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Geochemical implication of $^{87}Sr/^{86}Sr$ ratio of high-temperature deep groundwater in a fractured granite aquifer

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The Dongrae thermal water area located at the southeast margin of the Korean Peninsula is one of the oldest hot springs in Korea and has been used in spas since the 9th Century. In this paper, a geochemical significance of $^{87}Sr/^{86}Sr$ ratios from deep thermal water, groundwater, surface water and rainwater in the Dongrae area is discussed. The bedrock of this thermal water-bearing aquifer is composed of Mesozoic granitoids. For temperatures up to 71°C, the thermal water is Na–Cl type, whereas shallow cold groundwater is Ca(–Na)–HCO_3 type. $^{87}Sr/^{86}Sr$ ratios of the thermal water are in the 0.705651 ± 11–0.705696 ± 12 range and have remained nearly unchanged over the past 4 years (2004–2007). $^{87}Sr/^{86}Sr$ ratios of the shallow cold groundwater, surface water and rainwater range from 0.705781 ± 26 to 0.705789 ± 12, 0.706700 ± 14 and 0.707375 ± 11 respectively. $^{87}Sr/^{86}Sr$ ratios of the thermal water in the Dongrae area are lower than those of groundwater, surface water, rain water as well as aquifer bearing granite. These Sr isotopic signatures indicate that the circulation rate between thermal water and current meteoric water, including groundwater, surface water and rain water in the Dongrae area should be very slow. Therefore, the thermal water might be derived from a high temperature paleo-groundwater reservoir rather than from circulation of young meteoric water heated by current heat sources. Our data show that $^{87}Sr/^{86}Sr$ ratios may become an important time lag indicator for the groundwater cycle between deep and shallow groundwater in a fractured granite aquifer system.

Keywords: $^{87}Sr/^{86}Sr$ ratio, fractured granite aquifer, thermal water, time lag indicator, groundwater cycle

INTRODUCTION

Since the 1990s, strontium isotopes have been used extensively as a natural tracer of groundwater flow (Peterman and Stuckless, 1992; Bullen *et al.*, 1996; Johnson and DePaolo, 1994; McNutt *et al.*, 1990; McNutt, 2000; Frost *et al.*, 2002; Gosselin *et al.*, 2004; Klaus *et al.*, 2007). Although classified as a trace element, Sr often occurs in measurable quantities in most rock types and behaves geochemically like Ca. It is soluble in water in its +2 oxidation state. Groundwater acquires Sr during recharging and interactions with Sr-bearing minerals within a groundwater-bearing unit. When Sr is removed from water as a result of mineral precipitation or cation exchange, the isotopic composition of the remaining Sr is unaffected, whereas individual Sr concentrations may change as a result of these processes (Gosselin *et al.*, 2004). Gosselin *et al.* (2004) showed that Sr isotopes can provide information on the sources of solutes within water. Therefore, the Sr isotopic composition of groundwater records an intergrated signal of water-rock interaction along flow path and can be used as a dynamic tracer to constrain subsurface flow patterns.

In general, most thermal waters reaching temperatures above 40°C are clearly related to young volcanic or subduction areas. The thermal water is thus considered to be predominantly derived from mantle/magmatic sources related to volcanic activities. Because of its old and very stable tectonic and geological environments with no active or young volcanism, South Korea is thought to have a low geothermal potential. Nevertheless, most spas use thermal water distributed in the Mesozoic granitoid area of the Korean Peninsula. The Dongrae is one of such thermal water, and is the oldest hot spring in South Korea, which has been used for public bathing over the past 1200 years.

Groundwater aquifers including the Dongrae thermal water have already been extensively studied (Lee and Lim,

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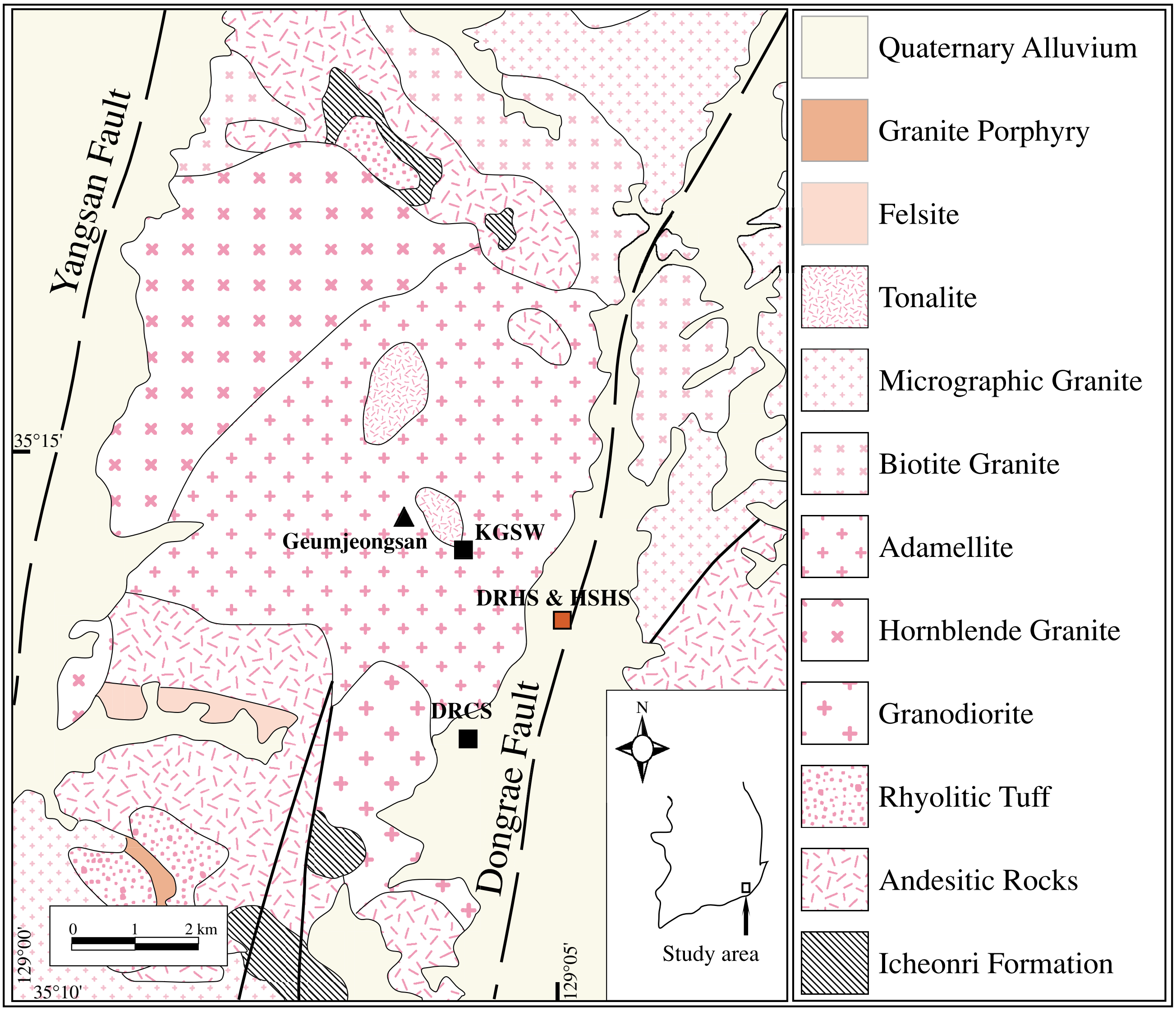

Fig. 1. Geological and sample location map in the Dongrae area, Busan, Korea. Red rectangle (DRHS & HSHS) are thermal waters, black rectangles (DRCS and KGSW) are groundwater and surface water, respectively.

