Geochemistry of Geothermal Waters in Korea: Environmental Isotope and Hydrochemical Characteristics I. Bugok Area*

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ABSTRACT : Hydrogeochemical and environmental isotope studies were undertaken for various kinds of water samples collected in 1995~1996 from the Bugok geothermal area. Physicochemical data indicate the occurrence of three distinct groups of natural water: Group I (Na-SO$_4$ type water with high temperatures up to 77°C, occurring from the central part of the geothermal area), Group II (warm Na-HCO$_3$-SO$_4$ type water, occurring from peripheral sites), Group III (Ca-HCO$_3$ type water, occurring as surface waters and/or shallow cold groundwaters). The Group I waters are further divided into two subtypes: Subgroup Ia and Subgroup Ib. The general order of increasing degrees of hydrogeochemical evolution (due to the degrees of water-rock interaction) is: Group III→Group II→Group I. The Group II and III waters show smaller degrees of interaction with rocks (largely calcite and Na-plagioclase), whereas the Group I waters record the stronger interaction with plagioclase, K-feldspar, mica, chlorite and pyrite. The concentration and sulfur isotope composition of dissolved sulfate appear as a key parameter to understand the origin and evolution of geothermal waters. The sulfate was derived not only from oxidation of sedimentary pyrites in surrounding rocks (especially for the Subgroup Ib waters) but also from magmatic hydrothermal pyrites occurring in restricted fracture channels which extend down to a deep geothermal reservoir (typically for the Subgroup Ia waters). It is shown that the applicability of alkali-ion geothermometer calculations for these waters is hampered by several processes (especially the mixing with Mg-rich near-surface waters) that modify the chemical composition. However, the multi-component mineral/water equilibria calculation and available fluid inclusion data indicate that geothermal waters of the Bugok area reach temperatures around 125°C at deep geothermal reservoir (possibly a cooling pluton). Environmental isotope data (oxygen-18, deuterium and tritium) indicate the origin of all groups of waters from diverse meteoric waters. The Subgroup Ia waters are typically lower in O-H isotope values and tritium content, indicating their derivation from distinct meteoric waters. Combined with tritium isotope data, the Subgroup Ia waters likely represent the older (at least 45 years old) meteoric waters circulated down to the deep geothermal reservoir and record the lesser degrees of mixing with near-surface waters. We propose a model for the genesis and evolution of sulfate-rich geothermal waters.

INTRODUCTION

Geothermal areas in Korea have mostly been studied in a regional scale, in terms of geological setting and general characteristics of thermal water compositions (Yang, 1971; Han, 1979; Kim, Nakai, 1981; Jeong, 1983; KIGAM, 1989, 1992). Progressive studies on the nature and evolution of geothermal water, including the age and origin, water/rock interaction, and interaction (mixing) between geothermal water and groundwater and/or surface water, have been very limited (Yum, 1993; Koh et al., 1994).

As a part of systematic study on geothermal waters in Korea, the Bugok geothermal area which is famous for hot springs with the highest in-situ water temperature in South Korea was chosen for this study. The Bugok area in the Changnyeong-Gun, Gyeongnam Province, is located approximately 50 km northwest of Pusan (Lat. 35° 30'N and Long. 128° 15'E). The exploitation of geothermal waters for commercial purposes in the Bugok area has begun around the early 1970s when the water level were located near the surface. Afterward, due to the rapid increase of water demands, the borehole depths for pumping-out of thermal groundwater has become progressively deeper. Around the 1980s, the groundwater level was reached around 200 m below the surface. Recently, the level is drawn down to around -400 m (but seasonally -450 m). For that reason, the pumping is recently regulated for both the protection of water resources and the reservation of contamination of geothermal waters. The well-head temperatures of geothermal waters from the Bugok area

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systematically decrease from central toward peripheral places.

Various types of natural water samples (thermal groundwater, cold groundwater, surface water) were sampled between June 1994 and August 1995 for this study. Environmental isotope compositions, including tritium, oxygen-18, deuterium and sulfur-34, were analyzed to elucidate the origin and hydrogeological characteristics of geothermal waters. Chemical compositions of waters were also studied systematically and compared with the environmental isotope data, in order to correlate the origin and evolution of geothermal water. In addition, both the calculation of multicomponent chemical equilibria in geothermal systems and its application to geothermometry also have been undertaken.

GEOLOGIC SETTING

The Bugok geothermal area is situated within the Gyeongsang Sedimentary Basin. The geology consists mainly of the Cretaceous Chindong Formation (which is represented by non-marine sedimentary rocks), with extrusions or intrusions of andesite and granodiorite at eastern and western parts of the study area (Fig. 1).

The Chindong Formation (about 1,500 m thick) is composed of shale, sandy shale and arkosic sandstone which are intercalated with thin tuffaceous or calcareous shale. General strikes and dips are about NS and 15°E, respectively. Owing to the intrusion of igneous rocks, the rocks were severely silicified along the contact zone. The lower part of this formation is characteristically composed of dark shale which commonly contains pyrites. Arkosic sandstone at the upper part is mainly composed of quartz, feldspars and andesitic rock fragments. The feldspars are altered to chlorites along cleavages. Within the andesitic rock fragments, plagioclase (oligoclase to andesine) and augite are abundant as phenocrysts and are partially or completely altered to chlorite and calcite.

The Chusan andesitic rocks occur at the eastern parts of the Bugok geothermal area, and consist of flows, sheets, dykes and intrusive bodies in occurrence. The rocks comprise andesite, augite andesite, hornblende andesite, trachyandesite and brecciated andesite, among which augite andesite is most common. The NS-trending dykes consist of andesite intruding all of the rocks described above. Diorite and granodiorite occur as dykes and stocks in the southwestern part of the study area.

Fault systems in the Bugok area consist of two sets: NS-trending, and EW-trending. The NS-trending faults are displaced by EW-trending ones. In many places, the fractures associated with these faults are infilled by calcite ($\pm$quartz) veins and veinlets. These veins and veinlets include scattered angular breccia fragments with variable size and orientation. According to Hwang and Yun (1993), the brecciation and vein formation took place due to hydraulic fracturing under high fluid-pressure environment (which was probably related to the high thermal gradient). It is noticeable that the calcite
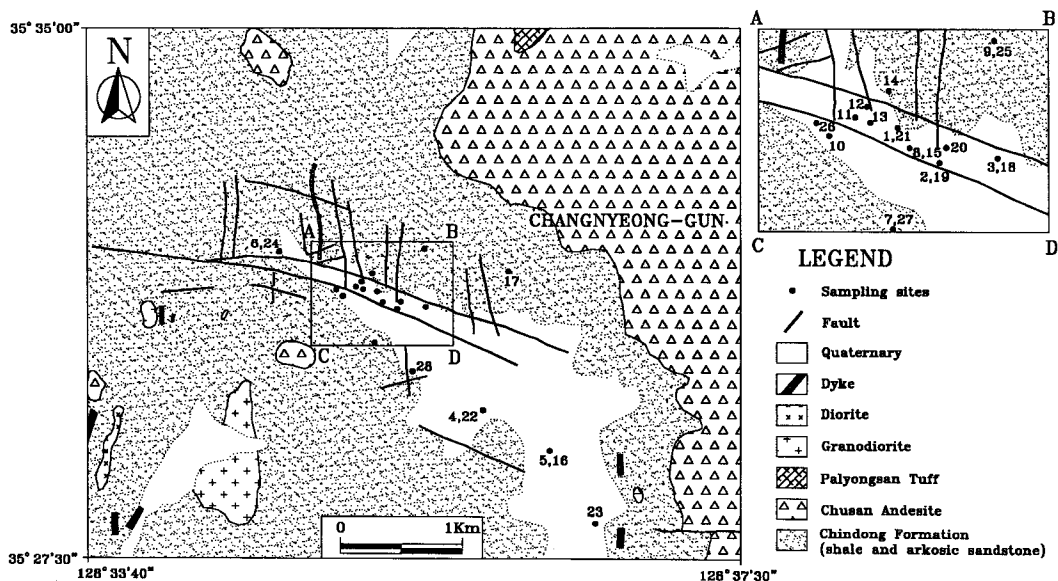

Fig. 1. Geological map of the Bugok geothermal area. Sampling locations are indicated by arabic figures. Drainage patterns are also shown.

