An occurrence of palygorskite in the Shetland Isles.

(With Plates XIV and XV.)

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I. INTRODUCTION.

IN May 1950 the writer received from Mr. Henry Burgess, of Spiggie, Shetland Isles, a specimen of a material which had been found by a local quarryman. The property of the material which had particularly attracted attention was that when it absorbed water it became soft and pliable and looked like wet leather. The specimen, measuring approximately $4 \times 2 \times 1$ inches, had a brownish iron-stained outer skin, and showed slight signs of foliation parallel to its length. Internally it consisted of a white to greyish-white compact material, in which were embedded portions of the syenitic country-rock. This white material has been shown to consist dominantly of the mineral palygorskite (attapulgite).

During the summer of 1952 the writer had an opportunity of visiting the site, and further specimens were found in situ, although the largest of these measured only about one inch.

II. FIELD RELATIONS.

The site where the palygorskite was found is the northernmost of four small quarries on the south-eastern flank of Noss Hill in South Mainland, Shetland Isles. The quarries, which are about $\frac{1}{3}$ mile WNW. of the farm of Bakkasetter, were being worked by the Zetland County Council for 'rotten granite' for use as road metal.

The exposed bedrock is a reddish coloured medium-grained syenite, which is markedly non-uniformly weathered, and is overlain by reddish sandy boulder clay of local origin, which in places is 10 or more feet thick. The rock has apparently been subjected to considerable hydrothermal alteration, as is shown by the presence of quartz-haematite veins, and epidote and epidote-haematite incrustations along joint planes. The palygorskite occurs in what appear to be roughly vertical crush-bands,

several yards wide, where the rock has a bleached appearance and is so highly altered that it is soft and friable and can be readily crumbled in the hand, and when wet is a non-plastic clayey grit. It is probable that the alteration in these zones is due to the action of hydrothermal solutions, as the rock is thoroughly decomposed at the lowest depths exposed (about 10 feet from the surface), whilst adjacent exposures of bedrock show a weathering crust only a fraction of an inch thick.

III. Mineralogy.

The fresh rock is composed of microcline-perthite, albite-oligoclase, orthoclase, quartz (rare), and normally less than 5 per cent. of ferromagnesian minerals. Usually it contains conspicuous elongated crystals of green actinolite, up to 5 mm. in length, which may be partially altered to fibrous pale olive-green nontronite. The amphibole and secondary nontronite invariably contain epidote as inclusions, and are often associated with granular aggregates of haematite and anatase. Epidote is a common constituent of the rock, being distributed throughout as yellow-green grains, often replacing felspar, and also occurring as veinlets, where it is often associated with haematite and quartz. Accessory minerals are apatite and zircon.

In thin sections of the decomposed rock the felspars show all gradations between relatively unaltered and completely altered grains, the albite-oligoclase being much more strongly attacked than the microcline. The epidote, haematite, and quartz remain unchanged, but the ferromagnesian minerals have been altered or destroyed. The clay occurs as a white to very pale greenish material, which has partially replaced the felspars, and also occurs in thin veins penetrating the decomposed rock. X-ray examination shows it to be a montmorillonoid giving a rational series of $(00l)$ reflections corresponding to d (001) 17·7 Å. for the glycerol-treated material: application of the lithium-saturation test (Greene-Kelly, 1952) shows that it is montmorillonite and not beidellite or nontronite.

The palygorskite occurs sparingly in irregular pocket-like masses and thin veinlets in the montmorillonitized rock. In thin section the mass of the palygorskite shows an intimate felted texture, the small fibres being interwoven and knotted through each other; but, marginally and around fragments of included rock, the fibres show a marked directional texture with their long dimensions parallel to the boundaries. This effect is shown by mass extinction of the fibres under crossed nicols, and is

