Minor Elements in Shallow-Water Deposits from Nanao Bay, Japan*

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Abstract: The minor elements Ni, Co, Cu, Zn, Pb, Cd, Cr, V, Mo, Zr and Ga were studied in 21 samples of shallow-water deposits from West, South and North Bays of Nanao. Ni (av. 14 ± 5 ppm), Co (av. 6 ± 2 ppm), Zn (av. 51 ± 7 ppm), V (av. 39 ± 6 ppm) and Mo (av. 0.5 ± 0.3 ppm) were not so much concentrated in these deposits as in pelagic deposits, but only Ga (av. 12 ± 3 ppm) shows concentration similar to that in pelagic sediment. It is characteristic of these deposits that Pb (av. 55 ± 6 ppm) and Zr (av. 101 ± 46 ppm) are notably abundant in them, compared with those of shallow-water deposits from all the coasts of Honshu, Japan, Korean coast and Gulf of Paria. The constancy of Co/Ni ratios was found in these deposits and red clays despite large difference in abundance of these elements in them. There are positive correlations between the contents of Ni, Zn and Ga and content of Al, and also between the contents of V and S.

1. Introduction

In the previous paper (YAMAMOTO, 1968) the analyses of major chemical constituents on the 21 samples of shallow-water deposits from West, South and North Bays of Nanao were reported with geological outline. In the present investigation the minor elements, Ni, Co, Cu, Zn, Pb, Cd, Cr, V, Mo, Zr and Ga in the same samples were determined.

The contents and the regional characteristics of distribution of elements in the deposits of each bay were clarified together with relations between the contents of major and minor elements. The comparison of abundance values of minor elements in these deposits with the average values of other shallow- and deep-sea sediments or of rocks is also discussed.

2. Samples and methods of analyses

Samples air-dried were pulverized, dried at $105-110^{\circ}\text{C}$ to a constant weight, and subjected to the analysis. The samples were classified into 3 groups [West Bay (Sample No. 1-5P), South Bay (Sample No. 6-10₁), and North Bay (Sample No. 11-19)] according to the geographical distribution.

Determinations of Ni, Co, Cu, Zn, Pb, Cd, Cr, V and Mo were done by the colorimetric method of SANDELL (1950) with some minor modifications (ISHIBASHI *et al.*, 1958, 1959, 1960, 1962, 1964; UEDA, 1957; YAMAMOTO, 1960). Zirconium was determined by the Alizaline S method of DEGENHARDT (1956), Gallium was analyzed fluorometrically by the method of NISHIKAWA (1958).

3. Results and discussion

The results of the analyses of minor elements in Nanao Bay deposits are given in Table 1. In Table 2, the average values for West, South and North Bays are shown. The determination was carried out with 10% of error. The ratios of each minor element concentration in the deposits and those in igneous or pelagic sediments are summarized in Figs. 1 and 2.

The conclusions drawn from the distributions are found in the paragraphs on differences below.

Nickel and Cobalt—The nickel and cobalt contents of these deposits range from 4 to 24 ppm and 2 to 12 ppm with the average of 14 ± 5 and 6 ± 2 ppm respectively.

The deposits of Nanao Bay show values little less than those of the shallow-water deposits of all the coasts of Honshu, Japan and of Korean coast in the average contents of these elements.

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Table 1. Minor elements of the shallow-water deposits in Nanao Bay.

Sample No.	1	2	3	4	5	5P	6	7	8	9	10	10 ₁	11	12	13	14	15	16	17	18	19
Ni	18	4	14	15	16	7	16	10	19	17	15	10	16	9	11	16	19	24	19	8	17
Co	3	4	5	2	6	7	6	5	5	7	6	7	6	2	8	9	8	9	12	5	5
Cu	19	21	11	15	66	9	20	56	17	15	15	17	38	21	23	24	35	32	26	64	15
Zn	31	27	41	47	29	13	73	54	51	54	56	40	46	28	61	61	98	97	46	38	79
Pb	30	78	29	32	50	11	42	42	44	47	75	67	64	46	66	63	75	74	76	62	77
Cd	0.61	0.04	0.02	0.04	0.20	0.20	0.09	0.10	0.22	0.07	0.09	0.11	0.11	0.08	0.04	0.04	0.06	0.06	0.09	0.04	2.07
Cr	36	15	23	16	45	18	42	22	16	61	24	22	19	13	40	79	16	17	48	21	37
V	34	57	44	36	17	3	67	31	56	72	54	46	30	17	34	42	47	39	44	17	22
Zr	152	88	127	141	126	54	113	41	36	37	80	71	82	31	124	155	150	161	154	33	163
Mo	0.7	0.6	0.4	1.4	1.0	0.7	0.4	0.5	0.8	0.6	0.4	0.4	0.2	0.2	0.2	0.3	0.6	0.7	0.2	0.3	0.4
Ga	17	16	15	18	14	8	16	11	14	13	10	9	12	10	9	13	12	11	14	7	12

Fig. 1. Ratios of average elemental abundance in deposits of Nanao Bay and igneous rocks. Ranges are indicated by the lengths of the horizontal lines, and averages by a short vertical line.

