

동래온천지역의 지열수와 지하수의 지화학적 특성

Geochemical Characteristics of Geothermal Water and Groundwater in the Dongrae Hot-Spring Area

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요약 / ABSTRACT

동래온천지역 지열수 및 그 주변지역 지하수의 수리지구화학적 특성을 밝히기 위해서, 20개의 시료(11개 지하수 시료와 9개 온천수 시료)를 채수하여 화학성분을 분석하였다. 지하수와 온천수의 화학적 성질을 조사하고 이들의 화학 조성을 비교·분석하였다. 요인분석과 상관분석을 통하여 화학분석 자료를 몇 개의 요인으로 묶어서 요인들간의 상호연관성을 고찰하였다. 파이퍼 다이어그램에 도시한 결과, 지하수는 Ca-HCO₃ 형에 그리고 온천수는 Na-Cl 형에 속하는 것으로 나타났다. 동래온천수의 염소이온 함량은 우리나라의 다른 화강암지역의 온천수보다 높게 나타난다. 온천수의 Na/Cl 비는 0.7~1.3이다. 상평형도에 의하면, 지하수는 카오리나이트 안정 영역에 놓인다. 한편, 온천수는 미사장석이나 카오리나이트 안정영역에 놓인다. Na-K, Na-K-Ca 및 Na-K-Ca-Mg 지온계에 의하면, 지하 심부의 지열대수층의 온도는 115~145°C로 추정된다.

주요어 : 동래온천, 지열수, 물-암석 반응, 지온계, 요인분석

Twenty water samples (eleven groundwater and nine geothermal water samples) were collected to elucidate hydrogeochemical characteristics of the groundwater and geothermal water in the Dongrae hot-spring area and its vicinity. Major and minor elements were analyzed for ground and geothermal water samples. Physicochemical properties of the groundwater and the geothermal water were examined and chemical composition of the two waters were compared. Factor and correlation analyses were

carried out to simplify the physicochemical data into grouping some factors and to find interaction between them. The groundwaters belong to Ca-HCO₃ type, while the geothermal waters belong to Na-Cl type. The Na and Cl concentrations in the Dongrae hot-spring area are higher than those of other granite areas in South Korea. The Na/Cl weight ratio ranges from 0.7 to 1.3 for the geothermal waters. On the phase stability diagram, groundwaters fall effectively in the field of stability of kaolinite, while geothermal waters fall in the stability field of microcline or kolinite depending on the chemical composition system. Based on the Na-K, Na-K-Ca and Na-K-Ca-Mg geothermometers, the geothermal reservoir is estimated to have equilibrium temperature between 115 and 145°C.

Key words : Dongrae hot-spring, geothermal water, water-rock interaction, geothermometer, factor analysis

INTRODUCTION

The study area (the Dongrae hot-spring area and its periphery) is located in southeastern coast of the Korean Peninsula and is the second largest city of the Republic of Korea (Fig. 1). The maximum value of heat flow in this area is higher than 100mW/m² (Lim et al., 1990) which is higher than normal values in the Korean Peninsula. The Dongrae hot-spring is situated and is very famous together with the Haeundae hot-spring located in the eastern seaside of Pusan city. At the same time, Pusan city is most heavily dependent on groundwater for divergent uses (domestic, potable and industrial uses) among the six large cities (Seoul, Pusan, Taegu, Kwangju, Incheon, and Daejeon). Therefore, it is very important to assess available groundwater resources of Pusan, to manage it reasonably, and to prevent it from pollution.

Nine thermal water samples (DH1-9) were collected from bathhouses (Nockcheon-Tang, Moonwha-Tang, Geumcheon-Tang, Joongang-Yeoguan, Cheonil-Tang, Oncheon-Yeoguan, Mansoo-Tang and Hyundae-Tang) and the municipal pumping station (Yangtang-Jang) in the Dongrae hot-spring area and eleven groundwater samples were also collected from Oncheon-Dong (sample numbers OC1-5) in May 1998, Sajik-Dong (sample numbers SJ1-3) and

Myongryun-Dong (sample numbers MR1-3) areas. The locations of 20 sampling sites are shown in Figs. 1 and 2. The groundwater boreholes are in the depth range 20-130m. Shallow groundwater is not deeper than 50 meters and intermediate groundwater ranges from 50m to 130m. The depth of geothermal boreholes are slightly more or less than 200m.

Chemical compositions of geothermal water and groundwater were analyzed statistically using computer program code SAS to understand the factors controlling the chemical property of the waters. Geochemical modeling was performed using AquaChem (Aqueous Geochemical Analysis, Plotting and Modelling) developed by Waterloo Hydrologic (1998) to elucidate some hydrogeochemical characteristics of the geothermal and ground waters, water-rock interaction, and chemical relation between them.

GEOLOGICAL AND HYDROGEOLOGICAL SETTING

The western part of the study area is occupied by the mountains of NNE-SSW direction wherein Mountain Geumjeong (790m) is located (Fig. 2). The eastern part is occupied by the small-scale mountains along NNE-SSW and NNW-SSE directions with lower altitude (the

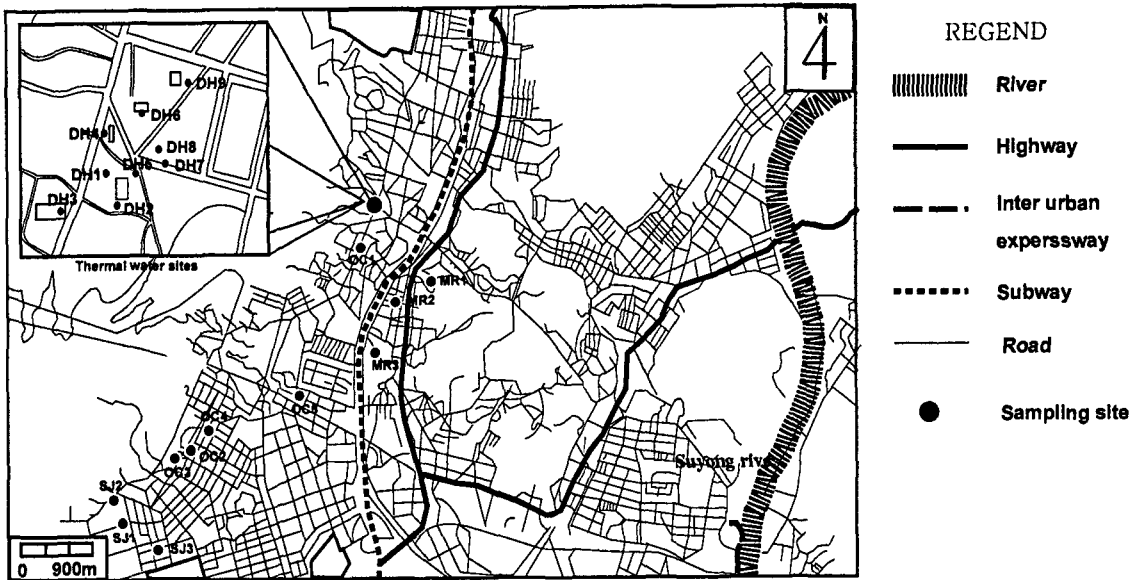


Fig. 1. Location and sample sites of the study area.

highest peak is Mountain Guweol of 450m than the western part. The Dongrae hot-spring is situated in the low plat area between the two parts where Dongrae fault covered by alluvium passes along NNE-SSW direction (Son et al., 1978). The main drainage of the area is related to the orientation of mountains and also related to the geological structures with numerous tributaries nearly perpendicular to the main trend.

The geology of the study area is composed of andesitic rocks belonging to Yucheon Group of Cretaceous, and Bulkuksa granites (biotite granite, adamellite, tonalite, granodiorite, and micrographic granite) intruding the andesitic rocks (Son et al., 1978). They outcrop in mountainous area and alluvial deposits cover the lower plat area.

