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Platinum and palladium abundances in marine sediments and their geochemical behavior in marine environments

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Abstract: A 284 marine sediments of terrigenous, hemipelagic and pelagic origin were collected from the different environments, i.e., in the seven sea areas around the Japanese islands (terrigenous sediments), on the Mariana Ridge (hemipelagic sediments), and in the Central Pacific (pelagic sediments). These samples were analyzed together with 31 lake sediments and 41 marine shales for Pt and Pd by atomic absorption spectrometry using a graphite furnace atomizer after solvent extraction separation. The average abundances of Pt and Pd are markedly higher in the pelagic sediments than the terrigenous sediments, with the hemipelagic sediments showing intermediate abundance. Most of the samples analyzed in this study are richer in Pt than Pd, whereas siliceous ooze collected from the central Pacific high productivity zone was generally richer in Pd than Pt. Although the Pt and Pd abundances and water depths of the sampling locations are not correlated, there are clear negative correlations between the Pt and Pd abundances and the sedimentation rates in the studied regions. It is considered that most of the Pt and Pd in marine sediments is originally derived from weathering of crustal materials, and both the elements have been precipitated and accumulated as the elemental and oxide forms by the involvements in biological transport processes. The great enrichments of Pt and Pd in pelagic sediments may result from the very low sedimentation rates and strongly oxidizing environments. The different vertical distributions of Pt or Pd and organic C concentrations in the central Pacific cores suggests that the formation of organometallic complexes of Pt and Pd, and migration of both elements during the early diagenesis are not so significant except in very rare cases. The crustal abundances for Pt and Pd are tentatively estimated as 2.7 ppb and 1.9 ppb, respectively.

Keywords: platinum, palladium, marine sediment, geochemical behavior, crustal abundance

1. Introduction

Platinum and Pd abundances in marine sediments have an important bearing on geochemical behavior of these elements in the marine environment and an economic significance for their resource potential. The geochemical behavior of Pt and Pd in coastal marine sediments collected from off Niigata, southeastern margin of the Japan Sea, have been investigated by the authors (Terashima *et al*., 1993). The results indicate that Pt and Pd are probably supplied to marine sediments in dissolved form through the rivers and sea waters and, to a lesser extent as discrete minerals. The inverse correlation between the Pt and Pd contents and redox potential of the sediments suggest that the dissolved Pt and Pd are converted by reduction to the metallic state in reducing environments. The Pt and Pd particles will be suspended in sea water, then be adsorbed on mineral surface and/or precipitated as hydroxide and sulfide. Although there are data reported for other regions (Crocket and Kuo, 1979; Crocket *et al*., 1973; Lee, 1983; Hodge *et al*., 1985, 1986; Goldberg *et al*., 1986; Koide *et al*., 1986; Colodner *et al*., 1992), detailed discussion on the geochemical behavior of Pt and Pd in terrigenous, hemipelagic and pelagic marine sediments has not been undertaken to date. The reported crustal abundances of Pt and Pd in the past have varied considerably.

In this paper, we report Pt and Pd contents in about 280 marine sediments and discuss the geochemical behavior of both elements in the marine environments. The crustal abundances of Pt and Pd are estimated based on the analytical results for lake sediments, terrigenous marine sediments, and marine shales.

2. Survey area and sample characteristics

Marine sediments were collected around the Japa-

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nese islands (Obama Bay, Surga Bay, south of Kii Strait, off Northeast Japan, the Japan Trench, the Ryukyu Trench and Shichito-Iojima Ridge) and on the Mariana Ridge and in the central Pacific (Fig. 1) during the period 1971-1981. Based on the distance from the continent, sediment geochemical characteristics and sedimentation rate, the sediments can be divided into three types, terrigenous (Obama Bay to Shichito-Iojima Ridge), hemipelagic (Mariana Ridge) and pelagic (central Pacific) as listed in Table 1.

The sediment from the Obama Bay, Suruga Bay and south of Kii Strait are composed of fine sand, silt and silty clay, and those from off Northeast Japan and the Japan Trench are mostly silty clay and clay. Generally, they include some thin layers of sand, tuff and pumice. As for the Ryukyu Trench and Shichito-Iojima Ridge, there are various types of sediments from gravel to clay, mainly silty clay to clay. Calcareous fragments are some times included for both types of sediment, with volcanogenic sediment dominant in the latter. The hemipelagic sediments from the Mariana Ridge are composed of silty clay to clay, and mostly include both calcareous and volcanogenic source materials. The pelagic sediments from both the northern and southern parts of the central Pacific, i.e. Mid-Pacific Mountains and Penrhyn Basin, respectively, are richer in pelagic clay and zeolitic mud. The central Pacific equatorial zone is abundant in siliceous ooze and siliceous mud, reflecting the high biological productivity. Although most sampling stations are situated below the Carbonate Compensation Depth (CCD), calcareous-rich sediments occur sporadically in the central and

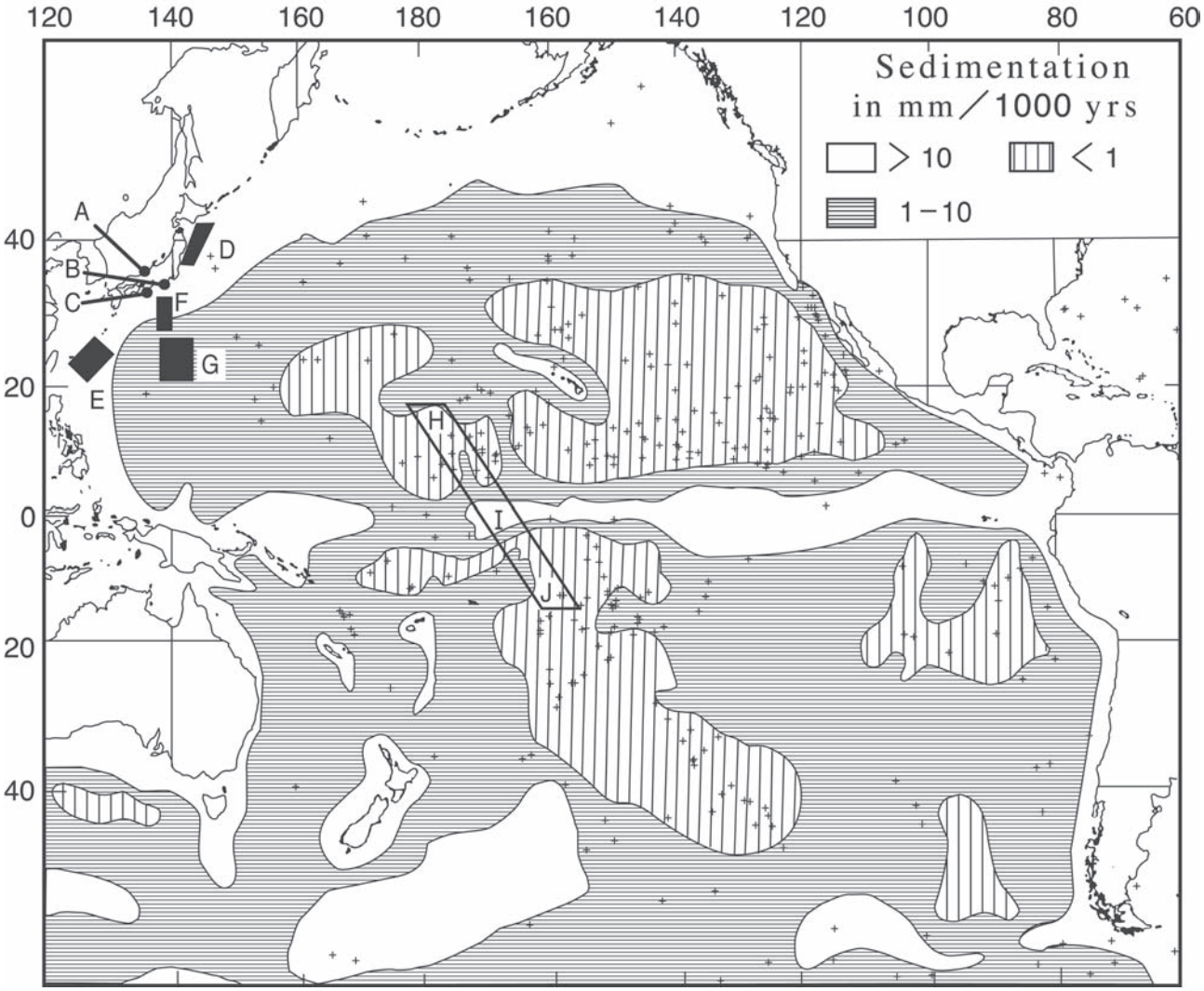

Fig. 1 Sampling areas (A to J) of studied marine sediments and sedimentation rates in the Pacific Ocean. The sedimentation rates are estimated originally by Lisitzin (1972) and revised by Piper and Williamson (1977). A: Obama Bay; B: Suruga Bay; C: south of Kii Strait; D: off Northeast Japan-the Japan Trench; E: the Ryukyu Trench; F: Shichito-Iojima Ridge; G: the Mariana Ridge; H: Mid-Pacific Mountains; I: Central Pacific Basin; J: Penrhyn Basin.

Table 1 Locality of studied marine sediments.

Sea area	Location	Water depth (m)	Distance from land (m)
Terrigenous sediments			
Obama Bay	35°-36°N, 135°-136°E	4-26	0.5-3
Suruga Bay	34°-35°N, 138°-139°E	17-2000	5-30
South of Kii Strait	33°-34°N, 134°-136°E	1355-2070	10-30
Off Northeast Japan	39°-43°N, 141°-144°E	750-4770	50-170
The Japan Trench	36°-44°N, 143°-149°E	5180-8805	200-350
The Ryukyu Trench	22°-27°N, 124°-131°E	1180-7110	300-800
Shichito-Iojima Ridge	27°-33°N, 139°-142°E	1403-4123	350-900
Hemipelagic sediments			
The Mariana Ridge	22°-27°N, 139°-145°E	1840-5975	1000-1500
Pelagic sediments			
Mid-Pacific Mountains	12°-17°N, 178°E-177°W	5027-5569	>3000
Central Pacific Basin (N)	6°-11°N, 172°-176°W	5429-6014	>3000
Central Pacific Basin (C)	1°S-5°N,166°-174°W	5087-5747	>3000
Central Pacific Basin (S)	1°-9°S, 160°-168°W	2959-5698	>3000
Penrhyn Basin	10°-15°S, 157°-160°W	5111-5690	>3000

N: northern part; C: central part; S: southern part.

southern parts of the Central Pacific Basin (Nakao and Mizuno, 1982).

It is well known that S present as sulfide in marine sediments is derived primarily from bacterial reduction of SO_4^{-2}. This bacterial actively occurs in reducing sediments. The sulfide content of the sediments is therefore one of the principal indicators of the redox conditions. Of the sediments studied, the samples from off Northeast Japan are contain the highest sulfide contents, while those from the Obama Bay and the Suruga Bay have relatively low sulfide contents (Terashima *et al.*, 1995). In the case of pelagic sediments, sulfide was not detected in any of the samples (Terashima *et al.*, 1982). The sedimentation rate contributes to the redox conditions of the sediments. In general, slower accumulation rates provide more oxidized conditions. An average accumulation rate for sediment from around the Japanese islands was estimated at more than 10 mm/k. y., whereas that of the Central Pacific was less than 10 mm/k. y. (Piper and Williamson, 1977; Fig. 1).

Although the geologic age of the studied sediments is partly unknown, five ages such as Holocene, Pleistocene, Pliocene, Miocene and Oligocene are recognized in the sediment cores from the central Pacific (Nakao and Mizuno, 1982; Nishimura, 1984, 1986), and the sediments younger than Pliocene were taken from other sea regions. The Jurasic to Paleogene marine shales were collected from Western Shikoku district (Ishihara *et al.*, 1985) and Neogene to Quaternary mudstones of Kanagawa prefecture were selected from about 600 m of drill core. Recent muddy sediments from the Lake Suwa, Lake Kasumigaura and Lake Biwa (Terashima *et al.*, 1986) were also analyzed for comparison together with estimation of crustal abundance.

3. Sampling and Analytical methods

Terrigenous sediments, from Obama Bay and Suruga Bay were collected using the Smith-McIntyre-type grab sampler. The uppermost part of the sample (ca. 0-5 cm) was selected for analysis. For the sediments from South of Kii Strait to the Japan Trench, a total of 16 sediment cores (2-6 m in length) were collected using a piston corer. The cores were sectioned every 2 to 20 cm and 3 to 6 representative samples from each core were selected. The sediments from the Ryukyu Trench, Shichito-Iojima Ridge and the Mariana Ridge have been collected using a cylinder type dredge sampler and a piston corer. Pelagic sediments were collected using a freefall grab, box corer and piston corer (Nakao and Mizuno, 1982). The samples collected from the upper 0-5 cm were labeled as surface samples, and those collected deeper than 5 cm were labeled as subsurface or core samples. All samples were air-dried, and ground to under 100 mesh. Analytical results for Au, Fe, Mn, Cu, Pb, Zn, Co, Ni, organic C, total S and sulfide have already been reported (Terashima *et al.*, 1982, 1983, 1986, 1995; Mita and Nakao, 1984; Mita *et al.*, 1982).

