Geochemical, stable isotope, and numerical modeling studies of *sake* and groundwater for identification of the location of *sake* production: A case study from Hakusan City, Japan

SHINGO TOMIYAMA,^{1*} TOMOKAZU HASHIGUCHI,² AKIRA UEDA,³ AKIKO KITAI,¹ HANAE IZU² and SHIGETOSHI SUDO²

¹Mitsubishi Materials Techno Corporation, 1-297 Kitabukuro-cho, Omiya-ku, Saitama 330-0835, Japan

²Safety and Quality Research Division, National Research Institute of Brewing,
3-7-1 Kagamiyama, Higashi-hiroshima, Hiroshima 739-0046, Japan

³Graduate School of Science and Engineering, University of Toyama, Gofuku 3190, Toyama 930-8555, Japan

(Received May 6, 2012; Accepted August 1, 2013)

Understanding the source and chemical characteristics of groundwater used for *sake* production is an important strategy for the quality management of *sake* brewing. Oxygen isotope ratios ($\delta^{18}\text{O}$) of 96 *sake* samples from 19 provinces in Japan were analyzed. A good correlation was found between the *sake* $\delta^{18}\text{O}$ values and groundwater $\delta^{18}\text{O}$ values taken from previously published data, where the $\delta^{18}\text{O}$ of *sake* is similar to that of the groundwater used in the *sake* breweries.

Detailed sampling of 19 *sake* and groundwater samples was conducted near a *sake* brewery in the Hokuriku district, central northern Japan (Ishikawa and Toyama Prefectures). The $\delta^{18}\text{O}$ of *sake* and groundwater in the area also showed a good correlation. Our findings indicate that the $\delta^{18}\text{O}$ of *sake* can be used to identify the locality of *sake* production. This has the potential to help prevent fraudulent representation of the area of production.

Water chemistry, hydrogen (δD) and oxygen ($\delta^{18}\text{O}$) isotopes of two groundwater and eighteen river water samples in Hakusan City, Ishikawa Prefecture, were analyzed to determine their origin and water flow patterns. The groundwater is of a Ca-HCO_3 type similar to river water. The results show that the groundwater used to produce the “Hakusan” brand of *sake* originates from river water at an altitude of 360 to 450 m. This is supported by groundwater flow modeling, which also indicates that the water was sourced 2–3 km away from the *sake* brewery. The combined geochemical and numerical modeling approach provides a good tool for determining the source of groundwater used in *sake* production.

Keywords: *sake*, oxygen isotope, Ishikawa, groundwater, modeling

INTRODUCTION

Large quantities of good quality groundwater are used for *sake* brewing. Groundwater contains several dissolved chemical components. Potassium is known to promote yeast fermentation, and calcium aids the extraction of *koji* enzymes (Brewing Society of Japan, 1996). The quality of *sake* is affected by the chemical composition of the local groundwater used in the brewing process. In recent times, fraudulent representation of the location of *sake* production and other products in the food sector has increased. Trace element and DNA analyses have been used to trace the origins of food products (e.g., Dion *et al.*, 2008; Adamo *et al.*, 2012), as well as stable isotope ratio analyses of light elements (Ueki, 2008; Nakashita *et al.*, 2008; Suzuki *et al.*, 2008). In addition, consumers are

increasingly expecting disclosure of the source of groundwater used for beverage production. Case studies of mineral waters from the flank of Mt. Fuji and the Gifu and Kanto plains have been conducted, including analysis of the stable isotopic compositions and numerical modeling of groundwater and river waters (e.g., Tomiyama *et al.*, 2009, 2010, 2011). However, a detailed study for *sake* has not yet been undertaken. Regulations have been put in place requiring producers to provide geographical information on bottle labels for the purpose of establishing regional brands and to provide appropriate information to consumers (National Tax Agency Notice No. 4, December 28, 1994). The *sake* brewed and manufactured in Hakusan City, in the northern part of central Japan is known by the brand name “Hakusan.”

There are many previous studies that traced the geographical sources of foods including water, wine, and milk by using multi-elemental and multi-isotope analyses (e.g., Kelly *et al.*, 2005; Marisa *et al.*, 2004; Chesson *et al.*, 2010). Crittenden *et al.* (2007) evaluated the suitability of multi-element isotope ratio analysis for determining

*Corresponding author (e-mail: tomiyama@mmc.co.jp)

Table 1. $\delta^{18}\text{O}$ values of sake in Japan

Sample No.	Sampling date*	Locality	$\delta^{18}\text{O}$ of sake (observed)	$\delta^{18}\text{O}$ of groundwater and river water** (estimated)
G11-26	17-Jan-2011	Asahikawa, Hokkaido	-11.5	-12.0
G11-30	17-Jan-2011	Oosaki, Miyagi	-9.4	-8.0
G11-31	17-Jan-2011	Oosaki, Miyagi	-9.5	-8.0
G11-32	17-Jan-2011	Oosaki, Miyagi	-9.6	-8.0
G11-33	17-Jan-2011	Oosaki, Miyagi	-8.6	-8.0
G11-34	17-Jan-2011	Nihonmatsu, Fukushima	-10.5	-9.0
G10-2195	3-Nov-2010	Nihonmatsu, Fukushima	-10.4	-9.0
G11-294	17-Jan-2011	Koriyama, Fukushima	-9.9	-9.0
G11-35	17-Jan-2011	Niigata, Niigata	-10.9	-10.0
G11-36	17-Jan-2011	Kashiwazaki, Niigata	-9.5	-10.0
G11-458	24-Jan-2011	Shibata, Niigata	-10.6	-10.0
G11-37	17-Jan-2011	Oume, Tokyo	-9.4	-9.0
G11-38	17-Jan-2011	Oume, Tokyo	-9.4	-9.0
G11-21	17-Jan-2011	Toyama, Toyama	-11.5	-10.0
G11-22	17-Jan-2011	Kurobe, Toyama	-11.7	-10.0
G10-2189	3-Nov-2010	Kaga, Ishikawa	-9.4	-9.0
G10-2190	3-Nov-2010	Kusu, Ishikawa	-8.9	-9.0
G10-2191	3-Nov-2010	Kanazawa, Ishikawa	-9.2	-9.0
G10-3312	17-Jan-2011	Kanazawa, Ishikawa	-9.9	-9.0
G10-3313	17-Jan-2011	Kanazawa, Ishikawa	-10.2	-9.0
G10-3314	17-Jan-2011	Kanazawa, Ishikawa	-9.0	-9.0
G10-3315	17-Jan-2011	Kanazawa, Ishikawa	-9.1	-9.0
G10-3316	17-Jan-2011	Kanazawa, Ishikawa	-9.5	-9.0
G10-3317	17-Jan-2011	Kanazawa, Ishikawa	-9.4	-9.0
G10-3307	17-Jan-2011	Kanazawa, Ishikawa	-10.2	-9.0
G10-2186	3-Nov-2010	Hakusan, Ishikawa	-8.8	-9.0
G10-2187	3-Nov-2010	Hakusan, Ishikawa	-9.3	-9.0
G10-2188	3-Nov-2010	Hakusan, Ishikawa	-9.5	-9.0
G10-2192	3-Nov-2010	Hakusan, Ishikawa	-9.3	-9.0
G10-2193	3-Nov-2010	Hakusan, Ishikawa	-9.4	-9.0
G10-3113	17-Jan-2011	Hakusan, Ishikawa	-8.8	-9.0
G10-3114	17-Jan-2011	Hakusan, Ishikawa	-8.7	-9.0
G10-3115	17-Jan-2011	Hakusan, Ishikawa	-9.1	-9.0
G10-3116	17-Jan-2011	Hakusan, Ishikawa	-8.8	-9.0
G10-3117	17-Jan-2011	Hakusan, Ishikawa	-8.2	-9.0
G10-3128	17-Jan-2011	Hakusan, Ishikawa	-9.3	-9.0
G10-3129	17-Jan-2011	Hakusan, Ishikawa	-9.4	-9.0
G10-3130	17-Jan-2011	Hakusan, Ishikawa	-9.5	-9.0
G10-3131	17-Jan-2011	Hakusan, Ishikawa	-9.0	-9.0
G10-3132	17-Jan-2011	Hakusan, Ishikawa	-9.4	-9.0
G10-3301	17-Jan-2011	Hakusan, Ishikawa	-9.2	-9.0
G10-3302	17-Jan-2011	Hakusan, Ishikawa	-9.4	-9.0
G10-3303	17-Jan-2011	Hakusan, Ishikawa	-9.4	-9.0
G10-3304	17-Jan-2011	Hakusan, Ishikawa	-9.3	-9.0
G10-3305	17-Jan-2011	Hakusan, Ishikawa	-9.5	-9.0
G10-2194	17-Jan-2011	Hakusan, Ishikawa	-9.1	-9.0
G10-3118	17-Jan-2011	Hakusan, Ishikawa	-9.2	-9.0
G10-3119	17-Jan-2011	Hakusan, Ishikawa	-9.2	-9.0
G10-3120	17-Jan-2011	Hakusan, Ishikawa	-9.3	-9.0
G10-3121	17-Jan-2011	Hakusan, Ishikawa	-9.5	-9.0
G10-3122	17-Jan-2011	Hakusan, Ishikawa	-9.2	-9.0
G10-3123	17-Jan-2011	Hakusan, Ishikawa	-8.8	-9.0
G10-3124	17-Jan-2011	Hakusan, Ishikawa	-8.7	-9.0
G10-3125	17-Jan-2011	Hakusan, Ishikawa	-9.0	-9.0
G10-3126	17-Jan-2011	Hakusan, Ishikawa	-9.0	-9.0
G10-3127	17-Jan-2011	Hakusan, Ishikawa	-8.9	-9.0
G10-3306	17-Jan-2011	Noto, Ishikawa	-8.7	-9.0
G10-3308	17-Jan-2011	Noto, Ishikawa	-8.8	-9.0
G10-3309	17-Jan-2011	Nomi, Ishikawa	-9.6	-9.0
G10-3310	17-Jan-2011	Tsubata, Ishikawa	-8.7	-9.0

