

DIAGENETIC ALTERATION OF PERLITE IN THE GURYONGPO AREA, REPUBLIC OF KOREA

JIN HWAN NOH¹ AND JAMES R. BOLES²

¹ Department of Geology, Kangweon National University, Chuncheon 200, South Korea

² Department of Geological Sciences, University of California, Santa Barbara, California 93106

Abstract—Perlite, which occurs at the contacts between dacite and lacustrine tuffs of Miocene age in the Guryongpo area, Korea, has undergone more sluggish and incomplete diagenetic alteration than the surrounding zeolitic tuffs. Alkali-clinoptilolite, mordenite, smectite, K-rich gel-like glass, low-cristobalite, and K-feldspar are characteristic diagenetic phases in the altered perlite.

Hydration of the glass to form perlite resulted in the expulsion of cations, mainly Na, from the glass into the pore fluid and in the relative enrichment of K in the perlite. Hydration of the glass also resulted in increased alkalinity of the pore fluid, which, in turn, affected the nature and behavior of subsequent glass dissolution. Textural observations and chemical data on the early diagenetic phases indicate a sequence of incongruent dissolution reactions, which depended on silica activity and alkalinity of the ambient pore fluid: Reaction (1) 12.5 perlitic glass + 3.88 K⁺ + 0.65 H⁺ + 15.4 H₂O = smectite + 9.5 gel-like glass + 4.03 Na⁺ + 0.25 Ca²⁺ + 10.55 H₄SiO₄ released Ca and silica which were consumed by reaction (2) perlitic glass + 0.1 Ca²⁺ + 0.1 H₄SiO₄ + 0.1 H⁺ + H₂O = clinoptilolite + 0.1 K⁺ + 0.2 Na⁺. The paragenesis from glass via smectite to alkali zeolites in most glass-bearing rocks may be explained by a sequence of such dissolution reactions. Still later reactions involved the transition from less-silicic clinoptilolite to an assemblage of silicic Na-clinoptilolite + mordenite and the crystallization of the gel-like glass to K-feldspar.

Key Words—Clinoptilolite, Diagenesis, Dissolution, Glass, Mordenite, Perlite, Smectite, Zeolite.

INTRODUCTION

Zeolites and associated secondary minerals delineate the mineralogical and chemical evolution of tuffaceous rocks undergoing diagenesis and low-grade burial metamorphism. Transitions of less stable zeolites (phillipsite, clinoptilolite, and heulandite) to more stable phases (mordenite, analcime, laumontite, and K-feldspar) have been well documented in various geologic environments (Coombs, 1954; Sheppard and Gude, 1968; Iijima and Utada, 1972; Boles and Coombs, 1975; Hay, 1977; Surdam and Sheppard, 1978).

Smectite is one of the most common authigenic minerals associated with zeolites in altered tuffaceous rocks. Incipient smectite formation prior to zeolitization is commonplace in most altered glass-bearing rocks (Hay, 1963; Sheppard and Gude, 1973; Dibble and Tiller, 1981). Yet, it is still not clear: (1) why the smectite generally preceded the zeolite, (2) how the Mg required for the formation of smectite was generated, and (3) whether or not the earlier-formed smectite was consumed in the subsequent zeolite formation.

Perlite, a hydrous glassy rock, occurs in lacustrine zeolitic tuffs in the Guryongpo area of the Republic of Korea (Figure 1). The perlite is partly altered to smectite and zeolites, but the rate of alteration appears to have been more sluggish, compared with surrounding zeolitic tuffs, due to its low permeability. Therefore, careful observations of the authigenic mineralization in the altered perlite should be helpful in understanding

the details of the alteration process. The present study deals with the occurrence and petrologic characterization of the perlite and the subsequent alteration process. The chief objective of this study was to delineate the interrelationship between hydration and dissolution of natural glass and the formation of authigenic minerals in the altered perlite.

METHODS OF STUDY

Samples were collected from quarry faces of the Nuldaeri Perlite Mine on the basis of their mode of occurrence and the degree of alteration. The samples consisted of fresh perlite, altered perlite, dacite, and zeolitic tuff. Samples of fresh perlite and adjacent altered perlite were specifically selected to determine chemical and mineralogical differences.

Petrographic identification of perlite and its alteration products was made by polarizing microscopy and scanning electron microscopy (SEM), combined with X-ray powder diffraction (XRD) analysis of bulk samples. The chemical composition of perlite and its zeolitic counterpart was determined by wet methods for major elements and by atomic absorption spectroscopy for minor elements. The water content was separately determined by a thermogravimetric method.

Zeolites and other authigenic minerals were chemically analyzed by an ARL model EXM-SM electron microprobe using 20-s counting intervals, a 15-kV accelerating voltage, and a 7.5-nA sample current. Three WDS spectrometers were used for the analyses of Mg,

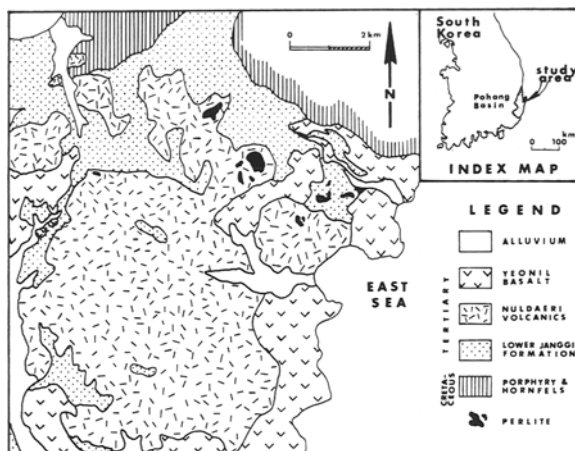


Figure 1. Geologic and index maps of the Guryongpo area, Republic of Korea.

Na, and Sr. The results of the zeolite analyses were checked and screened on the basis of the crystal chemical criteria of zeolites, such as water content by difference, framework composition, and degree of charge balance. Analyses having a balance error (E) of >10% were discarded following the suggestion of Gottardi and Galli (1985). A wide electron beam (100- μ m diameter) was used for the bulk microprobe analyses of the glassy components in the fresh and altered perlite following the method of Jezek and Noble (1978).

GENERAL GEOLOGY

The Guryongpo district, located in the northeastern margin of the Pohang basin, is the largest Tertiary sedimentary sub-basin in Korea (Figure 1). Sediments in the area were deposited in a Miocene lacustrine environment (Huzioka, 1972; Kim *et al.*, 1975; Bong, 1981) and rest nonconformably on porphyry and hornfels of Cretaceous age.

The Miocene sedimentary sequence, called the Lower Janggi Formation, consists of various pyroclastic units such as volcanic conglomerate, tuff, and tuffaceous sandstone. These pyroclastics were deposited in a lacustrine environment as a result of a subaqueous eruption of acidic to intermediate magma during or prior to the emplacement of the Nuldaeri Volcanics (Noh and Kim, 1986; Lee *et al.*, 1986). Most of the tuffaceous deposits are wholly or partly transformed to zeolitic rocks as a result of diagenetic alteration (Noh, 1985). The Nuldaeri Volcanics, which belongs to the calc-alkali rock series (Lee *et al.*, 1986), consists of early Miocene dacite with some trachyte and rhyolite.

