

On Minerals Associated with Ultrabasic Rocks, Found in the Vicinity of Common Boundaries of Shimane, Tottori, Okayama and Hiroshima Prefectures (VIII)

— Ca-montmorillonite from the Hirose Mine, Tottori Prefecture —

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Abstract

A Ca-montmorillonite has been altered from pyroxenite. The Ca-montmorillonite described in the paper is associated with a small amount of diopside. X-ray, differential thermal and chemical data of the Ca-montmorillonite are presented. A part of Ca occupies octahedral site replacing Mg^{+2} , and the exchangeable capacity of Ca presented in inter-layer is large.

Observation

The white Ca-montmorillonite occurs in the New Hirose level of the Hirose mine, Tottori Prefecture which is the lowest level of the mine. The mineral was found in a dyke form in ultrabasic rocks which belong to the Sangun geological formation. It seems that the mineral is hydrothermally altered from pyroxenite dyke which is mainly composed of diopside.

X-Ray Diffraction Data

X-ray powder diffraction patterns of the natural and heated specimens were obtained by a X-ray diffractometer with Cu-K α radiation and the spacings and intensities of the specimen are listed in Table 1.

The diffractions shown by powder diagrams of the montmorillonite minerals can be placed in two categories. One class consists of basal reflections, which vary with the state of hydration of the mineral, i. e., with the thickness and regularity of the water layers between the silicate sheets. The second class of diffraction consists of general diffractions which are characteristic of the structure of the montmorillonite layers themselves and are not dependent on the inter-layer hydration. These are hk bands,

which in general are the same for all montmorillonites. The differences shown by various montmorillonites are in details of spacings and relative intensities.

The X-ray powder data show that the white rock fragment is composed mainly of montmorillonite and small amounts of diopside. The intensity of 15.5 Å peak of the montmorillonite is stronger than those of the another peaks of the mineral as shown in Table 1. The powder pattern shows only basal reflections and two-dimensional scattering bands indicating a lack of stacking order, so that a three-dimensional cell cannot be strictly defined. The 1.52 Å dimension of the 06 reflection indicates that the mineral belongs to tri-octahedral montmorillonite group. Diopside peaks are seen more or less in the X-ray powder pattern. The dimension of (11, 02) of the specimen is larger something than that of normal montmorillonite.

The identification of changes in phase on heating the clay minerals has been made almost entirely by means of X-ray diffraction analyses. The samples were heated to various temperatures, allowed to cool, and then studied. The high temperature X-ray diffraction technique is providing information of great value in studies of the formation of minerals at elevated temperatures and of transformations at high temperatures.

Table 1. X-ray powder data for Ca-montmorillonite (bearing small amounts of diopside) from Hirose mine, Tottori Pref.

d (Å)	I	hkl
15.5	100	001
7.81	1	002
5.27	2	003
4.58	16	11; 02
3.534	2	
3.473	7	
3.278	7	024
3.069	8	005
2.998	7	
2.969	8	
2.903	5	
2.814	4	025
2.652	30	13; 20
2.557		
2.529		
2.430	1/2	
2.356	4	
2.327		
2.222	6	22; 04
2.163		
2.137		
1.924		
1.768	6	15; 24; 31
1.751		
1.629	2	244
1.605	8	245
1.585		
1.526	18	06; 33

The 001 dimension decreases to 15.0 Å at 300°C from 15.5 Å at normal temperature. The (11, 02) dimension increases to 4.62 Å at 300°C from 4.575 Å at normal temperature. Rapid loss of (OH) water takes place at 500°C, and also same amounts of (OH) are lost at 600°C. At this stage the basal spacing (001) shrink to 9.83 Å, but the distances of (11, 02), (13, 20) and (33, 06) are not almost changed. Further shrinkage takes place with heating to 700°C, yielding a minimum basal spacing of 9.56 Å; this powder pattern of dehydrated montmorillonite corresponds to the inter-layer distance in talc. Decomposition of the structure at the temperature is partly occurred and enstatite-like mineral is produced. The mineral is completely transformed to enstatite and amorphous material at 800°C. The peak and its intensity of enstatite at 900°C are almost equal to these at 800°C.

