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Thermal Behaviour of Some Montmorillonites with related their Chemical Compositions

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Abstract: Detailed chemical compositions of thirteen montmorillonites and their thermal behaviour by differential thermal and thermogravimetric analysis have been studied. Comparison of structural formulae with experimental results by thermal analysis gave evidence of that both substitutions of Fe for Al in octahedral and Al for Si in tetrahedral positions appear to affect dehydroxylation temperature, which is valid for the present samples. Further detailed study of this topic using well-known samples which have various degree of substitution will be justified.

INTRODUCTION

Differential thermal analysis(DTA) curves in the dehydroxylation region have been used for the classification of montmorillonite into "normal" or "abnormal" varieties depending on the temperature range in which dehydroxylation occurs. The endothermic peak system due to dehydroxylation shows a wide variation in peak temperatures. Normal montmorillonites give a dehydroxylation endotherm at about 700°C whereas abnormal varieties show either a single endotherm at about 550°C or a dual endothermic system between 550° and 650°C. The reasons for variation in dehydroxylation temperature have not yet been satisfactorily explained. Dual peaks in this region may be the result of "structural irregularities" (Grim, 1968) or mixing of layers (Grim and Kulbicki, 1961). Mackenzie (1957, 1970) suggested that variations in dehydroxylation peak temperature must be related to differences in bonding energies of hydroxyl groups in the structure. Schultz (1969) suggested that a lowering in dehydroxylation temperature is mainly a result of weak bonds due to large amounts of tetrahedral substitutions in the structure.

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The purpose of this paper is to describe the relationships between isomorphous substitution in the structure of montmorillonites and their thermal behaviours with particular reference to their dehydroxylation temperature.

MATERIALS AND METHODS

Thirteen samples were collected from the Tertiary sediments of Miocene age for the detailed investigations. Six of these were from the Janggi aera (Y-series), three from the Gampo area (G-series), three from the Haseo area (H-series), and one from the Pohang area (C-series). These samples represented montmorillonites found in each of the major Tertiary stratigraphic sequence in the area. Under 2 micron size fraction was obtained by the sedimentation method to obtain montmorillonite fractions of sufficient purity for chemical analysis, DTA and thermogavimetric analysis (TG).

Mineralogical composition and quantitative analysis of the purified samples were examined by X-ray diffraction (XRD) and infra-red analysis (IR). XRD and IR were made using a Philips generator with iron-filtered Co-ka radiation and Perkin-Elmer model 577 spectrometer with a NaCl prism, respectively. Stanton Redcroft equipments were used for thermal analysis.

All DTA and TG runs were made with a same heating rate of 15°C/min. TG curve was made with a dried nitrogrn atomosphere. All major elements, excluding Fe^{2+}/Fe^{3+} ratio and water content, reported in this study were obtained using inductively coupled plasma spectrometry by the method of Walsh (1980). FeO was determined by the amonium metavanadate method of Wilson (1955) and $H2O^-$ by TG.

STRUCTURAL FORMULAE

Structural formulae of montmorillonites were calculated by the method of Mackenzie (1960) from the chemical compositions shown in Table 1. Before structural formulae calculation, very careful correction of the chemical analysis is necessary to allow for the possible presence of mineral impurities, free iron oxide, silica, alumina, and exchangable cations (Foster, 1951; Osthaus; 1955; Mackenzie; 1960). Free silica and alumina were determined by the sodium carbonate method of Follet et al. (1965) and free iron oxide was measured by the sodium dithionite/citrate method of Mehra and Jackson (1960). Results from these treatments are not tabulated and discussed here in detail for the brevity. Amounts of extracted free silica ranged from 0.54~3.16 percent which corresponded to 1.1~5.3 percent of the total silica contents. Extracted alumina contents ranged from 0.23~1.69 percent, equivalent to 1.6~9 percent of the total alumina contents. Some samples, for example Y-11-1, Y-33-2, Y-16, H-5 and H-U-33, show relatively high free silica and alumina value which, if not allowed for in calculation of the structural formulae, could seriously affect the validity of these. Amounts of free iron extracted during the first treatment ranged from 0.20~1.71 percent while amounts extracted during the second treatment ranged from 0.08~0.77 percent. Only the first extracted iron oxide was substracted from the original analysis. The proportions of extracted to total iron were higher than the corresponding ratios for silica and alumina.

