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ORIGINAL PAPER

Mantle and crustal processes in the magmatism of the Campania region: inferences from mineralogy, geochemistry, and Sr–Nd–O isotopes of young hybrid volcanics of the Ischia island (South Italy)

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Abstract Ischia, one active volcano of the Phlegraean Volcanic District, prone to very high risk, is dominated by a caldera formed 55 ka BP, followed by resurgence of the collapsed area. Over the past 3 ka, the activity extruded evolved potassic magmas; only a few low-energy explosive events were fed by less evolved magmas. A geochemical and Sr–Nd–O isotope investigation has been performed on minerals and glass from products of three of such eruptions, Molara, Vateliero, and Cava Nocelle (<2.6 ka BP). Data document strong mineralogical, geochemical, and isotopic heterogeneities likely resulting from mingling/mixing processes among mafic and felsic magmas that already fed the Ischia volcanism in the past. Detailed study on the most mafic magma has permitted to investigate its origin. The mantle sector below Ischia underwent subduction processes that modified its pristine chemical, isotopic, and redox conditions by addition of $\leq$1 % of sediment fluids/melts. Similar processes occurred from Southeast to Northwest along the Apennine compressive margin, with addition of up to 2.5 % of sediment-derived material. This is shown by volcanics with poorly variable, typical $\delta^{18}O$ mantle values, and $^{87}Sr/^{86}Sr$ progressively increasing toward typical continental crust values. Multiple partial melting of this modified mantle generated distinct primary magmas that occasionally assimilated continental crust, acquiring more ^{18}O than ^{87}Sr. At Ischia, 7 % of Hercynian granodiorite assimilation produced isotopically distinct, K-basaltic to latitic magmas. A SW–NE regional tectonic structure gave these magmas coming from large depth the opportunity to mingle/mix with felsic magmas stagnating in shallower reservoirs, eventually triggering explosive eruptions.

Keywords Ischia · Mineral chemistry · Isotope geochemistry · Mingling/mixing · Mantle enrichment/ crustal contamination · Oxidizing fluids

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Introduction

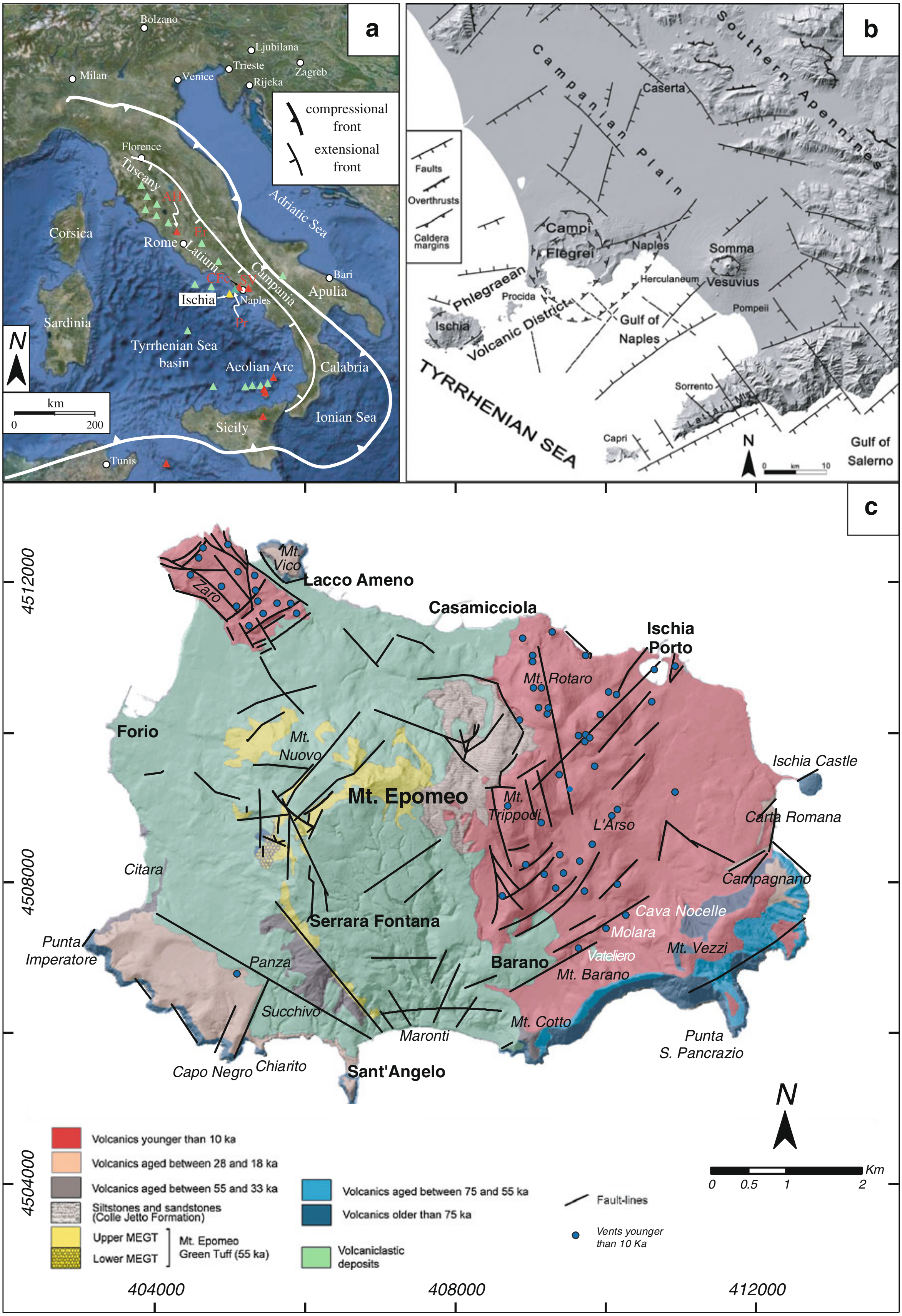
The combined use of radiogenic and stable isotopes in igneous petrology and volcanology has proven to be an invaluable tool in investigating different-scale processes such as mantle enrichment, crustal contamination, and magma mingling/mixing (e.g., James 1981; Bindeman 2008, and references therein). Discerning the effects of mantle and crustal processes on the geochemical and isotopic composition of a given magma batch is one of the most fascinating challenge for geochemists and petrologists. Furthermore, understanding role and mechanisms of open-system processes (e.g., crustal contamination, magma chamber recharge, volatile exsolution, and magma mingling/mixing) in the magmatic system feeding an active volcano may provide important contributions for volcanic hazards assessment and related risk mitigation (e.g., Wörner et al. 1985; Palacz and Wolff 1989; Orsi et al. 1995; Knesel et al. 1999; Sumner and Wolff 2003; Reubi and Nicholls 2005; Arienzo et al. 2009; Tonarini et al. 2009; Di Renzo et al. 2011). In particular, the significant role played by magma mingling/mixing (e.g., Bateman 1995; Clynne 1999, and references therein) in triggering many volcanic eruptions has widely been proven (e.g., Sparks et al. 1977; Huppert et al. 1982; Orsi et al. 1995; Folch and Martì 1998; Streck and Grunder 1999; Murphy et al. 2000; Nagakawa et al. 2002; Suzuki and Nakada 2007; Tonarini et al. 2009; Di Vito et al. 2011).

The Ischia volcanic island (Campania region, South Italy; Fig. 1a) offers a good opportunity to investigate genesis and evolution processes of potassic magmas, as well as relationships between composition of extruded magmas and structural position of the eruption vent. The Ischia volcanic system is still active and, also due to the explosive character of its volcanism, induces very high-potential volcanic hazards. The island is part of the Phlegraean Volcanic District (PVD; Orsi et al. 1996a) along with Procida and Campi Flegrei volcanic fields (Fig. 1b). Except for Procida, which activity ended 17.3 ka BP (Lirer et al. 1991), volcanic eruptions have occurred in historical times at both Ischia island (over the past 2.9 ka; last eruption: Arso, AD 1302) and Campi Flegrei caldera (last eruption: Monte Nuovo, AD 1538). In the last decades, many petrological studies have been carried out on PVD volcanoes in order to investigate the magmatic feeding systems, discriminate between mantle and crustal sources in the magmagenesis, and establish possible relationships between magmatic processes and structural features of each volcano, in order to achieve information useful for short- and long-term volcanic hazards assessment (e.g., Vezzoli 1988; Crisci et al. 1989; Civetta et al. 1991; Orsi et al. 1995; D'Antonio et al. 1999, 2007; Pappalardo et al. 2002; De Astis et al. 2004; Tonarini et al. 2004, 2009; Arienzo et al. 2009, 2010; Di Renzo et al. 2011, Di Vito et al. 2011; and references therein). However, most of these studies were focused on Campi Flegrei, whereas less attention has been devoted to Ischia that, thus, deserves further investigations.

Current views consider the Plio-Quaternary magmatism of the Tyrrhenian margin of Central-Southern Italy (Fig. 1a) to be a consequence of subduction processes related to the collision between Africa and Eurasia plates (e.g., Frezzotti et al. 2007, and references therein). In this framework, scarcity of volcanic rocks representative of primitive/primary magmas is a limitation relevant to the understanding of the PVD magmagenesis, in that it does not permit to investigate the mantle source region geochemical features prior to and after subduction (e.g., D'Antonio et al. 1999, 2007). On the other hand, the few K-basaltic lithic lava clasts occurring at Procida and Ischia are characterized by the lowest $^{87}Sr/^{86}Sr$ (0.7051) and highest $^{143}Nd/^{144}Nd$ (0.5127) ratios among Plio-Quaternary volcanics of Italy (Di Girolamo et al. 1995; D'Antonio et al. 1999), in which primitive mafic magmas with much higher Sr isotope ratios and lower Nd isotope ratios, have been extruded in centers located in northwestern Campania, Latium, and Tuscany (Fig. 1a; for example, Ellam et al. 1989; Conticelli et al. 2002; Avanzinelli et al. 2009). The relatively moderate LILE/HFSE and LREE/HREE ratios and the isotopic features of these PVD mafic rocks (MgO up to 10 wt%) can be confidently attributed to the mantle sector beneath the Campania region that, on these grounds, can be considered the least modified by subduction-related processes of the Plio-Quaternary magmatic provinces of Italy, as already outlined in some of the above-mentioned studies.

This paper presents and discusses the results of a study aimed at shedding light on mantle and crustal processes that have affected the magmas of the Ischia plumbing system in recent times. The study was carried out through combined mineral and glass chemistry, and Sr–Nd–O isotope investigations on the poorly evolved products of Molara, Vateliero, and Cava Nocelle eruptions. The investigated rocks were emplaced less than 2.6 ka BP by moderately explosive activity. This occurred through three vents located along a SW–NE–oriented tectonic structure located in the SE sector of the island and going through Procida and the Campi Flegrei caldera and, as such, being part of a regionally prominent fault system (Fig. 1b, c). The studied rocks are mostly shoshonite and latite in composition, and characterized by textural evidence for mingling/mixing already known in the literature (Vezzoli 1988, and references therein; Crisci et al. 1989; Di Girolamo et al. 1995). Data from separated phenocrysts and glass matrices reveal strong chemical and isotopic heterogeneities. In this work these features are discussed and interpreted as due to interaction processes between distinct magmatic components with different hybridization histories occurred along

Fig. 1 **a** Traces of the subduction-related compression and extension fronts along the Apennines chain (modified after Acocella and Funiciello 2006); *red triangles* (except Ischia, in *yellow*) are active volcanoes, *green triangles* are extinct volcanoes. Pr = Procida; CFc = Campi Flegrei caldera; SV = Somma-Vesuvius; AH = Alban Hills; Er = Mts. Ernici. **b** Structural sketch map of the Campanian Plain and surrounding Apennines (modified after Orsi et al. 2003). **c** Geological sketch map of Ischia (modified after Orsi et al. 2003). The Molara, Vateliero, and Cava Nocelle vents can be clearly located on the Southeastern sector of the island


a
Bolzano
Ljubilana
Milan
Venice
Trieste
Zagreb
Rijeka
compressional front
extensional front
Florence
Tuscany
Adriatic Sea
Corsica
Rome
Latium
Campania
Bari
Apulia
Ischia
Naples
Sardinia
Tyrrhenian Sea basin
Aeolian Arc
Calabria
Ionian Sea
Sicily
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km
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Southern Apennines
Campanian Plain
Caserta
Faults
Overthrusts
Caldera margins
Campi Flegrei
Naples
Somma
Vesuvius
Herculaneum
Phlegraean Volcanic District
Procida
Ischia
Gulf of Naples
Pompeii
Sorrento
TYRRHENIAN SEA
Capri
Gulf of Salerno
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4512000
4508000
4504000
404000
408000
412000
Mt. Vico
Lacco Ameno
Zaro
Casamicciola
Ischia Porto
Mt. Rotaro
Forio
Mt. Nuovo
Mt. Epomeo
Mt. Trippodi
L'Arso
Ischia Castle
Carta Romana
Citara
Campagnano
Serrara Fontana
Cava Nocelle
Molara
Mt. Vezzi
Punta Imperatore
Panza
Vateliero
Barano
Mt. Barano
Succhivo
Mt. Cotto
Maronti
Punta S. Pancrazio
Capo Negro
Chiarito
Sant'Angelo
N
Km
0 0.5 1 2
Volcanics younger than 10 ka
Volcanics aged between 28 and 18 ka
Volcanics aged between 55 and 33 ka
Siltstones and sandstones (Colle Jetto Formation)
Upper MEGT
Lower MEGT
Mt. Epomeo Green Tuff (55 ka)
Volcanics aged between 75 and 55 ka
Volcanics older than 75 ka
Volcaniclastic deposits
Fault-lines
Vents younger than 10 Ka

the above-mentioned SW–NE regional fault system. From our data, we conclude that at least one of these magmatic components is mafic in composition and, as such, it is potentially the best candidate to help investigating the geochemical features of the mantle source underlying Ischia and the Campania region.

