BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 1462—1468 (1966)

The Chlorine and Fluorine Contents of Tertiary Sediments on the Miura Peninsula

By Bunji IWASAKI, Kenzo KITAYAMA and Takashi KATSURA

Department of Chemistry, Tokyo Institute of Technology, Ookayama, Tokyo

(Received September 15, 1965)

Tertiary sediments were collected from the Miura group on the Miura Peninsula, and the total chlorine and fluorine in these sediments were determined colorimetrically, together with the water-soluble chlorine and fluorine. There was little correlation of the contents of insoluble chlorine and fluorine in the sediments to their locations and ages. The insoluble chlorine contents of the psammitic rocks were higher than those of the pelitic rocks, whereas the insoluble fluorine contents of the former were lower than those of the latter. There seemed to be a moderately negative correlation between the contents of insoluble chlorine and fluorine in the sediments. All the sediments analyzed contained very small amounts of water-soluble fluorine (0.001 to 0.002% F). The frequency distributions of the insoluble chlorine contents in both the psammitic and pelitic rocks were lognormal.

Studies of the chlorine content of sedimentary rocks have been published by Behne,[1] Akaiwa and Nishimura,[2] and Gulyaeva.[3] On the other hand, the fluorine content of sedimentary rocks has been studied by Koritnig,[4] Kokubu,[5] and Itkina.[6] These studies have chiefly been made in order to see whether or not the two halogens are useful as geochemical indicators of marine and fresh water sediments, and to obtain the average contents of the two halogens in sediments in order to estimate their geochemical balance. For the most part, the data described above were obtained from a very few samples, without considering the distribution of the two halogens in sedimentary rocks throughout a member, a smaller unit of stratigraphy, of a region. Among these studies, however, Akaiwa

1) W. Behne, *Geochim. et Cosmochim. Acta,* **3**, 186 (1953).
2) H. Akaiwa and M. Nishimura, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **84**, 721 (1963); **85**, 363 (1964).
3) L. A. Gulyaeva, *Doklady Akad. Nauk S. S. S. R.*, **86**, 911 (1951); L. A. Gulyaeva and E. S. Itkina, *Geokhimiya*, 524 (1962); L. A. Gulyaeva and I. F. Lositskaya, *Geokhim. i Gidrokhim. Neft. Mestorozhd., Akad. Nauk S. S. S. R., Inst. Geol. i Razrabetki Goryuch. Iskop.*, 40 (1963).
4) S. Koritnig, *Geochim. et Cosmochim. Acta,* **1**, 89 (1951).
5) N. Kokubu, *Memoirs Fac. Sci., Kyushu Univ. Ser. C, Chem.*, **2**, 95 (1956).
6) E. S. Itkina, *Geokhim. i Gidrokhim. Neft. Mestorozhd., Akad. Nauk S. S. S. R., Inst. Geol. i Razrabetki Goryuch. Iskop.*, 57 (1963).

and Nishimura[2] have made clear the vertical distribution of chlorine in two regions, i. e., the Yubari district, Hokkaido, and the Niigata district.

In this paper, an attempt will be made to see how the two halogens, chlorine and fluorine, in sediments vary vertically and horizontally throughout a member of a region, and to gain some information on the behavior of the two halogens in the sedimentary and diagenetic processes.

The tertiary sediments of the Miura group on the Miura Peninsula have been well studied in detail by many geologists[7] from the geological standpoint, and it has been said that no metamorphic process has affected these sediments. This is the reason why we chose this area for determining the chlorine and fluroine contents in sediments. After having collected the samples from this area, we determined colorimetrically the content of total and two water-soluble halogens in these samples. From the basis of the results obtained, we will discuss the following: 1) the horizontal and vertical distributions of the two halogens throughout a member; 2) their distributions among the various members formed in different geological ages; 3) the effect of the particle size of the sediments on their distributions, and 4) the correlation between the chlorine and fluorine contents in these sediments.

Experimental

Sample.—The Miura group is usually divided into three formations consisting of fourteen members. All members except the Tomioka member are composed of marine sediments, e. g., siltstone, silt, sandstone, sand, pebble conglomerate, breccia, and pyroclastic sediment. The number of the samples collected from each member is shown in Table I.

