

Saponite from Allt Ribhein, Fiskavaig Bay, Skye.

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Summary. This saponite, which is closely associated with zeolites such as stilbite, heulandite, thomsonite, and gonnardite, occurs in vesicles in basalt. It has the composition: $1.02M^+ (\text{Mg}_{3.54}\text{Mn}_{0.01}\text{Al}_{0.03}\text{Fe}_{0.08}) (\text{Si}_{14.95}\text{Al}_{1.01})\text{O}_{20}(\text{OH})_4$, according to a new method for calculating the ionic formulae of smectites: this method also enables determination of the temperature at which all sorbed moisture is removed—in this instance about 800° C. The exchangeable cations are largely Ca^{2+} . The chemical, thermal, and X-ray data are discussed with reference to other saponite samples. Electron-microscope examination showed a tendency to elongation in the direction of the *a*-axis. It is concluded that the saponite is of excellent purity and free from interstratification.

A VEIN of very pale blue, almost white, saponite was exposed during excavation of a water dam in Skye: this vein was said to be 5 to 6 feet long, about 1 foot deep, and up to 2 inches thick. Since the site is now covered with concrete, no more bulk material is available; however, some small pieces have recently been recovered from the spoil heap by Mr. R. H. S. Robertson.

The locality of the vein is on the small stream Allt Ribhein (map reference on the Ordnance Survey Popular Edition 1 inch map, sheet 34, 635545), which flows into Fiskavaig Bay, on the south side of Loch Bracadale. It is in an area of Skye where the lavas are notoriously vesicular. In the immediate neighbourhood of the dam the lava is cut not only by a sill, but also by a dyke. Some of the rock excavated was in an advanced state of decay, but this process of deep-weathering does not seem to account for the saponite.

The vesicles in the lava are often as much as 2 cm. in diameter. They may be filled with white zeolites (stilbite, heulandite, and thomsonite have been identified at this locality) or with saponite, or they may have an inner core of saponite surrounded by a rim of zeolite, which in two samples examined was largely gonnardite. From the evidence available it appears that the saponite was formed *after* and in a manner exactly similar to the more common zeolitic infillings. The contents of the amygdules have obviously been carried into the cavities dissolved in

water, which may itself have been of volcanic origin (see Harker and Clough, 1904).

Optical data. The saponite occurs in fan-shaped aggregates (fig. 1) rather similar to those described by Konta and Šindelář for the saponite from Čáslav. The optical data together with those for some other recently-described saponite samples are given in table I. The γ value is

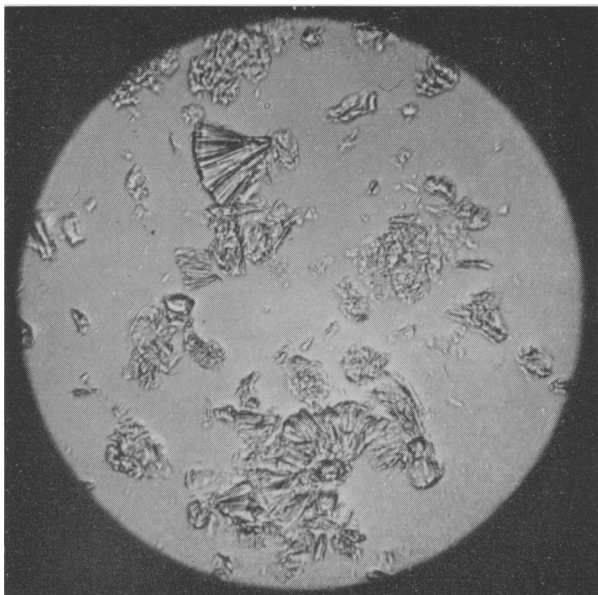


FIG. 1. Photomicrograph of saponite, Allt Ribhein, Skye.

somewhat higher than those quoted by Winchell (1951) for several low-iron saponites, but is similar to that for the Čáslav sample which has a fairly high iron content; values may, however, vary with the water content and with the exchangeable cation. The γ -index is parallel to the direction of elongation and the α is perpendicular to the principal cleavage plane. From electron-microscope data α corresponds to the direction of the c -axis, β to the b -axis, and γ to the a -axis.

