Clays and Clay Minerals, Vol. 23, pp. 1–9. Pergamon Press 1975. Printed in Great Britain

SWELLING AND STRUCTURAL ORGANIZATION OF SAPONITE

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(*Received* 1 *August* 1974)

Abstract—The structural formula of Kozákov saponite (Czechoslovakia) is as follows:

$$Na_{0.005}Ca_{0.22}K_{0.01}[Si_{3.30}Al_{0.68}Fe^{3+}{}_{0.02}][Mg_{2.50}Fe^{2+}{}_{0.26}Fe^{3+}{}_{0.24}]O_{10}(OH)_2.$$

Saturated with 6 different cations (Li, Na, K, Ca, Mg, Ba) its swelling in ethylene glycol, glycerol and water and its homogeneous hydration extents according to the relative humidity have been studied. Our results were compared with those found for montmorillonites, beidellites and vermiculites in order to estimate the respective influence of the surface charge density and the charge localization on the swelling properties. The three-dimensional organization of the saponite is more or less affected by random stacking faults and by multiple **b**/3 translations according to the exchangeable cation, the swelling state and the nature of the solvation liquid. Our experimental results indicate that the three-dimensional order met in the hydrated saponites can be explained by an anchoring of the layers towards each other by chains made up of cation–dipole interactions and of hydrogen bonds between negatively charged surface oxygens and the interlayer water. This type of interlayer link is relatively weak. It is therefore easy to introduce stacking faults in these edifices in particular by grinding of the samples.

INTRODUCTION

The mineral studied is found in Kozákov in Czechoslovakia. It was identified by Melka (1965) as a trioctahedral smectite and occurs with the appearance of amygdaloïdal cavities in a melaphyre-rock. We have determined its structural formula by chemical analysis

$$Na_{0.005}Ca_{0.22}K_{0.01}[Si_{3.30}Al_{0.68}Fe^{3+}{}_{0.02}]$$
$$[Mg_{2.50}Fe^{2+}{}_{0.26}Fe^{3+}{}_{0.24}]O_{10}(OH)_2,$$

i.e. a charge density of 0·46 for half a unit cell. Its experimental cation exchange capacity is 119 m-equiv./100 g of calcinated clay: this value coincides with the calculated exchange capacity.

The examination by electron microscopy (Fig. 1) confirms Weiss *et al.* observations (1955): this mineral exists in ribbon-shaped particles mixed with isometric particles. Electron-diffraction studies of this specimen verify that the particles are elongated parallel to the *a*-axis. The size of the particles is much larger than that which is usually encountered in smectites.

The saponite of Kozákov has been saturated with six different cations (Li, Na, K, Ca, Mg and Ba) and we have studied:

(a) its swelling in ethylene glycol, glycerol and water,

(b) its homogeneous hydration extents according to the relative humidity,

(c) its structural organization under the same conditions.

Our results were compared with those found for montmorillonites, beidellites and vermiculites in order to estimate the respective influence of the surface charge density and the charge localization.

SWELLING

The swelling in ethylene glycol, glycerol and water of 4 clay minerals saturated with the 6 exchangeable cations mentioned above have been studied.

These 4 clay minerals are: montmorillonite (an octahedrally charged smectite), beidellite, saponite and vermiculite (three tetrahedrally charged minerals). It is, however, only in the saponite and vermiculite that we find strictly the same distribution of the charges, i.e. an excess of positive charges in the octahedral sheet, consequently a more defined localization of negative charges on the oxygens of the silicate surface.

Ethylene glycol

With ethylene glycol liquid, saponite presents a behaviour similar to that of the other smectites, i.e. its swelling varies between 16·7 and 17 Å (Table 1). On the other hand, several authors showed that most of the time Mg–vermiculites give a complex at 14·3 Å.

Glycerol

With liquid glycerol, the saponite also presents a behaviour similar to the other smectites and its swelling varies between 17·8 and 18 Å, contrary to the majority of the vermiculites which swell to about 14·3 Å (Table 2).

However, we observed that the Li, Na, Ca, Mg–saponites present another weak reflection at 14·3 Å in addition to the 18 Å reflection. The intensity of this supplementary reflection is all the stronger when a gly-

https://doi.org/10.1346/CCMN.1975.0230101 Published online by Cambridge University Press

Table 1. Mean values of basal spacings d_{001} (Å) of ethylene glycol solvation complexes of smectites and vermiculites

Clay mineral \ Exchangeable cation	Li	Na	K	Ca	Mg	Ba
Montmorillonite						
(a)	16·9–17·1	17	17	17	17	17
(d)				16·9	15·3	
Beidellite						
(b)	17·00	16·86	14·7	16·88	16·95	16·7
(d)				16·7	16·8	
(e)	16·6	16·87	14	16·7	17·1	
Saponite	16·4	16·7	16·5	16·6	16·7	16·7
Vermiculite						
(c)	16·1	16·3 l.c. 14·8 h.c.		16·2 l.c. 15·6 h.c.	14·3 l.c. 14·3 h.c.	16·2 l.c. 16·0 h.c.
(d)				15·3	14·25	

(a) Brindley (1966).
(b) Beidellite from Black Jack Mine (Idaho); Weir (1960).
(c) Walker (1958): l.c., low-charge density vermiculite; h.c., high-charge density vermiculite.
(d) Harward, Carstea and Sayegh (1969). These values were obtained with ethylene glycol vapour. The beidellite used comes from Black Jack Mine (Idaho).
(e) Beidellite from Rupsroth (Germany); unpublished data given by R. Glaeser.

cerol is used almost without any water. On the contrary, it completely disappears when the sample has been ground, e.g. 5 min in an agate mortar.

