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Geochemistry of platinum and gold in ocean-floor ferromanganese crusts and nodules

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Abstract : Platinum and gold were analyzed for 76 hydrogenous ferromanganese crusts and nodules from the Ogasawara Plateau, the Antarctic Ocean and the central Pacific Ocean, using graphite furnace atomic absorption spectrometry after solvent extraction separation. The average platinum content is clearly higher in the Ogasawara Plateau (0.51 ppm) than in the Antarctic Ocean (0.16 ppm) and the central Pacific Ocean (0.14 ppm). The two growth stages are observed within the crusts from the Ogasawara Plateau, and the older one is richer in platinum. These analyses and earlier reference data suggest that platinum abundance greater than 0.5 ppm is encountered, in general, at water depths between 800 and 2000 m. Platinum enrichment may take place in the reduced marine environments of the oxygen depleted depths. Gold content ranges from less than 0.2 ppb to 2.73 ppb with the average of 0.45 ppb. The average gold content is clearly lower than that of the crustal abundance (5 ppb). The economical interest for gold in the marine hydrogenous ferromanganese oxides appears much smaller than the submarine hydrothermal sulfides.

Introduction

Platinum and gold abundances in ocean-floor ferromanganese oxides has important bearing on metal geochemistry in the marine environments and a great deal of economic interest as mineral resources. However, very few published data of platinum (AGIORGITIS and GUNDLACH, 1978 ; HALBACH *et al.*, 1984 ; HODGE *et al.*, 1985) and gold (HARRIS *et al.*, 1968 ; KEAYS and SCOTT, 1976 ; GLASBY *et al.*, 1978) are available for ferromanganese minerals from the world oceans. Even in a recent review by HAYNES *et al.* (1986) on Pacific manganese nodule chemistry covering seventy-four elements, only five data for platinum and ten for gold are cited, whereas there are 5000 data or more for manganese, iron, copper and nickel. The reason for the paucity of platinum and gold data may have been related to extremely low concentration and no reliable analytical method with convenient but sufficient sensitivity. Recently, a rapid and precise analytical method was established for platinum and gold (TERASHIMA, 1987, 1988) in ferromanganese oxides.

In this paper, we present analytical results of platinum and gold in 76 ferromanganese oxides from three different sea areas, and discuss their geochemical characteristics with the marine environments. Although a brief summary of the platinum abundance have been reported in a separate paper (TERASHIMA *et al.*, 1988), the major contents are included in

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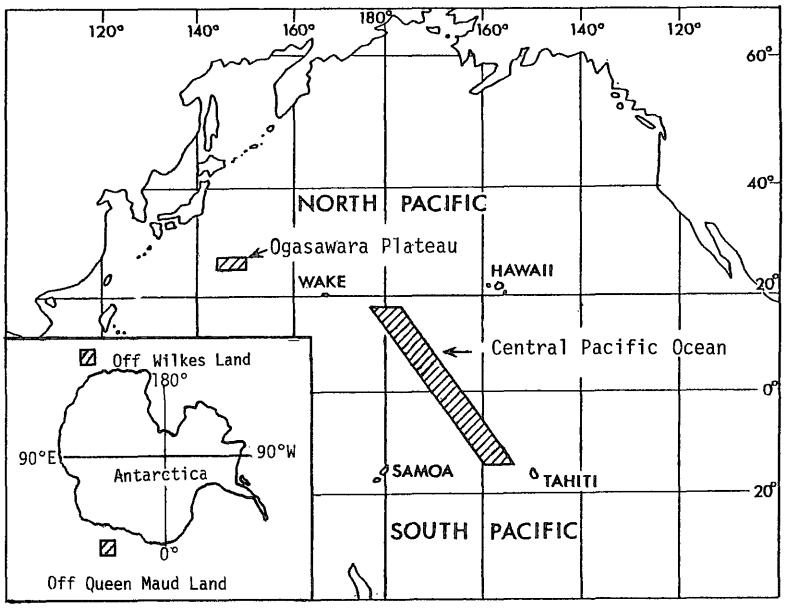

Fig. 1 Sampling locations of ferromanganese crusts and nodules.

this paper for more detailed discussion.

Analyzed samples

The ferromanganese oxides studied here are hydrogenous crusts and nodules from the Ogasawara Plateau, the Antarctic Ocean and the central Pacific Ocean (Fig. 1). The powdered 76 samples are aliquot part of those used for major and minor elements and mineral analyses (USUI and MOCHIZUKI, 1982 ; USUI *et al.*, 1987, 1988).

The Ogasawara Plateau is situated in the east of the Ogasawara-Mariana Arc, the West Pacific. Ferromanganese crusts were collected from the tops and the slopes of seamounts and the plateau at water depths between 790 and 2780 m. On some seamounts, ferromanganese nodules are often observed, but no significant compositional differences could be noticed between crusts and nodules at seamount (USUI *et al.*, 1987).

The eleven samples from the Antarctic Ocean were collected from three dredge hauls in the two regions; off Queen Maud Land and off Wilkes Land. The manganese nodules and crusts are composed of a hydrogenous mineral and distributed in the continental slope and basin floor off the East Antarctica. They are generally enriched in iron, but depleted in manganese and copper (USUI *et al.*, 1988).

Thirty-nine deep-sea manganese nodules were collected along two 4000 km-long transects from east of the Wake Island to the west of Tahiti in the central Pacific Ocean. Details of the major element chemistry of these nodules have been reported by USUI and MOCHIZUKI (1982).

Analytical method

Analytical methods of platinum and gold in ferromanganese oxides using graphite furnace atomic absorption spectrometry have been published (TERASHIMA, 1987, 1988). A brief summary of the procedure is as follows.

Platinum: The powdered sample of

Table 1 Analytical results of platinum and gold in two USGS manganese nodule reference samples.

