

A saponite from Krugersdorp district, Transvaal.

By E. R. SCHMIDT,

Geological Survey, Mines Department, Union of South Africa,

and H. HEYSTEK,

National Chemical Research Laboratory, South African Council
for Scientific and Industrial Research.

[Communicated by the General Secretary; taken as read June 11, 1953.]

I. INTRODUCTION.

AVAILABLE information on the clay mineral saponite shows an amazing degree of variation and considerable discrepancies, probably due to investigation of impure samples. The clay mineral described in this paper was essentially pure and furthermore it seems to represent a magnesium end-member of the montmorillonite group.

Optical, chemical, X-ray, and differential thermal data of this particular saponite are presented, as well as data on some associated minerals, namely, a chlorite, two antigorites, and a chrysotile-asbestos.

The influence of Mg^{++} , as the only natural occurring exchangeable base, on the nature of the X-ray diffraction and differential thermal diagrams leads to some interesting observations.

II. OCCURRENCE.

The white clay mineral identified as saponite occurs in a chrysotile-asbestos mine, on the farm Honingklip 72, Krugersdorp district. The mineral was found in the form of a vein in a fracture zone in rocks which probably belong to the Jamestown complex. These rocks are usually represented by massive serpentines and amphibolites. The rock immediately underlying the clay is an amphibolite containing numerous chloritoid needles. Overlying the clay is a rock consisting of chlorite and amphibole, which grades into material rich in zoisite.

In hand-specimens it can be seen that the soft, white clay passes into the hard chlorite-amphibole-rock through an intermediate stage of soft, greyish material consisting of chlorite and saponite.

The thickness of the vein varies from a fraction of an inch to about 6 inches, and in places it pinches out completely. The occurrence is extremely limited and the clay is therefore of no economic value.

III. DESCRIPTION AND OPTICAL DATA.

Samples of the clay and associated rocks were collected at the mine, as well as two samples of antigorite and a sample of the chrysotile-asbestos. Their optical properties are shown in table I.

TABLE I. Optic data.

Sample.	Optic sign.	α' .	Refractive indices ± 0.005 .	
			β .	γ .
Saponite	—	—	1.486–1.493	—
Antigorite, no. 1	—	1.55	—	1.555–1.565
Antigorite, no. 2	—	—	—	1.561
Chrysotile-asbestos	—	—	—	1.554
Chlorite	Positive	—	1.591	—

The clay varied in colour from nearly pure white to a brownish off-white, and had a soapy feel. The mean refractive indices of different samples of the clay varied from 1.486 to 1.493 (± 0.005). An electron microscope investigation of the clay showed the individual particles to be flat and flake-shaped with ill-defined edges.

Three serpentine samples chosen for investigation may be described as follows:

Antigorite, no. 1: Massive green antigorite consisting of flat flake-like particles.

Antigorite, no. 2: Bluish-green sample, harder than no. 1, consisting of long needle-like crystals compacted together. An electron micrograph indicated that this consisted of fibrous particles and, according to Selfridge (1), this should strictly be classified as chrysotile.

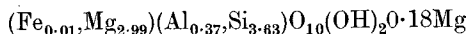
Chrysotile-asbestos: A typical sample.

The purified chlorite associated with the clay mineral saponite appeared as colourless particles under the petrographical microscope.

IV. CHEMICAL ANALYSIS.

From the chemical analyses of the chrysotile-asbestos and the antigorites listed in table II, it is apparent that there are no significant differences in the composition of the two structures, in agreement with the studies by Selfridge (1).

The analysis of saponite refers to the material dried at 110° C. From the analysis, the following formula is derived.



in which the 0.18 Mg represents exchangeable cations, consisting

almost wholly of Mg. The base-exchange capacity according to this is 89 milliequivalents per 100 g. of clay dried at 110° C.

Using the ammonium-acetate Kjeldahl distillation method of base-exchange determination, a base-exchange value of 100 m.e. NaOH per 100 g. clay dried at 110° C. was found for the saponite. In the extract, Mg⁺⁺ was the only exchangeable cation found to be present, and analysis gave a value of 2.03 % MgO based on the clay sample or 101 m.e. per 100 g. Bearing in mind possible errors in both the chemical analysis and the base-exchange analysis, the agreement between 89 and 100 must be regarded as good substantiation for the structural formula given above.

A comparison with other saponite samples quoted in the literature (2, 3) indicates that the present saponite is closer to the magnesium end-member of the montmorillonite group than any previously reported. The nearest is a saponite from Montreal, Canada, given as no. 77 in the paper of Ross and Hendricks (2).

