On some chloritic minerals associated with the basaltic Carboniferous rocks of Derbyshire.

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[Read June 15, 1926.]

THE occurrence of chloritic minerals as infillings of vesicular cavities in volcanic rocks is very common in rocks of all geological ages. Numerous chlorites have been described and analysed, but their classification and nomenclature are complicated by the fact that, as in the case with other hydrous alumino-silicates such as zeolites and clay minerals, the chlorites present a great variety of chemical compounds, usually of indefinite composition.

M. F. Heddle,¹ whose work on Scottish minerals is so very extensive, was the first to attempt the classification of chlorites according to their genesis. His classification is as follows:

(1) Chlorites—usually markedly crystalline, not decomposed by hydrochloric acid, principally occurring in metamorphic and sedimentary rocks.

(2) Saponites—usually cryptocrystalline or amorphous, readily decomposed by hydrochloric acid, occurring as products of decomposition of basic volcanic rocks.

A later classification of the chlorite group by G. Tschermak² bears a general resemblance to the foregoing, his orthochlorites and leptochlorites corresponding respectively with the chlorites and saponites of Heddle.

The chlorites under discussion in this paper naturally fall into the second subdivision, i.e. leptochlorites or saponites. Some chlorites in

¹ M. F. Heddle, Chapters on the mineralogy of Scotland. VI. Chloritic Minerals. Trans. Royal Soc. Edinburgh, 1879, vol. 29, p. 55; Min. Mag., 1880, vol. 4, p. 45.

² G. Tschermak, Sitzungsber. Akad. Wiss. Math.-naturw. Cl. Wien, 1891, vol. 100, Abt. I, p. 29.

Derbyshire have already been noticed and described by H. C. Sargent¹ and C. S. Garnett²; and the present paper, although quite independent, proceeds along the same line of investigation. It deals mainly with a chlorite found in a decomposed basalt of Calton Hill, the remaining chlorites associated with the upper and lower lavas of Derbyshire receiving but a cursory description for the purpose of comparison.

Calton Hill (4 miles from Buxton on the Buxton-Bakewell road) was opened up some few years ago as a road-metal quarry, with the result that a most interesting geological section became exposed. Only a very brief account of this will be given here, as it will form the subject of a separate paper in the near future. In this section the compact and fresh basalt (quarried for road-metal) is seen to invade an extremely decomposed vesicular basaltic lava ('toadstone') as well as the underlying stratified volcanic agglomerate and tuff. In places the decomposed lava still rests on the upper surface of the stratified pyroclastic material, but deeper down in the quarry the compact basalt has apparently been intruded along the junction of the lava and the tuffs, and has broken off and caught up large masses of the decomposed lava in its midst. There are several of those large 'xenolitic ' masses in the compact basalt.³

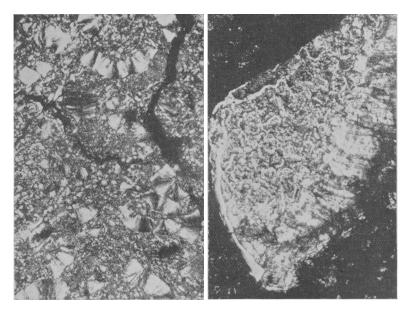
The decomposed basalt varies in colour from chocolate-brown to light brown shot with green. In places where it has been more exposed to weathering it is quite earthy and crumbles easily between the fingers. Under the microscope, this decomposed rock appears as a confused aggregate of chloritic material together with some specks of iron oxide and calcite. The original texture, looking like a well-erased palimpsest, only becomes visible under the crossed nicols. The felspar microlites, probably the last mineral to be affected by the process of decomposition, can be clearly observed under the crossed nicols. They are very turbid with ragged edges, but many of them still show the original twinlamellae and give almost straight extinction, a fact which suggests that the original felspar was of an alkaline variety, probably an oligoclase. The remaining ferromagnesian minerals are completely decomposed, but sometimes one can see clearly the outlines of a former olivine phenocryst.

