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Sulfur and Carbon Contents of Manganese Nodules from the Central Pacific, GH80-1 Cruise

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Abstract: One hundred and eleven manganese nodules from the north and south Central Pacific were analyzed for total sulfur and carbon. These samples were collected along two tracks of 2000 km long for each, running from east of the Wake island to west of Tahiti, in a Hakurei-maru cruise, GH80–1.

Total sulfur content ranges from 120 to 1590 ppm, and averages 650 ppm. Manganese and total sulfur contents are inverserly correlated for the nodules with higher manganese contents, whereas they appear to have rather positive correlation for those with lower manganese contents. Sulfur in the nodules is positively correlated with water soluble sodium. This suggests that sodium sulfate is the most important form of sulfur in the nodules.

The content of total carbon varies from 200 to 4180 ppm and averages 730 ppm. There are no clear correlations between total carbon and total sulfur contents. Sulfur and carbon are not enriched in the nodules as compared with the earth crust and deep-sea sediments. These facts may be due to different solubility in oxide form of these elements.

Introduction

Many data have been reported on the contents of major and minor elements in manganese nodules. But, as to the contents of sulfur and carbon, there are few data, and the geochemical characteristics of both elements in the nodules have not been discussed.

In this study, 111 manganese nodules from the north and south Central Pacific were analyzed for total sulfur and total carbon. The samples had been collected along two tracks of 2000 km long for each, running from east of the Wake island to west of Tahiti in the cruise GH80–1, Geological Survey of Japan. In order to know chemical forms and/or occurrences of both the elements, water soluble sodium, non-carbonate carbon, carbonate carbon, calcium and barium in some selected samples were determined.

Index map and localities of the analyzed samples are shown in Fig. 1 and Table 1, respectively. More details of the survey area and the comprehensive studies of the cruise have been reported by MIZUNO and NAKAO (1982), and the chemistry of these nodules, especially by USUI and MOCHIZUKI (1982).

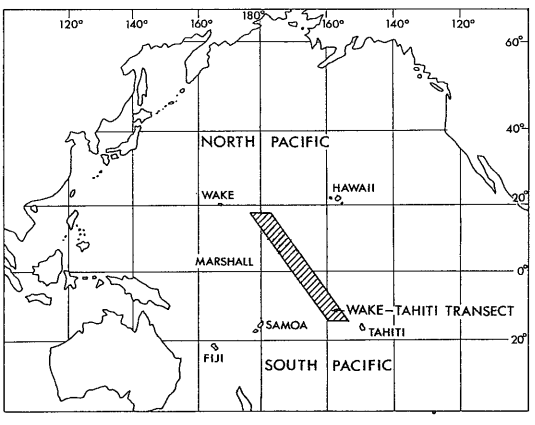

Fig. 1 Index map of the survey area.

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Table 1 Localities of the sampling stations.

Station No.	Latitude	Longitude	Depth (m)
Mid-Pacific Mountains			
1647	16°10.14′N	179°19.82′W	5292
1590	15°23.31′N	178°43.79′E	5287
1646	15°22.48′N	178°45.46′W	5537
1645	14°06.61′N	177°47.28′W	5068
1591	14°02.91′N	179°44.90′E	5550
1592	13°14.65′N	179°37.55′W	5596
Central Pacific Basin, Northern Part			
1593	11°54.16′N	178°36.28′W	5491
1643	11°49.41′N	176°05.47′W	5258
1642	11°06.38′N	175°30.07′W	5441
1594	11°06.91′N	178°00.01′W	5729
1641	9°46.81′N	174°31.04′W	5829
1595	9°46.68′N	176°59.02′W	6298
1640	8°57.86′N	173°53.91′W	5915
1596	8°57.56′N	176°23.96′W	6009
1639	7°40.26′N	172°56.77′W	5926
1597	7°38.13′N	175°14.54′W	5945
1638	6°48.65′N	172°15.46′W	5791
1599	5°29.19′N	173°47.67′W	4901
Central Pacific Basin, Central Part			
1601	3°17.83′N	172°10.51′W	5350
1635	3°16.42′N	169°40.10′W	5351
1635A	3°16.29′N	169°41.35′W	5349
1634	2°32.13′N	169°06.07′W	5087
1603	1°17.22′N	170°42.28′W	5479
1604	0°24.23′N	170°02.51′W	5457
Central Pacific Basin, Southern Part and North Tokelau Basin			
1631	0°58.61′S	166°20.89′W	5342
1606	1°45.07′S	168°26.20′W	5230
1629	2°53.00′S	164°57.31′W	5261
1607	3°02.12′S	167°29.91′W	5698
1628	3°30.50′S	164°09.94′W	4947
Manihiki Western Plateau and Manihiki Northeastern Basin			
1609	5°11.60′S	165°51.90′W	4397
1625	7°06.72′S	161°56.68′W	4650
1611	7°20.88′S	164°17.60′W	4155
1623	9°26.14′S	160°14.83′W	4561
Penrhyn Basin			
1622	10°16.35′S	159°35.57′W	5235
1621	11°35.38′S	158°34.91′W	5312
1616	12°20.07′S	160°30.89′W	5690
1620	12°26.44′S	157°57.20′W	5285
1619	13°34.03′S	157°06.01′W	5131
1617	13°47.40′S	159°28.35′W	5162
1618	14°29.61′S	158°52.98′W	5453
1618A	14°28.86′S	158°52.66′W	5530

Sample Preparation and Analytical Methods

For the purpose of removing adherent sea salt, all nodules were immersed in running water and then ion-free water. Air-dry nodules were ground to under 150 mesh. The ground samples were dried at 110°C for 3 hours, then removed into 40 ml of plastic bottles and kept in a desiccator. In most cases, the analyzed samples were prepared from the mixture of two or three nodules having different sizes for each group of samples collected with a box corer or a freefall grab.