A chemical analysis of the chlorite found closely associated with the saponite is also listed in table II.

TABLE II. Chemical analyses. (Analyst: D. Sampson.)

	Saponite	Chlorite.	Chrysotile- asbestos.	Antigorite no. 1.	Antigorite no. 2.
SiO ₂ ...	53.88	29.69	43.09	43.65	44.53
TiO ₂ ...	0.25	0.14	0.26	0.23	0.23
Al ₂ O ₃ ...	4.47	20.93	0.64	0.83	0.78
Fe ₂ O ₃ ...	0.60	10.26	1.14	2.47	1.01
MgO ...	31.61	27.13	40.90	39.52	41.13
CaO ...	—	—	—	—	—
Na ₂ O ...	0.01	0.03	0.04	0.04	0.04
K ₂ O ...	0.05	0.04	0.07	0.03	0.03
ign. loss ...	9.28	11.74	13.62	13.31	12.53
	<u>100.15</u>	<u>99.96</u>	<u>99.76</u>	<u>100.08</u>	<u>100.28</u>

V. X-RAY DIFFRACTION DATA.

X-ray powder diffraction patterns were obtained with a Philips high-angle spectrometer goniometer, type 42201/2, with Co-K α radiation (λ 1.78890 Å.) and an automatically recording Brown electronic strip-chart potentiometer. The X-ray patterns aided in identifying the minerals in the mixtures giving compound differential thermal curves (fig. 3) and in all cases substantiated the differential thermal curve findings.

In table III the *d* values and intensities of the saponite clay are

listed. The sample on which work in this paper is reported was exceptionally free from contaminating minerals. This was established by selecting a long series of samples from the seam and examining them by X-ray diffraction. The possible contaminants were serpentine and

TABLE III. X-ray data.

Saponite.		Chlorite.		Chrysotile- asbestos.		Antigorite no. 1.		Antigorite no. 2	
<i>d.</i>	Int.	<i>d.</i>	Int.	<i>d.</i>	Int.	<i>d.</i>	Int.	<i>d.</i>	Int.
14.65	vs	14.01	s	—	—	—	—	—	—
—	—	7.05	vvs	7.33	vs	7.29	vs	7.23	vs
—	—	—	—	—	—	—	—	5.25	w
4.87*	m	4.70	vs	—	—	—	—	4.71	w
4.56	s	—	—	—	—	4.54	m	—	—
—	—	—	—	4.46	s	—	—	—	—
—	—	—	—	4.03	m	—	—	3.99	mw
3.63*	m	—	—	3.64	vs	3.63	s	3.61	s
—	—	3.53	vs	—	—	—	—	—	—
—	—	—	—	—	—	—	—	3.33	w
2.94*	s	—	—	—	—	—	—	—	—
—	—	2.82	s	—	—	—	—	—	—
2.627	m	—	—	—	—	—	—	—	—
2.554	s	2.57	w	—	—	—	—	—	—
2.485		2.54		—	—	—	—	—	—
—	—	—	—	—	—	2.504	m	2.54	m
—	—	2.440	w	2.435	m	2.438	w	2.418	mw
—	—	2.362	w	—	—	—	—	—	—
—	—	2.252	w	—	—	—	—	—	—
—	—	—	—	—	—	2.148	w	2.161	w
2.081	w	2.025	s	—	—	—	—	—	—
—	—	1.881	vw	—	—	—	—	—	—
—	—	1.823	w	1.829	w	—	—	1.816	w
1.731	w	—	—	—	—	—	—	—	—
1.689	w	—	—	—	—	—	—	—	—
—	—	1.660	w	—	—	—	—	—	—
—	—	1.566	m	—	—	—	—	—	—
1.530	s	1.538	w	1.535	s	1.540	m	1.559	w
—	—	—	—	—	—	1.506	w	—	—
—	—	1.417	m	1.462	w	—	—	—	—
1.321	w	1.393	m	—	—	—	—	—	—
1.271	w	1.287	w	—	—	—	—	—	—

* Values apparently related to the fact that the saponite contains only Mg^{++} as the exchangeable base.

chlorite, pure samples of which were also available, so that the clay samples could be selected which gave X-ray diagrams completely free from peaks due to these minerals. The data for associated chlorites and serpentine minerals are also quoted in table III.

