Magmatism, mantle evolution and geodynamics at the converging plate margins of Italy

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Abstract: The Plio-Quaternary magmatism in the Tyrrhenian Sea area exhibits wide compositional variations, which cover almost entirely those observed for volcanic rocks worldwide. Some volcanoes (Etna, Iblei, Sardinia, etc.) range from tholeiitic to Na-alkaline, and display elemental and isotope signatures typical of FOZO and EM-1 ocean-island basalts (OIB). Other volcanoes (Aeolian Arc, Italian peninsula) range from calc-alkaline–shoshonitic to K-alkaline, exhibit typical 'subduction-related' trace element signatures (low Ta–Nb, high Rb–Cs–LREE), and show a large range of radiogenic isotope ratios, from mantle-like in the Aeolian Arc to crustal-like in central Italy. Geochemical data suggest that OIB-type magmatism originated in lithosphere–asthenosphere sources that were unaffected by recent subduction. In contrast, subduction-related magmas come from mantle sources that underwent Eocene to present mixing with various amounts and types of subducted crustal components. Fluxing of the mantle wedge by water-rich fluids from a mid-ocean ridge basalt-type slab occurred in the southern Tyrrhenian Sea, whereas interaction between peridotite and various types of sediments occurred in central Italy. These contrasting styles of mantle contaminations

relate to the nature (oceanic or continental) of the foreland, slab geometry and pre-metasomatic mantle compositions, which vary greatly along the Apennine arc and are the reason for the formation of the wide variety of orogenic magmas in Italy.

The Plio-Quaternary volcanism of the Tyrrhenian Sea area (Fig. 1) is well known for both historical and geological reasons. The activity of many Italian volcanoes, especially Etna, Vesuvius and Stromboli, has been the source of threat and destruction for local populations since early historical times. Their variable styles of eruption, from quiet Hawaiian-type lava effusions to mildly explosive Strombolian explosions, and to catastrophic Plinian eruptions, have been taken as models for volcanic activity worldwide.

A main reason for interest in the young volcanism of Italy arises from the extreme compositional variability of magmas, which is one of the main causes of contrasting eruptive styles. Magma compositions range from mafic to felsic and from subalkaline to ultra- alkaline, both potassic and sodic. If plotted on the total alkalis v. silica (TAS) diagram (Fig. 2), a scheme designated to classify volcanic rocks on a global scale (Le Maitre 2002), the Italian Plio- Quaternary volcanic rocks completely cover the diagram, indicating the coexistence of almost all magma types known on Earth in a relatively small area that has been at the converging boundaries between Africa and Europe from the Early Cretaceous to the present.

Except for some crustal anatectic granitoids and rhyolites mostly occurring in Tuscany (e.g. Poli 2004; Farina *et al*. 2012), the large majority of magmas are of ultimate mantle origin. Most if not all of them have undergone evolution processes during emplacement, which have significantly modified their compositions (e.g. Iacono Marziano *et al*. 2008; Lucchi *et al*. 2013*a*,*b*). However, a wealth of studies carried out in recent decades agree that much of the compositional variability observed in the Italian volcanic rocks, especially in the mafic ones, is primary, and reflects extremely variable mantle sources and conditions of partial melting (e.g. Hawkesworth & Vollmer 1979; Rogers *et al*. 1985; Ellam *et al*. 1988;

Beccaluva *et al.* 1991; Francalanci *et al.* 1993, 2007; Peccerillo 1999, 2005; De Astis *et al.* 2000; Conticelli *et al.* 2009*a*; Carminati *et al.* 2012). Understanding the reason for these complexities is of primary interest for the petrology and geochemistry of magmas and related mantle processes, not only in Italy but also in other converging plate settings.

In this paper we summarize the first-order petrological, geochemicalnd isotopic data on the recent to active magmatism in Italy, and discuss the main petrogenetic and geodynamic implications. We will particularly focus on subduction-related volcanism, which shows a complex and unique association of magma compositions, ranging from typical calc-alkaline to ultrapotassic and carbonatitic. We will use petrological, geochemical and field data to demonstrate that many components, of both mantle and crustal origin, contributed to magmatism. These include depleted and fertile peridotite from various mantle depths, mid-ocean ridge basalt (MORB)-derived fluids, and carbonate to silicic subducted metasediments. Finally, we will show that variable roles of these components generated heterogeneous mantle sources at both regional and local scales, which are the cause of the large variety of magma compositions observed at the surface.

Many models of the evolution of the Apennine–Maghrebian system have been proposed, but they are mainly based on sedimentological and geophysical data, and only the first-order characteristics of magmatism have been sometimes considered (e.g. Doglioni *et al.* 1999; Wortel & Spakman 2000; Faccenna *et al.* 2001, 2004, 2014; Di Stefano *et al.* 2009; Neri *et al.* 2009; Carminati *et al.* 2010; Giacomuzzi *et al.* 2012). However, the significance of along-strike compositional variation of the magmatism has received little attention. One of the objectives of this paper is to fill this gap, showing how consideration of single magmatic districts and their compositional characteristics can provide constraints to models of the geodynamic evolution of the Tyrrhenian Sea and Apennine–Maghrebide chain.

2. Summary of the geodynamic evolution of the Tyrrhenian Sea area

The Cretaceous to present evolution of the western Mediterranean Sea is the result of the convergence between the African and the European continents and intervening minor plates (e.g. Doglioni *et al.* 1999; Mantovani *et al.* 2002; Carminati *et al.* 2012). This process is responsible for the formation of the Alpine and Apennine chains, and of a number of extensional basins.

According to some researchers (e.g. Doglioni *et al.* 1999; Carminati *et al.* 2010) southward subduction of the European plate beneath Africa and Adria with consumption of the intervening Ligurian–Piedmontese ocean continued until the Eocene (Alpine subduction), when convergence and continental collision occurred along the Alpine–Betic belt (e.g. Dal Piaz 2010). Starting from the Lutetian a new subduction process (Apennine subduction) developed east of the Alpine–Betic collision belt, with northwestward dipping of Ionian oceanic lithosphere beneath the Alpine–Betic retrobelt (e.g. Carminati *et al.* 2010). However, a continuous westward subduction of the Adriatic plate beneath Iberia from the Late Cretaceous has been suggested by other researchers for the Apennine subduction system (e.g. Abbate *et al.* 1994; Buttinelli *et al.* 2014). Whatever the case, the Apennine subduction front migrated southeastward generating back-arc stretching and fragmentation of the Alpine–Betic belt, opening of the Ligurian–Provençal and Valencia basins(40–15 Ma) and separation of the Corsica–Sardinia block from the southern European margin. This was followed by opening of the Tyrrhenian Sea (*c*. 15 Ma to present), the counter-clockwise rotation of the Italian peninsula, and the migration of the Apennine compression front to its present position in the western Adriatic– Ionian area (e.g. Carminati *et al.* 1998, 2010, 2012; Doglioni *et al.* 1998, 1999; Faccenna *et al.* 2001; Cavazza & Wezel 2003; Sartori 2003; Pauselli *et al.* 2006).

Tyrrhenian Sea opening, differential collision of the Adriatic– Ionian foreland and the counter-clockwise rotation of the Italian peninsula generated a longitudinal stretching of the Apennines, seg-mentation of the subduction zone and the formation of several arc sectors separated by transverse tectonic lines of lithospheric importance (Fig. 1). These include the so-called 41° Parallel Line, which divides the northern and southern Tyrrhenian Sea basins, the Tindari–Letojanni fault systems and others (e.g. Serri 1990; Bruno *et al*. 2000; Rosenbaum *et al*. 2008; Turtù *et al*. 2013). It has beensuggested that tear-off fractures of the Adriatic–Ionian subducted slab occur along some of these faults. This allows asthenospheric mantle material to rise to shallower levels where it melts, contributing to the volcanic activity (Rosenbaum *et al*. 2008).

Both oceanic and continental lithosphere have been subducting beneath the southern European margin from the Eocene to present. In the northern sector of the Apennines, an early stage of oceanic crust consumption was followed by continental subduction, which involved about 170 km of lithosphere. In contrast, more than 700 km of oceanic lithosphere (Ionian lithosphere) have been subducted under Calabria and the southern Tyrrhenian Sea from the Eocene to present (Carminati et al. 2005).

Widespread magmatic activity occurred in the Tyrrhenian Sea area from the Eocene–Oligocene to present. It took place along margins of overriding plates (e.g. Aeolian Arc), in back-arc areas (e.g. Tyrrhenian Sea basin) and in the foreland (e.g. Iblei, Sicily Channel) (e.g. Peccerillo 2005; Carminati et al. 2010; Conticelli et al. 2010). Some magmas are directly related to subduction processes, show geochemical signatures typical of arc rocks (e.g. high La/Ta, Th/Nb, Rb/Zr, etc.), and are broadly referred to as ‘oro- genic’ (see the next section). Other magmas, emplaced in back-arc regions or along the African margin, have little or no arc ggeochemical signature (e.g. low La/Ta, Th/Nb, etc.) and are generally referred to as ‘anorogenic’ (e.g. Peccerillo 2005; Lustrino et al. 2013).

Orogenic magmatism related to Apennine subduction processes started in Provence (about 33–19 Ma; Rehault et al. 2012) and progressively shifted to Sardinia (c. 38–15 Ma), the Tyrrhenian Sea basin and the Italian peninsula (about 8 Ma to present), following the eastward retreat of the Apennine subduction front. Petrological compositions of magmas are mainly calc-alkaline, but the younger activity becomes enriched in potassium, with shoshonitic to ultrapotassic magmas abundantly erupted over the last million years (e.g. Lustrino et al. 2004; Peccerillo 2005; Conticelli et al. 2010). Currently active subduction-related volcanism occurs in the central–eastern Aeolian Arc (Vulcano, Stromboli) and in the Neapolitan area (Ischia, Campi Flegrei (Phlegrean Fields), Vesuvius). Some seamounts around the Aeolian Arc (e.g. Marsili) are also probably active. The zone of active volcanism is marked by the occurrence of a deep-focus Wadati–Benioff seismic zone that has been interpreted as related to subduction of the oceanic Ionian Sea floor beneath Calabria and the southern Tyrrhenian Sea (e.g. Panza et al. 2003; Chiarabba et al. 2008). Deep seismicity is virtually lacking in the western Aeolian Arc and in central Italy, and earthquake foci with a maximum depth of about 90 km have been detected beneath the northern Apennines (Carminati et al. 2005). However, the occurrence of subducted crust has been amply documented by VP–VS anomalies all along the Apennine–Maghrebian chain (e.g. Panza et al. 2007; Chiarabba et al. 2008; Neri et al. 2009; Faccenna et al. 2011; Giacomuzzi et al. 2012). Magmatism with 'anorogenic' compositions (12 Ma to present; Beccaluva et al. 2010; Lustrino et al. 2013) is distributed over a wide area from Sardinia to eastern Sicily and the Sicily Channel (Fig. 1). There is no clear age polarity for anorogenic magmas, although currently active volcanism is restricted to eastern Sicily and the Sicily Channel. Compositions range from mafic to felsic with tholeiitic to Na-alkaline and nephelinitic affinities (Lustrino & Wilson 2007). Anorogenic magmas are sometimes spatially associated with older orogenic rocks in some areas. This is particular evident in Sardinia, where a Late Eocene to Middle Miocene orogenic cycle related to the Apennine subduction was followed by Plio-Pleistocene anoro- genic magmatism that was contemporaneous with the main opening stages of the Tyrrhenian Sea (Carminati et al. 2010; Lustrino et al. 2013).

3. Petrological, geochemical and isotopic characteristics of magmatism in Italy

The compositional characteristics and activity of the Italian Plio- Quaternary magmatism have been the subject of many studies (e.g. Kilburn & McGuire 2001; Peccerillo 2005; Alagna et al. 2010; Beccaluva et al. 2010; Conticelli et al. 2010; Lucchi et al. 2013a; Lustrino et al. 2013). Therefore, only a summary of the most prominent data will be given in this paper.

As recalled above, the two broad groups of orogenic and anorogenic magmas have been distinguished, based on geodynamic setting of emplacement zones and compositions. The main characteristics of the two magma types are given Table 1. Some representative analyses are reported in Table 2.

Geochemical data, especially trace element data, allow better definition of these two groups of magmas. Overall, orogenic rocks contain variable abundances of the large ion lithophile elements (LILE: Rb, Cs, Ba, K, Th, U, LREE, etc.) but relatively low amounts of high field strength elements (HFSE: Ti, Ta, Nb, Zr, Hf, etc.). In contrast, ocean-island basalt (OIB)-type 'anorogenic' magmas are enriched in Ta and Nb, relative to LILE. Therefore, LILE/HFSE ratios differ widely between intraplate and arc rocks, and are used to discriminate the two magma types in Italy and elsewhere (e.g. Wood et al. 1979; Pearce 1982; Peccerillo 1985; Rogers et al. 1985; Pearce & Peate 1995; Lustrino et al. 2011). Use of discriminant trace element ratios gives better results if only 'primitive' mafic magmas with high MgO (c. 7–8 wt%) and Mg# (atomic ratio of $Mg/(Mg + Fe^{+2})$ ~ 0.7) are considered. These are little affected by evolutionary processes and are considered as the closest proxies of their mantleequilibrated 'primary' parental magmas.

Unfortunately, primitive rocks are extremely rare in Italy and a lower limit of MgO ≥ 4 wt% is adopted in this paper with the aim of handling a statistically significant number of data. We are well aware that these magmas have undergone significant evolution, which modified their compositional characteristics. However, fractional or equilibrium crystallization does not modify significantly the ratios of incompatible elements (i.e. those elements that strongly prefer to occur in the liquid rather than in the main rock-forming minerals, such as Cs, Rb, Th, U, Ta, Nb, Zr, etc.; e.g. Sha 2012), and radiogenic isotope signatures. Both can be modified by assimilation of wall rocks. It has been demonstrated that assimilation has been occurring in many Italian volcanoes, but the effects on trace element and radiogenic isotope ratios have been modest and much lower than variations exhibited by mafic magmas at regional and sometimes at local scales. Therefore, these variations represent pristine characteristics of magmas. The modest effects of assimilation on geochemical signatures of Italian magmas are due to high concentrations of incompatible elements, which effectively buffer variations of incompatible element ratios and radiogenic isotopes (e.g. Conticelli 1998; Peccerillo 2005; Lucchi et al. 2013b; Peccerillo et al. 2013). Therefore, incompatible element ratios in mafic magmas can be used confidently to infer the composition of primary melts and their mantle sources.

