

SYNTHESIS AND SWELLING PROPERTIES OF SAPONITES WITH INCREASING LAYER CHARGE

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Abstract—Nine synthetic Na-saponites with charge densities varying between 0.33 and 1.0 have been prepared. Their swelling properties and structural organization in water, ethylene glycol and glycerol show discontinuities in the physico-chemical behaviour of these samples. The layer charge densities caused changes in swelling properties and structural organization of the minerals. These changes also depended upon the nature of the solvation liquid and the interlayer cation involved.

Electron diffraction patterns of the Ba-saponites showed no abnormal diffusion making honeycomb-like patterns between Bragg reflections.

The results indicate criteria for estimating the layer charge of tetrahedrally substituted trioctahedral 2/1 phyllosilicates.

There is no upper limit until $x = 1$ for the layer charge x which is specific to the smectite-group. Consequently, the changes in the swelling properties observed when $x = 0.5$ – 0.6 and $x = 0.8$ – 0.9 come from the modifications of the interlayer structure, which are mainly a function of cation-liquid and silicate layer-liquid interactions. Consequently, there is an overlap between the saponite and the vermiculite mineral groups.

INTRODUCTION

Roy and his co-workers, since 1948, have studied the synthesis of clay minerals in order to prepare a series of samples belonging to the same group of minerals with only one variable parameter. The essential results obtained by Roy's group were published in 1961. However, it is often difficult to make a valid comparison of the physical-chemical properties of natural minerals because they have various parameters which can vary simultaneously as follows:

—the genesis (it can imply a morphological difference and sometimes a difference of chemical behaviour)

—the nature and number of the octahedral cations

—the total amount of the layer charge per half-unit cell (x)

—the localization of octahedral and/or tetrahedral substitutions which produce the layer charge (for example, two tetrahedrally charged smectites can have the same total layer charge x but a different net positive charge in the octahedral layer).

Iiyama and Roy (1963) prepared synthetic saponites. Using the identification criteria of Warshaw and Roy (1961), they concluded that hydrothermal and synthetic saponites could only be prepared if their charge did not exceed a value close to 0.6.

We have reexamined this question to see if their results could be explained differently depending on how one interprets the swelling properties and the X-ray diffraction patterns of the samples. A series of synthetic samples has therefore been prepared which were chemically similar to the saponite composition and whose charge was varied between 0.33 and 1.0.

Their general formula is thus:

$$\text{Na}_x(\text{Si}_{4-x-q}\text{Al}_{x+q})(\text{Mg}_{3-q}\text{Al}_q)\text{O}_{10}(\text{OH})_2,$$
where

$$0.33 \leq x \leq 1; q = 0 \text{ and } 0.2.$$

These saponites were saturated with six different cations (Li, Na, K, Ca, Mg and Ba) and their swelling characteristics upon solvations with water, ethylene glycol, and glycerol were studied. The structures of swelling saponites were three-dimensionally examined by X-ray powder diffraction. In addition, the collapsed Na and Ba-substituted samples were examined by electron microscopy and diffraction techniques. The results have been compared with those of natural saponites, beidellites and vermiculites where tetrahedral substitutions were present.

During this study, an attempt was made to determine the principal criteria which would enable an estimate of the layer charge of a saponite to be made.

DESCRIPTION OF THE SAMPLES

Experimental conditions

The synthetic saponites were prepared in a "Morey" bomb with an inner volume of 40 ml. The gels used for the synthesis were prepared according

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to the usual method from the following compounds: tetraethyl orthosilicate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 7\text{H}_2\text{O}$, Na_2CO_3 , HNO_3 , NH_4OH and ethanol.

To obtain strongly reactive gels, special care was taken, in the transformation of the nitrates to oxides; the heating temperature was limited to 600°C during 24 hr.

Approximately 12 g of the starting mixture was sealed with 15 ml of water into a gold tube 1.8 mm in dia. and placed in the bomb. The bomb was heated at 450°C in a regulated electric furnace. The pressure was estimated at 1500 bars during the run. After 15 days, the bomb was quenched, opened and the solid product was washed five times with water, using a centrifuge.

X-ray studies of the samples (with a diffractometer for oriented samples and a Guinier camera for random samples) showed that the crystalline products were pure but it was impossible to determine if a small amount of amorphous materials were also present. Because of the low synthesis temperature (450°C), it is sometimes difficult to avoid the formation of amorphous material during the bomb quenching.

Determination of the layer charge

Table 1 gives the theoretical structure formulae of the synthetic saponites obtained from the bulk composition of the starting mixture and their layer charge x determined by their cation exchange capacities (C.E.C.). The latter were obtained by displacing sodium with calcium chloride (Table 1, columns 4 and 5) and in some cases by displacing calcium with magnesium chloride (Table 1, column 6). The concentrations of Na and Ca in solutions were measured by atomic absorption spectrophotometry.

Table 1 shows a substantial difference between the theoretical and experimental layer charge densities for several samples ($x = 0.33$, $q = 0$; $x = 0.5$, $q = 0.2$; $x = 0.8$, $q = 0$; $x = 0.8$, $q = 0.2$ and $x = 1$, $q = 0.2$). These differences may arise from the presence of amorphous phases and from the existence of collapsed layers in the samples.

The presence of amorphous phases was observed by electron microscopy in sample no. 1 and the exist-

ence of collapsed layers was indicated for sample no. 9 by a peak at 9.8 \AA in the X-ray diffraction pattern.

Besides the presence of an amorphous or badly crystallized product, other factors such as the particle size or the heterogeneity in the particle size can be at the origin of our difficulties in the C.E.C. determination.

SWELLING AND STRUCTURE

Tables 2, 3 and 4 give basal spacings d_{001} of synthetic saponites which were dried and then put into contact with liquid water, ethylene glycol and glycerol for at least 48 hr, together with the basal spacings observed for several natural tetrahedrally substituted 2:1 phyllosilicates under the same conditions. The results are accurate to $\pm 0.1 \text{ \AA}$. Numbers in brackets indicate an irregular sequence. The other values correspond to homogeneous swellings, i.e. rational (00l) reflections.