	Platinum (ppm)		Gold (ppb)	
	Nod-A-1	Nod-P-1	Nod-A-1	Nod-P-1
TERASHIMA (1987 and 1988)	0.512±0.016	0.098±0.015	0.22±0.02	1.49±0.06
CHOWDHURY *et al.* (1983)	0.497±0.020	0.101±0.015	<4	<4
ARUSCAVAGE *et al.* (1984)	0.453±0.012	0.123±0.014	–	–

Nod-A-1 : Location, 31° 02′ N ; 78° 22′ W. Water depth, 788 m.
Nod-P-1 : Location, 14° 50′ N ; 124° 28′ W. Water depth, 4340 m.

about 0.1 g was decomposed with 8 ml of aqua regia and filtered. The filtrate was evaporated to dryness, then dissolved in 20 ml of 20 % tartaric acid by heating. After the addition of 0.5 ml of iron(III) chloride solution (20 mg Fe/ml) and 0.5 ml of 1 % 1,3-diphenylthiourea in acetone, the mixture was heated for 5 minutes in a boiling water bath. The solution was extracted with 1 ml of 1, 2-dichloroethane for 5 minutes. Platinum in the organic layer was determined by graphite furnace atomic absorption spectrometry.

Gold: The sample of about 0.5 g was decomposed with 15 ml of aqua regia, and evaporated until to about 2 ml. After the addition of 3 ml of 12 M hydrochloric acid, the solution was filtrated. Then 0.5 ml of iron(III) chloride solution(20 mg Fe/ml) and 4 ml of 2 % sodium fluoride solution were added, and diluted to about 20 ml with water. The solution was extracted with 1.5 ml of metylisobutylketone for 5 minutes. The aqueous layer was rejected, and the organic layer was washed for 2 min. with 10 ml of 0.6 M hydrochloric acid. Gold in the organic layer was also analyzed by graphite furnace atomic absorption spectrometry.

The detection limit of platinum for the methed is 0.05 ppm at the 2 standard deviation confidence level, and the relative standard deviations in the determination of more than 0.2 ppm platinum are less than 10 %. In determination of gold, 0.2 ppb is detected and the relative standard deviations for more than 0.4 ppb gold are less than 15 %. Analytical results of the USGS manganese nodule reference samples(FLANAGAN and GOTTFRIED, 1980) are also cited in Table 1 after TERASHIMA (1987, 1988). Although there is no available reference value for gold, the agreement between the present results and references data for platinum is fairly good.

Results and Discussion

Platinum abundance

Among all the studied samples, platinum abundance varies greatly from 0.05 to 2.39 ppm(Table 2), and averages 0.27± 0.34 ppm for the total 76 samples. Areal variation of platinum, gold, manganese, iron, copper, nickel, cobalt, zinc and lead in the studied three sea areas are summarized in Table 3, and comparison with some reported data for platinum and gold are given in Table 4. The ferromanganese oxides from the Ogasawara Plateau are most abundant in platinum(0.51 ppm), whereas the deep sea manganese nodules of the central Pacific Ocean are much depleted(0.14 ppm). The iron-rich manganese nodules and crusts from the Antarctic Ocean are depleted in platinum(0.16 ppm), as well as in manganese and copper.

The relationship between platinum contents in ferromanganese oxides and water depths of the sampling locations are plotted in Fig. 2, together with some reference

Table 2 Platinum and gold in ocean-floor ferromanganese crusts and nodules (110° C dried basis).

