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**The source and behavior of iodine dissolving in groundwater  
in the Mobara gas field, Japan  
(Research Document)**

June, 2002

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**The source and behavior of iodine dissolving in groundwater  
in the Mobarra gas field, Japan  
(Research Document)**

Gento Kamei\*

**ABSTRACT**

The groundwater of the Mobarra gas-field in Boso peninsula, eastern Japan, contains considerable amount, around 100 mg/L, of iodine besides dissolved methane. Twelve groundwater samples from gas-producing wells to the aquifer within the Kazusa Group in Mobarra and Naruto districts have been analyzed for iodine, pH, Eh,  $\text{HCO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SiO}_2(\text{aq})$ ,  $\delta\text{D}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}_{\text{CH}_4}$  and seventeen elements. There is a good correlation between the concentrations of the dissolved elements to those in marine algae. The principal source of the iodine is believed to be algae buried in the sediments and the iodine has been discharged to the porefluid during decomposition of the tissue.

The molar ratio of  $\text{I}/\text{Cl}^-$  in the groundwater increases from  $1.0 \times 10^3$  to  $2.2 \times 10^3$  with changing the depth from 2000 to 1000 meters below the surface and turns to decrease from  $2.2 \times 10^3$  to  $1.8 \times 10^3$  with going up from 1000 to 500 meters. This tendency may be caused by the variation of buried organisms due to changing the sedimentary environment. The observed variation in the ratio indicates that the iodine discharged in the pore fluid did not migrate significantly after the deposition of the formation.

This paper can be regarded as an English version of Japanese article written by Kamei, which was published on the 'Shigen Chishitsu (Resource Geology)' 51(2)145-151 (2000).

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## 茂原ガス田地下水中のヨウ素の起源と挙動

(研究報告)

亀井 玄人\*

## 要 旨

房総半島の茂原ガス田の地下水中には 100mg/L 程度の高濃度のヨウ素が、メタンとともに溶存している。茂原および成東地域において、上総層群を帯水層とする計 12 のガス井から得られた地下水試料について、ヨウ素、pH、Eh、 $\text{HCO}_3^-$ 、 $\text{NH}_4^+$ 、 $\text{SiO}_2(\text{aq})$ 、 $\delta\text{D}$ 、 $\delta^{18}\text{O}$ 、 $\delta^{13}\text{C}_{\text{CH}_4}$  と、さらに 17 元素濃度を分析した。これらの元素濃度と海生の藻類中のそれらとの間により相関を認めた。このことから、このヨウ素は堆積物中に埋没した藻類を起源とし、藻類の組織の分解にともなって、間隙水中に放出されたものと考えた。

地表を基準とする地下水の採取深度が 2000 から 1000m へ上昇するにつれ、溶存する I/Cl のモル比は  $1.0 \times 10^3$  から  $2.2 \times 10^3$  へ上昇した。しかし、さらに地表下 1000 から 500m の範囲では、 $2.2 \times 10^3$  から  $1.8 \times 10^3$  へ逆に低下していた。このような変化傾向の理由として、(1)堆積環境の変化に伴って、埋没される生物の種類が変化した、(2)生物の種類によって、体内に含まれるヨウ素の濃度が異なっていた、さらに(3)生物の分解にともなって堆積物の間隙水中に放出されたヨウ素は、堆積層中を顕著に移行しなかった、と考えた。

なお、本資料は筆者が資源地質に発表した論文（亀井,2001,資源地質 51(2),145-151）を基に一部変更を加えて英訳したものである。

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## 1. INTRODUCTION

The region in Japan where is of eastern coast of the Tokyo bay to central to northern part of the Boso peninsula is called as the Minami-Kanto gas field. The gas is predominantly composed of methane and is dissolving in groundwater originating in the Kazusa Group of which is composed of Plio-Pleistocene marine sedimentary rock. This groundwater also contains considerable amount (around 100 mg/L) of iodine as I<sup>-</sup> mostly. Neither IO<sub>3</sub><sup>-</sup> nor volatile iodineorganic compound, such as CH<sub>3</sub>I or C<sub>2</sub>H<sub>5</sub>I, has been detected. (Sangyo Sozo Kenkyusho,1995) . Uptake of marine organisms such as algae into the sediments has been thought as the reason why the iodine concentration is remarkably high (e.g.,Fukuda and Nagata,1982). However, little discussion has been proposed. to verify the model. The source and behavior of the iodine in the aquifer will be discussed in this study based on examinations of chemical composition of the groundwater and environmental conditions during the deposition of the geologic formations.

## 2. GEOLOGIC SETTING

The Kazusa Group in central-eastern part of the Boso peninsula of central Japan consists of 12 formations (Mitsunashi *et al.*, 1959), which are composed mostly of marine-based argillaceous rocks. The Kazusa Group is in total several thousands meters thick. The age of sedimentation ranges from about 15 to 0.5Ma successively. These formations were uplifted around 0.5Ma ago (Nirei,1993; Watanabe and Danhara,1996). These formations dip northwest and the younger formations are exposed in the northwestern portion of the investigated area (Fig.1). Each formation intercalates tuff layers composed of scoriae or volcanic ash. These tuff layers range from a few to tens of centimeters in thickness. Little alteration was observed for a volcanic glass shards in the Ohtadai Formation (See Fig.2, Kamei et al., 2000).

Lithofacies and fossil species of shells or foraminifera indicate sedimentary environments. Silt stone is predominant in the Namihana and Ohara formations of lower part of the Kazusa Group and slump bed is also partly

