

CHEMICAL COMPOSITION OF THREE MANGANESE NODULES FROM THE PACIFIC OCEAN¹

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ABSTRACT

Three manganese nodules from the Pacific Ocean have been analysed for 35 elements by using mainly spectrophotometric and spectrographic methods. Cu, Co, Ni, Zn, and Pb were found in amounts approaching 1%, which far exceeds their average concentrations in igneous rocks. On the other hand, elements having readily hydrolysable ions, such as Ga, Sc, Zr, Y, La and Ti, are present only in amounts comparable with their concentrations in igneous rocks. Sb, Bi, Be, and Cr were not detected. The hydrochloric acid-insoluble fraction of nodules is practically free of the heavy metals that are characteristic of the acid-soluble fraction; it consists principally of clay minerals, together with lesser amounts of quartz, apatite, biotite and sodium and potassium feldspars.

INTRODUCTION

One of the most interesting problems of marine geochemistry is the origin of the manganese deposits which have formed over large areas of the deep ocean floors. These deposits occur either as dark-coloured grains and coatings on the sea bed and on the debris above it, or as discrete concretions (so-called manganese nodules) which were first discovered during the CHALLENGER Expedition of 1873-76 (36).

Although manganese nodules are quite scarce in the Atlantic Ocean, where the sediment is poor in manganese, they are found in great abundance in some areas of the Pacific Ocean, where they have frequently been recovered in amounts as great as 50-100 kg. They usually occur in water deeper than 2000 m, but occasionally they have been found in water as shallow as 260 m (37). Nodules appear to be more abundant (25) on the top of outcrops of pre-Pleistocene sediments and on elevated areas of the ocean floor than in the surrounding depressions.

¹ The authors wish to thank the trustees of the British Museum (Natural History) for the gift of nodules taken at CHALLENGER Sts. 248 and 252.

Nodules are found principally on red clay deposits and are particularly abundant on the dark chocolate-coloured oozes which are rich in manganese. They also occur less frequently on radiolarian and globigerina ooze and even in blue muds formed under conditions of low redox potential (CHALLENGER Sts. 298 and 299).

Nodules, which vary in shape from almost spherical and ovoid types through irregular shapes to flattened slabs, occur in a wide range of sizes; spherical types range from 0.5 to 15 cm in diameter and flattened types may reach a size of 20 × 50 × 4 cm. Their surfaces, frequently reniform, appear to have been formed by amalgamation of a number of small nodules. In general, all nodules from a particular locality are roughly similar in shape but may differ greatly in size.

Generally, but not always, nodules are formed around a nucleus of different material which consists most frequently of pumice, volcanic glass or igneous rock, often much altered; less commonly, the nuclei consist of shark or fish teeth (sometimes those of extinct species), otoliths and bones of Cetaceans, or siliceous and calcareous sponges (2).

The majority of manganese nodules are built up of a series of concentric layers of alternating light and dark bands, which show the concretionary nature of the nodules. Sometimes, particularly in those specimens containing no nucleus, only the outer parts are banded, the inner part appearing homogeneous and much darker in colour. The concentric structure is often combined with a radial structure in which dendritic growths of manganese oxide penetrate inwards through several layers. The various forms of nodules and their internal structures are clearly shown by Murray and Renard (36: pls. I-IV, IX).

Chemically, the external portions of nodules consist principally of hydrated oxides of manganese and iron, in varying proportions, together with significant amounts of many other elements, particularly transition metals. They also contain variable amounts of adventitious matter, such as clay and mineral grains. Few of the early analyses of manganese nodules (36, 2) are satisfactory; frequently, major constituent elements were not determined, and in many cases the nucleus was included in the sample analysed.

The only reasonably complete analysis of a manganese nodule which can be traced is that by Gibson (36: 416-423), who determined 28 elements in some small nodules from the Pacific

(CHALLENGER St. 285). Owing to the rather primitive techniques available in his time, the analysis must be considered only semi-quantitative, but it did draw attention to the presence of considerable amounts of certain rare elements that are present in nodules.