Major elements and classification

A particularly useful scheme to classify mafic (MgO > 4 wt%) Plio-Quaternary volcanic rocks from Italy is a plot of ΔQ v. K2O/ Na2O. Such a diagram, modified after Sahama (1974), is partiparticularly valuable for orogenic magmas (Peccerillo 2005), which have wide ranges of K2O/Na2O ratios and variable degrees of silica saturation. Based on these petrological parameters, orogenic magmas are subdivided into calc-alkaline, shoshonitic, potassic alkaline and ultrapotassic (Fig. 3), with a very few arc tholeiites (Peccerillo 2005). Calc-alkaline and shoshonitic rocks have moderate potassium enrichments, and K2O/Na2O ratios ranging from lower to slightly higher than unity. Potassic rocks are slightly oversaturated to undersaturated in silica, and have intermediate K2O/Na2O ratios between shoshonitic and ultrapotassic rocks. Ultrapotassic rocks (K2O/Na2O > 2.5) are subdivided into Roman- type, kamafugites and lamproites. These three groups differ from each other in the degree of silica saturation as well as in many major element abundances (Table 2), as observed for analogous rock-types worldwide (e.g. Foley et al. 1987; Peccerillo 1992). Roman-type ultrapotassic mafic rocks have high CaO (up to 12– 14%) and Al2O3 (up to 20 wt%) and moderate Na2O (typically 2.5–3.5 wt%).

Kamafugites are strongly undersaturated in silica and show very high CaO (up to c. 20 wt% in the lavas), low Al2O3 (c. 8–12 wt%) and Na2O (c. 0.3–1.2 wt%) and extremely high To sum up, there is an increase in potassium in orogenic magmas from the western to the eastern Aeolian Arc, and from this region to the Neapolitan area and central Italy. Volumes of potassic and ultrapotassic rocks also increase northward, reaching a maximum in Latium where about 900 km3 of predominantly pyroclastic products have been emplaced in less than 0.8 Ma. In contrast, pyroclastic rocks are scarce or absent in Tuscany (Peccerillo 2005). Anorogenic magmas occur in Sardinia, the Tyrrhenian Sea basin (the island of Ustica and several seamounts), Sicily and the Sicily Channel (Fig. 1; Table 1). Rocks in Sardinia range from subalkaline (basalt to rhyolite) to transitional (basalt to trachyte) and alkaline (basanite to phonolite), and have lower CaO and higher K2O and K2O/Na2O than equivalent rocks from Sicily (e.g. K2O/Na2O ratios (up to 30). Lamproites range from slightly undersaturated to oversaturated in silica and have high Mg# (>0.7), rather high silica (SiO2 ~ 55–58 wt%), low to moderate abundances of CaO (c. 2.0–7.0 wt%), Al2O3 (c. 11–16 wt%) and Na2O (c. 1.0–2.0 wt%), and high K2O (typically 6–8 wt%) and K2O/Na2O ratios (up to 5.0). As is obvious, modal mineralogy also differs depending on the type of ultrapotassic magma. Lamproites are plagioclase- and leucite-free rocks and contain phlogopite and sanidine as main potassic minerals. In contrast, Roman-type rocks contain abundant leucite and plagioclase in the mafic compositions and biotite and sanidine in the evolved rocks. Kamafugites are feldspar-free and contain melilite, phlogopite and leucite.

Anorogenic mafic magmas have low to moderate K2O/Na2O ratios and variable degrees of silica saturation. These can be better classified by their normative mineralogy (Yoder & Tilley 1962) as quartz-tholeiites, olivine-tholeiites, Na-alkaline basalts, basanites and nephelinites (normative ne >20%), or by using alkali–silica nomenclature (Le Maitre 2002).

Regional distribution of magma types

Calc-alkaline rocks are almost ubiquitous in central–southern Italy, but are abundant in the Aeolian Arc where basalt, andesite, dacite and rhyolite lava flows and pyroclastic rocks build up large subaerial and submarine stratovolcanoes (Table 1). Shoshonitic and potassic rocks (ranging from trachybasalt to trachyte occur in the central–eastern Aeolian Arc, especially at Vulcano and Stromboli, but are also widespread in Campania, Latium and Tuscany. Roman-type ultrapotassic rocks are con centrated in Campania and Latium, where they form large stratovolcanoes (e.g. Vesuvius, Roccamonfina, Alban Hills and Vico), various monogenetic centres (e.g. Ernici) and some huge multicentre volcanic complexes (Sabatini and Bolsena) consisting of leucite tephrite and leucitite to leucite phonolites. Kamafugites occur as a few melilitite lava flows and pyroclastic deposits forming small monogenetic centres in the internal zones of the central Apennines (e.g. Umbria), where carbonate-rich pyroclastic rocks are also found (Peccerillo et al. 1988; Stoppa & Woolley 1997). Some kamafugites also occur at the Alban Hills (Peccerillo et al. 2010) and Ernici (Boari et al.

2009; Conticelli et al. 2010). Silica-undersaturated strongly alkaline lavas and pyroclastic rocks spanning the Na- and K-alkaline fields occur at the isolated volcano of Mt. Vulture (Fig. 3), associated with carbonatites (Stoppa & Woolley 1997; De Astis et al. 2006; D'Orazio et al. 2007). Finally, lamproitic rocks are restricted to Tuscany (Montecatini, Orciatico, Torre Alfina) with an older outcrop in Corsica (Sisco, 14 Ma), where they form a few small subvolcanic bodies and lava flows, associated with shoshonitic and calc-alkaline lavas, as well as with crustal anatectic magmas (Fig. 1; Table 1). To sum up, there is an increase in potassium in orogenic magmas from the western to the eastern Aeolian Arc, and from this region to the Neapolitan area and central Italy. Volumes of potassic and ultrapotassic rocks also increase northward, reaching a maximum in Latium where about 900 km3 of predominantly pyroclastic products have been emplaced in less than 0.8 Ma. In contrast, pyroclastic rocks are scarce or absent in Tuscany (Peccerillo 2005). Anorogenic magmas occur in Sardinia, the Tyrrhenian Sea basin (the island of Ustica and several seamounts), Sicily and the Sicily Channel (Fig. 1; Table 1). Rocks in Sardinia range from subalkaline (basalt to rhyolite) to transitional (basalt to trachyte) and alkaline (basanite to phonolite), and have lower CaO and higher K2O and K2O/Na2O than equivalent rocks from Sicily (e.g. Beccaluva et al. 2010; Lustrino et al. 2013). Compositions in Sicily range from tholeiitic to Na-alkaline and nephelinitic. Rocks are mainly mafic, but intermediate rocks also occur at Etna and Ustica, and peralkaline rhyolites dominate at Pantelleria. High-P ultramafic xenoliths are found in alkaline rocks from Sardinia and Iblei (e.g. Tonarini et al. 1996; Scribano et al. 2006; Beccaluva et al. 2010; Bianchini et al. 2010; Rocco et al. 2012).

Trace element geochemistry

Normalized diagrams of Italian mafic rocks, in which element abundances of each rock are divided by the concentrations of primitive mantle (Sun & McDonough 1989), are shown in Figure 4. Patterns of upper crustal rocks are also shown to highlight the similarity to some potassic or ultrapotassic rocks (Peccerillo & Martinotti 2006). The profiles of orogenic magmas are characterized by high enrichments in Cs, Rb, Ba, K, Pb and other LILE and negative spikes of HFSE, especially Ta and Nb (Fig. 4a and c). Similar features are also observed in many upper crustal rocks such as global subducted sediments (GLOSS) (Plank & Langmuir 1998) or crustal anatectic rhyolites and granitoids from Tuscany (Fig. 4d). In contrast, anorogenic magmas have a rather smooth upward-convex OIB-type pattern, sometimes with relative depletion in Cs, Rb and K (Fig. 4b). Mount Vulture (Fig. 4c) shows somewhat intermediate characteristics, being relatively depleted in HFSE, similar to orogenic rocks, but also in Rb and K, as observed in some anorogenic lavas (De Astis et al. 2006).

Another important feature emerging from trace element geochemistry is that, unlike many circum-Pacific volcanic arcs that show poorly variable along-strike incompatible trace element ratios (e.g. Miller et al. 1994; Singer et al. 2007), LILE/HFSE and LILE/LILE ratios of orogenic magmas in Italy vary widely, defining different trends for various regions. This is independent of the major element chemistry of magmas (Fig. 5). For instance, calc-alkaline to ultrapotassic rocks from Tuscany have different trace element ratios from the equivalent rocks from Campania and the Aeolian Arc. Another interesting case is that of the calc-alkaline to ultrapotassic rocks from Stromboli, Vesuvius and the Campania volcanoes, which define a single compositional trend for many trace element ratios, and differ from equivalent rocks from elsewhere in Italy. Therefore, incompatible element ratios allow several volcanic regions or provinces to be distinguished in Italy (Peccerillo 2002, 2005). These are schematically shown in Figure 1 and briefly described in Table 1. Many provinces are separated from each other by lithospheric faults, indicated by dashed lines in Figure 1. The newly defined magmatic provinces differ somewhat from those established long ago by Washington (1906), which were based on major element chemistry and mineralogy of volcanic rocks.

Isotope geochemistry

Anorogenic magmas from Etna and other Sicilian volcanoes have low Sr and high Nd isotope ratios (87Sr/86Sr ~ 0.703–0.704; 143Nd/144Nd ~ 0.5132–0.5128), falling close to or within the field of the so-called FOZO (focal zone) and HIMU (high-μ, i.e. high 238U/204Pb) mantle compositions with a trend toward DMM (depleted MORB mantle) (Fig. 6a; for definition of mantle compositions see Zindler & Hart 1986; Hofmann 1997; Stracke et al. 2005). The Plio-Quaternary rocks from Sardinia show a relatively narrow range of Sr isotopic signatures and more variable 143Nd/144Nd, with a few outcrops in southern Sardinia showing higher Nd isotope ratios than the large majority of volcanoes occurring in the central–northern part of the island.

Orogenic magmas define a continuous trend from Sicily to anatectic silicic rocks from Tuscany and the upper continental crust. Single regions plot in discrete fields along the general trend, and there is an overall increase of Sr isotope and a decrease of Nd isotope ratios passing from the western–central Aeolian Arc to Stromboli and the Campania area (Vesuvius, Campi Flegrei, and the offshore islands of Ischia, Procida, Ventotene and Ponza), and to central Italy (i.e. Latium and Tuscany) (e.g. Hawkesworth & Vollmer 1979; Vollmer & Hawkesworth 1980; Bell et al. 2004). Very strong isotopic variations are sometimes observed in mafic rocks from single volcanic areas or from single centres, such as at Ernici (87Sr/86Sr ~ 0.7065–0.7112) and Mt. Cimini in Tuscany (87Sr/86Sr ~ 0.7133–0.7157) (Poli et al. 1984; Frezzotti et al. 2007; Conticelli et al. 2009a,b, 2010, 2011, 2013). Hf and He isotope ratios also show wide ranges of compositions, from typical mantle to upper crustal values, although the number of data for these isotopes is much smaller (e.g. Marty et al. 1994; Gasperini et al. 2002; Martelli et al. 2008; Prelevic et al. 2010).

Lead isotope ratios of anorogenic magmas are also variable (206Pb/204Pb ~ 17.30–

20.00; 207Pb/204Pb ~ 15.50–15.70; 208Pb/204Pb ~ 37.40–39.60). Rocks from Sicily basically plot along the Northern Hemisphere Reference Line (NHRL). Sardinia has unradiogenic Pb isotope signatures close to the so-called EM-1 (Enriched Mantle-1) mantle composition (e.g. Gasperini et al. 2000, 2002; Lustrino et al. 2013), but a few southern occurrences show more radiogenic Pb isotope ratios and plot close to or within the field of Sicily rocks (Fig. 6b and c). Orogenic magmas (206Pb/204Pb ~ 18.50–19.80; 207Pb/204Pb ~ 15.60–15.90; 208Pb/204Pb ~ 38.40–39.80) plot above the NHRL, displaced toward upper crustal compositions such as marine sediments (Ben Othman et al. 1989), Tuscany crustal anatectic rocks (Vollmer 1976) or the basement rocks from Calabria (Rottura et al. 1991; Fig. 6b and c).

On a 206Pb/204Pb v. 87Sr/86Sr (and 143Nd/144Nd) diagram (Fig. 6d), anorogenic magmas from Etna, Iblei and Sicily Channel plot between HIMU, FOZO and DMM. Sardinia plots between FOZO and EM-1. Orogenic magmas define a hyperbolic trend between Etna (and FOZO), the EM-2 mantle composition and the Tuscany crustal anatectic magmas (i.e. the upper continental crust).

Petrogenetic implications of geochemical data

The large ranges of petrological, geochemical and isotopic compositions of magmatism in Italy require heterogeneous sources, and a variety of petrogenetic processes in their origin.

Anorogenic magmatism

OIB-type magmas from intraplate settings have been extensively studied because of the implications for mantle compositions and evolution, and for global geodynamic processes such as eemplacement of mantle plumes (see Foulger 2010). Hypotheses suggested by geochemical and experimental investigations are many and include melting of garnet- or spinel-peridotites at the lithosphere– asthenosphere boundary (e.g. Niu et al. 2011, and references therein), melting of pyroxenite bodies occurring in the upper mantle and derived from old subducted oceanic crust (e.g. Sobolev et al. 2005; Herzberg 2011), and melting of amphibole-rich lith- ologies in the lithosphere or at the lithosphere–asthenosphere boundary (e.g. Pilet et al. 2011; Dai et al. 2014).

Ideas on Italian OIB-type magmatism reflect the wide spectrum of hypotheses suggested for worldwide OIBs. The similarity between Sicily magmas and other OIB-type rocks in Europe has been suggested as evidence for a common origin by melting of mantle diapirs ascending from a very wide high S-wave velocity layer that is at a depth exceeding 400 km beneath Europe (Lustrino & Wilson 2007). This has been named the European Asthenospheric Reservoir (EAR) and it may represent the zone of accumulation of old subducted crust or an ancient plume head (Wilson & Downes 1991; Granet et al. 1995). However, a much deeper mantle plume has been suggested by Montelli et al. (2004) as a source of Etna, which also has a chemical contribution from the nearby Ionian subducting slab, based on boron isotopes and fluid-mobile elements (Tonarini et al. 2001). An origin in a lithospheric mantle strongly modified by metasomatic fluids coming from depth has been suggested for Iblei by some researchers (Trua et al. 1998; Beccaluva et al. 2010), with alkali basalt and nephelinites being formed by lower degrees of partial melting at higher pressures than tholeiites. Finally, the Sicily Channel magmas have been considered to be generated at the spinel–garnet transition zone (i.e. in the local asthenosphere) by Civetta et al. (1998) and Neave et al. (2012). In contrast, an interaction between asthenospheric and lithospheric melts has been suggested by Esperança & Crisci (1995) and Di Bella et al. (2008).

Anorogenic rocks from Sardinia have been divided into two groups, essentially on the basis of radiogenic isotope signatures (e.g. Lustrino et al. 2013). A few occurrences from the south have compositions not far from those of Sicily anorogenic magmas, and a similar provenance from the EAR can be envisaged (Lustrino et al. 2013). Much more puzzling is the origin of EM-1-type mamagmas that represent the bulk of anorogenic activity in Sardinia. Some researchers (e.g. Gasperini et al. 2000, 2002; Bell et al. 2004) advocate melting of mantle plume heads stored for a long time in the mantle, which ascended and melted at shallow levels during Plio-Quaternary times. Others (Lustrino et al. 2013, and references therein) suggest a more complex origin by melting of mantle sources that had undergone interaction with delaminated lower crustal rocks. Decreasing degrees of melting (from about 25 to 5%) at increasing depth (30–80 km) would generate subalkaline to alkaline magmas (Beccaluva et al. 2010, and references therein).

