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Chemical Studies of the Shallow-water Deposits. (4)

On the Chemical Constituents of the Shallow-water Deposits along the Sea-Coasts of Korea[1]

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In this paper, the results of anlaysis, carried out laying emphasis on K determination, of 10 kinds of the deposits from the east sea-coast, are described, and further, the generaized considerations of all the samples from all the sea-coasts of Korea are presented. From the summarized results of all samples, it is found that K is plentiful in these deposits and considerably enriched in the muds on the whole, though there are several exceptions mainly in the deposits from the sea-coast of the Korean Straits.

INTRODUCTION

In the previous papers[2], we have reported the chemical composition of 21 kinds of deposits from the west sea-coast of Korea, the sea-coast of the Korean Straits and a part of the east sea-coast. In this paper, the analytical results on 10 kinds of deposits from the east sea-coast are described, and further, summarizing these results and those of other coasts which have been already reported, the generalized considerations of all the samples from all the sea-coasts of Korea are presented.

SAMPLES

Locality is shown in Table 1.

All of these samples gathered from the east sea-coast are sands and there is no mud such as from the west sea-coast of Korea and the sea-coast of the Korean Straits. This is probably due to the fact that the efflorescences of weathered granite, gneiss and the like were carried by the rivers without being weathered into mud and deposited at the beach as they were, because the watersheds of mountain chains such as the Taebaek Mts., Kumgang Mt. and Hamgyong Mts. are close to the east sea-coast.

Types of the deposits are as follows :

K 20, K 22, K 26_2 : light yellowish brown sands,

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K 21 : yellowish white sand,

K 23, K 24 : light brown sands,

K 25, K 26_1, K 26_3, K 27 : grayish white sands.

In these samples, K 25 contains mud considerably, and K 22 and K 25 contain some shell fragments.

Table 1.

Sample No.	Locality
K 20	Imwon-ri, wondok-myon, Samchok-kun, Kangwon-do
K 21	Chumun-ri, Chumunjin-myon, Kangnung-kun, Kangwon-do
K 22	Haean-tong, Wonsanpu, Hamgyong-namdo
K 23	Hengchon, Songjin-ub, Songjin-kun, Hamgyong-pukto
K 24	Songshin-tong, Ouyang-myon, Kyongsong-kun, Hamgyong-pukto
K 25	Tokyoun-tong, Ochon-myon, Kyongsong-kun, Hamgyong-pukto
K 26_1	Bipa-tong, Songpyong-tong, Unggi-ub, Kyonghung-kun, Hamgyong-pukto
K 26_2	Ungsang-tong, Unggi-ub, Kyonghung-kun, Hamgyong-pukto
K 26_3	Unggi-tong, Unggi-ub, Kyonghung-kun, Hamgyong-pukto
K 27	Sosura-tong, Roso-myon, Kyonghung-kun, Hamgyong-pukto

EXPERIMENTAL PROCEDURE, RESULTS AND DISCUSSION

As the analytical method was referred to in the previous paper[3], it is not repeated here.

The analytical results of the air-dried samples are shown in Table 2. From this table we obtained the percentages of chemical constituents in the sea-salt-free samples dried at 105～110°C as shown in Table 3*. Summarising the results in Table 3 and those shown in the previous papers[2], we obtained Table 4, in which the average chemical composition of all the samples (31 kinds) from all the sea-coasts and the maximum, minimum and average values of each chemical constituent of muds (20 kinds)** and sands (11 kinds) are shown, respectively. The average chemical composition of red clays and rocks is also recited for the convenience of comparison in this table.

As obvious from Table 3, the SiO_2 content ranges 61.26～83.74 % and amounts to more than 70 % in all the samples except K 23, K24 and K 25. And it is especially high in K 20, K 21 and K 26_1, being about 80 % or more.

* We performed this calculation on the basis of the same assumption as in the previous paper[1].

** Sandy muds and clay are included.

Table 2. Chemical composition of the deposits.

