

Geochemistry of Geothermal Waters in Korea: Environmental Isotope and Hydrochemical Characteristics II. Jungwon and Munbyeong Areas*

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ABSTRACT: From the Jungwon and Munbyeong areas which are among the famous producers of the carbonate-type groundwaters in Korea, various kinds of natural waters (deep groundwater, shallow groundwater and surface water) were collected between 1996 and 1997 and were studied for hydrogeochemical and environmental isotope ($\delta^{34}\text{S}_{\text{SO}_4}$, $\delta^{18}\text{O}$, δD and tritium) systematics. Two types of deep groundwaters (carbonate type and alkali type) occur together in the two areas, and each shows distinct hydrogeochemical and environmental isotope characteristics. The carbonate type waters show the hydrochemical feature of the 'calcium-(sodium)-bicarbonate-(sulfate) type', whereas the alkali type water of the 'sodium-bicarbonate type'. The former type waters are characterized by lower pH, higher Eh, and higher amounts of dissolved ions (especially, Ca^{2+} , Na^+ , Mg^{2+} , HCO_3^- and SO_4^{2-}). Two types of deep groundwaters are all saturated or supersaturated with respect to calcite. Two types of deep groundwaters were both derived from pre-thermonuclear (about more than 40 years old) meteoric waters (with lighter O and H isotope data than younger waters, i.e., shallow cold groundwaters and surface waters) which evolved through prolonged water-rock interaction. Based on the geologic setting, water chemistry, and environmental isotope data, however, each of these two different types of deep groundwaters represents distinct hydrologic and hydrogeochemical evolution at depths. The carbonate type groundwaters were formed through mixing with acidic waters that were derived from dissolution of pyrites in hydrothermal vein ores (for the Jungwon area water) or in anthracite coal beds (for the Munbyeong area water). If the deeply percolating meteoric waters did not meet pyrites during the circulation, only the alkali type groundwaters would form. This hydrologic and hydrogeochemical model may be successfully applied to the other carbonate type groundwaters in Korea.

INTRODUCTION

The study on deep thermal and/or warm groundwaters is still in the early stage in Korea. Therefore, the nature and subsurface evolution of deep groundwaters, such as the relative age (recharge time), water-rock interaction, and mutual interaction between diverse waters (deep groundwater, shallow groundwater and surface water) have not been well understood (Yum, 1993; Koh *et al.*, 1994; Yun *et al.*, 1998). As an effort of systematic study on groundwaters in Korea, various kinds of natural waters (deep warm groundwater, shallow cold groundwater and surface water) from the Jungwon and Munbyeong areas (Fig. 1) were collected and examined for environmental isotopes and hydrochemical characteristics. The Jungwon area is located about 100 km southeast of Seoul, near the

Choongju City. The Munbyeong area is located about 150 km southeast of Seoul. Recently, these two areas are both famous for springs of the 'carbonate type' groundwater, which characteristically show the severe

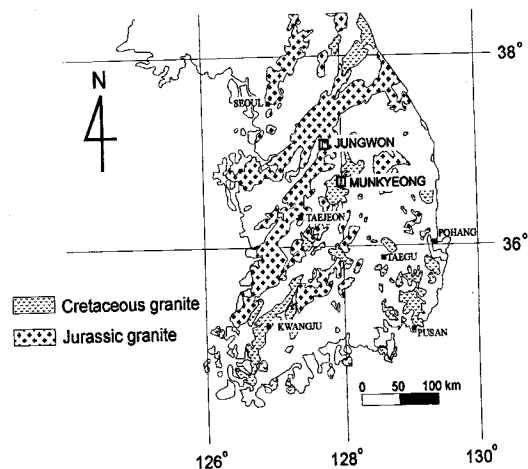


Fig. 1. Simplified geologic map of the Republic of Korea, showing locations of the Jungwon and Munbyeong areas.

* This paper was supported by NON DIRECTED RESEARCH FUND, Korea Research Foundation.

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outgassing of carbon dioxide and accompany the precipitation of brown-colored calcite. The 'carbonate type' waters show neutral to slightly acidic (<6.5) pH and high solute concentrations. It is interesting that although these two areas are different in geologic setting, the physicochemical features of the carbonate type groundwaters are quite similar. This fact probably reflect that the common process(es) of hydrogeochemical evolution control the formation and genesis of the 'carbonate type' groundwaters.

In this study, comparisons between the relatively mineralized groundwater and the dilute groundwater were undertaken in order to understand the subsurface hydrogeochemical processes of groundwater. The hydrogeologic processes such as water-rock interaction and mixing of different waters were also elucidated as major controls of groundwater chemistry. The main purpose of this study is to identify the origin and hydrogeochemical evolution of the 'carbonate type' groundwaters.

GEOLOGIC SETTING

The Jungwon area

Geology of the Jungwon area consists mainly of Precambrian gneisses (of the Kyonggi Gneiss Complex) and Mesozoic granitoids (biotite granite, porphyritic granite and some dykes), as shown in Fig. 2. The NW-trending Angsung fault separates the geology of the area into two divisions: granite largely in the northern part, and gneiss in the southern part. The Precambrian gneisses comprise banded biotite gneiss, schistose gneiss and granitic gneiss, and are intruded by biotite granite and several acidic to basic dykes. According to Kim (1985), the average mineralogical composition of the biotite granite is quartz (27.4%), K-feldspar (26.3%), plagioclase (38.0%), biotite (6.2%) and muscovite (1.6%) with rare amounts of apatite, zircon and opaque minerals.

Granitic gneiss hosts the Daehwa and Donsan hydrothermal W-Mo deposits (Fig. 2) which were famous W-Mo producers in Korea but are now closed. These W-Mo deposits are composed of numerous, NW-trending subparallel quartz ± calcite veins (usually about 50 cm thick) which fill the fractures of Precambrian granitic gneiss and Late Cretaceous (105 ± 5 Ma; Kim, 1985) biotite granite. A K-Ar age (88 ± 2 Ma) of vein muscovite from the Daehwa W-