Orogenic magmatism

The wide range of major element compositions shown by the most mafic (i.e. least modified) orogenic magmas in the Tyrrhenian Sea region implies that their parents were generated in mineralogically heterogeneous mantle sources, by variable degrees of partial melting at different T–P–Pfluid conditions (e.g. Peccerillo 1999, 2002; Conticelli et al. 2010).

The high abundance of potassic magmas of ultimate mantle origin is the most striking feature of orogenic magmatism in Italy. Their origin requires that K-rich phases, probably phlogopite, contributed significantly to melts during magma genesis. However, phlogopite (or other K-rich minerals) is generally an accessory phase of upper mantle rocks. This leads to the conclusion that the upper mantle beneath the Italian peninsula has an anomalous, phlogopite-rich composition. The variation of potassium coconcentrationsbserved at both regional and local scales, along with the large range of silica saturation, suggests variable contributions of K-rich minerals to melting, as a consequence of different intensity and type of mantle metasomatism and/or conditions of partial melting (e.g. Peccerillo 1999; Conticelli et al.

2010).

In contrast, the occurrence of calc-alkaline magmas in the western Aeolian Arc and the central island of Lipari calls for scarcity or absence of phlogopite in the mantle sources. Large degrees of mantle melting, triggered by abundant aqueous fluid, can be an additional explanation for the K-poor compositions of these rocks. Somewhat intermediate characteristics between those of the western Aeolian Arc and central Italy can be envisaged for the mantle wedge beneath the eastern Aeolian Arc, where potassic rocks appear, and for the Neapolitan volcanoes where K-rich magmas become abundant.

Experimental studies on simplified phlogopite-bearing mantle systems demonstrated that phlogopite melts incongruently giving potassium-rich melts with increasing degree of silica undersaturation at increasing pressure (Wendlandt & Eggler 1980a,b). This led to the suggestion of an origin of potassic and utrapotassic magmas in Italy by melting of phlogopite-bearing mantle rocks at pressures increasing from the oversaturated (lamproites) to undersaturated (kamafugites) magmas (e.g. Peccerillo et al. 1988). Other experiments have substantiated this hypothesis. Conceçao & Green (2004) investigated phlogopite + pargasite-bearing lherzolite and demonstrated that moderate degrees of melting (about 8% melt fraction and 4.5% H2O) at 1–1.5 GPa give silica-oversaturated moderately potassic liquids with compositions similar to shoshonites. Silica-oversaturated melts richer in potassium (K2O up to 6.7 wt%) and with K2O/Na2O ~ 1.0–6.7 (i.e. spanning the shoshonitic to lamproitic fields; Fig. 3) were obtained by Condamine & Médard (2014) by fluid-absent melting of phlogopite-bearing lherzolite and harzburgite at 1 GPa. Multiple-saturation studies exploring the liquidus phase relationships of ultrapotassic undersaturated rocks at high pressures with the presence of H2O + CO2 found that undersaturated magmas such as kamafugites or olivine lamproites can be formed by partial melting of phlogopite-bearing lherzolite or wehrlite at pressures around 2.5–3.5 GPa and temperature around 1000–1300°C (e.g. Edgar et al. 1976, 1980;

Thibault et al. 1992). It has to be noted, however, that high undersaturation for some rocks may also depend on shallow-level carbonate assimilation, a process well documented in some ultrapotassic volcanoes (Iacono Marziano et al. 2008; Peccerillo et al. 2010).

Trace element data give distinct and complementary information magma genesis and compositions of magma sources. A main incompatible trace element feature of all the mafic rocks from the Aeolian Arc and the Italian peninsula is their high LILE/ HFSE ratio, a typical arc signature. It is generally agreed that this signature reflects contamination of the mantle wedge by material released from subducted slab (e.g. Kessel et al. 2005; Grove et al. 2012). The nature of the slab and the mechanism of element transfer (H2O-rich fluids, supercritical fluids, hydrous melts, bulk-rock) can be variable and it has been concluded that the range of oro- genic rock compositions in Italy denotes modification of one or more of these factors for the different volcanic regions (e.g. Peccerillo 1999, 2002).

An important piece of information on the nature of mantle wedge contamination comes from Sr–Nd–Pb isotope variations of orogenic rocks that define mixing trends between FOZO (Etna) and the upper continental crust (Fig. 6). This provides a robust indication that mantle–crust interaction played a key role in the genesis of orogenic magmas. Northward increase of Sr isotope ratios and decrease of Nd isotope ratios suggest that the upper crustal contribution was minimal in the western sector of the Aeolian Arc and reached a maximum in southern Tuscany.

Interaction between crust and mantle end-members can occur during magma ascent to the surface (magma contamination) and/or by introduction of upper crustal material into the mantle, essentially during subduction (source contamination). Many studies have demonstrated that much of the regional variability of radiogenic isotope ratios in Italy is the effect of source contamination. As discussed above, magma contamination processes were ubiquitous, and had strong effects on oxygen isotope composition but not on Sr–Nd–Pb radiogenic isotope and incompatible element ratios (e.g. Rogers et al. 1985; Conticelli et al. 2002; Peccerillo 2005, and references therein).

Main petrogenetic conclusions

The main conclusions on the origin of Plio-Quaternary magmatism in Italy arising from major element, trace element and isotope data can be summarized as follows.

(1) Two broad groups of magmas, defined as orogenic and anorogenic, coexist in Italy. They have been erupted in distinct tectonic settings, and display different petrological and incompatible trace element signatures.

(2) Anorogenic magmas range from subalkaline to Na-alkaline and nephelinitic. Some rocks (e.g. in Sicily, Sicily Channel, Ustica) resemble very closely intraplate volcanic rocks occurring in several places in Europe and are supposed to derive by melting of diapirs ascending from a wide mantle layer (European Asthenospheric Reservoir) that is at depths exceeding 400 km. A few anorogenic rocks in southern Sardinia have composition and origin similar to those of Sicily magmas. In contrast, the bulk of the magmatism in the island shows EM-1 type isotope signatures that are unique in Europe and may originate by melting of a deep mantle plume or of an upper mantle modified by interaction with delaminated lower crustal rocks. Magmas were formed at variable depth in the local asthenosphere–lithosphere, with alkaline magmas being formed by lower degrees of melting and at greater depths than subalkaline magmas.

(3) Orogenic magmas range from calc-alkaline to ultrapotassic and display very variable major and trace element and radiogenic isotope signatures. These reveal mineralogically and geochemically and heterogeneous mantle sources.

(4) Radiogenic isotope data for orogenic magmas define mixing trends between Etna (FOZO) and the upper continental crust. This clearly suggests interaction between crust- and

mantle-derived components. The most likely explanation is that upper crustal material was added to the mantle source of orogenic magmas by subduction processes. Northward increase of Sr iso- tope and decrease of Nd–Pb isotope ratios suggest that crustal contribution to orogenic magmatism increases northward, with a maximum in southern Tuscany. In this region, Mg-rich mantle-derived rocks show trace element and radiogenic isotope signatures overlapping those of crustal anatectic magmas occur- ring in the same region.

(5) Values of trace element and radiogenic isotope ratios show strong regional variations, especially for orogenic magmas, and allow several compositionally distinct sectors (or magmatic provinces) to be distinguished. These reveal strong lateral heterogeneities of the mantle source compositions and are suggested to reflect the different nature of mantle metasomatic events, and various mechanisms of element transfer from the slab to the mantle wedge.

Element transfer and crust–mantle interaction in subduction zones

The petrogenetic framework summarized above has gained a gegeneralthough not unanimous acceptance among petrologists, at least for most of the first-order issues (e.g. Peccerillo 1999; Conticelli et al. 2002, 2010; Peccerillo et al. 2010; Lustrino et al. 2011; but see Bell et al. 2013). However, many problems remain, especially for orogenic magmatism. These pertain mainly to the mechanism of slab to mantle element transfer and to the petrogenetic and geodynamic significance of compositionally distinct magmatic provinces. Here, we briefly summarize studies on element behaviour and modalities of material transfer from slab to the mantle wedge in the subduction environment, as preliminary steps to the discussion of the subduction factory in Italy and the reasons for regional variation of magmas.

Element transfer in the subduction environment

Several experimental studies have been devoted to element mobility at high P–T conditions of subduction environments (e.g. Tatsumi et al. 1986; Schmidt & Poli 2003; Manning 2004; Bebout 2007, 2013; Gao et al. 2007; Antignano & Manning 2008). Among C–O–H volatile species, water is the dominant component and a main element-transfer agent, and its behaviour determines the type and amount of element transfer to the mantle wedge and magma generation in subduction zones (e.g. Poli & Schmidt 2002; Grove et al. 2012). Water can move as a relatively diluted solution, as a silicate-rich (supercritical) fluid (e.g. 50% silicates, 50% H2O) and in hydrous silicate melts (Manning 2004; Kessel et al. 2005; Sanchez-Valle 2013; Frezzotti & Ferrando 2015) depending on P and T conditions during subduction. Experimental studies have documented that at shallow depths typical of forearc settings (i.e. <100 km) aqueous fluids have a limited capability to transport chemical elements, although they are able to strongly fractionate fluid-mobile LILE over less mobile elements such as Th, REE and, in particular, HFSE (Kessel et al. 2005). Therefore arc magmas with low total abundances of incompatible elements but with high LILE/HFSE, and high Ba/Th, Rb/Th and Ba/La ratios, may be indicative of mantle sources that had been metasomatized by aqueous fluids released at relatively low P–T. At greater pressures (i.e. >100 km depth) and temperatures, silicate-rich supercritical aqueous fluids or hydrous silicate melts are the important carriers of chemical components. Kessel et al. (2005) demonstrated that the trace element load of aqueous fluids released from K-free MORB at 4–6 GPa and 700–1200°C is similar to that of hydrous melts. They are also characterized by high LILE/HFSE (e.g. Johnson & Plank 1999; Rudnick et al. 2000; Hermann & Rubatto 2009) but do not fractionate some LILE such as Ba, La and Th. Thus, high concentrations of LILE and poorly variable LILE ratios such as Ba/Th and Ba/La can be indicative of enrichments by supercritical fluids or hydrous silicate melts.

Although a significant release of pore and loosely bonded water occurs at shallow depths below 20 km, transfer of water and other components from the slab to the mantle wedge depends on the amount and nature of the hydrous phases that become unstable at increasing P–T conditions, and hence on the temperature distribution in the subduction environment. Relative trace element abundance in the slab fluids is governed by progressive break- down of subducted mineral phases at increasing temperature, such as phengite (LILE, and Ba), epidote (REE, Sr, Th, Pb), lawsonite (REE, Sr, Pb, Th, U), and allanite–monazite (La, Ce, Th) (Schmidt & Poli 1998, 2003; Hermann 2002a,b; Hermann et al. 2006; Hermann & Spandler 2008; Hermann & Rubatto 2009; Martin et al. 2011). On the other hand, the HFSE depletion is related to the stability of HFSE-rich minerals such as zircon (Zr, Hf) and rutile (Ti, Nb, Ta).

The complex dehydration reactions occurring in the slab are best summarized in a MORB + H2O phase diagram reporting predicted metamorphic facies and stability fields of hydrous phases for different slab P–T subduction paths (Fig. 7; Maruyama & Okamoto 2007, and references therein). Progressive water release at forearc depths from subducted crustal lithologies, such as metabasalts and metasediments, occurs only in relatively warm active subduction zones, corresponding to P–T paths 3 and 4 in Figure 7, which are the only geotherms to cut the wet solidus at sub-arc depths. These P–T paths, however, differ from thermal models of many modern subduction zones. Cooler and more com- mon geotherms do not cross the wet solidus at shallow depths, and the upper part of the slab crosses the blueschist to lawsonite- or zoisite-eclogite facies fields (P–T paths 1 and 2 in Fig. 7). According to Poli & Schmidt (2002), blueschists can contain 4 wt% H2O and release 3 wt% of water at eclogite transformation above 2 GPa (path 1 in Fig. 7). Therefore, during progressive cold subduction most of the incompatible element (e.g. K, LILE) budget can remain in stable hydrous phases contained in crustal lithologies (e.g. amphibole, phengite, epidote, lawsonite). As a consequence, whereas the amount of released fluids diminishes, the amount of solutes increases with depth.

In most active arcs, subducting crust consists of various proportions of basaltic and sedimentary rocks. Therefore, the modal proportions of hydrous phases vary considerably, depending on the composition of the downgoing slab, and are different for MORB-type crust, MORB + sediments and continental crust (e.g. Hacker 2008; van Keken et al. 2011). In volcanic areas that contain abundant potassic magmas with high LILE contents, one of the distinctive features of Italian magmatism, a major role for a K- and LILE-rich phase as source of these elements is required in the slab. Such a phase is best represented by phengite, which governs about 90% of the K and Rb budget in ultrahigh-pressure (UHP) metamorphic rocks. Its abundance is much greater in metasediments than in MORB, and its stability field extends to high P–T conditions (Fig. 7). Phengite breakdown along the deepest tracts of subduction zones generates fluids rich in LILE that are added to the mantle wedge at high pressure, favouring the formation of K-rich hydrous phases. Mantle phase relations in a CO_2–H_2O-saturated K-doped peridotite have been recently experimentally determined by Tumiati et al. (2013). The resulting model predicts metasomatic phase assemblages, and partial melting behaviour for phlogopite- and COH-bearing lherzolite, at redox conditions of wedge peridotites (see Malaspina et al. 2010). According to this study, olivine, orthopyroxene, phlogopite, and carbonates represent ubiquitous phases in a mantle wedge flushed by H_2O–CO_2 carbon-saturated fluids (Fig. 8). Phlogopite is one of the first phases to disappear over the solidus, indicating that early formed magmas have potassic compositions. Interestingly, if solidus conditions are attained at P > 2 GPa, near-solidus initial melts are carbonate-rich in composition (Fig. 8).

Physical models of slab–mantle wedge interaction

MORB are the main subducting rock types in many active volcanic arcs, but various amounts of sediments and slices of continental crust are also involved (e.g. Tera et al. 1986; Morris et al. 1990; Hacker 2008). Sediments and upper continental crust are much more enriched in incompatible elements than MORB and, therefore, fur-furnish bulk of incompatible element budget to the mantle wedge (Hermann et al. 2006; Bebout 2007, 2013; Hermann & Rubatto 2009; Marschall & Schumacher 2012). They are also able to modify dramatically radiogenic isotopic signatures of mantle peridotite.

Experimental investigations, geochemical studies and numerical modelling have suggested distinct physical and chemical frameworks of element transport from slab to mantle wedge. Most models suggest that hydrous fluids, supercritical fluids and/or H2O-rich melts are released from the subducting slab, migrate to the overlying mantle wedge, react with peridotite to promote incompatible element enrichment and partial melting ('flux melt- ing'; e.g. Schmidt & Poli 1998; Kessel et al. 2005; Kelley et al. 2010; Gerya & Meilick 2011). Fluids can originate from all types of subducted rock mentioned above, including altered oceanic crust, various types of sediments, and slices of upper continental crust (e.g. Hacker 2008). Radiogenic isotope signatures of erupted magmas can give information on source rocks of fluids.

