Geochemical Study on Lakes Mikata

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Lakes Mikata-goko were studied geochemically. Among the five lakes, Kugushi and Hiruga are salt-water lakes, while Mikata is a fresh-water lake. Lakes Suigetsu and Suga lie between a salt lake, Kugushi and a fresh-water lake, Mikata and therefore present interesting problem. In Lake Suigetsu, a distinct boundary of water layers exists at about 10 meter in depth, and under this boundary water stagnates for a long period. In this stagnant water, the quantities of dissolved components such as chloride, sulfur compounds, phoshorus *etc.* increase continuously with the depth, and near in the bottom hydrogen sulfide is formed by the reduction of sulfate. Hydrogen sulfide reacts with manganese contained in this lake to give interesting effect on the vertical variation of manganese.

INTRODUCTION

Mikata-goko (Mikata five lakes) lies in Mikata-gun, Fukui Prefecture, and consists of five lakes, Hiruga, Kugushi, Suigetsu, Mikata and Suga, the last of which seems to be a part of Suigetsu.. They are now connected together by narrow waterways, the Urami river (between Lakes Kugushi and Suigetsu), Saga tunnel (between Hiruga and Suigetsu), Seto channel (between Suigetsu and Mikata) and Horikiri channel (between Suga and Mikata). Lakes Hiruga and Kugushi open into Wakasa Bay in the Japan Sea through Hiruga waterway and the Hayase river, respectively as shown in Fig. 1.

All of these lakes were fresh-water lakes. before. By opening the above waterways, however, Lakes Hiruga and Kugushi became salt-water lakes, and sea water entered into Lakes Suigetsu and Suga. During the years 1932–1935, these waterways were enlarged in order to prevent floods and for the convenience of the water transportation. Immediately after the reconstruction work, large amounts of sea water flowed into Lake Suigetsu, increased hydrogen sulfide content of the whole part (surface through the bottom) of the lake and gave rise a great deal of damage to fishes. After this accident, called "Unusual or uncommom phenomenon in the Mikata Lakes", the examinations on the lakes have been repeated mainly by the staff of Fukui Fisheries Experiment Station[1].

An outline of the lakes[2] are listed in Table 1; among the five lakes, Suigetsu is located between a salt-water lake, Kugushi and a fresh-water lake, Mikata and therefore it is expected to give some interesting problems such as the erosion or the sedimentation which is caused by mixing the river water and the sea water. Hydrogen sulfide found in bottom layer is an example, which may be formed by

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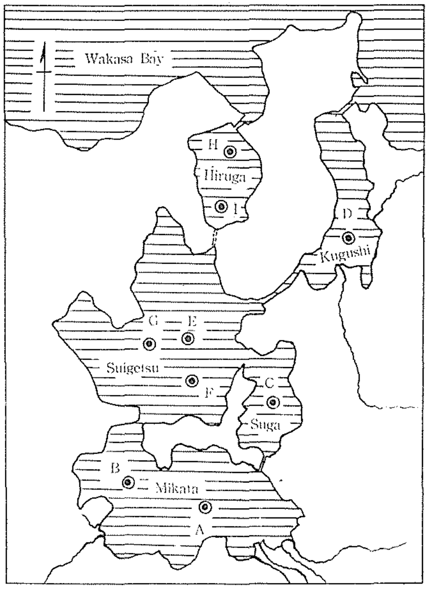

Fig. 1. Lake Mikata-goko.

Table 1.

Lake	Area (km^2)	Maximum Depth (m)	Average Depth (m)	Volume (km^3)	Quality
Mika	3.61	5.80	1.33	0.00484	Fresh-water
Suigetsu*	5.02	34.00	14.33	0.07165	Brackish-water
Kugushi	1.45	2.50	0.83	0.00117	Salt-water
Hiruga	4.16	38.50	14.33	0.04085	Salt-water

* Including Suga.

the reduction of the stagnant salt-water, as suggested by Yamamoto1).

On such a view point, the authors attempted to carry out the geochemical study on the Mikata Lakes, especially on Lake Suigetsu, and surveyed on December 5th, 1959, on April 24th and on August 1st and 2nd, 1960. In the first two surveys, the collection of water samples were made essencially on one fixed station, located in the deepest area of Lake Suigetsu, but finally, water samples were taken also from other stations and from other lakes. The temperature and pH value of the samples taken at various depths were measured and chemical analysis were carried out on the dissolved components such as chloride, hydrogen sulfide, total sulfur, manganese, total phosphorus, dissolved oxygen gas *etc.*

Results of the three surveys revealed the following informations. On Lake Suigetsu, a distinct boundary of water layers exists at about 10 meters in depth, and under this boundary water stagnates through out all seasons, in contrast with the freely moving upper layer. Hydrogen sulfide is found apparently even at the depth of 15 meters and its concentrations were 200 milligrams per liter or more in the samples taken at several meters above the bottom. However, in all samples, the quantities of total sulfur do not exceed the amount of sulfate-sulfur calculated from the sulfate-chloride ratio of sea water and therefore hydrogen sulfide has its origin in sea water. Lake Suigetsu is characteristic also in respect of relatively large amounts of manganese. Manganese content increases suddenly at around the boundary mentioned above, reaches maximum value just under this, and decreases gradually with the depth. The negative gradient in the lower layer may be attributed to the reaction with hydrogen sulfide, because the concentration of manganese is approximately the same to the value calculated from the solubility product of manganese sulfide. The composition of the water of the deepest lake, Hiruga, is identical with sea water, but small amount of manganese is found near the bottom. The nature of Lake Suga is almost the same to that of Lake Suigetsu, and it is reasonable because of its circumstance. The other salt lake, Kugushi and a fresh-water lake, Mikata are very shallow, and are not unusual.