It is well known that the solvation complexes tend to contain an integral number of layers of water or organic molecules between consecutive silicate layers. Consequently, we shall use the terms double-layer or single-layer complexes according to the thickness of the interlayer phase which can be expressed as $d_{001} - 9.4 \text{ \AA}$ (9.4 \AA being the thickness of a silicate layer).

Synthetic saponites reach their equilibrium state—i.e. their maximum expansion with a given solvation liquid—faster than natural minerals, especially if the latter are monocrystals. Thus the X-ray diffraction patterns of natural solvated minerals still showed, after 48 hr of contact, two d_{001} values which corresponded to low- and high-expansion states. After a further time of contact, the reflection intensity of the d_{001} -spacing of the low expansion state was gradually weakened and approached zero when equilibrium was reached. In addition, the swelling varies according to the experimental procedures: for example, immersion of the mineral in excess liquid or making a liquid-mineral paste from the powder. With ethylene glycol and glycerol, the second procedure was used.

The structural organization was described simply on the basis of a visual estimate of the X-ray powder patterns.

Table 1. Theoretical structural formulae and layer charge densities obtained from cation exchange capacities of synthetic saponites

Sample	Theoretical structural formula	x : layer charge density q : positive excess charge in octahedral sheet		x' (exchange Na, Ca)	x'' (exchange Na, Ca)	x''' (exchange Ca, Mg)
1	$\text{Na}_{0.33}(\text{Si}_{3.67}\text{Al}_{0.33})\text{Mg}_3\text{O}_{10}(\text{OH})_2$	$x = 0.33$	$q = 0$	0.50		0.43
2	$\text{Na}_{0.5}(\text{Si}_{3.5}\text{Al}_{0.5})\text{Mg}_3\text{O}_{10}(\text{OH})_2$	$x = 0.5$	$q = 0$	0.43	0.41	0.47
3	$\text{Na}_{0.5}(\text{Si}_{3.3}\text{Al}_{0.7})(\text{Mg}_{2.8}\text{Al}_{0.2})\text{O}_{10}(\text{OH})_2$	$x = 0.5$	$q = 0.2$	0.58		
4	$\text{Na}_{0.6}(\text{Si}_{3.3}\text{Al}_{0.8})(\text{Mg}_{2.8}\text{Al}_{0.2})\text{O}_{10}(\text{OH})_2$	$x = 0.6$	$q = 0.2$	0.55	0.52	0.56
5	$\text{Na}_{0.7}(\text{Si}_{3.1}\text{Al}_{0.9})(\text{Mg}_{2.8}\text{Al}_{0.2})\text{O}_{10}(\text{OH})_2$	$x = 0.7$	$q = 0.2$	0.74		
6	$\text{Na}_{0.8}(\text{Si}_{3.2}\text{Al}_{0.8})\text{Mg}_3\text{O}_{10}(\text{OH})_2$	$x = 0.8$	$q = 0$	0.60	0.65	0.68
7	$\text{Na}_{0.8}(\text{Si}_3\text{Al})(\text{Mg}_{2.8}\text{Al}_{0.2})\text{O}_{10}(\text{OH})_2$	$x = 0.8$	$q = 0.2$	0.59	0.56	0.60
8	$\text{Na}(\text{Si}_3\text{Al})\text{Mg}_3\text{O}_{10}(\text{OH})_2$	$x = 1$	$q = 0$	0.94		
9	$\text{Na}(\text{Si}_{2.8}\text{Al}_{1.2})(\text{Mg}_{2.8}\text{Al}_{0.2})\text{O}_{10}(\text{OH})_2$	$x = 1$	$q = 0.2$	0.35	0.39	0.38

Table 2. Basal spacings d_{001} (Å) upon water solvation: (a) swelling in water of the mineral after its preparation; (b) swelling in water of the air-dry mineral. x = layer charge per half unit cell; q = excess of positive charge in octahedral sheet. Reflection intensities: s: strong; w: weak; v.w.: very weak; diff: diffuse

Sample		Li	Na	Exchangeable cation		Mg	Ca	Ba
				(a)	(b)			
$x = 0.33$	$q = 0$	ind	15.3	15.7	15.7	18.8	18.8s 15.5w	18.8
$x = 0.5$	$q = 0$	ind	15.2	15.5	15.5	18.8	15.4	18.4
$x = 0.5$	$q = 0.2$	ind	15.2	15.6	15.6	18.8	15.4	18.4
$x = 0.6$	$q = 0.2$	ind	14.9	12.8	12.8	14.8	15.2	15.7
$x = 0.7$	$q = 0.2$	14.6 diff	14.9	12.8	12.8	14.6	15.1	15.7
$x = 0.8$	$q = 0$	14.6	14.9	12.8	(11.6)	14.5	15.0	15.4
$x = 0.8$	$q = 0.2$	14.6	14.9	12.8	(11.6)	14.5	15.0	15.4
$x = 1$	$q = 0.0$	14.6	14.9	12.8	10.0	14.4	14.9	14.8
$x = 1$	$q = 0.2$	14.6s 12.2w	14.9	10.0	10.0	14.4	14.9	14.7
Beidellite	(1)	ind	ind		12.55	18.58	18.6	18.38
	(2)	ind	15.2		12.7	18.6	{ 18.7w 15.4vw	
Saponite	(3)	ind	15.2		12.6	{ 18.9s 14.8w	{ 18.6w 15.4s	{ 18.5w 15.9vw
	(4)	ind	14.9		10.1	14.7	14.9	15.7
Vermiculite	(5)	15.07	14.76		10.57	14.47	15.41	15.41
	(7)	14.5	14.9		10.0	14.3	15.0	14.8

Values in parentheses are average values for irregular layer sequences.

(1) Beidellite from Black Jack Mine, Idaho; $x = 0.46$; Weir (1960).

