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PARTICULATE IRON IN THE BERING SEA *

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Introduction

The iron in marine water occurs in various forms. It is essential for all plants and animals. Cooper (1948a) catalogued a number of forms of iron contained in sea water, but is difficult to assay quantitatively more than two forms, the soluble and the particultate, where the distinction between them is arbitrarily dependent upon the porosity of the filter utilized for the separation. The greater portion of the iron in marine water may be in colloidal or other particulate forms, inasmuch as the solubility of ferric and ferrous hydroxides will allow but 0.5γ/L of iron exists as ionic species. As demonstrated by many investigators (Cooper, 1935; Thompson & Bremner, 1935; Rakestraw, Mancke & Beach, 1936), the distribution of iron in the sea seems usually very erratic. Lewis and Goldberg (1954) have pointed out the fact that the so-called soluble iron is quite uniformally dispersed throughout the oceans. Accordingly the erratic distribution of iron in the sea must be attributed to the random distribution of relatively large particles of iron compounds in suspension.

The particulate iron in marine water plays an important rôle in biogeochemical cycle in the ocean (Gran, 1933). Harvey (1937) has demonstrated that diatoms are able to assimilate ferric hydroxide or ferric phosphate in colloidal or particulate forms and to utilize it in their growth. Furthermore Goldberg (1952) observed that the marine diatom *Asterionella japenica* utilzed only particulate and/or colloidal iron as growth nutrient whereas ionically complex ferric iron as the citrate, ascorbate or artificial humate was not available for uptake. On the other hand, Goldberg (1954) considered the ability of the hydrated oxides of iron and manganese to adsorb ions from solution (*SCAVENGING*) in relation to some problems in marine sciences, and demonstrated that the distribution of some ionic species is influenced by their adsorbability by particulate iron and manganese oxides.

Few available data have ever been published on the distribution of iron, especially in the particulate form, in the pelagic waters of the North Pacific and the Bering Sea (Thompson & Bremner, 1935; Lewis & Goldberg, 1954), notwithstanding the important significance of the particulate iron in the field of the biogeochemistry of the ocean. Oceanochemical investigation of the particulate iron in the water of the Bering was undertaken by the author and his collaborators, in the summer of 1955, when on board the training ship "Oshoro-Maru" (617 tons) of the Faculty of Fisheries, Hokkaido University.

* Report from the "Oshoro-Maru" on oceanographic and biological investigations in the Bering Sea and Northern North Pacific in the summer of 1955. III. おしよろ丸北洋調査報告 No. 6 (1955年度)

This cruise of the "Oshoro-Maru" had been planned for participating in the North Pacific Oceanographic Expedition (NORPAC Expedition) coordinated by the oceanographic institutions of Japan, Canada and the United States. The "Oshoro-Maru" Expedition (Motoda & Fujii, 1956) in the summer of 1955 was conducted by Prof. Shigeru Motoda and a group of scientists from the Faculty engaged directly in research work connected with their specific interests.

The "Oshoro-Maru" departed from Hakodate on June 21, 1955, cruising northward, and arrived at the first station of the Expedition off the south-eastern coast of Kamchatka on June 26. The hydrographic casts and plankton sampling as well as gill-net operation were begun from this day. The routine observations were finished at the thirty-seventh station in the southwest of the Gulf of Alaska on the 21th of July. The problems of particulate iron in the water were studied using samples taken at the seven stations which are indicated in Figure 1 and summarized in Table 1.

