## Chlorophaeite in the dolerites (tholeiites) of Dalmahoy and Kaimes Hills, Edinburgh.

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The name chlorophaeite was given by John Macculloch<sup>1</sup> in 1819 to a mineral exhibiting striking colour change on exposure which he found at Craig nan Stàrdean (=Sgùrr Mòr) in the island of Rum. Sixty years later Professor Heddle<sup>2</sup> visited the type locality and redescribed the mineral, giving for the first time chemical analyses. He also noted an occurrence of the mineral in Canna. In 1908 A. Harker<sup>3</sup> showed that the rock which contained the chlorophaeite belongs to the mugearites.

Records of chlorophaeite are not always trustworthy since the term has been used somewhat loosely. Professor Heddle (loc. cit., p. 88) confirmed the occurrence at the Giant's Causeway, Co. Antrim, first recorded by Greg and Lettsom in their Manual of Mineralogy. Chlorophaeite is frequently mentioned by S. Allport<sup>4</sup> as a decomposition product of Carboniferous dolerites, and from his descriptions it seems clear that in several cases his 'chlorophaeite' is identical with the type mineral. J. D. Dana<sup>5</sup> accepted as chlorophaeite a mineral from the Faroe Islands analysed by Forchhammer, C. T. Clough<sup>6</sup> recorded two occurrences of chlorophaeite in vesicular basalts in the Cowal district of Argylshire. Chlorophaeite has been described by Solias and McHenry<sup>7</sup> from a basalt at Bunowen

<sup>1</sup> J. Macculloch, A description of the Western Isles of Scotland, 1819, vol. 1, p. 504.

<sup>2</sup> M. F. Heddle, Trans. Roy. Soc. Edinburgh, 1880, vol. 29, p. 84.

<sup>8</sup> A. Harkor, The geology of the small isles of Inverness-shire. Mem. Geol. Survey Scotland, 1908, p. 132.

<sup>4</sup> S. Allport, Quart. Journ. Geol. Soc. London, 1874, vol. 80, p. 529.

<sup>5</sup> J. D. Dana, System of Mineralogy, 5th edit., 1868, p. 510.

<sup>6</sup> C. T. Clough, Geology of Cowal. Mem. Geol. Survey Scotland, 1897, pp. 130, 170.

<sup>7</sup> W. J. Sollas and A. McHenry, Trans. Roy. Irish Acad., 1896, vol. 30, p. 742.

Tower in Galway; and the 'hullite' of E. T. Hardman<sup>1</sup> from Carnmoney Hill, near Belfast, is in all probability a variety of the same mineral.

The dolerites of Dalmahov and Kaimes Hills are well known through the descriptions given by S. Allport (loc. cit., p. 555), A. Geikie, <sup>2</sup> J. J. H. Teall,<sup>3</sup> and J. S. Flett,<sup>4</sup> and Flett has emphasized their unique character when compared with other Carboniferous dolerites of the Midland Valley of Scotland. In the course of a re-investigation of these dolerites undertaken by the writers it has been found that they are exceedingly rich in typical chlorophaeite. The mineral occurs throughout the sill, which shows marked textural and mineralogical variations, but it is most abundantly developed in the coarser modification where it makes up 15% or more of the rock. On a freshly fractured surface it appears as bright olive-green patches with a glassy lustre which suggest fresh olivine, but the colour of the mineral changes rapidly on exposure-first to a dark-green and finally to black with a pitch-like lustre. The finer-grained matrix of the rock at the same time darkens in colour in such a way as to make one suspect the presence there also of the same mineral. On weathered surfaces the mineral loses its lustre and becomes chocolate-brown in colour. Detailed description of the varying distribution of the chlorophaeite is reserved for a paper which will deal with the petrography of the dolerites. Meanwhile it may be noted that much of the mineral occurs in a fashion suggestive of the infilling of vesicular cavities; in a pegmatitic modification of the rock it appears in curious isolated groups of thin parallel veinlets; less frequently it forms thicker veins up to several inches in length. In thin section it is seen that the vesicular patches (fig. 1) occur usually in association with areas of intersertal mesostasis, and frequently the central chlorophaeite areas are surrounded by a rim of 'chlorite'. Much of the microscopic chlorophaeite is found as pseudomorphs after olivine, and it is seen to occur also interstitially in varying amount. The colour of the mineral in thin section varies from pale-green in very fresh rock, through darker shades of green and brownish-green to red in slices cut from surfaces which have been long exposed to weathering. Not infrequently the mineral is crowded with minute tubular bodies simulating micro-organisms (fig. 2). When the dolerite has been changed to 'white

<sup>&</sup>lt;sup>1</sup> E. T. Hardman, Proc. Roy. Irish Acad., 1878, ser. 2, vol. 3, p. 161; Rep. Brit. Assoc. (48th meeting, Dublin, 1878), 1879, p. 542.

