

XVII.—*On the Composition of Oceanic and Littoral Manganese Nodules.*

By J. Y. BUCHANAN, Esq., F.R.S. (With Map and Plate.)

(Read January 9, 1891.)

The following analyses were made some years ago, principally with the object of ascertaining the state of oxidation of the manganese in the nodules. The nodules examined came from three different localities, two of them oceanic and the third littoral. Samples marked I., II., and III. are from nodules brought up in the trawl on board the "Challenger," on 13th March 1874, in lat.  $42^{\circ} 42' S.$ , long.  $134^{\circ} 10' E.$  The depth of the water was 2600 fathoms, and the temperature of the bottom water  $0.2^{\circ} C.$  The density of the bottom water was 1.02570 at  $15.56^{\circ} C.$  Being from a high southern latitude, and therefore near the source of surface aeration, the water is highly charged with atmospheric gases, especially oxygen. It contained, per litre, 18.4 c.c. of mixed nitrogen and oxygen, of which 31.81 per cent. was oxygen, and 27.33 c.c., or 53.7 milligrammes, loosely-bound carbonic acid. The position of the station is about 400 miles south-west of the nearest part of the Australian coast, and about 500 miles west of Tasmania. It was the deepest water observed in the Antarctic voyage between the Cape of Good Hope and Melbourne. The haul was a very abundant one, and a few notes which I made at the time may be interesting:—"The water was found unexpectedly deep, the bottom being red clay, with some Foraminifera. The bag of the trawl came up quite full of this mud, with many animals and a large number of manganese nodules. These were of all shapes, and with the characteristic mammillated surface, which in some was accentuated to such a degree as to give them a botryoidal appearance, like specimens of Psilomelane. Many of them were perfectly spherical, others formed groups of spheres. One of these spherical nodules was found, on being broken, to contain a hard kernel of a mineral, giving a powder of the colour of bichromate of potash, with a conchoidal fracture and resinous lustre. Round this the spherical shells of manganese were gathered, and could be easily broken off with the fingers. Another nodule was noticed with the same yellow resinous-looking substance in the centre, but it mixed with the manganese forming part of the substance, and could not be detached from the surrounding shells. It has a light wine-yellow colour by transmitted light, and polarises light. Many flat pieces were observed, with horizontal stratification and botryoidal surface. Whether flat or spherical, the manganese was put on in layers, separated by very fine sheets of the mud of the locality. There was one nodule which had formed round the fragment of another, and therefore older nodule, the distinction between the two being well marked by the inclination of the mud sheets of the kernel to those of the shell. There were many where

the clay or mud formed a large percentage of the mass, either as interbedded layers or as pockets, and in some of these pockets Foraminifera were to be seen. Amongst the collection were two ear-bones of whales and a very fresh shark's tooth, covered with the incrustation. The occasional occurrence of icebergs at the surface was made probable by the presence of two pieces of granite, the one with a very thin covering, and the other with over one-eighth of an inch thickness of manganese. On the fracture of one of the pieces, it was evident that the manganese had filtered into the interior of the stone, colouring the quartz a beautiful amethyst purple."

This haul was remarkable in many ways; and not the least in being the only important haul which we got in the vicinity of continental land, and with no volcanic islands near. The samples taken for analysis were—

- I. The outer rind or shell of a spherical nodule, which was detached without any trace of the kernel. It was 10 millimetres thick.
- II. A similar piece, detached from another spherical nodule, but with traces of the kernel attached. It was also 10 millimetres thick.
- III. A piece of a horizontally stratified concretion, with botryoidal upper surface. It was 15 millimetres thick.

Samples marked IV. and V. are from one nodule. IV. is part of the outer rind, 13 millimetres thick, consisting of concentric layers, most of them mottled with reddish yellow spots, and separated by fine seams of purple-brown oxide of manganese, without yellow specks. V. is the kernel of the same nodule. It is harder than the rind, from which it easily splits away. It is nearly spherical, with a radius of 16 millimetres. At the centre is a small colourless piece of mineral matter.

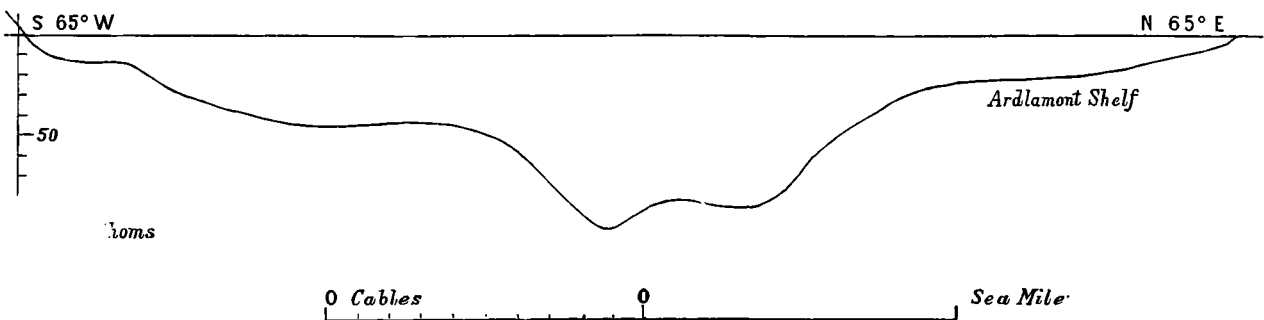
This nodule was one of an enormous haul made by the "Challenger" on the 12th July 1875 in the North Pacific, in lat.  $37^{\circ} 52'$  N., long.  $160^{\circ} 17'$  W. The depth of the water was 2740 fathoms. The temperature of the bottom water was  $1.0^{\circ}$  C., and its density at  $15.56^{\circ}$  C. was 1.02573. The gaseous contents of the water were—17.7 c.c. mixed nitrogen and oxygen, of which 16.95 per cent. was oxygen, and 21.48 c.c., or 42 milligrammes, carbonic acid per litre. It will be seen that the water contains very much less oxygen than was contained in the bottom water off the Australian coast. In fact, in this water the dissolved oxygen has been reduced to almost exactly half the amount which it contained when it left the surface. All over this district, where manganese greatly abounds, the dissolved oxygen has been reduced from 34 per cent. of the mixed gases, as at the surface, to from 16 to 22 per cent. at the bottom.

The position of this station lies midway between the Aleutian Islands and the Sandwich Islands, being 1000 miles distant from the nearest island of either group; it is 1600 miles distant from the nearest point of the North American continent in the same latitude. Hence, although there were many stations further from land than this, it can claim to be quite beyond the reach of any continental influence. The station from which samples I., II., and III. come, although comparatively close to the Australian coast,

may be said also to be practically beyond the sphere of its influence, as, owing to its climate, it is almost destitute of drainage.

The *Littoral Nodules*, samples M, N, P, Q, K, R, &c., are from Loch Fyne, one of the most important arms of the Firth of Clyde. They are from a lump of mud which came up on the fluke of the deep-sea kedge-anchor of the steam yacht "Mallard" after a series of temperature observations in the deepest part of the loch on the 21st September 1878.

The Firth of Clyde is the name given to the most remarkable group of fiord-like channels and sea lochs in the British Islands. They form a compact basin or depression, and it has been named after the principal stream which empties itself into it—the river Clyde. If we draw a straight line through the Craig of Ailsa and Sanda Island, at the extremity of the Peninsula of Cantyre, we shall have delineated the Firth seawards, and a line of soundings along this line discloses an almost perfectly uniform depth of water of from 23 to 25 fathoms. If we run a line of soundings at right angles to this line, we shall find the water deepening as we retire from the line whether we go northwards or southwards. If we go northwards we find the depth increase gradually and steadily as we pass the Island of Arran, whether by the main channel on the east, or by Kilbrennan Sound on the west; so that Arran stands, as it were, on an



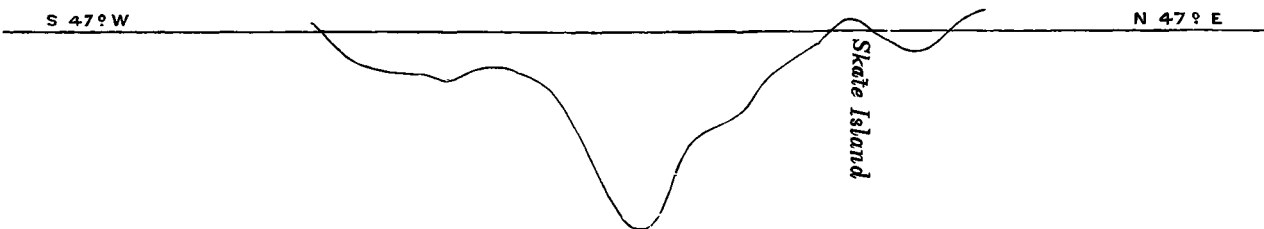
Loch Fyne. Section I.—Cantyre to Cowal.

inclined plane sloping northwards from the north of the Firth, attaining a depth of 90 fathoms off the N.E. point of the island, and continuing as a deep trough into Loch Fyne, with a maximum depth of 104 fathoms\* close to Skate Island and about three miles from the entrance of the loch. This deep trough only occupies a portion of the width of the loch, as is shown by the chart and sections. At its mouth the loch measures four nautical miles across, but the width of the portion of it over 50 fathoms in depth is only one mile. Both the loch, as a whole, and the deep channel contract until they reach a minimum of sectional area, where this deep spot is. Here the whole width across from Skate Island to the south shore is only 1.6 mile, and of this one-half, or

\* See Map.

