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# Occurrence and Genesis of Zeolites from the Tertiary Volcanic Sediments in the Guryongpo Area, Korea

## 浦項 九龍浦 지역 第3紀 火山堆積岩 中의 沸石鑛物의 産出狀態와 成因

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**ABSTRACT** : Clinoptilolite and mordenite are important constituents of the Nuldaeri Trachytic Tuff and Guryongpo Dacitic Tuff of the Tertiary Janggi Group which were deposited in a lacustrine environment. The diagenetic crystallization sequences of zeolites in different tuffaceous sediments and their chemical behaviors have been studied to know the process of their formation. The paragenetic sequence established from textural observations and chemical data : Ca-smectite→(Ca, K)-clinoptilolite→(K, Na)-mordenite, indicates that the chemical activities of alkalic ions and Si/Al activity ratio in pore fluids changed systematically with diagenetic alteration. The chemical trend of zeolite formation is characterized by decreasing Ca and Mg, non-variable Na and increasing K in the Nuldaeri Trachytic Tuff and by decreasing Ca and Mg, increasing Na and increasing-decreasing K in the Guryongpo Dacitic Tuff. The paragenesis from glass via smectite to alkali zeolites indicates a sequence of incongruent dissolution reactions and subsequent crystallization. Inhomogeneity in chemical composition of each zeolite may be attributed to such processes.

**요약** : 클라이놉타일로라이트와 모데나이트는 호소환경에서 퇴적된 제3기 장기층군에 속하는 눌대리조면암질 응회암과 구룡포데사이트질 응회암의 주요구성 광물이다. 이들 광물의 생성과정을 알아보기 위하여 서로 다른 응회암질 퇴적암에서 불석광물들의 속성정출순서와 이들의 화학적 동향에 대한 연구가 수행되었다. 현미경적 조직관찰과 화학조성으로부터 밝혀진 생성순서, 즉, Ca-스멕타이트 → (Ca, K)-클라이놉타일로라이트 → (K, Na)-모데나이트는 공극유체의 알칼리이온의 활동도와 Si/Al 활동도 비가 속성변질작용과 함께 체계적으로 변화했다는 것을 지시해준다. 불석광물형성의 화학적 진행 추이는 눌대리조면암질 응회암에서는 Ca와 Mg의 감소, K의 증가방향으로 그리고 구룡포데사이트질 응회암에서는 Ca와 Mg의 감소, Na의 증가 및 K의 증가-감소방향으로 진행되었다. 유리질 물질로부터 스멕타이트를 거쳐 알칼리 불석으로 이어지는 생성순서는 분해용융과 그 직후의 정출작용의 결과이다. 각 불석광물의 화학조성상의 불균질성은 이와 같은 광물생성과정에 기인한다.

## INTRODUCTION

Clinoptilolite and mordenite are the important constituent minerals of the Tertiary volcanic sediments in the Guryongpo area located in the southeastern corner of Korean peninsula. Noh and Kim (1982, 1989) gave textural evidences for the diagenetic formation of clinoptilolite and mordenite from tuffaceous volcanic sediments. Noh and Boles (1989) suggested that the paragenesis from glass via smectite to alkali zeolites in most glass-bearing rocks be explained by a sequence of incongruent dissolution reactions.

Detailed geological map of the area has been newly prepared from the field investigation for better understanding of geological environment of the formation of zeolites from the tuffaceous volcanic sediments. Detailed stratigraphy and volcanic sequences have been established from field mapping.

The field occurrence and microscopic tex-tures of zeolites and associated minerals were used to establish their paragenetic sequence. The process of formation of mordenite and clinoptilolite from volcanic materials in the diagenetic environment and the involved chemical reaction were the objectives of this study.

## MATERIALS AND METHODS

Samples for this study were collected from each of the formations designated on the geological map on the basis of their modes of occurrence and textures.

Mineralogy and textures of rocks were studied by using polarizing microscopy, scanning electron microscopy (SEM) and X-ray diffraction (XRD). The chemical compositions of zeolite minerals were determined by using the JEOL JXA-733 Superprobe at a 15 kV accelerating voltage, a 0.01 $\mu$A beam current and 5 $\mu$m beam diameter. Average counts (10 sec x 5 times) were employed in comparing the analyses with the natural silicate standards. Bence and Albee's (1968) method was used for calibration.

## GENERAL GEOLOGY

The Guryongpo area, located in the north-eastern margin of the Pohang basin, is a Tertiary sedimentary sub-basin in Korea (Figure 1). The geology of the area consists of the Janggi Group, Yeonil Basalt, and Guryongpo Andesite, all of Miocene age.

