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原 著

## An Application of Mn-impregnated Acrylic Fiber to the Determination of $^{226}\text{Ra}$ and $^{228}\text{Ra}$ in Hot Spring Waters

Tomoko NAKANO-OHTA<sup>1</sup> and Jun SATO<sup>2\*</sup>

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<sup>1</sup> Department of Nuclear Science and Engineering, Research Reactor Institute, Kyoto University<sup>2</sup> Department of Applied Chemistry, School of Science and Technology, Meiji University

### マンガ化合物を含浸させたアクリル繊維を用いた 温泉水中の $^{226}\text{Ra}$ と $^{228}\text{Ra}$ の定量

<sup>1</sup> 京都大学原子炉実験所, <sup>2</sup> 明治大学理工学部中野 (太田) 朋子<sup>1</sup>, 佐藤 純<sup>2</sup>

#### 要 約

マンガ化合物を含浸させたアクリル繊維を用いて東京地域に湧出する温泉水中の  $^{226}\text{Ra}$  と  $^{228}\text{Ra}$  の濃度を測定した。高塩濃度の水試料に対するこの方法の適用性は海水を用いて検討した。温泉水中の  $^{226}\text{Ra}$  は  $0.3\text{--}84\text{ mBq}\cdot\text{l}^{-1}$  の範囲にあり,  $^{228}\text{Ra}$  は  $0.2\text{--}104\text{ mBq}\cdot\text{l}^{-1}$  の範囲にあった。温泉水中の Ra 濃度の平均値は, NaCl 型の温泉水中の  $^{226}\text{Ra}$  では  $39\text{ mBq}\cdot\text{l}^{-1}$  で  $^{228}\text{Ra}$  では  $55\text{ mBq}\cdot\text{l}^{-1}$  であり, 単純アルカリ泉型のものでは  $^{226}\text{Ra}$  は  $0.6\text{ mBq}\cdot\text{l}^{-1}$  で  $^{228}\text{Ra}$  では  $0.8\text{ mBq}\cdot\text{l}^{-1}$  であった。NaCl 型の Ra 同位体の濃度は単純アルカリ泉型のものよりかなり高いことを示した。本邦のいくつかの温泉水中の  $^{226}\text{Ra}$  の平均濃度は NaCl 型では  $104\text{ mBq}\cdot\text{l}^{-1}$  で単純アルカリ泉型では  $9\text{ mBq}\cdot\text{l}^{-1}$  であり, これらの温泉でも, NaCl 型の  $^{226}\text{Ra}$  濃度は単純アルカリ泉型より高いことが示された。温泉水中の Ra の濃度は Ca 濃度との間に良い相関が見られ, さらに温泉水の pH の大小が Ra の濃度を左右していると見られた。

#### Abstract

Concentrations of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in hot spring waters from Tokyo area were observed by Mn-impregnated acrylic fiber. Applicability of the method to highly saline waters was examined by use of seawater. The concentrations of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in hot

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\* To whom all correspondences should be addressed.

spring waters ranged from 0.3 to 84 mBq · l<sup>-1</sup> and from 0.2 to 104 mBq · l<sup>-1</sup>, respectively. The average concentrations of the hot spring waters were 39 mBq · l<sup>-1</sup> for <sup>226</sup>Ra and 55 mBq · l<sup>-1</sup> for <sup>228</sup>Ra in NaCl type, and 0.6 mBq · l<sup>-1</sup> for <sup>226</sup>Ra and 0.8 mBq · l<sup>-1</sup> for <sup>228</sup>Ra in simple alkaline type, indicating that the concentrations of Ra isotopes in NaCl type were much higher than those in simple alkaline type. Average concentration of <sup>226</sup>Ra of some hot spring waters in Japan were 104 mBq · l<sup>-1</sup> for NaCl type and 9 mBq · l<sup>-1</sup> for simple alkaline type, indicating that the concentration of <sup>226</sup>Ra in NaCl type was also much higher than those in simple alkaline type. Concentrations of Ra isotopes are well correlated with Ca concentrations, and may be controlled by pH of hot spring waters.