Goldberg (14) has analysed nodules from 11 localities in the eastern Pacific Ocean for iron, manganese and nine other elements. His results (see Table I) represent the composition of the nodules (presumably excluding the nucleus but including any interstitial silicate). They show Fe/Mn ratios varying from 0.26 to 1.28 and demonstrate the considerable enrichment of manganese, copper, cobalt and nickel in the nodules compared with red clay or average igneous rocks. Goldberg claims he found linear relationships of the iron content with the titanium, zirconium and cobalt contents and of manganese with copper and nickel. Statistical examination of his figures reveals that there is no correlation of iron with zirconium or of manganese with copper, although there is a high degree of probability of a correlation of iron with titanium and cobalt.

TABLE I. COMPOSITION OF PACIFIC OCEAN MANGANESE NODULES IN PERCENT OF WEIGHT

Element	Gibson, in Murray & Renard, 36	Goldberg, 14		
		Minimum	Maximum	Average
Iron	10.00	6.18	20.3	13.8
Manganese	16.66	10.8	24.2	19.0
Nickel	0.77	0.16	1.15	0.46
Cobalt	0.22	0.066	0.71	0.28
Copper	0.30	0.17	1.81	0.55
Phosphorus	0.06	0.22	1.97	0.54
Aluminium	2.90	0.27	1.70	0.73
Titanium	0.06	0.27	1.25	0.81
Zirconium	—	0.0038	0.014	0.0064

Dietz (13) has discussed the occurrence of manganese concretions and nodules on the northeastern Pacific sea floor. He has presented analytical data for iron, manganese, cobalt and nickel in two nodules and three manganese crusts. One of these crusts (from the Gilbert Sea Mount) contained 3.1% CaO; 1.9% MgO; 8.4% SiO₂; 3.2% Al₂O₃; 0.50% P₂O₅; 0.13% V₂O₅; 0.90% TiO₂; 0.20% Mo; 0.55% S; 0.06% Cu; 11.0% insoluble.

Goldberg and Arrhenius (15) have published spectrographic data on the composition of a concretion which had formed around a steel fragment at a depth of 2000 m. This concretion was mainly composed of hydrous iron oxides together with 0.1% of manganese and appreciable amounts of metals characteristic of manganese nodules.

Numerous determinations of particular trace elements in manganese nodules have been carried out (Table II), particularly in connection with determinations of their rate of formation based on their content of radioactive elements.

TABLE II. OCCURRENCE OF TRACE ELEMENTS IN MANGANESE NODULES FROM THE PACIFIC OCEAN

Element	µg of Element per gm	Reference
Beryllium	Not detected*	21
Boron	500*	22
Cadmium	8-13	34
Gallium	4*	19
Lead	3450	39
Lead	27-2180 (mean 1740)	9
Niobium	24	42
Radium	1.2-25 × 10 ⁻⁶	40
Radium	up to 80 × 10 ⁻⁶	8
Scandium	4*	20
Thorium	1.3	29
Thorium	38-143	33
Thorium	24-124	16
Yttrium	10*	20

* CHALLENGER Expedition St. 286.

Until recently nothing has been known of the structure of iron and manganese compounds comprising the bulk of nodules, since they give only diffuse lines by the normal X-ray diffraction methods. In a valuable paper, Buser and Grütter (1) have shown that, in nodules containing only small amounts of iron, most of the manganese is in the form of δ-manganese dioxide together with manganese II manganite [3MnO₂·Mn(OH)₂·xH₂O]. The latter compound has a double layer structure; the main layers, which contain Mn⁴⁺ in six-fold co-ordination with O²⁻, are separated by 10 Å and contain between them a disordered layer of Mn²⁺ co-ordinated with O²⁻, OH⁻ and H₂O. In nodules containing iron, the Mn²⁺ in this intermediate layer is replaced by Fe³⁺ to form ferric manganite.

and some of the Mn^{4+} ions in the main layers may also be replaced by Fe^{3+} with the development of a charge. The majority of nodules contain more iron than can be accommodated as ferric manganite, and this is held as the highly adsorptive hydroxide, part of which may be converted into goethite (α - $FeOOH$). The Mn^{2+} in the intermediate layer may also be replaced by other polyvalent ions (such as those of cobalt, nickel, and the rare earths) with a high charge density. This probably explains the high concentrations of these elements in manganese nodules.

