

Dehydration of the montmorillonite minerals.

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INTRODUCTION.

STUDIES of the effect of dehydration at temperatures greater than 150° on sorption by montmorillonites have shown that small inter-layer cations such as lithium and magnesium promote an irreversible decrease in the amount of interlamellar sorption and a consequent marked fall in the cation exchange capacity as measured by conventional methods (1, 2, 3, 4). The other minerals of the group do not show this property (4), which is quite distinct from the supposed 'potassium fixation' reported in these minerals (5). This latter effect, which is small for montmorillonite, refers to the decreased rate of exchange of potassium as compared with smaller exchange cations especially after the potassium-saturated mineral has been dried at 100° C., and has been shown to be much more marked in mica-like minerals with silicate layers of higher charge density (e.g. illites and vermiculites (6)). The amount of water sorbed by potassium-saturated montmorillonite is not significantly affected by drying at temperatures below 400° C. although it is less than that of most other montmorillonites (3), due probably to the low hydration energy of the potassium ion (7).

In this paper the conditions leading to irreversible loss of internal surface are considered in greater detail. In the first part the susceptibility to irreversibility is considered for lithium-saturated minerals over the range of composition from montmorillonite to beidellite.¹ The end-members of this isomorphous series have been shown to differ markedly in their dehydration properties (4) and this has been made the basis for a simple test to distinguish them (8). Since, however, intermediate minerals exist, particularly in soils, it was thought desirable to investigate them also. The second part of this paper is concerned with the effect of only partly saturating the exchange complex of montmorillonite with lithium, the remaining ions being normal in their behaviour

¹ See appendix for remarks on the mineral 'beidellite'.

on dehydration. The effect on the internal surface of the two types of treatment is very similar, the difference being that in the first case the loss of surface is determined by the way the octahedral substitutions are distributed between silicate sheets, whereas in the second case it is determined by the way the two types of exchange cations spread themselves over the surface.

I. MONTMORILLONITE-BEIDELLITE SERIES.

Method.

The chief difficulty in carrying out this work was to find a number of analysed minerals whose unit cells have compositions intermediate between montmorillonite and beidellite. Unfortunately many of the samples that have been analysed were not pure and often no attempt had been made to distinguish between cations held superficially by the clay and those composing the silicate sheet. Foster (9) has emphasized the latter point with special reference to magnesium and found that several dioctahedral montmorillonite minerals formerly thought to have more than two out of the three octahedral positions filled with cations were actually nearly dioctahedral. Where silica, alumina, and iron oxides are closely associated with the clay mineral the problem of calculating the unit cell composition from total analyses is almost insoluble. Methods have been proposed whereby these impurities are selectively extracted by suitable reagents, and it has been shown that whereas the analyses indicated an unreasonable unit-cell composition, after correction not only was a reasonable unit-cell composition calculable but it often turned out to be nearly dioctahedral (10, 11). Such results increase confidence in selective solubility methods, but the necessity of relying on such empirical methods to arrive at unit-cell compositions can hardly be considered as satisfactory, since they require assumptions as to the amount of clay mineral attacked by the reagent.

The method used here to classify samples was based on the assumption that all the minerals investigated were strictly dioctahedral. The divalent cations not removed by repeated washing with ammonium acetate were assumed to originate from octahedral co-ordination in the clay mineral. Inspection of analyses given in the literature shows that magnesium is generally the only important divalent cation permissible in octahedral co-ordination.

The net charge was calculated from the exchange capacity. The justification for this procedure is that the samples were carefully selected,

purified by sedimentation, and examined by X-ray diffraction to avoid the possibility of contamination by non-expanding mica-like minerals. Analyses of the samples for potassium also served to confirm this point and provided a correction where necessary.

The percentage of the exchange capacity due to substitution of trivalent cations by magnesium was then taken as an index of the percentage of octahedral substitution. This method is admittedly an approximation, but in the light of present knowledge it is thought to give results which bear as much relation to the truth as the more conventional methods.

To carry out the dehydration tests the samples were first saturated with lithium, since lithium has been found to be the most active inter-layer cation. The samples were then heated at various temperatures up to 300° C. and the loss of internal surface tested by taking X-ray diffraction photographs of the samples after treatment with glycerol. Glycerol was used because the X-ray photographs of glycerol-treated samples showed comparatively simple two-component random interstratification effects and because the relevant calculations had been carried out (12). The surface readily available to glycerol has been found to be roughly comparable to that available to water vapour.

