地調月報 Bull. Geol. Surv. Japan, vol. 30 (8), p. 441–457, 1979 552.52+556.3 : 553.981(521.29) : 546.15

Geochemistry of Some Iodine-rich Rocks and Brines from the Mobara Gasfield, 50 km Southeast of Tokyo

Koji MOTOJIMA* and Takashi HIRUKAWA*

Abstract: Very high concentrations of iodine, up to 240 ppm in the marine mudstones and up to 112 mg/l in the brines, were recognized in the Mobara gasfield, some 50 km southeast of Tokyo.

The mudstone core samples of the Pliocene and Pleistocene ages were taken from three drilling sites and their contents of iodine, chlorine, and bromine were determined by neutron activation method. Two brine samples from two gas-iodine producing wells, having the reservoirs of the same geologic horizons from which the core samples were taken, were obtained and their contents of iodine, chlorine, bromine, calcium, magnesium, etc. were determined by volumetric, gravimetric, and atomic absorption methods.

All the samples were taken from the Kazusa group which is composed mainly of the alternation of sandstone and mudstone deposited under the neritic and bathyal conditions. The group is divided into eleven formations, and the maximum concentrations of iodine in both the rocks and brines were recognized in the middle part of the group, the Kiwada formation.

In the rocks, iodine is more abundant than bromine, on the contrary, in the brines bromine is more abundant. The relative abundance of iodine and bromine in the brines corresponds roughly to that of magnesium and calcium.

The values of the ratio of "I ppm in rock/I mgl^{-1} in brine" in the limited geologic horizons range from 1.22 to 1.72, and tend to increase towards the older formations. These values are changed field by field, for instance the value of the Okinawa gasfield, some 2,000 km southwest of Tokyo, is 0.59 and that of the Anadarko Basin, Oklahoma, is 0.0088. The difference of the values is likely to have been caused by the differences in depositional environment and diagenetic condition of the sedimentary rocks.

In accordance with the general geologic evidences, it can be supposed that the main portion of highly concentrated iodine in the Mobara gasfield was originated from seaweeds and diatoms.

1. Introduction

The South Kanto natural gas region, occupying more than 2,500 km^2 and filled with the Neogene and Pleistocene marine sediments, is one of the world's largest iodine fields, at present, and the Mobara gasfield is a centre for gas and iodine industries in the region. The field is situated about 50 km southeast of Tokyo and is made up of the reservoirs of dissolved-in-water type (Fig. 1 and Fig. 2).

In Japan, iodine has been industrially extracted from the brines associated with hydrocarbon gases and the production in 1975 reached 6,851 tons of which 84.7% was from the South Kanto gas region, 14% was from the Niigata oil-and-gas field, and the rest was from the Miyazaki gasfield.

In spite of the importance to the basis of iodine exploration, there is no literature which deals with the exact relationship between the iodine concentrations in sedimentary rocks and brines in the field. Since the geochemical study of iodine in connection with the exploration of hydrocarbon resources was conducted by one of the authors (MOTOJIMA, 1971), it has been expected to get some convenient samples from the Mobara gasfield. Fortunately, at his request to a natural gas company, in 1973, ten core samples of muddy rocks and two samples of brines were taken from the drilling sites

* Geochemistry and Technical Service Department

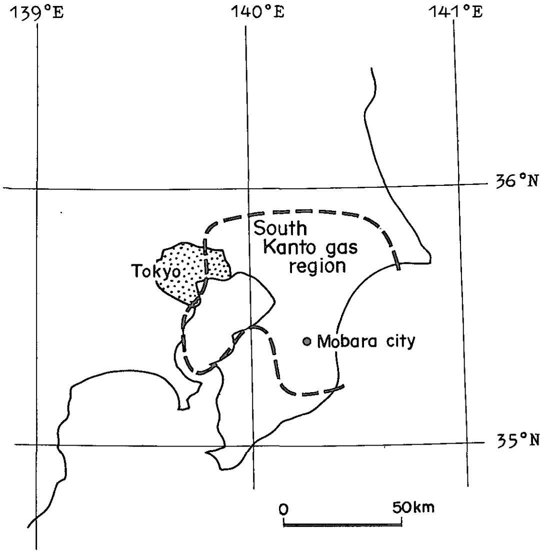

Fig. 1 Locality of Mobara gasfield.

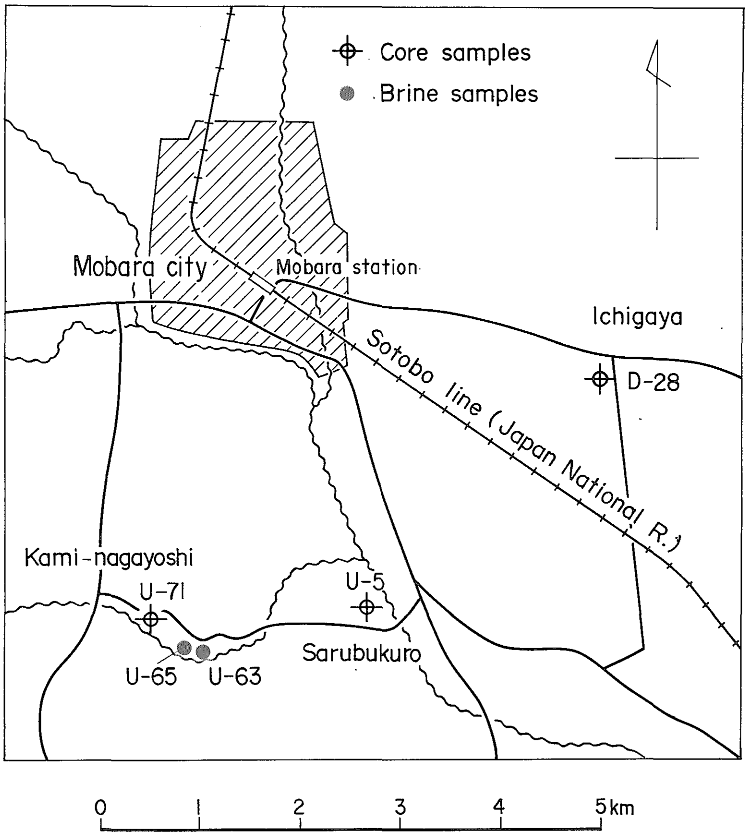

Fig. 2 Locality of five wells for sampling of cores and brines.

and gas-iodine producing wells under a convenient state for geochemical study.

