# Thermal and Mineralogical Characterization of Ca-Montmorillonite from Gampo Area.

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**Abstract :** Ten under 2 micron size fractions of the montmorillonite from Yongdongri area, Gyeongsangbug-Do were studied using X-ray powder diffraction, cation exchange measurement, differential thermal analysis, thermogravimetric analysis, differential thermal scanning calorimetry and chemical analysis. Montmorillonites occurring at same deposit show limited variation in chemical composition whereas in thermal properties they do not. Their dehydroxylation endothermic peaks are "abnormal" type with a small range of variation of peak temperature reflecting tetrahedral substitution of Al for Si. Data from DSC show that divalent-cation saturated montmorillonite has relatively a higher endothermic heat capacity than monovalent-cation saturated montmorillonite, indicating that cations with higher electronegativity hold more water molecules.

## INTRODUCTION

Bentonites are widespread and one of the most common authigenic minerals in the Gampo area where Tertiary volcanic and volcanic sedimentary rocks are widely distributed. Study on the mineralogy and genesis of bentonites from Tertiary sediments were made by some workers(Noh, et al., 1983; Moon, 1984). Thermal behaviour of montmorillonite occurring here has not been fully understood. Montmorillonites can be classified into "normal" or "abnormal" varieties depending on the dehydroxylation temperature(Green-Kelly, 1953) which are closely related to their chemical composition and structural features(Grim,1968; Grim and Kulbicki, 1961; Mackenzie, 1970; Schultz, 1969; Moon, 1985). Moon studied montmorillonite from the Tertiary sediments

occurring around this area and concluded no examples of completely "normal" or "abnormal" type existed, as those with an apparent single peak showed inflextion on either the low-temperature or high-temperature side of the endotherm. Those examined samples collected from various localities in terms of geography and stratigraphy showed relatively high variation in octahedral substitution. For this study, samples were collected systematically from one deposit in Yongdongri area. The present study is focused on whether or not Ca-montmorillonites occurring at same deposit show changes in thermal characteristics, assuming that these samples show limited variation on octahedral and tetrahedral substitutions.

## MATERIAL AND METHOD

Montmorillonite beds are intercalated in the upper part of the Yongdongri Tuff. These are generally parallel to the orientation of the bed(N20˚~50˚E, 10˚~30˚NW). The eleven montmorillonite samples were collected from this tuff are shown in Fig.1.

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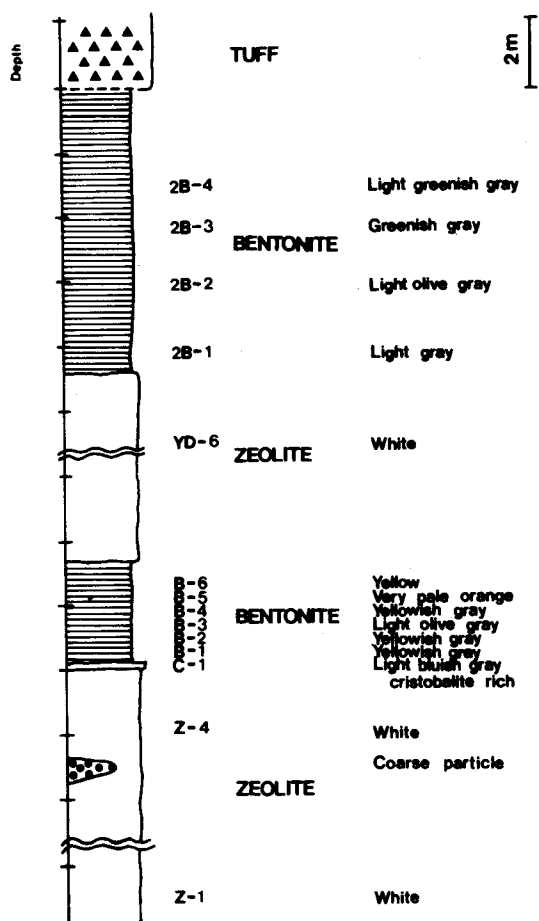**Div. of Mineralogy, KIER, Garibongdong, Gurogu, Seoul,

Depth

TUFF

2m

| 2B-4 | | Light greenish gray |
| 2B-3 | BENTONITE | Greenish gray |
| 2B-2 | | Light olive gray |
| 2B-1 | | Light gray |
| YD-6 | ZEOLITE | White |
| B-6 | | Yellow |
| B-5 | | Very pale orange |
| B-4 | BENTONITE | Yellowish gray |
| B-3 | | Light olive gray |
| B-2 | | Yellowish gray |
| B-1 | | Yellowish gray |
| C-1 | | Light bluish gray cristobalite rich |
| Z-4 | | White |
| | ZEOLITE | Coarse particle |
| Z-1 | | White |

Fig. 1. Columnar section of Yongdongri area showing montmorillonite—rich and zeolite beds.

