



Letter

New insights into the Aeolian Islands and other arc source compositions from high-precision olivine chemistry



Denis Zamboni^{a,b}, Jarek Trela^a, Esteban Gazel^{a,*}, Alexander V. Sobolev^{c,d}, Claudia Cannatelli^e, Federico Lucchi^f, Valentina G. Batanova^{c,d}, Benedetto De Vivo^b

^a Department of Geosciences, Virginia Tech, Blacksburg, VA, USA

^b Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli Federico II, Napoli, Italy

^c ISTerre, UMR 5275, CNRS, Université Grenoble Alpes, Grenoble, France

^d Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, Moscow, Russia

^e Department of Geology and Andean Geothermal Centre of Excellence (CEGA), Universidad de Chile, Santiago, Chile

^f Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Alma Mater Studiorum, Università di Bologna, Bologna, Italy

ARTICLE INFO

Article history:

Received 4 August 2016

Accepted 3 December 2016

Available online 15 December 2016

Keywords:

Mantle source

Olivine chemistry

Arc magmas

Aeolian arc

Melt oxidation state

ABSTRACT

The Aeolian arc (Italy) is characterized by some of the strongest along-the-arc geochemical variations in the planet, making it an ideal location to study the effect of subducting components in modifying the mantle source of island arc melts. Here, we use high-precision element concentrations in primitive phenocrystic olivine from basalts along the arc to elucidate the effects of mantle source modification by the subduction process. Olivines from this arc have Ni concentrations and Fe/Mn ratios that show similarity to peridotite sources that melted to produce mid-ocean ridge basalts. Nevertheless, they also have systematically lower Ca concentrations and Fe/Mn ratios that broadly overlap with olivines from the available global arc array. These phenocrysts also do not show significant variations in Ca as a function of olivine forsterite content. The global data suggest that all olivines crystallizing from island-arc melts have suppressed Ca concentrations and Fe/Mn ratios, relative to olivines derived from melts at intraplate and mid-ocean ridge settings suggesting elevated H₂O concentrations and higher oxidation state of the equilibrium melts. Based on olivine chemistry, we interpret a predominantly peridotite source (fluxed by subduction fluids) beneath the Aeolian Arc and also for other examples of arc-related lavas.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The physical and chemical evolution of the Earth is closely linked to the recycling of crustal materials and elements into subduction zones at convergent plate margins (Hofmann, 1997; Plank and Langmuir, 1993; Rudnick, 1995; Ryan and Chauvel, 2014; Zindler and Hart, 1986). The subducting slab at convergent plate boundaries undergoes metamorphic processes and introduces crustal materials, volatiles, and fluids (aqueous fluids, hydrous melts, or supercritical liquids) back into the mantle (e.g., Grove et al., 2012), resulting in a heterogeneous upper mantle. Although subduction processes generate geochemical heterogeneities in the mantle, the chemical relationship between erupted island arc basalts and subducted materials in the mantle wedge requires further evaluation. The Aeolian Islands (Italy) stand as a singular volcanic arc to study this link, as the lavas record some of the most extreme geochemical variations along-the-arc (see a comprehensive synthesis in Lucchi et al., 2013c).

Several geochemical studies (e.g., Francalanci et al., 2007; Peccerillo et al., 2013; Zamboni et al., 2016) suggested that the geochemical

variations of the mafic rocks along the arc reflect modification of the mantle wedge by subducting components. For example, the well-known negative correlation between ⁸⁷Sr/⁸⁶Sr (0.7034–0.7075) and ¹⁴³Nd/¹⁴⁴Nd (0.5129–0.5124) isotope ratios from west to east along the Aeolian Island Arc in a distance of less than 100 km is attributed to increasing metasomatism by subducting components (fluid and melt) along with local crustal contamination processes (e.g., anatexis in the source of Lipari, Di Martino et al., 2010, 2011). The study by Zamboni et al. (2016) used B and other fluid mobile elements (e.g., As, Li) coupled with melt mobile elements (i.e., Be) to distinguish the contributions of the subducting components along the Aeolian Arc system, and provided evidence for the presence of hydrous fluid components along the arc and the existence of a metasomatic melt component in the peripheral islands (Alicudi and Stromboli).

Our study aims to elucidate the effect of hydrous fluids and slab-melts in the mantle wedge with evidence beyond whole rock geochemistry. Olivine is the most abundant mineral in the upper mantle and is the first to crystallize from a basaltic melt, thus providing critical information on primary magma compositions. The investigation of trace element compositions (e.g., Ni, Mn, Ca, Cr, Ti; in abundances from 10s to 1000s of ppm) in olivine is a useful tool to infer the lithology of the mantle source (De Hoog et al., 2010; Sobolev et al., 2007). These trace

* Corresponding author.

E-mail address: egazel@vt.edu (E. Gazel).

element systematics have been previously used to discriminate between peridotite and pyroxenite sources (Barker et al., 2014; Gurenko et al., 2009a, 2009b, 2013; Herzberg, 2011; Herzberg et al., 2014; Søager et al., 2015; Sobolev et al., 2005, 2007). Olivines that crystallize from pyroxenite-derived melts record high Ni, low Ca, and high Fe/Mn and the partitioning of these elements is largely controlled by clinopyroxene and garnet in the source (Sobolev et al., 2005, 2007). Olivines interpreted to have crystallized from peridotite derived melts, e.g., mid-ocean ridge basalts (MORB), record lower Ni, higher Ca, and lower Fe/Mn relative to olivine crystallizing from pyroxenite sourced melts due to the effect of residual olivine in the source. These studies rely on the compositional control of Ni partitioning between olivine and melt. However, some studies show that the partition coefficient of Ni ($D_{Ni}^{ol/melt}$) in olivine depends also on temperature and olivines crystallizing at low pressures and temperatures from the melt originally in equilibrium with normal mantle olivine at high pressures and temperatures will have elevated Ni contents without the involvement of an olivine-free (pyroxenite) source (Li and Ripley, 2010; Matzen et al., 2013; Putirka et al., 2011). Recent experimental studies by Mallik and Dasgupta (2012, 2013, 2014) described elevated Fe/Mn ratios in melts obtained by mixtures of eclogite and peridotite derived melts in equilibrium with residues characterized by lower olivine modal abundance than in peridotite, but not necessarily olivine-free, as Mn content is also controlled by garnet in the source. Finally, oxidized melts, as commonly produced in arc settings, could crystallize olivine with significantly lower Fe/Mn in olivine as Fe^{3+} is less compatible in olivine than Fe^{2+} (Krivolutskaya et al., 2012).

The few available studies on subduction related rocks (Foley et al., 2013; Prelević et al., 2013; Straub et al., 2008) reported olivines with high Ni content and associated this characteristic to a source that

contains an olivine-free assemblage. It is imperative to distinguish between multiple source lithologies beneath the Aeolian Islands in order to characterize the subduction inputs involved in the magma genesis of this area. Here, we adopt a high-precision olivine chemistry approach (Batanova et al., 2015; Herzberg et al., 2014; Sobolev et al., 2005, 2007).