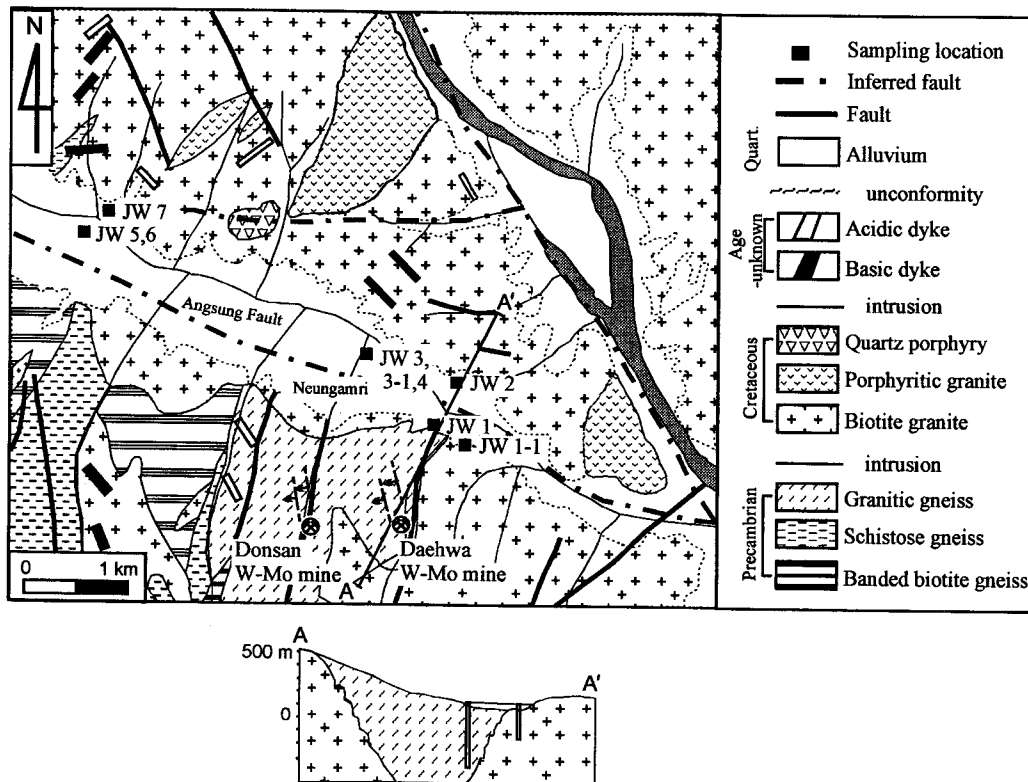


Fig. 2. Geologic map and cross section of the Jungwon area. Sampling locations, drainage pattern, and fault system are also shown.

Mo mine indicated that W-Mo mineralization occurred during Late Cretaceous (So *et al.*, 1983). Ore minerals of the Daehwa and Donsan mines are quite similar and comprise less than 10% of the total vein volume. The ore mineralogy consists mainly of molybdenite (MoS_2), wolframite ($(\text{Fe}, \text{Mn})\text{WO}_4$), pyrite (FeS_2), chalcopyrite (CuFeS_2), sphalerite ($(\text{Zn}, \text{Fe})\text{S}$), marcasite (FeS_2) and bismuthinite (Bi_2S_3) with minor amounts of galena (PbS) and pyrrhotite (Fe_{1-x}S). Gangue minerals are mainly quartz with subordinate muscovite, fluorite (CaF_2), calcite, siderite (FeCO_3) and ankerite ($\text{CaFe}(\text{CO}_3)_2$).

Geologic structures of the Jungwon area consist largely of NE- and NW-trending faults and associated fractures (Fig. 2), and largely control not only the surface drainage system but also possibly the groundwater flow pattern (Yum, 1993). Deep groundwater wells of the Jungwon area are located at crossing points between NW-trending faults (including the Angsung Fault) and NE-trending faults (Fig. 2). It is also noteworthy that the 'carbonate type' groundwater wells in the Neungamri area are commonly located near the Daehwa and Donsan W-Mo mines.

The Munkyeong area

Geology of the Munkyeong area consists mainly of the Ordovician limestone formation, Jurassic(?) sandstone formation and Cretaceous granitoids (Kim *et al.*, 1967; Fig. 3). The Ordovician limestone-rich formation, belonging to the Pugong-ri Formation of the Chosun Supergroup, is composed of light to dark gray-colored bedded limestone (lo-

wer part) and white to gray-colored massive limestone (upper part). The age-unknown Sangnaeri Formation occurs locally at southwestern part of the study area, and overlies the Pugong-ri Formation. It consists of black slate, chlorite schist, phyllite and metasandstone, and is intruded by the Baekhwa-ri hornblendite. The lowermost part of the Jurassic Dansan Formation (of the Daedong Supergroup) occurs at southeastern part of the study area, and is in the fault contact with the Pugong-ri Formation. It is composed mainly of pebble-bearing, coarse- to medium-grained sandstone. Fine-grained sandstone and shale with black colors occur as intercalations in sandstone, and contain several coal beds. The Cretaceous granitoids, consisting of a batholith of biotite granite and dykes of quartz porphyry and felsite, occur widely at northern part of the study area and intrude all of the rocks described above. The biotite granite contains quartz, feldspars, biotite and rare zircon.

The NE-trending and northwardly dipping, sub-parallel reverse or thrust faults (pre-Cretaceous) represent a major geologic structure in the Munkyeong area (Kim, 1986; Fig. 3), and probably control the surface drainage system and regional groundwater flow. Within the Munkyeong area occur typically several anthracite coal mines including the abandoned Bongmyong mine (Fig. 3). They occur in the Dansan Formation as several repeated beds which contain rare amounts of fine-grained pyrites. A 'carbonate type' thermal groundwater well (location MK-1 in Fig. 3) is situated about 1.5 km away from the Bongmyong mine.

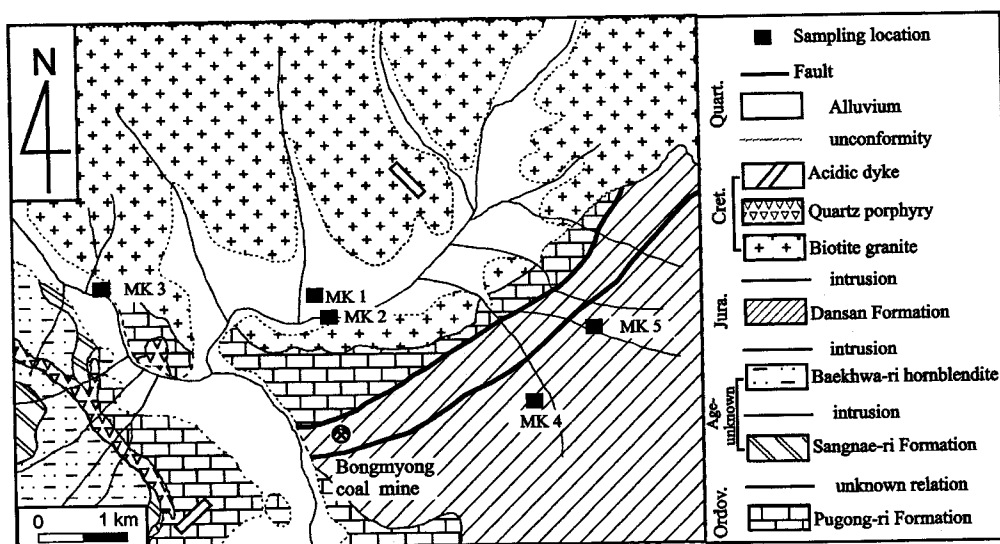


Fig. 3. Geologic map of the Munkyeong area. Sampling locations, drainage pattern, and fault system are also shown.