The core samples were analysed by Dr. Eisaku TAJIMA *et al.*, Gunma University, and the brines were analysed by Takashi HIRUKAWA, Geological Survey of Japan, respectively. The short note on the analytical work of the core samples has already appeared (TAJIMA *et al.*, 1975).

The very high concentrations of iodine were noticed in both the rocks and brines, and the present paper is focused on the relationship between the iodine content in rocks and brines in relation to the geologic horizons.

The authors wish to express their gratitute to Dr. Shizuo TOTANI, Faculty of Engineering of the University of Tokyo, for his kind arrangement to get samples. Thanks are also due to Mr. Toshio HONMA of the Kanto Natural Gas Development Company Ltd. for kindly supplying the valuable samples of cores and brines.

2. Geology of the Mobara Gasfield

The iodine-gas deposits of dissolved-in-water type in Japan, have been found in the marine sediments of the late Miocene, Pliocene, and Pleistocene ages.

In the South Kanto gas region, more than ten gasfields have been found and exploitated. Almost all gas reservoirs are in the thick marine sediments for which the "Kazusa group" has been named. The geologic ages of the group are from the late Pliocene to middle Pleistocene. The stratigraphic relation is shown in Fig. 3, and the boundary between the Pliocene and Pleistocene is supposed to be in the middle of the Umegase formation or in the top of the Ohara formation (FUKUTA, 1976). The

Fig. 3 Stratigraphy of the Kazusa group.

		Formation name	Rock facies	Thickness(m)
Post Kazusa group [Quaternary]		Narita group		
[Pliocene–Pleistocene]	Kazusa group	Kasamori formation	muddy f. sd. st–sdy. silt st	240–250
		Chonan f.	sd. st/mud st	110
		Kakinokidai f.	mud st (+sd. st)	80–90
		Kokumoto f. (Ko)	mud st, sd. st/mud st	240
		Umegase f. (U)	(sd. rich) sd. st/mud st	370
		Otadai f. (Ot)	(mud rich) sd. st/mud st	260–270
		Kiwada f. (Kw)	mud st	600–650
		Ohara f. (Oh)	(sd. rich) sd. st/mud st	180
		Namihana f.	(mud rich) sd. st/mud st	310
		Katsuura f.	(sd. rich) sd. st/mud st	350+
		Nonozuka f.	(andesitic) pyroclastics, conglomerate, sd. st	40–50
Kurotaki unconformity				
Pre Kazusa group [Tertiary]		Toyooka group		

f: fine
sd.: sand
sdy: sandy
st: stone

sd. st/mud st: alternation of sandstone and mudstone

(FUKUTA, 1976)

marine sediments of the Kazusa group are found in the area of some 12,000 km², and the maximum thickness is about 2,800 meters at the eastern part of the South Kanto gas region (Fig. 1).

The Kazusa group overlies unconformably the Toyooka group which is composed of marine sediments of the late Miocene and middle Miocene ages, and is overlain partial-unconformably by the marine sediments of the Narita group of the late Pleistocene age. The Kazusa group is divided into eleven formations. The lower Kazusa group consists of sand-rich sediments deposited under neritic to bathyal environments. The middle Kazusa group consists of silt, and the alternation of sand and silt deposited under bathyal environment. Almost all upper Kazusa group consists of the neritic sediments, however, the values of sand/mud ratio in the sediments gradually increase towards the upper part and this phenomenon corresponds to the fact that the depositional environments were changed from outer neritic to inner neritic.

The main gas-and-brine reservoirs are in the Kiwada, Otadai, and Umegase formations, especially the latter two have a high productivity for gas and brine.

The radiometric ages are as follows (FUKUTA, 1976):

middle of the Kokumoto formation ....0.7 my
boundary between the Umegase and Otadai formations........................0.9 my
upper part of the Ohara formation ....1.8 my
lowermost part of the Kazusa group ....less than 2.4 my

The general strike of the Kazusa group in the Mobara gasfield is NE–SW and the group inclines gently towards NW by about 5 degrees.

3. Samples

3.1 Rocks

At the drilling sites of the three wells were taken ten marine muddy core samples: four each from U–71 and U–5, and two from D–28 (Fig. 2 and Fig. 4).

The geologic horizons of the sampling points are shown in Fig. 4. The samples were taken from the formations between the Kokumoto and Ohara, namely, one from the Kokumoto, three from the Umegase, two from the Otadai, three from the Kiwada, and one from the Ohara.

The sampling depths from the landsurface ranged from 140 to 1,455 m. All the samples were muddy rocks with bluish grey in colour, and the average grain size was silt. The core samples were dried naturally.

3.2 Brines

The brine samples were taken in January, 1973 from the two gas-iodine wells for which the locations are shown in Fig. 2. The physical conditions of the two producing wells are listed in Table 1.

U–65 well, one of the two wells for sampling, produces gas and brine from the depths between 246 and 749 m, and this interval corresponds to the formations of the upper Umegase, lower Umegase, upper Otadai, and lower Otadai (Fig. 5). This well is a pumping well and hence the brine sample was taken by gas lift method.

U–63 well is located close to U–65, and the depths of the reservoirs are from 739 to 1,588 m,