1995; Han *et al*., 1999; Lee *et al*., 2001; Sung *et al*., 2001; Son *et al*., 2002). The geochemical composition of the geothermal water is mainly Na–Cl type, whereas that of shallow groundwater is mainly Ca(–Na)–HCO_3. Han *et al*. (1999) and Sung *et al*. (2001) suggested that the Na–Cl type of Dongrae thermal water was derived from seawater intrusion.

In a recent preliminary study, Lee *et al*. (2006) reported that Sr isotopic ratios of most South Korea's thermal waters were very similar to those of associated granite emplacements. In this study, we measured the $^{87}Sr/^{86}Sr$ ratio and chemical composition of Dongrae area thermal water from one representative well for four years in order to estimate variation and origin of $^{87}Sr/^{86}Sr$. The $^{87}Sr/^{86}Sr$ ratios of the groundwater, surface water and rain water were also analyzed to compare with those of the thermal water. The aim of this study is to determine if $^{87}Sr/^{86}Sr$ ratios can be used as a tracer to identify the groundwater cycle between deep and shallow groundwater aquifer in a fractured granitic rock area.

General Geology and Hydrogeology

The study area is located at the southeast margin of the Korean Peninsula and consists of granitoids and andesite (Fig. 1). Yun *et al*. (2005) reported that the granites were crystallized from calc-alkaline series and I-type granitic rocks which evolved from granodioritc magma

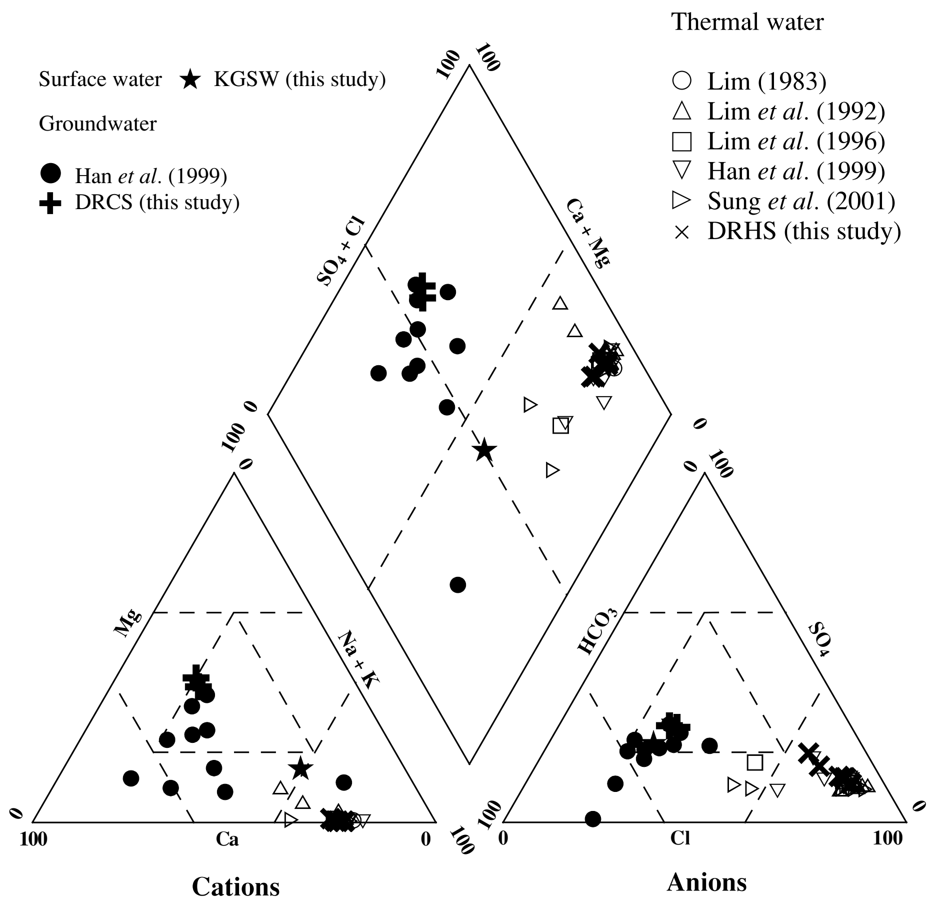

Fig. 2. Piper diagram of the Dongare area thermal water, groundwater and surface water. For comparison, data from previous literature were also plotted. The chemical compositions (particularly anions) of the thermal water from this study show that they experienced a different water-rock interaction than the groundwater.

into hornblende granite, adamellite, biotite granite, and finally micrographic granite through fractional crystallization of plagioclase. Based on trace element composition and REE patterns, the granitoids are continental margin arc calc-alkaline rocks produced in the subduction environment at 69.6 ± 1.9 Ma (2σ) with an initial Sr isotopic ratio of 0.70503 ± 0.00015 (Yun *et al.*, 2005).

The Dongrae thermal water occurs in the adamellite area and is enclosed by two major displacements (i.e., Yangsan fault and Dongrae fault) extending in an E–W direction (DRHS & HSHS in Fig. 1). The Yangsan fault is one of the most important geological structures in the southern part of the Korean Peninsula. The Dongrae thermal water occurs near to the Dongrae fault line. Ryu *et al.* (1999) argued that the Dongrae and Yangsan faults might be related to the flow route of the hot springs in the study area. The thermal water should thus be considered to flow along the E–W fault and to ascend along the Dongrae fault. Choi *et al.* (1984) also suggested that the shallow groundwater in the Dongrae area should follow mainly N60-80E trending fractures developed in the bed rocks. Son *et al.* (2002) suggested that the topographical basin formed at Sanjeong in Geumsongsan (see Fig. 1) might be considered as a major recharge area of groundwater around the study area. This suggests that groundwater flows from the western mountain range to the lower area of southeastern Dongrae.

The Dongrae thermal waters have naturally flowed out to the land surface for hundred of years. However, over the past 30 years, thermal waters in South Korea have been overpumped for baths. Therefore, there is no natural overflow in most Korean thermal waters, including Dongrae. In addition, the upper part of the bedrock aquifer in the thermal water areas has been encroached by nearby cold groundwater due to excessive pumping of deep thermal wells (Yum, 2000). At Dongrae, groundwater levels of thermal water have recently been lowered to 100 m below surface (Lee and Lim, 1995; Sung *et al.*, 1999). The cold groundwater levels range from 6 to 23 m (Han *et al.*, 1999).

