PYROMETAMORPHIC PROCESSES AT THE INTERFACE BETWEEN MAGMA AND PRODUCTS OF THE HYDROTHERMAL SYSTEM IN ACTIVE VOLCANOES: EVIDENCE FROM THE EJECTA OF STROMBOLI (AEOLIAN ISLANDS, ITALY)

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INTRODUCTION

This work is focused on the study of the igneous and contact metamorphic petrology of some volcanic ejecta, coupled with the investigation of hydrothermal processes underwent by the rocks of active volcanoes. In particular we are going to deal with rocks of Stromboli volcano as concerning: 1) the characterization of hydrothermally processes (alteration) suffered by the rocks of the crater area and the upper parts of the subvolcanic system, and 2) the mineralogical, petrological and geochemical study of some buchite to sanidinite ejecta erupted during recent, more violent eruptions (paroxystic explosions) of Stromboli.

Contrary to what you might expect studying the above two different groups of rocks (they would appear with no links between them) the low-P high-T contact metamorphism (pyrometamorphism) of Stromboli involve subsolidus recrystallization and partial melting of the shallow hydrothermally-altered rocks.

THE HYDROTHERMALLY-ALTERED EJECTA

In the uppermost system of an island arc active volcano like Stromboli, volcanic and subvolcanic rocks usually suffer the alteration processes induced by an acid-sulphate hydrothermal system. The circulation of acid fluids causes leaching in the rocks and, depending on the *p*H, temperature and interval time of exposure to the hydrothermal fluids, volcanics are going to show different alteration facies.

Hydrothermally-altered volcanics of the uppermost cone of Stromboli can be represented (as fresh rocks) by the present-day activity basalts or the more evolved andesite-trachite lavas of the older volcanostratigraphic periods (*e.g.* Vancori).

The material collected during various geological surveys consists of yellowish to brownish and locally damp decimetric ejecta (1 to 30 cm in size) often with a floury surface and a still recognizable scoriaceous oxidized core. In order to characterize the hydrothermally-altered products of Stromboli, samples were investigated using different methodologies:

- *p*H determinations, using a solution of 50 ml of deionized water (*p*H = 7) to dissolve 1 gr of rock powder, then measuring the new *p*H of the solution mostly deriving from sulphur and other minor ions (*e.g.* chlorine) contained in the altered rock.

- XRD analyses, in order to investigate secondary phases precipitated from the percolated hydrothermal fluids, those formed by leaching processes and the relict minerals of the original rock.

- Mass balance calculation using the isocon method, to estimate geochemical whole rock variations induced by hydrothermal fluids activity with respect to a possible fresh rock (*e.g.* a shoshonitic basalt of the Stromboli present-day activity).

The obtained data permitted to recognize three different alteration facies: intermediate argillic, advanced argillic and silicic. Intermediate argillic facies can be recognized in samples core that appear weakly altered. In this facies the first phase that suffered transformation, as the result of high-T hydrothermal fluids percolating through the rocks, is olivine. This latter is quite completely replaced by opaques, whereas clinopyroxene and plagioclase mostly survived to the leaching processes. Acidity of the solutions obtained with rocks of the intermediate argillic facies is between *p*H 4 and *p*H 6 and samples generally show a depletion of major and trace elements with respect to the compared fresh rock. In the advanced argillic facies, *p*H of the solutions is comprised between *p*H 2 and *p*H 4.5. Primary minerals mostly disappeared and only some partially dissolved plagioclase phenocrysts survived. In this alteration facies, sulphates, hydrous sulphates and hydroxysulphates are abundant: alunite [$KAl_3(SO_4)_2(OH)_6$], natroalunite [$NaAl_3(OH)_6(SO_4)_2$], pickeringite [$MgAl_2(SO_4)_4 \cdot 22(H_2O)$], polyhalite [$K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$], hexahydrite [$MgSO_4 \cdot 6(H_2O)$], millosevichite [$(Al,Fe^{3+})_2(SO_4)_3$], kieserite [$MgSO_4(H_2O)$], minamiite [$(Na,Ca,K)_2Al_6(SO_4)(OH)_{12}$], anydrite [$CaSO_4$], and rostite [$Al(OH)SO_4 \cdot 5H_2O$]. The advanced argillic facies samples are generally depleted in major and trace elements, excepting for some elements such as Al and Mg that entry the structural formulae of many secondary sulphates (Fig. 1). It is possible to appreciate also an enrichment of some trace elements (As, Pb, Bi, W, Zn) forming a strong covalent bond with oxygen and usually transported by fluids, thus entrapped in the altered rock because of crystallization of the secondary minerals. In the silicic alteration facies the original rock is replaced by amorphous to crystalline silica phases (*e.g.* cristobalite); in this case the calculated *p*H of the solutions is minor than *p*H 2. This alteration facies is characterized by thin films in the volcanic rocks, mostly produced by the action of very shallow to surface acid brines.

