

## ZEOLITES IN PYROCLASTIC DEPOSITS IN SOUTHEASTERN TENERIFE (CANARY ISLANDS)

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**Abstract**—The chemical and the mineralogical composition of a group of pumiceous tuffs associated with recent salic volcanic episodes from Tenerife (Canary Islands) have been studied. The investigation focused on the two main types of pyroclastic deposits of the zone: ash-flows and ash-falls. The samples can be classified chemically as trachytic and phonolitic rocks with an intermediate silica content and a high percentage of alkali cations ( $\text{Na}^+$  and  $\text{K}^+$ ). The mineralogical composition, determined by X-ray diffraction, scanning electron microscopy, and optical microscopy, shows the occurrence of zeolites (mainly phillipsite, with lesser chabazite and analcime), associated with the parent glass. K-feldspar (sanidine) and calcite are accessory minerals. Zeolites are significantly more abundant in the ash-flow deposits. Zeolite formation by hydrothermal weathering in closed-system conditions varies according to the nature and the origin of the pyroclastic deposits. Tenerife phillipsites differ from typical diagenetic, lacustrine, and deep-sea phillipsites, both in chemical and mineralogical features. Alkali cations exceed divalent cations in the unit-cell that, assuming a monoclinic symmetry, has the following parameters:  $a = 8.46\text{--}10.55 \text{ \AA}$ ,  $b = 14.21\text{--}14.40 \text{ \AA}$ ,  $c = 7.80\text{--}8.70 \text{ \AA}$ , and  $\beta = 105^\circ\text{--}110^\circ$ .

**Key Words**—Ash-fall, Ash-flow, Chemical analysis, Geoautoclave, Phillipsite, X-ray diffraction, Zeolites, Zeolitization.

### INTRODUCTION

The southeastern side of Tenerife Island is covered by phonolitic and trachytic salic pyroclasts that have been cited or described by many authors (Ridley, 1967; Alonso, 1986, 1989; and others). The available geochronological data (Abdel-Monem *et al.*, 1972; Ancochea *et al.*, 1990) place the eruption of these materials between the Middle Pleistocene and the Holocene.

The local pyroclastic rocks can be subdivided into three different groups with varied characteristics and origins (Alonso, 1986, 1989): ash-fall, ash-flow, and base-surge deposits. In ash-fall deposits, the size of the lithic and pumice fragments increases toward the emission center and, during their transport by the wind, a more or less marked inner stratification by granulometric selection is produced. The rapid temperature decrease of the fragments during transport leads to a loss of volatiles, mainly water vapour, to the atmosphere, and the subsequent weathering of the glass is very limited.

Ash-flows are formed in Vulcanian or Pelean eruptive phases, or by collapse of an eruptive column. In both cases, the fluidized mass, formed by a highly concentrated suspension of particles and gases at high temperature, is rapidly transported down the slope, generally with laminar flow. The ash-flow evolves, filling the valleys and the depressed areas. These materials contain a high proportion of water vapour, which can be kept at high temperature for weeks, months, or even years, whereby the intensity and the rate of chemical

reactions on the glass are significantly higher than for ash-fall deposits.

Base-surge deposits are quantitatively less significant than ash-fall or ash-flow deposits. They are generated by turbulent flows of low particle concentration formed by explosive eruptions of hydromagmatic type.

During the last 15 years, many studies on the genesis of zeolites in various geological materials and environments have been reported (Hay, 1978; Iijima, 1978; Surdam and Sheppard, 1978; Gottardi, 1989; and others). Gottardi (1989) discusses the importance of the hydrothermal process on the genesis of zeolites. Hawkins (1981) points out that the aqueous concentration of cyclic building units, the main constituents of zeolite structures, increases significantly in high-temperature systems. Also, weathering processes in volcanic glasses have been the subject of numerous experimental studies since the works of Ross and Smith (1955), where the importance of the hydration of volcanic glass as a first stage in weathering was emphasized. Based upon these reports and other data, Colella *et al.* (1978) concluded that such hydration processes represent the initial stages in the formation of zeolites.

