

Mineralogical and technical features of zeolite deposits from northern Latium volcanic district

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ABSTRACT. — Six pyroclastic formations from volcanic districts of northern Latium have been investigated. These formations were subjected to post-depositional diagenetic processes which gave rise to the crystallization of chabazite and subordinate phillipsite. Zeolite grades are greater than 50 wt% for most of the analysed samples. Generally, the phillipsite content does not exceed 20 wt%. The chemical composition of chabazite is quite variable as far as the different formations are considered, but Ca and K generally prevail over the other extraframework cations. A very high Ca content is responsible for incomplete cation exchange process, both due to the preferential selectivity of the zeolite towards cations of higher valence and to the steric hindrance of the «ingoing» cation. The cation exchange capacity of the bulk rock is not influenced by the joint presence of the two zeolites. The large available tonnages of these materials and the well known selectivity of chabazite towards many polluting cations offer good potential for applications in several technological fields.

RIASSUNTO. — Sono state studiate sei formazioni piroclastiche, appartenenti a diversi distretti vulcanici del Lazio settentrionale. Tali formazioni sono state zeolitizzate a seguito di processi diagenetici post-deposizionali che hanno dato luogo alla formazione

di cabasite e di subordinata phillipsite. Per la maggior parte dei campioni analizzati il contenuto in zeolite è superiore al 50% in peso, ed in generale il contenuto di phillipsite non ha mai superato il 20% in peso. La composizione chimica della cabasite è variabile da formazione a formazione, ma il Ca ed il K prevalgono sugli altri cationi scambiabili. L'elevato contenuto di Ca è la causa degli incompleti processi di scambio, sia per la maggiore affinità della zeolite verso cationi a carica maggiore, sia a causa dell'ingombro sterico dei cationi utilizzati per i processi di scambio. La presenza congiunta dei due tipi di zeolite non ha influenzato la capacità di scambio totale del campione tal quale. La vasta disponibilità, in termini di cubatura, di questi materiali e la ben nota selettività da parte della cabasite verso alcuni cationi inquinanti sembrano offrire buone possibilità di utilizzo in diversi settori tecnologici per i suddetti materiali.

KEY WORDS: *Chabazite, cation exchange capacity, northern Latium, phillipsite, quantitative evaluation, technological features, tuff.*

INTRODUCTION

Several formations of northern Latium, belonging to different volcanic districts, are

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zeolite-bearing (mainly chabazite, associated with subordinate phillipsite) (Passaglia *et al.*, 1990; de' Gennaro *et al.*, 1995a).

Recent researches proved the high potential of zeolitized volcanoclastites, particularly in technological processes. Fields of potential or current application of natural zeolitized products are:

- cation exchange, in particular for heavy-metal removal from wastewater (Colella, 1996; Pansini, 1996);
- cement production, where zeolites can be used in the preparation of pozzolanic cements (Sersale, 1991);
- traditional ceramic and tile production, substituting for commonly utilized raw materials (Di Bartolomeo *et al.*, 1996);
- zootechny, in particular animal feeding and composting (Tsitsishvili *et al.*, 1984);
- agriculture, as amendants in soils and slow-release fertilizer (Langella *et al.*, 1995; de' Gennaro *et al.*, 1995b).

The two last applications are well developed in Italy. The Italian average estimated production of natural zeolites was 25,000 t/y in 1996, with a constant growing rate that reached ~50,000 t/y in 1998, making the building industry the most developed utilization field for these materials.

On the basis of the above statements, it is necessary to obtain a more accurate knowledge of the individual volcanoclastic formations, in terms of the economic potential of the bulk deposit, its zeolite content, as well as a detailed crystal-chemical characterization, in order to better understand their technological properties. This is the purpose of the present research that was carried out on the most important formations of three major volcanic districts of Latium.

GEOLOGICAL SETTING

Vulsini volcanic district, Vico volcano and Sabatini volcanic district are, from north to south, the volcanic districts of northern Latium (fig. 1). Their age of activity ranges between

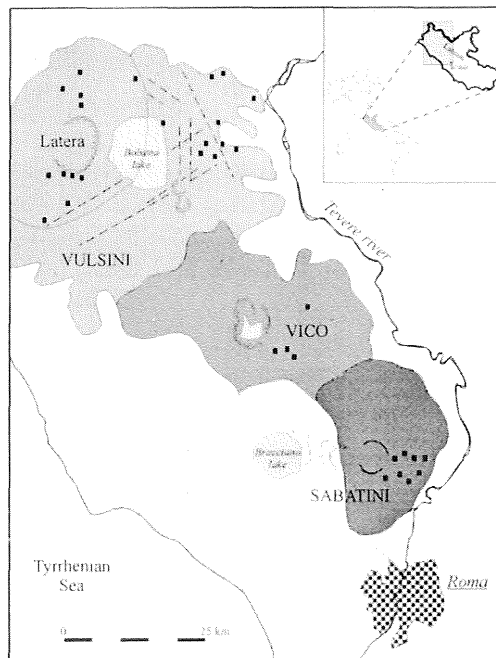


Fig. 1 – Sketch maps of northern Latium and sample locations (modified after Barbieri *et al.*, 1988).

600,000 and 127,000 y.B.P. According to several authors (Sparks, 1975; Nappi, 1991; Conticelli *et al.*, 1987; Nappi *et al.*, 1994b), the stratigraphic sequences of pyroclastic flows (fall, surge and flow) are consistent with the collapse of a sustained eruptive column.

Vulsini volcanic district (VVD)

The Vulsini volcanic district, (southern Tuscany-northern Latium) was active during the period 590,000-127,000 y.B.P. (Santi, 1991). The prevalent pyroclastic deposits cover an area of about 2,200 km² and are radially distributed with respect to the polygenetic calderas of Bolsena and Latera. On the basis of stratigraphic records, five main volcanic complexes have been identified: Paleobolsena, Bolsena, Montefiascone, Latera, and Neobolsena (Nappi *et al.*, 1995). As far as the potential economic resource is concerned, the

Orvieto-Bagnoregio formation from the Bolsena complex, the Sorano formation (D Ignimbrite), and the Onano formation from the Latera complex represent the most important products of this area.

Orvieto-Bagnoregio formation

The Orvieto-Bagnoregio formation (OBF) spread out about 333,000 y.B.P. (Santi, 1991), over the northeastern and eastern sectors of the district; its primary areal distribution, inferred from the recognized outcrops, is about 200 km² (Nappi *et al.*, 1994a).

The main ignimbritic deposit can be subdivided into two units: a lower multiple pumice flow deposit, composed of white to pale gray sanidine-bearing pumice set in an ashy matrix, and an upper orange coherent ignimbrite, containing sanidine and analcimized leucite-bearing black scoria, from which derives the Italian name «*Tufo rosso a scorie nere*». This lithified facies is mainly characterized by very large (up to 1 m in diameter) black scoriae, with analcimized leucite, reddish pumice, sanidine, and lava fragments in a generally fine-grained, cineritic to micropumiceous matrix. The formation also commonly appears in loose gray facies (Nappi, 1991). Although the deposit has an average thickness of about 10 m, it is much thicker in the distal outcrops at Bagnoregio, Lubriano, Porano, and Bardano, reaching its maximum of 60 m at the Orvieto cliff, as a consequence of the paleomorphology. The Orvieto-Bagnoregio formation is zeolitized in the yellow-reddish lithoid facies with prevailing chabazite; phillipsite occurs only locally, mainly in pumice.

