

CaK-clinoptilolite, KNa-chabazite, KNa-heulandite, KNa-erionite and Na-phillipsite from tuffaceous rocks, Province of the Mesa Central, Mexico

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ABSTRACT

This paper presents the occurrence, mineralogy and process of formation of CaK-clinoptilolite, KNa-chabazite, KNa-heulandite, KNa-erionite and Na-phillipsite in pyroclastic rocks from the Calvillo-Jalpa-Nochixtlán area in the Province of the Mesa Central, Mexico. CaK-clinoptilolite, $(\text{Si}_{30.600-30.150}\text{Al}_{5.760-5.220})(\text{Ca}_{1.890-1.800}\text{K}_{1.080-0.810}\text{Mg}_{0.540-0.450})\text{O}_{72}$, of 5.04–5.86 Si/Al, 0.83–0.86 Si/(Si+Al) and 0.26–0.31 (Na+K)/(Na+K+Ca+Mg) ratios, free of Na, crystallized from siliceous alkaline pore fluids and glasses of composition $(\text{Si}_{0.890-0.825}\text{Al}_{0.202-0.102})(\text{K}_{0.072-0.020}\text{Ca}_{0.020-0.010}\text{Fe}_{0.050-0.010})\text{O}_2$ in tuffaceous rocks northeast of Jalpa. KNa-heulandite, $(\text{Si}_{28.080}\text{Al}_{8.010})(\text{K}_{4.680}\text{Na}_{2.250}\text{Ca}_{0.270}\text{Fe}_{0.180})\text{O}_{72}$, KNa-chabazite, $(\text{Si}_{9.210-9.000}\text{Al}_{3.090-2.940})(\text{K}_{0.750-1.180}\text{Na}_{0.360-1.260}\text{Ca}_{0.150-0.030}\text{Fe}_{0.210-0.090}\text{Mg}_{0.380-0.210})\text{O}_{24}$, NaK-erionite, $(\text{Si}_{27.990}\text{Al}_{7.830})(\text{K}_{2.000})(\text{K}_{4.210}\text{Na}_{1.620}\text{Ca}_{0.090}\text{Fe}_{0.090}\text{Mg}_{0.180})\text{O}_{72}$, and Na-phillipsite, $(\text{Si}_{12.080}\text{Al}_{3.920})(\text{Na}_{3.160}\text{K}_{0.240}\text{Ca}_{0.160}\text{Fe}_{0.040})\text{O}_{32}$, of 2.91–3.57 Si/Al, 0.74–0.78 Si/(Si+Al) and 0.72–0.97 (Na+K)/(Na+K+Ca+Mg) ratios, dominant exchange cations K and Na, formed from siliceous alkaline high-pH fluids and glasses of composition $(\text{Si}_{0.910-0.833}\text{Al}_{0.170-0.092})(\text{K}_{0.101-0.050}\text{Na}_{0.033-0.027})\text{O}_2$ in tuffs northwest of Nochixtlán. The zeolites were formed in the Jalpa area by diagenetic alteration of the tuff; in the Nochixtlán area, enrichment of Na and formation of alkali-rich zeolites was attributed to alkaline saline brines in an open hydrologic system. They occur in Oligocene – early Miocene tuffaceous rocks associated to the volcanism of the Sierra Madre Occidental, exposed in the Calvillo–Jalpa–Nochixtlán area in the states of Aguascalientes and Zacatecas, in the Province of the Mesa Central, Mexico.

Keywords: CaK-zeolites, KNa-zeolites, zeolites, Mexico.

RESUMEN

Este trabajo presenta la ocurrencia, mineralogía y proceso de formación de CaK-clinoptilolita, KNa-chabazita, KNa-heulandita, KNa-erionita y Na-phillipsita en rocas piroclásticas del área de Calvillo-Jalpa-Nochixtlán, en la Provincia de la Mesa Central, México. CaK-clinoptilolita, $(\text{Si}_{30.600-30.150}\text{Al}_{5.760-5.220})(\text{Ca}_{1.890-1.800}\text{K}_{1.080-0.810}\text{Mg}_{0.540-0.450})\text{O}_{72}$, de relaciones 5.04–5.86 Si/Al, 0.83–0.86 Si/(Si+Al) y 0.26–0.31 (Na+K)/(Na+K+Ca+Mg), libre de Na, cristalizó de fluidos

de poro silíceos alcalinos y vidrios de composición $(\text{Si}_{0.890-0.825}\text{Al}_{0.202-0.102})(\text{K}_{0.072-0.020}\text{Ca}_{0.020-0.010}\text{Fe}_{0.050-0.010})\text{O}_2$ en tobas al noreste de Jalpa. KNa-heulandita, $(\text{Si}_{28.080}\text{Al}_{8.010})(\text{K}_{4.680}\text{Na}_{2.250}\text{Ca}_{0.270}\text{Fe}_{0.180})\text{O}_{72}$, KNa-chabazita, $(\text{Si}_{9.210-9.000}\text{Al}_{3.090-2.940})(\text{K}_{0.750-1.180}\text{Na}_{0.360-1.260}\text{Ca}_{0.150-0.030}\text{Fe}_{0.210-0.090}\text{Mg}_{0.380-0.210})\text{O}_{24}$, NaK-erionita, $(\text{Si}_{27.990}\text{Al}_{7.830})(\text{K}_{2.000})(\text{K}_{4.210}\text{Na}_{1.620}\text{Ca}_{0.090}\text{Fe}_{0.090}\text{Mg}_{0.180})\text{O}_{72}$, y Na-phillipsita, $(\text{Si}_{12.080}\text{Al}_{3.920})(\text{Na}_{3.160}\text{K}_{0.240}\text{Ca}_{0.160}\text{Fe}_{0.040})\text{O}_{32}$, de relaciones 2.91–3.57 Si/Al, 0.74–0.78 Si/(Si+Al) y 0.72–0.97 (Na+K)/(Na+K+Ca+Mg), cationes intercambiables dominantes K y Na, cristalizaron de fluidos de poro silíceos alcalinos de alto pH y de vidrios de composición $(\text{Si}_{0.910-0.833}\text{Al}_{0.170-0.092})(\text{K}_{0.101-0.050}\text{Na}_{0.033-0.027})\text{O}_2$ en tobas al noroeste de Nochixtlán. Las zeolitas se formaron, en Jalpa, por diagenesis de la toba; en Nochixtlán, el enriquecimiento de Na y la formación de zeolitas alcalinas se atribuye a la acción de salmueras alcalinas salinas, en un sistema hidrológico abierto. Las zeolitas ocurren en tobas del Oligoceno – Mioceno temprano asociadas al volcanismo de la Sierra Madre Occidental y expuestas en el área de Calvillo–Jalpa–Nochixtlán, estados de Aguascalientes y Zacatecas, en la Provincia de la Mesa Central, México.

Palabras clave: CaK-zeolitas, KNa-zeolitas, zeolitas, México.

INTRODUCTION

This paper presents the occurrence, mineralogy and process of formation of alkali-rich zeolites in volcanoclastic deposits in the states of Zacatecas and Aguascalientes in the Province of the Mesa Central, México. Alkali-rich zeolites are a not so common rarity, opposed to the widely distributed sedimentary zeolites clinoptilolite-heulandite and mordenite of CaKNaMg-exchange components. Alkali-rich zeolites have not been reported previously in Mexico. Known deposits of sedimentary zeolites in Mexico are mostly of clinoptilolite-heulandite, in the state of Oaxaca in the Province of the Sierra Madre del Sur (Wilson and Clabaugh, 1970; Mumpton, 1973; de Pablo, 1986), in the vicinity of Guanajuato and San Miguel de Allende in the Province of the Mesa Central (de Pablo *et al.*, 1996), in the Mexican Volcanic Belt (de Pablo and Chavez, 1996) and in the state of Sonora in the Basin and Range Province (Münch and Cochemé, 1993; Münch *et al.*, 1996). Extensive deposits of sedimentary zeolites are known in western United States, in the states of Arizona, California, Nevada and Oregon (Passaglia

and Sheppard, 2001), in Italy (Passaglia and Vezzalini, 1985) and elsewhere. Alkali-rich zeolites are known from western United States (Passaglia and Sheppard, 2001) and which generally have, relative to their equivalent Italian zeolites, less K and larger Si/Al ratios (Passaglia, 1970; De'Genaro and Franco, 1976; Passaglia and Vezzalini, 1985; Passaglia and Sheppard, 2001).

The formation of zeolites in volcanoclastic deposits is associated to the peculiarities of the precursor glass, the percolating fluids and the local environment, thus a close relationship prevails between the newly formed authigenic minerals and the chemistry of the glasses and pore fluids, which may change. The transformation to zeolites is possible in: (1) hydrologic closed alkaline saline systems, (2) hydrologic open systems, (3) marine environments, (4) hydrothermal systems, (5) geoautoclave systems and (6) by burial diagenesis (Hay and Sheppard, 2001). In this paper are presented the mineralogy and origin of CaK-, KNa- and Na-zeolites from the Province of the Mesa Central, Mexico. The area studied is known for a high incidence of pulmonary diseases (Reyes-Veyna, 2007). The interest is on the origin of the alkali-rich zeolites, contribute to the knowledge on the minerals, their occurrence in Mexico, possible harmful health effects and eventual technological interest. Mineral zeolites have economic interest as low-cost adsorbers in chemical and environmental applications, in agricultural practice and in animal feedstocks and husbandry (Mumpton, 1977); their commercial use in Mexico has been mostly limited to application as dimension stone, in agriculture and in animal feedstocks.

