

PETROLOGICAL AND GEOCHRONOLOGICAL STUDY OF MAGMATIC PRODUCTS AND MANTLE XENOLITHS FROM CENOZOIC SOUTHALPINE MAGMATIC PROVINCE (NORTH-EAST ITALY)

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INTRODUCTION AND AIMS

The Cenozoic Southalpine magmatic province (NE Italy), known in literature as Veneto Volcanic Province (VVP; *e.g.*, De Vecchi & Seda, 1995; Beccaluva *et al.*, 2001, 2007; Macera *et al.*, 2003, 2008; Fig. 1), is one of the widest magmatic districts of the Adria microplate, the northern continental promontory of the

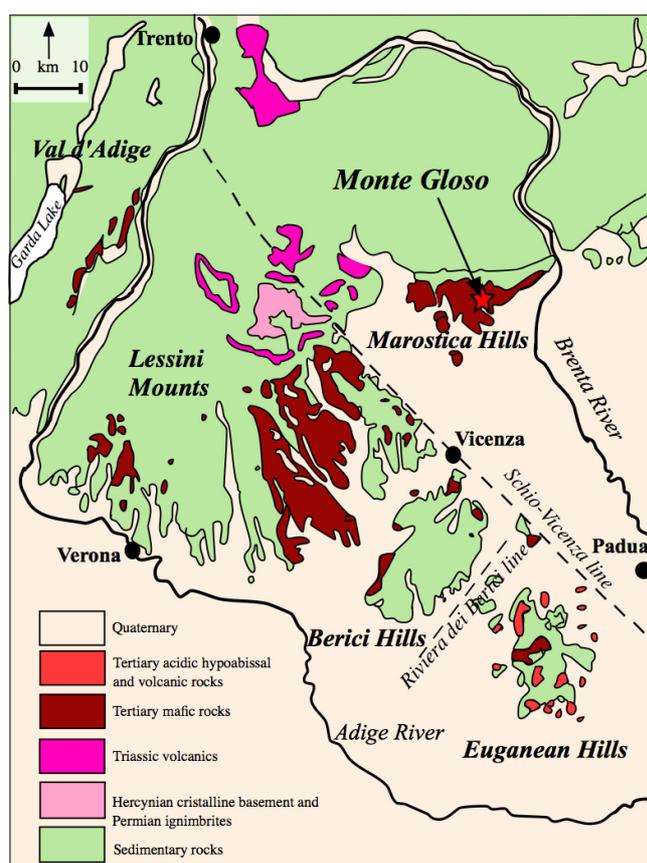


Fig. 1 - Geological map of the Veneto Volcanic Province (VVP; De Vecchi & Seda, 1995) and its five magmatic districts: Val d'Adige, Lessini Mts., Marosticano, Berici Hills, and Euganean Hills. The location of Monte Glosio, the xenolith site in the Marosticano magmatic district is also shown.

African plate (Beccaluva *et al.*, 2007). From late Paleocene to early Miocene, the VVP magmatic activities developed along a series of eruptive centers orientated NNW-SSE: Val d'Adige, Lessini Mts., Marosticano, Berici Hills, and Euganean Hills. Since the early '90s, extensive petrological studies were carried out on the VVP magmatism, mainly on the basic products. They comprise a wide compositional spectrum including (mela) M-nephelinites, basanites to the West (Val d'Adige and western Lessini Mts.), and predominantly alkali-basalts, transitional basalts and tholeiites to the East areas (eastern Lessini Mts. and Marosticano; De Vecchi & Seda, 1995; Beccaluva *et al.*, 2001, 2007; Macera *et al.*, 2003, 2008). Only in the Euganean Hills, volcanic and subvolcanic rocks range from subordinate basalts to prevalently acidic types, mostly quartz-trachytes and rhyolites (Milani *et al.*, 1999). According to Macera *et al.* (2003) and Beccaluva *et al.* (2007), the potassic affinity ($\text{Na}_2\text{O}/\text{K}_2\text{O} > 1$) and the incompatible element distribution (characterized by negative anomalies in Cs, Rb, K and positive anomalies in Nb and Ta) of the VVP magmatic products are features of the intraplate origin from ocean island basalt (OIB)- like mantle source.

