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Metasomatism in the lithospheric mantle and its relationships to magmatism in the Veneto Volcanic Province, Italy

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ABSTRACT. — A detailed textural and geochemical study was carried out on a suite of anhydrous, spinel-bearing peridotitic xenoliths hosted in alkaline basic lavas from the Veneto Volcanic Province (VVP). Lherzolites and harzburgites show metasomatic textures superimposed on primary, protogranular textures. On the basis of textural relationships, relative modal percentages and grain size between primary and secondary parageneses, three metasomatic textures were distinguished: Type A characterized by reaction areas around orthopyroxene and spinel, generating olivine, clinopyroxene and spinel secondary crystals; Type B by the abundant presence of glassy patches closely intergrown with olivine, clinopyroxene, spinel and feldspar; and Type C by reaction areas around clinopyroxene, giving rise to spongy or completely recrystallized clinopyroxenes.

Unmetasomatized lherzolites display flat REE patterns at about $2-3 \times$ chondrite, while metasomatized lherzolites and harzburgites show a classic spoon-shaped light (L) REE-enriched patterns. Major and incompatible element analyses of primary and secondary minerals (including glass), together with textural features and whole-rock data, allow the definition of at least two distinct events which affected the VVP lithospheric mantle. Geochemical features (including trace elements) of

primary clinopyroxenes and spinels, as well as whole-rock geochemistry, indicate that the initial process was of partial melting, followed by enrichment due to infiltration of a strong undersaturated Na-alkali silicate melt as suggested by secondary clinopyroxenes and coexisting glass. The measured Nd and Sr isotopic compositions of whole-rock and separated clinopyroxenes plot in a distinctive array originating from isotopically depleted compositions in the ⁸⁷Sr/⁸⁶Sr vs 143 Nd/ 144 Nd diagram (87 Sr/ 86 Sr = 0.702214-0.702543; 143 Nd/ 144 Nd = 0.51325-0.51329), close to the DM component, and trending towards the enriched low Nd - high Sr components (HIMU and EMI) recorded by the metasomatized peridotites $(^{87}Sr/^{86}Sr = 0.702951 - 0.70365, ^{143}Nd/^{144}Nd =$ 0.51297-0.51299). Late Cretaceous lamprophyric dykes, cutting the South Alpine Basement at Calceranica (Trento) and well reproducing the geochemical features of the inferred metasomatic melt, plot at the end of the enrichment trend of the VVP peridotites. These isotopic features, coupled with the other geochemical parameters, strongly suggest that a metasomatic agent interacted with the primary mantle assemblage, forming glass and feldspar (plus recrystallized olivine, clinopyroxene and spinel) as reaction products.

In the same diagram, VVP basic lavas lie within a field encompassing both the metasomatized xenoliths and the inferred metasomatic agent. On the basis of their incompatible element contents, the

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presence of amphibole and phlogopite in the VVP magma sources could be invoked. The incompatible element budget related to these minerals was compared with the metasomatic contribution in the mantle xenoliths, calculating the elemental distribution between primary and secondary phases. The strict analogy between incompatible element contents in VVP magma sources and VVP mantle xenoliths, together with their similar isotopic ratios, strongly suggest that the metasomatic agent responsible for the enrichment of the VVP magma sources was very similar to that affecting the VVP xenoliths. It is conceivable that a continuum metasomatic enrichment, starting at least from Late Cretaceous, progressively affected the upper portion of the VVP lithospheric mantle.

RIASSUNTO. — Una suite di noduli peridotitici di mantello anidro a spinello (lherzoliti ed harzburgiti) inclusi in vulcaniti basiche alcaline della Veneto Volcanic Province (VVP) è stata l'oggetto di un dettagliato studio petrografico e geochimico. Tre tipi di tessiture metasomatiche, impostate su tessiture primarie di tipo protogranulare, sono state distinte sulla base delle differenze riscontrate tra relazioni tessiturali, percentuali modali, dimensioni e habitus dei minerali costituenti la paragenesi primaria e quella secondaria: Tipo A, caratterizzato da reazioni attorno all'ortopirosseno ed allo spinello che producono cristalli secondari di olivina, clinopirosseno e spinelli; Tipo B, caratterizzato da cristalli di olivina, clinopirosseno, spinello e feldspato immersi in una matrice vetrosa; Tipo C, dove le reazioni, a spese del clinopirosseno, danno luogo a clinopirosseni spugnosi o completamente ricristallizzati.

Lherzoliti non metasomatizzate presentano un pattern piatto delle Terre Rare a circa 2-3 volte condrite, mentre lherzoliti e harzburgiti metasomatizzate mostrano un tipico pattern di arricchimento in terre Rare Leggere.

