STEVENSITE, A MONTMORILLONITE-TYPE MINERAL SHOWING MIXED-LAYER CHARACTERISTICS*

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ABSTRACT

X-ray and electron diffraction studies confirm that stevensite belongs to the montmorillonite group of minerals. The basal spacings are variable and show a poorly developed sequence of non-integral character. Some specimens show a long spacing of about 24–25 Å. Organic liquid complexes also show a poorly developed sequence of basal reflections and occasionally a long spacing of about 26 Å. Heat-treatment up to 400° C. reduces the basal spacing to about 9.6 Å. It is suggested that the mineral may have a mixed-layer sequence consisting normally of about 10 and 14 Å units, the latter showing swelling and shrinking characteristics; it may be described as a talc-saponite interlayered mineral. Electron micrographs are reproduced.

INTRODUCTION

Stevensite has recently been examined by Faust and Murata (1953) who have shown that it belongs to the montmorillonite group. The swelling characteristics which they report, namely a 001 spacing of 15.1 Å after treatment with ethylene glycol and "no easily detectable swelling" when a fragment is dropped in water, together with an abnormally low cation-exchange capacity, suggested to the writer that the mineral might have anomalous features as compared with others in this group. Dr. G. Switzer of the U. S. National Museum kindly supplied a specimen of stevensite (U.S.N.M. R 4719) from Springfield, New Jersey, a source from which Faust and Murata also obtained material. The mineral has been examined by *x*-ray diffraction using a Norelco Straumanis-type camera of diameter 11.46 cm. and Geiger counter recording spectrometers (General Electric XRD-3 and North American Philips high-angle instrument), and by electron diffraction and electron microscopy using RCA instruments. The swelling of the mineral in a series of organic liquids has been measured.

X-RAY AND ELECTRON DIFFRACTION ANALYIS

X-ray powder diagrams taken with specimens prepared in a variety of ways show a clearly defined pattern of the montmorillonite type, (Fig. 1, *a* and *b*). Faust and Murata indexed the diagram "on the basis of the work of Faust (1951) on the related mineral sauconite" in which a monoclinic formula was used. This does not conform with current views of diffraction by montmorillonite and similar minerals. The broadly

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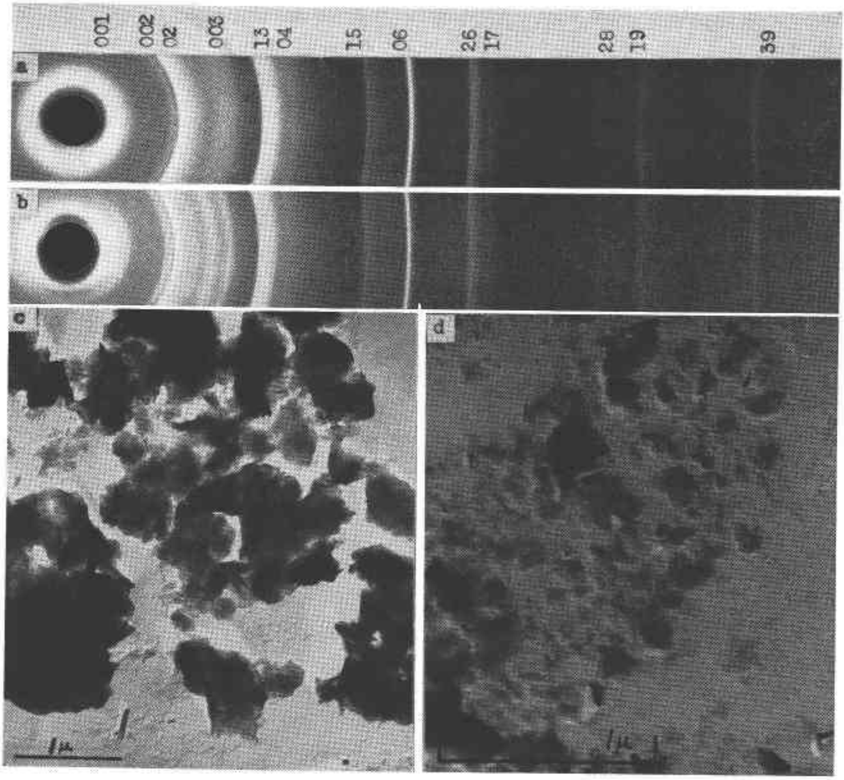