The mode of formation of manganese nodules has been the subject of much discussion, and the literature on their formation has been critically reviewed by Pettersson (41) and by Goldberg and Arrhenius (15). The latter workers postulate that positively charged colloidal hydrated iron oxide particles are deposited electrophoretically on oppositely charged nuclei, such as pumice, sharks' teeth, etc. The electropotentials of these nuclei are attributed to the flow of ocean water (a conductor) through the earth's magnetic field (*cf.* 14). Manganous ions brought to the sediment-water interface by various physical processes are oxidised to tetravalent manganese by oxygen under the catalytic action of the discharged iron oxide colloid. This tetravalent manganese oxide associates with the catalyst and, to a lesser extent, with divalent manganese hydroxide to form manganous and ferric manganites found by Buser and Grütter (7).

While this theory gives a possible explanation of the mechanism of formation of the commonest types of nodules in which the Mn:Fe ratio varies from *ca.* 1.5 to 4, it can not explain the existence of nodules with a ratio of 55 (0.8% Fe), such as that cited by Buser and Grütter (ALBATROSS St. 373).

The rate of accretion of manganese nodules has been estimated by Pettersson (40) and by von Buttlar and Houtermans (8) to be *ca.* 0.6–1.3 mm per thousand years. This figure must be regarded as minimal, since it is based on the assumption that all of the radium present in nodules was derived from seawater. The high thorium content of nodules, however, suggests that the ionium in sea water derived from uranium decay is also collected, and this in its turn will produce radium and so give an over-estimate of the rate of deposition (15).

In view of the small amount of reliable data on the occurrence of many of the less abundant elements in manganese nodules, specimens

collected by the CHALLENGER Expedition at three stations in the Pacific Ocean were analysed for 35 elements. In each case the nucleus of the nodule was removed before analysis. The origin of each sample is shown in Table III and descriptions of each are given below.

TABLE III. ORIGIN OF MANGANESE NODULES. ALL SAMPLES WERE TAKEN FROM A SEDIMENT OF RED CLAY

Challenger	Brit. Mus. Catalogue No.	Position		Depth (m)
		Lat.	Long.	
St. 248	M 313	37°41' N	177°04' W	5304
St. 252	M 316	37°52' N	160°17' W	5011
St. 276	—	13°28' S	149°30' W	4298

DESCRIPTIONS OF NODULES ANALYSED

CHALLENGER St. 248. At this station a large number of manganese nodules, together with many pumice stones and sharks' teeth, were collected by trawl. The specimen examined, *ca.* 7.5 cm in diameter, had a nucleus of much altered pumice surrounded by alternating light and dark bands. It was similar in external and internal structure to nodules shown by Murray and Renard (36: plate II, fig. 1; plate IX, fig. 4) and was typical of the majority of samples found at this station.

CHALLENGER St. 252. Hundreds of rounded or ellipsoidal manganese nodules were collected at this station, the largest ones being *ca.* 8–9 cm in diameter. The specimen examined, almost spherical with a diameter of *ca.* 7.5 cm, consisted of three zones: (i) a hard yellowish nucleus penetrated by dendrites of manganese; (ii) a dark layer of manganese oxides about 0.8 cm thick, (iii) an outer zone with concentric structure separated from the inner layer by a thin band of clay (?). This structure is analogous to that found by Murray and Renard (36) for other nodules from this station.

CHALLENGER St. 276. About 2001 of small manganese nodules, sharks' teeth, otoliths, pumice stones, and volcanic rock were taken at this station. The sample used for analysis consisted of five small and almost spherical nodules, having diameters ranging from 2–3 cm, closely resembling those shown by Murray and Renard (36: plate IV, figs. 7, 8). All had yellowish nuclei of much altered volcanic rock.