Andesitic rocks distribute in the southern part of the study area. They are composed of feldspar, pyroxene and hornblende. The Bulkuksa granites are composed of essential minerals (quartz, plagioclase, orthoclase, and biotite) and accessory minerals (hornblende, chlorite,

magnetite, sphene, and apatite).

The groundwater flows from the range of western mountains to the lower plat area (Dongrae-Ku and Geumjeong-Ku). Dongrae fault invisible in the field owing to alluvium and pavement is distinct on the satellite image. At the same time, Yangsan fault runs in the weatern part of Mountain Geumjeong with fault evidence at several sites in Yangsan area (Ryu and Kim, 1997). Dongrae and Yangsan faults may be related to the formation of the Dongrae hot-spring as developing secondary tension fault of NE-SW direction which may act water channel extending to at least 2-3km depth and heat the water (Ryu et al., 1999). The heated groundwater is considered to flow along the fault having E-W strike and to ascend at the area of the Dongrae hot-spring along Dongrae fault which is favorable ascending flow path. In addition, the shallow groundwater flows mainly N60-80E trending fractures developed in bedrocks (granite and andesitic rocks) (Choi et al., 1984).

The Korean Peninsula is not an area

associated with high potential geothermal energy as it is a part of the stable foreland of Far East Asia and is located far from the Circum-Pacific tectonic belt (Lim, 1995). Hence, it is inferred

that favorable geological structures (recharge and upflow channels) associated with intrusive body (Bulguksa granite) may contribute to heat geothermal water at the Dongrae hot-spring.

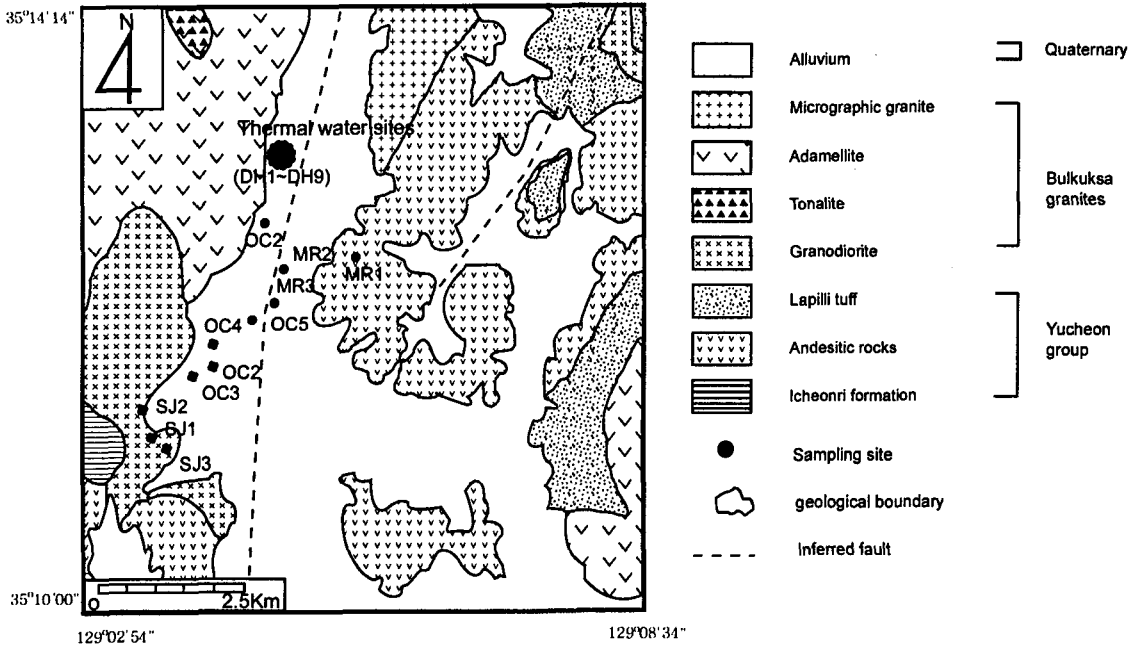


Fig. 2. Geological map of the study area (from Son et al., 1978).

SAMPLING AND ANALYSIS METHOD

At the same time with groundwater and geothermal water sampling, temperature, pH, electrical conductivity (EC), salinity and total dissolved solid (TDS) were measured using pH meter (Orion Model 250A), temperature thermistor (Sato Model SM-1250MC) and EC meter (Orion Model 115) in the field.

Bicarbonate and carbonate were analyzed in the field by the titration method. Cations were analyzed using the Atomic Absorption Spectrometer (Perkin Elmer 3100) and anions (F^- ,

Cl^- , NO_3^- , SO_4^{2-} and PO_4^{3-}) were analyzed using the Ion Chromatography (Dinex DX-300) at Korea Institute of Geology, Mining and Materials (KIGAM). Heavy metal ions were analyzed using PDV3000 at KIGAM. All water samples for the laboratory analysis were field-filtered with a $0.45\mu m$ filter. The water samples for cation analyses were acidified using 0.05N HCl for maintaining the sample with pH 2-3. The samples were chilled below $4^\circ C$ during transportation to the laboratory. To check the validity of the chemical analysis, charge balance errors were calculated.

RESULTS AND DISCUSSION

The chemical composition of nine geothermal water and eleven groundwater samples is presented in Table 1 with mean, standard deviation, variance, maximum and minimum values, and sample numbers.

PHYSICOCHEMICAL AND CHEMICAL CHARACTERISTICS

The temperature of groundwater ranges from 14 to 17.6°C with the average temperature of 16.4°C. On the other hand, the temperature of geothermal water ranges from 50.6 to 66.4°C with the average temperature of 58.4°C. The maximum temperature of 66.4°C were measured at the municipal pumping station. The temperature of the Dongrae hot-spring is relatively high among those of the hot springs in Korean Peninsula.

The electrical conductivity (EC) is an indicator of water quality in relation to inorganic constituents with increasing the concentration of total dissolved solids (TDS) and increase with depth due to the progress of water-rock interaction. EC of groundwater ranges from 240 to 705 $\mu\text{S}/\text{cm}$ with averaging 447 $\mu\text{S}/\text{cm}$ (Table 1). In contrast, geothermal water ranges from 1,044 to 1,689 $\mu\text{S}/\text{cm}$ with averaging 1,475 $\mu\text{S}/\text{cm}$ which is higher than the mean value of geothermal waters in South Korea. This is a characteristics of hot springs which situated near southeast or east coast of the Korean Peninsula (Dongrae, Haeundae, Pohang and Mageumsan hot springs) and may indicate the influence of saltwater at deep places (Lim, 1995). High EC of sample MR2 is believed to reflect anthropogenic influence (domestic or other wastes).

pH of groundwater ranges from 6.06 to 7.23 with averaging 6.74, whereas geothermal water ranges from 7.65 to 8.00 with averaging 7.83, as showing higher pH values in geothermal water

than in groundwater. This is due to much consumption of hydrogen ion in geothermal water than shallow groundwater originating from long-term water-rock interaction.

Cl^- concentration in groundwater averages 38.1mg/l with ranging from 18.8 to 47.6mg/l. In contrast, chloride concentration in geothermal water averages 362.4mg/l with ranging from 234 to 454mg/l (approximately ten times higher than groundwater). Thus, it corresponds to the trend that chloride concentrations increase with depth but not in a well-defined, continuous or predictable manner (Nordstrom et al., 1989). The salinity of the groundwater is derived from outside the rock (allochthonous) and or inside the rock (autochthonous) (Nordstrom et al., 1989). Chloride is used as an indicator of seawater influence. However, when the relation between Na^+ and Cl^- ions is not well established, it may be the result of water-rock interaction (Banks et al., 1995).