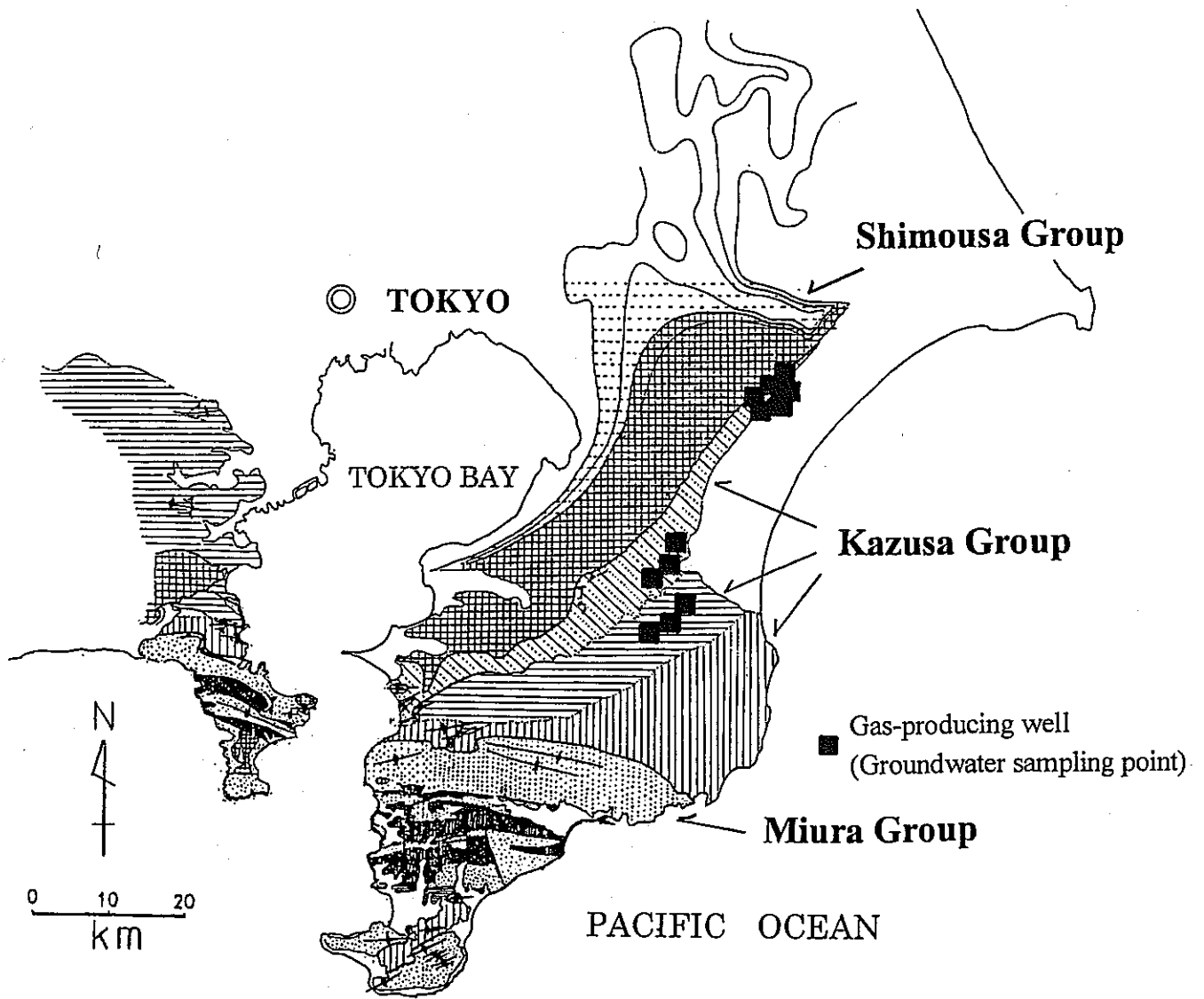
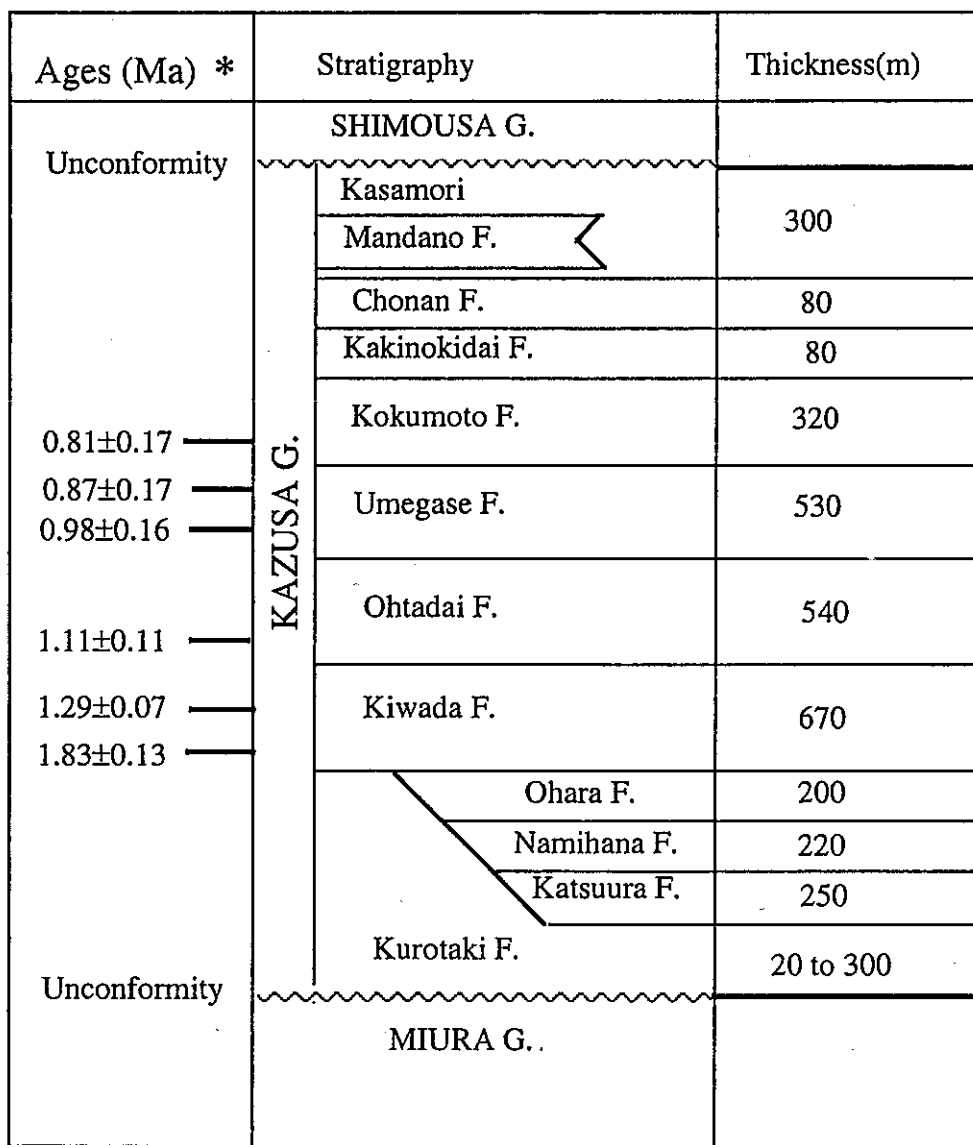


