Bulletin of the Geological Survey of Japan, vol. 41(10), p. 539-549, 1990 546.13 : 550.822 : 551.79(521.41)

On the chlorine content in the pore water from the central Niigata sedimentary basin

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KOMA, T. and SUZUKI, Y. (1990) On the chlorine content in the pore water from the central Niigata sedimentary basin. *Bull. Geol. Surv. Japan*, vol. 41(10), p. 539-549.

Abstract: The pore water in sediments of the Niigata basin is supposed to have been the same composition as the present sea water because all the sediments of the basin except for the Uonuma Group are marine origin. Nevertheless, the actual composition and concentration of the present pore water have changed largely from those of the sea water, due to the influence of meteoric water and chemical reaction with the solid sediment during the diagenetic stage.

In this paper, we present the content of the water-soluble chlorine in the well core samples from the Central Niigata Basin, and also describe the concentration of chlorine ion in core samples from the MITI wells, and those in the brine water from oil and gas fields. Finally, we discuss the diagenetic variation of the chlorine ion in pore water.

Chlorine in water-soluble fraction in rocks and brine water is higher in the central plain area and decreases both southward and toward the margins of the Niigata Sedimentary Basin. On the other hand, concentration of chlorine ion shows systematic vertical variation with the maximum at the intermediate depth. Chlorine in water-soluble fraction in rocks and brine water reaches to its maximum generally at the shallower depth than 1000 m in hilly area and between 1000 to 3000 m deep within the basin.

Taking the tectonic evolution of the Niigata Sedimentary Basin into account, the chlorine in water-soluble fraction in rocks and brine water is supposed to have been controlled by infiltrated meteoric water caused by the upheaval of the basin. Consequently, the water-soluble chlorine in the southern region and marginal areas of the basin has been diluted because these areas were uplifted in the earlier stage.

INTRODUCTION

The Niigata sedimentary basin mainly comprises marine sediments from the basal Nanatani Formation, so-called Green Tuff affinity during its initial stage, to the Teradomari, Shiiya, Nishiyama and Haizume Formations upward. However, the Uonuma Group, representing the final stage of the basin fill, changes to brackish to fresh water in the Uonuma District in the southern region of the basin, while it interfingers with the marine Nishiyama and Haizume Formations in the northern region (KOBAYASHI *et al.*, 1986). After the deposition of the Uonuma Group, the southern region of the basin began to uplift to form hilly to mountainous topography. The northern region still occupied a depo-center of thick strata which were, however, mostly fresh water with local brackish origin.

According to these depositional environments, the pore water is supposed to have been the same composition as the present sea water because all the sediments of the Niigata basin except for the Uonuma Group are marine origin. Nevertheless, the actual composition and concentration of the present pore water have changed largely from those of the sea water, due to the influence of meteoric water and chemical reaction with the solid sediment during the diagenetic stage.

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In this paper, we present the content of the water-soluble chlorine in the well core samples from the Central Niigata Basin, and also describe the concentration of chlorine ion in the core samples from MITI wells, and those in the brine water from oil and gas fields. Finally, we discuss the diagenetic variation of the chlorine ion in pore water.

Chlorine is commonly measured as an ion concentration per unit volume of brine water, and expressed as mg/l of Cl, for the convenience of direct comparison to chlorine concentration in sea water. On the other hand, however, chlorine is usually measured as water-soluble chlorine in weight percent for dried specimen (KOMA *et al.*, 1983). Chlorine ion concentration (mg/l) in pore water (KANEHARA *et al.*, 1958) and water-soluble chlorine (wt. %) are in high correlation (KOMA *et al.*, 1989), and those two values are consistent enough for the description of vertical variation of chlorine concentration in stratigraphic sequence. In this study, therefore, chlorine in the well core sample is expressed as water-soluble chlorine (wt. %) and that in the pore water sample from the MITI wells and the brine waters is expressed as chlorine ion concentration (mg/l).

If the bulk density and water content of the specimen are known, the chlorine ion concentration can be converted to the water-soluble chlorine content by the relation shown below, provided the density of pore water is assumed to be 1.

$$C_{dry} = \frac{C_w \times r}{100\,d - r} \times 10^{-4} \quad \cdots\cdots \quad (1)$$

C_{dry} : water-soluble chlorine (wt. %)
C_w : Cl^- concentration in pore water (mg/l)
d : bulk density
r : water content (vol. %)

SAMPLE ANALYZED

1500 argillaceous rock samples were analyzed for the water-soluble chlorine content, collected from 17 well cores in the Niigata oil and gas field (Fig. 1). It occupies the extent of 100 km in N-S and 50 km in E-W, where Itsuka-Machi, Suibara-Cho, and Izumozaki-Machi are located in the southern, northern and western margins respectively.