De Rita *et al.* (1986) hypothesized a zeolitization process of the ignimbrites from Vulsini and Sabatini volcanic districts related to the particular chemico-physical conditions of the volcanoclastites at the emplacement time. Vapour phases of hydromagmatic eruptions and pyroclastic flows contribute to create these favorable conditions which allow a quick silica and alkali leaching from the glassy matrix, necessary for the zeolitization process. All the pyroclastic flows of Vulsini volcanic district,

even if at different extent, are zeolitized, thus confirming the hydromagmatic character of the eruption.

Tufo Giallo Litoide (Sorano and Onano formation)

The Latera volcanic complex, developed in the western area of the Vulsini volcanic district, was prevalently characterized by plinian explosive eruptions over about 100 ky time interval, during which a series of moderate-size ignimbrites was emplaced (Nappi, 1969; Sparks, 1975). The *Tufo Giallo Litoide* (Nappi, 1969), also described as D Ignimbrite (Sparks, 1975) or «Sorano formation» (Vezzoli *et al.*, 1987), is a very fine grained trachytic deposit as much as a few tens of meters thick. The other main ignimbrite from the Latera complex (Onano formation) shows very similar volcanological features.

These formations locally contain several thin beds composed of pumice with reverse size-grading. The Sorano formation also gave rise to deep channels carved into the underlying formations. They have many common features with pyroclastic flows of hydromagmatic origin found in the Vulsini volcanic district (Nappi and Marini, 1986). The small pumice enclosed in the ash-sized matrix are rounded and contain spherical vesicles. From a volcanological point of view, these formations are related to an emplacement mechanism involving water-magma interaction, as they are classified as pyroclastic flows, characterized by an abundant fluid phase and emplacement temperatures of a few hundred degrees. Furthermore, they commonly were extensively zeolitized, leading to crystallization of predominant chabazite by the transformation of trachytic and/or phonolitic primary glass.

Vico volcano (VV)

The Vico volcano is characterized by mainly explosive activity, with the emplacement of at least four major ignimbrites, spanning in time from 200,000 to 150,000 y.B.P. Among these volcanic units, for its peculiar geological

features (spreading out over about 1,250 km² and reaching thickness up to 30 m, averaging 15-20 m), the C ignimbrite was selected for this study («*Tufo rosso a scorie nere*»). This volcanic unit consists of a lithified ash flow, with a fine-grained, yellowish-red matrix, containing black scoriae.

Sabatini volcanic district (SVD)

As with other volcanic districts of the Roman Magmatic Province, the volcanism of the Sabatini volcanic district is related to the distensional post-Miocene dynamics, leading to the Tyrrhenian basin formation. It is characterized by a diffuse areal activity, with a central main structure in the eastern sector. The activity was mainly explosive and emplaced several huge formations (*Tufi Varicolori della Storta*, *Tufo Rosso a Scorie Nere*). For its areal distribution and thickness, *Tufo Giallo della Via Tiberina* (TGVT), linked to Sacrofano caldera, is the most important. This pyroclastic flow (228,000 y.B.P., Fornaseri, 1985) is composed of an upper part that is incoherent and gray in color and by a lower thick (up to 30 m), yellow cineritic tuff that is lithified and characterized by pumice of varying size. Lenzi and Passaglia (1974), referring to pyroclastic flows of this region, analyzed both lateral and vertical variations of the zeolitization phenomena and proposed as the main factor of zeolitization the high temperature of the circulating solutions inside the deposit during its emplacement.

MATERIALS AND METHODS

For each investigated formation, representative samples were taken from small trenches dug where the materials were best exposed. Figure 1 reports the locations of the 58 collected samples. They were coned and quartered to obtain suitable material for successive mineralogical and technological characterization.

Rock mineralogy was investigated by X-ray powder diffraction (XRPD) (Philips

PW1730/3710) and scanning electron microscopy (Cambridge Stereoscan TP250).

Chabazite-enriched samples were obtained from the above tuffs by processes based on the greater friability and lower density of zeolite relative to other rock constituents (de' Gennaro and Franco, 1979). Zeolites were separated from the other crystalline phases using a mixture of heavy liquids (bromoform/acetone) at selected density, on a 0.25 and 0.15 mm (60-100 mesh) grain-size fraction. After each treatment, the purity was checked by XRPD. Whenever residual phases such as feldspars were recorded, the treatment was repeated with lower density solutions and by centrifugation (5000 rpm). This technique resulted in enriched zeolites (90-95%), the remainder being traces of feldspar and phillipsite.

Single crystals or clusters of chabazite, and subordinately phillipsite, obtained from the above mentioned 60-100 mesh fraction were embedded in epoxy resin and polished for microanalyses by electron microprobe (LINK AN10000 and Cambridge Stereoscan TP250). Whenever possible, glass shards were separated from the matrix and analyzed separately.

Cation-exchange capacity (CEC) of enriched chabazite samples was measured in column on 0.2 gram of the samples. The powders were micronized to increase the specific surface of the sample and to enhance the cation diffusion in each single grain. The adopted cross-exchange method is based on a preliminary Na- or K-exchange of the zeolite by percolation at 60°C with a 0.1M NaCl or KCl solution (Carlo Erba reagent grade) until the concentration of Na, K, Ca, and Mg in solution is near or equal to the blank. The exchange process is completed with 0.5M NaCl (or KCl) solutions (99.99% pure reagent Aldrich) until no further potassium (or sodium), calcium, and magnesium were detected in the eluate (Colella *et al.*, 1982; Pansini *et al.*, 1996). Concentration of the eluted cations was measured by atomic absorption spectrophotometry (Perkin Elmer 2100).

Quantitative mineralogical analyses were performed, utilizing a Netzsch Multiple Thermoanalyzer STA409, through the water-

vapour desorption technique (de' Gennaro and Colella, 1989). This method is based on the evaluation by thermogravimetry of the water content of a tuff, ignited at 900°C after previous heating at 240°C and 380°C, with each cycle followed by a cooling at room temperature. The water loss amount at 380°C and 900°C is attributed to zeolite (phillipsite and chabazite, respectively), while the water lost at 240°C and not reabsorbed is attributed to glass. The ratio between the water amount ascribed to zeolites and that of the pure phases reported in literature or estimated through TGA on pure phases gives the zeolite content of the raw sample.

To test the accuracy of these evaluations, XRPD Rietveld quantitative analyses on two representative samples, (Orvieto-Bagnoregio formation: sample LP3, Palombara; Sorano formation: sample 55, Piandirena) were performed.

An internal standard, α -Al₂O₃ (1 μ m, Buehler Micropolish) was added to each sample in the amount of 20.0 wt%. Powders with grain size <10 μ m were obtained using a Brinkmann Micro Rapid mill; such particle size allow us to override several problems such as particle statistics, primary extinction, microadsorption, and preferred orientation (Bish and Chipera, 1988; Klug and Alexander, 1974).

Phases present in the mixture (sanidine, albite, analcime, biotite, and clinopyroxene), other than zeolites, were recognised with qualitative XRPD. Also, amorphous material (glass) was detected.

Data were collected at the Los Alamos National Laboratory, Los Alamos (NM, USA) on a Siemens D500 automated diffractometer with CuK α radiation, incident- and diffracted-beam Soller slits, Kevex Psi solid-state Si(Li) detector, 2 θ range from 3° to 100°, step size 0.02° 2 θ and 105s counting time per step.