FIG. 1. (*a*) and (*b*)—*X*-ray powder diagrams of air-dry stevensite, with 00*l* and *hk* indices of the reflections. (*a*)—Random layer sequence, (*b*)—partial segregation of 10 and 14 Å layers. (*c*) and (*d*)—Electron micrographs of platinum-shadowed stevensite.

spreading diffraction bands represent coherent scattering from single layers of the mineral and monoclinic parameters do not exist, (see Brindley 1951, Brindley and Méring, 1951). The low-angle terminations of the bands correspond closely with *hk*0 positions in reciprocal space and the corresponding *d* values can be calculated from the layer parameters *a* and *b* or, for hexagonal layers, from a single parameter *a* or *b*.

The results of the diffraction analysis are summarized in Table 1. The first column gives the indices of the reflections which are of types 00*l* and *hk*. The intensities are visually estimated and the *x*-ray values are for specimens with a minimum of preferential orientation. The 00*l* spacings are variable and at the best correspond only roughly with an integral series; a precise basal spacing cannot be given. In addition, many of the counter-spectrometer records shown an indication of a weak reflection at about 24–25 Å; see, for example, figure 2*b* for an orientated air-

TABLE 1. INDEXED POWDER DIAGRAM OF AIR-DRY STEVENSITE
(from Springfield, N. J.; U.S.N.M. R 4719)

X-ray data; filtered CuKα radiation, $\lambda = 1.542$ Å
Electron data; 50 kV electrons calibrated with MgO, $a = 4.213$ Å

Indices	Intensities		Spacings, *d* (Å)			
	X-ray	Electron	*X*-ray	Electron	Calculated	Faust & Murata
—	—	—	24	—	—	—
~001	10+	—	11.2–12.4	—	—	14±
~002	2	—	4.89–4.96	—	—	—
02, 11	10	10+	4.54	4.53	4.56	4.55
~003	5	—	3.0–3.5	—	—	3.20
13, 20	9	10	2.618	2.64	2.635	2.63–2.53
04, 22	2	2	2.279	2.26	2.280	2.284
15, 24, 31	4	7	1.725	1.717	1.725	1.722
06, 33	9	10	1.520	1.514	1.520	1.526
26, 40	7	9	1.314	1.314	1.317	1.315
17, 35, 42	2	4	1.265	1.263	1.266	1.265
08, 44	—	1	—	1.139	1.140	—
28, 37, 51	1	2	1.047	1.043	1.046	—
19, 46, 53	3	5	0.994	0.989	0.995	0.990
0.10, 55	—	½	—	0.910	0.912	—
39, 60	3	5	0.879	0.877	0.878	0.879
57, 64, 1.11	—	½	—	0.815	0.819	—
0.12, 66	—	4	—	0.759	0.760	—
2.12, 59, 73	—	2	—	0.727	0.731	—
1.13, 68, 75	—	½	—	0.690	0.696	—
4.12, 80	—	1	—	0.653	0.658	—
3.13, 5.11, 82, 14.0	—		—		0.652	—

dry specimen sedimented on a glass plate. The *hk* spacings correspond to the low-angle terminations of the bands in all cases where there is a spreading of intensity towards higher angles. The calculated spacings are obtained from the formula,

$$(1/d)^2 = (3h^2 + k^2)/b^2$$

and the *b* parameter, 9.12 Å, is derived from the sharp 06 reflection. With CuKα radiation the *hk* reflections can be measured down to 0.879 Å. Electron diffraction diagrams taken by transmission through thin films mounted on collodion extend the range of measurements down to 0.652 Å. The latter are calibrated by reference to MgO using the spacings determined by Swanson and Tatge (1953). The *x*-ray values are considered to be accurate to about 0.2% and the electron values to about 0.5%. The agreement between the two sets of measurements and the calculated values is very close throughout. All *hk* reflections theoretically possible have been recorded. The index sum $(h+k)$ is always even in accordance with the centering of the layer unit. There is close agreement also with the experimental data of Faust and Murata which are listed in Table 1, but in the writer's opinion their indexing of the diagram in terms of monoclinic parameters is incorrect; they also list some indices with $(h+k)$ an odd number.

