

XXXII.—*On the Manganese Oxides and Manganese Nodules in Marine Deposits.**

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During the "Challenger" Deep-Sea Exploring Expedition a great many peculiar-looking manganese nodules or concretions were dredged from the floor of the ocean at great depths, chiefly in the Red Clay areas of the Pacific, but also in less abundance in the Red Clays of the Atlantic. In the other varieties of Deep-Sea deposits these nodules were much less abundant than in the Red Clays.

In still more recent soundings, both American and British ships have discovered in many regions of the Pacific and Indian Oceans a dark-brown coloured deposit containing a large amount of manganese dioxide, similar in character to the Red Clays from which the "Challenger" procured the largest hauls of manganese nodules. There is then every reason for supposing that manganese deposits and nodules are very widely distributed over the ocean's bed, especially in deep water at great distances from land. It was only occasionally that manganese nodules were present in any abundance in a Globigerina Ooze, and in these exceptional instances there was always much volcanic débris associated with the deposit. In the Blue Muds surrounding continental shores manganese nodules were rarely observed; still, on some rocks and boulders dredged from terrigenous deposits, a coating of manganese dioxide was observed on that portion of the stone which had projected above the surface of the mud.

The interest in these peculiar manganese deposits is much enhanced by the extraordinary organic and mineral associates of the manganese nodules in the centre of the South Pacific. In this region hundreds of sharks' teeth, many of them of gigantic size and

* Manganese, symbol, Mn; atomic weight, 55 (oxygen=16), is a metal closely resembling iron, with which it is most frequently associated. It is slightly magnetic. It has never been found native except in minute traces in meteorites. When eliminated from its ores it is of a greyish-white colour, resembling cast-iron; it has a specific gravity of about 7.2-8.0 (Mendelëff). The metal was first isolated in 1774 by Salier. For a long time there was confusion as to its name, and not till after the beginning of the present century was the name manganese generally adopted. The Latin (*manganesium*) is arbitrarily altered from magnesium, and is rarely used in technical works. *Magnesia* was the original name of the black oxide of manganese, which was used by the ancients for removing colouring matter from glass, and was generally confounded with the lodestone (*Magnes* and *Magnesium lapis*).

Its principal use is in the manufacture of ferro-manganese, which absorbs nine-tenths of the whole production. The dioxide of manganese, in connection with hydrochloric acid, is the means at present adopted to produce chlorine for bleaching purposes, but the decomposition of magnesium chloride, or the electrolysis of water with the production of peroxide of hydrogen, may altogether revolutionise this process of bleaching. Small quantities of manganese are in demand to clear glass coloured by iron; for certain alloys; for the manufacture of pottery, electric piles, and colours. Speaking generally, iron and manganese are the great pigments of nature. The annual production of manganese in 1891 was 316,000 tons, of which more than one-half was produced by Russia, principally from the Caucasus, where the mineral is very rich, containing 90 per cent. of dioxide; Germany, the United States, and Chili produce each between 25,000 and 40,000 tons annually; Cuba, France, and Belgium each between 15,000 and 20,000 tons; Great Britain Sweden, and Austria each between 5000 and 10,000 tons.

belonging to extinct species, dozens of ear-bones and other bones of cetaceans, myriads of small zeolitic crystals, cosmic spherules, and numerous fragments of highly altered volcanic rocks were brought up with the manganese nodules, and these bodies not unfrequently formed the nuclei around which the manganese was deposited. These manganese nodules, and the other interesting substances associated with them, are described and figured with considerable detail in the "Challenger" Report on Deep-Sea Deposits.*

In the present paper we propose to point out the distribution of the oxides of manganese in the geological series of rocks, in fresh and sea water, and in marine deposits, with special reference to our explorations in the lochs of the west of Scotland; to give an account of investigations undertaken to ascertain the source of the manganese present in marine deposits in the form of the higher oxides, and thereafter to discuss the various views that have been advanced to explain the formation and distribution of manganese concretions in marine deposits in general.

Manganese in Eruptive and Schisto-Crystalline Rocks.—Manganese is present in nearly all the crystalline rocks, generally only in such minute traces that it does not usually appear in analyses of these rocks owing to its not having been specially looked for. It increases in amount along with the iron, and is more abundant in the basic than in the acid series of rocks.† In some fragments of basic volcanic glass from the bed of the Pacific, MURRAY and RENARD found 0·34 and 0·44 per cent. of manganous oxide (MnO) present as silicates.‡ In a large number of rocks which we examined, the quantity of manganous oxide (MnO) ranged between 0·01 and 1·0 per cent. In the unaltered crystalline and schisto-crystalline rocks the manganese exists as protoxide in combination with silicic acid. When these rocks had undergone alteration, some of the manganese was present as carbonate.§

* See MURRAY and RENARD, *Deep-Sea Deposits Chall. Exp.*, London, 1891.

† The following are some of the manganese-bearing silicates (the numbers after the names indicate the percentage of MnO):—Paulite, 0·6; diallage, 5–20; augite, 0·3; acmite, 1–3; rhodonite, 54; hermanite, 47; ægerine, hornblende; pyrosinalite, 21; astrophyllite, 10; tephroite, 70; knabellite, 35; zephrolite; manganese-alumina garnet; pyrochlore, 7 (somewhat variable); tantalite, 1–6.

‡ MURRAY and RENARD, *op cit.*, p. 307.

§ I. In the following rocks, chiefly from the Clyde drainage area, the manganese oxide was soluble in carbonic and dilute acetic acids, therefore presumably present as carbonate:—

Felstone,	from	contained from	Per cent. MnO.
	Blackhill,		0·5 to 1·0
"	Devonside,	"	trace
"	Gourock (2 samples),	"	0·1 to 0·5
"	Innerleithen,	"	0·1 to 0·5
"	Lanark,	"	0·5 to 1·0
"	Lesmahagow (9 samples),	"	0·5 to 1·0
" (Green)	"	"	0·1 to 0·5
Breccia (calcareous),	Glenfalloch,	"	0·5 to 1·0
Limestone,	Kilsyth,	"	0·5 to 1·0
Mud (25 fathoms),	Cumbræ,	"	0·1 to 0·5
Sandstone (new red),	Hamilton,	"	0·5 to 1·0
Tuff (volcanic),	Eaglesham,	"	0·1 to 0·5

These silicates are in all probability the original source of all the carbonate and

II. In the following rocks the manganese occurred only partly in a soluble condition :—

		Per cent. MnO.
Mica-schist,	from Glenmorag,	0.1 to 0.5
Sandstone,	„ Lesmahagow,	0.5 to 1.0
Felstone,	„ Pentland Hills,	0.5 to 1.0
„	„ Clyde Area,	0.1 to 0.5
Basalt,	„ Castle Hill, Edinburgh,	0.01 to 0.1
Volcanic rocks,	„ Argyllshire,	0.1 to 0.5

III. In the following rocks the manganese was in an insoluble condition, probably silicate :—

		Per cent. MnO.
Pumice,	from Lipari,	0.5 to 1.0
„ (black)	„ Iceland,	0.5 to 1.0
„	„ Ascension,	0.1 to 0.5
Pumice tuff,	„ Rhineland,	0.1 to 0.5
Iceland „	„ Dannibora,	0.1 to 0.5
Felstone,	„ Coldstream,	0.1 to 0.5
„	„ Kilmalcolm,	0.5 to 1.0
Dolerite,	„ Kirk o' Shotts,	0.1 to 0.5
Greywacke,	„ Abington,	0.1 to 0.5
Granite,	„ Lanarkshire,	0.1 to 0.5
Melaphyr,	„ Bowling,	0.01 to 0.1
Serpentine,	„ Glenfalloch,	trace
Peridotite,	„ „	0.01 to 0.1

Besides the above-named rocks, about fifty others were examined for manganese, which was found to be present in amounts varying from traces to 0.5 per cent. of MnO.

Fresh Blue Muds, from various places in the estuaries of the Clyde and Forth, were examined and found to contain manganese partly as silicate and partly as carbonate. There was a slight trace of manganese found in some samples of Globigerina Ooze, but none in corals, boiler deposits, or siliceous sinter (from Iceland). A piece of coral (*Pleurocorallium johnsoni*, taken by the "Challenger," Station 3, 1525 fathoms), was coated on the outside with manganese dioxide, but internally there was no trace of manganese. Minute traces were found in kelp and in sea-weed ash.