Powder data sets were analyzed by the Rietveld method using the GSAS software package (Larson and von Dreele, 1995). Starting atomic coordinates of the structure were taken from literature: chabazite (Calligaris *et al.*, 1982), phillipsite (Rinaldi *et*

al., 1974), sanidine (Phillips and Ribbe, 1973), albite (Smith, 1974), diopside (Clark *et al.*, 1969), analcime (Mazzi and Galli, 1978) and biotite (Takeda and Ross, 1975).

Background was fitted using a cosine Fourier series (3–7 terms). For each crystalline phase lattice constants, phase fraction, profile coefficients (pseudo-Voigt function modelling diffraction peaks with Gaussian FWHM and Lorentzian broadening) and occupancy factors of extraframework sites and water molecules for zeolites were refined. A second order spherical-harmonic function (Popa, 1992) was applied to correct preferred orientation for feldspars. The total number of parameters refined was about 55 for each sample. Agreement factors for Rietveld refinements, R_p and R_{wp} (Larson and Von Dreele, 1995), were all within 0.10-0.17 and 0.10-0.20, respectively.

RESULTS AND DISCUSSION

Table 1 summarizes, for each sample reported in fig. 1, the locality, volcanic formation, and lithological and mineralogical features. For most of the investigated samples, the mineralogical composition is nearly homogeneous. The primary minerals are feldspars, mica, and a salitic clinopyroxene, and the authigenic minerals are chabazite and minor phillipsite. Clay minerals are rare and occur only in five samples. Analcime, probably related to the transformation of a primary leucite, is recognised mainly in the Orvieto-Bagnoregio and Onano formations. In any case this phase occurs always in very low amount (3-5 wt%). Calcite, often identified in samples from the Onano formation (Tufelle di Sopra outcrop) and from *Tufo Giallo della Via Tiberina* samples, is due to the calcareous clasts from the underlying sedimentary basement. Only a few samples bear only chabazite, and they are generally in the Orvieto-Bagnoregio and Onano formations. The genetic mechanisms of the studied volcanic products are not the aim of the present research. This subject is in progress with the contribution of volcanological expertise.

TABLE 1

Location, volcanic unit, lithological and mineralogical features of the investigated samples.

<i>Sample</i>	<i>Locality</i>	<i>Volcanic Unit</i>	<i>Description</i>	<i>Mineralogy</i>
1	Mercareccia	C Ignimbrite SVD	Red tuff with black scoriae	Chabazite, Phillipsite, Feldspars, Mica
111b	Rio Filetto	C Ignimbrite VV	Yellowish orange tuff	Chabazite, Feldspars, Mica, Phillipsite
118	Moca S. Elia	C Ignimbrite VV	Red tuff with black scoriae	Chabazite, Feldspars, Mica, Phillipsite
124	S. Susanna, SS. Flaminia	C Ignimbrite VV	Red tuff with black scoriae	Chabazite, Feldspars, Mica, Phillipsite
15	Rio Vicano	C Ignimbrite VV	Red tuff with black scoriae	Chabazite, Phillipsite, Feldspars, Mica
112	Pizzo Iella	C Ignimbrite VV	Red tuff with black scoriae	Chabazite, Feldspars, Mica, Phillipsite
128	Quercia Fagotta	C Ignimbrite VV	Red tuff with black scoriae	Chabazite, Feldspars, Mica, Phillipsite
223	Pizzo Iella	C Ignimbrite VV	Yellowish-red tuff	Chabazite, Feldspars, Mica, Phillipsite, Clays
237	Pizzo Iella	C Ignimbrite VV	Yellowish-red tuff	Chabazite, Feldspars, Mica, Phillipsite, Clays
247	Pizzo Iella	C Ignimbrite VV	Yellowish-red tuff	Chabazite, Feldspars, Mica, Phillipsite, Clays
251	Pizzo Iella	C Ignimbrite VV	Yellowish-red tuff	Chabazite, Feldspars, Mica, Phillipsite
257	Pizzo Iella	C Ignimbrite VV	Yellowish-red tuff	Chabazite, Feldspars
259	Pizzo Iella	C Ignimbrite VV	Yellowish-red tuff	Chabazite, Feldspars, Mica, Phillipsite
266	Pizzo Iella	C Ignimbrite VV	Yellowish-red tuff	Chabazite, Feldspars, Mica, Phillipsite
267	Pizzo Iella	C Ignimbrite VV	Yellowish-red tuff	Chabazite, Feldspars, Mica, Phillipsite
271	Pizzo Iella	C Ignimbrite VV	Yellowish-red tuff	Chabazite, Feldspars, Mica, Phillipsite
279	Pizzo Iella	C Ignimbrite VV	Yellowish-red tuff	Chabazite, Feldspars, Mica, Phillipsite
281	Pizzo Iella	C Ignimbrite VV	Yellowish-red tuff	Chabazite, Feldspars, Mica, Phillipsite
284	Pizzo Iella	C Ignimbrite VV	Yellowish-red tuff	Chabazite, Feldspars, Mica, Phillipsite
06G	Ponzano	OBF	Red yellow tuff with orange pumice	Chabazite, Augite, Feldspars
16T	Bagnoregio	OBF	Yellow tuff with abundant yellow-orange pumice	Chabazite, Feldspars
19Y	Lubriano	OBF	Red tuff with black scoriae and orange pumice	Chabazite, Phillipsite, Augite, Feldspars, Mica
20Z	Cantolla	OBF	Red tuff with black scoriae and orange pumice	Chabazite, Phillipsite
21AB	Orvieto	OBF	Orange tuff	Chabazite, Phillipsite, Feldspars
22AC	Bardano	OBF	Red tuff with black scoriae and orange pumice	Chabazite, Feldspars
23AD	Bardano	OBF	Red tuff with black scoriae and orange pumice	Chabazite, Phillipsite, Feldspars, Augite
SP	S.Procolo	OBF	Light yellow tuff with yellow pumice	Chabazite, Feldspars
LP	Palombara	OBF	Red tuff with black scoriae and orange pumice	Chabazite, Phillipsite, Feldspars
BTR	Bardano	OBF	Red tuff with black scoriae and orange pumice	Phillipsite, Chabazite, Feldspars
TAB	Bardano	OBF	Red tuff with black scoriae and orange pumice	Chabazite, Phillipsite, Feldspars, Mica

