Zeolitization processes in basic lavas of the Báucarit Formation, northwestern Mexico

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ABSTRACT

Basalts and basaltic andesites interbedded with sandstones in the molassic Báucarit Formation of northwestern Mexico show contrasting zeolite and clay assemblages in amygdales and in veins cross-cutting the flows. In amygdales, heulandite-clinoptilolite, chabazite, offretite/erionite and phillipsite are associated with a di-smectite clay. In veins, mesolite, analcime and stilbite are associated with minor clay, quartz and calcite. The low temperature nature of the zeolites and clays suggests that the infiltrating fluid had a temperature below 100°C and probably *ca.* 60°C. The absence of a pervasive alteration and a lack of correspondence between clay and host-rock chemistry suggest that this fluid was probably of a meteoric and fresh water character, which subsequently evolved into a more alkaline nature following interaction with glassy material in the interbedded mollassic sediments.

Key words: Mexico, Zeolite, Basin and Range, Low temperature metamorphism.

RESUMEN

Procesos de ceolitización en lavas básicas de la Formación Báucarit, noroeste de México. Los basaltos y andesitas basálticas interestratificados con areniscas en la formación molásica Báucarit del noroeste de México poseen asociaciones contrastantes de ceolitas y minerales arcillosos contenidas en amígdalas y en venas que atraviesan las coladas. En las amígdalas, heulandita-clinoptilolita, chabacita, offretita/erionita y phillipsita están asociadas con una di-esmectita. En las venas, mesolita, analcita y estilbita se asocian con cuarzo, calcita y cantidades menores de minerales arcillosos. La ausencia de una alteración pervasiva y la falta de correspondencia entre la composición química de los minerales arcillosos y la roca huésped sugieren una precipitación a partir de un fluido de origen externo. El carácter de baja temperatura de las ceolitas y minerales arcillosos sugiere que el fluido infiltrado tenía una temperatura inferior a 100°C y posiblemente cercana a 60°C. Este fluido era, probablemente, agua dulce de carácter meteórico que posteriormente evolucionó hacia una naturaleza más alcalina a consecuencia de su interacción con el material vítreo contenido en los sedimentos molásicos interestratificados.

Palabras claves: México, Ceolita, Basin and Range, Metamorfismo de baja temperatura.

Revista Geológica de Chile, Vol. 21, No. 2, p. 217-231, 12 Figs. 4 Tables, December 1994.

INTRODUCTION

The geology of the eastern region of the state of Sonora in northwestern Mexico is dominated by the mid-Tertiary Sierra Madre Occidental plateau, a K-rich rhyolitic ignimbrite plateau which developed during Oligocene times (McDowell and Clabaugh, 1979; Cameron *et al.*, 1980; Demant *et al.*, 1989). Following this major volcanic episode, early Miocene times were marked by a period of extensional tectonics which disrupted the ignimbritic sequences and produced a series of NNW-SSE trending basins and ranges (Fig. 1) (Montigny *et al.*, 1987).

The basins were infilled with coarse detrital continental molasse, composed mainly of volcanic detritus derived from the ignimbrite pile, which is now seen as a sequence of poorly bedded conglomerates and sandstones up to 400 m thick, known as the Báucarit Formation (King, 1939). At the base and intercalated with the sequence are basalts and basaltic andesites, with rarer rhyolitic tuffs present as flows and air fall horizons (Fig. 2). Age determinations on these volcanic rocks allow the age of the Báucarit Formation in eastern Sonora to be bracketed between 17 and 22 Ma (Bockoven, 1980; Pubellier, 1987; Bartolini *et al.*, 1992).

The thickest Báucarit successions are found in those basins lying to the west of the high Sierra Madre Occidental plateau, and to the east of the Sonoran Desert Province. In the latter region the Báucarit is overlapped by Recent alluvium. The Báucarit Formation is easily recognised by the fact that it forms relatively upstanding landforms. Similar molasse-filled basins occur in the southern part of Arizona, U.S.A., where the basin infill formations are known as the Nogales Formation, which is slightly younger than the Báucarit Formation at 13.5 and 13.8 Ma (Drewes, 1981).

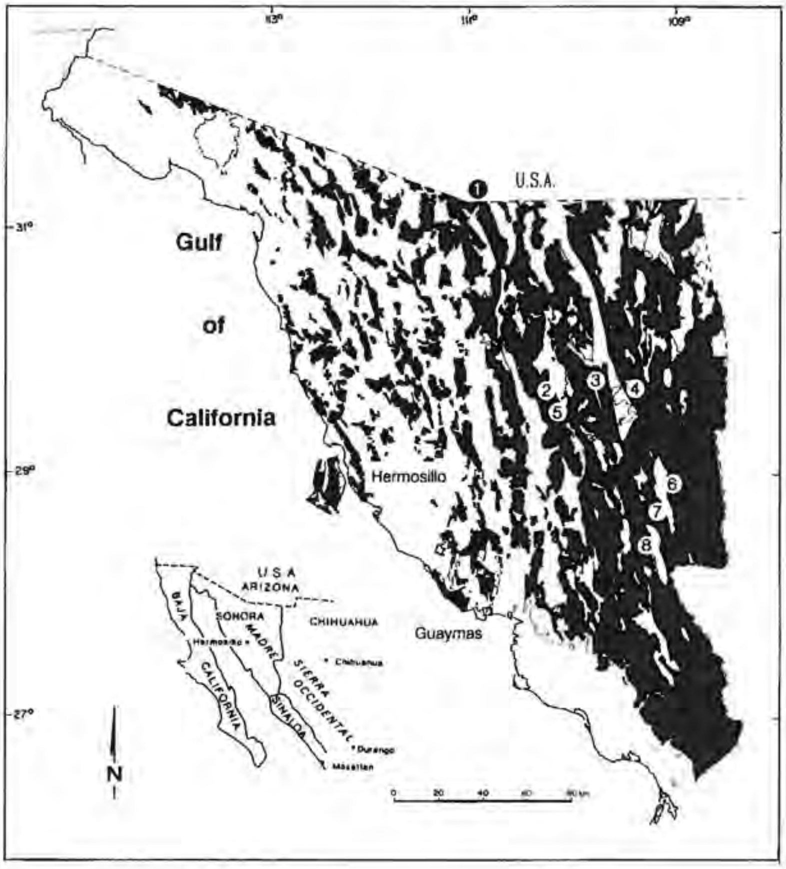

FIG.1. General location map of the Sonoran region showing the NNW-SSE trending basins (white areas) and ranges (black areas) and sample positions. Sample 1- Nogales (2378); 2- Huepac (2358); 3,4- between Mazocahui and Moctezuma (respectively 2356 and 2357); 5- La Labor (2363); 6- Sahuaripa (2364); 7- Arivechi (2365); 8- Tepoca (2367).

