Geochemical study of groundwater in the Sho river fan, Toyama Prefecture for heat usage by geothermal heat pump

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Chemical and isotopic (D, ¹⁸O) compositions of 40 shallow groundwater, 14 observation well water and 2 river water samples in the Sho river fan, Toyama, northern part of central Japan, were analyzed to examine their water quality, origins and water flow in order to obtain baseline geochemical data for application of groundwater to geothermal heat pump (Geo-HP). Water temperatures of the groundwaters in the observation wells are almost constant at 15°C from surface to *ca.* 60 m in depth and increase up to 25°C at depth of 200 m with the thermal gradient of 6°C/100 m. This geothermal gradient is twice as high as that of the other areas in Japan, suggesting existence of high temperature geothermal sources beneath this region and a high potential for heat usage in winter.

The isotopic results show that the groundwaters are a mixture of two big river waters (Sho and Oyabe rivers) and precipitation in the Sho river fan and that the contribution of infiltration from the Sho river has increased in recent 10 years. The Sho river has lower $\delta^{18}\text{O}$ values than the Oyabe river. The groundwaters shallower than 80 m depth are of a Ca–HCO₃ type. Deep groundwaters from observation wells were characterized by high in pH and HCO₃ compared to the shallow groundwaters due to ion exchange with rocks containing clay minerals. The deep groundwaters are almost saturated or oversaturated with respect to calcite and dolomite, becoming confined due to the presence of an impermeable layer. In this paper, formation of calcite and iron hydroxide scale inside pipes of the Geo-HP was discussed from the chemical compositions of groundwater to examine whether the water is applicable to geothermal heat pump or not.

Keywords: groundwater, heat usage, hydrogen isotope, oxygen isotope, scale, geothermal heat pump

INTRODUCTION

The minimum and maximum air temperature is 0°C in winter and 35°C in summer in central areas along the Japan Sea such as Toyama Prefecture, northern Central Japan. Also, a large amount of snow falls in winter. Most residents in Toyama use kerosene and electricity for house-heating and pay more than 500 USD per year for kerosene. Since the gigantic Tohoku earthquake of March 11, 2011 that resulted in the loss of the Fukushima Daiichi Nuclear power station, saving electric power has become an urgent necessity in Japan and alternative energy resources are being sought. In Toyama Prefecture, a large amount (1 million tons/year) of groundwater flows from the mountains (*ca.* 3000 m in altitude) to the Sea of Japan side within 100 km in distance (Toyama Prefecture,

2006), thus most rivers in Toyama Prefecture have the highest hydraulic gradient in Japan. Since the water temperature of shallow groundwater in Toyama is constant at 15°C throughout the year, the groundwater can be used for heat source of air conditioning of houses and industry in winter by using the temperature difference between air and groundwater.

The use of the geothermal heat pump (Geo-HP) is now spreading worldwide (e.g., Hutterer, 1997; Diao *et al.*, 2004; Lee and Hahn, 2006; Fujii *et al.*, 2007; Russo *et al.*, 2011). In particular, the open-type Geo-HP using groundwater has been often used because of the low cost (e.g., Wang *et al.*, 2012). In the open-type Geo-HP system, groundwater is pumped to the surface, heat-exchanged and returned to the aquifer through a reinjection well. In the closed-type Geo-HP system, anti-freezing fluid circulates through the U-tube installed in the underground to pick up the heat. The final goal of our study is to evaluate the applicability of groundwater as a heat source to air conditioning of houses and melting of road snow in this area. In summer, shallow groundwater, which is cooler than the atmospheric temperature, can be

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Fig. 1. Locality of the Sho river fan. (a) Watershed of the Sho river fan. (b) The detailed study area and sample localities of shallow groundwaters and river water in the Sho river fan. Solid circles indicate the shallow groundwater, solid squares the observation well, open triangles river water. Numbers in the sample locality correspond to those in Tables 1, 2 and 3. (c) Groundwater levels in the Sho river fan (modified from the Toyama Prefecture, 2006).

used for cooling houses. In this system, the quality and mode of water movement are important parameters for the use of groundwater. In addition, the effect of temperature change of groundwater after heat exchange on the later available heat should also be examined (e.g., Freedman *et al.*, 2012; Ni *et al.*, 2011). A constant supply of groundwater is required for the long use of the Geo-HP device. The quality of groundwater is also important to keep high heat exchange efficiency during the operation. Precipitation of some chemical components such as iron and calcium carbonate as a scale in the heat exchanger and water pipes has to be avoided (e.g., Andritsos and Karabelas, 2003; Lei *et al.*, 2011). Iron in anoxic groundwater is dissolved as ferrous ion (Fe^{2+}) and oxidized to ferric ion (Fe^{3+}) by oxidation upon contact with atmosphere and precipitates as iron hydroxide ($\text{Fe}(\text{OH})_3$) and iron carbonate (FeCO_3).

There are many works done on water movement in alluvium fan in the world (e.g., Mizutani and Oda, 1983; Li *et al.*, 2008; Hidalgo and Cruz-Sanjulian, 2001; Mizutani *et al.*, 2001; Chkirbene *et al.*, 2009; Yuan *et al.*, 2011; Vanderzalm *et al.*, 2011; Tsuchihara *et al.*, 2011). In this study, groundwaters and river waters in the Sho river fan were geochemically analyzed to determine the water flow and quality of groundwater in order to assess the potential use of the groundwater for Geo-HP. The statistics data such as water level fluctuation, flux and movement of groundwater in the Sho River fan should be consistent with the geochemical data (e.g., Tomiyama *et al.*, 2009, 2010, 2011). In the Sho river fan, groundwater has been used for industry, snow melting on the road and drinking. Excessive extraction of groundwater in the past resulted in the land subsidence in the northern part of the fan, creating permanent damage to the land surface. Such land subsidence has been reported elsewhere and the correlation between groundwater level and the change in morphology in the land subsidence has also been studied (e.g., Chen *et al.*, 2010).

