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Preliminary Report on the Geochemistry of Iodine, Bromine, and Chlorine in the Surface Samples of Cenozoic Marine Sediments from the Southern Part of Okinawa Main Island, Southwestern Japan

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Abstract: The contents of iodine, bromine, and chlorine in ten surface muddy rock samples of Pleistocene, Pliocene and Upper Miocene marine sediments from the southern part of Okinawa Main Island, were determined by neutron activation.

The average values of halogen contents are; Cl 48 ppm, Br 3.4 ppm, I 20 ppm, Cl/Br 16, Cl/I 3.3, and Br/I 0.20. Two samples with high content of iodine, 44 and 41 ppm, were taken from the geologically upper horizons, the Shinzato Formation and the upper member of the Yonabaru Formation, and the iodine content of the rest samples which were taken from the middle and lower members of Yonabaru Formation ranges from 6.6 to 27 ppm with the average value of 14.4 (±6.3) ppm. A positive correlation was observed between the iodine content in the rocks and the contents of inorganic carbon, O–N–S compounds in the bitumen.

1. Introduction

Among several iodine-gas fields in Japan that have ever been explored, the Okinawa Gasfield is located in the southern-most district.

The members of the Geological Survey of Japan, Ryukyu University, and the Industrial Research Institute of Okinawa Prefecture, have been engaged in the exploration of gas and iodine resources in the field. The main areal target of the exploration has been concentrated upon the southern part of Okinawa Main Island, occupying some 300 km² and filled with the Pleistocene, Pliocene and Upper Miocene marine sediments.

The contents of halogen in the groundwaters associated with natural gas from the gasfield were reported as follows: (MOTOJIMA *et al.*, 1970; FUKUTA *et al.*, 1970; Research Group of GSJ, 1971).

name of well	R–1	R–2	R–3
depth of reservoir (m)	405–435	312–364	470–851
formation	Tomigusuku	Tomigusuku	Tomigusuku
geologic age	upper Mioc.	upper Mioc.	upper Mioc.
Cl^- (mg/l)	8,050	11,370	19,500
Br^- (mg/l)	40.5	52.5	94
I^- (mg/l)	33.9	51.9	91

An attempt has been made to clarify the geochemical relation in the occurrence of halogens between rocks and groundwaters.

All the rock samples were taken by the members of the Research Group for Natural Gas Resources in the Okinawa Region, Geological Survey of Japan. The authors wish to express their gratitute to the members of the Group for providing the samples.

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2. Geology and samples

Figure 1 shows the geological map of the investigated area. The marine sedimentary rocks of Late Tertiary and Quaternary ages, the Shimajiri Group, are exposed and the beds trend northeast to southwest and dip southeast. On the basis of the data of NATORI (1979) and FUKUTA *et al.* (1970), the geologic sequence is as follows in descending order.

Formation	Thickness (m)	Lithology
Shinzato	250	Clayey silt, sand, ash, and pumice
	Up. m. 350	
Yonabaru	900 Mid. m. 500	Clayey silt
	Low. m. 50	
Tomigusuku	900+	Alternation of clayey silt, sand, shale, and sandstone

Micropaleontological data show that the formations were deposited under neritic to bathyal conditions. Concerning the geologic age of the formations, the Shinzato Formation is of the late Pliocene