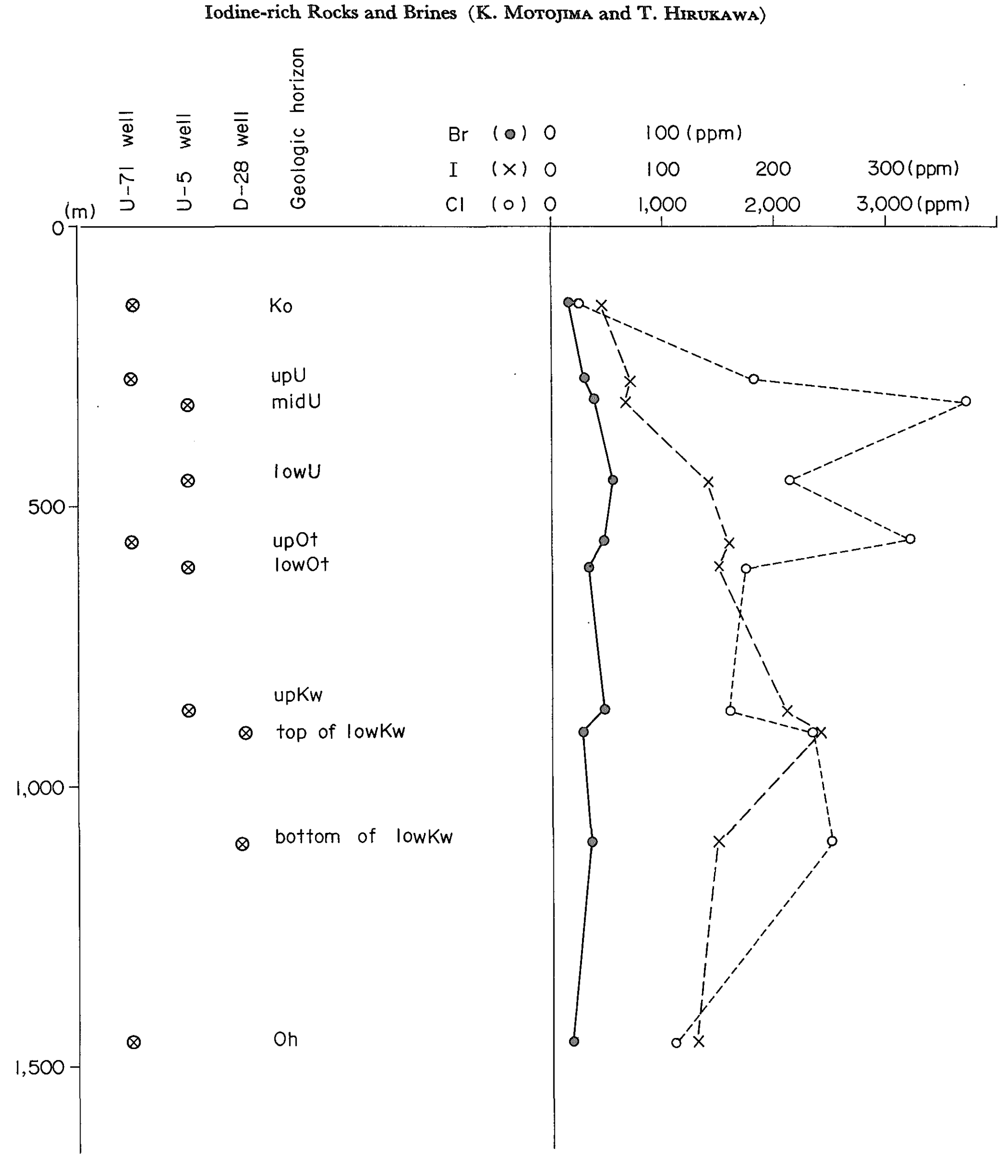

Fig. 4 Sampling depth, geologic horizon, and content of iodine, chlorine, and bromine for muddy core samples.

Table 1 Production of gas and water from U-63 and U-65 wells.

Name of well	U-65	U-63
Gas production (m^3/d)	1,460	8,190
Water production (kl/d)	421	333
Gas water ratio	3.5	24.6
Working pressure (kg/cm^2)	14.3	natural flow out
Water temperature (°C)	29.0	21.8
Date of measuring	13 May 1972	13 May 1972
Date of completion	21 Jan. 1971	21 Jan. 1971

Measured by Kanto Natural Gas Development Co. Ltd.

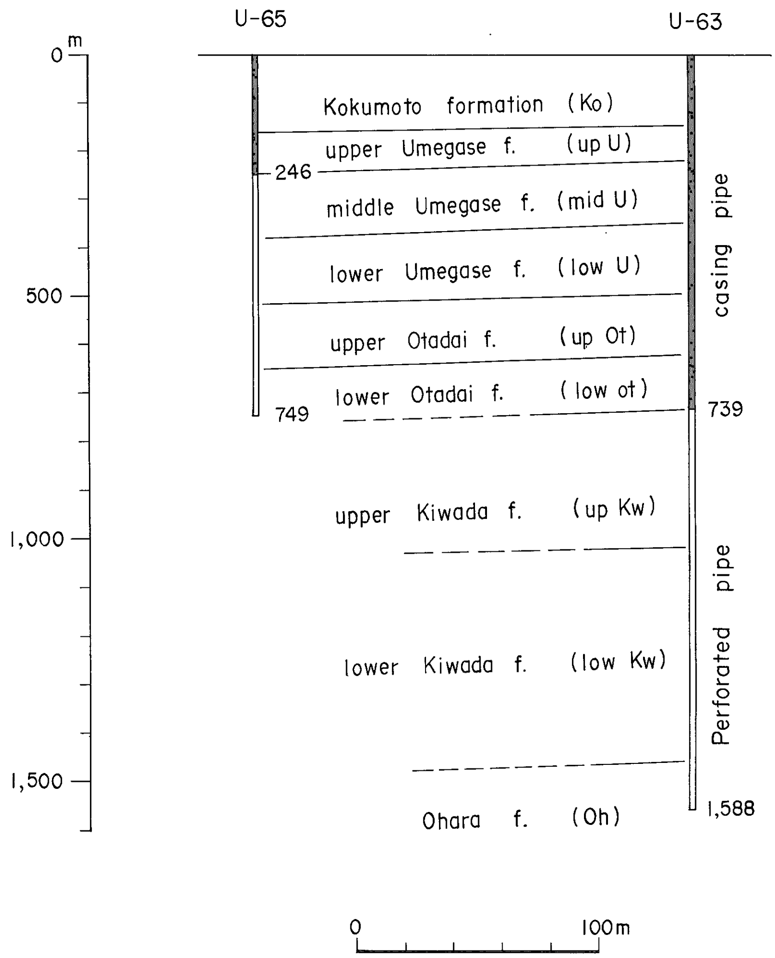

Fig. 5 Geologic horizons for sampling of brines

within this interval the formations of the upper Kiwada, lower Kiwada, and upper part of the Ohara were recognized. The brine flows out naturally from the well head with the temperature of 21.8°C.

4. Analytical Procedure

4.1 Rocks

The determination for iodine, chlorine, and bromine in the rocks was done by neutron activation method by TAJIMA *et al.* (1975) with the following techniques:

- The samples were broken into small chips, and were subsequently pulverized.
- 0.5 g of the pulverized sample was taken into a polyethylene tube and was sealed.
- The tube was put in a JAERI[1] JRR–3 type pneumatic tube having the radiation intensity of $f = 2 \times 10^{13}$ n/cm$^3 \cdot$ sec for 60 minutes.
- After the sample was activated, the alkali fusion was applied to the sample.

1) Japan Atomic Energy Research Institute

· The separation of iodine and bromine was conducted by distillation after fractional oxidation.
· The content of iodine and bromine was determined by γ-ray spectrometry with a sodium iodide scintillation detector.

