

# The Deep Plumbing System of Ischia: a Physico-chemical Window on the Fluid-saturated and CO<sub>2</sub>-sustained Neapolitan Volcanism (Southern Italy)

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RECEIVED AUGUST 2, 2011; ACCEPTED JANUARY 1, 2013  
ADVANCE ACCESS PUBLICATION FEBRUARY 20, 2013

*Ischia, a volcanic island located 18 miles SW of Naples (Southern Italy), is a densely populated active caldera that last erupted in AD 1302. Melt inclusions in phenocrysts of the Vateliero and Cava Nocelle shoshonite–latite eruptive products (6th to 4th centuries BC) constrain the structure and nature of the Ischia deep magmatic feeding system. Their geochemical characteristics make Ischia a natural borehole for probing the physico-chemical conditions of magma generation in mantle contaminated by slab-derived fluids or melts, largely dominated by CO<sub>2</sub>. Volatile concentrations in olivine-hosted melt inclusions require gas–melt equilibria at between 3 and 18 km depth. In agreement with what has already been demonstrated at the other neighboring Neapolitan volcanoes (Procida, Campi Flegrei caldera and Somma–Vesuvius volcanic complex), a major crystallization depth at 8–10 km has been identified. The analyzed melt inclusions provide clear evidence for CO<sub>2</sub>-dominated gas fluxing and consequent dehydration of magma batches stagnating at crustal discontinuities. Gas fluxing is further supported by selective enrichment in K owing to fluid-transfer during magma differentiation. This takes place under oxidized conditions ( $Fe^{3+}/\Sigma Fe \geq 0.3$ ) that can be fixed by an equimolar proportion of divalent and trivalent iron in the melt if post-entrapment crystallization of the host olivine is discarded. The melt inclusion data, together with data from the literature for other Neapolitan volcanoes, show that magmatism and volcanism in the Neapolitan area, despite differences in composition*

*and eruption dynamics, are closely linked to supercritical CO<sub>2</sub>-rich fluids. These fluids are produced by devolatilization of subducting terrigenous–pelagic metasediments and infiltrate the overlying mantle wedge, generate magmas and control their ascent up to eruption. Geochemical characteristics of Ischia and the other Neapolitan volcanoes reveal that the extent of fluid or melt contamination of the pre-subduction asthenospheric mantle wedge was similar among these volcanoes. However, differences in the isotopic compositions of the erupted magmas (more enriched in radiogenic Sr at Ischia, Campi Flegrei and Somma–Vesuvius with respect to Procida) and the amount of H<sub>2</sub>O in the plumbing system of these volcanoes (almost double at Ischia, Campi Flegrei and Somma–Vesuvius than at Procida) reflect the different flow-rates of deep slab-derived fluids or melts through the mantle wedge, which, in turn, control the amount of generated magma. The high bulk permeability of the lithosphere below Ischia, Campi Flegrei and Somma–Vesuvius, determined by the occurrence of intersecting NW–SE and NE–SW regional fault systems, favours fluid ascent and accumulation at crustal levels, with consequent larger magma production and storage than at Procida, located along the NE–SW system.*

KEY WORDS: CO<sub>2</sub>-fluxing; melt inclusions; redox state; trachybasalts; alkali enrichment

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## INTRODUCTION

Melt inclusions (MI) are droplets of melt trapped in phenocrysts (e.g. Roedder, 1984) along the pathways of magma evolution from deep to shallow zones of segregation and storage, up to extrusion. As such, they provide fundamental clues to and quantitative constraints on the physico-chemical conditions of magma storage, ascent and pre-eruptive degassing (e.g. Anderson *et al.*, 1989; Métrich & Clocchiatti, 1989; Blundy & Cashman, 2008; Barsanti *et al.*, 2009). The chemical compositions of MI are a powerful geochemical tool with which to characterize the magmatic feeding system of a volcano, providing data that can be integrated with the results of geophysical investigations. MI studies have become essential in understanding and quantifying magmatic processes, contributing to assessments of volcanic hazard at active volcanoes and particularly for defining likely eruption scenarios involving magma recharge over short to medium timescales (e.g. years to tens of years). MI-based retrieval of the gas composition coexisting with the melt at depth can represent a highly valuable complement to gas discharge measurements at surface (e.g. Aiuppa *et al.*, 2010; Arienzo *et al.*, 2010) and provide an essential tool to solve ambiguities concerning the magmatic versus hydrothermal origin of gas emissions at volcanic sites (e.g. Chiodini *et al.*, 2006).

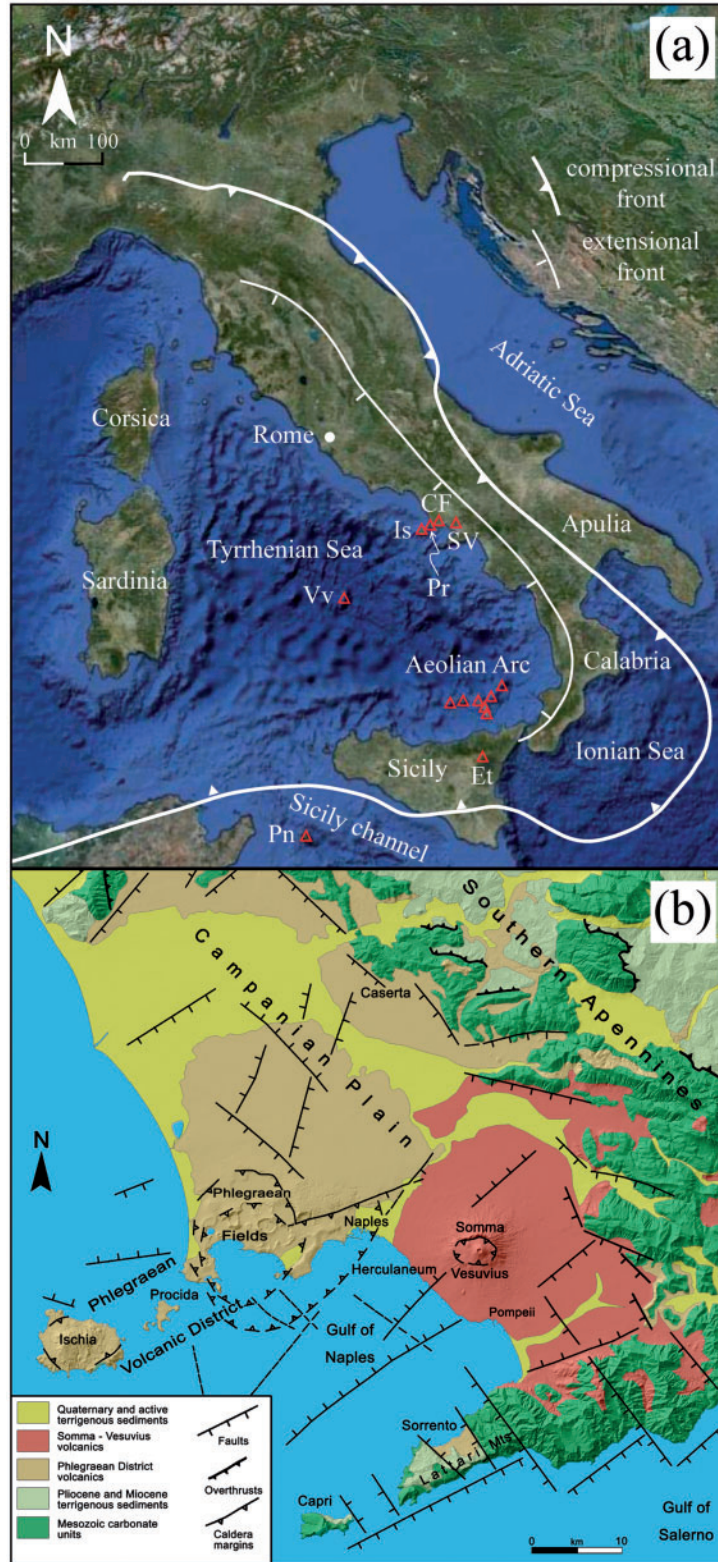
The island of Ischia is a densely populated resurgent caldera in the Gulf of Naples (Southern Italy) (Fig. 1). The last eruption was in AD 1302 and there has been ground deformation in historical times, recent seismicity and diffuse fumarolic and thermal-spring activity; these provide evidence for the state of activity of the magmatic feeding system, as well as information on hydrothermal potential and volcanic hazard (Buchner *et al.*, 1996; Orsi *et al.*, 2003; Sepe *et al.*, 2007; Sbrana *et al.*, 2009; Di Napoli *et al.*, 2011).

In such a framework, assessment of the processes occurring at variable depths within the magmatic feeding system is clearly an important task for the scientific community. In this study we have focused on MI in the products of eruptions fed by weakly differentiated magmas over the last 3 kyr. The specific aims were the definition of the architecture of the magmatic feeding system and evaluation of the relationships between deep and shallow transfer processes of subduction-related fluids or melts. The latter have been addressed by modelling the oxidation state and degassing processes within a CO<sub>2</sub>–H<sub>2</sub>O–H<sub>2</sub>S–SO<sub>2</sub>–silicate melt system and by discussing the variability of alkalis and halogens, to define the role played by fluids in driving magma ascent to the surface. In addition, we have explored the geochemical similarities and differences between Ischia and the other Neapolitan volcanoes and interpreted them in the context of the structural setting of the area, providing insights into the geodynamic processes that control the Neapolitan magmatism.

## GEOLOGICAL, PETROLOGICAL AND GEOCHEMICAL BACKGROUND OF ISCHIA

Ischia is the emergent top of a large volcanic complex that rises more than 1000 m above the sea floor. Together with Campi Flegrei (CF), Procida and Somma–Vesuvius (SV), it is one of the four Neapolitan volcanoes formed in the graben of the Campanian Plain along the Tyrrhenian Sea margin of the Apennines (Fig. 1) (Orsi *et al.*, 2003; Peccerillo, 2005). This margin has been affected by extensional processes since the Miocene as a consequence of the eastward migration of the Apennines in relation to a progressive eastward retreat of the subducting Ionian lithosphere (e.g. Jolivet *et al.*, 2009). Extension has occurred along mainly NW–SE normal and subordinate NE–SW transverse faults (Acocella & Funicello, 2006, and references therein). Ischia, Procida and CF are NE–SW aligned and constitute the Phlegraean Volcanic District (PVD) (Orsi *et al.*, 1996a). The Ischia system, as well as those of CF and SV, is associated with a complex setting of tectonic and volcano-tectonic features, located at the intersection of the NE–SW- and NW–SE-trending regional fault systems (Acocella & Funicello, 1999, 2006). The complex structural setting allows ascent of magmas as well as deep-to-shallow emplacement of major magma bodies. Ischia and CF are resurgent calderas (Orsi *et al.*, 1991, 1996a, 1999a; Acocella & Funicello, 1999; Acocella *et al.*, 2004), SV is a strato-volcano (Santacroce *et al.*, 2008), and Procida is a monogenetic volcanic field (De Astis *et al.*, 2004).

At Ischia, volcanism began prior to 150 ka BP and has continued intermittently, with quiescent periods lasting centuries to millennia, until the last eruption in AD 1302 (Vezzoli, 1988; Orsi *et al.*, 1996b; de Vita *et al.*, 2010). The volcanic and deformation history is dominated by the caldera-forming Monte Epomeo Green Tuff (MEGT) eruption at *c.* 55 ka (Vezzoli, 1988), during a period of activity that generated the most voluminous and devastating eruptions of the island (Brown *et al.*, 2008, and references therein). The MEGT caldera floor was later affected by resurgence through a simple-shearing mechanism that generated uplift of about 900 m, probably over the past 33 kyr (the age of the oldest deformed rocks), and tilting of differentially displaced blocks; the most uplifted one is Monte Epomeo (Orsi *et al.*, 1991) (Fig. 1). The post-MEGT volcanic history has been subdivided into three periods of activity on the basis of structural and volcanological evidence, as well as geochemical and isotopic variations of the magmas erupted through time (Civetta *et al.*, 1991). During the last period of activity, which began 10 kyr ago, volcanism was mainly concentrated at around 5 ka and over the past 3 kyr. In this period resurgence dynamics have determined the conditions for magma ascent mainly



**Fig. 1.** (a) Traces of the subduction-related compression and extension fronts along the Apennine chain, modified after Acocella & Funicello (2006). Is, Ischia; Pr, Procida; CF, Campi Flegrei; SV, Somma–Vesuvius; Vv, Vavilov; Et, Etna; Pn, Pantelleria. (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).

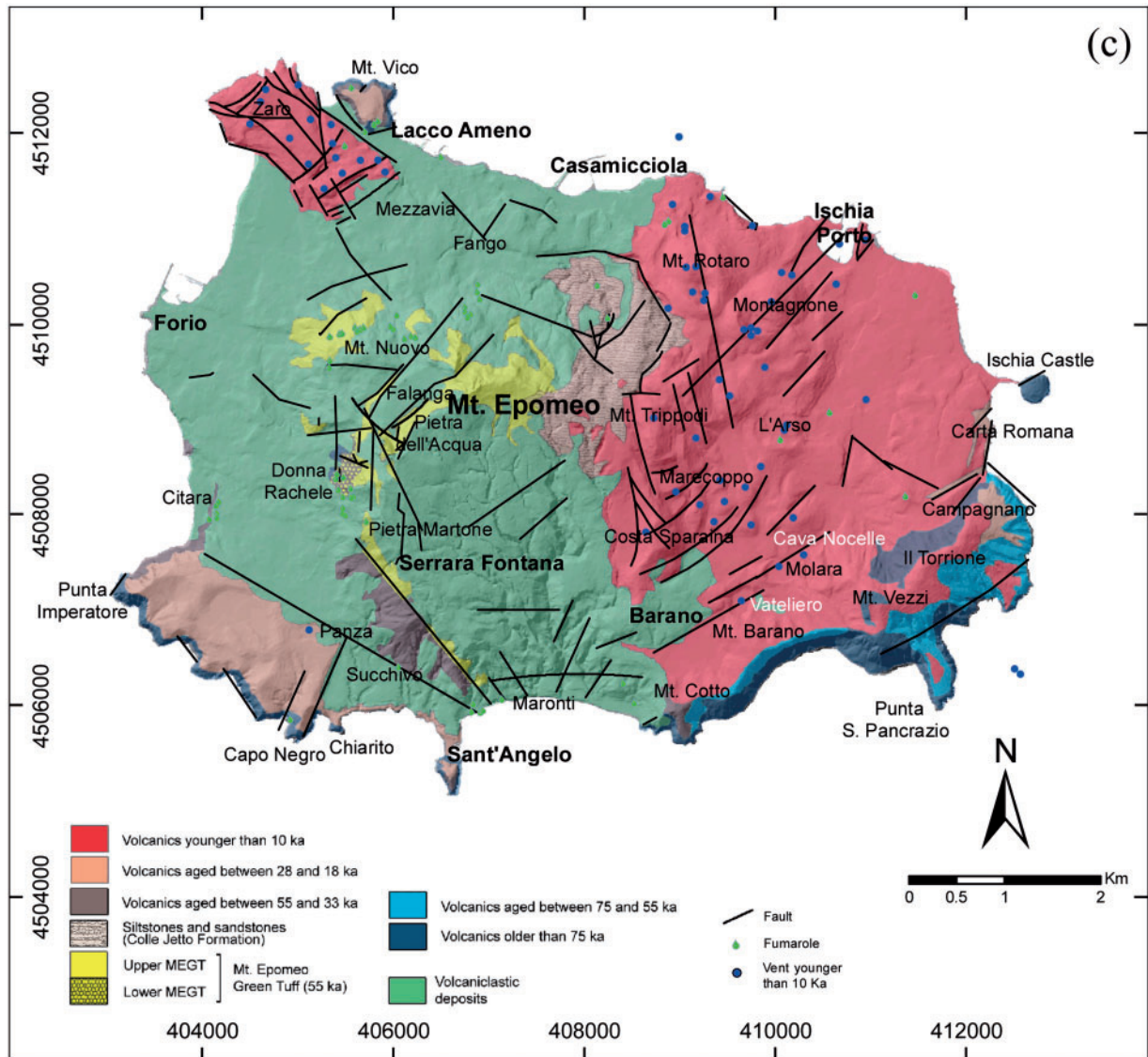
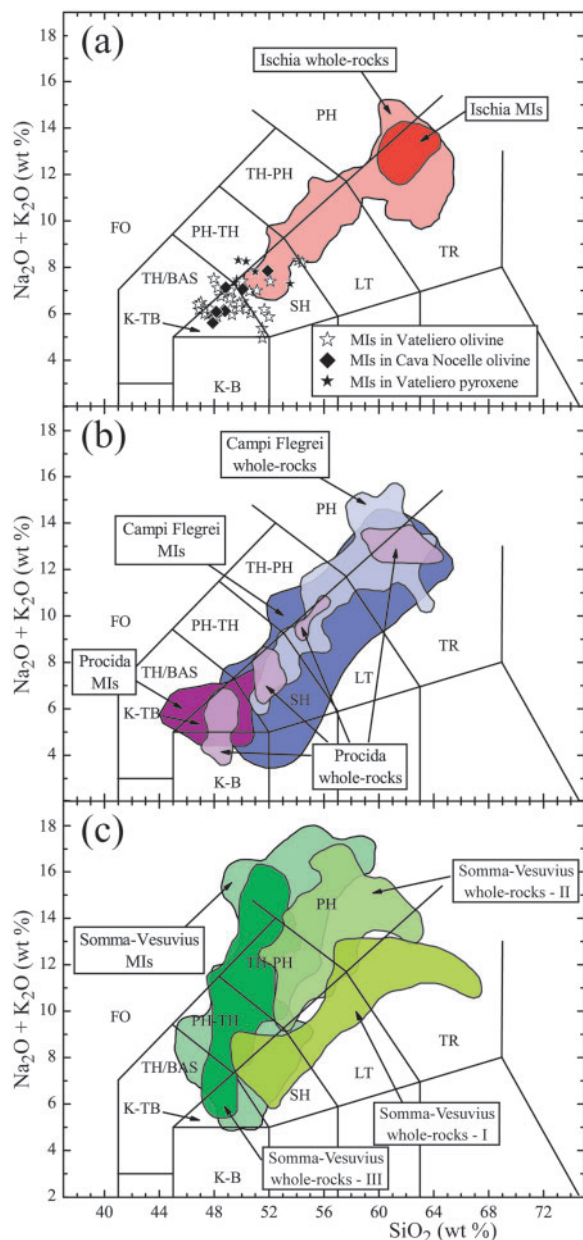


Fig. 1. (Continued).

to the east of the Monte Epomeo resurgent block, within the eastern sector of the island deformed by normal faults resulting from a tensile stress regime, and along portions of regional faults. The Molaro, Vateliero and Cava Nocelle eruptions took place along the NE–SW-trending fault system delimiting the southeastern sector of the island towards the north (Fig. 1). This portion of the transfer system acted as marginal faults during the MEGT caldera collapse. These eruptions were low-magnitude explosive events, characterized by magmatic and phreatomagmatic explosions generating sequences of scoria fallout layers and ash-surge beds, intercalated with subordinate pumice fallout deposits (de Vita *et al.*, 2010). On the basis of stratigraphic, geochronological and archeological evidence, the Molaro, Vateliero and Cava Nocelle eruptions followed

each other at short time intervals between the 6th and 4th centuries BC (de Vita *et al.*, 2010, and references therein).

Ischia volcanic rocks vary in composition from shoshonite to phonolite (Fig. 2a); the most abundant rock type is trachyte. The least evolved magmas were erupted during the 28–18 ka period of activity (Grotta di Terra shoshonitic dike, 28 ka) and over the past 3 kyr (Molaro, Vateliero, Cava Nocelle and Arso shoshonitic–latitic tephra; Fig. 1). The latter are characterized by petrographic, geochemical and isotopic features suggesting mingling or mixing among differently evolved, small magma batches, and entrapment of crystals inherited from previously erupted magmas (e.g. Civetta *et al.*, 1991; Piochi *et al.*, 1999; D'Antonio *et al.*, 2007, 2013).



**Fig. 2.** (a) Total alkalis vs silica (TAS, Le Maitre *et al.*, 1989) diagram showing the compositions of the analyzed MI compared with the compositional fields of Ischia whole-rocks (Ghiara *et al.*, 1979; Vezzoli, 1988; Crisci *et al.*, 1989; Orsi *et al.*, 1992; Di Girolamo *et al.*, 1995; D'Antonio *et al.*, 2007; Brown *et al.*, 2008) and MI (Sbrana *et al.*, 2009) from the literature. (b) TAS diagram for CF and Procida whole-rocks and MI from the literature (D'Antonio *et al.*, 1999a, 1999b; Piochi *et al.*, 1999; Signorelli *et al.*, 1999a; Webster *et al.*, 2003; De Astis *et al.*, 2004; Fulignati *et al.*, 2004; Marianelli *et al.*, 2006; Cannatelli *et al.*, 2007; Severs, 2007; Mangiacapra *et al.*, 2008; Tonarini *et al.*, 2009; Arienzo *et al.*, 2010; Di Vito *et al.*, 2011; Mormone *et al.*, 2011). (c) TAS diagram for SV whole-rocks and MI from the literature (Cioni *et al.*, 1995, 1998; Belkin *et al.*, 1998; Marianelli *et al.*, 1999, 2005; Signorelli *et al.*, 1999b; Cioni, 2000; Di Renzo *et al.*, 2007; Fulignati & Marianelli, 2007; Santacroce *et al.*, 2008). SV whole-rocks I, II and III represent those emplaced between  $22030 \pm 175$  and  $19265 \pm 105$  yr cal BP, between  $8890 \pm 90$  yr cal BP and AD 79, and between AD 79 and 1944, respectively (Santacroce *et al.*, 2008).

The deep structure of the Ischia caldera is poorly constrained. Modelling of magnetic data (Orsi *et al.*, 1999b) points to a large magma body at  $\sim 7$  km depth, which is either solidified or partly liquid, as the geothermal flux (Della Vedova *et al.*, 2001) suggests a solidus temperature of  $\sim 1000^\circ\text{C}$  at that depth. However, in the absence of seismic data, the role of petrology in assessing the characteristics of the deep magma storage system and magma crystallization depth is of fundamental importance. Eruption of shoshonitic to latitic magmas at the margin of the caldera and of differentiated magmas within it testifies to the ascent of weakly differentiated, CO<sub>2</sub>-rich magmas of deep provenance along regional faults and the occurrence of a shallow magma storage region beneath the caldera, in which the magmas evolve to trachyte and phonolite. The trachyte and phonolite storage region is relatively shallow with respect to the reservoir from which the shoshonitic–latitic magmas come. This is suggested by phenocryst-hosted MI studies from the Ischia trachytes and phonolites (Sbrana *et al.*, 2009) that yielded H<sub>2</sub>O contents up to 4 wt % but no CO<sub>2</sub> above the Fourier transform infrared (FTIR) spectroscopy detection limit. Accordingly, the occurrence of a relatively shallow magma reservoir ( $\sim 2$  km deep) over the last few thousands of years below the caldera, filled by hot ( $1000^\circ\text{C}$ ) trachytic magma, has been suggested. Gravity and magnetic data point to the occurrence of an intrusive crystalline body, with few and sparse partially molten portions (Paoletti *et al.*, 2009), below the caldera. These data are consistent with petrological and isotopic data, which suggest that the volcanic activity of the last 5 kyr was fed by isotopically distinct small magma batches (Civetta *et al.*, 1991; Piochi *et al.*, 1999; D'Antonio *et al.*, 2007, 2013), which differentiated and mixed prior to extrusion.

The isotopic characteristics of dissolved gases in thermal waters demonstrate that the Ischia hydrothermal system is supplied by a deep-seated gas component, characterized by CO<sub>2</sub> =  $97.7 \pm 1.2$  vol. % (on a water-free basis),  $\delta^{13}\text{C}_{\text{CO}_2} = -3.51 \pm 0.9\text{‰}$ , and  $^3\text{He}/^4\text{He} \sim 3.5$  Ra, probably of magmatic origin (Di Napoli *et al.*, 2009, 2011, and references therein). The latter value is significantly lower than that of Fo-rich olivines from the adjacent island of Procida, which yield the highest  $^3\text{He}/^4\text{He}$  ratios within the PVD (5 Ra; Piochi *et al.*, 2005; Martelli *et al.*, 2008).