The method of analyzing Pt and Pd in a variety geological reference materials using graphite furnace atomic absorption spectrometry has been published (Terashima, 1991). A brief summary of the procedure is as follows. If the sample contain more than about 0.5 % of organic carbon and/or sulfide sulfur, the samples are pre-heated to remove the carbon and sulfur. 0.5 to 2 g of sample containing less than 5 mg of Cu and 300 mg Fe was decomposed with 16 ml of aqua regia and 10 ml of hydrofluoric acid in a covered Teflon beaker. The mixture was evaporated to dryness, and

the evaporation was repeated with 8 ml of aqua regia until nearly dry, then dissolved in 10 ml of 6M hydrochloric acid by heating. After centrifugation, the supernatant was shaken with 15 ml of MIBK to remove Fe. The aqueous layer was transferred to another separatory funnel, and 0.5 ml of potassium iodide solution (100 g KI/100 ml) was added. Platinum and Pd were extracted into 0.2 ml of MIBK, and determined by graphite furnace atomic absorption spectrometry.

Detection limit is approximately 0.5 ppb for Pt and 0.2 ppb for Pd in a 2 g sample, and the time required for the determination of the two elements in 20 samples is estimated about 8 hours. Analytical results of 10 USGS rock reference samples are mostly agreed to those recently published data (Table 2). Average abundances of Pt, Pd and other elements in 51 international igneous rock and mineral reference materials are also cited after Terashima (1991) in Table 3. The concentrations of Pt and Pd in ultramafic and mafic rocks are clearly higher than those of intermediate and silicic rocks.

4. Results and discussion

4.1 Behavior of Pt and Pd in coastal marine sediments

The geochemical behavior of Pt and Pd in coastal marine sediments collected from the off Niigata, southeastern margin of the Japan Sea have been investigated by the authors (Terashima *et al.*, 1993). The results indicate that the Pt or Pd is generally enriched in the fine sediment fraction, and positively correlated with Cu, Pb and water depth. The inverse correlation between the Pt or Pd content and redox potential of the sediment suggest that significant amounts of Pt and Pd are supplied in their dissolved forms, and reduced to their metallic states. It is concluded that the Pt and Pd distribution in the coastal marine sediments are controlled by the geological characteristics of the studied area, grain size and redox potential of sediments, water depths, and dissolved O_2 concentration of sea water. Similar geochemical behavior of Pt and Pd may take place in the studied terrigenous marine sediments.

4.2 Regional variation

Analytical results of Pt, Pd, Au, Fe, Mn, Cu, Pb, Zn, Co, Ni, total S, organic C and Al in the studied samples are given in appendix Tables A-1 to A-3. Regional average variations for concentration of Pt, Pd and other elements are summarized in Table 4. Among all the terrigenous sediments, Pt content ranges from 2.7 ppb (South of Kii Strait) to 3.7 ppb (Obama Bay), and there is no large variations are recognized. The same tendency is shown for most other elements with the exception of Mn and Au. Mn content varies widely from 390 ppm (Off Northeast Japan) to 4739 ppm (Shichito-Iojima Ridge). In the region of Shichito-Iojima Ridge, recent submarine hydrothermal activity has been reported (Usui *et al.*, 1986), and the surface sediment is generally brownish, reflecting the presence of Fe and Mn oxides. The Mn contents in the most hydrothermal Mn minerals are significantly high, and Fe is very low (Usui *et al.*, 1986). The high concentrations of Mn

Table 2 Analytical results of Pt and Pd in ten U. S. Geological Survey reference materials. Literature values are given for comparison.

Sample	Pt (ppb)				Pd (ppb)			
	Terashima (1991)	Aruscavage *et al.*(1984)	Rowe and Simon(1971)	Basturk (1977)	Terashima (1991)	Aruscavage *et al.*(1984)	Rowe and Simon(1971)	Kontas *et al.* (1986)
AGV-1	1.2±0.2	<1	1.1	11.7	<0.2	<0.2	<0.5	2.0
BCR-1	0.6±0.3	<1	2.3	1.7	<0.2	<0.2	<0.5	2.7
BHVO-1	2.5±0.7	2.2±0.3			3.2±0.2	2.93±0.39		2.7
DTS-1	1.7±0.4	1.4, 1.8	1.7	5.8	<0.2	<0.2	<0.5	1.5
G-2	<0.5	<1	<0.5	5.9	<0.2	<0.2	<0.5	
GSP-1	<0.5	<1	<0.5	<1.9	<0.2	<0.2	<0.5	1.0
MAG-1	1.5±0.6	1.0, 1.0			1.9±0.4	0.8, 0.8		2.4
PCC-1	6.6±0.7	5.7±0.7	5.8	17.6	5.2±0.6	4.36±0.56	4.7	7.3
SDC-1	0.8±0.2	1.0, 1.2			0.6±0.2	0.6, 0.6		1.6
SGR-1	3.1±0.3	2.3, 3.6			5.0±0.8	3.6, 3.9		3.9

Table 3 Abundances of Si, Pt, Pd and other eight elements in 51 international igneous rock and mineral reference materials (modified after Terashima, 1991).

Rock type	(n)	Si (%)	Pt (ppb)	Pd (ppb)	Au (ppb)	Fe (%)	Mn (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)	Co (ppm)	Ni (ppm)
Ultramafic rocks	11	18.46	4.4	2.0	2.4	9.19	1441	40	8	224	89	1104
Mafic rocks	11	24.12	3.8	2.9	1.5	7.27	1719	73	14	123	43	110
Intermediate rocks	8	28.32	0.7	0.4	0.5	4.01	1286	28	39	131	12	28
Silicic rocks	21	32.76	<0.5	<0.2	1.4	1.46	387	16	41	61	7	7
All the samples	51	27.11	2.0	1.2	1.4	4.78	1046	35	28	120	34	269

Table 4 Regional average element contents.

Sea area	(n)	Pt (ppb)	Pd (ppb)	Au (ppb)	Fe (%)	Mn (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)	Co (ppm)	Ni (ppm)	Tatal-S (%)	Org. C (%)	Al (%)
Terrigenous sediments														
Obama Bay	10	3.7	1.7	2.1	4.71	903	47	23	110	19	36	0.16	0.97	6.97
Suruga Bay	14	3.1	2.3	1.7	3.70	581	31	19	93	14	28	0.14	0.80	6.98
South of Kii Strait	15	2.7	1.7	1.3	2.91	401	26	14	98	11	30	0.30	0.93	7.05
Off Northeast Japan	21	3.2	2.1	2.3	3.15	390	36	12	84	8	27	0.79	1.48	5.99
The Japan Trench	26	2.9	2.3	3.5	3.25	672	76	13	81	10	24	0.40	0.83	6.07
The Rhyukyu Trench	14	3.5	3.1	4.4	3.95	1856	77	28	91	21	58	n.d.	n.d.	7.34
Shichito-Iojima Ridge	8	3.6	3.7	6.1	3.58	4739	70	25	94	10	30	n.d.	n.d.	7.36
(Average)	(108)	3.1	2.3	2.9	3.49	1044	52	17	90	13	32	0.41	1.02	6.61
Hemipelagic sediments														
The Mariana Ridge	(23)	5.6	3.9	2.7	5.04	2446	122	25	99	23	37	n.d.	n.d.	6.84
Pelagic sediments														
Mid-Pacific Mountains	13	13.6	7.4	1.1	4.54	7543	361	36	156	122	268	0.20	0.21	7.65
Central Pacific Basin (N)	55	9.2	9.8	0.9	4.21	7580	464	35	173	117	232	0.31	0.19	6.83
Central Pacific Basin (C)	54	5.8	6.8	2.1	2.82	4380	282	23	89	55	132	0.35	0.25	4.53
Central Pacific Basin (S)	19	9.7	6.0	1.6	3.61	7641	304	41	95	92	178	0.30	0.23	4.28
Penrhyn Basin	12	22.8	8.6	1.1	7.42	15464	392	88	153	222	287	0.30	0.28	7.01
(Average)	(153)	9.5	8.0	1.4	3.94	7106	363	36	130	101	197	0.31	0.23	5.83

All the data are shown in air dried basis. n.d., not determined.

together with Au, and even distribution of Fe in the sediments from the Shichito-Iojima Ridge may be related to hydrothermal activity. Although the extraordinary high accumulations of anthropogenic Pt (Koide *et al*., 1986) or Pd (Lee, 1983) have been reported, the anthropogenic effects in the studied sediments are estimated to be negligible because the contents of Pt or Pd in these sediments are similar to those of igneous rock reference materials (Table 3).

Average abundances of Pt (5.6 ppb) and Pd (3.9 ppb) in the hemipelagic sediments from the Mariana Ridge are slightly higher than those in the terrigenous sediments, and the pelagic sediments of central Pacific are most dominant in Pt (9.5 ppb) and Pd (8.0 ppb) as shown in Table 4. There is a clear tendency for the sediments from both northern and southern parts of the Central Pacific to be richer in Pt and most transition metals than the central equatorial zone sediments, but Pd, Au, total S and organic C behaved in different manner (Table 4). This may be related to geological and geochemical characteristics of the study area. The organic C content was found to be very low in the pelagic sediments, suggesting an oxidizing environment. In general, Al is not enriched by the biological activities in the marine environment. In order to estimate the dilution effects of crustal material by biogenic material, concentration of Al was analyzed (Table 4). The central equatorial zone sediments are lower in Al than both northern and southern parts of the Central Pacific sediments, reflecting the high biological activity.

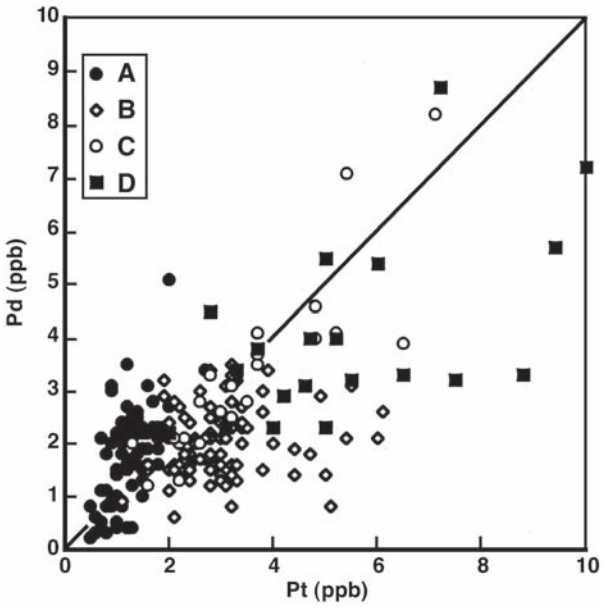

Fig. 2 Plot of Pt vs Pd content of the terrigenous and hemipelagic sediments. Most of the studied terrigenous sediments are plotted in the Pt rich area, whereas more than half of off Niigata sediments (Terashima *et al*., 1993) belong in Pd rich area. A: off Niigata; B: Obama Bay - the Japan Trench; C: the Ryukyu Trench and Shichito-Iojima Ridge; D: the Mariana Ridge.

4.3 Abundance ratio of Pt/Pd

In order to establish the distribution pattern of Pt/Pd ratios in the crustal materials, all the data containing of off Niigata sediments are plotted in Figs. 2 (terrigenous and hemipelagic sediments) and 3 (pelagic sediments). In the case of terrigenous sediments, more than

80 % samples are plotted in the Pt rich area, with the exception of samples of off Niigata, which are rather richer in Pd. As for the pelagic sediments, the sediments from both the Mid-Pacific Mountains and Penrhyn Basin are clearly richer in Pt than Pd, whereas sediments from the central Pacific equatorial zone are relatively abundant in Pd. The relationship between the vertical variation of seven elements (Pt, Pd, Co, Ni, Cu, Mn and Fe) and deposition age of the sediments on three representative cores from the Central Pacific Basin are shown in Fig. 4. The estimation of age was based on the micropaleontological data and a study of remnant magnetism of the sedimentary sequences (Nishimura, 1984, 1986; Joshima and Nishimura, 1984; Yamazaki, 1986). Analyzed samples of core P220 were selected from middle Miocene strata with the deposition age of 8.5 to 14.7 Ma. In this core, Pd is richer than Pt throughout the whole geologic period. On the other hand, the Pt/Pd ratios of two sediment cores P204 and P207 are significantly variable, and Pt rich sediments accumulated in strata younger than Pliocene age (Fig. 4).

