# The occurrence of palygorskite, near Ipswich, Queensland.

By LILLIAN E. ROGERS, M.Sc.,<sup>1</sup> A. E. MARTIN, B.Sc., F.R.I.C.,<sup>2</sup> and K. NORRISH, M.Sc., PH.D.<sup>1</sup>

Commonwealth Scientific and Industrial Research Organization.

[Taken as read November 4, 1954.]

# INTRODUCTION.

I N the course of an investigation on the determination of soil carbonates a sample of dolomite, from the Ibis dolomite quarry, Mt. Flinders, Queensland, was examined by X-ray diffraction and found to contain palygorskite.<sup>3</sup> As this appears to be the first recognition of the occurrence of the mineral in Australia and as it has a number of commercial uses (e.g. as a drilling mud, catalyst, decolorizer, and absorbent), further work was undertaken.

### GEOLOGY OF THE AREA.

Jensen (3) has described the development of the igneous rocks in the area, with special reference to the Flinders and Fassifern volcanoes. A general description of the Moreton district is given by Jones (4), but with little direct information on the Flinders dolomite. David (5) refers to the area and describes the Redbank series between Ipswich and Brisbane within an area of 18 miles by 12, as 'outcrops of freshwater beds . . . consisting of 300 feet of clays, shales and sandstone overlain by 500 feet of basalt. . . . Just east of Ipswich it is overlain . . . by the (Tertiary) Silkstone series of mudstones, shales and sandstones, dolomitized and silicified limestones with *Planorbis* and marly clays, with two interbedded flows of basalt; the total thickness is about 400 feet.'

It seems, therefore, that the dolomite found in the Ipswich area was deposited in fresh-water lakes during Tertiary times. The occurrence of palygorskite in the area is in keeping with those previously reported in the U.S.A. at Attapulgus (6), in France (7), and South Africa (8), where the palygorskite is associated with limestones of lacustrine origin.

<sup>1</sup> Division of Soils, C.S.I.R.O., Adelaide, South Australia.

<sup>2</sup> Division of Soils, C.S.I.R.O., Brisbane, Queensland.

<sup>3</sup> Palygorskite and attapulgite are synonymous. Palygorskite is used here as it has historic precedence (1, 2).

#### PALYGORSKITE FROM QUEENSLAND

#### DESCRIPTION OF THE QUARRY.

The Ibis dolomite quarry, Mt. Flinders (grid reference 857499, Flinders map, 1 mile series) is situated in the area covered by the Silkstone series. In the vicinity of the quarry the upper portions of the hillocks are composed of dolomite, basalt occurring farther downhill. Basalt also occurs as a capping on the tops of some of the hills. The dolomite is quarried after the removal of the shallow overlying black soil. In the quarry the dolomite occurs as massive blocks with horizontal and vertical cracks. Throughout the deposit there occur horizontal and vertical bands, 4–12 inches thick, of a pinkish-grey, shaly clay (palygorskite), in which hard brownish cores (mainly sepiolite) are distributed irregularly. At the level of the floor of the quarry a thicker deposit, 2 feet deep, of greenish clay occurs (this may be partly downwash from the quarry face) overlying a similar but pinkish clay which is at least  $1\frac{1}{2}$  feet thick (both clays contain palygorskite, montmorillonite, and dolomite).

Samples were taken from the main quarry only, but a visit to several adjacent hills which were being quarried indicated that they were similar to the main site.

### MINERALOGY OF THE MT. FLINDERS DEPOSITS.

1. Dolomite.—X-ray diffraction analyses indicated that the large blocks from the quarry were mainly dolomite with a palygorskite impurity. Treatment of the dolomite with 0.1 N HCl left a residue which gave an X-ray diffraction pattern in very good agreement with that given by Bradley (9) for pure palygorskite.

2. *Palygorskite.*—X-ray diffraction analysis indicated that the shaly clay occurring as bands was very pure palygorskite. The green and pink clays from the floor of the quarry each contained palygorskite and mont-morillonite with a little dolomite.