TABLE 1, *continued*

<i>Sample</i>	<i>Locality</i>	<i>Volcanic Unit</i>	<i>Description</i>	<i>Mineralogy</i>
03D	Bolsena	OBF	Red yellowish tuff with small pumice	Chabazite, Phillipsite, Analcime, Feldspars
44	Montorio	Onano	Red tuff	Chabazite, Phillipsite, Feldspars, Mica
50	Onano	Onano	Red tuff	Chabazite, Phillipsite, Feldspars, Analcime, Mica
51	Strada Sorano-Montorio	Onano	Red tuff	Chabazite, Phillipsite
91	Ischia di Castro	Onano	Yellow tuff with abundant pumice	Chabazite, Feldspars
97	Cittalda	Onano	Yellow tuff	Chabazite, Feldspars, Mica, Phillipsite, Calcite
105	Carchiana	Onano	Lithoid yellow tuff	Chabazite, Feldspars, Phillipsite, Calcite
145	Tufelle di Sopra. Cellere	Onano	Yellow tuff	Chabazite, Feldspars, Mica, Phillipsite, Calcite
154	Tufelle di Sopra. Cellere	Onano	Yellow tuff	Chabazite, Feldspars, Mica, Phillipsite, Calcite
157	Tufelle di Sopra. Cellere	Onano	Yellow tuff	Chabazite, Feldspars, Mica, Phillipsite, Calcite
164	Tufelle di Sopra. Cellere	Onano	Yellow tuff	Chabazite, Feldspars, Mica, Phillipsite, Calcite
165	Tufelle di Sopra. Cellere	Onano	Yellow tuff	Chabazite, Feldspars, Mica, Phillipsite, Calcite
168	Tufelle di Sopra. Cellere	Onano	Yellow tuff	Chabazite, Feldspars, Mica, Phillipsite, Calcite
04E	Acquapendente	Onano	Yellow tuff with abundant pumice	Chabazite, Phillipsite
181	La Selva	Onano	Yellow tuff	Chabazite, Feldspars, Mica, Phillipsite, Clays
195	La Selva	Onano	Yellow tuff	Chabazite, Feldspars, Mica, Phillipsite
202	La Selva	Onano	Yellow tuff	Chabazite, Feldspars, Mica, Phillipsite
54	Strada Canino-Valentano	Sorano	Lithoid yellow tuff	Chabazite, Feldspars, Mica
55	Ischia di Castro	Sorano	Yellow tuff	Chabazite, Phillipsite
69	Pian di Rena	Sorano	Yellow tuff	Chabazite, Feldspars, Mica
70	Piana Perina (Riano)	TGVT	Yellow tuff	Chabazite, Phillipsite, Feldspars, Mica, Clays
71	Piana Perina (Riano)	TGVT	Yellow tuff	Chabazite, Phillipsite, Feldspars, Calcite
72	Piana Perina (Riano)	TGVT	Yellow tuff	Chabazite, Phillipsite, Feldspars, Calcite
129	Riano	TGVT	Yellow tuff	Chabazite, Phillipsite, Feldspars, Mica, Calcite
Z1-Z7-Z13	Ercoli Quarry	TGVT	Yellow tuff	Chabazite, Phillipsite, Feldspars, Mica, Calcite
Z14-Z19				
Z2-Z3	Incecchi Quarry	TGVT	Yellow tuff	Chabazite, Phillipsite, Feldspars, Mica, Calcite
Z9-Z10-Z16	Mandroni Quarry	TGVT	Yellow tuff	Chabazite, Phillipsite, Feldspars, Mica, Calcite
Z4-Z5-Z6	Perina	TGVT	Yellow tuff	Chabazite, Phillipsite, Feldspars, Mica, Calcite
Z8-Z17	SICAT Quarry	TGVT	Yellow tuff	Chabazite, Phillipsite, Feldspars, Mica, Calcite
Z15-Z18	Ponte Storto	TGVT	Yellow tuff	Chabazite, Phillipsite, Feldspars, Mica, Calcite
Z11-Z12	Quarry	TGVT	Yellow tuff	Chabazite, Phillipsite, Feldspars, Mica, Calcite

TABLE 2
Chemical analyses (wt%) and formulas (calculated on 24 oxygens) of chabazites from selected samples.

Sample	1	15	111b	112	124	237	247	257	259	267	281	6G	19Y	20Z	21AB	22AC	23AD	LP0	TAB1	SP	44	50	
<i>Fmt.</i>	C SVD	C VV	C VV	C VV	C VV	C VV	C VV	C VV	C VV	C VV	C VV	OBF	OBF	OBF	OBF	OBF	OBF	OBF	OBF	OBF	OBF	OBF	OBF
SiO ₂	51.49	50.54	49.66	52.37	49.04	50.89	51.46	51.21	51.36	50.84	51.07	52.90	51.97	52.53	51.18	53.79	50.78	50.88	50.35	51.85	49.93	49.63	
Al ₂ O ₃	18.91	18.14	18.19	17.92	18.52	18.17	17.96	18.41	17.96	17.86	17.66	17.37	17.36	17.47	16.84	17.67	16.59	16.98	16.80	17.08	18.19	18.48	
Fe ₂ O ₃	0.12	1.03	0.82	0.56	0.20	1.40	0.69	0.31	0.24	1.44	0.61	0.25	0.56	0.68	0.23	0.49	0.11	0.25	0.29	0.22	0.67	0.08	
MgO	0.67	0.56	0.47	0.78	0.34	0.57	0.68	0.58	0.77	0.69	0.81	0.73	0.84	0.91	0.79	0.62	0.53	0.72	0.64	0.59	0.56	0.43	
CaO	7.13	4.61	5.48	5.12	6.15	4.87	6.09	6.24	6.32	5.95	5.80	5.45	5.46	6.06	5.24	6.81	6.73	5.88	5.77	5.70	4.72	6.44	
Na ₂ O	0.37	0.56	0.46	0.60	0.38	0.34	0.27	0.40	0.21	0.47	0.36	0.29	0.92	0.38	0.62	0.20	0.31	0.60	0.53	0.20	0.53	0.44	
K ₂ O	3.46	6.75	6.35	4.77	5.26	7.48	3.78	4.07	3.53	4.63	4.00	4.39	3.97	4.04	4.54	3.80	3.09	3.36	3.56	4.47	7.09	4.25	
H ₂ O	17.50	17.50	18.50	17.50	20.00	16.50	19.00	18.50	19.00	18.00	19.00	18.50	19.00	18.00	20.00	17.00	21.50	21.00	21.50	20.00	18.00	20.00	
Sum	99.65	99.69	99.93	99.62	99.89	100.22	99.93	99.72	99.39	99.88	99.31	99.88	100.08	100.07	99.44	100.38	99.64	99.67	99.44	100.11	99.69	99.75	
Si	8.361	8.353	8.307	8.532	8.296	8.329	8.479	8.427	8.494	8.375	8.490	8.649	8.556	8.547	8.609	8.595	8.626	8.590	8.592	8.631	8.278	8.347	
Al	3.619	3.533	3.586	3.440	3.692	3.504	3.487	3.570	3.501	3.467	3.460	3.347	3.368	3.354	3.338	3.327	3.321	3.378	3.379	3.351	3.554	3.663	
Fe	0.015	0.128	0.103	0.069	0.025	0.172	0.086	0.038	0.030	0.178	0.076	0.031	0.069	0.083	0.029	0.059	0.014	0.032	0.037	0.028	0.084	0.010	
Mg	0.162	0.138	0.117	0.189	0.086	0.139	0.167	0.142	0.190	0.169	0.201	0.178	0.206	0.221	0.198	0.148	0.134	0.181	0.163	0.146	0.138	0.108	
Ca	1.240	0.816	0.982	0.894	1.115	0.854	1.075	1.100	1.120	1.050	1.033	0.955	0.963	1.056	0.944	1.166	1.225	1.064	1.055	1.017	0.838	1.160	
Na	0.116	0.179	0.149	0.189	0.125	0.108	0.086	0.128	0.067	0.150	0.116	0.092	0.294	0.120	0.202	0.062	0.102	0.196	0.175	0.065	0.170	0.143	
K	0.717	1.423	1.355	0.991	1.135	1.562	0.794	0.854	0.745	0.973	0.848	0.916	0.834	0.838	0.974	0.774	0.670	0.724	0.775	0.949	1.499	0.912	
H ₂ O	9.474	9.643	10.318	9.505	11.281	9.003	10.438	10.150	10.477	9.886	10.531	10.084	10.429	9.765	11.217	9.056	12.177	11.821	12.232	11.100	9.950	11.215	
Si/Al	2.31	2.36	2.32	2.48	2.25	2.38	2.43	2.36	2.43	2.42	2.45	2.58	2.54	2.55	2.58	2.58	2.60	2.55	2.54	2.58	2.33	2.28	
Na/K	0.16	0.13	0.11	0.19	0.11	0.07	0.11	0.15	0.09	0.15	0.14	0.10	0.35	0.14	0.21	0.08	0.15	0.28	0.23	0.07	0.11	0.16	
E%	-0.53	0.64	-3.15	2.80	0.87	-4.12	3.65	2.99	2.02	-2.66	0.83	2.28	-2.81	-4.62	-3.54	-3.92	-4.82	-0.30	-0.20	0.34	-1.91	1.99	
K/Ca	.58	1.74	1.38	1.11	1.02	1.83	.74	.78	.67	.93	.82	.96	.87	.79	1.03	.66	.55	.68	.94	.93	1.79	.79	
M/D	.59	1.68	1.37	1.09	1.05	1.68	.71	.79	.62	.92	.78	.89	.96	.75	1.03	.64	.57	.74	.82	.87	1.71	.83	

