

Chemical Studies on the Ocean. (LXXI)

Cobalt Content of Shallow-water Deposits. (2)

Masayoshi ISHIBASHI, Shunzo UEDA and Yoshikazu YAMAMOTO*

(Ishibashi Laboratory)

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The authors have determined the cobalt content of 59 kinds of the deposits from the sea-coasts of Honshū (Japan) and Korea, and discussed these results together with those of the previous paper.

For 110 Japanese samples the cobalt content ranges from trace to 0.002% (mean value 0.0005%), and for 30 Korean samples from 0.0001 to 0.0019% (mean value 0.0008%).

They have further investigated the cobalt content of the several fractions of the two samples by mechanical analysis.

INTRODUCTION

In the preceding paper¹⁾, the authors reported on the cobalt content of 81 kinds of shallow-water deposits from the sea-coasts of Japanese Main Island. In this paper, we report the content of cobalt in 59 kinds of deposits from the sea-coasts of Japanese Main Island and Korea, and summarizing these results and those shown in the previous paper, present generalized considerations concerning all the samples.

The results of analysis of the several fractions into which two kinds of deposits were divided by mechanical analysis are also described.

EXPERIMENTAL PROCEDURE, RESULTS AND DISCUSSION

The determination of cobalt was carried out as described previously¹⁾.

The cobalt content of the deposits is shown in Table 1, in which the nickel content²⁾ is also cited for the purpose of investigating the relation of cobalt to nickel.

(1) On the Cobalt Content of the Shallow-water Deposits

Now, as we have analysed 140 kinds of deposits which were collected at the sea-coasts around Japanese Main Island and Korea, i. e. 80 kinds of Japanese sands, 30 kinds of Japanese muds**, 11 kinds of Korean sands and 19 kinds of Korean muds*, we are going to discuss the analytical results together with those shown in the previous paper.

* 石橋雅義, 上田俊三, 山本善一

**Samples of sandy mud and clay are included.

Table 1. Cobalt content of the shallow-water deposits.*

Sample No.	Locality	Type of deposits	Co content 10 ⁻³ %	Ni content 10 ⁻³ %	Co/Ni
83	Suna, Hasunuma-mura, Sanbu-gun, Chiba-ken	Light brown sand	0.4	1.1	0.36
84	Hama-machi, Anesaki, Anesakimachi, Ichihara-gun, Chiba-ken	Blackish gray sand	1.3	1.3	1.00
85	Hon-machi, Funabashi-shi, Chiba-ken	Light blackish brown sand	0.5	1.0	0.50
86	Kanazawa-machi, Isogo-ku, Yokohama-shi, Kanagawa-ken	Grayish sand	0.7	1.1	0.64
87	Ōiso, Ōiso-machi, Naka-gun, Kanagawa-ken	Blackish sand	1.2	2.0	0.60
88	Sakawa, Sakawa-machi, Ashigaranoshimo-gun, Kanagawa-ken	Blackish sand	2.0	3.9	0.51
89	Usami-mura, Tagata-gun, Shizuoka-ken	Blackish brown sand	0.7	2.2	0.32
90	Tago, Tagonoura-mura, Fuji-gun, Shizuoka-ken	Blackish gray sand	0.5	2.0	0.25
91	Chihama, Chihama-mura, Ogasa-gun, Shizuoka-ken	Light blackish gray sand	0.1	0.9	0.11
92	Hamana, Arai-machi, Hamana-gun, Shizuoka-ken	Light blackish gray sand	0.3	1.5	0.20
111	Namiita, Shishiori-mura, Motoyoshi-gun, Miyagi-ken	Grayish sandy mud	1.5	2.7	0.56
93	Namiita, Shishiori-mura, Motoyoshi-gun, Miyagi-ken	Grayish mud	1.7	1.6	1.06
94	Shizukawa-machi, Motoyoshi-gun, Miyagi-ken	Grayish white sand	1.2	3.2	0.38
95	Ōmagari, Yamoto-machi, Monou-gun, Miyagi-ken	Light brown sand	0.5	1.1	0.45
96	Nakahama, Sakamoto, Sakamoto-mura, Watari-gun, Miyagi-ken	Light yellowish gray sand	0.1	0.4	0.25
97	Shin-mach, Ukedo, Ukedo-mura, Futaba-gun, Fukushima-ken	Light brownish gray sand	0.7	0.6	1.17
98	Naka-machi, Yotsukura-machi, Iwaki-gun, Fukushima-ken	Light yellowish gray sand	0.2	0.3	0.67
99	Kawajiri, Toyoura-machi, Taga-gun, Ibaraki-ken	Light brownish gray sand	0.1	0.7	0.14
100	Akashi, Namino-mura, Kashima-gun, Ibaraki-ken	Light brownish gray sand	0.4	1.1	0.36
101	Yoshimi, Tajiri-mura, Sennan-gun, Ōsaka-fu	Yellowish brown sand	0.05	0.5	0.10
110	Kamiya-machi, Kishiwada-shi, Ōsak-fu	Yellowish brown sand	0.2	0.2	1.00
102	Shiomi-machi, Izumiōtsu-shi, Ōsaka-fu	Light yellowish brown sand	0.2	0.2	1.00
103	Hamazume-mura, Takeno-gun, Kyōto-fu	Light brown sand	0.4	1.7	0.24
104	Iwagahana, Yōrō-mura, Yoza-gun, Kyōto-fu	Light brown sand	0.2	0.6	0.33
109	Shimasaki, Miyazu-machi, Yoza-gun, Kyōto-fu	Yellowish brown sand	0.2	0.9	0.22
105	Higashikanzaki, Kanzaki-mura, Kasa-gun, Kyōto-fu	Light brownish gray sand	0.2	1.8	0.11