Experimental procedure.

The samples suspected of containing a dioctahedral montmorillonite mineral were first submitted to a preliminary examination, which consisted of taking an X-ray photograph of the powder specimen treated with glycerol. About fifty samples containing a substantial proportion of a dioctahedral montmorillonite mineral were re-examined by saturating them with lithium, heating them to 200° C. overnight, and again testing their reaction with glycerol. The samples could be divided into three main groups, those that gave a rational 18° kX spacing, those giving a rational 9·5° kX spacing, and those showing considerable central scatter and an irrational sequence of 00 l reflections. Representatives from each group were chosen and purified by dispersion to a 1 % suspension and passing through a Sharples supercentrifuge, the fraction less than 0·1 μ being retained. This fraction was concentrated by further centrifuging or by flocculation with calcium chloride. A little of the resultant gel was dried on a glass slide to provide oriented flakes and the remainder was washed with ammonium acetate until ammonium-saturated and then with alcohol until the excess ammonium acetate was removed.

The oriented flakes were cut from the glass slides, placed in small weighing bottles, and washed with 3N lithium chloride followed by alcohol until chloride-free. Samples of the flakes were heated at 100°, 150°, 200°, 250°, and 300° C., and soaked in glycerol at 80° C. overnight. X-ray photographs were taken with slit-collimated cylindrical cameras of 9 cm. diameter and filtered copper or cobalt radiation.

The exchange capacity of the samples was determined by distilling the ammonia in a semi-micro distillation apparatus after adding 2 ml. of 40 % sodium hydroxide. The exchange capacity thus determined compared favourably with that found by standard methods, and the results with duplication gave a reproducibility of ± 3 m.e./100 gm. for an exchange capacity of 100 m.e./100 gm.

The analyses for magnesium, potassium, iron, and calcium were carried out on the ammonium-saturated sample by evaporating the sample in hydrofluoric acid and taking the residue up in nitric acid. The resultant solution was analysed for the elements mentioned using the Lundegårdh spectrographic method. An accuracy of about ± 6 % of the amount present could be expected.

Results.

The results of analyses of the samples selected as representative of the montmorillonite-beidellite series are given in table I. Information concerning the source of samples is also included.

TABLE I. Chemical analyses and base-exchange capacity of the montmorillonite-beidellite series.

No.	Locality.	Exchange capacity m.e./100 gm.	Total analysis* in %			m.e./100 gm. of exchange capacity due to Mg.	% octa- hedral substitution.
			K ₂ O,	Fe ₂ O ₃ ,	MgO.		
1.	Black Jack mine, Idaho ...	94	0.2	0.7	0.16	4	4
2.	Plain of Akkar, Safita, Syria (IS17) ...	110	0.0	12.8	1.60	40	36
3.	Hathi-Ki-Dhani, India	73	0.0	7.6	1.20	30	41
4.	Unter-Rupsroth, Rhön	113	0.0	0.0	2.06	51	45
5.	Wyoming ...	89	0.0	4.4	2.48	62	70
6.	British Columbia ...	81	0.0	2.2	2.54	63	78
7.	Redhill, Surrey ...	82	0.0	7.4	2.78	70	85
8.	Elliots, Antigua ...	90	0.67	7.3	3.38	84	93†

* % CaO less than 0.1 %.

† Including 0.67 % K₂O in total charge, this value would reduce to 81 %.

Source of materials—

1, G. Nagelschmidt (14). 2, A. Muir. 3, Burmah Oil Co. 4, U. Hofmann. 5, F. W. Berk and Co., London. 6, Imperial Institute (no. Ca A 128). 7, Fullers Earth Union (no. XLCT). 8, Imperial Institute (no. L 158).

The X-ray results given in table II were interpreted by means of the spacing near 9 kX. It was concluded from the diffraction patterns that

the variations of spacing observed between samples was due to a two-component randomly interstratified system; the components being near 9.4 and 17.7 kX. This case has been investigated by Brown and Greene-Kelly (12), who calculated proportions of each component which would be required to produce a given sequence of basal reflections. The proportions 'p' of the 17.7 kX spacing were read off from fig. 2a¹ in the above paper after corrections had been applied to allow for small changes in the 'c' values of the two components. The results are included in table II.