In order to better constrain the nature and evolution of the lithospheric mantle source of the VVP magmatism a detailed petrological

study (major and trace element) and $T\text{-}\Delta\log f\text{O}_2$ estimates of a newly found suite of mantle xenoliths from the Marosticano district were performed. Previous studies of Val d'Adige and Lessini Mts. mantle xenoliths reveal variably depleted mantle domains subsequently enriched by one or more episodes of alkali-silicate metasomatism (Morten *et al.*, 1989; Siena & Coltorti, 1989; Beccaluva *et al.*, 2001; Gasperini *et al.*, 2006). In

this frame, the mantle xenoliths suite from Marosticano could extend the knowledge of the VVP Sub Continental Lithospheric Mantle (SCLM). Moreover, for the first time, *in-situ* Re-Os isotopic measurements on sulfides were performed on the VVP mantle domain, in particular on sulfides of Val d'Adige, Lessini Mts., and Marosticano peridotites (Brombin *et al.*, 2018). This made it possible to determine the age of the main melting event of the VVP mantle section, that progressively transformed fertile asthenospheric material into a depleted, buoyant lithosphere (Alard *et al.*, 2002).

Despite the deep petrological and geochemical knowledge of the VVP magmatic products and their source, the geodynamic mechanism that triggered this magmatism is still puzzling. According to the prevalent hypothesis, the VVP magmas have been related to upwelling of mantle diapirs through a slab window (*e.g.*, Macera *et al.*, 2003) after the European slab detachment at 35 Ma, following the Europe/Adria collision (*e.g.*, Rosenbaum & Lister, 2005).

New high-resolution $^{40}\text{Ar}/^{39}\text{Ar}$ measurements of basic and acidic lavas from selected key locations of Val d'Adige, Marosticano, Lessini Mts., and Euganean Hills districts were performed in this work in order to constrain *i*) the temporal evolution of the VVP magmatism, and *ii*) the relationship between Cenozoic magmatism VVP and Alpine orogenetic events.

ANALYTICAL TECHNIQUES

Bulk rock major compositions of mantle xenoliths and magmatic products from Val d'Adige, Lessini Mts., and Marosticano districts were determined by Wavelength Dispersive X-Ray Fluorescence Spectrometry (WDXRF) on pressed powder pellets using an ARL Advant-XP spectrometer at the Department of Physics and Earth Sciences, University of Ferrara (Italy). Bulk trace element compositions were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) using a Thermo Series X-I spectrometer at Department of Physics and Earth Sciences, University of Ferrara.

Major and trace elements of magmatic products from Euganean Hills district were determined by X-Ray Fluorescence Spectrometry (XRF) on glass bead samples at the Department of Geosciences, University of Padova (Italy), using Phillips PW1404.

In-situ major element compositions of minerals (olivine, pyroxene, and spinel) from xenoliths and host magmatic products were analyzed using CAMECA SX50 Electron MicroProbe (EMP) at the Department of Geosciences, University of Padova (Italy).

In-situ trace element concentrations in clinopyroxene and orthopyroxene of mantle xenoliths were obtained by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) at the Department of Earth Sciences, University of New Hampshire (USA) using an Analyte Excite 193 nm excimer laser plumbed into a Nu instruments AttoM high resolution ICP-MS.

In-situ Re-Os data on sulphides of Val d'Adige, Lessini Mts., and Marosticano mantle xenoliths were obtained by Laser Ablation Multicollector Inductively Coupled Plasma Mass Spectrometry (LA-MC-ICPMS) using a Nu Plasma multi-collector ICP-MS system (Nu005) at the ARC Centre of Excellence for Core to Crust Fluid Systems (Macquarie University, Sydney, Australia).

For $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology of VVP magmatic products, granulate (size fraction of 90-250 μm) constituted by groundmass was prepared for basanitic and basaltic samples from Val d'Adige, Lessini Mts., and Marosticano districts; granulate (size fractions of 150-215 μm and 215-315 μm) constituted by K-rich phenocrysts (plagioclase, amphibole, biotite, sanidine, and feldspar) was prepared for basaltic trachyandesites, trachyandesites, trachytes, and rhyolites from the Euganean district. The groundmass and mineral separates were loaded into Cd- aluminum discs together with the neutron fluence monitors (GA1550 biotite and FCs) for the irradiation at TRIGA Reactor at Oregon State University (USA). The plateau age and isochrons were obtained measuring the Ar isotopic ratios through laser step-heating with *i*) MAP 215-50 and *ii*) ARGUS VI mass spectrometers at Curtin University within the Western Australian Argon Isotope Facility (WAAIF) of the John

de Laeter Centre, and *iii*) Nu Instruments Noblesse magnetic sector noble gas mass spectrometer at the Noble Gas Geochronology Laboratory of the University of Vermont.