Table 1. Physicochemical data of water samples from the Bugok geothermal area (unit of concentration=mg/l)

Sample no.	Water type (group)	Sampling date	Sampling depth (m)	pH	Eh (mV)	Temp. (°C)	Cond. (µS/cm)	Na	K	Mg	Ca	Cl	SO$_4$	HCO$_3$[1]	CO$_3$[1]	NO$_3$	SiO$_2$	Fe	Zn	Sr	F
1	Ia	June 1994	-250(?)	8.69	-113.4	77.2	453.1	75.1	3.6	0.0	4.3	8.2	124	24.2	1.1	0.1	72.7	0.01	0.1	0.1	2.5
2	Ib	June 1994	-350	8.50	-99.3	65.3	539.7	90.5	4.9	0.1	8.7	14.4	160	48.5	1.4	0.1	62.0	0.01	0.0	0.1	2.0
3	II	June 1994	?	9.74	-164.4	33.8	334.3	60.5	0.5	0.2	2.6	18.6	51	41.5	14.8	0.1	42.1	0.10	0.0	0.1	2.6
4	II	June 1994	-325	9.56	-153.3	28.8	337.5	58.3	0.5	0.2	3.1	20.3	47	41.7	9.0	0.1	25.7	0.01	0.0	0.1	1.7
5	III	June 1994	?	7.74	-43.1	19.8	396.4	18.0	1.1	8.5	48.0	22.8	37	162.9	0.5	5.5	20.5	0.01	0.0	0.5	0.2
6	III	June 1994	-230	7.86	-50.3	25.3	318.6	9.2	1.0	5.4	47.0	5.1	20	158.8	0.7	3.4	21.4	0.02	0.3	0.1	0.1
7	II	June 1994	-450	8.95	-120.4	47.0	362.2	58.3	1.6	0.1	4.8	22.2	66	42.2	2.9	0.1	40.6	0.01	0.1	0.1	1.2
8	Ib	June 1994	?	9.02	-136.9	71.6	507.6	81.9	3.9	0.2	6.7	11.3	146	10.4	1.0	0.1	66.3	0.01	0.0	0.1	2.3
9	III	June 1994	-15	8.20	-69.2	18.5	282.4	7.3	0.5	10.5	40.0	2.5	24	151.0	1.2	1.9	12.0	0.01	0.0	0.1	0.1
10	Ia	Aug. 1995	-375	8.83	-109.7	55.2	369.5	76.0	4.6	0.2	6.2	8.4	113	49.6	2.9	0.1	79.2	0.08	0.0	0.4	2.3
11	Ib	Aug. 1995	-350	8.25	-67.4	60.6	462.2	65.0	6.1	1.9	24.0	19.2	103	79.4	1.3	2.3	53.5	0.01	0.0	0.7	1.1
12	Ib	Aug. 1995	-240(?)	8.24	-76.1	72.3	532.4	100.0	6.9	0.0	12.0	15.9	185	50.1	0.9	0.1	70.6	0.01	0.0	0.5	1.4
13	Ib	Aug. 1995	-300	8.23	-78.3	73.1	511.5	95.0	6.5	0.0	11.0	12.9	188	37.8	0.6	0.1	77.0	0.01	0.0	0.5	1.9
14	Ib	Aug. 1995	-400	8.33	-83.2	76.7	493.6	91.0	6.0	0.0	13.0	12.9	188	30.5	0.6	0.1	77.0	0.01	0.0	0.6	2.1
15	Ib	Aug. 1995	-400	8.14	-73.7	71.6	482.5	90.0	6.5	0.0	8.2	22.2	147	59.0	0.8	0.1	68.5	0.01	0.0	0.2	1.4
16	III	Aug. 1995	-310	7.63	-39.1	19.3	472.5	28.0	1.6	7.9	54.0	27.5	41	169.0	0.4	3.0	23.5	0.01	0.3	1.5	0.2
17	III	Aug. 1995	-150	7.65	-37.3	24.0	402.2	11.0	0.9	9.6	47.0	13.3	15	165.8	0.4	8.0	23.5	0.01	0.2	0.6	0.1
18	II	Aug. 1995	-420	9.98	-167.2	32.7	292.1	65.0	0.8	0.0	1.1	17.8	55	25.2	15.5	0.1	36.4	0.06	0.0	0.2	2.5
19	Ib	Aug. 1995	-350(?)	8.23	-79.4	64.1	635.1	110.0	9.8	0.1	18.0	20.3	240	42.5	0.8	0.1	66.3	0.01	0.0	0.7	1.3
20	Ib	Aug. 1995	-350	8.69	-103.4	59.9	418.3	84.0	5.2	0.0	5.7	23.9	121	30.0	1.3	0.1	64.2	0.12	0.0	0.3	1.6
21	Ia	Aug. 1995	?	8.57	-113.5	75.5	415.2	78.0	5.0	0.0	3.8	11.6	123	35.6	1.3	0.1	81.3	0.01	0.0	0.3	2.5
22	II	Aug. 1995	-325	9.52	-139.0	29.3	310.5	72.0	0.6	0.1	3.0	21.3	71	39.2	7.9	0.2	27.8	0.01	0.0	0.2	1.2
23	III	Aug. 1995	-80	7.63	-33.9	16.2	433.5	15.0	1.3	11.0	57.0	35.0	14	142.1	0.3	38.3	25.7	0.01	0.0	0.6	0.1
24	III	Aug. 1995	-500	7.99	-56.0	33.3	385.6	22.0	1.4	3.8	43.0	9.9	33	133.7	0.9	1.1	30.0	0.01	0.2	0.7	0.2
25	III	Aug. 1995	0	7.82	-45.6	22.8	334.8	7.0	0.6	8.4	39.0	3.1	24	133.0	0.5	0.1	15.8	0.01	0.0	0.4	0.1
26	Ia	Aug. 1995	-275	8.90	-123.8	66.7	362.5	77.0	6.1	0.0	3.2	8.8	116	33.2	2.4	0.1	83.4	0.10	0.0	0.2	2.6
27	II	Aug. 1995	-450	9.34	-135.7	45.4	361.5	67.0	2.5	0.0	7.6	24.7	80	32.1	5.5	0.1	42.8	0.01	0.0	0.1	1.0
28	II	Aug. 1995	-100(?)	9.42	-136.7	39.8	342.3	75.0	1.3	0.1	6.2	32.0	60	50.1	9.5	0.1	38.5	0.01	0.0	0.1	0.7

[1] Calculated from the measured alkalinity and pH data using the computer code SOLVEQ (Reed, 1982)

breccia veins are preferentially developed in the Bugok geothermal area.

SAMPLING AND ANALYTICAL METHODS

Water sampling was carried out from totally twenty-eight locations between 1994 and 1995. The sampling sites are shown in Fig. 1. Temperatures of waters systematically decrease toward peripheral sites in the geothermal area. Water samples are categorized into three major types, based on the temperature and sampling locations (Fig. 1, Table 1): 1) Group I=hot ($55.2°$~$77.2°C$) groundwaters from the central part of the Bugok geothermal area; 2) Group II=warm ($28.8°$~$47.0°C$) groundwaters from the peripheral part; and 3) Group III=cold ($<33.3°C$) water either from streams or from shallow groundwater wells at the vicinity of the geothermal area. The Group I waters are further divided into two subtypes (Ia and Ib), based on the water chemistry and genesis (see below). All waters, except stream waters, were sampled from drilling wells for com- mercial or drinking purposes.

The pH, Eh, temperature and electrical conductivity of water samples were measured *in situ* with potable meters (Orion 290A and 190). Measurement of alkalinity was performed in the field by acid titration. Samples for chemical analyses were filtered using 0.45 μm cellulose membrane filters. Samples for cation analysis were acidified to pH of <2.0 by adding few drops of 50% ultrapure HNO_3.

