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En-route formation of silica-undersaturated magmas through interaction at shallow crustal levels: insights from nephelinites of the Hyblean Plateau, Southern Italy

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Summary

Neogene to Quaternary volcanic rocks from the Hyblean area (Southeastern Sicily) mostly consist of basalts with both alkaline and tholeiitic affinity, erupted in most cases in submarine settings. Minor basanites and nephelinites also occur. Nephelinites mark the resuming of the eruptive activity in this area during Late Miocene, after a non-magmatic period of about 50 Ma, either in form of diatremes or lava flows. Hence, nephelinitic lavas were the final volcanic products on Early Pleistocene. This work is based on whole rock analyses from literature and original in situ investigations by SEM-EDS/WDS of juvenile clasts from tuff-breccia deposits related to diatremic eruptions and lava flow effusions, together with a new unique sampling of a Quaternary lava flow in the area of the San Demetrio quarries, with all samples coming from the northern part of the Hyblean Plateau. Texture of samples varies from subaphyric (especially in the diatremic facies) to highly porphyritic, containing olivine, Ti-rich augite and Ti-magnetite phenocrysts immersed in a groundmass of Ti-augite, nepheline, abundant apatite, Fe-Ti oxide micrograins, rare reacting orthopyroxene and micro-phenocrysts pertaining to minerals of the sodalite group. The groundmass is also characterized by scarce amounts of interstitial glass, often enriched in S, Cl and P, with either haüyne-like or feldspar-like compositions. In the latter case, acicular μm-sized plagioclases are also immersed in the glass. All samples display exceptional chemical heterogeneity, a feature even more emphasized among the residual glass compositions. It is

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also worth noting that the coexistence of nephelinites and alkali basalts occurs at the scale of the same outcrop, as in the case of the San Demetrio lava flow. The origin of Hyblean nephelinites has been previously related to the influence of metasomatic agents, represented by carbonatitic melts, acting into the mantle source. A new perspective has been provided here, implying that the final, extreme heterogenous compositions of these Hyblean ultramafic volcanic rocks can originate from ascending basaltic magmas that have assimilated variable amounts of phyllosilicates and evaporite-like salts.

Keywords: Hyblean Plateau; Nephelinite; Diatreme; Lava flow; Crustal interaction; Phyllosilicate; Evaporite.

Formazione di magmi sottosaturi in silice attraverso interazione sin-eruttiva a livelli crostali superficiali: esempi dalle nefeliniti del Plateau Ibleo, Italia meridionale

Riassunto

Le rocce vulcaniche dell'area Iblea (Sicilia sud-orientale) di età Neogenico-Quaternaria sono costituite principalmente da basalti ad affinità alcalina e tholeiitica, per lo più emessi in ambiente sottomarino, associati a basaniti e nefeliniti. Le nefeliniti, presenti in facies diatremica o colate laviche, segnano la ripresa dell'attività eruttiva in quest'area durante il Miocene superiore, dopo un periodo di inattività durato circa 50 milioni di anni. Le lave nefelinitiche rappresentano dunque gli ultimi prodotti vulcanici del Pleistocene inferiore. Questo lavoro include analisi su roccia totale e indagini in situ SEM-EDS/WDS condotte su clasti juvenili provenienti da depositi tufacei e brecciati correlati a eruzioni diatremiche ed effusioni laviche, unitamente al campionamento unico di una colata lavica Quaternaria presente nell'area delle cave di San Demetrio. Tutti i campioni provengono dalla parte settentrionale del Plateau Ibleo. La tessitura dei campioni varia da subafirica (presente soprattutto in facies diatremica) a fortemente porfirica, con olivina, augite ricca in Ti e fenocristalli di Ti-magnetite immersi in una pasta di fondo composta da Ti-augite, nefelina, abbondante apatite, microliti di ossido di Fe-Ti, raro ortopirosseno e microfenocristalli appartenenti a minerali del gruppo della sodalite. La pasta di fondo è inoltre caratterizzata da vetro interstiziale, spesso arricchito in S, Cl e P e avente composizione simile a haüyna o feldspato. In quest'ultimo caso, è stata osservata anche la presenza di plagioclasio aciculare di dimensioni micrometriche immerso nel vetro interstiziale. Tutti i campioni mostrano un'eccezionale eterogeneità chimica, un carattere enfatizzato tra le composizioni dei vetri residuali. Inoltre, all'interno dello stesso affioramento si è spesso osservata la coesistenza di nefeliniti e basalti alcalini, proprio come nel caso della colata lavica di San Demetrio. L'origine delle nefeliniti iblee è stata precedentemente correlata all'azione di agenti metasomatici, rappresentati da fusi carbonatitici, nella sorgente mantellica. Questo studio apre nuove prospettive sull'origine delle nefeliniti, suggerendo che le composizioni estremamente eterogenee di queste rocce vulcaniche ultramafiche possano essere correlate alla risalita di magmi basaltici in grado di assimilare quantità variabili di fillosilicati e deposi salini di natura evaporitica durante il percorso verso la superficie.

Parole chiave: *Plateau Ibleo; Nefelinite; Diatrema; Colata lavica; Interazione crostale; Fillosilicato; Evaporite.*

1. Introduction

In several continental and oceanic anorogenic zones, sequences of volcanic rocks mainly consist of basalts, both tholeiitic and alkaline, and subordinately of nephelinites (e.g., Gill, 2010 and references therein). While there are no doubts regarding the mantle origin of basalts, the scientific community is not completely in agreement regarding the genesis of nephelinites. Excluding an origin by differentiation of basaltic magmas, the most acknowledged hypothesis able to explain the formation of nephelinites is their primary production in the deep, convective mantle by low degrees of partial melting of metasomatized peridotites (e.g., Best, 2003; Philpotts and Ague, 2009, and references therein). The scientific community agrees on the fact that carbonatitic melts of deep origin metasomatize the mantle source (Schmidt et al., 2024 and references therein), producing enrichment in various incompatible elements, especially LILEs. However, the compositional heterogeneity of anorogenic volcanic rocks, especially in oceanic island contexts, can be also ascribed to the interaction of magmas of asthenospheric provenance with metasomatized rocks in the lithospheric mantle or with crustal rocks (e.g., Davidson and Bohrson, 1998; Best, 2003; Philpotts and Ague, 2009, and references therein).

As regards the nephelinites of the Hyblean Plateau, their origin from partial melting of a mantle metasomatized by carbonatitic melts is the most accredited hypothesis in the scientific literature (cf. Beccaluva et al., 1998; Trua et al., 1998). However, Scribano and Viccaro (2013; 2014) and, later, Correale et al. (2019) have put forward the preliminary idea that the Hyblean nephelinitic magmas may have originated at crustal levels following the interaction between a basaltic magma (s.l.) and altered mafic rocks that constitute the remains of an abyssal, Permo-Triassic hydrothermal system. Some convincing points of this new hypothesis are related to the presence in some Hyblean nephelinites of minerals rich in sodium, sulphur and chlorine, such as haüyne, and to the marked compositional heterogeneity of the volcanic products both in terms of major and trace elements.

The present work is therefore aimed at providing further evidence, essentially based on new observations on bulk rock compositions and in situ compositional data acquired by SEM-EDS/WDS on various nephelinitic samples referred to both diatremes and lava flows in the northern sector of the Hyblean Plateau, able to support the idea that the final composition of the silica undersaturated volcanic rocks in the area has been strongly influenced by interaction and contamination processes occurred at shallow crustal levels.

2. Geochemical and volcanological background of the Hyblean volcanic rocks

The Hyblean Plateau (Sicily, Southern Italy; Fig. 1) has been interested by multiple phases of volcanism, which showed significantly different geochemical and volcanological characteristics over time (Behncke et al., 2004). Well data place the oldest volcanic manifestations, which are mainly represented by mafic volcanic rocks and rare gabbros in the Triassic (Cristofolini, 1966).

These are mostly alkali basalts with trace element concentrations and Sr-Nd-Pb isotope ratios consistent with those of oceanic island basalts (Rocchi et al., 1998). Other eruptive manifestations date back to Upper Cretaceous and include alkali basalts that are found as fragments of highly altered pillows and hyaloclastites.

They crop out discontinuously under horizons of rudist limestones in the areas of Capo Passero, Porto Palo and along the Ionian coast from Siracusa to Augusta in a rather complex structural framework (Fig. 1; Carbone et al., 1981; 1984; Lentini et al., 1996).

Other volcanic events, Miocenic in age, characterize the eastern and northeastern part of the Hyblean Plateau (Fig. 1). These outcrops provide evidence of a peculiar explosive activity, rather spatially and temporally limited, which has generated a series of diatremes whose juvenile products are poorly differentiated melts, ranging from alkali basalts to nephelinites (e.g., Schmincke et al., 1997; Scribano et al., 2007; Suiting and Schmincke, 2009; 2010; 2012). The latest volcanic events in the Hyblean area, which follow the previous period without interruption, are Plio-Pleistocenic in age. They include lava flows of tholeiitic basalts with E-MORB affinity and other alkaline effusive products represented by basanitic and nephelinitic flow units emplaced both in subaqueous and subaerial environments (Beccaluva et al., 1998; Correale et al., 2018). During the Upper Pliocene, eruptive rates increased and were accompanied by the northward migration of the volcanic activity. Alkaline volcanic rocks have rather primitive composition, as evidenced by their Mg# >60 and their Ni (>200 ppm) and Cr (>250 ppm) contents.