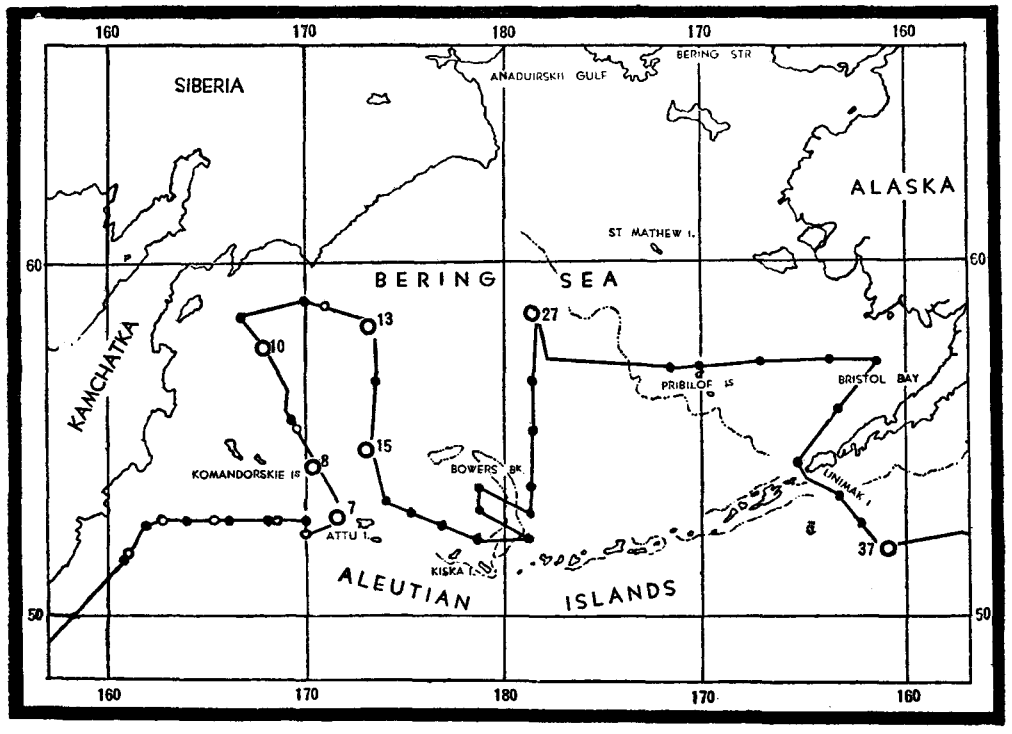

Fig 1. Observation station on the OSHORO-MARU EXPEDITION in the summer of 1955

Experimental

1. *Collection and Pretreatment of Water Samples*

Measured sample of 500 ml (or 250 ml) sea water, collected in Nansen bottles, was passed through a molecular filter. The filter was dried in the dryer equipped with two

ultra-red lamps for about ten minutes until quite dry, put into a polyethylene envelope and sealed by heating for preservation without external contamination. The sealed filters were brought to the laboratory of the Faculty of Fisheries of the University and subjected to chemical determination.

The molecular filter utilized in the present investigaton was "Membranfilter Grob 3" (made in Germany), whose porosity is 500 mμ.

2. Determination of Particulate Iron on the Filter

Particulate iron separated on the dried filter was determined colorimetrically by means of α, α'-bipyridyl method which was utilized by Lewis and Goldberg (1954).

The molecular filter was taken out from the sealed emvelope, and placed in 30 ml Kjeldahl flask containing 5 ml of perchloric acid. Heat was applied until no further evolution of acid fumes was observed. When cooled, 1 ml of 1.2N HCl and 10 ml of water was added, after which the contents were transferred to a 50-ml measuring flask. The Kjeldahl flask was rinsed with two 10 ml portions of water. The combined solutions were treated with 1 ml each of 10% hydroxylamine hydrochloride, 50% sodium acetate, and 0.4% bipyridyl solutions. After the sample was diluted to 50 ml, its optical density was determined in an A. K. A. Photoelectric Tube Colorimeter (Kotaki-Seisakusho Ltd.) at 530 mμ with utilization of a S-53 Filter attached to the colorimeter.

