

Mineral chemistry profile: a valuable approach to unravel magma mixing processes in the recent volcanic activity of Stromboli, Italy

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ABSTRACT. — A mineral chemistry study including compositional zoning profiles on clinopyroxene and plagioclase has been performed on pyroclastic deposits of recent Stromboli (with an age of about 2-3 ka), erupted just before the setting of the typical present-day Strombolian activity (Post-Pizzo series). The mineral chemistry characterisation of samples from the bottom and top of the Post-Pizzo series has revealed a complex magmatic history recorded by mineral phase compositional variations.

These data suggest that the initial phase of the eruptive period of Post-Pizzo series was characterised by repeated arrival of mafic magmas emphasized by several changes in the crystal compositions. After the magma hybridization, the system nearly recovered its initial composition by associated continuous fractional crystallisation, thus establishing a nearly steady-state dynamics of the magma system. The arrivals of mafic magma batches became more important during the late Post-Pizzo eruptive period, leading in the final stage to a more mafic magma composition, similar to that of the basaltic products erupted by the present-day activity. This plumbing system behaviour reminds the dynamics driving the pre-eruptive processes responsible of the present-day Strombolian activity. Accordingly, the Post-Pizzo series seems to represent the period during which the magmatic conditions for the present-day activity were developed. The micro-analytical approach using zoning profiles can be considered a powerful tool in

revealing magma mixing processes and in helping to clarify the dynamics of magmatic systems.

RIASSUNTO. — Il presente lavoro riguarda lo studio microanalitico dettagliato volto alla determinazione sia delle caratteristiche composizionali delle fasi mineralogiche, sia delle variazioni composizionali lungo profili nucleo-bordo su clinopiroseni e plagioclasti. Tale studio è stato condotto sulle rocce della sequenza piroclastica dello Stromboli recente (serie Post-Pizzo, con età intorno a 2-3 ka) che è stata messa in posto poco prima dell'inizio dell'attuale attività vulcanica Stromboliana. La caratterizzazione composizionale delle fasi mineralogiche costituenti i campioni alla base e al tetto della sequenza piroclastica della serie Post-Pizzo ha messo in evidenza una complessa storia evolutiva.

I dati indicano che la fase iniziale della serie eruttiva del periodo Post-Pizzo è stata caratterizzata da ripetuti arrivi di magmi più femici, come testimoniato dalle brusche variazioni composizionali delle fasi mineralogiche. Dopo il completo mescolamento, il sistema riacquisiva la sua composizione iniziale attraverso continui processi di cristallizzazione frazionata, stabilendo così una dinamica di tipo stazionario. L'arrivo di magma femico nel sistema più superficiale ha probabilmente assunto una maggiore importanza nella fase finale del periodo eruttivo Post-Pizzo, determinando lo stabilirsi di un magma con composizione più femica e simile a quella dei prodotti basaltici eruttati dall'attuale attività Stromboliana. Questo comportamento del

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sistema magmatico ricorda la dinamica dei processi pre-eruttivi che generano l'attività vulcanica attuale. Pertanto, la serie Post-Pizzo sembra rappresentare il periodo durante il quale si svilupparono, nel sistema magmatico, le condizioni per l'instaurarsi della presente attività Stromboliana. L'approccio microanalitico, con la determinazione dei profili di zonazione composizionale delle fasi mineralogiche, rappresenta uno strumento fondamentale al fine di mettere in evidenza processi di mescolamento tra magmi e chiarire la dinamica dei sistemi magmatici.

INTRODUCTION

Igneous mineral phases usually vary their chemical compositions with changing of physical and/or chemical conditions of crystallization. It is possible to connect each zone and compositional change in crystals with formation conditions and interpret them in term of evolution and plumbing system dynamics. Plagioclase and clinopyroxene are particularly useful. Major element zonation in plagioclase reflects changes in magma composition, temperature, pressure and volatile content (Tsuchiyama, 1985; Smith and Brown, 1988; Johannes *et al.*, 1994). Combining major element with trace element gives a powerful tool for deciphering the origin of zoning (Giletta and Casserly, 1994; Ginibre *et al.*, 2002; Pietranik *et al.*, 2006). The dependence on crystal chemistry and crystallization conditions of distribution coefficients of trace element (Sr, Ba and Fe) in plagioclase have been experimentally constrained (Ren *et al.*, 2003; Lundgaard and Tegner, 2004). Complex zoning texture are commonly shown by clinopyroxene from volcanic rocks (e.g., Dobosi, 1989; Simonetti *et al.*, 1996; Morgan *et al.*, 2004) and have been variably ascribed to Fe-Mg diffusion during decompression (Morgan *et al.*, 2004), to magma mixing (Simonetti *et al.*, 1996; Cioni *et al.*, 1998), to mingling processes and to polybaric crystallization (Francalanci *et al.*, 2005). In particular, compositional gradients of Fe-Mg diffusion in clinopyroxene have been used to determine pre-eruption residence time of crystals (Morgan *et al.*, 2004), whereas chemical and isotopic crystal profile have been proved to be useful in constraining the geometry of the plumbing system (Francalanci *et al.*, 2005).

Micro-analytical techniques are extremely useful in providing spatial resolution needed to determine temporal changes recorded by mineral phases in volcanic rocks. Mineral profile technique, aimed to track mineral chemistry variations during growth of volcanic mineral phases, have been recently used (e.g., Chertkoff and Gardner, 2003) in order to constrain timescale of magma processes.

This paper reports the results of a microprobe study with mineral profiles on clinopyroxene and plagioclase, applied to the juvenile components of a recent pyroclastic sequence (Post-Pizzo series) from Stromboli. The peculiarity of this Post-Pizzo activity, occurred about 2-3 ka ago, is that its plumbing system dynamics seems to be the precursor dynamics of the present-day Strombolian activity. The micro-analytical approach has demonstrated to be an important tool in tracking and deciphering changes of crystal formation conditions pointing to recognise key processes of magma evolution.

