MONTMORILLONITE

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Abstract

Montmorillonite (including nontronite) probably varies in composition between the following end-member formulas: $4(Al, Fe)_2O_3 \cdot 16SiO_2 \cdot 20H_2O$, $6(Al, Fe)_2O_3 \cdot 12SiO_2 \cdot 22H_2O$, $6MgO \cdot 3(Al, Fe)_2O_3 \cdot 12SiO_2 \cdot 25H_2O$, and $6MgO \cdot 2(Al, Fe)_2O_3 \cdot 14SiO_2 \cdot 24H_2O$. These variations are shown on a (partial) triangular prism on which 52 analyses are plotted. The optical properties vary very little except with variations in the Al-Fe''' series.

Introduction

In 1935 Marshall,[1] gave good evidence for the conclusion that montmorillonite is essentially $Al_4(OH)_{12}Si_8O_{12}(OH)_8$, in which Si may be replaced (in part) by Al, and Al may be replaced (in part) by Mg. To a less extent he concluded that Si may be replaced by P and perhaps by Fe''' and Ti; also Al may be replaced entirely by Fe''', or in part by Ti, Fe'', Mn, Ca, and Na.[2] He also showed that structurally montmorillonite consists of repetitions of one $Al_4(OH)_{12}$ layer and two $Si_4O_6(OH)_4$ layers. In this respect it differs from kaolinite which consists of repetitions of one $Al_4O_4(OH)_8$ layer and one Si_4O_6 layer.

Derivation of End-Member Formulas

If the formula of montmorillonite be doubled, for convenience, it becomes $Al_8(OH)_{24}Si_{16}O_{24}(OH)_{16}$ or $4Al_2O_3 \cdot 16SiO_2 \cdot 20H_2O$. This may be accepted as one end-member of the montmorillonite system. Since Si may be replaced (in part) by Al, Si_{16} might become $Si_{15}Al$, $Si_{14}Al_2$, $Si_{13}Al_3$, etc. If the uneven numbers are omitted (for convenience in writing the oxide formulas) the series becomes: Si_{16}, $Si_{14}Al_2$, $Si_{12}Al_4$, $Si_{10}Al_6$, and corresponding oxide formulas are $4Al_2O_3 \cdot 16SiO_2 \cdot 20H_2O$, $5Al_2O_3 \cdot 14SiO_2 \cdot 21H_2O$, $6Al_2O_3 \cdot 12SiO_2 \cdot 22H_2O$, and $7Al_2O_3 \cdot 10SiO_2 \cdot 23H_2O$ (the number of H_2O molecules being assumed to be such as will keep the total number of oxygen atoms constant). It is at present unknown how far this replacement of Si by Al can proceed; two analyses of natural minerals (1 and 2) give the ratio: $7Al_2O_3 . 10SiO_2$ almost exactly and a few others have a little more than $6Al_2O_3$ to $12SiO_2$, but since analyses of these minerals are almost inevitably made on clay-like masses rather than on single crystals or aggregates of crystalline material of one kind, it seems probable that the material analyzed may include some bauxite or limonite in certain cases.

[1] *Zeit. Krist.*, **91**, 433 (1935).

[2] Noll (*Chem. Erde*, **10**, p. 129) has shown that Be may be present in large amount. One per cent of CuO is present in analysis 35. Analyses 33, 39, and 51 are K-montmorillonites.

There is little doubt that the replacement goes at least to $6Al_2O_3 \cdot 12SiO_2$; it will be assumed that this is a second end-member.

Considering next the replacement of Al by Mg, Noll[3] has proved that montmorillonite can be made artificially containing as much as 15.30 per cent of MgO. This is considerably more than has ever been found in any natural mineral and may reasonably be taken as the maximum that is possible. Noll's analysis may be expressed as $6MgO \cdot 3Al_2O_3 \cdot 12SiO_2 \cdot$