0·8 mile, is occupied by a shallow tongue, with about 20 fathoms, projecting from the south shore. The deep channel, with over 50 fathoms, is here contracted to little over 0·3 mile. It will be seen from these data that dredging in the deepest water is difficult, because it implies drifting; and as the deep channel, besides being narrow, makes here a sort of elbow or sinuosity, as if there had been foldings in a vertical plane, it would seem to be impossible, as I generally found it to be in practice, to drift for any distance in any direction without rapidly getting into shallower water.

The chart is taken from Admiralty Charts Nos. 2133 and 2321, on the scale of 2 inches to the sea mile. Where the depth is less than 30 fathoms it has been left uncoloured, depths over 30 fathoms have been coloured blue, and those over 80 fathoms dark blue, showing the trend of the deepest parts. The great constriction at Skate Island, with the deepest spot lying immediately on one side, is well shown both in



Loch Fyne. Section II.—Cantyre to Cowal through 20-fathom bank and Skate Island.

the map and in Sections II. and III. In Section II. the area of the whole section is 52,190 square fathoms; that of water lying at a greater depth than 30 fathoms is 17,940 \* square fathoms. In Section III. these quantities are 61,500 and 21,500 square fathoms. For comparison with these we have Section I. at the mouth of Loch Fyne and Section VI. at the widest part, towards Loch Gilp. In the former of these the total area is 154,820 square fathoms, and the area of water over 30 fathoms is 61,920 square fathoms; in the latter these figures are 129,200 and 67,500. Sections IV. and V. show transition stages from the

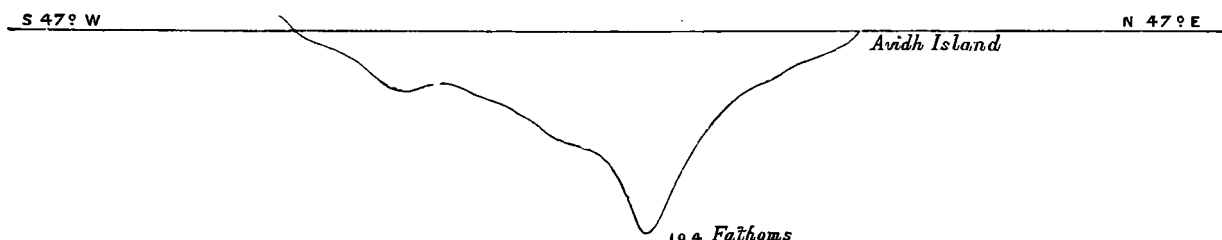


Section IIA.—The same as Section II. on natural scale.

narrowest to the widest portions of the landward portions of the loch. Section IIA. is constructed on a uniform scale of lengths and depths, and gives the natural proportions at the narrowest points.

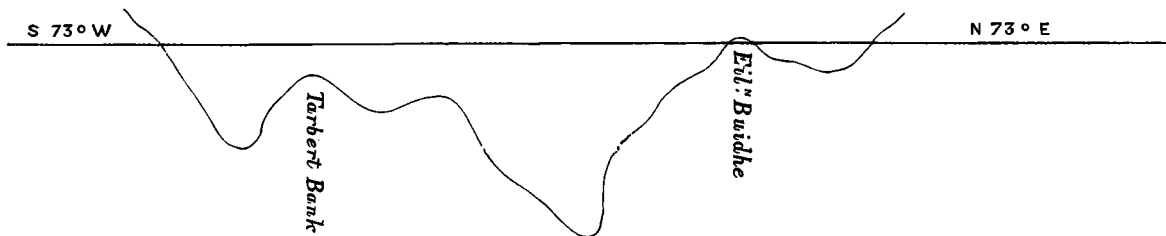
\* In marine charts the unit of distance is always the nautical mile, which is equal to one minute of arc of a great circle of the globe, and it is subdivided into 10 cables of 100 fathoms each; so that the nautical mile is 1000 fathoms. Hence, in applying the decimal system to geographical measurements, the fathom is the natural unit so long as we retain the subdivision of the circumference of the circle into degrees and minutes as at present. The metre and kilometre are very inconvenient and clumsy in this respect.

As the locality where the nodules are found is very restricted, it is important to fix its position as nearly as possible. Now, there is not much difficulty in fixing a vessel's position in a direction up and down the loch. Skate Island and adjacent features make it possible to get good leading marks in a direction perpendicular to the coast, but to find her place on this line is very difficult, as there is no feature that gives any leading, and there is nothing near and in the right direction to take bearings from; still, with careful work, it was always possible to find the spot. Thus, on the day in question, 21st September 1878, the first sounding gave exactly 104 fathoms, and everything was done to drop the anchor in the same spot; yet, when it was let go, it took the ground in 60 fathoms, the vessel having drifted, owing to the south-westerly breeze, towards the north shore. The



Loch Fyne. Section III.—Cantyre to Cowal through deepest spot parallel to Section II.

cable was immediately brought to the winch and the anchor hove up, though it required a good deal of humouring to get it out of the ground. The anchor was not brought quite up to the bows, but, when about 5 fathoms of cable were still out, the yacht was steamed out to the proper position and the anchor immediately dropped, and the depth, as given by the wire-rope cable, was as nearly as possible 104 fathoms. More cable was then given, until 150 fathoms were out. It must be remembered that I was using a small kedg-



Loch Fyne. Section IV.—Cantyre to Cowal through Tarbert Bank and Eiln. Buidhe.

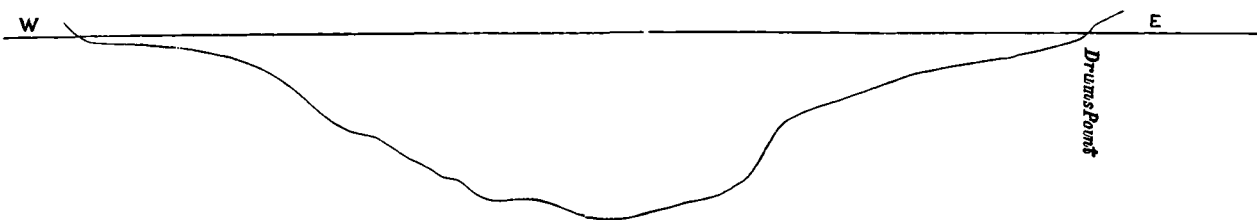
anchor of ordinary type and weighing half a hundredweight, and my object was simply to anchor the vessel in the deepest water so as to be able to take temperatures and collect samples of water at leisure and without having to manœuvre the vessel. Although the anchor had not dragged, she had tailed before the south-west wind so far toward the north shore that when I put over the sounding-line with a number of deep-sea ther-

mometers, bottom was struck at 60 fathoms. On getting up the anchor, and after heaving in the extra cable which had been paid out, I sounded when the cable was up and down, and found exactly 104 fathoms, so that the anchor had held and remained in the deep place while the ship swung into water that was 44 fathoms shallower. When



Loch Fyne. Section V.—Knapdale to Cowal through Barmore and Black Harbour.

the anchor was brought up, a large mass of clay and dead shells, principally *Pecten*, was sticking to one of the flukes; and this was the specimen which contained the manganese nodules, which at that time were not supposed to exist anywhere out of the deepest oceans. As the anchor held firmly in the first instance in 60 fathoms, and was not



Loch Fyne. Section VI.—Knapdale to Cowal through widest part.

examined before being lowered into the 104-fathom spot, it might be held to have picked up the sample in 60 fathoms, and kept it all the time it was holding the ship in 104 fathoms; but this is not likely. On 24th September 1878 the anchor was again dropped in apparently exactly the same spot, and it brought a quantity of clay and shells exactly like those of the 21st, but containing no nodules. On 1st October a few nodules were got in the deep trough; and dredging in 50 fathoms on the north side and in 40 fathoms on the south side none were found. On the south side the ground was very rough and rocky in 40 fathoms.

Although everything went to show that the abundance of nodules really occurred in the deep trough, it was disappointing that I could never get complete confirmation. On 15th July 1881, however, I was again successful, for the anchor-dredge brought up a large bagful of mud, containing abundance of nodules. On this occasion the position of the ship was carefully watched, showing that she dragged over about half a mile of ground, beginning in 100 fathoms and gradually shoaling to 85 fathoms, when the

anchor was brought up. There can, therefore, be no longer any doubt that it is really in the deep trough that the nodules occur, and only in a very limited area of it.

