- same enlarged. *c.* Portion of a branch still further enlarged. From the Hamilton Group.
- FIG. 21.—*Retepora Phillipsi*, Nich. *a.* Fragment of the natural size. *b.* Fragment in which the outer non-celluliferous layer has been removed, showing the bases of the cells, enlarged. From the Corniferous Limestone.
- FIG. 22.—*Fenestella magnifica*, Nich. *a.* Portion of the polyzoary, natural size. *b.* Fragment of the same, enlarged. From the Corniferous Limestone.
- FIG. 23.—*Fenestella marginalis*, Nich. *a.* A fragment, of the natural size. *b.* A portion of the same, enlarged. *c.* A portion of a branch still further enlarged, viewed from behind, and showing the large marginal and the minute central cells. From the Corniferous Limestone.
- FIG. 24.—*Fenestella filiformis*, Nich. *a.* Fragment, natural size. *b.* Portion of the same enlarged. From the Corniferous Limestone.
- FIG. 25.—*a.* *Spirorbis omphalodes*, Goldfuss, of the natural size and enlarged. *b.* *Spirorbis Arkenensis*, Nich., of the natural size and enlarged. *c.* A dextral example of the same, enlarged. From the Hamilton Formation.
- FIG. 26.—*Ortonia intermedia*, Nich. *a.* One of the tubes enlarged. *b.* Another example in which the annulations are greatly extended laterally, enlarged. From the Hamilton Formation.

III.—ON THE SUBSTITUTION OF ZINC FOR MAGNESIUM IN MINERALS.

By EDWARD T. HARDMAN, F.R.G.S.I.¹

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IN the GEOLOGICAL MAGAZINE of last October² I have noticed the occurrence of zinc in small quantities in the White Limestone (Chalk) of the Co. Tyrone, and also in the overlying basalt. When that paper was read,³ exception was taken to the latter part of it, on the ground that the metal in question had never been known to exist in rocks of igneous origin; but as my analysis seemed perfectly trustworthy, I saw no reason to modify it on the objections then put forward. Since then, whilst making an investigation—with a different object—on a specimen of basalt from another locality in the neighbourhood of that whence the one originally examined was obtained, I succeeded in again finding zinc in it; and I think it well to mention the fact now, as an *addendum* to, and as confirming my former statement.

The specimen was procured at a place called Curglasson, near Stewartstown, from the heart of a quarry by the roadside; being more than a mile north of the spot whence the basalt referred to in my former communication was obtained. The rock was carefully examined qualitatively for all the metals precipitable from an acid solution by sulphuretted hydrogen. Iron and alumina were then precipitated, and the filtrate examined with the utmost caution. On the addition of ammonium sulphide, a distinct white precipitate appeared. As it was probable that a little lime might have been brought down by a trace of carbonic acid in the re-agents, the precipitate was filtered off, re-dissolved in hydrochloric acid, and re-precipitated. (a) It was again re-dissolved, evaporated to dryness, and strongly ignited, to drive off ammonia, etc. A small quantity of the residue, *which was deliquescent*, was mixed with carbonate of soda,

¹ This paper formed part of a communication read before the Royal Irish Academy, January 26, 1874.

² Vol. X, page 434.

³ Before the Royal Geological Society of Ireland, June 11, 1873.

and exposed before the blowpipe on charcoal. The support became covered with the usual zinc oxide incrustation, which, treated with nitrate of cobalt, gave a vivid green. The fused bead and support were levigated with water in an agate mortar, when numerous spangles of white metal were seen, which, when treated with a drop of water very slightly acidulated with hydrochloric acid, dissolved with evolution of hydrogen. As the solution (a) could only contain zinc, with a trace of ferrous iron, and of lime, this experiment was conclusive.

The above results were obtained with separate portions of the rock, treated in the following different ways:—

- (1). The powdered rock was fused in a platinum crucible with carbonate of soda.
- (2). The powdered rock was boiled in strong hydrochloric acid.
- (3). The powdered rock was boiled in nitro-hydrochloric acid.

It is somewhat remarkable that only a trace of titanium was observed in this specimen.