## SAMPLING

For this study, tephra from Vateliero and Cava Nocelle were chosen for analysis because they are among the least evolved magmas erupted at Ischia volcano. They were sampled at the type localities where the units have been recently redefined (de Vita *et al.*, 2010). The sampled volcanic rocks are either composite pumice samples or single scoria fragments. From the stratigraphic sequence of the Vateliero tephra, we collected and analyzed two composite

pumice samples representative of a basal surge bedset overlying a paleosol (sample Vat A), and a fallout deposit at the top of the stratigraphic sequence (sample Vat B). At Cava Nocelle we collected four scoria samples representative of distinct intervals in the strombolian activity. For MI studies we analyzed the stratigraphically intermediate sample (I Cn 2), which is the only one containing glassy MI.

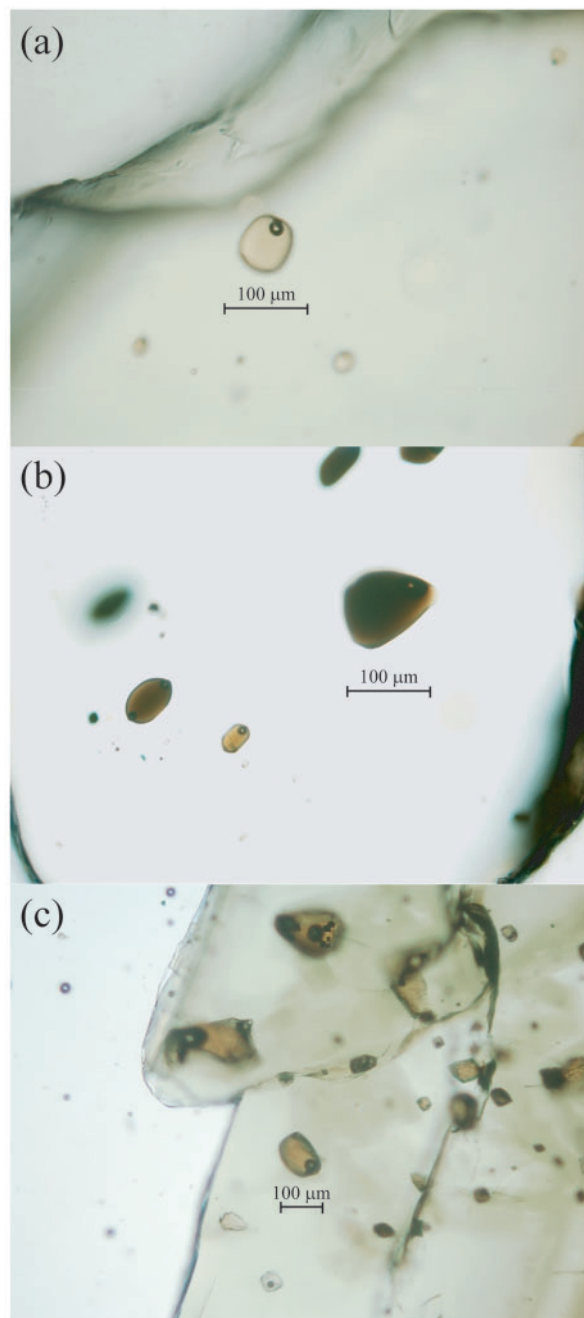
## ANALYTICAL METHODS

### Sample preparation and analytical details

Samples were washed several times in deionized water, then dried and crushed to particles <1 cm in an agate mortar and sieved. Olivine and clinopyroxene phenocrysts were handpicked under a binocular microscope from crushed pumice fragments for MI studies. The selected crystals were mounted on microscope slides with an epoxy resin soluble in acetone (Crystalbond). Doubly polished sections of phenocryst-hosted MI were prepared by grinding and polishing the host minerals first with abrasive papers and then with 0.3 µm alumina powder (water was used as lubricant). Sample thicknesses were measured via a Mitutoyo micrometer.

Analyzed MI are generally glassy or two phase (glass + shrinkage bubble), indicating a rapid quench (Lowenstern, 1994) and likely preservation of local-scale equilibrium between the trapped melt and the host mineral (Fig. 3). FTIR analyses of *c.* 80 MI trapped in both olivine and clinopyroxene phenocrysts were carried out at the Istituto Nazionale di Geofisica e Vulcanologia (INGV), sezione di Napoli, Osservatorio Vesuviano, using an FTIR Nexus™ spectrometer from Nicolet, equipped with a heated ceramic (Globar) source, a KBr beamsplitter and an MCT detector. A high-pressure dry air (CO<sub>2</sub> <7 ppm) line was used to purge the system. For each spectrum 1000 scans at 4 cm<sup>-1</sup> were obtained. The investigated spectral domain ranges from 4000 to 650 cm<sup>-1</sup>. H<sub>2</sub>O and CO<sub>2</sub> concentrations were determined via the Beer–Lambert law (Ihinger *et al.*, 1994). Density was estimated for each sample using the method of Lange & Carmichael (1987). The extinction coefficients used are 63.9 ± 2 L mol<sup>-1</sup> cm<sup>-1</sup> for the peak of H<sub>2</sub>O at 3550 cm<sup>-1</sup>, whereas for CO<sub>2</sub>, dissolved as CO<sub>3</sub><sup>2-</sup>, we used 308 ± 110 L mol<sup>-1</sup> cm<sup>-1</sup> for the peak at 1515 cm<sup>-1</sup> (Behrens *et al.*, 2009). The latter value matches well that calculated using the empirical equation of Dixon & Pan (1995) for basalts, and is consistent with that determined for shoshonitic experimental glasses (Vetere *et al.*, 2011). For the CO<sub>2</sub> absorption background correction, we subtracted from each acquisition the spectrum of a degassed glass of as similar as possible composition and thickness. The resulting spectrum was processed using the Jandel ‘Peak Fit’ package<sup>©</sup>.

Crystal and MI compositions including S and Cl were determined by electron microprobe. Electron microprobe



**Fig. 3.** Transmitted light photomicrographs of (a) Vatellero olivine-hosted MI, (b) Cava Nocelle olivine-hosted MI and (c) Vatellero pyroxene-hosted MI.

(EMP) analyses were carried out using a JEOL JXA 8200 with wavelength-dispersive spectrometry (WDS) and energy-dispersive spectrometry (EDS) combined at the INGV sezione di Roma, Italy. During the EMP-WDS analyses the operating conditions were 15 kV accelerating voltage and 7 nA probe current, providing signal stability. A probe diameter of 5 µm, with a final spot size of about

7  $\mu\text{m}$ , was used to reduce alkali migration during glass analysis. The elements Na, F, Si, K, and Ca were analysed first and simultaneously. Counting time was 10 s on both peak and background; data reduction was carried out using the ZAF correction routine, provided within the JEOL software package. The following materials were used as standards for the various elements (in parentheses): (1) for glass analyses: fluorite (F), albite (Na), island basalt BIR-1 (Mg, Al, Si, Ca, Fe), orthoclase (K), sodalite (Cl), barite (Ba), nickel metal (Ni), titanium oxide (Ti), apatite (P), chromite (Cr) and spessartine (Mn); (2) for olivine analyses: forsterite (Mg, Si), pargasite, (Al, Ca), almandine (Fe) and albite (Na). For the glass analyses, the maximum uncertainties were: 3.5% for Si, Al, Mg, Fe, Ca, K and Na; 17% for Cl and S; 24% for P, F and Cr; Ni contents were generally near or below the detection limit, implying uncertainties up to 30%. For the olivine analyses, the maximum uncertainties were: 2% for Si, Mg and Fe; 10% for Ca; near or below detection limit for Ni, Mn and Cr.

The major element compositions (oxides) of the analyzed MI are reported in Table 1, both recalculated to 100 wt % on an anhydrous basis and recalculated at 100 wt % after re-equilibration using the Petrolog3 software package (Danyushevsky & Plechov, 2011), together with the volatile species  $\text{H}_2\text{O}$  (wt %),  $\text{CO}_2$ , S and Cl (ppm). The compositions of the host olivine and pyroxene, together with the original EMPA data for MI, are reported in the Supplementary Data (available for downloading at [www.http://petrology.oxfordjournals.org/](http://petrology.oxfordjournals.org/)).

### Procedure for MI post-entrapment correction and consequences on the redox state

We used the Maurel & Maurel (1982) equation for spinel–liquid equilibrium to calculate the FeO/MgO ratio of the magma crystallizing Cr-bearing spinel and olivine in the composition range  $\text{Fo}_{89}$  to  $\text{Fo}_{81}$ . D'Antonio *et al.* (2013) provided compositional data for Cr-spinels that we assumed were in equilibrium with MI compositions representative of the melts trapped by such olivines during magmatic differentiation (I-Vat-A.1 ol3 incl1 and I-Vat-B.1 ol6, Table 1).

Because re-equilibration between the host olivine and MI appears to have been complete, as shown by the sharp boundaries between them (Fig. 4), we lack any constraints to establish the initial  $\text{FeO}_{\text{tot}}$ , unless we fix arbitrarily the oxygen fugacity and consequently compute the melt  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio. Therefore, we assume that the measured MI  $\text{FeO}_{\text{tot}}$  values correspond to the FeO contents of a melt that equilibrated with Cr-bearing spinel. Then, by adopting the FeO/MgO ratios from the melt–spinel equilibrium (from 0.875 to 1.608 for pairs involving spinels trapped within olivines ranging between  $\text{Fo}_{89}$  and  $\text{Fo}_{81}$  respectively), we determined that the maximum MgO contents

consistent with the (non-corrected)  $\text{FeO}_{\text{tot}}$  of Vat-A.1 ol3 incl1 and Vat-B ol6 MI are 6.97 and 3.58 wt % (Table 1).

We then calculated which redox conditions the Petrolog3 software package (Danyushevsky & Plechov, 2011) returned for the selected samples based on the corrected composition. As shown by D'Antonio *et al.* (2013) this occurs for  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios varying from 0.2 (for melts trapped in  $\text{Fo}_{89}$  olivines) to 0.3 (for melts trapped in  $\text{Fo}_{79}$  olivines), making the correction for olivine crystallization less important for the more differentiated compositions. The following linear relationship can be established between olivine molar composition and melt redox state ( $\text{Fe}^{3+}/\Sigma\text{Fe}$  molar ratio in melt):

$$\left. \frac{\text{Fe}^{3+}}{\Sigma\text{Fe}} \right|_{\text{molar}}^{\text{melt}} = -0.0081 \left. \frac{\text{Fe}}{\text{Mg} + \text{Fe}} \right|_{\text{molar}}^{\text{olivine}} + 0.9088.$$

Corrections for all MI were made using Petrolog3, by imposing the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio corresponding to the above equation. The post-entrapment crystallization of the host olivine involves a fraction of 10% at most from the trapped MI.

Redox states up to  $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.3$ , corresponding to MI corrected for post-entrapment crystallization, represent an alternative scenario to that given by the nearly equivalent divalent and trivalent iron proportions. This yields redox estimates that, although more conservative than that obtained by considering the non-corrected MI, reveal that the Ischia magmas are very oxidized, exceeding the nickel–nickel oxide (NNO) buffer by more than one log unit.

## RESULTS

The analyzed pumice fragments have variable vesicularity (40–60 vol. %). They are highly porphyritic and glomeroporphyritic, with 25–40 vol. % of euhedral phenocrysts and microphenocrysts of feldspar, clinopyroxene, olivine, biotite, opaque oxides and apatite, in order of decreasing abundance.

The host olivines are euhedral crystals,  $\sim 1$  mm long and characterized by Fo contents ranging from 89 to 79 mol % (Table 1). The olivine-hosted MI are glassy and usually large (up to 300  $\mu\text{m}$  in length), but small inclusions are also present. In the same crystal rounded and elongated MI can coexist. They both contain one large or several small shrinkage bubbles (Fig. 3a and b). Under the petrographic microscope the MI are dark brown to light brown in colour. Their compositions (Table 1) range from K-trachybasalt to shoshonite (Fig. 2a). Tiny inclusions of dark red oxide (probably chromite) occur in a few olivine phenocrysts.

The analysed clinopyroxene phenocrysts are euhedral and vary in color from green to black. Clinopyroxene-hosted MI in samples from the Vateliero tephra have irregular shapes, with rims less sharp than those hosted in

Table 1: Original melt inclusion compositions and re-equilibrated compositions using Petrolog

|   | Vat A<br>1__ol1           | Vat A<br>1__ol2           | Vat A<br>1__ol3<br>(inc1) | Vat A<br>1__ol3<br>(inc2) | Vat A<br>1__ol3<br>(inc3) | Vat A<br>1__ol3<br>(inc4) | Vat A<br>1__ol4<br>(inc1) | Vat A<br>1__ol4<br>(inc2) | Vat A<br>1__ol5<br>(inc1) | Vat A<br>1__ol5<br>(inc2) | Vat A<br>1__px1 |
|---|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|-----------------|
| <i>Original compositions normalized to 100% on an anhydrous basis</i> |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                 |
| SiO <sub>2</sub>  | 48.63                     | 52.45                     | 54.74                     | 54.46                     | n.a.                      | n.a.                      | 52.04                     | n.a.                      | 49.65                     | 49.62                     | 51.15           |
| TiO <sub>2</sub>  | 1.40                      | 1.52                      | 1.57                      | 1.51                      | n.a.                      | n.a.                      | 1.80                      | n.a.                      | 1.81                      | 1.90                      | 1.10            |
| Al <sub>2</sub> O <sub>3</sub>  | 18.19                     | 18.72                     | 18.63                     | 18.61                     | n.a.                      | n.a.                      | 17.52                     | n.a.                      | 18.05                     | 18.13                     | 19.83           |
| FeO <sub>t</sub>  | 7.75                      | 6.25                      | 5.57                      | 5.51                      | n.a.                      | n.a.                      | 6.82                      | n.a.                      | 8.85                      | 8.69                      | 6.94            |
| MnO   | 0.15                      | 0.20                      | 0.08                      | 0.09                      | n.a.                      | n.a.                      | 0.16                      | n.a.                      | 0.10                      | 0.18                      | 0.22            |
| MgO   | 4.02                      | 3.20                      | 2.71                      | 2.80                      | n.a.                      | n.a.                      | 3.66                      | n.a.                      | 3.62                      | 3.16                      | 3.54            |
| CaO   | 13.31                     | 9.38                      | 7.71                      | 7.99                      | n.a.                      | n.a.                      | 11.01                     | n.a.                      | 10.27                     | 10.70                     | 7.56            |
| Na <sub>2</sub> O   | 2.28                      | 3.64                      | 4.05                      | 3.90                      | n.a.                      | n.a.                      | 3.63                      | n.a.                      | 3.12                      | 3.13                      | 3.47            |
| K <sub>2</sub> O  | 3.63                      | 3.81                      | 4.22                      | 4.43                      | n.a.                      | n.a.                      | 2.60                      | n.a.                      | 3.62                      | 3.59                      | 4.92            |
| P <sub>2</sub> O <sub>5</sub>   | 0.64                      | 0.83                      | 0.74                      | 0.70                      | n.a.                      | n.a.                      | 0.76                      | n.a.                      | 0.90                      | 0.90                      | 1.27            |
| Total   | 100.00                    | 100.00                    | 100.00                    | 100.00                    |                           |                           | 100.00                    |                           | 100.00                    | 100.00                    | 100.00          |
| <i>Re-equilibrated compositions using Petrolog v3.1.1.2</i>           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                 |
| SiO <sub>2</sub>  | 48.28                     | 51.98                     | 54.16                     | 54.21                     | n.a.                      | n.a.                      | 51.63                     | n.a.                      | 49.39                     | 49.22                     |                 |
| TiO <sub>2</sub>  | 1.33                      | 1.46                      | 1.54                      | 1.49                      | n.a.                      | n.a.                      | 1.74                      | n.a.                      | 1.78                      | 1.85                      |                 |
| Al <sub>2</sub> O <sub>3</sub>  | 17.25                     | 18.02                     | 18.35                     | 18.34                     | n.a.                      | n.a.                      | 16.97                     | n.a.                      | 17.78                     | 17.63                     |                 |
| Fe <sub>2</sub> O <sub>3</sub>  | 1.85                      | 1.47                      | 1.46                      | 1.42                      | n.a.                      | n.a.                      | 1.67                      | n.a.                      | 2.71                      | 2.71                      |                 |
| FeO   | 6.15                      | 4.94                      | 4.36                      | 4.25                      | n.a.                      | n.a.                      | 5.33                      | n.a.                      | 6.50                      | 6.50                      |                 |
| MnO   | 0.14                      | 0.19                      | 0.08                      | 0.09                      | n.a.                      | n.a.                      | 0.15                      | n.a.                      | 0.10                      | 0.18                      |                 |
| MgO   | 6.15                      | 4.94                      | 3.58                      | 3.42                      | n.a.                      | n.a.                      | 5.07                      | n.a.                      | 4.08                      | 4.09                      |                 |
| CaO   | 12.63                     | 9.03                      | 7.59                      | 7.88                      | n.a.                      | n.a.                      | 10.66                     | n.a.                      | 10.12                     | 10.41                     |                 |
| Na <sub>2</sub> O   | 2.17                      | 3.50                      | 3.98                      | 3.84                      | n.a.                      | n.a.                      | 3.52                      | n.a.                      | 3.07                      | 3.04                      |                 |
| K <sub>2</sub> O  | 3.45                      | 3.67                      | 4.16                      | 4.37                      | n.a.                      | n.a.                      | 2.52                      | n.a.                      | 3.57                      | 3.49                      |                 |
| P <sub>2</sub> O <sub>5</sub>   | 0.60                      | 0.80                      | 0.73                      | 0.69                      | n.a.                      | n.a.                      | 0.74                      | n.a.                      | 0.89                      | 0.88                      |                 |
| Total   | 100.00                    | 100.00                    | 100.00                    | 100.00                    | 0.00                      | 0.00                      | 100.00                    | 0.00                      | 100.00                    | 100.00                    |                 |
| Cl  | 4140                      | 3000                      | 2140                      | 2220                      |                           |                           | 1380                      |                           | 3000                      | 2850                      | 3660            |
| S   | 1435                      | 880                       | 900                       | 725                       |                           |                           | 1310                      |                           | 1580                      | 1565                      | 1810            |
| Fo (mol %)  | 85.8                      | 86.1                      | 84.0                      | 83.7                      |                           |                           | 85.0                      |                           | 78.5                      | 78.5                      |                 |
| H <sub>2</sub> O (wt %)   | 1.05                      | 1.26                      | 1.76                      | 1.19                      | 1.01                      | 1.01                      | 1.78                      | 1.91                      | 1.62                      | n.a.                      | 2.02            |
| CO <sub>2</sub> (ppm)   | 1440                      | 622                       | 283                       | 176                       | b.d.l.                    | 333                       | 1167                      | 1120                      | 1556                      | n.a.                      | 216             |
| MI thickness (µm)   | 108                       | 60                        | 58                        | 58                        | 58                        | 58                        | 68                        | 68                        | 85                        |                           | 50              |
| <i>P</i> (MPa), non-corrected MI                                      | 186.7                     | 142.7                     | 106.1                     | 71.6                      |                           |                           | 97.3                      | 207.6                     | 202.5                     | 264.6                     | 101.5           |
| Depth (m), non-corrected MI   | 7622                      | 5827                      | 4337                      | 2930                      |                           |                           | 3976                      | 8473                      | 8268                      | 10801                     | 4150            |
| <i>P</i> (MPa), corrected MI  | 186.1                     | 127.7                     | 92.3                      | 55.4                      |                           |                           | 70.6                      | 206.6                     | 188.9                     | 273.3                     | 71.9            |
| Depth (m), corrected MI   | 7598                      | 5217                      | 3774                      | 2269                      |                           |                           | 2889                      | 8434                      | 7713                      | 11154                     | 2942            |
| <i>T</i> from Petrolog (°C)   | 1052                      | 1066                      | 1077                      | 1077                      |                           |                           | 1062                      |                           | 1067                      | 1036                      |                 |
|   | Vat A<br>1__px2<br>(inc1) | Vat A<br>1__px2<br>(inc2) | Vat A<br>1__px2<br>(inc3) | Vat A<br>1__px3           | Vat A<br>1__px4           | Vat A<br>1__px5           | Vat A<br>1__px6<br>(inc1) | Vat A<br>1__px6<br>(inc2) | Vat A<br>1__px6<br>(inc3) | Vat A<br>ol1              | Vat A<br>ol2    |
| <i>Original compositions normalized to 100% on an anhydrous basis</i> |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                 |
| SiO <sub>2</sub>  | n.a.                      | 50.13                     | 50.05                     | n.a.                      | n.a.                      | n.a.                      | 49.87                     | 53.93                     | 51.31                     | 50.47                     | 47.97           |
| TiO <sub>2</sub>  | n.a.                      | 1.15                      | 1.02                      | n.a.                      | n.a.                      | n.a.                      | 1.32                      | 1.30                      | 1.18                      | 1.94                      | 1.50            |
| Al <sub>2</sub> O <sub>3</sub>  | n.a.                      | 19.99                     | 19.95                     | n.a.                      | n.a.                      | n.a.                      | 20.84                     | 19.76                     | 20.67                     | 17.42                     | 17.83           |

(continued)



