

*Illite occurring in decomposed granite at Ballater,
Aberdeenshire.*

By R. C. MACKENZIE, B.Sc., Ph.D., G. F. WALKER, B.Sc., Ph.D.,
and R. HART, B.Sc., Ph.D.

Macaulay Institute for Soil Research, Aberdeen.

[Read August 26, 1948; Clay Minerals Group at International Geological
Congress, London.]

DURING soil survey in the Deeside district of Aberdeenshire, a light greenish-yellow clay-like material was observed penetrating and coating the altered rock along a vein in a granite outcrop freshly exposed in road-widening operations one mile north-east of Ballater. The material occurs in a crush-band in the rock, and the alteration is apparently due to the action of water, but since the band was still highly altered at the base of the exposure (about 25 feet from the surface) it is not certain from the field relationships whether the water was of hydrothermal origin or whether it percolated from the surface.

Samples collected at various points along the crush-band were separated into various particle-size fractions by the usual sedimentation and supercentrifuge technique, using ammonia as the dispersing agent. Samples of particle-size greater than 1.4μ equivalent spherical diameter were preserved for microscopic examination, while the finer fractions were examined by X-ray, chemical, and thermal methods.

EXPERIMENTAL.

Standard methods were employed for the chemical analyses (1), while the cation exchange capacities were determined by a method similar to that of Jackson and Truog (2). A sintered alumina specimen-holder of capacity 0.2 gram and a ceramic block were used in the differential thermal analysis apparatus, the thermocouple arrangement (chromel-alumel) being identical with that of Grimshaw, Heaton, and Roberts (3). The control mechanism has, however, been made automatic by inserting a constant voltage transformer and a rheostat run by a synchronous motor. Both the temperature trace and the differential trace are recorded on the same chart. The temperatures quoted below are corrected to the temperature of the sample at the peak (3). Dehydration curves were obtained by weighing the material after heating it for one hour at temperatures increasing by 50° C.

Mineralogical data.—The fresh rock is a coarse- to medium-grained pink granite, the tint being due to the colour of the orthoclase felspar. The principal minerals are quartz, orthoclase, oligoclase, and biotite, the biotite being very sparing in amount and the orthoclase in part perthitic. The accessory minerals are zircon, sphene, fluorite, apatite, and iron oxides.

The decomposed rock, mottled pink and light greenish-yellow, crumbles readily in the hand and is confined to a narrow vein running

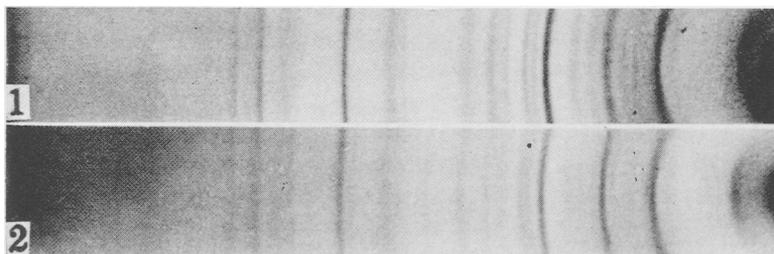


FIG. 1. Powder diffraction photographs of illites: 1, Ballater, $< 1.4 \mu$; 2, Fithian, Illinois.

roughly vertical. The clay mineral, which has a platy character, occurs as a light greenish-yellow soft scale on the decomposed rock and rubs readily off the rock face. It is also found as a network through the decomposed rock and running in cracks in and partly replacing the decomposed felspar. Under the microscope it is nearly colourless. The optical data together with those for illite (4, 5) and hydromuscovite (6) are shown in table I. The figures agree with those for illite rather than those for hydromuscovite, especially in the size of the optic axial angle.

TABLE I. Optical data.

	Illites			Hydromuscovite Ogofau, S. Wales (6).
	Ballater.	South Wales (5).	Fithian, Ill. (4).	
α ...	1.568	1.572	1.555	—
β ...	1.590	1.587	—	1.575
γ ...	1.593	1.600	1.588	1.580
$\gamma - \alpha$	0.025	0.028	0.033	—
2V	small	small	small	large

X-ray data.—Powder photographs of the separated material ($< 1.4 \mu$ equivalent spherical diameter) confirm its micaceous character. Comparisons with the published diagrams of other clay micas (table II and fig. 1) reveal a closer resemblance to the Illinois (4) and South Wales

TABLE II. X-ray data.

