PRIMARY MAGMAS, FRACTIONATION MODELLING AND MANTLE SOURCE OF ETNEAN LAVAS

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INTRODUCTION

Mt. Etna, 3343 meters high, is the highest european volcano and one of the most active in the world. In the last decades several eruptive events caused the closure of the "Fontane Rosse" Airport of Catania for few days and the destruction of edifices and roads along the southern (Rifugio Sapienza and Nicolosi) and northern flank (Piano Provenzana) of the volcano. In order to reduce the risk connected to these events, it is necessary to understand the eruptive dynamics starting from the deep "roots" of the volcano. The investigation of the deep and shallow feeding system of Mt. Etna, and subsequently of his mantle source, could give us some information about the eruptive style, thus helping to predict future volcanic events and to reduce their hazard.

GEOLOGICAL BACKGROUND

Mt. Etna is located in the northeastern sector of Sicily region in a complex geodynamic contest, at the intersection of the Maghrebian Chain, the Peloritani Mountains and the Iblean foreland (Catalano & D'Argenio, 1982) and has an oval base area of 1418 km² (47 km N-S and 38 Km E-W) (Tanguy et al., 1997). The tectonic setting of Mt. Etna is due to the interaction between regional tectonic dynamics and local processes concentrated into the Etnean area. It grew up at the intersection of three main regional fault system: I) Tindari-Giardini lineation, directed NW-SE and connected with the Ibleo - Maltese Escarpment towards SE; II) Messina-Fiumefreddo fault System, oriented NE-SE; III) Kumeta-Alcantara fault System, directed ENE-WSW, that intersects the other lineations just north of the volcanic edifice. Recently The Ibleo-Maltese Escarpment assumed a more important role than Messina-Fiumefreddo and Kumeta-Alcantara Systems. It is considered as the superficial expression of a main regional asymmetric rifting (Torelli et al., 1998). The geodynamic behavior of the volcanic edifice seems to be controlled by flank instability processes, like the oriental sector eastward dislocation. This is named "Valle del Bove", a horseshoe shaped depression, 7 kilometers long and 5 kilometers wide, bounded by steep wall up to 700-800 meters (Nicotra et al., 2011). It is interpreted as the result of a complex interaction between regional tectonic stresses and the gravity on the volcanic edifice. Pernicana Fault and Trecastagni and Tremestieri Faults identify respectively the northern and southern margin of this unstable sector (Azzaro, 1999).

Volcanological evolution

In this work, a new volcanological evolution that could integrate all data from previous works (Branca *et al.*, 2008, and reference therein) was implemented.

Tholeiitic and transitional phase (500 - 220 ka ago): the volcanic activity started about 500 ka ago (Gillot *et al.*, 1994), several kilometers southeastward the actual Mt. Etna position, with fissural and submarine volcanism with tholeiitic affinity. Tanguy *et al.* (1997), in their detailed work, recognized three main type of eruptive products with peculiar petrographic and geochemical features: *Olivine-tholeiites*, *Pigeonite-tholeiites*, *Transitional tholeiites*.

Ancient alkaline volcanism - AAV (220-60 ka ago): about 220 ka ago the volcanic activity shifted northward along the Ionian coast with fissural eruptions of Na-alkaline products (Tanguy *et al.*, 1997; Branca *et al.*, 2008). This first alkaline stage generated a shield volcano, 15 km in diameter (oriented N-S) and 7 kilometers southeastward the current volcano edifice (Branca *et al.*, 2008).

About 121 ka ago the volcanic activity migrated (westward) to the "Valle del Bove" area and was characterized by the emplacement of the polygenic volcanic centers of "Tarderia" (106 ka ago) and "Rocche" (102 ka ago) recording the beginning of a central conduit type volcanic activity (Branca *et al.*, 2008). Afterwards, some others ancient alkaline centers took place, named Calanna, Triglioletto I and II, Zoccolaro, Vavalaci-Belvedere, Giannicola, Salfizio and Cuvigghiuni. Trifoglietto is the largest volcanic center developed from 80 to 60 ka ago.

