

## Italian zeolitized rocks of technological interest

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Received: 20 October 1995/Accepted: 10 April 1996

**Abstract.** Large areas of Italian territory are covered by thick and widespread deposits of zeolite-bearing volcanoclastic products. The main zeolites are phillipsite and chabazite spread over the whole peninsula, and clinoptilolite recorded only in Sardinia. A trachytic to phonolitic glassy precursor accounts for the formation of the former zeolites characterized by low Si/Al ratios ( $\leq 3.00$ ), while clinoptilolite is related to more acidic volcanism. The genesis of most of these zeolitized deposits is linked to pyroclastic flow emplacement mechanisms characterized by quite high temperatures and by the presence of abundant fluids. The main utilization of these materials has been and still is as dimension stones in the building industry. Currently, limited amounts are also employed in animal farming (dietary supplement, pet litter and manure deodorizer) and in agriculture as soil improvement and slow-release fertilizers. New fields of application have been proposed for these products on account of their easy availability, very low cost, their high-grade zeolites (50–70%), and good technological features such as high cation exchange capacities and adsorption properties.

minerogenetic processes leading to their formation have received substantial stimulus. In particular, studies have focused on the products of Quaternary volcanism in central-southern Italy, although researches highlighting the presence of zeolitized materials within the Apennine sedimentary successions and Sardinian pyroclastites have also been completed.

The extremely complex question of zeolitization has been tackled, taking into account both mineralogical and all the geological, volcanological, petrographical and geomagnetic information required to draw up valid genetic models. Valuable contributions to our knowledge of zeolitization processes have also been provided by laboratory simulations, which followed the evolution of the chemical and mineralogical composition of fluids and solid phases respectively, in the course of the interaction between volcanic glass and solutions.

The present study updates knowledge on Italian zeolitized volcanoclastic rocks and the perspectives for their exploitation in technological fields.

Active volcanism, both continental and insular, occurring in Italy mainly during the last million years, gave rise to the emplacement of huge volcanoclastic deposits. Many of them were then subjected to syn- and post-depositional minerogenetic processes which resulted in the formation of zeolites and clay minerals. Zeolites, formed in either submarine or lacustrine products or continental deposits, originate by transformation of a parent volcanic glass after interaction with alkaline solutions.

Many outcrops are of particular interest due to their high zeolite content. This resource, for its economic value, cannot be neglected, and Italian contractors must pay particular attention to the wide applications of zeolites in many technological fields.

On the basis of these considerations, during the last 25 years research on these Italian products and on the

### Analytical methods

The analytical data given in this work are both from previous published sources and, in some cases, original ones presented for the first time in this work.

The mineralogical investigations on zeolitized materials were carried out using a Philips PW 1730 diffractometer with  $\text{CuK}_\alpha$  radiation. Pure phases were obtained using the enrichment and separation methods described by de'Gennaro and Franco (1979). The chemical analyses were performed with a Link AN 10000 apparatus in the energy dispersive mode at 15 kV on selected crystals, linked to a scanning electron microscope (Stereoscan Cambridge 250 TP). A Netzsch STA-409 apparatus was used for thermogravimetric and thermogravimetric analyses, the latter also allowing the evaluation of zeolite content according to the methods proposed by Colella et al. (1982), de'Gennaro et al. (1984) and de'Gennaro and Colella (1989). Cation exchange capacity was evaluated following

**Table 1.** Mineralogical composition of the zeolitized rocks described in this study

Volcanic district	Age	Samples	Phases	Sources of data
Vulsini	0.6–0.13 Ma	47(20) <sup>a</sup>	Ch, Ph, S, Cpx, B	(1) (2) (3)
Vico	0.2–0.15 Ma	3(2)	Ch, Ph, S, Cpx, B	(1) (4)
Sabatini	0.6–0.37 Ma	31	Ch, Ph, S, Cpx, B	(5)
Colli Albani	0.7–0.50 Ma	9	Ch, Ph, B, Lc	(3) (6)
Monti Ernici	0.7–0.11 Ma	6	Ph, Cpx, B, Ca, Ol, Ga	(7)
Roccamonfina	1.5–0.05 Ma	3	Ch, Pl, Cpx, B	(6) (8) (9)
Somma-Vesuvio	A.D. 79	–	Ch, S, Cpx, B, Lc	(10)
Campi Flegrei (NYT)	12.000 y BP	28	Ph, Ch, S, Cpx, B	(3) (6) (8) (11) (12)
Campi Flegrei (CI)	33.000 y BP	9(3)	Ch, Ph, S, Cpx, B	(1) (3) (6) (9) (11) (13)
Monte Vulture	0.83–0.30 Ma	17(14)	Ch, Ph, Pl, B, Lc	(1) (3) (8)
Ponza	4.53–4.32 Ma	–	Mor, S, Cr, Il, Sm	(14)
Sardinia (north)	32–15 Ma	2	Cl, Q, S, Pl, B, Cr, Sm	(15) (16)
Sardinia (south)	32–15 Ma	(7)	Ch, An, Lau, Epi, St	(1)
Apennine chain (north)	40 Ma	–	Ph, Heu, An, Sm, Ca, Q, S, B	(3) (17)
Apennine chain (south)	1 Ma	6	Ph, An, Ch, Sm, Il	(18)

<sup>a</sup> In brackets samples analyzed in this study

Sources of data: (1) this study; (2) Granato et al. 1991; (3) Passaglia and Vezzalini 1985; (4) Langella and Adabbo 1994; (5) Carnevali et al. 1994; (6) Passaglia et al. 1990; (7) de'Gennaro et al. 1982a; (8) Ciambelli et al. 1980; (9) de'Gennaro and Franco 1988; (10) de'Gennaro et al. 1981; (11) de'Gennaro et al. 1987; (12) de'Gennaro et al. 1982b; (13) de'Gennaro et al. 1984; (14) Passaglia et al. 1995; (15) de'Gennaro et al. 1995b; (16) Ghiara et al. 1995; (17) Minguzzi et al. 1987; (18) Adabbo et al. 1994.

Ch, chabazite; Ph, phillipsite; Cl, clinoptilolite; Heu, heulandite; An, analcime; Lau, laumontite; Epi, epistilbite; St, stilbite; Mor, mordenite; S, K-feldspar; Pl, Plagioclase; Q, quartz; Cpx, clinopyroxene; B, biotite; Lc, leucite; Ca, calcite; Ol, olivine; Ga, garnet; Cr, cristobalite; Il, illite; Sm, smectite

the technique described by Colella et al. (1982). CEC values of the whole rock also permitted measurement of the zeolite content, given the cation exchange capacity (measured and calculated) of the pure phases.

The volcanic districts considered, their age, the mineralogical phases, the number of reported analyses of zeolites, and the sources of data are given in Table 1.

### Geological setting and mineralogical features of zeolite-bearing rocks

Figure 1 is a sketch map of the largest outcrops of zeolitized pyroclastic deposits in Italy; they are mainly located on the western side of the Apennine chain, between Tuscany and Lucania (Basilicata), and in northern Sardinia. Moreover, pyroclastic layers of various thickness, sometimes deeply zeolitized, are widespread in the sedimentary sequences of the Apennine chain.

The Tyrrhenian belt of the central-southern Apennines was involved in volcanic activity which developed at two different periods from 4.4 Ma to historical times, with a pause of 0.5 Ma between 1.75 and 1.25 Ma BP (Savelli 1986; Zitellini et al. 1986). This break represents the boundary between the first phase, characterized by acidic volcanism in the northernmost part of the Apennine chain, and the second phase, marked by a potassic alkaline composition widely spread over the whole area.

#### Vulsini district

This is the northernmost volcanic district. Its activity (0.6 Ma BP) gave rise to the emplacement of both lava

flows and pyroclastites, covering an area of about 2200 km<sup>2</sup>.

Chronological reconstruction of volcanic events is quite difficult and not always unanimously accepted by researchers. Nappi et al. (1987) hypothesized magmatic and phreatomagmatic activity in four major volcanic complexes: Paleo-Bolsena, Bolsena, Latera and Montefiascone.

The Vulsini district is characterized by fall deposits and surges, some larger ignimbrites, and a series of small-scale pyroclastic flows. The following formations are recognized:

- Civitella d'Agliano Formation* (Nappi 1991): linked to the Paleo-Bolsena activity. The outcrops, of limited extent, are mainly concentrated in Civitella d'Agliano, Castell'Ottieri and the southern part of Tuscania. The deposit is lithoid, characterized by a coarse-grained matrix and sanidine- and analcimized leucite-bearing pumice.
- Small-scale pyroclastic flows* (Nappi et al. 1987): generally considered as belonging to the first cycle of the activity of the Bolsena complex, characterized by trachytic or trachyandesitic rocks with a potassic series (KS) affinity. The outcrops are mainly located near Bolsena.
- Orvieto-Bagnoregio Formation* (Nappi 1991): thick outcrops of this ignimbrite, emplaced after the most powerful eruptive event of the Bolsena district, cover the northeastern sector of this area. It appears to be composed of two not easily distinguishable flow units, the lower trachytic and the upper latitic. Its most widespread facies is a wine-red lithoid tuff; the ashy to micropumiceous matrix contains black and gray pumice, leucite and sanidine phenocrysts and lava fragments from the basement.



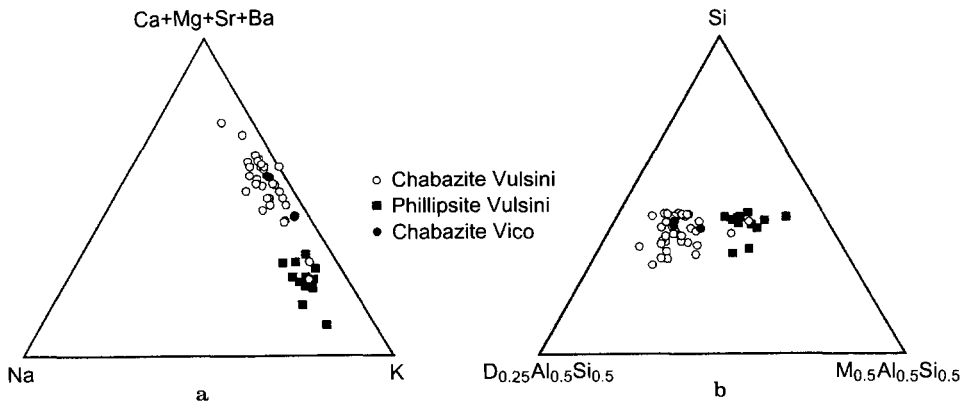
Fig. 1. Sketch map of the main outcrops of zeolitized pyroclastic deposits in Italy

- d. *Montefiascone Ignimbrite* (Marini and Nappi 1986): emplaced during the first stage of the activity of the Montefiascone complex, this is composed of a succession of five flow units. It outcrops in the south-eastern sector of the district and its main facies is a dark gray siltar with pumice, many rounded lava blocks, sedimentary lithics and mafic holocrystalline nodules in a glassy matrix.
- e. *Latera Volcanic Complex* (Nappi 1991): strombolian or effusive activity characterizes the first stage of this complex, followed by paroxysmal explosive activity with the emplacement of the "lower trachytic ignimbrite" (Nappi 1969a, b). This is followed by seven major and minor ignimbrites emplaced over a period of about 110 000 years (from 278 000 to 166 000 y BP). Reconstruction of events is quite complex owing to the presence within the ignimbrite of several flow units due to different conditions of water-magma interaction. Sparks (1975) proposed a stratigraphic succession characterized by six main ignimbrites (identified by letters A to F) and six pyroclastic falls. Activity ended with the emplacement of the Pitigliano formation, composed of more units with distinct lithological features.