Chemical analyses of montmorillonites usually show minor amounts of titanium oxide. manganese oxide, and phosphorus pentoxide. Amount of the last two oxides are usually ignored during structural formula calcuations. However, TiO_2 contents in some samples such as Y-22 and Y-33-2 etc were greater than 1 percent. Deer, Howie and Zusman (1966) stated that Ti may replace Si in small amounts. The pre-

Table 1 Chemical analysis of <2 micron size fractions of the montmorillonites.

Sample	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	$H2O^+$	$H2O^-$	Total
Y-13	54.01	18.57	3.30	0.46	2.23	1.92	0.19	0.58	0.51	0.11	0.08	5.04	12.96	99.95
Y-11-1	60.36	14.20	2.11	0.32	2.65	1.87	0.07	0.47	0.30	0.09	0.11	3.58	13.82	99.96
Y-22	50.64	17.64	5.90	0.93	2.31	2.30	0.34	0.77	1.22	0.21	0.02	4.95	12.65	99.90
Y-33-2	48.92	16.79	7.42	0.83	2.35	2.13	0.14	0.19	1.39	0.26	0.02	5.04	14.42	99.91
Y-3-1	46.75	17.22	8.07	0.61	2.93	2.13	0.01	0.35	1.57	0.12	0.12	5.73	14.05	99.93
Y-16	56.65	17.62	3.52	0.42	1.82	1.74	0.09	0.23	0.42	0.07	0.06	4.71	12.67	100.06
G-46	52.98	15.61	1.22	0.59	4.47	2.64	0.14	0.09	0.21	0.05	0.03	4.10	17.80	99.93
G-66-2	52.11	15.45	4.67	0.77	3.25	2.63	0.06	0.02	0.68	0.06	0.02	4.60	15.60	99.91
G-YD-2	55.57	15.77	2.54	1.84	2.36	2.20	0.11	0.10	0.34	0.06	0.12	4.20	14.60	99.80
H-5	57.53	14.88	4.66	0.56	1.60	1.97	0.15	0.14	0.37	0.05	0.02	4.22	13.80	99.94
H-G-39	48.85	17.49	5.91	0.49	2.49	2.42	0.24	0.61	1.26	0.18	0.00	4.65	15.35	99.95
H-U-33	56.95	14.25	3.04	0.73	2.91	2.41	0.11	0.10	0.50	0.09	0.03	4.10	14.70	99.92
C-84	54.54	15.71	3.02	0.61	3.30	2.37	0.02	0.12	0.25	0.05	0.00	4.22	16.00	100.21

Table 2 Structural formale of the montrillonites.

Sample No.	Tetrahedral		Octahedral				Total cations Oct.	Lattice charge		CEC(meq/100g)	
	Si^{4+}	Al^{3+}	Al^{3+}	Fe^{3+}	Fe^{2+}	Mg^{2+}		Oct.	Total	1	2
Y-13	7.72	0.28	3.00	0.40	0.07	0.61	4.08	0.44	0.72	98	115
Y-11-1	7.39	0.11	3.03	0.18	0.05	0.79	4.05	0.69	0.80	110	122
Y-22	7.67	0.33	2.64	0.65	0.14	0.64	4.07	0.57	0.90	121	114
Y-33-2	7.69	0.31	2.50	0.83	0.13	0.63	4.09	0.49	0.80	106	107
Y-3-1	7.79	0.21	2.60	0.60	0.09	0.80	4.09	0.62	0.83	112	120
Y-16	7.77	0.23	3.11	0.42	0.06	0.46	4.05	0.37	0.60	82	95
G-46	7.96	0.04	2.81	0.13	0.07	1.08	4.09	0.88	0.82	126	116
G-66-2	7.93	0.07	2.67	0.49	0.10	0.76	4.02	0.81	0.87	118	107
G-YD-2	7.91	0.09	2.90	0.29	0.26	0.59	4.04	0.73	0.82	111	101
H-5	7.71	0.29	2.85	0.61	0.09	0.45	4.00	0.49	0.78	105	111
H-G-39	7.60	0.40	2.61	0.61	0.09	0.45	4.07	0.44	0.84	113	122
H-U-33	7.88	0.12	2.76	0.38	0.10	0.79	4.04	0.78	0.90	122	113
C-84	7.98	0.02	2.93	0.20	0.08	0.82	4.03	0.81	0.83	114	112