In the literature, X-ray data for saponites are not very reliable, the most quoted data (4, 5) being those of Kerr where the spacings vary

from those found by the authors (table IV), while the data listed by Midgley (6) appear to have been obtained on a saponite containing talc as an impurity, as distinctive talc peaks are listed. As the present saponite is of an extreme type and of high purity, the data in table III should prove useful for future identification.

TABLE IV. Comparison of X-ray data for saponite.

Saponite.		Saponite heated to 600° C.		Saponite heated and rehydrated.		Saponite, Kerr* (1937).	
<i>d.</i>	Int.	<i>d.</i>	Int.	<i>d.</i>	Int.	<i>d.</i>	Int.
14.65	vs	—	—	14.65	s	--	—
—	----	9.59	vs	9.59	m	—	—
4.87†	m	—	—	—	—	—	—
4.56	s	4.56	s	4.57	s	4.51	s
—	—	—	—	—	—	4.06	m
3.63†	m	—	—	—	—	—	—
—	—	3.16	s	3.15	s	—	—
—	—	—	—	—	—	3.01	m
2.94†	s	—	—	—	—	—	—
2.627	m	—	—	2.627	} m	—	—
2.554	} s	2.602	} m	2.615		2.54	s
2.485		2.495		2.45	w		
2.081	w	--	—	—	—	—	—
1.731	w	--	—	1.726	w	1.74	m
1.689	w	—	—	1.687	w	—	—
1.530	s	1.529	m	1.529	m	1.52	s
1.321	w	—	—	—	—	1.32	m
1.271	w	—	—	—	—	1.29	m

* Amer. Min., 1937, vol. 22, p. 541. [M.A. 7-99.]

† Values apparently related to the fact that the saponite contains only Mg⁺⁺ as the exchangeable base.

The basal spacing of 14.65 Å. shifted to 16.49 on treating the clay with ethylene glycol, proving that this clay should be placed within the montmorillonite group, while the (060) spacing of 1.53 Å. indicates a trioctahedral montmorillonite. On being heated at 450° C. for three hours the basal peak moved down to 9.59 Å. and the general X-ray pattern became that of talc (table IV). When the heated sample was again left in moist air for a few days, rehydration occurred and resulted in the basal peak moving up to 14.65 Å. There was not, however, a complete return to the original X-ray diffraction diagram (see table IV) as peaks at 4.87, 3.63, and 2.94 did not return, while that at 3.16 remained unchanged. As noted later, a small peak on the differential thermal diagram also failed to reappear. These observations opened up the possibility that an impurity was present, which was responsible

for the above peaks, but which decomposed irreversibly on dehydration. In order to test this point, exchangeable Mg^{++} was completely replaced by NH_4^+ and by Na^+ . The peaks at 4.87, 3.63, and 2.94 disappeared in both samples. Furthermore, on reconverting the NH_4 -saponite back to a Mg -saponite, the peaks returned. It is clear, therefore, that these peaks are not due to an impurity, but to presence of exchangeable Mg^{++} ions in unheated saponite. Heating apparently produces an irreversible change in structure in that these reflections peculiar to presence of Mg^{++} ions no longer appear. The problem is an interesting one, and further work is being carried out, which it is hoped to report in a later paper.

At lower temperatures the change to the talc pattern could not be made to take place, but samples heated to 600° C. and 700° C. for two hours each showed similar behaviour to that heated at 450° C., though rehydration was somewhat slower. At 780° C. for two hours, the talc pattern was produced again, but only slight signs of rehydration in moist air were apparent. It appears that the reactivity of the 'talc' formed from saponite decreases as the temperature of its formation increases.

On comparing the X-ray data of the chrysotile-asbestos with those of the antigorites no. 1 and no. 2, it can be seen that there is some resemblance but not complete agreement. The d values of antigorite no. 2 seem to lie between that of the asbestos and the antigorite no. 1. This is consistent with the needle-like or partly fibrous nature of the antigorite no. 2.

VI. DIFFERENTIAL THERMAL ANALYSIS.

The differential thermal apparatus at the Mineralogical Laboratory, Geological Survey, used for this investigation consisted of:

(1) A horizontal alundum muffle-tube furnace wound with Kanthal A wire, similar in construction to the one described fully by Gruver (7).

(2) A Variac (type V-20 HM) continuously adjustable transformer used as the manual power control of the heating rate of the furnace (15° C. per minute in all curves given).

(3) A Cambridge spot-light galvanometer (30 mm. per microamp. sensitivity) for measurement of the e.m.f. from the differential thermocouple.