Modelling of the geodynamic regimes during subduction fur- ther illustrates how element transfer from slab to mantle wedge can occur by a two-stage process where physical mixing between slab rock and peridotite is followed by mantle modification and melting at shallower depth in the mantle wedge (e.g. Gerya et al. 2006; Castro & Gerya 2008; Castro et al. 2010; Marschall & Schumacher 2012). During a first stage, various types of subducted rocks (basalts, sediments, slices of continental crust) are transported along the subduction channel to the mantle wedge where they mix with peridotite to form hydrous mélanges at the slab–mantle interface. The low density of mélange triggers instability and the formation of cold diapirs or 'plumes' that buoyantly rise toward the hotter corner of the mantle wedge. Here, plumes release aqueous fluids and melts that flux the plume margins and the overlying mantle peridotite. Melting occurs essentially at margins of the dia- pirs and in the overlying peridotite, both fluxed and enriched in mobile elements. Therefore, the volatile-element enrichments observed in many arc rocks would reflect release of fluids from the internal parts of diapirs, rather than or in addition to direct flow from the slab. Conversely, those magmas enriched in some poorly mobile elements such as Th, Be and REE could be derived by melting of dehydrated diapir rocks (Marschall & Schumacher 2012). Experimental studies have shown that melting in the ascending mixed diapirs produces silicic magmas with trondhjemite and granodiorite compositions, which can be responsible for formation of the Cordilleran-type granitoid magmatism occur- ring in many orogenic areas (Castro et al. 2010).

6 Origin of orogenic magmatic provinces in Italy

The petrological and geochemical variability of orogenic rocks in Italy requires different roles of several components in the origin of the magmatism as well as different physical models of mantle wedge contamination and partial melting. Here we focus on single volcanic provinces to constrain components involved in magmatism, and discuss models of mantle metasomatism and partial melting that better fit the observed petrological, geochemical and field evidence.

Western–central Aeolian Arc

The dominant calc-alkaline mafic to intermediate rocks in the western Aeolian Arc and the central island of Lipari, the low abun- dances of LILE relative to other orogenic rocks in Italy, as well as the Sr–Nd–Pb isotope signatures close to FOZO and Etna, all suggest an origin of parent magmas by high degrees of melting in a mantle wedge fluxed by fluids released from a MORB-type slab, with little or no participation of sediments (De Astis et al. 2000; Peccerillo et al. 2013). The negligible role of sediments makes improbable a model of subduction–mélange diapir formation, which requires for its initiation thick piles of sediment (see Behn et al. 2011). Therefore, the most suitable physical model of wedge metasomatism in the western Aeolian Arc is the release of H2O- rich fluid by an oceanic slab at shallow depths, and fluid influx into the mantle wedge that promotes moderate LILE enrichments and large degrees of partial melting. Low concentrations at normal (N)-MORB level of some fluid-immobile elements, such as the HFSE Ta and Nb, in some islands (Salina and Lipari) suggests a depleted MORB-type pre-metasomatic mantle. However, higher abundances of these elements at Alicudi (up to 10 times primitive mantle; Fig. 4c) has been interpreted as evidence for a role of OIB- type components, possibly provided by inflow of asthenosphere from the foreland or from the Tyrrhenian Sea back-arc region (Peccerillo et al. 2013).

Stromboli and Campania volcanoes

Active volcanism occurs in this area, which is also characterized by a Wadati–Benioff seismic zone with earthquake foci increasing northwestward and reaching depths of about 450 km beneath the southern Campania area (e.g. Chiarabba et al. 2008). The dominance of shoshonitic and K-alkaline magmas in this area and the higher Sr and lower Nd–Pb isotope ratios imply that the mantle sources were more enriched in upper crustal material than those in the western–central Aeolian Arc. On the other hand, Ba/Th and Ba/La ratios reach high values in this region, a feature that is typically attributed to aqueous fluids. This all suggests that fluids released by a MORB-type slab and metasediments were responsible for source metasomatism in this area (e.g. Tommasini et al. 2007; Peccerillo et al. 2013). The increase in potassium from Stromboli to Vesuvius suggests that the bulk of potassium was released away from the subduction front. Such a process could be related to the wide stability field of phengite. This formed in the subducted metasediments (e.g. Behn et al. 2011), survived to great depths along the subduction zone, and broke down at high P–T to release its load of K–Rb above the deepest sectors of the slab. A role for an OIB-type component is suggested by high contents of the HFSE Ta and Nb (Serri 1990; De Astis et al. 2000, 2006). Such a component has been provided by inflow of asthenospheric mantle from the African plate, around the margin of the subducting slab (Peccerillo 2001; Peccerillo et al. 2013).

Mount Vulture

This isolated volcano is situated in a particular geodynamic setting, at the margins of the southern Apennine thrust front and on the western edge of the Apulia foreland (Fig. 9). Its peculiar tectonic setting is reflected by magma compositions that are different from those of any other Italian volcano. The Vulture rocks range from K- to Na-rich, and have many subduction-related geochemical signatures such as high Th/Ta and LREE/Nb, but are also depleted in K and Rb, as are many OIB-type rocks (Fig. 4). Some carbon- atites are also present, a unique case for subduction-related envi- ronments (Stoppa & Woolley 1997; D'Orazio et al. 2007). Therefore, geochemical data suggest equal contributions by both subduction-type and OIB-type components, in agreement with the peculiar geological setting of this volcano (De Astis et al. 2006). The causes of partial melting are also still poorly understood. There is no clear evidence of extension and associated mantle upwelling that could indicate decompression melting. Neither there are seismic indications of active subduction in the area. A solution could be that magmatism is related to redox mantle melt- ing, as hypothesized by Foley (2011) for several magmas, includ- ing carbonatites. Redox melting is unlikely in subduction settings because of the low thermal gradients. However, in this case active subduction has ceased and a tear-off of the slab has been hypoth- esized (see next section) with an increase of temperatures that may have triggered redox melting.

The Roman Province

Overall, the abundance of potassic magmatism, incompatible element patterns and radiogenic isotope signatures close to GLOSS and upper continental crust (Taylor & McLennan 1985; Plank & Langmuir 1998) suggest widespread mantle contamination by sub- ducted upper crustal components in the Roman Province. A mantle composition similar to the Alpine orogenic peridotites of Finero and Ulten (e.g. Zanetti et al. 1999; Rampone & Morten 2001) that have phlogopite as the main K-bearing metasomatic phase, often coexisting with amphibole and carbonates (Sapienza et al. 2009), can be envisaged for the source of Roman magmas. Experimental evidence discussed above suggests that melting of phlogopite- bearing lherzolite or wehrlite at high pressure generates undersaturated ultrapotassic magmas, whereas melting at lower pressure produces potassic melts (Wendlandt & Eggler 1980a,b; Conceçao & Green 2004; Condamine & Médard 2014). The large volumes of erupted magmas and the strong explosivity index of volcanism require wide sections of mantle melting and occurrence of high quantities of volatiles in the source, probably H2O and CO2.

Geochemical modelling based on trace element ratios and Sr isotope signatures led to the suggestion of mixed carbonate–silicic sediments (marls) as likely contaminants in the Roman Province (Peccerillo et al. 1988), a hypothesis supported by recent investigation (e.g. Avanzinelli et al. 2009). Marly sediments provide both H2O and CO2 to the mantle wedge. Moreover, melts at 8 GPa from marls have incompatible element patterns similar to Roman rocks (Grassi et al. 2012) and could be suitable contaminants for the mantle wedge in this region. Introduction of H2O + CO2 lowers the solidus of peridotite more than is done by H2O or CO2 alone (Foley et al. 2009), thus promoting extensive melting and favouring large-scale explosive volcanism. It should be noted that the foreland in this sector of the Apennines is represented by the Adriatic plate, which has continental-type characteristics, distinct from the oceanic-type Ionian Sea foreland (e.g. Panza et al. 2007; Giacomuzzi et al. 2012; Speranza et al. 2012).

Poorly variable and crustal-like Ba/Th, Ce/Sr and other element ratios indicate that there was no fractionation among these incompatible trace elements. This requires extensive breakdown and participation in melting of both Ba- and Th–REE-rich phases such as phengite and allanite, which can be accomplished by transfer to the mantle wedge by melted metasediments or supercritical fluids. In contrast, variable LILE/HFSE ratios such as La/Nb and Th/Ta, which reach values not observed in any common rocks, require that some phases containing Ta–Nb were left in the residue at
some stage of magma formation and/or contamination of mantle sources by sedimentary materials (e.g. Grassi et al. 2012).

The formation of phlogopite in the mantle wedge is related to input of potassium by breakdown of K-rich phases, especially phengite. The absence of calc-alkaline magmas in the Roman Province suggests little loss of aqueous fluids at shallower depths. In the case of subduction along a low geothermal gradient not only partial melting of crustal rocks in the slab is not expected, but also dehydration is limited, as subducting oceanic and continental rocks retain most of the LILE-rich hydrous phases (e.g. lawsonite, phengite, and epidote sensu lato) to a depth greater than 90–100 km (Fig. 7). This has been seen clearly in high-pressure (HP)–UHP complexes from the Alpine belt, which have subducted along a cold geotherm (5–7° km^{-1}) to depths greater than 100 km and do not show depletion of most LILE (e.g. Rb, Ba, Sr, Th, U) compared with bulk sediment or upper crust composition (Busigny et al. 2003; Ferrando et al. 2009; Frezzotti & Ferrando 2015).

The proposed model for the origin of magmatism in the Roman Province can be explained by mantle phase relations expected in a CO_2–H_2O-saturated K-doped peridotite system, illustrated on a subduction geodynamic model (Fig. 8; Tumiati et al. 2013, and references therein). Large amounts of carbonate and pelitic sediments from the Adriatic plate are transported and mixed along the subduction channel to the mantle wedge. Mixing of sedimentary components is required by the poorly variable compositions for radiogenic isotopes of Roman magmas. Rayleigh–Taylor instability is triggered in the metasedimentary pile and evolves in diapiric structures that ascend buoyantly into the mantle wedge. Melt and/ or fluid from the diapir interact with the surrounding mantle, extensively modifying its mineralogical and geochemical composition. Release of K and incompatible elements occurs by dissolution or melting of phengite, which did not undergo breakdown during subduction, as the temperatures necessary for dissolution or melting of hydrous phases were not reached at the top of the actively subducting slab. Partial melting of a mineralogically and geochemically heterogeneously enriched hydrous mantle at pressure higher than 1.5–2 GPa would generate K-rich magmas. Very subordinate fractions of carbonate-rich melts can be generated if such a C–O–H–K-rich mantle wedge reaches temperatures only slightly above its solidus (Fig. 8; Tumiati et al. 2013). These low fractions of melts, being extremely reactive, are not supposed to reach the surface unless extremely violent eruptions occur (Frezzotti & Touret 2014). In contrast, it is much more plausible that carbonate-rich melts are consumed on reaction with mantle minerals, providing a source for fluxes of CO_2 towards the exo-sphere (Frezzotti et al. 2009, 2011; Frezzotti & Touret 2014). This can explain the large CO_2 degassing in the Roman Province (e.g. Frezzotti et al. 2010; Chiodini et al. 2013).

The Intra-Apennine Province

The few monogenetic volcanoes with ultrapotassic kamafugitic compositions occurring in the internal zones of the central Apennines (Umbria, Abruzzi and Latium regions) display incompatible trace element patterns and radiogenic isotope signatures that are very similar to those of mafic rocks of the Roman Province. This suggests a similar origin and geodynamic significance. The low abundances of Na2O and Al2O3 and the high CaO of kamafugites have been explained by assuming that the parent rock of the magmas was formed by a restitic harzburgite that had been affected by re-fertilization by CaO-rich sedimentary material (Peccerillo et al. 1988). Some carbonate-rich pyroclastic rocks have been observed in the Intra-Apennine Province and may represent carbonatitic magmas (e.g. Stoppa & Woolley 1997), whose presence is expected in the mantle model reported in Figure 8. However, there is strong geochemical isotope and geological evidence suggesting that carbonate-rich rocks in the internal zones of the Apennines are kamafugitic magmas that have undergone considerable interaction with sedimentary carbonates (Peccerillo 2005, and references therein).

Ernici and Roccamonfina

This zone is here considered as a geographical and petrological transition zone from Stromboli–Campania to the Roman Province (see also Peccerillo 2002, 2005). The small volumes of exposed magmas have contrasting geochemical features. Some rocks have calc-alkaline to potassic compositions, with trace element and isotopic signatures similar to those of analogous rocks from Stromboli–Campania volcanoes; others are similar to ultrapotassic Roman-type and kamafugitic rocks (Frezzotti et al. 2007; Boari et al. 2009; Conticelli et al. 2009b; Nikogosian & van Bergen 2010). Notably, the calc-alkaline and shoshonitic magmas are younger than the ultrapotassic activity (Boari et al. 2009). The occurrence of variably enriched magmas suggests a com- plexly zoned upper mantle affected by superimposition of multi- ple metasomatic events with Roman-type and Campania-type characteristics.

Tuscany

This magmatic province is characterized by the occurrence of both mantle-derived and crustal anatectic magmas (e.g. Poli 2004), and exhibits some of the most puzzling and apparently contrasting petrological and geochemical features observed in Italy. Mantle-derived magmas, ranging from calc-alkaline to lamproitic, show very primitive compositions (Mg# up to 75; Ni up to 300–400 ppm, Cr up to 600–700 ppm in poorly porphyritic or aphyric rocks), and sometimes contain mantle-derived ultramafic xenoliths (e.g. Peccerillo et al. 1988; Conticelli 1998). However, these rocks also show the closest similarities to upper crustal rocks for incompatible element and radiogenic isotope signatures (Figs 4 and 5). Volumes of magmatic rocks are modest and there is scarcity to absence of pyroclastic products, two features that contrast with the large-volume and highly explosive volcanism of the Roman Province and other volcanic regions in Italy. Peccerillo et al. (1988) demonstrated that some key geochemical and isotopic signatures of Tuscany mafic magmas (e.g. Ce/Sr, Rb/Sr, Sr isotope ratios) could be successfully modelled by assuming a mantle source contaminated by large amounts (at least 20 wt%) of metapelites or analogous upper crustal rock types (e.g. S-type metagranites), with little or no participation of carbonates. The close similarity of incompatible element patterns between Tuscany mafic rocks and metasediments (Fig. 4) requires extensive element transfer to the mantle wedge, which can be accomplished by large degrees of sediment melting (Peccerillo & Martinotti 2006). Such a contamination process is strikingly distinct from that envisaged for the nearby Roman and Intra-Apennine provinces, a conclusion corroborated by recent geochemical and isotopic investigations (Conticelli et al. 2002, 2010; Avanzinelli et al. 2009; Prelevic et al. 2008, 2010). Moreover, the highly 'primitive' characters of some rocks, especially lamproites, and their moderate or low concentrations of Na2O and CaO suggest a residual harzburgite as the pre-metasomatic mantle rock, probably representing the local lithosphere (e.g. Peccerillo et al. 1988).

