On the Micas of the Three Rock Mountain, Co. Dublin.

By Professor J. P. O'Reilly, Roy. Coll. of Science, Dublin.

[Read April 14th, 1896.]

THE micas presented by the granites of the Co. Dublin have been analysed by Haughton, and determined by him to be margarodites and lepidomelanes (see *Proc. Roy. Irish Ac.* Vol. VI. 1855, pp. 176-79, and *Quart. Journ. Geol. Soc.* Vol. XV. 1859, p. 129). In this latter paper he says:—"In my first paper on the Granites of Leinster (*Quart. Journ. Geol. Soc.* Vol. XII. 1856, p. 171), I have mentioned the black mica which is found accompanying the white margarodite of the Leinster granite in small flakes, and noticed the curious fact that these flakes are sometimes physically embedded in the plates of white mica without injuring their fissility or lustre, but always effecting a reduction of about 20° in the angle between the optic axes of the latter."

In the first mentioned paper ("On the Chemical Composition and Optical Properties of the Mica of the Dublin, Wicklow and Carlow Granites") he thus describes the first specimen examined:—"No. 1. Mica from the Three Rock Mountain, Co. Dublin; gray, transparent, containing specks or flakes of a bronze-coloured or black mica."

He further adds, when speaking of the deviation of this mica from the formula found to result from his analysis:—"The mica which deviates the most from this formula is the mica of the Three Rock Mountain, and this deviation may possibly be due to the presence of grains of black mica, which also occurs in the mass of the granite, and of which I was unable to obtain a sufficient quantity for chemical or optical examination; the quantity of protoxides in the Three Rock Mica is somewhat in excess of that required by the formula."

The author of the present paper having frequently had occasion to pass by the road which leads over the east end of the Three Rock Mountain into Glencullen, had his attention drawn to the micas which show themselves in the stones and boulders forming the walls and fences of the fields along the road. These micas are relatively large, very pearly in lustre, and almost without exception, when large, show a zonal

structure due to the linear arrangement of the bronze and brown specks or flakes, and very generally the central part of the mica is filled with these same flakes or patches, but with larger dimensions. Struck by this character, and desirous of examining the relations of the constituent parts, I collected from time to time a large number of these micas from the stones and boulders, and also from a portion of a mica band or vein which occurs on the north side of the mountain, in the midst of the stone quarries which extend over this face.

I proposed to mechanically separate the white or colourless portion of the micas from the bronze or black specks, and to have each part thus separated chemically examined. The task of separation was undertaken by Miss Mary Robertson, M.A., then engaged in research work in the laboratory of the Royal College of Science, under the direction of Professor Hartley; and after some weeks of tedious and careful picking, enough of the separated materials was obtained to allow of the proposed analysis being undertaken. The following is the Report which she furnished as to the result:—

"Chemical Laboratory,

"Roy. Coll. of Sci., Dublin, May 4th, 1889

"Sir,—With regard to the sample of mica submitted to me for analysis, I have made the following observations. The mica is essentially white or colourless, but contains black specks, generally occurring in the centre of the crystal, *i.e.* in hexagonal shape, and leaving the centre comparatively clear. In cleaving the mica, black stains were often visible, coinciding in shape with a speck underneath, The specks usually broke away with comparative ease from the surrounding white portion. One black portion was found of rather larger size than usual, which had the hexagonal shape of the large crystals.

"In preparing for the analysis, the crystals were split, and the black specks separated and collected under the microscope. The white portion was also carefully collected, and freed from any black specks. Separate analyses were made of the two substances so obtained.

"The quantities available were so very small that only a quantitative analysis could be made; but in the course of this analysis search was made for substances which might occur.