Analysis No.	Sample No.	Latitude (N)	Longitude (E)	Depth (m)	Pt (ppm)	Au (ppb)	Mn (%)	Fe (%)	Cu (%)	P (%)
Ogasawara Plateau										
1	D 845-6	26°25.8′	144°16.8′	2780	0.20	0.50	18.14	18.58	0.065	0.37
2	D 849-10 C	25°59.2′	143°29.9′	2390	0.20	n. d.	17.42	17.30	0.041	0.44
3	-10 N				1.10	0.28	21.39	11.39	0.100	2.36
4	D 851-14	26°10.0′	144°15.1′	905	0.77	0.42	11.50	7.42	0.097	7.27
5	-15				2.39	<0.2	32.08	7.30	0.264	0.91
6	-18				0.62	<0.2	24.65	16.38	0.060	0.52
7	D 853-12	26°09.8′	144°10.9′	790	0.23	<0.2	12.92	5.48	0.059	6.86
8	D 854-14	26°04.9′	144°21.1′	955	1.12	<0.2	22.95	10.21	0.081	1.43
9	D 856-4	25°56.1′	144°16.5′	1870	0.06	<0.2	14.37	19.42	0.038	0.42
10	D 858-1 A	25°18.9′	143°54.8′	1515	0.29	<0.2	21.70	18.90	0.041	0.56
11	-1 B				0.33	<0.2	24.90	14.50	0.057	0.39
12	-1 C				0.76	<0.2	24.19	7.88	0.097	3.98
13	D 859-5	25°13.4′	143°55.7′	1560	0.80	<0.2	20.62	10.91	0.130	2.99
14	-11				0.79	<0.2	22.94	13.84	0.081	0.33
15	D 862-1	25°16.3′	144°04.9′	2500	0.14	0.33	15.87	19.46	0.073	0.35
16	D 866-1 A	26°10.3′	145°04.1′	1250	0.13	<0.2	12.42	15.87	0.092	0.31
17	-1 B				0.19	0.30	19.09	16.40	0.074	0.48
18	D 867-1	26°15.0′	145°09.3′	1100	0.18	0.31	21.41	18.17	0.046	0.54
19	-3				0.43	<0.2	27.65	5.98	0.082	3.68
20	D 869-2	26°54.1′	145°30.4′	1250	0.12	<0.2	23.25	14.00	0.070	0.43
21	D 879-9	25°50.8′	147°47.9′	1410	0.58	0.36	15.10	17.61	0.086	0.52
22	D 881-1	25°45.1′	147°59.5′	1375	0.20	<0.2	22.48	17.08	0.048	0.51
23	D 883-1	25°47.8′	146°44.8′	1470	0.86	<0.2	24.77	4.77	0.151	4.13
24	D 884-1	25°47.6′	146°47.0′	1395	0.22	<0.2	21.52	15.16	0.078	0.58
25	D 886-1 A	27°06.0′	145°12.5′	1880	0.14	0.35	18.50	19.03	0.045	0.46
26	-1 B				0.47	<0.2	19.35	9.79	0.087	3.91
Antarctic Ocean										
27	D 603-30	65°38.4′ S	33°24.9′	2363	0.12	0.24	8.27	22.02	0.05	n. d.
28	-2				0.15	0.49	12.56	23.30	0.05	n. d.
29	-1				0.10	0.23	6.15	20.19	0.12	n. d.
30	D 602-38 A	65°35.7′ S	33°22.1′	3222	0.18	0.25	15.78	20.81	0.13	n. d.
31	-38 B				0.14	<0.2	15.97	21.94	0.13	n. d.
32	-35				0.16	0.75	14.27	20.17	0.12	n. d.
33	-21				0.20	0.30	14.37	20.95	0.14	n. d.
34	-25				0.23	0.65	12.77	20.50	0.16	n. d.
35	D 401-1	62°40.2′ S	139°43.5′	3890	0.18	n. d.	14.68	16.85	0.09	n. d.
36	-2				0.19	1.39	14.81	16.12	0.09	n. d.
37	-3				0.10	0.37	11.00	15.80	0.08	n. d.
Central Pacific Ocean										
38	F G 192-2	15°23.61′	178°44.01′	5306	0.12	0.87	13.42	9.45	0.29	n. d.
39	F G 194-1	13°14.65′	179°37.55′ W	5596	0.08	0.28	25.64	8.92	0.86	n. d.
40	F G 195-1	11°54.16′	178°36.28′ W	5491	0.10	0.41	26.16	7.88	0.93	n. d.
41	F G 196-1 in	11°06.91′	178°00.01′ W	5729	0.14	0.23	23.39	16.21	0.42	n. d.
42	-4 out	11°04.77′	177°58.28′ W	5870	0.14	0.23	23.88	15.47	0.50	n. d.
43	F G 197-1	9°46.68′	176°59.02′ W	6298	0.15	0.20	25.77	11.57	0.88	n. d.
44	-2	9°45.93′	176°58.33′ W	6293	0.14	0.45	21.05	16.33	0.37	n. d.
45	F G 198-2	8°56.76′	176°23.44′ W	6129	0.13	0.39	15.93	10.90	0.43	n. d.
46	-3	8°55.96′	176°22.94′ W	6120	0.14	0.45	16.42	13.73	0.43	n. d.

(Table 2 continued)

Analysis No.	Sample No.	Latitude (N)	Longitude (E)	Depth (m)	Pt (ppm)	Au (ppb)	Mn (%)	Fe (%)	Cu (%)	P (%)
47	F G 199-2	7°38.21′	175°14.43′ W	5936	0.09	0.48	24.65	6.96	1.28	n. d.
48	F G 203-1	3°17.45′	172°10.38′ W	5349	0.13	0.30	28.61	5.27	1.78	n. d.
49	-2	3°17.24′	172°10.34′ W	5335	0.10	0.50	30.37	5.59	1.90	n. d.
50	B-9	1°45.07′ S	168°26.20′ W	5230	0.08	2.35	23.66	19.77	0.31	n. d.
51	P 161	3°02.12′ S	167°29.91′ W	5698	0.25	0.75	22.19	14.03	0.50	n. d.
52	F G 209-1	3°02.21′ S	167°29.09′ W	5690	0.08	0.42	16.55	13.81	0.35	n. d.
53	-2	3°02.13′ S	167°29.16′ W	5692	0.11	0.32	16.84	13.37	0.42	n. d.
54	B 11	7°20.88′ S	164°17.60′ W	4155	0.07	0.44	6.29	6.90	0.20	n. d.
55	B 15 out	13°47.40′ S	159°28.35′ W	5162	0.17	0.81	18.05	24.97	0.17	n. d.
56	F G 219-2 out	13°47.15′ S	159°28.26′ W	5147	0.13	0.52	18.52	25.22	0.17	n. d.
57	F G 220-2	14°29.69′ S	158°53.13′ W	5438	0.09	0.43	20.28	9.25	0.75	n. d.
58	F G 221-1 irr.	14°29.49′ S	158°52.59′ W	5484	0.15	0.44	10.50	15.22	0.27	n. d.
59	-2	14°29.37′ S	158°52.53′ W	5484	0.17	0.29	20.39	15.14	0.39	n. d.
60	F G 224-1	11°35.57′ S	158°34.72′ W	5317	0.16	<0.2	21.44	16.78	0.30	n. d.
61	B 20 burr	9°26.14′ S	160°14.83′ W	4561	0.13	0.59	15.99	6.85	0.56	n. d.
62	B 21	7°06.72′ S	161°56.68′ W	4650	0.14	0.45	11.08	6.45	0.43	n. d.
63	F G 234-1	0°59.02′ S	166°20.41′ W	5390	0.15	0.44	26.02	9.44	1.16	n. d.
64	F G 239-2	3°16.30′	169°41.29′ W	5358	0.05	0.80	10.55	11.25	0.41	n. d.
65	F G 244-1 (Sr)	8°58.05′	173°53.34′ W	5901	0.10	0.58	25.87	6.57	1.10	n. d.
66	F G 245-2	9°46.92′	174°30.77′ W	5839	0.10	0.27	26.63	6.39	1.30	n. d.
67	F G 246-1	11°06.26′	175°29.50′ W	5430	0.16	1.01	22.41	15.68	0.39	n. d.
68	F G 246-2	11°06.19′	175°29.45′ W	5429	0.12	0.44	22.06	14.72	0.44	n. d.
69	F G 247-1	11°49.40′	176°04.87′ W	5253	0.22	<0.2	20.78	14.17	0.36	n. d.
70	-2	11°49.36′	176°04.84′ W	5256	0.17	0.35	23.97	15.43	0.44	n. d.
71	B 30	14°06.61′	177°47.28′ W	5068	0.16	0.48	20.01	16.84	0.44	n. d.
72	B 31	15°22.48′	178°45.46′ W	5537	0.14	2.73	22.03	12.48	0.65	n. d.
73	F G 250-1	15°22.79′	178°45.21′ W	5512	0.14	0.39	17.22	10.13	0.40	n. d.
74	-2	15°22.74′	178°45.17′ W	5526	0.22	0.33	23.72	13.94	0.50	n. d.
75	B 32	16°10.14′	179°19.82′ W	5292	0.13	0.65	22.99	11.05	0.69	n. d.
76	F G 251-1	16°10.17′	179°19.87′ W	5292	0.23	2.31	24.13	16.17	0.38	n. d.

