NOTES AND NEWS

A NOTE ON SOME PROPERTIES OF SYNTHETIC MONTMORILLONITES

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While it has been known for several decades that montmorillonites can be synthesized in the laboratory (1, 2) very little further systematic work has been done to determine either the compositional limits of montmorillonite formation or the properties of the phases obtained. In the meantime the whole field of clay mineralogy has advanced rapidly and has had to contend with the fact that there was relatively little control on the purity or composition of the natural minerals to which detailed attention was given. Hydrothermal investigations (3, 4, 5, 6) recently have encountered montmorillonite phases in the systems Al_2O_3—SiO_2—H_2O, MgO—Al_2O_3—SiO_2—H_2O and Na_2O—Al_2O_3—SiO_2—H_2O, where chemically "known" and mineralogically homogeneous phases were prepared and the equilibrium thermal dissociation temperature determined as a function of decomposition. Other workers (7, 8) have determined the cation exchange capacities of synthetic montmorillonites.

As part of a more detailed investigation of the properties of clay minerals, we undertook to prepare and examine a large number of montmorillonite phases. Roy and Roy (6) already have described some of the results on the 1:1 layer, kaolin-serpentine type structures. Since the more complete cataloguing of properties of a large number of such phases extends over some years, it is considered worthwhile to report briefly the earlier results of such synthetic work. The methods and equipment used have been described in several earlier publications (3, 4). The phases formed are identified in every case by powder *x*-ray diffraction techniques. Equilibrium is presumed on the basis of successively longer runs with given compositions. If the same phase or phase assemblage appears to remain unchanged after a few weeks, and if in each case the total composition may reasonably be fitted in with the composition of the phases present, this is taken as an equilibrium assemblage. In the past we have shown neither patterns nor given the *x*-ray diffraction data for these montmorillonite phases since they are quite analogous to those of natural montmorillonites. However, *x*-ray data are now being compiled for end-member synthetic montmorillonites of known compositions. The crystallinity of the samples is examined under the electron microscope, and has been shown to be as good or better

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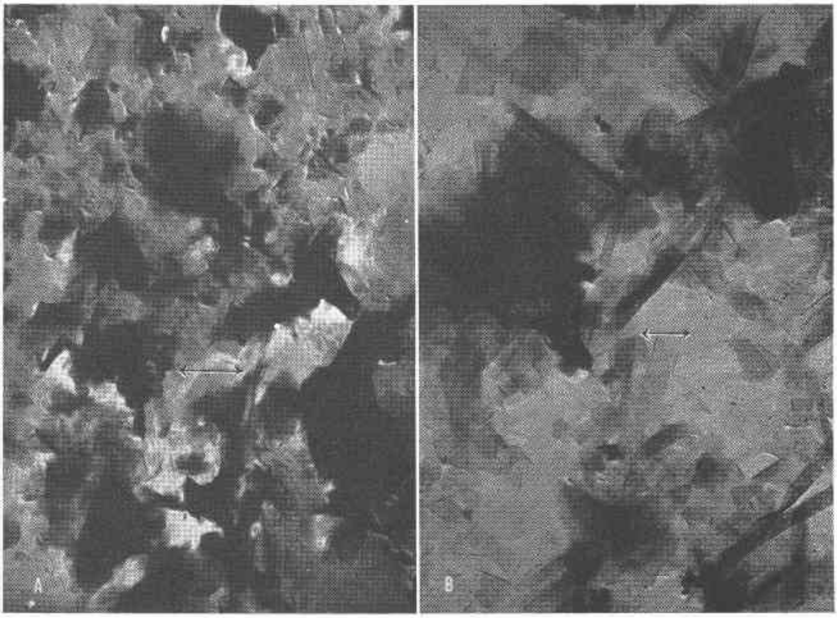