Na^+ concentration in groundwater averages 29.05mg/l with ranging from 13.0 to 67.4mg/l, while geothermal water averages 222.8mg/l with ranging from 170 to 253mg/l. Na^+ is the most abundant alkali element, and exists in minerals. Thus, Na^+ in surface water or groundwater originates from the dissolution of plagioclase or from seawater intrusion and sea fog near coast.

The Na/Cl weight ratio for the geothermal water (0.6) is slightly higher than the seawater ratio of 0.55 (Fig. 3). Therefore, it is considered that there was introduction of Na^+ as well as the mixing of more saline water with dilute meteoric water (Nordstrom et al., 1989). Fig. 4 is a semi-log plot of the same data and shows two distinct slopes, a steep slope from 18.8 to 47.6 mg/l of Cl and a gentle slope at higher Cl concentrations. High Na/Cl weight ratios for the steep slope are very typical of river waters, rainwaters, fresh groundwaters and groundwaters

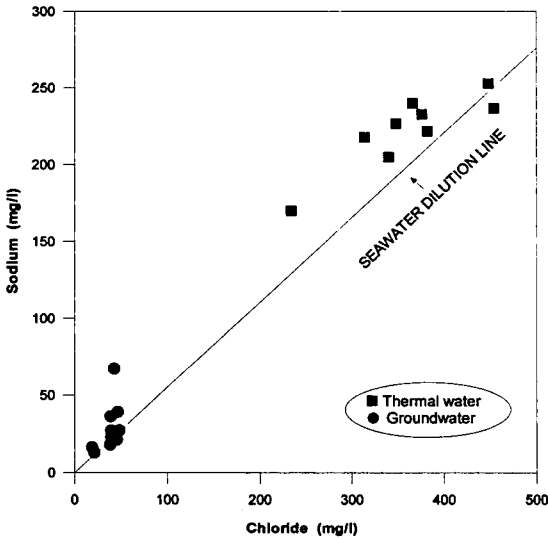


Fig. 3. Sodium concentration plot against chloride concentration for the groundwater and thermal water samples.

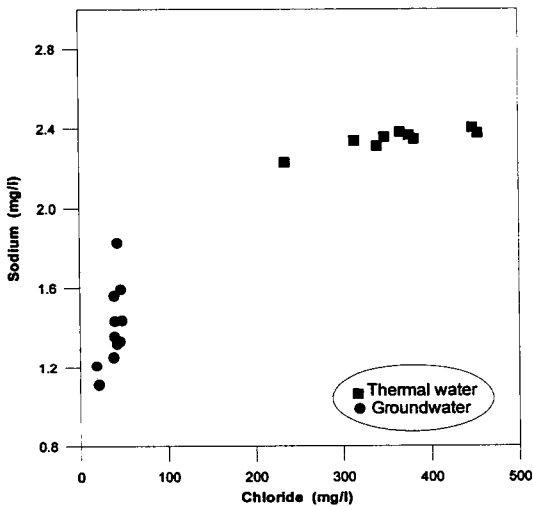
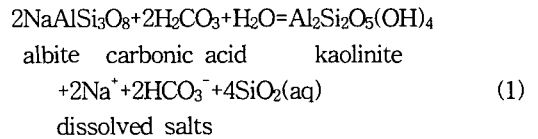


Fig. 4. Semi-log plot for sodium and chloride concentrations for the groundwater and thermal water samples.

dominated by halite dissolution (Nordstrom et al., 1989). Low ratios tend to occur when another cation (usually Ca) becomes equal to or more than Na ions.

SO_4^{2-} concentration in groundwater averages 36.24 mg/l with ranging from 1.87 to 59.34 mg/l, whereas SO_4^{2-} concentration in geothermal water averages 74.0 mg/l with ranging from 52.0 to 83.7 mg/l (Table 1). Thus, high concentration of SO_4^{2-} in geothermal water may derive from sulfides (pyrite, chalcopyrite and so on) in depth.

Average concentration of HCO_3^- in groundwater is 129.5mg/l with minimum 64.0 and maximum 242.6mg/l, whereas that in geothermal water is 92.7mg/l and lower than in groundwater except 318.8mg/l at DH9 whose reason is indistinct. In general, HCO_3^- concentration is higher at shallow level because H_2CO_3 is more abundant associated with CO_2 gas in soil and weathered zone (Nesbitt and Young, 1984):



Ca^{2+} concentration in groundwater averages 37.46mg/l with ranging from 13.7 to 78.9mg/l, whereas Ca^{2+} concentration in geothermal water averages 53.73mg/l with ranging from 30.7 to 65.2mg/l. Ca^{2+} in the water samples may be derived from the weathering of plagioclase.

K^+ concentration in groundwater averages 3.40 mg/l with ranging from 0.58 to 15.10mg/l whereas K^+ concentration in geothermal water averages 5.37mg/l with ranging from 3.84 to 6.38mg/l. K^+ ion in geothermal water may be related to the dissolution of K-feldspar or mica. However, K^+ concentration in groundwater shows wider standard deviation than geothermal water. This indicates that K^+ ion in groundwater may be derived from anthropogenic sources as well as natural sources (dissolution of K-feldspar and mica or cation exchange within some clays). K^+ concentration at MR2 and MR3 is much higher

Table 1. Chemical composition and other data of the water samples in study area.