Table 1. Previous results from hot spring and groundwater research performed in Dongrae and surrounding area, Korea

Site	Name	Sampling date	Well depth (m)	*T* (°C)	pH	EC (μS/cm)	F (mg/L)	Cl (mg/L)	SO_4 (mg/L)	HCO_3 (mg/L)	Na (mg/L)	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Sr (mg/L)	
Hot Spring																
D1		May, 1991	220	35.4	7.74	972	0.8	212	33.2	49.2	111	43.7	2.67	5.18	0.21	Lim *et al*., 1992
D2		May, 1991	175	33	7.83	876	0.6	206	32.0	46.2	95	47.2	1.92	8.66	0.20	
D3		May, 1991	230	49.3	8.19	1638	1.5	310	49.5	38.6	181	47.6	5.67	1.8	0.24	
DH-1	Nokcheon-tang	May, 1991	150	62.2	7.51	1763	1.6	387	70.2	58.0	231	61	6.36	0.26	0.36	
DH-4	Jungang-Motel	May, 1991	115	66.6	7.74	2220	1.8	404	69.6	47.2	234	58.9	6.68	5.49	0.32	
DH-7	Mansoo-tang	May, 1991	120	66.6	8.18	2560	1.9	460	75.5	29.8	273	63.6	6.65	2.11	0.68	
DH-8	Hyundae-tang	May, 1991	110	62.1	7.92	2100	1.8	402	71.9	53.7	245	57.7	6.38	0.32	0.53	
DH-9	Yangtangjang	May, 1991	120	65.5	7.46	2440	1.8	439	74.4	40.3	259	61.7	6.17	1.69	0.65	
DH1	Nokcheon-tang	May, 1996	200	61.3	8.09	1520	1.5	380	42.0	72.0	231	62.9	5.08	0.49	—	Lim *et al*., 1996
C5	Yangtangjang	May, 1996		71	8.3	1780	1.79	445	82.9	30.0	255	71	6.2	1.47	—	
DH-1	Nokcheon-tang	May, 1998	200	66.4	7.69	1688	2.12	448	82.8	41.2	253	65.2	6.09	0.1	—	Han *et al*., 1999
DH-2	Moonwha-tang	May, 1998	210	62.7	7.82	1476	2.01	366	72.6	64.0	240	55.2	5.98	0.13	—	
DH-3	Geumcheon-tang	May, 1998	107	50.6	7.94	1526	1.89	376	77.0	51.9	233	58.6	5.55	0.14	—	
DH-4	Jungang-Motel	May, 1998	210	55	8	1044	1.48	234	52.0	76.3	170	30.7	3.84	0.08	—	
DH-5	Cheonil-tang	May, 1998	210	62	7.74	1395	1.54	314	74.4	77.8	218	49.2	5.05	0.17	—	
DH-6	Oncheon-Motel	May, 1998	210	63	7.65	1463	1.73	348	73.2	48.8	227	51.1	5.03	0.12	—	
DH-7	Mansoo-tang	May, 1998	210	53.7	7.77	1439	1.55	340	74.0	103.7	205	53.9	5	0.28	—	
DH-8	Hyundae-tang	May, 1998	210	60.4	7.89	1551	1.94	382	77.0	51.9	222	54.6	5.38	0.11	—	
DH-9	Yangtangjang	May, 1998	210	52.1	7.91	1689	1.87	454	83.7	318.8	237	65.2	6.38	0.17	—	
DW01		Oct, 19, 1999	140	68.1	7.94	1567	1.60	357	52.0	31.0	262.1	70.5	8.1	0.1	1.31	Sung *et al*., 2001
DW02		Oct, 19, 1999	120	63	7.82	1432	1.60	322	49.0	46.0	242.6	61.1	7.1	0.2	1.12	
DW03		Oct, 19, 1999	110	46.2	7.79	921	0.40	141	38.0	165.0	168.2	37.1	4.6	0.2	0.71	
DW04		Oct, 1999	130	59.3	7.8	1441	1.10	282	48.0	52.0	231.6	55.1	4.8	0.2	1.06	
DW05		Nov, 18, 1999	110	52.9	7.71	1432	1.20	305	51.0	34.0	219.4	56.4	7.3	0.2	1.05	
DW06		Oct, 19, 1999	130	56.4	8.08	1443	1.40	302	48.0	64.0	228.3	63.7	7.3	0.3	1.23	
DW07		Oct, 19, 1999	150	29.1	7.19	1063	0.50	163	36.0	156.0	153.2	71.4	2.9	0.7	1.25	
DJH*		Jun, 2000	720	40	8.22	463	1.55	61.8	18.4	127.0	78.7	12.4	1.01	0.39	0.12	Moon *et al*., 2000a

Site	Name	Sampling date	Well depth (m)	T (°C)	pH	EC (μS/cm)	F (mg/L)	Cl (mg/L)	SO_4 (mg/L)	HCO_3 (mg/L)	Na (mg/L)	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Sr (mg/L)	
Groundwater																
DNH*		Jul, 2000	648	26.5	6.75	25520	0.09	9580	1260	32.7	4030	1420	14.2	491	14.80	Moon *et al.*, 2000b
MR1		May, 1998	100	17.6	7.23	455	0.42	38	50.4	100.6	17.9	56.1	0.58	6.17	—	Han *et al.*, 1999
OC1		May, 1998		17	6.57	442	0.07	46.3	49.2	103.7	39.2	42.1	1.69	8.47	—	
OC2		May, 1998		16.5	7.05	466	0.1	45.4	41.7	109.8	21.4	33	0.89	21.3	—	
SJ1		May, 1998	87	16.9	6.06	365	0.05	41.9	29.7	64.0	20.8	30.8	1.04	9.93	—	
OC3		May, 1998		16.3	6.39	592	0.08	39.4	56.6	167.8	27.2	43.2	1.24	20.2	—	
SJ2		May, 1998		14.7	6.8	240	0.07	18.8	16.9	65.6	16.2	19.7	0.78	7.35	—	
MR2		May, 1998	23	16.6	6.37	705	0.15	47.6	59.3	216.6	37.4	78.9	15.1	7.71	—	
MR3		May, 1998	20	14	6.71	450	0.18	38.6	41.5	137.2	36.4	37.7	8.1	4.15	—	
CC4		May, 1998	130	16.9	6.74	439	0.05	39.3	38.2	114.4	22.7	29.2	1.19	17.1	—	
CC5		May, 1998	113	16.8	7.19	503	0.18	42.6	1.9	242.6	67.4	13.7	6.21	5.78	—	
SJ3		May, 1998	100	17.2	7.03	285	0.07	21.3	13.3	102.2	13	27.5	0.61	7.26	—	

**DJH and DNH are boreholes being developed recently, which are located about 1 km northeast and 6 km southeast from DRHR hole. The distance between DNH and the southeastern coast is about 5 km.*

Sampling and Analytical Methods

Thermal water sampling for DRHS hole was carried out seven times between 2004 and 2007, mainly in March, in order to assess the overall variation of its chemical composition. For comparison, in March 2007 other thermal waters were sampled from two HSHS holes, located about 300 m west of DRHS. In 2007, rain water was also sampled at Dongrae at the beginning of the rainy season. In November 2007, cold groundwater (DRCS hole) and surface water were collected to compare with thermal water.