The stable isotopic compositions of groundwater and river waters in the Sho river fan have been determined previously (Mizutani and Oda, 1983; Kato *et al.*, 1984; Takaoka and Mizutani, 1987; Mizutani *et al.*, 1987; Miyamoto, 2000). Mizutani and Oda (1983) reported that a significant difference exists in δD and $\delta^{18}\text{O}$ values between the waters of the Sho and Oyabe rivers and indicated that the aquifers in the eastern half of the Sho river fan were recharged by the Sho river water and those in the western half by the Oyabe river water. They also noted contribution of the precipitation and finally demonstrated 5 water sources for groundwaters in the Sho river fan.

SAMPLE LOCALITY AND ANALYTICAL PROCEDURES

The Sho river fan is located in the western part of

Toyama prefecture and spreads between Nanto and Takaoka cities (Fig. 1a), where two big rivers, Sho and Oyabe, flow along the edge of the fan (Fig. 1b). The geology of the study area consists of unconsolidated coarse-grained andesitic breccia derived from the surrounding mountains. Confined aquifer does not exist between Nanto and Takaoka, because there is no permeable clay layers in the gravel layer. The permeability of the gravel layer is reported as 10^{-2} cm/sec (Toyama Prefecture (2006)). Two or three clay layers are present between the two rivers in the northern, sea side part of the fan, where the lower aquifer is confined. In some areas of Takaoka city, water head is *ca.* 2 m above the ground surface. The Sho and Oyabe rivers originate from mountains with the altitude of 1,625 m and 1,572 m and flow to the ocean 115 km and 68 km away with the flow rates of 34 m³/sec and 24.3 m³/sec, respectively (Fig. 1a). The highest elevation of the catchment area is 1,020 m for the Sho river and 260 m for the Oyabe river. Annual precipitation is 3,200 mm at Shirakawa where the Sho river originates, and 2,300 mm in Takaoka area (ocean side). The size of the Sho and Oyabe rivers area are 1,180 km² and 682 km², respectively. The groundwater levels are shown in Fig. 1c which indicates groundwaters flowing radially from top to end of the fan. The flow velocity of the shallow groundwater (above 60 m depth) has been estimated to be 250 m/day at Tonami, the top area of the fan along Sho river (Takahashi *et al.*, 2003). They used deuterium-enriched and NaCl solutions to evaluate the velocity. Mizutani and Oda (1983) estimated the water flow rate of 10 to 13 m/day for the deep groundwater (confined aquifer) in the northern part of the fan.

The study area and water sampling sites are provided in Fig. 1b. Three types of water samples are collected; shallow groundwater, groundwater from observation wells, and river waters. In this study, the groundwaters outside the fan (the vicinity of Takaoka) were also investigated, for the area around Takaoka was not included in the previous study. They were analyzed for their chemical and isotopic compositions. Water samples were collected in 100 ml and 250 ml plastic bottles. Water temperature, pH, EC, and Eh were measured at the sampling site using a thermometer, a pH meter (Shindengen, KS-701), EC meter (Horiba, B-173) and Eh meter (TOA, RM-12P), respectively. Alkalinity was determined using standard titration with HCl. Dissolved ion concentrations were measured using conventional methods. The major cations (Na, K, Ca, Mg) and anions (Cl , NO_3 , SO_4) in the filtered samples were analyzed with an ion chromatograph (Metrohm 761 Compact IC). The charge balances of the obtained results are within $\pm 5\%$ and the analytical uncertainties on dissolved ion concentrations are also within 5%. SiO_2 was analyzed with a UV-VIS spectrophotometer (SHIMADZU UVmini-1240). Iron concentration was

Table 1. Sample locality, temperature, pH, EC and ORP of shallow groundwaters and river waters in the Sho River fan area