Gli elementi maggiori e gli elementi in traccia incompatibili delle fasi mineralogiche primarie e secondarie e del vetro, insieme a considerazioni di tipo tessiturale e ai dati di roccia totale, hanno permesso la ricostruzione di almeno due eventi che hanno influenzato l'evoluzione petrologica del mantello litosferico della VVP. Un primo evento di fusione parziale, suggerito dalle caratteristiche geochimiche (inlcusi gli elementi in traccia) dei clinopirosseni e spinelli primari e dalle analisi di arricchimento per interazione della matrice peridotitica con un fuso Na-alcali silicatico fortemente sottosaturo, come indicato dai clinopirosseni secondari e dal vetro coesistente. Le

composizioni isotopiche di Sr e Nd degli xenoliti, misurate sia su roccia totale che su clinopirosseni separati, presentano un caratteristico andamento dalle lherzoliti non metasomatizzate (87Sr/86Sr =0.702214-0.702543; ¹⁴³Nd/¹⁴⁴Nd = 0.51325-0.51329) isotopicamente impoverite (DM) alle peridotiti metasomatizzate (87Sr/86Sr = 0.702951-0.70365; ¹⁴³Nd/¹⁴⁴Nd = 0.51297-0.51299) che mostrano un arricchimento verso le componenti a basso Nd-alto Sr tipo HIMU e EMI. Nel diagramma ⁸⁷Sr/⁸⁶Sr vs ¹⁴³Nd/¹⁴⁴Nd una serie di dicchi lamprofirici del Cretaceo superiore, che tagliano il basamento delle Alpi Meridionali nei dintorni di Calceranica (Trento) e che presentano caratteristiche geochimiche molto simili a quelle ipotizzate per il fuso responsabile del metasomatismo, ricadono all'estremità del trend di arricchimento mostrato dalle peridotiti della VVP. Le caratteristiche isotopiche ed i parametri geochimici indicano chiaramente un modello di reazione, dove un agente metasomatizzante interagisce con la paragenesi primaria di mantello formando vetro, feldspato (più olivina, clinopirosseno e spinello ricristallizati) come prodotti di reazione.

Nello stesso diagramma le lave basiche della VVP delineano un campo che comprende sia gli xenoliti metasomatizzati che l'agente metasomatico. Gli arricchimenti in elementi incompatibili di queste lave sono coerenti con un modello petrologico che prevede la presenza nelle rispettive sorgenti di mantello di anfibolo e flogopite. La somiglianza della distribuzione degli elementi in traccia incompatibili in queste due fasi con quella relativa alle fasi metasomatiche analizzate nei noduli peridotitici, unitamente ai rapporti isotopici molto simili di lave e xenoliti arricchiti, suggeriscono una forte analogia tra l'arricchimento delle sorgenti delle lave ed il metasomatismo osservato negli xenoliti. E' probabile che i processi di arricchimento, iniziati almeno nel Cretaceo Superiore, abbiano continuato ad agire arricchendo progressivamente porzioni via via più superficiali del mantello litosferico della VVP.

KEY WORDS: Veneto Volcanic Province, basic alkaline magmatism, metasomatism.

INTRODUCTION

In the southern-central sector of the South Alpine domain basaltic rocks are widespread. These Upper Palaeocene to Upper Oligocene volcanic rocks vary in composition from nephelinites to tholeiites, and are distributed from Rovereto in the west to the Marostican Hills in the east over an area of 1500 km², thus representing a rather wide mantle section. The more silica-deficient types contain a wide variety of deep-seated xenoliths. Although various petrological works have been published on these xenoliths (e.g. Morten, 1987; Siena and Coltorti, 1989; Siena and Coltorti, 1993; Beccaluva et al., 2001a), a detailed study integrating the geochemistry of the xenoliths and that of the mafic alkaline volcanic rocks was not undertaken. The present paper allows a comparison between metasomatic style, basaltic source enrichments and partial melting processes in the subcontinental lithospheric mantle of the South Alpine domain.

Metasomatic processes are clearly recorded in many xenoliths, as evidenced by the presence of several metasomatic textures. This study uses xenoliths from the key localities of Pilcante and Passo Buole in the westernmost sector (Lagarina Valley, Southern Trentino), San Giovanni Ilarione, Mt. Madarosa and Mt. Guarda in the central sector (Alpone-Chiampo Valley), and Mt. di Gloso in the easternmost sector (Marostican Hills) (fig.1). Outcrop locations, together with a detailed petrographic description of the peridotites, can be found in Morten (1987) and Siena and Coltorti (1989).

In this paper, relationships between the metasomatic textures and chemical characteristics of primary and secondary phases (including glass) of the VVP mantle xenoliths are evaluated, in order to investigate the links between metasomatism and magmatism in the complex geochemical evolution of the Veneto lithospheric mantle. This provides insight into issues such as infiltration and metasomatic modifications of the lithospheric mantle by melts, as well as basic constraints on mineralogical and geochemical compositions of the VVP mantle sources.

GEOLOGICAL SETTING

The Veneto Volcanic Province (VVP) is situated in the southern-central sector of the

Southern Alps. Its magmatic products are mainly represented in the Lessini Mts., an area delimited by the Valsugana Line (to the north), Brenta River (to the east), Po Plain (to the south) and Adige River (to the west) (fig.1).

In this area lithospheric thinning is limited, with the Moho at a depth of about 28 km and deepening toward the surrounding areas (Morelli, 1951; Slejko *et al.*, 1987). Thinning predates or is coeval with volcanic episodes (Barbieri *et al.*, 1982). The small volume of erupted volcanics, together with the high percentage of undifferentiated magmas spanning a wide compositional spectrum, coherently resembles the volcanological characteristics of a low-volcanicity rift (Barberi *et al.*, 1982). Accordingly, this magmatism can be considered a passive rift, most probably as a consequence of the Africa-Europe collision.

On the basis of different tectono-magmatic features the VVP can be subdivided into three major sectors: Western Lessini-Southern Trentino, Eastern Lessini, and the Marostican Hills.