Sample No.	K 20	K 21	K 22	K 23	K 24	K 25	K 26_1	K 26_2	K 26_3	K 27
	%	%	%	%	%	%	%	%	%	%
Drying loss	0.64	0.15	1.25	0.82	1.33	2.95	0.34	0.34	0.65	0.46
Ignition loss	1.57	0.43	3.43	1.78	1.57	5.08	0.69	0.83	0.16	0.11
Fe_2O_3	1.81	0.87	2.41	7.53	3.63	5.73	2.05	2.05	2.76	1.64
Al_2O_3	9.95	9.10	12.49	12.50	15.97	9.64	10.97	13.23	16.01	14.78
MnO	0.03	0.02	0.05	0.11	0.03	0.07	0.03	0.04	0.01	0.03
CaO	0.87	0.80	4.14	7.40	2.46	3.07	2.22	2.36	2.82	2.57
MgO	0.75	0.28	1.06	4.95	1.11	1.22	0.87	1.00	0.85	0.87
K_2O	2.05	3.24	2.38	1.65	2.96	2.43	2.16	2.25	2.82	2.28
Na_2O	1.20	1.80	1.08	2.18	4.76	3.32	2.82	3.59	4.33	3.87
SiO_2	80.45	83.58	70.84	60.73	65.12	65.68	78.52	74.79	69.76	72.64
SO_3	0.06	0.12	0.15	0.34	0.45	0.34	0.12	0.05	0.20	0.25
Cl	0.10	0.02	0.39	0.02	0.03	1.19	0.32	0.27	0.27	0.17
P_2O_5	0.05	0.03	0.06	0.17	0.09	0.05	0.05	0.04	0.05	0.08
CO_2	—	—	2.70	—	—	1.69	—	—	—	—
N	0.01	0.02	0.02	0.03	0.02	0.04	0.01	0.01	0.02	0.03

Table 3. Chemical composition of the deposits on sea-salt-free and dry basis (Calculated from Table 2).

Sample No.	K20	K21	K22	K23	K24	K25	K26_1	K26_2	K26_3	K27
	%	%	%	%	%	%	%	%	%	%
Fe_2O_3	1.82	0.87	2.46	7.60	3.68	6.04	2.07	2.07	2.79	1.65
Al_2O_3	10.03	9.12	12.74	12.61	16.19	10.16	11.07	13.34	16.19	14.89
MnO	0.03	0.02	0.05	0.11	0.03	0.07	0.03	0.04	0.01	0.03
CaO	0.88	0.80	4.21	7.46	2.49	3.19	2.23	2.37	2.84	2.58
MgO	0.75	0.28	1.04	4.99	1.13	1.15	0.84	0.98	0.83	0.86
K_2O	2.07	3.25	2.42	1.66	3.00	2.53	2.17	2.26	2.84	2.30
Na_2O	1.14	1.79	0.81	2.19	4.81	2.57	2.60	3.42	4.18	3.77
SiO_2	81.11	83.74	72.26	61.26	66.03	69.21	79.25	75.42	70.56	73.20
SO_3	0.05	0.12	0.10	0.34	0.46	0.21	0.08	0.02	0.17	0.23
P_2O_5	0.05	0.03	0.06	0.17	0.09	0.05	0.05	0.04	0.05	0.08
CO_2	—	—	2.75	—	—	1.78	—	—	—	—
N	0.01	0.02	0.02	0.03	0.02	0.04	0.01	0.01	0.02	0.03
Na_2O+K_2O	3.21	5.04	3.23	3.85	7.81	5.10	4.77	5.68	7.02	6.07
K_2O/Na_2O	1.82	1.82	2.99	0.76	0.62	0.98	0.83	0.66	0.68	0.61

Table 4. Summary of the results obtained*.