The Janggi Group consists of the Janggi Conglomerate, Nuldaeri Trachytic Tuff, Guryongpo Dacitic Tuff, massive dacite and breccia dacite, in ascending order. The sediments in the area were deposited in a lacustrine environment

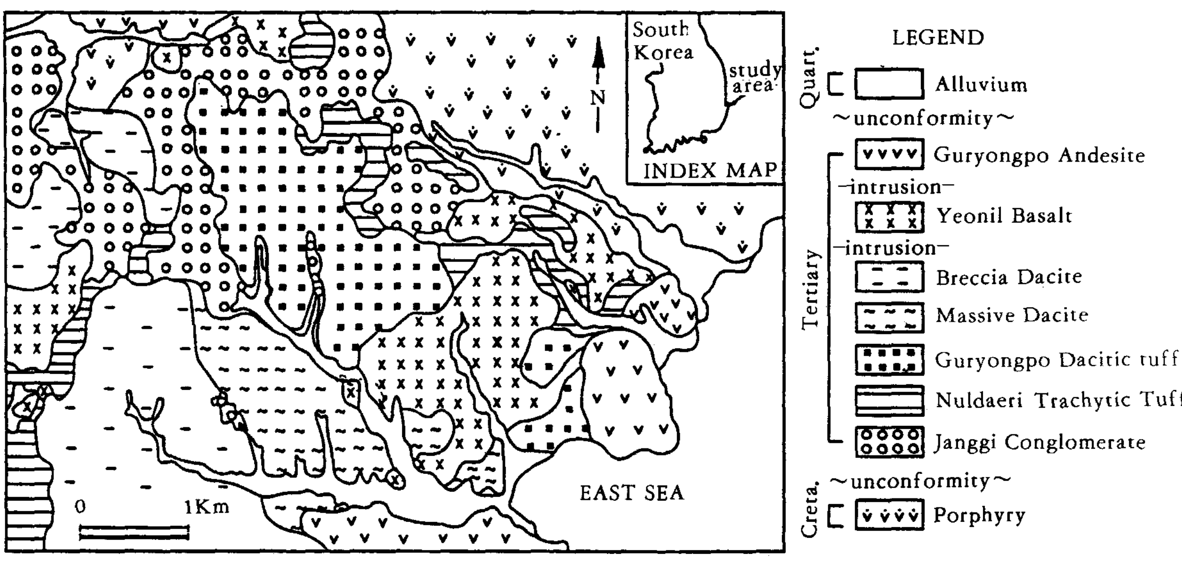


**Fig. 1.** Geologic map of the Guryongpo area, Korea.

(Huzioka, 1972; Kim et al., 1975; Bong, 1981) and rest nonconformably on porphyry and hornfels of Cretaceous age.

The Nuldaeri Trachytic Tuff consists of various volcanic units such as volcanic breccia, tuff and tuffaceous sandstone. Most of the fine-grained tuffs in the Nuldaeri Trachytic Tuff are wholly or partly transformed to zeolitic rocks and minor bentonite as a result of diagenetic alteration.

The Guryongpo Dacitic Tuff lies directly on the Janggi Conglomerate or the Nuldaeri Trachytic Tuff. It consists of various volcanic units such as breccia and tuff. The perlite occurs as large or small blocks, and sandy particles in the Guryongpo Dacitic Tuff. They are wholly or partly altered to smectite and/or zeolite as a result of diagenetic alteration.

The massive dacite and breccia dacite are the volcanics which are possibly related to the deposition of volcanic sedimentary sequence. The Yeonil Basalt and Guryongpo Andesite intrude the Janggi Group.

## RESULTS

### Occurrence of Zeolites

The Nuldaeri Trachytic Tuff contains clinoptilolite and mordenite as major constituent minerals. On the basis of mineralogy and texture, it is subdivided into five units in ascending order:(1) grey chert-like mordenite-rich rock, (2) green and brown mordenite-clinoptilolite rock, (3) green, porcellainic, clinoptilolite-rich rock, (4) white yellow, mordenite-rich rock, and (5) sandstone and tuff. The thickness of each unit varies from place to place from several meters to about 50 m. The mordenite-rich rocks are more dense and hard than the clinoptilolite-rich rock. Bentonitic mudstone is partly intercalated in the upper part of the Nuldaeri Trachytic Tuff.

The Guryongpo Dacitic Tuff contains clinoptilolite and mordenite as minor consti-tuents. The perlite and dacitic glass are its major constituents. Both partly transformed to smectite and/or clinoptilolite and mordenite.

