

## DISCRIMINATING MAGMA SOURCES BENEATH THE AEOLIAN ISLANDS, ITALY

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### INTRODUCTION

The Aeolian Islands, in the southern Tyrrhenian Sea (Italy), have been a subject of study for centuries and, at present time, this archipelago is still an interesting location because of its important structural, volcanological, and petrological variations.

The collision between the African and Eurasian plates and the related geodynamic evolution of the Mediterranean area, in particular the Miocene-Quaternary opening of the Tyrrhenian Sea, determined the present tectonic structure of the Italian region. The Aeolian Islands originated by the steep northwestern subduction of the Ionian Plate below the Calabrian orogenic arc, which also rolled back toward southeast (Gvirtzman & Nur, 2001; Chiarabba *et al.*, 2008). 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 oceanic basin.

The arc is subdivided into the western, central and eastern sectors based on petrological, geochemical, and geophysical data (De Astis *et al.*, 2003 and reference therein). At present time, the western area (Alicudi and Filicudi) is considered not active, whereas the volcanic activity is present in Vulcano (central segment) and Stromboli (eastern segment). The Aeolian subaerial activity developed recently (250 - 270 ka, Lucchi *et al.*, 2013) and is characterized by rocks of different degrees of magma evolution with calc-alkaline through potassic compositions and by relevant variations in isotopic signatures and trace elements (for further details see Zamboni *et al.*, 2016).

Geochemical variations in magmas from the western to the eastern sector of the Aeolian Islands are considered to be some of the largest along-arc variations in the world (*e.g.*, Peccerillo, 2005; Peccerillo *et al.*, 2013).  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  isotope ratios showed a severe change in these values along the volcanic front. Current interpretations (Francalanci *et al.*, 2007; Peccerillo *et al.*, 2013) suggest that these signatures are controlled by a depleted mantle source at Alicudi that gets gradually enriched from west to east along the arc. This may be due to an increasing role for subduction components or crustal contamination. However, crustal contamination cannot account for the entire geochemical variation along the arc as it requires unrealistic extents of assimilation (details in Zamboni *et al.*, 2016); therefore, the regional geochemical trends recorded in the mafic lavas in the Aeolian Arc are most likely controlled by the addition of subduction components to the mantle wedge in the form of fluids and/or melts.

We investigated which slab-derived components (*i.e.*, slab fluids or melts derived from the subducting crust and/or sediments) control the extreme along-arc variations in the geochemical signatures of these magmas using new B, Be, Li, and As data from olivine bearing mafic lavas, representative of primitive magmas largely unaffected by crustal contamination (*e.g.*, De Astis *et al.*, 2000; Peccerillo, 2005).

Furthermore, we adopted the minor and trace elements in olivine approach (Sobolev *et al.*, 2007) to characterize the mantle lithologies in order to understand if differences in mantle source compositions might control the along arc variations. We evaluated if a possible influence from a pyroxenitic source at the edges of the arc, in addition to the peridotitic source, could result in the isotopic and geochemical variations described in the literature using high-precision microprobe analyses on olivine crystals from the same samples collected for the B and Be analyses, a technique never applied to the Aeolian Islands mafic magmas.

## BORON AND BERYLLIUM

In the fieldwork campaign, we collected samples on the island of Alicudi, Filicudi, Salina, and Stromboli. We revisited and sampled outcrops of well-studied units of olivine-bearing basalts, based on studies (Lucchi *et al.*, 2013 and reference therein) suggesting that these units are the most mafic in the arc and they do not show any evidence of crustal contamination (for details see Zamboni *et al.*, 2016).

All the samples were processed in the geochemistry laboratory at the Department of Geosciences at Virginia Polytechnic Institute and State University (USA). Major element compositions were determined with X-ray fluorescence (XRF) at Virginia Tech where also additional trace element compositions for Stromboli were collected by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Trace elements contents from the island of Alicudi, Filicudi, and Salina were determined by solution ICP-MS at the USF Center for Geochemical Research at the University of South Florida together with Be and Li contents (also for Stromboli). Boron and arsenic contents were determined by solution ICP-MS. For methods and standard statistics see Zamboni *et al.* (2016).

The samples collected (whole rock compositions are provided in Zamboni *et al.*, 2016) range in composition from calc-alkaline to high potassium basalt to andesite. Stromboli rocks display a significant separation between lavas with high potassium contents ( $K_2O > 3.5$  wt.%) that belong to the potassic series and other samples that plot in a range between the calc-alkaline and shoshonitic series.

