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THE STRUCTURAL RELATIONSHIP OF NONTRONITES AND MONTMORILLONITE

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INTRODUCTION

Nontronites have been regarded quite often as iron kaolinites, though some investigators (1) are inclined to group them among the zeolites. On account of the extremely fine-grained nature of all the nontronites the only hope for the solution of this problem lies in the investigation by means of *x*-rays. By the use of the powder method the writer will show that nontronites including morencite, pinguite, faratsihite, stilpnochloran and chloropal are like montmorillonite in structure. They are, therefore, layer structures, very similar to vermiculites but unlike kaolinite. They have no resemblance to the structures of zeolites.

The writer wishes to express his thanks to Mr. Russell Wayland for his assistance in measuring and calculating over forty films, and to the Graduate School of the University of Minnesota whose grants made this study possible. He is also indebted to Dr. W. F. Foshag and Dr. E. P. Henderson of the United States National Museum for most of the specimens investigated.

MINERALS USED

1. Nontronite, Peta Luma, California. United States National Museum specimen. Greenish lemon yellow veinlets in a reddish brown decomposed brecciated rock. Contains considerable amounts of calcite.
2. "Morencite," Arizona Central Mine, Morenci, Arizona. United States National Museum specimen No. 86033. Described by W. Lindgren and W. F. Hillebrand, *Am. Jour. Sci.*, vol. **18**, p. 455, 1904. Sample used contains a little quartz and some unidentified impurities.
3. "Faratsihite," Faratsiho, Madagascar. United States National Museum No. 95754. Described by M. A. Lacroix, *Bull. Soc. Mineral.*, vol. **37**, p. 231, 1914.
4. Nontronite, White Oak Creek about three miles east of Bakersville, North Carolina. Received from E. P. Henderson, United States National Museum. Contains some brownish stains.
5. "Pinguite," Geilsdorf, Saxony. United States National Museum No. R4881. Greenish lemon yellow, compact.
6. "Stilpnochloran," Gobitschau, Moravia. Light brown fibrous-looking material.

This specimen was obtained through the kindness of Dr. Julius Holzner who described it in two papers (see references).

7. Nontronite, Mt. Magnitnaya, Ural Mountains. Mixed with other silicates. Greenish yellow, fibrous looking. The powder photograph of this nontronite is not included in table 1 on account of a number of lines belonging to impurities.
8. Montmorillonite ("bentonite"), unknown locality. Dense pinkish white specimens.

X-RAY DATA

Of all the layer structures investigated by the writer nontronites and montmorillonite yield the poorest powder spectrum photographs. This is undoubtedly due chiefly to the extremely small size of the individual particles. It may also be caused by a certain lack of parallelism of layers in individual "books." This absence of parallelism would exist in addition to common block structure phenomena and could be due to distortion in the layers themselves or unequal distribution of H_2O content between them.

Though the lines are broad and diffused they are good enough to give the interplanar distances (d) and intensities (I) recorded in table 1. Fe radiation from a modified Ksanda ion tube was used. Exposures were twenty-four hours at 10 MA and 30 KV. The radii of the cameras were 57.3 mm. The powders mounted on silk threads with collodion were not over 0.8 mm. in diameter. Montmorillonite was *x*-rayed in the same manner and its lines (given in table 1) agree with the powder spectrum photograms of other investigators of montmorillonite (5, 9, 10). Certain changes in the lines of nontronites occurred when the minerals were partially dehydrated over periods of thirty hours at 300°C. The essential changes are recorded in table 1. The distances for which no changes are indicated remained practically unaltered in the dehydrated material. The same statement applies to specimens almost completely dehydrated at 575°C. (twenty hours heating in air).

Three samples were *x*-rayed after their powders had been placed in water for four days. An attempt was made to keep the powders moist by means of a wick in contact with the mounting threads during the exposure.* That the attempt was successful is shown in table 1 by the increases of the distances for lines No. 1. It was not possible, however, to ascertain the amount of H_2O in the powders actually *x*-rayed.

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* Glass tubes could not be used for containers of these moist powders because Fe radiation is largely absorbed by the glass.

INTERPRETATION OF DATA

The agreements between the lines of the nontronites and montmorillonite are obvious in table 1, that is if one makes allowance for the difference in the sizes of the Al and Fe″ ions. The agreement is even more striking in a comparison of the films themselves which, however, do not lend themselves well to photographic reproduction.