2. Geologic setting

The collision between the African and Eurasian plates and the related geodynamic evolution of the Mediterranean area is responsible for shaping the present day volcanic and tectonic setting of the Italian region. The Aeolian Islands originated during the steep northwestern subduction of the Ionian Plate beneath the Calabrian orogenic arc and the plate's rollback toward southeast (Chiarabba et al., 2008; Gvirtzman and Nur, 2001). The archipelago consists of seven volcanic islands (Alicudi, Filicudi, Salina, Lipari, Vulcano, Panarea, and Stromboli) and several seamounts (i.e., Palinuro, Marsili) inside and around the Marsili back-arc basin (Fig. 1). The arc is subdivided into the western, central and eastern sectors based on structural, geochemical, and volcanological criteria (e.g., De Astis et al., 2003). Presently, the western area (Alicudi and Filicudi) is not considered volcanically active while young eruptions occur on Vulcano (central segment) and Stromboli (eastern segment). The Aeolian subaerial activity is geologically recent (250–270 ka, Lucchi et al., 2013a, 2013b; Forni et al., 2013) and is characterized by mafic volcanic rocks having calc-alkaline through potassic compositions with extreme variations in trace elements and in radiogenic isotope signatures (e.g., Peccerillo et al., 2013). The highest Nd isotopic (0.512894) and lowest Sr (0.703433) contents characterize the most primitive basalts in the archipelago on the island of Alicudi, with ratios similar to Etna lavas (e.g., Peccerillo et al., 2004). In contrast,

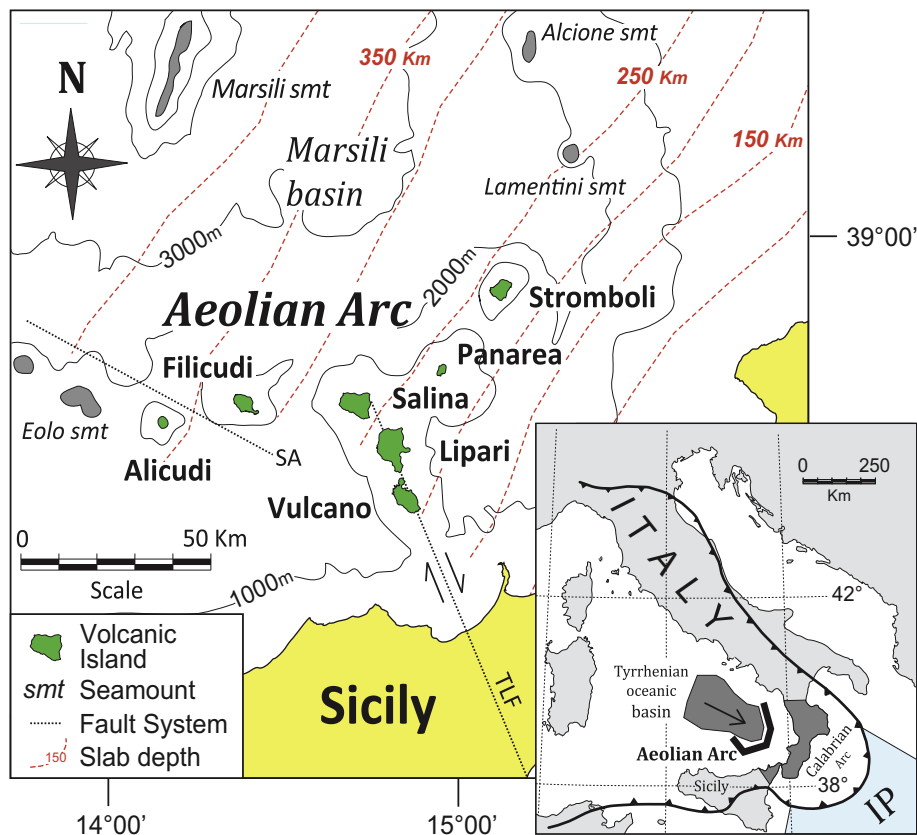


Fig. 1. Scheme of the Apennine-Maghrebi fold-and-thrust belt (barbed lines) of the central Mediterranean region, representing the actual evolution of the Southern Tyrrhenian Sea-Calabrian arc region (after Ventura, 2013), and the geomorphology and bathymetric setting of the Aeolian Islands together with surrounding seamounts (modified from Zamboni et al. (2016)). The red dashed lines represent the depth contours of the Wadati-Benioff zone from Faccenna et al. (2011). Abbreviations: IP = Ionian Plate; SA = Sisisfo-Alicudi Fault System; Smt = seamount; TLF = Tindari-Letojanni Fault System.

these values systematically change, moving toward the eastern sector, in which Stromboli's rocks display the highest $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic content (0.707550) and the lower $^{143}\text{Nd}/^{144}\text{Nd}$ value (0.512460), resembling Vesuvius lavas (e.g., Peccerillo, 2001).

3. Materials and methods

We collected mafic samples ($\text{MgO} > 8 \text{ wt\%}$) on the islands of Alicudi, Filicudi, Salina, and Stromboli based on studies that suggested that the units collected are not only the most mafic but, do not show strong evidence for crustal contamination (with the possible exception being Alicudi) (e.g., Francalanci et al., 2013; Lucchi et al., 2013a; Lucchi et al., 2013b; Lucchi et al., 2013d). For additional geologic background, Lucchi et al. (2013c) presented a comprehensive geologic description and history of the Aeolian Islands and the units selected for this study. Sample location coordinates and whole rock major and trace element chemical compositions are provided in Zamboni et al. (2016). For Stromboli, we collected olivine from both the calc-alkaline and the potassic lavas. We processed the samples in the geochemistry laboratory at the Department of Geosciences at Virginia Tech. Olivine phenocrysts were handpicked from the most mafic units, mounted in epoxy, and hand-polished with diamond suspensions. The polished epoxy disks were then carbon coated with a 20 nm film using a Q150TE high-vacuum carbon coater. We performed high precision major (Si, Fe, Mg), minor and trace (Ni, Mn, Ca, Al, Cr, Co, Ti, Zn, P and Na) element analyses on the olivine phenocrysts using the JEOL JXA-8230 Superprobe at the Institute des Sciences de la Terre (ISTerre), University Joseph Fourier, Grenoble, France.

Samples were analyzed using the method described by Batanova et al. (2015) with an accelerating voltage at 25 keV and a beam current of 900 nA. Major elements were analyzed with an ED spectrometer with element count times of 500 s for Si, Fe, and Mg. Minor and trace elements were analyzed by WD spectrometer. Element counts were as follows: 160 s for Na, 180 s for Al, 160 s for Co, 180 s for Zn, 180 s for Ca, 160 s for P, 180 s for Ti, 90 s for Cr, 160 s for Mn, and 80 s for Ni. The San Carlos olivine standard (USNM111312-44, Jarosewich et al., 1980) was analyzed as an unknown 3 times every 30 measurements in order to monitor potential instrumental drift and to estimate accuracy and precision. The results yield precision better than 10 ppm (2 standard errors) for trace elements and 0.06 wt% (2 standard errors) for Fo content of San Carlos olivine analyses. A detailed discussion on the EMPA protocol can be found in Batanova et al. (2015). Standards and statistics for the olivine analyses are given in Table 1 in Supplementary Materials.

4. Results

The new high precision major and trace element compositions in olivines from our Aeolian basaltic samples are reported in Table 1 of Supplementary Materials. We conducted 133 high precision olivine analyses for Alicudi, 92 for Filicudi, 183 for Salina, and 105 for Stromboli. The peripheral islands (Stromboli, Alicudi) are characterized by higher forsteritic content (high Mg-number) than the central sector of the arc (Fig. 2). The Mg-numbers of olivines from Alicudi are the highest with 92.21, while Stromboli reaches values up to 90.77. It is noteworthy to mention the low and constant Mg-numbers for the olivine representing the potassic rock series (67.87–75.88). Olivines from Filicudi reach a maximum value of 86.84, while those from the central sector (Salina) have Mg-numbers as high as 87.55.