### Diagenetic Fabrics

Zeolitic rocks of the Nuldaeri Trachytic Tuff occur as thick beds showing massive fabric or faint stratification. They show congruent relation to the intercalated sandstone or mudstone. In addition, they contain rock fragments of various size. It is often found that the rock fragments are smectitized. The wholly or partly smectitized or zeolitized perlite fragments are abundantly found in the Guryongpo Dacitic Tuff. The field occurrence of zeolitic rocks suggests their sedimentary nature of the precursor materials, although someone suggests hydrothermal origin. Diagenetic features including replacement, dissolution and precipitation textures are abundantly found in the zeolitic rocks.

Macroscopic as well as microscopic replacement features are abundantly found in the zeolitic rocks. Macroscopic replacement textures are easily found in some part of the Nuldaeri Trachytic Tuff and in the perlite fragments in the Guryongpo Dacitic Tuff. Most of perlite fragments are wholly or partly replaced by smectite and/or zeolite. Replacement of perlite by smectite and/or zeolite begins along its margin or cracks and advances outward. Distinct zoning from fresh perlite to its altered equivalents is common (Noh and boles, 1989). Smectite is found as the first alteration product occurring as thin rim along the wall of the perlitic cracks, whereas clinoptilolite and mordenite are found in the moderately and highly altered zones, respectively.

The mineral distribution is usually discernible by color. The smectite-, clinoptilolite-, and mordenite-rich parts are yellowish, brownish white and greenish, respectively. The greenish color may be related to the high Fe content in low-cristobalite (Noh and Boles, 1989). Mordenite-