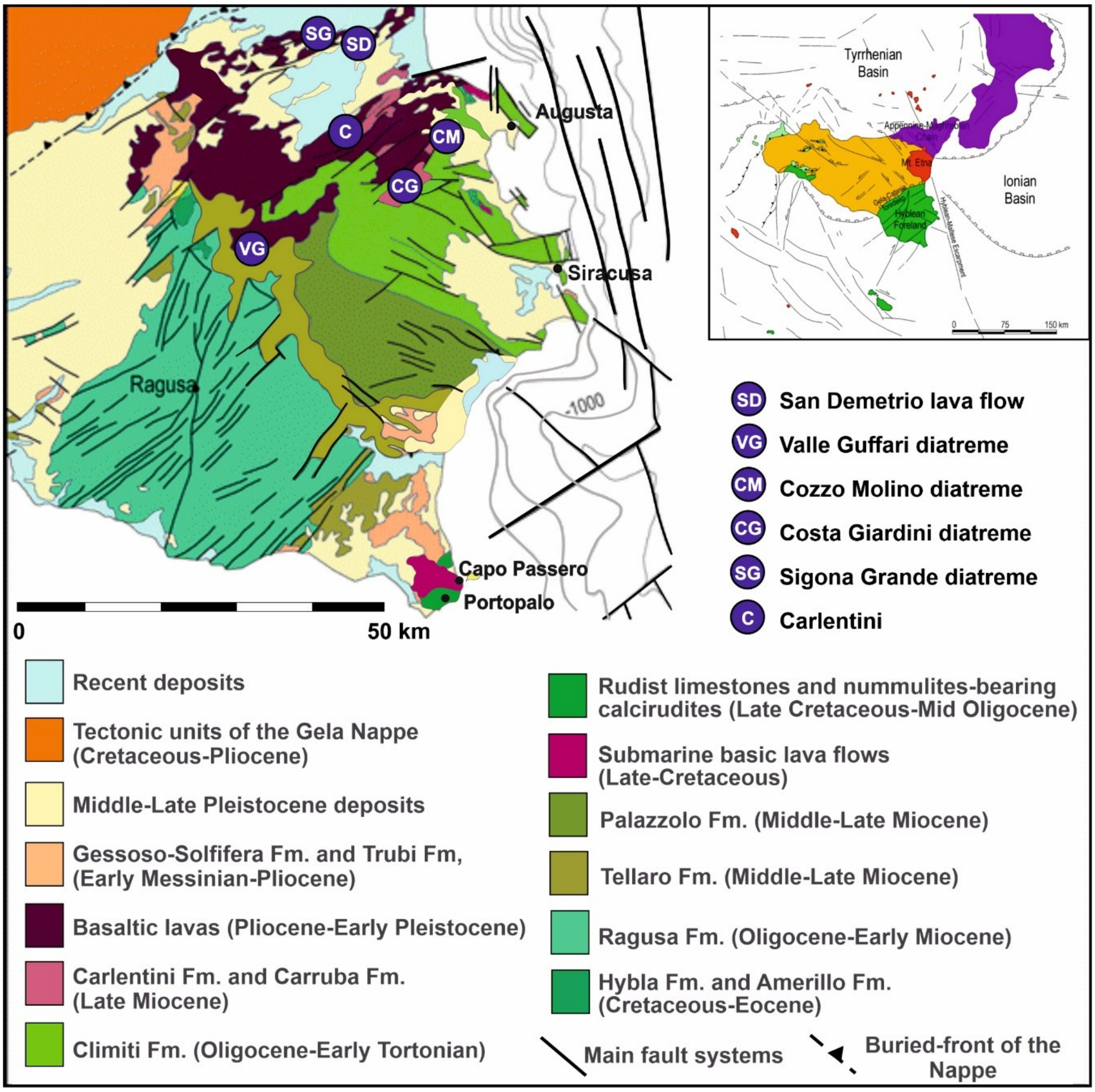

Fig. 1. Simplified geodynamic framework of Southern Italy (inset) and geological sketch map of the southeastern corner of Sicily modified after Carbone et al. (1984).

This implies fast ascent that prevented compositional modifications related to fractional crystallization processes. According to Trua et al. (1998), the Sr-Nd isotope compositions of the Plio-Pleistocene volcanic rocks are very close to those of MORBs, while the distribution of trace elements is more similar to those of OIB-type magmas, also suggesting that crustal contamination processes are substantially absent. The large serial range of erupted products has been ascribed to compositionally heterogeneous mantle sources located at different depths (Beccaluva et al., 1998). In this framework, the most superficial source gave rise to tholeiitic and transitional basalts for partial melting degrees between 10 and 30%, whereas those located at intermediate depths produced alkali basalts and basanites for partial melting degrees between 4 and 10%. Finally, the deepest source (i.e., about 90 km), after being metasomatized by alkaline and/or carbonatitic melts, originated nephelinitic magmas for partial melting degrees in the order of 3-4%. Scribano et al. (2009) have suggested that mantle sources feeding the Hyblean volcanism can be ascribed to a depleted lithospheric mantle re-fertilized by clinopyroxenite veins with variable quantities of accessory phases such as aluminous spinel, garnet, hydrous and carbonate minerals. Low degrees of partial melting could have emphasized the role of pyroxenitic veins and hydrous minerals, leading to the formation of primary magmas with alkaline affinity. Higher degrees of partial melting could have instead led to the production of tholeiitic magmas through dilution of the chemical effects related to melting of the pyroxenitic veins. In this context, Scribano et al. (2009) have also highlighted that contamination of basaltic magmas with hydrothermally-altered ultramafic rocks at crustal levels could explain the remarkable compositional heterogeneity observed for the Hyblean volcanic rocks over space and time.

3. Petrological characteristics of the Hyblean nephelinites

The Hyblean nephelinites can be found both in diatremic facies and lava flows. Nephelinites of the diatremes constitute the juvenile tephra deposited in the breccia infilling of diatremes and in the tuff-ring surrounding the diatreme crater edge. The best exposed diatremes of the Hyblean Plateau, Miocenic in age, are those of Sortino, Valle Guffari and Cozzo Molino (Fig. 1). Among these, the diatremes of Cozzo Molino and Valle Guffari are extraordinarily rich in ultramafic xenoliths (Scribano, 1987; Sapienza and Scribano, 2000; Sapienza et al., 2005; 2007; Scribano et al., 2006; Ciliberto et al., 2009; Scribano et al., 2009; Viccaro et al., 2009). Conversely, the nephelinitic lava flows are represented by subaerial units with evident columnar fissures that cover the temporal range from the Messinian to Pleistocene. They also bear partly resorbed xenoliths of variable size, from 2 cm to a few mm, and xenocrysts of olivine and Mg-rich orthopyroxene, presumably deriving from mantle peridotites. The silica undersaturation of the Hyblean Plateau reflects not only in the occurrence of nepheline, but also in the abundance of olivine (being sometimes melanephelinites) and, in some cases, in the occurrence of minerals belonging to the sodalite group (mostly haüyne). From a macroscopic point of view, the Hyblean nephelinites are very similar to the alkali basalts, either in terms of density (between 2.7 and 3.1 g/cm^3) or the dark grey color. They present textures varying from subaphyric, especially in diatremic facies, to strongly porphyritic (porphyricity index P.I. up to ~50) with augitic clinopyroxene and olivine among the most abundant phases in phenocrysts. Augitic clinopyroxene, nepheline, apatite, titanite and Fe-Ti oxides characterize the groundmass

(Tonarini et al., 1996; Beccaluva et a., 1998; Trua et al., 1998; Scribano et al., 1996, 1997, 2009, 2014; Sapienza et al., 2000).

The geochemical analyses of the Hyblean nephelinites available in the scientific literature present aspects that are partly consistent with those of worldwide nephelinites (cf. Tonarini et al., 1996; Schmincke et al., 1997; Beccaluva et al., 1998; Trua et al., 1998; Sapienza et al., 2000; Scribano et al., 2006; Suiting and Schmincke, 2009). Among these, the SiO_2 content (<42 wt.%) and the rather high concentrations of Ba, Sr, Th, Ta, Nb, LREE, Pb and P (ppm). In particular, the enrichment in Sr, Ba, LREE, the high CaO/Al_2O_3 ratio (between 1.0 and 1.5) and the high P_2O_5 concentrations (up to 2.6 wt.%) are all features in accordance with low degrees of mantle partial melting (e.g., Beccaluva et al., 1998). The Hyblean nephelinites also show geochemical characteristics similar to those of alkali basalts, such as: 1) Sr and Nd isotope compositions consistent with depleted mantle sources (Tonarini et al., 1996); 2) Sr-Nd-Pb isotope compositions and Th/Yb - Nb/Yb ratios consistent with those of OIB magmas; 3) concentrations of K_2O, TiO_2, Zr, Hf and Y similar to those of other alkaline mafic products cropping out in the Etna region (e.g., Viccaro and Cristofolini, 2008; Viccaro et al., 2011; Viccaro and Zuccarello, 2017).

4. Sampling and analytical methods

Nephelinites of this study come from various Miocenic tuff-breccia deposits related to diatremic eruptions and lava flow effusions from the northern sector of the Hyblean Plateau (Figs. 1 and 2).

