

## **GENESIS AND DIFFERENTIATION OF ANCIENT Mt. ETNA MAGMAS (ELLITTICO VOLCANO, 45-15 KA): A MULTIDISCIPLINARY APPROACH FROM GEOLOGY TO MELT INCLUSIONS**

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### INTRODUCTION

The Ellittico eruptive center is the first big central edifice in the volcanic history of Mt. Etna. It directly precedes the present-day eruptive phase of Recent Mongibello (RM), with the formation of a huge elliptical caldera in the last phases of its “life”. Products of the Ellittico are still well visible in several areas of the present-day Mt. Etna, with the best exposure along the walls of Valle del Bove (VdB). The whole of the characteristics of the Ellittico volcano resemble those of the RM, and the very fact that it developed in a limited time-span (45-15 ka) makes this center as an ideal natural laboratory of volcanic processes at Mt. Etna. In order to have a comprehensive insight on the evolution of the Ellittico, several points have been studied and discussed: 1) the mantle source of Ellittico magmas and their processes of partial melting; 2) the shallow plumbing system (geometry, depth of magma storage, differentiation processes); 3) the transition-phase between Ellittico and RM.

### GEOLOGICAL SURVEY

Geological survey allowed us to define a complete volcano-stratigraphic sequence of the Ellittico volcano (Fig. 1), divided in four major volcano-stratigraphic Units, here informally defined: the Serra delle Concazze (SdC) Unit, the Rocca della Valle (RdV) Unit, the Pizzi Deneri (PdN) Unit and the Piano delle Concazze (PdC) Unit (Fig. 1). Except for SdC and PdC Units (see below), all products show radial dips from the present-day Summit Crater area toward the lower flanks of the edifice, with directions and dip respectively ranging from N10-20°E to N70-80°E and from 25° to 10°. In the PdN area the sequence of the Ellittico is cut by the walls of an elliptical caldera having 4-5 km of diameter.

The SdC Unit crops out only at the base of the SdC3 section (Fig. 1) and is constituted by ~ 20 thin (up to 1 m) lava flows interlayered with thin layers of pyroclastic fall deposits and breccias. Its lowermost limit does not crop out, whilst the uppermost one is marked by a 15 m thick layer constituted by angular blocks in a coarse matrix (Fig. 1). Products of this Unit have a different orientation from the above products of RdV and PdN Units, dipping toward South and having N180° of orientation and 5-10° of inclination angle.

The RdV Unit constitutes the frame of the Ellittico volcanic edifice, with a maximum thickness of ~ 500 m. It is mostly made up of an alternating of lavas, pyroclastites and epiclastites. Lava flows constitutes about the 50% in height (Fig. 1), with a quite homogeneous thickness (1-3 m). Pyroclastic products constitute about the 35% of total height of the entire Unit (Fig. 1) and have been interpreted as fallout deposits, with only two levels recognized as pyroclastic flow deposits. Epiclastites, mostly interpreted as wet and dry lahars, constitutes about the 15% of the entire height of the RdV Unit, with single thickness up to 25-30 m (Fig. 1). Values of strike, dip and dip angle of this Unit (see above for the