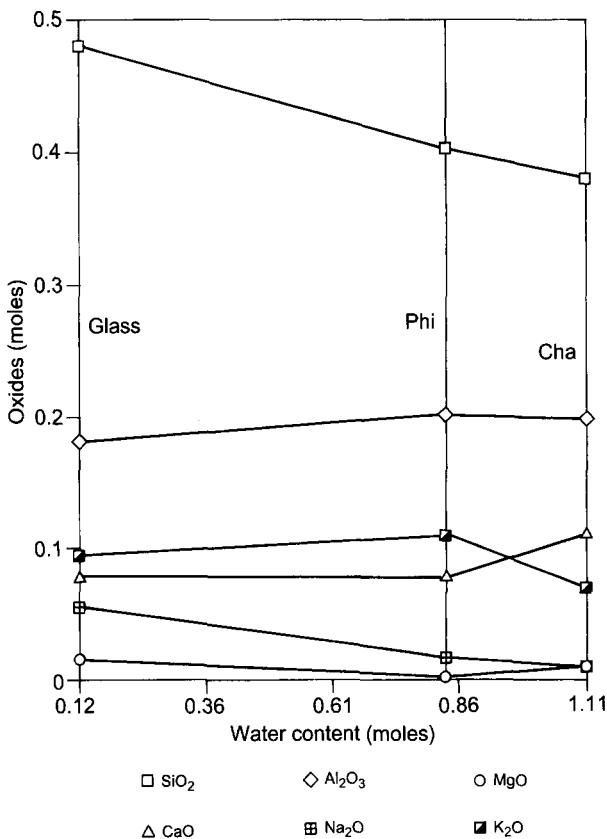
*Mineralogical features of the main zeolitized layers and genetic hypothesis.* The largest ignimbrites previously mentioned show chabazite – phillipsite assemblages, and sometimes analcime, derived from transformation of

glasses ranging from trachyte to phonolite. Chabazite, the prevailing zeolite, is widespread in the rock, while phillipsite is mainly concentrated in pumice. This is probably due to particular physical-chemical conditions which developed a microenvironment more suitable to phillipsite crystallization (Granato et al. 1991). Many chemical analyses of these zeolites and of the parent glass, from the literature or carried out for the present work, give a quite complete picture both of their composition and of the system from which they originated during glass-to-zeolite transformation. Chabazite generally has a calcic-potassic composition, except for two samples particularly rich in potassium from the Orvieta-Bagnoregio Formation and the "small-scale pyroclastic flows". Phillipsite is almost always potassic (Fig. 2a, b). Since the parent glass always showed a homogeneous composition (trachytic or trachytic-phonolitic) the chemical changes during the glass-to-phillipsite-to-chabazite transformation are well represented by Fig. 3. For both zeolites it is evident that there is a decrease in the Si/Al ratio, which is almost always higher in phillipsite than chabazite, and an appreciable decrease in sodium; an increase of calcium in chabazite and of potassium in phillipsite is also observed. However, it is difficult to explain what happens to the excess Si and Na which are lost in the process.

The emplacement of these ignimbrites is linked to paroxysmal eruptive processes which established a system characterized by high temperatures (some hundreds of degrees) and wet conditions probably related to phreatomagmatic explosions (De Rita et al. 1986; Nappi et al. 1994). Interaction between the fluids and the prevailing glassy fraction of these products was favored both by the high reactivity and low Si/Al ratio ( $\cong 2.60$ ) of the alkaline glass as well as by the high temperature of the system, and resulted in chabazite and phillipsite crystallization. Therefore, it is possible that the zeolitization process began with emplacement and developed in quite a short time. The hypothesis that the mineralogical process breaks off as the system cools down is supported by the absence of more stable phases, particularly low-temperature feldspar, and by laboratory simulations (de'Gennaro et al. 1988; de'Gennaro and Colella 1991). As discussed later, this kind of mechanism is applicable to all the volcanic deposits of central-southern Italy related to pyroclastic flow emplacement. It could also be, in a sense, related to the "geoautoclave" hypothesis proposed by Aleksiev and Djourova (1975) for high-silica volcanic products and by Lenzi and Passaglia (1974) for trachytic-to-phonolitic rocks. Gottardi (1989) excluded the possibility that the phenomenon could be considered as "diagenetic" since the system reaches temperatures higher than 200 °C. Furthermore, the frequent presence of unzeolitized or slightly zeolitized layers of various thickness at the top and the bottom of the ignimbrite is further evidence of the role played by the emplacement temperature and the abundance of fluids in the zeolitization process. Whenever present, the slight zeolitization of these products is restricted to the areas at the bottom of and contiguous to the "hot" ignimbrite where the influence of temperature was more pronounced. It cannot be excluded that the grain size of the products has a determining role in the process (Gottardi 1989). On the other hand there is occasional



**Fig. 2.** a Mole plot of exchangeable cation content in chabazites and phillipsites of the Vulsini and Vico districts and b chemical variability of the same phases, D, divalent cations; M, monovalent cations



**Fig. 3.** Oxide variations during glass-to-phillipsite-to-chabazite transformation, plotted against the water content of each phase, for the Vulsini district. Note that SiO<sub>2</sub> values have been divided by 2 for the purpose of the plot

macroscopical evidence of a grain size difference between zeolitized and unzeolitized materials.

**Feasibility of applications.** The pyroclastic flows of the Vulsini district have been thoroughly exploited, mainly to produce dimension stones for the building industry. At the moment, about ten quarries are still active and some of them have almost reached the bottom of the deposit. However, these materials are of definite economic interest, especially because of the constant high-grade of chabazite

from the stratigraphical and volumetric points of view (Table 2). Nevertheless, questions of landscape alteration or environmental impact due to intense exploitation cannot be neglected. It is therefore to be hoped that mining activity will take into account these aspects while still allowing the exploitation of these materials in specific technological fields (agriculture, cation exchange, animal farming, etc.).

#### Vico district

The activity of the Vico complex developed over a period of about 0.8 Ma (from 0.9 to 0.09 Ma BP) and covered the pre-existing Cimino volcano. It is characterized by predominantly explosive activity and an alkaline-potassic composition. Stratigraphical reconstructions identify four main cycles. The most interesting materials from the technological point of view are those associated with the youngest period of volcanic activity, in particular four major ignimbrites (A, B, C, D) emplaced between 0.2 and 0.15 Ma. The third one (ignimbrite C), also called *Tufo rosso a Scorie Nere* (red tuff with black scoriae), covers an area of about 1250 km<sup>2</sup> and reaches distances of about 25 km from the vent (Locardi 1965).

This ignimbrite, in the southeast and southwest parts of the outcrop, touches an analogous formation of the Sabatini district so that in the past both were considered as a single product of the Vico volcano. It is an ash flow of variable thickness, lithified or welded near its emission area (Langella and Adabbo 1994). The fine reddish-yellow matrix contains black phonolitic scoriae, many feldspar fragments, and lithic clasts of various origins (Cioni et al. 1987).

**Mineralogical features of the main zeolitized layers and genetic hypothesis.** The *Tufo Rosso a Scorie Nere* or ignimbrite C formation (Locardi 1965), in the morphologically lowest area of deposition, may reach thicknesses of more than 30 m, with average values of 10–15 m. The only epigenetic minerals in the formation are chabazite and phillipsite, the former uniformly distributed within the rock, the latter particularly concentrated in pumice. Table 3 and Fig. 2 show the analyses and the representative points of three chabazites which are rich in potassium and

**Table 2.** Zeolite content and CEC values for some samples from the Vulsini district

Formation	Zeolite content <sup>a</sup>			CEC (cation exchange capacity)		
				Calculated	Measured <sup>b</sup>	
	Minimum	Maximum	mean	Chabazite	Phillipsite	Chabazite
Orvieto-Bagnoregio Small-scale pyroclastic flows	32.80	74.90	53.85	3.33		3.10
Montefiascone	50.60	82.80	66.70			
Latera	63.00	78.70	70.85	3.45	3.82	3.28

<sup>a</sup>Thermogravimetric determination (de'Gennaro and Colella 1989)

<sup>b</sup>Determined according to Colella et al. (1982)

**Table 3.** Chemical analyses of zeolites from some volcanic districts considered here

Location	Vico District			Sabatini District		Roccamonfina			Monte Vulture			
	Ignimbrite C formation			Tufo Giallo della Via Tiberina					Tufi chiari (pale tuffs)			
	Pizzo lella <sup>a</sup> Chabazite	Pizzo lella <sup>b</sup> Chabazite	Faliska quarry <sup>c</sup> Chabazite	Riano <sup>n</sup> = 19 Chabazite	Riano <sup>n</sup> = 12 Phillipsite	Sessa Aurunca <sup>d</sup> Chabazite	Rocca- monfina <sup>e</sup> Chabazite	Colle Friello <sup>f</sup> Chabazite	Glass	<sup>n</sup> = 10 Chabazite	<sup>n</sup> = 2 Phillipsite	Analcime
SiO <sub>2</sub>	51.21	51.07	49.66	49.91	51.84	50.48	46.03	50.84	62.24	51.20	52.96	56.77
Al <sub>2</sub> O <sub>3</sub>	18.41	17.66	18.19	17.93	18.36	19.27	19.36	18.00	18.31	18.19	18.58	20.15
Fe <sub>2</sub> O <sub>3</sub>	0.31	0.61	0.82	0.13	0.13	0.55	1.31	0.00	1.55	0.54	0.62	0.55
MgO	0.58	0.81	0.47	0.49	0.28	0.30	0.55	0.88	0.07	0.59	0.45	0.30
CaO	6.24	5.80	5.48	5.78	3.45	5.73	5.68	4.76	1.20	5.88	3.24	0.54
Na <sub>2</sub> O	0.40	0.36	0.46	0.49	1.20	0.43	0.67	0.67	5.27	1.02	4.15	9.77
K <sub>2</sub> O	4.07	4.00	6.35	4.99	8.88	6.53	6.02	4.96	6.88	3.74	3.94	2.29
H <sub>2</sub> O	18.50	19.00	18.50	20.28	18.86	16.80	19.99	17.84	4.11	18.50	15.80	10.00
Si	8.43	8.49	8.31	8.42	11.27	8.27	7.94	8.47	58.57	8.44	11.30	33.70
Al	3.57	3.46	3.59	3.57	4.70	3.72	3.94	3.53	20.31	3.53	4.67	14.10
Fe	0.04	0.08	0.10	0.02	0.02	0.07	0.17	0.00	1.10	0.07	0.11	0.25
Mg	0.14	0.20	0.12	0.12	0.09	0.07	0.14	0.22	0.09	0.14	0.14	0.27
Ca	1.10	1.03	0.98	1.04	0.80	1.01	1.05	0.85	1.21	1.04	0.74	0.34
Na	0.13	0.12	0.15	0.16	0.51	0.14	0.22	0.22	9.62	0.33	1.72	11.25
K	0.85	0.85	1.35	1.07	2.46	1.36	1.32	1.05	8.26	0.79	1.07	1.74
H <sub>2</sub> O	10.32	10.53	10.32	11.41	11.49	9.18	11.49	9.91	12.89	10.17	11.24	19.79
O	24	24	24	24	32	24	24	24	160	24	32	96
E%	2.99	0.83	-0.27	-0.14	-1.11	-0.50	-3.70	0.34	-0.87	1.53	2.54	-0.70
Si/Al	2.36	2.45	2.31	2.36	2.40	2.22	2.02	2.40	2.88	2.39	2.42	2.39
Na/K	0.15	0.14	0.11	0.15	0.21	0.10	0.17	0.21	1.16	0.42	1.60	6.48

<sup>a</sup>Borehole number 4.14 m below ground level; <sup>b</sup>Borehole number 5.15 m below ground level; <sup>c</sup>Langella and Adabbo 1994; <sup>d</sup>Passaglia et al. 1990; <sup>e</sup>Ciambelli et al. 1980; <sup>f</sup>de'Gennaro et al. 1995a; <sup>g</sup>mean analyses on "n" samples

calcium in good agreement with the composition of the parent glass (Langella and Adabbo 1994).