Major elements data are taken from USUI *et al.* (1987, 1988), and USUI and MOCHIZUKI (1982 ; calculated from the air dried basis). n. d., not determined.

Table 3 Areal variation of average metal contents of ferromanganese oxides.

Sea area	(n)	Pt (ppm)	Au* (ppb)	Mn (%)	Fe (%)	Cu (%)	Ni (%)	Co (%)	Zn (%)	Pb (%)
Ogasawara Plateau	(26)	0.51	0.18	20.43	13.57	0.08	0.48	0.56	0.07	0.18
Antarctic Ocean	(11)	0.16	0.48	12.79	19.88	0.11	0.15	0.27	0.06	0.09
Central Pacific Ocean	(39)	0.14	0.61	20.65	12.57	0.60	0.75	0.31	0.08	0.09
All the samples	(76)	0.27	0.45	19.44	13.97	0.35	0.57	0.39	0.07	0.12

* Gold value less than 0.2 ppb is assumed as 0.1 ppb Au for calculation of average.
(n) : Number of samples.

Table 4 Comparison for platinum and gold contents in ferromanganese oxides of this study and reference data.

Sea area	(n)	Pt (ppm)	Au (ppb)	Reference	
Ogasawara Plateau	(26)	0.51±0.50	0.18±0.13	This study	
Antarctic Ocean	(11)	0.16±0.04	0.48±0.38	This study	
Central Pacific Ocean	(39)	0.14±0.05	0.61±0.58	This study	
Central Pacific seamount areas	(11)	0.42±0.27	n. g.	HALBACH *et al.*	(1984)
Pacific Ocean	(10)	0.26±0.30	n. g.	HODGE *et al.*	(1985)
Atlantic, Pacific and others	(19)	n. g.	2.90±2.00	HARRISS *et al.*	(1968)
Mid-Atlantic Ridge	(3)	n. g.	0.28±0.14	KEAYS and SCOTT	(1976)
Pacific Ocean and others	(5)	n. g.	0.32±0.30	GLASBY *et al.*	(1978)

n. g., not given

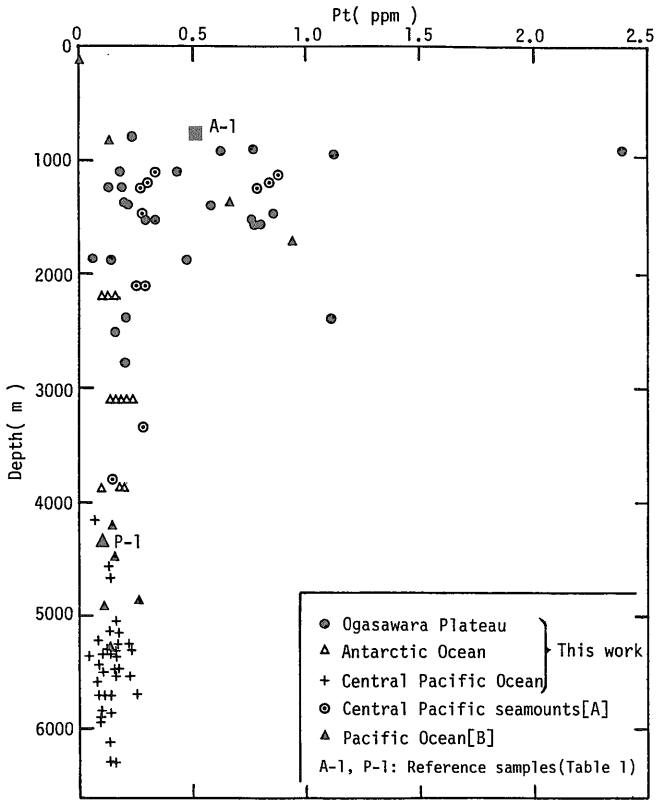

Fig. 2 Relationship between platinum contents in ferromanganese oxides and water depths of the sampling locations (modified after TERASHIMA *et al.*, 1988). The data [A] for Figures 2 through 6 are from HALBACH *et al.* (1984), and [B] from HODGE *et al.* (1985).

data for ferromanganese crusts from the Central Pacific seamounts (HALBACK *et al.*, 1984) and for ferromanganese minerals collected sporadically from the Pacific Ocean (HODGE *et al.*, 1985). The results show that the water depth dependency of platinum abundance is consistent to those in the present results and references data; the highest platinum abundance greater than 0.5 ppm is encountered

Table 5 Variation of platinum contents of two subsamples from three different ferromanganese crusts from the Around the Ogasawara Plateau.