Sample name	Sample date	Latitude	Longitude	Altitude	Temp. (°C)	pH	EC (mS/m)	ORP (mV) Pt*
1	2011.8.12	36°45'19.10"	136°58'19.44"	7	21.3	7.62	29.5	-9
2	2011.8.12	36°44'16.81"	136°56'41.87"	11	14.5	7.46	37.1	79
3	2011.8.12	36°43'0.54"	136°55'13.97"	16	25.0	7.50	10.0	81
4	2011.8.12	36°43'9.70"	136°56'34.29"	12	15.6	7.77	25.3	86
5	2011.8.12	36°41'43.97"	136°54'12.96"	21	15.8	7.09	19.6	109
6	2011.8.12	36°40'45.53"	136°53'9.19"	26	18.0	6.88	18.7	139
7	2011.8.12	36°39'39.21"	136°53'34.68"	31	16.4	6.20	14.8	138
8	2011.8.12	36°39'15.22"	136°51'26.47"	34	13.6	7.57	13.0	104
9	2011.8.12	36°37'49.74"	136°53'35.45"	40	17.5	7.61	11.1	69
10	2011.8.12	36°37'25.66"	136°54'56.93"	47	17.1	7.58	12.2	93
11	2011.8.12	36°36'51.76"	136°53'51.05"	45	14.0	6.93	16.4	85
12	2011.8.12	36°35'51.96"	136°55'4.90"	55	16.0	6.36	14.5	93
13	2011.8.12	36°36'35.32"	136°56'32.81"	64	21.4	7.08	16.1	119
14	2011.8.12	36°35'59.01"	136°59'7.19"	83	16.1	7.60	13.8	103
15	2011.8.27	36°43'57.93"	137° 1'39.54"	11	15.4	7.89	11.7	75
16	2011.8.27	36°44'11.93"	136°59'53.02"	7	14.0	7.57	12.0	67
17	2011.8.27	36°44'0.96"	136°58'25.27"	8	14.2	7.60	17.7	86
18	2011.8.27	36°42'42.85"	136°57'56.37"	14	14.0	7.56	16.8	108
19	2011.8.27	36°41'0.33"	136°56'43.72"	26	15.9	6.58	18.1	126
20	2011.8.27	36°40'53.73"	136°54'52.16"	25	14.8	6.73	18.9	146
21	2011.8.27	36°40'12.83"	136°55'27.11"	31	17.3	7.72	16.7	95
22	2011.8.27	36°39'21.81"	136°54'44.75"	38	14.4	6.67	13.7	100
23	2011.8.27	36°38'1.36"	136°56'8.83"	50	16.3	6.55	17.9	68
24	2011.8.27	36°35'2.99"	136°56'44.91"	78	13.7	6.67	11.1	127
25	2011.8.27	36°37'28.79"	136°57'39.45"	61	26.3	6.55	15.7	120
26	2011.8.27	36°37'55.59"	136°59'18.91"	59	16.1	7.33	9.7	120
27	2011.8.27	36°39'26.96"	136°58'49.95"	42	18.6	6.58	13.4	112
28	2011.8.27	36°39'46.10"	136°57'32.66"	37	14.9	6.99	16.1	116
29	2011.8.27	36°40'27.09"	136°58'24.55"	30	15.8	6.74	16.0	720
30	2011.8.27	36°41'43.58"	136°58'29.55"	21	15.2	6.56	12.7	374
31	2011.8.27	36°42'41.37"	136°59'26.01"	15	13.9	7.15	26.0	315
32	2011.8.27	36°42'4.72"	137° 0'7.12"	17	12.2	7.92	8.9	286
33	2011.9.7	36°43'17.08"	137° 3'15.12"	10	14.9	6.48	13.7	217
34	2011.9.7	36°40'4.13"	137° 1'31.81"	36	14.4	6.77	10.5	183
35	2011.9.7	36°37'15.54"	137° 0'36.40"	70	21	6.26	14.1	163
36	2011.9.7	36°34'15.01"	136°59'5.85"	114	18.2	6.7	8.9	186
37	2011.9.7	36°30'20.74"	136°54'8.11"	169	14.1	7.4	28.7	37
38	2011.9.7	36°33'22.68"	136°54'19.31"	81	14.8	6.52	10.5	201
39	2011.9.7	36°45'36.03"	137° 0'24.23"	4	17.3	6.57	88.0	9
40	2011.9.7	36°45'28.29"	137° 2'54.69"	3	15.4	7.48	13.3	114
SR	2011.8.12	36°37'20.84"	136°59'57.74"	63	24.9	7.69	8.2	102
OR	2011.8.12	36°37'3.52"	136°53'56.18"	45	23.5	7.79	13.7	61

*Measured with a Pt electrode.

determined by ICP-MS at the Naka Institute of Mitsubishi Materials Corp.

The hydrogen and oxygen isotope ratios were determined by a stable isotope analyzer for H₂O by the use of

a diode laser-based infrared spectrometer. The results were reported relative to V-SMOW2 with an analytical precision of 1‰ for δD and 0.3‰ for δ¹⁸O, respectively.

Table 2. Chemical and stable isotope compositions of shallow groundwaters and river waters in Sho River fan area