	Depth	T(Wa)	pH	Cond	SiO ₂	Ca	K	Mg	Na	Fe	Zn	Cu	Pb	Mn	Al	F	Cl	NO ₃	SO ₄	HCO ₃	PO ₄	NH ₄	As	Se	(+/-)		
MFI	100	17.6	7.23	455	39.8	56.1	0.56	6.17	17.9	0.008	0.016	0.058	0	0	0	0.42	38	9.25	50.4	100.6	0	0.05	0	0.002	1.04		
OC1		17	6.57	442	53	42.1	1.69	8.47	39.2	0.068	0.025	0.039	0	0	0.026	0	0.07	46.3	3.9	49.2	0	0.05	0	0.001	1.11		
OC2		16.5	7.05	466	31.9	33	0.89	21.3	21.4	0.03	0.013	0.049	0	0	0	0.1	45.4	10	41.7	109.8	0	0.13	0	0	1.05		
SJ1	87	16.9	6.06	365	36.1	30.8	1.04	9.93	20.8	0.024	0.004	0.033	0	0	0	0.05	41.9	7.42	29.7	64	0	0.03	0	0.001	0.9		
OC3		16.3	6.39	592	31	43.2	1.24	20.2	27.2	0.016	0.015	0.04	0	0	0	0.08	39.4	6.75	56.6	167.9	0	0.15	0	0	0.97		
SL2		14.7	6.8	240	28.7	19.7	0.78	7.35	16.2	0.027	0.006	0.029	0	0	0	0.07	18.8	5.8	16.9	65.6	0	0.03	0	0.01	1.13		
MF2	23	16.6	6.37	705	21.8	78.9	15.1	7.71	37.4	0.003	0.317	0.026	0	0	0	0.15	47.6	13.1	59.3	216.6	0	0.07	0	0.006	1.04		
MF3	20	14	6.71	450	18	37.7	8.1	4.15	36.4	0.034	0.01	0.022	0	0	0	0.18	38.6	2.24	41.5	137.2	0	0.25	0	0.001	0.94		
OC4	130	16.9	6.74	439	38.1	29.2	1.19	17.1	22.7	0.067	0.207	0.024	0	0	0	0.05	39.3	8.67	39.2	114.4	0	0.12	0	0.001	1		
OC5	113	16.8	7.19	503	31.2	13.7	6.21	5.78	67.4	0	0.079	0.018	0	0	0	0.18	42.6	0.03	1.87	242.6	0	0.08	0	0.002	0.81		
SL3	100	17.2	7.03	285	33.1	27.5	0.61	7.26	13	0.053	0.004	0.019	0	0	0	0.07	21.3	2.98	13.3	102.2	0	0.02	0	0.001	1.04		
Groundwater	Min	14	6.06	240	18	13.7	0.58	4.15	13	0	0.004	0.018	0	0	0	0.05	18.8	0.03	1.87	64	0	0.02	0	0	0.001	1.04	
	Max	17.6	7.23	705	53	78.9	15.1	21.3	67.4	0.067	0.317	0.058	0	0	0	0.42	47.6	13.1	59.3	242.6	0	0.25	0	0	0.001	1.04	
	Average	16.409	6.74	449.273	32.973	37.445	3.403	10.493	29.055	0.032	0.063	0.032	0	0	0	0.129	38.109	6.376	36.243	129.5	0	0.069	0	0	0.001	1.02	
	St. Dev.	1.067	0.371	129.232	9.27	17.975	4.624	6.069	15.54	0.027	0.013	0.013	0	0	0	0.108	9.506	3.853	18.709	57.567	0	0.069	0	0	0	0.069	
	Dev. Coeff	6.623	5.508	28.765	28.113	48.002	135.683	57.837	53.465	86.389	163.47	39.598	0	0	0	83.808	24.943	60.423	51.623	44.453	0	77.362	0	0	0	77.362	
	Var%	20	16	66	62	83	96	81	81	100	99	69	0	0	0	88	61	100	97	74	0	92	0	0	0	92	
DH1	200	66.4	7.69	1688	46.2	65.2	6.03	0.1	253	0.063	0.015	0	0	0	0	2.12	448	0.19	82.8	41.2	0	0	0	0	0	0.95	
DH2	210	62.7	7.82	1476	47.9	55.2	5.96	0.13	240	0.051	0.014	0.018	0	0	0	2.01	366	0.03	72.6	64	0	0	0	0	0	0.001	1.02
DH3	107	50.6	7.94	1526	46.4	58.6	5.55	0.14	233	0.057	0.01	0.017	0	0	0	1.89	376	3.95	77	51.87	0	0	0	0	0	1	
DH4	210	55	8	1044	45.6	30.7	3.84	0.08	170	0.06	0.01	0.016	0	0	0	1.48	234	2.01	52	76.3	0	0	0	0	0	0.99	
DH5	210	62	7.74	1395	41.1	49.2	5.05	0.17	218	0.047	0.008	0.012	0	0	0	1.54	314	1.16	74.4	77.8	0	0	0	0	0	1.02	
DH6	210	63	7.65	1463	46.2	51.1	5.03	0.12	227	0.067	0.047	0.014	0	0	0	1.73	348	0.8	73.2	48.8	0	0	0	0	0	1.3	
DH7	210	53.7	7.77	1439	51.3	53.9	5	0.28	205	0.035	0.056	0.014	0	0	0	1.55	340	0.49	74	103.7	0	0	0	0	0	0.91	
DH8	210	60.4	7.89	1551	55.2	54.6	5.38	0.11	222	0.042	0.022	0.013	0	0	0	1.94	382	0.79	77	51.87	0	0.01	0	0	0	0.88	
DH9	210	52.1	7.91	1689	56.7	65.2	6.38	0.17	237	0.047	0.021	0.011	0	0	0	1.87	454	0	83.7	316.8	0	0.01	0	0	0	0.7	
Thermal water	Min	50.6	7.65	1044	41.1	30.7	3.84	0.08	170	0.012	0.008	0.001	0	0	0	1.48	234	0	52	41.2	0	0	0	0	0	0	
	Max	66.4	8	1689	56.7	65.2	6.38	0.28	253	0.067	0.056	0.018	0	0	0	2.12	454	3.95	83.7	316.8	0	0.01	0	0	0	0.7	
	Average	58.433	7.823	1474.556	48.511	53.744	5.367	0.144	222.778	0.049	0.022	0.014	0	0	0	1.792	362.44	1.047	74.078	92.704	0	0	0	0	0	0.94	
	St. Dev.	5.643	0.12	191.423	4.981	10.283	0.761	0.059	24.194	0.017	0.018	0.002	0	0	0	0.228	66.931	1.258	9.194	86.941	0	0	0	0	0	0.94	
	Dev. Coeff	9.658	1.529	12.982	10.268	19.152	14.188	40.827	10.833	34.622	79.934	15.905	0	0	0	12.723	18.467	120.235	12.411	93.783	0	0	0	0	0	0.94	
	Var%	24	4	38	28	53	40	71	33	82	86	39	0	0	0	30	48	100	38	87	0	0	0	0	0	0	
	Sample No	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	

than the other groundwater samples and may suggest anthropogenic origin.

SiO₂ concentration in groundwater averages 32.97mg/l with ranging from 18.0 to 53.0mg/l whereas SiO₂ concentration in geothermal water averages 49.51mg/l with ranging from 41.1 to 56.7mg/l. SiO₂ is introduced to the water due to the dissolution of silicate minerals which is most abundant in rocks.

Mg²⁺ concentration in groundwater averages 10.49mg/l with ranging from 4.15 to 21.30mg/l whereas that in geothermal water averages 0.14mg/l with ranging from 0.08 to 0.28mg/l. At high temperature, Mg²⁺ concentrations decrease rapidly as forming chlorite, illitic mica, montmorillonite and, less commonly, dolomite (Muffler and White, 1969). In general, the main source of Mg²⁺ ion in shallow groundwater is the dissolution of dolomite or Mg-containing minerals (Lee et al., 1997).

F⁻ concentration in groundwater averages 0.13mg/l with ranging from 0.05 to 0.42mg/l, whereas F⁻ concentration in geothermal water averages 1.79mg/l with ranging from 1.48 to 2.12mg/l as being much higher than in groundwater. F⁻ concentration is reported relatively higher in granite, schist and gneiss than other types of rock (Lee et al., 1997). Also, F⁻ concentration is often high around the fluorite mines as fluorite (CaF₂) contains F⁻. In the study area, F⁻ ion could be related to hornblende and apatite (Ca₅(Cl, F, OH)(PO₄)₃) (Hem, 1985). One explanation of higher F⁻ ion in thermal water is that F⁻ amount by adsorption is higher at shallow depth than deep place owing to abundant clay minerals (gibbsite, kaolinite, and halloysite) at shallow depth (Hem, 1985).

NO₃⁻ concentration in groundwater averages 6.38mg/l with ranging from 0.03mg/l at SJ3 to 13.1mg/l at MR2 and with standard deviation 3.85mg/l. In contrast, NO₃⁻ concentration in geothermal water averages 1.05mg/l with ranging

up to 3.95mg/l and with lower standard deviation (1.26mg/l) than groundwater. This means that geothermal water is less affected by anthropogenic sources than shallow groundwater.

Heavy elements (Cd, Pb, Mn, and Al) were hardly detected except small amount of Fe and Zn.

GEOHERMAL AND GROUND WATER TYPES

Concentration of dissolved ions is changed with depth. However, if the water-rock interaction occurs in the same geological condition, the relative concentration will not vary with depth. The water compositions were plotted on the Piper diagram (trilinear diagram) which shows major cations and anions in milliequivalents per liter (Fig. 5) for comparing the waters, detecting mixing of waters of different composition and identifying some of the chemical processes during the water circulation (Hem, 1985). The sampled waters are grouped as Ca-HCO₃ type for groundwater region and Na-Cl type for geothermal water region, respectively. Ionic equivalent abundances for cations and anions in groundwater show Ca>Na>Mg>K and DIC>Cl>SO₄>F, respectively. However, sample number OC2 shows much abundance in Na⁺ ion than other samples. Ionic equivalent abundances for cations and anions in geothermal water show Na>Ca>Mg>K and for anions Cl>SO₄>DIC>F, respectively.