So far, the possibility of zeolite occurrence in pyroclastic deposits in southeastern Tenerife has not been considered in the literature despite the fact that both the nature of the pyroclastics and the geologic conditions of the zone are very favourable for zeolite formation. They are similar to other geologic environments, in which zeolite minerals have been reported to occur (Hay, 1978; Gottardi and Galli, 1985). The

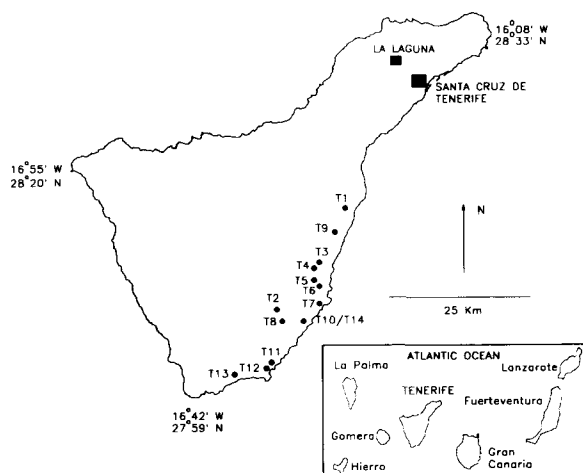


Figure 1. Geographic location of the samples.

aim of this paper is to report the chemical composition, the abundance, and the mineralogy of zeolites associated with pyroclastic silic materials in the southeastern side of Tenerife Island. Comments on their genesis will also be made.

#### EXPERIMENTAL METHODS AND MATERIALS

Criteria used for sample selection included the geological origin of the beds (ash-flow or ash-fall), their potential exploitability, and the absence of alternative uses (agricultural or urban) for zeolite-containing areas. The approximate geographic locations of the sampled sites are shown in Figure 1.

X-Ray Microanalysis (XRM) of phillipsite crystals was performed by averaging several points in four specimens of five representative samples using a Kevex-Quantimex microprobe, operated at 15.0 KeV and 15 nA beam current. Microprobe data were normalized to 100 wt. % by adding water determined by thermogravimetric analysis (TGS-2 Perkin Elmer at 20° min<sup>-1</sup> in air atmosphere).

The mineralogical composition was studied by X-ray powder diffraction analysis (XRD), SEM, and petrographic analysis of thin sections. Quantitative analysis by XRD (Phillips PW-1720 diffractometer at 40 kV and 30 mA) was performed by the method of Chung (1974), using NaCl as the internal standard. The unit-cell parameters of phillipsite were obtained by applying the TREOR indexing software.

#### RESULTS AND DISCUSSION

##### *Chemical and mineralogical composition of the samples*

From the chemical viewpoint, the whole rocks (data not shown) can be classified as phonolitic and, in some cases, as trachytic and trachyandesitic (Le Bas *et al.*,

Table 1. Mineralogical composition of the samples (by weight %).

Sample	Type	PHI	CHA	ANA	CAL	SAN	GLA
T1	AFL	6	tr	0	tr	12	82
T2	AFW	57	3	5	tr	7	28
T3	AFL	12	0	0	5	7	76
T4	AFL	0	tr	tr	2	0	98
T5	AFL	3	0	tr	0	2	95
T6	AFW	36	0	0	0	11	53
T7	AFW	30	0	0	0	8	62
T8	AFW	60	0	0	1	14	25
T9	AFL	13	0	tr	0	9	78
T10	AFW	24	tr	tr	0	5	71
T11	AFW	27	0	4	1	10	58
T12	AFW	21	0	tr	5	11	63
T13	AFW	21	tr	1	7	7	64
T14	AFW	35	0	0	1	14	50

Key: AFL = Ash-Fall; AFW = Ash-Flow; PHI = Phillipsite; CHA = Chabazite; ANA = Analcime; CAL = Calcite; SAN = Sanidine; GLA = Volcanic glass and other minor constituents not detected by XRD (augite, plagioclase, ilmenite, and hauyne); tr = traces.