¹ H. C. Sargent, On a spilitic facies of Lower Carboniferous lava-flows in Derbyshire. Quart. Journ. Geol. Soc. London, 1918, vol. 73 (for 1917), p. 11.

² C. S. Garnett, On a peculiar chlorite-rock at Ible, Derbyshire. Min. Mag., 1923, vol. 20, p. 60; The 'toadstone-clays' of Derbyshire. Min. Mag., 1923, vol. 20, p. 151.

³ The occurrence of a decomposed lava entrapped in a fresh olivine-dolerite sill at Ible, near Matlock, has been already recorded by C. S. Garnett (loc. cit.), and it may be possible to compare this occurrence with that of Calton Hill. Comparison of sections of this rock with sections of the decomposed spilitic basalt lava (the base of the upper lava at Knot Low) leads to the conclusion that it represents essentially the same rock, but in various stages of decomposition.

The decomposed basalt is highly vesicular, and the vesicles, which are more or less evenly distributed throughout the rock, are completely filled with a dark chloritic mineral. The latter, much more compact



F1g. 1.

FIG. 2.

- Fig. 1. Micro-section of chlorite, spherulites in groundmass, from Calton Hill, Derbyshire. Crossed nicols. ×100.
- F16. 2. Micro-section of chlorite, filling a vesicle and partly replaced by calcite, from Miller's Dale, Derbyshire. $\times 25$.

than the rock in which it is embedded, can easily be separated by hand in the form of almond-shaped or nut-shaped nodules. At first sight the rock resembles a volcanic tuff with devitrified glassy lapilli embedded in it. Several blocks of decomposed lava containing abundant vesicular infillings were carefully crushed by hand and the chloritic nodules separated from the groundmass. The weight of each portion was separately determined and the following proportions were obtained : chloritic nodules 12.89, decomposed basalt 87.11, total 100.00. The specific gravity of the whole rock (groundmass + chlorite) is 2.34, and that of the groundmass (including the pore-space) 2.33; several determinations of the sp. gr. of the chlorite ranged from 2.386 to 2.396, giving an average of 2.393.

The chloritic nodules from the rock were afterwards graded according to size, and the number in each grade was counted. The result was a typical frequency distribution curve with a maximum at 0.6 mm. approximately, and with a sharp slope towards zero and a more gentle one in the opposite direction. This gives some idea of the size of the blow-holes of which the nodules are the exact casts, and of their distribution in the lava. The nodules show a great variety in shape, those of the larger size being more irregular, those of the average size (2-10 mm.) almond-shaped, and those of the smallest size (below 2 mm.) spherical. There were also others dumb-bell shaped.

The colour of chlorite is dark green, passing to light green on the surface of the nodules, and bluish-green along cracks. The hardness is slightly over 2. Streak pale green. Greasy feel. Infusible before the blowpipe. Soluble in hydrochloric acid with the separation of flocculent gelatinous silica.

Under the microscope, the chlorite is pale green, and appears as an aggregate of fibrous spherulites (usually not complete) embedded in a fine groundmass also consisting of spherulites and sheaves of fibres, but of a much smaller size (fig. 1). Between crossed nicols fine second-order colours are shown. The fibres give straight extinction with positive elongation. Pleochroism is very weak or altogether absent. The refractive index of the aggregate (determined by the method of immersion, in sodium-light) was found to be 1.563 + 0.003.