Sample name	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ⁻	SiO ₂	Fe	δD	δ ¹⁸ O
	mg/L									μg/L	‰	
1	19.21	3.77	14.29	20.73	13.43	0.59	6.04	153.72	37.24	2.51	-47	-8.5
2	12.37	2.13	6.23	62.97	13.42	0.86	4.16	215.94	31.51	2.38	-45.8	-8.1
3	11.24	4.69	1.24	3.85	10.80	3.10	3.26	28.79	59.77	3.57	-47.6	-8.8
4	8.98	1.34	5.88	37.00	8.82	7.74	7.95	129.32	13.39	2.38	-55.2	-9.2
5	8.07	1.00	5.34	25.04	10.37	2.83	10.41	88.45	31.29	2.38	-52.5	-8.9
6	9.11	0.99	6.12	22.71	8.63	2.63	10.08	87.84	29.54	2.38	-53.6	-9.1
7	7.01	1.08	2.95	16.86	8.28	4.43	10.29	50.02	20.41	2.41	-56.5	-9.5
8	7.72	7.15	4.72	4.92	11.14	24.41	12.39	9.76	16.68	2.40	-46.5	-8.7
9	6.57	0.88	2.45	10.15	6.16	3.50	6.54	38.43	15.04	2.38	-54.7	-9.3
10	7.44	0.88	2.77	12.53	8.44	3.93	7.69	42.09	19.15	2.38	-53.6	-9.2
11	10.41	0.93	4.64	16.22	8.26	4.46	7.55	73.20	29.60	2.38	-49.8	-8.7
12	8.68	0.78	4.42	13.65	7.26	3.72	7.36	59.17	17.54	2.40	-53.8	-8.9
13	6.20	1.09	2.81	21.71	6.78	5.90	11.10	62.22	19.94	2.42	-53.2	-9.0
14	4.96	0.85	2.73	19.61	5.30	3.02	7.48	62.22	14.66	2.39	-61.2	-10.4
15	5.21	0.77	2.55	15.16	4.11	1.45	7.40	54.26	22.50	2.38	-64	-10.5
16	6.09	0.81	2.72	15.08	4.02	1.76	6.42	55.87	20.41	2.41	-62.6	-10.4
17	6.81	1.04	4.62	22.99	5.79	3.81	8.59	84.18	20.64	2.42	-59.6	-9.7
18	6.48	1.11	3.66	21.22	7.32	5.69	10.68	68.59	20.89	2.37	-56.2	-9.0
19	7.06	1.22	3.10	24.18	8.48	7.07	13.33	67.07	19.55	2.39	-51.3	-9.0
20	8.45	1.32	3.79	22.97	16.17	4.80	13.19	59.78	23.93	2.42	-50.8	-9.0
21	7.79	1.36	2.63	21.58	8.76	5.73	17.79	53.04	20.39	2.53	-51.8	-8.9
22	7.22	0.95	2.01	15.28	9.39	3.88	11.72	43.04	17.98	2.38	-53.4	-9.0
23	6.51	1.11	3.63	24.84	7.14	5.23	9.58	74.42	19.69	2.61	-54.2	-9.3
24	4.88	1.36	1.70	13.31	4.96	7.44	8.50	33.55	10.60	2.37	-55.7	-9.2
25	5.66	1.05	3.02	21.19	6.27	4.80	9.18	64.25	18.61	2.39	-54.4	-9.4
26	4.13	0.78	1.76	11.71	3.89	2.02	8.21	36.36	12.65	2.39	-62.3	-10.0
27	5.16	0.88	2.50	12.98	4.70	2.89	8.92	48.80	17.13	2.39	-60.9	-9.8
28	5.76	1.02	3.30	21.31	6.51	4.41	10.06	64.66	18.17	2.40	-57.4	-9.7
29	6.62	1.03	3.17	19.80	7.56	4.91	10.76	62.05	19.37	3.09	-56.9	-9.3
30	5.63	1.18	1.71	15.92	6.69	5.91	10.07	34.16	14.88	2.39	-56	-9.7
31	24.35	1.46	3.32	21.89	8.80	4.50	79.95	34.51	14.55	2.39	-62	-10.1
32	5.09	0.61	1.64	12.36	3.72	1.42	9.66	40.87	21.59	2.38	-64.6	-10.6
33	8.15	1.11	3.99	12.80	8.34	5.20	10.15	45.26	21.14	2.40	-52	-9.3
34	5.58	0.94	2.06	11.38	5.78	2.43	7.77	37.75	13.29	2.39	-58.5	-9.9
35	9.12	1.28	3.24	12.81	12.44	3.39	8.29	44.50	15.30	2.62	-55	-9.0
36	5.11	1.35	1.92	7.98	7.31	3.04	6.41	24.68	10.18	2.39	-62.1	-9.8
37	11.75	1.32	10.01	36.13	9.44	1.65	8.32	160.77	38.57	2.59	-48.6	-8.4
38	7.88	1.33	2.86	6.71	7.54	6.49	8.65	26.60	15.09	2.40	-50.6	-8.8
39	63.52	5.73	35.06	79.22	128.22	1.20	12.16	441.95	46.76	2.99	-63.6	-10.4
40	7.68	0.72	3.78	13.68	4.31	1.53	8.42	60.56	21.72	2.43	-62.5	-10.2
SR	3.18	0.66	1.02	7.62	2.49	0.61	5.36	28.55	8.99	2.56	-66.2	-10.7
OR	5.00	1.08	1.87	8.65	4.45	0.96	6.24	33.51	8.86	2.75	-59.7	-9.5

RESULTS AND DISCUSSION

The chemical and isotopic compositions of water samples are shown in Tables 1 to 4 and Figs. 1 to 8, where the sample numbers correspond to those in Fig. 1b.

Temperature, EC and ORP profiles of groundwater in the observation well (P3)

In one of the observation wells, Kamizeki (P3 in Fig. 1b and Table 3), water temperature, EC, ORP, and pH were measured as a function of depth (Fig. 2) using a

Table 3. Sample locality of groundwaters in observation wells. Sample numbers correspond to those in Fig. 1

Sample name	Sampling date	Latitude	Longitude	Depth (m)	Altitude (m)	Temp. (°C)	pH	EC (mS/m)	ORP (mV) Pt*
P1	2011.8.10	36°44'48.43"	137°5'26.44"	30	3	20.1	8.06	14.8	-110
P2-0	2011.8.10	36°46'13.64"	137°2'17.78"	0	3	37.8	8.92	44.3	28
P2-33	2011.8.10	36°46'13.64"	137°2'17.78"	33	3	28.7	8.99	47.5	3
P2-67	2011.8.10	36°46'13.64"	137°2'17.78"	67	3	25.3	9.18	48.9	-80
P2-100	2011.8.10	36°46'13.64"	137°2'17.78"	100	3	24.9	9.16	61.0	-128
P3-0	2011.8.10	36°43'44.27"	137°0'36.48"	0	14	38.3	8.42	49.6	35
P3-50	2011.8.10	36°43'44.27"	137°0'36.48"	50	14	25.0	8.32	50.1	-172
P3-107	2011.8.10	36°43'44.27"	137°0'36.48"	107	14	24.7	8.11	52.7	-188
P4	2011.8.11	36°36'33.07"	136°57'54.80"	33	73	19.6	7.72	16.6	85
P5	2011.8.11	36°34'43.98"	136°53'35.44"	33	59	17.6	7.97	13.7	-170
P6	2011.8.11	36°38'28.64"	136°54'5.06"	33	40	17.2	8.65	8.7	25
P7	2011.8.11	36°42'3.25"	136°56'16.90"	0	19	31.8	8.37	15.8	37
P8	2011.9.13	36°39'10.85"	136°56'36.85"	20	42	22.7	8.85	8.7	87
P9	2011.9.9	36°42'47.96"	137°0'34.67"	50	13	13.8	8.28	11.4	76

*Measured with a Pt electrode.