The Basal Reflections; Evidence for a Mixed-Layer Structure

The occurrence of a 24–25 Å reflection, taken in conjunction with the poorly developed and non-integral basal reflections suggests a mixed-layer structure containing layers of about 9.5–10 and 14–15 Å thickness. A partially regular alternation of two such layers would account for a weak reflection at about 24–25 Å. If integral sub-multiples of 9.5, 10, 14 and 15 Å units are set out as follows:

15.0		7.5	5.00	3.75	3.00	2.50		2.14
14.0		7.0	4.67	3.50	2.80		2.33	2.00
	10.0		5.00	3.33		2.50		2.00
	9.5		4.75	3.17			2.37	1.90

then an irregular or imperfectly regular alternation of the two components would be expected to give scattering maxima around 12 Å, 4.8–4.9 Å, 3.2–3.5 Å and 2.0–2.1 Å. The first three are in accordance with the observed results. The 4.8–4.9 Å line is sharp and constant from one specimen to another, while the 12 Å and 3.2–3.5 Å lines are broad, and variable (c.f. Figs. 1*a* and *b*).

Méring (1951) has discussed theoretically how partial order in a sequence of layers influences the diffraction effects. Partial order may occur as a tendency towards either segregation of the two components, or their regular alternation. Both tendencies have been observed with stevensite. Some specimens (see Fig. 1*b*) show the 11–12 Å line spreading outwards towards 10 and 14 Å and the 3.2–3.5 Å line almost splitting into two separate components with continuous scattering between them. This represents a tendency towards segregation of the components. More commonly there is no splitting of the 11–12 Å line nor of the 3.3 Å line which remains very broad. This, together with the occurrence of the 24–25 Å line, represents a tendency towards alternation of the two components (see Fig. 1*a*); the long spacing is shown only in spectrometer records).

It appears that stevensite is a rather variable material and contains layers of two kinds which show a tendency in some fragments to segregate, and in others to give a partial alternation. The question which has