The mud of 21st September 1878 was divided in two equal portions, one of which was preserved and the other was analysed mechanically. It was separated into three constituents, the nodules, the shells, and the residue, a sandy clay. The number of nodules thus obtained was 83, and they weighed 142·7 grammes, whence the mean weight of a nodule was 1·7 gramme. Packed as closely as possible in a graduated cylinder of 37 millimetres internal diameter, they occupied a length of 130 millimetres, reaching to 146 c.c. on the graduation. I then poured in 100 c.c. water, which stood at 158 c.c. Hence the volume of the nodules was 58 c.c., and the average volume of one was 0·7 c.c., and their density 2·46. The shells were all dead, and principally *Pecten*; they weighed 35 grammes. The following was the mechanical composition of the mud:—

Nodules, . . . . .	141 grammes.	30 per cent.
Shells, . . . . .	35 "	7½ "
Sandy Clay, . . . . .	289 "	62½ "
	<hr/> 465 "	<hr/> 100 "

Of twenty-two nodules which were split open, sixteen contained soft nuclei of about the size of a pea, and apparently very rich in manganese. One of these nuclei was so slightly attached to the rind as to fall out when the nodule was split. The rind is always very hard and gritty, and when the oxides of iron and manganese are removed by hydrochloric acid, it falls into a mass of sand, similar to that which makes up a large proportion of the rind. This agrees with the idea that the nodules are agglomerations of the mud found *in situ*, and cemented by the ochreous oxides. One nodule (No. 24) was interesting, as showing the complete soft kernel, loose, in a cavity of mud, the rind not having as yet formed, although it was evidently forming, the mud being stained from the inner wall of the shell outwards. No. 25 was a similar nodule, only the kernel had no free space round it. The mud round it was stained yellow. This seems to be very general with the growing nodule; the oxide of iron spreads itself in front of the oxide of manganese. A little of the yellow shell gives no manganese reaction with hydrochloric acid. A nodule of the size of a pea was found, resembling the others perfectly, except that it contained  $\text{Fe}_2\text{O}_3$ , and no  $\text{MnO}_2$ . Very careful examination of the mud from which the nodules and shells had been removed showed that perfect nodules exist down to the size of a pin-head, and all through the mud there were specks showing where probably nodules had begun to form. Although so near the shore, the mud contains hardly any pebbles larger than a grain of sand. This shows conclusively that the nodules have not been washed down into their present position; and that they have been formed *in situ* is further shown by the fact that the mud round them is generally stained yellow with ferric oxide. A number of nodules were picked out for illustration and analysis.

In the Plate, fig. 1 represents a nodule which was found attached to the rim of a dead pecten shell. It is represented in one and a half times the natural size.

Figs. 2 and 2*a* represent, in twice natural size, a nodule entirely filling up a shell.

Figs. 3, 3*a*, and 3*b* represent, in twice natural size, (3) a nodule found attached to a dead pecten shell; (3*a*) the under side of the nodule, showing bases of attachment; and (3*b*) a view of the shell, showing surfaces of attachment.

Fig. 4, in one and a half times natural size, shows a remarkable nugget-shaped nodule.

Fig. 5, in twice natural size, shows a pear-shaped nodule, with stem of attachment.

Fig. 6, in twice natural size, shows a spherical nodule of the commonest form.

Figs. 7 and 7*a* show a nodule split through the middle, and with a semi-detached nucleus. The half of the kernel protrudes in fig. 7, and the corresponding cavity is visible in fig. 7*a*.

All these nodules were got on 21st September 1878.

The nodules taken for analysis are as follows:—M and N (called Nos. 10 and 14 in original notes) were chosen as average specimens. P was a rather softer and Q a rather more stony nodule. K and R are the kernels and rinds respectively of five nodules. These nodules were split, and the kernels and rinds separated as carefully and as completely as possible. Their approximated weights were—

Kernels,	.	.	.	.	1·127 grammes.
Rinds,	.	.	.	.	10·710 „
Total,	.	.	.	.	<hr/> 11·837 „

S is an average sample taken from a number of nodules pounded up and mixed.

The analyses of these samples was undertaken at first only to show the state of oxidation of the manganese. In the case of the Loch Fyne nodules, it was carried further, with a view of showing the nature of the other principal constituents. The analyses under the letters X, Y, and Z constitute together a complete analysis, though it was not at first intended to be such, otherwise the whole of the requisite material would have been prepared and extracted at once. These analyses were made in 1879 by Dr GEORGE M'GOWAN, F.R.S.E., now of Bangor, and were carried out with the greatest care and attention.

#### ANALYTICAL METHOD FOLLOWED FOR THE DETERMINATION OF THE STATE OF OXIDATION OF THE MANGANESE.

The analysis of these nodules was conducted as follows (any particular point relating to any one nodule will be given in detail along with the analysis of that nodule):—



A. The nodules were reduced to an impalpable powder in an agate mortar, and were not dried previous to analysis.

B. In two separate portions (of about 2 decigrams each) the *available oxygen* was determined by Bunsen's iodometric method.

C. Two portions, of about 0.5 grams each, were dissolved in about 5 c.c. of pure strong hydrochloric acid, in a small covered beaker, heat being applied cautiously at first to prevent loss by effervescence of chlorine. The mixture was then evaporated to dryness over a water-bath, covered with a glass shade; the residue, when free from all excess of acid, moistened with a few drops of strong hydrochloric acid, and the *insoluble residue* filtered off, ignited, and weighed.

(a) *Insoluble Residue*.—This insoluble residue was kept in a corked tube, and afterwards fused with  $(\text{NaK})\text{CO}_3$  (in the proportion of about four parts of carbonate to one of residue) for the estimation of silica. The filtrate from the silica was examined *qualitatively* for the bases present.

(b) The *filtrate* from the insoluble residue was treated with a moderate excess of pure carbonate of baryta. In practice about 2 grams were required. This was added in a state of cream to the liquid in a small flask. The flask was corked and allowed to stand some hours, being shaken occasionally. The liquid was then filtered off, and the precipitate, after thorough washing, tested for manganese with carbonate of soda on platinum foil.

D. To the filtrate from the carbonate of baryta precipitate excess of sodium acetate was added, so that there should be not less than  $3\text{C}_2\text{H}_4\text{O}_2$  to  $\text{HCl}$  in the solution (in practice 15 to 20 c.c. of a 1 in 10 solution of  $\text{Na}\bar{\text{A}}$  were added). Before adding the acetate it is well to drop in a little acetic acid, otherwise an immediate precipitation of barium salt occurs. Bromine in excess was then added to the sufficiently dilute fluid, and the flask corked and placed in a moderately warm place for some time. Gentle warming at first greatly aids the precipitation of the  $\text{MnO}_2$ . When the manganese had begun to deposit, and the liquid in the flask was at a temperature of about  $50^\circ$ , it was removed to a colder place (at the ordinary temperature of the room), and allowed to stand over-night. If necessary, a little more bromine was first added; this is regulated by practice. Next day the flasks were heated in order to drive off all superfluous bromine, a few drops of alcohol being added towards the end to get rid of the last traces. When the solution became perfectly colourless it was filtered, all the  $\text{MnO}_2$  that came easily out of the flask being thrown on the filter and washed with boiling water. The *filtrate* was tested first for more  $\text{MnO}_2$  with  $\text{Na}\bar{\text{A}}$  and bromine, and then for nickel and copper (*vide* below).

(a) The *filter*, on which was the bulk of the  $\text{MnO}_2$  precipitate, was dried. When dry, the  $\text{MnO}_2$  was returned to the original flask (on the sides of which some  $\text{MnO}_2$  remained sticking), the filter was ignited, and its ash also dropped into

the flask. This manganese precipitate was then dissolved in a few drops of strong HCl, the chlorine boiled off, and the solution slightly diluted. It was found that the  $\text{MnO}_2$  always brought down some baryta with it, and this was separated by precipitation with a few drops of sulphuric acid. This solution was then filtered from the  $\text{BaSO}_4$ ; evaporated to dryness over a water-bath to get rid of all excess of hydrochloric acid; the residue taken up with water; the solution filtered again if necessary; and the manganese precipitated by pure carbonate of soda solution, only a very slight excess being used. The  $\text{MnCO}_3$  was washed first by decantation, then dried, and ignited to  $\text{Mn}_2\text{O}_4$ .

The filtrate from the  $\text{MnCO}_3$  was always kept over-night, when sometimes a second minute precipitate came down. The  $\text{Mn}_2\text{O}_4$  was kept, and the nickel and cobalt in it determined afterwards.