Concentrations of major cations were measured by the atomic absorption spectrometer (AAS) and inductively coupled plasma-atomic emission spectrometer (ICP-AES). Major anions were measured by the ion chromatography (IC). Oxygen and hydrogen isotope compositions of waters, relative to the Vienna SMOW standard, were determined through the conventional CO_2 equilibration method (at $25°C$) and the reduction with Zn metal (at $450°C$), respectively. Relative errors of analysis are within $0.1‰$ for oxygen-18 and within $1.0‰$ for deuterium. Tritium contents (TU) of waters were measured by the liquid scintillation counting (during 500 minutes) after the electrolytical enrichment (from a sample weight of 600 g to 20 g). The pre-
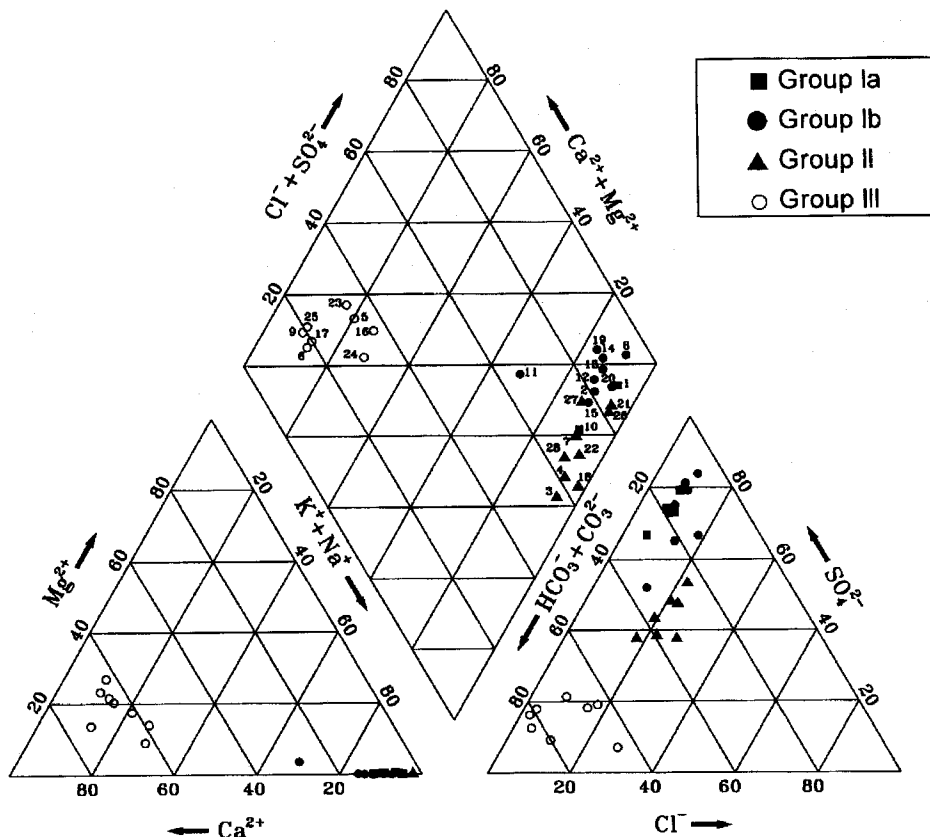

Fig. 2. Trilinear compositional diagrams showing chemical characteristics of various waters from the Bugok geothermal area.

cision of the tritium analysis is about 1.0 TU. For the determination of sulfur isotope compositions (relative to the Canyon Diablo Troilite standard) of waters, aqueous sulfates were precipitated as $BaSO_4$ by adding $BaCl_2$ solution. These obtained barium sulfate was reduced to Ag_2S by using the Thode solution (Thode *et al.*, 1961) and thereafter was combusted with Cu_2O to produce SO_2 for mass spectrometric analysis. The accuracy of the sulfur isotope measurements is better than 0.2‰.

WATER CHEMISTRY AND GEOTHERMOMETRY

Physicochemical data and classification of waters

Data of *in-situ* measurements and hydrochemical compositions of various kinds of waters from the Bugok geothermal area are summarized in Table 1.

The pH and temperature of the Group I waters (hot groundwater) range from 8.1 to 9.0 and from 55.2° to 77.2°C, respectively. Those of the Group II waters (warm groundwater) are 9.0 to 10.0 and 28.8° to 47.0°C. The Group III waters (cold, surface water and shallow groundwater) are weakly alkaline (pH= 7.6 to 8.2) with temperatures mostly less than 25°C. The redox potentials (Eh; mV) of the Group I, II, and III waters range from -137 to -67, from -167 to -120, and from -69 to -34, respectively. Ranges of the electrical conductivities (μS/cm) of the Group I, II, and III waters are 363 to 635, 292 to 362, and 282 to 473, respectively. Therefore, each group water shows distinct data of temperature, pH, Eh and to a less extent electrical conductivity.

Hydrochemical compositions of water samples are plotted in trilinear equivalence diagrams (Fig. 2). The Group I and II waters are characterized by the relatively significant enrichments of alkali metals (Na^++ K^+), whereas the Group III waters are relatively enriched in Ca^{2+}. In terms of anion contents, the Group I waters are typically enriched in SO_4^{2-}, whereas the Group III waters in carbonates (HCO_3^- +CO_3^{2-}). The Group II waters show the transitional area having intermediate anion compositions between the Group I and Group II waters. Therefore, the typical geothermal waters (Group I) belong to the Na-SO4 type, whereas the peripheral warm groundwater (Group II) and the cold water (Group III) have the characteristics of the Na-Ca-SO4 type and Ca-HCO3 type, respectively.

Water/rock interaction

The Group I (especially the subgroup Ib) and Group

II waters are typically enriched not only in sulfate but also in most cations (especially, alkali metals such as Na^+ and K^+), as shown in Fig. 3. Compared to the Group II waters, the Group I waters are characterized by the following features: 1) higher temperature; 2) higher contents of dissolved SO_4^{2-}, Na^+, K^+, F^- and TDS; 3) higher Eh and lower pH values. It is noteworthy that among the Group I waters, sulfate is more enriched in the Group Ib waters (Fig. 3B). The Group III waters are characterized by lower pH and higher Eh, and are depleted in SO_4^{2-}, Na^+, K^+ and F^-, compared with the Group I and II. Therefore, the sulfate distribution appears to be a key parameter for understanding the origin and evolution of the geothermal waters at Bugok. Here, it is very important to know the origin of sulfate that is enriched in the Group I waters.

Combined with geologic setting (and mineralogy of surrounding rocks), the probable sources of sulfate are as follows: 1) oxidation of H_2S gas derived from deep geothermal reservoir (possibly, the cooling pluton), and 2) oxidation of sulfide minerals (mainly pyrite) in surrounding sedimentary rocks. We prefer the latter explanation, because the pyrite oxidation
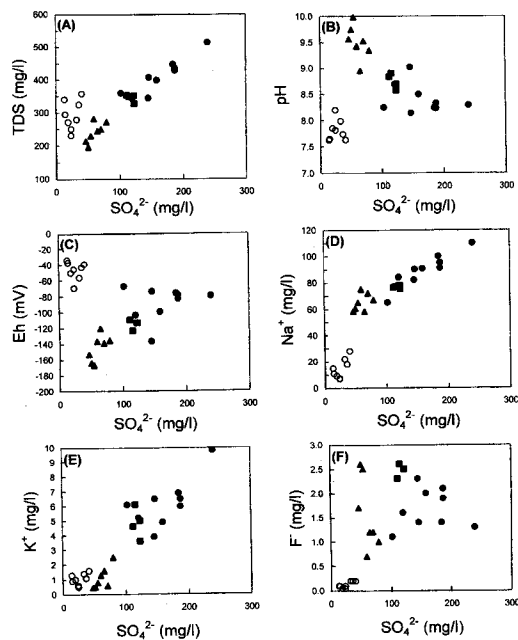

Fig. 3. Relationships between SO_4^{2-} content and values (or contents) of TDS, pH, Eh, Na^+, K^+ and F^- in various groups of waters from the Bugok geothermal area. Sulfate is a key component for understanding the origin and evolution of the geothermal water. Symbols are the same as in Fig. 2.

only would effectively form sulfate-rich acidic water which was subsequently capable of reacting intensively with silicate minerals in surrounding rocks (see also the "Sulfur isotope: source of sulfate" in the "ENVIRONMENTAL ISOTOPES" section).