Geological, volcanological, and petrological outlines of Ischia

The island of Ischia is an active volcanic field located at the Northwestern corner of the Gulf of Naples (South Italy; Fig. 1b). A complex interplay among tectonism, volcanism, volcano-tectonism, erosion, and sedimentation has characterized the history of the island (e.g., Buchner 1986; Vezzoli 1988; Orsi et al. 1991, 1992, 1996b; de Vita et al. 2006, 2010; Brown et al. 2008; Sbrana et al. 2009). Volcanism began prior to 150 ka BP and continued, with centuries to millennia long quiescence periods, until the last eruption, occurred in AD 1302. Early volcanism culminated with the caldera-forming Mt. Epomeo Green Tuff eruption (MEGT; 55 ka) followed by block resurgence of the caldera floor, that began after ca. 33 ka BP. Resurgence dynamics influenced the last period of activity, begun 10 ka BP, and mainly concentrated around two major periods at 5.5 and over the past 2.9 ka, when magmas ascended mainly within the Eastern portion of the island and along pre-existing regional faults (Fig. 1c) (Orsi et al. 1991).

Volcanic products vary in composition from shoshonite to slightly peralkaline trachyte and phonolite, the latter two being the most abundant rock types (e.g., Vezzoli 1988, and references therein; Crisci et al. 1989; Civetta et al. 1991; Orsi et al. 1992; Di Girolamo et al. 1995; Piochi et al. 1999; D'Antonio et al. 2007; Brown et al. 2008). They also exhibit large variability in Sr, Nd, Pb, O and B isotopic values (Civetta et al. 1991; Turi et al. 1991; Orsi et al. 1992; Piochi et al. 1999; Slejko et al. 2004; D'Antonio et al. 2007; Avanzinelli et al. 2009, and references therein). Heterogeneities in $^{87}Sr/^{86}Sr$ ratios of magmas erupted over the past 55 ka highlight a complex behavior of the feeding system, characterized by alternation of closed-system conditions, and replenishment by new, isotopically distinct magmas, with evidence for either crustal contamination or mixing processes. The latter process was operative mostly over the past 10 ka (Civetta et al. 1991; Piochi et al. 1999;

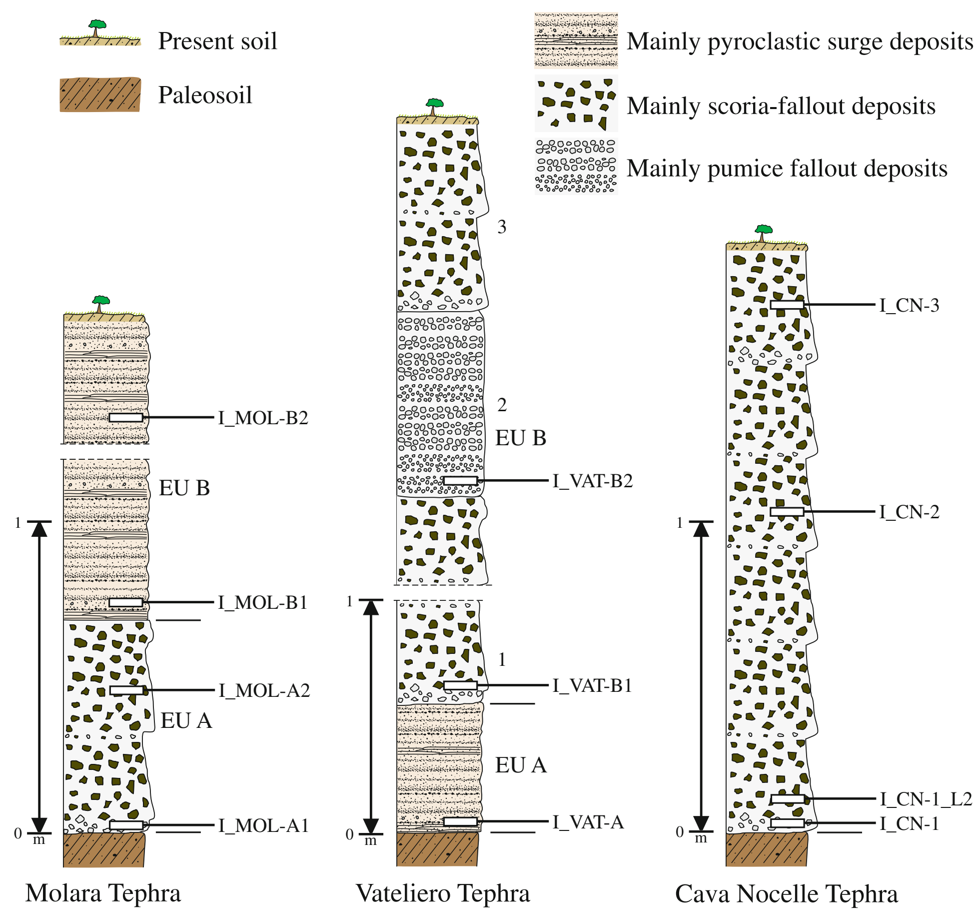


Fig. 2 Schematic stratigraphic sequences of Molara, Vateliero, and Cava Nocelle deposits (redrawn after de Vita et al. 2010) showing the position of rock samples collected for the present study. EU = erupted unit

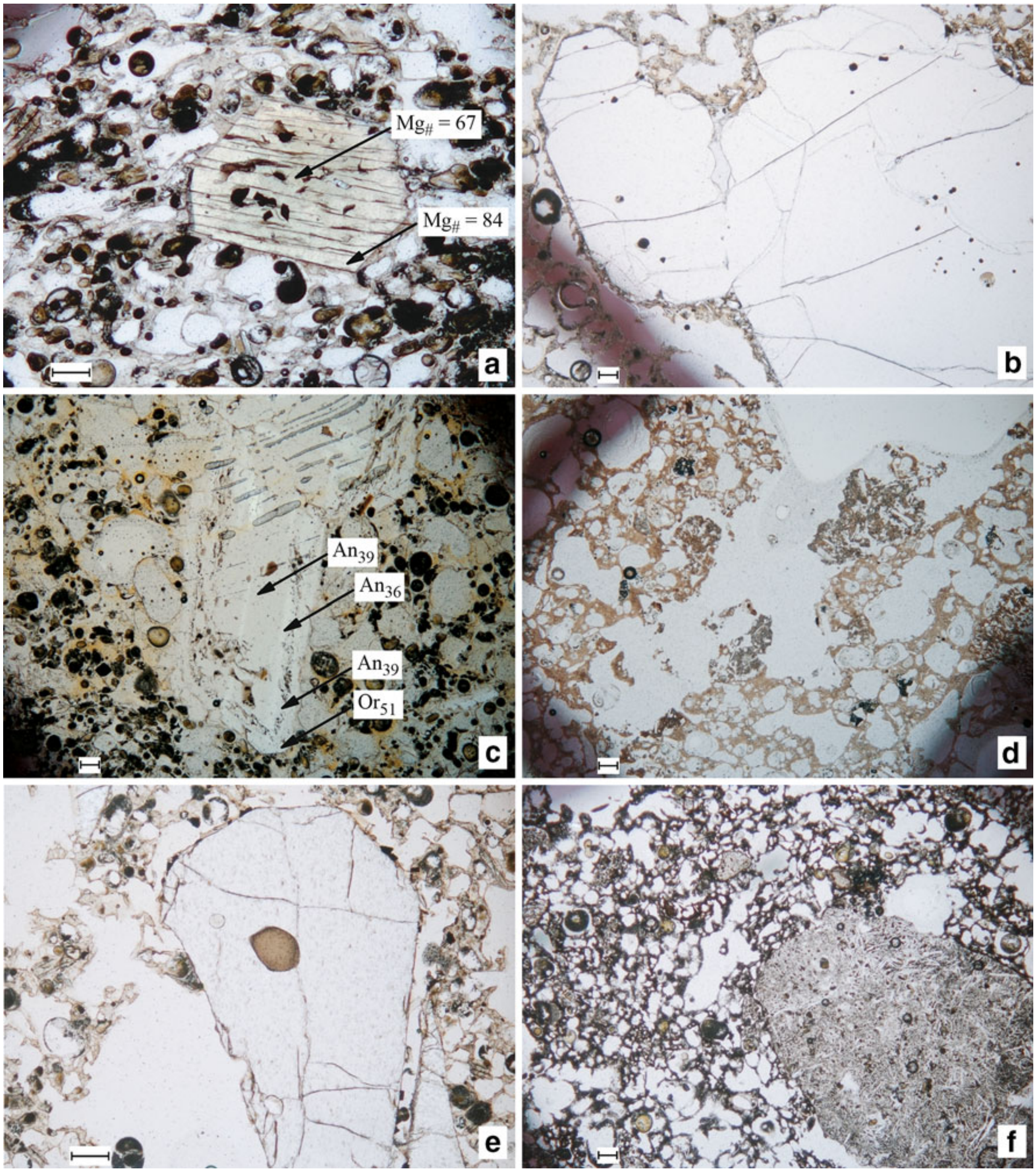


Fig. 3 Photomicrographs in plane-polarized light showing the main textural and mineralogical features of the investigated volcanic rocks from Ischia island. The *horizontal bar* in each microphotograph is 100 μm long. **a** reversely zoned clinopyroxene phenocryst in Vateliero Tephra; **b** Mg-rich olivine phenocrysts (Fo_{89-88}) with a few Cr-spinel (*cr*-number = 0.58) inclusions, in Vateliero Tephra; **c** oscillating zoned feldspar phenocryst in a *felsic* sample from Molara Tephra; **d** differently colored patches of groundmass in Cava Nocelle Tephra; **e** large glass inclusion of K-trachybasaltic composition trapped in Mg-rich olivine phenocryst (Fo_{85-84}) in Vateliero Tephra; **f** *felsic* (alkali-feldspar-rich) lithics trapped in the groundmass of a sample from Cava Nocelle Tephra

D'Antonio et al. 2007). The volcanic system is still active, as testified by the intense volcanism and seismic activity in historical times and widespread hydrothermalism (e.g., Vezzoli 1988, Orsi et al. 1996b; de Vita et al. 2006, 2010; Di Napoli et al. 2009, 2011; Sbrana et al. 2009).