The Western Lessini-Southern Trentino sector extends from Mt. Baldo to the west and the Castelvero fault to the east. Volcanism, mainly submarine, dating from Upper Palaeocene to Middle Eocene, is principally characterized by hyaloclastites, tuffs and pillow lavas. Massive lava flows are volumetrically subordinate. Nephelinites, basanites and alkali basalts are the most common magmas, though transitional basalts and rare tholeiites are also present.

The Eastern Lessini sector is delimited by the Castelvero fault to the west and the Schio-Vicenza line to the east. The beginning of volcanism was coeval with that of the Western sector but it extends to the Upper Oligocene. Volcanism was interrupted during the Upper Eocene to Lower Oligocene, while the main activity phase was in the Middle Eocene. Volcanic products in this area are characterized by tuffs and lava flows, with several spectacular column-jointing eruptive necks, such as those of Vestena, San Giovanni Ilarione, Mt. Bolca, Montecchio di Crosara,



Fig. 1 - Geological sketch map of Veneto Volcanic Province (VVP). The main xenolith locations are also indicated.

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Mt. Madarosa, etc. With a thickness up to 400 metres, they constitute the most representative volcanic sequence of the VVP. Basanites, alkali basalts, transitional basalts and tholeiites occur in this area, with alkaline products slightly more abundant.

The Marostican sector is delimited westward by the Schio-Vicenza line, and eastward by the Brenta River. Volcanism mainly developed during the Oligocene, with few, uncertainly dated episodes during the Palaeocene (Laverda River) and Miocene (Sarcedo). Effusive activity predominated over the explosive types, becoming subaerial after the Middle Oligocene and being related to various necks (Mt. di Gloso, Contrà di Pascolara). Transitional and tholeiitic basalts are more abundant with respect to basanites and alkali basalts.

To summarize; in the western sector (Western Lessini-Southern Trentino) volcanic activity began in the Upper Palaeocene and ended in the Middle Eocene; in the central sector (Eastern Lessini) volcanism dates from the Upper Palaeocene to Upper Oligocene with prolonged quiescence between the Middle Eocene and Middle Oligocene; and in the eastern sector (Marostican Hills) activity mainly developed in the Oligocene, most probably ending in the Upper Oligocene. Nephelinites and basanites decrease, while transitional basalts and tholeiites increase eastward. A similar trend can be observed for effusive, subaerial activity which is more developed eastward. Hence there is evidence for an eastward temporal shift of magmatic activity, related to a compositional change of erupted lavas (Barbieri et al., 1982; De Vecchi and Sedea, 1995; Beccaluva et al., 2000).

Petrography

Xenoliths range from 5 to 20 cm in diameter and exhibit sharp contacts with the host basalts. Most are fresh, except those of Passo Buole where abundant calcite veins cross-cut the xenoliths. They comprise anhydrous peridotites, varying from coarse- to mediumgrained protogranular (Mercier and Nicolas, 1975) four-phase spinel lherzolites, and minor harzburgites. Protogranular textures are represented by well-equilibrated (unzoned) assemblages of large olivine (often kinked) and orthopyroxene crystals (up to 2 mm), with curviplanar boundaries and interstitial, smallersized clinopyroxenes and spinels (up to 1 mm). Exsolution lamellae are found in both pyroxenes. Most of the xenoliths have been affected to varying degrees by metasomatic infiltrations, with reaction textures developed to greater or lesser degrees (fig. 2).

Three types of textures were identified on the basis of primary and secondary mineral textural relationships, grain size, shapes and relative modal abundance (particularly for glass).

Type A: orthopyroxene and spinel represent the main reacting phases, followed in some cases by clinopyroxene (figs. 2a,b). Orthopyroxene shows a reaction rim composed of secondary clinopyroxene and olivine, while spinel is zoned with a brown core and dark rim.

Type B: glass is the predominant phase. It is dark to pale brown, and may be associated with quenched feldspars or with a secondary assemblage made up of olivine, feldspar, clinopyroxene and spinel in decreasing order of abundance (fig. 2c).

Type C: cloudy, spongy clinopyroxene predominates. The re-crystallized portion may cover the whole crystal or, more often, only the marginal portions (fig. 2d).

At this point some abbreviations may be introduced. All primary minerals are identified by 1 (ol1, cpx1, sp1)(fig. 2a) but for orthopyroxene, which is never found as a secondary mineral. Secondary olivine is named ol2 (figs. 2b,c,d). Secondary clinopyroxenes growing in the re-crystallized marginal portions of orthopyroxene (Type A texture) and clinopyroxene (Type C texture) are named cpx2-O and cpx2-C respectively, while the inner portion of spongy clinopyroxene is named cpxSpo (figs. 2a,d). Dark, vermicular secondary spinel or dark rims surrounding large primary crystals are named S1-sp, while dark, subhedral to euhedral crystals are named



Fig. 2 – Microphotographs of the three main textural types. *a*) and *b*) Type A texture: *ol*1, *opx*, *cpx*1 and *sp*1 indicate primary minerals; *ol*2, secondary olivine; S1-sp, S1-type secondary spinel; *cpx*2-O, secondary clinopyroxene after orthopyroxene, *R*-*fld* and *I*-*fld*, rim feldspar around spinel and intergranular feldspar respectively.



Fig. 2 – c) Type B texture: S2-sp, S2-type secondary spinel; gl, glass; other abbreviations as in figs. a and b. d) Type C texture: cpxSpo, spongy clinopyroxene; cpx2-C, secondary clinopyroxene after clinopyroxene; other abbreviations as in figs. a and b.

