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GEOCHEMICAL INVESTIGATIONS OF SALINIZED GROUNDWATER USING ENVIRONMENTAL ISOTOPES

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SYNOPSIS

Geochemical investigations of salinized groundwater in the Motooka area, west of Fukuoka City, Japan were carried out. The measured tritium concentrations in shallow groundwater system are higher than those of deeper groundwater system. From the results of hydrogen-oxygen isotope ratio plotting on the mixing line of meteoric water and seawater, it was inferred that the deeper groundwater is affected by seawater. ^{14}C isotope dating of a shell that was collected at the depth of approximately 2m from the core samples of B2 indicated its age to be about 2000 years. Accordingly, the salinized groundwater in this area suggests that it was originally below the sea bottom. Furthermore, it was found that the environmental isotopes of salinized groundwater should be utilized as the index of the geochemical properties as well as characterization of the water quality using Piper diagram.

INTRODUCTION

Generally, flow rate of fresh water in shallow groundwater is quicker than that of salinized groundwater in deeper part. Evolving processes in quality of the salinized groundwater changes differences of kind of geological matrix in aquifer and contact time between the geological matrix and the salinized groundwater. Therefore, in the area where salinized groundwater problem occurs, in order to evaluate the quantities of water for agricultural use and the water resources to be developed, it is necessary to understand the evolving processes of salinized groundwater quality on geochemistry. Ikeda (1) showed that the quality changes of salinized groundwater could be explained by ion exchange reaction, because most chemical compositions of salinized groundwater were determined by the composition of exchangeable cation in soil matrix. On the other hand, Wicks et al. (2) indicated that the evolving processes of salinized groundwater quality with changing of depth was explained by the dissolution/precipitation reaction and diagenesis of the water-rock interaction of Calcite, Dolomite and Gypsum. Price et al. (3) performed geochemistry consideration of the change in chemical species at a mixing rate of the seawater to groundwater besides investigation of dissolution/precipitation reaction of the carbonate minerals in salinized groundwater.

In this study, geochemical investigations were carried out and quality evolving processes of salinized groundwater was performed in Motooka area, west of Fukuoka City, Japan with the use of chemical species analysis and environmental isotope analysis as a primary consideration.

OUTLINE OF INVESTIGATION AREA

The investigation area of salinized groundwater is located in Motooka, west of Fukuoka City. The sampling site of this area is shown in Fig. 1, and the well depths are shown in Table 1. The land in this area is used for industrial greenhouses, paddy fields, field farms, and groundwater is used

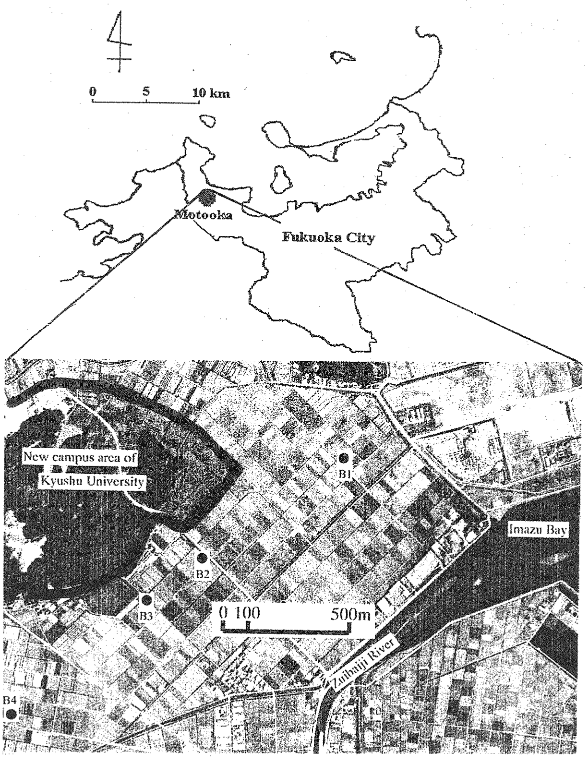

Fig.1 Map of Motooka in Fukuoka City with field site locations.

Table 1 Depth of sampled groundwater.

Sampling site	Depth(m)	Symbol
B1	10	B1-10
B1	30	B1-30
B2	10	B2-10
B2	30	B2-30
B3	10	B3-10
B3	30	B3-30
B4	10	B4-10
B4	50	B4-50

for agricultural use especially the industrial greenhouses. The land reclamation for the new campus area of Kyushu University is progressing according to schedule, around the investigation wells. However, due to decreasing groundwater recharge concerns regarding saltwater intrusion have been raised.