It is necessary to take this observation into account when smectites are differentiated from vermiculites by their swelling in the magnesium state in glycerol.

The different possible steps of swelling of a mineral in a liquid are mainly function of cation–liquid and silicate layer–liquid interactions in the interlayer space. If these interactions are modified, either because a second liquid was added (dilution of glycerol with water), or because stacking faults were caused through grinding, the energetic state of the structure and therefore the type of the swelling, can then be modified. In the least ground sample, the presence of two types of swelling enables one to think that there may be some heterogeneity either in the charge localization or in the size.

Water

Table 3 gives the mean values of basal spacings d_{001} upon water solvation of the 4 clay minerals which have been mentioned above and which are saturated with the six usual cations. The state of maximum hydration in which the layers lose their parallelism has been called 'indeterminate' (ind.). The results included in this table have been differently presented in Table 4.

With the Li cation, the layers of the 4 phyllosilicates are completely dispersed. Therefore, they have been grouped in the same place. However, it is well known

Table 2. Mean values of basal spacings d_{001} (Å) of glycerol solvation complexes of smectites and vermiculites

Clay mineral \ Exchangeable cation	Li	Na	K	Ca	Mg	Ba
Montmorillonite						
(e)			18 or 13·8			
(a)	ind.	17·8	18	17·6	17·8	17·8
(d)				17·3	17·4	
Beidellite						
(f)	18·0	18·0	13·7	17·7	17·9	17·9
(b)	17·6	17·7	13·90	17·60	18·00	
(d)				14·6 s	14·4	
Saponite	18·1 s 14·4 vw	18·1 s 14·3 vw	18·2	17·9 s 14·4 vw	18·1 s 14·3 vw	18·1
Vermiculite (c)	14·3	14·8		17·6 l.c. 14·3 h.c.	14·3	17·6 l.c. 14·3 h.c.

(a) Montmorillonite from Wyoming; Brindley (1966).
(b) Beidellite from Black Jack Mine (Idaho); Weir (1960).
(c) Walker (1958): l.c., low-charge density vermiculite; h.c., high-charge density vermiculite.
(d) Harward, Carstea and Sayegh (1969). These values are obtained with glycerol vapour for the montmorillonites and the beidellite of Black Jack Mine and with liquid glycerol for the vermiculites.
(e), (f) Unpublished data given by R. Glaeser; (e) montmorillonite from Wyoming and Camp-Berteaux; (f) beidellite from Rupsroth.

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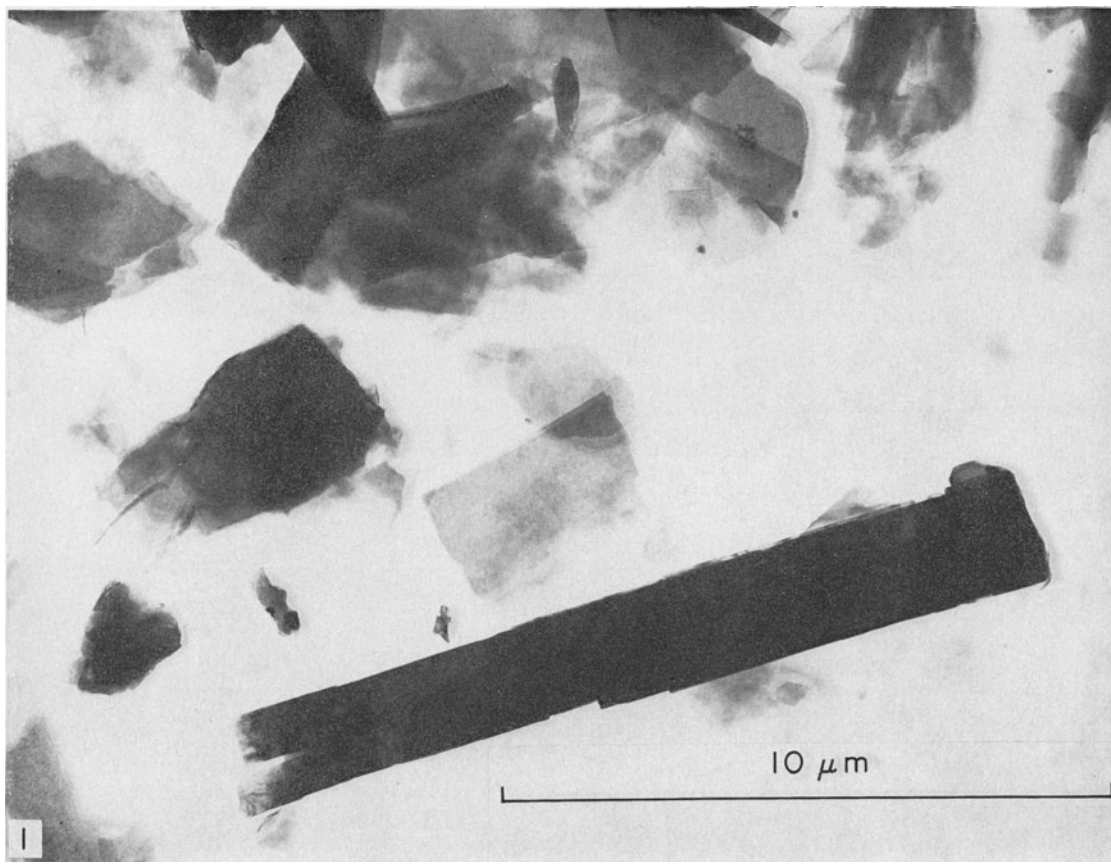

Fig 1. Electron micrograph of a specimen of Kozákov sample.