Table 1: Continued

|   | Vat A<br>1_px2<br>(inc1) | Vat A<br>1_px2<br>(inc2) | Vat A<br>1_px2<br>(inc3) | Vat A<br>1_px3               | Vat A<br>1_px4               | Vat A<br>1_px5               | Vat A<br>1_px6<br>(inc1)     | Vat A<br>1_px6<br>(inc2)     | Vat A<br>1_px6<br>(inc3)     | Vat A<br>ol1        | Vat A<br>ol2 |
|---|--------------------------|--------------------------|--------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|---------------------|--------------|
| FeOt  | n.a.                     | 6.89                     | 7.57                     | n.a.                         | n.a.                         | n.a.                         | 7.09                         | 6.66                         | 5.88                         | 7.00                | 7.70         |
| MnO   | n.a.                     | 0.16                     | 0.17                     | n.a.                         | n.a.                         | n.a.                         | 0.17                         | 0.18                         | 0.17                         | 0.10                | 0.12         |
| MgO   | n.a.                     | 3.99                     | 3.04                     | n.a.                         | n.a.                         | n.a.                         | 3.38                         | 3.07                         | 3.39                         | 3.67                | 3.68         |
| CaO   | n.a.                     | 8.06                     | 9.05                     | n.a.                         | n.a.                         | n.a.                         | 8.71                         | 7.14                         | 8.53                         | 11.97               | 14.32        |
| Na <sub>2</sub> O   | n.a.                     | 3.12                     | 3.26                     | n.a.                         | n.a.                         | n.a.                         | 3.04                         | 4.16                         | 3.25                         | 3.57                | 1.99         |
| K <sub>2</sub> O  | n.a.                     | 5.25                     | 4.28                     | n.a.                         | n.a.                         | n.a.                         | 4.37                         | 3.19                         | 4.62                         | 3.00                | 4.01         |
| P <sub>2</sub> O <sub>5</sub>   | n.a.                     | 1.27                     | 1.60                     | n.a.                         | n.a.                         | n.a.                         | 1.20                         | 0.61                         | 1.00                         | 0.85                | 0.88         |
| Total   | 0.00                     | 100.00                   | 100.00                   |                              |                              |                              | 100.00                       | 100.00                       | 100.00                       | 100.00              | 100.00       |
| <i>Re-equilibrated compositions using Petrolog v3.1.1.2</i>           |                          |                          |                          |                              |                              |                              |                              |                              |                              |                     |              |
| SiO <sub>2</sub>  |                          |                          |                          |                              |                              |                              |                              |                              |                              | 49.92               | 47.53        |
| TiO <sub>2</sub>  |                          |                          |                          |                              |                              |                              |                              |                              |                              | 1.84                | 1.42         |
| Al <sub>2</sub> O <sub>3</sub>  |                          |                          |                          |                              |                              |                              |                              |                              |                              | 16.47               | 16.88        |
| Fe <sub>2</sub> O <sub>3</sub>  |                          |                          |                          |                              |                              |                              |                              |                              |                              | 1.58                | 1.82         |
| FeO   |                          |                          |                          |                              |                              |                              |                              |                              |                              | 5.59                | 6.08         |
| MnO   |                          |                          |                          |                              |                              |                              |                              |                              |                              | 0.09                | 0.11         |
| MgO   |                          |                          |                          |                              |                              |                              |                              |                              |                              | 6.16                | 6.09         |
| CaO   |                          |                          |                          |                              |                              |                              |                              |                              |                              | 11.33               | 13.56        |
| Na <sub>2</sub> O   |                          |                          |                          |                              |                              |                              |                              |                              |                              | 3.38                | 1.88         |
| K <sub>2</sub> O  |                          |                          |                          |                              |                              |                              |                              |                              |                              | 2.84                | 3.80         |
| P <sub>2</sub> O <sub>5</sub>   |                          |                          |                          |                              |                              |                              |                              |                              |                              | 0.80                | 0.83         |
| Total   |                          |                          |                          |                              |                              |                              |                              |                              |                              | 100.00              | 100.00       |
| Cl  |                          | 3830                     | 3960                     |                              |                              |                              | 4270                         | 1880                         | 3870                         | 1830                | 3650         |
| S   |                          | 2295                     | 1940                     |                              |                              |                              | 2070                         | 1825                         | 1960                         | 1336                | 1672         |
| Fo (mol %)  |                          |                          |                          |                              |                              |                              |                              |                              |                              | 87.2                | 85.9         |
| H <sub>2</sub> O (wt %)   | 1.72                     | 0.82                     | 1.67                     | 1.69                         | 0.91                         | 2.01                         | 2.02                         | 1.83                         | 1.63                         | 3.64                | 3.17         |
| CO <sub>2</sub> (ppm)   | b.d.l.                   | 168                      | 868                      | b.d.l.                       | b.d.l.                       | b.d.l.                       | b.d.l.                       | b.d.l.                       | 281                          | 1907                | 2473         |
| MI thickness (μm)   | 70                       | 70                       | 70                       | 70                           | 90                           | 57                           | 64                           | 64                           | 64                           | 32                  | 36           |
| <i>P</i> (MPa), non-corrected MI                                      |                          | 70.9                     | 183.2                    |                              |                              |                              |                              |                              |                              | 87.3                | 288.5        |
| Depth (m), non-corrected MI   |                          | 2900                     | 7482                     |                              |                              |                              |                              |                              |                              | 3570                | 11774        |
| <i>P</i> (MPa), corrected MI  |                          | 41.1                     | 154.8                    |                              |                              |                              |                              |                              |                              | 73.8                | 316.2        |
| Depth (m), corrected MI   |                          | 1686                     | 6324                     |                              |                              |                              |                              |                              |                              | 3019                | 12903        |
| <i>T</i> from Petrolog (°C)   |                          |                          |                          |                              |                              |                              |                              |                              |                              | 1055                | 1025         |
|   | Vat A<br>ol3             | Vat A<br>ol4             | Vat A<br>ol5 (inc1)      | Vat A<br>ol5 (inc1)<br>spot1 | Vat A<br>ol5 (inc1)<br>spot2 | Vat A<br>ol5 (inc1)<br>spot3 | Vat A<br>ol5 (inc1)<br>spot4 | Vat A<br>ol5 (inc1)<br>spot5 | Vat A<br>ol5 (inc1)<br>spot6 | Vat A<br>ol5 (inc2) | Vat A<br>ol6 |
| <i>Original compositions normalized to 100% on an anhydrous basis</i> |                          |                          |                          |                              |                              |                              |                              |                              |                              |                     |              |
| SiO <sub>2</sub>  | 48.87                    | 47.47                    | 47.97                    | 47.96                        | 47.31                        | 47.92                        | 47.72                        | 47.74                        | 47.26                        | 48.11               | 48.38        |
| TiO <sub>2</sub>  | 2.00                     | 1.68                     | 1.24                     | 1.20                         | 1.45                         | 1.41                         | 1.54                         | 1.37                         | 1.48                         | 1.23                | 1.85         |
| Al <sub>2</sub> O <sub>3</sub>  | 17.30                    | 18.37                    | 17.09                    | 17.39                        | 17.50                        | 17.28                        | 17.27                        | 17.22                        | 17.58                        | 17.73               | 18.84        |
| FeOt  | 7.01                     | 8.67                     | 8.03                     | 7.98                         | 8.03                         | 7.85                         | 8.18                         | 8.21                         | 7.99                         | 7.59                | 8.01         |
| MnO   | 0.13                     | 0.24                     | 0.14                     | 0.14                         | 0.16                         | 0.15                         | 0.17                         | 0.19                         | 0.09                         | 0.15                | 0.15         |
| MgO   | 3.96                     | 3.77                     | 4.23                     | 4.34                         | 4.22                         | 4.25                         | 4.00                         | 3.80                         | 3.46                         | 3.98                | 3.32         |

(continued)

Table 1: Continued

|   | Vat A<br>ol3 | Vat A<br>ol4 | Vat A<br>ol5 (inc1) | Vat A<br>ol5 (inc1)<br>spot1 | Vat A<br>ol5 (inc1)<br>spot2 | Vat A<br>ol5 (inc1)<br>spot3 | Vat A<br>ol5 (inc1)<br>spot4 | Vat A<br>ol5 (inc1)<br>spot5 | Vat A<br>ol5 (inc1)<br>spot6 | Vat A<br>ol5 (inc2) | Vat A<br>ol6         |
|---|--------------|--------------|---------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|---------------------|----------------------|
| CaO   | 12.43        | 11.85        | 14.34               | 14.07                        | 14.34                        | 14.14                        | 14.36                        | 14.44                        | 14.89                        | 14.17               | 10.65                |
| Na <sub>2</sub> O   | 2.74         | 2.75         | 2.07                | 2.09                         | 2.10                         | 2.01                         | 1.99                         | 2.19                         | 2.13                         | 2.08                | 3.17                 |
| K <sub>2</sub> O  | 4.06         | 3.79         | 4.10                | 4.07                         | 4.12                         | 4.16                         | 4.07                         | 4.05                         | 4.32                         | 4.19                | 4.39                 |
| P <sub>2</sub> O <sub>5</sub>   | 1.50         | 1.40         | 0.79                | 0.77                         | 0.77                         | 0.83                         | 0.70                         | 0.78                         | 0.79                         | 0.77                | 1.24                 |
| Total   | 100.00       | 100.00       | 100.00              | 100.00                       | 100.00                       | 100.00                       | 100.00                       | 100.00                       | 100.00                       | 100.00              | 100.00               |
| <i>Re-equilibrated compositions using Petrolog v3.1.1.2</i>           |              |              |                     |                              |                              |                              |                              |                              |                              |                     |                      |
| SiO <sub>2</sub>  | 48.46        | 47.19        | 47.58               | 47.58                        | 46.93                        | 47.58                        | 47.29                        | 47.28                        | 46.83                        | 47.75               | 48.09                |
| TiO <sub>2</sub>  | 1.91         | 1.63         | 1.18                | 1.15                         | 1.38                         | 1.35                         | 1.46                         | 1.29                         | 1.39                         | 1.18                | 1.80                 |
| Al <sub>2</sub> O <sub>3</sub>  | 16.51        | 17.83        | 16.30               | 16.64                        | 16.67                        | 16.54                        | 16.35                        | 16.24                        | 16.55                        | 17.00               | 18.26                |
| Fe <sub>2</sub> O <sub>3</sub>  | 1.59         | 2.37         | 1.90                | 1.89                         | 1.92                         | 1.86                         | 1.94                         | 1.94                         | 1.89                         | 1.81                | 2.32                 |
| FeO   | 5.58         | 6.57         | 6.33                | 6.29                         | 6.39                         | 6.19                         | 6.45                         | 6.47                         | 6.30                         | 5.97                | 6.14                 |
| MnO   | 0.12         | 0.23         | 0.13                | 0.13                         | 0.15                         | 0.14                         | 0.16                         | 0.18                         | 0.08                         | 0.14                | 0.15                 |
| MgO   | 6.05         | 4.97         | 6.27                | 6.23                         | 6.24                         | 6.13                         | 6.36                         | 6.36                         | 6.12                         | 5.83                | 4.28                 |
| CaO   | 11.87        | 11.50        | 13.68               | 13.46                        | 13.66                        | 13.54                        | 13.60                        | 13.62                        | 14.02                        | 13.57               | 10.38                |
| Na <sub>2</sub> O   | 2.61         | 2.67         | 1.97                | 2.00                         | 2.00                         | 1.92                         | 1.88                         | 2.06                         | 2.01                         | 1.99                | 3.09                 |
| K <sub>2</sub> O  | 3.87         | 3.68         | 3.91                | 3.89                         | 3.93                         | 3.98                         | 3.85                         | 3.82                         | 4.07                         | 4.02                | 4.28                 |
| P <sub>2</sub> O <sub>5</sub>   | 1.43         | 1.36         | 0.75                | 0.74                         | 0.73                         | 0.79                         | 0.66                         | 0.74                         | 0.74                         | 0.74                | 1.21                 |
| Total   | 100.00       | 100.00       | 100.00              | 100.00                       | 100.00                       | 100.00                       | 100.00                       | 100.00                       | 100.00                       | 100.00              | 100.00               |
| Cl  | 2530         | 3150         | 4070                | 3880                         | 3410                         | 3870                         | 3310                         | 3710                         | 4140                         | 3900                | 2960                 |
| S   | 2144         | 1868         | 1892                | 1672                         | 1892                         | 2020                         | 1608                         | 1648                         | 1988                         | 1784                | 1656                 |
| Fo (mol %)  | 87.0         | 81.8         | 85.8                | 85.8                         | 85.8                         | 85.8                         | 85.8                         | 85.8                         | 85.8                         | 85.6                | 80.9                 |
| H <sub>2</sub> O (wt %)   | 2.83         | 3.35         | 2.25                | 2.25                         | 2.25                         | 2.25                         | 2.25                         | 2.25                         | 2.25                         | 2.53                | 2.78                 |
| CO <sub>2</sub> (ppm)   | 933          | 603          | 1837                | b.d.l.                       | b.d.l.                       | b.d.l.                       | b.d.l.                       | b.d.l.                       | b.d.l.                       | 1667                | 304                  |
| MI thickness (μm)   | 41           | 31           | 53                  | 53                           | 53                           | 53                           | 53                           | 53                           | 53                           | 42                  | 37                   |
| <i>P</i> (MPa), non-corrected MI                                      | 194.7        | 176.3        | 236.8               |                              |                              |                              |                              |                              |                              | 224.6               | 127.9                |
| Depth (m), non-corrected MI   | 7949         | 7200         | 9666                |                              |                              |                              |                              |                              |                              | 9168                | 5223                 |
| <i>P</i> (MPa), corrected MI  | 190.3        | 171          | 250.6               |                              |                              |                              |                              |                              |                              | 232.7               | 118.3                |
| Depth (m), corrected MI   | 7770         | 6983         | 10228               |                              |                              |                              |                              |                              |                              | 9498                | 4834                 |
| <i>T</i> from Petrolog (°C)   | 1062         | 1053         | 1057                | 1064                         | 1057                         | 1059                         | 1044                         | 1035                         | 1014                         | 1045                | 1051                 |
|   | Vat A<br>ol7 | Vat A<br>ol8 | Vat A<br>ol9        | Vat A<br>ol10                | Vat A<br>ol11                | Vat A<br>ol12 (inc1)         | Vat A<br>ol12 (inc2)         | Vat A<br>ol13                | Vat A<br>ol15                | Vat A<br>ol16       | Vat A<br>ol17 (inc1) |
| <i>Original compositions normalized to 100% on an anhydrous basis</i> |              |              |                     |                              |                              |                              |                              |                              |                              |                     |                      |
| SiO <sub>2</sub>  | n.a.         | 50.90        | 50.71               | n.a.                         | n.a.                         | n.a.                         | n.a.                         | n.a.                         | 50.22                        | 51.85               | 51.45                |
| TiO <sub>2</sub>  | n.a.         | 1.93         | 1.69                | n.a.                         | n.a.                         | n.a.                         | n.a.                         | n.a.                         | 1.28                         | 1.51                | 1.40                 |
| Al <sub>2</sub> O <sub>3</sub>  | n.a.         | 16.66        | 18.55               | n.a.                         | n.a.                         | n.a.                         | n.a.                         | n.a.                         | 18.45                        | 17.71               | 19.83                |
| FeO <sub>t</sub>  | n.a.         | 6.18         | 7.07                | n.a.                         | n.a.                         | n.a.                         | n.a.                         | n.a.                         | 7.19                         | 5.94                | 6.13                 |
| MnO   | n.a.         | 0.21         | 0.14                | n.a.                         | n.a.                         | n.a.                         | n.a.                         | n.a.                         | 0.15                         | 0.06                | 0.14                 |
| MgO   | n.a.         | 4.18         | 3.62                | n.a.                         | n.a.                         | n.a.                         | n.a.                         | n.a.                         | 3.42                         | 3.56                | 3.23                 |
| CaO   | n.a.         | 12.00        | 11.30               | n.a.                         | n.a.                         | n.a.                         | n.a.                         | n.a.                         | 12.34                        | 13.50               | 10.11                |
| Na <sub>2</sub> O   | n.a.         | 3.38         | 3.63                | n.a.                         | n.a.                         | n.a.                         | n.a.                         | n.a.                         | 2.51                         | 1.78                | 3.49                 |
| K <sub>2</sub> O  | n.a.         | 3.63         | 2.60                | n.a.                         | n.a.                         | n.a.                         | n.a.                         | n.a.                         | 3.79                         | 3.20                | 3.57                 |

(continued)

Table I: Continued

|   | Vat A<br>ol7         | Vat A<br>ol8       | Vat A<br>ol9       | Vat A<br>ol10 | Vat A<br>ol11 | Vat A<br>ol12 (inc1) | Vat A<br>ol12 (inc2) | Vat A<br>ol13 | Vat A<br>ol15 | Vat A<br>ol16 | Vat A<br>ol17 (inc1) |
|---|----------------------|--------------------|--------------------|---------------|---------------|----------------------|----------------------|---------------|---------------|---------------|----------------------|
| P <sub>2</sub> O <sub>5</sub>   | n.a.                 | 0.93               | 0.67               | n.a.          | n.a.          | n.a.                 | n.a.                 | n.a.          | 0.65          | 0.88          | 0.66                 |
| Total   |                      | 100.00             | 100.00             |               |               |                      |                      |               | 100.00        | 100.00        | 100.00               |
| <i>Re-equilibrated compositions using Petrolog v3.1.1.2</i>           |                      |                    |                    |               |               |                      |                      |               |               |               |                      |
| SiO <sub>2</sub>  | n.a.                 | 50.44              | 50.44              | n.a.          | n.a.          | n.a.                 | n.a.                 | n.a.          | 49.82         | 51.27         | 51.06                |
| TiO <sub>2</sub>  | n.a.                 | 1.85               | 1.66               | n.a.          | n.a.          | n.a.                 | n.a.                 | n.a.          | 1.23          | 1.43          | 1.36                 |
| Al <sub>2</sub> O <sub>3</sub>  | n.a.                 | 15.95              | 18.18              | n.a.          | n.a.          | n.a.                 | n.a.                 | n.a.          | 17.77         | 16.80         | 19.23                |
| Fe <sub>2</sub> O <sub>3</sub>  | n.a.                 | 1.34               | 1.84               | n.a.          | n.a.          | n.a.                 | n.a.                 | n.a.          | 1.79          | 1.33          | 1.51                 |
| FeO   | n.a.                 | 4.98               | 5.42               | n.a.          | n.a.          | n.a.                 | n.a.                 | n.a.          | 5.59          | 4.80          | 4.88                 |
| MnO   | n.a.                 | 0.20               | 0.14               | n.a.          | n.a.          | n.a.                 | n.a.                 | n.a.          | 0.14          | 0.06          | 0.14                 |
| MgO   | n.a.                 | 6.13               | 4.48               | n.a.          | n.a.          | n.a.                 | n.a.                 | n.a.          | 5.07          | 5.94          | 4.53                 |
| CaO   | n.a.                 | 11.49              | 11.07              | n.a.          | n.a.          | n.a.                 | n.a.                 | n.a.          | 11.89         | 12.81         | 9.81                 |
| Na <sub>2</sub> O   | n.a.                 | 3.24               | 3.56               | n.a.          | n.a.          | n.a.                 | n.a.                 | n.a.          | 2.42          | 1.69          | 3.38                 |
| K <sub>2</sub> O  | n.a.                 | 3.48               | 2.55               | n.a.          | n.a.          | n.a.                 | n.a.                 | n.a.          | 3.65          | 3.04          | 3.46                 |
| P <sub>2</sub> O <sub>5</sub>   | n.a.                 | 0.89               | 0.66               | n.a.          | n.a.          | n.a.                 | n.a.                 | n.a.          | 0.63          | 0.83          | 0.64                 |
| Total   |                      | 100.00             | 100.00             |               |               |                      |                      |               | 100.00        | 100.00        | 100.00               |
| Cl  |                      | 2440               | 1120               |               |               |                      |                      |               | 3040          | 2280          | 1960                 |
| S   |                      | 1904               | 1508               |               |               |                      |                      |               | 1472          | 1208          | 1072                 |
| Fo (mol %)  | n.a.                 | 88.5               | 83.1               |               |               |                      |                      |               | 84.3          | 87.7          | 85.1                 |
| H <sub>2</sub> O (wt %)   | 2.66                 | 3.41               | 3.44               | 3.07          | 2.91          | 2.04                 | 1.96                 | 3.07          | n.a.          | n.a.          | 3.47                 |
| CO <sub>2</sub> (ppm)   | 251                  | 639                | 2830               | 2771          | 705           | b.d.l.               | b.d.l.               | 1764          | n.a.          | n.a.          | 1243                 |
| MI thickness (μm)   | 38                   | 30                 | 30                 | 34            | 39            | 29                   | 29                   | 27            |               |               | 31                   |
| P (MPa), non-corrected MI   | 107.0                | 181.3              | 355.2              | 335.2         | 171.0         |                      |                      | 267.7         |               |               | 240.5                |
| Depth (m), non-corrected MI   | 4373                 | 7404               | 14495              | 13680         | 6981          |                      |                      | 10927         |               |               | 9817                 |
| P (MPa), corrected MI   | 93.8                 | 171.6              | 379.3              | 362.7         | 163.1         |                      |                      | 278.8         |               |               | 238.5                |
| Depth (m), corrected MI   | 3835                 | 7007               | 15476              | 14799         | 6661          |                      |                      | 11378         |               |               | 9735                 |
| T from Petrolog (°C)  |                      | 1084               | 1056               |               |               |                      |                      |               | 1031          | 1015          | 1053                 |
|   | Vat A<br>ol17 (inc2) | VatB<br>ol1 (inc1) | VatB<br>ol1 (inc2) | VatB<br>ol2   | VatB<br>ol3   | VatB<br>ol4          | VatB<br>ol5          | VatB<br>ol6   | VatB<br>ol7   | VatB<br>ol8   | VatB<br>ol9          |
| <i>Original compositions normalized to 100% on an anhydrous basis</i> |                      |                    |                    |               |               |                      |                      |               |               |               |                      |
| SiO <sub>2</sub>  | n.a.                 | n.a.               | n.a.               | n.a.          | n.a.          | n.a.                 | 50.44                | 51.86         | 49.66         | 49.72         | 48.64                |
| TiO <sub>2</sub>  | n.a.                 | n.a.               | n.a.               | n.a.          | n.a.          | n.a.                 | 1.60                 | 1.49          | 2.20          | 1.33          | 1.95                 |
| Al <sub>2</sub> O <sub>3</sub>  | n.a.                 | n.a.               | n.a.               | n.a.          | n.a.          | n.a.                 | 18.05                | 16.24         | 18.46         | 18.06         | 18.34                |
| FeO <sub>t</sub>  | n.a.                 | n.a.               | n.a.               | n.a.          | n.a.          | n.a.                 | 6.95                 | 6.45          | 7.47          | 7.50          | 7.38                 |
| MnO   | n.a.                 | n.a.               | n.a.               | n.a.          | n.a.          | n.a.                 | 0.15                 | 0.16          | 0.19          | 0.16          | 0.10                 |
| MgO   | n.a.                 | n.a.               | n.a.               | n.a.          | n.a.          | n.a.                 | 3.31                 | 4.06          | 3.33          | 3.44          | 3.71                 |
| CaO   | n.a.                 | n.a.               | n.a.               | n.a.          | n.a.          | n.a.                 | 10.48                | 13.75         | 10.58         | 13.08         | 11.34                |
| Na <sub>2</sub> O   | n.a.                 | n.a.               | n.a.               | n.a.          | n.a.          | n.a.                 | 3.47                 | 2.52          | 3.19          | 2.55          | 2.84                 |
| K <sub>2</sub> O  | n.a.                 | n.a.               | n.a.               | n.a.          | n.a.          | n.a.                 | 4.00                 | 2.90          | 3.86          | 3.45          | 4.33                 |
| P <sub>2</sub> O <sub>5</sub>   | n.a.                 | n.a.               | n.a.               | n.a.          | n.a.          | n.a.                 | 1.55                 | 0.59          | 1.06          | 0.73          | 1.37                 |
| Total   |                      |                    |                    |               |               |                      | 100.00               | 100.00        | 100.00        | 100.00        | 100.00               |
| <i>Re-equilibrated compositions using Petrolog v3.1.1.2</i>           |                      |                    |                    |               |               |                      |                      |               |               |               |                      |
| SiO <sub>2</sub>  | n.a.                 | n.a.               | n.a.               | n.a.          | n.a.          | n.a.                 | 50.13                | 51.11         | 49.35         | 49.23         | 48.33                |
| TiO <sub>2</sub>  | n.a.                 | n.a.               | n.a.               | n.a.          | n.a.          | n.a.                 | 1.57                 | 1.39          | 2.15          | 1.27          | 1.89                 |
| Al <sub>2</sub> O <sub>3</sub>  | n.a.                 | n.a.               | n.a.               | n.a.          | n.a.          | n.a.                 | 17.68                | 15.20         | 18.07         | 17.23         | 17.78                |

(continued)