EXPERIMENTAL

Preparation of Samples. Each nodule was cut into sections, the nucleus and other heterogeneous materials were removed, and it was then powdered to pass through an 80 mesh sieve. In order to remove any interstitial salts derived from seawater (*e. g.*, the sample from Ch. St. 276 contained 0.50 % Cl⁻ and 0.47 % SO₃), the powdered sample was boiled in 200 times its own weight of water. The cold liquid was allowed to stand overnight. The residue, separated by filtration, was washed with hot water and then dried at 110°; in each case the sample contained less than 0.01 % Cl⁻ and 0.02 % acid-soluble SO₃.

Separation of the acid-insoluble fraction. The fine powder (10 g) was treated with 50 ml of concentrated hydrochloric acid and evaporated to dryness on the waterbath. The dry residue was treated with 15 ml of perchloric acid and heated on a hot plate until dense white fumes were evolved. When the sample had cooled, 200 ml of 0.5 N perchloric acid were added; this mixture was then heated on the waterbath with constant stirring, and the liquid was filtered through a weighed sintered glass crucible. The insoluble residue, after it had been thoroughly washed by decantation, was transferred to the filter, dried at 110°, and reweighed. The filtrate and washings were combined and diluted to 500 ml; this solution was used for the determination of most of the elements of the acid-soluble fraction.

Analysis of the insoluble fraction. Determination of the principal components of the insoluble fraction was carried out as described by Riley (45). Trace elements were determined spectrographically (1).

Analysis of the acid-soluble fraction. The methods used to determine elements in the acid-soluble fraction are summarised in Table IV. In general, the analyses were performed on the solution prepared as described above. In certain cases, however, when spectrographic determinations were made or when volatile elements (such as chromium, boron, or germanium) were determined, the powdered nodule was used. The amount of the element in the soluble part was estimated by subtraction of its weighted concentration in the insoluble part.

TABLE IV. SUMMARY OF METHODS OF ANALYSIS USED FOR ACID-SOLUBLE FRACTION OF MANGANESE NODULES

Element	Method	Reference
Aluminium	Spectrophotometric, as aluminium oxinate	45
Antimony	Spectrographic - detection limit 30 ppm	
Barium	Spectrographic	1
Beryllium	Spectrographic - detection limit 10 ppm	1
Bismuth	Spectrographic - detection limit 10 ppm	
Boron	Spectrophotometric, as boron-turmeric complex	Unpublish.*
Cadmium	Spectrophotometric, as dithizonate	34
Calcium	Gravimetric, as oxalate	51
Chromium	Spectrophotometric with diphenylcarbazide	48
Cobalt	Spectrophotometric, as thiocyanate	48
Copper	Spectrophotometric, as diquinoyl complex	47
Gallium	Spectrophotometric, as Rhodamine B chlorogallate	12
Germanium	Spectrophotometric, as phenylfluorone complex	6
Iron	Volumetric	30
Lanthanum	Spectrographic	1
Lead	Spectrophotometric, as dithizonate	48
Magnesium	Gravimetric, as magnesium pyrophosphate	51
Manganese	Volumetric (potentiometric titration)	32
Molybdenum	Spectrophotometric, as thiocyanate	48
Nickel	Spectrophotometric, as dimethylglyoxime complex	48
Phosphorus	Spectrophotometric, as molybdenum blue complex	35
Potassium	Flame photometric	45
Scandium	Spectrographic	1
Silver	Spectrographic	1
Sodium	Flame photometric	45
Strontium	Spectrographic	1
Thallium	Spectrographic	1
Tin	Spectrographic	1
Titanium	Spectrophotometric, with hydrogen peroxide	48
Tungsten	Spectrophotometric, as thiocyanate	48
Vanadium	Spectrophotometric, as oxinate	48
Yttrium	Spectrographic	1
Zinc	Spectrophotometric, as dithizonate	48
Zirconium	Spectrographic	1
Available oxygen	Volumetric	30
Water	Gravimetric	46
Carbon dioxide	Gravimetric	46

* Greenhalgh and Riley.