Ellittico (60-15 ka ago): about 60 ka ago, the main Etnean feeding system moved northwestward inducing the development of the Ellittico Center, the large Stratovolcano which constitutes the skeleton of the actual edifice (more than $\frac{1}{3}$ of the whole volcanic edifice). About 15 ka ago, four sub-plinian eruptions partially destroyed the Ellittico Center (Branca *et al.*, 2008) producing several km³ of trachytes as fall and pyroclastic flow deposits. These events generated a 4×3 kilometers wide caldera filled by the subsequent Recent Mongibello products and lavas (Tanguy *et al.*, 1997; Branca *et al.*, 2008, and reference therein).

Recent Mongibello (15 ka ago - present day): the last 15 ka volcanic persistent activity formed the Recent Mongibello Volcano over-imposed on the Ellittico caldera (Tanguy *et al.*, 1997; Branca *et al.*, 2008). Its activity is characterized by different eruptive mechanisms related to the presence of an extensional tectonic regime. About 2 ka the Recent Mongibello summit area collapse generated the "Caldera del Lago" filled by the current summit craters products. All these lavas and products belong to Na-alkaline series and in lesser extent to K-alkaline series although, since 1971, the K-affinity prevails on the Na-one.

SAMPLING AND ANALYTICAL METHODS

A representative number of rocks were sampled for each evolutionary stage of Mt. Etna volcanic activity in order to have a complete framework. This sampling helped also to complete the analyses for both Tholeiitic and AAV periods which are rather scarce in literature. All samples were analyzed for whole-rock major and trace elements using X-ray fluorescence (Thermo ARL Advant XP). Intensities were corrected for matrix effects following the method of Lachance & Trail (1996). Loss on Ignition (L.O.I.) was determinate by gravimetric method. 26 Representative samples were selected for Th, U, and REE analyses by means of Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Plasma Quad 2Plus VG Elemental). Both major and trace element analyses were carried out at the Department of Physics and Earth Sciences of the University of Ferrara. Major and minor elements for olivines, clinopyroxenes, plagioclases, amphiboles, spinels and apatites were carried out by an electron microprobe (EMP-Cameca SX-50) at laboratories of Padova, IGG-CNR, using both energy and wavelength dispersive spectrometry (EDS and WDS).

GAS AND VOLUME ESTIMATION

Gas

One of the main features of Mt. Etna is represented by the persistent degassing from summit craters. Upon their migration from the source region toward the Earth's surface, magmas release volatile species into the gas phases after a decrease in their solubility inside the melt. These may induce magma fragmentation during strombolian activity and lava fountaining generating a significant hazard (Cashman *et al.*, 2000). Two important volatile species are represented by SO₂ and CO₂. Mt. Etna is one of the largest SO₂ emission source even during non-eruptive periods. Measurements of the SO₂ volcanic plume and of CO₂ soil emissions indicate an average SO₂ outflux between 0.31 and 7.7 Mt yr⁻¹ (average of 2.04 Mt yr⁻¹ during non eruptive periods; Ferlito *et al.*, 2014) and a CO₂ average output of 13 ± 3 Mt yr⁻¹ (Allard *et al.*, 1991). Regard to CO₂ Mt. Etna produces about the 15% of the global volcanic emission. D'Alessandro *et al.* (1997) calculated the involvement of 0.7 km³/y of magma in generating the estimated CO₂ emission rate. However, Calvari *et al.* (1994) measured a lava emission rate in the order of 0.035 km³/y for the 1971-1995 period (GPS techniques were used to measure the lava thickness enabling to calculate the final volume and emission rate), that is 1/20 of the value requested to balance

the gas emissions. This reveals a very low ratio between erupted and degassed magma and opens a lively debate that affects other well studied volcanoes that exhibit continued degassing in the absence of significant magma eruptions. Allard *et al.* (1994, and references therein), suggest the intrusion of huge amounts of magma and/or the presence of convective movements within the conduits and magma chambers. The undegassed and volatile-rich magma rises the conduit while the degassing one increases his density and can: I) convects back down into the volcanic conduit; II) mixes in large and deep reservoir; III) intrudes the country rock (Witham, 2011).

