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Hydration states in interlayer of hydromuscovite

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Hydration states of hydromuscovites under conditions of 80% and 50% R.H. and glycerol solvation after saturation with various kinds of cations in the expandable interlayers were examined by means of Fourier transform analysis.

At 80% R.H., Ca-saturated specimens showed one- and two-layer hydration states of expandable layer and the ratios of two-layer to one-layer hydration states decrease with increasing the proportions of mica layer components. At 50% R.H., Ca-saturated specimens indicated a decrease in two-layer hydration and an increase in one-layer hydration as compared with those of the specimens at 80% R.H. Glycerol solvated complexes of Mg-saturated specimens showed that the specimens contain one-layer glycerol complexes with spacing of about 12.5Å.

These hydration states of the hydromuscovites are different from those of smectites and expandable layers of regularly interstratified mica/smectites, and it is considered to be due to their high layer charge in expandable layer.

Introduction

The AIPEA Nomenclature Committee has shown the classification scheme for the phyllosilicates related to clay minerals based on its layer type (ratio of tetrahedral to octahedral sheets in one repetitive unit structure) and charge density. Although, the Committee recommended that the definition of mica is 2 : 1 layer type clay minerals with layer charge of 1 per formula unit, it has written that "the status of illite (or hydromica), sericite, etc. must be left open at present, because it is not clear whether or at what level they would enter the Table (Bailey, 1980); many materials so designated may be interstratified". At present, many studies have been conducted to clarify the mineralogical properties of these minerals (Grim *et al.*, 1937; Kodama, 1957; Kodama, 1962; Hower and Mowatt, 1966; Shimoda, 1970, etc.). As to the chemical composition, these micas show excess of water and deficiency of potassium in interlayer positions and aluminum in tetrahedral sheets as compared with theoretical composition of muscovites, suggesting that the layer charge of the former is slightly lower than that of latter (Hower and Mowatt, 1966). As to the structure of interstratification, these micas include two types of minerals, one is interstratified mica/smectite with small amounts of expandable layers, the other is pure mica with no interstratification structure (Shirozu and Higashi, 1972).

The present study deals with the hydration states in the interlayers of hydromuscovites (interstratified mica/smectites with small amounts of expandable layers) and their nature of interstratifications.

Specimens

Five hydromuscovites with small amounts of expandable layers were examined in this study. They are as follows;

H1: Specimen from Tenei, Fukushima Prefecture (Kawano, 1988).

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H2 : Specimen from Makurazaki, Kagoshima Prefecture.

H3 : Specimen from Tenei, Fukushima Prefecture (Kawano, 1988).

H4 : Specimen from Silver Hill, Montana, U.S.A. (Hower and Mowatt, 1966) supplied from the Source Clays Repository of The Clay Minerals Society.

H5 : Specimen from Aira, Kagoshima Prefecture (Kawano and Tomita, 1988).

The chemical analysis of specimen H2 was carried out by usual wet method. The chemical analyses and structural formulae for these specimens are listed in Table 1.

Table 1. Chemical analyses and structural formulae for hydromuscovites

	H1	H2	H3	H4	H5
SiO_2	49.04	46.69	48.06	55.10	48.98
TiO_2	0.13	0.05	0.09	0.63	0.02
Al_2O_3	28.30	34.12	31.31	22.00	33.82
Fe_2O_3	4.43	0.48	0.51	5.28	0.58
FeO	-	-	-	1.34	-
MnO	0.04	0.01	0.51	-	0.01
MgO	0.81	0.59	1.04	2.80	0.61
CaO	0.58	0.07	0.64	0.02	0.02
Na_2O	0.34	1.18	1.18	0.08	1.33
K_2O	7.14	6.25	6.61	8.04	5.99
$(NH_4)_2O$	-	-	-	-	1.30
P_2O_5	0.26	-	0.21	-	-
$H_2O(+)$	5.54	7.95	6.48	6.40	5.25
$H_2O(-)$	4.08	2.70	3.81	1.00	1.86
Total (%)	100.69	100.09	99.96	102.69	99.82
Tetrahedral					
Si	3.37	3.20	3.31	3.66	3.25
Al	0.63	0.80	0.69	0.34	0.75
Octahedral					
Al	1.66	1.96	1.85	1.38	1.89
Fe^{3+}	0.23	0.02	0.03	0.26	0.03
Fe^{2+}	-	-	-	0.07	-
Mg	0.07	0.02	0.09	0.28	0.06
Ti	0.01	0.00	0.00	-	0.00
Sum	1.97	2.01	1.97	1.99	1.98
Interlayer					
Ca	0.04	0.01	0.05	-	0.00
Na	0.05	0.16	0.16	0.01	0.18
K	0.63	0.55	0.58	0.68	0.51
NH_4	-	-	-	-	0.20
Mg	0.01	0.04	0.02	-	-
X^+	-	-	-	0.03	-
Sum	0.72	0.76	0.81	0.72	0.89
Total charge	0.78	0.79	0.87	0.72	0.89