$$E\% = \frac{(Al + Fe) - [Na + K + 2(Ca + Mg)]}{[Na + K + 2(Ca + Mg)]} * 100$$

M/D= Monovalent/Divalent

TABLE 2, continued

Sample	51	97	154	157	164	181	212	4E	54	55	69	70	71	72	Ercoli	Incecchi	Mandrioni	P.Storto	Perina	Quarry	Sicat
<i>Fmt.</i>	Onano	Onano	Onano	Onano	Onano	Onano	Onano	Onano	Sorano	Sorano	Sorano	TGVT	TGVT	TGVT	TGVT	TGVT	TGVT	TGVT	TGVT	TGVT	TGVT
SiO ₂	49.15	50.45	49.23	50.17	49.74	48.29	49.02	47.59	50.19	45.73	48.68	49.35	50.27	50.19	49.78	49.46	50.07	49.95	49.94	49.71	51.20
Al ₂ O ₃	18.92	18.95	19.27	19.43	17.49	20.45	20.68	19.09	17.51	21.75	18.83	18.01	17.80	18.13	18.16	18.24	17.60	18.04	17.98	17.50	17.63
Fe ₂ O ₃	0.32	0.27	0.18	0.27	0.09	0.29	0.33	0.16	0.15	0.00	0.34	0.12	0.03	0.05	0.08	0.30	0.10	0.20	0.07	0.13	0.07
MgO	0.51	0.63	0.35	0.38	0.40	0.44	0.51	0.19	0.54	0.19	0.77	0.63	0.57	0.52	0.47	0.51	0.40	0.58	0.57	0.46	0.48
CaO	6.33	6.86	5.87	6.23	5.35	7.59	8.02	7.53	6.50	8.58	5.87	5.20	5.14	6.16	6.44	5.48	5.19	5.44	5.50	6.09	6.09
Na ₂ O	0.32	0.42	0.50	0.35	0.23	0.59	0.30	0.44	0.22	0.47	0.47	0.76	0.50	0.48	0.53	0.57	0.56	0.38	0.58	0.37	0.21
K ₂ O	5.06	3.53	5.56	6.19	5.26	4.52	3.78	3.69	3.57	3.92	4.93	5.59	5.12	4.96	4.15	6.10	5.44	5.43	5.22	4.40	4.81
H ₂ O	19.00	18.50	19.00	16.50	21.00	18.00	17.50	21.00	20.50	19.50	20.00	20.00	20.00	19.00	20.31	19.15	20.46	19.57	19.67	21.40	19.00
Sum	99.61	99.61	99.96	99.52	99.56	100.17	100.14	99.69	99.18	100.14	99.89	99.66	99.43	99.49	99.92	99.80	99.83	99.58	99.53	100.04	99.49
Si	8.238	8.313	8.230	8.218	8.502	7.976	8.002	8.144	8.497	7.711	8.224	8.371	8.488	8.395	8.383	8.326	8.490	8.411	8.418	8.470	8.524
Al	3.737	3.680	3.796	3.751	3.523	3.981	3.978	3.850	3.494	4.322	3.749	3.600	3.542	3.574	3.604	3.618	3.517	3.580	3.572	3.513	3.459
Fe	0.040	0.033	0.023	0.033	0.012	0.036	0.041	0.021	0.019	0.000	0.043	0.015	0.004	0.006	0.011	0.037	0.013	0.026	0.008	0.016	0.009
Mg	0.127	0.155	0.087	0.093	0.102	0.108	0.124	0.048	0.136	0.048	0.194	0.159	0.143	0.130	0.117	0.128	0.102	0.145	0.144	0.117	0.119
Ca	1.137	1.211	1.051	1.093	0.980	1.343	1.403	1.387	1.179	1.550	1.062	0.945	0.930	1.104	1.162	0.988	0.942	0.981	0.993	1.111	1.086
Na	0.104	0.134	0.162	0.111	0.076	0.189	0.095	0.146	0.072	0.154	0.154	0.250	0.164	0.156	0.174	0.186	0.184	0.123	0.190	0.122	0.068
K	1.082	0.742	1.186	1.293	1.147	0.952	0.787	0.806	0.771	0.843	1.062	1.210	1.103	1.058	0.892	1.310	1.177	1.167	1.123	0.955	1.021
H ₂ O	10.618	10.164	10.590	9.011	11.968	9.913	9.524	11.982	11.571	10.962	11.265	11.311	11.259	10.596	11.404	10.749	11.568	10.985	11.053	12.157	10.547
Si/Al	2.20	2.26	2.17	2.19	2.41	2.00	2.01	2.11	2.43	1.78	2.19	2.33	2.40	2.35	2.33	2.30	2.41	2.35	2.36	2.41	2.46
Na/K	0.10	0.18	0.14	0.09	0.07	0.20	0.12	0.18	0.09	0.18	0.14	0.21	0.15	0.15	0.20	0.14	0.16	0.11	0.17	0.13	0.07
E%	0.63	2.01	4.74	-0.68	4.04	-1.56	1.10	1.07	0.58	3.10	0.54	-1.84	3.79	-2.91	-0.54	-2.97	1.97	1.10	-0.43	-0.55	-1.17
K/Ca	.95	.61	1.13	1.18	1.17	.71	.56	.58	.65	.54	1.00	1.28	1.19	.96	0.77	1.33	1.25	1.19	1.13	0.86	0.94
M/D	.94	.64	1.18	1.18	1.13	.79	.58	.67	.64	.62	.97	1.32	1.18	.98	0.83	1.34	1.30	1.15	1.15	0.88	0.90

$$E\% = \frac{(Al + Fe) - [Na + K + 2(Ca + Mg)]}{[Na + K + 2(Ca + Mg)]} * 100$$

M/D= Monovalent/Divalent

However, on the basis of the current knowledge it likely seems that the deposits emplaced at quite high temperatures, in any case lower than those necessary for the welding of the products. The joint action of the temperature and the meteoric waters and/or groundwaters could have favored the glass leaching and the consequent zeolitization.

Table 2 gives chemical analyses and atoms per formula unit of the investigated chabazites. Chabazites from the C ignimbrite of Vico Volcano are characterized by a Si/Al ratio of 2.25-2.48. A relatively large range was determined for sample 15 to sample 237 (2.25-2.48), but samples 247 to 281 display a narrow range (2.36-2.45). These groups can also be distinguished on the basis of the extraframework cations. The first group is characterized by higher K content, respect to Ca, while Na and Mg are similar but far lower than the other two cations. In the second group, Ca is the predominant extraframework cation, and Na and Mg have similar values compared to the first group. These differences could be related to different composition of the original glass; however, because of the intense alteration of the rocks, only in rare cases (a few samples of the Vulsini volcanic district) the glass was analyzed. It cannot be excluded, however, that cationic exchange processes took place after the zeolite formation. In this case, it would be very difficult, indeed, to explain how these processes affected only some layers of a given formation at the same location.