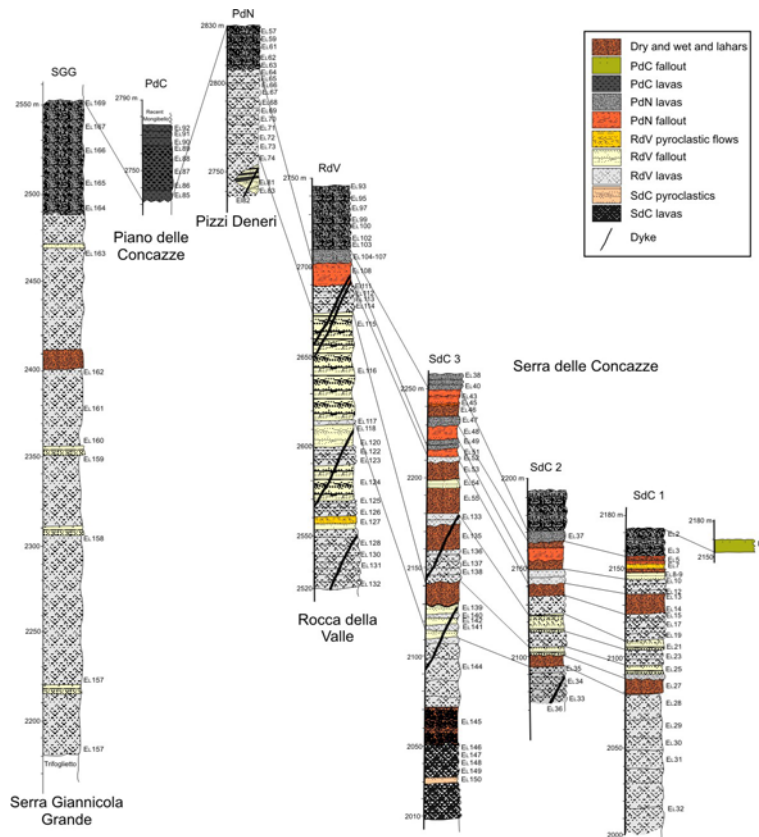


Fig. 1 - Stratigraphic sections and correlations of the volcanic succession of the Ellittico, cropping out on the northern and western walls of Valle del Bove. Labels of stratigraphic sections and samples are indicated.

entire NVdB) clearly suggest a same point of emission located in the area of the actual Summit Craters of Mount Etna.

The PDN Unit represents the highest part of the sequence of the Ellittico (Fig. 1) and constitutes the last eruptive phase prior to caldera-forming processes. The PdN Unit has the same radial orientations and dip of the RdV Unit and is mainly constituted by 1-2 m thick PI-rich porphyritic lava flows, locally named “Cicirara”, very uncommon at Mount Etna. Fallout deposits of the PdN Unit constitute < 5% of total height as they are limited to few levels of lapilli in a fine (< 1 mm) yellow ashy matrix at the base of Cicirara lava flows (Fig. 1).

The PdC Unit is located in the summit area (PdC area, Fig. 1). This 50 m thick Unit is constituted of 6 lava flows with very variable thickness (1.5-20 m) and a sub-horizontal (~ 5°) dip toward N100°E, with its basal flow unit (EL85 sample) considered as one of the first after the caldera-forming phase. A level of fallout pyroclastics (EL1 sample), outcropping on the northern flank of SdC and lying on Cicirara lavas, has been also attributed to this Unit (Fig. 1).

Faults are well visible on the NVdB, all dip toward SE with constant strike and dip angle (respectively N59°E to N72°E and 50-70°) and are normal with a left-lateral movement. A total of 51 dykes (up to 3 m in thickness) has been counted and measured, with N50-80°E directions of intrusion.

## PETROGRAPHY AND MINERAL CHEMISTRY

Lava flows of the Ellittico have a porphyritic texture with Porphyritic Index ranging between 10 and 60 (PI in vol.%). The mineralogical assemblage is constituted by phenocrysts of An<sub>38-85</sub> plagioclase and augitic clinopyroxene in similar proportions (~ 80 vol.% of total phenocrysts), followed by Fo<sub>51-90</sub> olivine (8-12 vol.%), Ti-magnetite oxides (< 3 vol.%) and apatite (< 3 vol.%). In 3 samples it has been recognized the occurrence of brown amphibole (< 1 vol.%) and in 1 sample (EL85) those of phlogopite (~ 3 vol.%). Mesostasis textures are quite variable, ranging from crypto- to holo-crystalline, with intersertal and pilotassytic structures among the most frequent. Groundmass is made by Pl (65-75 vol.%), Cpx (< 20 vol.%), Ol (< 5%) and Ti-mt (< 5%). The main petrographic difference between the volcano-stratigraphic Units is the variable size and proportions of mineral phases: for example, it can be clearly distinguished a group of Pl-rich porphyritic lavas (crystals up to 1.5-2 cm), locally known as “Cicirara”, which constitute the frame of the PdN Unit.

