Seasonal Movements of Phosphorus and Iron Compounds, Dissolved Hydrogen Sulfide, and Others in Anoxic Seawater at Lake Hamana[§]

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The sea bottom in the vicinity of the center of Lake Hamana in Japan forms a sea basin, and anoxic seawater appears in this bottom layer in summer. We examined the seasonal movements of phosphorus and iron compounds, dissolved hydrogen sulfide, and others in this anoxic seawater with a view to investigating their elution processes from the sediments of the sea basin into the anoxic seawater. Some parts of the elution phenomena of these components from the sediments of the sea basin in Lake Hamana into the anoxic seawater in summer will be described in the present work.

The sea bottom in the vicinity of the center of Lake Hamana in Japan forms a sea basin. Anoxic seawater appears in this bottom layer in summer because the hydrosphere in the basin becomes a reducing atmosphere at a high temperature as a result of the small tidal currents and the decomposition of dead marine organisms such as plankton deposited on the sea floor. However, very little information is available in the literature on the seasonal movements of phosphorus and iron compounds, dissolved hydrogen sulfide (DHS), and others, in the anoxic seawater occurring in a sea basin such as Lake Hamana.

We ourselves have reported previously analytical methods for dissolved inorganic phosphorus (DIP) and organic phosphorus (DOP)[1-3] and DHS[4,5] eluted from the sediments of the sea basin in Lake Hamana into the anoxic seawater. By applying mainly our analytical methods, we have now examined the seasonal movements of DIP, DOP, iron(II) and iron(III) ions, DHS, and others in the anoxic seawater occurring in the sea basin, with a view to investigating geochemically their elution processes from the sediments.

Experimental

Analytical Procedure for DHS. Sample solutions (4-ml volume) from different water depths are introduced from Kitahara's bottle into a 10-ml syringe containing 4 ml of an acetone solution of hydroxylamine hydrochloride(0.2%). After the removal of an air bubble, the syringe is shaken gently, then most of the mixed sample solution is transferred into a 7-ml dark plastic bottle. The bottle is immediately sealed and stored at 0 °C. The DHS in the stored solution is determined by means of gas chromatography under the conditions shown in Table 1.

Table 1. Analytical Conditions for the Determination of Dissolved Hydrogen Sulfide by Means of Gas Chromatography

Column temperature	110 °C
Injection temperature	150 °C
H_2 pressure	0.75 kg cm^{-2}
Air pressure	1.30 kg cm^{-2}
Carrier gas	Nitrogen, 90 ml min^{-1}
Injection volume	2 µl
Glass column	1.1×3.2 mm i.d.
Packing material	Porapak N (50—80 mesh)

The initial DHS concentration in anoxic seawater is determined by reference to previously prepared calibration and decay curves for DHS at a rate of about 0.5% per hour over a 24-h period after sampling. For further details, the reader should refer to Refs. 4 and 5.

Analytical Procedure for DIP and DOP, and for Fe(II) and Fe(III). The DIP and DOP and the Fe(II) and Fe(III) in anoxic seawater are determined by the heteropoly-blue method[1,3] and by 1,10-phenanthroline spectrophotometry[6] respectively.

Results and Discussion

The water samples were taken using Kitahara's bottle from different water depths (at intervals of about 1 m) at two Stations, A and B, in Lake Hamana.[5] The sea bottom of Station A, in the vicinity of the center in Lake Hamana, forms the deepest sea basin (about 12 m) in the lake, while Station B, used as a control for A, stands at one end of this sea basin.

Figure 1 shows the seasonal variations in the dissolved oxygen (DO), the salinity, the pH, and the temperature at different water depths of Stations A and B at roughly monthly intervals for the year in 1983. It may be observed from the results shown in Fig. 1 that DO decreased gradually with the increase

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in the water depth from near 4 m of Station A in March to September, closely approaching zero at the deep water depths of 7 to 11 m in May to September; the pH in seawaters of Station A showed a decreasing