Table 4. Chemical and stable isotopic compositions of groundwaters in observation wells at Sho River fan area. Sample numbers correspond to those in Fig. 1

Sample name	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ⁻	SiO ₂	Fe	δD	δ ¹⁸ O
	mg/L									μg/L	‰	
P1	14.28	1.66	5.35	7.41	8.70	0.000	0.96	68.63	6.35	69.83	-48.4	-7.2
P2-0	94.50	6.40	1.50	5.40	79.00	0.000	1.10	138.78	2.00	4.26	-45.1	-7.3
P2-33	97.20	5.30	1.60	6.30	82.00	0.000	1.00	131.15	3.90	10.76	-51.4	-8.2
P2-67	102.50	6.00	1.50	5.75	97.00	0.000	0.75	126.27	17.40	226.28	-52.3	-8.4
P2-100	235.50	12.00	5.00	16.50	317.50	0.000	0.50	129.32	38.20	237.32	-55.6	-9.0
P3-0	55.70	3.10	29.20	15.40	20.40	0.000	0.00	277.55	11.40	2.51	-51.0	-8.2
P3-50	50.00	2.60	29.00	29.80	19.00	0.000	0.00	308.05	19.30	23.02	-54.6	-8.7
P3-107	46.30	2.60	27.70	41.50	17.60	0.000	0.00	326.96	32.60	78.80	-57.1	-9.1
P4	5.73	0.95	3.08	25.30	6.23	0.050	3.20	94.55	10.80	2.60	-57.4	-9.7
P5	10.73	1.25	2.30	10.28	4.63	0.000	1.10	62.22	10.45	3.26	-46.9	-8.5
P6	8.33	0.95	0.65	7.83	8.85	0.000	0.13	37.21	0.90	2.57	-50.6	-9.5
P7	9.98	1.38	5.33	11.33	12.58	0.025	0.18	63.44	6.95	55.50	-42.9	-6.5
P8	7.26	3.81	0.59	13.57	1.58	0.168	6.33	58.56	12.40	274.33	-55.0	-8.9
P9	4.59	0.88	0.79	6.54	4.62	0.023	0.04	28.67	0.30	9.13	-55.7	-9.3

water monitoring system (MP-TROLL9000). It is noted that the water temperature is almost constant at 15°C between 10 to 80 m and increases monotonously up to 23°C at 220 m depth. The EC value normalized at 25°C decreases from 56 to 42 mS/m at the surface zone and increases up to 65 mS/m with increasing depth (Fig. 2). The ORP increases from -220 to -100 mV with depth. A strainer tube installed between 160 to 175 m depth allowed groundwater to flow into the well. The EC and temperature profiles show that the groundwater can be divided into 3 layers; 10 to 60 m, 60 to 160 m and the deep-layer except for the surface layer (surface to 10 m).

Groundwater samples were collected at the depth of 0 (surface), 50, and 100 m using a water sampler (Table 3). If there is only one strainer in the deep part of the well, water chemistry would have been the same at all depths. The observed variations imply that the water with different EC and temperature mixes above the strainer depth due to casing break.

The most important characteristic of groundwater profile in the observation well is the high geothermal gradient of *ca.* 6°C/100 m below a depth of 80 m. The high geothermal gradient suggests existence of a high temperature heat source exists under the study area.

Fig. 2. Variation with depth in water temperature (a), EC (b), ORP (c) and pH (d) of groundwater in the Kamizaki observation well P3.

δD and $\delta^{18}O$ values of water samples

The δD and $\delta^{18}O$ values of shallow groundwaters vary from -46.5 to -64.6‰ and from -8.1 to -10.6‰ , respectively (Table 2), whereas those of well waters are relatively high (δD : -46.9 – -57.1‰ and $\delta^{18}O$: -7.2 – -9.3‰ ; Table 4 and Fig. 3). Water sample from Sho river has the lowest δD (-66.2‰) and $\delta^{18}O$ (-10.7‰) values (Fig. 3) of the samples. Most of the water samples plot along a meteoric water line defined as $\delta D = 8\delta^{18}O + d$ (Craig, 1961; Dansgaard, 1964) where d indicates the Y-intercept. Two meteoric water lines in Fig. 3 were quoted from Satake *et al.* (1984), where d is 10 in summer and 30 in winter for precipitation in Toyama City, 20 km east of the Sho river fan. The δD and $\delta^{18}O$ values of Toyama precipitation were monitored from 1982 to 1995 as shown in Table 5. The range of variation is reproduced as an open box in Fig. 3.