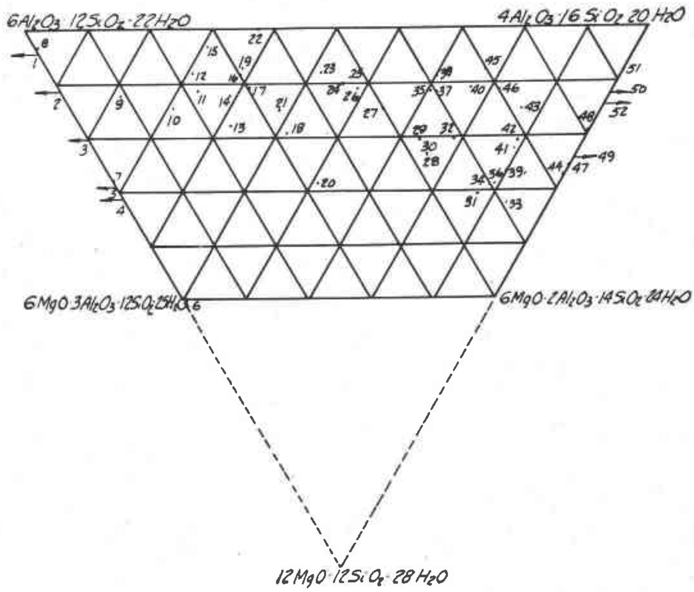

FIG. 1. Montmorillonite analyses plotted on (part of) a triangle having $4Al_2O_3 \cdot 16SiO_2 \cdot 20H_2O$, $6Al_2O_3 \cdot 12SiO_2 \cdot 22H_2O$, and $12MgO \cdot 12SiO_2 \cdot 28H_2O$ at its corners, Al standing for Al, Fe''', Ti and Cr, and Mg for Mg, Fe'', Mn, Ca.

$20H_2O$. As compared with the formula, $6Al_2O_3 \cdot 12SiO_2$, obtained above, this shows a replacement of just half the Al atoms by Mg atoms. If all the aluminum could be replaced by magnesium, the formula would be $12MgO.12SiO_2$ (with H_2O). It seems impossible that this is an end-member of montmorillonite, but it is convenient to use it as if it were. Then it is possible (disregarding other variations) to represent montmorillonite analyses on a triangle having $4Al_2O_3 \cdot 16SiO_2$, $6Al_2O_3 \cdot 12SiO_2$, and $12MgO \cdot 12SiO_2$ at its corners, as in Fig. 1. Fifty-two analyses of montmorillonite (including beidellite, bentonite, leverrierite, and nontronite[4]) have been

[3] *Chem. Erde*, **10**, 129 (1936).

[4] Chemically, attapulgite belongs in this system, but it seems to differ in crystal structure, as shown by de Lapparent, J. (*Bull. Soc. Fr. Min.*, **61** p. 253) and Bradley, W. F.: *Am. Mineral.*, **25**, 405 (1940).

plotted on the diagram; the distribution of the points representing these analyses indicates that the probable end-member formulas are:

1. $4Al_2O_3 \cdot 16SiO_2 \cdot 20H_2O$
2. $6Al_2O_3 \cdot 12SiO_2 \cdot 22H_2O$
3. $6MgO \cdot 3Al_2O_3 \cdot 12SiO_2 \cdot 25H_2O$
4. $6MgO \cdot 2Al_2O_3 \cdot 14SiO_2 \cdot 24H_2O$

The writer would suggest that the first end-member should be designated leverrierite. Marshall states that the chief replacement in beidellite is Al for Si; accordingly the second formula is apparently the end-member most fittingly called beidellite.

As indicated by the arrows along the margins of the drawing a few analyses contain an excess of Al_2O_3 (due to admixed bauxite?) and a few contain an excess of SiO_2 (due to admixed quartz or cristobalite?). Of course, these analyses suggest the possibility of a greater replacement of Si by Al, and *vice versa*, than recognized in the drawing, but if more Al_2O_3 were present it is difficult to understand why kaolinite would not form instead of montmorillonite.

In calculating the position of each analysis on Fig. 1, Al is assumed to include Fe''' (and Ti and Cr, if they are present). Also Mg is assumed to include Fe'', Mn, and Ca. Alkalies have been disregarded entirely; they are present in such small quantity (except in analyses 33, 39, and 51) that the resulting error is not important; K is important in analyses 33, 39, and 51, but, as noted by Ross and Shannon,[5] it seems to replace H, or H_2O, rather than Mg or Al.