In this contest, mixing represents the main mechanism that may be able to reduce the volatile concentration in magma arriving at an open volcanic vent in a degassing system (that is lower than in melt inclusions analyses). Following Ferlito *et al.* (2014) the solution of magma convection presents some important weakness: *i*) does not explain why new magmas batches can emplace, lose their volatiles content and does not erupt; *ii*) the loss of volatiles induces undercooling, promotes crystallization and should "close" the open conduit; *iii*) all the degassed magma will have to be rearranged beneath the volcanic edifice. The estimated amount of degassed and cold basaltic magma is $3 \cdot 10^5$ m³ every day and it would be too large if compared with the plutonic complex recognized by Patanè *et al.* (2006).

Ferlito *et al.* (2014) support the presence of a CO_2 flux within the Etnean feeding system, because CO_2 exsolves at considerable depths. The CO_2 acting as volatiles carrier (because changes the CO_2 -H₂O equilibrium of fluxed magma), induces the H₂O exsolution at depth, causing loss of H₂O from the system (Armienti *et al.*, 2013). This can justify the high emissions of H₂O without frequent magma eruptions. Unfortunately the migration mechanism of H₂O is still a not well understood process that necessitate a long series of experimental works (Ferlito *et al.*, 2014).

Volume estimation

One of the aims of this study was to obtain an estimation of the magmatic products related to the Etnean activity. First was necessary to calculate the volcanic edifice volume, taking into account the reconstruction of the sedimentary basement underlying Mt. Etna. Neri & Rossi (2002), starting from geoelectric data and hydrogeological studies drew a substratum map. Evaluating both literature data and hydrogeological studies of private and public companies, Neri & Rossi (2002) reconstructed the sedimentary basement morphology comparing direct and indirect information on the same detected area. A specific software, that makes tridimensional elaborations of topographic data, was used to calculate the emitted products volume as a simple difference between the actual topographic surface and the reconstructed substratum. The final result is a volume of 374 km³ with an emission rate of 1250 m³/y, which was calculated taking into account that most of the volcanic edifice developed in the last 100 ka. (Neri & Rossi, 2002).

MELT INCLUSIONS

Silicate melt inclusions represent trapped silicate melt that can give us important information on the evolution of the magma. This is possible only on the condition that they remained isolated from the enclosing magma after their entrapment (Frezzotti, 2001). Studies of melt inclusions in early crystallization phases allow the characterization of primary magmas, whereas in differentiated products they can provide information on the petrological evolution of the magmas. Olivine, represents the best mineralogical phase for the MI study because give us the compositions of primary melts and it is less prone to fracturing. Kamenetsky & Clocchiatti (1994, 1996) found a range of compositions for Etnean magmas varying from tholeiitic, transitional to alkaline basalts that could not be related by fractional crystallization but only by partial melting of the mantle source. Another important outcome in studying MI is given by the measurements of their H₂O and CO₂ content. At Mt. Etna several authors analyzed the volatiles contents of MI entrapped in olivines (Métrich *et al.*, 2004; Spilliaert *et al.*, 2006); they obtained a value of 3.5 wt.% of H₂O and 4000 ppm of CO₂ for MI trapped at 400 and 100 MPa on recent erupted lavas (2001 and 2002-2003 eruptive events). These high values are normally related to metasomatized mantle source in subduction geodynamic settings. A lot of authors (Faccenna *et al.*, 2011, and

reference therein) hypothesize the interaction with metasomatizing fluids from the near eolian subduction slab. Other possible explanation for the high H₂O content in etnean magmas could be: *i*) supercritical fluids carrying alkali Cl-complexes migrating from the deeper to the shallower portion of the pumbling system (Ferlito & Lanzafame, 2010; Ferlito *et al.*, 2014); *ii*) involvement of volatile-bearing phases (amphibole and/or phlogopite) in the partial melting of an heterogeneous and variably enriched mantle source (Beccaluva *et al.*, 1998; Viccaro & Cristofolini, 2008, Alesci *et al.*, 2013).