In the present experiments, all of the reagents were utilized of Reagent Grade, and various pretreatments were employed for most of them for the purpose of removing any trace impurity of iron, previous to their preparation of reagent solutions:

Solution of recrystallized hydroxylamine hydrochloride was treated with o-phenanthlorine solution and the colored ferroin complex was extracted with redistilled iso-amyl alcohol until no further red color appeared. The same pretreatment was also applied to the solution of sodium acetate. Glacial acetic acid and hydrochloric acid were respectively distilled, but only perchloric acid was utilized without any treatment because of the practical difficulty of its purification. The sixty percent solution of perchloric acid (Wako Junyaku Co.) used in the present experiments contains 0.3 γ/ml of iron as impurity. The distilled water was used after passing further the columns of ion exchange resins for rendering completely free from iron.

If the reagent solutions are properly purified, the only extraneous iron comes from the perchloric acid and the molecular filter. The blank test showed the existence of 1.6 γ iron in average, of which the portion from the filter was 0.4 γ.

Results and Discussion

Data obtained from the present investigation are summarized in Table 1. A typical example of vertical distribution of the particulate iron is plotted in Figure 2 in comparison with the other physical and chemical data (Fac. Fish. Hokkaido Univ. 1956; Kato, 1957)

measured in the present expedition. In these figures, the "turbidity" was determined on board by the scattering intensity method just after collecting the water sample, and is indicated as Coleman Nepheros Unit.

Table 1. Particulate iron in the Bering Sea

Os 7 (53°02′-N, 172°00′-E)		Os 8 (54°30′-N, 170°33′-E)		Os 10 (57°41′-N, 167°59′-E)		Os 13 (58°30′-N, 173°15′-E)		Os 15 (55°10′-N, 173°17′-E)		Os 27 (58°49′-N, 178°43′-W)		Os 37 (52°15′-N, 161°09′-W)	
Depth m	Fe γ/L	Depth m	Fe γ/L	Depth m	Fe γ/L	Depth m	Fe γ/L	Depth m	Fe γ/L	Depth m	Fe γ/L	Depth m	Fe γ/L
0	226	0	20	0	72	0	71	0	32	0	38	0	51
10	67	10	8	10	26	10	13	10	8	8	13	10	11
25	38	25	6	25	34	25	16	24	6	21	7	25	25
50	60	50	6	50	14	50	77	48	8	42	9	50	8
75	82	75	2	75	64	75	7	72	8	60	6	75	2
100	14	98	8	99	100	98	16	92	2	100	12	100	5
150	8	147	15	150	27	148	10	138	20	141	8	150	8
200	19	197	14	200	15	197	17	184	4	169	2	200	13
292	10	295	3	269	8	278	19	276	2	240	13	298	12
392	21	394	15	365	20	370	20	369	5	302	2	398	21
492	3	493	6	460	27	464	11	460	2	361	11	498	14
591	12	593	3	555	26	554	8	554	8	478	6	597	14
785	10	792	8	740	8	754	20	749	7	625	17	796	17
990	40	980	9	935	25	942	22	939	5	799	12	994	20
1184	6	1177	15	1162	14	1170	8	1120	2	1053	12	1193	8
1485	3	1472	3	1456	18	1460	15	1400	8	——	——	1492	18
——	——	1989	11	——	——	——	——	——	——	——	——	——	——

A number of oceanographic observations in the Bering Sea (Barnes & Thompson, 1938; Watanabe et al, 1954; Mishima & Nishizawa, 1955; Koto, 1957) may demonstrate the following hydrographic features of the Bering.

The deep waters below about 200 meters are similar to these in the subarctic region of the North Pacific, on the basis of temperatures, salinities, and dissolved oxygen values at stations within the Bering to the south of the Aleutian Chain. At the intermediate region ranging at depths of about 75 to 200 meters, characteristic layers of cold waters of which the salinities are approximately similar to those of the upper layers were observed at all stations in the Bering. The temperature minimum of the dicothermal layer was found near 150 meters level, and an oxygen minimum appeared usually at the upper level of the dicothermal layer. Accordingly, as pointed out by Barnes and Thompson (1938), the depth of the temperature minimum in the dicothermal layer may represent the depth to which convection currents reach in the winter season.