S2-sp (figs. 2a,b,c). Feldspars crystallizing in fine aggregates within the dark spinel rim are named rim feldspar (*R-fld*), while crystals intertwined with glass are named intergranular feldspar (*I-fld*)(figs. 2b,c).

A general equation, summarising the above mentioned reaction textures, may be written as follows:

> ol1+opx+cpx1+sp1+melt=ol2+cpx2(cpx2-O,cpx2-C)+sp2(S1-sp,S2-sp)++fld(R-fld,I-fld)+glass

ANALYTICAL METHODS

REE, U and Y concentrations were analysed by Inductively Coupled Mass Spectrometry (ICP-MS) using a VG Plasma Quad2 Plus at the Earth Science Department, University of Ferrara (Italy). Precision and accuracy were estimated < 10% for all the elements well above the detection limit. The international standard JP-1 (peridotite at $0.1 \times$ chondritic REE) was regularly spaced out every four samples, showing for REE a precision within 20% and an average error of 15% with respect to the ICP-MS analyses carried out by Makishima and Nakamura (1997) on the same reference material. Using the same analytical procedure, an average error of 7% was obtained for the international standards UB-N (serpentine at $1 \times$ chondritic REE) and J-Gb1 (gabbro at $10 \times$ chondritic REE) with respect to the recommended values (Govindaraju, 1989).

Major element analyses (minerals and glasses) were carried out at the C.N.R- Centro di Studio per la Geodinamica Alpina, Padua (Italy), by a Cameca-CAMEBAX electron microprobe. The acceleration voltage was 15kV, with a beam current of 15nA and counting time of 20s for each element in minerals, whereas in glasses Na and K counting times were reduced to 10s to minimize alkali loss. Natural and synthetic minerals were used as standards, and the PAP data reduction program was used for matrix corrections.

Trace element contents of minerals and

glasses from highly representative samples were analysed by Secondary Ion Mass Spectrometry (SIMS) with a Cameca IMS 4f instrument at the C.N.R.- Centro Studi per la Cristallografia e Cristallochimica (C.S.C.C.), Pavia (Italy). REE, Y, Zr and Ti were carried out in clinopyroxenes, while the same elements plus Rb, Sr and Ba were analysed in feldspars and glasses. Reference standards, analytical procedures, accuracy and precision of the method are reported in Bottazzi *et al.* (1994).

Sr and Nd isotopic analyses were obtained at the Istituto di Geocronologia e Geochimica Isotopica, University of Pisa (Italy). Samples were first washed with ultrapure water, then leached with 6M HCl for 4 hours under a hot plate. Samples were repeatedly rinsed with double distilled H₂O, ultrasonically washed, and then dissolved with HF-HNO₃ mixtures. Sr and Nd were extracted by conventional cationexchange chromatographic technique, and the isotope ratios were measured in dynamic mode on a Finnigan MAT262 multicollector thermal ionization mass spectrometer (TIMS).

WHOLE-ROCK CHEMISTRY

Bulk compositions and modal abundances for VVP xenoliths are consistent with progressive depletion of the rocks by partial melting (Beccaluva et al., 2001a). The decrease in modal clinopyroxene is accompanied increasingly by depleted higher MgO/(MgO+FeO)*100 (mgv) whole-rock values (fig. 3a). Two samples (Fe-lherz), with cpx modal percentages (20-24%) similar to those theoretically assigned to primitive lherzolite, are unusually enriched in FeO (11.52-11.31 wt%), departing from the main trend. Peridotites from Passo Buole have very high CaO (and low Al₂O₃) contents, reflecting the strong alteration processes affecting these xenoliths.

Highly incompatible elements (e.g. Sr and Zr), as well as moderately incompatible elements (e.g. Y and heavy REE (HREE) show a weak negative correlation with mgv for most



Fig. 3 – Modal clinoproxenes *a*) and Ni contents *b*) vs whole-rock mgv (mol MgO/(MgO+FeO)*100) in VVP peridotites. Symbols: squares, Pilcante; triangles, Passo Buole; circles, M. Madarosa; diamonds, San Giovanni Ilarione. Filled and open symbols represent herzolites and harburgites respectively, while crosses indicate the two Fe-lherzolites.

of the VVP xenoliths. Ni is positively correlated with mgv, consistent with its compatible character during melt-peridotite equilibrium with the Fe-lherz plotting at the fertile end of the trend (fig. 3b). Chondritenormalized REE (plus Ti and Zr) distribution patterns of protogranular lherzolites are flat pattern at about 2-3 × chondrite, whereas lherzolites with metasomatic textures show classic spoon-shaped patterns (Beccaluva *et al.*, 2001a). Metasomatized harzburgites, in contrast with the normally refractory character of these rocks, have total REE contents comparable to those of lherzolites (Beccaluva *et al.*, 2001a).

MAJOR AND TRACE ELEMENT MINERAL CHEMISTRY

Major and trace element data for minerals and glasses from VVP mantle xenoliths has been provided by Beccaluva *et al.* (2001a). However, in order to better understand the fundamental processes of melting and metasomatism that shaped the lithospheric mantle beneath the VVP region, an additional brief description of the main geochemical features of the constituent phases in relation to the different textural types will be given here.