PETROGRAPHY

Mt. Etna rocks show peculiar petrographic features for each evolutionary stage. The tholeiitic samples have ophitic to poorly porphyritic textures with P.I. (Porhyritic Index) ranging from 5 to 15 vol.%. Phenocrysts, including olivine (on average 63%), clinopyroxene (21%), plagioclase (18%) and Cr-spinel (13%), are settled in a microcrystalline groundmass. Clinopyroxene ranges from diopside to salite in composition (Tanguy et al., 1997). High dimension plagioclase phenocrysts have labradoritic composition. Products and lavas from AAV show higher P.I. (on average 35-40 vol.%) than tholeiites with abundant and large labradoritic plagioclase phenocrysts (75%), followed by clinopyroxene (13%), amphibole (9%), Ti-magnetite (7%), and olivine (6%) in a glassy to microcrystalline groundmass. Amphiboles, founded in several samples (up to 25-30%) are abundant and markedly pleochroic. These optical characters conform to those of the Ti-rich calcic amphibole classified as kaersutite. Ellittico lavas are the most evolved terms emitted by Mt. Etna and show petrographic features similar to AAV ones. They have a porphyiritc texture (on average P.I. = 35-40 vol.%) with abundant plagioclase (on average 71%, from andesine to bytownite), olivine (15%), clinopyroxene (11%), and Ti-magnetite (5%) phenocrysts in a glassy to microcrystalline groundmass. Samples from Recent Mongibello have a more primitive character with lower P.I (on average 25-30 vol.%) and abundant olivine. Andesitic and labradoritic plagioclase is still the most common phase (on average 60%) followed by olivine (20%) clinopyroxene (15%) and Ti-magnetite (5%). Textural relationships between phenocrysts indicate early crystallization of olivine, clinopyroxene, and Ti-magnetite, followed by massive crystallization of plagioclase.

WHOLE-ROCK GEOCHEMISTRY

All lavas sampled in this work were plotted together with published data for major elements in a Total Alkali Silica diagram (Fig. 1). Two main trends are observable, a first one tholeiitic and a second one alkaline, that comprises AAV, Ellittico and Recent Mongibello products. Lavas from Recent Mongibello are the most primitive and are classified as hawaiites and mugearites.

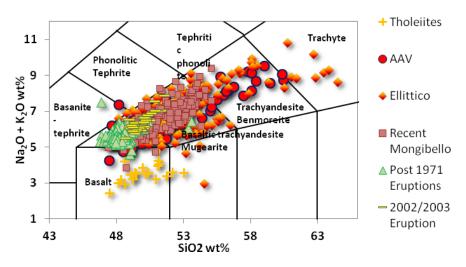


Fig. 1 - Total Alkali vs. Silica of the Mt. Etna products.

 K_2O/Na_2O vs. K_2O diagram (Fig. 2) point out the presence of two distinct alkaline trends, a first one sodic and second one potassic. Samples from AAV period are among the most evolved terms but always show a sodium affinity. In the last decade a lot of authors (Viccaro & Cristofolini, 2008 and reference therein) observed a shift from sodic to potassic alkaline terms starting from the 1971 eruption. This is shown in Fig. 2 where most of the post-1971 products fall in the K-alkaline series (trachybasalts and basaltic trachyandesites).

Many authors tried to justify this K-enrichment (that could not be related to simple crystal fractionation) suggesting several models that failed to explain the phenomenon satisfactorily. However, several lavas from Ellittico and pre-1971 Recent Mongibello are classified as potassic terms (Fig. 2) indicating that this shifting is not prerogative of the last 40 years (Ferlito & Lanzafame, 2010).

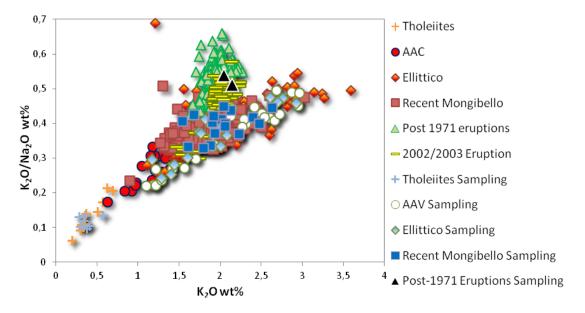


Fig. 2 - K₂O/ Na₂O vs. K₂O Archer Diagram for Mt. Etna products.