Lewis and Goldberg (1954) pointed out in respect to the vertical distribution of iron

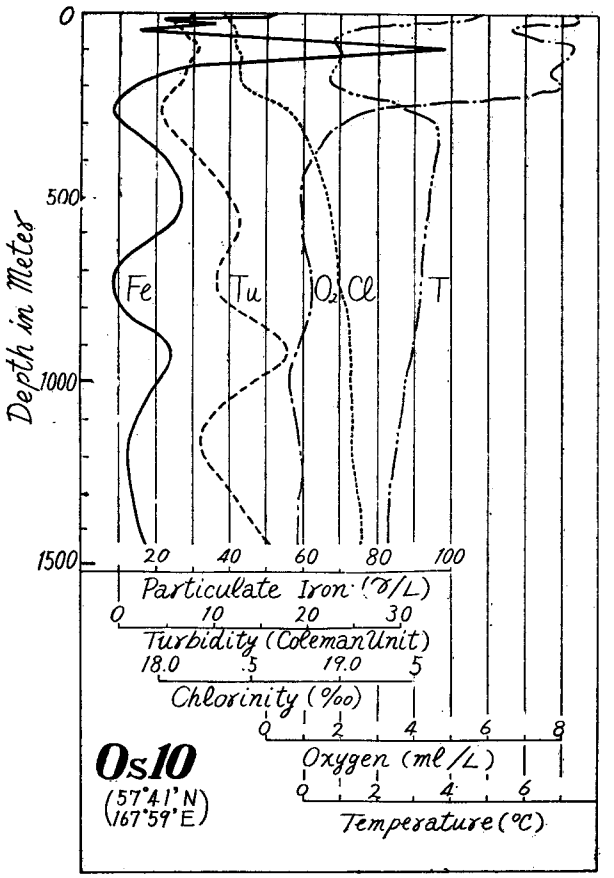

Fig 2. Vertical distribution of particulate iron contents with relation to the other properties of water

in the Bering that the particulate iron in waters deeper than 500 meters averages 4.5 γ/L whereas is shoaler waters the values were ofttimes higher and showed a wide variation with depth. In accodance with the hydrographical features as noted above, it seems not always adequate to discuss the vertical variation of the iron values dividing the column of water into two portions at the depth of 500 meters. Now the present investigation showed that the particulate iron is usually accumulated in rather more advance at depths less than 200 meters and possesses a wide range of scatter whereas in the deeper layer below 200 meters the amount of particulate iron seems rather small and to be changing with depth within comparatively narrow ranges.

Table 2 indicates the average contents and standard deviations corresponing to the particulate iron at the present stations.

Table 2. Average and standard deviation of particulate iron (γ/L)

Station	< 200 m		> 200 m		All Samples	
	Average	Std. dev.	Average	Std. dev.	Average	Std. dev.
7	76.5	68.6	13.8	11.0	41.2	54.0
8	9.1	5.7	8.7	4.7	8.9	5.2
10	48.1	28.8	18.0	6.7	31.1	24.5
13	29.8	28.1	15.6	4.9	21.8	20.2
15	12.1	9.6	4.8	1.9	8.0	7.7
27	11.9	10.5	10.0	4.3	10.9	8.1
37	15.8	15.5	15.2	4.0	15.5	11.0
	28.7		12.2		19.5	

As shown in Table 2, the amount of particulate iron averages 28.8 γ/L in waters

of the upper layers above 200 meters whereas 12.2 γ/L in the deeper water, and the average content is 19.6 γ/L in the waters at all stations. Although the above averages seem to indicate a fairly large content of particulate iron in comparison with data of Lewis and Goldberg (1954), they appear to indicate a relatively small contents than was found in waters off the northwestern coast of the United States (Thompson & Bremner, 1953). In respect to the iron content in sea waters ranging from the surface to the layer deeper than 1000 meters, some of available estimates are summarized in Table 3, inspection of which suggest that the present averages do not always appear excessively abundant in comparison with the others.