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Table 3. Mean values of basal spacings d_{001} (Å) of water solvation complexes of smectites and vermiculites

Clay mineral \ Exchangeable cation	Li	Na	K	Ca	Mg	Ba
Montmorillonite	ind.	ind.	(1) { ind. / 15·5	19·1	19·4	18·7
Beidellite						
(2)	ind.	15·2	12·7	{ 18·7 s / 15·4 vw	18·6	
(3)	ind.	ind.	12·55	18·6	18·58	18·38
Saponite	ind.	15·2	12·6	{ 18·6 vw / 15·4 s	{ 18·9 s / 15·7 vw	{ 18·5 s / 15·9 vw
Vermiculite	(1) { ind. / 15	14·9	(1) { 12·6 / 10·4	14·9	14·7	15·7

(1) According to the origin and the history of the sample.
(2) Beidellite from Rupsroth (Germany); unpublished data given by R. Glaeser.
(3) Beidellite from Black Jack Mine (Idaho); Weir (1960).

that the highly charged vermiculites give a two-water layer hydrate, therefore a second localization of the vermiculites.

With the Na cation, the layers of montmorillonite and some beidellites are completely dispersed and a two-water layer hydrate for other beidellites, saponites and vermiculites is observed.

With potassium, montmorillonite alone can give a complete dispersion of the layers, unless it has been subjected to some dehydration and hydration cycles (Mamy, personal communication). The K–beidellite and K–saponite give a single water-layer hydrate.

Saturated with calcium, montmorillonite gives a three-water layer hydrate. Ca–beidellite also gives mostly this hydrate, plus a two-water layer hydrate in a small quantity. The phenomenon is on the contrary reversed with the saponite, i.e. there is mostly a two-water layer hydrate and a three-water layer one in a small quantity. Vermiculite gives a two-water layer hydrate. Therefore, there is a transition from montmorillonite to vermiculite through beidellite and saponite which clearly shows the passage through clay minerals where the two swelling states are presented.

Thus, two equilibrium states with the same mineral and the same liquid can be observed, as it has been noticed before with the Li, Na, Ca and Mg–saponites in glycerol. But if a Ca–saponite is ground, the formation of the three-layer water hydrate is favoured. Going further, if the swelling in water is preceded by a swelling in ethylene glycol (with a complete elimination of this pre-swelling liquid) a three-water layer homogeneous hydrate can be obtained.

The Mg and Ba–saponite give a mixture chiefly made up of a three-water layer hydrate and in a much weaker quantity, a two-water layer one.

Thus, in Table 4, the hydration states clearly vary as a function of several factors; namely, the nature of the exchangeable cation, the surface charge density since the vermiculites are systematically in the group of the least hydrated minerals and the charge localization. We indeed observe that, on the one hand, the octahedrally charged mineral (montmorillonite) is always in the group of the most hydrated minerals. On the other hand, if saponite and beidellite are compared, both having very similar charge densities, the excess of positive charges in the octahedral sheet of the saponite, gives it a weaker aptitude to hydration, and thus it behaves nearly like a vermiculite.

Eventually, other factors influence the swelling of these clay minerals, in particular—and we will come

Table 4. Classification of the minerals according to the swelling in water and the exchangeable cation

Hydration state \ Exchangeable cation	Li	Na	K	Ca	Mg	Ba
Indetermined	M B S V	M B	M			
3 Water layers				M B (S)	M B S	M B S
2 Water layers	V	B S V	M	(B) S V	(S) V	(S) V
1 Water layer			B S V			
0 Water layer			V			

M: montmorillonite
B: beidellite
S: saponite
V: vermiculite
} in water

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back to this matter later on—the type of layer stacking in the case where these layers can be hydrogen bonded by the solvation liquid. This stacking can be modified either by grinding or by hydration and dehydration cycles as it can be seen in the K–montmorillonites.

HYDRATION EXTENT

The ground samples introduced in capillaries were subjected to diminishing pressures of water vapour at a constant temperature of 20°C. When equilibrium was reached, one sample of each cation was removed and sealed immediately for X-ray examination.

The variations of basal spacings d_{001} according to the relative humidity and nature of exchangeable cation, are represented in Figs. 2–7. In Figs. 2 and 7, the hydration extents of beidellite and hectorite have been represented such as they have been determined by Glaeser and Méring (1968).

Na cation (Fig. 2)

In the Na–saponite and the Na–beidellite, three distinct horizontal steps are observed which are superimposed and which correspond to the dehydrated mineral, to the mono-water layer hydrate and to the two-water layer hydrate respectively. These two smectites have a positive charge deficiency in the tetrahedral sheets. These homogeneous hydration extents are characterized by the presence of a rational series of reflections (001).

During the transition of the mono-water layer hydrate to the two-water layer hydrate, we observe an interstratification phenomenon in a narrow field of relative humidity (about 10 per cent). This same phenomenon can be observed in the case of the other two alkaline cations and it is represented in Figs. 2–4 by vertical lines.

The hydration extents of Na–hectorite have also been represented in order to show the clear differences existing between this clay mineral with a positive charge deficiency in the octahedral sheet and the other clay minerals with a positive charge deficiency in the tetrahedral sheets. It can be seen on the one hand that there is no longer a horizontal step and on the other hand that the interstratification extents are much more important.

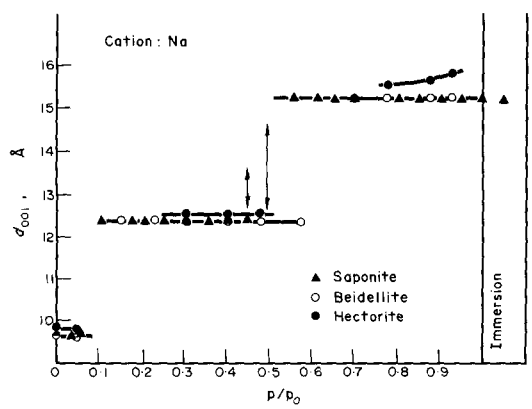

Fig. 2. Basal spacings upon hydration of Na-saturated samples.