probably due to clay movement and compaction after formation. The fibres have straight (or nearly straight) extinction, and positive elongation. It is possible to obtain from the mass of interwoven fibres an interference figure which shows 2V negative about 15°. The mean refractive index is $1·520±0·005$, and the birefringence is low.
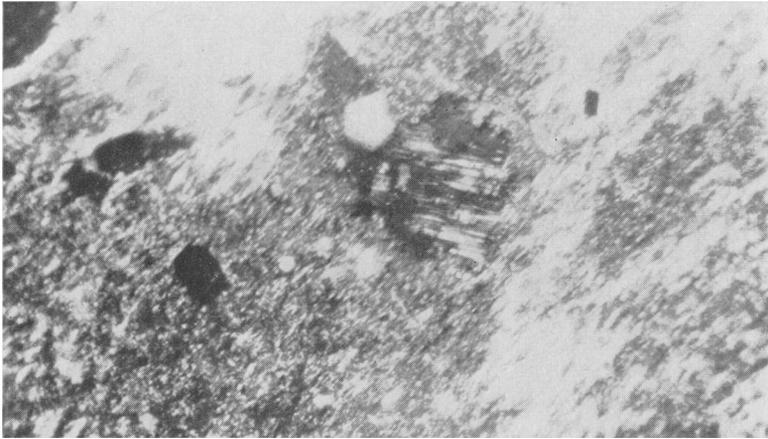

Fig. 1. Thin section of palygorskite, with included relatively unaltered plagioclase felspar. Crossed nicols. × 66.

The felspars occur as inclusions in various stages of alteration, from relatively unaltered grains (fig. 1) to completely replaced 'ghost' relics. The dominant feature is one of replacement, as relatively few unaltered grains are present. Numerous small crystals of high refractive index occur scattered throughout, and have the appearance of shattered epidotes.

IV. X-RAY ANALYSIS.

In 1879 Heddle described under the name of pilolite a number of specimens of 'mountain leather' or 'mountain cork' from different localities and geologic occurrences. The similarity of pilolite to the Bakkasetter mineral and also to palygorskite occurring in mineralized granite at Tafraout, Morocco (Caillère, 1951), suggested the identity of these mineral types. It is interesting to note that one of Heddle's specimens also occurred in veins in decomposing granite at the Burn of Daugh, Cabrach, Aberdeenshire.

X-ray photographs of the Bakkasetter specimen, Heddle's pilolite

from the Cabrach, Aberdeenshire, pilolite (mountain leather) from Naw-
ton, North Riding, Yorkshire, and mountain leather from Seaton,
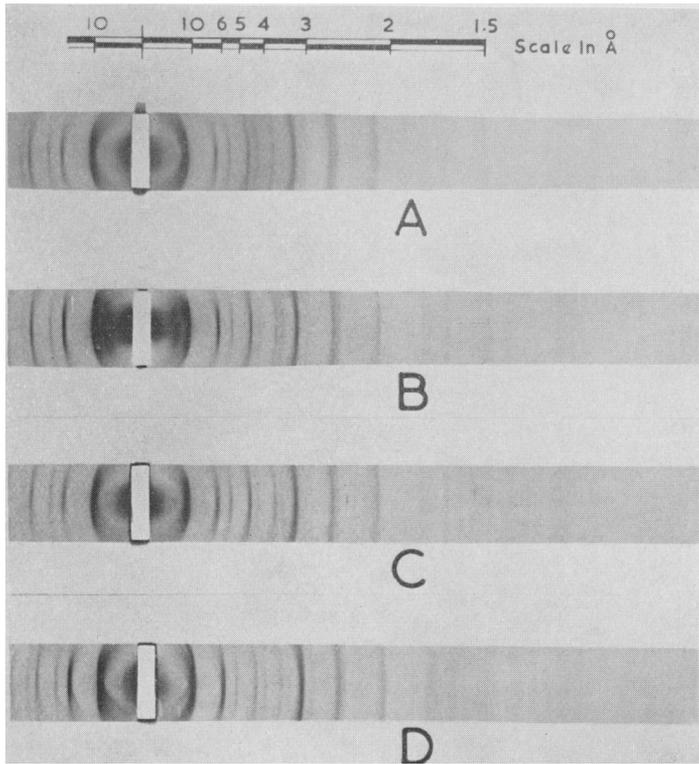Devonshire,[1] are identical, and agree closely with powder data given by

FIG. 2. X-ray diffraction diagrams of palygorskites: A, Bakkasetter, Shetland
Isles, 2–0·5 μ; B, Bakkasetter, Shetland Isles, < 0·5 μ; C, Cabrach, Aberdeenshire;
D, Nawton, Yorkshire.