For this formation too, the emplacement mechanism explains the widespread, uniform zeolitization within the deposit as a consequence of interactions between still-hot fluids and a particularly reactive trachyphonolitic glass. The eruptive event, which probably caused the emplacement of a single unit as well as preserving chemical-physical conditions for long enough, gave rise to a constant zeolitization (zeolite grades between 58 and 73%) as shown by the core samples from a mining survey near Civita Castellana (Langella and Adabbo 1994).

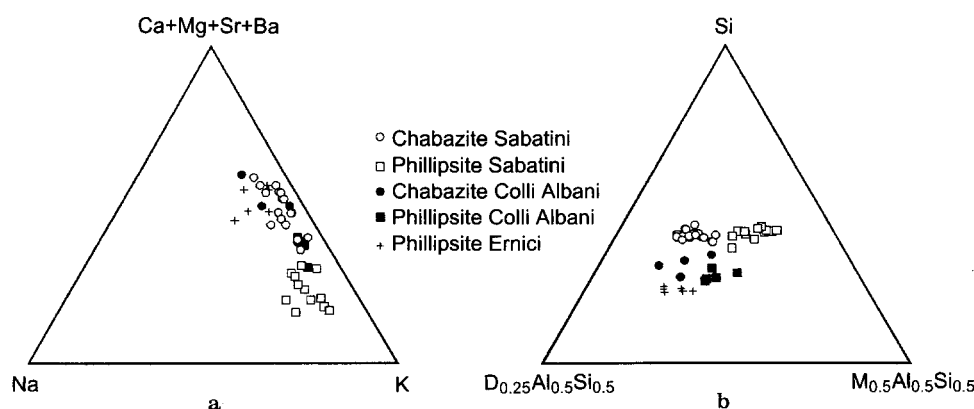
The marked concentration in pumice of phillipsite could be related to the establishment of a locally different

physical-chemical environment probably due to a distinct chemical composition of pumice and ashy matrix.

*Feasibility of applications.* Some quarries in the *Tufo Rosso a Scorie Nere* formation are already being exploited for the production of dimension stone for the building industry. The high-zeolite grades of these deposits also make them of high technological and economic interest.

#### *Sabatini district*

Volcanic activity here started about 0.6 Ma BP and lasted for about 550 000 y involving several eruptive centers. It



**Fig. 4.** a Mole plot of exchangeable cation content in chabazites and phillipsites of the Sabatini, Colli Albani and Monti Ernici districts and b chemical variability of the same phases, *D*, divalent cations; *M*, monovalent cations

was mainly explosive, with the emplacement of huge amounts of pyroclastic materials (Conticelli et al. 1989). The formations of the *Tufo Giallo della via Tiberina* or *Tufo di Sacrofano*, *Tufo Rosso a Scorie Nere* and *Tufo Varicolori della Storta* are all linked to the activity of the Sacrofano volcano, located in the eastern part of the district. For technological purposes, the first is a useful material. It is the product of a pyroclastic flow from a crack in the caldera dated at  $228\,000 \pm 6000$  years BP (Fornaseri 1985). The flow, which lies directly on Plio-Pleistocene sediments, extends throughout the eastern sector of the Sabatini area (Cioni et al. 1987). It filled the paleo-valleys which flowed into the river Tevere on the right, forming a series of tongues which reached their maximum thickness near the river.

The upper part of the formation, 4–5 m thick, is cohesionless and gray in color (Nappi et al. 1979). The yellow lithified part is composed of a very fine-grained matrix incorporating pumice of various sizes. The matrix also contains K-feldspar, pyroxene and mica phenocrysts, lava fragments and xenoliths of the sedimentary basement. Zeolites are very abundant and chabazite is generally prevalent over phillipsite (Langella and Adabbo 1994).

The deposit reaches a thickness of some tens of meters near Riano (Rome) and is thoroughly exploited for dimension stone, in order to satisfy demand by the construction industry working on the urban expansion of Rome and its suburbs.

**Mineralogical features of the main zeolitized layers and genetic hypothesis.** The tuff is characterized by a fine-grained yellow matrix, quite rich in yellow pumice. There are abundant volcanic and calcareous clasts, up to 10 cm in diameter. XRD examination shows the presence of chabazite, K-feldspar, calcite, biotite and phillipsite. In thin section, the primary minerals are prevalent K-feldspar and subordinate clinopyroxene and biotite. The rock is vitrophyric with porphyritic structure and abundant calcareous clasts.

Table 3 shows the mean chemical composition of chabazite and phillipsite. The representative points of each zeolite are plotted in Fig. 4a, b. Both chabazite and phillipsite are rich in potassium, the latter more than the former.

The deep zeolitization of the *Tufo Giallo della Via Tiberina* formation, emplaced by a pyroclastic flow

**Table 4.** CEC mean values and mean zeolite content of samples from the Sabatini District

Phase	CEC <sup>a</sup> (calculated)	CEC (measured)	Zeolite content <sup>b</sup>	Zeolite content <sup>c</sup>	Zeolite content <sup>d</sup>
Chabazite	3.49			49.7	
Phillipsite	3.64			7.5	
Whole rock		2.04	57	57.2	61

<sup>a</sup> Mean value; <sup>b</sup> calculated by CEC; <sup>c</sup> calculated by thermogravimetry; <sup>d</sup> from Carnevali et al. (1994)

mechanism, bears on the minerogenetic process previously described (see Vulsini district Sect.). Here again, hot fluids within the deposit allowed the transformation of the original trachy-phonolitic glass to chabazite and phillipsite. A similar genetic hypothesis (the “geoautoclave” proposed by Aleksiev and Djourova 1975) has been suggested for the *Tufo Rosso a Scorie Nere*, another flow unit connected to the activity of the Sabatini volcanoes (Lenzi and Passaglia 1974). However, these deposits do not show evidence of high-pressure conditions implied by the term geoautoclave. In this case, the term describes a thermally well-insulated system where the temperature of the fluids is preserved for a long time.

**Feasibility of applications.** The area around Riano (Rome) contains a large number of quarries for the production of dimension stone for the building industry. It is however known that small amounts of quarry dust are sometimes supplied to local cement factories producing pozzolanic cements.

Table 4 details the cation exchange capacities of the two zeolites and the mean zeolite contents, obtained either by thermogravimetry or from the literature (Carnevali et al. 1994). Furthermore, close sampling of a 43 m thick quarry wall (sample taken every meter) was performed in order to verify stratigraphical variation in zeolite grades. A range of 50.4–61.0% was recorded, confirming a virtual homogeneity due to the emplacement of a single flow unit during the depositional event.

Their homogeneity, high zeolite contents and abundant available volumes make these deposits of reliable interest not only for the production of building stone but above all

for use in technological fields such as agriculture, since they significantly improve plant height and other plant parameters (Langella et al. 1991). Their utilization for the abatement of polluting metal cations ( $\text{Cr}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ) has also been proposed (Pansini and Colella 1989; Pansini et al. 1993; Colella et al. 1995).

### Colli Albani

The volcanic products of this district cover an area of about 1500 km<sup>2</sup>, from the southern side of Rome to the Piana Pontina. Activity developed over a period of time longer than 0.6 Ma, in the course of which various centers emitted lava flows and above all great volumes of pyroclastics. The *complesso dei tufi inferiori* (0.5–0.28 Ma) is composed of a thick succession of pyroclastites, both incoherent (*pozzolana*) and lithified (tuffs). In the latter, the *Tufo Lionato* is so called because of its tawny colour.

The volcanic activity of the Colli Albani ended with a series of large phreatomagmatic eruptions which gave rise to several multiple craters. The activity of these vents produced a sequence of pyroclastic deposits, locally called *peperini* (Franco and de'Gennaro 1980).

*Mineralogical features of the main zeolitized layers and genetic hypothesis.* The most important zeolitized formation related to the activity of the Colli Albani is the *Tufo Lionato* formation, a phillipsite- and chabazite-bearing tuff. It has a reddish-yellow matrix and contains black or yellow scoriae, lithic clasts, and biotite and pyroxene fragments. Scoria vesicles are commonly filled with phillipsite microcrystals (de'Gennaro et al. 1995a).

The most common zeolite in the *Tufo Lionato* is phillipsite, detectable in almost all levels and rarely associated with chabazite, generally in the upper part of the formation. Only in a few outcrops is chabazite the prevailing zeolite. The current knowledge of this formation is insufficient to clearly explain the stratigraphical distribution of the two zeolites. It is probably linked to local physico-chemical conditions (i.e. temperature, alkalinity, different availability of alkaline cations, etc.) which are sometimes more favorable to chabazite crystallization.

Figure 4a,b shows the compositional variations of some phillipsites and chabazites of this formation (Passaglia and Vezzalini 1985; Passaglia et al. 1990; de'Gennaro et al. 1995a). Both zeolites were derived by transformation of a basanitic to leucititic glass with a Si/Al ratio near 2, thus favoring the formation of zeolites with lower ratios (mean value for phillipsites = 1.74; mean value for chabazites = 1.91). Also noteworthy is the high calcium content, which may either be connected to the chemical composition of the original glass or to exchange processes following zeolite crystallization. As explained in the next section on Monti Ernici, calcium cannot be completely removed from zeolites by exchange with NaCl solutions (Carnevali et al. 1994), thus supporting the hypothesis that at least some calcium took part in the zeolitization process, probably without playing any role in determining its structural type.

Zeolitization affected the deposit extensively and the zeolite grade sometimes exceeds 80%, as in the case of the

*Paliano* tuff where phillipsite amounts to 47.8% and chabazite 34% (Carnevali et al. 1994).

The post-depositional minerogenetic process may be related to the pyroclastic flow eruptive mechanism, aided by abundant fluids and by temperatures of some hundreds of degrees. This is confirmed by the presence of pipe structures, whose wall surfaces are coated with some mm-thick phillipsite patinas (*Paliano* tuff), and of columnar fissures in many outcrops of the *Tufo Lionato* near Campoleone (Franco and de'Gennaro 1980), testifying to the still-high temperature of the deposit after lithification.

*Feasibility of applications.* The *Tufo Lionato* has historically been used as dimension stone in Rome. Many quarries were exploited until the beginning of the 1970s. Eventually the continual urban expansion of Rome reached the quarrying area itself, step by step causing the end of exploitation. Although the tuff is one of the few prevalently phillipsite-bearing deposits in Italy, together with the Neapolitan yellow tuff, the relaunching of intensive exploitation does not seem to be proposed. The outcrops farthest from built-up areas (i.e., Campoleone and Paliano) could be employed for local use, e.g., in animal farming. In fact, at the moment this is the main field of application for Italian phillipsite-bearing products, and there are many cattle and sheep farms in this area.