TABLE II. Results of X-ray examination of the minerals after glycerol treatment. The interlayer spacing is given in kX, followed by 'p' proportion expanded.

No.	Untreated.	Heated				
		100°.	150°.	200°.	250°.	300° C.
1.	8.9 R	8.9 R	8.9 R	8.9 R	8.9 R	8.9 R
	1.0	1.0	1.0	1.0	1.0	1.0
2 (a).	8.9 R	8.9 R	8.9 R	9.0	9.0	9.1
	1.0	1.0	1.0	0.7	0.7	0.5
3 (b).	8.9 R	8.9 R	8.9 R	9.1	9.2	9.3
	1.0	1.0	1.0	0.5	0.3	0.2
4.	8.9 R	n. d.	9.0	9.1	9.1	9.2
	1.0	n. d.	0.7	0.5	0.5	0.3
5.	8.9 R	8.9 R	9.4 R	9.4 R	9.5 R	9.4 R
	1.0	1.0	0.0	0.0	0.0	0.0
6 (c).	8.9 R	8.9 R	9.2	9.6 R	9.6 R	9.6 R
	1.0	1.0	0.4	0.0	0.0	0.0
7.	8.9 R	8.9 R	9.0	9.4 R	9.4 R	9.4 R
	1.0	1.0	0.0	0.0	0.0	0.0
8.	8.9 R	8.9 R	9.2	9.4 R	9.4 R	9.4 R
	1.0	1.0	0.3	0.0	0.0	0.0

(a), Lines broad, few orders; a typical soil clay mineral. (b), Kaolinite present. (c), Cristobalite present.

R, reflection is a member of rational 00l sequence. n.d. not determined.

In fig. 1 the percentages of octahedral substitution in the different minerals are plotted against the value of 'p' after heating the lithium-saturated mineral to 200° C. It can be seen that according to the conditions of the test, above 70 % octahedral substitution there is little expansion, but below this value there is a rise in 'p' reaching the half-expanded state at about 40–45 % octahedral substitution. Unfortunately it was not possible to obtain a beidellite containing about 20 % octahedral substitution, but it seems likely that such a mineral would be little affected by the treatment. Nontronites generally contain about

¹ The ordinates in fig. 2c in reference 12 should read 2.95, 3.05, 3.15 kX instead of 2.8, 3.0, and 3.2 kX.

0.8–1.0 % MgO and probably lie in the region 20–40 % octahedral substitution and their behaviour to the test is compatible with afore-going results. Here again lack of sufficient amounts of samples of adequate purity did not permit detailed examination. It is noteworthy that of the fifty dioctahedral minerals investigated only five were not montmorillonites.

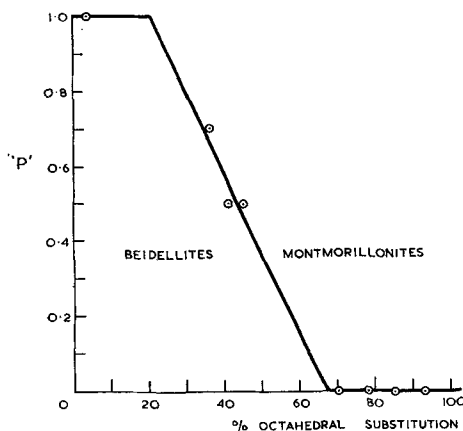


FIG. 1. Relation between the loss of internal surface after treatment and the percentage of octahedral substitution. Heating temperature 200° C.

Discussion.

Hofmann and Klemen (1) have suggested that the anomalous loss of expansion by lithium-montmorillonite after drying is due to the migration of lithium ions from the interlayer position to the vacant octahedral sites. They argue that this would tend to reduce the effective silicate sheet charge and make the mineral approach a non-expanding pyrophyllite-type structure.