Although clay- to silt-sized specimen is usually selected for the chlorine analyses, all the samples were collected in every 10 m interval from the cores including arenaceous sections in the present study. Geological profile transecting through the Amaze R-4, Umeda R-1, and Mitsuke SK-1 wells is shown in Figure 2.

ANALYTICAL METHOD

Water-soluble chlorine (Cl^- : H_2O) was measured with the Sulfuric Acid Chlorine Ion Analyzer (model S-04B, Seishin Seiyaku K. K.) according to the procedure described below.

A 1.0 g of pulverized sample is well ingrained with 10 ml of distilled water, and chlorine is extracted with ultrasonic vibrator for 1 hour. The extracted aliquot is then centrifuged for the sulfuric acid chlorine ion analyzer, which is composed of liquid chromatography and photoelectric colorimeter (KOMA *et al.*, 1983).

DISTRIBUTION OF WATER-SOLUBLE CHLORINE CONTENT (Cl^- : H_2O wt. %)

Vertical fluctuation of water-soluble chlorine ion contents from the respective core samples is shown in Figure 3, which indicates that the water-soluble chlorine content varies with the well site, and with the depth in the same site. Figure 4 shows a schematic distribution of the water-soluble chlorine content in each site.

The core samples of the northern region were taken from the Kakuta R-2, Uchino R-1, Furutsu R-1, and Asahi R-30, and Shirane Observation wells. The water-soluble chlorine content is shown to be extremely high, mostly more than 0.05%, in the horizon shallower than 800 m deep of the western sites of the Kakuta R-2 and Uchino R-1 wells. In the Kakuta R-2 well, however, chlorine content decreases rapidly downward to less than 0.1% below the 800 m depth. The next highest contents are observed from the

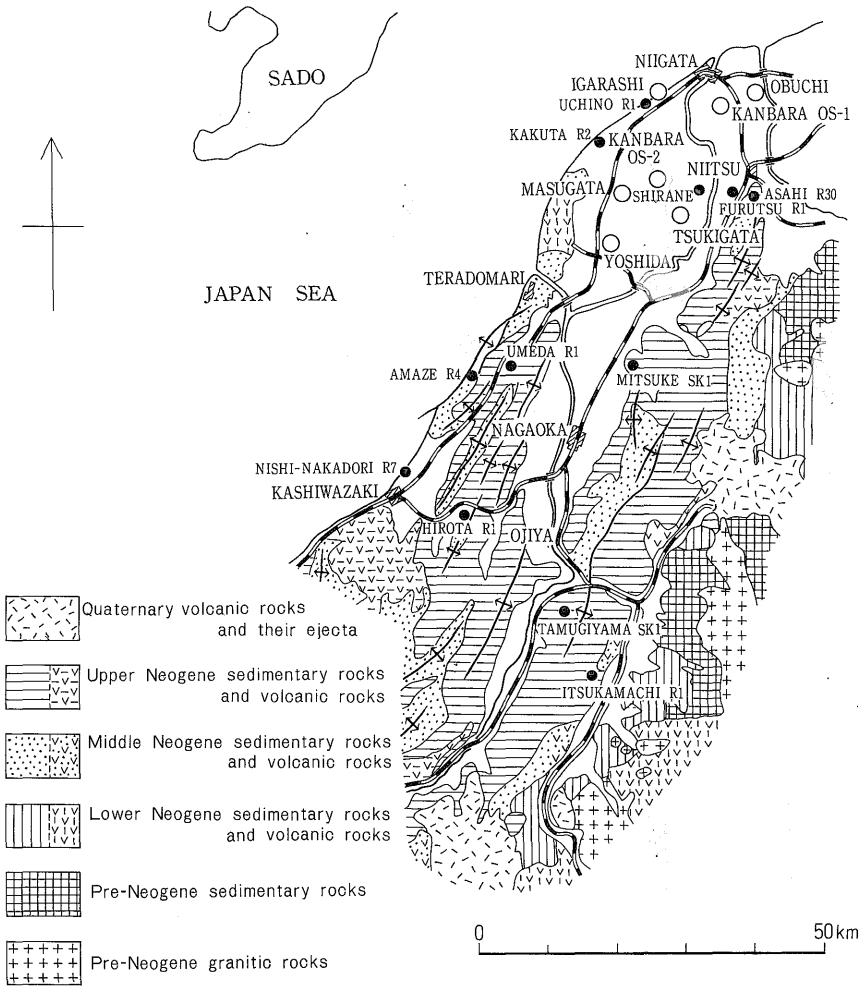

Fig. 1 The location of wells for analysis of samples in the Niigata oil and gas field. (modified after the Japanese Association for Petroleum Technology, 1983)