Key words : Mn-impregnated acrylic fiber, radium-226, radium-228, hot spring water, Tokyo area

キーワード : マンガン化合物を含浸させたアクリル繊維, ラジウム 226, ラジウム 228, 温泉水, 東京地域

## 1. Introduction

As <sup>226</sup>Ra and <sup>228</sup>Ra are progenies of <sup>238</sup>U and <sup>232</sup>Th, respectively, the concentrations of <sup>226</sup>Ra and <sup>228</sup>Ra are essentially dependent on the U and Th concentration in the source rocks. Thorium-230 and <sup>232</sup>Th, parents of <sup>226</sup>Ra and <sup>228</sup>Ra, respectively, are supposed to be insoluble in hot spring waters with chemical character of neutral and/or alkaline type. The <sup>226</sup>Ra and <sup>228</sup>Ra in the hot spring waters are supplied from the relevant rock into water, including chemical leaching from the relevant rock and by the  $\alpha$ -recoil ejection from Th isotopes on the surface of the rock. Assuming that the leaching efficiency between Ra isotopes from the relevant rock into the hot spring water is equal to each other, the variation in the activity ratio of Ra isotopes in the hot spring waters may be dependent on the age of hot spring water (Nakano-Ohta and Sato, 2005) or due to the mixing of waters of different origin in highly varying proportions. Thus the concentration of <sup>226</sup>Ra and <sup>228</sup>Ra is expected to be useful tracer on the hydrological aspects of natural waters.

Radium isotopes (<sup>226</sup>Ra and <sup>228</sup>Ra) in hot spring waters have been determined by co-precipitation with BaSO<sub>4</sub> followed by  $\alpha$ -ray spectrometry,  $\gamma$ -ray spectrometry or liquid scintillation spectrometry (Ikeda, 1955 ; Sugihara, 1970 ; Horiuchi and Murakami, 1978 ; Horiuchi *et al.*, 1979 ; Kanroji *et al.*, 1980 ; Kametani and Matsumura, 1983 ; Yamamoto *et al.*, 1994 ; Chu and Wang, 2000). However, Ba reagents frequently contain small but significant amounts of <sup>226</sup>Ra of a fraction of 1 Bq/g. The amount of <sup>226</sup>Ra impurity in BaCl<sub>2</sub> · 2H<sub>2</sub>O reagents from 3 major chemical reagent makers in Japan was observed to be in the range of 20–100 mBq · g<sup>-1</sup> (Saito *et al.*, 2002), which may contaminate with several mBq of <sup>226</sup>Ra in the co-precipitation process of sample waters. Though the separation procedure including co-precipitation of <sup>226</sup>Ra with Ba reagents may be applied to the hot spring water having high concentration of <sup>226</sup>Ra of 1,000 mBq · l<sup>-1</sup> or more, it is not preferable for hot spring waters having low concentration of <sup>226</sup>Ra to separate it with BaSO<sub>4</sub>, especially for a minute amount of <sup>226</sup>Ra of less than 10 mBq · l<sup>-1</sup>. Yamamoto *et al.* (1989) also pointed out that the amount of <sup>226</sup>Ra impurity in Ba reagents ranged from 100 to 400 mBq · g<sup>-1</sup> and proposed the procedure to eliminate <sup>226</sup>Ra impurity from Ba compounds by cation exchange separation using CyDTA (cyclohexanedia-minetetraacetic acid) as eluant. Co-precipitation procedures with BaSO<sub>4</sub> were reported for

<sup>226</sup>Ra in natural waters, including seawater, of  $1 \text{ mBq} \cdot \text{l}^{-1}$ , using Ra-free Ba reagent (Yamamoto *et al.*, 1994) or Ba reagent with the known amount of Ra contents. Recently, Saito *et al.* (2002) developed an ion exchange procedure for Ra isotopes in hot spring waters, which was free from the contamination of Ra isotopes from reagent.

Moore (1976) reported that Mn-impregnated acrylic fiber could collect <sup>228</sup>Ra from a large amount of seawater : 100 g of the Mn-impregnated acrylic fiber could collect up to 500 dpm of <sup>228</sup>Ra in seawater, which was equivalent to 1,500 l or more of seawater. Collection of Ra isotopes by Mn-impregnated acrylic fiber has been applied to various natural waters (Moore, 1976 ; Ku *et al.*, 1980 ; Yamada and Nozaki, 1986 ; Nozaki and Tsunogai, 1990 ; Kasemsupaya *et al.*, 1993).