THE MANTLE SOURCE OF VVP MAGMATISM

The VVP magmatic products analyzed in this work are basanites and basalts from Val d'Adige, Lessini Mts., and Marosticano, and basaltic andesites, basaltic trachyandesites, trachyandesites, trachytes, and rhyolites from Euganean Hills. The geochemical compositions of the less evolved rocks (*i.e.*, basic-ultrabasic rocks) could be used as proxies of nature and evolution of the VVP mantle source. The primitive-mantle normalized trace element patterns of VVP basic-ultrabasic samples show *i*) an increase from Rb to U, *ii*) a progressive decrease of the incompatible trace elements from Nb, and *iii*) strong enrichment in Light Rare Earth Elements (LREE) compared with Heavy Rare Earth Elements (HREE) [(La/Yb)_N: 14.4-22.0] (Fig. 2). These features are observed also in previous studies on the VVP, which interpreted the trace element patterns as the result of an intraplate origin from OIB-like mantle source (Milani *et al.*, 1999; Beccaluva *et al.*, 2007; Macera *et al.*, 2008; Fig. 2). However, VVP patterns of this study are distinguishable from that of the average OIB (McDonough & Sun, 1995) for: *i*) enrichment in LILE relative to HFSE (Ba/La: 10.7-19.2; average OIB: 9.4) and *ii*) positive anomalies in Ba, Sr, and P (Fig. 2). These features are commonly observed in carbonatite metasomatized mantle xenoliths (Ionov *et al.*, 1996), which are carried by silicic basaltic melts derived from peridotitic sources (*e.g.*, Wood & Corgne, 2010).

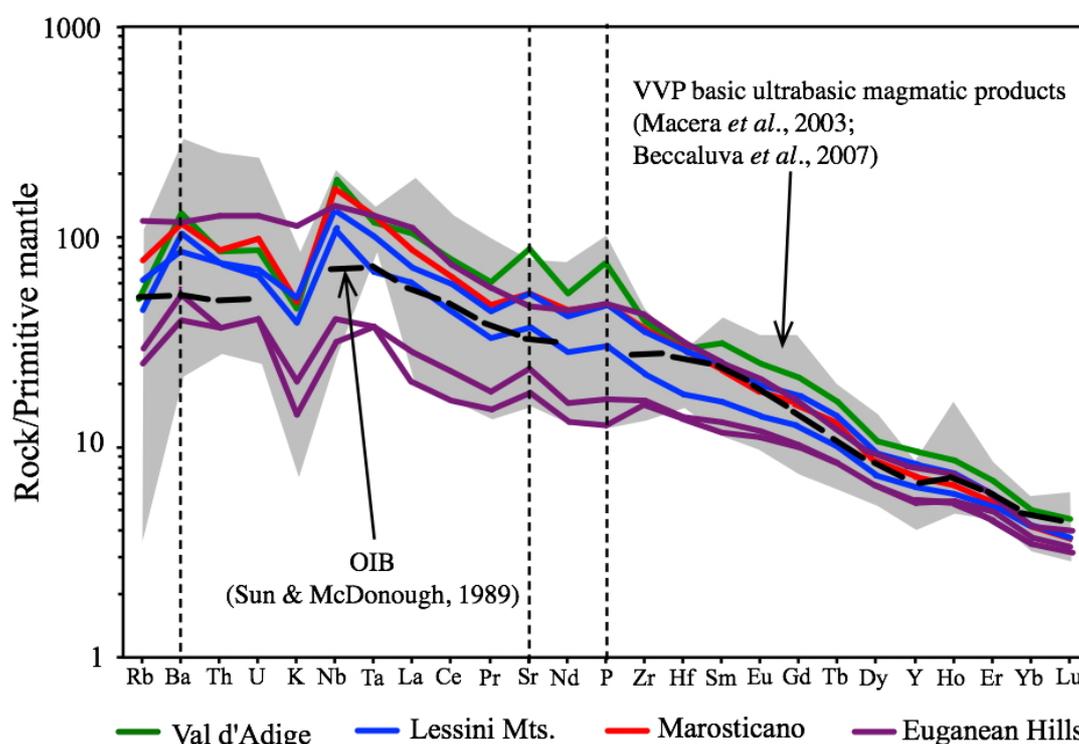


Fig. 2 - Primitive mantle-normalized trace elements patterns for basic-ultrabasic rocks from Val d'Adige, Lessini Mts., Marosticano, and Euganean Hills. The patterns of literature samples from Val d'Adige and Lessini Mts. (Macera *et al.*, 2003, Beccaluva *et al.*, 2007) are represented with a shadowed area. Typical ocean island basalt (OIB; Sun & McDonough, 1989) is indicated with a black dashed line. Primitive mantle values are from McDonough & Sun (1995).