The mineral was subjected to chemical analysis with the following results:

| | | Weight %. | | | | Molecular %. | | | |
|------------------------------|-------|-----------|-------|-----|-----|--------------|---|-------|--|
| SiO_2 | | | 35.92 | | ••• | 26.28 | | 26.28 | |
| TiO ₂ | ••• | ••• | nil | ••• | | — | | - | |
| Al_2O_3 | | | 12.20 | ••• | ••• | 5.25 | Ĵ | 7.34 | |
| Fe_2O_3 | ••• | ••• | 7.59 | ••• | | 2.09 | ſ | . 01 | |
| \mathbf{FeO} | ••• | | 4.66 | ••• | ••• | 2.85 | ٦ | | |
| MgO | | ••• | 21.82 | | | 23.80 | 7 | 28.08 | |
| CaO | | | 1.82 | ••• | ••• | 1.43 | J | | |
| CO_2 | ••• | •••• | 0.13 | ••• | ••• | | | | |
| $ m H_{2}O$ at 105° | | ••• | 6.50 | ••• | ••• | 15.86 | Ĵ | 38.30 | |
| ${ m H}_2{ m O}$ ign | ition | ••• | 9.20 | | ••• | 22.44 | 5 | | |
| | | | | | | | | | |
| | | | 99.84 | | | 100.00 | | | |

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The following approximate formula is derived from this analysis:

13H₂O.10R"O.2.5R"'₂O₃.9SiO₂,

or, disregarding the water lost at 105° C.:

 $7.5 H_2O$, 10R''O, $2.5 R'''_2O_3$, $9SiO_2$.

It is obvious that according to its chemical composition this chlorite may be placed in the group embracing such minerals as delessite, diabantite, ripidolite, berlauite, &c. Nevertheless, it differs from these minerals in certain respects, viz. its lower specific gravity and the absence of pleochroism. In its specific gravity it stands somewhere between the delessite-diabantite group and the saponite group. In certain respects it may be well compared with certain varieties of saponite, such as 'bowlingite' and 'cathkinite'.1 All these leptochlorites are typical 'colloform' minerals and probably pass by imperceptible gradations into one another. The degree of hydration is probably one of the principal factors regulating their morphological characters and their specific gravity, but the latter is also a function of the relative proportion of the heavier metallic oxides. Arranging in the following table certain minerals belonging to the group (serpentine and chlorophaeite being also added for comparison) according to the increasing proportion of water, we notice a gradual decrease in the specific gravity. The position of the Calton Hill chlorite is clearly seen in this table. Without introducing a new mineral name we may simply call it a variety of delessite.

| | | | | $H_{9}O$ | | | |
|------------------|--------------|---------------------|-----------|------------------|---------|----------|----------------------|
| Mineral. | Locality. | Author. | Sp. gr. | $(+\bar{R_2}0).$ | R''0. 2 | R‴203 | . SiO ₂ . |
| Serpentine | (theoretical | formula) | 2.20-2.70 | 9 | 13.5 | | 9 |
| Diabantite | (theoretical | formula) | 2.80 | 9 | 12 | 2 | 9 |
| Chlorite (no. 8) | Ible | Garnett | 2.52 | 9 | 10 | 2 | 9 |
| Chlorite | Darley Dale | Garnett | 2.79 | 10 | 11 | 2 | 9 |
| Ripidolite | Cape Wrath | Heddle | 2.823 | 12 | 12 | 3 | 9 |
| Delessite | St. Cyrus | Heddle | 2.652 | 12 | 13 | 2.5 | 9 |
| Chlorite | Calton Hill | Tomkeieff | 2.393 | 13 | 10 | 2.5 | 9 |
| Griffithite | California | Larsen & Steiger | 2.309 | 13 | 8 | 1.5 | 9 |
| Delessite | Dumbuck | Heddle | 2.598 | 14.5 | 12 | 3 | 9 |
| Berlauite | Berlau | Schrauf | · | 15 | 11 | 2.5 | 9 |
| Saponite | Perthshire | Heddle | 2.235 | 18 | 10 | 1.5 | 9 |
| Chlorophaeite | Dalmahoy | Campbell & Lunn | 1.81 | 27 | 5 | 2 | <u>9</u> |

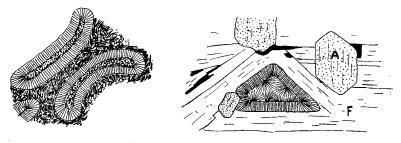
¹ M. F. Heddle, The Mineralogy of Scotland, 1901, vol. 2, p. 139.