□ : 22 Red clays from the Pacific (GOLDBERG and ARRHENIUS)
 ■ : 22 Red clays from the North Pacific (TATSUMOTO)
 Fig. 2. Ratios of average elemental abundance in deposits of Nanao Bay and the Pacific pelagic sediments. Ranges are indicated by the lengths of the horizontal lines, and averages by a short vertical line.

Table 2. Average minor elements in the shallow-water deposits of three groups from Nanao Bay.

	Deposits of West Bay (6 specimens)	Deposits of South Bay (6 specimens)	Deposits of North Bay (9 specimens)	All deposits of Nanao Bay (21 specimens)
Ni	12±5ppm	15±3ppm	15±5ppm	14±5ppm
Co	5±2	6±1	7±3	6±2
Cu	24±19	23±15	31±14	27±16
Zn	31±11	55±10	62±24	51±7
Pb	38±21	53±13	67±7	55±6
Cd	0.22±0.21	0.11±0.05	0.29±0.63	0.22±0.43
Cr	25±12	31±16	32±20	30±5
V	32±18	54±12	32±11	39±6
Zr	115±34	63±28	117±51	101±46
Mo	0.8±0.5	0.5±0.5	0.3±0.4	0.5±0.3
Ga	15±2	12±2	11±2	12±3

Comparing with the average figures of other workers (TATSUMOTO, 1956; GOLDBERG and ARRHENIUS, 1958; SANDELL *et al.*, 1943), the average contents of nickel and cobalt in these deposits are depleted than in red clays or igneous rocks.

The average ratio of Co to Ni in Nanao Bay sediments is 0.43 and is in good agreement with that of sediments of the Pacific red clay (0.50, GOLDBERG *et al.*, 1958; 0.37, TATSUMOTO, 1956) or that of hydrolyzate (0.4, RANKAMA, 1950), in spite of a great differences exist on the contents of Ni and Co among them.

As shown in Fig. 3, a positive correlation between the contents of nickel and aluminum was found. A similar relation can be found between the contents of cobalt and aluminum.

Copper and Zinc—The average copper content in these deposits is 27±16 ppm ranging from 9 to 66 ppm, and the zinc ranges from 13 to 98 ppm with the average of 51±7 ppm.

The average values of copper and zinc in the deposits in Nanao Bay, are less than those in pelagic sediments or in igneous rocks.

The average Cu/Zn ratio for these deposits, 0.53, agrees those of 0.45 and 0.53 for igneous rocks (SANDELL and GOLDICH, 1943; LUNDEGARDH, 1946, 1947), but differ from that of 0.73 for red clay (TATSUMOTO, 1956).

The relation between the contents of zinc and aluminum is shown in Fig. 4.

Fig. 3. Relationship between the contents of nickel and aluminum in deposits of Nanao Bay.

There is a positive correlation between the contents of zinc and nickel with 0.95 of correlation factor, as is shown in Fig. 5, as well as a similar relation can be surmised between those of zinc and cobalt.

Lead—The lead contents of these deposits range from 11 to 78 ppm with the average of 55±6 ppm. The average lead content of these deposits

Fig. 4. Relationship between the contents of zinc and aluminum in deposits of Nanao Bay.

Fig. 5. Relationship between the contents of zinc and nickel in deposits of Nanao Bay.

is remarkably higher than those of the shallow-water deposits from all the coasts of Honshu, Japan, Korean coast and Gulf of Paria, or that of igneous rocks, and is in the same order of magnitude with values on the pelagic sediments in the North Pacific given by TATSUMOTO (1957).

No clear relationship between the contents of lead and major elements is found, but there is a tendency that sediments with high concentration of lead are generally rich in the contents of nickel, cobalt and zinc.

Cadmium—The cadmium content ranges from 0.04 to 2.07 ppm with the average of 0.22 ± 0.43 ppm. The average content of cadmium in Nanao Bay sediments is in the same order of magnitude with those of igneous rocks.

Chromium and Vanadium—The average content of chromium in the sediments of Nanao Bay is 30 ± 5 ppm, and the content is particularly lower than those in red clays (93 ppm) and igneous rocks (200 ppm).

There can not be found any correlation between chromium and aluminum contents of the deposits, despite there are similarity of their chemical properties, ionic size and ionic charge.

EMERY (1960) stated that the abundance of chromium in several cores are closely paralleled with calcium and strontium, but in Nanao Bay deposits, no clear relationship of chromium to calcium can be found.

In these deposits the vanadium contents are remarkably low in Sample 5P (3 ppm), and relatively high in Samples 9 and 14 (72 and 42 ppm). The average vanadium content of the deposits (39 ± 6 ppm), is particularly lower than those in the red clays (450 ppm from the Pacific or in igneous rocks (150 ppm).

A positive relation of vanadium to sulfur is found in the deposits, as shown in Fig. 6. This is attributable that in an anoxic condition, vanadium precipitate in a sediment as sulphide V_2S_5 as pointed by RANKAMA (1950).

Fig. 6. Relationship between the contents of vanadium and sulfur in deposits of Nanao Bay.