Greene-Kelly (4) showed that only magnesium- and lithium-montmorillonite showed a marked dehydration hysteresis. This would be expected since the two ions are of the same size and would fit easily in the octahedral positions in the silicate sheet. Trioctahedral montmorillonite minerals were also shown to re-expand freely after lithium saturation and dehydration, and this is also to be expected, since no vacant octahedral sites are available for the migrating ions. Among the dioctahedral minerals, beidellites and nontronites were also found to be free from the hysteresis, and the results of this paper have shown that there is a correlation between the percentage of octahedral substitution and the

loss of expansion. These results could be explained if it were assumed that migration is only permissible when the silicate sheet charge is due to octahedral substitution. If all ions of the correct size migrate on dehydration then the effect on the expanding properties of the mineral will depend on the way the tetrahedral and octahedral substitutions occur in the mineral. If they occur so that all of one crystallite is tetrahedral and all of another octahedral, then after treatment there should be two sets of $00l$ reflections, one due to the expanded and the other due to unexpanded crystallites. On the other hand, if each crystallite consists of randomly interstratified silicate sheets each possessing only tetrahedral or octahedral charge, then the effect of the treatment will be to produce three concentrations of interlayer cations, namely zero, half the normal number, and normal number of exchange cations per unit cell. Clearly the X-ray photograph of the glycerol-saturated specimen is liable to be complex, with the characteristic X-ray effects associated with random interstratification. The case where the silicate sheets are all similar in composition and contain both octahedral and tetrahedral substitution is interesting, since it will show the effect of decreasing the silicate sheet charge on the balance between the attractive force between the sheets and the repulsive force due to the sorption energy of the interlayer molecule. Random interstratification would not be expected in this case. It is probable that as the sheet charge decreases, the glycerol-treated mineral will show a sudden loss of expanding properties as the mineral approaches the pyrophyllite structure. In most of the cases studied there seems to have been random interstratification of 9.5 and 17.7 kX, and this suggests that there are differences in composition between the silicate sheets.

II. LITHIUM-SODIUM-MONTMORILLONITE.

Experimental procedure.

Pairs of 0.5 gm. samples of a purified montmorillonite from Redhill, Surrey, were washed five times with normal solutions of mixed lithium and sodium chlorides. They were washed free of chloride ions with alcohol-water mixtures and one of each pair was then heated to 200° C. The samples were washed with ammonium acetate, the washings being analysed spectrographically for lithium, sodium, and calcium. The samples were then freed from excess ammonium acetate with alcohol and analysed for ammonia. To determine the change of internal

surface, flakes containing known proportions of lithium and sodium were heated to 200° C. and the decrease of surface area determined by taking X-ray photographs of the glycerol-treated specimens as in part I.

Results.

Table III gives the results of the exchange capacity and X-ray measurements. It will be noticed that the calcium content is included with the

TABLE III. Relation between sodium introduced and sodium recovered after heating. The fraction, 'p', of the internal surface available to glycerol is also shown. (Exchange capacity of the unheated montmorillonite is 85 m.e./100 gm.)

m.e. (Na ⁺ + Ca ⁺⁺) per 100 gm. introduced.	m.e. (Na ⁺ + Ca ⁺⁺) per 100 gm. washed off after heating.	m.e. (Li ⁺) per 100 gm. washed off after heating.	'p'.
5	5	15	n. d.
15	8	11	n. d.
20	12	10	0.1
26	17	12	n. d.
27	20	12	0.25
48	29	15	1.0
57	45	16	1.0
70	65	6	1.0
79	74	5	1.0

n. d., not determined.

sodium content because of the difficulty of removing all the calcium from the exchange complex, and at low sodium values its contribution is appreciable. On the average about 3 milliequivalents of calcium per 100 gm. remained.

It will be seen that in general an appreciable amount of the sodium introduced was recovered after heating. The internal surface available to glycerol after heating is low at low sodium contents but rapidly increases to that of the fully expanding material when about 50 % of the exchange complex is sodium. All the heated samples still contained some exchangeable lithium; the lithium-saturated and heated mineral had a residual exchange capacity due to lithium of 15–20 m.e./100 gm. In fig. 2 the correlation of internal surface of heated samples with the exchange capacity measurements is made. It is interesting to note that X-ray photographs of heated lithium-sodium-montmorillonite treated with glycerol did not show any evidence of a 14 Å. reflection or its contribution to a mixed layer system.