The lower montmorillonite bed is about 9 meters thick with a yellowish grey colour of exposed or newly exposed surfaces and green colour for buried surfaces.

Contact between montmorillonite and adjacent zeolite beds is very sharp. The lower zeolite shows a "dish structure" which could have been formed during the consolidation of rapidly deposited sediments in water due to the upward escape of water(Pederson et al., 1977), whereas montmorillonites do not show any clear sedimentary structure. The only observable structure on montmorillonite horizons is a faint laminae developed in the lower part of the

bed. The montmorillonites are very soft and friable.

The bulk samples were first analyzed by X-ray diffraction(XRD) to determine the mineralogical composition of bulk samples. Montmorillonites contents were quantified by XRD and the ethylene glycol monoethyl ether(EGME) surface area measurement. Under 2 micron size fractions were obtained by sedimentation method in order to get as pure as possible montmorillonite for chemical and thermal analysis. Purified and Ca-saturated montmorillonites were examined by XRD and wet chemical method for $Fe^{2+}$.$H_2O$ was determined by the thermogravimetry. Chemically characterized samples were then studied by the differential thermal(DTA), thermogravimetric(TG) and differential scanning calorimetry(DSC) analysis using of SEIKO TG/DTA 30 and DSC 20 thermal analysis equipment. Applied sample weight and heating rate in this study was 40mg and 12℃°min, respectively for TG and DTA. For the DSC, 20mg sample and 10℃/min heating rate was used. For thermal studies, montmorillonites were saturated with various cations such as Na, K, Mg, Ca and Ba. Cation exchange capacities(CEC) and total exchangeable cations of the montmorillonites were determined by the $NH_4OAc$ method.

## RESULT AND DISCUSSION

### Mineralogy and Mineral Chemistry

All the bulk samples consist mainly of montmorillonite with more than four other minerals as impurities such as feldspar, cristobalite, quartz, mica (mainly biotite) and zeolite as summarized in Table 1.

Montmorillonite content calculated from an EGME surface area values assuming that 1m² of clay surface required $2.86 \times 10^{-4}$g EGME for a monolayer coverage(Carter et al., 1965) range from 40-65% indicating that impurity contents are very high. In every sample examined, the basal reflections of the montmorillonite range between 15.3-16.4Å indicating that predominant cations are divalent. The d-spacing of

**Table 1.** Mineralogical compositions of the bulk samples.

| Sample No. | Predominant mineral | Other clay minerals | Non clay minerals | Montmorillonite (001) spacing (Å) |
|---|---|---|---|---|
| B - 1 | Mont | Mi | Fd, Cr, Q | 16. 1 |
| B - 2 | Mont | Mi | Fd, Cr, Q, Cl | 15. 7 |
| B - 3 | Mont | Mi | Cr, Fd, Q | 15. 6 |
| B - 4 | Mont | Mi | Cr, Fd, Q | 15. 3 |
| B - 5 | Mont | Mi | Fd, Cr, Q | 16. 0 |
| B - 6 | Mont | Mi | Fd, Cr, Q, Cl, Md | 16. 4 |
| 2 B - 1 | Mont | Mi | Fd, Cr, Q | 16. 0 |
| 2 B - 2 | Mont | Mi | Cr, Fd, Q | 16. 1 |
| 2 B - 3 | Mont | Mi | Fd, Cr, Q | 15. 9 |
| 2 B - 4 | Mont | Mi | Fd, Q, Cr | 15. 7 |

Mont;montmorillonite, Mi;mica, Fd;feldspar, Cr;cristobalite, Q ;quartz, Cl ;clinoptilolite, Md;mordenite.