MATERIALS AND METHODS

Materials

The tuffs discussed herein are part of the Cenozoic volcanic that extends over the Mesa Central, in the states of Zacatecas and Aguascalientes in Mexico. The area of study extends approximately 25,000 km², between the 103°40' – 102°00'W longitude and the 22°00' – 21°15'N latitude; it is located to the west of the city of Aguascalientes and south of Calvillo, Zacatecas, and includes the towns of Jalpa and Nochixtlán. The geology setting of the area was introduced in a previous publication (de Pablo *et al.*, 2013). The dominant lithology are the Oligocene-Miocene rhyolitic tuffs and rhyolite-ignimbrites associated with the volcanism of the Sierra Madre Occidental; exposed in the area are Miocene andesites and basalts, Pliocene calcareous conglomerates, conglomerates and shales. The tuffs were sampled at different locations and which together with mineralogical and compositional data have been presented (de Pablo *et al.*, 2013).

Methods

The mineralogy and petrography of the tuffs were determined by the usual procedures of optical microscopy, X-ray powder diffraction (XRD) and X-ray fluorescence (XRF). X-ray powder diffraction (XRD) analyses were performed using a Siemens diffractometer with filtered CuK α radiation on powdered bulk material and clay-sized fractions scanned at 1° 2 θ min⁻¹. Whole-rock major and trace elements analyses were performed by X-ray fluorescence (XRF) on bulk powders fused as glass beads. Total Fe was analyzed by XRF and calculated as FeO; methods to differentiate Fe³⁺ from Fe²⁺ were not considered. Loss on ignition was determined by wet chemistry (de Pablo *et al.*, 2013). XRD characterization of some zeolites was limited due to the difficulty of obtaining adequate amounts for their detection. Heulandite and clinoptilolite were differentiated by their framework composition: minerals with the framework ratio Si/Al < 4 were labeled as heulandite and those with Si/Al > 4 were labeled as clinoptilolite, after the recommended nomenclature of the Commission on New Minerals

and Mineral Names of the International Mineralogical Association (Coombs *et al.*, 1997, 1998).

The morphology, microtexture and composition of minerals were initially determined by scanning electron microscopy (SEM) at 25 kV operating voltage coupled with energy dispersive X-ray (EDX) analysis, on unpolished fragments that were carbon-coated when analyzed for composition and gold-coated when studied morphologically. More precise studies were performed by high resolution scanning electron microscopy (HRSEM) using a JEOL 2000FX scanning electron microscope operated at an acceleration voltage of 200 kV and equipped with a double inclined sample holder with a resolution of 3.1 Å and an EDX Oxford ISIS spectrometer with a resolution of 136 eV at 5.39 keV. The chemical compositions determined by EDX were obtained at short time periods to avoid alkali volatilization, from selected areas of uniform morphology and mineralogy presumably larger than the cross section of the incident electron beam (de Pablo *et al.*, 2013).

RESULTS

The dominant lithology in the area is an assemblage of ignimbrite and rhyolitic tuffs of Oligocene-Miocene age (de Pablo *et al.*, 2013). Variations in the chemical composition (Table 1), mineralogy (Table 2) and stratigraphic position of the tuffs allowed recognition of four distinct groups (de Pablo *et al.*, 2013). Group 1, located 10 km northeast of Jalpa, elevation 1334 m, comprises tuffs of comparatively low contents of SiO₂ and MgO and high contents of Al₂O₃, Fe₂O₃ and K₂O (sample 2 in Tables 1 and 2). Group 2, 20 km northeast of Jalpa, elevation 1350 m, where the tuffs are noted by the unusual association of cristobalite, tridymite and minor alunogen-alunite to feldspar, plagioclase, heulandite-clinoptilolite and smectite and by comparatively high contents of SiO₂ and low of Al₂O₃, Fe₂O₃, CaO, Na₂O, Rb and Ba (sample 3 in Tables 1 and 2). Group 3, 90 km northwest of Nochixtlán at elevations of 1370 m and 1440-1478 m and east of Calvillo at elevations of 1521-1570 m, includes tuffs of high and low SiO₂/Al₂O₃ ratio and high contents of MgO, Sr, Ba and Y and predominant authigenic heulandite-clinoptilolite and smectite (samples 14, 12, 13, 1 and 15 in Tables 1 and 2). Group 4, northwest of Nochixtlán, elevation 1780-1880 m, includes tuffs noted by the presence of primary quartz and authigenic smectite, high contents of Na₂O, K₂O, Rb, Y and Nb and low of MgO, CaO, Sr and Ba (samples 10 and 11 in Tables 1 and 2).

The contents of major and trace elements in the tuffs relative to Zr are presented in Figure 1. Zirconium was selected as an indicator of differentiation because of its incompatibility. From low to high concentrations of Zr slight descending compositional trends are shown by SiO₂ and Na₂O and upward trends are exposed by Al₂O₃ and MgO that depict continuous compositional changes in the tuffs. High concentrations of SiO₂ and low of Al₂O₃, Na₂O and K₂O occur in tuffs from the 1350 m elevation site northeast of Jalpa, opposed to the more abundant K₂O and Na₂O noted in tuffs from the 1880 m elevation site northwest of Nochixtlán. Differences in the ignition loss imply hydration and reaction with H₂O, H⁺ and H₃O⁺.

Changes in the mineralogy of the tuffs among the four groups are significant (Table 2, Figure 2). X-ray diffraction data showed the presence of predominant heulandite-clinoptilolite and minor smectite at intermediate elevations in Group 3. Northeast of Jalpa, in Group 2 at an elevation of 1350 m, primary cristobalite and tridymite are significant and northwest of Nochixtlán, in Group 4 at an elevation of 1880 m, quartz crops. Altogether, XRD data depict an extensive area of tuffs zeolitized to predominant heulandite-clinoptilolite. The tuffs from groups 2 and 4 showed the most relevant changes and were selected for presentation in further detail, represented respectively by sample

Table 1. Chemical composition of the rhyolitic tuffs. Analyses by XRF (from de Pablo *et al.*, 2013).

	Sample								
	11	10	15	1	12	13	14	3	2
Group	4	4	3	3	3	3	3	2	1
Elevation (m)	1880	1780	1570	1521	1478	1440	1370	1350	1334
SiO ₂ (wt%)	67.27	73.31	63.76	64.38	69.76	71.13	64.65	71.49	64.30
TiO ₂	0.20	0.21	0.43	0.37	0.30	0.33	0.37	0.33	0.42
Al ₂ O ₃	16.08	11.49	13.16	13.13	10.55	10.63	12.34	10.80	13.50
Fe ₂ O ₃	2.10	2.34	2.73	2.75	2.37	2.91	2.98	1.32	3.16
MnO	0.03	0.12	0.02	0.04	0.03	0.02	0.07	0.01	0.04
MgO	0.60	0.44	1.14	0.74	1.36	0.79	1.55	1.55	0.43
CaO	0.67	1.45	2.22	2.33	2.54	2.31	3.00	1.09	2.44
Na ₂ O	2.78	1.40	0.28	2.20	0.95	1.22	0.56	0.64	0.90
K ₂ O	6.98	5.18	4.05	2.72	2.30	2.56	2.52	1.86	2.57
P ₂ O ₅	0.05	0.07	0.07	0.10	0.07	0.01	0.13	0.08	0.07
Ign loss	3.11	3.77	12.10	11.18	9.97	7.94	12.14	12.05	10.99
Rb (ppm)	233	140	106	116	137	122	102	40	114
Sr	39	49	870	334	505	522	846	314	398
Ba	495	633	983	947	785	1605	1283	747	903
Y	58	80	28	30	26	21	37	14	28
Zr	212	175	280	214	187	171	264	232	223
Nb	10	11	8	8	3	4	8	8	6
V	23	119	20	38	32	43	32	34	44
Cr	30	18	7	5	21	12	12	8	10
Co	7	5	6	8	7	6	6	7	8
Ni	6	10	8	8	9	7	9	7	9
Cu	5	5	9	12	10	15	11	13	14
Zn	74	74	77	72	65	103	86	18	78
Th	14	14	9	10	7	6	9	10	10
Pb	13	13	13	10	7	8	18	15	14

3, location 102°50'W longitude, 21°42'N latitude, elevation 1350 m, northeast of Jalpa and by sample 11, location 102°47'W longitude, 21°26'N latitude, elevation 1880 m, northwest of Nochixtlán.