Hofmann, Endell and Wilm (5) have given us an interpretation of the montmorillonite structure with which the writer agrees except for some of the indices they assigned to their reflections. According to them montmorillonite is built up of layers as pyrophyllite and talc (6) with this difference, however, that H_2O is present between the layers. The distance between centers of layers is determined by the amount of H_2O available. Under water, for example, it is as high as 19.6 Å. The spacing, therefore, is entirely dependent on the percentage of H_2O in the specimen. The writer has shown a similar structure for vermiculite (this journal, vol. **19,** p. 571, figs. 1 and 2) with this difference, however: The spacing appears to be constant (14.2 Å) over a wide range of H_2O content. It decreases to that of talc (9.2 Å) at some relatively high temperature. It has not been possible so far to fix this temperature definitely.

Since the basal pinacoid reflections seem to be the only ones which alter their positions with changing H_2O in montmorillonite, Hofmann, Endell and Wilm assume that the unit cell is orthorhombic and assign (hk0) indices to the stationary reflections. It is doubtful whether they are correct in their assumption, for montmorillonite lines are too diffuse to measure them very accurately. If the cell is monoclinic as found for all similar structures, the reflections might still appear unchanged after contraction of the lattice. Table 1 illustrates this point for nontronites. Leaving basal reflections out of consideration only a few essential changes occur. The other reflections also seem to show shifts but of insignificant magnitude when considering such poorly crystallized material.

The dimensions of the unit cell of nontronite, averaging the first six specimens of table 1, would be, on the basis of hexagonal SiO_4 layers, $a_0 = 5.23$ Å and $b_0 = 9.06$ Å. The values for montmorillonite are correspondingly smaller. The distance $d_{(002)}$ for laboratory-dry material varies between 12.4 and 14.7 Å, depending on the amount of H_2O. Since the angle β is unknown, c_0 cannot be evaluated. It is probable that the unit cell is two layers high as it is in most of

TABLE 1
POWDER DIAGRAMS OF NONTRONITES, Fe RADIATION

No.	1		2		3		4		5		6		Paulusbrunn*		Montmoril-lonite		Indices
	d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	
1	14.7	7–8	12.4	3	13.9	4	13.9	6	14.1	8–10	13.4	5–8	Obscured by arrangement of camera		15.0	8	200
2			7	*ind*	7.1	1 *ind*	7	*ind*									
3	4.93	1β	4.95	0.5β	4.87	0.5β	4.97	1β	5.02	1β	4.99	0.5β			4.92	1β	
4	4.48	3	4.48	2–3	4.44	3	4.50	4	4.55	3–4	4.51	3	4.56	*st*	4.45	3	
5	4.26	0.5 *ind*	4.14	1	3.94	0.5 *ind* β					4.18	1	4.12	*ss*			
6			3.55	1	3.54	2	3.42	1–2					3.52	*ss*			
7													3.13	*s*			
8			2.84	0.5	2.79	0.5	2.80	0.5	2.80	0.5–1	2.82	0.5	2.82	*s*	2.81	*ind*	
9	2.72	0.5	2.68	1							2.68	0.5					
10	2.571	1–2	2.573	1–2	2.588	1–2			2.584	2	2.577	2	2.562	*mst*	2.535	2	
11	2.476	1–2	2.501	1–2	2.507	1 *ind*	2.521	2 *vb*									
12			2.437	1–2							2.436	2	2.436	*ss*	2.43	*ind*	
13	2.267	0.5	2.259	0.5–1	2.272	0.5 *vb*	2.2	*ind*	2.28	*ind*			2.242	*ss*	2.228	0.5	
14			2.180	0.5–1							2.180	0.5–1 *vb*					
15			2.071	0.5									2.115	*ss*			
16	2.046	0.5	1.995	0.5–1													
17	1.859	1	1.884	0.5					1.862	0.5	1.888	0.5–1	1.884	*ss*	1.851	0.5	
18	1.795	0.5											1.808	*ss*			
19			1.712	1–2	1.720	0.5–1	1.716	0.5–1	1.718	1			1.739	*s*			
20	1.701	0.5									1.708	1–2	1.690	*s*	1.688	1	
21	1.657	0.5	1.659	1	1.678	1	1.670	1	1.670	1	1.665	1–2			1.643	1	
22	1.618	0.5			1.632	0.5–1	1.629	0.5									
23			1.560	0.5							1.556	0.5	1.583	*ss*			
24	1.500	2*b*	1.506	2–3	1.519	2	1.517	3	1.517	3–4	1.505	4	1.528	*st*	1.494	3	060
25					1.481	2	1.478	1									
26	1.462	0.5	1.449	0.5	1.451	0.5					1.444	0.5	1.450	*ss*	1.415	0.5	
27	1.409	0.5	1.391	0.5					1.390	0.5			1.401	*ss*			
28	1.345	0.5											1.363	*ss*			
29					1.307	0.5	1.305	1 *b*	1.304	0.5–1	1.299	0.5	1.314	*s*	1.285	1	
30	1.284	0.5–1 *b*			1.281	0.5	1.282	0.5	1.280	0.5							
31			1.253	0.5–1	1.263	0.5–1	1.260	1	1.263	1	1.254	0.5	1.268	*s*	1.241	0.5	
32	1.236	0.5			1.231	0.5–1											