Olivines from the peripheral islands are characterized by higher Ni contents with respect to those from the central sector (Fig. 3A). Olivines from Alicudi have the highest Ni values in the arc (maximum of 3243 ppm), followed by Stromboli calc-alkaline-derived olivines with ~2604 ppm. In contrast, olivines from Filicudi and Salina are characterized by lower Ni contents (1046 and 2232 ppm, respectively). Olivines from all the islands have Fe/Mn ratios of ~60, with the exception of a

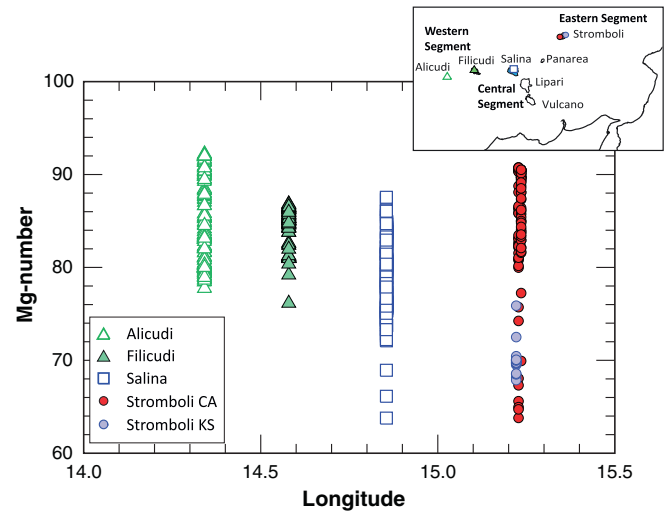


Fig. 2. Variation of olivine Mg-numbers from the most mafic rocks along the Aeolian Islands. The island of Alicudi is characterized by the highest Mg-number of 92.21. Mg-number is defined as $100 \times \text{MgO} / (\text{MgO} + \text{FeO})$. Alicudi, Filicudi, Salina, and Stromboli are color-coded.

small subgroup from Alicudi, that displays elevated values up to 74. Calcium concentrations display two populations of crystals in Alicudi for forsteritic olivine (Mg number ~90), with one population reaching almost 2000 ppm and the other characterized by values less than 1000 ppm (Fig. 3C). The majority of the olivines from the other islands display Ca concentrations in the range between 1000 and 2000 ppm. Olivines from the potassic rock of Stromboli range between 2000 and 2500 ppm Ca, with a maximum of 2369 ppm.

5. Discussion and conclusions

We used the minor and trace element geochemical compositions of olivines from the most primitive erupted magmas along the Aeolian Arc to distinguish which source lithology (peridotite or olivine-free “pyroxenite”) melted to produce the observed arc basalts (Herzberg, 2011; Sobolev et al., 2005, 2007). We present our data with olivine derived from primary magmas modeled from an ~anhydrous peridotitic source (e.g. MORB) and schematic trends for the liquid lines of descent (LLD) of olivine and the cotectic fractionation olivine + clinopyroxene (ol + cpx), as described in Herzberg (2011). Nickel contents in most of the Aeolian olivines (Fig. 3A) match the olivine LLD modeled from melts derived from a peridotite source or are even more depleted in Ni. The Fe/Mn ratios of most Aeolian olivines are the same or lower than predicted for olivine from peridotite sourced parental melts (Fig. 3B). These together imply for the dominant role of peridotitic source for the studied Aeolian magmas. The only exception is the high-Ni olivine subgroup from Alicudi that can't be explained by simple fractional crystallization (Figs. 3 and 4). This subgroup of olivines is characteristically higher in Ni, Fe/Mn, and lower in Ca than olivines from the other Aeolian Island olivines and is indicative of a crystallization from a source that includes a pyroxenite component. These two groups also show distinct Ti crystallization trends, inconsistent with derivation from the same source. The high-Ni olivines are markedly lower in Ti (less than 50 ppm) than the low-Ni olivine group that display elevated Ti contents (up to 73 ppm). The low Ti concentrations in the high-Ni olivine could reflect the sequestration of Ti by rutile in a pyroxenite source. The elevated Ni contents in olivine subgroup from Alicudi are unlikely to be explained by temperature dependence of Ni partition between olivine and melt (e.g. Li and Ripley, 2010; Matzen et al., 2013; Putirka et al., 2011) because these are arc magmas that are not particularly hot compared to other geologic environments such as intraplate plume-related magmatism.

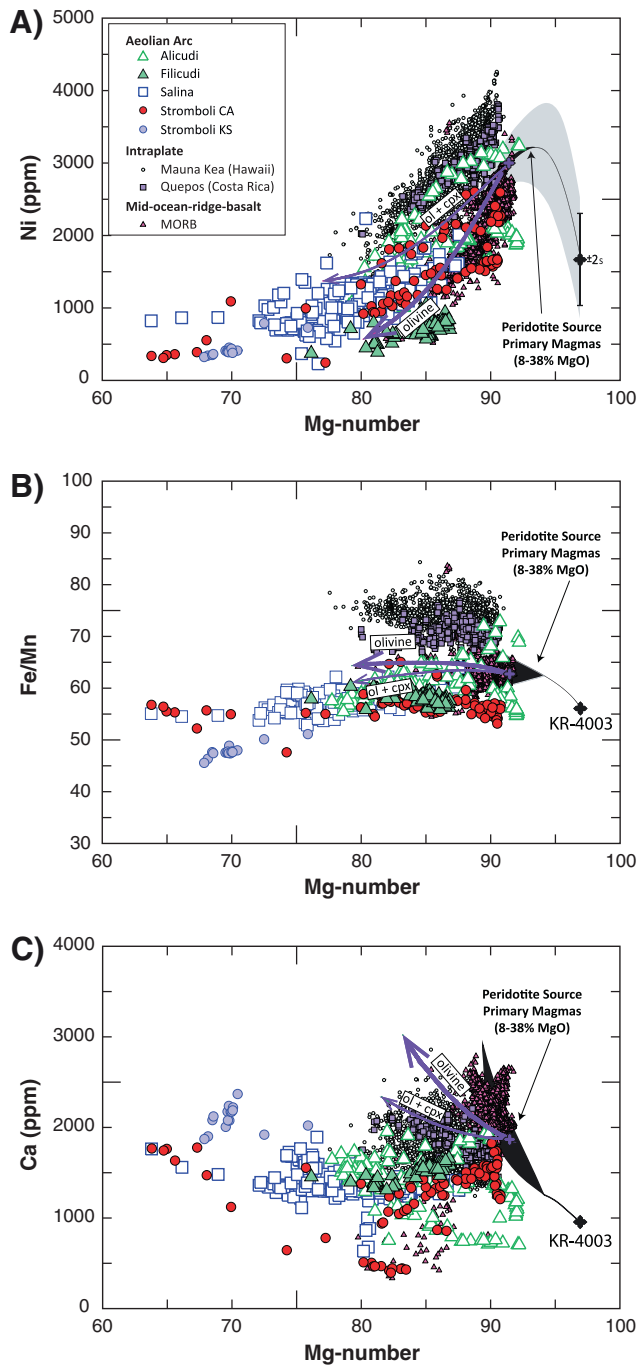


Fig. 3. Mg-number versus Ni (A), Fe/Mn (B), and Ca (C) for Aeolian Islands olivines compared to peridotite source derived olivines (MORB, Sobolev et al., 2007) and pyroxenite source derived olivines (Mauna Kea, Sobolev et al., 2007; Quepos, Trela et al., 2015). Schematic liquid lines of descent for derivative melts from fertile peridotite KR-4003 are shown for olivine (thick purple line) and cotectic crystallization of olivine + clinopyroxene (thin purple line).