Physical parameters such as temperature, pH, electric conductivity (EC) were measured in the field using portable equipments (Orion model 290A and 130). Pumped thermal water and cold groundwater samples were collected once physical properties such as temperature, pH and EC values were stabilized.

All samples were filtered with a precleaned plastic filter fitted with a 0.45 μm pore size membrane. All sample bottles were acid-washed and rinsed at least three times with distilled water. Water samples for major and trace element determinations were collected in polyethylene bottles and acidified with ultrapure nitric acid to pH < 1.

Cation (Ca^{2+}, Mg^{2+}, Na^+, K^+, and Sr^{2+}) and SiO_2 concentrations were analyzed using an inductively coulpled plasma-atomic emission spectrometer (ICP-AES, Jobin Yvon 38) and an atomic absorption spectrometer (AAS, Perkin Elmer 5100). Anion concentrations were determined for Cl^-, SO_4^{2-}, NO_3^-, and Br^- by ion chromatography (Dionex 300).

For Sr isotope composition, Sr was separated using the standard cation exchange technique. The Sr isotopic ratios were measured using a VG 54-30 thermal ionization mass spectrometer at the Korea Basic Science Institute in Daejeon. Over the course of isotopic analyses, measurements of the standard NBS987 gave a $^{87}Sr/^{86}Sr$ ratio of 0.710247 ± 0.000003 (N = 30, 2σ error). The total chemical blank was less than 50 pg for Sr.

Results

The chemical composition of the thermal water and groundwater are listed in Tables 1 and 2. The chemical composition of thermal water from the selected well over a period of four years is given in Table 2 along with surface water, shallow groundwater and rainwater. Data collected in this study as well as older data sets (1973–2001) within the study area are plotted in Fig. 2.

Thermal water temperature at Dongrae over the past 18 years ranges from 29.1°C to 71°C, while that of DRHR over a period of 4 years ranges from 57.5°C to 63.4°C. The Dongrae thermal water is of Na–Cl type with a pH in the 7.2–8.3 range, whereas the chemical composition of

Table 2. Physical and chemical properties of hot and cold springs in the Dongrae area, Korea

Site		Sampling date	Well depth (m)	*T* (°C)	pH	EC (μS/cm)	F (mg/L)	Cl (mg/L)	Br (mg/L)	SO_4 (mg/L)	HCO_3 (mg/L)	Na (mg/L)	Ca (mg/L)	K (mg/L)	Mg (mg/L)	SiO_2 (mg/L)	Br/Cl
Thermal water																	
DRHS-01[1]	129°05′02.0″ E 35°13′02.6″ N	Feb, 2004	300	61	8.34	1542	1.60	251.9	1.64	75.6	45.8	219.0	58.5	6.79	0.165	51.3	0.00649
DRHS-02		Aug, 2004	300	57.7	7.48	1472	1.57	223.3	1.09	88.5	76.3	186.0	51.6	7.01	0.194	48.6	0.00488
DRHS-03		Mar, 2005	300	61	7.85	1540	1.59	358.4	1.18	80.6	72.0	194.4	51.9	5.45	0.2	57.1	0.00328
DRHS-04		Mar, 2006	300	62.8	8.02	1463	1.69	382.3	1.23	81.8	67.1	204.8	59.5	5.04	1.28	401.0	0.00321
DRHS-05		Mar, 2007	300	63.4	7.93	1551	1.69	368.0	1.46	66.3	54.9	243.0	59.7	5.37	0.2	51.3	0.00397
DRHS-06		Jun, 2007	300	63	7.90	1521	1.75	371.0	0.90	69.0	54.0	194.0	55.1	4.97	0.04	53.5	0.00243
DRHS-07		Nov, 2007	300	62.1	7.92	1515	1.66	341.0	1.03	72.9	56.4	228.0	55.3	4.51	0.15	22.5	0.00302
HSHS-A[2]	129°04′54.3″ E 35°13′11.9″ N	Mar, 2007	230	58	7.68	1385	1.40	303.0	0.79	62.0	51.9	208.0	63.2	6.14	0.63	54.6	0.00261
HSHS-B[2]	129°04′54.4″ E 35°13′11.8″ N	Mar, 2007	170	49.5	7.44	1158	0.99	238.0	0.60	52.7	65.6	166.0	55.8	4.87	2.23	57.3	0.00252
Groundwater																	
DRCS-01	129°04′12.0″ E 35°12′09.0″ N	Mar, 2007	130	8.6	7.31	623	0.08	48.0	0.13	62.3	126.6	30.2	45.5	1.63	27.7	50.1	0.00271
DRCS-02		Nov, 2007	130	16.4	7.13	630	0.1	52.2	0.1	62.1	123.6	28.7	45.9	1.29	30	23.2	0.00192
Surface water																	
KGSW	129°04′22.0″ E 35°14′04.0″ N	Nov, 2007	0	13.5	7.3	69.4	0.08	5.3	—	5.85	16.8	7.62	2.83	0.37	1.04	9.24	—
Precipitation																	
DRP20070625[3]	129°05′02.0″ E 35°13′02.6″ N	Jun, 2007	—	—	4.3	42.9	0.3	0.5	<0.05	5.32	4.58	0.29	0.66	0.07	0.19	<0.1	—
Sea water																	
Busan[4] (near to study area)				16.9	8.24	50356	2.30	19020	66.8	1773	134	10636	1280	406	1280	—	0.00351

[1] *Jungang Spa. The same well with DH4 in Table 1.*
[2] *Heochimcheong Spa. A and B mean hole number.*
[3] *DRP20070625 was collected at the same site with DRHS.*
[4] *Sung et al. (2001).*

Table 3. Sr isotopic composition of the thermal water, groundwater, surface water and rainwater at the Dongrae area, Korea

