

POST-EMPLACEMENT MINEROGENETIC PROCESSES IN UPPER TUFO GIALLO DELLA VIA TIBERINA (LATIUM): A MINERALOGICAL AND VOLCANOLOGICAL APPROACH

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INTRODUCTION

The authigenic mineralization processes have been traced to describe the different local condition. The present research deals with the characterization of the authigenic mineralization in the Upper Tufo Giallo della Via Tiberina (UTGVT), a pyroclastic deposits cropping out in a widespread area north of Rome.

The purposes of the present work are:

1. An accurate investigation of the volcanological features of UTGVT, aimed at pointing out the possible presence of different eruptive units within the formation.
2. The mineralogical and petrographical characterization of the products of these different units, aimed at defining the zeolite content and investigating the type of zeolites and their stratigraphical and areal distribution. These characterizations aimed at hypothesizing a minerogenetic model able to explain the genesis of the different authigenic phases (chabazite, phillipsite, feldspar) in the UTGVT pyroclastic deposits.
3. The evaluation of the physical and mechanical properties of the products of the UTGVT, taking into account the variation of the minero-petrographic features.

GEO-VOLCANOLOGICAL SETTING

The UTGVT was mainly an explosive deposits sourcing at the Sacrofano vent. The deposit is made up of three distinct sub-unit (a, b and c), separated by two ash layers, the age of which ranges between 551 ka and 547 ka (Karner *et al.*, 2001; Nappi & Mattioli, 2003).

The UTGVTa is a massive yellow ash deposit with scoria, lava and non-metamorphosed sedimentary lithic fragments, white pumice and accretionary lapilli. The base of UTGVTa has a 10-cm thick horizon, rich in lava, sedimentary lithic clasts and pumice. The upper part of this unit is a fine-grained, bedded ash with abundant accretionary lapilli.

The UTGVTb is an ignimbrite with similar petrographic characteristic to the UTGVTa.

The UTGVTc has one meter of alternating planar and cross-bedded ash, lapilli, and pumice rich layers at its base, and it is interpreted to be linked to surge and pyroclastic fall deposit (Karner *et al.*, 2001; Nappi & Mattioli, 2003).

FIELD INVESTIGATIONS

The sampling area of UTGVT was selected through the study of previous papers dealing with the products of this formation (Karner *et al.*, 2001; Lombardi *et al.*, 2006), and the detailed field investigations in order to define the accessibility and the suitability to the sampling of the whole area and to define the stratigraphic relationships of the mentioned three flow units (in three main investigated outcrops km 13-12.7, Perina and Cannetaccio quarries) with the pre-volcanic basement (Fig. 1).

Field investigations allowed to reconstruct the *i*) geometry of the deposits, and *ii*) the stratigraphy of the products. These two aspects showed the variable thickness of the deposits, due to the pre-volcanic basement, represented by the paleo-Tiber river valley. This feature determined a very high variability of thickness inside a limited area (80 m in Cannetaccio, 15 m at km 13 quarry). The stratigraphy of the formation allowed to distinguish three distinct flow units (UTGVTa, UTGVTb, UTGVTc). Field data show that the thickness of units

is not constant. Whenever the formation reaches highest thickness, no clear evidence of the presence of overlapping flow units, can be pointed out; probably the discontinuity layers between units was erased from the subsequent flow unit.

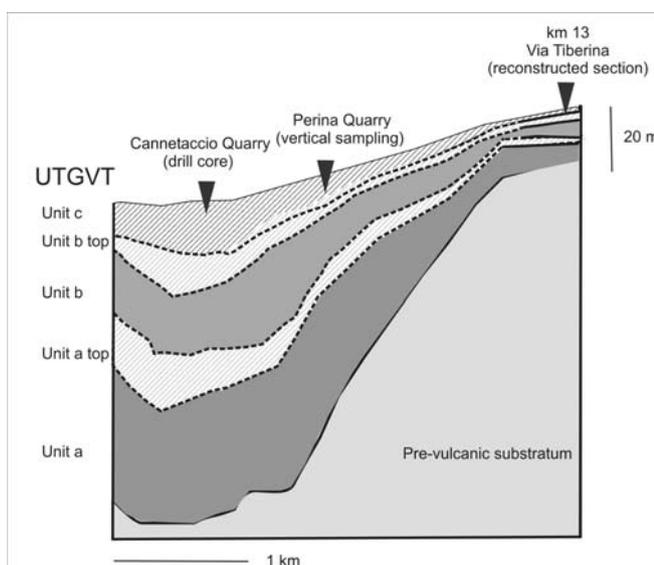


Fig.1 - Stratigraphic relationship between investigated outcrops and pre-volcanic basement.