TABLE 1 (*Continued*)

Essential Changes After Heating at 300°C.

No.	1		2		3		4		5		6		Paulusbrunn*		Montmorillonite		Indices
	d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	
1	14.0	2	disappeared		disappeared		disappeared		13.8	4–5	disappeared						002
1*a*	none		9.87	2–3					9.90	1	9.56	2–3			9.8#		002
7*a*	none		3.169	2 *b*	3.085	*ind*	none		3.118	1	3.123	3					
11*a*	*ind*		2.514	2–3	2.498	2 *b*	2.472	1 *vb*	2.476	1 *vb*	2.496	2					
Essential Changes After Dehydration at 575°C.																	
1*a*	9.72	2	9.56	4	9.61	2	9.17	2	9.37	3	9.37	3			9.6#		002
7*a*	3.160	2	3.169	3	3.126	2	3.107	2	3.134	3	3.126	3					
11*a*	2.466	1 *vb*	2.517	2–3	2.462	1 *vb*	2.447	1 *vb*	2.475	1 *vb*	2.47	*ind*					
			2.452	1 *vb*													
Essential Changes When X-rayed While Moist																	
1	15.8	6			15.8		14.9										002

β = line definitely caused by K_β radiation.
b = outer edge of broad line.
vb = outer edge of very broad line.
ind = indistinct edge of line.
* Diagram by Noll (1). *st* = strong, *s* = weak, *ss* = very weak, *m* = medium.
# After Hofmann, Endell and Wilm (5).

the other layer-structures. The density determinations of nontronites are unreliable on account of the fluctuations of the distances between layers. They should, however, be greater than 2.2 for laboratory-dry material.

CHEMICAL CONSIDERATIONS

One finds little encouragement in the perusal of the chemical mineralogy of nontronites. The analyses vary between very wide limits, and different mineral names apply to the same species. It is certain now that nontronite, morencite, pinguite, chloropal (1), faratsihite, and stilpnochloran are structurally identical and should be called nontronite though faratsihite might just as well be classed as beidellite according to its analysis in table 2. Four analyses are given in this table. While specimens Nos. 2 and 3 come from the type localities, it is probable that the samples x-rayed would not be exactly like the analyzed material of table 2. Stilpnochloran No. 6 is exactly like the x-rayed material according to Dr. J. Holzner who had suspected* that it is nontronite. The water content might be different, however, due to a change in climatic conditions. In connection with this material the findings of Holzner (3 and 4) that it absorbs large amounts of thallium are very interesting. Thallium replaces calcium and water according to Holzner.

The unit cell of the proposed structure of nontronite (for illustration see this journal, vol. **19**, p. 571, fig. 2) contains 16 Si positions of which four or even more could be occupied by Al, as in the micas. It also has 8 to 12 (Al, Fe''', Fe'', Mg) positions between the Si_4O_{10} layers. The total number of occupied cation positions then is somewhere between 24 and 28. If *for the present discussion we consider the small amounts of* Fe'' *and Mg trivalent* the number will be close to 24. If just 12 positions of the 16 possible ones were occupied by Si, table 2 shows how many positions would be occupied by available (Fe''', Al Fe'' Mg) ions. There is evidently a deficiency of such ions unless Si occupies from 12.5 to 14 positions.† If we make the further assumption—which is reasonable—that the number of O and OH ions is fairly constant in the structure, we arrive at the following structural formula:

$$OH_8(Fe''', Al)_{8+n/3}(Si_{16-n}(Al, Fe''')_n)O_{40}\cdot mH_2O.$$

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* Written communication.