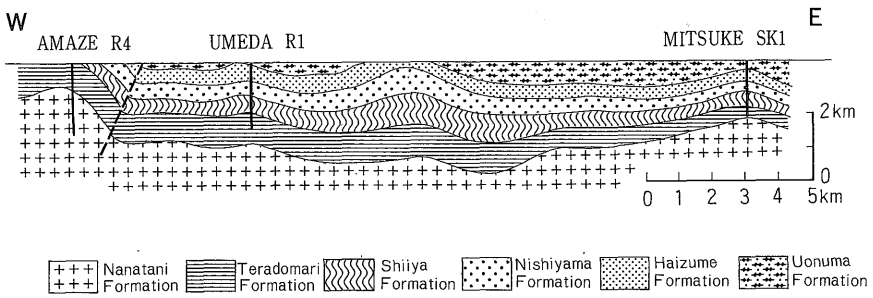

Fig. 2 A geologic cross-section from Amaze R-4 to Mitsuke SK-1 in the central part of the Niigata oil and gas field.

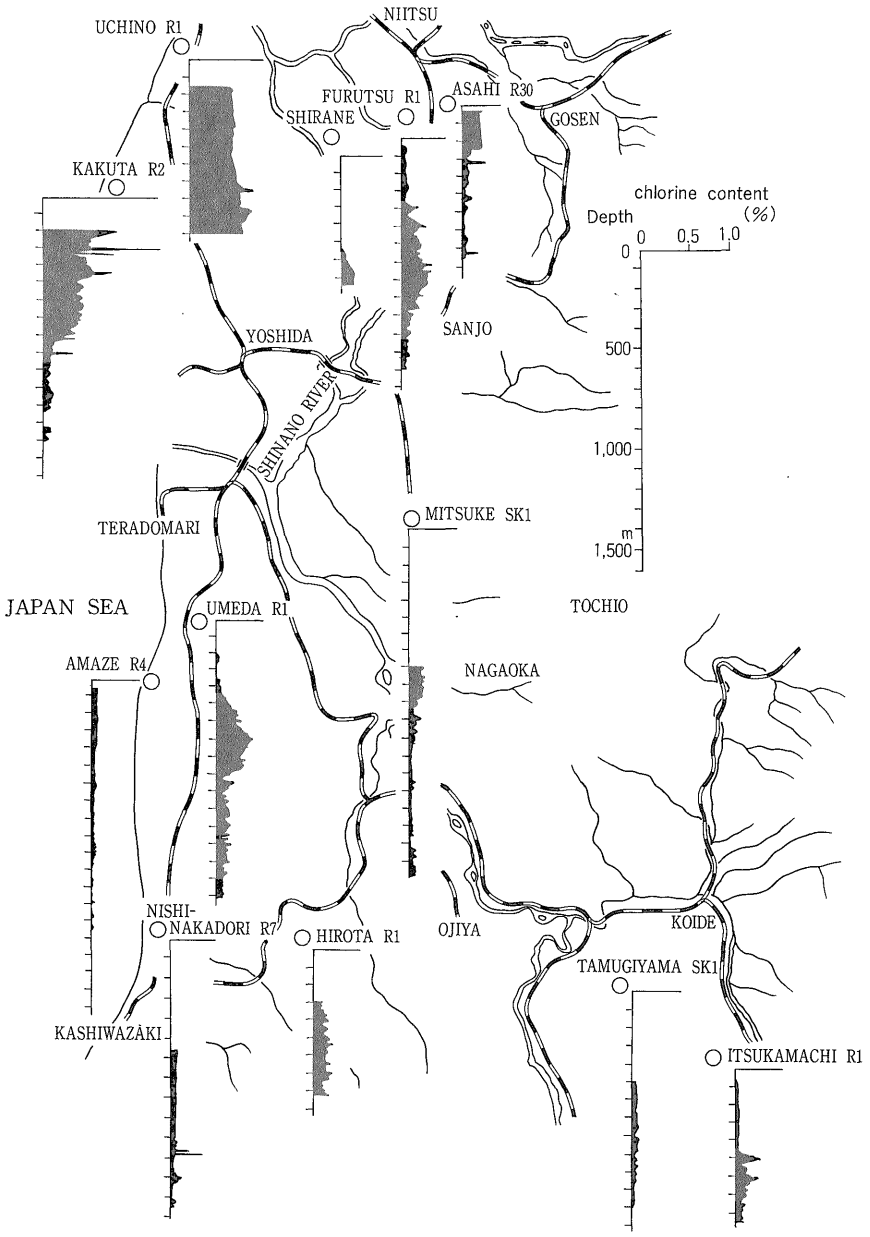

Fig. 3 Water-soluble chlorine content in the wells in the Niigata oil and gas field.