* Results are shown on the sea-salt-free and dry basis.

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106	Wakamiya, Takahama-machi, Ōi-gun, Fukui-ken	Greenish black sand	1.8	3.9	0.46
107	Shirahige, Obama-machi, Onyū-gun, Fukui-ken	Grayish brown sand	0.4	1.1	0.36
108	Jshishinbo, Natsume-mura, Sakai-gun, Fukui-ken	Brown sand	0.4	1.3	0.31
K 1	Puna, Yongchon-kun, Pyongan-pukto	Dark brown mud	n.d.	n.d.	—
K 2	Osong-tong, Taesan-myon, Sonchon-kun, Pyongan-pukto	Dark brown mud	0.9	2.6	0.35
K 3	Hampal-ri, Hanchon-myon, Pyongwon-kun, Pyongan-namdo	Dark brown mud	1.0	1.8	0.56
K 4	Okyangki-ri, Chinnampopu, Pyongan-namdo	Dark brown mud	1.0	2.8	0.36
K 5	Yonghoto-ri, Tongnam-myon, Ongjin-kun, Hwanghae-do	Dark brown mud	0.6	1.3	0.46
K 6	Chinjong-ri, Sonwon-myon, Kanghwa-kun, Kyonggi-do	Dark brown mud	0.7	2.0	0.35
K 7	Tongjoung-ri, Soukmun-myon, Tangjin-kun, Chungchong-namdo	Dark brown mud	0.7	2.7	0.26
K 8	Sopinchon, Kunsanpu, Cholla-pukto	Dark brown mud	1.0	2.8	0.36
K 9	Namchang-ri, Pukpyong-myon, Haenam-kun, Cholla-namdo	Dark brown mud	0.9	2.2	0.41
K10	Mayang-ri, Taeku-myon, Kangjin-kun, Cholla-namdo	Dark brown mud	1.3	2.5	0.52
K11	Haeon, Kuhangshine, Yosub, Yosukun, Cholla-namdo	Dark brown mud	1.1	1.4	0.79
K12 ₁	Royang-ri, Kumnan-myon, Hadong-kun, Kyongsang-namdo	Dark brown sandy mud	0.7	1.6	0.44
K12 ₂	Royang-ri, Kumnan-myon, Hadong-kun, Kyongsang-namdo	Dark brown mud	1.0	2.8	0.36
K13	Sonjin-ri, Yongkyoun-myon, Sachon-kun, Kyongsang-namdo	Dark brown sandy mud	0.8	1.4	0.57
K14	Tupu-ri, Samsan-myon, Kosong-kun, Kyongsang-namdo	Dark brown mud	0.4	2.2	0.18
K15	Shinjon-ri, Sanyang-myon, Tongyong-kun, Kyongsang-aamdo	Dark brown sandy mud	1.0	1.4	0.71
K16	Kyonghwa-tong, Chinhae-ub, Changwon-kun, Kyongsang-namdo	Brown mud	1.3	1.8	0.72
K17	Chedok-ri, Ungchon-myon, Changwon-kun, Kyongsang-namdo	Dark brown mud	0.8	0.9	0.89
K18	Bangou-ri, Tong-myon, Ulsan-kun, Kyongsang-namdo	Yellow clay	0.9	1.7	0.53
K19 ₁	Pohang-tong, Pohang-ub, Yongil-kun, Kyongsang-pukto	Dark brown mud	1.9	7.8	0.24
K19 ₂	Pohang-tong, Pohang-ub, Yongil-kun, Kyongsang-pukto	Light yellowish brown sand	0.4	0.3	1.33
K20	Imwon-ri, Wondok-myon, Samchok-kun, Kangwon-do	Light yellowish brown sand	0.3	0.8	0.38
K21	Chumun-ri, Chumunjin-myon, Kangnung-kun, Kangwon-do	Yellowish white sand	0.1	0.4	0.25
K22	Haeon-tong, Wonsanpu, Hamgyong-namdo	Light yellowish brown sand	0.5	0.4	1.25
K23	Hengchon, Songjin-ub, Songjin-kun, Hamgyong-pukto	Light brown sand	0.5	2.3	0.22
K24	Songshin-tong, Ouyang-myon, Kyongsong-kun, Hamgyong-pukto	Light brown sand	0.7	1.2	0.58