TABLE V. COMPOSITION OF ACID-INSOLUBLE MATTER FROM MANGANESE NODULES. DRIED AT 110°. PERCENT BY WEIGHT

	Challenger Stations		
	248	252	276
% Insol.	32.61	26.09	32.19
SiO ₂	73.90	72.10	72.70
Al ₂ O ₃	10.16	10.65	10.89
Fe ₂ O ₃	0.93	1.00	1.01
TiO ₂	0.55	0.60	0.54
MnO	0.02	0.02	0.02
P ₂ O ₅	0.33	0.25	0.19
CaO	0.94	0.91	0.89
MgO	0.64	0.80	0.63
Na ₂ O	2.08	2.32	2.16
K ₂ O	1.50	1.80	1.71
H ₂ O	8.90	10.00	9.10
	99.95	100.45	99.84

MINOR ELEMENTS (PPM)*

St. No.	Ba	Co	Cu	Ga	Ni	Pb	Sn	Sr	V	Zr
248	260	3	30	3	6	5	<10	80	25	600
276	200	3	20	4	5	5	<10	110	18	450

* Ag, Be, La, Mo, Sc and Tl not detected.

DISCUSSION

The nodules examined contained between 26 and 33 % of acid-insoluble material of similar composition (see Table V). Microscopic examination of thin sections of the nodules showed the presence of large amounts of clay minerals together with small amounts of quartz grains, apatite needles, hornblende and low temperature sodium or potassium feldspar. These minerals were concentrated in the light coloured concentric bands. The rather drastic method used for the removal of the acid-soluble part of the nodules has probably caused a loss of some sodium and potassium and of lesser amounts of other elements from the clay minerals, hence their amounts in the insoluble matter may be slightly underestimated.

With the exception of barium, titanium and zirconium, the insoluble fractions were almost free of those elements which are strongly concentrated in the soluble fraction. It is probable that

these three elements occur in the nodules in the form of barite, rutile and zircon, respectively, which were derived from red clay in which the nodules were found. These minerals are unreactive and insoluble and occur in most Pacific Ocean deposits in appreciable amounts.

Analyses of the acid-soluble parts of the nodules are shown in Table VI together with the abundance of relevant elements in seawater and the concentration factors (mean concentration [in ppm] of element in soluble fraction of nodule/concentration [ppm] of element in sea water).

The penultimate column of figures in Table VI was compiled after a critical survey of the data for the abundance of elements in sea water, collected by Richards (44). No values were available for the concentration of many trace elements in deep ocean waters. In such cases, values for surface or near surface waters were used; it must be realised that such samples may be quite different in trace metal content from those obtained in deep water. Hence there may be an error of about one order of magnitude in the concentration factors given.

The concentrations of manganese and iron found in the three nodules examined were similar to the averages given by Sverdrup (50) but were greater than any of those reported by Goldberg (14). Many of the minor elements, such as zinc, copper, nickel and lead, are much enriched in the soluble part of the nodules compared with the lithosphere and are present in economically recoverable amounts. The values for nickel and cobalt agree well with the linear relationships found by Goldberg between manganese and nickel and between cobalt and iron concentrations respectively.

The average Co/Ni ratio for the nodules (0.38) is close to the value of 0.40 found by Goldschmidt (18) for hydrolysate sediments. The Zn/Cd ratio (660) is similar to that found for igneous rocks (530); apparently little differentiation of the two elements occurs during weathering, transport to the sea, adsorption and deposition in the nodules.

Relative to the iron content, the titanium and zirconium concentrations are lower and higher respectively than those reported by Goldberg. The amounts of gallium, scandium and yttrium are about 3-4 times greater than those found by Goldschmidt and Peters for a nodule from CHALLENGER St. 286 (Table II). The concentrations of these elements and those of a number of others, such as