Table 2.

	Sampling Station		Maximum Depth (m)	Sampling Depth (m)	Date and Time	Weather	Temp. °C
1st Survey*	E	Suigetsu	34.8	0, 2, 5, 10, 15, 20, 25, 30, 33,	XII. 5. 1959 2.15–3.50 p.m.	rain	13.3
	C	Suga	12.5	5, 10,	XII. 5. 1959 4.10–4.20 p.m.	rain	13.3
2nd Survey*	E	Suigetsu	34.8	0, 2, 5, 10, 12, 15, 20, 25, 30, 34,	IV. 24. 1960 8.45–10.10 a.m.	fine	20.7
3rd Survey**	A	Mikata	2	1.5, 1.9,	VIII. 1.1960 9.45–10.06 a.m.	fine	31.8
	B	Mikata	2	1.5, 1.9,	VIII. 1. 1960 10.20–10.32 a.m.	fine	31.9
	C	Suga	12.5	5, 7, 10, 12,	VIII. 1. 1960 10.51–11.05 a.m.	fine	31.8
	D	Kugushi	2	0, 2,	VIII. 1. 1960 11.39–11.45 a.m.	fine	32.6
	E	Suigetsu	34.8	0, 2, 5, 7, 10, 12, 15, 20, 25, 30, 33, 34,	VIII. 1. 1960 2.30–3.20 p.m.	fine	33.0
	F	Suigetsu	31.8	5, 10, 20, 30,	VIII. 1. 1960 3.28–3.40 p.m.	fine	32.8
	G	Suigetsu	34.5	5, 10, 15, 20, 30,	VIII. 1. 1960 3.45–4.07 p.m.	fine	32.5
	H	Hiruga	39.9	5, 10, 20, 30, 39,	VIII. 2. 1960 9.06–9.31 a.m.	fine	30.4
	I	Hiruga	35.0	10, 20, 30, 34,	VIII. 2. 1960 9.44–9.51 a.m.	fine	30.8

Components measured or determined

* Temperature, pH, Chloride, Hydrogen Sulfide, Oxidizable Sulfur, Manganese, Total Phosphorus

** Same to the above two surveys, except Hydrogen Sulfide and Total Phosphorus ; Hydrogen Sulfide was calculated from Oxidizable Sulfur.

EXPERIMENTAL RESULTS AND DISCUSSION

Water samples were collected with a Kitahara's Water Sampler, Model B (content 500 ml.). Spectrophotometric measurement were carried with a Hitachi's Photoelectric Spectrophotometer, Model EPU-2A, using 1 cm. quartz cells, and a Horiba's Glass electrode pH Meter, Model III was used for the pH measurements.

Outlines of the sampling are summerized in Table 2. Temperature and pH value were measured immediately after the sampling, and the chemical analysis was carried as soon as possible, for the samples stored in 100 ml, 250 ml. or 500 ml. polyethylene bottles.

Temperature and pH Value

Variation of temperature and pH value are graphically shown in Fig. 2 and Fig. 3. As shown in Fig. 2-a, in the deep part of Lake Suigetsu, the differences of the temperature by the season are very small, and therefore, it is expected that the temperature of bottom water may be constant, considering the influence of atmospheric temperature. pH values show that water is-almost neutral. It is doutful, however, whether the reading of pH meter shows true value or not, because the samples contained large amounts of oxidizable compounds.

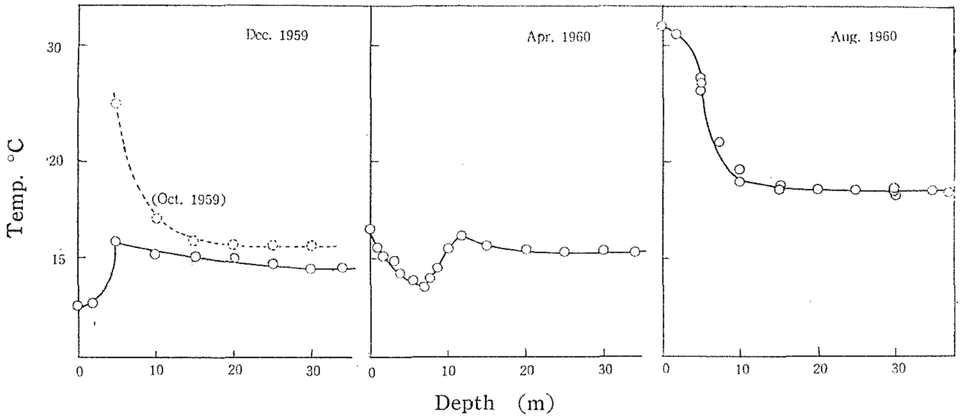

Fig. 2-a. Temperature (seasonal variation at station E).