High-resolution scanning electron microscopy of the rhyolitic tuff cropping 20 km northeast of Jalpa (sample 3) shows rhyolitic glasses of 78.22–80.01 wt% SiO₂, free of Na and Mg, K>Ca, of 4.07–5.65 Si/Al, 0.80–0.88 R [R=Si/(Si+Al)] and 0.50–0.80 alkali [(Na+K)/(Na+K+Ca+Mg)] ratios, occurring as irregular non-vesicular fragments over 30 µm in size (Figure 3a, composition 3.4.1 in Table 3), slabs ~150 nm thick and 800 nm long (Figure 3b, compositions 3.9.1 and 3.9.2 in Table 3) and thinner irregular slabs of round edges (Figure 3b). These thin slabs occasionally are oriented around orthogonal empty spaces and are crowned by vesicular glass (Figure 3c, compositions 3.14.1 and 3.14.2 in Table 3). Glass spheres of 50–100 nm in diameter formed (Figure 3d, composition 3.11.1 in Table 3). A more siliceous glass of 84.67 wt% SiO₂, no Na and Mg, 8.68 Si/Al, 0.89 R and 0.94 alkali ratios fills voids between crystals (Figure 3e, composition 3.37.1 in Table 3).

The authigenic mineralogy includes blocky, tabular and pseudo hexagonal thick crystals 2–10 µm thick and 10–20 µm long of clinoptilolite of 5.86–5.04 Si/Al, 0.85–0.83 R and 0.31–0.26 alkali ratios, Ca>K, dominant exchange cations (DEC) Ca, K, subordinate exchange cation (SEC) Mg, free of Na, in vesicles and fissures (Figure 3f, 3g, 3h, compositions 3.32.2, 3.34.1, 3.35.1 in Table 3) (Coombs *et al.*, 1997). This clinoptilolite differs from the clinoptilolite from the Suchilquitongo

Formation, Etna, Oaxaca, which is sodic, K+Na>Ca+Mg and 5.05–4.31 Si/Al, 0.83–0.81 R and 0.59–0.53 alkali ratios, DEC K, Ca, Na, SEC Mg and from clinoptilolite from the Chichíndaro Formation, San Miguel Allende, Guanajuato, which is sodic, 4.49 Si/Al, 0.81 R and 0.69 alkali ratios, DEC K, Ca, Na, SEC Mg (de Pablo, 1986; de Pablo *et al.*, 1996; de Pablo and Chavez, 1996). Differences in the Si, Al and alkalis contents depict distinct degrees of framework ordering and channel occupancy between the clinoptilolite from Jalpa and the clinoptilolite from the Suchilquitongo and the Chichíndaro Formations (Armbruster and Gunter, 2001). Clinoptilolite of high R ratio occurs in rhyolitic tuffs at Cañadón Hondo, Patagonia, Argentina (Mason and Sand, 1960); of low alkali ratio is known from the Báucarit Formation, Mexico (Münch and Cochemé, 1993) and Na-free clinoptilolite crops in the Malpais Hill, Arizona (Wise and Tschernich, 1976). The composition and morphology of the clinoptilolite from Jalpa has some resemblance to tabular dachiardite. Dachiardite of 0.86 R ratio has been described from Altoona, Washington (Wise and Tschernich, 1978) and of Ca>Na from Elba Island, Italy (Gottardi, 1960; Vezzadini, 1984), Yellowstone National Park, Wyoming (Bargar *et al.*, 1987) and from the Kagoshima and Ogasawara Islands, Japan (Nishido and Otsuka, 1981; Passaglia and Sheppard, 2001).

Irregular thick wavy glassy slabs of a composition that resembles heulandite, of 2.64–2.30 Si/Al, 0.72–0.70 R and 0.60–0.51 alkali ratios, DEC Na, Ca and minor K, enclose empty orthogonal cavities (Figure 3i, compositions 3.38.1 and 3.38.2 in Table 3). Heulandite of high alkali

Table 2. Minerals in the rhyolitic tuffs. Analyses by XRD and optical microscopy (from de Pablo *et al.*, 2013).

	Sample								
	11	10	15	1	12	13	14	3	2
Group	4	4	3	3	3	3	3	2	1
Elevation (m)	1880	1780	1570	1521	1478	1440	1370	1350	1334
heulandite-clinoptilolite	-	-	X	X	X	X	X	X	X
crystalite	-	-	-	-	-	-	-	X	-
tridymite	-	-	-	-	-	-	-	X	-
quartz	X	X	-	-	-	-	-	-	-
smectite	X	X	X	X	X	X	X	X	X
plagioclase	X	X	X	X	X	X	X	X	X
feldspar	X	X	X	X	X	X	X	X	X
alunogen-alunite	-	-	-	-	-	-	-	X	-
glass	X	X	X	X	X	X	X	X	X

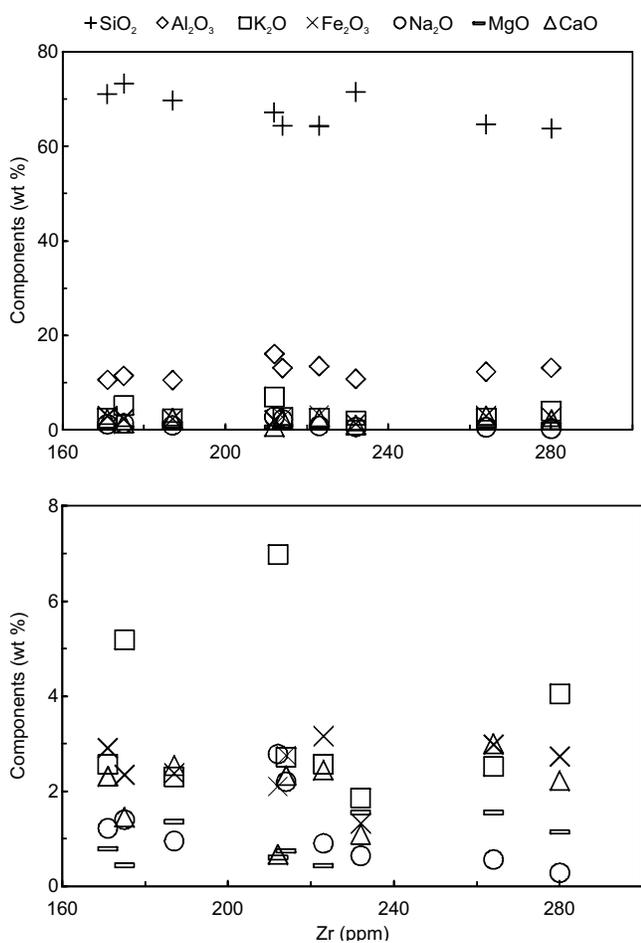


Figure 1. Chemical composition variation diagrams of rhyolitic tuffs from Jalpa and Nochixtlán.

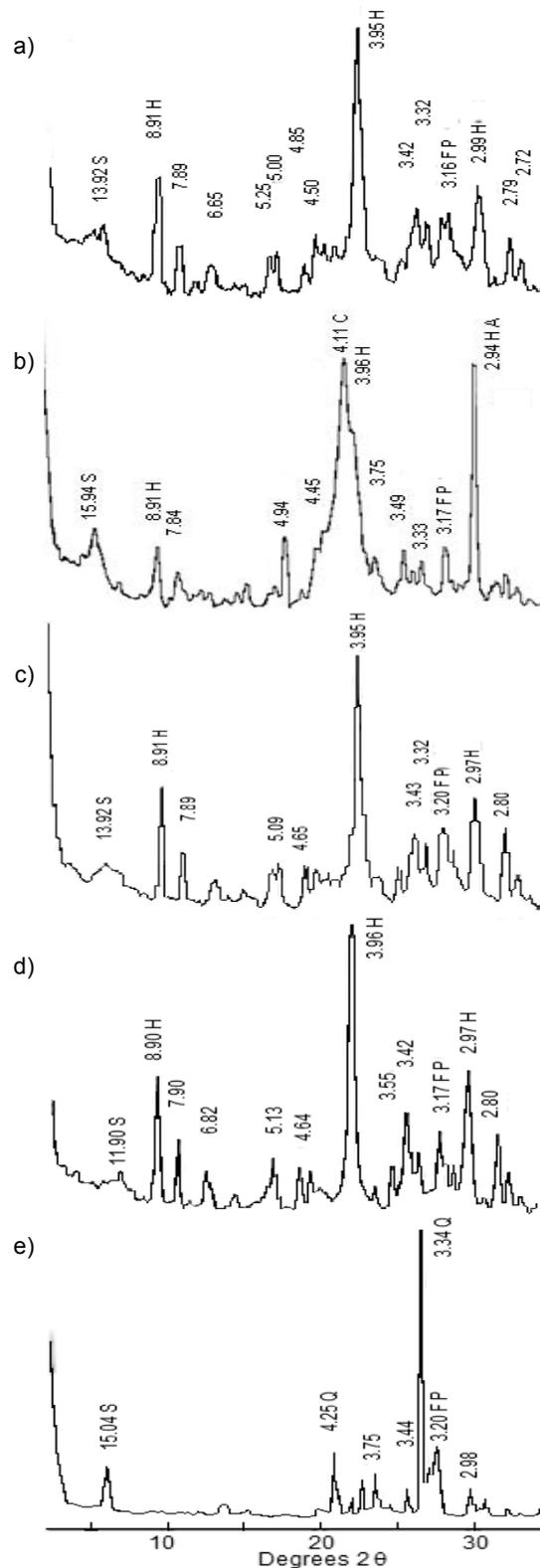


Figure 2. X-ray diffraction patterns of rhyolitic tuffs: (a) sample 2, 10 km northeast of Jalpa, elevation 1334 m; (b) sample 3, 20 km northeast of Jalpa, elevation 1350 m; (c) sample 14, 90 km northwest of Nochixtlán, elevation 1370 m; (d) sample 15, 20 km east of Calvillo, elevation 1570 m; (e) sample 11, 11 km northwest of Nochixtlán, elevation 1880 m. S smectite, H heulandite-clinoptilolite, Q quartz, P plagioclase, F feldspar, C cristobalite, T tridymite, A alunogen-alunite.