Indices.	Illites						Hydromuscovite	
	Ballater		South Wales (5).		Gilead, Ill. (4).		Ogofau, Wales (7).	
	<i>d.</i>	<i>I.</i>	<i>d.</i>	<i>I.</i>	<i>d.</i>	<i>I.</i>	<i>d.</i>	<i>I.</i>
002	9.9	s	10.0	vs	9.98	s	9.98	s
004	4.9	m	5.0	m	4.97	w	5.02	s
110	4.45	vs	4.46	vs	4.47	s	4.51	m
111	4.28	w	—	—	—	—	—	—
022	4.10	w	—	—	4.11	vw	—	—
113̄	3.87	m	—	—	—	—	—	—
023	3.64	mw	—	—	3.7	vw	3.62	s
114̄	—	—	—	—	3.4	vw	—	—
006	3.35	vs	3.32	vs	3.31	m	3.34	vs b
114	—	—	—	—	3.2	vw	—	—
025, 115̄	3.09	mw d	2.97	vw	2.98	w	3.09	s
115	2.85	m d	2.80	vw	2.84	vw	2.89	s
202̄	2.56	vs	2.55	vs	2.56	s	2.59	vs
133̄, 202	2.45	mw	2.44	w	2.44	w	2.470	m
204̄, 133	2.39	m	2.37	mw	2.38	m	2.390	s
221̄	2.235	mw	2.23	} w	2.24	m	2.27	} w
223̄	—	—	2.17		2.18	w	2.18	
206̄, 043	2.14	m	2.14	m	2.11	w	2.135	s
0010	1.988	m	1.98	m	1.98	m	1.994	vs
206	1.940	w	—	—	—	—	—	—
208	—	—	—	—	—	—	1.715	vw
2010̄, 312	1.647	m d	1.64	m	1.65	w	1.648	s
060, 331̄	1.497	s	1.49	vs	1.50	s	1.505	s
0014	—	—	—	—	—	—	1.416	vw
337̄	—	—	—	—	—	—	1.380	vw
335	1.342	mw d	1.34	w	1.34	vw	1.350	} m
							1.336	
400	1.294	m	—	—	—	—	1.297	m
402	1.266	w	—	—	—	—	—	—
0016	1.243	mw	1.24	w	1.24	w	1.245	w

The Ballater illite was photographed with Fe- $K\alpha$ radiation in a 9 cm. camera. *d*-spacings in Ångström units and intensities estimated visually. vs = very strong; s = strong; ms = medium strong; m = medium; mw = medium weak; w = weak; vw = very weak; d = diffuse; b = broad.

illites (5) than to the Ogofau hydromuscovite (7). There are, however, a number of lines on the Ballater illite diagram (e.g. at 4.28 Å. and 3.87 Å.) which do not appear on those of the other illites quoted, although they occur in the muscovite and sericite data given by Grim, Bray, and Bradley (4), and are here indexed accordingly.

Apart from a slight increase in the unit-cell height, heat treatment at 300° and 540° C. has no appreciable effect on the structure, but at 625° C. a few lines of the pattern, viz. those at 3.87, 2.85, and 2.14 Å., tend to

become weaker and at 750° C. they have disappeared completely. At 1000° C. recrystallization to γ -alumina takes place.

Photographs of oriented aggregates treated with glycerol (8) indicate the presence of a very small amount of montmorillonite (1 % or less in the $< 1.4\mu$ fraction). A slight tail to the 10 Å. line extending inwards to about 11.5 Å. is also observed on the aggregate photographs and suggests that the illite may be breaking down to form montmorillonite. Decrease in the particle-size of the specimen increases the relative quantity of the latter mineral, so that in the $< 0.4\mu$ fraction about 2 % is present, and in the $< 0.2\mu$ fraction about 5 % (fig. 2).

Chemical data.—Chemical analyses of three fractions (X-ray diagrams in fig. 2) are listed in table III, together with an analysis of the fresh felspar and published data for other illites (4, 5) and for hydromuscovite (6). Ballater illite, sample 3, was collected from a different part of the section and was red in colour due to the presence of free iron oxide,

which is recorded separately in the analysis. Since the calcium content of all three samples was approximately equal to or less than the cation exchange capacity, and since all samples were coagulated with calcium chloride during separation, the analytical figures were corrected for lime, hygroscopic moisture, and free iron oxide, and are recalculated to 100 %. These figures are given in columns 1c, 2c, and 3c. Because of its small montmorillonite content, sample 1 (column 1c) is taken for comparison with two other illites, hydromuscovite, and the fresh felspar.