It is also shown in Fig. 3. that among the groundwater samples (Group I and II) the sulfate-rich waters have the lowest pH and highest Eh values. This fact also supports that the oxidation of pyrite played an important role to control the chemistry of hot and warm groundwaters (Group I and II). The larger degrees of the interaction between more acidic waters with larger sulfate contents and rocks, the larger amounts of cations such as Na^+ and K^+ (therefore, the associated higher TDS values) were dissolved in waters (Fig. 3D, E). The pyrite oxidation and subsequent interaction with rocks could release increased alkali ions through the breakdown of Na-rich plagioclase and K-bearing minerals (mica and K-feldspar) within sedimentary rocks and/or granite.

For the successful explanation of the genesis of the Group I waters, however, we should demonstrate the reason why for the Group I waters the SO_4^{2-} concentrations are relatively high but the pH is not acidic (>8.1). This may indicate that the protons produced by the pyrite oxidation were less than those consumed by the dissolution of feldspars, which could result in the pH increase (in fact, if albite was reacted with water, 1 proton in aqueous phase was consumed for each mole of Na^+ released). For example, if the observed concentration of Na+ for the sample no. 21 (78 mg/l) was formed through the interaction between albite and water, the hydrogen ion of about 3 mmoles should have been consumed to result in a pH increase. We conclude that the Group I waters (pH=8.1 to 9.0), compared to the Group II waters (pH=9.0 to 10.0), represent the groundwaters that were evolved through larger degrees of involvement (mixing) of more acidic waters derived from pyrite oxidation.

Fig. 3. also shows that the concentrations of Na^+ and K^+ in the Group I and II waters have positive linear correlations with the sulfate concentration. These trends can be explained by the following mechanisms: 1) mixing of hotter sulfate-rich waters (which earlier formed by the pyrite oxidation and are represented as the Group I and II waters) with cooler and more dilute waters (i.e., surface water and/or downward cold groundwater, corresponding to the Group III waters), or 2) progressive interaction of cooler and more dilute waters with wallrock sulfides. We prefer the first mechanism, because clear classification in chemical compositional changes are ob-

served among each group of waters (Fig. 3).

The breakdown of plagioclase, carbonates, biotite and chlorite would also increase the Ca^{2+} and Mg^{2+} contents. However, the measured concentrations of Ca^{2+} and Mg^{2+} are relatively too low (Table 1). In high-pH waters, Ca^{2+} and Mg^{2+} are usually transfered to the solid phase and, therefore, their contents in water are controlled by mineral precipitation. It is also remarkable that the contents of dissolved carbonates (equally, the alkalinity) in the Group I and II waters are almost constant below 80.7 mg/l (on the other hand, >133.5 mg/l for the Group III waters; Table 1), regardless of pH and SO_4^{2-} contents. This indicates the saturation state of waters with respect to carbonates. In fact, the saturation index (S.I.) of calcite in waters, calculated using the computer code SOLVEQ (Reed, 1982), shows that all groups of waters in the Bugok area are nearly saturated or supersaturated with respect to calcite (Fig. 4).

The Group I waters are more enriched in SiO_2 (53.5 to 83.4 mg/l) than other group waters (<42.8 mg/l; Table 1). However, it is also noteworthy that the silica concentration of the Group I waters are relatively constant. In general, variation of the silica content in geothermal waters is mainly controlled by temperature, pH and quartz precipitation (Tonani, 1980; Fournier, 1981). We suggest that the observed constancy of silica content in the Group I waters implies either a small difference in deep-seated geothermal reservoir's temperatures (see below) or the partial precipitation of silica associated with the cooling of upflowing less-alkaline waters during the ascent (from a reservoir toward the surface) (Fournier, 1981).

The Group I waters also tend to have higher concentrations of F^- (up to 2.7 mg/l) than the Group
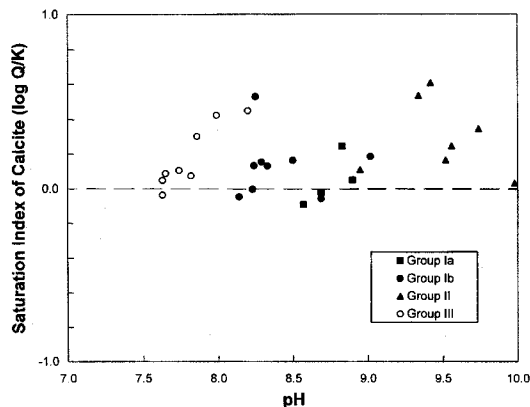

Fig. 4. Calculated saturation indices (S.I.) of calcite in terms of pH of waters from the Bugok area. All waters are nearly saturated or supersaturated with respect to calcite.

III (surface) waters (Fig. 3F). Most natural fresh waters contain about 0.1 mg/*l* F⁻, and the active thermal and mineral spring waters in Japan contain higher amounts of F⁻ (average 1.9 mg/*l*; Sugawara, 1967). We suggest that the relatively enriched F ion in the Bugok geothermal waters is originated from the fluids upflowing from deep-seated · geothermal reservoir.

Geochemical evolution of geothermal waters

As discussed above, the Group I and II waters have been undergone the following subsequent processes: 1) heating of deeply circulating meteoric waters, accompanying some degrees of dissolution of carbonates and plagioclase in rocks near the circulation pathways, resulting in the pH increase (up to about 10.0) and the formation of the Ca-HCO₃ type water → 2) deeper penetration (as indicated by environmental isotope data; see the following section) and reaction with pyrite-rich aquifer rocks (possibly near the thermal reservoir at depths), resulting in the formation of more acidic sulfate-rich waters → 3) subsequent larger degrees of dissolution of carbonates and silicates (including K-feldspars, mica and chlorite, in addition to plagioclase) in rocks around their pathways → 4) some chemical changes not only through the precipitation of some minerals (including calcite and silica, due to their attainment to saturation or supersaturation states) but also through the mixing with cooler and more dilute waters (corresponding to the Group III waters) at near-surface (It must be noted that these two changes resulted in the increase of pH up to 8.90). If the circulating waters were evolved largely the first and fourth processes without the second and third ones, merely the Group II waters formed. On the other hand, the Group I waters record all of the previous processes.

The important role of pyrites in the geochemical evolution of the Group I waters is evidenced by the fact that pyrites are commonly observed in drill-cores for the development of geothermal waters in the Bugok area. Sulfur isotope data of these pyrites (δ³⁴S_CDT=3.3 and 3.4‰) indicate their hydrothermal origin (Ohmoto and Rye, 1979). Furthermore, the sulfur isotope data of pyrites likely indicate the presence of a cooling granitic pluton (as the source of hydrothermal sulfur and geothermal water) at depths.

Here, we must discuss the relationship between the Subgroup Ia waters (e.g., sample nos. 1, 10, 21, 26; Table 1) and the Subgroup Ib waters. Compared with the Subgroup Ib geothermal waters, the Subgroup Ia geothermal waters are characterized by the lower

contents of TDS, sulfate and alkali ions (Na⁺, K⁺), lower Eh values, and higher values of pH and F⁻ (Fig. 3). As discussed above, these differences also can be explained by the difference in the degrees of mixing with pyrite-related waters. The Subgroup Ia waters record lesser degrees of the mixing, and were evolved mainly through interaction with relatively larger amounts of more pyrite-poor rocks. Possibly, the pyrite-poor rock is a granitic pluton at considerable depths, which served as a supplier of heat and F⁻. This interpretation is also supported by sulfur isotope, oxygen-hydrogen isotope and tritium data (see following section).