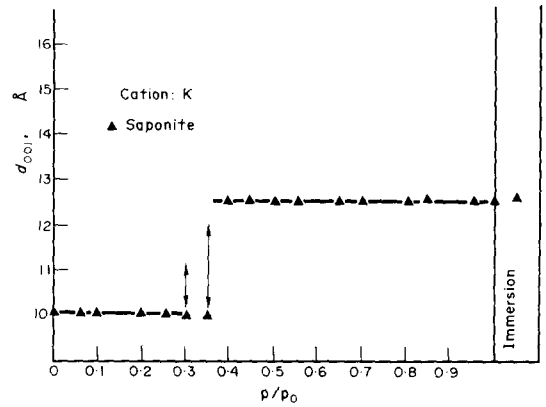

Fig. 3. Basal spacings upon hydration of K-saturated samples.

Calvet (1972), Glaeser and Méring (1968) and other authors have shown that the hydration curve of Na–montmorillonite is of the same type as that which we are here describing for hectorite. On the contrary, Mamy and Le Renard (1970) have observed that Na–phlogopite has homogeneous hydration extents characterized by horizontal steps similar to those which we have shown for the smectites with substitutions in the tetrahedral sheets.

Furthermore, it has been shown that, in the tetrahedrally charged phyllosilicates, Na–beidellite (Glaeser and Méring, 1968) and Na–vermiculite (Van Olphen, 1965), the hydration isotherms produce two steps, one being at the level of the single-water layer hydrate, the other at that of the two-water layer hydrate, whereas this phenomenon cannot be obtained with Na–montmorillonite and Na–hectorite.

These two factors, namely, the hydration curves with horizontal steps and hydration isotherms with steps are indicative of tetrahedrally charged Na–clay minerals. Glaeser *et al.* (1967) had already noticed, from their beidellite studies, that a third factor was to be linked with the two previous ones—a three-dimen-

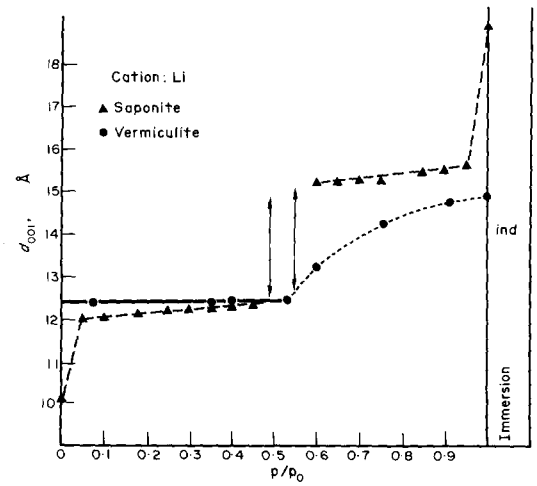

Fig. 4. Basal spacings upon hydration of Li-saturated samples.

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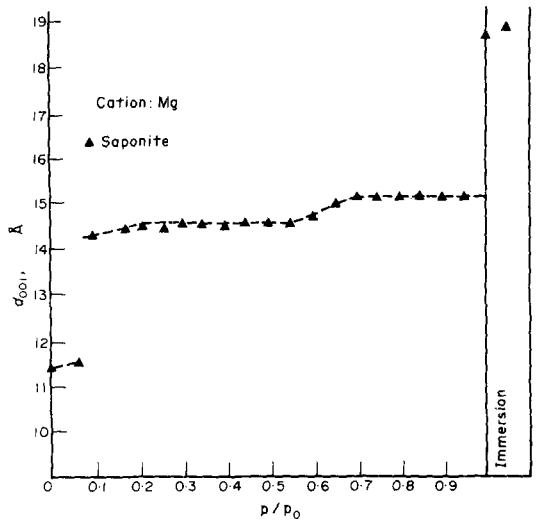

Fig. 5. Basal spacings upon hydration of Mg-saturated samples.

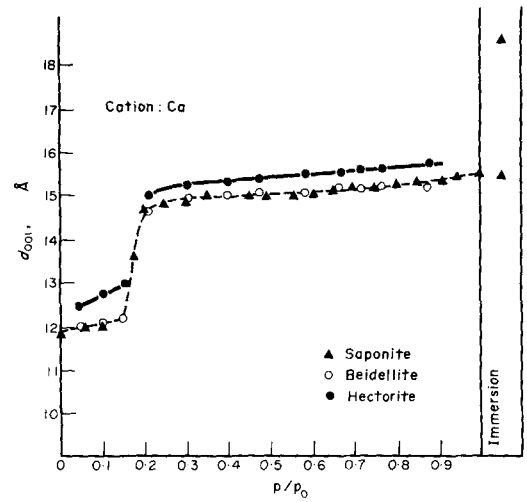

Fig. 7. Basal spacings upon hydration of Ca-saturated samples.

sional crystalline organization. We will come back to this matter later on but it can be already noticed that it is especially with the Na cation that the hydrated saponite presents the best three-dimensional organization.

K cation (Fig. 3)

The K–saponite presents homogeneous hydration extents for the dehydrated mineral and the single-water layer hydrate. On the contrary several authors have shown that the hydration curve of the K–montmotillonite did not present any clear horizontal step but that its slope varied according to the relative humidity.

Li cation (Fig. 4)

With the Li cation, saponite indicates five possible states of hydration but none is characterized by an horizontal step. On the contrary, the Li–vermiculite from Benahavis, ground for a long time, presents a homogeneous hydration extent when the relative humidity is less than 55 per cent. Beyond this value we can only notice interstratified states.