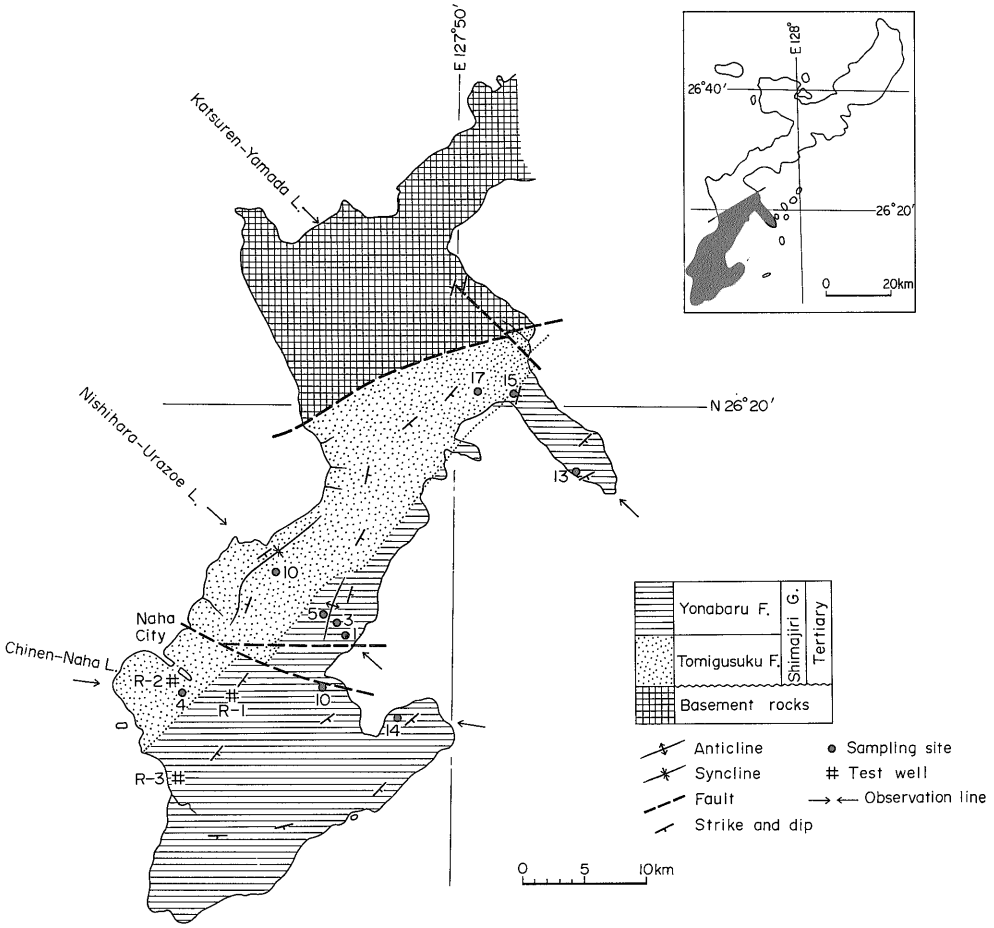

Fig. 1 Geological map of the middle and southern parts of Okinawa Main Island (FUKUTA *et al.*, 1970).

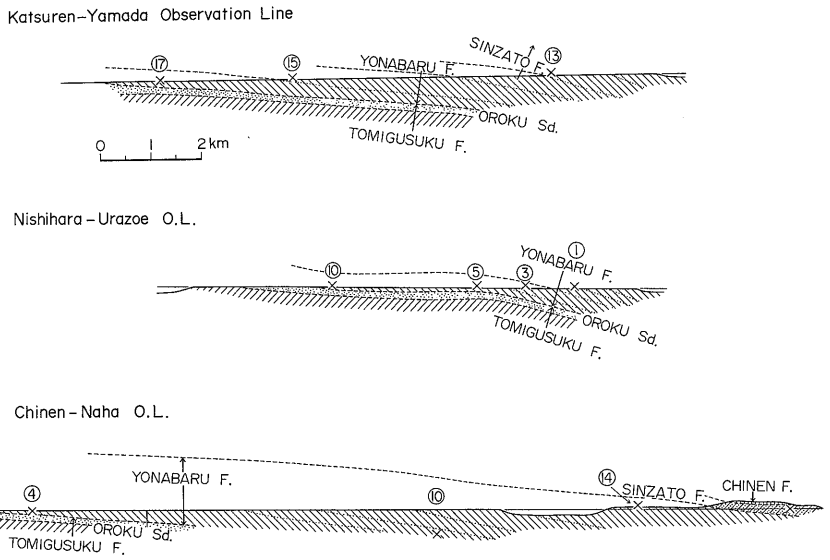

Fig. 2 Sampling points of rocks on the geological profiles (Maki *et al.*, 1970).

to Pleistocene in age, and the upper and middle members of Yonabaru Formation are of Pliocene age, while the lower member of Yonabaru and the Tomigusuku Formation are of Miocene age. The approximate radiometric ages are as follows (Tsuchi and W. G., 1979).

Shinzato Formation	2–3 my
Yonabaru F.	3–5.5 my
Tomigusuku F.	5.5–8.5 my

In the northern part, Mesozoic rocks lie in fault contact with the Shimajiri Group, while in the southern part, the Mesozoic basement exists underneath the Shimajiri Group.