The conglomerates and sandstones of the Báucarit have a zeolite cement which is dominated by heulandite-clinoptilolite minerals associated with minor amounts of clay minerals and calcite (Cochemé *et al.*, 1988; Münch and Cochemé, 1993). Rhyolitic fragments within the Báucarit are also altered to zeolites. Cochemé *et al.* (1988) and Münch and Cochemé (1993) attributed the process of zeolitization to hydrothermal fluids that were related to heating developed during an extensional-related very low grade metamorphic episode. However, the effects of any such fluids and the extent of alteration in the interbedded basic lavas have not previously been assessed. In this paper the authors investigated the character of alteration in basalts and basaltic andesites interbedded with the Báucarit sedimentary rocks in order to compare the alteration mineralogy with that in the sediments. In particular, the authors drew comparisons between the zeolitic and clay minerals, and assessed the role of whole rock composition on the secondary mineralogy. In addition, the authors considered the findings of this investigation in the light of previous accounts of the origin of the zeolite and clay minerals of the Báucarit sedimentary rocks by Cochemé *et al.* (1988) and Münch and Cochemé (1993).

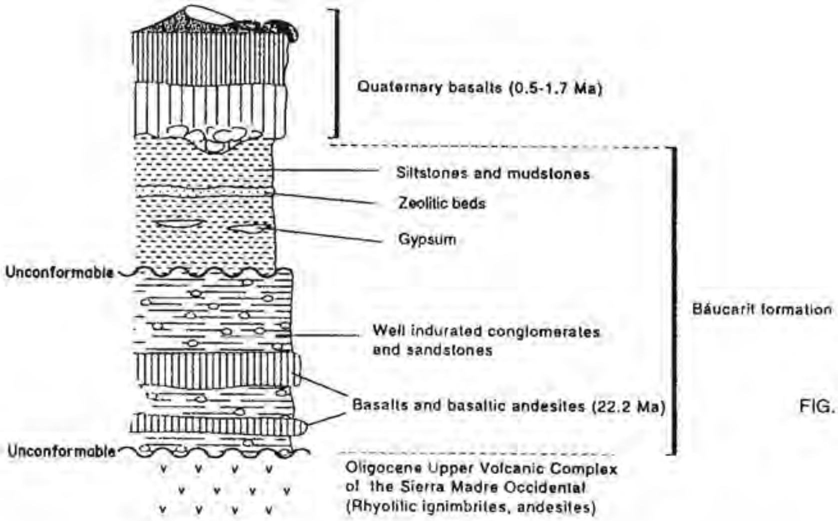

FIG. 2. Schematic section through the Báucarit Formation (Moctezuma basin; ages from Paz, 1992) showing the stratigraphic setting of the various basalts examined.

FIELD SAMPLING AND ANALYTICAL METHODS

Miocene lavas from the Báucarit Formation were sampled from seven localities in Sonora, while an equivalent lava flow was also sampled from Nogales in southern Arizona, U.S.A. (Fig. 1). Samples from east and west of Moctezuma, Huepac and Nogales are inter-Báucarit flows, while the three localities at La Labor, Arivechi and Tepoca are flows from the base of the Báucarit Formation; the stratigraphic position of the samples collected southeast of Sahuaripa is not clearly established.

Whole rock analyses were undertaken at Marseille on nonamygdaloidal facies using Atomic Absorption (AA) for MnO, Na_2O and K_2O, and ICP for other elements. Observation of the samples and analysis of minerals were undertaken using various equipment at laboratories in Bristol, Cardiff, Marseille and Montpellier: petrographic, X-ray diffraction (XRD), scanning electron microscopy (SEM) with an X-ray energy dispersive detector (EDX) and electron microprobe (EMPA). Due to the instability of zeolites under the microprobe beam only analyses with $E<10\%$ have been utilised in this discussion ($E\% = 100[Al(Na+K)-2(Ca+Mg+Sr+Ba)]/[Na+K+2(Ca+Mg+Sr+Ba)]$; Passaglia, 1970).

PRIMARY MINERALOGY AND GEOCHEMISTRY

As most lavas are amygdaloidal, the authors performed whole rock analyses only on the massive part of a flow. Non-vesicular facies were not found in the flow corresponding to the sample 2356. Major element composition for six basalts and basaltic andesites from the Báucarit Formation are presented in table 1. Chemically the flows are similar to other mid-Tertiary basic lavas widespread in Sonora, *i.e.*, akin to continental tholeiites with calc-alcaline affinity (Demant *et al.* 1989). They show a range in SiO_2 from 46-57 wt%, combined with high K_2O (1-2.6%), Al_2O_3 (16-18%), TiO_2 (0.9-2.5%) and P_2O_5 (0.4-1.2%), and low MgO (2.6-4.5%) and CaO (7.2-8.1). Total iron as Fe_2O_3 ranges between 6.7-12.7 %, but FeO total lacks any enrichment with fractionation. High H_2O content and Fe_2O_3/FeO ratio indicate secondary alteration.

The sampled flows are mostly aphyric and have intergranular to pilotaxitic textures. Plagioclase is the dominant feldspar and primary compositions (EPMA) are normally preserved, ranging from $An_{73}Or_1$ to An_{40}-Or_6 in sample 2364. Clinopyroxene, again typically unaffected by alteration, is augitic, with compositions in the range Wo_{50-35} En_{53-39} Fs_{19-2}. In contrast, olivine is usually altered, but where preserved, the primary composition is in the Fo_{70-75} range. Titanomagnetite is modally abundant.

TABLE 1. MAJOR ELEMENT COMPOSITION OF BASIC LAVAS FROM THE BÁUCARIT FORMATION.

Locality	Huepac	La Labor	Sahuaripa	Arivechi	Tepoca	Nogales
Sample	2358	2363	2364	2365	2367	2378
SiO_2	50.42	49.26	48.49	56.95	53.26	46.54
TiO_2	1.27	1.07	2.48	0.73	0.88	2.36
Al_2O_3	16.89	17.91	15.96	17.28	16.90	16.53
Fe_2O_3	6.69	7.91	9.51	4.46	6.37	10.50
FeO	1.61	0.97	1.58	1.99	2.05	1.94
MnO	0.23	0.11	0.19	0.24	0.17	0.18
MgO	3.92	4.48	3.51	2.61	4.00	4.02
CaO	7.95	7.72	7.91	7.23	8.05	8.02
Na_2O	3.54	3.43	3.70	3.56	3.29	3.15
K_2O	2.57	1.42	1.99	2.26	1.87	1.02
P_2O_5	0.68	0.37	1.16	0.41	0.50	0.57
H_2O+	2.35	2.65	1.82	2.02	1.95	2.67
H_2O-	1.07	1.92	0.82	0.75	0.87	1.87
Total	**99.19**	**99.22**	**99.12**	**100.49**	**100.16**	**99.37**

SECONDARY ALTERATION FEATURES

Field and petrographic examination of basalts and basaltic andesites from the Báucarit Formation showed that alteration assemblages have developed in three settings, namely within the body of the rock, as amygdale infillings, and as cross-cutting veins. The most noticeable effect seen, is the rimming of vesicle walls with clay minerals of various colours and the infilling of voids with zeolites and variable amounts of calcite and quartz.