Fig. 1 Groundwater sampling localities on the geologic map cited from Mitsunashi et al.(1959)





\* Watanabe and Danhara(1996)

Fig. 2 Stratigraphy of Plio-Pleistocene at the central-eastern part of the Boso Peninsula (Nakajima,1978)

predominant in the Ohara formation. Estimated depth of water is from 700 to 1500 meters based on the fossils of shelfishes and foraminifera (Kitazato, 1986), the sedimentation environment is considered as a lower submarine fan to an ocean floor (Ito et al., 1992). The Kiwada formation is composed mainly of siltstone. This intercalates a turbiditic sandstone especially in eastern part of the Boso peninsula (Nakajima, 1978). The environmental condition for the deposition is estimated to be an upper part of continental slope based on benthos fossils (Ishiwada, 1964, Aoki, 1968). The Ohtadai and Umegase formations are composed mainly of sediments including turbidite at continental slope to at lower continental shelf (Nakajima, 1978). Igarashi (1994) studied the effect of ocean currents along the eastern coast of the Honshu islands (The warmer stream going up north, 'Kuroshio' and the colder stream going south, 'Oyashio') to deposition environment based on the analyses of fossils of planktonic foraminifera. The results suggested that the environmental condition for the Kiwada to middle Ohtadai formations was predominantly affected by Kuroshio and was little affected by gushing stream caused by a collision of Oyashio to the continental slope. During the sedimentation from the upper Ohtadai to the upper Umegase formations, on the other hand, the environment turned to be near the border between Kuroshio and Oyashio so that gushing stream actively occurred.

Those of the Kiwada to the Kokumoto Formation show a continental slope to lower continental shelf, and those of the Kakinokidai to the Kasamori Formation suggest a neritic sea to tidal zone environment (e.g. Ishiwada, 1964; Aoki, 1968; Nakajima, 1978; Ito and Katsura, 1993). In short, the younger formations indicate the shallower sea as their sedimentary environments.

As mentioned above, a deposit of iodine and natural gas dissolved in groundwater is embedded in the Kazusa Group. Many wells pumping out the groundwater are in operation in the studied region. There is an interface between the groundwater dissolving iodine and natural gas and permeating surface water in this region. The depth of the interface is around 150m beneath the surface at the west of the investigated region (Nirei, 1993).

### 3. SAMPLES

Table 1 The groundwater samples for chemical analysis.

|   |                    |           |           |           |                    |           |
|---|--------------------|-----------|-----------|-----------|--------------------|-----------|
| Sample                                    | No.1               | No.2      | No.3      | No.4      | No.5               | No.6      |
| District                                  | Mobara             | Mobara    | Mobara    | Mobara    | Mobara             | Mobara    |
| Collection depth (m)<br>below the surface | 797-1202           | 742-1200  | 743-1301  | 852-1302  | 717-1140           | 517-949   |
| Geologic<br>formations**                  | Otd.,Kwd.          | Otd.,Kwd. | Otd.,Kwd. | Otd.,Kwd. | Umg.,Otd.          | Umg.,Otd. |
| Sample                                    | No.7*              | No.8*     | No.9*     | No.10*    | No.11*             | No.12*    |
| District                                  | Narutoh            | Narutoh   | Narutoh   | Narutoh   | Narutoh            | Narutoh   |
| Collection depth (m)<br>below the surface | 1351-1947          | 1585-1868 | 1234-1791 | 1427-1800 | 1450-1800          | 1098-1492 |
| Geologic<br>formations**                  | Kwd.,Ohr.,<br>Nmh. | Ohr.,Nmh. | Kwd.,Ohr. | Kwd.,Ohr. | Kwd.,Ohr.,<br>Nmh. | Kwd       |

\*Okada and Tanaka (1999)

\*\*Umg;Umegase F., Otd;Ohtadai F., Kwd;Kiwada F., Ohr;Ohara F., Nmh;Namihana F.

Twelve groundwater samples from gas-producing wells were examined: six samples from the Mobarā district in the Boso Peninsula were analyzed and six data reported by Okada and Tanaka(1999)for the Narutoh district were also adopted to this study. Table 1 shows collection depth beneath the surface for each gas-producing well and its corresponding to the formations. As seen in the Fig.2, the aquifers are Namihana, Ohara, Kiwada, Ohtadai and Umegase formation in this order from the lower part of the Kazusa group.

#### 4. METHODOLOGY

There are four possibilities as sources of elements including iodine. Namely, (1) seawater, (2) minerals constituting stratum, (3) organisms involved in stratum and (4) permeating water from the surface. With respect to the (1) and (2), the author compared the calculated values of chemical composition of solution originating from seawater of which has been equilibrated with minerals constituting the Kazusa formation with the measured those of sampled groundwater. The details of the calculations will be mentioned after. As possibility (3), marine algae and/or foraminifer can be assumed. Because foraminifera generally live together with algae, the author assumed a process that the elements including iodine discharge into the groundwater with the decomposition and the elements have been preserved. The concentration ratio of an element in algae to in seawater was compared with that of the same element in groundwater to in seawater in order to confirm the assumed process. The ratios in terms of 19 elements, Li, B, F, Na, Mg, Al, Si, S, Cl, K, Ca, Ti, Cr, Fe, Se, Br, Sr, I and Ba, which are major elements generally dissolved in groundwater or have a tendency to be enriched into living algae or to be expelled from it. The concentration of Si and of S was evaluated as  $\text{SiO}_2$  and  $\text{SO}_4^{2-}$ , respectively. To check the possibility (4) mentioned above, hydrogen and oxygen stable isotopic ratios,  $\delta D$  and  $\delta^{18}\text{O}$ , were also determined for the groundwater. All groundwater samples from the Mobarā district were filtrated through a molecular weight cut-off 10000, then were analyzed. Values of temperature, pH and Eh were obtained for the

Table 2 Methods of analysis for the groundwater samples.