The constituents to be determined were water temperature, pH, electric conductivity (EC), dissolved oxygen, oxidation reduction potential(ORP), Cl^-, NO_3^-, SO_4^{2-}, Na, K, Mg, Ca, Mn, Fe, ^3H, δD, $\delta^{18}O$, $\delta^{13}C$, and ^{14}C. In addition, ^{14}C activity in the shell was taken from the B2 boring core samples to determine the age of stratum deposit, was measured.

For groundwater samples, we measured water temperature, pH, electric conductivity (EC), ORP. Furthermore, we measured cation concentrations of Na, K, Mg, Ca, Mn, Fe by using atomic absorption spectrometry and anion concentrations of Cl^-, NO_3^-, and SO_4^{2-} by using ion chromatography. ^3H by the combined use of the electrolysis condensing method and a liquid scintillation measuring method, δD, $\delta^{18}O$ by uranium reduction balance method and H_2O-CO_2 balance method of the atomic absorption spectrometry. ^{14}C measurement by JNC(Japan Nuclear Fuel Cycle Development Institute) Tono Geoscience Center, Japan tandem type acceleration machine was used for mass analysis measurement. For ^{14}C measurement accuracy, refer to Sheng Xu (4) for literature references.

Measurement of numerical value of isotope ratio, δ

$$\delta = [(Rx - Rs)/Rs] \times 1000 \quad (\text{‰}) \tag{1}$$

where, R expresses corresponding contrast (D/H, $^{18}O/^{16}O$ and $^{13}C/^{12}C$), x and s, express a sample and the quality (standard mean ocean water: SMOW) of a standard, respectively. The accuracy and reproducibility of isotopic values are ± 1‰ for hydrogen, ± 0.1‰ for oxygen and ± 0.2‰ for carbon. With regards to measurement of chemical species by the atomic absorption spectrometry and the ion chromatography, dilution (5000 times) of high magnification was required to measure the concentrations due to the samples with high concentrations. HCO_3^- concentration was calculated from the balance of equivalent concentrations between cation and anion.

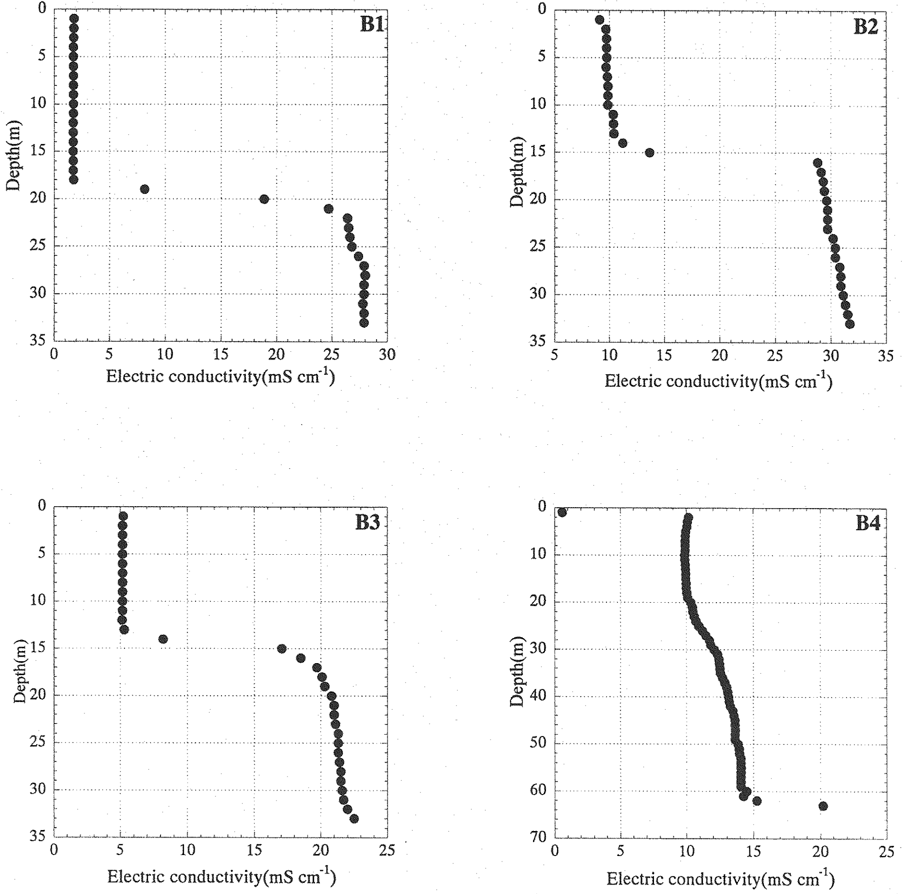

Fig.2 Profile of electric conductivity(EC).