4.2 Brines

The following methods were adopted for the analysis of the brines.

alkalinity—titration with hydrochloric acid solution

Cl^-—titration with silver nitrate solution

NH_4^+—colorimetric method with Nessler's reagent

K^+, Na^+—atomic absorption method

Ca^{2+}, Mg^{2+}—titration with EDTA solution

total Fe—colorimetric method with potassium thiocyanate solution

HBO_2—titration with sodium hydroxide solution

$KMnO_4$ consumption—$KMnO_4$ consumption under alkaline condition

SO_4^{2-}—gravimetric method after getting precipitates of barium sulphate

I^-, Br^-—Br^- and I^- are oxidized to bromic acid ion and iodate acid ion with sodium hypochlorite under the pH conditions of 5–7. The excess oxidizing reagent is decomposed with sodium formate. Bromic acid ion and iodate acid ion are determined by titration with iodometry, and the sum of Br^- and I^- is obtained. When the pH value of water sample is lowered below 2 and oxidized with sodium hypochlorite, I^- alone will be oxidized to iodate acid ion, while Br^- to only free bromine. Therefore, after the excess oxidizing reagent is decomposed with sodium formate, bromine is expelled from the water sample by boiling, and the content of I^- can be determined. After determining the content of $Br^- + I^-$ and I^-, the content of Br^- can be calculated by the equation of $(Br^- + I^-) - I^- = Br^-$.

According to the above stated principle, after the preparation of the reagents, the titration of $Br^- + I^-$ was conducted with N/200 sodium thiosulphate standard solution with an indicator of starch solution until the water sample becomes colourless under the acidic condition of pH value lower than 2. The titration for I^- was conducted under the same pH condition.

5. Results and Discussion

5.1 Rocks

In Table 2, the content of chlorine, bromine, and iodine in the ten core samples is shown.

Very high content of iodine is noted in the table. Two core samples from the Kiwada formation have the iodine content of 240 and 210 ppm, and the values probably are of the largest numbers for the mudstones in the world. Five samples contain iodine of 130–160 ppm, and all the rest of the samples are 44–72 ppm in iodine content.

The content of bromine in the mudstones is less than that of iodine, and as is stated later, the quantitative relation between iodine and bromine in the mudstones is just the reverse of that in the brines taken from the reservoirs of the same geologic horizons.

The chlorine content in the rocks ranges from 170 to 3,700 ppm. The lowest value, 170 ppm, is found in the shallowest sample, and according to the authors' experiences, the core sample from 140 m

Table 2 Geological and chemical data of core samples from Mobara gas-iodine field.

Number of core sample	Rock	Depth from land-surface (m)	Name of well **	Geologic horizon	Cl* (ppm)	Br* (ppm)	I* (ppm)	I/Cl ×10³
1	mudstone	140	U–71	Kokumoto formation	170	14	44	258
2	〃	275	U–71	up Umegase f.	1,800	28	72	40
3	〃	315	U– 5	mid Umegase f.	3,700	38	67	18
4	〃	455	U– 5	low Umegase f.	2,100	54	140	67
5	〃	563	U–71	up Otadai f.	3,200	46	160	50
6	〃	609	U– 5	low Otadai f.	1,700	33	150	88
7	〃	868.5	U– 5	up Kiwada f.	1,600	47	210	131
8	〃	904	D–28	top of low Kiwada f.	2,400	29	240	100
9	〃	1,100	D–28	bottom of low Kiwada f.	2,500	35	150	60
10	〃	1,455	U–71	Ohara f.	1,100	20	130	118

* Chemical analysis: TAJIMA *et al.* (1975).
** These wells belong to Kanto Natural Gas Development Co. Ltd.

Table 3 Chemical composition of groundwaters from Mobara gas-iodine field.

Name of well Interval of perforated pipe (m) Geologic horizons of reservoirs	Kanten U–63 739–1,588 up Kiwada formation, low Kiwada f. and Ohara f.	Kanten U–65 246–749 up Umegase formation, low Umegase f. up Otadai f. and low Otadai f.
pH	8.0	8.0
alkalinity (as HCO_3^- mg/l)	1,235	917
SO_4^{2-} (mg/l)	1.1	0.7
Cl^- (〃)	19,090	16,500
Br^- (〃)	145	118
I^- (〃)	112	105
NH_4^+ (〃)	191	173
K^+ (〃)	272	241
Na^+ (〃)	11,300	9,570
Ca^{2+} (〃)	210	182
Mg^{2+} (〃)	426	384
total Fe (〃)	2.77	3.17
HBO_2 (〃)	53.9	42.1
$KMnO_4$ consumption (〃)	302	291

Chemical analysis: HIRUKAWA, T., Sept. 1973
Sampling: Kanto Natural Gas Development Co. Ltd. Jan., 1973

deep has probably been flushed by meteoric water and hence the main portion of chlorine has already been moved from the rock. Furthermore, in accordance with the authors' analytical data on the core samples from other gas, oil, and coal fields, in general, the vertical distributional trend of chlorine content in the interstitial waters of the Pliocene and Pleistocene mudstones has been expressed by a smoothed curve. Therefore, the chlorine content of the samples which is shown in Fig. 4 might have been greatly controlled by the porosity or the compactional condition of the rocks.

The vertical distribution of iodine, bromine, and chlorine in the rocks is shown in Fig. 4. Iodine increases gradually towards the deeper part, and the maximum value is observed at the depth of 904 m, and in the parts deeper than this, the iodine content decreases gradually to 1,455 m deep in the Ohara formation.

5.2 Brines

The chemical composition of the two brine samples is shown in Table 3. In the table, very high concentrations of iodine and bromine are noted, namely, in the brines from U–63 and U–65 wells, the content of iodine is 112 and 105 mg/*l*, respectively, and that of bromine is 145 and 118 mg/*l*. Thus the contents for iodine are lower than those for bromine. As stated above, this relationship is just reversal to that observed for the rocks.

The pH value is 8.0 for the two brines, and the value is largely controlled by the content of HCO_3^-. In the natural gas from the Mobara gasfield, the percentage of carbon dioxide is generally lower than 1.0, and the pH value of the brines tends to slightly alkaline condition.

One notified relationship is seen in Table 3, that is, the contents for calcium, 210 and 182 mg/*l*,

Table 4 Iodine, bromine, chlorine, and organic carbon content in the Japanese muddy marine sediments.