Table 1. (continued)

Sample No.	Sampling date*	Locality	$\delta^{18}\text{O}$ of <i>sake</i> (observed)	$\delta^{18}\text{O}$ of groundwater and river water** (estimated)
G11-23	17-Jan-2011	Katuyama, Fukui	-9.4	-9.0
G11-24	17-Jan-2011	Obama, Fukui	-8.9	-9.0
G11-25	17-Jan-2011	Fukui, Fukui	-9.4	-9.0
G11-27	17-Jan-2011	Kiso, Nagano	-11.0	-12.0
G11-28	17-Jan-2011	Suwa, Nagano	-12.0	-11.0
G11-29	17-Jan-2011	Ina, Nagano	-10.6	-11.0
G11-306	24-Jan-2011	Nirasaki, Yamanashi	-10.5	-10.0
G11-297	17-Jan-2011	Tajimi, Gifu	-9.1	-9.0
G11-299	17-Jan-2011	Mizunami, Gifu	-9.0	-9.0
G11-298	17-Jan-2011	Hazu, Aichi	-8.1	-9.0
G11-302	24-Jan-2011	Kyoto, Kyoto	-7.7	-7.5
G11-307	24-Jan-2011	Kyoto, Kyoto	-7.9	-8.0
G11-301	24-Jan-2011	Nishinomiya, Hyogo	-7.4	-7.5
G11-452	24-Jan-2011	Nishinomiya, Hyogo	-7.6	-8.0
G11-453	24-Jan-2011	Nishinomiya, Hyogo	-7.5	-8.0
G11-454	24-Jan-2011	Kobe, Hyogo	-7.5	-8.0
G11-455	24-Jan-2011	Kobe, Hyogo	-8.0	-8.0
G11-456	24-Jan-2011	Kobe, Hyogo	-7.8	-8.0
G11-303	17-Jan-2011	Tsuyama, Okayama	-8.3	-8.0
G11-304	17-Jan-2011	Tsuyama, Okayama	-8.3	-8.0
G11-305	17-Jan-2011	Tsuyama, Okayama	-7.9	-8.0
G11-451	24-Jan-2011	Futukaichi, Hiroshima	-8.0	-8.0
G10-2888	11-Jan-2011	Higashi-hiroshima, Hiroshima	-7.7	-8.0
G10-2889	11-Jan-2011	Higashi-hiroshima, Hiroshima	-7.7	-8.0
G10-2890	11-Jan-2011	Higashi-hiroshima, Hiroshima	-7.6	-8.0
G10-2891	11-Jan-2011	Higashi-hiroshima, Hiroshima	-7.6	-8.0
G10-2892	11-Jan-2011	Higashi-hiroshima, Hiroshima	-7.8	-8.0
G11-457	24-Jan-2011	Higashi-hiroshima, Hiroshima	-8.4	-8.0
G11-308	24-Jan-2011	Higashi-hiroshima, Hiroshima	-8.4	-8.0
G10-2196	3-Nov-2010	Yasuda, Kochi	-7.4	-7.0
G11-39	17-Jan-2011	Sagawa, Kochi	-7.3	-7.0
G11-40	17-Jan-2011	Sagawa, Kochi	-7.5	-7.0
G11-295	17-Jan-2011	Kami, Kochi	-7.3	-7.0
G11-296	17-Jan-2011	Kochi, Kochi	-8.1	-7.0
G11-300	24-Jan-2011	Kumamoto, Kumamoto	-7.3	-7.5
G11-459	24-Jan-2011	Uruma, Okinawa	-5.7	-4.9

*Collected sake samples bottled at the sake brewery.

**The $\delta^{18}\text{O}$ values of nearby groundwater and rivers were estimated from figure 3 of Mizota and Kusakabe (1994) and averaged data from Agata *et al.* (2001).

the source of cow milk produced in Australasia. They showed that the oxygen isotope ratio ($\delta^{18}\text{O}$) and carbon isotope ratio ($\delta^{13}\text{C}$) reflected isotopic variations due to latitudinal and climatic variability in different regions, and concluded that isotope analysis can help identify the geographic source of dairy products. Papesch and Horacek (2009) examined the $\delta^{18}\text{O}$ of water in beer and demonstrated that a sample of beer labeled as premium brand was, in reality, an inferior brand. Suzuki *et al.* (2008) examined the carbon and nitrogen contents and the $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and ($\delta^{14}\text{N}$) isotope ratio of polished rice in order to develop a simple method to determine its geographical source. They showed that such chemical and isotopic parameters were potentially useful for rapid and regular dis-

crimination of geographical source of the polished rice.

In this study, the $\delta^{18}\text{O}$ of *sake* samples from all over Japan were analyzed for the first time. The $\delta^{18}\text{O}$ of the *sake* samples was compared to the $\delta^{18}\text{O}$ values reported in the literature for shallow groundwater and river water near the *sake* breweries (Mizota and Kusakabe, 1994; Agata *et al.*, 2001). A detailed analysis of the $\delta^{18}\text{O}$ of *sake* and the $\delta^{18}\text{O}$, hydrogen isotopes (δD), and other geochemical characteristics of groundwater samples from the Hokuriku district, northern central Japan, was also conducted. The data were used to determine the source of groundwater used for brewing “Hakusan” *sake*. Numerical modeling was also applied to estimate the history of the groundwater used in the *sake* brewery.

Fig. 1. Locations of sake samples in this study. The study area (Hokuriku district) is shown in the inset.

Fig. 2. Locality of sake and groundwater samples in the Hokuriku district. The $\delta^{18}\text{O}$ values of groundwaters are divided into 6 groups as shown by marks with an interval of 0.5‰. The Hakusan area is shown in the inset.

SAKE AND GROUNDWATER SAMPLE LOCATIONS

Ninety six *sake* samples were collected in Japan during November 2010 to January 2011 (Fig. 1) and analyzed for $\delta^{18}\text{O}$. These were then compared with $\delta^{18}\text{O}$ values of groundwater and river water reported by Mizota and Kusakabe (1994) and Agata *et al.* (2001) (Table 1). We found a good correlation between the $\delta^{18}\text{O}$ of *sake* and groundwater collected in the same area.

Nineteen *sake* and groundwater samples were obtained from 17 *sake* breweries in central northern Japan (Ishikawa and Toyama Prefectures) in April–May 2011 (Table 2 and Fig. 2). In order to examine the source of groundwater and the mode of water flow around the *sake* brewery, two groundwaters and eighteen river waters were collected in Hakusan City, Ishikawa Prefecture (Table 3 and Fig. 3) for chemical and stable isotope analyses (δD and $\delta^{18}\text{O}$). The river water samples are divided into three groups based on their location: alluvial fan (D–T), talus (DGf), or hill (AGf) (Table 3 and Fig. 3).