Table 1. Physicochemical data of various kinds of waters from the Jungwon and Munkyeong areas

Area	Sample no.	Water type ¹⁾	Sampling date	Drilling depth (m)	Temp.	pH	Eh (mV)	EC ($\mu\text{S}/\text{cm}^2$) ²⁾	TDS ³⁾	Dissolved constituents (mg/l)										
										Na	K	Mg	Ca	SiO ₂	Cl	SO ₄	HCO ₃	CO ₃	NO ₃	F
Jungwon	JW 1	H; carb.	May-96	558	29.4	6.3	34.0	3427	3306	300.0	18.0	44.0	464.0	102.7	22.5	25.1	2327	n.d.	tr.	2.2
			Jul-97		32.8	6.3	38.0	3525	3154	310.0	17.3	38.3	415.0	104.0	19.9	23.6	2223	n.d.	0.7	2.2
			Aug-97		30.6	6.4	40.4	2580	3071	314.8	15.9	46.5	366.7	100.2	23.7	19.5	2181	n.d.	0.1	2.2
	JW 1-1	C	Jul-97	60	23.5	7.3	-31.4	293	284	38.7	2.0	4.0	24.3	26.0	23.4	18.9	144	n.d.	n.d.	3.1
			Aug-97		24.9	7.6	-38.2	268	301	48.0	1.8	3.6	23.5	27.6	22.3	11.3	161	n.d.	0.2	2.2
	JW 2	H; carb.	May-96	250	23.7	6.1	58.3	2136	2008	120.0	2.9	44.0	307.0	90.0	11.9	6.0	1423	n.d.	tr.	3.1
	JW 3	H; carb.	May-96	200	24.1	6.1	54.5	876	1208	84.0	2.4	21.0	176.0	94.1	12.2	8.8	805	n.d.	0.9	3.4
			Jul-97		21.9	6.0	47.9	1333	1231	97.6	2.8	24.1	168.4	90.1	13.7	10.4	821	n.d.	n.d.	3.1
	JW 3-1	C	Jul-97	25	17.4	6.9	-6.2	512	221	13.2	3.1	4.0	31.2	23.1	8.7	16.6	118	n.d.	2.7	0.4
	JW 4	C	May-96	60	14.7	6.8	10.6	246	310	30.0	1.2	2.9	46.0	25.7	9.2	16.0	175	n.d.	3.2	0.6
JW 5			Jul-97		17.0	6.4	23.9	182	215	13.2	3.1	4.0	30.7	15.6	8.3	16.0	120	n.d.	3.2	0.4
			May-96	60	14.7	7.2	-10.8	127	155	17.0	1.0	1.6	16.0	17.3	6.1	13.2	75	n.d.	6.2	1.6
			Jul-97		16.1	7.0	-11.3	62	176	14.9	1.6	2.4	21.4	18.0	6.2	12.5	93	n.d.	5.1	1.0
			Aug-97		16.0	7.1	-9.6	55	167	12.4	1.1	2.3	19.0	23.0	7.4	5.3	94	n.d.	1.1	1.2
			May-96	400	24.8	9.4	-134.0	176	219	64.0	n.d.	tr.	2.4	17.3	7.2	3.4	107	5.0	tr.	13.0
Munkyeong	JW 6	H; alk.	May-96		25.4	9.2	-134.8	309	239	68.2	1.2	n.d.	2.1	16.3	5.8	4.7	111	15.0	0.1	14.1
			Jul-97		25.8	9.1	-130.8	289	232	65.9	0.5	n.d.	2.0	16.3	7.4	5.3	105	15.0	1.1	13.6
	JW 7	C	May-96	25	12.6	6.9	0.8	114	134	8.2	1.2	2.3	17.0	17.5	6.7	13.5	58	n.d.	9.1	0.8
			Jul-97		13.8	6.7	4.0	125	141	8.5	1.6	3.3	19.1	16.7	6.5	11.0	65	n.d.	8.7	0.4
	MK 1	H; carb.	Aug-97	200	30.2	6.4	47.8	2260	2059	86.6	3.2	41.8	364.4	24.8	10.9	73.3	1452	n.d.	0.9	1.4
MK 2	S	Aug-97		26.5	8.2	-78.9	209	140	5.1	1.5	4.2	24.3	11.3	6.1	43.4	30	n.d.	13.8	0.1	
MK 3	H; alk.	Aug-97	900	30.4	9.1	-125.0	135	124	23.4	0.2	n.d.	8.6	19.5	5.3	5.3	40	9.0	0.7	4.2	
MK 4	C	Aug-97	15	23.3	6.1	53.0	23	25	2.1	0.2	0.4	2.3	5.1	4.2	3.2	7	n.d.	0.5	0.1	
MK 5	S	Aug-97		22.0	4.7	135.0	1056	975	3.4	2.2	44.4	187.4	13.7	2.1	715.8	5	n.d.	0.5	0.5	

¹⁾ H; deep warm groundwater (alk.; alkali type; carb.; carbonate type). C; shallow cold groundwater. S; surface water. ²⁾ EC; electrical conductivity. ³⁾ TDS; total dissolved solid. nd.; not detected; tr.; trace.

SAMPLING AND ANALYTICAL PROCEDURE

Sampling of various kinds of natural waters (deep warm groundwater, shallow cold groundwater and surface water) from total 14 locations (9 locations from the Jungwon area, and 5 locations from the Munkyeong area; Figs. 2 and 3) was carried out between May 1996 and August 1997 (Table 1). Sampling sites of cold groundwater were very adjacent to those of warm groundwater.

Physical properties of groundwater, such as pH, oxidation-reduction potential (Eh), temperature and electric conductivity (EC), were measured *in situ* using portable meters (Model Orion 290A and Orion 130) which were corrected by standard solutions. Samples were filtered through 0.45 μm pore-size nitrate membrane filter, and were carried to the laboratories in the high-density polyethylene bottles. Samples for cation analysis were acidified by adding a few drops of conc. HNO_3 solution. Alkalinity of waters was measured *in situ* by using standard titration method immediately after sampling.

Major dissolved ionic constituents in waters were analyzed at the Center for Mineral Resources Research (CMR) in Korea University by using the inductively coupled plasma-atomic emission spectrometry (ICP-AES; Model Perkin Elmer Optima 3000) for cations, and ion chromatography (IC; Model Dionex 120) for anions.