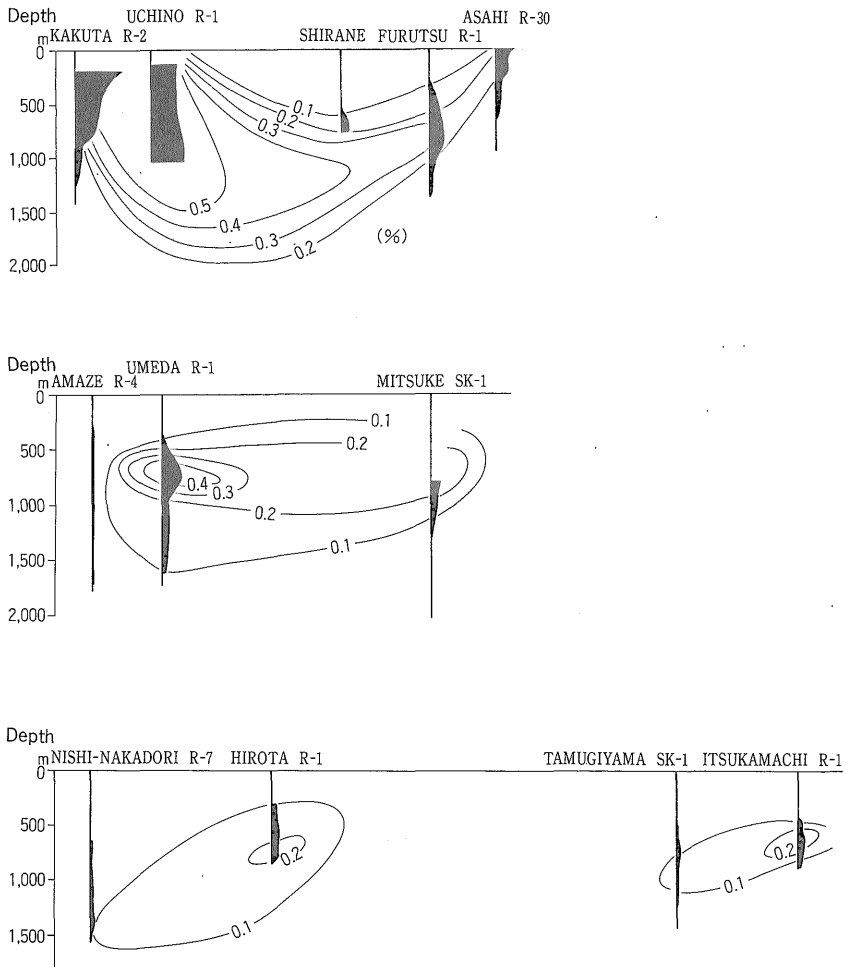

Fig. 4 Generalized water-soluble chlorine content in the wells in the Niigata oil and gas field.

400 to 1000 m subsurface interval of the Furutsu R-1 well (0.3% in maximum) and the horizon shallower than 250 m deep in the Asahi R-30 well (about 0.2%), both of which are located in the eastern side. The chlorine contents decrease in the Furutsu R-1 well to less than 0.1% above the 350 m depth and 0.5% below the 970 m depth. In the Asahi R-30 well, the content also decreases above the 350 m depth to less than 0.5%. In the Shirane Observation well, the content is less than 0.01% above the 500 m depth, which is the minimum value observed in the northern region, however, it gradually increases downward upto about 0.2% at the 700 m depth, and also seems to increase in the far deeper horizon.

In the central region, three cores are analyzed from the Amaze R-4, Umeda R-1, and Mitsuke SK-1 wells. The highest water-soluble chlorine content is observed in the Umeda R-1 well where the value is more than 0.2% in the 300 to 900 m interval, especially high at the 700 m depth to be more than 0.4%, while it decreases to less than 0.1% at the 900 m and the greater depths. In the Amaze R-4 and Mitsuke SK-1 wells which are located on the both sides of the Umeda R-1 well, the contents are generally less than 0.2%.

Among the core samples in the southern region, i.e., the Nishinakadori R-7, Hirota R-1, Tamugiyama SK-1 and Itsukamachi R-1 wells, the average water-soluble chlorine content is

highest in the Hirota R-1 well to be as much as 0.2%. The next highest value is observed in the Itsukamachi R-1 well from the depth of 450 m and deeper, to be more than 0.3% at maximum although the shallower horizon contains generally less water-soluble chlorine, 0.1 to 0.2% within the 450 to 350 m depth interval and less than 0.1% in the 350 m and shallower depths. Only small content, less than 0.1%, of water-soluble chlorine is observed in the Tamugiyama SK-1 and Nishinakadori R-7 wells.

Summarizing the above description, water-soluble chlorine content is generally high in the northern region and decreases to the south, because the maximum value exceeds 0.5% in the northern region while the average is 0.4% in the central and 0.2% in the southern regions.