(2) Beidellite from Rupsroth (Germany); $x = 0.54$; Glaeser's results published in Suquet *et al.* (1975).

(3) Saponite from Kozakòv, Czechoslovakia; $x = 0.45$; Suquet *et al.* (1975).

(4) Vermiculite from Benahavis, Spain; $x = 0.53$; Suquet *et al.* (1975).

(5) Vermiculite from Culsagee Mine, Macon County, North Carolina; $x = 0.65$; Barshad (1950).

(7) Vermiculite derived from a Madagascar powdered phlogopite; $x = 0.89$.

Swelling and structure with water: swelling

K cation. We have measured the swelling properties in two cases: (i) immediately after synthesis (the sample was never dried) or (ii) after dipping the air-dried sample in water. In both cases, the expansion was the same for all the cations except for potassium. Columns (a) and (b) of Table 2 show that, after being dried, the high-charge K-saponites gave an expansion inferior to that shown after their initial preparation.

It must be noted that the potassium hydrates give a smaller number of diffuse basal reflections (00l) than the hydrates obtained with other cations. The lack of a strict periodicity in the direction perpendicular to the sheet plane may be probably related to the low electrostatic field strength of this large univalent ion.

In water, all the potassium saponites with layer charge inferior or equal to 0.5 gave a two-layer hydrate, which is not the case of the K-beidellites.

Na cation. Na-saponites gave a well-ordered two-layer hydrate whatever their layer charge. The d_{001} values of these two-layer hydrates fluctuated between 15.3 and 14.9 Å; there is not a continuous variation of d_{001} according to the layer charge.

It appeared that the smaller spacings corresponded to saponites with a high layer charge and vice versa.

Li cation. It is known that, with water, Li-vermiculites give either a complete layer dispersion or a two-layer hydrate according to their geological origin and the sample charge. Our study shows that there is a

gap at layer charge $x = 0.6$ and that at a higher layer charge the expansion is limited to a two-layer hydrate except that when $x = 1$ and $q = 0.2$ the two-layer and one-layer hydrates were simultaneously observed.

Mg and Ba cations. Table 2 shows that Ba and Mg cations produced homogeneous three-water layer hydrates when the layer charge was inferior to 0.6. Above this value, a two-layer hydrate was observed as with Li, Na and Ca cations.

Ca cation. The three-layer hydrate was observed only with very low-charge saponites ($x \leq 0.33$). Above this value, all Ca-saponites gave a two-water layer hydrate.

These results enable us to suggest a hypothesis to explain the double swelling (18.6 and 15.4 Å) observed with natural Kozakòv Ca-saponite immersed for a long time in water (Table 2). The chemical analysis and the cation exchange capacity of this mineral indicated that its mean layer charge was 0.45. Since this mineral exhibited a weak peak at 18.6 Å and a strong peak at 15.4 Å, the mean layer charge can be explained by a mixture having a layer charge as low as 0.33 together with a layer charge higher than 0.45. Such heterogeneity within a mineral sample is quite plausible as it has been found in other layer silicates by several authors (Lagaly and Weiss, 1969; Glaeser and Mering, 1975).

Swelling and structure with water: structure

Three-layer hydrates. These can be obtained with Mg- and Ba-saponites and have a turbostratic struc-

ture. This hydration state, although very disordered, gives rational X-ray reflections (00l).

Two-layer hydrates. Most of them have a partially ordered structure of V_1 type with a number of random translation faults along Ox (de la Calle *et al.*, 1975). The stacking is such that layers are displaced randomly relative to others by $\pm \frac{b}{3}$. This is seen in powder X-ray diffraction patterns by a band (02), (11) and by discrete reflections belonging to the series (20l), (13l) and two reflections (060) and ($\bar{3}$ 32) (Figure 9, Suquet *et al.*, 1975).

In addition, the number of faults varies with the nature of the interlayer cation. Thus for samples with $x = 1$ and $q = 0$, the reflection broadening and the diffusion intensity on the [20l][13l] rows of the reciprocal lattice show that the relative number of faults increases as follows:

$$\text{Mg} \approx \text{Na} \approx \text{Li} < \text{Ca} \approx \text{Ba}.$$

High charge Na-saponites have a three-dimensional structure of V_{III} type (de la Calle *et al.*, 1975) with a great degree of disorder.

K-saponites. The one- or two-layer hydrated K-saponites are very poorly ordered. This may be related to their basal spacings d_{001} which are not so well defined as for the other cations.

The high-charge K-saponites collapse to 10 Å in water. The number of random faults in these structures is much greater than in the dehydrated phase of the natural Kozaköv K-saponite (Suquet *et al.*, 1975).

Swelling and structure with ethylene glycol: swelling

Three swellings stages are expected to be observed when a 2/1 phyllosilicate is saturated with ethylene glycol (Brindley, 1966).

—*a swelling between 16.0 and 17.1 Å.* Such a swelling was observed with the smectite group (17.0 ± 0.1 Å) and the low-charge vermiculites (16.2 ± 0.1 Å). It has been shown by several authors (MacEwan, 1948; Reynolds 1965; Chassin, 1972) that it corresponded to an arrangement of double-layers of glycol molecules between the silicate layers.

—*a 14.3 Å swelling* obtained with high-charge vermiculites saturated with magnesium. It was identified as a single-layer complex (MacEwan, 1948; Brindley, 1966)

—*a 12.9 Å swelling* obtained with Llano Na-vermiculite whose layer charge is particularly high ($x = 0.9$). This phase as studied by Bradley *et al.* (1963) corresponds to the formation of a single layer of glycol molecules in the interlayer space with a molecule arrangement obviously different from the preceding one.

The synthetic saponites described here have enabled us to identify these swelling steps and to study their ability according to the nature of the exchangeable cation and the layer charge density (Table 3).

Double-layer glycol complexes. These can be obtained with Ca and Ba cations for a wide range of layer charge ($0.33 \leq x \leq 1$).