The $\delta^{18}\text{O}$ and δD values of waters were analyzed by the gas/isotope ratio mass spectrometry (Model Finnigan MAT 252) at CMR. For the measurement of δD values, we used the H/Device (Finnigan Co.) which is a new apparatus for an automatic reduction of H_2O to H_2 by using Cr metal. The $\delta^{34}\text{S}$ values of dissolved SO_4^{2-} in waters were measured by the gas/isotope ratio mass spectrometry (Model Finnigan MAT 230C at the Institute of Mineral Deposits of China at Beijing). For the measurement, the dissolved SO_4^{2-} was precipitated as BaSO_4 by adding concentrated BaCl_2 solution. The precipitated BaSO_4 samples were purified using appropriate chemical treatments, and were changed to SO_2 gas by the V_2O_5 oxidation method. The stable isotopic data are reported in δ values (in per mil) relative to the Vienna SMOW standard for oxygen and hydrogen, and the Canyon Diablo Troilite standard for sulfur. Standard errors of each analysis are $\pm 0.1\%$ for O and S, and $\pm 2\%$ for H. The tritium contents (unit=T.U.) of waters were measured at Korean Atomic Energy Research Institute (KAERI) by a liquid scintillation counter (Model Packard 3255) after the electrolytic enrichment process.

RESULTS AND DISCUSSIONS

Chemical composition

pH and Eh

Measured physicochemical data of water samples from the Jungwon and Munkyeong areas are summarized in Table 1. Drilling depths of deep warm groundwaters range from about 200 to 900 m, whereas those of shallow cold groundwaters are 15 to 60 m. Therefore, the cold groundwater samples mostly represent the shallowly circulated waters which are similar to the local surface waters. Each groundwater sample does not show any recognizable physicochemical changes with their sampling time.

Primarily based on pH conditions, deep warm groundwaters from the two areas are distinctly divided into two main groups: the carbonate type waters with pH values between 6.0 and 6.4 (e.g., JW 1, JW 2, JW 3 and MK 1); and the alkali type waters with high pH values between 9.1 and 9.4 (e.g., JW 6 and MK 3). These two type waters represent different hydrologic and hydrogeochemical processes at depths. Each type of deep groundwater from the two areas shows very similar and narrow pH values: for the carbonate type waters, 6.0 to 6.4 from the Jungwon area, and 6.4 from the Munkyeong area; and for the alkali type waters, 9.1 to 9.4 from the Jungwon area, and 9.1 from the Munkyeong area. This fact indicates that each water type from the two areas was evolved through similar hydrogeochemical processes, although the geologic setting is different. The pH values of shallow cold groundwaters and surface waters range from 6.1 to 7.6 and from 4.7 to 8.2, respectively. Exceptionally, a relatively low pH value (4.7) for a surface water from the Munkyeong area (sample MK 5) resulted from oxidation of abandoned, pyrite-bearing, coal waste dumps at upstream sites.

The oxidation-reduction potential (Eh) of groundwaters also varies systematically with the water type: in a general decreasing order, carbonate type deep groundwater (34.0 to 58.3 mV) > shallow cold groundwater (-38.2 to 53.0 mV) > alkali type deep groundwater (-134.8 to -125.0 mV). Therefore, deep groundwaters also can be divided into two distinct groups according to the Eh values. It is noteworthy that the carbonate type groundwaters show higher degrees of oxidation state; but the alkali type groundwater show remarkably lower reducing state.

Fig. 4 shows the pH-Eh relationships of all kinds of water samples. The carbonate type deep groundwaters have lowest pH and highest Eh values, whereas the alkali type deep groundwaters have highest pH and

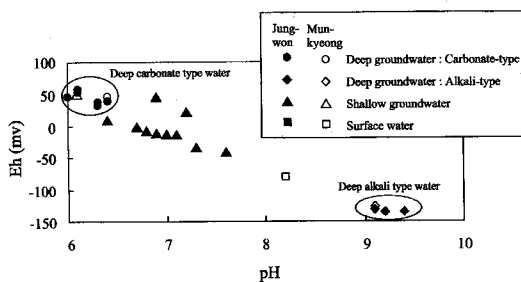


Fig. 4. Eh-pH relationship of various kinds of waters from the Jungwon and Munkyeong areas.

lowest Eh values. Cold groundwaters and surface waters are plotted between these two type waters. As indicated by the vicinity of W-Mo or coal mines (Figs. 2 and 3; see also "Geologic Setting"), it is likely for the observed pH-Eh values of the carbonate type waters to reflect the effect of mixing of acid-sulfate mine waters with general alkali type waters. Oxidation of sulfide minerals (mainly pyrites) either in W-Mo veins of the Daehwa and Donsan mines or in coal beds of the Bongmyong mine possibly formed the low pH and high Eh mine waters which contain significant amounts of dissolved solids (Baas Becking *et al.*, 1960), as discussed below. This idea is supported by the fact that typical alkali type groundwaters (samples JW 6 and MK 3) occur at distal sites from the mines (Figs. 2 and 3).

Distribution of dissolved ions

Chemical composition and TDS (and EC) data of water samples are also shown in Table 1. The TDS values of deep (200 to 900 m from the land surface) warm groundwaters range widely from 124 to 3,306 mg/l. The carbonate type waters show higher degrees of mineralization (TDS=1,208~3,306 mg/l) than the alkali type waters (TDS=124~239 mg/l), although these two type waters were pumped out from wells with similar drilling depths. This also indicates that these two type waters have undergone a different geochemical evolution along flow paths during the circulation. As suggested above, the carbonate type waters are closely related to the local preferential dissolution of sulfides (mainly pyrite) in W-Mo or coal mines. Shallow (15 to 60 m deep) cold groundwaters have remarkably lower TDS values (25 to 301 mg/l) than nearby deep groundwaters, indicating that the circulating depth and/or water/rock reaction time largely controlled the chemistry of groundwaters in crystalline bedrocks. A low pH (4.7) surface water from the Munkyeong area (sample MK 5) has an abnormally high TDS value (975 mg/l), due to the influx of TDS-rich mine waters.

Typically, all of the carbonate type deep groundwaters have high alkalinity (HCO_3^- contents=805~2,327 mg/l) and show similar chemical features (Table 1). Owing to the very high alkalinity, brown-colored (due to the coprecipitating Fe oxide) calcites are precipitated when the waters are pumped out.

General decreasing orders of absolute abundances of major ions in deep warm groundwaters are as follows (Table 1): for the carbonate type water, $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{SO}_4^{2-} \approx \text{Cl}^-$; and for the alkali type water, $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$ and $(\text{HCO}_3^- + \text{CO}_3^{2-}) > \text{Cl}^- \geq \text{SO}_4^{2-}$. It is obvious that two types of deep groundwaters show different chemical characteristics: the 'calcium (-sodium)-bicarbonate (-sulfate) type' for the carbonate type water; and 'sodium-bicarbonate type' for the alkali type water. Based on these observed hydrochemical characteristics, along with major mineral constituents in surrounding rocks, it is suggested that deep warm groundwaters of the Jungwon and Munkyeong areas were evolved largely through preferential dissolution of calcite and Na-rich plagioclase with lesser degrees of dissolution of mica (or K-feldspar) and Cl-bearing hydroxyl silicates such as biotite and amphibole (Hem, 1992; Yu *et al.*, 1994; Hounslow, 1995; Park *et al.*, 1997). Relatively high Mg^{2+} contents (21.0 to 46.5 mg/l; Table 1) in deep carbonate type groundwaters also indicate the large degrees of dissolution of biotite and chlorite in surrounding rocks.