(4) In addition to the 50 ohms resistance of the galvanometer, an external resistance of 150 ohms was used in the circuit in the case of all

the differential thermal curves, except that of saponite where 50 ohms was used.

(5) A nickel block sample holder.

(6) A temperature thermocouple and a differential thermocouple, both made of Pt-Pt 13 % Rh wire, 0.3 mm. in diameter.

Differential thermal analysis curves for each of the samples are shown in figs. 1-3. The differential thermal curve for the chlorite (fig. 1) found in association with the clay mineral is typical (5) with two strong endothermic peaks at 690° and 840° C. respectively.

As also in the case of X-ray diffraction, the rather unusual saponite, hectorite, has been examined closely by differential thermal analysis, but satisfactory data on the more usual saponites do not exist. A reference sample of hectorite was examined and the curve in fig. 1 agrees closely with the published curve (4), though, in the present case, it has been extended from 1100° to 1200° C., giving rise to additional peaks. The saponite sample was quite different both from hectorite and from montmorillonite. The composite low-temperature endothermic peaks at 170-245° C. are analogous to the behaviour of Ca-montmorillonite, but the low-temperature endothermic peak at 320° C. was found to be also related to the fact that this particular saponite occurs naturally with Mg^{++} as the only exchangeable base. Complementing the X-ray diffraction results, it was found that this endothermic peak at 320° C. disappeared when the clay was heated to 450° C. or above and then allowed to rehydrate. It also disappeared when the Mg^{++} was replaced by either NH_4^+ or Na^+ , but when the NH_4 -clay was again changed to the Mg-clay, the 320° C. endothermic peak reappeared on the differential thermal curve. No endothermic peaks appeared between 550° and 750° C., as is usual for montmorillonites. Weak peaks in this region have been reported by Caillère and Hénin (3) for some saponites, but were probably due to impurities (see below). The authors found only one sharp high-temperature endothermic peak at 895° C. which is typical for talc, and above this up to 1200° C. no further changes occurred. The high-temperature behaviour was thus completely different from hectorite and montmorillonite. On the other hand, it is to be expected from the X-ray behaviour cited earlier, as, on complete removal of adsorbed water, the mineral gives a talc-like pattern, and except in its ability to rehydrate on exposure to water, presumably behaves like talc at high temperatures. As in the case of talc, X-ray examination showed that enstatite was formed on elimination of OH groups at 895° C. It may be noted that

removal of adsorbed water according to the differential thermal diagram is complete at about 400° C. The change to a talc-like pattern cited earlier occurs only after three hours at 450° C. Further, at still higher temperatures, the 'talc' loses its ability to rehydrate. One must infer

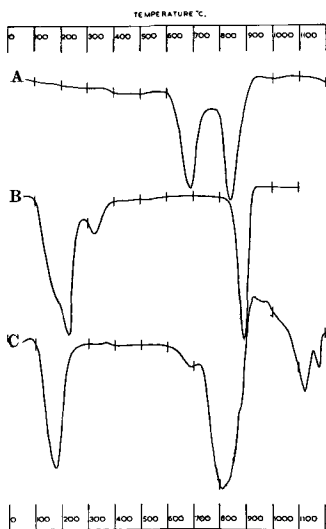


FIG. 1

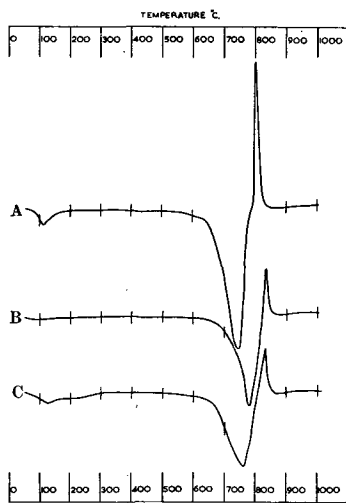


FIG. 2

FIG. 1. Differential thermal curves of: (A) a chlorite, (B) Krugersdorp saponite, (C) hectorite.

FIG. 2. Differential thermal curves of some serpentine minerals: (A) antigorite no. 1; (B) antigorite no. 2; (C) chrysotile-asbestos.

that the change to talc and the loss of rehydration properties both take place between 400° and 850° C. during the differential thermal run, but that neither change produces sufficient thermal effects to record on the differential thermogram. Both are probably due to removal of very small traces of adsorbed water.

