HYDROTHERMAL CONVERSION OF TRACHYTIC GLASS TO ZEOLITE. 3. MONOCATIONIC MODEL GLASSES

Maurizio de' Gennaro,[1] Alessio Langella,[2] Piergiulio Cappelletti,[1] and Carmine Colella[3]

[1] Dipartimento di Scienze della Terra dell'Università Federico II, Via Mezzocannone 8, 80134 Napoli, Italy
[2] Università del Sannio, Via Caio Ponzio Telesino, 11, 82100, Benevento, Italy
[3] Dipartimento d'Ingegneria dei Materiali e della Produzione dell'Università Federico II, Piazzale V. Tecchio 80, 80125, Napoli, Italy

Abstract—Experiments on zeolitization were conducted on four synthetic monocationic glasses (Na, K, Ca, or Mg-rich glass) with Si/Al molar ratios of 2.67, similar in acidity to many volcanic glasses of partially zeolitized Italian tuffs. The products of the hydrothermal treatment at 100, 150, and 200°C of single glasses or glass mixtures with deionized H_2O or monosaline solutions (NaCl, KCl, $CaCl_2$) were characterized by X-ray diffraction, thermal, microscopic and chemical analyses. Chemical analyses of mother liquors were also performed. Mineral assemblages, containing chabazite, phillipsite, analcime, and K-feldspar, very similar to those found in altered, volcaniclastic alkali-trachytic or trachytic glass deposits were produced. Potassium was essential to chabazite and phillipsite crystallization, although phillipsite was obtained also in Ca-Na mixed systems. Sodium was necessary for analcime formation. Calcium plays only a secondary role in zeolitization, and magnesium does not favor zeolite crystallization but promotes the formation of smectite. Glass composition determines the mineral assemblages obtained and hence in those commonly found in nature.

Key Words—Analcime, Chabazite, Glass-to-Zeolite Conversion, Phillipsite, Synthesis, Trachytic Glasses, Zeolite Synthesis.

INTRODUCTION

Zeolites of pyroclastic and epiclastic deposits generally form by the action of natural fluids on volcanic glass. Usually the type and chemical composition of resultant zeolites are strongly dependent on the chemical composition of the starting material, although other physical and chemical factors may play a prominent role in the thermodynamics and kinetics of zeolite formation. For example, different zeolites, often with similar chemical composition, may arise from the same starting material, as is illustrated by the Neapolitan Yellow Tuff, occurring in outcrops in the Naples volcanic district as far as the northernmost area of the Phlegraean Fields (Scarpati *et al.*, 1993; Orsi *et al.*, 1995). This tuff is part of a huge volcaniclastic deposit emplaced ~12 Ka ago. The upper, unlithified part of this formation is called "pozzolana" and consists of glass shards with an alkali-trachytic composition with a slight trachytic to latitic trend from the bottom to the top (Di Girolamo *et al.*, 1984; Orsi *et al.*, 1995). The zeolitization of this glassy precursor by the action of fluids, in a genetic environment linked to the eruptive mechanism (de' Gennaro *et al.*, 1995), gave rise to phillipsite, subordinate chabazite and, in some cases, analcime (de' Gennaro *et al.*, 1982a, 1987a). The former two zeolites show a very similar chemical composition, except for small differences in exchangeable cations (de' Gennaro and Langella, 1996).

The physico-chemical factors controlling crystallization of phillipsite and chabazite remain unresolved. The problem was previously approached using experiments simulating the hydrothermal conversion of natural trachytic glass in deionized H_2O (de' Gennaro *et al.*, 1988), which gave rise to zeolite crystallization at or below 200°C. A gel-like phase formed as an intermediate stage of conversion, although zeolite apparently nucleated from the liquid phase. The synthesized authigenic phases were phillipsite, analcime and feldspar, and the most important parameters affecting zeolitization appeared to be the cationic composition, the alkalinity, and temperature (de' Gennaro and Colella, 1991; de' Gennaro *et al.*, 1992). Further studies investigated the reaction of the same glass with seawater (de' Gennaro *et al.*, 1993). In this study, phyllosilicates (smectite and illite) were synthesized, depending on the Mg available in solution, along with the expected framework silicates (phillipsite, analcime, and feldspar). The overall similarity of the phase assemblages in the different experiments demonstrates the dominant role played by the chemistry of the starting glass. Ghiara and Petti (1996) confirmed previous observations, as well as the formation of an "amorphous layer" where Al, Ca, and Mg ions are partially absorbed on the surface of the reacting glass. The influence of the type of hydrologic system (open *vs.* closed) developed in the Neapolitan yellow tuff was also considered by Passaglia and Vezzalini (1985) and by Carnevali *et al.* (1994). Scanning electron microscope (SEM) observations showed that phillipsite crystallization often preceded chabazite, although a later formation of phillipsite could not be excluded in some cases (Scherillo and Scherillo, 1990; de' Gennaro and Langella, 1996).

Table 1. Chemical analyses of natural and synthetic glasses (reactant) and of synthesized phases (products) as wt. %.

	SiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O	Si/Al	$\Sigma Cz_c/Al^2$
Reactant									
Natural glass[1]	56.61	17.98	2.82	1.88	4.37	4.03	7.23	2.67	1.51
Na-glass	62.07	19.77	—	—	—	18.15	—	2.67	1.51
K-glass	56.20	17.90	—	—	—	0.68	24.90	2.67	1.51[3]
Ca-glass	62.28	19.85	—	—	16.42	0.27	0.12	2.67	1.51[4]
Mg-glass	64.88	20.67	—	12.23	—	0.60	0.13	2.67	1.51[5]
	SiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O	Si/Al	E%[7]
Product[6]									
$Na-P1_8$ (Na-glass + H_2O)	55.78	18.60	0.06	0.07	0.04	10.50	0.14	2.54	5.26
Ana_8 (Na-glass + H_2O)	61.37	19.23	0.07	0.16	0.02	11.13	0.03	2.71	2.38
Ana_8 (Na-glass + Ca soln.)	60.80	19.07	0.02	0.09	0.04	11.26	0.05	2.71	1.02
Cha_6 (K-glass + Na soln.)	45.23	18.60	0.10	0.16	0.89	1.32	14.88	2.06	−8.32
Cha_{15} (Na-glass + K-glass + H_2O)	47.42	18.25	0.02	0.32	1.12	1.97	11.06	2.20	1.07
Phi_{12} (K-glass + Na soln.)	50.24	18.41	0.04	0.16	0.42	1.44	15.13	2.31	−7.51
Phi_{15} (Na-glass + K-glass + H_2O)	52.73	17.23	b.d.l.	0.13	0.48	2.90	10.23	2.20	1.09
Phi_6 (Ca-glass + Na soln.)	55.08	18.60	0.33	0.51	8.82	2.05	0.13	2.51	−10.77
Phi_6 (Ca-glass + Na soln.)	54.60	18.50	0.11	0.24	0.06	11.25	0.31	2.50	−5.41