The Molara, Vateliero, and Cava Nocelle eruptions

Molara, Vateliero, and Cava Nocelle monogenetic volcanoes, together with those of Fiaiano (ca. 1.05 ka) and Arso (AD 1302), are among the few centers that have extruded relatively poorly evolved magmas in recent times at Ischia. They are located in the Southeastern sector of the island, along a SW–NE tectonic lineament, that is part of a N60E trending, prominent regional fault system, passing through the island of Procida and the Campi Flegrei caldera (Fig. 1b, c; for example, Orsi et al. 1991, 1996a; Acocella and Funiciello 2006; de Vita et al. 2010). Each of these three volcanoes has produced a pyroclastic sequence (Fig. 2), recently re-defined, described in detail, and named the Molara Tephra, Vateliero Tephra, and Cava Nocelle Tephra (de Vita et al. 2010). Although radiometric ages are not available for these sequences, on the basis of archeological evidence, Molara and Vateliero eruptions have been dated at the VI–IV century BC, whereas the Cava Nocelle event must be slightly younger, as its deposits are stratigraphically comprised between the Molara Tephra and the Cretaio Tephra (II century AD) (de Vita et al. 2010, and references therein). Molara and Vateliero eruptions were characterized by complex alternating magmatic and phreatomagmatic phases, that built up the Molara scoria cone, and the Vateliero maar. Cava Nocelle eruption was dominated by Strombolian activity that built up a scoria cone. The products of these eruptions were variably classified as trachybasalt, shoshonite, latite, and trachyte by various authors using different classification schemes (e.g., Vezzoli 1988, and references therein; Crisci et al. 1989; Di Girolamo et al. 1995; D'Antonio et al. 2007).

Samples selection and analytical methods

For the purposes of this study, the pyroclastic sequences of the Molara Tephra, Vateliero Tephra, and Cava Nocelle Tephra were newly sampled at the same type localities where the units have been recently re-defined (de Vita et al. 2010). The collected volcanic rocks are pumice and (rarely welded) scoria fragments representative of the entire eruption sequences (Fig. 2). Each sample was composed of many juvenile clasts, carefully selected on the basis of freshness. After petrographic observations, the samples were prepared for the determination of the following: (1) major and minor oxide contents on minerals and glass by EMPA techniques; (2) major and minor oxide, and trace element contents on whole-rocks by XRF and LA-ICP-MS techniques; (3) Sr and Nd isotopic compositions on whole-rocks, separated minerals, and glass, and (4) O isotopic compositions on separated single minerals, by TIMS techniques. A detailed description of sample preparation techniques and analytical methods is reported in Appendix A of the electronic supplementary material.

Results

Petrography of the rocks

The investigated volcanic rocks are either pumice or scoria fragments, with vesicularity ranging from 60 through 40 to 10 vol. % in a welded scoria sample (I_CN1-L2). All samples are strongly porphyritic and glomero-porphyritic, with 25–40 vol. % phenocrysts and microphenocrysts of feldspar, clinopyroxene, olivine, biotite, magnetite, and apatite, in decreasing abundance. On the basis of macroscopic color, parageneses, and relative abundance of minerals, most of the samples are *mafic*, and only two are *felsic* (I_MOL-B1 and I_MOL-B2).

At hand-specimen scale, and particularly on separated crystals, three differently colored types of clinopyroxene phenocrysts were distinguished in most *mafic* samples: green Cpx, dark Cpx, and black Cpx (abbreviations following Whitney and Evans 2010). Also, two types of olivine phenocrysts were distinguished in some *mafic* samples, a light Ol and a yellow Ol. Under the microscope, in plane-polarized light, the green and black Cpx are pale and dark green, respectively, whereas the dark Cpx owes its color to many glass and/or magnetite inclusions. Furthermore, many Cpx individuals display either normal or reverse zoning, the latter characterized generally by a wider, dark green core surrounded by a thinner, light green rim (Fig. 3a). Conversely, Ol phenocrysts are usually homogeneous in color. Tiny inclusions of dark red opaque oxide occur sometimes in Ol individuals showing partially rounded margins (Fig. 3b) and kink banding. Feldspar is mostly plagioclase, and subordinately sanidine in *mafic* samples, with a reverse abundance in *felsic* rocks. Biotite and magnetite phenocrysts are often rounded and sometimes embayed. Sieve-textured cores, oscillating zoning, and an outer rim of sanidine are common in Pl phenocrysts (Fig. 3c). Non-zoned sanidine phenocrysts also occur in *felsic* samples.

The groundmass texture is mostly felty, and subordinately intersertal, hypohyaline, and fluidal in *mafic* samples, and either holoyaline or cryptocrystalline in *felsic* samples. Variable amounts of acicular feldspar (not resolvable), Cpx, Mag, and rare Ol and amphibole microlites are dispersed in the mostly glassy groundmass of *mafic* samples. The groundmass shows significant variations in color (from light gray to black), occurring as either strips or patches in single fragments (Fig. 3d). Glass occurs also as melt inclusions (MIs) of variable size in most phenocrysts (Fig. 3e) of Cava Nocelle and Vateliero Tephra. Interestingly, cm- to sub-mm-sized *felsic* lithic fragments are included in most *mafic* rocks. They are fine-grained, light brown, with dominant Sa, subordinate Cpx, Bt, and Mag phenocrysts in a either holohyaline or

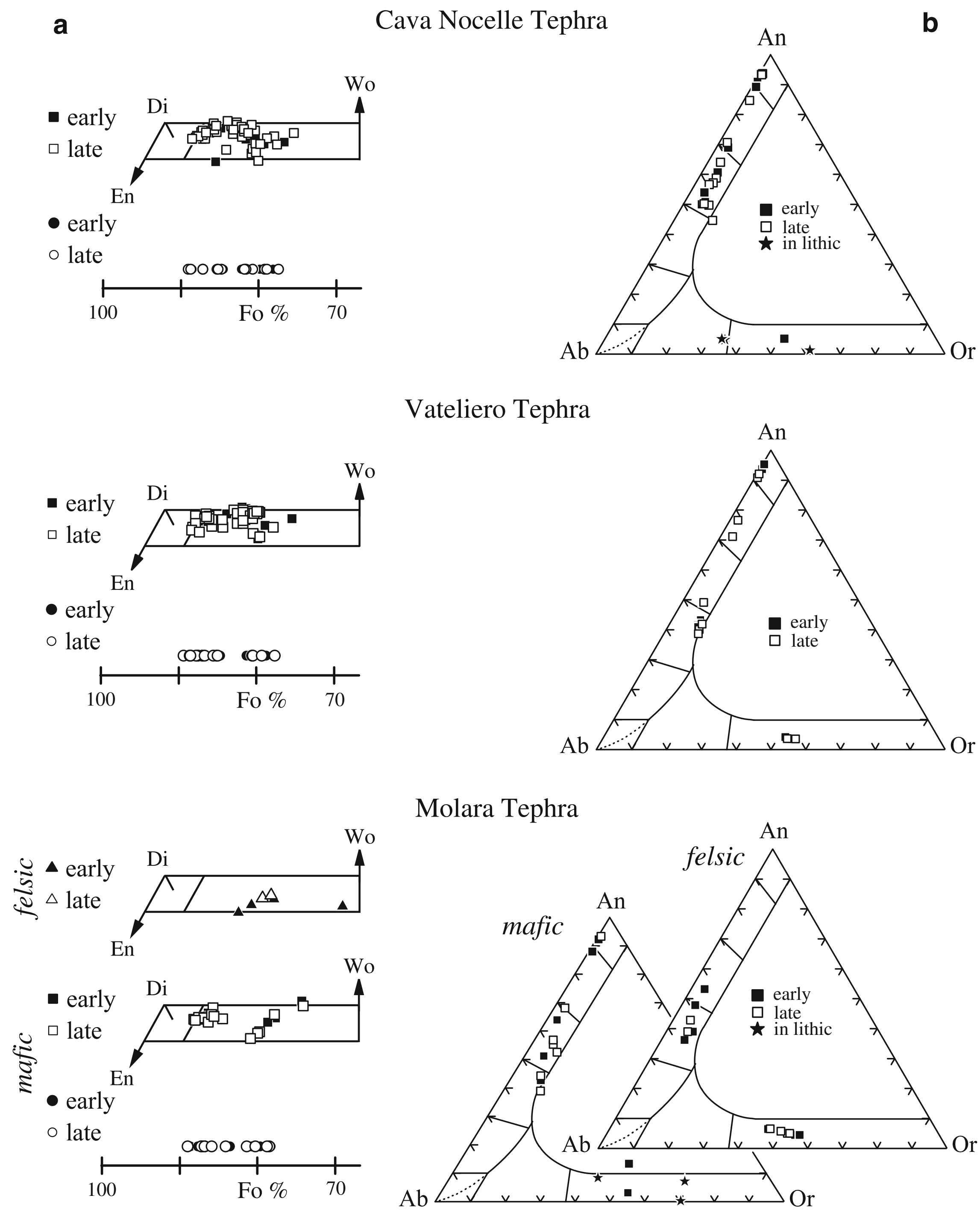


Fig. 4 **a** Portion of the pyroxene quadrilateral classification diagram Di-Hd-En-Fs (Rock 1990), and bar of forsterite mol % (Fo) variation, showing all clinopyroxene and olivine crystals analyzed in the selected volcanic rocks from Molara (both *mafic* and *felsic*), Vateliero (*mafic*), and Cava Nocelle (*mafic*) Tephra. Di = diopside; Hd = hedenbergite; En = enstatite; Fs = ferrosilite; Wo = wollastonite. Early = phenocryst cores; late = phenocryst rims, microphenocrysts and microlites. **b** Ternary classification diagram Ab-An-Or for feldspars showing all analyzed plagioclase and alkali-feldspar crystals. Ab = albite; An = anorthite; Or = orthoclase. Early = phenocryst cores; late = phenocryst rims, microphenocrysts and microlites

holocrystalline felsic groundmass. Thus, their texture and mineralogy are different with respect to those of host-rock (Fig. 3f). The margins of these lithics are mostly rounded and undulated, suggesting a plastic behavior during cooling of the host-rock; only sometimes they are sharp, with a dark glassy rim of the host groundmass.

Mineral chemistry

A detailed (ca. 400 single analyses) mineral chemistry investigation of the selected volcanic rocks was carried out in order to better characterize the compositional variability of the mineral species highlighted by macro- and microscopic observations. EMP analyses were made on both separated phenocrysts to be characterized isotopically (see later), and 12 polished thin sections. Representative analyses of minerals are reported in Appendices B through D of the electronic supplementary material, the others are available on request. All analyzed clinopyroxenes, olivines, and feldspars are plotted in the diagrams of Fig. 4.

Clinopyroxene

The majority of Cpx in *mafic* rocks are ferroan diopside, with subordinate diopside and rare magnesium-rich augite (Yavuz 2001; Fig. 4a). Ferroan diopside is mostly aluminian ± ferroan ± ferrian ± chromian, and sometimes also subsilicic; sometimes, it is chromian ferroan. Diopside is mostly chromian, less frequently aluminian chromian. The rare magnesium-rich augite is aluminian ± chromian. The Cpx in the Molara Tephra *felsic* rocks is mostly (aluminian) ferroan diopside, but one (aluminian ferroan) magnesium-rich augite. The green Cpx identified macroscopically corresponds to the most Mg-rich diopside and ferroan diopside phenocrysts and will be reported hereafter as Mg-rich Cpx; the black Cpx is either iron-rich ferroan diopside or magnesium-rich augite and will be reported as Fe-rich Cpx; the dark Cpx is always intermediate in composition and will be reported as Mg-poor Cpx. The whole chemical variation of Cpx in all *mafic* samples is noteworthy, with *mg*-numbers ranging from 0.92 to 0.64, with small differences for Cpx from the three sequences. Instead, the *mg*-numbers in the *felsic* samples from Molara Tephra vary from 0.78 to 0.54, in agreement with the evolved character of host-rock. Normal and reverse zoning is quite common in Cpx phenocrysts and microphenocrysts (Fig. 3a). Cpx crystals with distinct compositions occur together in every single sample. Similar Cpx compositional ranges were previously found in latitic and trachytic volcanics from Molara, Vateliero, Cava Nocelle, Fiaiano, and Arso sequences (Di Girolamo et al. 1995; Piochi et al. 1999), although not as Mg-rich as those observed here.