TABLE I. THE NUMBER OF THE SAMPLES COLLECTED FROM THE VARIOUS MEMBERS

Misaki formation	
Misakimachi member	10
Aburatsubo member	5
Kamakura formation	
Shimoyamaguchi member	2
Zushi member	35
Ikego member	6
Kanazawa formation	
Hukazawa member	2
Nojima member	5
Hayashi member	2
Ohuna member	12
Koshiba member	1
Nakazato member	7
Tomioka member	4
Total	91

7) H. Akamine, S. Iwai, Y. Naruse, S. Ogose, M. Omori, Y. Seki, K. Suzuki and K. Watanabe, *Geoscience* (*Chikyukagaku*), No. 30, 1 (1956); T. Mitsunashi and K. Yazaki, *J. Japanese Association of Petroleum Technologist* (*Sekiyu Gizyutsu Kyokaishi*), **23**, 16 (1958), etc.

The members are presented in the order of the stratigraphical sequence. Only a few specimens were collected from most of the members, while thirty-five samples were collected from the Zushi member in order to ascertain the horizontal and vertical distributions of its two elements. The locations of the samples are shown in Fig. 1.

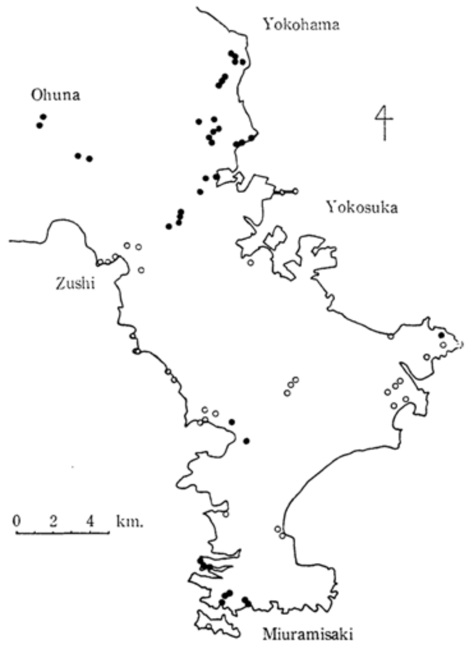


Fig. 1. The location of samples.
○ The samples from the Zushi member
● The samples from the other member

About 1 kg. of a sample was collected from each point and dried in the sunshine. Then about 100 g. of each 1 kg. was split away from the central part of the sample and crushed with a steel mortar. After about 100 g. of the sample had been quartered, about 25 g. of the sample was ground to fineness with an agate mortar in order to make a chemical analysis.

Analytical Methods.—The total chlorine was determined by the method of Iwasaki et al.[8] with some improvements. The water-soluble chlorine was determined by the thiocyanate method[9] after extraction as described in a previous paper.[10] The total fluorine was determined as follows: After about 1.00 g. of the sample had been fused with sodium peroxide in a nickel crucible, the melt was leached with a small amount of water and treated with an excess of sulfuric acid, and the fluorine was steam-distilled as fluosilicic acid. The total fluorine in distillate was colorimetrically determined by the method of Kamada et al.[11] The water-soluble

8) I. Iwasaki, T. Katsura and N. Sakato, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zassi*), **76**, 1116 (1955).
9) A. Tomonari, ibid., **83**, 693 (1962).
10) B. Iwasaki and T. Katsura, This Bulletin, **37**, 1827 (1964).
11) M. Kamada and T. Onishi, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **80**, 275 (1959).

fluorine was determined by the same method after the same extraction and separation processes as were for water-soluble chlorine.

Duplicated analyses were made for all of the samples, and it may safely be said that the precision of the present determination of chlorine is within ±5%, while that of fluorine is within ±10%, over the whole range obtained here. The fluorine contents of the standard rock samples, W-1 and G-1, and the basaltic rock samples of O-sima Volcano, A-15 and H-13, were determined in order to confirm the accuracy of our present results. The results are shown in Table II, together with the results of other authors. As is shown in Table II, our values are fairly well consistent with the data of Yoshida.