The process adopted for the comparative estimation of manganese was the colour-test, obtained when the material under examination was fluxed with potassium and sodium carbonates and a little pure potassium nitrate. The fused mass, on cooling, gives the green colour characteristic of manganates—even when manganese is only present in minute traces. Comparison with a standard series of coloured fluxes, each containing a known amount of manganese varying from 0.01 to 1.0 per cent., was an easy, quick, and at the same time a comparatively accurate, method of estimating the quantity of manganese present. The proportion of manganese existing in the rocks under the various conditions of carbonate, silicate, and higher oxides might be roughly determined by thorough trituration and treatment with carbonic acid in aqueous solution; but the expenditure of time involved in the prosecution of this process renders the substitution of dilute acetic acid for carbonic acid advisable, the dilute acetic acid attacking the carbonate alone. The amount of peroxide present was determined as usual by the Bunsen process, *i.e.*, by taking advantage of its power of liberating chlorine from hydrochloric acid. Crystalline silicates, even when reduced to the finest state of division, are only very gradually decomposed by carbonic acid. We found that all the manganese which is combined with carbonic acid in the rocks is thus rapidly extracted by the use of dilute acetic acid, and can be determined by evaporating the solution so obtained to dryness, and treating the dried residue with fluxing materials at a red heat, or by actual precipitation by the general methods in use for manganese determination. We can thus determine the proportion of manganese existing in a rock or mineral as carbonate. If, however, the manganese exists partly as carbonate and partly as silicate, we obtain the portion present as carbonate in the acetic acid solution, and the portion existing as silicate or the higher oxides in the insoluble residue.

The process adopted by us for the determination of the quantity and state of combination of the manganese in a rock sample was as follows :—

(1) Exactly 1 gramme of the sample, reduced to a fine powder, was intimately mixed with 4 grammes of the fusion mixture already referred to (20 parts Na_2CO_3 , 26 parts K_2CO_3 , 1 part KNO_3), and heated in a platinum crucible over the blow-pipe until tranquil fusion supervened. The liquid mass was then poured out upon a porcelain slab and allowed to cool. The quantity of manganese present in the fused magma was ascertained by comparing its colour with that of the series of standard coloured fluxes. This gave the total percentage of manganese in the sample.

(2) Another portion from the same pulverised sample, weighing 1 gramme, was exhausted with dilute acetic acid (to extract the carbonates), and the amount of manganese in the residue determined colorimetrically after fusion

higher oxides of manganese found either in sedimentary strata or in the ores of veins.*

The Ores of Manganese.—The ores of manganese and iron are almost the only metalliferous minerals that occur in stratified beds. The manganese ores are as widely distributed as those of iron, but they are only rarely found in any considerable quantity, while those of iron are often present in very extensive beds. The principal manganese ores are oxides, and so intimate is their connection with those of iron that manganese occurs as a constituent in all iron ores; manganese dioxide was at one time, indeed, regarded as an iron ore. The ores of iron and manganese have evidently had a similar origin. In the United States, nodules of manganese dioxide form the bulk of the manganese ores, and they either are or were embedded in calciferous shales. They occur in pockets or sheets, the individual nodules varying from the size of a pin's head to masses weighing tons. In Russia, Chili, and other countries the manganese ores appear, from the descriptions, to be similar to those of the United States, and to have been laid down under similar physical conditions. The manganese and iron ores occur in the stratified rocks of all geological formations, and they appear to have had their origin in the disintegration of the crystalline rock-masses of the region in which they are found. The manganiferous minerals and ores of veins and lodes have, in all probability, had a similar origin in the alteration of the crystalline rocks of the vein-walls and deposition from aqueous solution.†

as in (1). The deficit (*i.e.*, the difference between the above two determinations) due to exhaustion with dilute acetic acid we assume to be present as carbonate of manganese.

In many of the rocks and minerals examined in this manner we found the manganese wholly combined with carbonic acid, in others partly with carbonic acid and partly with silicic acid; in some cases it is present as peroxide; it may exist in all three forms in the same rock, whilst in the majority of minerals it exists combined with silicic acid alone.

The felstones of the upper area of the Clyde basin seem to contain all their manganese in a soluble condition, presumably as carbonate. These rocks effervesce on treatment with dilute acids. If the deposits of the Clyde Sea-Area contain more peroxide than the deposits of other similar areas, this may be due to the soluble condition of the manganese in these felstones. In the laboratory, when a portion of these rocks was simply fused or fritted without fluxing material, the carbonic acid was expelled, and the bases were found in the cooled mass to be combined with silicic acid alone, as a silicate or silicates insoluble even in strong hot hydrochloric acid. Even when ten per cent. of carbonate of lime was added to the pulverised felstone, and the mixture fused, the silicates in the fritted material were insoluble, showing the acid nature of this class of rocks. This experiment shows that in the presence of silicic acid (or acid silicates) carbonates are decomposed by heating, silicic acid taking the place of the carbonic acid expelled, and also that the manganese found in these rocks has really been infiltrated as carbonate into even the heart of the felstone. These felstones are hard compact rocks, and contain no water which can be expelled even at 400° F. (204°·4 C.), nor do they absorb water, even when soaked in it for twenty-four hours.

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* Professor CLARKE estimates that manganese makes up about 0·08 per cent. of the earth's crust. (*Bull. Phil. Soc. Washington*, vol. xi. p. 138, 1892).

† The following are the principal manganese minerals:—Pyrolusite, (MnO₂); hausmannite, (Mn₃O₄); braunite, (Mn₂O₃); manganite, (Mn₂O₃, H₂O); psilomelane, (MnO₂, united with some protoxide, as of Mn.Ba.K₂ or H₂); dialogite (MnCO₃).

The following are oxides—Jacobsite, crednerite, chalcophanite, franklinite, pyrochroite.

Sulphide (blende)—Alabandine (MnS).

Anhydrous Carbonates—Breunnerite, siderite, mangano-calcite.

Hydrated Sulphates—Lankite, mellardite.

Hydrated Phosphates (the numbers are percentages of MnO in the mineral)—Fillowite (40), heterozite, dicksonite (25), fairfieldite (16), neddingtonite (46), eosporite (24), childrenite (9), tuplite.

Some of the manganese present as carbonate in the deeper parts of veins may, however, have been derived by emanations directly from the internal metallic nucleus.*

Dendrites and Coatings of Manganese Dioxide.—The surfaces of rocks containing manganese, on exposure to moist air, become gradually coloured a dirty-brown by the deposition of manganese dioxide, and the internal cracks of many rocks become lined with very beautiful dendrites of the same substance. Even limestones and coral-reef rocks present similar markings where exposed to running water. In the case of coral islands, the manganese which sometimes discolours the coral rock can be traced to the decomposition of the pumice and volcanic minerals, occasionally abundant in the red earths of these islands.

During the past few years we have examined a large number of the streams flowing into sea lochs connected with the drainage area of the Firth of Clyde in Scotland. On the stones and sandy particles forming the beds of these streams, as well as on the faces of exposed cliffs over which water trickles, abundant deposits and coatings of manganese dioxide were observed. The brilliant shining black lustre of the surfaces of many of the rolled pebbles was due to this oxide.†

Manganese Dioxide in Suspension in Fresh and Sea Waters.—A considerable quantity of water from various streams flowing into the Clyde Sea-Area was carefully filtered, and on the filters we found traces of manganese in an insoluble condition.‡ This manganese was present as dioxide, which we believe to have been derived from the mutual attrition of the manganese-coated stones in the beds of the streams, especially during floods. Traces of manganese were also obtained on the filters through which large quantities of sea-water had been passed. This was the case with samples both from the Clyde Sea-Area and from the open Atlantic. This manganese was probably present as dioxide associated with the fine clayey matter which is held in suspension in sea-water, even in some samples collected at great distances from land.§

After the water from the Clyde streams was carefully filtered, manganese was found to be present in solution in nearly all the samples in combination with carbonic and humic acids. The manganese was always more abundant in solution towards the head waters of the streams, especially near deposits of peat.|| Its less abundance towards the

* L. de Launay, *Formation des gîtes Métallifères*, p. 232; M. SARALP, *Le Manganese des Pyrénées*, (*Memoirs de l'Académie des Sciences de Toulouse*, 1893).

† Stones and sand coated and aggregated with manganese dioxide, and often presenting a polished surface and black metallic lustre, were observed in the River Clyde (Stonebyres Falls, Rutherglen, Underbank) and its tributaries the Mousewater, Hallhill, Diller, Devon, Teiglam, Craignethan, Birkwood, Poniel, Powtrail and Shortcleugh Burns, and Cander and Fence Waters; also in the streams flowing directly into the Clyde Sea-Area, as Sea Mill Water, Skelmorlie and Fairlie Burns (Wemyss Bay), and the streams falling into Loch Fyne, Loch Ranza, Loch Goil, and Campbelltown Loch. At Middleton Farm, Loch Fyne, there occurs a sandy deposit containing 0·7 per cent. MnO_2 , and at Dundee there is found in alluvium, interlayered with red sand, a black sand containing 2·5 to 3 per cent. MnO_2 .

‡ Water was examined in this way from the Clyde, Nethan, Mousewater, Hagshaw Burn, Loch Ranza Burn, and Glen Morag Burn.