1986). These rocks are alkalic, which should influence the chemical composition and the origin of zeolites. High proportions of alkali cations would indicate that highly alkaline pH values are likely in pore water in the tuff. This fact is extremely important for explaining the mechanism of zeolite genesis. In an alkaline environment, Si and Al are rapidly dissolved from volcanic glass, thus providing the main constituents of zeolites.

Trachytic and phonolitic tuffs have been reported to bear zeolites, especially in Italian deposits (Gottardi and Galli, 1985). According to these authors, phillipsite is the most common zeolite species, although chabazite may also be found in large amounts (Sersale, 1978). In these environments, the zeolite origin is usually attributed to a diagenetic mechanism, probably in hydrologically open systems (Sersale, 1978; Passaglia *et al.*, 1990). Furthermore, zeolites grown in such environments are quite different from those occurring in lacustrine deposits, formed from more acidic (rhyolitic) tuffs.

The presence of phillipsite, chabazite, and analcime was confirmed by quantitative XRD analysis (Table 1). Phillipsite is the most abundant, while chabazite and analcime are reduced minor species or traces. K-feldspar (sanidine) and calcite were detected as accessory minerals. The weight percent of glass (and trace minerals) was calculated by subtracting the sum of crystalline phases from 100. The most important aspect of these results is that phillipsite (and zeolites in general) are more abundant in the ash-fall deposits than in the ash-flows. In fact, the phillipsite-poorest ash-flows (T12 and T13) contain almost twice as much phillipsite as the most phillipsite-rich ash-fall (T9). The difference is much greater when considering the average phillips-

