

V.—*Manganese in the Sea.*

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TO the geologist, the mineralogist and the chemist, two of the observations made during the voyage of the Challenger are of especial interest. One of these observations is the occurrence over vast areas of the deep sea bottom of a peculiar red clay, containing silica, peroxide of iron, and alumina. The other discovery to which I refer has been described by Sir Wyville Thomson as the occurrence throughout this red clay of nodules of "nearly pure peroxide of manganese." To these nodules, as well as to the red clay, an organic origin has been assigned. But the immediate source of so much manganese is hard to find, for this element is by no means an abundant constituent of animal or vegetable organisms. The difficulty is, however, somewhat lessened when the manganese nodules are submitted to a more minute chemical examination. From two correspondents I have received an ample supply of these curious concretions, accompanied by a suggestion that they should be submitted to chemical analysis.

The specimens were from two localities in the Pacific. In the centre of one of the nodules was a core of indurated red clay: in two other specimens analysed, fragments of pumice occupied the middle of the concretion. All the specimens were almost homogeneous, so far as ordinary chemical and physical tests were capable of showing.

The material had, however, been deposited in several concentric layers, which, in some part of the nodules could be successively removed. In some of the specimens (which were *not* submitted to analysis) a very fine layer of a paler substance separated the blackish manganese layers from each other.

The following are the chief characters of the nodules:—Hardness 3.5, Specific gravity 1.89. Colour brownish black: streak somewhat shining: powder, between blackish brown and clove-brown: fragile; fracture, rough conchoidal.

In the closed tube this mineral gives out much water having a slightly alkaline reaction. Before the blowpipe it contracts, becomes black, and fuses at the edges. With hydrochloric acid chlorine is evolved, and silica separated as the mineral dissolves.

Qualitative analysis shows that the powdered nodules, from which any clay cores, &c., have been carefully removed, contain a small quantity of the salts of sea-water. Cold water removed from a powdered sample just .71 per cent. of chlorine in the form of chlorides of sodium, magnesium, &c. The mineral used for the subsequent quantitative determinations was not, however, thus washed, but had been merely powdered and exposed for an hour or two to the air. The following are the numerical details of my analyses.

I.—5295 gram lost .13 gram  $H_2O$  in vacuo over sulphuric acid.

The above vacuum-dried mineral gave .053 gram  $H_2O$  when heated in a current of air, the water being weighed in a chloride-of-calcium tube. The platinum boat lost .001 gram more than the chloride of calcium absorbed, showing the original state of peroxidation of the manganese: a slight yellowish sublimate occurred in this experiment.

II.—.412 gram of mineral (from a large nodule) lost .107 gram in vacuo, and .047 gram at a red heat. These figures correspond, respectively, to 25.97 and 11.31 per cent. of water.

III.—.301 gram gave .07 gram  $Fe_2O_3$  and  $Al_2O_3$ .

„ „ .0795 „  $Mn_2O_4$

„ „ .0315 „  $SiO_2$

IV.—.3015 „ „ .0705 „  $Fe_2O_3$  and  $Al_2O_3$

„ „ .08 „  $Mn_2O_4$

„ „ .031 „  $SiO_2$

V.—.5295 „ „ .0175 „  $Al_2O_3$

From the above results, (excluding analysis II), the following mean percentages of the chief constituents of the “manganese” nodules are calculated:—

	in 100 parts.
Water lost <i>in vacuo</i> . . . . .	24.55
Water retained at 100°C but evolved at a red heat . .	10.00
Manganese dioxide . . . . .	30.22
Ferric oxide . . . . .	20.02

Alumina .. .. .	3.30
Silica .. .. .	10.37
Chlorine .. .. .	.71
Mg, Ca, Cu, Na, Cl, P <sub>2</sub> O <sub>5</sub> &c. .. .. .	.83
	100.00

It would be rash to assume from the above data, which represent the average amount of the several constituents of a few only of these nodules, that we have here a new and definite mineral. If, however, many other analyses of numerous homogeneous specimens from diverse localities of the deep sea bottom should yield the same or nearly-related results, then the singularity of the mode of formation, of the occurrence, and of the composition of these concretions should constitute no bar to their recognition as a distinct mineral species under such a name as *Pelagite*. It would at present be impossible to assign a formula to this 'pelagite,' but the analyses I have quoted correspond pretty closely to a compound expressed by the formula  $2 \text{MnO}_2, \text{Fe}_2\text{O}_3, \text{SiO}_2, 12 \text{aq}$ . It would appear probable that the red clay, which is so constantly found associated with these black nodules, is itself a hydrated silicate of alumina and ferric oxide.

I stated at the commencement of the present note that the black nodules have been invariably described as nearly pure black oxide of manganese. I have examined 11 characteristic specimens or fragments—some large and some small, but have not yet met with any specimens notably free from iron &c. than those analysed above. Yet these nodules, black grains, concretions, are always described as "peroxide of manganese," (Proc. Roy. Soc. xxiii. p. 45. Nov. 1874). In the address by Sir Wyville Thomson at Glasgow (11 Sept. 1876. See Report, revised by the author, in "Nature," vol. xiv, p. 492) he uses the same expression, "nearly pure peroxide of manganese." As this passage from his address contains Sir Wyville Thomson's latest description of these black nodules, I quote it here *in extenso*.

"Over the whole bottom of the Pacific, or a very large part of it, we find red clay, and particularly in the North Pacific, where there is a great depth of water. The red clay has all through it nodules, which vary from the size of sago, or a canary seed to the size of a child's head or an orange, composed of nearly pure peroxide of manganese. These are found in enormous quantity. The trawl sent down to the bottom in those regions brings up masses of concretions, much resembling lumps of the mineral known as *wad*, almost all of which contain as a kernel in the interior, a fish's tooth, or a little bit of sponge, or some fossil

of some kind, which has formed the nucleus round which the manganese has accumulated. This is altogether a most peculiar and novel observation. In the Atlantic, and all over the bottom of the sea we find manganese in minute bits, but in the North Pacific particularly, these pieces are in very great quantity and attain a large size. This is a phenomenon which we are as yet unable to explain, and I do not know that there is any analogous instance in any of the older formations."

Postscript, October 6, 1876.—So far was the above account of my results written when I received No. 170 of the Proc. Roy. Society containing the "Report from the Challenger." From Mr. Buchanan's notice of the class of black oceanic nodules which form the subject of the present note, it is evident that he has fully recognised their complex composition. He gives no quantitative results at present, but promises further inquiry in this direction. Meanwhile, the present communication may serve as a slight corrective to the wide-spread statement copied into newspapers and periodicals of all kinds, English and Foreign, that all these dark-coloured oceanic concretions consist almost exclusively of pure black oxide of manganese. And, further, it may prove of some slight use and interest as affording an independent analysis for comparison with the authoritative conclusions which are promised by Mr. Buchanan.