In order to better constrain the nature of the VVP mantle source, the geochemistry of mantle xenoliths commonly hosted in the alkaline lavas (*i.e.*, basanite and nephelinites) was also taken in account. According to

previous studies (Beccaluva *et al.*, 2001; Gasperini *et al.*, 2006), Val d'Adige and Lessini Mts. mantle xenoliths exhibit geochemical characteristics of off-craton lithospheric mantle affected by Na-alkaline silicatic metasomatism. To enlarge the knowledge of the mantle portion beneath the VVP, a recently discovered occurrence of mantle peridotites from Monte Glosio (MG; Fig. 1) in Marosticano district was investigated in this work. The Marosticano anhydrous harzburgites and lherzolites exhibit the complete spinel facies assemblage and pyrometamorphic textures. The analyses for major elements show that the Marosticano lherzolites and harzburgites have got higher contents in restitic components (*i.e.*, Mg, Ni, Cr) than the mantle domain beneath the other VVP districts (Lessini Mts. and Val d'Adige), but similar to those observed for the on-craton peridotites worldwide (*e.g.*, Kaapval Craton, Boyd, 1989; Siberia Craton and Greenland Craton, Kelemen *et al.*, 1998; Fig. 3a-b). Therefore, the petrological characterization of Marosticano mantle lherzolites and harzburgites seems to introduce a cratonic component in the geodynamic evolution of the Adria microplate system (Brombin *et al.*, 2018).

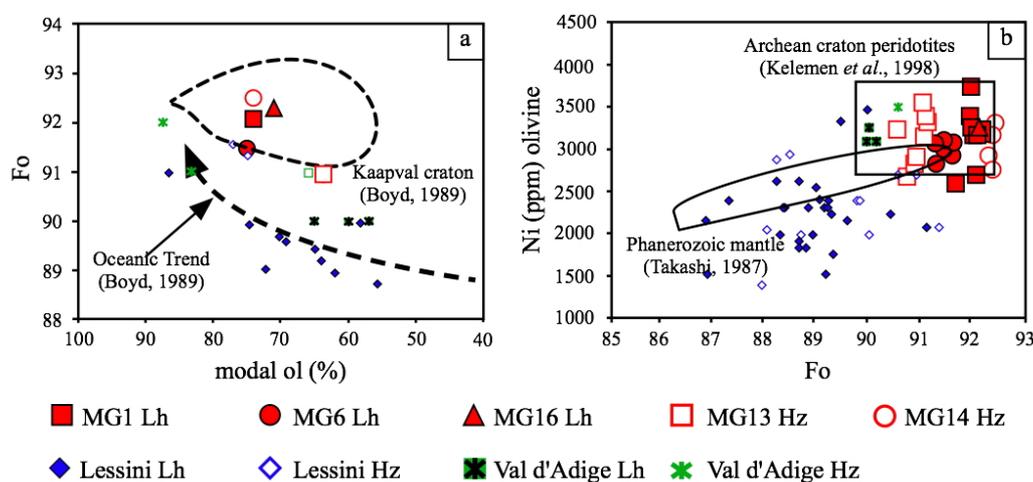


Fig. 3 - (a) Forsterite [$Fo = 100 \times Mg/(Mg+Fe)_{mol}$] compositions versus modal olivine for Val d'Adige, Lessini Mts., and Marosticano (MG) mantle peridotites; the "oceanic trend" is from Boyd (1989). (b) Ni (ppm) versus Fo of olivines; fields from Archean craton both garnet and spinel peridotites (Kelemen *et al.*, 1998), and Phanerozoic mantle array (Takahashi, 1987) are also plotted. Filled and open symbols are for lherzolite (Lh) and harzburgite (Hz), respectively. For comparison Lessini Mts. (Beccaluva *et al.*, 2001; Gasperini *et al.*, 2006; Morten *et al.*, 1989; Siena & Coltorti, 1989) and Val d'Adige (Gasperini *et al.*, 2006) xenoliths are also reported.