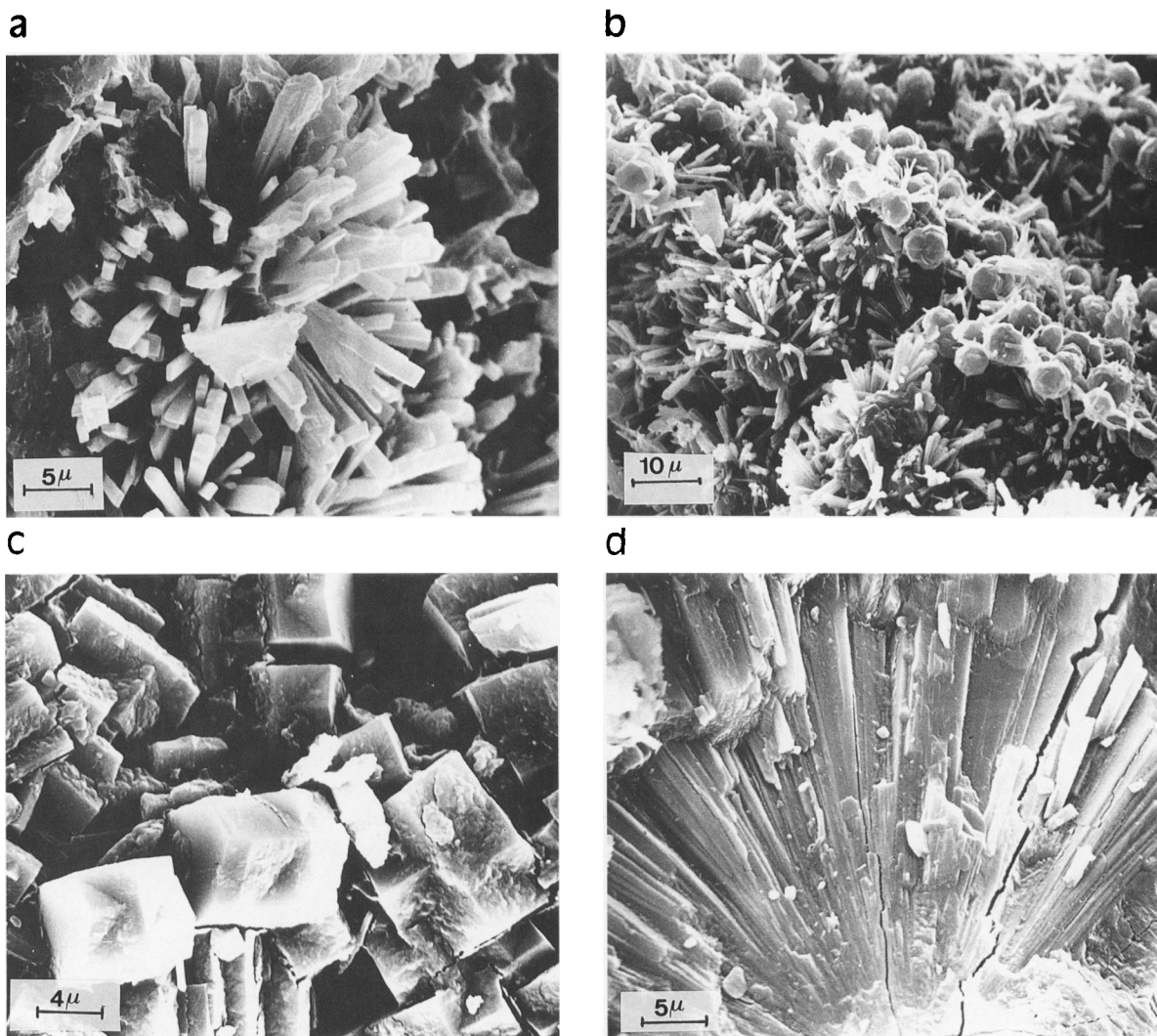


Figure 2. SEM photomicrographs of typical zeolite occurrences. a. Radiating clusters of phillipsite crystals (sample T8). b. Analcime crystals overlying radiating fibrous crystals of phillipsite (sample T2). c. Blocky chabazite (sample T2). d. Weathered glass showing radiating structures (sample T8).

ite content of both types of deposits. The significance of this finding with regard to the zeolite genesis will be discussed below.

The SEM also shows the ubiquitous occurrence of zeolites (Figure 2) intimately associated with the parent glass. Phillipsite, occurring in radiating clusters, is by far the most abundant zeolite mineral (Figure 2a). Analcime (Figure 2b) and blocky chabazite (Figure 2c) can also be distinguished, but in minor quantities. Analcime crystals always appear over phillipsite ones, suggesting that they grew later, at the expense of phillipsite. The characteristic fan-shaped structures seen on weathered glass (Figure 2d) have a genetic relationship with the growth and development of phillipsite crystals (Mumpton and Ormsby, 1976). Other minor phases not detected by XRD (augite, plagioclase,

ilmenite, etc.) were observed in thin sections under crossed Nicols.

#### *Chemistry and mineralogy of phillipsite*

A detailed chemical and mineralogical study of phillipsite was carried out on five representative rock samples. The other zeolite species, chabazite and analcime, were not studied because of their low abundance.

The chemical composition of the phillipsite is shown in Table 2. In principle, and from a chemical viewpoint, Tenerife phillipsite seems similar to those described by Passaglia *et al.* (1990), but the alkali cation content is markedly higher. On the other hand, Tenerife phillipsite is less silicic and even more alkalic than the diagenetic, lacustrine species described by Shepard and Fitzpatrick (1989) in saline, alkaline-lake de-

Table 2. Chemical composition (weight %) of five phillipsite samples.