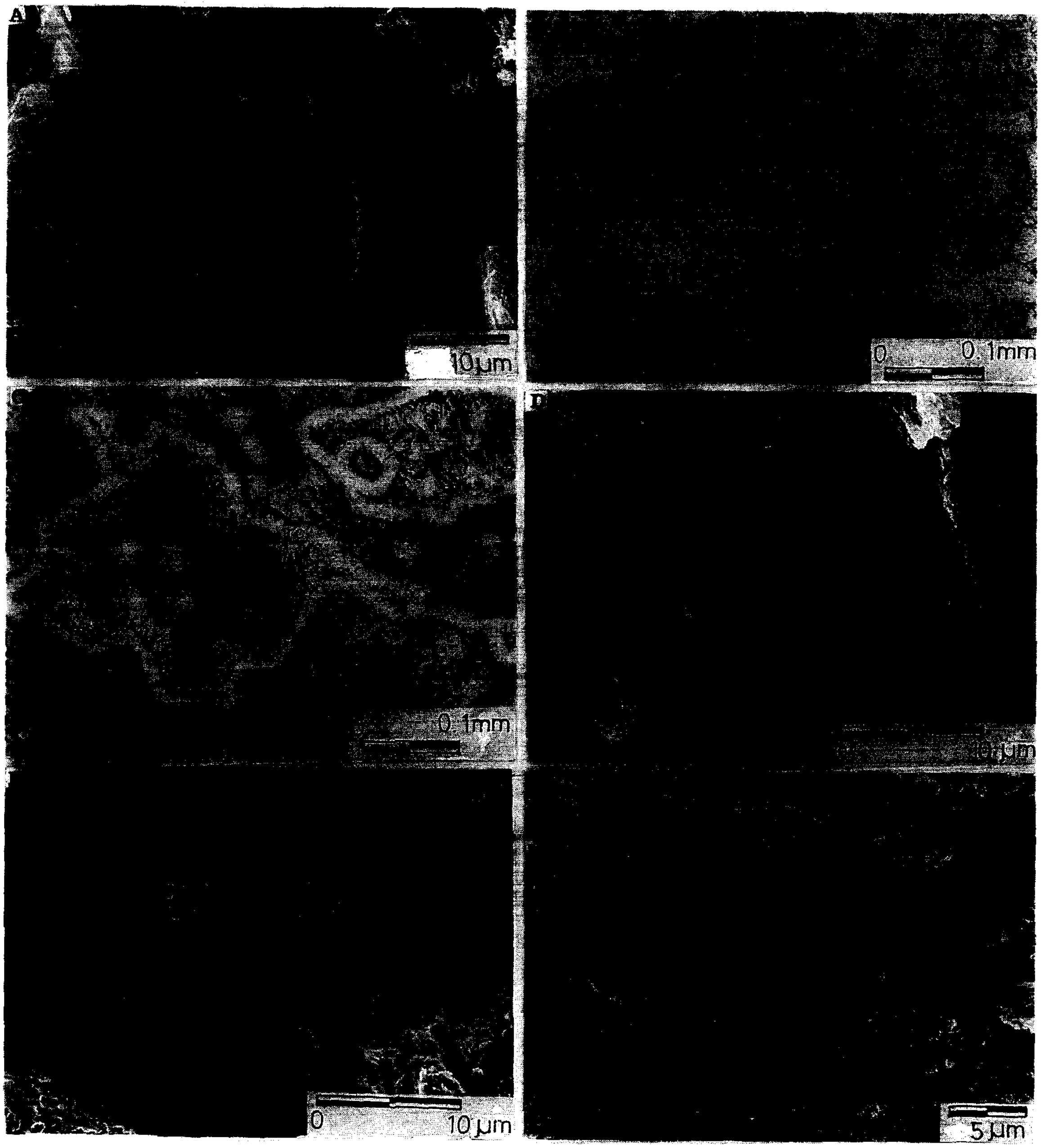


**Fig. 2.** Photomicrographs showing occurrence of clinoptilolite. (A) Scanning electron micrograph showing crystallization of smectite in dissolution cavities of glass (g) and replacement of glass by clinoptilolite (c). (B) Alteration of glass shards to crypotocrystalline clinoptilolite and crystallization of lath-shaped clinoptilolite crystals (lc) in dissolution cavity. (C) Precipitation of rim clinoptilolite (rc) and lath-shaped clinoptilolite (lc) in dissolution cavities of glass shards. (D) Scanning electron micrograph showing the incipient growth of smectite (s) on glass shard (g) and precipitation of clinoptilolite (c) in the smectite cavity. (E) Scanning electron micrograph showing lamellar or the lath-shaped clinoptilolite (c) seen through the broken window of smectite (s) walls. (F) Association of glass (g) with clinoptilolite (c).

rich part is also rich in low-cristobalite.

The glass shards in the vitric tuff are usually replaced by cryptocrystalline clinoptilolite (Figures 2A and 2B) or mordenite (Figure 3A). The original textural pattern of vitric tuff is considerably preserved in the zeolitic rocks (Figure 2B). It is also observed that the gel-like glass (Noh and Boles, 1989) showing colloform surface transformed to mordenite (Figure 3E).

Dissolution and precipitation features are abundantly found in the vitric tuff (Figures 2A and 2C). The cavities formed by dissolution of glass shards are filled with smectite (Figure 2A), or lined with narrow smectite (Figure 2D), clinoptilolite band (Figure 2C) and the remaining cavities are wholly or partly filled with lath-shaped clinoptilolite crystals projecting from the wall (Figures 2B, 2C, 2D and 2E), or with fibrous mordenite (Figure 3E). It is also observed that clinoptilolite fills the interior of smectite walls (Figure 2E). Fibrous or woolly mordenite is found independently (Figure 3E) or in association with clinoptilolite in interstices of replacement mordenite (Figure 3B). It is also observed that woolly mordenite occurs in the cavity of clinoptilolite (Figure 3D). Figure 3C shows the precipitation of clinoptilolite and mordenite near the glass-smectite interface. In some sample, the acicular mordenite grows perpendicular to the collofrom suface of massive gel-like glass (Figure 3E). Mordenite is also associate with quartz vein. Low-cristobalite is associated with fibrous and radiating mordenite (Figure 3F).

## Paragenesis

Textural analysis of zeolitic rock suggests that the zeolite minerals formed as results of mineral-pore water reactions. The alteration of the Nuldaeri Trachytic Tuff and Guryongpo Dacitix Tuff seems to begin with dissolution of glass and precipitation of semctite (Figure 2A). As the glass dissolution proceeded to a considerable stage, clinoptilolite formed by replacement of remaining glass and subsequent precipitation from pore fluid in cavities (Figures 2B and 2C). Shard glass and its initial alteration product (smectite) are metastably persist after crystallization of clinoptilolite (Figure 2D). At a moderate stage of alteration, clinoptilolite and mordenite formed (Figure 3C). At and advanced stage of alteration, mordenite and low-cristobalite co-precipitated (Figure 3F). K-feldspar was iden-tified in the advanced stage of alteration of perlite (Noh and Boles, 1989), but it is not found in the vitric tuff.

## Chemical Composition

The chemical composition of clinoptilolite and mordenite are significantly variable from sample to sample, and even in one and the same sample (Tables 1 and 2). The chemical variations of clinoptilolite and mordenite are shown in the histograms in Figure 4. The weight % of K, Ca, Na and Mg in clinoptilolite are considerably different between the early-formed rim and the late formed lath-shaped clinoptilolites. Si and Al are not significantly variable. The Si/Al ratios are high in the rim clinoptilolite (4.5-5.0) compared with lath-shaped clinoptilolite (4.5). The rim clinoptilolite is rich in Ca, whereas the lath-shaped clinoptilolite is rich in K. The former is rich in Mg compared with the latter. However, both are low in Na (Figure 4). The lath-shaped clinoptilolite in the Guryongpo Dacitic Tuff is significantly high in K compared with that of the Nuldaeri Trachytic Tuff.