§ See MURRAY and IRVINE, "Silica in Modern Seas," *Proc. Roy. Soc. Edin.*, vol. xviii. p. 243, 1891.

|| The samples in which manganese was found in solution came from Clyde River and its tributaries, as, for example, Mouse Water, Hagshaw Burn, Hallhill Burn, Skelmorlie Burn, Glen Morag.

mouths of the streams was evidently due to the oxidation of the carbonate and its consequent deposition on the stones of the bed of the stream as dioxide. We have, on the other hand, examined large quantities of carefully-filtered sea-water from various regions of the open ocean, but have never been able to detect manganese in solution, although, as above stated, we have found traces of manganese in the clayey matter in suspension in many of the sea-waters we have examined. The soluble bicarbonate of manganese, which, as we have seen above, exists in the water of fresh-water streams, is probably all deposited as dioxide on meeting with the alkaline and oxygenated water of the ocean. It is generally stated that all elementary substances can be detected in solution in ocean water; still, as a matter of fact, all the samples of normal sea-water which we have had under examination have not yielded any traces of manganese in solution.* A large number of deposits from the boilers of sea-going steamships were likewise examined for manganese, but no traces were found. These investigations seem conclusively to show that manganese is not present in solution in the normal sea-waters of the ocean, and consequently the material for the formation of the manganese nodules, so abundant in the abysmal regions of the deep sea, cannot be derived from solution in the waters of the open ocean.

Manganese in Mud-Waters.†—It has been shown that the sea-water associated with the deposits on the floor of the ocean has a very different composition from the normal superincumbent sea-water. A further examination of these mud-waters, and of the changes taking place in the muds, has furnished important indications as to the source and

* To determine the limits of detection of manganese in sea-water, standardised solutions of pure chloride of manganese (in sea-water) were prepared, and after boiling with excess of bromine for some time the precipitated MnO_2 was estimated. With solutions containing from 1 part in 15,000 to 1 part in 100,000, the separation was rapid and apparently complete, and the precipitated dioxide was collected on a filter and weighed, after ignition, as Mn_2O_4 ; with solutions containing 1 part in 1,000,000, MnO_2 separated out after boiling with bromine for some time. On treating a solution of 1 part $MnCl_2$ in 10,000,000 of sea-water, the precipitate of MnO_2 , after prolonged boiling with bromine, was quite distinct, but in this case appeared as a brown scum on the surface of the liquid, and formed a distinct brown ring round the walls of the white porcelain basin above the evaporating surface of the liquid.

Having established this point, we endeavoured to find manganese by this method in fresh, clear, filtered sea-water, obtained from the German Ocean. Two gallons were evaporated until the contained sea-salts began to crystallise out. The liquid was filtered clear of deposited sulphates and carbonates, and treated with bromine. There was not even the faintest trace of coloration. The basin in which this sea-water was evaporated was washed with hot hydrochloric acid, so as to decompose carbonates thrown down during evaporation, and the filtered liquid so obtained exactly neutralised with ammonia, and thereafter treated with bromine. In this case there was not the faintest trace even of coloration. We therefore conclude that in the sea-water samples examined by us, manganese, if present, could not have been there to a greater extent than 1 part in 10,000,000.

To confirm the above by more delicate tests, the two portions from the sea-water—viz., the strong brine and the residue of salts treated with hydrochloric acid—were boiled down until most of the salts had crystallised out. The crystals were separated, washed with pure hydrochloric acid, and the washings added to the mother liquor, which was then evaporated to dryness, and ignited to drive off ammoniacal salts. This residue—in which we assume any manganese present in solution in the original sea-water would appear—was then fused with carbonates of potash and soda and a little potassium nitrate. The fluxed mass when cold was absolutely milk-white. This result (when the extreme delicacy of this method of detecting manganese is taken into account) points to the conclusion that manganese is not present in solution in ordinary sea-water, at least within the chemical limits of observation at our disposal, and therefore ordinary sea-water cannot provide the material for the formation of manganese nodules.

† MURRAY and IRVINE, "On the Chemical Changes which take place in the Composition of the Sea-Water associated with Blue Muds on the Floor of the Ocean," *Trans. Roy. Soc. Edin.*, vol. xxxvii. p. 481, 1893.

mode of accumulation of the manganese dioxide in the deposits dredged from some regions of the sea-bed. The following details with reference to the manganese in these mud-waters illustrates the difference between these mud-waters and samples of normal sea-water:—

I. Water filtered from the Blue Mud taken from a depth of 6 fathoms in the sea-water quarry at Granton during February 1892, was found after standing in a bottle for two years to give a deposit of manganese dioxide amounting to 0·045 grammes per kilogramme, equivalent to 0·06 grammes MnCO_3 originally in solution, or equal to one part MnCO_3 in 16,600 of water.

II. In water filtered from the Blue Mud from the same quarry during March 1894 we found manganese in solution amounting to 0·0315 grammes of MnCO_3 per kilogramme, or one part in 31,700 of water. In water immediately overlying this mud we found, at the same time, manganese in solution amounting to 0·0034 grammes of MnCO_3 per kilogramme, or one part in 300,000 of water. In the same place, and at the same date, in water taken 18 inches above the surface of the mud, there were found distinct traces of manganese in solution. The sea broke into this quarry forty years ago. At the present time there is a distinct black coloration all around the rocky walls of the quarry between high and low water marks, due to a deposit of manganese dioxide—the deposit being apparently more abundant on a built portion, where the lime pointing is exposed at the joints to the action of the water. At some places the stones and shells in the channel, by which the sea-water flows in and out of the quarry at each tide, are likewise coated with a thin deposit of manganese dioxide. The salt-water was examined as it entered the quarry with the flowing tide, and it was not found to contain any manganese in solution.

The mud at the bottom of the quarry is made up of a mass of fine detrital matter, in which are small crystals of quartz, felspar, hornblende, augite, mica, magnetite, and other minerals. When dried in the air this mud was found to contain about 0·1 per cent. of manganous oxide (MnO), present partly as carbonate and partly as silicates. It therefore seems evident that the manganese dioxide on the walls of this quarry and on the stones in the tidal entrance has its origin in the carbonate of manganese in solution in the sea-water associated with the mud, and that this carbonate, in its turn, is derived from the decomposition of the minerals contained in the mud.

III. Sea-water filtered from mud from Granton Harbour (depth 2 fathoms) in March 1894 contained manganese carbonate in solution amounting to 0·008 grammes per kilogramme, or 1 part in 120,000 of water.

IV. Sea-water filtered from a grey-coloured mud obtained in a depth of 20 to 25 fathoms, off the Tan Buoy, Cumbrae, in the Clyde, gave distinct indications of manganese in solution, but not nearly in such abundance as in the waters from the muds in Granton Quarry and Granton Harbour.

V. Sea-water filtered from a brownish-black mud obtained in a depth of 22 to 29 fathoms, off Castle Bay, Little Cumbrae, contained manganese in solution amount-

ing to 0·0114 grammes of MnCO_3 per kilogramme, or 1 part MnCO_3 in about 94,000 of water.

VI. Sea-water filtered from a Blue Mud obtained off Balloch Pier, Cumbrae, in a depth of 25 fathoms, contained manganese in solution as MnCO_3 amounting to 0·0105 grammes per kilogramme, or 1 part of MnCO_3 in about 95,000 parts of water. This mud, as well as that obtained off the Little Cumbrae, contained, in addition to quartz, many volcanic minerals and rock fragments, some of them much altered.

All our experiments seem to show that in the oozy pulp formed by the sea-water, organic matter, and the mineral constituents, active chemical changes must necessarily be taking place. This mud, when completely freed from adherent sea-water salts by washing with distilled water, gave no indication of manganese peroxide by the Bunsen test; but, on fusing the washed mud with alkaline carbonates, the characteristic colour of the mass showed manganese to be present in the silicates. It may be taken for granted, then, that the carbonate of manganese in these mud-waters is derived either (1st) from the direct decomposition of the rock-fragments in the mud by the alkaline carbonates in the sea-water, or (2nd) from the reduction of the higher oxides of manganese by the organic matter in the muds; for, as we will show later on, in the presence of decomposing organic matter, deoxidation takes place in the muds, and soluble bicarbonate of manganese is formed. Both these processes, doubtless, take place in most marine deposits. The great increase of alkalinity owing to the formation of sulphides must give these mud-waters a great power in decomposing silicates and setting free the bases to combine with the carbonic acid always present in excess in mud-waters.* The influence of carbonate of lime in rendering silicic acid soluble through the formation of calcium silicate must also be important in initiating chemical changes in many deep-sea deposits.

Rate of Oxidation of the Bicarbonate of Manganese in Sea-Water.—In the foregoing paragraphs we have frequently referred to the oxidation of the carbonate of manganese and the subsequent deposition of the dioxide. A number of laboratory experiments were undertaken with the object of arriving at some idea of the rate at which these changes take place:—

I.	One part of bicarbonate of manganese was added to	10,000	parts of sea-water.
II.	„ „ „	30,000	„
III.	„ „ „	100,000	„

The most dilute portion (III.) was the first to change by oxidation of the bicarbonate into dioxide of manganese, which attached itself to the walls of the vessel. The other portions (I. and II.) separated more slowly; but, in all three experiments, the oxidation of the whole of the bicarbonate was completed in the course of a few months. There can be little doubt that the separation of the whole of the dioxide would have taken place much more rapidly had the water been aërated by constant agitation. The water

* See MURRAY and IRVINE, *Trans. Roy. Soc. Edin.*, vol. xxxvii. p. 485.

in the dilute portion (III.) being much more abundant relatively to the manganese than in the other portions consequently offered much more dissolved oxygen, and thus led to a more rapid oxidation. It thus appears that manganese cannot long remain in solution in sea-water even as bicarbonate, but must soon be deposited as dioxide.