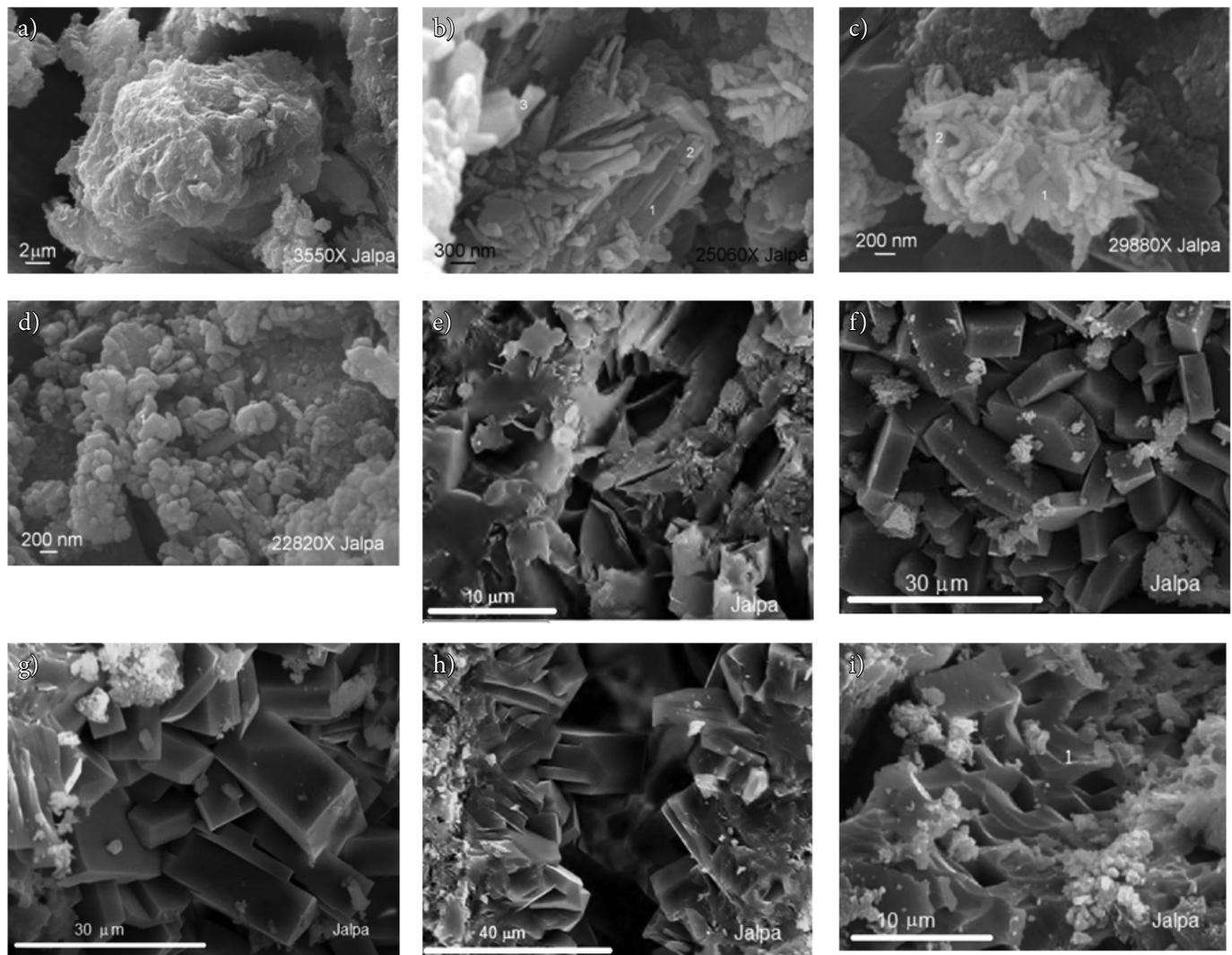


Figure 3. High resolution scanning electron microscopic images from the rhyolitic tuff from Jalpa, sample 3: (a) glass (composition 3.4.1 in Tables 3, 6); (b) glass (1, 2, compositions 3.9.1 and 3.9.2 in Tables 3, 6); (c) glass (1, 2, compositions 3.14.1 and 3.14.2 in Tables 3, 6); (d) glass spheres (1, composition 3.11.1 in Tables 3, 6); (e) glass (composition 3.37.1 in Tables 3, 6); (f) clinoptilolite (composition 3.32.2 in Tables 3, 6); (g) clinoptilolite (composition 3.34.1 in Tables 3, 6); (h) clinoptilolite (composition 3.35.1 in Tables 3, 6); (i) heulandite (compositions 3.38.1 and 3.38.2 in Tables 3, 6).

ratio was found in burial diagenetic clay-rich horizons in Denmark (Nornberg, 1990) and high alkali ratio almost K-free crystals are known from Yellowstone National Park, Wyoming (Bargar and Beeson, 1981), from the Shimane Prefecture, Japan (Minato and Aoki, 1978), Caravaca, Spain (Vannucci *et al.*, 1992) and the Barstow Formation in California (Sheppard and Gude, 1969; Passaglia and Sheppard, 2001).

The tuff that crops 11 km northwest of Nochixtlán at an elevation of 1880 m (sample 11), contains $\sim 16 \mu\text{m}$ quartz crystals of predominant hexagonal bipyramidal faces and diminished prismatic faces that depict crystallization from the melt (Figure 4a, composition 11.35.1 in Table 4). Smaller quartz crystals are enclosed by 67.63 wt% SiO_2 glass (Figure 4f, composition 11.34.1 in Table 4). Albite crystals are noted (Figure 4b, composition 11.21.1 in Table 4).

The glasses in sample 11 show a wider range of composition than the glasses from sample 3. In sample 11 there are glasses of 91.86–81.06 wt% SiO_2 , low 9.54–5.52 wt% Al_2O_3 , free of Na, 13.89–7.27 Si/Al, 0.93–0.88 R and 0.92–0.50 alkali ratios, non-vesicular (Figures 4c, 4d, compositions 11.25.1, 11.25.2, 11.24.1 in Table 4). They associate to

less siliceous glasses of 86.98–76.74 wt% SiO_2 , 10.97–7.52 wt% Al_2O_3 , 1.55–1.28 wt% Na_2O , 9.84–4.90 Si/Al, 0.91–0.83 R and 1.00–0.92 alkali ratios which form small lens-shaped shards (Figure 4c, compositions 11.25.3 to 11.25.6 in Table 4) and to lower-temperature glasses of dacitic and trachydacitic composition of 67.63–65.01 wt% SiO_2 , 7.09–3.17 wt% K_2O , 3.13–2.51 wt% MgO , free of Na, low 3.20–2.43 Si/Al, 0.76–0.71 R and 0.60–0.43 alkali ratios, often occurring around irregular and roughly orthogonal cavities (Figures 4e, 4f, 4g, compositions 11.37.1, 11.34.1 and 11.39.1 in Table 4) (Le Bas *et al.*, 1986).

Intimately associated with the glasses are crystallites of rhombohedral pseudocubic morphology and ‘herschelitic’ habit of chabazite, $\sim 0.25 \mu\text{m}$ in size, 3.13–2.91 Si/Al, 0.76–0.74 R and 0.89–0.72 alkali ratios, DEC K, Na, SEC Mg and essentially free of Ca (Figure 4d, compositions 11.24.2 and 11.24.3 in Table 5). Chabazite crystallites of 0.89 alkali ratio, DEC Na, K, SEC Mg and very minor Ca are on phillipsite in vesicles (Figure 4i, composition 11.20.2 in Table 5). These chabazites have an R ratio greater than the 0.73–0.68 R ratio of the Italian hydrothermal chabazites (Passaglia, 1970; De’Genaro

Table 3. Composition of minerals from sample 3.