Due to their peculiarity, major elements oxides of the apatite and phlogopite crystals of the EL85 and EL87 samples (PdC Unit) have been analyzed with EMPA. Apatite crystals (~ 1 vol.%) have a prismatic and an acicular habitus and, due to their high F content, may be classified as fluorapatite. Euhedral brown mica occurs exclusively within lava vesicles of the sample EL85 as crystals 0.2 to 2 mm in size; their high F concentrations allow us to classify them as fluorophlogopite. The anionic positions are mainly occupied by F (~ 1.7 a.f.u.) and scarce Cl. Finally, these micas and the edges of lava vesicles in sample EL85 are surrounded by a 10 to 200 nm-thick film of a SiO<sub>2</sub>-rich colorless amorphous phase, formed by multi-stage accretion layers slightly different in composition.

Textural relationships indicate that olivine and Ti-magnetite are the first crystallizing phases, followed in turn by clinopyroxene, plagioclase, amphibole, apatite and phlogopite (at times).

## WHOLE ROCK GEOCHEMISTRY

Major elements concentrations were measured by means of XRF, whereas REE and trace elements by means of ICP-MS. The Ellittico lavas are constrained into the hawaiite-mugearite-benmoreite fields of the TAS diagram (Fig. 2), with pyroclastics that show a more scattered distribution. One of the most important features is a real compositional “jump” of the PdN lavas toward more evolved compositions. Averaged chondrite normalized REE of the products of the Units show a very similar pattern with a clear overall fractionation. The Primordial mantle (PM) normalized diagram confirms a slight enrichment in LILE and HFSE of the Ellittico rocks. Cl and F whole-rock concentrations of the EL85 benmoreite, measured by means of SEM-EDS raster analyses, are respectively of 0.20 wt.% and 0.34 wt.%, which are significantly higher than the data available on Ellittico benmoreites.

The isotopic compositions of Sr-Nd-Pb of 15 representative lava samples were measured by TIMS, whereas oxygen isotopic data for 10 selected samples were obtained after extraction by bromine pentafluoride.

The <sup>87</sup>Sr/<sup>86</sup>Sr ratio ranges between 0.703281 and 0.703423, with the two lava samples of PdC Unit (EL85 and EL87) that exhibit the more enriched Sr isotopic composition (Fig. 3). Although no evident correlations occur, a general increase of the <sup>87</sup>Sr/<sup>86</sup>Sr values with time was evidenced.

The <sup>143</sup>Nd/<sup>144</sup>Nd ratio ranges between 0.512877 and 0.512928 (Fig. 3), with a negative correlation with time. RdV values of <sup>143</sup>Nd/<sup>144</sup>Nd are almost constant and very similar to those of PdN lavas; EL85 and EL87 lava samples of the PdC unit also have similar values, ranging 0.512889-0.512900. In a