The most significant change in the alteration of the felspar to illite is the almost complete removal of soda. The potash content, however, appears to have been very little affected. An appreciable rise in the alumina, iron, magnesia, and water contents, or decrease in the silica content is also observed.

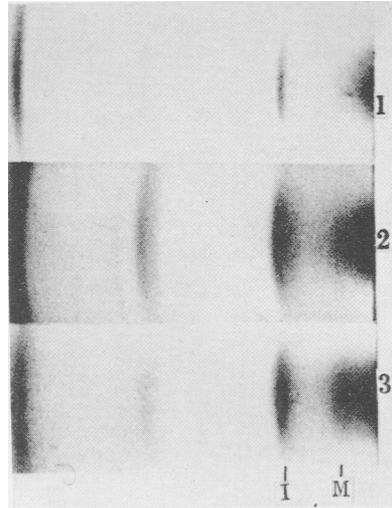


FIG. 2. Aggregate diffraction photographs of Ballater illite: 1, $< 1.4\mu$; 2, $< 0.4\mu$; 3, $< 0.2\mu$. (I, illite line; M, montmorillonite line.)

TABLE III. Chemical analyses.

	1.	2.	3.	1c.	2c.	3c.	4.	5.	6.	7.
SiO ₂ ..	49.26	49.01	48.95	51.26	50.36	52.76	51.22	47.55	46.54	66.34
TiO ₂ ..	0.05	0.07	0.07	0.05	0.07	0.08	0.53	0.64	0.17	0.04
Al ₂ O ₃ ..	28.97	29.45	26.74	30.15	30.26	28.83	25.91	32.45	36.37	19.18
Fe ₂ O ₃ ..	2.27	2.30	2.44	2.36	2.36	2.63	4.59	0.76	0.72	0.28
FeO ..	0.57	0.70	0.46	0.59	0.72	0.50	1.70	1.85	0.36	0.11
MnO ..	0.04	0.05	0.08	0.04	0.05	0.09	—	—	—	0.00
CaO ..	0.67	0.19	0.91	nil	nil	nil	0.16	0.06	0.22	0.25
MgO ..	1.32	1.52	1.68	1.37	1.56	1.81	2.84	1.70	0.50	0.05
K ₂ O ..	7.47	7.66	5.44	7.77	7.87	5.86	6.09	6.22	8.06	8.62
Na ₂ O ..	0.13	0.37	0.16	0.13	0.38	0.17	0.17	1.05	0.46	5.13
H ₂ O + ..	6.03	6.20	6.74	6.28	6.37	7.27	7.14	7.73	6.31	0.32
H ₂ O - ..	3.22	2.78	5.52	nil	nil	nil	1.45	nil	0.52	0.12
	100.00	100.30	99.86	100.00	100.00	100.00	101.80	100.01	100.23	100.44
SiO ₂ : Al ₂ O ₃	2.89	2.82	3.11	3.36	2.49	2.17	—
SiO ₂ : R ₂ O ₃	2.75	—	—	3.02	2.45	2.14	—
SiO ₂ : K ₂ O	10.32	—	—	13.20	11.96	9.05	—

1-3. Illite, Ballater, Aberdeenshire. Analyst, R. C. Mackenzie. Total in no. 3 includes free Fe₂O₃ 0.67 (not determined in nos. 1 and 2). No. 1 of fraction < 1.4 μ; 2, < 0.4 μ; 3, < 0.2 μ.

1c-3c. Ditto recalculated.

4. Illite, Fithian, Illinois. Ref. (4).

5. Illite, South Wales. Ref. (5).

6. Hydromuscovite, Ogofau, South Wales. Ref. (6).

7. Felspar, Ballater. Analyst, R. C. Mackenzie.

The silica-sesquioxide and silica-alumina ratios are similar to those of the other illites and higher than those of hydromuscovite. The ferrous iron, magnesia, and alkali contents, and the silica-potash ratio are, on the other hand, intermediate between those of the illites and those of hydromuscovite, while the water content is similar to that of hydromuscovite.