Estimation of geothermal reservoir temperature

Assuming that the chemical composition of geothermal water were preserved after the interaction with igneous rocks at depths, we can estimate the temperature of the geothermal reservoir. Fig. 5. shows the compositional plots of geothermal waters (Group I and II) from the Bugok area in a Giggenbach's (Giggenbach, 1988). Characteristics of the Na/K and K/Mg geothermometers are also compared in the diagram. In general, it is known that the Na/K geothermometer reflects the long-term conditions of the geothermal system, whereas the K/Mg geothermometer gives the informations on the last chemical processes occurred during the circulation. It is also noteworthy that the Mg concentration is expressed as the square root; for this reason the mixing processes are represented by non-linear lines, unless the Na/K ratio remains practically unchanged.

All of the waters from the Bugok area are plotted in the region below the full equilibrium line (Fig. 5).
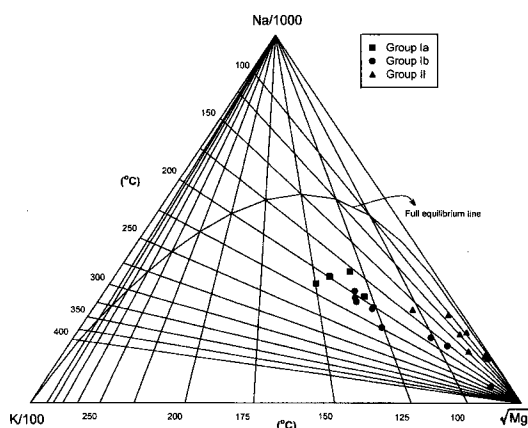

Fig. 5. Triangular plots of Na, K and Mg as a function of temperature of geothermal reservoir (after Giggenbach, 1988). The Mg values are represented as square roots.

It is also noteworthy that the plots of the Group I waters tend to be aligned on a linear line going from a Mg corner toward the plots of the Subgroup Ia waters. This trend indicates that the geothermal waters from the Bugok area largely form a single compositional family, and were evolved largely through the progressive mixing between two end members: a Mg-rich water (probably the near-surface water), and a relatively Mg-poor water (which is represented by the Subgroup Ia waters). Therefore, the Subgroup Ia waters (sample nos. 1, 10, 21, 26) record most intensively the composition of the original geothermal waters which formed in the geothermal reservoir. As suggested above, the more Mg-rich, Subgroup Ib waters (sample nos. 2, 8, 11, 12, 13, 14, 15, 19, 20) formed by larger mixing with pyrite-related waters during their upflow, compared to the Subgroup Ia.

The alignments of plots in Fig. 5 also reflect not only the extents of attainment to equilibrium among considered cations but also the applicability of certain geothermometries. The plots of the Group I waters are aligned near a 200°C Na-K isothermal line, but do not match with any specific K-Mg geothermometric line. This indicates the partial disequilibrium between K and Mg, likely due to the mixing of various amounts of the Mg-rich waters. The degrees of chemical disequilibrium between K and Mg were greatest for the Group II waters.

The application of the Na-K geothermometer yields too high temperatures for the Group I waters (200°±25°C; Fig. 5), probably due to the relative deficiency of Na in comparison with the saturation condition with respect to albite (see also below). On the other hand, the application of the K-Mg geothermometer gives lower and variable temperatures (<100° to 150°C; Fig. 5), likely due to the later mixing with Mg-rich cold groundwater or the uptake of K (possibly as illite). Therefore, the reasonable reservoir temperatures are thought to exist between these two ranges.

Additionally, various chemical geothermometers have been developed to predict the reservoir temperatures in geothermal system (Fournier, Rowe, 1966; Fournier and Truesdell, 1973; Truesdell, 1976; Fournier, 1979; Tonani, 1980; Fournier, 1981; Fournier, Potter, 1982; Arnorsson, 1983; Nieva, Nieva, 1987; Giggenbach, 1988). These geothermometers are all based on the assumption that specific temperature-dependent mineral/solute equilibria are attained in the geothermal reservoir. Because they use only a few chemical components analyzed, variable temperatures can be frequently predicted for a same fluid. These temperature variation may be due to the lack of equilibration between solutes and minerals or due to additional processes (including mixing with cold water in the upflow). Therefore, it is desirable to have an approximate approach that optimizes the use of the available analytical data and allows the validity of the assumption of specific solution/mi-

Table 2. Estimated reservoir temperatures of geothermal waters from the Bugok area, using various published geothermometers

Sample no.	Water type (group)	pH	In-situ temp. (°C)	Estimated temperature (°C)										
				QC[1]	QA[1]	CH[1]	NaK[1]	Na/K[2]	Na/K[3]	Na/K[4]	NaK[5]	NaKCa[6]	Na/K[7]	K/Mg[7]
1	Ia	8.69	77.2	120.1	118.3	91.7	161.1	123.6	130.3	149.2	119.9	143.1	180	92
2	Ib	8.50	65.3	112.1	111.4	83.0	169.5	133.9	139.8	157.3	129.7	146.2	188	102
7	II	8.95	47.0	92.3	94.4	61.8	126.6	82.6	92.1	115.4	80.6	115.0	147	75
8	Ib	9.02	71.6	115.5	114.3	86.6	160.7	123.1	129.8	148.7	119.4	140.8	179	93
10	Ia	8.83	55.2	124.6	122.0	96.6	177.4	143.8	148.8	165.1	139.1	151.4	195	97
11	Ib	8.25	60.6	105.0	105.3	75.3	211.6	187.7	188.6	198.5	180.8	159.1	227	74
12	Ib	8.24	72.3	118.6	117.0	90.1	187.1	156.0	160.0	174.6	150.7	156.8	204	127
13	Ib	8.23	73.1	123.1	120.8	95.0	186.5	155.2	159.2	173.9	150.0	156.2	204	133
14	Ib	8.33	76.7	123.1	120.8	95.0	183.7	151.7	156.0	171.2	146.6	152.4	201	126
15	Ib	8.14	71.6	117.1	115.7	88.4	190.6	160.4	164.0	178.0	154.9	160.4	208	133
19	Ib	8.29	64.1	115.5	114.3	86.6	207.3	182.0	183.5	194.3	175.4	167.7	223	126
20	Ib	8.69	59.9	113.8	112.9	84.9	179.1	145.8	150.7	166.7	141.1	154.7	197	133
21	Ia	8.57	75.5	125.9	123.2	98.1	181.6	149.0	153.6	169.2	144.1	158.5	199	143
26	Ia	8.90	66.7	127.3	124.4	99.6	197.8	169.7	172.4	185.0	163.7	170.4	214	150
27	II	9.34	45.4	94.7	96.4	64.3	144.9	104.1	112.2	133.3	101.2	126.3	164	104
28	II	9.42	39.8	90.0	92.3	59.3	102.0	54.7	65.6	91.4	53.6	99.1	123	72

QC, QA and CA=silica geothermometers; others=alkali-ion geothermometers [Data sources: [1] Fournier (1981), [2] Tonani (1980), [3] Arnorsson (1983), [4] Nieva, Nieva (1987), [5] Truesdell (1976), [6] Fournier, Truesdell (1973), [7] Giggenbach (1988)].

neral equilibria to be tested. Table 2 summarizes the reservoir temperatures calculated from available silica and alkali ion geothermometers.

Recently, Reed, Spycher (1984) have proposed that the best estimate of reservoir temperature can be obtained by considering simultaneously the states of equilibrium between a specific water and many geothermal minerals as a function of temperature [here, the dependancy of equilibrium constants to pressure is negligible because the pressure range in geothermal systems are too low (1-200 bars) to effect the constants]. If a group of minerals converges to the equilibrium at a particular temperature, this temperature reflect the most reasonable reservoir temperature (or at least the source aquifer temperature of the specific water considered) (e.g., Pang, Armannsson, 1989; Tole et al., 1993). Reed and Spycher (1984) also proposed that through this approach we can distinguish the degrees of equilibrium states between a geothermal water and minerals and therefore the causes of disequilibrium (i.e., boiling or fluid-fluid mixing).

As an example of the calculation of multi-component mineral equilibria (based on the computer code SOLVEQ), a log Q/K versus temperature diagram for one of the Group Ia waters from the Bugok area (sample no. 21) is shown in Fig. 6. The minerals chosen for the calculation are geothermal alteration minerals which might be precipitated owing to the attainment to saturation states in our waters. However, we must note that this new approach of reservoir's temperature estimation also remains some problems because of the fundamental difficulty in obtaining reasonable analyses of aluminium in water. Nevertheless, the hypothetical aluminium concentration can be applied for each temperature by forcing the water to

attain at equilibrium state with respect to microcline. We used the calculated aluminium contents for the calculations of the Q/K diagram.