FIG. 1. Electron micrographs of synthetic montmorillonites in the $Na_2O—Al_2O_3—SiO_2—H_2O$ system. (*A*) On the left—typical thin sheets curled at the edges; (*B*) On the right—synthesized at a higher temperature and containing more silica

$$\left(\frac{Na_2O}{6}\cdot Al_2O_3\cdot 4SiO_2 \text{ as compared to } \frac{Na_2O}{6}\cdot Al_2O_3\cdot 3SiO_2 \text{ for } A.\right)$$

shows somewhat greater regularity in habit. Closer comparison will show the presence of the same curled sheets in both.

than that of the natural material (see Fig. 1); the products at the higher temperature giving very much sharper crystal outlines than have previously been observed in montmorillonites. The relation of morphology to both composition and conditions of formation should again prove to be of interest as in the case of the kaolinite-serpentine series. Single crystal electron diffraction studies carried out at the same time did not yield any significantly new data.

Another property which is often difficult to obtain accurately in a natural product is the cation exchange capacity. The fine-grained "amorphous" material (which is frequently a contaminant in natural samples) usually has a very high exchange capacity and the common gangue minerals have low exchange capacities. These contaminants are usually difficult to remove completely. Likewise, dispersions present a problem and a restricted particle size range usually is required for dependable results. These factors are eliminated with the synthetic clays. This has been recognized also by Karsulin and Stubican (8) who have related cation exchange capacity with the substitution of Mg for Al in synthetic montmorillonites. Our determinations have been made by the Bower and Truog (9) method which has been checked for reproducibility and shown in our case to be accurate to about ±3%.

In the table below are listed the properties of one of the many compositions studied and is an example of the program in progress.

TABLE 1

Composition	1/6 $Na_2O \cdot Al_2O_3 \cdot 4SiO_2$.
Conditions of synthesis	400° C., 15,000 psi H_2O, 2 weeks.
Habit	Uniform, clear, well-defined crystals approaching lath-like habit.
Equilibrium decomposition temperature	480° C. at 15,000 psi H_2O.
Decomposition products of above	Paragonite and pyrophyllite+albite.
Exchange capacity (M.e. Mn^{++}/100 g.)	96.
Basal spacing (glycol solvated)	17.0 Å.

The powder *x*-ray diffraction data are listed in Table 2.

TABLE 2. POWDER DATA ON SAMPLE OF TABLE 1

d	*Int.*	*hkl*
17.0	vs	001
8.50	ms	002
5.65	w	003
4.82	w	
4.42	s	
4.23	vw	004
3.73	w	
3.40	ms	005
2.83	w	006
2.57	wd	
1.71	vw	
1.65	vw	
1.50	ms	060(?)
1.34	wd	00, 13
1.24	wd	00, 14

Abbreviations used: vs = very strong, s = strong, ms = moderately strong, w = weak, wd = weak diffuse, vw = very weak.

Montmorillonites have now been prepared by various workers in this laboratory with a wide variety of compositions, some of which are listed in Table 3.

Table 3

*Pure	$Al_2O_3—SiO_2—H_2O$	And with systematic additions of Na and Mg and Ca to yield typical beidellites.
Pure	$MgO—SiO_2—H_2O$	With systematic additions of Al to yield typical saponites.
	$NiO—SiO_2—H_2O$	With systematic additions of Al yielding pimelites (?).
	$ZnO—SiO_2—H_2O$	With systematic additions of Al to yield sauconites.
	$Ga_2O_3—SiO_2—H_2O$	. . . .
	$Cr_2O_3—SiO_2—H_2O$	With additions of Al to yield "volchonskoite (?)"- like phases

* The pure members contain no other ions whatever within experimental error, unlike earlier work. The "addition" of Al^{3+} is not, of course, to be taken in the mechanical sense.