OCCURRENCE AND PETROGRAPHY OF PERLITE

The most striking field characteristic in the mode of occurrence of the perlite is its presence in both volcanic

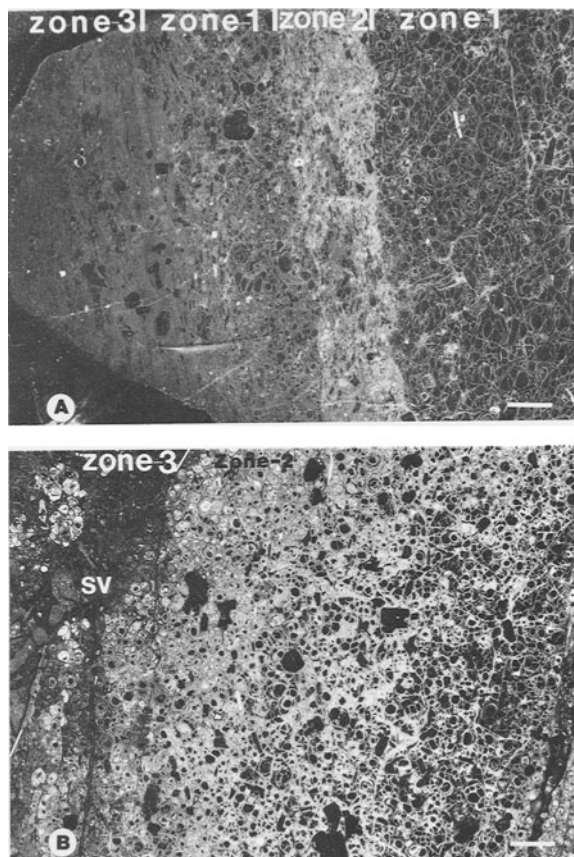


Figure 2. Negative thin section view of partially altered perlite showing characteristic alteration modes. A. Typical alteration zoning of fresh perlite (zone 1), slightly altered perlite (zone 2), and severely altered perlite (zone 3). Note characteristic rounded perlitic cracks and fresh perlitic glass in zone 1 (dark) at right. Original perlitic fabric is mostly obliterated in greenish zeolitic part (zone 3). Numerous plagioclase phenocrysts (black) and some biotite (white, elongated) and iron oxide (white, rectangular) phenocrysts are not altered. Scale bar is 0.3 cm. B. Diagenetic alteration mode in zones 2 and 3. Note that alteration is apparently controlled by original perlitic cracks. Modified perlitic fabric is well preserved in zone 2. Some segregation veinlets (sv) in zone 3 contain low-cristobalite, mordenite, and Na-clinoptilolite. Scale bar is 0.2 cm.

and sedimentary sequences (Figure 1). In the dacite, the perlite occurs as nodular or breccia-like masses near contacts with the Lower Janggi Formation. The boundary between the perlite and surrounding dacite is remarkably sharp and obvious because of the striking difference in physical character between these rocks. Perlite also occurs as a bed-like body of pyroclastic aggregates or small nodules in the lower part of the Lower Janggi Formation. The surrounding tuff is green and zeolitic; the original tuffaceous materials have been altered to clinoptilolite and mordenite. In the sedimentary unit, the perlite fragments are a few centimeters to tenths of a centimeter in size and occur most-

Table 1. Chemical analyses (wt. %) of dacite, perlite, altered perlite, perlitic glass, and gel-like glass by wet and electron microprobe methods.

	D-1	FP-1	FP-2	AP-1	PG-1	G-1
SiO ₂	69.88	69.01	68.41	66.50	69.32	66.34
TiO ₂	0.30	0.22	0.23	0.19	0.22	0.18
Al ₂ O ₃	15.80	14.10	14.12	11.95	13.51	15.05
Fe ₂ O ₃	1.63	1.00	0.97	0.71	1.15 ¹	1.24 ¹
FeO	0.59	0.45	0.50	0.25	n.d.	n.d.
MnO	0.06	0.07	0.09	0.04	0.10	0.08
MgO	0.48	0.39	0.35	0.44	0.50	0.64
CaO	1.89	1.57	1.63	1.60	1.34	1.05
Na ₂ O	4.32	3.20	3.87	4.43	3.73	0.95
K ₂ O	3.13	3.94	3.33	2.01	3.47	8.65
H ₂ O+	1.66	5.77	6.23	7.25	6.66 ²	5.82 ²
H ₂ O-	0.34	0.24	0.24	4.58	n.d.	n.d.
P ₂ O ₅	0.07	0.04	0.04	0.03	n.d.	n.d.
Total	100.15	100.00	100.01	99.98	100.00	100.00

Symbols: D-1 = bulk analyses of dacite by a wet method, FP-1, FP-2 = bulk analyses of fresh perlite by a wet method, AP-1 = bulk analyses of altered perlite (green, zeolitic) by a wet method, PG-1 = mean value of the perlitic glass by electron microprobe, G-1 = mean value of the gel-like glass by electron microprobe.

¹ Total iron.

² Total water calculated by difference.

ly as fragmental aggregates mixed with tuffaceous materials.

The perlite is dark gray to black, dense, and has a vitreous appearance. In thin section, most specimens exhibit the characteristic perlitic texture of concentric cracks (Figures 2 and 3A). The perlite consists by volume of silicic glass (93.1%), plagioclase (5.9%), biotite (0.6%), opaque minerals (0.4%), and traces of hornblende, apatite, zircon, and sanidine. Phenocrysts in the perlite are the same as those in the surrounding dacite in both abundance and composition. In addition, the compositions of plagioclase phenocrysts (An₃₂–An₄₇) in the perlite are also similar to those (An₃₁–An₄₂) in the dacite. SiO₂ (68–69 wt. %) and total alkali (7.1–7.3 wt. %) contents of the fresh perlite indicate that the rock can be chemically classified as a dacite. Petrochemical affinity between the perlite and the Nuldaeri Volcanics was suggested by Lee *et al.* (1986). The perlite characteristically contains 6.0–6.5 wt. % total water (Table 1).

DISCUSSION

Mode of diagenetic alteration

Most petrologists believe that obsidian is the non-hydrated precursor of perlite (Fisher and Schminke, 1984). Obsidian, however, was not found in this area. The spatial and lithologic relationships between perlite and associated dacite strongly suggest that dacite was the parental rock of the perlite in the Guryongpo area. The process of perlite formation, i.e., the hydration of dacite, is also inferred from the limited occurrence of perlite and its altered products near or within the sedimentary tuff. In other words, the rapid cooling and subsequent hydration of dacite, which are necessary for the formation of perlite, must have occurred as a

result of localized subaqueous extrusion of dacitic magma during the deposition of the tuff unit. During extrusion, the marginal parts of the dacite probably came directly in contact with fresh water, and thereby became successively hydrated.

Most of the perlite has been partially or wholly altered to smectite and/or zeolite. The characteristic dark gray color of perlite was drastically changed to dull brown or green during this alteration. Perlite within the sedimentary tuff was more severely altered than that within the dacite. The dull brown rock contains abundant smectite and clinoptilolite, but the green rock is comparatively smectite-free and contains clinoptilolite, mordenite, and silica minerals as major secondary components.

Distinct zoning from fresh perlite to its altered equivalents is common, not only in the outcrop but in hand specimen. For descriptive purposes, three alteration zones have been designated: zone 1 for the fresh perlitic part, zone 2 for the dull brown part, and zone 3 for the green part (Figure 2A). The initial alteration of the perlite apparently occurred along the concentric cracks that are characteristic in the fresh perlite. As the alteration advanced, the perlitic cracks became diffuse and indistinct as a result of smectite crystallization in their peripheral margins (Figures 2B and 3B). The remnant perlitic texture was generally preserved in zone 2, but was ultimately obliterated by the crystallization of zeolites and silica minerals as segregation veinlets in zone 3. Throughout the alteration, the composition of the plagioclase phenocrysts remained unchanged.