Chemical data. The chemical analysis of a Ca-saturated sample is compared with some published analyses in table I. The two Skye samples are very similar in composition. The cation-exchange capacity of the Allt Ribhein material is 109 m.e. per 100 g., the exchangeable cations in the natural sample being about 92% Ca^{2+} and 8% Mg^{2+} . Several

analyses given by Heddle (1879, see Harker and Clough, 1904) appear, from their high CaO content, also to refer to essentially Ca-saturated material, but it is doubtful whether the Quirang sample was pure as the CaO content is considerably higher than would be expected for a sample of normal cation-exchange capacity and the Na₂O content is also high:

TABLE I. Chemical analyses and optical data for saponite.

	1.	2.	3.	4.	5.	6.
SiO ₂ ...	43.62	42.50	53.88	50.01	54.74*	40.46
TiO ₂ ...	0.00	—	0.25	< 0.04	—	—
Al ₂ O ₃ ...	5.50	5.06	4.47	3.89	8.93*	10.15
Fe ₂ O ₃ ...	0.66	0.85	0.60	0.21	0.43*	3.56
FeO ...	—	—	—	—	—	4.89
CaO ...	2.85	3.27	—	1.31	2.65*	1.94
MgO ...	24.32	23.95	31.61	25.61	33.28*	20.71
MnO ...	0.06	0.22	—	—	—	0.24
Na ₂ O ...	0.08	0.45	0.01	—	—	0.25
K ₂ O ...	0.04	0.17	0.05	—	—	0.32
H ₂ O—105° C.	—	15.52	} 9.28 {	7.28	—	13.33†
H ₂ O—300° C.	17.42	—		—	14.09	—
H ₂ O+	5.48	8.16		12.02	5.01	4.24
Σ ...	100.03	100.15	100.15	100.37	—	100.23‡
α ...	1.490	—	—	1.511	—	1.513
β ...	1.531	—	1.486 to 1.493	—	—	—
γ ...	1.534	—	—	1.514	1.498	1.536
γ—α ...	0.044	—	—	0.003	0.004 to 0.007	0.023

1. Allt Ribhein, Skye. (Anal. J. B. Craig).

2. Quirang, Skye (Heddle, 1879).

3. Krugersdorp, Transvaal (Schmidt and Heystek, 1953).

4. Milford, Utah, U.S.A. (Cahoon, 1954).

5. Groeschlattengrün, Germany (Weiss, Koch, and Hofmann, 1955).

6. Čáslav, Czechoslovakia (Konta and Šindelář, 1955).

* Determined on ignited weight.

† 160° C. ‡ Includes P₂O₅ 0.14.

it may, therefore, have been contaminated with zeolites. The preponderance of exchangeable Ca²⁺ is paralleled in the zeolitic infillings, which usually consist of lime or soda-lime zeolites with lime as the principal base (Harker and Clough, 1904).

The usual method of calculating the smectite structural formula is that of Ross and Hendricks (1945), based upon the assumption that each structural unit contains 20 oxygen and 4 hydroxyl ions giving it a total negative valency of 44. No account is taken of the measured H₂O+ content. On this basis the saponites for which analyses were quoted in table I have the formulae indicated in table II (a).

An alternative method of calculation of the structural formula using the measured H_2O+ content may be derived by modifying the calculation of Brown and Norrish (1952) for the hydrous micas. If one assumes the oxygen and water contents obtained by analysis to be divided up according to the proportions $20 O^{2-}:4 OH^-:x H_2O$, where xH_2O is the

TABLE II. Ionic formulae for saponites (reference nos. see table I).

(a) By the method of Ross and Hendricks (1945).

	1.	2.	3.	4.	5.	6.
M^+ ...	1.02	1.48	0.83	0.42	1.22	1.08
Mg ...	5.82	5.87	5.96	5.74	5.90	4.70
Fe^{3+} ...	—	—	—	—	—	0.64
Mn ...	0.01	—	—	—	—	0.02
Al ...	0.04	0.03	—	0.12	0.06	0.22
Fe^{3+} ...	0.08	0.10	0.02	0.02	0.04	0.42
Ti ...	—	—	0.02	—	—	—
Si ...	7.00	7.02	7.24	7.48	6.26	6.34
Al ...	1.00	0.98	0.72	0.52	1.24	1.66
Fe ...	—	—	0.04	—	—	—
O ...	20	20	20	20	20	20
OH ...	4	4	4	4	4	4

(b) By new method.