Table 3. Iron estimates in oceanic waters

	Location	Depth(m)	Fe in γ/L	
			Soluble	Total
1.	U.S. Coast, Northwest Atlantic	0-3830	5	21
2.	Northeast Pacific	0-2000	8	25
3.	Southern Japan (Open Ocean)	0-1009	—	10
4.	Off SE. Honshu and S. Shikoku (Japan)	0-1554	—	9.5
5.	Suruga-Wan (Japan)	0-1000	—	27
6.	North Pacific, Bering Sea	0-3500	3.5	8
7.	Bering Sea	0-1989	(3.5)	23.5
8.	Bering Sea	200-1989	(3.5)	15.7

1. Rakestraw, N.W., Mahncke, H.E. & Beach, E.F. 1936; Ind. Eng. Chem. (Anal), 8: 136-138.
2. Thompson, T.G. & Bremrer, R.W. 1935; J. Cons. int. Explor. Mer, 10: 38-47.
3. Anonyous, 1951; Res. mar. Obsns., Tokyo, 6: 52-56.
4. Kawamoto, T. 1952; Sea and Sky, 29: 112-116.
5. Anonymous (b) 1939; J. Oceanogr., Kobe, 12: 37-71.
6. Lewis, G.J. & Goldberg, E.D. 1954; J. Mar. Res., 13: 183-196.
7. Kato, K. 1956; in the present paper.
8. Do

It was usually observed at most of stations that the amount of particulate may change in parallel with the turbidity of the water. A greater or less discrepancy of distributions between the iron particles and the turbidity observed seldom in certain levels of waters may be attributed principally to the temporary supplies of larger particles of iron or to the scattering of populations of micro plankton.

Striking accumulation of particulate iron are apt to cover the boundary between two bodies of waters of which the physical and chemical properties differ from each other, for example, at the thermocline intermediate between the warm surface water and the cold dicothermal water. Such accumulation of suspended particles of iron will be influenced by more or less diminution of decending velocities of particles owing to the higher density of the lower water mass, but, of course, some of these accumulations seem sometimes to be attributable to biological activities of microganisms propagating very actively at the border between these waters, judging from the corresponding oxygen

minimum developed at the depth.

At almost all of stations observed in the Bering, a belt of dicothermal layer of cold water thrusts in between the surface and the subarctic waters as described above. A comparatively thin layer of abundant particulate iron is found at the upper border of the dicothermal layer, whilst beneath the lower limit of the dicothermal layer extends a fairly pronounced accumulation of iron over a few hundred meters of depth range (Stations Os 7, 8, 10 and 13). It is of great interest that this characteristic profile of iron distribution is similar to that of the turbidity of the corresponding bodies of waters.

Since the amount of iron in sea water at a given depth will be no doubt influenced, as suggested in Figure 2 by various factors controlling the oceanographic conditions, it is very interesting to consider the distribution of iron in relation to the hydrographic features of the Bering Sea. A certainly close correlationship may be found between the amount of iron and the dissolved oxygen value at a given depth. That is to say, iron maximum is likely to occur at the same depth as oxygen minimum, as illustrated in Figure 3 in which several lines connecting iron maxima coincide respectively with those of corresponding oxygen minima. Such coincidency may demonstrate that particles of oxydizable iron accumulated abundantly as well as respiratory organisms have consumed a good amount of dissolved oxygen at the iron maximum layer. Furthermore these maximum lines of iron illustrated in Figure 3 will also suggest some trend of hydrographic movement of the waters in the Western Bering.