WITHIN FLOW (NON-AMYGDALOIDAL DOMAIN)

Petrographic examination of the collected samples has shown that in the main the lavas have been only slightly altered. The main alteration has been the formation of various phyllosilicate minerals which account for the high hydration shown by the rock analyses (Table 1). No zeolite minerals have been found in the body of the investigated samples.

On a regional scale, olivine is typically altered to iddingsite. The high oxydation ratio and low MgO content of the rock is attributed to leaching during alteration of olivine crystals, but this process might also be related to the original cooling of the lavas. Clay present in olivine and associated with iddingsite has a chemistry similar to that of clay in the groundmass (Table 2), apart from sample 2367 in which it has a montmorillonite composition. A total non-interlayer cation (Si+Al+Fe+Mg+Mn) *versus* Al diagram (Fig. 3) shows that these clays fall very close to the ideal tri-octahedral saponite composition.

Clay minerals are not developed ubiquitously. In the plagioclases there is a patchy development of clay minerals either at the centres of crystals or forming narrow alteration zones coinciding with primary oscillatory chemical zones. The clays in the feldspars show a clear chemical relationship to the host in that they are Al-rich (>20% Al_2O_3) varieties (Table 2). The noninterlayer cation (Si+Al+Fe+Mg+Mn) *versus* Al diagram shows that these clays are di-octahedral varieties of a beidellite character (Fig 3).

Clay in the groundmass contrasts sharply in chemistry to that occurring in feldspars in being relatively Al-poor and Mg-rich (Table 2), although they are similar to those found in altered clivines and again are representative of a typical tri-octahedral saponite as shown in Fig. 3.

TABLE 2. REPRESENTATIVE ELECTRON MICROPROBE ANALYSES OF CLAY MINERALS IN DIFFERENT SITES FROM LAVAS OF THE BAUCARIT FORMATION, NORTHWESTERN MEXICO. THE ATOMIC PROPORTIONS ARE BASED ON 28 OXYGENS.

Site	plagioclase					olivine					groundmass	
Sample No.	2363-1	2367-1	2367-2	2367-3	2378-1	2364-1	2364-2	2364-3	2364-4	2364-5	2364-6	2365-1
SiO_2	50.61	47.90	49.80	48.97	53.70	52.04	52.18	52.70	53.56	53.72	52.44	51.65
TiO_2	0.00	0.00	0.01	0.09	0.62	0.01	0.00	0.00	0.00	0.02	0.01	0.00
Al_2O_3	23.86	21.40	20.92	22.45	20.95	1.63	1.70	1.80	1.80	1.68	1.73	2.59
FeO*	0.82	2.27	4.03	3.71	3.21	1.65	0.61	0.54	0.53	0.35	0.46	3.84
MnO	0.02	0.00	0.04	0.00	0.06	0.05	0.01	0.01	0.05	0.00	0.00	0.00
MgO	6.73	6.60	5.27	4.42	3.26	25.69	26.43	26.15	26.19	26.66	26.24	20.86
CaO	2.17	1.11	2.00	2.02	0.92	0.25	0.37	0.50	0.44	0.40	0.42	0.73
Na_2O	0.01	0.18	0.00	0.00	0.13	0.06	0.12	0.10	0.08	0.09	0.03	0.13
K_2O	0.19	0.76	0.65	0.65	0.46	0.13	0.07	0.07	0.09	0.05	0.09	0.15
Total	**81.71**	**80.22**	**82.72**	**82.31**	**83.31**	**81.51**	**81.49**	**81.87**	**82.74**	**82.97**	**81.42**	**79.95**
Si	9.00	9.11	9.27	9.14	9.74	9.91	9.88	9.92	9.97	9.96	9.92	10.10
Ti	0.00	0.00	0.00	0.01	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	5.02	4.80	4.59	4.94	4.48	0.37	0.38	0.40	0.39	0.37	0.39	0.60
Fe	0.12	0.36	0.63	0.58	0.49	0.26	0.10	0.09	0.08	0.05	0.07	0.63
Mn	0.00	0.00	0.01	0.00	0.01	0.01	0.00	0.00	0.01	0.00	0.00	0.00
Mg	1.79	1.87	1.46	1.23	0.88	7.29	7.46	7.34	7.27	7.37	7.40	6.08
Ca	0.42	0.23	0.40	0.40	0.18	0.05	0.08	0.10	0.09	0.08	0.09	0.15
Na	0.00	0.07	0.00	0.00	0.05	0.02	0.04	0.04	0.03	0.03	0.01	0.05
K	0.11	0.18	0.15	0.15	0.11	0.03	0.02	0.02	0.02	0.01	0.02	0.04
Mg/(Fe+Mg)	0.91	0.84	0.70	0.68	0.64	0.97	0.99	0.99	0.99	0.99	0.99	0.91
Si+Al+Fe+Mg	15.97	16.14	15.95	15.89	15.59	17.82	17.82	17.75	17.71	17.75	17.78	17.40