GEOLOGICAL SETTING AND SAMPLE SELECTION

Stromboli is the northernmost island of the Aeolian island arc in the Tyrrhenian sea. The subaerial part of the main cone was built up during the last 100 ka (Gillot and Keller, 1993) through mainly effusive activity and minor explosive eruptions. The volcanological history of Stromboli was characterised by seven main periods of activity alternated with several caldera, flank and sector collapses. In particular, four collapses affected the NW part of the cone after 13 ka, leading to the formation of the Sciara del Fuoco scar and the crater terrace, where the present-day activity takes place (Hornig-Kjarsgaard *et al.*, 1993; Pasquarè *et al.*, 1993; Tibaldi, 2001) (Fig. 1). The rock composition displays large variations, from calc-alkaline (mainly basaltic-andesites), to potassic-alkaline (potassic trachybasalts and shoshonites), through high-K calc-alkaline (high-K basalts to high-K andesites) and shoshonitic (shoshonitic basalts to few trachytes) (e.g., Francalanci *et al.*, 1989; Hornig-Kjarsgaard *et al.*, 1993). The Recent period of activity, younger than 5.6 ± 3.3 ka (Gillot and Keller, 1993), mainly includes the shoshonitic basalts of the Pizzo Sopra la Fossa pyroclastic cone, the high-K basaltic lavas of S. Bartolo and

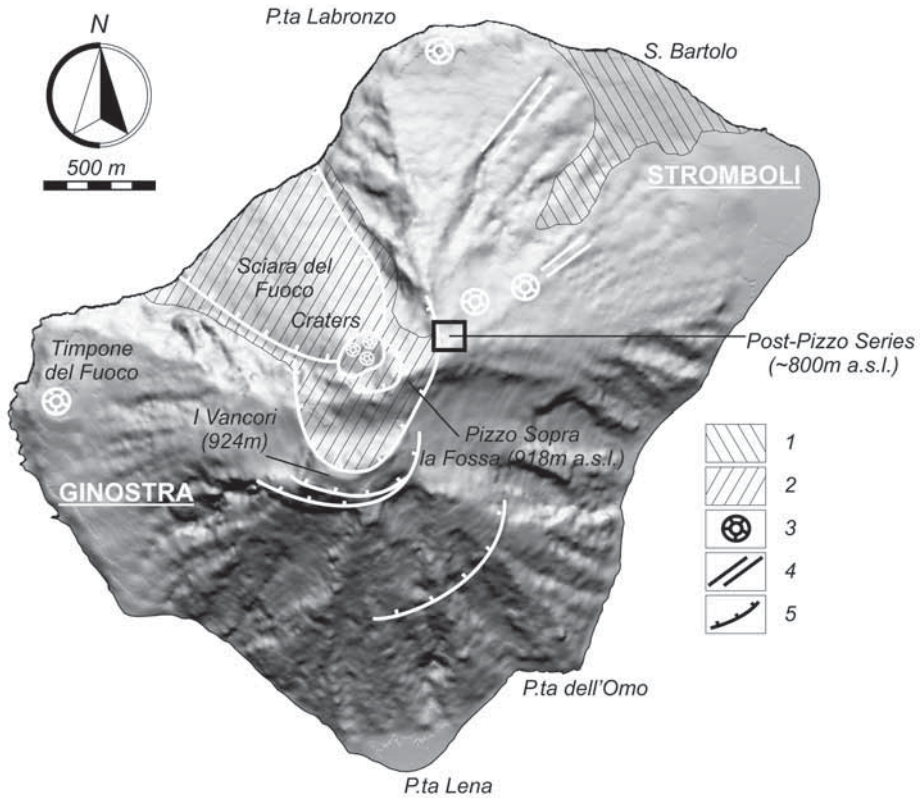


Fig. 1 – Topographic map of the subaerial part of Stromboli volcano with reported deposits of the Recent period (from Hornig-Kjarsgaard *et al.*, 1993) and the tectonic structures (from Pasquarè *et al.*, 1993). Legend: 1, San Bartolo lavas; 2, Pizzo Sopra la Fossa pyroclastic deposits and products of the present-day activity; 3, eruptive vents; 4, eruptive fractures; 5, caldera and sector collapses. Modified from Francalanci *et al.* (2004).

the products of the present-day activity being shoshonitic basalts in composition.

A 2 meter thick series of pyroclastic deposits has been also recognised between the Pizzo Sopra la Fossa deposits and the present-day products (Post-Pizzo series), cropping out on top of Liscione in discordance with Upper Vancori and Pizzo Sopra la Fossa deposits (Fig. 1). The latter deposits, in particular, are here represented by a small outcrop of yellowish, fine-grained and thinly stratified pyroclastic surges, similar to the surges found on the top of Pizzo Sopra la Fossa cone. This outcrop is nearly vertically cut by the Pizzo sector collapse and the Post-Pizzo series is emplaced in clear discordance at the contact with the collapse surface. The Post-Pizzo series is

constituted by levels of grey scoriaceous spatters with reddish surfaces and a variable thickness between 20 to few cm, which sometimes also form quite continuous strata. They alternate with thin and discontinuous layers of yellowish and massive fine-grained tuffs. The uppermost scoriaceous spatters nearly form a continuous stratum mantling the previous topography, and they are covered by the widespread “cow dung” scoriaceous bombs emplaced by the paroxysms of the present-day activity. These spatters testify the occurring of lava fountain activity, more energetic in respect with the present-day Strombolian activity. The eruption period of the Post-Pizzo series, with an inferred age of 2-3 ka (Gillot and Keller, 1993; Rosi *et al.*, 2000; Arrighi *et al.*, 2004), is deduced by its stratigraphic

position, directly between the deposits of Pizzo Sopra la Fossa cone and the scoriaceous bombs of the present-day activity paroxysms.

The present-day Strombolian activity usually consists of periodic moderate explosions ejecting around the craters black scoriaceous bombs, lapilli and ash. This activity is sometimes broken by effusive eruptions and more energetic explosions (paroxysms). The usual Strombolian activity and lava flows are fed by a volatile-poor, highly porphyritic magma, whereas a volatile-rich magma, with a very low phenocryst content, is also erupted as light pumice during paroxysms (Bonaccorso *et al.*, 1996; Francalanci *et al.*, 1999, 2004; Bertagnini *et al.*, 1999). The highly porphyritic magma resides and evolves in a continuously erupting, crystallising and replenished shallow reservoir, in which a steady-state condition is maintained. The volatile-rich magma represents the replenishing magma from a deeper reservoir. Mixing with refilling fresh magmas plus fractional crystallisation are, therefore, the pre-eruptive evolutionary processes of the magmas feeding the present-day activity (Francalanci *et al.*, 1999, 2004, 2005; Métrich *et al.*, 2001). The occurrence of these processes seems to have been crucial for the onset of the persistent Strombolian activity, which began between III and VII century A.D. (Rosi *et al.*, 2000). To shed light on the processes leading to the setting of the present-day persistent activity, we undertook a detailed micro-analytical study of the rocks from the Post-Pizzo series which were erupted just before the present-day products. The pre-eruptive processes recognised along the Post-Pizzo series will be useful for understanding how the dynamics of the plumbing system precursor of the present-day activity started.