TABLE II. ANALYTICAL DATA OF THE STANDARD ROCKS (fluorine content %)

	Yoshida[a)]	Ingamells[b)]	Jeffery[c)]	The present authors
G-1	0.066	0.069—0.074	0.0629	0.059
W-1	0.024	0.030—0.031	0.0290	0.021
H-3[d)]	0.012			0.009
A-15[d)]	0.012			0.009

a) M. Yoshida, Doctral Thesis, Tokyo Institute of Technology (1962).
b) C. O. Ingamells, *Talanta*, **9**, 507 (1962).
c) P. G. Jeffery, *Geochim. et Cosmochim. Acta*, **26**, 1335 (1962).
d) The basaltic rock in 1950—1951 from O-sima volcano.

Results

Tables III-a and III-b give the insoluble chlorine and fluorine contents of the tertiary sediments on the Miura Peninsula, together with the water-soluble chlorine and fluorine contents.

Table III-b shows the findings on pairs of the sediments, e. g., siltstone and sandstone, and silt and sand, which were contiguous to one another.

TABLE III-a. THE CHLORINE AND FLUORINE CONTENTS OF THE TERTIARY SEDIMENTS IN THE MIURA PENINSULA

Sample No.	W-Cl %	I-Cl %	W-F %	I-F %	Remarks
Shimoyamaguchi member					
2807	0.005	0.028			P
0404-1	0.003	0.004			P
Zushi member					
2801	0.008	0.009	0.002	0.024	S
3106	0.006	0.009			S
3107	0.002	0.010	0.001	0.032	S
0301	0.002	0.010	0.002	0.033	S
0302	0.004	0.011	0.001	0.026	S
0303	0.004	0.033	0.002	0.031	S
0401	0.17	0.01	0.001	0.013	B
0402	0.008	0.021	0.001	0.015	S
0403	0.003	0.060	0.001	0.015	B
0404-2	0.45	0.00	0.001	0.021	P
0405	0.20	0.01	0.001	0.029	S
0406	0.009	0.022	0.001	0.009	S
0407	0.004	0.010	0.002	0.033	S
0501	0.003	0.061	0.001	0.009	B
0501-1	0.003	0.030	0.001	0.017	Ss
0502	0.034	0.007	0.001	0.011	B
0503	0.006	0.009	0.002	0.021	S
0504	0.066	0.016			S
0505	0.15	0.00	0.001	0.017	S
0601	0.002	0.011	0.001	0.032	S
0603	0.010	0.018	0.001	0.028	S
0604	0.004	0.012	0.001	0.028	S
0605	0.009	0.019	0.001	0.018	S
0607	0.011	0.024	0.001	0.031	S
0701	0.021	0.003	0.001	0.024	S
0702	0.019	0.003	0.001	0.031	S
Ikego member					
2916	0.006	0.023			Py P
2917	0.008	0.013			S
2918	0.003	0.017	0.002	0.027	S
2918-1	0.012	0.020			S
0606	0.005	0.046			P
0606-1	0.25	0.00			Py Ss
Hukazawa member					
0204	0.92	0.00	0.001	0.009	Ss
0204-1	1.49	0.00			Ss
Nojima member					
0203	0.004	0.017			S
2913	0.35	0.00			Ss
2915	0.15	0.01			Ss
Hayashi member					
3112	0.002	0.038			P
3113	0.002	0.010			Sand
Ohuna member					
2908	0.002	0.016			Ss
2909	0.20	0.00			S
2911	0.004	0.007			S
2912	0.001	0.007			S
0201	0.003	0.007			S
0201-1	0.002	0.008			S
0202	0.007	0.010	0.001	0.025	S
0703	0.003	0.012			S
0705	0.004	0.008	0.001	0.042	S
0706	0.004	0.022	0.001	0.018	S
Koshiba member					
0.704	0.082	0.001			Sand
Nakazato member					
0704-1	0.39	0.00			Silt
Tomioka member					
2901	0.003	0.008			Silt
2902	0.014	0.005			Silt
2903	0.003	0.008	0.000	0.024	Silt
2904	0.005	0.005	0.001	0.030	Silt