Table 1: Continued

|   | Vat A<br>ol17 (inc2) | VatB<br>ol1 (inc1) | VatB<br>ol1 (inc2) | VatB<br>ol2  | VatB<br>ol3  | VatB<br>ol4  | VatB<br>ol5  | VatB<br>ol6   | VatB<br>ol7   | VatB<br>ol8         | VatB<br>ol9         |
|---|----------------------|--------------------|--------------------|--------------|--------------|--------------|--------------|---------------|---------------|---------------------|---------------------|
| Fe <sub>2</sub> O <sub>3</sub>  | n.a.                 | n.a.               | n.a.               | n.a.         | n.a.         | n.a.         | 1.94         | 1.40          | 2.17          | 1.86                | 1.83                |
| FeO   | n.a.                 | n.a.               | n.a.               | n.a.         | n.a.         | n.a.         | 5.38         | 5.30          | 5.72          | 5.89                | 5.74                |
| MnO   | n.a.                 | n.a.               | n.a.               | n.a.         | n.a.         | n.a.         | 0.15         | 0.15          | 0.19          | 0.15                | 0.10                |
| MgO   | n.a.                 | n.a.               | n.a.               | n.a.         | n.a.         | n.a.         | 4.05         | 6.97          | 4.05          | 5.47                | 5.06                |
| CaO   | n.a.                 | n.a.               | n.a.               | n.a.         | n.a.         | n.a.         | 10.26        | 12.87         | 10.36         | 12.48               | 10.99               |
| Na <sub>2</sub> O   | n.a.                 | n.a.               | n.a.               | n.a.         | n.a.         | n.a.         | 3.40         | 2.35          | 3.12          | 2.43                | 2.75                |
| K <sub>2</sub> O  | n.a.                 | n.a.               | n.a.               | n.a.         | n.a.         | n.a.         | 3.92         | 2.71          | 3.78          | 3.29                | 4.20                |
| P <sub>2</sub> O <sub>5</sub>   | n.a.                 | n.a.               | n.a.               | n.a.         | n.a.         | n.a.         | 1.52         | 0.55          | 1.04          | 0.70                | 1.33                |
| Total   |                      |                    |                    |              |              |              | 100.00       | 100.00        | 100.00        | 100.00              | 100.00              |
| Cl  |                      |                    |                    |              |              |              | 1810         | 2500          | 1860          | 2770                | 2760                |
| S   |                      |                    |                    |              |              |              | 1212         | 1538.5        | 1464          | 1624                | 1792                |
| Fo (mol %)  |                      |                    |                    |              |              |              | 81.8         | 88.7          | 80.9          | 84.6                | 84.4                |
| H <sub>2</sub> O (wt %)   | 3.3                  | 3.2                | 1.93               | 2.64         | 2.52         | 2.76         | 1.58         | 1.56          | 2.38          | 2.04                | 2.7                 |
| CO <sub>2</sub> (ppm)   | 1102                 | 2313               | 1206               | 2053         | 4409         | 862          | 1708         | 1664          | 1468          | 1976                | 697                 |
| MI thickness (µm)   | 35                   | 43                 | 43                 | 42           | 30           | 27           | 44           | 65            | 40            | 34                  | 41                  |
| P (MPa), non-corrected MI   | 216.9                | 307.4              | 211.0              | 285.4        | 423.1        | 185.4        | 263.0        | 212.6         | 252.8         | 246.8               | 173.6               |
| Depth (m), non-corrected MI   | 8854                 | 12545              | 8614               | 11649        | 17261        | 7571         | 10733        | 8678          | 10317         | 10075               | 7090                |
| P (MPa), corrected MI   | 219.0                | 329.0              | 198.7              | 295.5        | 464.0        | 178.2        | 273.4        | 218.8         | 260.1         | 264.5               | 165.3               |
| Depth (m), corrected MI   | 8940                 | 13425              | 8112               | 12059        | 18930        | 7276         | 11158        | 8932          | 10616         | 10795               | 6750                |
| T from Petrolog (°C)  |                      |                    |                    |              |              |              | 1054         | 1049          | 1049          | 1023                | 1062                |
|   | VatB<br>ol10         | VatB<br>ol11       | VatB<br>ol12       | VatB<br>ol13 | VatB<br>ol14 | VatB<br>ol15 | VatB<br>ol16 | Vat B<br>ol17 | Vat B<br>ol18 | I_Cn2<br>ol1 (inc2) | I_Cn2<br>ol1 (inc1) |
| <i>Original compositions normalized to 100% on an anhydrous basis</i> |                      |                    |                    |              |              |              |              |               |               |                     |                     |
| SiO <sub>2</sub>  | 51.03                | 50.20              | 49.56              | n.a.         | n.a.         | n.a.         | n.a.         | 52.34         | 48.41         | n.a.                | n.a.                |
| TiO <sub>2</sub>  | 1.27                 | 1.68               | 1.34               | n.a.         | n.a.         | n.a.         | n.a.         | 1.76          | 1.31          | n.a.                | n.a.                |
| Al <sub>2</sub> O <sub>3</sub>  | 17.63                | 18.34              | 18.23              | n.a.         | n.a.         | n.a.         | n.a.         | 16.46         | 19.22         | n.a.                | n.a.                |
| FeOt  | 6.62                 | 6.40               | 6.94               | n.a.         | n.a.         | n.a.         | n.a.         | 6.16          | 7.67          | n.a.                | n.a.                |
| MnO   | 0.18                 | 0.10               | 0.08               | n.a.         | n.a.         | n.a.         | n.a.         | 0.11          | 0.13          | n.a.                | n.a.                |
| MgO   | 3.81                 | 3.24               | 3.95               | n.a.         | n.a.         | n.a.         | n.a.         | 3.94          | 3.75          | n.a.                | n.a.                |
| CaO   | 12.83                | 12.84              | 12.87              | n.a.         | n.a.         | n.a.         | n.a.         | 12.75         | 13.00         | n.a.                | n.a.                |
| Na <sub>2</sub> O   | 2.61                 | 3.03               | 2.61               | n.a.         | n.a.         | n.a.         | n.a.         | 3.36          | 2.39          | n.a.                | n.a.                |
| K <sub>2</sub> O  | 3.45                 | 3.47               | 3.64               | n.a.         | n.a.         | n.a.         | n.a.         | 2.55          | 3.48          | n.a.                | n.a.                |
| P <sub>2</sub> O <sub>5</sub>   | 0.57                 | 0.70               | 0.77               | n.a.         | n.a.         | n.a.         | n.a.         | 0.58          | 0.64          | n.a.                | n.a.                |
| Total   | 100.00               | 100.00             | 100.00             |              |              |              |              | 100.00        | 100.00        |                     |                     |
| <i>Re-equilibrated compositions using Petrolog v3.1.1.2</i>           |                      |                    |                    |              |              |              |              |               |               |                     |                     |
| SiO <sub>2</sub>  | 50.47                | 49.74              | 49.18              | n.a.         | n.a.         | n.a.         | n.a.         | 51.78         | 48.01         | n.a.                | n.a.                |
| TiO <sub>2</sub>  | 1.20                 | 1.60               | 1.29               | n.a.         | n.a.         | n.a.         | n.a.         | 1.68          | 1.26          | n.a.                | n.a.                |
| Al <sub>2</sub> O <sub>3</sub>  | 16.71                | 17.51              | 17.54              | n.a.         | n.a.         | n.a.         | n.a.         | 15.70         | 18.43         | n.a.                | n.a.                |
| Fe <sub>2</sub> O <sub>3</sub>  | 1.48                 | 1.47               | 1.62               | n.a.         | n.a.         | n.a.         | n.a.         | 1.36          | 1.92          | n.a.                | n.a.                |
| FeO   | 5.33                 | 5.08               | 5.49               | n.a.         | n.a.         | n.a.         | n.a.         | 4.95          | 6.05          | n.a.                | n.a.                |
| MnO   | 0.17                 | 0.10               | 0.08               | n.a.         | n.a.         | n.a.         | n.a.         | 0.10          | 0.12          | n.a.                | n.a.                |
| MgO   | 6.20                 | 5.37               | 5.67               | n.a.         | n.a.         | n.a.         | n.a.         | 6.07          | 5.51          | n.a.                | n.a.                |

(continued)

Table 1: Continued

|   | VatB<br>ol10 | VatB<br>ol11 | VatB<br>ol12 | VatB<br>ol13 | VatB<br>ol14 | VatB<br>ol15 | VatB<br>ol16 | Vat B<br>ol17 | Vat B<br>ol18        | I_Cn2<br>ol1 (inc2)  | I_Cn2<br>ol1 (inc1) |
|---|--------------|--------------|--------------|--------------|--------------|--------------|--------------|---------------|----------------------|----------------------|---------------------|
| CaO   | 12.16        | 12.26        | 12.38        | n.a.         | n.a.         | n.a.         | n.a.         | 12.16         | 12.46                | n.a.                 | n.a.                |
| Na <sub>2</sub> O   | 2.47         | 2.89         | 2.51         | n.a.         | n.a.         | n.a.         | n.a.         | 3.21          | 2.29                 | n.a.                 | n.a.                |
| K <sub>2</sub> O  | 3.27         | 3.31         | 3.50         | n.a.         | n.a.         | n.a.         | n.a.         | 2.43          | 3.34                 | n.a.                 | n.a.                |
| P <sub>2</sub> O <sub>5</sub>   | 0.54         | 0.67         | 0.74         | n.a.         | n.a.         | n.a.         | n.a.         | 0.55          | 0.61                 | n.a.                 | n.a.                |
| Total   | 100.00       | 100.00       | 100.00       |              |              |              |              | 100.00        | 100.00               |                      |                     |
| Cl  | 3200         | 2290         | 2720         |              |              |              |              | 1800          | 2480                 |                      |                     |
| S   | 1399         | 1328         | 1492         |              |              |              |              | 1312          | 1508                 |                      |                     |
| Fo (mol %)  | 87.5         | 86.6         | 86.2         |              |              |              |              | 88.1          | 84.5                 |                      |                     |
| H <sub>2</sub> O (wt %)   | 2.37         | 2.15         | 3.52         | 1.27         | 2.46         | 2.9          | 1.68         | 1.63          | 4.25                 | 1.37                 | 1.94                |
| CO <sub>2</sub> (ppm)   | 1716         | 2100         | 3956         | b.d.l.       | b.d.l.       | 2350         | 1352         | 1614          | 847                  | b.d.l.               | b.d.l.              |
| MI thickness (μm)   | 45           | 33           | 33           | 14           | 45           | 43           | 45           | 39            | 30                   | 41                   | 41                  |
| <i>P</i> (MPa), non-corrected MI                                      | 236.9        | 256.9        | 394.5        |              |              | 307.6        | 223.4        | 226.4         | 210.9                |                      |                     |
| Depth (m), non-corrected MI   | 9669         | 10484        | 16096        |              |              | 12550        | 9120         | 9242          | 8608                 |                      |                     |
| <i>P</i> (MPa), corrected MI  | 244.7        | 271.3        | 438.0        |              |              | 326.0        | 209.3        | 229.8         | 208.3                |                      |                     |
| Depth (m), corrected MI   | 9988         | 11072        | 17870        |              |              | 13303        | 8544         | 9380          | 8504                 |                      |                     |
| <i>T</i> from Petrolog (°C)   | 1047         | 1019         | 1055         |              |              |              |              | 1059          | 1047                 |                      |                     |
|   | I_Cn2<br>ol2 | I_Cn2<br>ol3 | I_Cn2<br>ol4 | I_Cn2<br>ol5 | I_Cn2<br>ol6 | I_Cn2<br>ol7 | I_Cn2<br>ol8 | I_Cn2<br>ol9  | I_Cn2<br>ol10 (inc1) | I_Cn3<br>ol10 (inc2) | I_Cn2<br>ol11       |
| <i>Original compositions normalized to 100% on an anhydrous basis</i> |              |              |              |              |              |              |              |               |                      |                      |                     |
| SiO <sub>2</sub>  | n.a.         | n.a.         | n.a.         | 49.08        | n.a.         | 50.44        | 49.19        | n.a.          | 52.27                | 49.27                | 48.27               |
| TiO <sub>2</sub>  | n.a.         | n.a.         | n.a.         | 1.23         | n.a.         | 1.62         | 1.88         | n.a.          | 1.57                 | 1.57                 | 1.34                |
| Al <sub>2</sub> O <sub>3</sub>  | n.a.         | n.a.         | n.a.         | 17.66        | n.a.         | 18.37        | 16.89        | n.a.          | 18.91                | 19.09                | 17.48               |
| FeOt  | n.a.         | n.a.         | n.a.         | 6.50         | n.a.         | 6.91         | 7.77         | n.a.          | 6.99                 | 8.07                 | 7.47                |
| MnO   | n.a.         | n.a.         | n.a.         | 0.07         | n.a.         | 0.06         | 0.10         | n.a.          | 0.04                 | 0.07                 | 0.13                |
| MgO   | n.a.         | n.a.         | n.a.         | 4.41         | n.a.         | 3.50         | 4.31         | n.a.          | 2.78                 | 3.02                 | 4.05                |
| CaO   | n.a.         | n.a.         | n.a.         | 14.17        | n.a.         | 11.27        | 12.30        | n.a.          | 8.89                 | 10.85                | 15.04               |
| Na <sub>2</sub> O   | n.a.         | n.a.         | n.a.         | 2.19         | n.a.         | 3.63         | 2.92         | n.a.          | 3.90                 | 2.97                 | 2.02                |
| K <sub>2</sub> O  | n.a.         | n.a.         | n.a.         | 4.02         | n.a.         | 3.50         | 3.25         | n.a.          | 4.00                 | 4.23                 | 3.63                |
| P <sub>2</sub> O <sub>5</sub>   | n.a.         | n.a.         | n.a.         | 0.67         | n.a.         | 0.72         | 1.39         | n.a.          | 0.64                 | 0.87                 | 0.57                |
| Total   |              |              |              | 100.00       |              | 100.00       | 100.00       |               | 100.00               | 100.00               | 100.00              |
| <i>Re-equilibrated compositions using Petrolog v3.1.1.2</i>           |              |              |              |              |              |              |              |               |                      |                      |                     |
| SiO <sub>2</sub>  | n.a.         | n.a.         | n.a.         | 48.65        | n.a.         | 49.87        | 48.80        | n.a.          | 51.94                | 48.93                | 47.80               |
| TiO <sub>2</sub>  | n.a.         | n.a.         | n.a.         | 1.17         | n.a.         | 1.53         | 1.81         | n.a.          | 1.54                 | 1.53                 | 1.26                |
| Al <sub>2</sub> O <sub>3</sub>  | n.a.         | n.a.         | n.a.         | 16.81        | n.a.         | 17.36        | 16.26        | n.a.          | 18.53                | 18.62                | 16.48               |
| Fe <sub>2</sub> O <sub>3</sub>  | n.a.         | n.a.         | n.a.         | 1.40         | n.a.         | 1.56         | 1.86         | n.a.          | 2.07                 | 2.42                 | 1.68                |
| FeO   | n.a.         | n.a.         | n.a.         | 5.25         | n.a.         | 5.51         | 6.10         | n.a.          | 5.29                 | 6.00                 | 5.96                |
| MnO   | n.a.         | n.a.         | n.a.         | 0.07         | n.a.         | 0.06         | 0.10         | n.a.          | 0.04                 | 0.07                 | 0.12                |
| MgO   | n.a.         | n.a.         | n.a.         | 6.62         | n.a.         | 6.04         | 5.95         | n.a.          | 3.51                 | 3.97                 | 6.66                |
| CaO   | n.a.         | n.a.         | n.a.         | 13.48        | n.a.         | 10.65        | 11.84        | n.a.          | 8.71                 | 10.58                | 14.18               |
| Na <sub>2</sub> O   | n.a.         | n.a.         | n.a.         | 2.08         | n.a.         | 3.43         | 2.81         | n.a.          | 3.82                 | 2.90                 | 1.90                |
| K <sub>2</sub> O  | n.a.         | n.a.         | n.a.         | 3.83         | n.a.         | 3.31         | 3.13         | n.a.          | 3.92                 | 4.13                 | 3.42                |
| P <sub>2</sub> O <sub>5</sub>   | n.a.         | n.a.         | n.a.         | 0.64         | n.a.         | 0.68         | 1.34         | n.a.          | 0.63                 | 0.85                 | 0.54                |

(continued)

Table 1: Continued

|   | I_Cn2<br>ol2         | I_Cn2<br>ol3         | I_Cn2<br>ol4         | I_Cn2<br>ol5       | I_Cn2<br>ol6        | I_Cn2<br>ol7        | I_Cn2<br>ol8        | I_Cn2<br>ol9        | I_Cn2<br>ol10 (inc1) | I_Cn3<br>ol10 (inc2) | I_Cn2<br>ol11       |
|---|----------------------|----------------------|----------------------|--------------------|---------------------|---------------------|---------------------|---------------------|----------------------|----------------------|---------------------|
| Total   |                      |                      |                      | 100.00             |                     | 100.00              | 100.00              |                     | 100.00               | 100.00               | 100.00              |
| Cl  |                      |                      |                      | 3830               |                     | 2580                | 1260                |                     | 1500                 | 3450                 | 4440                |
| S   |                      |                      |                      | 1912               |                     | 1404                | 1616                |                     | 1092                 | 1952                 | 1828                |
| Fo (mol %)  |                      |                      |                      | 88.7               |                     | 87.3                | 85.4                |                     | 80.3                 | 79.7                 | 87.3                |
| H <sub>2</sub> O (wt %)   | 1.82                 | 1.97                 | 3.15                 | 3.63               | 3.66                | 2.7                 | 3.13                | 3.69                | 2.05                 | n.a.                 | 2.35                |
| CO <sub>2</sub> (ppm)   | b.d.l.               | b.d.l.               | 3435                 | 3421               | 3832                | 1949                | 483                 | 3818                | b.d.l.               | n.a.                 | 2298                |
| MI thickness (μm)   | 27                   | 30                   | 38                   | 34                 | 33                  | 41                  | 36                  | 34                  | 44                   | 44                   | 40                  |
| P (MPa), non-corrected MI   |                      |                      | 373.8                | 352.1              | 397.3               | 286.9               | 157.9               | 397.0               |                      |                      | 308.9               |
| Depth (m), non-corrected MI   |                      |                      | 15250                | 14368              | 16209               | 11709               | 6447                | 16196               |                      |                      | 12607               |
| P (MPa), corrected MI   |                      |                      | 412.3                | 389.8              | 447.8               | 304.7               | 146.6               | 447.4               |                      |                      | 271.5               |
| Depth (m), corrected MI   |                      |                      | 16822                | 15904              | 18269               | 12434               | 5988                | 18253               |                      |                      | 11081               |
| T from Petrolog (°C)  |                      |                      |                      | 1068               |                     | 1057                | 1077                |                     | 1053                 | 1029                 | 1039                |
|   | I_Cn2<br>ol12 (inc1) | I_Cn2<br>ol12 (inc2) | I_Cn2<br>ol12 (inc3) | Vat A<br>ol2 (inc) | Vat A<br>ol3 (inc2) | Vat A<br>ol3 (inc1) | Vat A<br>ol4 (inc1) | Vat A<br>ol4 (inc2) | Vat A<br>ol4 (inc3)  | Vat A<br>ol6 (inc1)  | Vat A<br>ol6 (inc3) |
| <i>Original compositions normalized to 100% on an anhydrous basis</i> |                      |                      |                      |                    |                     |                     |                     |                     |                      |                      |                     |
| SiO <sub>2</sub>  | 48.54                | n.a.                 | n.a.                 | 48.75              | 48.88               | 47.02               | 47.74               | 47.62               | 47.12                | 48.90                | 49.18               |
| TiO <sub>2</sub>  | 1.28                 | n.a.                 | n.a.                 | 1.55               | 1.91                | 1.69                | 1.62                | 1.60                | 1.67                 | 1.31                 | 1.63                |
| Al <sub>2</sub> O <sub>3</sub>  | 17.76                | n.a.                 | n.a.                 | 18.17              | 18.09               | 18.50               | 18.89               | 19.15               | 18.93                | 18.07                | 17.92               |
| FeO <sub>t</sub>  | 7.37                 | n.a.                 | n.a.                 | 6.82               | 8.47                | 9.25                | 8.58                | 8.42                | 8.66                 | 7.37                 | 6.95                |
| MnO   | 0.18                 | n.a.                 | n.a.                 | 0.15               | 0.17                | 0.19                | 0.18                | 0.18                | 0.17                 | 0.13                 | 0.14                |
| MgO   | 3.81                 | n.a.                 | n.a.                 | 3.59               | 3.21                | 3.52                | 3.07                | 3.40                | 3.39                 | 3.67                 | 3.14                |
| CaO   | 14.37                | n.a.                 | n.a.                 | 13.43              | 10.48               | 11.87               | 11.97               | 11.00               | 11.69                | 13.81                | 12.90               |
| Na <sub>2</sub> O   | 2.13                 | n.a.                 | n.a.                 | 2.27               | 3.03                | 2.53                | 2.74                | 2.86                | 2.81                 | 2.35                 | 2.72                |
| K <sub>2</sub> O  | 4.00                 | n.a.                 | n.a.                 | 4.08               | 4.48                | 4.18                | 4.34                | 4.49                | 4.26                 | 3.73                 | 4.15                |
| P <sub>2</sub> O <sub>5</sub>   | 0.55                 | n.a.                 | n.a.                 | 1.19               | 1.29                | 1.26                | 0.88                | 1.26                | 1.29                 | 0.66                 | 1.27                |
| Total   | 100.00               |                      |                      | 100.00             | 100.00              | 100.00              | 100.00              | 100.00              | 100.00               | 100.00               | 100.00              |
| <i>Re-equilibrated compositions using Petrolog v3.1.1.2</i>           |                      |                      |                      |                    |                     |                     |                     |                     |                      |                      |                     |
| SiO <sub>2</sub>  | 47.99                | n.a.                 | n.a.                 | 48.30              | 48.57               | 46.73               | 47.39               | 47.31               | 46.83                | 48.40                | 48.66               |
| TiO <sub>2</sub>  | 1.20                 | n.a.                 | n.a.                 | 1.47               | 1.86                | 1.64                | 1.56                | 1.55                | 1.62                 | 1.23                 | 1.54                |
| Al <sub>2</sub> O <sub>3</sub>  | 16.62                | n.a.                 | n.a.                 | 17.22              | 17.63               | 17.96               | 18.21               | 18.57               | 18.35                | 17.02                | 16.88               |
| Fe <sub>2</sub> O <sub>3</sub>  | 1.67                 | n.a.                 | n.a.                 | 1.55               | 2.46                | 2.69                | 2.40                | 2.38                | 2.41                 | 1.69                 | 1.60                |
| FeO   | 5.95                 | n.a.                 | n.a.                 | 5.43               | 6.27                | 6.84                | 6.44                | 6.41                | 6.51                 | 5.86                 | 5.51                |
| MnO   | 0.17                 | n.a.                 | n.a.                 | 0.14               | 0.17                | 0.18                | 0.17                | 0.17                | 0.16                 | 0.12                 | 0.13                |
| MgO   | 6.70                 | n.a.                 | n.a.                 | 6.01               | 4.24                | 4.69                | 4.62                | 4.61                | 4.69                 | 6.32                 | 5.86                |
| CaO   | 13.45                | n.a.                 | n.a.                 | 12.73              | 10.21               | 11.53               | 11.54               | 10.66               | 11.33                | 13.02                | 12.15               |
| Na <sub>2</sub> O   | 2.00                 | n.a.                 | n.a.                 | 2.15               | 2.96                | 2.46                | 2.64                | 2.77                | 2.72                 | 2.21                 | 2.56                |
| K <sub>2</sub> O  | 3.74                 | n.a.                 | n.a.                 | 3.87               | 4.37                | 4.06                | 4.18                | 4.35                | 4.13                 | 3.51                 | 3.91                |
| P <sub>2</sub> O <sub>5</sub>   | 0.51                 | n.a.                 | n.a.                 | 1.13               | 1.26                | 1.22                | 0.85                | 1.22                | 1.25                 | 0.62                 | 1.20                |
| Total   | 100.00               |                      |                      | 100.00             | 100.00              | 100.00              | 100.00              | 100.00              | 100.00               | 100.00               | 100.00              |
| Cl  | 3900                 |                      |                      | 3166.67            | 3010.00             | 3280                | 3710.00             | 3510.00             | 3236.67              | 3613.33              | 2733.33             |
| S   | 1972                 |                      |                      | 2156.67            | 2111.67             | 2707.5              | 2020.00             | 2031.67             | 1976.67              | 2270.00              | 2236.67             |
| Fo (mol %)  | 87.4                 |                      | 90.7                 | 87.1               | 80.2                | 80.2                | 81.2                | 81.3                | 81.3                 | 86.8                 | 86.7                |

(continued)

