study of Palæophytology, and has sought to determine the affinities of palæozoic genera and species with those of existing forms. With this view he has described the fructification of a number of carboniferous ferns and lycopods. He has compared the plant remains of several British coalfields with each other, and with those of the coalfields of other countries. The most important results of his investigations have appeared in our *Transactions*.

On the Occurrence of Sulphur in Marine Muds and Nodules, and its bearing on their Mode of Formation. By J. Y. Buchanan, Esq., F.R.S.

(Read December 1, 1890.)

In the first section of the cruise of the "Challenger," that from Tenerife to Sombbrero, the existence was established of deep-sea muds, perfectly free from carbonate of lime, consisting mainly of silicates mixed with ochreous material, principally hydrated oxides of iron and manganese, and of local concentrations of these materials in the form of nodules and of coatings or incrustations on dead calcareous matter. The qualitative composition of these concentrations was carefully determined, and it was particularly noted that whether in the form of nodules or of incrustations they were aggregations of the general materials of the bottom, and not concretions or coatings of pure hydrous oxides.

On the section between Bermuda and the Azores some very suggestive specimens were got from the bottom on 27th June 1873, when the ship dredged in 1675 fathoms in lat. $38^{\circ} 18' N.$, long. $34^{\circ} 48' W.$ A number of light-coloured concretions were brought up which were much perforated by worm-holes, the walls of which were all stained blackish brown. The substance of the concretions consisted of carbonate of lime and silicates, and the black lining of the holes was peroxide of manganese. The various specimens obtained on this occasion showed the deposition of oxide of manganese in various stages, from those which showed only specks or stains to those containing a considerable percentage.* The most remarkable fact, however, was the close association of the oxide of manganese, especially at its first appearance, with the work of

* They are described in my report, *Proc. Roy. Soc.*, 1876, vol. xxiv. p. 606.

annelids, and this produced a strong conviction that the occurrence of peroxide of manganese at the bottom of the sea depended in some way or other on the organic life existing there.

After this comparatively little manganese was met with, until, on approaching the south coast of Australia, a large haul was obtained from a depth of 2600 fathoms in lat. $42^{\circ} 42' S.$, long. $134^{\circ} 10' E.$ and throughout the whole of the Pacific, when the trawl was put over in water sufficiently deep and sufficiently far from land, it rarely failed to collect abundance of manganese nodules, of all shapes and sizes, and surrounding all kinds of nuclei. Concretions also were obtained from time to time, recalling those of the North Atlantic above referred to. Thus, on the plateau of the Kermadec Islands, large lumps of a tufaceous sandstone were brought up, which were much perforated by serpular borings, and these were lined with peroxide of manganese. At the first station after leaving Japan, and on the landward side of the deep gully which runs parallel with the islands, a large haul was obtained, chiefly of pumice, tuff, and volcanic mud concretions. These were much perforated by worms, and the holes were lined with black oxide of manganese. One concretion, a portion of which is on the table, was broken open in the plane of one of the worm-holes, and the worm was found dead in it.* On another portion a dead worm was found adhering, and on removing it a black stain was found below it consisting of peroxide of manganese. The connection of the peroxide of manganese with the life of these animals was very marked in this case, and continued to occupy my attention from time to time, though without arriving at any satisfactory solution, during the cruise. It must not be forgotten that an invariable feature of the nodules was that they gave off abundance of alkaline and empyreumatic-smelling water on being heated, which served further to connect them with the organic world.

After the return of the "Challenger" I did a good deal of dredging in the summers of several years (1877–1882) in the seas on the west coast of Scotland, and on the 21st September 1878 I brought up from the deepest parts of Loch Fyne (104 fathoms) a quantity of sandy mud, with large quantities of dead pecten shells, and along with them true manganese nodules, with all the outward

* The body of this worm was tested and found free from manganese.

characteristics of those from the greatest depths of the open ocean; and this similarity was maintained on chemical examination. The dredging anchor must on this occasion have been dropped in the very richest part of the deposit; for the mud, which had undergone no concentrating process, was found, on being submitted to mechanical analysis, to consist of rather over 30 per cent. of nodules.* This was a very remarkable discovery; for although peroxide of manganese was not wanting in the shallower dredgings of the "Challenger," it existed only as coatings and similar deposits and not as nodules, which were believed to be dependent for their formation on the conditions obtaining in very deep water. After this particular attention was paid to the occurrence of manganese in all dredgings, and it was found to be abundant all round our coasts as a coating on shells, and more especially as the binding and colouring matter of worm tubes; but no nodules were anywhere found except in the deep part of Loch Fyne. Some years afterwards Mr Murray found them in great abundance on the Skelmorlie Bank in the Firth of Clyde in 10 fathoms.