Chabazites from the Orvieto-Bagnoregio formation display a relatively high Si/Al ratio (2.54-2.60), varying in a very narrow range. These are the only chabazites, among the investigated ones, having Ca greater than K (except for sample 21AB), and having Na and Mg in subordinate amounts.

Chabazites from the Onano formation are characterized by a high variability of the Si/Al ratio, ranging between 2.00 and 2.41. As far as the extraframework cations are concerned, Ca and K clearly prevail over the others, but no clear relationship is evident among them.

The composition of chabazites from the

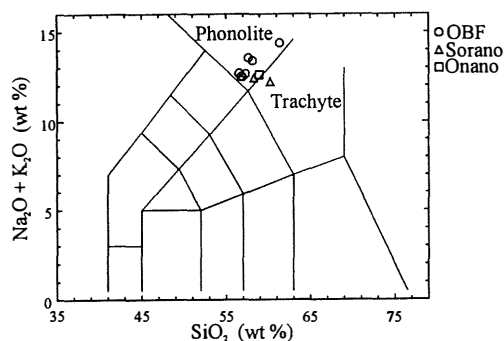


Fig. 2 - T.A.S. diagram for the considered glasses (modified after Le Bas *et al.*, 1986).

Sorano formation is mostly variable. Here is recorded the lowest Si/Al ratio (1.78, sample 55), and Ca is the predominant cation.

The chemical composition of glasses separated from selected samples and from the literature are reported in Table 3. Fig. 2 shows their petrographical classification (phonolites and, subordinately, trachytes) according to the T.A.S. diagram (Le Bas *et al.*, 1986). The Si/Al ratio is always higher in the glasses than in the derived authigenic phases, but the most striking features are the Na decrease during the glass-to-chabazite conversion and a higher Ca concentration in chabazites. No particular trend of K content in the glass and in the zeolite was recognized.

Chabazites from *Tufo Giallo della Via Tiberina* also display a very wide Si/Al range and variable Ca and K contents. The joint occurrence of phillipsite (Table 4) and chabazite confirms the potassic environment for these zeolites, but evidences as well the higher Ca content with respect to Na. In this case, the high Ca content of these zeolites can be attributed to the contribution of calcareous clasts to the solution that circulated in the deposit.

Ternary diagrams (figs. 3a and 3b) show a summary of the whole data set. As far as the cationic population is considered (fig. 3a), regardless of the kind of zeolite, the Na content is relatively constant and lower than that of the corresponding glass. On the other hand, notwithstanding a wide variability of K and

TABLE 3

Chemical analyses (wt%) and Barth's anhydrous standard cell content (calculated on 160 oxygens) of glasses from selected formations.

Sample	06G	19Y	20Z	23AD	BTR	B*	M*	#	B1^	PL°
<i>Fmt.</i>	OBf	OBf	OBf	OBf	OBf	OBf	OBf	Onano	Sorano	Sorano
SiO ₂	54.39	59.44	55.14	53.47	52.59	55.60	55.73	57.80	56.14	58.24
TiO ₂	0.49	0.35	0.53	0.40	0.50	-	-	0.51	0.44	0.46
Al ₂ O ₃	17.00	18.05	17.35	17.13	16.90	18.50	18.90	18.55	18.28	18.94
FeO	4.29	2.12	4.16	4.39	4.55	-	-	3.44	-	2.12
Fe ₂ O ₃	-	-	-	-	-	6.04	5.82	-	4.63	-
MnO	0.31	0.09	0.11	0.12	0.12	-	0.10	-	0.12	0.02
MgO	0.84	0.18	0.73	1.10	1.05	0.88	1.08	0.60	0.84	0.95
CaO	3.77	2.51	3.71	4.40	4.59	4.20	2.48	4.42	3.34	3.91
Na ₂ O	2.98	3.62	3.76	3.32	4.13	3.91	3.56	3.44	3.96	1.59
K ₂ O	9.83	10.32	8.96	8.49	7.40	8.58	8.28	8.91	8.00	10.21
H ₂ O	6.00	3.50	5.50	7.00	8.00	2.20	3.72	2.10	4.25	3.20
Total	99.90	100.18	99.95	99.82	99.83	99.91	99.67	99.77	100.00	99.64
Si	55.142	57.223	55.235	54.644	54.322	54.235	54.770	55.483	55.113	56.102
Ti	0.374	0.253	0.399	0.307	0.388	-	-	0.368	0.325	0.333
Al	20.311	20.479	20.482	20.631	20.572	21.267	21.890	20.985	21.149	21.501
Fe	3.637	1.707	3.485	3.751	3.930	4.927	4.783	2.761	3.801	1.708
Mn	0.217	0.060	0.076	0.085	0.086	-	0.068	-	0.081	0.013
Mg	1.269	0.258	1.090	1.675	1.616	1.279	1.582	0.858	1.229	1.364
Ca	4.095	2.589	3.981	4.817	5.079	4.389	2.611	4.545	3.513	4.035
Na	5.857	6.756	7.302	6.578	8.270	7.394	6.783	6.402	7.537	2.969
K	12.712	12.673	11.449	11.067	9.750	10.676	10.381	10.910	10.018	12.546
H ₂ O	20.619	11.234	18.369	23.851	27.551	7.103	12.189	6.721	13.911	10.277
Si/Al	2.71	2.79	2.70	2.65	2.64	2.55	2.50	2.64	2.61	2.61
Na/K	0.46	0.53	0.64	0.59	0.85	0.69	0.65	0.59	0.75	0.24

*de' Gennaro et al., 1987; ^Passaglia et al., 1990; #Adabbo & Langella, 1994; °Granato et al., 1991

Ca+Mg values, a sharp distinction between chabazite and phillipsite fields can be drawn (figs. 3a and 3b).

SEM observations confirmed the widespread presence of chabazite in all the investigated formations, and particularly the Orvieto-Bagnoregio formation. This zeolite is preferentially concentrated in the vugs of the rock (fig. 4a) and is associated only to a minor extent with phillipsite (fig. 4b). Contrary to what observed for other Italian volcanic deposits no genetic relationship was recognised

between the two zeolites. Phillipsite is particularly concentrated in pumice where it coats the walls and fills the cavities; here the crystals are generally larger, up to several tens of mm (fig. 4c). The *Tufo Giallo della Via Tiberina* formation, unlike the others, shows an unresolved association of chabazite and phillipsite (fig. 4d).

Table 5 shows, for some selected chabazites, total cation exchange capacities (CEC) as well as the contribution of each extraframework cation. The calculated CECs are also reported

TABLE 4

Chemical analyses (wt%) and formulas (calculated on 32 oxygens) of phillipsites from selected samples.