### Monti Ernici

This is a small complex located in the central part of the Valle Latina, about 70 km south of Rome. The emission centers were active from 0.7 to 0.1 Ma and formed small scoria cones, while lava and pyroclastic flows occurred directly from fractures within the calcareous ridge of the Monti Ernici. In particular, there are some pyroclastic flows on the southeastern side of the ridge, near Patrica and Supino (Frosinone) and along river valleys. They show typical features of coarse-grained volcanic breccias, with pale gray matrix containing magmatic and sedimentary lithics, pyroxene and mica phenocrysts and, subordinately, olivine and garnet. Their cement is prevalently zeolitic and locally calcitic near the rim of calcareous clasts (de'Gennaro and Franco 1971).

*Mineralogical features of the main zeolitized layers and genetic hypothesis.* The volcanoclastites of this district are linked to phreatomagmatic eruptions and often suffered zeolitization. Phillipsite is in most cases the only zeolite; chabazite is rare or absent (de'Gennaro et al. 1982a).

A peculiar feature of these phillipsites is their unusually high contents of magnesium and calcium when compared to other Italian sedimentary zeolites (e.g. Colli Albani; see previous Sect.). This cationic composition is in agreement with the low Si/Al ratio (average 1.6). The DTA curves (de'Gennaro et al. 1982a) show an endothermic effect at about 380 °C, related to the high Ca/(Na + K) ratio of the zeolites. This feature is also evident from Fig. 4a, b.

It is likely that the solution interacting with the original volcanic glass already had a cationic complement, deriving either from a calcareous water-bearing stratum or from the presence within the flow of many calcareous

clasts. A consequence of this is the neoformation of calcite coatings observed in thin sections. The composition of the zeolite should therefore, on one hand, reflect that of the original glass (e.g., Si/Al) and, on the other, that of the solution from which it was nucleated (e.g., concentration of Ca). This means that the compositions, as already observed in the Colli Albani and as regards Italian zeolites, typically plot in the chabazite field (Fig. 4a, b). All these observations indicate that in this case the role played by alkali and alkaline-earth cations in defining the type of structure has been neglected, whereas other factors such as solution pH and temperature may have greater importance (de'Gennaro et al. 1993).

It is difficult to establish whether or not the presence of Ca and Mg is the consequence of exchange processes which occurred after the crystallization of a typically potassic-sodic phillipsite. Currently, this appears to be the most likely hypothesis as regards Mg, whose presence in solution favors the crystallization of phyllosilicates (de'Gennaro et al. 1993; de'Gennaro and Colella 1992). Conversely, the considerable difficulty observed in removing the Ca from these zeolites by cation exchange weakens the hypothesis (Langella et al. 1993). The low Si/Al ratio of the phillipsites requires about 6 Al atoms per unit cell and means that the structural position occupied by Ca prevents complete replacement of the bivalent cation by two monovalent ones, since this would involve total site occupancy and give rise to electrostatic repulsive behavior (Carnevali et al. 1994). All these observations therefore indicate that the low Si/Al ratio of the original glass, together with the chemico-physical conditions of the system, favored the crystallization of a zeolite with a low Si/Al ratio and thus with the second extraframework position necessarily already partially occupied by Ca.

*Feasibility of applications.* These products, although among the few Italian phillipsite-bearing volcanic deposits, are not consequently exploitable, due to the smallness of the outcrops, their location at quite a high altitude, and the low zeolite grade (approximately 20–30%) measured by comparison of the CECs of the zeolite and of the bulk rock.

#### *Roccamonfina Volcano*

This is the northernmost volcanic center of the Campania region and covers an area of about 300 km<sup>2</sup>. Roccamonfina is a Pleistocene composite volcano, located at the intersection of two fracture systems related to post-Miocene distensive tectonics: the Apenninic (NW–SE) and anti-Apenninic (NE–SW) systems (Capaldi et al. 1985). Its activity, which started about 1.5 Ma ago, was characterized by two main eruptive cycles, separated by the formation of a caldera.

High-K rocks (HKS) predominated in the first cycle, with leucitites and leucitic phonolites (Appleton 1972) which formed a fairly regular strato-volcano.

After caldera formation, the second cycle was characterized by low-potassium products (LKS), predominantly leucite-free and varying in composition from trachybasalt to trachyte. The formation of white trachytic tuff marks

the beginning of the second cycle at about 0.3 Ma (Gianetti and Luhr 1983).

Later eruptive activity was confined to the caldera and its margins, producing lava domes, and to minor vents e.g. Colle Friello (Stanzione and de'Gennaro 1968) with related pyroclastites. The activity of Roccamonfina certainly ended before the Campanian Ignimbrite eruption (about 33 000 y BP) (Di Girolamo 1968a; Capaldi et al. 1985).

*Mineralogical features of the main zeolitized layers and genetic hypothesis.* The volcanic activity of Roccamonfina was both effusive, with the emission of many lava flows, and explosive, with the emplacement of large volumes of pyroclastic falls. The latter did not undergo any secondary mineralization or zeolitization. The only zeolitized formations of technological interest in this district are in the Sessa Aurunca area and in the northern part of the region, both ascribed to pyroclastic flow eruptive mechanisms (Di Girolamo 1968b; de'Gennaro and Stanzione 1970). Also in this case, the transformation of the original phonolitic-tephritic (Di Girolamo 1968b) and latitic (de'Gennaro et al. 1995a) glasses to chabazite was favored by the hot fluids permeating the deposit at the time of emplacement. In particular, the activity of Colle Friello emplaced a latitic tuff now characterized by a fine, pale zeolitized matrix with lithic fragments and a few crystals of plagioclase, pyroxene and brown mica (de'Gennaro and Stanzione 1970).

Table 3 displays the chemical analyses of three chabazites from different sites, the first two belonging to the former leucitic cycle and the third to the trachytic cycle, as also confirmed by the different Si/Al and Na/K ratios.

*Feasibility of applications.* The tuffs of the northern area have been exploited by the building industry. Only local use of these materials, particularly in agriculture, is foreseeable, in order to avoid landscape alteration or environmental impact.

#### *Somma-Vesuvio Volcano*

Together with the Phlegraean Fields, the Somma-Vesuvio volcanic complex, located ESE of Naples, is an area of active volcanism. Geologically, Somma-Vesuvio is a morphological high in a structural low, represented by the Pianura Campana (Campanian Plain). It is a strato-volcano which produced variably undersaturated leucite-bearing products belonging to the basanite-leucite series. The beginning of activity is uncertain, although deep bore-holes indicate that it is older than 0.3 Ma (Bernasconi et al. 1981).

Four periods have been distinguished on the basis of Rittmann's (1933) interpretation: primordial, ancient and young Somma Periods, and the Vesuvio Period, during which the formation of the Great Cone of Vesuvius took place within the terminal caldera of Somma, after the eruption of Pompei (AD 79).

Recently the presence of only leucite-bearing undersaturated primary magmas (basanites, tephrites and leucitites) has been shown at Somma-Vesuvio, as well as



low-pressure differentiated products (phonolite-tephrites and phonolites) (Di Girolamo et al. 1979; Cortini and Hermes 1981; Di Girolamo and Rolandi 1984).

The eruption of AD 79 emplaced great amounts of pyroclastic products with different eruptive mechanisms due to different water-magma interaction ratios; they include pumice falls alternating with various surges and flows such as the Ercolano flow (Sigurdsson et al. 1985). The Ercolano tuff is a pale yellow lithified pyroclastite with a fine matrix containing pumice and lithic lapilli of various sizes, associated with a few crystals of augite, feldspar, biotite and, more rarely, leucite. Non-volcanic materials (carbonized wood and fragments of sedimentary substratum) may also be found.

*Mineralogical features of the main zeolitized layers and genetic hypothesis.* Zeolitized products of Somma-Vesuvio outcrop only in a few sectors of the volcano and have scientific rather than technological interest. In 1976, de'Gennaro and Franco reported the presence of K-chabazite within the pyroclastic flow which buried Ercolano in AD 79. Further investigations showed that a potassic composition is common to all the chabazites of the zeolitized formation linked to this eruption (de'Gennaro et al. 1981; Franco and Rolandi 1978). This type of zeolite and its chemical composition are both definitely related to the original glass belonging to the high-potassium series, whereas its genesis is ascribed to the interaction of the glass with hot fluids. The emplacement temperature of these flows ranges between 350° and 100°C (Kent et al. 1981).

*Feasibility of applications.* The remarkable landscape, and the tourist and archaeological interest of this area, precludes the setting up of mineral exploitation activities. In fact, many quarries producing aggregate and paving stone have already been closed and others will be in the near future, as part of new planning of the Vesuvian region which foresees the establishment of a national park.

### *Campi Flegrei*

The Campi Flegrei (Phlegraean Fields) are an area of active volcanism located in the Piana Campana near a large NE-SW structural depression (Ippolito et al. 1975; Ortolani and Aprile 1985).

Its volcanic activity began about 50 000 years ago and was characterized by a large number of eruptions from various vents. On the basis of field observations, their products were ascribed by De Lorenzo (1904) to three main eruptive periods. The most important products of the first period are the *Piperno*, the *Breccia Museo* formation and the *Ignimbrite Campana* (Campanian ignimbrite). The *Tufo Giallo Napoletano* (Neapolitan yellow tuff) is the most important product of the second period. Those of the third period are mostly loose pyroclastics (ash, lapilli, pumice, etc.) which erupted from vents in the central-eastern part of the area.

More recent works, based on both stratigraphic correlation and absolute age determinations (Rosi et al. 1983;

Di Girolamo et al. 1984a, Rosi and Sbrana 1987), subdivide this volcanic activity into four main phases.

The first phase involved violent activity linked to the *Ignimbrite Campana*, (hereafter CI) dated at 33 000 years ago. Three other phases of activity followed the CI. The first eruption led to a succession of events, both submarine and subaerial, giving rise to the formation of trachytic tuffs among which the most widespread is the *Tufo Giallo Napoletano* (hereafter NYT) (12 000 y BP) (Alessio et al 1971). The second cycle (10 500–8000 y BP), characterized by prevailing subaerial activity, emplaced mainly trachytic pyroclastic products. Lavas and pyroclastites ranging in composition from trachyte to trachyphonolite were erupted during the last cycle, which started about 4000 y BP and closed in historical times (AD 1538) with the formation of Monte Nuovo (Pozzuoli, Naples).