The δD and $\delta^{18}O$ values of river waters were periodically analyzed between 1980 and 1982 (Mizutani and Oda, 1983) of which variations for the Sho and Oyabe rivers are shown in Fig. 3 as solid and open circles, respectively. The averaged δD and $\delta^{18}O$ values are -63.3‰ and -10.4‰ for the Sho river and -55.2‰ and -9.4‰ for the Oyabe

Table 5. δD and $\delta^{18}O$ values of Precipitation at Toyama City

Year	Precipitation (mm)	δD (‰)	$\delta^{18}O$ (‰)
1982	1555	-54	-8.8
1983	2871	-54	-9.3
1984	2224	-50	-9.5
1985	2969	-56	-9.4
1986	—	—	—
1987	1281	-43	-7.4
1988	1731	-52	-8.8
1989	—	—	—
1990	—	—	—
1991	1984	-54	-8.8
1992	1816	-48	-8.6
1993	2213	-54	-8.0
1994	1411	-37	-7.1
1995	1756	-48	-8.3
Averaged*	1982	-51	-8.6

*Weighted mean averaged values of δD and $\delta^{18}O$.
Data reproduced from Satake *et al.* (1984).

Fig. 3. δD vs. $\delta^{18}O$ relationship of water samples in the Sho river fan. Open triangles indicate the shallow groundwater, solid squares the Sho and Oyabe rivers, open circles the observation well water (above 80 m), and solid circles the observation well water (below 80 m). The box indicates the range of isotopic variations for precipitation in Toyama city (averaged data for 5 years since 1991 measured by Satake, unpublished). Solid and broken circles correspond to the range of variation for the Sho (S.R.) and Oyabe (O.R.) river waters (data from Mizutani and Oda, 1983). Two solid lines indicate the local meteoric water lines in the winter and summer at Toyama City (Satake *et al.*, 1984).

Fig. 4. Distribution of $\delta^{18}\text{O}$ values of shallow groundwater collected in 2011 in the Sho river fan.

river, respectively (Mizutani and Oda, 1983), almost similar to the present results (Table 2). In Fig. 3, the range of variation in δD and $\delta^{18}\text{O}$ values of the Sho river (solid circle in Fig. 3) is smaller than that of the Oyabe river (broken circle). As mentioned before, the Sho river originates from high altitude, whereas the Oyabe river comes from lower mountains. These geographical differences caused large variations in δD and $\delta^{18}\text{O}$ values of the two rivers due to a large difference in the isotopic values of the source precipitation.

The observed δD and $\delta^{18}\text{O}$ values of shallow groundwaters in the Sho river fan are consistent with the ranges of averaged precipitation and river waters of the area (Fig. 3). The contour of $\delta^{18}\text{O}$ distribution are shown in Fig. 4. We can see that two groundwaters derived from the Sho and Oyabe rivers infiltrate to the central part of the fan. Along the Oyabe river, the $\delta^{18}\text{O}$ values of groundwater are -8.5 to -9‰ which are higher than the river water $\delta^{18}\text{O}$ value (-9.5‰). This means that shallow groundwaters around the Oyabe river are a mixture of river water and precipitation. In contrast, the $\delta^{18}\text{O}$ values of shallow groundwater along the Sho river are similar to those of river water (-10.7‰). These results show that the Sho river water infiltrates at the top of the fan and discharges at the end of the fan. Though the Oyabe river

Fig. 5. Distribution of the chemical type of shallow groundwaters and river waters in the Sho river fan. The chemical type is shown by the inserted hexa-diagrams. The solid hexagons correspond to the chemical type of the river waters. Solid circle shows the groundwater No. 39 that has a high EC value. The five arrows in the figure mean the water sources of groundwaters in the Sho river fan as demonstrated by Mizutani and Oda (1983). The contour is given in 10 m interval. The highest altitude is 150 m a.s.l. at the southernmost end of the fan.

Fig. 6. The Piper diagram for water samples in the Sho river fan. Open triangles indicate the shallow groundwater, solid squares the Sho and Oyabe rivers, open circles the observation well water (above 80 m), and solid circles the observation well water (below 80 m). Solid circle shows groundwater in well P3. The water was observed to change from the Na-HCO₃ to NaCl types with increasing depth.

Fig. 7. Relationship between Ca+Mg and HCO₃ concentrations of the Sho river fan waters. Open triangles indicate the shallow groundwater, solid squares the Sho and Oyabe rivers, open circles the observation well water (above 80 m), and solid circles the observation well water (below 80 m). Broken line corresponds to dolomite dissolution. Solid and broken circles show the range of variation for the shallow and deep groundwaters, respectively.

Fig. 8. Saturation index of (a) calcite and (b) dolomite as a function of pH. Open triangles indicate the shallow groundwater, solid squares the Sho and Oyabe rivers, open circles the observation well water (above 80 m), and solid circles the observation well water (below 80 m).

flows near the Nanto city (see Fig. 1b), $\delta^{18}\text{O}$ value of groundwater around Nanto is almost -8‰ (Fig. 4). The groundwater of this region is strongly influenced by the precipitation.

Chemical compositions

All shallow groundwaters have weakly acid to alkaline with pH values ranging from 6.20 to 7.89 (Table 1). In contrast, those of groundwaters from the observation wells (shallow water above -80 m and deep below -80 m) are relatively high to be 7.72 to 9.18 (Table 3). The EC values are 8.9 to 37.1 mS/m except for sample No. 39

Fig. 9. Distribution of Ca concentration (mg/L) in shallow groundwaters in the Sho river fan.

(solid circle in Fig. 5. EC = 88 mS/m). These results are almost similar to those reported by Miyamoto (2000). The EC values of groundwaters in the observation well vary from 8.7 to 52.7 mS/m (Table 3), relatively high compared to shallow groundwaters. In the upper part of the fan, the shape of the hexa-diagrams for shallow groundwaters is similar to that of river waters (solid hexagons in Fig. 5). This suggests that both river waters infiltrate into the fan in the upper area. Shallow groundwaters in the central and lower part of the fan are characterized by high Ca and HCO_3 concentrations (Fig. 5). Furthermore, the flow of groundwater in the fan can be divided into five water systems (arrows in Fig. 5) based on the chemical compositions as suggested by Mizutani and Oda (1983).