TABLE VI. COMPOSITION OF ACID-SOLUBLE FRACTION OF MANGANESE NODULES

CHALLENGER St. Soluble Percent	Weight % Oxides in Soluble Fraction			Weight % Element Ex- cluding H ₂ O and CaCO ₃			Mean	Conc. of Element in Sea Water ($\mu\text{g/l}$)	Concn. Factor	Reference	
	248	252	276†	248	252	276					
	67.39	73.91	67.81	—	—	—	—	—	—	—	
<i>Element</i>	<i>Oxide</i>										
Aluminium	Al ₂ O ₃	6.04	2.00	4.72	4.23	1.36	3.27	2.95	10	3 × 10 ⁶	49
Antimony	Sb ₂ O ₃	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	—	—	—	—
Barium	BaO	0.58	0.51	0.41	0.69	0.59	0.48	0.59	50	1 × 10 ⁵	17
Bismuth	Bi ₂ O ₃	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	—	0.2	—	38
Beryllium	BeO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	—	0.03	—	28
Boron	B ₂ O ₃	0.010	—	0.013	0.004	—	0.005	0.005	4500	11	50
Cadmium	CdO	0.0011	—	0.0007	0.0013	—	0.0008	0.0010	0.1	1.0 × 10 ⁵	34
Calcium	CaO	2.10	1.54	3.49	0.42	0.01	0.40	0.27	4 × 10 ⁵	6.7	50
Chromium	Cr ₂ O ₃	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	0.05	>10 ⁶	27
Cobalt	CoO	0.17	0.22	0.28	0.17	0.22	0.29	0.23	0.4	5.0 × 10 ⁶	27
Copper	CuO	0.80	0.44	0.45	0.85	0.45	0.47	0.59	2***	3 × 10 ⁶	4
Gallium	Ga ₂ O ₃	0.0029	0.0021	0.0025	0.0029	0.0021	0.0023	0.0024	0.03	8 × 10 ⁵	11
Germanium	GeO ₂	0.0007	—	0.0009	0.0007	—	0.0008	0.0007	0.06	1.2 × 10 ⁵	6
Iron	Fe ₂ O ₃	21.44	23.73	28.60	19.85	21.34	26.14	22.44	<1.0**	>2.2 × 10 ⁷	3
Lanthanum	La ₂ O ₃	0.02	0.01	0.03	0.03	0.02	0.04	0.03	0.3	10 ⁶	17
Lead	PbO	0.15	0.22	0.25	0.19	0.26	0.30	0.25	5	5 × 10 ⁵	38
Magnesium	MgO	0.90	0.10	0.01	0.71	0.08	0.01	0.27	1.3 × 10 ⁶	2.1	50
Manganese	MnO	31.62	34.73	28.79	32.41	34.57	29.14	32.04	ca. 1***	3.2 × 10 ⁵	26

Molybdenum	MoO ₃	0.060	0.075	0.060	0.050	0.060	0.052	0.054	12	4 × 10 ⁴	5
Nickel	NiO	0.53	0.69	0.53	0.56	0.69	0.55	0.60	2	3 × 10 ⁶	31
Phosphorus	P ₂ O ₅	0.30	0.27	0.34	0.17	0.15	0.20	0.17	variable	—	—
Potassium	K ₂ O	1.45	1.45	1.33	1.60	1.54	1.40	1.51	3.8 × 10 ⁵	40	50
Scandium	Sc ₂ O ₃	0.0015	0.0008	0.0015	0.0013	0.0006	0.0010	0.0010	0.04	3 × 10 ⁵	17
Silver	Ag ₂ O	0.0016	0.0015	0.0015	0.0020	0.0018	0.0020	0.0019	0.15	1.3 × 10 ⁶	38
Sodium	Na ₂ O	3.37	2.56	2.56	3.30	2.44	2.48	2.74	1.05 × 10 ⁷	2.6	50
Strontium	SrO	0.18	0.09	0.07	0.20	0.10	0.08	0.13	8 × 10 ³	1.6 × 10 ²	10
Thallium	Tl ₂ O	0.009	0.011	0.008	0.012	0.014	0.010	0.013	<0.01	>10 ⁷	38
Tin	SnO ₂	0.03	0.04	0.03	0.03	0.04	0.03	0.03	3	1.0 × 10 ⁵	38
Titanium	TiO ₂	0.56	1.11	0.71	0.45	0.85	0.56	0.56	1	6 × 10 ⁶	23, 24
Tungsten	WO ₃	0.006	—	0.012	0.007	—	0.010	0.009	0.1	0.9 × 10 ⁶	27
Vanadium	V ₂ O ₅	0.071	0.071	0.125	0.053	0.051	0.090	0.064	3	2 × 10 ⁵	27
Yttrium	Y ₂ O ₃	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.3	1.0 × 10 ⁵	17
Zinc	ZnO	0.70	0.51	0.67	0.74	0.53	0.70	0.66	5	1 × 10 ⁶	17
Zirconium	ZrO ₂	0.015	0.014	0.012	0.015	0.010	0.012	0.012	—	—	—
Available oxygen		6.10	7.40	6.10	—	—	—	—	—	—	—
Water	H ₂ O	22.43	20.75	18.47	—	—	—	—	—	—	—
Carbon dioxide	CO ₂	1.30	1.20	2.40	—	—	—	—	—	—	—
Oxide oxygen		—	—	—	33.25	34.63	33.28	—	—	—	—
Totals		100.08	99.76	100.48	100.00	100.00	100.00	—	—	—	—

