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

—— Saponite from the Wakamatsu mine, Tottori Prefecture ——

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Abstract

A saponite of clay mineral described in this paper is pure and represents a magnesium rich member of the montmorillonite group. X-ray, differential and chemical data of this saponite are presented. The influence of Mg^{+2}, as the exchangeable base, on the nature of the X-ray diffraction and differential thermal diagrams leads to some interesting problems.

Occurrence

The grey clay mineral identified as saponite occurs in south level of the Wakamatsu imine, Tottori Prefecture. The mineral was found in a vein form in a fracture zone in ultrabasic rocks which belong to the Sangun metamorphic zone, and the occurrence is extremely limited. These rocks are usually represented by massive serpentinized harzburgites and chloritites of the non-regional metamorphic or slightly metamorphic terrane. The soft, grey clay portion passes into chlorite through an intermediate stage of soft greyish material consisting of chlorite and saponite. The thickness of the vein varies from 10 cm to about 30 cm. It seems that the saponite results mainly from the weathering of ultrabasic rock in condition of poor drange when magnesium is not removed.

Structure

X-Ray Diffraction Patterns

X-ray powder diffraction patterns of the natural and heated specimens were obtained with a Shimazu X-ray diffracometer, with Cu-K radiation (α : 1.5418 Å) and the d values and intensities of the specimen are listed in Table 1. The specimen was free from contaminating minerals, so X-ray diagrams completely free from peaks due to serpentine and chlorite. The 020 and 110 reflections of the specimen show asymmetric powder lines with a sharp cut off on the low angle side and a tail extendings high angles. The patterns show the only (001) and (hk) reflections, true (hkl) reflections being absent because of lack of crystallographic order in super position of the structural layers.

Table 1. X-ray data for saponite and its heated specimens.

	Normal temp.		300°C			400°C		500°C		600°C	
hkl	d	I	d	I	hkl$^+$	d	I	d	I	d	I
001	14.8	100	14.7	43		14.13	2				
					002	10.98 9.83	1	9.83	12	9.77	15
002	7.32*	2									
003	4.89*	3	4.87	1							
02,11	4.61	9	4.63	6	020,11$\bar{1}$	4.62˙	5	4.62	5	4.62	5
004	3.68	1									
12	3.43	1/2								3.33⁚	1/2
					006	3.25 3.21	1	3.20	1/2	3.18	8
005	2.95*	5									
13,20	2.637 2.606 2.543	11	2.652 2.614 2.515	9		2.641					
					200,13$\bar{2}$	2.618˙	2	2.618	2	2.607	2
					132,20$\bar{4}$	2.529˙ 2.455	3	2.478	2	2.512	2
					134,20$\bar{6}$					2.295	1
24,31,15	1.743	1/2	1.743	1		1.743	1			1.737	1/4
06,33	1.536	7	1.536	7	060,33$\bar{2}$	1.536	7	1.536	9	1.535	4

hkl : saponite, hkl$^+$: talc,
d* : contains mainly Mg^{-2} as the exchangeable base.
d˙ : saponite and talc, d⁚ : quartz.

Table 1. (*continued*)

	700°C		800°C		900°C	
hkl	d	I	d	I	d	I
	9.51*	3				
211	3.255	1	3.238	2	3.215	3
240,221	3.152	4	3.121	5	3.126	9
160	2.871	16	2.849	20	2.840	17
311 022 340,251	2.543 2.512 2.462	8	2.501 2.481 2.468	15	2.515 2.504 2.481	14

* : talc, no symbol : enstatite.

Thermal Changes

The lattice spacings corresponding to the (001) series vary with the heat treatment of the mineral as the following description. On heating at 300°C for one hour the reflection 7 Å becomes extinct, and loss their interlamellar water reversibly. On being heated at 400°C for one hour the basal peak moves down to 10.98 Å and 9.83 Å, and the general X-ray pattern begins to appear that of talc as shown in the table. When the sample was heated at 500°C for one hour, the X-ray pattern of dehydrated saponite becomes similar to that of talc, showing that the (001) peak is reduced to about 9.8 Å. The specimen heated to 600°C for one hour showed similar behavior as that heated at 500°C. It seems that the reactivity decreases as the temperature of its formation elevates. With heating at 700°C for one hour, the X-ray pattern of enstatite appears, but at higher temperatures, where detachment of (OH) ions takes place, the X-ray pattern deteriorates considerably as shown in the table.