The analyses show that Al may be replaced by Fe''' in any amount from 0 to 100 per cent. To show this graphically, a three-dimensional figure is necessary, as provided in Fig. 2, in which the vertical axis represents 100 (Fe'''+Ti+Cr) divided by Fe'''+Ti+Cr+Al. The iron end-member formulas are:

1. $4Fe_2O_3 \cdot 16SiO_2 \cdot 20H_2O$
2. $6Fe_2O_3 \cdot 12SiO_2 \cdot 22H_2O$
3. $6MgO \cdot 3Fe_2O_3 \cdot 12SiO_2 \cdot 25H_2O$
4. $6MgO \cdot 2Fe_2O_3 \cdot 14SiO_2 \cdot 24H_2O$

These are the probable limits of variation in composition of the mineral commonly known as nontronite, but this is merely the ferric iron end of the montmorillonite system. Analysis 45 is the original chloropal or unghwarite. Accordingly it may be reasonable to designate $4Fe_2O_3 \cdot 16SiO_2 \cdot 20H_2O$ as chloropal.

The tenor of H_2O in montmorillonite varies notably, apparently good analyses ranging all the way from 15 to 25 per cent, but the usual amount is about as given in the formulas; though the evidence that some end members contain more than others is not conclusive. Formulas are written with varying tenor of water so as to keep the total number of oxygen atoms constant.

[5] *Jour. Am. Ceram. Soc.*, **9**, 77 (1926).