In addition, the $Fo = 91.5$ and $Cr\# = 60.0$ of Marosticano olivine and spinel, respectively, suggest high degrees of partial melting ($> 25\%$; *e.g.*, Bernstein *et al.*, 2007) occurring at high melting temperature typical of old mantle thermal regime (*i.e.*, Archean or Paleoproterozoic mantle; Walter, 2003), that would imply the clinopyroxene consumption in the spinel stability field. Therefore, the observed Marosticano clinopyroxene are secondary in nature with a metasomatic legacy as expected from clinopyroxene of peridotites from on-craton setting (Grégoire *et al.*, 2003). In fact, *i)* enrichment in Th, U, Rb, and LREE, but depletion in both HREE and HFSE (*e.g.*, Ta, Zr and Hf; Fig. 4a) and *ii)* REE patterns that mimic those of clinopyroxene equilibrated with a synthetic carbonatitic melt at 1100-1150°C and 1.5-2.0 GPa (Klemme *et al.*, 1995; Fig. 4b) suggest that clinopyroxenes in both lherzolites and harzburgites were formed by the interaction between restitic peridotite and carbonatitic/CO₂-rich silicatic metasomatic melts.

The metasomatic melt could be also responsible for the equilibrium temperatures (923-1117°C) and oxidizing conditions [$\Delta \log fO_2$ (FMQ) = -0.6 +1.1], anomalously high for a proper cratonic environment (Foley, 2011), but similar to the off-craton VVP xenoliths [885-966°C; $\Delta \log fO_2$ (FMQ) = -1 +1; Siena & Coltorti, 1993; Gasperini *et al.*, 2006; Beccaluva *et al.*, 2007]. Using the equation of Stagno & Frost (2010) the calculated

dissolved CO_2 mole fractions for the inferred metasomatic agent are close to 1.0, indicating that CO_2 was the largest component of such melt and it probably played an oxidizing role. In this frame, the positive Eu anomaly exhibited by some Marosticano clinopyroxene (Fig. 4a) may be the adjustment effect of the interplay between crystal chemistry and redox conditions during metasomatism, as it was demonstrated that with the increase of $f\text{O}_2$ Eu^{3+} became more compatible than Eu^{2+} in the augite structure and can partition into the crystallizing pyroxene (Karner *et al.*, 2010).

Despite the different geochemical features, Marosticano, Val d'Adige, and Lessini Mts. mantle portions show similarities in Re-Os ages calculated from *in-situ* isotopic measurements on mantle sulfides. The Re-Os model ages (T_{MA}) for the entire VVP domain range between 2.0 and 2.8 Ga, with one value at 3.1 ± 0.08 Ga, confirming the derivation of Marosticano peridotites from ancient (cratonic) mantle and also suggesting a “hidden” cratonic signature for Val d'Adige and Lessini Mts. lithospheric mantle.