An original, unique sampling of a Quaternary lava flow in the San Demetrio quarries has been also added to the diatremic and lava flow samples collected by Prof. Vittorio Scribano during field campaigns conducted in the '80s and '90s. In addition to common petrographic investigations, polished thin sections were subjected to more advanced in situ analyses in order to obtain quantitative information on the mineralogical phases and their major element abundances.

Data have been acquired with a Tescan Vega II LMU scanning electron microscope (SEM) at the Earth Sciences Section of the Department of Biological, Geological and Environmental Sciences of the University of Catania. The instrument is equipped with an EDAX Neptune XM4-60 EDS micro-analyzer that operates through an energy dispersive system characterized by an ultra-thin Be window coupled with an EDAX LEXS WDS (wavelength dispersive low energy X-ray spectrometer) system calibrated for light elements. Data were acquired at 20 kV of acceleration voltage, with beam current of about 2 nA, obtaining precision and accuracy on the investigated elements in the range of 3-5%, verified by repeated analyses of internationally certified standards during the analytical runs.

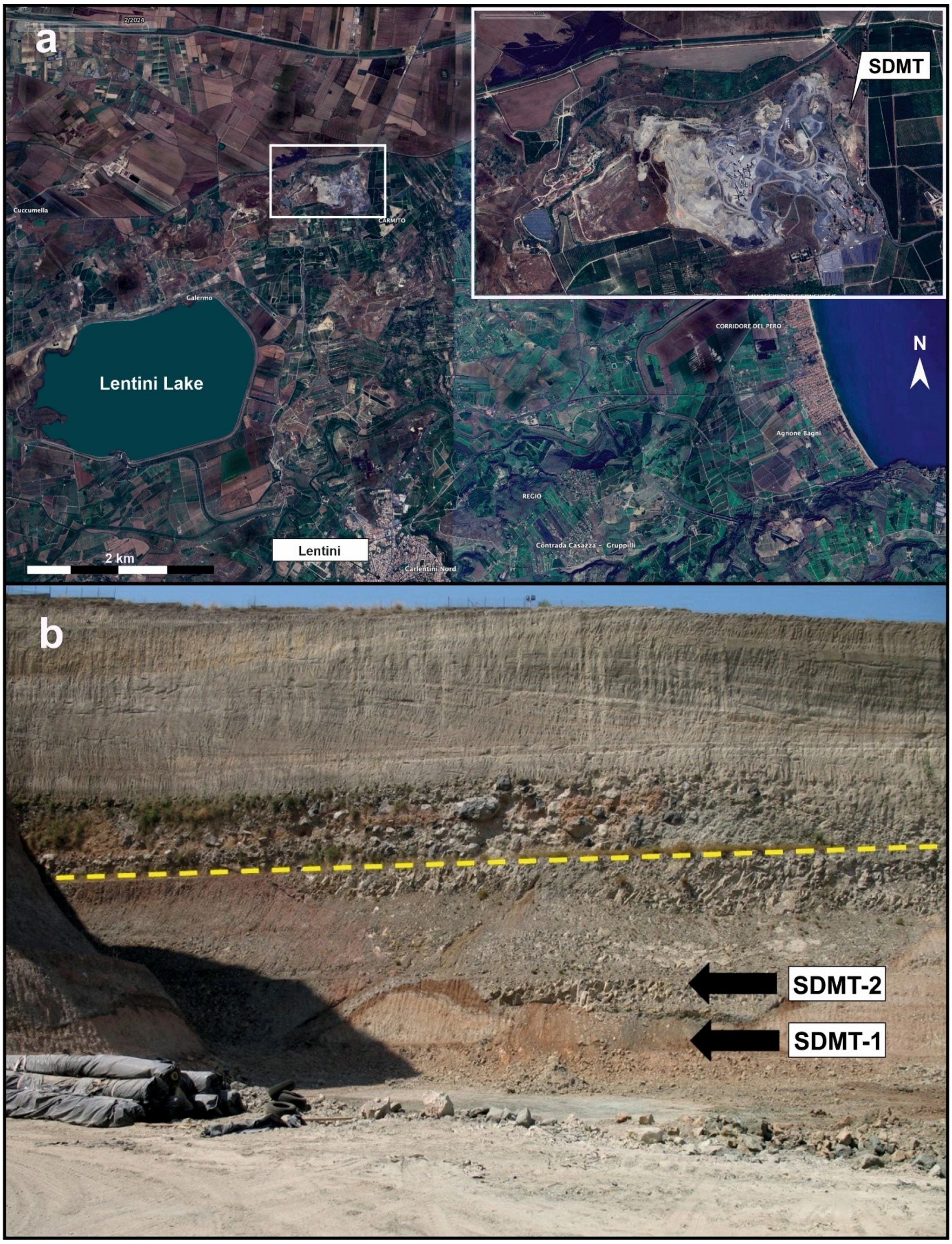

Fig. 2. a) Location of the San Demetrio quarries in the northeastern area of the Lentini Lake with position of the SDMT lava flow samples; b) outcrop of the San Demetrio lava flow with position in the sequence of the SDMT-1 nephelinitic sample and the SDMT-2 alkali basaltic one. The yellow dotted line marks the upper limit of the San Demetrio lavas.

New whole rock data on two samples of the San Demetrio lava flow have been also integrated with analyses of Hyblean nephelinites available from literature (Tonarini et al., 1996; Schmincke et al., 1997; Beccaluva et al., 1998; Trua et al., 1998; Sapienza et al., 2000; Scribano et al., 2006; Suiting and Schmincke, 2009). Original data have been obtained at the Earth Sciences Section of the Department of Biological, Geological and Environmental Sciences of the University of Catania by means of the Philips PW2510 spectrometer with correction for matrix effects. The loss on ignition (L.O.I.) was obtained by precision gravimetric methods and corrected for the oxidation of Fe^{2+}. The fine powder was also analyzed with integrated ICP-AES and ICP-MS mass spectrometry methods in order to obtain the trace element concentrations. Samples were previously digested and completely dissolved by sodium peroxide fusion in graphite crucibles and diluted with HNO3. Analyses were then obtained with a Perkin Elmer ELAN 6100 mass spectrometer used at the SGS laboratories in Canada. Calibration series on internationally certified reference materials ensure analytical precision better than 7% for all the trace elements analyzed.

5. Results

Volcanic rocks have textures from subaphyric to markedly porphyritic, with porphyricity index (P.I.) up to ~50 vol.%, in line with observations from past studies. Juvenile clasts from tuff-breccia diatremic deposits are in general significantly less crystallized than lava flow samples, which exhibit the highest P.I. Augitic clinopyroxene rich in titanium is the most abundant phase and is present both as phenocrysts with sizes of 2-5 mm and microlites in the groundmass (Fig. 3a). Olivine is found exclusively as zoned phenocrysts with Fo_{86} to Fo_{82} and size between 200 μm and 1 mm. The most crystallized products display olivine and augitic clinopyroxene also as abundant porphyroclasts. Ti-magnetite is also found in the phenocryst assemblage. The groundmass is mainly composed of Ti-augite, nepheline, abundant apatite, titanite, Fe-Ti oxides, rare reacting orthopyroxene and limited glassy portions (Fig. 3b).

Micro-crystals of haüyne and other minerals of the sodalite group are frequently found in diatreme and lava flow samples (Figs. 3a, 3c and 4a-b). These show dimensions varying from 200 to 500 μm and represent ~25% of the total crystal volume. They have often skeletal textures and rarely euhedral habitus. These crystals can be colorless, faintly blue, violet or black. They are sometimes surrounded by a thin opaque brownish-blackish acicular rim (Fig. 3d). They can contain glassy drops and microlites similar to those of the groundmass in the central portion, which can be replaced in some cases by phyllosilicates or fluid inclusions (Fig. 3d). Crystals are often zoned: variations in the Ca/Na and S/Cl ratios can shift the compositions towards the fields related to haüyne, lazurite and nosean. Fragments of xenocrysts and µm-sized inclusions, observable only through electron microscope, are present in the groundmass of all samples, with a clear prevalence in those coming from the diatremic facies. In situ analyses conducted on these fragments suggest that some of them can be referred to minerals falling within the haüyne-lazurite range (Fig. 4a-b; Table 1).