Sample name		Sampling date	$^{87}Sr/^{86}Sr$	2σ	Sr (μg/L)	1/Sr
DRHS-01	thermal water	Feb, 2004	0.705691	0.000008	1060	0.0009
DRHS-02		Aug, 2004	0.705686	0.000010	883	0.0011
DRHS-03		Mar, 2005	0.705694	0.000010	902	0.0011
DRHS-04		Mar, 2006	0.705688	0.000010	1253	0.0008
DRHS-05		Mar, 2007	0.705672	0.000012	1080	0.0009
DRHS-06		Jun, 2007	0.705677	0.000012	1080	0.0009
DRHS-07		Nov, 2007	0.705696	0.000012	1117	0.0009
HSHS-A		Mar, 2007	0.705666	0.000012	1110	0.0009
HSHS-B		Mar, 2007	0.705651	0.000011	880	0.0011
DRCS-01	groundwater	Mar, 2007	0.705781	0.000026	384	0.0026
DRCS-02		Nov, 2007	0.705789	0.000012	408	0.0025
KGSW	surface water	Nov, 2007	0.706700	0.000014	30	0.0333
DRP20070625	rain water	Jun, 2007	0.707375	0.000011	1	1.0000
KJ-2*	granite		0.707041	0.000012	229900	0.000004
KJ-4			0.722915	0.000014	21600	0.000046
KJ-6			0.718773	0.000012	28700	0.000035
KJ-9			0.708007	0.000012	113500	0.000009
KJ-11			0.708401	0.000011	110300	0.000009
KJ-12			0.715372	0.000011	38500	0.000026
KJ-15			0.708836	0.000011	99100	0.000010

**Tha data for the granite were reported from Yun et al. (2005).*

the shallow cold groundwater is of Ca(–Na)–HCO_3 type with pH ranging 6.1–7.3. The electric conductivity (EC) of Dongrae thermal water ranges from 463 to 2560 μS/cm, whereas that of groundwater ranges from 240 to 705 μS/cm (see Tables 1 and 2). Groundwater at DNH hole, located about 6 km southeast from DRHR, shows a high EC value of 25520 μS/cm. The average chloride concentration in shallow groundwater is less than 50 mg/L, whereas in most thermal waters, it reaches values higher than 300 mg/L. The anionic equivalence in the geothermal water is $Cl^- > SO_4^{2-} > HCO_3^-$, whereas that of groundwater is $HCO_3^- > Cl^- > SO_4^{2-}$, suggesting they experienced different water-rock interaction.

The Sr isotope ratios of the Dongrae area thermal water, groundwater and rain water are given in Table 3. The $^{87}Sr/^{86}Sr$ ratios of the thermal water ranges between 0.705651 ± 11 and 0.705696 ± 12. The overall variations of $^{87}Sr/^{86}Sr$ ratios from the thermal waters, groundwater, surface water and rainwater are plotted in Fig. 3. Figure 3a shows the difference of $^{87}Sr/^{86}Sr$ ratios of thermal water, groundwater, surface water and rainwater at Dongrae. Figure 3b shows the variations of $^{87}Sr/^{86}Sr$ ratios of the thermal water from DRHS hole over the past four years. The Sr concentration of the thermal water ranges from 880 to 1253 μg/L. The $^{87}Sr/^{86}Sr$ ratios of the groundwater samples are 0.705781 ± 26 and 0.705789 ± 12, which are higher than those of the thermal water. The $^{87}Sr/^{86}Sr$ ratio of the surface water sample is 0.706700 ± 14, which is also higher than those of the thermal water. The Sr concentrations of groundwater and surface water are 384–408 μg/L and 30 μg/L, respectively. The $^{87}Sr/^{86}Sr$ ratio of rainwater is 0.707375 ± 11, which is higher than both the thermal water and groundwater. However, the concentration of Sr is very low with a value of 1 μg/L.

Discussion

Origin and Geochemical implications of $^{87}Sr/^{86}Sr$ ratio in the thermal water

One of the peculiar geochemical characteristics of the Dongrae thermal water is that the $^{87}Sr/^{86}Sr$ ratios of the thermal water are lower than those of shallow groundwater, surface water, rainwater and the present $^{87}Sr/^{86}Sr$ ratio of the host granitic rocks (Figs. 3a and 3c). The other is that they have very constant $^{87}Sr/^{86}Sr$ ratios over the past four years (Fig. 3b). In addition, the thermal waters $^{87}Sr/^{86}Sr$ ratios values, ranging between 0.705651 ± 11 and 0.705696 ± 12, are similar to the initial $^{87}Sr/^{86}Sr$ ratio of 0.70503 ± 0.00015 from the granites in the study area (Yun *et al.*, 2005).

An isotopic ratio in groundwater at any given point is a product of both the isotopic ratio of solute transported from remote areas and that acquired from local rock by chemical reaction (Johnson and Depaolo, 1997). Sr is transported by advection and dispersion and the $^{87}Sr/^{86}Sr$ ratio of the water is influenced by Sr transferred from solid phases by dissolution and/or ion exchange. Moreover, the chemical behavior of Sr in groundwater is