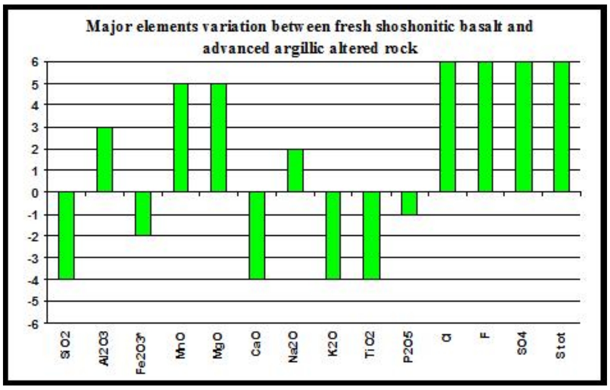

Fig. 1 – Mass balance calculation (isocon method) that measures the major elements variation of an advanced argillic rock, with respect to a fresh shoshonitic basalt of Stromboli. Variation less then –1000% = -6. Between –1000% and –100% = -5. –100 and –75% = -4. –75% and –50% = -3. –50% and –25% = -2. –25% and –5% = -1. –5% and +5% = 0. +5% and +25% = 1. +25% and +50% = 2. +50% and +75% = 3. +75% and +100% = 4. +100% and +1000% = 5. Variation more than +1000% = 6.

We pointed out a “scale” of the Stromboli hydrothermally-altered rocks on the basis of their different buffer property by alkaline hydrolysis (reducing the acidity of the volcanic fluids), due to the persisting hydrothermal leaching processes.

THE PIROMETAMORPHIC EJECTA

Pyrometamorphism is a kind of very high-temperature (high-T) and low-pressure (low-P) contact metamorphism, in which not only subsolidus mineralogical transformation processes are involved, but also partial melting of the protoliths and subsequent crystallization of phases from the anatectic liquid. Products of the pyrometamorphism are comprised within the buchite and sanidinite rocks facies. Buchite rocks consist of a partially or almost completely glassy rock resulting from intense high-T low-P contact metamorphism, while the sanidinite facies indicates an almost subsolidus crystallization giving rise to a sanidine-syenite composition. The main phases found in the buchite and sanidinite rock facies are: sanidine, cordierite, orthopyroxene, sillimanite, mullite, spinel and opaque minerals. In an active volcano like Stromboli, pyrometamorphic processes are induced in protolith rocks by the contact with basaltic magma. In order to form sanidinite or buchite facies the protoliths should be represented by arenitic or pelitic bulk rock compositions. At Stromboli these latter can be searched in the volcano basement, or among the altered products of the hydrothermal system.

Eight groups of buchite ejecta, erupted during different paroxystic explosions of Stromboli were sampled around the summit crater area and the upper flanks of the volcano. The pyrometamorphic ejecta are 1 to 100 cm in size and, in hand specimen, are vitreous to microcrystalline with lithologic heterogeneities at the mesoscale. They are always coated by the shoshonitic basaltic scoria of the present-day activity of Stromboli.

Studying the eight groups of buchite-sanidinite xenoliths it was possible to clarify the mineralogical and chemical heterogeneities at the microscale, also in the same sample. Microstructural features and mineral assemblages allowed to distinguish four facies of the Stromboli pyrometamorphic ejecta.