The dehydrated sample of Li–saponite does not give a rational series of reflections (00*l*) and this characterizes a particularly unstable hydration state.

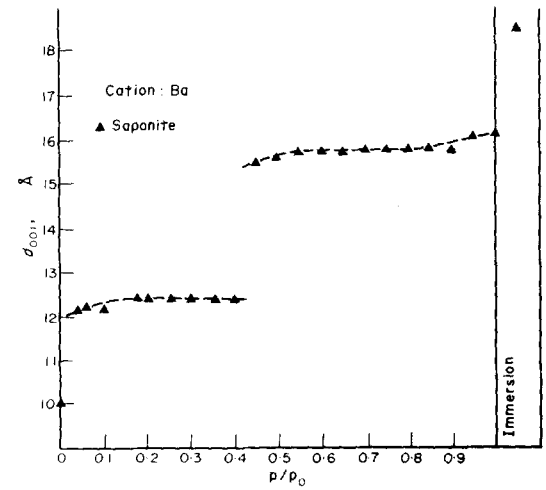

Fig. 6. Basal spacings upon hydration of Ba-saturated samples.

Mg cation

The hydration curve of the Mg–saponite indicates the existence of a mono-water layer hydrate and a two-water layer hydrate. Contrary to the Na–saponite, there is a clear variation of the value of d_{001} for the two-water layer hydrate which varies according to the relative humidity.

Ba cation

Saturated with the Ba cation, the saponite indicates four states of hydration. There again, for the mono- or two-water layer hydrates, steps as clear as those met in the Na–saponite cannot be found.

With the Mg and Ba cations, it has been shown that the hydration curves of montmorillonite present a more important slope within each hydration extent than in the case of the corresponding saponites.

Ca cation

In Fig. 7, we do not observe either the clear horizontal steps of the hydration curves of Na– and K–saponites but slightly inclined lines, superimposed on those obtained by Glaeser and Méring (1968) with Ca–beidellite. In the same figure, the Ca–hectorite hydration extent has been represented. It may be noted that the thickness of the interlayer water is greater for this mineral.

THREE-DIMENSIONAL CRYSTALLINE STRUCTURE

We have studied the organization of the layers in relation to one another in the saponite, it being understood that we were only interested in the homogeneous

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hydration state, excluding all of the factors associated with interstratification.

In contrast with the octahedrally charged smectites, it is well known that the tetrahedrally charged smectites, beidellites and saponites, produce an X-ray diffraction pattern indicating a more or less complete three-dimensional crystalline structure. Glaeser *et al.* (1967) have already shown that the type of organization is not dependent upon the high charge of the layer. We have achieved the same results with a charge of 0·46, much inferior to the limit of 0·55 set by several authors (Weiss *et al.*, 1955), and we have observed a three-dimensional organization in the saponite.

We have used powder diffraction patterns and patterns obtained with oriented films of clay. The latter technique employed either stationary film or precession camera.

We were thus able to follow the evolution of the diffusion of X-rays on two families of rows of the reciprocal lattice $[02l]^*$–$[11l]^*$ and $[20l]^*$–$[13l]^*$ which are indicative of the whole of the order parameters of the mineral.

The turbostratic state is defined as a random stacking of the silicate layers and the loss of periodicity is achieved by random translations or by random rotations. The powder diffraction pattern then indicates the series (00*l*) and the bands (02) and (20). Such is the case for hectorite. We define three-dimensional order as a strictly periodic ordered organization of the layers in space. The deviation from three-dimensional order can proceed either from random stacking faults, or from multiple **b**/3 translations. α and β will respectively be called the rate of random faults and that of multiple **b**/3 faults. It can be considered that α (the probability that a layer $(n + 1)$ is in random position in relation to a layer n) is equal to zero in a three-dimensional organized phyllite and equal to unity in a turbostratic structure. In our samples, the absolute value of α will not be estimated but we will only draw an approximate classing of this rate of faults in reference to the broadening of (20*l*) reflexions. Multiple **b**/3 faults can be shown by the more or less complete vanishing of the discreet reflexions with $k \neq 3n$, and in particular by the series (02*l*), at the benefit of a continuous diffusion along the rows. In the same way, we cannot, at the present stage of our studies, quantitatively determine the absolute value of β, and this is so, moreover, because the (02*l*) reflexion broadening expresses the sum of both factors, α and β.

Three-water layer hydrate

They are obtained with the Mg–, Ba– and Ca–saponites immersed in water. They present a three-dimensional organization where the number of random faults increases from Mg and Ba to Ca. It must be noticed that the three-water layer Ca–saponite can be obtained only when the sample has been subjected to a previous treatment in ethylene glycol or once the

Table 5. X-ray powder diffraction data for the two-water layer Kozákov saponite (obtained with a Guinier De Wolff camera and monochromatized $\lambda K\alpha$ Co radiations; Si as standard)

Intensity	Indices	$d_{observed}$ (Å)	$d_{calculated}$ (Å)
vvvs	001	15·29	15·32
w	002	7·65	7·66
w	003	5·10	5·10
vs	020	4·61	4·616
	110		4·595
vvw	$\bar{1}11$	4·529	4·528
vvw	021	4·418	4·420
m	111	4·284	4·284
m	$\bar{1}12$	4·125	4·127
vw	022	3·954	3·954
vw	004	3·828	3·829
vvw, br	$\bar{1}13$	3·599	3·600
vw	023	3·424	3·424
vw	113	3·256	3·256
m, br	005	3·063	3·063
vvw	$\bar{2}01$	2·662	2·662
s	200	2·648	2·648
m	$\bar{2}02$	2·598	2·598
s	201	2·560	2·560
s	202	2·418	2·418
w	$\bar{2}04$	2·307	2·307
w, br	203	2·245	2·247
vvw, br	134	2·126	2·128
m	$\bar{3}11$	1·7454	1·7456
vw	$\bar{2}42$	1·7259	1·7255
vw	241	1·7145	1·7144
vw	311	1·7015	1·7017
vvs	060	1.5389	1·5388
vs	$\bar{3}32$	1·5320	1·5317
w	$\bar{3}33$	1·5092	1·5093
	331		1·5090

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product has been prepared with an extensively ground powder.