Sample location	Sample No.	Pt (ppm)	Sample No.	Pt (ppm)	Sample No.	Pt (ppm)
Upper (younger) layer	D 858-1 A	0.29	D 866-1 A	0.13	D 886-1 A	0.14
Lower (older) layer	D 858-1 C	0.76	D 866-1 B	0.19	D 886-1 B	0.47

Data taken from Table 2.

at water depths generally between 800 and 2000 m.

In some ferromanganese crusts and nodules of the Ogasawara Plateau, the two growth stages are observed (USUI *et al.*, 1987). The deposition of the older crust layer sequence is associated with the formation of phosphorite composed of fine-grained apatite. The younger crust layer started to grow after the phosphorite episode, and it is richer in cobalt and iron than the older one in most cases. In order to examine the distribution of platinum within a single crust sample, analyses were made on two or three subsamples from the upper (younger) to lower (older) crust layers of three different crusts from the Ogasawara Plateau. The older crust layer is more enriched in platinum than the younger one as shown in Table 5.

Similar tendency of platinum distribution has been described in the older and younger crust layers from the Central Pacific seamounts (HALBACH *et al.*, 1984). According to the results of HALBACH and PUTEANUS (1984) and HALBACH (1986), the growth period of the older crust layer continued from about 16 to 9 Ma ago, and the younger crust formation started to grow around 8 Ma ago. Although there are no age data for ferromanganese crusts of the Ogasawara Plateau, the occurrence and chemical and mineral compositions are almost similar to those of the Central Pacific seamounts crusts. USUI *et al.* (1987) considered that the ferromanganese oxides of both Ogasawara Plateau and Central Pacific seamounts may be correlated with each other.

Gold abundance

Gold content ranges from less than 0.2 ppb to 2.73 ppb, and averages 0.45 ± 0.49 ppb. The average gold content in the ferromanganese oxides from the Ogasawara Plateau (0.18 ppb, gold value of less than 0.2 ppb is tentatively assumed as 0.1 ppb for calculation of average) is significantly lower than that of the manganese nodules from the Antarctic Ocean (0.48 ppb), and the central Pacific Ocean (0.61 ppb), as shown in Table 4.

In order to compare the gold contents in ocean-floor sediments with those of ferromanganese oxides, nine various types of sediments from the central Pacific Ocean are analyzed (Table 6). The value of gold varies from 0.55 to 4.22 ppb with the average of 1.85 ppb. The results mean that the ferromanganese nodules from the central Pacific Ocean are more depleted in gold than the sediments.

Among all the references data for gold in ocean-floor ferromanganese oxides, the data for manganese crusts from the Mid-Atlantic Ridge (0.11, 0.36 and 0.36 ppb; KEAYS and SCOTT, 1976), and for manganese nodules from the Southwestern Pacific Basin and other regions (0.13, 0.16, 0.28 and 0.84 ppb; GLASBY *et al.*, 1978) are more or less similar to those of the present study as shown in Table 4 and Fig. 3. However, the average value of gold by HARRISS *et al.* (1968) for manganese nodules from the world oceans (2.90 ± 2.00

Table 6 Gold contents in ocean floor sediments from the central Pacific Ocean (110° C dried basis).

Sample No.	Sediment type	Latitude (N)	Longitude (W)	Depth (m)	Au (ppb)
B -2	Zeolite-rich clay	15°23.31′	178°43.79′ E	5287	1.21
P 161	Siliceous mud	3°02.12′ S	167°29.91′	5698	1.00
B 16	Pelagic clay	14°29.61′ S	158°52.98′	5453	1.35
B 21	Clayey nanno ooze	7°06.72′ S	161°56.68′	4650	2.26
B 24	Calcareous siliceous ooze	0°58.61′ S	166°20.89′	5342	4.22
B 29	Siliceous fossil-rich clay	9°46.81′	174°31.04′	5829	2.49
P 178	ditto	11°06.38′	175°30.07′	5441	0.55
B 31	Zeolite-rich clay	15°22.48′	178°45.46′	5537	1.54
B 32	Zeolitic mud	16°10.14′	179°19.82′	5292	2.06

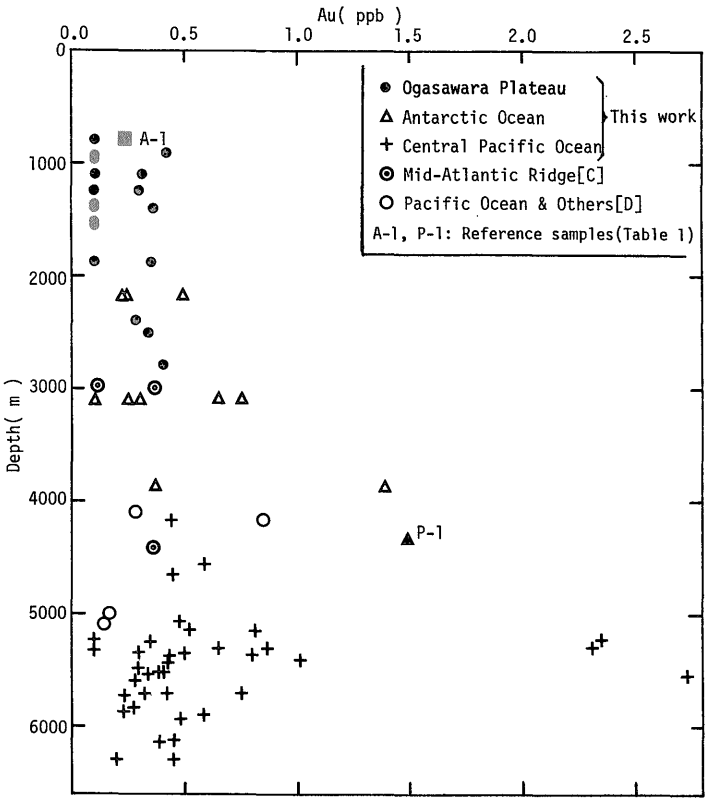

Fig. 3 Relationship between gold contents in ferromanganese oxides and water depths of the sampling locations. The data [C] and [D] are from KEAYS *et al.* (1976) and GLASBY *et al.* (1978), respectively.

ppb, n=19) is significantly higher than those of the present study (Table 4). As the crustal abundance of gold estimated as 5 ppb (MASON, 1958), the economical interest for gold in the marine ferromanganese oxides may be much smaller than the submarine hydrothermal sulfides.