Restitic buchite facies

In these buchite xenoliths the incipient partial melting conditions of the pyrometamorphic processes and the disequilibrium crystal growths did not completely transform the protoliths (on mineralogical and microstructural point of view). In fact pseudo-porphyritic microstructures and restitic phenocrysts (Fig. 2) are still well recognizable even though pyrometamorphic Mg-cordierite and orthopyroxene coexist with interstitial yellowish to brownish glass. Restitic plagioclase phenocrysts (An_{58-83}; up to 1 mm in size) are ubiquitous. Skeletal armalcolite ($(Mg_{0.5}Fe^{2+}{}_{0.5}Ti_2O_5)$) crystals follow the dissolved habitus of biotite that provided titanium for this oxide metamorphic crystallization.

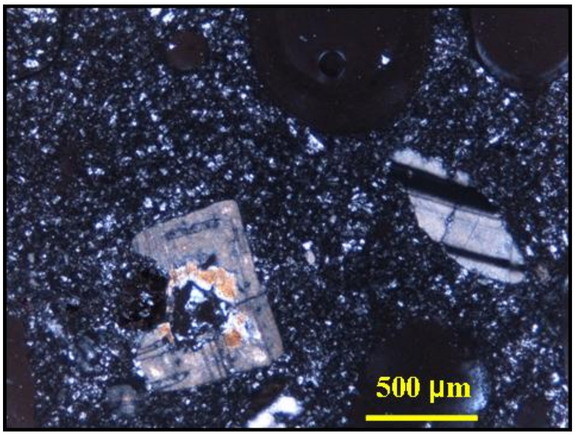

Fig. 2 – Relict plagioclase phenocrysts in a microcrystalline cordierite bearing groundmass.

Cordierite buchite facies

This is the main facies among the studied buchite ejecta and samples are whitish to light grey in hand specimen. Xenoliths are characterized by the presence of ubiquitous Mg-cordierite (Mg# 82-92; Fig. 3) associated with minor amount of Ca-rich plagioclase (An_{80-95}; locally at the cordierite microcryst cores) ± orthopyroxene ± glass ± rutile ± armalcolite ± sillimanite ± restitic plagioclase phenocrysts. Synchrotron powder diffraction data performed on some samples of cordierite indicate an orthorhombic symmetry; nevertheless TEM examination showed the presence of transformation twinning from the high-T

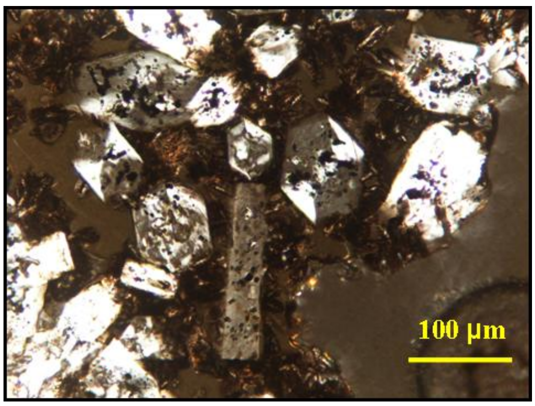

Fig. 3 – Tabular and hexagonal cordierite crystals with sector twinning and partially resorbed core, dispersed in a sillimanite + glass groundmass.

metastable hexagonal symmetry (indialite) to the orthorhombic cordierite. This means a crystallization from a liquid, at a temperature up to 1000°C and a pressure less than 1 kbar.

Plagioclase-rimmed mullite buchite facies

This buchite facies is black and white in colour, resembling in hand specimen an obsidianaceous to fine-grained rock, depending on the amount of glass (often more than 70 vol.%). Microcrystalline Mg-cordierite and Ca-rich plagioclase are often associated and dispersed in a glass + mullite assemblage with the same features described for the cordierite buchite facies. Veins of mullite + cordierite due to different cooling rate can locally occur. Contacts between the peraluminous xenoliths and the shoshonitic basalt are constituted by plagioclase palisades formed by Ca-rich plagioclase (An_{51-92}) + spinel (Sp_{51-77}) ± mullite, according to the following reaction: clinopyroxene + mullite (or Al-rich melt) = Ca-plagioclase + spinel.

Tridymite buchite facies

This is a subordinate facies among the Stromboli pyrometamorphic ejecta and it can be observed at the contact zone between the coating shoshonitic basalt and the xenoliths themselves, both in the cordierite buchite and the mullite buchite facies.