Concentrations of Ra isotopes in hot spring waters were reported to be  $1 \sim 632 \text{ mBq} \cdot \text{l}^{-1}$  for <sup>226</sup>Ra and  $0.2 \sim 1,000 \text{ mBq} \cdot \text{l}^{-1}$  for <sup>228</sup>Ra (Sato *et al.*, 1975 ; Horiuchi *et al.*, 1979 ; Kanroji *et al.*, 1979 ; Yamamoto *et al.*, 1994 ; Saito, 2005 ; Nakano-Ohta and Sato, 2006). Though the highly concentrated Ra isotopes in hot spring waters can be determined with several tens liters of sample water, Ra of low concentration requires sample volume larger than 100 l. This paper deals with effective collection and determination for the concentration of <sup>226</sup>Ra and <sup>228</sup>Ra in seawaters and various hot spring waters including highly saline hot spring waters with a large volume of 100 l in Tokyo area. The present study consists of two procedures : (1) collection of <sup>226</sup>Ra and <sup>228</sup>Ra in seawater and hot spring water of 100 l by a column of Mn-impregnated acrylic fiber and (2) determination of <sup>226</sup>Ra and <sup>228</sup>Ra by  $\gamma$ -ray spectrometry.

## 2. Experiments

### 2.1 Sampling sites and samples

Surface seawater from Tokyo Bay was sampled at Umizuri Park, Kawasaki. Figure 1 shows sampling sites of hot spring waters and the geology in Tokyo area (Omori, 1989). Hot springs located in Tokyo area are grouped into three localities : (1) metropolitan area, (2) Tama area and (3) Okutama area (Kanroji *et al.*, 2000). Chemical characteristics of the hot spring waters belong to (1) NaCl and NaHCO<sub>3</sub> type for metropolitan area, (2) NaCl and NaHCO<sub>3</sub> type for Tama area, and (3) simple alkaline type for Okutama area. Evaporated residues of hot spring waters ranged from 98 to 580 mg  $\cdot$  l<sup>-1</sup> for Okutama area, from 150 to 2,053 mg  $\cdot$  l<sup>-1</sup> for Tama area and from 2,000 to 32,050 mg  $\cdot$  l<sup>-1</sup> for metropolitan area (Kanroji *et al.*, 2000 ; Kanroji, 2005, *priv. com.*), indicating that the evaporated residues in the hot spring waters from the metropolitan area were much higher than those from Okutama area and Tama area.

Hot spring waters and surface seawaters were stored in 20 l polyethylene bottles for transportation.

### 2.2 Analytical method

The Mn-impregnated acrylic fiber was prepared after the procedure given by Moore (1976). Briefly, 100 g of acrylic fiber (Hamanaka Co. Ltd.) was put into 1 l of  $0.3 \text{ mol} \cdot \text{l}^{-1}$  solution of KMnO<sub>4</sub> for 3 h at 70°C to form Mn-impregnated acrylic fiber, and the product was rinsed well with deionized water and dried completely in an electric drier oven at 50°C. The