- (b) The *filtrate* from the  $\text{MnO}_2$  precipitate with bromine was, in the case of the "Challenger nodules," neutralised with  $\text{NH}_4\text{OH}$ , and then excess of  $\text{NH}_4\text{HS}$  added, the flask filled up and corked, and allowed to stand for one or more days. Generally a minute black precipitate, accompanied by much barium sulphate, came down. This was filtered off, ignited, dissolved in HCl, the solution evaporated to dryness in a small basin, the residue taken up with water, and preferably a drop of  $\text{H}_2\text{SO}_4$ , and filtered. In the filtrate the nickel oxide was precipitated by a drop or two of pure caustic potash. After ignition this precipitate was always tested for purity. It is better, however (and this was done in the case of the Loch Fyne nodule), to neutralise the filtrate from the  $\text{MnO}_2$  with  $\text{NH}_4\text{OH}$ , add  $\text{NH}_4\text{HS}$ , and then acetic acid in excess, and pass  $\text{H}_2\text{S}$  gas through the gently-warmed solution (as is done in the separation of  $\text{MnO}$  from  $\text{NiO}$  and  $\text{CoO}$ ). Thus, after standing over-night, minute traces of nickel came down, which remained dissolved in the  $\text{NH}_4\text{HS}$  solution.

E. The  $\text{Mn}_2\text{O}_4$  *precipitates* were dissolved in a few drops of strong HCl in a small basin, the solution evaporated to dryness over the water-bath, taken up with water, and the solution filtered. To the filtrate, after neutralising any trace of acid present with  $\text{NH}_4\text{OH}$ , sulphide of ammonium and acetic acid were added, and sulphuretted hydrogen gas passed through the gently-warmed solution to precipitate the nickel and cobalt as sulphides. After standing over-night (the flask being full and corked) this precipitate was filtered off, and the filtrate treated in the same manner with ammonia, ammonium sulphide, acetic acid, and sulphuretted hydrogen. In this way a minute additional precipitate was obtained. The two precipitates were dried, ignited, and dissolved together in hydrochloric acid, and exactly the same process gone through again, so as to get rid of all traces of manganese. The second two precipitates of cobalt and nickel sulphides were again dried, ignited, redissolved in hydrochloric acid, the solution evaporated to dryness, the residue taken up with water, and this solution filtered. The

nickel and cobalt in the filtrate were then precipitated by a few drops of pure caustic potash. This precipitated the nickel and cobalt together. The precipitate was ignited and weighed as  $\text{NiO} + \text{Co}_3\text{O}_4$ . It was then again dissolved in hydrochloric acid, all excess of acid evaporated off, the residue taken up with water, the solution filtered into a small beaker, and gently evaporated down. During this evaporation very often a minute quantity of silica and ferric hydrate came down, and the solution had to be refiltered. After the liquid became very concentrated—reduced to a few drops, in fact—the cobalt was precipitated as double nitrite of cobalt and potassium. A solution of 1 in 4 nitrite of potassium was used.

- (a) The *cobalt precipitate*, after being filtered off and washed with acetate of soda, was dissolved in water or dilute hydrochloric acid, the filter ignited, and the ash added to the solution. The solution was evaporated to dryness, water added, and the solution filtered. The cobalt was then precipitated by caustic potash solution. It was ignited to  $\text{Co}_3\text{O}_4$ .
- (b) To the *filtrate* from the potassium nitrite precipitate excess of hydrochloric acid was added, the solution evaporated, and the nickel precipitated by caustic potash. It was found necessary to redissolve this nickel precipitate and reprecipitate it, on account of the relatively very large quantity of potassium chloride which had to be washed out of it. This gave the nickel as  $\text{NiO}$ . The nickel and cobalt precipitates were afterwards tested in the dry way.

#### TABULAR LIST OF NODULES SUBMITTED TO ANALYSIS.

##### *Oceanic Nodules—*

Nos. I., II., and III. are from a locality 400 miles south of the Australian coast, in lat.  $42^\circ 42'$  S., long.  $134^\circ 10'$  E. Depth, 2600 fathoms. I. is from the outer rind of a large spherical nodule, and it was detached without any trace of the kernel. II. is a similar piece taken from the outside shell of a smaller spherical nodule, with traces of an augitic kernel. III. is a piece of a horizontally-stratified nodule with botryoidal upper surface.

Nos. IV. and V. are from the same nodule, which was collected on the 12th July 1875 in the North Pacific in lat.  $37^\circ 52'$  N., long.  $160^\circ 17'$  W. Depth, 2740 fathoms. IV. is a portion of the outer shell, 13 millimetres thick, consisting of concentric layers, most of them mottled with reddish-yellow spots. V. is the kernel of the same nodule, and is harder than the rind, from which it easily splits away. It was nearly spherical and with 16 millimetres radius. At the centre was a small colourless piece of mineral.

##### *Littoral Nodules—*

These are all from Loch Fyne in 104 fathoms (see page 3). M, N, P, and Q are separate selected nodules; K and R are the kernels and rinds of five nodules.

The analytical details have been collected in a series of tables, as follows:—

TABLE I.—*Determination of Available Oxygen by the Iodometric Method.*

Number of Sample.		Weight of Sample taken (grammes).	Volume of Hyposulphite used (c.c.).	Equivalent Weight of		Oxygen per cent.	Equivalent per cent. of MnO <sub>2</sub>
				Iodine (grammes).	Oxygen (grammes).		
		<i>a</i>	<i>b</i>	$c = 0.01231b.$	$d = 0.063c.$	$e = 100 \frac{d}{a}$	$f = 5.4375e.$
I.	1.	0.1711	12.07	0.14856	0.009358	5.47	29.74
	2.	0.2698	19.06	0.23465	0.01478	5.48	29.80
II.	1.	0.1815	13.52	0.16647	0.010486	5.78	31.43
	2.	0.1734	13.03	0.16040	0.010104	5.82	31.65
III.	1.	0.1802	12.20	0.1502	0.009463	5.25	28.55
	2.	0.1620	11.05	0.13601	0.0085677	5.29	28.76
IV.	1.	0.1924	10.10	0.12439	0.0078356	4.07	22.13
	2.	0.1650	8.657	0.106567	0.0067129	4.07	22.13
V.	1.	0.1514	8.306	0.102246	0.00644	4.25	23.13
	2.	0.1731	9.65	0.11875	0.0073546	4.25	23.13
M	1.	0.1768	9.03	0.11113	0.007001	3.96	21.53
	2.	0.2210	11.30	0.1391	0.008762	3.96	21.53
N	1.	0.1859	5.936	0.07307	0.004603	2.48	13.48
	2.	0.2547	8.17	0.10057	0.006335	2.47	13.54
P	1.	0.1754	8.18	0.10073	0.006345	3.62	19.67
	2.	0.2117	9.77	0.1203	0.007578	3.58	19.47
Q	1.	0.1945	8.43	0.10375	0.006535	3.36	18.27
	2.	0.1815	7.83	0.09636	0.00607	3.34	18.18
K	1.	0.1116	8.94	...	...	6.25	34.00
	2.	0.1004	8.153	...	...	6.33	34.43
	3.	0.0553	4.401	...	...	6.21	33.77
R	1.	0.2286	9.96	0.12296	0.007746	3.39	18.43
	2.	0.3070	13.43	0.16446	0.01036	3.37	18.32

TABLE II.

TABLE II.—*Determination of Insoluble Residue.*

Number of Sample.		Weight of Sample taken (grammes).	Weight of Insoluble Residue (grammes).	Insoluble Residue per cent.	Weight of Insoluble Residue taken for SiO <sub>2</sub> Estimation.	Weight of SiO <sub>2</sub> (grammes).	SiO <sub>2</sub> per cent.	
							In Insoluble Residue.	Equivalent in Nodules.
							$f = 100 \frac{e}{d}$	$g = \frac{b}{a} f$
I.	1.	0.5290	0.1088	20.56	0.0958	0.0819	85.45	17.46
	2.	0.4733	0.0961	20.30				
II.	1.	0.4802	0.0815	16.96	0.1475	0.1278	86.75	14.75
	2.	0.6001	0.1018	16.95				
	3.	0.5254	0.0894	17.01				
III.	1.	0.5633	0.0937	16.63	0.1291	0.1127	87.26	14.68
	2.	0.5839	0.0983	16.83				
	3.	0.5566	0.0937	16.83				
IV.	1.	0.5035	0.1386	27.52	0.1727	0.1442	83.47	23.09
	2.	0.5248	0.1453	27.68				
	3.	0.4943	0.1358	27.63				
V.	1.	0.5015	0.1001	19.95	0.1139	0.0961	84.34	16.86
	2.	0.4825	0.0967	20.03				
M	1.	0.4977	0.1469	29.51	0.1631	1.1388	85.10	25.24
	2.	0.5516	0.1646	29.83				
N	1.	0.5021	0.1395	27.78	0.1377	0.1161	84.28	23.55
	2.	0.5321	0.1496	28.10				
P	1.	0.4639	0.1491	32.13	0.1458	0.1217	83.44	26.83
	2.	0.4767	0.1535	32.17				
Q	1.	0.5045	0.1463	28.99	0.1436	0.1208	82.70	23.94
	2.	0.5110	0.1478	28.91				
R	1.	0.5814	0.1717	29.56	...	...	...	...
	2.	0.5144	0.1503	29.21				