In my former note on this subject, I endeavoured to account for the presence of zinc by the supposition that it existed as a distinct mineral, and pointed out the possibility of its being introduced by the infiltration of water; but subsequent examination and consideration has led me to what appears to be the true clue. Zinc is very closely allied to magnesium in characteristics and behaviour, both in the metallic state and in combination with other elements. In many points the resemblance is very strong;¹ their salts have a similar composition, and these, as well as the natural compounds, or minerals, are isomorphous.² Consequently, following the law of isomorphism, they should be mutually replaceable; and wherever we find the one in any quantity, we should expect to find the other encroaching on it. It is curious that while in most mineralogical treatises the interchangeability of the protoxides of iron, manganese, calcium, and magnesium is laid down, that of zinc with these, so far as I am aware, has not been yet shown,³ and in the very few instances in which zinc is given as an accessory metal, its presence seems to be considered rather as an accidental circumstance, than as the result of any chemical law. In few cases has it been given in the composition of a mineral, unless when present in such quantity as to make a very serious item in the analyses, as in those of Automolite, or zinc spinel (20 to 35 per cent. of Zn O), and Franklinite (17 per cent. Zn O); while in most minerals traces of Mn, Fe, Mg, are constantly recorded as replacing part of the essential metals.

Believing, therefore, that zinc compounds might thus be calculated to occur in most magnesian rocks or minerals, I have tried several, and so far the result has almost exceeded my expectations, for in every single case the metal was proved. As yet I have merely

¹ Fownes' *Manual of Chemistry*, 10th ed. p. 393; also Galloway's *Qualitative Analysis*, p. 49.

² *Supra cit.*; also Dana's *Manual of Mineralogy*, p. 74.

³ Although in one or two cases implied.

satisfied myself with regard to its presence, reserving the quantitative determination until I shall have completed the testing of a number of specimens; but it may be worth while to mention the rocks and minerals already searched.

1. *Granite*.—Wicklow and Wexford range variety:¹ from Graigue-na-spiddoge, near Carlow.—Obtained from heart of quarry: (a) A very coarse-grained light grey rock, porphyritic in parts, containing white mica, together with a dark greenish magnesian variety; also tourmaline. The portion taken for analysis was prepared in such a way as to contain a preponderance of mica, and four analyses of this were made in the wet, as well as others in the dry, way, ere I allowed myself to be perfectly satisfied as to the presence of zinc. The quantity of this was very small, as was of course to be expected. Traces of copper and lead were also noticed.

(b.) *Mica*.—After many searches at the same quarry, I was fortunate enough to find a mass of mica sufficiently large for analysis with the blowpipe. It was mostly white, but contained laminae of green mica. About four grains were treated on charcoal before the blowpipe, with carbonate of soda. Two metals were reduced, which proved to be copper and zinc. The zinc spangles dissolved with rapid evolution of hydrogen in a barely acid solution of hydrochloric acid. The solution evaporated to dryness, moistened with nitrate of cobalt, and heated on charcoal, gave the characteristic green reaction.²

2. *Serpentine* (?).—A green soft steatitic rock from Garrarus Strand, near Tramore, Co. Waterford. This rock occurs among Silurian limestones and slates, near masses and dykes of felstone, etc. Some of the limestone can be distinctly seen to pass into Serpentine. Examined qualitatively for zinc: found it present in fair quantity, all the re-actions being most distinct.

This rock contains about 8 per cent. of water, and 11 per cent. of carbonic acid (CO₂).³

3. *Basalt*.—Already described.

4. *Black Mica*.—In a gneissose or granitic rock. Locality unknown. Specimen from Geological Survey collection.⁴ The mica is perfectly black, and occurs in quantity in small flakes thickly massed together.

About four grains were treated at a time before the blowpipe with carbonate of soda. After fusion the mass yielded a notable quantity of copper, a very appreciable amount of zinc, and a trace of a metal which seemed to be lead. All the characteristic tests for zinc were answered very distinctly.

5. *Chlorite schist* (? *Talc schist*).—With inclosed grains of glauconite (?). From Geological Survey Collection. The examination with the blowpipe gave two metals, both in very appreciable

¹ Leinster Granite.

² The zinc most probably occurs here in the dark magnesian mica.

³ It is therefore not entirely metamorphosed.

⁴ The specimens from the Survey Collection were obtained by the kind permission of Prof. Hull, F.R.S., Director of the Geological Survey of Ireland.

quantity, viz. copper and zinc. The zinc re-actions were very pronounced.

6. "*Mountain Leather*."—Variety of asbestos. From Portlock's Collection, Geological Survey Museum, Dublin. Locality unknown; but associated with asbestos and other basaltic minerals from Antrim. Zinc very apparent, all the re-actions being perfectly unmistakable. A trace of lead (?) was also observed.