The formula for Ballater illite on the basis of 24SiO₂ is: 2.4(K,Na)₂O. 1.2MO.8.8R₂O₃.24SiO₂.10H₂O. This is intermediate between the illite formulae given by Grim, Bray, and Bradley (4) (2K₂O.3MO.8R₂O₃. 24SiO₂.12H₂O), and by Nagelschmidt and Hicks (5) (2.5(K,Na)₂O.1.3MO. 9.9R₂O₃.24SiO₂.13H₂O) for alkalis and sesquioxides, but somewhat lower than either in monoxides and water. It differs considerably, however, from the formula for hydromuscovite (2.9(K,Na)₂O.0.7MO. 11.3R₂O₃.24SiO₂.10.8H₂O) except for the water content.

Because of isomorphous replacements a more valid comparison is probably that on the basis of the ionic composition, taking O + OH = 48 (table IV). Here it will be noted that in Ballater illite the relative amounts of O and OH are similar to those in hydromuscovite; the amounts of Si and Al in tetrahedral positions and the total number of ions in octahedral positions are similar to those in Fithian illite; and the amounts of Al in octahedral positions and of alkalis are intermediate between those in Fithian illite and in hydromuscovite.

The cation exchange capacities of samples 1 and 3 (table III) are,

respectively, 23.2 and 42.0 milliequivalents/100 gm. Correcting the latter figure for 5% montmorillonite of cation exchange capacity 100 m.e./100 gm., the exchange capacity becomes 39 m.e./100 gm., both samples being thus in the illite range (20–40 m.e./100 gm.).

TABLE IV. Chemical (ionic) composition on the basis of (O,OH) = 48.

	Muscovite.	Hydromuscovite.	Ballater Illite.	South Wales Illite.	Fithian Illite.
K	4	2.7	2.5	2.0	2.0
Na	—	0.2	0.1	0.5	0.1
Ca	—	—	—	—	—
Mg	—	0.2	0.5	0.6	1.1
Fe ⁺²	—	0.1	0.1	0.4	0.4
Fe ⁺³	—	0.1	0.5	0.1	0.8
Al	8	7.1	6.2	5.8	4.9
Ti	—	—	—	0.1	0.1
Al	4	4.0	2.9	3.9	2.9
Si	12	12.0	13.1	12.1	13.1
O	40	37.1	37.2	34.9	35.9
OH	8	10.9	10.8	13.1	12.1

Thermal data.—Differential thermal analysis curves of a considerable number of samples from the same exposure were all similar (curves 3, 4, and 5, fig. 3). After the hygroscopic moisture peak there occurs a very broad peak in the region 560–600° C. followed by a sharp, well-defined peak at 713° C. Curves obtained with the same apparatus for illite from Fithian, Illinois, and from South Wales are shown in the same figure (curves 1 and 2, respectively). All the curves are for 200 mg. samples except curve 5 which is for a 170 mg. sample. Correcting the areas of the peaks in curve 5 to 200 mg., the areas of the three peaks at 713° C. are approximately the same, with, if anything, a slight decrease towards the smaller particle-size. The difference in thermal reaction between the type illite and the Ballater material, which is very striking, is discussed below.

Dehydration curves for the same three samples are shown in fig. 4 (nos. 2, 4, and 5) in which curves 1 and 3 are reproduced from the data published by Nagelschmidt and Hicks (5) and by Grim, Bray, and Bradley (4) respectively. Instead of the single 'step' observed in their curves at about 350–550° C. the Ballater material shows two distinct 'steps' at 400–500° C. and 550–650° C., corresponding to the two peaks on the thermograms shown in fig. 3. The first 'step' in these curves apparently increases in size with decrease in particle-size, while the second 'step' decreases.