	Composition (wt%)											
	3.4.1	3.9.1	3.9.2	3.14.1	3.14.2	3.11.1	3.37.1	3.32.2	3.34.1	3.35.1	3.38.1	3.38.2
SiO ₂	79.40	79.36	79.60	78.22	80.01	78.84	84.67	80.69	79.29	78.98	66.04	63.16
Al ₂ O ₃	11.92	12.18	13.66	16.29	14.77	13.80	8.42	11.85	12.94	13.41	21.35	23.23
K ₂ O	1.39	3.14	2.03	3.02	3.25	2.45	5.44	1.79	2.24	1.94	0.82	0.70
CaO	1.73	1.21	1.77	0.98	1.05	1.66	0.54	4.75	4.48	3.70	6.33	7.58
FeO	5.57	4.10	2.94	1.49	0.92	3.25	0	0	0	0	0.91	0.78
Na ₂ O	0	0	0	0	0	0	0	0	0	0.22	4.55	4.22
MgO	0	0	0	0	0	0	0	0.91	1.04	1.72	0	0.32
Si ⁴⁺	3.39	3.40	3.37	3.30	3.37	3.35	3.56	3.40	3.35	3.33	2.90	2.79
Al ³⁺	0.60	0.61	0.68	0.81	0.73	0.69	0.41	0.58	0.64	0.66	1.10	1.21
K ⁺	0.08	0.17	0.11	0.16	0.17	0.13	0.29	0.09	0.12	0.10	0.05	0.04
Ca ²⁺	0.08	0.06	0.08	0.04	0.05	0.08	0.02	0.21	0.20	0.17	0.29	0.36
Fe ²⁺	0.20	0.15	0.10	0.05	0.03	0.12	0	0	0	0	0.03	0.03
Na ⁺	0	0	0	0	0	0	0	0	0	0.02	0.38	0.36
Mg ²⁺	0	0	0	0	0	0	0	0.05	0.06	0.11	0	0.02
O ⁼	8	8	8	8	8	8	8	8	8	8	8	8
Si/Al	5.65	5.57	4.96	4.07	4.62	4.86	8.68	5.86	5.23	5.04	2.64	2.30
Si/(Si+Al)	0.85	0.85	0.83	0.80	0.82	0.83	0.89	0.85	0.84	0.83	0.72	0.70
Si/(Al+Fe)	4.24	4.47	4.32	3.84	4.43	4.14	8.68	5.86	5.23	5.04	2.56	2.25
alkali ratio*	0.50	0.74	0.58	0.80	0.77	0.62	0.94	0.26	0.31	0.30	0.60	0.51
Mineral	gl	gl	gl	gl	gl	gl	gl	cl	cl	cl	gl	gl

*Alkali ratio = (K+Na)/(K+Na+Ca+Mg), gl: glass, cl: clinoptilolite.

and Franco, 1976; Passaglia and Vezzalini, 1985) but similar to the sedimentary calcic chabazite from the John Day Formation, Oregon (Sheppard and Gude, 1970; Passaglia and Sheppard, 2001) and to chabazite from the Big Sandy Formation, Arizona (Sheppard and Gude, 1973). Chabazite of 0.78 R ratio has been observed in rhyolitic tuffs and a ratio R of 0.77 is known for chabazite from 'closed systems' (Sheppard *et al.*, 1978).

Erionite of 3.57 Si/Al, 0.78 R and 0.97 alkali ratios, DEC K, Na, SEC Mg, Ca, occurs in bundles of prismatic crystals in vesicles (Figure 4h, composition 11.23.1 in Table 5). The R ratio of this erionite is within the range of 0.79–0.68 common to sedimentary erionite but, whereas its exchange cations are K and Na, the general rule is to have K and Ca and rarely Na as exchangeable cations (Passaglia *et al.*, 1998; Passaglia and Sheppard, 2001). This erionite has the composition $K_{6.21}Na_{1.62}Ca_{0.09}Mg_{0.18}(Al_{7.83}Si_{27.99})O_{72}$, more potassic than the erionite-K, $K_4Na_2Ca(Al_8Si_{28})O_{72}$, from Rome, Oregon (Ballarino *et al.*, 2009) and distinct from the erionite-Ca and erionite-Na from the erionite series (Dogan and Dogan, 2008).

Phillipsite amygdaloidal of 3.08 Si/Al, 0.76 R and 0.95 alkali ratios, DEC Na, K, SEC Ca, an unusually high content of 0.79 Na⁺ per 8O²⁻ and almost no K⁺, (Ca+Mg)/(Na+K) 0.047, Na/(Na+K) 0.93 (Figure 4i, compositions 11.20.1 Table 5) occurs in vugs; its composition approaches that of analcime (Passaglia and Sheppard, 2001).

Heulandite thick slabs and blocky crystals of high cationic and low Si contents have 3.51 Si/Al, 0.78 R and 0.96 alkali ratios, 0.32 Na/Na+K, Na+K>Ca+Mg, DEC K, Na, SEC Ca (Figure 4d, composition 11.24.4 in Table 5). The R ratio is normal for heulandite in sediments; a ratio of 0.85 is known for mineral from rhyolitic tuffs of Canadon Hondo, Argentina (Mason and Sand, 1960); the alkali ratio ranges from 0.07 in sedimentary crystals from silicic volcanic sandstone of the Baucarit Formation, Mexico (Münch and Cochemé, 1993) to 1.0 in crystals from a burial diagenetic clay-rich horizon in a chalk

soil from Sangstrup Klint, Denmark (Nornberg, 1990). The 0.32 Na/Na+K ratio ranges from 0 in Na-free crystals to 0.94 in almost K-free crystals from Yellowstone National Park, Wyoming (Bargar and Beeson, 1981). Heulandite of Na+K>Ca+Mg ratios is known in samples from deep-sea sediments and burial diagenetic sediments (Boles and Wise, 1978; Vannucci *et al.*, 1992; Ogihara, 1994; Passaglia and Sheppard, 2001).

Anorthoclase occurs as few rare thick crystals of defective cation content (Figure 4j, composition 11.17.1 in Table 5). Crystals show a pitted surface on which mineralized strings 1600 nm long and 350–400 nm diameter of possible cemented glass bubbles that resemble microbes grew (Figure 4k, composition 11.18.1 in Table 5). Thin hexagonal crystallites of fayalite occur in Fe-rich glass (Figure 4l, composition 11.15.1 in Table 5).

The empirical formulas and the compositions of minerals are shown in Table 6 and Figure 5. Glasses and zeolites define compositional trends (Figure 5). In the Jalpa district occur glasses of 84.67–78.22 wt% SiO₂, 8.68–4.07 Si/Al and 0.89–0.80 R ratios, framework modifiers K and Ca, free of Na and Mg. Clinoptilolite free of Na crystallized from these glasses and pore fluids when the ratios were 5.86 Si/Al and 0.85 R (Figure 5a). Glasses coexist with lower-temperature glasses of 66.04–63.16 wt% SiO₂, 2.64–2.30 Si/Al and 0.70–0.72 R ratios, higher contents of Na and Ca and lower of K (Figure 5a). In the Nochixtlán area, glasses of 91.86–81.06 wt% SiO₂, free of Na, 13.89–7.27 Si/Al, 0.93–0.88 R and 0.92–0.50 alkali ratios coexist with glasses of 86.98–76.74 wt% SiO₂, 1.55–1.28 wt% Na₂O, 9.84–4.90 Si/Al, 0.91–0.83 R and 1.00–0.92 alkali ratios and with dacitic glasses of 67.63–65.01 wt% SiO₂, 7.09–3.17 wt% K₂O, free of Na, 3.20–2.43 Si/Al, 0.76–0.71 R and 0.60–0.43 alkali ratios. When the ratios were Si/Al<3.57 and R<0.78 KNa-chabazite, KNa-heulandite, NaK-erionite and KNa-phillipsite crystallized (Figure 5b). Glasses and zeolites show continuous compositional correlations: diminishing contents of SiO₂,