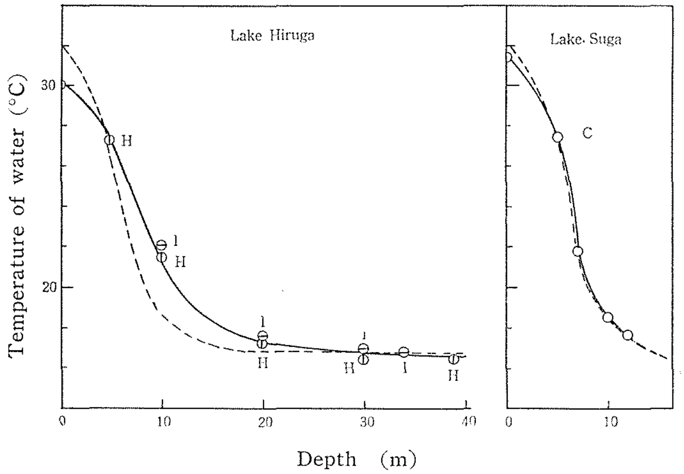

Fig. 2-b. Temperature (variation with depth, Aug. 1960).

---- Lake Suigetsu (station E)

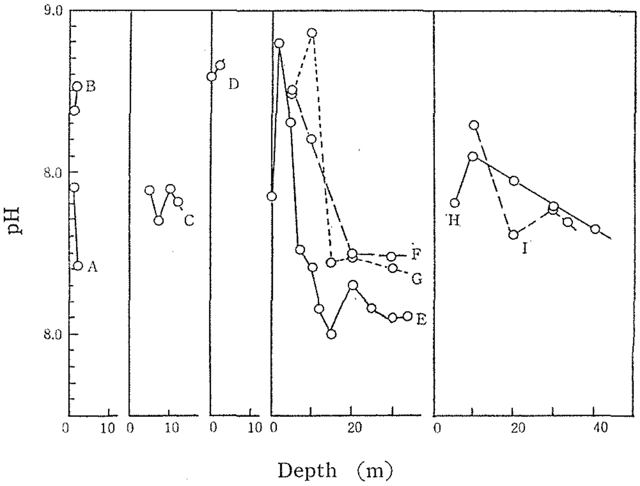

Fig. 3. pH values (Aug. 1960).

Chloride

Chloride was determined volumetrically by Mohr's method, and the results are shown in Fig. 4. Data obtained on Lakes Kugushi and Hiruga show that these are salt-water lakes, while data on Lake Mikata indicate that it is scarcely affected by the influence of sea water. In Lake Suigetsu, the concentrations of chloride increase with the depth, but not uniformly. There is sudden change at the depth of about 10 meter, and the existence of a boundary of water layers is expected. Under this discontinuous place, the concentration of chloride remains unchanged through all seasons, and at the same depth, it is independent also of the sampling stations, as seen in Fig. 4-b.

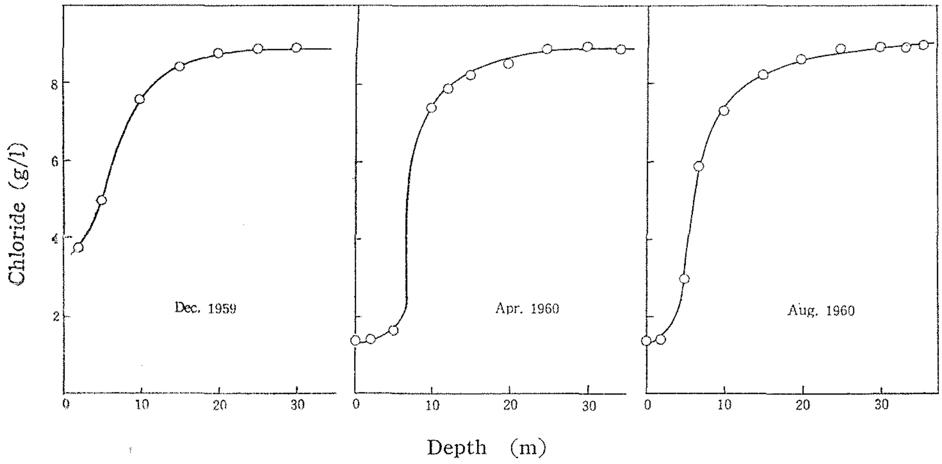

Fig. 4-a. Chloride (seasonal variation at station E).