The olivine Ni data from the Stromboli calc-alkaline series also display two distinct trends (Fig. 3A). Nevertheless, in this case they can be explained by a higher Ni trend (at a given Mg#) that resulted from earlier ol + cpx cotectic crystallization, relative to the low-Ni trend. This may reflect higher crystallization pressures that would initiate early cpx fractionation. Fe/Mn values in the Aeolian olivines are even markedly lower than estimated for peridotite-sourced magmas (Fig. 3B). This could exclude a significant role of pyroxenitic lithologies

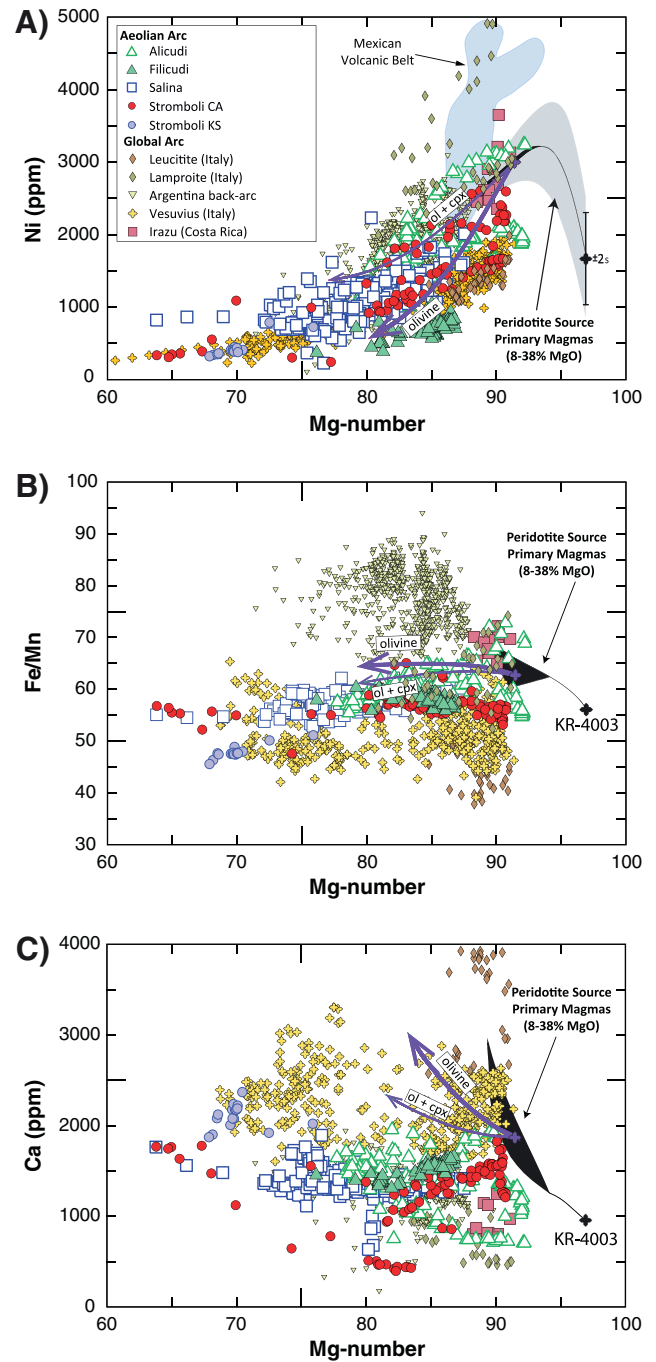


Fig. 4. Plots of Mg-numbers versus Ni (A), Fe/Mn (B), and Ca (C) for subduction related olivines. Data from Aeolian Islands (this study), Irazu (Ruprecht and Plank, 2013), Vesuvius (Redi, 2014, PhD thesis), Argentina back-arc (Søager et al., 2015), and leucite-lamproite (Ammannati et al., 2016). Irazu olivines represent averages of the most forsteritic points (Mg-number > 88) of each sample traverse core to rim.

in the sources, but most likely it reflects the oxidized conditions for the crystallizing magmas (Krivolutskaya et al., 2012).

Calcium contents in Aeolian olivines are lower than expected for olivines crystallizing from an anhydrous peridotite source (Fig. 3C). This may result from an alternative peridotite source hydrated by subduction fluids. Experimental data show that the main effect of H₂O on the partitioning behavior of Ca between olivine and melt is to decrease the partition coefficient ($D_{Ca}^{ol/melt}$), as $D_{Ca}^{ol/melt}$ is a function of olivine Mg-number, and suppressed with increasing H₂O (Feig et al., 2006; Gavrilenko et al., 2016). This effect is mostly observed in olivines with depleted Ca concentrations, relative to those crystallizing from a

nominally anhydrous source, e.g., MORB. The represented olivine liquid lines of descent (LLD) and the corresponding peridotite source (Herzberg, 2011) were modeled for anhydrous magmas. We note that H_2O is not considered to have a great effect on $D_{Ni}^{ol/melt}$ and $D_{Fe/Mn}^{ol/melt}$. Volcanic arcs commonly contain high H_2O contents, on average ~4 wt% (Plank et al., 2013), thus the water effect on Ca partitioning requires further evaluation. In the case of the Aeolian Islands, water contents from olivine (Fo 88–91) hosted melt inclusions range 2–4 wt% for Vulcano (Clocchiatti et al., 1994; Gioncada et al., 1998) and 2–3 wt% for Alicudi (Sorbadere et al., 2012), while for Stromboli olivine (Fo 83–89) hosted melt inclusions contain 2–4 wt% of H_2O (Métrich et al., 2001, 2010).

We first compared our Aeolian Islands high precision olivine data with olivine compositions from different mid-ocean ridge and intraplate volcanic settings derived from pyroxenite, peridotite, or a mixture of the two sources. The Aeolian olivines partially overlap with MORB olivines that are consistent with peridotite source melting (Herzberg, 2011; Sobolev et al., 2007). Only very few high-Ni samples from Alicudi overlap with the intraplate olivines (Fig. 3A). This can be seen in Fig. 3B where several high forsteritic samples of Alicudi with high Fe/Mn ratios overlap with intraplate olivines. In contrast, the low Ca contents are not consistent with either an anhydrous pyroxenite or peridotite source. We suggest that the differences between the Aeolian olivine compositions and the intraplate olivine data (characterized by high Ni and low Mn and Ca) are due to the different origins of the respective melts. For example, both Mauna Kea and Quepos (accreted Galapagos track in Costa Rica) olivines were interpreted as crystallizing from pyroxenite-derived primary magmas (Sobolev et al., 2007; Trela et al., 2015).