TABLE III-b. THE CHLORINE AND FLUORINE CONTENTS OF THE TERTIARY SEDIMENTS IN THE MIURA PENINSULA

Sample No.	W-Cl %	I-Cl %	W-F %	I-F %	Remarks
Misakimachi member					
0102	0.006	0.050	0.001	0.001	Py Ss
0102-1	0.41	0.00	0.001	0.021	S
0103	0.029	0.011			S
0103-1	0.003	0.022			Ss
0104	0.027	0.018	0.000	0.023	S
0104-1	0.005	0.037	0.001	0.007	Ss
0105	0.12	0.00			S
0105-1	0.008	0.030			Ss
0106	0.024	0.015			S
0106-1	0.006	0.029			Ss
Aburatsubo member					
0107	0.38	0.00	0.001	0.010	S
0107-1	0.055	0.05			Py P
0107-2	0.019	0.033			Py Ss
0108	0.082	0.03			Ss
0108-1	0.006	0.042			S
Zushi member					
3108	0.003	0.070	0.002	0.028	S
3108-1	0.002	0.025	0.002	0.018	Ss
3108-2	0.002	0.012			S
0101	0.019	0.008	0.002	0.030	S
0101-1	0.006	0.021			Ss
0506	0.018	0.002	0.001	0.026	S
0506-1	0.004	0.016	0.002	0.017	Ss
0602	0.004	0.013	0.000	0.027	S
0602-1	0.004	0.016	0.002	0.021	Ss
Nojima member					
2914	0.003	0.027	0.002	0.009	P
2914-1	0.012	0.020	0.001	0.018	S
Ohuna member					
2910	0.007	0.010	0.002	0.028	S
2910-1	0.009	0.09	0.001	0.033	Ss
Nakazato member					
2905	0.001	0.008			Sand
2905-1	0.003	0.003			Silt
2906	0.001	0.007	0.001	0.018	Silt
2906-1	0.001	0.007	0.001	0.014	Sand
2907	0.002	0.005			Silt
2907-1	0.002	0.006			Sand

Abbreviation used in Tables III-a and III-b has the following meaning:
W-Cl, water-soluble chlorine content; I-Cl, insoluble chlorine content; W-F, water-soluble fluorine content. I-F; insoluble fluorine content.
B, breccia; P, pebble conglomerate; Py P, pyroclastic pebble conglomerate; Py Ss, pyroclastic sandstone; S, siltstone; Ss, sandstone.

Discussion

Water-soluble Chlorine. — As is shown in Tables III-a and III-b, the water-soluble chlorine contents range from 0.001 to 1.5%. The samples containing a large amount of water-soluble chlorine seem to be contaminated with sea-water; they were collected on or near the coast. Therefore, we will omit the data which can be suspected of being contaminated with sea-water.

The frequency diagrams of the water-soluble chlorine contents of psammitic and pelitic rocks are shown in Fig. 2.

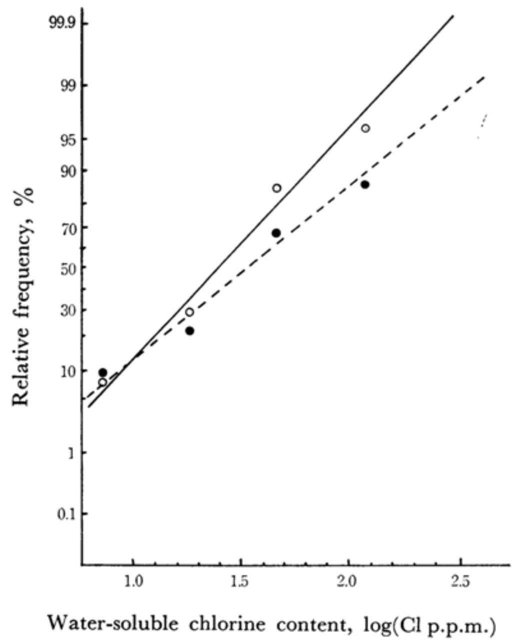
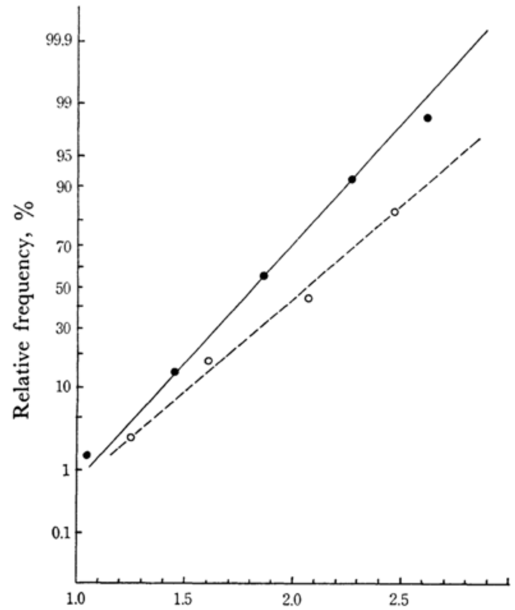