The temperatures for the attainment to equilibrium states, and therefore the probable reservoir temperatures, are estimated to be about 120° to 130°C (Fig. 6). In comparison, the other calculated temperatures for the sample no. 21 are as follows (Table 2): 144° to 199°C from Na-K thermometers (Truesdell, 1976; Tonani, 1980; Fornier, 1981; Arnorsson, 1983; Nieva, Nieva, 1987; Giggenbach, 1988), 143°C from an K-Mg thermometer (Giggenbach, 1988), and 159°C from an Na-K-Ca geothermometer (Fournier and Truesdell, 1973). These values are more or less higher than the temperature (near 125°C) obtained from a log Q/K diagram. Therefore, we suggest that albite and K-feldspar apparently were not approached to chemical equilibrium with the water at deep reservoir. Fig. 6 also shows that the subsurface mineral assemblage including quartz, kaolinite and muscovite were in equilibrium with the Subgroup Ia waters.

We collected hydraulic fracture-filling calcites from drillcores (see "GEOLOGIC SETTING") and measured for homogenization temperatures of fluid inclusions. Aqueous liquid-rich fluid inclusions (measured numbers=38) in the calcites have homogenization temperatures of 66° to 183°C (mean=128°C), which are in good agreement with the thermodynamically estimated temperature. Conclusively, we consider that the deep geothermal reservoir likely has the temperatures around 120°~130°C (or slightly higher temperatures). This temperature condition may be used to estimate the potential of development of geothermal energy in the Bugok area.

ENVIRONMENTAL ISOTOPES

In order to elucidate the origin, evolution and recharge time of geothermal waters in the Bugok area, 14 data of sulfur isotope of dissolved sulfates and 28 data of oxygen and hydrogen isotopes and tritium content of waters were obtained (Table 3).

Sulfur isotope: source of sulfate

The measured $\delta^{34}S_{SO4}$ values (relative to CDT) range widely from 2.3 to 13.9‰ (Table 3). Within this range, each group water has an unique value as follows: 12.9 to 13.9‰ for the Subgroup Ia waters; 2.3 to 8.1‰ for the Subgroup Ib waters; 2.4 to 7.9‰ for the Group II waters; and 6.3 to 12.7‰ for the Group III waters. It is noteworthy that the Subgroup Ia waters have much higher $\delta^{34}S_{SO4}$ values than other group waters. In particular, the values of the Sub-
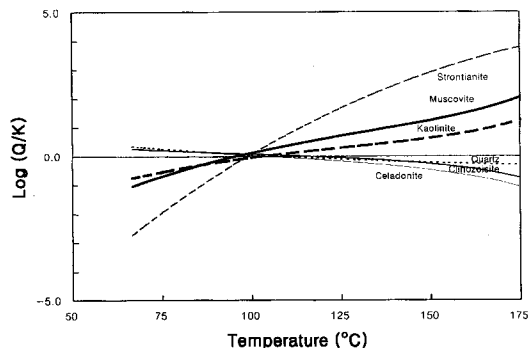

Fig. 6. A temperature versus log Q/K diagram showing the coprecipitation equilibrium condition for alteration minerals (for the sample no. 25). The probable equilibrium temperature is about 100° to 125°C, which is much lower than the well-head temperature (67°C).

Table 3. Isotopic compositions of water samples from the Bugok geothermal area

Sample no.	Water type	$\delta^{18}O$ (‰)	δD (‰)	Tritium (TU)	$\delta^{34}S_{SO4}$ (‰)
1	Ia	-9.0	-62.2	0.1	–
2	Ib	-8.7	-61.7	3.8	–
3	II	-8.1	-59.7	3.1	–
4	II	-7.7	-55.2	6.6	–
5	III	-7.4	-51.1	6.5	–
6	III	-8.0	-51.6	6.4	–
7	II	-8.2	-54.3	5.3	–
8	Ib	-8.9	-61.1	2.1	–
9	III	-8.0	-51.3	8.1	–
10	Ia	-8.9	-60.7	0.1	13.9
11	Ib	-8.0	-56.1	3.3	–
12	Ib	-8.3	-56.2	2.3	–
13	Ib	-8.7	-58.9	1.9	8.0
14	Ib	-8.9	-59.7	0.5	8.1
15	Ib	-8.2	-56.7	5.1	3.8
16	III	-7.3	-52.2	6.3	6.3
17	III	-7.8	-51.8	5.7	–
18	II	-8.0	-52.4	2.6	4.7
19	Ib	-8.4	-57.7	3.4	2.3
20	Ib	-8.2	-53.1	4.3	6.6
21	Ia	-9.0	-61.9	0.0	13.5
22	II	-7.6	-52.1	4.1	2.4
23	III	-7.5	-50.5	8.9	12.7
24	III	-7.6	-51.0	6.8	–
25	III	-7.9	-52.8	7.8	–
26	Ia	-9.0	-60.3	0.5	12.9
27	II	-8.1	-54.3	5.0	6.1
28	II	-7.7	-52.9	5.4	7.9

group Ia waters are higher than those of the Subgroup Ib waters. These data suggest the presence of several different sources (at least two) of sulfur, including an isotopically heavier source (at least ≥ 13.9‰) and a lighter source (down to 2.3‰).

The lighter sulfur source may include general fresh river waters which may include anthropogenically derived atmospheric sulfur. For the Bugok area, this external source can be applied to the Group II and III waters that contain minor amounts of sulfate. For the heavier sulfur source, we pay attention to the pyrite in surrounding rocks (including the aquifer rock itself). Hydrochemical data of the sulfate-rich, Group I waters indicate the prevalence of this source, as discussed above.

Combined with the geology and observed hydrochemical data, however, the distinct $\delta^{34}S_{SO4}$ values between the Subgroup Ia and Ib waters likely suggest the involvement of two different genetic types of pyrite (hydrothermal and sedimentary). The high $\delta^{34}S_{SO4}$ values (12.9 to 13.9‰) for the Subgroup Ia waters possibly indicate the derivation of sulfate

from kinetic oxidation of hydrothermal (magmatic) pyrites ($\delta^{34}S$ value=3.3~3.4‰; see above) occurring in hydraulic fractures as pathways of geothermal waters. According to Harrison, Thode (1957), the kinetic-controlled chemical oxidation of reduced sulfur (and sulfides) forms the SO_4^{2-} enriched in ^{34}S [however, the degrees of ^{34}S enrichment is much lower than the equilibrium fractionation (up to about 40 to 50‰ at temperatures between 80° and 130°C; Ohmoto, Rye, 1979). Furthermore, the $\delta^{34}S_{SO4}$ values for the Group I waters likely exclude the sulfate sulfur derived from bacterial sulfide oxidation and associated kinetic fractionation, as this process results in progressively ^{34}S-depleted SO_4^{2-} (Pearson, Rightmire, 1980). Although we could not obtain the $\delta^{34}S$ values of sedimentary pyrites in surrounding sedimentary rocks, relatively low $\delta^{34}S_{SO4}$ values (2.3 to 8.1‰) for the Subgroup Ib waters may indicate the derivation of sulfate probably from isotopically lighter sedimentary pyrites during the deep circulation of waters.

In summary, the observed hydrochemical and $\delta^{34}S_{SO4}$ data of the Group I waters indicate that two kinds of pyrites have involved in the formation of the waters. This at least two-source model for sulfates in the Group I waters well explains the interesting result that the Subgroup Ia waters with characteristics of more evolved water rather contains less amounts of sulfate than the chemically less-evolved Subgroup Ib waters.