"I find that the white portion contains as follows:—

Weight taken for analysis—for bases	...	1·1056 grm.
,, ,, ,, ,, for alkalies	...	0·6075 ,,
Loss by ignition ...	...	4·710 per cent.
SiO_2	...	39·414 ,,
(Cuprous Oxide) Cu_2O	...	3·654 ,,
Al_2O_3	..	33·738 ,,
Fe_2O_3...	...	1·418 ,,
MnO	...	1·244 ,,
MgO	...	1·344 ,,
CaO	..	0·955 ,,
Li_2O	...	0·642 ,,
Na_2O	...	2·675 ,,
K_2O	..	9·430 ,,
Total	...	99·224 ,,

"An analysis of the black mica was also made, but copper and iron seemed to be present in varying quantities, so that different portions gave varying results.

"It was then found that on treating the dark specks with hydrochloric acid, the colouring matter dissolved, leaving a residue of white mica. A portion so treated gave on analysis:—

Residue insoluble in HCl		45·14 per cent.
Ferric Oxide, containing traces of Mn	...	45·14 ,,
Cuprous Oxide	...	9·78 ,,
(The amount taken for analysis having been 0·0101 grm.)	...	100·06 ,,

"The copper was very carefully estimated in another portion of the dark substance, and found to amount to 22·5 per cent. Cu_2O; the alkalies in the same portion were 13·70 per cent., estimated as soda.

"The iron was estimated in another portion of the dark substance, and found to amount to 25·35 per cent. of Fe_2O_3. Hence the copper and iron appear to occur in varying proportions in the dark substance.

"A portion of the loss by ignition is due to *hydrofluoric acid*, traces of which were found; none was observed in the substance after ignition, though carefully tested for.

"A portion of the original substance, containing both the white and the black bodies, was used to estimate the combined water, and gave the following result:—

Water driven off at 100°C.	0·2506	per cent.
,, ,, ,, between 100° and 240° ...	0·1058	,,
Thus showing that the loss on heating to 240°C. was	0·3564	,,

"(Signed) MARY W. ROBERTSON, M.A."

Comparing this analysis with that of Dr. Haughton already referred to (given in *R. Irish Ac. Proc.* Vol. VI. 1855, p. 177), and which is mentioned as "No. 1, Mica from the Three Rock Mountain, Co. Dublin; gray transparent, containing specks or flakes of a bronze coloured or black mica," the following differences appear—

	Miss Robertson's.	Dr. Haughton's.
SiO_2 ...	39·414 per cent.	43·47 per cent.
Al_2O_3 ...	33·738	31·42
Fe_2O_3 ...	1·418	4·79
CaO ...	0·955	1·38
MnO ...	1·244	——
MgO ...	1·344	1·13
K_2O ...	9·430	10·71
Na_2O ...	2·675	1·44
Li_2O ...	0·642	——
Cu_2O ...	3·654	——
Loss by ignition	4·710	5·43
	99·224	99·77

It may be remarked that the amount of SiO_2 in the analysis of Miss Robertson is lower by 4·056 per cent. than that of Haughton, and lower than any example of muscovite cited by Dana in the edition of 1892, p. 617, wherein the extreme values for SiO_2 are 49·34 per cent. and 43·67 per cent. Assuming Miss Robertson's determination of the silica to be quite correct, the amount found, 39·414, would correspond rather with a biotite, and in this respect would harmonise with Haughton's remark as to the reduction of the angle of the axes. The other values correspond fairly well; what however is remarkable is the high value for the

cuprous oxide, Cu_2O = 3·654 per cent. The element copper is not unknown, as a constituent of the micas, since in the list given by Dana it occurs in two cases, one amongst the analyses of damourites, &c., and the other in the analysis No. 61 of "*Œllacherite*" from the Pfitsch-thal with an amount of CuO = 0·31. In both cases the copper is given as cupric oxide. However, there is evidence that it may occur in relatively large quantities in certain minerals of the chloritic group, as is shown by Sterry Hunt, in his *Mineral Physiology*, 1886, p. 357, where he describes, under the name of "Venerite," a mineral containing, according to the analysis of Hawes, 17·58 per cent. of CuO, and referred to the chlorites.