Olivine

Olivine in all the investigated samples is classified as chrysolite, with forsterite (Fo) content variable from 89.2 to 77.0 mol %; the range of Fo variation is about the same for Ol from the three sequences (Fig. 4a). Light and yellow Ol phenocrysts correspond to more and less magnesian

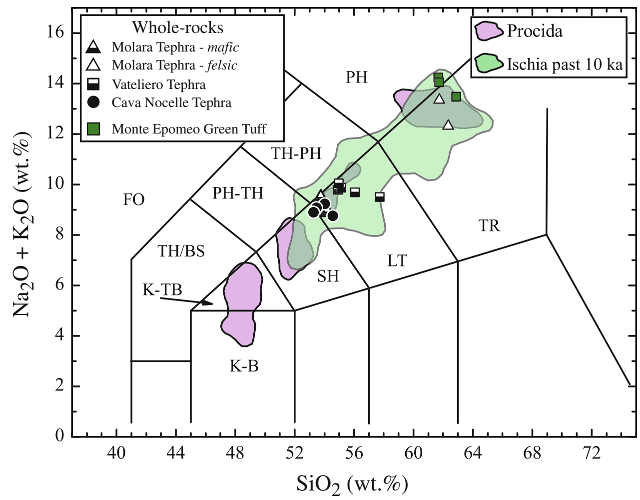


Fig. 5 Total Alkali versus Silica classification diagram (TAS; Le Maitre et al. 1989) showing the composition of the investigated Ischia volcanic rocks (data from Appendix E, electronic supplementary material). All analyses were plotted after normalization to 100 % on water-free basis, according to recommendation by I.U.G.S. (Le Maitre et al. 1989). K-B = K-basalt; K-TB = K-trachybasalt; SH = shoshonite; LT = latite; TR = trachyte (these rock names are relative to a K-alkaline series); TH/BS = tephrite/basanite; PH-TH = phonotephrite; TH-PH = tephriphonolite; PH = phonolite. The *green* and *pink* fields encompass the composition of past 10 ka Ischia, and Procida volcanic rocks, respectively, from the literature (data from Vezzoli 1988, and references therein; Crisci et al. 1989; Orsi et al. 1992; Di Girolamo et al. 1995; Piochi et al. 1999; D'Antonio et al. 1999, 2007; De Astis et al. 2004). The MEGT data are from Brown et al. (2008)

varieties. Two distinct groups have been recognized: (1) Mg-rich group 1 with Fo content ranging from 89 to 85 mol % and (2) Mg-poor group 2 with Fo from 83 to 77 mol %. The phenocrysts are generally homogeneous in composition; sometimes slight, normal chemical zoning has been detected. One case of significant reverse zoning has been measured in a phenocryst from Cava Nocelle Tephra, with Fo content from 80.3 at the core to 81.5 mol % at the rim. A similar compositional range ($Fo_{87–72}$) was measured in Ol from Molara, Vateliero, and Cava Nocelle sequences by Di Girolamo et al. (1995), whereas Ol from Fiaiano and Arso Tephra ($Fo_{83–70}$; Piochi et al. 1999) has been reported to be Mg poor.

Feldspars

Feldspar in the investigated *mafic* rocks is dominantly plagioclase, displaying either normal or reverse or sometimes complex chemical zoning. Compositions range from almost pure anorthite (An_{95}), through bytownite and labradorite, to andesine (An_{39}) (Fig. 4b). While the An-richest and labradorite-to-andesine compositions are more frequent, bytownite is scarce. Rare sanidine occurs as either isolated phenocrysts or in glomerocrysts, with composition

Or_{55-52}. Sometimes sanidine is observed as the late-stage rim of large plagioclase phenocrysts (e.g., Fig. 3c). In Molara Tephra *felsic* samples, plagioclase varies from labradorite to andesine (An_{53-36}); the co-existing alkali-feldspar is sanidine (Or_{55-45}). Even larger compositional ranges were measured in feldspars from Molara, Vateliero, Cava Nocelle, Fiaiano, and Arso sequences (Di Girolamo et al. 1995; Piochi et al. 1999), that is, plagioclase from An_{95} to An_{20}, and alkali-feldspar from Or_{74} to Or_{11}.

Opaques

The most common opaque is Ti-magnetite with ca. 30 % ulvöspinel component. It occurs as microphenocrysts, both isolated and in glomerocrysts with Cpx, Pl and Bt, and as microlites in the groundmass. Sometimes, it also occurs as microlites trapped in Cpx and Bt phenocrysts. The other opaque is a chromium-rich spinel, found exclusively as microlites in some Ol phenocrysts with Fo content from 89 to 81 mol % (Fig. 3b). The *mg*-number and *cr*-number of these Cr-spinels are in the range 0.66–0.52 and 0.58–0.28, respectively, correlating with decreasing forsterite content of the host olivine crystal.

Other mineral phases

Black mica is quite common in all analyzed volcanic rocks. It occurs both as phenocrysts and microphenocrysts, and sometimes in glomerocrysts along with Pl, Cpx, and opaques. It is quite rich in TiO_2 and classifies as ferroan–phlogopite and as Mg-biotite (IMA-1998; Yavuz 2003). Fluor–apatite is commonly found as accessory phase, included in Bt and Cpx. Rare calcic amphibole was found in the groundmass of a sample from Vateliero Tephra, classified as a potassian-titanian magnesiohastingsite (IMA-04; Yavuz 2007).

Whole-rock chemistry

The samples of Molara, Vateliero, and Cava Nocelle sequences (Appendix E, electronic supplementary material) have been plotted in the TAS classification grid (Fig. 5) and compared with the compositional fields of volcanic rocks emplaced at Ischia over the past 10 ka and at Procida. Moreover, the composition of samples representative of the Mt. Epomeo Green Tuff (Brown et al. 2008, and references therein) has also been plotted. All samples representative of the Vateliero Tephra classify as latite, with a small variation of silica from 54.98 to 57.82 wt% (on anhydrous basis), but no significant variation of total alkalis. The Molara Tephra is bimodal, as the two samples from eruption unit A classify as latite, whereas the two samples from eruption unit B fall in the trachyte field.

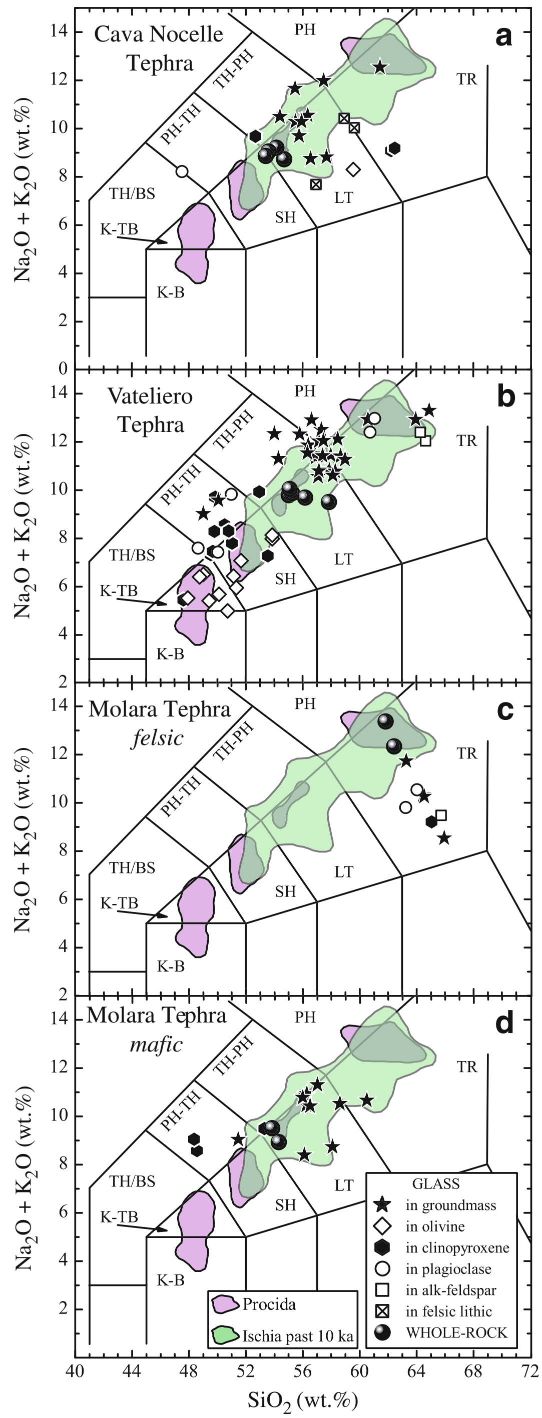


Fig. 6 TAS diagrams showing the composition of all glass analyzed in the selected volcanic rocks from **a** Molara (*mafic*), **b** Molara (*felsic*), **c** Vateliero (*mafic*), and **d** Cava Nocelle (*mafic*) sequences. The olivine-hosted MIs analyses were plotted after correction for post-entrapment crystallization (see text, and Appendix I). All analyses were plotted after normalization to 100 wt% on water-free basis, according to recommendation by I.U.G.S. (Le Maitre et al. 1989). Colored fields and abbreviation names as in Fig. 5

Three samples from Cava Nocelle Tephra classify as latite, whereas one sample falls in the shoshonite field close to the limit with the latite field. The latter four samples are the least evolved among those investigated in this paper (MgO between 3.78 and 3.53 wt%). All samples are mildly alkaline, with Na_2O-2.0≪ K_2O (according to Le Maitre et al. 1989), and silica-undersaturated, with normative nepheline in the range 1.0–7.1 wt%, but one sample, with no normative nepheline and 5.9 wt% normative hypersthene (C.I.P.W. norms are reported in Appendix F of the electronic supplementary material). The alkaline character is mirrored by high contents of alkaline and alkaline earth (Rb, Cs, Sr, Ba), as well as high-field strength (Zr, Nb, Hf, Ta) elements. light rare earth element patterns are strongly enriched over heavy REE (Appendix G, electronic supplementary material) and show a negative Eu anomaly deepening from *mafic* (Eu/Eu* = 0.93–0.80) to *felsic* samples (Eu/Eu* = 0.42–0.40). Transition metal (e.g., Sc, V, Cr, Co, Ni) concentrations are relatively low even for the least differentiated samples.

Glass chemistry

Electron microprobe measurements (112) have been carried out on glass, both in the groundmass and melt inclusions (MIs) trapped in minerals (Ol, Cpx, Pl, Sa). Of the 59 analyses of MIs, 12 are in olivine phenocrysts, thus potentially affected by post-entrapment crystallization. The latter has been taken into account by re-calculating each analyses through the Petrolog 3.1 software package (Danyushevsky and Plechov 2011). Representative groundmass glass and Cpx- and Fsp-hosted MIs compositions are listed in Appendix H, whereas the uncorrected/re-calculated analyses of olivine-hosted MIs are listed in Appendix I of the electronic supplementary material. The extreme variability of the analyzed glass is evident in the TAS classification grid (Fig. 6), although the scatter might be attributed partly to the uncertainty of EMPA (see Appendix A). The glass analyzed in samples of Vateliero Tephra is the most variable in both total alkalis and silica, especially when compared to the limited variation of whole-rock composition (Fig. 6b). The glass in the groundmass of the mafic rocks is unusually heterogeneous. It is mostly latitic in composition, however, glass of phono-tephritic, tephri-phonolitic, phonolitic, and trachytic composition also occurs. There is a rough correlation between groundmass glass color and composition, darker zones being less evolved with respect to lighter ones. The composition of MIs is even more variable than the glass in the groundmass. Glass trapped in Ol is mostly K-trachybasalt and shoshonite. Glass trapped in Cpx is mostly shoshonite and phono-tephrite, in some cases K-trachybasalt, tephri-phonolite, or trachyte; MIs in Pl are mostly phono-tephrite, sometimes tephrite or trachyte. Only the glass trapped in sanidine phenocrysts, and that in the groundmass of *felsic* samples from Molara Tephra (Fig. 6c), is trachyte. The large compositional range is well documented by highly variable MgO contents that range from 6.79 to 0.02 wt% (on anhydrous basis). The C.I.P.W. norm reveals that glass of basic and intermediate compositions is silica-undersaturated (normative nepheline up to ca. 12 wt%), whereas felsic glass is either silica-undersaturated or silica-oversaturated (normative quartz up to ca. 10 wt%). Overall, the composition of analyzed glass extends that of the past 10 ka whole-rocks of Ischia (green field in Fig. 6) toward both less and more evolved as well as more silica-undersaturated compositions. Moreover, the mafic glass found in latites of the Ischia rocks is comparable to the most primitive rocks of Procida (pink field in Fig. 6). Groundmass glass of Fiaiano and Arso sequences is much less variable, with MgO ranging from 2.62 to 0.48 wt% (Piochi et al. 1999).