Treatment with Ammonium Nitrate (NH_4NO_3)

The peaks of spacings at 7.32, 4.89, 3.68 and 2.95 Å are not seen in the specimen heated at 400°C. These peaks are not due to an impurity, but to presence of exchangeable Mg^{+2} ions in unheated saponite. The spacings of the specimen after treatment with ammonium nitrate are shown in Table 2, A. On treating the specimen with ammonium nitrate, exchangeable Mg^{+2} are completly replaced by NH^{4}_{+} and then the values of those peaks apparently are related to the fact that the saponite contains almost Mg^{+2} as exchangeable base. It is clear therefore that these peaks are due to presence of exchangeable Mg^{+2} ions in the unheated specimen as mentioned above. The (001) spacings decrease from 14.8 Å (unheated) to 12.6 Å (treated), and the (004) peaks decrease from 3.68 Å to 3.14 Å. From the table it is realized that the basal intensities of (001) and (004) of the specimen treated with ammonium nitrate are stronger than those of the natural specimen.

Table 2. Saponite treated with each of Ammonium nitrate and Ethylen glycol.

			A.		B.	
	Untreatment		Treatment with Ammonium nitrate		Treatment with Ethylen glycol	
hkl	d	I	d	I	d	I
001	14.8	100	12.6	145	16.7	63
002	7.32*	2			8.31	5
003	4.89*	3			5.51	2
02,11	4.61	9	4.60	6	4.58	4
004	3.68	1	3.14	17		
12	3.43	1/2				
005	2.95*	5			3.34	13
13,20	2.637 2.606 2.543	11	2.622	4	2.797 2.622	5
24,31,15	1.743	1/2				
06,33	1.536	7	1.537	4	1.535	7

* : contains mainly Mg^{+2} as the exchangeable cation.

Treatment with Ethylen Glycol (CH_2OH. CH_2OH)

The X-ray data of the specimen soaked in ethylene glycol is shown in Table 2, B. The basal spacings of 14.8 Å (001), 7.32 Å (002), 4.48 Å (003) and 2.95 Å (005) are shifted to 16.7 Å, 8.31 Å, 5.51 Å and 3.34 Å respectively as seen in the table on treating the specimen with ethylene glycol, proving that this specimen should be placed within the montmorillonite group, while the (060) spacing of 1.536 Å indicates a tri-octahedral montmorillonite.

Structure

To form saponite structure the alumina in the octahedral layer of the montmorillonite structure would be almost completly replaced by magnesia. Therefore the only difference in the structure for saponite would be a slightly thicker unit cell due to the substitution of the larger magnesium.

The position of the 060 reflection can be used to indicate the di-octahedral or tri-octahedral nature of a montmorillonite. The specimen is tri-octahedral montmorillonite which is based on the formula and structure of talc.

Substituted ammonium ions are taken up by the specimen and result in interplanar spacing 12 Å as described above. Polar organic liquid such as ethylen glycol is adsorbed in integral numbers of layers and yield regular layer sequences with characteristic basal spacings. Ethylen glycol gives rise to a basal reflection at 16.7 Å and an integral series of higher orders as denoted above. The number of layers of water molecule is influenced to some extent by the nature of the interlayer cations, magnesium montmorillonite (saponite) usually having two layers per cell and $d_{001} \approx 14.8$ Å as the specimen. In montmorillonite water is readily adsorbed between the structure layers and the basal spacing can vary over a wide range. The specimen is swellng clay mineral in that can taken up water or organic liquid between the structural (inter-layer) layers, and it shows marked cation exchange property.

Montmorillonite can be prepared containing inter-layer cations which are to varying degrees exchangeable. Some of the Mg^{+2} ions occupy inter-layer sites and contribute to the cation exchange capacity. Generally the replacing power of ions with higher valency is greater and their replaceability is less, so that magnesium is more firmely held. The principal cause of cation exchange in montmorillonite is the unbalance of charge in the fundamental layers and not the presence of unsatisfied surface valencies.