de Lapparent (1935) and by Bradley (1940) for samples of attapulgite
from Attapulgus, Georgia, U.S.A. Reproductions of the X-ray photo-
graphs are given in fig. 2, except that of the Devonshire specimen which

[1] The specimens from Aberdeenshire, Yorkshire, and Devonshire were
supplied by the courtesy of H.M. Geological Survey, London. The specimen
(23789) from Seaton, Devonshire, occurs in fissures in the New Red (Keuper) Marl.
Nawton, North Riding, Yorkshire, is in an area of Corallian rocks, and the matrix
of this specimen (2953) is consistent with its having come from this source; it
probably occurs in fissures in Corallian limestone.

showed the presence of gypsum in addition. The strongest line on the pattern at about 10·5 Å. is distinctive, and readily distinguishes the palygorskites from the sepiolites which give a spacing at about 12 Å.

Minor amounts of montmorillonite occur associated with the Bakkasetter palygorskite. The montmorillonite is concentrated in the finest size-fractions, and occurs only in minor amounts in the particle-size range greater than $0·5\mu$ (fig. 2, A and B). The X-ray pattern of the fine fraction also shows very faint lines at 7 Å. and 3·5 Å which can be ascribed to kaolin.

V. CHEMICAL ANALYSES.

A partial chemical analysis of the Bakkasetter mineral is shown in table I, col. 1, and is in good agreement with those of other palygorskites quoted in the literature (table I, cols. 2–4) except for the slightly higher value for alumina. This is probably due to the presence of small amounts of montmorillonite as an impurity.

TABLE I. Chemical analyses of palygorskite, &c.

	1.	2.	3.	4.	5.
SiO_2	52·35	51·17	51·00	54·04	51·52
TiO_2	—	—	—	0·32	0·48
Al_2O_3	15·44	13·73	12·89	9·83	17·15
Fe_2O_3	2·12*	1·55	0·09	3·52	5·65
FeO	—	0·31	2·68	0·19	0·32
MnO	—	—	0·08	—	—
MgO	6·60	6·40	7·54	9·07	2·80
CaO	0·14	2·89	—	1·69	1·72
Na_2O	—	—	0·27	0·08	0·15
K_2O	—	—	0·44	0·57	0·85
H_2O+	12·00	13·24 ⎫	24·74	10·93	8·55
H_2O-	10·32	10·29 ⎭		10·00	11·22
	98·97	99·58	99·73	100·24	100·41

* Total iron determined as Fe_2O_3.

1. Palygorskite, Bakkasetter, Shetland Isles. Analyst, C. Bloomfield.
2. Palygorskite, Nijni-Novgorod, Russia. (Caillère, 1936.)
3. Pilolite, Cabrach, Aberdeenshire. (Heddle, 1879.)
4. Attapulgite, Attapulgus, Georgia, U.S.A. (Kerr et al., 1950.)
5. Montmorillonite, Amory, Mississippi, U.S.A. (Kerr et al., 1950.)

The analyses of palygorskites show a marked resemblance to those of montmorillonites, particularly in their water-contents (cf. table I, col. 5). The main difference is that in the palygorskites magnesia is present in excess of the amount normally present in montmorillonites, and as a group they appear to lie between beidellite-montmorillonite and the

magnesium-rich clay minerals such as sepiolite (meerschaum) and saponite. Bradley (1940), however, has concluded that attapulgite has an amphibole-type structure, thus confirming an earlier suggestion by Nagelschmidt (1938) that in these minerals, channels of water between amphibole-like chains play the part of the inter-layer water in montmorillonites.

The exchangeable cations present in the palygorskite and in the associated altered syenite were determined spectrographically after leaching the samples with neutral normal ammonium acetate. These data and the experimentally determined values of the total exchange capacity are given in table II.

TABLE II. Exchangeable cations in milligram-equivalents.