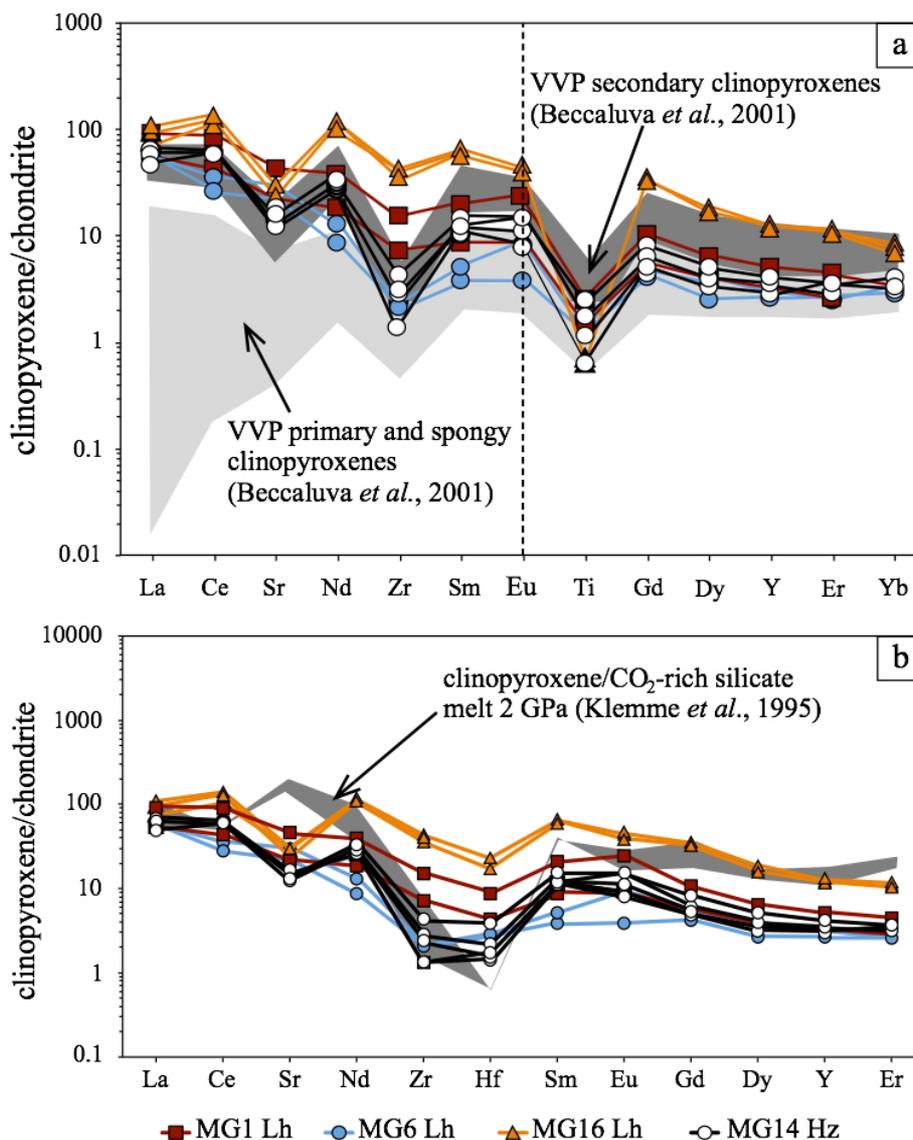


Fig. 4 - (a) Trace element compositions of Marosticano clinopyroxene (MG) compared with the overall VVP clinopyroxene shadowed areas: data from Beccaluva *et al.* (2001). (b) REE patterns of Marosticano clinopyroxene (MG) compared with modeled clinopyroxene formed by carbonatitic/ CO_2 -rich silicate melt applying $\text{D}^{\text{clinopyroxene/melt}}$ calculated at pressure of 2 GPa and temperature of 1100-1150°C (Klemme *et al.*, 1995); shadowed area. Chondrite values are from Sun & McDonough (1989). Filled and open symbols are for Lherzolite (Lh) and harzburgite (Hz) respectively.

These results allow a re-interpretation of the geodynamic evolution of the VVP lithosphere. The Marosticano domain can be interpreted as a vestige of an Archean/Proterozoic cratonic keel, whose signature was not erased by the carbonatite/CO₂-rich silicatic metasomatism, whereas the xenoliths from the Lessini Mts. and Val d'Adige are remnants of circumcratonic domains compositionally rejuvenated by infiltration of asthenosphere-derived melts, whose upwelling could be induced by the retreatment of the European slab after the Adria/Europe collision (Fig. 5).

