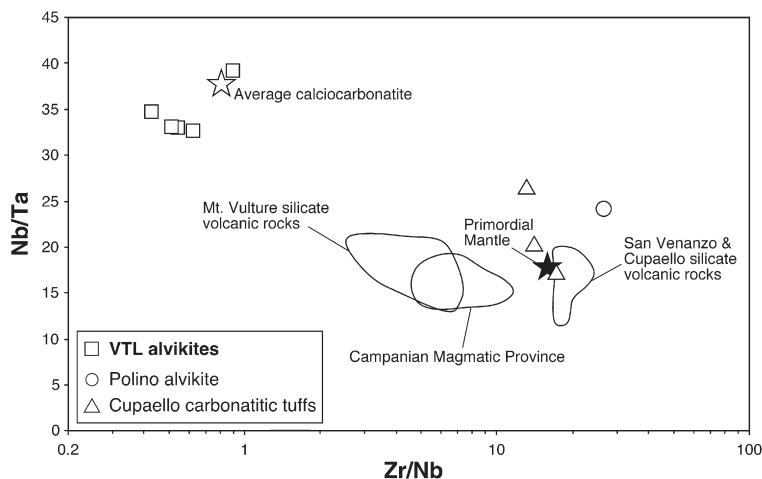


Fig. 10. Plot of Nb/Ta vs. Zr/Nb for the Vallone Toppo di Lupo alvikites and other Italian carbonatites. In the diagram are also reported the fields for the silicate volcanic rocks from Mt. Vulture, San Venanzo and Cupaello, and the Campanian Magmatic Province (Somma-Vesuvius, Campi Flegrei, Ischia and Procida). The white and black stars represent the Nb/Ta and Zr/Nb values for the average calciocarbonatite of Chakhmouradian (2006) and the Primordial Mantle of McDonough and Sun (1995), respectively. Data sources: Vallone Toppo di Lupo and Polino alvikites, this work; Cupaello carbonatitic tuffs, Stoppa and Woolley (1997) and Stoppa and Cundari (1995); Mt. Vulture silicate volcanic rocks, De Astis et al. (2006), and this work; Cupaello, San Venanzo and Campanian Province silicate volcanic rocks, Peccerillo (2005) and reference therein.

of Mt. Vulture rocks are intermediate between those observed for the intra-plate-type, Plio–Quaternary magmas from southern Italy (e.g. Mt. Etna, Hyblean Mts.) and the enriched values of the Roman Province volcanoes (e.g. Peccerillo, 2005 and reference therein). According to Beccaluva et al. (2002), Mt. Vulture magmas were produced by low-degree melting of a deep lithospheric mantle enriched in Na-alkaline/carbonatite melts and furtherly modified by the addition of a subduction-related component. De Astis et al. (2006), proposed that Mt. Vulture is sourced by an African-type mantle (FOZO-HIMU-type), flowing westward in response to the detachment of the downgoing Adria Plate, and modified by melts released from the sedimentary cover of this latter.

Looking with more detail into the Sr–Nd isotope diagram of Fig. 7, it can be noted that the volcanic rocks and mantle xenoliths from Mt. Vulture define two rough trends: the first one, that includes most of the volcanic samples, is characterized by nearly constant $^{143}\text{Nd}/^{144}\text{Nd}$ values (average $^{143}\text{Nd}/^{144}\text{Nd}=0.51270\pm 1$) and widely variable $^{87}\text{Sr}/^{86}\text{Sr}$; the second trend shows a rough negative correlation between the Sr and Nd isotope ratios. Samples forming this trend are the Mt. Vulture carbonatites (VTL alvikites and sövite ejecta), the melilitite dike from Prete della Scimmia, the S. Caterina melilitite-bearing mela-foidite lava, the foidite from Piana Ferriera (western sector of the volcano), three samples from the maars of the Monticchio Lakes, and most of the mantle xenoliths. The melilitite from Prete della Scimmia and the

foidite from Piana Ferriera, that, as shown above, have Sr–Nd isotope compositions close to the VTL alvikites, show the most radiogenic Pb isotope composition, whereas the S. Caterina mela-foidite and the rocks from the Monticchio Lakes maars have Pb isotope ratios very close to those of the VTL alvikites. The boron isotope compositions are in accordance with the other isotope data: indeed, the VTL lava has a $\delta^{11}\text{B}$ value close to the values measured for the melilitite-bearing samples (Table 4). Mt. Vulture volcanics, carbonatite included, are depleted in B relative to other highly incompatible elements (es. Th, Nb, La). In the diagram of Fig. 8, where the $\delta^{11}\text{B}$ is plotted against the Nb/B ratio, Mt. Vulture samples have $\delta^{11}\text{B}$ values in the same range of the nearby Campanian Magmatic Province (D’Antonio et al., 2007), but are generally characterized by higher Nb/B ratios.

