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Fluoride and Borate-Boron in Interstitial Water of Marine Sediment

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Fluoride and borate-boron were determined in interstitial waters of core sediments from the Northwest Pacific.

The values of the fluoride to chloride concentration ratio in the interstitial waters are nearly equal to or lower than that in normal sea water, and derease with depth in the sediment core. And the values of borate-boron to chloride concentration ratio in the interstitial waters are higher than that in normal sea water, and show the trend to decrease with depth in the sediment core. The depletion of fluoride and borate-boron in interstitial waters in deep parts of sediment is probably due to the interaction with solid phase of the sediment.

Introduction

Fluoride and borate-boron are important anions as major constituents of sea water. They have roughly equal residence times in the ocean and similar concentrations in river waters and sea water. Then, it is expected that fluoride and borate-boron behave similarily in sea water. However, they are different in their removal processes in sea water due to the difference in their chemical natures (Kanamori, 1970). Thus, it seems to be interesting to compare the geochemical behaviors of fluoride and borate-boron in marine environments.

Many researchers have investigated the distribution and behavior of fluoride and borate-boron in open sea water (Greenhalgh and Riley, 1963; Riley, 1965; Brewer et al., 1970; Bewers, 1971; Kester, 1971; Kullenberg and Gupta, 1973; Kanamori et al., 1974). And these results indicate that the high concentrations of fluoride and borate-boron and the high ratios of fluoride and borate-boron to chlorinity are observed in bottom waters of some deep oceans. Kanamori et al. (1974) suggested that such high ratios of fluoride and borate-boron to chlorinity in bottom sea waters may be attributable to the supplies of fluoride and borate-boron from the same source in ocean floor to bottom sea water. For the mechanisms on the abnormal distributions of fluoride and borate-boron in bottom sea waters, it is helpful to clarify the behaviors of fluoride and borate-boron in interstitial waters contacted with bottom sediments.

Several papers on fluoride and borate-boron in interstitial waters have been published (Shishkina, 1966; Kitano et al., 1969; Windom, 1971; Kitano and Furukawa, 1972). However, little has been known about the distribution and behavior of fluoride and borate-boron in interstitial waters in deep oceans.

The purpose of this paper is to clarify the vertical distribution and behavior of fluoride and borate-boron in interstitial waters of deep sea sediments.

Experimental Procedures

Core samples were taken during Vega Expedition (KH–78–1) of the research vessels *Hakuho Maru* of Ocean Research Institute, the University of Tokyo in 1978. Three deep sea sediment samples studied are: (1) red clay from the Northwest Pacific, Stn. L–1: 16°46N, 136°36E), (2) greenish gray clay from the Northwest Pacific, Stn. M–4–1: 26°14N, 129°38E) and (3) calcareous clay from the Northwest Pacific, Stn. M–5: 26°10N, 131°08E). Manganese nodules (three pebles with 3 to 5 cm in diameter) were found near the surface of Stn. L–1 sediment.

Each of these sediment core samples was separated into 5 or 10 cm vertical sections on board, and was kept at 3 ± 2°C. The interstitial waters from these sediment samples were squeezed with a syringe squeezer at 3 ± 2°C within one week after collection. The interstitial waters were filtered at squeezing with 0.45 μm Millipore filter placed inside of the squeezer.

The following analytical methods were used.

Fluoride: Colorimetry with lanthanum-alizarin complexone mixed reagent (Greenhalgh and Riley, 1961).

Borate-boron: Colorimetry with curcumin (Grinstead and Sinder, 1967).

Chloride: Titration with silver nitrate standard solution.

Results and Discussion

Table 1 shows the concentrations of fluoride, borate-boron and chloride with depth in sediment core (expressed as weight per liter) in the interstitial waters from Stn. L–1 sediment, Stn. M–4–1 sediment and Stn. M–5 sediment. Chloride concentrantions in most interstitial waters are within 19 to 20 g/l, which is close to that in normal sea water.

Figure 1 plots fluoride to chloride concentration ratio and borate-boron to chloride concentration ratio in interstitial waters of the sediments, against the depth in sediment core. From this figure, it is seen that the values of $[F^-]/[Cl^-]$ and $[\text{Borate-B}]/[Cl^-]$ in the interstitial waters decrease slightly with depth to reach minimum values at 200 to 300 cm depth in the sediments and then increase with further increasing depth.