Because of the dominant effect of water on the partitioning behavior of Ca in olivine, it is necessary to compare and contrast our Aeolian olivine data with the limited available high-precision olivine data from arc settings (Fig. 4). In the Ni vs. Mg# systematic (Fig. 4A) we observe that the Irazu (Costa Rica) and Argentinian back-arc olivines only, though overlap with the few relatively high Ni Alicudi's data. Vesuvius olivines plot near the Aeolian data, though exhibit trends lower in Ni and Fe/Mn and higher Ca at any given Mg# (Fig. 4A–C). These trends are also observed in most suprasubduction-related olivines and are thought to result from the more oxidized mantle wedge compared with intraplate mantle sources (e.g., Krivolutskaia et al., 2012) implying that the use of olivine Fe/Mn from magmas produced in arc-related settings should be interpreted with caution as a source lithological discriminator, by always considering the internal consistency with Ni and other trace elements. The Argentinian data (Søager et al., 2015) are characterized by high Fe/Mn ratios (Fig. 4B) that exceed the modeled bound of 70 for observed olivines of a peridotite source provenance (Herzberg, 2011), indicating a pyroxenitic source mixing with a peridotitic metasomatized mantle by fluids (Søager et al., 2015). Irazu olivines (Fo > 88) also display slightly higher Fe/Mn values and Ni, suggesting the need of a pyroxenitic component in the generation of these lavas (Fig. 4A). In terms of Ca contents, the Irazu and Argentinian olivines are similarly low than the Aeolian Islands ones (Fig. 5C). This observation can be readily explained by the influence of H_2O on the partitioning of Ca (Behrens and Schulze, 2000; Gavrilenco et al., 2016), as mentioned before, and supports a fluid fluxed source for the Aeolian lavas, as well as for Irazu and Argentina back-arc examples. In contrast, Vesuvius olivines are characterized by higher Ca contents (>2000 ppm), similar to data from the leucites and lamproites found in Italy, (Ammannati et al., 2016) and interpreted as a carbonated source. This source is probably related to metasomatism of the mantle wedge through melting of subducted carbonated pelites and/or reactions with the carbonates in the crust (Ammannati et al., 2016; Dallai et al., 2011; Jolis et al., 2013).

In order to evaluate global trends and minimize the effect of crystal fractionation, we filtered the available global olivines database to obtain primitive compositions, selecting Mg-numbers >87. In Fig. 5A and B we represent data as averages (1 standard deviation) and plot Mn/Fe ratios against parameters useful to emphasize differences in source lithology and geodynamic settings (Sobolev et al., 2007). Fig. 5A

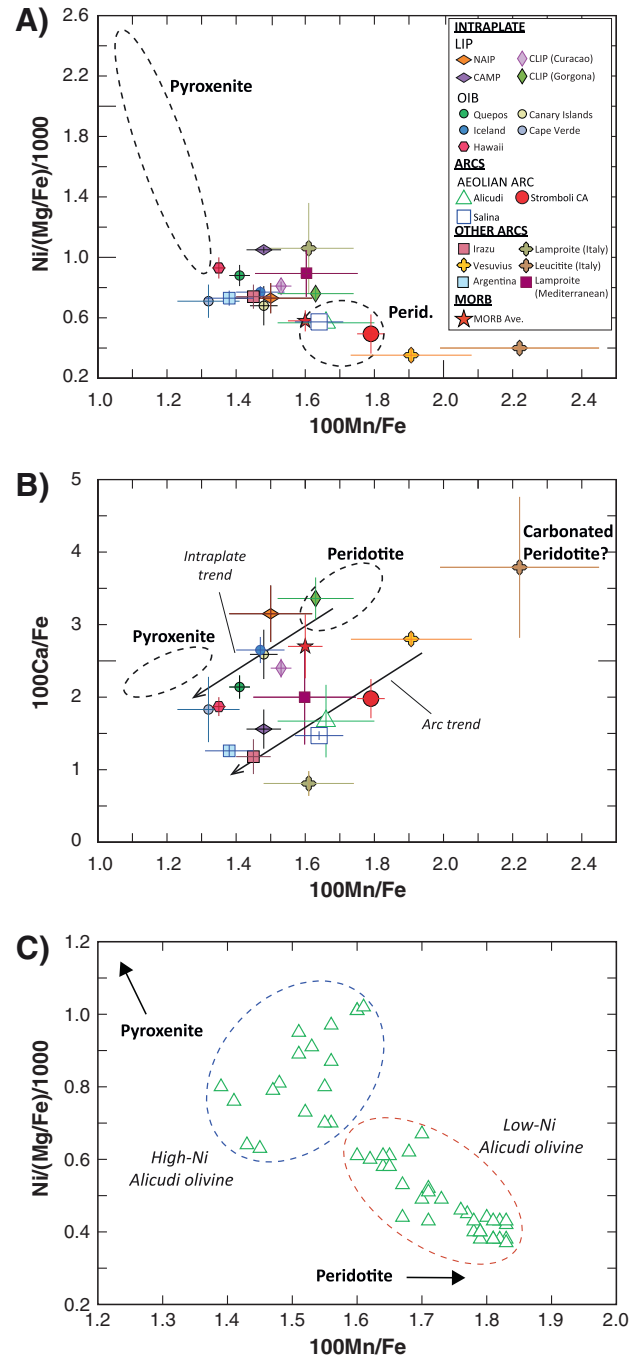


Fig. 5. Plot of $Ni/(Mg/Fe)/1000$ and $100Mn/Fe$ vs. $100Ca/Fe$ used to discriminate between pyroxenite and peridotite source lithology. All the data are plotted as averages (1 standard deviation) for forsterite content ranging between 87 and 93. (A) General trend from magma crystallized principally by a pyroxenite olivine free source through a peridotite source in agreement with the global array of Sobolev et al. (2007). Noteworthy are the Aeolian samples overlapping the peridotite end-member. (B) General pyroxenite–peridotite trend is separated into an “intraplate trend” (high Ca/Fe) and an “arc trend” characterized by low Ca/Fe values. Global olivine data: Ocean Island Basalt (OIB), Hawaii (Sobolev et al., 2007), Quepos (Trela et al., 2015), Canary Islands (Gurenko et al., 2009a, 2009b), Cape Verde (Barker et al., 2014), Iceland (Spice et al., 2016); Mid-Ocean Ridge Basalt (MORB) (Sobolev et al., 2007); Arc, Irazu (Ruprecht and Plank, 2013), Argentina back-arc (Søager et al., 2015), Vesuvius (Redi, 2014, PhD Thesis), leucite-lamproite (Ammannati et al., 2016), Mediterranean lamproite (Prelević and Foley, 2007); Large Igneous Province (LIP), Curacao (Trela et al., 2015), Gorgona (Coogan et al., 2014), Central Atlantic Magmatic Province (CAMP) (Whalen et al., 2015), North Atlantic Igneous Province (NAIP) (Spice et al., 2016). (C) Graph highlighting the bimodal distribution of olivine trace element characteristics for Alicudi. The wide range of olivine compositions for this island can be explained by olivine crystallization from two distinct melts sourced from pyroxenite (high-Ni group) and peridotite (low-Ni group) sources.

shows 100Mn/Fe vs. Ni/(Mg/Fe)/1000 and defines a clear array between olivines derived from pyroxenite and peridotite sources. The Aeolian Islands olivines clearly plot within the peridotite end-member, with the exception of the high-Ni group of Alicudi olivines. The differences in trace element systematics between the two Alicudi olivine groups highlight the significance of having two lithologically distinguishable sourced (peridotite and pyroxenite) melts in the generation of Alicudi olivine (Fig. 5C). In contrast, Vesuvius olivines plot outside the area defined by the pyroxenite–peridotite end-members, but with composition similar to Stromboli olivines. The composition of these olivines might represent a third lithological end-member, e.g., a peridotite metasomatized by carbonatitic melts (Ammannati et al., 2016) found in some arc settings and/or olivine crystallization from an oxidized melt (Krivolutskaya et al., 2012).