<sup>&</sup>lt;sup>2</sup> A. Geikie, Trans. Roy. Soc. Edinburgh, 1879, vol. 29, p. 518.

<sup>&</sup>lt;sup>3</sup> J. J. H. Teall, British Petrography, 1888, p. 190.

<sup>&</sup>lt;sup>4</sup> J. S. Flett, The neighbourhood of Edinburgh. Mem. Geol. Survey Scotland, 1910, p. 291.

trap' the chlorophaeite is completely replaced by areas of carbonates in which these tubules can still be recognized. In partially altered rock the associated 'chlorite' seems to be replaced by carbonates more readily than the chlorophaeite.

The larger patches of chlorophaeite have a mamillated surface and show a laminated internal structure. The streak is brownish; fracture markedly conchoidal; hardness about  $1\frac{1}{2}$ ; density  $1.81 \pm .$  In Dana's 'System of Mineralogy' and in most text-books chlorophaeite is said to



FIG. 1.

possess cleavage in two directions. Cleavage, however, is not mentioned by Macculloch or Heddle and is certainly wanting in all the materials (including that from the type locality) examined by the writers.

Nearly all the chlorophaeite at Dalmahoy and Kaimes is isotropic, but it occasionally consists in part of small fibres polarizing slightly, as noted by Lacroix <sup>1</sup> in the 'hullite' of Carnmoney Hill. In a few instances we have noted the development along the fractures of a scaly chloritic mineral which has grown apparently at the expense of the original substance. Tested by immersion in oils of known refractive index the freshest

<sup>1</sup> A. Laeroix, Bull. Soc. Franç. Min., 1885, vol. 8, p. 432.

FIG. 2.

FIG. 1. Chlorophaeite patches in delerite.  $\times$  46. FIG. 2. Chlorophaeite showing structures simulating micro-organisms.  $\times$  200.

chlorophaeite was found to have a refractive index of  $1.498 \pm .$  It is attacked rapidly by cold hydrochloric acid, leaving a residue of gelatinous silica.

The analysis by W. H: Herdsman shown in column A was made on material carefully separated from the larger patches in the rock of Ravelrig quarry, Dalmahoy. We quote for comparison Heddle's analysis (I) of chlorophacite from Sgurr Mor, Rum, and Hardman's analysis (II) of 'hullite' from Carnmoney Hill, Pelfast. No. II a is a recalculation of no. II with total H<sub>2</sub>O given the same value as in A.

|                                |     |        | А.    | Ι.     | 11.    | II a. |
|--------------------------------|-----|--------|-------|--------|--------|-------|
| $SiO_2$                        |     |        | 32.95 | 36.00  | 39.437 | 32-35 |
| TiO <sub>2</sub>               |     | •••    | 0.62  | -      |        | _     |
| $Al_2O_3$                      |     |        | 5.40  |        | 10.350 | 8.49  |
| Fe <sub>2</sub> O <sub>3</sub> |     |        | 12.37 | 22.80  | 20.720 | 17.00 |
| FeO                            |     |        | 9.18  | 2.46   | 3.699  | 3.03  |
| MnO                            |     |        | 0.33  | 0.50   | trace  | trace |
| MgO                            |     |        | 4.75  | 9.50   | 7.474  | 6.13  |
| CaO                            |     | •••    | 3.05  | 2.52   | 4.484  | 3.68  |
| Na <sub>2</sub> O              |     |        | 1.68  | trace  |        |       |
| $K_2O$                         | ••• |        | 0.36  | trace  | -      | —     |
| H <sub>2</sub> O at 105°C      |     |        | 23.90 | *      |        |       |
| $H_2O + 105^{\circ}C.$         |     | 5.20 § | 26.46 | 13.618 | 29.10  |       |
|                                |     |        | 99.79 | 100.24 | 99.782 | 99-78 |

A. Chlorophaeite from Ravelrig quarry, Dalmahoy; Analyst, W. H. Herdsman.

I. Chlorophaeite from Sgurr Mor, Rum; Analyst, M. F. Heddle, 1880.

II. Hullite from Carnmoney Hill, Belfast; Analyst, E. T. Hardman, 1878.

II a. Recalculation of no. II with  $H_2O$  as 29.10 %.

\* Loses 19-227 at 100°C.

Chlorophaeite is always amorphous. Consideration of the values of its refractive index, specific gravity, and hardness in relation to its chemical composition clearly exclude the possibility of its being a glass.<sup>1</sup> Its physical and chemical characters, on the other hand, suggest strongly that the mineral is a 'colloid'. Lacroix (loc. cit.) has expressed the opinion that the 'hullite' of Carnmoney Hill, which we regard as a variety of chlorophaeite, is of a colloidal nature. The mamillary habit together with the laminated or scaly and occasionally spherulitic characters bring it under the 'minerals of colloform structure' of Rogers.<sup>2</sup> The occurrence

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<sup>&</sup>lt;sup>1</sup> See W. O. George, The relation of the physical properties of natural glasses to their chemical composition. Journ. Geol., 1924, vol. 32, p. 353.