1 : Calculated CEC from the lattice charge. CEC=(Total lattice charge/unit cell weight) $\times 1000 \times 100$ meq/100g.
2 : measured CEC by the silver thiourea method of Chhabra et al. (1975).

sence of anatase in the under 2 micron fractions was noted and it was assumed that the bulk of the TiO_2 was present as this mineral. Consequently, Ti was omitted from calculations.

Calculated structural formulae and related data are listed in Table 2.

Substitution of Al^{3+} for Si^{4+} in tetrahedral positions occurs, the extent ranging from 0.02 to 0.33atoms per unit cell. The percentage of lattice charge originating from tetrahedral substitution ranges from 4 to 47 percent. Generally, the Y-series of samples and H-5 and H-U-33 show relatively high tetrahedral substitution (38-47 percent). More than 85 percent of the lattice charge is due to substitution in the octa hedral sheet in the remaining samples, mainly of the G-series. Amounts of tetrahedral Al^{3+} are important for distinguishing between beidelite and montmorillonite. All of the present samples are montmorillonites on the basis of Weir and Greene-Kelly's (1962) definition.

Total negative lattce charges range from 0.60 to 0.92 per unit cell. A reasonably good agreement exists between calculated CEC from the structural formula and measured CEC. Differences between them generally do not exceed 20 percent; such differences are generally acceptable (Mering, 1975).

In early studies (Ross and Hendricks, 1945) and also in some recent investigations, the total number of octahedral cations in the unit cell was as high as 4.44, mainly as a result of increased subsititution of Mg^{2+} for Al^{3+}. However, the majority of workers consider that total octahedral cations are close to 4.00, which is the ideal amount for dioctahedral clays (Foster, 1951; Osthaus, 1955; MacEwan, 1961). Totals of octahedral cations in the present samples are also close to 4.00, ranging from 4.02 to 4.09 per unit cell.

Weaver and Pollard (1975) reported that tetrahedral Al^{3+} contents in 101 montmorillonite-beidellite samples ranged erom 0.00 to 0.66, with an average of 0.16 per unit cell. This statistical data is probably of limited significance to the present samples because it also includes beidellite data. However it suggests that tetrahedral Al^{3+} contents vary widely in montmorillonite. On the basis of the tetrahedral Al^{3+} contents of the present samples, H-G-39 is

close to the boundary between montmorillonite and beidellite. By comparison of total Al^{3+} and tetrahedral Al^{3+} contents, there is a tendency for tetrahedral Al to increase with an increase in total Al. Ramberg (1952) suggested that when substitution of Al for Si in silicate structuers occurs, the electronegativity of the oxygen decreases and the Fe/Mg ratio is likely to increase. This relationship was observed in the present samples. For example, samples Y-33-2, Y-22, H-5 and H-G-39 which are relatively high in tetrahedral Al gave high Fe/Mg ratios. This increase of Fe in high Al-montmorillonites probably resulted from compensation of charge deficiency due to substitution of Al for Si in tetrahedral positions.