It is evident that a wide compositional latitude is possible in montmorillonite structures, especially in systems such as $MgO—Al_2O_3—SiO_2—H_2O$ where several ions can proxy for each other. The only limitation which appears to emerge in addition to the obvious ones of the electrostatic neutrality and the structure appears to be one of the limit on the charge of the layer. Assuming that base exchange capacity is also variable enhances the compositional area over which a single crystalline phase can form, although this point is very difficult to prove experimentally.

Acknowledgments

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References

1. Ewell, R. H., and Insley, H. (1935), Hydrothermal synthesis of kaolinte, dickite, beidellite and nontronite: *J. Res. Natl. Bur. Stand.*, **15,** 173.
2. Noll, W. (1944), New investigations in water-silicate systems: *Kolloid Zeits.*, **107,** 181.
3. Roy, Rustum, and Osborn, E. F. (1954), The system $Al_2O_3—SiO_2—H_2O$: *Am. Mineral.*, **39,** 853–885.
4. Roy, Della M., and Roy, Rustum (1955), Synthesis and stability of minerals in the system $MgO—Al_2O_3—SiO_2—H_2O$: *Am. Mineral.*, **40,** 147–178.
5. Sand, L. B., Roy, Rustum, and Osborn, E. F. (1953), Stability relationships of some minerals in the system $Na_2O—Al_2O_3—SiO_2—H_2O$: *Am. Mineral.* (abstract), **39,** 341.
6. Roy, Della M., and Roy, Rustum (1954), An experimental study of the formation and properties of synthetic serpentines and related layer silicate minerals: *Am. Mineral.*, **39,** 957–975.

7. Ormsby, W. C., and Sand, L. B. (1953), Base exchange: An analytical tool for mixed layer aggregates: *Proc. Second National Clay Conference,* Publication 327, National Academy of Science-National Research Council, Washington, D. C. (1954).
8. Karsulin, M., and Stubican, VI (1954), On the structure and properties of synthetic montmorillonite: *Monats. Chem.,* **85,** 343–358.
9. Bower, C. A., and Truog, E. (190), Base exchange capacity determination of soils and other materials: *Ind. Eng. Chem., Anal. Ed.,* **12,** 411–413.

OPTICAL ANOMALIES IN ARFVEDSONITE FROM GREENLAND

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Many alkali amphiboles fail to show complete extinction on (010) between crossed nicols, not even in monochromatic light. The phenomenon was observed by Eskola and Sahlstein (1930) on three amphiboles of the arfvedsonite-riebeckite series, on two alkali amphiboles later called eckermannite by Adamson (1944), on one specimen of hastingsite and one of taramite. The incomplete extinction was found only in sections roughly parallel with (010). On (100), striations parallel with the trace of the *c*-axis were noted.

At that time, no closer experimental study of the phenomenon was made. It was only assumed that the amphiboles, originally crystallized as a homogeneous phase, have later been subjected to exsolution and are now perthitic. The lath-shaped strips are arranged in such a way that the *c*-axis and the (010) plane are common for the exsolved amphibole components.

Later, the incomplete extinction of certain alkali amphiboles, particularly of those belonging to the arfvedsonite-riebeckite series, have been mentioned by a number of Japanese authors (Sato, 1936; Iwao, 1939; Hori, 1942; Inoue, 1950; Yagi, 1953). The phenomenon seems to be very common in alkali-rich amphiboles.

To explain the optical anomalies pointed out above, a specimen of arfvedsonite from Kangerdluarsuq, Greenland (this Institute Collection No. 3436), was studied with more modern equipment. The incomplete extinction on (010) and the striated structure on (100) are very clearly seen on this mineral. Chemical analysis and optical properties of arfvedsonite No. 3436 are given in Table 1.

The material for the chemical analysis was purified by centrifuging in Clerici's solution. The purity of the final powder was tested under the microscope. The optical properties were determined in the usual manner. For determining the optical orientation and for quantitative measurement of the pleochroism and of the degree of non-extinction, thin sections were cut parallel with (010) and (100). On the section (010) it was found that the direction of maximum absorption (=optical α) is parallel with