Olivine: primary olivines (*ol*1) in both unmetasomatized and metasomatized



Fig. 4 – crv (Cr/(Cr+A1)*100) vs mgv (Mg/(Mg+Fe)*100) diagrams of primary (*sp*1; filled symbols) and secondary (S1-*sp*, S2-*sp*; open symbols) spinels from VVP mantle xenoliths. Symbols: circles, lherzolites; squares, harzburgites.

lherzolites show a slightly lower Fo content than in harzburgites. As stated by Beccaluva *et al.* (2001a), irrespective of lithologies, secondary olivines are characterized by higher CaO contents and tend to have higher FeO with respect to *ol*1, suggesting that metasomatic processes (related to melt invasion) lowered the Fo content of olivine.

Orthopyroxenes in harzburgites have a higher mgv=Mg/(Mg+Fe) (90.93-91.95) than those in lherzolites (88.63-92.02). Orthopyroxenes in harzburgites are enriched in Cr₂O₃ and depleted in Al₂O₃ with respect to those in lherzolites.

Spinels show a wide compositional range. In the mgv vs crv (Cr/(Cr+Al)) diagram they depict an almost continuous trend from sp1 to S2-sp (fig. 4). Primary spinels (sp1) are usually zoned, with the core characterized by higher mgv and lower crv than the rim. Sp1 in lherzolites tend to have higher mgv (66.57-84.97) and lower crv contents (8.28-23.89) than those in harzburgites (mgv, 69.58-78.74; crv, 25.89-38.25)(fig. 4), as expected by partial melting processes.

SI type spinels: these spinels are typical of reaction areas, and represent intermediate compositions between *sp*1 and *S*2-*sp* type spinels. They display a wide compositional range in terms of both mgv (61.04-77.89) and crv (23.08-55.17).

S2 type spinels: these spinels represent the last product (within spinels) of metasomatic reaction, and are more abundant in Type B texture. Accordingly, they present the most restricted range of mgv and crv, together with the lowest mgv (51.05-59.40) and highest crv (60.20-70.86) (fig. 4).

Clinopyroxene: mgv of primary clinopyroxenes (cpx1) ranges between 86.65 and 94.42, with those from harzburgites being restricted to the higher values (92.40-94.42). Cpx1 in lherzolites have higher Al₂O₃ and Na₂O and contents than in harzburgites,



Fig. 5 $-Al_2O_3$ contents of *cpxl vs* crv (Cr/(Cr+Al)*100) of coexisting *spl*. Curve is after Brown *et al.* (1980) for Massif Central peridotite xenoliths. Symbols: filled circles, unmetasomatized lherzolites; open circles, metasomatized lherzolites; open squares, harzburgites; crosses, Fe-lherzolites.

consistent with principal control by partial melting. The Al₂O₃ content in cpx1 correlates with crv of the coexisting sp1 and decreases (more rapidly than Al_2O_3 in the coexisting opx) with increasing crv of sp1 (fig. 5). All these data are consistent with the experimental partial melting results where clinopyroxene is consumed before other phases (Mysen and Kushiro, 1977). Noticeably, cpx1 in three metasomatized lherzolites (SG12, MA7 and MA15) are anomalously enriched in Al, deviating conspicuously from the variation pattern of fig. 5, while cpx1 and sp1 of Fe-lherz follow the partial-melting trend, but present higher refractory degrees than expected from whole-rock geochemistry (fig. 5).

Both secondary clinopyroxenes (cpx2-C and cpx2-O) are depleted in Al₂O₃ (0.37-4.59wt%) and Na₂O (0.48-0.85wt%) and, on the whole, present lower mg values (84.34-92.94) with respect to primary clinopyroxene (fig. 6). Cpx2-C is, however, remarkably enriched in TiO₂ (0.29-1.87wt%) and FeO (2.18-4.66wt%) and depleted in SiO₂ (50.16-53.86wt%) with respect to cpx2-O (TiO₂, 0.05-0.36wt%; FeO, 2.52-3.23wt%; SiO₂, 53.20-55.90wt%)(fig. 6). On the other hand, cpx2-O presents a more restricted range of mgv (91.17-92.90) with respect to cpx2-C (84.34-92.94).

Spongy clinopyroxenes (cpxSpo) are characterized by a wide geochemical variation (SiO₂, 49.62-55.27wt%; Al₂O₃, 0.67-8.53wt%; Na₂O, 0.32-2.12wt%; TiO₂, 0.09-0.52wt%), spanning the whole compositional range from primary to secondary clinopyroxenes. The inner portions of the crystals, less affected by reaction, can have compositions similar to those of primary clinopyroxene, whereas the outer portions (almost completely reacted) may lie within the compositional range of secondary crystals (fig. 6).

Primary clinopyroxenes in lherzolites and harzburgites have flat MREE (Sm-Dy) to HREE (Er-Yb) patterns at about 10 \times (comparable to fertile mantle clinopyroxenes) and 3 \times chondrite respectively and the LREE (La-Nd) varying from depleted to enriched. The clinopyroxenes of this group display systematically negative Ti and Zr negative anomalies with Ti anomalies being more pronounced in harzburgites.

Spongy clinopyroxenes have no distinctive trace element signature, ranging in composition from characteristic *cpx*1 (mainly crystal cores) to typically LREE-enriched secondary clinopyroxenes (crystal rims) of *cpx*2-C types.

The secondary clinopyroxenes have REE profiles steadily enriched from Yb to La, with high LREE concentrations and deep Ti and Zr negative anomalies. These patterns are similar to those of clinopyroxenes from various mantle occurrences interpreted as reflecting interactions with metasomatic melts (Coltorti *et al.*, 1999 and references within).