TABLE III.—*Determination of Manganese, Nickel, and Cobalt.*

Number of Sample.	Weight of Sample taken (grams).	Weight of $\text{Mn}_2\text{O}_3 + \text{NiO} + \text{Co}_3\text{O}_4$ (grams).	Per cent. of $\text{Mn}_2\text{O}_3 + \text{NiO} + \text{Co}_3\text{O}_4$ in Nodules.	Weight of Mixed Oxides taken for Ni and Co Estimation.	Weight of $\text{NiO} + \text{Co}_3\text{O}_4$ (grams).	Per cent. of $\text{NiO} + \text{Co}_3\text{O}_4$ in Nodules.	Per cent. of $\text{MnO}$ in Nodules.	Total Weight of $\text{NiO} + \text{Co}_3\text{O}_4$ (grams).	Weight of $\text{Co}_3\text{O}_4$ (grams).	Per cent. of $\text{Co}_3\text{O}_4$ in Nodules.	Weight of $\text{NiO}$ (grams).	Per cent. of $\text{NiO}$ in Nodules.
	$a$	$b$	$c = 100 \frac{b}{a}$	$d$	$e$	$f = 100 \frac{eb}{ad}$	$g = 0.99(c-f)$	$h = e_1 + e_2$	$i$	$k = 100 \frac{1.033i}{a_1 + a_2}$	$l$	$m = 100 \frac{b}{a_1 + a_2}$
I. 1.	0.5290	0.1526	28.84	0.1524	0.0063	1.20	25.71	0.0128	0.0019	0.19	0.0116	1.11
I. 2.	0.4733	0.1377	29.08	0.1371	0.0065	1.38	25.76	0.0077	0.0008	0.19	0.0062	1.32
II. 1.	0.4802	0.1463	30.46	0.1452	0.0077	1.61	26.94	0.0066	0.0011	0.21	0.0049	0.90
III. 1.	0.5633	0.1509	26.81	0.1496	0.0066	1.21	23.91	0.0051	0.0001	0.19	0.0034	0.68
IV. 1.	0.5035	0.1056	20.97	0.1048	0.0051	0.99	18.69	0.0088	0.0031	0.34	0.0040	0.42
V. 1.	0.5015	0.1076	21.49	0.2084	0.0088	0.92	19.30	0.0088	0.0031	0.34	0.0040	0.42
V. 2.	0.4825	0.1043	21.61	0.3525	0.0024	0.02	31.36	0.00024	0.00024	0.02		
M. 1.	0.4977	0.1679	33.74	0.3525	0.0024	0.02	31.34	0.00024	0.00024	0.02		
M. 2.	0.5516	0.1859	33.72	0.3100	0.0024	0.02	27.90	0.00024	0.00024	0.02		
N. 1.	0.5021	0.1507	30.02	0.3100	0.0024	0.02	27.91	0.00024	0.00024	0.02		
N. 2.	0.5321	0.1598	30.03	0.2891	0.00044	0.05	28.56	0.00044	0.00044	0.05		
P. 1.	0.4639	0.1427	30.76	0.2891	0.00044	0.05	28.52	0.00044	0.00044	0.05		
P. 2.	0.4767	0.1464	30.71	0.3167	0.00054	0.03	29.45	0.00034	0.00034	0.03		
Q. 1.	0.5045	0.1588	31.48	0.3167	0.00054	0.03	29.29	0.00034	0.00034	0.03		
Q. 2.	0.5110	0.1611	31.53	0.3167	0.00054	0.03	37.15	0.00034	0.00034	0.03		
K. 1.	0.2673	0.1068	39.94	0.3167	0.00054	0.03	29.72	0.00034	0.00034	0.03		
K. 2.	0.5814	0.1858	31.95	0.3167	0.00054	0.03	29.49	0.00034	0.00034	0.03		
R. 1.	0.5144	0.1631	31.70	0.3167	0.00054	0.03						
R. 2.	0.5144	0.1631	31.70	0.3167	0.00054	0.03						

TABLE IV.—*Oceanic Nodules. (Summary of Results.)*

Number of Sample.	Insoluble Residue per cent.	*Per cent. SiO <sub>2</sub> in	Oxygen per cent.	MnO per cent.	Co <sub>2</sub> O <sub>3</sub> per cent.	Ni <sub>2</sub> O <sub>3</sub> per cent.	Formula of Peroxide.
I.	20.56 20.30	(17.46) 85.45	5.47 5.48	23.71 23.76	... 0.19	... 1.23	(MnO <sub>1.946</sub> ) MnO <sub>1.901</sub>
II.	16.95 17.01 16.96	... (14.75) 86.75	... 5.78 5.82	... ... 26.94	... ... 0.19	... ... 1.46	... (MnO <sub>1.954</sub> ) MnO <sub>1.908</sub>
III.	16.83 16.83 16.63	... (14.68) 87.26	5.25 5.29 5.28	... ... 23.91	... ... 0.21	... ... 1.00	... (MnO <sub>1.979</sub> ) MnO <sub>1.937</sub>
IV.	27.68 27.63 27.52	... (23.09) 83.47	... 4.07 4.07	... ... 18.69	... ... 0.19	... ... 0.75	... (MnO <sub>1.951</sub> ) MnO <sub>1.926</sub>
V.	19.95 20.03	(16.86) 84.34	4.25 4.25	19.30 19.41	... 0.34	... 0.47	(MnO <sub>1.974</sub> ) MnO <sub>1.941</sub>

In calculating the "Formula of Peroxide" the MnO equivalents of the Co<sub>2</sub>O<sub>3</sub> and Ni<sub>2</sub>O are taken in the lower ones, and only the MnO found is taken in calculating those in brackets.

TABLE V.—*Littoral Nodules. (Summary of Results.)*

Number of Sample.	Insoluble Residue per cent.	*Per cent. SiO <sub>2</sub> in	Oxygen per cent.	MnO per cent.	Co <sub>2</sub> O <sub>3</sub> per cent.	NiO and CuO.	Formula of Peroxide.
M	29.51 29.83	(25.24) 85.10	3.96 3.96	31.36 31.34	... 0.02	Decided traces of copper were present in all the samples. The traces of nickel were so small as to be doubtful.	... MnO <sub>1.562</sub>
N	27.78 28.10	(25.55) 84.28	2.48 2.49	27.90 27.91	... 0.02		... MnO <sub>1.394</sub>
P	32.13 32.17	(26.83) 83.44	3.62 3.58	28.56 28.52	... 0.05		... MnO <sub>1.558</sub>
Q	28.99 28.91	(23.94) 82.70	3.36 3.34	29.25 29.30	... 0.03		... MnO <sub>1.507</sub>
K	... ... ...	... ... ...	6.25 6.33 6.21	... ... 37.15	... ... ...		... ... MnO <sub>1.75</sub>
R	29.56 29.21	... ...	3.39 3.37	29.72 29.49	... ...		... MnO <sub>1.505</sub>

\* The upper numbers, in brackets, refer to the original substance, the lower ones to the Insoluble Residue.

In connection with these Tables it may not be amiss to quote the analyses which I made of some nodules in 1876, and published in the *Proceedings* of this Society.\* The samples analysed were from four different localities, two of which are identical with those from which the nodules I.-V. came.

Nos. 2, 4, and 5 were from the same place, No. 2 being the matter collected round a shark's tooth as nucleus, Nos. 4 and 5 being the outside rinds of ordinary nodules.

The results are given in the following Table, the numbers being in many cases the means of several observations :—

Locality.		No.	A Insoluble Residue.	B O	C MnO <sub>2</sub>	D MnO	E Fe <sub>2</sub> O <sub>3</sub>	F Al <sub>2</sub> O <sub>3</sub>	G H <sub>2</sub> O	Na <sub>2</sub> O
Lat.	Long.									
13° 52' S.	149° 17' W.	2	17.55	6.13	33.30	27.18	...	...	...	...
...	...	4	15.30	5.92	32.23	...	23.86	...	...	...
...	...	5	15.30	6.49	35.28	...	24.85	...	10.2	...
37° 52' N.	160° 17' W.	6	36.24	6.49	24.41	...	20.16	3.83	7.70	5.98
42° 42' S.	134° 10' E.	7	17.98	7.54	41.11	33.53	18.04	2.55	7.31	...
22° 21' S.	150° 17' W.	8	21.74	5.19	28.20	...	24.52	7.67	8.54	8.5

A is the residue which remains undissolved after treating the mineral with strong hydrochloric acid, evaporating to dryness and redissolving. In No. 5 it contains 55.16 per cent. silica, and in No. 6, 82.27 per cent.

B is the available oxygen determined by Bunsen's method.

C is the MnO<sub>2</sub> equivalent to the available oxygen.