In order to make the relationship between the Pt and Pd abundances and geologic age of sediment clear, the average Pt and Pd abundances were calculated for different ages of the sediment, selected from major four types of sediments such as zeolitic clay, pelagic clay, siliceous mud and siliceous ooze, all collected from the Central Pacific (Table 5). Among all the four types, the Pt abundance and Pt/Pd ratios all increase if the age decreases. Holocene to Pleistocene sediments are then richer in Pt than Pd. These results imply that the Pt and Pd abundances in the sediments vary according to the sedimentation age. The relationship between Pt and Pd abundances and geologic age was therefore investigated for Recent lake sediments together with Jurassic to Quaternary marine shales collected from the Japanese islands. The results are summarized in Table 6. In the case of marine shales, the Pt abundances increase if the age decrease, and all of them are rich in Pt than Pd. However, recent lake sediments from the Lake Biwa are richer in Pd (2.6 ppb) than Pt (2.0 ppb), and the marine sediments from off Niigata are also richer in Pd than Pt (Table 6). These results indicate that systematic variation of Pt abundances and Pt/Pd ratios for sediment ages had been restricted to several sea regions especially in the Central Pacific. As for the terrigenous sediments, the Pt/Pd ratios and both elements abundances are controlled by the geological

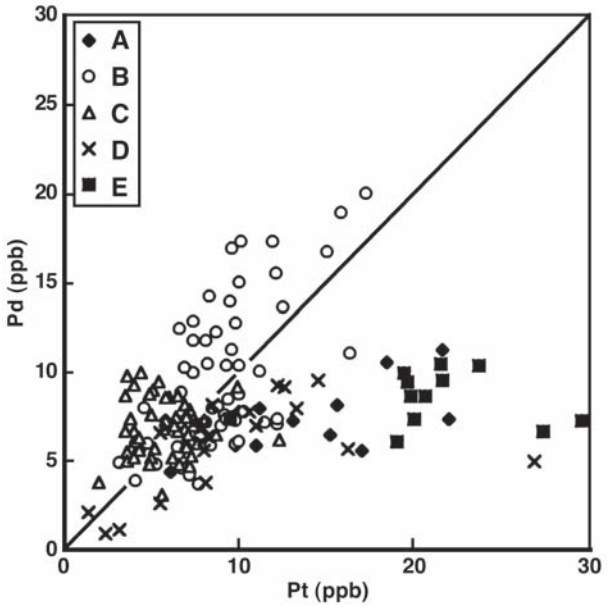

Fig. 3 Plot of Pt vs Pd content of the pelagic sediments. The sediments from both northern and southern parts of the Central Pacific are richer in Pt than Pd, and the central equatorial zone sediments are dominant in Pd than Pt. A: Mid-Pacific Mountains; B, C and D: northern, central and southern parts of the Central Pacific Basin; E: Penrhyn Basin.

Table 5 Average abundances of Pt and Pd on the different geologic ages of selected four types sediments from the Central Pacific.

Sediment type	(n)	Pt(ppb)	Pd(ppb)	Pt/Pd
Zeolitic clay				
Holocene-Pleistocene	6	16.7	6.0	2.8
Miocene	14	10.4	13.6	0.8
Avg.	(20)	12.3	11.3	1.1
Pelagic clay				
Holocene-Pleistocene	18	11.7	7.3	1.6
Pliocene	7	8.5	9.6	0.9
Miocene	4	10.7	14.2	0.8
Avg.	(29)	10.8	8.8	1.2
Siliceous mud				
Holocene-Pleistocene	14	7.7	6.7	1.2
Pliocene	2	6.7	6.7	1.0
Avg.	(16)	7.5	6.7	1.1
Siliceous ooze				
Holocene-Pleistocene	6	6.6	5.4	1.2
Pliocene	4	6.4	5.2	1.2
Miocene	22	4.8	7.5	0.6
Oligocene	2	3.5	6.3	0.6
Avg.	(34)	5.2	6.8	0.8
All the samples				
Holocene-Pleistocene	44	10.4	6.7	1.6
Pliocene	13	7.5	7.8	1.0
Miocene	40	7.4	10.3	0.7
Oligocene	2	3.5	6.3	0.6
Avg.	(99)	8.6	8.3	1.0

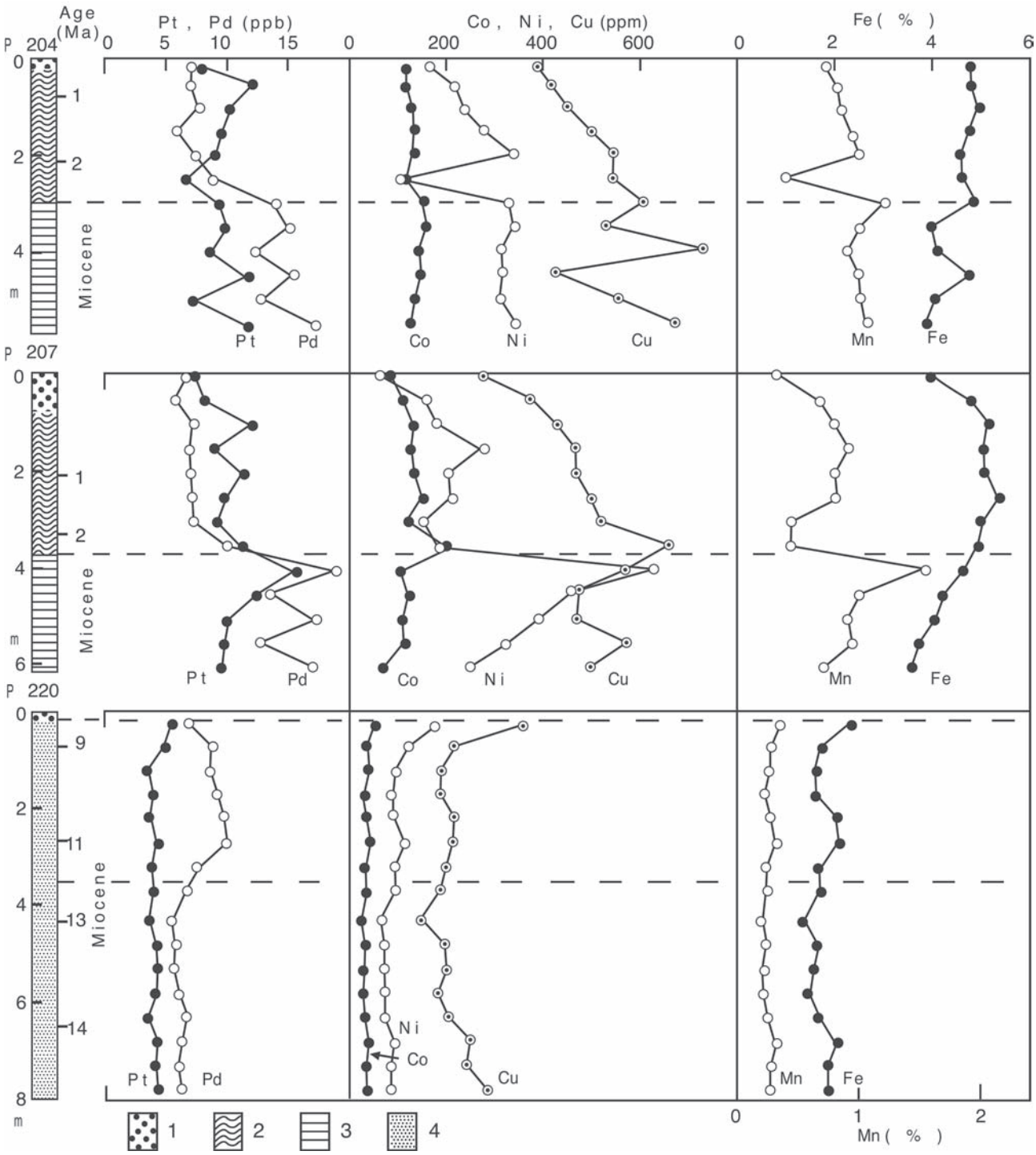

Fig. 4 Vertical variation of Pt, Pd and other 5 elements in the selected three piston cores from the Central Pacific Basin. Sampling localities are as follows.

Core no.	Locality	Water depth (m)
P 204	9°04.93' N, 174°02.60' W	5936
P 207	8°41.24' N, 174°04.25' W	6014
P 220	3°15.30' N, 169°40.79' W	5371

Dotted line means existence of hiatus. Abbreviation for sediment type: 1, siliceous clay; 2, pelagic clay; 3, zeolitic clay; 4, siliceous ooze.

characteristics of the major significant sources of the sediments.

4.4 Relationship to Pt and Pd abundances in ferromanganese minerals

Platinum and Pd abundances in ferromanganese minerals have been reported in several papers (Harriss *et al*., 1968; Halbach *et al*., 1984, 1989; Hodge *et al*., 1985; Goldberg *et al*., 1986; Koide *et al*., 1986; Hein *et al*., 1988, 1990; Terashima *et al*., 1988; Usui and Terashima, 1997; Stuben *et al*., 1999). Among all the references, the average Pt abundances are clearly higher in ferromanganese crusts from seamounts than in the deep-sea manganese nodules. In general, a Pt abundance greater than 0.5 ppm, which is over a hundred times the crustal abundance, is observed at water depths between 800 and 2800 m. On the contrary, Pd abundance of both the seamounts crusts and deep-sea nodules is more or less similar to that of marine sediments. Then the Pt/Pd ratios in the ferromanganese minerals vary greatly between 47 and 3000 (Goldberg, 1987).

The relationship between the water depths of sampling locations, and Pt or Pd abundances in the sediments are shown in Fig. 5. The Pt and Pd rich sedi-

Table 6 Abundances of Pt, Pd and other seven elements of three fresh water lakes sediments, off Niigata marine sediments, and Quaternary to Jurassic marine shales.

Sample	Age	Locality		Pt	Pd	Fe	Mn	Cu	Pb	Zn	Co	Ni
			(n)	(ppb)	(ppb)	(%)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Muddy lake sediments	Recent	Nagano pref., Lake Suwa	8	5.7	1.2	5.20	1089	63	26	106	19	38
		Ibaraki pref., Lake Kasumigaura	16	5.1	1.3	5.50	1148	46	17	90	12	24
		Shiga pref., Lake Biwa	7	2.0	2.6	4.80	2993	74	45	168	18	40
Sandy to muddy marine sediments	Recent	Off Niigata, SE of the Japan Sea	81	1.2	1.6	4.27	2035	21	35	95	10	37
Marine shale	Quaternary	Kanagawa pref., Kazusa Group	7	4.8	1.7	4.08	606	27	13	78	12	30
	Neogene	Kanagawa pref., Kazusa Group	9	4.0	1.5	4.48	640	39	15	84	13	31
	Paleogene	Western Shikoku, Shimanto Terrane	7	3.5	1.4	3.68	397	33	17	93	n.d.	n.d.
	Cretaceous	Western Shikoku, Shimanto Terrane	6	2.5	1.5	3.49	555	39	19	88	n.d.	n.d.
	Cretaceous	Western Shikoku, Ryoke Terrane 6	2.4	0.9	2.02	232	24	22	68	n.d.	n.d.	
	Jurassic	Western Shikoku, Chichibu Belt	6	2.2	1.1	3.66	580	26	27	85	n.d.	n.d.

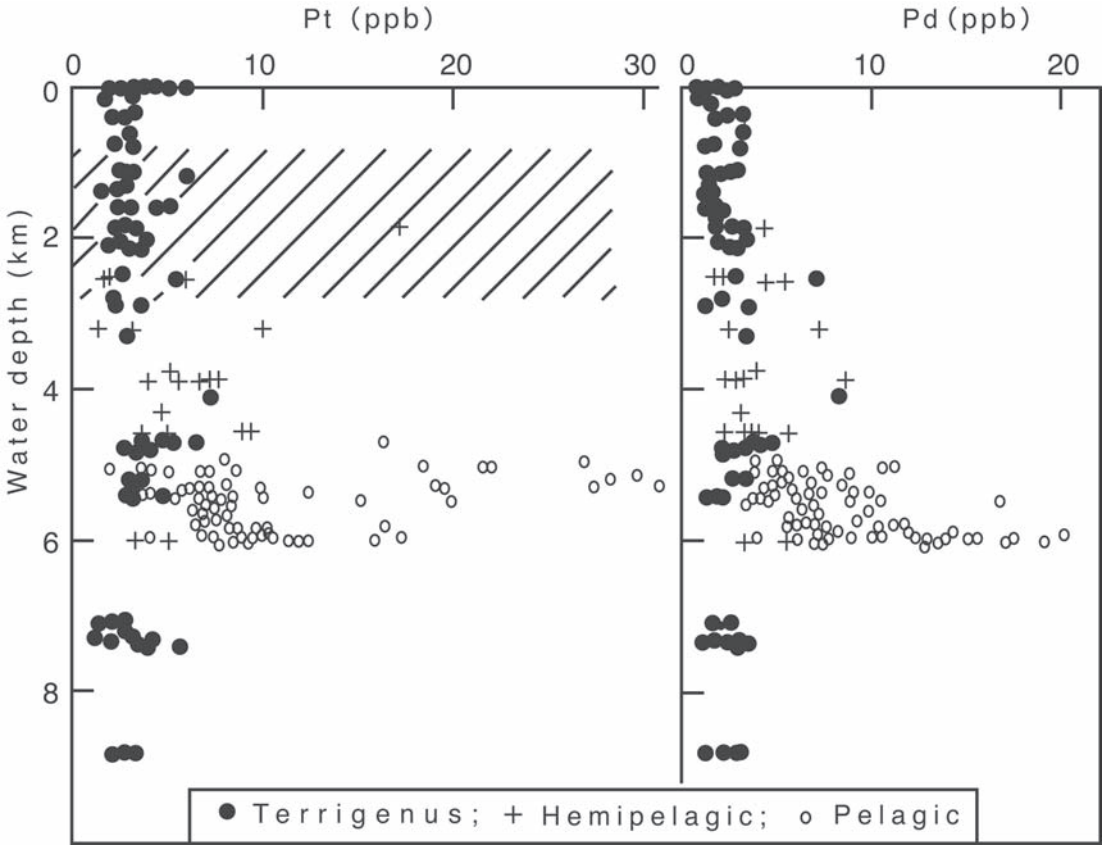

Fig. 5 Plot of Pt and Pd content in the sediments vs water depth of the sampling location. Platinum rich ferromanganese crusts (>0.5 ppm) are generally observed from the shaded (800-2000 m) water depths.

ments are distributed at water depths between 2000 and 6000 m, and there is no clear difference in the Pt and Pd abundances depending upon the water depths. In addition, the variations of Pt/Pd ratios in the marine sediments are very small (<5.4). The different enrichment behavior of Pt and Pd in ferromanganese minerals and marine sediments may arise mainly from redox conditions of environments. Platinum is more enriched in strongly oxidizing conditions, Pd may have the same tendency, but the effects are too weak to be certain.