K25	Tokyoun-tong, Ochon-myon, Kyongsong-kun, Hamgyong-pukto	Grayish white sand	0.7	0.7	1.00
K26 ₁	Bipa-tong, Songpyong-tong, Unggi-ub, Kyonghung-kun, Hamgyong-pukto	Grayish white sand	0.4	0.7	0.57
K26 ₂	Ungsang-tong, Unggi-ub, Kyonghung- kun, Hamgyong-pukto	Light yellow- ish green sand	0.3	0.3	1.00
K26 ₃	Unggi-tong, Unggi-ub, Kyonghung- kun, Hamgyong-pukto	Grayish white sand	0.4	0.9	0.44
K27	Sosura-tong, Roso-myon, Kyonghung-kun, Hamgyong-pukto	Grayish white sand	0.3	0.9	0.33

From the experimental results, it is seen that the content of cobalt in the shallow-water deposits is comparatively high in the blackish sands collected at the sea-coasts of Aomori, Iwate, Kanagawa and some other Prefectures, and so is in the fine muds from the sea-coasts of Okayama, Miyagi and some other Prefectures and west and south coasts of Korea, while it is remarkably low in the yellowish or brownish sands collected from Hiroshima, Yamaguchi, Ōsaka and Kyōto and some other Prefectures. In general the cobalt content is higher in muds than in sands.

Summarizing the analytical results of all the samples, we obtained the data given in Table 2.

Table 2. Summary of the results obtained.