MATERIALS AND METHODS

Lithified and unlithified samples were taken from two abandoned quarries between 12.7 and 13 km of Tiberina road. Lithified samples were also taken from four active quarries along the Tiberina road managed by “Cave Riunite srl”, namely the Cannetaccio, Perina and SICAT quarries, located between km 11 and km 12 of the consular road, and from the Fantini quarry, located at the km 7.50.

Samples were ground, coned and quartered and entirely sieved < 100 mesh; finally, the powders were quartered again to obtain suitable material for further laboratory analysis.

For the purposes of present research, the collected samples were analyzed by means of: X-ray powder diffraction (XRPD), X-ray fluorescence spectrometry (XRF), optical microscopy (OM), scanning electron microscopy (SEM) equipped with energy dispersive X-ray microanalysis (EDS). In order to understand the lithification process uniaxial compressive strength test were carried out (UNI EN 1926; 2000).

RESULTS

The XRPD data shows that samples are composed by the following mineralogical phases: feldspars, calcite, mica-biotite, clay minerals (smectite) and zeolites (such as chabazite, phillipsite, and analcime).

Chabazite is the main zeolite followed by phillipsite, whereas analcime is present only in samples belonging to km 12.7-13 and Cannetaccio quarries. The joint occurrence of these zeolites, within the UTGVTa and UTGVTb suggests suitable temperatures for zeolitization by interaction of fresh glass with water; this water that can be attributed to eruption type (phreatomagmatic), but also to paleo-Tiber river and meteoric waters. The uppermost unit UTGVTc shows occurrence of analcime as main zeolite and low content of phillipsite, suggesting unsuitable temperature for zeolitization. This unit was cooled soon after emplacement and its high content of analcime is associated to the analcimization of leucite phenocrysts (Giampaolo & Lombardi, 1994). The feldspar content of km 13-12.7 samples can be attributed to a primary phase (sanidine). Fig. 2 shows the vertical variation of the main mineralogical phases.

Wherever deposit preserves high temperature for a long time, zeolites evolves toward a more stable phase (authigenic feldspars, adularia-like). As chabazite content decreases, feldspar percentage increases and

vice-versa, this process confirms the crystallization of feldspar at the expense of chabazite (Fig. 3), favored by high temperature for a long time, a condition suitable for feldspatization process, that was likely reached in this quarry due to the highest thickness of the whole UTGVT succession (about 70 m).

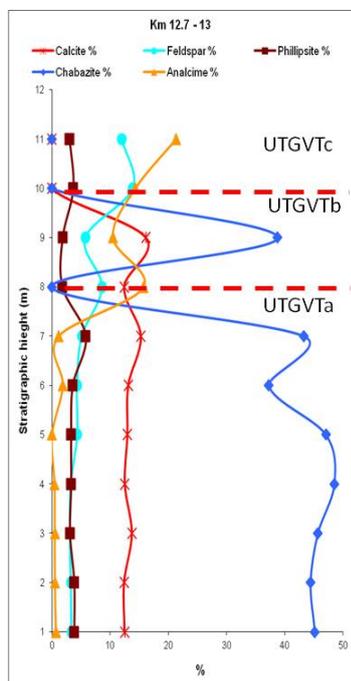


Fig. 2 - Reconstructed stratigraphy of samples from km 12.7 and km 13 quarries. The red dotted line indicate the inferred position of discontinuities between sub-unit a to b, and b to c. As regard to stratigraphic height, from 1 m to 8 m correspond to UTGVTa unit, from 8 m to 10 m correspond to UTGVTb, up to 10 m correspond to UTGVTc.