Assuming for the moment that the copper found in the Three Rock Mountain mica by Miss Robertson exists in combination with SiO_2, it is presumable that such a silicate of copper should to some extent influence the colour of the white mica, since no colourless silicate of copper so far is known. Now the samples analysed by Haughton as well as the material used by Miss Robertson seem to have been equally devoid of colour (macroscopically examined), and are described as being *gray and transparent*.

Under the microscope, however, most of these transparent gray and colourless muscovites of the locality mentioned show black specks, more or less minute, and for the most part round like blots of ink, or exceptionally somewhat hexagonal.

These minute specks may be tenorite (CuO), and the fact that, according to Jenzsch, the artificially prepared tenorite is rhombic and possesses a perfect basal cleavage would favour the presumption. They might equally be *melaconite*, which also presents itself in a scaly form, and occurs interlaminated with chlorite. The *melaconite* of Vesuvius is stated by Dana to be frequently hexagonal, and sometimes triangular in shape. The different forms presented by the black specks would best agree with this interpretation, and with other characteristics of the muscovites now considered.

It must be remembered that the specimens examined by Miss Robertson were from different points of the mountain, and that some particular point, say the mica vein mentioned, may really have furnished the copper samples.

The muscovites of the Three Rock Mountain and vicinity present other characteristics which connect themselves with those already considered, and come out when thin cleavage plates are examined under the microscope. For the most part the plates show a zonal structure, the zones being mainly composed of irregularly bounded brown patches, sometimes showing

a rough hexagonal form with rounded corners and only rarely clearly defined hexagonal or triangular forms: these patches are evidently very thin and intermixed with the plates of muscovite, but so that the patches cover one the other quite irregularly as regards outline, giving rise thus to composite patches of quite jagged contour. With these brown patches and lying between them occur black specks and spots smaller in extent, evidently connected with the brown ones, generally round, sometimes fringed with a less black or very dark gray mineral; lastly, here and there in the majority of plates examined from the Three Rocks Mountain, but sparingly and quite microscopically appear what may be designated "blue micas" (?), which contrast markedly with the brown and black spots by the perfect geometrical regularity of their forms.

The largest individual specimen examined did not exceed 0·5 mm. in breadth, and generally they are quite microscopic but very distinct (see Pl. iv.). The predominant forms are seemingly perfect equilateral triangles, hexagons resulting from the truncation of the angles of such triangles, perfect hexagons and occasionally forms of rectangular shape or of an L shape pointing to the existence of rhombic cleavages in the mineral. Their colour presents all the shades of blue from faintly purple to most intense blue, such as Prussian blue or the cobalt blues of pottery ware; exceptionally a faint but distinct rose tint is met with, and more frequently the blue is so intense as to appear black. The contours are always strictly geometrical, and the angles formed by the sides perfectly sharp and well defined. The plates are evidently very thin, and may be seen, even in thinly cleaved micas, covering one another; they are translucent, and under polarised light they behave isotropically.

Apart from the colour, their form and their conditions of relation to the containing mica would favour the opinion of their being micas, but the colour, or rather colours, presented by them would lead to their being referred to one or other of the minerals characterised by blue colours. As regards the black triangular plates, there is every reason for connecting them with the black spots or patches already referred to, and consequently considering them as melaconite; on the other hand, it is reasonable to see in the blue triangular plates always present with the black ones a variety or an altered form of the same mineral, such as for instance a chrysocolla ($CuO.\ SiO_2+2aq$) altered from the melaconite or tenorite. This presumption would be in accordance with the translucence and low refrangibility of the plates, the forms and the analysis, but can only be taken as a presumption until further examination of them has fixed their

true nature; as, however, there are other minerals characterised by a blue colour and allied to the micas, it is necessary to examine whether one or other of them may not better correspond to the characters presented by the mineral in question. Dana mentions amongst such minerals Diphanite and Vaalite.