(060) peak was $1.50\pm 0.01$Å indicating that all examined montmorillonites are dioctahedral. Comparing the mineralogical composition, there is no significant variation with respect to stratigraphical variation in this occurrence. It is worth to note that although quartz is the one of the common accessory minerals, it occurs only as a minor constituent in spite of the abundance of quartz in stratigraphically adjacent tuffaceous sandstones and sandstones.

Purified montmorillonite obtained by the sedimentation method contains appreciable amounts of non-clay minerals as impurities, but impurity content was clearly less than that of the bulk sample. Impurities were identified by XRD and quantified by the Mackenzie's method(1960). After impurity correction, calcu-lated structural formulae were calculated and related data are listed in Table 2.

Substitution of Al for Si in tetrahedral positions range from 0.08 to 0.18 atoms per unit cell. Total negative lattice charge originating from octahedral substitution range 78-90 percent. By Weir and Green-Kelly's definition(1962), all of these samples are montmorillonites. As expected variations in tetrahedral and octahedral substitution of all the present samples are smaller than those of samples occurring different localities in the Tertiary sediments as previously reported by Moon(1985). They still show some degree of variations but are relatively limited, indeed, even though they occur in the same bed. The total numbers of octahedral cations in the unit cell are

**Table 2.** Structural formulae of of the montmorillonites.

| Samle No. | Tetrahedral | | Octahedral | | | | Total cations in octahedral | Layer charge | |
|---|---|---|---|---|---|---|---|---|---|
| | Si | Al | Al | $Fe^{3+}$ | $Fe^{2+}$ | Mg | | Octahedral (%) | Total (eq. /unit cell) |
| B - 1 | 7.89 | 0.11 | 2.80 | 0.50 | 0.03 | 0.67 | 4. 00 | 86. 42 | 0.81 |
| B - 2 | 7.82 | 0.18 | 2.94 | 0.41 | 0.03 | 0.62 | 4. 00 | 78. 31 | 0.83 |
| B - 3 | 7.87 | 0.13 | 2.91 | 0.42 | 0.02 | 0.65 | 4. 00 | 83. 75 | 0.80 |
| B - 4 | 7.85 | 0.15 | 2.90 | 0.42 | 0.04 | 0.69 | 4. 05 | 79. 45 | 0.73 |
| B - 5 | 7.88 | 0.12 | 2.60 | 0.54 | 0.14 | 0.81 | 4. 09 | 85. 00 | 0.80 |
| B - 6 | 7.83 | 0.17 | 2.85 | 0.55 | 0.03 | 0.51 | 3. 94 | 80. 90 | 0.89 |
| 2 B - 1 | 7.86 | 0.14 | 2.72 | 0.47 | 0.07 | 0.80 | 4. 06 | 83. 13 | 0.83 |
| 2 B - 2 | 7.86 | 0.14 | 2.56 | 0.47 | 0.12 | 0.94 | 4. 09 | 84. 95 | 0.93 |
| 2 B - 3 | 7.92 | 0.08 | 2.96 | 0.37 | 0.09 | 0.54 | 3. 96 | 90. 36 | 0.83 |
| 2 B - 4 | 7.90 | 0.10 | 2.98 | 0.39 | 0.06 | 0.56 | 3. 99 | 86. 67 | 0.75 |

**Table 3.** Cation exchange capacities and extractable cations for under 2 micron size fractions.

| Sample No. | CEC (meq/100g) | | | Extractable cation (meq/100g) | | | | |
|---|---|---|---|---|---|---|---|---|
| | [1]Calculated | [2]Measured | [3]Corrected | K | Ca | Mg | Na | Total |
| B − 1 | 110.5 | 72.2 | 83.3 | 5.7 | 38.3 | 22.5 | 3.9 | 70.4 |
| B − 2 | 113.7 | 76.4 | 93.4 | 5.9 | 38.3 | 20.0 | 4.2 | 68.9 |
| B − 3 | 109.5 | 71.8 | 87.2 | 6.1 | 35.6 | 24.5 | 4.5 | 70.7 |
| B − 4 | 99.7 | 75.1 | 91.1 | 4.2 | 36.2 | 26.8 | 2.9 | 70.1 |
| B − 5 | 108.2 | 68.0 | 79.1 | 6.6 | 38.8 | 18.0 | 4.6 | 67.5 |
| B − 6 | 121.4 | 61.9 | 78.0 | 5.7 | 37.3 | 13.3 | 3.9 | 60.2 |
| *2 B − 1 | 113.0 | 66.3 | 91.7 | 1.8 | 41.3 | 15.2 | 2.6 | 60.9 |
| *2 B − 2 | 126.3 | 68.7 | 96.5 | 5.0 | 47.0 | 26.2 | 3.2 | 81.4 |
| *2 B − 3 | 113.6 | 60.6 | 81.1 | 1.7 | 36.1 | 19.3 | 2.0 | 59.1 |
| 2 B − 4 | 102.6 | 67.9 | 74.7 | 2.2 | 41.4 | 20.2 | 2.3 | 66.1 |