Hakusan City is located in the western part of Ishikawa prefecture alongside the Tedori River. This river flows within the Tedori alluvial fan, which spreads between Nomi City and the southern part of Kanazawa City. Figure 3 shows the study area and water sampling sites. The alluvial fan has an area of 191 km² and its catchment area is greater than 750 km². The main fan has a concentric shape, and the elevation and slope of the ground are about

90 m and 1/130 at the top, and 5 m and 1/200 at the edge, respectively (Tsuchihara *et al.*, 2011). The basement of the study area consists of (from lower to upper layers): Miocene green tuff and rhyolite, Pleistocene sedimentary layers (lower layer of sand gravel (D–T), clay, and upper alluvial gravel (DGf)) and alluvial sand gravel deposits (AGf) (Hokuriku Agriculture Report, 1977). The groundwaters are also divided into three groups: D–T, DGf, and AGf. The groups DGf and AGf correspond to deep and shallow groundwaters, respectively (Watanabe, 2002).

There are ~20 *sake* breweries in the southern part of the Ishikawa prefecture, many of which operate in the Tedori alluvial fan. The *sake* brewery studied in this work is situated on the flank (190 m in altitude) of a hill along the Tedori River, 7 km inland from the tip of the fan (Fig. 3). The groundwater used in the brewery is pumped from a well 100 m deep.

ANALYTICAL PROCEDURES

At the sampling site, pH, electrical conductivity (EC), and oxidation reduction potential (ORP) were measured using a pH meter (Shindengen, KS-701), EC meter (Horiba, B-173), and ORP meter (TOA, RM-12P), respectively. Dissolved ion concentrations were measured using conventional methods. All geochemical water analy-

Table 2. $\delta^{18}\text{O}$ values of sake and groundwaters from the Hokuriku district. Numbers of sake brewery correspond to those in Fig. 2

Brewery No.	Locality	Sake			Groundwater		
		Sampling date*	Observed $\delta^{18}\text{O}$ (‰)	Averaged** $\delta^{18}\text{O}$ (‰)	Sampling date	Sample No.	Observed $\delta^{18}\text{O}$ (‰)
A	Wajima, Ishikawa	30-Apr-2011	-8.5	-8.7	30-Apr-2011	W-10	-8.1
A	Wajima, Ishikawa	30-Apr-2011	-8.7	-8.7	30-Apr-2011	W-10	-8.1
A	Wajima, Ishikawa	30-Apr-2011	-8.8	-8.7	30-Apr-2011	W-10	-8.1
B	Wajima, Ishikawa	30-Apr-2011	-8.2	-8.1	30-Apr-2011	W-12	-8.3
B	Wajima, Ishikawa	30-Apr-2011	-8.0	-8.1	30-Apr-2011	W-12	-8.3
C	Noto, Ishikawa	30-Apr-2011	-8.8	-8.1	30-Apr-2011	W-13	-8.3
D	Nakanoto, Ishikawa	1-May-2011	-9.0	-9.0	1-May-2011	W-14	-8.6
D	Nakanoto, Ishikawa	1-May-2011	-9.0	-9.0	1-May-2011	W-14	-8.6
E	Kaga, Ishikawa	3-Nov-2010	-9.4	-9.4	28-Apr-2011	W-1	-8.2
E	Kaga, Ishikawa	28-Apr-2011	-9.3	-9.4	28-Apr-2011	W-1	-8.2
E	Kaga, Ishikawa	28-Apr-2011	-9.5	-9.4	28-Apr-2011	W-1	-8.2
F	Kanzawa, Ishikawa	17-Jan-2011	-9.0	-9.1	28-Apr-2011	W-6	-8.2
F	Kanzawa, Ishikawa	17-Jan-2011	-9.1	-9.1	28-Apr-2011	W-6	-8.2
G	Kanzawa, Ishikawa	17-Jan-2011	-9.5	-9.4	1-May-2011	W-19	-8.9
G	Kanzawa, Ishikawa	17-Jan-2011	-9.4	-9.4	1-May-2011	W-19	-8.9
G	Kanzawa, Ishikawa	3-Nov-2010	-9.2	-9.4	1-May-2011	W-19	-8.9
H	Tsubata, Ishikawa	17-Jan-2011	-8.7	-8.7	28-Apr-2011	W-7	-8.2
H	Tsubata, Ishikawa	17-Jan-2011	-8.7	-8.7	28-Apr-2011	W-7	-8.2
I	Hakusan, Ishikawa	17-Jan-2011	-9.3	-9.3	28-Apr-2011	W-3	-9.0
I	Hakusan, Ishikawa	17-Jan-2011	-9.4	-9.3	28-Apr-2011	W-3	-9.0
I	Hakusan, Ishikawa	17-Jan-2011	-9.2	-9.3	28-Apr-2011	W-3	-9.0
I	Hakusan, Ishikawa	17-Jan-2011	-9.2	-9.3	28-Apr-2011	W-3	-9.0
I	Hakusan, Ishikawa	17-Jan-2011	-9.3	-9.3	28-Apr-2011	W-3	-9.0
I	Hakusan, Ishikawa	17-Jan-2011	-9.5	-9.3	28-Apr-2011	W-3	-9.0
I	Hakusan, Ishikawa	17-Jan-2011	-9.2	-9.3	28-Apr-2011	W-3	-9.0
J	Hakusan, Ishikawa	3-Nov-2010	-8.8	-8.9	28-Apr-2011	W-4	-8.7
J	Hakusan, Ishikawa	17-Jan-2011	-8.8	-8.9	28-Apr-2011	W-4	-8.7
J	Hakusan, Ishikawa	17-Jan-2011	-8.7	-8.9	28-Apr-2011	W-4	-8.7
J	Hakusan, Ishikawa	17-Jan-2011	-9.0	-8.9	28-Apr-2011	W-4	-8.7
J	Hakusan, Ishikawa	17-Jan-2011	-9.0	-8.9	28-Apr-2011	W-4	-8.7
J	Hakusan, Ishikawa	17-Jan-2011	-8.9	-8.9	28-Apr-2011	W-4	-8.7
K	Hakusan, Ishikawa	17-Jan-2011	-9.2	-9.4	28-Apr-2011	W-5	-9.5
K	Hakusan, Ishikawa	17-Jan-2011	-9.4	-9.4	28-Apr-2011	W-5	-9.5
K	Hakusan, Ishikawa	3-Nov-2010	-9.4	-9.4	28-Apr-2011	W-5	-9.5
K	Hakusan, Ishikawa	3-Nov-2010	-9.3	-9.4	28-Apr-2011	W-5	-9.5
K	Hakusan, Ishikawa	3-Nov-2010	-9.5	-9.4	28-Apr-2011	W-5	-9.5
L	Hakusan, Ishikawa	3-Nov-2010	-9.3	-9.3	28-Apr-2011	W-5	-9.5
L	Hakusan, Ishikawa	17-Jan-2011	-9.4	-9.3	28-Apr-2011	W-5	-9.5
L	Hakusan, Ishikawa	17-Jan-2011	-9.5	-9.3	28-Apr-2011	W-5	-9.5
L	Hakusan, Ishikawa	17-Jan-2011	-9.0	-9.3	28-Apr-2011	W-5	-9.5
L	Hakusan, Ishikawa	17-Jan-2011	-9.4	-9.3	28-Apr-2011	W-5	-9.5
M	Asahi, Toyama	1-May-2011	-9.7	-9.7	1-May-2011	W-15	-10.3
N	Kurobe, Toyama	1-May-2011	-11.7	-11.7	1-May-2011	W-16	-11.1
N	Kurobe, Toyama	1-May-2011	-11.6	-11.7	1-May-2011	W-16	-11.1
N	Kurobe, Toyama	1-May-2011	-11.4	-11.7	1-May-2011	W-16	-11.1
N	Kurobe, Toyama	1-May-2011	-11.9	-11.7	1-May-2011	W-16	-11.1
O	Kurobe, Toyama	1-May-2011	-10	-10.0	1-May-2011	W-17	-9.4
P	Iwase, Toyama	1-May-2011	-11.5	-11.5	1-May-2011	W-18	-9.6
Q	Tonami, Toyama	30-Apr-2011	-10.3	-10.4	28-Apr-2011	W-8	-9.8

*Collected sake samples bottled at the sake brewery.

**The $\delta^{18}\text{O}$ values of nearby groundwater and rivers were estimated from figure 3 of Mizota and Kusakabe (1994) and averaged data from Agata et al. (2001).

