

原 著

## Geochemical Study of Water and Gas Samples from Funagoya Spa in Fukuoka Prefecture, Japan

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### 福岡県船小屋温泉の温泉水とガス成分の地球化学的研究

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#### 要 旨

福岡県筑後市の船小屋温泉およびみやま市の長田鉱泉から湧出する鉱泉水、炭酸成分および希ガスの起源を明らかにするために、鉱泉水および付随ガスの化学・同位体分析を行った。鉱泉水の安定同位体組成 ( $\delta D$  および  $\delta^{18}O$ ) から、船小屋温泉および長田鉱泉の鉱泉水はいずれも天水起源であることが示された。また、付随ガス中の  $^3\text{He}/^4\text{He}$  比と  $^4\text{He}/^{20}\text{Ne}$  比の関係より、船小屋温泉水中には大気起源 He の混入はほとんどなく、マントル起源および地殻起源の He が混合したものであることが示された (マントル起源 He : 60%, 地殻起源 He : 40%, 大気起源 He : 0.1% 以下)。C/ $^3\text{He}$  と  $\delta^{13}\text{C}$  の関係より、付随ガス中の  $\text{CO}_2$  に占める炭素の起源を推算したところ、マントル起源  $\text{CO}_2$  (Mantle derived  $\text{CO}_2$ ) が 35%, 海成炭酸塩起源  $\text{CO}_2$  (Marine carbonate  $\text{CO}_2$ ) が 56%, 堆積有機炭素 (Sedimentary organic carbon) が 9% という結果が得られた。さらに、付随ガス中の  $\text{CH}_4/(\text{C}_2\text{H}_6 + \text{C}_3\text{H}_8)$  比と  $\text{CH}_4$  中の  $\delta^{13}\text{C}$  の解析により、付随ガス中の  $\text{CH}_4$  は地下深部における有機物の熱分解によって生じたことが示唆された。

キーワード：炭酸泉、ヘリウム、全溶存炭酸、安定同位体、起源、筑後平野

#### Abstract

We studied mineral water and associated gases of Funagoya spa, and mineral water of Nagata spa, in Fukuoka Prefecture to identify the sources of their respective waters, inorganic carbon components, and noble gases. The stable isotope composition ( $\delta D$  and  $\delta^{18}O$ ) of the mineral waters showed that the waters of the Funagoya and Nagata spas originate from rainwater. However, the relation between the  $^3\text{He}/^4\text{He}$  ratio and  $^4\text{He}/^{20}\text{Ne}$  ratio in the

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associated gases indicates that He flowing out from Funagoya spa contains almost no He derived from the atmosphere : it originates from deep underground (mantle-derived He, 60% ; crustal He, 40%). Furthermore, the relation between  $C/{}^3\text{He}$  and  $\delta^{13}\text{C}$  in the associated gases shows that mantle-derived  $\text{CO}_2$  accounts for 35%, deep subducted marine carbonate for 56%, and sedimentary organic carbon for 9%. Furthermore, analyses of the  $\text{CH}_4/(\text{C}_2\text{H}_6 + \text{C}_3\text{H}_8)$  ratio and the  $\delta^{13}\text{C}$  of  $\text{CH}_4$  in the associated gases suggests that the  $\text{CH}_4$  from the Funagoya spa is produced from thermogenic decomposition of deep organic sediments.

Key words : Carbonate spring, helium, dissolved inorganic carbon, stable isotope, origin, Chikugo plain

## 1. Introduction

Fukuoka Prefecture's Funagoya and Nagata spas are well-known carbonated springs in Japan. They were discovered by the Arima Clan during the late Edo Period (1810) on the north side of the Yabe River, and by the Yanagawa/Tachibana Clans on the south side of the river (Urakawa, 2011). The respective spas prospered during the Meiji to the Showa Periods, with peak visitation by as many as 20,000 bathers annually. Dozens of mineral spring wells have been drilled on both sides of the river, including those at the Funagoya and Nagata spas (Urakawa, 2011). The dissolved inorganic carbon (DIC) concentration covers a wide range from about 50 ppm to 1,000 ppm or more (Urakawa, 2011). In recent years, the springs have attracted attention for the medical effects of their high DIC (namely  $\text{CO}_2$ ) concentrations. Associated gases are discharged together with mineral waters from the most deeply drilled wells in the Funagoya spa area.