Mordenite in the Nuldaeri Trachytic Tuff is significantly rich in K compared with that in the Guryongpo Dacitic Tuff, whereas the latter is significantly rich in Na compared with the former. Earlier mordenite is K-type, whereas late mordenite is (K, Na)-type. The Si/Al ratios of mordenite is higher in the Nuldaeri Trachytic Tuff than in the Guryongpo Dacitic Tuff.

Some differences in chemical composition are

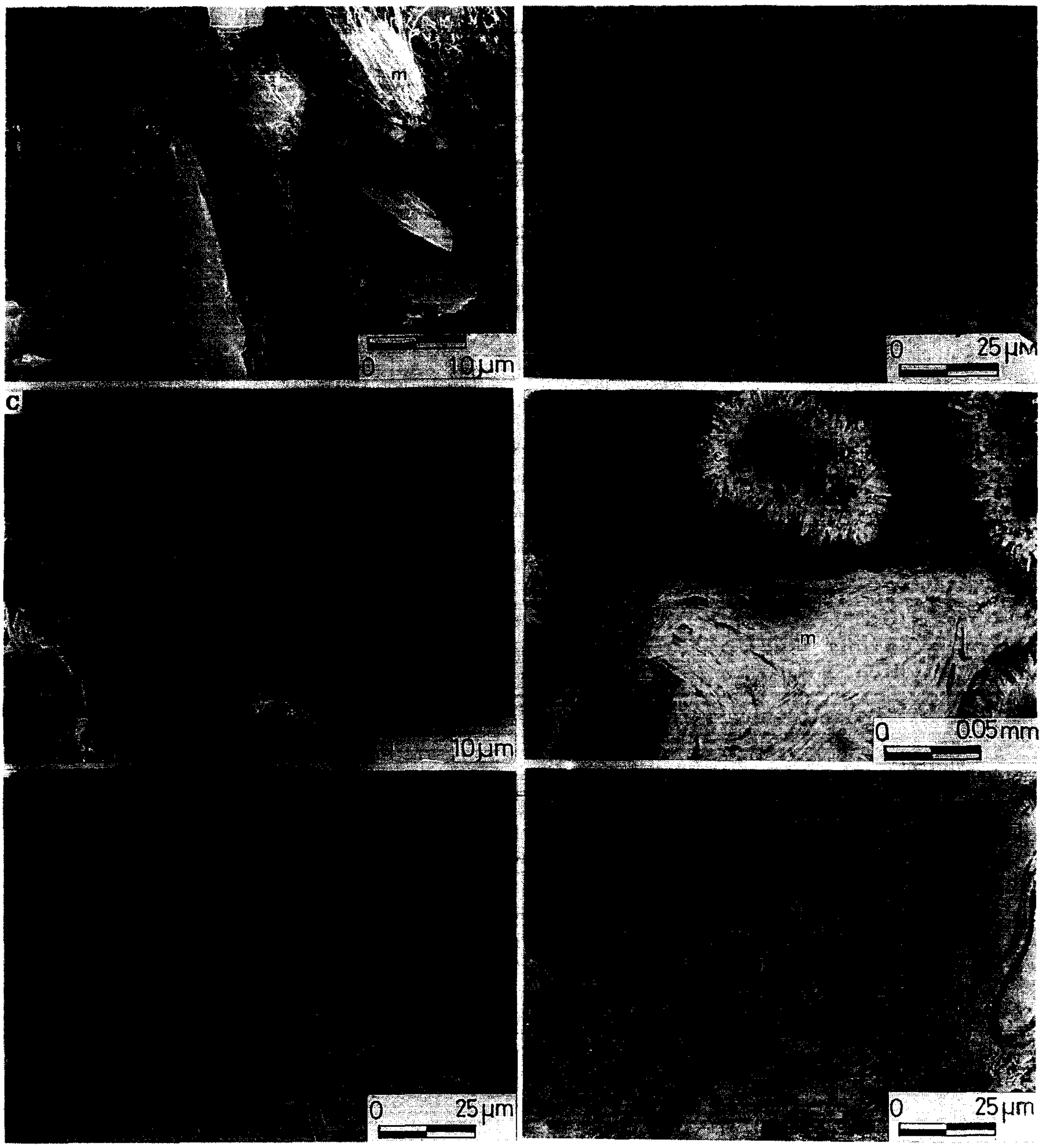


**Fig. 3.** Photomicrographs showing occurrence of mordenite. (A) Fibrous mordenite (m) formed from glass (g). (B) Clinoptilolite (c) and mordenite (m) formed by reaction of gel-like glass (g) with pore fluid. Note the transformation of glass to mordenite. (C) Precipitation of clinoptilolite (c) and mordenite (m) near the glass (g)-smectite (s) interface. (D) Independent crystallization of lath-shaped clinoptilolite (c) and wooly mordenite (m) in a cavity. (E) Crystallization of fibrous mordenite in interstices of colloform glass (g). Note Partial replacement of glass by mordenite fibers. (F) Crystallization of low-cristobalite (cr) and fibrous mordenite (m) in cavity.

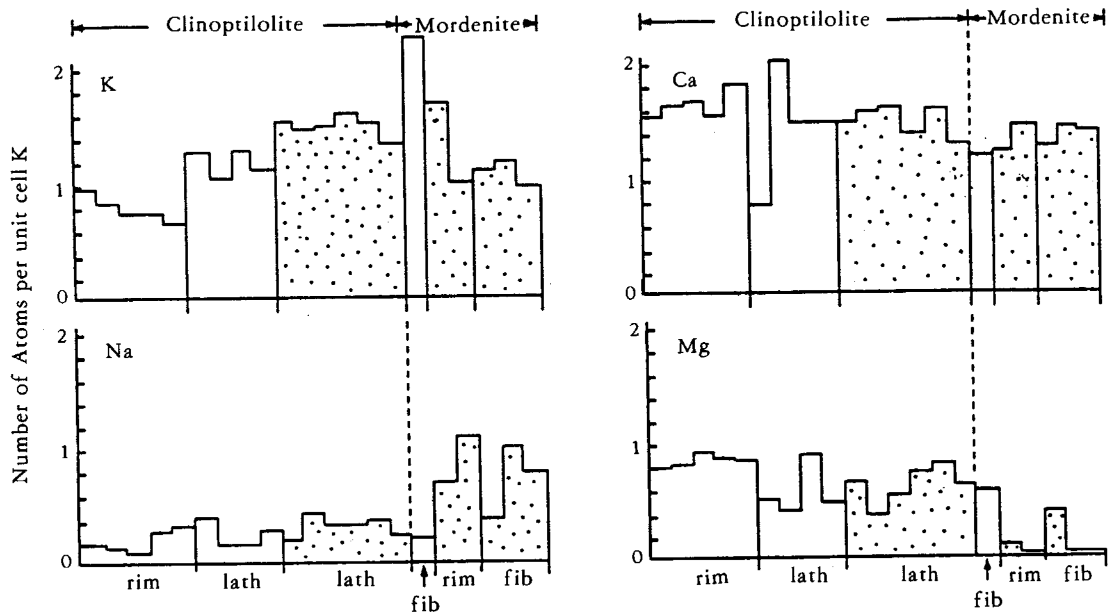