Two instrumental methods were used to determine the concentrations of the elements under consideration: (i) Infrared absorption photometry after combustion for total sulfur, total carbon and non-carbonate carbon (TERASHIMA, 1979). (ii) Atomic absorption spectrometry for sodium, calcium and barium. The coefficient of variation of the infrared absorption photometry after combustion was 5–10%, and that of the atomic absorption spectrometry was 3–5%. Outlines of the analytical procedures are given below.

Analyses of total sulfur and total carbon: Weigh 0.1 g of the ground sample into a ceramic crucible and keep for two hours in a drying oven at about 140°C to remove the moisture. Cover the surface with iron powder (ca. 0.6 g) and add tungsten chips (ca. 1.3 g). Heat the crucible in a furnace for 35–60 seconds at ca. 1800°C. Then read out the contents of total sulfur and total carbon directly by the infrared absorption photometer.

Analysis of non-carbonate carbon. Weigh 0.2 g of the ground sample into a ceramic crucible. Add about 1.5 ml of concentrated hydrochloric acid and place on an hot plate at about 130°C in a fume hood. After evaporating to dryness, place for 20–30 minutes in a drying oven at about 150°C to remove residual hydrochloric acid. Cover the residue with ca. 0.6 g of iron powder and ca. 1.3 g of tungsten

chips, and proceed as described above for total sulfur and carbon.

Analysis of water soluble sodium: Weigh 0.2 g of the ground sample into a 50 ml test tube with a stopper. After adding water to the volume, shake the mixture for about 1 minute. Allow to stand for more than two days, and then determine sodium in the supernatant solution by an atomic absorption spectrophotometer using an air-acetylene flame.

Analyses of calcium and barium. Weigh 0.1 g of the ground sample into a Teflon beaker, and add 4 ml of concentrated hydrochloric acid and 2 ml of 30% hydrogen peroxide. After standing for 5 minutes at room temperature, add 5 ml of hydrofluoric acid, and evaporate to dryness at about 180 °C. Add 5 ml of diluted hydrochloric acid (1+1), and repeat the evaporation. Add 2.5 ml of diluted hydrochloric acid (1+1) and 5 ml of water, and heat gently to dissolve the salt. Transfer the solution into a 25 ml of volumetric flask, and add 2.5 ml of potassium chloride solution (30 mg/ml K) and 1 ml of strontium chloride solution (40 mg/ml Sr), then dilute to the volume. Determine calcium and barium in the solution by an atomic absorption spectrophotometer using an air-acetylene flame for calcium and a nitrous oxide-acetylene flame for barium.

Results and Discussion

The contents of total sulfur, total carbon and water soluble sodium in 111 nodule samples are listed in Table 2, in southeastward order of their geographical localities. The results for non-carbonate carbon, carbonate carbon, calcium oxide and barium in selected 37 nodules are listed in Table 3. The values of carbonate carbon are obtained by subtracting non-carbonate carbon from the total carbon.

General aspect

The content of total sulfur varies from 120 to 1590 ppm, averages 650 ppm in the survey area. For total carbon, the content ranges from 200 to 4180 ppm, and averages 730 ppm. The average contents of total sulfur and total carbon in the deep-sea sediments from the same survey areas are 3300 ppm and 5400 ppm, respectively (TERASHIMA, unpublished). The results indicate that both the elements are less enriched in the manganese nodules than in the sediments.

Sulfur appears to exist as the compounds of sulfate or sulfide in marine sediments. The sulfide sulfur is easily removed from the samples by ignition at high temperature. So, the selected fifteen nodules (Nos. 3, 4, 11, 30, 35, 48, 52, 57, 64, 73, 81, 85, 92, 93 and 94) were analyzed after igniting at 500 °C for 60 minutes. However, there was no clear difference in the results between the samples ignited at 500 °C and only drying at 140 °C for 2 hours. This suggests that the sulfur in the nodules is not sulfide sulfur but is present in the form of sulfate.

Non-carbonate carbon content ranges from 200 to 1400 ppm, 300–700 ppm in most cases. Also carbonate carbon has a range from 10 ppm to 3680 ppm, being commonly 100–1000 ppm (Table 3). Calcium carbonate ($CaCO_3$) is the most common mineral of carbonate carbon in deep-sea sediments. Therefore, there may be some calcium carbonate as an impurity in the nodules. However, Fig. 2 shows the existence of much excess of calcium oxide in the nodules. The excess calcium oxide may be in the form of phosphate.

Relationship between regional variations and nodule types

Regional variations of the average contents of total sulfur, total carbon, water soluble sodium and manganese are listed in Table 4. The contents of total sulfur and total carbon on the samples from southern part in the survey area, i.e. the Manihiki Western Plateau, Manihiki Northeastern Basin and Penrhyn Basin, are slightly higher than those of northern part, i.e.,

Table 2 Analytical results of total sulfur, total carbon and water soluble sodium for manganese nodules from the GH80–1 cruise.