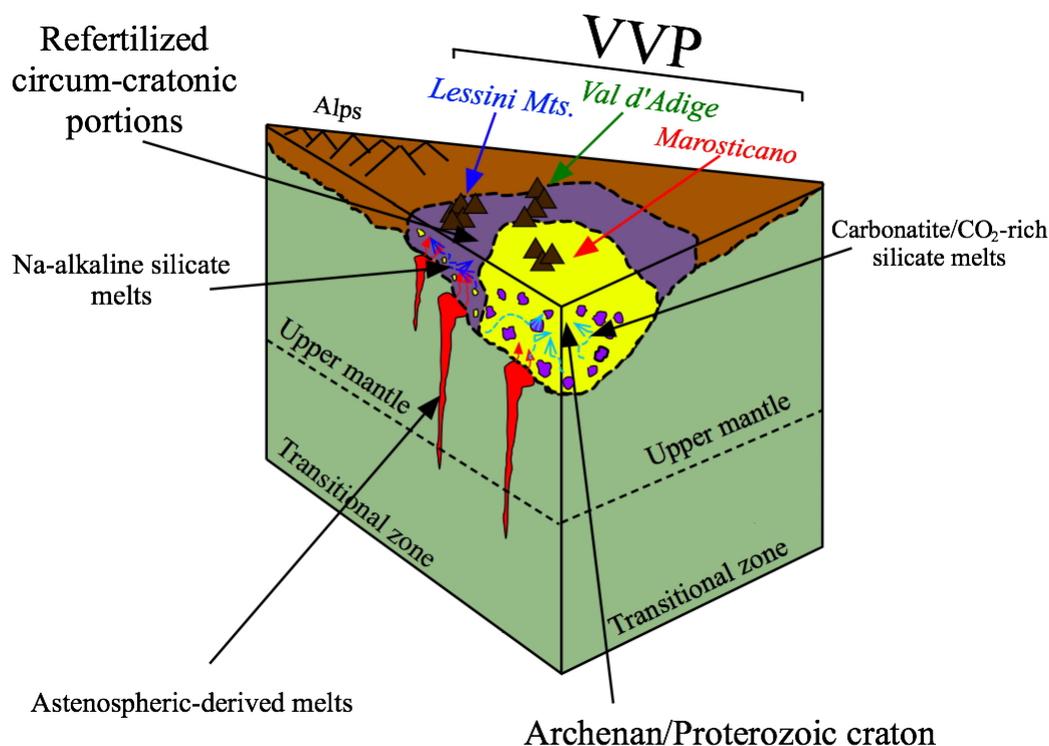


Fig. 5 - Schematic model of processes significant in the evolution of the lithospheric mantle beneath Veneto Volcanic Province (VVP) during the European/Adria collision. See explanation in the text.

THE TEMPORAL EVOLUTION OF THE MAGMATIC ACTIVITY OF THE VVP AND GEODYNAMIC IMPLICATIONS

The biostratigraphic literature allows to reconstruct the temporal evolution of the magmatic activity in the VVP. According to these data the VVP products erupted discontinuously during a time-span of 30 Ma, interbedded with the Paleocene to Miocene in age Southalpine sedimentary cover (Scaglia Rossa, limestones and marls) and becoming progressively younger towards the south and east (Savelli & Lipparini, 1979; Piccoli *et al.*, 1981; Luciani, 1989; De Vecchi & Sedeà, 1995; Beccaluva *et al.*, 2007; Bassi *et al.*, 2008). However, in a complex geodynamic framework, such that of the Alpine realm, the integration of stratigraphic records with reliable radiometric ages is essential to infer the origin and evolution of the VVP magmatism.

Several authors provided already radiometric ages using different methods. Barbieri & Medizza (1969), Savelli & Lipparini (1979), and Zantendeschi (1994) dated the VVP products using the K-Ar and Rb-Sr methods. However, such dating techniques are no longer in use, because they are affected by systematic problems, therefore their reliability is questionable. Visonà *et al.* (2007) and Bartoli *et al.* (2014) dated zircons hosted in basanites of Lessini Mts. and in xenoliths in trachytes of Euganean Hills using the U-Pb technique. However, the magmatic origin of these zircons is uncertain.

In this work, new $^{40}\text{Ar}/^{39}\text{Ar}$ radioisotopic ages of magmatic products from VVP are combined with the literature biostratigraphic data to reconstruct the history of the magmatic activity. According this reconstruction, the first eruptions occurred in the late Paleocene in the western districts (*i.e.*, Val d'Adige and Lessini Mts.), however these activities could be not dated because of the pervasive alteration of the subaqueous volcanic products. In the early Eocene the magmatic activity went on only in the Lessini Mts. district. The middle Eocene (Lutetian-Bartonian) is considered the climax of the VVP volcanism with basic eruptions in Val d'Adige, Lessini Mts., (Val d'Adige: 41.98 ± 0.20 Ma – 40.73 ± 0.24 Ma; Lessini Mts: 45.21 ± 0.11 Ma – 38.73 ± 0.44 Ma; Fig. 6) and Euganean Hills (Piccoli *et al.*, 1981). During the early Oligocene in Euganean Hills both basic and acidic eruptions took place in a time-span possibly shorter than 0.2 Ma (32.35 ± 0.09 Ma – 32.09 ± 0.29 Ma; Fig. 6), while only basic eruptions occurred in Marosticano (Savelli & Lipparini, 1979). In this latter district, magmatic episodes were recorded until the end of the early Miocene (~ 22 Ma; Fig. 6).