Fig. 2. Cumulative frequency distribution of water-soluble chlorine content of sediments.
○ Psammitic rocks
● Pelitic rocks

In this paper, we will divide all the sediments into two rock types. One is the psammitic rock type, in which sandstone, sand, pebble conglomerate, breccia, and pyroclastic sediment are included, and the other is the pelitic rock type, in which siltstone and silt are included. As is shown in Fig. 2, these two types of sediments show approximate lognormalities, rather than normalities. Provided that the frequency diagrams of the water-soluble chlorine contents of both psammitic and pelitic rocks obey the lognormal distribution, we obtain the geometrical means of the water-soluble chlorine contents of the two types of rock as 0.002 and 0.003 per cent respectively. From these values, it is clear that the samples which are not likely to be contaminated with sea-water contain very small amounts of water-soluble chlorine. Judging from their geometrical means, no significant effect caused by particle size was found on the distribution of water-soluble chlorine in these rock types. However, the water-soluble chlorine contents of the pelitic rocks are frequently higher than those of the psammitic rocks, as Table III-b shows. The tendency may be explained by saying that the pelitic rocks are much more retentive of chlorine than the psammitic rocks because of the larger adsorption surface and the lower permeability of the pelitic rocks.

Insoluble Chlorine.—The insoluble chlorine contents range from 0.00 to 0.09%. Figure 3 gives the frequency diagrams of the insoluble chlorine contents of the psammitic and pelitic rocks.



Insoluble chlorine content, log(Cl p.p.m.)

Fig. 3. Cumulative frequency distribution of insoluble chlorine content of sediments.
○ Psammitic rocks
● Pelitic rocks

They also show the lognormal distributions. We obtain the geometrical means of the insoluble chlorine contents of both psammitic and pelitic rocks as 0.011 and 0.006% respectively.

Figure 4 gives the horizontal and vertical distributions of the insoluble chlorine contents of the pelitic rocks in the Zushi member.

As Tables III-a and III-b show, the insoluble chlorine contents range from 0.00 to 0.070%. The terms "coast" and "deep sea" imply coastal and deep sea conditions during the age when the sediments were formed. The alphabetical letters on the right hand side of Fig. 4 indicate the names of the pyroclastic key beds. The thickness of the sediments among each key bed is arbitrarily drawn. We cannot find any regularity in the distribution of insoluble chlorine in the Zushi member from Fig. 4; this means that one specimen, or even a few specimens, collected from a member may not be truly indicative of the insoluble chlorine content. Also, it may be seen that the insoluble chlorine contents of the sediments can not be related to their sedimentary ages.

Water-soluble Fluorine.—As is shown in Tables III-a and III-b, the water-soluble fluorine contents range from 0.001 to 0.002%. Such small amounts of the water-soluble fluorine in the sediments are in striking contrast to the larger amounts of the water-soluble chlorine in the sediments previously shown. It is, however, clear that the water-soluble fluorine content may only slightly be influenced by the contamination of sea-water, because sea-water contains only 1.4 p.p.m. fluorine.