In order to take samples from the fresh-looking outcrops, three observation lines were selected from the north to the south, these are the Katsuren–Yamada Observation Line, the Nishihara–Urazoe O.L., and the Chinen–Naha O.L. as shown in Figure 1. Figure 2 shows the sampling points on the geological profiles. The samples of grey silt were taken for the determination of iodine, bromine, and chlorin econtents. All these samples were already analysed for organic materials (Maki *et al.*, 1970).

3. Analytical procedure

The determination for iodine, chlorine, and bromine in the rocks was done by neutron activation method by Tajima and Akaiwa (1971) with the following techniques:

The crushed rock samples of 1 g were sealed in polyethylene vials and irradiated in the pneumatic tube of the JRR–2 reactor at a flux of 8×10^{13} n/cm^2 · sec for 20 min. Samples and monitors were fused with sodium hydroxide in nickel crucibles, in the presence of carriers. The fusion cake was dissolved in water and acidified to about 2M H_2SO_4. Fe^{3+} was added to oxidize I^- to I_2, and I_2 was distilled into sodium sulfate solution. $KMnO_4$ was then added to oxidize Br^- and Cl^- to Br_2 and Cl_2, and these elements were separated from mother solution by distillation. Chemical yields were measured chlorimetrically for iodine and potentiometrically for chlorine and bromine.

The distillates were counted on a γ-ray spectrometer, consisting of 3 in. × 3 in. NaI(Tl) crystal and a 400-channel pulse height analyser. The following γ-rays were measured: ^{128}I, 0.445 MeV; ^{38}Cl,

Table 1 Halogen content in surface

Name of observation line	Sample number	Geologic horizon	Rock	Cl ppm	Br ppm	I ppm	Br/Cl $\times 10^3$	I/Cl $\times 10^3$	I/Br	Cl/Br
Katsuren–Yamada	13	Shinzato	silt	63	6.5	44	103	698	6.8	9.7
〃	15	mid Yonabaru	〃	58	4.3	16	74	276	3.7	13
〃	17	low Yonabaru	〃	34	1.7	8.2	50	241	4.8	20
Nishihara–Urazoe	1	mid Yonabaru	〃	39	2.1	6.6	54	169	3.1	19
〃	3	〃	〃	61	3.4	13	56	213	3.8	18
〃	5	〃	〃	33	3.7	27	112	818	7.3	8.9
〃	10	low Yonabaru	〃	33	1.8	13	55	394	7.2	18
Chinen–Naha	4	〃	〃	58	3.0	18	52	310	6.0	19
〃	10	mid Yonabaru	〃	66	2.6	13	39	197	5.0	25
〃	14	up Yonabaru	〃	36	4.6	41	128	1140	8.9	7.8

(TAJIMA *et al.*, 1972)

1.60 and 2.17 MeV; ^{82}Br, 0.55 and 0.78 MeV. The activity measurement for ^{82}Br was done after one day cooling.

4. Results

Analytical results on ten samples from the Shinzato to the lower member of Yonabaru Formation are shown in the left half of Table 1. The values of average content of halogens and the corresponding standard deviations are as follows:

element	range	average value	standard deviation
Cl	36–63 ppm	48.1 ppm	14.1 ppm
Br	1.7–6.5 ppm	3.4 ppm	1.5 ppm
I	6.6–44 ppm	20 ppm	13.1 ppm
Cl/Br	7.8–25	15.8	5.7
Cl/I	0.88–5.9	3.3	1.7
Br/I	0.11–0.32	0.20	0.07
Br/Cl $\times 10^3$	39–128	72	31
I/Cl $\times 10^3$	169–1140	446	328
I/Br	3.1–8.9	5.7	1.9

It is clearly shown in Table 1 that two samples, K–Y no. 13 and C–N no. 14, which were taken from geologically upper horizon, the Shinzato Formation and the upper member of Yonabaru Formation, have extremely high values in iodine and bromine contents, 44 and 41, and 6.5 and 4.6. By omitting these values for calculation, the following results are obtained for eight samples from the middle and lower members of Yonabaru Formation.

element	range	average value	standard deviation
Br	1.7–4.3 ppm	3.0 ppm	1.0 ppm
I	6.6–27 ppm	17.3 ppm	10.7 ppm
Cl/Br	8.9–25	17.6	4.8
Cl/I	1.2–5.9	3.8	1.5
Br/I	0.14–0.32	0.21	0.07
Br/Cl $\times 10^3$	39–112	62	23

samples from Okinawa Gasfield.