Distribution of Manganese Nodules and Manganese Dioxide Coatings in the Marine Deposits of the Clyde Sea-Area.—The manganese dioxide which coats the stones in the beds of the streams flowing into the Clyde Sea-Area is, as we have shown, rubbed off—especially during floods—and carried to the sea along with ferric oxide and other detrital matters. Soon after reaching the salt-water the greater part of this detrital matter is thrown down not far from the shores, and forms the Blue Muds which cover the bottom in all the deeper reaches of the Clyde basins. In this Blue Mud, as we have seen, active chemical reactions take place, many of them initiated by the action of the decomposing organic matters always associated with these deposits. The sulphates of the sea-water are, in these circumstances, deoxidised, and the sulphur of the hydro-sulphuric acid combines with the iron, forming sulphide of iron, which is unaffected by the presence of the carbonic or humic acids in the mud, and hence remains a permanent constituent of the deposit, giving it, indeed, its blue or black colour. The sulphide of manganese, formed at the same time and in the same manner, is not, however, permanent, but is at once decomposed by the carbonic acid present in the mud-waters, sulphuretted hydrogen being evolved and bicarbonate of manganese formed.* Even the loosely-combined carbonic acid of the bicarbonates in sea-water effects this decomposition.

There is, however, another way in which bicarbonate of manganese may originate in these mud-waters. The increased alkalinity induced by the above changes gives to the water associated with the mud greater solvent power over silica and silicates, and those mineral particles of the deposit which may contain manganese are slowly decomposed, and, along with other carbonates, carbonate of manganese is formed which, as we have seen, may remain for a short time in solution, but, on meeting the oxygen in the overlying sea-water, is soon deposited as dioxide.†

A large number of laboratory experiments were conducted with the view of studying these various reactions, among them the following:—

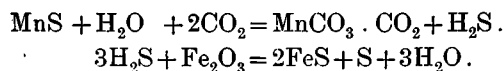
I. Sulphide of manganese and excess of ferric hydrate were suspended in water through which carbonic acid was passed. The sulphuretted hydrogen, resulting from the

* See IRVINE and GIBSON, *Proc. Roy. Soc. Edin.*, vol. xviii. p. 54, 1891.

† If we take the Blue Mud extending over an area of 1 square mile and 1 foot in depth as containing one half of its weight of water (equal to 867,700,000 lbs.), and holding 1 part of MnCO_3 in 95,000, we will have a total amount of 9134 lbs. MnCO_3 per square mile, and if we take the amount found in the water immediately overlying the mud in Granton Quarry as representing what occurs in the Clyde area, *i.e.*, 1 part in 300,000, we have per square mile of water 1 foot deep (weighing 1,735,400,000 lbs.) 5785 lbs. MnCO_3 , or a total, including that obtained from the mud and from the water overlying it, of 14,919 lbs., or 23 lbs. per acre of surface available for nodule formation. Of course there may be much more, as there must be a continuous removal of MnCO_3 by tidal action; but, considering the extent of the floor of the Clyde basin, even the amount here estimated is very great.

Taking the amount of flow at Lanark at 15,000 cubic feet per second, holding 1 part manganese in 28,000,000 of water, this represents a daily quantity of over 1 ton carried by that river to the sea. This is manifestly a low approximation, as the flow is much augmented by tributaries between this point and the sea.

action of carbonic acid and water on the sulphide of manganese, combined with the iron present, forming sulphide of iron. This reaction took place so long as there was excess of ferric hydrate, and may be thus represented:—



II. Sea-water, starch solution (to represent non-nitrogenous organic matter), and carbonate of manganese were placed in a vessel, and allowed to stand for several days at a temperature of 80° F. (26°·67 C.). It was found that sulphuretted hydrogen was continuously given off till all the sulphates present in the sea-water were decomposed, bicarbonate of manganese ($\text{MnCO}_3 \cdot \text{CO}_2$) being at the same time formed. It was noticed that the carbonate of manganese oxidised much more rapidly in alkaline fluids than in pure water; and sea-water, it must be remembered, is probably always alkaline.

III. Powdered deep-sea manganese nodules were placed in sea-water along with decomposing mussel-flesh. In a few days the sulphates of the sea-water had been reduced to sulphides; and while the sesquioxide of iron present in the nodules was thrown down as insoluble sulphide of iron, the manganese dioxide was first reduced to sulphide, but finally appeared in the sea-water as soluble bicarbonate of manganese.

These experiments show that manganese dioxide cannot exist for any time in muds where there is a large quantity of decomposing organic matter, such as is nearly always present in the Blue Muds of the Clyde Sea-Area and similar deposits around continental lands. This result is in complete harmony with the actual observations as to the distribution of manganese oxides, made known by means of the dredge and trawl. What is known as the Clyde Sea-Area consists of a series of submarine basins, separated from each other by submarine barriers. The depth of the basins ranges from 30 to 106 fathoms, and the depth of water over the intervening ridges varies from 3 to 15 fathoms. In all the deeper parts of the basins there is a bluish mud, in which, as a rule, no manganese nodules are found, but on the immediate surface of the deposit of Blue Mud there is a surface layer with a reddish or light-grey colour, in which deposits of manganese dioxide do occur. When stones are dredged from these muds many of them are, as a rule, surrounded by a dark ring of manganese dioxide, marking the depth to which they have been embedded in the mud. The whole upper surface of the stones has likewise a slight coating of manganese, while the portion imbedded in the mud is free from these manganese deposits.

The submarine ridges between the different lochs or basins are usually covered with rocks and stones, many of which are dark coloured from a coating of manganese dioxide. Very little mud is, as a rule, deposited on the shallower parts of these ridges, owing to their being continually washed by tidal currents. Mud is, however, deposited among the stones a few fathoms deeper on either side of these ridges, and some hollows or small depressions on the barriers are filled with mud, in which small manganese nodules are frequently found in great abundance. The larger stones in the positions here indicated all showed the dark ring of manganese marking out the line between the mud and water. The deposits

of manganese on some of the stones at the water-line were 3 or 4 inches in thickness. The nodules varied in size from 2 inches to $\frac{1}{16}$ of an inch in diameter, and all showed a concentric arrangement of parts. The general appearance of the stones and nodules is shown by the sections in figures 1, 2, 3, and 4.

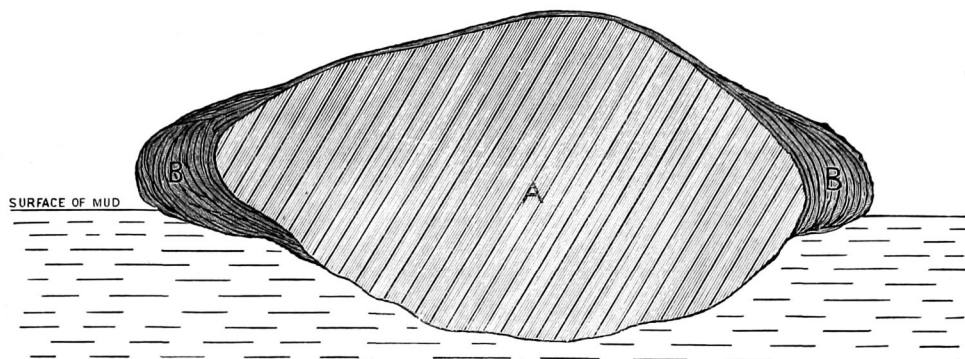


FIG. 1.—Schistose Boulder from the Barrier, Loch Goil, $\frac{1}{10}$ natural size. A, boulder of Mica schist. B, layers of Manganese dioxide.

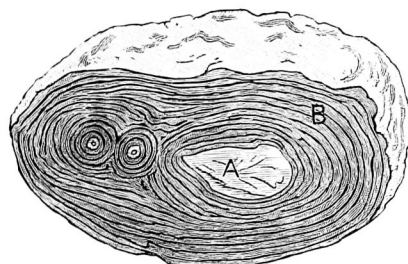


FIG. 2.—Section of Loch Striven Nodule (natural size). The layers of Manganese dioxide (B) have been deposited round a piece of slate (A).



FIG. 3.—Section of small Nodule from Loch Goil (natural size).

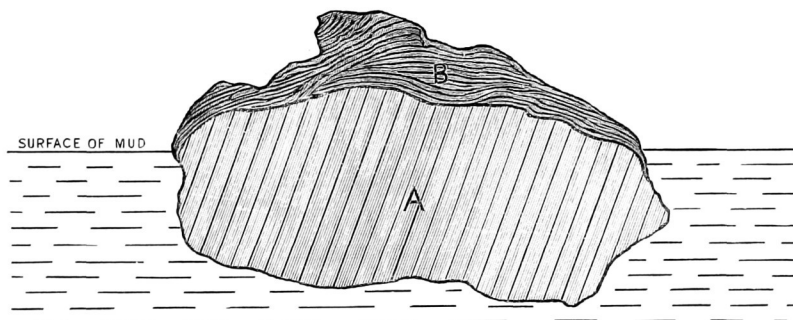


FIG. 4.—Section of Boulder of Schist from Loch Fyne, showing Manganese Deposit ($\frac{1}{3}$ natural size). A, boulder of schistose rock. B, layers of Manganese dioxide.