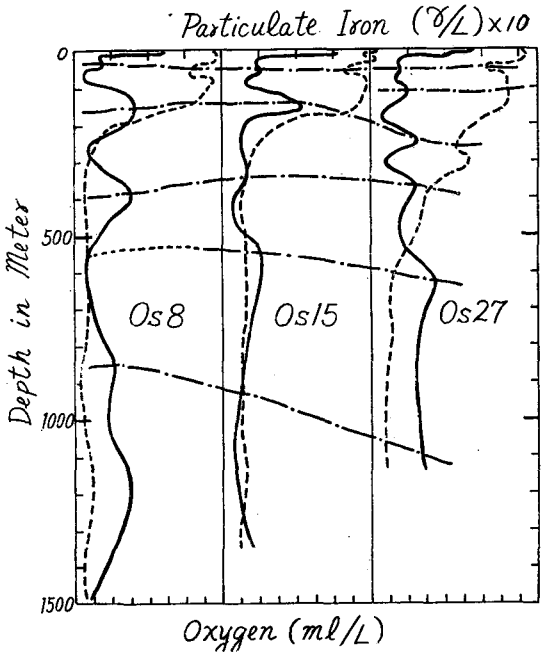

Fig. 3. Correlation of particulate iron content to dissolved oxygen values

Thompson and Bremner (1935) pointed out that a high total iron was observed at the region of minimum layer of dissolved oxygen ranging 800 to 1200 meters, and suggested that the iron maximum layer would be due to the very fine particles which had previously existed in the water when it had approximate contact with the sea bottom. In the present investigation, the maximum layers of the iron somewhat resembling the above feature were found at the levels of similar depth range. But that iron maximum corresponding to oxygen minimum, as illustrated in Figure 3, may be but a case of several maxima usually occurring in the present area, and then it seems not necessarily adequate to judge that

the iron maximum could be attribute to the water which had sometimes contacted with the sea bottom.

An enormous amount of iron was accumulated in the surface water as well as in the intermediate layer near 1000 meter level at Station Os 7, although it is difficult to adduce any causes for these abundant accumulation of particulate iron. An exceedingly concentrated suspension of iron in the surface water would consist of iron particles comparatively poor in number but larger in size, judging from the discrepancy between the iron-content and the turbidity (intensity of light scattering) of the water. So, that feature may suggest either some new supply of terrestrial substances from land not to far off the station or biochemical assimilation of iron by strinking propagation of phytoplankton (Motoda, 1956, private communication). While the coincidency of distribution curves of the content and the turbidity in the deeper layer may suggest that a good amount of fine particles of iron would suspend in the intermediate water at about 1000 meters depth.

The author is much indebted to Dr. Shigeru Motoda, leader of the oceanographic expedition in the summer of 1955, Professor of the Faculty of Fisheries, Hokkaido University, for his untiring encouragement during the investigation. To professor Noboru Suzuki of the Faculty, grateful acknowledgement is due for giving facilities for the work. The author also offers his heart-felt gratitude to Assistant Professor Takeji Fujii, Captain of the Training Ship, "Oshoro-Maru", of the Faculty, for kindly help during the cruise of research.

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Summary

1. Determination was made of particulate iron retained on the molecular filter through which had been passed the water samples collected from seven stations in the Bering Sea during the Oshoro-Maru Expedition in the summer of 1955.

2. In the layer above 200 meters, the particulate iron shows higher values (28.7 γ/L in average) varying within a fairly wide range, whereas in the deeper water lower but less variable values (12.2 γ/L in average) are observed. All of samples obtained from the Bering average 19.6 γ/L.

3. At most stations, the amount of particulate iron varies vertically in parallel with the turbidity (intensity of light scattering) of the water.

4. Remarkable accumulations of particulate iron are apt to extend over the boundary

between two different bodies of waters.

5. It is of great interest that iron maximum is likely to occur at the depth of oxygen minimum. That may be attributed to the consumptions of dissolved oxygen by oxidizable iron particles and/or by biological activities of marine biosphere.

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