Table 3. Water chemistry and stable isotope values of groundwaters in the Hokuriku district. Sample numbers correspond to those in Table 2 and Fig. 2

Sample No.	pH	Tem. (°C)	ORP (mV)	EC (mS m ⁻¹)	Chemical composition (mg L ⁻¹)						Type of water	Stable isotope ratio (‰)			
					Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	HCO ₃ ⁻		SO ₄ ²⁻	NO ₃ ⁻	δD	δ ¹⁸ O
W-1	6.9	13	162	3.2	14	3.5	10	4.7	20	39	12	6.3	Na-HCO ₃	-45.0	-8.2
W-2	7.1	10.5	176	12.4	7.2	1.1	8.4	1.6	9.5	24	8.2	3.3	Ca-HCO ₃	-48.5	-9.1
W-3	8	13	170	22	9.0	0.7	21	11	7.3	110	18	0.2	Ca-HCO ₃	-47.9	-9.0
W-4	7.1	13.5	190	5.9	6.4	2.6	1.2	0.9	11	6.8	4.1	0.5	Na-Cl	-47.8	-8.7
W-5	7	14	201	14.7	6.9	0.9	17	3.3	7.9	53	13	3.0	Ca-HCO ₃	-55.0	-9.5
W-6	6.6	12	226	19.4	14	1.5	18	4.7	13	54	28	1.3	Ca-HCO ₃	-43.3	-8.2
W-7	7	10.5	173	19.4	17	1.1	12	5.9	26	55	5.9	3.9	Na-HCO ₃	-44.9	-8.2
W-8	7	14	204	11.3	6.5	0.6	11	3.3	6.1	44	5.8	2.5	Ca-HCO ₃	-56.7	-9.8
W-9	6.6	12.5	212	8.2	12	0.3	2.5	0.8	13	12	5.2	1.8	Na-Cl	-47.2	-8.6
W-10	6.8	12	218	16.7	18	2.1	7.2	4.1	26	32	7.6	6.7	Na-Cl	-44.8	-8.1
W-11	7.1	13	209	20	23	1.3	13	4.9	32	58	6.3	2.5	Na-HCO ₃	-42.2	-7.8
W-12	7.3	11.5	202	22	31	3.3	4.6	4.2	53	16	12	1.1	Na-Cl	-44.9	-8.3
W-13	7.3	13	215	13.3	12	1.0	8.6	3.9	12	52	1.9	1.2	Na-HCO ₃	-47.1	-8.3
W-14	7.5	13	203	12.9	10	1.9	7.7	3.6	10	48	1.9	0.5	Na-HCO ₃	-46.6	-8.6
W-15	6.8	12	227	13.9	5.6	1.4	16	3.2	6.4	50	11	3.7	Ca-HCO ₃	-61.4	-10.3
W-16	7.5	12.8	208	11.1	4.7	1.1	12	3.0	5.0	41	8.5	2.6	Ca-HCO ₃	-66.7	-11.1
W-17	6.4	15	244	11.2	6.8	1.3	10	2.7	6.4	38	5.8	6.3	Ca-HCO ₃	-55.0	-9.4
W-18	7.3	15	228	22	6.2	2.2	32	6.2	6.2	110	14	6.8	Ca-HCO ₃	-58.6	-9.6
W-19	7.7	—	220	—	14	3.4	19	7.2	9.9	92	12	3.4	Ca-HCO ₃	-49.7	-8.9

Sample numbers correspond to those in Table 2 and Fig. 2.

Fig. 3. A detailed map of the study area (Hakusan, Ishikawa Prefecture). Water quality is shown using Stiff-diagrams. The solid lines represent the area covered by the numerical modeling. ●, River water from the alluvial fan area; ●, River water from the talus area; ○, River water from the hill area; ■, Groundwater at Hakusan brewery.

ses were conducted at the Mitsubishi Materials Techno Corporation Analytical Center. The filtered water samples were analyzed for major anions (Cl^- and SO_4^{2-}) with a Dionex ICS-2000 ion chromatograph using an IonPac As22 column. Water samples were filtered in the laboratory 2 or 3 days after collection using a filter which is

0.22 μm size. Alkalinity was determined via a standard HCl titration. Cations were analyzed using a Dionex DX-320J ion chromatograph.

Oxygen isotope ratios were determined by the automated CO_2 equilibration method (Epstein and Mayeda, 1953) for both *sake* and groundwater samples. To ascer-

Fig. 4. The observed $\delta^{18}\text{O}$ values of sake (this study) vs. shallow groundwaters and river waters in Japan after Mizota and Kusakabe (1994) and Agata *et al.* (2001). The solid line shows the 1:1 correlation of $\delta^{18}\text{O}$ values of water samples.

tain if alcohol content (*ca.* 15 wt%) affects the sake $\delta^{18}\text{O}$, we analyzed $\delta^{18}\text{O}$ values of distilled water containing 0, 5, 10, 15, and 20 wt% of reagent ethanol. The average $\delta^{18}\text{O}$ values of triple analyses of each sample increased slightly from $-12.15 \pm 0.05\text{‰}$ at 0 wt% ethanol to $-11.94 \pm 0.03\text{‰}$ at 20 wt% ethanol. This indicates that alcohol content could influence sake $\delta^{18}\text{O}$ by up to $\sim 0.2\text{‰}$. Given the large isotopic variation between the samples, we did not consider this important, and did not correct for this in our analyses.

The hydrogen isotope ratios of groundwater samples were determined via the Zn reduction method (Coleman *et al.*, 1982). The $\delta^{18}\text{O}$ and δD were measured with a mass spectrometer (Optima, VG Micromass Co. Ltd.) and reported relative to V-SMOW2 with an analytical precision of 0.1‰ for $\delta^{18}\text{O}$ and 1‰ for δD .

RESULTS AND DISCUSSION

$\delta^{18}\text{O}$ values of sake in Japan

The $\delta^{18}\text{O}$ values of 96 sake samples varied from -12.0 to -5.7‰ and showed a regional pattern of low values in northern Japan and high values in southern Japan, reflecting the latitude effect (Table 1). The $\delta^{18}\text{O}$ values of groundwater supplied to individual sake breweries were estimated from values reported by Mizota and Kusakabe (1994). In Okinawa Prefecture, southern Japan, for which Mizota and Kusakabe (1994) did not report any data, we used an average of the $\delta^{18}\text{O}$ values of 3 spring waters near the sake brewery given in Agata *et al.* (2001) (Table

Fig. 5. (a) Outline of sake brewing procedures. (http://www.japansake.or.jp/sake/english/pdf/no_2.pdf). (b) $\delta^{18}\text{O}$ of sake during brewing process (Hashiguchi *et al.*, 2011). Open and closed symbols correspond to water samples during sake brewing of two Daiginjo and two Honjozo sakes, respectively.

1). Figure 4 shows a good correlation between the $\delta^{18}\text{O}$ values of sake and the reported $\delta^{18}\text{O}$ of surface and shallow groundwaters. These results indicate that there is no large isotopic fractionation between sake and the shallow groundwater that is used for its production.

The outline of sake-brewing process is shown in Fig. 5a. Non-sticky japonica rice (a short-grained variety of rice) is suitable for sake brewing. Many types of premium

Table 4. $\delta^{18}\text{O}$ values of sake throughout the various brewing stages

Brewing stages of sake	$\delta^{18}\text{O}$ of sake (‰)			
	Number of samples	Maximum	Minimum	Average
Groundwater	4	−7.4	−7.4	−7.4
Moromi	4	−6	−6.3	−6.2
Gensyu	4	−7.6	−7.8	−7.7
Sake	4	−7.6	−7.7	−7.6

sake are made from this rice. Since the outer layers of unpolished rice contain large amounts of fats, minerals, and proteins that spoil the flavor of sake, the rice is polished to remove the outer layer using a high speed mill. Normally, the outer 30% of the grain is removed, leaving the central 70%. For *ginjo-shu*, the outer 40% or more of the grain may be removed. After milling, the polished rice is washed in water to remove the bran and is soaked in water. When the grain has absorbed an amount of water equivalent to 30% of its weight, it is removed from the water and steamed for one hour.

Following this, it is necessary to use enzymes to break down the starch in the rice and to convert it to sugar (yeast fermentation). The enzymes play a number of roles, finely shredding the starch to convert it into sugar, breaking down proteins, and producing peptides and amino acids. For making sake, a substance called kome-koji (*koji* rice) is used. The *koji* rice is made by cultivating *koji*-fungi on steamed rice. The *koji*-fungus (*Aspergillus oryzae*) is a beneficial and safe variety of mold. In about two days, the steamed rice is entirely covered with *koji*-fungi. As the *koji*-fungi grow, they produce enzymes, which accumulate in the *koji*.