Assuming the extreme case that fluorite is a main carrier of fluorine in sediments and that the solution extracted is an aqueous solution saturated with

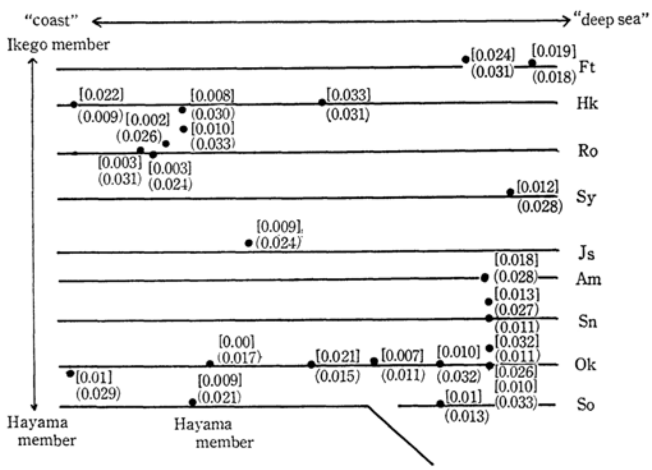


Fig. 4. Vertical and horizontal distributions of insoluble chlorine and fluorine in the Zushi member.
[ ] Insoluble chlorine content
( ) Insoluble fluorine content

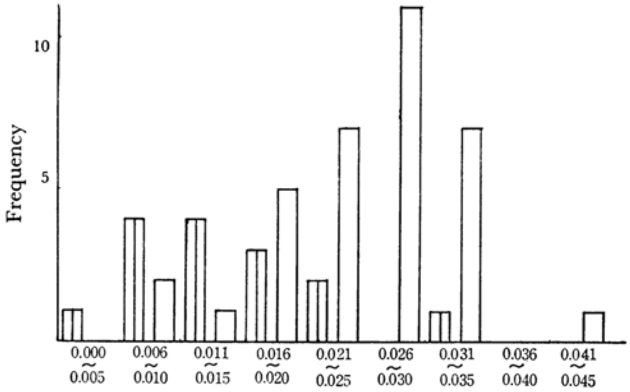


Fig. 5. Frequency distribution of insoluble fluorine contents of the psammitic and pelitic rocks.
Psammitic rocks
Pelitic rocks

fluorite (13.1 mg. fluorite per liter at 0°C[12]) in the case of water-soluble fluorine from 1 g. of a sample with 20 ml. of water, the fluorine content of the solution may be expected to become 0.013%. Actually, the water-soluble fluorine contents of samples were about ten times smaller than that calculated above. Therefore, it is thought that fluorine in these sediments does not exist as fluorite but as other forms.

Insoluble Fluorine.—As Tables III-a and III-b show, the insoluble fluorine contents of the sediments range from 0.001 to 0.042%. Figure 5 gives the frequency diagrams of the insoluble fluorine contents of both psammitic and pelitic rocks.

They seem to have neither normal nor lognormal distributions. Provided that they show normalities, we obtain the arithmetical means of psammitic and pelitic rocks as 0.025 and 0.014% respectively. The mean insoluble fluorine content of the former is twice as much as that of the latter. As may be seen in Fig. 5 and Table III-b, it is evident that the insoluble fluorine contents of the pelitic rocks are higher than those of the psammitic rocks, as has already been pointed out by Koritnig.[4] It is generally believed that the amounts of OH-bearing minerals in pelitic rocks are higher than those of psammitic rocks; thus, assuming that hydroxide ions in these minerals are replaced by fluoride ion in an aqueous solution, it may be reasonable to say that fluorine is concentrated in pelitic rocks.

Figure 4 gives the horizontal and vertical distributions of the insoluble fluorine in the Zushi member. As is shown in Tables III-a and III-b, the insoluble fluorine contents range from 0.009 to 0.033%. Figure 4 does not, however, show any trend in the distribution of insoluble fluorine in the Zushi member horizontally or vertically.

The Correlation between the Content of Insoluble Chlorine and of Fluorine in the Sediments.—Figure 6 shows the correlation between the contents of insoluble chlorine and fluorine in the sediments.