In the same summer of 1878 I made a number of observations in the channel off the north-east part of the Island of Arran, where the water reaches a depth of 90 fathoms. A galvanised iron bucket was used as dredge, with a weight attached behind, and one before it; so that its action was rather to skim the surface than to dig into the lower layers of the bottom. It brought up a quantity of a very fine red mud, in which manganese grains could be detected, not apparently differing from those found in oceanic red clays. In the process of levigation, when the mud was stirred up with water and the light flocculent portion poured off, the heavier portion which had settled to the bottom of the vessel had the appearance of having been cast into elongated pellets. When these were stirred up again with water they were partially broken up into flocculent matter, which was poured off, leaving again pellets as before; and this could be continued until the whole of the mud had been washed away as flocculi, produced by the breaking up of these pellets. In the case of the particular mud under description, hardly anything in the shape of sand or coarser material remained behind. The ground-fauna, chiefly ophiurids, seemed to be abundant; and the pellets

* *Nature*, 1878, vol. xviii. p. 628.

above described were the casts excreted by these creatures, which subsist on what nutriment they can pick up by triturating and passing the sand or mud through their bodies. In some of these animals the triturating apparatus takes formidable proportions, as in sea-urchins; and it is probable that the sand found at low water owes its state of comminution largely to these animals and to worms, such as the ordinary lob-worm used for bait. When examining deep-sea clays in the "Challenger" I had observed the pellet formation, without, however, being able to refer it to any probable cause. Now, however, it became probable that the same causes are at work in deep as in shallow seas, and that the matter forming the bottom of the sea is being continually passed and repassed through the bodies of the numerous tribes of animals which demonstrably subsist on the mud and its contents.

In the following season, 1879, I made an extended cruise through the greater part of the waters of the west coast of Scotland, visiting most of the deeper spots, and paying particular attention to the occurrence of coprolitic mouldings of the mud. Thus, on 16th June 1879, dredging in the deep part of the Sound of Raasay in 155 fathoms,* "a little mud came up. It was a fine gray clay, which effervesced with acids and smelled of H_2S . On washing a quantity of it there remained the coprolitic masses and very little fine sand. There appeared to be a good deal of carbonate in a very fine state of division. There were very few shell particles visible, and the effervescence of what looked like flocculent clay was not inconsiderable." At the time I explained this flocculent carbonate as having been produced out of the silicates of the mud by the ground animals forming sulphide of calcium, which was transformed into carbonate by the carbonic acid of the water. On the following day another haul was got in the same locality and with similar results; it is noted that—"Sticking to the outside of the bag were many legs of ophiurids, which will account for the coprolites." When attention had once been paid to it, the coprolitic moulding of the mud, when of a suitable consistency, was found to be practically universal round our shores.†

* From deck-book of Steam Yacht "Mallard," 1879.

† Later, in the year 1886, when in charge of the expedition to survey the Gulf of Guinea in the steamship "Buccaneer," I found the same thing practically

Shore muds, that is, the terrigenous deposits which are found all along the shores of continents, and even at great depths—generally present the characteristic appearance of a reddish surface layer, overlying a bluish substratum. This characteristic is observed in deposits even far out at sea, and, where it is not masked by large amounts of calcareous matter, is evidently due to the oxidation of the bluish ferrous salts, on their coming in contact with the sea water, which always contains dissolved oxygen.

A very remarkable example of a blue clay—for it was too tenacious to be called a mud—was obtained in the Sound of Jura, and it was particularly noticeable for the amount of sulphides which it contained, and instructive by their complete disappearance on drying. It is worthy of more particular mention.

On 6th July 1879 the anchor dredge was put over in the Sound of Jura, where a depth of 120 fathoms was marked on the chart. It did not hold, and the yacht drifted, dragging it over the ground in a northerly direction before the wind and tide. Suddenly it hooked the ground, and brought the vessel up with a great strain on the cable. In heaving up it was with difficulty that the anchor was broken out of the ground; and when it was brought to the surface the bag was full of a fine, unctuous, very tenacious blue clay, with some of the reddish-brown surface mud covering it. There were a few pieces of broken shell and rock, also smooth and rounded pebbles, which seemed to occur principally in the part separating the surface mud from the blue clay, but there was very little of this kind of matter. The whole bagful, weighing more than

universal all along the African coast, and developed in a most remarkable manner on the coast flat within a considerable radius of the mouth of the river Congo. Here it was necessary to introduce a new designation for muds, and in this district the most frequent entries in the deck-book as to the nature of the bottom are “cop. m.,” meaning coprolitic mud. These so-called coprolites were almost jet black and of the size of mice droppings, and they were covered with the same substance in flocculent form, or were free from it, according to the scour of the tide in the locality. It was best developed in comparatively shallow water, and more especially in a depth of 50 fathoms, when the large ash bucket, to the use of which as a dredge I found it convenient to revert, came up full of these coprolites, without any flocculent matter whatever. All along the coast the mud of the locality was moulded in a similar way, though it was not so striking. When the course of the cruise took us across the open ocean to Ascension, and thence northwards, we were able to trace the transition of the more earthy shore coprolites into the more mineralised and glauconitic pelagic ones.

1 cwt., consisted almost entirely of homogeneous blue clay of a tenacity similar to the clay dug for brickmaking, and quite different from ordinary "blue muds." The clay was rather foul-smelling, and gave off abundance of sulphuretted hydrogen when treated with hydrochloric acid. It was so tenacious that it was impossible to break it up in water for the purpose of levigation, which is always very easily accomplished with ordinary muds. A considerable portion of it was dried and taken for analysis. It was found that, as soon as dry, not a trace of sulphide was to be found; but the mass of the clay was permeated with fine particles of oxide of iron, each of which represented a previous particle of sulphide. A specimen of this clay is on the table. The contrast between the fresh moist clay, which was thoroughly impregnated with sulphides, and the dried clay, without a trace of them, was very striking.*

The fact then had been demonstrated that the mud is being continually passed and repassed through the bodies of animals inhabiting the bottom of the sea. In doing so the mineral matter of which it consists comes in contact with the organic secretions of the animals, mixed with sea water, and is ground up along with them in the milling organs of the animals.