To discriminate between melt and fluid components typical of a subduction zone, we used trace elements that are compatible in either hydrous fluids or melts. The high field strength elements (HFSE, *e.g.*, Nb, Ta, Zr, and Th) and middle to heavy rare earth elements (MREE and HREE, respectively) preferentially partition into melts and are not mobilized by aqueous fluids. In contrast hydrous fluids preferentially mobilize the alkali metals (*e.g.*, K and Rb), the alkaline earth metals (*e.g.*, Ba and Sr) and U. Similarly, light REE (*e.g.*, La) are mobilized more easily by hydrous fluid than the rest of the REE (*e.g.*, Elliott, 2003).

In the Aeolian Islands commonly used ratios of fluids related elements to those mobilized only in melts (*e.g.*, Ba/Nb, U/Th, and Sr/La) are systematically higher in the central segment of the arc (Salina), compared to the lower ratios of the external islands (particularly Stromboli) that suggests an increased contribution of silicate melt components. These along-arc variations imply that fluids play a major role in the transport of elements into the mantle wedge beneath the central region of the arc (Salina), whereas under Stromboli and, to a lesser extent, under Alicudi a silicate melt is the dominant contributing component (details and figures in Zamboni *et al.*, 2016).

We analyzed the trace element concentrations of fluid mobile elements (*e.g.*, B, As, and Li), and Be, a melt-soluble element, as they are good geochemical indicators of subduction components.

Boron, like Li and As, is considered to be an excellent tracer for the dehydration of the subducting slab due to its highly fluid mobile nature in sediments and oceanic crust during the subduction process and because of its extreme depletion in the upper mantle (Leeman & Sisson, 1996; Bebout *et al.*, 1999; Plank, 2014; Ryan & Chauvel, 2014). Boron budgets in the Aeolian Islands are increasing from West to East, with Alicudi and Filicudi characterized by the lowest average B contents ( $\approx 7$  ppm) and Stromboli showing the highest average ( $\approx 20$  ppm). Calc-alkaline rocks in Stromboli have the highest B content (30 ppm). Lithium and As contents vary similarly to B. This increment in B, Li, and As abundances toward the eastern segment of the arc is best explained by hydrous fluid inputs derived from the dehydrating subducting slab and sediments, as also evident by other trace element systematics (figures and details in Zamboni *et al.*, 2016).

Beryllium is another element enriched in marine sediments and altered oceanic crust, but highly depleted in the upper mantle, mimicking the terrestrial distribution pattern of boron (*e.g.*, Ryan, 2002; Ryan & Chauvel, 2014). Its behavior is very different with respect to elements, like B, as it is immobile in hydrous fluids, but highly mobile in silicate melts derived from the subducting slab (Ryan, 2002). Beryllium contents in the calc-alkaline lavas from across the archipelago are broadly similar (1-2 ppm, the highest are from the peripheral islands). In contrast, the potassic samples from Stromboli are strongly enriched in Be (5-7 ppm), as well as in

other incompatible trace elements (*e.g.*, Th, Nb, and La). This behavior can be explained by partial melting of a source that is largely enriched in incompatible trace elements, including Be, by subducted sediments transported by the Ionian slab. The role of silicate melts in Stromboli is also evident when the different Be abundances from all the samples are plotted against B or other fluid mobile elements (*e.g.*, As and Li) in respect to upper mantle (UM) values. This comparison provides a clear separation between two compositional trends, on which we suggest two different sources for the calc-alkaline and potassic rocks of Stromboli: 1) for the calc-alkaline magmas a source metasomatized by a fluid component derived from the oceanic slab and 2) a source enriched with a sediment melt component for the potassic rocks (figures and details in Zamboni *et al.*, 2016).

The presence of a dominant sediment-melt component in the genesis of potassic lavas was also supported by several experimental works which suggested that silica-undersaturated alkaline arc lavas could be produced via the reaction of sediment-derived siliceous melt with peridotite in the mantle wedge (Avanzinelli *et al.*, 2008; Mallik & Dasgupta, 2013). More recently, an experimental study by Mallik *et al.* (2015) demonstrated that ultrapotassic magmas (resembling the ones from Stromboli) could be generated by mantle reaction with hydrous sediment-derived melts.

In order to support our results we also compared our new B, Be, and trace element data with samples from the Phlegrean Fields, along with other well studied volcanic arcs and arc segments in the world by assembling a dataset via the GEOROC database (details in Zamboni *et al.*, 2016).

The low ratios (2-15) of B/Be for most of the Aeolian Islands samples make this Italian arc analogous to Cascades and Mexican Volcanic Belt. We notice the same similarity in several plots using well-known ratios used to distinguish between fluid and melt components (*e.g.*, Th/Nb vs. La/Nb) as slab-derived metasomatizing agents in the different arcs. Our results show how the Aeolian Islands (in particular Stromboli) are similar to Cascades, Sunda Arc, Phlegrean Fields, and for some extents Mexican Volcanic Belt, all controlled by a melt-dominated component, whereas the fluid component dominates in the Izu-Bonin, Marianas, Kamchatka, and Tonga Arcs. Other global arcs (*i.e.*, Aleutians) are characterized by different proportions of subduction components (diagrams description in Zamboni *et al.*, 2016).