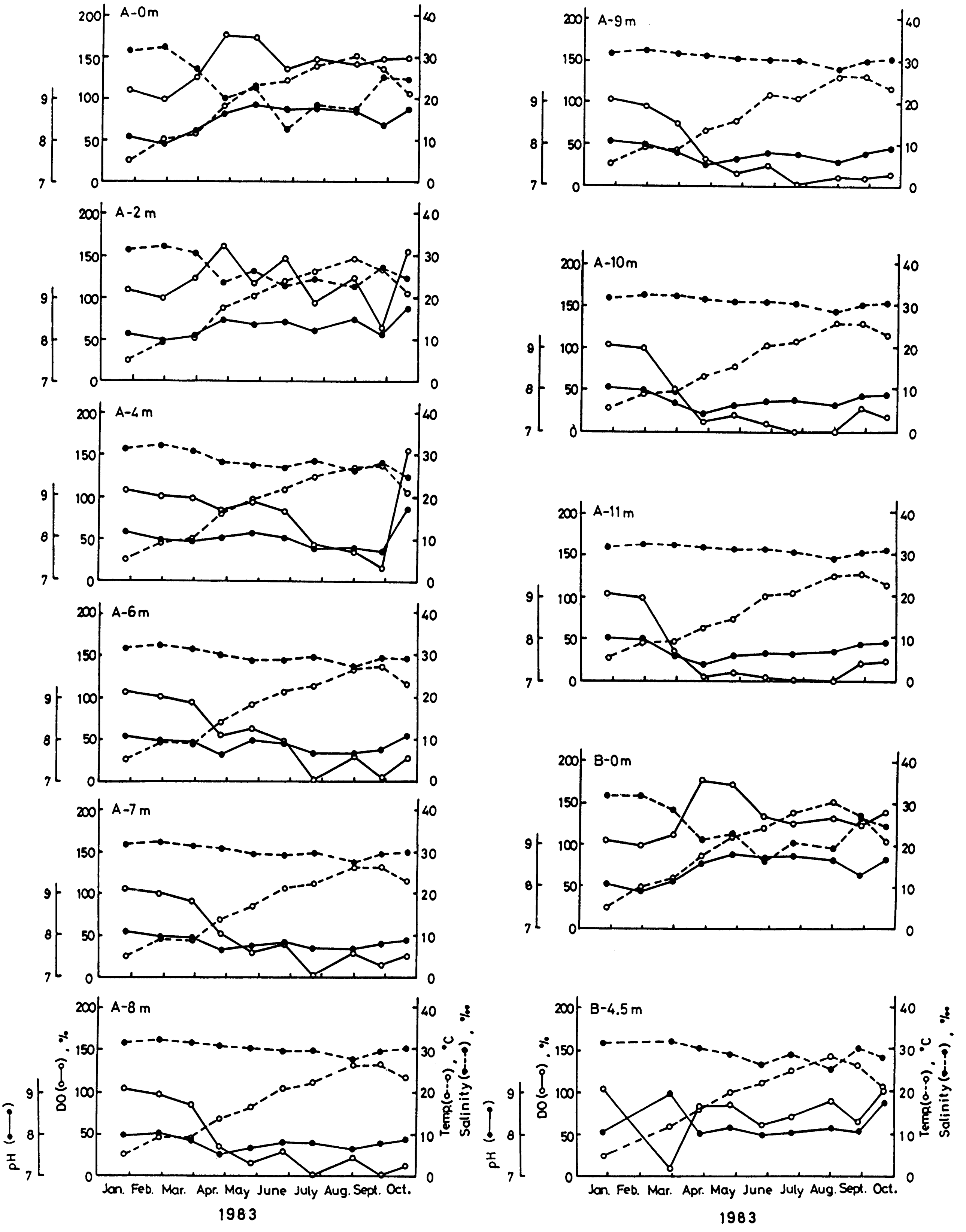

Fig. 1. Seasonal variations of dissolved oxygen, salinity, pH, and temperature in the seawater at different water depths of the stations A and B in 1983.

trend like DO with the increase in the water depth from near 4 m in March to September, while the water temperature reached a maximum near 30 °C at every water depth in August or September. From such changes in the DO and the pH, it can be estimated that the sea basin of Station A rises from a water depth of about 4 m and that its bottom layer presents a reducing atmosphere from March to September.