**Fig. 4.** Histograms showing non-homogeneity of clinoptilolite and mordenite. Clinoptilolite occurs as cryptocrystalline rime of dissolution cavities or cavity-filling lath-shaped crystals, whereas mordenite occurs as cryptocrystalline mass or fibers in the Nuldaeri Trachytic Tuff (not dotted) and Guryongpo Dacitic Tuff (dotted).

**Table 1.** Electron microprobe analyses of clinoptilolite.

| | 27-2* | 1-5* | 29-7* | B1-2B+ | B1-2C+ | B1-2D+ |
|---|---|---|---|---|---|---|
| $SiO_2$ | 64.73 | 63.85 | 63.75 | 67.01 | 65.64 | 60.81 |
| $TiO_2$ | 0.02 | – | – | – | 0.01 | 0.01 |
| $Al_2O_3$ | 12.22 | 11.69 | 11.73 | 12.17 | 11.08 | 12.11 |
| $Fe_2O_3$ | 0.13 | – | 0.04 | 0.02 | 0.03 | 0.13 |
| MnO | 0.05 | 0.04 | – | – | 0.01 | 0.05 |
| MgO | 1.25 | 1.17 | 1.23 | 0.78 | 0.95 | 1.12 |
| CaO | 3.63 | 3.20 | 2.41 | 3.25 | 2.72 | 3.03 |
| $Na_2O$ | 0.37 | 0.17 | 0.25 | 0.39 | 0.39 | 0.41 |
| $K_2O$ | 1.15 | 1.43 | 2.56 | 2.61 | 2.73 | 2.54 |
| Total | 83.55 | 81.55 | 81.97 | 86.23 | 83.56 | 80.21 |
| Si/Al | 4.49 | 4.63 | 4.61 | 4.67 | 5.03 | 4.26 |

* From the Nuldaeri Trachytic Tuff.
+ From the Guryongpo Dacitic Tuff.