Experimental method

Fractions less than 2 μm were obtained by usual sedimentation method, and were saturated with Ca^{2+}, Na^{+} and Mg^{2+} by treatment with 1N $CaCl_2$, NaCl and $MgCl_2$ solution. After the removal of excess salt by washing with 80% ethanol, the homoionic specimens were oriented on glass slides.

X-ray diffraction analysis was carried out by Rigaku diffractometer using CuK_α radiation under the conditions of 80% and 50% relative humidities for Ca-saturated specimens, 50% relative humidity for Na-saturated specimens, and glycerol solvated complexes of Mg-saturated specimens. The basal spacings were obtained from d-values of the center half the height of basal reflections and intensities were determined by step scan method. The control of humidity was made by ordinary humidifier and dehumidifier equipment. These instruments were run in the x-ray room and humidities were checked by hygrometer.

The hydration states in expandable layers and nature of the interstratifications were examined by means of Fourier transform analyses, and the equation employed in this calculation was formulated by MacEwan (1956) and can be written as

$$W(R)=\sum_l \frac{I}{E\,|F_l|^2}\cos 2\pi\mu_l R,$$

where function $W(R)$ is defined as the probability of finding another layer at a distance R from any layer. I, the integrated intensity, E, the geometric factor, $|F_l|^2$, the square of the layer structure factor and μ_l, the reciprocal spacing. $(1+\cos^2 2\theta/\sin 2\theta)$ was used for the factor E. The layer structure factors were taken from Cole and Lancucki (1966) for hydrous dioctahedral mica type layers.

Results

Hydration states of Ca-saturated specimens at 80% R.H.

Basal spacings and intensities of Ca-saturated specimens obtained under the condition of 80% R.H. are listed in Table 2. Fig. 1 shows Fourier transforms of basal reflections for the five specimens. These transforms show three fundamental components (A, B and C) with spacings of about 10, 13 and 15.4Å, which are assigned to mica layer, expandable layer of one-layer hydration and that of two-layer hydration, respectively. Table 3 shows calculated and observed heights of peaks from Fourier transforms of basal reflections for Ca-saturated hydromuscovites at 80% R.H. The calculated heights of peaks were determined by

Table 2. Spacings (Å) and intensities of basal reflections for Ca-saturated hydromuscovites at 80% R.H.

H1		H2		H3		H4		H5	
d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
11.5	1000	10.7	1000	10.4	1000	10.3	1000	10.2	1000
5.04	265	5.05	323	5.02	314	5.03	166	5.02	242
3.290	531	3.319	427	3.309	448	3.325	433	3.339	325
2.521	36	2.521	26	2.512	19	2.509	21	2.514	16
1.993	151	1.998	130	1.995	133	1.996	114	2.006	91
1.654	1	1.655	2	1.654	1	1.667	3	1.658	1
1.424	7	1.427	7	1.426	5	1.425	9	1.430	3
1.251	10	1.252	7	1.251	5	1.247	8	1.251	4