In summary, the Sr–Nd–Pb–B isotope data indicate that the VTL alvikites are genetically related to the silicate magmas that fed Mt. Vulture volcano, and, in particular, they show a close relationship with some of the melilitite-bearing rocks (e.g. the S. Caterina mela-foidite).

As stated above, a significant feature of Mt. Vulture magmatism is the occurrence of two trends in the Sr–Nd isotopic space (Fig. 7). The first trend, characterized by constant and high $^{143}\text{Nd}/^{144}\text{Nd}$ and variable $^{87}\text{Sr}/^{86}\text{Sr}$, might be ascribed to a fluid-dominated enrichment process in the mantle source of these magmas; this trend will not be furtherly discussed in this study. The second trend is characterized by a covariation of Sr and Nd

isotope ratios, and includes the VTL alvikites and the mantle xenoliths. According to [Downes et al. \(2002\)](#), the Sr–Nd isotopic variability of the Mt. Vulture mantle xenoliths reveals the occurrence of metasomatic processes induced by silicate melts, possibly subduction-related, on a previously depleted lithospheric mantle.

6.2. Petrogenesis of the VTL alvikites

Experimental studies on model and natural systems at high pressures have shown that melting of carbonate-bearing peridotites yields magnesiocarbonatite liquids (e.g. [Dalton and Wood, 1993](#); [Wyllie and Lee, 1998](#); [Lee et al., 2000](#) and reference therein). Further experimental work at lower pressures has shown that carbonatitic liquids obtained as solidus melting of carbonated wehrlites have much higher Ca/Mg ratios, and that magnesiocarbonatite liquids rising through the lithospheric mantle may react with peridotites forming wehrlites and becoming progressively calcitic ([Dalton and Wood, 1993](#); [Lee and Wyllie, 2000](#)). However, these experiments indicate a maximum molar Ca/(Ca + Mg) of the reacted carbonate liquids of ~ 0.88 . Due to their low content of MgO, the VTL alvikites show molar Ca/(Ca + Mg) > 0.90 . The juvenile carbonatite fraction of the VTL alvikites should have an even higher Ca/(Ca + Mg) ratio, considering that part of the Mg of the bulk rock is held by clinopyroxene, amphibole and phlogopite xenocrysts. The whole-rock Mg# (molar Mg/(Mg + Fe)) of the VTL alvikites is < 0.51 , and the juvenile carbonate fraction should have an even lower Mg# due to the occurrence of Mg-rich silicate xenocrysts. Such low values of Mg# are not appropriate for primary carbonatite magmas in equilibrium with mantle olivine ([Eggler, 1989](#)). [Stoppa and Principe \(1998\)](#) found mantle debris in the cores of the calciocarbonatite lapilli from the Monticchio Lakes, and took this evidence as a proof of the near-primary nature of the carbonatite. To date, we did not find any unambiguous mantle-derived material (xenocrysts or xenoliths) inside the VTL alvikites, that are otherwise charged with xenocrysts and xenoliths from the sedimentary and volcanic pile. In conclusion, the geochemistry (Ca/Mg and Mg/Fe ratios) and petrography (absence of mantle debris) of the VTL alvikites do not support their primary nature.

The frequent intimate association of carbonatites with highly silica-undersaturated, alkaline, silicate rocks, coupled with field and melt inclusions evidences, gave rise to the hypothesis that carbonatitic magmas could be generated through liquid immiscibility (e.g. [Koster van Groos and Wyllie, 1963](#)). The existing experimental data on carbonate-silicate liquid immiscibility

give variable and contrasting informations about the extent of liquid immiscibility at various pressures and about the compositions of the conjugate liquids. However, [Kjarsgaard \(1998\)](#) was able to obtain calciocarbonatite liquids with very high Ca/(Ca + Mg) ratios (> 0.95) and moderate alkali contents, through low-pressure (0.2–0.5 GPa) liquid immiscibility experiments. The starting material for these experiments was a natural Mg-poor nephelinite with 10 wt.% CaCO₃ added. Interestingly, some of the 0.2 GPa experimental runs contained melilite in addition to the immiscible carbonate and silicate liquids.