Fig. 5B clearly shows that olivines crystallizing from hydrous peridotite-derived liquids (as in an arc setting) systematically show lower Ca concentrations and lower Mn/Fe ratios, relative to those that crystallized from nominally anhydrous sources, e.g., OIBs and MORB. This trend is subparallel to the intraplate trend, yet shows similar variations between peridotite and pyroxenite end members. Detailed hydrous peridotite and pyroxenite melting experiments and analysis of derived olivine phenocrysts will place better constraints on the mantle source end-member compositions in subduction zone settings. We suggest that the intraplate trend is related to the almost anhydrous conditions that characterized OIB melts, while the arc trend highlights the effect of H₂O on the partitioning behavior of Ca between melt and olivine (Berndt et al., 2005; Feig et al., 2006; Libourel, 1999) and higher oxidation of Fe. A water diffusion study by Behrens and Schulze (2000) suggests that hydrous species strongly bond to Ca-complexes in melts, thus resulting in a decrease of calcium activity in the melt and an overall decrease in calcium concentrations in crystallizing olivine. The effects of temperature, pressure, and oxygen fugacity are considered to be negligible factors controlling the calcium contents of olivine. Therefore, calcium concentrations in primitive olivine phenocrysts from island arcs may be a more useful indicator of H₂O concentrations in primary melts.

With the exception of some samples from the island of Alicudi, the dominant role of a peridotite source for the Aeolian Islands is a surprising result, given the fact that melt components have been identified in the peripheral islands (Zamboni et al., 2016). This new evidence suggests that although from a trace-element and isotopic perspective the three different components that play a role in producing magmas beneath the Aeolian Islands are peridotite, subducted oceanic crust, and sediments (e.g. Francalanci et al., 2007; Peccerillo and Frezzotti, 2015; Peccerillo et al., 2013), contrary to Mexico (Straub et al., 2008), and Argentina (Søager et al., 2015) the source composition is a hydrated peridotite. We suggest that the ratio of silica-rich melt (from the subducting oceanic crust) to peridotite increases and as a consequence, the source can evolve from re-fertilized peridotite to olivine-bearing pyroxenite, and finally olivine-free pyroxenite depending on the proportion of silicic melts that can react with peridotite, and the convection processes in the mantle wedge. Additionally, it is also possible that high degrees of partial melting, common in the presence of water in arc settings, obscure the role of melting pyroxenitic veins in a dominant peridotitic mantle. Finally, carbonatitic melts with very low silica activities could react with orthopyroxene to produce olivine (Neumann et al., 2002) and thus, reverting the reaction produced by silica-rich melts, thus adding more complexity to the metasomatic reactions that result in arc magmas.

Finally, we suggest that the use of Fe/Mn and Ca in olivines as tracers of mantle source lithology in island arc settings (as they have used for intraplate magmas) should be used with caution. Iron partitioning between olivine and melt is sensitive to the state of oxidation of the melt (which may be more oxidized in arc settings) and $D_{Ca}^{ol/melt}$ is suppressed in hydrous melts. Therefore, the use of nickel concentrations in olivine, coupled with other geochemical data (whole rock major and trace element), provides internal consistency to infer the source

lithology in arc settings, as $D_{Ni}^{ol/melt}$ is not significantly affected by the state of oxidation or H₂O content of the melt.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.lithos.2016.12.004>.

Acknowledgments

We are grateful to an anonymous reviewer and Dr. Chusi Li for their constructive comments. We appreciate the efforts of Dr. Andrew Kerr for the handling of this manuscript. This project was supported in part by award EAR-1249412 to E.G. The participation of A.V.S. and V.G.B. and partial analysis of olivine were funded by the Russian Science Foundation grant number 14-17-00491 (to A.V.S.).

References

- Ammannati, E., Jacob, D.E., Avanzinelli, R., Foley, S.F., Conticelli, S., 2016. Low Ni olivine in silica-undersaturated ultrapotassic igneous rocks as evidence for carbonate metasomatism in the mantle. *Earth and Planetary Science Letters* 444, 64–74.
- Barker, A.K., Holm, P.M., Troll, V.R., 2014. The role of eclogite in the mantle heterogeneity at Cape Verde. *Contributions to Mineralogy and Petrology* 168, 1–15.
- Batanova, V.G., Sobolev, A.V., Kuzmin, D.V., 2015. Trace element analysis of olivine: high precision analytical method for JEOL JXA-8230 electron probe microanalyser. *Chemical Geology* 419, 149–157.
- Behrens, H., Schulze, F., 2000. Compositional dependence of water diffusivity in aluminosilicates glasses and melts. In: Rammlmair, J.M., Oberthür, T., Heimann, R.B., Pentinghaus, H. (Eds.), *Applied Mineralogy in Research, Economy, Technology and Culture*, Proceedings of the 6th International Conference on Applied Mineralogy. Balkema, Rotterdam, pp. 95–98.
- Berndt, J., Koepke, J., Holtz, F., 2005. An experimental investigation of the influence of water and oxygen fugacity on differentiation of MORB at 200 MPa. *Journal of Petrology* 46, 135–167.
- Chiarabba, C., De Gori, P., Speranza, F., 2008. The southern Tyrrhenian subduction zone: deep geometry, magmatism and Plio-Pleistocene evolution. *Earth and Planetary Science Letters* 268, 408–423.
- Clocchiatti, R., Del Moro, A., Gioncada, A., Joron, J.L., Mosbah, M., Pinarelli, L., Sbrana, A., 1994. Assessment of a shallow magmatic system: the 1888–90 eruption, Vulcano Island, Italy. *Bulletin of Volcanology* 56 (6–7), 466–486 Dec 1.
- Coogan, L.A., Saunders, A.D., Wilson, R.N., 2014. Aluminum-in-olivine thermometry of primitive basalts: evidence of an anomalously hot mantle source for large igneous provinces. *Chemical Geology* 368, 1–10.
- Dallai, L., Cioni, R., Boschi, C., D’Orlando, C., 2011. Carbonate-derived CO₂ purging magma at depth: influence on the eruptive activity of Somma-Vesuvius, Italy. *Earth and Planetary Science Letters* 310, 84–95.
- De Astis, G., Ventura, G., Vilardo, G., 2003. Geodynamic significance of the Aeolian volcanism (Southern Tyrrhenian Sea, Italy) in light of structural, seismological, and geochemical data. *Tectonics* 22 (n/a-n/a).
- De Hoog, J.C.M., Gall, L., Cornell, D.H., 2010. Trace-element geochemistry of mantle olivine and application to mantle petrogenesis and geothermobarometry. *Chemical Geology* 270, 196–215.
- Di Martino, C., Frezzotti, M.L., Lucchi, F., Peccerillo, A., Tranne, C.A., Diamond, L.W., 2010. Magma storage and ascent at Lipari Island (Aeolian archipelago, Southern Italy) at 223–81 ka: the role of crustal processes and tectonic influence. *Bulletin of Volcanology* 72, 1061–1076.
- Di Martino, C., Forni, F., Frezzotti, M.L., Palmeri, R., Webster, J.D., Ayuso, R.A., Lucchi, F., Tranne, C.A., 2011. Formation of cordierite-bearing lavas during anatectesis in the lower crust beneath Lipari Island (Aeolian arc, Italy). *Contributions to Mineralogy and Petrology* 162, 1011–1030.
- Faccenna, C., Molin, P., Orecchio, B., Olivetti, V., Bellier, O., Funicello, F., Minelli, L., Piomallo, C., Billi, A., 2011. Topography of the Calabria subduction zone (southern Italy): clues for the origin of Mt. Etna. *Tectonics* 30 (n/a-n/a).
- Feig, S.T., Koepke, J., Snow, J.E., 2006. Effect of water on tholeiitic basalt phase equilibria: an experimental study under oxidizing conditions. *Contributions to Mineralogy and Petrology* 152, 611–638.
- Foley, S.F., Prelevic, D., Rehfeldt, T., Jacob, D.E., 2013. Minor and trace elements in olivines as probes into early igneous and mantle melting processes. *Earth and Planetary Science Letters* 363, 181–191.
- Forni, F., Lucchi, F., Peccerillo, A., Tranne, C.A., Rossi, P.L., Frezzotti, M.L., 2013. Stratigraphy and geological evolution of the Lipari volcanic complex (central Aeolian archipelago). *Geological Society, London, Memoirs* 37, 213–279.
- Francalanci, L., Avanzinelli, R., Tommasini, S., Heuman, A., 2007. A west–east geochemical and isotopic traverse along the volcanism of the Aeolian Island arc, southern Tyrrhenian Sea, Italy: inferences on mantle source processes. *Geological Society of America Special Papers* 418, 235–263.
- Francalanci, L., Lucchi, F., Keller, J., De Astis, G., Tranne, C.A., 2013. Eruptive, volcano-tectonic and magmatic history of the Stromboli volcano (north-eastern Aeolian archipelago). *Geological Society, London, Memoirs* 37, 397–471.
- Gavrilenko, M., Herzberg, C., Vidito, C., Carr, M.J., Tenner, T., Ozerov, A., 2016. A Calcium-in-Olivine Geohygrometer and its Application to Subduction Zone Magmatism: *Journal of Petrology* 57 (9), 1811–1832.