Subscript for synthesized phases is reaction time in days.
[1] Data from de' Gennaro *et al.*, 1988.
[2] C: alkaline or alkaline-earth cation; z_c: valence of C.
[3] 1.57, including the Na_2O impurity.
[4] 1.54, including the Na_2O and K_2O impurities.
[5] 1.56, including the K_2O impurity.
[6] Symbols as in Figures 1 and 2.
[7] Percent balance error, $100[1 - (Na + K + 2Ca + 2Mg)/Al]$.

The present study examines more closely the role of cations, either in the precursor glass or in the contact solution, in the transformation of trachytic glass into phase assemblages characteristic of Neapolitan yellow tuff and other Italian tuffs (phillipsite, chabazite, and/or analcime).

MATERIALS AND METHODS

Four glasses were prepared at the "Stazione Sperimentale del Vetro di Murano (Venice)", having a chemical composition of a typical alkali-trachytic pumice from the Phlegraean Fields where Si/Al = 2.67, ΣCz_c = 1.51, in which C is a cation and z_c is its valence (de' Gennaro *et al.*, 1988; 1993), and each glass contained only one metal ion of Na, K, Ca, or Mg, apart from impurities. Table 1 reports the chemical compositions of these glasses, referred to as Na-glass, K-glass, Ca-glass, and Mg-glass, compared with that of the natural pumice from the Astroni volcano in the Phlegraean Fields.

Hydrothermal reactions were performed in 40 ml Teflon-lined stainless-steel containers using 1 g of powdered glass (grain size <10 μm). The following experimental conditions were employed: reaction temperature: 100, 150, or 200°C; reaction time: 6 h to 38 d; solid-to-liquid ratio: 1/10; contact solution: deionized H_2O or 0.05 M NaCl, KCl, $CaCl_2$, or $MgCl_2$ solutions. Some tests were performed by mixing two different glasses (Na-K, Na-Ca, K-Ca) in the proportions of 1/3, 1/1, or 3/1. Experiments were performed at

autogenous water-vapor pressure (100°C = 101.3 kPa; 150°C = 475.9 kPa; 200°C = 1539.1 kPa) without stirring.

Reactions were interrupted at predetermined times and the containers opened while still hot. To prevent $Al(OH)_3$ precipitation, an aliquot of solution was sampled and acidified with HCl; solids were separated from the remaining liquids by gooch filters, washed with deionized H_2O, and dried overnight at 80°C. Solids were characterized by X-ray diffraction (Philips PW 1730-3710), thermal analysis (multiple thermoanalyzer Netzsch STA 409), and scanning electron microscopy (SEM) (Cambridge 250 TP). Whenever possible, chemical analyses of the synthesized products were performed using a Link AN 10000 microanalyzer system. Cations in solutions were analyzed by atomic absorption spectrophotometry (Perkin-Elmer 2100) and silica was analyzed by colorimetry (Secoman 500).

RESULTS

Reactions of single glasses with deionized H_2O

Figures 1 and 2 summarize the results of the hydrothermal conversions in H_2O of Na-glass and K-glass, respectively, as a function of temperature and reaction time. Lines in the figures roughly bound the crystallization domains of single phases or phase assemblages. Similar experiments were performed with Ca-glass and Mg-glass, but in the former case no zeolite crystallization occurred, and in the latter only formation of
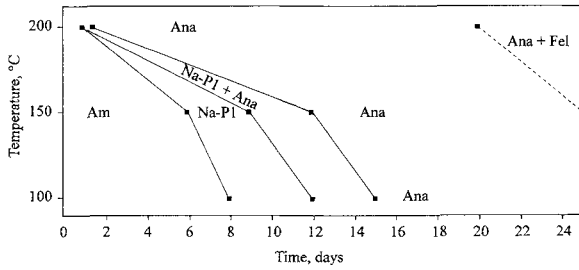
Figure 1. Crystallization sequences for the Na-glass–H$_2$O system as a function of temperature and reaction time. Am: no crystallization; Na-Pl: gismondine-like zeolite; Ana: analcime; Fel: feldspar.
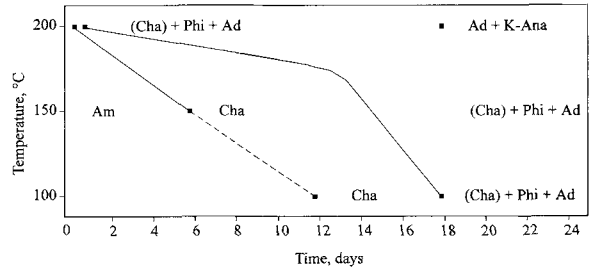

Figure 2. Crystallization sequences for the K-glass–H$_2$O system as a function of temperature and reaction time. Am: no crystallization; Cha: chabazite; Phi: phillipsite; Ad: adularia. Parentheses indicate a small quantity of phase.

smectite was obtained after a three week long experiment at 200°C. These figures clearly show the influence of temperature and time on the reaction of glass. The most stable phases (analcime and feldspar) crystallized early at higher temperatures and appeared after longer reaction times at low temperatures. In the early stages of reaction, the sodic system produced Na-Pl, a zeolite having no natural counterpart (Baerlocher and Meier, 1972). During the reaction, analcime formed and became the dominant phase, along with feldspar for the longest reaction times (Figure 1). Reactions of K-glass with H$_2$O produced chabazite at short reaction times, which transformed with time into phillipsite +

adularia (Figure 2). Long-duration experiments at 200°C produced possible crystallization of a K-rich analcime, identified in part by its low water content (2.8%), compared to the Na-rich analogue (>8%) (Barrer and Hinds, 1953).