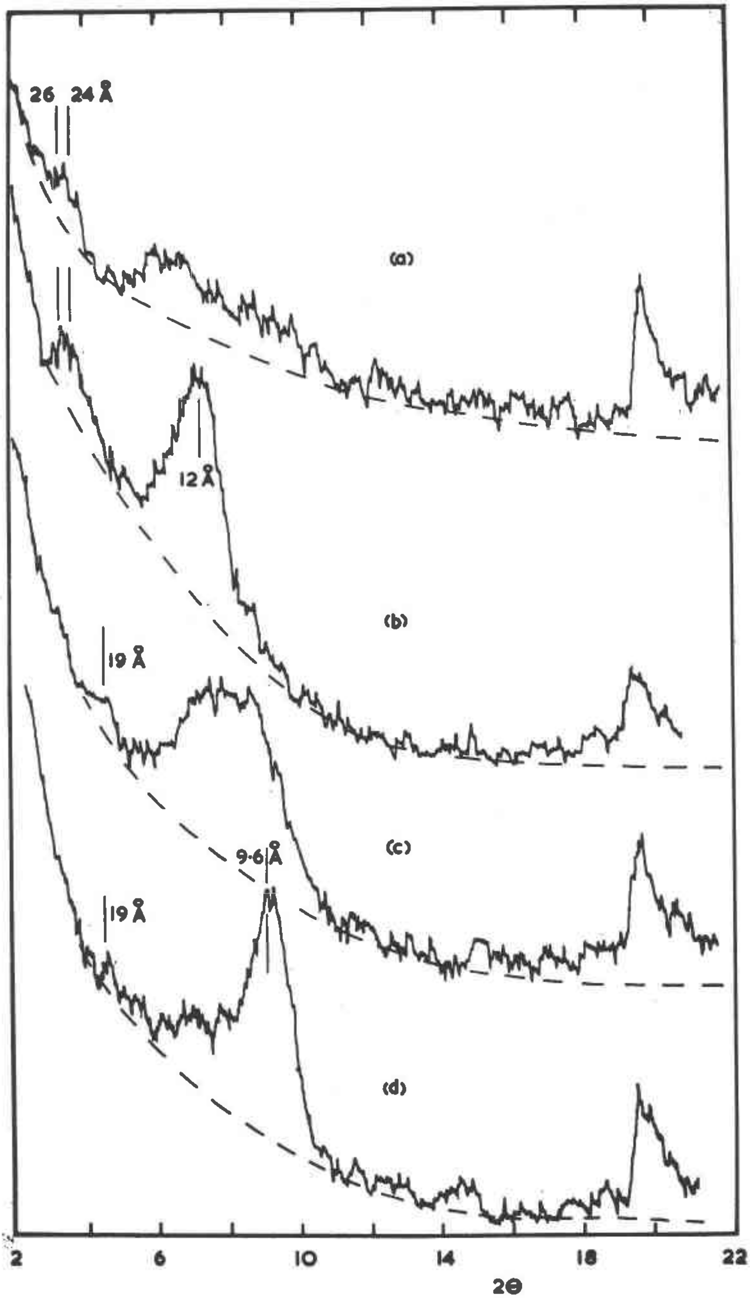

FIG. 2. Geiger counter spectrometer records for stevensite. (*a*) Water-wet material. (*b*) Air-dry material oriented on glass slide. (*c*) Air-dry material heated for 1 hr. at 105° C. and immediately *x*-rayed. (*d*) Material heated for 3 days at 400° C.

to be considered is whether the two kinds of layers are basically different, or whether they arise from a largely fortuitous difference in degree of hydration of the layers. Information bearing on this question may be obtained by studying the hydration and dehydration of the mineral and its organic complexes.

(a) *Hydration tests:* A specimen kept in water for 3 days and *x*-rayed in a moist condition with a counter spectrometer gave continuous scattering from 14–7.5 Å and clear evidence of a long spacing at about 25 Å (see Fig. 2*a*). Similar data were obtained with other water-wet specimens and there was no indication that wetting the mineral produced a more uniformly hydrated system.

(*b*) *Dehydration tests:* Low temperature heat-treatment up to 400° C. produced a collapse of the basal spacing to about 9.6 Å and the following reflections were observed: 9.6 Å, medium-strong and clearly defined, but with intensity spreading towards longer spacings (see Fig. 2*d*); 4.8 Å, weak and not fully resolved from the 4.5 Å band; 3.18 Å, medium-strong and clearly defined; 1.92 and 1.22 Å, both weak and broad. These reflections correspond to the orders 1, 2, 3, 5 and 8 from a basal spacing of 9.6 ± 0.1 Å. Traces of a long spacing of about 19 Å are found (see Figs. 2*c* and *d*) but the evidence is uncertain. It is clear that the 14–15 Å layers collapse in a similar manner to hydrated montmorillonite layers, and a more regular structure is produced. Any differences now remaining between the layers are too small to be detected with any degree of certainty.

Since montmorillonite-organic complexes normally give a well-ordered sequence of basal reflections, numerous attempts were made to expand the stevensite layers in a similar way. The results are described in the following section.

ORGANIC COMPLEXES OF STEVENSITE

The swelling of stevensite in a number of organic liquids, mainly dihydric alcohols, has been investigated with a Geiger counter spectrometer which easily records spacings to 30 Å. Oriented layers obtained by sedimentation and randomly oriented specimens have been used. The results of many tests show that the number, sharpness and regularity of the reflections are much inferior to those obtained with montmorillonite-organic complexes. A first order reflection at about 17–18 Å spacing is usually the only clearly defined basal reflection. A weak second order at about 8.5–9.5 Å often appears. Higher orders are weak and diffuse and cannot be reliably correlated with a particular basal spacing. Evidence is obtained occasionally of a longer spacing and one complex with glycerol showed a clearly defined spacing of 26 Å, but higher orders could not be detected.

TABLE 2. "FIRST" ORDER SPACINGS OF ORGANIC LIQUID COMPLEXES WITH STEVENSITE

Organic Complex	d (Å)
ethylene glycol	17.0
1.3 propane diol	18.2
1.4 butane diol	17.3
1.5 pentane diol	18.0
1.12 polyethylene diol	17.3
ethylene glycol mono-butyl ether	13.8
diethylene glycol	16.7
glycerol	17.7

The available evidence points to an irregular layer sequence of spacings of about 17 and 10 Å. The curves calculated by Brown and MacEwan (1951) for such a sequence having a predominance of 17 Å layers show a "first" order at about 17 Å or a little higher spacing, a "second" order at about 9 Å together with higher orders which cannot be reliably identified in the spectrometer traces.