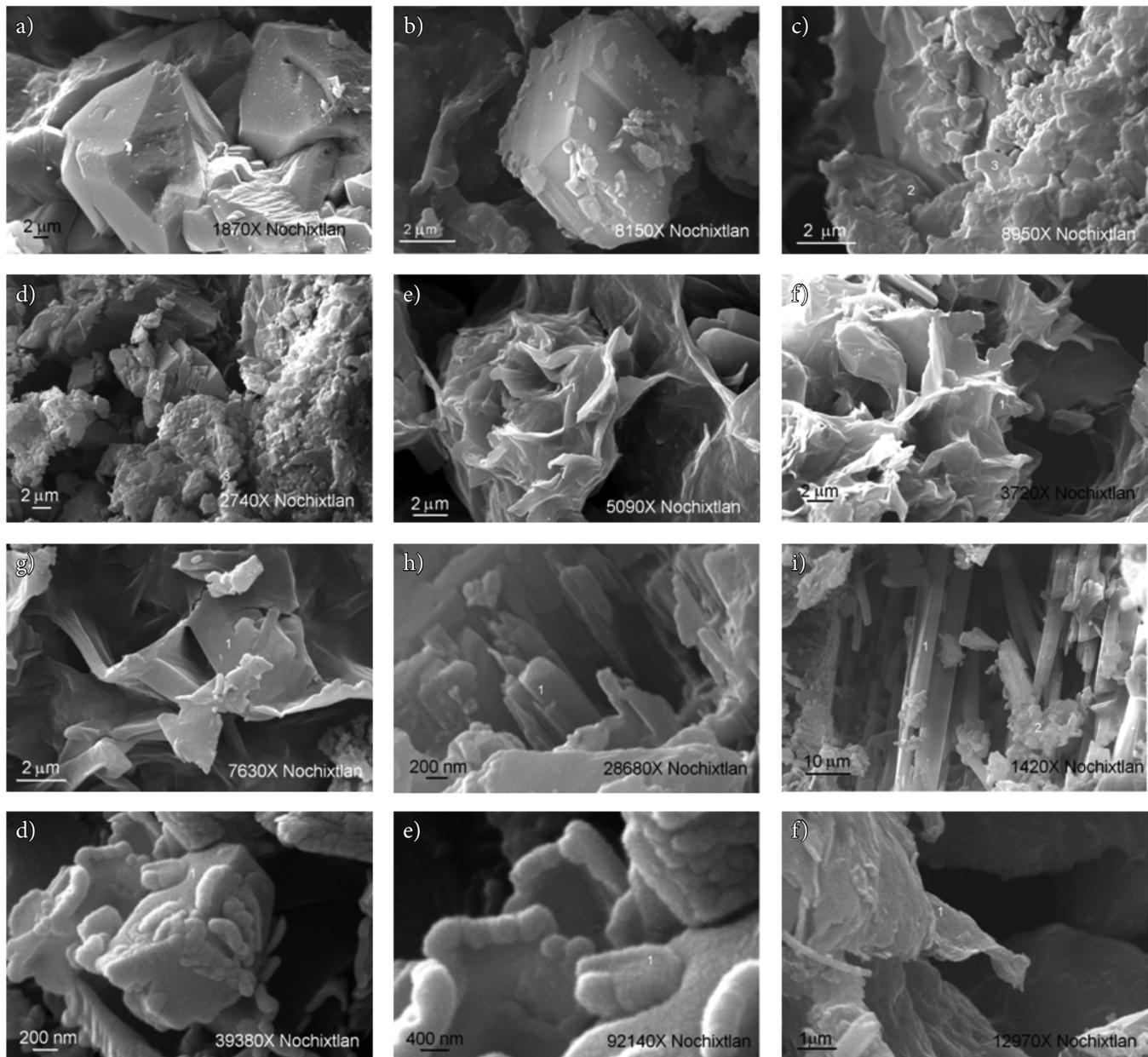


Figure 4. High resolution scanning electron microscopic images from the rhyolite tuff from Nochixtlán, sample 11: (a) quartz (1, composition 11.35.1 in Tables 4, 6); (b) 1 albite (composition 11.21.1 in Tables 4, 6); (c) glass (1, 2, 3, 4, 5, 6, compositions 11.25.1-11.25.6 in Tables 4, 6); (d) glass (1, composition 11.24.1 in Tables 4, 6), chabazite (2, 3, compositions 11.24.2, 11.24.3 in Tables 5, 6), heulandite (4, composition 11.24.4 in Tables 5, 6); (e) glass (1, composition 11.37.1 in Tables 5, 6); (f) glass (1, composition 11.34.1 in Tables 5, 6); (g) glass (1, composition 11.39.1 in Tables 5, 6); (h) erionite bundles of prismatic crystals (1, composition 11.23.1 in Tables 5, 6); (i) phillipsite (1, composition 11.20.1 in Tables 5, 6), chabazite (2, composition 11.20.2 in Tables 5, 6); (j) anorthoclase (1, composition 11.17.1 in Tables 5, 6); (k) 1 feldspatic silication (composition 11.18.1 in Tables 5, 6); (l) fayalite in glass (composition 11.15.1 in Tables 5, 6).

and of the Si/Al and R ratios correspond to increasing concentrations of Al_2O_3 , K_2O , Na_2O and CaO (Figure 5c). The correlations extend to the SiO_2 -glass spherules filled with tridymite and cristobalite-tridymite nanocrystals and the high-temperature AlFe-rich minerals kyanite, Fe-cordierite, Fe-amphibole and fayalite- and lepysheres of cristobalite-tridymite in vesicles in the glasses from Jalpa (Figure 5d) (de Pablo et al., 2013).

The distribution of the framework cation modifiers in glasses and zeolites is shown in Figure 6. In the Na-CaMg-K system the glasses from Jalpa fall on the CaMg-K axis, not far from clinoptilolite which is

more calcic and displaced towards the Ca corner of the system (Figure 6). Residual sodic glasses from Jalpa fall towards the central part of the system. The Na-free glasses from Nochixtlán are on the CaMg-K axis and those containing Na are closer to the Na-K axis; chabazite, heulandite, phillipsite and erionite move towards the central part of the system (Figure 6). When the zeolite framework is incorporated in the system $(CaMg)_{0.25}Al_{0.50}Si_{0.50}O_2-SiO_2-(NaK)_{0.50}Al_{0.50}Si_{0.50}O_2$, glasses and zeolites remain in the upper half of the system; those from Jalpa stay closer to the SiO_2 corner and those from Nochixtlán are displaced towards the central part of the system and above the 50-50 line (Figure 7).

Table 4. Composition of minerals from sample 11.

	Composition (wt%)											
	11.35.1	11.21.1	11.25.1	11.25.2	11.24.1	11.25.3	11.25.4	11.25.5	11.25.6	11.37.1	11.34.1	11.39.1
SiO ₂	100	66.39	91.86	81.06	91.58	80.34	76.74	86.98	86.31	65.01	67.63	66.87
Al ₂ O ₃	0	20.53	5.52	9.54	6.63	10.97	13.31	7.52	7.87	20.33	17.89	23.41
K ₂ O	0	1.35	1.24	8.34	1.13	6.28	7.44	3.70	4.23	3.17	7.09	3.75
CaO	0	2.95	0.31	0.06	0.25	0.06	0.39	0.10	0.15	0.97	1.66	1.27
FeO	0	0.48	0.19	0.45	0.40	0.23	0.58	0.28	0.17	7.69	3.22	1.59
Na ₂ O	0	8.30	0	0	0	1.55	1.54	1.42	1.28	0	0	0
MgO	0	0	0.87	0.55	0	0.57	0	0	0	2.83	2.51	3.13
Si	4	2.93	3.75	3.49	3.73	3.44	3.33	3.64	3.62	2.89	3.01	2.89
Al	0	1.07	0.27	0.48	0.32	0.55	0.68	0.37	0.39	1.07	0.94	1.19
K	0	0.08	0.06	0.46	0.06	0.34	0.41	0.20	0.23	0.18	0.40	0.21
Ca	0	0.14	0.01	0.00	0.01	0.00	0.02	0.00	0.01	0.05	0.08	0.06
Fe	0	0.02	0.01	0.02	0.01	0.01	0.02	0.01	0.01	0.29	0.12	0.06
Na	0	0.71	0	0	0	0.13	0.13	0.11	0.10	0	0	0
Mg	0	0	0.05	0.04	0	0.04	0	0	0	0.19	0.17	0.20
O	8	8	8	8	8	8	8	8	8	8	8	8
Si/Al	0	2.74	13.89	7.27	11.66	6.25	4.90	9.84	9.28	2.70	3.20	2.43
Si/(Si+Al)	1	0.73	0.93	0.88	0.92	0.86	0.83	0.91	0.90	0.73	0.76	0.71
Si/(Al+Fe)	1	2.69	13.39	6.98	11.30	6.14	4.76	9.58	9.05	2.12	2.84	2.31
alkali ratio*		0.85	0.50	0.92	0.86	0.92	0.96	1.00	0.97	0.43	0.61	0.45
Mineral	q	al	gl									

*Alkali ratio = (K+Na)/(K+Na+Ca+Mg), q: quartz, al: albite, gl: glass.

Table 5. Composition of minerals from sample 11.