Figures 3 and 4 summarize the results of the chemical analyses of the mother liquors for reactions with H$_2$O at 200°C and 150°C, respectively. The pH trends for solutions in contact with Na-glass and K-glass are very similar at both temperatures (Figures 3a and 4a). The highest values were consistently obtained in the first stages of reaction, and coincide with the beginning of crystallization because of the dissolution of the
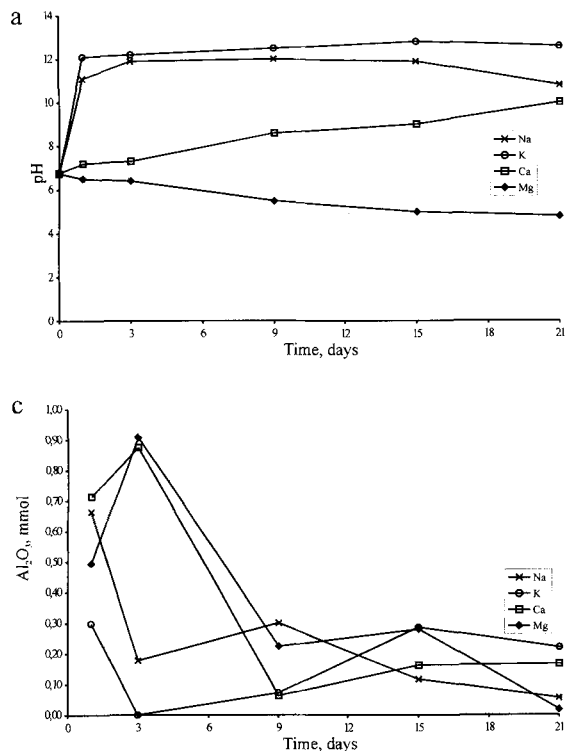

Figure 3. Concentration trends of pH, SiO$_2$, Al$_2$O$_3$, and alkaline and alkaline-earth cations in the mother liquors as a function of time for four glasses reacted with H$_2$O at 200°C.
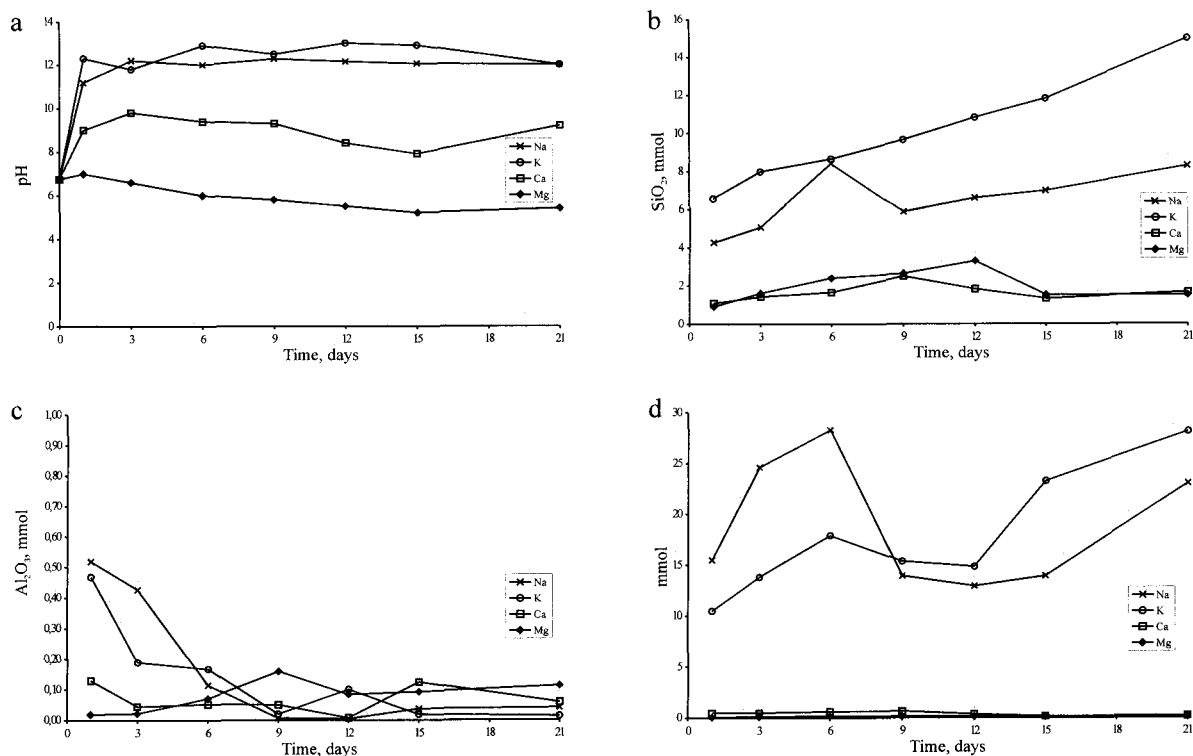
Figure 4. Concentration trends of pH, SiO_2, Al_2O_3, and alkaline and alkaline-earth cations in the mother liquors as a function of time for four glasses reacted with H_2O, at 150°C.

most reactive surface layers (Figures 1 and 2). Experiments with Ca-glass produced lower pH values, which increased very slowly to pH ~11. Mg-glass tended to generate octahedrally coordinated layers, resulting in a continuous pH decrease, in agreement with the results of previous investigations on the interaction between natural trachytic or shoshonitic glasses and seawater (de' Gennaro and Colella, 1992; de' Gennaro et al., 1993; Ghiara and Petti, 1996). Consistent with the pH trends, SiO_2 content rapidly reached the highest values in the first stages of reaction of Na-glass and K-glass at 200°C (Figure 3b), whereas it constantly increased at 150°C (Figure 4b). SiO_2 content slightly decreased for experiments starting from Ca-glass at 200°C, whereas for Mg-glass SiO_2 content remained nearly constant. The same experiments at 150°C showed, for both glasses, a slight increase in SiO_2 content followed by a decrease in the latter half of the experiment. The Al_2O_3 concentration was typically variable, but always very low if compared with other cations, and it decreased as a function of time (Figures 3c and 4c). However, data from the literature for Al_2O_3 are rather controversial, suggesting that different temperature or cooling rate of the solution can remarkably affect its evolution (de' Gennaro et al., 1993). Na and K concentrations quickly reached and maintained high

values in the relevant (Na, K) systems (Figures 3d and 4d), and Ca and Mg concentrations remained low.

Reactions of single glasses with heteroionic solutions

The results of glass-to-zeolite conversions at 150°C in the presence of heteroionic solutions, i.e., reactions with 0.05 M solutions containing a cation other than that present in the glass, are summarized in Figure 5. Experiments with aqueous Mg were not performed for two reasons. First, the presence of this ion in solution causes a pH reduction during the first stage of reaction with trachytic glasses upon crystallization of a Mg-smectite (stevensite) (de' Gennaro et al., 1993). Second, interaction with Na- or K-glass causes a pH increase which greatly reduces the solubility of $Mg(OH)_2$.