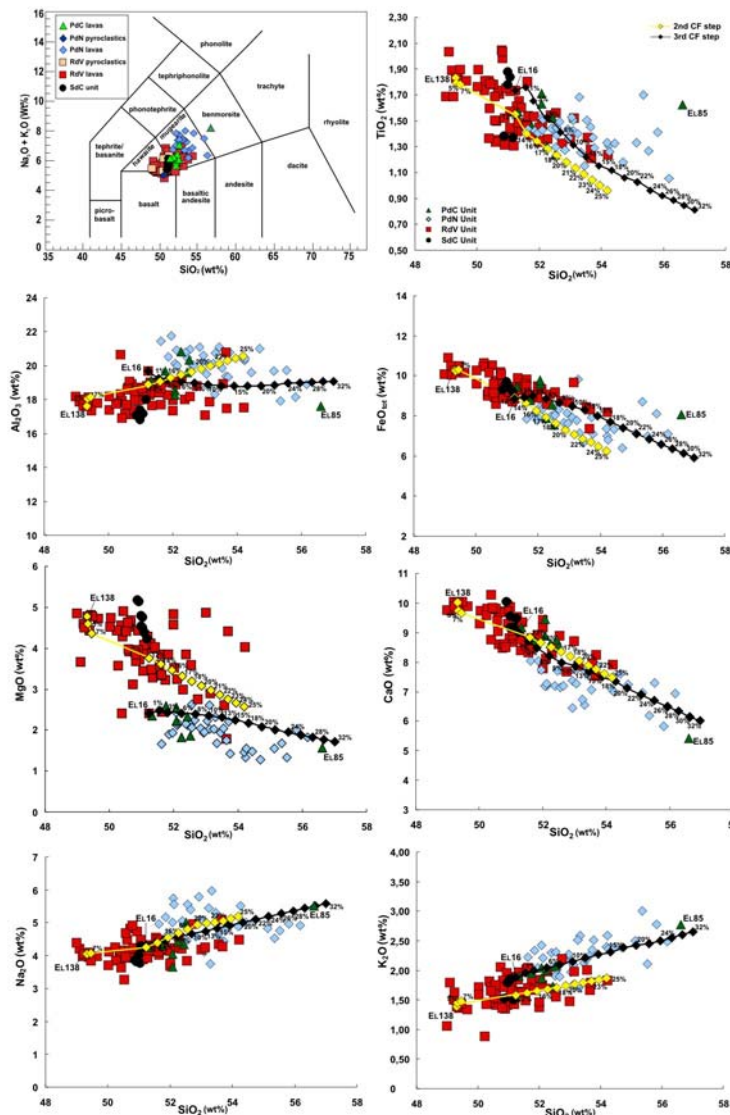


Fig. 2 - TAS and selected major elements variation diagrams of sampled products. With the yellow and black lines are indicated the 2<sup>nd</sup> and 3<sup>rd</sup> step of crystal fractionation simulated with MELTS.

$^{87}\text{Sr}/^{86}\text{Sr}$  vs.  $^{143}\text{Nd}/^{144}\text{Nd}$  space, analyzed samples define a marked negative correlation which lies along the mantle array and results well comparable to the whole Mt. Etna Sr-Nd isotope data set.

Pb isotope compositions for the Ellittico lava samples vary considerably.  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios range between 19.145 and 20.007,  $^{207}\text{Pb}/^{204}\text{Pb}$  ratios between 15.634 and 15.688,  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios between 38.912 and 39.691 (Fig. 3). The Pb-Pb isotope diagrams reveal a positive correlation between  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  with  $^{206}\text{Pb}/^{204}\text{Pb}$ , with the EL33 and EL37 samples (RdV and PdN units respectively), having the most depleted isotopic composition in lead.

The  $\delta^{18}\text{O}$  values for representative samples of the Ellittico eruptive center range between +6.7 and +7.5‰, which, although slightly higher, are well comparable to those of mantle derived magma. The highest enrichment in  $\delta^{18}\text{O}$  values occur in some RdV and PdN lavas and not in those of the PdC Unit, which are the most enriched in major and trace elements and in Sr-Nd-Pb isotopic ratios.