The DIC of the mineral waters, a particularly interesting characteristic of the Funagoya and Nagata spas, is probably attributable to the decomposition of organic matter by methanogens, under anaerobic conditions, buried at a depth of a few hundred meters underground (Urakawa, 2011). However, that inference has not been proven. Many unclear aspects remain. For this study, samples of mineral waters and associated gases discharged from Funagoya and Nagata spas were examined to ascertain, based on the samples' chemical and isotopic composition, the water sources and their inorganic carbonate components and noble gases.

## 2. Sampling and analyses

On 1 November 2010, mineral water and accompanying bubble gases were sampled at Funagoya spa (point A), and mineral water was collected from Nagata spa (point B, Fig. 1). The water temperature and pH were measured at the sites. The water samples were subjected to chemical analyses of the major components and dissolved inorganic carbon ( $\text{DIC} = \text{CO}_{2(\text{aq})} + \text{HCO}_3^- + \text{CO}_3^{2-}$ ), stable isotope analysis of water ( $\delta\text{D}$  and  $\delta^{18}\text{O}$ ), and carbon stable isotope measurement of DIC ( $\delta^{13}\text{C}$ ) using the method described by Sakai *et al.* (2011). The respective measurement precisions of isotope analyses for  $\delta\text{D}$ ,  $\delta^{18}\text{O}$ , and  $\delta^{13}\text{C}$  were  $\pm 1.0\text{‰}$ ,  $\pm 0.1\text{‰}$ , and  $\pm 0.2\text{‰}$ .

Bubble gases were collected using the following three techniques [**Gas samples 1-3**] in accordance with the items that were analyzed.

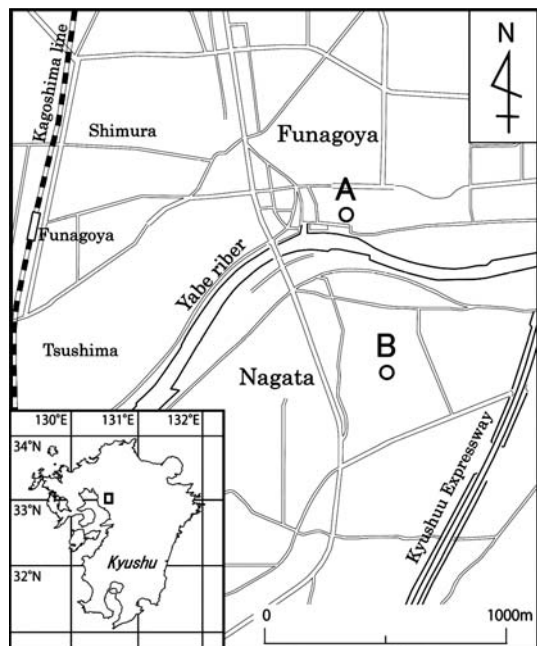


Fig. 1 Mineral springs investigated in this study :  
A, Funagoya spa ; B, Nagata spa.

**[Gas sample 1]** Gas bubbles were temporarily trapped in a soft plastic bag (equipped with cocks) using a plastic funnel of about 20 cm diameter. The gas was transferred immediately to a gas collection vessel (a large glass syringe) containing 5M KOH aqueous solution. The carbon dioxide gas ( $\text{CO}_2$ ), which is thought to constitute most of the volume of gases, was thereby absorbed into the alkali solution. Through repeated collection, it was possible to obtain an adequate volume of the gas component that had not been absorbed into the alkali solution (residual gas, 'R gas'). The gas was then brought back to the laboratory. Chemical composition data for  $\text{CO}_2$ ,  $\text{N}_2$ , Ar, He,  $\text{H}_2$ ,  $\text{CH}_4$ , and  $\text{O}_2$  were obtained from these samples. In accordance with Iwakura *et al.* (2000),  $\text{CO}_2$  was measured from the alkali solution using the  $\text{CO}_2$  electrode method. However,  $\text{N}_2$ , Ar, He,  $\text{H}_2$  and  $\text{CH}_4$