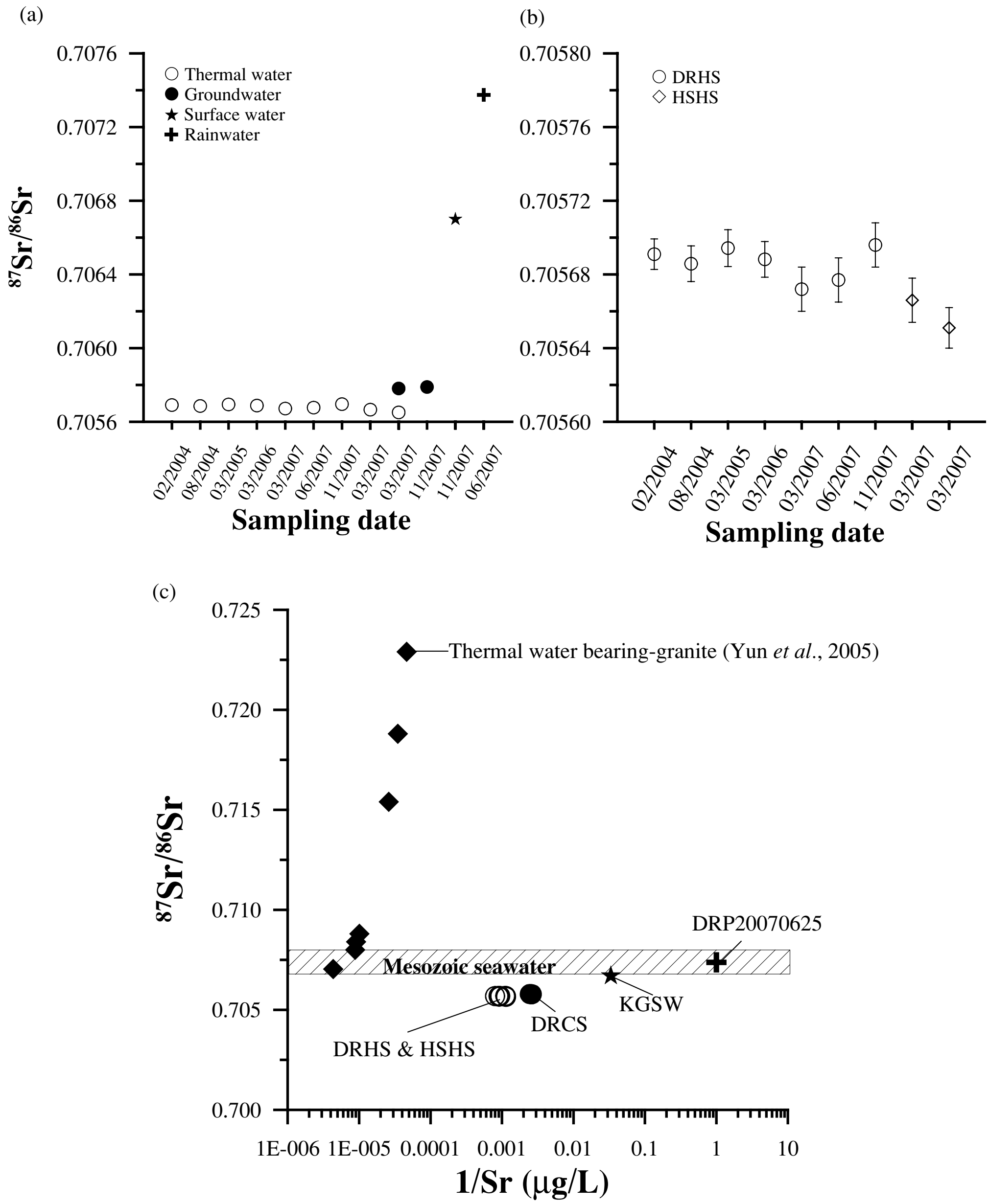

Fig. 3. (a) $^{87}Sr/^{86}Sr$ ratios of the thermal water, groundwater, surface water and rainwater. (b) Variation of $^{87}Sr/^{86}Sr$ ratios over a period of 4 years in the thermal waters. (c) Plot of the $^{87}Sr/^{86}Sr$ versus the 1/Sr for the thermal water (DRHS & HSHS), groundwater (DRCS), surface water (KGSW) rainwater (DRP20070625) and present $^{87}Sr/^{86}Sr$ ratio of the granitoids. The range of the $^{87}Sr/^{86}Sr$ ratio in the Mesozoic seawater was given by Denison et al. (1994). $^{87}Sr/^{86}Sr$ ratios of the granitoids are by Yun et al. (2005).

strongly controlled by the nature of the aquifer matrix (Vuataz *et al*., 1988). Water temperature, the presence of fracture filling mineral and the chemical composition of the water also are important factors on the chemical behavior of Sr in groundwater. In these systems, ion exchange reactions between solute and certain minerals occur rapidly and therefore exert an important influence on the solute isotope ratios of exchanged elements (Drever, 1988; Bishop and Lloyd, 1990; Bullen *et al*., 1996; Johnson and DePaolo, 1997). Zuddas *et al*. (1995) showed that in determining the fluid isotopic composition, biotite played an important role in the initial stage of interaction. Hence, as a result of long-term interaction in near-equilibrium systems, natural fluids should reach the same signature as the host rock. Thus, the $^{87}Sr/^{86}Sr$ ratio of groundwater is inexorably pushed towards the

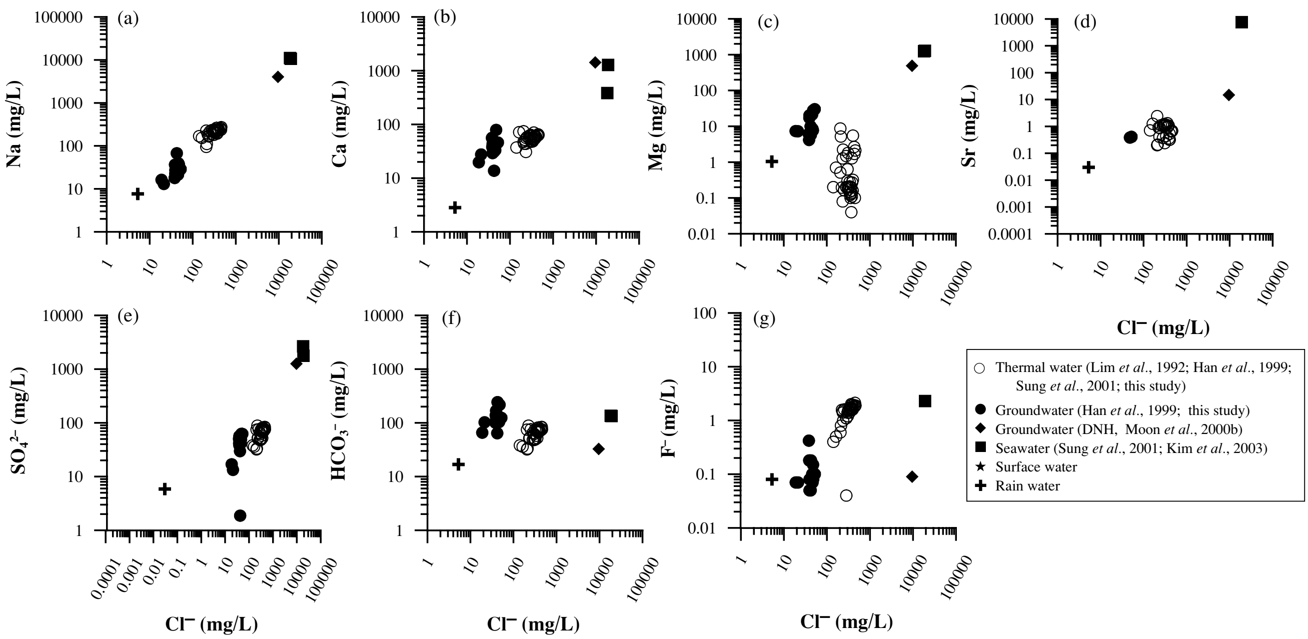

Fig. 4. Correlation diagram of Cl versus other ions in the thermal water, groundwater and rainwater.

average value of the country rock (Stettller and Allègre, 1978). However, waters ascending rapidly in open channels are unlikely to reach full equilibration (Graham, 1992). $^{87}Sr/^{86}Sr$ ratio of the Dongrae thermal water is similar to the host rock initial $^{87}Sr/^{86}Sr$ ratio rather than its present $^{87}Sr/^{86}Sr$ ratio. This suggests that the $^{87}Sr/^{86}Sr$ ratio of the thermal water could be derived from water-rock interaction with a $^{87}Sr/^{86}Sr$ ratio similar to the initial value of the source material of the Dongrae area granites. However, it may be difficult to prove that the very low Sr isotope ratio of the Dongrae thermal water was produced by water-rock interaction at the time of the emplacement of the host granite and consequently, the very low value from the Dongrae thermal water remains open to further studies. Nevertheless, the relationship between the $^{87}Sr/^{86}Sr$ ratios of thermal water and those of groundwater, surface water and rain water suggests that the Sr isotope signatures in the Dongrae thermal water might reflect water-rock interaction (exchange) in a closed system over a long period of time under geological conditions similar to the formation of oil reservoirs. Kebede *et al.* (2008) identified paleo-groundwaters with age ranging between 2,300 and 3,000 years based on ^{14}C age of groundwater from Ethiopian rift volcanic aquifers. This study serves as an example of very slow water cycling of deep groundwater in a fractured aquifer system. The geochemical characteristics of $^{87}Sr/^{86}Sr$ ratios of the Dongrae thermal water indicate that it might also be a product by paleo-groundwater-rock interaction rather than that of groundwater-rock interaction with current water cycle.