The chemical composition of these nodules differs only slightly from that of those taken in the deep sea, and this difference arises from the greater abundance of mineral particles and their different nature, quartz and other continental minerals being almost

absent from the deep-sea samples, but abundant in those from the Clyde area. The manganese is also more completely oxidised in the deep-sea samples.*

* *Partial Analyses of Several Clyde Nodules (Anderson).*

	Nodules from off Skate Island, Lower Loch Fyne, in 104 Fathoms.						Nodules from off Paddy's Rocks, Upper Loch Fyne, in 20 Fathoms.			Nodules from off Skelmorlie Bank, in 11 Fathoms.		
	Percentage Composition.		Composition after Deducting Water.		Composition after Deducting Water and Insoluble Matter.		Percentage Composition.	Composition after Deducting Water.	Composition after Deducting Water and Insoluble Matter.	Percentage Composition.	Composition after Deducting Water.	Composition after Deducting Water and Insoluble Matter.
	Rinds.	Kernels.	Rinds.	Kernels.	Rinds.	Kernels.						
Manganese Oxide, MnO . . .	24·830	33·657	39·294	44·367	59·429	62·710	16·420	30·151	41·538	16·656	28·543	39·616
Peroxide Oxygen, O . . .	4·846	7·096	7·669	9·354	11·599	13·221	3·720	6·831	9·410	3·366	5·768	8·006
Ferric Oxide, Fe ₂ O ₃	7·117	13·068	18·004	6·960	11·927	16·554
Alumina, Al ₂ O ₃	1·758	3·228	4·447	1·890	3·239	4·195
Insoluble in Hydrochloric Acid	21·410	22·190	33·882	29·251	14·930	27·415	...	16·310	27·950	...
Loss on Ignition . . .	40·040	28·870	48·020	43·890
Formula of Peroxide . . .	MnO _{1·86}	MnO _{1·93}	MnO ₂	MnO _{1·89}

Partial Analysis of a Manganese coating on a stone from Loch Fyne (see Fig. 4).

The substance was broken, and the Fine Particles separated from the Coarse by levigation, and dried in air.

Manganese coating was divided into Fine Washings = 63·03 per cent.
 ,, ,, Coarse Particles = 36·97 ,,
 100·00

		Fine Washings.		Coarse Particles.	
		Percentage Composition.	Composition after Deducting Water.	Percentage Composition.	Composition after Deducting Water.
Insoluble in Hydrochloric Acid	Water, H ₂ O	12·615	...	17·434	...
	Manganese Dioxide, MnO ₂	57·930	66·293	58·560	70·925
	Ferric Oxide, Fe ₂ O ₃	3·220	3·685	1·960	2·374
	Alumina, Al ₂ O ₃	1·120	1·282	0·910	1·102
	Silica, SiO ₂	9·000	10·300	6·810	8·248
	Ferric Oxide, Fe ₂ O ₃	trace	trace	trace	trace
	Alumina, Al ₂ O ₃	3·750	4·291	2·410	2·919
	Total Insoluble in Acid,	(14·020	16·044	10·040	12·160)

The main difference between the two analyses is the larger quantity of iron and clayey matter present in the Fine Washings, and a corresponding increase of manganese in the Coarse Particles.

		Manganese Nodule from Outer Side of Barrier, Loch Goll, in 15 fathoms, 16/11/91 (see fig. 3).							Manganese Nodule from Loch Striven, off Clapochlar Point, in 30 fathoms, 12/4/92 (see fig. 2).						
	a	b	c	d	e	f	g	a	b	c	d	e	f	g	
	Aqueous Extract.	Acetic Acid Extract (2% % Acid).	Hydrochloric Acid Ex- tract.	Insoluble Matter.	Total Composition.	Composition after de- ducting the Water.	Composition after de- ducting the Water, and Insoluble Matter, and Aqueous Extract.	Aqueous Extract.	Acetic Acid Extract (2% % Acid).	Hydrochloric Acid Ex- tract.	Insoluble Matter.	Total Composition.	Composition after de- ducting the Water.	Composition after de- ducting the Water, and Insoluble Matter, and Aqueous Extract.	
Water,	26.980	16.470	
Manganous Oxide, MnO	...	Tr.	33.232	...	33.232	46.172	61.005	...	0.740	33.680	...	34.420	41.717	64.750	
Ferric Oxide, Fe ₂ O ₃	...	0.221	5.485	Tr.	5.706	7.928	10.475	...	0.459	3.520	0.933	4.912	5.954	7.485	
Alumina, Al ₂ O ₃	...	0.470	1.136	3.749	5.355	7.440	2.948	...	0.155	1.088	3.060	4.303	5.216	2.338	
Cupric Oxide, CuO	0.255	...	0.255	0.354	0.468	0.250	...	0.250	0.303	0.470	
Cobalt Oxide, CoO	Tr.	...	Tr.	Tr.	Tr.	Tr.	...	Tr.	Tr.	Tr.	
Calcium Oxide, CaO	Tr.	1.419	0.260	...	1.679	2.333	3.082	Tr.	1.224	0.330	...	1.554	1.884	2.923	
Magnesia, MgO	Tr.	1.560	1.093	0.277	2.930	4.071	4.870	Tr.	1.213	1.075	0.285	2.573	3.119	4.304	
Alkalies (Na ₂ O and K ₂ O)	0.955	0.690	0.304	0.820	2.769	3.847	1.825	0.495	1.131	0.660	1.055	3.341	4.050	3.369	
Phosphoric Acid, P ₂ O ₅	0.382	0.531	0.701	0.350	0.424	0.659	
Sulphuric Acid, SO ₃	0.220	0.220	0.306	...	0.180	0.180	0.218	...	
Chlorine, Cl	0.880	0.880	1.223	...	0.406	0.406	0.492	...	
Carbonic Acid, CO ₂	0.550	0.764	1.010	0.242	0.293	0.455	
Silica, SiO ₂	...	0.316	0.279	10.799	11.394	15.830	1.092	...	0.274	0.223	23.024	23.321	28.509	0.935	
Peroxide Oxygen, O	6.564	9.120	12.050	6.345	7.690	11.936	
Organic Carbon, C	0.258	0.358	0.474	0.200	0.242	0.376	
[Subtract basic Ox- gen = Chlorine].	0.199	0.199	0.277	...	0.092	0.092	0.111	...	
	1.856	4.676	42.044	15.645	98.955	100.000	100.000	0.989	5.196	40.826	28.357	98.975	100.000	100.000	

Formula of Peroxide = MnO_{1.57}
Loss on Ignition = 32.423 %

Formula of Peroxide = MnO_{1.82}
Loss on Ignition = 21.238 %

After separation from the iron and alumina the manganese was precipitated as carbonate, ignited to Mn₂O₃, and extracted with acetic acid, re-ignited and weighed. The peroxide oxygen was estimated by dissolving the chloride, obtained after adding a small amount of hydrochloric acid, into a solution of potassium dichromate, and titrating with a standard solution of ferrous sulphate. The phosphoric acid was precipitated by the molybdenum process and the organic carbon by oxidising with chromic acid by means of strong sulphuric and chromic acids. The carbonic acid itself had to be estimated by boiling a portion of the nodule in a solution of sulphuric acid, sulphate of silver, and ferrous sulphate, and passing the carbonic acid into baryta water of decinormal strength. The water was estimated directly by igniting the nodule, mixed with oxide of lead, in a platinum boat, and absorbing the water in a calcium-chloride tube. The loss on ignition would seem to consist of the following:—

Oxygen = Acid = 4.068
Carbonic Acid = 0.260
Organic Carbon = 0.250
Water (by difference) = 27.847
32.423

3.750
0.242
0.200
17.087
21.238

In both cases the water found by difference is about 0.5% higher than the water found directly. Column f shows the percentage composition of the nodules when calculated free from water, and the total raised to 100. Column g shows the probable percentage composition of the nodules when calculated free from water, sea-salts, and insoluble matter, and would perhaps represent the composition of the more purely ferro-manganese portion of the nodule, which would be formed by chemical reactions as described in this paper. The insoluble matter is no doubt a mixture of quartz-sand and clay, mechanically entangled.