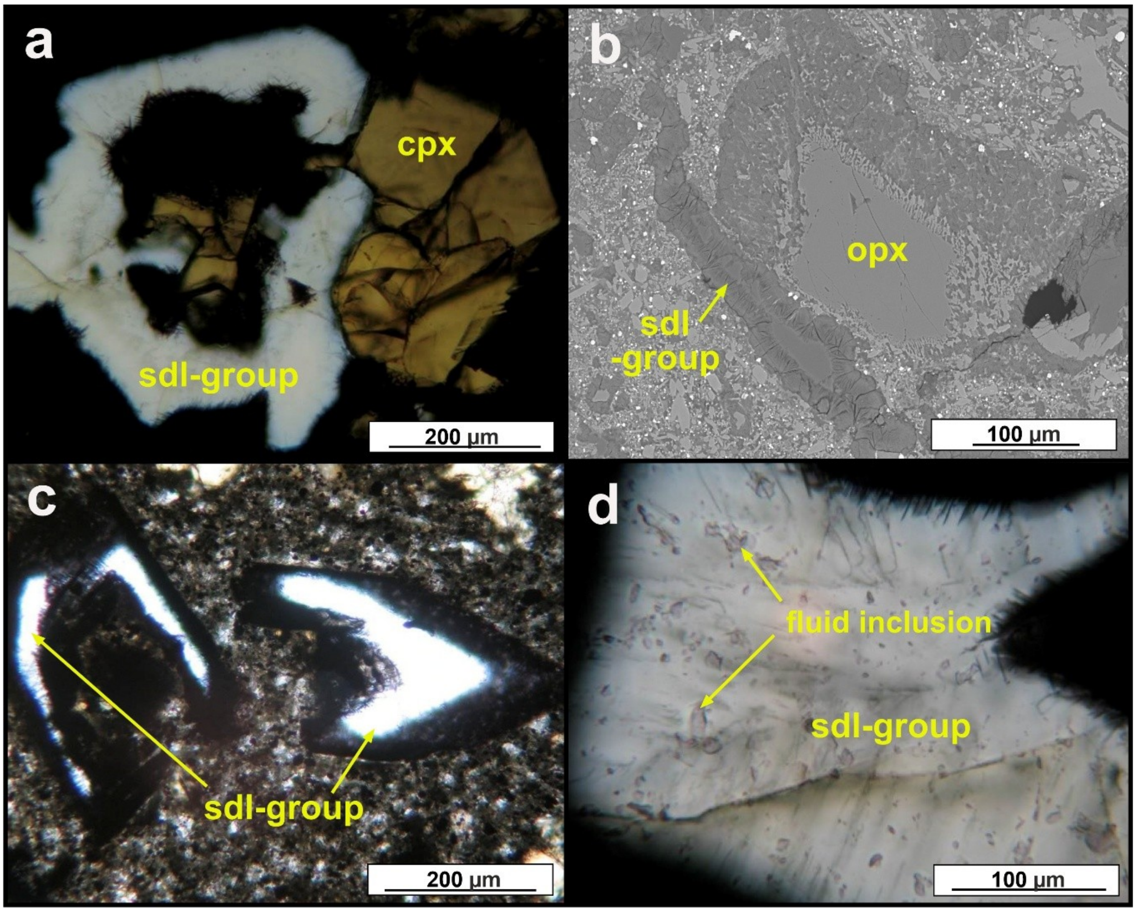

Fig. 3 a) Skeletal mineral of the sodalite-group (sdl-group) in association with an augitic clinopyroxene (cpx) phenocryst found in the lava flow sample SDMT-1 (photo under optical polarizing light, 20× magnification); b) Back-scattered SEM image of a reacting orthopyroxene crystal (opx) found in a tuff-breccia juvenile clast of diatremic deposits; c) Minerals of the sodalite group surrounded by a typical brownish-blackish reaction rim found in the lava flow sample SDMT-1 (photo under optical polarizing light, 20× magnification); d) Detail of the clear portion of a sodalite group mineral found in the lava flow sample SDMT-1 showing a consistent amount of micrometric fluid inclusions (photo under optical polarizing light, 40× magnification).

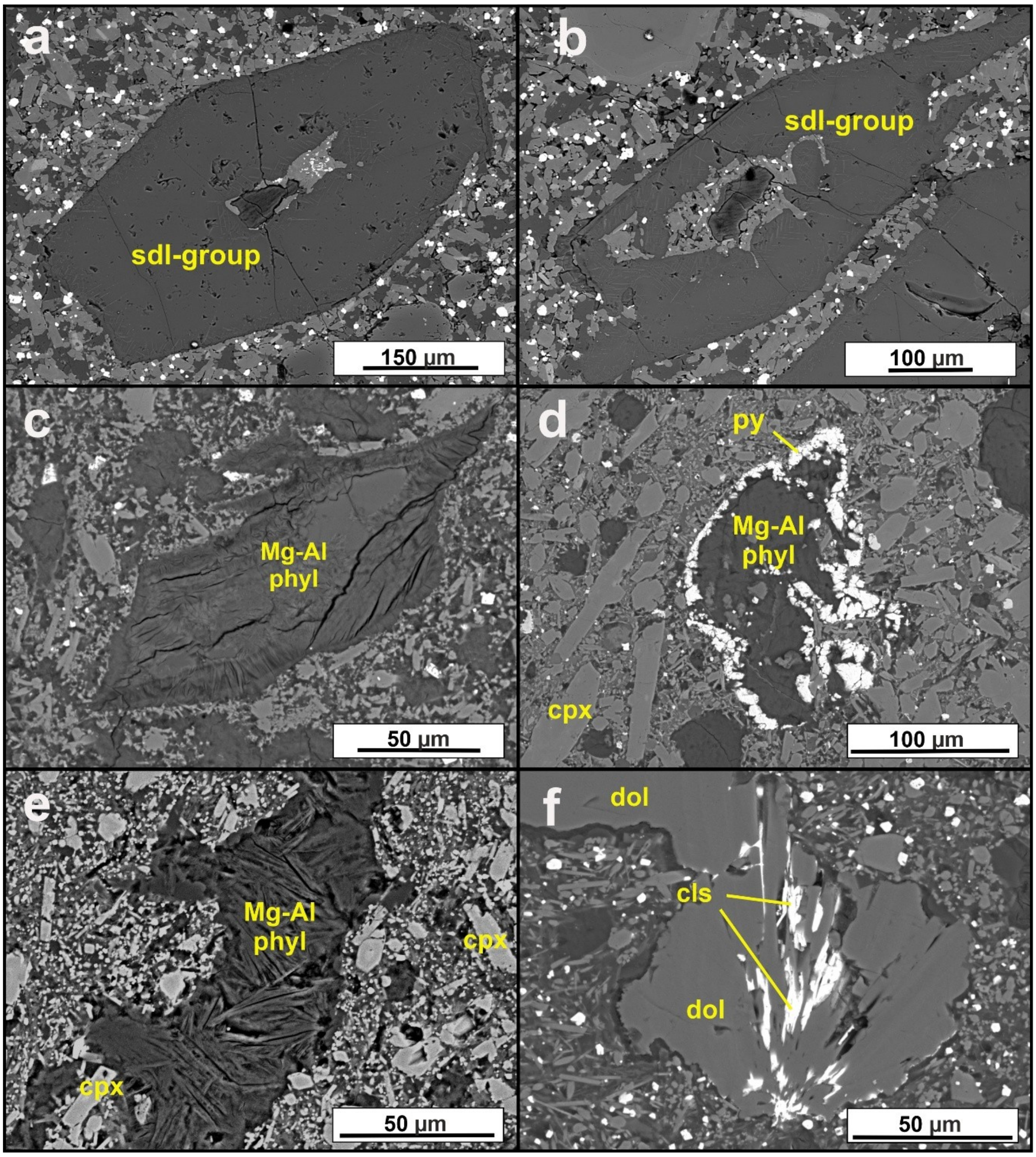

Fig. 4. a) and b) Back-scattered SEM images of crystals referred to minerals of the sodalite group (haüyne zoned to sodalite) found in the lava flow sample SDMT-1. The central portion of crystals is generally constituted by microlites similar to those visible in the groundmass; edges of the external and inner portions of the crystals are characterized by thin lamellae of opaque minerals; c), d) and e) Back-scattered SEM images showing some examples of the abundant micrometer-size Mg-Al phyl ascribed to phyllosilicates with interlayered chlorite/smectite structures found in the diatreme tuff-breccia juvenile clasts; clasts are occasionally bordered by pyrite (py), as shown in the panel d); f) Back-scattered SEM image of a micrometer-size xenocryst found in a tuff-breccia juvenile clast: the pale gray mineral is dolomite (dol), the white one is celestine (cls).

Mineral phase	**Rock type**	**SiO_2**	**TiO_2**	**Al_2O_3**	**FeO_{tot}**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**P_2O_5**	**Cl**	**S**	**Cr_2O_3**	**SrO**
Clinopyroxene	L	44.48	2.93	11.40	6.47	11.61	19.17	1.45	0.66	0.94	0.20	0.70	-	-
Clinopyroxene	L	45.88	1.72	16.65	9.09	11.91	11.92	0.54	0.54	0.53	0.03	1.17	-	-
Clinopyroxene	L	52.73	1.43	9.52	7.41	9.81	16.59	2.17	0.20	0.13	0.03	-	-	-
Clinopyroxene	L	45.37	2.79	13.71	10.54	9.42	11.99	2.91	1.25	1.83	0.06	-	0.13	-
Clinopyroxene	L	46.62	1.98	13.75	8.65	10.43	12.73	3.55	0.92	1.17	0.13	-	0.07	-
Clinopyroxene	L	51.54	1.67	16.01	5.54	7.36	10.29	6.10	0.45	0.74	0.11	-	0.19	-
Clinopyroxene	L	48.12	3.14	11.38	6.61	9.93	17.74	2.08	0.85	-	0.00	-	0.15	-
Clinopyroxene	D	47.40	2.06	12.94	9.06	12.01	12.78	1.45	1.60	0.66	0.00	-	0.05	-
Clinopyroxene	D	45.02	4.13	8.73	7.42	12.03	21.41	0.45	0.12	0.09	0.07	-	0.52	-
Opx	D	56.78	0.16	0.91	5.74	35.33	0.37	0.23	0.08	0.00	0.06	-	0.34	-
Mg-Al phyllosilicate	D	48.89	0.32	14.27	7.05	25.76	0.81	1.89	0.62	0.07	0.11	0.21	-	-
Mg-Al phyllosilicate	D	44.37	1.48	18.10	10.58	14.76	5.81	0.63	2.74	1.36	0.09	-	0.07	-
Mg-Al phyllosilicate	D	40.02	0.69	25.26	11.89	16.50	4.31	0.25	0.51	0.28	0.15	-	0.15	-
Feldspar	D	58.82	-	26.57	0.41	0.44	1.85	11.53	0.25	0.07	0.06	-	-	-
Feldspar	D	56.48	0.85	24.35	1.32	0.77	7.75	6.91	1.33	-	0.12	-	0.12	-
Feldspar	D	62.90	0.85	21.05	0.58	0.79	1.80	6.72	4.88	0.44	-	-	-	-
Feldspar	D	58.73	0.12	25.58	0.18	0.19	0.20	14.36	0.26	0.15	0.05	-	0.18	-
Celestine	D	-	2.46	7.01	4.05	3.53	21.77	1.53	0.88	-	0.09	22.58	0.20	35.90
Sodalite-group	L	32.52	-	27.41	1.39	0.38	7.68	15.12	1.36	-	0.81	13.35	-	-
Sodalite-group	L	32.81	-	27.42	0.98	0.48	8.55	14.36	1.51	-	0.51	13.38	-	-
Sodalite-group	L	33.21	-	27.41	0.81	0.39	8.67	14.14	1.38	-	0.45	13.54	-	-
Sodalite-group	L	32.19	-	27.18	1.61	0.37	7.59	14.99	1.39	-	0.81	13.86	-	-
Sodalite-group	L	32.42	-	27.00	2.02	0.44	7.59	13.98	1.39	-	0.74	14.45	-	-
Sodalite-group	L	32.93	-	27.52	0.81	0.31	8.50	14.47	1.39	-	0.60	13.47	-	-
Sodalite-group	L	33.52	-	28.10	2.07	0.20	5.78	15.29	1.04	-	2.03	11.95	-	-
Sodalite-group	L	32.93	-	26.57	1.10	1.62	8.36	15.64	1.32	-	0.40	12.06	-	-