The double-layer glycol complex can also be formed with the following cations and layer charge densities:

$$\begin{aligned} &\text{Mg when } x \leq 0.7; \\ &\text{Li and Na when } x \leq 0.8; \\ &\text{K when } x \leq 0.5. \end{aligned}$$

The thickness of this complex varies greatly, as indicated by their basal spacings which varied from 15.2 Å (Ca: $x = 1.0$, $q = 0.2$) to 16.8 Å (Mg: $x = 0.33$, $q = 0$). This suggests a high flexibility in the arrangement of glycol molecules in the interlayer space.

Single-layer glycol complexes (14.3 Å). This phase is seen only with Mg and when the layer charge density is high ($x > 0.7$). It should be noticed that this layer charge is higher than the value generally taken for distinguishing smectites from vermiculites. Undoubtedly this result arises for the Mg ion because of its small size and high electrostatic field strength.

Single-layer glycol complex (12.2–12.9 Å). The 12.9 Å phase has been obtained with Llano- Na-vermiculite by several authors (Bradley *et al.*, 1963; Chassin, 1972). Similar results were obtained with high layer charge synthetic Na-saponites and with Na-vermiculite formed from a Madagascar phlogopite ($x = 0.89$).

Li-cations also gave a single-layer complex with a layer thickness of 12.2 Å which is slightly smaller than the ordinary single-layer glycol complex of 12.9 Å. This certainly relates to the small size of this cation.

“*Zero-layer glycol complex*”. It is formed when the layer charge density is high ($x \geq 0.8$ with potassium and $x = 1$ with sodium). Ethylene glycol molecules could no longer penetrate between the layers, since the interlayer spaces were closed.

It can therefore be concluded that saponites in contact with glycol have four swelling states which are distinguished from the d_{001} -spacings of complexes (16.7 Å, 14.3 Å, 12.9 Å and 10.0 Å) with a clear predominance of the 16.7 Å state.

In addition, a comparison of Table 3 with Table 2 shows that, for high values of the layer charge, glycol expands the saponites less readily than water. This phenomenon is more obvious in the case of alkaline interlayer cations than in the case of alkaline-earth interlayer cations.

Furthermore, Table 3 shows the influence of a charge excess in the octahedral sheet. It can be observed, particularly for the Na-saponites, with a given layer charge ($x = 0.8$ or $x = 1$). The presence of $\text{Mg}^{2+} \rightarrow \text{Al}^{3+}$ substitutions in the octahedral layers causes a less expansion. When $x = 1$ and $q = 0.2$, glycol did not expand the saponite completely, while glycol formed a one-layer complex with Na-saponite with $x = 1$, $q = 0$.

Swelling and structure with ethylene glycol: structure

Double-layer glycol complex. It was shown by Reynolds (1965) that the glycol molecules of the double-layer complex are oriented perpendicular to

Table 3. Basal spacings d_{001} (Å) upon ethylene glycol solvation. x = layer charge density per half unit cell; q = excess of positive charge in octahedral sheet. Reflection intensities: s; strong; w: weak; diff: diffuse. Values in parentheses are average values for irregular layer sequences.

Sample		Li	Na	Exchangeable cation			
				K	Mg	Ca	Ba
$x = 0.33$	$q = 0$	16.6	16.7	16.8	16.8	16.6	16.7
$x = 0.5$	$q = 0$	16.5	16.7	16.8	16.6	16.7	16.6
$x = 0.5$	$q = 0.2$	16.5	16.7	16.8	16.6	16.6	16.6
$x = 0.6$	$q = 0.2$	16.3	16.6	(13.6) diff	16.3	16.3	16.4
$x = 0.7$	$q = 0.2$	16.2	16.5	(13.6) diff	16.2	16.1	16.3
$x = 0.8$	$q = 0$	16.1	16.2	(13.6)s (10.2)w	16.0w 14.2s	16.0	16.2
$x = 0.8$	$q = 0.2$	16.1	16.1s 12.8w	10.2 diff	14.3	15.9	16.1
$x = 1$	$q = 0$	12.2	12.8	10.2	14.3	15.3	16.0
$x = 1$	$q = 0.2$	12.2	12.8s 9.8s	9.8	14.2	15.2	16.0
Beidellite	(1)	17.00	16.86	14.7	16.95	16.88	16.7
	(2)	16.6	16.87	13.7	17.1	16.7	
Saponite	(3)	16.4	16.7	16.7	16.7	16.6	16.7
	(6)	{ 16.1 l.c. 16.0 h.c. (15.9)w	{ 16.3 l.c. (14.8) h.c.		{ 16.3 l.c. 14.3 h.c.	{ 16.2 l.c. (15.6) h.c.	{ 16.2 l.c. 16.0 h.c.
Vermiculite	(7)	12.2	12.8	10.1	14.2	15.2	16.0
	(8)		12.9				

- (1) Beidellite from Black Jack Mine, Idaho; $x = 0.46$; Weir (1960).
- (2) Beidellite from Rupstroth, Germany; $x = 0.54$; Glaeser's results published in Suquet *et al.* (1975).
- (3) Saponite from Kozakòv, Czechoslovakia; $x = 0.45$; Suquet *et al.* (1975).
- (5) Vermiculite of Culsagee Mine, Macon County, North Carolina; $x = 0.65$; Barshad (1950).
- (6) Walker (1958): l.c.: low-charge vermiculite $0.6 \leq x \leq 0.7$ h.c.: high-charge vermiculite $x = 0.8$.
- (7) Vermiculite obtained from a Madagascar powdered phlogopite; $x = 0.89$.
- (8) Vermiculite from Llano; $x = 0.9$; Bradley *et al.* (1963).

(001), and by Chassin (1972) that they exist in the "gauche" form as in liquid.

These two studies were carried out on montmorillonite-glycol complexes whose basal spacing d_{001} is equal to 17.0 ± 0.1 Å. Saponite-glycol complexes, however, gave the d_{001} -spacing ranging from 15.2 to 16.8 Å, suggesting that the organization of glycol molecules in saponite is different from that in montmorillonite due to differences in layer charge densities.