Envelopes of the analyzed samples (representative rocks of each magmatic suite) for both tholeiitic and alkaline types show a marked upward convexity with positive spikes for Th, U and La and negative in Rb, K, Hf, Ti and Y. The depletion in Hf and Ti is not so frequent in Na-alkaline magmas from intraplate geodynamic settings (Wilson, 1989). These anomalies are typical of the Etnean analyses present in literature, but a comparison between pre- and post-1971 lavas shows how the K-alkaline terms are instead enriched in Rb, K, and other LILE.

FRACTIONATION MODELING

An alternative method to melt-inclusions to obtain the primary magmas features is represented by the development of backward fractionation models (an "indirect method") that, starting from real and primitive analyzed magmas, allow to reconstruct the "primary" and un-fractionated compositions.

In this work two different kind of fractionation models are presented with the aim of *i*) describing the differentiation processes of each Etnean magmatic series and *ii*) reconstructing primary melts and compare them with bibliographic data. They were modeled by means of major and trace element mass balance calculations using major element whole rock and *in situ* mineralogical phases analyses (olivine, clinopyroxene, plagioclase and spinel). The least differentiated samples were chosen and used as starting melt for both backward and direct fractionation modelling. They were then used for modeling whole-rock trace element contents for the parental magma, using Rayleigh fractionation model (and relative Kd downloaded from the GERM database,

<u>http://earthref.org/GERM/</u>). Mineral proportions and total amount of fractionated material were then used to calculate the trace element contents of the differentiated magma.

Average fractionation modeling percentages from the primary (real for tholeiites and reconstructed for alkaline series) to the evolved compositions (Table 1) show similar relative proportions for phases of the alkaline suites. Tholeiites are the most primitive and include the separation of orthopyroxene and Cr-spinel (Table 1).

AAV, Ellittico and pre-1971 Recent Mongibello display similar amount of fractionated gabbroic material without considerable difference in the relative percentages of the mineralogical phases. Separated olivine ranges from 47.2 to 52.2%, clinopyroxene from 18.7 to 22.8%, plagioclase from 15.5 to 19.9% and Ti-Mt from 11.4 to 14.2%. Post-1971 model is quite different because the arrival magma (Pm2 from 2002-2003 Eruption, Giacomoni *et al.*, 2012) is less differentiated with a Mg# of 49.8% (Table 1).

Mg#	Thol. 72.4 - 52.4	AVV 66.8 - 34.3	Ellittico 66.6 - 42.6	pre-1971 66.2 - 35.9	post-1971 67.3 - 49.8
Срх	13.9	22.8	19.7	18.7	8.3
Орх	28.9	-	-	-	-
Plg	14.7	15.5	16.7	19.9	7.2
Sp	15.4	13.1	11.4	14.2	6.7
Tot	100	100	100	100	100
Tot fract. %	53.1	43.1	40.9	52.16	26.1

 Table 1 - Summary of the complete fractionation models (from the primary reconstructed magma to the evolved term) for

 each Etnean evolutionary period.

MELTING MODELING

Mt. Etna is one of the most studied volcano in the world, especially in the last 40 years; nevertheless, the nature of his mantle source is still debated because mantle xenoliths have never been found. The scarcity of direct information could be balanced through melt modeling that take into account the reconstructed primary and the whole-rock and *in situ* analyses of mantle xenoliths from the near Iblean magmatic province. In this context, Mt. Iblei mantle source, could represent a realistic paragenesis to take into account for comparison. In this work five models were developed, representative of each Etnean periods, to constrain the entire magmatic cycle. In addition "primary" and un-fractionated magmas, compatible with a direct origin by partial melting processes, were used. Only tholeiites show primitive features and do not necessitated of backward reconstructions to obtain the original composition. Mantle Source S_1 , from Beccaluva *et al.* (1998), was chosen for the tholeiitic modeling whereas S_2 was used for the alkaline suites reconstructions. This overview lets us to distinguish two main partialmelting regimes for the Etnean magmas one for the productions of tholeiitic magmas and one for the alkaline successive suites. The S_1 mantle source generates tholeiitic lavas by partial melting degrees in the order of 16-17%. The calculation shows negative olivine and high positive orthopyroxene and amphibole melting proportions. The S₂ peridotitic composition represents the mantle source of AAV, Ellittico and Recent Mongibello products. Primary reconstructed alkaline magmas result to be generated by about 7% of partial melting degree that is lower than in previous mentioned tholeiitic model. In this case, olivine is still negative in melting proportions but with lower percentages (from -13.7 to -10.3%), whereas less orthopyroxene (22-25.3%) and more clinopyroxene (29.6-31.8%) is necessary to take into account the primary alkaline melt composition. For this alkaline regime, the involvement of spinel in the partial melting is negative and amphibole reaches 55.8%. The largest difference is given by the presence of phlogopite in the alkaline groups melting, which is