In view of the E-W direction, the content is generally higher in the western parts in three region, i. e., it is lower in the central sites than the western sites such as the Uchino and Kakuta wells in the northern region ; in the central region, the western sites such as Umeda well are also higher in chlorine content than the central sites except for the westernmost Amaze well where the content is extremely low ; and in the southern region, the Hirota and Itsukamachi wells shows relatively higher values.

As to the relation between the depth and content of water-soluble chlorine, it is depicted that the maxima tend to appear at the intermediate depth, not the deeper nor shallower horizons. The horizon of the maximum of each well is ; 200 to 500 m in the Kakuta, 900 to 1000 m in the Uchino, about 800 m in the Furutsu, and about 200 m in the Asahi wells in the northern region ; about 800 m in the Umeda, shallower than 900 m in the Mitsuke, and about 300 m in the Amaze wells in the central region ; and about 500 m in the Itsukamachi and 900 to 1000 m in the Tamugiyama wells in the southern region, although distinct variation of the content is rather hard because it is generally very low in the southern region.

As summarized above, water-soluble chlorine content in the bedrock samples tends to be high to the north and decreases to the south in the Niigata basin. Also apparent is the tendency that the maxima generally occur in the horizon shallower than 1000 m deep, which can be called hanging lens below the surface.

CHLORINE ION CONCENTRATION (mg/l) IN PORE WATER FROM THE MITI AND GS WELLS

There are several MITI wells in the central part of the Niigata Sedimentary Basin which penetrated more than 3000 m deep during 1963 to 1971 (Japan. Assoc. Petr. Tech., 1973). The concentration of chlorine ion in pore water from these wells is described below.

In the northern region of the Niigata basin where three test wells, that is, the Shimoigarashi, Kanbara GS-2, and Obuchi wells are available, chlorine ion concentration tends to be high in the western sites. In case of the Shimoigarashi well, the concentration is above 10,000 mg/l between the 1000 to 4000 m depth. However, it is only between the 1000 to 3000 m depth that the concentration is more than 10,000 mg/l in the Kanbara GS-2, the maxima at the 2000 m depth exceeds 20,000 mg/l. In the Obuchi well, it is only around the 1500 m depth that the concentration is above 10,000 mg/l.

In the central region, the northern Masugata and Tsukigata wells show the higher chlorine ion concentration, where the maxima are 15,000 mg/l between the 2000 to 4000 m depth and 19,000 mg/l at the 2000 m depths respectively, while in the southern Kanbara GS-1 well the maximum does not exceed 15,000 mg/l at any depth, being as much as 10,000 mg/l between the 1000 to 3000 m depth.

In the southern region, only the Yoshida well is available where the concentration is more than 10,000 mg/l between the 3000 to 4000 m depth, and the maximum reaches to 15,000 mg/l.

Concerning to the relation with the depth, it is also shown that chlorine ion concentration has the maximum at the intermediate depth and decreases both upward and downward, as is the case for the water-soluble chlorine contents.