Figure 2 shows the seasonal variation in the contents of DIP, Fe(II), Fe(III), and DHS in the seawater at different water depths of Stations A and B at roughly monthly intervals for the year of 1983. The following points particularly attract attention among the results shown in Fig. 2:

(a) The DIP increased remarkably with the increase in water depth from near 3 m of Station A in roughly inverse interrelation to the DO and the pH in the summer season (June to September), while the DOP was 10 ppb or less at every water depth of both stations at all times. Therefore, the DOP was not

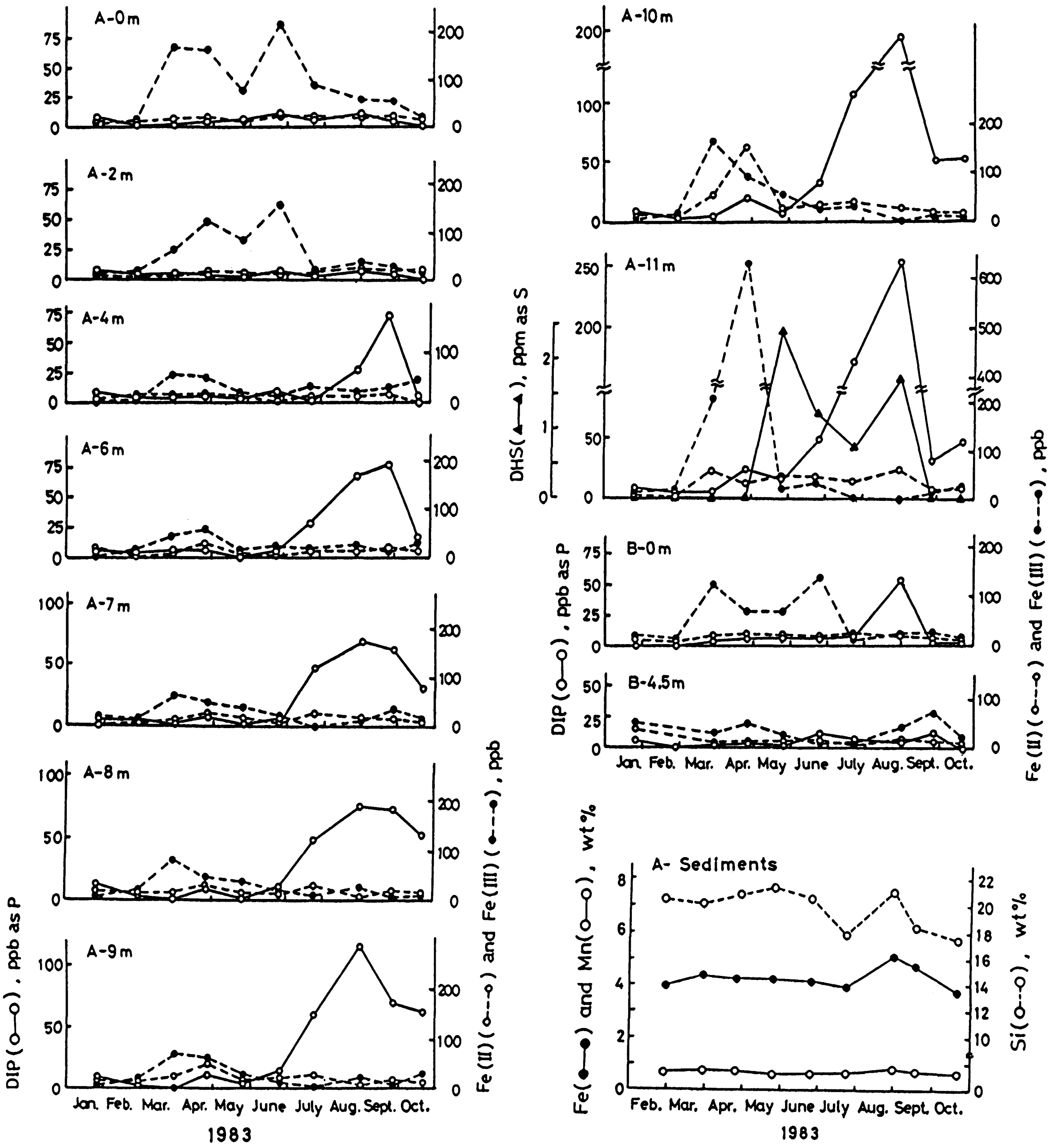

Fig. 2. Seasonal variations of dissolved inorganic phosphorus, Fe(II), Fe(III), and dissolved hydrogen sulfide in the seawater at different water depths of the stations A and B, and those of some elements in the sediments at the station A in 1983.

plotted in Fig. 2.