Chemical composition of the alteration zones

Changes in major element chemistry during hydration of rhyolitic glass and obsidian have been well es-

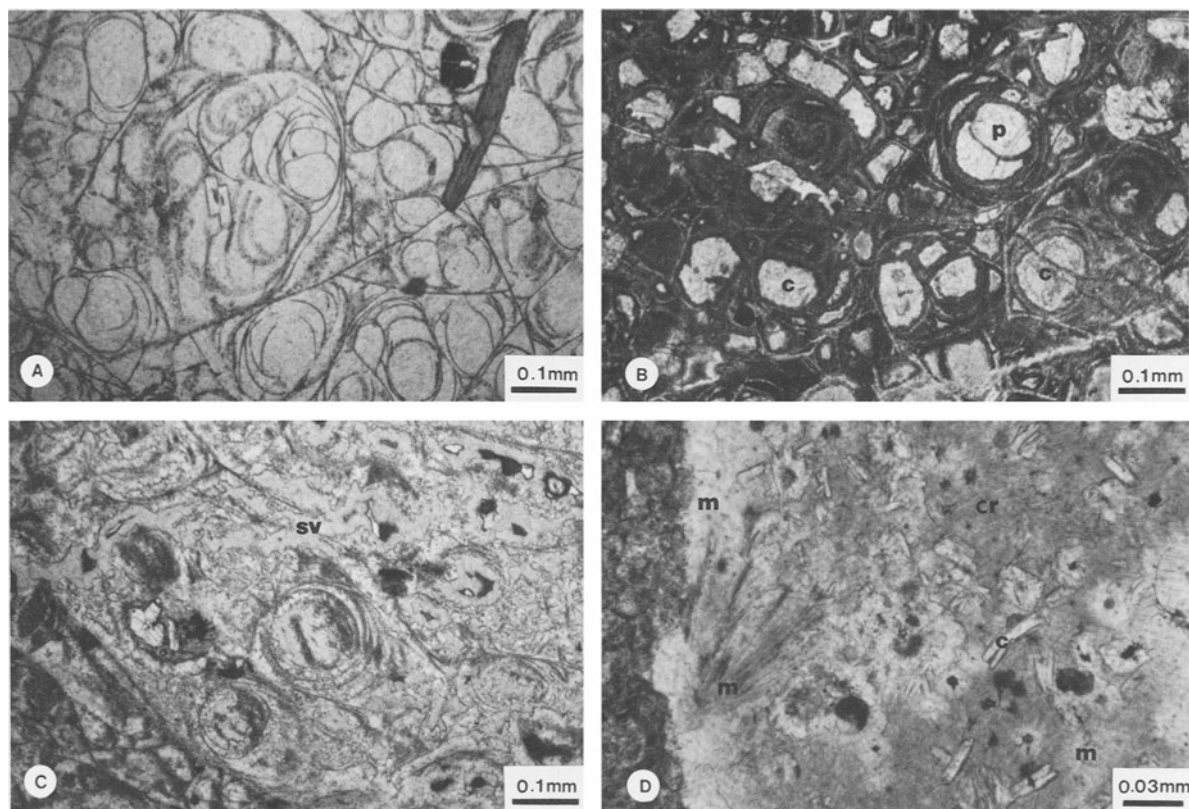


Figure 3. Photomicrographs showing characteristic appearance of the perlite and its alteration modes. A. Typical perlitic fabric in zone 1. Phenocrysts are biotite, plagioclase, and an iron oxide mineral. B. Intense smectite alteration accompanying gel-like glass along perlitic cracks in zone 2. Note remnant perlitic glass (white, p) or clinoptilolite-2 (dull white, c) in inner part of the crack. C. Zeolitic alteration in the zone 3. Original perlitic texture is severely modified by precipitation of clinoptilolite-3, mordenite, and low-cristobalite as segregation veinlets (upper, sv) and fillings in dissolved central cavities (lower). D. Enlarged view of segregation veinlet in Figure 3C. Fibrous and radiating mordenite aggregates (m) and prismatic clinoptilolite-3 clusters (c) are perched in the low-cristobalite (cr) matrix of veinlet.

tablished (Lipman, 1965; Jezek and Noble, 1978). To compare the chemical compositions of fresh perlite and its altered equivalents, we have used the electron microprobe to avoid including primary phenocrysts. These phenocrysts of plagioclase and iron oxides (totally about 7 vol. % of the rock) are not precursors of zeolite and smectite and can be ignored in considering the glass hydration reaction. Generally, good agreement was found between bulk-rock wet chemical and electron microprobe spot analyses for the fresh perlite (Table 1), especially considering that the wet chemical analysis unavoidably included minor clay minerals in perlitic cracks and phenocrysts.

The chemical composition of the glassy matrix in the altered perlitic rock is significantly different in the three alteration zones (Fig. 4). The wt. % of Na, K, Ca, and H₂O are significantly different in the different zones. Mg also appears to be variable, but its abundance is insignificant. The H₂O contents of the glass are as much as 8 wt. %, depending on the degree of alteration. Si

and Al are about the same in all zones. During hydration of the glass, a significant loss of Na, a slight loss of Ca, and a slight gain of K occurs in the perlite, the same as noted for obsidian altered to perlite (Jezek and Noble, 1978).

The alkali/alkaline earth ratios decrease with alteration of the perlite due to the loss (about 0.8 wt. %) of total alkalis during alteration (Figure 4A). As seen on the ternary diagram of (Na₂O + CaO)-(K₂O + MgO)-H₂O (Figure 4B), the (Na₂O + CaO)/H₂O ratios, are more variable than those of (K₂O + MgO)/H₂O. In addition, Na₂O and CaO vary chiefly with respect to H₂O, whereas the Na₂O/CaO ratios are strikingly uniform, regardless of the degree of alteration (Figure 4C). The Na₂O/CaO ratios of samples from zone 1 (2.8–3.2) are greater than those from zones 2 and 3 (1.1–1.3), due probably to intense Na leaching from the glass into the pore solution during the diagenetic alteration. The more variant trend of the K₂O/(CaO + Na₂O) ratio (Figure 4F) compared to those of the Na₂O/K₂O

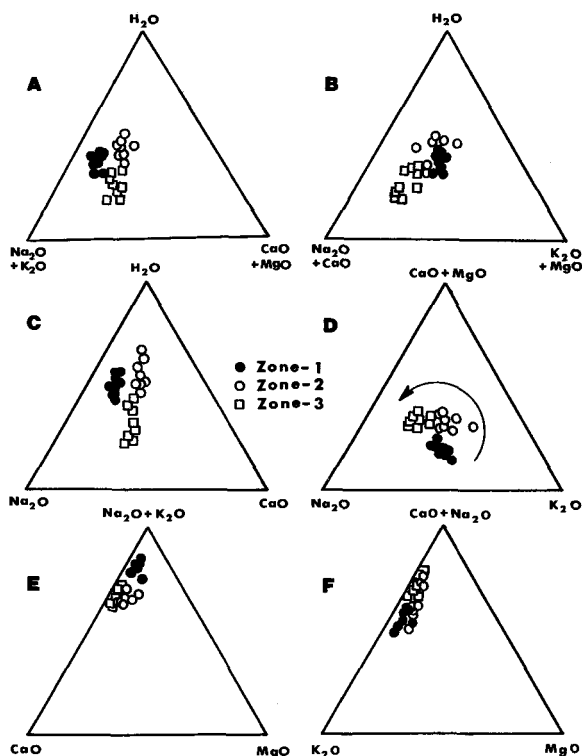


Figure 4. Ternary diagrams between H_2O and cation oxides, showing chemical change of glassy matrix parts of altered perlite during diagenetic alteration. Arrow in Figure 4D reflects trend of cation change within the glass precursor during alteration (cf. diagram showing the change of cation abundances of zeolites in Figure 5A).

(Figure 4D) and the $CaO/(Na_2O + K_2O)$ (Figure 4E) strongly suggests that the substitution $(2Na,Ca) = 2K$ took place in the glassy precursors during the diagenetic alteration.

Paragenesis and chemistry of zeolites and associated minerals

Clinoptilolite and mordenite occur as cryptocrystalline aggregates in association with smectite, low-cristobalite, and K-feldspar in the altered perlite. Clinoptilolite occurs in zones 2 and 3 as fillings of secondary cavities that resulted from dissolution of the perlitic glass, whereas mordenite is common together with low-cristobalite mainly in zone 3. Smectite typically occurs as a thin rim along the original perlitic cracks in zones 1 and 2. Late-formed low-cristobalite and K-feldspar are characteristic authigenic phases in zone 3. The late-formed cristobalite occurs as replacements of smectite and is green in hand specimen as well as in thin section. This may be related to the high Fe content (total Fe as $Fe_2O_3 =$ about 0.3 wt. %) in the silica mineral.