In the northern region, the maxima are located

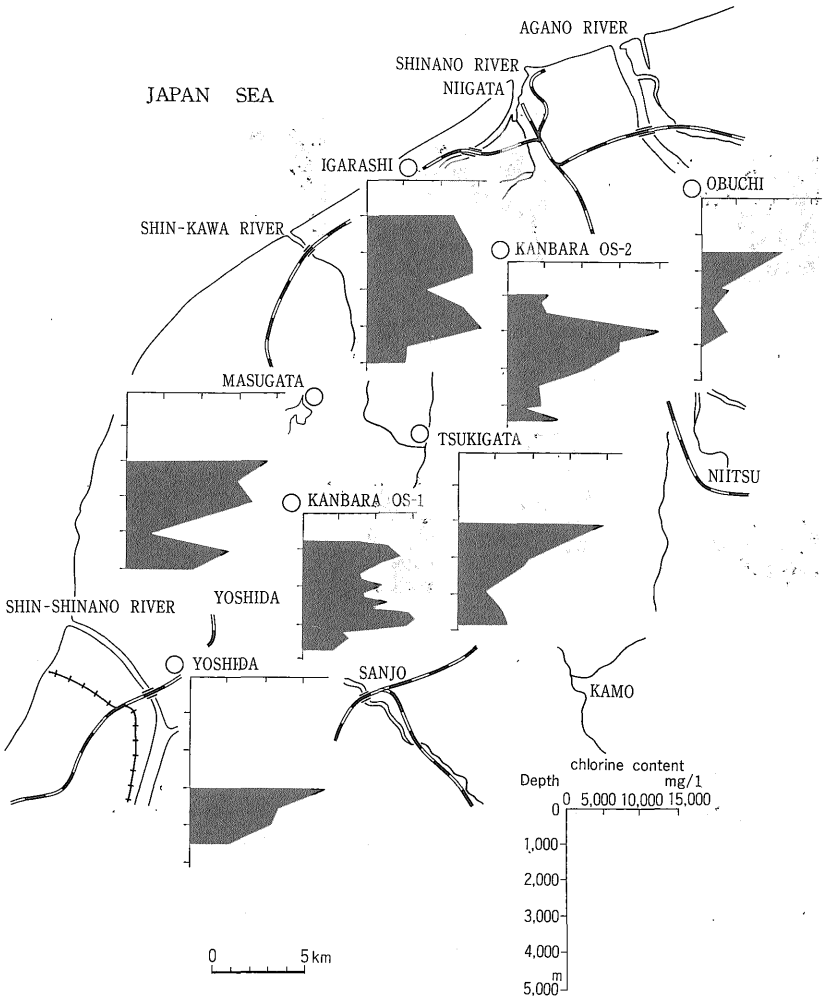

Fig. 5 Chlorine iron content in pore water in the sedimentary rocks from the cores of wells in the Niigata oil and gas field.

at the 2000 to 4000 m depth in the Shimoigarashi, 2000 m depth in the Kanbara GS-2, and above the 1500 m depth in the Obuchi wells.

In the central region, the maxima are located at the 2000 to 3000 m in the Masugata, and above the 2000 m in the Tsukigata wells. In the Kanbare GS-1 well, the concentration shows rather complicated vertical fluctuation where the two maxima are identified at the 1200 and 3000 m depths and the concentration seems to decrease both the shallower and deeper horizons.

In the southern Yoshida well, the maximum is located above the 3000 m depth, and the concentration decreases downward.

To summarize the above description, the chlorine ion concentration reaches the maximum at the intermediate depth and decreases both upward and downward as is the case for water-soluble chlorine content in pore water. The depth of the maxima is generally between 1500 and 3000 m deep, and tends to be deeper in more southerly and closer to the hilly area wells.

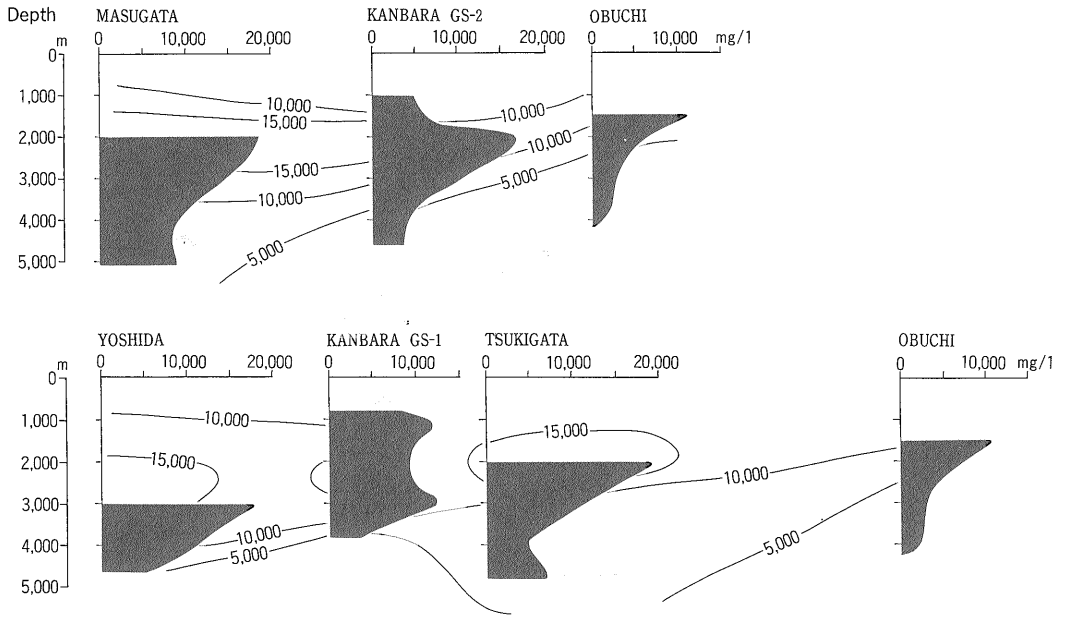

Fig. 6 Generalized chlorine iron content in pore water in the sedimentary rocks from the cores of wells in the Niigata oil and gas field.

CHLORINE ION CONCENTRATION (mg/l) IN BRINE WATER FROM OIL AND GAS FIELD

It is generally accepted that the chlorine ion concentration in brine water accompanied with petroleum and natural gas tends to be higher in the center of the sedimentary basin and decreases to its margins (Japan. Assoc. Petr. Tech., 1983). This is also the case for the Niigata Sedimentary Basin, where the oil and gas fields with high concentration of chlorine ion more than 20,000 mg/l in their brine water, are all located in the central part, such as Shiunji, Higashiniigata, and Kumoide gas fields (Fig. 7). In contrast, chlorine concentration is very low in oil fields in the margin of the basin, and the concentration tends to decrease from the center to the margins of the basin, such as the Nishiyama and Niitsu oil fields where the maxima are 190 and 120 mg/l respectively.