1. Caluculated CEC = (total lattice charge/formula weight) × 1000 × 100

2. Measured CEC by using of ammonium acetate

3. Corrected CEC result from impurity correction

*; reported value from the bulk sample

close to 4.00, which is ideal amount for dioctahedral clays(Foster, 1951 ; Newman and Brown, 1987), ranging from 3.97 to 4.07 per unit cell indicating calculated structural formulae were valid.

Four bulk samples and seven under 2 micron size fractions were analyzed for total exchangeable cations and exchange capacities using the ammonium acetate method. Results for the measured CEC and calculated CEC from the structural formulae with corrected CECs on the impurity free basis are given in Table 3.

The predominant exchangeable cations in the present samples áre Ca and Mg as expected from XRD data. The percentage of divalent cations to the total exchangeable cations was more than 83 percent in all the present samples. Corrected CECs from the directly measured values are lower than calculated CECs from the structural formulae. The cause of such difference is uncertain but the incomplete exchange reaction is probably responsible for this. However, corrected CEC values are in fairly good agreement with the calculated CEC.

### Thermal Characteristics of Montmorillonite

### Differential thermal analysis

DTA curves of the present samples are shown in Fig.2.

DTA curves of the montmorillonite can be separated into three parts: Low-temperature region (<300°C) related to sorbed water, the dehydroxylation region (400-800°C) and high temperature region (>800°C) related to mineralogical transformation. First two parts were considered here. All show a single low-temperature endothermic peak with a poorly defined shoulder on the high temperature side of the peak with temperature of the first peak ranging between 80-93°C and of the second between 158-166°C. Exchangeable cation composition of these samples are almost identical to each other, therefore such a big differences in peak temperature is not expected. Differences in peak area can explain variations in amount of absorbed water from sample to sample. Endothermic temperatures of the first two parts of DTA curves are reported in Table 4.

The dehydroxylation endothermic peak system lie between 612°C and 674°C. "Normal" montmorillonite shows a single dehydroxylation endotherm at about 700°C whereas "abnormal" montmorillonite give either a single endotherm at about 550°C or a dual peak between 550°C and 650°C. On the basis of dehydroxylation
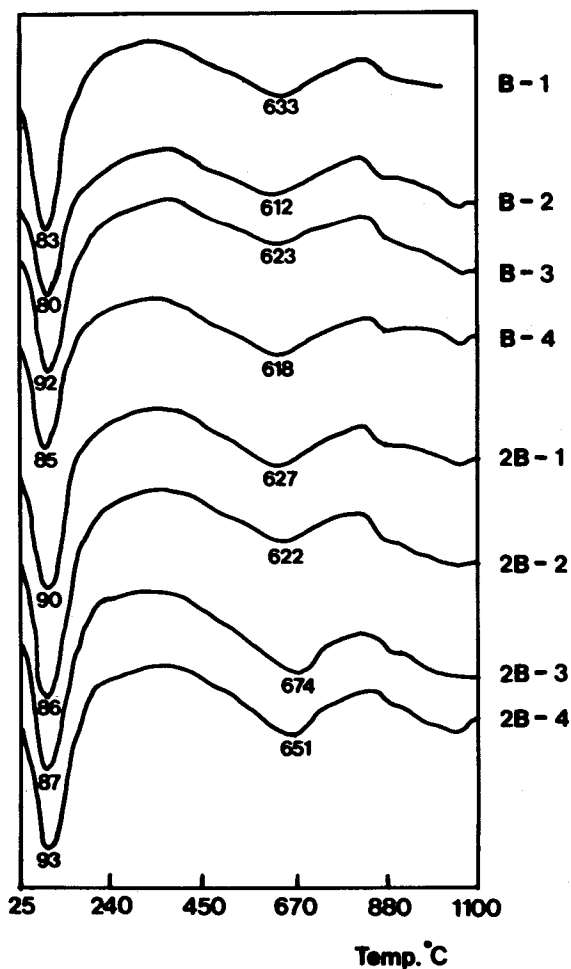
behaviours the present samples can be considered "abnormal" type. No other type was recognized. It suggests that montmorillonite occurred in same stratigraphic horizon appear to have identical thermal character. Because dehydroxylation temperatures of the present samples are lower than that of the "normal" type and dehydroxylation endothermic shows an inflection on the lower-temperature side. As shown in Fig.2, all DTA curves are similar but there is a small variation in endothermic temperature. As suggested by Schultz(1969) and Moon(1985), dehydroxylation temperature does increase with decrease of in tetrahedral substitution Al for Si. Even samples showing a limited range of tetrahedral substitutions and belonging to the same abnormal type, such relationship appears as plotted in Fig.3.