A most extensive series of dredgings was conducted during several years in nearly all parts of the Clyde Sea-Area, and so constant were the conditions under which the manganese deposits occurred that Captain TURBYNE, of the yacht "Medusa," could usually point out with certainty the situations in which they might be procured by the dredge. There is one apparent exception, viz., the very deepest spot in the whole area (106 fathoms), in Lower Loch Fyne. The nodules from this place were described several years ago by Mr J. Y. BUCHANAN.* This deep hole is very limited in extent, and the nodules found in it occur only in one place, and that at the very deepest point. The hole is situated off Skate Island, towards which, from the Cantyre shore, there runs a submerged tongue or ridge, so that the water passing through this narrow gully to supply the whole of the upper parts of Loch Fyne is much confined, and motion of the water takes place at a greater depth here than at other parts of the area. With reference to currents, then, this deep hole resembles the hollows filled with mud on the ridges and barriers.†

In addition to the deposits of manganese dioxide on stones, and in the form of nodules, many of the living and dead shells found in the deeper parts of the district are coated with this substance—for instance, those of *Astarte sulcata*, *Nucula sulcata*, *Pecten septemradiatus*, *Cyprina islandica*, *Corbula gibba*, *Venus fascicula*, *Venus casina*, *Scrobicularia alba*, *Buccinum undatum*, *Fusus antiquus*. Many of the dead fragments of *Lithothamnion calcareum* from the shallow dredgings are black coloured, and thoroughly impregnated with deposits of manganese dioxide.

A survey of the foregoing facts seems to show conclusively that the bicarbonate of manganese, which we have found in solution in the sea-water associated with the Blue Muds of the Clyde sea-basins, has been derived either from the deoxidation of the dioxide carried into the sea by streams along with other detrital matters, through the decomposition of organic matter in the presence of the sulphates of the sea-water, or directly from decomposition in the mud of manganese-bearing silicates present among the

* See BUCHANAN, *Trans. Roy. Soc. Edin.*, vol. xxxvi. p. 459, 1891.

† Captain Turbyne, of Mr Murray's yacht "Medusa," writes as follows as to the manganese dredging in the Clyde Sea-Area:—"Regarding the nodules being in pot-holes, I consider that I have absolute proof of that on the outer side of the barrier of Loch Goil. In the first place, we were dredging from the outside toward the barrier or up the loch, on the slope, as I thought, between the mud and harder ground. In this case we ought to have been shallowing our soundings, but after towing for a short time the dredge suddenly began to dip, which was seen from the angle of the wire, and more had to be run out; then we suddenly came fast, and had to heave up, and this was the haul in which the nodules were got. They differed from those at Skelmorlie Bank in being much larger, and to the unaided eye they seemed perfectly smooth and quite round. In the second place, after finding the nodules I tried to get more both on this and on several other occasions; but though we tried to strike the spot as nearly as possible, it was only after dredging up and down the loch and in close sections across it, that we again hit on the spot. For these reasons I have come to the conclusion that the nodules are found in a hole of small extent. This is the only instance in my experience in which I am certain that the nodules were taken from a small hole. In my opinion the slopes of Skelmorlie Bank and Minard Narrows are full of small holes containing mud and manganese nodules where the tide meets with an obstruction. The 106 fathom-hole has always been a mystery to me. I often thought that if the nodules were formed in that deep hole, why don't we get them off Brodick in 95-97 fathoms, which part is practically a continuation of the trough in which the 106 fathom-hole is situated? Surely this submarine tongue you mention and the small size of the 106 fathom-hole has got something to do with it. I can say nothing about under-currents at the deep hole, but there is a strong surface-current at spring-tides, as we rapidly got out of position, and it is well known to fishermen and others that, with the wind against the tide, a nasty sea is met with off Skate Island."

mineral particles of the mud itself. It is probably derived from both these sources. Further, this bicarbonate, on escaping in solution from the mud into the overlying water, takes up oxygen, and is deposited in a higher state of oxidation on any objects which may lie on or project above the surface of the mud. In this way we may account for the tonsure-like rings of dioxide of manganese which surround many stones, and for the deposits on the shells of the molluscs living in the immediate surface layers of the muds.

The formation of manganese nodules on the immediate surface of the deposit, on the tops of the barriers, and in the pit-like depressions, is most probably to be accounted for by the more abundant supply of oxygen, or by the diminished amount of decomposing organic matter in these positions.

In those deep parts of the Clyde basins, where there is little motion from tidal or other currents, the bicarbonate of manganese in the mud-water would gradually ooze out into the overlying water, and be slowly carried along till deposited as dioxide near the tops of the ridges, where motion is more rapid and oxygen more abundant. In the muds of the Clyde Sea-Area there is most probably a continual and very slow shifting of the dioxide of manganese deposits from one position to another, for if a partially embedded stone, covered on its upper surface with a deposit of manganese dioxide, should become more deeply embedded from the accumulation of the deposit, the lower portions of the dioxide would be reduced by this deoxidising mud, and the manganese, passing through the state of sulphide and bicarbonate, would ultimately be transferred to some other point higher up on the stone, or to a still greater distance, before being again laid down as dioxide. There would thus always be a tendency for the manganese dioxide to accumulate in the surface layers of a Blue Mud deposit, as well as at certain favourable points, such as in the little hollows filled with mud, over which the water is continually changing, or where there is an absence of decomposing organic matter.

When viewed in this light, the amount of the manganese, in relation to the whole mass of the deposits being laid down on the floor of the ocean, may not be so great as some dredgings, at points where accumulation has taken place, would lead us to suppose.

Manganese Nodules and Manganese Dioxide Deposits in the Deep Sea.—The dredgings, trawlings, and soundings conducted in recent years by the "Challenger" and other deep-sea exploring expeditions, show that deposits containing a large quantity of manganese dioxide are very widely distributed. Over large areas of the Mid-Pacific and Mid-Indian Oceans there is a dark chocolate-coloured deposit, usually in depths beyond 2200 fathoms. Whenever dredgings have taken place on this chocolate-coloured clay, large numbers of manganese nodules have always been procured, associated with sharks' teeth, ear-bones of whales, and the other peculiar substances mentioned in the opening paragraphs of this paper.

In some few places in the Pacific, the Globigerina Oozes, which occur at lesser depths than the Red Clay, have also this deep chocolate colour due to the minute grains

of manganese dioxide disseminated throughout the deposit. When dredgings have been obtained in these Globigerina deposits, many manganese nodules have been procured, but they were not accompanied by large numbers of sharks' teeth, bones of cetaceans, zeolitic crystals, and cosmic spherules, as in the case of the Red Clays. Very many minute particles of basic volcanic rocks, most of them in an altered condition, were, however, present in these dark chocolate coloured Globigerina Oozes.

The one outstanding fact connected with the distribution of manganese nodules in the abysmal regions of the ocean is, that wherever they occur in great abundance, they are accompanied by numerous fragments and lapilli of basic volcanic rocks, and many of these, on examination, are found to be in an advanced state of alteration. For instance, a typical Globigerina Ooze is usually of a white or rose colour, and the inorganic residue, insoluble in dilute acids, consists of clayey matter, oxides of iron, and a few mineral particles chiefly of volcanic origin, along with fragments of pumice. In such a typical deposit, a few grains of manganese dioxide may be observed attached to some of the

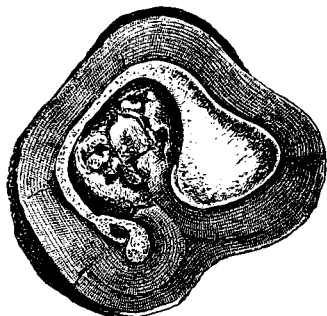


FIG. 5.—Tympanic bone of *Mesoplo-don* (?) very deeply embedded in depositions of manganese (natural size). Station 160; 2600 fathoms. Southern Indian Ocean.

Foraminiferal shells, or in the residue after removal of the carbonate of lime by dilute acid. As a rule, no manganese nodules are procured by dredging on such a typical Globigerina Ooze. A Globigerina deposit with the same species of Foraminifera, the same percentage of carbonate of lime, laid down in similar latitudes and under similar physical conditions, but containing much volcanic débris of a basic character, is, however, of a dark chocolate colour, and contains many manganese nodules.

Indeed, all observations go to show that the quantity of manganese dioxide in these abysmal deposits is in direct relation to the abundance and basic character of the erupted rocks and minerals associated with them, and the extent to which these minerals and rock particles have undergone alteration.

In the Blue Muds, which in deep water surround continental land and cover the bottoms of enclosed or partially enclosed seas, no manganese nodules similar to those from the central regions of the ocean basins have as yet been obtained in dredgings. In a good many instances, however, stones and boulders have been dredged from Blue Muds or other terrigenous deposits, with the upper or emerged surfaces coated with manganese. Markings of this substance were also found on some shells, fragments of pumice, and phosphatic concretions which evidently had lain on the immediate surface of the mud. The Blue Muds in deep water have a thin red-coloured watery layer on the surface, and beneath this the deposit is of a dark blue colour, and often smells strongly of sulphuretted hydrogen. These deeper layers contain much decomposing organic matter, like the muds of the Clyde Sea-Area, and in them no deposits of manganese have as yet been found other than mere traces; but manganese dioxide was found coating objects lying on the immediate surface layer, and, as in the case of the Clyde mud, these

deposits doubtless arise from the oxidation of the bicarbonate of manganese, which oozes or seeps out of the dark-coloured reducing layers beneath.