The participation of abundant silicic material (such as meta-granites, metapelites or turbidites) in contamination of the mantle wedge in Tuscany favours a model of transport of bulk upper crustal rocks along the slab and formation of cold diapirs by Rayleigh– Taylor instability (Gerya & Yuen 2003; Marschall & Schumacher 2012). We suggest that mafic magmas with variable enrichments in potassium, incompatible elements and radiogenic isotopes originated from mantle rocks inside or around the mélange diapir, which were affected by different intensities of metasomatism by silicic melts from the sedimentary components of the plume.

7 Geodynamic implications

Careful consideration of orogenic magmatism and its variation at the local and regional scales can give important information to help clarify mantle dynamics and the nature of the subduction processes in Italy. A synthesis of the relationships between magmatic provinces and subduction processes along different arc sectors of the Apennine–Sicilian Maghrebide chain is schematically shown in Figure 9.

The Tindari–Letojanni tectonic line is a main cross-arc structural divide between the western and eastern sectors of the Aeolian Arc, which show distinct volcanological, petrological and geochemical features. The low to moderate enrichment in incompatible elements and the mantle-like isotope signatures of calc-alkaline magmas in the western Aeolian Islands have been interpreted as an indication of mantle sources fluxed by low-pressure aqueous fluids released from a MORB-type crust. VP tomographic models suggest the occurrence of a discontinuous slab in the upper mantle, with the shallower and deeper segments separated by a low-velocity anomaly (e.g. Faccenna et al. 2001; Neri et al. 2009). We suggest that the deep slab could represent a detached fragment of the oceanic crust, which dehydrated at shallow depths to promote magmatism and is now sinking into the mantle, giving sporadic seismic activity (Orecchio et al. 2014).

Stromboli and the Campania volcanoes share many geochemical and isotopic signatures, which support an origin in compositionally similar sources (Peccerillo 2001). Geochemical data are best explained by assuming mantle wedge contamination by fluids coming from a MORB-type crust plus sediments. The occurrence of OIB-type trace element signatures in the Stromboli and Campania volcanoes has led to the suggestion of an inflow of asthenosphere from the Ionian plate into the mantle wedge, across a slab window (De Astis et al. 2000; Peccerillo 2001; Peccerillo et al. 2013). Notably, a slab window has been also modelled by geophysical data (e.g. Chiarabba et al. 2008; Neri et al. 2009; Giacomuzzi et al. 2012), providing an interesting case of similar conclusions reached by distinct and independent geochemical and geophysical investigations. The geochemical affinities between Stromboli and Campania support a geodynamic model suggesting that a single continuous slab was initially subducting beneath the southern Apennines and the eastern Aeolian Arc, from the Apulia block to the Ionian Sea. A tear in the slab occurred in the Apulia sector and propagated horizon- tally southward, according to a mechanism of slab detachment as described by Wortel & Spakman (2000) and Spakman & Wortel (2004). The southern segment of the slab, still attached to the Ionian foreland, collapsed inside the upper mantle, retreated southeastward, and dehydrated to induce partial melting beneath the eastern Aeolian Islands to Campania. Sinking and southeast-ward retreat of the slab also promoted suction of asthenospheric Ionian mantle around the margin of the slab (e.g. Gvirtzman & Nur 1999; Panza et al. 2007; Peccerillo et al. 2013). Mount Vulture is located in the northern edge of the slab tear zone and its magmas are the result of interaction between comparable amounts of OIB and subduction components. OIB components could be provided by mantle inflow from the foreland, whereas the subduction component was probably furnished by fragments from the sinking margins of the detached slab. The two components are characterized by distinct redox conditions, which could have triggered partial melting (Foley 2011) favoured by increasing ambient temperature following slab detachment.

Ernici and Roccamonfina volcanoes are located between Campania and the Roman Province, behind a second-order arc situated between the major arcs of the northern Apennines and southern Apennines–Calabria (e.g. Satolli & Calamita 2008). Magmatism is scarce and CO2 flux and heat flow are much lower than in Campania, Latium and Tuscany (Della Vedova et al. 2001; Chiodini et al. 2013). Rock compositions show similarities to those of Roman and Campania volcanoes (e.g. Frezzotti et al. 2007; Boari et al. 2009; Conticelli et al. 2009b). Moreover, VS anomalies, which are well observed in the upper mantle beneath the southern and northern Apennines, are absent or less clear in the Ernici–Roccamonfina area (Giacomuzzi et al. 2012). We suggest that the upper mantle in this sector was affected by two stages of metasomatism, respectively related to subduction processes of the northern Apennine and southern Apennine–Ionian slabs. The younger age of calc-alkaline and shoshonitic volcanoes with respect to Roman-type ultrapotassic rocks may reflect a younger age for the Campania-type metasomatic event.

The Roman Province and the Intra-Apennine volcanoes are both the effects of mantle metasomatic modification by addition of abundant mixed carbonate–siliceous sediments to lherzolite and harzburgite. These sediments were provided by the subduction of the Adriatic plate beneath the northern Apennines, a process that started in the Miocene, after consumption of the oceanic crust (e.g. Carminati et al. 2010). Because the subduction front in the western Adriatic Sea is very close to volcanic areas, a steeply dipping slab could be inferred. However, we envisage that sediment subduction and mélange diapirs could have formed further away from the sub- duction front, and were successively shifted eastward by corner flow processes.

Finally, the calc-alkaline to ultrapotassic magmas of the Tuscany Province are contiguous, partially coeval and overlapping in space with the Roman Province (Fig. 1; Table 1). However, there is strong compositional and volcanological discontinuity between the two provinces, which suggests different mantle contamination histories.

The timing and the physical model of mantle metasomatism in Tuscany are debated. Serri et al. (1993) accepted that different types of sediments contaminated the upper mantle beneath Tuscany and the Roman Province, but suggested that both were related to the Miocene to Quaternary subduction and delamination of the Adriatic plate. However, this leaves unexplained why the two provinces show strikingly different petrological, geochemical and volcanological characteristics. Therefore, distinct modalities of contamination processes are required by geochemical data.

Peccerillo & Martinotti (2006) noticed that an association of lamproitic, calc-alkaline and shoshonitic rocks, with compositions similar to those in Tuscany, also occurs in the Western Alps (about 30 Ma) and in the Betic Cordillera of southeastern Spain (from 23 to 6 Ma; see Prelevic et al. 2008, 2010). The close compositional affinities between all these occurrences were interpreted evidence for a similar style and a single stage of mantle contamination. It was suggested that contamination of the upper mantle in these zones took place during the east-verging Cretaceous– Oligocene subduction of the European plate beneath the African margin, when Tuscany, the Betic Cordillera and the Western Alps represented the border of the overriding Alpine–Betic belt (e.g. Carminati et al. 2010). Successively, the new west-verging Apennine subduction of Ionian lithosphere started east of the Alpine collision zone, which was dismembered, subjected to lithospheric boudinage and dragged eastward by back-arc spreading. It has been long recognized that Tuscany is a portion of the Alpine chain that migrated eastward during opening of the northern Tyrrhenian Sea behind the Apennine compression front (e.g. Doglioni et al. 1998, 1999). The petrological characteristics of mafic magmas support various degrees of melting at low pressure of a phlogopite-bearing harzburgite (Condamine & Médard 2014), representing remnants of old contaminated and dismembered lithosphere (e.g. Peccerillo et al. 1988). Melting occurred in and around subducted mélanges, which were formed during Alpine convergence. Eastward decrease in age of magmas reflects a shift in the same direction of back-arc thermal anomalies, behind the eastward migrating subduction front (e.g. Balestrieri et al. 2011). Starting from the Early Miocene, the Apennine subduction involved the Adriatic continental plate, which was responsible for a second stage of mantle contamination by mixtures of silicic and carbonate sediments. This essentially affected the Roman Province, but its consequences are also recognizable in some Tuscan centres (e.g. Tolfa–Manziana–Cerite, Radicofani; Pinarelli 1991; Bertagnini et al. 1995; Peccerillo et al. 2008). In contrast, the geochemical signatures of older Alpine contamination events are difficult to see in the magmas of the Roman Province, probably because the very great younger contamination by the Adriatic slab covered the previous evolution history of the mantle wedge. An additional possibility is that back-arc extension, which increases southward from Tuscany to Latium, completely dismembered and eroded older lithospheric mantle in the Roman Province, thus deleting the previous contamination history.

8 Summary and conclusions

(1) Based on geodynamic setting and on major and trace element compositions, two broad groups of Plio-Quaternary magmas are recognized in the Tyrrhenian Sea area, and have been indicated as 'orogenic' and 'anorogenic'. The former are mainly related to sub- duction processes of the Ionian–Adriatic plate beneath the south- ern European margin. They have calc-alkaline to ultrapotassic petrochemical affinity, and are characterized by high values of

Th/ Ta, Ba/Nb and other LILE/HFSE ratios. Anorogenic magmas occur in back-arc settings (e.g. Sardinia and some volcanoes in the southern Tyrrhenian Sea) and on the margin of the African foreland (Iblei, Etna, Sicily Channel). They range from tholeiitic to Na-alkaline and nephelinitic, have low LILE/HFSE ratios, low 87Sr/86Sr and high 143Nd/144Nd, resembling intraplate igneous rocks occurring in several places in Europe. Plio-Quaternary anorogenic volcanism from central–northern Sardinia has a peculiar unradiogenic Pb–Nd isotopic composition that is unique in Europe, and resembles EM-1 OIB-type rocks.

(2) Anorogenic magmas from Sicily, the Sicily Channel and the Tyrrhenian Sea are believed to derive from melting at various depths of mantle diapirs ascending from a high S-wave velocity layer occurring beneath Europe (European Asthenospheric Reservoir). A contribution by subduction components is recognized at Etna. A plume head or an upper mantle contaminated by delaminated lower continental crust has been suggested as a source of magmas in central–northern Sardinia.

(3) Orogenic magmas display very variable major element, trace element and radiogenic isotope compositions that allow several magmatic provinces to be distinguished. These were formed by melting of mineralogically and geochemically different mantle sources, which were contaminated by distinct types and abundances of subduction-related components.

(4) Radiogenic isotope data for orogenic mafic rocks define mixing trends between Sicily anorogenic magmas and upper continental crust indicating mantle contamination (metasomatism) by subducted upper crustal material. The northward increase of Sr isotope ratios and decrease of Nd isotope ratios suggest a greater contribution by continental crust in the northern sectors (Tuscany and Roman Province) than in the southern ones (Aeolian Arc and Campania).

(5) Trace element and radiogenic isotope variation of orogenic magmas reveals that different types of slab-derived materials were responsible for mantle contamination in

different sectors of the Italian peninsula. In particular, aqueous fluids from a MORB-type slab contaminated the mantle wedge beneath the western Aeolian Arc; similar fluids, but with a significant contribution from sediments, had a key role in the metasomatism of the mantle wedge in the eastern Aeolian Arc and Campania (Vesuvius, Campi Flegrei, Ischia, Pontine Islands). Melts from upper crustal rocks were responsible for mantle contamination in the Roman and Tuscany provinces.

(6) Mantle metasomatism beneath Tuscany was provided by siliceous rocks with little or no carbonate participation. Trench turbidites of continental origin, metapelites and/or slices of cocontinental crust are possible contaminants. Metasomatism occurred much earlier than onset of the magmatism (Miocene to Quaternary), during the Cretaceous to Oligocene subduction of the European plate beneath the northern African margin.

(7) Contamination of the mantle wedge beneath the Roman Province was accomplished by addition of mixed siliceous–carbonate (marly) sediments. These were provided by subduction of the Adriatic continental plate that started in the Early Miocene, after the consumption of oceanic lithosphere in the northern Apennine sector of the arc. However, the mantle source of the Roman magmas was also probably affected by contamination during Alpine subduction. If this is the case, the upper mantle in this region was modified by two superimposed contamination processes, which may be an explanation for the great abundances of potassic magmas.

(8) Physical processes of mantle contamination in both the Roman and Tuscany provinces are envisaged as transport of sediments or other upper crustal rocks along the subduction channel, formation of mélanges of subducted rocks and peridotites, ascent of mélange diapirs by Rayleigh–Taylor instability, dehydration, and melting in the diapirs and the surrounding modified mantle.

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Table 1. *Volcanological and compositional characteristics and ages of volcanic provinces in Italy*