Sample	Ercoli	Incechi	Mandroni	P. Storto	Perina	Quarry	BTR
<i>Fmt.</i>	TGVT	TGVT	TGVT	TGVT	TGVT	TGVT	OBF
SiO ₂	52.12	50.24	52.48	52.18	50.60	52.55	51.39
Al ₂ O ₃	18.58	19.84	18.28	18.16	17.50	18.18	17.23
Fe ₂ O ₃	0.05	0.20	0.12	0.32	0.22	0.05	0.24
MgO	0.21	0.50	0.19	0.78	0.23	0.22	0.20
CaO	3.44	4.62	3.37	3.51	3.59	2.27	1.55
Na ₂ O	1.23	0.65	1.47	1.25	1.15	0.97	1.18
K ₂ O	9.00	8.80	8.73	7.66	8.76	10.45	11.30
H ₂ O	15.47	15.15	15.17	16.00	17.65	15.00	17.00
Total	100.08	100.00	99.79	99.86	99.69	99.69	100.09
Si	11.264	10.884	11.325	11.294	11.302	11.388	11.434
Al	4.731	5.065	4.649	4.632	4.607	4.643	4.518
Fe	0.009	0.033	0.019	0.052	0.036	0.008	0.040
Mg	0.068	0.161	0.060	0.252	0.077	0.071	0.066
Ca	0.796	1.072	0.778	0.814	0.859	0.527	0.369
Na	0.513	0.273	0.614	0.525	0.496	0.408	0.509
K	2.481	2.432	2.402	2.115	2.496	2.889	3.207
H ₂ O	11.146	10.942	10.913	11.546	13.140	10.838	12.611
Si/Al	2.38	2.15	2.44	2.44	2.45	2.45	2.53
Na/K	0.21	0.11	0.26	0.25	0.20	0.14	0.16
E%	0.18	-2.06	-0.93	-2.89	-5.27	3.35	-1.52
K/Ca	3.12	2.27	3.09	2.60	2.91	5.48	8.69
M/D	3.46	2.19	3.60	2.48	3.20	5.51	8.54

$$E\% = \frac{(Al + Fe) - [Na + K + 2(Ca + Mg)]}{[Na + K + 2(Ca + Mg)]} * 100$$

M/D = Monovalent/Divalent

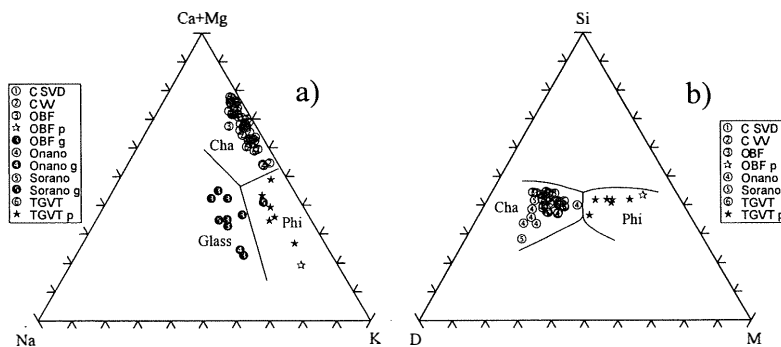


Fig. 3 – Ternary diagrams for zeolites and glasses. a) exchangeable cation content; b) chemical variability. TGVTp and OBFp refer to phillipsite, solid dots refer to glasses. D = Divalent ions, M = Monovalent ions.

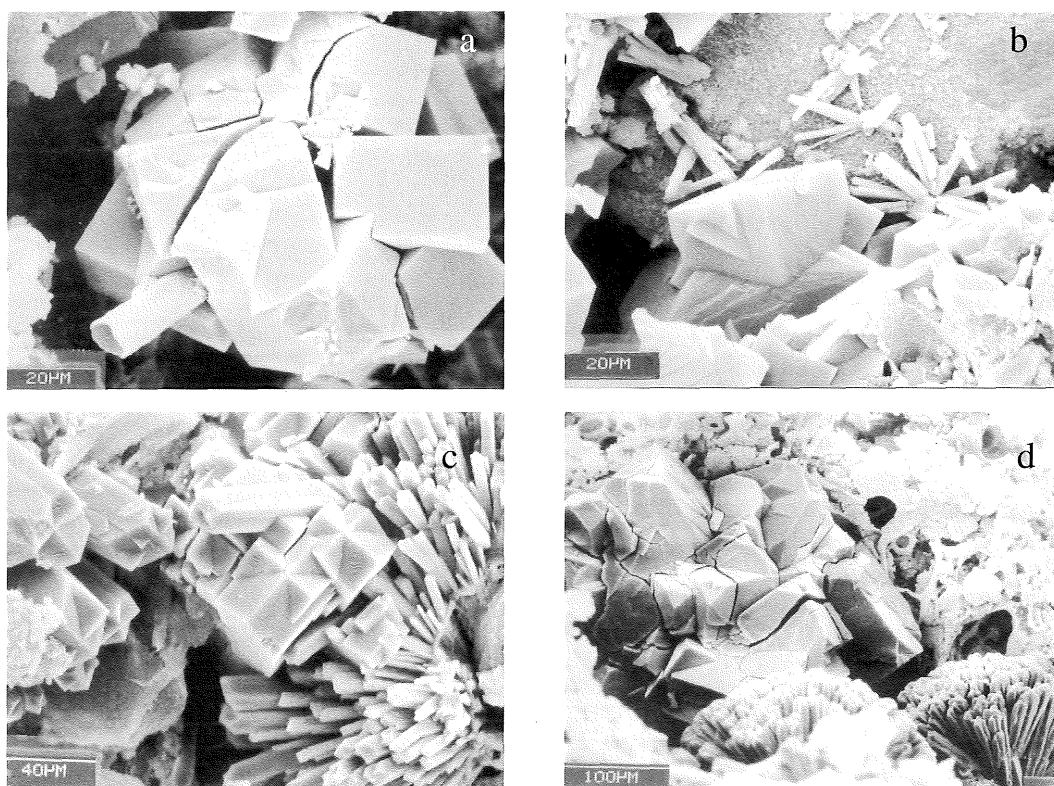


Fig. 4 – SEM micrographs: a) sample LP3, rhombohedral chabazite crystals in rock vugs; b) sample SP, small chabazite crystals associated with clusters of acicular phillipsite; c) sample 247, phillipsite crystal aggregates in pumice; d) sample 129, rhombohedral chabazite crystals associated with phillipsite aggregates.

for comparison. Only for chabazite from C ignimbrite (Vico Volcano) and from *Tufo Giallo della Via Tiberina* is the calculated value almost equal to the experimental CEC, whereas the other zeolites show an incomplete exchange process. In most cases, moderate CEC reductions (3-7%) were recorded, except for chabazites from the Onano and Sorano formations where the reduction is remarkable (15%). As far as the contribution of CECs from individual cations is concerned, Ca and Mg data refer to the NaCl solution exchange inasmuch as they were higher (on average 0.05-0.1 meq/g for Ca and 0.01-0.02 meq/g for Mg) than those obtained with KCl solutions.

It appears that the difficulty in removing all Ca and Mg prevents the exchange from

attaining completion. The extent to which the exchange is not complete increases with an increase of the framework charge density of various chabazite samples. This finding is in agreement with the Eisenmann theory (Eisenmann, 1962; Sherry, 1969; Colella, 1996), according to which the selectivity of a given zeolite for cations of higher valence increases with the intensity of the electrical field generated by its framework anion. The fact that lower Ca and Mg exchange levels may be attained by performing the exchange with K rather than with Na may be related to the larger steric hindrance of K which further hinders cation exchange.

The concentration of the ingoing cation in the contact solution greatly affects the

TABLE 5

Calculated and measured CEC for some investigated chabazites and their framework charge density.