Cl/I	Br/I	Bitumen ppm	Hydrocarbon ppm	Org. C %	Inorg. C %	Degree of hydrocarbonization	O–N–S % in bitumen	compounds ppm in rock
1.4	0.15	339	70	0.34	1.84	0.0177	42.3	144
3.6	0.27	399	78	0.72	1.00	0.0093	22.7	91
4.1	0.21	372	132	0.51	0.92	0.0223	24.8	92
5.9	0.32	352	45	0.58	0.59	0.0067	41.7	147
4.7	0.26	598	75	0.65	0.00	0.0099	17.8	106
1.2	0.14	308	38	0.57	1.57	0.0057	44.2	136
2.5	0.14	145	36	0.45	1.04	0.0069	49.7	72
3.2	0.16	373	154	0.22	1.03	0.0602	31.0	116
5.1	0.20	526	205	0.36	1.14	0.0490	41.7	219
0.88	0.11	343	72	0.57	1.36	0.0109	20.0	38

(Maki *et al.*, 1970)

$I/Cl \times 10^3$	169–818	327	210
I/Br	3.1–7.3	5.1	1.6

The iodine content for each formation is summarized as follows:

formation	average (ppm)	range (ppm)	number of samples
Shinzato F.	44	44	1
Up. m. Yonabaru F.	41	41	1
Mid. m. Yonabaru F.	15	6.6–27	5
Low. m. Yonabaru F.	13	8.2–18	3

5. Discussion

The data on Table 1 will be compared with the previous ones obtained from some regions in Japan (Akaiwa *et al.*, 1977; Akaiwa *et al.*, 1978).

Although these rocks were deposited in a marine condition, the average chlorine content is low, 48.1($\pm$14.1) ppm. In the Niigata Oilfield, 300 km north of Tokyo, the chlorine content of surface mudstone samples is also low, ranging from 16 to 68 ppm with the average value of 45 ppm. However, in the case of the Niigata Oilfield, the values of core samples range from 620 to 1,200 ppm (Akaiwa *et al.*, 1977), and those in the Mobara Gasfield, 50 km southeast of Tokyo (Tajima *et al.*, 1975), from 1,100 to 3,200 ppm. Both the Niigata and Mobara Fields are located in the Neogene to Pleistocene marine sedimentary basins. A difference in the chlorine content between the surface samples and the core samples strongly suggests that the flushing effect by meteoric water is quite remarkable in the exposed rocks.

Bromine content ranges from 1.7 to 6.5 ppm with the average value of 3.4($\pm$1.5) ppm. Comparing the values of Okinawa with those of Niigata, having the range of 0.3–3.2 ppm with the average value of 1.2 ppm, the rocks from the former region are about 3 times more abundant in bromine than the latter.

Iodine content ranges from 6.6 to 44 ppm with the average value of 20($\pm$13.1) ppm. The values are higher than those of Niigata, 0.13–2.5 ppm with the average value of 0.71 ppm.

The mutual ratios of Cl/Br, Cl/I, and Br/I are 15.58($\pm$5.7), 3.3($\pm$1.7), and 0.20($\pm$0.07), respec-