	Composition (wt%)									
	11.24.2	11.24.3	11.24.4	11.23.1	11.20.1	11.20.2	11.17.1	11.18.1	11.15.1	
SiO ₂	68.59	70.11	69.97	60.70	69.24	68.36	69.93	68.92	21.44	
Al ₂ O ₃	20.03	19.02	16.95	16.33	19.13	19.08	18.83	19.86	7.72	
K ₂ O	4.46	6.71	9.07	11.96	1.09	5.33	5.06	7.75	3.47	
CaO	1.01	0.23	0.53	0.27	0.96	0.35	0.71	0.16	1.38	
FeO	1.86	1.53	0.54	0.39	0.27	0.86	0.51	1.32	65.99	
Na ₂ O	2.20	1.40	2.94	2.04	9.31	4.94	4.97	1.99	0	
MgO	1.84	1.00	0	0.31	0	1.08	0	0	0	
Si	3.00	3.07	3.12	3.11	3.02	3.02	3.07	3.04	1.49	
Al	1.03	0.98	0.89	0.87	0.98	0.99	0.97	1.03	0.63	
K	0.25	0.38	0.52	0.69	0.06	0.30	0.28	0.44	0.31	
Ca	0.05	0.01	0.03	0.01	0.04	0.02	0.03	0.01	0.1	
Fe	0.07	0.06	0.02	0.01	0.01	0.03	0.02	0.05	3.85	
Na	0.19	0.12	0.25	0.18	0.79	0.42	0.42	0.17	0	
Mg	0.12	0.07	0	0.02	0	0.07	0	0	0	
O	8	8	8	8	8	8	8	8	8	
Si/Al	2.91	3.13	3.51	3.57	3.08	3.05	3.16	2.95	2.37	
Si/(Si+Al)	0.74	0.76	0.78	0.78	0.76	0.75	0.76	0.75	0.70	
Si/(Al+Fe)	2.73	2.73	3.43	3.53	3.05	2.96	3.10	2.81	0.33	
alkali ratio*	0.72	0.86	0.96	0.97	0.95	0.89	0.96	0.98	0.97	
Mineral	ch	ch	he	er	ph	ch	an	fs	fa	

*Alkali ratio = (K+Na)/(K+Na+Ca+Mg), ch: chabazite, he: heulandite, er: erionite, ph: phillipsite, an: anorthoclase, fs: feldspatic, fa: fayalite.

Table 6. Empirical formulas of minerals from the rhyolitic tuffs, samples 3 and 11.

Sample 3		
3.4.1	glass	(Si _{0.847} Al _{0.150}) K _{0.020} Ca _{0.020} Fe _{0.050} O ₂
3.9.1	glass	(Si _{0.850} Al _{0.152}) K _{0.042} Ca _{0.015} Fe _{0.037} O ₂
3.9.2	glass	(Si _{0.842} Al _{0.170}) K _{0.027} Ca _{0.020} Fe _{0.025} O ₂
3.14.1	glass	(Si _{0.825} Al _{0.202}) K _{0.040} Ca _{0.010} Fe _{0.012} O ₂
3.14.2	glass	(Si _{0.842} Al _{0.182}) K _{0.042} Ca _{0.012} Fe _{0.007} O ₂
3.11.1	glass	(Si _{0.837} Al _{0.172}) K _{0.032} Ca _{0.020} Fe _{0.030} O ₂
3.37.1	glass	(Si _{0.890} Al _{0.102}) K _{0.072} Ca _{0.005} O ₂
3.32.2	clinoptilolite	(Si _{30.600} Al _{5.220}) (Ca _{1.896} K _{0.810} Mg _{0.450}) O ₇₂
3.34.1	clinoptilolite	(Si _{30.150} Al _{5.760}) (Ca _{1.800} K _{1.080} Mg _{0.540}) O ₇₂
3.35.1	clinoptilolite	(Si _{29.970} Al _{5.940}) (Ca _{1.530} K _{0.900} Na _{0.180} Mg _{0.999}) O ₇₂
3.38.1	glass	(Si _{0.720} Al _{0.275}) K _{0.012} Ca _{0.058} Fe _{0.007} Na _{0.095} O ₂
3.38.2	glass	(Si _{0.697} Al _{0.302}) K _{0.010} Ca _{0.090} Fe _{0.007} Mg _{0.005} O ₂
Sample 11		
11.35.1	quartz	SiO ₂
11.21.1	albite	(Si _{2.930} Al _{0.070}) (Al _{1.000}) (Na _{0.710} Ca _{0.140} K _{0.080} Fe _{0.020}) O ₈
11.25.1	glass	(Si _{0.937} Al _{0.067}) K _{0.015} Ca _{0.002} Fe _{0.002} Mg _{0.012} O ₂
11.25.2	glass	(Si _{0.872} Al _{0.120}) K _{0.115} Fe _{0.005} Mg _{0.001} O ₂
11.24.1	glass	(Si _{0.932} Al _{0.080}) K _{0.015} Ca _{0.002} Fe _{0.002} O ₂
11.25.3	glass	(Si _{0.860} Al _{0.137}) K _{0.085} Na _{0.032} Fe _{0.002} Mg _{0.010} O ₂
11.25.4	glass	(Si _{0.832} Al _{0.170}) K _{0.102} Na _{0.032} Ca _{0.005} Fe _{0.005} O ₂
11.25.5	glass	(Si _{0.910} Al _{0.092}) K _{0.050} Na _{0.027} Fe _{0.002} O ₂
11.37.1	glass	(Si _{0.722} Al _{0.267}) K _{0.045} Ca _{0.012} Fe _{0.072} Mg _{0.047} O ₂
11.34.1	glass	(Si _{0.752} Al _{0.235}) K _{0.100} Ca _{0.020} Fe _{0.030} Mg _{0.042} O ₂
11.39.1	glass	(Si _{0.722} Al _{0.297}) K _{0.052} Ca _{0.015} Fe _{0.015} Mg _{0.050} O ₂
11.25.6	glass	(Si _{0.905} Al _{0.097}) K _{0.057} Na _{0.025} Ca _{0.002} Fe _{0.002} O ₂
11.24.2	chabazite	(Si _{9.000} Al _{3.090}) (K _{4.750} Na _{0.570} Ca _{0.150} Fe _{0.210} Mg _{0.360}) O ₂₄
11.24.3	chabazite	(Si _{9.210} Al _{2.940}) (K _{1.140} Na _{0.360} Ca _{0.030} Fe _{0.180} Mg _{0.210}) O ₂₄
11.24.4	heulandite	(Si _{28.080} Al _{8.010}) (K _{4.680} Na _{2.250} Ca _{0.270} Fe _{0.180}) O ₇₂
11.23.1	erionite	(Si _{27.990} Al _{7.830}) (K _{2.000}) (K _{4.210} Na _{1.620} Ca _{0.090} Fe _{0.090} Mg _{0.180}) O ₇₂
11.20.1	phillipsite	(Si _{12.080} Al _{3.920}) (Na _{3.160} K _{0.240} Ca _{0.160} Fe _{0.040}) O ₃₂
11.20.2	chabazite	(Si _{9.060} Al _{2.970}) (Na _{1.260} K _{0.900} Ca _{0.060} Fe _{0.090} Mg _{0.210}) O ₂₄
11.17.1	anorthoclase	(Si _{3.070}) (Al _{0.970}) (Na _{0.420} K _{0.280} Ca _{0.030} Fe _{0.020}) O ₈
11.18.1	feldspatic	(Si _{3.040}) (Al _{1.030}) (K _{0.440} Na _{0.170} Ca _{0.010} Fe _{0.050}) O ₈
11.15.1	fayalite	(Si _{0.745} Al _{0.315}) (Fe _{1.925}) Ca _{0.050} K _{0.155} O ₄

DISCUSSION

In the Jalpa district, Provincia de la Mesa Central, occurs clinoptilolite, DEC Ca, K, free of Na, 5.86 Si/Al, 0.85 R and 0.31–0.26 alkali ratio, distinct from clinoptilolite of DEC K, Na, Ca from the Sulchiquitongo Formation, Oaxaca and from the Chichindaro Formation, Guanajuato, and of possible different degree of framework ordering and channel occupancy. In the Nochixtlán district crop heulandite, DEC Na, K and significant 0.96 alkali ratio known only from few worldwide locations and deep-sea sediments; chabazite, DEC K, Na, 0.76 R ratio, comparable to chabazite from the John Day Formation; erionite, DEC K, Na, free of Ca, a rarity compare to erionite that normally contains Ca and K and seldom Na; phillipsite, DEC Na and only minor K.

Minerals and glasses resulted from the fractionation of a precursor explosive magma into a high-temperature Fe-rich magma from which high-temperature AlFe-minerals crystallized and into an immiscible siliceous melt. The siliceous melt cooled from a high-temperature SiO₂-rich liquid, predominant in the Jalpa district, to a lower temperature more aluminous liquid common to the Nochixtlán district; upon cooling, the framework cation modifiers Na, K and Ca and the framework former Al progressively increased their concentration. (Roedder 1951; Muan 1957; Muan and Osborn 1965; Thompson et al., 2007; de Pablo et al. 2013). In Jalpa, CaK-clinoptilolite free of Na, of 80.69–78.98 wt% SiO₂, 5.86–5.04 Si/Al, 0.85–0.83 R and 0.31–0.26

alkali ratios was formed in veins and amygdules from altered glass of similar composition and from siliceous pore fluids of low alkalinity. The transformation of the Na-free glass to smectite may have raised the activity of Si and Ca in the pore fluid, eventually leading to the crystallization of clinoptilolite in a relatively high-temperature environment free of Na. Associated residual AlCaNa-glasses of low Si content did not intervene in the formation of the zeolite. In Nochixtlán, chabazite, heulandite, erionite and phillipsite, of 70.11–60.70 wt% SiO₂, 3.57–2.91 Si/Al, 0.78–0.74 R and 0.97–0.72 alkali ratios crystallized from siliceous alkaline high-pH pore fluids in an environment of comparatively lower temperature. Pore fluids removed Na, K, Al and Si from glasses of SiO₂ content higher than the zeolites and which in the present case were over 76 % SiO₂. Zeolitization implied desilication of glass and displacement of Na, K and minor Ca to the pore fluid. Zeolites crystallized from glasses altered through hydration, H₂O, H⁺ and H₃O⁺ interdiffusion and from enriched pore fluids. Once the structure of the glass was opened and the glass saturated with water, formation of gel and crystallization of zeolites was simple, with the Si free to diffuse outwards to attain equilibrium with the surrounding aqueous fluid. In Jalpa, the diagenetic alteration of the tuff was significant. In Nochixtlán, the notable enrichment of Na and crystallization of NaK-rich zeolites is attributed to reaction with alkaline saline brines in an open hydrologic system, without formation of saline minerals.