Geologic age	Formation name	Depth from landsurface (m)	Cl (ppm)	Br (ppm)	I (ppm)	Organic carbon (wt%)
Niigata oilfield, 300 km north of Tokyo						
Neogene	Shiiya	115	620	2.1	0.81	
〃	〃	205	1,100	1.8	0.84	
〃	Teradomari	385	1,200	1.8	1.7	
〃	Nanatani	455	1,100	3.6	2.8	
			(AKAIWA *et al.*, 1977)			
Tomioka district, Gunma Prefecture, 100 km north of Tokyo						
Miocene		35.5		1.6	2.2	0.84
〃		41.9		1.4	2.0	0.73
〃		51.0		1.4	1.9	0.69
〃		58.1		1.6	2.0	0.86
〃		65.2		2.6	2.2	0.94
〃		71.7		2.3	2.5	0.79
			(AKAIWA *et al.*, 1978)			
Okinawa gasfield, 2,000 km southwest of Tokyo						
Pliocene	Shinzato	surface	63	6.5	44	0.34
〃	up Yonabaru	〃	36	4.6	41	0.57
〃	mid Yonabaru	〃	58	4.3	16	0.72
〃	〃	〃	39	2.1	6.6	0.58
〃	〃	〃	61	3.4	13	0.65
〃	〃	〃	33	3.7	27	0.57
〃	〃	〃	66	2.6	13	0.36
Miocene	low Yonabaru	〃	34	1.7	8.2	0.51
〃	〃	〃	33	1.8	13	0.45
〃	〃	〃	58	3.0	18	0.22
			(MOTOJIMA *et al.*, 1972)			

Table 5 Iodine, bromine, and organic carbon content in the sediments outside Japan.

Sample	Br (ppm)	I (ppm)	Organic carbon (wt%)
argillaceous sandstone (Portageville, N.Y.)		37.6±0.5	
chalk—limestone (Dover, England)		29 ±7	
argillaceous limestone (Trenton Falls, N.Y.)		8 ±2	
charty limestone (LeRoy, N.Y.)		23 ±7	
argillaceous shale (Rochester, N.Y.)		13 ±3	
calcarious shale (Lima, N.Y.)		38 ±10	
		(BECKER *et al.*, 1972)	
Kimmeridge Shales, England	13	34	36.8
Kimmeridge Coal, England	16	72	71.4
		(COSGROVE, 1970)	
recent marine sediments off Namibia, Africa	500±	2,000±	8±
		(PRICE *et al.*, 1977)	
recent seaweed: *Laminaria* sp.	1,380	510–8,000	
recent coral: *Gorgonia* sp.	16,200	69,200	
		(VINOGRADOV, 1953)	
recent marine sediments, Barents Sea	257	828	2.35
〃 〃	92	400	1.04
〃 〃	7	26	1.31
		(PRICE *et al.*, 1970)	
Paleozoic core sample, shale, Anadarko, Oklahoma		8.25	
〃 〃 〃 〃		12.3	
Paleozoic core sample, limestone, Anadarko, Oklahoma		10.4	
		(COLLINS *et al.*, 1971)	

are lower than those for magnesium, 426 and 384 mg/*l*.

Hydrogencarbonate ion (HCO_3^-) content is 1,235 and 917 mg/*l*, respectively, and these are the common values for ordinary natural gas brines from the relatively high gas potential fields.

Concerning the content of SO_4^{2-},since there is no evaporite and sulphate rock in the sedimentary sequence of the Mobara gasfield and the brine shows a negative value of redox potential, around minus 50–100 mV, SO_4^{2-} contents are 1.1 and 0.7 mg/*l*.

The chlorine contents are 19,090 and 16,500 mg/*l*, and are close to those of the ocean waters, approximately 20,000 mg/*l*. One notified point is that the chlorine content in the U–63 brine which is flowing out naturally from the deeper parts is higher than that in the U–65 brine. In the Japanese Neogene oil and gas fields, two vertical distributional trends of chlorine content in brines have been recognized, one is the increase in chlorine towards the deeper parts, and the other is reversal. However, in the cases of the brines from the Pliocene and Pleistocene marine sediments, the majority are the former case, and hence the distributional trend recognized in the present research is one of the normal cases.

5.3 Relation between the iodine content in the rocks and that in the brines with reference to the geologic horizons

The content of iodine, bromine, chlorine, and organic carbon in the Japanese muddy marine

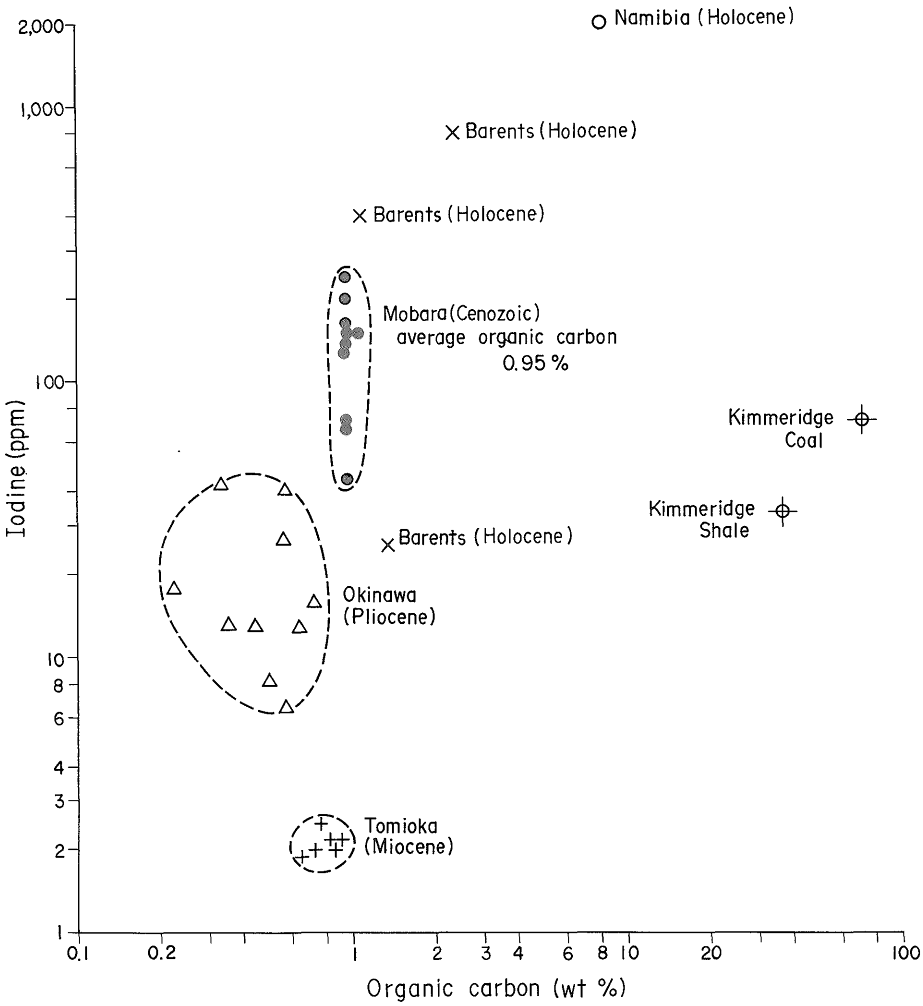

Fig. 6 Relation between iodine and organic carbon in sediments.

sediments of the Neogene is shown in Table 4, and that in the sediments outside Japan in shown in Table 5.