	Korean all samples (31 kinds)	Korean muds (20 kinds)			Korean sands (11 kinds)			Red clays [a]	Red clays [b]	Igneous rocks [c]	Shales [c]	Sandstones [c]
		Maximum	Minimum	Average	Maximum	Minimum	Average					
	%	%	%	%	%	%	%	%	%	%	%	%
Fe_2O_3	5.71	13.82	3.56	7.16	7.60	0.87	3.08	8.93	11.84	7.30	6.74	1.40
Al_2O_3	14.26	19.48	9.26	15.14	16.19	9.12	12.68	17.35	22.70	15.34	15.40	4.77
MnO	0.05	0.20	trace	0.06	0.11	0.01	0.04	0.99	1.78	0.124	—	—
CaO	2.66	6.93	0.89	2.37	7.46	0.80	3.19	2.64	1.85	5.08	3.11	5.50
MgO	1.45	3.20	0.64	1.56	4.99	0.28	1.25	3.62	2.69	3.49	2.44	1.16
K_2O	2.34	3.09	1.07	2.31	3.25	1.66	2.39	2.78	2.96	3.13	3.24	1.31
Na_2O	2.40	7.37	0.78	2.27	4.81	0.81	2.64	5.38	1.54	3.84	1.30	0.45
SiO_2	67.39	73.54	53.88	64.40	83.74	61.26	72.82	56.70	54.15	59.14	58.10	78.33
SO_3	0.32	1.56	0.09	0.40	0.46	0.02	0.17	—	0.20	0.13	0.64	0.07
P_2O_5	0.09	0.20	0.05	0.11	0.17	0.03	0.07	0.48	0.30	0.299	0.17	0.08
CO_2	0.50	3.16	—	0.39	3.30	—	0.71	—	—	0.101	2.63	5.03
N	0.07	0.19	0.01	0.10	0.04	0.01	0.02	—	—	—	—	—
Na_2O+K_2O	4.74	10.41	2.29	4.58	7.81	3.21	5.03	8.16	4.50	6.97	4.54	1.76
K_2O/Na_2O**	0.98	2.40	0.41	1.02	2.99	0.61	0.91	0.52	1.92	0.82	2.49	2.91
Drying loss***	2.59	10.78	0.81	3.46	2.95	0.15	1.02	—	—	—	—	—
Ignition loss***	3.64	7.92	1.52	4.69	5.08	0.11	1.74	—	—	—	—	—

* The chemical composition of sea-deposits is shown on the sea-salt-free and dry basis, but as for that of rocks, it is cited for comparision from the original as it is.

** For the convenience of comparison, particularly in this table, average value of K_2O/Na_2O was calculated from average K_2O and average Na_2O.

*** The rerults are expressed on the air-dry basis.

(*a*) Average chemical composition fo 16 kinds of red clays by Hamaguchi[5].

(*b*) Average chemical composition of 6 kinds of red clays by Ishibashi and Harada[6].

(*c*) Average chemical composition of igneous rocks, shales and sandstones[7]

The Fe_2O_3 content is high in the sands which have low content of SiO_2, especially high in K 23 and K 25, being 7.60 % and 6.04 %, respectively, whereas it is low in those which have high content of SiO_2, being about 2 % or lower in many of them, especially low in K 21 which has the highest content of SiO_2, being 0.87 %.

The Al_2O_3 content varies considerably with samples, ranging 9.12～16.19 %. Though there are some exceptions, Fe_2O_3 and Al_2O_3 are impoverished in samples of high SiO_2 content and plentiful in those of low SiO_2 content.

The CaO content is exceedingly high in K 23 and comparatively high in K 22 which contains some shell fragments, but low in K 20 and K 21 which have high content of SiO_2.

As for the MgO content, it is low on the whole, being about 1 % or lower in all the samples except K 23.

As for the P_2O_5 and MnO contents, they are slightly high in K 23, showing the maximum values, 0.17 % and 0.11 %, respectively, while low in the others, being less than 0.1 %.

From the above it is seen that K 23 is considerably different from the others by showing the minimum content of SiO_2 and the maximum content of Fe_2O_3, CaO, MgO and the like.

As for alkalies, these deposits from the east sea-coast seem to be rich in K_2O on the whole, showing mostly more than 2 % K_2O. The Na_2O content is also more than 2 % in all the sands except K 20, K 21 and K 22, therefore, the Na_2O $+K_2O$ content is considerably high in general, being more than 4 % in many samples.

Next, on the basis of the values presented in Table 4, generalized considerations of all the samples from all the sea-coasts are described.

Comparing the average chemical composition of muds with that of sands, noticeable differences in the content of SiO_2 and Al_2O_3 are observed.

On the processes of sedimentation it is generally said that weathered materials of the rocks are transported by the action of water, wind, ice and the like, being sorted physically and chemically, and the coarse-grained particles with a diameter above 2 mm mostly consist of chemically unaffected rock and mineral material, but in the particles with a diameter of 2～0.02 mm quartz becomes to be an essential constituent and with the decrease in particle size, the content of aluminum silicates and consequently that of Al_2O_3 increases[8].

Results in Table 4 show the excellent agreement with the above mentioned, and it is recognized that the muds are poor in SiO_2 and rich in Al_2O_3 comparing with the sands. The Fe_2O_3 content is also considerably higher in muds than in sands.