Figure 6 shows a trilinear diagram of the chemical compositions of all water samples. Shallow groundwaters and river waters are mainly of a Ca-HCO_3 type with a few exceptions. Water samples from observation wells plot widely in Fig. 6. The EC values of groundwaters in well P3 (solid circle in Fig. 6) increase with increasing depth (Fig. 2) with the associated chemical change from Na-HCO_3 to NaCl types. It is thought that seawater flows into the deep part.

The $\text{Ca} + \text{Mg}$ concentrations of water samples increase linearly with increasing HCO_3 as shown in Fig. 7, where the broken line indicates dolomite dissolution. The linearity implies that the shallow groundwaters become enriched in Ca, Mg, and HCO_3 due to dissolution of dolomite. In contrast, the groundwaters in the observation wells are plotted below the broken line. In Fig. 7, solid

Fig. 10. (a) Distribution of $\delta^{18}\text{O}$ difference in shallow groundwaters between 2000 and 2011. The 2000 data were quoted from Miyamoto (2000). (b) Temporal change of the boundary between the Sho and Oyabe water systems from 1965 to present (after Mizutani and Oda, 1983 for data in 1965 and 1983, and Miyamoto, 2000 for 2000).

and broken circles show the ranges of observed chemical variations of the shallow (above 80 m) and deep (below 80 m) groundwater in wells P2 (Nomachi) and P3 (Kamizeki). Our shallow and deep samples are plotted as open and solid circles, respectively. Sodium concentration in groundwaters from the observation wells is higher than that in shallow groundwater in the Sho river fan and correlates with K concentration (Tables 2 and 4). Groundwaters in the observation well are enriched in Na and K and depleted in Ca through ion exchange with clay minerals that underlie the northern part of the fan. The

Fig. 11. Distribution of Fe concentration ($\mu\text{g/L}$) in shallow groundwaters in the Sho river fan.

pH values of deep groundwater also become higher than the shallow groundwater.

The saturation indices of calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) were calculated to discuss the source of Ca and Mg and also to examine the possibility of precipitation of such minerals during heat exchange by Geo-HP. Saturation Index (S.I.) is defined by;

$$\text{S.I. (Saturation Index)} = \log(Q/K) \quad (1)$$

where Q and K are, respectively, activity product ($a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}}$ in the case of calcite) and solubility product ($((\text{Ca}^{2+})(\text{CO}_3^{2-}))$) of minerals. If $\text{S.I.} > 0$, the fluid is saturated with respect to the minerals. The chemical code PHREEQC (Parkhurst and Appelo, 1999) was used in this study. The obtained S.I. values of water samples are plotted against pH as shown in Fig. 8. The S.I. of calcite and dolomite increases with increasing pH, and above pH8, groundwater should be saturated with respect to these minerals. Groundwaters in the observation wells are oversaturated because of their high pH and high Ca and HCO_3^- concentrations. The S.I. of gypsum (CaSO_4) was also calculated, but it was always below unity, or gypsum undersaturated. These results imply that shallow groundwater derives essentially from river waters that infiltrated into underground and enriched in Ca and HCO_3^- due to dissolution of carbonate minerals such as calcite and dolomite. Carbonate rocks are observed in the several formations in the Sho river fan (Sumi *et al.*, 1989). The hydrolysis and dissolution reactions of limestone and dolomite to form dissolved bicarbonate, calcium and

Fig. 12. Saturation index of (a) ferrihydrite ($\text{Fe}(\text{OH})_3$) and (b) goethite (FeOOH) as a function of Fe concentration. Open triangles indicate the shallow groundwater, solid squares the Sho and Oyabe rivers, open circles the observation well water (above 80 m), and solid circles the observation well water (below 80 m).

magnesium ions can be described as (Appelo and Postma, 2005):

If CO_2 is available from the atmosphere and/or decom-

Fig. 13. A map showing the areas where an open type or closed type Geo-HP is recommended in the Sho river fan (See text). 1: Open type Geo-HP can be used, but iron scale may cause a problem. 2: Open type Geo-HP can be used without any scaling problem. 3: Open type Geo-HP can be used with necessary of monitoring the change of water flow. 4: Closed type Geo-HP is recommended. 5: Closed type Geo-HP is recommended. Groundwaters with high EC value may induce calcite scaling. 6: Not recommended to any type of Geo-HP, because of high salinity from sea water contamination.

position of organic matter, the equations are;

Calcium and magnesium ions in the groundwaters from alluvial fans are often correlated, and these components are considered to derive from dissolution of carbonate minerals (e.g., Hidalgo and Cruz-Sanjulian, 2001; Chkirbene *et al.*, 2009). These rocks are the most likely source of Ca and Mg in the groundwaters.

Figure 9 is a contour map of Ca distribution in the shallow groundwaters. It is noted that the 20 mg/L contour is widely found in the central part of the fan. In the Sho river fan, basement rocks form depression in the central part of the fan and its minimum depth is estimated to be ~ 300 m (Miyamoto, 2000). This means that part of shallow groundwater infiltrates into deeper part of the central part of the fan and discharges in the northern part of the fan as confined groundwater. During this process, shallow groundwaters acquire Na, K and HCO_3 as noted by Miyamoto (2000).