The dominant component in the subduction will depend on the thermal structure of the arc. Systematics in arc B/La vs. Ba/La display how the Aeolian Islands forms a trend with Cascades, Sunda Arc, and Mexican Volcanic Belt at low B/La consistent with the mixing of a “hot” slab-derived B source and the UM (Ryan & Chauvel, 2014). This is different than arcs as Izu-Bonin, Marianas and Central America (Honduras-Nicaragua), which involve contributions of a “cool” slab-derived B source (*i.e.*, subduction-related serpentinite; Tonarini *et al.*, 2007; Ryan & Chauvel, 2014). The “cool” fluid-mobile element component is not evident in Aeolian lavas, but the fact that they show boron enrichment along the arc it is a clear indication that a slab-derived fluid component is involved.

This observed geochemical signature, that suggests a sediment melt component, is in contrast with results of global thermal models for subduction systems. In fact, the model of Syracuse *et al.* (2010) describes different pressure-temperature (P-T) paths of subducting slabs that depict the subduction of the Ionian slab beneath Calabria as one of the coldest subduction zones on Earth. Unfortunately, Syracuse *et al.* (2010) results come from a two-dimensional model that does not consider the 3D complications of lateral or trench-parallel asthenospheric mantle flow, due to slab rollback or slab windows (Buttles & Olson, 1998; Schellart, 2008). The asthenospheric mantle flow was already suggested by several studies as the responsible for the geochemical variation in the northern segment of the Cascades, Sunda Arc and the heterogeneous mantle under the Mexican Volcanic Belt (details and references in Zamboni *et al.*, 2016).

Seismic studies and numerical models in the southern Tyrrhenian area (*e.g.*, Chiarabba *et al.*, 2008; Faccenna *et al.*, 2011) suggest the presence of African-related asthenospheric flow around the edges of the narrow Ionian Plate due to a slab tear caused by the rollback motion of the Ionian slab (Gvirtzman & Nur, 1999; Gutscher *et al.*, 2016). We consider this hot asthenosphere flow the responsible for the sediment melt component at the borders of the Aeolian arc.

## THE OLIVINE PERSPECTIVE

The geochemical variability of arc magmas depends on the introduction of upper crust material into the mantle source by subduction processes. One approach to study the origin of these mantle end-members is by the analyses of minor element of olivine phenocrysts from melts produced in arc-related basalts. Three different lithological mantle end-members were identified, *e.g.*, peridotite, subducted oceanic crust, and sediments (oceanic and terrigenous) on the basis of olivine chemistry.

Sobolev *et al.* (2007) described how melts of pyroxenite are characterized by highly forsteritic olivines (Fo > 90) with high Ni, low Ca and Mn contents, and high Fe/Mn ratio, in comparison to olivine from peridotite source-derived melts. These contents resulted from the interaction of silica rich melts (derived from the slab or from pyroxenitic/eclogitic lithologies in intraplate setting) with peridotites that caused the formation of an olivine-free pyroxenite. Melts from this hybrid pyroxenitic source will be Ni-rich melts compared to peridotite-derived melts because there is no residual olivine phase in the source. Nickel is less compatible in the pyroxenite, whereas Ca and Mn (higher bulk partition coefficient) are more compatible in pyroxenite source lithologies.

We performed high precision major (Si, Fe, and Mg), minor, and trace (Ni, Mn, Ca, Al, Cr, Co, Ti, Zn, P, and Na) element analyses on olivine phenocrysts from the most mafic lava and scoria (MgO bulk content > 6 wt.%) from Alicudi, Filicudi, Salina, and Stromboli; only the potassic rocks of Stromboli have MgO > 4 wt.%. We analyzed more than 500 olivine data points by means of the JEOL JXA-8230 Superprobe at the Institute des Sciences de la Terre (ISTerre), University Joseph Fourier, Grenoble, France, following the analytical protocol described in Batanova *et al.* (2015).

The peripheral islands are characterized by higher forsteritic content (high Mg-number) than the central sector of the arc; Alicudi have the highest with 92.21 while Stromboli reaches values up to 90.77. In contrast, olivine phenocrysts from Filicudi reaches 86.84, while the majority of Salina olivines are characterized by Mg-numbers around 80. Olivines from the potassic rock of Stromboli have low and constant forsterite (< 75).