Chemical compositions of relatively Mg-rich (G-46) and Fe-rich montmorillonites (Y-33-2) in the present samples show the limits of composition. These based on Mg and Fe ions in octahedal positions are:

$(Si_{7.69}\ Al._{04})(Al_{2.81}\ Fe._{13}{}^{3+}\ Fe._{07}{}^{3+}\ Mg_{1.08})O_{20}(OH)_4$ and $(Si_{7.69}\ Al_{1.31})\ Al_{2.50}\ Fe._{83}{}^{3+}\ Fe._{13}{}^{2+}\ Mg._{63})O_{20}\ (OH)_4$.

These two examples show a relatively large variation in octahedral substitution even though they are stratigraphically and geographically close and have an almost similar sedimentation environment. The cause of such a variation is uncertain but the different composition of the original source materials is probably the main cause of such a comopositional variation.

DIFFERENTIAL THERMAL ANALYSIS

DTA curves of the present samples are shown in Fig. 1. All show a double low-temperature endothermic peak system with temperatures of the firrst peak ranging between 120~152°C and of the second between 177~204° C. Differences in peak area of the first endotherm indicate variations in amount of absorbed water, even though the clays were equilibrated at the same

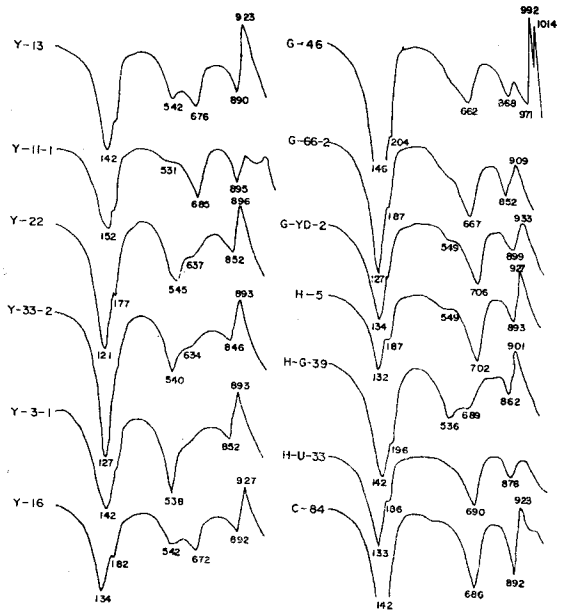

Fig. 1 DTA curves for thirteen Ca-saturated montmorillonites.

room-temperature conditions. In some samples, e.g. Y-11-1, Y-33-2 and Y-3-1, the second endothermic peak related to the cation-coordinated water (Mackenzie et al., 1958; Nemecz, 1962) appears only as a poorly defined shoulder to the main peak; this may reflect minor differences in the exchangable cation assemblage (divalent vs. monovalent) but it should be noted that the definition of this second peak is very much dependant on the magnitude of the first peak.

Base-line shifts are observed on all the DTA curves, this being due to instrummental factors. The dehydroxylation endothermic peak system shows much variation. On the basis of their dehydroxylation behaviour the samples can be divided into three groups: (1) those showing a single dehydroxylaion peak at a relatively high temperature (most of the Y-series of samples), (2) those showing a single endothermic peak at about 540°C (most of the H- and G-series of samples) and (3) those showing a dual dehydroxylation endothermic peak system (sam-

ples Y-13, Y-16 and H-G-39). No examples of completely "normal" or "abnormal" types were observed, as those with an apparently single dehydroxylation peak showed an inflexion on either the low-temperature or high-temperature side of the endotherm, respectively.

The high-temperature DTA behaviours characterized by an S-shaped peak system in most of the present samples. Samples Y-ll-l, G-46, G-66-2 and H-U-33 show very weak exothermic peaks at around 900°C. Strong, sharp exothermic peaks at 992 and 1014°C in sample G-46 probably correspond to high-temperature β-cristobalite and β-quartz development (Grim et al., 1961).

THERMOGRAVIMETRIC ANALYSIS

TG curves of montmorillonite show three distinct water losses: (1) an initial rapid loss of absorbed water and part of the cation coordinated water up to approximately 200°C, (2) a gently sloping plateau between this temperature and 550°C and (3) a region of hydroxyl water loss, initally relatively rapid but which may extend gradually to 1000°C.