- Gioncada, A., Clocchiatti, R., Sbrana, A., Bottazzi, P., Massare, D., Ottolini, L.A., 1998 Nov 1. Study of melt inclusions at Vulcano (Aeolian Islands, Italy): insights on the primitive magmas and on the volcanic feeding system. *Bulletin of Volcanology* 60 (4), 286–306.
- Grove, T.L., Till, C.B., Krawczynski, M.J., 2012. The role of H₂O in subduction zone magmatism. *Annual Review of Earth and Planetary Sciences* 40, 413–439.
- Gurenko, A.A., Hoernle, K.A., Sobolev, A.V., Hauff, F., Schmincke, H.-U., 2009a. Source components of the Gran Canaria (Canary Islands) shield stage magmas: evidence from olivine composition and Sr–Nd–Pb isotopes. *Contributions to Mineralogy and Petrology* 159, 689–702.
- Gurenko, A.A., Sobolev, A.V., Hoernle, K.A., Hauff, F., Schmincke, H.-U., 2009b. Enriched, HIMU-type peridotite and depleted recycled pyroxenite in the Canary plume: a mixed-up mantle. *Earth and Planetary Science Letters* 277, 514–524.
- Gurenko, A.A., Geldmacher, J., Hoernle, K.A., Sobolev, A.V., 2013. A composite, isotopically-depleted peridotite and enriched pyroxenite source for Madeira magmas: insights from olivine. *Lithos* 170–171, 224–238.
- Gvirtzman, Z., Nur, A., 2001. Residual topography, lithospheric structure, and sunken slabs in the central Mediterranean. *Earth and Planetary Science Letters* 187, 117–130.
- Herzberg, C., 2011. Identification of source lithology in the Hawaiian and Canary Islands: implications for origins. *Journal of Petrology* 52, 113–146.
- Herzberg, C., Cabral, R.A., Jackson, M.G., Vidito, C., Day, J.M.D., Hauri, E.H., 2014. Phantom Archean crust in Mangaia hotspot lavas and the meaning of heterogeneous mantle. *Earth and Planetary Science Letters* 396, 97–106.
- Hofmann, A., 1997. Mantle geochemistry: the message from oceanic volcanism. *Nature* 385, 219–229.
- Jarosewich, E., Nelen, J.A., Norberg, J.A., 1980. Reference samples for electron microprobe analysis. *Geostandards Newsletter* 4, 43–47.
- Jolis, E.M., Freda, C., Troll, V.R., Deegan, F.M., Blythe, L.S., McLeod, C.L., Davidson, J.P., 2013. Experimental simulation of magma–carbonate interaction beneath Mt. Vesuvius, Italy. *Contributions to Mineralogy and Petrology* 166, 1335–1353.
- Krivolutskaya, N.A., Sobolev, A.V., Mikhailov, V.N., Plechova, A.A., Kostitsyn, Y.A., Roschina, I.A., Fekiacova, Z., 2012. Parental melt of the Nadezhdinsky formation: geochemistry, petrology and connection with Cu–Ni deposits (Noril'sk area, Russia). *Chemical Geology* 302–303, 87–105.
- Li, C., Ripley, E.M., 2010. The relative effects of composition and temperature on olivine-liquid Ni partitioning: statistical deconvolution and implications for petrologic modeling. *Chemical Geology* 275, 99–104.
- Libourel, G., 1999. Systematics of calcium partitioning between olivine and silicate melt: implications for melt structure and calcium content of magmatic olivines. *Contributions to Mineralogy and Petrology* 136, 63–80.
- Lucchi, F., Santo, A.P., Tranne, C.A., Peccerillo, A., Keller, J., 2013a. Volcanism, magmatism, volcano-tectonics and sea-level fluctuations in the geological history of Filicudi (western Aeolian archipelago). *Geological Society, London, Memoirs* 37, 113–153.
- Lucchi, F., Gertisser, R., Keller, J., Forni, F., De Astis, G., Tranne, C.A., 2013b. Eruptive history and magmatic evolution of the island of Salina (central Aeolian archipelago). *Geological Society, London, Memoirs* 37, 155–211.
- Lucchi, F., Peccerillo, A., Keller, J., Tranne, C.A., Rossi, P.L., 2013c. The Aeolian Islands Volcanoes. *Geological Society of London*.
- Lucchi, F., Peccerillo, A., Tranne, C.A., Rossi, P.L., Frezzotti, M.L., Donati, C., 2013d. Volcanism, calderas and magmas of the Alicudi composite volcano (western Aeolian archipelago). *Geological Society, London, Memoirs* 37, 83–111.
- Mallik, A., Dasgupta, R., 2012. Reaction between MORB–eclogite derived melts and fertile peridotite and generation of ocean island basalts. *Earth and Planetary Science Letters* 329–330, 97–108.
- Mallik, A., Dasgupta, R., 2013. Reactive infiltration of MORB–Eclogite-Derived carbonated silicate melt into fertile peridotite at 3 GPa and genesis of alkalic magmas. *Journal of Petrology* 54, 2267–2300.
- Mallik, A., Dasgupta, R., 2014. Effect of variable CO₂ on eclogite-derived andesite and lherzolite reaction at 3 GPa—implications for mantle source characteristics of alkalic ocean island basalts. *Geochemistry, Geophysics, Geosystems* 15, 1533–1557.
- Matzen, A.K., Baker, M.B., Beckett, J.R., Stolper, E.M., 2013. The temperature and pressure dependence of nickel partitioning between olivine and silicate melt. *Journal of Petrology* 54, 2521–2545.
- Métrich, N., Bertagnini, A., Landi, P., Rosi, M., 2001. Crystallization driven by decompression and water loss at Stromboli volcano (Aeolian Islands, Italy). *Journal of Petrology* 42, 1471–1490.
- Métrich, N., Bertagnini, A., Di Muro, A., 2010. Conditions of magma storage, degassing and ascent at Stromboli: new insights into the volcano plumbing system with inferences on the eruptive dynamics. *Journal of Petrology* 51, 603–626.
- Neumann, E.R., Wulff-Pedersen, E., Pearson, N.J., Spencer, E.A., 2002. Mantle xenoliths from Tenerife (Canary Islands): evidence for reactions between mantle peridotites and silicic carbonatite melts inducing Ca metasomatism. *Journal of Petrology* 43, 825–857.