Treatment with Organic Substances

Organic substances readily adsorbed in montmorillonite are the polyhydric alcohols such as glycol and glycerol, and the molecules have some polar character. Polar molecules are held by a C-H-O bond, and large numbers of (OH)

Table 1. (continued)

After 300°C		After 500°C		After 600°C		(hkl)
d (Å)	I	d (Å)	I	d (Å)	I	
15.0	15	9.83	36	9.83	17	(001)
4.62	7	4.61	9	4.60	5	(11, 02)
				3.534	2	
3.507	2					
3.100	4	3.100	3	3.084	11	
				3.003		
3.003	10	3.008	9	2.903	14	(13, 20)
2.667	16	2.667	18	2.656		
2.571		2.571		2.571		
2.543		2.536		2.543		
1.629	1			1.631	2	(244)
				1.616	4	(245)
1.531	8	1.531	5	1.533	9	(33, 06)

Table 1. (continued)

d (Å)	After 700°C		After 800°C		After 900°C		
	I	hkl	d (Å)	I	d (Å)	I	hkl
9.56	16	002					
4.575	1	020, 11 $\bar{1}$					
3.215	12	006					
3.187	14	240, 221*	3.187	17	3.187	17	240*
2.988	14	231*	2.988	14	2.989	16	231*
2.955	1						
2.903	1	160*	2.885	14	2.894	5	160*
					2.862	7	151*
2.652	8	200, 13 $\bar{2}$	2.648	5	2.652	8	241*
2.560	1/2	311*	2.564	2	2.557	4	311*
2.529	12	132, 20 $\bar{1}$; 022*	2.552	16	2.522	16	022*
1.926	1						
1.713	1/5						
			1.642	2	1.642	2	
1.626	2		1.622	2	1.622	3	
1.584	4		1.583	4	1.580	4	
1.528	5	060, 33 $\bar{2}$					

no symbol : talc, * : enstatite

ions are required to form these bond. Under certain circumstances, both glycerol and ethylen glycol form inter-layer complexes with the montmorillonites. The rate and degree of complex formation are related to the surface charge on the silicate tayers, to the type of inter-layer cation present and to crystal size. With glycerol, but not with ethylene glycol, the hydration state of the mineral immediately prior to complex formation is of some importance. The ability of montmorillonite to imbibe double sheets of

inter-layer glycerol ($d_{001} = 17.7 \text{ \AA}$) and ethylen glycol ($d_{001} = 17 \text{ \AA}$) molecules respectively was reported by MacEwan (1944, 1946) and Bradley (1945). The adsorbed water enters the inter-lamellar region, where it is associated with the exchangeable cation. The lattice swells to accomodate the intercalated water.

Water adsorption by inter-lamellar complexes of ethylene glycol and montmorillonite has been obtained by X-ray technique. Since identification of expanding-lattice clay minerals are frequently based on X-ray diffraction measurments of changes observed in the c -direction of the unit cell when the organic liquids are added to the clays, a more detailed study of these reactions was undertaken and is reported herein.

Treatment with Ethylen Glycol

Montmorillonites possess the property of adsorbing organic molecules between the individual silicate layer with a consequent shift in the c -dimension, depending on the size and configuration of the organic molecule. Such resulting montmorillonite-organic complexes have a high degree of regularity, yielding sharp (001) lines of many orders. The X-ray data (Table 2) of the specimen after treatment with glycol provides a sharp (001) reflection at 16.4 \AA .

Table 2. X-ray data for Ca-montmorillonite after treatment with glycol

d (Å)	I	hkl
16.4	64	001
8.42	1	002
4.23	1/3	004
3.427	2	
3.363	1/5	005
3.033	2	
2.979	4	
2.629	2	
2.546	6	
2.505	1/15	
1.575	1	
1.525	9	

montmorillonite. The material treated with glycerol shows eight orders of the basal reflection. They occur at essentially the same position as with the corresponding montmorillonite reflections, but the intensities are markedly different, as shown by the table 3. This shows that, apart from the different (hk) spacings, the relative intensities of the (001) reflections would give a means of distinguishing this material from normal montmorillonite.