reflected in the higher primary Na_2O and K_2O magma contents. Comparing pre- and post-1971 partial melting models, a higher contribution of phlogopite (from 9.79 to 13.6%, for the more recent primary reconstructed composition) is shown. This evidence can partially justify the different original K_2O wt.% contents observed prevalently in the last 40 years products.

CONCLUSIONS

This work furnished a complete overview of the entire evolutionary cycle of Etnean magmatism. The stratigraphically controlled sampling from Tholeiitic to Recent Mongibello periods gave us the possibility to investigate the variations in the petrographic and geochemistry features of the emitted magmas and in the eruptive styles. By means of these direct studies it was possible to reproduce deep fractionation processes and improve the knowledge on the Etnean feeding system. Mass balance modeling allowed to identifie five original magmas (Tholeiites, AAV, Ellittico, pre-1971 and post-1971 Recent Mongibello) with "primary" features, representing unfractionated terms. They were compared to melt inclusions data (from literature) showing realistic compositions. Starting from the reconstructed primary magmas the most evolved lavas for each series were obtained. On average an estimation of about 40% of material should be considered beneath the volcano taking account the entire volume of the products emitted by the volcano. According to Neri & Rossi (2002), if the whole volcano edifice amounts to 374 km³, about 150 km³ of magma should be left behind from the magma on its way from the mantle to the surface (Tanguy et al., 1997, hypothesize the beginning of magma fractionation at 10 Kbar pressure). As confirmed by seismic tomography a positive P-wave anomaly (Patanè et al., 2006) underneath the volcanic edifice is noticed and Allard et al. (2006) hypothized that the absence of significant magma emissions could be balanced by the presence of an un-erupted, 10 km wide, intrusive body extending from the crystalline basement for 5 km inside the lower crust (its volume could be 3-4 times greater than the exposed volcanic succession one). Patanè et al. (2006) suggested that magma ascent can occur through this plutonic body. This calculation allowed us to give a first estimation of the entire magma volume produced by the Etnean source in his magmatic evolution. However this assumption is in contrast to the volume estimation obtained by the fractionation modeling. The value of 150 km³, derived from mass balance calculations applied to the Neri & Rossi (2002) study, is about 9 times smaller than Allard et al. (2006) estimation. Ferlito et al. (2014) further support our hypothesize stating that is not necessary the presence of such a wide intrusive body to produce the volume of magma erupted and the massive magmatic gasses released. They suppose the presence of a volatile flushing inside the primitive magma that resides into the plumbing system. This process allows H₂O content to overcome the saturation threshold, exsolving and promoting eruption of primitive and volatile-rich magma. Another aim of this work was to investigate the Etnean mantle source, and it was possible only using Iblean mantle xenoliths from Beccaluva et al. (1998).

The results showed two evident different sources for tholeiites and alkaline suites that are attributable to Mt. Iblei modeling from Beccaluva *et al.* (1998). Post-1971, prevalently K-alkaline terms, derived probably from the same mantle source S_2 of pre-1971 products that melt in different proportions with a more involvement of phlogopite. This could partially explain the shifting to potassium affinity that is not prerogative of recent lavas but is evidenced in AAV and Ellittico stages too. Modal proportions of melted peridotite showed the same percentage of phlogopite in AAV, Ellittico and post-1971 models (about 13%) and a lower participation in pre-1971 calculation (about 9%). This is in agreement with Ferlito & Lanzafame (2010) that recognized a cyclic recurrence of potassium term in Mt. Etna magmatic evolution.

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