4.5 Geochemical behavior of Pt and Pd in marine environments

The inter-element relationships in the studied marine sediments are listed in Table 7. The strong positive correlation of Pt with most transition metals in the hemipelagic and pelagic sediments implies that these elements are enriched as a result of similar geochemical behavior. According to recent studies of the geochemical behavior of Pt and Pd during weathering in the supergene environments, the most probable forms of dissolved Pt or Pd in natural waters are believed to be as the hydroxide, chloride, or organometallic complexes; the relative geochemical mobility of Pd is generally greater than that of Pt (Fuchs and Rose, 1974, Taufen and Marchetto, 1989; Wood and Vlassopoulos, 1990). The vertical distribution of Pt and Pd concentrations in Pacific Ocean waters shows nutrient-type profiles, with Pt values increasing from about 100 pg/l in shallow water (200 m) to 300 pg/l in deeper water (>2000 m). At the same time, Pd values increase from 20 to 60 pg/l (Hodge *et al.*, 1985). Causes for the enrichment of Pt in marine ferromanganese

Table 7 Correlation coefficient matrix for studied sediments.

	Water depth	Pt	Pd	Au	Fe	Mn	Cu	Pb	Zn	Co	Ni	Total-S	Org. C
	Terrigenous sediments (n=108)												
Pt	-0.05												
Pd	0.23	0.52											
Au	0.39	0.13	0.36										
Fe	-0.08	0.46	0.40	0.01									
Mn	0.04	0.17	0.27	0.40	0.10								
Cu	0.64	0.45	0.71	0.54	0.33	0.27							
Pb	-0.14	0.26	0.26	0.50	0.48	0.35	0.28						
Zn	-0.21	0.18	0.08	0.17	0.51	0.12	0.08	0.34					
Co	0.03	0.47	0.43	0.13	0.73	0.18	0.51	0.59	0.33				
Ni	-0.04	0.27	0.28	0.14	0.53	0.39	0.33	0.57	0.37	0.66			
Total-S	0.04	0.03	0.01	0.05	-0.08	-0.30	-0.06	-0.32	-0.02	-0.54	0.20		
Org. C	-0.05	0.14	0.28	0.30	-0.11	-0.30	0.13	-0.05	0.17	-0.28	0.08	0.37	
Al	-0.11	0.29	0.30	0.03	0.79	0.22	0.14	0.51	0.68	0.64	0.57	-0.13	-0.32
	Hemipelagic sediments (n=23)												
Pt	-0.16												
Pd	0.06	0.46											
Au	0.22	0.10	0.38										
Fe	-0.02	0.74	0.46	0.02									
Mn	-0.11	0.69	0.19	-0.19	0.83								
Cu	-0.11	0.80	0.46	0.01	0.89	0.86							
Pb	-0.51	0.75	0.15	-0.21	0.66	0.85	0.80						
Zn	-0.30	0.62	0.08	-0.28	0.78	0.92	0.76	0.86					
Co	-0.23	0.78	0.23	-0.22	0.85	0.96	0.91	0.92	0.91				
Ni	-0.13	0.72	0.17	-0.24	0.79	0.95	0.88	0.88	0.89	0.98			
Total-S	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		
Org. C	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Al	0.12	0.34	0.28	-0.16	0.76	0.58	0.55	0.30	0.63	0.52	0.49	n.d.	n.d.
	Pelagic sediments (n=153)												
Pt	-0.06												
Pd	0.45	0.31											
Au	-0.09	-0.16	-0.09										
Fe	0.25	0.68	0.24	-0.07									
Mn	0.10	0.75	0.42	-0.18	0.82								
Cu	0.44	0.40	0.45	-0.20	0.55	0.61							
Pb	-0.03	0.72	0.18	-0.13	0.80	0.80	0.34						
Zn	0.42	0.38	0.55	-0.28	0.47	0.50	0.65	0.34					
Co	0.19	0.81	0.35	-0.24	0.86	0.85	0.62	0.81	0.53				
Ni	0.22	0.67	0.51	-0.22	0.53	0.76	0.73	0.47	0.57	0.73			
Total-S	0.18	-0.04	0.18	0.25	-0.07	0.03	0.18	-0.08	0.02	-0.12	-0.03		
Org. C	0.06	0.05	0.06	0.80	0.20	0.10	-0.05	0.17	-0.15	0.02	-0.08	0.18	
Al	0.55	0.47	0.37	-0.15	0.78	0.57	0.73	0.45	0.64	0.69	0.58	-0.15	0.04

minerals have been suggested as: (1) adsorption of $Pt(OH)_2^o$ onto the surface of Mn and Fe oxyhydroxide minerals (Stuben *et al*., 1999); (2) reduction of the divalent form and co-precipitation in elemental form with MnO_2 (Halbach *et al*., 1989); (3) Oxidation from the divalent to the insoluble tetravalent form (Hodge *et al*., 1985; Halbach *et al*., 1989); and (4) association of Pt with organic complexes (Hein *et al*., 1988).

In O_2-depleted environments, the dissolved complex would be decomposed by reduction to the metallic state, and precipitation of Pt and Pd in sea water with sediment particles may then take place. A negative correlation can therefore be expected between the Pt or Pd concentration and the redox potential of the sediments. In fact, a negative correlation is observed in the off Niigata sediments (Terashima *et al*., 1993). The relationship between Pt, Pd, Au and organic C concentrations, and the sampling depth below the ocean bottom for the sediments studied are shown in Fig. 6. In the case of pelagic sediments, the surface samples have greater range (low to high) in Au and organic C concentrations, while deeper sediments are depleted in both elements. This same trend is not present in the Pt or Pd concentrations (Fig. 6). As for the terrigenous sediments, there is no clear vertical trend for Pt, Pd, Au or organic C concentrations. To evaluate the different vertical trends of the data, Pt, Pd, Au, organic C, and five transition metals in the five short cores from the Mid-Pacific Mountains (core A), Central Pacific Basin (B, C, and D), and Penrhyn Basin (E), data are shown in Fig. 7. The Au and organic C content tends to decrease with increasing core depth. No such trend occurs for the Pt, Pd and five transition metals except in core A. It has been considered that Au in the terrigenous sediments is present mostly in the elemental form, whereas about half of Au in the pelagic sediments existed in the form of organometallic complexes. The most probable cause of the vertical change of Au in the pelagic sediments is therefore upward migration of Au-organometallic complexes during early diagenesis (Terashima *et al*., 1995). The vertical profiles of Pt and Pd in the core B to E are clearly different from those of Au and organic C (Fig. 7). This may suggest that the formation of organometallic complexes of Pt and Pd, and the migration of both elements during early diagenesis are not so significant. However, the considerable enrichment of Pt and some transition metals in the uppermost part of core A (Fig.7) is prob-

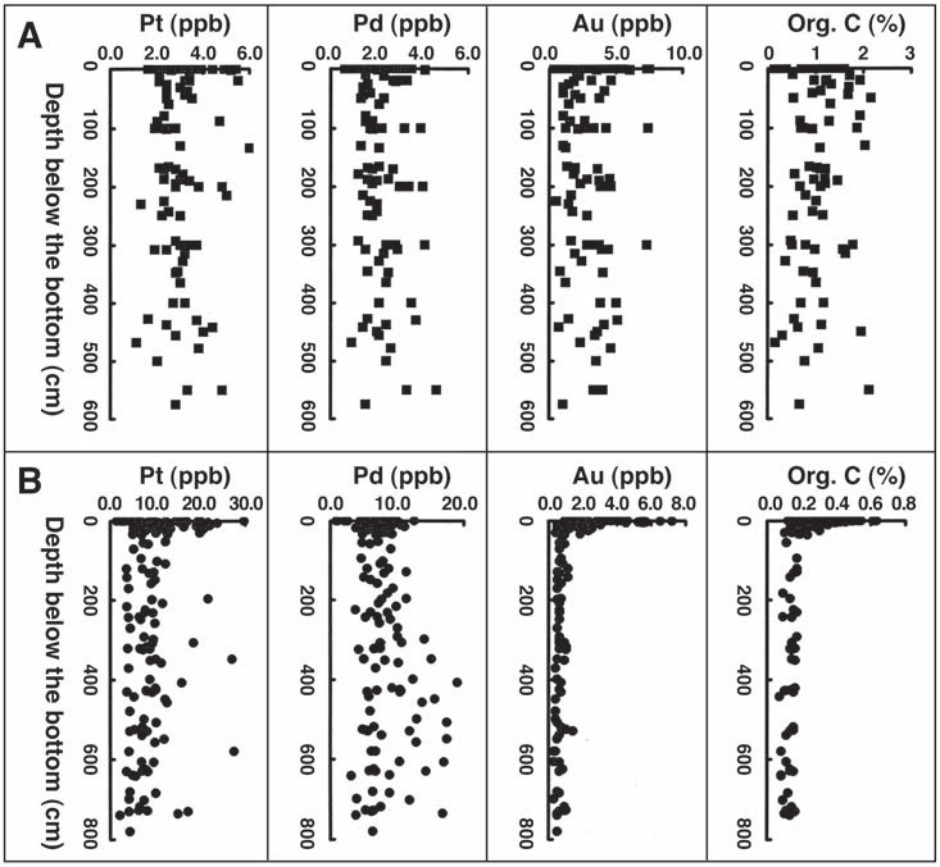

Fig. 6 Plots of Pt, Pd, Au and organic C content of the terrigenous (A) and pelagic (B) sediments vs sampling depth below the ocean bottom. The pelagic surface sediments have greater range in Au and organic C contents, while deeper sediments are depleted, and the trend is not shown in other cases.

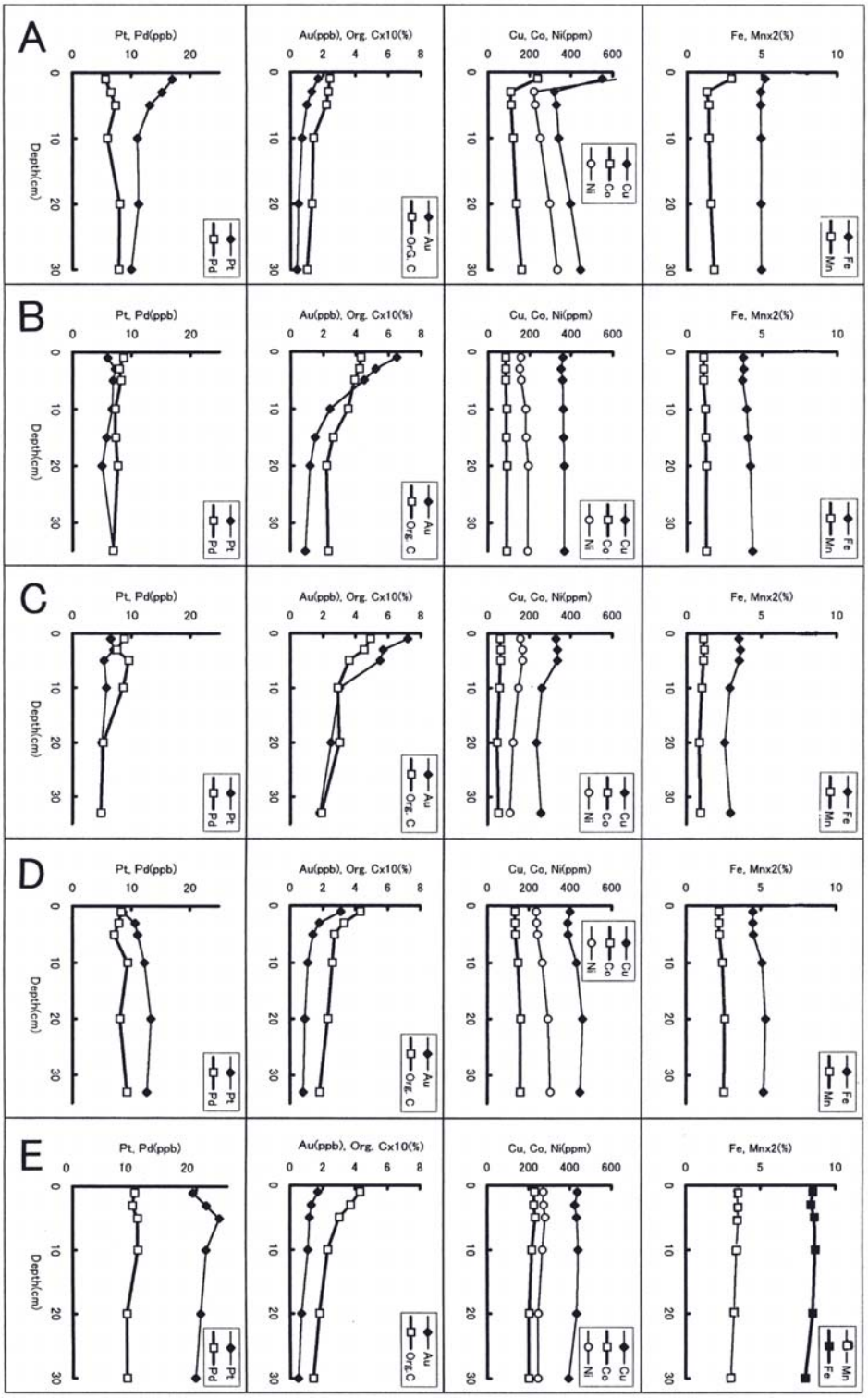

Fig. 7 Vertical change of Pt, Pd and other elements in the selected five box cores from the Central Pacific. Sampling localities and sediment types are as follows.