Chlorites occurring in vesicles of lavas at other localities in Derbyshire.

The upper lava of Derbyshire is well exposed in Miller's Dale, where the limestone quarries in some places facilitate its study. Both the upper and the lower portions of this lava are extremely vesicular, and the latter was identified by Sargent as a spilite. In his paper (loc. cit.) dealing with spilites, Sargent also mentions some of the minerals occurring in the vesicles, including a fibrous chlorite. Examination of a section of this rock, from Knot Low, shows that, besides a great deal of rather turbid chloritic material in the groundmass, there is also a quite distinct, well-crystallized fibrous chlorite filling up the vesicles. In many places this chlorite is replaced by other minerals, such as calcite or quartz. As already mentioned, this rock is somewhat similar to that of Calton Hill, but is in a less advanced stage of decomposition.

The upper vesicular portion of the upper lava, as occurring in the limestone quarry to the south of the railway line, is quite different from that of Knot Low. It is light grey in colour, and apparently greatly calcified (the rock immediately above it is a limestone). Numerous lath-shaped felspars (oligoclase ?) are embedded in a semi-aphanitic groundmass, mainly composed of a dark green chlorite. Vesicles are filled with secondary calcite (chalcedony in places), but some of them still preserve the original chloritic infilling. This chlorite is dark green in colour with a dull lustre and hardness 2-3. Only very small fragments of this chlorite could be scraped out from the vesicles, but even in the purest of them one could detect the presence of calcite. After a short treatment of one of these fragments with cold hydrochloric acid, the specific gravity was determined by means of heavy liquids as This figure may be somewhat too high owing to the presence of 2.538.some calcite within the chlorite. An attempt was then made to determine the approximate amount of water. The results, expressed in round figures, are : H₂O at 105° C. 10 %, H₂O lost on ignition 20 %, total 30 %. Even taking into consideration a certain loss on ignition due to CO₂ derived from the calcite present in the chlorite, this still represents a high percentage of water.

Under the microscope, this chlorite appears much darker than the Calton Hill chlorite and possesses a totally different structure. Even under a low-power objective one can see clearly that it is formed of an aggregate of bacteria-like bodies imbedded in a semi-amorphous (cryptocrystalline ?) groundmass (fig. 2). Under a high-power objective the structure of these bacteria-like bodies is seen to consist of an elongated, sometimes dumb-bell-shaped core, composed of granular semi-amorphous green material, and surrounded by a layer of a fibrous white mineral (fig. 3). The groundmass is also composed of a similar granular stuff, together with very minute radiating anisotropic clusters of spherulites. The microstructure of this chlorite is somewhat similar to that of the chlorophaeite from Dalmahoy Hill near Edinburgh, described by R. Campbell and J. W. Lunn,¹ though the individual bacteria-like bodies in our chlorite are much larger than in the Dalmahoy Hill specimens. This fact and the large amount of water present, suggest that we have here a chlorite which, although not a typical chlorophaeite, may belong to the same group. The white fibrous mineral may be some variety of zeolite.



F1G. 3.

FIG. 4.

FIG. 3. Chlorite from Miller's Dale. Enlargement of bacteria-like bodies in fig. 2. $\times 130$.

FIG. 4. Palagonite from Miller's Dale, infilling spaces between felspar (F) and augite (A), $\times 330$.

Similar chlorite with a well-defined bacteria-like structure was also observed filling the vesicles of the top portion of the lower lava at Ravens Tor, near Miller's Dale.