Considering, however, that *iolite* has been determined by Dr. Joly to exist in the granites of the neighbouring valley of Glencullen, distant from the Three Rock Mountain only about $1\frac{1}{2}$ mile (see *Sc. Proc. Roy. Dub. Soc.* 1886, Vol. V. part 2), and that the colour of the plates corresponds well in a number of cases with that of iolite (Berlin blue in different intensities), the question arises Do the other characteristics presented by the plates correspond to those shown by iolite? Certain of the angles of the apparently equilateral triangles were measured, and while one gave 60°, another more carefully handled gave 61°18′. Now this would rather point to a rhombic mineral, having a prism angle approaching 120°, as in the case of iolite, and $\infty P\breve{\infty}$ cleavage as presented by this mineral (see fig. c, Pl. VI.). Lastly, if there be supposed a composition plane parallel to ∞P, the triangular form presented by the mineral becomes intelligible (see fig. g, Pl. VI.), giving for the angle at the summit 60°50′, and for the two basal angles 59°35′. This twinning being assumed, an explanation is afforded of the little *notch* presented so frequently by the plates on one of the sides of the triangle, as shown in one of the figures (fig. a of Pl. VI.). Lastly, the fig. c same plate points to alterations along a section taken as $\infty P\breve{\infty}$, and so far confirms the rhombic character of the mineral. From the co-existence of the different characters it may reasonably be assumed that the mineral in question is "iolite" in a more or less altered state, and then, according to Dana, tending to the "division of the prism into plates parallel to the base." The largest of these plates met with was only 0·5 mm. broad, and is represented on fig. 2, Pl. IV. The notch referred to is here also observable, as also on many of the black triangles and hexagonal forms shown on Pl. IV., and seems to connect them so far with the blue plates.

The brown patches so characteristic of the micas, as indeed of many other muscovites, were studied by G. Rose (see *Monats-ber. der Acad. Berlin*, 1869, p. 339); he noted that generally the white colourless mica surrounds the brown ones. He concluded that the black to brown tablets were ironglance, while Dana and Brush considered the black plates to be magnetic iron, the red ironglance, and the yellow hydrated oxide (see Zirkel, *Elemente d. Mineralogie, von* C. F. Naumann, 1881, p. 571).

The black patches present themselves under two forms, or rather three:

regular triangles or hexagonal forms, perfectly opaque; blebs or blots equally opaque, but irregular in form, and frequently "dusted" or sprinkled, as it were, between the plates of mica; and lastly, round patches, grayish rather than black, the tint graduating in intensity from the centre to the circumference, as indicated on Pl. VII. These are remarkable in that the centre of figure is frequently marked by the presence of a microlite, perfectly transparent and colourless as a rule; seemingly of the same nature as the many similar microlites which show themselves in most of the mica plates examined. What the exact relation may be that seems to exist between the central microlite and the black patch has not been ascertained so far.

In all the micas examined, the presence of the rod-like voids which have been frequently noticed by most observers was recognised and in certain cases they appear filled with a product of decomposition having an earthy appearance of a yellowish colour.

The brown patches generally found in the centre of the mica plate, and having seemingly no relation of arrangement with the sides of the crystal, are frequently surrounded by a zone of smaller brown patches and brownish crystallites, generally forming a line parallel to the sides of the prism, and therefore having a rhombic or hexagonal outline. This zonal structure is markedly present in the micas from the east side of the Three Rock Mountain. Its general character is indicated by the enlarged drawing shown on Plate V., on which is also indicated the remarkable banded structure observable in the mica plate when held in a plane of about 45° with the line of vision, and then examined with a lens. These bands generally lie outside the zone of small brownish patches, and but rarely extend to the margin of the plate. They would seem to be connected with stages of growth of the mica crystal. The small brownish patches already referred to seem at first sight to have no relation of direction with the principal lines of the mica plate; but more carefully examined, they frequently show themselves as lying nearly perpendicular to the direction of the zone, just as crystals lining a cavity of a rock stand out more or less normally from the sides.