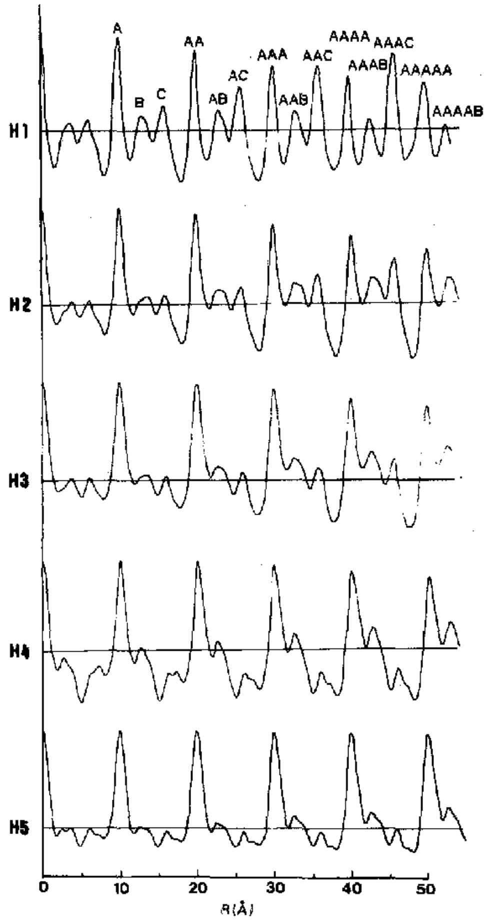

Fig. 1. Fourier transform of basal reflections for Ca-saturated hydromuscovites at 80% R.H.

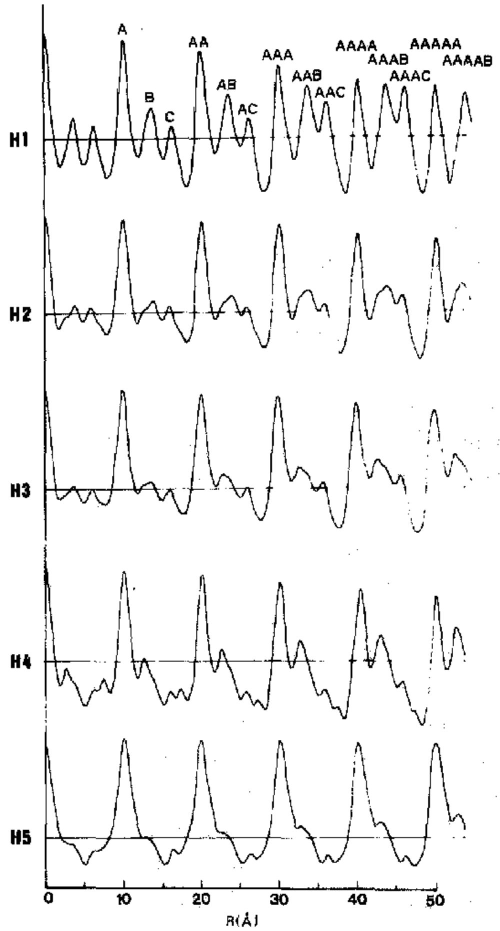

Fig. 2. Fourier transform of basal reflections for Ca-saturated hydromuscovites at 50% R.H.

the method of MacEwan (1956), and observed heights of peaks were obtained from heights of peaks in Fourier transform. The values for calculated and observed heights of peaks A, B and C represent proportions of component layers. The results suggest that specimens H1, H2 and H3 are composed of three component layers, which are mica layer, expandable layer of one-layer hydration and that of two-layer hydration, while specimens H4 and H5 are composed of two component layers, which are mica layer and expandable layer of one-layer hydration. The existing ratios of one-layer to two-layer hydration increase with increasing the proportions of mica layer components.

Hydration states of Ca-saturated specimens at 50% R.H.

Table 4 shows the basal spacings and intensities of Ca-saturated specimens at 50% R.H. Under the humidity condition, the first order reflection shifts slightly to higher angle while the third and fifth order reflections shift to lower angle compared with those of the specimens under the condition of 80% R.H. Fig. 2 shows Fourier transforms for Ca-saturated specimens at 50% R.H. These transforms indicate that expandable layers of two-layer hydration decrease and those of one-layer hydration

Table 3. Calculated and observed heights of peaks from Fourier transform of basal reflections for Ca-saturated hydromuscovites at 80% R.H.