RESULTS AND DISCUSSION

Vertical distribution of electric conductivity

Figure 2 shows the vertical distribution of electric conductivity. Electric conductivity(EC) was carefully measured 1m intervals from the surface in the observation boring wells. Rapid increases of EC at the depth of 20m in B1, the depth of 15m in B2, the depth of 15m in B3 were observed respectively and obvious interfaces between freshwater and saltwater were found to appear. B4 with a depth of 2m where EC of 0.5mS cm^{-1} to 10mS cm^{-1} was found to have a sudden increase and EC gradually increased from a depth of 20m to nearly 60m. At the depth over 60m a sudden change of EC occurred. B4 with a depth of 1m, showed EC of 0.5 mS cm^{-1} which is below fresh water value. B1, B2 and B3 of shallow part have EC values of 2-10 mS cm^{-1} usually these EC values are not suitable for agricultural use. Near the observation wells the land is used for industrial greenhouses, paddy fields and farm field. In particular geographical environment inappropriate fertilizers may have been used and this factor probably contributed to high values of EC in this area.

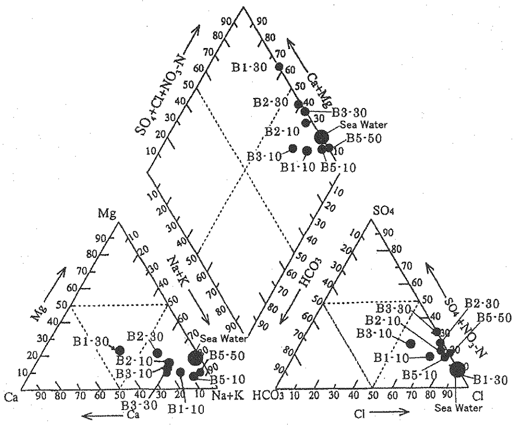

Fig.3 Piper diagram in Motooka.

Table 3 Tritium concentrations of sampled groundwater.

Sampling site	Tritium conc. (TR)
B1-10	0.8
B1-30	less than 0.3
B2-10	4.4
B2-30	less than 0.3
B3-10	4.1
B3-30	0.5
B4-10	1.1
B4-50	less than 0.3

Table 2 Fraction of seawater in Motooka (meq L^{-1}).

Motooka B 1–30	Seawater	Sample	Mix	React	Fresh water
Na^+	485.00	116.00	265.15	−149.15	13.60
K^+	10.60	0.65	5.70	−5.05	0.09
Mg^{2+}	110.20	69.00	59.53	9.47	1.55
Ca^{2+}	21.40	123.00	12.73	110.27	2.82
Cl^-	566.00	308.00	308.00	0.00	12.80
$(NO_3^-)+(HCO_3^-)$	2.40	10.00	2.60	7.40	2.82
SO_4^{2-}	58.60	18.10	32.41	−14.31	2.44
fsea	100.00	53.36			

Motooka B 2–30	Seawater	Sample	Mix	React	Fresh water
Na^+	485.00	221.00	234.82	−13.82	53.90
K^+	10.60	0.41	4.56	−4.15	0.20
Mg^{2+}	110.20	72.50	52.69	19.81	11.10
Ca^{2+}	21.40	82.70	17.34	65.36	14.40
Cl^-	566.00	272.00	272.00	0.00	59.40
$(NO_3^-)+(HCO_3^-)$	2.40	53.31	7.92	45.39	11.91
SO_4^{2-}	58.60	51.30	29.40	21.90	8.29
fsea	100.00	41.97			

Motooka B 3–30	Seawater	Sample	Mix	React	Fresh water
Na^+	485.00	153.00	169.48	−16.48	37.50
K^+	10.60	0.37	3.24	−2.87	0.16
Mg^{2+}	110.20	36.10	37.20	−1.10	6.67
Ca^{2+}	21.40	54.50	14.42	40.08	11.50
Cl^-	566.00	189.00	189.00	0.00	31.30
$(NO_3^-)+(HCO_3^-)$	2.40	48.40	13.47	34.93	18.10
SO_4^{2-}	58.60	42.40	21.82	20.58	6.43
fsea	100.00	29.49			