Table I: Continued

|                             | L_Cn2<br>ol12 (inc1) | L_Cn2<br>ol12 (inc2) | L_Cn2<br>ol12 (inc3) | Vat A<br>ol2 (inc) | Vat A<br>ol3 (inc2) | Vat A<br>ol3 (inc1) | Vat A<br>ol4 (inc1) | Vat A<br>ol4 (inc2) | Vat A<br>ol4 (inc3) | Vat A<br>ol6 (inc1) | Vat A<br>ol6 (inc3) |
|-----------------------------|----------------------|----------------------|----------------------|--------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| H <sub>2</sub> O (wt %)     | 1.84                 | 2.47                 | 2.49                 | 3.33               | 2.33                | 2.33                | 2.51                | 1.90                | 1.28                | 3.43                | 3.65                |
| CO <sub>2</sub> (ppm)       | 2112                 | 4462                 | 4601                 | 2632.28            | 882                 | 294                 | b.d.l.              | b.d.l.              | b.d.l.              | 2872                | 1058                |
| MI thickness (μm)           | 47                   | 47                   | 47                   | 32                 | 36                  | 36                  | 33                  | 33                  | 33                  | 35                  | 35                  |
| P (MPa), non-corrected MI   | 225.4                | 368.8                | 432.4                | 309.1              | 207.3               | 113.7               |                     |                     |                     | 322.4               | 217.9               |
| Depth (m), non-corrected MI | 9200                 | 15047                | 15049                | 12615              | 8464                | 4645                |                     |                     |                     | 13157               | 8896                |
| P (MPa), corrected MI       | 252.99               | 467.9                | 476.7                | 334.60             | 206.8               | 107.8               |                     |                     |                     | 355.4               | 219.2               |
| Depth (m), corrected MI     | 10326                | 19089                | 19448                | 13653              | 8442                | 4406                |                     |                     |                     | 14502               | 8948                |
| T from Petrolog (°C)        | 1034                 |                      |                      | 1028               | 1046                | 1040                | 1018                | 1048                | 1038                | 1031                | 1012                |

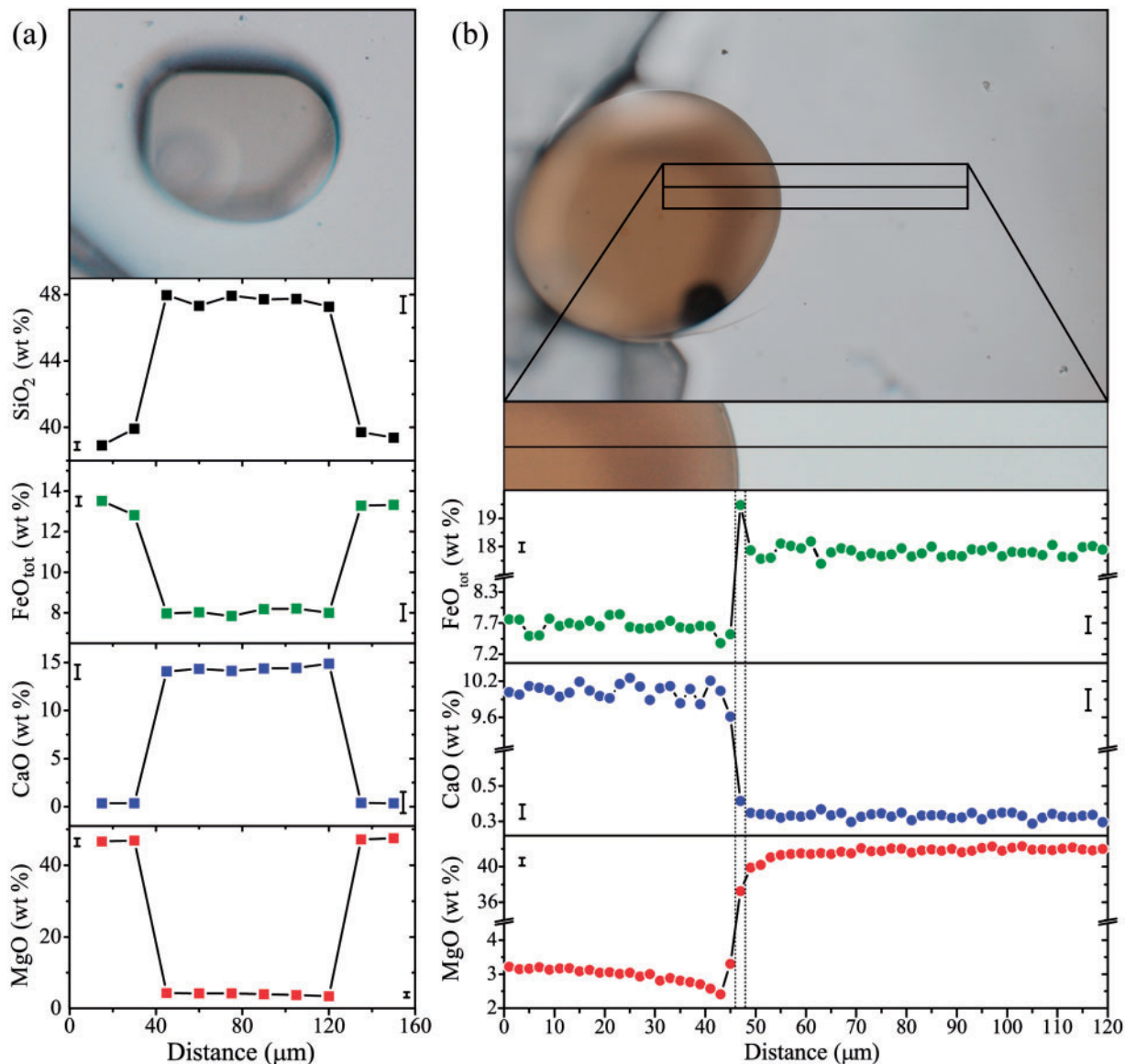
|   | Vat A<br>ol6 (inc2) | Vat A<br>ol7 (inc) | Vat A<br>ol7 glass | Vat A<br>ol8 (inc1) | Vat A<br>ol8 (inc2) | Vat A<br>ol9 | Vat A<br>ol10 | Vat A<br>ol11 | Vat A<br>ol14 | Vat B2<br>ol1 |
|---|---------------------|--------------------|--------------------|---------------------|---------------------|--------------|---------------|---------------|---------------|---------------|
| <i>Original compositions normalized to 100% on an anhydrous basis</i> |                     |                    |                    |                     |                     |              |               |               |               |               |
| SiO <sub>2</sub>  | 48.61               | 50.61              | 49.39              | 48.79               | 49.08               | 47.62        | 48.18         | 50.63         | 49.51         | 47.47         |
| TiO <sub>2</sub>  | 1.40                | 1.34               | 1.20               | 1.61                | 1.49                | 1.32         | 1.91          | 2.11          | 1.66          | 1.51          |
| Al <sub>2</sub> O <sub>3</sub>  | 18.20               | 17.30              | 18.40              | 18.14               | 17.55               | 18.91        | 18.29         | 18.48         | 18.51         | 17.05         |
| FeOt  | 7.25                | 6.48               | 7.66               | 6.54                | 6.84                | 7.66         | 8.28          | 7.18          | 7.86          | 7.98          |
| MnO   | 0.15                | 0.15               | 0.18               | 0.11                | 0.12                | 0.16         | 0.15          | 0.10          | 0.14          | 0.09          |
| MgO   | 3.38                | 3.65               | 3.86               | 3.07                | 3.50                | 3.80         | 3.22          | 2.98          | 3.85          | 3.99          |
| CaO   | 14.11               | 13.83              | 11.87              | 14.33               | 14.18               | 13.90        | 11.49         | 9.62          | 10.41         | 15.20         |
| Na <sub>2</sub> O   | 2.38                | 2.77               | 2.77               | 2.56                | 2.43                | 2.04         | 2.98          | 4.04          | 3.05          | 2.14          |
| K <sub>2</sub> O  | 3.88                | 3.35               | 3.96               | 3.92                | 3.91                | 3.87         | 4.17          | 3.69          | 4.17          | 3.84          |
| P <sub>2</sub> O <sub>5</sub>   | 0.64                | 0.51               | 0.72               | 0.92                | 0.89                | 0.72         | 1.33          | 1.16          | 0.84          | 0.74          |
| Total   | 100.00              | 100.00             | 100.00             | 100.00              | 100.00              | 100.00       | 100.00        | 100.00        | 100.00        | 100.00        |
| <i>Re-equilibrated compositions using Petrolog v3.1.1.2</i>           |                     |                    |                    |                     |                     |              |               |               |               |               |
| SiO <sub>2</sub>  | 48.11               | 50.17              | 48.82              | 48.30               | 48.56               | 47.22        | 47.82         | 50.34         | 49.23         | 47.03         |
| TiO <sub>2</sub>  | 1.32                | 1.28               | 1.13               | 1.51                | 1.40                | 1.26         | 1.84          | 2.06          | 1.63          | 1.42          |
| Al <sub>2</sub> O <sub>3</sub>  | 17.13               | 16.58              | 17.30              | 17.06               | 16.51               | 18.02        | 17.64         | 18.06         | 18.14         | 16.04         |
| Fe <sub>2</sub> O <sub>3</sub>  | 1.67                | 1.49               | 1.75               | 1.46                | 1.53                | 1.87         | 2.29          | 1.95          | 2.15          | 1.83          |
| FeO   | 5.76                | 5.15               | 6.09               | 5.23                | 5.47                | 6.09         | 6.31          | 5.43          | 6.04          | 6.34          |
| MnO   | 0.14                | 0.14               | 0.17               | 0.10                | 0.11                | 0.15         | 0.14          | 0.10          | 0.14          | 0.08          |
| MgO   | 6.11                | 5.57               | 6.58               | 5.90                | 6.28                | 5.83         | 4.69          | 3.98          | 4.58          | 6.64          |
| CaO   | 13.27               | 13.26              | 11.16              | 13.47               | 13.33               | 13.24        | 11.08         | 9.39          | 10.19         | 14.30         |
| Na <sub>2</sub> O   | 2.24                | 2.66               | 2.60               | 2.41                | 2.29                | 1.94         | 2.88          | 3.95          | 2.99          | 2.01          |
| K <sub>2</sub> O  | 3.65                | 3.21               | 3.72               | 3.69                | 3.68                | 3.69         | 4.03          | 3.61          | 4.09          | 3.61          |
| P <sub>2</sub> O <sub>5</sub>   | 0.60                | 0.49               | 0.68               | 0.87                | 0.84                | 0.69         | 1.28          | 1.13          | 0.82          | 0.70          |
| Total   | 100.00              | 100.00             | 100.00             | 100.00              | 100.00              | 100.00       | 100.00        | 100.00        | 100.00        | 100.00        |
| Cl  | 3975.00             | 2440.00            | 4570               | 3590.00             | 3766.67             | 3873.33      | 2696.67       | 1613.33       | 3507.50       | 4403.33       |
| S   | 2240.00             | 1288.33            | 1840               | 2357.50             | 2166.67             | 2361.67      | 2071.67       | 1853.33       | 2040.00       | 1968.33       |
| Fo (mol %)  | 86.7                | 86.7               | 86.9               | 87.5                | 87.6                | 85.3         | 81.7          | 81.9          | 82.1          | 86.7          |
| H <sub>2</sub> O (wt %)   | 3.79                | 3.21               | 4.34               | 2.73                | 2.98                | 2.20         | 3.33          | 2.04          | 3.88          | 1.88          |
| CO <sub>2</sub> (ppm)   | 3159                | 2419               | 567                | 4489                | 2982                | 2354         | 814           | 1111          | 2014          | 1725          |
| MI thickness (μm)   | 35                  | 35                 | 35                 | 33                  | 33                  | 38           | 39            | 30            | 31            | 46            |
| P (MPa), non-corrected MI   | 342.5               | 295.7              | 198.8              | 378.4               | 317.0               | 250.7        | 204.5         | 227.3         | 327.2         | 189.5         |

(continued)

Table 1: Continued

|   | Vat A<br>ol6 (inc2) | Vat A<br>ol7 (inc) | Vat A<br>ol7 glass | Vat A<br>ol8 (inc1) | Vat A<br>ol8 (inc2) | Vat A<br>ol9 | Vat A<br>ol10 | Vat A<br>ol11 | Vat A<br>ol14 | Vat B2<br>ol1 |
|---|---------------------|--------------------|--------------------|---------------------|---------------------|--------------|---------------|---------------|---------------|---------------|
| Depth (m), non-corrected MI   | 13976               | 12069              | 8115               | 15441               | 12936               | 10231        | 8347          | 9280          | 13354         | 7739          |
| <i>P</i> (MPa), corrected MI  | 379.6               | 316.0              | 191.4              | 440.2               | 352.9               | 270.0        | 202.9         | 228.1         | 340.2         | 224.6         |
| Depth (m), corrected MI   | 15488               | 12895              | 7814               | 17959               | 14400               | 11019        | 8283          | 9311          | 13882         | 9168          |
| <i>T</i> from Petrolog (°C)   | 1013                | 1032               | 1063               | 993                 | 1020                | 1034         | 1032          | 1050          | 1082          | 1039          |
|   | Vat B2<br>ol2       | Vat B2<br>ol3      | Vat B2<br>ol4      |                     |                     |              |               |               |               |               |
| <i>Original compositions normalized to 100% on an anhydrous basis</i> |                     |                    |                    |                     |                     |              |               |               |               |               |
| SiO <sub>2</sub>  | 49.16               | 49.49              | 46.71              |                     |                     |              |               |               |               |               |
| TiO <sub>2</sub>  | 1.60                | 1.24               | 2.05               |                     |                     |              |               |               |               |               |
| Al <sub>2</sub> O <sub>3</sub>  | 18.61               | 19.37              | 19.96              |                     |                     |              |               |               |               |               |
| FeOt  | 8.27                | 7.18               | 7.75               |                     |                     |              |               |               |               |               |
| MnO   | 0.18                | 0.10               | 0.15               |                     |                     |              |               |               |               |               |
| MgO   | 3.25                | 3.25               | 3.10               |                     |                     |              |               |               |               |               |
| CaO   | 10.78               | 12.23              | 13.21              |                     |                     |              |               |               |               |               |
| Na <sub>2</sub> O   | 3.01                | 2.45               | 2.79               |                     |                     |              |               |               |               |               |
| K <sub>2</sub> O  | 4.12                | 3.94               | 3.32               |                     |                     |              |               |               |               |               |
| P <sub>2</sub> O <sub>5</sub>   | 1.02                | 0.74               | 0.95               |                     |                     |              |               |               |               |               |
| Total   | 100.00              | 100.00             | 100.00             |                     |                     |              |               |               |               |               |
| <i>Re-equilibrated compositions using Petrolog v3.1.1.2</i>           |                     |                    |                    |                     |                     |              |               |               |               |               |
| SiO <sub>2</sub>  | 48.82               | 49.16              | 46.35              |                     |                     |              |               |               |               |               |
| TiO <sub>2</sub>  | 1.56                | 1.20               | 1.95               |                     |                     |              |               |               |               |               |
| Al <sub>2</sub> O <sub>3</sub>  | 18.13               | 18.81              | 18.94              |                     |                     |              |               |               |               |               |
| Fe <sub>2</sub> O <sub>3</sub>  | 2.46                | 1.91               | 1.92               |                     |                     |              |               |               |               |               |
| FeO   | 6.20                | 5.53               | 6.07               |                     |                     |              |               |               |               |               |
| MnO   | 0.18                | 0.10               | 0.14               |                     |                     |              |               |               |               |               |
| MgO   | 4.19                | 4.49               | 5.40               |                     |                     |              |               |               |               |               |
| CaO   | 10.50               | 11.87              | 12.54              |                     |                     |              |               |               |               |               |
| Na <sub>2</sub> O   | 2.93                | 2.38               | 2.65               |                     |                     |              |               |               |               |               |
| K <sub>2</sub> O  | 4.01                | 3.83               | 3.15               |                     |                     |              |               |               |               |               |
| P <sub>2</sub> O <sub>5</sub>   | 0.99                | 0.72               | 0.90               |                     |                     |              |               |               |               |               |
| Total   | 99.97               | 100.00             | 100.01             |                     |                     |              |               |               |               |               |
| Cl  | 3010.00             | 3393.33            | 1780.00            |                     |                     |              |               |               |               |               |
| S   | 2061.67             | 2113.33            | 1223.33            |                     |                     |              |               |               |               |               |
| Fo (mol %)  | 80.0                | 82.7               | 84.6               |                     |                     |              |               |               |               |               |
| H <sub>2</sub> O (wt %)   | 2.87                | 2.67               | 1.78               |                     |                     |              |               |               |               |               |
| CO <sub>2</sub> (ppm)   | 1688                | 2177               | 1042               |                     |                     |              |               |               |               |               |
| MI thickness (μm)   | 42                  | 35                 | 33                 |                     |                     |              |               |               |               |               |
| <i>P</i> (MPa), non-corrected MI                                      | 278.9               | 254.0              | 155.3              |                     |                     |              |               |               |               |               |
| Depth (m), non-corrected MI   | 11381               | 10366              | 6344               |                     |                     |              |               |               |               |               |
| <i>P</i> (MPa), corrected MI  | 291.5               | 286.0              | 155.0              |                     |                     |              |               |               |               |               |
| Depth (m), corrected MI   | 11896               | 11672              | 6330               |                     |                     |              |               |               |               |               |
| <i>T</i> from Petrolog (°C)   | 1042                | 1021               | 1000               |                     |                     |              |               |               |               |               |





**Fig. 4.** (a) Variations of SiO<sub>2</sub>, FeO<sub>tot</sub>, CaO and MgO (wt %) across host olivine (sample Vat A, olivine 5; Supplementary Data) and entrapped melt inclusion (Table 1). The abrupt transitions suggest that no appreciable re-equilibration has occurred. (b) Transect of ~120 μm at 2 μm intervals (60 points) through the MI–olivine boundary, showing abrupt chemical variations (FeO<sub>tot</sub>, CaO and MgO), but also a narrow, 2–3 μm thick, transition zone in which FeO<sub>tot</sub> and MgO contents are higher and lower, respectively, than in the surrounding olivine. The size of error bars is related to analytical uncertainties reported in the text.

olivine, and lengths varying up to 200 μm. The analysed MI are shoshonitic and phono-tephritic in composition (Fig. 2a); these coexist with large oxide crystals (Fig. 3c). The host clinopyroxene phenocrysts, 1–1.5 mm long, are diopsidic in composition [Ca<sub>46–48</sub>, Mg<sub>41–47</sub> (Fe<sup>3+</sup>, Fe<sup>2+</sup>, Mn)<sub>6–11</sub>] (see Supplementary Data).

The analysed MI, hosted either in olivine or in clinopyroxene phenocrysts, are less evolved than either the whole-rocks, classified mostly as latite, or the residual glasses (Fig. 2a). They are compositionally similar to MI

hosted in the least differentiated Minopoli and Fondo Riccio products from CF, and Solchiaro products from Procida (Fig. 2b); they also partially overlap with the less alkaline MI from SV magmas (Fig. 2c).

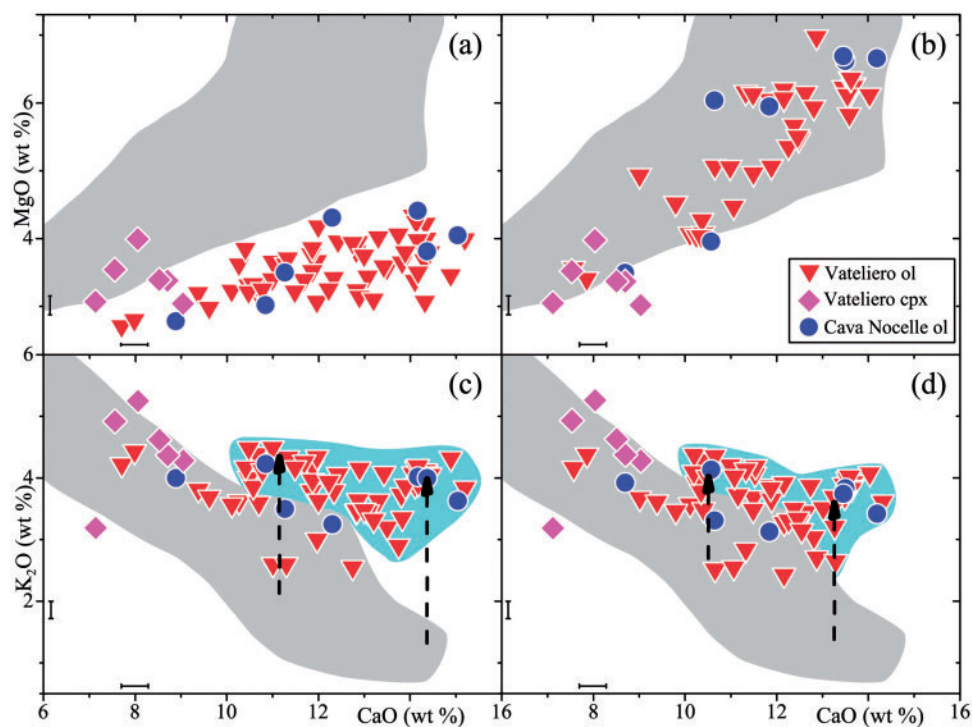
No compositional variations were observed between an host olivine phenocryst and its entrapped melt inclusion (Fig. 4a; Table 1).

An additional transect of ~120 μm at 2 μm interval (60 points, accelerating voltage 15 kV; dwell time 10 s; probe current  $1.4 \times 10^{-8}$  A) through the MI–olivine boundary

(Fig. 4b) shows abrupt chemical variations, but also a narrow, 2–3  $\mu\text{m}$  thick, transition zone in which  $\text{FeO}_{\text{tot}}$  and  $\text{MgO}$  contents are higher and lower, respectively, than in the surrounding olivine. Moreover, the concentration profile of  $\text{CaO}$ , the diffusion of which is much slower than that of  $\text{MgO}$  and  $\text{FeO}$  (Danyushevsky *et al.*, 2003), does not display any intermediate value at the olivine–MI boundary. These features can be ascribed either to post-entrapment crystallization on the olivine wall or to the position of the probe crystals (TAPH for Mg, PETJ for Ca and LIFH for Fe) relative to the surface of the MI at its edge, which cannot be horizontal when approaching the boundary with olivine, because of the different abrasion of olivine and MI during sample preparation. Because we cannot definitely establish that the measured compositions record the original MI–host crystal equilibrium, we discuss below results for two scenarios (non-equilibrated and re-equilibrated MI). We then consider either that their measured compositions record the original MI–host crystal equilibrium, or that complete re-equilibration took place during magma evolution, with the post-entrapment formation of a very thin crystalline layer along the MI rim (Gaetani & Watson, 2000).

FTIR spectra of the analyzed MI show water and in most cases carbonate peaks. The detected  $\text{H}_2\text{O}$  and  $\text{CO}_2$  contents range from 0.9 to 4.3 wt % and from 170 to 4,600 ppm, respectively, and decrease with decreasing  $\text{CaO}$  content (Table 1).