Magmatic province	Main magmatic centres and ages (in Ma)	Volcanology	Petrology–geochemistry
Orogenic magmatism			
Tuscany (8.5–0.3 Ma)	*Acid intrusions*: Elba (8.5–6.3), Montecristo (7.1), Giglio (5), Campiglia–Gavorrano (5–4.3). Various hidden intrusions at Larderello–Amiata (<5) *Acid lavas*: San Vincenzo (4.5), Roccastrada (2.5), Amiata (0.3), Cimini (1.3–1.1), Tolfa–Cerite–Manziana (4.2–1.8) *Mafic centres*: Capraia (7.7–4.8), Elba (5.8), Orciatico and Montecatini (4.1), Radicofani (1.3), Cimini (0.9), Torre Alfina (0.8). The Sisco lamproitic dyke (14) in Corsica is often considered as belonging to the Tuscany Province	Felsic rocks: granitoid rocks, aplites, pegmatites. Monogenetic lava flows and domes, and polygenetic cones (Amiata). A few ignimbrites (Cimini, Cerite); no pyroclastic rocks in other centres Mafic rocks: small extrusive and subvolcanic bodies. Stratovolcano at Capraia. Few or no pyroclastic products	Mafic magmas: calc-alkaline, shoshonitic and ultrapotassic (lamproites) rocks, nearly saturated in silica, with high MgO. LILE abundances and $^{87}Sr/^{86}Sr$ (*c.* 0.708–0.717) increase from calc-alkaline to lamproitic compositions Felsic magmas: metaluminous to peraluminous rocks originated by crustal anatexis (acid rocks) plus mixing between these and various types of mafic magmas and crustal melts. $^{87}Sr/^{86}Sr \sim 0.712–0.723$, with highest values in rocks with no evidence of mixing with mafic magmas (e.g. Roccastrada and some San Vincenzo rhyolites)
Intra-Apennine Province (0.6–0.3 Ma)	San Venanzo (0.26), Cupaello (0.64), Polino (0.25), Acquasparta, Oricola (0.53), etc.	Monogenetic pyroclastic centres and rare lavas (San Venanzo and Cupaello)	Ultrapotassic melilititic (kamafugites) composition. Carbonate-rich pyroclastic rocks of uncertain origin. Similar trace element patterns and radiogenic isotope composition ($^{87}Sr/^{86}Sr \sim 0.710–0.711$) to mafic rocks of the Roman Province
Roman Province (Latium) (0.8–0.006 Ma)	Vulsini (0.6–0.13), Vico (0.4–0.09), Sabatini (0.8–0.09), Alban Hills (0.6–0.006)	Large multicentre volcanic complexes and stratovolcanoes with polygenetic calderas formed prevalently by pyroclastic rocks and minor lavas	Roman-type potassic (trachybasalt to trachyte) and ultrapotassic (leucite tephrite to phonolite) rocks with high enrichments in LILE (K, Rb, Cs, Th, LREE, etc.) and depleted in HFSE (Ta, Nb, Zr). High $^{87}Sr/^{86}Sr \sim 0.709–0.711$
Ernici (or Mid Latin Valley) – Roccamonfina (0.7–0.1 Ma)	Ernici: Pofi, Ceccano, Patrica, etc. (0.6–0.25), Roccamonfina (0.6–0.05)	Monogenetic pyroclastic and lava centres (Ernici or Mid Latin Valley), and a stratovolcano with a central caldera and intra-caldera domes (Roccamonfina)	Silica-undersaturated Roman-type leucite-bearing ultrapotassic rocks, and younger Campania-type saturated to slightly undersaturated calc-alkaline to potassic rocks. The latter show lower LILE and radiogenic Sr than ultrapotassic rocks
Campania (including Ponza and nearby islands) (4 Ma–present)	Somma–Vesuvius (0.03–AD 1944), Campi Flegrei (0.3–AD 1538), Ischia (0.15–AD 1302), Procida (0.05–0.01), Ponza (4–1), Palmarola (1.5), Santo Stefano (1.2–0.6), Ventotene (0.9–0.1). Buried calc-alkaline volcano (2 Ma)	Stratovolcanoes and multicentre complexes mostly formed by pyroclastic rocks with minor lavas. Rhyolitic lavas and pyroclastic rocks at Ponza and Palmarola. Calc-alkaline rocks found by deep borehole drillings or as rare xenoliths	Shoshonitic–potassic (trachybasalt to trachyte) and ultrapotassic (leucite tephrite to phonolite) rocks, less enriched in LILE and radiogenic Sr ($^{87}Sr/^{86}Sr \sim 0.705–0.708$) than equivalent Roman rocks, but similar to Stromboli potassic rocks
Vulture (0.7–0.1 Ma)	Vulture, Melfi	Stratovolcano with a summit caldera, intracaldera maars and some parasitic centres formed by dominant pyroclastic rocks and lavas	Mildly to strongly silica-undersaturated Na–K-rich (variable K/Na) melilitites, tephrites, phonolites, foidites with haüyne. Late carbonatites. Intermediate OIB- and arc-type trace element signatures
Aeolian Arc (0.27 Ma–present)	Alicudi (0.1–0.03), Filicudi (0.25–0.03), Salina (0.25–0.016), Vulcano (0.12–AD 1888), Lipari (0.27–AD 1220), Panarea (0.15–0.008), Stromboli (0.2–present)	Large stratovolcanoes with some calderas, formed by alternating pyroclastic rocks and lavas. Active volcanism in the central–eastern sector of the arc	Dominant calc-alkaline (basalt–andesite–rhyolite) compositions in the western–central arc. Dominant shoshonitic and potassic rocks at Vulcano and Stromboli. More primitive radiogenic isotope compositions in the western–central islands. Silicic rocks are concentrated in the central island of the archipelago (Lipari, Vulcano)
Southern Tyrrhenian sea floor (12 Ma–present)	Cornacya (12), Anchise, Sisifo, Enarete, Eolo, Lametini, Alcione, Palinuro, Marsili Sites 650 and 651	Seamounts of various ages, shape and volume. Marsili is a 60 km NE–SW elongated ridge, rising *c.* 3000 m above the actively spreading Marsili basin	Shoshonitic to calc-alkaline and arc-tholeiitic compositions
Anorogenic magmatism			
Sicily (7 Ma–present)	Etna (0.5–present), Iblei (7–1.5), Ustica (0.75–0.13), Pantelleria (0.3–0.005), Linosa (1–0.5), Sicily Channel seamounts (Miocene to AD 1891), ODP	Stratovolcanoes, diatremes, small plateaux, cinder cones, tuff cone and tuff rings, etc. Active volcanism at Etna and in the Sicily Channel (AD 1831 and 1891)	Tholeiitic to Na-alkaline rocks (basanite, hawaiite, trachyte) at Etna, Iblei, Linosa. Na-transitional basalts to peralkaline trachyte and rhyolite at Pantelleria. Trace element and isotopic signatures typical of FOZO–OIB-type rocks
Sardinia (12–0.1 Ma)	Isola del Toro (12), Capo Ferrato (*c.* 5), Montiferro (4–2), Orosei–Dorgali (4–2), Monte Arci (3.7–2.3), Logudoro (3–0.1)	Stratovolcanoes, basaltic plateaux and monogenetic centres	Mafic to silicic subalkaline, transitional to Na-alkaline rocks, sometimes with a K-affinity. Variable radiogenic isotope compositions, mostly with EM-1 characteristics, unique in Europe
Southern Tyrrhenian sea floor (7–0.1 Ma)	Magnaghi (3), Marsili, Vavilov, Aceste, Prometeo, ODP Sites 654 and 655, DSDP Site 373	Seamounts and lava fields	MORB-type tholeiite, Na-transitional and alkaline basalt to trachyte compositions

Modified after Peccerillo (2005). ODP, Ocean Drilling Program; DSDP, Deep Sea Drilling Project.

Table 2. *Selected compositions of Plio-Quaternary volcanic rocks from Italy*

	Anorogenic rocks								Orogenic rocks		
Sample:	Etna tholeiitic basalt	Etna alkali basalt (1974)	Iblei tholeiitic basalt	Pantelleria transitional basalt	Pantelleria peralkaline rhyolite	Sardinia mugearite	Sardinia hawaiite	Sardinia basaltic andesite	Alicudi calc-alkaline basalt	Alicudi andesite	Lipari rhyolite
Reference:	1	1	2	3	3	4	4	4	5	5	6
SiO_2	49.18	47.79	50.98	47.60	68.90	54.75	49.28	54.51	50.83	57.42	72.79
TiO_2	1.47	1.61	1.71	2.46	0.48	1.46	2.65	1.48	0.75	0.75	0.16
Al_2O_3	17.20	18.53	15.83	17.40	9.20	16.83	13.97	15.47	17.25	18.05	12.23
Fe_2O_3	9.58	3.35	3.05	3.08	3.84	8.95	10.52	10.87	3.80	3.53	1.82
FeO	–	6.31	7.77	7.73	5.03	–	–	–	4.67	2.83	–
MnO	0.15	0.17	0.15	0.16	0.30	0.18	0.16	0.12	0.15	0.11	0.10
MgO	8.73	6.15	7.30	4.98	0.21	4.24	8.92	6.26	7.47	3.16	0.17
CaO	9.27	10.30	8.73	10.60	0.79	5.93	8.37	6.58	10.65	7.07	0.66
Na_2O	3.20	3.40	2.96	3.74	6.32	3.6	4.62	3.83	2.48	3.79	3.76
K_2O	0.35	1.83	0.20	0.76	4.14	3.23	1.01	0.71	1.01	2.08	4.58
P_2O_5	0.38	0.41	0.33	0.50	0.02	0.84	0.51	0.17	0.29	0.37	0.01
LOI	0.39	0.15	1.01	0.98	0.87	–	–	–	0.64	0.84	3.80
Sc	25	28	26	34	5	11	18	17	37	22	3
V	169	327	177	110	5	79	168	143	223	159	–
Cr	36	–	280	–	12	37	321	246	296	46	–
Co	45	42	47	–	25	18	40	37	35	19	–
Ni	144	34	217	85	2	31	232	125	70	19	1
Rb	5.5	46	3	15	266	66	46.8	14.1	23	23	271
Sr	455	1203	315	495	6	593	1140	532	700	606	13
Y	22	28	29	25	247	33.5	21.4	17.9	18	17	43
Zr	99	195	125	153	2403	313	298	86	83	56	181
Nb	17	43	17	32	422	54	70	9.8	7	7.3	31
Cs	0.17	1.0	0.09	0.10	3.23	1.4	0.7	0.3	0.65	0.95	16.3
Ba	142	640	128	230	69	1023	1230	311	347	260	6.2
La	20	56	16	21	269	51	65	14	21	19	40
Ce	40	108	32	45	488	105	116	27	42	38	82
Pr	4.8	12.6	4.19	5.90	55	12.7	13.7	3.8	4.01	4.2	9.5
Nd	20	49	17.75	24.3	193	50	48	18.1	18.3	18	34.0
Sm	4.7	9.3	4.65	5.5	37.8	9.8	7.96	4.6	3.59	3.54	8.10
Eu	1.59	2.73	1.77	1.97	4.45	3.16	2.55	1.65	1.24	0.95	0.12
Gd	4.7	7.4	–	5.9	41.7	8.0	6.7	4.2	3.44	4.11	6.1
Tb	0.74	1.07	0.85	0.82	6.30	1.21	0.92	0.63	0.55	0.50	1.11
Dy	4.2	5.4	4.96	4.22	35.6	6.50	4.38	3.28	2.86	3.42	6.6
Ho	0.8	1.01	0.99	0.82	7.40	1.21	0.77	0.64	0.60	0.63	1.41
Er	2.1	2.58	2.31	1.98	19.6	3.1	2.0	1.44	1.70	1.78	4.2
Tm	0.31	0.34	0.35	0.27	2.92	0.42	0.28	0.21	0.23	0.26	0.64
Yb	2.09	2.11	2.06	1.67	17.87	2.80	1.60	1.20	1.79	1.53	4.22
Lu	0.25	0.32	0.30	0.25	2.67	0.39	0.22	0.16	0.29	0.28	0.61
Hf	2.48	4.3	3.14	3.10	46	6.9	7.3	2.4	1.76	1.34	5.4
Ta	0.88	2.28	0.80	1.75	18.6	3.5	4.5	0.7	0.41	0.36	2.4
Pb	1.3	6.3	1.08	1.10	16.7	3.5	5.9	1.4	5.15	3.3	24.4
Th	2.22	7.2	1.22	1.87	36.7	7.8	9.4	1.6	3.40	3.02	38.8
U	0.49	2.16	0.35	0.5	11.6	1.9	1.7	0.3	0.98	0.89	11.8
$^{87}Sr/^{86}Sr$	0.703147	0.703564	0.70297	0.703098	0.704280	0.70437	0.70437	0.70495	0.70386	0.70357	0.705710
$^{143}Nd/^{144}Nd$	0.512924	0.512877	0.51311	0.512989	0.512963	0.512746	0.512598	0.51232	0.51284	0.51288	0.51254
$^{206}Pb/^{204}Pb$	19.449	19.844	19.444	19.595	19.696	18.93	18.07	17.67	19.322	19.362	19.357
$^{207}Pb/^{204}Pb$	15.626	15.676	15.623	15.557	15.647	15.66	15.58	15.57	15.629	15.662	15.697
$^{208}Pb/^{204}Pb$	39.142	39.538	39.003	38.990	39.260	39.06	38.23	37.84	39.086	39.220	39.320

(*continued*)

Table 2. *(continued)*

	Orogenic rocks									
Sample:	Stromboli present-day lava	Stromboli potassic basalt	Vesuvius 1944 lava	Vulture foidite	San Venanzo (Umbria) kamafugite	Vulsini leucite tephrite	Torre Alfina lamproite Tuscany	Radicofani shoshonite Tuscany	Roccastrada rhyolite Tuscany	Elba granodiorite Tuscany
Reference:	7	7	8	9	10	11	12	13	14	15
SiO_2	49.51	51.69	48.91	42.50	41.33	46.14	56.00	54.50	73.40	68.24
TiO_2	0.960	0.90	1.03	1.17	0.59	0.83	1.33	0.89	0.24	0.48
Al_2O_3	18.01	17.22	19.30	16.8	12.23	17.82	12.98	16.97	14.10	15.42
Fe_2O_3	2.90	1.70	1.10	9.45	2.05	3.80	0.89	0.93	1.11	
FeO	5.60	5.96	6.71	–	4.01	4.67	4.90	5.07	1.10	2.92
MnO	0.16	0.15	0.16	0.19	0.11	0.15	0.094	0.11	0.04	0.04
MgO	6.50	6.22	3.72	4.69	12.99	5.69	8.76	8.09	0.29	1.34
CaO	10.87	9.11	8.46	12.7	15.55	11.54	5.41	7.54	0.85	2.44
Na_2O	2.68	2.21	1.54	4.00	1.03	1.89	0.97	1.95	2.48	3.32
K_2O	2.12	3.97	8.24	5.08	8.91	6.24	7.57	3.26	5.03	4.12
P_2O_5	0.42	0.54	0.84	1.13	0.39	0.50	0.56	0.20	0.13	0.20
LOI	0.29	0.30	0.24	1.39	0.81	0.73	0.45	0.49	1.58	0.78
Sc	27	27.6	25	15	21	20	13	26	4.8	8.0
V	219	192	230	271	117	302	123	170	13	33.0
Cr	100	153	48	7	844	20	560	409	11	27.0
Co	27	25.2	23	30	41	37	34	25	2.7	7.0
Ni	38	34.6	26	20	149	40	370	137	19	12.0
Rb	72	123	307	153	463	402	443	214	430	292
Sr	730	750	885	2550	1742	1395	726	343	59.79	188
Y	26	27	23	69	36	34	36	24	33	18.2
Zr	161	187	206	478	261	262	601	211	122	143
Nb	22	25	40	112	12.9	12	32	14.5	14	11.9
Cs	4.86	9.81	17.5	10.3	38	26	35	18.0	–	33.9
Ba	1010	1540	2090	2780	625	870	1285	666	140	343
La	40	44.7	51	277	63	71	111	49.5	28	32.0
Ce	82	92.5	102	512	152	155	296	111	59	64.0
Pr	9.6	11.8	12.5	55	18	17.7	35	13.5	–	7.6
Nd	38	48.5	47	199	72	70	143	50.0	27.51	28.0
Sm	7.5	10.2	9.4	34	13.9	12.7	24.0	8.30	6.68	5.5
Eu	1.95	2.49	2.36	7.3	2.65	2.67	4.5	1.83	0.48	0.80
Gd	7.45	9.48	7.76	23.8	9.29	9.57	15.0	6.1	–	4.10
Tb	0.93	1.14	0.85	3.15	1.09	1.24	1.8	0.82	0.94	0.62
Dy	4.84	5.54	4.25	14.8	6.54	5.90	6.5	4.70	–	3.30
Ho	0.90	0.98	0.75	2.39	1.03	1.06	1.20	0.95	–	0.6
Er	2.54	2.65	2.13	5.4	2.62	2.56	3.2	2.51	–	1.57
Tm	0.33	0.34	0.26	0.65	0.31	0.35	0.37	0.35	–	0.22
Yb	2.21	2.21	1.9	3.8	2.02	2.42	2.2	2.10	2.75	1.35
Lu	0.35	0.34	0.25	0.53	0.35	0.34	0.33	0.36	0.33	0.18
Hf	3.67	4.82	4.0	–	7.38	5.98	15.0	6.6	3.56	0.69
Ta	1.12	1.34	1.9	5.8	0.77	0.59	2.00	1.0	2.12	1.73
Pb	17.1	22.4	21	67	21.8	38	66	32	43	50
Th	16.7	20.9	19.45	72	33	30	61	30	21	19.6
U	4.61	6.15	6.30	18.7	6.53	6.80	13.0	4.2	16.7	3.8
$^{87}Sr/^{86}Sr$	0.706246	0.707550	0.707228	0.705918	0.710369	0.71020	0.71623	0.71383	0.71863	0.715345
$^{143}Nd/^{144}Nd$	0.512550	0.512474	0.512474	0.512709	0.512081	0.51213	0.51209	0.51218	–	0.512164
$^{206}Pb/^{204}Pb$	19.070	19.082	19.021	19.28	18.735	18.779	18.663	18.672	18.685	18.687
$^{207}Pb/^{204}Pb$	15.677	15.687	15.696	15.718	15.661	15.653	15.656	15.669	15.655	15.671
$^{208}Pb/^{204}Pb$	39.067	39.104	39.151	39.351	38.928	39.015	38.858	38.981	38.865	38.902

References: 1, Armienti *et al*. (2004); Pb isotopes are from Giacobbe (1993). 2, Trua *et al*. (1998), average of six samples. 3, Esperança & Crisci (1995). 4, Lustrino *et al*. (2013). 5, Lucchi *et al*. (2013*b*); Peccerillo *et al*. (2013); Sr–Nd–Pb isotope ratios are average of four basalts and four andesites. 6, Gioncada *et al*. (2003). 7, Francalanci *et al*. (1989, 2013); Tommasini *et al*. (2007). 8, Paone (2008); Conticelli *et al*. (2010). 9, D'Orazio *et al*. (2007). 10, A. Peccerillo (unpubl. data). 11, De Astis *et al*. (2000); Gasperini *et al*. (2002). 12, P. Barnekow & A. Peccerillo (unpubl. data). 13, Conticelli *et al*. (2011). 14, Average of 30 samples; Hawkesworth & Vollmer (1979); Giraud *et al*. (1986); Pinarelli *et al*. (1989); Peccerillo (2005). 15, Farina *et al*. (2012); Pb isotopes are average values of three granodiorites from Monte Capanne batholith from Vollmer (1976).