were analyzed using a gas chromatograph using  $\text{O}_2$  as the carrier gas. The  $\text{O}_2$  in the gas sample was obtained by calculating, based on the ideal gas state equation using those analysis values, the R gas volume, the atmospheric temperature, and the pressure inside the laboratory. Then the  $\text{CO}_2$  that had been absorbed into the alkali solution was reacted with  $\text{Sr}(\text{OH})_2$ , thereby isolating it as  $\text{SrCO}_3$  for carbon stable isotope measurements ( $\delta^{13}\text{C}$ ) using the same method as that used for DIC.

**[Gas sample 2]** A funnel was used to collect gas bubbles directly, together with a small amount of hot spring water, in a 10 mL or 20 mL glass bottle with a rubber septum. Using the method described in Ohsawa *et al.* (2010), data of the relative composition of  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$  with respect to  $\text{CH}_4$  were obtained from the sample, as were data related to the carbon stable isotope ratio ( $\delta^{13}\text{C}$ ) of these compounds. During transport and storage, external air was blocked by tipping the glass bottle onto its side and setting it so that the connection point with the septum was sealed with hot spring water, thereby preventing sample gas leakage and air contamination.

**[Gas sample 3]** Gas bubbles were collected, using a funnel, into a Pyrex glass gas-sampling bottle equipped with a stop cock on both ends. Data for the  $^3\text{He}/^4\text{He}$  ratio and  $^4\text{He}/^{20}\text{Ne}$  ratio were obtained from this sample using a magnetic sector mass spectrometer by the Environment Department of Kyuden Sangyo Co., Inc. The respective uncertainty errors in the  $^3\text{He}/^4\text{He}$  ratio and  $^4\text{He}/^{20}\text{Ne}$  were estimated as 1% and 10%.

Table 1 Chemical and isotopic data of spring waters and bubble gases in Funagoya and Nagata mineral springs, Fukuoka Prefecture.

		Funagoya	Nagata
spring waters	Water temp (°C)	23.5	23.1
	pH	5.6	5.0
	Na (mg/L)	63.5	14.8
	K (mg/L)	3.9	2.4
	Mg (mg/L)	21.8	4.1
	Ca (mg/L)	22.0	23.2
	Cl (mg/L)	18.4	16.5
	SO <sub>4</sub> (mg/L)	8.9	17.1
	HCO <sub>3</sub> (mg/L)	217	64.8
	DIC (mg/L)	1000 as CO <sub>2</sub>	1200 as CO <sub>2</sub>
	$\delta$ D H <sub>2</sub> O (‰)	-43.9	-43.5
	$\delta$ <sup>18</sup> O H <sub>2</sub> O (‰)	-7.54	-6.55
	$\delta$ <sup>13</sup> C DIC (‰)	-6.99	-7.38
bubble gases	CO <sub>2</sub> (%)	91.2	
	N <sub>2</sub> (%)	6.95	
	CH <sub>4</sub> (%)	1.73	
	Ar (%)	0.043	
	O <sub>2</sub> (%)	0.031	
	He (ppm)	68	
	C <sub>2</sub> H <sub>6</sub> (ppm)	25	
	H <sub>2</sub> (ppm)	3.5	
	C <sub>3</sub> H <sub>8</sub> (ppm)	0.9	
	$\delta$ <sup>13</sup> C CO <sub>2</sub> (‰)	-4.13	
	$\delta$ <sup>13</sup> C CH <sub>4</sub> (‰)	-43.1	
	$\delta$ <sup>13</sup> C C <sub>2</sub> H <sub>6</sub> (‰)	-39.2	
	<sup>3</sup> He/ <sup>4</sup> He	6.64 × 10 <sup>-6</sup>	
<sup>4</sup> He/ <sup>20</sup> Ne	273		