† Sample 276 also contained 2.3 ppm HgO₂, 62 ppm ThO₃ and 110 ppm CoO₂ in whole nodule.

* Concentration factor = mean concentration of element in nodules ($\mu\text{g/g}$) / concentration of element in sea water ($\mu\text{g/ml}$).

** Very variable—figure given is for average total iron, in samples from depths of more than 2000 m.

*** Known to be very variable.

zirconium and vanadium, are similar to their abundances in the lithosphere.

Since the majority of the minor elements of the nodules are probably adsorbed directly from sea water (15), a consideration of the concentration factors should prove useful. These factors range from over 3×10^7 for manganese and iron down to values of less than 40 for elements which occur in major amounts in sea water. The latter elements are mainly those forming hydroxides with ionic bonds, which, according to Wickman (52), are not strongly adsorbed; their amounts in the soluble part are relatively small. It is almost certain that some of the sodium and potassium shown in the analyses (Table VI) has been dissolved from the insoluble fraction during the opening up of the nodules.

The majority of other elements have concentration factors lying between 10^5 and 10^6 . These include elements occurring in sea water in a cationic form as well as elements co-ordinated with chlorine or oxygen, such as copper or tungsten and vanadium (43) respectively, which occur as anions. Elements such as scandium, titanium and zirconium, which have ions that are readily hydrolysed, probably exist in sea water in the form of positively charged colloidal hydrated oxides (43: 235). Such colloidal particles are probably readily adsorbed by oppositely charged manganite or other particles.

Elements such as cobalt, nickel, copper, zinc and lead, which are strongly concentrated in the nodules and which have high concentration factors, probably occur in sea water in ionic form, either as cations or as anionic chloro-complexes. These elements, which have high charge densities, are probably removed from sea water by chemisorption on colloidal ferric hydroxide or on the intermediate layers of the manganites, as described by Buser and Grütter (7).

The presence of appreciable amounts of thallium in the nodules is of interest, since this element has not been detected in seawater. Unpublished work in these laboratories has shown that its concentration is less than $0.01 \mu\text{g/l}$. In the nodules, thallium is probably in the trivalent state on account of their high redox potential.

Antimony, bismuth and beryllium were sought spectrographically but were not detected in any of the nodules; their concentrations must be less than *ca.* 10 ppm. In addition, chromium was not detected either chemically or spectrographically and its concentration must be less than 5 ppm; the absence of chromium is rather surprising since it occurs in amounts varying from 0.003 to 0.01% in

pelagic red clay (Unpublished) and since Goldberg and Arrhenius (15) found 0.002% in a ferric oxide concretion. The redox potential of the nodules is sufficiently high to ensure that any chromium present is oxidised to the chromate ion.

The atomic ratios Mn/available oxygen lead to the formulae $\text{MnO}_{1.88}$, $\text{MnO}_{1.94}$ and $\text{MnO}_{1.94}$ for the oxide of manganese in the nodules from CHALLENGER Sts. 248, 252 and 276 respectively. These deficiencies of oxygen are in agreement with structures of the ferric and manganous manganites which constitute the nodules. On the other hand, Dittmar (36) found an O:Mn ratio slightly greater than 2; this is probably attributable to errors in the analytical method used for the determination of manganese.

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