The Reducing Action of organic matter on sulphates has long been known, and its importance as an agent in geological metamorphosis was thoroughly recognised by Bischof.†

The effect of Trituration in promoting the chemical decomposition of silicates by water was demonstrated by Daubrée,‡ more particularly in the case of Felspar. I found the observations to hold good also for Augite. Clear crystals of this mineral from the Tristan da Cunha group, when pulverised with water in an agate mortar, rendered the water alkaline to turmeric paper.

It is evident therefore that at the bottom of the sea a number of conditions occur together, which are favourable to the production of chemical change. The ground animals, in the search of food, pass the mud through their bodies, grinding it up, and bringing it

* A condensed account of my views of the part played by the sulphates of the sea water in the production of the ochreous deposits on the bottom of the ocean, and of the carbonate of lime of the shells of the Mollusca, is published in the *Reports of the British Association* (York), 1881, p. 584.

† Bischof, *Lehrbuch der Chemischen und Physikalischen Geologie* (1863), i. 31, 358.

‡ Daubrée, *Geologie Experimentale*, i. 268.

thoroughly into contact at the moment of comminution with the sea water and the digestive secretions of the animal. The action of these secretions on the sulphates in the sea water is to produce sulphides, and the actions of the sulphides on the ochreous matter of the bottom is to produce sulphides of iron and manganese. Even if the bottom were covered with felspathic or augitic sand, the sulphides, acting on these silicates in the moment of partial decomposition, would convert the ochreous oxides by degrees into sulphides. That the volcanic material, lava, dust, scoriæ, pumice, which forms the bulk of the unaltered material of the bottom of the ocean, is so dealt with by the animals, is evident from the specimen from the Pacific on the table, which is not a singular specimen, but rather a typical one.

Having extracted what nutriment they can from the mud, the animals reject it, containing a certain proportion of sulphides of iron and manganese. These sulphides, it is well known, are exceedingly unstable in presence of water and oxygen, and if they come to lie on the surface of the mud, where they are exposed to the action of the sea water, which always contains dissolved oxygen, they must be quickly transformed into oxides. In the oxidation of ferrous sulphide by this process there is always separation of free sulphur, which, however, is to a great extent further oxidised; but it is probable that some would persist. If then the process just described represents at all what takes place in nature, we should expect to find in the ochreous deposits (the hydrous oxides of iron and manganese) some relics of their connection with the organic world. These are not wanting. All the deep-sea muds and manganese concretions, of every diversity of form, gave without exception, when freshly collected and heated in a tube over the lamp, a large quantity of ammoniacal water. It was important to see if sulphur could be detected. And here it is well to bear in mind that in the case of a "blue mud," which may contain unaltered sulphide, the sulphur found in the dried sample will come at least in part from that sulphide, and will be due to the oxidation by the atmosphere in the process of drying. In the case of an oceanic "red clay" or manganese nodule, where no blue matter is present, any sulphur which is found may be properly ascribed to oxidation on the bottom of the sea.

Acting on these considerations, in the winter of 1880–81, a number of muds and nodules were examined with a view to the detection, and if possible the estimation, of free sulphur.

Estimation of Sulphur in Muds.

A certain quantity of the clay, dried at about 80°, was put into a bottle with a known weight of chloroform. The stopper was tied down, and it was then put into a water-bath for about an hour at about the temperature of boiling chloroform (61° C.). It was then allowed to cool, filtered into a weighed fractionating flask, and washed twice with a little more chloroform. The chloroform was then distilled off, and the residue heated slightly and weighed.

The residue was treated with hot nitric and hydrochloric acids, diluted, and filtered if necessary, barium chloride solution added, allowed to stand, filtered, and the precipitate of barium sulphate weighed.

In the first few samples the barium sulphate was not weighed, but the quantity of sulphur judged by the amount of barium sulphate precipitated.

At first bisulphide of carbon was used, but it was departed from, because, although perfectly pure, and leaving no trace of sulphur on evaporation, it was thought that it would be well to use a solvent not containing any sulphur. A portion of the blue clay from the Sound of Jura, which when fresh contains much sulphide, was in the dried state tested with both solvents, with the following results.

Treatment with Bisulphide of Carbon.—A quantity of the clay was pounded and dried at about 80°. 50·00 grammes were put into a bottle with 236·0 grammes of bisulphide of carbon, and allowed to stand all night. A weighed portion of the carbon bisulphide was then taken out and put into a weighed flask, and the carbon bisulphide distilled off, and the residue weighed. 0·28 per cent. of sulphur was found in this way.

The sulphur dissolved completely in a small quantity of bisulphide. Next day another portion of carbon bisulphide was taken out and put into a weighed flask, distilled, and the residue weighed. This gave 0·33 per cent. of sulphur.

The bisulphide was tested to see whether it contained any free sulphur; it turned out to be very nearly pure.

Treatment with Chloroform.—Another 50·00 grammes of clay were treated with 183·6 grammes of chloroform. The mixture was heated for an hour on the water-bath at about the temperature of boiling chloroform (61° C.). A portion of the chloroform was then taken out, evaporated, and the residue weighed. This gave 0·39 per cent. of sulphur.

There was very little oil present in the residue, which was nearly pure sulphur.