table 2 continued

Site	amygdales (beidellitic clays)						amygdales (saponitic clays)					
Sample No.	2367-4	2378-2	2378-3	2378-4	2378-5	2378-6	2363-3	2363-4	2363-5	2364	2364-1	3264-2
SiO_2	47.84	51.49	52.62	53.36	53.53	56.49	49.22	49.45	49.56	51.52	49.27	50.77
TiO_2	0.00	0.32	0.16	0.43	0.07	0.53	0.00	0.03	0.03			
Al_2O_3	21.05	19.80	22.68	13.21	22.06	19.38	6.45	6.41	6.32	3.39	3.44	3.64
FeO*	0.28	2.60	0.81	2.55	0.30	2.92	0.90	0.74	0.90	0.43	0.40	0.35
MnO	0.28	0.00	0.09	0.02	0.00	0.06	0.00	0.05	0.04			
MgO	9.07	3.55	3.24	7.31	3.85	3.84	22.22	23.74	22.08	21.38	21.00	21.12
CaO	1.94	1.18	0.91	1.11	1.08	1.28	0.71	1.04	0.95	1.84	1.53	1.55
Na_2O	0.00	0.00	0.07	0.96	0.13	0.04	0.00	0.02	0.00	0.05	0.05	0.06
K_2O	0.33	0.59	0.28	2.20	0.57	0.84	0.00	0.02	0.06	0.09	0.11	0.06
Total	**880.79**	**79.53**	**80.86**	**81.15**	**81.59**	**85.38**	**79.50**	**81.50**	**79.94**	**78.70**	**75.80**	**77.55**
Si	8.98	9.77	9.67	10.14	9.74	10.00	9.54	9.39	9.56	10.06	10.00	10.05
Ti	0.00	0.05	0.02	0.06	0.01	0.07	0.00	0.00	0.00	0.00	0.00	0.00
Al	4.66	4.43	4.91	2.96	4.73	4.04	1.47	1.43	1.44	0.78	0.82	0.85
Fe	0.04	0.41	0.12	0.41	0.05	0.43	0.15	0.12	0.15	0.07	0.07	0.06
Mn	0.04	0.00	0.01	0.00	0.00	0.01	0.00	0.01	0.01	0.00	0.00	0.00
Mg	2.54	1.00	0.89	2.07	1.04	1.01	6.42	6.72	6.35	6.22	6.35	6.23
Ca	0.39	0.24	0.18	0.23	0.21	0.24	0.15	0.21	0.20	0.39	0.33	0.33
Na	0.00	0.00	0.02	0.35	0.05	0.01	0.00	0.01	0.00	0.02	0.02	0.02
K	0.08	0.14	0.07	0.53	0.13	0.19	0.00	0.00	0.01	0.02	0.03	0.02
Mg/(Fe+Mg)	0.98	0.71	0.88	0.84	0.96	0.70	0.98	0.98	0.98	0.99	0.99	0.99
Si+Al+Fe+Mg	16.22	15.61	15.59	15.58	15.57	15.49	17.58	17.66	17.50	17.14	17.24	17.18

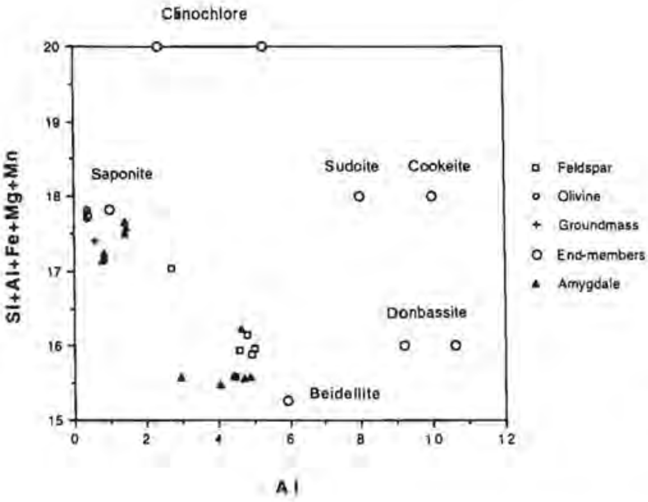

FIG. 3. Total non-interlayer cations (Si+Al+Fe+Mg+Mn) *versus* total Al diagram showing clay composition in relation to host mineral, amygdale or groundmass position.

AMYGDALE INFILL MINERALS

Vesicles in the Báucarit lavas are generally either empty or partially filled with varying amounts of clays, zeolites, calcite and quartz. The typical relationship present is that the vesicles are rimmed by a thin coat of clay which is of variable colour from blue through grey to green. This often forms a coat on which zeolites grew, clearly indicating the clays were precipitated first although there are some vesicles in which zeolites and other minerals are present in the absence of clays. Rarely clays have precipitated on the surfaces of other secondary minerals such as quartz (Fig. 4), which indicates the earlier growth of such minerals. Even more rarely, zeolites are seen protruding through a later zeolite overgrowth (see below).

CLAY MINERALS

The chemistry of vesicle clays shows two sharply contrasting types with aluminium-rich di-octahedral beidellite and trioctahedral, saponite types being present (Fig. 3). Interestingly, XRD patterns of all examined clays, whether of differing colour or chemistry, are similar and a typical pattern is shown in Fig. 5. The air-dried pattern shows a low profile with only very weak peaks except for the first strong peak at 14Å. On glycolation a much more definitive pattern is obtained, with a strong basal 001 spacing near 17Å and with a subsequent series of higher order peaks that approximate a rational series. These features are indicative of a swelling clay of a smectite character, with only a low proportion of a mixed-layer component. Measurements based on the 002 peak spacing for five samples from which clay was separated indicate that the smectite content is in excess of 80%. These XRD characters are in accord with the clay chemistry (Fig. 3), indicative of near end-member di- and tri-octahedral types.

ZEOLITE MINERALS

Various zeolites have been identified in amygdales from the lavas and representative analyses are presented in table 3.

Heulandite-clinoptilolite

Minerals belonging to the solid solution series heulandite-clinoptilolite are the most abundant zeolites found in the vesicles and are present in samples 2364, 2365, 2367 and 2378. They typically show tabular forms, flattened on 010, are up to 500 µm in length (Fig. 6), and commonly occur in aggregates on clay minerals which line the amygdales. Cochemé *et al.* (1988) reported heulandite to be the dominant zeolite cementing the sandstones of the Báucarit Formation.

Representative microprobe analyses from heulandite-clinoptilolite minerals in the basalts and basaltic andesites show a range in compositions related chiefly to variations in the contents of SiO_2, K_2O,

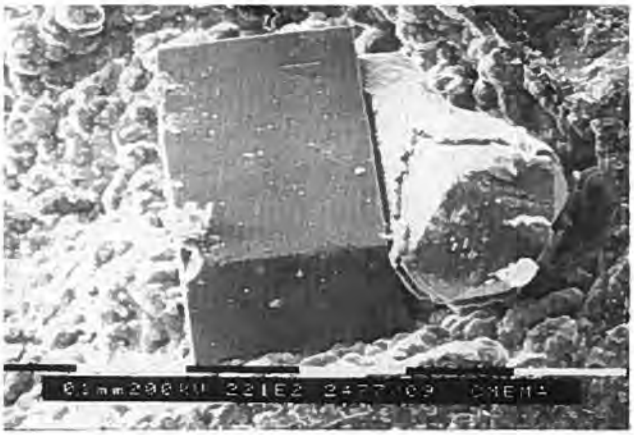

FIG. 4. SEM photomicrograph showing clay precipitate on a quartz crystal (sample 2356). The large blocky crystal is a chabazite.