The zeolitized tuffs from Jalpa and Nochixtlán have low content of zeolites, insufficient to be of economic interest. The tuffs from Jalpa contain the health-hazardous minerals cristobalite-tridymite, tridymite, SiO₂-glass, amorphous and cryptocrystalline silica, and siliceous glasses and clinoptilolite of not well-defined health effects. The tuffs from Nochixtlán enclose erionite of known health-damaging effects and potentially damaging heulandite, chabazite and phillipsite. The high alkali content of the tuffs could preclude their application in agricultural practice and the association of quartz should result inconvenient for their use in animal feedstocks.

CONCLUSIONS

Sedimentary CaK-clinoptilolite occurs in the vicinity of Jalpa, state of Zacatecas; it crystallized from Na-free glasses and siliceous pore fluids of low alkalinity. Alkali-rich KNa-chabazite, KNa-heulandite, KNa-erionite and Na-phillipsite occur northwest of Nochixtlán, Aguascalientes; they formed from Ca-low glasses and siliceous highly alkaline pore fluids. Zeolites in Jalpa may have formed by diagenetic alteration of the tuffs while zeolitization and alkali enrichment in Nochixtlán is attributed to alkaline saline brines, in an open hydrologic system.

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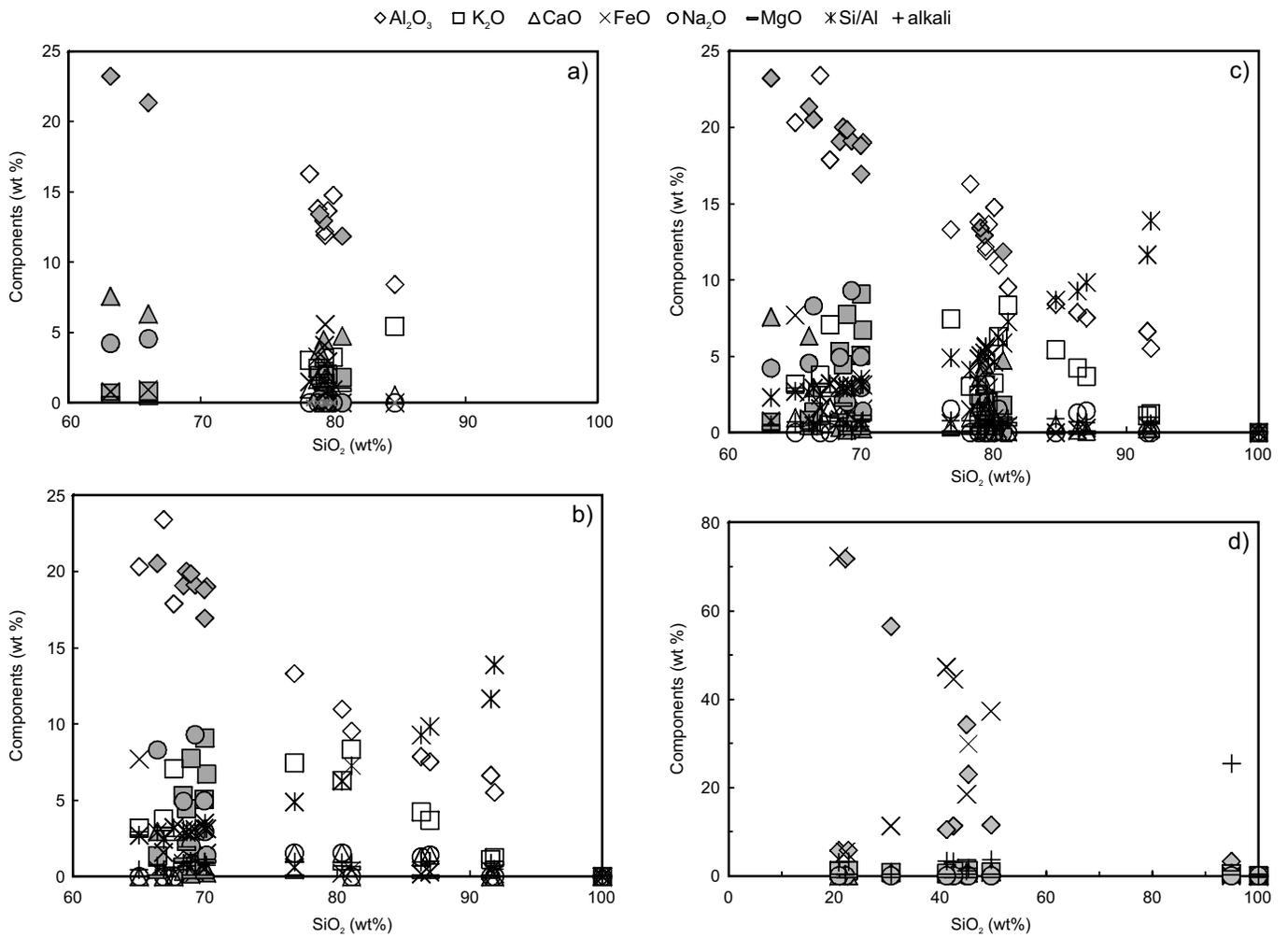


Figure 5. Chemical composition variation diagrams of minerals and glasses in tuffs from: (a) Jalpa, (b) Nochixtlán, (c) Jalpa and Nochixtlán, (d) Jalpa, FeAl-silicates in the tuff. Symbols light glasses; dark zeolites and FeAl-silicates; the ordinate axis represents components (wt%) and ratios.

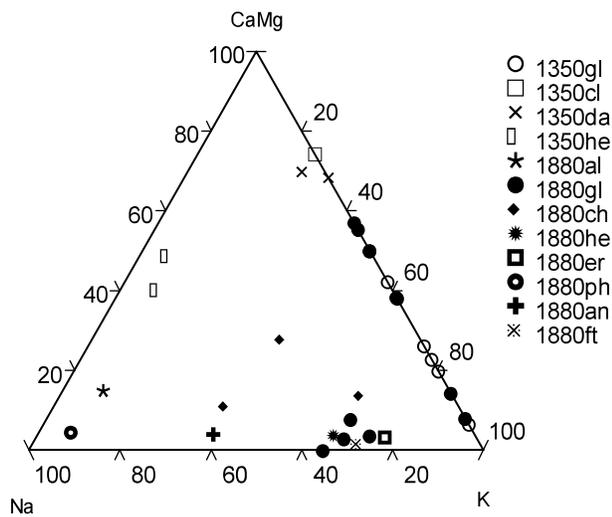


Figure 6. Cation modifiers and exchangeable in glasses and zeolites (in mol%).

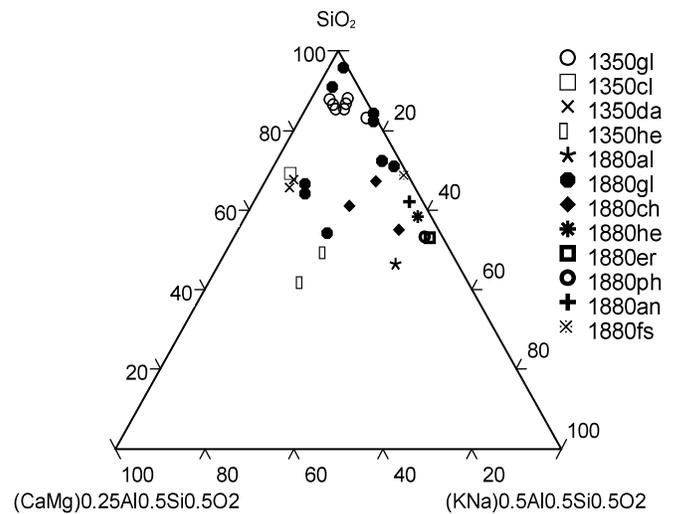


Figure 7. Composition of glasses and zeolites in the system $(\text{CaMg})_{0.25}\text{Al}_{0.5}\text{Si}_{0.5}\text{O}_2\text{-SiO}_2\text{-}(\text{KNa})_{0.5}\text{Al}_{0.5}\text{Si}_{0.5}\text{O}_2$ (in mol%).

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