According to the classification scheme of geothermal waters proposed by Giggenbach (1991), the waters

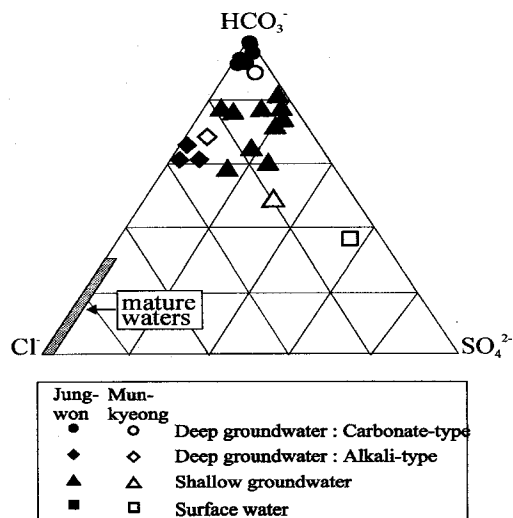


Fig. 5. Triangular plots of molar proportions of Cl^- , HCO_3^- and SO_4^{2-} in various kinds of waters from the Jungwon and Munkyeong areas. The ranges of typical 'mature' and 'peripheral' waters from Giggenbach (1991).

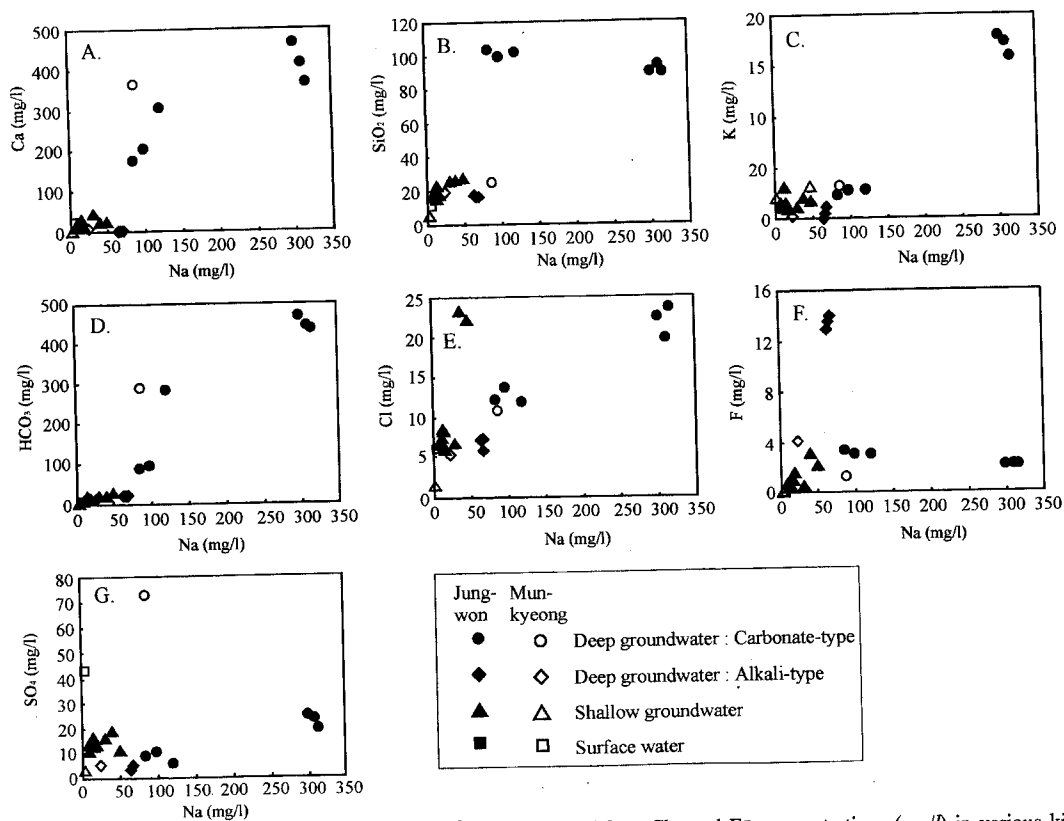


Fig. 6. Plots of Na⁺ concentration (mg/l) versus Ca²⁺, SiO₂, K⁺, HCO₃⁻, Cl⁻ and F⁻ concentrations (mg/l) in various kinds of waters from the Jungwon and Munkyeong areas.

of the Jungwon and Munkyeong areas belong to the 'peripheral' waters (Fig. 5). Fig. 6 shows the correlations of the Na⁺ concentration against concentrations of Ca²⁺, SiO₂, K⁺, HCO₃⁻, Cl⁻, F⁻ and SO₄²⁻. The contents of Ca²⁺, SiO₂, K⁺, and HCO₃⁻ show nearly positive correlations with increasing Na⁺, indicating progressively larger degrees of dissolution of calcite and feldspars.

Shallow cold groundwaters have low TDS contents and commonly show a chemical feature of the 'sodium (-calcium)-bicarbonate' type with general abundances of Na⁺ ≅ Ca²⁺ > Mg²⁺ > K⁺ and HCO₃⁻ ≫ SO₄²⁻ ≅ Cl⁻ (Table 1). Among these cold groundwaters, the water with relatively higher TDS content (sample JW 1-1) tends to have a behavior of Na⁺ > Ca²⁺, possibly indicating the aggressive dissolution of plagioclase in addition to calcite in surrounding rocks. Surface waters from the Munkyeong area are relatively enriched in Ca²⁺, Mg²⁺ and SO₄²⁻, which indicates the effect of mine waters.

The deep (400 m below from surface) alkali type groundwater from the Jungwon area (sample JW 6) characteristically contains high amounts of F⁻ (13.0~14.1 mg/l; Table 1). Most natural fresh waters contain

less than 1 mg/l F⁻ (Hem, 1992), but some alkali waters may contain more than 1 mg/l F⁻ due to its desorption from kaolinite (Hounslow, Back, 1985). This F⁻ desorption is greatest at pH conditions of >7.5 and <4, and lowest around 6 (Hounslow, 1995). However, it is unlikely at Jungwon that the F⁻ was derived by desorption from kaolinite, because we cannot successfully explain quite low F⁻ contents (0.4 to 1.6 mg/l) in nearby shallow cold groundwaters (samples JW 5 and JW 7). We consider that the observed high F⁻ (and Cl⁻) contents possibly resulted from the dissolution of biotite and apatite which contain F⁻ at OH⁻ sites (Nordstrom *et al.*, 1989). According to Tsusue *et al.* (1981), apatite and biotite from Korean Cretaceous granites typically contain appreciable amounts of F⁻ and Cl⁻. On the other hand, the lower F⁻ contents (<3.4 mg/l; Table 1) in the carbonate type deep groundwaters may be explained by the adsorption onto kaolinite at pH conditions near 6.