The Post-Pizzo pyroclastic sequence has been sampled in stratigraphic order to have good timescale constraints. The micro-analytical study with the determination of mineral zoning profile has been performed on two black scoria samples belonging to two different levels of scoriaceous spatter strata: one sample is from the bottom (STR276) and the other from the top of the sequence (STR275). The choice of the samples at different stratigraphic level led to a fully evaluation of the variations in the mineral chemistry and favoured their interpretation in term of changes in

crystallisation conditions, evolution and plumbing system dynamics.

ANALYTICAL METHODS

Chemical compositions of mineral phases were determined using a microprobe JEOL 8600 Superprobe at CNR-IGG of Florence, Earth Science Department, University of Florence. The microprobe is equipped with four spectrometer and operating conditions are 15 kv and 10 nA. Matrix effects were corrected following the Bence and Albee (1968) method. Analytical data on reference samples show a good precision with a coefficient of variation lower than 3% on major elements, in accordance with estimated precision and accuracy given by Vaggelli *et al.* (1999).

Chemical compositions of crystal cores and rims were determined on olivine, clinopyroxene and plagioclase for a total of 58 crystals analyzed from the two selected samples. Representative analyses are given in table 1. The compositions of outer cores and inner rims were also determined on the larger crystals. On selected clearly zoned crystals of clinopyroxene and plagioclase, mineral compositions were determined along traverse of mineral profile from core to rim using 10 μm spacing between each point of analysis, for a total of 70-200 spots on single crystals. This allowed to obtain a complete zoning profile from core to rim of clinopyroxene and plagioclase, also permitting an estimation of the width of zoned bands. With a 5 μm spot size and 10 μm spacing, the resolution of each point is fairly good ensuring a complete covering of a traverse with limited overlapping between each point. When dealing with step-scanning technique it is necessary to consider the convolution effect, which depends on the excitation process and instrumental factor. As shown by Ganguly *et al.* (1988), however, the convolution effect decreases with the increasing length and decreasing value of standard deviation and is negligible for a profile length of about 15 μm .

The crystals for chemical profiles were chosen among larger and clearly zoned phenocrysts, with the aim of reconstructing the history and growth conditions of crystals and thus deciphering variable physical-chemical conditions of the

magma plumbing system during the Post-Pizzo series emplacement.

RESULTS

The rocks of the Post-Pizzo series are characterised by quite high porphyritic index (~25-30%). Plagioclase, clinopyroxene and olivine constitute the mineral phases present in all samples of the sequence. These phases are found as phenocrysts and micro-phenocrysts as well as in the groundmass. Plagioclase is the most abundant phase followed by clinopyroxene, although the latter is found as larger phenocryst. Phenocrysts are mainly constituted by clinopyroxene and olivine both as single crystals and glomeroporphyritic aggregates, whereas plagioclase prevails among the micro-phenocrysts and in the groundmass laths. Zoning of clinopyroxene phenocrysts are well evident under petrographic observation. The diopsidic composition is locally found as cores and/or light-coloured bands. Plagioclase crystals often show sieved textures in repeated zones around the cores. No evident disequilibrium textures between mineral rims and the groundmass are present.

The bottom sample STR276 is a shoshonite with 53.1 wt.% of silica and 2.8 wt.% of K_2O , whereas the top sample STR275 is a shoshonitic basalt with $SiO_2 = 49.6$ wt.% and $K_2O = 2.1$ wt.%. The two samples are also well differentiated on the basis of CaO and MgO contents, with bottom sample having 8.9 wt% of CaO and 4.2 wt% of MgO, whereas the top sample has CaO of 10.8 wt% and MgO of 6.3 wt%.

Chemical compositions of olivine, clinopyroxene and plagioclase have been determined for several crystals from both samples, for a total of 58 crystals (Table 1). The analysed crystals span over a range of sizes belonging to phenocrysts, micro-phenocrysts and groundmass populations. This ensures a fairly good representativeness of crystal population and help to monitoring changes of magma chamber conditions during crystallization.

Olivine of the top sample (STR 275) is definitively more forsteritic (Fo_{70-73}) in respect with olivine belonging to the bottom sample (STR 276) (Fo_{61-68}). In addition, olivine from the top sample is quite homogeneous in composition, whereas

olivine crystals from the bottom sample show slightly more variable compositions (Fig. 2a).

The differences in composition among clinopyroxene crystals between the bottom and the top samples are less straightforward. Indeed, clinopyroxene from the top sample spans from Mg# [molar $Mg/(Mg + Fe^{2+})$] of 0.71 to 0.90, whereas that from the bottom sample has Mg# ranging from 0.70 to 0.86. The latter, moreover, shows a clear bimodality in composition with lower Mg# in the crystal cores and rims (Mg# = 0.70-0.75) in respect with intermediate portion of crystals (Mg# = 0.79-0.86) (Fig. 2b). Comparing only the rim compositions, which are considered to represent the compositions in equilibrium with the groundmass, the clinopyroxene rims of the bottom sample show lower Mg# than those of the top sample (Fig. 2b).

Plagioclase crystals from both samples show a variable composition and are less distinguishable between the two samples. Plagioclase from the top sample ranges between Anorthite 36-83% (An_{36-83}), whereas those from the bottom sample are slightly less variable in composition (An_{51-91}) (Fig. 2c). Groundmass crystals are generally the less anorthitic plagioclase of each sample, with An_{40} and An_{62} in the top sample and An_{51} and An_{55} in the bottom sample. Plagioclase rims of the top sample are An-richer than those of the bottom sample. Plagioclase populations of the bottom sample are characterised by compositional bimodality which is slightly different from what observed for the clinopyroxene population of the same sample. Two different crystal populations are evident also in this case: the first one is characterised by crystal rims and few cores having An_{55} to An_{62} , the second one is characterised by several cores and subordinate rims having An_{72-91} (Fig. 2c).