**Table 2.** Electron microprobe analyses of clinoptilolite.

| | 28-19* | B1-2B+ | B1-3A+ | B1-2C+ |
|---|---|---|---|---|
| $SiO_2$ | 67.94 | 68.05 | 66.31 | 66.52 |
| $TiO_2$ | – | 0.02 | 0.03 | – |
| $Al_2O_3$ | 11.93 | 10.22 | 11.92 | 10.50 |
| $Fe_2O_3$ | 0.10 | 0.06 | 0.07 | 0.04 |
| MnO | – | – | 0.02 | – |
| MgO | 0.06 | 0.05 | 0.84 | 0.05 |
| CaO | 2.91 | 2.83 | 2.37 | 2.89 |
| $Na_2O$ | 1.13 | 0.90 | 0.24 | 1.21 |
| $K_2O$ | 2.03 | 1.61 | 3.70 | 1.70 |
| Total | 85.10 | 83.74 | 85.50 | 82.91 |
| Si/Al | 5.27 | 5.65 | 4.72 | 5.38 |

* From the Nuldaeri Trachytic Tuff.
+ From the Guryongpo Dacitic Tuff.

found between the massive rim and fibrous mordenites in the Guryongpo Dacitic Tuff. The massive rim mordenite is rich in Na and poor in Mg compared with the fibrous mordenite in cavities. It is significant that clinoptiolite and mordenite show considerable non-homogeneity in chemical composition on a microscopic scale as shown in Figure 4. Present study shows that zeolites in both the Nuldaeri Trachytic Tuff and Guryongpo Dacitic Tuff are characterized by low contents of Na and (Ca+Mg) as compared with those in the altered perlite (Noh and Boles, 1989).

## DISCUSSION

Textures of zeolite and associated minerals, and their chemical compositions give important information for the trend of diagenetic alteration of glass in the tuffaceous sedimentary rocks. In altered tuffs, smectite typically occurs lining or filling the cavities (Figure 2A), and zeolites occur replacing shards of filling shard cavities father from the glass-smectite interface. During the initial crystallization of smectite from the perlitic glass, a K-enriched non-crystalline phase (gel-like glass) and pore fluid form (Noh and Boles, 1989). The partial dissolution of glass to form smectite and gel-like glass tends to liberate more silica and sodium into the pore fluid. The increased alkalinity and silica activity of the pore fluid may have facilitated complete dissolution of remnant glass and the simultaneous precipitation of zeolite (Noh and Boles, 1989). Precipitation of clinoptilolite and mordenite near the glass-smectite interface (Figure 3C) suggests the incongruent dissolution and subsequent crystallization from pore fluids. A decreasing alkalinity of the pore fluid after the complete dissolution may be inferred from the precipitation of more silicic types of zeolite and silica minerals in the late stage.

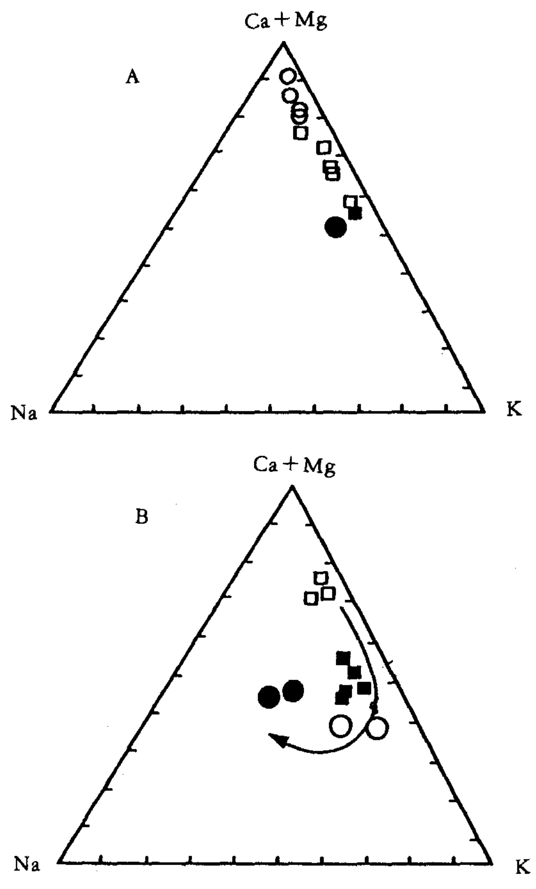


**Fig. 5.** (Ca+Mg)-Na-K ternary digrams showing differences in cations abundance of zeolites in the Nuldaeri Trachytic Tuff (A) and Guryongpo Dacitic Tuff (B). Arrow shows paragenetic trend in zeolite formation. Small open circle: smectite. Open square: rim clinoptilolite. Filled square: lath-shaped clinoptilolite. Large open circle: rim mordenite. Filled circle: fibrous mordenite.