The amount of inter-layer water adsorbed varies according to the type of montmorillonite, the nature of the inter-layer cations and the physical conditions. Magnesium montmorillonite (saponite) usually take up two layers of water molecules in each space. The inter-layer water is essentially water of hydration surrounding the replaceable cation, and this leads to a characteristic basal spacing. Among the many cations which can enter the inter-layer spaces of montmorillonite, an important one is the ammonium ion.

Montmorillonites are so poorly crystalline that X-ray data of single crystal are unobtainable. The X-ray powder patterns show only basal reflections and two dimentional scattering bands indicating a lack of stacking order, so that a three-dimensional cell can not be strictly defined. The X-ray diffraction pattern is typical of a tri-octahedral montmorillonite.

Cell Dimensions

X-ray reflection indices of the montmorillonite group are generally shown as (001) and (hk). The saponite that have a high content of exchangeable Mg^{+2} cations may show definite signs of hkl reflections, and perhaps ought to be included with the vermiculites than the montmorillonites. If the (hk) spacings of the specimen are chosen most availably, then the equations to solve the cell dimensions of the specimen are expressed as the following description:

$$Q_{20\bar{2}} = (1/d_{20\bar{2}})^2 = 4a^{*2} + 4c^{*2} 8c^* a^* \cos \beta^* \qquad (1)$$

$$Q_{005} = (1/d_{005})^2 = 25c^{*2} \qquad (2)$$

$$Q_{310} = (1/d_{310})^2 = 9a^{*2} + b^{*2} \qquad (3)$$

$$Q_{060} = (1/_{060})^2 = 36b^{*2} \qquad (4)$$

From (1), (2), (3) and (4),

$a^* = 0.1878$ since $a = 5.36$ Å,

$b^* = 0.1085$ since $b = 9.22$ Å,

$c^* = 0.0678$ since $c = 14.75$ Å (variable),

$\beta^* = 83°53'$ since $\beta = 96°7'$.

Chemistry

The difficulty of distinguishing adsorbed from constitutional water, leads some workers to ignore the H_2O_+ figure and to calculate other ions on the basis of 22 oxygen equivalents. Mackenzie (1957) showd how a formula may be calculated using the H_2O_+ figure assuming that all hydrogen present is in the 4(OH) ions and in the adsorbed water. This method yields the same results as that based on 22 oxygen equivalents. The two methods have been used to derive the number of ions, so that where a number of water molecules per formula unit is given, this corresponding to water held beyond the temperature at which H_2O_- was determined, in most cases 105°−110°C. Dual role of Mg is as an octahedral and an exchange cation.

Substitutions in octahedral or tetrahedral sites by ions of lower valency are accompanied by the addition of an equivalent number of inter-layer cations. The average extent of such substitution requires 0.66 monovalent cations (or their equivalent) per formula unit, and these ions are in general exchangeable. The exchangeable cation indicates the particular substitution in the structure which gives rise to the balancing negative charge. Up to one atom of Al^{3+} and/or Fe^{3+} may apparently be present in the octahedral layers. Also some Fe^{2+} may substitute for Mg^{2+}.

In montmorillonite substitution is almost entirely in Y site, while in saponites it takes place principally in the Z site. There does not appear to be a solid solution series between the di-and tri-octahedral members, considering from the total number of Y ions. In the tri-octahedral minerals, saponite usually contains some trivalent ions in Y sites and has correspondingly more Al replacing Si.

Differential Thermal Analysis

Differential thermal analysis curve for the specimen is shown in Fig. 1. It is evident from the differential thermal curve for the specimen that the low-temperature peak system consists of three peaks, the first two of which overlap partly. The multiple low temperature strong endothermic peaks at 129°C and 171°C are caused by removal of adsorbed water from the external surfaces and inter-layers respectively, but the low temperature endothermic peak at 303°C is related to the fact that this particular saponite occurs naturally with Mg^{+2} as the only exchangeable cation. Replacement of Al by Mg lowers the temperature of the third endothermic peak. Thus the initial part of the curve is a function of the exchangeable ion and pretreatment. The change to a talc-like pattern cited earlier appears only after one hour at 400°C. Dehydroxylation does not therefore occur until about 500°C. It is infered that the change to talc are taken place at about 600°C during the differential thermal run. The writer found that the thermal curve of the specimen shows a little broad endothermic peak at about 634°C. It may be noted that loss of constitutional water (OH) according to the differential thermal diagram begins at about 600°C and rapid loss of (OH) water takes place at about 634°C. The initial dehydration product in this case is probably silica judging from the X-ray pattern at 600°C. At this stage the basal spacing has shrunk to about 9.7 Å. This spacing corresponds nearly to the inter-layer distance in talc as mentioned above. The doubling of the final peak supports on a single endothermic peak would give an impression of doubling, since the specimen give a exothermic peak in the