Alteration of the hydrated glass (i.e., perlite) seemed to begin by dissolution of the glass and crystallization of smectite along perlitic cracks. As the alteration pro-

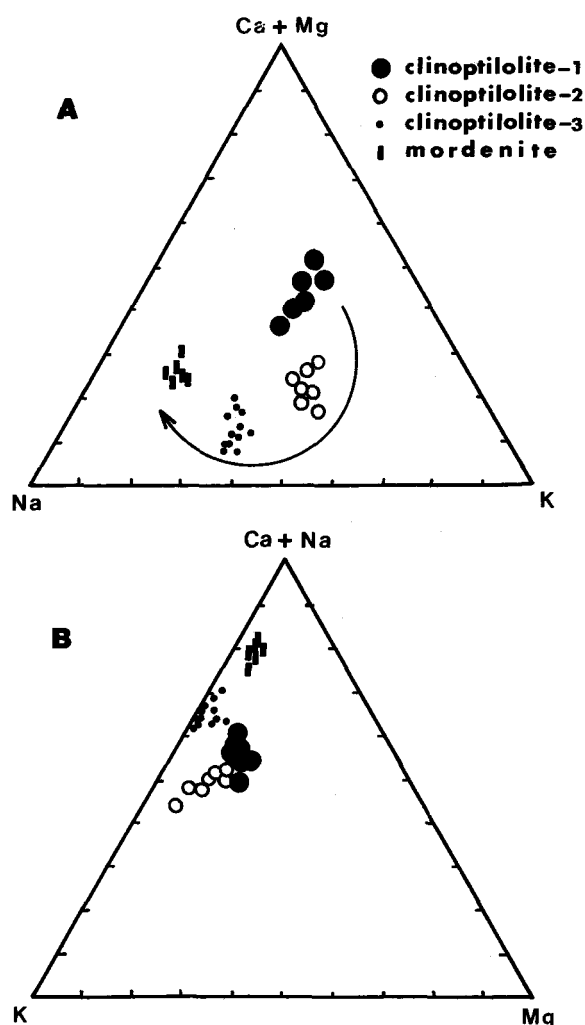


Figure 5. Ternary diagrams showing differences in cation abundances of zeolites. Arrow reflects paragenetic trend in zeolite formation.

ceeded, glass dissolution with continued precipitation of the smectitic rims advanced inward. In the central part of rounded remnant glass, the remaining glass was completely dissolved and clinoptilolite precipitated (Figures 2B and 3B). The modified perlitic fabric which resulted from rimming of smectite along the original perlitic cracks is easily identified in zone 2 (Figure 3B). At the advanced stage of alteration (i.e., in zone 3), clinoptilolite, mordenite, and low-cristobalite were co-precipitated as disseminated spots or segregation veinlets, thereby partially obliterating the modified perlitic fabric (Figure 3C). Based on the authigenic mineralization and concurrent textural change, authigenic mineral assemblages in zones 2 and 3 appear to be, in order of paragenetic sequence: (1) smectite + clinoptilolite; (2) clinoptilolite + cristobalite; (3) clinoptilolite + mordenite + cristobalite; and (4) cristobalite

Table 2. Representative electron microprobe analyses of zeolites.

	Clinoptilolite					Mordenite	
	1-1	2-1	2-2	3-1	3-2	4-1	4-2
SiO ₂	69.28	67.43	67.97	67.94	67.33	72.26	71.35
Al ₂ O ₃	13.49	12.19	12.17	12.49	11.66	11.12	10.56
Fe ₂ O ₃ ¹	0.74	0.30	0.04	0.22	0.01	0.23	0.07
MgO	0.82	0.84	0.08	0.05	0.06	0.20	0.20
CaO	2.48	2.16	1.00	1.22	0.98	2.00	1.71
SrO	0.08	0.35	0.92	0.95	0.97	0.09	0.13
BaO	0.78	0.26	0.04	0.28	0.12	0.11	0.20
Na ₂ O	1.75	1.45	2.83	3.12	3.23	3.05	2.99
Total	91.96	87.61	88.62	89.25	87.36	90.39	88.30
Si/Al	4.36	4.70	4.75	4.63	4.91	5.51	5.74
E(%) ²	9.48	5.45	7.73	6.97	3.57	5.92	6.70

Symbols: 1-1 = clinoptilolite-1 in perlitic crack, 2-1, 2-2 = clinoptilolite-2 in central dissolved cavities, 3-1, 3-2 = clinoptilolite-3 in silica veinlets, 4-1, 4-2 = mordenite in silica veinlets.

¹ Total iron.

$$^2 E(\%): \frac{(Al + Fe) - (Na + K) - 2(Mg + Ca + Sr + Ba)}{(Na + K) + 2(Mg + Ca + Sr + Ba)} \times 100.$$

+ K-feldspar. Assemblages 1 and 2 are in zone 2, and assemblages 3 and 4 are in zone 3.

Clinoptilolite in the Guryongpo area can be paragenetically divided into three types: (1) clinoptilolite-1, a rare phase, associated with the earliest-formed smectite in the modified perlitic cracks, (2) clinoptilolite-2, precipitated in the central cavities resulting from complete dissolution of remnant glass, and (3) clinoptilolite-3, occurring with mordenite in the silica veinlets or precipitated as fillings in the dissolved cavities of zone 3. Clinoptilolite-2 is generally coarser (> 2 mm) than the other types and is the chief zeolite in zone 2. These three types of clinoptilolites differ in chemical composition, especially in cation abundance and Si/Al ratios (Table 2 and Figure 5). Clinoptilolite-1 is less silicic and comparatively Ca-rich in composition, whereas clinoptilolite-3 exhibits a higher Si/Al ratio and a higher abundance of alkalis, especially Na. Clinoptilolite-2 is intermediate not only in its exchangeable cation composition but also in its Si/Al ratio. A distinct linear relationship between Si/Al ratio and total alkali abundance is obvious for the alkalic zeolites (Figure 6).

During the progressive crystallization of zeolites, the zeolite chemistry seems to have changed systematically, as represented in Figure 5. Zeolite chemistry, including that of mordenite, probably reflects chemical activity of ions in pore fluids at the time of precipitation. Therefore, a chemical compensation of cations between glassy precursors and pore fluids during zeolitization can be illustrated by the clockwise chemical trend in the (Ca + Mg)-Na-K ternary diagram of zeolites (Figure 5A) and the counterclockwise trend in cation composition of remnant glass (Figure 4D). The progressive alteration suggests that the diagenetic alteration of perlite occurs under an isochemical condition without significant addition of elements, except

for H₂O, from outside. Furthermore, components were progressively leached from the glass to supply the precipitating zeolites.

Glass dissolution and formation of diagenetic phases

In altered tuffs, smectite typically occurs as a thin rim surrounding glass shards. Later-formed zeolites occur in shard cavities farther from the glass-smectite interfaces (Sheppard and Gude, 1968, 1969, 1973). In addition, the formation of K-feldspar from zeolite has been well documented in altered tuffs under various conditions (Iijima and Hay, 1968; Surdam and Parker, 1972; Sheppard and Gude, 1968, 1969, 1973).