It was reported that high substitution of Mg by Fe in the octahedral layer decreases the dehydroxylation temperature(Heller-Kallai and
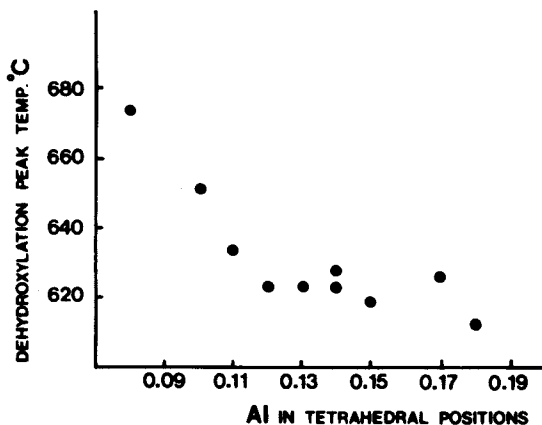
**Fig. 2.** DTA curves of some selected montmorillonites from Yongdongri area.

**Table 4.** Endothermic peak temperatures of the two regions.

| Sample No. | Low temperature endothermic peak (℃) | Dehydroxylation peak temperature (℃) |
|---|---|---|
| B — 1 | 83 | 633 |
| B — 2 | 80 | 612 |
| B — 3 | 92 | 623 |
| B — 4 | 85 | 618 |
| B — 5 | 92 | 622 |
| B — 6 | 90 | 625 |
| 2 B — 1 | 90 | 627 |
| 2 B — 2 | 86 | 622 |
| 2 B — 3 | 87 | 674 |
| 2 B — 4 | 93 | 651 |

**Fig. 3.** Relationship between major dehydroxylation peak temperatures and Al in tetrahedral positions.

Rozenson, 1980). This cannot be monitored in the present samples. It might be due to the fairly constant cation number in octahedral position.

### Thermogravimetric analysis

Thermogravimetric curves of the present samples are shown in Fig.4.

All the samples give typical TG curves of montmorillonites. Rapid initial losses continue about 200°C with plateau region following up to
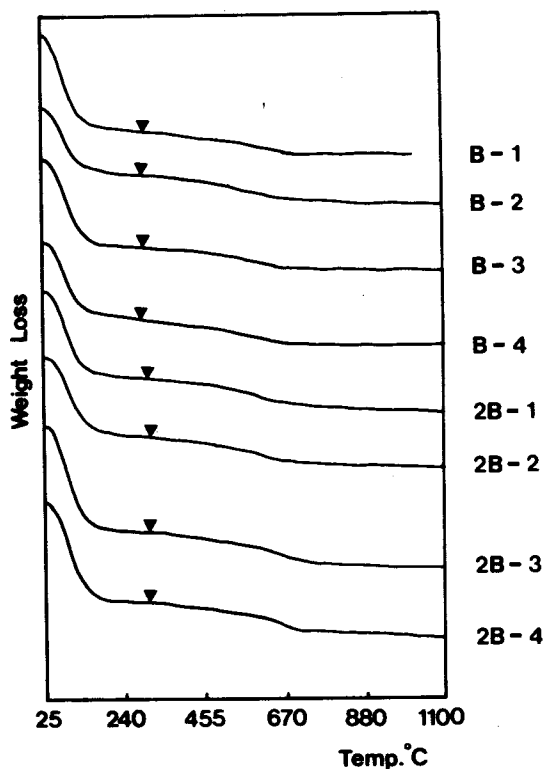


Fig. 4. TG curves of various cation saturated montmorillonites.

about 500°C reflecting losses of cation coordinated and hydroxyl water. Finally hydroxyl water loss appears. In Fig.4, triangular symbols are mid-point temperature of the plateau region and assigned the water loss above this to hydroxyl water using of Schultz's method(1969).