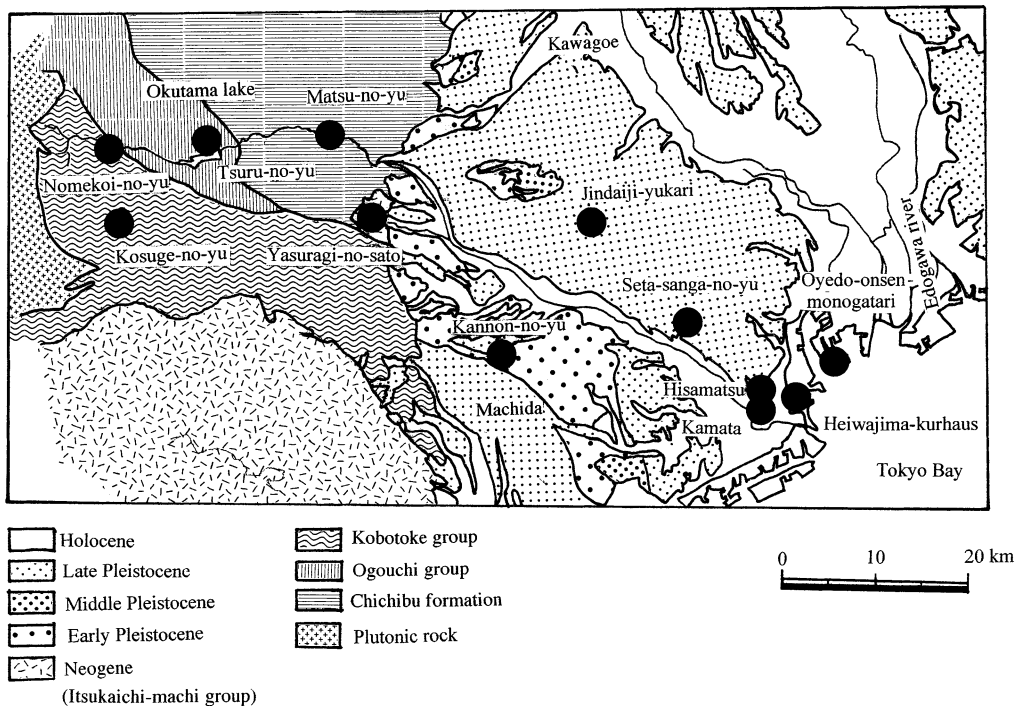


Fig. 1 Sampling sites of hot spring waters in Tokyo area (modified from Omori (1989)).

chemical form of the Mn compound deposited on the acrylic fiber and chemical properties of the Mn-impregnated acrylic fiber are described in detail elsewhere (Ohta *et al.*, 2004).

The polycarbonate column consists of three sub columns (3.5 cm inner diameter, 30 cm long) of 31 g of Mn-impregnated acrylic fiber connected in series with each other by putting plastic net between the columns. Sample waters were passed through the column with a flow rate of less than  $2\text{ l} \cdot \text{min}^{-1}$ . This collection procedure for  $^{226}\text{Ra}$  in 100 l water sample required 2.5 hours.

This analytical method was applied to seawater, highly saline hot spring water of NaCl type,  $\text{NaHCO}_3$  type and simple alkaline type. Hot spring waters of 66~100 l were passed through the column. Two Mn-impregnated acrylic fibers in the first and the second columns were combined to be packed into one air-tight tin canister (76 mm  $\phi$ , 24 mm H). The Mn-impregnated acrylic fibers which collected Ra isotopes were stored for 1 month for  $\gamma$ -ray spectrometry in order that  $^{214}\text{Pb}$  and  $^{228}\text{Ac}$  reached the radioactive equilibrium with  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ , respectively. Radioactivity of  $^{214}\text{Pb}$  and  $^{228}\text{Ac}$  were determined by the 351 keV and the 911 keV  $\gamma$ -rays, respectively. Detailed discussion on the present spectrometry is described by Saito *et al.* (2002).

Table 1 Concentrations of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ , and  $^{228}\text{Ra}/^{226}\text{Ra}$  activity ratio in hot spring waters from Tokyo area

Chemical character	Sampling date	$^{226}\text{Ra}/\text{mBq} \cdot \text{l}^{-1*}$	$^{228}\text{Ra}/\text{mBq} \cdot \text{l}^{-1*}$	$^{228}\text{Ra}/^{226}\text{Ra}$	Depth**/ m
<b>NaCl type</b>					
Oyedo-onsen-monogatari <sup>a)</sup>	Dec 9, 2005	84±2	104±4	1.2±0.1	1300
Heiwajima-kurhaus <sup>a)</sup>	Dec 26, 2004	58±2	94±4	1.9±0.1	2000
Kannon-no-yu <sup>b)</sup>	April 3, 2005	43±1	73±1	1.7±0.1	1500
Seta-sanga-no-yu <sup>a)</sup>	Dec 6, 2005	21±0.5	23±1	1.1±0.1	1700
Jindaiji-yukari <sup>a)</sup>	July 4, 2005	10±0.2	12±1	1.2±0.1	1500
Tenryo-no-yu <sup>d)</sup>	Aug 8, 2003	18±1	21±1	1.3±0.1	1600
Average		39	55	1.4	
<b>NaHCO<sub>3</sub> type</b>					
Kamata <sup>a)</sup>	Dec 26, 2004	1.2±0.2	3.0±0.4	2.5±0.5	100
Hisamatsu <sup>a)</sup>	July 2, 2005	0.49±0.09	0.73±0.20	1.5±0.5	60
Average		0.85	1.9	2.0	
<b>Simple alkaline type</b>					
Nomekoi-no-yu <sup>c)</sup>	May 14, 2003	0.30±0.08	0.24±0.04	0.8±0.3	1300-1500
Tsuru-no-yu <sup>c)</sup>	May 20, 2003	0.94±0.26	0.63±0.04	0.7±0.2	300
Matsu-no-yu <sup>c)</sup>	May 14, 2003	0.66±0.08	1.1±0.11	1.7±0.3	30
Kosuge-no-yu <sup>c)</sup>	July 12, 2005	0.43±0.10	0.62±0.15	1.4±0.5	1500
Yasuragi-no-sato <sup>c)</sup>	May 10, 2005	0.62±0.06	1.2±0.2	1.9±0.2	1300-1500
Average		0.6	0.8	1.3	

\* Errors represent the counting statistics.