The blue-coloured layers of those muds situated in deep water near shore gradually disappear towards the central parts of the ocean basins, the deposit passing into Globigerina, Pteropod, and Radiolarian Oozes and Red Clays. These latter deposits have generally one uniform colour throughout, of being usually red, chocolate, rose, or dull grey. No trace of a blue layer beneath a red-coloured surface one can be detected in these abysmal deposits. Apparently the organic matter, which reaches the bottom in these

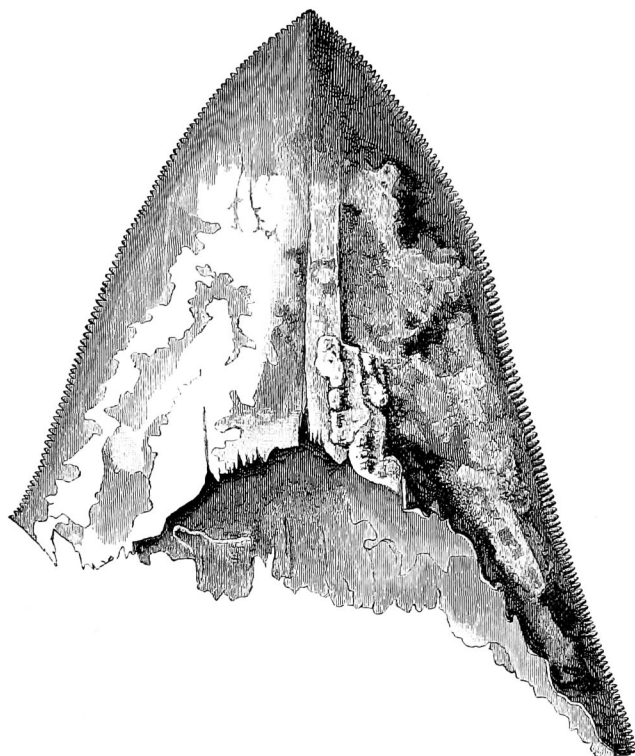


FIG. 6.—Tooth of *Carcharodon megalodon* (natural size). This is the largest specimen taken during the cruise of the "Challenger." Station 281; 2385 fathoms. South Pacific.

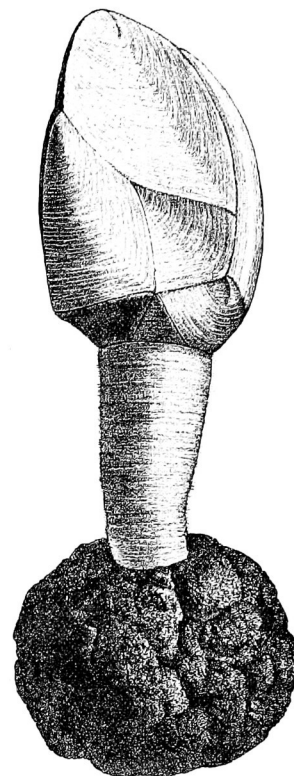


FIG. 7.—Manganese nodule with *Scalpellum darwini* growing on it. Station 299; 2160 fathoms. South Pacific.

abysmal regions, is less abundant than nearer shore, and probably the rate of accumulation is so slow that the decomposing organic matter is never covered up, as in the case of the Blue Muds. At all events, when deoxidation of the sulphates in sea-water does take place in the Red Clays or Globigerina Oozes, it never results in the formation and permanent addition of any large quantity of sulphide of iron to the deposit, as in the case of the Blue Muds, the iron being nearly all in the form of sesquioxide, and hence the whole deposit, at least to the depth of 18 inches, is of a red colour. In the case of the Blue Muds, the thin red-coloured watery layer on the surface becomes gradually converted into the blue layers beneath with the growth of the deposit.

In some cases it was observed that large light-yellow-coloured patches occurred in the red and chocolate clays, arising apparently from the decomposition of some organic body at the discoloured spot, so that even in these abysmal deposits the same deoxidation changes do take place as in the Blue Muds, and there may be a tendency to the production of manganese nodules, on or near the surface, at the expense of the dioxide of manganese in the deeper layers. We know that many of the deep-sea nodules were formed on the very surface of the deposit, and even projected above it, the upper portion of the nodule giving attachment to Hydroids, Polyzoa, Annelids and other organisms.

All the manganese nodules from the dredging or trawling at any one of the "Challenger" stations have a strong family likeness, being similar in their general form and size. So marked was this resemblance, that Mr MURRAY, or his assistant, could at sight with certainty indicate the station from which any given specimen was procured.

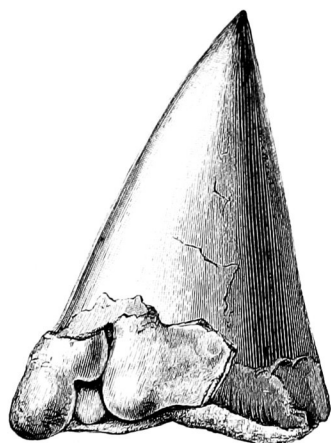


FIG. 8.—Large tooth of *Oxyrhina* (*Oxyrhina trigonodon* ?), about the largest specimen taken during the cruise (natural size). Station 276; 2350 fathoms. South Pacific.

Sometimes they were all flattened and of an oval shape, with a well-marked upper and under surface; nodules of this shape were evidently formed on the immediate surface of the deposit. At other stations they were pear-shaped, and in these instances the small end was embedded in the mud, while the large end projected above the deposit. In other localities all the nodules were round, at one station being about half an inch, and at another one or two inches in diameter. At one place in the South Pacific the surface of a Red Clay had been covered by a fall of volcanic ashes over an inch in depth, the whole deposit had then become a hardened mass, and subsequently was broken into fragments by some disturbance at the bottom. Large slabs, consisting of the upper layers of this deposit, were brought up in the trawl, and it could be seen that many of the manganese nodules had been situated on the very surface of the Red Clay previous to the fall of ash, while only a few had been completely embedded in the deeper layers of the Red Clay. There is, then, much evidence to show that even in the abysmal regions the manganese nodules are more abundant in the surface, than in the deeper, layers of the deposit. That these nodules do, however, occur at least a foot beneath the surface is proved by some small ones having been found at that depth in the sounding-tube.

General conclusions with reference to the Manganese Dioxide in Marine Deposits.—From the foregoing considerations it may be inferred that the manganese of the dioxide present in marine deposits was originally combined with the silica in the crystalline rocks of the earth's crust. Through the alteration and decomposition of these crystalline rocks the manganese was converted into bicarbonate. In terrestrial rocks and in the beds of streams this bicarbonate is deposited as dendrites and coatings of manganese dioxide. If any bicarbonate of manganese reaches the sea in the waters of rivers it is almost immediately deposited as manganese dioxide on meeting the alkaline sea-water. The

dioxide of manganese found on terrestrial rocks may be carried to the ocean, and widely distributed over the sea-bed along with other detrital matters. In marine deposits, mineral particles, derived from the disintegration of the crystalline rocks of the earth's crust, are everywhere present. In some regions the fragments derived from the disintegration of the acid series of rocks predominate, in others the fragments from the basic series. These minerals and rock fragments undergo alteration in the soft oozy deposit, in the same way as the rocks on the terrestrial surfaces. The manganese in the silicates is converted into bicarbonate of manganese, which is deposited as manganese dioxide wherever there is a sufficient supply of oxygen. Experience has shown that nodules of manganese are much more abundant in all those areas where the basic series of rocks predominate, and this is evidently connected with the greater abundance of iron and manganese in these rocks.

Manganese dioxide is a very stable and insoluble substance, and it might be supposed

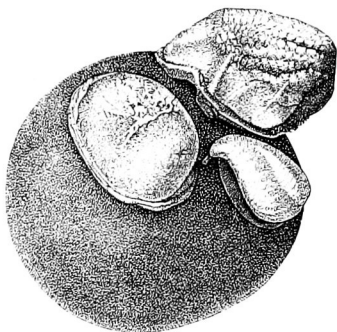


FIG. 9.—Manganese nodule with two Tunicates (*Styela squamosa* and *Styela bythica*) and a Brachiopod attached. Station 160 ; 2600 fathoms. Southern Indian Ocean.

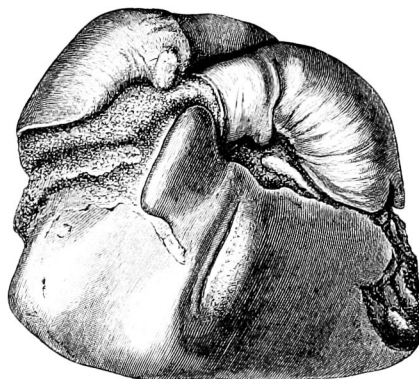


FIG. 10.—Petrous and tympanic bones of *Mesoplodon* (species allied to *layardi*), outer surfaces covered with manganese (natural size). Station 286 ; 2335 fathoms. South Pacific.

that when once formed in marine deposits it would be permanent. We have shown that there is, however, sufficient evidence, that, owing to repeated deoxidation and reoxidation, the manganese in marine deposits is continually being transferred from one position on the floor of the ocean to another. Wherever decomposing organic matter is present in the muds, deoxidation of the sulphates of the sea-water and of the manganese dioxide in the deposits takes place with the formation of sulphides of iron and manganese. The sulphide of iron is stable and remains in the deposit, but the sulphide of manganese, being unstable in the presence of carbonic acid, passes to bicarbonate of manganese and on meeting with a supply of oxygen is once more deposited as dioxide of manganese at some not very distant spot. It appears, then, that the manganese dioxide in marine deposits, whether originally derived from the decomposition of the rocks of the land surfaces or from the minerals forming part of the marine deposits, is continually shifting its position. The chemical processes in operation tend to favour its accumulation towards the surface of marine deposits, or in those areas on the ocean floor where there is a relatively small

amount of decomposing organic matter in the deposits at the bottom. In this way there may have been a gradual transference of manganese from the continents towards the remoter recesses of the abysmal regions from the earliest geological times, for, in the abysmal regions, where there is relatively a small amount of organic matter, and where the rate of accumulation of the deposit is slowest, the manganese dioxide would be more stable than in other areas.