	1.	2.	3.	4.	5.	6.
M^+ ...	1.02	1.35	0.75	0.42	1.18	1.09
Mg ...	5.84	5.86	5.98	5.75	5.91	4.72
Fe^{2+} ...	—	—	—	—	—	0.64
Mn ...	0.01	0.03	—	—	—	0.03
Al ...	0.03	—	—	0.17	0.05	0.19
Fe^{3+} ...	0.08	—	—	0.03	0.04	0.42
Ti ...	—	—	0.02	—	—	—
Si ...	6.99	6.92	7.22	7.49	6.75	6.32
Al ...	1.01	0.97	0.71	0.51	1.25	1.68
Fe ...	—	0.11	0.07	—	—	—
O ...	20	20	20	20	20	20
OH ...	4	4	4	4	4	4

excess sorbed moisture not removed at 105° C. (or any other temperature that may be chosen), one can derive the equations:

$$n[O^{2-}] = 20 + 4 + x \tag{1}$$

and
$$n[H^+] = 4 + 2x, \tag{2}$$

where n is the factor by which the ionic proportions of oxygen, $[O^{2-}]$, and hydrogen, $[H^+]$, obtained from the analysis must be multiplied to obtain the final formula. Combination of equations (1) and (2) gives:

$$2n[O^{2-}] - n[H^+] = 44. \tag{3}$$

Using the values of n calculated from equation (3), the formulae in table II (b) are obtained for the saponite samples previously referred to.

The Quirang and the Krugersdorp samples appear to require tetrahedral substitution of Fe^{3+} . However, since both appear to be virtually true saponite end-members, any slight errors in analysis would be magnified; in addition, the Quirang sample, as previously mentioned, was probably impure. For the Krugersdorp saponite both methods of calculation require a small amount of tetrahedral Fe^{3+} , the charge balance on the new basis is satisfactory, and the calculated cation-exchange capacity of 96 m.e. per 100 g. agrees with the measured value of 100 m.e. per 100 g. (Schmidt and Heystek, 1953). Thus, it may be that the very small octahedral Fe^{3+} content is true (cf. cronstedtite, which is believed to have considerable tetrahedral Fe^{3+}). In general the formulae obtained by the two methods differ only in detail.

In addition to giving the structural formula, however, this new method enables one to measure the amount of excess hygroscopic moisture in the $\text{H}_2\text{O}+$ content. Thus, from equation (1):

$$x = n[\text{O}^{2-}] - 24$$

and

$$x/n \times 18 = \% \text{ excess moisture.}$$

For the Allt Ribhein sample the excess hygroscopic moisture in the $\text{H}_2\text{O}+$ figure is 1.74 %; thus, from the dehydration curve (fig. 3), the sorbed water would appear not to be completely removed below about 800° C. This is in agreement with experiment, since the material heated to 750° C. rehydrates quite rapidly on exposure to the atmosphere. A similar calculation for the Čáslav sample indicates a temperature of about 600–700° C. for complete removal of sorbed water.

This method of calculation has interesting possibilities for smectites, since it should enable reasonably accurate determination of the total sorbed water content, which is not readily measured experimentally. Only by applying it to analyses of pure samples can it be checked, and for several known to the author it appears to give satisfactory results. Many of the published analyses for smectites are, unfortunately, for impure material from which little information of value can be derived.