Amongst these small brownish patches occur frequently small prismatic crystals, quite regular in form, and presenting angles which would point to rhombic or monoclinic forms. Certain of them are markedly dichroic, and show strong absorption—so much so indeed that sections which are nearly invisible when in one section-plane of the nicol, become nearly black or very intense brown when brought into the other. A certain number of them show reddish-brown in one plane of the nicol and

greenish in the other, tints characteristic of hypersthene, but the absorptions are quite equal to those presented by the hornblende series. No indication, however, of a hornblende cleavage was remarked. These crystals are quite microscopic, but from the sharpness of the outlines the angles are measurable. The colour is generally somewhat redder and the lustre greater than in the case of the brown mica plates, while the refrangibility is evidently great.

While occupied with these micas and continuing to collect from the eastern side of the Three Rock Mountain only, circumstances led me to look for large sized micas on the western side, at the point known as Barnaculla. Here a vein of very micaceous granite was shown me evidently having undergone fissuring and pressure, the mica plates which it shows presenting a certain parallelism of direction and crumpling, the rock possessing a gneissose character. These micas are often two cm. in length and show regular forms, that is, are more or less hexagonal or rhombic in outline. They proved to be somewhat harder than the micas of the east side, cleaving with more resistance and showing on the cleaved faces undulations, seemingly the consequence of pressure. The examination of the cleaved plates of these micas showed differences of constitution, as regards the micas of the east side of the mountain, very interesting, and so general throughout as to be in all probability characteristic of a large extent of rock. One of the peculiarities presented by them is a certain crumpling or fluting along the margin of the cleaved plate, see Pl. V., as if the crystal had been subjected to pressure and strain parallel to the directions of the sides of the crystal. This crumpling extends to a certain distance into the field of the plate, and is associated, as in the case of the micas of the east side, with the zonal line structure already referred to, as also with a similar zonal arrangement of small mica specks or flakes, with however the marked distinction that while in the micas of the east side examined no green patches or flakes showed themselves, they seem to dominate the brown patches in the cleaved plates from Barnaculla and to characterise them very distinctly. These green patches present, on the whole, outlines less jagged than the brown ones of the east side: the forms are often regular, and somewhat hexagonal in shape. The colour is generally that of a green olive oil, drops of which the micas frequently resemble; the lustre is weaker than that of muscovite, and corresponds to that of certain biotites and the generality of chlorites. The figures (*a*) and (*b*) of Pl. vii. give illustrations of their appearance under the microscope. In (*a*) the mineral is penetrated with minute grayish and blackish granules,

while in (*b*) the granules are larger, seemingly of the same nature as the mineral itself, and show stumpy prismatic forms not sufficiently regular in any of the specimens examined to allow of trustworthy measurements being made. With this granular structure is intimately allied the development of reticulated and brush structures, made up of opaque brown lines or needles and intersecting at angles seemingly in relation with the crystal forms of the mica. Every gradation of reticulated structure may be observed, from the merest outline to the complete filling up of the crystal space. Examples are shown on Pls. VI. and VII. Such reticulations are characteristic of rutile, and are well-known occurrences in quartz and also in biotites. When the network shows forms with an angle of about 60°, as occurs in the specimens examined, the structure represents the "sagenite" of Saussure. The examples presented by Pl. VII. (*c*) and (*d*), correspond well with that form; but in nearly every plate of green mica examined, there were present these brown reticulations in more or less advanced stages. They are referred to by Zirkel in his article on biotite, in his last edition of his *Lehrbuch d. Petrographie*, Vol. I. pp. 330-333 (1893). He examines very fully the question as to whether these reticulations are to be considered of primary or of secondary formation, and cites the different authorities for and against. His conclusion is that in reality the apparently contradictory statements of the observers cited may be reconciled by admitting that in biotites rutile may exist as of primary formation. In those of Barnaculla the occurrences are so frequent and general that every degree of development of formation may be observed, and as green micas exist therein which show no rutile needles, it is reasonable to assume that the reticulations are of secondary formation This is to a certain extent borne out by the fact that in certain plates a last stage of decomposition may be seen, whereby the needles seem to become earthy, to lose distinctness of outline, and assume forms markedly dendritic, as shown in Plate vii. Judging from the colour and other characters presented by this last stage of decomposition, it may be assumed that it represents the titanomorphite state.