No.	Station No.	Sample No.	Nodule type	Total sulfur (ppm)	Total carbon (ppm)	Water soluble sodium (%)	Manganese* (%)
1	1647	B 32	D_S	170	550	0.13	21.07
2		FG 251–1	Fs	620	640	0.20	20.93
3		FG 251–2	D_3/Ss	1120	700	0.47	19.98
4	1590	B 2	DPs/IDPs	1090	760	0.23	20.59
5		FG 192–1	IDPs/Ds	420	760	0.20	19.51
6		FG 192–2	S_S/D_3	450	1090	0.23	12.35
7	1646	B 31	D_3/DPs/Ls	350	420	0.26	20.42
8		FG 250–1	Ls/Ds	250	580	0.14	15.81
9		FG 250–2	DPs/Ls	680	650	0.21	20.77
10	1645	B 30	D_3/DPs	730	330	0.18	17.58
11		FG 249–1	DPs/IDPs	1140	720	0.42	20.47
12		FG 249–2	DPs/IDPs	1000	740	0.32	18.98
13	1591	FG 193–1	Sr	260	540	0.20	22.09
14		FG 193–2	Sr/SEr	390	1340	n.d.	18.61
15	1592	FG 194–1	DPs/IDPs (SEr)	500	390	0.21	23.46
16		FG 194–2	DPs/(Sr)	390	400	0.21	26.88
17	1593	FG 195–1	Sr/SEr (DPr)	570	440	0.23	23.96
18		FG 195–2	DPs/(Sr)	710	790	0.29	22.70
19	1643	FG 247–1	DPs/IDPs	850	740	0.24	18.10
20		FG 247–2	DPs/IDPs	920	670	0.32	20.61
21	1642	FG 246–1	DPs/IDPs	990	660	0.45	19.15
22		FG 246–2	DPs/IDPs	500	1290	0.32	19.13
23	1594	FG 196–1 In.	IDPs/DPs	700	440	0.23	20.11
24		FG 196–1 Ou.	IDPs	160	500	0.14	20.09
25		FG 196–2 In.	DPs/IDPs	620	340	0.24	22.16
26		FG 196–2 Ou.	DPs	170	590	0.15	19.88
27		FG 196–3	V	670	470	0.21	20.29
28		FG 196–4 In.	DPs/IDPs	240	740	0.17	20.20
29		FG 196–4 Ou.	DPs	600	510	0.24	20.59
30		FG 196–5 In.	DPs	770	1410	0.24	19.85
31		FG 196–5 Ou.	DPs	320	810	0.16	20.34
32	1641	B 29	Sr/SPr/Dr/Db	380	200	0.23	30.48
33		FG 245–1	Sr/SEr	650	520	0.35	24.00
34		FG 245–2	Sr/SEr	590	490	0.28	24.43
35	1595	FG 197–1	IDPs/DPs	830	520	0.23	22.95
36		FG 197–2	IDPs/DPs/(SEr)	1000	400	0.33	18.15
37		FG 197–3	IDPs	220	360	0.16	7.33
38	1640	FG 244–1 (Sr)	Sr/SEr	400	730	0.21	23.95
39		FG 244–1 (slab)	Sr	440	580	0.16	21.61
40		FG 244–2	Sr/SEr	410	610	0.23	24.68
41	1596	FG 198–1	IDPs	530	530	0.22	16.67
42		FG 198–2	IDPs	380	540	0.19	14.33
43		FG 198–3	IDPs	400	650	0.17	14.57
44		FG 198–4	IDPs	360	850	0.20	13.45
45	1639	FG 243–1	Dr/Sr	160	2180	n.d.	31.96
46		FG 243–2	Sr/Vr	170	900	n.d.	28.17
47	1597	FG 199–1	SPr/Sr	720	560	0.35	21.84
48		FG 199–2	SPr/Sr	740	560	0.31	22.35

(continued)