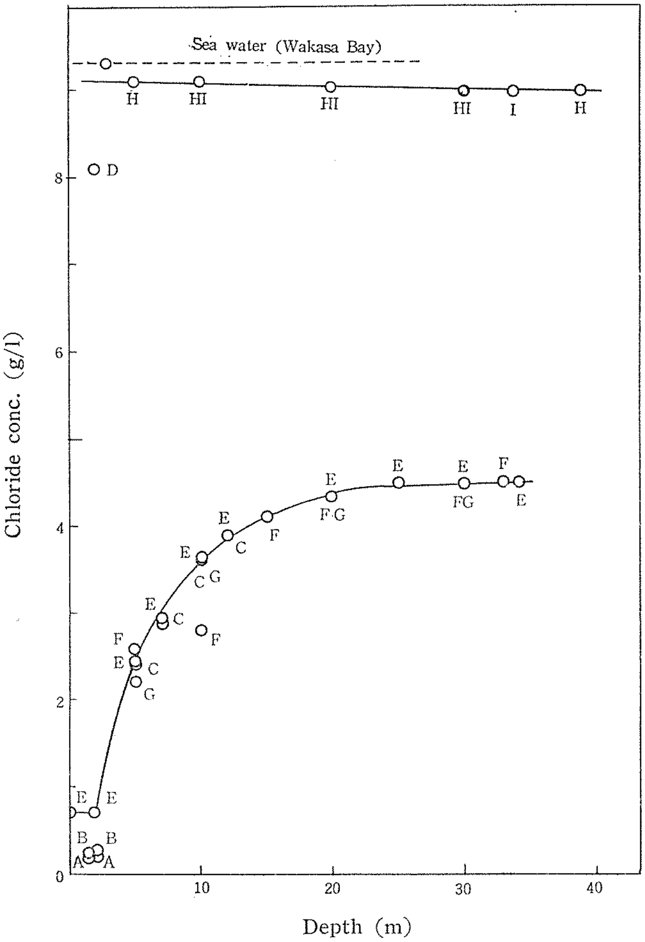

Fig. 4-b. Chloride (at various stations, Aug. 1960).

Sulfur Compounds*

Hydrogen sulfide was determined by precipitating as cadmium sulfide in acetic acid medium, followed by dissolving the separated precipitate with hydrochloric acid in the presence of iodine, and by backtitrating excess iodine with a standard solution of thiosulfate. Total oxidizable sulfur compounds were also measured by iodometry, but without any pretreatment. Total sulfur was determined by the chelatometric titration, after oxidizing the alkalized sample water with bromine, and then separating sulfate as barium salt.

Results are summarized in Fig. 5. Hydrogen sulfide is found in Lakes Suigetsu and Suga only. In the other lakes, the quantities of other oxidizable sulfur compounds were also negligible. In Suigetsu, hydrogen sulfide is found remarkably at

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* In the third survey, the amount of hydrogen sulfide was not determined, but calculated from the amount of oxidizable sulfur, by multiplying the latter by 0.852, the mean value of the ratio $\left(\frac{H_2S\text{-}S}{Oxi\text{-}S}\right)$, which was obtained from the results in second survey.

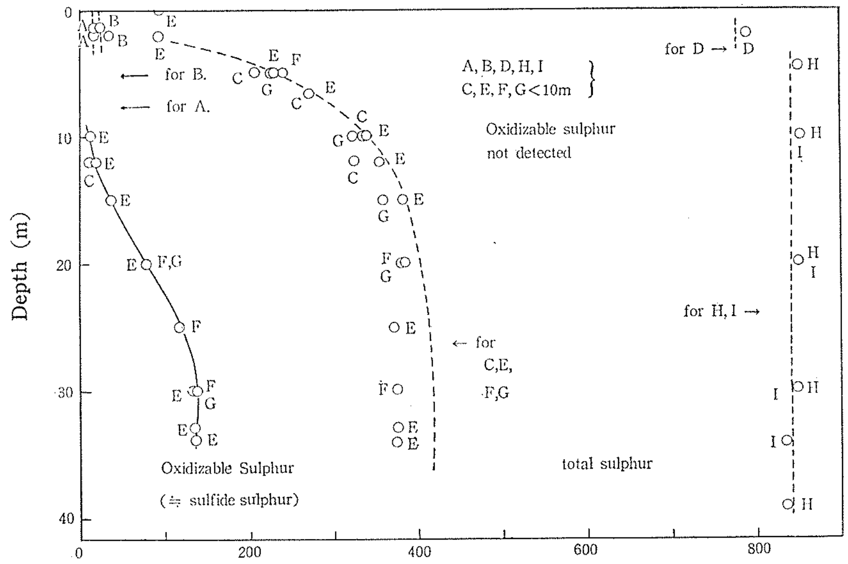
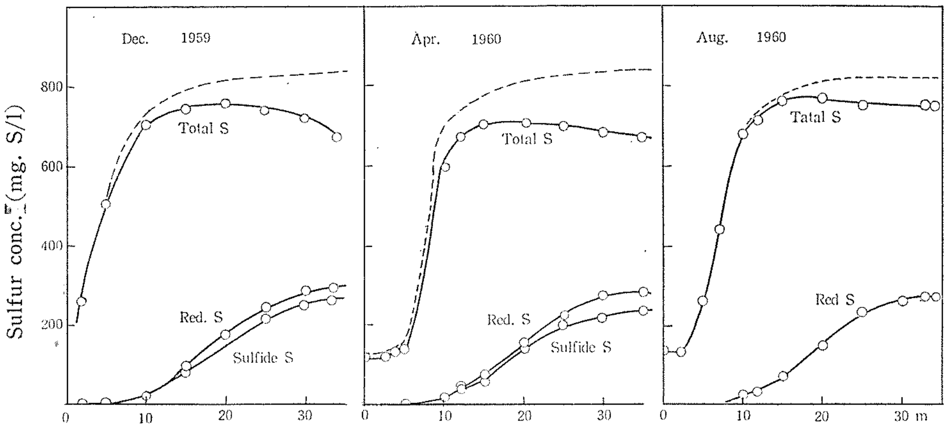


Fig. 5-a. Sulfur compound (at various stations, Aug. 1960).
- - - - - Total sulfur calculated from chloride.