On selected crystals, core to rim compositional profiles on plagioclase and clinopyroxene from both samples have been performed. Plagioclases of the sample collected at the bottom of the Post-Pizzo series are characterised by An contents variable from 52 to 86% (Fig. 3). Although plagioclase compositions are quite variable from core to rim, no clear systematic pattern of such variations is evident. Plagioclase 1 (p11) shows a general normal zoning with an An-richer core (up to An_{86}) than the rim (An_{52-60}). The first 0.3 mm of the core-rim profile show a constant composition,

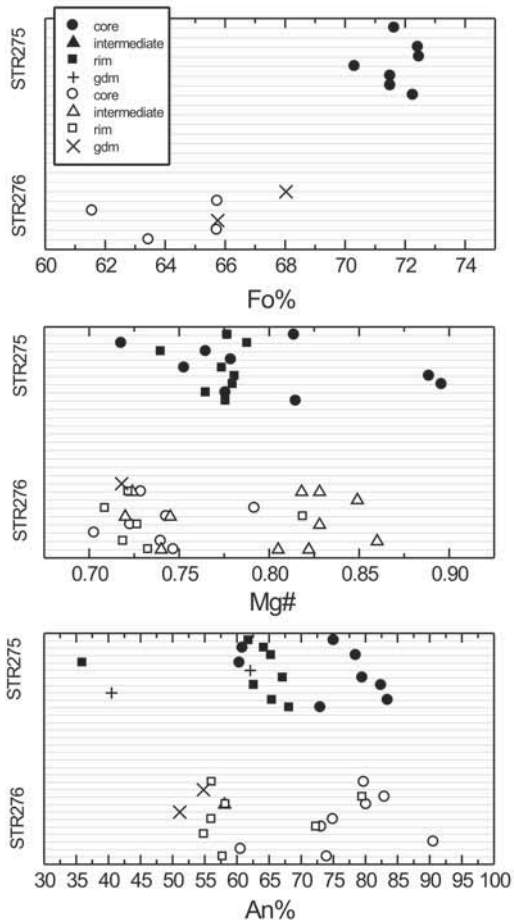


Fig. 2 – Core-rim compositional variations in olivine (a), clinopyroxene (b) and plagioclase (c) crystals of STR275 (top sample = filled symbols) and STR276 (bottom sample = open symbols) samples, using Fo%, Mg# and An% content, respectively. Core-rim compositional variations of each single crystal are reported along the same horizontal line. Compositions of groundmass (gdm) microlites are also shown.

then the chemical profile of this crystal is more complex showing an oscillatory zoning. The zoning profile of plagioclase 2 (p12) is simpler, with a variable pattern of composition from core to outer-core (An_{56-84}) and the An-richer compositions characterising the inner part of the crystal. This suggests that there is no any clear zoning pattern revealed by plagioclases, at least for the portion

of crystal analysed. It is worthy noting that the bimodality in composition, with a compositional gap at 62-72 An%, shown by distinct analyses on cores and rims of plagioclase crystal population (Fig. 2c) is not evident from mineral profile of the two analysed phenocrysts, which indeed span the whole range of compositions between An_{86} and An_{52} . It is possible that the compositional gap is more apparent than real due to the fact that in the case of punctual analysis only cores and rims have been analysed thus “sampling” the most probable composition among cores and rims.

Clinopyroxene crystals from the bottom sample show quite different compositional patterns. Core-rim zoning profiles performed on two different crystals show complex patterns with clear oscillatory zoning from Fe-richer composition of cores and rims ($Mg\# = 0.70-0.74$) to Mg-richer composition ($Mg\# = 0.79-0.86$) of intermediate (outer core or inner rim) zones of the crystals. In particular, clinopyroxene 1 (cpx1) is characterised by two peaks of Mg-rich compositions shown by the intermediate parts of the crystal, whereas the rim is even Fe-richer than the core, with a smooth decreasing of Mg# in the last 350 μm analysed (730 μm is the total length of core-rim profile). On the other hand, crystal 2 (cpx2) show a more complex and asymmetric pattern, with a general increase of Mg# from core to rim (0.72 to 0.83) along the profile 3. This increase, however, is not continuous, but it is characterised by several peaks (at least 3) of progressively Mg-richer compositions. Each peak is quite well defined with an almost constant width of 200 μm . Along the profile 2 of cpx2, after a 300 μm core with Mg# of 0.71-73, there is a quite large intermediate zone (400 μm) with high Mg# (0.78-0.82), followed by a 100 μm rim with composition similar to the core.

The mineral chemistry analyses have shown that the top sample is characterised by quite uniform composition of minerals. Indeed, few large variations were observed in phenocrysts and micro-phenocrysts of plagioclase and clinopyroxene. For this reason, only one zoning profile on clinopyroxene has been performed on this sample. The choice of analyzing a profile of a clinopyroxene is devoted to the fact that the clinopyroxene zoning is usually larger than that of plagioclase. The chemical zoning profile of a clinopyroxene from the top sample is definitively