Treatment with Glycerol

The glycerol test when applied to this material showed to behave quite like a normal montmorillonite, giving a strong reflection at 17.5 \AA . There seems to be no reasonable doubt therefore that the material is a true

Table 3. X-ray data for Ca-montmorillonite after treatment with glycerol

d (Å)	I	hkl
17.5	72	001
8.93	10	002
7.60	4	11; 02
4.47	10	004
3.817	4	22; 04
3.527	2	005
3.453	4	
3.273	2	
3.048	8	
2.959	12	006
2.633	8	
2.546	12	007
2.307	1	
1.920	12	009
1.768	4	0.0.10
1.705	1	
1.527	10	

Differential Thermal Analysis

The temperature at which the dehydration begins corresponds to be start of the endothermic reaction. The temperature of the peak of the endothermic deflection varies, depending on the details of the procedure followed, the character of the reaction involved, and the material being studied. An endothermic peak at between 100° and 300°C, which represents either the loss of sorbed moisture (generally small) from the ionic complexes or the loss of adsorbate from the molecular complexes. In the case of the clay minerals, differential thermal analyses show characteristic endothermic reactions due to dehydration and to loss of hydroxyl water from the crystal structure, and exothermic reactions due to the formation of new phases at elevated temperatures. Differential thermal analysis curve for the specimen is shown in Fig.1. It is evident from the

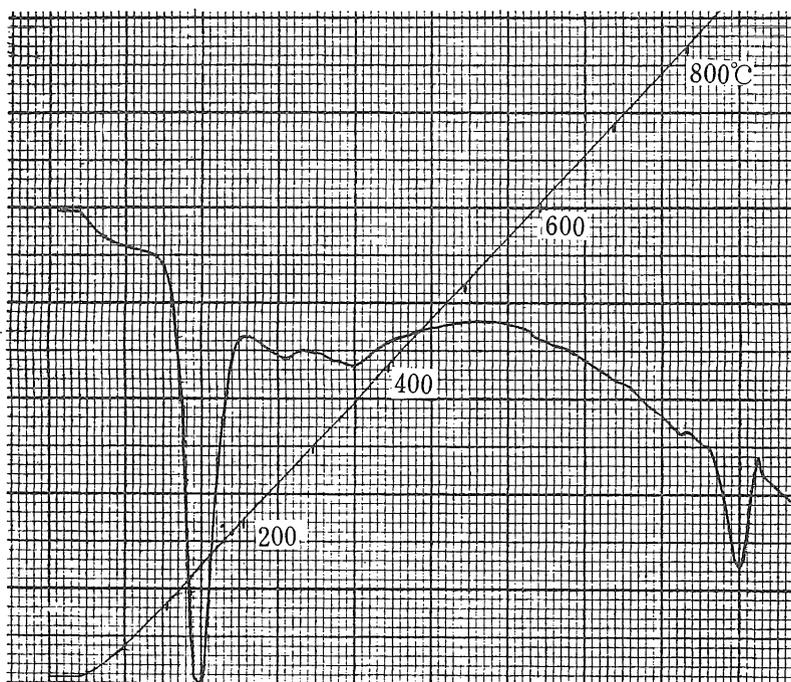


Fig. 1 Differential thermal analysis curve for the Ca-montmorillonite from New level of the Hirose mine, Tottori pref.

differential thermal curve for the specimen that the low temperature peak system consists of three peaks. The low temperature sharp strong endothermic peak at 141°C is due to non-clay impurity and is caused by removal of adsorbed water as mentioned above from the external surfaces and inter-layers respectively, but the low temperature endothermic peaks at 261°C and 355°C is related to the fact that this particular Ca-montmorillonite occurs naturally with only Ca as the exchangeable cation. Namely, the two low temperature small peaks are related to Ca of inter-layer. The endothermic peak near 500°C is generally caused by the loss of hydroxyl water from the crystal structure of a typical montmorillonite, but the peak is not observed in the specimen. All of the adsorbed

water can be removed at temperatures below 300°C and, if sufficient time is allowed, at considerably lower temperatures for some montmorillonites. Most samples of montmorillonite exhibit two high-temperature endothermic reactions which begin and reach maxima within the approximate range of 500° to 750° and 800° to 900°C. Small endothermic peak at 784°C is indicated that adsorbed inter-layer water was completely expelled. The endothermic peak at 866°C, which is prominent for the specimen, and which is followed by an exothermic peak at 894°C. According to the new hypothesis, hydroxyl ions can occur in the tetrahedral layers as statistical substitutions in a manner analogous to the substitution of (OH), for SiO₂. The high temperature endotherm is interpreted as evidence of the occurrence of hydroxyls in tetrahedral configuration. The endothermic peak is associated with the break down of the unhydrated montmorillonite (talc-like material) to an amorphous material from which new phase enstatite crystallize. There X-ray diagrams show a marked weak pattern of the unhydrated montmorillonite and the appearance of weak and diffuse pattern is due to the new enstatite phases. The endothermic peaks are due to the absorption of heat during the change from unhydrated montmorillonite to amorphous material. The type of structural rearrangement for enstatite accompanying the loss of hydroxyl of the unhydrated montmorillonite is important in determining the temperature of the main dehydroxylation peak. The nature of the exchangeable cation effects the size of the high temperature peaks, suggesting that quite small changes in composition have a marked effect. The size of the endothermic peak may depend upon the nature of the mineral, and it may be related to the amount of octahedral substitution. The temperatures at which the endothermic peaks occur are correlated with the hydration energies of the cations.