Table 1. Major oxide concentrations of representative mineral phases of the Hyblean nephelinites. L: lavas; D: diatremes.

It is important to underline, however, that methods based exclusively on chemical analyses do not allow to calculate the precise amount of sulfide ions located in the tetrahedral structure of the sodalite group minerals, making the characterization of these phases within the group very complex.

SEM-EDS/WDS observations and measurements have also revealed the presence of other micrometric fragments in the groundmass attributable to carbonates and sulphates like dolomite and celestine, along with a dominant presence of phyllosilicates (Fig. 4c-f; Table 1). These phyllosilicates are rich in Mg and poor in Ca, with Al contents compatible with mixed layered structures such as chlorite/smectite. These Mg-Al phyllosilicates are sometimes surrounded by thin pyrite rims (Fig. 4d). This rather complex assemblage is completed by sporadic patches of interstitial glass (Fig. 5) often enriched in S, Cl and P, displaying either a haüyne-like or feldspar-like compositions, and spanning both the alkaline and peralkaline fields (Fig. 6; Table 2). In the feldspar-like glass patches, acicular microlites of plagioclase are unusually present, suggesting a certain degree of SiO_2 saturation of the residual melt (Fig. 5; Tables 1 and 2).

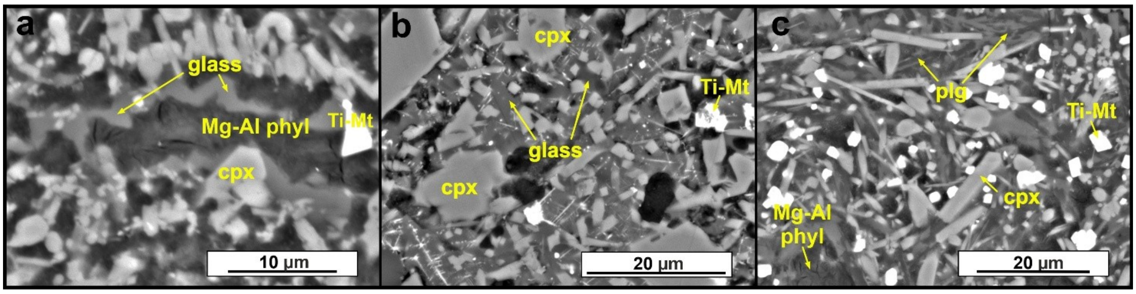

Fig. 5. SEM images of the groundmass in clasts of the juvenile lava characterizing the diatremic facies; a) silicate glass with a rough feldspar composition (pale gray) enclosing a micro-xenolith of the Mg-Al rich phyllosilicate. In general, the lava displays a considerable amount of disseminated micrometer-sized clasts of the same nature; b) Detail of the groundmass of a juvenile clast from the Valle Guffari tuff-breccia deposit, where the interstitial glass displays an almost stoichiometric haüyne composition; c) typical microcrystalline groundmass texture of the diatreme juvenile lava. Raster analyses by SEM-EDS/WDS testifies, in some cases, 10 wt.% normative nepheline, slight peralkaline character, lack of modal feldspathoids and modal occurrence of plagioclase with andesine composition. Other zones of the same juvenile clast provide glass compositions with 9 wt.% of normative quartz and metaluminous character (as Na_2O drops down to ca. 2 wt.%), emphasizing the significant chemical heterogeneity even at the scale of the same clast.

Glass	SiO_2	TiO_2	Al_2O_3	FeO_{tot}	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	S	Cr_2O_3
RG_1	43.33	0.80	21.80	6.74	1.23	8.63	7.90	2.71	3.66	1.59	1.57	0.06
RG_2	52.11	1.25	21.06	7.38	1.62	5.26	3.92	4.54	1.37	0.48	0.87	0.13
RG_3	37.43	0.29	26.44	3.16	0.87	4.72	12.04	1.78	0.84	1.48	10.95	0.00
RG_4	46.92	0.18	32.30	1.32	0.45	6.68	11.01	0.56	0.08	0.10	0.20	0.18
RG_5	46.44	0.34	32.44	1.56	0.36	7.05	9.77	0.12	0.19	0.06	1.51	0.16
RG_6	43.63	0.14	32.61	1.04	0.45	0.46	15.40	5.95	0.06	0.08	0.08	0.09
RG_7	55.07	0.33	21.31	1.46	0.26	5.86	10.75	0.38	4.58	-	-	-
RG_8	50.56	3.02	16.51	6.66	2.09	15.39	1.51	2.46	1.39	0.19	-	0.19
RG_9	51.26	3.28	16.03	7.03	2.30	13.45	1.15	3.63	1.33	0.23	-	0.30
RG_10	48.21	3.41	15.15	8.24	4.84	15.18	1.89	1.43	1.52	0.14	-	0.00
RG_11	52.05	1.48	20.60	3.23	2.40	11.84	5.28	1.28	1.63	0.08	-	0.14
RG_12	53.71	1.80	20.63	4.19	1.05	9.81	5.23	1.86	1.44	0.12	-	0.17
RG_13	58.66	1.33	22.84	2.20	0.46	4.84	6.49	2.97	-	0.07	-	0.12
RG_14	61.28	0.90	18.51	2.06	2.22	4.40	5.42	4.86	0.21	0.03	-	0.12
RG_15	62.20	0.46	18.81	1.27	1.48	2.95	5.60	6.40	0.64	0.09	-	0.10

Table 2. Major element composition of the residual glass (RG) in clasts of the juvenile lava characterizing the diatremic facies.

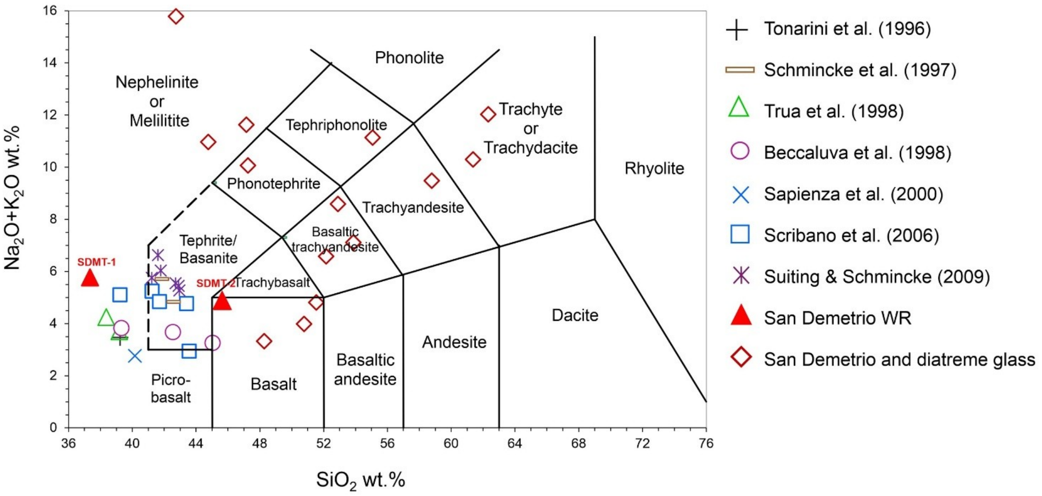

Fig. 6. Total Alkali vs. Silica diagram (Le Maitre, 2002) with plotted compositions of the Hyblean nephelinites available from literature (data from Tonarini et al., 1996; Schmincke et al., 1997; Beccaluva et al., 1998; Trua et al., 1998; Sapienza et al., 2000; Scribano et al., 2006; Suiting and Schmincke, 2009), the original whole rock data of the SDMT-1 and SDMT-2 lava flow samples and the original data of residual glasses found in various juvenile samples from the Hyblean diatremes and lava flows.