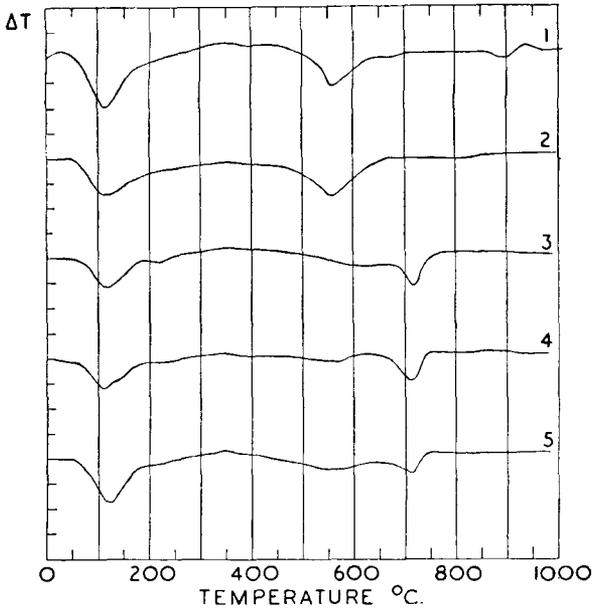


FIG. 3. Differential thermal analysis curves of illites.
 1, Fithian, Illinois. 2, South Wales. 3, Ballater, $< 1.4 \mu$.
 4, Ballater, $< 0.4 \mu$. 5, Ballater, $< 0.2 \mu$.

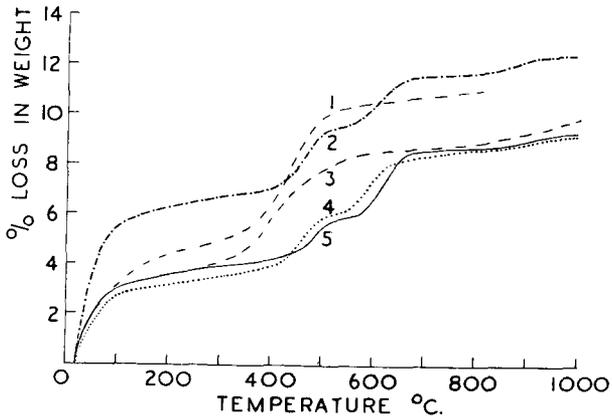


FIG. 4. Dehydration curves of illites.
 1, South Wales. 2, Ballater, $< 0.2 \mu$. 3, Fithian, Illinois.
 4, Ballater, $< 0.4 \mu$. 5, Ballater, $< 1.4 \mu$.

DISCUSSION.

The X-ray and optical data presented above agree with the classification of the clay mineral as illite rather than as hydromuscovite. The chemical data, while in some respects revealing similarities to hydromuscovite, are, in general, in fairly good agreement with those for illite. The rather ill-defined nature of the term 'sericite', which has frequently been quoted as an alteration-product of feldspar (9), makes its use unsuitable for the Ballater mineral. The probable sequence of events in the alteration of the rock would appear to be:



The main points of interest lie in the thermal characteristics of the mineral, which so far as can be ascertained are different from those of any other illite (10). Some similarity may be noted to the thermograms given by Bates (11) for the fine fraction of a mica concentrate from slate, but there the peak at 640° C. is assigned to chlorite of which there is no sign in the X-ray diffraction photographs of our material.

The 713° C. peak might on superficial examination be attributed to montmorillonite: cf. the peak at 700° C. on the thermogram of 'glimmerton' from Sárospaták, Hungary (12). However, the size of this peak (which is, e.g., in curve 3, fig. 3, much larger than would be expected for < 1% montmorillonite) as well as its relative constancy in area over the range < 1-5% montmorillonite (fig. 3) rules out this possibility. The apparent very slight decrease in the area of the peak as the particle-size decreases suggests that it is due to the illite. The disappearance of some illite lines in the X-ray pattern after heating in the region 625-750° C. supports this interpretation. The area of the broad peak on the thermogram is very difficult to measure accurately, but there appears to be, generally, a slight decrease with increasing particle-size. This, together with the corresponding decrease in the 400-500° C. 'step' on the dehydration curve, would seem to be associated with the montmorillonite component.

Further support for the above interpretation was obtained from a thermogram of material collected from a different part of the exposure which X-ray examination showed to contain about 20% montmorillonite and 80% illite. On this curve the 713° C. peak had disappeared and the broad peak (568° C.) increased very considerably in size, approximately to the extent required by an increase from 5 to 20% montmorillonite. Increase in the sensitivity of recording showed that the single broad peak observed actually consisted of two overlapping peaks,

one at 568° C. and the other at 713° C. The attribution of the 713° C. peak to illite is thus confirmed.

This conclusion would add still another type of illite to those already distinguished by Caillère and Hénin (13), all these types having similar X-ray patterns, but differing in their differential thermal curves—a position similar to that occurring in the antigorite group (14). In view of the thermal reactions of the Ballater mineral it is evident that caution must be observed in attributing a peak at about 700° C. to the presence of montmorillonite without some additional evidence.