Oxide	T3	T7	T8	T9	T12
SiO <sub>2</sub>	52.11 (0.62)	51.04 (0.89)	52.07 (0.82)	51.84 (0.31)	50.98 (1.15)
Al <sub>2</sub> O <sub>3</sub>	17.28 (0.74)	21.11 (1.10)	19.25 (1.46)	19.28 (0.48)	20.85 (0.94)
Fe <sub>2</sub> O <sub>3</sub>	1.18 (0.07)	1.37 (0.15)	1.43 (0.35)	1.61 (0.09)	1.02 (0.14)
CaO	3.86 (0.33)	1.12 (0.26)	1.22 (0.51)	2.49 (0.15)	2.44 (0.20)
MgO	0.97 (0.11)	0.18 (0.05)	0.38 (0.25)	0.78 (0.18)	0.26 (0.17)
Na <sub>2</sub> O	6.99 (0.16)	6.26 (0.24)	7.55 (0.82)	7.66 (0.41)	8.69 (0.26)
K <sub>2</sub> O	5.84 (0.21)	7.56 (0.30)	5.84 (0.94)	5.11 (0.35)	3.64 (0.37)
H <sub>2</sub> O	11.73	12.02	11.30	10.98	11.87

The numbers in brackets show the standard deviation.

posits. The alkali cation content, that seems to be the most distinctive characteristic, approaches the composition of the deep-sea species described by Stonecipher (1978).

The unit-cell composition and parameters are shown in Table 3. The sum of Si + Al in the unit cell is greater than 16, so other possible structure-forming cations (e.g., Fe<sup>+3</sup>) were not included in the zeolite framework. The compositional range, as compared with those of other phillipsites reported in literature, is given in Figure 3. Tenerife phillipsites are, in fact, different from those occurring in diagenetic (Passaglia *et al.*, 1990) and lacustrine (Sheppard and Fitzpatrick, 1989) environments, and they also differ from the deep-sea species described by Stonecipher (1978). Tenerife phillipsites are intermediate between the diagenetic and the deep-sea ones. Alkali cations exceed divalent cations

in all samples, and Na exceeds K. Phillipsites formed in hydrologically closed systems, deep-sea environments, and arid soils are usually Na-rich species, whereas phillipsites grown in hydrologically open systems from alkalic glasses are K-rich. This relationship was attributed by Passaglia *et al.* (1990) to the higher selectivity of phillipsite for K, which cannot be exerted in closed-system, marine, or arid conditions. It also seems to be true in Tenerife phillipsites.

With regard to the unit-cell parameters, TREOR does not provide good indexing values for d-values below 2 Å, so this value was chosen as the minimum limit. Italian phillipsites are quite different from Tenerife phillipsite, as they show higher values for the c-axis (higher than 14 Å) and, therefore, greater unit-cell volumes (above 2000 Å<sup>3</sup>, de' Gennaro and Franco, 1985; Passaglia *et al.*, 1990). The unit-cell parameters given by Gottardi and Galli (1985) and Sheppard and Fitzpatrick (1989) are closer to those of Tenerife phillipsite, although the β angle determined for Tenerife phillipsite is significantly lower (105°–110° vs 124°). The Miller indices of phillipsite (Table 4), as well as the unit-cell parameters shown in Table 3, were determined assuming a monoclinic symmetry for the mineral (Rinaldi *et al.*, 1974; Gottardi and Galli, 1985; von Balmoos, 1990).