The layer stacking in this double-layer complex changes from turbostratic (weak layer charge, maximum expansion, Figure 1b) to semi-ordered (high layer charge, minimum expansion) while some reflections (00l) become weak. However, the synthetic structure is always more disordered than the Kozakòv sample (Figure 1a).

A semi-ordered structure is one which is ordered along Ox but is disordered along Oy. Such is the case of the V_1 structure where the $\pm \frac{1}{2}$ translations are entirely random. However, these structures have a certain number of random faults in the direction Ox. For the layer charge, $x = 0.5$, $q = 0.2$, the relative number of random translation faults along Ox increases according the following order:

$$K \simeq Na < Mg.$$

The structure of the double-layer complex of Ca-saponite is very disordered and the Li-samples are nearly turbostratic.

Single-layer glycol complex (14.3 Å). The layer stack-

ing is always semi-ordered and of V_1 type (random $\pm \frac{1}{2}$ translations) in the single-layer complex with a basal spacing of 14.3 Å (Figure 1c). The number of translation faults along Ox is small in this complex.

Up to now, there has been no definite evidence of the arrangement of glycol molecules in interlayer spaces.

It is interesting to notice that the Mg-glycol complex gives the same basal spacings (14.3 Å) and stacking type (V_1) as are found in the two-layer Mg-vermiculite-water complex.

Single-layer glycol complex (12.2–12.9 Å). The X-ray study (Bradley *et al.*, 1963) and i.r. study (Chassin, 1972) of the Na-vermiculite glycol complexes have shown that the molecules are adsorbed in the form "trans" and with the chain OCCO perpendicular to the *ab* plane.

The X-ray powder diffraction pattern corresponding to this phase shows that the layer stacking is disordered along Oy (Figure 1d).

Swelling and structure with glycerol: swelling

Table 4 contains the basal spacings upon glycerol solvation of both synthetic saponites and natural minerals (beidellite, saponite and vermiculite). As shown by Brindley (1966), our observations can be divided into 3 groups according to the kinds of exchangeable cations:

—With Li, Mg and Na cations, the boundary between the double-layer complex ($d_{001} \simeq 18.0$ Å)

Table 4. Basal spacings d_{001} (Å) upon glycerol solvation. x : layer charge density per half unit cell; q : excess of positive charge in octahedral sheet. Reflection intensities: s: strong; w: weak. Values in parentheses are average values for irregular layer sequences

Sample		Exchangeable cation					
		Li	Na	K	Mg	Ca	Ba
$x = 0.33$	$q = 0$	18.0	18.1	18.1	18.1	17.9	18.1
$x = 0.5$	$q = 0$	18.0	18.1	18.1	18.1	17.9	18.1
$x = 0.5$	$q = 0.2$	18.0	18.1	18.1	18.1	17.9	18.1
$x = 0.6$	$q = 0.2$	14.3	14.2	(13.8)	14.3	17.9	18.1
$x = 0.7$	$q = 0.2$	14.2	14.2	(13.8)	14.3	17.9	18.1
$x = 0.8$	$q = 0$	14.2	14.2	10.2	14.3	17.9	(17.9) (14.2)
$x = 0.8$	$q = 0.2$	14.2	14.2	10.2	14.3	17.9	(17.9) (14.2)
$x = 1$	$q = 0$	14.2s 12.2s	(13.3)	10.2	14.3	14.3	14.0
$x = 1$	$q = 0.2$	14.1w 12.2s	(11.7) 9.8	9.9	14.3	14.2	14.0
Beidellite	(1)	17.6	17.7	13.90	18.00	17.60	17.90
	(2)	18.0	18.0	13.7	17.9	17.7	
Saponite	(3)	18.1 s 14.4 w	18.1 s 14.3 w	18.2	18.1 s 14.3 w	17.9*	18.1
	(6)	14.21 l.c. 14.3 h.c.	14.8		14.3	17.6 l.c. 14.3 h.c.	17.61 l.c. 14.3 h.c.
Vermiculite	(5)	14.33	14.33	10.64	14.33	14.18	14.33
	(7)	14.2w 12.2s	(13.3) (12.2)	10.1	14.3	14.4	14.1

(1) Beidellite from Black Mine, Idaho; $x = 0.46$; Weir (1960).

(2) Beidellite from Rupsroth, Germany; $x = 0.54$; Glaeser's results published in Suquet *et al.* (1975).

(3) Saponite from Kozakov, Czechoslovakia; $x = 0.45$; Suquet *et al.* (1975).

* A weak reflection at 14.4 Å is observed in a few cases.

(5) Vermiculite from Culsagee Mine, Macon County, North Carolina; $x = 0.65$; Barshad (1950).

(6) Walker (1958): l.c.: low-charge vermiculite $0.6 \leq x \leq 0.7$. h.c.: high-charge vermiculite $x = 0.8$.

(7) Vermiculite obtained from a Madagascar powdered phlogopite; $x = 0.89$.

and the single-layer one ($d_{001} \approx 14.3$ Å) appears at the layer charge where $x = 0.6$.

—With Ca and Ba, larger divalent ions, the boundary between the double-layer complexes ($d_{001} = 18.0 \pm 0.1$ Å) and the single-layer one ($d_{001} = 14.2 \pm 0.2$ Å) appears at the layer charge $x = 0.8$.

Strontium would have an identical behaviour.

—According to Brindley (1966), Rb, Cs and NH_4 , large, univalent cations lead to the formation of a single-layer complex ($d_{001} = 14.3$ Å) with smectites and 10–11 Å phase with high-charge vermiculites.

Our results for the K cation were different from Brindley's. Indeed, all the K-synthetic saponites show that, when $x < 0.6$, a double-layer complex exists ($d_{001} \approx 18.0 \pm 0.1$ Å) and all other cations also produce such a complex. When $x \geq 0.8$, the crystalline structure with K did not expand ("zero layer"). Between these two layer charges, interstratified structures were formed.