Oxygen-18 and deuterium: origin and hydrology of water

The oxygen and hydrogen isotope compositions of waters from the Bugok geothermal area are shown in Table 3. The ranges of $\delta^{18}O$ and δD values (relative to Vienna SMOW) of each group water are as follows: for the Subgroup Ia water, -9.0 to -8.9‰ and -62.2 to -60.3‰; for the Subgroup Ib water, -8.9 to -8.0‰ and -61.7 to -53.1‰; for the Group II water, -8.2 to -7.6‰ and -59.7 to -52.1‰; and for the Group III water, -8.0 to -7.3‰ and -52.8 to -51.1‰. The general order of increasing O and H isotope values is Subgroup Ia → Subgroup Ib → Group II → Group III (Fig. 7). This variation indicates that each group water were derived from distinct waters with unique O and H isotope compositions.

Fig. 7. also shows that all groups of waters from the Bugok area show wide isotopic compositions but are clustered along the worldwide meteoric water line (Craig, 1961). The absence of recognizable oxygen isotope shift is likely related to the relatively low reservoir temperature (around 125°C; see "WATER CHEMISTRY AND GEOTHERMOMETRY"), be-
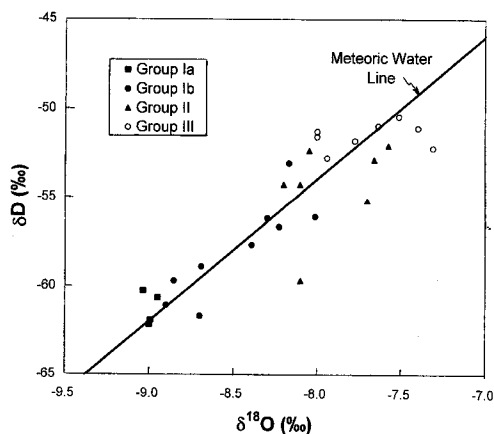
Fig. 7. Plots of $\delta^{18}O$ versus δD values for various groups of waters from the Bugok geothermal area.

cause the low-temperature water is hardly sufficient to yield a large oxygen isotope exchange with ^{18}O-enriched rocks (Taylor, 1974). Worldwide, well-known modern geothermal waters (with temperatures up to 250 to 300°C) also show the derivations from regional meteoric waters but show considerable oxygen isotope shift (up to 18‰; Truesdell and Hulston, 1980).

The isotopic distinction of geothermal waters (Group I) into two clusters (Subgroup Ia and Subgroup Ib) coincides exactly with the grouping deduced from systematics of hydrochemical and sulfur isotope data (see above), and evidences that the geothermal waters have derived from at least two sources. Therefore, it is apparent that for the generation of geothermal waters there are two main sources of meteoric waters with different O and H isotope compositions. If considered the fact that the sequence of increasing O and H isotope values varies systematically toward the shallower water groups, the Subgroup Ia waters (e.g., sample nos. 1, 10, 21, 26) likely represent the most typical geothermal waters that circulated deeply and then upflowed from a deep geothermal reservoir (possibly a cooling pluton). On the other hand, the Subgroup Ib waters (e.g., sample nos. 2, 8, 11, 12, 13, 14, 15, 19, 20) represent the less typical geothermal waters which mixed with sedimentary pyrite-derived waters.

We suggest that the Subgroup Ia waters should have the restricted fluid flow along fault-related pathways extending to a deep geothermal reservoir, and do not significantly mix with other surface or near-surface waters. For the deep circulation, the meteoric waters should have longer recharge paths starting from a high-altitude condition. Considering the observed altitude effect in Korea (about 0.19‰ in $\delta^{18}O$ value per each 100 m height; Kim, Nakai,

1988), the elevation of the recharge area for the Subgroup Ia waters was probably about 400 m higher than those for other group waters.

Tritium content: recharge time of water

Tritium contents (unit: TU) of water samples from the Bugok geothermal area are listed in Table 3. The values vary systematically with the water group: in a general decreasing order, Group III waters (5.7 to 8.9 TU) → Group II waters (2.6 to 6.6 TU) → Subgroup Ib waters (0.5 to 5.1 TU) → Subgroup Ia waters (0.0 to 0.5 TU).

It is remarkable that tritium in the Subgroup Ia waters is almost free. Referring the long-term monitored tritium contents in rain water samples from the Pohang City and KAERI of Taejon (IAEA, 1992; Koh et al., 1996), these remarkably low tritium contents indicate that the Subgroup Ia waters represent the old meteoric waters recharged during pre-thermonuclear (before 1953) times (IAEA, 1992). The time elapsed since the thermonuclear period was too long to have significant tritium left in meteoric waters recharged before the thermonuclear period. As the source of geothermal waters, we exclude the recent (post-thermonuclear period) meteoric waters.

The Group III waters have relatively high tritium contents (5.7 to 8.9 TU). This values agree well with those for recent rain waters in Korea (4.6 to 34.2 TU; Ahn and Koh, 1995). In reference, tritium contents of recent rain waters collected at KAERI in Taejon decreased annually with time and most recently are about 10 TU (Ahn, Koh, 1995). Therefore, shallow groundwaters in the Group III waters likely represent the meteoric waters recharged recently. The Group II
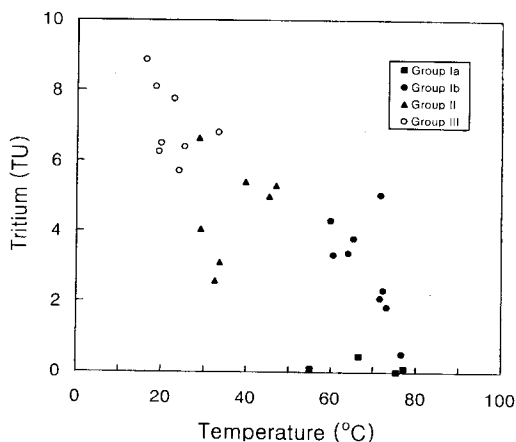

Fig. 8. Relationship between tritium content and in-situ well-head temperature for various groups of waters from the Bugok geothermal area.

Table 4. Summary and comparison of physicochemical characteristics of each group water from the Bugok geothermal area.

	Group Ia	Group Ib	Group II	Group III
Water type	Na-SO$_4$	Na-SO$_4$	Na-Ca-SO$_4$	Ca-SO$_4$
T (°C)	55 to 77	60 to 77	29 to 47	16 to 33
pH	8.6 to 8.9	8.1 to 9.0	9.0 to 10.0	7.6 to 8.2
Eh (mV)	-124 to -110	-137 to -67	-167 to -120	-69 to -34
SO$_4^{2-}$ (mg/l)	113 to 124	103 to 240	47 to 80	14 to 41
Na$^+$+K$^+$ (mg/l)	79 to 83	71 to 120	59 to 76	8 to 30
δ^{18}O (‰)	-9.0 to -8.9	-8.9 to -8.0	-8.2 to -7.6	-8.0 to -7.3
δD (‰)	-62 to -60	-62 to -53	-60 to -52	-53 to -51
Tritium (TU)	0.0 to 0.5	0.5 to 5.1	2.6 to 6.6	5.7 to 8.9
δ^{34}S$_{SO4}$ (‰)	12.9 to 13.9	2.3 to 8.1	2.4 to 7.9	6.3 to 12.7

waters have intermediate tritium contents between the Group I and Group III waters, clarifying the interpretation that compared to the Group I waters, the Group II waters involve the significant contribution from cold surficial waters.

The older recharge age (more than 45 years old) for the Group I waters possibly indicates the longer and deeper circulation flow path from an distant recharge area. Fig. 8. shows the relationship between tritium content and in-situ temperature for all groups of waters from the Bugok area. There is a general tendency of increasing temperature with decreasing tritium content (and therefore the age) of waters. This trend indicates that the older age meteoric waters (Group I) circulated deeply down to the geothermal reservoir and then were heated-up significantly. During the longer residence, larger amounts of ions (and TDS) were dissolved through water/rock interaction. On the other hand, the Group II and III waters with shorter subsurface residence times represent the meteoric waters that have circulated at shallower crustal levels and therefore have not been sufficiently heated-up.