Isotopic composition of whole-rocks and separated glass and minerals

Sr, Nd and O isotope ratios of representative Molara, Vateliero, and Cava Nocelle Tephra samples (whole-rocks,

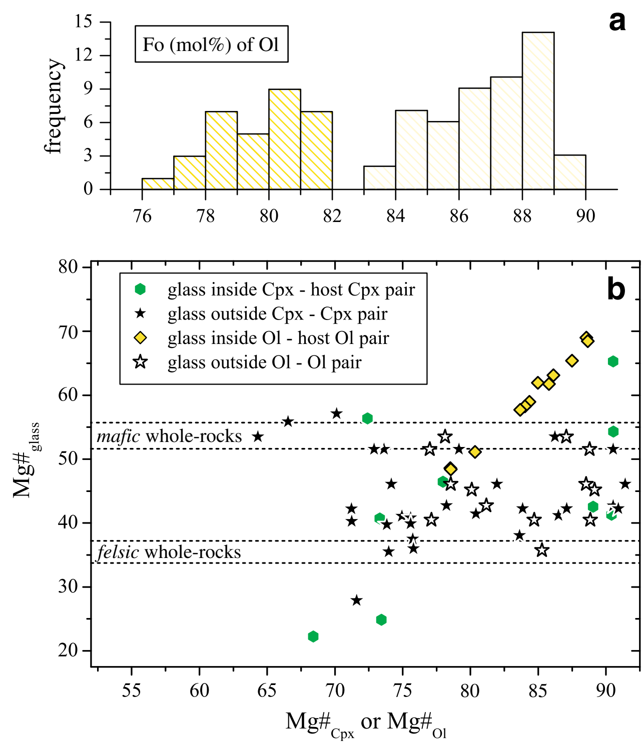
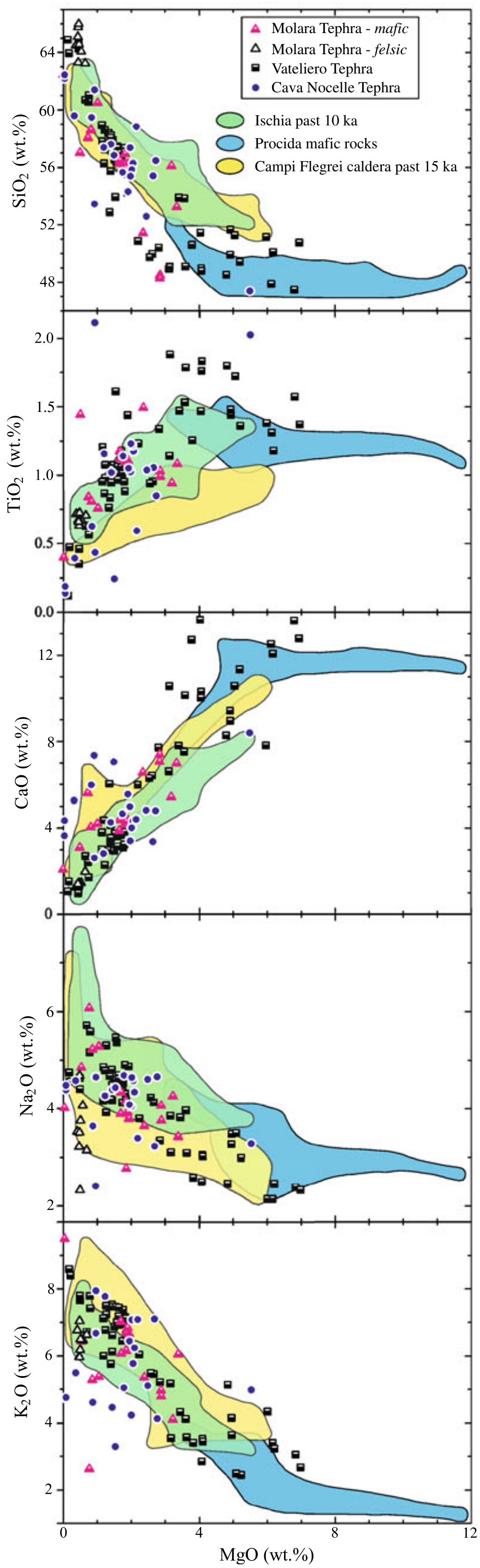


Fig. 7 **a** Frequency histogram showing the chemical composition of all Ol crystals analyzed in the investigated Ischia volcanic rocks. **b** binary diagram of Mg# (= 100 × *mg*-number for Cpx; = Fo mol. % for Ol) of crystal versus either trapped (i.e., MI) or host (i.e., groundmass) glass. The Mg# variation ranges for *mafic* and *felsic* whole-rocks are shown as *dashed lines*



◀ **Fig. 8** Binary diagrams of selected major oxides versus MgO wt%, used as a differentiation index, showing the composition of all glass analyzed in the investigated Ischia volcanic rocks. *Green field* whole-rock composition of past 10 ka volcanic rocks of Ischia (references as in Fig. 5); *blue field* whole-rock composition of K-basaltic to K-trachybasaltic volcanic rocks of Procida (D'Antonio et al. 1999, 2007 and references therein); *yellow field* whole-rock composition of past 15 ka volcanic rocks of Campi Flegrei caldera (D'Antonio et al. 2007 and references therein; Tonarini et al. 2009; Di Vito et al. 2011)

separated minerals, and glass) are listed in Appendix J (electronic supplementary material). Sr and Nd isotopic compositions of the analyzed whole-rock samples vary well beyond the analytical uncertainty (see Appendix A), from 0.70631 to 0.70648, and from 0.51259 to 0.51254, respectively. These ranges are slightly different from those reported in the literature for different samples from the three volcanic centers under investigation ($^{87}Sr/^{86}Sr$ = 0.70620–0.70635; $^{143}Nd/^{144}Nd$ = 0.51261–0.51254; Civetta et al. 1991; D'Antonio et al. 2007). The reason of this discrepancy will be discussed later. Even more variable, with respect to whole-rock samples, are the Sr and Nd isotope ratios of separated minerals and, subordinately, glass. The different types of clinopyroxene exhibit the largest $^{87}Sr/^{86}Sr$ ranges, between 0.70617 and 0.70697. It is interesting that Mg-rich Cpx has average $^{87}Sr/^{86}Sr$ higher than that of both Mg-poor and Fe-rich Cpx; moreover, the lowest $^{87}Sr/^{86}Sr$, that is 0.70617–0.70622, were measured in Fe-rich Cpx of Molara Tephra trachytes. The $^{143}Nd/^{144}Nd$ ratio of Mg-rich Cpx is also significantly variable, ranging from 0.51252 to 0.51250, and different from that of Fe-rich Cpx, ranging from 0.51256 to 0.51253.

The olivine separates also displays a large range of $^{87}Sr/^{86}Sr$, from 0.70631 to 0.70663, the Mg-rich having on average higher values than Mg-poor varieties. Since Ol is extremely poor in Sr, these values probably reflect the composition of glass inclusions within the olivines. Even lower is the $^{87}Sr/^{86}Sr$ detected in plagioclase separated from *mafic* samples, variable from 0.70600 to 0.70650. Sanidine has more homogeneous values, from 0.70597 to 0.70613, as well as biotite, from 0.70604 to 0.70617.

The Sr and Nd isotope ratios of glass separated from the groundmass of *mafic* samples range from 0.70628 to 0.70641, and from 0.51255 to 0.51253, respectively. In one *mafic* sample from Vateliero Tephra (I_VAT-A), dark and light glass shards have $^{87}Sr/^{86}Sr$ of 0.70638 and 0.70623, and $^{143}Nd/^{144}Nd$ of 0.51254 and 0.51252, respectively. Finally, the glass in trachyte from Molara Tephra has distinct, homogeneous isotopic composition of Sr and Nd, 0.70608 and 0.51256, respectively. Overall, the ranges of $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ measured in separated minerals and glass are much larger than those of whole-rocks studied here. However, this large range is surprisingly similar to that of all volcanic rocks emplaced at Ischia over

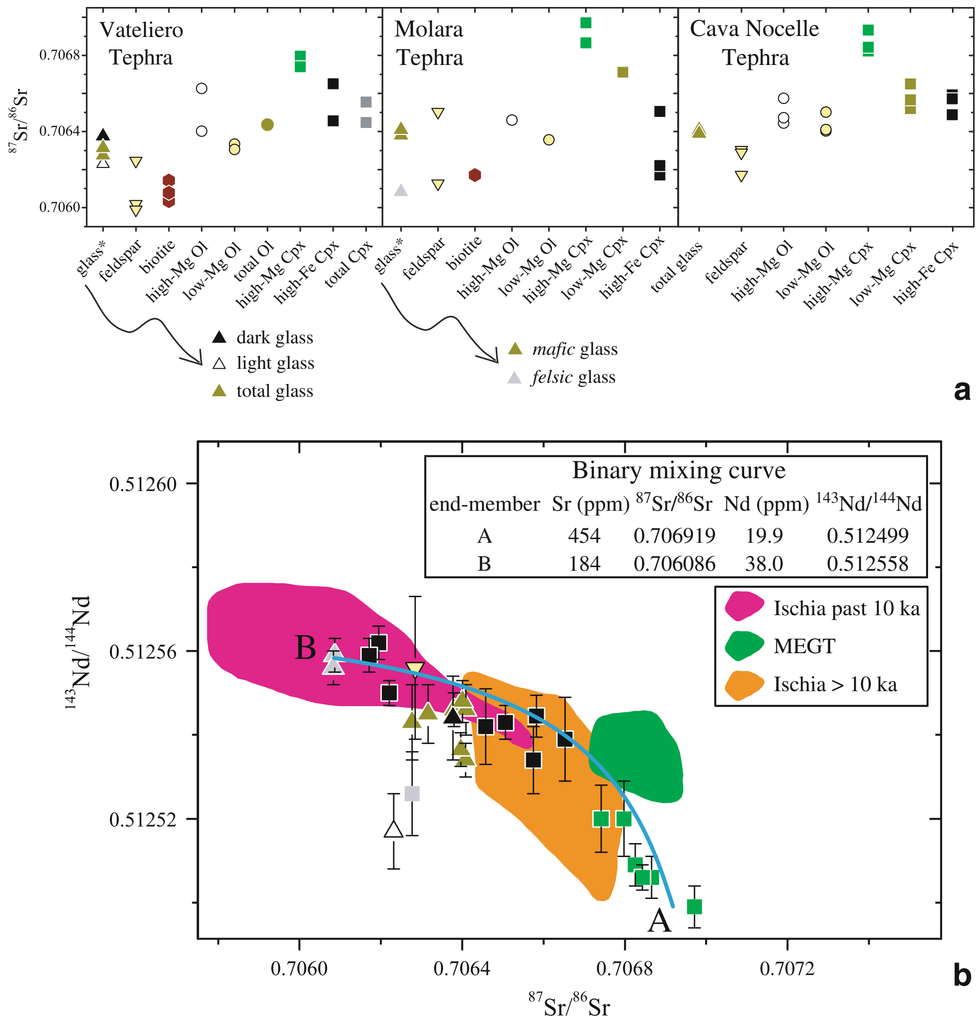


Fig. 9 **a** $^{87}Sr/^{86}Sr$ variation for separated minerals and glass of the Vateliero, Molara, and Cava Nocelle Tephra (data from Appendix J, electronic supplementary material). The *error bar* is included in symbols. Total Cpx stands for a Cpx separate including differently colored crystals. *Light glass* and *dark glass* were separated optically from a single sample; *mafic* glass and *felsic* glass were separated from samples with variable composition (i.e., *mafic* and *felsic*, respectively; Appendix E, electronic supplementary material). **b** $^{87}Sr/^{86}Sr$ versus $^{143}Nd/^{144}Nd$ binary diagram showing all separated minerals and glass of the investigated Ischia volcanic rocks (data from Appendix J, electronic supplementary material). The *error bar* for $^{87}Sr/^{86}Sr$ is included in symbols. Data fields for other Ischia whole-rocks, both younger and older than 10 ka, including MEGT, from the literature (D'Antonio et al. 2007), and unpublished from the authors are shown for comparison. The *blue curve* represents a binary mixing process between two end-members A and B, calculated through the Langmuir et al. (1978) equation; numerical parameters of the mixing hyperbola are given in the *inset*. See text for further details

the past 10 ka (0.7058–0.7070; Civetta et al. 1991; Orsi et al. 1992; Piochi et al. 1999; Slejko et al. 2004; D'Antonio et al. 2007). A more restricted range of $^{87}Sr/^{86}Sr$ values, from 0.70603 to 0.70682, was detected in Cpx, Ol, feldspars, and glass separated from latites and trachytes of the Fiaiano and Arso eruptions (Piochi et al. 1999).