When high-charge saponites saturated with Na and K cations are considered, the situation is the same as with ethylene glycol: some or all of the layers no longer expand in glycerol.

In high-charge synthetic ($x = 1$, $q = 0$ and $x = 1$, $q = 0.2$) and natural [vermiculite referred to as (7)]

Li-minerals, the reflection at 12.2 Å which corresponds to a low-expansion state gradually weakens versus time.

The Ba-saponites ($x = 0.8$, $q = 0$ and $x = 0.8$, $q = 0.2$) given irregular sequences which versus time tend towards the equilibrium state at 14.2 Å.

The high-charge synthetic ($x = 1$, $q = 0$ and $x = 1$, $q = 0.2$) and natural [vermiculite referred to as (7)] Na-minerals give interstratified sequences which tend towards 9.8 and 14.2 Å states. The equilibrium states are reached slowly at 20°C and more readily at 90°C.

Table 4 shows that, as with glycol, the relation between the excess positive charge q of the octahedral layer and the expansion properties. For the same layer charge, when the sample contains $\text{Mg}^{2+} \rightarrow \text{Al}^{3+}$ substitutions in octahedral sheet, it can be observed:

—either the presence of a second state of weaker expansion (such as is the case for Na with $x = 1$, $q = 0$ and $x = 1$, $q = 0.2$).

—or the increased X-ray reflection intensity for the 12.4 Å phase present (such as is the case for Li with $x = 1$, $q = 0$ and $x = 1$, $q = 0.2$).

The existence of two expanded phases with synthetic saponites in glycerol is consistent with the hypothesis of heterogeneity of the charge distribution

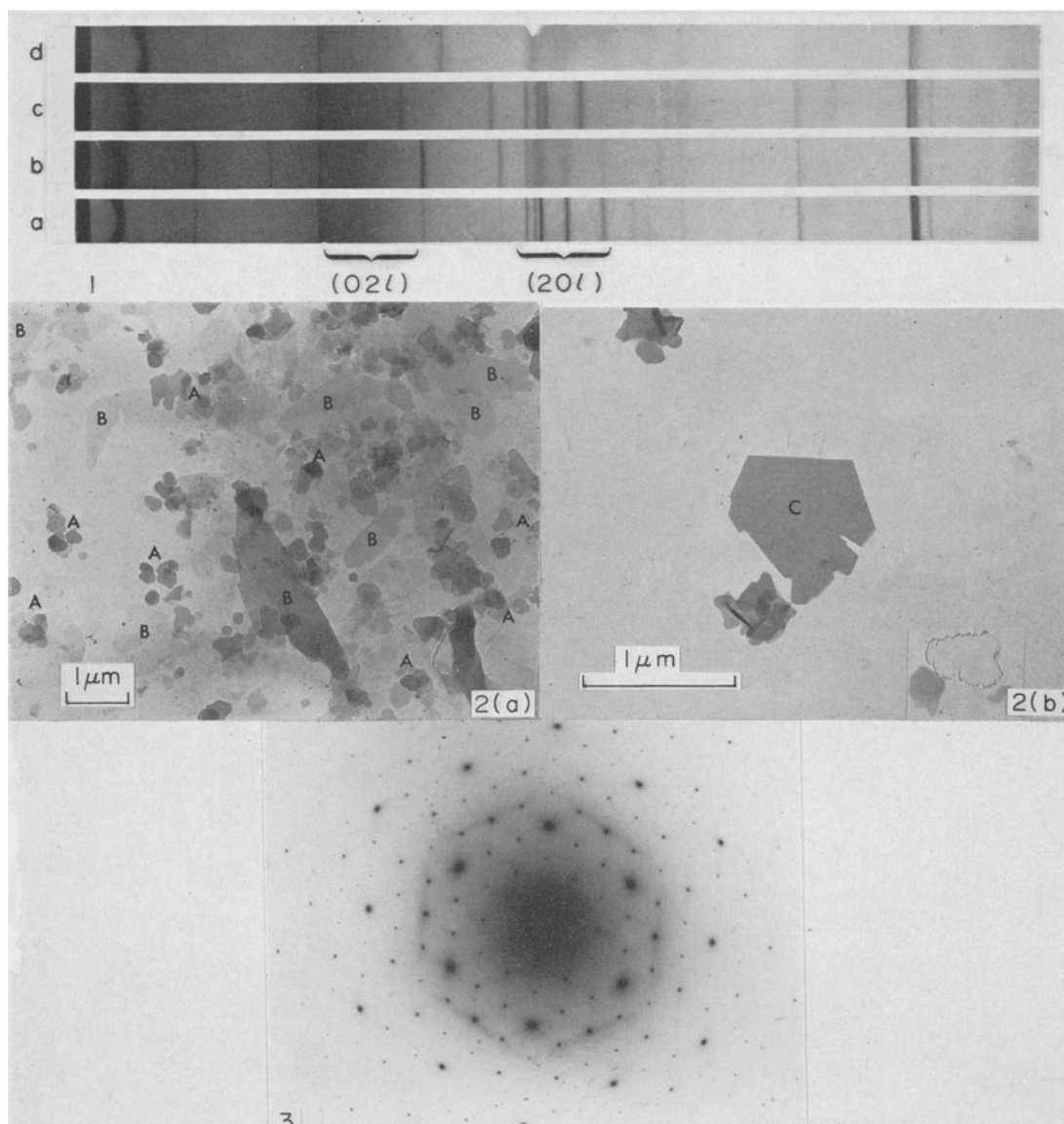


Figure 1. X-ray powder diffraction patterns of glycol complexes of synthetic and natural minerals ($K\alpha$ Co radiation): (a) Na-saponite (Kozakóv): $x = 0.45$; $d_{001} = 16.7 \text{ \AA}$; (b) Na-saponite (synthetic): $x = 0.5$ $q = 0.2$; $d_{001} = 16.7 \text{ \AA}$; (c) Mg-saponite (synthetic): $x = 1$ $q = 0$; $d_{001} = 14.3 \text{ \AA}$; (d) Na-saponite (synthetic): $x = 1$ $q = 0$; $d_{001} = 12.8 \text{ \AA}$.