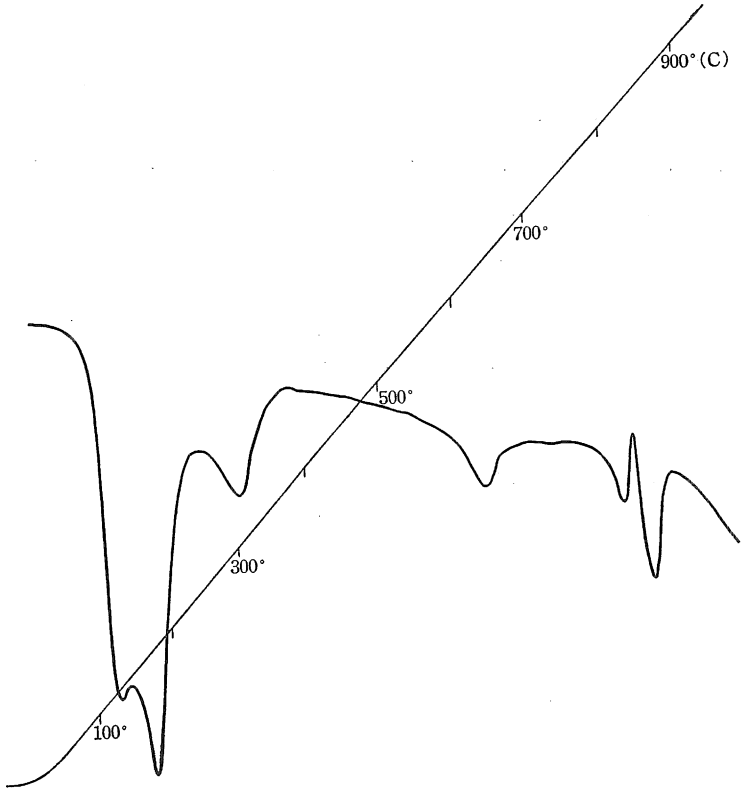

Fig.1 Differential thermal curve for the saponite from the Wakamatsu mine, Tottori Pref.

829°C. The temperatures of the double endothermic peaks between 800°C and 900°C of the specimen are 812°C at lower temperature side and 850°C at higher temperature side respectively. The high temperature exothermic effect is preceded by an endothermic effect, corresponding to the partial release of hydroxyl water from the talc-like phase which is formed at a low temperature by the removal of interlayer water and/or constitutional water (OH). That only partial dehydroxylation occurs at this stage is indicated by the presence of a second endothermic effect at a higher temperature. The fact that the release of hydroxyl water take places in two stages is evident by the two endothermic peaks on the differential thermal curve. X-ray diffraction pattern of the specimen taken from an electric furnace at appropriate temperature denotes that the temperature of the exothermic peak corresponds with that for the crystallization of enstatite. High magnesium and low iron content tend to raise the temperature of the first exothermic peak and in such case enstatite is formed depending upon the amount of Mg present in the original compound. The double endothermic peaks are attributed to the final breakdown of the structure after all (OH) has been expelled. The double endothermic peaks in the 800°~900°C region correspond to dehydroxylation with the formation of enstatite and amorphous silica, namely

$$Mg\,Si_5O_{20}(OH)_4 \longrightarrow 6MgSiO_3+2SiO_2+2H_2O.$$

The completion of the second effect should be correspond to the final disappearance of the talc-like phase. It is said that a distinct double endothermic peak of the saponite group always appears between 700°C and 900°C.

Chemical Analysis

The chemical analysis of the specimen and atomic ratios (ion numbers) calculated from the analysis is listed in Table 3. From the table, the following formula is derived :

Table 3. Analysis of saponite from the Wakamatsu mne, Tottori Prefecture.