D is the MnO found by weighing as Mn<sub>3</sub>O<sub>4</sub>.

E is the Fe<sub>2</sub>O<sub>3</sub> found by titration with SnCl<sub>2</sub>.

F is the alumina found by subtracting the Fe<sub>2</sub>O<sub>3</sub> found in E from the weight of the precipitate with acetate of soda.

G is the water expelled on ignition ; it is obtained by deducting two-thirds of the oxygen found in B from the loss of weight by ignition.

The samples were dried for ten or twelve hours at 140° C., and therefore the percentages are higher than those in Table IV., the samples in it having been analysed air-dried.

From these Tables it will be seen that nodules from all localities have similar composition. The most important difference between the littoral and the oceanic nodules is, that in the former the manganese is less highly oxidised than in the latter. In the oceanic nodules, when we consider the manganese alone, the peroxide is very little short of MnO<sub>2</sub> ; in the littoral ones it is very little over Mn<sub>2</sub>O<sub>3</sub>. In both oceanic and littoral ones the manganese is more highly oxidised in the kernels than in the rinds ; this difference is particularly marked in the littoral ones. Nickel, cobalt, and copper are probably present in

\* *Proc. Roy. Soc. Edin.*, 1876, vol. ix. p. 287.



all, but their relative proportions are different in the littoral and in the oceanic nodules. Cobalt can be determined in both, and ranges from 0·02 per cent. in Loch Fyne nodule M to 0·34 per cent. in oceanic nodule V. Nickel is present in large though variable quantity in the oceanic nodules, as much as 1·46 per cent. of oxide in II., falling to 0·47 per cent. in V. In the Loch Fyne nodules the presence of nickel was doubtful. Copper was present in both classes of nodule. In the oceanic ones, however, the traces were not always very distinct, whilst in the Loch Fyne ones they were very pronounced. In testing for thallium, it was sufficient with oceanic nodules to moisten a piece of the size of a bean with HCl and place it in a platinum triangle over a Bunsen burner to get a strong thallium line in the spectroscope. Thallium could not be detected in this way in the Loch Fyne nodules.

The insoluble residues were always tested quantitatively, and consisted, besides silica, of alumina and ferric oxide, with smaller quantities of lime and magnesia. The silica, however, of the Loch Fyne nodules was largely quartz, which was not the case with the oceanic nodules. The percentage of insoluble residue varies much in both sorts, but it is always greater in the Loch Fyne ones than in the oceanic ones. The percentage of silica in the Loch Fyne nodules varies very little from 25, leaving from 2 to 6 per cent. of bases in the insoluble residue. In the oceanic nodules, excepting IV., the silica varies between 14·68 and 17·46 per cent., leaving from 2 to 3 per cent. bases in the residue. In IV. the amount would be  $4\frac{1}{2}$ . In the kernels (K) the moisture driven off at 100°, the carbonic acid, and the  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$  were determined, and we have the following tabulated summary:—

*Sample K—Kernels of Loch Fyne Nodules.*

Carbonic acid, . . . . .	0·83 per cent.
Moisture at 100° . . . . .	8·23 „
Available oxygen, . . . . .	6·26 „
MnO, . . . . .	37·15 „
$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ , . . . . .	4·78 „
CuO, . . . . .	trace
NiO, . . . . .	doubtful trace.

The insoluble residue was not determined.

In order to obtain some knowledge of the other constituents of the Loch Fyne nodules, a number of nodules were pounded up and mixed, so as to form an average sample in which the determinations were to be made. They contained a certain amount of soluble matter from the sea water, and, if it had been intended at first to make a complete analysis, the whole of this sample would have been extracted at once. This was not done, and the various portions, X, Y, and Z, have been treated separately. Particulars follow.

X. *General Analysis.*

A sample of air-dried Loch Fyne nodules was thoroughly extracted with boiling water. The weight taken was 5·0405 grammes, and the insoluble portion, when dried at 100°, was found to weigh 4·5458.

A. *Estimation of Moisture.*—0·1910 of the sample was dried at 100°, and found to lose 0·0010 grammes, *i.e.*, the percentage of water in it driven off at 100° is 0·53.

B. *Estimation of the Oxygen reducible by Hydrochloric Acid.*—0·1195 grammes were boiled with strong hydrochloric acid. The chlorine liberated was passed into a solution of potassium iodide, and the amount of iodine liberated found by titration with sodium hyposulphite. There was found to be 4·104 per cent. of available oxygen, representing 22·32 per cent. of  $\text{MnO}_2$ .

C. *Estimation of Weight lost on Ignition.*—0·1263 grammes were strongly heated over a Bunsen flame. The loss of weight was found to be 0·0224 grammes; that is, 17·74 per cent.

D. *Estimation of Insoluble Residue,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Co}_2\text{O}_3$ .*—2·0880 grammes were treated with strong hydrochloric acid in a covered beaker, the mixture evaporated to dryness over a water-bath, the residue moistened with a few drops of strong hydrochloric acid, taken up with water, and the solution filtered.

The insoluble residue was heated over the water-bath with a strong solution of carbonate of soda. The heating was carried on for about forty-five minutes, water being occasionally added to keep the solution of constant strength. The solution was then decanted through a filter, more carbonate of soda solution added to the insoluble residue, and the same process repeated. This was done altogether three times. What remained undissolved was washed, ignited, and weighed. It was found to weigh 0·5790 grammes, that is, 27·73 per cent., consisting of silica and silicates, which resist the action of sodium carbonate solution.

The silica which had dissolved in the sodium carbonate was precipitated from it by hydrochloric acid as usual, filtered, ignited, and weighed. It weighed 0·11928 grammes, that is, 5·71 per cent. of soluble silica.

The *filtrate* from the insoluble residue was treated with excess of carbonate of baryta to precipitate the iron and alumina. The precipitate was filtered off and redissolved in hydrochloric acid, the baryta present precipitated with sulphuric acid and filtered off, the filtrate made up to 250 c.c. volume, and two estimations of  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$  made.

100 c.c. (= 8352 grammes of substance) gave 0·03368 grammes,  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ , *i.e.*, 4·03 per cent.; 75 c.c. (= 6264 grammes of substance) gave 0·02568 grammes,  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ , *i.e.*, 4·09 per cent. The two precipitates of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  were united and fused with bisulphate of potash. An insoluble residue of silica, weighing 0·00898 grammes, was found. This represents 0·61 per cent. of silica in the nodules, which, when added to the previously found 5·71 per cent., gives altogether 6·32 per cent.

Also, subtracting 0·61 from 4·06 (the average of the iron and alumina estimations), we find 3·45 per cent. of  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ .

In 50 c.c. of the above-mentioned 250 c.c. solution 0·00676 grammes of iron were found by titration with stannous chloride. This is equivalent to 2·31 per cent. of  $\text{Fe}_2\text{O}_3$  in nodules. Subtracting from 3·45, there remains 1·14 per cent.  $\text{Al}_2\text{O}_3$ .

In the *filtrate* from the barium carbonate precipitate the manganese was not estimated, but the cobalt was. It was separated by means of sulphide of ammonium and acetic acid, as usual, then precipitated as Fischer's salt with nitrite of potash, and this precipitate dissolved in HCl, and the cobalt reprecipitated with a few drops of carbonate of soda solution. It should be mentioned that, before treatment with sulphide of ammonium and acetic acid, sulphuric acid was added to precipitate the excess of barium; to the filtrate from  $\text{BaSO}_4$  sodium carbonate was added to precipitate both manganese and cobalt, and this precipitate dissolved up and the cobalt separated. 0·00049 grammes of  $\text{Co}_2\text{O}_3$  were found, representing 0·025 per cent. of  $\text{Co}_2\text{O}_3$  in the nodules.

*E. Estimation of Carbonic Acid.*—0·1792 grammes of nodules were treated with solution of phosphoric acid, the carbonic acid gas liberated passed into baryta water of known strength, and the excess of baryta determined by titration with hydrochloric acid. 0·015905 grammes of  $\text{Co}_2$  were found, representing 8·87 per cent. of carbonic acid in the nodules.

Another estimation was made; 0·1704 grammes of nodules were found to contain 0·015285 grammes of carbonic acid gas, that is, 8·91 per cent.

*F. Estimation of Phosphoric Acid.*—0·7162 grammes of nodules were converted into chlorides by treatment with HCl (the insoluble residue being removed in the usual way), and the solution made up to 250 c.c.

125 c.c. of the solution was treated with acetate of soda, and the phosphoric acid obtained as a precipitate of ferric phosphate. This precipitate was fused with bisulphate of potash and the fused mass dissolved in water. There was just a mere trace of insoluble matter. To this acid solution a very slight excess of pure sodium carbonate was added to neutralise any free sulphuric acid present, and then excess of nitric acid. The solution was then evaporated down, large excess of ammonium molybdate added, and the solution allowed to stand in a warm place till all the phosphoric acid was precipitated. The precipitate was filtered off and dissolved in ammonia, and the phosphoric acid precipitated with magnesia mixture as usual. The precipitate was ignited and weighed. It weighed 0·00319 grammes ( $\text{Mg}_2\text{P}_2\text{O}_7$ ), representing 0·57 per cent.  $\text{P}_2\text{O}_5$ .