Two-water layer hydrate

The number of random faults increases as follows:

$$Na < Mg < Ca < Ba < Li.$$

It seems that other multiple **b**/3 faults appear in some samples, particularly in the Mg–saponites. We observe in Fig. 8 the development of the crystalline organization from the reflexions (02*l*) and (20*l*) in the two extreme cases, either a two-water layer Na–saponite or a two-water layer Li one.

It is observed, if the grinding is sufficient, that there is a similarlity between the Mg–saponite and Mg–vermiculite patterns (Fig. 9), as we noticed when studying five samples of vermiculite of diverse origins (Kenya, Benahavis, Madagascar, Prayssac and Beni-Buxera).

The presence of a number of multiple **b**/3 faults, particularly large in the Mg–saponites and vermiculites, is to be considered in relation to the vermiculite structure as described by Shirozu and Bailey (1966). These authors have shown that we pass from the parent phlogopite to the vermiculite, not only by swelling and K–Mg exchange, but also by translation of **b**/3 of one layer out of two. This kind of shift caused during the weathering of phlogopite by the hydrated magnesium cations, can hardly be conceived without a relatively important number of faults. The nearly complete vanishing of the discreet (02*l*) reflexions in the powder patterns can thus be explained. With saponite, the fact that multiple **b**/3 shifts are observed with more difficulty can perhaps be linked with the weaker layer charge.

Figure 10 illustrates the grinding influence on the two-water layer Ca–saponite. The increase of grinding (from top to bottom in Fig. 10) results in a nearly total vanishing of the reflexions of type (02*l*) and (20*l*).

Na–saponite has the best organization state. This can be correlated with the fact that the two-water layer Na–saponite has a hydration range (as a function of the relative humidity) characterized by a strictly horizontal step.

A continuing study of the two-water layer Na–phlogopite polytypism enables one to conclude that this mineral is a one-layer polytype of the type Ia-2 if one refers to Brown and Bailey's terminology (1962). The two-water layer Na– and Ca–saponites present the same polytype (one layer Ia-2), which can be observed in the powder and precession patterns.

A comparison of the positions and intensities of the reflexions observed between the powder patterns of the two-water layer Na– and Ca–saponites and that of the two-water layer Na–phlogopite, enabled one to index these reflexions (Table 5) and to establish the unit cell parameters for the natural mineral:

$$\begin{aligned} a &= 5{,}333\,\text{Å} \\ b &= 9{,}233\,\text{Å} \\ c &= 15{,}42\ \text{Å} \\ \beta &= 96°66 \end{aligned}$$

Single-water layer hydrate

The number of random faults α increases as follows:

$$Na \simeq K < Ca \simeq Ba < Mg < Li.$$

It is difficult, at the present stage of our study, to estimate anything about the number of β faults of single-water hydrate but it appears to us that β is more important in the mono-water layer hydrate than in the two-water layer ones. This observation, however, is linked with our conclusions in the present study about the hydrated phlogopites.

It must be added that the same distribution of intensities of the (20*l*) reflexions with the Na, K and Ca cations can be observed whereas the Ba and Mg cations give a different distribution. In this latter case the distribution is similar to that presented by the mono-water layer Mg–vermiculite. The observed differences in these intensities are likely to be related to the layer stacking type characteristic of each cation series, but as no study is yet made about the single-water layer mica structures, we cannot go further in the interpretation.

The good structural organization of the mono-water layer Na– and K–saponites can be related with the fact that the hydration ranges, as a function of the relative humidity, are characterized by perfectly horizontal steps (Figs. 2 and 3).

With Na–saponite, we have verified that the passage of the mono-water layer hydrate to the two-water layer one implied an improvement in the three-dimensional organization, which is due to a shift of the layers.

It has been observed also that grinding increased the number of random faults in the mono-water layer hydrates.

Dehydrated minerals

The number of random faults varies as follows:

$$K \simeq Ba < Na.$$

No multiple **b**/3 faults in addition to random faults are observed.

Evidently dehydration particularly affects the Na–saponite structural organization which is no longer the mineral with the best three-dimensional organization. However, dehydration improves the Ba– and K–saponites' three-dimensional organization, because these voluminous cations lie in hexagonal holes in the oxygen surface of two adjacent layers, thus commanding an order from one layer to another.

Figure 11 gives the diffraction pattern obtained by the precession camera with an oriented film of dehydrated K–saponite. It can be seen the three rows of the reciprocal lattice: the row $[00l]^*$, the superimposed ones $[02l]^*$, $[11l]^*$ and $[\bar{1}1l]^*$ and finally the superimposed rows $[20l]^*$, $[13l]^*$ and $[\bar{1}3l]^*$. These rows do not present a continuous diffusion but discreet reflections (in the form of an arc of a circle) indicative of a three-dimensional organization. These rows are shown in Fig. 12. The reflexions corresponding to the dehydrated K–saponite are represented by arcs of a circle.