MI geochemical data (Table 1) show that with decreasing  $\text{CaO}$  (used as a differentiation index),  $\text{SiO}_2$ ,  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  increase, whereas  $\text{TiO}_2$  and  $\text{FeO}_{\text{tot}}$  decrease, in agreement with the general differentiation trend of the eruptive products from Ischia (Civetta *et al.*, 1991) and the other volcanic centres of the PVD (e.g. D'Antonio *et al.*, 1999b; Tonarini *et al.*, 2009; Arienzo *et al.*, 2010; Di Vito *et al.*, 2011).  $\text{CaO}/\text{Al}_2\text{O}_3$  ratios and  $\text{MgO}$  both decrease slightly, testifying to contemporaneous crystallization of olivine and Mg-rich pyroxene. However,  $\text{MgO}$  only decreases from 4 to 3 wt %, with a mean value of  $\sim 3.6$  wt % (Fig. 5a), whereas  $\text{CaO}$  spans the entire range displayed by the Neapolitan volcanoes, thus suggesting buffering of  $\text{MgO}$  values during magmatic differentiation. The low  $\text{MgO}$  content is rather unusual considering the highly forsteritic composition of the host olivines (as high as 89 mol %; Table 1). Within the same  $\text{CaO}$  interval the other PVD volcanic rocks are characterized by  $\text{MgO}$  values from 4 to



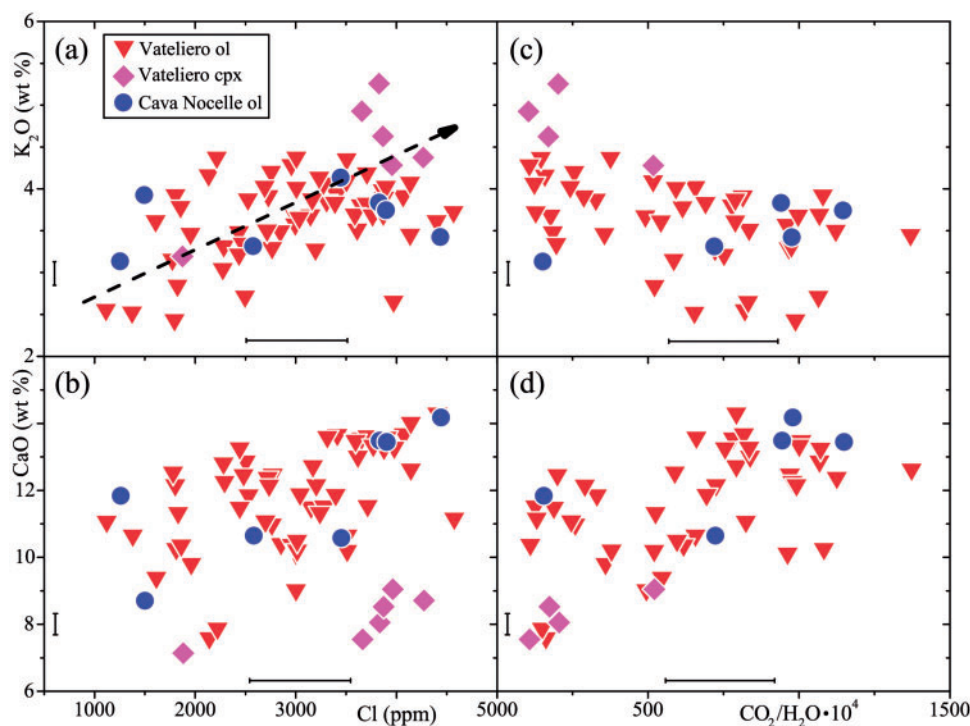
**Fig. 5.** (a)  $\text{MgO}$  and  $\text{CaO}$  covariation in Ischia MI compared with the trend of magmatic differentiation at Neapolitan volcanoes (original data). The Ischia MI display a nearly constant  $\text{MgO}$  value around 3.6 wt %, suggesting  $\text{MgO}$  buffering during progressive fractional crystallization. The gray field delimits the range of PVD whole-rocks and glassy groundmass from Procida samples, based on data from the literature (D'Antonio *et al.* 1999a, 2007; De Astis *et al.*, 2004; Mormone *et al.*, 2011). (b)  $\text{MgO}$  and  $\text{CaO}$  covariation for re-equilibrated MI compositions. The MI data overlap the PVD compositional field, with  $\text{MgO}$  contents spanning a wide range of values. (c) Covariation of  $\text{K}_2\text{O}$  and  $\text{CaO}$ . The light grey field delimits the data points that have  $\text{K}_2\text{O}$  and  $\text{CaO}$  contents plotting outside the PVD compositional field. Arrows indicate processes that may have occurred in addition to crystallization, such as fluid fluxing. (d) As (c), but showing re-equilibrated MI data. The size of error bars is related to analytical uncertainties reported in the text.

10 wt % (Severs, 2007; Mangiacapra *et al.*, 2008; Mormone *et al.*, 2011; Esposito *et al.*, 2011; Fig. 5a). Although at Ischia primitive magmatic rocks are absent, K-basaltic lithic blocks with MgO contents up to 10 wt % occur in the adjacent island of Procida (D'Antonio *et al.*, 1999a, 2007; Fig. 2b). Therefore, the Ischia olivines may have equilibrated in a magma more mafic than that trapped in the MI, as suggested by sparse kink-banding and chromium-rich spinel inclusions (D'Antonio *et al.*, 2013). Because we lack constraints on the initial  $\text{FeO}_{\text{tot}}$  of the trapped magma in the MI, unless arbitrarily imposing the oxygen fugacity, hence the melt  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio, we applied the Maurel & Maurel (1982) equation to estimate the MgO/FeO ratio theoretically by characterizing the parental liquid coexisting with Cr-spinels prior to post-entrapment olivine crystallization. Subsequent application of the PETROLOG3 code (Danyushevsky & Plechov, 2011), using the inferred  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio, allows the effect of post-entrapment olivine crystallization on the MI composition to be computed by adding olivine back into the glass composition until a liquid in equilibrium with the Fo content of the host-olivine phenocryst is obtained (D'Antonio *et al.*, 2013). The CaO vs MgO covariation in the re-equilibrated MI compositions displays a trend in good agreement with that of the PVD magmas, with the highest

values matching the field of Procida glassy groundmasses (Fig. 5b).

In Fig. 5c and d the variation of CaO vs  $\text{K}_2\text{O}$  is illustrated for the non re-equilibrated and the re-equilibrated MI compositions, respectively. In both cases  $\text{K}_2\text{O}$  contents increase with decreasing CaO. However, the data do not define a coherent trend ascribable to magmatic differentiation alone. The variability largely exceeds the analytical error and thus suggests K- and, to a lesser extent, Ca-enrichment. The CaO vs  $\text{K}_2\text{O}$  covariation of the re-equilibrated MI compositions (Fig. 5d) is little affected by post-entrapment crystallization of olivine, in agreement with microprobe profiles (Fig. 4). If we assume that post-entrapment crystallization affected only the CaO and  $\text{K}_2\text{O}$  contents, back-projecting the MI data into the PVD field would require crystallization of the trapped melt exceeding 20%, under extremely reduced and unrealistic redox conditions that are characterized by the absence of trivalent iron. Therefore, the large variability displayed by these two oxides needs to be explained by additional processes.

Figure 6a shows a positive correlation between  $\text{K}_2\text{O}$  and Cl in the MI. On the other hand, no clear correlation is observed between CaO and Cl (Fig. 6b), similar to the CaO vs  $\text{K}_2\text{O}$  covariation (Fig. 5c and d). Figure 6c and d illustrates the covariation of  $\text{K}_2\text{O}$  and CaO with the



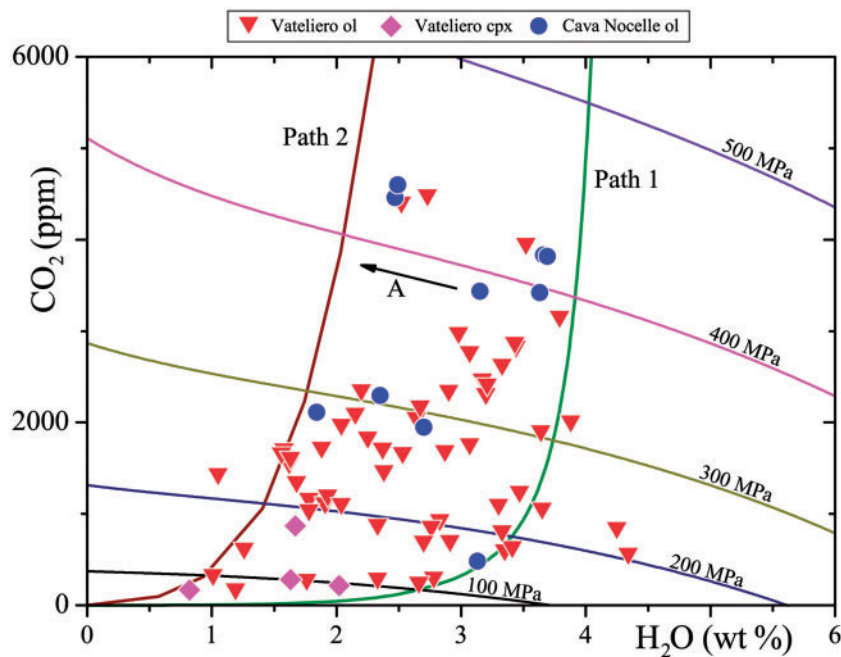
**Fig. 6.** CaO and  $\text{K}_2\text{O}$  variations (wt %) in MI (in the K-trachybasalt–shoshonite compositional range) vs Cl content (ppm) (a, b) and  $\text{CO}_2/\text{H}_2\text{O} \times 10000$  melt ratio (c, d). Fluid-phase transfer of Cl and K, owing to fluxing of a  $\text{CO}_2$ -rich gas phase, determines enrichments in K and Cl (and in Ca to a lesser extent) overlapping the trend of fractional crystallization (see text for details). The size of error bars is related to analytical uncertainties reported in the text.

$\text{CO}_2/\text{H}_2\text{O}$  ( $\times 10\,000$ ) melt ratio. Whereas CaO and  $\text{CO}_2/\text{H}_2\text{O}$  ( $\times 10\,000$ ) both decrease with differentiation,  $\text{K}_2\text{O}$  is not clearly correlated with  $\text{CO}_2/\text{H}_2\text{O}$ . The lack of significant correlations suggests that magma evolution towards low-pressure conditions (i.e. decreasing  $\text{CO}_2/\text{H}_2\text{O}$ ) was not accompanied by a unique trend of degassing and fractional crystallization. Rather, variable events of  $\text{CO}_2$ -rich fluid infiltration ( $\text{CO}_2$ -fluxing) may have occurred during magmatic differentiation. This is highlighted by the Cava Nocelle MI data, which show a decrease in  $\text{K}_2\text{O}$ , CaO,  $\text{CO}_2/\text{H}_2\text{O}$  ratio and Cl contents with depressurization.

The variation of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  contents in MI is compared with computed saturation isobars at 100, 200, 300, 400 and 500 MPa in Fig. 7 for an average trachybasaltic composition. Calculations assume the non-ideal, composition-dependent model of Papale *et al.* (2006). The isobars were computed at 1393 K, by analogy with the shoshonites studied by Cannatelli *et al.* (2007) and Mangiacapra *et al.* (2008). Computation of the saturation surfaces is appreciably affected by the relative FeO and  $\text{Fe}_2\text{O}_3$  proportions in the melt and was carried out consistently with  $\text{Fe}^{2+}/\text{Fe}^{3+}=1$ . The crude approximation of measured  $\text{FeO}_{\text{tot}}$  equal to divalent iron oxide gives Fe–Mg distribution coefficients ( $K_D$ ) between MI and host olivines that are too low ( $K_D \sim 0.16$  on average). Olivine–melt  $K_D$  should be around 0.3 (Roeder & Emslie, 1970) for these compositions.  $K_D$  values of  $\sim 0.3$  for all the studied

MI and coexisting olivines are achieved only by setting  $\text{Fe}^{2+}/\text{Fe}^{3+}=1$  (Table 1). This corresponds to very high oxidation states ( $\Delta\text{NNO} \sim 2\text{--}3$ ; the higher the equilibration pressure and water content, the higher the oxidation state), based on the approach of Moretti & Papale (2004) and Moretti (2005). Errors (not shown in Fig. 7 for the sake of clarity) correspond to the saturation model uncertainty (Papale *et al.*, 2006), and are  $\sim 15\%$  for  $\text{H}_2\text{O}$  and  $\sim 20\%$  for  $\text{CO}_2$ . A background degassing path (Path 1 in Fig. 7) bounding  $\text{H}_2\text{O}\text{--CO}_2$  pairs towards the  $\text{H}_2\text{O}$ -rich side has been determined, as for the Agnano–Monte Spina, Minopoli 2 and Fondo Riccio eruptions at CF (Mangiacapra *et al.*, 2008; Arienzo *et al.*, 2010). Path 1 is characterized by total water ( $\text{H}_2\text{O}^{\text{tot}}$ ) and carbon dioxide ( $\text{CO}_2^{\text{tot}}$ ) contents of 4.25 wt % (corresponding to the highest measured water contents) and 2.1 wt %, respectively. The former is higher than, whereas the latter is similar to, the values characterizing the CF MI. The bounding degassing path towards the  $\text{H}_2\text{O}$ -poor side (Path 2 in Fig. 7) is representative of a gas-buffered system with a constant  $\text{CO}_2^{\text{gas}}/\text{H}_2\text{O}^{\text{gas}}$  ratio of five (molar).

Entrapment pressures calculated for the  $\text{H}_2\text{O}\text{--CO}_2$  pairs vary from 70 to 430 MPa (from 40 to 480 MPa for the re-equilibrated dataset), and correspond to depths between 2.8 and 17.2 km (1.7 and 19.5 km for the re-equilibrated dataset) (Fig. 8), using an average crustal density of  $2.500\text{ kg m}^{-3}$  (P. Capuano, personal



**Fig. 7.** Variation of  $\text{H}_2\text{O}$  vs  $\text{CO}_2$  in MI compared with the degassing trends (Paths 1 and 2) from the Papale *et al.* (2006) model. Isobars are plotted for trachybasaltic composition; computation was performed at 1393 K. The background degassing Path 1, bounding the  $\text{H}_2\text{O}\text{--CO}_2$  MI pairs towards the  $\text{H}_2\text{O}$ -rich side, is characterized by total water ( $\text{H}_2\text{O}^{\text{tot}}$ ) and carbon dioxide ( $\text{CO}_2^{\text{tot}}$ ) contents of 4.25 wt % and 2.1 wt %, respectively. Path 2, towards the  $\text{H}_2\text{O}$ -poor side, is that of a gas-buffered system (along the direction indicated by arrow A) with a constant  $\text{CO}_2^{\text{gas}}/\text{H}_2\text{O}^{\text{gas}}$  ratio of five (molar). Error bars (not shown) are 15% for  $\text{H}_2\text{O}$  and 23% for  $\text{CO}_2$ .

communication). For the investigated eruptions, a vertically extended magmatic plumbing system emerges with possibly a major crystallization or storage region at  $\sim 200$  MPa, according to the data clustering.

## DISCUSSION

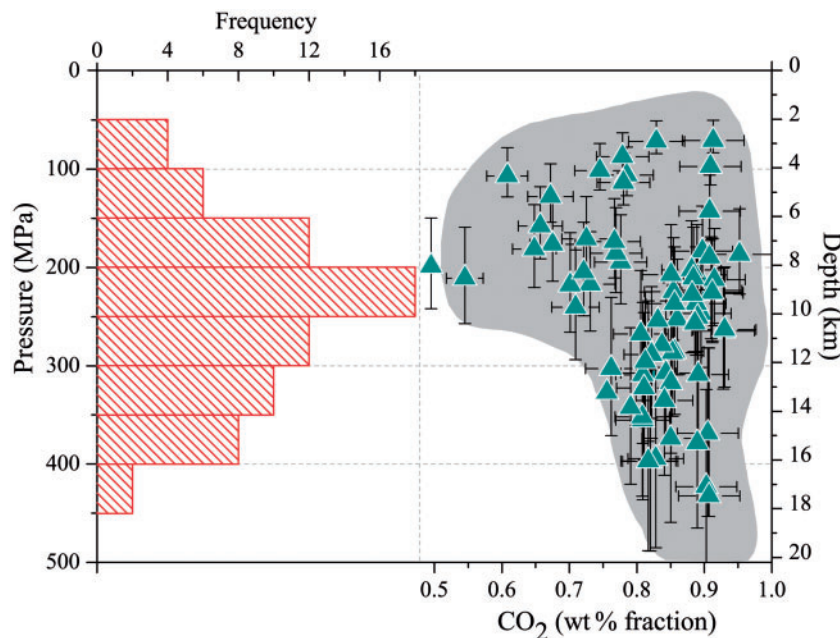
The MI data obtained as part of this study can be used to investigate the physico-chemical conditions of magmatic differentiation in the presence of fluid transfer and infiltration. Mixing or mingling processes of variably evolved magma batches are an additional factor that might also contribute to the observed variations. However, mixing or mingling processes would mirror the variations of major oxides caused by fractional crystallization and would not explain the large scatter displayed, for instance, in the CaO vs K<sub>2</sub>O (Fig. 5c and d), Cl vs K<sub>2</sub>O and Cl vs CaO plots (Fig. 6a and b) and CO<sub>2</sub>/H<sub>2</sub>O ( $\times 10\,000$ ) vs K<sub>2</sub>O (Fig. 6c).

Alternatively, different alkali-rich magma components could be involved in the genesis of the deep parental magma. However, in the PVD alkalinity and silica-undersaturation degrees do not show significant time variations (e.g. D'Antonio *et al.*, 1999a, 1999b, 2007, 2013; De Astis *et al.*, 2004), corroborating the hypothesis of geochemically similar parental magmas, which may have been modified *en route* to the surface (see below). Because

these magmas stagnated at mid-crustal levels, where they differentiated and were partly contaminated, presumably by the local Hercynian continental crust (Pappalardo *et al.*, 2002; Tonarini *et al.*, 2004; D'Antonio *et al.*, 2007; Di Renzo *et al.*, 2011, and references therein), small compositional differences can be ascribed to crustal contamination by *c.* 2 wt % of a granodioritic crust. Nevertheless, the resulting compositional changes are too small to explain the large scatter in K<sub>2</sub>O vs CaO (Fig. 5c and d).

Consistent with recent findings (Rust *et al.*, 2004; Spilliaert *et al.*, 2006; Mangiacapra *et al.*, 2008; Vigoroux *et al.*, 2008; Barsanti *et al.*, 2009; Aiuppa *et al.*, 2010; Arienzo *et al.*, 2010; Edmonds *et al.*, 2010; Oppenheimer *et al.*, 2011) we discuss below how the Ischia MI data highlight the role played by fluid percolation through the magmatic feeding system (i.e. fluxing), causing dehydration, CO<sub>2</sub> enrichment, high gas/melt ratios in the fluxed magma, and selective enrichment in elements such as the halogens and potassium (Collins *et al.*, 2009; Ferlito & Lanzafame, 2010).

Furthermore, our results allow exploration of the interplay between tectonic structures and ascending deep slab fluids to the Campanian Plain volcanoes, where the presence of CO<sub>2</sub> in magmas is well documented through analyses of MI in phenocrysts from (1) Procida K-trachybasalts (Esposito *et al.*, 2011; Mormone *et al.*, 2011), (2) CF shoshonitic to latitic Minopoli 2 and Fondo



**Fig. 8.** Pressure and equivalent depth vs gas composition for the analyzed MI. H<sub>2</sub>O–CO<sub>2</sub> pairs in MI suggest a nearly continuous 18–3 km depth range for crystallization and degassing (original data). The Gaussian distribution of crystallization depths throughout the plumbing system, with a mode between 200 and 250 MPa, is related to a main magma crystallization depth at 8–10 km, in agreement with observations at Campi Flegrei. In such an interval magmas stagnate and differentiate, as shown by the CO<sub>2</sub> gas proportion decreasing down to 50 wt %. The grey shaded field encompasses the pressure–depth and CO<sub>2</sub> gas proportion calculated by using the composition of the re-equilibrated MI and slightly expands the pressure–depth range of the original data. The size of error bars is related to model uncertainties reported in the text.

Riccio, and trachytic Agnano–Monte Spina products (Mangiacapra *et al.*, 2008; Arienzo *et al.*, 2010), and (3) tephri-phonolites of the post AD 1631 activity of Vesuvius (Marianelli *et al.*, 1999). Our results, together with these data, show that magmatic degassing in the Campanian Plain takes place at significant depths.

### Physico-chemical aspects

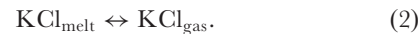
#### *Chemical variability and fluid transfer*

Because a significant role for mixing between initially different magmas can be discarded, the upper limit of the CaO vs K<sub>2</sub>O variation is probably due to a process of K (and to some extent Ca) enrichment (Fig. 5c and d) superimposed upon a fractional crystallization process (roughly coincident with the gray field in Fig. 5). Figure 6a shows a positive correlation between K<sub>2</sub>O and dissolved Cl, varying from an initial K<sub>2</sub>O = 2.5 wt % and Cl<sub>melt</sub> = 1000 ppm, up to ~4.5 wt % and ~4500 ppm. The data are significantly scattered and do not plot along a well-defined or unique trend of differentiation (dashed line in Fig. 6a is shown for qualitative purposes only). This reflects anomalous enrichments not related to fractional crystallization but determined by the transfer of a halogen-rich, alkali-bearing gas phase, as suggested for Mt. Etna (Ferlito & Lanzafame, 2010) and Procida (Mormone *et al.*, 2011). On the other hand, the lack of correlation between CaO and Cl (Fig. 6b) suggests that differentiation (i.e. CaO decrease) is not accompanied by a simple increase in Cl content.

When crystallization is coupled to degassing, a magma rising along a single ascent path should display decreasing CO<sub>2</sub>/H<sub>2</sub>O, with concomitant increase in incompatible element concentrations, such as K (prior to alkali-feldspar crystallization), and decrease in CaO. Despite the generally negative correlation between CaO and CO<sub>2</sub>/H<sub>2</sub>O (Fig. 6d), the positive correlation between K<sub>2</sub>O and Cl (Fig. 6a) and the lack of any correlation between CaO and Cl (Fig. 6b), as well as between CO<sub>2</sub>/H<sub>2</sub>O and K<sub>2</sub>O (Fig. 6c), strengthen the hypothesis that infiltration by fluids rising from great depth (CO<sub>2</sub>-fluxing) leads to K<sub>2</sub>O and Cl enrichment. This process is compatible with the high total amount of volatiles ( $\approx \text{H}_2\text{O}^{\text{tot}} + \text{CO}_2^{\text{tot}}$ ) in the Ischia parental magmas (~6 wt %), which, in turn, is consistent with previous estimates for the volcanism of Southern Italy (Scaillet & Pichavant, 2005).

The infiltration process, which is well exemplified by the Cava Nocelle MI data (see the positive correlation between CO<sub>2</sub>/H<sub>2</sub>O and K<sub>2</sub>O; Fig. 6c), strongly controls the measured K<sub>2</sub>O variability, superimposed on the normal trend of fractional crystallization.

Gas fluxing controls the observed K enrichment by stripping K from the melt to the gas phase as KCl. By considering KCl and HCl as the most important gas species, the following chemical reactions can be written:



From their equilibrium constants

$$\log a_{\text{KCl}_{\text{melt}}} = \log a_{\text{KCl}_{\text{gas}}} - \log K_2 = \log \frac{a_{\text{HCl}_{\text{gas}}}}{a_{\text{H}_2\text{O}_{\text{gas}}^{1/2}} \quad (3)$$

$$+ \log a_{\text{K}_2\text{O}_{\text{melt}}} + \log K_1.$$

Consequently, for a non-crystallizing melt (i.e.  $X_{\text{K}_2\text{O}} = \text{const}$ ), an increase in the  $a_{\text{HCl}_{\text{gas}}}/a_{\text{H}_2\text{O}_{\text{gas}}^{1/2}}$  ratio causes an increase of  $a_{\text{KCl}_{\text{melt}}}$ , and hence  $X_{\text{KCl}_{\text{melt}}}$ . Because at constant pressure this ratio would increase in response to CO<sub>2</sub>-fluxing and dehydration, reaction (1) explains experimental data showing that the Cl fluid–melt partition coefficient decreases when CO<sub>2</sub> is added to an H<sub>2</sub>O–Cl–melt system (Alletti *et al.*, 2009). Similar to the mechanism proposed to explain increasing Cl contents in zoned hornblende (Humphreys *et al.*, 2009), this suggests that Cl and K enrichment in a melt can be an indirect consequence of the transfer of a CO<sub>2</sub>-dominated, KCl-bearing gas phase fluxing through the magmatic system at variable depths. To a lesser extent, this process could also induce Ca enrichment, because of the presence of CaCl<sub>2</sub> in the magmatic gases (Symonds & Reed, 1993) that infiltrate the plumbing system. However, the predominance of K enrichment makes gas fluxing a process that essentially occurs at constant CaO (Fig. 5c and d).