The authors wish to thank Dr. G. Nagelschmidt, St. Austell, for a sample of illite from South Wales, and Mr. D. B. Honeybourne, Building Research Station, for a sample of illite from Fithian, Illinois.

Summary.—A clay occurring in an altered vein in a granite at Ballater, Aberdeenshire, has been examined by optical, X-ray, chemical, and thermal methods. The clay mineral is classified as illite although its thermal data are different from those of any illite so far described. As distinct from the usual illite thermograms, which show a peak in the region 500–600° C., this mineral shows two peaks: a broad one at 550–600° C. and a sharp one at 713° C. A small amount of montmorillonite is found as a contaminant, but this is insufficient to account for the 713° C. peak, while the area of this peak increases as the montmorillonite content decreases. This peak therefore is assigned to illite.

References.

1. I. M. KOLTHOFF and E. B. SANDELL, *Textbook of quantitative inorganic analysis*. 2nd edit., New York, 1943.
A. W. GROVES, *Silicate analysis*. London, 1937. [M.A. 6–483.]
2. M. L. JACKSON and E. TRUOG, *Proc. Soil Sci. Soc. Amer.*, 1939, vol. 4, p. 136.
3. R. W. GRIMSHAW, E. HEATON, and A. L. ROBERTS, *Trans. Brit. Ceram. Soc.*, 1945, vol. 44, p. 81.
4. R. E. GRIM, R. H. BRAY, and W. F. BRADLEY, *Amer. Min.*, 1937, vol. 22, p. 813. [M.A. 7–12.]
5. G. NAGELSCHMIDT and D. HICKS, *Min. Mag.*, 1943, vol. 26, p. 297.
6. A. BRAMMALL, J. G. C. LEECH, and F. A. BANNISTER, *Min. Mag.*, 1937, vol. 24, p. 516.
7. G. NAGELSCHMIDT, *Zeits. Krist.*, 1937, vol. 97, p. 518. [M.A. 7–94.]
8. D. M. C. MACEWAN, *Nature*, 1944, vol. 154, p. 577; *Journ. Soc. Chem. Ind.*, 1946, vol. 65, p. 298. [M.A. 10–27, 369.]
9. See, e.g. F. H. NORTON, *Amer. Min.*, 1937, vol. 22, p. 1; 1939, vol. 24, p. 1; 1941, vol. 26, p. 1; N. P. PETERSON, C. M. GILBERT, and G. L. QUICK, *Econ. Geol.*, 1946, vol. 41, p. 820; G. M. SCHWARTZ, *ibid.*, 1947, vol. 42, p. 319.
10. S. B. HENDRICKS and L. T. ALEXANDER, *Soil Sci.*, 1939, vol. 48, p. 257; RUSSELL and HADDOCK, *Proc. Soil Sci. Soc. Amer.*, 1941, vol. 5, p. 90; SCHAFFER and RUSSELL, *Soil Sci.*, 1942, vol. 53, p. 353; GRIM and ROWLAND, *Amer. Min.*, 1942,

- vol. 27, pp. 746, 801; GRIM, *ibid.*, 1947, vol. 32, p. 493; BATES, *ibid.*, 1947, vol. 32, p. 625; GRIM and BRADLEY, *ibid.*, 1948, vol. 33, p. 50; CAILLÈRE and HÉNIN, *Ann. Agron.*, 1947, vol. 17, p. 23; SPEIL, BERKELHAMER, PASK, and DAVIES, *Tech. Paper, U.S. Bur. Mines*, 1945, no. 664.
11. T. F. BATES, *Amer. Min.*, 1947, vol. 32, p. 625. [M.A. 10-365.]
 12. R. E. GRIM and R. A. ROWLAND, *Amer. Min.*, 1942, vol. 27, p. 746, 801 [M.A. 9-76.]; for X-ray data see E. MAEGDEFRAU and U. HOFMANN, *Zeits. Krist.*, 1937, vol. 98, p. 38.
 13. S. CAILLÈRE and S. HÉNIN, *Ann. Agron.*, 1947, vol. 17, p. 23.
 14. S. CAILLÈRE, *Bull. Soc. Franç. Min.*, 1936, vol. 59, p. 163. [M.A. 6-475.]