# Chemical Studies on the Ocean. (LXXI)

## Cobalt Content of Shallow-water Deposits. (2)

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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 paper[1], 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 papar, 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 previously[1].

The cobalt content of the deposits is shown in Table 1, in which the nickel content[2] 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.

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**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, Osaka-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.

| | | | | | |
|---|---|---|---|---|---|
| 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 | Haean, Kuhangshine, Yosu-ub, Yosu-kun, 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 | Haean-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 yellowish 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% |
| $Fe_2O_3$ | 2.01 | 2.22 | 3.29 | 6.21 | 7.57 |
| $TiO_2$ | 0.17 | 0.24 | 0.31 | 0.79 | 0.73 |
| $Al_2O_3$ | 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 $Fe_2O_3$, $TiO_2$ and MnO contents, while it is inversely proportional to the $SiO_2$ content. And we can see in Figs. 5-9 (Sample 112) that the cobalt content is approximately proportional to the $Fe_2O_3$, $Al_2O_3$, MnO and MgO contents, and inversely proportional to the $SiO_2$ content.

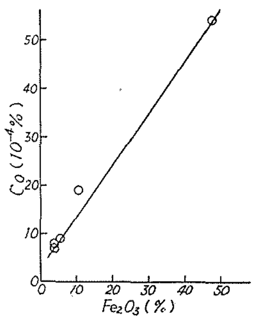

Fig.1. Co-$Fe_2O_3$.

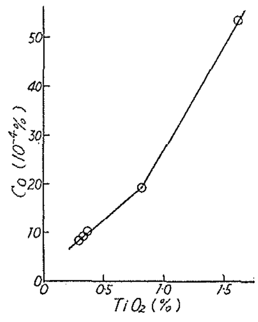

Fig.2. Co-$TiO_2$.

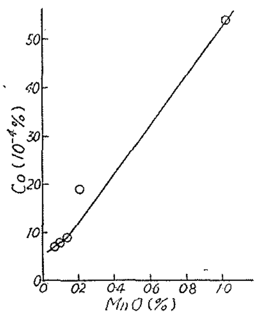

Fig.3. Co-MnO.

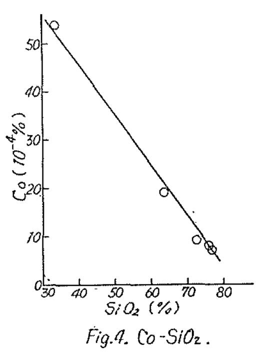

Fig.4. Co-$SiO_2$.

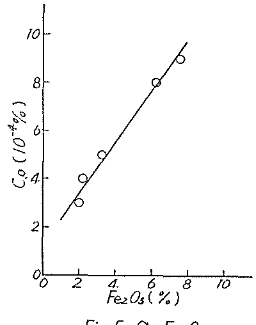

Fig.5. Co-$Fe_2O_3$

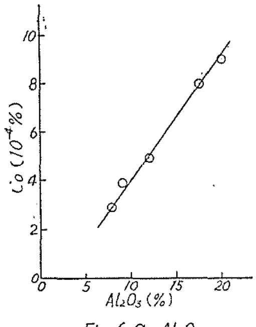

Fig.6. Co-$Al_2O_3$.

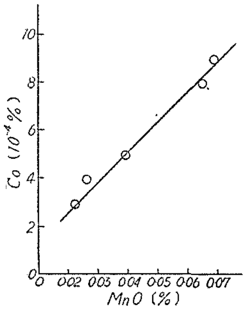


Fig. 7. Co-MnO

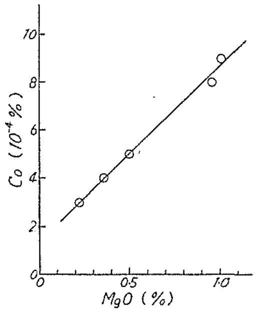


Fig. 8. Co-MgO.

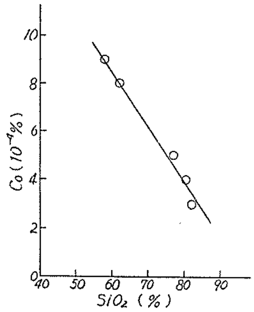


Fig. 9. Co-$SiO_2$.

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).