Number of samples		Co content (10 ⁻³ %)		
		Minimum	Maximum	Average
Total samples from Japan	110	Trace	2.0	0.5
sands	80	Trace	2.0	0.4
muds	30	0.2	1.7	0.7
Total samples from Korea	30	0.1	1.9	0.8
sands	11	0.1	0.7	0.4
muds	19	0.4	1.9	1.0

As seen from Table 2, in the case of total samples as well as muds the mean value of cobalt content of the Japanese samples is slightly lower than that of the Korean samples, while in the case of sands both give the same mean values. Furthermore, it is observed that the average content of cobalt in muds is higher than that in sands in both Japanese and Korean samples. Next, it is worthy of notice that the average cobalt content of the shallow-water deposits is much lower than that of the deep-sea deposits such as red clay, which is of the order of 50g/ton.*

There is some parallelism between the cobalt content and the nickel content, though there are many exceptions. Because of the predominance of nickel over

* Average of 22 samples of red clay collected at the North Pacific Ocean (M. Tatsmoto, *J. Chem. Soc. Japan*, **77**, 1637 (1956)).

cobalt, the ratio Co/Ni is less than 1 in most cases. For sands the ratio ranges 0—1.67 (mean value 0.48) and for muds it ranges 0.13—1.06 (mean value 0.43).

Between the content of cobalt and those of common elements, there seems to be no definite relation applicable to all the samples. Though there are many exceptions, it is seen that the cobalt content is high in the deposits which are low in SiO_2 and high in Fe_2O_3 , MgO , etc., while it is low in those which are high in SiO_2 and low in Fe_2O_3 , MgO , etc.

Between the cobalt content in the deposits and the geology of the land adjacent to the locations sampled, it is difficult to find definite relationship, because the deposits may have originated in remote places, and been carried to the sites by the river water and/or sea current.

(2) On the Cobalt Content of the Several Fractions of the Deposits Divided by Mechanical Analysis

Owing to the possibility that the cobalt content of the shallow-water deposits may be affected by the nature of source rocks and other factors, it is difficult to find the generalized relations between the content of cobalt and those of other constituents in the deposits from various localities. Therefore, we divided the deposit by mechanical analysis into five fractions and analysed each fraction in order to find the relation between the grain size and the chemical composition, and at the same time, to investigate how the cobalt content varies with the contents of other constituents.

Samples 46 and 112* were used in this experiment.

Results obtained are shown in Tables 3 and 4.

It is obvious from these tables that as the grain size of fraction becomes smaller, cobalt, iron, titanium, manganese and calcium increase in Sample 46

Table 3. Analyses of each fraction of Sample 46.

Fractions	1	2	3	4	5
Grain size	>0.5mm	0.5—0.25mm	0.25—0.1mm	0.1—0.08mm	<0.08mm
Size composition	2.05%	28.72%	52.73%	15.86%	0.64%
Fe_2O_3	4.06	4.11	5.69	10.76	47.79
TiO_2	0.28	0.32	0.35	0.78	1.51
Al_2O_3	9.29	9.81	10.15	10.76	6.27
MnO	0.07	0.10	0.14	0.21	1.02
CaO	1.86	2.85	3.28	5.10	5.50
MgO	1.46	1.16	2.38	4.95	4.03
SiO_2	76.90	76.07	72.78	63.63	33.36
Co	0.0007	0.0008	0.0009	0.0019	0.0054

* Greenish deposit ; collected at the sea-coast of Higashiura-machi, Chita-gun, Aichi-ken.

Table 4. Analyses of each fraction of Sample 112.

Fraction	1	2	3	4	5
Grain size	>0.5mm	0.5—0.25mm	0.25—0.1mm	0.1—0.05mm	<0.05mm
Size composition	11.69%	25.79%	14.47%	13.91%	34.14%
Fe ₂ O ₃	2.01	2.22	3.29	6.21	7.57
TiO ₂	0.17	0.24	0.31	0.79	0.73
Al ₂ O ₃	7.28	8.48	11.50	17.12	19.69
MnO	0.023	0.027	0.04	0.066	0.07
CaO	1.75	1.08	1.37	1.61	1.47
MgO	0.22	0.36	0.50	0.96	1.01
SiO ₂	82.22	80.58	77.18	62.22	58.13
Co	0.0003	0.0004	0.0005	0.0008	0.0009

and cobalt, iron, aluminum, manganese and magnesium increase in Sample 112, while silicon decreases in both samples.