We represented the olivine compositions of the Aeolian Islands samples as a function of Mg-number with the modeled peridotitic source for anhydrous magma (*e.g.*, intraplate magma) and a schematic olivine and cotectic (olivine + clinopyroxene (ol + cpx)) fractionation trends described in Herzberg (2011). Our data shows Ni contents for the most forsteritic olivine in agreement with values typical of olivines from a mantle peridotitic source (2800-3100 ppm, Herzberg *et al.*, 2013). Alicudi olivines have the highest Ni contents and also show a clear dichotomy with few olivines with higher contents and other with lower contents. The group at higher Ni resembles a cotectic fractionation path while the lower Ni group and olivines from Stromboli, Salina, and Filicudi reflect the typical olivine fractional crystallization trend from a peridotite. Similar observations can be made with Fe/Mn, whereas Ca contents are lower than expected for olivines crystallizing from a peridotitic source (< 2000 ppm). We suggest that the low Ca concentrations are related to a hydrous peridotite source, because the study of Feig *et al.* (2006) determined from experimental data that Ca partition coefficient between olivine and melt is a function of olivine Mg-number, and it decreases with increasing H<sub>2</sub>O resulting in olivines with depleted Ca concentrations.

In order to support the hypothesis of a peridotite source for the Aeolian Islands, we compared our high precision olivine data with olivine compositions from different volcanic settings in the world inferred to derive from pyroxenite, peridotite or a mixing of the two sources. The compared results for Ni, Ca, and Fe/Mn show how the Aeolian olivine resemble the MORB olivines consistent with a peridotite source melting (Sobolev *et al.*, 2007; Herzberg, 2011) and, in contrast, how different are these olivines with respect to olivine deriving from sources in which a pyroxenite component played a significant role (*e.g.*, Mauna Kea and Quepos; Sobolev *et al.*, 2007; Trela *et al.*, 2015). In comparison with olivines from a subduction setting, it is noteworthy that every olivine from every arc are characterized by low Ca contents (H<sub>2</sub>O effect), whereas those from Vesuvius are characterized by higher Ca contents (> 2000 ppm) that may be related to the melting subducted carbonated sediment and crust. Also, most of the Vesuvius olivines overlap with the Aeolian olivines.

Additionally, we created a database with other available high precision global olivine datasets (*e.g.*, Cape Verde, Iceland, CAMP). This database was filtered to obtain primitive olivine compositions characterized by Mg-numbers > 87 and to eliminate the effects of fractional crystallization on olivine chemistry.

The data averages (one standard deviation) were plotted in diagrams against parameters from Sobolev *et al.* (2007). The diagram 100Mn/Fe vs. Ni/(Mg/Fe)/1000 defined a clear array between pyroxenite derived olivines and the peridotite derived olivines. Olivines from Hawaii, Quepos, and Cape Verde plotted next to the pyroxenitic endmember; in contrast, MORB and Aeolian Islands olivine plotted perfectly in the peridotite spot endmember supporting our previous observations. Olivine from other localities derived from sources influenced by different proportions of pyroxenite and peridotite. On the other hand, Vesuvius olivines plotted outside the area defined by the pyroxenite-peridotite array with compositions similar to Stromboli olivines. The composition of these olivines may represent a third endmember on the Sobolev array, a carbonated peridotite.

Similar observations can be made from the diagram 100Mn/Fe vs. 100Ca/Fe in which two trends are clearly separated. At higher Ca there is an “intraplate trend” that largely corresponds to the pyroxenite-peridotite array described above, with Hawaii, Cape Verde and Quepos characterized by important contributions from a pyroxenite source, opposing MORB and Gorgona olivines derived from a predominantly peridotite source. At lower Ca there is an apparent “arc setting trend” subparallel to the intraplate trend that shows similar variations between a peridotite and pyroxenite endmembers. The arc setting trend is composed of olivines crystallized from hydrous peridotite derived liquids and systematically contain lower Ca concentrations. We suggest that the intraplate trend is related to the almost anhydrous conditions that characterized OIB magmas, whereas the arc trend highlights the effect of H<sub>2</sub>O on the partitioning of Ca in the sources of subduction related volcanoes.

## CONCLUDING REMARKS

The Aeolian Islands exhibit significant along-arc geochemical variations. Based on the systematics of B, Be, Li, and As contents in the Aeolian lavas, fluids from the subducting altered oceanic lithosphere influence the whole arc and a sediment melt component is present at the edges of the Aeolian arc, recognizable in the potassic lavas in Stromboli. The presence of hot asthenosphere inflow could explain either the melt component signature and why the Aeolian Islands shares geochemical similarities to hot subduction zones like the Cascades and the Mexican Volcanic Belt.

The high precision olivine data of the Aeolian Islands exhibit Ni, Mn, and Ca contents typical of olivines crystallized from primary magmas and derived from a peridotite source like the average MORB. Arc derived melts form a trend at lower Ca contents subparallel to the array between a pyroxenite and a peridotite endmembers.

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