Depth (m)
Fig. 5-b. Sulfur compound (seasonal variation at station E).
- - - - total S calculated from chloride as sea water
Red.S=Oxidizable Sulfur

15 meter in depth, and below this depth the concentrations increase with the depth. Under 30 meter in depth, it is more than 200 milligrams per liter. The behavior of oxidizable sulfur compounds is similar to hydrogen sulfide (Fig. 5-a), and the molar ratio of the latter to the former is from 0.85 to 0.90. Results in the three surveys give slight differences (Fig. 5-b), but it is doubtful whether the differences are due to the seasonal changes or not. Amounts of sulfate sulfur on Lakes Kugushi, Hiruga and Mikata are approximately equal to the value calculated from the concentration of chloride, using the composition of sea water as the basis. With all

samples from Lakes Suigetsu and Suga, total amounts of sulfur are not more than the calculated value, but frequently less. These are shown by dotted line in Figs. 5-a and 5-b. This indicates that hydrogen sulfide originated from the reduction of sulfate, a component of sea water which exists in the depth of the lakes. The defficiency may be caused by the diffusion of hydrogen sulfide to the upper layer and the loss in the sampling.

Manganese

Manganese was determined colorimetrically by permanganate method (periodate oxidation), after organic materials were destroyed and chloride was converted to perchlorate by fuming with perchloric acid. Manganese is found in some samples taken from Lakes Suigetsu, Suga and Hiruga, but not in Lakes Kugushi and Mikata, and the contents in the first two lakes were remarkably great, while only a small amount was detected in the third, even near the bottom. In Lake Suigetsu, the vertical change of manganese content is remarkable as shown in Figs. 6-a and 6-b.

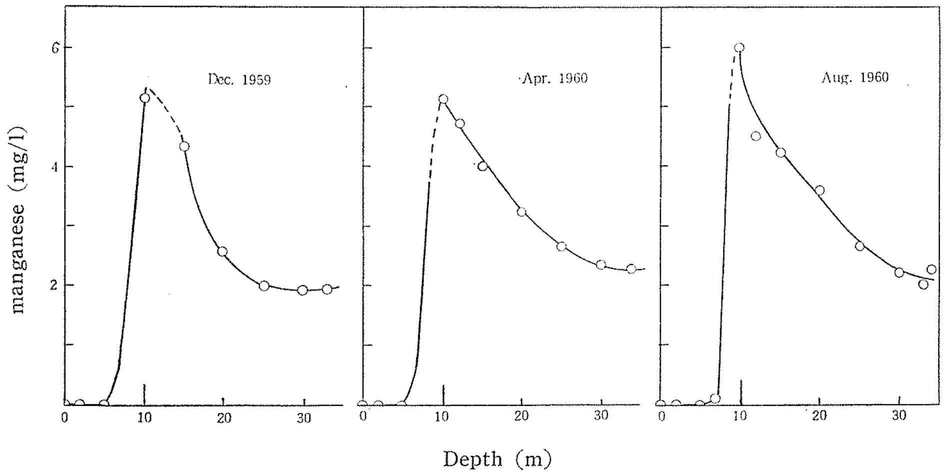
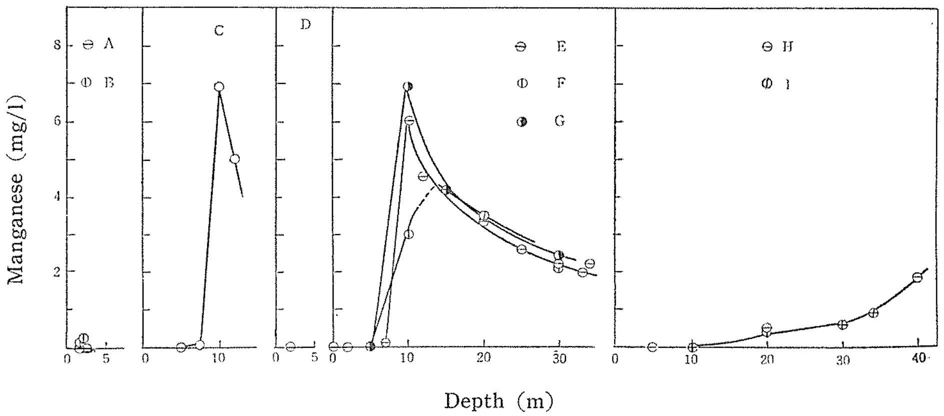


Fig. 6-a. Manganese (station E).



Eig. 6-b. Manganese (Aug. 1960).

Manganese does not exist in surface layer, but with approrching to the boundary of water layers it increases rapidly and reaches a maximum just under this boundary. The reason for this sudden increase can be explained as follows. In the surface layer, the strong stream makes manganese to distribute, but in the lower layer, the vartical mixing does not occur and the loss of manganese to the surface layer is very little. On the other hand, a distinct negative gradient seen in stagnant lower layer, is due to the formation of manganese sulfide, as discussed later. The seasonal variation of manganese contents may not be important, and the concentration in Lake Suga is almost similar to that in Lake Suigetsu.

The pink color developement, often observed in Lake Suigetsu, must be attributed to manganese which formes some organic compounds by the action of bacteria, because the concentration of ferric iron is very low.

Total Phosphorus

For the determination of total phosphorus, the spectrophotometric method by solvent extraction as phosphomolybdate complex was applied, after organic phosphorus compounds were decomposed by fuming with perchloric acid. Analysis were carried on samples taken from Lake Suigetsu, in the first and second surveys, and the results are represented in Fig. 7. Phosphorus seems to be resulted from dead organismus, and its high concentration and no seasonal variation indicate that the bottom water of the lake has been stagnating for a long period.