According to the Stiff diagram (Fig. 6), groundwater shows Ca-HCO₃ type except Na-HCO₃ type at OC5 which is puzzling. On the other hand, geothermal water shows Na-Cl type. The shapes of the Stiff diagram are similar for all geothermal-water samples representing the same origin, while those are different for groundwater samples.

Using stable isotope data in the Dongrae hot-spring (Lim et al., 1992), δD and δ¹⁸O for

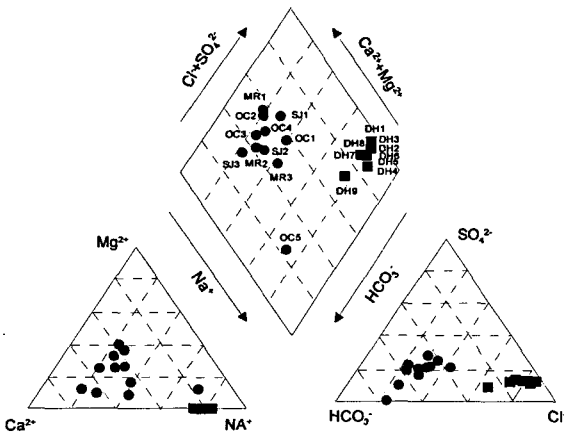


Fig. 5. Piper diagram of groundwater and thermal water samples from the study area.

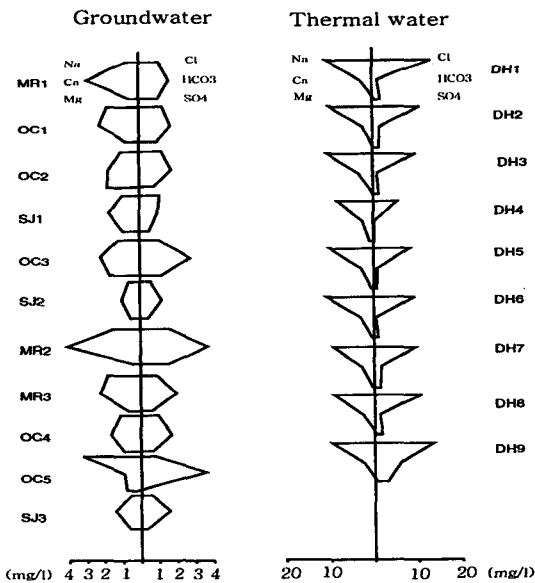


Fig. 6. Stiff diagram of groundwater and thermal water samples from the study area.

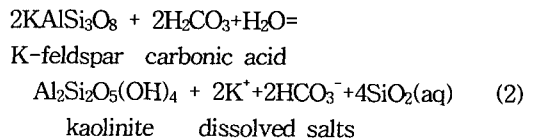
all data lie on and close to the meteoric water line, with values ranging from -48.7 to 51.8‰, and ranging from -7.3 to -7.8‰, respectively, thus indicating meteoric origin. These values are within mean values in South Korea (-80 to -4

0‰ for δD and -11 to -4‰ for δ¹⁸O) (Joo et al., 1992).

FACTOR ANALYSIS

To simplify individual independent variables into grouping some factors, factor analysis using statistical package SAS was conducted for groundwater and geothermal water. SiO₂, Ca²⁺, K⁺, Mg²⁺, Na⁺, Fe, Zn, Cu, F⁻, Cl⁻, NO₃⁻, SO₄²⁻, HCO₃⁻ and NH₄⁺ were used as independent variables. Principal component analysis (PCA) was used as factor extraction model and eigenvectors with eigenvalues larger than 1.000 were retained as factors. To maximize the variance of the loadings on the factors, varimax orthogonal rotation technique was employed.

As a factor analysis for groundwater, Ca²⁺, NO₃⁻, SO₄²⁻ and EC belong to factor 1 (Table 2), Na⁺, HCO₃⁻, EC and Cl⁻ belong to factor 2, and SiO₂, Mg²⁺ and K⁺ belong to factor 3. Data comprising factor 1 are considered to be influenced by anthropogenic sources. However, weak correlation between them demonstrates a variety of contamination sources. Na⁺, HCO₃⁻, K⁺ and Cl⁻ belonging to factor 2 could mainly be derived from the dissolution of plagioclase and K-feldspar. In contrast, high correlation coefficient between Na⁺ and HCO₃⁻ (0.80), and between K⁺ and HCO₃⁻ (0.713) indicate incongruent dissolution of albite as eq. (1) and that of K-feldspar, respectively:



As SiO₂, Mg²⁺, and K⁺ belonging to factor 3 show weak correlation between them, they may be related to separate reaction independently. The percentages of variance explained by factor 1,

factor 2 and factor 3 are 33.1%, 31.9% and 18.7%, respectively, and totaling 83.7%. The communality explains the amount of variance of each variable retained in the three factors. The communality for Mg^{2+} is the lowest among the

variables as 0.5412.

As a factor analysis for geothermal water (Table 3), EC, Ca^{2+} , K^+ , Na^+ , F^- , Cl^- and SO_4^{2-} belong to factor 1, Na^+ , HCO_3^- , and SiO_2 , Mg^{2+} and HCO_3^- belong to factor 2. Data comprising

Table 2. Varimax factor matrix of chemical constituents and factor scores for the groundwater.

Variable	Factor1	Factor2	Factor3	Communality
Conductivity	0.6111	0.7636	-0.09	0.9649
SiO ₂	-0.1095	-0.0681	0.8130	0.6776
Ca	0.8734	0.2008	-0.2454	0.8634
K	0.3100	0.5943	-0.7025	0.9427
Mg	0.3756	-0.0265	0.6321	0.5413
Na	-0.3421	0.9177	-0.1278	0.9756
Cl	0.4416	0.7537	0.3101	0.8592
NO ₃	0.8994	-0.1514	0.0550	0.8348
SO ₄	0.8987	0.1406	0.1593	0.8528
HCO ₃	0.0230	0.8695	-0.3322	0.8669
Eigenvalue	4.2244	2.7229	1.4319	
Percent of variance explained by factor	33.1464	31.9101	18.7354	
Cumulative percent of variance	33.1464	65.0566	83.7920	

Table 3. Varimax factor matrix of chemical constituents and factor scores for the thermal water.

Variables	Factor1	Factor2	Communality
Conductivity	0.9427	0.2875	0.9714
SiO ₂	0.2834	0.7020	0.5730
Ca	0.9298	0.3047	0.9574
K	0.9332	0.2727	0.9452
Mg	-0.1040	0.7112	0.5167
Na	0.9742	-0.0240	0.9496
F	0.9169	-0.1890	0.8764
Cl	0.9399	0.3007	0.9738
NO ₃	-0.2777	-0.4943	0.3214
SO ₄	0.8888	0.3224	0.8940
HCO ₃	0.1109	0.8240	0.6913
Eigenvalue	6.8033	1.8670	
Percent of variance explained by factor	62.6785	24.0243	
Cumulative percent of variance	62.6785	86.7028	

factor 1 could be related with by geothermometer with high correlation among them. Especially, Na^+ and Cl^- derive from the same origin with high correlation coefficient (0.884). As SiO_2 , Mg^{2+} and HCO_3^- belonging to factor 2 show weak correlation between them, they may be related to the mixing between geothermal water and cold water. The percentages of variance explained by factor 1 and factor 2 are 62.7% and 24.0%, respectively (total is 86.7%). The communality explains the amount of variance of each variable retained in the two factors.