Wherever manganese dioxide has once been deposited, a relatively rapid nodular formation there takes place in the clay or ooze, owing to the acidiferous properties of this dioxide, which, decomposing the carbonate of manganese in solution, produces manganous-manganic oxide, it may be Mn_3O_4 or a mixture of MnO and MnO_2 . This manganous-manganic oxide in the hydrated condition gradually becomes fully oxidised into dioxide; in this way we may account for the fact that the inner layers of some nodules are found to be more highly oxidised than the outer layers.

To the same action of manganese dioxide as an acid we may probably attribute the presence of calcium, nickel, cobalt, copper, and other metals in the nodules, for this dioxide would decompose the carbonates of any of these substances if present in the oozy Blue Mud or clay by uniting with their protoxides. In these soft oozes and clays the most favourable conditions are likewise present for the deposition of the manganese in concentric layers around a nucleus, similar in many respects to the urinary calculi found in the organs of many mammalia.

Theories concerning the Origin of Manganese Nodules in Marine Deposits.—Ever since the discovery of large numbers of manganese nodules by the “Challenger” Expedition on certain parts of the floor of the ocean, there has been much discussion both with regard to the source of the manganese and the mode of formation of these concretionary bodies.

GÜMBEL,* after an analysis of some of the “Challenger” specimens, referred the formation of the nodules to the action of submarine springs holding manganese in solution, which would be precipitated upon contact with sea-water. The rounded form of the nodules he believed to be due to repeated turnings and rollings on the bed of the ocean. It is almost certain that this distinguished geologist would not have held these opinions, could he have seen the large number and variety of nodules procured by the “Challenger” Expedition in many regions of the ocean. The form and distribution of the various nodules and coatings would have convinced him that submarine springs could not have had anything to do with their formation.

A cosmic or meteoric origin has been assigned to the oxides of manganese and iron in the manganese nodules.† MURRAY and RENARD have shown that magnetic spherules containing native iron and nickel, and certain spherules, called chondres, composed largely of silicates are present in deep-sea deposits, and have brought forward almost conclusive

* GÜMBEL, *Sitzb. d. k. Bayer. Akad. d. Wiss.*, Bd. viii. p. 189, 1878; Forschungsreise S.M.S. “Gazelle,” Th. ii. p. 103.

† See LOCKYER, *Nature*, vol. xxxviii, p. 521, 1888; HICKSON, *The Fauna of the Deep Sea*, p. 38, London, 1894.

evidence that these spherules have an extra-terrestrial origin.* But these cosmic spherules make up a very small part of the whole deposit. While admitting that a very small quantity of the iron and a still smaller quantity of the manganese in abysmal deposits have originated in the fall of meteorites to the earth, still it is undoubted that the great bulk of the manganese and iron in the manganese nodules has been derived from terrestrial rocks.

DIEULAFAIT,† from an examination of some samples of sea-water from the Atlantic and Indian Oceans, came to the conclusion that manganese existed in sea-water in the form of soluble bicarbonate, which becoming oxidised at the surface of the sea then fell to the bottom as oxides, and there took on a concretionary form. We have shown that, while manganese carbonate exists in the water associated with the clays, muds, and oozes at the bottom of the ocean, yet, so far as our researches go, there are no traces of manganese in solution in the great body of oceanic water. Traces of manganese, however, may be found in suspension in almost any sample of ocean water, associated with the suspended clayey matter which is nearly always present. This view of DIEULAFAIT, as well as that of RENARD,‡ that the greater part of the manganese accumulated at the bottom of the ocean has been derived from manganese in solution in the waters of the ocean, must therefore be abandoned. Besides, the distribution of the manganese dioxide in marine deposits in no way corresponds to what would take place did it fall to the bottom everywhere on oxidation of its carbonate at the surface of the ocean, even taking into consideration the rate of accumulation of the different kinds of deposits.

Mr J. Y. BUCHANAN, the chemist of the Challenger Expedition, has referred the origin of manganese nodules to the intervention of living organisms, it being held that the fine mud which some deep-sea organisms pass through their alimentary canals undergoes chemical changes, sulphuretted hydrogen and sulphides of iron and manganese being formed, the latter becoming subsequently oxidised. Those animals, such as Annelids, Holothurians and other Echinoderms, which obtain their food in this way, feed only on the thin red-coloured surface-layer of a Blue Mud. The excreta found in this layer are all red-coloured, so that if sulphide of iron be formed within the bodies of the animals, it must again be reoxidised after evacuation. The blue colour of the excreta found in the deeper layers is no doubt due to sulphide of iron, but this blue colour is an effect of the accumulation of the deposit as a whole, and arises from the decomposition of the organic matters imprisoned in the deeper layers by the gradual accumulation at the surface of the deposit. It has been shown that sulphide of manganese cannot exist under the same conditions as the sulphide of iron, but immediately passes into carbonate of manganese, which again passes to dioxide in the presence of the oxygen of the superincumbent sea-water. These changes take place not directly through the action of living organisms, but through the decomposition of organic débris present in the muds. Did the formation of manganese nodules in any way depend directly on the activity of living

* MURRAY and RENARD, *Deep-Sea Deposits Chall. Exp.*, pp. 327-336.

† DIEULAFAIT, *Comptes rendus*, tom. xcvi. p. 718, 1883.

‡ MURRAY and RENARD, *Deep-Sea Deposits Chall. Exp.*, p. 372, note.

organisms, we would expect them to be more abundant where marine organisms are especially numerous; the reverse is, however, the case. On coral reefs, Blue Muds, and Globigerina Oozes, manganese nodules are usually rare or entirely absent, although animal life is especially abundant in these areas. On the other hand, where living organisms are relatively rare or least numerous, as for instance around some volcanic islands and in the deepest recesses of the ocean, there we meet with depositions of dioxide of manganese and manganese nodules in the greatest abundance. It follows, then, that the mineralogical nature of the deposit has most to do with the rarity or abundance of manganese nodules, and not the greater or less abundance of living organisms.

In a recent publication Professor JUDD,* misled apparently by some supposed analogies, has argued that the manganese, the iron, and the other rarer metals, found in manganese nodules "must have been separated from their state of diffusion in sea-water" by organic agency. In the decomposition of all organic structures, it may be admitted that the chemical changes are initiated by bacteria, but with this exception it does not appear that organisms play any part in those changes which result in the formation of the manganese-iron nodules in marine deposits. In the foregoing pages we have shown satisfactorily that the formation of manganese nodules is due to purely chemical reactions taking place in marine deposits on the floor of the ocean, and not to secretion by organisms. Professor JUDD's views on this matter are rejected as inadmissible by all investigators who have devoted their attention to the problem.

In his first preliminary paper on Manganese in Deep-Sea Deposits, published in 1877, MURRAY† pointed out the association of large numbers of manganese nodules with the great abundance of basic volcanic débris in the deep-sea deposits at many localities. He held that the manganese dioxide originated in the decomposition of the manganiferous volcanic materials in the deposits through the action of carbonic acid, the carbonate of manganese formed passing gradually in the presence of the oxygen of the sea-water to the higher oxides of manganese. All the investigations described in this paper, indeed all subsequent researches on the subject, seem to confirm this view, which may now be regarded as firmly established. BISCHOFF long ago showed that the rocks which furnish iron and manganese ores contain both these metals as silicates of the protoxides, and that water which had permeated these rocks held carbonates of these metals in solution. "There can be," he says, "no doubt that the sesquioxide of manganese that occurs in manganese ores originates from carbonate of manganese."‡ More recently BOUSSINGAULT§ discussed the formation of coatings of manganese dioxide in various regions, and arrived at conclusions similar to those of BISCHOFF and MURRAY. The distribution and localisation of manganese dioxide on the floor of the ocean at the present time is thus shown to be strictly comparable with the corresponding subaërial phenomena, modified by the peculiar conditions which obtain on the floor of the ocean.

* *Fortnightly Review*, January 1894, p. 73.

† On the Distribution of Volcanic Débris over the Floor of the Ocean, *Proc. Roy. Soc. Edin.*, vol. ix. p. 255, 1877.

‡ Bischoff, *Chemical Geology*, vol. iii. p. 508, English edition.

§ *Annales de Chimie et de Physique*, ser. 5, tom. xxvii. pp. 289-311, 1882.