Figure 2. Shapes of Na-saponites as observed by electron microscopy (Philips EM 300 microscope; 80 kV):

- | | |
|---|-------------------------------------|
| A: round and platy | } from sample $x = 0.5$ $q = 0.2$; |
| B: angular and platy | |
| C: partially outlined (hexagonal) platy from sample $x = 1$ $q = 0$. | |

Figure 3. Electron diffraction pattern of a single crystal of Na-saponite ($x = 1$, $q = 0$). With the (001) plane perpendicular to the electron beam.

in Kozakòv saponite. Indeed, its behaviour in water suggested that the mineral whose mean layer charge is 0.45 contained a small proportion of layers with weaker charge (about 0.3).

At present, in comparison with synthetic saponites, it can be added that this natural mineral also contains a minor part whose charge is superior or equal to 0.6; when saturated with Li, Na, or Mg cations and dipped into glycerol, the mineral gives two peaks of $18.0 \pm 0.1 \text{ \AA}$ with a strong intensity and of 14.3 \AA with a low intensity.

It can therefore be concluded that the Kozakòv saponite contains layers whose surface charge varies between 0.3 and 0.6 with a certain statistical distribution whose median is close to 0.45.

Swelling and structure with glycerol: structure

Double layer glycerol complex probably has a semi-ordered structure similar to the double-layer glycol complex. For a surface charge density equal to 0.5 ($q = 0.2$), the relative number of translation faults along Ox increases according the following order:



Double-layer complexes obtained with Ba and Li cations have a turbostratic structure.

Single-layer glycerol complexes exhibited a semi-ordered structure of V_1 type. The relative number of random translation faults along Ox, indicated by a broadening of the reflections of the series (20l) (11l) varies as follows:



The high charge Ca-saponite-glycol complexes showed a V_V structure. Intensities and positions of the (20l) (13l) reflections are modified. This type of structure has already been observed in a two-layer hydrate of high-charge Ca-vermiculites (de la Calle *et al.*, 1977).

The single-layer glycerol complexes of high-charge Ba- and Li-saponites had a very disordered structure which was almost turbostratic.

Discussion

From these results, synthetic saponites may be classified

(1) according to their layer charge determined from cation exchange capacity measurements (Table 1, columns 4, 5 and 6). The samples are then classified in the following order: 1, 2, 4, 3, 7, 6, 5 and 8 (sample 9 cannot be classified because its C.E.C. has been altered by the presence of collapsed layers within the mineral);

(2) according to their theoretical layer charge (Table 1, column 3) based on their chemical composition.

Tables 2, 3 and 4 give the basal spacings in the presence of water, ethylene glycol, and glycerol and clearly show that expansions decrease in the order of the classification established from the theoretical formulae and not from the C.E.C. measurements.

ELECTRON MICROSCOPIC AND MICRODIFFRACTION STUDIES

Morphology

Elongated lath-shaped particles, as observed by Suquet *et al.* (1975) on the Kozakòv sample, were rather uncommon in the synthetic materials examined. The most common shapes of particles observed were round and platy, angular platy and partially outlined (hexagonal) platy. They are indicated by A, B and C, respectively in electron micrographs given in Figure 2.

Small round and platy particles (A) were predominant in samples 1, 2, 3, 4 and 5 whose layer charge was low or moderate. The mean size of particles (A) varied between 0.08 and $0.3 \mu\text{m}$. On the contrary, the abundance of angular and platy particles (B) increased with the layer-charge, i.e. their abundance increased in order of samples 1, 2, 3, 4, 5, 6 and 7. The greatest size of these particles was about $3\text{--}3.5 \mu\text{m}$ and their smallest one was about $0.2\text{--}0.4 \mu\text{m}$.

Rather well-outlined angular (hexagon-like) platy particles (C) were observed only in the highest charged samples ($x = 1$). Their greatest size was about $1\text{--}3 \mu\text{m}$ and their smallest about $0.25 \mu\text{m}$. In addition, aggregates consisting of short and fine rod or needle-like particles were noticeably observed in sample 1 and occasionally in some others (2, 4 and 7). Poorly crystalline (amorphous like-materials) were observed in samples 1 and 2.

Microdiffraction

Regardless of total layer charge and interlayer cations (Na, Ba), relatively thick particles of saponites gave microdiffraction patterns showing very little diffuse streaks, but relatively thin particles showed pronounced diffuse streaks which are slightly curved and spread in the three directions parallel to $[11]^*$, $[01]^*$ and $[\bar{1}1]^*$ (Figure 3). These diffuse scatterings have been previously observed in synthetic Ba-saponite and beidellite, in Ba-beidellite II from Unterrupsroth (Germany) (Besson *et al.*, 1973), in microcrystallized Ba-muscovite (Kodama, 1975) and in Ba- and Na-saponite from Kozakòv (Czechoslovakia). Since similar abnormal streaks were observed in talc (Kodama, 1975), they cannot be related to interlayer-cationic configurations. It is likely to be due to some distortion within the silicate layers such as a deformation of oxygen arrays in the layers. Since the microdiffraction data suggested that certain two-dimensional disorders should occur within planes parallel to (110), (010) and $(\bar{1}10)$, it is considered that oxygen atoms are partially dislocated along the corresponding directions, that is, $[110]$, $[010]$ and $[\bar{1}10]$, probably due to puckering of layers and disordered ditrigonal nature of oxygen hexagons in silicate layers (Kodama, 1975). It is also possible that thermal effects play a part in these diffuse scatterings.