The plateau region is of critical importance to hydroxyl water determinations because this region contains overlapping losses of cation-coordinated water and hydroxyl water. Neuman (1963) and Morgan(1974) attempted to separate cation-coordinated water from hydroxyl water loss by the use of slow heating rates but were not successful. Even by maintaining isothermal conditions at various temperatures within the plateau region, these two losses could not be separated. Schultz (1969) arbitrarily chose the mid-point of the plateau and assigned the water loss above this to hydroxyl water. He found that the hydroxyl water content determined by this method was greater than the ideal 4(OH) per unit cell and concluded that this "excess water" appeared to be the major factor controlling dehydroxylation temperature. Morgan (1974) queried Schultzs conclusion both on the basis of the arbitrary choice of the temperature at which dehydroxylation was assumed to begin and the facts that no account was taken of buoyancy corrections which have a larage effect on the small dehydroxylation weight loss (about 4-5 percent). He attempted to define the temperature on the TG curves at which dehydroxylation started by back calculation from constant weight at 1000°C, using the hydroxyl water content determined from the structural formulae.

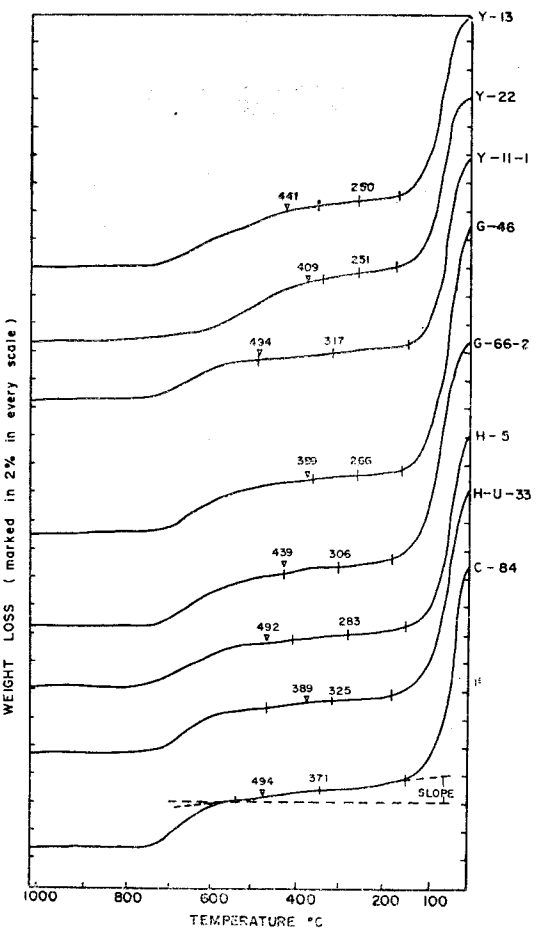

Fig. 2 TG curves of some representative montmorillonites (triangular symbol is back calculated temperature from the structural formula and middle bar is mid-point temperature of the plateau region).

Table 3 Data from thermogravimetric curves of montmorillonites.

Sample No.	Temperature range of plateau (°C)	Mid-point temperature of plateau (°C)	Slope of plateau (°)	Wt. loss from the mid-point (%)	Calculated temperature* (°C)
Y-13	172-339	250	7.0	5.04	441
Y-11-1	158-496	317	6.5	3.58	494
Y-22	178-336	251	9.5	4.95	409
Y-33-2	172-331	245	8.7	5.04	431
R-3-1	191-378	287	10.5	5.98	—
Y-16	189-403	285	9.0	4.71	402
G-46	178-369	266	5.5	4.10	389
G-66-2	190-439	306	7.0	4.60	439
G-YD-2	151-441	286	5.5	4.20	513
H-5	170-420	283	5.6	4.22	492
H-G-39	186-386	278	8.5	4.65	426
H-U-33	186-476	325	6.8	4.10	389
C-84	170-561	371	7.8	4.22	494

* the temperature obtained by back-calculation of the hydroxyl water from the structural formulae.