As for the CaO content, it is lower in muds than in sands, though it is also affected by the amount of shell fragments in samples, while the MgO content is slightly higher in the former than in the latter.

As for the SO_3, P_2O_5 and N contents, those in muds are higher than those in sands.

The Na_2O and K_2O contents in muds are both similar to those in sands, respectively.

Now, as for the K_2O content in muds, it is exceedingly high in most of the deposits, amounting to $2\sim3$ %, though it is less than 2 % mainly in several muds from the sea-coast of the Korean straits. As the causes of such a notable accumulation of K in muds, we surmise the following mechanism of enrichment. Namely, granitic rocks which may be rich in K, distribute widely in Korea and are in conditions to be readily weathered. The colloids which are formed out of silica, aluminum, iron and the like resulted from the weathering of these rocks have strong adsorptive power for K^+ and may prevent the escape of K originated in mother rocks by adsorption, and when they are brought into contact with the sea-water, they perhaps precipitate, adsorbing K^+ in sea-water, thus causing the accumulation of K in shallow-muds. Further, it is surmised that the deposits may become rich in K by halmyrolysis according to the marine environment.

Next, comparing the average chemical composition of these deposits with that of red clays, igneous rocks, shales and sandstones, we get the following conclusions.

1. SiO_2 : In shallow-water deposits it is higher than in red clays, igneous rocks and shales, but lower than in sandstones.
2. Fe_2O_3 and Al_2O_3 : In muds they are generally similar in igneous rocks and shales, but lower than in red clays and higher than in sandstones. In sands they are lower than in red clays, igneous rocks and shales, but higher than in sandstones.
3. CaO and MgO : The average CaO content in muds is lower than in igneous rocks, shales and sandstones, but similar in red clays. The average MgO content in muds is lower than in red clays, igneous rocks and shales, but higher than in sandstones. The average CaO content in sands is lower than in igneous rocks and sandstones, and similar in shales, but higher than in red clays. The average MgO content in sands is lower than in red clays, igneous rocks and shales, but similar in sandstones. The average content of MgO is higher than that of CaO in red clays, while as for shallow-water deposits the former is lower than the latter both in muds and in sands.
4. MnO : In shallow-water deposits it is lower than in igneous rocks and red clays, especially lower than in red clays.
5. P_2O_5 : In shallow-water deposits it is lower than in red clays, igneous rocks and shales, but similar in sandstones.
6. K_2O and Na_2O : The average K_2O content in shallow-water deposits is slightly lower than in red clays and comparatively lower than in igneous rocks and

shales, but exceedingly higher than in sandstones. The averege Na_2O content in shallow-water deposits is lower than in igneous rocks, but higher than in shales and sandstones. And it is lower than in red clays by Hamaguchi, but higher than in red clays by Ishibashi and Harada.

The average Na_2O+K_2O content in shallow-water deposits is lower than in red clays by Hamaguchi and igneous rocks, but similar in red clays by Ishibashi and Harada and shales, and higher than in sandstones. The average K_2O/Na_2O value in shallow-water deposits is lower than in red clays by Ishibashi and Harada, shales and sandstones, but similar in igneous rocks and higher than in red clays by Hamaguchi.

REFERENCES

(1) This investigation was partly presented at the Annual Meeting of the Chemical Society of Japan on April 5, 1941.
(2) M. Ishibashi, *J, Agr. Chem. Soc. Japan*, **16**, 245 (1940); **17**, 67 (1941); M. Ishibashi and S. Ueda, This Bulletin, **33**, 165 (1955).
(3) M. Ishibashi, *J. Agr. Chem. Soc. Japan*, **17**, 67 (1941).
(4) M. Ishibashi and S. Ueda, This Bulletin, **33**, 165 (1955).
(5) H. Hamaguchi, *J. Chem. Soc. Japan*, **63**, 1689 (1942).
(6) M. Ishibashi and Y. Harada, *J. Chem. Soc. Japan*, **59**, 569 (1938).
(7) F. W. Clarke, "The Data of Geochemistry," U. S. Geol. Survey, Bull. 770, 5. Ed., p. 34 Washington (1924).
(8) K. Rankama and Th. G. Sahama, "Geochemistry", p. 195 (1949).