Platinum enrichment

NOHARA (1987) pointed out that the

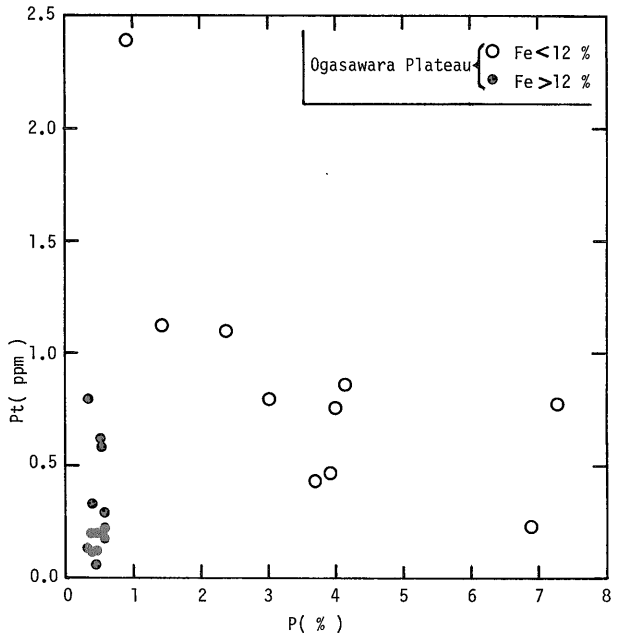

Fig. 4 Relationship between platinum and phosphorus.

adsorption of metal ions by phosphorite may be an important bearing in the formation of seamount ferromanganese crusts. In order to know the relationship between platinum and phosphorus contents, phosphorus was analyzed in the ferromanganese oxides from the Ogasawara Plateau (Table 2). As shown in Fig. 4, the samples containing 1 to 3 % phosphorus seem much dominant in platinum. The contents of phosphorus tend to increase with decreasing iron contents, and high phosphorus contents greater than 0.9 % are encountered at the samples containing less than 12 % iron (Fig. 4).

As for the process of platinum enrichment in the ferromanganese crusts from the Central Pacific seamounts, HALBACH (1986) considered that the following overall redox reaction appears under the conditions of the oxygen minimum zone:

$$Mn^{2+} + PtCl_4^{2-} + 2\,H_2O \rightarrow Pt^0 + MnO_2 + 4\,Cl^- + 4\,H^+$$

According to the reaction, a positive correlation is expected between platinum and manganese in the ferromanganese oxides. The correlation coefficients among platinum and other metals in the studied three sea areas are given in Table 7. Although a medium positive correlation is observed among platinum and manganese in both samples of the Ogasawara Plateau ($r=0.55$) and Antarctic Ocean ($r=0.64$), there is no clear positive correlation in the central Pacific nodules (Fig. 5, $r=0.17$). Platinum and iron are correlated negatively in the Ogasawara Plateau ($r=-0.57$) and the Central Pacific seamounts (HALBACH *et al.*, 1984), but there are no negative correlation in the Antarctic Ocean and the central Pacific Ocean (Fig. 6, Table 7). These differeces may reflect the different process of ferromanganese oxides formation at the individual sea regions.

The data on oxygen concentrations in sea water of the northwestern Pacific Ocean (KLINKHAMMER and BENDER, 1980) imply that the oxygen minimum zone may appear in the Ogasawara Plateau region. In the oxygen depleted depths, the reduc-

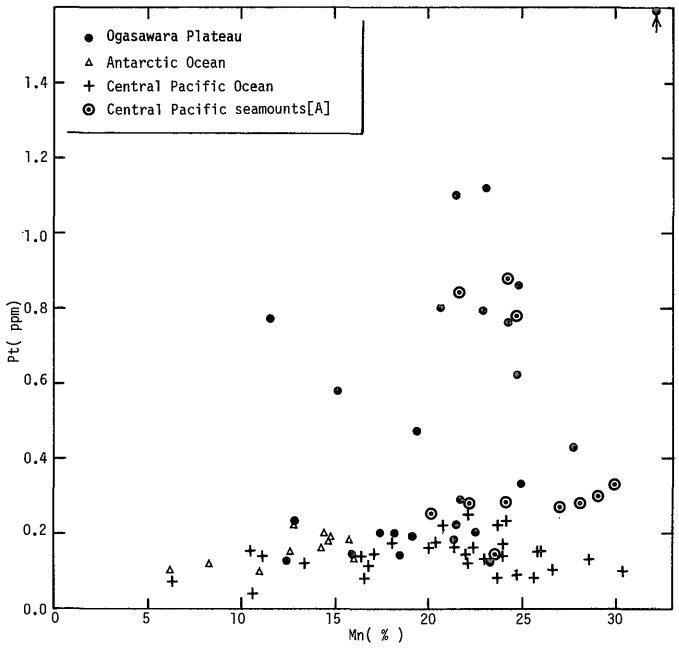

Fig. 5 Relationship between platinum and manganese.

ing reactions through which Mn (IV) is reduced to Mn (II), Fe (III) to Fe (II), and Pt (II) to Pt (0), may commonly occur. The Pt (0) are easily precipitated, whereas the Mn (II) and Fe (II) are rather stable in sea water. This suggests smaller growth rate and great enrichment of platinum in the ferromanganese oxides generated in the oxygen depleted marine environments. The strong positive correlation of platinum with copper (Fig 7, r= 0.87) implies that the both elements are enriched during similar geochemical behavior in the Ogasawara Plateau. Compared with ferromanganese crusts of the Ogasawara Plateau, deep-sea manganese nodules from the central Pacific Ocean are clearly rich in copper (Fig. 7). This may be related that copper in the deep-sea manganese nodules are presumably derived both hydrogenetically from sea water and diagenetically from ocean-floor sediments, whereas the metal in the ferromanganese crusts from the Ogasawara plateau consists mainly from sea water origin.