In summary, the carbonate type groundwaters are characterized by following physicochemical features: active degassing of CO₂ from dissolved carbon species, and subsequent precipitation of deep brown-

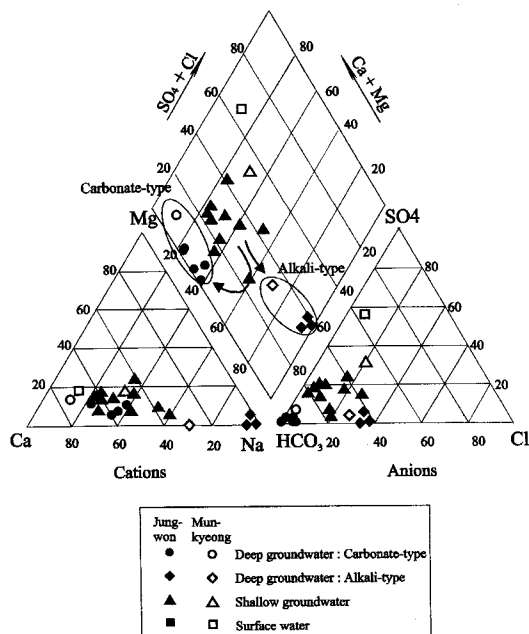


Fig. 7. Piper's diagram showing chemical compositions of various kinds of waters from the Jungwon and Munkyeong areas. Arrows indicate probable evolution paths of waters.

colored calcite; low pH and high Eh values; and relative enrichments of TDS, HCO₃⁻, Ca²⁺, SO₄²⁻, K⁺ and Mg²⁺. On the other hand, the alkali type groundwaters are characterized by the high pH and low Eh; relative enrichments of F⁻ and Na⁺; and relative depletion in TDS, Ca²⁺, Mg²⁺ and SO₄²⁻.

Fig. 7 shows the plots of chemical compositions of waters on the Piper's diagram. Arrows indicate the probable hydrogeochemical evolution paths which can be summarized as follows: TDS-poor, Ca²⁺-HCO₃⁻ type (for shallow cold groundwaters, mainly through the congruent dissolution of calcite) → Na⁺-HCO₃⁻ type (for the alkali type deep groundwaters, mainly through the successive dissolution in the order of plagioclase and F⁻- and Cl⁻-bearing biotite) → TDS-rich, Ca²⁺-HCO₃⁻ type (for the carbonate type deep groundwaters, mainly through mixing of acid mine waters formed by oxidation of pyrite, which subsequently enhanced the dissolution of carbonates and silicate minerals including Mg-bearing chlorite and biotite).

Calculation of the saturation index (S.I.) of calcite in waters (Fig. 8), using the computer program SOLVEQ (Reed, 1982), shows that deep warm groundwaters from the Jungwon and Munkyeong areas are nearly saturated or supersaturated with respect to calcite, whereas shallow cold groundwaters are yet undersaturated and are progressively evolved toward the saturation

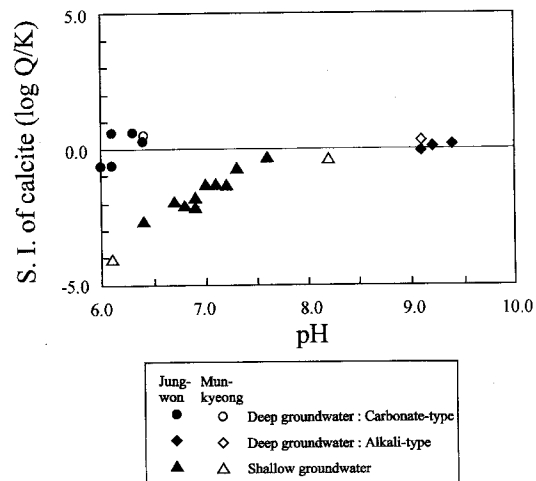


Fig. 8. Calculations of saturation indices (S. I.) of calcite in various kinds of waters from the Jungwon and Munkyeong areas, using the computer code SOLVEQ (Reed, 1982).

state with increasing pH (due to the increasing water/rock interaction).

Environmental isotopes

In order to elucidate the origin and recharge time of groundwaters, nine sulfur isotopes of dissolved sulfates, nineteen oxygen and hydrogen isotopes of waters, and seventeen tritium isotopes of waters were determined (Table 2).

Sulfur isotope of sulfate

The $\delta^{34}\text{S}_{\text{SO}_4}$ (relative to CDT) values of all kinds of waters range widely from 3.6 to 27.6‰. Within this wide range, each type water has a unique and uniform value: for the carbonate type deep groundwater, 24.2 to 27.6‰ from the Jungwon area, and 6.1‰ from the Munkyeong area; for shallow cold groundwater from the Jungwon area, 3.6 to 7.6‰; and for surface water from the Munkyeong area, 5.0‰ (however, the alkali type groundwaters could not be measured due to the lack of precipitated BaSO₄). It is interesting that the values of the carbonate type deep groundwater are much higher (by >16‰) than those of other type waters. This probably reflects different source(s) of sulfur in waters.

According to the pilot study of Mizutani *et al.* (1980), the $\delta^{34}\text{S}_{\text{SO}_4}$ values of the Han River water in Korea largely reflect the geologic setting of the drainage system. In general, the sulfate-sulfurs derived from sedimentary sulfate minerals have positive $\delta^{34}\text{S}$

Table 2. Sulfur, oxygen and hydrogen isotope data, and tritium contents of various kinds of waters from the Jungwon and Munkyeong areas