The standard weight ratio of steamed rice, *koji*, and water placed in the fermentation tank is 1:0.25:1.63. In the sake *moromi* (main mash), the enzymes in *koji* decompose the steamed rice while the yeast simultaneously ferments the resulting sugars in a single tank. The fermentation temperature is usually in the range of 8–18°C. The fermentation process takes 3–4 weeks, yielding an alcohol content of 17–20%. When the fermentation is complete, the *moromi* is passed through a cloth filter and the un-decomposed rice and yeast are removed, leaving new sake. This process may be done by placing the *moromi* in a cloth bag. A machine is used to apply pressure to the bag from above. Pressure may also be applied horizontally, similar to a beer mash filter press. The cake left over from the process is called *sakekasu* (filtered sake cake). Some turbidity remains after this filtration process. The liquid is left to stand at low temperature until particles precipitate as sediment. The clear supernatant is transferred into another tank and then filtered to produce a clear liquid. After sedimentation and filtering, most

sake undergoes pasteurization (*hi-ire*) at a temperature of 60–65°C before storing. The purpose of pasteurization is to sterilize the liquid, and at the same time render any enzymes inactive. The heating of sake during the pasteurization process alters the aroma and leaves it with an unrefined taste. For this reason, it is allowed to age for six months to one year. The alcoholic content of sake aged in tanks is 17–20%, the same as at the mash filtration stage. As this level is too high for consumption with meals, brewers often add water to reduce the alcohol level to around 15% before bottling. They may also filter and pasteurize it again, if necessary.

Table 4 and Fig. 5b show the $\delta^{18}\text{O}$ values of *moromi* and two types of sake (*genshu* and *sake*) and groundwater used for sake brewing (Hashiguchi *et al.*, 2011). *Genshu* is the sake obtained after *moromi* filtration but prior to the addition of water to adjust the alcohol content. The average $\delta^{18}\text{O}$ value of water in *moromi* is 1.2‰ higher than that of the corresponding groundwater, whereas the values of *genshu* and *sake* are very similar to those of groundwater. This means that isotopic fractionation occurs in the water during the production of *moromi* but there is no significant difference between the groundwater and sake $\delta^{18}\text{O}$ after the removal of *moromi*. This result is in accord with the fact that there is no significant difference between the $\delta^{18}\text{O}$ of sake and the local shallow groundwater and river water as shown in Fig. 4.

Suzuki *et al.* (2009) demonstrated that the $\delta^{18}\text{O}$ values of Japanese rice vary from $+25.1 \pm 0.6\text{‰}$ at Okinawa (southern Japan) to $+19.7 \pm 0.5\text{‰}$ at Hokkaido (northern Japan). They generally correlate to the $\delta^{18}\text{O}$ values of local surface waters in the same province, with isotopic fractionation between the rice and water of $\sim 30\text{‰}$. This large fractionation might be due to absorption of local surface water into plant cells and change of the water structure.

During the brewing of sake, the rice absorbs groundwater at room temperature and water content increases from a few % to $\sim 30\%$. Then, the rice is steamed and mixed with groundwater in the ratio of 1.63:1 as described above. During the fermentation process, the $\delta^{18}\text{O}$ of the *moromi* increases to become 1.2‰ greater than that of the groundwater (Fig. 5b). The reason for this enrichment

Fig. 6. Observed $\delta^{18}\text{O}$ values of sake and groundwaters in the Ishikawa Prefecture (solid circles) and Toyama Prefecture (open circles) of the Hokuriku district. The solid line shows the 1:1 correlation between $\delta^{18}\text{O}$ values of water samples.

of ^{18}O in the *moromi* cannot be explained presently. It is possible that oxygen molecules in the *moromi* might be exchanged with oxygen isotopes in CO_2 . In this study, the $\delta^{18}\text{O}$ values of water in samples were determined with the CO_2 -water equilibration method without distillation of water from *sake*. We observed only a slight isotopic difference (up to $\sim 0.2\text{‰}$) between distilled waters and those mixed with alcohol (5–20 wt%) and concluded that there is no large effect on the $\delta^{18}\text{O}$ values of *sake* resulting from the presence of alcohol. After formation of *moromi*, *genshu* is obtained by filtration, where more than 75% in volume is water and the remaining 25% is mainly alcohol. Then, groundwater is added to adjust the alcohol content to form *sake*. The $\delta^{18}\text{O}$ of the *sake* returns to a value similar to that of the groundwater during these processes.

$\delta^{18}\text{O}$ values of sake and groundwater in the Hokuriku district

Figure 6 plots the $\delta^{18}\text{O}$ values of *sake* from the Hokuriku district against those of local groundwaters. There is no significant difference between the *sake* and groundwater $\delta^{18}\text{O}$ values. It is noted that the $\delta^{18}\text{O}$ values in the Ishikawa Prefecture are higher than those in Toyama. Figure 7 shows the relationship between the δD and $\delta^{18}\text{O}$ values of shallow groundwaters. A plot of all the data along a local meteoric water line defined as $\delta\text{D} = 8\delta^{18}\text{O} + 21.1$. Mizota and Kusakabe (1994) reported low δD and $\delta^{18}\text{O}$ values in the mountain districts of central Japan ($>3,000$ m). The low $\delta^{18}\text{O}$ values of the Toyama groundwater indicate a high mountain origin for this water.

Fig. 7. Relationship between δD and $\delta^{18}\text{O}$ of groundwaters in the Hokuriku district. Solid line shows the local meteoric water lines in this region ($\delta\text{D} = 8\delta^{18}\text{O} + 21.2$).

δD and $\delta^{18}\text{O}$ values of water samples in the Hakusan area

There are ~ 20 *sake* breweries in the southern Ishikawa prefecture. Many of them including the *sake* “Hakusan” are located in the Tedoru alluvial fan. In order to know the source and the mode of groundwater flow that supplies water to the “Hakusan” brewery, *sake* samples from four breweries were analyzed. The $\delta^{18}\text{O}$ values of water in the *sake* samples are shown in Table 5. The *sake* breweries produce two types of *sake* (*daiginjo* and *honjozo*), which differ in their quality. $\delta^{18}\text{O}$ values are almost constant (within $\pm 0.3\text{‰}$) in individual *sake* breweries (Table 5).

The δD and $\delta^{18}\text{O}$ values of river water from the alluvial fan are -44.7 to -71.2‰ and -8.4 to -11.1‰ , respectively, (Table 6 and Fig. 8). Most samples plot along the meteoric water line with $d = 18.5$ in the study area (Fig. 8). A clear difference is observed in the isotopic compositions of the three groups of river waters. The hill area river waters have lower isotopic ratios than the other areas, with δD of -62.9 to -71.2‰ and $\delta^{18}\text{O}$ of 9.9 to -11.1‰ (Table 6). There is no clear difference in the δD and $\delta^{18}\text{O}$ values between river water samples from the southern (R-5, R-6, and R-7) and northern (R-3, R-8, and R-9) parts of the study area (Fig. 9). The river water samples from the talus area have higher δD (-53.8 to -44.5‰) and $\delta^{18}\text{O}$ values (-9.0 to -8.4‰) than those from the alluvial fan area, where δD ranges between -61.5 and -56.5‰ and $\delta^{18}\text{O}$ between -10.0 and -9.4‰ (Table 6).

Figure 9 shows the distribution of $\delta^{18}\text{O}$ values of all samples in this study area. There is a tendency of increasing $\delta^{18}\text{O}$ from mountainous regions to coastal sites. The δD and $\delta^{18}\text{O}$ values of the Tedoru River, a major river in

Table 5. $\delta^{18}\text{O}$ values of sake from 4 breweries in the Hakusan City study area

Sake brewery	$\delta^{18}\text{O}$ of sake (‰)			$\delta^{18}\text{O}$ of groundwater (‰)
	Number of samples	Maximum	Minimum	
A	5	−9.2	−9.5	−9.3
B	5	−9.2	−9.5	−9.4
C	5	−9.0	−9.5	−9.3
D	5	−8.7	−9.0	−8.9

this area, increase from -71.2‰ and -11.1‰ at R-5, the most upstream sample to -58.1‰ and -9.7‰ at R-15, the most downstream sample, respectively (Fig. 9). Stable isotopic compositions of groundwater and river waters in the Ishikawa prefecture have been previously reported (e.g., Mizota and Kusakabe, 1994; Tomita *et al.*, 2004; Tsuchihara *et al.*, 2011). From these results, the δD and $\delta^{18}\text{O}$ of river waters vary from -80 to -60‰ and -12 to -9‰ , respectively, similar to those obtained in this study. Tsuchihara *et al.* (2011) found an altitude effect as shown by the following equation:

$$\delta^{18}\text{O} = -0.0022h - 8.0 \quad (R^2 = 0.71) \quad (1)$$

where h is the altitude of the river water sample site. The change in the δD and $\delta^{18}\text{O}$ in the Tedor River from upstream to downstream might reflect an altitude effect (Dansgaard, 1964; Waseda and Nakai, 1983).