A chemical analysis of the clay separate (less than 0.002 mm.) of the pure palygorskite is given in table I. It is almost identical with South African palygorskite (8), but differs from most other published analyses in that there is a little less alumina but correspondingly more magnesia. No calcium was found and this is probably an indication of the high purity of the material analysed. During the separation of the clay it was treated with 0.2n HCl, so that any carbonate would have been removed. Most published analyses show several per cent. CaO, but since calcium probably cannot occur in the lattice of the mineral and since only about 1 % CaO can be accounted for as exchangeable cations, any excess over this is most likely due to contamination.

					, j			
			1.	2.	3.	4.	5.	6.
$SiO_2$			59.09	61.60	59.02	75.50	61.17	59.72
TiO <sub>2</sub>			0.99		0.66	0.14	0.23	0.49
$Al_2O_3$			6.84	6.82	9.64	1.06	1.69	0.30
${ m Fe_2O_3}{ m FeO}$			$4 \cdot 21$	0.87	$\left\{ \begin{array}{c} 3 \cdot 70 \\ 0 \cdot 25 \end{array} \right\}$	1.84	2.92	_
CaO			(< 0.01)	0.67	2.22	0.51	0.80	0.60
MgO			14.12	14.22	9.96	12.61	20.01	26.70
$H_{2}O +$			14.18	14.16	11.98	8.08	12.82	11:70
&c.					2.64			0.41
Total			99.43	98·34	100.07	99.74	99.64	99.92
$H_2O -$	•••		8.00		9.12	7.70	11.68	8.18
Exchang	e capac	eity						
m.e./l	00 g.		5.74	20	<b>21</b>	_		

TABLE I.	Chemical	analyses of	f palygorskite	and sepiolite.
(P	ercentages	calculated	on oven-drv	basis.)

1. Palygorskite, Mt. Flinders, Queensland,  $< 2\mu$ .

2.

Dornboom, South Africa. H<sub>2</sub>O given as ignition loss. (Heystek and Schmidt, 8.)

3. Attapulgus, Georgia, U.S.A. (Bradley (9) recalculated to oven-dry basis.)

4. Sepiolite, Mt. Flinders, Queensland.

5. Mt. Flinders. Calculated, deducting chert, assuming an average of ,, 61 % SiO<sub>2</sub> for sepiolite.

Yavapai County, Arizona. (Kauffman (10), recalculated to oven-dry 6. •• basis.)

Total exchange capacity determinations were carried out on acidwashed samples by an equilibrium method using normal ammonium acetate at pH 7.0. It is seen from table I that the exchange capacity is appreciably lower than that usually quoted in the literature for this mineral. This is thought to be due partly to clumping of the sample in the reagent, as saturation of the raw material (containing 72 % of the < 0.002 mm. fraction) under vacuum to displace all entrapped air gave a value of 7.34 m.e./100g. This is still greatly below the accepted exchange capacity and the discrepancy has yet to be explained. One sample from the floor of the quarry gave a value of 34.15 m.e./100g., but this material is known to be contaminated with montmorillonite.

The palygorskite clay was heated at 100° C. intervals to 1000° C. and diffraction patterns were obtained for each temperature. The diffraction data agreed, in general, with those of Longchambon (11, 12). The 10.5 Å. line became faint at 550° C. when a 9 Å. line began to appear. The mineral was converted to  $\alpha$ -cristobalite and enstatite at 850° C.

536

3. Sepiolite.—The hard brownish cores in the shaly clay were identified by X-ray diffraction as sepiolite with some chert and a little palygorskite. The cores were covered by a crust intermediate in properties between the brown core and the clay, and this contained about equal amounts of palygorskite and sepiolite with a little chert.

The brown cores were hard and dense and this departure from the normal physical properties of sepiolite is to be explained by its impregnation with chert. A chemical analysis of the material of the core is given in table I. If sepiolite is considered to contain 54 %  $SiO_2$ , then the sample contains 34 % free  $SiO_2$ .

X-ray diffraction patterns of heat-treated samples were in reasonable agreement with the results given by Migeon (13). The 12 Å. line of sepiolite disappeared at 850° C. and at that temperature the mineral changed to enstatite and  $\alpha$ -cristobalite. Migeon did not detect the cristobalite phase until 1100° C. in the heated sepiolite. As the sepiolite found in the quarry was intimately mixed with chert, the temperature at which the  $\alpha$ -cristobalite phase first appears is difficult to determine.