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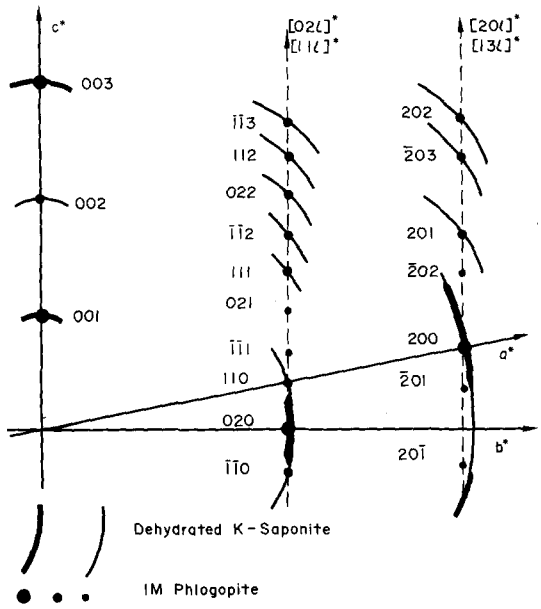

Fig. 12. Scheme representing two superimposed precession photographs. The first one (with arcs of a circle) corresponds to a film of dehydrated K–saponite and the second (with spots) corresponds to a film of K–phlogopite.

The spots correspond to the reflexions which would be given in the same conditions by a 1M or 3T polytype phlogopite. The spot surface is proportional to the intensity of the reflexions. The accurate correspondence between the two results makes it possible to establish that the K–saponite polytype is 1M or 3T.

Glycerol–saponite and ethylene glycol–saponite complexes

Whatever the nature of the exchangeable cation, these complexes have a small number of random faults but very numerous multiple **b**/3 stacking faults.

CONCLUSION

Our study aims at proving that the three-dimensional order in hydrated saponites can be explained only by an anchoring of the layers towards each other, and therefore only by the existence of chains mobilizing a part of the interlayer water to form, through the intermediary of the exchangeable cations, relatively rigid bridges from one layer to another.

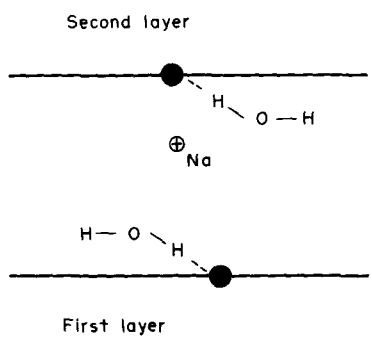

Fig. 13.

These chains may be developed as shown in Fig. 13, from cation–dipole interactions and from hydrogen bonds with some negatively charged surface oxygens as Farmer and Russell (1971) have already put forward.

This type of interlayer link is relatively weak and thus it is easy to introduce stacking faults particularly by grinding. In this case few modifications are likely to exist in the cation–dipole interactions, but a breaking of the hydrogen bonds is more likely to occur between the silicate layer and the hydration shell of the exchangeable cation.

The possibility to form hydrogen bonds implies a precise localization of the negative charges on the layer silicate surface and this is possible in the tetrahedrally charged minerals. It is thus explained that three-dimensional organization can occur only in this phyllosilicate family or at least in the minerals where the greatest part of the charge deficiency comes from tetrahedral substitutions. Glaeser *et al.* (1967), then Schultz (1969), have shown that the majority of beidellites were mixed, i.e. they are octahedrally and tetrahedrally charged smectites, and it is only beyond a certain critical value of the tetrahedral charge that beidellites are three-dimensionally organized (personally communicated by R. Glaeser).

X-ray diffraction study of different samples of mixed beidellite shows that in these samples the three-dimensional organization is inferior to that of the Kozákov saponite where there is no charge deficiency in the octahedral sheet.

The fact that a part of the interlayer water is engaged in hydrogen bonds with the layer surface is certainly not extraneous to the properties and reactivity differences noticed between the interlayer water in saponites and montmorillonites. Indeed, various authors, in particular Hecht *et al.* (1966), Russell (1965), Russell and Farmer (1964) and Doner and Mortland (1971) at the end of their nuclear magnetic resonance and infrared studies have shown that in saponites, the affinity for water is much bigger than in montmorillonites, but that, on the contrary, the proton mobility is here much weaker. Saponites do not give any protonation phenomenon similar to those met in montmorillonites, and this absence of protonation is no doubt to be linked with the greater thermal stability of these minerals, the dehydroxylation appearing at a temperature higher in saponites than in montmorillonites.

Acknowledgements—The authors thank Professor Nicolas and Mr. P. Douillet for the determination of the structural formula, Mr. G. J. Ross for measuring the cation exchange capacity, Mrs. E. Copin for technical assistance and Professor G. W. Brindley for his help in the English translation.

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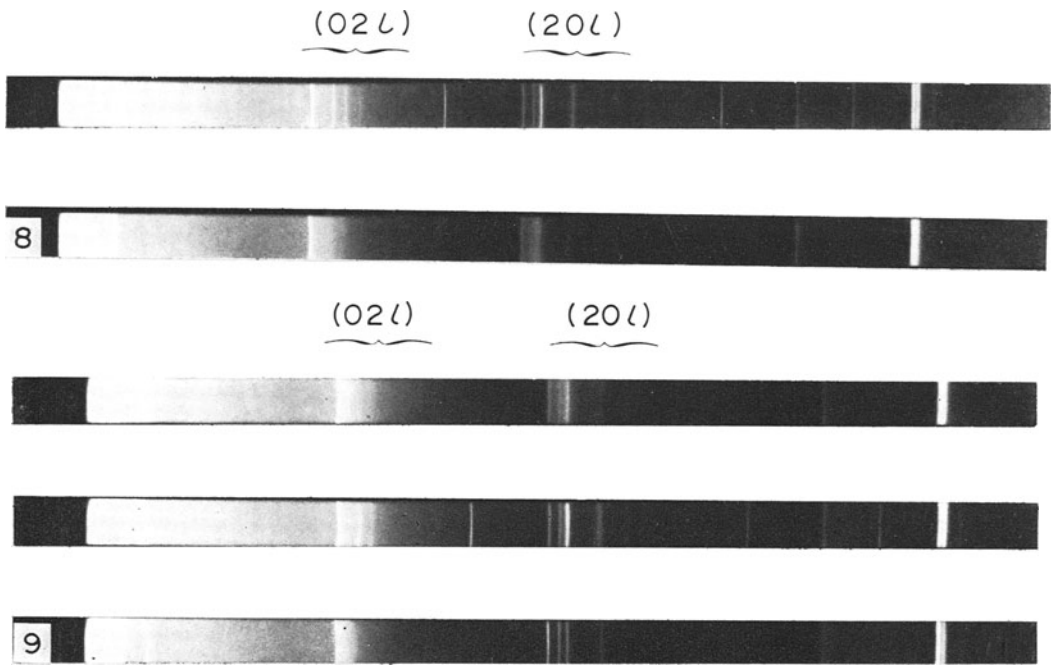