WATER-ROCK INTERACTION

To reveal the distribution of aqueous species and saturation state of some minerals, several modeling codes are used: WAETRQ4F (Ball and Nordstrom, 1991), MINTEQA2 (Allison, Brown, and Novo-Gradac, 1990), PHREEQC (Parkhurst, 1995), NETPATH (Plummer et al., 1991) and AQUACHEM (Waterloo Hydrologic, 1998). In this

study, AQUACHEM and PHREEQC are used for calculating activity and saturation index of some minerals, and plotting phase stability diagram.

According to the saturation indices for major chemical species in groundwater and geothermal water of the study area (Table 4), the groundwaters are undersaturated with respect to most minerals (calcite, aragonite, dolomite, siderite, gypsum, anhydrite, fluorite, amorphous silica and CO_2 gas) except chalcedony and quartz. In contrast, the geothermal waters are in equilibrium or slightly supersaturated with respect to most minerals except calcite, aragonite, chalcedony and quartz. This means that the undersaturated minerals (in case of their existence in the rocks) can dissolve in groundwater and geothermal water.

The saturation index of quartz, dolomite, calcite and gypsum is plotted against pH on Fig. 7. The saturation index of calcite and dolomite increase with the decrease of pH. In contrast,

Table 4. Saturation index (=Log(IAP/KT)) of the study area.

Sample No	Calcite	Aragonite	Dolomite	Siderite	Gypsum	Anhydrite	Fluorite	SiO2(a)	Chalcedony	Quartz
MR1	-0.568	-0.717	-1.846	-2.317	-1.914	-2.158	-1.721	-0.519	0.347	0.799
OC1	-1.347	-1.496	-3.151	-1.925	-2.042	-2.287	-3.397	-0.388	0.479	0.934
OC2	-0.956	-1.106	-1.869	-1.824	-2.228	-2.474	-3.201	-0.605	0.264	0.721
SJ1	-3.341	-3.491	-6.936	-4.192	-2.337	-2.582	-3.780	-0.549	0.313	0.768
OC3	-1.337	-1.487	-2.775	-2.575	-2.009	-2.256	-3.297	-0.615	0.255	0.712
SJ2	-1.622	-1.774	-3.470	-2.272	-2.731	-2.981	-3.625	-0.635	0.241	0.703
MR2	-1.000	-1.150	-2.776	-3.241	-1.766	-2.012	-2.504	-0.770	0.099	0.555
MR3	-1.170	-1.322	-3.107	-2.024	-2.138	-2.389	-2.567	-0.831	0.047	0.512
OC4	-2.465	-2.614	-4.924	-1.612	-2.279	-2.524	-3.828	-0.531	0.337	0.792
OC5	-0.829	-0.979	-1.796	-	-3.899	-4.145	-3.036	-0.617	0.251	0.706
SJ3	-2.194	-2.344	-4.725	-1.570	-2.692	-2.937	-3.506	-0.595	0.271	0.725
DH1	0.057	-0.061	-2.232	-5.220	-1.750	-1.670	-0.834	-0.824	-0.107	0.209
DH2	0.277	0.157	-1.587	-5.166	-1.863	-1.819	-0.912	-0.787	-0.061	0.264
DH3	0.187	0.060	-1.746	-4.695	-1.840	-1.903	-0.853	-0.719	0.040	0.396
DH4	0.232	0.108	-1.611	-4.908	-2.196	-2.222	-1.325	-0.761	-0.014	0.330
DH5	0.241	0.121	-1.490	-4.888	-1.885	-1.848	-1.178	-0.847	-0.119	0.208
DH6	-0.024	-0.143	-2.192	-4.809	-1.877	-1.830	-1.067	-0.800	-0.075	0.249
DH7	0.336	0.211	-1.107	-4.428	-1.877	-1.914	-1.081	-0.694	0.057	0.405
DH8	0.218	0.097	-1.768	-5.901	-1.844	-1.822	-0.931	-0.712	0.020	0.351
DH9	0.967	0.841	-0.135	-4.018	-1.821	-1.872	-0.888	-0.642	0.114	0.465

* Parenthetical letter a designates amorphous.

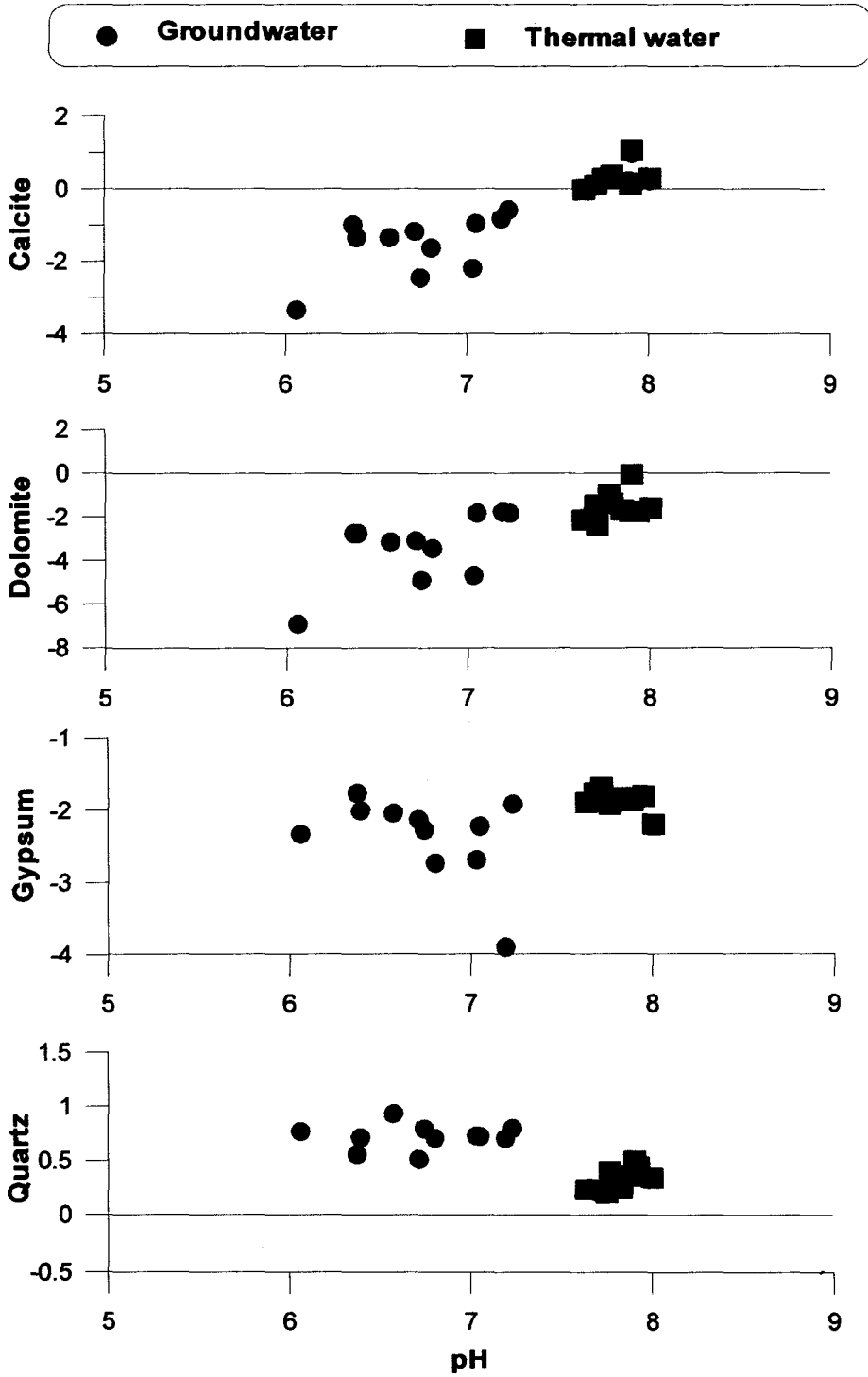


Fig. 7. Saturation indices of calcite, dolomite, gypsum and quartz against pH in the study area.