This point appeared within the plateau region for the four samples examined and its temperature increased as the dehydroxylation character become normal.

Some selected TG curves are shown in Fig.2 and results are listed in Table 3. All the samples shown in Fig. 2 gave typical TG curves showing rapid weight losses up to 190°C, a plateau region, and then a moderately rapid hydroxyl water loss. The first rapid weight loss exceeded the weight loss observed on drying the clays at 105-115°C. No evidnce of two dehydroxylation stages was apparent from the TG curves (cf. DTA results). However, the plateau region of the samples showing normal DTA behaviour finished at higher temperatures then that of the abnormal type.

The slope of the plateau region varies depending on the valency of the exchangable cations, with divalent-cation saturated montmorllionites showing a greater slope than monovalent-cation saturated montmorillonites(Mielenz et al., 1955). Slopes of the plateau region ranged from 5.5 (G-46) to 10.5 (Y-3-1) degrees, the Y-series of samples having relatively higher slope angles than those of the H-and G-series of samples. All the present samples were saturated with Ca and therefore variations in the exchangable cation assemblage are not the cause of these differences in slope.

RELATIONSHIP BETWEEN DEHYDROXYLATION BEHAVIOUR AND STRUCTURAL CHEMISTRY

Dehydroxylation behaviour of the present samples show "abnormal" or "normal" type but no sample shows completely one of those. However, differences between abnormal and normal dehydroxylation behaviour are reflected by differences in structural chemistry. Lower tetrahedral substitution of Al^{3+} for Si^{4+} was apparent in samples showing normal dehydroxylation behaviour, generally the G-and H-series of samples and C-84. Increase in tetrahedral substitution has been cited Schultz (1969) as a factor in lowering of dehydroxylation temperature. In Fig. 3 the dehydroxylation peak temperatures of the present samples have been plotted against tetrahedral Al^{3+} content. There is no linear relationship but the peak temperature does de-

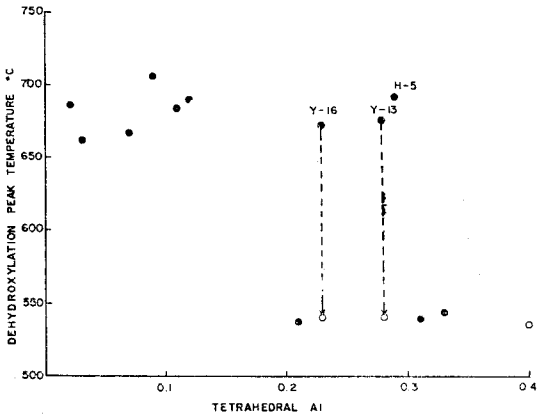

Fig. 3 Relationship between major dehydroxylation peak temperature and Al in tertrahedral positions (open circle represent smaller dehydroxylation endotherm temperature in case of dual peak system).

crease with increase of tetrahedral. Samples in which tetrahdral Al^{3+} is greater than 0.2 plotted in the region of lower dehydroxylation temperatuie. Even though samples Y-13, Y-16 showed dual dehydroxylation behaviour, no samples which had a tetrahedral Al^{3+} smaller than 0.2 plotted in the region of low dehydroxylation temperature. This observation suggests that tetrahedral subsitution is closely related to the dehydroxylation temperature.

Tettenhorst and Johns (1966) suggested that dual dehydroxylation endotherms are related to an asymmetric layer-charge distribution within the clay structure. This is not the case for the present samples. The charge distribution curves of all these are asymmetric but not all show a dual peak system.

Despite no reflection of double endotherm or inflection point on the TGA curves were observed, the dehydroxylation endotherm, in fact, was either dual or single with an inflection point or shoulder in all the samples except for H-U-33 which was not defined enough to obtain the deviding point. The deviding point were obtained from the DTA curves which lie at

Table 4 Dehydroxylation temperature and weight loss up to deviding point.