Tridymite buchite consist of about 90 vol.% tridymite, associated with pyroxene and minor amount of titanite, plagioclase and rutile. At the interface between tridymite and the host basalts a microcrystalline corona of clinopyroxene, locally associated with a needle shape Al-rich phase is commonly present.

Most of the buchite samples are peralluminous with compositions reflecting the facies heterogeneities at the meso-microscale. Restitic buchite and cordierite buchite facies show a similar bulk-rock composition with SiO_2 57-68%, Al_2O_3 18-26% and a significant amount of MgO (up to 6%) and K_2O (up to 5%). The plagioclase-rimmed mullite buchite facies is enriched in Al_2O_3 (31-34%) with respect to SiO_2 (56-60%), with minor amount of MgO (< 2%), and K_2O (< 6%); FeO is high (up to 12%). The tridymite buchite facies show SiO_2 85-91% and Al_2O_3 2-5%. All the xenoliths show a facies heterogeneity due to different bulk rock compositions in the same xenolith at the meso and microscale (Fig. 4).

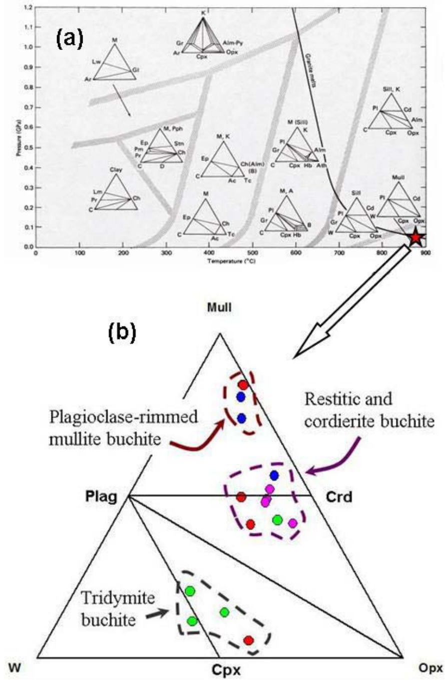

Fig. 4 – (a) Petrologic grid for metamorphic rocks; (b) ACF (mullite - wollastonite - orthopyroxene) diagram for the bulk rock compositions of 4 xenoliths (green, red, blue, violet). It is worth noting chemical heterogeneities in the same xenolith (same colour).

DISCUSSION

Looking for the protolith rock of the buchite xenoliths, it was disregarded the hypothesis of a protolith from the basement of the volcano because of some mineralogical, microstructural, chemical and isotopic incompatibility between the studied buchite/sanidinite xenoliths and the Stromboli continental crust, consisting of units of the Kabilo-Peloritano-Calabride domain. Instead, it was possible to recognize lots of similarities between the studied buchite xenoliths and the Stromboli ejecta hydrothermally-altered ejecta. The pseudo-porphyritic microstructures and the presence of relicts of plagioclase phenocrysts in many of the buchite xenoliths, testify a porphyritic microstructure in the protoliths, well before pyrometamorphic transformations. In addition, high contents of some trace elements such as As, Bi, Pb, W and Zn observed in the hydrothermally-altered products of Stromboli was also detected in some pyrometamorphic xenoliths. Facies heterogeneities observed in the buchite xenoliths are closely matched with the different alteration facies characterizing the hydrothermally-altered volcanic ejecta. As a matter of fact, the intermediate argillic alteration facies (peraluminous), heated to magmatic temperature (at low-P), can originate the cordierite buchite facies. In the same way, the advanced argillic facies (much more enriched in Al) could form the plagioclase-rimmed mullite buchite facies. Finally the tridymite buchite facies, often formed at the edge of some xenoliths, may be the result of pyrometamorphic processes on rocks with a silicic alteration facies.

The evidence reported above seems to demonstrate that the buchite/sanidinite xenoliths ejected at Stromboli during recent violent explosions, can originate from the hydrothermally-altered rocks of the volcano, through pyrometamorphism (*i.e.* at the interface between the altered volcanics and the basaltic magma in the feeder dyke system of Stromboli).