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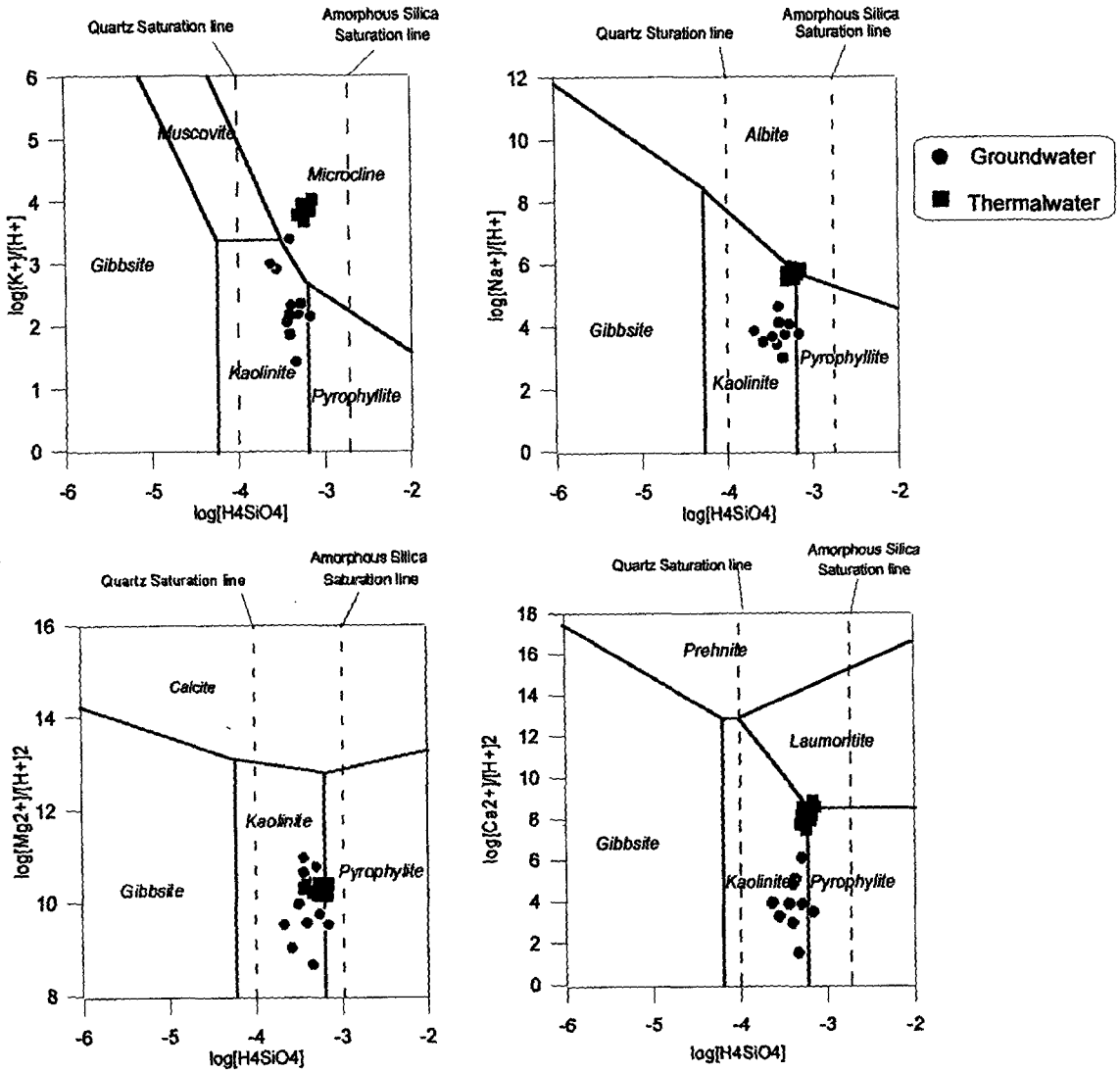


Fig. 8. Phase stability diagrams for some minerals in the $K_2O-Al_2O_3-SiO_2-H_2O$, $Na_2O-Al_2O_3-SiO_2-H_2O$, $CaO-Al_2O_3-SiO_2-H_2O$ and $MgO-Al_2O_3-SiO_2-H_2O$ at 298K and 1 atm.

gypsum and quartz do not show any clear trend with variation of pH. This can be explained by decrease of calcium carbonate solubility with the increase of pH.

The phase stability diagrams for logarithmic ionic activity of $[Ca^{2+}]/[H^+]^2$, $[Mg^{2+}]/[H^+]^2$, $[Na^+]/[H^+]$, $[K^+]/[H^+]$ vs. $[H_4SiO_4]$ demonstrate that groundwater samples fall effectively in the

field of stability of kaolinite representing lower temperature supergenic conditions. On the other hand, the geothermal water samples fall in the stability field of microcline for $K_2O-Al_2O_3-SiO_2-H_2O$ system, at the boundary of kaolinite-pyrophyllite-albite for $Na_2O-Al_2O_3-SiO_2-H_2O$ system, in the stability field of kaolinite near to pyrophyllite for $MgO-Al_2O_3-SiO_2-H_2O$

system and at the boundary of kaolinite-laurmontite-pyrophyllite for $\text{Ca}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system (Fig. 8). The phase stability diagrams are based on the thermodynamic data given by Helgeson et al. (1978) and Bowers et al. (1984). From the phase stability analysis, shallow groundwater occurring from granite in Dongrae area is in disequilibrium condition with feldspar and will continuously react with feldspar, while geothermal water reached equilibrium condition with feldspar.

CATION GEOTHERMOMETRY

Cation geothermometer is widely used to estimate geothermal reservoir temperature from hot springs and geothermal wells. Several cation geothermometers can be applied to geothermal waters: Na-K (Fournier, 1983; Arnorsson, 1983; Giggenbach et al., 1983), Na-K-Ca (Fournier and Truesdell, 1973), Na-K-Ca-Mg (Fournier and Potter, 1979), Na/Li (Fouillac and Michard, 1981), Li/Mg (Kharaka and Mariner, 1986) and Na-K-Mg (Giggenbach, 1988). The assumptions for the application of geothermometers involve: 1) temperature-dependent reactions, with adequate supply of constituents in the local reservoir rocks; 2) thermal water-rock equilibration with specific mineral assemblages at high reservoir temperatures; 3) rapid rising of thermal water from the reservoir to the surface; 4) negligible reaction in transit at lower temperatures, so that reservoir composition is retained; and 5) absence of dilution or mixing with other waters at intermediate depths (White, 1970). In reality, recognition and reconstruction of chemical equilibrium properties in a geothermal system from water analyses is complicated in many cases due to complex history of rising hot water (mixing of waters and degassing, or a combination of the two). Dilution and mixing of hot water with surficial waters during ascent to the surface commonly occurs in geothermal

systems (Fournier, 1977; Giggenbach, 1988).

Giggenbach (1988) proposed a geothermometer that is composed of a triangle with Na/100, K/100 and $\sqrt{\text{Mg}}$ at the apices and is in order to classify waters as fully equilibrated with rock at given temperatures, partially equilibrated, and immature (dissolution of rock with little or no chemical equilibrium). In order to render the plot applicable at all salinities, relative square root of Mg concentration in introduced (Giggenbach, 1988). The Na/1000-K/100- $\sqrt{\text{Mg}}$ triangular diagram is a combined method of the Na-K and K- $\sqrt{\text{Mg}}$ geothermometers. The Na/K is little affected by mixing with shallow waters, and generally indicates temperatures of deep equilibrium (Lahlou Mimi et al., 1998). In contrast, the K- $\sqrt{\text{Mg}}$ geothermometer is very sensitive to cooling and admixing of shallow waters. The full equilibrium curve is for reservoir water compositions corrected for loss of steam owing to decompressional boiling. Uncorrected waters will be plotted slightly above the full equilibrium line. Thus, the Na-K-Mg geothermometer allows a clear distinction between waters suitable or unsuitable for the application of cation geothermometry (Giggenbach, 1988). At the same time, it allows deeper equilibrium temperatures and the effects of a variety of processes (i.e. re-equilibrium and mixing of waters of different origins for a large number of samples).