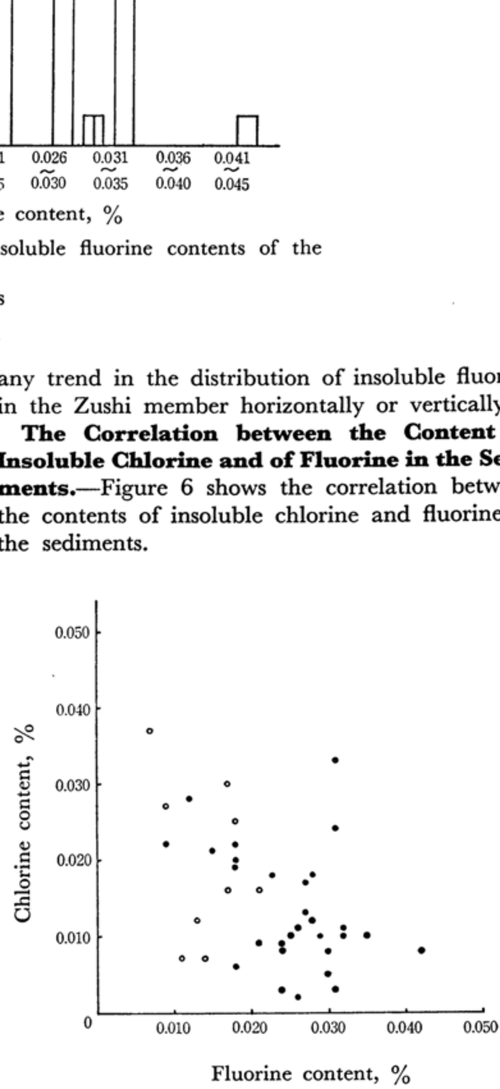


Fig. 6. Relationship between the contents of insoluble chlorine and fluorine of sediments.
○ Psammitic rocks
● Pelitic rocks

This shows a moderately negative correlation. Indeed, we have very little knowledge of the properties of OH-bearing minerals in sedimentary rocks, by which property some sort of replacement reaction might be expected to occur between halide and hydroxide ions. However, if we simply assume that the effective amount of hydroxide ions in the

12) F. Kohlrausch, *Z. physik. Chem.*, **50**, 355 (1904-5); **64**, 121 (1908).

sediments is constant and that the hydroxide ions are completely replaced by fluoride and chloride ions, there will be a negative correlation between the contents of fluorine and chlorine. As has been seen in Fig. 6, fluorine is more concentrated in pelitic rocks than in psammitic rocks, and concentrations above 0.02% fluorine are found exclusively in pelitic rocks. This may be attributed to the larger electronegativity and the smaller ionic radius of the fluoride ion than those of the chloride ion.

Conclusion

We may conclude from the above discussions that; 1) there is little correlation between the contents of insoluble chlorine and fluorine in the sediments and their sedimentary locations and ages; 2) it is almost impossible to estimate the contents of both insoluble chlorine and fluorine in a given member of sediments by using only one specimen geologically regarded as representative of the sediment in the member; 3) the insoluble chlorine contents of the psammitic rocks are higher than those of the pelitic rocks, whereas the insoluble fluorine contents of the former are lower than those of the latter; 4) there seems to be a moderately negaitve correlation between the contents of insoluble chlorine and fluorine; 5) all the sediments analyzed contain very small amounts of water-soluble fluorine (0.001 to 0.002% F), and 6) the frequency distributions of the insoluble chlorine contents in both psammitic and pelitic rocks are approximately lognormal.

The authors wish to express their thanks to Dr. Takashi Mitunashi, Geological Survey of Japan, for his valuable advice and criticism in the field observations. They are also much obliged to Dr. Sunao Ogose, the University of Tokyo, for his advice in the collection of the samples. They wish also to express their thanks to Professor Iwaji Iwasaki, Tokyo Institute of Technology, for his encouragement throughout this study. The expenses of this reseach were defrayed by a Scientific Reseach Encouragement Grant from the Ministry of Education, to which the authors' thanks are due.