\*\* The depth of bore-hole of hot-spring.

<sup>a)</sup> Metropolitan area

<sup>b)</sup> Tama area

<sup>c)</sup> Okutama area

<sup>d)</sup> Yamanashi Pref.

### 3. Results and discussion

#### 3.1 Surface seawater

Prior to the determination of the Ra isotopes in hot spring water,  $^{226}\text{Ra}$  in seawater was determined by the Mn-impregnated acrylic fiber. Surface seawater (100 l) from Tokyo Bay sampled at Umizuri Park, Kawasaki, was passed through the column. The Mn-impregnated acrylic fiber recovered from each column was dried to be packed into three canisters separately.

The total amount of  $^{226}\text{Ra}$  in the initial water sample can be estimated by the calculation given as follows :

$$C_1 = C_0 \cdot \alpha$$

$$C_2 = (C_0 - C_1) \cdot \alpha$$

$$\therefore \alpha = 1 - (C_2 / C_1)$$

$$\therefore C_0 = C_1 / [1 - (C_2 / C_1)]$$

Table 2 Concentrations of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ , and  $^{226}\text{Ra}/^{226}\text{Ra}$  activity ratio in hot spring waters in Japan (Yamamoto *et al.*, 1994 ; Saito *et al.*, 2002)

Chemical character	$^{226}\text{Ra}/\text{mBq} \cdot \text{l}^{-1}$	$^{228}\text{Ra}/\text{mBq} \cdot \text{l}^{-1}$	$^{228}\text{Ra}/^{226}\text{Ra}$
<b>NaCl type</b>			
Kagahachiman <sup>*)</sup>	2.08±0.27	3.09±0.66	1.5±0.3
Nakanomiya <sup>*)</sup>	45.2±0.8	37.5±1.1	0.83±0.02
Iwama <sup>*)</sup>	5.48±0.52	12.3±1.8	2.2±0.3
Keinakyo <sup>*)</sup>	4.77±0.33	6.11±0.71	1.3±0.1
Tatsuno-kuchi <sup>*)</sup>	112±4	174±11	1.6±0.1
Misasa 1 <sup>**)</sup>	48±1	112±5	2.3±0.1
Misasa 2 <sup>**)</sup>	52±9	101±16	1.9±0.4
Onogawa 1 <sup>**)</sup>	351±36	525±64	1.5±0.2
Onogawa 2 <sup>**)</sup>	344±25	565±42	1.6±0.2
Arima 1 <sup>**)</sup>	203±14	64±26	0.33±0.14
Arima 2 <sup>**)</sup>	69±10	49±14	0.71±0.22
Hijiori <sup>**)</sup>	14±2	32±3	2.2±0.4
Average	104	140	1.5
<b>Simple alkaline type</b>			
Nakano-yu <sup>*)</sup>	4.50±0.44	9.72±1.61	2.2±0.3
Akahodani <sup>*)</sup>	11.3±0.8	3.74±0.34	3.7±0.3
Gero <sup>*)</sup>	2.13±0.41	4.70±1.58	2.2±0.6
Nozawa <sup>*)</sup>	0.95±0.24	2.76±0.77	2.9±0.3
Miyano-hara <sup>*)</sup>	25±1	28±3	1.1±0.1
Average	9	10	2.4

<sup>\*)</sup> Yamamoto *et al.* (1994).

<sup>\*\*)</sup> Saito *et al.* (2004).

where  $C_0$  is the total amount of  $^{226}\text{Ra}$  in the initial seawater sample,  $C_1$  is the amount collected from the initial water sample by Mn-impregnated acrylic fiber in the first column,  $C_2$  is the amount collected by the second column from the sample water after passing through the first column, and  $\alpha$  is the collecting coefficient of  $^{226}\text{Ra}$  for each 31 g of Mn-impregnated acrylic fiber. The third column is the back-up column for the break-through of  $^{226}\text{Ra}$  from the second column. The amount of  $^{226}\text{Ra}$  collected by the third column may be  $C_3 = C_0 \cdot (1 - \alpha)^2 \cdot \alpha$ .