Rock protoliths of five buchite xenolith groups were focused in much more detail. In fact, the high content of some trace elements such as Hf and Zr observed in some of the buchite ejecta, is only comparable with that of the most evolved products of the Stromboli subaerial activity: latites and trachytes of the Upper Vancori period (13 ky). Hf and Zr are considered immobile trace elements during hydrothermal alteration processes, thus their enriched pattern in the buchite xenoliths, is the result of an enriched pattern in the hydrothermally-altered protoliths as well. There are also additional microstructural indications that agree with a protolith coming from the evolved products of the Upper Vancori period: first of all the presence of skeletal armalcolite that seems to nucleate following the pre-existing habitus of biotite phenocrysts. Biotite dissolution/breakdown can provide the Ti, Mg and Fe necessary for the subsolidus crystallization of armalcolite and, among the subaerial products of Stromboli, phenocrysts of biotite are only present in the Upper Vancori latites and trachytes.

These considerations provide insights into the environment of crystallization of the buchite facies. In fact, all the structural models of the volcano suggest contact between the present-day basaltic magma in the feeder system and the Upper Vancori wall rock latites and trachites in the very shallow level of volcano edifice at a depth between few tens to few hundred metres below the present-day active craters of Stromboli.

The above interpretation matches with phase equilibria of the minerals found in the buchite xenoliths indicating pyrometamorphic processes in the very shallow subvolcanic system of Stromboli ($P < 1$kbar). In addition, it was possible to estimate the temperature of the Stromboli pyrometamorphism between 850°C (through sillimanite-mullite equilibrium and tridymite stability) and 1140°C (temperature of the Stromboli basaltic magma of the present-day activity).

CONCLUSIONS

Buchite xenoliths sampled in the summit craters area of Stromboli record some pyrometamorphic processes occurring in the upper part of an active basaltic/andesitic stratovolcano. Studying the buchite rocks ejected during recent paroxysms of the present-day activity of Stromboli, it was possible to detect the complex history that may transform extrusive lithotypes to pyrometamorphic rocks. For some buchite ejecta, microstructural, mineralogical and trace elements evidence indicates that hydrothermally-altered latites and trachytes from the Upper Vancori period are the best candidates for protoliths of the buchite xenoliths. The volcanic rocks became peraluminous (and locally high-silica) through the activity of the acid-sulphate hydrothermal system of the volcano. When the magma of the persistently active feeder dyke of Stromboli interacts with the hydrothermally-altered wall rocks, pyrometamorphic processes may occur.

Contact between basaltic magma and wall rocks induce high-T, low-P contact metamorphism and incipient partial melting of the latter, with subsequent subsolidus crystallization and/or nucleation of minerals from the anatectic liquid. When violent eruptions occur, rapid rise of magma can stress the wall rocks, resulting in the fragmentation of the buchite and sanidinite facies rocks that can be erupted as ballistic ejecta (Fig. 5).

Pyrometamorphism at the interface between the magma and the hydrothermally-altered rocks can be difficult to detect because of the transient character of the phenomena. Nevertheless as already suggested by Wood (1994) it could be a rather common geological process which may occur at the magmatic/hydrothermal system of many active basaltic/andesitic volcanoes throughout the world.

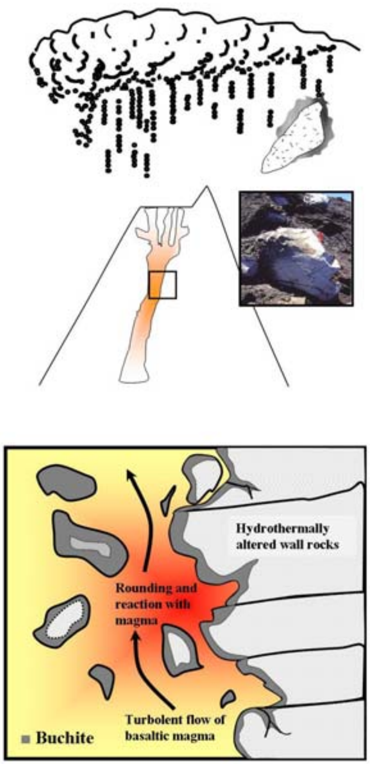

Fig. 5 – Sketch describing buchite rock formation at the magma/wall rocks interface. During rapid rise of magma in the conduit, fragment of buchite rocks can be erupted as ballistic ejecta. From Grapes (2006), modified.

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