Two groundwater samples collected on different days at the same location have almost identical values (-47.9 and -50.2‰ for δD and -9.0 and -8.8‰ for $\delta^{18}\text{O}$). These values are similar to those of river water from the talus area collected at 200–500 m in altitude, higher than the other river waters. From Eq. (1), the groundwater (W-1 and W-2) is considered to have originated at an altitude of 360–450 m. These results may imply that the groundwaters at the *sake* brewery might come from river waters that infiltrated into the talus area. Tsuchihara *et al.* (2011) examined the seasonal variation in $\delta^{18}\text{O}$ values of shallow and deep groundwaters in a well (well PU, Fig. 3) in the central part of the alluvial area (40 m in altitude, close to the R-11 sampling site) over a 2-year period (July 2008 to July 2010). They reported an increase in $\delta^{18}\text{O}$ values of the shallow groundwater from -8.5 to -7.5‰ with increases in groundwater levels and precipitation. In contrast, the $\delta^{18}\text{O}$ of deep groundwater showed little variation and remained almost constant at $-9.4 \pm 0.2\text{‰}$. These values are similar to those observed of groundwaters at the *sake* brewery in this study but higher than that of R-11 river water sample (-9.9‰ ; Table 6). Tsuchihara *et al.* (2011) demonstrated that Cl concentration of shallow groundwaters decreased from 17 to 6 mg/L with increasing infiltration of river water. This was es-

Fig. 8. Relationship between δD and $\delta^{18}\text{O}$ of groundwaters in the Hakusan area. Solid line shows the meteoric water line in this region ($\delta\text{D} = 8\delta^{18}\text{O} + 18.5$). ●, River water from the alluvial fan area; ●, River water from the talus area; ○, River water from the hill area; ■, Groundwater.

timated using an end-members mixing analysis (Hooper *et al.*, 1990; Ladouche and Weng, 2005). In our study, two groundwater samples show Cl concentrations of 7.3 and 15 mg/L and $\delta^{18}\text{O}$ of -8.8 and -9.0‰ . These chemical and isotopic differences may reflect a different river water infiltration ratio.

Chemical compositions of water samples in the Hakusan area

The chemical and isotopic compositions of groundwater (W-1) and river water (R-1 to R-18) are shown in Table 6 and Figs. 10 and 11. All samples are weakly alkaline (pH = 7.1 to 8.8). The river water samples are characterized by lower EC values (5–20 mS/m) than those of groundwater (22 and 27 mS/m) in the study area. In particular, samples from the talus area (R-2, R-4, and R-18) have lower EC values (5.0–8.1 mS/m) than the other river waters (Table 6).

The groundwater used for the *sake* production is taken

Table 6. Chemical and isotope compositions of water samples in the Hakusan area

Sample No.	Sampling date	Sample localities	Sample group	pH	Tem. (°C)	ORP (mV)	EC (mS m ⁻¹)	Chemical composition (mg L ⁻¹)						Stable isotope ratio (‰)			
								Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻	δD	δ ¹⁸ O
R-1	11-Nov-2011	Alluvial fan	AGF	7.3	15	94	15.2	6.5	1.4	13	2.1	6.5	47	12	1.9	-56.5	-9.4
R-2	11-Nov-2011	Talus	DGf	7.7	14	136	7.8	5.1	0.7	4.5	1.8	5	17	11	1	-53.8	-9
R-3	11-Nov-2011	Hill	D-T	7.9	12.5	143	14.1	7.2	1	14	2.6	6.8	49	16	1.2	-62.9	-10.3
R-4	28-Apr-2011	Talus	DGf	7.1	10	212	5	5.9	1.9	0.6	0.9	9.4	4.5	4.5	1.1	-44.5	-8.5
R-5	11-Nov-2011	Hill	D-T	8.8	9.5	167	20	9.9	1.3	17	4.8	15	53	28	0.8	-71.2	-11.1
R-6	11-Nov-2011	Hill	D-T	8.1	12	153	9.4	4.2	0.7	7.8	3.3	2.5	48	2.7	0.4	-63.5	-9.9
R-7	11-Nov-2011	Hill	D-T	7.9	14	142	12.2	6.1	0.9	10	3.2	6.5	44	13	0.7	-66.7	-10.4
R-8	11-Nov-2011	Hill	D-T	7.9	13	158	16.5	9.1	1.2	17	3	9.4	54	22	1.2	-66.9	-10.6
R-9	11-Nov-2011	Hill	D-T	7.9	14.5	144	14	7.6	1	13	2.6	7.1	45	16	1.4	-62.3	-10
R-10	11-Nov-2011	Alluvial fan	AGF	7.9	14	157	11.9	6	0.8	11	2.4	6.1	41	12	1	-60.8	-9.7
R-11	11-Nov-2011	Alluvial fan	AGF	8.1	15	155	11.9	6	0.9	11	2.3	6.1	41	12	1.4	-61.5	-9.9
R-12	11-Nov-2011	Alluvial fan	AGF	8.8	17	126	11.6	5.9	1.1	11	2.2	6.1	41	13	1.1	-60.5	-9.6
R-13	11-Nov-2011	Alluvial fan	AGF	8.1	17	128	12.3	6.7	1	11	2.2	6.8	40	12	1.4	-58.7	-9.8
R-14	11-Nov-2011	Alluvial fan	AGF	8.2	15	120	12	6.1	0.9	11	2.3	6.1	41	12	1.4	-59.3	-9.8
R-15	11-Nov-2011	Alluvial fan	AGF	8.1	17	146	12.7	6.6	0.9	12	2.4	7	42	13	1.6	-58.1	-9.7
R-16	11-Nov-2011	Alluvial fan	AGF	8.2	14	158	11.8	6.1	0.9	11	2.3	6.5	40	12	1.3	-60.9	-9.9
R-17	11-Nov-2011	Alluvial fan	AGF	7.9	13.5	165	11.6	6	0.8	11	2.3	6.2	41	12	1.4	-60.9	-10
R-18	11-Nov-2011	Talus	DGf	7.5	15	155	8.1	7.8	1.2	2.8	2.2	6.7	21	5.1	1.2	-47.9	-8.4
W-1	11-Nov-2011	Talus	DGf	7.9	15	580	27	14	0.7	23	12	15	130	18	0.1	-50.2	-8.8
W-1	28-Apr-2011	Talus	DGf	8	13	170	22	9	0.7	21	11	7.3	110	18	0.2	-47.9	-9

D-T, lower layer of sand gravel; DGf, middle clay and upper alluvial gravel; AGf, alluvial sand gravel deposits.
Sample numbers correspond to those in Fig. 3.

Fig. 9. Spatial distribution of $\delta^{18}\text{O}$ values of water samples in the Hakusan area. Inset shows the δD (□) and $\delta^{18}\text{O}$ (■) values of the Tedorì river waters.

from a depth of 100 m. Samples from this depth were collected in April and November, 2011. The April sample was slightly lower in Na^+ , Cl^- , and HCO_3^- than the November sample. This result suggests little seasonal variation in chemical composition of groundwater at this location. Figure 10 shows that river waters from the alluvium fan and hill areas are almost identical, with chemical compositions of $\text{Ca}^{2+}\text{--HCO}_3^-$ type. In contrast, the river waters from the talus area, R-2, R-4, and R-18 are of $\text{Na}^+\text{--Ca}^{2+}\text{--HCO}_3^-$, $\text{Na}^+\text{--Cl}^-$, and $\text{Na}^+\text{--HCO}_3^-$ types,

respectively. Tsuchihara *et al.* (2011) reported chemical compositions of shallow and deep groundwaters in the Tedorì alluvial fan that were similar to those of this study. The deep groundwaters in the southern part of the Tedorì River reported by Tsuchihara *et al.* (2011) have the same chemical compositions as river waters from the talus area in this study. In contrast, the shallow groundwaters in the southern part of the Tedorì River were enriched in Na^+ , K^+ , and HCO_3^- . These results imply that deep groundwaters in the southern part of the Tedorì River

Fig. 10. Trilinear diagrams for the water samples in Hakusan area. ●, River water from the alluvial fan area; ●, River water from the talus area; ○, River water from the hill area; ■, Groundwater.

derive from river waters that infiltrate at the talus area.