	Wt. %	Mols		Atom. ratios		Ditto when 0 =22
SiO_2	43.25	721	Si	721		6.571
TiO_2	0.01	0.1	Ti	0.1		0.001
Al_2O_3	7.39	73	Al	146		1.330
Fe_2O_3	1.51	9	Fe^3	18		0.164
FeO	0.22	3	Fe^2	3		0.027
MnO	0.14	2	Mn	2		0.018
NiO	0	0	Ni	0		0
MgO	28.61	715	Mg	715		6.517
CaO	0.26	5	Ca	5		0.046
Na_2O	0.03	0.5	Na	1		0.009
K_2O	0.01	0.1	K	0.2		0.002
H_2O_+	13.80	767	H_+	1534	(OH)	4.00
H_2O_-	4.81		H_-	534	$*H_2O\pm$	4.61
	100.04		O	3447.8		
			$*H_2O_+$	2.90	adsorbed water	
			H_2O_-	1.71		

(Analyst : J. Kitahara)

$(Mg_{0.63}, Ca_{0.05}, Na_{0.01}, K_{0.002})_{0.69}[(Mg_{5.89}, Fe^{3}_{0.06}, Fe^{2}_{0.03}, Mn_{0.02}, Ti_{0.001})_{6.00}]^{VI}[(Si_{6.57}, Al_{1.33}, Fe^{3}_{0.10})_{8.00}]^{IV}O_{20}(OH)_4 \cdot 2.90\,H_2O$.

In which, the 0.69 value represents exchangeable cations, consisting almost Mg. The present specimen is closer to the magnesium rich member of the montmorillonite group.

Table3. *(continued)*

	Numbers of ions (atoms)	
Si	6.57	8.00
Al	1.33	
Fe^3	0.10	
Al	–	6.00
Ti	0.001	
Fe^3	0.06	
Ni	0	
Fe^2	0.03	
Mn	0.02	
Mg	5.89	
Mg	0.63	0.69
Ca	0.05	
Na	0.01	
K	0.002	
(OH)	4.00	
H_2O	2.90	
M*	1.27	

M* : total charge on inter-layer cations.

The usual method of calculating the montmorillonite structural formula is that of Ross and Hendricks (1945), based upon the assumption that each structural unit contains 20 oxygen and 4 hydroxyl ions giving negative valency of 44. If one assumes the water contents obtained by analysis to be divided up according to the proportions $4OH^-$: nH_2O, where nH_2O is the excess sorbed moisture not removed at 110°C, one can derive the equation :

$$p[H^+] = 4+2n,$$

where $p = 9.79$ is the ionic proportion (atomic ratio) of hydrogen H, obtained from the analysis. This enables one to measure the amount of excess hygroscopic moisture in the H_2O_+ content. Thus from the equation :

$$n = \frac{p[H^+]-4}{2} = 2.90.$$

The excess hygroscopic moisture in the H_2O_+ :

$$H_2O\% \text{ (Wt.)} = \frac{\text{atom. ratio of (OH)} - 4.00}{\text{atom. ratio of (HO)}} = \frac{13.80 \cdot 5.79}{9.79} = 8.16.$$

This method of calculation should enable accurate determination of the total sorbed water content, which is not readily measured experimentally.

Conclusions

A saponite was discovered by the writer in a fracture zone of serpentinite in south level of the Wakamatsu mine, Tottori Prefecture. The grey clay mineral identified as saponite was investigated by X-ray, differential thermal and chemical analyses. The accumulated data can be summarized as follows :

(1) An X-ray diagram that proved this mineral to be of the tri-octahedral expanding lattice type gives a basic talc structure on dehydration. Certain of the X-ray spacings are not characteristic of the saponite, but only of the presence of exchangeable Mg^{+2} ions in unheated specimen.

(2) The endothermic peaks at 129° and 173°C of a differential thermal curve are caused by removal of adsorbed water. The endothermic peak at 303°C is related to exchangeable Mg^{+2} in the unheated specimen. A broad shallow endothermic effect centered at 634°C is considered to be connected to the formation of talc-like mineral. The endothermic peaks at 812° and 851°C are caused by the expulsion of structural water (OH). The exothermic peak at 829°C is due to be generated of enstatite.

(3) Chemical analysis indicates that this specimen to be an example of a magnesium rich member of the montmorillonite group with a formula as mentioned above.

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