No.	Station No.	Sample No.	Nodule type	Total sulfur (ppm)	Total cardon (ppm)	Water soluble sodium (%)	Manganese* (%)
49	1638	FG 242–1	Sr/Dr	430	730	0.19	26.90
50		FG 242–2	Ir/Vr/SPr	120	840	0.13	28.36
51	1599	FG 201–2	Sr	530	730	0.20	14.47
52		FG 201–3	Sr	900	3160	0.18	8.76
53		FG 201–4	Sr/SPr	640	410	0.27	21.55
54	1601	B 6	Sr	430	520	0.18	26.74
55		FG 203–1	Sr	350	410	0.19	26.66
56		FG 203–2	Sr	400	410	0.22	28.33
57	1635	B 26	Sr/Dr	1310	480	0.34	29.38
58		FG 238–1	Sr/Dr	430	620	n.d.	26.59
59		FG 238–2	Sr/Dr	370	390	0.23	28.86
60	1635A	FG 239–1	IDPs/r/DPs/r	770	580	0.25	15.99
61		FG 239–2	IDPr/Dr	320	760	0.19	9.58
62		D 377	Ir/Vr/Sr	330	920	n.d.	7.14
63	1634	FG 237–1	IDPs/r/DPs/r	830	590	0.29	22.51
64		FG 237–2	IDPs/r/DPs/r	1040	590	0.41	23.32
65	1603	FG 205–1	Sr	550	790	n.d.	26.84
66		FG 205–2	SPr/Sr	540	520	0.20	25.95
67	1604	FG 206–2	Sr	480	1520	n.d.	19.65
68	1631	B 24	Sr	530	440	0.32	24.72
69		FG 234–1	SPs/r/Ss/r	650	390	0.26	23.78
70		FG 234–2	SPs/r/Ss/r	740	520	0.38	22.46
71	1606	B 9	DPs	1070	280	0.28	20.12
72		FG 208–2	Sr/SEr	200	1010	0.15	4.85
73	1629	B 23	Ir/IDPr/Sr/Ls+r	1060	730	0.31	18.04
74		FG 232–1	Sr/Ds/r/Ls+r	890	470	0.29	21.23
75		FG 232–2	Sr/SEr	550	490	0.23	27.00
76	1607	P 161	DPs/SPs	670	590	0.27	19.64
77		FG 209–1	IDPs	800	470	0.24	14.57
78		FG 209–2	IDPs	600	480	0.18	14.90
79	1628	FG 231–2	Ir	370	630	0.17	26.39
80	1609	FG 211–2	DPs/IDPs	930	1220	0.22	19.43
81	1625	B 21	DPs/Ds	700	470	0.27	10.29
82		FG 228–1	Ss/Is	420	2140	n.d.	7.62
83	1611	B 11	Vs	350	560	0.18	5.76
84		FG 213–1	Vs	210	740	0.18	6.85
85	1623	B 20 Sur.	Ss/SPs	1590	510	0.48	18.98
86		B 20 Bur.	Ss	730	430	0.29	14.67
87	1622	FG 225–1	Ss/Ds	530	990	0.14	18.08
88	1621	B 19	Ds	1500	410	0.36	18.57
89		FG 224–1	Ss/Ds	880	430	0.23	18.63
90		FG 224–2	DPs/Ls	950	560	0.33	18.91
91	1616	B 14	Ss/Ls/(SPs)	940	490	0.23	19.29
92		FG 218–2	Ss/DPs/Fs	1220	4180	0.20	13.66
93	1620	B 18	Ds	970	490	0.19	20.25
94		FG 223–1	Ss/SEs	1310	400	0.44	19.18
95		FG 223–2	Ss/SEs	990	730	0.35	19.33
96	1619	FG 222–1	DPs/Lr+s	980	620	0.30	18.74
97		FG 222–2	DPs/SPs/ISs	930	610	0.25	20.05

(continued)

No.	Station No.	Sample No.	Nodule type	Total sulfur (ppm)	Total carbon (ppm)	Water soluble sodium (%)	Manganese* (%)
98		B 17	SPs/IDPs	890	590	0.21	21.94
99	1617	B 15 In.	Ss	1330	400	0.27	18.67
100		B 15 Ou.	Ss	160	1210	0.14	15.56
101		FG 219–1 In.	Ss/DPs/IDPs	1540	960	0.57	17.58
102		FG 219–1 Ou.	Ss	120	1800	0.12	13.00
103		FG 219–2 In. #1	Ss	770	420	0.23	18.61
104		FG 219–2 In. #2	Ss	1360	450	0.44	17.46
105		FG 219–2 Ou.	Ss	120	1220	0.14	15.67
106	1618	B 16 Irr.	Ss	430	920	0.16	11.16
107		B 16 Sph.	Ss	820	580	0.23	20.59
108		FG 220–2	Ss/ISs	670	540	0.24	18.66
109	1618A	FG 221–1 Sph.	ISs/DPs/Ss	930	620	0.31	20.13
110		FG 221–1 Irr.	ISs	360	1100	0.16	9.57
111		FG 221–2	ISs/DPs	910	620	0.26	18.08

Nos. 1–16, Mid-Pacific Mountains; 17–53, Central Pacific Basin, Northern Part; 54–67, Central Pacific Basin, Central Part; 68–79, Central Pacific Basin, Southern Part and North Tokelau Basin; 80–86, Manihiki Western Plateau and Manihiki Northeastern Basin; 87–111, Penrhyn Basin.
In.: Inner; Ou.: Outer; Sph.: Sphere; Irr.: Irregular; Sur.: Surface; Bur.: Buried.
*Data taken from USUI and MOCHIZUKI (1982).

the Mid-Pacific Mountains, Central Pacific Basin and North Tokelau Basin. This may be related to nodule type and/or bathymetric or geographical environment of nodule occurrence. Table 5 shows the average contents of some elements on typical four types of nodules. Total sulfur, total carbon and water soluble sodium are relatively enriched in s-type nodules which are poorer in manganese than r-type nodules. The Ss-type nodules are most abundant in both total sulfur and total carbon; and these nodules frequently occur in the southern part of the survey area.

Correlation among some elements

Manganese and total sulfur are correlated inversely on the nodules with high manganese (more than about 18%) contents. Those with low manganese (less than 18%) contents, however, appear to have a rather positive correlation, as shown in Fig. 3. The result was nearly the same as the relationship between manganese and iron contents (MOCHIZUKI *et al.*, 1981). This may be related to chemical characteristics of manganese during the nodule formation. The relationship between iron and total sulfur contents are shown in Fig. 4. There exists postitive correlation in most of the s-type nodules, but this correlation is ambiguous in the r-type ones. There are clear differences in the total sulfur contents between inner zone and outer zone of some selected nodules. In most cases, total sulfur is more abundant in the inner zone than the outer zone, as shown in Fig. 4.

The content of total carbon varies in a wide range for the nodules with low manganese contents (less than about 20%), whereas it tends to be restricted to relatively narrow range on those with high manganese (more than 20%) contents, as shown in Fig. 5. There are no clear correlations between total carbon and total sulfur contents.