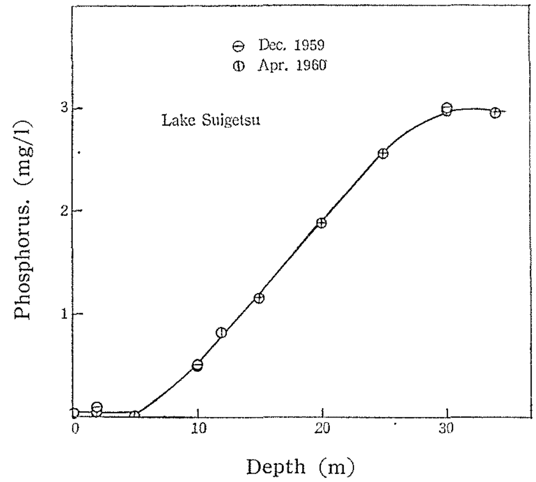


Fig. 7. Phosphorous compound.

Dissolved Oxygen Gas

Dissolved oxygen was measured by Winkler's method, using glass stoppered bottles (oxygen bottle), and results are shown in Fig. 8. The depth corresponding to the disappearance of oxygen is greater in Lake Hiruga than in Lake Suigetsu, and in the stagnant layer of the latter oxygen is not contained at all. This indicates that the vertical mixing occurs in the former, but scarcely in the latter.

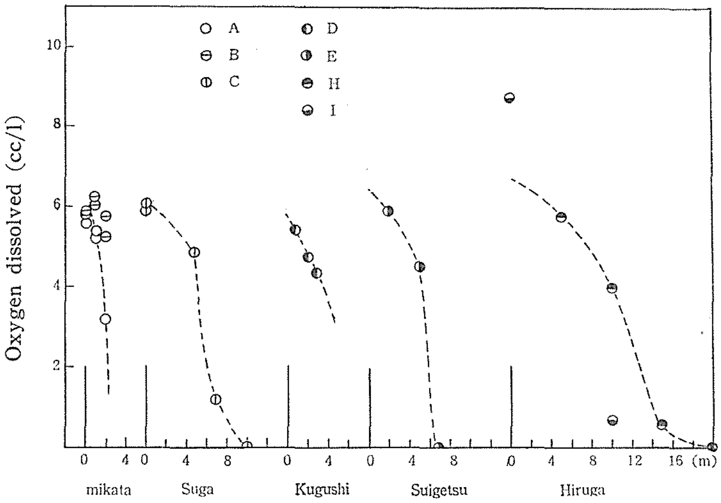


Fig. 8. Dissolved oxygen (Aug. 1960).

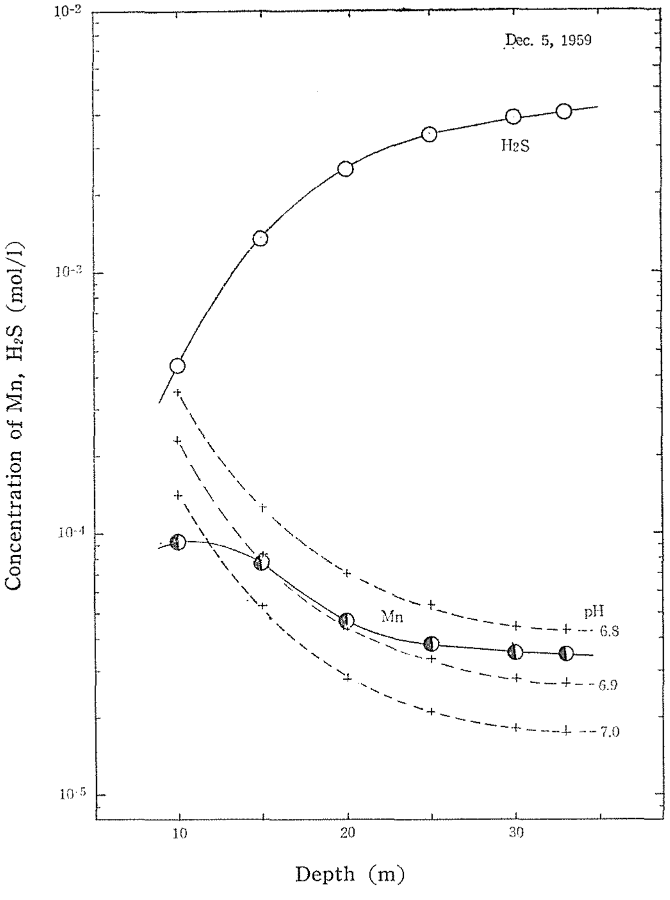


Fig. 9-a H_2S-Mn Relation.

Since the decreses of manganese contents in the under layer of Lake Suigetsu seems to be caused by the reaction with hydrogen sulfide, the possibility of this reaction was examined by an approximate calculation.