X-ray and thermal data. The X-ray diffraction patterns were typical of a trioctahedral smectite, but contamination with a very small quantity of coarse-grained zeolite was noted. The differential thermal curve is compared with those for some other saponites in fig. 2. It will be noted that the curves fall into two distinct groups depending upon the presence or absence of the peak at about 600° C. Weiss, Koch, and Hofmann (1955) attribute this peak to the dehydroxylation reaction and the final endothermic peak to the crystallization of enstatite from 'anhydro-

saponite', but their interpretation is based upon X-ray results for material heated to above 700° C. for some 200 hours, a period much too long to give valid comparison with the differential thermal curve. Both the Allt

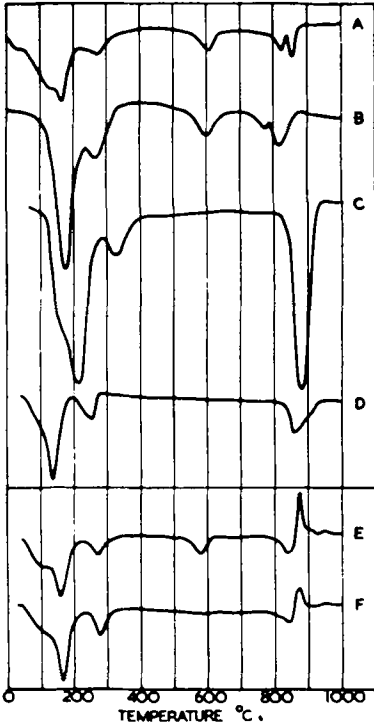


FIG. 2. Differential thermal curves for saponites (*A*—Cornwall, England; *B*—Groschlattengrün, Germany, after Weiss, Koch, and Hofmann, 1955; *C*—Krugersdorp, Transvaal, after Schmidt and Heystek, 1953; *D*—Allt Ribhein, Skye) and vermiculites (*E*—Kenya; *F*—West Chester, Pennsylvania, U.S.A.).

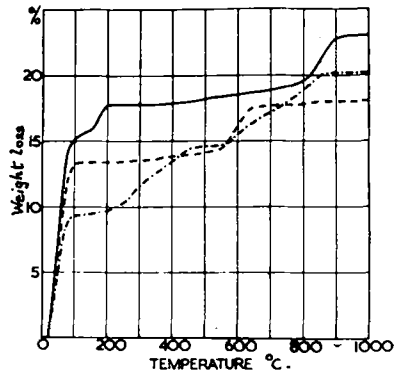


FIG. 3. Dehydration curves for saponite, Allt Ribhein, Skye (—); montmorillonite, Wyoming, U.S.A. (---); vermiculite, West Chester, Pennsylvania, U.S.A. (-·-·-).

Ribhein material and the Cornwall sample when heated to 700° C. in the differential thermal apparatus give the X-ray pattern of talc: dehydroxylation does not therefore occur until about 800–900° C., and the final peak must represent this reaction. Crystallization to enstatite probably occurs simultaneously. This mechanism is confirmed by the dehydration curve in fig. 3.

Comparison of the saponite dehydration curve with those for montmorillonite and vermiculite (fig. 3) shows that dehydroxylation occurs at a higher temperature than that of montmorillonite, and that the curve shows much sharper breaks between the various phases of water loss than that for vermiculite.

It seems, therefore, that the attribution of the 600° C. peak remains to be explained. Cole and Hosking (1957), after considering the structural similarity of saponite, vermiculite, and chlorite, suggest that saponite and chlorite may, like vermiculite and chlorite, form random intergrowths that are difficult to detect by X-ray examination, but are readily detected by differential thermal analysis. They attribute the 600° C. peak, therefore, to interleaved chlorite. It would not require many interleaved brucite layers to give rise to a chlorite peak of the size observed on curves *A* and *B*—cf. the effect of interleaved brucite layers on the vermiculite curve (curves *E* and *F*, fig. 2). X-ray examination of the Cornish material showed a very small amount of kaolinite contamination, but this does not seem sufficient to give a peak of the magnitude observed. The doubling of the final peak supports the suggestion of Cole and Hosking (1957), since magnesian chlorites give a strong exothermic peak in the 800° C. region and this superposed on a single endothermic peak would give an impression of doubling. Pronounced doubling is only observed with samples giving the 600° C. peak.