It is generally known that sulfide sulfur in the coastal marine sediments is produced by compensation of sulfate sulfur during the process of bacterial sulfate reduction. The bacterial sulfate reduction occurs only in the

Table 3 Contents of non-carbonate carbon, carbonate carbon, calcium oxide and barium in selected manganese nodules from the GH80–1 cruise.

No.	Non-carbonate carbon (ppm)	Carbonate carbon (ppm)	Calcium oxide (%)	Barium (%)
1	400	150	1.71	0.20
3	530	170	2.25	0.16
4	390	370	2.53	0.14
8	400	180	1.75	0.15
11	430	290	2.38	0.18
18	300	490	4.12	0.14
22	240	1050	2.35	0.17
30	300	1110	2.27	0.13
32	200	<10	2.31	0.18
33	430	90	1.82	0.12
34	380	110	1.83	0.12
35	300	220	1.86	0.17
37	300	60	1.67	0.05
39	500	80	2.08	0.12
44	660	190	1.35	0.10
48	420	140	1.85	0.09
52	1400	1760	7.28	0.05
56	380	30	2.35	0.15
61	410	350	2.26	0.13
64	330	260	2.28	0.22
72	770	240	0.98	0.04
76	580	10	2.24	0.14
79	370	260	2.24	0.20
80	960	260	2.52	0.13
81	470	<10	2.31	0.09
83	410	150	1.51	0.05
85	410	100	2.66	0.13
87	690	300	2.46	0.12
92	500	3680	9.24	0.13
93	380	110	2.28	0.13
94	320	80	2.63	0.16
96	440	180	2.39	0.15
100	880	330	2.26	0.14
102	1160	640	1.97	0.14
105	960	260	2.66	0.16
106	520	400	2.94	0.07
110	770	330	2.42	0.09
Average	521	390	2.54	0.13

Nos. same as Table 2.

absence of oxygen, and the sulfur and organic matter contents are positively correlated in most cases. There was no positive correlation between total sulfur and non-carbonate carbon in the manganese nodules. The results may

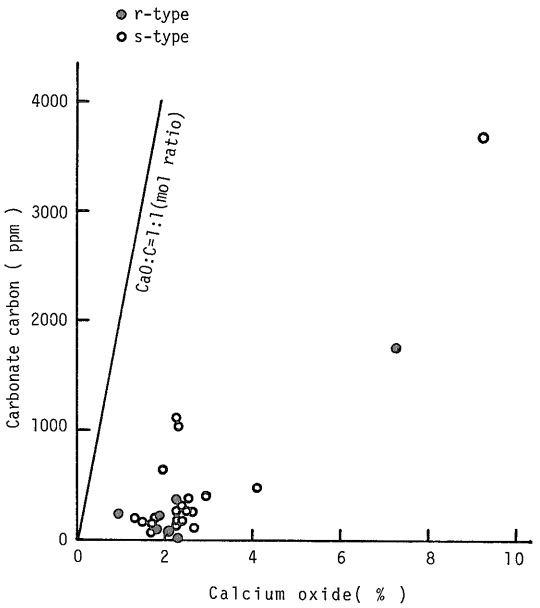

Fig. 2 Relation between calcium oxide and carbonate carbon.

indicate that the reaction of bacterial sulfate reduction is impossible in the strongly oxidizing conditions of the Central Pacific Basin, and there sulfide sulfur may not be produced.

Occurrence of sulfur

Barite ($BaSO_4$) is most common among sulfur-bearing minerals which widespread in deep-sea sediments. In this study, barium content of some selected nodules was determined in order to seek possibility of the barite contained in the studied samples. The content ranges from 0.04 to 0.22%, and averages 0.13%. The results clearly indicates that the barium contents are too low to consume sulfur in the nodules to form barite. Furthermore, there is no clear correlation between barium and sulfur contents; whereas the barium is positively correlated with manganese, as given in Fig. 6. The similar tendency for correlation of barium and manganese has been reported by PIPER *et al.* (1977).

The relationship between water soluble sodium and total sulfur contents are presented in Fig. 7. There is clear positive correlation

Table 4 Average contents based on their localities.

Area	(n)	Total sulfur (ppm)	Total carbon (ppm)	Water soluble sodium (%)	Manganese (%)
Mid-Pacific Mountains	16	598	663	0.24	19.97
Central Pacific Basin, Northern Part	37	535	742	0.23	20.76
Central Pacific Basin, Central Part	14	582	650	0.25	22.68
Central Pacific Basin, Southern Part, and North Tokelau Basin	12	678	542	0.26	19.81
Manihiki Western Plateau, and Manihiki Northeastern Basin	7	704	867	0.27	11.94
Penrhyn Basin	25	864	854	0.26	17.56
Average	111	650	730	0.25	19.53