Peak	H1 Spacing (Å)	H1 Calculated height	H1 Observed height	H2 Spacing (Å)	H2 Calculated height	H2 Observed height	H3 Spacing (Å)	H3 Calculated height	H3 Observed height
A	10.0	0.68	0.68	10.0	0.85	0.85	10.0	0.93	0.93
B	12.8	0.12	0.12	13.8	0.07	0.07	13.7	0.04	0.04
C	15.9	0.20	0.20	15.9	0.08	0.08	16.0	0.03	0.03
AA	20.0	0.59	0.59	20.1	0.79	0.79	20.0	0.90	0.90
AB	22.8	0.17	0.17	22.8	0.13	0.13	22.7	0.10	0.10
AC	25.8	0.24	0.34	25.9	0.08	0.16	25.9	0.00	0.06
AAA	29.9	0.50	0.48	30.1	0.74	0.71	30.0	0.86	0.84
AAB	32.7	0.20	0.16	32.8	0.17	0.19	32.7	0.14	0.19
AAC	35.8	0.25	0.48	35.9	0.08	0.26	35.8	0.00	0.12
AAAA	39.9	0.43	0.40	40.1	0.68	0.60	40.0	0.83	0.77
AAAB	42.7	0.22	0.10	42.9	0.21	0.22	42.7	0.17	0.25
AAAC	45.8	0.25	0.56	45.8	0.08	0.38	45.7	0.00	0.19
AAAAA	49.9	0.37	0.36	50.1	0.64	0.49	50.0	0.80	0.68
AAAAB	52.6	0.23	0.04	52.9	0.25	0.22	52.7	0.20	0.30

Peak	H4 Spacing (Å)	H4 Calculated height	H4 Observed height	H5 Spacing (Å)	H5 Calculated height	H5 Observed height
A	10.0	0.97	0.97	10.0	0.99	0.99
B	12.6	0.03	0.03	12.4	0.01	0.01
AA	20.0	0.95	0.95	20.1	0.99	0.99
AB	22.6	0.05	0.11	22.5	0.01	0.05
AAA	30.0	0.93	0.91	30.1	0.98	0.98
AAB	32.6	0.07	0.18	32.5	0.02	0.10
AAAA	40.0	0.90	0.85	40.2	0.98	0.96
AAAB	42.7	0.10	0.25	42.6	0.02	0.14
AAAAA	50.0	0.88	0.79	50.2	0.97	0.94
AAAAB	52.7	0.12	0.31	52.6	0.03	0.19

Table 4. Spacings (Å) and intensities of basal reflections for Ca-saturated hydromuscovites at 50% R.H.

H1 d(Å)	H1 I	H2 d(Å)	H2 I	H3 d(Å)	H3 I	H4 d(Å)	H4 I	H5 d(Å)	H5 I
11.1	1000	10.5	1000	10.4	1000	10.3	1000	10.2	1000
5.03	222	5.01	365	5.01	302	5.01	159	5.01	236
3.344	418	3.329	505	3.314	413	3.322	371	3.337	320
2.546	3	2.507	25	2.507	17	2.505	26	2.512	14
2.004	110	2.005	169	1.999	122	1.996	108	2.005	94
1.658	2	1.654	1	1.650	1	1.663	3	1.662	1
1.422	5	1.431	7	1.427	4	1.429	8	1.430	3
1.251	8	1.251	7	1.250	5	1.249	8	1.251	5

increase as compared with those of the specimens at 80% R.H.

Hydration states of Na-saturated specimens at 50% R.H.

Under the condition of 50% R.H., the first order reflection of Na-saturated specimens shifts to higher angle and the third and fifth order reflections shift to lower angle than those of Ca-saturated specimens (Table 5). These behaviors are caused by shrinkage of expandable layers. The Fourier transforms for Na-saturated specimens at 50% R.H. (Fig. 3) show that expandable layers of two-layer hydration decrease and those of one-layer hydration increase as compared with those of Ca-saturated specimens at 50% R.H.

Glycerol solvated complexes of Mg-saturated specimens

Basal spacings and intensities of glycerol solvated complexes for Mg-saturated specimens are given in Table 6. The first order basal reflection of the specimen H1 (11.5Å)

Table 5. Spacings (Å) and intensities of basal reflections for Na-saturated hydromuscovites at 50% R.H.