Area	Sample no.	Water type ¹⁾	Sampling date	$\delta^{34}\text{S}_{\text{SO}_4}$ (‰)	$\delta^{18}\text{O}$ (‰)	δD (‰)	Tritium (T.U.)
Jungwon	JW 1	H; carb.	May-96	N.D.	-10.4	-72.3	0.0
			Jul-97	27.6	-10.4	-70.9	0.8
			Aug-97	N.D.	N.D.	N.D.	0.8
	JW 1-1	C	Jul-97	3.7	-8.2	-58.0	N.D.
	JW 2	H; carb.	May-96	N.D.	-9.8	-69.0	3.1
	JW 3	H; carb.	May-96	N.D.	-9.4	-66.7	0.3
			Jul-97	24.2	-9.7	-68.8	0.5
	JW 3-1	C	Jul-97	6.6	-8.0	-55.7	6.5
	JW 4	C	May-96	N.D.	-8.0	-58.7	6.8
			Jul-97	7.6	-7.9	-54.9	N.D.
	JW 5	C	May-96	N.D.	-8.6	-60.7	9.2
			Jul-97	3.6	-8.1	-57.2	N.D.
			Aug-97	N.D.	N.D.	N.D.	7.2
	JW 6	H; alk.	May-96	N.D.	-9.8	-71.6	2.0
			Jul-97	N.D.	-9.6	-68.8	1.0
			Aug-97	N.D.	N.D.	N.D.	1.1
	JW 7	C	May-96	N.D.	-8.6	-62.0	9.0
Jul-97			4.8	-8.0	-55.9	N.D.	
Munkyeong	MK 1	H; carb.	Aug-97	6.1	-9.9	-70.5	0.3
	MK 3	H; alk.	Aug-97	N.D.	-9.4	-66.6	0.7
	MK 4	C	Aug-97	N.D.	-10.3	-75.5	7.3
	MK 5	S	Aug-97	5.0	-9.7	-68.3	N.D.

¹⁾ H; deep warm groundwater (alk.; alkali type, carb.; carbonate type), C; shallow cold groundwater, S; surface water. N.D.; not determined.

values, whereas those from sedimentary sulfide minerals are characterized by negative $\delta^{34}\text{S}$ values. The sulfate-sulfurs derived from sulfides in igneous rocks most often have $\delta^{34}\text{S}$ values near 0‰. Based on the geologic settings of the Jungwon and Munkyeong areas, which are characterized by the paucity of sulfate-bearing sedimentary rocks, we consider that the measured $\delta^{34}\text{S}_{\text{SO}_4}$ values (3.6~7.6‰) for shallow (<60 m deep) cold groundwaters and surface waters may reflect the major contribution of igneous and/or hydrothermal sulfides in surrounding rocks. However, we cannot rule out the contribution of anthropogenically derived atmospheric sulfur.

The high $\delta^{34}\text{S}_{\text{SO}_4}$ values (24.2 to 27.6‰) of the carbonate type deep groundwaters from the Jungwon area probably indicate the derivation of sulfate from kinetic oxidation of ore sulfides ($\delta^{34}\text{S}$ value=2.4 to 4.4‰; So *et al.*, 1983, Shelton *et al.*, 1987) in W-Mo veins. According to Harrison and Thode (1957), the kinetic-controlled chemical oxidation of reduced sulfur (and sulfides) at temperatures between 18° and 50°C forms the SO_4^{2-} enriched in ^{34}S by 22‰ (which is quite lower than the equilibrium fractionation of about 70‰; Ohmoto and Rye, 1979). Furthermore, our $\delta^{34}\text{S}_{\text{SO}_4}$ values likely exclude the origin

through the bacterial kinetic fractionation during sulfide oxidation because this process rather results in ^{34}S -depleted SO_4^{2-} (Pearson and Rightmire, 1980).

Although we could not obtain the $\delta^{34}\text{S}$ value of pyrite in coal beds from the Munkyeong area, relatively low $\delta^{34}\text{S}_{\text{SO}_4}$ values (5.0 and 6.1‰) of the carbonate type groundwater and surface water may indicate the mixing of sulfate from isotopically lighter sedimentary pyrites. Nevertheless, the $\delta^{34}\text{S}_{\text{SO}_4}$ values of the carbonate type groundwaters from the Jungwon and Munkyeong areas support the involvement of acid mine waters in genesis, as was also indicated by hydrochemical data.

Oxygen and hydrogen isotopes of water

The whole ranges of $\delta^{18}\text{O}$ and δD values (relative to SMOW) of all kinds of waters from the Jungwon and Munkyeong areas are -7.9 to -10.4‰ and -54.9 to -72.3‰, respectively (Table 2). It is noteworthy that within these wide ranges each type water has unique isotope values forming distinct clusters in a $\delta^{18}\text{O}$ versus δD diagram (Fig. 9). The values are as follows: for the carbonate type deep groundwater, $\delta^{18}\text{O}$ =-9.4 to -10.4‰, and δD =-66.7 to -72.3‰ from the Jungwon area, and $\delta^{18}\text{O}$ =-9.9‰ and δD =-70.5‰ from the Munkyeong

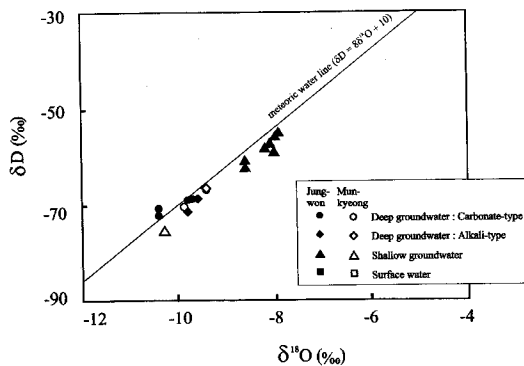


Fig. 9. $\delta^{18}\text{O}$ versus δD diagram of various kinds of waters from the Jungwon and Munkyeong areas.

area; for the alkali type deep groundwater, $\delta^{18}\text{O}=-9.6$ and -9.8‰ and $\delta\text{D}=-68.8$ and -71.6‰ from the Jungwon area, and $\delta^{18}\text{O}=-9.4\text{‰}$ and $\delta\text{D}=-66.6\text{‰}$ from the Munkyeong area; for shallow cold groundwater, $\delta^{18}\text{O}=-7.9$ to -8.6‰ , and $\delta\text{D}=-54.9$ to -62.0‰ from the Jungwon area, and $\delta^{18}\text{O}=-10.3\text{‰}$ and $\delta\text{D}=-75.5\text{‰}$ from the Munkyeong area; and for surface water from the Munkyeong area, $\delta^{18}\text{O}=-9.7\text{‰}$ and $\delta\text{D}=-68.3\text{‰}$.

The $\delta^{18}\text{O}$ versus δD diagram (Fig. 9) indicates that all kinds of waters from the Jungwon and Mun-

kyeong areas were derived from local meteoric waters. All data also plot along or near the worldwide meteoric water line, with no recognizable oxygen-shift. Some of the geothermal waters from modern geothermal systems (e.g., Lanzarote, Wairakei/Broadlands, the Geysers, Steamboat Springs, Salton Sea, Yellowstone Park) show considerable oxygen-shift from meteoric water composition (by up to 18‰; Truesdell and Hulston, 1980). On the other hand, the absence of recognizable oxygen isotope shift for deep warm groundwaters from the Jungwon and Munkyeong areas likely results from high water/rock ratio and/or relatively low reservoir temperature (Taylor, 1974).