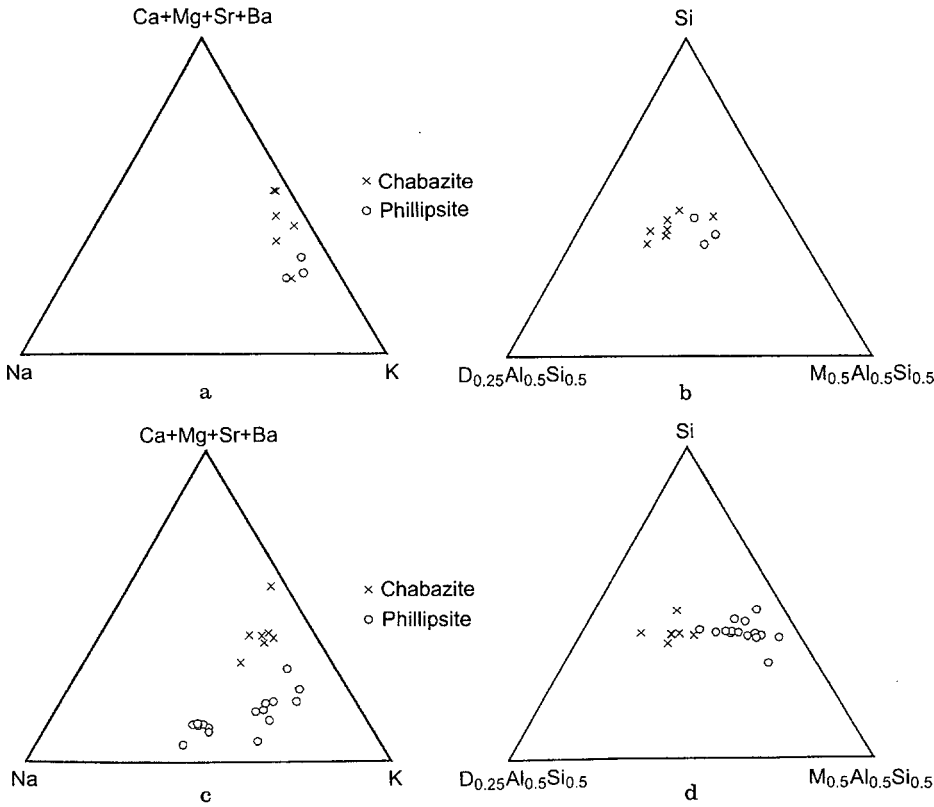
The activity of the Campi Flegrei is currently characterized by post-volcanic phenomena (fumarole and hydrothermal activity on the island of Ischia and in the Bacoli-Lucrino, Solfatara and Agnano craters).

*Mineralogical features of the main zeolitized layers and genetic hypothesis.* As previously reported, the most important products of the Campi Flegrei are the CI and the NYT.

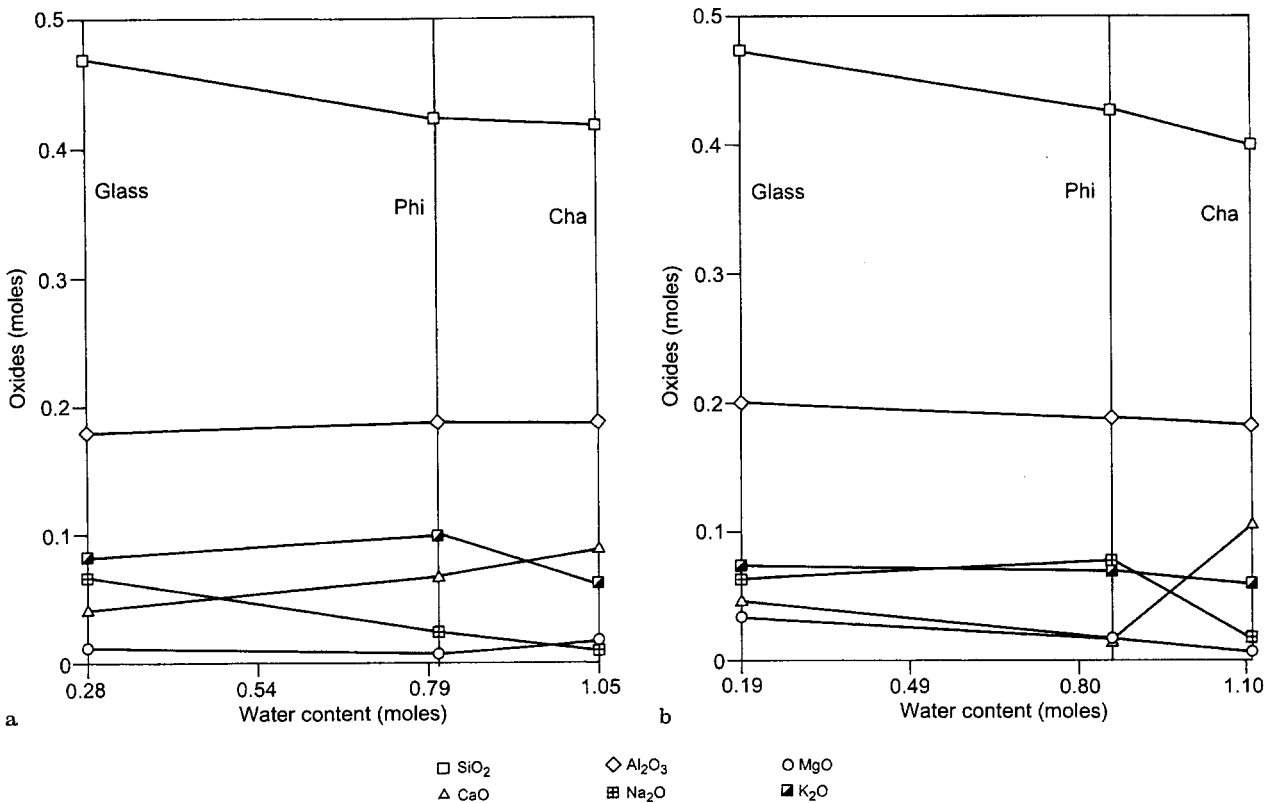
The Campanian Ignimbrite is characterized by two facies: one gray and lithoid with epigenetic feldspar, and one yellow, also lithoid, and zeolitized even in the most distal areas. The yellow facies of the *Ignimbrite Campana* is commonly considered to be a predominantly chabazite-bearing product, but this is only partially true. In fact, in some distal outcrops (e.g. S. Mango sul Calore, Avellino, about 75 km from the presumed vent), chabazite definitely prevails over phillipsite (cha = 61%, phi = 9%) (Langella et al. 1995), while more proximal outcrops (e.g. Tufino near Naples, about 35 km from the presumed vent) have phillipsite slightly higher than chabazite (cha = 19%, phi = 30%) (Langella et al. 1995).

The chemical composition of chabazites and phillipsites from the CI available from the literature (de'Gennaro et al. 1984; de'Gennaro et al. 1987; de'Gennaro and Franco 1988; Passaglia and Vezzalini 1985; Passaglia et al. 1990) is shown in Fig. 5a, b. Slight differences between the two zeolites are evident. In particular, alkali cations prevail in phillipsite and alkaline-earth cations in chabazite. Potassium is definitely higher than sodium in the two zeolites. Figure 6a shows the compositional variations occurring during the transformation of the alkali trachytic-trachytic glassy precursor to phillipsite and chabazite (de'Gennaro et al. 1995a).

The Neapolitan yellow tuff covers an area smaller than that of the CI and expands from Naples to Lago Patria and Aversa to the northwest and northeast, respectively. Its origin was a complex eruption giving rise to pyroclastic falls and flows. Scarpati et al. (1993) identified two units: lower (unit A), mainly composed of incoherent fall and flow deposits with thicknesses ranging from 10 m in the proximal areas to 1 m in the distal ones; and upper (unit B) with two facies, lithoid at the bottom (NYT) and incoherent (*pozzolana*) at the top. The greatest thicknesses are 60 and 20–25 m, respectively.



**Fig. 5a–d.** Mole plot of exchangeable cation content in chabazites and phillipsites of **a** the *Ignimbrite Campana* (Campanian ignimbrite) and **c** *Tufo Giallo Napoletano* (Neapolitan yellow tuff) and **b,d** chemical variability of the same phases, *D*, divalent cations; *M*, monovalent cations



**Fig. 6a, b.** Oxide variations during glass-to-phillipsite-to-chabazite transformation, plotted against the water content of each phase, for the **a** *Ignimbrite Campana* and **b** *Tufo Giallo Napoletano*. Note that SiO<sub>2</sub> values have been divided by 2 for the purpose of the plot

**Table 5.** Zeolite grades and CEC values of phillipsites and chabazites from the Campanian ignimbrite and Neapolitan yellow tuff

Location	CEC (Cha)		CEC (Phi)		Tuff CEC	Zeolite content <sup>a</sup>	Zeolite content <sup>b</sup> Cha + Phi (Total)
	Measured	Calculated	Measured	Calculated			
CI S.Nicola (Ce)	3.69	3.53	3.47	3.55	1.73	51	
CI Tufino (Na)	3.67	3.59	3.39	3.40	2.10	67	19 + 29 (48)
CI S.Mango (Av)	3.12	3.14					61 + 9 (70)
NYT Nuovo Policlinico (Na)	3.46	3.47			2.20	64	62 + 6 (68)
NYT Grotta del Sole (Na)	3.62	3.60	3.86	3.81	2.28	63	56 + 4 (60)
NYT Monte Barbaro (Na)	3.79	3.72					

<sup>a</sup>Calculated by CEC; <sup>b</sup>calculated by thermogravimetry

The NYT is generally characterized by predominant phillipsite and subordinate chabazite (de'Gennaro et al. 1982b). Many chemical analyses of the two zeolites are also available for this formation (see references in Table 1); their compositions mainly differ in alkali and alkaline-earth contents (Fig. 5c,d). Figure 6b shows that phillipsite contains almost equal amounts of Na and K, whereas chabazite is rich in Ca but low in Na.

Views are discordant regarding the genesis of these minerals. On the basis of chemical and mineralogical data, and from comparisons with phillipsites and chabazites of different minerogenetic environments, some authors believe that the process was a consequence of interactions between glass and pore-water in a "hydrological open system" (Passaglia et al. 1990; Sersale 1978). The hypothesis was already proposed by Hay and Sheppard (1977) who also considered the high reactivity of low-silica glass from alkaline volcanoclastites. The vertical and lateral change from *Pozzolana* to *Tufo Giallo Napoletano*, according to these authors, was a proof of a "hydrological open system". As regards the NYT, Scherillo and Scherillo (1990) hypothesized that zeolitization was partly favored by the condition of the glass shards, which they called "expanded pozzolana", as well as by the presence of a water-bearing stratum.

However, a full interpretation of these two formations should take into account the following considerations:

- The emplacement temperature of the CI of about 400°–600°C (Di Girolamo et al. 1984b; Incoronato 1990) did not allow widespread zeolitization. In fact the lithification (gray facies) is due to feldspar crystallization and to welding phenomena (Di Girolamo 1968a), while zeolitization took place only in the distal parts of the deposits or where the material cooled down after contact with groundwater (Di Girolamo and Morra 1987). For this reason the CI shows no precise stratigraphical relation between gray and yellow facies; only sometimes (S. Nicola la Strada, Caserta) does the first grade into the other laterally and vertically. In other places, only gray (S. Agata dei Goti, Benevento) or yellow facies (S. Mango sul Calore, Avellino; Tufino, Naples) are present, the former sometimes not greatly lithified.
- The NYT is a pyroclastic flow connected to a phreatomagmatic eruption (Scarpate et al. 1993;

Capaldi et al. 1987) emplaced at temperatures of 200°–300°C (Incoronato 1990). The zeolitized yellow facies of the NYT has the incoherent *pozzolana* at the top, and unit A (Scarpate et al. 1993) almost always un lithified and unzeolitized at the bottom. Zeolite grades broadly vary in a vertical direction (de'Gennaro et al. 1990). The degree of welding of the NYT formation progressively decreases from the emission center towards the periphery (Piana Campana) (Scarpate et al. 1993), as a consequence of cooling and perhaps volatile loss within the pyroclastite.

The lack of zeolitization in the lower part of the proximal facies of unit A where the total thickness of the formation often reaches about 70–80 m, and in the distal facies of both units (A and B) (total thickness between 10 and 20 m), seems to confirm the hypothesis that the layers of the deposit which cooled down rapidly or were almost lacking in fluids were not affected by zeolitization.