A general feature of these systems, with a few exceptions, is the reduction of the induction time, compared with the analogous experiments in H_2O (Figures 1 and 2). Phillipsite crystallizes in most systems, whereas chabazite forms in K-bearing systems and, contrasting with what occurs in natural systems, always precedes phillipsite crystallization.

A limited number of analyses of the mother liquors were performed (Figure 6). The most striking feature is that the cation concentration of the starting alkaline
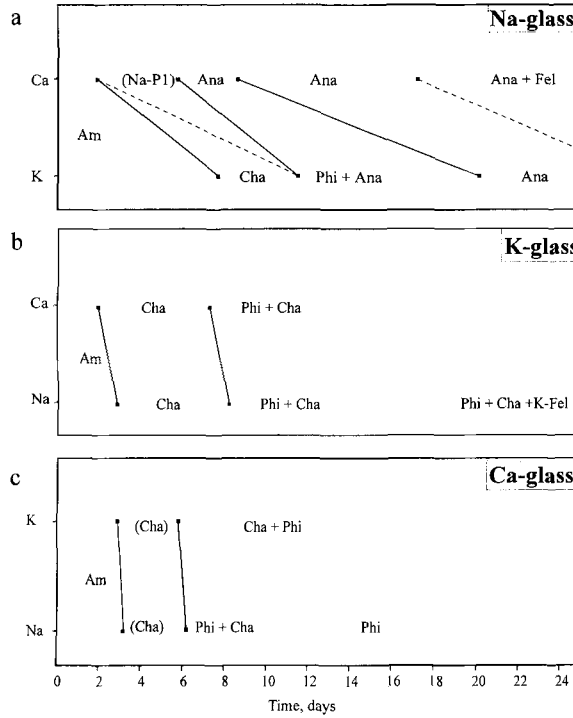
Figure 5. Phase assemblages as a function of time in different glass-monosaline solution systems at 150°C. Cation originally present in solution is given on the Y-axis; symbols as in Figures 1 and 2.
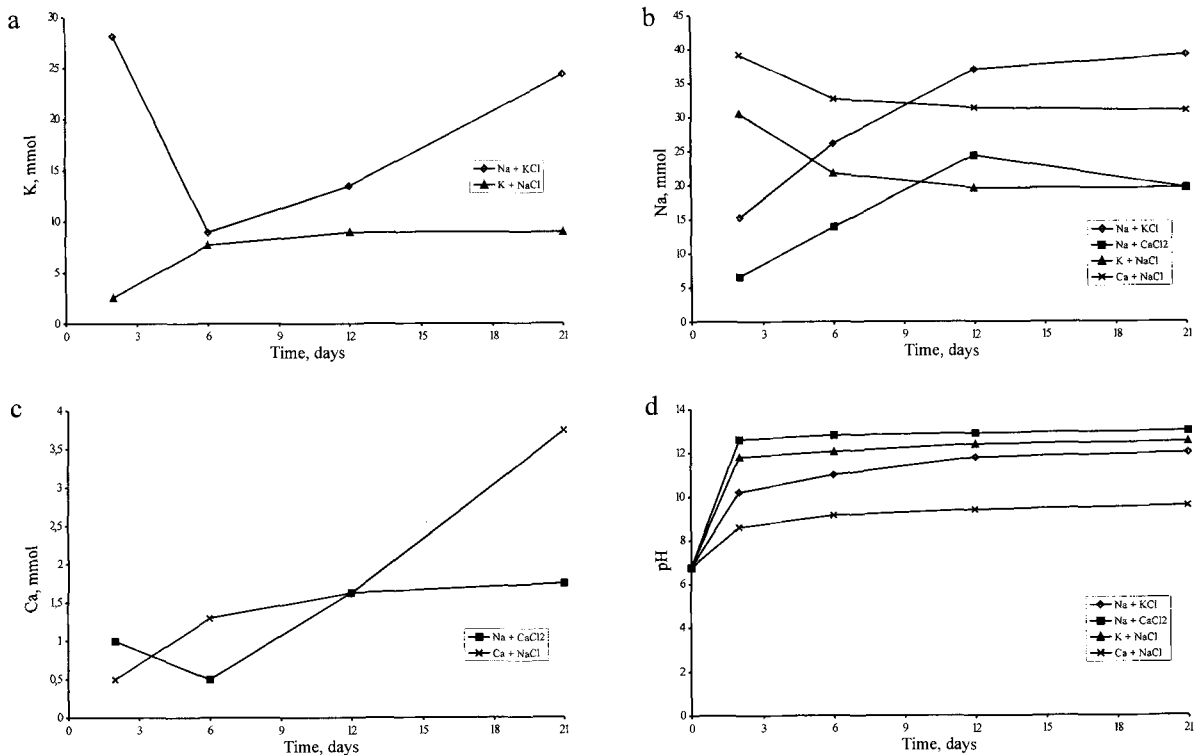

Figure 6. Concentration trends of pH, Na, K, and Ca in the mother liquors as a function of time for Na-, K-, Ca-glasses reacted with heteroionic solutions water, at 150°C.

Table 2. Crystallization products in mixed-glass-H_2O systems at 150°C.[1]

Glass system	Glass ratio	Time: 8 d	Time: 15 d	Time: 21 d
Na-K	1/3	Am	Cha > Phi	Cha > Phi
	1/1	Am	Phi ≈ Cha	Phi ≈ Cha
	3/1	Am	Phi > Cha	Phi > Cha
Na-Ca	1/3	Am	Phi	Phi
	1/1	Am	Phi	Phi
	3/1	Am	Phi	Phi
K-Ca	1/3	Am	Cha ≫ Phi	Cha ≫ Phi
	1/1	Am	Cha ≫ Phi	Cha ≫ Phi
	3/1	Am	Cha ≫ Phi	Cha ≫ Phi

[1] Symbols as in Figure 2.

Table 3. Concentrations of the main species in mother liquors of mixed glass-H_2O systems after 15 days of reaction at 150°C.