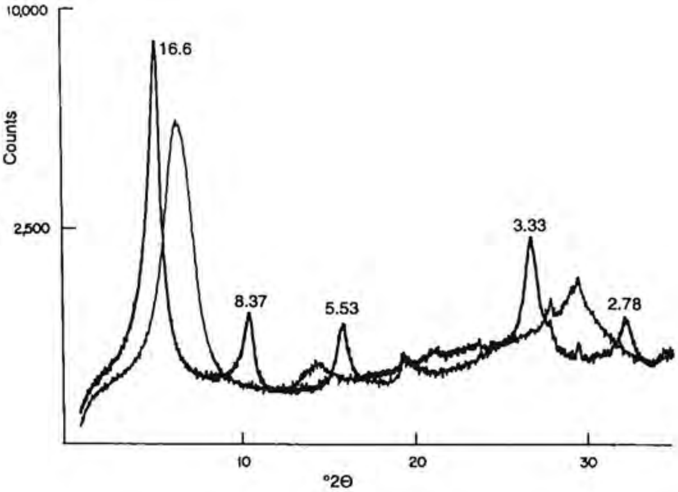

FIG. 5. XRD pattern of <2,μm clay separate from sample 2363, indicative of a swelling smectitic type. Profile in heavier pattern is for glycolated pattern and lighter pattern is for air dried sample. «d» values given for glycolated sample (Cu Kα radiation)

FIG. 6. SEM photomicrograph showing tabular form of heulandite-clinoptilolite crystals (Sample 2365).

TABLE 3. REPRESENTATIVE ELECTRON MICROPROBE ANALYSES OF ZEOLITES IN AMYGDALES FROM BASIC LAVAS OF THE BÁUCARIT FORMATION

	chabazite	erionite-offretite			heulandite			phillipsite	
Sample No.	**2356-105**	**2365-74**	**2365-73**	**2365-79**	**2364-120**	**2367-5R**	**2378-f**	**2365-76**	**2364-D**
Oxygens	**Cx =24**		**Ox =36**			**Ox =72**		**Ox =32**	
SiO_2	50.42	59.84	58.26	55.54	67.82	62.92	64.80	59.16	65.16
Al_2O_3	22.21	16.77	17.24	17.08	12.25	16.43	12.90	17.27	18.07
Fe_2O_3t	0.03	0.07	0.00	0.03	0.07	0.00	0.23	0.00	0.00
MgO	0.00	1.29	1.52	1.55	0.48	0.14	1.15	0.01	2.38
CaO	11.14	3.95	4.17	4.62	4.22	7.99	4.79	3.09	3.72
Na_2O	0.14	0.61	0.13	0.04	0.25	0.52	0.09	0.70	0.04
K_2O	1.60	4.12	3.81	3.12	2.39	0.53	1.13	9.64	3.47
Total	**85.54**	**86.65**	**85.14**	**81.98**	**87.48**	**88.53**	**85.09**	**89.86**	**92.84**
Si	7.90	13.57	13.42	13.28	29.71	27.54	29.10	11.91	12.12
Al	4.10	4.48	4.68	4.81	6.32	8.47	6.83	4.10	3.96
Fe	0.00	0.01	0.00	0.01	0.02	0.00	0.08	0.00	0.00
Mg	0.00	0.44	0.52	0.55	0.31	0.09	0.77	0.00	0.66
Ca	1.87	0.96	1.03	1.18	1.98	3.75	2.30	0.67	0.74
Na	0.04	0.27	0.06	0.02	0.21	0.44	0.08	0.27	0.01
K	0.32	1.19	1.12	0.95	1.34	0.30	0.65	2.47	0.82
Total	14.23	20.92	20.83	20.80	39.90	40.59	39.81	19.42	18.32
Si/Al	1.93	3.03	2.87	2.76	4.70	3.25	4.26	2.91	3.06
E%	0.03	5.68	9.31	8.50	3.41	0 72	0.44	0.26	8.81

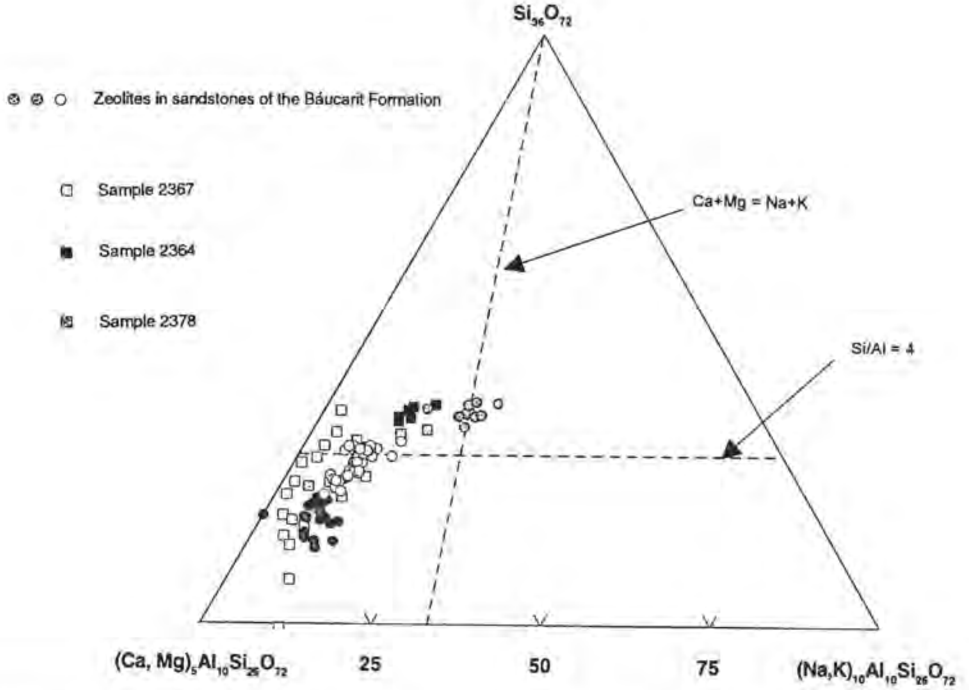

FIG. 7. Mole plot of heulandites and clinoptilolites in upper part of the triangle $Si_{36}O_{72}$ - (Ca,Mg$_{18}$ Al$_{36}$O$_{72}$ - (Na,K)$_{36}$Al$_{36}$O$_{72}$ (after Alietti *et al.*, 1977) to show comparison in chemistry of heulandite-clinoptilolite minerals from basic rocks and sandstones of the Báucarit Formation.