The oxygen isotopic compositions measured by laser fluorination (see Appendix A) on separated olivine and clinopyroxene crystals, both as single, large individuals and groups of smaller phenocrysts, vary outside analytical uncertainty. Olivine $\delta^{18}O$ values vary from 5.55 to 6.16 ‰, with no systematic variations in Mg-rich and Mg-poor types. A slightly larger range of $\delta^{18}O$ has been detected in Cpx, from 5.77 to 6.50 ‰, the Mg-rich type being the most variable. These $\delta^{18}O$ values are among the lowest ever detected in Plio-Quaternary K-alkaline volcanics of Italy (Dallai et al. 2004, 2011; Frezzotti et al. 2007; Santo and Peccerillo 2008).

Discussion

Our results show: (1) distinct olivine and clinopyroxene crystals populations; (2) extremely wide compositional range of glass of *mafic* samples, both in groundmass and trapped in crystals, in disagreement with the quite homogeneous whole-rock chemistry; (3) wide isotopic ranges in separated minerals and glass. All these features suggest that open-system evolution must have been a major process in the Ischia plumbing system before and/or during the short time span in which Molara, Vateliero, and Cava Nocelle eruptions took place (ca. 2.5–2.1 ka BP). In the following, our mineralogical, geochemical, and isotopic data will be discussed in terms of interaction among compositionally distinct magma batches resulting from different mantle and crustal sources, and with respect to the Ischia plumbing system and its regional tectonic setting.

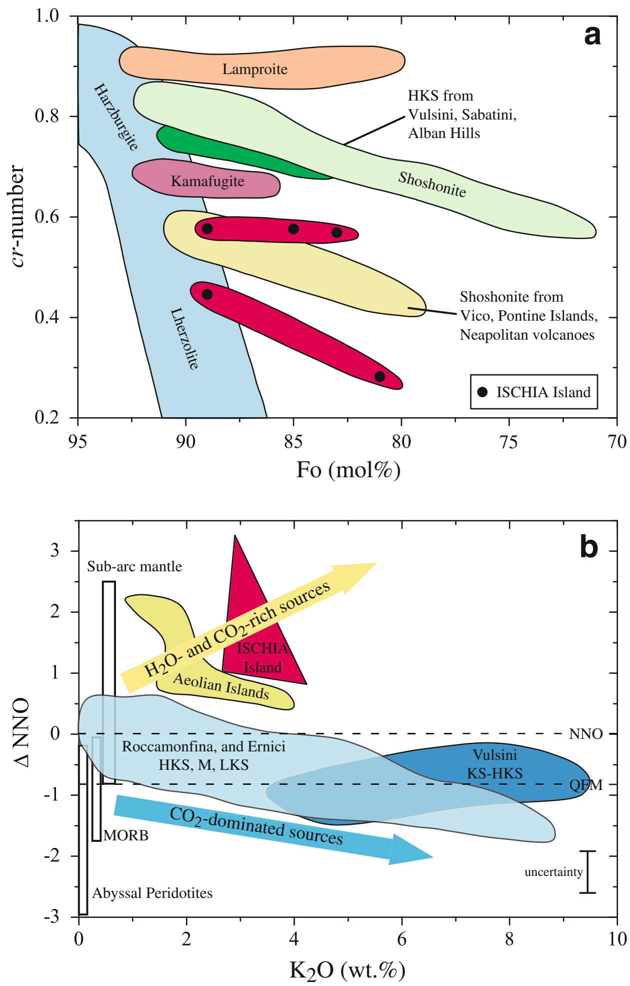


Fig. 10 **a** *cr*-number of spinel versus Fo content (mol %) of host olivines for Ischia, compared to those of volcanic rocks belonging to different potassic and ultrapotassic series from Plio-Quaternary volcanic centers of Italy (simplified after Conticelli et al. 2004). **b** Oxygen fugacity values of Ischia MIs, expressed as 10log units relative to the Ni-NiO (NNO) buffer, versus K_2O contents compared to those of volcanic rocks belonging to different potassic alkaline series from Plio-Quaternary volcanic centers of Italy (simplified after Nikogosian and van Bergen 2010). The red triangular field encompasses redox conditions for Ischia potassic mafic magmas estimated as explained in Appendix K; see text for further details

Mineral and glass chemistry evidence for mingling/mixing processes

The whole-rock chemistry of *mafic* samples exhibits limited variations (e.g., MgO between 3.78 and 2.82 wt%), which at least in part must be due to fractional crystallization (FC). However, the large compositional variability of minerals and glass requires additional magmatic processes. For instance, the most Mg-rich diopsides and ferroan diopsides, so rich in chromium (Cr_2O_3 up to 1.13 wt%), appear too primitive in comparison to the relatively differentiated shoshonitic to latitic host-rocks, with low Cr contents (61–32 ppm). Rather, these Cpx must have formed in Cr-rich, more mafic liquid(s). Also, the Mg-rich olivines (Fo up to 89 mol %) are clearly too primitive with respect to their evolved host-rocks (Fig. 4a). The frequency histogram of Fig. 7a clearly shows two distinct populations of Ol having Fo content one ca. 87 mol % another ca. 80 mol %. The two modes are separated by a small compositional gap. Similar histograms would show two modes also for Cpx and Pl phenocrysts. Two distinct populations of Ol and Pl (but not Cpx) crystals were already recognized by Crisci et al. (1989) for some trachybasalts (i.e., shoshonites in the TAS classification diagram) and latites from the same volcanic centers here investigated.

If the Ol and Cpx phenocrysts were in equilibrium with their groundmass glass, the Mg# of phenocryst-host glass pairs should exhibit a positive correlation. This can be checked in Fig. 7b, where the Mg# of crystal–glass pairs can be compared to that of whole-rocks, shown as horizontal dashed lines. The wide scatter of data points is a clear evidence that most crystals are not in equilibrium with their host glass. The only notable exception is the good positive correlation between Mg# of Ol crystals and that of their trapped melts, although this correlation is partly a result of the recalculation of MIs for post-entrapment crystallization.

Disequilibrium between host and phenocrysts (Cpx and Ol) can be explained as the result of mingling and/or mixing processes among magmas either crystallizing at variable pressure or having different degrees of chemical evolution (e.g., Dobosi and Fodor 1992; Zhu and Ogasawara 2004; Gioncada et al. 2005; Ohba et al. 2007). Less conclusive is the variable plagioclase composition. Indeed, Pl phenocrysts with An content as high as 95 mol % (Fig. 4b) occurring in evolved rocks might derive from either a Ca–Al-rich mafic melt or a H_2O-rich evolved magma (e.g., Panjasawatwong et al. 1995). Furthermore, the mafic composition of glass trapped in some Pl crystals, that is, shoshonite, tephrite, phono-tephrite with silica generally less than 52 wt% (Fig. 6) suggests that they equilibrated in magmas less evolved with respect to the shoshonitic to latitic host-rocks that are, strictly, intermediate.

Harker diagrams (Fig. 8) show well the extremely wide chemical variability of the glass, extending the range described by the past 10 ka products of Ischia (green fields) toward less evolved compositions, spanning much of the PVD compositional range. Usually, the composition of glass of groundmass and within phenocrysts is expected to be more evolved than that of the host-rock, giving information on the most evolved end of the liquid line of descent in volcanic suites showing no evidence for open-system processes (e.g., Toothill et al. 2007). This is clearly not the case for the glass analyzed in the present work, being frequently less evolved than the composition of host-rocks (Fig. 6). A similar, though much narrower variability of glass composition has been detected in Cpx- and Ol-hosted MIs from mafic to felsic PVD volcanic rocks (Cannatelli et al. 2007; Mangiacapra et al. 2008; Arienzo et al. 2010; Esposito et al. 2011; Mormone et al. 2011). Arienzo et al. (2010) and Esposito et al. (2011) have interpreted this as evidence for mingling/mixing among magmas with variable degree of chemical evolution. The same conclusion is here put forward to explain the extremely variable composition detected in glass of the studied Ischia sequences.

In summary, the quite homogenous whole-rock latitic composition might suggest complete mixing between mafic and felsic melts; instead, the large variability of mineral and glass chemistry testifies to mingling in the genesis of Molara, Vateliero, and Cava Nocelle hybrid rocks.

Isotopic evidence for mingling/mixing processes

Given the strong mineral and glass disequilibria displayed by Molara, Vateliero, and Cava Nocelle sequences, their whole-rock Sr and Nd isotope ratios are strictly a reflection of different proportions of phenocrysts and glass with variable isotopic compositions. That might be a reasonable explanation for the variable range of $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios measured in whole-rock samples of the studied tephra (Civetta et al. 1991; D'Antonio et al. 2007; present work) that are, thus, meaningless.

Figure 9 highlights that all mineral and glass separates from the investigated samples define a unique negative correlation trend of Sr and Nd isotopes, between two end-members: a high $^{87}Sr/^{86}Sr$ and low $^{143}Nd/^{144}Nd$ end-member, including all Mg-rich Cpx and some Mg-rich Ol, and a low $^{87}Sr/^{86}Sr$ and high $^{143}Nd/^{144}Nd$ one, including glass from *felsic* samples of Molara Tephra, and a few Fe-rich Cpx. Since both isotopic ratios vary, low-temperature alteration processes, that might have mobilized Sr but not Nd, can be confidently ruled out. Thus, our data are best explained by the interaction of two types of magma, each with its own crystal load: one with lower $^{87}Sr/^{86}Sr$ and higher $^{143}Nd/^{144}Nd$ ratios, similar to magmas which fed the past 10 ka Ischia activity (magenta field), and another with higher $^{87}Sr/^{86}Sr$ and lower $^{143}Nd/^{144}Nd$ ratios, similar to magmas which fed older Ischia eruptions (orange field).

Modeling binary mixing relies on the definition of two end-members (Langmuir et al. 1978). The mafic end-member is likely represented by high-Mg Cpx. The only PVD mafic volcanic rocks that have high-Mg Cpx in equilibrium with the groundmass are K-basaltic enclaves of Procida island (Solchiaro eruption; D'Antonio et al. 1999). The Sr and Nd contents of their olivine-hosted MIs (Esposito et al. 2011) and the isotopic composition of Molara Tephra high-Mg Cpx define this mafic end-member. The felsic end-member should be equivalent to a typical past 10 ka trachyte of Ischia (e.g., from Cretaio eruption), and its isotopic composition can be assumed as that of the felsic glass of Molara Tephra. The calculated binary mixing curve (Fig. 9b) fits separated mineral and glass data quite well, considering the uncertainty in isotope data. However, some data points do not fall close to the mixing curve