Geochemical significance of the chemical composition in the thermal water: the origin of the brackish thermal water and the relationship between thermal water and shallow groundwater

Figure 4 is a correlation diagram between chloride ion and other ions in rain water, groundwater, thermal water and seawater at Dongrae and its surrounding area. Except Mg, the concentrations of Na, Ca and Sr in rain water, groundwater, thermal water and seawater have a linear relationship with Cl. Such trend suggests that the thermal water should ultimately originate from the meteoric water cycle. Oxygen and hydrogen isotopic data summarized in the literature (Lim *et al.*, 1992; Sung *et al.*, 2001; Kim *et al.*, 2003) also indicate that local precipitation is the ultimate source of the geothermal water (Fig. 5).

The Dongrae thermal water is brackish deep groundwater in the 66–70°C temperature range. In a fractured crystalline rock aquifer system, the introduction of cold groundwater into geothermal water aquifer is related with two major processes: 1) partially penetrating casing of the thermal wells, and 2) downward movement of cold groundwater through the leaky aquitard. However, the current geochemical compositions of the Dongrae area thermal water do not show a geochemical characteristic due to input of shallow groundwater into the deep geothermal water. Pinpointing the origin of the dissolved ions in the Dongrae area thermal water may be helpful in understanding the thermal water heat source as well as the water cycle among precipitation, surface water (including seawater) and groundwater.

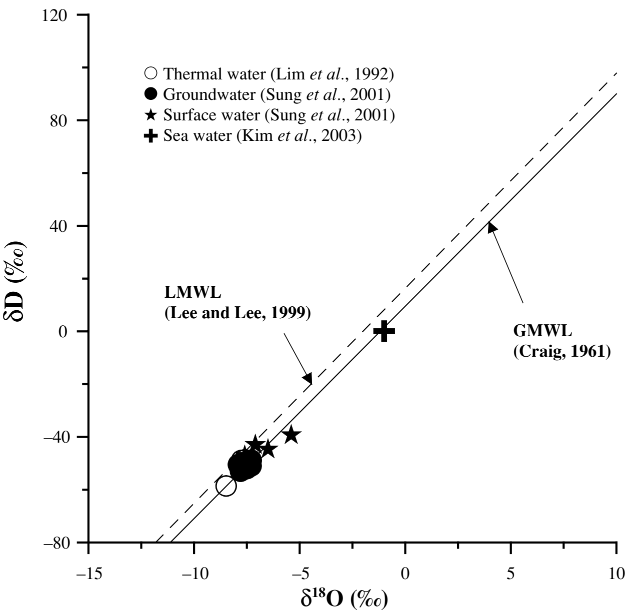

Fig. 5. Plot of δD vs. $\delta^{18}O$ of the thermal water, groundwater, surface water and seawater in Korea. LMWL and GMWL represent the local meteoric water line in South Korea (Lee and Lee, 1999) and the global meteoric water line (Craig, 1961), respectively.

Based on the spectrum analysis of long-term monitored groundwater level and electric conductivity in well DNH, Lee *et al.* (2001) and Sung *et al.* (2001) argued that the current seawater should be encroaching into the Dongrae thermal water through fractures which were developed at a greater depth and extended to the neighboring coast. The chemical compositions of the groundwater from a vertical borehole DNH of 648 m (Moon *et al.*, 2000b) are similar to those of seawater, however, its water temperature is slightly high (26.5°C). This suggests that the groundwater at the DNH hole might be partly influenced by current seawater and thermal water. However, even though the chemical composition of groundwater at the DNH hole is similar to that of seawater, the DNH hole is deeper than other thermal water holes at Dongrae and the water temperature of the DNH hole is much lower than that of the Dongrae thermal water. This suggests that the aquifer at the DNH hole should be different from that of the Dongrae thermal water.

Figure 6 is a variation diagram of Br/Cl ratio vs. other chemical component ratios from the thermal water, groundwater and seawater. In Figs. 6a and 6b, the Br/Cl ratios of the thermal water, groundwater and seawater show an increasing trend with increase of pH and Na/Cl ratio. The positive relationship between Br/Cl and Na/Cl suggests that the brackish component of thermal water should be derived from sea water. However, there is no correlation with Ca/Cl, K/Cl and Mg/Cl. Also, the Mg/Cl ratio of the thermal water is lower than those of groundwater and seawater (Figs. 6c–e). The $^{87}Sr/^{86}Sr$ ratio of the thermal water during last 4 years is constant and much lower than that of seawater, thus suggesting that the thermal water was not affected by current seawater. Seawater typically has a Br concentration of around 67 mg/L and a Br/Cl ratio of 0.0035 (Leybourne and Goodfellow, 2007). Over a period of 4 years, the Br/Cl ratio of the Dongrae thermal water decreased from 0.00649 to 0.00243 (Table 2). This strongly suggests that the Dongrae thermal water are not influenced by current seawater intrusion. Therefore, the geochemical characteristics of dissolved ions and $^{87}Sr/^{86}Sr$ ratio of the thermal water show that the brackish component in the Dongrae thermal water is most likely a remnant of paleo-seawater intrusion rather than a current sea water intrusion through the shallow groundwater aquifer located above the Dongrae thermal aquifer.

Heat source of the Dongrae thermal water

Generally, the origin of geothermal water can be explained by one of the following mechanisms: 1) geothermal water principally originated from meteoric water, and derived from heating of the static meteoric water reservoir by thermal conduction and convection, 2) a heat source, such as magma, is in contact with a reservoir in an area with volcanic activity and cold water in the reservoir is heated by contact with the heat source and rises in accordance to Darcy's law, and 3) juvenile water from a buried crystallizing magmatic source follows fracture zones and mixes with static meteoric reservoir. In granite aquifer, it is very difficult to define the origin of the thermal water because we cannot find the heat source directly. Nevertheless, based on geochemical characteristics we may be able to derive the heat source of the Dongrae thermal water.