---

|   |   |
|---|---|
| Na, K                                     | : Flame spectrometry                                |
| Li, Mg, Ca, Fe,:                          | Atomic absorption spectrophotometry                 |
| Cl , F, Br, SO <sub>4</sub> <sup>2-</sup> | : Ion chromatography                                |
| I   | : Iodometric titration                              |
| B, Al, Ba, Sr                             | : ICP   |
| HCO <sub>3</sub> <sup>-</sup>             | : Acid-base titration (at each collection locality) |
| SiO <sub>2</sub>                          | : Absorption spectrophotometry (molybdenum yellow)  |
| Cr, Se, Ti                                | : ICP-Mass  |
| $\delta$ D, $\delta$ <sup>18</sup> O      | : Mass spectrometry                                 |

---

Table 3 Chemical compositions of the groundwaters from the Mobara gas field and of seawater

|                                      | Groundwater |          |                    |                    |        |        |                    |                     |                    |                      |                     |                    | Seawater* |
|--------------------------------------|-------------|----------|--------------------|--------------------|--------|--------|--------------------|---------------------|--------------------|----------------------|---------------------|--------------------|-----------|
|                                      | No.1        | No.2     | No.3               | No.4               | No.5   | No.6   | No.7**             | No.8**              | No.9**             | No.10**              | No.11**             | No.12**            |           |
| Gas-producing wells                  | No.1        | No.2     | No.3               | No.4               | No.5   | No.6   | No.7**             | No.8**              | No.9**             | No.10**              | No.11**             | No.12**            |           |
| Collection Date                      | 92.7.7      | 99.11.26 | 92.7.7<br>99.11.26 | 92.7.7<br>99.11.26 | 92.7.8 | 92.7.9 | 78.9.7<br>80.11.13 | 75.10.28<br>82.5.13 | 78.9.8<br>82.5.13  | 75.10.28<br>80.11.14 | 74.12.17<br>77.4.19 | 78.9.8<br>82.5.13  |           |
|                                      |             |          |                    |                    |        |        | 84.6.25<br>88.3.23 | 79.5.7<br>88.3.23   | 84.6.25<br>88.3.23 | 84.6.25<br>88.3.23   | 88.3.23             | 84.6.25<br>88.3.23 |           |
| Water temperature(°C)                | 27.8        | 22.9     | 28.3               | 23.9               | 24.0   | 24.9   | 38.3               | 39.8                | 36.9               | 39.5                 | 35.0                | 33.5               |           |
| pH                                   | 7.86        | 7.82     | 7.80               | 7.67               | 7.94   | 7.74   | 7.58               | 7.56                | 7.59               | 7.58                 | 7.41                | 7.60               |           |
| Eh(mV)(vs.S.H.E)                     | -50         | -27      | -46                | -21                | -73    | -52    |                    |                     |                    |                      |                     |                    |           |
| Li (mg/kgH <sub>2</sub> O)           |             | 0.7      | 0.7                | 0.5                |        |        |                    |                     |                    |                      |                     |                    | 0.17      |
| B                                    |             | 3.3      | 3.5                | 3.1                |        |        | 3.5                | 3.1                 | 3.3                | 3.2                  | 3.3                 | 3.1                | 4.5       |
| HCO <sub>3</sub> <sup>-</sup>        | 903         |          | 995                | 934                | 970    | 897    | 669                | 570                 | 700                | 672                  | 531                 | 750                |           |
| NH <sub>4</sub> <sup>+</sup>         | 256***      | 252***   |                    | 255***             |        |        | 197                | 163                 | 205                | 181                  | 169                 | 224                |           |
| F                                    |             | 15.6     | 2.4                | 7.9                |        |        |                    |                     |                    |                      |                     |                    | 1.3       |
| Na                                   | 10700       | 11100    | 10400              | 10485              | 7410   | 9390   | 11220              | 10600               | 11140              | 11280                | 10900               | 11320              | 10800     |
| Mg                                   | 315         | 328      | 337                | 315                | 223    | 362    | 306                | 280                 | 304                | 310                  | 280                 | 314                | 1290      |
| Al                                   |             | 0.3      | 0.3                | 0.3                |        |        |                    |                     |                    |                      |                     |                    | 0.0008    |
| SiO <sub>2</sub>                     | 70          | 64       | 73                 | 63                 | 64     | 61     |                    |                     |                    |                      |                     |                    | 6         |
| SO <sub>4</sub> <sup>2-</sup>        |             | 1.2      |                    | 0.6                |        |        | 0.0                | 0.0                 | 0.4                | 0.3                  | 0.0                 | 0.3                | 2700      |
| Cl                                   | 18800       | 17400    | 19300              | 17700              | 13500  | 17300  | 19440              | 19575               | 19480              | 19380                | 19525               | 19372              | 19500     |
| K                                    |             | 365      |                    | 353                |        |        | 362                | 368                 | 359                | 368                  | 362                 | 338                | 399       |
| Ca                                   | 229         | 257      | 219                | 244                | 145    | 174    | 318                | 333                 | 286                | 328                  | 350                 | 260                | 413       |
| Ti                                   |             | 0.617    | 0.623              | 0.571              |        |        |                    |                     |                    |                      |                     |                    | <0.00096  |
| Cr                                   |             | 0.014    | 0.01               | 0.009              |        |        |                    |                     |                    |                      |                     |                    | 0.0002    |
| Fe                                   | 1.43        |          | 2.66               | 2.49               | 1.22   | 2.25   |                    |                     |                    |                      |                     |                    | 0.00006   |
| Se                                   |             | 1.17     | 1.07               | 1.11               |        |        |                    |                     |                    |                      |                     |                    | 0.00013   |
| Br                                   | 136         | 155      | 134                | 143                | 96     | 122    | 124                | 112                 | 129                | 125                  | 118                 | 136                | 67        |
| Sr                                   |             | 7.3      | 7.4                | 7.1                |        |        |                    |                     |                    |                      |                     |                    | 7.6       |
| I                                    | 131         |          | 128                | 137                | 84     | 111    | 83                 | 71                  | 86                 | 75                   | 72                  | 103                | 0.056     |
| Ba                                   |             | 2.7      | 2.8                | 2.0                |        |        |                    |                     |                    |                      |                     |                    | 0.014     |
| δ D (‰)                              | -0.4        |          | 1.9                | 6.7                | -0.8   | -3.2   |                    |                     |                    |                      |                     |                    |           |
| δ <sup>18</sup> O (‰)                | -1.93       |          | -1.90              | -1.94              | -2.61  | -2.53  |                    |                     |                    |                      |                     |                    |           |
| δ <sup>13</sup> C <sub>CH4</sub> (‰) |             |          |                    |                    |        |        | -67.4              |                     | -67.0              | -67.9                | -68.6               | -66.0              |           |

\*Faure (1998), \*\*Okada and Tanaka (1999) \*\*\*Higuchi : Personal communication

groundwater just after pumping out. Table 2 shows adopted analytical methods for each component in the groundwater.