#### Origin of zeolites

The genetic relationship between the type of deposit and the zeolitization of the volcanic glass seems to be clear. The ash-flow samples contain greater amounts of phillipsite and less volcanic glass than the ash-fall samples. In contrast, ash-falls typically show the association volcanic glass-feldspar with minor percentages of zeolites (Table 1). The formation of zeolite species is closely related to the hydrothermal, post-depositional processes that affected some of the pyroclastic units in southeastern Tenerife. In spite of the lack of data on the horizontal distribution of zeolites in the different pyroclastic levels, a diagenetic origin does not seem justifiable because the pluviometry conditions in the area (less than 250 mm per year, Kunkel, 1976), very similar to those in the recent geological past of the island, do not favour the infiltration of meteoric water to promote the hydration reactions in

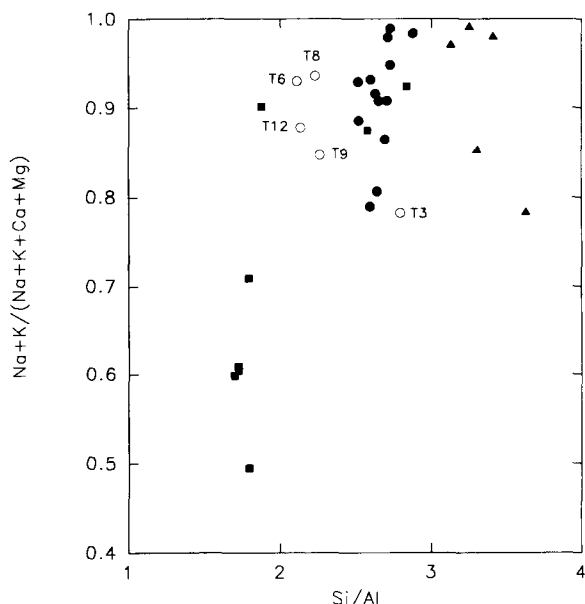


Figure 3. Diagram showing the chemical composition of Tenerife phillipsites vs other phillipsites described in literature, according to their alkali content and their Si/Al ratio. Open circles correspond to Tenerife phillipsites, and the solid figures are as follows: ■ Passaglia *et al.* (1990), ● Stonecipher (1978), ▲ Sheppard and Fitzpatrick (1989).

Table 3. Unit-cell content based on 32 atoms, and unit-cell parameters (monoclinic symmetry assumed).

Element	T3	T7	T8	T9	T12
Si	11.79	10.90	11.03	11.07	10.86
Al	4.22	5.16	4.94	4.89	5.09
Ca	0.84	0.25	0.28	0.56	0.55
Mg	0.31	0.09	0.05	0.24	0.08
Na	2.74	2.56	3.25	3.09	3.56
K	1.41	1.98	1.59	1.36	0.98
H <sub>2</sub> O	10.48	10.21	10.42	10.13	10.32
Si/Al	2.79	2.11	2.23	2.26	2.13
Si/(Si + Al)	0.73	0.67	0.69	0.69	0.68
a	8.46	8.74	8.75	10.55	10.47
b	14.40	14.33	14.21	14.33	14.34
c	7.80	8.59	8.70	8.53	8.10
$\beta$	105.13	109.18	110.14	108.81	107.58
V (Å <sup>3</sup> )	918.3	1016.9	1016.1	1222.2	1160.2

volcanic glass and the subsequent zeolitization processes.

The term "geoautoclave," independently coined by Lenzi and Passaglia (1974) and Aleksiev and Djourova (1975), has been used to describe this zeolitization in other volcanic units (Gottardi, 1989). The former found an ignimbrite homogeneously composed of chabazite, limited by two tuffs, one above and one below the ignimbrite. Despite their chemical composition being similar to the ignimbrite, both tuffs lacked zeolites. Gottardi (1989) pointed out that zeolitization of the ignimbrite cannot be explained by an open-system process and attributed zeolitization to the high vapour pressure and the high temperature inside the ignimbrite after its deposition.

Several researchers have provided experimental evidence of this mechanism by synthesizing zeolites in similar conditions to those existing inside an ash-flow or an ignimbrite (Colella *et al.*, 1978; Höller and Wirsching, 1978; de' Gennaro *et al.*, 1988). Höller and Wirsching (1978) observed the association phillipsite-analcime-chabazite, when treating finely powdered phonolitic glass with distilled water in closed system at 200°C and autogenous pressure. According to the authors, the grinding of the starting material constitutes a difference from natural conditions, but it is assumed only to accelerate the alteration rate without affecting the kind of minerals being formed.