H1		H2		H3		H4		H5	
d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
10.6	1000	10.4	1000	10.4	1000	10.3	1000	10.2	1000
5.08	115	5.04	197	5.01	308	5.03	120	5.01	324
3.296	247	3.312	289	3.322	478	3.324	358	3.337	473
2.498	9	2.507	16	2.507	21	2.504	16	2.509	24
2.008	57	2.010	85	2.002	153	2.001	90	2.004	155
1.653	9	1.657	1	1.658	1	1.667	2	1.660	1
1.419	3	1.425	3	1.429	7	1.425	7	1.430	6
1.248	4	1.251	3	1.250	7	1.246	7	1.251	7

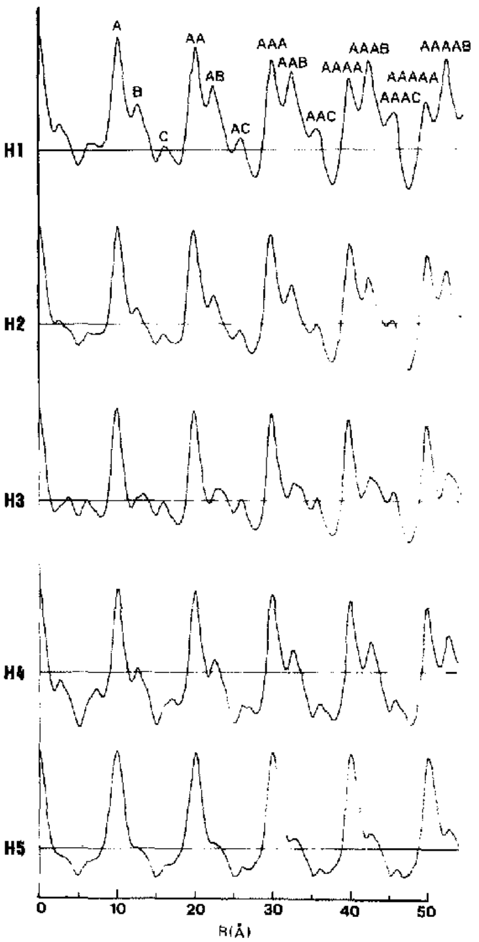

Fig. 3. Fourier transform of basal reflections for Na-saturated hydromuscovites at 50% R.H.

splits into two reflections (13.4 and 9.4Å), and that of other four specimens shifts slightly to higher angle. Fig. 4 shows Fourier transforms of basal reflections for the specimens. These transforms suggest that the specimens contain about 12.5 (B) and 18 (D) Å component layers, which are assigned to expandable layers with one-layer glycerol complexes and those with two-layer glycerol complexes. The restricted expansion with glycerol for 12.5Å component layers of Mg-saturated specimens agrees with the swelling behavior of vermiculite (Walker, 1957, 1958).

Discussion and Summary

Hydration states and nature of the interstratifications of the hydromuscovites were examined by means of Fourier transform method under the conditions of 80% and 50% R.H. for Ca- and Na-saturated specimens and glycerol solvated complexes of Mg-saturated specimens.

Under the condition of 80% R.H., Ca-saturated specimens H1, H2 and H3 show interstratifications of three component layers, which are mica layer, expandable layer of one-layer hydration and that of two-layer hydration. The existing ratios of expandable layer of two-layer hydration to that of one-layer decrease with increasing the proportions of

Table 6. Spacings (Å) and intensities of basal reflections for glycerol solvated complexes of Mg-saturated hydromuscovites

H1		H2		H3		H4		H5	
d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
13.4	245								
9.9	1000	9.9	1000	10.0	1000	10.1	1000	10.1	1000
4.88	194	4.96	327	4.96	342	4.98	175	5.01	339
3.352	455	3.357	478	3.334	489	3.336	544	3.345	479
2.525	28	2.518	28	2.512	25	2.584	44	2.511	29
1.998	109	2.001	128	1.998	132	1.996	182	2.002	150
1.646	4	1.654	4	1.661	2	1.667	4	1.656	3
1.422	5	1.429	6	1.425	5	1.428	10	1.429	5
1.250	5	1.254	7	1.245	5	1.248	16	1.251	8