Fluoride The trends of the vertical change in the value of $[F^-]/[Cl^-]$ are similar in interstitial waters of Stn. L–1, Stn. M–4–1 and Stn. M–5 sediments, as seen from Fig. 1. But the values of $[F^-]/[Cl^-]$ in the interstitial waters of these three sediments are different from each to other. That is, the values follow the following order:

Table 1. Fluoride, borate-boron and chloride concentrations in interstitial waters of marine sediments in Northwest Pacific.

Core	Core depth (cm)	F^- (mg/*l*)	Borate-B (mg/*l*)	Cl^- (g/*l*)	$F/Cl \times 10^5$	$Borate\text{-}B/Cl \times 10^4$
Stn. L–1 sediment	0–5	1.54	5.3	19.38	7.94	2.7
	5–10	1.50	5.1	19.15	7.83	2.7
	15–20	1.49	5.5	19.38	7.68	2.8
	30–35	1.39	6.3	19.54	7.11	3.2
	50–60	1.38	5.8	19.27	7.16	3.0
	70–80	1.33	5.6	19.14	6.94	2.9
	100–110	1.39	5.9	19.35	7.18	3.1
	150–160	1.37	5.4	19.38	7.06	2.8
	200–210	1.32	5.9	19.30	6.83	3.0
	250–260	1.18	5.8	19.28	6.11	3.0
	300–310	1.16	4.8	19.22	6.03	2.5
	350–360	1.26	5.4	19.23	6.55	2.8
	400–410	1.30	5.5	19.72	6.59	2.8
	450–460	1.28	6.2	19.18	6.67	3.3
	Mean	1.32	5.6	19.32	6.98	2.9
Stn. M–4–1 sediment	0–10	1.16	5.5	19.13	6.06	2.9
	20–30	1.21	5.6	19.33	6.25	2.9
	40–50	1.15	5.4	19.43	5.91	2.8
	60–70	1.31	4.8	19.40	6.75	2.5
	80–90	1.23	5.1	19.35	6.35	2.6
	100–110	—	6.1	21.91	—	2.8
	130–140	1.27	5.0	19.74	6.43	2.5
	160–170	1.16	5.0	19.45	5.96	2.6
	190–200	1.13	4.6	19.44	5.81	2.4
	Mean	1.20	5.2	19.69	6.19	2.7
Stn. M–5 sediment	0–10	1.31	5.8	19.37	6.76	3.0
	20–30	1.36	5.4	19.29	7.06	2.8
	40–50	1.27	6.1	19.67	6.45	3.1
	60–70	1.35	5.6	20.67	6.53	2.7
	80–90	1.32	5.0	19.94	6.61	2.5
	100–110	1.33	5.2	19.60	6.78	2.7
	118–123	1.39	4.8	19.58	7.09	2.4
	160–170	1.27	4.7	19.38	6.55	2.4
	190–200	1.27	4.7	19.69	6.45	2.4
	220–230	1.21	4.9	19.39	6.24	2.5
	250–260	1.24	4.8	19.37	6.40	2.5
	280–290	1.27	5.4	19.68	6.45	2.7
	310–325	1.21	5.3	20.21	5.98	2.6
	Mean	1.29	5.2	19.68	6.56	2.6