Core	Locality	Depth (m)	Sediment type
A	15°22.48' N, 178°45.46' W	5537	zeolitic clay
B	4°41.39' N, 173°11.89' W	5584	siliceous mud
C	1°16.04' N, 168°09.97' W	5359	siliceous ooze
D	5°27.32' S, 163°46.01' W	4995	siliceous mud
E	13°47.40' S, 159°28.35' W	5162	pelagic clay

ably due to upward migration of dissolved elements from the deeper sediment layers. In very rare cases, the diagenetic migration of Pt may arise. Colodner *et al*. (1992) has demonstrated that post-depositional mobility of Pt, Ir and Re in recent abyssal marine sediments.

The zeolitic sediments are generally formed in very low sedimentation environments (Nakao and Mizuno, 1982; Nishimura, 1984, 1986). An average Pt and Pd abundances in the zeolitic clay are higher than those of other sediments (Table 5). This may indicate that the sedimentation rates of marine sediments greatly affect the Pt and Pd abundances. The estimated sedimentation rates for the Pacific Ocean which taken from Piper *et al*. (1977) are shown in Fig. 1. The sampling locations of studied terrigenous sediments with low abundances of Pt and Pd are mostly situated in the high sedimentation rate area (>10 mm/k.y.), whereas the pelagic sediments of most dominant in Pt and Pd are observed from the very low sedimentation rate area (<1 mm/k.y.). Hemipelagic sediments with the moderate abundances of both elements belong to the intermediate sedimentation rate area (1-10 mm/k.y.). It is considered that therefore Pt and Pd are probably precipitated as the hydroxide, oxide and/or elemental forms by the involvement in biological transport processes, and this time occur in same degrees of preferential enrichment according to the biogenic activity, especially in Pd in the central Pacific equatorial zone sediments.

4.6 Consideration of crustal abundances

The crustal abundances of Pt and Pd reported in the past have varied. In order to estimate crustal abundances of Pt and Pd, published values (Goldschmidt, 1954; Taylor, 1964; Mason, 1966; Bowen, 1979; Levinson, 1980; Taylor and McLennan, 1995; Wedepohl, 1995) were collected and are listed in Table 8, together with recent value for cosmic abundance (McDonough and Sun, 1995). Among all the data for crustal abundance, Pt or Pd value varies greatly from 0.4 to 10 ppb, and the Pt/Pd ratios changed from 0.5 to 1.0. The cosmic abundance (McDonough and Sun, 1995) of Pt or Pd is 50-2000 times higher than that of crustal abundance. The abundance ratios of Mn/Pt, Cu/Pt, Co/Pt, Mn/Pd, Cu/Pd or Co/Pd for cosmic abundance are therefore much lower than those of crustal abundance (Table 8). Halbach *et al*. (1989) discovered some cosmic spherules in the ferromanganese crusts, and Harriss *et al*. (1968) calculated an upper limit on the mass accretion rate of interplanetary matter to the earth to be 60 tons/day over the surface of the earth. If the samples analyzed in this study contain significant amounts of cosmic materials, the abundance ratios of Mn/Pt to Co/Pd can be expected to low. However, the ratios of Mn/Pt to Co/Pd of all the studied samples are

Table 8 Comparison of some geological abundances of Pt, Pd and other eight elements, and the abundance ratios for selected elements.

	(n)	Pt (ppb)	Pd (ppb)	Au (ppb)	Fe (%)	Mn (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)	Co (ppm)	Ni (ppm)	Mn/Pt $X10^3$	Cu/Pt $X10^3$	Co/Pt $X10^3$	Mn/Pd $X10^3$	Cu/Pd $X10^3$	Co/Pd $X10^3$
Cosmic abundance																	
McDonough & Sun (1995)		1010	550	140	18.1	1920	120	2.47	310	500	10500	1.9	0.1	0.9	3.5	0.2	0.9
Crustal abundance																	
Goldschmidt (1954)		5	10	1	5.00	1000	70	16	80	40	100	200.0	14.0	8.0	100.0	7.0	4.0
Taylor (1964)		n.g.	n.g.	4	5.63	950	55	12.5	70	25	75						
Mason (1966)		10	10	4	5.00	950	55	13	70	25	75	95.0	5.5	2.5	95.0	5.5	2.5
Bowen (1979)		1?	0.6?	1.1	4.10	950	50	14	75	20	80?						
Levinson (1980)		2	4	4	n.g.	950	55	12.5	70	25	75	475.0	27.5	12.5	237.5	13.8	6.3
Taylor & McLennan (1995)		n.g.	1	3	7.07	1400	75	8	80	29	105				1400.0	75.0	29.0
Wedepohl (1995)		0.4	0.4	2.5	4.32	716	25	14.8	65	24	56	1790.0	62.5	60.0	1790.0	62.5	60.0
This study*		2.7	1.9	3.4	3.96	1328	40	24	93	13	33	491.9	14.8	4.8	698.9	21.1	6.8
Sediments and sedimentary rocks (this study)																	
Lake sediments	31	4.5	1.5	n.d.	5.30	1549	57	26	112	15	31	344.2	12.7	3.3	1032.7	38.0	10.0
Terrigenous marine sediments	189	2.3	2.0	3.4	3.82	1469	39	25	92	12	34	638.7	17.0	5.2	734.5	19.5	6.0
Hemipelagic marine sediments	23	5.6	3.9	2.7	5.04	2446	122	25	99	23	37	436.8	21.8	4.1	627.2	31.3	5.9
Pelagic marine sediments	153	9.5	8.0	1.4	3.94	7106	363	36	130	101	197	748.0	38.2	10.6	888.3	45.4	12.6
Marine shales	41	3.3	1.4	n.d.	3.60	513	32	18	83	13	31	155.5	9.7	3.9	366.4	22.9	9.3

*An average value of lake sediments, terrigenous marine sediments and marine shales; n.g.:not given; n.d.:not determined.

clearly higher than those of the cosmic abundance ratios (Table 8). This suggests that the Pt or Pd derived from cosmic material is not so significant.

The Pt/Pd ratio of this study for lake and marine sediments, and marine shales varies from 1.2 to 3.0, and that of international igneous rock reference materials and sea water is 1.7 (Table 3) and about 5 (Goldberg, 1987), respectively. These results indicate that Pt abundance of the crustal materials are higher than that of Pd. As shown in Table 8, the values of Mn and Cu in the hemipelagic and pelagic sediments are higher than those of crustal abundances. In this study therfore, the average values of Pt (2.7 ppb) and Pd (1.9 ppb) for 281 samples containing 31 lake sediments, 189 terrigenous marine sediments and 41 marine shales are tentatively recommended as the crustal abundance (Table 8).

5. Conclusions

Platinum and Pd in the marine sediments are more abundant in the Central Pacific than the coastal areas around the Japanese islands. Among all the studied sediments and sedimentary rocks, Pt is generally higher than Pd. However, Pd-rich sediments, especially siliceous ooze, are observed in the Central Pacific high productivity zone along the equator. Although the Pt and Pd abundances and water depths of the sampling locations are not correlated, there are clear negative correlation between the Pt and Pd abundances and sedimentation rates of the studied regions. It is considered that most parts of Pt and Pd in the marine sediments are derived mainly from crustal materials, and are precipitated as the elemental and oxide forms by the involvements in biological transport processes. The global distribution patterns of Pt and Pd have been controlled by the supplying amounts of crustal and biogenic sources materials. The crustal abundances of Pt and Pd are tentatively estimated 2.7 ppb and 1.9 ppb, respectively, based on analytical data for 281 sediments and sedimentary rocks.

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Table A-1 Analytical results for marine sediments.

Sample No.	Station No.	W. D. (m)	Location (cm)	Pt (ppb)	Pd (ppb)	Au (ppb)	Fe (%)	Mn (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)	Co (ppm)	Ni (ppm)	T.S (%)	Org. C (%)	Al (%)
Obama Bay																
1	I-1	7	Surface	3.8	1.5	0.5	4.10	800	20	12	88	19	21	0.06	0.23	6.14
2	I-2	9.1	Surface	2.2	2.0	1.5	4.28	630	38	19	99	16	27	0.11	0.81	6.78
3	IV-3	20.7	Surface	3.3	1.3	1.1	4.00	670	23	18	82	15	30	0.21	0.82	6.67
4	IV-4	23.3	Surface	2.0	1.1	3.2	3.78	740	20	17	82	14	34	0.17	0.76	6.83
5	IV-6	26	Surface	3.2	1.6	1.3	4.50	970	32	26	90	17	40	0.17	1.19	7.20
6	VI-2	12.2	Surface	5.4	2.1	2.3	5.19	830	73	31	123	21	50	0.21	1.35	n.d.
7	X-2	4.4	Surface	4.9	2.9	3.5	5.73	1380	89	36	140	23	41	0.20	1.59	8.31
8	X-3	4.4	Surface	5.1	0.8	1.2	4.40	610	60	13	116	19	21	0.04	0.20	6.46
9	X-4	4.5	Surface	3.0	2.1	2.2	4.98	820	50	22	122	20	46	0.15	1.18	7.41
10	X-5	4	Surface	4.4	1.9	4.1	6.10	1580	68	37	159	24	54	0.29	1.53	n.d.
Suruga Bay																
11	39	20	Surface	2.1	0.6	0.3	1.88	480	8	14	49	9	14	0.06	0.13	6.51
12	40	70	Surface	6.1	2.6	2.3	3.52	620	32	23	102	13	24	0.12	0.69	7.83
13	41	418	Surface	2.2	2.7	1.7	3.60	470	33	25	99	11	28	0.12	0.80	7.52
14	42	356	Surface	3.3	3.2	1.5	3.60	440	28	25	97	14	28	0.13	0.89	7.52
15	43	180	Surface	1.6	1.5	0.6	4.43	530	9	15	88	14	16	0.08	0.34	5.40
16	44	2000	Surface	3.9	3.4	2.2	4.34	550	47	19	90	15	27	0.22	0.84	7.30
17	45	1330	Surface	3.0	1.6	1.9	3.52	490	35	20	99	16	29	0.20	1.31	7.30
18	46	595	Surface	3.2	3.3	1.5	3.53	490	36	18	90	10	27	0.15	1.21	7.20
19	47	135	Surface	3.2	0.8	0.5	3.20	1020	4	19	69	10	8	0.19	0.37	4.76
20	106	367	Surface	2.7	1.7	2.3	4.03	530	32	17	97	15	21	0.21	1.12	7.30
21	107	1128	Surface	2.6	3.0	1.8	3.96	520	46	15	101	14	34	0.13	1.06	7.46
22	108	823	Surface	3.1	3.1	3.1	4.20	800	40	20	102	15	40	0.17	1.07	n.d.
23	109	400	Surface	3.2	2.5	2.9	4.03	480	51	23	114	16	45	0.15	1.03	7.52
24	110	17	Surface	2.9	2.5	1.4	4.00	720	32	14	100	17	55	0.08	0.36	7.15
South of Kii Strait																
25	334	1355	20-32	2.4	1.6	1.4	2.92	370	29	13	94	13	36	0.18	1.32	6.88
26			84-94	2.0	1.5	1.5	2.80	360	24	12	101	9	33	0.33	1.27	6.67
27			164-172	2.1	1.6	1.9	2.80	360	22	12	103	11	28	0.34	1.02	6.88
28			244-253	2.2	1.6		2.81	330	21	13	243	8	25	0.40	1.14	n.d.
29			342-350	2.9	1.6	0.8	3.58	550	22	13	116	14	44	0.39	0.74	7.36
30			423-432	1.6	1.6	1.4	3.41	540	21	12	81	15	40	0.35	0.54	7.46
31	327	1566	37-44	2.4	1.7	1.0	2.78	350	26	12	82	11	28	0.13	0.92	7.15
32			210-220	5.0	1.4	1.6	2.87	400	25	15	85	12	27	0.30	0.78	7.41
33			440-444	4.4	1.4	0.7	3.08	400	27	14	79	11	28	0.34	0.62	7.57
34			570-580	2.8	1.5	1.0	3.20	420	24	15	79	11	31	0.35	0.66	n.d.
35	353	1645	55-64	2.5	2.1	1.4	2.83	370	31	15	83	11	31	0.24	1.30	6.88
36			220-230	2.3	1.7	0.5	2.84	410	23	15	87	10	26	0.39	1.00	7.09
37			290-295	2.8	1.2	1.6	2.26	410	19	10	69	12	9	0.26	0.47	6.03
38	318	2070	17-25	2.1	2.8	1.8	2.71	400	37	15	88	12	32	0.20	1.20	6.93