It is worth noting that fluid percolation through the magmatic plumbing system has already been invoked as one of the processes responsible for the anomalous enrichment in K, Sb, Cl and F at CF (Villemant, 1988), Procida (Mormone *et al.*, 2011) and Mt. Etna (Ferlito & Lanzafame, 2010, and references therein). In magmas erupted at SV, volatile influx has also been inferred to account for a  $\delta^{18}\text{O}$  increase (with decreasing MgO) (Ayuso *et al.*, 1998), although the main agent for the potassium enrichment in the SV eruptive products (tending to ultra-potassic) must be sought in either phlogopite in the mantle source (Peccerillo, 2005, and references therein) or crustal contamination by limestone (Iacono-Marziano *et al.*, 2009).

#### *Magma crystallization and degassing: the redox connection*

An intriguing observation is the nearly constant, low MgO contents (~3.6 wt %; Fig. 5a) in the Ischia K-trachybasaltic and shoshonitic MI trapped in olivines covering a broad compositional range (Fo from 79 to 89 mol %), as well as in the few analyzed clinopyroxenes. This feature is shared with some weakly evolved CF and SV products (Marianelli *et al.*, 1999; Mangiacapra *et al.*, 2008; unpublished data by the authors), whereas the primitive eruptive products of the neighbouring Procida volcanic field (Fig. 1), although geochemically almost

indistinguishable (e.g. Peccerillo, 2005), are characterized by MgO contents of up to ~12 wt %, as shown by both whole-rocks (D'Antonio *et al.*, 1999a) and MI hosted in highly forsteritic olivine (Fo = 85–90 mol %; Severs, 2007; Esposito *et al.*, 2011; Mormone *et al.*, 2011). If we discard the hypothesized post-entrapment evolution of MI, their low Mg content could be a primary feature resulting from fast growth of the MI-trapping olivine crystals, with consequent relative Mg-enrichment in the host crystal and Mg-depletion in the trapped melt. However, this process should lead to zoned olivines, which have not been observed in the analyzed samples (Table 1; Supplementary Data). Moreover, such a mechanism does not necessarily account for the observed MgO buffering around 3.6 wt % (Fig. 5a), and demands that Mg diffusion in the liquid is slower than the crystal growth. Because diffusion does not occur at a constant rate, it is useful to compare the time needed by diffusion to cover a characteristic diffusion distance with the time required by olivine to grow by the same length.

Following Zhang (2008), we define the diffusion distance as that for which the concentration of MgO in the melt is halfway between the hypothetical compositional extremes. Specifically, the diffusion distance is halfway between the primitive Procida melt composition and the analyzed Ischia MI. We then consider  $x_{\text{mid}} = \gamma(Dt)^{1/2}$ , where  $x_{\text{mid}}$  is the mid-concentration distance,  $D$  is the Mg-diffusion coefficient ( $\sim 10^{-13} \text{ m}^2 \text{ s}^{-2}$  at the temperature of interest; Roselieb & Jambon, 2002),  $\gamma$  takes the value of 0.95 for half-space diffusion, and  $t$  is time. Assuming the size of MI as a diffusion distance ( $x_{\text{mid}} = 100 \mu\text{m}$ ), 110 000 s are needed to reach mid-concentration (i.e. Mg-diffusion is around 100 times faster than olivine growth) by considering a crystal growth rate around  $10^{-11} \text{ m s}^{-1}$  [i.e. comparable with, or even faster than, those of olivines in basalt (Mangan, 1990)]. Assuming a value of  $x_{\text{mid}}$  close to 1 cm [i.e. exceeding the size of the largest Ischia olivines (3–4 mm)], Mg-diffusion and crystal growth yield comparable timescales ( $\sim 30$  years), a condition that still ensures crystal–melt chemical equilibrium. Therefore, we discard the role of competing diffusive processes in the melt and crystal growth in determining the lower MgO content of Ischia MI with respect to those from Procida.

In line with a recent study of Hawaiian magmas (Matzen *et al.*, 2011), we link the low Mg content of the Ischia MI to a high redox state. The Ischia MI provide an excellent example in which divalent and trivalent iron species are abundant in the system and in equimolar proportions, thus appearing as the effective redox couple buffering the oxygen potential of the whole system and imposing the low-Mg conditions for the liquid–olivine equilibrium ( $K_{\text{D}} = 0.3$ ; Roeder & Emslie, 1970). Tests run with the MELTS code (Ghiorso & Sack, 1995) show that an Ischia melt composition with MgO ~4 wt % can

precipitate a forsteritic olivine (Fo = 85 mol %) only at NNO > 3, for a temperature of 1180°C, dissolved H<sub>2</sub>O = 3 wt % and  $P$  set at 3 kbar (roughly in line with our MI results). Under these conditions,  $\text{Fe}^{2+}/\text{Fe}^{3+}$  is ~1. More forsteritic olivine (up to Fo<sub>90</sub>) can be obtained, at (liquidus) temperatures of 1210°C, by further increasing the oxidation state up to NNO  $\approx$  +5. For lower oxygen fugacity, such as NNO, the crystallizing olivine is more fayalitic (Fo = 78 mol %;  $T = 1120^\circ\text{C}$ ). By raising the MgO content of the initial melt to 8–9 wt %, highly forsteritic olivines (Fo ~90 mol %) are at the liquidus for more normal redox conditions (i.e. between QFM and NNO) and for relatively higher temperatures of either 1250°C, if dissolved H<sub>2</sub>O = 3 wt %, or 1270°C, if dissolved H<sub>2</sub>O = 1 wt %. The latter is the case for the most primitive Procida volcanic products, as indicated by (1) the occurrence of H<sub>2</sub>O-poor MI in highly forsteritic olivines (H<sub>2</sub>O < 2 wt %; 85 mol % < Fo < 90 mol %; Severs, 2007; Esposito *et al.*, 2011; Mormone *et al.*, 2011), (2) measured FeO/Fe<sub>2</sub>O<sub>3</sub> ~ 3 (by weight) in whole-rocks (D'Antonio *et al.*, 1999a), and (3) estimated FeO/Fe<sub>2</sub>O<sub>3</sub> ~ 2 (by weight) in MI (Mormone *et al.*, 2011), which requires Fe<sup>2+</sup> being dominant over Fe<sup>3+</sup> to attain the olivine–liquid equilibrium (or  $K_{\text{D}} = 0.3$ ).

Although such high oxidation state conditions challenge the MELTS software limits, these results corroborate the interrelation between an unusually high oxidation state ( $\Delta\text{NNO} > 3$ ), high olivine forsterite contents (85–90 mol %) and low (~4 wt %) MgO contents of the analyzed Ischia MI. Moreover, the high oxidation states predicted here are consistent with recent evidence that sub-arc mantle is 1–4 log units more oxidized than mid-ocean ridge basalt (MORB)- or ocean island basalt (OIB)-source mantle (Evans *et al.*, 2012) and, particularly, with the  $f\text{O}_2$  estimates from Ischia Cr-rich spinel inclusions. Application of the Maurel & Maurel (1982) equation to these samples predicts relative  $f\text{O}_2$  values falling between NNO + 1.5 and NNO + 3.3 for mafic magmas equilibrated with Fo<sub>89</sub> olivines (D'Antonio *et al.*, 2013). The lower  $f\text{O}_2$  value is relative to MI compositions corrected for the effects of post-entrapment crystallization of olivine (re-equilibrated dataset), whereas the second value relates to the original dataset. Also, for the first and most conservative case (NNO + 1.5), Ischia shows the most oxidized source conditions so far recognized for central–southern Italian magmas (Nikogosian & Van Bergen, 2010; D'Antonio *et al.*, 2013).

It is important, however, to note the impossibility of coupling the Cr-spinel data with the whole-rock compositions of Ischia mafic magmas in the frame of the the Maurel & Maurel (1982) equation. Primitive Ischia whole-rocks have FeO<sub>tot</sub>/MgO values lower than the  $(\text{Fe}^{\text{II}}\text{O}/\text{MgO})_{\text{Maurel\&Maurel}}$  melt ratio (0.9 from Cr-spinels hosted in Fo<sub>89</sub> olivines). Therefore, the whole-rocks, probably

because of olivine accumulation, do not have enough iron to be representative of the parental magmas. On the other hand, the MI, with their low MgO and  $\text{FeO}_{\text{tot}}/\text{MgO} > 1 > (\text{Fe}^{\text{II}}\text{O}/\text{MgO})_{\text{Maurel\&Maurel}}$ , can be considered as such.

The large difference in oxidation state between the Ischia and Procida magmas probably results from variations in the amount of water, which is much greater at Ischia (up to 4 wt %) than at Procida (<2 wt %; Severs, 2007; Esposito *et al.*, 2011; Mormone *et al.*, 2011). For temperatures below 1200°C along the geothermal gradient, and in the presence of abundant water, the magma continues evolving along the olivine liquidus by substantially increasing the oxidation state of the system.

Owing to the large proportion of oxygen they carry,  $\text{H}_2\text{O}-\text{CO}_2$  fluids oxidize any magmas that they permeate. On the one hand, recently it has been shown that strong iron oxidation, caused by  $\text{CO}_2$  fluxing, produces a maximum local oxygen fugacity around  $\text{NNO} + 3$  to  $\text{NNO} + 3.5$  (Simakin *et al.*, 2012). On the other hand, the possible role of  $\text{H}_2\text{O}$  as an oxidizing agent in magmas has been explored by Kelley & Cottrell (2009), who showed its efficiency in subduction environments for its enhanced mobility in the fluid phase transferred from the slab. Although the subducting plate is intrinsically at a high oxygen fugacity, and clearly supplies the  $\text{H}_2\text{O}$  flux into the overlying mantle wedge, the mechanism by which the oxidized signature is transferred from the slab is poorly understood. The above researchers have suggested that the relation between Fe oxidation state and magmatic  $\text{H}_2\text{O}$  content at subduction zones may result from the oxidized state of the subducted oceanic lithosphere (e.g. iron in marine sediments is highly oxidized;  $\text{Fe}^{2+}/\text{Fe}^{3+} \sim 0.22$ ). It is likely that supercritical fluids released from the de-volatilizing slab form aqueous complexes of oxidized iron that migrate upwards, transferring their oxidized signature to the resultant mantle wedge melts (e.g. Gaetani & Grove, 2003). Nevertheless, adoption of this model for iron oxidation (Ottonello *et al.*, 2001; Moretti, 2005) shows that for a given  $f\text{O}_2$ , increasing the water fugacity, and hence the water content in the melt, decreases the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio, without the necessity of invoking any transfer of oxidized iron complexes from the de-volatilizing slab (Moretti & Ottonello, 2003; Moretti & Papale, 2004).

Additional evidence for the Ischia high oxidation state is provided by S degassing. In fact, a high oxidation state, well above  $\text{NNO}$ , favours S dissolution in the melt (Moretti & Papale, 2004), retarding its release to late depressurization stages. Based on the available MI data for the Ischia and Procida K-trachybasalts, we have modelled the S behaviour choosing an initial value  $S \sim 1500$  ppm, corresponding to the S content of the deepest MI (hosted

in a  $\text{Fo}_{86}$  olivine; Fig. 9) among those analyzed for S (Table 1). Moreover, a value of 1500 ppm for S content was also measured in the least evolved, most  $\text{CO}_2$ -rich MI from Procida (Esposito *et al.*, 2011; Mormone *et al.*, 2011) and in the least degassed shoshonitic MI from CF (Mangiaccapra *et al.*, 2008). Because of the very high S solubility at high pressure under oxidized conditions, we assumed its initial content to be representative of the total amount in the parental magma and used it to model the different conditions of sulphur release between Procida and Ischia.

Model runs for degassing in the  $\text{CO}_2-\text{H}_2\text{O}-\text{H}_2\text{S}-\text{SO}_2$ -melt system (Moretti & Papale, 2004) for a non-crystallizing magma ascending in closed system, clearly show that under oxidizing conditions (fixed by  $\text{Fe}^{2+}/\text{Fe}^{3+} = 1$ , corresponding to  $\text{NNO} + 3$ ) the system does not degass appreciably, and keeps its initial value of S at 1500 ppm down to a dissolved  $\text{H}_2\text{O}$  content less than 1 wt % or 20 MPa (dashed black curves in Fig. 9a and b, respectively). Conversely, if the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio is around 10 (corresponding to  $\log f\text{O}_2$  around  $\text{NNO}$ ) S degassing takes place immediately, resulting in a complete loss of S at  $\text{H}_2\text{O}$  content less than 1 wt % or in a loss of 400 ppm of S at 300 MPa (dotted black curve in Fig. 9a and b), in response to the lower solubility of S with respect to water under reduced conditions. For an oxygen fugacity corresponding to  $\text{NNO} + 1.5$  (i.e. considering the re-equilibrated MI compositions) S-degassing takes place at around 280–300 MPa (continuous black line in Fig. 9b).

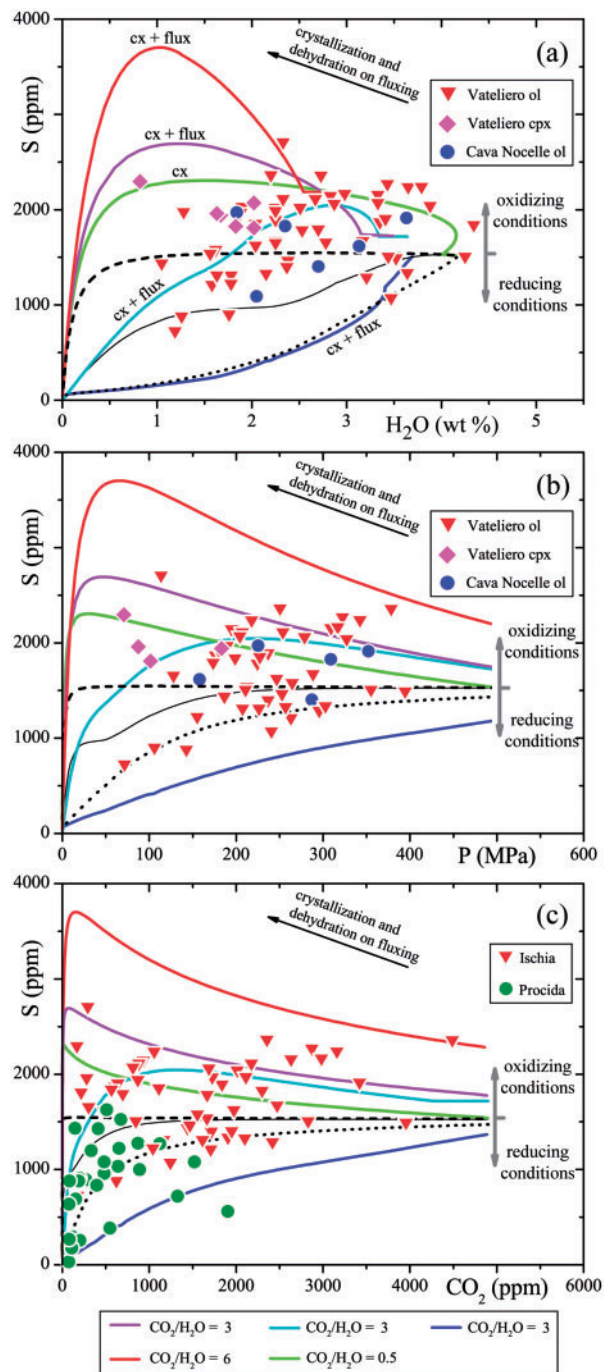
These behaviours well discriminate reduced and oxidized domains in the S vs  $\text{H}_2\text{O}$  and S vs pressure diagrams (Fig. 9a and b), but cannot explain the S-enrichment up to 2300 ppm. Such an enrichment can, however, be accounted for by considering the joint effect of crystallization and fluid fluxing. The amount of fractional crystallization has been evaluated using the Petrograph 2beta code (Petrelli *et al.*, 2005), using the composition of two analysed MI, ICn2 ol5 and Vat A ol6, representative of a primitive and a more evolved Ischia melt, respectively (Table 1). The results suggest that the daughter magma can be derived from the parent magma by subtraction of *c.* 36 wt % of a mineral assemblage dominated by Mg-rich clinopyroxene and Ca-rich plagioclase, with a small amount of K-feldspar, Mg-rich olivine and Ti-magnetite ( $\Sigma r^2 = 0.55$ ; see Supplementary Data for details).

The role of crystallization is then introduced into the modelling by using the following simple linear relationship, which returns 36 wt % of crystallization from 500 MPa to 0.1 MPa:

$$M_{xx}(\text{wt}\%) = -0.07P(\text{MPa}) + 34.9 \quad (4)$$

in which  $M_{xx}$  is the amount of crystallized magma. The value of 500 MPa for the beginning of crystallization is





**Fig. 9.** Effects of crystallization, redox state, fluxing and depressurization on S concentration in multicomponent degassing melts. Dashed, continuous and dotted black curves in (a)–(c) represent closed-system degassing ( $H_2O^{tot} = 4.25$  wt %,  $CO_2^{tot} = 2.1$  wt %,  $S^{tot} = 0.15$  wt %) of the ‘unfluxed’ and non-crystallizing magma ( $Fe^{3+}/\Sigma Fe = 0.5$  for the dashed curve,  $Fe^{3+}/\Sigma Fe = 0.3$  for the continuous curve, calculated by using the composition of the MI corrected for post-entrapment crystallization). The dotted black curve refers to reduced conditions. Bold coloured lines in (a)–(c) account for crystallization, and for different degrees of  $CO_2$  enrichment, given as a mass ratio with respect to  $H_2O$ . Green, magenta and red curves were calculated for  $Fe^{3+}/\Sigma Fe = 0.5$ , varying  $CO_2^{tot}/H_2O^{tot}$  from 0.5 to

close to the largest computed saturation pressure (480 MPa for the re-equilibrated MI dataset). Crystallization alone, without fluxing, generates a degassing curve under closed-system conditions that preserves the initial  $CO_2^{tot}/H_2O^{tot}$  ratio (0.5 by mass), demands initial  $H_2O$  enrichment, and can only partially account for the high S values (higher than 2000 ppm) at low pressure and water contents (turquoise line in Fig. 9a and b). It is also necessary to introduce the effect of fluxing (by adding  $CO_2$  and increasing the  $CO_2^{tot}/H_2O^{tot}$  ratio from 0.5 to three and then to six by mass) to achieve degassing patterns matching the high S points in both diagrams (magenta and red curves in Fig. 9a and b).

A major outcome of our modelling is that only the combination of (1) high oxidation state, (2) crystallization on magma ascent [in terms of simple mass removal based on equation (4)] and (3) fluxing and consequent melt dehydration allows reproduction of the high-S (>2000 ppm)–low- $H_2O$  (<1 wt %) data points. If the system is reduced (Fig. 9a and b), S solubility is so depressed that fluid fluxing ( $CO_2^{tot}/H_2O^{tot} = 3$  by mass) and crystallization (blue curves in Fig. 9a and b) do not reproduce the S enrichment, and melt desulphurization occurs, as for dehydration. The latter is very probably the case for S in the Procida MI (Severs, 2007; Esposito *et al.*, 2011; Mormone *et al.*, 2011), which is much less abundant than in the Ischia MI, at a similar  $CO_2$  content (Fig. 9c). This suggests that S was stripped into the gas phase under much more reduced conditions (Moretti & Papale, 2004).

The alkali variability and the constancy of iron oxidation state, as well as the MgO content of the non-corrected MI compositions, lead us to conclude that the dehydration displayed by the MI is due to  $CO_2$ -fluxing rather than diffusive re-equilibration of water driven by proton diffusion (e.g. Massare *et al.*, 2002; Gaetani *et al.*, 2011). In fact, proton diffusion would alter the  $Fe^{2+}/Fe^{3+}$  ratio, thus producing scattered values. On the other hand, a full-equilibrium scenario allows modelling of all the data, including S loss.

**Fig. 9** Continued

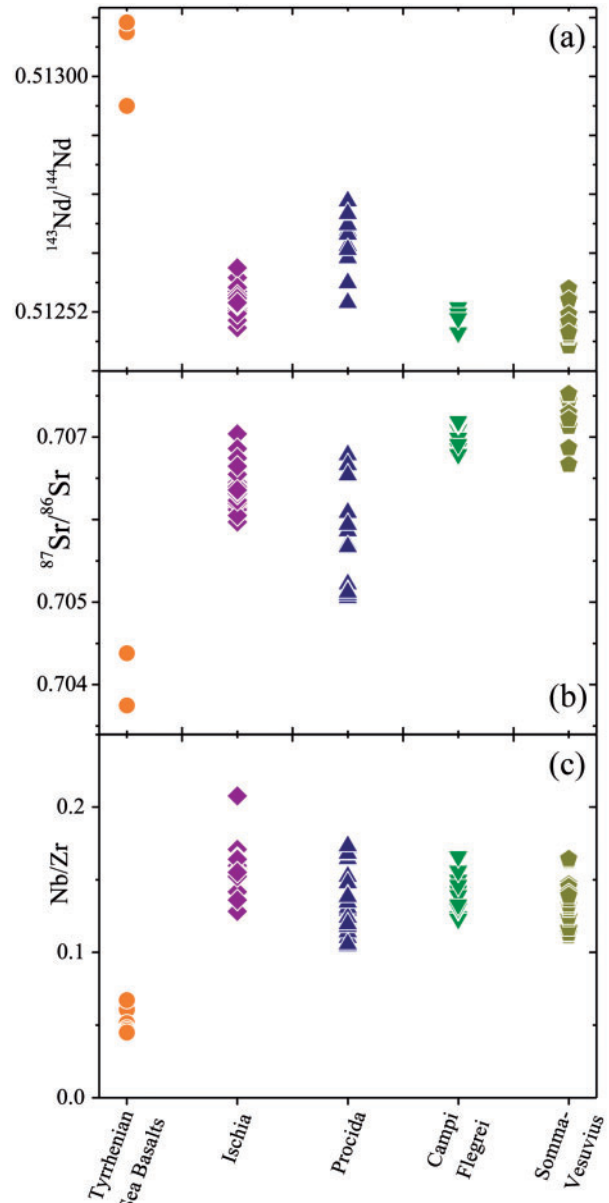
three up to six by mass; the cyan curve is for  $Fe^{3+}/\Sigma Fe = 0.3$  and  $CO_2^{tot}/H_2O^{tot} = 3$  by mass (see Appendix). The dark blue line accounts for crystallization and fluxing ( $CO_2^{tot}/H_2O^{tot} = 3$  by mass) under reduced conditions. (c) illustrates the  $CO_2$  vs S covariation in MI from Ischia (this study) and Procida (Severs, 2007; Esposito *et al.*, 2011; Mormone *et al.*, 2011), starting from a common initial S content of 1500 ppm. Accounting for fluxing + crystallization yields S enrichment only under oxidized conditions (i.e. Ischia); that is, for  $Fe^{3+}/\Sigma Fe \geq 0.3$  (or  $\log fO_2 \geq NNO + 1.5$ ). The higher the oxidation state, the greater the melt enrichment in S. In contrast, reduced conditions (i.e. Procida) do not favour S enrichment, leading to S depletion even at high dissolved  $CO_2$  contents (i.e. pressure). The black arrow in the upper right of (a) is a qualitative vector indicating that coupled crystallization and fluxing of a melt evolving under oxidizing conditions yields strong dehydration and S enrichment).

### Geodynamic relations and the role of ascending CO<sub>2</sub>-dominated fluids in determining magma evolution at Ischia and the other Neapolitan volcanoes

The information provided thus far by the MI data makes the Ischia magmatic plumbing system a natural crustal borehole that can shed light on melt–fluid coexistence conditions, particularly on the presence of a CO<sub>2</sub>-dominated supercritical fluid phase rising from mantle depths. Such knowledge, together with the available data for the other Neapolitan volcanoes, can be used to investigate the relationships between these volcanoes, which all have plumbing systems extending to mantle depths (Peccerillo, 2005).