				1.	2.	3.
Ca	...	...	...	5·80	n.d.	6·00
Mg	...	...	...	27·60	n.d.	16·30
Mn	...	...	...	0·11	n.d.	0·03
K	...	...	...	0·86	n.d.	0·29
Na	...	...	...	1·02	n.d.	0·46
				35·39		23·08
Exchange capacity				35·9	27·4	23·4

1. Palygorskite, Bakkasetter, Shetland Isles.
2. Pilolite, Cabrach, Aberdeenshire.
3. Montmorillonitized syenite, Bakkasetter, Shetland Isles.

Assuming that the palygorskite (table II, col. 1) contains 10 % montmorillonite of exchange capacity 90 m.e./100 g., the exchange capacity of the palygorskite is 30 m.e./100 g., which corresponds closely to the value obtained for the sample from the Cabrach (table II, col. 3), but is slightly higher than data given by Caldwell and Marshall (1942), who report values ranging from 18 to 25·3 m.e./100 g. for samples of the attapulgite clay.

VI. DIFFERENTIAL THERMAL ANALYSIS.

The thermal curve given by the Shetland palygorskite is shown in fig. 3, together with published curves of other palygorskites given by Syromyatnikov (1946) for a specimen from the Gorky region, U.S.S.R., and by Caillère and Hénin (1947) for specimens from Attapulgus, Georgia, U.S.A., and Taodeni, Sahara.

All these thermograms are characterized by two endothermic reactions in the low-temperature region at about 200° C. and 300–350° C., and

another endothermic reaction at 500–550° C. In addition the Taodeni mineral shows a well-marked endothermic peak at about 750° C. The
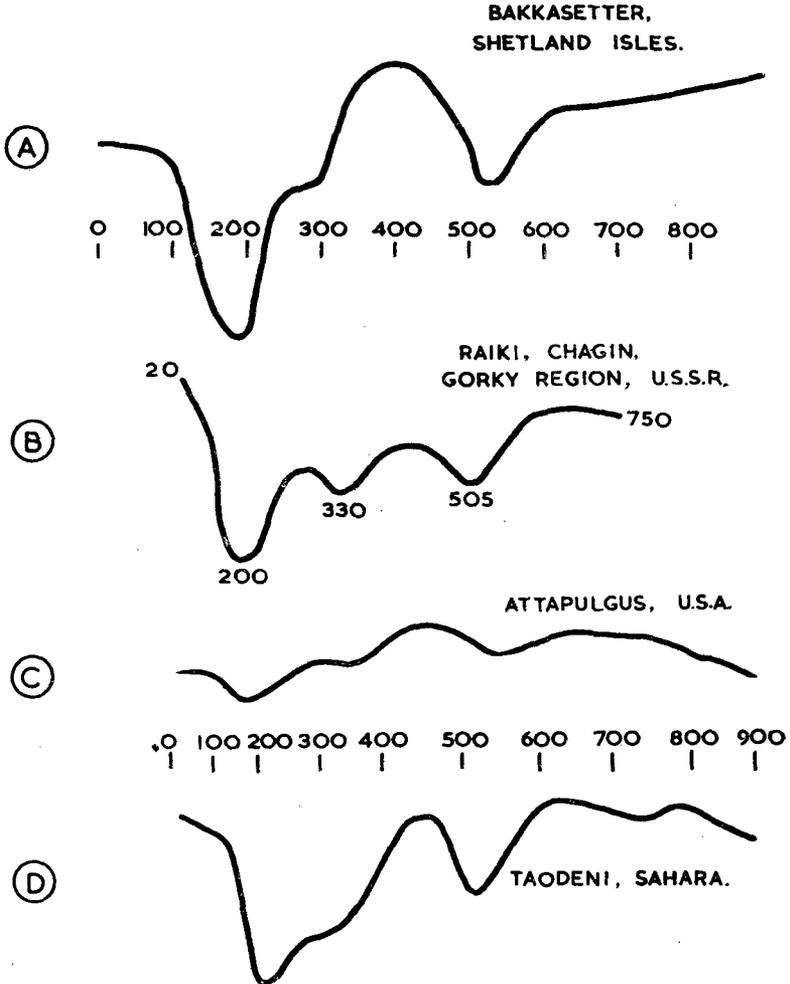

BAKKASETTER, SHETLAND ISLES.

Ⓐ

0 100 200 300 400 500 600 700 800

RAIKI, CHAGIN, GORKY REGION, U.S.S.R.