The slope of the plateau region of these studied samples are almost identical ranging from 4 to 6 degree when TG curves were made with full chart paper as 100%. Cation composition and the percentage of divalent cations to

the total are also identical as shown in Table 3. Mielenz et al.(1955) reported that the slope of the plateau region was affected by the valency of the exchangeable cation. They concluded that monovalent-cation saturated montmorillonites show a smaller slope in the plateau region than that of a divalent-cation saturated one. Moon(1985) queried their conclusion on the basis of variation of slope in the Ca-saturated montmorillonites and suggested that variation in the exchangeable cation assemblage is not the sole cause of the difference in slope of the plateau region. Concerning DSC results from the various cation-saturated montmorillonites from this study, generally divalent-cation saturated montmorillonites have slightly higher endothermic heat capacities. If the montmorillomtes have higher endothermic heat capacities (which is saturated with divalent-cations), they should have a greater slope in the plateau region than those of monovalent-cation saturated montmorillonites. Considering this, divaient cation saturated montmorillonite should show a greater slope than monovalent-cation saturated montmorillonite. It indicates that valency of exchangeable cations do effect the slope of the plateau region in some extent.

Reaction mechanics of this region in still uncertain but the generally low—temperature endothermic reaction is closely related to its cation composition and relative water content, as suggested by many workers.

In a high temperature region reflecting losses of hydroxyl water is initially rapid but may continue gradually up to 1100°C. Hydroxyl water loss above 800°C is very limited. No characteristic of this region can be recognizable considering variation of DTA curves of this region.

### Differential scanning calorimetry

DSC between 25–400°C : The main advantage of DSC over DTA is that it is quantitative for change in enthalpy and heat capacity.

Consequently can be it used to determine not only enthalpy change but also the total energy any specific temperature range (Fripiat, 1982 ;

**Table 5.** DSC results and charge densities of under 2 micron size fractions of the montmorillonites and bulk samples.

| Samlpe No. | Endothermic heat capacity (mJ/mg) | | Endothermic temperature (℃) | Charge density* (eq./unit cell) |
|---|---|---|---|---|
| | < 2 size fractions | bulk samples | | |
| B − 1 | 372.2 | − | 123 | 0.15 |
| B − 2 | 371.7 | 272.8 | 126 | 0.15 |
| B − 3 | 421.4 | − | 122 | 0.15 |
| B − 4 | 321.4 | 206.8 | 124 | 0.13 |
| B − 5 | 311.0 | − | 123 | 0.14 |
| B − 6 | 336.5 | − | 121 | 0.17 |
| 2 B − 2 | 447.5 | 263.5 | 121 | 0.17 |
| 2 B − 3 | 357.0 | 327.5 | 128 | 0.15 |
| 2 B − 4 | 461.9 | − | 121 | 0.16 |

−; not determined

*; charge density was calculated from the structural formula

Mackenzie, 1980).

For DSC analysis a sealed sample container was used but it was pinholed. Measured heat capacities of the purified montmorillonites (under 2 micron size fractions), bulk samples and calculated charge densities are listed in Table 5.

Charge densities are calculated from the CECs derived from structural formulae assuming that the surface area of the montmorillonite is 750㎡/g. Endothermic temperatures of DSC ranges between 121-128℃ and are about 30-40℃ higher than those of DTA results. This is indication of slow heat escape due to sealing of the sample container. Endothermic heat capacities of the purified montmorillonite range from 311 to 461 mJ/mg and those of some bulk samples range between 206 and 327 mJ/mg which is considerably lower than those of purified samples. This is mainly due to the anhydrous mineral impurities in the bulk samples. Absolute values of heat capacities show relatively wide variation due mainly to differences in moisture content, eventhough the samples were equilibrated at the same room temperature condition as noted in DTA and TG, and variations of impurities from one sample to another. For DSC analysis carefully controlled experimental conditions and humidity were required but the instrument used here did not strictly control that. However, relationship between charge densities and endothermic heat capacities shows some degree of agreement, probably reflecting the fact that higher layer charged montmorillonite lead to tighter bonds between the clay layer and cations.