Water quality usable for geothermal heat pump

Water movement is one of the key parameters for utilizing a geothermal heat pump. Figure 10a shows the difference in $\delta^{18}\text{O}$ values of groundwaters between 2000 (Miyamoto, 2000) and 2011. It indicates that most shallow groundwaters in 2011 are depleted in $\delta^{18}\text{O}$ up to 0.75‰ compared to those in 2000. This means that contribution of the Sho river water into groundwater increased over time. Figure 10b shows the boundary between the groundwater originated from the Sho and Oyabe rivers. The boundaries were drawn using the $\delta^{18}\text{O}$ distribution, water level and pH (the 1965 and 1982 boundaries were taken from Mizutani and Oda (1983)). It is seen that the 1965 boundary was located in the western part of the fan, whereas the 2000 boundary shifted eastward. The 2011 boundary stayed almost the same in the northern part of the fan, but it shifted slightly westward in the southern part. Mizutani and Oda (1983) demonstrated that the Sho river water infiltrated into the main part of the fan. They also stated that the recharge area moved from the top to end of the fan because of reduction in flow rate and lowering of the riverbed. The 2011 boundary moved to the west in the top of the fan as stated above. It is interpreted that the amount of water infiltration from the Sho river increased in recent 10 years.

The quality of groundwater is a key parameter for geothermal heat pump. The EC values of shallow groundwaters were 8.8 to 37.1 mS/m and almost the same or higher than those of river waters (8.2 and 13.7 mS/m). Saturation index calculations indicate that most of the shallow groundwaters are undersaturated with respect to calcite at 15°C except for 4 samples (Fig. 8). Calcite may precipitate in the system during heat exchange in heat pump for the 4 groundwaters. Groundwaters may be heated up to 40°C in heat exchanger in summer. The SI at this temperature is -0.2 , so some more shallow water may be saturated with calcite. However, the majority of water is still undersaturated. This suggests that scaling by calcite deposition will not be a problem in the study area.

Dissolved iron is a potential component of scaling during heat pumping. Iron in groundwater under reducing condition generally exists as ferrous ion (Fe^{2+}) and is oxidized by atmospheric O_2 to ferric ion (Fe^{3+}) at the surface. Ferric ion will precipitate in the well and piping. Ferrihydrite ($\text{Fe}(\text{OH})_3$) and goethite (FeOOH) are commonly observed in the scale of groundwater wells (e.g., Schwertmann and Murad, 1983; Charette and Sholkovitz, 2002). In this study, iron concentrations in waters were analyzed (Tables 2, 4). They vary from 2.4 to 3.6 $\mu\text{g/L}$ (Fig. 11) and 2.6 to 274 $\mu\text{g/L}$ for shallow and deep groundwaters, respectively. Saturation indices of ferrihydrite ($\text{Fe}(\text{OH})_3$) and goethite (FeOOH) were calculated from the observed ORP values and the chemical compositions of water samples (Figs. 12a and b). In this

calculation the PHREEQC code was used where the observed ORP values were used for the oxidation-reduction potential (Pe). Most of the shallow groundwaters are saturated with respect to ferrihydrite (except for 6 samples) and goethite. Part of iron in the groundwater will precipitate in the heat exchanger during heat pumping. Kushita *et al.* (2012) has tested an open-type heat pump at the Nanto City (Fig. 1b) for one year. They compared the power requirement for the first and second floors of a house where the test was performed. Cool air was supplied only to the first floor from the heat pump. It was found that electric consumption was saved to 60% in the first floor. After this test, a small amount of brown colored deposit was observed in the heat exchanger after 1 year use. The XRF analysis indicated that it contained iron as a major component. This iron precipitate is thought to be come from corrosion of iron casing pipe of the well, but precipitation of iron from groundwater cannot be ruled out. These results demonstrated that groundwater with low Fe^{2+} concentration and low ORP can be used for an open-type heat pump. In contrast, groundwaters with high ORP need to pay attention for the iron oxide precipitation. The oxidation-reduction potential of groundwater is a key parameter for the iron precipitation, and eventually in maintaining a heat pump.

Figure 13 shows six areas where geothermal heat pump can be used in the study area. Area 1 is recommended for an open type Geo-HP. Iron scale may cause a problem in this area. An open type Geo-HP can be used in area 2 without any scaling problem. An open type Geo-HP can also be used in area 3, but the water flow has to be monitored because the flow may change with time (Fig. 10b). In the area 4 where most groundwaters are originated from meteoric precipitation, therefore the water level fluctuates depending on precipitation amount. A closed type Geo-HP system can be used without any problem. In the areas 5 and 6, a closed type Geo-HP is recommended, because calcite scaling and corrosion by high Cl concentration are expected if the open type Geo-HP is used.

CONCLUSIONS

Groundwater samples at the Sho river fan, Toyama Prefecture, Japan were geochemically examined to assess the applicability of groundwater to heat usage for air conditioning and melting of road snow. The shallow groundwaters are of meteoric origin and of a Ca-HCO_3 type. High geothermal gradient (twice as much as the other areas in Japan) found in the observation wells suggests existence of high geothermal sources under this region. The Sho river fan can be classified into 6 areas where either an open type or closed Geo-HP is better used, depending on the quality of groundwater from each area. The shallow groundwaters in most part of the study area

are appropriate for heat usage by an open-type heat pump system. In some groundwater with high ORP, iron precipitation in the heat exchange is possible and Fe concentration should be monitored for the open type Geo-HP. A closed type Geo-HP is recommended for groundwater which is oversaturated with iron and calcite precipitations, because of possible scaling by the precipitates in the pipes used in the closed type system.

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