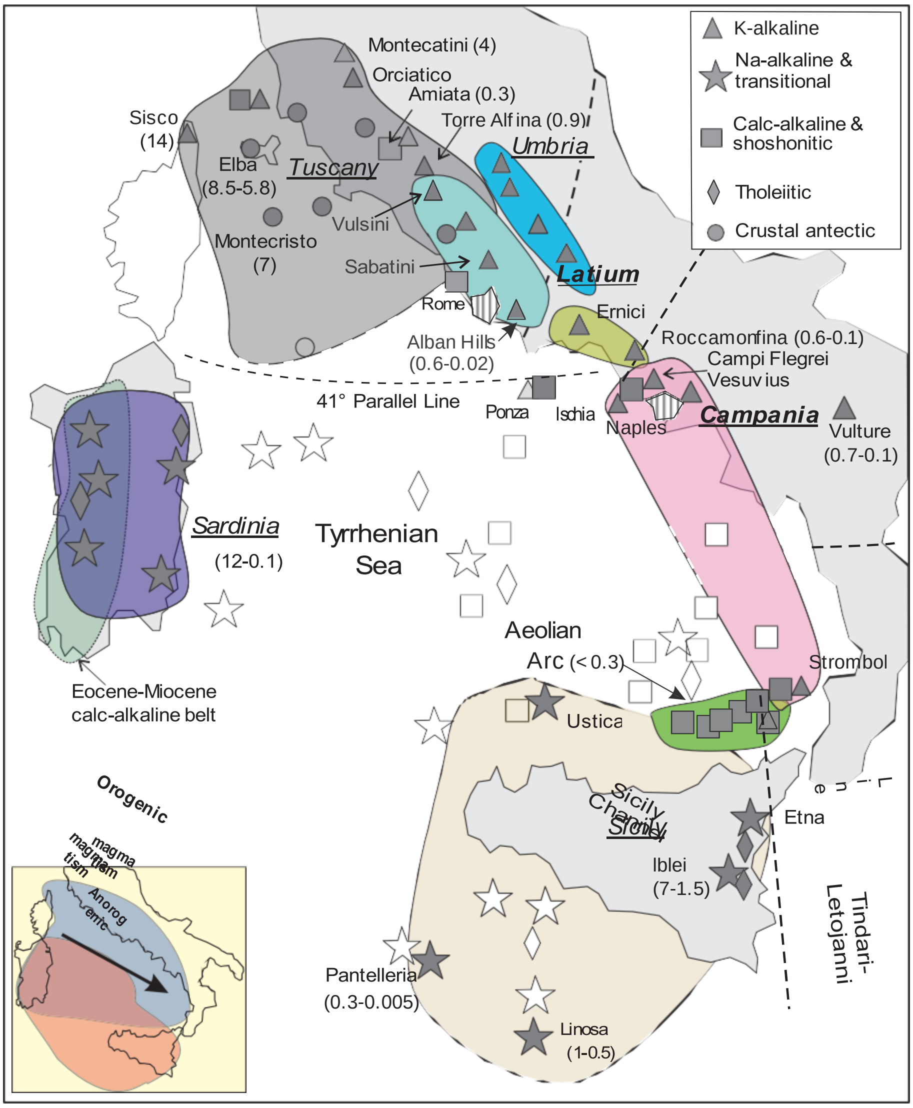

Fig. 1. Distribution of Plio-Quaternary magmatism in Italy (numbers in parentheses are ages in Ma). Site of Eocene–Miocene calc-alkaline volcanic belt of Sardinia is also reported. Open symbols indicate submarine volcanoes. Volcanic provinces are those defined in Table 1 and in the text. Dashed lines indicate main transverse tectonic lines Inset shows areal distribution of orogenic and anorogenic magmas. Arrow shows migration of orogenic magmatism with time. Modified after Peccerillo (2005

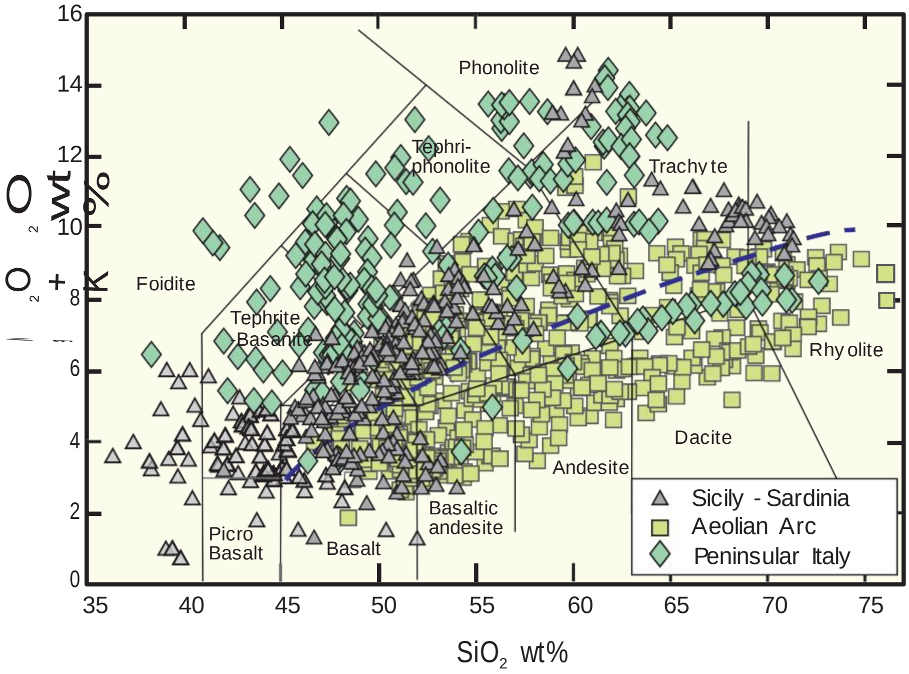

Fig. 2. Total alkalis v. silica (TAS) classification diagram for Plio- Quaternary volcanic rocks in Italy (Le Maitre 2002). Only a limited number of samples have been reported to avoid excessive symbol crowding in this and other figures. Carbonatitic rocks from Mt. Vulture have not been plotted. The dashed line divides the subalkaline and the alkaline fields of Irvine & Baragar (1971). (For data sources for this and the following figures see Table 2 legend and Peccerillo (2005).)

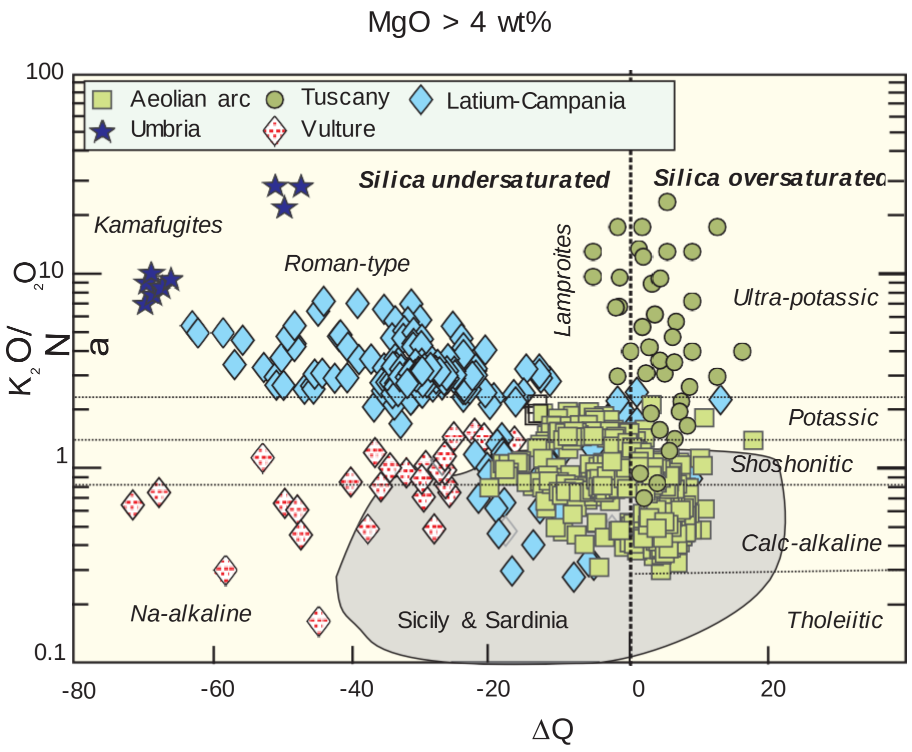

Fig. 3. Classification diagram of orogenic mafic rocks (MgO > 4.0 wt%) in Italy based on K2O/Na2O (wt%) ratio and degree of silica saturation. ΔQ is the algebraic sum of normative quartz minus undersaturated minerals (nepheline, leucite, kalsilite, olivine). Rocks with ΔQ < 0 are undersaturated in silica whereas rocks with ΔQ > 0 are oversaturated in silica. Silica-saturated rocks have ΔQ ~ 0. Grey area indicates compositions of mafic anorogenic rocks from Sicily, the Sicily Channel and Sardinia. Carbonatitic rocks from Mt. Vulture are not plotted.

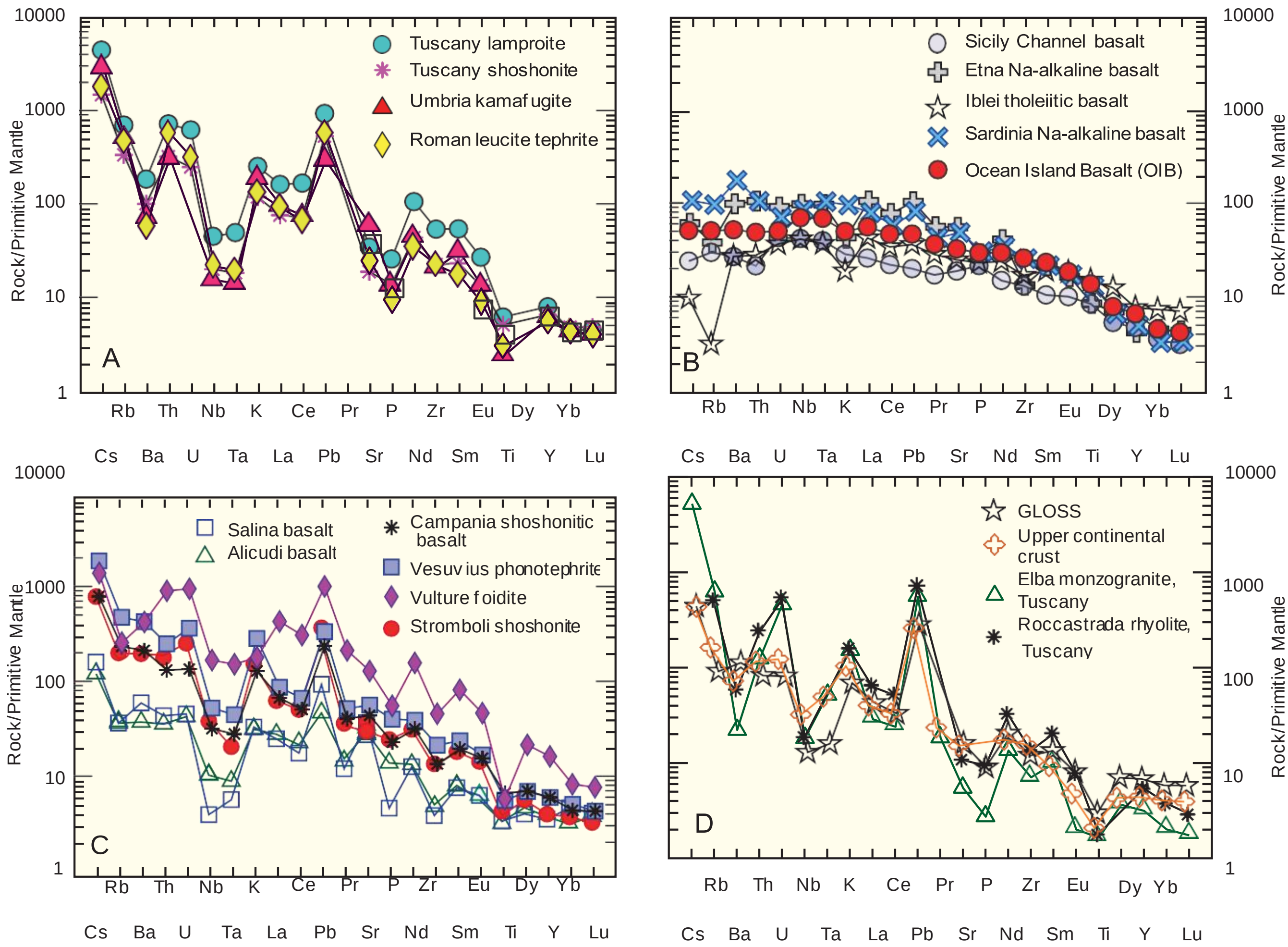

Fig. 4. Patterns of incompatible elements normalized to primitive mantle compositions for representative Italian Plio-Quaternary orogenic (**a**, **c**) and anorogenic (**b**) mafic rocks, and for some upper crustal rocks (**d**). Average ocean-island basalt (OIB) and primitive mantle normalizing values are from Sun & McDonough (1989). Data on upper continental crust and global subducted sediments (GLOSS) are from Taylor & McLennan (1985) and Plank & Langmuir (1998).