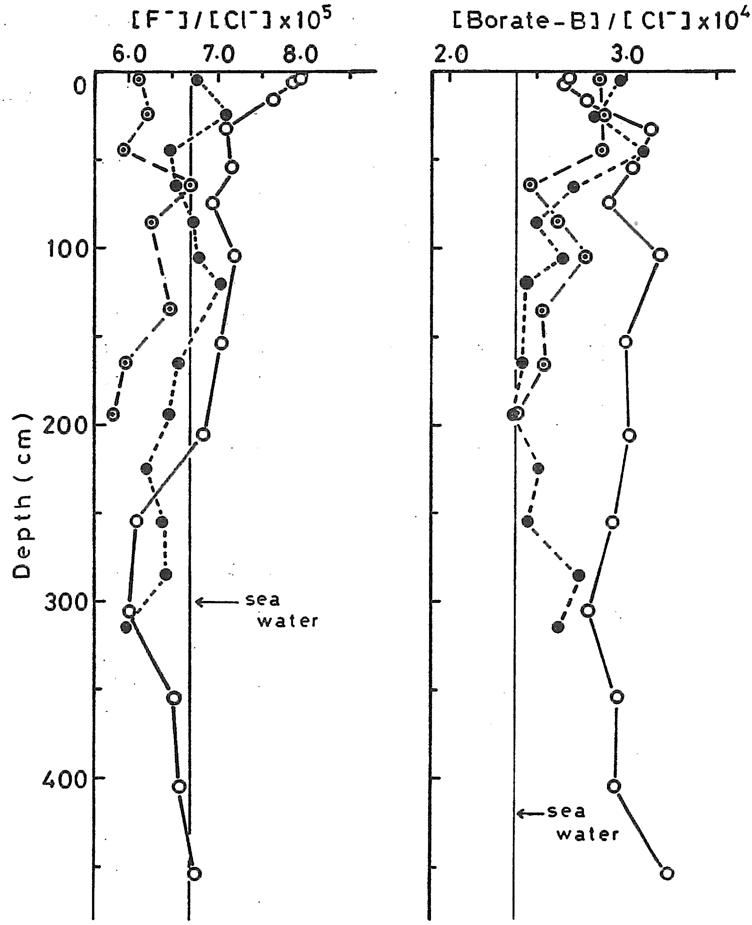

Fig. 1. Vertical profiles of [F⁻]/[Cl⁻] and [Borate-B]/[Cl⁻] in interstitial waters in three pistone cores.

○ Stn. L–1 sediment
◎ Stn. M–4–1 sediment
● Stn. M–5 sediment

Stn. L–1 sediment > Stn. M–5 sediment > Stn. M–4–1 sediment.

The value of [F⁻]/[Cl⁻] in normal sea water is about 6.7×10^{-5} (Greenhalgh and Riley, 1963; Riley, 1965). The values of [F⁻]/[Cl⁻] in the interstitial waters from the upper parts of Stn. L–1 sediment and Stn. M–5 sediment are a little higher than or nearly equal to that in sea water, except the very high value of [F⁻]/[Cl⁻] in the interstitial waters near the surface of Stn. L–1 sediment (0–35 cm), whereas the values in their deep parts are lower than that in sea water. It is noted that manganese nodules were found in the surface sediment at Stn. L–1. It is unclear whether or not the very high concentration of fluoride in the interstitial water at the surface of Stn. L–1 sediment has some connection with the existence of manganese nodules there. The values for Stn. M–4–1 sediment are lower than that in sea water throughout the entire sediment. These facts may suggest that fluoride is removed from interstitial water through diagenetic processes. In order to clarify the removal of fluoride from interstitial water, the interaction between fluoride in interstitial water and sediment contacted with the water should be examined. It has been known that fluoride is easily incorporated into calcium phosphate minerals such as apatite. Apatite is formed directly from interstitial water or through the transformation of calcium carbonate to apatite in marine sediments (Anglejan, 1968; Brooks et al., 1968). Therefore, fluoride is expected to be incorporated with apatite (Kramer, 1965; Kitano et al., 1978). But the occurrence of apatite in the sediments studied has not been detected. Clay minerlas are a major constituent of the sediments used in this study. Although clay minerals are not expected to act an important role in the removal of fluoride from interstitial water (Bower and Hatcher, 1967; Carpenter, 1969), the role of clay minerals can not be always neglected. The depletion of fluoride in the interstitial waters remains to be clarified.

Borate-boron The values of [Borate-B]/[Cl^-] in interstitial waters decrease with depth, except those at Stn. L–1. In contrast to [F^-]/[Cl^-], the values of [Borate-B]/[Cl^-] in interstitial waters are higher than that in sea water ([Borate-B]/[Cl^-]$\approx 2.4\times10^{-4}$), especially those in Stn. L–1 sediment are very high. These observations suggest that the behavior of borate-boron is different from that of fluoride in interstitial water during sedimentation and diagenetic processes.

It was known that borate-boron is easily adsorbed on clay minerals, especially on illite. Thus, the depletion of borate-boron in interstitial water at deep parts of sediments may be due to the adsorption of borate-boron on clay minerals contacted with the water.

The enrichment of borate-boron and the high value of [Borate-B]/[Cl^-] in interstitial water relative to overlying water were also observed in interstitial waters in the inlets of Juneau glacier and Tracy Arm (Kitano et al., 1969). The Kitano's study and also the present study make it possible to conclude that borate-boron is easily enriched in interstitial water near the surface of sediments, although the reason for this enrichment still remains unsolved.

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