Table A-1 Continued

Sample No.	Station No.	W. D. (m)	Location (cm)	Pt (ppb)	Pd (ppb)	Au (ppb)	Fe (%)	Mn (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)	Co (ppm)	Ni (ppm)	T.S (%)	Org. C (%)	Al (%)
39			97-107	2.4	1.8	2.1	2.80	350	34	20	77	10	31	0.26	0.92	7.36
Off Noutheast Japan																
40	464	750	28-33	3.0	1.4	1.0	3.41	590	25	12	76	9	23	0.49	1.68	6.88
41			78-82	2.3	1.5	1.0	2.81	300	25	12	76	8	29	0.70	1.92	5.45
42			127-132	3.0	1.3	1.0	2.83	290	25	11	70	7	30	0.85	2.03	5.40
43	467	1150	37-50	3.2	1.4	1.9	3.12	320	28	13	99	5	40	0.91	1.67	0.00
44			127-140	6.0	2.1	1.2	3.86	430	28	13	90	6	43	1.36	1.08	6.46
45			157-175	2.5	2.1	1.3	3.96	460	30	14	88	6	48	1.36	0.86	7.41
46			235-250	2.5	2.0	1.7	3.76	480	32	14	91	8	53	1.33	0.93	7.09
47			358-372	3.0	2.4	1.2	3.82	470	26	12	99	6	41	1.52	1.00	6.93
48	470	1650	6-17	3.4	2.3	2.2	3.00	350	27	11	90	4	23	0.79	1.70	5.77
49			190-200	2.8	1.8	2.3	3.46	520	27	10	90	5	20	0.95	1.19	6.62
50			310-320	3.2	2.3	1.9	3.37	390	37	12	104	8	29	0.90	1.61	6.40
51	479	1850	18-22	3.4	2.7	3.1	2.83	390	38	12	89	8	18	0.60	1.92	5.03
52			98-102	2.6	1.7	1.2	3.35	500	32	15	72	13	21	0.49	0.68	7.15
53			168-172	2.8	2.7	1.9	3.50	410	41	15	90	14	28	0.78	1.09	6.67
54			248-252	3.0	1.8	2.8	3.16	490	24	12	61	11	18	0.46	0.52	6.35
55	476	4770	48-52	3.5	2.3	3.7	2.34	270	53	10	82	8	17	0.37	2.15	4.71
56			98-102	2.8	2.2	4.2	2.44	260	58	10	79	7	17	0.39	1.86	4.71
57			188-192	3.4	2.0	3.7	3.10	390	43	10	73	9	18	0.45	1.45	6.09
58			298-302	3.4	2.4	3.3	2.67	330	44	9	81	7	18	0.53	1.77	5.35
59			448-452	4.0	2.0	3.6	2.63	260	63	7	80	6	13	0.60	1.95	4.71
60			548-552	3.3	3.3	4.0	2.70	280	60	8	88	6	20	0.73	2.11	4.71
The Japan Trench																
61	450	5180	18-22	3.2	3.3	4.6	3.32	470	104	15	100	14	31	0.47	0.96	6.09
62			298-302	3.0	2.6	2.8	4.35	520	77	19	93	18	41	0.51	0.78	6.93
63	442	5400	80-95	4.7	1.8	2.6	3.98	400	73	18	90	15	36	0.20	0.67	7.04
64			172-185	3.1	1.2	1.8	2.96	460	21	13	68	9	19	0.58	0.55	6.35
65			320-335	3.1	2.1	2.4	4.06	530	64	16	97	12	31	0.12	0.36	7.46
66			450-462	2.8	2.1	3.4	4.17	430	54	17	97	8	30	0.16	0.30	7.30
67	455	7050	0-20	2.1	1.5	2.0	2.62	770	36	14	55	4	8	0.17	0.51	6.25
68			160-180	2.3	1.8	3.6	3.06	560	43	9	85	5	15	0.63	1.19	5.77
69			340-355	2.8	2.5	4.0	2.66	840	77	10	74	5	20	0.39	0.94	5.35
70			430-445	2.4	2.4	4.1	2.82	560	83	11	75	6	21	0.40	1.11	5.24
71	438	7300	30-45	3.3	1.6	4.1	3.80	550	70	14	99	12	33	0.80	1.10	6.88
72			180-195	3.0	1.6	2.8	3.70	520	68	19	95	12	29	0.68	0.96	6.83
73			300-315	2.4	1.5	3.9	3.82	550	65	19	93	13	36	0.74	0.97	7.04
74			460-475	1.1	0.9	2.3	3.50	640	16	11	74	10	13	0.40	0.15	6.83
75	471	7330	180-194	2.3	2.5	4.5	2.87	350	85	11	83	6	21	0.51	1.18	5.29
76			300-315	1.9	2.9	4.4	3.04	370	94	10	91	7	25	0.57	1.56	5.77
77			470-485	3.8	2.6	4.6	3.31	450	89	13	96	10	27	0.42	1.05	6.30
78	447	7400	18-22	5.5	3.1	4.6	3.01	380	95	15	71	10	18	0.22	1.22	5.82
79			198-202	3.8	3.0	4.3	3.38	520	98	12	77	10	20	0.58	1.10	5.66
80			398-402	3.2	3.5	5.0	3.32	400	104	12	74	9	20	0.54	1.16	5.66
81	449	8805	48-52	2.4	1.3	2.3	2.52	1000	60	13	69	9	7	0.17	0.53	5.93
82			98-102	1.9	3.2	3.3	2.91	990	110	14	68	13	18	0.20	0.74	5.24
83			198-202	2.8	3.4	3.8	2.80	1100	108	14	75	14	25	0.18	0.67	5.40
84			298-302	3.2	2.8	3.7	2.43	1650	89	6	71	11	21	0.18	0.50	5.19
85			398-402	2.7	2.1	3.8	3.30	1570	82	8	62	13	23	0.41	0.68	5.08
86			498-502	2.0	2.4	3.5	2.71	900	101	12	76	15	23	0.13	0.76	5.19
The Ryukyu Trench																
87	207	1830	Surface	3.2	3.1	5.5	2.15	1260	41	21	63	10	38	n.d.	n.d.	4.66
88	206	2490	Surface	2.6	2.8	5.0	2.45	1000	50	21	67	10	32	n.d.	n.d.	5.29
89	389	7110	0-4	2.6	2.0	3.5	5.03	1250	61	25	111	19	64	n.d.	n.d.	8.95

Table A-1 Continued

Sample No.	Station No.	W. D. (m)	Location (cm)	Pt (ppb)	Pd (ppb)	Au (ppb)	Fe (%)	Mn (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)	Co (ppm)	Ni (ppm)	T.S (%)	Org. C (%)	Al (%)
90			98-102	2.2	2.0	2.7	5.12	510	31	28	112	17	60	n.d.	n.d.	8.95
91			228-232	1.3	2.0	1.4	4.71	680	36	24	103	15	54	n.d.	n.d.	8.84
92	399	2880	Surface	2.2	1.3	0.5	0.74	1000	42	24	30	9	50	n.d.	n.d.	1.96
93	200	1180	Surface	2.3	2.1	1.7	2.62	460	23	28	63	11	25	n.d.	n.d.	4.87
94	193	2930	Surface	3.7	3.5	7.5	3.10	1180	61	25	81	14	42	n.d.	n.d.	6.67
95	202	5715	0-4	5.2	4.1	6.0	4.77	3450	122	35	108	30	80	n.d.	n.d.	8.63
96			98-102	6.5	3.9	7.4	4.92	2800	121	33	108	33	75	n.d.	n.d.	8.68
97			198-202	4.8	4.0	4.6	4.73	2960	122	31	107	33	63	n.d.	n.d.	8.73
98			298-302	3.7	4.1	7.3	4.91	2850	113	32	102	30	72	n.d.	n.d.	8.84
99			428-432	3.7	3.7	5.1	5.00	3080	120	32	106	30	74	n.d.	n.d.	8.63
100			548-552	4.8	4.6	3.3	5.07	3500	135	36	108	33	76	n.d.	n.d.	9.05
Shichito-Ioujima Ridge																
101	RC-317	1403	Surface	1.6	1.2	15.2	2.60	2460	32	54	107	4	8	n.d.	n.d.	6.93
102	307	2154	Surface	3.2	2.5	4.6	2.99	7760	57	23	92	8	53	n.d.	n.d.	5.77
103	322	2105	Surface	3.0	2.6	n.d.	3.02	10600	50	22	100	6	48	n.d.	n.d.	n.d.
104	341	2224	Surface	3.5	2.8	5.0	3.00	9500	50	17	101	8	44	n.d.	n.d.	n.d.
105	358	2540	Surface	5.4	7.1	n.d.	4.88	2500	104	19	87	15	25	n.d.	n.d.	n.d.
106	362	2784	Surface	2.1	2.1	2.2	3.30	1710	41	12	86	7	12	n.d.	n.d.	n.d.
107	P445	3303	Surface	2.8	3.3	7.3	2.45	2000	93	30	92	9	30	n.d.	n.d.	n.d.
108	P443	4123	Surface	7.1	8.2	2.4	6.39	1380	130	20	86	25	20	n.d.	n.d.	9.37
The Mariana Ridge																
109	1534	3835	0-4	4.2	2.9	6.0	4.60	2180	112	23	91	16	21	n.d.	n.d.	5.98
110			98-102	5.5	3.2	2.6	6.24	1410	143	13	91	19	18	n.d.	n.d.	7.36
111			198-202	7.5	3.2	4.0	4.58	1400	91	22	80	15	28	n.d.	n.d.	6.30
112			298-302	4.0	2.3	2.6	3.34	1480	60	25	68	12	23	n.d.	n.d.	5.72
113			398-402	6.5	3.3	3.3	4.47	1800	152	24	79	15	28	n.d.	n.d.	6.19
114	1532	4535	0-4	8.8	3.3	4.6	5.46	3000	132	24	114	21	32	n.d.	n.d.	7.20
115			98-102	5.0	2.3	2.8	4.45	2610	100	20	87	17	25	n.d.	n.d.	6.25
116			198-202	9.4	5.7	3.2	4.96	1350	105	19	87	16	22	n.d.	n.d.	6.40
117			298-302	4.7	4.0	3.4	5.33	2460	147	20	92	19	29	n.d.	n.d.	7.41
118			498-502	3.7	3.8	3.0	5.64	1900	99	20	95	20	23	n.d.	n.d.	7.30
119	1493	2480	Surface	2.0	2.2	1.7	3.95	1700	42	21	101	11	8	n.d.	n.d.	6.35
120	1494	2538	0-4	6.0	5.4	2.3	4.50	1460	131	35	85	17	14	n.d.	n.d.	6.19
121			98-102	2.8	4.5	1.6	4.32	1460	121	24	81	16	15	n.d.	n.d.	6.03
122	1496	2525	Surface	1.8	2.2	1.6	4.48	1700	54	18	100	8	8	n.d.	n.d.	7.41
123	1501	3195	8-12	1.3	2.5	1.6	4.31	1900	68	20	132	11	13	n.d.	n.d.	7.36
124			78-82	3.1	2.3	1.7	3.06	790	64	19	67	7	9	n.d.	n.d.	5.13
125	1517	5975	Surface(a)	3.3	3.4	0.4	5.62	3510	99	9	97	20	34	n.d.	n.d.	7.52
126			Surface(b)	5.0	5.5	3.1	5.73	4160	188	23	114	43	120	n.d.	n.d.	7.15
127	1500	3740	Surface	5.2	4.0	2.8	4.40	3010	103	28	109	20	30	n.d.	n.d.	6.99
128	1516	4280	63-67	4.6	3.1	0.5	4.60	1610	118	16	88	15	30	n.d.	n.d.	7.94
129	1508	3200	Surface	10.0	7.2	2.8	5.38	2120	131	25	90	24	22	n.d.	n.d.	6.83
130	1512	1840	Surface	17.1	4.4	0.5	9.61	10300	365	97	245	134	275	n.d.	n.d.	8.47
131	1507	3850	Surface	7.2	8.7	6.4	6.90	2950	183	21	94	25	28	n.d.	n.d.	7.89
Mid-Pacific Mountains																
132	1647	5292	Surface	6.1	4.4	1.9	4.76	5000	268	32	132	99	148	0.26	0.34	8.31
133	1590	5287	Surface	9.8	5.9	1.1	4.35	6000	347	33	219	116	210	0.23	0.27	8.01
134	1646	5537	0-2	17.0	5.6	1.7	5.21	14800	550	59	158	237	630	0.16	0.24	7.46
135			2-4	15.2	6.5	1.3	4.92	6600	320	33	132	108	220	0.17	0.23	7.83
136			4-6	13.1	7.3	1.0	4.93	7200	330	36	134	110	226	0.17	0.22	7.73
137			9-11	11.0	5.9	0.7	4.96	7300	340	37	140	119	250	0.16	0.14	7.78
138			19-21	11.2	8.0	0.5	4.96	7900	397	42	144	134	297	0.17	0.13	7.73
139			29-31	10.0	7.8	0.4	4.98	9000	446	44	145	160	334	0.20	0.10	7.67
140	1645	5068	Suface	n.d.	n.d.	2.0	4.48	5000	274	31	126	94	138	0.24	0.37	8.22