The content of iodine and that of organic carbon in the sediments relate positively each other as shown in Fig. 6. In the figure, although the points for the Mobara gasfield occupy the middle part in iodine content, these points occupy the highest part in the area for the sediments older than the Pleistocene age. The average value of the organic carbon content of the 31 surface samples from the Kazusa group is 0.95% and that of hydrocarbons is 53 ppm, and hence the average value of the degree of hydrocarbonization is

degree of H.C. $= 53 \times 0.86/9{,}500 = 0.0048$

(YAGISHITA, 1962). Thus, it can be understood that the rocks are under the unmaturated stage for the generation of oil.

The content of iodine in the Kimmeridge coal was reported to be 72 ppm (COSGROVE, 1970) and this value has been estimated to be the highest one for sediment in the world.

It is a well known fact that the recent marine sediments sometimes have very high concentrations of iodine, and as is shown in Table 5 and Fig. 6, some recent sediments off the Namibia Coast and in the Barents Sea have the iodine content from 2,000 to 400 ppm. However, the decrease in iodine content towards the depths in the Recent sediments is very rapid compared with that in organic carbon content (PRICE *et al.*, 1970 and 1977).

Thus, it is more convenient to discuss separatly the content of iodine on the old sediments and in the Recent sediments. Standing on this side, the iodine content in the surface rock samples in the Okinawa Main-Island must be noted for their high values. It has been mentioned that these surface samples probably have had some pollution from the recent ocean water because of the close distance to the ocean from the sampling sites. However, as far as the iodine content is concerned, the check analysis of a few samples from the surface and underground has proved that the degree of the pollution is less than 20% (unpublished data, TAJIMA, AKAIWA, and MOTOJIMA).

The muddy rocks of the Tomioka district, 100 km north of Tokyo, contain only 2 to 3 ppm of iodine.

Thus, it is possible to conclude that the mudstones in the Mobara gasfield have extremely high concentrations of iodine.

In the next place, the relation between the iodine content in rocks and that in brines is examined using three examples, the Mobara gasfield, the Okinawa gasfield, and the Anadarko Basin.

(1) Mobara gasfield

As already explained, the two maximum concentrations of iodine in the rocks, 210 and 240 ppm, were found in the upper Kiwada formation and in the top of lower Kiwada formation.

The average iodine content in the rocks from the middle Umegase to the lower Otadai formations is 129 ppm, and the average value of chlorine content in the same interval is 2,675 ppm. Thus the average value of $I/Cl \times 10^3$ is 48.2. The iodine content of U–65 brine, obtained from the same horizons, is 105 mg/*l*, and the ratio of $I/Cl \times 10^3$ is 6.36.

By the same calculation, the followings are obtained for the interval between the upper Kiwada and the Ohara formations.

· average iodine content in the rocks is 183 ppm
· average chlorine content in the rocks is 1,900 ppm
· average $I/Cl \times 10^3$ in the rocks is 96.3

The iodine content of U–63 brine, obtained from the same horizons, is 112 mg/*l*, and the ratio of $I/Cl \times 10^3$ is 5.87.

Thus, the above calculated results are summarized as follows:

	mid U–low Ot	up Kw–Oh
I in rocks	129 ppm	183 ppm
C*l* in rocks	2,675 ppm	1,900 ppm
$I/Cl \times 10^3$ in rocks	48.2	96.3
	U–65 (246–749 m)	U–63 (739–1,588 m)
I in brines	105 mg/*l*	112 mg/*l*
C*l* in brines	16,500 mg/*l*	19,090 mg/*l*
$I/Cl \times 10^3$ in brines	6.36	5.87
I ppm in rocks/I mg l^{-1} in brines	1.23	1.63
I ppm/C*l* mg $l^{-1} \times 10^3$ in rocks/in brines	7.58	16.4

From the summarized results the followings are recognized.

1. Iodine content both in the rocks and brines is more abundant in the deeper and older parts than in the shallower and younger ones.
2. The I/*Cl* ratio in the rocks from the deeper and older parts is higher than that in the shallower and younger ones.
3. On the contrary, the I/*Cl* ratio in the brines from the deeper parts is lower than that from the shallower ones.
4. The values of the ratio of "I ppm in rock/I mg l^{-1} in brine" for the two intervals are 1.23 and 1.63, and the value of the deeper samples is higher.
5. The values of I/*Cl* $\times$ 10^3 in rock/brine are 7.58 for the shallower interval and 16.4 for the deeper one.

Further examinations are necessary to get the detailed relation between the iodine content in the rocks and that in the brines. The values of I/*Cl* ($\times$ 10^3) in the rocks are shown in Table 2, and the vertical distribution of the values, except for the samples from the depths of 140 and 275 m which are likely to have been flushed by meteoric waters, shows the increase from 18 to 131 corresponding to the formations of the middle Umegase to the upper Kiwada. The value in the top of lower Kiwada formation is still 100, and at the bottom of lower Kiwada formation the value decreases to 60. However, the mudstone from the Ohara formation shows nearly the maximum value, 118, and the reason for this is likely to have had the weak flushing by the groundwaters with relatively low concentration of chlorine or to have the diagenetic changes of the rocks. According to ISOMURA (1967), the brines with relatively low content of chlorine were sometimes noticed in the Ohara formation.