In the first ten samples the BaSO_4 was not weighed, but the residue was always oxidised and the presence of sulphur proved by the formation of sulphuric acid. When sulphur was found constantly and in appreciable quantity, I then decided to weigh it, the operation being, from an analytical point of view, an advantageous one, as the sulphate of barium weighed weighs seven times more than the sulphur to be estimated. By far the largest amount of sulphur is contained in the clay from the Sound of Jura, which, in its fresh state, contained large quantities of sulphides, which were completely oxidised on drying. The 0·197 grammes of residue may be taken to be pure sulphur, which makes about 0·4 per cent. By far the greater part, if not the whole, of this sulphur was formed by oxidation during drying. Had it been possible to collect and examine separately the reddish-brown surface layer, we should, no doubt, have found very much less sulphur, but it would have been mainly due to oxidation by the oxygen of the bottom water.

The “oil,” which is extracted from all the muds along with the sulphur, and which varies a good deal in quantity, is due to the animal débris intimately mixed with the mud and with the materials of the nodules, which are made up, for the most part, of the materials of the bottom.

Nos. 2 and 3.—The manganese nodules of the 12th July 1875, from the North Pacific, in lat. 37° 52' N., long 160° 17' W., came from a depth of 2740 fathoms, where they appear to have been exceptionally abundant. Those of the 16th September 1875 came from a locality where they were equally abundant. The water was a little shallower, being 2350 fathoms, in lat. 13° 28' S., long. 149° 30' W. In both the samples of these nodules examined, the weight of the residue is considerable, but as there was a little oil in both cases it is not possible to give the percentage of sulphur.

No. 4.—The mud from the Sound of Raasay, off the west coast of Ross-shire, was dredged from 150 fathoms, and consisted of very fine soft grey mud, which on washing left a large residue of coprolitic pellets.

No. 5 is a similar mud from Loch Duich, also in Ross-shire; it harboured many annelids.

No. 6 is from the station in Loch Fyne, where, for the first time, manganese nodules were obtained in comparatively shallow water. It is a sandy clay with many dead shells.

No. 7 is the red clay from 90 fathoms in the Firth of Clyde, off the north-east part of the Island of Arran, which has already been referred to. It is a very fine red ochreous mud, much resembling the oceanic clays. On washing, it is found to be almost completely moulded into coprolitic pellets, and supports an abundant ground fauna. Like oceanic clays, on careful washing, grains of peroxide of manganese can be isolated, and it contains over 1 per cent. of phosphoric acid.

No. 8 is red clay from lat. 18° 56' N., long. 59° 35' W., depth 2975 fathoms, in the western basin of the North Atlantic.

No. 9 is a coating of peroxide of manganese from an oceanic concretion, but the locality has been omitted to be noted.

No. 10 is mud from 115 fathoms in the channel between the Island of Searba and the Garvelloch Islands, about twenty miles S.W. of Oban. Peroxide of manganese is very abundant here as a coating on dead shells.

No. 11 is from the upper basin of Loch Fyne, in 60 fathoms. The mud here contains a remarkably large amount of sulphur. The upper basin of a sea loch is, as regards many of its conditions, and notably as regards the nature of the mud at its bottom, in a state intermediate between that of the open sea and that of a fresh-water lake. The mineral constituents are usually in a lower state of oxidation than outside; and this is accompanied by, and partly due to, the relatively large amount of vegetable débris from the land. All these circumstances may retard the disappearance of the sulphur.

Nos. 12 and 13 are globigerina oozes from the Pacific and the Atlantic respectively, their particular locality not noted.

No. 14 is from the same locality as No. 10.

No. 15 is from a position north-east of the Island of Rum, in 147 fathoms, soft grey mud.

No. 16 is a blue mud, from 2050 fathoms in the Celebes Sea.

No. 17 is a glauconitic mud from the east coast of Australia, in 410 fathoms, lat. $34^{\circ} 13' S.$, long. $151^{\circ} 38' E.$

No. 18 is a diatomaceous mud from the Antarctic Ocean, in 1950 fathoms, lat. $53^{\circ} 55' S.$, long. $148^{\circ} 35' E.$

No. 19 is a red clay dredged on the 13th March 1874, in 2600 fathoms, lat. $42^{\circ} 42' S.$, long. $134^{\circ} 10' E.$ Along with the mud a large quantity of manganese nodules was brought up.

No. 20 is a radiolarian ooze from the North Pacific, lat. $12^{\circ} 40' N.$, long. $152^{\circ} 1' W.$, depth 2900 fathoms.

Nos. 21 and 22 are again samples of globigerina ooze from the Atlantic and the Pacific respectively. These samples differ from Nos. 12 and 13 inasmuch as the Pacific sample now contains more sulphur than the Atlantic one.

No. 23 is the insoluble residue left after treating a nodule from the same locality as No. 2 with hydrochloric acid and ferrous chloride. The difference is very remarkable. In No. 2 the sulphur was not determined—that is, the barium sulphate produced by its oxidation was not weighed; but it was one of these samples which showed that the amount present was so appreciable that it was worth while determining it as accurately as possible, so that it is certain that it must have contained at least an average amount. In the case of the natural nodule (No. 2) the weight of chloroform residue per 100 grammes substance was 29 milligrammes; in the case of the extracted nodule No. 23 it is 2 milligrammes, and the weight of sulphate of barium is put down as 1 decimilligramme. In fact, the sulphur in the nodule had disappeared under the treatment.