Now, based on the data in these tables, the relation of cobalt to other constituents is shown in Figs. 1-9. As seen in Figs. 1-4 (Sample 46), the cobalt content is approximately proportional to the Fe₂O₃, TiO₂ and MnO contents, while it is inversely proportional to the SiO₂ content. And we can see in Figs. 5-9 (Sample 112) that the cobalt content is approximately proportional to the Fe₂O₃, Al₂O₃, MnO and MgO contents, and inversely proportional to the SiO₂ content.

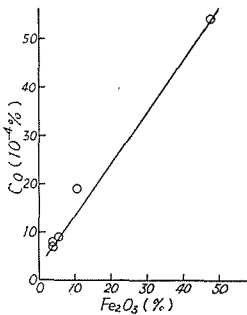
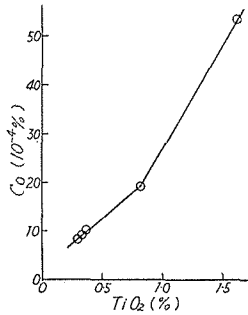
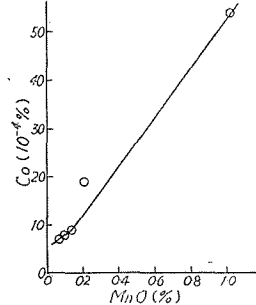
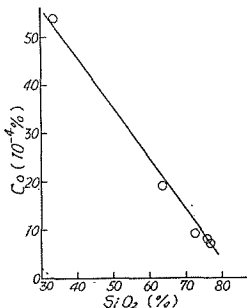
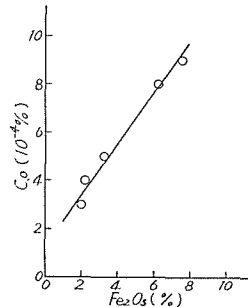
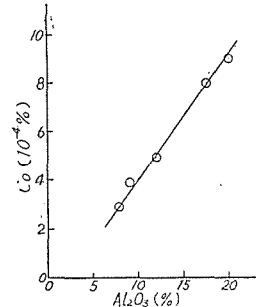
Fig. 1. Co-Fe₂O₃.Fig. 2. Co-TiO₂.

Fig. 3. Co-MnO.

Fig. 4. Co-SiO₂.Fig. 5. Co-Fe₂O₃.Fig. 6. Co-Al₂O₃.

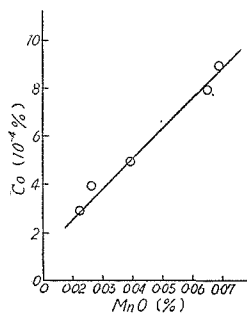


Fig. 7. Co-MnO

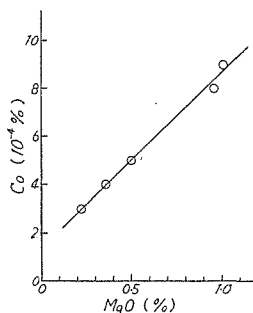


Fig. 8. Co-MgO.

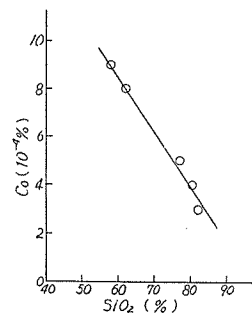


Fig. 9. Co-SiO₂.

Figs. 1~9. Relations between the content of cobalt and those of other constituents. Figs. 1~4 for Sample 46, and Figs. 5~9 for Sample 112.

From the above results, we presume that the cobalt content in these two samples is related especially to the iron content.

REFERENCES

- (1) M. Ishibashi, S. Ueda and Y. Yamamoto, *This Bulletin*, **37**, 26 (1959).
- (2) M. Ishibashi and S. Ueda, *Reports of Investigation for Development of Marine Resources in the Japanese National Commission for UNESCO*, **1**, 102 (1955).