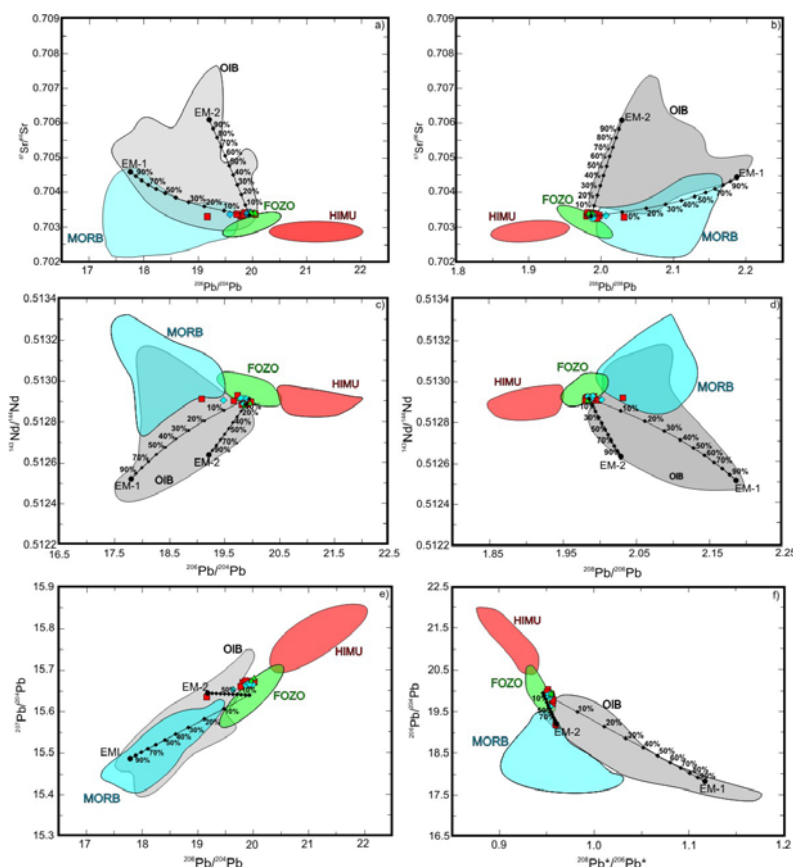


Fig. 3 - Pb vs. Sr, Nd and Pb isotope ratios for selected Ellittivo volcanic rocks. Data for fields from Stracke *et al.* (2005) and references therein. Legend as in Fig. 2. In the diagrams the results from modelling of a binary FOZO - EM-1 and FOZO - EM-2 mixing are shown. Data for FOZO, EM-1 and EM-2 end-member are derived from GeoRoc database (<http://georoc.mpch-mainz.gwdg.de/georoc>).

OLIVINE-HOSTED MELT INCLUSIONS

Major elements compositions of analyzed olivine phenocrysts and hosted Melt Inclusions (MI), plus their Cl and S contents were determined by means of SEM/EDS, whereas H<sub>2</sub>O and CO<sub>2</sub> contents by using  $\mu$ -FTIR. Unfortunately, only three pyroclastic products (EL8, EL54, EL124) resulted useful for this type of analysis. Olivines are Fo<sub>63-82</sub> and contain 20-120  $\mu$ m two-phases MI with brownish glass, opaque oxides and a contraction bubble. Only inclusions without opaque oxides were analyzed.

In the EL8 sample, MI show an evolved geochemical signature, low amounts of dissolved H<sub>2</sub>O (0.06-0.31 wt.%) and are CO<sub>2</sub>-free (Fig. 4); however, the high Cl and S contents (up to 0.47 and 0.15 wt%), show as these inclusions do not underwent a post-trapping degassing. In the EL54 sample, MI present a trend of differentiation along an ideal liquid line of descent, with negative correlations between SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, CaO and MgO. MI of the EL54 sample present high values of CO<sub>2</sub> (up to 1734 ppm) and of H<sub>2</sub>O (up to 1.32 wt.%; Fig. 4), which good agree with the high Cl and S contents. The EL124 sample inclusions have a similar trend with respect to the EL54 one, variable H<sub>2</sub>O (0.37-1.78 wt.%) and CO<sub>2</sub> (up to 1200 ppm; Fig. 4); their high Cl and S contents (up to 0.53 and 0.17 wt.%) show as these inclusions cannot be considered as degassed.

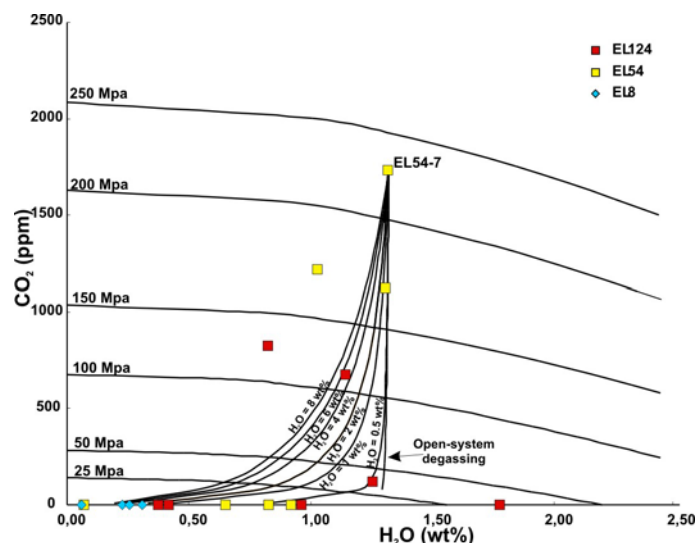


Fig. 4 - H<sub>2</sub>O vs. CO<sub>2</sub> contents in melt inclusions trapped in olivines of the EL8, EL54 and EL124 samples. Isobars and degassing trends were calculated using VOLATILECALC and for a temperature of 1140°C. 250 to 200 MPa were calculated at 47.5 wt.% of SiO<sub>2</sub>, 150-100 MPa at 48 wt.% SiO<sub>2</sub>, whereas 50 to 25 MPa isobars at 48.5 wt.%. Closed-system degassing curves are computed from 0.5 to 8 wt.% of initial gas phase coexisting with the melt at ~ 250 MPa.