## 5. RESULTS

Table 3 indicates chemical compositions of the groundwater samples and those of seawater, which was cited from Faure (1998).

In-situ measured temperature shows 22.9 to 28.3°C (average 25.3°C) in the Mobara district and 33.5 to 39.8°C (av. 37.2°C) in the Narutoh district. Similarly, pH falls into a range from 7.67 to 7.94 (av. 7.81) in the Mobara district and from 7.41 to 7.60 (av. 7.55) in the Narutoh district (Data of the Narutoh district were cited from Okada and Tanaka, 1999). Eh was measured for samples from the Mobara district and falls into the range from -21 to -73mV (av. -45mV, vs. S.H.E).

With respect to major, minor and trace elements, Na<sup>+</sup> and Cl<sup>-</sup> are predominantly and these concentrations are fairly close to those of seawater. Hydrogen and oxygen stable isotopic ratios are also similar to those of seawater ( $\delta D = -3.2$  to  $+6.7\%$ ,  $\delta^{18}O = -1.90$  to  $-2.61\%$ ). Values of  $\delta^{13}C$  of methane separated from groundwater in the Narutoh district indicate -66.0 to -68.6‰ (Okada and Tanaka, 1999) and suggest that microbe activities could be concerned in the methane production, according to Matsumoto (1994).

## 6. DISCUSSIONS

In order to test the possibilities (1) and (2) mentioned above, the author compared calculated chemical composition of the seawater which has leached to be an equilibrium to rock forming minerals of the Kazusa Group with measured that of the groundwater. In addition, the influence of uptaking algae during sedimentation was evaluated to examine the possibility (3). In terms of the possibility (4), the influence of permeating surface water could be small. Because the hydrogen and oxygen stable isotopic ratios and concentrations of Na<sup>+</sup> and Cl<sup>-</sup> of the groundwater suggest that seawater has been significantly involved in the development of the groundwater chemistry.

Table 4 Abundance of constituent minerals in an argillaceous rock of the Ohtadai formation in the Kazusa group (Kamei et al., 2000).

|                     |     |
|---------------------|-----|
| quartz              | +++ |
| plagioclase         | ++  |
| montmorillonite     | +   |
| chlorite            | +   |
| illite              | .   |
| calcite             | +   |
| $\alpha$ -tridymite | .   |
| K-feldspar          | .   |
| clinoptilolite      | .   |
| pyrite              | .   |
| siderite            | .   |
| hornblende          | .   |

Marks are: +++; abundant, ++; major, +; minor, and .; trace.



Table 5 Calculated and measured chemical composition of the groundwater

|            | Input (Seawater) | Calculated* | Analyzed** |
|------------|------------------|-------------|------------|
| pH         | 7.68             | 8           | 7.78       |
| pe         | -0.761           | -3.793      | -0.761     |
| Li (mol/L) | 2.45E-05         | 2.45E-05    | 9.08E-05   |
| B          | 4.16E-04         | 4.16E-04    | 3.05E-05   |
| C          | 1.14E-02         | 3.42E-05    | 1.14E-02   |
| F          | 6.84E-05         | 6.84E-05    | 4.53E-04   |
| Na         | 4.70E-01         | 2.37E-03    | 4.57E-01   |
| Mg         | 5.31E-02         | 1.45E-03    | 1.26E-02   |
| Al         | 1.97E-08         | 1.47E-05    | 1.11E-05   |
| Si         | 9.97E-05         | 8.32E-05    | 1.10E-03   |
| S          | 2.81E-02         | 2.81E-02    | 4.16E-06   |
| Cl         | 5.50E-01         | 5.50E-01    | 5.19E-01   |
| K          | 1.02E-02         | 7.61E-13    | 9.18E-03   |
| Ca         | 1.03E-02         | 2.93E-01    | 6.54E-03   |
| Ti         | 0                | 0           | 2.95E-06   |
| Cr         | 3.85E-09         | 3.85E-09    | 2.12E-07   |
| Fe         | 1.07E-09         | 2.96E-03    | 3.60E-05   |
| Se         | 1.65E-09         | 1.65E-09    | 1.42E-05   |
| Br         | 8.39E-05         | 8.39E-05    | 1.60E-03   |
| Sr         | 8.67E-05         | 8.67E-05    | 8.33E-05   |
| I          | 4.41E-07         | 4.41E-07    | 7.72E-04   |
| Ba         | 2.18E-09         | 2.18E-09    | 1.82E-05   |

\*Using the software 'PHREEQC'

Reactions to albite, anorthite, calcite, chlorite, K-feldspar, muscovite (as a substitute of illite), pyrite, quartz, siderite and tremolite (as a substitute of hornblende) were considered.

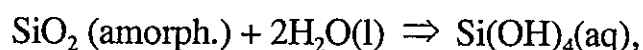
\*\*Average of the groundwater samples in Table 3.

## 6.1 Mineral-seawater chemical equilibrium

The author calculated chemical composition of the seawater which has leached to be an equilibrium to rock forming minerals of the Kazusa Group using a computer software, 'PHREEQC (Purkhurst, 1995). Temperature was assumed to be 25°C based on the measured value. Chemical composition of seawater was cited from Faure(1998). Based on the mineral composition of an argillaceous rock from the Ohtadai formation (Table 4, Kamei et al., 2001), the mineral assemblage was assumed as follows: albite, anorthite, calcite, chlorite, K-feldspar, muscovite (as a substitute of illite), pyrite, quartz, siderite, tremolite (as a substitute of hornblende).

In terms of pH and a redox potential (pe) as requirements for the calculation, values of 7.68 and -0.761(V) were adopted respectively based on measured data of the groundwater. In many elements except Li, B, Cl, Br and Sr, remarkable discrepancies have been seen in their between the calculation and the measuring (Table 5). This result suggests that other processes excepting mineral-seawater reaction significantly contribute evolution of the groundwater chemistry.

Volcanic glass shards and diatom fossils are contained in strata of the Kazusa Group. Consequently, effect of dissolution of glass and of amorphous silica was also considered to the evolution of aqueous silica content in the groundwater. Namely,



$\log K = -2.71$  (Nordstrom and Munoz, 1994) so that solubility of  $\text{SiO}_2(\text{amorph.})$  is calculated to be  $1.22 \times 10^{-3} \text{ mol/kgH}_2\text{O}$ . On the other side, average concentration of  $\text{SiO}_2(\text{aq})$  in the groundwater is  $1.10 \times 10^{-3} \text{ mol/kgH}_2\text{O}$  and there is a good agreement each other. Thus, dissolution process of volcanic glass and diatom fossils could significantly contribute the evolution of aqueous silica concentration of the groundwater.