CONCLUSIONS

Various kinds of natural waters, including the central high-temperature geothermal waters, the peripheral warm groundwaters, and the surface waters and shallow cold groundwaters, were collected from the Bugok area which is famous for the occurrence of sulfate-rich geothermal waters in Korea. Systematic hydrogeochemical and environmental isotope studies were undertaken, in order to elucidate the nature (grouping), origin and evolution (including the geothermal reservoir temperature, water/rock interaction, and fluid-fluid mixing, etc.) of the geothermal waters. Major results of studies are summarized as follows:

(1) Based on physicochemical data, waters from

the Bugok area are grouped into three distinct types (Table 4): 1) Group I, typical geothermal waters with high in-situ temperatures (55°~77°C) and intermediate pH (8.1~9.0) and Eh (-137 to -67 mV) values; 2) Group II, peripheral warm groundwaters with intermediate temperatures (29°~47°C), high pH (9.0~10.0) and low Eh (-167 to -120 mV) values; 3) Group III, surface waters and cold groundwaters which are very similar with general fresh surface waters. Hydrochemical types of each group water are: Na-SO$_4$ type for the Group I waters; Na-Ca-SO$_4$ type for the Group II waters; and Ca-HCO$_3$ type for the Group III waters. Therefore, the general sequence of increasing degrees of hydrogeochemical evolution is Group III → Group II → Group I. All groups of waters are saturated or supersaturated with respect to calcite.

(2) The Group I waters are further divided into two subtypes: Subgroup Ia and Subgroup Ib. Compared to the Subgroup Ib waters, the Subgroup Ia waters are characterized by higher pH (8.6~8.9) and F$^-$ contents, lower Eh values, and lower TDS, SO$_4^{2-}$ (113~124 mg/l), Na$^+$ and K$^+$ contents. The Subgroup Ia waters are thought to represent the most typical geothermal waters that upflowed restrictedly along fault fractures from a deep geothermal reservoir.

(3) Careful examination of hydrochemical data shows that the sulfate is a key aqueous constituent for understanding the origin and evolution of geothermal waters in the Bugok area. Based on the hydrochemical and sulfur isotope data and field observation, it is likely that there were at least two sources of sulfate in geothermal waters (additionally, atmospheric anthropogenic sulfur possibly involved in the Group II and III waters). These are: 1) hydrothermal pyrites (with δ^{34}S values of about 3.5‰, indicating the precipitation from a magmatic sulfur) occurring largely in pathways of geothermal waters; and 2) sedimentary pyrites in surrounding sedimen-

tary rocks (possibly with lower $\delta^{34}S$ values). The $\delta^{34}S$ values of sulfate in waters vary systematically with the water group: 12.9~13.9‰ for the Subgroup Ia waters; 2.3~8.1‰ for the Subgroup Ib waters; and 2.4 to 12.7‰ for the Group II and III waters. The higher $\delta^{34}S_{SO4}$ values of the Subgroup Ia waters indicate the derivation of sulfate mainly from oxidation of magmatic hydrothermal pyrites, whereas those of the Subgroup Ib waters indicate the large involvement of sedimentary pyrites. Examinations of water-rock interaction indicate that the Group I waters were evolved mainly through dissolution of Na-plagioclase, K-feldspar, mica and chlorite with the involvement of two genetic types of pyrite, whereas the Group II and III waters largely through dissolution of calcite and Na-plagioclase.

(4) The application of various alkali-ion geothermometers yields appreciably different reservoir temperatures (between the range of 100° to 214°C), indicating either the lack of equilibrium states between the ions considered (especially Mg) and hydrothermal minerals and/or the mixing with near-surface waters during the upflow. Combined with homogenization temperatures $(130° \pm 60°C)$ of fluid inclusions in hydrothermal calcites, the computation of fluid/mineral equilibria indicates the likely reservoir temperatures around 125°C. This estimated temperature can be used to evaluate the exploitability of geothermal energy in the Bugok area.

(5) The $\delta^{18}O$ and δD data of waters from the Bugok area indicate the derivation of all groups of waters from meteoric waters. The absence of recognizable oxygen isotope shift reflects relatively low temperatures of the deep geothermal reservoir. The O and H isotope data vary systematically with the water group: in a general increasing order, Subgroup Ia → Subgroup Ib → Group II → Group III. This indicates that each group water was derived from isotopically distinct meteoric water. A simple calculation, based on the altitude effect on the O isotope composition, suggests that the Group I waters have been recharged from the land surface which is about 400 m higher in elevation than the Group II waters. Tritium contents of the Subgroup Ia waters approach zero, whereas those of other group waters are relatively high (up to 8.9 TU) and increase in the same sequence observed for O and H isotope data. Combining with hydrochemical data, this indicates that typical geothermal waters (Subgroup Ia) were recharged during the pre-thermonuclear period (before 1953), whereas the Subgroup Ib waters include the mixing effect (during the uprising) with younger shallower waters which involved the sedimentary pyrite-derived waters.

(6) The following scenario is suggested for the genesis of geothermal waters in the Bugok area: the older age (at least 45 years old) meteoric waters (responsible for the Subgroup Ia waters) circulated deeply down to a geothermal reservoir (possibly, a granite body with some latent heat) and then were heated (up to 125°C); during the longer subsurface residence, larger amounts of ions including sulfates and alkali ions were enriched through water/rock interaction; during the upflowing along restricted channels, both the sedimentary pyrite-derived thermal groundwaters and cold near-surface waters mixed locally. Our proposed model may be also applied to understand the genetic environments of the other sulfate-rich geothermal waters in Korea.

ACKNOWLEDGEMENTS

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한반도 지열수의 지화학적 연구: 환경동위원소 및
수문화학적 특성 I. 부곡 지역

윤성택 · 고용권 · 김천수 · 소칠섭

요   약 : 1995~1996년중 부곡 지열수 지역에서 채수한 유형별 자연수를 대상으로 수문지구화학 및 환경동위원소 연구를 수행하였다. 연구 지역에는 물리화학적으로 뚜렷히 구분되는 세 유형의 자연수, 즉 (1) 군집 I (지열수 지역의 중심부에서 산출되고 최대 77℃의 용출 온도를 갖는 Na-SO$_4$ 유형), (2) 군집 II(외곽부에서 산출되며 다소 낮은 온도를 갖는 Na-HCO$_3$-SO$_4$ 유형) 및 (3) 군집 III (지표수나 천층 냉각 지하수로서 Ca-HCO$_3$ 유형)이 함께 산출된다. 군집 I은 Ia 및 Ib로 세분된다. 수문지구화학적 진화는 수-암 반응의 증가에 따라 군집 III → II → I의 순으로 진행되었다. 군집 II 및 III의 자연수는 비교적 낮은 수-암 반응, 특히 방해석 및 Na-사장석의 용해 반응에 의해 형성되었지만, 군집 I은 사장석, K-장석, 백운모, 녹리석, 황철석 등과의 높은 수-암 반응에 의해 형성되었다. 용존 황산염의 농도 및 황동위원소 조성은 지열수의 기원 및 진화를 해석하는데 중요한 정보가 된다. 용존 황산염은 퇴적 기원 황철석의 산화에 의해 생성되거나 (군집 Ib의 경우), 또는 열수의 상승 통로인 단열대에 존재하는 마그마 열수 기원 황철석의 용해에 의해 생성되었다 (군집 Ia의 경우). 지열 저장지의 온도 규명을 위한 알칼리 이온 지온계의 적용성은 화학조성을 변화시키는 요인들, 특히 마그네슘이 풍부한 지표수와의 혼합에 의해 제한된다. 그러나 다성분 광물/물 평형계에 대한 열역학적 계산 및 유체포유물 실험 결과, 심부 지열 저장지 (냉각중인 화성암체?)의 온도는 125℃에 이르는 것으로 판단된다. 환경동위원소 (산소-수소, 삼중수소) 연구에 의하면, 자연수는 모두 상이한 층진 특성을 갖는 강우로부터 기원하였다. 특히 군집 Ia의 물은 심부 지열 저장지까지 심부 순환한 오래된 (40년 이상) 강우로부터 기원하였으며 지표부 물과의 혼합 정도도 낮다. 본 논문에서는 황산염이 풍부한 국내 지열수의 성인 및 진화에 관한 모델을 제시한다.