Feldspars range between labradorites and Na-sanidine compositions (K₂O, 0.47-7.64wt%) (fig. 7). On the whole, feldspars in VVP xenoliths cover the same compositional range as Baikal and Yitong feldspars (Ionov et al., 1995; Xu et al., 1996) and, noteworthy, are quite distinct from feldspars in host lavas (fig. 7a). They show a noticeable chemical variation in relation to both lithology and textural position. Feldspars in harzburgites are generally more alkali-rich (Na₂O, 5.89-7.50wt%; K₂O, 1.23-7.64wt%) with respect to feldspars in lherzolites which, on the other hand, are richer in anorthite (An, 2.93-54.02)(fig. 7b). In the same reaction areas, feldspars in spinel rims (R-fld) are usually enriched in anorthite (An_{2,93-54,02}Ab_{43,42-} _{63,54}Or_{2,57-40,4}) while interstitial feldspars (*I-fld*) (An_{2.86-46,73}Ab_{48,27-65,35}Or_{3.09-43,93}) are enriched in orthoclase (fig. 7c).

Taking into account the small crystal size and textural position, only one intergranular feldspar (*I-fld*) was analysed for trace element composition. Its pattern is similar to those of associated glasses with lower amounts of all incompatible elements except Ba, Sr and Eu, which present positive anomalies (antithetic to those observed in glasses), supporting equilibrium conditions with glasses (Beccaluva *et al.*, 2001a).

Glasses have high silica (55.90-65.43wt%), Al₂O₃ (14.29-22.44wt%) and alkali (Na₂O,



Fig. 6 – Major element patterns of spongy (cpxSpo) and secondary clinopyroxenes (cpx2-C, cpx2-O) normalized to primary clinopyroxene (cpx1) from VVP mantle xenoliths.



4.07-9.67wt%; K_2O , 3.58- 8.28wt%) contents, their composition being comparable to those of mantle glasses worldwide (Coltorti *et al.*, 2000a). In the chondrite-normalized diagram they exhibit significant but variable enrichments in LREE (La/Sm=7.96-19.29) and incompatible elements, together with a remarkable Sr, Ba and Eu depletion, which was considered by Beccaluva *et al.* (2001a) to be related to glass/feldspar equilibrium conditions.

FELDSPAR AND GLASS FORMATION

Several hypotheses have recently been put forward for the origin of mantle glasses. These range from: products of i) host magma infiltration (i.e. Garcia and Presti, 1987); ii) decompression melting of hydrous phases during rapid ascent (Frey and Green 1974; Francis, 1976; Gamble and Kyle 1987); iii) in situ melt products derived from prexisting metasomatic phases, such as amphibole and phlogopite (+clinopyroxene) (Yaxley and Kamenetsky, 1999; Chazot et al., 1996a; Chazot *et al.*, 1996b; Yaxley *et al.*, 1997); *iv*) small fraction partial melts generated under anhydrous or C-H-O fluid-saturated conditions (Draper and Green, 1997); or else v) reaction products between pristine mantle assemblages and infiltrating metasomatizing agents which, at the same time, may induce melting by lowering the solidus (Siena et al., 1991; Siena and Coltorti, 1993; Hauri et al., 1993; Schiano and Clocchiatti, 1994; Neumann and Wulff-Pedersen 1997; Coltorti et al., 1999).

Coltorti *et al.* (2000a) report evidence clearly favouring the last hypothesis, with mantle glasses representing the most useful tool for identifying the nature of the metasomatizing agent. Accordingly, several diagrams aimed at discriminating between various groups of metasomatic melts have been proposed.

In the Na/K vs normative minerals diagram, the Lessinian mantle glasses form a coherent trend, ranging from strongly silicaundersaturated to silica-oversaturated terms, with Na₂O/K₂O ratios ranging between 0.64 and 2.14. The glasses plot in the area related to Na-alkali silicate metasomatism which, together with the absence of any Ti or Zr negative anomalies and high Ti/Eu ratios (6821-13624), suggest that the original metasomatic agent was an alkaline silicate melt (fig. 8a,b) (Coltorti *et al.*, 1999; 2000a).

A major and incompatible trace element composition of the inferred metasomatizing melt was calculated by Beccaluva *et al.* (2001a); this calculated composition is similar to that of the Late Cretaceous lamprophyric dykes from Calceranica, an area north of Mt. Lessini (Galassi *et al.*, 1994).

The relative abundance of feldspar in the metasomatic assemblage of VVP xenoliths deserves some attention. Feldspar is reported in several mantle xenolith occurrences worldwide (Yaxley et al., 1991; Dautria et al., 1992; Ionov et al., 1995; 1996; Qi et al., 1995; Vaselli et al., 1995), but has only been addressed in three recent papers (Ionov et al., 1995; Xu et al., 1996; Ionov et al., 1999) where an unclearly-defined alkali-rich (potassic?) fluid is invoked as responsible for its formation. They largely occur also as megacrysts, although anorthoclase and sanidine in compositions, in Late Palaeozoic vents form Scotland (Aspen et al., 1990). According to Upton et al. (1999) they are related to smallfraction melts produced from metasomatized mantle.