During the initial crystallization of smectite from the perlitic glass of the Guryongpo area, a K-enriched (K₂O = 8.2–10.4%) phase, which is noncrystalline by XRD analysis, was noted (Table 1, Figure 7). This phase has also been reported in obsidian-perlite pairs by Jezek and Noble (1978), and following their work, we refer to this phase as gel-like glass. The gel-like glass occurs near smectite-perlitic glass interfaces and develops farther from the perlitic glass than the smectite, forming a typical micro-scale zoning of gel-like glass-smectite-perlitic glass in zone 2 (Figure 8). The gel-like glass is isotropic and pale yellowish green in thin section. SEM observations of the gel-like material indicate it is formless and generally more abundant than smectite (Figure 8C). Clinoptilolite-1 occurs locally at smectite-perlitic glass interfaces, but does not occur in the gel-like material (Figure 8D). As the alteration proceeded, the zones of smectite and the gel-like glass around perlitic glass became broader and more conspicuous. The initial micro-scale zoning was generally maintained until the remnant perlitic glass dissolved and subsequently, clinoptilolite-2 precipitated. As the crystallization of clinoptilolite-2 began, the advanced

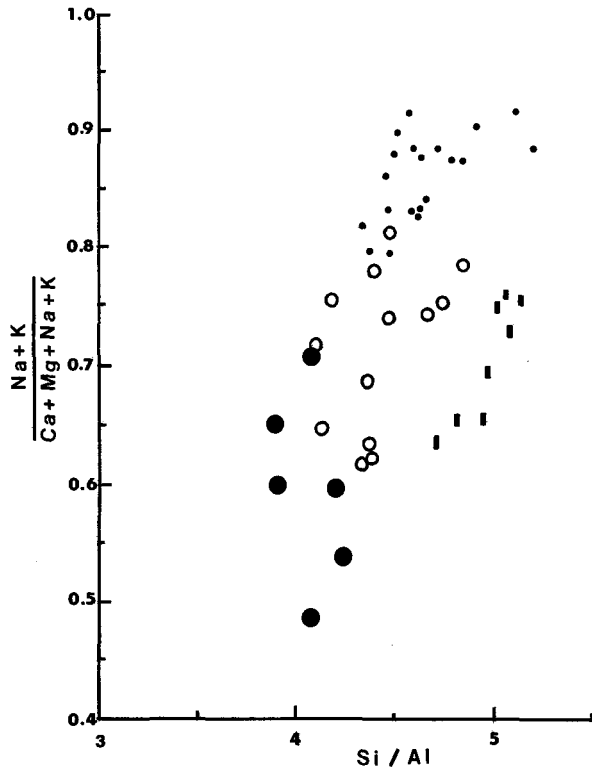


Figure 6. Plot of alkali abundance ratios vs. Si/Al ratios in clinoptilolite and mordenite. Symbols are the same as in Figure 5.

micro-scale zoning of gel-like glass-smectite-clinoptilolite-2 was locally formed in zone 2 (Figure 9A). These two types of early micro-scale zonations indicate that the dissolution behavior and kinetics of the glass dissolution are the main influences on the paragenesis of early-formed authigenic solid phases. The following three modes of chemical leaching of the glass were probably operative in the diagenetic alteration of the perlite: (1) successive hydration and Na-depletion of the volcanic glass forming perlite, (2) sluggish, partial dissolution at the smectite-perlitic glass interfaces, and (3) rapid, complete dissolution of the remnant perlitic glass.

The first leaching process probably corresponded to a perlitization of the original dacitic glass, which was accompanied by a slight gain of K and a significant loss of Na during simple hydration. In other words, as Hay (1963) discussed for the altered tuffs in the John Day Formation, any loss of Na during hydration of glass was not totally compensated for by a gain of K, and thus, required an equivalent anion (i.e., oxygen). The depletion of Na can be considered a hydrolysis reaction, $\text{Na}_2\text{O} + \text{H}_2\text{O} = 2\text{Na}^+ + 2(\text{OH})^-$, which ultimately yields an increase in alkalinity. In addition, the hydration-hydrolysis reaction during perlitization can be represented as the following simplified equation:

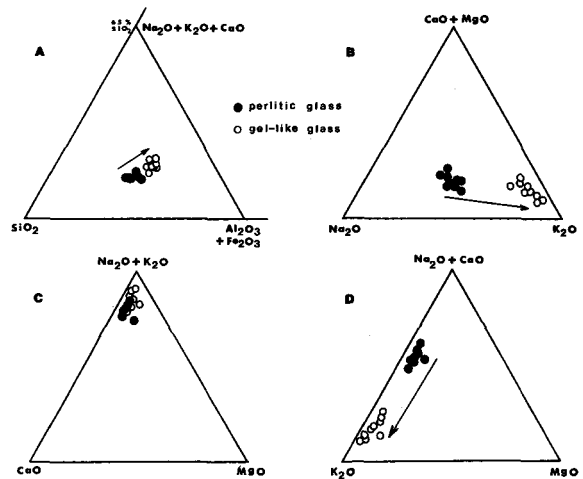
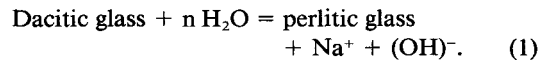
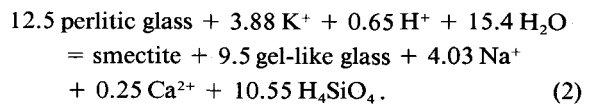


Figure 7. Ternary diagrams showing chemical differences of perlitic glass and gel-like glass.



The perlitization process appears to have been a preliminary stage to the subsequent glass dissolution related to the formation of smectite and gel-like glass.

Due to the increasing pH of the lacustrine pore water, the partial dissolution that accompanied the formation of the smectite and the gel-like glass was probably initiated along the perlitic crack surfaces. The smectite and gel-like glass are not intergrown but form distinct micro-scale zones. The gel-like glass also occupies the outer zone from the smectite to perlitic glass interfaces (Figure 8A and 8C). The spatial relationship between these early-formed phases suggests that the gel-like glass precipitated from the residual solution immediately after the smectite crystallized, *in situ*, by the sluggish incongruent dissolution of the perlitic glass, rather than by simultaneous precipitation from the pore solution. The suggestion may be confirmed by the fact that the larger the smectite rim around the perlitic glass fragment, the more gel-like glass is found in the perlitic cracks (Figure 8C). From the paragenetic relationship among these early diagenetic phases, including the perlitic glass and their chemical compositions (Table 3), the incongruent dissolution reaction may be illustrated on the assumption that Al is immobile:



Dissolution reaction (2) is based on the assumption that Mg is totally fixed in the solid products. In this case, Fe is also simultaneously fixed. Another possible dissolution reaction, however, may be suggested due to the fact that the liberated K from perlitic glass tends