Concentration of chlorine ion thus changes across the axis of the basin, but it also shows a variation along the axis. The concentration in 5,500 to 26,000 mg/l in the Higashiniigata gas field in the northern region, while it decreases southward to 18,000 mg/l in the Mitsuke and 13,000 mg/l in the Tamugiyama oil fields. This trend is also observed further southeastward to the Gosen Plain, where the concentration is reduced to 5,500 to 13,000 mg/l in the Kuwayama gas field.

These variations of the chlorine ion concentration in brine water from oil and gas fields indicate that chlorine in the brine are closely related to water-soluble chlorine content in bed rocks. In other words, pore water chlorine is generally enriched to the north and lower to the south, and, at the same time, concentrated in the central-western part decreasing both eastward and westward. In more detail, water-soluble chlorine content is higher in the Umeda R-1 than in Mitsuke SK-1 wells while the chlorine ion concentration in brine water is in vice versa. This inconsistency seems to be due to the complicated circulation system of ground water which influenced the variation of chlorine ion distribution.

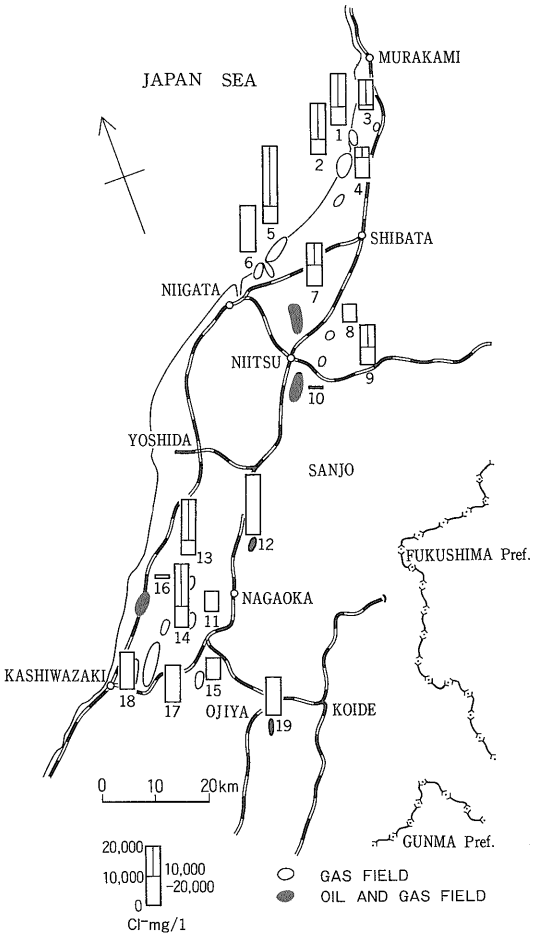

Fig. 7 Chlorine content in brine water in the Niigata oil and gas field.

1. Shin-Tainai (6,000-17,000 mg/l)
2. Nakajo (5,000-17,000 mg/l)
3. Hirakida (1,000-10,000 mg/l)
4. Shiunji (6,500-10,000 mg/l)
5. Higashi-Niigata (5,500-26,000 mg/l)
6. Matsuzaki (15,300 mg/l)
7. Minami-Aga (7,000-14,000 mg/l)
8. Minami-Suibara (6,000 mg/l)
9. Kuwayama (5,500-13,000 mg/l)
10. Niitsu (13-120 mg/l)
11. Kanbara (6,500 mg/l)
12. Mitsuke (18,000 mg/l)
13. Fujiikawa (4,500-18,000 mg/l)
14. Kumoida (7,000-20,500 mg/l)
15. Katagai (7,000 mg/l)
16. Nishiyama (190 mg/l)
17. Yoshii (12,000 mg/l)
18. Higashi-Kashiwazaki (12,000 mg/l)
19. Tamugiyama (13,000 mg/l)

DIAGENETIC CHANGE OF CHLORINE ION CONCENTRATION

The original concentration of chlorine ion is supposed to have been similar to sea water, as much as 19,000 mg/l, except for the Uonuma Group. During later stages, pore water was expelled from the sediments due to compaction by deep burial and authigenic mineralization. In addition, upheaval of the provenance and the basin itself caused the infiltration of meteoric water, which diluted the chlorine ion in pore water (SUDO, 1967).