The theoretical concentration of manganous ion, (Mn^{++}), is obtained from the solubility product of manganese sulfide, Ks, and the dissociation constant of hydrogen sulfide, Kd, as follows.

$$Ks=[Mn^{++}][S^{--}]=7\times10^{-16}$$

$$Kd=\frac{[H^+]^2[S^{--}]}{[H_2S]}=10^{-22}$$

therefore

$$[Mn^{++}]=\frac{Ks}{Kd}\times\frac{[H^+]^2}{[H_2S]}=7\times10^6\times\frac{[H^+]^2}{[H_2S]} \qquad (1)$$

and

$$\log[Mn^{++}]=6+\log 7-2pH-\log[H_2S] \qquad (2)$$

if expressed as a logarithmic equation.

The concentrations of manganese analysed, and the calculated values which were obtained from the equation (1) by introducing the concentration of hydrogen

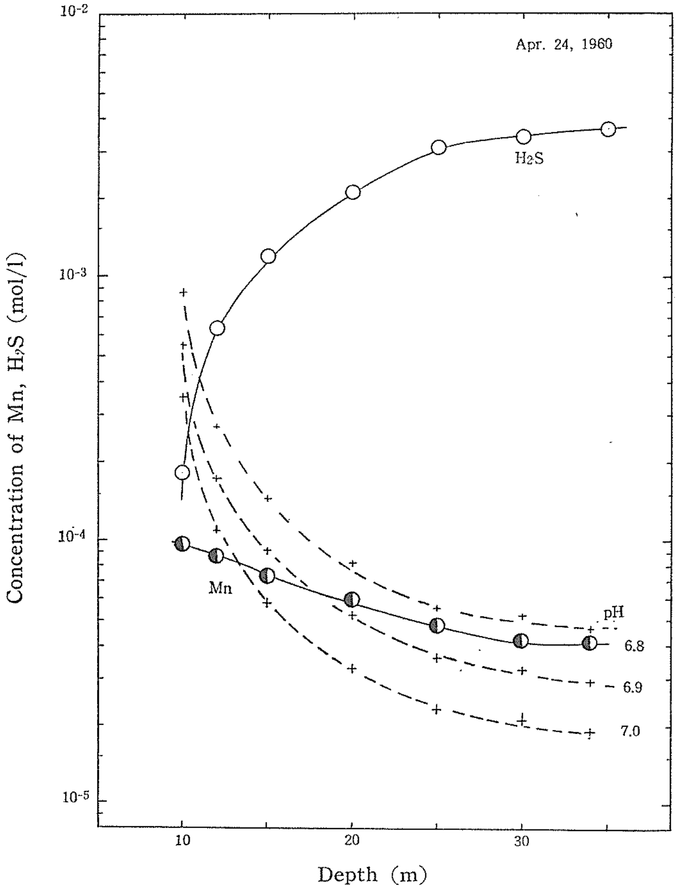


Fig. 9-b H_2S-Mn relation.

sulfide and by assuming pH value of 6.8, 6.9 and 7.0, are shown in Fig. 9, as a function of the depth. The straight lines in Fig. 10. represent the equation (2) with various pH values, while the points indicate the analytical results in all samples containing manganese.

Under the depth of 15 meter, both values gave approximately the same magnitude, although the experimental values deviate to positive direction with the depth. The reason for this deviation may be that a part of manganese in the forms other than ionic, such as suspended colloidal sulfide, was also determined. Considering this, the assumption that manganese reacts with hydrogen sulfide to precipitate its sulfide, must be true. In the above calculation, the assumed value of pH was used because the reading of pH meter was thought to be uncertain on such samples containing large amounts of sulfide or sulfite.

As previously mentioned repeatedly, water under the boundary layer of Lake Suigetsu stagnated for a long time. This is concluded by the analytical results of almost all components. The reason for this can be explained as follows.

In this lake, the influx of both sea and land water are expected. However, because Lake Kugushi and the Urami river which is a passage of sea water, are very sharrow in comparison with Suigetsu, and the Urami river is very narrow,

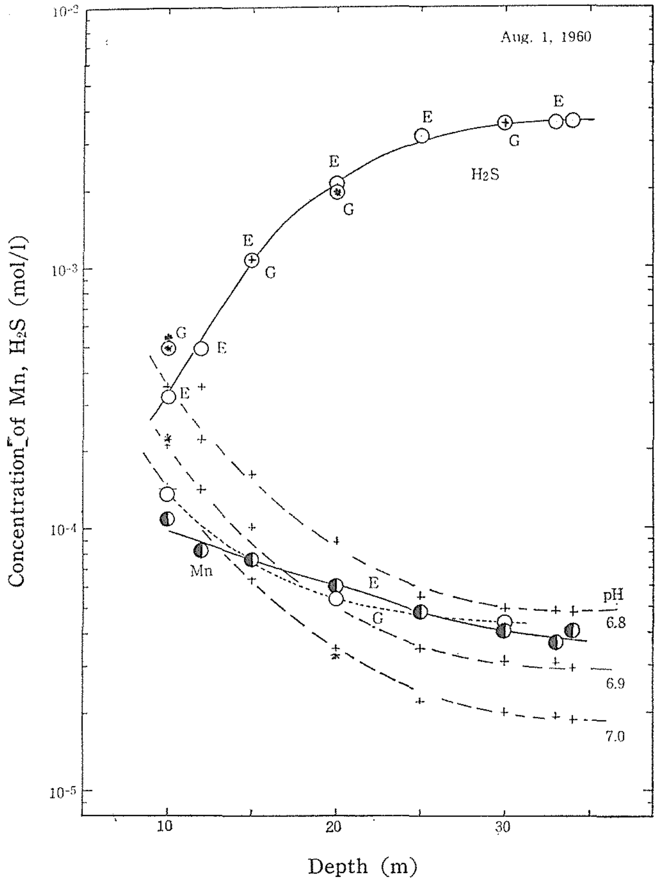


Fig. 9-c. H_2S-Mn relation.