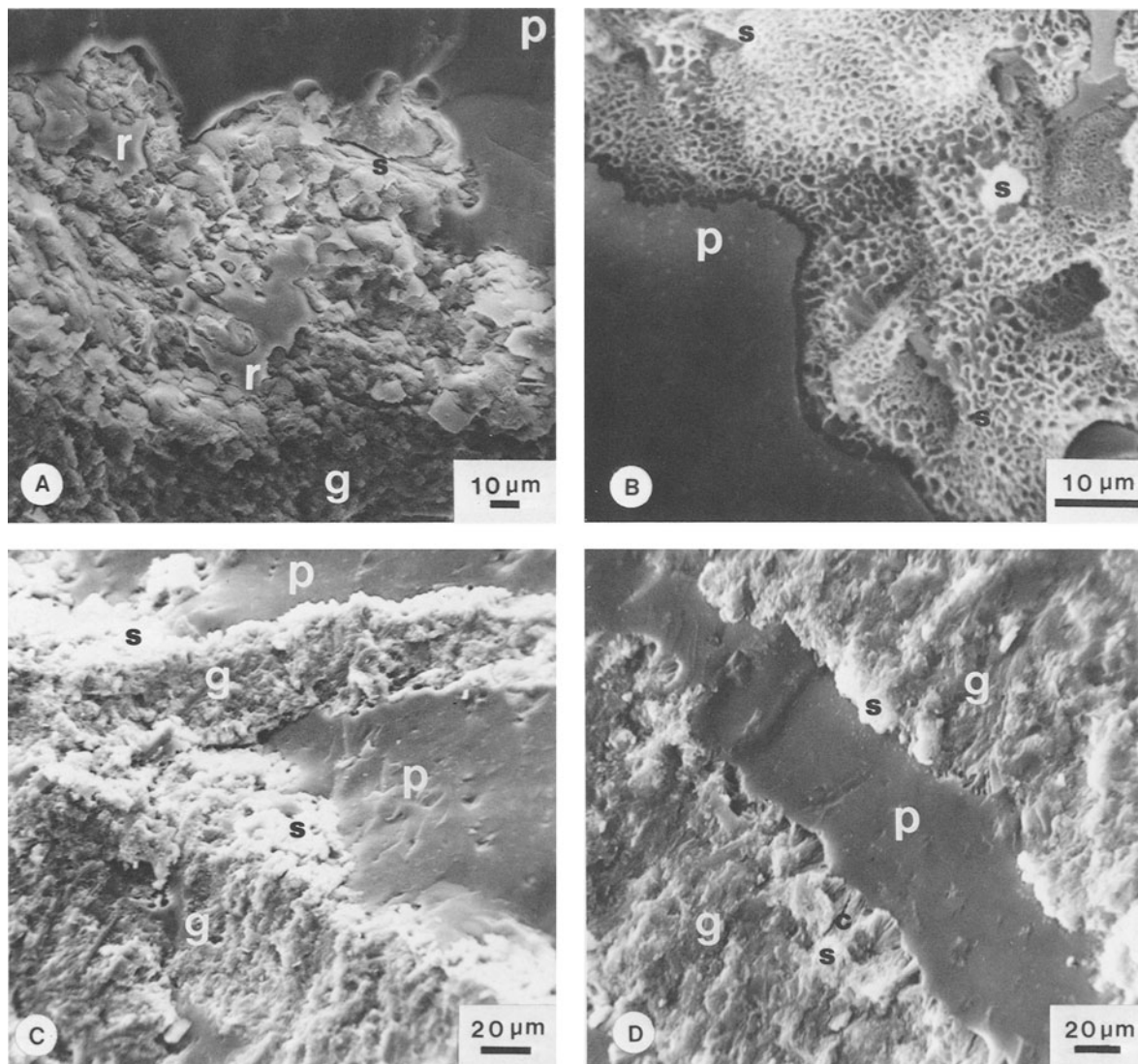
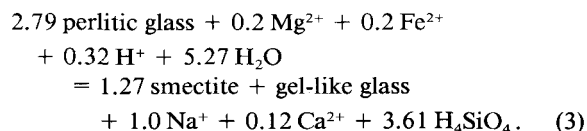


Figure 8. Scanning electron micrographs showing typical spatial relations among perlitic glass, smectite, and gel-like glass during initial partial dissolution. A. Typical initial partial dissolution of perlitic glass (p) to form smectite (s) and gel-like glass (g). Remnant glass patches (r) are visible in the smectite zone. B. Enlarged view of perlitic glass (p)-smectite (s) contacts in Figure 8A. C. A micro-scale zoning of smectite (s) and gel-like glass (g) around perlitic glass precursor (p). Note abundance of gel-like glass over smectite. D. Remnant perlitic glass (p) rimmed by smectite (s) or clinoptilolite-1 (c) on both sides. A gel-like glass (g) occupies outside of contacts.

to be fixed in the gel-like glass. This reaction can be written as follows:

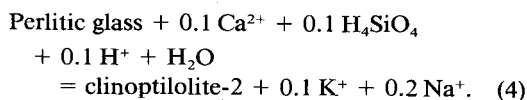


Reaction (3) requires an external source of Mg and Fe. The source of Mg and Fe cannot be explained here because the perlitization that occurred immediately prior to the dissolution reaction appears not to have

been related to Mg migration as previously mentioned. In addition, the relative width ratio (nearly 3) of gel-like glass zone/smectite zone as determined by scanning electron microscopy (Figure 8C) reasonably supports the idea that reaction (2) was operative rather than reaction (3).

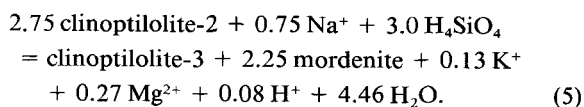
A different dissolution process was probably responsible for the subsequent crystallization of clinoptilolite-2 from the remnant perlitic glass. From SEM observations, the second stage dissolution appeared to have yielded only a coarser-grained clinoptilolite-2, without accompanying dissolution cavities or other zeolites

(Figures 9A and 9B). The advanced dissolution reaction can be illustrated on the assumption that Al is immobile:



Comparison between incongruent dissolution reactions (2) and (4), which are relevant to smectite and zeolite formation, respectively, indicates that reaction (4) occurred as a consequence of incipient reaction (2). In other words, the partial dissolution to form smectite and gel-like glass tended to liberate more silica and sodium into the pore fluid, as seen in the reaction (2). The increased alkalinity and silica activity of the pore fluid may have facilitated complete dissolution of remnant glass and the simultaneous precipitation of clinoptilolite-2.

A decreasing pH of the pore fluid after the complete dissolution may be inferred from the fact that more-silicic types of zeolites and silica minerals subsequently precipitated instead of clinoptilolite-2, as indicated by Mariner and Surdam (1970) in their experiments on dissolution of glass. As the alkalinity of pore fluid decreased, clinoptilolite-2 drastically transformed to clinoptilolite-3 and mordenite. The clinoptilolite-3 and mordenite are intergrown as cavity-fillings, where no reaction textures are observed (Figure 3D). A dissolution-precipitation process may be suggested here by the fact that incipient clinoptilolite-2 generally occupies whole cavities resulting from glass dissolution and locally occurs in contact with residual glass, whereas later-formed clinoptilolite-3 and mordenite accompany some dissolved cavities and are not associated with residual glass (cf. Figures 9A, 9B, 9C, and 9D). The initial diagenetic phases (i.e., smectite and gel-like glass) are metastably persistent, however, despite subsequent higher silica activity in the pore fluid. The result is a series of micro-scale zones, gel-like glass-smectite-clinoptilolite-3-mordenite (Figure 9C). The zeolite transition from clinoptilolite-2 to clinoptilolite-3 + mordenite can be written as:



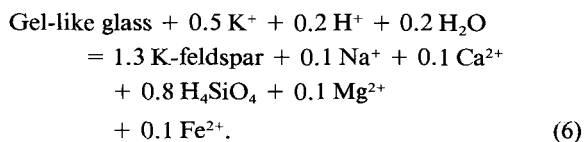
The products of reaction (5) are obviously favored by higher activities of silica and Na. Most of the Na liberated from earlier glass dissolution reactions could be fixed in the products of this reaction.

K-feldspar has never been reported as a direct alteration product of glass in tuffaceous rocks (Surdam, 1977); however, the formation of K-feldspar, which formed at the expense of the K-rich, gel-like glass, is

Table 3. Average composition of glass and diagenetic phases determined from electron microprobe data.