*Estimation of Lime and Magnesia.*—120 c.c. of the above-mentioned 250 c.c. solution (equivalent to 0·3438 grammes nodules) were treated with sulphide of ammonium, filtered, the ammonium sulphide in the filtrate destroyed by means of hydrochloric acid, evaporated and filtered from sulphur, and the lime precipitated twice with ammonium oxalate as usual. After the second precipitation the calcium oxalate (which seemed to contain alumina) was redissolved, and the lime precipitated a third time with ammonium oxalate. The precipitate was filtered, ignited, and dissolved in hydrochloric acid. It

weighed 0.0433 grammes. The solution was just rendered alkaline with ammonia. This precipitated the trace of alumina. It was filtered and weighed, and found equal to 0.00414 grammes. Subtracting this from 0.0433 grammes, we have 0.03919 grammes of  $\text{CaCO}_3$ , that is, 6.38 per cent. of  $\text{CaO}$ .

The sulphide of ammonium precipitate, together with the small precipitate of alumina, was worked up for any lime that might be present in it as phosphate. It was ignited, dissolved in hydrochloric acid, the solution evaporated. The phosphoric acid, iron, and alumina present were precipitated by adding acetate of soda. In the filtrate from this the manganese was precipitated with ammonium sulphide. In the filtrate from the manganese sulphide a small additional quantity of lime was obtained on addition of ammonium oxalate; 0.09154 grammes of  $\text{CaCO}_3$  were thus obtained. This is 0.45 per cent. of  $\text{CaO}$  of the nodules. Adding this to the previously found 6.38 per cent., we have altogether 6.83 per cent. of  $\text{CaO}$  in the nodules.

The filtrates from the oxalate of lime were evaporated down, and the ammonium salts driven off. The residue was taken up with hydrochloric acid and water, and filtered. Ammonia and phosphate of soda were added. A precipitate was obtained, which was filtered off, ignited, and weighed as  $\text{Mg}_2\text{P}_2\text{O}_7$ . It weighed 0.03366 grammes, representing 3.53 per cent. of  $\text{MgO}$  in the substance. Another estimation gave 4.08 per cent. of  $\text{MgO}$ .

G. *Estimation of Moisture at 162° C.*—0.6215 grammes of substance were exposed in a small bath to a temperature of 162° for about forty minutes. The water driven off was collected in a calcium chloride tube. It was found after heating that the substance had lost 0.0085 grammes (1.37 per cent.), while the calcium chloride tube had gained 0.0098 grammes (1.57 per cent.); mean, 1.47.

H. *Estimation of Carbon (by combustion).*—0.6215 grammes were ignited with pure lead chromate and oxide of copper in a stream of air free from  $\text{CO}_2$ . The carbonic acid given off was collected in a soda-lime tube, and found to weigh 0.0596 grammes, that is, 9.59 per cent. As 8.89 per cent. of carbonic acid as such were found in the substance, this gives us 0.70 per cent. of carbonic acid due to organic carbon, or 0.20 per cent. of organic carbon.

#### Y. *Estimation of MnO and Alkalies.*

5.3893 grammes of the same sample of air-dried Loch Fyne nodules were boiled with water as before, filtered, and the filtrate evaporated. The residue, which crystallised out when dried at 110°, weighed 0.1240 grammes, that is, 2.30 per cent. of the nodules were found soluble in water. The insoluble part was dried at 100°, and separated from the filter-paper. The latter was then ignited, and the ash added to the rest. The whole was then air-dried, and this air-dried mass was used for analysis.

A. *Estimation of Moisture (driven off at 150°–160°).*—0.3609 grammes were heated in a small bath, and the water driven off absorbed by a calcium chloride tube. The heating continued for over half an hour. The substance was found to have lost 0.0194 grammes (5.33 per cent.), while the calcium chloride gained 0.0183 grammes. The

moisture in X is 1.47 per cent. and in Y 5.53 per cent.; the difference is 4.06. Therefore, 95.94 parts of Y are equivalent to 100 parts of X, and we must multiply the results in Y by 1.042 to make them comparable with those in X.

B. *Estimation of Alkalies.*—3.7014 grammes were dissolved in hydrochloric acid, and the insoluble part removed as usual. The solution was made up to 250 c.c.; 100 c.c. of this solution was used for the estimation of the alkalies. In the first place, however, the barium hydrate and ammonium carbonate to be used in the separation were tested for their purity. 5.518 grammes of barium hydrate were dissolved in water, and carbonic acid gas passed through the solution to saturation. The whole was then boiled and filtered. The barium carbonate precipitate was dried and roughly weighed. It weighed from 2.95 to 3 grammes, *i.e.*, about 47.6 per cent. of  $\text{Ba(OH)}_2$  in the barium hydrate used, the rest being water. The filtrate from the barium carbonate was evaporated nearly to dryness in a platinum basin, a little barium carbonate which settled out was filtered off, and the filtrate evaporated to dryness. The residue was redissolved in water, refiltered, evaporated to dryness again, and weighed. It weighed 0.0017 grammes, *i.e.*, 0.031 per cent. of alkalies as chloride in the baryta hydrate. *N.B.*—This hydrate of baryta had previously been recrystallised.

The *ammonium carbonate* was then tested. It was a solution of 1 part of salt in 5 of water. 5 c.c. of it were evaporated to dryness in a platinum basin, and the residue ignited, and then moistened with hydrochloric acid and ignited again. It weighed 0.0012 grammes, therefore 1 c.c. of the ammonium carbonate solution leaves 0.00024 grammes of residue.

To the above-mentioned 100 c.c. solution (containing 1.4805 grammes of substance) 4.088 grammes of barium hydrate were added. It dissolved completely, and the whole was allowed to stand over-night. Next morning carbonic acid gas was passed through the turbid solution to saturation, and the solution boiled to get rid of excess of carbonic acid gas; it was then filtered. The *precipitate* was dried and transferred to the original flask in which precipitation took place, and the ignited filter ash added.

The *filtrate* was evaporated down to a bulk of from 25 to 50 c.c., and the barium and calcium present precipitated by the addition of 5.5 c.c. of ammonium carbonate. This precipitate was dried and added, along with its filter ash, to the flask in which were the other bases and excess of barium carbonate. The reason for doing this was, that on evaporation of the filtrate from the bases, a further small quantity of a dark-brown precipitate ( $\text{MnO}_2$ , most likely) came down.

The filtrate from the ammonium carbonate precipitate was evaporated to dryness in a platinum basin, the ammonium salts driven off, and redissolved in water. A good deal of grey powder, probably barium carbonate, remained undissolved. This was added to the precipitate of bases mentioned above. The filtrate was evaporated to dryness and ignited. It weighed 0.0279 grammes. This, then, is the weight of alkalies as chlorides. When dissolved in water it left a mere trace of insoluble matter, coloured with carbon. This was filtered off, ignited, and weighed. It weighed 0.0004 grammes.

Thus, to find the weight of alkalis as chlorides in the 1.4805 grammes of nodules used, we have to subtract from 0.0279 grammes 0.00132 grammes (residue left by 5.5 c.c. ammonium carbonate solution) + 0.00127 (which is the residue in 4.088 grammes of barium hydrate) + 0.0004 (insoluble matter). This leaves 0.02491 grammes (or 1.68 per cent.) of alkalis weighed as chlorides.

The *potassium* in the above alkaline salts was estimated by means of platinic chloride. 0.01356 grammes of the double chloride of potassium and platinum ( $2\text{KCl} \cdot \text{PtCl}_4$ ) were found—that is, 0.01356 grammes of potassium chloride in 1.4805 grammes of nodules, or 0.91 per cent. of KCl. This is equivalent to 0.45 per cent. of  $\text{K}_2\text{O}$ , leaving 0.41 per cent. of  $\text{Na}_2\text{O}$ .

The error due to the ratio of potash to soda in the nodules being different from that in the reagents can be but trifling.

*C. Analysis of the Precipitate of Bases obtained in separating the Alkalies.*—Dissolved this precipitate in hydrochloric acid, and made up the solution to 250.85 c.c.

*Estimation of Manganese.*—Took 100 c.c. of the above solution (0.5902 grammes nodules). Evaporated to dryness to get rid of excess of acid, took up the residue with water, and, as usual, added barium carbonate to precipitate iron and alumina. In the filtrate precipitated the manganese, as usual, as  $\text{MnO}_2$  by means of bromine, filtered off the  $\text{MnO}_2$ , dissolved it in hydrochloric acid, removed any baryta as  $\text{BaSO}_4$ , evaporated solution to dryness, took up with water, and precipitated the manganese with sodium carbonate as  $\text{MnCO}_3$ . Filtered, ignited to  $\text{Mn}_3\text{O}_4$ , and weighed. The  $\text{Mn}_3\text{O}_4$  weighed 0.19646 grammes (or 33.29 per cent.). This is equivalent to 30.96 per cent. of  $\text{MnO}$  (including cobalt) in the nodules.