On the other hand, the platinum hexachlorocomplex $[P_t\ (IV)\ Cl_6]^{2-}$ would be a very stable species in oxygenated sea water (HALBACH, 1986). Thus the deep sea manganese nodules from the central Pacific Ocean are less enriched in platinum reflecting the oxidizing environments, and there are no clear correlations between platinum and other metals (Table 7). Although we have no available data for oxygen concentrations in sea water of the Antarctic Ocean, we may speculate that there will be relatively much oxygen dissolved in bottom water because of lower activity of marine organisms and low temperature of sea water promoted by the Antarctic Bottom Currents. Consequently low platinum abundance is possibly related to the oxidizing environments.

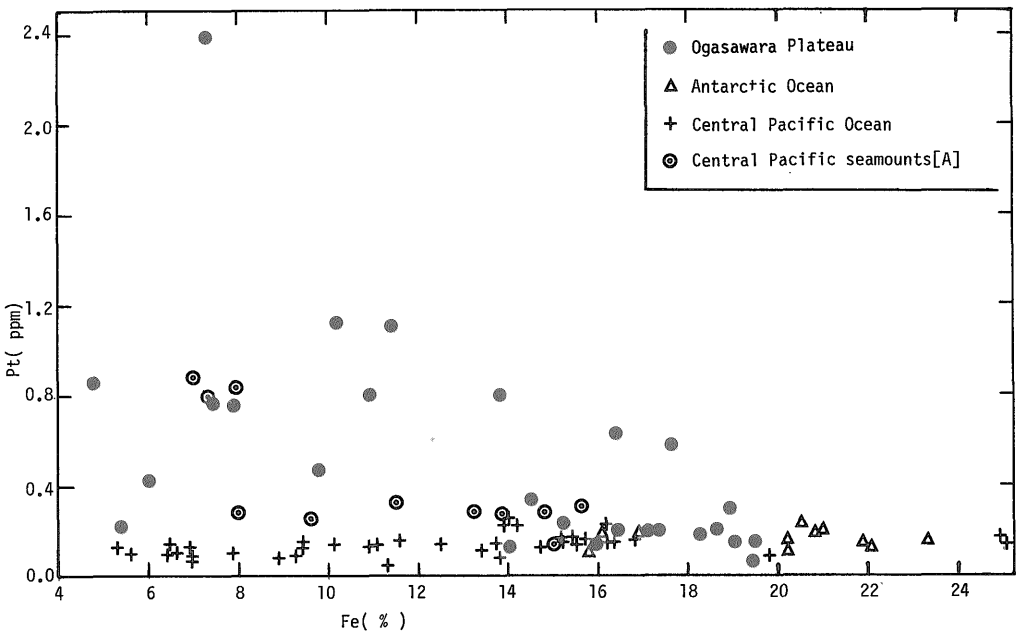

Fig. 6 Relationship between platinum and iron.

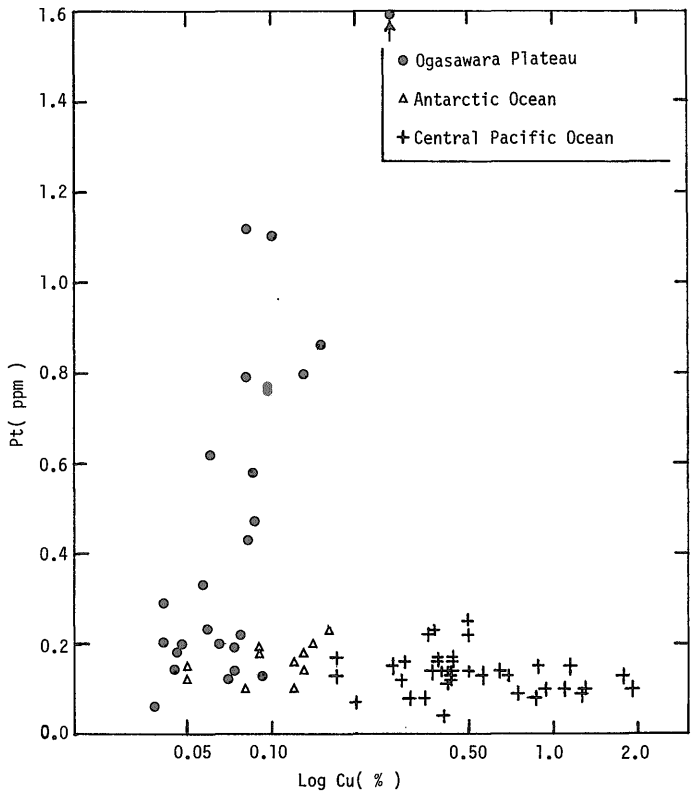

Fig. 7 Relationship between platinum and copper.