Both the upper and the lower portions of the lava are affected by weathering. However, it was possible to obtain a fresh specimen of this lava from the middle portion, of which the outcrop can be found in some old disused quarries near Miller's Dale. In these the basalt weathers spheroidally and some of the cores of the spheroids are composed of compact dark grey basalt. Under the microscope, this basalt appears to be quite fresh, with the exception of olivine, which is completely serpentinized. Felspar apparently exists in two generations: felspar-laths (labradorite) and a more acid allotriomorphic felspar of a later stage of

¹ B. Campbell and J. W. Lunn, Chlorophaeite in the dolerites (tholeiites) of Dalmahoy and Kaimes Hills, Edinburgh. Min. Mag., 1925, vol. 20, p. 435. crystallization. Augite is present in the form of semi-idiomorphic granules, and iron-ore in the form of granules and rods. All lacunae between the felspar-laths and augite-grains are occupied by a certain amount of allotriomorphic felspar of the second generation and by a large quantity of a light brownish-green mesostasis. In certain places this mesostasis is seen to pass into, or encroach upon, the felspar of the second generation. This mesostasis consists entirely of anisotropic material in the form of a fibrous spherulitic aggregate, somewhat similar to the chlorite of Calton Hill. It is non-pleochroic, gives straight extinction along the fibres, shows bright polarization colours, and has a refractive index higher than Canada balsam. The walls of every lacuna are lined with a fibrous layer of this mineral, and a more or less irregular spherulitic aggregate fills up the remaining space (fig. 4). In places it is interpenetrated by rods of iron-ore. There is but little doubt that this substance is the so-called palagonite.

D. N. Wadia, in his work on a palagonite-bearing dolerite, states the opinion, 'that palagonite is not a definite mineral, but an amorphous decomposition product of variable composition formed *in situ* within the rock'.¹ He also found that in this particular rock palagonite was formed not only at the expense of glass alone, but also as a product of decomposition of the ferromagnesian constituents. In our case, however, all augite is perfectly fresh, as also the iron-ore. The palagonite of the Miller's Dale basalt must be, therefore, either the product of alteration of the original glassy mesostasis, or an autogenous product formed from the hydrated residual liquor during the final stages of the crystallization of the magma.

L. I. Fermor, in his most interesting work on Deccan basalts, has described many varieties of palagonite and secondary chlorite, and is of the opinion that the great part of the palagonite in the Bhusawal traps represents the original glassy mesostasis which has become devirified and transformed into an aggregate of chlorites (delessite or diabantite).

'Treated generally, palagonite may perhaps be regarded as a hydrous glassy substance of variable composition formed partly by hydration of the primary glass and partly at the expense of augite (?again largely hydration) and ironore, and with much more difficulty at the expense of felspar (? by replacement). In colour it ranges through orange and brown to brownish green and bright green, and the material of all colours may become "devitrified" and anisotropic in spherulites and concentric-radiate layers, with in all cases a positive elongation to the fibres. The clear orange and brown varieties, both isotropic and

¹ D. N. Wadia, Palagonite-bearing dolerite from Nagpur: suggestion regarding the nature and origin of palagonite. Rec. Geol. Survey, India, 1925, vol. 58, p. 342. anisotropic, constitute chlorophæite, whilst the anisotropic green form is probably identical with delessite or celadonite.'¹

It is quite possible that in many cases the chloritic palagonite may be formed from glass or augite, but there are certain facts which suggest that the palagonite in the Miller's Dale basalt is a primary and not a secondary mineral. As already mentioned, all the augite in this basalt is perfectly fresh and therefore this source of origin is excluded. The palagonite is more or less uniform throughout the rock and not a trace or indication of any original glassy substance is seen. This, together with the presence of a regular radiate layer lining the walls of every lacuna, precludes the possibility that palagonite is a product of devitrification of glass, such as we may observe in many rhyolites and pitchstones. The original glass has either been completely dissolved and redeposited in the form of a fibrous aggregate; or, what the present author thinks to be more probable, the glass has never been formed at all and the palagonite is an autogenous mineral formed during the final stages of the consolidation of the lava.