There are multiple evidences in favor of an origin of Mt. Vulture carbonatites through liquid immiscibility: 1) the carbonatites are closely associated to melilitites, foidites and phonolites, potentially representing their parental or conjugate silicate liquids; 2) the Sr–Nd–Pb–B isotope composition of the VTL alvikites is very close to some melilite-bearing rocks from the volcano; 3) the VTL carbonatites frequently contain melilite xenocrysts and melilite-bearing xenoliths; 4) silicate-carbonate melt inclusions in apatite phenocrysts have been found by [Solovova et al. \(2005\)](#) in a phonolitic nephelinite bomb embedded in the Monticchio Lakes carbonatitic tuffs.

The trace-element enrichment/depletion of the VTL alvikites with respect to their potential silicate conjugates, should be consistent with the available experimental data on the trace-element partitioning between immiscible silicate-carbonate liquids. In [Fig. 9](#) are plotted the concentrations of selected elements of the average VTL alvikite (average of the four samples less contaminated by sedimentary rocks), normalized to the composition of three melilitite-bearing rocks from Mt. Vulture (VTR 4, Melfi foidite; VM 11, Prete della Scimmia melilitite; VU 621, S. Caterina mela-foidite; [Table 3](#)). The compositions of these rocks could possibly approximate that of the silicate liquid conjugate to the VTL alvikite. With respect to the melilitite-bearing rocks from Mt. Vulture, the VTL alvikite is highly depleted in the alkaline elements K, Na, Rb and Cs, and in Zr and Ti; whereas, it is enriched by more than a factor of two in U, Sr, Ba, La, Ce, Nb and P.

The distribution of the HFSE in the VTL alvikites is particularly interesting. In the diagram of [Fig. 10](#), the Nb/Ta ratios have been plotted versus the Nb/Zr ratios. The VTL alvikites are characterized by high Nb/Ta ratios (33–39) and low Zr/Nb ratios (0.4–0.9); these values are similar to those of the average calciocarbonatite (Nb/Ta = 38, Zr/Nb = 0.82; [Chakhmouradian, 2006](#)), and very different from those measured for the silicate volcanic rocks from Mt. Vulture and the Campanian Province, and for the IAV rocks (San Venanzo, Cupaello, Polino).

The experimental carb-liq/sil-liq partition coefficients determined by Veksler et al. (1998b) in model systems very rich in alkalis, are in agreement with the VTL alvikites enrichment factors for Ba and Sr, that are both highly enriched in the carbonatite liquid, and for Ti and Zr, that are enriched in the silicate liquid. The other elements considered in the study of Veksler et al. (1998b) (Nb, Ta, REE), except La, are partitioned preferentially in the silicate liquid. However, these experimental data demonstrate that carbonate/silicate liquid unmixing is an efficient process for decoupling Nb from Ta ($K_D^{Nb/Ta}$ carb-sil ~ 5.1), Nb from Zr ($K_D^{Nb/Zr}$ carb-sil ~ 54) and LREE from HREE ($K_D^{La/Tm}$ carb-sil ~ 4.4), as observed for the VTL alvikites with respect to the melilite-bearing silicate rocks (Figs. 9, 10). The experimental study of the distribution of Th, Pb and U between immiscible carbonate and silicate liquids by Jones et al. (1995) indicates that these elements are preferentially partitioned in the silicate liquid. This is in contrast with the enrichment observed in the VTL alvikites for these elements, in particular U. In conclusion, the relative distribution of a series of relevant trace elements in the VTL alvikites and some melilite-bearing rocks, taken as potential conjugate silicate liquids, are for many aspects compatible with a process of liquid unmixing. The observed discrepancies could be ascribed both to an inaccurate knowledge of the composition of the actual silicate conjugate liquid and to the uncertainties of the still scarce experimental trace-element partitioning data, which were all obtained in alkali rich model systems.