Motooka B4–50	Seawater	Sample	Mix	React	Fresh water
Na^+	485.00	118.00	116.67	1.33	88.80
K^+	10.60	0.40	1.23	−0.83	0.52
Mg^{2+}	110.20	11.90	14.29	−2.39	7.03
Ca^{2+}	21.40	8.58	10.89	−2.31	10.10
Cl^-	566.00	118.00	118.00	0.00	84.10
$(NO_3^-)+(HCO_3^-)$	2.40	7.93	11.46	−3.53	12.15
SO_4^{2-}	58.60	19.80	13.60	6.20	10.20
fsea	100.00	7.03			

Piper diagram and water quality characteristics

Water quality characteristic of B1-30 as shown by the Piper diagram in Fig. 3 was classified into alkaline carbonate type $(Ca(HCO_3)_2$ freshwater. Other samples (B1-10, B2-10, B2-30, B3-10, B3-30, B4-10, B4-50) were classified into alkaline non-carbonate type (Na_2SO_4 or NaCl). Cl^- showed a dominant anion compared to $SO_4^{2-}+NO_3^-$. It is seen from Fig.2 that the deep groundwater of B1 to B4 is salinized groundwater. Unlike the chemical properties of B2 to B4, B1-30m samples had a high Ca^{2+} content. The geology of B1-30 is schist and those of the depths of other points are weathered granite. Generally, when a schist forms, it is assumed that cation exchange capacity is larger than weathered granite. It is considered because more Ca^{2+} is released due to the cation exchange between Na^+ and Ca^{2+} than in other points (1),(5).

Mixing rate of sea water intrusion

The chemical reactions during fresh/salt water displacements can be deduced more specifically by calculating a composition based on conservative mixing of saltwater and freshwater, and by comparing the conservative concentrations with those actually found in the water analysis (5). The concentration of an ion i, by conservative mixing of seawater and fresh water is:

$$m_{i,mix} = f_{sea} \cdot m_{i,sea} + \left(1 - f_{sea}\right) \cdot m_{i,fresh} \qquad (2)$$

where m_i is the concentration of i (meq/L), f_{sea} is fraction of seawater in mixed water, and subscripts *mix*, *sea* and *fresh* indicate the conservative mixture, and end members seawater and fresh water.

Any change in concentration $m_{i,react}$ as a result of reactions (not of mixing) then becomes simply:

$$m_{react} = m_{i,sample} - m_{i,mix} = m_{i,sample} - \left(f_{sea} \cdot m_{i,sea} + \left(1 - f_{sea}\right) \cdot m_{i,fresh}\right) \qquad (3)$$

where $m_{i,sample}$ is the actually observed concentration in the sample.

The fraction of seawater is normally based on Cl^- concentration of the sample. Chloride is assumed to be a conservative parameter. The Cl^- based fraction of seawater is:

$$f_{sea} = \frac{m_{Cl^-,sample} - m_{Cl^-,fresh}}{m_{Cl^-,sea} - m_{Cl^-,fresh}} \qquad (4)$$

If there is no source of Cl^- but seawater, $m_{Cl^-,fresh}=0$ which simplifies (4) to:

$$f_{sea} = \frac{m_{Cl^-,sample}}{566} \qquad (5)$$

where Cl^- concentration is expressed in meq/L, and the Cl^- concentration of 35‰ seawater is set at 566 meq/L. Cl^- concentration of ocean water is assumed to be constant everywhere on earth.

The results of the fraction of seawater in all observation wells using equations(2)-(5) are shown in Table 2. The concentrations at the depth of 10m in all observation wells are adopted as background freshwater concentrations of each well. The mixing rate of seawater intrusion in all observation wells, B1-30(53%), B2-30(42%), B3-30(29%) and B4-50(7%) were shown in decreasing order. It is thought that the decrease of the mixing rate of seawater in order of B1 to B4 is related to the distance from the sea.

Tritium concentration

Age presumption of the groundwater by tritium can be determined, when it is assumed that the groundwater flow is a single flow path as the piston flow without mixture of new and old groundwater. However, since the actual groundwater may be composed of various groundwater origins, it is difficult to estimate the age of groundwater. As deep groundwater in observation wells is infiltrated by seawater, age presumption of groundwater by tritium should also take the influence into consideration. Table 3 shows the tritium concentration in observation wells. Kakiuchi et al. (6) have reported that the tritium concentration of the surface ocean water is 0.3-3.4TR in east of the Pacific Ocean and India Ocean. Their seawater samples were collected between 19 Dec., 1996 and 18 Feb., 1997. The groundwater sampling date of the area under investigation was 18 Feb., 2000, and the difference in sampling date is about 3 years. Here, the correction of tritium concentration after a period of 3 years was not taken into consideration. By using both the mixing rate of seawater and the measured concentrations of tritium at deep samples in the wells, the tritium concentration in the salinized groundwater, except the effect of tritium in the seawater can be calculated by means of the following equation.