ISOMURA (1967) reported the values of the ratio of I/*Cl* $\times$ 10^3 in the brines in both the Mobara and Otaki gasfields as follows:

Mobara gasfield		Otaki gasfield	
mid U–low U	5.77		
mid U–up Ot	5.82		
low U–low Ot	6.34		
Kw	6.91	Ot–up Kw	7.75
		Kw	7.08
		Kw–Oh	6.45
		Kw–Nm–Ku	6.11

Nm—Namihana formation
Ku—Katsuura formation

Thus it is obvious that the value of I/*Cl* ratio of the brines in the Mobara gasfield increases gradually from the Umegase formation to the Kiwada formation, and that in the Otaki gasfield decreases from the Otadai-upper Kiwada formations to the Kiwada–Namihana–Katsuura formations. Comparing these two gasfields, it is clear that the maximum I/*Cl* ratio in the brines was recognized in the interval between the Otadai and the Kiwada formations.

The average content of iodine in the brines from the Mobara gasfield is as follows (ISOMURA, 1967):

mid U–low U	average I (mg/*l*)	85.0
mid U–up Ot	〃	96.8
low U–low Ot	〃	112.0
Kw	〃	116.2

Therefore, the roughly estimated values of the ratio of "I ppm in rock/I mg l^{-1} in brine" are as follows:

mid U–low U	1.22
mid U–up U	1.26
low U–low Ot	1.34
Kw	1.72

The general distributional trend of the values of the ratio of "I in rock/I in brine" shows the gradual increase from the middle Umegase formation to the Kiwada formation.

It is clear that when the content of iodine in the rocks increases then that in the brines increases correspondingly, furthermore the values of the ratio of I/C*l* both in the rocks and brines increase.

(2) Okinawa gasfield

The mudstone samples from the surface of the ground of the Okinawa gasfield have relatively high iodine contents 6.6–44 ppm, as explained above (Table 4). The average iodine content is 20.0 ppm for the ten samples. Since the samples were taken from the landsurface and the retention of chlorine in the ordinary mudstones is weaker than that of iodine, the values of I/C*l* ratio had no geochemical meaning, and hence only the quantitative comparison on the iodine concentrations in the rocks and brines of the same geologic horizons is discussed here.

The chemical composition of the brine from the Okinawa R–1 well was reported as follows (Motojima *et al.*, 1970):

depth of the reservoirs—405–435 m

geologic horizon—Tomigusuku formation (upper-most)

chemical composition (mg/*l*)—

pH	7.8	Cl^-	8,050	I^-	33.9
Br^-	40.5	HCO_3^-	248	SO_4^{2-}	2.8
NH_4^+	26.1	K^+	25.9	Na^+	5,030
Ca^{2+}	147	Mg^{2+}	59.0		

This brine has some noticiable characteristics compared with those from the Mobara gasfield, for instance,

· Ca^{2+}/Mg^{2+} ratio is 2.49

· HCO_3^- is less than 300 mg/*l*

· ratio of I/Br is 0.84.

The value of $I/Cl \times 10^3$ is calculated to be 4.21 which is lower than those of the Mobara gasfield, 5.77–7.75.

The quantitative relation of the iodine content in the rocks and brines is considered in the next place. The average iodine content in the rock is 20.0 ppm and in the brine is 33.9 mg/*l*, thus the value of the ratio of "I ppm in rock/I mgl^{-1} in brine" is 0.59, which is lower than those of the Mobara gasfield, 1.22–1.72. In the Mobara gasfield, these values gradually increase towards the older formations, however, since the geologic age of the gas-bearing formations in the Okinawa gasfield is older than that of the Mobara gasfield, it must be considered that the values of the ratio of "I in rock/I in brine" have been controlled by many geologic factors, such as the depositional environment of the sediments, the kind of the organic materials in the sediments, etc.

(3) Anadarko Basin, Oklahoma, U.S.A.

Some Anadarko Basin Brines have very high concentrations of iodine (COLLINS, 1969). The brines were obtained from the Pennsylvanian and Mississippian sediments and the type of brine was Na–Ca–*Cl*. The highest value of iodine content in the brines is 1,400 mg/*l*, and in this case the content of bromine is 470 mg/*l*, and that of chlorine is 98,000 mg/*l*. The value of I/*Cl* ($\times 10^3$) is 14.3, which is higher than those of the Mobara gasfield.

The maximum content of hydrochloric acid reachable iodine in the core samples of shale and calcite from the Anadarko Basin were 12 and 11 ppm, respectively.

In 1971, COLLINS reported again the content of iodine in the core samples of shales and limestones from the Anadarko Basin. This time, he used a neutron activation analysis to determine iodine content. The maximum concentration of iodine was 12.3 ± 1.5 ppm in the shale sample, and the geologically corresponding brine contains 1,400 mg/*l* of iodine. In this case, the value of the ratio of "I ppm in rock/I mg l^{-1} in brine" is 0.0088. The value is very small and to be noted, compared with those in the Mobara and Okinawa gasfields, 1.22–1.72 and 0.59

5.4 Origin of iodine

According to VINOGRADOV (1953), dried seaweeds contain up to 8,000 ppm of iodine and corals contain up to 69,200 ppm of iodine. Very high content of iodine in some marine diatoms was also reported by him in the same book.

The sediments of the Kazusa group were deposited under neritic to bathyal conditions, and it is supposed that organic materials derived from the seaweeds and planktonic organisms were deposited in the muddy sediments of the group. Some chemical components of the brines from the Mobara gasfield still have the feature of the Recent ocean water, for instance the relative abundance of calcium and magnesium. The chemical type of the brines in the Mobara gasfield is Na–*Cl*–HCO_3, and the pH values are nearly 8.0. Thus, iodine liberated by the anaerobic decomposition of organic matter in the sediments was transferred into the brines. However, the iodine content in the rocks is still very high. From the standpoint of the maturation of organic matter in rocks, the organic matter of the Kazusa group is still in the under-maturated stage for the generation of petroleum.

As for iodine in the Anadarko Basin, the chemical type of brines is Na–Ca–*Cl*, and geologic age of the reservoirs is Paleozoic. Generally, the carbonate rocks contain the organic materials (kerogen) which were probably derived from seaweeds. In the case of the Anadarko Basin, there is high probability that iodine in such sediments was originated from seaweeds and corals, as already pointed out by COLLINS in 1971.

As a tentative conclusion, it is supposed that the seaweeds, diatoms, and some corals may have supported the high concentration of iodine in the rocks and brines.

6. Summary

(1) In the Mobara gasfield, ten mudstone samples and two brine samples were taken from the Kazusa group of the Pliocene and Pleistocene ages.

(2) Very high concentrations of iodine were recognized in both the mudstones and brines, up to 240 ppm and 112 mg/*l*, respectively.