The amounts of  $^{226}\text{Ra}$  collected on the Mn-impregnated acrylic fibers were 93 mBq for the first column and 24 mBq for the second column. The amount of  $^{226}\text{Ra}$  in the third column was less than the detection limit. The  $\alpha$  is calculated by the amounts of  $^{226}\text{Ra}$  collected on the Mn-impregnated acrylic fibers of the first and the second column to be 0.73, and the amount of  $^{226}\text{Ra}$  in the initial seawater sample is estimated to be  $C_0 = 127$  mBq. The amount of  $^{226}\text{Ra}$  is calculated to be 6.5 mBq for  $C_3$  and 2.7 mBq in the drain water, suggesting that the amount of  $^{226}\text{Ra}$  passed through the three columns of the Mn-impregnated acrylic fibers is 2% of the total amount of  $^{226}\text{Ra}$  in 100 l of the seawater sample. The  $^{226}\text{Ra}$  concentration in this seawater sample was  $1.3 \text{ mBq} \cdot \text{l}^{-1}$ . Seawater (127 l) from Tokyo Bay also sampled at Umizuri Park was passed through the set of the three columns. Two Mn-impregnated acrylic fibers in the first

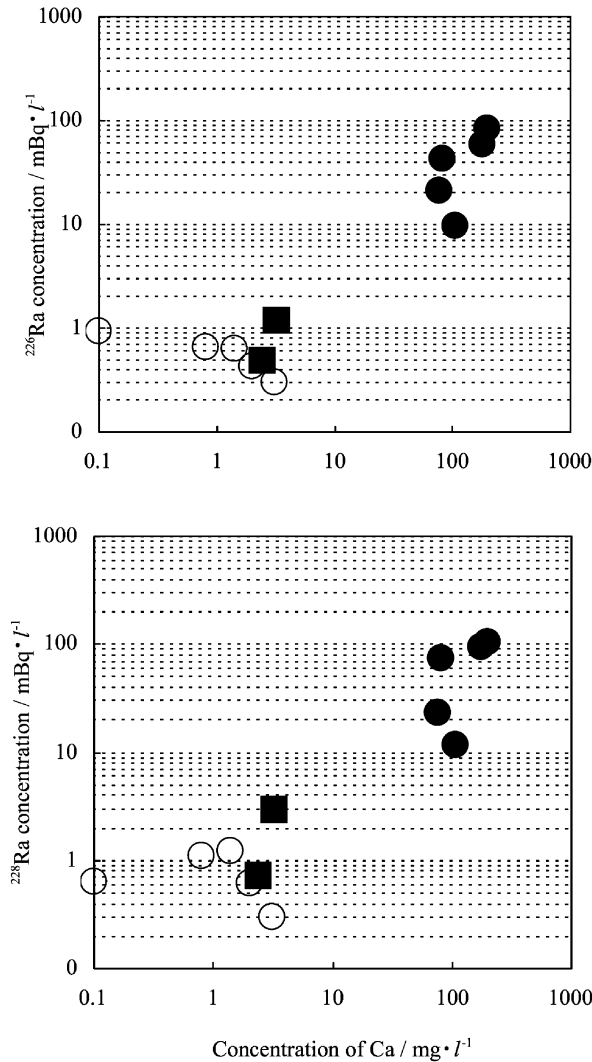


Fig. 2 Correlation between concentrations of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ , and Ca in hot spring waters from Tokyo area.

● : NaCl type, ■ : NaHCO<sub>3</sub> type, ○ : simple alkaline type.

and the second column were combined and packed into a canister for  $^{226}\text{Ra}$  analysis with the view of reducing counting duration in case of a large number of samples. The concentration of  $^{226}\text{Ra}$  in this seawater sample was  $1.1 \text{ mBq} \cdot \text{l}^{-1}$ . Concentration of  $^{226}\text{Ra}$  in seawater could be estimated by the amounts of  $^{226}\text{Ra}$  collected on the combined Mn-impregnated acrylic fiber of the first and second columns, and the volume of sample water. This procedure will result in an underestimation of a few percent of  $^{226}\text{Ra}$  content, though it is in the order of magnitude of the counting error for  $\gamma$ -ray spectrometry. The presently observed concentrations of  $^{226}\text{Ra}$  in surface seawaters from Tokyo Bay are similar to those in previous results (Yamada and Nozaki, 1986).