Table A-1 Continued

Sample No.	Station No.	W. D. (m)	Location (cm)	Pt (ppb)	Pd (ppb)	Au (ppb)	Fe (%)	Mn (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)	Co (ppm)	Ni (ppm)	T.S (%)	Org. C (%)	Al (%)
141	1591	5569	Surface	5.8	7.3	1.3	5.00	4300	303	31	126	84	142	0.11	0.22	7.62
142	1644	5027	5-17	22.0	7.4	0.5	3.85	5000	255	29	128	122	295	0.18	0.16	7.97
143			192-202	21.6	11.3	0.7	2.99	10700	357	32	170	125	415	0.25	0.13	6.74
144			302-312	18.4	10.6	0.9	2.74	10600	518	34	286	97	259	0.31	0.14	6.22
145	1593	5491	Surface	15.6	8.2	1.7	5.40	6200	348	35	145	102	184	0.17	0.25	7.78
Central Pacific Basin(N)																
146	1642	5441	20-30	8.3	6.1	0.5	4.53	5300	384	35	140	86	138	0.35	0.17	8.28
147			90-100	6.8	4.6	0.7	4.56	5900	443	30	140	100	157	0.33	0.17	7.85
148			220-230	7.7	3.7	0.6	4.65	6800	505	33	153	117	203	0.29	0.15	7.46
149			320-330	7.2	4.2	1.0	4.40	6200	544	27	149	107	199	0.35	0.14	7.48
150			420-430	10.0	10.4	0.6	4.29	6700	591	29	124	107	178	0.34	0.14	7.49
151			520-530	5.3	4.8	1.0	4.42	7900	583	33	159	137	240	0.30	0.14	7.60
152			620-630	7.8	6.5	0.8	3.96	7000	611	30	159	118	217	0.26	0.13	7.84
153			680-690	10.0	8.8	0.6	3.87	7700	626	33	154	129	263	0.22	0.12	7.48
154			730-740	15.0	16.8	0.5	4.20	11000	396	35	143	151	291	0.19	0.10	7.85
155	1642	5429	Surface	4.8	6.0	1.7	4.87	4400	353	26	132	84	148	0.31	0.29	6.72
156	1641	5829	Surface	9.6	7.5	2.2	4.05	5200	443	26	128	83	147	0.27	0.38	7.31
157	2026	5936	12-17	8.1	7.2	0.9	4.78	7300	391	47	127	119	168	n.d.	n.d.	8.03
158			49-54	12.2	7.1	0.7	4.83	8160	417	52	155	121	219	n.d.	n.d.	7.65
159			99-104	10.3	7.8	0.6	4.98	8600	451	49	160	128	239	n.d.	n.d.	8.03
160			146-151	9.8	6.0	0.5	4.80	9360	499	40	168	138	279	n.d.	n.d.	7.31
161			196-201	9.2	7.6	0.5	4.60	10300	545	47	156	136	344	n.d.	n.d.	6.79
162			246-251	6.7	8.9	0.6	4.62	4030	541	53	159	115	113	n.d.	n.d.	7.06
163			296-301	9.5	14.0	0.6	4.87	12200	605	57	224	158	333	n.d.	n.d.	7.47
164			346-351	10.0	15.1	0.5	3.99	10100	530	42	341	162	346	n.d.	n.d.	7.58
165			396-401	8.7	12.3	0.5	4.11	9010	728	50	414	147	315	n.d.	n.d.	7.52
166			446-451	12.1	15.6	0.4	4.78	10600	423	39	548	149	318	n.d.	n.d.	8.11
167			496-501	7.4	12.9	0.4	4.08	10240	556	40	241	139	313	n.d.	n.d.	7.34
168			546-551	11.9	17.4	0.5	3.91	10690	673	35	233	127	346	n.d.	n.d.	6.25
169			696-701	4.1	3.9	0.3	0.20	480	42	8	38	3	12	n.d.	n.d.	0.41
170	1640	5901	Surface	6.5	5.8	1.8	4.53	6200	404	26	128	90	196	0.28	0.29	6.46
171	1640	5915	5-20	10.0	6.1	1.1	4.47	6600	385	31	127	104	160	0.27	0.24	7.83
172			127-137	8.5	8.0	0.6	4.52	9700	516	36	141	134	307	0.35	0.15	7.36
173			227-237	9.4	8.5	0.6	4.38	9200	521	37	138	124	240	0.37	0.16	7.28
174			287-297	7.4	10.0	0.6	4.43	3900	478	31	139	117	105	0.35	0.17	7.42
175			347-357	8.8	8.1	0.9	4.38	12000	637	38	151	147	348	0.33	0.16	7.52
176			427-437	9.3	10.4	0.7	4.60	11900	507	40	153	152	305	0.27	0.15	7.67
177			525-534	8.1	11.8	1.4	4.05	8000	481	31	161	121	218	0.32	0.13	7.44
178			625-635	8.3	14.3	0.6	3.72	8700	512	32	182	125	306	0.36	0.15	7.18
179			725-735	17.2	20.1	0.6	3.64	9100	387	32	179	140	294	0.35	0.16	6.72
180	1596	6009	Surface	4.6	8.0	2.1	4.63	5200	380	30	123	95	148	0.25	0.29	6.51
181	2049	6014	5-10	7.6	6.9	1.2	4.00	3340	275	49	345	89	70	n.d.	n.d.	7.16
182			55-60	8.4	5.9	0.9	4.79	6730	374	33	117	115	162	n.d.	n.d.	8.04
183			105-110	12.2	7.4	0.8	5.17	8000	430	36	159	135	185	n.d.	n.d.	7.44
184			155-160	9.0	7.0	0.7	5.04	9090	464	47	158	129	283	n.d.	n.d.	8.00
185			205-210	11.5	7.2	0.6	5.08	7880	467	45	161	138	207	n.d.	n.d.	7.72
186			255-260	9.8	7.3	n.d.	5.37	8130	497	43	211	154	217	n.d.	n.d.	7.47
187			305-310	9.3	7.4	0.6	4.98	4500	518	50	149	123	151	n.d.	n.d.	7.41
188			355-360	11.2	10.1	n.d.	4.92	4370	657	45	186	202	192	n.d.	n.d.	8.15
189			405-410	15.8	19.0	0.7	4.62	15400	567	42	226	111	633	n.d.	n.d.	7.63
190			455-460	12.5	13.7	n.d.	4.20	10110	475	35	206	128	463	n.d.	n.d.	7.86
191			505-510	10.1	17.4	0.5	4.05	9020	468	33	183	111	395	n.d.	n.d.	6.83
192			555-560	9.8	12.8	n.d.	3.73	9390	573	35	269	120	324	n.d.	n.d.	6.73
193			605-610	9.6	17.0	0.6	3.59	7040	497	27	217	73	250	n.d.	n.d.	6.64

Table A-1 Continued

Sample No.	Station No.	W. D. (m)	Location (cm)	Pt (ppb)	Pd (ppb)	Au (ppb)	Fe (%)	Mn (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)	Co (ppm)	Ni (ppm)	T.S (%)	Org. C (%)	Al (%)
194	1639	5926	Surface	n.d.	n.d.	3.2	3.71	4600	386	21	106	84	147	0.32	0.48	6.53
195	1598	5962	Surface	6.6	12.5	3.7	3.55	4500	293	28	95	80	109	0.35	0.43	6.47
196	1638	5839	Surface	3.2	4.9	2.8	3.87	3900	290	23	104	68	107	0.32	0.31	5.61
197	1638	5791	10-20	16.3	11.1	1.0	4.53	8200	456	49	152	130	221	0.34	0.17	7.44
198			124-134	9.6	11.3	0.5	4.14	8800	491	34	162	116	244	0.36	0.17	6.67
199			424-434	8.2	10.5	n.d.	2.13	5000	211	4	97	66	178	0.38	0.10	3.65
200			602-612	6.9	10.3	0.3	2.29	5600	265	8	83	76	158	0.33	0.11	4.13
201			697-707	7.4	11.8	n.d.	2.50	5200	255	18	112	66	134	0.33	0.09	4.71
Central Pacific Basin(C)																
202	1599	5245	Surface	4.1	6.3	2.3	3.32	4200	275	31	96	66	145	0.25	0.26	4.55
203	1600	5584	0-2	6.0	8.6	6.5	3.75	5450	360	27	100	82	156	0.40	0.43	5.61
204			2-4	7.2	7.9	5.2	3.79	5430	352	26	99	82	151	0.32	0.42	5.61
205			4-6	6.9	8.2	4.5	3.70	5430	358	26	100	83	158	0.31	0.39	5.61
206			9-11	6.7	7.2	2.4	4.00	6060	362	27	106	88	180	0.29	0.35	5.82
207			14-16	5.8	7.3	1.5	4.09	6250	365	26	107	87	182	0.29	0.26	5.82
208			19-21	5.0	7.6	1.2	4.24	6470	368	26	108	90	193	0.28	0.22	6.19
209			33-36	6.9	6.8	0.9	4.40	6480	370	25	115	90	191	0.32	0.23	6.25
210	1636	5747	5-12	7.0	6.0	1.9	3.52	4300	264	20	81	80	124	0.35	0.29	5.88
211			116-126	7.1	5.5	1.1	3.77	6000	289	36	166	79	133	0.33	0.17	6.48
212			226-236	7.6	6.0	n.d.	3.74	7500	304	36	130	87	193	0.37	0.17	6.25
213			316-326	6.5	6.7	1.0	4.76	7000	360	41	110	98	146	0.32	0.16	7.10
214			416-426	9.9	9.2	n.d.	4.68	7000	400	39	118	100	145	0.38	0.16	6.67
215			514-524	7.1	6.5	0.7	4.35	7300	356	36	112	96	204	0.37	0.15	6.51
216			624-634	7.0	5.8	n.d.	3.62	5700	343	33	102	80	133	0.38	0.13	5.79
217			714-724	6.4	7.5	0.9	3.33	4500	313	26	134	62	102	0.39	0.14	5.54
218	1601	5350	Surface	n.d.	n.d.	4.0	3.33	8000	409	26	116	75	252	0.41	0.61	4.78
219	1635	5351	Surface	n.d.	n.d.	4.2	2.72	3100	308	16	8	7	153	0.41	0.47	4.99
220	2583	5371	20-25	5.7	6.8	0.6	2.34	3450	362	27	101	55	179	n.d.	n.d.	3.97
221			68-73	5.1	9.0	0.6	1.73	2860	220	13	62	39	124	n.d.	n.d.	3.12
222			118-123	3.5	8.7	n.d.	1.62	2720	191	9	55	42	100	n.d.	n.d.	3.12
223			168-173	4.0	9.3	0.5	1.63	2330	189	8	56	34	91	n.d.	n.d.	3.12
224			213-218	3.6	9.8	n.d.	2.06	2760	214	20	65	36	96	n.d.	n.d.	3.55
225			268-273	4.4	10.0	0.5	2.11	3160	216	17	69	44	119	n.d.	n.d.	3.71
226			318-323	3.8	7.4	n.d.	1.68	2410	200	10	59	32	97	n.d.	n.d.	3.02
227			368-373	4.0	6.7	0.4	1.71	2600	193	11	59	35	98	n.d.	n.d.	3.07
228			427-432	3.6	5.5	n.d.	1.37	2040	151	9	42	26	70	n.d.	n.d.	2.59
229			477-482	4.3	5.9	0.4	1.64	2450	200	17	53	35	75	n.d.	n.d.	3.02
230			527-532	4.3	5.6	n.d.	1.59	2240	202	16	49	31	75	n.d.	n.d.	2.96
231			577-582	4.1	6.1	0.4	1.46	2190	185	28	47	29	66	n.d.	n.d.	2.81
232			627-632	3.5	6.7	n.d.	1.66	2580	204	33	53	31	76	n.d.	n.d.	3.02
233			697-684	4.3	6.3	0.5	2.08	3190	248	21	67	42	98	n.d.	n.d.	3.71
234			727-732	4.1	6.1	n.d.	1.90	2710	242	22	60	35	87	n.d.	n.d.	3.71
235			777-782	4.3	6.3	0.5	1.90	2710	284	16	62	35	88	n.d.	n.d.	3.76
236	1602	5389	Surface	n.d.	n.d.	4.6	3.31	4000	285	20	88	66	115	0.41	0.52	5.20
237	1634	5087	50-60	7.2	4.7	0.6	3.01	4900	293	32	88	51	126	0.34	0.11	5.22
238			138-148	3.6	5.0	1.1	3.69	6000	340	29	92	80	144	0.33	0.13	6.14
239			238-248	4.0	5.2	n.d.	3.71	6100	387	25	116	88	199	0.35	0.14	6.09
240			318-328	8.7	6.5	0.6	3.05	7000	418	21	169	70	260	0.38	0.13	5.52
241			438-448	5.2	5.7	n.d.	1.18	2200	218	4	67	17	98	0.37	0.07	2.03
242			535-545	7.0	7.6	0.6	1.36	2800	281	1	128	22	155	0.49	0.11	2.24
243			635-645	4.9	8.8	n.d.	1.02	1800	163	<1	104	5	65	0.41	0.08	1.73
244			735-745	2.0	3.8	0.5	0.69	1000	92	3	57	4	21	0.30	0.13	0.87
245	1603	5479	0-15	7.4	7.0	1.4	3.22	4200	331	19	101	58	180	0.42	0.29	5.10
246			237-247	6.3	7.0	n.d.	1.79	2000	206	<1	55	25	130	0.40	0.09	3.55