Ⓑ

20

750

330   505

200

ATTAPULGUS, U.S.A.

Ⓒ

.0 100 200 300 400 500 600 700 800 900

Ⓓ

TAODENI, SAHARA.

FIG. 3. Differential thermal analysis curves of palygorskites.

first very marked peak on the thermograms almost certainly corresponds to the loss of interstitial or sorbed water, and the higher peak at 300–350° C. probably corresponds to the 'less mobile' water which occurs associated with magnesium or aluminium in octahedral co-ordination in

the structure proposed by Bradley (1940). The marked peak at 500–550° C. would correspond to the loss of structural (OH) groups, and it is noteworthy that X-ray diagrams of palygorskites heated above 400° C. show a marked modification, the strong spacing at about 10·5 Å. being replaced by a diffuse halo and the other lines on the diagrams also being considerably altered.

VII. Electron micrographs.

The extremely fibrous nature of the Attapulgus clay has been demonstrated by Marshall et al. (1942), and electron micrographs of the British palygorskites studied reveal a similar development of crystal habit. The Shetland palygorskite (pl. XIV, A) occurs in bundles of extremely elongated lath-shaped crystals. The broader laths are seen to be parallel aggregates of smaller units, which give the appearance of striations parallel to the length, and cause step-like terminations at the ends, although the ends of individual laths are fairly regular. It is probable that the smaller units result mainly from the cleavage of the broader laths. The average breadth of the units appears to be about 30 mμ. The laths must be very thin, as, when they overlap, the outlines of the underlying ones can easily be seen. Evidence for the presence of a tubular structure, such as occurs in halloysite, is lacking.

The micrographs of the other palygorskites exhibit similar characteristics showing single laths and bundles of laths, together with mineral impurities of an entirely different habit in the Cabrach and Devon specimens (pl. XIV, B and XV, B). In the micrograph of the Devon palygorskite it is probable that the additional material is mainly gypsum, as this has been shown to occur finely admixed with the palygorskite.

VIII. Discussion.

The palygorskite described in this paper occurs in association with montmorillonitized syenite. The exchange complex of the altered syenite, in agreement with the occurrence of magnesium-bearing clay minerals, is saturated dominantly with magnesium ions, and it seems clear that the alteration involved the introduction of magnesium solutions from elsewhere than the parent-rock. In the field the juxtaposition of highly decomposed and essentially unweathered syenite suggests that the alteration of the rock is not due to atmospheric weathering, but to the action of hydrothermal solutions, which have permeated the rock mass subsequent to its emplacement, and which have preferentially acted along zones of weakness, such as crush-bands or shear-zones.

A hydrothermal mode of origin has also been suggested by Caillère (1951) for palygorskite occurring in granite at Tafraout, Morocco, but it should be noted that many of the occurrences of this mineral are under conditions which preclude this mode of formation. Perhaps the commonest occurrences are in association with calcareous sediments, in situations where montmorillonite would be expected. Probably a particular chemical composition of the system, especially in regard to the relative abundance of magnesium and aluminium, is the controlling factor in the formation of these minerals.

Note on nomenclature.—The name *palygorskite* has been adopted in this paper, as it was first used to describe these minerals by Ssaftschenkow (1862). The name was taken from that of a mining district in the Urals. In 1879 Heddle described (with chemical analyses) minerals known as 'mountain leather' or 'mountain cork', and showed that specimens from several localities in Scotland and from different geologic environments had closely similar physical characteristics and chemical compositions, and should therefore be regarded as a definite mineral species. He suggested the name *pilolite* ($\pi\hat{\imath}\lambda o\varsigma$, felt) because of their felted character. Friedel (1901, 1907) described similar minerals occurring in the Haute-Loire and the Pyrénées-Orientales under the name of *lassallite*.

Fersman (1908, 1913) defined the palygorskite minerals, mainly from their chemical composition, distinguished them from the sepiolites, and also classified pilolite and lassallite with the palygorskites. The term *attapulgite* was introduced by de Lapparent (1935), who studied specimens from Mormoiron, France, and Attapulgus, U.S.A., but a comparison of their properties with those of the palygorskites shows no significant differences. In view of this it is suggested that the name attapulgite should be discontinued.