## 6.2 Algae contribution to the groundwater chemistry

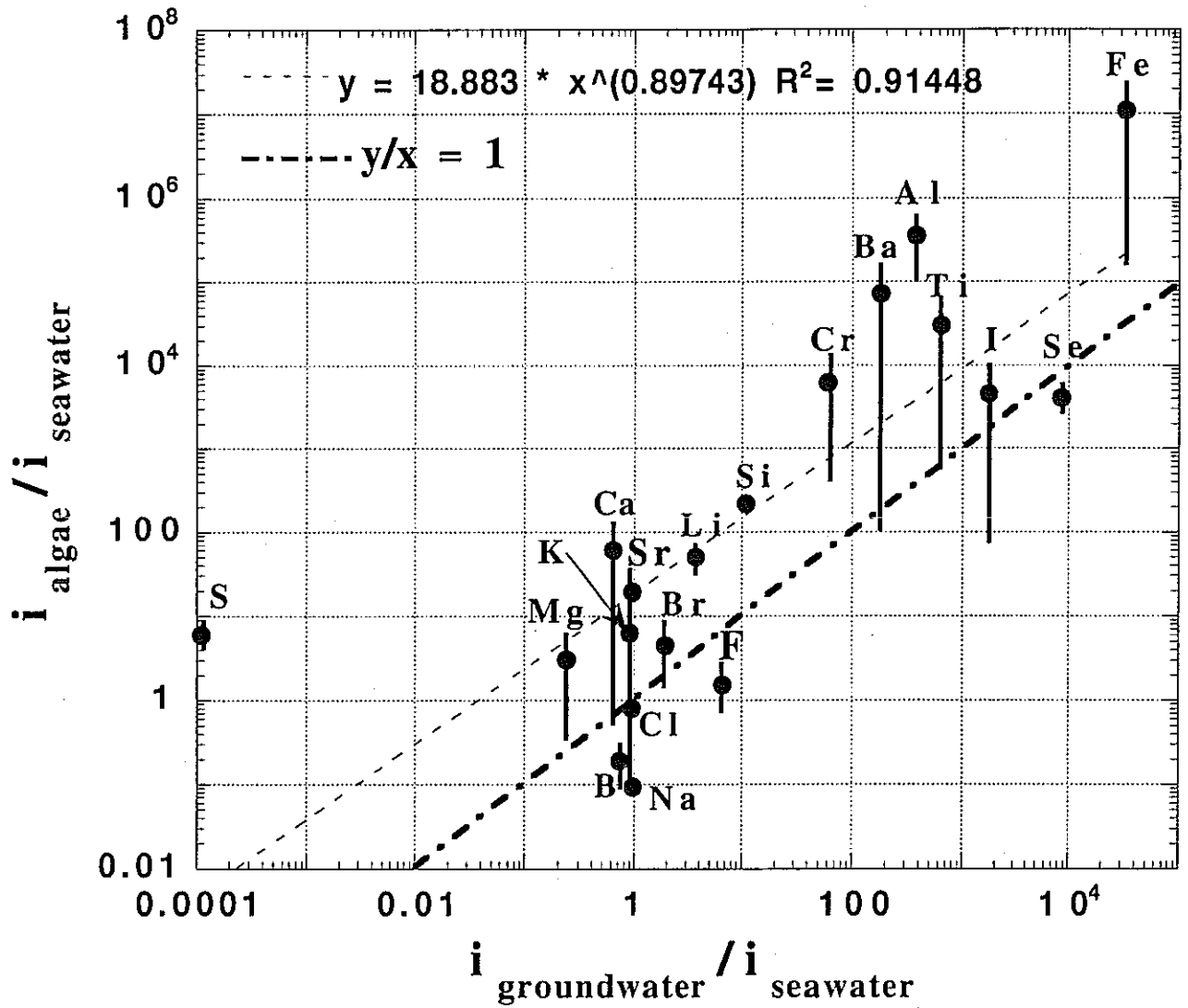


Fig. 3 Ratio of the specific elemental concentration in groundwater in the Mobara gas-field to that in seawater versus the ratio of in living algae to in seawater.

In this paper, algae refers to diatom and brown, red and green algae. Figure 3 indicates a relation between the ratio of elemental concentration in living algae to that in seawater (Condensation Coefficient, Hanya,1978) and that in groundwater to in seawater. Although condensation ratios of several elements widely vary there is a fairly good correlation between them. This fact indicates remarkable contribution by algae to chemical evolution of the groundwater. The author assumed that the algae was decomposed after taking in sediments and some elements constituting the body was then discharged in porefluids in the sediments. Halogen, including iodine, tends to be plotted along the line of  $y/x = 1$  in Fig.3. On the other hand, other elements tend to be plotted in a field of  $y/x > 1$ . This reason may be explained as follows: Halogen exists as anion in groundwater and so that it is excluded into porefluid (i.e. groundwater) by the Coulomb power between it and minerals negatively electrified, such as clay. Other elements, however, precipitate as minerals and/or adsorb onto minerals such as clay. On the assumption that all iodine was discharged into porefluid during a decomposition process of algae taken in sediments, a mass-balance of iodine was quantitatively examined:

For 1L of wet sediment, including groundwater, the iodine concentration and the porosity is assumed to be 100 mg/L and 42% (based on the value of the Ohtadai formation, Inami,1981), respectively. Accordingly, contained amount of iodine in this 1L of this sediment is

$$100 \times 0.42 = 42 \text{ mg.}$$

where, amount of iodine in seawater and from mineral was ignored.

Contained iodine amount varies from 4 to 500 mg for live algae (Hanya, 1978).