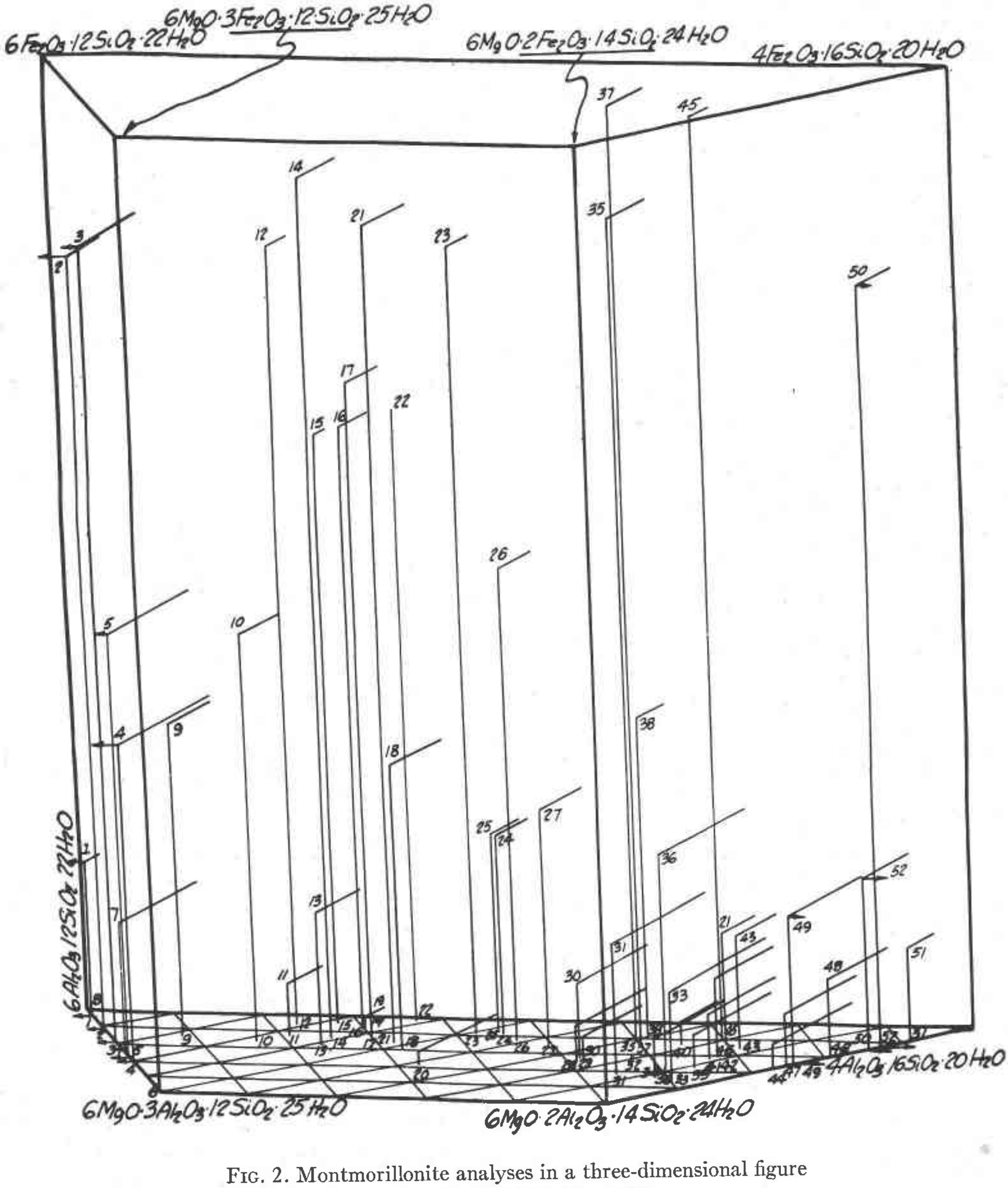

FIG. 2. Montmorillonite analyses in a three-dimensional figure whose base is shown in Fig. 1.

Optic Properties as Related to Composition

It is well known that the indices of refraction of montmorillonite (including nontronite) vary considerably with variations in the tenor of water. For example, Larsen and Steiger[6] show that nontronite from Woody, California, with 13.06% H_2O at ordinary temperature has an index of 1.585, which rises to 1.615 at 75°C. with 3.40% H_2O and to 1.67 at 210°C. with 1.80% H_2O. Other writers have noted similar data for ordinary montmorillonite. For example, Kerr[7] states that the indices of

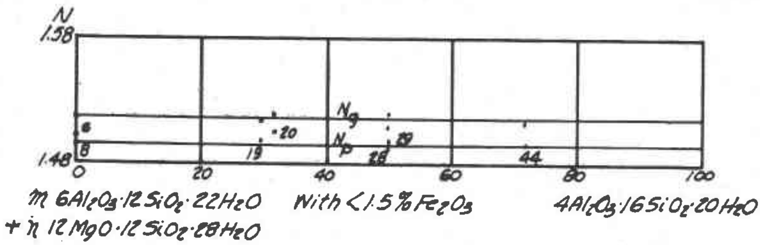

Fig. 3. Indices of refraction of montmorillonites (containing less than 1.5% Fe_2O_3) with varying replacement of Si by Al.

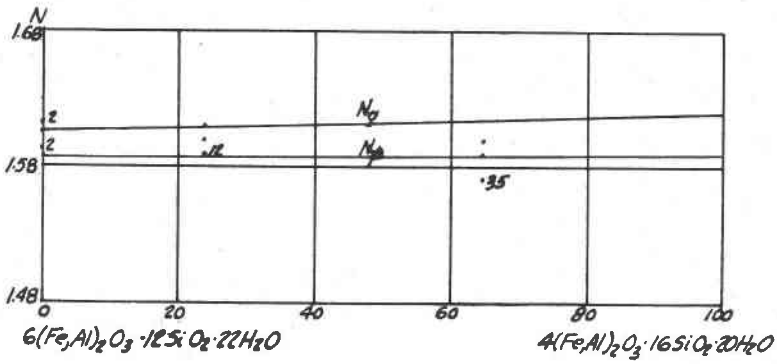

Fig. 4. Indices of refraction of montmorillonites (or nontronites) with much Fe_2O_3 (between 10 and 13% atomic Al).

refraction of montmorillonite from France and from Styria rise appreciably even at ordinary temperature if allowed to stand in a desiccator. Such variations probably explain the fact that Kerr reports the indices of the mineral from France as 1.506 and 1.485 while Ross and Shannon[8] report the indices of the same mineral of the same composition as 1.527 and 1.504, and also Larsen and Wherry[9] report that the indices of mont-

[6] *Am. Jour. Sci.*, **15,** 1 (1928).
[7] *Am. Mineral.*, **17,** 192 (1932).
[8] *Jour. Am. Cer. Soc.*, **9,** 77 (1926).
[9] *Jour. Wash. Acad. Sci.*, **7,** 208 (1917).

morillonite from Beidell, Colorado, increase in immersion liquids from 1.575 and 1.470 to 1.602 and 1.558, while Ross and Shannon give the indices of this same mineral as 1.536 and 1.494. It is probably due to these facts that it seems to be impossible to find the exact relations between variations in composition and in optical properties.