From comparisons of mineralogical and volcanological data, zeolitization in these formations was evidently a very complex phenomenon for which it is premature to give a definitive account, considering all the events which occurred. It may finally be discussed as a diagenetic process, in its widest meaning (Bates and Jackson 1980). However, the currently available information is not enough to unambiguously define the process leading to zeolitization of the NYT. An assessment of the proposed model will be possible at the end of the research in progress by the authors, which aims to reach a detailed understanding of the zeolitization phenomena within the different units of NYT, considering their stratigraphical position and the relation with the hypothesized vents (proximal or distal facies). Further evidence may be provided by the comparison between the epigenetic phases of the main Phlegraean pyroclastic formations and their emplacement mechanisms (fall, flow, surge).

*Feasibility of applications.* Table 5 reports the zeolite grades and the cation exchange capacities of phillipsite and chabazite from the CI and NYT, which underlie the technological importance of these two materials.

The CI is currently exploited only for the production of dimension stone for the building industry. In 1992, eight active quarries in the provinces of Caserta and Avellino produced about 500 000 tons of material. The overall

potential of this formation was estimated at greater than 17350 million cubic meters, distributed over about 15 outcrops with a mean chabazite content of 58% (Aiello and Porcelli 1974).

The high content of phillipsite makes the NYT deposits of great economic importance. At present, within the whole Phlegraean area, 16 quarries are still active and are mainly exploited for the building industry. In 1992 the total production was about 1 million tons. However, the waste material from these particular workings (quarry dust) is marketed for technological uses involving zeolites, particularly phillipsite. About 25000 tons/year are used for the production of animal feed, pet litter and animal farming, as well as additives for agricultural use.

Urban expansion in the outcrop areas of the NYT, as well as interest in the landscape, urgently necessitate specific studies aiming at evaluating the available amounts, the environmental impact of exploitation activities, and landscape restoration at the end of exploitation.

### Monte Vulture

Unlike the volcanoes described until now, the Vulture volcano is located on the external front of the Apennine chain. It is an isolated strato-volcano, geographically on the border of a recent tectonic depression called the Fossa Bradanica.

Activity in Vulture began 830 000 y ago and went on for 500 000 y (Capaldi et al. 1985). The products of this strato-volcano are undersaturated rocks with potassic to sodic transitional characters (Melluso et al. 1995), emitted during three main phases. The first phase gave essentially phonolitic-trachytic ignimbrites, the intermediate one was characterized by undersaturated products (basanite, foidite, tephrite), and the final one by lava flows and subordinate pyroclastic flows (Hieke Merlin 1967; De Fino et al. 1982) with a prevailing tephritic composition (Morra and Melluso, personal communication).

The *Tufo Carpatto*, a typical trachytic pyroclastic flow, belongs to the first period of activity and is one of the most characteristic varieties of zeolitized (chabazite) tuffs of Monte Vulture (Sersale 1960; Lenzi 1988).

Columnar jointing, abundance of pumice and absence of large xenoliths are particular features of the outcrops.

*Mineralogical features of the main zeolitized layers and genetic hypothesis.* Sersale (1960) first reported the presence of zeolites, and particularly chabazite, as an epigenetic phase within the *Tufo Carpatto* of Monte Vulture.

Recently, a detailed study on many volcanoclastic outcrops revealed that only products connected with ignimbrite-type volcanic mechanisms were diffusely zeolitized. The others had been subjected to alteration processes which led to the formation of halloysite, often associated with illite, mixed-layer minerals, chlorite and smectite. Analcime is sometimes present; traces of chabazite and phillipsite are rare (Lenzi 1988).

These observations (Lenzi 1988) were also confirmed by the many analytical data collected over the last few years by the authors of the present paper and their working group, on samples from the pyroclastic formations of

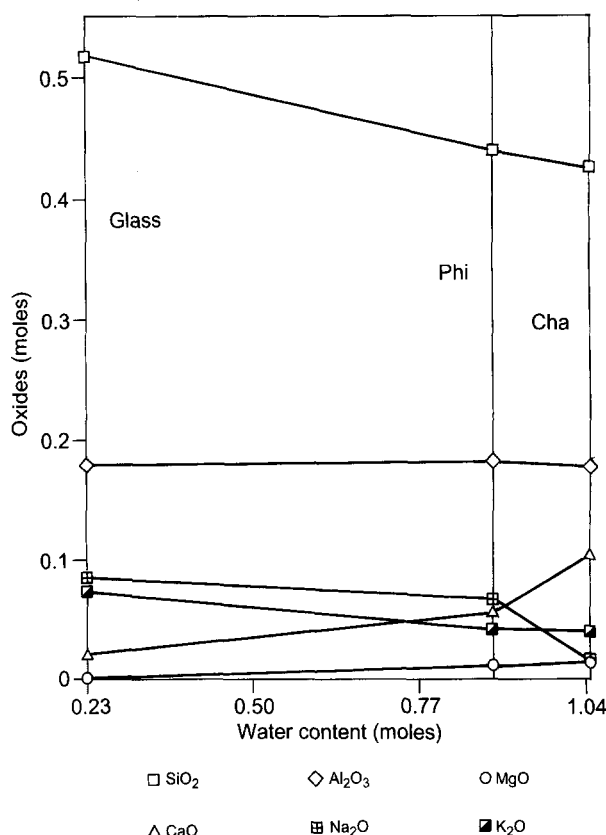
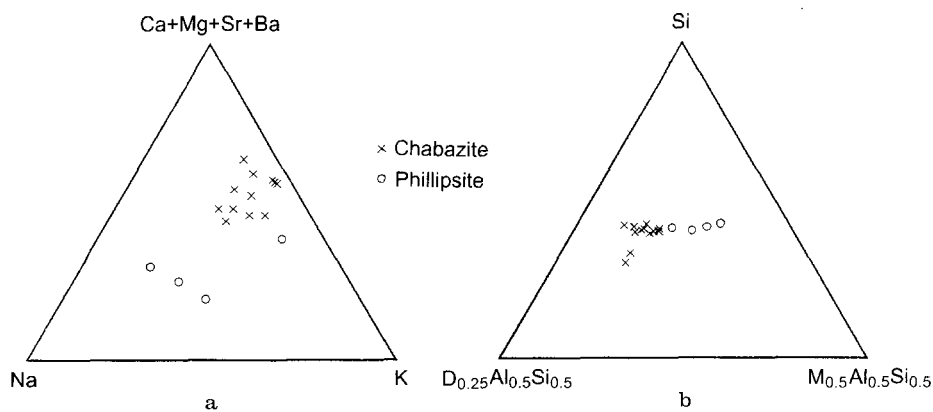


Fig. 7. Oxide variations during glass-to-phillipsite-to-chabazite transformation, plotted against the water content of each phase, for the Vulture district. Note that SiO<sub>2</sub> values have been divided by 2 for the purpose of the plot

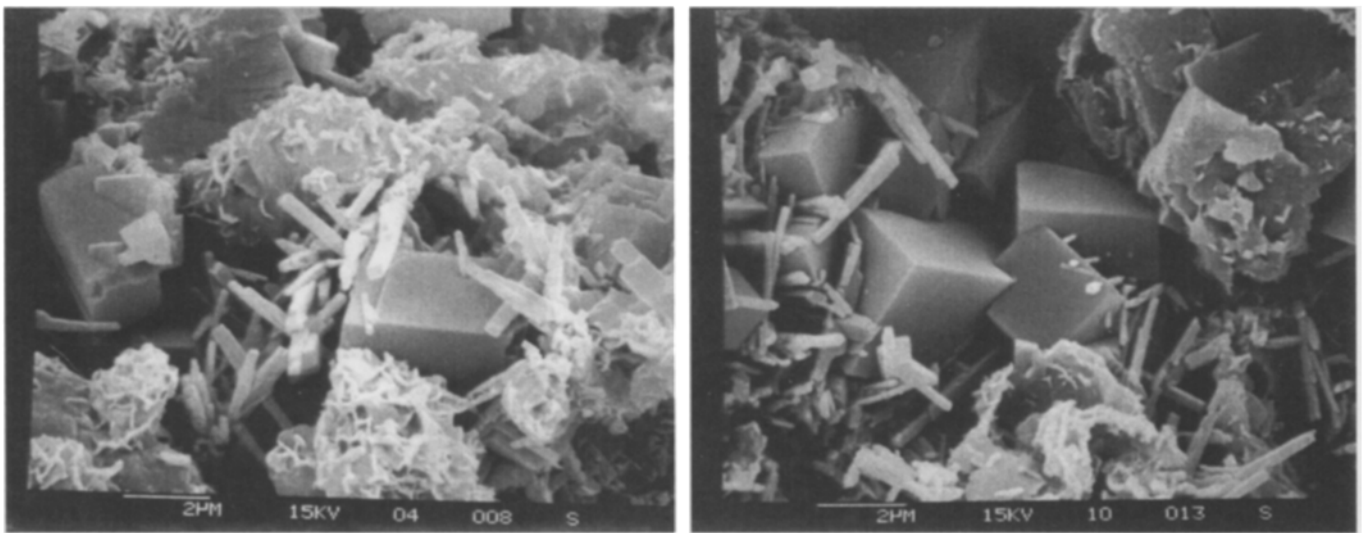
Monte Vulture. Complete classification of the zeolites and their chemical composition related to that of the original glass was also carried out. The result was that on the whole zeolitization involved only the tuffs (*tufi chiari*) in ignimbritic facies, with the formation of chabazite and subordinate phillipsite. All the other formations (pale tuffs in lahar facies, dark tuffs, fluvial-lacustrine deposits, and products of final activity) are locally analcimized and frequently altered to halloysite.

The abundance of chabazite meant that many more analyses could be carried out on it than on the subordinate phillipsite. Comparisons between the mean chemical compositions of the unaltered trachy-phonolitic glass and of the two zeolites (Table 3) showed a decrease in the Si/Al ratio (glass = 2.88, phi = 2.42; cha = 2.39), a slight increase in the Na/K ratio in phillipsite, and a marked decrease in that of chabazite (glass = 1.16, phi = 1.6; cha = 0.42) (Fig. 7) in agreement with the well-known influence of these two cations in solution on the crystallization of one of them. Phillipsite crystallization is favored by mixed sodic-potassic environments; chabazite by more potassic ones (Aiello and Colella 1975). Figure 8a, b shows the cationic distribution of the two zeolites.

Comparisons of mineralogical and volcanological data indicate that, as in the previously mentioned deposits, zeolitization started at the moment of emplacement, as a consequence of interactions between trachy-phonolitic glass and hot fluids permeating the deposit. This is



**Fig. 8.** **a** Mole plot of exchangeable cation content in chabazites and phillipsites of the Vulture district and **b** chemical variability of the same phases, *D*, divalent cations; *M*, monovalent cations



**Fig. 9.** SEM micrographs of chabazite embedding phillipsite crystals from the *Tufo Chiari* (pale tuff) Formation (Monte Vulture)

confirmed by the observation that only the ignimbritic facies, characterized by high emplacement temperatures and abundant fluids, are deeply zeolitized, while the other facies are not, or were only slightly involved in this mineralogical process, probably because of quick cooling and/or the lack of mineralizing fluids. The constant presence of analcime in all the formations may be related either to transformation of leucite (as confirmed by the high potassium contents of some analcimes in pale tuff from the Piana dei Gelsi) or to direct crystallization immediately after emplacement at very high temperatures (de'Gennaro and Colella 1991). Both interpretations are useful to explain the predominance of chabazite over phillipsite. As previously mentioned, chabazite mostly crystallizes in low Na/K ratio systems. Laboratory simulations on glasses ranging in composition from trachyte to phonolite showed that the Na/K ratio in solution is constantly high, thus determining an environment favorable to the crystallization of phillipsite (de'Gennaro et al. 1988; Ghiara et al. 1993). Analcimisation of leucite may remove sodium from the system, leading to more suitable environmental conditions for the crystallization of chabazite. Obviously, the formation of small amounts of phillipsite, also

detected in XRD examination, cannot be excluded in the first stage of interaction. SEM observations of chabazite embedding phillipsite crystals seem to support this genetic hypothesis (Fig. 9a, b).