Various cation—Ba, Ca, Mg, Li, Na and K—saturated montmorillonites were studied and the results are shown in Fig.5.

Saturation was achieved by 1N chloride salt of Ba, Mg, Ca, K and Na and 3N for Li. The endothermic peak due to the loss of absorbed water is single, double or triple for certain cations depending on relative humidity (Hendricks et al., 1940). As shown in Fig. 5, some of the present samples show single peak while the others show double peak. According to Hendricks et al. (1940), monovalent-cation saturated montmorillonite with a low humidity shows a single peak, indicating appeared in monovalent-cation saturated samples in this study, indicating relative humidity is more than 40%. Assuming that the relative humidity of present samples are almost identical.

Correlations between electronegativity of various cations and endothermic heat capacities were considered. The results are shown in Fig. 6.

The electronegativities for Mg, Ca, Ba, Li, Na and K are 1.2, 1.0, 0.9, 1.0, 0.9 and 0.8, respectively, quoted from Pauling (1960). Mason and Moore(1982) stated that the degree of hydration depends not only on the size of
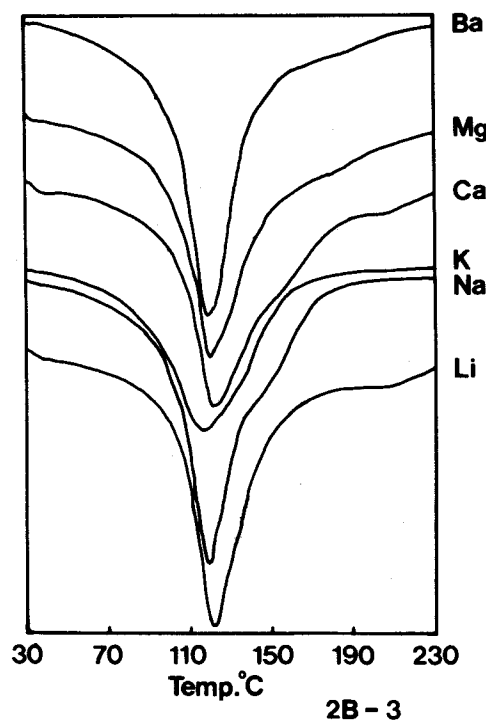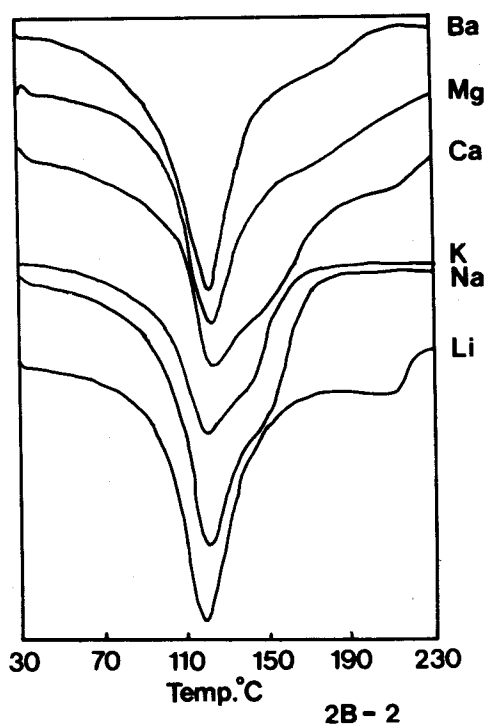
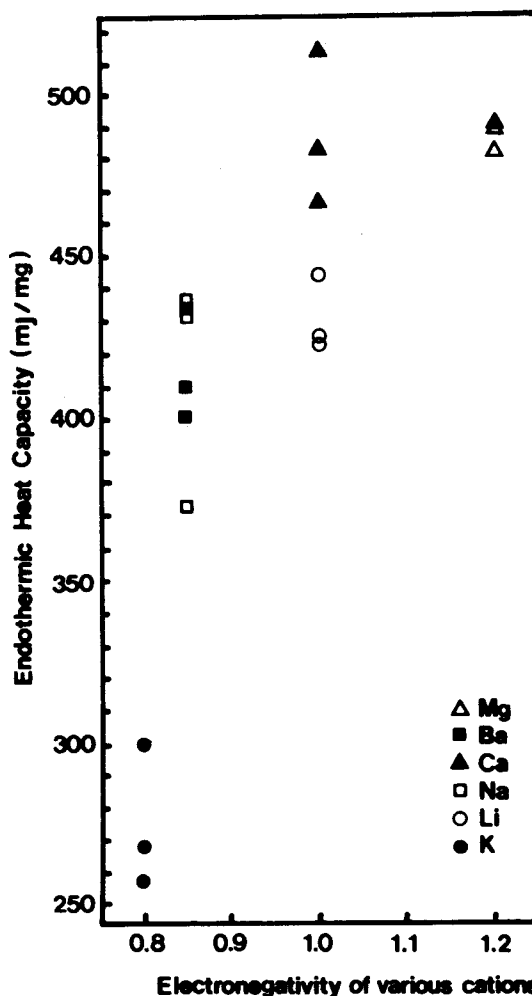**Fig. 5.** DSC curves of various cation saturated montmorillonites.