The Neapolitan volcanoes show striking morpho-structural similarities, highlighted by seismic reflection data (Bruno *et al.*, 2003), magnetic data (Paoletti *et al.*, 2009), and the relationships between the location of eruptive vents and magma compositions (Civetta *et al.*, 1991; D'Antonio *et al.*, 1999b; Piochi *et al.*, 2005; De Astis *et al.*, 2006; Di Renzo *et al.*, 2011). Ischia and CF are located at the intersection of NE–SW- and NW–SE-trending fault systems, and are characterized by large, caldera-forming eruptions and resurgence of the caldera floor, suggesting the presence of large, shallow magma chambers. Both volcanoes mostly extruded differentiated (trachyte–phonolite) magmas during the caldera-forming eruptions through vents located within the caldera floor. Weakly differentiated magmas (shoshonite–latite) have been erupted only by vents located along portions of faults of the NE–SW system, most of which have acted as marginal faults during caldera collapses (e.g. the Arso, Vateliero and Cava Nocelle eruptions at Ischia, and the Minopoli and Fondo Riccio eruptions at CF). Conversely, the Procida volcanic field has erupted relatively small volumes of mainly weakly differentiated magma (K-basalt to shoshonite) through vents aligned along faults of the NW–SE transfer system. Trachytic to phonolitic Plinian and sub-Plinian eruptions, accompanied by summit caldera collapses at SV, are located at the intersection of the NE–SW and NW–SE fault systems, also suggesting the presence of a large, shallow magma chamber.

The geochemical relationships between the parental magmas can be considered in terms of their Sr and Nd isotopic compositions and the high field strength element (HFSE/HFSE) (Nb/Zr) ratio along an idealized transect from the Tyrrhenian Sea [MORB: Ocean Drilling Program (ODP) Leg 107, site 655 on the Gortani Ridge, western Vavilov Basin; Gasperini *et al.*, 2002, and references therein], through Ischia, Procida, CF and SV (Fig. 10). The plotted isotopic and chemical data refer to CF rocks younger than 39 ka (i.e. before the caldera-forming Campanian Ignimbrite eruption; Fisher *et al.*, 1993), and SV rocks older than 22 ka. These were selected because they do not show significant evidence of crustal



**Fig. 10.** Nd (a) and Sr (b) isotope, and Nb/Zr (c) variations along an idealized transect extending from the Tyrrhenian Sea through the Neapolitan volcanoes. Data from Gasperini *et al.* (2002), Pappalardo *et al.* (2002), De Astis *et al.* (2004, 2006), Piochi *et al.* (2004), D'Antonio *et al.* (2007), Di Renzo *et al.* (2007) and Pabst *et al.* (2008).

contamination, unlike the younger products (e.g. Pappalardo *et al.*, 2002; D'Antonio *et al.*, 2007; Di Renzo *et al.*, 2007, 2011). The Ischia magmas are geochemically and isotopically similar to the SV least contaminated magmas older than 22 ka and the CF magmas younger than 39 ka (D'Antonio *et al.*, 2007).

All the Neapolitan volcanoes have a similar geochemical signature (e.g. Nb/Zr ratio), which is different from that of the Tyrrhenian Sea basalts, despite differences in

composition and eruptive style, and variable amounts of crustal assimilation, mixing, and fractional crystallization during their evolution to recent times (e.g. Civetta *et al.*, 1991; Ayuso *et al.*, 1998; Fulignati *et al.*, 1998; Piochi *et al.*, 1999; Gilg *et al.*, 2001; Tonarini *et al.*, 2004; De Astis *et al.*, 2006; D'Antonio *et al.*, 2007; Di Renzo *et al.*, 2007, 2011; Arienzo *et al.*, 2009, 2011; Iacono-Marziano *et al.*, 2009, and references therein).

The geochemical signature of all the Neapolitan volcanoes (Fig. 10) reflects the involvement of either a MORB-type (D'Antonio *et al.*, 2007, and references therein) or an OIB-type mantle source (De Astis *et al.*, 2006, and references therein), partially modified by subducting slab derived fluids and melts.

Procida is located between CF and Ischia (Fig. 1) along a NE–SW strike-slip tectonic feature that approximately follows the dip of the subducting slab. With such a configuration, and contrary to what is observed, a larger involvement of the water-poor, MORB- (or OIB)-type mantle source component would be expected at Ischia rather than Procida, because the former is located at a greater distance from the subducting slab, which dips towards the Tyrrhenian Sea. A possible explanation for such an unexpected result could be in the crystallization of magmas ponding at mid-crustal depths: the larger the extent of crystallization, the higher the degree of water enrichment, as differentiation tends to concentrate the most soluble volatile components. However, this explanation is not supported by the very limited chemical difference between Ischia and Procida MI (Fig. 2a and b). An alternative hypothesis is that the difference in initial H<sub>2</sub>O concentration (~4 wt % at Ischia and <2 wt % at Procida), reaching the highest values at greatest depth (~14 km at Procida and ~18 km at Ischia), indicates a different H<sub>2</sub>O content in the deep slab-derived fluid source. The lower H<sub>2</sub>O/CO<sub>2</sub> ratio in the source below Procida could be related to a larger contribution of a (water-poor) transitional (T)-MORB (or OIB) mantle source component than at Ischia, CF and SV, as supported by the variation of large ion lithophile elements (LILE) relative to HFSE (not shown), and radiogenic isotopes in the products of these volcanic systems (Fig. 10). However, owing to the location of Ischia and CF with respect to Procida, such a hypothesis would need a nearly punctiform slab breakthrough or tear to allow the ascent of the 'pristine' mantle component below Procida. Similarly, changes in H<sub>2</sub>O content related to slab surface temperature (Plank *et al.*, 2009) would demand a very localized peak of temperature, which again would be in contradiction to the relative location of CF, Procida and Ischia with respect to the subducting slab. At subduction zone depths (>100 km; e.g. Chiarabba *et al.*, 2008) these two scenarios seem very unlikely in light of the short Ischia–Procida and Procida–CF distances (<5 km). Moreover, published data (Fig. 10)

reveal that the higher content of magmatic H<sub>2</sub>O at Ischia, CF and SV (up to 4 wt %) with respect to Procida (<2 wt %) (Severs, 2007; Mormone *et al.*, 2011), and the consequent difference in redox state, is reflected in the geochemical signature of the eruptive products. They show an appreciable difference between Procida on the one side and Ischia, CF and SV on the other side. In fact, whereas the HFSE/HFSE ratios (Nb/Zr) are similar for all these volcanoes, pointing to a common pre-subduction mantle, different Sr, Nd, Pb and B isotope ratios (the latter two not shown) for Procida with respect to the other volcanoes require a different mobilization of deep slab-derived fluids in the overriding plate.

We suggest that the heterogeneity of the highly oxidized Campanian mantle source region is due to large volumes of hot, CO<sub>2</sub>-rich, oxidizing fluids coming from subduction slab-derived pelagic sediments (D'Antonio *et al.*, 2013), which can explain the observed variability in the chromium number of olivine-hosted spinels in the Neapolitan volcanic rocks.

The above geochemical features, and the initial water contents, which are lower at Procida than at the other Neapolitan volcanoes, could be related to the areal distribution and interplay between the NW–SE normal faults and the NE–SW transfer faults dissecting the Campanian Plain. Following Doglioni (1996) and Italiano *et al.* (2000), we postulate that the faults affecting the Neapolitan volcanic area are deep lithospheric structures. They permit the ascent of fluids released from the subducted slab that accumulate at the base of the lithosphere. These are mostly tapped beneath Ischia, CF and SV, where the intersecting fault systems generate a particularly high crustal permeability, thus favouring not only ascent of deep fluids or melts but also their horizontal drainage and the formation of large magma chambers (Figs 1 and 11). Crustal dissection also favours accumulation of deep fluids involved in caldera resurgence processes.

The characteristics of the Procida magma feeding system, such as (1) the relatively small amount of H<sub>2</sub>O in the parental melts, (2) isotopic compositions less enriched in radiogenic Sr, Pb and unradiogenic Nd, and (3) modest amounts of magma production, are inferred to be a consequence of the reduced input of deep fluids, owing to the lower crustal permeability compared with that beneath Ischia, CF and SV. Fluid connectivity at Procida is achieved only occasionally, thus preventing long-term crustal storage of magma and fluids, which are directly transferred to the surface along the transfer fault planes, whenever they are characterized by strong vertical permeability. From this perspective, the pressure interval for relatively fast magma ascent at Procida (from 350 MPa to volcanic venting; Mormone *et al.*, 2011) can be taken as a rough measure of the depth reached by the transfer faults (13–14 km). The relatively short residence

time of fluids and melts below Procida (compared with Ischia, CF and SV) owing to such a straight connection from mid-crustal depths to the surface is also supported by the high  $^3\text{He}/^4\text{He}$  values at Procida (around 5 R/Ra; Piochi *et al.*, 2005). In contrast,  $^3\text{He}/^4\text{He}$  values are significantly lower wherever large magma bodies have formed in the crust at the intersection of NE–SW and NW–SE tectonic features, and where there is more pronounced addition of radiogenic He from the crust (Chiodini *et al.*, 2010).

The structural conditions generated by the intersection of the NW–SE normal faults and NE–SW transfer faults below Ischia, CF and SV are suitable for the formation of large magma chambers and large residual crystal mushes (e.g. De Natale *et al.*, 2006; D'Antonio, 2011; see below) in which interaction with deep fluid and new magma batches can explain why the Ischia and CF products record strong mineralogical and isotopic disequilibria (Civetta *et al.*, 1991; Di Renzo *et al.*, 2011).

Another interesting similarity between Ischia, CF and SV is the common occurrence of one or more mid-crustal low-velocity layers, at least 1 km thick (e.g. Auger *et al.*, 2001), lying roughly at the same depth below the volcanoes. The extent of such layers at 8–9 km depth (equivalent to a pressure of  $\sim 200$  MPa) suggests some lateral continuity between the magma storage systems within the Neapolitan volcanic area. This layer is volatile-rich and acts as a valve controlling the upward transfer of magmas and fluids, giving rise to shallower magma chambers that feed both hydrothermal systems and surface eruptions. We speculate that the occurrence of such a mid-crustal magma reservoir may be linked to the widespread  $\text{CO}_2$ -dominated plume rising through the crust (e.g. Chiodini *et al.*, 2004; Frezzotti *et al.*, 2009) and infiltrating the volcanic plumbing systems through the deep lithospheric faults that dissect both crust and mantle on a small scale (Acocella & Funicello, 1999). The occurrence of such lithospheric faults also within the Apennine chain (Italiano *et al.*, 2000; Chiodini *et al.*, 2004, 2010) may suggest efficient drainage of the same deep slab-derived fluids through the crust, enhanced by the presence of  $\text{CO}_2$  (Fig. 11). Not surprisingly, and despite the absence of detectable deep magma bodies, He isotope ratios in the Southern Apennines reach maximum values (5–6 R/Ra) in those areas characterized by the largest  $\text{CO}_2$  emissions (at Mefite d'Ansanto; Chiodini *et al.*, 2010; see also Fig. 11).

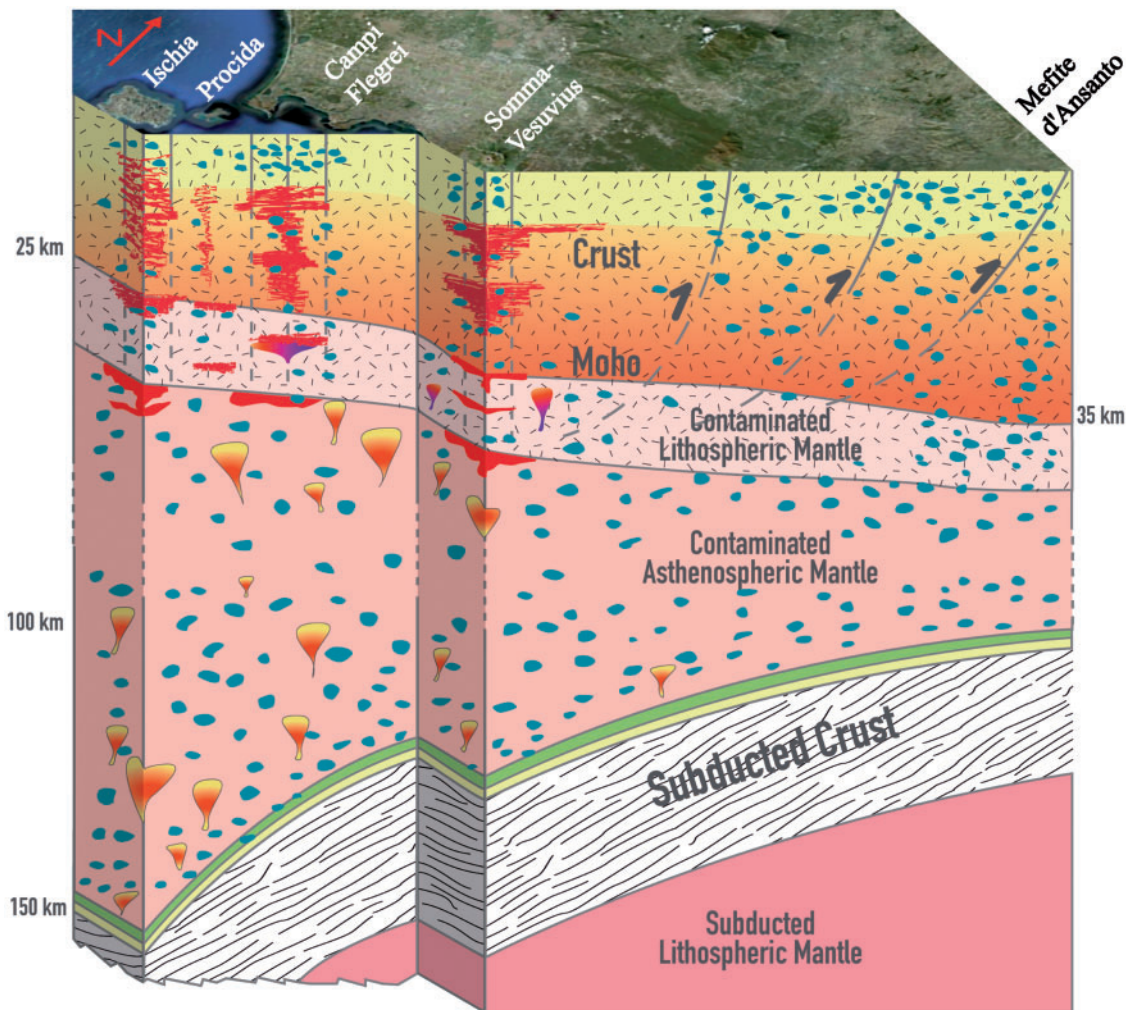
The generation of supercritical fluids owing to deep  $\text{CO}_2$  release is thus an important process within the Neapolitan volcanic region, as evidenced by: (1) widespread and deep-generated diffuse  $\text{CO}_2$  degassing (both at volcanic and non-volcanic sites; Chiodini *et al.*, 2004, 2010; Frezzotti *et al.*, 2009); (2) the occurrence of  $\text{CO}_2$ -rich melts at all the Neapolitan volcanoes (Marianelli *et al.*, 1999, 2005; Severs, 2007; Mangiacapra

*et al.*, 2008; Arienzo *et al.*, 2010); (3) evidence for fluid transfer (fluxing) through the magmatic systems at CF (Villemant, 1988; Mangiacapra *et al.*, 2008; Arienzo *et al.*, 2010), Procida (Mormone *et al.*, 2011) and SV (Ayuso *et al.*, 1998; Quarenì *et al.*, 2007); (4) low P-wave seismic velocity, high seismic attenuation, and high anomalies in P/S wave velocity ratios. These data indicate that magmatic fluids are produced at a depth of about 150 km and stored in the lower crust or uppermost mantle (Chiarabba *et al.*, 2008).

The occurrence of an extensive plume of  $\text{CO}_2$ -dominated fluid, rising from great depth along preferential lithospheric pathways, highlights the important role of fluids in promoting chemical exchange (metasomatism) with the surrounding rocks (including the mantle wedge) and percolated magmas (e.g. Berkesi *et al.*, 2012). Recently, the deep origin of such a gas plume was explained in terms of deep  $\text{CO}_2$ -rich magmas generated by melting of carbonated crustal rocks subducted at  $\sim 150$  km depth, which release  $\text{CO}_2$  because of depressurization on their ascent (Frezzotti *et al.*, 2009). Although we cannot precisely assess the exact origin of the widespread  $\text{CO}_2$  emissions at the surface (e.g. breakdown vs melting of carbonated slab metasediments), we can confidently state that there is strong evidence that breakdown of limestones of marine origin at crustal depths plays only a minor role.

Within the Neapolitan area, Ischia samples the relatively most undisturbed supercritical fluid because interaction with the melt phase occurs under high fluid/melt ratios, as evidenced by both the total volatile content of the magmas (Fig. 7) and the huge discharge of magmatic fluids (Di Napoli *et al.*, 2009, 2011). Additionally, high fluid/melt ratios suggest that at great depths the ascending supercritical fluids may induce melting of existing crystal mushes (e.g. Gaetani & Grove, 2003) and then mobilize small batches of fluid-rich magma, contributing to Sr isotope disequilibrium between early olivine, diopside and glass (e.g. Piochi *et al.*, 1999).

In this context, the mafic magmas erupted at Ischia during the last 10 kyr could represent magma batches formed under hydrous and oxidized conditions by melting of a mush compositionally akin to the Procida mafic rocks. Iron is the most abundant multiple valence element within the magma mush system, and during fluid-induced melting it would buffer the redox state at  $\text{Fe}^{2+}/\text{Fe}^{3+} \sim 1$  for the whole range of olivine compositions (from  $\text{Fo}_{79}$  to  $\text{Fo}_{89}$ ) and non-corrected melt inclusion compositions (e.g. Giggenbach, 1996). This allows extraction from the mush of only the little Mg-content needed to achieve equilibrium with highly forsteritic olivine and would explain the occurrence of Mg-depleted and Mg-rich (MgO up to 12 wt %; Severs, 2007) MI within early crystallizing olivines ( $\text{Fo} > 80$  mol %) from closely spaced, or even the same, magmatic reservoirs, such as those feeding the Ischia and



**Fig. 11.** Schematic cross-section of the asthenosphere and lithosphere below the Neapolitan volcanoes showing the relationships between the magmatic plumbing systems, the regional tectonic regime and the deep subduction system. A widely and uniformly degassing layer at the top of the subducting slab (down to ~150 km depth beneath the Neapolitan volcanoes; Chiarabba *et al.*, 2008), related to the breakdown of  $\text{CO}_2\text{-H}_2\text{O}$ -bearing terrigenous and/or pelagic metasediments, supplies volatiles to the overlying asthenosphere and lithosphere, which are both contaminated by the ascent of supercritical fluids and melts. The asthenosphere is uniformly affected by exchange with the rising fluids. In contrast, the nearly 50 km thick lithosphere is contaminated by rising fluids along preferential paths coincident with the NE–SW transfer and NW–SE normal fault systems. In the Neapolitan region most of the magma transfer and accumulation occurs at the intersections between these two fault systems (Ischia, Phlegraean Fields and Somma–Vesuvius), whereas volcanic centres such as Procida that developed on top of the transfer fault system experience much less magma production. Traces of the NW–SE normal fault systems correspond to vertical shaded planes, whereas the NE–SW transfer fault systems are in the plane of the paper. Deep  $\text{CO}_2$ -rich fluids (but not magmas) also rise to the surface in the compressional setting of the Apennine chain (Fig. 1) along one such plane. (See text for further details.)

Procida volcanism. Moreover, mush remelting could generate Ca-rich MI but not the low  $\text{CaO}/\text{Al}_2\text{O}_3$  (~0.6) MI trapped in  $\text{Fo} > 87$  olivines (e.g. I Cn2.7; Table 1), which alternatively could be explained by infiltration of residual melts not in equilibrium with their hosts.

A similar situation can be expected at CF and SV, where voluminous crystal mushes at depth have been suggested (De Natale *et al.*, 2006; D'Antonio, 2011), and mineralogical and isotopic disequilibria in the erupted magmas have been demonstrated (e.g. Di Renzo *et al.*, 2011, and references therein). Therefore, melting of crystal mushes by

reactive porous fluid fluxing (e.g. Gaetani & Grove, 2003), and consequent magma chamber reactivation, is here suggested as much more likely than pure mantle diapirism.

## CONCLUSIONS

This study has shown that an exsolved  $\text{CO}_2$ -rich gas phase coexists with Ischia magmas throughout the crust, at least in the upper 18 km. The emerging picture highlights a composite system with magma stored at variable depths that can experience both nearly isobaric degassing upon

crystallization (decrease of the  $\text{CO}_2/\text{H}_2\text{O}$  ratio) and crystallization upon dehydration (increase of the  $\text{CO}_2/\text{H}_2\text{O}$  ratio) owing to fluxing from deep crustal or even mantle depths. The occurrence of a fluxing phase, already identified at CF (Mangiacapra *et al.*, 2008; Arienzo *et al.*, 2010), explains the relatively low magma production compared with magmatic fluid discharge, especially if considering the potential role that fluid infiltration may play in remelting resident crystal mushes.

The mid-crustal 200–250 MPa fluid saturation zone (8–10 km depth) in the Ischia vertically extended magmatic plumbing system (3–18 km depth) provides evidence for a major region of magma stagnation and gas fluxing similar to CF (Mangiacapra *et al.*, 2008; Zollo *et al.*, 2008) and SV (Auger *et al.*, 2001). The occurrence of such a mid-crustal magma layer below the active Neapolitan volcanoes is rather surprising, but suggests a causal link common to the entire Neapolitan volcanic region. Such a causal mechanism involves the interplay between regional structures (NW–SE normal and NE–SW transfer faults) and a widespread deep volatile source, derived from subducting metasediments. The hypothesis that the Neapolitan magmatism and volcanism are sustained by  $\text{CO}_2$ -dominated supercritical fluids is corroborated by several lines of evidence, such as the widespread diffuse  $\text{CO}_2$ -rich gas emissions detected at the surface, seismic features compatible with deep (150 km) slab devolatilization and fluid accumulation in the mantle wedge, the occurrence of  $\text{CO}_2$ -rich melts, fluid fluxing through the magmatic systems, and metasomatic fluid release from subduction zone depths.

The efficiency of this deep fluid transfer from the subducting slab upwards varies according to the permeability of the overlying lithosphere. Permeability increases in those sectors in which NW–SE normal and NE–SW transfer fault systems intersect (Ischia, CF, and SV). Consequently, the different connectivity that can be established from subduction zone depths upwards also explains the variability in both  $\text{H}_2\text{O}$  content measured in the deep magmas (up to 4 wt % at SV, CF and Ischia and <2 wt % at Procida) and magma production rates. Intersection of NW–SE and NE–SW structures and consequent dissection of the lithosphere promotes variable ascent of subduction fluids contaminating the mantle wedge, hence offering a key to explain the geochemical similarities and differences between Procida, Ischia, CF and SV, and, particularly, the major variations in redox state that profoundly affect the chemistry (e.g. Mg content) of the magmas beneath the Neapolitan volcanic area.

The demonstration of a common volatile source component for the Neapolitan volcanism contributes to our understanding of the basic process of magma production at mantle depths and the transfer of these magmas to shallow levels where they differentiate, mix and mingle in magma

chambers necessarily supersaturated in volatiles. Shedding light on the mechanisms that transfer magma and fluids from deeper to shallower levels of the magmatic plumbing systems improves our ability to understand the causes and dynamics of episodes of unrest taking place in one of the most densely populated volcanic areas of the world.

## ACKNOWLEDGEMENTS

The authors warmly thank Francesca Di Laura and the graphical laboratory (INGV-Roma) for graphic rendition of Fig. 11, Andrea Cavallo (INGV, Roma) for providing valuable technical support during microprobe analyses, and Antonio Carandente (INGV-OV) for his technical support with FTIR analyses. R.M. thanks Monica Piochi for helpful discussions on Ischia and Procida magmatism. Constructive reviews by Nicole Metrich, Jake Lowenstern and an anonymous reviewer helped us to improve the paper substantially.

## FUNDING

The work was carried out with the financial support of INGV-DPC (2004–2006 V3.2 project ‘Ischia’), PRIN-MIUR 2008 and PRIN-MIUR 2009 projects.

## SUPPLEMENTARY DATA

Supplementary data for this paper are available at *Journal of Petrology* online.

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