CaO and MgO (Table 3), as illustrated in figure 7, which also shows the field of heulandite-clinoptilolite minerals from sandstones of the Báucarit Formation. Mumpton (1960) used the thermal property of heulandite group minerals to distinguish between heulandite and clinoptilolite. However, the small size of the crystals in the vesicles negated their separation and hence the use of the Mumpton (1960) classification. Instead, the authors followed the method of Boles (1972) to distinguish heulandite and clinoptilolite, with the latter having a Si/Al ratio of >4, and heulandite <4. Both heulandite and clinoptilolite occur in amygdales of the lavas, as indeed do both occur in the Báucarit sandstones. Clinoptilolite is present in sample 2364 from Sahuaripa, with Si/Al ratios in the range 4.4-4.7. In comparison with analyses presented by Gottardi and Galli (1985), they are relatively rich in CaO (as indeed are such minerals from the Báucarit sandstones; Münch and Cochemé, 1993) and relatively poor in K_2O. Analyses from Tepoca (sample 2367) plot, with few exceptions, in the heulandite field and are characterized by very low contents of total alkalies compared with the representative analyses of Gottardi and Galli (1985). In particular, they have negligible amounts of Na_2O, although they are similar to heulandite analyses given by Viereck *et al.* (1982) from Icelandic basalts. Heulandite analyses from Nogales (sample 2378) show higher concentrations of K_2O than those from Tepoca, as well as markedly higher MgO, but lower CaO. Particularly, the compositions from sample 2378 show a virtual overlap with heulandites from the Báucarit sandstones. The differences in chemistry, and in particular, the content of SiO_2, in the various zeolites in the Báucarit do not show a correlation with the whole rock compositions (Tables 1 and 3).

Chabazite

Chabazite is found in samples from the Moctezuma area (2356, and 2357) and Sahuaripa (2364). It occurs as well formed rhombohedral crystals (resembling cubes, Fig. 8) up to 1 mm across, typically on clay which lines the amygdales. There is little compositional variation in the chabazite analyses (Table 3) and they are characterized by high CaO and low total alkalis, particularly negligible contents of Na_2O, in comparison to analyses presented by Gottardi and Galli (1985) with the exception of a single analysis (from Val di Fassa, Italy).

Offretite/erionite

Hexagonal, striated prismatic crystals, terminated by a basal pinacoid face, and up to 50 µm long and 5 µm across were found in two samples, namely 2365 (Arivechi) and 2364 (Sahuaripa). These forms are similar to those of both erionite and offretite. They occur in association with clay minerals, in places resting on a coat of clay minerals, in other cases protruding through the coat (Fig. 9). Two microprobe analyses (Table 3) of these prisms are more similar to offretite than erionite, in having markedly low Na_2O contents (0.04-0.13 wt %), and high CaO (4.17-4.62 wt%). A third analysis (Table 3), however, has a composition closer to that of erionite. This is demonstrated by following the chemical scheme suggested by Wise and Tschernich (1976) to distinguish between these two zeolites. Offretite has Ca+Mg > K+Na and *vice versa* in erionite. If this is correct, then it appears that both phases are present, and intergrowths of the two minerals are, in fact, quite common (Gottardi and Galli, 1985). In addition, in sample 2364 erionite with a fibrous form is present, illustrated in figure 10.

Phillipsite

K-rich zeolites have been identified in two samples, 2365 (Arivechi) and 2364 (Sahuaripa). In sample 2364 the mineral forms radiating aggregates up to 4 mm across which lie on clay minerals which line the amygdales (Fig. 11). The rosettes have a hollow centre. In sample 2365 the mineral occurs as framboidal crystal aggregates. Representative analyses are given in table 3 which show slight compositional differences between the phases in the two samples. In sample 2364, two of the analyses are relatively low in K_2O, and have compositions which recalculate to the formula $K_{0.8-1.3}$ $(Ca_{0.7-1.3}$ $Mg_{0-1.3})$ $(Al_4$ $Si_{12}O_{32}).xH_2O$, which is broadly similar to the compositions of some phillipsite analyses listed by Tschernich (1992). However, the majority of the analyses recalculate to a formula K_2 $Na_{0.1}$ $Ca_{0.7-0.9}$ $(Al_4$ $Si_{12}O_{32}).xH_2O$, which are characterised by K_2O contents in excess of those usually found in phillipsite. X-ray diffraction patterns of both of these phases give patterns for phillipsite, despite the high K_2O contents in the second group. Table 4 lists the powder diffraction data for these high-K phillipsites. Interestingly, these appear to be some of the highest K_2O contents for phillipsite which have yet been published.

FIG. 8. SEM photomicrograph showing well-formed rhombohedral chabazite crystals (sample 2364).

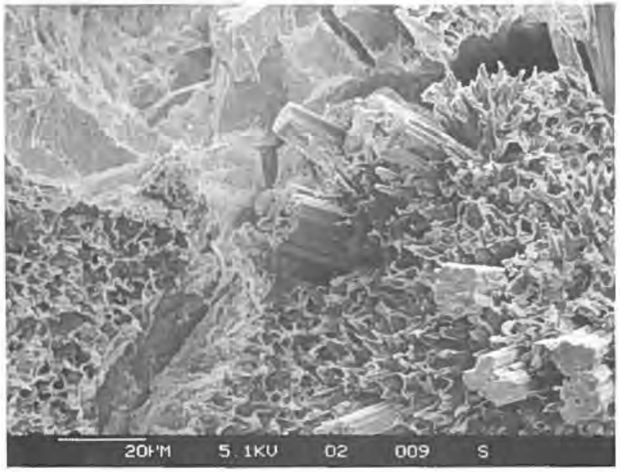

FIG. 9. SEM photomicrograph offretite/erionite prismatic-needle crystals growing on, and through a thin clay rim to a vesicle (sample 2364).

FIG. 10. SEM photomicrograph showing fibrous erionite associated with chabazite and growing through clay (sample 2364).

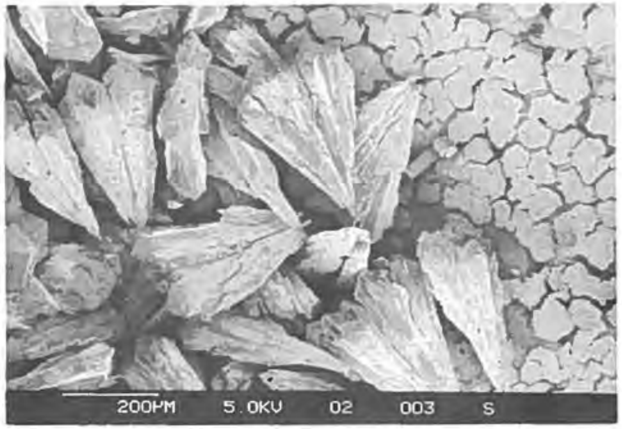

FIG. 11. SEM photomicrograph showing rosettes of K-rich phillipsite growing on a clay rim to vesicle (sample 2364).

VEIN MINERALS

Vein infillings cutting the basalt lavas were sampled at two localities, namely La Labor (2363) and Tepoca (2367). Both occurrences are from the basal parts of the Báucarit Formation. Generally, the veins are no wider than *ca.* 5 cm, and commonly bifurcate or form anastomosing systems. Country rocks adjacent to the veins are typically altered, a feature readily observable in the field. In contrast to the amygdale infill zeolites, however, those in the veins are coarsely crystalline, with individual crystals commonly measurable on the centimetre scale. As detailed below, the mineralogy of the veins is different to that seen in the amygdales, with mesolite, analcime and stilbite present along with minor clay, quartz and calcite.