**Fig. 6.** Relationship between endothermic heat capacity and electronegativity of various cations.

ion but also on the intensity of the charge on its surface. Results of study also show that montmorillonite with higher electronegativity hold more water molecules, therefore the endothermic heat capacity for the separated water molecule from this is of a high value. Among these various cation-saturated montmorillonites, generally, potassium having relatively low electronegativity, show lower endothermic heat capacity than other cations. It is obvious that ionic potential is of great influence for the hydration of an ion.

## CONCLUSION

Mineral chemistry of the present samples revealed that there are limited variations of substitution of Al for Si in tetrahedral position and substitution of $Fe^{3+}$, $Fe^{2+}$ and Mg for Al in octahedral position eventhough they occurred at same locality. Substitution in tetrahedral position ranging from 0.08 to 0.18 atom per unit cell. Schultz(1969) classified smectites into six different types depending on their thermal properties and chemical constitution. Using Schultz's classification most of the present samples can not be fixed into any one of his classifications. Many members of the montmorillonite series could not be fixed in this classification probably due to the net layer charge caused by oxidation of iron in the structure at the weathered or exposed surface as suggested by Schultz(1969). Brigatti and Poppi(1981) stated that substituion of Al for Si in the tetrahedral sheet not show significant variance. Thermal properties of the present samples are somewhat unique but almost identical each other. On the basis of dehydroxylation behaviour, all the present samples are of the "abnormal" type because dehydroxylation temperatures are lower than that of the "normal" type appearing at about 700℃ with endothermic peaks as an inflection on the lower-temperature side. No other type was observable. It indicates that such a small variation in mineral chemistry probably does not influence its thermal properties. In other words, montmorillonite occurred in the same stratigraphic and geographic locality appear to have identical thermal characters even if their chemical composition vary in a limited range.

Although the exact mechanism of the internal substitution how to affect to the dehydroxylation peak temperature is not known with certainty, it can be monitored in this study that dehydroxylation peak temperature does decrease with increase in tetrahedral substitution Al for Si eventhough their variations are limited. Data provided by TG and DSC is that divalent-cation saturated montmorillonite has higher endothermic heat capcity reflecting that montmorillonite with higher electronegativity hold more water. Endothermic heat capacities must be examined with a greater precision using carefully controlled experimental conditions of DSC and moisture of the sample and then these interpretations can be fully reconciled.

## ACKNOWLEDGEMENTS

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# 甘浦地域 Ca-몬모릴로나이트의 熱的 및 鑛物學的 特性

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요약 : 甘浦地域의 용동리에서 龍洞里凝灰岩내에 배태되는 Ca-몬모릴로나이트들은 비록 同一層準에서 産出되나 制限的이지만 化學組成의 差異가 나타난다. 이들의 열적특성은 "비정상型"으로 나타나며, 탈수와 관계된 흡열반응피크의 溫度는 사면체내의 Si를 치환한 Al의 양적비에 따라 약간변화된다. 이러한 사실은 제한적인 화학조성의 변화는 열적특성에 큰 영향을 미치지 못함을 지시한다. 시차주사열량 측정결과 2가의 양이온으로 치환 된 시료의 경우 1가의 양이온으로 치환된 시료보다 흡열용량이 증가되는 경향을 보이므로 시료내의 우세한 양이온의 종류를 예상할 수 있으며, 전기음성도가 큰 이온일 수록 더 많은 물분자를 取함을 알수있다.