None of the analyses published of Irish micas show the presence of titanic acid, although in the series given by Dana for muscovite and for biotite TiO_2 is frequently indicated as present; in the case of the muscovites only in small quantities (to 1·52 per cent.), but in that of biotite more frequently and in more notable quantities (up to 4·73 per cent.). In the rocks of Bray Head, however, it has been shown to exist, and a more extended and careful series of analyses would in all probability show its presence in the micas of the Dublin granites, more especially in

the biotites, taking the "sagenite" reticulations herein described as indications of such presence.

Note on the presence of copper in the mica of Glencullen, Co. Wicklow (referred to in Professor O'Reilly's paper "On the Micas of the Three Rock Mountain").

(Extract of letter from Mr. Charles Darling, Assoc.R.C.S. Dublin, Demonstrator in Chemistry at the Royal Military College, Woolwich, 3rd March, 1899.)

"I have much pleasure in forwarding you the figures of my analysis of the Glencullen mica, taken from my college note book:—

SiO_2	...	42·99 per cent.
Cu_2O	...	0·10 ,,
MnO	...	0·06 ,,
FeO	...	2·69 ,,
Al_2O_3	...	34·44 ,,
CaO	...	0·54 ,,
MgO	...	0·77 ,,
K_2O	...	13·27 ,,
Na_2O	...	trace ,,
H_2O	...	5·05 ,,
		99·91 ,,

"The cuprous oxide, as you will observe, is much less in quantity than was found to be the case with the Three Rock Micas. I believe in the latter case the Cu_2O crystals were distinctly visible, and were traced out under the microscope by Miss Robertson. In the sample provided me by Professor Hartley no such operation was possible; but there can be no possible doubt as to the presence of the copper in the proportion stated, as I made the estimation three times with the same result. The quantity being small, a colorimetric method was adopted, the *modus operandi* being as follows:—

"The mica was fused with mixed carbonates of soda and potash until decomposed; then treated with strong HCl and taken to dryness to render the SiO_2 insoluble; treated again with HCl and filtered. The filtrate was then saturated with H_2S, the copper precipitate filtered off, and after washing with H_2S water, was dissolved in boiling dilute HNO_3. Excess of ammonia was now added, so as to produce the blue colour, and the solution transferred to one of two graduated tubes having the same bore.

The second tube contained a solution made by dissolving a known quantity of metallic copper in HNO^3 and adding excess of ammonia. One or the other was then diluted until the tints were matched."

Note on Miss Robertson's Analysis of the Three Rock Mountain Mica.

By Professor W. N. HARTLEY, F.R.S., Royal College of Science, Dublin.

[Communicated April 26th, 1897.]

IN the analysis of mica executed by Miss Robertson for Professor O'Reilly in my laboratory, and under my guidance and advice, it will be observed that the copper is stated to be present as cuprous oxide Cu_2O. There was no evidence whatever of its being cupric oxide CuO. That the whole of the copper was present as Cu_2O in the sample analysed was shown by the following tests, which were made by me at the time:—

1. The microscopic examination of the mica showed the presence of no black, green or blue particles, such as would be characteristic of a cupric compound. 2. The colour of the mica, which was reddish, was seen to be caused by crystalline spangles of a bright red colour, many of them more or less of a ruby or garnet tint. 3. These coloured particles dissolved easily in warm hydrochloric acid, leaving the mica clear and colourless. 4. The hydrochloric acid solution was brown, and on dilution with water became turbid from a precipitation of what can only have been white cuprous chloride. 5. The particles of mica which were coloured gave a red glass by fusion with borax. This would not have been the case with a cupric compound.

There being no evidence whatever of the copper being in two different states of oxidation, the analytical results were calculated upon the evidence afforded by the above tests, for which the quantity of material available was very small.