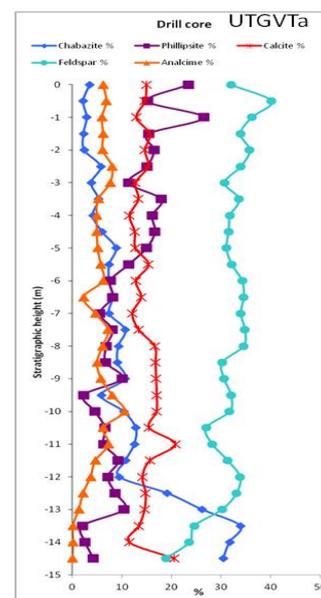


Fig. 3 - Vertical variation of feldspar, calcite and zeolitic minerals: chabazite, phillipsite and analcime. The whole drill core belongs to the middle part of UTGVTa unit.

The conditions that favored the chabazite crystallization (Ca-K environment) are testified by chemical analysis of bulk-rocks. The XRF data show the occurrence of high Ca concentrations in the bulk rocks ($\text{CaO} > 10 \text{ wt.}\%$), which was never observed in others Italian zeolitized volcanoclastic formations (Langella *et al.*, 2013). The high Ca concentrations were early attributed to the presence of carbonatic clasts, belonging to sedimentary basement, but further investigations showed a widespread occurrence of Ca within the rocks.

OM observations showed a clear distinction between primary and authigenic minerals. OM observations showed presence of carbonatic clasts and they also allowed to identify the presence of a second generation of calcite that filled fractures of the rock. The occurrence of secondary calcite could suggest an initial acidic solution that dissolves the carbonatic clasts; this determines a buffer effect on the pH of solution, with hydrolysis and dissolution of the glassy fraction. The progressive increase of pH (alkaline environment) led the reaction among CaO and the CO_2 in solution, with the consequent precipitation of secondary calcite. In order to verify the differences between the aforementioned two types of calcite, back-scattering electron (BSE) investigations were carried out, that allowed to obtain elements distribution inside of the investigated sample. The Fig. 4 shows the comparison between two thin section portions where are visible the aforementioned two types of calcite.

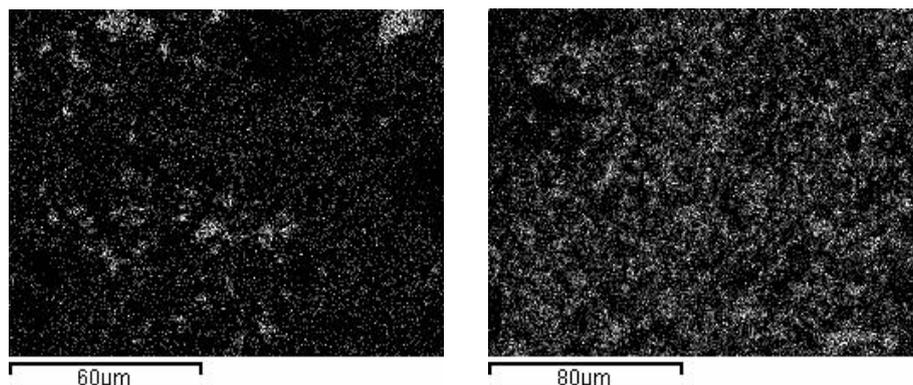


Fig. 4 - BSE images: Ca maps of element distribution; left: carbonatic clasts indicated by light color zones, concentrated to a restricted area; right: secondary calcite indicated by a wide spread of calcium.

SEM observations confirmed the initial acidic environment, as testified by the occurrence of glassy shards totally devitrified and replaced by clay minerals (smectite). The altered glassy shards are associated with chabazite crystals. These features could suggest the following early crystallization sequence: glass \rightarrow smectite \rightarrow chabazite. This zeolite was concentrated in the vugs of the rock. SEM observations revealed that clusters of phillipsite are only concentrated in pumice. Probably the chemical condition (sodic-potassic environment) allowing the crystallization of phillipsite has been maintained in pumice. Chabazites and phillipsite crystals are observed in association with authigenic feldspars; this confirms the transformation from a metastable phase (zeolites) to more stable phase (Fig. 5).