No. 24 is from Loch Fyne, in 87 fathoms, opposite Otter House, and a little further up the loch than the station No. 6, but both of them in the outer loch, as opposed to No. 11, which is in the upper and semi-enclosed basin. The contrast between No. 24 and No. 11 is remarkable. In the upper basin the amount of the chloroform residue per 100 grms. substance was 74 milligrms., and 10 milligrms. of it was sulphur. In the outer loch there were only 17 milligrms. of residue and 1 milligrm. sulphur.

No. 25 is a very remarkable white clay from the bottom of Loch Ness, and therefore a fresh-water formation. It occurs in a small area opposite Urquhart Castle, and, in various depths, often covered by a thin layer of peaty substance; but in some places, in depths of about 30 fathoms, the sounding-tube brings up the white clay alone. It was observed also in Loch Oich. It is chemically quite distinct from the marine clays, being much more acid. The amount of matter extracted by chloroform is enormous, being 374 milligrms. per 100 grms., most of which is oil or wax, but containing 4 milligrms. of oxidisable sulphur. It is not impossible that in this case the sulphur may exist as an organic compound; and the amount of oily matter in the clay is interesting in the indication which it gives of the possible mode of formation of our oil-bearing shales.

No. 26 is from the anchorage of Isle Oronsay in the Sound of Sleat.

No. 27 is from a depth of 87 fathoms off Garroch Head, in the Firth of Clyde. Both in this case and in that of No. 26 the amounts of residue and of sulphur are insignificant.

Sulphur was thus detected in all these samples and determined in the greater number of them. Putting aside shallow water coast muds, the largest amounts of sulphur are found in the Celebes Sea (No. 16), in the Diatomaceous ooze of the Antarctic (No. 18), and in the Radiolarian ooze of the Pacific (No. 20). So far, therefore, as it goes, we have the evidence of the sulphur in favour of former organic agency. It is worthy of remark that the property of giving off alkaline water on heating has in the course of years disappeared, and in its place the nodules on being heated give off acid vapours, which, it is true, contain some ammonia, but along with an excess of nitric acid, which is without doubt due to the gradual oxidation of the nitrogenous matter. It is possible that the finely divided sulphur may diminish and finally disappear in the same way. But in 1881, there was still enough to be easily determined. Let us consider the chemical reactions more closely.

When a mud containing ferrous sulphide is treated with dilute hydrochloric acid, the sulphide dissolves with evolution of sulphuretted hydrogen, so long as there is no substance present which has a decomposing action on the sulphuretted hydrogen. If there be

ferric salt either mixed with the mud or in the solution, then it is reduced to ferrous salt, with the destruction of the equivalent amount of H_2S and separation of sulphur. If the ferric salt be in excess, no sulphuretted hydrogen makes its appearance at all. The reaction is very simple—

because the 2HCl appears on both sides of the equation, and is in fact unnecessary. A *trace* of free acid is no doubt necessary, and it is turned over and over again in the reaction of indefinite quantities of FeS on Fe_2Cl_6 , after the manner of a catalytic action.

The same reaction takes place if we use ferric sulphate in place of ferric chloride.

It is evident, therefore, that if we have a sample of mud containing sulphide, and we mix it thoroughly with a solution of Fe_2Cl_6 or $\text{Fe}_2(\text{SO}_4)_3$, we shall have in the ferric salt reduced a measure of the decomposable sulphide present. The ferrous salt can be readily determined by permanganate of potash or otherwise. It will be seen from the above equation that one molecule FeS decomposes one molecule Fe_2Cl_6 with the formation of three molecules FeCl_2 , so that the FeS in the mud is one-third of the ferrous salt found.

In order to make some preliminary experiments, a mixture of 100 grms. alum and 30 grms. ferrous sulphate were dissolved in about $\frac{3}{4}$ litre of water and precipitated with ammonia and sulphide of ammonium. The precipitate was thoroughly washed by repeated decantations, the flask being always filled up to the neck, and corked and allowed to settle. When it was completely washed the surplus water was poured off, and the precipitate, suspended in about $\frac{1}{2}$ litre of water, was preserved in a well-stoppered reagent bottle. The precipitate consists of alumina and sulphide of iron, and may therefore be taken as an imitation of a simple form of mud. I made some experiments to see with what amount of agreement in the results one could titrate a number of different samples of the same mud.

Three flasks were placed side by side, and into each 50 c.c. suspended FeS mud were measured. The mixture of $\text{FeS} + \text{Al}_2\text{O}_3$ was

thoroughly shaken up, then run into a narrow graduated cylinder, holding 50 c.c., which was emptied into the flask and then washed once into it with distilled water. To each of the flasks was then added 10 c.c. of the reddish-brown but still acid, ferric sulphate solution, and the contents shaken. In a few seconds the black colour of the sediment had disappeared entirely, being replaced by a yellowish-red precipitate, which disappeared for the most part on the addition of dilute sulphuric acid. Water was then added to bring up the volume to 250 c.c., and the titration was effected with permanganate of potash solution (1 litre containing $\frac{\text{KMnO}_4}{50}$ grms.). The three portions of 50 c.c. required each 11.6, 11.6, and 11.7 c.c. permanganate respectively. We see then that a suspended precipitate can be measured off about as accurately as a dissolved salt.