6.3. Mt. Vulture carbonatites: a geodynamic perspective

With very few exceptions, carbonatite rocks are limited to continental settings; in particular, they occur within rifted cratons and, more rarely, close, or within, orogenic belts (e.g. Atlas, Morocco; Wagner et al., 2003;

northern Pakistan; Le Bas et al., 1987), whereas they are completely absent above currently active subduction systems, both oceanic and continental. As inferred for Mt. Etna volcano (Doglioni et al., 2001), Mt. Vulture is located along a supposed deep vertical tear in the slab (Fig. 11; Doglioni et al., 1994; Schiattarella et al., 2005). The slab underneath the Southern Apennines has been highlighted by seismic tomography (De Gori et al., 2001), and the low grade of deep seismicity can be ascribed to a number of factors such as: 1) the low or absent rate of present convergence at the front of the Southern Apennines (Pieri et al., 1997; Patacca and Scandone, 2001); 2) the shallower brittle behavior of the continental lithosphere with respect to the oceanic slab to the south (Carminati et al., 2002); 3) the stretched or thinned slab at depth due to the along arc lengthening of the subduction lithosphere while retreating (Doglioni, 1995).

The supposed vertical rupture of the slab and the consequent creation of an along-dip slab window is mainly related to the differential slab retreat to the NW and SE of the Tremiti, Mattinata and Ofanto transfer zone (Fig. 11). It is accepted that at the time of the Vulture emplacement, the slab retreat of the Southern Apennines slowed down, decreasing the rate of accretion (if any) and determining an inversion from compressive to extensional tectonics (e.g., Hippolyte et al., 1994). However, this change of stress field corresponds to the growth of the foreland anticline (the “Apulian swell”) which indicates a mechanical continuity for transmitting the compressive stress made by the mantle and acting on the slab. This process has been interpreted for buckling the foreland continental lithosphere in a 100 km wide anticline (Doglioni et al., 1994). The area of tear separating the remaining active slab retreat in the central northern Adriatic with respect to the Puglia region is confined between the Ofanto and Tremiti alignments which would correspond to deep vertical tears in the slab

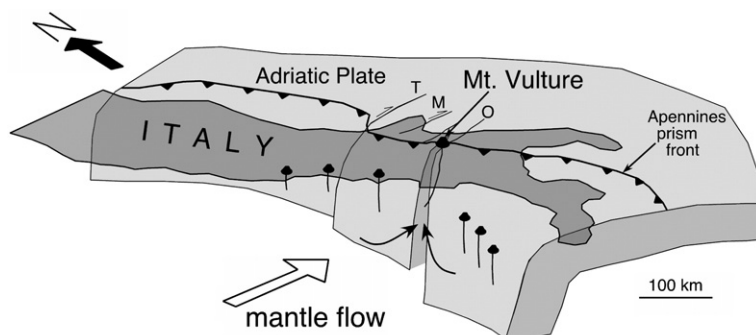


Fig. 11. Cartoon showing the vertical slab window inferred beneath the Southern Apennines. The relative eastward mantle flow enriched of fluids/melts from the Adria Plate subduction could have converged and flowed into the slab tear sourcing Mt. Vulture volcano. T, Tremiti line (E–W); M, Mattinata line (E–W); O, Ofanto graben (ENE–WSW).

allowing differential retreat, possibly controlled by the variation in buoyancy of the thicker (100–110 km) continental lithosphere at the Southern Apennines front (Calcagnile and Panza, 1981). It is worth noting the contemporary evolution of the supposed deep and vertical slab tear and the Vulture volcanic activity, suggesting a common relation.

The slab retreat can be generated either by slab pull, or by the eastward mantle flow predicted by the so-called westward drift of the lithosphere, or by both processes. Whatever the cause, slab retreat must be either compensated or pushed by the mantle, that means in both cases the mantle is flowing eastward (Doglioni et al., 1999). The eastward flow of the mantle when encroaching a vertically ruptured slab could penetrate the window, carrying volatiles and/or melts formed laterally on the slab upper plane, then flowing and rising into the area where the slab is missing. This geodynamic picture possibly accounts for the anomalous tectonic setting of Mt. Vulture, that is located on the external hinge zone of the Apennine subduction zone (Fig. 11a, 11), and whose age matches the Pleistocene time of the tear development.