4. Chert.—Chert was a contaminant of most of the samples examined and was identified by the strong diffraction line at 4.1 Å and 2.5 Å. When pure it gives a diffraction pattern similar to but not identical with that of  $\beta$ -cristobalite (14). Gruner (15) discusses the occurrence of cristobalite in bentonites and fuller's earth.

5. Soil.—A rendzina soil overlies the dolomite outcrop at this quarry. An examination of the clay fraction of the soil showed palygorskite with small amounts of sepiolite, dolomite, calcite, quartz, chert, and montmorillonite. Palygorskite has been observed as a clay mineral of brown desert soils in Syria (16) and terra rossa soils in the south of France (7), but there was no indication in these reports as to whether the mineral was a constituent of the underlying limestones. The presence of palygorskite in the clay fraction of this soil probably indicates relatively mild pedogenic processes leading to the genesis of the rendzina.

## MINERALOGY OF THE QUEEN'S PARK BORE.

To determine the extent of the palygorskite occurrence, other dolomites from the area were examined. Through the courtesy of the Queensland Geological Survey, samples from a deep bore, NS2/1944 (17), at Cribb's estate (NW. corner of portion 131, Queen's Park, Ipswich), were made available for study. This site is about 17 miles NNE. from the Ibis quarry. The bore was put down to a depth of 903 feet, and basalt occurred at the following depths: 125–130, 235–283, 333–388,

# 538 L. E. ROGERS, A. E. MARTIN, AND K. NORRISH ON

and between 414 and 760 feet, interlayered with soft brown mud. Between these flows dolomitic clays were found. The following gives the results of the X-ray analysis of the samples which were available:

- 120 feet: dolomite and montmorillonite with traces of palygorskite and kaolin.
- 209, 213, 215, 218 feet: palygorskite and dolomite.
- 220 feet: palygorskite, dolomite, and montmorillonite.
- 300, 308, 315 feet: palygorskite and dolomite.
- 384 feet: dolomite and palygorskite.
- 393 feet: dolomite, sepiolite, and trace of palygorskite.
- 790 feet: quartz and montmorillonite.
- 805 feet: quartz, montmorillonite, and kaolin.

Taking local variations into account, the dolomite deposits down to 393 feet appear to be very similar to those found in the Flinders quarry. It therefore appears that palygorskite and sepiolite may occur fairly widely in limestones of the Ipswich area.

### ORIGIN OF THE PALYGORSKITE.

Dunstan (18), in a report on the suitability of Flinders dolomite for cement manufacture, considered that the dolomite deposit was formed by a combination of lime from local calcareous sandstone, with magnesia from decomposed basalt. It is now considered, however, that the sandstone is non-calcareous. Nevertheless, there seems no reason why both the calcium and magnesium could not have come from the weathering of the basalt. The tropical weathering of basalt consists largely in the removal of alkali and alkaline earth metals and silicon. Iron and aluminium, as shown by their concentration in tropical soils forming from basalt, tend to be retained. In the present instance, the calcium, magnesium, and silicon from the basalt appear to have been deposited in lakes as dolomite, sepiolite, and chert. Subsequent additions of aluminium probably altered much of the sepiolite to palygorskite.

Longchambon (19) has observed that palygorskite appears to be formed by the alteration of pyroxenes and amphiboles, and in a later paper (12) he proposed that palygorskite is derived from sepiolite by the isomorphous replacement of magnesium by aluminium. Although palygorskite and sepiolite appear to be related they are not isostructural, and more work, particularly on the structure of sepiolite, will be necessary before the relationship of these two minerals is understood. Heystek and Schmidt (8) suggest that, in the Transvaal deposit, palygorskite has been derived from montmorillonite. There is no evidence at the Mt. Flinders deposit supporting this hypothesis and it appears that, in the Ipswich area, palygorskite is formed from sepiolite.