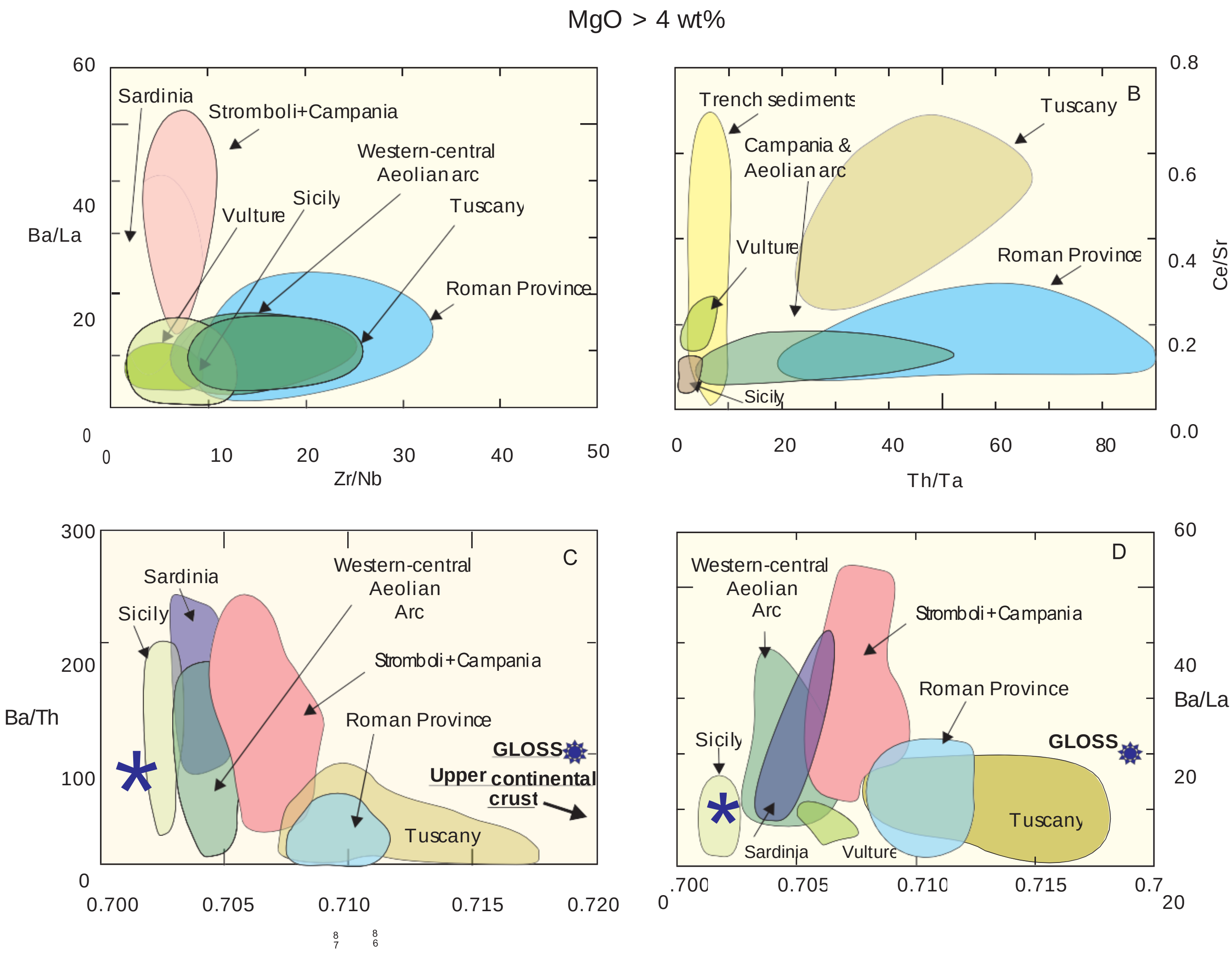

Fig. 5. Variation of incompatible element ratios and $^{87}Sr/^{86}Sr$ for mafic rocks from Italy. Trench sediments and GLOSS (global subducted sediments) are from Plank & Langmuir (1998). Asterisk indicates primitive mantle composition of Sun & McDonough (1989).

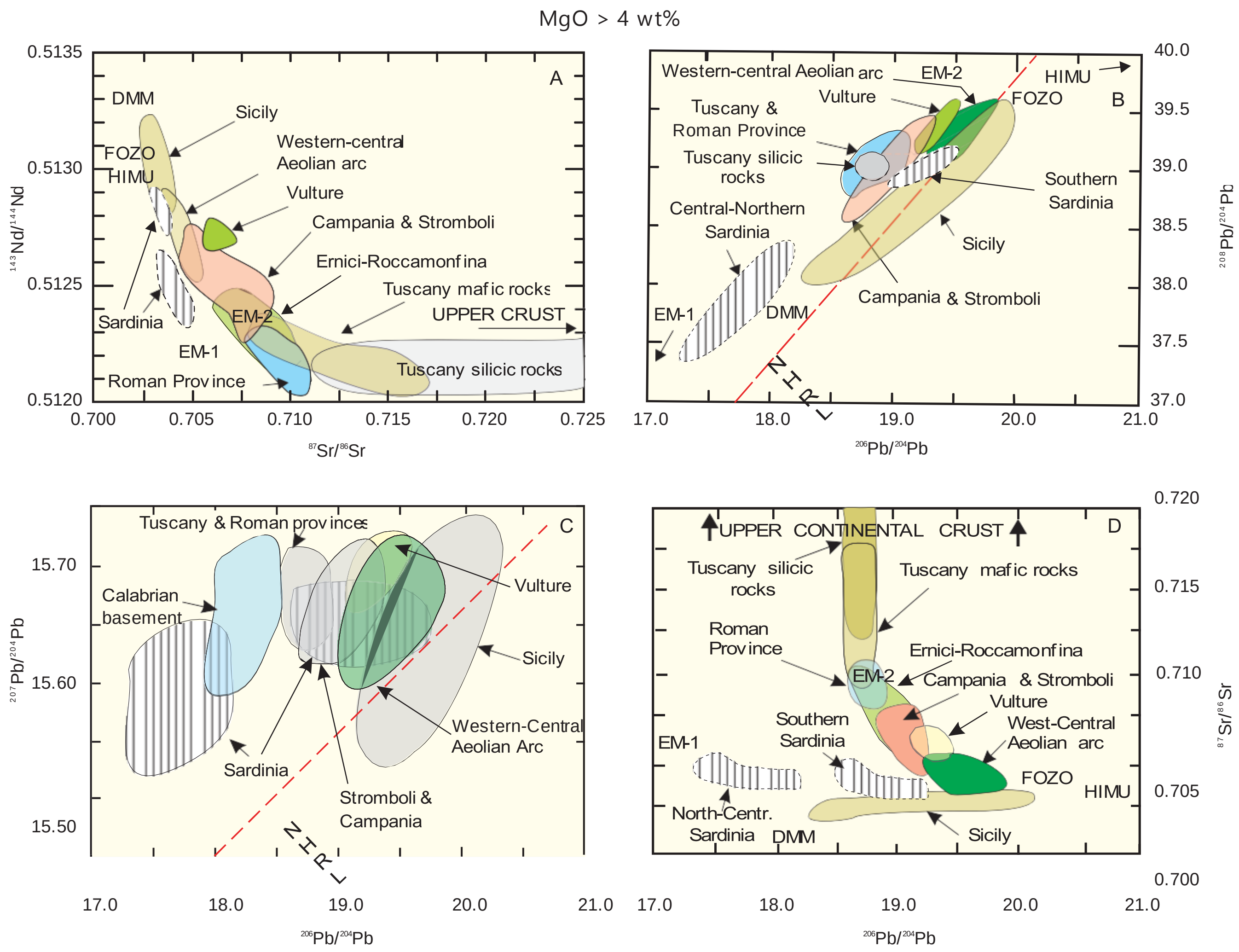

Fig. 6. Sr–Nd–Pb isotope compositions of Plio-Quaternary mafic volcanic rocks in Italy. Compositions of some mantle end-members (HIMU, FOZO, DMM, EM-1, EM-2) and Northern Hemisphere Reference Line (NHRL) are shown (Zindler & Hart 1986; Stracke *et al.* 2005; Jackson & Dasgupta 2008). Data for Calabria basement rocks are from Rottura *et al.* (1991).

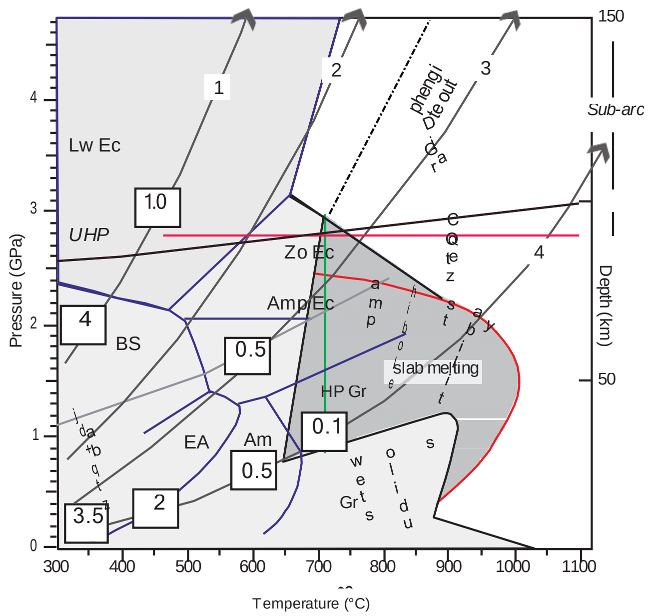

Fig. 7. Schematic diagram showing the *P–T* evolution of subducted slabs (MORB + H_2O system) along different subduction-zone geotherms (1, 2, 3 and 4), modified after Poli & Schmidt (2002), Maruyama & Okamoto (2007) and Bebout (2013). The light blue areas indicate hydrous metamorphic rocks. Estimates of H_2O content of the subducted oceanic crust along the different geotherms are indicated (wt%; white squares). The orange area indicates slab melting *P–T* conditions. Ec, eclogites facies; Am, amphibolite facies; EA, epidote amphibolite facies; Gr, granulite facies; BS, blueschist facies; HP Gr, high-pressure granulite; Lw Ec, lawsonite eclogite; Amp Ec, amphibole eclogite; Zo Ec, zoisite eclogite; UHP, ultrahigh-pressure metamorphic domain.

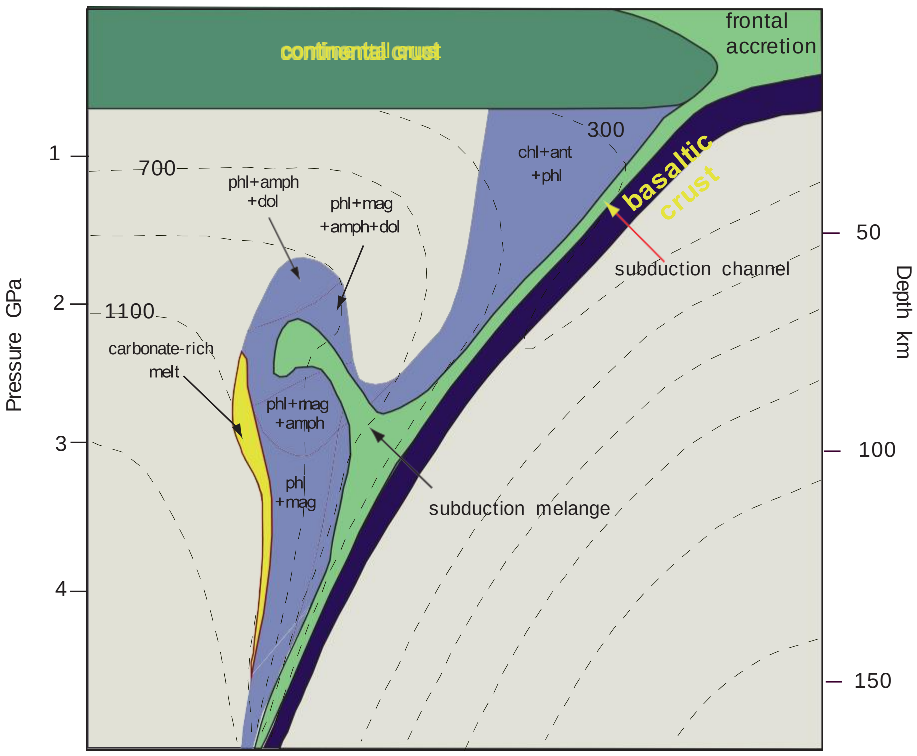

Fig. 8. Schematic illustration of emplacement of sediment diapirs in subduction zones (Gerya & Meilick (2011), along with phase relations of CO2–H2O-saturated peridotite in the K2O–Na2O–CaO–FeO–MgO–Al2O3–SiO2 (KNCFMAS) C–O–H system (Tumiati et al. 2013). Redrawn from Tumiati et al. (2013).

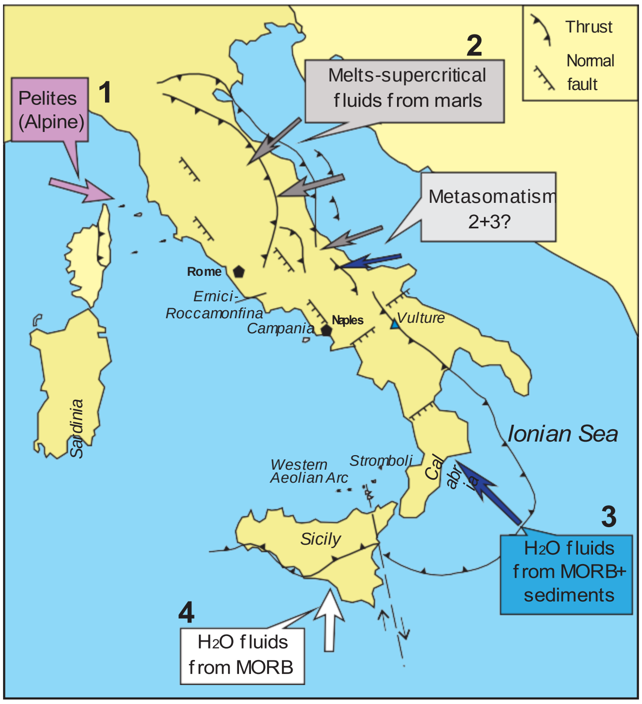

Fig. 9. Sketch map illustrating mantle wedge contamination by subduction processes, for the various sectors of the Apennines and Sicilian Maghrebides. Contamination 1: accomplished by introduction of pelitic sediments or other siliceous rocks (turbidites or slices of continental crust) during Alpine eastward subduction of the European plate beneath the northern African–Adriatic plate, in the area that Tuscany and northern Latium. Contamination 2: occurred by introduction of mixed carbonate plus siliceous sediments during Miocene to Recent subduction of the continental Adriatic plate beneath the Northern Apennine arc. Contamination 3: occurred beneath the eastern Aeolian Arc and the Campania volcanoes, by fluids released from currently subducting Ionian oceanic slab and associated sediments. Contamination 4: performed by fluids coming from an oceanic-type slab with negligible or no sediment participation. Processes 2 and 3 were both occurring beneath the Central Apennines (Ernici–Roccamonfina area).