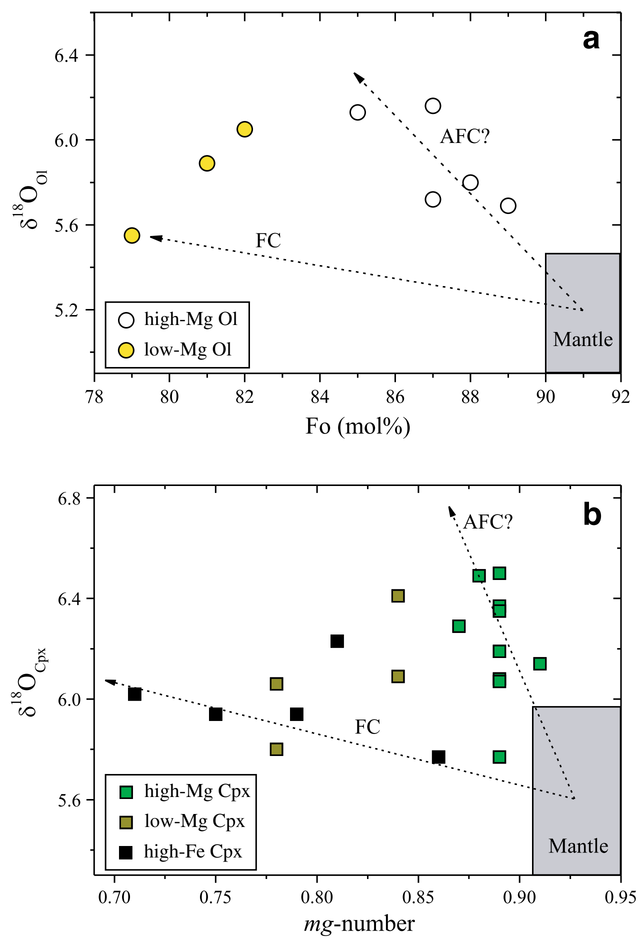
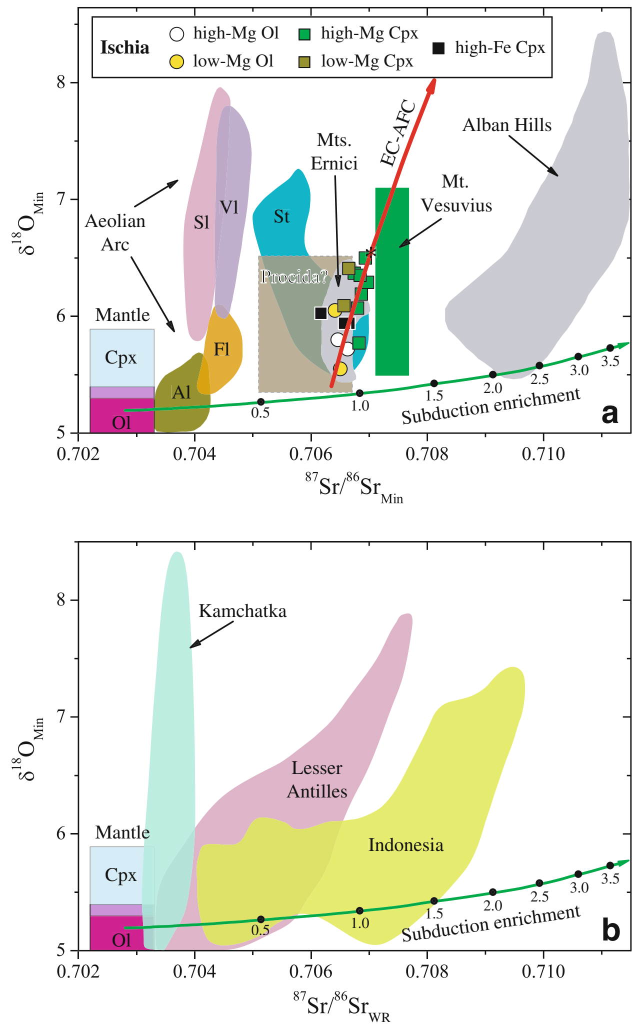


Fig. 11 $\delta^{18}O$ versus **a** Fo mol % (Ol) and **b** *mg*-number (Cpx) binary diagrams for separated minerals of the investigated Ischia volcanic rocks (Appendix J, electronic supplementary material). FC = fractional crystallization; AFC = assimilation + fractional crystallization



◀ **Fig. 12** **a** $\delta^{18}O$ versus $^{87}Sr/^{86}Sr$ binary diagram for separated minerals of the investigated Ischia volcanic rocks (Appendix J, electronic supplementary material) compared with data from other volcanic centers located along the Apennine compressive margin of Italy. Available $\delta^{18}O$ literature data on Cpx and/or Ol crystals have been plotted against the $^{87}Sr/^{86}Sr$ of host whole-rocks in order to draw data fields for Alban Hills (Dallai et al. 2004; Gaeta et al. 2006), Mts. Ernici (Frezzotti et al. 2007), and Aeolian Arc (Peccerillo et al. 2004; Santo and Peccerillo 2008, and references therein). Key for abbreviations: Al = Alicudi; Fl = Filicudi; Sl = Salina; Vl = Vulcano; St = Stromboli. The box for Procida island has been drawn using whole-rock Sr isotope literature data (D'Antonio et al. 1999; De Astis et al. 2004), by hypothesizing that their $\delta^{18}O$ values are similar to those of Ischia island (this work). The box for Mt. Vesuvius has been drawn using Sr isotope literature data on younger than 4-ka whole-rocks (Santacroce et al. 1993; Cioni et al. 1995) and O isotope literature data on Cpx and Ol crystals (Dallai et al. 2011). The *green curve* represents a source enrichment process involving MORB mantle to which fluids/melts from pelagic sediments have been added in different percentages indicated by numbers on dots ($R = ([Sr]m/[O]m)/([Sr]c/[O]c) = 0.03$). Numerical parameters used in the modeling are listed in Table 1. The *red curve* represents an AFC process involving a primitive magma segregated by the subduction-modified mantle sector below Ischia that crystallizes and assimilates Hercynian continental crust; the black asterisk indicates O-Sr isotopic values resulting from 7 % of assimilated mass. Numerical parameters used in the modeling are listed in Table 2. **b** $\delta^{18}O$ versus $^{87}Sr/^{86}Sr$ binary diagram for some relevant volcanic island arcs: Lesser Antilles (Van Soest et al. 2002, and references therein); Indonesia (Java Island and Banda Arc; Handley et al. 2010, and references therein); and Kamchatka (Bindeman et al. 2004, and references therein). The fields include $\delta^{18}O$ data on Cpx and/or Ol plotted versus $^{87}Sr/^{86}Sr$ on whole-rocks

suggesting processes more complex than the simple binary mixing.

Inferences for mantle and crustal components and processes

Since our data define possible mantle and crustal end-members, we can make inferences on their origin and composition. One relevant aspect of the mantle source of Ischia magmas, its redox state, can be assessed considering mafic minerals. Olivine crystals characterized by Fo content >80 mol % host mafic MIs with MgO content as high as 6.9 wt% (after re-calculation for post-entrapment crystallization, see Appendix I). Moreover, these crystals host chromium-rich spinel microlites (Fig. 3b), and some of them are kink banded, a feature typical of olivine grown in the deep lithosphere. All this suggests that the host olivines may have equilibrated in a magma more mafic than the one represented by the latitic host-rocks. The *cr*-number values of the analyzed Ischia Cr-spinels are peculiar with respect to those of other Italian Plio-Quaternary potassic and ultrapotassic volcanic rocks (Fig. 10a) and demand a fertile, lherzolitic mantle. Even though our data on Cr-spinels are limited in number, noteworthy is that two of them hosted in high-Mg Ol fall on distinct positions along the mantle array of Fig. 10a. This strengthens further the hypothesis that the heterogeneity of the Campania mantle source region is likely due to chemical exchanges with fluids/melts coming from subduction slab-derived pelagic sediments (e.g., D'Antonio et al. 1999, 2007; Tonarini et al. 2004). Indeed, following Kelley and Cottrell (2009), huge amounts of hot and oxidizing fluids involved in subduction settings increase the oxidation state of sub-arc magmas. Therefore, the most mafic magmas of Ischia should be characterized by high $Fe^{3+}/\Sigma Fe$ values, hence oxygen fugacity, in agreement with the high water content detected in MIs (Moretti et al. 2013; Appendix K, electronic supplementary material), and the general redox properties of hydrous melts (Moretti and Ottonello 2003; Moretti 2005).

Application of the Maurel and Maurel (1982) equation to representative melt-Cr-spinel pairs allowed us to evaluate the range of oxidation states characterizing the Ischia parental mafic magmas. Our educated guess for oxygen fugacity values calculated under variable possible conditions (Appendix K, electronic supplementary material) is

Table 1 Parameters used for the subduction enrichment modeling of Fig. 12 using Sr–O isotopes

End-member	Composition	Sr ppm	$^{87}Sr/^{86}Sr$	K_dSr	$\delta^{18}O$ ‰	O wt%	R*	References
MORB mantle	Peridotite	10	0.7028		5.2	43.7	0.03	1, 2, 3
Pelagic sediment	Clay	208	0.7170	0.53	18.0	52.1		4

* R = ([Sr]m/[O]m)/([Sr]c/[O]c), where m = mantle or magma, and c = contaminant. Key for references: (1) GERM reservoir database (http://earthref.org/GERM/); (2) Mattey et al. 1994; (3) Eiler 2001; (4) Rollinson 1993. O wt% calculated from major oxide compositions

Table 2 Parameters used for the EC-AFC modeling of Fig. 12 using Sr–O isotopes

Equilibration parameters—transition from K-basalt to latite					
T_{eq}	Equilibration temperature	900 °C			
$T_{l,m}$	Magma liquidus temperature	1,300 °C			
T^0_m	Initial magma temperature	1,350 °C			
$T_{l,a}$	Wall-rock liquidus temperature	980 °C			
T^0_a	Initial wall-rock temperature	400 °C			
T_s	Wall-rock solidus temperature	780 °C			
$C_{p,m}$	Magma isobaric specific heat capacity	1,484 J/kg K			
$C_{p,a}$	Assimilant isobaric specific heat capacity	1,388 J/kg K			
Δh_{cry}	Crystallization enthalpy	396,000 J/kg			
Δh_{fus}	Fusion enthalpy	354,000 J/kg			
Geochemical parameters					
	Sr	$^{87}Sr/^{86}Sr$	D_0	O	$\delta^{18}O$
Magma	500 ppm	0.7063	0.9	47 wt%	5.4 ‰
Assimilant	280 ppm	0.7130	0.8	50 wt%	12.0 ‰

Average O and Sr isotope data of assimilant (Hercynian granodiorite) from Ayuso et al. (1994) and Rottura et al. (1991), respectively

D_0 Bulk distribution coefficient

used to expand the ΔNNO versus K_2O diagram of Nikogosian and Van Bergen (2010) for Italian potassic volcanics (Fig. 10b). The diagram shows that Ischia products plot at conditions of oxygen fugacity that can be even higher than those of Aeolian Islands, enlarging the fO_2 upper limits of island arc magmas in case the correction for post-entrapment olivine crystallization is not applied. Together, the two fields of Aeolian Islands and Ischia point toward a trend opposite to the one displayed by the potassic and ultrapotassic volcanics of central Italy, generally characterized by a gentle decrease of oxygen fugacity at increasing K_2O. We speculate that the high oxidation state of Ischia and Aeolian Islands is the effect of abundant subduction-derived hydrous fluids, whereas the trend of slight decreasing fO_2 at increasing K_2O content of alkaline magmas feeding volcanoes of central Italy represent nearly anhydrous systems, dominated by CO_2 infiltration and/or carbonate assimilation (e.g., Conticelli et al. 2004; Dallai et al. 2004, 2011; Frezzotti et al. 2007; Avanzinelli et al. 2009).

The most mafic glass, detected in Vateliero Tephra olivine crystals, is K-trachybasaltic in composition, with chemical features close to those of the least evolved products of PVD found at Procida, ranging from K-basalt to K-trachybasalt (Figs. 6, 8). Thus, K-basaltic primary melts can be inferred to feed the Ischia plumbing system. Given their potassic (and related trace elements) character, such primary melts were generated by partial melting of a mantle sector likely made up of amphibole- or phlogopite-bearing spinel-peridotite, by analogy with petrogenetic hypotheses on the generation of mildly potassic melts which fed the Plio-Quaternary volcanism of Italy (e.g., Ellam et al. 1989; D'Antonio et al. 1999; Conticelli et al. 2002; Avanzinelli et al. 2009; Nikogosian and van Bergen 2010). Trace element and isotopic features of Ischia, as well as of Procida volcanics, suggest that this mantle sector can be considered as the least modified one by subduction-related sedimentary components in the framework of Plio-Quaternary magmatism of Italy (e.g., Civetta et al. 1991; Piochi et al. 1999; D'Antonio et al. 1999, 2007; Conticelli et al. 2002, 2004; De Astis et al. 2004; Tonarini et al. 2004; Avanzinelli et al. 2009; this work). This feature may appear to contradict the abundant subduction-derived hydrous fluids inferred for the PVD mantle sector. However, the contradiction is easily reconciled if we consider the different role of H_2O and CO_2 in the slab-derived fluids. They derive from devolatilization of carbonate-bearing pelagic sediments, the most likely sedimentary material of the slab (e.g., Ellam et al. 1989; D'Antonio et al. 1999, 2007; Conticelli et al. 2002; Avanzinelli et al. 2009; Nikogosian and van Bergen 2010) that, below the Campania region, is thought to be oceanic, whereas it should be continental below Latium and Tuscany regions (e.g., Sartori 2003). In case of carbonate rock incipiently subducted, the huge release of CO_2 could favor partial melting conditions leading to high potassium enrichments (e.g., Edgar 1987; Conticelli et al. 2002). This can apply particularly to the CO_2-dominated ultrapotassic magmas of the Latium and Tuscany regions, in line with the ΔNNO versus K_2O correlation (Nikogosian and van Bergen 2010; Fig. 10b). On the other side, potassic magmas of the Campania region, and Stromboli in the Aeolian Arc, show much larger proportions of H_2O (up to 4 wt% in MIs) than CO_2, suggesting much larger oxidation states. This difference may be attributed to (1) a lower proportion of carbonate in the metasomatic agent below Campania, than below Latium and Tuscany: this would agree with a different nature of the subducting slab, that is, oceanic versus continental; (2) different depths of partial melting of the contaminated mantle: the deeper the partial melting, the higher the partial pressure of CO_2, and the greater the degree of silica undersaturation and potassium content (e.g., Edgar 1987); (3) a combination of the two.