References.

BRADLEY (W. F.), 1940. Amer. Min., vol. 25, p. 405. [M.A. 8–81.]
CAILLÈRE (S.), 1936. Bull. Soc. Franç. Min., vol. 59, p. 352.
—— 1951. Compt. Rend. Acad. Sci. Paris, vol. 233, p. 697.
CAILLÈRE (S.) and HÉNIN (S.), 1947. Ann. Agron., vol. 17, pt. 1, p. 23.

CALDWELL (O. G.) and MARSHALL (C. E.), 1942. Univ. Miss. Agr. Expt. Sta. Rea. Bull. 354.

FERSMAN (A), 1908. Bull. Acad. Imp. Sci. St. Pétersbourg, ser. 6, vol. 2, p. 255.

—— 1913. Mém. Acad. Imp. Sci. St. Pétersbourg, ser. 8, vol. 32, no. 2, p. 323.

FRIEDEL (G.), 1901. Bull. Soc. Franç. Min., vol. 24, p. 12.

—— 1907. Bull. Soc. Franç. Min., vol. 30, p. 80.

GREENE-KELLY (R.), 1952. Nature, vol. 170, p. 1130.

HEDDLE (M. F.), 1879. Min. Mag., vol. 2, p. 206.

KERR (P. F.) et al., 1950. Amer. Petroleum Inst., Project 49, Prelim. Report no. 7. [M.A. 11–216.]

LAPPARENT (J. de), 1935. Compt. Rend. Acad. Sci. Paris, vol. 201, p. 481. [M.A. 6–150.]

MARSHALL (C. E.) et al., 1942. Soil Science, vol. 54, p. 149.

NAGELSCHMIDT (G.), 1938. Nature, London, vol. 142, p. 114.

SSAFTSCHENKOW (T. v.), 1862. Verh. Russich-Kaiser. Gesell. Min. St. Petersburg, p. 102.

SYROMYATNIKOV (F. V.), 1946. Voprosy Min., Geokhim. i Petr., Fersman memorial volume, Acad. Sci. U.S.S.R., p. 142. [M.A. 10–553.]

EXPLANATION OF PLATES XIV AND XV.

Electron micrographs of palygorskite.
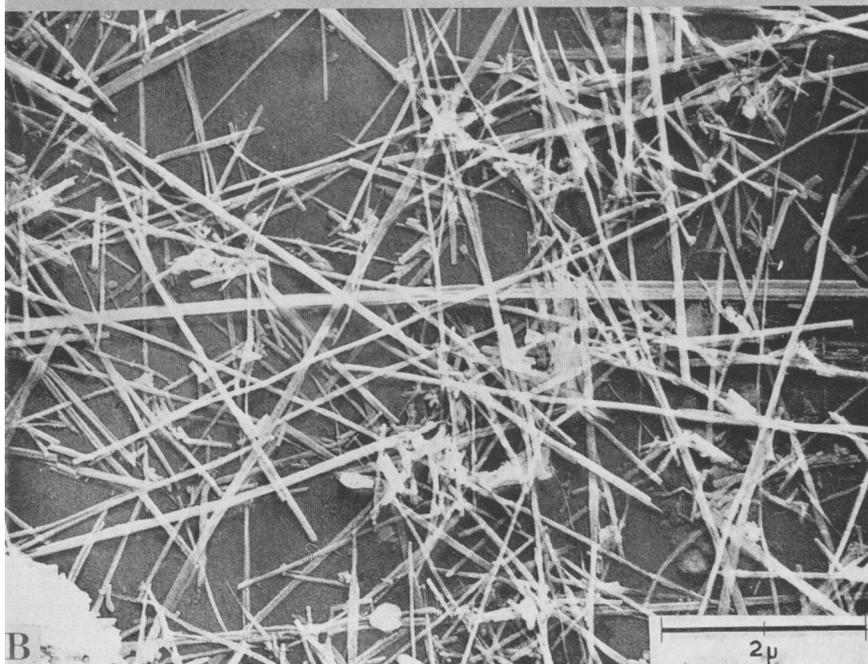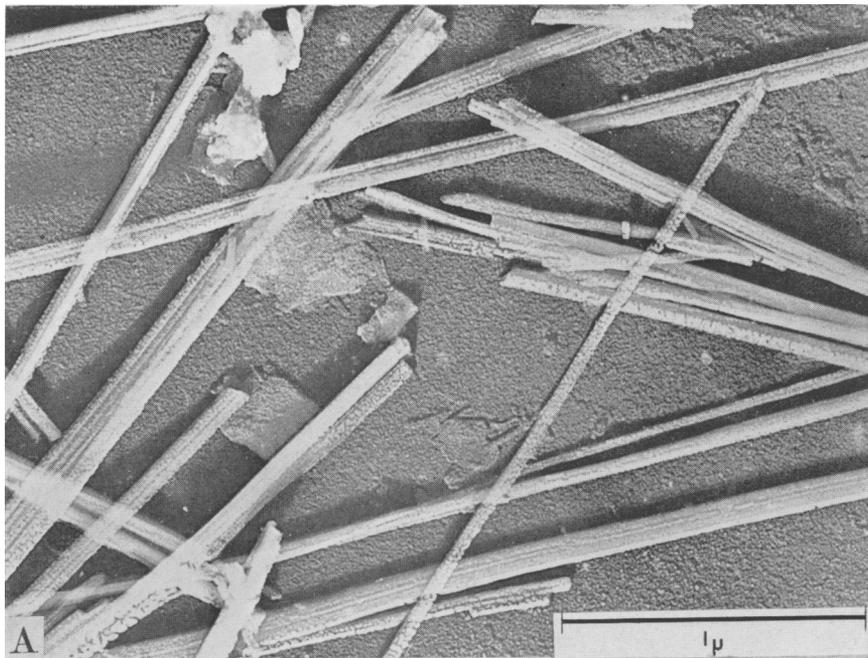(Reduced about $\frac{2}{3}$ from the magnifications indicated.)