Chemistry

Inter-layer Molecules

Calcium montmorillonite usually take up two layers of water molecules in each space. The inter-layer water is essentially of hydration surrounding the replaceable cation, and this leads to a characteristic basal spacing. Among

Table 4. Treatment with ammonium nitrate

hkl	d	I
11, 02	4.57	8
	3.466	4
024	3.302	11
	3.234	
005	3.069	4
	2.998	8
13, 20	2.656	30
	2.618	
	2.564	
	2.529	
	2.315	
15, 24, 31	1.766	3
	1.645	4
	1.626	4
	1.583	5
06, 33	1.528	13

the many cations which can enter the inter-layer spaces of montmorillonites; an important one is the ammonium ions. As the exchangeable capacity of calcium is large, calcium is not easily substituted by ammonium ion (NH₄NO₃). The X-ray data for the specimen treated with NH₄NO₃ are as shown in Table 4.

Cation Exchange

Calcium is commonly occurring exchangeable cation. Generally the replacing power of ions with higher valency is greater and their replaceability is less, so that calcium is more firmly held. The principal cause of cation exchange in montmorillonite is the unbalance of charge in the fundamental layer. In mont-

morillonite the exchange capacity is considerably larger when determined with Ca^{2+} than with Na^+ . The specimen is closely related to the tri-octahedral montmorillonite as mentioned above. The exchange capacity of cation is in excess on the basis of the positive charge deficiency within the composite sheets.

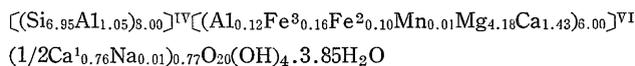
Chemical Analysis

The specimen was analyzed by wet process. The result and numbers of ions are shown in Table 5. The chemical formula of the specimen is similar to that of talc in which substitutions by ions of lower valency in octahedral or tetrahedral sites are accompanied by the addition of an almost equivalent number of inter-layer Ca ions. Such substitution is 0.77 additional monovalent ($1/2 \text{Ca}$, Na) ions per formula unit. The substitution of Si by Al is taken mainly in the Z site. Substitution other than Z site is

Table 5. Analysis of Ca-montmorillonite from Hirose mine, Tottori pref.

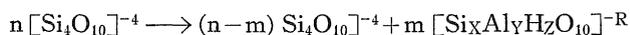
	Wt. %	Mols.		Nos. of ions when 0 = 22
SiO_2	47.70	795	Si	6.953
TiO_2	0	0	Ti	0
Al_2O_3	6.84	67	Al	1.172
Fe_2O_3	1.47	9	Fe^3	0.157
FeO	0.78	11	Fe^2	0.096
NiO	0	0	Ni	0
MnO	0.06	1	Mn	0.009
MgO	19.12	478	Mg	4.180
CaO	11.60	207	Ca	1.810
Na_2O	0.03	0.5	Na	0.009
K_2O	0	0	K	0
H_2O_+	4.52	251	OH	4.00
H_2O_-	7.52	418	H_2O	3.851
	99.81			

Chemical formula of Ca-montmorillonite :



(Analyst : J. Kitahara)

also shown in the table. Tetrahedral position is principally occupied by Al ions as already mentioned. Octahedral sites contain small amounts of Al, Fe^3 , Fe^2 and Mn, and comparatively a large amount of Ca. The specimen is tri-octahedral mineral contained some trivalent ions in Y sites. Ca occupies an octahedral and an exchangeable cation. When the total ions of Y site are coincided to its ideal value, Ca is designated in part as an exchangeable cation. The total of tetrahedral and octahedral charges almost corresponds to that of an exchangeable cation. The general expression for the proposed isomorphous substitutions can be written :



where $X+Y+Z/4 = 4$, and $R = X+2Y+Z/4 = 4+Y$. This expression is written in such a way as to preserve the original charge of the silica sheet except for the increase in negative charge which will accompany each Si — Al. The total number of 6 coordinated cations in the unit cell, according to the above formula, is 6, quite equal to the theoretical 6 for a tri-octahedral layer.

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