One possibility is that deep groundwater ascending along major faults is heated due to a geothermal gradient with high heat anomaly or heat production caused by radioactive element such as U, Th and K. But, the water temperature of the Dongrae thermal water has not changed in spite of severe lowering of the groundwater table over the past 100 years. The lowering of deep groundwater table implies a lack of supply of meteoric water from surface or shallow cold groundwater. Such a lack of water supply from surface can force thermal water temperatures to increase. However, the Dongrae thermal water does not have such phenomenon. In addition, Lee *et al.* (2007) reported that heat flow and heat production across Korea were similar, regardless of petrography or formation age of lithology. They concluded that heat production is unlikely to have a first-order importance in determining surface heat flow distribution in Korea. This suggests that the Dongrae thermal water can not be heated due to

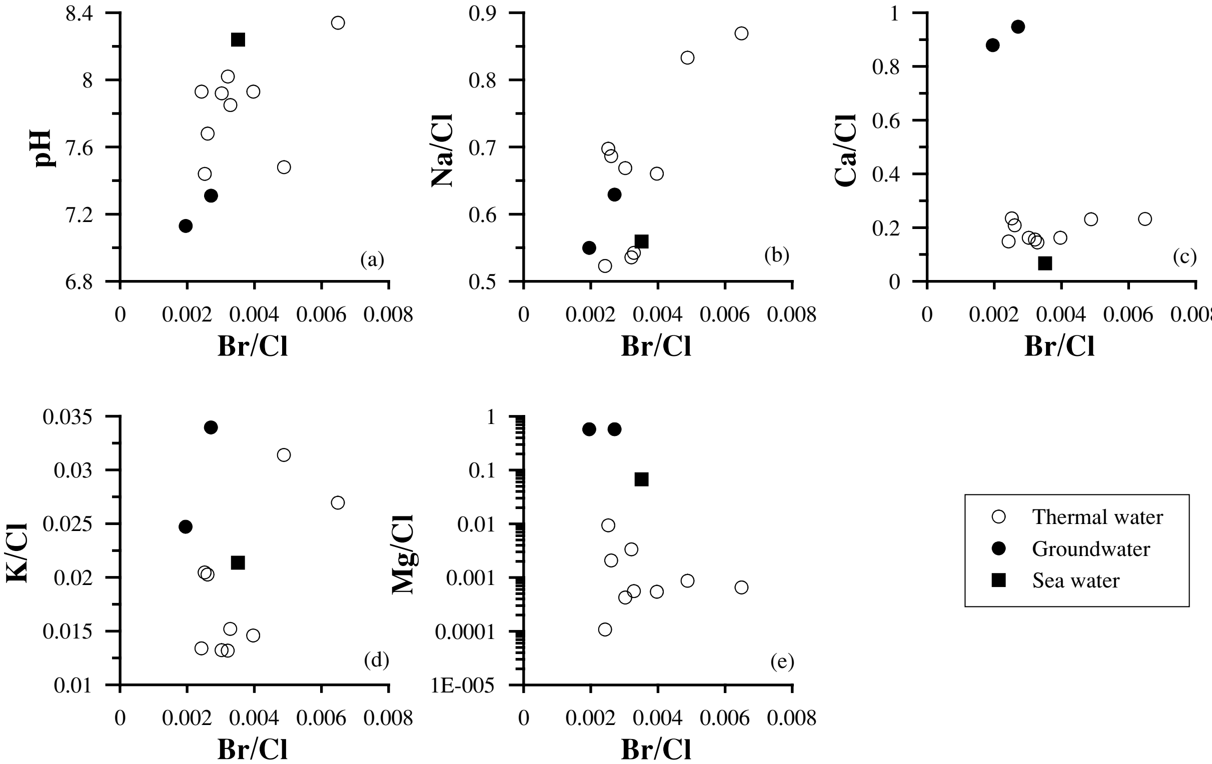

Fig. 6. Correlation diagram of Br/Cl ratio versus (a) pH, (b) Na/Cl, (c) Ca/Cl, (d) K/Cl and (e) Mg/Cl ratio and temperature versus Mg/Cl ratio among thermal water, groundwater and sea water.

geothermal gradient with high heat anomaly or heat production caused by radioactive element such as U, Th and K along the major faults.

Another possibility is the genetic relationship with Cretaceous granite emplacement. As previously mentioned, the Dongrae thermal water shows very constant water temperatures despite a severe drawdown of groundwater table. The chemical composition data for the thermal water from literature also shows relatively constant value over the last 40 years (Park, 1968; Lim, 1983, Lim *et al.*, 1992, 1996; Han *et al.*, 1999; Sung *et al.*, 2001; this study). Consequently, differences in chemical composition between the thermal water and shallow cold groundwater suggest that they should have experienced different water-rock interaction. The $^{87}Sr/^{86}Sr$ ratios of the thermal water have not changed over the last four years and are lower than those of the shallow cold groundwater, surface water, rain water and aquifer-bearing host rock. All of these characteristics indicate that the $^{87}Sr/^{86}Sr$ ratios of the thermal water should be a product of an old groundwater-rock interaction. So, the present water temperature of the Dongrae thermal water may be derived from old groundwater-heat source rather than current heat source-groundwater interaction. Unfortunately, we do not know the age of the thermal water. It may be useful to carry out C-14 dating for the thermal water to determine whether the $^{87}Sr/^{86}Sr$ ratio of the Dongrae thermal water is a product of old groundwater-heat source or not.

Summary and Conclusions

The Dongrae thermal water is one of the oldest hot springs in Korea and has been used as a spa for more than 1200 years. In this study, we measured the Sr isotopic ratio and chemical composition of the thermal water from one representative well over a period of four years in order to identify both the geochemical significance of this Sr isotopic ratio as well as the heat source of the Dongrae thermal water. At its highest temperature of 71°C, the Dongrae thermal water is of Na–Cl type with an electric conductivity (EC) of 876–2560 μS/cm and pH of 7.5–8.3, whereas the chemical composition of the shallow cold groundwater is Ca(–Na)–HCO_3 type with a low EC of 240–705 μS/cm and a pH of 6.1–7.3. The $^{87}Sr/^{86}Sr$ ratios of the thermal waters range from 0.705651 ± 11 to 0.705696 ± 12 and remained nearly unchanged over the past 4 years (2004–2007). The $^{87}Sr/^{86}Sr$ ratios of the shallow cold groundwater, surface water and rainwater range from 0.705781 ± 26 to 0.705789 ± 12, 0.706700 ± 14 and 0.707375 ± 11, respectively. The $^{87}Sr/^{86}Sr$ ratios of the

Dongrae area thermal water are lower than those of groundwater, surface water, rain water as well as granite bearing aquifer. This suggests that the circulation rate between thermal water and current meteoric water, including groundwater, surface water and rain water in the Dongrae area should be very slow.

The relationship between Cl and other constituent ions of the rain water, groundwater, thermal water and seawater suggests that thermal water are likely derived from meteoric water. However, concentrations of the dissolved ions in the thermal water derived from deep groundwater are higher than those of surrounding shallow groundwater and the Br/Cl ratio of the thermal water shows a decreasing trend over the four years. The thermal water has a very constant $^{87}Sr/^{86}Sr$ ratio and a lower $^{87}Sr/^{86}Sr$ ratio than that of the shallow cold groundwater and precipitation. The $^{87}Sr/^{86}Sr$ ratio of the thermal water is also lower than the present $^{87}Sr/^{86}Sr$ ratio of the thermal water-bearing rock. Therefore, it can be concluded that the Dongrae thermal water is likely a remnant of paleo-groundwater with seawater component-rock interaction rather than encroachment of current seawater intrusion. In this study, we show that $^{87}Sr/^{86}Sr$ ratio of deep groundwater can be used as a tracer to resolve the time lag of groundwater cycle between deep and shallow groundwater in a fractured granite aquifer system.

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