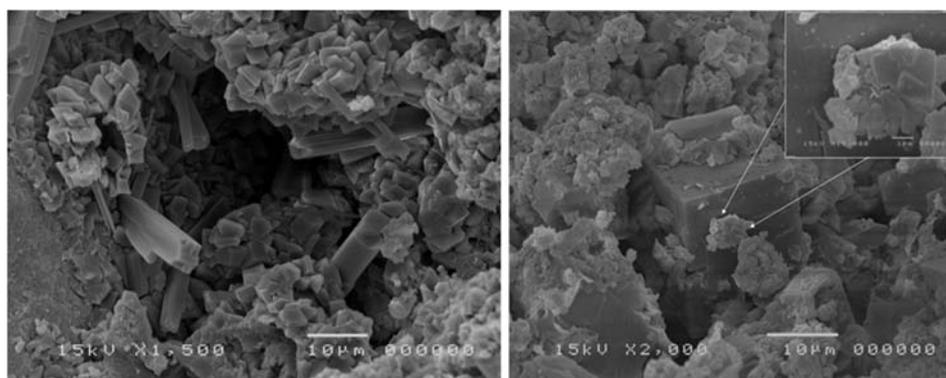
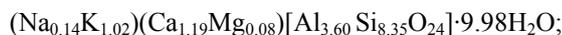
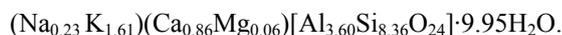


Fig. 5 - SEM micrographs, left, authigenic feldspar (adularia) associated with phillipsite crystals; right, authigenic feldspar (adularia) associated with rhombohedral chabazite.

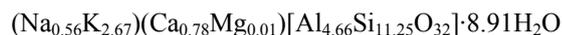
In order to understand the chemical composition of system (volcanic glass - solution), which led to the minerogenesis of zeolites, chemical analysis of chabazite and phillipsite were carried out by EDS microanalysis. Chemical data of chabazite showed a variable calcium and potassium content. Two average chemical formulas were calculated: the first for the calcic-potassic type:



the second for the potassic-calcic character of chabazites:



The chemical composition of phillipsite is quite constant, and denotes its potassic-calcic character, with the following average chemical formula:



On the basis of SEM observations, that allow to distinguish pyrogenic and authigenic feldspars, chemical analyses were carried out, in order to identify their possible compositional differences.

Authigenic feldspars have an higher K content (> 95 wt.%) than the sanidine (\leq 90 wt.%); the chemical composition, along with SEM observations, identify this authigenic mineral as adularia.

The secondary crystallization of authigenic minerals such as zeolites and feldspars and the presence of secondary calcite progressively enhance the physical properties of the deposit. In order to verify the relationship between mineralogy and compressive strenght (Table 1), a quantitative mineralogical analysis was performed on a set of samples subjected to UCS test. The Table 1 also reveals a direct proportion between compressive strength and feldspar percentage, higher UCS value coincides with higher feldspar content. Petrophysical characterization reveals higher compressive strength values of the UTGVT (about 6 MPa), compared to others volcanoclastic deposit (for example the NYT formation with a mean UCS of 3 MPa; Di Benedetto, 2011).

Table 1 - RIR values of UCS samples, with the corresponding UCS values.
Error in brackets = $\sqrt{\sigma_1^2 + \sigma_2^2 + \dots}$ (Chipera & Bish, 1995); amorphous % by difference.