Diagenetic phases	Composition
Perlitic glass	$\text{K}_{0.3}\text{Na}_{0.4}\text{Ca}_{0.1}\text{Mg}_{0.1}\text{Fe}_{0.1}\text{Al}_{1.1}\text{Si}_{4.8}\text{O}_{12} \cdot 1.6 \text{ H}_2\text{O}$
Gel-like glass	$\text{K}_{0.8}\text{Na}_{0.1}\text{Ca}_{0.1}\text{Mg}_{0.1}\text{Fe}_{0.1}\text{Al}_{1.3}\text{Si}_{4.7}\text{O}_{12} \cdot 1.4 \text{ H}_2\text{O}$
Smectite	$(\text{K}_{0.03}\text{Na}_{0.02}\text{Ca}_{0.05})(\text{Mg}_{0.3}\text{Fe}_{0.3}\text{Al}_{1.4})\text{Si}_{4.0}\text{O}_{10}(\text{OH})_2$
Clinoptilolite-2	$\text{K}_{0.2}\text{Na}_{0.2}\text{Ca}_{0.2}\text{Mg}_{0.1}\text{Al}_{1.1}\text{Si}_{4.9}\text{O}_{12} \cdot 3 \text{ H}_2\text{O}$
Clinoptilolite-3	$\text{K}_{0.1}\text{Na}_{0.4}\text{Ca}_{0.1}\text{Mg}_{0.05}\text{Al}_{1.0}\text{Si}_{5.0}\text{O}_{12} \cdot 3 \text{ H}_2\text{O}$
Mordenite	$\text{K}_{0.1}\text{Na}_{0.4}\text{Ca}_{0.2}\text{Al}_{1.0}\text{Si}_{5.1}\text{O}_{12} \cdot 3 \text{ H}_2\text{O}$
K-feldspar	KAlSi_3O_8

common in zone 3. The K-feldspar mainly occupies concentric cavities outside smectite rims. Petrographic evidence for a paragenetic relationship between K-feldspar and alkalic zeolites is lacking in the altered perlite. The chemical comparison of the K-feldspar and the gel-like glass suggests that the complete dissolution of the K-rich, gel-like glass would have produced a local K-supersaturation in the pore fluid and, thereby, favored the K-feldspar formation. The reaction can be written as follows:



The K liberated from zeolite reactions (4) and (5) would be fixed in the K-feldspar formation.

Throughout zeolite reactions (3) and (4), low-cristobalite behaved as a geochemical niche for excess silica (Figure 9D). In addition, a green low-cristobalite commonly occurs as replacements of smectite in the zone 3. The transformation from smectite to an iron-bearing, green, low-cristobalite probably occurred at the highest silica activity in the pore fluid.

SUMMARY AND CONCLUSIONS

Successive perlitization and further diagenetic alteration of the original dacite to form zeolites via perlite to altered perlite evidently occurred to varying degrees even on a fine scale. The perlitic cracks of the perlite appear to have played a major role as channels through which additional lacustrine water was introduced, thereby allowing the resultant diagenetic phases to form three types of assemblages, each characterized by micro-scale zonings. From early to late they are: (1) gel-like glass-smectite-perlitic glass, (2) gel-like glass-smectite-clinoptilolite-2, and (3) gel-like glass-smectite-

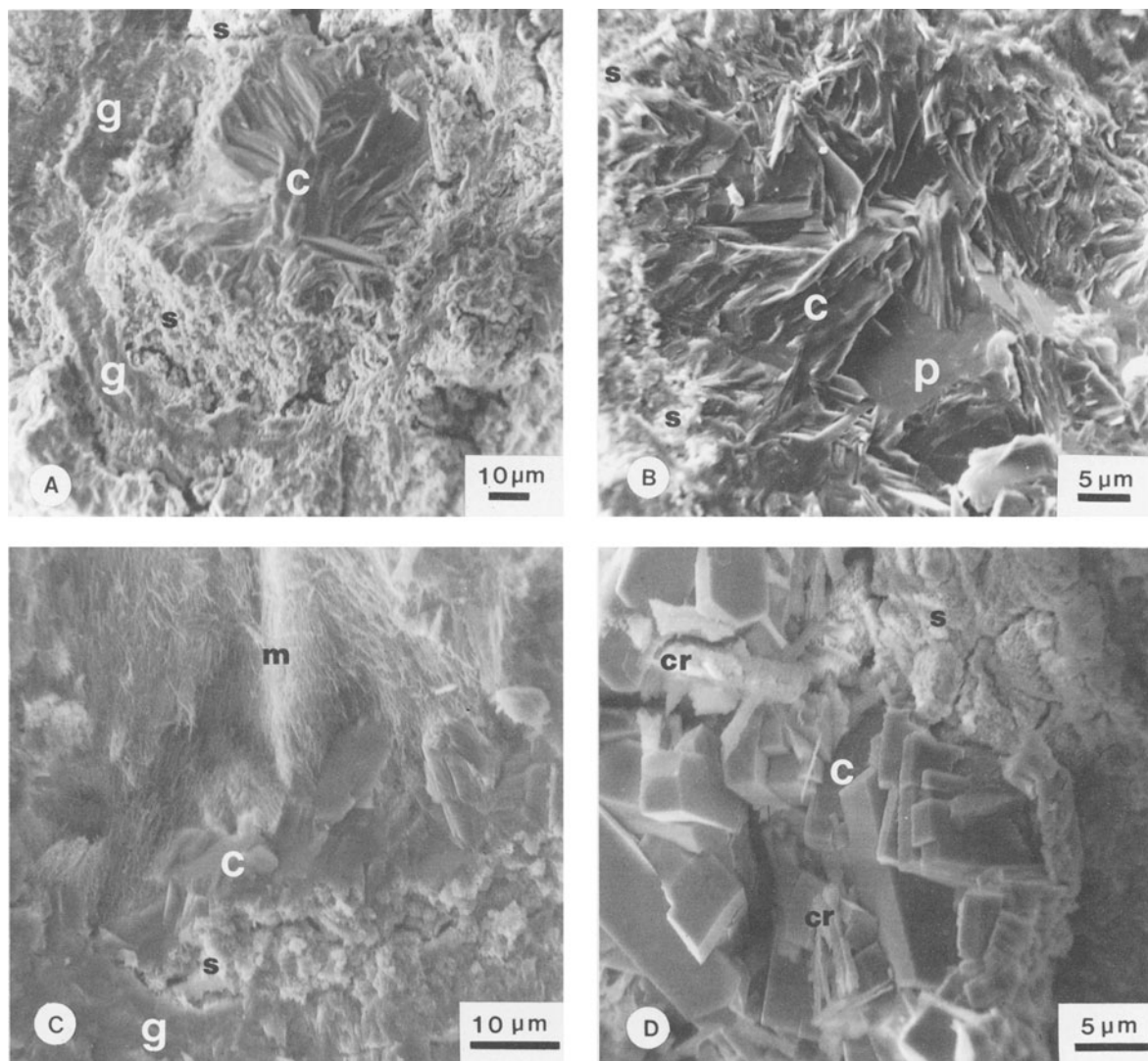


Figure 9. Scanning electron micrographs showing advanced types of micro-scale zoning controlled by original perlitic fabric. A. Gel-like glass (g)-smectite (s)-clinoptilolite-2 (c) zoning. B. Crystallization relationship of clinoptilolite-2 (c) from remnant perlitic glass (p). Note smectite (s) occupying outer area. C. Gel-like glass (g)-smectite (s)-clinoptilolite-3 (c)-mordenite (m) zoning. Note sutured trace of original perlitic crack in gel-like glass zone. D. Precipitation of clinoptilolite-3 (c) and minor low-cristobalite (cr) on smectite (s)-rimmed cavity wall (cf. mode of occurrence of clinoptilolite-3 to that of clinoptilolite-2 in Figure 9B).

clinoptilolite-3 and mordenite. During the hydration of the glass, which presumably continued until about 8 wt. % water had been added, the glass lost Na and gained K. The depleted Na may have undergone hydrolysis in the pore fluid, thereby causing an increase of alkalinity in the pore fluid. The increasing alkalinity in the pore fluid unquestionably affected the dissolution behavior of the perlitic glass and, subsequently, the diagenetic mineral assemblages.