Table A-1 Continued

Sample No.	Station No.	W. D. (m)	Location (cm)	Pt (ppb)	Pd (ppb)	Au (ppb)	Fe (%)	Mn (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)	Co (ppm)	Ni (ppm)	T.S (%)	Org. C (%)	Al (%)
247			637-647	5.6	3.1	n.d.	1.33	1100	157	2	41	18	100	0.36	0.08	2.93
248	1633	5359	0-2	6.5	8.7	7.2	3.50	5610	330	24	92	58	156	0.32	0.49	4.87
249			2-4	7.0	7.5	5.7	3.61	5800	336	27	93	61	168	0.34	0.45	5.19
250			4-6	5.4	9.5	5.5	3.52	5620	336	26	95	61	168	0.33	0.36	4.87
251			9-11	5.8	8.6	3.0	2.91	5010	262	31	81	55	148	0.27	0.29	4.45
252			19-21	5.0	5.2	2.5	2.57	4300	235	31	72	45	122	0.24	0.30	3.81
253			32-34	4.9	4.8	1.8	2.96	4700	258	30	79	52	107	0.27	0.19	4.29
254	1632	5255	20-30	6.6	4.8	0.7	2.75	4600	280	27	97	54	89	0.32	0.14	4.16
255			312-322	8.0	7.3	1.0	3.83	7200	373	28	252	80	149	0.37	0.15	6.05
256			522-532	7.3	5.3	n.d.	3.22	5600	346	24	93	63	143	0.38	0.15	5.41
257			722-732	6.2	5.2	1.0	2.89	6400	346	22	87	62	183	0.41	0.13	4.71
258	1604	5457	Surface	n.d.	n.d.	5.5	3.01	3500	272	28	74	47	100	0.40	0.63	5.23
259	1605	5455	6-16	n.d.	n.d.	1.7	3.29	4500	225	43	85	53	110	0.29	0.24	4.84
260	1631	5342	Surface	12.3	6.2	3.6	3.38	3900	231	28	81	53	100	0.42	0.54	4.82
Central Pacific Basin(S)																
261	1630	5537	15-34	7.7	7.3	2.3	4.27	6000	242	32	123	77	110	0.29	0.30	5.84
262			423-433	7.9	6.9	n.d.	4.34	7400	329	38	112	90	154	0.31	0.11	5.49
263			723-733	8.2	6.4	0.9	4.42	7400	281	34	114	98	159	0.30	0.11	5.54
264	1639	5261	Surface	n.d.	n.d.	3.3	3.41	4000	260	33	86	72	140	0.43	0.44	5.13
265	1607	5698	15-30	8.0	5.6	0.9	5.69	9700	260	49	121	83	100	0.28	0.14	6.91
266	1607	5690	Surface	5.5	6.6	2.1	5.70	6300	246	41	120	72	109	0.27	0.25	6.03
267	1628	4947	10-25	8.1	3.8	0.9	2.24	4700	189	37	64	58	100	0.25	0.28	3.02
268			343-353	26.9	5.0	n.d.	4.48	15300	986	33	198	152	632	0.45	0.14	6.29
269	1609	4395	Surface	1.4	2.1	1.2	0.47	980	52	22	16	8	20	0.16	0.15	0.64
270	1627	4995	0-2	8.5	8.2	3.1	4.49	11000	400	47	108	132	235	0.37	0.43	5.13
271			2-4	10.6	7.8	1.8	4.48	11000	388	44	110	132	237	0.36	0.33	4.98
272			4-6	11.0	7.0	1.4	4.50	11200	391	46	111	134	241	0.33	0.27	5.19
273			9-11	12.2	9.3	1.1	5.10	12200	430	42	126	147	265	0.35	0.26	5.61
274			19-21	13.3	8.0	0.9	5.33	13000	460	46	131	160	292	0.35	0.23	5.82
275			32-34	12.6	9.2	0.8	5.21	12700	448	42	127	158	304	0.39	0.18	5.82
276	1625	4650	Surface	5.5	2.6	1.5	2.03	4900	180	36	56	59	106	0.23	0.19	2.28
277		4650	Surface	16.2	5.7	2.1	2.56	3200	233	47	67	87	144	0.32	0.31	3.13
278	1612	4805	Surface	14.5	9.6	1.3	5.00	13600	412	126	134	154	313	0.36	0.29	4.87
279	1624	3889	Surface	3.2	1.1	0.9	0.27	860	41	21	12	3	12	0.18	0.12	0.37
280	1623	4561	Surface	n.d.	n.d.	1.4	1.71	4600	130	36	50	59	58	0.21	0.20	1.67
281	1613	2952	Surface	2.4	0.9	1.7	0.15	420	24	19	10	1	7	0.17	0.13	0.21
Penrhyn Basin																
282	1622	5235	5-20	19.0	6.1	0.6	5.96	9400	363	60	118	144	214	0.18	0.17	7.94
283			178-188	30.8	8.5	n.d.	5.78	9700	312	81	129	327	402	0.29	0.09	6.42
284			575-585	27.4	6.7	0.3	5.69	9100	328	74	147	256	389	0.27	0.08	6.44
285	1621	5312	Surface	n.d.	n.d.	1.5	6.60	18300	412	92	149	248	358	0.26	0.41	6.86
286	1616	5690	Surface	n.d.	n.d.	1.5	7.45	15300	383	105	143	192	223	0.33	0.45	7.06
287	1620	5285	Surface	19.6	9.5	1.2	6.41	18200	412	113	145	231	347	0.31	0.35	6.70
288	1619	5111	Surface	29.6	7.3	1.4	7.45	16000	367	99	139	206	267	0.34	0.36	6.73
289	1617	5162	0-2	19.4	10.0	1.7	8.49	17200	436	82	172	228	270	0.35	0.43	7.04
290			2-4	21.6	9.6	1.3	8.38	17500	424	87	172	225	273	0.35	0.37	7.09
291			4-6	23.7	10.4	1.2	8.61	17600	433	87	173	232	280	0.33	0.30	7.15
292			9-11	21.5	10.5	1.1	8.65	17000	439	89	175	215	266	0.32	0.23	7.15
293			19-21	20.6	8.7	0.7	8.50	16200	432	86	171	202	246	0.30	0.18	7.20
294			29-31	19.8	8.7	0.5	8.01	15200	393	78	159	200	244	0.28	0.14	7.41
295	1618	5453	Surface	20.0	7.4	1.2	7.86	19800	349	92	146	197	244	0.35	0.37	6.90

n.d.: not determined.

Table A-2 Analytical results for lake sediments.

Sample No.	Station No	Location (cm)	Pt (ppb)	Pd (ppb)	Fe (%)	Mn (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)	Co (ppm)	Ni (ppm)
Lake Suwa											
296	2	0-15	5.1	1.4	4.81	1150	65	27	108	17	29
297		30-45	5.8	1.3	5.56	1350	63	32	116	19	47
298		80-101	5.7	1.4	4.92	1220	60	24	102	16	45
299	3	15-30	5.6	1.2	6.06	1450	69	27	120	20	45
300		30-60	5.8	1.2	4.98	1080	84	24	109	20	54
301		60-80	4.9	1.3	4.86	1040	57	23	117	20	41
302	11	25-35	6.6	1.0	5.00	680	53	25	101	19	23
303		80-92	6.3	1.0	5.02	740	51	23	78	17	22
Lake Kasumigaura											
304	10	18-23	11.1	2.2	5.88	1150	66	33	130	10	38
305		28-33	5.1	1.5	5.76	740	57	16	92	9	35
306		38-43	4.4	1.4	5.48	560	57	14	83	11	28
307		73-78	4.6	1.1	5.23	520	51	17	96	15	32
308		93-98	6.6	1.2	5.93	900	46	14	82	12	25
309		108-113	5.7	1.5	5.29	1600	41	12	73	9	19
310		118-123	4.7	1.0	6.10	1310	40	11	74	10	21
311		128-133	4.0	1.3	5.92	1600	35	11	75	10	19
312	99	15-30	5.1	1.6	4.76	910	65	24	93	15	23
313		65-70	3.5	1.5	5.47	800	50	23	98	18	30
314		125-130	4.5	1.1	5.80	1960	29	19	89	12	15
315		145-150	4.4	0.8	5.80	1830	33	16	87	14	23
316	125	19-24	6.7	1.2	5.40	950	62	26	110	16	24
317		39-44	3.7	1.0	5.77	930	56	16	89	15	25
318		109-114	3.3	1.0	5.33	1530	27	15	83	10	15
319		139-144	3.6	0.7	4.63	1070	21	10	80	9	14
Lake Biwa											
320	31	0-5	2.2	2.8	4.69	4380	82	50	161	20	38
321	38	0-5	2.2	2.7	4.92	4320	79	39	172	19	44
322	42	0-5	2.0	2.6	4.93	2500	82	47	180	19	43
323	76	0-5	2.2	2.5	4.58	2880	74	40	160	18	40
324	77	0-5	1.8	2.0	5.00	2950	72	35	138	17	41
325	130	0-5	1.7	2.4	4.50	1920	66	54	180	17	38
326	131	0-5	2.0	3.0	4.66	2000	65	53	183	18	33

Table A-3 Analytical results for marine shales.

Sample No.	Locality	Original sample no.	Pt (ppb)	Pd (ppb)	Fe (%)	Mn (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)
	Ryoke Terrane, Izumi G., Cretaceous								
327		70s-285	1.8	1.5	1.88	230	31	26	87
328		70s-309	2.5	0.8	3.24	460	19	25	89
329		70s-310	2.4	1.0	3.02	460	18	21	66
330		70s-311	2.2	0.7	1.12	80	16	16	52
331		70s-315	3.2	0.6	1.17	80	40	32	75
332		70s-201	2.0	0.8	1.68	80	21	14	37
	Chichibu Terrane, Chichibu B., Jurassic								
333		70s-255	2.1	1.4	4.39	620	40	14	93
334		70s-118	2.6	1.8	4.09	460	23	23	107
335		70s-231	2.8	0.9	3.67	850	31	20	84
336		70s-249	2.5	0.9	3.35	390	23	46	77
337		70s-211	1.6	0.8	3.53	460	22	22	78
338		70s-245	1.8	0.7	2.90	700	16	34	73
	Shimanto Terrane, North Uwa B., Cretaceous								
339		70s-101	3.0	1.1	3.45	390	35	26	95
340		70s-105	1.4	1.6	4.12	620	50	20	111
341		70s-63	3.7	3.0	4.45	1550	66	16	100
342		70s-109	1.6	0.7	3.02	310	15	12	80
	Shimanto Terrane, South Uwa B., Cretaceous								
343		70s-47	1.6	1.3	2.63	150	40	14	66
344		70s-84	3.4	1.2	3.29	310	27	23	75
	Shimanto Terrane, Nakasuji B., Paleogene								
345		70s-76	2.0	0.8	3.68	770	57	28	98
346		70s-11	3.5	0.9	2.34	160	18	11	72
347		70s-14	5.5	2.7	3.67	310	35	14	118
	Shimanto Terrane, Shimizu B., Paleogene								
348		70s-10	3.3	0.9	4.24	460	18	23	105
349		70s-22	3.6	1.9	4.45	620	49	18	93
350		70s-7	3.3	2.0	3.85	230	33	8	87
351		70s-6	3.3	0.9	3.54	230	18	14	80
	Kawasaki drill hole, Kanagawa pref., Quaternary								
352		59.9 m	3.5	1.7	3.62	490	34	14	87
353		109.6 m	4.0	0.9	6.20	850	32	14	78
354		144 m	8.5	2.6	3.91	470	31	14	91
355		213 m	4.0	1.6	3.72	740	15	9	67
356		275 m	6.1	1.1	3.59	490	27	15	78
357		337 m	3.9	1.5	4.08	490	32	17	85
358		339 m	3.6	2.2	3.46	710	16	9	62
	Kawasaki drill hole, Kanagawa pref., Neogene								
359		361.1 m	5.7	1.7	4.00	510	36	16	88
360		379.9 m	5.2	1.8	4.38	610	38	18	84
361		446 m	3.8	1.2	5.34	740	37	14	83
362		470.7 m	2.6	1.4	4.55	850	40	15	85
363		500 m	4.8	1.0	3.98	560	37	15	82
364		513 m	4.2	1.5	4.65	740	35	15	80
365		558.4 m	3.7	1.4	4.26	540	43	16	81
366		585 m	4.7	1.6	4.03	470	44	14	85
367		608 m	1.7	1.9	5.11	740	45	14	86

海底堆積物中の白金とパラジウムの存在量とその地球化学的挙動

寺島　滋・三田直樹・中尾征三・石原舜三

要　旨

日本列島周辺海域(陸源性堆積物)，マリアナ海嶺(半遠洋性堆積物)，太平洋中央部(遠洋性堆積物)で採取された海底堆積物284試料について，溶媒抽出分離―黒鉛炉原子吸光法によりppbレベルの微量の白金(Pt)とパラジウム(Pd)の正確な存在量を定量し，地球化学的挙動を考察した．比較のため，湖沼堆積物及び堆積岩類も分析した．遠洋性堆積物は，陸源性堆積物に比べ平均値で約3倍のPt, Pdを含有しており，半遠洋性堆積物は中間的な含有量であった．多くの試料は，PdよりもPtに富む特徴が認められたが，赤道付近の生物生産が活発な海域にはPdに富む珪質堆積物が分布しており，生物濃縮の可能性を示唆している．試料を採取した地点の水深とPt, Pdの含有量の間には一定の傾向は存在しないが，堆積速度との間には負の関係があり，堆積速度の遅い海域で高濃度を示す．深海底堆積物におけるPt，Pdの供給源として宇宙物質の影響が指摘されているが，Mn/Pt, Cu/Pt等の存在比は宇宙物質のそれよりも地殻物質に類似している．地殻物質の風化・変質により溶出したPt, Pdが，主として難溶性の酸化物態あるいは還元されて元素態となり，鉄やマンガン等の遷移金属とともに海底堆積物に移行すると考えた．堆積層内におけるPt, Pd等の鉛直分布の特徴から，初期続成作用に伴う移動と濃集の影響は，極く一部を除いて無視できると判断された．これまでに報告されたPt, Pdの地殻存在量(Pt, Pdとも0.4-10 ppb)にはかなりのばらつきが認められるが，本研究で陸源性堆積物，湖底堆積物，堆積岩等合計281試料の分析値から算出した地殻存在量はPt 2.7 ppb，Pd 1.9 ppbである．