*Feasibility of applications.* The pale tuffs of the ignimbrite facies were exploited in the past by the building industry. There are some inactive quarries in the Piana dei Gelsi, near Barile, and south of Vallone Macera. These particular locations and their limited size make these tuffs useful only locally, mainly in agriculture.

#### *Arcipelago Pontino*

The Arcipelago Pontino is composed of one major island, Ponza, and six minor ones distributed over a distance of about 50 km, near the bay of Gaeta, in the Tyrrhenian.

All these islands, except Zannone, are made up of volcanic rocks lying on a sedimentary basement. The volcanic activity of Ponza was not continuous, but had two phases. The first (4.53 – 4.32 Ma), mainly submarine, emplaced rhyolitic lava flows and hyaloclastites; the

second, alkali-trachytes in a subaerial environment (Savelli 1987).

*Mineralogical features of the main zeolitized layers and genetic hypothesis.* The silica-rich volcanoclastic materials outcropping in the northern part of Ponza have undergone considerable weathering which led to the formation mainly of clay minerals (smectite and mixed interlayered illite-smectite) (Pozzuoli 1986, 1991; Pozzuoli et al. 1987) and, in the lower part of the deposit, of mordenite together with sanidine, cristobalite, illite and smectite (Passaglia et al. 1995).

Pozzuoli et al. (1987) proposed an alteration model for the pyroclastic succession, based upon analyses of clay minerals from drilling core samples from Cala Fontana. It provides for the action of a hydrothermal system, fed either by waters from the sedimentary basement or meteoric waters, and heated by a heat flow linked to the volcanic activity of the island. Ascending hydrothermal fluids were characterized by higher temperatures (315–370 °C) and pH values around 6 in the lower part of the deposit and by lower temperatures (125–230 °C) and a higher pH (7–7.5) in the upper part. The influence of seawater is excluded.

Based upon careful mineralogical and crystallochemical study of the mordenite in the most zeolitized layer and comparisons with data from the literature, Passaglia et al. (1995) arrived at conclusions similar to those described. The particular concentration of mordenite in a layer 90 m from the top of the formation led these authors to exclude zeolitization due to a typical “hydrological open system”. The diagenetic alteration of the rhyolitic glass is explained as the result of the heating of meteoric waters as a consequence of post-volcanic activity. The transition from smectite to mordenite towards the bottom is due to “an unusually high local pH”.

*Feasibility of applications.* The bentonite outcrop of Cala Fontana was exploited for many years until the mid-1970s. At present, further exploitation of the mordenite-rich layer is not proposed, both because of technical difficulties and also because of intense tourist activity in the Pontine Islands.

### *Sardinia*

Sardinia and Corsica are made up of continental crust 30 km thick (Morelli et al. 1967, 1976) and are usually considered to be a continental microplate, rotated counterclockwise and translated with respect to Europe (Alvarez 1972; Nairn and Westphal 1968; De Jong et al. 1969; Coulon et al. 1974; Westphal et al. 1976; Beccaluva et al. 1985). Their displacement coincided and was accompanied by widespread “andesitic and ignimbritic” volcanism. This volcanism is commonly interpreted as belonging to an orogenic association (Coulon 1977; Beccaluva et al. 1989) and is related to the subduction of oceanic lithosphere in a NNW direction beneath the European plate (Coulon 1977; Tapponier 1977) in response to the relative motion of the African and European plates since Cretaceous-middle Eocene times.

The Oligo-Miocene calcalkaline volcanism of Sardinia, dated from ~32 to ~15 Ma (Araña et al. 1974; Beccaluva et al. 1985; Morra et al. 1994), is characterized by a close field association of “andesites” with minor basalts and ignimbrites ranging in composition from dacites to rhyolites. These ignimbrite sequences have been interpreted as the products of partial melting of continental crust, at least in the northern sector (Coulon et al. 1978; Beccaluva et al. 1987).

*Mineralogical features of the main zeolitized layers and genetic hypothesis.* The hydrothermal zeolites of Sardinia have been widely studied (Alberti 1986), whereas knowledge of zeolites in the Tertiary volcanoclastites is very limited. In the second half of the 1980s research on the volcanic deposits of southern Sardinia revealed the presence of chabazite, laumontite, epistilbite, stilbite and analcime, whose concentrations are not economically viable. Table 6 shows analyses of these zeolites.

Recent research on the ignimbrites of northern Sardinia reveals the presence of many clinoptilolite deposits (de’Gennaro et al. 1995b; Ghiara et al. 1995). One published analysis is also reported in Table 6. This investigation, still in progress, shows zeolite concentrations ranging from 31% to 53%, which make these products of great economic interest, partly because they are the only Italian deposits of clinoptilolite.

Available data are not sufficient to formulate a valid genetic hypothesis or to indicate possible fields of application.

### *Pyroclastic layers from sedimentary successions of the Apennine chain*

The presence of pyroclastic layers of Oligocene, Miocene and Plio-Pleistocene age in marine and continental terrigenous sequences of the Apennine chain has been known for several years (Guerrera and Veneri 1989). These layers are mainly composed of pyroclastic and epiclastic materials, easily recognizable within the stratigraphic succession due to their greater hardness with respect to the surrounding sediments. They have thicknesses ranging from a few centimeters to some meters. The space-time distribution of these products shows that they progressively migrated towards the external Apennine areas, and that stronger volcanic activity occurred during the Aquitanian-Burdigalian-Langhian compared with the post-evaporitic Messinian.

On the whole, the chemical composition of these pyroclastic products indicates their origin from orogenic calcalkaline magmas.

Omitting detailed descriptions of the numerous deposits, which may be found in Guerrera and Veneri (1989), some indications of the space-time distribution and composition of these volcanites may be given:

- a. The upper-Oligocene-lower Miocene, volcanoclastic products are characterized by an andesitic composition and are mainly located in the sedimentary successions of the northern Apennines (both pyroclastic and

**Table 6.** Chemical analyses and formulae of zeolites from southern Sardinia

	Chabazite M. Oladri	Analcime M. Oladri	Laumontite Sarroch	Epistilbite Sarroch	Epistilbite Predicasu	Stilbite S. Margherita	Stilbite Siliqua	Clinoptilolite Logudoro <sup>a</sup>
SiO <sub>2</sub>	52.03	58.50	52.40	56.92	57.89	58.18	57.11	67.33
Al <sub>2</sub> O <sub>3</sub>	18.02	20.47	20.70	17.24	17.14	14.87	15.87	12.17
Fe <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.09	0.03	0.00	0.00	0.01	0.00
MgO	0.61	0.03	0.05	0.33	0.03	0.16	0.24	1.09
CaO	7.76	0.13	8.78	7.15	7.74	4.88	4.88	2.53
Na <sub>2</sub> O	0.27	11.95	1.62	2.23	1.48	2.05	2.53	0.87
K <sub>2</sub> O	1.20	0.11	1.59	0.21	0.48	2.25	2.52	2.39
H <sub>2</sub> O	20.00	8.60	14.80	15.70	14.90	17.90	17.20	13.40
Si	8.54	34.03	16.38	17.65	17.79	27.64	27.06	29.75
Al	3.49	14.03	7.63	6.30	6.21	8.33	8.86	6.34
Fe	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.00
Mg	0.15	0.02	0.02	0.15	0.01	0.11	0.17	0.72
Ca	1.37	0.08	2.94	2.38	2.55	2.48	2.48	1.20
Na	0.09	13.48	0.98	1.34	0.88	1.89	2.32	0.75
K	0.25	0.08	0.63	0.08	0.19	1.36	1.52	1.35
H <sub>2</sub> O	10.95	16.68	15.42	16.23	15.27	28.36	27.18	19.74
O	24	96	48	48	48	72	72	72
R	0.71	0.71	0.68	0.74	0.74	0.77	0.75	0.82
M	0.18	0.99	0.23	0.36	0.28	0.55	0.59	0.51
Si/Al	2.45	2.42	2.15	2.80	2.87	3.32	3.05	4.69
E%	3.30	1.89	1.10	- 2.76	0.22	- 1.42	- 3.05	6.19

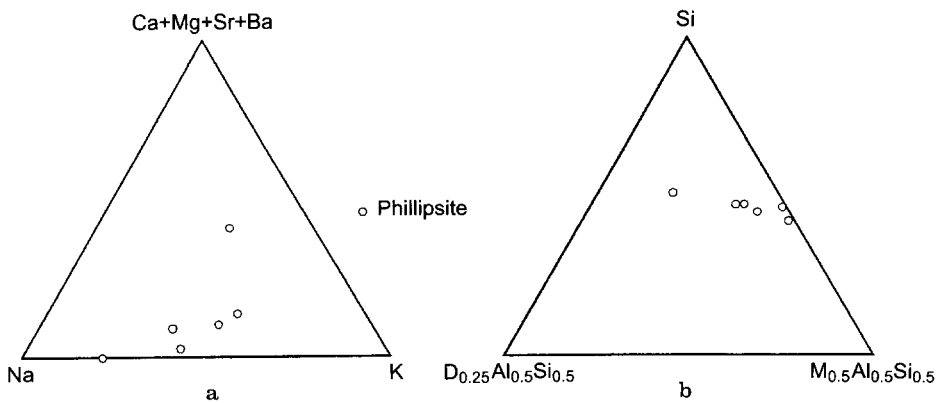
<sup>a</sup> De'Gennaro et al. 1995b

- epiclastic depositional processes) and in the northern part of the Sicilian chain (epiclastic deposits);
- Pyroclastic layers of acidic to intermediate composition characterize the period of time between the Aquitanian and the Langhian throughout the area, both peninsular and insular; the thickest deposits are found in southern Sardinia and the central-northern Apennines (Gianello and Gottardi 1969), and the thinnest in the southern Apennines (Perrone 1987; Zupetta et al. 1984; Crisci et al. 1988);
  - In central and southern Sicily and in the southern Apennines, there is a concentration of layers with composition ranging from acidic to mafic, between the Serravallian and pre-evaporitic Messinian (Spadea and Carmisciano 1974; Di Girolamo et al. 1986; Crostella and Vezzani 1964);
  - The evaporitic and post-evaporitic Messinian is generally characterized by rhyolitic and rhyodacitic products, particularly in the Marche foredeep domain, although some layers in the southern Apennines have also been reported (Di Girolamo et al. 1986; Di Nocera and Torre 1987);
  - Rhyolitic volcanoclastic layers of lower Pliocene age have been recorded in Puglia (Di Girolamo et al. 1986); some others of basaltic to ultramafic type have also been reported in Sicily;
  - Variable chemical composition, from acidic to mafic, characterizes the prevalent pyroclastic products of southern Italy, of middle-upper Pliocene to lower Pleistocene age (Lentini 1969a, b);
  - The products of Pleistocene age are also essentially pyroclastics and are mainly located in the Fossa Bradanica (southern Apennine) and in Valdarno (central-northern Apennines); the former have acidic to mafic composition (Spadea 1986; Capaldi et al. 1979; Adabbo

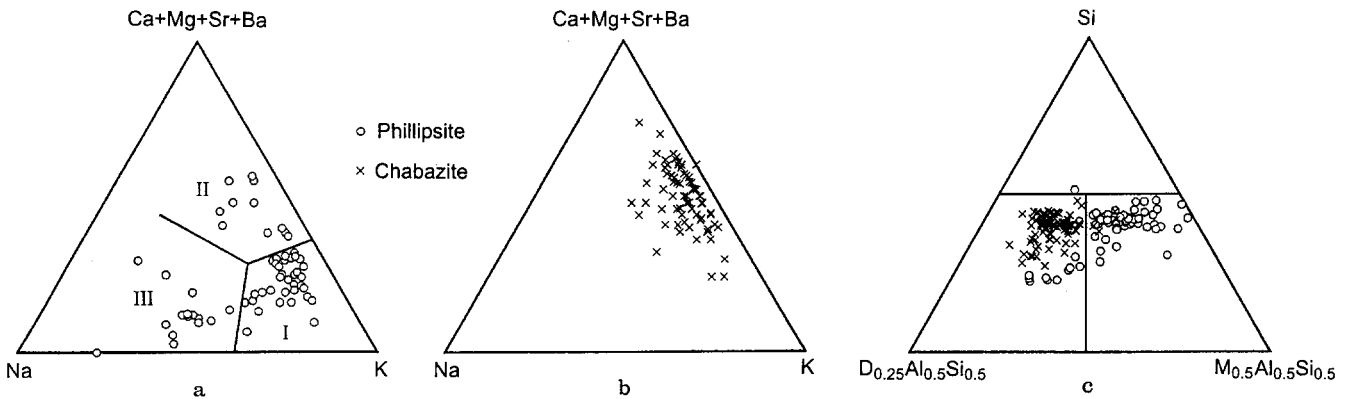
et al. 1994), and the latter are generally of acidic type.