Table 7 Inter-element relationships in ferromanganese oxides (after TERASHIMA *et al.*, 1988)

(a) Ogasawara Plateau (n=26)

	Pt	Au	Mn	Fe	Cu	Co	Ni	Zn
Au	−0.17							
Mn	0.55	−0.45						
Fe	−0.57	0.35	−0.30					
Cu	0.87	−0.16	0.46	−0.59				
Co	0.39	−0.05	0.49	0.03	0.14			
Ni	0.64	−0.46	0.72	−0.74	0.70	0.12		
Zn	0.53	−0.30	0.27	−0.76	0.63	−0.16	0.76	
Pb	0.45	0.13	0.53	0.16	0.20	0.71	0.07	−0.23

(b) Antarctic Ocean (n=11)

	Pt	Au	Mn	Fe	Cu	Co	Ni	Zn
Au	0.45							
Mn	0.64	0.27						
Fe	0.00	−0.55	−0.09					
Cu	0.52	−0.08	0.33	0.06				
Co	0.65	0.82	0.56	−0.46	−0.09			
Ni	0.74	0.43	0.85	−0.34	0.59	0.57		
Zn	−0.01	−0.44	−0.01	0.86	0.02	−0.49	−0.21	
Pb	0.46	0.05	0.21	0.52	−0.22	0.40	−0.05	0.38

(c) Central Pacific Ocean (n=39)

	Pt	Au	Mn	Fe	Cu	Co	Ni	Zn
Au	0.06							
Mn	0.17	0.04						
Fe	0.38	0.21	−0.09					
Cu	−0.25	−0.14	0.67	−0.66				
Co	0.54	0.31	0.28	0.80	−0.43			
Ni	−0.18	−0.06	0.67	−0.68	0.96	−0.40		
Zn	−0.23	0.02	0.73	−0.55	0.92	−0.24	0.93	
Pb	0.50	0.19	0.11	0.88	−0.52	0.89	−0.53	−0.40

Geochemical distribution of some metals

The concentration of manganese, iron, cobalt, nickel, copper, zinc, lead, platinum, and gold in the ferromanganese oxide are listed in Table 8, in comparison with those of the earth crust and sea water. The enrichment factor of gold in the ferromanganese oxides against the earth crust (0.1) is extremery low as compared to that of other metals (3 to 194, Table 8). This may arise from chemical characteristics of gold during the ferromanganese oxide formation while leaving out gold in sea water. The concentration of gold in sea water estimated 0.01 ppb, and the value is nearly the same to that of manganese, but much higher than cobalt, lead and platinum (Table 8).

The enrichment factor of platinum in the ferromanganese oxides against the earth crust (54) is almost similar to that of nickel (71), copper (78) or lead (80). These facts indicate that only platinum could not be especially enriched in the ferromanganese oxides. HALBACH *et al.* (1984) considered that the platinum and other metals in ferromanganese crusts are originally derived from the crustal mate-

Table 8 Geochemical distribution of some metals.

Metal	Ferromanganese oxide (This work) [A]		The earth crust (MASON, 1958) [B]		Sea water (NOZAKI, 1985) [C]		Enrichment factor [A/B]	Enrichment factor [A/C]
Mn	19.44	(%)	0.10	(%)	0.01	(ppb)	194	1944.0×10^7
Fe	13.97		5		0.04		3	349.3×10^7
Co	0.39		0.0023		0.002		170	195.0×10^7
Ni	0.57		0.0080		0.5		71	1.1×10^7
Cu	0.35		0.0045		0.1		78	3.5×10^7
Zn	0.07		0.0065		0.4		11	0.2×10^7
Pb	0.12		0.0015		0.002		80	60.0×10^7
Pt	0.000027		0.0000005		0.0002		54	0.1×10^7
Au	0.000000045		0.0000005		0.01		0.1	45

rials, and that the alteration of basaltic rocks in the ocean-floor may be a potential source of the metals.

Conclusions

Platinum is markedly enriched in ferromanganese oxides over gold compared to their crustal abundance or sea water values. The average platinum content is clearly higher in the seamounts ferromanganese crusts than in the deep-sea manganese nodules. In general, platinum abundance greater than 0.5 ppm which equivalent to a hundredfold of crustal abundance are observed at water depths between 800 and 2000 m. Platinum enrichment may take place in the reduced marine environments of the oxygen depleted depths.

Gold content in the deep-sea ferromanganese nodules is rather richer than that of the seamounts crusts. There is no essential positive or negative correlation between gold and other metals. An average gold content in the studied ferromanganese oxides is clearly lower than that of deep-sea sediments or crustal abundance. The economical interest for gold in the marine hydrogenous ferromanganese oxides may be much smaller than the platinum.

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海底鉄マンガン酸化物中の白金・金の地球化学的研究

寺島　滋・臼井　朗・中尾征三・三田直樹

要　旨

マンガンクラストやマンガン団塊中の白金および金は未利用貴金属資源として注目されてきたが，これまでに公表された分析値は極めて少ない．本研究では，小笠原海台，南極周辺，太平洋中央部から得た非熱水起源の鉄マンガン酸化物76試料について溶媒抽出分離-黒鉛炉原子吸光法により白金および金を定量した．

白金は，深海底のマンガン団塊に比べて海山域のマンガンクラストに多く含有される傾向があり，小笠原海台周辺では平均 0.51 ppm, 最高値は 2.39 ppm を示した．白金含有量 0.5 ppm 以上の鉄マンガン酸化物は，水深 800–2000 m の海域に分布する傾向があり，これは海水中溶存酸素極小層において白金が沈殿しやすく，逆にマンガン，鉄等が沈殿しにくいためと考えられた．

金は，海山域のクラストよりも深海底のマンガン団塊でやや高い傾向があった．しかし，最も金に富む太平洋中央部の試料でも平均 0.61 ppb であり，これは地殻存在量の 1/10 程度である．海水中には，コバルト，鉛よりも多く，マンガンと同程度の金が溶存していると考えられており，金は非熱水起源の鉄マンガン酸化物には濃集しにくいものと思われた．

（受付：1988 年 9 月 12 日；受理：1989 年 1 月 26 日）