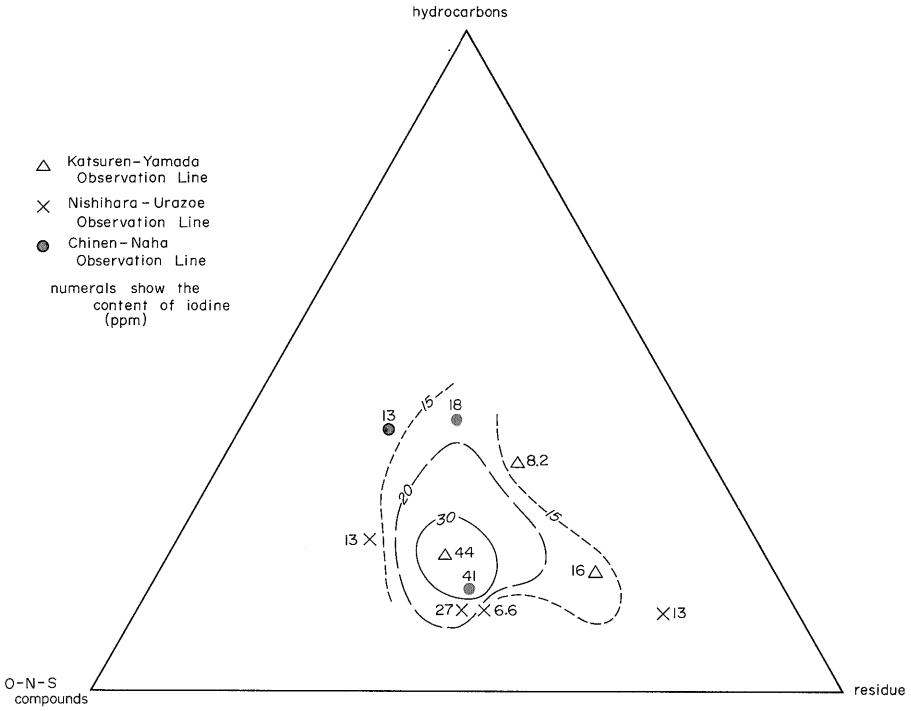

Fig. 3 Relation between the composition of bitumen and the content of iodine.

tively. Comparing the values with those of Niigata, 62, 120, and 2.0, one could find that the values of Okinawa are extremely low. It should be noted that iodine is 3 to 9 times concentrated to bromine, and the iodine contents are higher than those of bromine in all the samples from Okinawa.

As already pointed out, the iodine contents in the upper horizons, the Shinzato Formation and the upper member of Yonabaru Formation, are remarkably more abundant than those in the lower horizons. Geological and paleontological studies (FUKUTA *et al.*, 1970) revealed that the Shinzato Formation and the upper member of Yonabaru Formation might be deposited under the marine environment having slightly low salinity waters.

The organic geochemical data (MAKI *et al.*, 1971) shown in the right half of Table 1 indicate that the iodine content is also high in the samples with high content of inorganic carbon.

Figure 3 shows the relationship between the iodine content and the composition of bitumen. The highest values in iodine content are plotted in the central-lower portion of a triangular diagram. Therefore, iodine is concentrated in the area in which both O–N–S compounds and the residues on chromatograph column are relatively abundant but hydrocarbons are less abundant. Thus, from the standpoint of the maturation of organic materials in sedimentary rocks, it is supposed that iodine has been concentrated in the rocks under moderate organic maturation. The relationship stated above is also understood by the data of the degree of hydrocarbonization shown in Table 1.

By comparing the present data with the others, from the standpoint of the relationship between the contents of iodine and organic carbon (MOTOJIMA, 1971; MOTOJIMA *et al.*, 1979), it is recognized that the rocks from Okinawa show very high value in iodine content.

MOTOJIMA (1971) pointed out that two groups of groundwaters associated with natural gas have been recognized in the Okinawa Gasfield, as far as the I/*Cl* ratio is concerned. Group A has the value of

about 5/1,000, and Group B about 2.5/1,000. The groundwaters of the Group A have been produced from the areas near the Katsuren–Yamada and Chinen–Naha Observation Lines, while those of the Group B from near the Nishihara–Urazoe Observation Line. It was also reported (Maki *et al.*, 1970) that the samples from the Nishihara–Urazee Line have high organic carbon content and low value in the degree of hydrocarbonization, compared with those from both the northern and southern parts of the gasfield. In spite of the difference in the above stated two points, no distinct difference is recognized on the concentrations of iodine and bromine in the rocks as shown in Table 1.

As already explained in the introduction, the values of I/C*l* and I/Br ratios of the groundwaters are calculated as follows:

	I/C*l*	I/Br
R–1	33.9/8,550=4.0/1,000	0.84
R–2	51.9/11,370=4.6/1,000	0.99
R–3	91/19,500=4.7/1,000	0.97

The reservoirs of the three wells are all in the Tomigusuku Formation, therefore it is impossible to correlate the data of the surface rocks directly with those of groundwaters. However, from the viewpoint of the generation and migration of the groundwaters and natural gases, it is plausible to consider that the groundwater in the Tomigusuku Formation has been affected in its nature by the Yonabaru Formation. In fact, the downward migration of groundwaters and natural gases in the Okinawa Gasfield was recognized at R–3 well (Fukuta *et al.*, 1970).