PLATE XIV.

FIG. A.   Bakkasetter, Shetland Isles.   × 60,000.

FIG. B.   Cabrach, Aberdeenshire.   × 20,000.
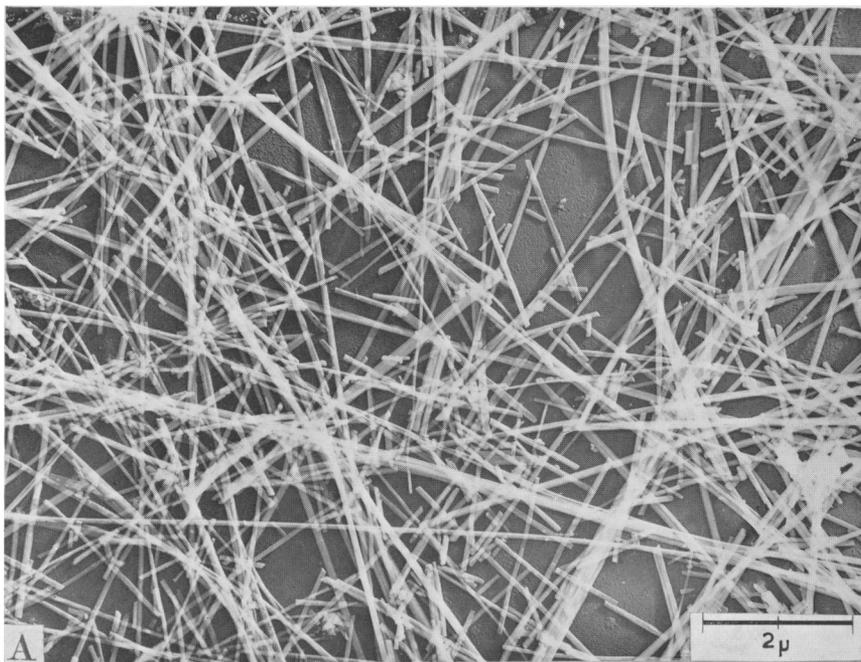
PLATE XV.

FIG. A.   Nawton, North Riding, Yorkshire.   × 15,000.

FIG. B.   Seaton, Devonshire. The white patches are probably gypsum.   × 14,000.

I. Stephen: Electron micrographs of palygorskite

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