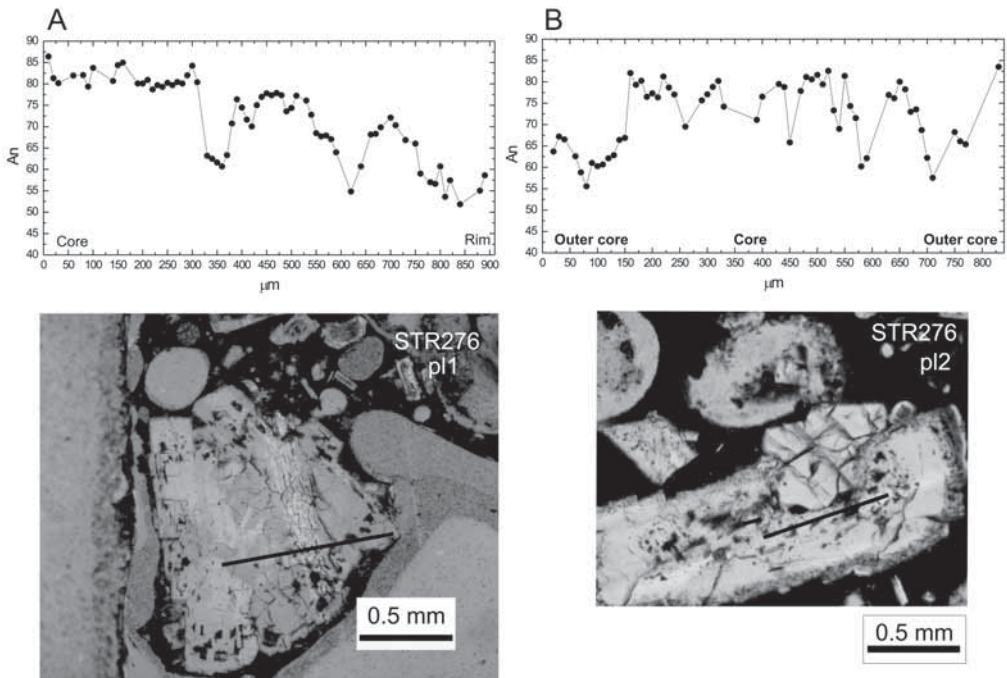


Fig. 3 – Chemical zoning profiles of plagioclase crystals of STR276 sample (bottom sample of the analysed sequence of the Post-Pizzo series). Variation of the An% contents is plotted versus the length of the mineral profile shown by the heavy line in the microphotograph of the corresponding analysed mineral. A) plagioclase 1 (pl1): the length of the traverse is 900 μm and 67 analyses were performed. This profile crosses the mineral from core to rim; B) pl2: the length of the traverse is 830 μm and 59 points were performed.

simpler (Fig. 5). This is a large clinopyroxene (2 mm core-rim length) characterised by a quite smooth chemical profile and a slight increase of Mg# from core (0.75) to rim (0.76-0.77). Only one narrow zone with Mg# down to 0.71 is present (Fig. 5).

DISCUSSION AND CONCLUSION

Chemical composition of mineral phases gives precious indications regarding their growth history; thus it is possible to infer variations occurred in the magma chamber during the crystallization. Plagioclase is the most sensitive mineral phases concerning variations in physical (i.e., pressure and temperature) or chemical conditions (Smith and Brown, 1988; Johannes *et al.*, 1994). On the

other hand, mineral chemistry of clinopyroxene is less sensitive to variations of physical conditions, but it is a good indicator of chemical changes in the magma plumbing system (Dobosi, 1989; Simonetti *et al.*, 1996; Cioni *et al.*, 1998; Morgan *et al.*, 2004). Olivine, given its simple structure promptly records the variable physical and/or chemical conditions which might occur in the magma chamber during the crystallization, thus a rapid equilibrium is favoured (Philpotts, 1990). Polybaric crystallization and decompression are the main causes of pressure and temperature variation and they represent, along with volatile contents, one of the main factors influencing plagioclase chemistry. Magma mixing and mingling processes can determine compositional changes and temperature variations of variable intensity in the magma chamber, thus affecting not

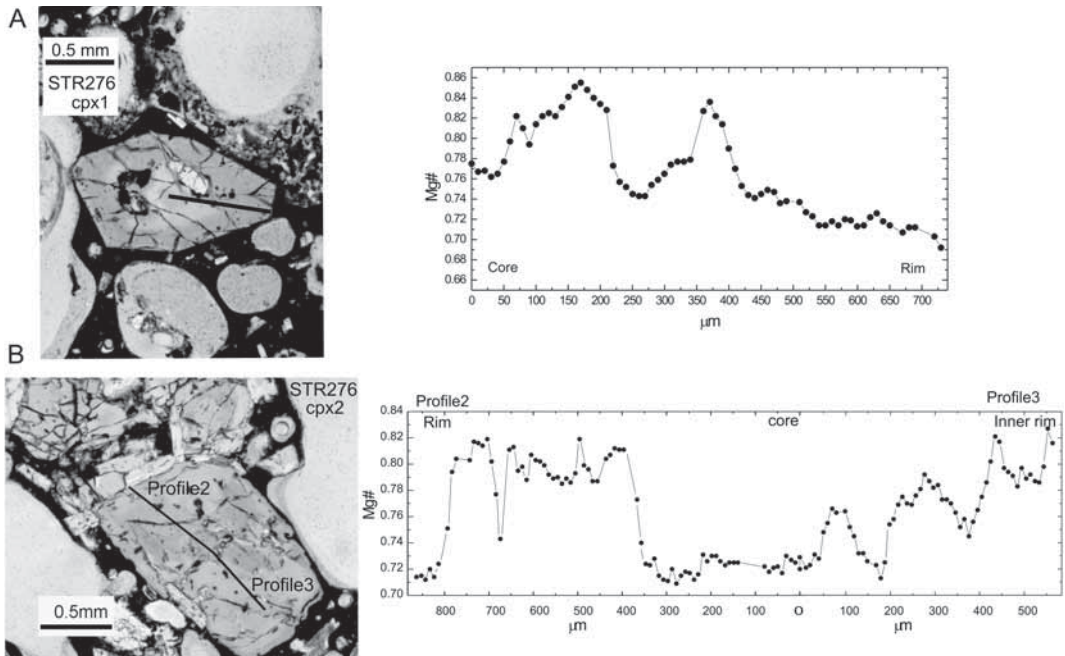


Fig. 4 – Chemical zoning profiles of clinopyroxene crystals of STR276 sample (bottom sample of the analysed sequence of the Post-Pizzo series). Variation of the Mg# contents is plotted versus the length of the mineral profile shown by the heavy line in the microphotograph of the corresponding analysed mineral. A) clinopyroxene 1 (cpx1): the length of the traverse is 740 μm and 49 analyses were performed. The profile crosses the clinopyroxene from core to rim; B) cpx2: two different profiles (profile 2 and profile 3), consecutive one to each other, cross the mineral from a rim to the other inner-rim. A total of 132 points of analysis have been performed for a total length of these profiles of ~ 1.46 cm.

only the composition of the crystallizing mineral phases but in more extreme cases even the type of mineral phases.

The mineral phases analysed on the rocks of the Post-Pizzo series have shown quite large compositional variations, which are higher within the single samples in respect with the variations found between the two samples. These characteristics suggest a complex plumbing system dynamics and they will be interpreted in the light of pre-eruptive magmatic processes. It can be reasonable to suppose that the general main compositions of the mineral rims represent the compositions in equilibrium with the liquid just before the eruptions. Olivine are generally not zoned and the olivine crystals from the top sample are clearly Fo-richer than the olivine crystals from the bottom sample (Fig. 2a), suggesting a less

evolved liquid composition for the top sample. This indication is clearly supported by both clinopyroxene and plagioclase populations (Fig. 2 b and c). Indeed, rims from the top sample are Mg-richer and An-richer, respectively, in respect with crystal rims of the bottom sample. The evidence that crystals from the top sample grew in a less evolved magma in respect with the mineral host magma of the bottom sample, perfectly agrees with the whole rock chemistry. Indeed, the top sample (STR 275) has a basaltic composition, whereas the bottom sample (STR 276) is a shoshonite. A decreasing degree of magma evolution from the bottom to the top of the Post-Pizzo sequence is, therefore, present.