Major oxide concentrations of the San Demetrio lava flow have been plotted on the Total Alkali vs. Silica diagram (Le Maitre, 2002) together with those of nephelinites referred to both diatremes and lava flows available from literature (Fig. 6; Table 3; data from Tonarini et al., 1996; Schmincke et al., 1997; Beccaluva et al., 1998; Trua et al., 1998; Sapienza et al., 2000; Scribano et al., 2006; Suiting and Schmincke, 2009). Despite the rather similar petrographic characteristics of both samples, they exhibit two markedly distinct compositions.

The SDMT-1 has a SiO_2-undersaturated composition typical of other Hyblean nephelinites, with higher MgO, CaO, Na_2O and F contents with respect to the SDMT-2 sample, which is an archetypal alkali basalt. In general, the Hyblean nephelinites show large chemical variability in terms of major oxide concentrations (Fig. 6; Table 3). Indeed, Na_2O varies from ~2 to ~5 wt.% and the sum of alkalis from ~2.8 to ~7 wt.%; MgO and CaO range both between ~9 and ~16 wt.%. For what regards the trace element distribution, the Primordial Mantle-normalized (PM; McDonough et al., 1992) REE patterns for all the considered products exhibit comparable trends (Fig. 7a), suggesting rather similar ratios between LREEs and HREEs. Conversely, the PM-normalized (McDonough et al., 1992) trends of incompatible elements evidence a certain heterogeneity among the considered nephelinitic products (Fig. 7b). Major variability is observed in the concentrations of Ba, Nb, La and, to a minor extent, of Th, U and Sr. This feature appears accentuated in the SDMT-2 alkali basalt, which displays a pronounced negative anomaly of Ba if compared to the SDMT-1 nephelinite. Finally, samples provided by Schmincke et al. (1997) and Suiting and Schmincke (2009) display significantly lower Nb/La than all the products considered, with marked depletion in this ratio especially in samples from diatremes (Fig. 7b).

	SDMT-1	SDMT-2
SiO_2	36.2	44.01
TiO_2	3.64	2.89
Al_2O_3	13.3	12.51
FeO_{tot}	13.1	12.63
MnO	0.24	0.15
MgO	9.34	6.65
CaO	14.11	11.5
Na_2O	4.1	3
K_2O	1.49	1.66
P_2O_5	1.4	1.41
F	1360	890
LOI	2.6	3.92
Cr	100	117
Ni	93	124
V	346	213
Cu	96	87
Rb	34.5	33.8
Ba	1170	146
Th	11.1	8.3
U	2.86	2.34
Nb	127	91
Ta	6.6	4.6
La	79.4	99.7
Ce	143	180
Pr	16.5	16.9
Sr	1530	1140
Nd	62.7	64.9
Sm	11.6	12.4
Zr	229	267
Hf	5	6
Eu	3.68	3.7
Gd	9.63	10.1
Tb	1.39	1.41
Dy	7.14	7.17
Y	40	27.4
Ho	1.29	1.27
Er	3.28	3.24
Tm	0.41	0.4
Yb	2.6	2.4
Lu	0.38	0.33
Co	47.7	44.8
Cs	0.4	0.4

Table 3. Major oxide and trace element concentrations of the San Demetrio lava flow.

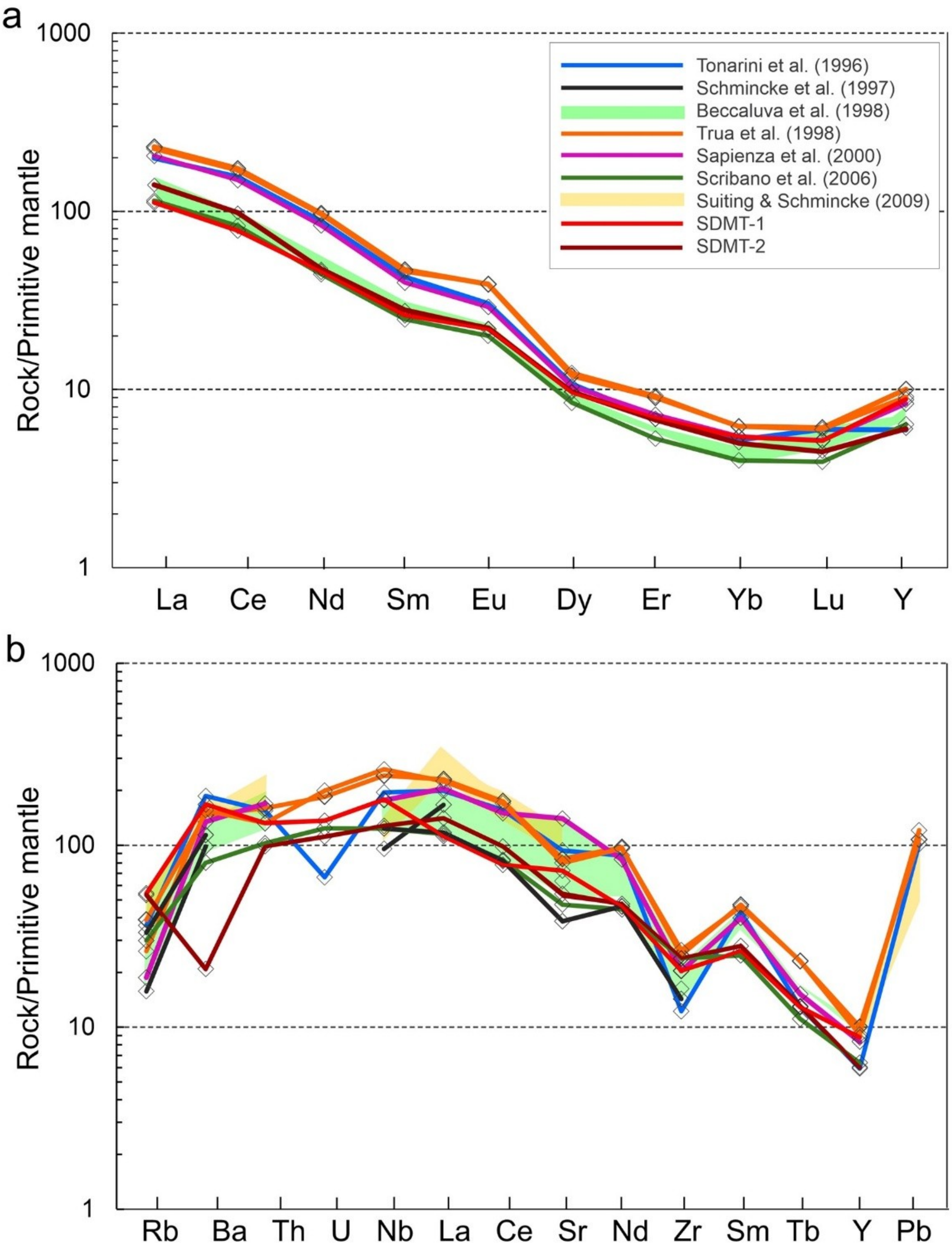

Fig. 7. Primordial Mantle normalized (McDonough et al., 1992) diagrams for REE (a) and the incompatible trace elements (b) of the Hyblean nephelinites available from literature (data from Tonarini et al., 1996; Schmincke et al., 1997; Beccaluva et al., 1998; Trua et al., 1998; Sapienza et al., 2000; Scribano et al., 2006; Suiting and Schmincke, 2009) and the SDMT-1 and SDMT-2 lava flow samples.

6. Discussion

The scientific community agrees that production of nephelinitic magmas needs of a lherzolitic-harzburgitic mantle modified by metasomatic agents of deep origin, which are represented by carbonatitic melts with low viscosity and enrichment in volatiles (e.g., Yaxley et al., 1991; Hauri et al., 1993; Ionov et al., 1995). Carbonatitic melts have carbonate composition with SiO_2 contents generally lower than 4 wt.% (Schmidt et al., 2024 and references therein). They are characterized by strong enrichments in Ba (BaO can exceed even 20 wt.%) with barite often found as primary mineral. Among the most abundant trace elements there are Sr (SrO even >5 wt.%), Co, Cr, Ni, V, Th, U and Nb (mainly contained in pyrochlore, with values exceeding 1200 ppm). They also exhibit significant REE contents, with high LREE/HREE ratios. Various hypotheses have been advanced regarding the genesis of carbonatites (Schmidt et al., 2024 and references therein). They could form by exsolution, at the liquid state, from a SiO_2-undersaturated silicate melt rich in alkalis and CO_2 (with concentrations of at least 5 wt.%). In this regard, experimental data have demonstrated that silicate and carbonatitic melts can coexist as distinct liquid phases at specific P-T conditions (Koster van Groos and Wyllie, 1963; Lee and Wyllie, 1998). Alternatively, they could be primary magmas generated by partial melting of a carbonated peridotite (CO_2 >5 wt.%; Lee et al., 2000). Other models suggest they could represent the residue of fractional crystallization of CO_2-rich phonolitic magmas (Veksler et al., 1998). In this case, the carbonatitic residual liquid could react with the surrounding rocks altering their chemistry. Finally, they could originate, together with basanitic melts, from amphibole harzburgites and spinel websterites permeated by aqueous fluids and CO_2. For the genesis of nephelinitic melts, the reaction between the metasomatic agent represented by carbonatites and the mantle would cause transformation of orthopyroxene into clinopyroxene, shifting the pristine lherzolitic-harzburgitic peridotite into a wehrlitic composition. This interaction is able to produce desilication of the basaltic magma produced by partial melting and enrichment in volatiles, alkalis and incompatible elements (mainly LREE, Sr, Nb and P), producing negative anomalies in Zr and Ti and fractionation of Nb/Ta and Zr/Hf (Beccaluva et al., 1992).