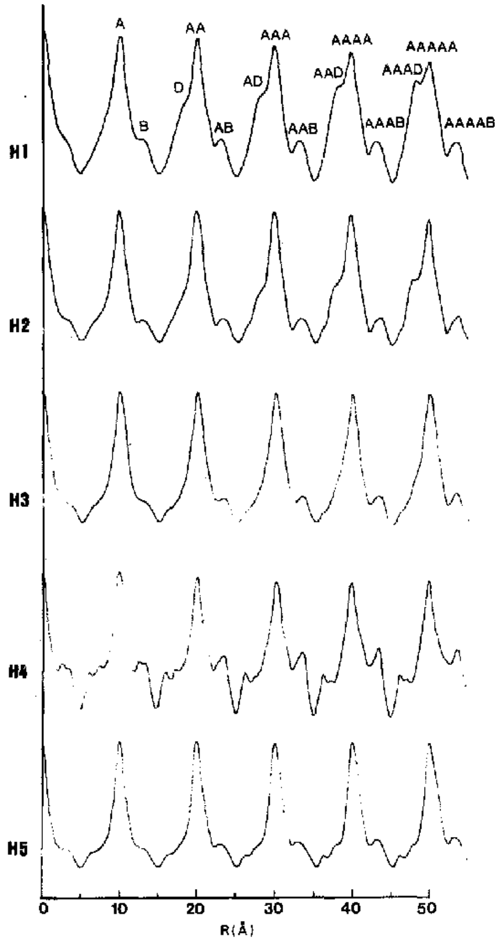

Fig. 4. Fourier transform of basal reflections for glycerol solvated complexes of Mg-saturated hydromuscovites.

mica layer components. Specimens H4 and H5, which have larger proportions of mica layer than those of the above three specimens, show interstratifications of two component layers, which are mica layer and expandable layer of one-layer hydration. Glaeser and Méring (1968), Suquet *et al.* (1975) and Watanabe and Sato (1988) reported the basal spacings of Ca-saturated smectites under the conditions of various relative humidities, and pointed out that Ca-saturated smectites retain two layers of water molecules in interlayer positions in the range of relative humidities between about 30% and 90% R.H. Similar expansion characteristics of expandable layer of regularly interstratified mica/smectites have been reported by Matsuda (1984). The hydration states in the interlayers of hydromuscovites examined in this study show inhomogeneity of one- and two-layer hydration states, and the ratios of two-layer hydration to one-layer decrease with increasing the proportions of mica layer components. These hydration states may be the result of high layer charge and inhomogeneous charge density distribution in expandable layers.

Under the condition of 50% R.H., the Ca-saturated specimens show a little decrease in two-layer hydration, and Na-saturated specimens show further decrease in two-layer hydration and increase in one-layer hydration. Although, the x-ray diffraction data demonstrated shrinking behaviors of expandable layers, the expandable layers of two-layer hydration did not show continuous contraction. The changes of hydration states of expandable layers indicate that the values of layer charge are higher than those of regularly interstratified mica/smectites and usual smectites, and the values increase with increasing the proportions of mica layer components. The Fourier transforms of glycerol solvated complexes of Mg-saturated specimens also indicate the presence of high charge expandable layers which have vermiculite-like expansion properties.

The differences of hydration behaviors of hydromuscovites from those of regularly interstratified mica/smectites and usual smectites are considered to be due to high layer charge in expandable layers of the hydromuscovites.

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ハイドロマスコバイトの層間水和状態

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ハイドロマスコバイトの膨潤層層間陽イオンを様々の陽イオンで交換後，相対湿度 80%，50% およびグリセロール処理後の水和状態をフーリエ変換によって検討した。

Ca 飽和試料は相対湿度 80% の条件で膨潤層層間に一層と二層の水分子層が存在し，雲母層の増加に伴い一層の水分子層を持つ膨潤層比率の増加が認められた。相対湿度 50% の条件では二層の水分子層を持つ膨潤層が減少し，一層の水分子層を持つ膨潤層が増加した。Mg 飽和後のグリセロール処理では 12.5Å の面間隔を持つ一層のグリセロール分子複合体が認められた。

これらの層間水和状態はスメクタイトおよび規則型雲母/スメクタイト混合層鉱物とは異なり，膨潤層の高い層電荷に起因するものと思われる。