Mesolite

Mesolite occurs in samples 2363 and 2367 as divergent aggregates of needle-like crystals up to 9 mm long with acicular habit, associated with and occurring on analcime. Identification was confirmed by XRD with Si, Al and Ca as major components and Na, Mg, K and Fe as minor components detected by EDX analysis.

Analcime

Analcime forms distinctive euhedral trapezohedra up to 3 mm across, associated with and forming a base to mesolite in samples 2363 and 2367. Identification was by XRD, supported by EDX analysis showing the presence of only Na, Al and Si in the spectrum.

Stilbite

Stilbite was identified in sample 2367 forming single euhedral crystals or radiating aggregates of crystals up to 10 mm in length. The crystals are pseudo-orthorhombic and tabular in shape, being flattened on [010]. Identification was confirmed by XRD analysis.

TABLE 4. XRD PATTERN OF HAND-PICKED K-RICH PHILLIPSITE MINERAL FROM AMYGDALES IN SAMPLES 2364 AND 2365; XRD PATTERN LISTED IN COLUMNS 1 AND 2 IS THAT GIVEN FOR PHILLIPSITE ($K_{0.8}Na_{0.7}Ca_{0.7}Fe_{0.08}F\,Al_{2.8}O_{16.39}H_2O$) by Harada *et al.* (1967). Card No. 20-923 ASTM index.

ASTM 20-923		Sample No. 2364		Sample No. 2365	
d (Å)	Rel. int. %	d (Å)	Rel. int. %	d (Å)	Rel. int. %
		9.41	2		
8.19	6	8.18	3		
7.19	100	7.13	100	7.18	100
6.41	12	6.41	3	6.42	14
5.37	10	5.39	6	5.38	3
5.06	25	5.06	7		
4.98	18	4.98	5		
4.69	4				
4.31	10	4.33	30		
4.13	40	4.12	12	4.13	13
4.07	14			3.91	4
3.96	6	3.96	4	3.68	9
3.70	4	3.68	2		
3.54	6	3.56	4		
3.47	6	3.47	2		
3.26	30	3.26	9		
3.19	85	3.19	58	3.19	56
3.14	35	3.16	6		
2.93	14	2.95	4		
2.89	6				
2.86	4				
2.75	20	2.75	12	2.73	5
2.70	35	2.69	7		
2.67	10			2.68	4
2.58	6	2.57	5	2.56	5
				1.77	4
				1.72	
				1.60	5
				1.54	
				1.45	

ALTERATION PROCESS

The alteration process affecting basalts of the Báucarit Formation has been such, that the products are concentrated in the amygdales and in cross-cutting veins. Generally, in the main body of the lavas the primary igneous minerals, with the exception of olivine, are unaffected by the process, suggesting that the fluid did not pass pervasively through the flows.

There is a contrast between the assemblages present as amygdale infillings and as vein infills. The amygdales have assemblages dominated by relatively K- and Ca-rich zeolites, in particular heulandite/clinoptilolite, along with variable amounts of clay, quartz and calcite. The vein assemblages, in contrast, are dominated by relatively Na- and Ca-rich zeolites, including mesolite and analcime, which are not found in the amygdales. In addition, quartz and clay minerals are of only minor abundance in the vein assemblages. This suggests that the varying assemblages formed under different conditions.

Zeolite mineral assemblages in both the amygdale and vein assemblages are dominated by varieties indicative of formation at very low temperatures. For example, in hydrothermal systems in Iceland, chabazite, erionite/offretite, mesolite and phillipsite are stable at temperatures below 100°C (Kristmannsdóttir and Tómasson, 1978). While heulandite, stilbite and analcime may also form at temperatures below 100°C, they can also be precipitated from fluids at temperatures greater than 100°C. In the Báucarit basalts there are no zeolites such as laumontite, which typically replace other zeolites at temperatures greater than *ca.* 100°C. Accordingly, the authors believe that the zeolites all formed at temperatures below 100°C. The low temperature character of the assemblages is also indicated by the clay mineral types present in the basalts and their compositions. XRD analyses show that the clay minerals are of a smectitic character, being di- and trioctahedral varieties with <20% of mixed-layer chlorite content. Such minerals are also typical of low temperature conditions; in geothermal systems in Iceland, for example, Kristmannsdóttir (1979) and Schiffman and Fridleifsson (1991) recognised smectitic varieties of clay at temperatures from <60 °C to a maximum of 200°C. Analyses of the clays in the Báucarit lavas show a range in MgO/(MgO+FeO) ratios. Those clays lining vesicles typically have MgO/(MgO+FeO) ratios >0.70, showing no relationship to the whole rock ratios, which are <0.50 (Fig. 12). In contrast, those in plagioclase show markedly lower MgO/(MgO+FeO) ratios, but again show no correlation with whole rock ratios (Fig. 12). These features are taken as indicating a lack of equilibration between clay mineral and whole rock compositions, a feature which is typical of mafic phyllosilicates at very low (diagenetic) grades of metamorphism. At higher grades, such as in the prehnite-pumpellyite facies, there is a strong linear relationship between whole rock and chlorite MgO/(MgO+FeO) ratios (Fig. 12; Bevins *et al.*, 1991; Robinson *et al.*, 1993).

The features outlined above suggest that, the infiltrating fluid and the components for crystallization of the zeolite assemblages are being derived largely from a source external to the basalts. As discussed earlier, many of the zeolites reported from the Báucarit lavas have also been recorded in basalts affected by hydrothermal alteration associated with geothermal systems such as in Iceland. In the Báucarit sequences, however, the alteration is developed across the whole north-west Sonoran region within disparate and isolated basins. Most geothermal systems, in contrast, tend to be of more localized extent geographically. Moreover, in that case, geothermal fluids become evolved during ascent, leading in some cases to low pH waters which often give rise to kaolinite or alunite in pervasively altered rocks, or alternatively the fluid may become silica saturated and lead to local silicification. Neither of these types of alteration are