## DISCUSSION AND CONCLUSIONS

### *The mantle source of the Ellittico volcano*

The main features of the mantle source of Mt. Etna can be obtained only through indirect studies (*e.g.* the isotopic ones), chiefly due to the lack of mantle xenoliths in its products. In order to be sure to have isotopic composition not modified by external process of contamination such as crustal assimilation, modeling through Langmuir binary mixing of this process between isotopic ratios of the Ellittico and a “Calabrian-like” continental crust was performed, confirming, as proposed by several authors, that crustal assimilation is not a relevant process at Mt. Etna.

Mineralogy and degree of partial melting of the Ellittico mantle source have been studied by using the *modus operandi* of Class & Goldstein (1997). Mantle-equilibrated volcanics of the Ellittico have been compared with the most primitive Etnean alkaline rock sample (et75 from Armienti *et al.*, 1988), as the behavior of their most incompatible trace elements could reflect those of their source. The “enrichment ratio” of Th ( $E_{Th}$ ; Class & Goldstein, 1997), calculated as:

$$E_{Th} = [ C_{Th,FL} ] / [ C_{Th,FH} ] = [ F_H \cdot (1 - (1 - F_H)^{1/D}) ] / [ F_L \cdot (1 - (1 - F_L)^{1/D}) ]$$

could be approximated to the value of  $F_H/F_L$  as  $D_{Th} \ll 0.001$ , and for the Ellittico magmas varies from 1.88 to 2.23. If a high degree of partial melting  $F_H$  of ~ 6-8% is assumed for the et75 sample, the  $E_{Th}$  of Ellittico magma is consistent with a  $F_L$  value of 3-4%.

With regard of mantle source mineralogy, the  $E_i$  has been esteemed for the other trace elements and has been plotted in diagram together with those of a Grt- and Sp-lherzolite and with an Amph/Phlog-peridotite (Fig. 5). Our results suggest the occurrence of amphibole and/or phlogopite, together with the “classical” mineral assemblage (ol, opx, cpx, grt), in the Ellittico mantle source.

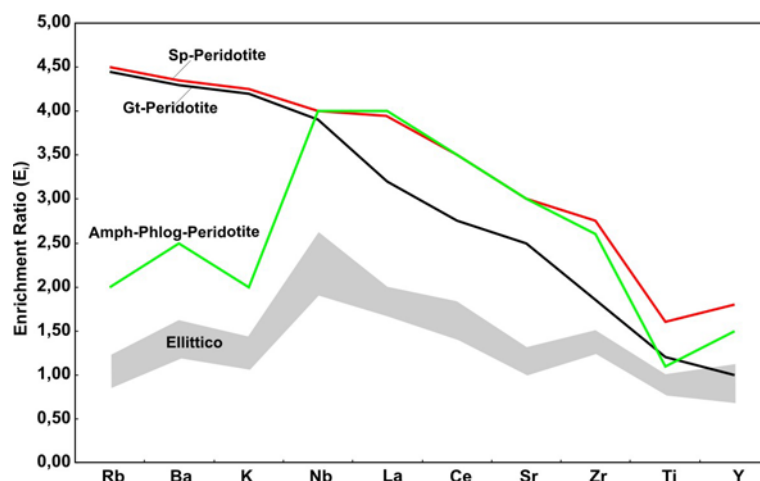


Fig. 5 - Enrichment ratio ( $E_i$ ) patterns calculated by partial melting of spinel (sp), garnet (grt) and hydrous-phase bearing peridotites (amphibole and phlogopite). Partial melting modeling was run at FL = 2%. Modal proportions are: spinel peridotite ol:opx:cpx:sp = 58:30:10:2; garnet peridotite ol:opx:cpx:grt = 60:25:9:6; hydrous phase bearing peridotite ol:opx:cpx:grt:phl:amph = 3:22:3:1:1. Best-fit for Ellittico volcanics is obtained by melting of a hydrous-phase-bearing peridotite.