Glass system	Glass ratio	SiO_2, mmol	Na, mmol	K, mmol	Ca, mmol
Na-K	1/3	6.40	5.52	6.91	—
	1/1	5.81	6.52	2.94	—
	3/1	7.64	8.70	3.71	—
Na-Ca	1/3	0.95	5.44	—	0.027
	1/1	1.74	19.75	—	0.008
	3/1	2.95	27.62	—	0.011
K-Ca	1/3	0.90	—	1.25	0.019
	1/1	2.41	—	2.63	0.013
	3/1	2.58	—	4.60	0.015

solutions was greatly reduced following the beginning of the interaction. Some specific results for selected systems are described.

Na-glass–KCl solution. Chabazite and then phillipsite crystallization began on the eighth day (Figure 5a). The aqueous K concentration decreased during the first 10 days (Figure 6a), and the aqueous Na concentration increased until the fifteenth day, when abundant analcime formed (Figures 6b and 5a). With the exception of lower starting values, the pH trend was similar to that observed in the Na-glass–H_2O system (Figure 6d).

Na-glass–$CaCl_2$ solution. The aqueous Na concentration progressively increased (Figure 6b), whereas the Ca concentration decreased to very low values after the second day of reaction (Figure 6c), in response to the crystallization of Na-P1, analcime, and for longer times, K-feldspar (Figure 5a). The pH value after two days was near 13 (Figure 6d).

K-glass–NaCl solution. A rapid increase of K until the sixth day of reaction was followed by near constant values (Figure 6a). Na values also decreased to the sixth day and then remained constant (Figure 6b). Chabazite crystallization occurred after about three days and was followed by phillipsite formation after eight days of reaction (Figure 5b). The pH trend was similar to that observed in the K-glass–H_2O system (Figure 6d).

Ca-glass–NaCl solution. Na values slightly decreased up to the sixth day and then remained constant (Figure 6b). The aqueous Ca concentration ranged between 0.50–4 mmol. The highest pH value recorded was 9.5 (Figure 6d). Chabazite was the first phase to crystallize, in low amounts, followed after six days by phillipsite (Figure 5c).

Reactions of glass mixtures with deionized H_2O

Synthesis starting from mixtures of two glasses and H_2O gave results consistent with the previous data (Table 2). Experiments confirm that phillipsite forms pref-

erentially in all systems between the eighth and the fifteenth day of reaction, whereas chabazite crystallizes only in K-bearing systems. The relative amounts of the two zeolites appear to depend on the glass proportions in the mixture. Once again Ca-glass does not appear to promote the crystallization of phillipsite and chabazite.

Table 3 reports the composition of the mother liquors after 15 days of reaction. The concentrations of alkaline cations in solution are apparently related to the glass ratio only for the Na-K glass mixture. For Na-Ca and K-Ca glass systems, the alkaline cations in solution always predominate over Ca, regardless of the glass ratio. The silica concentration appears strongly related to the content of Na-glass or K-glass in the mixture.

SEM observations and microanalysis

The progressive transformation of glass during the reactions was followed by selected SEM observations. In the first stages of reaction, the glass shard surfaces showed intense pitting (Figure 7a–7c), clearly indicative of attack starting on high surface-energy areas. In some cases, dissolution-crystallization developed preferentially along glass fractures (Figure 7d). In the early stages, Mg-glass produced a thin patina, consisting of a thick net, presumably a gel-like phase which is a precursor of smectite crystallization (Figure 7e and 7f).

Figure 8 shows the crystallization sequence in the K-glass–H_2O system at 200°C. After about one day a chabazite-like phase appeared (Figure 8a), which was nearly replaced by phillipsite after about two days (Figure 8b). Both zeolites transformed into analcime after 18 days (Figure 8c) and then into adularia (Figure 8d) at longer reaction times (>20 days).

Table 1 also reports the microanalyses of select synthesized phases, from which we conclude: (1) Phillipsite and chabazite have a Si/Al ratio lower than the original glass, typical of natural occurrences; (2) High concentrations of Na are present in zeolite Na-P1, in
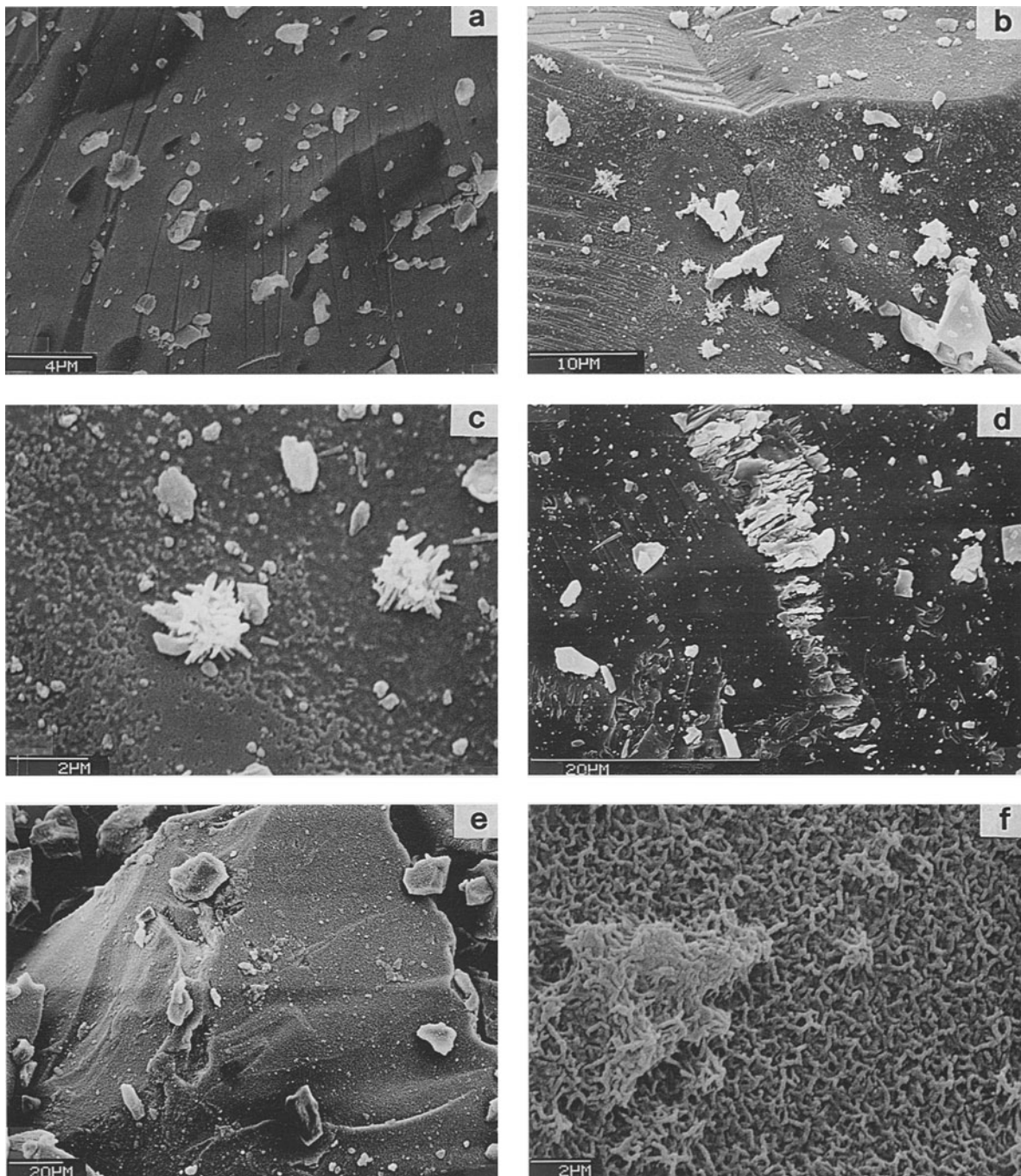
Figure 7. a, b, c: SEM micrographs of glass shards showing intense pitting on high surface-energy areas. (a) Na-glass + H$_2$O, 200°C, 1 d; (b) Na-glass + H$_2$O, 150°C, 6 d; (c) detail of Figure b; (d) (Na-glass + KCl solution, 150°C, 4 d), crystallization on glass shards preferentially concentrated along fractures; (e) (Mg-glass + H$_2$O, 200°C, 8 d), glass shards coated by a thin patina constituted by a thick net; (f) probably representing a gel-like phase.