Fig. 8. X-ray powder diffraction patterns of the two-water layer hydrate of Na–saponite (plus Si) and Li–saponite. (λ Kα Co radiation).

Fig. 9. X-ray powder diffraction patterns of the two-water layer hydrates. (λ Kα Co radiation). From top to bottom: Mg-saponite (ground), Mg–saponite (plus Si), Mg–vermiculite (from Beni-Buxera).

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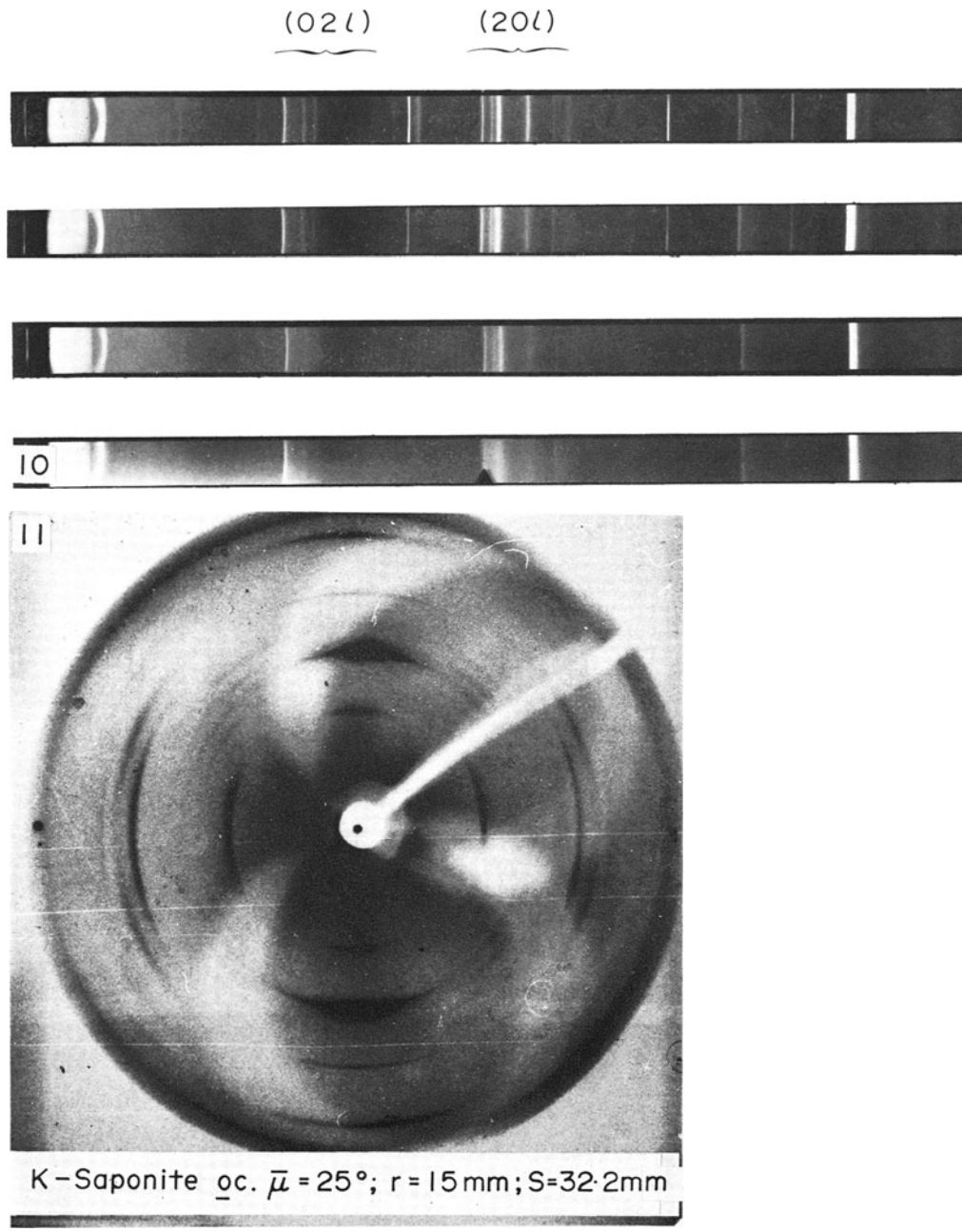

Fig. 10. Influence of grinding upon the two-water layer hydrate of Ca–saponite. From top to bottom: Saponite from Kozákov (natural plus Si); Ca–saponite (plus Si); Ca–saponites (ground); (λ Kα Co radiation).

Fig. 11. Precession photograph of a film of dehydrated K–saponite ($\bar{\mu}$= 25; Cu Kα).

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