It seems highly probable, therefore, that the Cornwall and Groschlattengrün 'saponites' are in reality interstratified chloritic-saponites, and the Allt Ribhein and Krugersdorp (as well as the Čáslav) samples are true saponites. The initial part of all these curves is, of course, a function of the exchangeable ion and pretreatment: the slight doubling of the second peak on curve *D*, fig. 2, may be due to the small amount of magnesium present (Mg-saturated material gives a peak at about 275° C. and Ca-saturated at about 260° C.).

Electron-microscope data. Electron-microscope examination showed the saponite to be platy with a notable tendency to elongation (figs. 4, 5*a*), some thin crystals being apparently folded over at right angles in the manner observed by Cahoon (1954) for the Milford material (fig. 4). Single crystal electron-diffraction patterns (fig. 5*b*) showed the elongation to occur uniformly in the direction of the *a*-axis, and gave the cell-dimensions $a = 5.3 \text{ \AA}$., $b = 9.2 \text{ \AA}$. This value for the *b*-axis compares well with the value of 9.21 \AA . calculated theoretically from the composition by the formula of Brindley and MacEwan (1953).

Conclusion. The Allt Ribhein material would thus appear to be a

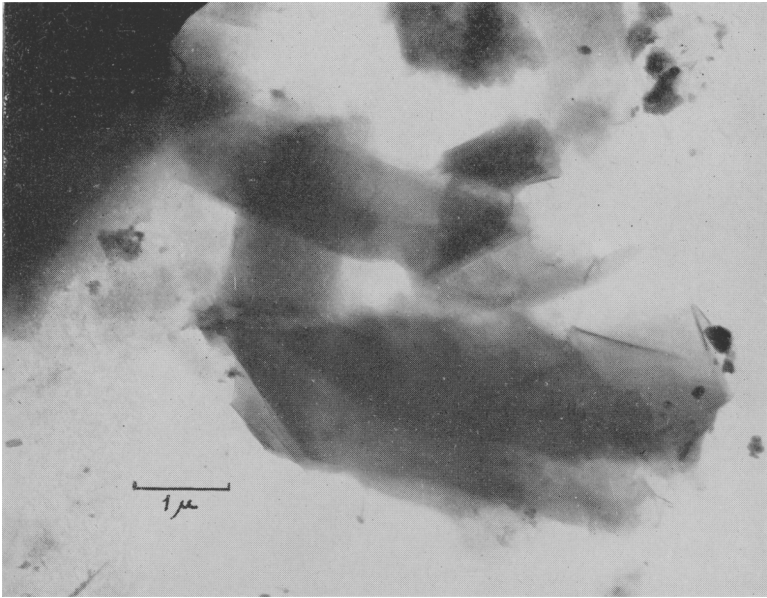


FIG. 4. Electron micrograph of saponite, Allt Ribhein, Skye.

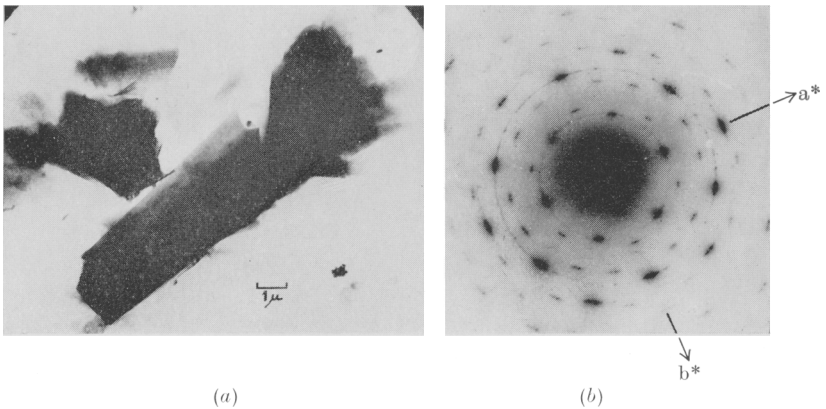


FIG. 5. Electron micrograph (a) and electron-diffraction pattern (b) of saponite, Allt Ribhein, Skye. Same crystal in same orientation used for both photographs.

good saponite of low iron content and free from interstratification; it occurs in platelets elongated along the a -axis. It is probable that the material from Quirang described by Heddle was similar.

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