The metasomatic event able to generate compositional heterogeneities in the Hyblean mantle has been placed at depths between 70 and 90 km with pressures varying between 2.0 and 3.5 GPa (cf. Beccaluva et al., 1998). Lower depths are in fact incompatible with the presence of carbonates since their devolatilization would lead to formation of CO_2 and lime residue. Following these authors, low degrees (3-4%) of partial melting of this carbonated mantle gave rise to nephelinitic magmas which, due to decompression linked to transtensive tectonics, ascended rapidly throughout the crust without experiencing significant fractionation and contamination by the surrounding rocks. The high volatile content of the Hyblean nephelinitic magmas and their possible final interaction with deep aquifers could have been the cause for the violent diatreme explosions. The high trace element concentrations, mainly LILE and REE, the isotope ratios and the finding in some websteritic xenoliths of Ti-poor pargasite and Al-Cr-rich clinopyroxene are all features consistent with the hypothesis of mantle genesis of these nephelinites. In particular, the enrichment in incompatible elements could represent an important clue towards the contamination by deep metasomatic agents. Indeed, some Hyblean nephelinites have non-chondritic Zr/Hf and Nb/Ta ratios that are coherent with source contamination by a carbonatitic melts (Trua et al., 1998).

Some inconsistencies must be, however, highlighted within this framework. Interactions between mantle peridotite and carbonatitic magmas should occur at depths compatible with those of the garnet facies. Studies conducted on ultramafic xenoliths do not support, however, the role of such a deep mantle in the Hyblean Plateau. The abundance of Yb, Y and the low Zr/Y ratios (<10) found in nephelinites suggest superficial re-equilibration of magmas, which occurred in the spinel peridotite field (Bianchini et al., 1999). Furthermore, carbonatitic metasomatism should not lead to important variations in the HFSE content, while the Hyblean nephelinites show enrichments in some of these elements with respect to common alkali basalts (Fig. 7; cf. Tonarini et al., 1996; Trua et al., 1998; Beccaluva et al., 1998). This last feature is emphasized even at the scale of the same outcrop, being the nephelinitic sample of the San Demetrio lava flow (SDMT-1) enriched in U, Th, Nb, as well as in some LILE such as Ba and Sr with respect to the coexisting SDMT-2 alkali basalt (Fig. 7). Specifically, the Ba content of the San Demetrio is particularly high. The extreme variability of fluid-mobile elements such as Ba and Sr, among others, in the Hyblean nephelinites seems therefore to be linked to interaction processes with aqueous fluids rather than to partial melting of a carbonated mantle. All these features make unreasonable the production of nephelinitic magmas from a large mantle portion metasomatized by the same agent, as they should appear more homogeneous from both a chemical and mineralogical point of view. Indeed, preliminary evidence already available in literature (Scribano and Viccaro, 2013; 2014; Correale et al., 2019), along with the detailed observations and measurements by SEM-EDS/WDS on the Hyblean nephelinites conducted in this work, clearly put into evidence significant heterogeneities in terms of constituents and of the groundmass compositions (Figs. 5 and 6). These appear to be strongly related to contributions external to the juvenile magma in terms of xenocrysts and mineral/rock fragments (Fig. 4), and culminate with the odd coexistence at the scale of the same lava flow unit of both nephelinitic and alkali basaltic compositions as in the San Demetrio site (Fig. 2) or the presence of silica saturation in various portions of the glassy groundmass of tuff-breccia juvenile clasts and lava flows (Fig. 6).

Similar cases were recorded in various oceanic environments worldwide. As an example, the Sugar Loaf alkali basalt lava flow in Honolulu (Hawaii Islands) coexists with nephelinitic lenses with pegmatitic-like structure (Clague, 2014). These lenses have textural, chemical and isotopic characteristics very different from those of the host alkali basaltic magma. On a similar line of reasoning, Kent et al. (1999) suggested that the marked heterogeneity in K, Cl and other incompatible elements observed in many pillow-rim and fragmental glasses from the Loihi seamount could be the result of extensive assimilation of a seawater-derived, Cl-rich component, during magma storage and ascent. Clague et al. (1995) explained the comparable heterogeneity observed in submarine Kilauea lavas through the same processes, whereas Michael and Schilling (1989), Jambon et al. (1995) and Michael and Cornell (1998) proposed analogous processes for some volcanic rocks at mid-ocean ridges. These small-scale compositional heterogeneities observed worldwide, along with those making peculiar the Hyblean volcanic rocks, cannot be therefore considered as derived by deep metasomatic processes, but conversely through contamination experienced at shallow, crustal levels. Indeed, deep processes involving significant volumes of the mantle should be able to originate heterogeneous products through space and time, of course, but definitely more homogeneous at least at the scale of the same outcrop/flow unit.

In light of all the above-mentioned evidence, the Hyblean nephelinites could result from mingling/mixing in variable proportions between two significantly distinct terms: 1) a basaltic magma with tholeiitic or alkaline seriality; 2) SiO_2-poor components enriched in alkalis, sulphur and halogens (fluorine and chlorine), among these the widespread Mg-Al phyllosilicates, carbonates and sulphates observed under the electron microscope and largely common in all the Hyblean nephelinites, especially in diatremic facies. Considering the models proposed for the Hyblean lithospheric section, these exotic components in the magma can have two principal derivations. In the classic geological view, they could be ascribed to the Tortonian clayey and Messinian evaporitic levels (e.g., Carbone et al., 1984). However, if this could rather easily explain the Messinian to Quaternary volcanic activity, some problems arise for some of the first Upper Tortonian diatremes, being the evaporitic levels still not formed at that time. Recent works proposed, as an alternative, that a large part of the unexposed section of the Hyblean lithosphere could have a serpentinitic nature also enriched in deep-seated evaporite-like salts such as Ca-Mg sulfates, halite, carbonates and minor phosphates (Scribano et al., 2007; Ciliberto et al., 2009; Manuella et al., 2012; 2013; 2015). Since the serpentinization process requires pure H_2O, the involved seawater-derived serpentinizing fluid will undergo total desalinization. This means that about 10.5 kg of salts can be deposited for each cubic meter of serpentinized peridotite. Salts can then be deposited in pores, fractures and major tectonic discontinuities of the serpentinite wall rocks (Carbone et al., 2014). Consequently, hot aqueous fluids deriving from local dehydration of the serpentinite at the contact with the ascending basaltic magma can form highly mobile saline brines. The latter, at their supercritical state, allow the salt assimilation by slightly superheated basaltic magma a thermodynamically viable process.

Although the nature of these exotic fragments has not been fully clarified yet, they represent in any case relics of the shallow crustal section tapped by the rising magma, and their occurrence in the erupting system is consistent with low degrees of homogenization due to the short-term, shallow depth of interaction.

7. Conclusions and implications

Petrographic and analytical observations carried out by SEM-EDS/WDS on some nephelinites coming from tuff-breccia diatremic deposits and lava flows of the northern part of the Hyblean Plateau open new horizons to elucidate the processes at the origin of silica-undersaturated products characterizing this area. Heterogeneity observed at the outcrop scale (e.g., San Demetrio lava flow), extendable to the hand sample and to the thin section, is consistent with interaction processes occurred at crustal levels between basaltic magmas with tholeiitic or alkaline seriality and undersaturated components in SiO_2 but enriched in alkalis, sulphur and halogens. Assimilation of these fragments caused the en-route hybridization of basaltic magmas, modifying its pristine rheological and compositional character and producing desilication coupled with alkalis enrichment, i.e. the specific ingredients for the making of nephelinitic magmas.

One last consideration regards the volatile content of these magmas. Despite the nature of the shallow crustal section in the Hyblean area, the explosive behavior of the erupting magmas is evidence of interaction with water. In the classic view, magma intrusion/emplacement into wet clayey and evaporitic sediments and/or shallow water depth is an easy way to boost sediment dehydration and steam expansion, finally making maar-like eruptions (cf. Schmincke et al., 1997; Suiting and Schmincke, 2009; 2010; 2012). Conversely, Scribano et al. (2007) proposed that the genesis of the Hyblean diatremes could be connected to dehydration of an ultramafic basement pervasively hydrated for about 50 Ma (i.e., from the Upper Cretaceous to the Lower Miocene; cf. Longaretti et al., 1991) by the first basaltic magmas of the Miocene-Quaternary eruptive cycle. Serpentinized peridotites can store large quantities of water (from 250 to 400 kg/m^3; Carlson, 2001). Their dehydration, due to the interaction with the ascending basaltic magma, can lead to a violent expansion of pressurized steam and therefore to eruptions with a highly explosive character.

In this regard, the non-magmatic interval of fluid recharge would explain the limited temporal distribution of the Hyblean diatremes, which are exclusively Upper Miocenic in age (i.e., Tortonian and Messinian; e.g., Schmincke et al., 1997 and references therein).