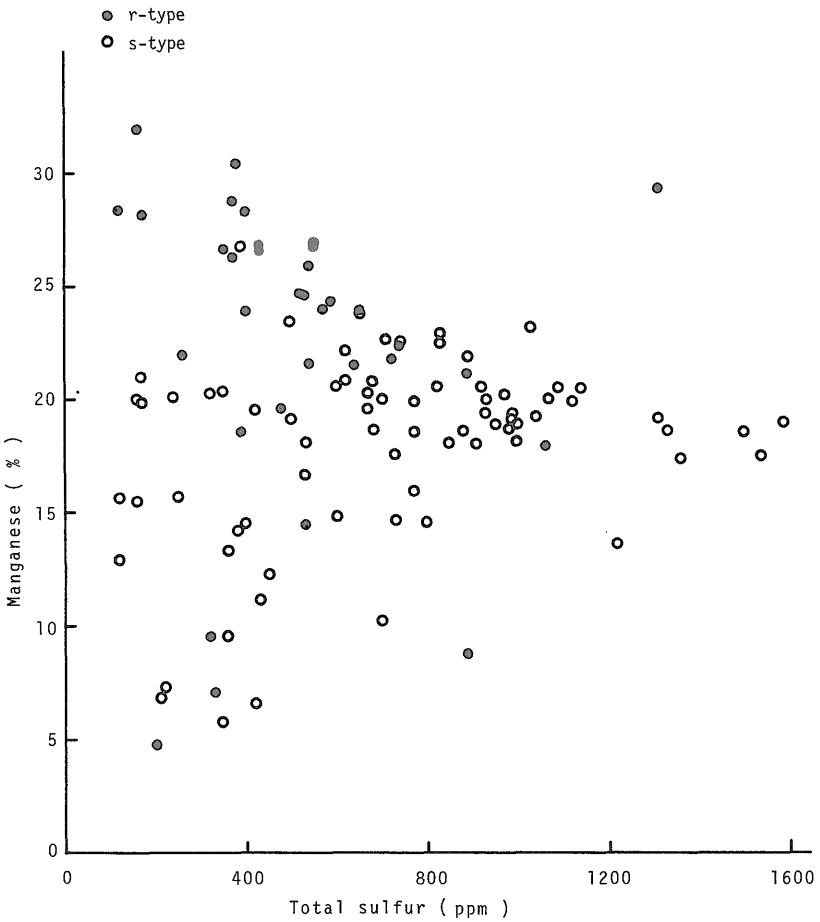

Fig. 3 Relation between total sulfur and manganese.

Table 5 Average contents based on nodule types.

Type	(n)	Total sulfur (ppm)	Total carbon (ppm)	Water soluble sodium (%)	Manganese (%)
Sr	26	510	728	0.23	23.25
Ss	13	845	1033	0.27	16.32
DPs	23	775	705	0.27	20.04
IDPs	10	554	556	0.21	15.65
r-type	26	510	728	0.23	23.25
s-type	46	746	765	0.25	18.03

throughout both s- and r-type nodules. Concentration ratios of sulfur to sodium are calculated for both sea water and sodium sulfate (Na_2SO_4), and the results are illustrated with broken lines in the figure. The ratios for the manganese nodules are plotted parallel to the sodium sulfate line and the plots are diagonal to the sea water line. These facts imply that the sulfur in the nodules may not be originated in the remaining sea water in the samples but occur as sodium sulfate.

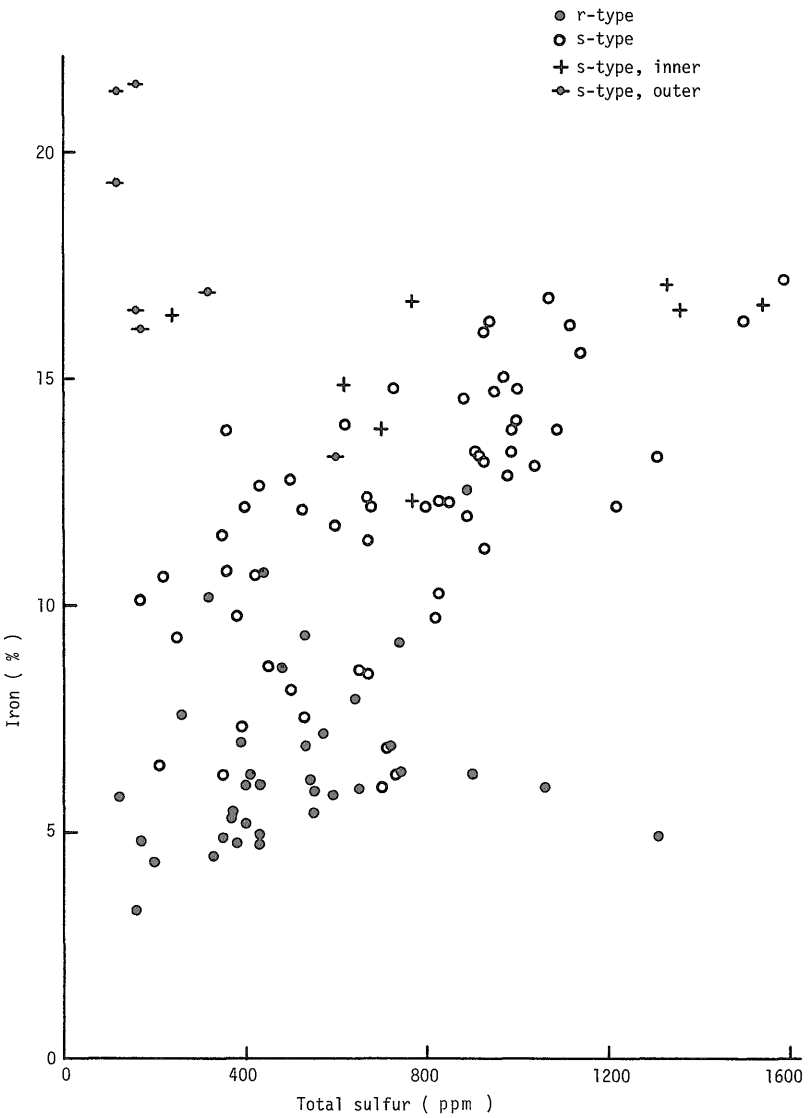

Fig. 4 Relation between total sulfur and iron.