Clinopyroxene crystals from the bottom sample are characterised by strong oscillatory zoning with sharp compositional changes (Fig. 2b). In

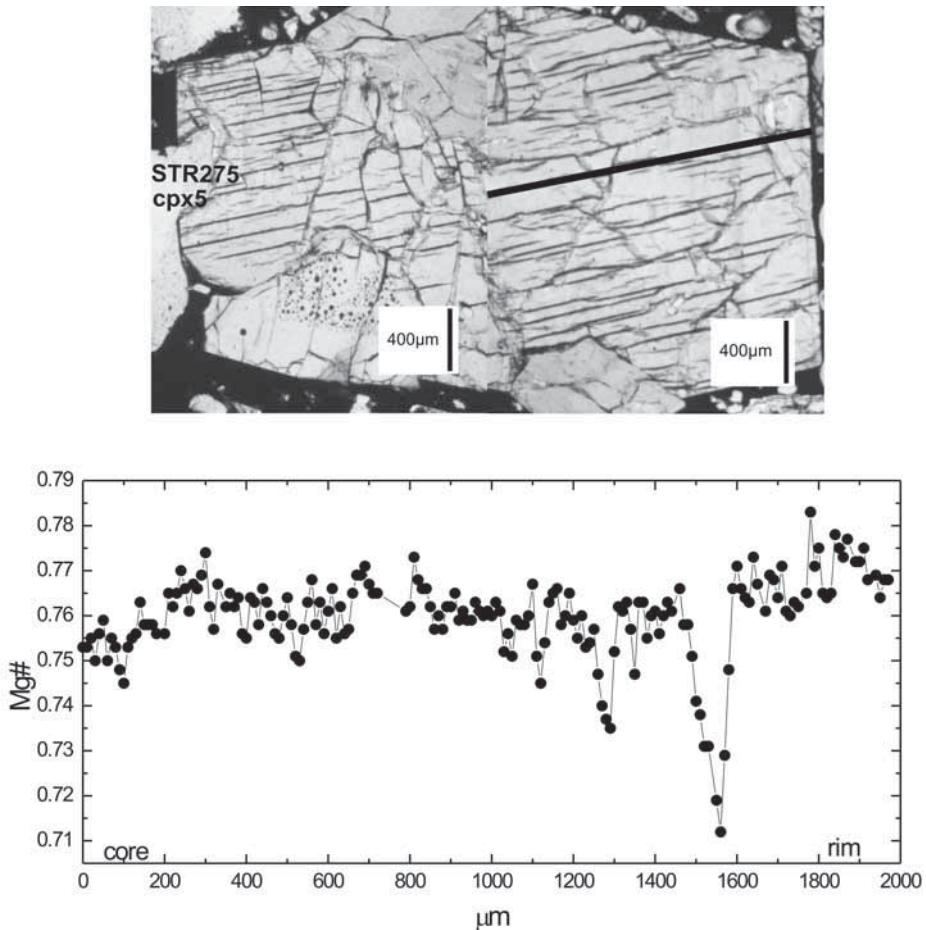


Fig. 5 – Chemical zoning profile of clinopyroxene crystal of STR275 sample (top sample of the analysed sequence of the Post-Pizzo series). Variation of the Mg# contents is plotted versus the length of the mineral profile shown by the heavy line in the microphotograph (composed by two pictures) of the corresponding analysed mineral. A total of 183 points of analysis have been performed for a total length of these profiles of ~2 cm. The profile crosses the mineral from core to rim.

particular, both zoning profiles of cpx1 and cpx2 show two-three Mg-richer zones characterising the inner part of the crystals. These zones are quite wide and their occurrence is at almost constant interval in each crystal (~ 200 μm). The presence of these bands with different composition indicates that the growing crystal recorded variations in the magma composition. Since these zones are clearly Mg-richer than the core of the crystal, magma composition became more mafic during the crystal

growth. This clearly suggests repeated arrivals of mafic magmas into the reservoir of STR276 magma. It is interesting to note that after the arrival of the mafic magma, the crystal composition became Fe-richer again. In some cases (cpx1 and profile 2 of cpx2, Fig. 4) the exact composition showed by the crystal core has been recovered. Thus, the crystal recorded the arrivals of new mafic magmas and equilibrated with this new composition, crystallising the Mg-richer zones. Fractional

crystallization processes continued after this mixing event thus determining the evolution of the whole system toward a more evolved composition sometimes close to those observed prior of the mafic magma arrival. This process repeated several time (at least three) during the growth of the two analysed clinopyroxene minerals. As suggested by the fact that after each arrival of magmas, the clinopyroxene returned more or less to their original composition, it is possible to hypothesize that the system remained in a sort of steady state, characterised by the repeated arrival of batches of mafic magmas associated to successive fractional crystallisation. This did not lead to an abrupt change of the whole magma composition, at least in the initial phase of Post-Pizzo series.

The clear bimodal composition observed for a major number of clinopyroxene analysed (Fig. 2b) seems to confirm the evidence arisen from the two clinopyroxene compositional profiles. Indeed, the Mg-richer compositions of the intermediate portions of crystals (outer-core and inner-rim) and the more Fe-richer compositions of the cores and rims is a clear indicator of a perturbation of the system during the growth of intermediate portion of crystals and a recovering of the "normal" state toward the end of the crystallization of the analysed phenocryst and micro-phenocryst populations. The perturbation can be represented by the arrival of several pulses of new mafic magmas, whereas the recovering of a "normal" state indicates that chemical composition of the whole magma body was not so different from those characterising the initial crystallization of crystals (cores of crystals).

There are, however, some differences among the two analysed profiles of clinopyroxene crystals from the bottom sample. Cpx1 is characterised by a Mg-poorer rim suggesting that after the pulses of more mafic magmas the system not only recovered the original composition of the magma body, but also followed a normal evolutionary path of fractional crystallization. Profile 3 of cpx2 is, instead, characterised by a general evolution towards Mg-richer compositions than the core, and the recovering of the initial composition after each pulse of mafic magma is not complete. Profile 2 of cpx2, on the other hand, shows that this crystal has a thin outer rim with a composition similar to that of its core.