<sup>&</sup>lt;sup>2</sup> A. F. Rogers, Journ. Geol., 1917, vol. 25, p. 518. [Min. Abstr., vol. 1, p. 378.]

of structures simulating micro-organisms (fig. 2) recalls the frequent presence of these in artificial gels.<sup>1</sup> In the present case the possibility of organic origin does not of course arise. The isotropic character of chlorophaeite cannot be questioned, and the fact that it sometimes shows anomalous double refraction is in keeping with the character of many gel minerals.<sup>2</sup> The chlorophaeites from different localities have the same *approximate* chemical composition while not attaining the *definite* chemical composition of crystalline minerals. The content of water is very high but shows considerable variation. Experiments to determine the dehydration curve might yield interesting results. Worthy of note, too, in the present connexion is the fact that the chlorophaeite of Dalmahoy loses 23.90% of H<sub>2</sub>O at 105° C. without any sign of decrepitation.

The most striking character of chlorophaeite is the rapidity with which it changes colour when first exposed—a property which gives a ready means of distinguishing it from other 'chloritic' minerals. The complete change from pale olive-green to black takes place in ninety minutes; the first stage, from pale to dark green, is very rapid, occupying only fifteen minutes. Professor Heddle (loc. cit., p. 86) considered that this phenomenon was due to molecular change, A. Harker (loc. cit., p. 133) regarded it as physical rather than chemical, while C. T. Clough (loc. cit., p. 130) speaks of the mineral as changing colour when exposed to light. The following experiments indicate rather that the change is due to oxidation. A freshly broken piece of the rock rich in chlorophaeite was placed in an atmosphere of carbon dioxide. After four hours the colour change was scarcely perceptible. This experiment shows that the rapid change in colour is inhibited by the absence of oxygen, and, since the experiment was conducted in bright sunlight, it indicates also that light is not the cause. The change from pale-green to black was induced artificially by heating a fragment in the oxidizing part of a Bunsen-flame for about thirty seconds; on prolonged heating, the chlorophaeite assumed the reddish-brown colour seen in the natural rock along joint-planes and on surfaces long exposed to weathering. The experiments demonstrate that the chlorophaeite retains its original colour when kept in a non-oxidizing atmosphere and changes colour rapidly in the presence of oxygen. The extreme rapidity of the first natural colour change from pale to dark green suggests the action of a catalytic agent, and in this connexion the presence of a small percentage of manganese oxide may be significant.

<sup>1</sup> See A. Scott, Fourth Report on Colloid Chemistry, Brit. Assoc. Adv. Sci. 1922, p. 214. [Min. Abstr., vol. 2, p. 297.

<sup>2</sup> See A. Scott, loc. cit., p. 216.

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It may be of interest to note here several other new records of chloro-A specimen of dolerite in the Edinburgh University collection phaeite. labelled 'Burntisland Harbour' is richer in chlorophaeite than any rock we have examined. So far we have not succeeded in getting the chlorophaeite-rich material in situ, but the mineral is present in considerable amount in slices of the lowest and middle sills of Burntisland. Chlorophaeite has been noted also in the dolerite (tholeiite) of John's Burn, Balerno, and it is common as a vesicle mineral in the basalt of the Lion's Haunch, Arthur's Seat. In the Heddle collection of thin slices in University College, Dundee, typical chlorophaeite is present in dolerites from the Ascrib Island, Skye, and from the rock of Umaolo, south-west of Canna, and in a trachybasalt, labelled Killellan, presumably from the Carboniferous lava belt of southern Kintyre. We have observed the mineral also in a tholeiite of Salen type from the shore at Pennyghael, Mull [Geological Survey collection (14541)].<sup>1</sup> Mrs. Janette F. P. Robertson has sent us specimens of two chlorophaeite-bearing tholeiites; one occurs as a sill on the shore between Ganavan and Dunstaffnage Castle, Oban, the other as a dike at Rudha-na-Lice, Kerrera.

We are indebted to Dr. H. H. Thomas and Mr. E. B. Bailey for their kindness in allowing us to compare our rock slices with Geological Survey slices of rocks from Mull, Rum, and Canna, and to Mr. Innes of St. Andrews University for an opportunity of examining the chlorophaeite sections from the Heddle collection in University College, Dundee. We wish also to thank Professor Charlesworth of Belfast who sent us specimens of the basalt of Carnmoney Hill.

<sup>1</sup> Tertiary and post-Tertiary geology of Mull. Mem. Geol. Survey Scotland, 1924, p. 285.