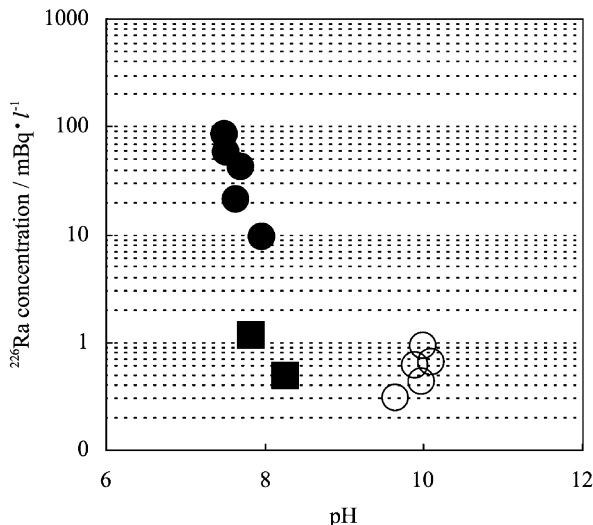


Fig. 3 Correlation between concentrations of  $^{226}\text{Ra}$  and pH of hot spring water from Tokyo area.

● : NaCl type, ■ :  $\text{NaHCO}_3$  type, ○ : simple alkaline type.

### 3.2 Hot spring water

Table 1 lists concentrations of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in hot spring waters classified by chemical characteristics along with the depth of bore-hole of respective hot spring. The concentrations of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in the hot spring waters ranged from 0.3 to  $84 \text{ mBq} \cdot \text{l}^{-1}$  and from 0.2 to  $104 \text{ mBq} \cdot \text{l}^{-1}$ , respectively. The average concentrations were  $39 \text{ mBq} \cdot \text{l}^{-1}$  for  $^{226}\text{Ra}$  and  $55 \text{ mBq} \cdot \text{l}^{-1}$  for  $^{228}\text{Ra}$  in NaCl type, and  $0.6 \text{ mBq} \cdot \text{l}^{-1}$  for  $^{226}\text{Ra}$  and  $0.8 \text{ mBq} \cdot \text{l}^{-1}$  for  $^{228}\text{Ra}$  in simple alkaline type, indicating that the concentrations of Ra isotopes in NaCl type were 70 times higher than those in simple alkaline type.

Table 2 lists the reported concentrations of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in hot spring waters from Japan classified by NaCl type and simple alkaline type. The  $^{226}\text{Ra}$  concentration in hot spring water in Tables 1 and 2 ranged from 2 to  $351 \text{ mBq} \cdot \text{l}^{-1}$  for NaCl type and from 0.3 to  $25 \text{ mBq} \cdot \text{l}^{-1}$  for simple alkaline type, and the averaged concentration was  $74 \text{ mBq} \cdot \text{l}^{-1}$  for NaCl type and  $4.8 \text{ mBq} \cdot \text{l}^{-1}$  for simple alkaline type, also indicating that the concentrations of  $^{226}\text{Ra}$  in NaCl type were much higher than those in simple alkaline type and that the concentrations of Ra isotopes may be dependent on the chemical characteristics of hot spring water.

Smaller activity ratios of  $^{228}\text{Ra}/^{226}\text{Ra}$  in hot spring waters from Nomekoi-no-yu, Tsuru-no-yu, Nakanomiya, Arima 1 and Arima 2 suggest that these hot spring waters are older than the others (Nakano-Ohta and Sato, 2005).

Figure 2 shows the correlation between the observed concentrations of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  and the concentration of Ca for hot spring waters from Tokyo area (Kanroji, 2005, *priv. com.*). The correlation coefficient ( $r^2$ ) between concentration of  $^{226}\text{Ra}$  and concentration of Ca is 0.86. The good correlation between concentrations of Ra isotopes and Ca suggests that Ra isotopes may have been leached chemically from the rocks in the aquifer. Figure 3 shows the variation



in the concentration of <sup>226</sup>Ra with pH values. The average pH values are 7.7 for NaCl type and 9.9 for simple alkaline type, indicating that the hot spring water with lower pH contains higher concentration of Ra isotopes, suggesting that the leaching process mentioned above may be controlled by pH of hot spring waters.

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