When it is 250 mg, to provide 42 mg of iodine,

$$42 / 250 \times 1000 = 168 \text{ g}$$

is needed as live algae for 1L of wet sediment. This amount was more discussed based on the following assumption. As mentioned above, occurrence of an oceanic upstream should be considered at a sedimentation field of the upper Ohtadai formation. Production rate of organic carbon is assumed to be  $300 \text{ gC} / \text{m}^2 / \text{y}$  for such environment based on Suzuki (1997). When 1% of this organic carbon is taken into a sediment, the annual amount is  $3 \text{ gC} / \text{m}^2$ . The deposition rate, on the other side, is assumed to be  $10^{-4} \text{ m/y}$

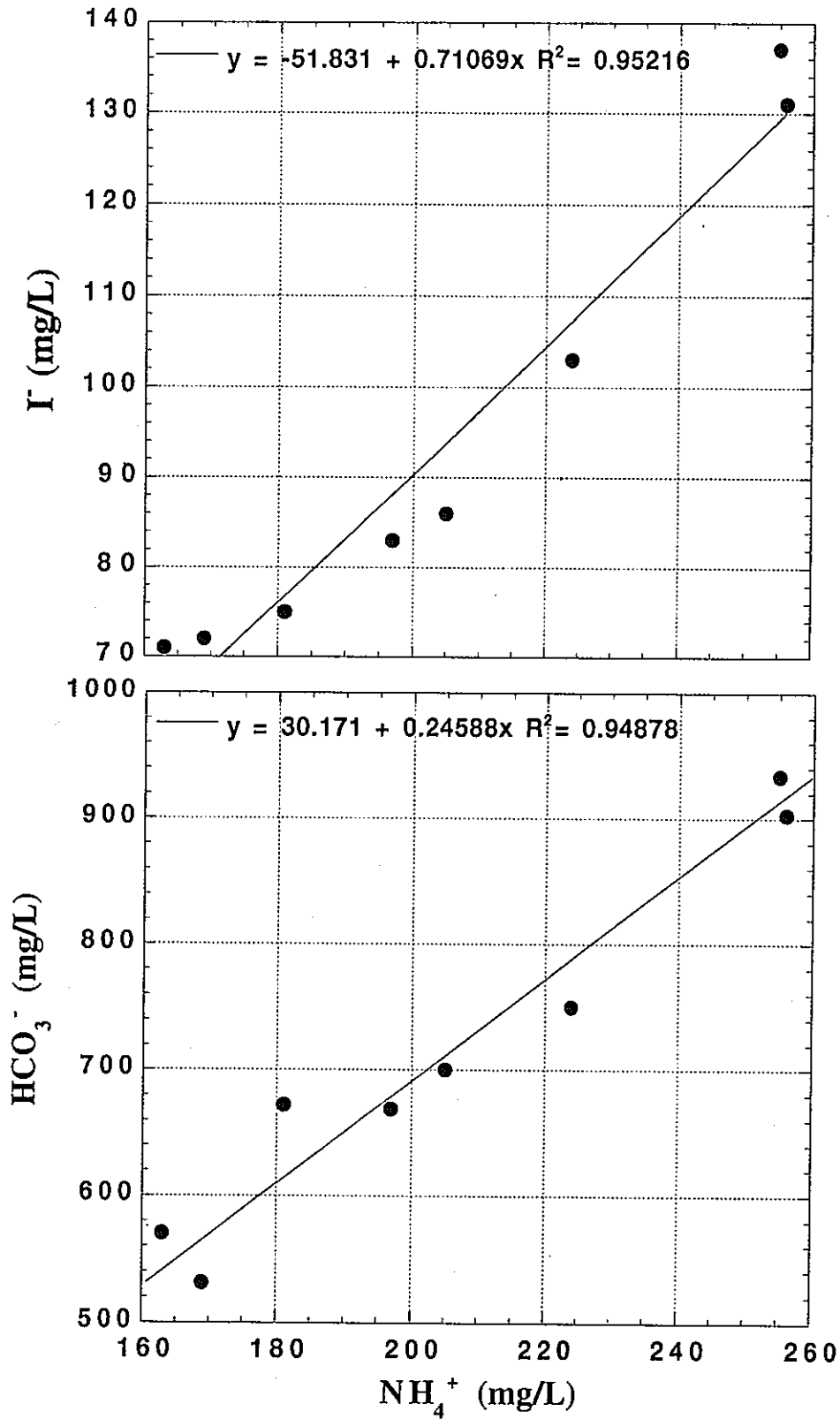


Fig. 4 Relationships between the molar concentration of ammonium and that of iodine, and of bicarbonate, dissolving in groundwater in the Mobarra gas-field.