These geochronological results depict also a possible new Adria/Europe geodynamic scenario. The Alpine magmatism has been generally interpreted as an effect of upwelling of mantle diapirs through a slab

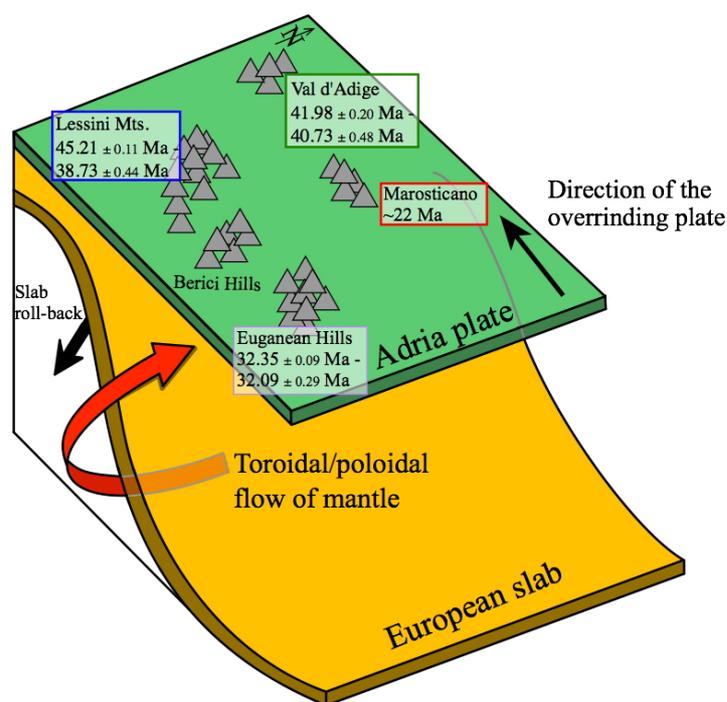


Fig. 6. - Schematic model showing toroidal/poloidal flow beneath the Adria plate around the edge of the European slab. See explanation in the text.

window after the European slab detachment, which occurred ~ 35 Ma (*e.g.*, Rosenbaum & Lister, 2005). However, the VVP $^{40}\text{Ar}/^{39}\text{Ar}$ radioisotopic ages provide evidence for a pre-Oligocene magmatic activity ruling out the slab breakoff as the possible triggering mechanism of the VVP magmatism.

Therefore, another alternative geodynamic model must be proposed. According to recent high-resolution isotropic and anisotropic tomographic profiles the subducting European slab is continuous from the Western Alps to the Central Alps and nearly vertical (Zhao *et al.*, 2016; Hua *et al.*, 2017). It means that since the Europe/Adria collision occurred in the Eastern Alps in early Paleocene (~ 65 Ma), the European slab became progressively steeper and retreated toward west in response to roll-back mechanisms (Rosenbaum *et al.*, 2002). The effects of retreating slabs is well documented

by analytical laboratory solutions, 3D experiments and numerical modeling, which demonstrate that near the lateral edge of the slab the asthenospheric material located below the slab escapes laterally producing vigorous toroidal/poloidal mantle flow (*i.e.*, horizontal and vertical rotational vortex-like components of mantle motion; Funicello *et al.*, 2006; Piromallo *et al.*, 2006; Faccenna *et al.*, 2011). Likewise, the retreatment of the European slab could have caused the upwelling of a toroidal/poloidal flow, which drove the decompression melting in the mantle wedge beneath the VVP and induced the magmatism (Fig. 6). The migration and rejuvenation of the magmatism southeastward within the VVP could be due to overriding Adria plate moving faster than the retreating European slab.

CONCLUSIONS

This contribution presents an integrative study of both magmatic products and mantle xenoliths from the Veneto Volcanic Province shedding new lights on the geodynamic framework of the Southeastern Alpine domain. The petrological and geochronological characterizations of VVP mantle xenoliths revealed that the Val d'Adige and Lessini Mts. mantle domains are circumcratonic portions refertilized and rejuvenated by asthenospheric-derived melts, whose upwelling was induced by the retreatment of the European slab after the Adria/Europe collision. Only in the Marosticano mantle domain the vestige of a cratonic portion variably affected by carbonatite/CO₂-rich silicate metasomatism is preserved. Such metasomatism is confirmed also by the trace element patterns of the VVP magmatic products, which revealed an OIB-like mantle source metasomatized by carbonatitic melts.

The geochronological study of the VVP magmatic products allowed a review of the triggering mechanism of the VVP magmatism. The first VVP eruptions are pre-Oligocene in age, ruling out the hypothesis of relationship between the magmatism and the European slab detachment, occurred at 35 Ma. In addition, new tomographic images revealed the European slab is continuous and nearly vertical. Therefore, in this study a new geodynamic model is proposed: a decompression melting of the sub-lithospheric mantle material beneath the VVP due to a toroidal/poloidal flow, which was induced by the progressive retreatment and steepness of the European slab. It is also speculated that the migration and rejuvenation of the magmatism southeastward is due to overriding Adria plate moving faster than European slab retreatment.

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