### 3. Results and discussion

Table 1 presents results of chemical and isotope analyses of the samples of the spring waters and the associated bubble gas. Just like Nagata spa, the Funagoya spa is a mineral spring with water temperature of less than 25°C. The hydrogen/oxygen stable isotope compositions of the spring waters (Table 1) roughly resemble those of meteoric water ( $\delta$  D = 8  $\delta$  <sup>18</sup>O + 10; Craig, 1961), thereby indicating that these are shallow ground waters derived from rainwater. The Funagoya spa is classified as a carbonated spring (HCO<sub>3</sub> type), as is the Nagata spa. The Funagoya spring water has Na-HCO<sub>3</sub> type water quality, indicating that the ground water has undergone considerable geochemical evolution. However, the main cation in the Nagata spring water is Ca, indicating that the initial water quality of the shallow ground water. The major component of the associated gas of the Funagoya spring water is CO<sub>2</sub>, but it does not contain negligible amounts of CH<sub>4</sub> (Table 1). Therefore, it appears that methane fermentation (2CH<sub>2</sub>O → CH<sub>4</sub> +

CO<sub>2</sub>) of sedimentary organic compounds is involved in the formation of the carbonate spring. One might infer that the spring water is shallow ground water of meteoric origin which has undergone some process of hydrochemical evolution. Nevertheless, the geochemical characteristics of the He and CO<sub>2</sub> in the associated gas indicate that the origin of the spring water is not so simple.

Figure 2 [A] shows the <sup>3</sup>He/<sup>4</sup>He ratio and <sup>4</sup>He/<sup>20</sup>Ne ratios of the associated gas of the Funagoya spring water (Table 1), as displayed on a <sup>3</sup>He/<sup>4</sup>He-<sup>4</sup>He/<sup>20</sup>Ne diagram, as in the case of the Hitoyoshi Basin Hot Springs (Ohsawa *et al.*, 2011). When the model calculation method described in Shimizu *et al.* (2005) was used to find the contribution rates of He types from different sources in the associated gas, the results revealed that mantle-derived He accounted for 60%, crustal He for 40%, and atmospheric He for 0.1% or less.

The δ<sup>13</sup>C value for CO<sub>2</sub> (-4.13 ‰ : 2.86 ‰ heavy with respect to DIC attributable to isotope fractionation accompanying gas liberation) reveals that the water contains deep-origin CO<sub>2</sub>. However, the possibility cannot be denied, based on δ<sup>13</sup>C only, that CO<sub>2</sub> is derived from material containing marine carbonate and sedimentary organic carbon. Therefore, this point was investigated by plotting the data on a graph of C/<sup>3</sup>He versus δ<sup>13</sup>C (Sano and Marty, 1995) (Fig. 2 [B]). Just as in the case of He, the contribution rates of carbon from different sources in CO<sub>2</sub> of the associated gas can be estimated (Sano and Marty, 1995). Results show that mantle-derived CO<sub>2</sub> accounted for 35%, marine carbonate was 56% and sedimentary organic carbon was 9%. As explained

above, most He and CO<sub>2</sub> in associated gases were of deep origin, which attests to the fact that these gases, rising from deep underground, flow into a shallow groundwater system and thereby