The Ca^{2+} and $(\text{Ca}^{2+} + \text{Mg}^{2+})$ concentrations of water samples increase with increasing HCO_3^- as shown in Fig. 11, where the dotted lines correspond to calcite and dolomite dissolution lines. From the chemical compositions of groundwater samples, the saturation indices (S.I.) of calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) were calculated using the following equation:

$$\text{S.I.} = \log(Q/K), \quad (2)$$

where Q and K are the mineral's (calcite i.e., $(\text{Ca}^{2+})(\text{CO}_3^{2-})$) activity and solubility products, respectively. If $\text{S.I.} > 0$, the fluid is saturated with respect to a mineral, that mineral would be precipitated. The chemical code PHREEQC (Parkhurst and Appelo, 1999) was used in this study. The S.I. values obtained for the groundwater samples collected in April and November, 2011 were the same: -0.15 for calcite and -0.37 for dolomite. Enrichment of Ca^{2+} and HCO_3^- is due to dissolution of carbonate minerals such as calcite and dolomite. The hydrolysis and dissolution reactions of limestone and dolomite to form dissolved bicarbonate, calcium, and magnesium ions can be described following Appelo and Postma, 2005:

Fig. 11. Relationship between Ca and HCO_3^- (a), and $\text{Ca} + \text{Mg}$ and HCO_3^- (b) of groundwaters in the Hakusan area. The broken lines indicate stoichiometric dissolution of calcite (a) and dolomite (b). ●, River water from the alluvial fan area; ●, River water from the talus area; ○, River water from the hill area; ■, Groundwater.

Ca^{2+} and Mg^{2+} in the groundwaters within alluvial fans throughout the world have shown a good correlation. These components are considered to come from dissolution of carbonate minerals (e.g., Hidalgo and Cruz-Sanjulian, 2001; Chkirbene *et al.*, 2009). Carbonate rocks are commonly observed at the location of the sake brewery in the Tedor fan (Obara, 1961). These rocks are a likely source of groundwater Ca^{2+} and Mg^{2+} .

Fig. 12. Schematic vertical section showing flow direction and recharge of river water and groundwater in the Hakusan area.

Modeling of groundwater movement

Figure 12 shows a schematic model showing flow direction and discharge of groundwater. The $\delta^{18}\text{O}$ and δD values of two groundwaters are similar to those of river water from the talus area collected at 200–500 m altitude. A three-dimensional numerical groundwater flow model was used to estimate the flow of groundwater at a particular *sake* brewery. Table 7 shows the conditions used for the numerical model. The modeling area covers $30 \text{ km} \times 30 \text{ km} \times 2 \text{ km}$ (Fig. 13a). The surface geometry was reproduced from a digital elevation model (DEM) and pasted on a numerical model of the ground surface. The DEM data was taken from “Digital Map 50 m Grid (Elevation)” of the Geographical Survey Institute. The hydrogeological parameters used in the model are given in Table 7 for the fan deposit, Neogene sediment, Tedori Formation, and Pre-Neogene granitic rocks. The surface strata, excluding alluvial fan deposits, were treated as weathered layers with high permeability. The surface boundary condition was specified by the recharge rates ranging from 0.21 to 0.86 mm/day. Zero meter water pressure head was assumed for the coast and rivers. The amount of rainfall in this area was calculated from the annual precipitation (AMeDAS data at Komatsu, Yoshino Hakusan, and Shiramine Hakusan), evaporation rate, and river runoff (Maruyama *et al.*, 2012). The bottom and sides of the model were assumed to be impermeable boundaries. The program code used in this study was Dtransu-3D-EL advection-dispersion analysis, a three-dimensional saturated-unsaturated seepage flow calculation code (Hishiya *et al.*, 1999). The pre- and post-processor software is G-TRAN/3D for Dtransu-3D. The permeability (k) for the numerical analysis area was taken from a database which was collected from literatures about permeability of sediments and rocks in Japan (Umeda *et*

Table 7. Basic design and physical parameters used in this study for flow simulation

(a) Boundary conditions	
Top (Ground surface):	Infiltration ($0.21\sim0.86 \text{ mm d}^{-1}$)
River:	Pressure head (0 m)
Side and bottom:	Impermeable
(b) Finite element method grid	
Number of elements:	51942
Number of layers:	6 (minimum thickness is 10 m)
(c) Method of analysis	
Saturated three-dimensional seepage analysis	
(d) Lithology and Hydraulic conductivity ($k \times m \text{ s}^{-1}$)	
Alluvial fan deposits:	7.0×10^{-4}
Tertiary strata:	1.3×10^{-7}
Tedori group:	9.2×10^{-10}
Granitic rocks:	9.6×10^{-10}

al., 1995).

The distribution of water pressure head in the Tedori alluvial fan is shown in Fig. 13b. The model results match well with observed data, showing that the depth of water table at the end of the fan is shallower than 2 m (Okuyama, 2010) and increases in depth towards the north. Figure 13b also shows that the water table of the alluvial fan is located beneath the ground surface at the end of the fan (Tedori Iseki) and is nearly 18 m deep in the central fan (Taiheiji). The calculated and measured water tables were 2 m deep at Tedori Iseki; and the calculated water table was 18 m, and the measured water table 20 m deep at Taiheiji. The calculated water tables are in close agreement with the observed levels, indicating that the model accurately represents the water flow in the study area.

(a)

(b)

(c)

Fig. 13. Three-dimensional simulation of groundwater flow in the Hakusan area. (a) Blocks for simulation of water flow, (b) Distribution of calculated water heads (dashed line) obtained from the flow simulation. Two closed circles (Iseki and Taiheiji) indicate groundwater wells. The calculated water heads are close to the observed water heads. (c) Stream lines of groundwater in the lower (black) and upper (gray) aquifer toward the sake brewery. Broken circle indicates the recharge area of groundwater for the sake brewery. The grid lines in (c) show the terrain of the area.

Figure 13c shows the results of the prediction analysis. Solid lines show the calculated trace lines for the source of groundwater for *sake* brewing for which recharge occurs at the 440–540 m elevation and has a flow path 2–3 km long (broken circle in Fig. 13c). The effect of pumping depth in the well on the water source is examined. The Darcy flow rate of groundwater in the calculation was 0.0002–0.015 m/day. The actual flow rate using the effective porosity of 0.02 is 0.01–0.75 m/day. Groundwater flow predicted by the above numerical analysis is consistent with the results from stable isotope and water chemistry analyses. These results suggest that the combination of geochemical and numerical modeling techniques provides a useful tool to predict the source of groundwater.

CONCLUSIONS

“Hakusan,” one of the premium brand *sakes* in Japan, is brewed in Hakusan City, Ishikawa. In this study, the water chemistry and δD and $\delta^{18}O$ contents of groundwater used in the *sake* brewing process and the surrounding river waters were analyzed to estimate its source. The results indicate that the groundwater used in the “Hakusan” brewery comes from mountain slopes at 360–450 m altitude. The 3-D modeled groundwater flow, which is independent of the geochemical method, also supports this view. Our study indicates that simultaneous analyses of numerical and geochemical techniques can help estimate the source and water movement of groundwater used in *sake* production. The observed $\delta^{18}O$ of 96 *sake* samples in 19 provinces in Japan showed a good correlation with that of corresponding groundwater. This indicates that the $\delta^{18}O$ of *sake* is a useful parameter to identify the location of *sake* production, which will help prevent fraudulent representation of the location of *sake* production.

Acknowledgments—The authors wish to thank to the members of *sake* brewery in Hakusan City for allowing us to sample groundwaters used for *sake* production. The authors wish to thank the members of Mitsubishi Materials Techno Corp., especially A. Miyaoka for oxygen isotopic analyses of water samples. N. Okakita is also acknowledged for analyzing oxygen isotope compositions of alcohol containing water samples. C. Mizota, F. Yanagisawa, and M. Kusakabe are acknowledged for their critical comments and for improving the English used in this manuscript.

REFERENCES

Adamo, P., Zampella, M., Quétel, C. R., Aversano, R., Piaz, F., Tommasi, N., Frusciante, L., Iorizzo, M., Lepore, L. and Carputo, D. (2012) Biological and geochemical markers of the geographical origin and genetic identity of potatoes. *J. Geochem. Explor.* **121**, 62–68.