(b) The maxima of Fe(II) and DIP, even in a small peak, were simultaneously observed at the deep water depths from 7 to 11 m near the sediments of Station A around April.

(c) On the other hand, the peaks of Fe(III) at the same deep water depths appeared from March to April and had almost disappeared already when the DIP and a large amount of the DHS appeared in the anoxic seawater in the early summer season.

(d) However, the concentrations of Fe(III) in the seawater samples collected from the surface to a water depth of near 2 m of Stations A and B were higher than those in the anoxic seawater at the middle water depths of both stations from March to April, while they had the two maxima from March to the early summer season.

(e) The considerable amounts of DHS, which are several times as much as the DIP or Fe(II) contents, were detected at a water depth of 11 m of Station A in the summer season when the DIP appeared in the anoxic seawater.

(f) The seasonal variations of some elements in the surface layer of the sediments at the sea basin of Station A are shown in Fig. 2. It is evident from these results that considerable amounts of iron at least exist in the sediments, and that these seasonal curves of Fe and Si both have a miximum in summer. On the other hand, the Fe and Mn in plankton collected near the sea surface at Station A in August in 1983 constituted dry percentages of 3.5 and 0.05 respectively.

Figure 3 shows the vertical profiles of DIP, Fe(II),

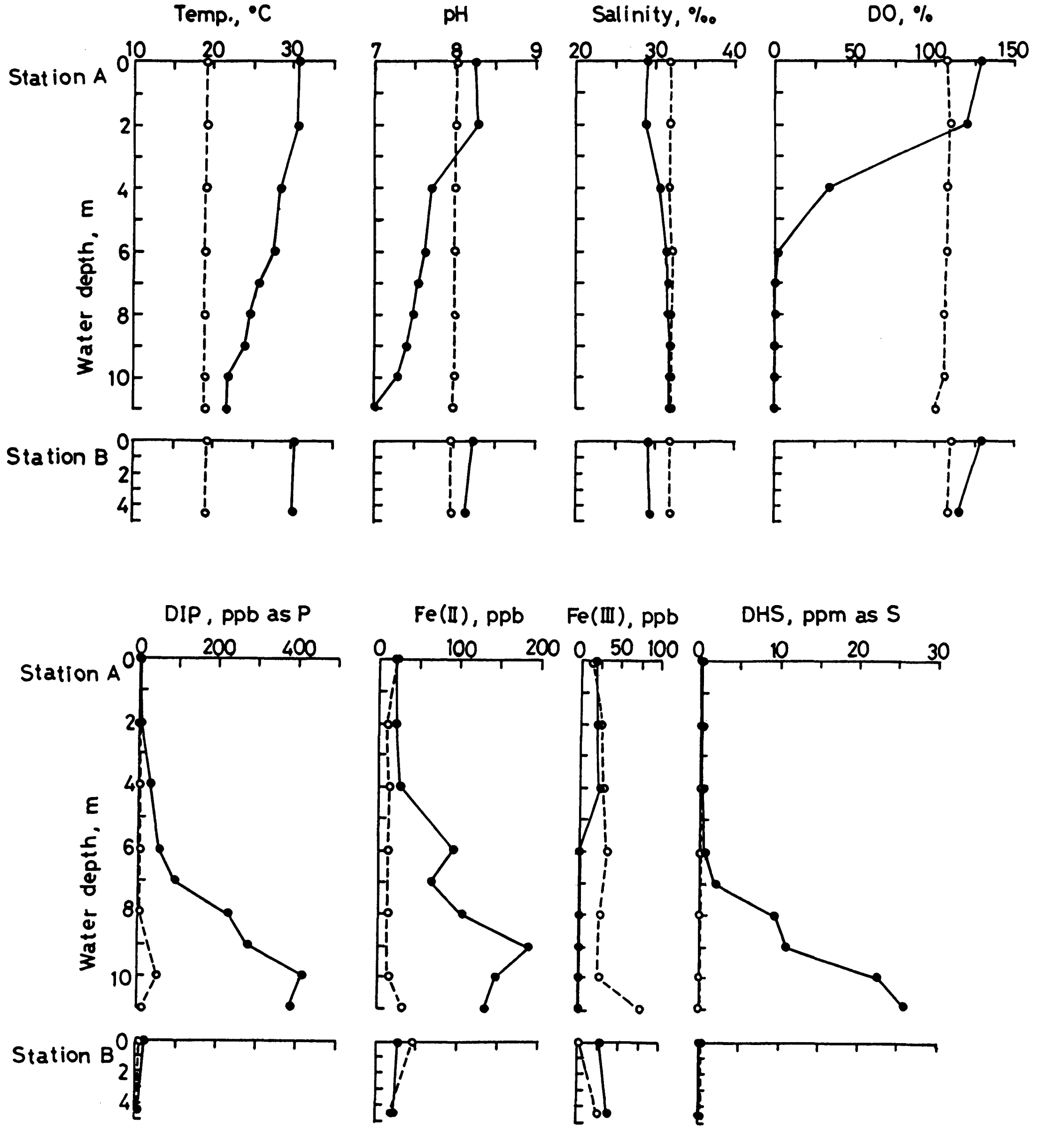

Fig. 3. Vertical profiles of dissolved inorganic phosphorus, Fe(II), Fe(III), dissolved hydrogen sulfide, and others in the seawater at the stations A and B in 1984. ●—●: in September, 1984, O---O in October, 1984.

Fe(III), DHS, and others in the anoxic seawater at Stations A and B in September and October in 1984. Since in Japan it was a relatively cold summer in 1984, and since, besides, some typhoons hit Lake Hamana in the summer, the anoxic seawater had not developed fully until the end of August that year. It is apparent