The average Cr/V ratio in the deposits, 0.77, agrees with those of 0.76, 0.79 and 0.74 for shallow-water deposits from all the coasts of Honshu, Japan, Korean coast and the Gulf of Paria (HIRST, 1962). The average Cr/Fe ratio, 0.09×10^{-2} in the deposit of Nanao Bay, is in the same order of magnitude with those of 0.10×10^{-2} , 0.10×10^{-2} , and 0.14×10^{-2} in the deposits from all the coasts of Honshu, Japan and Korean coast, and the sands from the Gulf of Paria and the red clays of the Pacific, respectively.

Zirconium—Zirconium content of these deposits show an appreciable extent of variation ranging from 31 to 163 ppm.

The average zirconium content of the deposits, 101 ± 46 ppm, is 2–4 times higher than 27–48 ppm of the deposits of all the coasts of Honshu, Japan and 44–65 ppm of Korean coast, but is about half as much as 180 ppm of deep-sea sediments or 220 ppm of igneous rocks.

The highest zirconium content among these deposits is 163 ppm of Sample 19, which is characterized by higher concentrations of other minor elements such as cadmium, zinc and lead. It is found that zirconium contents are high in the deposits rich in aluminum and phosphorus. On the contrary, there is little correlation between the contents of zirconium and titanium despite notable similarity of their general characters.

Molybdenum—The average molybdenum content is 0.5 ± 0.3 ppm ranging from 0.2 to 1.4 ppm.

HIRST (1962) found that the molybdenum contents of Paria sediments range from 0.01 to 1.1 ppm which is in good agreement with the present result of molybdenum content in Nanao Bay deposits. While, OKABE (1961) reported a little higher content of molybdenum of 1.0 to 4.7 ppm for coastal marine sediment in Japan. As to the molybdenum contents of lithosphere, the average value is about 1 ppm (KURODA and SANDELL, 1954; VINOGRADOV, 1958).

No relation between the contents of molybdenum and iron, aluminum and manganese can be seen in these deposits, despite the similarity their geochemical behaviors.

Gallium—Gallium is known as one of environmental discriminators with boron, lithium and

vanadium. From such point of view, the abundance and behavior of gallium in marine sediments may be worth paing attention.

The gallium contents of these deposits range from 7 to 18 ppm with the average of 12 ± 3 ppm which is somewhat lower than the averages, 19, 15 and 22 ppm for deep-sea sediments, igneous rocks and muds from Gulf of Paria (HIRST, 1962), respectively. The similar concentration of gallium was reported by present authors (1966) and POTTER *et al.* (1963) for the shallow-water, marine or fresh-water sediments.

It is to be noted that gallium, unlike the other minor elements, such as nickel, cobalt, copper, zinc, vanadium and molybdenum, is characterized as the element of no remarkable accumulation in deep-sea sediments.

In Fig. 7 a positive relation of gallium to aluminum in these deposits is shown. Probably this relation is caused by the similarities of their chemical properties and ionic radii of gallium and aluminum ions, 0.62 and 0.57 Å, respectively, as pointed out by RANKAMA (1950) and HIRST (1962).

The average Ga/Al ratio for the deposits, 0.16 ± 10^{-3} , is a little less than the ratios of 0.12×10^{-3} and 0.23×10^{-3} for deposits from various small islands and Paria sediments, respectively. The average Ga/Al ratios of groups W, S and N are 0.20×10^{-3} , 0.16×10^{-3} and 0.14×10^{-3} respectively.

Fig. 7. Relationship between the contents of gallium and aluminum in deposits of Nanao Bay.

Fig. 8. Relationship between the contents of gallium and cobalt in deposits of Nanao Bay.

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七尾湾浅海底土の微量元素

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要旨 七尾湾西湾, 南湾, および北湾から採取した21個の浅海底土試料中の微量元素, ニッケル, コバルト, 銅, 亜鉛, 鉛, カドミウム, クロム, バナジウム, モリブデン, ジルコニウム, ガリウムを定量した. これらの微量元素のうち, ニッケル (平均値 14 ± 5 ppm), コバルト (平均値 6 ± 2 ppm), 亜鉛 (平均値 51 ± 7 ppm), バナジウム (平均値 39 ± 6 ppm), モリブデン (平均値 0.5 ± 0.3 ppm) は遠洋深海堆積物ほど, これらの浅海堆積物には濃縮されていない. ガリウム (平均値 12 ± 3 ppm) は両堆積物中にはほぼ同じ程度の存在量を示す. 鉛 (平均値

55 ± 6 ppm) とジルコニウム (平均値 101 ± 46 ppm) は本州, 朝鮮沿岸および Paria 湾からの浅海堆積物に比較すると, 七尾湾堆積物にかなり多い点が注目される.

また七尾湾浅海堆積物と深海堆積物の赤粘土を比べると両者のニッケルとコバルト含量に大きな差異があるにもかかわらず, Co/Ni の比がほぼ一定であることがわかった.

ニッケル, 亜鉛, ガリウム含量とアルミニウム含量との間には正の相関々係があり, またバナジウム含量と硫黄含量との間にも同様の関係が認められる.