Sample No.	Start of dehydroxylation endotherm on DTA curves 1 (degree C)	Deviding point on dehydroxylation endotherm. 2 (degree C)	Weight loss temperature range 1 & 2 (percent)
Y-13	383	603	2.40
Y-11-1	400	584	1.05
Y-22	363	620	3.40
Y-33-2	366	606	3.35
Y-3-1	356	603	4.15
Y-16	400	598	2.30
G-46	402	594	1.35
G-66-2	363	576	1.40
G-YD-2	440	605	1.10
H-5	391	603	1.15
H-G-39	361	609	2.95
H-U-33	439	—	—
C-84	361	549	0.75

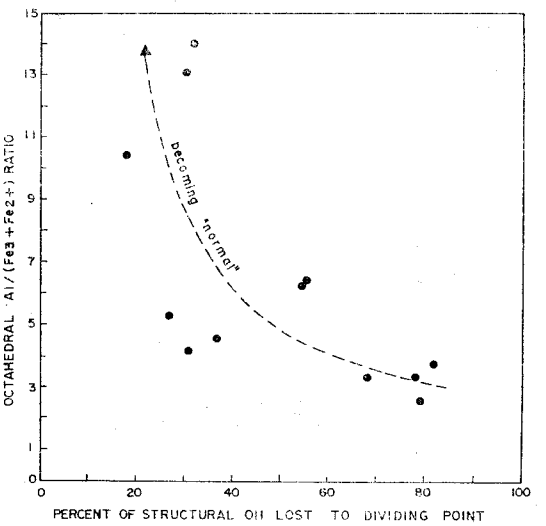

Fig. 4 Structural (OH) lost up to deviding point against octahedral $Al/(Fe^{3+}+Fe^{2+})$ ratio.

about 600°C in most samples (Table 4). Hydroxyl water lost below deviding point temperature obtained from the corresponding TGA curves. these water losses range from 0.75 (C-84) to 4.15 (Y-3-1) percent were plotted against the ratio of $Al/(Fe^{3+}+Fe^{2+})$ in octa-

hedral position (Fig. 4). It shows a reasonably good negative correlation between them. This observation suggests that octahedral substitutions of Fe for Al may also influence the dehydroxylation temperature, normal montmorillonites having higher octahedral Al:Fe ratios. This both substitutions of Fe for Al in octahedral and Al for Si in tetrahedral positions appear to affect crystal distortion and unstable crystal network which were could probably reduced the dehydrxylation temperature. Those are valid for the present samples but undoubtly there will be some other factors to influence dehydrxylation behaviour.

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몬모릴로나이트의 화학조성과 열적성질의 관계

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요약 : 경상도 연일, 감포 및 하서지역의 삼기층에서 산출되는 13개 몬모릴로나이트에 대한 화학조성과 열적성질을 연구하였다. 이들의 화학조성으로 부터 계산된 결정구조식은 사면체내의 Si^{4+}는 Al^{3+}에 의하여 단위격자당 0.02에서 0.33 원자가 치환되었으며 전체 층간부전하의 4~47%가 사면체내의 치환에서 유래되고 있다. 대부분의 시료는 85% 이상의 부전하는 팔면체내의 치환에 의해서 유래되고 있었다. 몬모릴로나이트의 결정구조식과 시차열 및 열천평곡선에 의한 열적특성 결과를 비교 검토한 결과 몬모릴로나이트의 팔면체내의 Al의 Fe에 의한 치환 및 사면체내의 Si의 Al에 의한 치환 모두가 dehydroxylation 온도를 감소시키는 결과를 초래했다. 이러한 관계는 금번 실험된 시료들에서는 충분한 정의 관계를 보였으나, 팔면체 및 사면체내에서의 치환정도가 현저히 다른 시료로서 연구한 결과가 이와 일치된다면 일반적인 현상으로 받아 들일 수 있을 것이다.

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