7. *Augite*.—Very large crystals in a trappean ash. Locality unknown. From Geological Survey Collection. About four or five grains of the powdered mineral, fused with carbonate of soda on charcoal, yielded a sufficiency of metal to identify with certainty. Besides zinc, copper was present. All the zinc re-actions were most distinct.

All the above minerals and rocks were selected at random, on account of containing, or being themselves, magnesian compounds, and they are numbered in the order in which they were examined, every one resulting in "a find." In many cases the examination by the blowpipe and its immediately connected wet tests was found to be amply sufficient to prove the presence of the metal; especially as from the comparatively large amount of the substance under investigation taken,—four or five grains,¹—there was little possibility of error. But where the result was at all doubtful, it was confirmed by one or more analyses in the wet way.

The amount of zinc appeared to be most plentiful where the largest quantity of magnesium existed; but as I am as yet only concerned in proving the *presence* of the former metal in the above minerals, I am not now in a position to positively assert this; deferring the quantitative analyses until I have continued the investigation so far as to enable me to select the most typical examples for estimation. In the mean time these notes on the subject may not be without some interest, bearing as they do on a matter of much importance from a mineralogical as well as a chemical standpoint.

It may be thought that the zinc might as well be considered to replace the other members of the isomorphous group, which are known to occur in traces and occasionally in quantity in some of these minerals. But this would be a replacement of a replacing element; and I believe it is invariably considered that the accessory metal substitutes itself for part of the essential one. On this ground alone, all the minerals here referred to being strictly magnesian ones, the zinc must be regarded as replacing magnesium. At the same time I do not doubt that in other instances where there is no magnesium, it may be equally found to replace any of the other members. But when we remember the affinities of the two metals, it will hardly be considered a far-fetched notion to suppose, that were a preference possible, the zinc would associate itself with the magnesium, in the same way as some other metals act towards each other, notably the Platinic group; which possessing a very peculiar relation to one

¹ This was rendered possible by the use of paraffin oil in the blowpipe lamp, by which a very large and hot flame was procured, capable of decomposing a much larger quantity of rock. For reductions, and where great heat is required in blowpipe analysis, it will be found most useful where gas is unattainable.

another independently of their isomorphism—which is not thorough—are nearly always found together.

It will be seen that the majority of the minerals examined are species that are most often found in nature forming component parts of igneous rocks, while two rocks of that class are themselves included.

IV.—THE VOLCANIC HISTORY OF IRELAND.

Being the Anniversary Address delivered to the Royal Geological Society of Ireland, February 11th, 1874.

By Professor EDWARD HULL, M.A., F.R.S., President;
Director Geological Survey of Ireland.

(Concluded from page 150.)

(PLATE X.)

Carboniferous Period.—The Lower Carboniferous rocks, both of the North of England, of Scotland, and of Ireland, afford examples of contemporaneous volcanic action of considerable intensity. The so-called “toad-stones” of Derbyshire, and the great sheets of melaphyre, porphyrite, and ashes of the central valley of Scotland, forming the Kilpatrick, Campsie, and Dalry Hills, appear to have been erupted over the bed of the same sea as that in which were poured out similar materials in County Limerick, forming the well-known Carboniferous volcanic rocks of “the Limerick Basin.” These rocks have been already so fully described by several observers, that I shall confine myself to a very short description, such as is essential to the brief history of volcanic action which I am here endeavouring to draw up.¹

The trap-rocks of the Limerick basin, ably described by Professor Apjohn, belong to at least two consecutive periods of eruption; both, however, included in the Carboniferous Limestone period, and are disposed in concentric sheets round a tract of Upper Limestone shale which occupies a district around Ballybrood. The “Lower trap-band” is more important and continuous than the Upper, and along with beds of ash and agglomerate is found in several tracts to the north and west of the band itself. In several spots both to the north and south of the “Lower trap-band,” are isolated bosses of trap, such as those of Knockdirk, Carnanagh Fort, Cullon, and Maddyboy, which may be regarded as the old “necks” or volcanic throats, from which the sheets of trap and ashes have been erupted or blown out, but from which they are now disconnected by denudation.

As regards the composition of these rocks, notwithstanding the variety of names they have received, microscopic examination shows them to belong, with few exceptions, to that series of old augitic lavas usually called “melaphyres,” which have undergone considerable alteration from their original condition. The base is for the most

¹ The composition of the Knockdirk trap is essentially so different from that of the other masses, that I suspect it to belong to an older period of eruption. See author's paper on “The Microscopic Structure of the Limerick Trap-rocks,” *GEOLOGICAL MAGAZINE*, 1873, Vol. X. p. 153, Pl. VIII.