The external resemblance between the palagonite in the central portion of the upper lava and the chlorite infilling the vesicles at its peripheries (Calton Hill chlorite) suggests that they may be genetically related. The albitization of the peripheral portion of the lava flow and the infilling of vesicles with fibrous chlorite (and in some cases by albite, as mentioned by Sargent) were certainly prior to the intrusion of the compact basalt of Calton Hill (late Carboniferous or Permian), and therefore long before the present agents of weathering came into action. The facts supporting this contention are as follow:

(1) The black compact basalt of Calton Hill is perfectly fresh, while the enclosed lava is greatly decomposed.

(2) Observations of the products of atmospheric weathering of Derbyshire lavas fail to reveal the formation of the finely radio-spherulitic type of chlorite; on the contrary this type of chlorite tends to be destroyed and replaced by an earthy chlorite greatly contaminated by brown hydrated iron oxides. (These lavas on weathering, as was shown by Garnett and also observed by the present author, are gradually losing the ferromagnesian constituents, and pass first into a green clay and finally into a white clay which consists mainly of a hydrous aluminosilicate).

¹ L. L. Fermor, On the basaltic lavas penetrated by the deep baring for coal at Bhusawal, Bombay Presidency. Rec. Geol. Survey, India, 1925, vol. 58, p. 183.

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(3) In places where the upper portion of the lava is seen *in situ* below the limestone, there is a tendency for the chlorite infilling the vesicles to be replaced by calcite, quartz, &c., without any formation of secondary chlorite.

(4) Fragments of dark green chlorite, similar to that found in the decomposed lava at Calton Hill and in the vesicles of the upper and the lower lava at Miller's Dale, were found among the stratified tuffs underlying the lava at Calton Hill. These fragments of chlorite were obviously derived from an underlying lava (probably the lower lava) during the volcanic outburst preceding the eruption of the upper lava.

We may surmise, therefore, that the albitization and chloritization of the lava occurred at a later stage in the crystallization of the magma, and the infilling of vesicles soon after its final solidification, probably under the influence of hot magmatic solutions (autopneumatolysis).¹

The chlorites found in the basaltic lavas of Derbyshire can thus be classified according to their genesis, as follows:

(1) Primary chlorite (palagonite), found in the mesostasis of lavas.

(2) Chlorite of the post-volcanic phase (autopneumatolitic), found infilling vesicles.

(3) Secondary chloritic material, a product of atmospheric weathering, found in abundance in the crust of weathering of lavas and in the green clays resulting from such weathering.

I wish to express my thanks to Mr. H. C. Sargent, who kindly sent me some specimens of the spilitic lavas of Derbyshire, and also to Miss M. Illington, B.Sc., who has assisted me in writing up this paper.

1 O. O. Baklund (H. G. Backlund), The basalt of Bolshezemelsck tundra, Trav. Musée Géol. Pierre le Grand, Acad. Sci. St. Pétersbourg, 1911, vol. 4 (for 1910), pp. 75-97, has described a chloritic substance occurring in amygdules and mesostasis of a basalt from Siberia. It is dark brownish green in colour, feebly double-refractive and radial-fibrous in structure. In the mesostasis it can be sharply distinguished from the glass. In its chemical composition it resembles hullite. The author of that paper thinks that it is not a secondary product infilling vesicles, nor a product of alteration of glass, but that its origin could be explained by the assumption that 'the magma after the crystallization of felspar (and augite) has separated into two immiscible portions, so that one of them solidified as glass containing some skeletal crystals of magnetite formed before or simultaneously with the glass, while the remaining portion of the magma, which contained the greater, part of the water vapours originally present in the liquid magma, acquired an abnormal composition and solidified in a colloidal state, forming a mixture of hydrogels with some adsorbed oxides' (pp. 93-94). This hypothesis advanced by O. O. Baklund can be offered as another plausible explanation of the genesis of amygdaloidal and mesostatic chlorite in Derbyshire lavas.