analcime derived from Na-glass, and particularly in a Na-rich phillipsite formed in the Ca-Na mixed system (Table 1); (3) Chabazite and phillipsite obtained from the system K-glass + NaCl are rich in K and differ only by their Si/Al ratio, which is higher in phillipsite; and (4) The system Ca-glass + NaCl can produce phillipsite with variable cation composition, either rich in Ca or Na.
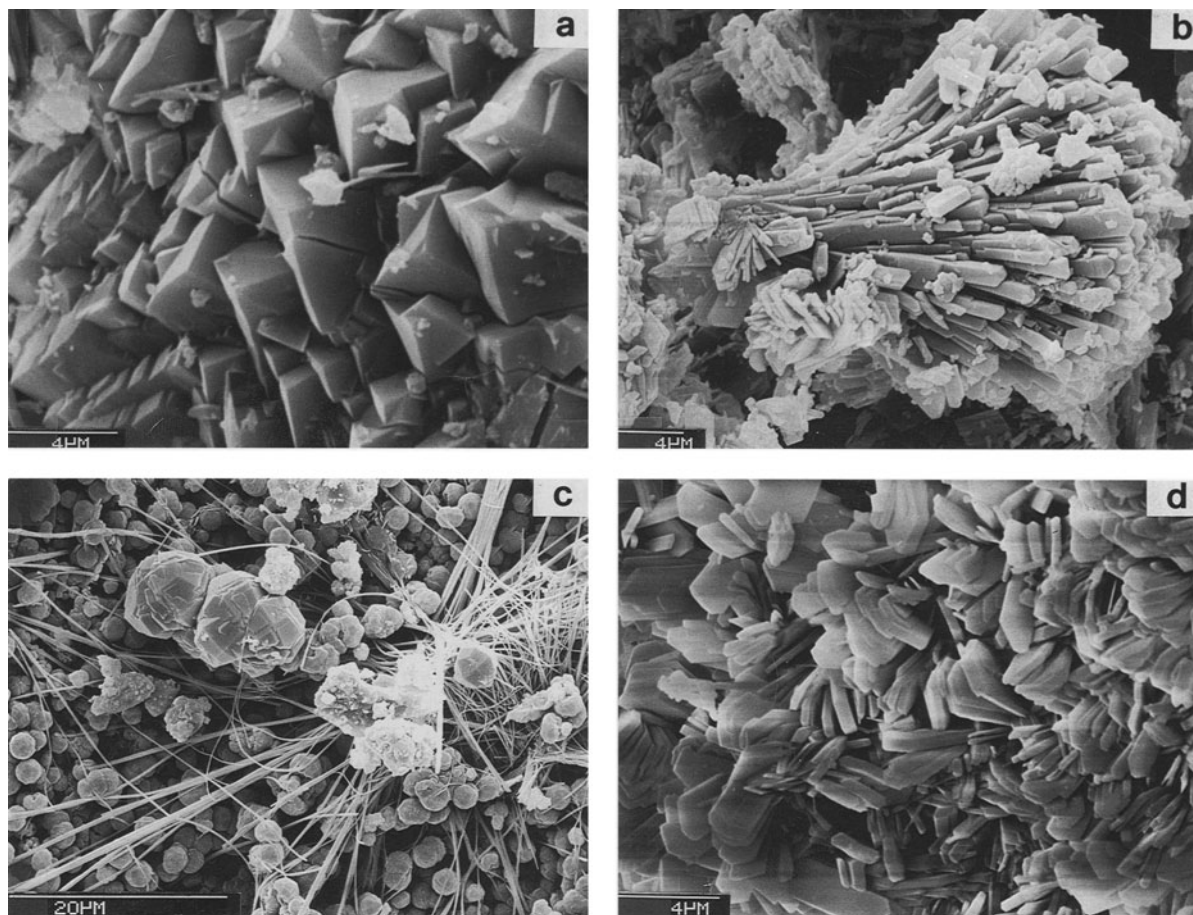
Figure 8.   SEM micrographs showing the crystallization sequence in the K-glass–H₂O system at 200°C. (a) Chabazite crystallized after 1 d; (b) Phillipsite aggregates formed after 2 d; (c) Analcime crystallized after 18 d; and (d) Adularia obtained for longer reaction times (22 d).

DISCUSSION

We discuss below our results based on the physical and chemical parameters in zeolite crystallization from the model glasses as they relate to the natural zeolitization of trachytic glass.

Temperature

Temperature does not appear to play a critical role in the crystallization of the observed zeolites. Over the temperature range examined, temperature primarily affected the reaction kinetics and did not significantly affect the resultant phase assemblages.