The alkali/alkaline earth ratios increase with alteration of glass as seen on the (Ca+Mg)-Na-K ternary diagram (Figure 5). K varies chiefly with respect to (Ca+Mg), whereas Na is considerably uniform except in the late stage. Chemical compositions of minerals showing the sequential crystallization probably reflect the chemical activity of ions in pore fluids at the time of precipitation and the trend of chemical variation. Therefore, the chemical variation in the pore fluid during mineral formation by alteration of glass can be illustrated by the clockwise chemical trend in the (Ca+Mg)-Na-K ternary diagram (Figure 5). Some difference in the chemical trend of zeolite formation in found between the Nuldaeri Trachytic Tuff and Guryongpo Dacitic Tuff. The chemical trend of zeolite formation is characterized by decreasing Ca and Mg, non-variable Na, and increasing K in the Nuldaeri Trachytic Tuff, and by decreasing Ca and Mg, increasing Na and increasing-decreasing K in the Guryongpo Dacitic Tuff. This difference may be due to the difference in the chemical compositions of parent materials.

Based on the above discussion, the following scenario for mineral formation is suggested. The partial dissolution of glass was the beginning of diagenetic alteration. The glassy materials in the tuff reacted with pore fluid to form smectite, clinoptilolite, or mordenite, depending on the physicochemical environment during diagenesis. Formation of smectite by an initial hydrolysis of shard glass took place at relatively low (Na+K)/H activity ratio (Hemley, 1962). However, the continued hydration of glass resulted in increased alkalinity (Noh and Boles, 1989) and concentration of alkali ions (Hay, 1963). This raised (Na+K)/H activity ratio of the pore fluid, providing a more suitable environment for the formation of alkali zeolites. Clinoptilolite formed from pore fluid with relatively high Si/Al activity ratio. The (Ca, Mg)-clinoptilolite formed early as a replacement product of glass shards, whereas the K-rich clinoptilolite precipitated late in cavities. K-mordenite formed not only as a replacement product of shard glass and gel-like glass but also as crystallization product from pore fluid with higher Si/Al activity ratio. In the Guryongpo Dacitic Tuff, K-mordenite is followed by (Na,K)-mordenite

Although Noh and Boles (1989) showed that mordenite did not form directly at the expense of a glass precursor in perlite, some mordenite formed directly at the expense of shard glass (Figure 3A). Mordenite occurs independently or in associated with clinoptilolite in cavities (Figure 3B). It seems that the early formed gel-like glass (Noh and Boles, 1989) also reacted with pore fluids in the same way as shard glass. Some of clinoptilolite and mordenite crystallized by this reaction (Figure 3B). The reaction involving the transition of less silicic clinoptilolite to an assemblage of silicic Na-rich clinoptilolite and mordenite in the alteration of perlite (Noh and Boles, 1989) is not found in vitric tuff. Independent precipitation of Na-or K-rich mordenite is observed in cavities having clinoptilolite lining (Figure 3D) in the non-perlitic tuffs. K-feldspar formed from the K-rich gel-like glass at a late stage of diagenetic alteration of perlite (Noh and Boles, 1989) but it is not found in the non-perlitic tuffs.

## CONCLUSIONS

The formation of diagenetic zeolites from different tuffaceous sediments are controlled by the chemical composition of parent materials. The diagenetic crystallization sequence established from textural observations and chemical data is Ca-smectite→ (Ca, K)-clinoptilolite→ (K, Na)-mordenite, which indicates that the chemical activities of alkalic ions and Si/Al activity ratio in pore fluids changed systematically with diagenetic alteration. The chemical trend of zeolite formation is characterized by decreasing Ca and Mg, non-variable Na and increasing K in the Nuldaeri Trachytic Tuff, and by decreasing Ca and Mg, increasing Na and increasing-decreasing K in the Guryongpo Dacitic Tuff. This paragenesis indicates a sequence of incongruent dissolution reactions and crystallization from pore fluids. The significant non-homogeneity in chemical composition of zeolites on a micros-copic scale suggests the mon-homogeneity in the pore fluids.

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