Agata, S., Satake, H. and Tokuyama, A. (2001) Chemical characteristics and isotopic compositions of spring and river waters in Okinawa Island. *Chikyukagaku (Geochemistry)*, **35**, 27–41 (in Japanese with English abstract).

Appelo, C. A. J. and Postma, D. (2005) *Geochemistry, Groundwater and Pollution*. 2nd ed., AA Balkema, Amsterdam, 649 pp.

Brewing Society of Japan (ed.) (1996) *Text of the Latest Brewing Technology*, 30 pp.

Chesson, L. A., Podlesak, D. W., Erkkila, B. R., Cerling, T. E. and Ehleringer, J. R. (2010) Isotopic consequences of consumer food choice: Hydrogen and oxygen stable isotope ratios in foods from fast food restaurants versus supermarkets. *Food Chem.* **119**, 1250–1256.

Chkirbene, A., Tsujimura, M., Charef, A. and Tanaka, T. (2009) Hydro-geochemical evolution of groundwater in an alluvial aquifer: Case of Kurokawa aquifer, Tochigi prefecture, Japan. *Desalination* **246**, 485–495.

Coleman, M. L., Shepherd, T. J., Durham, J. J., Rouse, J. E. and Moore, G. R. (1982) Reduction of water with zinc for H-isotope analysis. *Anal. Chem.* **54**, 993–995.

Crittenden, R. G., Andrew, A. S., LeFournour, M., Young, M. D., Middleton, H. and Stockmann, R. (2007) Determining the geographic origin of milk in Australasia using multi-element stable isotope ratio analysis. *Int. Dairy J.* **17**, 421–428.

Dansgaard, W. (1964) Stable isotopes in precipitation. *Tellus* **16**, 436–438.

Dion, M. A., Luykx, M. and Saskia, M. R. (2008) An overview of analytical methods for determining the geographical origin of food products. *Food Chem.* **107**, 897–911.

Epstein, S. and Mayeda, T. (1953) Variation of the $^{18}O/^{16}O$ ratio in natural waters. *Geochim. Cosmochim. Acta* **4**, 213–224.

Hashiguchi, T., Izu, H., Sudo, S., Tomiyama, S., Miyaoka, A., Koizumi, Y. and Kitai, A. (2011) Comparison of oxygen isotopic compositions between *sake* and the source water. *The Fifth Meeting of Discussion Group of Analysis for Labeling Origin*, The Japan Society for Analytical Chemistry, Saitama, Japan, P3 (in Japanese).

Hidalgo, M. C. and Cruz-Sanjulian, C. (2001) Groundwater composition, hydrochemical evolution, and mass transfer in a regional detrital aquifer (Baza basin, southern Spain). *Appl. Geochem.* **16**, 745–758.

Hishiya, T., Nishigaki, M. and Hashimoto, N. (1999) The Three Dimensional numerical analysis method for density dependent groundwater flow with mass transport. *Proceedings—Japan Society of Civil Engineers* **638**, 59–69.

Hokuriku Agriculture Report (1977) Hydrogeology and groundwater in Ishikawa Prefecture, Hokuriku Agriculture Report, 58 pp.

Hooper, R. P., Christophersen, N. and Peters, N. E. (1990) Modeling streamwater chemistry as a mixture of soilwater end-members—an application to the Panola Mountain catchment, Georgia, U.S.A. *J. Hydrol.* **116**, 321–343.

Kelly, S., Heaton, K. and Hoogewerff, J. (2005) Tracing the geographical origin of food: The application of multi-element and multi-isotope analysis. *Trends Food Sci. Tech.* **16**, 555–567.

- Ladouche, B. and Weng, P. (2005) Hydrochemical assessment of the Rochefort marsh: Role of surface and groundwater in the hydrological functioning of the wetland. *J. Hydrol.* **314**, 22–42.
- Marisa, C., Almeida, R., Teresa, M. and Vasconcelos, S. D. (2004) Does the winemaking process influence the wine $^{87}\text{Sr}/^{86}\text{Sr}$? A case study. *Food Chem.* **85**, 7–12.
- Maruyama, T., Noto, F., Yoshida, T., Nakamura, K., Horino, H., Murashima, K. and Takimoto, H. (2012) Analysis of water balance at the Tedor River alluvial fan areas in Japan. *J. Japan Soc. Hydrol. and Water Resour.* **25**, 20–29 (in Japanese with English abstract).
- Mizota, C. and Kusakabe, M. (1994) Spatial distribution of δD – $\delta^{18}\text{O}$ values of surface and shallow groundwater from Japan, south Korea and east China. *Geochem. J.* **28**, 387–410.
- Nakashita, R., Suzuki, Y., Akamatsu, F., Iizumi, Y., Korenaga, T. and Chikaraishi, Y. (2008) Stable carbon, nitrogen, and oxygen isotope analysis as a potential tool for verifying geographical origin of beef. *Anal. Chim. Acta* **617**, 148–152.
- Obara, N. (1961) Report on the engineering geology of the proposed dam site at Gomijima along the river Tedor, Ishikawa prefecture. *Report of Geological Survey of Japan* **12**, 72–76 (in Japanese with English abstract).
- Okuyama, T. (2010) Hydrogeological survey of Tedor-gawa fan. *Proceedings of the Annual Meeting of the Japanese Society of Irrigation, Drainage and Rural Engineering*, 244–245 (in Japanese).
- Papesch, W. and Horacek, M. (2009) Forensic applications of stable isotope analysis: Case studies of the origins of water in mislabeled beer and contaminated diesel fuel. *Science and Justice* **49**, 138–141.
- Parkhurst, D. L. and Appelo, C. A. J. (1999) Users Guide to PHREEQC (Version2)—A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations, Water-Resources Investigations Report, U.S. Department of the Interior, U.S. Geological Survey, 99-4259.
- Suzuki, Y., Chikaraishi, Y., Ogawa, N. O., Ohkouchi, N. and Korenaga, T. (2008) Geographical origin of polished rice based on multiple element and stable isotope analyses. *Food Chem.* **109**, 470–475.
- Suzuki, Y., Nakashita, R., Akamatsu, F. and Korenaga, T. (2009) Multiple stable isotope analyses for verifying geographical origin and agricultural practice of Japanese rice samples. *Bunseki Kagaku* **58**, 1053–1058 (in Japanese with English abstract).
- Tomita, J., Sakaguchi, A., Satake, H., Nakamura, T. and Yamamoto, M. (2004) Isotopic geochemical study of hot and mineral springs around Hakusan volcano. *Annual Report of Kanazawa University* **20051201**, 80–81.
- Tomiya, S., Ii, H., Miyaike, S., Hattori, R. and Ito, Y. (2009) Estimation of the sources and flow system of groundwater in Fuji–Gotenba area by stable isotopic analysis and groundwater flow simulation. *Bunseki Kagaku* **58**, 865–872 (in Japanese with English abstract).
- Tomiya, S., Ii, H., Uehara, T. and Wakita, T. (2010) Stable isotopic analysis and groundwater flow simulation as potential tools for estimating groundwater sources used for food materials. *Nippon Shokuhin Kagaku Kogaku Kaishi* **57**, 32–39 (in Japanese with English abstract).
- Tomiya, S., Ueda, A., Kitai, A. and Aoi, S. (2011) Estimation of the sources of groundwater used for food materials in Sayama city, Saitama prefecture, by geochemical methods and numerical simulation. *Bunseki Kagaku* **60**, 131–142 (in Japanese with English abstract).
- Tsuchihara, T., Yoshimoto, S., Ishida, S. and Imaizumi, M. (2011) Classification of recharge sources of groundwater in a paddy dominant alluvial fan based on geochemical and isotopic analyses. *Bulletin of the National Institute for Rural Engineering* **211**, 21–34 (in Japanese with English abstract).
- Ueki, T. (2008) Food labeling and authentication technology. *Nippon Shokuhin Kagaku Kogaku Kaishi* **55**, 405–409 (in Japanese).
- Umeda, K., Yanagisawa, K. and Yoneda, S. (1995) Construction of database of hydraulic conductivities on land of Japan. *Journal of Groundwater Hydrology* **37**, 69–77 (in Japanese).
- Waseda, A. and Nakai, N. (1983) Isotopic compositions of meteoric and surface waters in Central and Northeast Japan. *Geochem. J.* **17**, 83–91.
- Watanabe, K. (2002) Natural environment in Tedor River: Groundwater in Tedor fan. *Chigakukyouiku (Geochemistry)*, **55**, 149–172 (in Japanese).