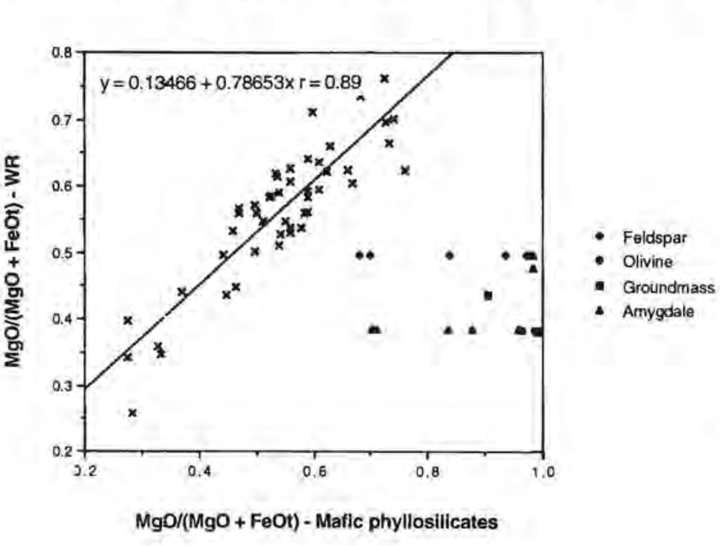

FIG.12. Plot of MgO/(MgO+FeOt) ratios in whole rock compared to that of mafic phyllosilicates. Greenland and Welsh samples (crosses) are taken from Bevins *et al.* (1991) and Robinson *et al.* (1993).

seen anywhere in the area studied. Rather, the alteration style is monotonous over a very large area (in excess of 100,000 km^2).

The assemblages seen in the Báucarit basalts do, however, show a very strong resemblance to zeolite/clay assemblages normally associated with the low-temperature alteration of thick non-marine sequences of silicic tuffaceous volcanics. Sheppard and Gude (1973) described the presence of analcime, clinoptilolite, erionite and chabazite with less abundant phillipsite and mordenite arising from the low temperature alteration of silicic, vitric tuffs interbedded in the lacustrine Big Sandy Formation of Pliocene age in Arizona. From textural evidence the main generation of the zeolites was attributed to a solution-precipitation process as the volcanic glass reacted with the interstitial pore water. However, no zonation of the type commonly seen in saline lake deposits (Hay, 1978) has been observed in either the Báucarit lavas or the Báucarit sandstones.

Several examples of similar zeolite assemblages have been attributed to a process involving the circulation of low temperature meteoric fluid in an open hydrologic system, associated with interaction with silicic glass. For example, Walton (1975) reported abundant clinoptilolite and analcime in the Veja Group (Oligocene) of Texas, while Barrows (1980) described heulandite, clinoptilolite, mordenite, analcime, thomsonite(?), erionite and chabazite(?) in thick Miocene volcaniclastic sequences in the southern Desatoya Mountains, Nevada. In both cases, alteration was attributed to the breakdown of unstable silicic glass .

The basalts studied here are interbedded with clastic rocks of the Báucarit Formation which consist of abundant ignimbritic debris, while the Miocene bed rock to the Báucarit basins is K-rich ignimbrites of the Sierra Madre Occidental. Cochemé *et al.* (1988) reported that the ignimbritic (silicic lithic) fragments in the Báucarit Formation are altered to heulandite/clinoptilolite, whereas those of the Sierra Madre outcrop are unaffected. In these circumstances, it appears that the origin of the zeolites described here, can be largely related to externally-derived fluids whose chemical character was a function of the degree of interaction with silicic volcanics within the basin successions.

Besides temperature, however, the distribution of clay/zeolite assemblages is also highly controlled by additional parameters including the composition, salinity and alkalinity of the fluid phase from which the minerals precipitated. Precipitation of clay minerals is favoured by a hydrous fluid with a fresh-water character (near neutral pH) whereas the heulandite/clinoptilolite series would be favoured more by water with high salinity and alkalinity (Hay, 1978). The presence of high silica minerals belonging to the heulandite/clinoptilolite series and the tetrasilicic nature of the phyllosilicates suggest that the fluid had a high $a\text{SiO}_2$ high Si/(Al+Fe^{3+}) (Garrells and Christ, 1965; Hess, 1966), high alkali ion to hydrogen ion activity, and high log[$a\text{Ca}^{2+}/(a\text{H}^+)$] (Bowers and Burns 1990). This fluid most probably relates to alteration of alkali-rich siliceous volcanic shards and lithics which released abundant alkalies into solution. This would lead to a high $a\text{SiO}_2$ and also a high $a\text{CaO}$ giving rise to precipitation of relatively high-Si and high-Ca zeolites.

In contrast, the presence of mesolite, analcime and stilbite in the veins, phases which are not found in the amygdales of the lavas, and the general absence of clays, suggest a fluid of contrasting composition to that related to the amygdale infilling. In particular, it indicates a fluid of greater salinity, alkalinity and lower $a\text{SiO}_2$, and increased log[$a\text{Na}/a\text{H}^+$] (Bowers and Burns, 1990) for generation of the vein assemblages. Both parageneses would also appear to have precipitated from fluids with a low content of CO_2 indicated, in particular, by the scarcity of calcite.

The changes in the fluid composition suggest an evolution in the chemical character of the invading fluid. Initially, the fluid that was associated with clay deposition would have been of low salinity and alkalinity. Precipitation of heulandite/clinoptilolite on this clay indicates a trend to increasing salinity and alkalinity, with high Ca and Si activity Finally, the vein deposition was associated with fluids having an even higher salinity and alkalinity, and increasing Na activity, but with decreasing Si activity.

The sequential nature of the parageneses suggests that they are more of a time-dependent than distance-dependent origin. Accordingly, therefore, we envisage a model of infiltration by a fluid initially of a fresh-water character which then evolved through interaction with basalts and crystallization of clays but also to an increase in the extent of alteration of silicic glass shards, resulting in an increase in the Na+K to H ratio, to a situation more conducive to zeolite crystallization (Sheppard and Gude, 1973). The final fluid, again perhaps depleted in Si and Ca as a result of precipitation of the heulandite/clinoptilolite minerals in particular, then evolved into a more alkali-rich fluid with lower silica activity that was expelled through fracture zones resulting in the observed vein mineral assemblage.

CONCLUSIONS

Zeolite and clay mineral assemblages in basic lavas of the Báucarit Formation imply very low temperature alteration, most probably below 100°C. The regional character, and the lack of any obvious zonation of assemblages, rule out geothermal-type alteration and saline-lake precipitates, respectively. The assemblages present are consistent with circulation of meteoric water in an open hydrologic system. Initially the fluids were of low alkalinity (near neutral pH) and had low salinity. These fluids reacted with the sandstones and basalts leaching, in particular Mg, resulting in the precipitation of the smectitic clays. Alteration of abundant shardic and lithic (glassy) fragments in the Báucarit sandstones led to an increase in the alkalinity of the original near-neutral pH fluids . This led to increased $a\mathrm{SiO_2}$ and $a\mathrm{CaO}$, and to precipitation of the zeolite minerals. Crystallization of the zeolites led to chemical evolution of the fluid towards lower $a\mathrm{SiO_2}$, but even higher pH; from these fluids, the various vein zeolite minerals precipitated.

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