Discussion.

When the amounts of inactive ions (sodium and calcium) were less than 50 % of the total exchange capacity, fig. 2 shows that about 65 % of the sodium and calcium introduced was recovered after the mineral had been heated. In this range of composition, the internal surface

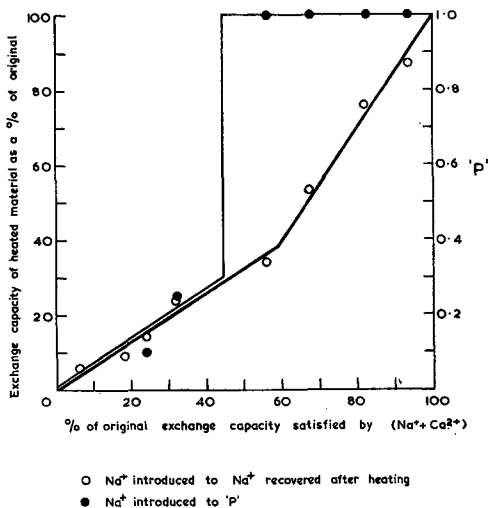


FIG. 2. Relation between the internal surface and exchangeable sodium available after treatment and the amount of sodium introduced. Heating temperature 200° C.

available to glycerol appeared to be comparable with the amount of sodium recovered. This suggests that the freely exchangeable sodium ions are concentrated in that part of the interlamellar space which is freely expanding. The remaining 35 % of the sodium introduced which is not freely exchangeable is presumably miscible with the lithium ions and consequently trapped when the latter migrate and the sheets are irreversibly brought together.

When the exchange complex contained above about 50 % sodium a marked change occurred. The X-ray results indicated that a high proportion of the internal surface became freely available to glycerol and at the same time there commenced an upward trend in the amount of sodium recovered. The composition of the fixed cations when this sudden expansion occurred was about 30 % sodium ions and the remainder lithium. It is interesting to note that when most of the surface

was available to glycerol the amount of sodium recovered was still somewhat less than that introduced. This may be a reflection of the slightly different penetrating power of water and glycerol.

The fact that lithium-saturated and heated montmorillonites always give some exchangeable lithium the amount of which appears to be independent of the composition of the mineral (for more than 70 % octahedral substitution) suggests that these cations are attached to sites external to the crystallites and these cations differ fundamentally from the interlamellar cations in their behaviour on dehydration. It is interesting to note that even if a high proportion of the sodium introduced is recovered and the crystallites appear to expand fully with glycerol, the amount of lithium recovered is small. This suggests that these lithium ions are fixed even though the interlamellar surface is available and this would confirm the Hofmann and Klemen migration theory, since the lithium ions should be in octahedral sites. However, the lithium ions exchange freely at higher temperatures, because heated lithium-montmorillonite will exchange all the lithium in decinormal sodium chloride at 250° C. It is concluded, therefore, that the migration of the lithium ions occurs freely at 200–300° C., the direction of migration depending on the external conditions. This may be related to the instability of an ion which is too small for the co-ordination in which it finds itself. Migration to the octahedral sites satisfies both this requirement and that of being near the seat of charge in the silicate layer. The reverse migration is presumably due to the greater stability of a hydrated lithium ion in interlayer positions than that of an unhydrated lithium ion in octahedral co-ordination.

CONCLUSION.

The study of the two closely related systems, lithium-montmorillonite-beidellite and lithium-sodium-montmorillonite, has shown that neither system is a uniform one. In the former case it seems that there must be differences in composition between silicate sheets bound in the same crystallite, and in the latter case the majority of the sodium ions segregate to form a sodium-rich 'phase'.

The effect of heating on the internal surface available to glycerol of the lithium-saturated montmorillonite-beidellite is shown to be correlated with the amount of octahedral substitution; less than 70 % leading to some glycerol penetration. Likewise the study of the lithium-sodium-montmorillonite system indicated that, if there was less than

70 % lithium ions in the interlamellar spaces, expansion occurred after heating. No evidence of an intermediate state of expansion at 14 Å. was found. The migration of the lithium ions on heating lithium-saturated montmorillonites appears to explain fully all the experimental data.

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APPENDIX. A NOTE ON NOMENCLATURE.