Time

Time was a significant parameter for these systems, primarily because of metastability of zeolites. In the system Na-glass + H₂O, the sequence Na-P1 → analcime was clearly recognizable (Figure 1), whereas in the system K-glass + H₂O, the sequence chabazite → phillipsite → adularia + K-analcime was observed (Figure 2). In mixed systems (Figure 5), the sequence chabazite → phillipsite, followed by K-feldspar in the presence of K-glass and by analcime in the presence of Na-glass was typically found.

Alkali and alkaline-earth cations

Cations exerted a clear structure-directing role in the crystallization of zeolites from glasses. Chabazite and phillipsite crystallization required the presence of K, although both zeolites formed occasionally in mixed Na-Ca systems (Figure 5c; Table 2). Note that in these systems limited K is present as an impurity in Ca-glass. Analcime and Na-P1 required sodic environments (Figures 1 and 5a), although an analcime-like phase was obtained in the system K-glass + H₂O (Figure 2). By contrast, Ca did not appear to play a determining role in zeolite crystallization. However the presence of Ca appeared to produce phillipsite or chabazite, where Na or K was also present, respectively. The presence of Ca in some phillipsite obtained from the Ca-glass + NaCl system may indicate that this cation enters the zeolite structure during formation and

not as a consequence of cation exchange. The different Ca content in the two phillipsites obtained after six days of reaction in the Ca-glass + NaCl system is explained by Ghiara and Petti (1996). They showed that the interaction of shoshonitic glasses and H_2O lead to an initial crystallization of a Ca-rich phillipsite which is replaced by a K-rich phillipsite after longer reaction times. The rapid crystallization may favor the coexistence of a "first generation" Ca-rich phillipsite with a "second generation" Na-rich phase. These results may explain the occurrence of Ca-rich phillipsite in particular geological systems such as those of pyroclastic flows of the Mt. Ernici district (Central Italy) (de' Gennaro *et al.*, 1982b). In fact, these phillipsites are characterized by the impossibility of total Ca substitution for Na or K by cation exchange (Langella *et al.*, 1993; Carnevali *et al.*, 1994).

Glass-H₂O interaction

The glass-H_2O interaction begins with glass hydrolysis and the consequent increase of pH in solution, which further favors glass dissolution. According to Hawkins (1981), the concentration of SiO_2 in solution can provide insight on the dissolution process and on zeolite formation. Crystallization begins after a few hours of interaction, when the SiO_2 concentration reaches high values. As the interaction continues, an equilibrium between glass dissolution and zeolite crystallization is attained and silica in solution remains nearly constant. Alkaline cations show a similar trend, except for Na which is slightly depleted as analcime crystallizes. The low concentration of SiO_2 in solution for Ca and Mg-glass experiments does not favor crystallization of zeolites. Synthesis with Mg-glass, however, produces a smectite-like phase in the final stage of reaction, despite the low silica concentration. In this system, the reaction process is characterized by glass dissolution, immediately followed by precipitation of a gel-like phase. The low pH favors six-fold coordination of Al, thus promoting the crystallization of smectite (De Jong *et al.*, 1983). The great difference in solubility between the alkali glasses and the alkaline-earth glasses is noteworthy, as well as their very different reactivity.

Glass-solution interaction

According to Shiraki and Iiyama (1990), the first stage of reaction with monosaline solutions involves exchange of solution cations with the glass. This exchange process explains the observed initial decrease of cation concentration in solution. The rapid Ca reduction in $CaCl_2$ solution as the pH increases may be related to precipitation of the fairly soluble hydroxide. In fact, after only two days of reaction, the pH of the solution is >12, giving rise to precipitation of most of the Ca present.

In the presence of various mixed-cation systems the synthesized mineral assemblages are very similar to those found as products of epigenetic transformation of trachytic glass. This is evidence of the decisive role played by the glass composition on the phases formed and on the typical phillipsite-chabazite-analcime assemblages usually found in trachytic volcaniclastic deposits, such as in Italy, Germany, and Canary Islands (de' Gennaro *et al.*, 1995; de' Gennaro and Langella, 1996). In fact, the above phases are the only zeolites formed in nature by the transformation of glasses with a Si/Al ratio ranging between 2.33–2.88 (de' Gennaro *et al.*, 1987a; 1987b). The only example of crystallization of a different assemblage from a basaltic glass (Si/Al ~2.90) is that reported by Ibrahim and Hall (1995), who described a Quaternary volcaniclastic formation from Jordan, where an unusual faujasite-phillipsite occurrence in some basal layers was found. The authors ascribe the crystallization of faujasite to the presence of very dilute solutions. Elsewhere, alteration of silica-rich glasses produces phillipsite and silica-rich zeolites such as clinoptilolite and mordenite (Gianello and Gottardi, 1969; Sheppard, 1971).

CONCLUSIONS

The alteration of synthetic glasses with a Si/Al ratio (2.67) similar to that of natural trachytic glasses (*i.e.*, Phlegraean Fields) at 200°C leads to phillipsite and chabazite when H_2O is the interacting solution. In these systems, pH and composition of the solution change as a consequence of glass leaching. The formation of phillipsite and chabazite, however, requires K. Calcium is not important in zeolite crystallization in trachytic glasses, whereas Na leads to analcime formation.

These results explain the mutual occurrence of phillipsite and chabazite in zeolitized products of many volcanic districts. In natural systems containing K, Na, and Ca, the relative abundance of these two zeolites is related to the prevailing concentration of any of these cations in the genetic system. For instance chabazite, as a dominant authigenic phase in zeolitized volcaniclastics, is often related to a system characterized by a Ca/K ratio lower than Ca/Na, such as in K-chabazite-rich tuff from Vesuvius (de' Gennaro *et al.*, 1987a; 1987b).

The composition of the contact solution is important for low-reactive glasses. For example, the Ca-glass + H_2O system does not lead to crystallization under the experimental conditions of the present study. In the other systems with H_2O, no substantial differences in phase assemblages were noted. In contrast, heteroionic solutions obviously favored crystallization of chabazite and phillipsite.

Experimental crystallization sequences show that chabazite consistently precedes phillipsite. This occurrence is unique from that found in nature, where in

the few cases observed phillipsite is normally embedded in chabazite crystals, demonstrating that chabazite is a late-formed phase (de' Gennaro and Colella, 1991). These different findings can be ascribed to a more complex composition of natural glasses in terms of alkaline and alkaline-earth cations. Finally, it cannot be excluded that a different cationic composition of the solutions occurs prior to their reaction with the volcanic glass.