- Peccerillo, A., 2001. Geochemical similarities between the Vesuvius, Phlegraean Fields and Stromboli Volcanoes: petrogenetic, geodynamic and volcanological implications. *Mineralogy and Petrology* 73, 93–105.
- Peccerillo, A., Frezzotti, M.L., 2015. Magmatism, mantle evolution and geodynamics at the converging plate margins of Italy. *Journal of the Geological Society* 172, 407–427.
- Peccerillo, A., Dallai, L., Frezzotti, M.L., Kempton, P.D., 2004. Sr–Nd–Pb–O isotopic evidence for decreasing crustal contamination with ongoing magma evolution at Alicudi volcano (Aeolian arc, Italy): implications for style of magma–crust interaction and for mantle source compositions. *Lithos* 78, 217–233.
- Peccerillo, A., De Astis, G., Faraone, D., Forni, F., Frezzotti, M.L., 2013. Compositional variations of magmas in the Aeolian arc: implications for petrogenesis and geodynamics. *Geological Society, London, Memoirs* 37, 491–510.
- Plank, T., Langmuir, C.H., 1993. Tracing trace elements from sediment input to volcanic output at subduction zones. *Nature* 362 (6422), 739–743.
- Plank, T., Kelley, K.A., Zimmer, M.M., Hauri, E.H., Wallace, P.J., 2013. Why do mafic arc magmas contain ~4 wt% water on average? *Earth and Planetary Science Letters* 364, 168–179.
- Prelević, D., Foley, S.F., 2007. Accretion of arc-oceanic lithospheric mantle in the Mediterranean: evidence from extremely high-Mg olivines and Cr-rich spinel inclusions in lamproites. *Earth and Planetary Science Letters* 256, 120–135.
- Prelević, D., Jacob, D.E., Foley, S.F., 2013. Recycling plus: a new recipe for the formation of Alpine–Himalayan orogenic mantle lithosphere. *Earth and Planetary Science Letters* 362, 187–197.
- Putirka, K., Ryerson, F.J., Perfit, M., Ridley, W.I., 2011. Mineralogy and composition of the oceanic mantle. *Journal of Petrology* 52, 279–313.
- Redi, D., 2014. Pyroxene and olivine chemistry as an indicator of melt evolution. A contribution to the understanding of Somma-Vesuvius eruptive behaviour. (PhD Thesis). Dipartimento Di Scienze Della Terra, dell'Ambiente e Delle Risorse, Università Di Napoli Federico II.
- Rudnick, R.L., 1995. Making continental crust. *Nature* 378, 571–578.
- Ruprecht, P., Plank, T., 2013. Feeding andesitic eruptions with a high speed connection from the mantle. *Nature* 500, 68–72.
- Ryan, J.G., Chauvel, C., 2014. The subduction-zone filter and the impact of recycled materials on the evolution of the mantle. In: *Treatise of Geochemistry*, 2nd ed. AGU, Washington, D.C., pp. 479–508.
- Saager, N., Portnyagin, M., Hoernle, K., Holm, P.M., Hauff, F., Garbe-Schönberg, D., 2015. Olivine major and trace element compositions in Southern Patagonia Basalts, Argentina: evidence for pyroxenite–peridotite melt mixing in a back-arc setting. *Journal of Petrology* 56, 1495–1518.
- Sobolev, A.V., Hofmann, A.W., Sobolev, S.V., Nikogosian, I.K., 2005. An olivine-free mantle source of Hawaiian shield basalts. *Nature* 434, 590–597.
- Sobolev, A.V., Hofmann, A.W., Kuzmin, D.V., Yaxley, G.M., Arndt, N.T., Chung, S.L., Danyushevsky, L.V., Elliott, T., Frey, F.A., Garcia, M.O., Gurenko, A.A., Kamenetsky, V.S., Kerr, A.C., Krivolutskaia, N.A., Matvienkov, V.V., Nikogosian, I.K., Rocholl, A., Sigurdsson, I.A., Sushchevskaya, N.M., Teklay, M., 2007. The amount of recycled crust in sources of mantle-derived melts. *Science* 316, 412–417.
- Sorbadere, F., Schiano, P., Métrich, N., 2012. Constraints on the origin of nepheline-normative primitive magmas in island arcs inferred from olivine-hosted melt inclusion compositions. *Journal of Petrology* (Oct 11:egs063).
- Spice, H.E., Fitton, J.G., Kirstein, L.A., 2016. Temperature fluctuation of the Iceland mantle plume through time. *Geochemistry, Geophysics, Geosystems* 17, 243–254.
- Straub, S.M., LaGatta, A.B., Martin-Del Pozzo, A.L., Langmuir, C.H., 2008. Evidence from high-Ni olivines for a hybridized peridotite/pyroxenite source for orogenic andesites from the central Mexican Volcanic Belt. *Geochemistry, Geophysics, Geosystems* 9 (n/a-n/a).
- Trela, J., Vidito, C., Gazel, E., Herzberg, C., Class, C., Whalen, W., Jicha, B., Bizimis, M., Alvarado, G.E., 2015. Recycled crust in the Galápagos Plume source at 70 Ma: implications for plume evolution. *Earth and Planetary Science Letters* 425, 268–277.
- Ventura, G., 2013. Kinematics of the Aeolian volcanism (Southern Tyrrhenian Sea) from geophysical and geological data. *Geological Society, London, Memoirs* 37, 3–11.
- Whalen, L., Gazel, E., Vidito, C., Puffer, J., Bizimis, M., Henika, W., Caddick, M.J., 2015. Supercontinental inheritance and its influence on supercontinental breakup: the Central Atlantic Magmatic Province and the breakup of Pangea. *Geochemistry, Geophysics, Geosystems* 16, 3532–3554.
- Zamboni, D., Gazel, E., Ryan, J.G., Cannatelli, C., Lucchi, F., Atlas, Z.D., Trela, J., Mazza, S.E., De Vivo, B., 2016. Contrasting sediment melt and fluid signatures for magma components in the Aeolian Arc: implications for numerical modeling of subduction systems. *Geochemistry, Geophysics, Geosystems* (n/a-n/a).
- Zindler, A., Hart, S., 1986. Chemical geodynamics. *Annual Review of Earth and Planetary Sciences* 14, 493–571.