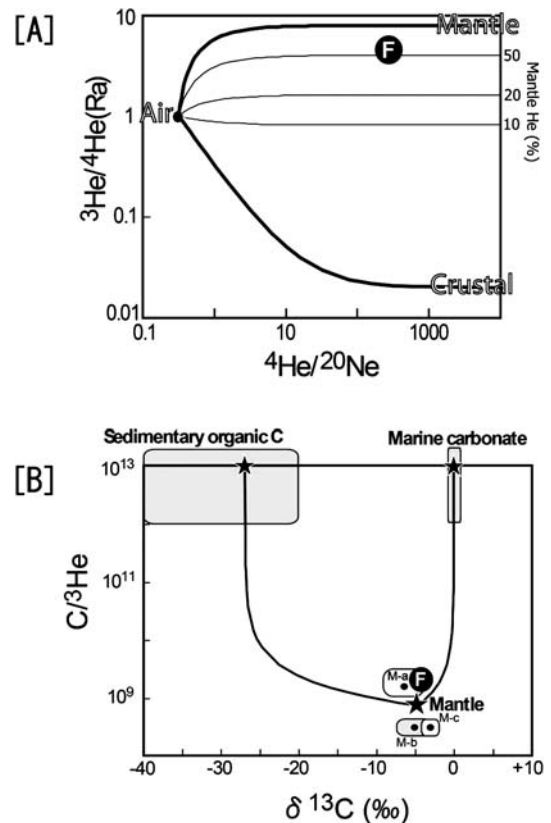


Fig. 2 [A] Plot of <sup>3</sup>He/<sup>4</sup>He versus <sup>4</sup>He/<sup>20</sup>Ne ratios for the Funagoya gas sample obtained for this study. The upper thick line represents the mixing line between air and upper mantle components. The lower thick line is a mixing line for air and crust components. The three medium lines show trajectories for mixing between air and deep-originated gas for various mantle helium components of 10, 20, and 50%. F, Funagoya spa ; B, Nagata spa.

[B] Correlation between C/<sup>3</sup>He ratio and δ<sup>13</sup>C of DIC for the Funagoya sample. The figure also shows model end members for mantle (M-a, Sano and Marty, 1995 ; M-b, Deines, 2002 ; M-c, Nishio *et al.*, 1998), marine carbonate (Sano and Marty, 1995), and sedimentary organic carbon (mean value of those described in Sano and Marty (1995), Deines (2002), and Nishio *et al.* (1998)). The tie lines of the model end members are mixing lines. F, Funagoya spa.

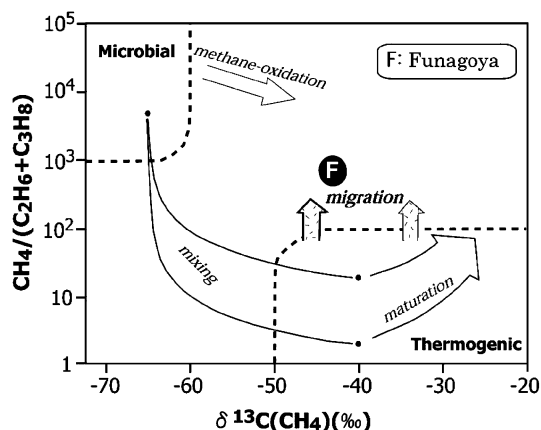


Fig. 3  $\delta^{13}\text{C}$  of  $\text{CH}_4$  and the  $\text{CH}_4/(\text{C}_2\text{H}_6 + \text{C}_3\text{H}_8)$  ratio of the gas sample from Funagoya spa expressed as the Barnard Diagram, which is generally used for discrimination of origin of  $\text{CH}_4$  and interpretation of physical and chemical processes of hydrocarbon gases. F, Funagoya spa.

produce a carbonated spring.

Figure 3 portrays an agrochemical discrimination diagram, called a 'Barnard Diagram', which is widely used in the field of organic geochemistry (Ohsawa *et al.*, 2010). The diagram shows the  $(\text{CH}_4/(\text{C}_2\text{H}_6 + \text{C}_3\text{H}_8))$  ratio against  $\delta^{13}\text{C}$  of  $\text{CH}_4$ , thereby enabling one to trace transitions in physicochemical processes such as the  $\text{CH}_4$  origin and the maturation process of hydrocarbon gases. The  $\text{CH}_4$  in gases from Funagoya spa is produced by thermogenic decomposition of shallow organic sediments, as explained by assuming that  $\text{CH}_4$  produced deep underground has migrated to the surface. Even if  $\text{CO}_2$  were produced by the microbial oxidation of methane, it would retain the same chemical and isotopic compositions as  $\text{CH}_4$ . However, as

demonstrated by Waseda *et al.* (2002), a great difference exists between the  $\delta^{13}\text{C}$  of  $\text{CO}_2$  and that of  $\text{CH}_4$  (see Table 1). Therefore, they are unlikely to have similar origin. It seems reasonable to infer that hydrocarbon gases including  $\text{CH}_4$  are added to the shallow groundwater from some external source, as are He and  $\text{CO}_2$ .

In future studies, the authors would like to conduct a similar investigation of other carbonated springs around the Chikugo River in the Tsukushi Plain, with characteristics reportedly resembling those of the Funagoya spa (Urakawa, 2011).

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