Although montmorillonite is well established as a mineral, the somewhat rarer occurrences of beidellite had caused the existence of the mineral to be questioned (13). There is, however, little doubt that the mineral exists. Nagelschmidt discussed two beidellites (14), one of which was the type specimen from Beidell and the other a pure sample from Black Jack mine, Idaho. X-ray examination showed both samples were dioctahedral montmorillonites and the analytical results left no doubt that they should be classified as beidellites, since they were low in magnesium and ferrous iron. They contained only traces of potassium. The latter specimen has been used in this work and provides a nearly perfect end-member for the montmorillonite-beidellite series.

The results of Ross and Hendricks (15) have shown that the montmorillonite-beidellite series is probably continuous with no natural dividing boundary and have left the classification of the minerals of the series to be established arbitrarily. It is here suggested that it would be convenient if the term beidellite were reserved for those minerals with less than 50 % of their silicate sheet charge due to octahedral substitutions and montmorillonite for those in which it is more than 50 %. The term nontronite should be restricted to beidellite-type minerals high in iron and low in aluminium, and the term should not be used for possible nontronite-like minerals which derive most of their charge from octahedral substitutions and for which a new name should be proposed.

References.

1. HOFMANN (U.) and KLEMEN (R.), 1950. Verlust der Austauschfähigkeit von Lithiumionen an Bentonit durch Erhitzung. *Zeits. Anorg. Chem.*, vol. 262, pp. 95-99.
2. GREENE-KELLY (R.), 1952. Irreversible dehydration in montmorillonite. *Clay Minerals Bulletin*, vol. 1, pp. 221-225.

3. GONZALEZ GARCIA (F.), 1950. Silicates del grupo de la montmorillonita. *Anales de Edafología y Fisiología Vegetal*, Madrid, vol. 9, p. 149.
 4. GREENE-KELLY (R.), 1953. Irreversible dehydration in montmorillonite, Part II. *Clay Minerals Bulletin*, vol. 2, pp. 52-56.
 5. RANEY (W. A.) and HOOVER (C. D.), 1946. The release of artificially fixed potassium from kaolinite and montmorillonitic soils. *Proc. Soil Sci. Soc. Amer.*, vol. 11, pp. 231-237.
 6. BARSHAD (I.), 1948. Vermiculite and its relation to biotite as revealed by base exchange reactions, X-ray analysis, differential thermal curves, and water content. *Amer. Min.*, vol. 33, pp. 655-678. [M.A. 10-462.]
 7. NORRISH (K.), 1954. The swelling of montmorillonite. *Discussion of Faraday Society on Flocculation* (to be published).
 8. GREENE-KELLY (R.), 1953. The identification of montmorillonoids in clays. *Journ. Soil Sci.*, vol. 4, pp. 233-237.
 9. FOSTER (M. D.), 1951. The importance of exchangeable magnesium and cation-exchange capacity in the study of montmorillonitic clays. *Amer. Min.*, vol. 36, pp. 717-730. [M.A. 11-455.]
 10. ——— 1953. Geochemical studies of clay minerals III. *Geochim. Cosmochim. Acta*, vol. 3, pp. 143-154.
 11. EARLEY (J. W.), OSTHAUS (B. B.), and MILNE (I. H.), 1953. Purification and properties of montmorillonite. *Amer. Min.*, vol. 38, pp. 707-724. [M.A. 12-492.]
 12. BROWN (G.) and GREENE-KELLY (R.), 1954. X-ray diffraction by a randomly interstratified clay mineral. *Acta Cryst.*, vol. 7, pp. 101-103.
 13. PASK (J. A.) and DAVIES (B.), 1945. Thermal analysis of clay minerals and acid extraction of alumina from clays. U.S. Bureau of Mines, Tech. Paper no. 664, pp. 56-81.
 14. NAGELSCHMIDT (G.), 1938. On the atomic arrangement and variability of the members of the montmorillonite group. *Min. Mag.*, vol. 25, pp. 140-155.
 15. ROSS (C. S.) and HENDRICKS (S. B.), 1945. Minerals of the montmorillonite group: their origin and relation to soils and clays. *Prof. Paper U.S. Geol. Surv.*, no. 205-B. [M.A. 10-26.]
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