Sample	Calculated CEC (meq/g)					Measured CEC (meq/g)					Charge density
	Ca	Mg	Na	K	Total	Ca	Mg	Na	K	Total	C/cm ³
70	1.85	0.32	0.25	1.19	3.61	1.83	0.25	0.25	1.20	3.53	705
71	1.83	0.29	0.16	1.08	3.36	1.82	0.22	0.19	1.07	3.30	689
55	3.06	0.10	0.15	0.83	4.14	2.45	0.10	0.17	0.80	3.52	838
181	2.71	0.22	0.19	0.96	4.08	2.18	0.15	0.19	0.96	3.48	783
212	2.86	0.25	0.10	0.80	4.01	2.56	0.20	0.10	0.80	3.66	783
257	2.22	0.29	0.13	0.87	3.51	2.20	0.26	0.13	0.88	3.47	701
281	2.07	0.41	0.12	0.85	3.45	2.03	0.40	0.12	0.85	3.40	724
112	1.82	0.38	0.19	1.01	3.40	1.84	0.36	0.19	1.02	3.41	677
111b	1.96	0.24	0.15	1.35	3.70	1.95	0.23	0.15	1.35	3.68	724
SP	2.04	0.30	0.06	0.95	3.35	1.87	0.22	0.06	0.95	3.10	654
20Z	2.16	0.46	0.12	0.86	3.60	2.10	0.35	0.12	0.86	3.43	771

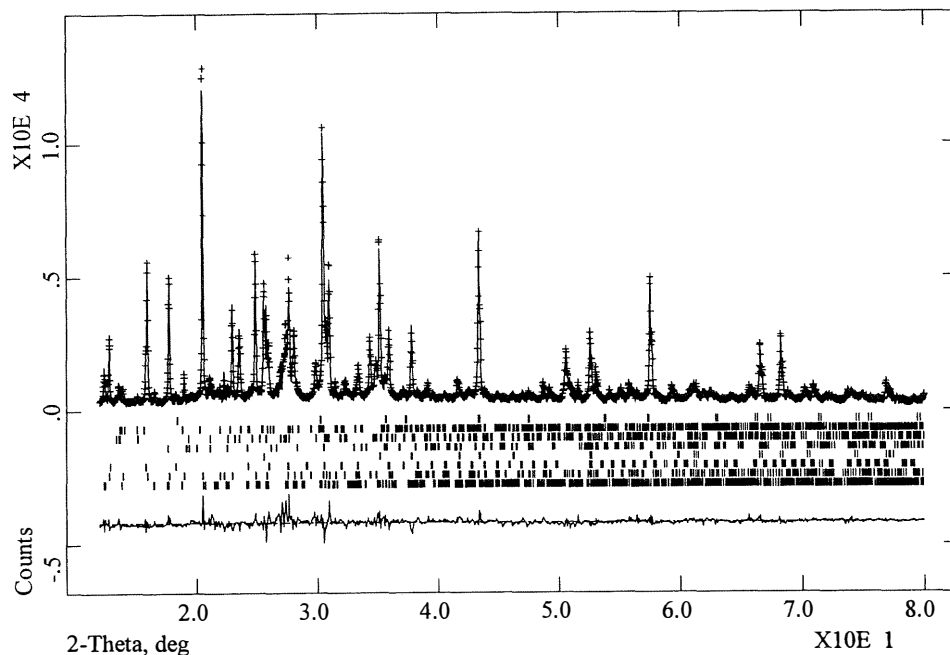


Fig. 5 – Observed (crosses), calculated (line) and difference (bottom line) patterns for LP3 sample, XRPD Rietveld analyses. Vertical bars mark calculated phase reflections, from bottom to top: phillipsite, chabazite, analcime, Al₂O₃, biotite, sanidine, albite, and clinopyroxene.

TABLE 6

Cation exchange capacity (CEC) for selected samples of raw zeolitic tuff.

Sample	Formation	CEC (meq/g)
111b	C Ign. VV	2.6
112	C Ign. VV	2.2
118	C Ign. VV	2.7
124	C Ign. VV	2.5
257	C Ign. VV	2.3
281	C Ign. VV	2.5
SP	OBF	2.2
LP3	OBF	2.4
91	Onano	2.8
105	Onano	2.7
145	Onano	2.1
168	Onano	1.9
181	Onano	2.4
212	Onano	2.4
129	TGVT	2.0
70	TGVT	2.1
Z8	TGVT	2.0

completeness of the exchange (Torraca *et al.*, 1998), and therefore the molality of the solution used (0.5) could not have been sufficient for the complete exchange. More concentrated solutions were utilized by Alberti *et al.* (1982) and by Passaglia (1978), obtaining the nearly complete removal of Ca and Mg from chabazites displaying high framework charge density.

CEC data on raw materials for some investigated samples are listed in Table 6. All values are higher than 2 meq/g (except for sample 168=1.9) with a maximum of 2.8 meq/g (sample 91). The wide range of values depends on the variable total amount of effective zeolite, whereas no relationship was found between this parameter and the relative concentration of chabazite and phillipsite. This is a further confirmation of the similar cation exchange capacity of phillipsite and chabazite

TABLE 7

Zeolite grade (%) of selected samples, evaluated by water adsorption/desorption (TGA), Rietveld method (Rietveld), and cation exchange capacity (CEC) method.

Sample	TGA		Rietveld		CEC Total zeolite
	CHA	PHI	CHA	PHI	
1	58	6			
129	45	8			57
44	71	2			
50	51	12			
51	70	9			
145	51	10			
165	53	7			
168	43	7			
181	47	16			67
195	47	20			
202	30	20			
212	43	14			66
54	77	-	65.6	-	70
55	58	13			68
69	73	-			
15	55	4			
223	51	21			
231	41	24			
237	57	3			
247	57	16			
251	57	13			
257	52	10			66
259	52	13			
266	52	6			
271	45	21			
281	52	15			72
284	49	13			
O6G	61	11			
16T	61	4			
19Y	40	14			
20Z	50	10			
21AB	37	11			
22AC	66	9			
23AD	54	13			
SP	58	8			64
TAB1	52	11			
LP3	57	10	58.6	5.4	68
LP0	48	14			

that was proven for other Italian zeolitized products (de' Gennaro and Langella, 1996; Carnevali *et al.*, 1994). Therefore, the joint presence of phillipsite (never exceeding 20 wt%) and chabazite does not seem to affect the total CEC of the raw materials for their use in wastewater treatment of polluting cations, towards which these two zeolites have a similar selectivity.

The zeolite content was evaluated on selected samples using two different methods: the water vapor adsorption/desorption technique and by comparing the CEC of *tout venant* with that of pure phases, whenever available. On two samples (LP3 and 55), Rietveld XRPD quantitative analyses were also performed (fig. 5). Table 7 summarizes these results which are in good agreement. The prevailing amount of chabazite is confirmed, as well as the total zeolite content which is higher than 60 wt%, except for two samples.

CONCLUSIONS

The research carried out on the main volcanoclastic formations of northern Latium allowed us to evaluate their potentiality as a source of economic minerals. The main results can be summarized as follows:

- All the investigated deposits (Orvieto-Bagnoregio formation, Onano and Sorano formations from Vulcini volcanic district, Cignimbrite from Vico volcano, and Cignimbrite and *Tufo Giallo della via Tiberina* from Sabatini volcanic district) consist of chabazite-rich tuffs.

- The chabazite content is 37-72 wt%, with a minor amount of phillipsite; the overall grade of zeolites is higher than 50 wt%.

- The CEC of the investigated materials is, on average, higher than those of other European deposits that are characterized by very high amounts of clinoptilolite (Tsitsishvili *et al.*, 1984).

These properties, the large available tonnage of the materials, and their well known selectivity towards several polluting cations,

demonstrate that the investigated materials can be advantageously employed in several industrial processes involving wastewater treatment and, above all, zootechny and agriculture.

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