The oxygen and strontium isotopic characteristics of the investigated Ischia olivine and clinopyroxene phenocrysts can help to better constrain the meaning of the regional geochemical and isotopic variations found in Plio-Quaternary volcanic rocks of Italy. Closed-system fractional crystallization processes (FC) of magmas with different alkalinity and SiO_2 in the range 48–74 wt% increase $\delta^{18}O$ of about 0.3–0.4 ‰ only (e.g., Bindeman 2008). The overall variation of about 1 ‰ detected in the analyzed Ischia minerals requires additional processes such as assimilation of continental crust. Olivine crystals have $\delta^{18}O$ in the range 5.55–6.16 ‰, thus never falling in the range of upper mantle olivine (5.2 ± 0.2 ‰; Mattey et al. 1994; Eiler 2001), although some values are very close to the higher end. Interestingly, the most Mg-rich Ol crystals display increase of $\delta^{18}O$ at decreasing Fo content, whereas the lowest $\delta^{18}O$ value is shown by an evolved crystal with Fo ca. 79 mol % (Fig. 11a). Similar features arise after examination of $\delta^{18}O$ versus *mg*-number variation in Cpx crystals (Fig. 11b). The higher number of data available for Cpx better highlights the variety of possible FC and AFC trends starting from a slightly modified mantle source (upper mantle Cpx has $\delta^{18}O$ of 5.6 ± 0.3 ‰; Mattey et al. 1994; Eiler 2001). Again, the most Mg-rich Cpx crystals display the steepest increase of $\delta^{18}O$ at decreasing *mg*-number, suggesting that more mafic, hence hotter magmas assimilated continental crust during fractional crystallization. Thus, variable evolution processes can be suggested for the Ischia magmas, from closed-system FC of mafic magmas originally derived from a mantle source only slightly enriched in ^{18}O with respect to “unmodified” mantle, to assimilation + fractional crystallization (AFC) processes that significantly increased ^{18}O, as well as ^{87}Sr, of such magmas. Moreover, the scatter of data points in the diagrams of Fig. 11 may be a further evidence for mingling/mixing processes among variably contaminated magmas. Indeed, such variable FC-AFC evolution processes likely generated the isotopically distinct end-members recognized in the Sr–Nd isotope space (Fig. 9) that interacted in the Ischia plumbing system over the past 2.9 ka. Conversely, the lowest $\delta^{18}O$ value, detected in a Fe-rich single phenocryst, can be the result of either interaction with hydrothermal fluids (e.g., Thirlwall et al. 1997; Lassiter and Hauri 1998), or trapping of magnetite, both known to fractionate oxygen isotopes increasing ^{16}O (e.g., Harris et al. 2000).

The sensitivity of coupled oxygen and strontium isotopes as a tool to identify the involvement of crustal (i.e., sedimentary) components in magmatic processes is well known. In particular, downward- and upward-convex curves in the O-Sr isotope space may discriminate between mantle source enrichment and AFC processes in subduction settings, respectively (e.g., James 1981; Van Soest et al. 2002; Bindeman et al. 2004; Handley et al. 2010). Now, we use O-Sr isotope data of Ol and Cpx crystals from Molara, Vateliero, and Cava Nocelle Tephra in order to constrain mantle versus crustal processes under the PVD, and we compare our data with available literature data from other Italian Plio-Quaternary volcanic centers, such as Alban Hills, Mts. Ernici, Mt. Vesuvius, and Aeolian Islands (Fig. 12). For these, laser fluorination oxygen isotope data were recently obtained on olivine and/or pyroxene phenocrysts (Dallai et al. 2004, 2011; Peccerillo et al. 2004; Frezzotti et al. 2007; Santo and Peccerillo, 2008), proven to be much more reliable with respect to conventional fluorination analysis on whole-rock (e.g., Eiler et al. 1997; Dobosi et al. 1998; Bindeman 2008, and references therein). It is clearly evident that there is a progressive increase of both $\delta^{18}O$ values and $^{87}Sr/^{86}Sr$ ratios from the Aeolian Arc, through Procida, Ischia (largely overlapping the fields of Mts. Ernici and Stromboli) and Mt. Vesuvius, to Alban Hills. At a closer look, moreover, the minerals least enriched in ^{18}O and ^{87}Sr of each volcanic center, if considered together, appear to be progressively displaced toward significantly higher $^{87}Sr/^{86}Sr$ ratios and slightly higher $\delta^{18}O$ values. As suggested for the magmagenesis in several subduction settings worldwide (e.g., Van Soest et al. 2002; Bindeman et al. 2004; Handley et al. 2010), this trend can be achieved through a mantle enrichment process by sedimentary material, such as subduction involving an oceanic lithospheric slab carrying a few hundreds meters cover of pelagic clays. Indeed, a few weight percents of fluids/melts from this material added to a depleted-MORB mantle sector would increase much more its ^{87}Sr, and less its ^{18}O, given the much greater difference in Sr content relative to O between mantle and sediments. Such a mantle source process (subduction enrichment) has been modeled through the Langmuir et al. (1978) binary mixing equation (parameters of end-members given in Table 1). The modeling (green curve in Fig. 12a) foresees addition to a depleted-MORB mantle of about 0.2–0.3 wt% of pelagic sediment fluids/melts for Aeolian islands (except Stromboli), about 0.5–1 wt% for Ischia, Procida as well as Stromboli and Mts. Ernici, about 1.2 wt% for Mt. Vesuvius, and 2–2.5 wt% for Alban Hills, in substantial agreement with previous modeling (e.g., D'Antonio et al. 1999, 2007; Tonarini et al. 2004; Santo and Peccerillo, 2008; Avanzinelli et al. 2009). Partial melting of such mantle source regions, each modified by a different amount of subduction slab-derived fluids/melts, generated a variety of primary melts throughout the Tyrrhenian margin of Italian peninsula. After segregation from the mantle source, each of these magmas rose toward the surface and suffered open-system evolution processes that increased its Sr , and especially O isotope ratios, thus describing steep trends in the O-Sr isotope space. At Ischia, these processes are likely responsible also for the variable Sr and Nd isotopic values of mineral and glass separates (Fig. 9); the same might have occurred at other volcanic centers in Italy.

The infiltration of abundant, hot, and oxidizing fluids from the subducting slab, as recorded by the unusually high oxidation state of Cr-spinels hosted in early crystallizing olivine, may have facilitated the chemical and thermal diffusion and exchange between mafic magmas and surrounding crustal rocks. As already suggested for Campi Flegrei and Mt. Vesuvius magmas, a good candidate for the assimilant could have been Hercynian intrusives, supposed to compose the crustal basement underneath the Campania region (Pappalardo et al. 2002; Di Renzo et al. 2007, 2011). Actually, the role of Mesozoic limestone as an assimilant candidate, invoked for Alban Hills (Dallai et al. 2004), Mts. Ernici (Frezzotti et al. 2007), and Mt. Vesuvius (Dallai et al. 2011), cannot be ruled out for the Ischia magmas. However, given the generally higher $\delta^{18}O$ values of Mg-rich Ol and Cpx phenocrysts from Molara, Vateliero, and Cava Nocelle sequences with respect to Mg-poor ones (Fig. 11), contamination of Ischia magmas must have occurred during an early stage of evolution, when hot mafic magmas were rising through the continental crust in the 10–18 km depth range, as suggested by equilibration pressure of melt inclusion data (Moretti et al. 2013), thus pointing toward the Hercynian basement as a more likely assimilant. Energy-constrained assimilation plus fractional crystallization modeling (EC-AFC; Spera and Bohrson 2001) applied to the Ischia minerals provided the red curve in Fig. 12a that explains their O-Sr isotope variability with assimilation of up to 7 % of Hercynian granodiorite, by a K-basaltic to latitic crystallizing magma (parameters given in Table 2).

The complex sequence of mantle and crustal processes recognized for many Italian volcanoes must be quite the rule at subduction zones worldwide, as volcanic rocks of island arcs such as Kamchatka, Lesser Antilles, and Indonesia exhibit very similar O-Sr isotope variations (Fig. 12b). Indeed, the least enriched in ^{18}O and ^{87}Sr rocks of these island arcs follow the same subduction enrichment curve and, as such, represent primary magmas derived from mantle sectors progressively contaminated by pelagic clay-derived fluids/melts. Moreover, AFC processes affect the successive evolution of these primary magmas while rising through continental crust, as testified by steep data fields in the O-Sr isotope space. Unfortunately, such a comparison for other volcanic arcs is hampered by lack of O isotope data on mafic minerals.

Conclusions

The results of the petrological investigation of hybrid volcanic rocks from Molara, Vateliero, and Cava Nocelle young volcanic centers at Ischia have permitted to (1) describe in greater detail their already known textural and mineralogical disequilibria, (2) put forward more hypotheses on genesis and differentiation processes of the feeding magmas from mantle to crustal depths and (3) stress the relationship between composition of the erupted magmas and structural setting. The detailed characterization of both chemical and Sr–Nd–O isotopic features of glass and minerals from a number of representative rock samples has allowed us to document complex mingling/mixing processes as the most likely explanation for the origin of these disequilibria and to hypothesize that both mafic and felsic magmas were involved in the complex interplay of open-system processes.

Notwithstanding the significant textural, mineralogical, geochemical, and isotopic disequilibria of these hybrid volcanic rocks, it has been possible to get some important inferences for the processes occurred in the mantle and crust sectors underlying Ischia island, extending the results to other Plio-Quaternary volcanic centers of Italy. Combining oxygen and strontium isotopic characteristics of olivine and clinopyroxene phenocrysts of the investigated Ischia rocks, and comparing our data with those from other Italian volcanic centers, a common link can be found among the least ^{18}O-enriched minerals (Fig. 12): their strong increase in radiogenic ^{87}Sr at very gently increasing $\delta^{18}O$ values, similar to those of MORB mantle, might be the result of progressive mantle source enrichment processes. The latter can be the result of increasing addition of sedimentary components (both oxidizing fluids and melts from pelagic clays, carrying K and related trace elements) to this mantle sector, as a consequence of the subduction related to the Apennine orogenesis and Tyrrhenian Sea basin opening. Furthermore, it has been inferred that, in some cases, primitive melts from these modified mantle sectors experienced AFC-type processes, likely favored by sediment-derived, hot, and oxidizing fluids rising through both the mantle wedge and overlying continental crust. In the case of Ischia, these processes occurred likely in the deep continental crust and were responsible for further, steep increase in $\delta^{18}O$ values and moderate increase in $^{87}Sr/^{86}Sr$ ratios at decreasing *mg*-number of Cpx and Fo content of Ol phenocrysts. The assimilant might have been Hercynian granodiorite crust, as it has been modeled for Campi Flegrei and Mt. Vesuvius magmas; however, the role of limestone in some of these volcanic centers can also be taken into account.

In conclusion, different primary mafic magmas, coming from large depths and carrying distinct isotopic features inherited from deep FC and AFC processes, generated mafic to felsic magmas with variable O-Sr–Nd isotope ratios. These magmas interacted in shallower reservoirs of the Ischia plumbing system. This has occurred many times during Ischia's volcanic history, as the isotopic features of mixing end-members recognized in the Molara, Vateliero, and Cava Nocelle volcanics are similar to those of either older or younger than 10 ka BP magmas (Fig. 9). Mingling/mixing processes among magmas characterized by different chemical and isotopic composition are shared by other volcanoes of the PVD located along the N60E trending, regional fault system, passing through Ischia and Procida islands and possibly the Campi Flegrei caldera (Fig. 1). This prominent tectonic structure must play a significant role in giving mafic magmas coming from large depth the opportunity to meet felsic magmas stagnating in shallower reservoirs, eventually triggering explosive eruptions (e.g., Orsi et al. 1991, 1996a; Acocella and Funiciello 2006; Vezzoli et al. 2009; Tonarini et al. 2009; de Vita et al. 2010; Di Renzo et al. 2011; Moretti et al. 2013).

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