Acknowledgements.—The authors wish to acknowledge valuable discussions with Professor W. H. Bryan and Dr. Dorothy Hill (Geology Department, Queensland University); and to thank Mr. C. C. Morton (Queensland Government Geologist, Department of Mines, Queensland) and Mr. T. D. Dimmick (Department of Mines, Queensland) for valuable discussions, allowing access to data, and the bore samples from Cribb's estate. Mr. R. T. McGeoch, owner of the Ibis dolomite quarry, is thanked for his co-operation and assistance in supplying samples.

#### References.

- CAILLÈRE (S.) and HÉNIN (S.), X-ray identification and structures of clay minerals. Edited by G. W. BRINDLEY. Mineralogical Society, London, 1951, p. 234.
- 2. BRINDLEY (G. W.) and McEWAN (D. M. C.), Structural aspects of the mineralogy of clays and related structures. Ceramics: A Symposium. British Ceramic Soc., London, 1953, p. 15.
- 3. JENSEN (H. J.), Notes on the geology of the Mt. Flinders and Fassifern districts, Queensland. Proc. Linn. Soc. N.S.W., 1909, vol. 34, p. 67.
- 4. JONES (O. A.), The Tertiary deposits of the Morton district, S.E. Queensland. Proc. Roy. Soc. Queensland, 1926, vol. 38, p. 23.
- DAVID (T. W. E.), The Geology of the Commonwealth of Australia. London, 1950, vol. 1, p. 545.
- KERR (P. F.) and KULP (J. L.), Reference clay localities—United States. Reference clay minerals; A. P. I. Research Project, 49; Preliminary Report, 1951, no. 2, pp. 95–98. [M.A. 11–169, 12–212.]
- MICHAUD (R.), CERIGHELLI (R.), and DROUINEAU (G.), Sur les spectres de rayons X des argiles extraites de sols méditerranéens. Compt. Rend. Acad. Sci. Paris, 1945, vol. 222, pp. 94–95.
- HEYSTEK (H.) and SCHMIDT (E. R.), The mineralogy of the attapulgitemontmorillonite deposit in the Springbok Flats, Transvaal. Trans. Geol. Soc. South Africa, 1954, vol. 56 (for 1953), pp. 99, 115.
- BRADLEY (W. F.), The structural scheme of attapulgite. Amer. Min., 1940, vol. 25, pp. 405-413. [M.A. 8-81.]
- KAUFFMAN (A. J.), Fibrous sepiolite from Yavapai County, Arizona. Amer. Min., 1943, vol. 28, pp. 512-520. [M.A. 9-123.]
- LONGCHAMBON (H.), Sur les propriétés caractéristiques des palygorskites. Compt. Rend. Acad. Sci. Paris, 1936, vol. 203, pp. 672–76. [M.A. 7–100.]
- Sur les caractéristiques des palygorskites. Compt. Rend. Acad. Sci. Paris, 1937, vol. 204, pp. 55-58. [M.A. 7-101.]
- MIGEON (G.), Contribution à l'étude de la définition des sépiolites. Bull. Soc. Franç. Min. 1936, vol. 59, pp. 6-134. [M.A. 6-477.]
- DWYER (F. P.) and MELLOR (D. P.), An X-ray study of opals. Journ. Roy. Soc. N.S.W., 1934, vol. 68, pp. 47-50. [M.A. 6-8.]

### 540 L. E. ROGERS, A. E. MARTIN, AND K. NORRISH: PALYGORSKITE

- GRUNER (J. W.), Abundance and significance of cristobalite in bentonites and fuller's earth. Econ. Geol., 1940, vol. 35, pp. 867–875. [M.A. 8–83.]
- 16. MUIR (A.), Notes on the soils of Syria. Journ. Soil Sci., 1951, vol. 2, pp. 163-181.
- Queensland Dept. of Mines, Published log of the Ipswich bore. Queensland Govt. Mining Journ., 1953, vol. 54, p. 361.
- DUNSTAN (B.), Queensland Portland Cement Company's deposit at Flinders and Gore. Queensland Govt. Mining Journ., 1913, vol. 14, p. 187.
- LONGCHAMBON (H.), Sur les constituants minéralogiques essentiels des argiles, en particulier des terres à foulon. Comp. Rend. Acad. Sci. Paris, 1935, vol. 201, pp. 483-485. [M.A. 6-236.]