The poorly developed sequence of basal reflections and the occasional appearance of a long spacing in the region of 26 Å constitute the main evidence for a mixed-layer structure from the organic complexes.

Table 2 records the "first" order spacings observed for a number of stevensite-organic complexes. The smaller expansion to 15 Å found by Faust and Murata is not confirmed.

ELECTRON MICROGRAPHS

Electron micrographs of stevensite are reproduced in Figs. 1*c* and 1*d*. The mineral was crushed and lightly ground in a mortar, dispersed in water and allowed to sediment; fine fractions about 1μ and 0.1μ in size on collodion films were examined before and after platinum shadowing. The appearance of the mineral is closely similar to that of many montmorillonites. The finest fraction, Fig. 1*d*, shows very thin plates with irregular outline. The 1μ fraction, (Fig. 1*c*), consists largely of irregular aggregates, the edges of which appear to show curled fragments.

DISCUSSION

The diffraction data confirm and extend those given by Faust and Murata. The mineral is of the expanding layer type and has a *b* parameter of 9.12 Å which is in accordance with its trioctahedral composition (c.f. talc, $b=9.10$; hectorite, $b=9.16$, vermiculite, $b=9.18$–9.20).

The long spacing of about 24–25 Å from air-dry material and about

26 Å from organic complexes are consistent with an interlayering of 9.5–10 and 14–15 Å layers in the air-dry material and 9.5–10 and 17–18 Å layers in the organic complexes. Low temperature heat-treatment gives a basal spacing of about 9.6 Å which results from a collapse of the 14 Å layers. It appears that the mineral is composed of two kinds of layers, of which one is capable of expanding and collapsing like the layers in montmorillonite, and the other appears to remain stable at about 9.5–10 Å.

The question arises whether the presence of these two kinds of layers can be correlated with the low cation-exchange capacity reported by Faust and Murata. If the exchangeable cations are associated with only the swelling part of the mineral then the exchange capacity of the swelling part is correspondingly greater. It is not justifiable to claim this as support for the mixed-layer hypothesis since there is no a priori reason why the exchange capacity should not be as small as the value which is reported. The differential thermal analyses given by Faust and Murata provide no direct indication of the presence of two kinds of layers, but it may be significant that, in their comparison of stevensite with the magnesian montmorillonite, saponite, they find the low temperature endotherm associated with the removal of interlayer water is only about half as large for stevensite as for saponite, the weights of the samples being very similar. This result is consistent with there being fewer hydrated layers in stevensite, but this evidence must be accepted cautiously since the hydration of montmorillonite-type minerals depends considerably on the humidity of the atmosphere and the nature of the exchange cations.

The hypothesis that stevensite consists of swelling and non-swelling or hydrated and non-hydrated layers may be linked with the suggestion, discussed by Faust and Murata, that it "might be a hydrated form of talc." Now talc itself has a basal spacing of about 9.4 Å. Stevensite, when dehydrated, gives a spacing of 9.6 ± 0.1 Å, which could be interpreted as an average of 9.4 Å and a value suitably larger than 9.6 Å depending on the proportions of the two components. The basal spacings of air-dry stevensite may also be interpreted in terms of talc-like layers of spacing 9.4 Å and hydrated layers with a spacing of 14–15 Å. The chemical analyses of stevensite given by Faust and Murata show very little K_2O and the CaO, also small, is largely exchangeable. There is no chemical evidence, therefore, to suggest that the non-swelling layers are mica-like with a spacing of about 10 Å.

The combined evidence of the present work and that of Faust and Murata is that stevensite consists of talc-like layers, some of which (like those in normal talc) do not swell in water and in organic liquids, and others (due to an octahedral ion deficiency as pointed out by Faust and Murata) have exchangeable cations and swell like montmorillonite (or saponite) layers. Since Mg occupies most of the octahedral positions, it seems reasonable to describe the mineral as a talc-saponite interlayered mineral; this comes close to the earlier description of it as a hydrated talc.

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