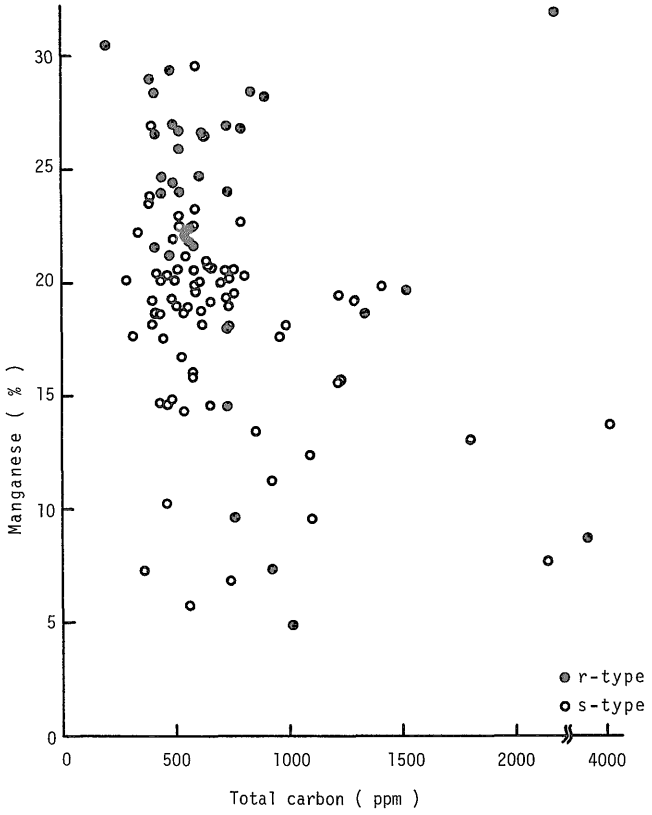

Fig. 5 Relation between total carbon and manganese.

Table 6 Geochemical distribution of some elements.

Element	Mn-nodule (wt.%) Mero (1962)* [A]	Earth crust (wt.%) Mason (1958) [B]	Deep-sea sediments (wt.%) Mita *et al.* (1982) [C]	Sea water ($\times 10^{-7}$ g/kg) Turekian (1969)	Concentration ratio [A/B]	Concentration ratio [A/C]
S	0.065**	0.052	0.33***	9040000	1.25	0.20
C	0.073**	0.032	0.54***	280000	2.28	0.14
Cr	0.001	0.020	n.g.	2	0.05	—
Co	0.35	0.0023	0.011	3.9	152	31.8
Cu	0.53	0.0045	0.040	9	118	13.3
Mn	24.2	0.10	0.78	4	242	31.0
Ni	0.99	0.008	0.021	66	124	47.1
Pb	0.09	0.0015	0.004	0.3	60	22.5
Zn	0.047	0.0065	0.015	50	7.2	3.1

*Average (n=54) of the Pacific Ocean nodules. **This study. ***Unpublished data by Terashima (1982). n.g.: Not given.

Comparison with geochemical distribution of some other elements

Geochemical distribution of sulfur (total), carbon (total), chromium, cobalt, copper, manganese, nickel, lead and zinc for manganese nodules (Mero, 1962), the earth crust (Mason, 1958), deep-sea sediments (Mita *et al.*, 1982) and sea water (Turekian, 1969) are listed in Table 6. Concentration ratios are calculated against earth crust (manganese nodule/earth crust) and deep-sea sediments (manganese

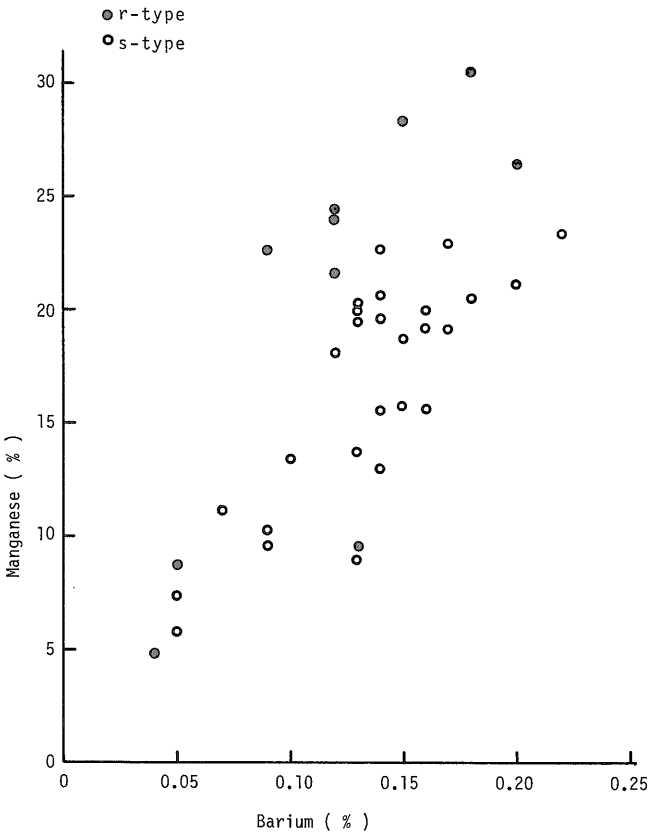

Fig. 6 Relation between barium and manganese.