*$\text{BaCO}_3$  Precipitate.*—Dried this precipitate, redissolved it in hydrochloric acid, and precipitated the baryta with sulphuric acid. Evaporated the solution over water-bath to get rid of excess of acid. Took up with water, filtered from traces of insoluble matter, diluted, and precipitated with a slight excess of ammonia, boiling till all excess was expelled. The precipitate of  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$  when ignited weighed 0.0266 grammes. Fused it with bisulphate of potash in order to see if silica was present. 0.00194 grammes of the fused mass was insoluble, leaving 0.0246 grammes of  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ , i.e., 4.17 per cent.

To make the figures obtained for the alkalis and manganese comparable with those obtained in X, we have in both cases used substances extracted with water, and therefore free from soluble matter; but in X the substance was used dried at  $100^\circ$ , while in Y it was exposed to the air after extraction, and was therefore in an air-dry condition. X contained 1.47 per cent. moisture, which was driven off at  $162^\circ \text{C}$ .; Y contained 5.53 per cent., the difference being 4.06. Therefore 95.94 parts of Y are equivalent to 100 parts of X, and we must multiply the results in Y by 1.042, and we have  $\text{MnO} = 32.23$  per cent.,  $\text{K}_2\text{O} = 0.47$  per cent., and  $\text{Na}_2\text{O} = 0.43$  per cent.

Some of the same air-dried samples of nodules were examined without being extracted with boiling water, or rather the extraction formed part of the analysis.

A. *Estimation of Moisture driven off at 180°*.—0·8078 grammes of nodules (unextracted) were heated in an air-bath to 180°. The heating was continued for about three hours, two hours being between 160° and 180°. The loss of weight was found to be 0·0363 grammes (4·50 per cent.).

B. *Estimation of Matter soluble in Water*.—8·8078 grammes were (after the moisture had been driven off) extracted with hot water. The solution was evaporated to dryness, ignited, and weighed. It weighed 0·0169 grammes, that is, 2·09 per cent. of the nodules.

The dry residue was redissolved and tested for *potash*, and found to contain a little.

C. *Estimation of Insoluble Residue, Manganese, Iron, and Alumina*.—Treated what was insoluble in water of the above 0·8078 grammes with hydrochloric acid, and separated the silica and silicates as usual. The insoluble residue weighed 0·26106 grammes, equal to 32·32 per cent.

The *filtrate* from the insoluble residue was made up to 100 c.c. 50 c.c. of the solution (equal to 0·4039 grammes of nodules) were used for manganese estimation, and 0·1349 grammes of  $\text{Mn}_3\text{O}_4$  found. This gives 31·11 per cent. of  $\text{MnO}$ .

The *iron and alumina* were precipitated by barium carbonate in 100° c.c. of the solution. (It was the filtrate from this precipitate that was used for the manganese estimation.) The precipitate was redissolved in hydrochloric acid, the baryta present precipitated with sulphuric acid, and iron and alumina precipitated from the filtrate from the barium sulphate. 0·0146 grammes of  $\text{Fe}^2\text{O}_3 + \text{Al}_2\text{O}_3$  were found, representing 3·60 per cent. in the nodules. This was fused with bisulphate of potash, and found free from silica.

To make the figures comparable with those of X, we have 2·09 soluble matter and 4·05 moisture, together 6·14; from which we deduct 1·47 moisture in X, leaving 4·67; whence 95·33 of Z are equivalent to 100 of X. We must therefore multiply the figures obtained in Z by 1·049. We have then  $\text{MnO} = 32·62$  per cent., insoluble residue = 33·90 per cent., and  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 = 3·77$  per cent. After making all reductions we have—

*Insoluble Residue*.—In X 34·05 per cent., and in Z 33·90 per cent. As the soluble silica was determined in X, and the value of the total residue in Z agrees closely, we take the values for X, namely, soluble  $\text{SiO}_2$  6·32 per cent., and remainder of residue 27·73; together, 34·05 per cent.

$\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ .—As the figure found in Z for the sum of these constituents agrees sufficiently with that found in X, we take the value for the individual constituents found in it, namely,  $\text{Fe}_2\text{O}_3$ , 2·31 per cent., and  $\text{Al}_2\text{O}_3$ , 1·44 per cent.

*Manganese*.—The results obtained in Y and Z agree well, and we take the mean, 32·43 per cent. of  $\text{MnO}$ .

*Loss on Ignition*.—The amount of substance taken for this determination was 0·1263 grammes. Recent experiments show that it would lose about three-sevenths of its available oxygen on ignition, and it may therefore be safely concluded that all the

CO<sub>2</sub> would be driven off, also all the water, and two-thirds of the available oxygen. We have then—

Moisture removed at 162°, . . .	1·47 per cent.
CO <sub>2</sub> , . . .	8·87 "
3/7 available oxygen, . . .	1·76 "
Balance, . . .	5·64 "
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Total loss found, . . .	17·74 "

We have then the following composition :—

Moisture, . . .	1·47 per cent.
Carbonic acid, . . .	8·89 "
Available oxygen, . . .	4·10 "
MnO, . . .	32·43 "
Co <sub>2</sub> O <sub>3</sub> , . . .	0·025 "
CuO, . . .	traces
Fe <sub>2</sub> O <sub>3</sub> , . . .	2·31 per cent.
Al <sub>2</sub> O <sub>3</sub> , . . .	1·14 "
CaO, . . .	6·83 "
MgO, . . .	4·08 "
K <sub>2</sub> O, . . .	0·47 "
Na <sub>2</sub> O, . . .	0·43 "
P <sub>2</sub> O <sub>5</sub> , . . .	0·57 "
Soluble SiO <sub>2</sub> , . . .	6·32 "
Balance of insoluble residue, . . .	27·73 "
Do., loss on ignition, . . .	5·64 "
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	102·43 "

If we assign the CO<sub>2</sub> first to the CaO and then to the MgO, we shall have—

CaCO <sub>3</sub> , . . .	12·20 per cent.
MgCO <sub>3</sub> , . . .	5·17 "
MgO, . . .	2·41 "

#### ANALYSIS OF THE MUD IN WHICH THE NODULES FROM LOCH FYNE WERE FOUND.

The mud was air-dried, and had been freed from manganese nodules and shells. The moisture, carbonic acid, available oxygen, manganous oxide, and insoluble residue were determined, with the following results :—

Moisture at 162° C., . . .	5·92 per cent.
Carbonic acid, . . .	2·55 "
Available oxygen, . . .	merest trace.
MnO, . . .	0·71 per cent.
Insoluble residue, . . .	74·26 "
CuO, . . .	distinct traces.



With regard to the available oxygen, 0·5750 grammes were taken, and, after boiling with strong HCl as usual, the solution of potassium iodide remained colourless. On adding a little starch solution to it, however, a slight purple tint was produced, which the smallest drop of hyposulphite sufficed to decolorise. There is, therefore, only the smallest possible trace of  $\text{MnO}_2$  present, and the 0·71 per cent.  $\text{MnO}$  is really present as  $\text{MnO}$ .

#### ANALYSIS OF PECTEN SHELLS PICKED OUT OF THE LOCH FYNE MUD.

*Qualitative Analysis.*—These shells were well scrubbed with pure water, so as to free them from all adhering mud, and then air-dried. They contained—

Organic matter,	.	.	A little.
$\text{CO}_2$ ,	.	.	A large amount.
$\text{SO}_3$ ,	.	.	Small amount.
$\text{SiO}_2$ ,	.	.	Very small amount.

No metals precipitable by  $\text{H}_2\text{S}$  in HCl solution. Very small precipitate with sulphide of ammonium—

$\text{CaO}$ ,	.	.	Very large amount (no $\text{BaO}$ ).
$\text{MgO}$ ,	.	.	Trace.

*Qualitative Estimation of  $\text{MnO}$  and  $\text{P}_2\text{O}_5$ .*—1·5695 grammes were treated with dilute HCl. There was very little organic matter present, which shows that the shells were very old. The insoluble residue was filtered, ignited, and weighed; it weighed 0·0063 grammes = 0·4 per cent. insoluble residue. To the filtrate from the insoluble residue added  $\text{Fl}_2\text{Cl}_6$  and precipitated all the  $\text{P}_2\text{O}_5$  with acetate of soda. In the filtrate from this the manganese was precipitated with bromine. The following results were obtained :—

Insoluble residue,	0·40 per cent.
$\text{P}_2\text{O}_5$ ,	0·09 „
$\text{MnO}$ ,	1·00 „



MR. BUCHANAN ON MANGANESE NODULES.