The differences registered by the two crystals of the bottom sample are not easy to explain, one possible explanation can be found imagining that at some point cpx1 was "isolated" from the influence of the mafic magma pulses. Indeed, it is possible to suggest that cpx1 and cpx2 crystallised in different portions of the magma chamber. Cpx1 crystallised in a portion in which efficient crystal fractionation prevailed in the end on mixing with refreshing magma. Whereas cpx2, which registered Mg-richer composition for most of the intermediate portion of the crystal unless a thin rim, was growing in a portion of the magma chamber in which inputs of more mafic magma and mixing were more efficient. It is hard to decipher the exact position of these different portions, but it seems obvious that cpx1 grew in a portion less affected by mixing processes as could be represented by the external or upper parts of the magma chamber. On the other hand, it is probable that cpx2 was located in a zone characterised by efficient mixing between the new mafic magma and the magma already resident in the system. A similar condition could be found in the lower or central parts of the magma reservoir. The cpx2 also has a thin rim with the Mg-poorer composition ($Mg\# = 0.71-0.73$) typical of the clinopyroxene rims of this sample and in equilibrium with the liquid composition at the time of the eruption (Fig. 2b). This indicates that, shortly before the eruption or during the eruption, the cpx2 was included in the more evolved magma present in the system (probably in the magma portion in which cpx1 was growing) and grew in equilibrium with it. The more complex growth history of cpx2 is also testified by the asymmetry shown by the two zoning profiles analysed on it. This asymmetry could be due to resorption processes variably acting on the different portion of the crystal and linked to the arrivals of more mafic and hotter magmas than the host magma of cpx2 core. Indeed, profile 3 registered repeated arrivals of less evolved magmas, whereas profile 2 could be determined by a more extensive resorption during the last episode of mafic magma input. After that, profile 2 of the cpx2 registered the whole crystallisation history up to the eruption.

From all above, it is clear that cpx1 and cpx2 from the bottom sample show a more complex history in respect with plagioclase. Compositional variations of plagioclase are quite similar to those

shown by clinopyroxene although the zoning pattern is less clear and provide contrasting indications. Indeed, the general normal zoning of pl1, with also steep and rapid oscillatory zoning in the middle-external portion of the crystal, is a close behaviour to that observed for cpx1. Pl2 shows almost uniform composition with high An content (up to 85%) in the core and oscillatory zoning towards lower An content (up to about 60%) in the outer core, similarly to the inner part of pl1. Plagioclase crystals seem to have followed a normal fractional crystallization path given their general decrease of An contents from core to rim (Figs. 2 and 3), with only oscillatory zoning pointed out by the peaks at higher An contents in the intermediate part of crystals. Chemistry of plagioclase is extremely sensible to P, T and magma volatile content variations. In particular, an increase of fluid pressure of magma determines the crystallization of an An-richer plagioclase and the resorption of Ab-richer crystals which were in equilibrium with previous conditions. Accordingly, it is possible to suggest that the arrival of more mafic and less degassed magma would have determined an increase of volatile contents of the system, thus causing the crystallization of An-rich plagioclase and the contemporaneous resorption of already formed Ab-richer crystals. Thus, the observed An-rich compositions of plagioclase cores could represent the effect of increasing in volatile due to the arrival of mafic magma and resorption of previously crystallised minerals. In this view, the normal zoning of plagioclase will reflect the recovering of the "normal" state of the system and the lack of An-poorer cores may be due to the complete resorption of this cores by the newly arrived more mafic magmas.

Looking to chemistry of clinopyroxene in more details, it is well known that its Al content is extremely sensitive to the changing of physical-chemical conditions. The increase of Al content can be determined by the increase of P, T, fO_2 and by the decrease of SiO_2 in the magma. The increasing of Al_{tot} with Al^{IV} has been experimentally demonstrated to be correlated with T increasing (Thompson, 1974). The positive correlation shown by clinopyroxene populations of both samples, therefore, (Fig. 6a) can be related to a T variation. In particular, the high Al_{tot} and Al^{IV} shown by some intermediate portions of clinopyroxene from the

bottom sample, suggests higher crystallization T for that portions of crystals. At the same time an increase of P might be suggested by the positive correlation of Al^{VI} and Al_{tot} (Fig. 6b) as experimentally found by Pemberton and Offler, (1985). Contrastingly, the increase of Al^{IV} and Al^{VI} indicate a decrease of pressure (Francalanci, 1993). Therefore, the high Al^{IV} , Al^{VI} and Al_{tot} cannot be attributable to P variations. The increase of Al contents in clinopyroxene can also be correlated with decreasing of silica contents in the magma (Campbell and Borley, 1974). Nevertheless, the higher Si, at the same Al contents, of clinopyroxene from the top sample (Fig. 6c), which is also the less evolved, suggests that the Si contents of clinopyroxene are not correlated with the silica content of the host magma. At the same time, clinopyroxene from the top sample have lower Fe^{3+} contents which are slightly correlated with Al^{VI} (Fig. 6d). This could suggest a lower fO_2 for the top sample which determines lower Fe^{3+} in the liquid and consequently for the clinopyroxene. Due to stoichiometric balance, a higher Al^{VI} in the octahedral site of clinopyroxene is therefore necessary (Fig. 6d). The higher Al^{VI} for the top sample determines a lower Al^{IV} and consequently higher Si at the same Al_{tot} content (Fig. 6c). The observed chemistry of clinopyroxene populations, therefore, does not seem to indicate a significant difference of P and T between the two samples, but probably a lower fO_2 during the magma crystallization of the top sample. Probably, the differences in the main compositions of host magma, although evident from whole rocks, are not so strong to be registered by the clinopyroxene chemistry.