Quarry	Sample	Smectite %	Chabazite %	Phillipsite %	Feldspar %	Calcite %	Total %	Amorphous	UCS (MPa)
Cannetaccio	CV_1	10 (\pm 1)	24 (\pm 1)	4 (\pm 1)	27 (\pm 5)	10 (\pm 1)	75 (\pm 9)	25	8.87
	CV_3	9 (\pm 1)	27 (\pm 1)	5 (\pm 1)	26 (\pm 9)	11 (\pm 1)	78 (\pm 13)	22	8.49
	CV_6	10 (\pm 1)	21 (\pm 1)	4 (\pm 1)	22 (\pm 10)	15 (\pm 1)	73 (\pm 14)	27	7.36
Perina	C2_0	7 (\pm 1)	29 (\pm 2)	5 (\pm 1)	15 (\pm 3)	17 (\pm 1)	73 (\pm 8)	27	5.69
	C2_6	8 (\pm 1)	39 (\pm 2)	7 (\pm 1)	20 (\pm 3)	12 (\pm 1)	86 (\pm 8)	14	6.12
	C2_7	11 (\pm 2)	35 (\pm 2)	6 (\pm 1)	17 (\pm 7)	11 (\pm 1)	81 (\pm 13)	19	6.97
Fantini	C4_1	9 (\pm 1)	55 (\pm 3)	4 (\pm 1)	13 (\pm 3)	12 (\pm 1)	93 (\pm 9)	7	5.44
	C4_2	8 (\pm 1)	53 (\pm 3)	3 (\pm 1)	13 (\pm 6)	10 (\pm 1)	86 (\pm 12)	14	6.17
	C4_3	10 (\pm 1)	58 (\pm 3)	6 (\pm 1)	11 (\pm 4)	8 (\pm 1)	64 (\pm 10)	6	4.67
	C4_4	9 (\pm 1)	55 (\pm 3)	5 (\pm 1)	10 (\pm 4)	11 (\pm 1)	90 (\pm 10)	10	4.41
	C4_5	8 (\pm 1)	62 (\pm 3)	4 (\pm 1)	11 (\pm 4)	10 (\pm 1)	95 (\pm 10)	5	4.73
	C4_6	9 (\pm 1)	54 (\pm 3)	3 (\pm 1)	8 (\pm 4)	13 (\pm 1)	87 (\pm 10)	13	4.77

CONCLUSIONS

The reconstruction of the minerogenetic processes that affected the UTGVT formation was carried out taking into the account both volcanological and mineralogical features.

Results of volcanological characterization allowed to ascribe the deposit to a pyroclastic flow-like emplacement mechanism. The occurrence of dune structures in unlithified layers and the presence of accretionary lapilli within the deposits suggested a strong interaction between water and magma. It is well known that the water-magma interaction mechanism favored the formation of authigenic minerals (de' Gennaro *et al.*, 2000; Langella *et al.*, 2013).

Results of mineralogical studies led to hypothesize that post-emplacment process developed in several successive stages. The minerogenetic model can be described as follows:

1. the initial acidic solution began to circulate within the deposit, causing the glass alteration with subsequent formation of smectite;

2. the acidic solution also interacted with the carbonatic clasts, occurring within the deposit, thereby causing an increase of Ca^{2+} ion in the solution;

3. the growing of pH toward higher values and the hydrolysis of glass determine the increase of K and Na in solution. It is well known (de' Gennaro *et al.*, 1999) that a calcic-potassic environment favours the crystallization of chabazite. This process explained the prevalence of chabazite in the whole investigated sections. Only for longer reaction time, phillipsite crystallized;

4. as the pH increased, the crystallization of secondary calcite was favoured, with a subsequent decrease of Ca and an indirect increase of K in the solution. This led to a suitable condition for the crystallization of phillipsite and chabazite. Chemical analyses of K-rich zeolites confirm this hypothesis;

5. chemical composition of zeolites (phillipsite and chabazite) is in agreement with those findings; both phases are potassic-calcic. In chabazites the extra-framework cation content can be summarized as follow: $\text{Ca} > \text{K} \gg \text{Na}$, whereas in phillipsites $\text{K} > \text{Ca} \gg \text{Na}$;

6. in the portions of the deposits, where temperature was maintained for longer times, conditions suitable for the crystallization of adularia-like feldspar were obtained.

The better petro-physical features of UTGVT can be attributed to the occurrence of calcite. Wherever zeolitization should evolve toward more stable phases (like authigenic feldspars), a further improvement in the geotechnical characteristic of this deposit could be observed.

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