from the vertical profiles shown in Fig. 3 that, in September at Station A, the DIP, Fe(II), and DHS were simultaneously eluted from the sediments of the sea basin into the anoxic seawater under the conditions at DO$\approx$0, and that they then diffused gradually into the upper layer, whereas in October at Station A the DO has already reached saturation at every depth and so hardly any vertical changes with the water depth were observed. The variations shown in Fig. 3 correspond quite well to those shown in Fig. 2.

The molalities at each maximum in the seasonal-variation curves for DIP, Fe(II), Fe(III), and DHS at the water depth of A-11 m (Fig. 2) were 8.19, 1.07, 11.3, and 74.5 mmol m^{-3} respectively, while those for DIP, Fe(II), and DHS at the water depth of A-11 m in September (shown in Fig. 3) were 12.3, 2.38, and 754 mmol m^{-3} respectively.

Conclusion

On the basis of the above-mentioned experimental facts, we reached the following conclusions regarding the elution phenomena of DIP, Fe(II), Fe(III), and DHS from the sediments of the sea basin in Lake Hamana into the anoxic seawater in summer:

(1) The DIP is undoubtly eluted, together with a large amount of DHS and a small amount of Fe(II), from the sediments of the sea basin into anoxic seawater under the conditions of the water near the sediments at DO$\approx$0 and at water temperatures$\approx$20—30 °C in the summer season (see (a), (e) and Fig. 3 in Results and Discussion). The tendency for DIP to decrease with shallowing the water depth may be caused by the diffusion of the tidal current or by its being taken as nutrition by the plankton living in the shallow water layer. Such elutions of DIP and DHS from the sediments into the anoxic seawater in summer season might result mainly from the decomposition of dead plankton deposited on the surface of the sea basin according to a chemical reaction, represented by Richards,$^{7)}$ which proceeds from the action of anaerobic bacteria in the sediments at the reducing atmosphere under the above-mentioned conditions.