In fig. 2 antigorites nos. 1 and 2 are compared with chrysotile-asbestos. It can be seen that no. 2 and the asbestos give about identical curves in conformity with the view that as no. 2 consists of fibrous crystals, it should be classified as a chrysotile. These two curves vary from that of the antigorite no. 1, in the endothermic reaction being less intense. These results agree with the work of Nagy and Bates (8) and their conclusion that chrysotile has the lowest chemical and thermal stability of the minerals in the serpentine group.

The possible effect of impurities with the clay mineral saponite was next examined. Natural samples which were found by X-ray examination to contain chlorite and/or serpentine are illustrated in fig. 3 and show additional thermal peaks. Curve A was a sample containing chlorite, curve B was a similar sample with a higher proportion of chlorite, and curve C was a sample with both chlorite and serpentine.

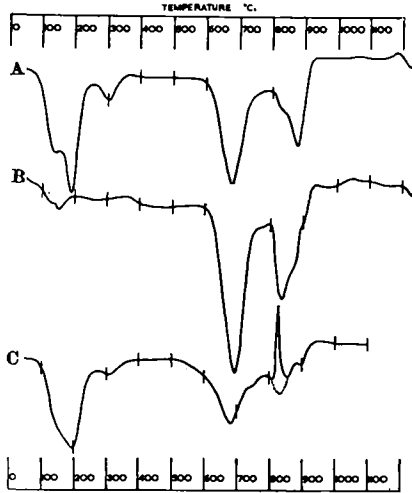


FIG. 3. Differential thermal curves of natural mixtures: (A) saponite and chlorite; (B) chlorite and saponite; (C) saponite, chlorite, and antigorite.

VII. CONCLUSIONS.

A white soapy clay mineral identified as saponite was investigated by optical, chemical, X-ray, and differential thermal analyses. The accumulated data can be summarized as follows:

- (1) A refractive index β varying between 1.486 and 1.493.
- (2) A chemical analysis that indicated this saponite to be an example of a magnesium end-member of the montmorillonite group with a formula $(\text{Fe}_{0.01}, \text{Mg}_{2.99})(\text{Al}_{0.37}, \text{Si}_{3.63})\text{O}_{10}(\text{OH})_2 \cdot 0.18 \text{ Mg}$.
- (3) An X-ray diagram that proved this mineral to be of the trioctahedral expanding lattice type that gives a basic talc structure on dehydration. Certain of the X-ray spacings are not characteristic of

saponite in general, but only of the presence of exchangeable Mg^{++} ions in unheated saponite.

(4) A differential thermal curve showing endothermic peaks at 225–326° C. and at 895° C. Complete rehydration occurred after the mineral was heated to 450° C. and as high as 700° C. The 326° C. endothermal peak is related to exchangeable Mg^{++} in the unheated clay.

The clay mineral occurred in a vein in massive serpentines and amphibolites, and some of the associated minerals, namely, two antigorites, a chrysotile asbestos, and a chlorite are also described. The one antigorite which was not massive but had a fibrous structure showed other properties also intermediate between that of the massive antigorite and the chrysotile-asbestos, and most probably should be classified as a chrysotile.

Acknowledgement.—This paper is published with the permission of the South African Council for Scientific and Industrial Research and of the Department of Mines.

References.

1. G. C. SELFRIDGE, An X-ray and optical investigation of the serpentine minerals. *Amer. Min.*, 1936, vol. 21, pp. 463–503. [M.A. 6–476.]
 2. C. S. ROSS and S. B. HENDRICKS, Minerals of the montmorillonite group: their origin and relation to soils and clays. Prof. Paper U.S. Geol. Survey 1945, no. 205-B, pp. 23–79. [M.A. 10–26.]
 3. S. CAILLÈRE and S. HÉNIN, The properties and identification of saponite (bowlingite). *Clay Minerals Bull.*, 1951, vol. 1, no. 5, pp. 138–144.
 4. P. F. KERR *et al.*, Reference clay minerals, American Petroleum Institute. Research Project 49, 1951. Columbia University, New York.
 5. G. W. BRINDLEY, editor, X-ray identification and crystal structures of clay minerals. 1951, Mineralogical Society, London. [M.A. 11–253.]
 6. H. G. MIDGLEY, A serpentine mineral from Kennack Cove, Lizard, Cornwall. *Min. Mag.*, 1951, vol. 29, pp. 526–530.
 7. R. M. GRUVER, Precision method of thermal analysis. *Jour. Amer. Ceram. Soc.*, 1948, vol. 31, pp. 323–328.
 8. B. NAGY and T. F. BATES, Stability of chrysotile asbestos. *Amer. Min.*, 1952, vol. 37, pp. 1055–1058. [M.A. 12–180.]
-