An assumption is made on the geochemical correlation between the rocks and groundwaters. In the rocks, the mean values of I/C*l* and I/Br are 446/1,000 and 1.9, which are very high values compared with those of the groundwaters. Though the high value of I/C*l* of the surface rock samples is well explained through the flushing of chlorine by meteoric water as already explained, the value of I/Br may have been controlled by the processes of the decomposition, maturation, and migration of the despersed organic materials and interstitial waters in the rocks.

Further investigations using core samples will give some information to solve the problem.

6. Summary

(1) Ten grey silt samples were taken from the outcrops of the marine Shimajiri Group of Pleistocene, Pliocene and Miocene ages in the Okinawa Gasfield, occupying the southern part of Okinawa Main Island.

(2) The contents of iodine, bromine, and chlorine were determined by neutron activation and the following results were obtained.

element	range (ppm)	average value (ppm)
C*l*	36–63	48
Br	1.7–6.5	3.4
I	6.6–44	20
I/Br	3.1–8.9	5.7
Br/C*l*$\times 10^3$	39–128	72
I/C*l*$\times 10^3$	169–1,140	446

(3) The geologic sequence in descending order is the Shinzato Formation, the Yonabaru Formation (the upper member, middle member, and lower member), and the Tomigusuku Formation.

The iodine content ranges from 44 and 41 ppm in the Shinzato Formation and the upper member of Yonabaru Formation to 6.6–27 ppm in the middle and lower members of Yonabaru Formation.

(4) The rocks from the Okinawa Gasfield are more abundant in iodine content than those from the Niigata Oilfield.

(5) As a general trend, the rocks with high content of inorganic carbon have high iodine content.

(6) The rocks with high iodine content are in the moderate stage of the maturation in terms of organic materials (kerogen).

(7) This study will also reveal how halogens have been supplied to the surface samples from the present sea water. Further investigations using core samples will reveal the geochemical relation of halogen between the rocks and groundwaters.

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地名英和対応表

Shimajiri	島尻	Yamada	山田
Shinzato	新里	Nishihara	西原
Yonabaru	与那原	Urazoe	浦添
Tomigusuku	豊見城	Chinen	知念
Katsuren	勝連	Naha	那覇

沖縄ガス田の地表で採取した新生界海成泥岩中のヨウ素，臭素，および塩素に関する知見

本島公司・田島栄作・赤岩英夫

要旨

日本には，さく井によって調査されたヨード－ガス田が，北から南にかけていくつもある．沖縄本島南部を占める沖縄ガス田は，これらの中で最も南に位置するものであり，そこは地質調査所，琉球大学，および沖縄県工業試験所などの専門家によって20年来調査・研究が続けられている．

当地に発達する新生界は，島尻層群といわれる海成層からなり，その層序は上から次のようである．

層名	層厚 (m)			岩相
新里	250			主にシルト，砂
与那原	900	上部	350	主にシルト
		中部	500	
		下部	50	
豊見城	900＋			シルト・砂互層

新里層は更新世-鮮新世に，上・中部与那原層は鮮新世に，下部与那原層と豊見城層は上部中新世に属する．豊見城層に不整合で覆われる基盤岩は中生代に属する．

10コの地表のシルト試料が島尻層群からとられ，中性子放射化分析され，次の結果がえられた．

元素	分布 (ppm)	平均 (ppm)
Cl	36-63	48
Br	1.7-6.3	3.4
I	6.6-44	20

ヨウ素の含有量は，新里層と上部与那原層で41および44ppmと多く，中部と下部与那原層では6.6–27ppmと少ない．しかもこれらの値を，同じ程度のCl量を示す新潟油田の地表泥岩試料のものと比較すると，沖縄において著しくヨウ素が多い．また，沖縄では，ヨウ素が無機炭素の多い試料と，有機物の熟成度が中程度の試料とに多い傾向がある．シルト試料では，ヨウ素が臭素よりも多いが，試料がとられた層からおよそ100–300m下位にある豊見城層上部のガス層から得られた地下塩水では，この関係は逆である．今後，コア試料と，その試料と同一層準からとられた地下塩水試料についての，地球化学的研究が必要である．筆者らは，すでにコア試料中のハロゲンの定量を終っているので，本論文に引き続いて，以上の点を中心にとりまとめ発表する予定である．

（受付：1979年7月31日；受理：1979年8月17日）