We prefer the geodynamic frame delineated above to the alternative slab detachment models proposed for the Mediterranean region by other authors (Wortel and Spakman, 2000) and applied to Mt. Vulture magmatism by De Astis et al. (2006). Indeed, a wide horizontal tear in the slab should imply a larger proportion of Adriatic mantle in the source of Mt. Vulture, as well as in the sources of the other volcanoes of the Italian peninsula, and does not account for its peculiar tectono-magmatic evolution. In addition, a westward inflow of Adriatic mantle through the large window created by slab detachment is not favoured by the general eastward mantle flow required by the slab rollback, by the plate motion in the hotspot reference frame, and by the shear wave splitting analysis that shows E–W trending anomalies shifting to NW–SE approaching the Apennines slab (Baccheschi et al., 2007). This flow pattern in the mantle rather supports a west to east mantle flow, consistently with the aforementioned issues. The occurrence of highly silica-undersaturated alkaline rocks associated to carbonatites at Mt. Vulture, is an evidence of low-degree mantle melting at pressures $> \sim 2.0$ GPa under high $\text{CO}_2/\text{H}_2\text{O}$ ratio (e.g. Eggler, 1978). Bearing in mind the geodynamic frame above outlined, and the orogenic chemical signature of Mt. Vulture rocks, we speculate that a genetic link between Tertiary subduction under the southern Italian peninsula and the carbonatation of the mantle source of Mt. Vulture magmas could exist. Taking into account the abundance of marine

carbonate rocks within the upper portion of the sedimentary sequence of the Adriatic lithosphere, it is likely that the sediments subducted below the southern Italian peninsula contained a significant amount of marine carbonates plus a fraction of sedimentary organic carbon. The metasomatized mantle wedge below the Campanian/Tyrrhenian region flows eastward and eventually joins the Adriatic mantle beneath Mt. Vulture area through its injection into the vertical slab window, creating the hybrid source of the CO_2 -rich, silica-undersaturated, magmas feeding Mt. Vulture volcano. In particular, the Sr–Nd isotope similarity between the VTL alvikites, the melilite-bearing rocks and the most isotopically enriched xenoliths from the Mt. Vulture lithospheric mantle (Fig. 7), suggests that the magmas parental to the alvikites were generated in the lithospheric mantle by low-degree melting, preferentially involving the metasomatic component.

7. Conclusions

The extrusive carbonatites, forming lavas, dikes and tuffs, found at Vallone Toppo di Lupo, within the Pleistocene volcanic pile of Mt. Vulture (Southern Apennines, Italy), are medium- to fine-grained rocks made of Sr–Ba–LREE-rich calcite, Na-melilite, LREE-rich apatite, Ti-magnetite, monticellite and accessory perovskite-type phases. A variable fraction of crustal xenolithic materials (igneous and sedimentary rocks and xenocrysts) is also present. Based on the petrographical, chemical and O–C–Sr–Nd–Pb–B isotope data obtained in this study, we conclude that:

- the studied carbonatites are alvikites showing high to very high concentrations of Sr, Ba, U, LREE, Nb, P, F, Th, high Nb/Ta and LREE/HREE ratios, and low contents of Ti, Zr, K, Rb, Na and Cs. These chemical features are commonly observed for calciocarbonatites world-wide;
- the isotope compositions of C and O of the carbonate fraction, though modified by secondary processes, are compatible with a mantle source and rule out a significant involvement of shallow, sedimentary, carbonate rocks in the genesis of these rocks. The high incompatible element content of the alvikites supports the same conclusion;
- the chemical and Sr–Nd–Pb–B isotope compositions indicate that the studied alvikites are genetically related to the silicate volcanic rocks from Mt. Vulture, particularly to some melilite-bearing rocks;

- the carbonatite liquid crystallizing to form the studied alvikites did not represent a primary magma rising directly from the mantle, but most likely originated by liquid unmixing at shallow level, starting from a CO₂-rich melilitite/nephelinite parental melt;
- Mt. Vulture magmas are sourced in a hybrid mantle produced by the interaction between the Adriatic mantle and the metasomatized mantle wedge flowing eastward from the Campanian/Tyrrhenian region. The interaction between these mantle reservoirs is allowed by the occurrence of a vertical tear in the retreating Adriatic lithospheric slab;
- the CO₂-rich nature of the mantle source of Mt. Vulture, able to generate silicate melts evolving to carbonatite, is related to the input of marine carbonates and sedimentary organic carbon, carried at mantle depths by the subduction of the Adriatic lithosphere.

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