*Mineralogical features of the zeolitized layers and genetic hypothesis.* Figure 1 shows the location of the pyroclastic layers in which the presence of zeolite has been ascertained. Generally they have thicknesses lower than one meter, and only a few centimeters in some cases. Locally they are thicker, e.g. in Garbagna (7 m, or about 4 m) (Passaglia et al. 1990; Sersale et al. 1962), Albarasca and Ramata, near Voghera (up to 2 m) (Minguzzi et al. 1987; Morandi and Tateo 1991), and near Craco (province of Matera) (one layer 2 m thick) (Adabbo et al. 1994).

Pyroclastic layers within the marly-arenaceous successions of the central-northern Apennines (Oligo-Miocene) may be referred to rhyodacitic-dacitic (Mezzetti 1969; Passaglia and Vezzalini 1985) or sometimes trachytic (Minguzzi et al. 1987) volcanism. The glassy fraction underwent post-depositional alteration which led to the crystallization of phillipsite (often Ba-rich) and heulandite (Passaglia and Vezzalini 1985; Minguzzi et al. 1987). The presence of zeolite with a high Si/Al ratio (3.10), such as heulandite in the Garbagna formation, is a proof of the origin of these zeolites from an acidic glass (Passaglia and Vezzalini 1985). The inhomogeneous zeolitization of the pyroclastic layers led Gottardi (1989) to conclude that the minerogenetic process did not develop in a sedimentary marine environment and to hypothesize zeolitization after the emersion of the succession, in a sort of hydrologic open system, further supported by the quite low sodium content (Fig. 10a-uppermost point) (Passaglia et al. 1990). The difference in permeability between the pyroclastic layers and the marly sediments certainly favored saturation and stagnation of water within the layers and a consequent increase in the interaction with glassy



**Fig. 10.** **a** Mole plot of exchangeable cation content in phillipsites from the pyroclastic layers in sedimentary successions of the Apennine chain and the **b** chemical variability of this phase, *D*, divalent cations; *M*, monovalent cations



**Fig. 11** Mole plot of exchangeable cation content in **a** Italian sedimentary phillipsites and **b** chabazites. Chemical variability of Italian sedimentary chabazites and phillipsites, *D*, divalent cations; *M*, monovalent cations

grains. Conversely, the Ba-rich phillipsite in some layers of the same Oligo-Miocene succession is explained as the result of hydrothermal alteration (interaction with hot sea-water near the emission center and subsequent dispersion over a wider area) (Minguzzi et al. 1987).

Many pyroclastic layers interbedded with argillaceous sediments outcrop in the southern Apennines near Matera, with radiometric ages ranging between  $0.98 \pm 0.15$  Ma (Pisticci) and  $1.14 \pm 0.09$  Ma (Montalbano Ionico) (Capaldi et al. 1979). They are composed of a glassy matrix varying from rhyolite and high-K andesite to trachyte; only the latter underwent post-depositional alteration, leading to clay minerals (smectite and illite) and zeolite (phillipsite, rarely analcime and occasionally chabazite). Phillipsite, according to the composition of the parent glass, shows a Si/Al ratio ranging between 2.82 and 2.46, and sodium often prevailing over potassium. In Fig. 10a, b, the representative points fall in the typical field of deep-sea zeolites (Stonecipher 1978; Sheppard et al. 1970). This consideration, together with the presence of smectite and homogeneous zeolitization of all the trachytic outcrops, further supports the origin of these zeolites as due to the interaction of a trachytic precursor with sea-water in a low-alkaline system (Adabbo et al. 1994).

Lastly, the glasses with a higher Si/Al ratio were not involved in secondary zeolitization, probably due to their young age (about 1 Ma). In fact, these products have lower reactivity, which requires much longer interaction times as well as drastic physical-chemical conditions.

*Feasibility of applications.* On the basis of these considerations, it is clear that the possibility of exploiting these deposits is limited only to the thickest outcrops of the northern Apennines, (e.g. Garbagna), and mainly for phillipsite which is sometimes higher than 70% (Passaglia and Vezzalini 1985).

There is a request for a licence by one of the largest Italian cement manufacturers to exploit the Garbagna deposit for white cement (Giorcelli, personal communication), but this work was never completed.

## Conclusions

Many zeolite deposits of volcanic origin occur in Italy. Some of them have economic importance due to the presence of high grades of phillipsite, chabazite, and sometimes clinoptilolite (Sardinia).

The first two zeolites mostly derive from trachytic and/or phonolitic glasses. A rhyodacitic precursor is hypothesized for the zeolites (phillipsite and heulandite) from the Antognola pyroclastic layer in the Apennines; clinoptilolites from Sardinia are related to high-silica glasses.

Phillipsite and chabazite compositions are quite variable, particularly in exchangeable cations. Figure 11a summarizes all the phillipsites considered in this work. Three fields can be distinguished. Field I is characterized by high K values and comparable Na and Ca contents; fields II



and III show higher values of Ca and Na respectively. It should be noted that no relation is apparent between the genetic environments of phillipsites and their distribution in the diagram; those belonging to distinct sedimentary and diagenetic contexts fall in three different fields, but at the same time those from the same formation are sometimes distributed in more than one field.

Chabazites scatter in just one field along the Ca-K side in Fig. 11b, since the Na content is always very low.

In Fig. 11c, both zeolites fall below the line indicating a Si/Al ratio of 3.00, with the sole exception of the Garbagna phillipsite. This is in good agreement with the chemical composition of the parent glasses, which are characterized in most cases by a Si/Al ratio  $\leq 3$ , and for the Garbagna phillipsite by a more silicic glass (rhyolitic-rhyodacitic). Most chabazites plot on the left side of the triangle and phillipsites on the right, thus confirming the different selectivity of the two zeolites towards alkali and alkaline-earth cations. The different behaviour of the calcic phillipsites from Monti Ernici and Colli Albani and the potassic chabazites from Somma-Vesuvio and some outcrops of Monti Vulsini is once again confirmed.

There are no chemical compositions which can definitely be related to a specific genetic environment: in fact, zeolites with definitely different geneses, such as those from the Vulsini ignimbrites and those from the pyroclastic layers of the Apennine chain, lie in the same field of the diagram.

As concerns the post-depositional minerogenetic process it is supposed that zeolitization of the pyroclastic flows started with emplacement and was favored by the high temperatures of fluids within the deposits. Emplacement temperatures higher than 300°–400°C (i.e., in the Campanian ignimbrite) did not allow zeolitization, leading to feldspar crystallization.

The lack of vertical variation in the mineralogy of the Italian deposits, which are sometimes homogeneous (i.e., volcanoes from Lazio region) and in other cases variable (i.e., Neapolitan yellow tuff), as well as the absence of unzeolitized products at the top of them seems to exclude the action of circulating fresh waters.

Fall deposits connected with large flow units are never zeolitized, but are sometimes clayey. In particular, distal outcrops of the Neapolitan yellow tuff, even in deposits more than 10 m thick, are unzeolitized.

There is therefore a direct relation between the eruptive mechanism and the zeolitization process. In fact, diagenetic zeolitization in pyroclastic flow conditions occurs only in deposits characterized, at the time of emplacement, by wet conditions and temperatures of some hundreds of degrees. This high temperature in the central part of the deposit is maintained for several weeks, while the rapid loss of fluids leads the layers close to the surface to quick cooling (Fisher and Schmincke 1984). This genetic hypothesis seems to be applicable to almost all the flow units considered in the present work. The degree of zeolitization is often high and constant within the same deposit (i.e., ignimbrite C from Civita Castellana, Vico District). The only exception, in some outcrops of NYT where frequent and irregular variations of zeolite content have been recorded, cannot be ascribed to a diagenetic process due to interaction of fresh pore water with the volcanic glass, but

rather to a depositional mechanism characterized by the emplacement of subsequent flows with slightly different fluids and temperatures. In the ignimbrites of Sardinia, the zeolitization is most likely due to circulation of hydrothermal fluids linked to the Oligo-Miocene calc-alkaline volcanism. On the other hand, interaction with fresh waters is responsible for zeolitization of the pyroclastic layers within the sedimentary successions of the Apennine chain.

Most of the deposits mentioned have been or still are intensely exploited for building products. In contrast, many technological uses have been proposed but not yet implemented, as testified by the abundant literature on this subject (Colella et al. 1987 and references therein; Colella et al. 1991 and references therein). At the moment, limited amounts of these products are used. The Italian industries which handle and market this product turn out about 25 000 tons per year. More than the 60% is from the NYT formation, while the remaining part is from the chabazite-bearing deposits in northern Lazio.

The predominant use of this material is in animal farming, as a dietary supplement, manure deodorizer and bedding for stock-breeding. Another application is in the cement industry where this product is used for the production of pozzolanic cements. However, the intermittent utilization in this field does not allow us to quantify the amounts employed. Both phillipsitic and chabazitic materials can also be usefully employed in agriculture, particularly for their high contents of available potassium (Langella et al. 1991; 1995; de'Gennaro et al. 1995c). In this context, the importance should be emphasized of the NYT, the *Tufo Lionato* and some outcrops of the CI, on account of their high phillipsite grade. In fact this zeolite was proved to be highly selective towards ammonium (Colella et al. 1984) and is therefore the most suitable for zootechnical purposes. Consequently, it is necessary to plan the exploitation of these deposits with appropriate techniques and subsequent restoration of the ground, particularly in areas of high touristic value. The zeolitized pyroclastic layers of the Apennine chain cannot be considered a valid alternative to the deposits mentioned, owing to the expense of exploitation and the highly exchangeable Ba contents of some deposits which are disadvantageous for their utilization in agriculture and zootechny.

Lastly, these zeolites may be advantageously used in cationic exchange applications (Pansini et al. 1993), although their economic use must consider many other aspects linked to the chemical-physical composition of waste products.

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Editorial handling: A. Hall