The isotopic compositions of the Ellittico volcanics reveal as the principal mantle component is a FOZO one (Fig. 3), generally attributed to recycling of oceanic crust with a different composition and age than the rarer HIMU source. Furthermore, as the sole FOZO component seems to be not enough to account for the observed evolution, our modeling showed that the addition of variable amounts between 0 and 10% of an EM-1 - type component (generally ascribed to the recycling of ancient pelagic sediments) to a dominant FOZO is able to explain the isotopic variability of Ellittico magmas (Fig. 3).

#### *The shallow plumbing system of the Ellittico Volcano*

Whole rock geochemistry of the Ellittico volcano showed a wide compositional range. In order to have an idea about the possible ways of evolution of the Ellittico magmas, the role of differentiation processes, and in particular of crystal fractionation, on them has to be established. Here, an attempt of modeling of crystal fractionation (CF) of major elements into three steps has been performed by using MELTS software (Fig. 2).

The first step simulates conditions of deep crystallization from a magma formed by partial melting of the upper mantle and still in equilibrium with it. Simulations showed that a first phase of crystal settling of an ultra-mafic mineral assemblage occurs in the deepest portion of the Ellittico feeding system (Fig. 6).

The second step simulates a polybaric CF at shallow depth (9-5 km; Fig. 6). Results show as the compositional variation of the SdC and RdV Units are explained by fractionation of 5-26% of augitic Cpx (6-16%), Pl (4-19%;  $\sim An_{79}$ ), Sp ( $\sim 5\%$ ) and traces ( $< 1\%$ ) of Ap (Fig. 2). Considering that RdV lavas were mostly emitted from the Ellittico central craters, this mineral assemblage suggests that the shallow feeding system of this volcano had a geometry very similar to the present-day of Mt. Etna. Conversely, the PdN and the PdC Units do not follow the simulated liquid line of descent (Fig. 2), being



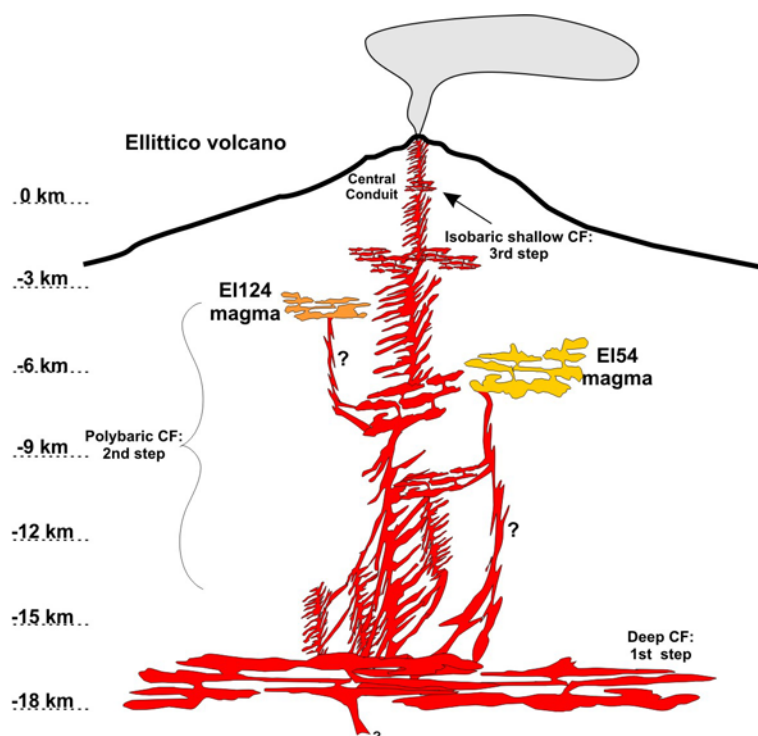


Fig. 6 - Sketch of the shallow Ellittico feeding system showing a possible model for the EL54 and EL124 magmas. Depths of magma ponding derive from VOLATILECALC simulations (see text).

enriched/depleted in most of the major elements. This step of CF has been also simulated and confirmed through a Rayleigh model for trace elements.