$$TR_{calc} = \frac{TR_{meas.} - T_{sea} f_{sea}}{1 - f_{sea}} \qquad (6)$$

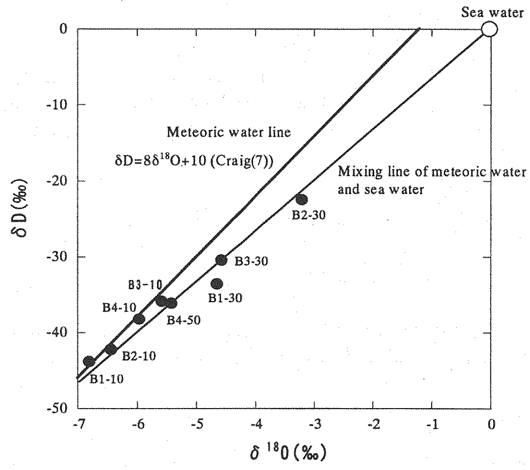

Fig.4 δ D and δ ^{18}O values of groundwater in all sampling points.

where T_{sea} is the tritium concentration in the seawater, $TR_{meas.}$ is the tritium concentration at B1-30, B2-30, B3-30, B5-50, $TR_{calc.}$ is the tritium concentration in the salinized groundwater except the effect of tritium in the seawater at deep sites in the wells. As a result of calculation using equation(6) T_{sea}=1.85TR (1.85TR is the arithmetic average of 0.3TR and 3.4TR), in case of B3-30, since it was $TR_{meas.}$ =0.5TR, T_{sea}=1.85TR, f_{sea}=0.295, it was set out to $TR_{calc.}$=-0.065. The same results which showed minus tritium concentrations($TR_{calc.}$) were recognized in each of the samples B1-30, B2-30, B4-50. Therefore, as the results of calculation using T_{sea}=1.85TR as a tritium concentration in the seawater showed minus, it was found that T_{sea}=1.85TR was too large. It seems reasonable to suppose that the tritium concentration of the seawater in a salinized groundwater is zero (i.e., T_{sea}=0TR). From the results of examining the tritium concentration as T_{sea}=0TR, it was assumed that the deep groundwater of B1~B4 was not mixed with the shallow one.

Hydrogen-oxygen isotope ratio

Figure 4 shows the relation between the hydrogen-oxygen isotope ratio in all sampling points. The origin of groundwater at every 10m depth samples were derived from precipitation because of plotting on the meteoric water line. On the other hand, B2, B3 with depths of 30m, B4 with a depth of 50m were plotted on the mixing line of meteoric water and seawater. It was inferred that the deeper groundwater is affected by seawater.

Age assumption of stratum formation by ^{14}C dating method

Generally, the ^{14}C content in a dead organism temporally decreases due to the termination of a source of new ^{14}C supply. The ^{14}C dating results of a broken piece of shell that was collected at the depth about 2-10m from the core samples B2 is shown in Table 4. It was found that the investigated area about 2000 years before the age measurement results of the shell extracted with the depth of 2m was the seabed. In depths deeper than 4m, it was found that it is the stratum formed from ca. 6000 years to ca. 7000 years. Therefore, although the investigated area was originally the sea, the sea gradually changed into land due to the sand sedimentation from the river and the artificial reclamation. Thereafter, it is thought that the shallow fresh groundwater was formed by rain.

Table 4 ^{14}C activity.

Sample	Depth(m)	$\delta^{13}C$	^{14}C(pMC)	+/-	Libby age(yr)	+/-
plant(root)	0.2	-13.9	111.45	0.53	modern	
shell	1.9	0.92	76.64	0.46	2137	49
shell	2.8	0.33	55.57	0.34	4720	49
shell	3.7	-1.9	45.39	0.29	6344	51
shell	4.3	-0.09	44.44	0.3	6514	53
shell	5.27	-3.33	41.14	0.28	7134	55
shell	9.9	-1.86	41.37	0.28	7090	55

CONCLUSIONS

The findings of this study are as follows:

Although the concentration level was also generally low and the age of groundwater was not presumed about tritium. It was revealed for B1, B2, B3, B4 that the deep groundwater was not mixed with the shallow one. From the results of hydrogen-oxygen isotope ratio, it was concluded that the origin of shallow groundwater was precipitation. On the other hand, the deeper groundwater was affected by seawater.

According to ^{14}C isotope dating, the salinized water in this area is thought to be originally below the sea bottom.

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