Furthermore, the elutions of Fe(II) and DIP may occur by their changing chemically from very slightly soluble $FePO_4$ in water to hardly soluble $Fe_3(PO_4)_2$ in the sediments at the above-mentioned reducing state and by the dissociation of the $Fe_3(PO_4)_2$ with the drop in the pH(<7) of the interstitial water in the sediments according to the following Eqs. 1 and 2:$^{8)}$

$$FePO_4 \xrightarrow{\text{reducing state}} Fe_3(PO_4)_2 \qquad (1)$$

$$Fe_3(PO_4)_2 \xrightleftharpoons{pH<7} 3Fe^{2+} + 2PO_4^{3-} \qquad (2)$$

Such inference does not contradict the experimental fact that the maxima of Fe(II) and DIP at the deep water depths, even in a small peak accompanying the decrease in DO around April, appeared simultaneously in Fig. 2(see (b) and Fig. 3 in Results and Discussion).

(2) The Fe(II) appearing in the anoxic seawater from the sediments around April, as is shown in Fig. 2, and in August or September, as is shown in Figs. 2 and 3, may be rapidly oxidized to Fe(III) in the shallow water layer by the DO according to the following Eq. 3:

$$Fe(II) \xrightarrow{O_2(DO)} Fe(III) + e^- \qquad (3)$$

(3) The peaks appearing in the seasonal-variation curves of Fe(III) at the deep water depths of Station A from March to April, as is shown in Fig. 2 (see (c) in Results and Discussion), may result from a slight dissociation of $Fe(OH)_3$ as a hardly soluble precipitate in water with the drop in the pH of the interstitial water in the sediments, as is shown in Fig. 1, and/or from the above-mentioned oxidation of Fe(II) by the DO (see (b) and (f)).

From the experimental findings that the concentrations of Fe(III) in the water near the surface of Stations A and B were higher than those in the anoxic seawater at the middle water depths of both stations for the above period, and that they had their two maxima in the season from March to early summer, as is shown in Fig. 2 (see to (d) in Results and Discussion), it can also be thought that some organic substances serving as chelators for Fe(III) which are produced from plankton living in the seawater near the sea surface may contain some Fe(III), or that on the occassion of sampling, a little plankton containing Fe(III) may be taken into the water samples (see (f) in Results and Discussion).

(4) The rapidly decaying phenomena, especially at the bottom layers, of Fe(II) and Fe(III) in the seasonal-variation curves at different water depths of Station A, as is shown in Fig. 2 (see (b), (c), and (d) in Results and Discussion) when the DIP and the large amounts of DHS appeared just in the anoxic seawater in the early summer season might be only an apparent decrease resulting from the formation$^{8)}$ of FeS or FeS·S as a hardly soluble precipitate with the DHS, according to Eqs. 4 and 5:

$$2Fe^{3+} + H_2S \longrightarrow 2Fe^{2+} + S\downarrow + 2H^+ \qquad (4)$$

$$Fe^{2+} + S^{2-} \longrightarrow FeS\downarrow \qquad (5)$$

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References

1) N. Ichinose, C. Shimizu, H. Kurokura, T. Inui, and K. Kadohata, *Bunseki Kagaku,* **31**, 532 (1984).

2) N. Ichinose, C. Shimizu, H. Kurokura, and T. Inui, *F. Z. Anal. Chem.,* **316**, 791 (1983).

3) N. Ichinose, H. Kanai, and K. Nakamura, *Anal. Chim. Acta,* **156**, 345 (1984).

4) N. Ichinose, K. Adachi, and C. Shimizu, *J. Chromatogr.,* **292**, 393 (1984).

5) N. Ichinose, C. Shimizu, K. Okamoto, T. Inui, and K. Adachi, *Anal. Sci.,* **3**, 131 (1987).

6) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, New York (1959).

7) F. A. Richards, in "Chemical Oceanography," Vol. 1, ed by J. P. Riley and G. Skirrow, Academic Press, London (1965), pp. 623—634.

8) K. Sugawara, T. Koyama, and E. Kamata, *J. Earth Sci., Nagoya Univ.,* **5**, 60 (1957).