A further step of iso-baric CF at very shallow depth (< 3 km; Fig. 6) has been tried to explain the Cicirara lavas (PdN Unit), starting from the composition of one of the last RdV mugearites (EL16; Fig. 2). The resulting liquid line of descent (Fig. 2) good agrees with the compositional variability of the PdN lavas, as they could be explained with the fractionation of 1-28% of a variable mineral assemblage constituted by 4-24% of Pl ( $\sim An_{65}$ ), 2-10% of augitic Cpx and 1-6% of Ti-mt. However, also this step of crystallization cannot definitively explain the evolved composition of the EL85 sample as it turns to be enriched in  $TiO_2$ ,  $FeO_{tot}$  and  $K_2O$  (Fig. 2). This last step of CF has been also simulated and confirmed through a Rayleigh model for trace element. Therefore, a further step of CF added to the polybaric one could be able to explain the geochemical variation observed in the PdN Cicirara lavas. However, this simulation can provide only an indication on the real causes of formation of these Pl-phyric lavas; a further detailed work on compositional profiles of plagioclase phenocrysts is needed to understand the processes of differentiation, recharge and crystallization in the shallow feeding system of the Ellittico.

The study of olivine-hosted MI in pyroclastics of the Ellittico provided information on the volatiles content of the Ellittico magmas (maximum values:  $H_2O$  1.78 wt.%,  $CO_2$  1733.8 ppm; Fig. 4). The reliability of these values is confirmed by the Cl-S contents of the MI, which correspond to a near undegassed Etnean magma. Furthermore, these anomalous contents are indication of magma batches in closed-system conditions in the uppermost portion of the volcanic succession of the Ellittico (Fig. 4).



VOLATILECALC simulations (Fig. 4) confirmed such hypothesis and suggested depths at which shallow magma reservoirs were located. The reservoir of the EL54 pyroclastics ponded at 5-6.5 km (160-210 MPa), those of the EL124 sample at 3-4 km (100-120 MPa) below the vents, whilst a very shallow depth of entrapment of MIs can be inferred for the EL8 sample (Figs. 5 and 6). Our results revealed that geometry of the feeding system and depth of magma storage at Mt. Etna have not changed in the last 45 ka, with the magmas that, in their road to surface from the mantle source, pond at several levels corresponding to the main lithological discontinuities present beneath the volcano edifice (Fig. 6).

#### *The Ellittico-Mongibello transition phase*

The PdC Unit presents characters that certainly attribute it to an intra-calderic succession. The exceptional occurrence of F-rich minerals (*i.e.* fluorophlogopite and fluoroapatite) in the basal flow (EL85 sample) of the PdC Unit and in some coevals benmoreitic products at Mt. Calvario (low SW flank of Mt. Etna; Gianfagna *et al.*, 2007) could provide important clues for assessing some geochemical and volcanological aspects of the transition-phase between Ellittico and RM.

Crystal fractionation cannot explain the EL85 lava compositions, as it results selectively enriched in Ti, Fe, K, Ba, Rb, La, Sm, Nd with respect to the calculated curve of melt evolution. Also measured F and Cl contents showed an anomalous high amount in such elements. The selective enrichment of these elements may be an evidence of particular processes of differentiation, such as the volatile-induced differentiation. This process suggests a volatile transfer (metal-halogen complexes) from a deeper more basic and hotter magma toward an uppermost one, which is therefore selectively enriched in some elements. The last phases of “life” of the Ellittico eruptive center good agree with the model of volatile-induced differentiation as the residual “PDN-like” magma in the shallow feeding system of the Ellittico could have evolved toward a “EL85-like” one, which was in turn metasomatized by upward migrating volatiles. This occurred also into localized and peripheral portion of the volcano, as testified by the occurrence of F-rich minerals in the Mt. Calvario area.

The occurrence of the fluorine-bearing phases and the SiO<sub>2</sub>-rich amorphous phase surrounding the fluorophlogopite crystals within vesicles, testify their nucleation and grown during and/or after the lava emplacement. During the final stages of crystallization (syn- and/or post-eruptive), the high solubility of F even at low pressure joined to the high P and K concentrations in the melt, allowed first the crystallization of fluorapatite in the groundmass followed in turn by fluorophlogopite within the lava vesicles, probably in a very late stage of “pneumatolytic” post-eruption growth. Fluorophlogopite crystallization has been followed by condensation of a SiO<sub>2</sub>-rich amorphous phase, consequence of the high amount of F available in the system.

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