It is evident, then, that if we have a mud containing FeS and other ferrous compounds decomposable by HCl, we can determine first the FeS by adding Fe_2Cl_6 and titrating a portion with permanganate; then the other ferrous compounds, by adding HCl and titrating another portion with permanganate, due account being kept of the weights and volumes used. In order to try the method in practice, three soundings were made;—on 30th September 1881 in the Sound of Raasay, off Croulin Island, 120 fathoms; and on the 1st October 1881 in Loch Duich, in 49 and 51 fathoms. The first of these represents more or less the conditions in the open sea of coast waters; the last two represent the conditions in a semi-enclosed loch basin. The Sound of Raasay mud was a light grey mud, with no offensive qualities. Both samples from Loch Duich were very foul smelling. All three samples were tightly stoppered up in their wet condition, and examined on 20th and 21st October 1881 in my laboratory in Edinburgh. I unfortunately had no suitable ferric solution afloat with me so as to treat them immediately. In the three weeks that both muds from Loch Duich were kept in bottles, the surface layer got completely oxidised, and on opening the bottles the smell was gone; but, on breaking through the surface layer, the unaltered black mud was exposed with all its original qualities, including its peculiar odour.

The following was the method used in the case of the Loch Duich

mud from 49 fathoms. Two portions of the damp unaltered mud were weighed out; one portion, 6·724 grms., was dried at 100° C., and the other, 7·881 grms., was treated with deep red Fe_2Cl_6 in a 100 c.c. flask, which was then filled up to the mark with water. 50 c.c. of this solution, containing 3·94 grms. damp mud, were acidified with sulphuric acid and titrated with permanganate ($\frac{\text{KMnO}_4}{50}$ grms. per litre), using 1·9 c.c. To the remaining 50 c.c. with sediment (the volume of which may here be neglected) were added 4 c.c. of strong hydrochloric acid (12·5 HCl grms. per litre), filled up to the mark, and allowed to settle. 50 c.c. of this solution, containing 1·97 grms. damp mud, were further acidified with sulphuric acid and titrated with the same permanganate, of which 1·7 c.c. were used. A litre of the above permanganate oxidises 5·6 grms. iron from the ferrous to the ferric state. In the first operation, 50 c.c. solution used 1·9 c.c. permanganate, therefore the whole amount of mud, 7·881 grms., when treated with ferric chloride, would require 3·8 c.c. = 0·0213 gm. iron.

After treatment with hydrochloric acid a quantity of solution equivalent to 1·97 grms. wet mud required 1·7 c.c. permanganate, so that 7·881 grms. mud would require 6·8 c.c. when treated with both HCl and Fe_2Cl_6 , which represents 0·0381 gm. iron. Therefore, total iron found by

Permanganate in HCl + Fe_2Cl_6 solution,	.	.	0·0381 gm.
Deduct Iron found in Fe_2Cl_6 solution,	.	.	0·0213 „

Leaves Iron present as Ferrous Salt extracted by	}	0·0168 „
Hydrochloric Acid,		

Of the 0·213 gm. iron found in the first solution we have seen that only one-third is to be reckoned as belonging to the mud, and to be taken as forming FeS , so that in 7·881 grms. wet mud we have 0·0071 gm. iron present as sulphide, equal to 0·0112 gm. FeS , and 0·0168 gm. iron present as ferrous oxide extracted by hydrochloric acid, equal to 0·0216 gm. FeO .

The 6·724 grms. wet mud weighed when dried at 100° C., during which it was oxidised as well as dried, 2·011 grms., equal to a loss of 70·1 per cent. Therefore the dry mud is 29·9 per cent. of the damp mud taken. The 7·881 grms. damp mud therefore represent

2·3564 grms. dry mud, and therefore we find that the mud taken as dry contains 0·47 per cent. FeS and 0·92 per cent. FeO in some other easily decomposable combination.

The other samples were treated in the same way, and in the Loch Duich mud, from 51 fathoms, 0·94 per cent. FeS + 0·65 per cent. FeO were found. It is remarkable that the amount of F_2S should be so small in such offensive muds.

In the outside mud from 120 fathoms in the Sound of Raasay only 0·05 per cent. FeS and 0·1 per cent. FeO were found.

In connection with this mud, which contained some shell debris, the method was found to be less applicable than to muds free from calcareous matter. The reason is obvious; because, on adding a neutral ferric solution to a mud containing carbonate of lime, precipitation of the ferric oxide by the lime immediately commences. This would not really interfere with the reaction, because the FeS would reduce the precipitated Fe_2O_3 all the same, and the ferrous salt can still be determined by permanganate; but in truly calcareous bottoms this action is troublesome, and the method will require special study in this direction. In the semi-enclosed basins of the sea lochs, which, as has already been observed, form a transition between the open sea and fresh-water lakes, the bottom resembles more nearly that of the fresh-water lakes, in the absence of mollusca, and in the abundance of organic matter of vegetable origin, than that of the open sea with its abundant and varied ground fauna. It differs from those of fresh-water lakes in being bathed by sea-water largely impregnated with sulphates. Consequently it is in the inner basins of sea lochs that the conditions for a constant production of sulphides are present, while the same conditions are hostile to the presence of calcareous organisms. Hence it is in these basins that the greatest quantities of sulphides are found, and it is in their muds that the above method is most applicable.