The picture arisen from these data suggests that the initial phase of the Post-Pizzo series was characterised by repeated arrivals of mafic magma batches in the shallow magma reservoir, registered by the intermediate portions of mineral phases. Nevertheless, the final residual magma composition does not significantly changed as testified by rims of crystals having almost the same composition of the crystal cores. Mineral chemistry of the top sample (STR275) suggests slightly different processes for the last phase of the Post-Pizzo series. Mineral phases from this sample show some compositional variations but there is no a clear zoning pattern and, while olivine

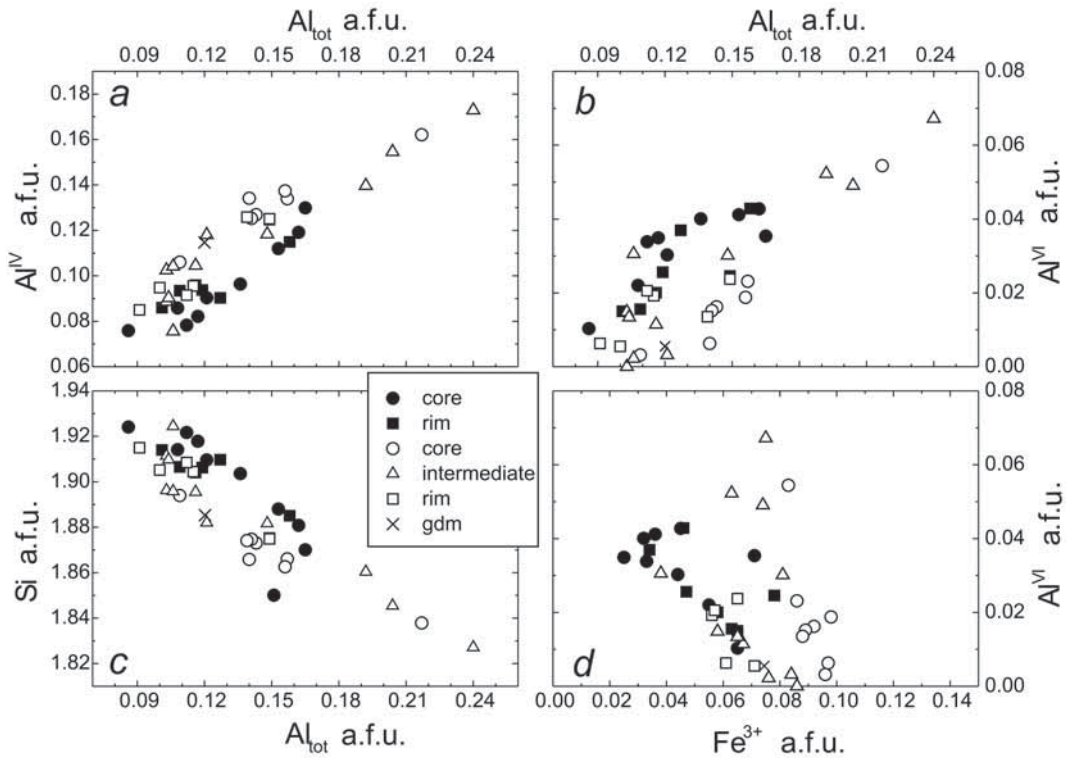


Fig. 6 – Diagrams of Al^{IV} , Al^{VI} and Si versus Al_{tot} (a, b and c) and Al^{VI} versus Fe^{3+} (a.f.u.) showing chemical variations of clinopyroxene from Post-Pizzo series samples. Symbols: filled black symbols: STR275 (top sample); open symbols: STR276 (bottom sample); gdm = groundmass crystal.

have a very constant composition, clinopyroxene and plagioclase populations are more variable and show Mg-richer and An-richer cores, respectively (Figs. 3-5). This clearly suggests a tendency toward a normal magma evolution by fractional crystallization of the observed mineral phases. The crystallising magma have a more mafic composition in respect with that initially presents in the magma chamber and represented by the bottom sample. Looking at the general composition of whole crystal population of the top sample (Fig. 2), it is clear that, on average, these crystals show more mafic composition in respect with crystal population of the bottom sample. This is obvious for olivine and for plagioclase and clinopyroxene rims. Recalling that mineral phases of the bottom samples are characterised by bimodality, it is clear

that the whole top sample is characterised by mineral phases having a more mafic composition than the crystal population of the base sample. This suggests that the arrival of new mafic magma batches not only characterised the initial phases of Post-Pizzo series period, but probably continued with a higher importance than crystal fractionation during the entire period determining a changing of the composition of the whole magma body toward the more mafic composition of the final stage of the Post-Pizzo series. The top sample, therefore, represents the composition of the final mixed magma which underwent to successive crystallisation as testified by the normal zoning of plagioclase and clinopyroxene. The Mg-richer and An-richer compositions of clinopyroxene and plagioclase, respectively, are similar in the bottom

and top samples, indicating that these minerals belong to the same magmatic system which is refilled with time by the same mafic magmas.

Mineral chemistry study associated with compositional zoning profile is a powerful tool in deciphering the history of crystallization of mineral phases and revealing physical and chemical modification occurred in the magma chamber during the growth of mineral phases. Mineral chemistry characterisation of the bottom and top samples of the Post-Pizzo series pyroclastic sequence revealed a complex history registered by mineral phases. The initial phase of Post-Pizzo series eruptive period was characterised by repeated arrival of new batches of more mafic magmas registered by more mafic composition of intermediate portions of clinopyroxene and cores of plagioclase populations of the bottom sample. After the complete mixing of these batches of mafic magmas with the whole magma body resident in the magma chamber, the system recovered its initial (i.e. pre-mixing) composition by fractional crystallisation processes. The arrival of mafic magma batches probably became more important, in respect with the fractional crystallisation processes, during the entire Post-Pizzo eruptive period. Thus, the continuous mixing between these mafic batches and the main magma body determined in the final stage a change towards a more mafic magma composition as registered by the less evolved compositions shown by mineral phases from the top sample.

During the Post-Pizzo eruptive period a steady-state dynamics of the magma system, with repeated arrivals of refreshing magmas and successive mineral crystallisation from the hybrid liquids, was established. This can be considered a precursor of the dynamics of the present-day steady-state activity whose persistent eruptive character is due to repeated refilling with deep-sited volatile-rich magmas (Francalanci *et al.*, 1999, 2004, 2005; Bertagnini *et al.*, 1999; Rosi *et al.*, 2000; Metrich *et al.*, 2001). This type of pre-eruptive evolutionary processes have characterised the plumbing system after the Pizzo Sopra la Fossa pyroclastic eruptions, as pointed out by the mineral chemistry composition of the Post-Pizzo series, erupted just before the setting of the typical present-day Strombolian activity. During the eruptive period of the Post-Pizzo series,

therefore, the conditions in the magma system for the development of the present-day activity were matured. In the Post-Pizzo eruptive period, however, the refilling magmas were never erupted, contrarily to what usually occurs in the present-day paroxysms. Accordingly, it might be hypothesised a possible shallower feeding magma system for the present-day activity in respect with the previous Post-Pizzo eruptive period. As final remark it has been pointed out that the micro-analytical zoning profile approach is a powerful tool in revealing magma mixing processes and helping to clarify the dynamics of the Stromboli plumbing system.

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