As described in the Petrography chapter and shown in fig. 2b, VVP mantle xenolith feldspar always occurs associated with spinel, but in two different textural positions, corresponding to different feldspar compositions. Their compositional range well matches that reported from Baikal (Ionov et al., 1995) and Yitong (Xu et al., 1996), and is distinctly separated from the feldspar of the host lavas, thus making it improbable that they originated by magma infiltration (fig. 7a). Feldspars in lherzolitic rocks tend to be richer in CaO than those in harzburgitic ones (fig. 7b), thus suggesting a whole-rock control on the feldspar compositions. On the other hand, a textural control is suggested by the compositional



Fig. 8 – Major and trace element glass discrimination diagrams (after Coltorti *et al.*, 2000a). *a*) and *b*) open squares, VVP glasses. *b*) filled squares, glasses from carbonatite-metasomatized xenoliths (Comores, Coltorti *et al.*, 1999; Samoa, Hauri *et al.*, 1993; Spistbergen, Ionov, 1998; Mongolia, Ionov *et al.*, 1994); crosses, glasses from K-alkali silicate metasomatized xenoliths (Cape Verde, Coltorti *et al.*, 2000b; Yitong, Xu *et al.*, 1996).

variation of *R*-fld and *I*-fld, the former being richer in CaO (and Al₂O₃) with respect to the latter (which, on the other hand, is obviously richer in K₂O and SiO₂) (fig. 7c). Concomitantly, spinel composition becomes depleted in Al₂O₃ from *sp*1 to *S*1-*sp*, thus providing aluminium for feldspar formation. The relationships between bulk rock, textural position and feldspar composition (in equilibrium with glass) favour the hypothesis of feldspar growth by a reaction mechanism between an infiltrating metasomatising melt and the pre-existing parageneses.

VVP LITHOSPHERE METASOMATISM AND VVP MAGMA SOURCES

Beccaluva et al. (2000) highlighted the similarity between the trace element patterns of the VVP lavas (nephelinites to basanites) and the inferred metasomatic agents, thus suggesting a possible link between metasomatism and magmatism. The VVP magmas were generated from progressively deeper sources, with a concomitant decrease of the partial melting degree (25-2%) from tholeiites to nephelinites. Magmas, ranging from tholeiitic to basanitic, were produced from the same alkali silicate-metasomatized lherzolitic mantle source (S1, modally characterized by amphibole and phlogopite), whereas a different source affected by carbonatite metasomatism (S2) is required for the production of nephelinites (Beccaluva et al., 2000).

Mantle xenoliths from the VVP obviously cannot be considered as the source of VVP magmatism, being sampled by the host lavas at shallower lithospheric levels. However, if we compare the trace element contents of source S1 with those of the metasomatized MA7 and SG12 lherzolites, they do share some similarities (fig. 9a).

To account for the geochemical characteristics of VVP magmas (tholeiites to basanites) the presence of 9% amphibole and 1% phlogopite in the S1 source was invoked

(Beccaluva et al., 2000), which may be considered the result of previous metasomatism. On the other hand, the metasomatic enrichment of VVP mantle xenoliths can be evaluated by taking into account the trace element contents of secondary parageneses (clinopyroxenes, feldspars and glasses). Their modal percentages were obtained by matching major element mass balance calculations with whole-rock trace element contents. The satisfactory results obtained (fig. 10) allow the separation of the metasomatic contribution to the whole trace element budget of VVP mantle xenoliths, which may be compared with the inferred geochemical enrichment of the S1 source, mainly represented modally by the presence of amphibole and phlogopite. The comparison is illustrated in fig. 9b, where trace element contents of amphibole and phlogopite (S1 source) fall almost completely within the range delimited by MA7 and SG12 secondary parageneses. Thus the metasomatic fluids responsible for the enrichment of the S1 source have geochemical features analogous to those responsible for the metasomatic features observed in the VVP mantle xenoliths.

A further constraint comes from the isotopic data reported in fig. 11. VVP lavas and metasomatized xenoliths cover a restricted range (Table 1), most of which plot close to the high U/Pb (HIMU-type; Zindler and Hart, 1986) ocean island magmas. A few samples are shifted toward an enriched mantle component, as also suggested by Pb isotopic data on VVP lavas (Beccaluva et al., 2000), indicating a minor role for an EMII-like component. All samples are lower in ⁸⁷Sr/⁸⁶Sr and higher in ¹⁴³Nd/¹⁴⁴Nd than Bulk Earth (BE), supporting the origin of VVP lavas from a mantle source previously affected by a time-integrated incompatible element depletion, followed by (multiple?) enrichment and metasomatic processes. Primary, unmetasomatized peridotites (14D3 and 18D, separate clinopyroxene) plot near the DM component, while metasomatized xenoliths (SG2 and MA2;



Fig. 9 – *a*) Comparison between trace element composition of metasomatized VVP mantle xenoliths and modelled VVP magma (basanite to tholeiite) sources (S1, Beccaluva *et al.*, 2000). *b*) comparison between metasomatic contribution in VVP mantle xenoliths and calculated amphibole and phlogopite enrichment in S1 source. Numbers refer to calculated modal percentages of S1, SG12 and MA7. Amph, amphibole; ph, phlogopite; other abbreviations as in fig. 2.



Fig. 10 – Primordial Mantle (PM)-normalized trace element distribution of metasomatized VVP mantle xenoliths (solid lines) vs calculated (dashed lines) distribution on the basis of major element mass balance modelling. Normalized values from Sun and McDonough (1989)

whole-rock analyses), enriched in ⁸⁷Sr/⁸⁶Sr and depleted in ¹⁴³Nd/¹⁴⁴Nd, plot near the HIMU isotopic component. It should be noted that the lamprophyric dykes, thought to be the best analogues of the metasomatic melt, fall in the same position as the enriched xenoliths, right at the end of this trend. Similarly, the VVP lavas (including lavas from the Euganean Hills, Milani *et al.*, 1999) plot in the same position as the metasomatized xenoliths and the metasomatic agent, thus strongly supporting a link between the metasomatic agent reacting with the VVP xenoliths and that which affected the mantle source of VVP lavas.