But careful study of the data shows that replacement of Si by Al has very little effect upon the optical properties. This is shown graphically in Figs. 3 and 4. All reliable data on montmorillonite containing very

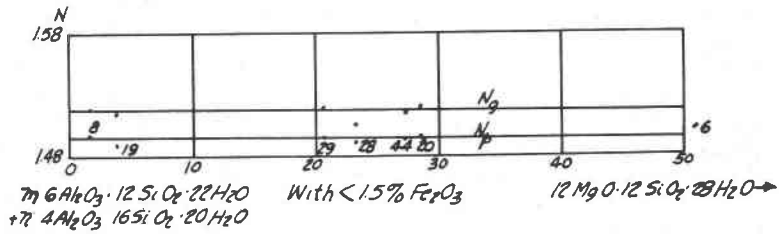

FIG. 5. Indices of refraction of montmorillonites (containing less than 1.5% Fe_2O_3) with varying replacement of Al by Mg.

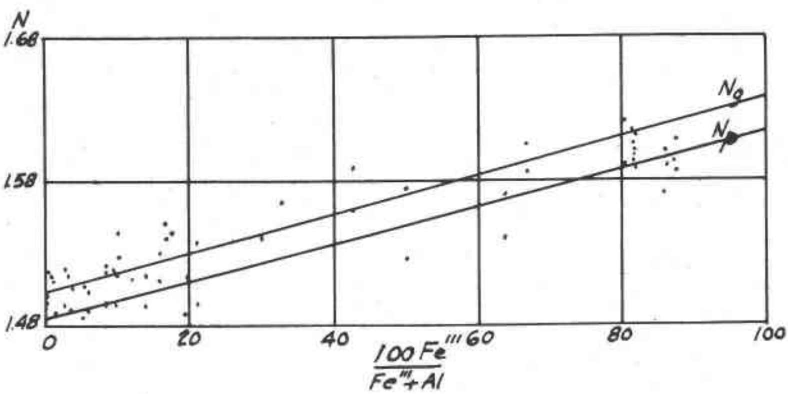

FIG. 6. Indices of refraction of montmorillonites with varying replacement of Al by Fe.

little iron ($100Fe'''/Fe'''+Al<4$) are included in Fig. 3; all data for samples with much iron ($100Fe'''/Fe'''+Al=80$–87) except 21 and 23 (excluded on account of unsatisfactory optical data) are included in Fig. 4. Replacement of Al by Mg also has very little effect on the optical properties; this is well shown by the similarity in properties between samples 8 and 6, as well as by Fig. 5.

On the other hand replacement of Al by Fe produces a marked effect on the optical properties, as shown on Fig. 6, which is based solely on this relation, because other replacements have no important effect. It is probable that variations from the rectilinear relationship are due in large part to variations in tenor of water.