The following scenario for mineral paragenesis seems plausible although the exact timing of reactions (1) through (6) is uncertain. The release of components by

some reactions and their consumption in others suggest that the reactions may occur simultaneously. Alteration of the perlite was apparently dependent on two different incongruent dissolutions, as summarized in Figure 10. A micro-scale zoning of the smectite and gel-like glass around the glass precursor suggests that smectite was formed by a leaching process just prior to the deposition of the gel-like glass by a sluggish dissolution of the perlitic glass which began along the original perlitic cracks (i.e., $12.5 \text{ perlitic glass} + 3.88 \text{ K}^+ + 0.65 \text{ H}^+ + 15.4 \text{ H}_2\text{O} = \text{smectite} + 9.5 \text{ gel-like glass} + 4.03 \text{ Na}^+ + 0.25 \text{ Ca}^{2+} + 10.55 \text{ H}_4\text{SiO}_4$). This reac-

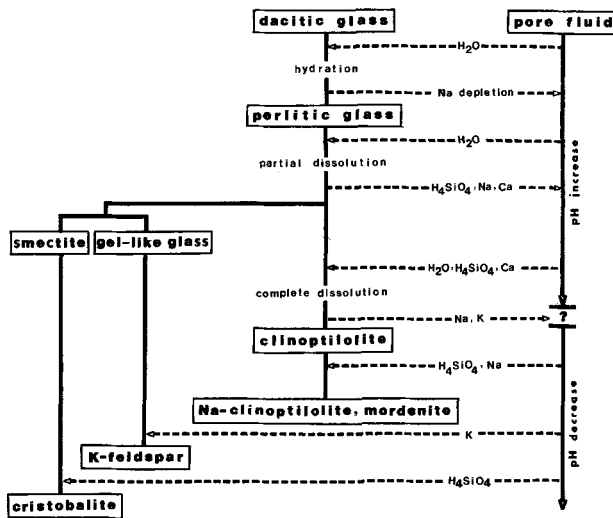


Figure 10. Flow diagram showing diagenetic reaction pathways and paragenetic sequences of authigenic phases in altered perlite.

tion produced the resultant Si, Na, and Ca in the products which would favor subsequent crystallization of zeolites instead of earlier formed smectite and the gel-like glass.

With increasing pH and silica activity of the pore fluid, the dissolution of the remnant glass became more complete and produced the subsequent precipitation of alkalic zeolites from clinoptilolite-2 to clinoptilolite-3 + mordenite. The association of early-formed diagenetic phases and later-formed alkalic zeolites in discrete micro-scale zones suggests that early-formed smectite and gel-like glass were not consumed as a precursor during subsequent zeolite formation. Clinoptilolite-2 was formed as a result of a more rapid and complete dissolution of residual perlitic glass at a higher alkalinity and silica activity of the pore fluid (i.e., perlitic glass + 0.1 Ca^{2+} + $0.1 \text{ H}_4\text{SiO}_4$ = clinoptilolite-2 + 0.1 K^+ + 0.2 Na^+). Mordenite did not form directly at the expense of a glass precursor but coprecipitated with Na-rich clinoptilolite-3 at the expense of incipient clinoptilolite-2 from a pore fluid supersaturated with respect to silica. Finally, K-feldspar formed not from zeolites but from the K-rich gel-like glass at a later stage of the diagenetic alteration.

ACKNOWLEDGMENTS

This study was financially supported by a post-doctoral research fellowship (Noh) from the Korea Science and Engineering Foundation during 1987. We are very grateful to Dave Pierce of the University of California at Santa Barbara for his technical assistance in the SEM and electron microprobe studies. We also appreciate the stimulating suggestions of Professor Soo Jin Kim of Seoul National University in the initial stage of the

study. The manuscript was improved as a result of critical reviews by F. A. Mumpton, R. A. Sheppard, M. Utada, and R. Coffman.

REFERENCES

- Boles, J. R. and Coombs, D. S. (1975) Mineral reactions in zeolitic Triassic tuff: *Geol. Soc. Amer. Bull.* **86**, 163–173.
- Bong, P. Y. (1981) Palynology of the Janggi area: *Report Geol. Miner. Resources Korea* **10**, 103–136.
- Coombs, D. S. (1954) The nature and alteration of some Triassic sediments from Southland, New Zealand: *Trans. Roy. Soc. New Zealand* **82**, 65–109.
- Dibble, W. E. and Tiller, W. A. (1981) Kinetic model of zeolite paragenesis in tuffaceous sediments: *Clays & Clay Minerals* **29**, 323–330.
- Fisher, R. V. and Schmincke, H.-U. (1984) *Pyroclastic Rocks*: Springer-Verlag, Berlin, 327 pp.
- Gottardi, G. and Galli, E. (1985) *Natural Zeolites*: Springer-Verlag, Berlin, 380 pp.
- Hay, R. L. (1963) Stratigraphy and zeolitic diagenesis of the John Day Formation of Oregon: *Univ. California Publ. Geol. Sci.* **42**, 199–262.
- Hay, R. L. (1977) Geology of zeolites in sedimentary rocks: in *Mineralogy and Geology of Natural Zeolites*, F. A. Mumpton, ed., Miner. Soc. Amer. Short Course Notes 4, 53–63.
- Huzioka, K. (1972) The Tertiary floras of Korea: *J. Mining College Akida Univ.* **5**, 1–83.
- Iijima, A. and Hay, R. L. (1968) Analcime composition in tuffs of the Green River Formation of Wyoming: *Amer. Mineral.* **53**, 184–200.
- Iijima, A. and Utada, M. (1972) A critical review on the occurrence of zeolites in sedimentary rocks in Japan: *Japan J. Geol. Geogr.* **42**, 61–83.
- Jezek, P. A. and Noble, D. C. (1978) Natural hydration and ion exchange of obsidian: *Amer. Mineral.* **63**, 266–273.
- Kim, B. G., Cheong, C. H., and Kim, S. J. (1975) Stratigraphical studies on the lignite beds in Yeongil area: *J. Geol. Soc. Korea* **11**, 240–252.
- Lee, M. W., Won, C. K., and Noh, J. H. (1986) Geology of Guryongpo area: *J. Korea Earth Sci. Educ. Soc.* **5**, 15–21.
- Lipman, P. W. (1965) Chemical comparison of glassy and crystalline volcanic rocks: *U.S. Geol. Surv. Bull.* **1201-D**, 24 pp.
- Mariner, R. H. and Surdam, R. C. (1970) Alkalinity and formation of zeolites in saline alkaline lakes: *Science* **170**, 977–980.
- Noh, J. H. (1985) Mineralogy and genesis of zeolites and smectites from Tertiary tuffaceous rocks in Yeongil area: Ph.D. thesis, Seoul National Univ., Seoul, Korea, 142 pp.
- Noh, J. H. and Kim, S. J. (1986) Zeolites from Tertiary tuffaceous rocks in Yeongil, Korea: in *7th Int. Zeolite Conf., Tokyo, 1986*, Y. Murakami, A. Iijima, and J. W. Ward, eds., Kodansha, Tokyo, Elsevier, Berlin, 59–66.
- Sheppard, R. A. and Gude, A. J., 3rd (1968) Distribution and genesis of authigenic silicate minerals in tuffs of Pleistocene Lake Tecopa, Inyo County, California: *U.S. Geol. Surv. Prof. Pap.* **597**, 38 pp.
- Sheppard, R. A. and Gude, A. J., 3rd (1969) Diagenesis of tuffs in the Barstow Formation, Mud Hills, San Bernardino County, California: *U.S. Geol. Surv. Prof. Pap.* **634**, 35 pp.
- Sheppard, R. A. and Gude, A. J., 3rd (1973) Zeolites and associated authigenic silicate minerals in tuffaceous rocks of the Big Sandy Formation, Mohave County, Arizona: *U.S. Geol. Surv. Prof. Pap.* **830**, 36 pp.
- Surdam, R. C. (1977) Zeolites in closed hydrologic systems: in *Mineralogy and Geology of Natural Zeolites*, F. A.

- Mumpton, ed., *Miner. Soc. Amer. Short Course Notes* **4**, 65–92.
- Surdam, R. C. and Parker, R. D. (1972) Authigenic aluminosilicate minerals in tuffaceous rocks of the Green River Formation, Wyoming: *Geol. Soc. Amer. Bull.* **83**, 689–700.
- Surdam, R. C. and Sheppard, R. A. (1978) Zeolites in saline, alkaline-lake deposits: in *Natural Zeolites: Occurrence, Properties, Use*, L. B. Sand and F. A. Mumpton, eds., Pergamon Press, Elmsford, New York, 145–174.

(Received 15 December 1987; accepted 21 June 1988; Ms. 1746)