The sulphuretted muds, however, are so alterable by atmospheric influences that it is essential that they should be treated immediately on collection. For this purpose weighed wide-mouthed bottles with good stoppers should be provided. When a specimen of mud is brought up from the bottom, a sample of it is immediately taken with a spatula and put into one

of these bottles containing a known quantity of ferric chloride solution, at least sufficient to completely cover the sample of mud. Another sample, as nearly similar to the first as possible, is taken and stoppered in another bottle for drying. In this way a large amount of valuable information might be gained; but it will be evident from the nature of the case that the actual figures obtained in any one particular case are affected by a considerable possible error.

In the month of June 1881 I carried out a number of laboratory experiments bearing on this subject, using the sulphides of different metals of the iron group. These bodies were all prepared in the same way, namely, by precipitating the sulphates with sulphide of ammonium, and washing by decantation in stoppered bottles, always filled up quite full. A quantity of hydrated ferric oxide was also prepared by precipitating ferric chloride with ammonia and washing. All of these precipitates, when thoroughly washed, were preserved suspended in distilled water in well-stoppered reagent bottles.

Ferrous Sulphide and Ferric Oxide.—When quite neutral these substances do not react on one another, at least at once. But if the water has the slightest acid reaction reduction of the sesquioxide and production of sulphur take place rapidly. A mixture of Fe_2O_3 and FeS in water and quite neutral was corked up and allowed to stand for five days, when the sediment was found to be separated into two sharply-defined layers—the upper red, consisting of the oxide, and the lower black, of the sulphide. When brought together, therefore, in presence of nothing but distilled water, there is no appreciable resultant action.

Manganous Sulphide can be preserved perfectly under distilled water in well-stoppered bottles filled to the neck. A considerable quantity was prepared in the summer of 1881, and, when thoroughly washed, it was put away in three separate bottles. The contents of only one bottle were used for experimental purposes, and the upper part of it got coloured immediately black with oxide of manganese, from the oxidation of the flakes of sulphide which adhered to the surface of the upper part of the bottle, left dry when some of the water and precipitate had been poured out. This took place at the time, and was to be expected. The two other bottles, which were

filled up with the manganous sulphide at the time of preparation, have never been opened since, though they have all the time been exposed to the light, and are exactly in the condition in which they were when bottled nine and a half years ago. There is no trace of oxidation.

Manganous Sulphide and Hydrous Ferric Oxide.—Both substances are used, suspended in distilled water. If the ferric oxide be cautiously added to the sulphide of manganese, and both suspended in water, the red patches are seen to disappear, and the general colour of the suspended matter becomes rather lighter in colour than the MnS , and there is no formation of FeS . If further additions of Fe_2O_3 be made, red flakes deposit themselves. They do not appear to be unaltered Fe_2O_3 , but are exactly like the “red cherty particles” of manganese bottoms. On still further additions of Fe_2O_3 , the colour changes quickly, though not instantaneously, to black, with, however, a large admixture of white particles, the two being easily seen to be perfectly distinct. There is also a quantity of precipitated sulphur which remains floating in the liquid long after the heavy matter has subsided.

Prosecuting this line of experiment, I made three mixtures in suitable flasks.

No. 1 contained MnS and Fe_2O_3 , the MnS being in excess. There was formation of red cherty particles, but nothing black.

No. 2. The same substances, but containing the Fe_2O_3 in excess; the mixture quickly turned black.

No. 3. The same as No. 2, only it was made up with warm water, and it turned black almost at once.

These experiments were repeated, and with the same results. The above flasks, Nos. 1, 2, and 3, were corked up and allowed to stand over night. No. 1 contained numerous black particles, as well as red cherty ones, and an excess of MnS as well as sulphur. Nos. 2 and 3 were much as they had been the night before, except that the white particles had almost entirely disappeared, as also all red particles. The reactions are considerably accelerated by heat.

On examining the contents of each of these flasks, no peroxide of manganese was found, but large quantities of sulphide of iron. The likeness in the red flakes to the cherty particles of the bottom muds in the manganese districts of the South Pacific, and of the

kernels of some manganese nodules was very striking. It is not improbable that the first action of the MnS on the Fe_2O_3 may be accompanied by the formation of mixed oxides of iron and manganese; but there is much to be done in this direction in the strictly quantitative investigation of the interaction of the insoluble, but not inert, compounds of this as well as of other groups of metals.

Ferric Sulphate and Manganous Sulphide.—Experiments were now made, using the iron as a ferric salt in solution, and for this purpose ferric sulphate was used. It was made as nearly neutral as possible by addition of ammonia. The MnS was, as before, suspended in distilled water.

On adding ferric sulphate to excess of MnS, the formation of FeS is immediate.

On adding a large excess of $\text{Fe}_2(\text{SO}_4)_3$ the FeS is decomposed, there is formation of basic salt, and on dissolving it with H_2SO_4 the solution contains large quantities of ferrous sulphate.

On experimenting with solution of ferrous sulphate it was found that excess of MnS precipitates the iron completely as FeS, acting exactly like an alkaline sulphide.

The rationale, therefore, of the above reaction is very simple. Thus

∴ adding (1) and (2) we have

which is identical with (1), and by adding more MnS we get the conditions of equation (2), and so on, repeating the cycle.

Hence, if we add MnS to excess of $\text{Fe}_2(\text{SO}_4)_3$, we should get reduction of the ferric salt without formation of FeS. On adding excess of MnS, we get formation of FeS, and then on adding excess of $\text{Fe}_2(\text{SO}_4)_3$ we get back to the same state of things as at first.