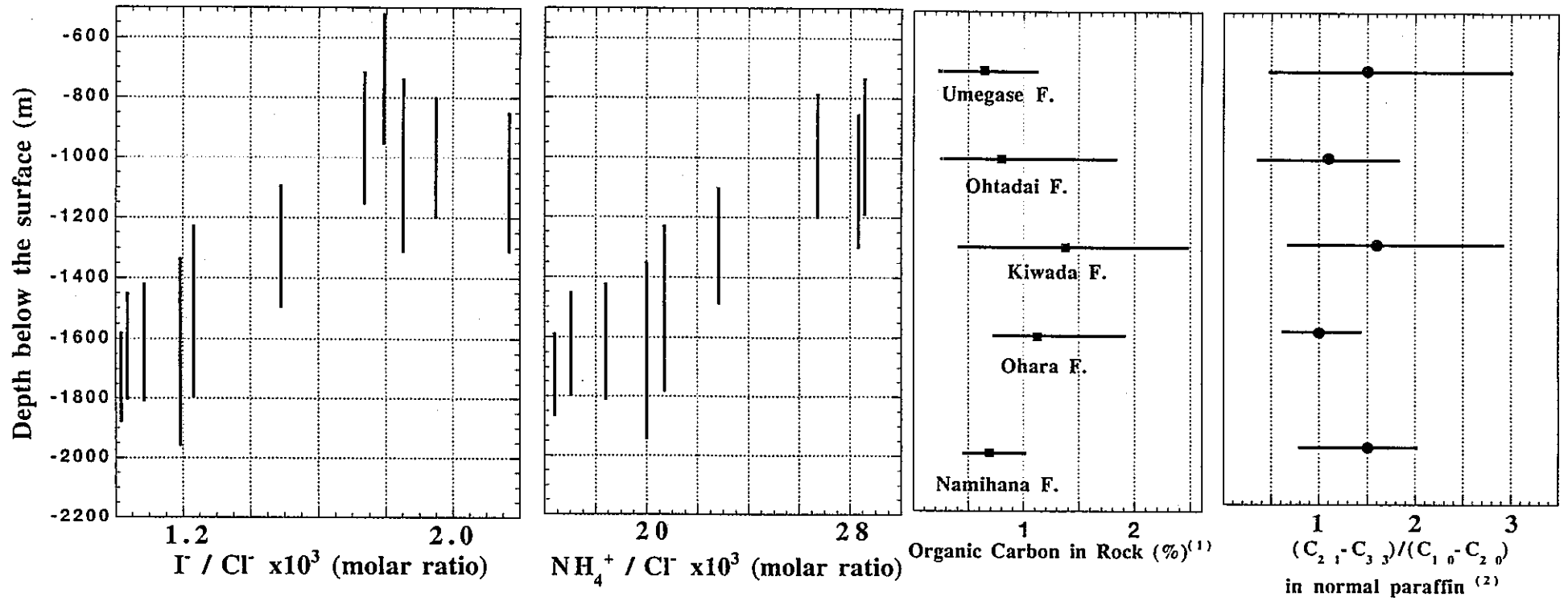


Fig. 5 Relationships between the depth below the surface in the Mobara gas-field and ionic molar ratio of I<sup>-</sup>/Cl<sup>-</sup>, NH<sub>4</sub><sup>+</sup>/Cl<sup>-</sup>, organic carbon in rock (Ref.1, Koma et al.,1983) and (C<sub>21</sub>-C<sub>33</sub>)/(C<sub>10</sub>-C<sub>20</sub>) in normal paraffin in rock (Ref.2, Yonetani et al.,1983).

based on the rate at a field within 1000 km east from the Honshu island of Japan (Kobayashi, 1977). From the assumed rate, carbon concentration in wet sediment is calculated to be 30 gC / L. When the carbon content by percentage is 50 %, the dry weight of organisms in 1L of the sediment is  $30 / 0.5 = 60$  g/L.

When the water content is 70%, the live (wet) weight in 1 L of the sediment is  $60 \times 1 / (1 - 0.7) = 200$  g/L.

Therefore, algae could be considered as an origin of the iodine from the view point of provided amount into the sediment.

### 6.3 The origin of iodine and its behavior in geologic formations

The relation between the iodine and algae is moreover discussed here. Algae taking into a sediment could be decomposed by microbe activity and bicarbonate and ammonium ion could be produced through the process. If iodine is released into the porefluid of a stratum from the algae during the decomposition, a positive correlation could be seen between concentration of iodine and of bicarbonate as well as ammonium. As seen in Fig.4, there is a good agreement between  $[\text{NH}_4^+]$  and  $[\text{I}^-]$ , as well as a relation between  $[\text{NH}_4^+]$  and  $[\text{HCO}_3^-]$ , so that it is suggested that the iodine be derived from an organisms, such as algae.

Figure 5 shows the relations between the groundwater collection depth (beneath the surface) and chemical concentration ratios for the groundwater, i.e.  $\text{I}^- / \text{Cl}^-$  and  $\text{NH}_4^+ / \text{Cl}^-$ , organic carbon amount in a rock sample from the Umegase, Ohtadai, Kiwada, Ohara and Namihana formations (Koma et al., 1983) and carbon number ratio, i.e.  $(\text{C}_{21}-\text{C}_{33}) / (\text{C}_{10}-\text{C}_{20})$ , in normal paraffin in a rock from each formation (Yonetani, 1983). Organic matter derived from a land plant (e.g. that in peat or lacustrine sediment) has generally larger value for the  $(\text{C}_{21}-\text{C}_{33}) / (\text{C}_{10}-\text{C}_{20})$  (Yonetani, 1983). From the value, we can consequently estimate the more or less of the quantity of land plant taken into a stratum (In Figure 4, the author plotted a value of organic carbon and of carbon number ratio at a horizon, which is considered as a center of the geologic formation). Figure 4 indicates that both of  $\text{I}^- / \text{Cl}^-$  and of  $\text{NH}_4^+ / \text{Cl}^-$  are low at a depth corresponding to the Ohara formation and increase with going upward. These indicate maximum at the Ohtadai formation and  $\text{I}^- / \text{Cl}^-$  turns to be slightly lower at the Umegase formation. The variation of organic carbon amount in rock

has a similar trend. The amount increase from the lower formation and has the greatest number at the Kiwada formation but it decreases with going upper.

The values of  $(C_{21}-C_{33})/(C_{10}-C_{20})$  tend to be higher in the Kiwada and Umegase formation. This fact suggests that comparatively larger amount of land plants be supplied for these formations.

On the basis of these discussions and the account in the previous chapter of 'Geologic Setting', the sedimentary environment and features of the sediment are concluded as follows for the Ohtadai formation of which the groundwater has the highest I/Cl in concentration ratio:

1. A continental slope to a lower continental shelf. Turbidites are observed.
2. A warm ocean stream, 'Kuroshio', was predominantly. An upward ocean stream occurred at the latter to last stage of sedimentation.
3. Amount of land plants taken in is comparatively low.

Organisms, mainly algae, which live in these environment may be comparatively rich in iodine. Inversely, iodine is less in a sediment on a lower submarine alluvial fan and/or on an ocean floor (e.g. the Ohara formation). The organisms living in such environment may not have significant amount of iodine. With respect to the Kiwada formation, the amount of organic carbon is comparatively higher but that of iodine is lower compared with those in the Ohtadai formation because supplied amount of land plants might be higher during the deposition. Namely, the author infers that organisms species vary with changing sedimentation environment so that iodine amount in organisms also vary. Moreover, the similarity between the variation trend of iodine concentration with the groundwater collection depth and that of ammonium and/or of organic carbon may suggest that the iodine has not remarkably migrate from each formation since the deposition.

## 7. CONCLUSION

In order to make clear the origin and behavior of iodine dissolving in groundwater of the Mobarra gas-field in Japan, chemical composition of the water has been examined. Decomposition of algae taken in a sediment could significantly contribute to the evolution process of the chemical composition in addition to the chemical reaction between seawater and the minerals forming the geologic formation. The correlation between iodine concentration and ammonium or bicarbonate may suggest a remarkable



contribution of the algae decomposition process.

In a extent from the Namihana to the Umegase formations in the Kazusa group, the I/Cl<sup>-</sup> concentration ratio for the groundwater gradually increase with going upward and indicate a maximum at the Ohtadai formation. Then it turns to slightly decrease at the Umegase formation. Reported value of the carbon number ratio (C<sub>21</sub>-C<sub>33</sub>)/(C<sub>10</sub>-C<sub>20</sub>) in normal paraffin in organic matter containing in the rock indicates that the more amount of land plants might be supplied during the deposition of the Kiwada and Umegase formations but the more marine organisms for the Ohtadai formation. Organisms species vary with changing sedimentation environment so that iodine amount in organisms might vary. The variation of concentrations of iodine, ammonium in groundwater and of organic carbon in rock with changing horizons of the groundwater collection may suggest little migration of iodine since the depositions of these geologic formations.

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