TABLE 1. DATA USED IN FIGS. 1–6

	Si atoms for 24 non O(+H) atoms	$6Al_2O_3 \cdot 12SiO_2 \cdot 22H_2O$	$12MgO \cdot 12SiO_2 \cdot 28H_2O$	$4Al_2O_3 \cdot 16SiO_2 \cdot 20H_2O$	$\frac{100(Fe'''+Cr+Ti)}{Fe'''+Cr+Ti+Al}$	Sign	2V	N_g	N_m	N_p	N_g-N_p	G
1.	10.29	96.0	4.0	—	16.9			1.550		1.540	.01	
2.	10.30	88.4	11.6	—	81.4	+	Sm.	1.612	1.604	1.592	.02	2.296
3.	11.18	79.7	20.3	—	87.4	−	26°	1.608	1.593	1.585	.023	2.289
4.	11.23	68.6	31.4	—	33.2	−	30°	1.585	1.585	1.559	.026	
5.	11.34	71.3	28.7	—	32.9				1.564			
6.	11.94	48.9	51.1	—	0.0				1.50			
7.	11.99	72.1	27.9	—	14.2			1.588		1.569	.019	
8.	12.00	96.3	3.7	—	0.3			1.518		1.495	.023	
9.	12.35	78.4	12.9	8.7	23.4	−	0°	1.578	1.578	1.538	.04	2.498
10.	12.70	69.4	14.5	16.0	42.9	−	30°	1.588	1.588	1.559	.029	
11.	12.84	67.1	11.7	21.2	5.9	−	16°	1.549		1.517	.032	
12.	12.90	69.5	8.1	22.4	81.9	+	40°	1.610	1.600	1.589	.021	2.271
13.	12.92	58.3	18.0	23.7	17.9				1.544			2.40
14.	13.03	61.1	12.5	26.3	90.5	−	Sm.	1.573		1.569	.004	
15.	13.10	69.3	3.1	27.6	61.4							
16.	13.19	61.3	9.0	29.7	63.5	−	29°					
17.	13.22	58.8	11.2	30.0	69.0			1.605		1.585	.020	
18.	13.26	48.4	19.7	31.9	30.3				1.542			
19.	13.29	60.0	7.8	30.2	1.4			1.513		1.488	.025	
20.	13.30	39.5	28.2	32.3	0.9	−		1.517		1.494	.023	
21.	13.31	52.1	15.1	32.7	86.7	−	Sm.	1.575		1.571	.004	
22.	13.48	62.9	—	37.1	63.9			1.57		1.54	.03	
23.	13.66	48.8	8.0	43.2	83.8				1.57–1.63			
24.	13.83	44.3	10.1	45.6	21.0			1.536		1.494	.042	
25.	13.87	43.5	9.7	46.8	21.2		Sm.	1.536		1.494	.042	
26.	13.90	40.1	11.2	47.7	50.2			1.572		1.523	.049	
27.	13.98	35.8	14.4	49.8	22.8							
28.	14.07	24.3	23.5	52.2	3.9			1.506		1.490	.016	
29.	14.11	26.6	20.8	52.5	2.8			1.520		1.495	.025	
30.	14.14	24.1	23.2	52.7	8.3				1.520		.007	
31.	14.22	11.6	31.0	57.4	14.0		16–24°	1.513		1.492	.021	
32.	14.23	20.9	20.8	58.3	0.0							
33.	14.27	6.7	32.7	60.6	9.3	−	12–25°	1.565		1.543	.021	
34.	14.39	11.6	28.9	59.5	3.8				1.480			1.98
35.	14.40	29.1	11.3	59.6	86.0	−	66°	1.60	1.59	1.57	.03	
36.	14.40	10.3	29.0	60.7	23.2				1.546–1.553			2.03
37.	14.41	27.9	12.0	60.1	98.2	−	Sm.	1.585	1.585	1.57	.015	2.495
38.	14.46	29.6	8.9	61.5	34.0							
39.	14.52	9.9	26.8	63.3	3.7	−	15–27°	1.550		1.528	.022	
40.	14.56	24.5	10.9	64.6	1.7							
41.	14.69	10.2	22.9	66.9	5.4	−	13–24°	1.508		1.484	.024	
42.	14.73	10.5	21.5	68.0	9.1	−	7–19°	1.515		1.493	.022	
43.	14.74	13.3	15.3	71.4	12.3				1.558			
44.	14.78	—	27.3	72.7	3.1		16–24°	1.513		1.492	.021	
45.	14.80	21.6	8.2	70.2	96.7							
46.	14.80	18.6	11.7	69.7	11.8				1.51±			
47.	14.96	—	25.9	74.1	5.8			1.506		1.490	.016	
48.	15.27	—	19.3	80.7	8.5	−	15–22°	1.515		1.492	.023	
49.	15.49	—	24.0	76.0	15.9	−		1.53		1.51	.02	
50.	15.74	—	12.4	87.6	80.5			1.62		1.59	.03	2.29
51.	15.86	—	8.6	91.4	10.3			1.545		1.525	.02±	
52.	16.52	—	14.6	85.4	19.9	−	18°	1.514		1.487	.027	

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