It has been shown (Besson *et al.*, 1973) that microdiffraction patterns of tetrahedrally charged smectites,

beidellites and saponites, did not show any abnormal honeycomb-shaped diffusion around Bragg reflection. Such abnormal diffusions have been observed on Ba-forms of K-depleted illites and muscovites (Besson *et al.*, 1974; Kodama, 1975) and on Ba-saturated Kenya vermiculites (Besson, 1972). Similar observations by X-ray diffraction were also reported on Kenya Ba-vermiculite monocrystals. (Alcover *et al.*, 1974).

Ba-saturated Benahavis (Spain) and Kenya vermiculites whose layer charges were 0.53 and 0.74, respectively, were also examined by electron diffraction in order to compare with results above mentioned. Honeycomb-shaped diffuse-scatterings were regularly observed in Kenya vermiculites and only in some particles of Benahavis vermiculite.

All of these observations therefore suggest that the existence of honeycomb-shaped diffuse scatterings is neither necessarily related to a layer charge density superior to 0.6, nor to a vermiculite character of the mineral.

DISCUSSION AND CONCLUSION

There is no charge limit at 0.6 for the Na-saponite structure. Thus it is necessary to modify the previous conclusions of Iiyama and Roy (1963). Recently, Carman (1974) also drew similar conclusions. The maximum layer charge ($x = 1$) corresponds to the occupation of all pseudo-hexagonal cavities by a Na-cation.

It must be noticed that we did not succeed in preparing hydrothermal synthetic Ca-saponites with a layer charge of 1. All the products obtained during these experiments either contained calcite or Ca-feldspars along with one or more poorly crystallized phases.

In the Na-saponite series with increasing charges several results were pointed out:

—an expansion of d_{001} spacing by solvation became greater as the layer charge decreased, whatever the solvation liquid and the exchangeable cation nature;

—a three-dimensional order, becoming more imperfect (i.e. a disorder in the layer stacking) as the layer charge decreased.

Although it was thought that organic liquids had greater expansion properties for the collapsed structure than water, Tables 2, 3 and 4 clearly indicate that it is not the case and that the high-charge ($x \geq 0.9$) minerals saturated with Na and K cations expand more easily in water than in ethylene glycol or glycerol. This does not contradict Glaeser and Mering's results (1967). These authors indeed observed that ethylene glycol gave the best expansion for a Li-montmorillonite heated at 225°C. In this case, the nature of the clay was changed on heating because of the migration of lithium into the octahedral sheet.

Finally we can propose several criteria for evaluating the layer charge of a saponite:

(a) *the action of water on minerals saturated with Li, Mg and Ba cations.* When x is inferior to 0.6, a

three-layer hydrate is obtained with Mg and Ba cations whereas when x is superior to 0.6, a two-layer hydrate is obtained.

With the Li cation, a two-layer hydrate is obtained when x is superior to 0.6. When the layer charge is equal or inferior to this value, the swelling is unlimited.

(b) *the action of ethylene glycol on K, Mg, Li and Na samples.* With the K cation, a double-layer complex is observed when x is inferior to 0.6.

With the Mg cation, the layer charge boundary between the double-layer and the single-layer complex appears at $x = 0.8$.

With Li and Na cations, the double layer complex (16.1 Å–16.7 Å) is obtained when the layer charge is inferior to 1. When $x = 1$, a single-layer complex is obtained.

(c) *the action of glycerol on samples saturated with Li, Na, Mg, K and Ca cations.* With Li, Na, Mg and K cations, a double-layer complex of glycerol molecules (18.0 ± 0.1 Å) appears when the layer charge is inferior to 0.6. The single-layer complex (≈ 14.3 Å) is obtained when the layer charge density is superior to 0.6, with Li, Na and Mg cations. With K cation and with a layer charge equal or superior to 0.8, glycerol yields a 10 Å phase.

With the Ca cation, the limit between the double-layer and the single-layer complex appears when the layer charge is between 0.8 and 1.

Finally, a question may be raised: what is the fundamental difference between a high-charge saponite and a low-charge vermiculite ($0.5 < x \leq 0.6$)? Many scientists and particularly Wear and White (1951), Barshad (1950, 1954), Weaver (1958), Walker (1958), Warshaw and Roy (1961), Harward and Brindley (1965); Besson *et al.* (1973) and Robert (1975) have tried to determine criteria for distinguishing vermiculites and smectites.

Up to now, phyllosilicates with a charge density inferior to 0.6 are considered as smectites whereas those with a charge density superior to 0.6 are considered to be transformed micas.

This classification is based upon five principal criteria:

- the total layer charge as indicated by C.E.C.,
- the swelling in glycerol and ethylene glycol,
- the collapse of structure when saturated with potassium and the subsequent rehydration,
- the order-disorder state of their layer stacking, and
- some abnormal diffusions in microdiffraction patterns.

None of the results brought out in this study enables us to make a clear distinction between the high-charge saponite and a low-charge vermiculite. Instead, the layer charge density cannot be considered as a criterion since synthetic saponites exist with a layer charge varying between 0.33 and 1.0.

The comparison between the swelling properties of synthetic saponites in water, ethylene glycol, and gly-

cerol and of the natural tetrahedrally-charged minerals has shown that there are some discontinuities in the physico-chemical behavior of these minerals. These discontinuities depend upon the cation exchange capacity, the solvation liquid and the layer charge density, but not upon the type of mineral (saponite or vermiculite).

The ability of K-substituted phyllosilicates to collapse and rehydrate has not been fully studied. The observations made on K-saponites suggest that this ability also depends upon the layer charge density and not upon the nature of the mineral.

The three-dimensional structural organization of a clay mineral is variously changed with complex factors; therefore it is difficult to differentiate saponites from vermiculites. It is already known that the three-dimensional order of a crystalline structure largely depends upon the physical treatment (grinding in particular). In addition, this study shows that the stacking perfection of tetrahedrally substituted smectites also depends upon chemical factors such as the exchangeable cation, the solvation liquid and the layer charge.

Although the presence of honeycomb-shaped diffuse scatterings has been indicated to be a potential criterion for high-charge mica type minerals, because of difficulty for obtaining consistent results such a distinction by electron diffraction method is not a decisive criterion.

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