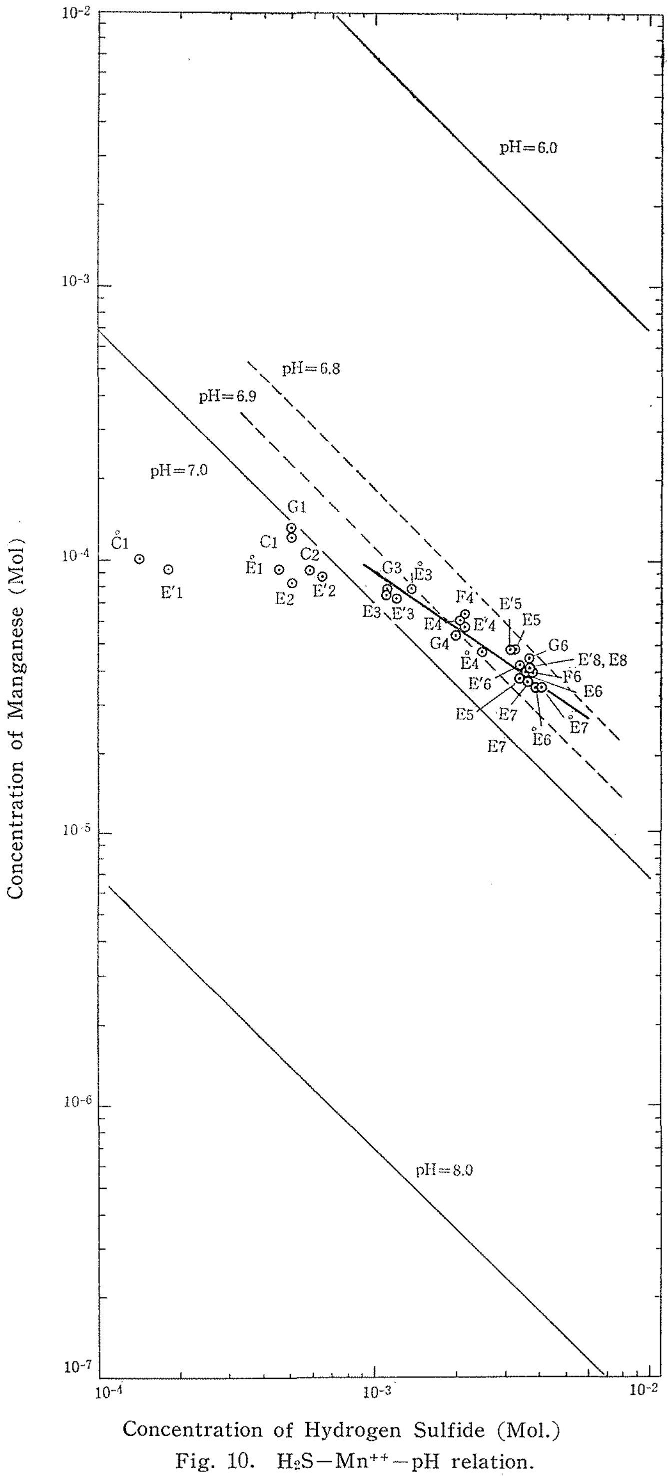


Fig. 10. $H_2S-Mn^{++}-pH$ relation.

C, E, F, G : Aug. 1960 ; E′ : Apr. 1960 ; $\overset{\circ}{C}$, $\overset{\circ}{E}$: Dec. 1959 at station C, E, F or G.
1 : 10m ; 2 : 12 m ; 3 : 15 m ; 4 : 20 m ; 5 : 25 m ; 6 : 30 m ; 7 : 33 m ; 8 : 34 m in depth.
Example. E′8=sampled at 34m. of station E, Apr. 1960.

the amount of sea water inflowed is relatively small, and less than the land water from Lake Mikata, as proved by the low concentration of chloride near the surface on Lake Suigetsu. Therefore, difference in the specific gravities of water is brought about in layers, in the same way as shown in the vertical change of chloride, from the surface water to the bottom water which contains sea water entered by the opening of the Urami river. This difference of specific gravity prevents the vertical movement of water, and by this reason and the circumstance that the Urami river and Lake Mikata is sharrow, the water in deeps can neither flow out nor return to the sea.

The conditions in Lake Hiruga are very different, because the lake is connected continuously with the sea and sea water flows in and out freely. There is no distinct difference in chlorinity between the surface and the depths, and so the vertical mixing is expected as in ordinary lakes.

In the present work, the origin of manganese was not studied, and no attempt was made to the biological problem, although the presence of manganese and of variable sulfur compounds indicated the inhabit of bacteria. Further studies will be made on these important problem.

SUMMARY

The geochemical studies were carried on Lakes Mikata-goko, especially on Lake Suigetsu, and the dissolved components were determined. Analytical results were investigated and the origin of hydrogen sulfide and the behavior of manganese of Lake Suigetsu were discussed.

The authors wish to express their gratitude to the Chemical Group, Kyoto Girl's High School, for their assistance during this study.

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