The VVP nephelinites have a different geochemical signature from the basanite to tholeiite lavas, particularly in their more pronounced Ti and Zr negative anomalies (fig. 12). Beccaluva *et al.* (2000) attributed these features to a carbonatite-metasomatized mantle source (S2). No evidence of this deeper event, whose isotopic characteristics are identical to the alkali-silicate which generated the S1 source, has, however, been recorded in the VVP mantle xenoliths, where only Na-alkali silicate metasomatism has been reported (Coltorti *et al.*, 2000a; Beccaluva *et al.*, 2001a). Tholeiite to nephelinite magmas from

the Iblean Plateaux share similar geochemical features to those of the VVP (fig. 12). suggesting that the deeper lithospheric portions were also affected by carbonatitic fluids (Beccaluva et al., 1998). A spatial distribution between different metasomatic styles may thus be envisaged, with carbonatite preferably metasomatizing the deeper lithospheric portion. This fact may also be generalized on a wider scale, comparing nephelinites and basanites from various localities world-wide. In fact, in the Zr/Sm vs Ti/Eu diagram (fig. 12), the most undersaturated lavas tend to plot in the lower left part of the diagram, i.e. the portion which, on the basis of the geochemical features of mantle glasses, has been referred to carbonatite metasomatism (fig. 8b) (Coltorti et al., 2000a).

In the case of the VVP, it may even be possible that the metasomatism of lava sources and that of mantle xenoliths was the result of a unique event, which progressively affected the shallower portions of lithospheric mantle at different times. Alternatively, two distinct events (with similar geochemical and isotopic features) could have affected various lithospheric portions at different times.

Table 1
Sr and Nd isotopic data for VVP mantle xenoliths and lamprophyric dyke from Calceranica
Standard deviation = 2σ .

		⁸⁷ Sr/ ⁸⁶ Sr	¹⁴³ Nd/ ¹⁴⁴ Nd
Clinopuroxenes			
Pilcante	10D1	0.703125 ± 9	
Pilcante	10D8	0.703120 ± 5	
Pilcante	10D15	0.702951 ± 11	
Pilcante	18D	0.702543 ± 8	0.513291 ± 16
Passo Buole	14D3	0.702214 ± 18	0.51325 ± 36
Whole-rock			
Mt. Madarosa	MA 2	0.70365 ± 16	0.51297 ± 12
San Giovanni Ilarione	SG 2	0.70317 ± 16	0.512994 ± 12
Late Cretaceous Lamprophyre			
Calceranica	Calc 38	0.703667 ± 30	0.512893 ± 4



Fig. 11 – ¹⁴³Nd/¹⁴⁴Nd vs ⁸⁷Sr/⁸⁶Sr diagram of VVP lavas and xenoliths, as well as of Late Cretaceous lamprophyric dyke from Calceranica. Fields of Iblean lavas and xenoliths (D'Orazio *et al.*, 1997; Beccaluva *et al.*, 1998), Sardinian lavas and xenoliths (Lustrino, 1999; Beccaluva *et al.*, 2001b), Euganean Hills (Milani *et al.*, 1999) and Central Europe (Wedepohl and Baumann 1999) are also reported.

CONCLUSIONS

Several pyrometamorphic textures have been found overprinted on the original protogranular texture, with an increase in the modal amount of glass (and secondary phases) from Type A to Type B textures. The reactions led to the formation of new phases such as glass and feldspar at the expense of primary phases (olivine, orthopyroxene, clinopyroxene and spinel), which are partially re-absorbed in Type A and progressively disappear (or recrystallize with different composition) in Type B textures.

These complex textural and chemical characteristics are the result of a multistage evolution of the mantle material. The last event recorded by the xenoliths is a metasomatic reaction caused by infiltration of an exotic melt into a variably depleted peridotite matrix. Major and trace element glass composition, makes it possible to define the nature of this exotic, metasomatic melt which was strictly comparable with Late Cretaceous lamprophyric dykes from Calceranica (Trento).

The analogy between inferred VVP lava sources, metasomatic melt and VVP xenolith enrichments seems suggest a link between metasomatism and magmatism, the latter probably resulting from a longer period of melt/peridotite reaction processes acting in the deeper lithospheric portions. On the basis of the geochemical features of mantle glasses and



Fig. $12 - (Zr/Sm)_N vs$ (Ti/Eu)_N diagram for nephelinites (Neph) and basanites (Bsn) from Veneto Volcanic Province (VVP; Beccaluva *et al.*, 2000), Iblei (Ib; Beccaluva *et al.*, 1998), Cape Verde (CV; Gerlach *et al.*, 1988; Romagnoli, 1992), Gran Comore (GC; Deniel, 1998; Class and Goldstein, 1997), Samoa (S; Palacz and Saunders, 1986), Canary Islands (C; Hoernle and Schminke, 1993) and Hawaii (Hw; Clague and Frey, 1982).

undersaturated (nephelinites and basanites) magmas, a general model is envisaged which involves carbonatite and alkali silicate metasomatisms impregnating the base of the lithosphere, while an alkali silicate metasomatism alone commonly affects its uppermost portions.

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