(3) In the mudstones, iodine is more abundant than bromine, while, in the brines, the reversed

relation is observed.

(4) In both the mudstones and brines, the maximum content of iodine is observed in the Kiwada formation which occupies nearly the middle of the Kazusa group.

(5) The values of the ratio of "iodine content in rock/iodine content in brine" increase towards the older formations.

(6) The high concentrations of iodine in the rocks and brines might have been caused by some geologic conditions, such as the depositional environment, the diagenesis of the sedimentary rocks. It is suggested by the geologic evidences that the large portion of iodine in the Mobara gasfield was originated from seaweeds and diatoms.

References

AKAIWA, H., TAJIMA, E. and AIZAWA, S. (1977) Chlorine, bromine and iodine as geochemical indicators for depositional paleoenvironment. *Chikyu-kagaku* [*Geochemistry*], vol. 11, p. 58–62 (in Japanese with English abstract).

————, ———— and ———— (1978) Bromine and iodine contents of sedimentary rocks from Tomioka, Gunma prefecture, Japan. *Chikyu-kagaku* [*Geochemistry*], vol. 12, p. 1–14 (in Japanese with English abstract).

BECKER, V. J., BENNET, J. H. and MANUEL, O. K. (1972) Iodine and uranium in sedimentary rocks. *Chem. Geol.*, vol. 9, p. 133–136.

COLLINS, A. G. (1969) Chemistry of some Anadarko Basin Brines containing high concentrations of iodine. *Chem. Geol.*, vol. 4, p. 169–187.

————, BENNETT, G. H. and MANUEL, O. K. (1971) Iodine and algae in sedimentary rocks associated with iodine-rich brines. *Geol. Soc. Amer. Bull.*, vol. 82, p. 2607–2610.

COSGROVE, M. E. (1970) Iodine in the bituminous Kimmeridge Shales of the Dorset Coast, England. *Geochim. Cosmochim. Acta*, vol. 34, p. 830–836.

FUKUTA, O. (1976) Iodine-gas deposits of dissolved-in-water type in Japan. *Tennengasu* [*Natural Gas*], vol. 19, no. 9, p. 14–27 (in Japanese).

ISOMURA, T. (1967) Studies on the brine water of the Kujukuri gas field—Especially on the distribution of halogens—. *Jour. Japanese Assoc. Mineral. Petrol. Econ. Geol.*, vol. 58, p. 188–200 (in Japanese with English abstract).

MOTOJIMA, K. *et al.* (1970) Report of the 3rd phase survey for the natural gas resources of Ryukyu Islands (Part 10)—Production test of Naha No. 1 test well—. *Bull. Geol. Surv. Japan*, vol. 21, p. 499–502 (in Japanese with English abstract).

————,(1971) Iodine in oil and gas fields—Especially on the geochemical consideration of the prospecting for iodine deposits. *Bull. Geol. Surv. Japan*, vol. 22, p. 559–574 (in Japanese with English abstract).

————, AKAIWA, H. and TAJIMA, E. (1972) Geochemical consideration on the iodine content in the marine Neogene mudstones in the southern part of Okinawa main-island. *Preprint of the Annual Meeting of the Geochemical Society of Japan*, p. 80 (in Japanese).

PRICE, N. B., CALVERT, S. E. and JONES, P. G. W. (1970) The distribution of iodine and bromine in the sediments of the Southwestern Barents Sea. *Jour. Marine Res.*, vol. 28, p. 22–34.

————, ———— and ———— (1977) The contrasting geochemical behaviors of iodine and bromine in recent sediments from the Namibian shelf. *Geochim. Cosmochim. Acta*, vol. 41, p. 1769–1775.

TAJIMA, E., NAKATA, N. and AKAIWA, H. (1975) Halogen content in mudstones from Mobara area, Chiba prefecture. *Preprint, 32nd Meeting, Japan Chem. Soc.*, p. 919 (in Japanese).

VINOGRADOV, A. P. (1953) The elementary chemical composition of marine organisms. *Sears Found. Marine Res., Mem.*, 11.

YAGISHITA, H. (1962) Distribution of hydrocarbons in Neogene rocks of Niigata as a clue to the recognition of petroleum source rock. *Jour. Japanese Assoc. Petrol. Technologists*, vol. 27, p. 256–296 (in Japanese with English abstract).

地名英和対応表

Kasamori	笠森	Namihana	浪花	Chonan	長南	Katsuura	勝浦
Kakinokidai	柿ノ木台	Nonozuka	野々塚	Kokumoto	国本	Kurotaki	黒滝
Umegase	梅ケ瀬	Toyooka	豊岡	Otadai	大田代	Kazusa	上総
Kiwada	黄和田	Mobara	茂原	Ohara	大原	Otaki	大多喜

茂原ガス田の非常によう素含有量の多い泥岩および塩水の地球化学

本島　公司・比留川　貴

南関東ガス田地域はまた世界最大のよう素田でもあって，その中には10以上のガス田が発見され開発されている．東京の南東およそ 50km に位置する茂原ガス田は，これら諸ガス田の中でも，ガスおよびよう素工業の両面から最も重要なものである．南関東のよう素とガスの産出する地層は，海成の鮮新–洪積世の上総層群である．茂原ガス田の3つの掘さく井から10個の泥岩コア試料と，2つの産出井から2個の塩水試料が，いづれも上総層群から採取された．

泥岩中のよう素含量は，最高 240ppm が下部黄和田層の頂部で測定され，また塩水中のよう素含量は 112mg/l に達した．泥岩中によう素が多い地層から産出する塩水中にはやはりよう素が多い．よう素含量は，黄和田層に最も多く，順次上位の大田代層，梅ケ瀬層，国本層へと減少し，さらに下位の大原層でも減少する．

泥岩中ではよう素含量のほうが臭素含量よりも多いが，いっぽう同じ層準から採取した塩水中では逆でよう素含量のほうが少ない．

泥岩中のよう素含量 (ppm)/ 塩水中のよう素含量 (mg/l) の比の値は，1.22–1.72であり，この値は上位層から下位層へ向って増加する傾向を示す．さらに，この値は，沖縄ガス田の1例で0.59，オクラホマ州のアナダルコ盆地で0.0088であることから考えて，地層の堆積環境や続成作用に大いに影響されるようである．

茂原ガス田のよう素の重要部分は，海藻と珪藻に由来しているように思われる．

(受付：1979年2月22日；受理：1979年3月20日)