† Note the similarity to glauconite in this respect (8).

TABLE 2

ANALYSES AND ATOMIC DISTRIBUTION

					No. of Ions in Unit Cell			
	2	3	6	Paulus-brunn*	2	3	6	Paulus-brunn*
SiO_2	45.74	41.60	36.45	40.02	12.0	12.0	12.0	12.0
TiO_2	trace	.13	0.02	—	(14.1)	(12.8)	(12.8)	(13.5)
Al_2O_3	1.98	22.68	6.03	10.55				
Fe_2O_3	29.68	15.22	34.24	26.16	8.7	11.4	11.2	10.0
FeO	0.83	0.54	none	1.37	(10.5)	(12.2)	(12.0)	(11.3)
MgO	3.99	0.11	0.97	—				
CaO	1.61	0.60	1.91	—				
MnO	trace	—	0.04	—				
K_2O	0.20	0.22	0.35	—				
Na_2O	0.10	0.16	none	—				
H_2O-	8.84	5.71	11.01	13.25	12.2	18.0	22.2	21.8
H_2O+	5.08	13.02	9.20	8.58	(14.3)	(19.2)	(23.7)	(24.5)
FeS_2	0.66	—	—	—				
P_2O_5	0.18	0.21	0.31	—				
Total	98.89	100.20	100.53	99.93				
Sp. Gr.	—	2.523	—	—	n=1.9	n=3.2	n=3.2	n=2.5

2. Lindgren and Hillebrand, analysts.
3. M. A. Lacroix, analyst.
6. J. Holzner, analyst.
* W. Noll, analyst.

Based on this formula the calculated numbers of ions in a unit cell for the analyzed samples are recorded as numbers in parentheses in table 2; *n* values are also given. In general, then, the value of *n* lies between 1 and 4 and that of *m* between 8 and 22 for air-dried nontronite. The same formula may be used for the isomorphous montmorillonite in which case *n* approaches zero. Beidellite which according to Larsen and Steiger (2, p. 18) is very similar to nontronite would have a value of *n* between 1 and 3. As a matter of fact the analysis No. 3 of faratsihite approaches beidellite more closely (2, p. 15) than nontronite. No other beidellite was available to the writer.

It appears from all the available information that the capacity for giving off and reabsorbing water between the layers is greatest in montmorillonite in which $n=0$ or close to 0. It might be thought then that the occupation of 16 Si positions by Si is the deciding factor. On the other hand, the Al: Fe''' ratio may control the absorption process—that is, the more Al present the greater the capacity for H_2O when the mineral is kept moist. It is hoped to continue this phase of the study when more analyzed material is available.

On account of its similar formula hisingerite from several localities was *x*-rayed. It gives about five broad, indistinct bands which agree with the most intense lines of nontronite except for line No. 1 which could not be identified in hisingerite. The amorphous character of the mineral, therefore, seems to be established.

Conclusions

An *x*-ray investigation of nontronite, morencite, pinguite, faratsihite, chloropal, and stilpnochloran shows that these so-called species are structurally identical. It is highly probable that beidellite, hoeferite, müllerite and graminite according to Larsen and Steiger also have the same structure.

The structure is practically identical with that of montmorillonite (bentonite). Therefore, montmorillonite, beidellite, and nontronite form an isomorphous completely miscible series. As in montmorillonite the H_2O content of nontronites may fluctuate. Since they are layer structures the H_2O content controls the distances between layers. These distances vary between 9.2 Å at 575°C. and 15.8 Å if the sample is kept moist during *x*-ray exposure. The dimensions for a_0 and b_0 average 5.23 Å and 9.06 Å, respectively. When dehydrated at 575°C. nontronite is very similar to pyrophyllite in structure. The structural formula of this series is probably best expressed as follows:

$$OH_8(Al,\ Fe''')_{8+n/3}(Si_{16-n}(Al,\ Fe''')_n)O_{40}\cdot mH_2O.$$

This is based on the assumption that O and OH are constant and the small amounts of Mg, Fe'' are counted in as trivalent. The value of n will be between 0 and 4. Since the composition of these isomorphous mixtures depends largely on their environment during formation, n for nontronites probably is rarely much below 2, and may be as high as 4. For montmorillonite on the other hand n will usually be smaller than 1. The value of m lies between 8 and 22 for air-dried material.

Hisingerite appears to be amorphous. The four or five indistinct bands visible in the films agree, however, with the intense lines of nontronite.

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