The reaction of equation (1) can be obtained by very cautiously adding small quantities of suspended MnS to a very large excess of

$\text{Fe}_2(\text{SO}_4)_3$. Still there is always local formation of FeS which disappears on mixing, so that the reaction is really that of the whole cycle. The action, therefore, of MnS on soluble iron salts is in the first instance to reduce whatever is in the ferric state to the ferrous, and then at once to precipitate the ferrous salt as sulphide, a managanous salt taking the place of the ferrous salt in the solution.

When added in great excess to solutions of nickel sulphate, managanous sulphide precipitates it as NiS . When added to solution of sulphate of zinc, it either does not precipitate it at all or only very slightly at ordinary temperatures. Sulphide of zinc was not found to precipitate manganese sulphate solution.

As the result, then, of the observations and experiments which have been recited I was led to believe that the principal agent in the comminution of the mineral matter found at the bottom of both deep and shallow seas and oceans is the ground fauna of the sea, which depends for its subsistence on the organic matter which it can extract from the mud.

In order to fit them for collecting their nutriment in this way the animals have been fitted with different forms of masticating or milling apparatus, so as to thoroughly deal with the matter which they pass through their bodies. It has been shown that most silicates are decomposed to a certain extent when ground or pulverised under water; so that the mere mastication of the sand or mud in presence of pure water would have a decomposing action on the silicates which it contains. This action is much assisted, in the case of marine animals, by the fact that the water which they pass through their bodies along with the sand is charged with sulphates. These are easily reduced to sulphides by the action of the organic matter of the secretions of the animals. The resulting sulphide at once suffers double decomposition with any oxide of iron or manganese which is present as such in the mud, or may be being set at liberty from silicates under the decomposing influence of trituration under water. The sulphides of manganese and iron so formed are in course of nature extruded by the animals, and if exposed to the sea water on the surface of the mud are quickly oxidised, the manganese taking priority. The mud below the surface layer, in localities where ground life is abundant, remains blue, being protected by the oxidation of what is above it.

At the bottom of the ocean the mineral matter is thus exposed to a reducing process due to the life of the animals which inhabit it, and to an oxidising process due to the oxygen dissolved in the water. Other things being equal, the redness or blueness of a mud or clay depends on the relative activity of these processes. They also exercise a controlling or modifying influence on one another. For, although marine animals are much less sensitive to variation in the amount of oxygen in their atmosphere than terrestrial animals, it is certain that there must be a limit to the deficiency of oxygen which each animal can support; and when this limit is approached, its reducing activity is diminished, or, it may be, extinguished. The water in the course of circulation is being continually renewed, and, meeting with a diminished amount of freshly reduced matter, it is able to push the oxidation of the mud to a greater depth. It is easily conceivable that in many of the deep parts of the ocean the amount of ground life may be so limited that the water has no difficulty in oxidising at once its ejecta; and these conditions would be favourable to the formation of a red clay or chocolate mud according to the preponderance of iron or manganese.

While dealing with this subject it is proper to refer to Darwin's book on *Vegetable Mould and Earthworms*, which was published in 1881. His masterly investigations in the kindred department of the part played by earthworms in the formation of the terrestrial soil strengthened me much in my belief in the soundness of the views above developed as to the formation of marine muds. Indeed, to a certain extent he extends his views himself to the case of marine muds. At page 256, after noticing that it is due to the milling action of the gizzards of worms that the supply of exceedingly finely divided mineral matter, which is removed from the surfaces of every field by every shower of rain, is constantly renewed, he adds in a note: "This conclusion reminds me of the vast amount of extremely fine chalky mud which is formed within the lagoons of many atolls, where the sea is tranquil and waves cannot triturate the blocks of coral. The mud must, so I believe, be attributed to the innumerable annelids and others animals which burrow into the dead coral, and to the fishes, Holothurians, &c., which browse on the living corals." Darwin further gives an

approximate numerical result or estimate of the work of earth-worms which is interesting. At page 258 he says: "Nor should we forget, in considering the power which worms exert in triturating particles of rock, that there is good evidence that on each acre of land which is sufficiently damp and not too sandy, gravelly, or rocky for worms to inhabit, a weight of more than 10 tons of earth annually passes through their bodies and is brought to the surface."

On a Simple Pocket Dust-Counter.

By John Aitken, Esq.

(With a Plate.)

(Read December 1, 1890.)

It is now a year and a half since I communicated to this Society a description of a portable form of apparatus for enabling us to count the number of particles of dust in the atmosphere. The working of that instrument in my hands has been most satisfactory, and though it has occasionally given trouble, yet it has not given more than might have been expected. Though that apparatus has worked quite pleasantly with me, and enabled a beginning to be made of an investigation into the amount, and the effects, of dust in our atmosphere, yet very few have as yet followed up this line of inquiry. This has probably been owing to there being something in the complicated nature of the apparatus which has deterred others from joining in the work. I therefore determined to see if a simpler, and at the same time a reliable, form of the apparatus could not be devised.

After the experience gained in making thousands of observations with the portable apparatus, I have acquired an acquaintance with its weak points, and a knowledge of what it would be necessary for an instrument of this kind to do under the different conditions in which it would be required to work, and I may now sum up the indictment against the portable apparatus under the following heads:—It is too complicated; it has too many weak points; it is too heavy; it has an unnecessarily wide range for meteorological work; and it is too expensive. If an instrument could be con-