ACKNOWLEDGMENTS

REFERENCES

Baerlocher, Ch. and Meier, W.M. (1972) The crystal structure of synthetic zeolite Na-P1, an isotype of gismondine. *Zeitschrift für Kristallographie*, **135**, 339–354.

Barrer, R.M. and Hinds, L. (1953) Ion-exchange in crystals of analcite and leucite. *Journal of the Chemical Society*, 1879–1883.

Carnevali, R., Gualtieri, A., and Passaglia, E. (1994) Quantitative determination of zeolite component in Italian pyroclastites by the Rietveld analysis of X-Ray powder patterns. *Materials Engineering*, **5**, 211–221.

de' Gennaro, M. and Colella, C. (1991) The critical role of temperature in the natural zeolitization of volcanic glass. *Neues Jahrbuch Für Mineralogie-Monatshefte*, **8**, 355–362.

de' Gennaro, M. and Colella, C. (1992) Experimental clay formation through the action of hot saline waters on volcanic glass. *Mineralogica et Petrographica Acta*, **35A**, 275–282.

de' Gennaro, M. and Langella, A. (1996) Italian zeolitized rocks of technological interest. *Mineralium Deposita*, **31**, 452–472.

de' Gennaro, M., Franco, E., Langella, A., Mirra, P., and Morra, V. (1982a) Le phillipsiti dei tufi gialli del napoletano. *Periodico di Mineralogia*, **51**, 287–310.

de' Gennaro, M., Franco, E., Langella, A., Mirra, P., and Morra, V. (1982b) Le zeoliti delle piroclastiti dei Monti Ernici. La phillipsite dei peperini. *Acta Naturalia "L'Ateneo Parmense"*, **18**, 163–173.

de' Gennaro, M., Franco, E., Rossi, M., Langella, A., and Ronca, A. (1987a) Epigenetic minerals in the volcanoclastic deposits from central-southern Italy: A contribution to zeolite genesis. *Rendiconti dell' Accademia di Scienze Fisiche e Matematiche Napoli*, Special Issue, 107–131.

de' Gennaro, M., Di Girolamo, P., Mirra, P., and Morra, V. (1987b) Phillipsite in some pyroclastic flows from Tenerife (Canary Islands). *Rendiconti dell' Accademia di Scienze Fisiche e Matematiche Napoli*, Special Issue, 133–159.

de' Gennaro, M., Colella, C., Franco, E., and Stanzione, D. (1988) Hydrothermal conversion of trachytic glass into zeolite. I: Reactions with deionized water. *Neues Jahrbuch Für Mineralogie-Monatshefte*, **4**, 149–158.

de' Gennaro, M., Colella, C., Pansini, M., and Langella, A. (1992) Reconstruction of a natural zeolitization process through laboratory simulations. In *Ninth International Zeolite Conference*, R. von Balmoos, J.B. Higgins, and M.M.J. Treacy, eds., Butterworth-Heinemann, Boston, **2**, 207–214.

de' Gennaro, M., Colella, C., and Pansini, M. (1993) Hydrothermal conversion of trachytic glass into zeolite. II Reactions with high-salinity waters. *Neues Jahrbuch Für Mineralogie-Monatshefte*, **3**, 97–110.

de' Gennaro, M., Adabbo, M., and Langella, A. (1995) Hypothesis on the genesis of zeolites in some european volcaniclastic deposits. In *Natural Zeolites '93*, D.W. Ming and F.A. Mumpton, eds., Brockport, New York, 51–67.

De Jong, H.W.S., Schramm, C.M., and Parziale, V.E. (1983) Polymerization of silicate and aluminate tetrahedra in glasses, melts, and aqueous solutions—IV. Aluminium coordination in glasses and aqueous solutions and comments on the aluminium avoidance principle. *Geochimica et Cosmochimica Acta*, **47**, 1223–1236.

Di Girolamo, P., Ghiara, M.R., Lirer, L., Munno, R., Rolandi, G., and Stanzione, D. (1984) Vulcanologia e petrologia dei Campi Flegrei. *Bollettino della Società Geologica Italiana*, **103**, 349–413.

Ghiara, M.R. and Petti, C. (1996) Chemical alteration of volcanic glasses and related control by secondary minerals. Experimental studies. *Aquatic Geochemistry*, **1**, 329–354.

Gianello, A. and Gottardi, G. (1969) Sulla zeolitizzazione del livello cineritico detto "Tripoli di Contignaco". *Mineralogica et Petrographica Acta*, **15**, 5–8.

Hawkins, D.B. (1981) Kinetics of glass dissolution and zeolite formation under hydrothermal conditions. *Clays and Clay Minerals*, **29**, 331–340.

Ibrahim, K. and Hall, A. (1995) New occurrences of diagenetic faujasite in the Quaternary tuffs of north-east Jordan. *European Journal of Mineralogy*, **7**, 1129–1135.

Langella, A., de' Gennaro, M., Pansini, M., Colella, C., and Cantalini, C. (1993) Thermal stability of some Italian natural phillipsites. In *Proceedings of Journées Mediterranéenes de Calorimétrie et d'Analyse Thermique '93*, N. Balbi, ed., Sammarcelli, Biguglia (France), 229–232.

Orsi, G., Civetta, L., D'Antonio, M., Di Girolamo, P., and Piochi, M. (1995) Step-filling and development of a three-layer magma chamber: The Neapolitan Yellow Tuff case history. *Journal of Volcanology and Geothermal Research*, **67**, 291–312.

Passaglia, E. and Vezzalini, G. (1985) Crystal chemistry of diagenetic zeolites in volcanoclastic deposits of Italy. *Contribution to Mineralogy and Petrology*, **90**, 190–198.

Scarpati, C., Cole, P., and Perrotta, A. (1993) The Neapolitan Yellow Tuff—A large multiphase eruption from Campi Flegrei, Southern Italy. *Bullettin of Volcanology*, **55**, 343–356.

Scherillo, A. and Scherillo, M. (1990) I Campi Flegrei e la stratigrafia napoletana. *Quaderni Accademia Pontaniana*, **11**, 138 pp.

Sheppard, R.A. (1971) Zeolites in sedimentary deposits of the United States—A review. In *Molecular Sieve Zeolites*, R.F. Gould, ed., *American Chemical Society, Advances in Chemistry Series*, **101**, 279–310.

Shiraky, R. and Iiyama, J.T. (1990) Na-K ion exchange reaction between rhyolitic glass and (Na,K)Cl aqueous solution under hydrothermal conditions. *Geochimica et Cosmochimica Acta*, **54**, 2923–2931.