As aforementioned, there are only restricted horizons between the 1000 to 3000 m depth in the northern region of the Niigata Sedimentary Basin where the present chlorine ion concentration nearly corresponds to that of sea water. The concentration is lower in all the other regions, particularly low in the southern region and marginal hilly areas. This evidence indicates that the upheaval of the Niigata Sedimentary Basin initiated both in the southern region and marginal areas where the dilution of pore water by infiltrated meteoric water primarily started. The infiltration took place through the shallower and deeper stratigraphic horizons, which preserved the less diluted pore water with high chlorine concentration as a hanging lens in between.

Finally, high concentration of chlorine ion in brine water from oil and gas fields has the maximum in the central area of the basin and decreasing toward its margins.

SUMMARY

Chlorine in water-soluble fraction in rocks and brine water is higher in the central plain area and decreases both southward and toward the margins of the Niigata Sedimentary Basin. On the other hand, concentration of chlorine ion shows systematic vertical variation with the maximum at the intermediate depth. Chlorine in water-soluble fraction in rocks and brine water reaches to its maximum generally at the shallower depth than 1000 m in hilly area and between 1000 to 3000

m deep within the basin.

Taking the tectonic evolution of the Niigata Sedimentary Basin into account, the chlorine in water-soluble fraction in rocks and brine water is supposed to have been controlled by infiltrated meteoric water caused by the upheaval of the basin. Consequently, the water-soluble chlorine in the southern region and marginal areas of the basin has been diluted because these areas were uplifted in the earlier stage.

Acknowledgements: We wish to thank Dr. Yoshio WATANABE of Fuel Resources Department of the Geological Survey of Japan for his reviewing and rewriting the manuscript.

Thanks are also extended to the Teikoku Oil Company and the Japan Petroleum Exploration Company for offering the core samples, and Mrs. Akiko KUSUDA for the preparation of the manuscript.

REFERENCES

KANEHARA, K., MOTOJIMA, K., ISHIWADA, Y. (1958) Core test, In Natural Gas. Asakura-Syoten, Tokyo, p. 187-203.

KOBAYASHI, I., TATEISHI, M., YASUI, S., KAZAOKA, O., KUROKAWA, K., ABURAI, H. and WATANABE, K. (1986) Stratigraphy and paleoenvironment of Nishiyama and Haizume Formations and Uonuma Group in Niigata Sedimentary Basin. *Jour. Geol. Soc. Japan*, vol. 92, p. 375-390.

KOMA, T., SUZUKI, Y. and KODAMA, K. (1983) Forms of sulfur, carbon, chlorine and iron compounds and their depositional environment in the Kazusa Group, the Boso Peninsula, central Japan. *Bull. Geol. Surv. Japan*, vol. 34, p. 191-206 (in Japanese with English abstract).

———, ——— and TOGASHI, S. (1989) Geochemical and Mineralogical study of Plio-Pleistocene mudstones taken from some holes drilled in the southeast part of Kanto Plain, Central Japan. *Jour. Japan. Assoc. Pet. Technol.*, vol. 54, p. 1-17.

SUDO, Y. (1967) Geochemical study of brine from oil and gas fields in Japan. *Jour. Japan Assoc. Pet. Technol.*, vol. 32, p. 286-296.

The Japanese Association for Petroleum Technology (1973) Petroleum Mining Industry and Technology of Japan. Ratesu, Tokyo, p. 104-174.

The Japanese Association for Petroleum Technology (1983) Handbook of Petroleum Mining Industry. Ratesu, Tokyo, p. 708-714.

新潟堆積盆地中央部の地層中の塩素含有量分布について

狛　武・鈴木尉元

要　旨

新潟堆積盆地を構成する地層は魚沼層群をのぞいて海成層であり，地層に含まれる間隙水は現在の海水とほぼ同じ組成をもっていたに違いない．しかし現在各層に含まれ間隙水は海水とは濃度および組成において非常に異なってしまっている．

新潟堆積盆地中央部に掘られた坑井コア中の水溶性塩素量，および基礎試錐のコア試験による間隙水の塩素イオン濃度，さらに油田・ガス田鹹水中の塩素イオン濃度を検討し，間隙水がどのように変化してきたかを検討した．

新潟堆積盆地の地層中の水溶性塩素含有量（油田・ガス田鹹水の塩素イオン濃度を含む，以下略）は，新潟平野において高く，南方に，また周辺の丘陵地域に向かって低くなる．しかし，水溶性塩素濃度は深さによって変化し，一般に浅部においても深部に向かっても小さくなり，最大の水溶性塩素濃度を示す深さは，丘陵地では一般に 1000 m 以下であり，新潟平野では 1000 ないし 3000 m である．

新潟堆積盆地の地史から，水溶性塩素含有量は，堆積盆地の隆起にともなう陸水侵入によって主として決定され，早期に隆起した堆積盆地南部ならびに周辺地域では水溶性塩素含有量は小さくなる傾向を示した．

（受付：1990年 5 月23日；受理：1990年 6 月14日）