Table 7 Solubility of some oxide (After HODGMAN *et al.*, 1962).

Oxide	Crystalline form	Solubility in grams per 100 ml of water
SO_2	gas or liquid	22.8 (0°C)
CO_2	gas or liquid	0.348 (0°C)
CrO_3	rhombic	166 (15°C)
CoO	cubic	insoluble
CuO	cubic	insoluble
MnO	cubic	insoluble
MnO_2	rhombic	insoluble
NiO	cubic	insoluble
PbO	tetragonal	0.0017 (20°C)
PbO	rhombic	0.0023 (22°C)
ZnO	hexagonal	0.00016 (29°C)

nodule/deep-sea sediments). Except for chromium, the concentration ratios of metals such as cobalt, copper, manganese, nickel, lead and zinc in the nodules against the earth crust and the deep-sea sediments range from 7.2 to 242, and 3.1 to 47.1, respectively. Chromium is significantly low in the nodule, so that the ratio is the least against the earth crust (0.05). Sulfur and carbon in the nodules are also low, and the concentration ratios are 1.25 and 2.28 against the earth crust, and 0.20 and 0.14 against deep-sea sediments.

It is generally known that manganese in the nodules occurs as mixture of manganese dioxide. Occurrence of other metals such as cobalt, copper, nickel, lead and zinc has not been proved exactly. But these metals may also be in the form of various oxides, because solubility of the oxides is lower than that of hydroxides in most cases. The values of solubility for some selected oxides, are listed in Table 7. The solubility of chromium trioxide is the highest (166), and that of sulfur dioxide (22.8) and

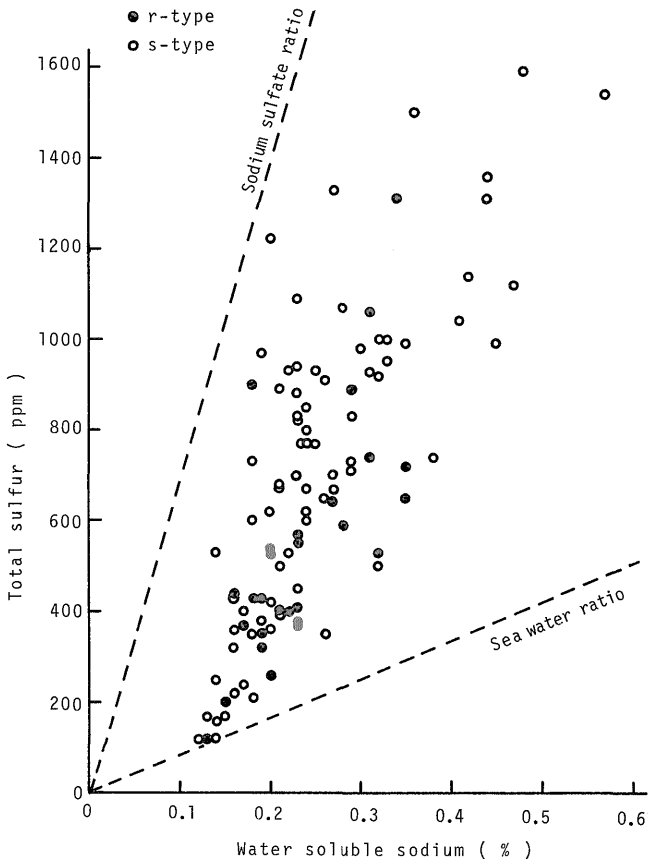

Fig. 7 Relation between water soluble sodium and total sulfur.

carbon dioxide (0.348) is also relatively high. However, other metal oxides are clearly low (probably less than 0.003). This difference of the solubility, together with availability in sea water, may be related to the lower concentration of chromium, sulfur and carbon in the manganese nodules.

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マンガン団塊中の硫黄と炭素

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要　旨

中央太平洋海盆から得られたマンガン団塊111試料について全硫黄と全炭素を定量し，さらにこれら元素の存在形態と地球化学的性質を知る目的で一部の試料について非炭酸塩炭素，ナトリウム(水溶性)，カルシウム，バリウムなどを定量した．用いた分析方法は全硫黄，全炭素，非炭酸塩炭素は燃焼-赤外吸収法であり，他の元素は原子吸光法である．

全硫黄の含有量は120-1590 ppmで，平均値は650 ppmであった．マンガン量との関係では，マンガン含有量が高い（約18%以上）試料では逆相関，低い試料では正の相関が認められた．加熱試験や水溶性ナトリウムとの関係などからマンガン団塊中の硫黄はすべて硫酸塩として存在し，特に硫酸ナトリウムとして含有される可能性が大きい．

全炭素の含有量は200-4180 ppmで，平均値は730 ppmであった．そして炭酸塩炭素（平均390 ppm, n=37）に比べて非炭酸塩炭素（平均521 ppm, n=37）がやや多く含有される．

硫黄，炭素，クロムは，マンガン，ニッケル，銅などに比べてマンガン団塊中に濃縮されない元素である．これら元素の酸化物の水に対する溶解度を比較した結果，硫黄，炭素，クロムの溶解度が他の金属元素に比べて著しく大きいことがわかった．マンガン団塊中の各種元素の存在量を規制する要因の一つとして，各元素の海水中の存在量と酸化物の溶解度の差が重要と思われる．

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