De' Gennaro *et al.* (1988) carried out experiments of hydrothermal weathering of trachytic glasses, almost chemically identical to those described in this paper, with distilled water in closed system at temperatures ranging from 60° to 200°C and autogenous water pressure. These authors observed a rapid glass dissolution and gel formation as an intermediate stage in growth of zeolite species. The sequence of occurrence of zeolites, as a function of the reaction time, found by the authors is as follows:

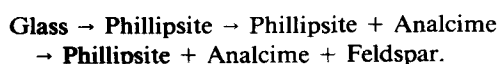


Table 4. Miller indices calculated for phillipsite in sample T8 using the TREOR indexing software.

2 $\theta$ obs.	2 $\theta$ calc.	<i>d</i> (Å)	<i>h</i> / <i>k</i> / <i>l</i>	<i>h</i>	<i>k</i>	<i>l</i>
	10.754			1	0	0
10.828	10.821	8.164	10	0	0	1
	12.360			-1	0	1
	12.430			1	1	0
12.444	12.448	7.107	48	0	2	0
	12.488			0	1	1
13.798	13.845	6.412	16	-1	1	1
16.484	16.478	5.373	15	1	2	0
	16.522			0	2	1
17.567	17.576	5.044	30	-1	2	1
	17.733	4.997	11	1	0	1
20.582	20.560	4.312	13	-2	0	1
	21.636			1	3	0
21.672	21.670	4.097	39	0	3	1
	21.724			1	2	1
22.445	22.492	3.958	5	-1	3	1
	22.502			2	1	0
	24.105	3.696	9	-2	2	1
	25.684	3.466	21	-2	1	2
27.335	27.326	3.260	16	1	4	0
	27.353			0	4	1
	27.424			2	0	1
	27.897			-2	2	2
27.940	27.943	3.191	100	-2	3	1
	28.019			-1	4	1
	28.023			-1	3	2
	28.721	3.106	11	2	3	0
	30.329	2.945	15	1	2	2
32.558	32.571	2.748	19	-2	0	3
	32.619			-2	4	1
	33.275			3	1	0
	33.309			2	4	0
33.322	33.330	2.688	20	1	5	0
	33.343			-1	2	3
	33.353			0	5	1
	33.401			0	4	2
35.246	35.269	2.544	9	0	2	3
	35.909	2.498	6	2	0	2
	37.506	2.396	9	2	4	1
	37.539			1	4	2
40.510	40.503	2.225	5	-2	5	2

This could describe almost exactly the mineral association in our samples, except the sanidine in Tenerife samples seems to be primary and not a result of glass weathering. Furthermore (and according to these authors), the occurrence of chabazite might be produced during the cooling of the ash-flow due to its lower crystallization temperature. There is no direct evidence supporting this idea from the data presented in this paper, so it must be regarded as a hypothesis.

Subsequently, and on the basis of the obtained results, it can be concluded that zeolites (and particularly phillipsite) in the pyroclastic silic rocks of Tenerife have their origin in the action of water vapour trapped within the pores of the glass particles. The water vapour rapidly reacted with volcanic glass at high temperature and closed-system conditions, thus promoting its hydration and dissolution and the subsequent nucleation and growth of zeolite crystals. Moreover, the alkali-rich parent glass would induce a raise of pH that is necessary for the mobilization of Si and Al to form the different zeolite species found here. This idea is supported by two pieces of evidence. The first is the occurrence of analcime, the most Al-rich zeolite species, which is characteristic of strongly alkaline environments. The second is the high alkali cation content of Tenerife phillipsite. This characteristic is very significant and, together with the crystallographic features shown in Table 3, distinguishes Tenerife phillipsite from other well-known phillipsites described in the literature.

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