Geothermal water and shallow groundwater in the study area were plotted in the (Na/1000)-(K/100)-($\sqrt{\text{Mg}}$) diagram (Fig. 9). The geothermal waters plots under the full equilibrium line and are aligned near 140°C Na-K isothermal line, but do not lie on any specific K-Mg geothermometric line (Fig. 9). This may indicate the partial disequilibrium between K and Mg due to the mixing between shallow groundwater and deep geothermal water in

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equilibrium with the geothermal reservoir. The geothermal water rising from geothermal reservoir may be cooled by conduction of heat to the surrounding rock, by boiling, by mixing with cold water, or by a combination of these processes (Fournier, 1979).

In general, the Na-K geothermometer is used to estimate temperatures in deeper parts of geothermal system where waters reside for relatively long time. The Fournier (1983) Na-K geothermometer yields temperature estimates for geothermal water which range between 115°C and 125°C (Table 5). On the other hand, Na-K geothermometer (Arnorsson, 1983) yields temperature estimates for geothermal water which range between 120°C and 130°C. The Na-K-Ca geothermometer (Fournier and Truesdell, 1973) and the corrected Na-K-Ca-Mg geothermometer (Fournier and Potter, 1979) yields the same temperatures between 109°C and 116°C. These four geothermometers yields lower temperature than the Na-K geothermometer (Giggenbach et al., 1983) which yields the estimates between 135°C and 146°C. The Na-K geothermometer (Giggenbach, 1983) matches with the Giggenbach (1988) Na-K-Mg geothermometer well.

Based on the above several geothermometers, the deep temperature in the geothermal reservoir

may be between 115 and 145°C (average 130°C).

The geothermal gradient in the south-eastern part of the Korean Peninsula is over 28°C/km which is higher than the mean geothermal gradient throughout South Korea of 26.9°C/km (Lim, 1995) with the mean annual air temperature 14°C in Pusan area (Han, 1999). Using those values and fluid temperature 130°C in Dongrae geothermal reservoir, the reservoir could be situated at 4.1km depth.

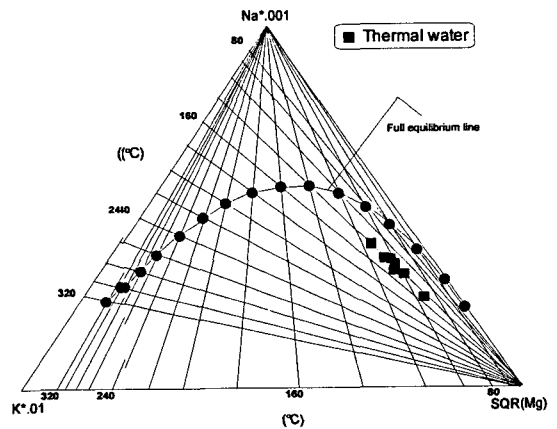


Fig. 9. Triangular plots of Na, K and Mg as a function of temperature of the geothermal reservoir (after Giggenbach, 1988). The Mg values are represented as square roots.

Table 5. Chemical geothermometers for the thermal waters.

Sample No	Meas. T °C	Na-K ^a °C	Na-K ^b °C	Na-K ^c °C	Na-K-Ca ^d °C	Na-K-Ca Mg corrected ^e °C
DH1	66.4	124.4	119.2	139.5	112.0	112.0
DH2	62.7	126.2	121.1	141.3	113.7	113.7
DH3	50.6	123.9	118.7	138.9	111.2	111.2
DH4	55.0	121.2	115.8	136.1	109.2	109.2
DH5	62.0	122.5	117.1	137.5	110.4	110.4
DH6	63.0	120.2	114.7	135.1	108.9	108.9
DH7	53.7	125.1	120.0	140.2	111.0	111.0
DH8	60.4	124.8	119.6	139.9	111.7	111.7
DH9	52.1	130.3	125.5	145.5	115.6	115.6

^a Arnorsson(1983); ^b Fournier(1983); ^c Giggenbach et al.(1983); ^d Fournier and Truesdell(1973); ^e Fournier and Potter(1979).

CONCLUSIONS

Nine geothermal water samples and eleven cold groundwater samples were collected from the Dongrae hot-spring and its vicinity. The water samples were analyzed in the field and the laboratory. Hydrogeochemical study was carried out to elucidate some of chemical characteristics of geothermal and ground waters each other and comparison of chemical properties between them. Major results of the study are followed:

1. The temperature of groundwater ranges from 14 to 17.6°C with the average temperature 16.4°C, while temperature of geothermal water ranges from 50.6 to 66.4°C with the average temperature 58.4°C.

2. pH of groundwater ranges from 6.06 to 7.23 whereas geothermal water ranges from 7.65 to 8.00. EC of groundwater with ranging from 240 to 705 $\mu\text{S}/\text{cm}$ is lower than that of geothermal water with ranging from 1044 to 1689 $\mu\text{S}/\text{cm}$.

3. Mean values of major ion concentrations in geothermal waters are higher than in ground waters except Mg^{2+} and HCO_3^- ions. HCO_3^- concentration is higher at shallow level than deep level because H_2CO_3 is more abundant associated with CO_2 gas in soil and weathered zone. Mg^{2+} concentrations decrease rapidly as forming chlorite, illitic mica and montmorillonite at higher temperature.

4. Ionic equivalent abundances for cations and anions in the ground water show $\text{Ca} > \text{Na} > \text{Mg} > \text{K}$ and $\text{DIC} > \text{Cl} > \text{SO}_4 > \text{F}$, respectively. In contrast, ionic equivalent abundances in the geothermal water show $\text{Na} > \text{Ca} > \text{Mg} > \text{K}$ for cations and $\text{Cl} > \text{SO}_4 > \text{DIC} > \text{F}$ for anions.

5. According to the Piper diagram, the ground water belongs to $\text{Ca}^{2+}\text{-HCO}_3^-$ type, while the geothermal water belongs to $\text{Na}^+\text{-Cl}^-$ type.

6. The Na/Cl weight ratio for the geothermal water indicates that there was introduction of

Na^+ ion as well as the mixing of more saline water with dilute meteoric water.

7. According to the factor analysis for the groundwater, factor 1 are considered to be influenced by anthropogenic sources, and factor 2 could mainly be related with the dissolution of plagioclase and mica. However, SiO_2 , Mg^{2+} , and K^+ belonging to factor 3 may be related to separate reaction independently. Factor 1 for the geothermal water could be related with by geothermometer and factor 2 may be related to the mixing between geothermal water and cold water.

8. According to the saturation indices, the ground waters are undersaturated with respect to most minerals (calcite, aragonite, dolomite, siderite, gypsum, anhydrite, fluorite, amorphous silica and CO_2 gas) except chalcedony and quartz, while the geothermal waters are in equilibrium or slightly supersaturated with respect to most minerals except calcite, aragonite, chalcedony and quartz.

9. On the phase stability diagram, the groundwater samples lie in the field of stability of kaolinite, while the geothermal water samples lie in the stability field of microcline or kaolinite depending on the chemical composition system.

10. Based on the $\text{Na-K-}\sqrt{\text{Mg}}$, Na/K , Na-K-Ca and Na-K-Ca-Mg geothermometers, the deep temperature in the geothermal reservoir may be between 115 and 145°C.

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동래온천지역의 지열수와 지하수의 지화학적 특성

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