The persistent association of nephelinitic magmas with diatremic eruptions supports the hypothesis of their derivation through interaction with a shallow crustal section constituted by clayey and evaporitic components. Indeed, the volcanic activity migrating northwards during the Quaternary should have affected progressively marginal portions of such layers, presumably less enriched by fluids. Result of this more limited fluid interaction is represented by the effusive emplacement of lava flows. Chemical heterogeneities characterizing the Hyblean ultramafic rocks, either as whole rocks or residual glasses in tuff-breccia juvenile clasts and lava flows, can be therefore due to non-complete homogenization of clayey and evaporitic components within the magma, to a non-uniform distribution of the brines produced by crustal dehydration and to the extremely variable depths and timescales of interaction.

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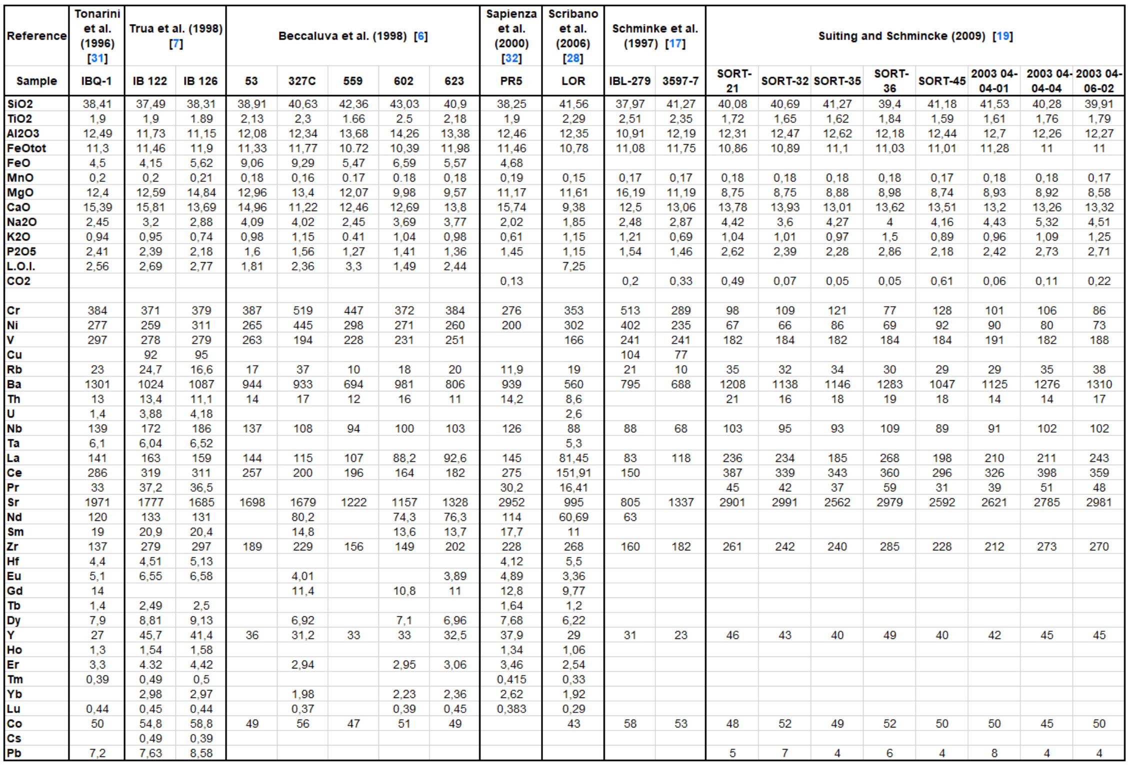
Supplementary table



Reference	**Tonarini et al. (1996) [31]**	**Trua et al. (1998) [7]**		**Beccaluva et al. (1998) [6]**					**Sapienza et al. (2000) [32]**	**Scribano et al. (2006) [28]**	**Schminke et al. (1997) [17]**		**Suiting and Schmincke (2009) [19]**							
Sample	**IBQ-1**	**IB 122**	**IB 126**	**53**	**327C**	**559**	**602**	**623**	**PR5**	**LOR**	**IBL-279**	**3597-7**	**SORT-21**	**SORT-32**	**SORT-35**	**SORT-36**	**SORT-45**	**2003 04-04-01**	**2003 04-04-04**	**2003 04-06-02**
SiO2	38,41	37,49	38,31	38,91	40,63	42,36	43,03	40,9	38,25	41,56	37,97	41,27	40,08	40,69	41,27	39,4	41,18	41,53	40,28	39,91
TiO2	1,9	1,9	1.89	2,13	2,3	1.66	2.5	2,18	1,9	2,29	2,51	2,35	1,72	1,65	1,62	1,84	1,59	1,61	1,76	1,79
Al2O3	12,49	11,73	11,15	12,08	12,34	13,68	14,26	13,38	12,46	12,35	10,91	12,19	12,31	12,47	12,62	12,18	12,44	12,7	12,26	12,27
FeOtot	11,3	11,46	11,9	11,33	11,77	10.72	10,39	11,98	11,46	10,78	11,08	11,75	10,86	10,89	11,1	11,03	11,01	11,28	11	11
FeO	4,5	4,15	5,62	9,06	9,29	5,47	6,59	5,57	4,68											
MnO	0,2	0,2	0,21	0,18	0,16	0.17	0.18	0,18	0,19	0,15	0,17	0,17	0,18	0,18	0,18	0,18	0,17	0,18	0,18	0,17
MgO	12,4	12,59	14,84	12,96	13,4	12,07	9,98	9,57	11,17	11,61	16,19	11,19	8,75	8,75	8,88	8,98	8,74	8,93	8,92	8,58
CaO	15,39	15,81	13,69	14,96	11,22	12,46	12,69	13,8	15,74	9,38	12,5	13,06	13,78	13,93	13,01	13,62	13,51	13,2	13,26	13,32
Na2O	2,45	3,2	2,88	4,09	4,02	2,45	3,69	3,77	2,02	1,85	2,48	2,87	4,42	3,6	4,27	4	4,16	4,43	5,32	4,51
K2O	0,94	0,95	0,74	0,98	1,15	0.41	1,04	0,98	0,61	1,15	1,21	0,69	1,04	1,01	0,97	1,5	0,89	0,96	1,09	1,25
P2O5	2,41	2,39	2,18	1,6	1,56	1,27	1,41	1,36	1,45	1,15	1,54	1,46	2,62	2,39	2,28	2,86	2,18	2,42	2,73	2,71
L.O.I.	2,56	2,69	2,77	1,81	2,36	3,3	1,49	2,44		7,25										
CO2									0,13		0,2	0,33	0,49	0,07	0,05	0,05	0,61	0,06	0,11	0,22
Cr	384	371	379	387	519	447	372	384	276	353	513	289	98	109	121	77	128	101	106	86
Ni	277	259	311	265	445	298	271	260	200	302	402	235	67	66	86	69	92	90	80	73
V	297	278	279	263	194	228	231	251		166	241	241	182	184	182	184	184	191	182	188
Cu		92	95								104	77								
Rb	23	24,7	16,6	17	37	10	18	20	11,9	19	21	10	35	32	34	30	29	29	35	38
Ba	1301	1024	1087	944	933	694	981	806	939	560	795	688	1208	1138	1146	1283	1047	1125	1276	1310
Th	13	13,4	11,1	14	17	12	16	11	14,2	8,6			21	16	18	19	18	14	14	17
U	1,4	3,88	4,18							2,6										
Nb	139	172	186	137	108	94	100	103	126	88	88	68	103	95	93	109	89	91	102	102
Ta	6,1	6,04	6,52							5,3										
La	141	163	159	144	115	107	88,2	92,6	145	81,45	83	118	236	234	185	268	198	210	211	243
Ce	286	319	311	257	200	196	164	182	275	151,91	150		387	339	343	360	296	326	398	359
Pr	33	37,2	36,5						30,2	16,41			45	42	37	59	31	39	51	48
Sr	1971	1777	1685	1698	1679	1222	1157	1328	2952	995	805	1337	2901	2991	2562	2979	2592	2621	2785	2981
Nd	120	133	131		80,2		74,3	76,3	114	60,69	63									
Sm	19	20,9	20,4		14,8		13,6	13,7	17,7	11										
Zr	137	279	297	189	229	156	149	202	228	268	160	182	261	242	240	285	228	212	273	270
Hf	4,4	4,51	5,13						4,12	5,5										
Eu	5,1	6,55	6,58		4,01			3,89	4,89	3,36										
Gd	14				11,4		10,8	11	12,8	9,77										
Tb	1,4	2,49	2,5						1,64	1,2										
Dy	7,9	8,81	9,13		6,92		7,1	6,96	7,68	6,22										
Y	27	45,7	41,4	36	31,2	33	33	32,5	37,9	29	31	23	46	43	40	49	40	42	45	45
Ho	1,3	1,54	1,58						1,34	1,06										
Er	3,3	4.32	4,42		2,94		2,95	3,06	3,46	2,54										
Tm	0,39	0,49	0,5						0,415	0,33										
Yb		2,98	2,97		1,98		2,23	2,36	2,62	1,92										
Lu	0,44	0,45	0,44		0,37		0,39	0,45	0,383	0,29										
Co	50	54,8	58,8	49	56	47	51	49		43	58	53	48	52	49	52	50	50	45	50
Cs		0,49	0,39																	
Pb	7,2	7,63	8,58										5	7	4	6	4	8	4	4

Table S1. Major and trace element compositions of the Hyblean nephelinites available in the scientific literature.