It is remarkable that shallow cold groundwaters from the Jungwon area have heavier $\delta^{18}\text{O}$ and δD values (by about 2‰ and 14‰, respectively) than nearby deep warm groundwaters. Deep groundwaters, regardless of their types, have similar O and H isotope compositions. These results indicate the distinct hydrologic evolution between deep warm groundwaters and shallow cold groundwaters. In other words, each of the deep groundwaters and shallow cold groundwaters represents the meteoric water recharged during different times and/or through distinct circulation flow paths (with different residence time).

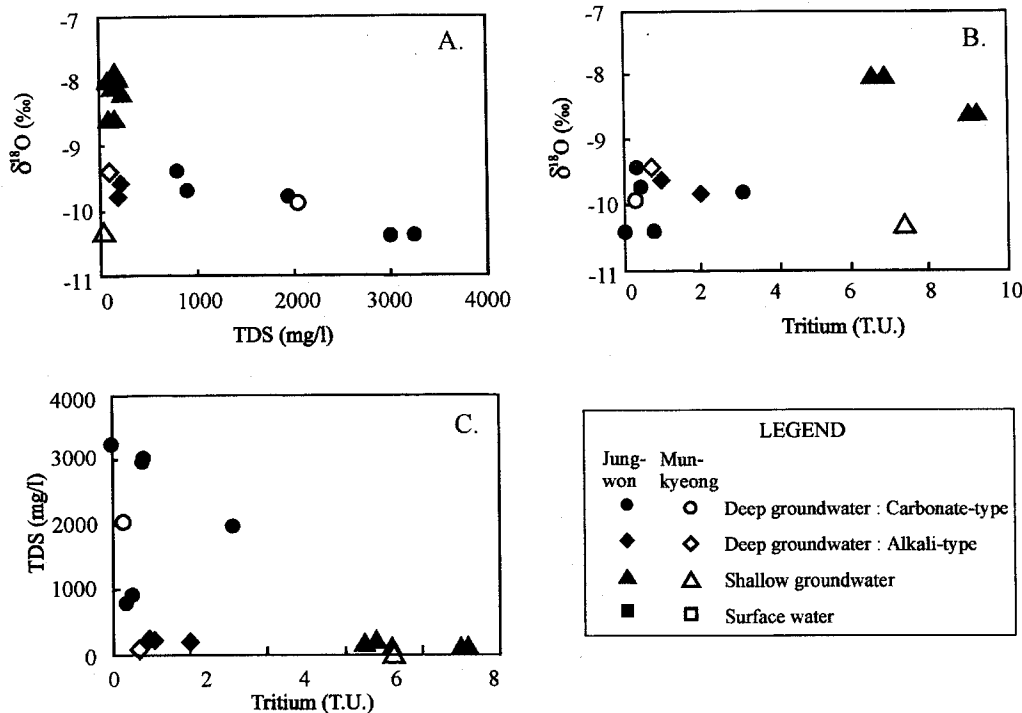


Fig. 10. Relationships among $\delta^{18}\text{O}$ value (‰), TDS content (mg/l), and tritium content (T.U.) in various kinds of waters from the Jungwon and Munkyeong areas.

Tritium content of water

Different kinds of waters have distinct tritium contents as follows (Table 2): for the carbonate type deep groundwater, 0.0 to 3.1 T.U. (0.0 to 3.1 T.U. from the Jungwon area, and 0.3 T.U. from the Munkyeong area); for the alkali type deep groundwater, 0.7 to 2.0 T.U. (1.0 and 2.0 T.U. from the Jungwon area, and 0.7 T.U. from the Munkyeong area); and for shallow cold groundwater, 6.5 to 9.2 T.U. (6.5 to 9.2 T.U. from the Jungwon area, and 7.3 T.U. from the Munkyeong area). Deep warm groundwaters have much lower tritium contents than shallow cold groundwaters, indicating the older recharge age of deep groundwaters. The older recharge age possibly indicates the longer circulation flow path.

Fig. 10 shows the relationships among the tritium, $\delta^{18}O$ and TDS data for various kinds of waters. The carbonate type deep groundwaters with lower $\delta^{18}O$ but higher TDS values have the lowest tritium contents. This relationship clearly indicates that compared with cold groundwaters, warm groundwaters represent the older meteoric waters (with lower $\delta^{18}O$ values) which had the longer residence time at depths. During the longer residence, larger amounts of ions (and TDS) were dissolved through water/rock interaction. The high TDS values for the carbonate type deep groundwaters, however, were more controlled by lower pH conditions which resulted in larger degrees of dissolution of silicates and carbonates. This is also suggested by lower TDS values for the alkali type deep groundwaters.

The accurate estimation of groundwater age is very difficult, as most of the samples obtained from wells may represent the waters mixed with younger surficial waters during the pumping-up. Table 3 shows the general relationship between groundwater age and tritium concentrations (Hendry, 1988). Based on this data, deep warm groundwaters (0.0 to 2.0 T.U., except the sample JW 2) seem to have originated from the "pre-bomb (pre-thermonuclear)" water [more than 40 years old; if we consider the publication date (about 10 years ago) as well as the

half-life of tritium (12.43 years; Hendry, 1988, Attendorf and Bowen, 1997)], whereas shallow cold groundwaters (6.5 to 9.2 T.U.) seem to be younger (<40 years old). Among the deep warm groundwaters, the sample JW 2 with slightly high tritium content (3.1 T.U.) may indicate some degrees of the mixing with surface and/or cold groundwaters.

We can calculate the likely percolating rates of groundwaters at depths, based on the comparison of tritium data for nearby two waters from different depths and on the half-life of tritium (Hendry, 1988; Attendorf and Bowen, 1997). In the Jungwon area, we can consider two ideal cases of the percolation path in a relatively impermeable granite: path A, between the samples JW 3 (average 0.4 T.U. and 200 m deep; Table 1 and Fig. 2) and JW 3-1 (6.5 T.U. and 25 m deep); and path B, between JW 5 (average 8.2 T.U. and 60 m deep) and JW 6 (average 1.37 T.U. and 400 m deep). Some assumptions are required for this calculation as follows: one water comes only through chemical evolution from nearby another water; neither mixing nor dilution occurred during the evolution; and the water flow directions formed toward the shortest path. The estimated durations and rates of percolation are about 50 years and 3.5 m/yr for the path A, and about 33 years and 10 m/yr for the path B. These values can be considered as an estimate of rapid groundwater flow in a crystalline granitic rock.

CONCLUSIONS

Various kinds of natural waters (deep warm groundwater, shallow cold groundwater, surface water) were collected from the Jungwon and Munkyeong areas which are among the famous localities of the carbonate type spring waters in Korea. Major results of hydrogeochemical and environmental isotope studies are summarized as follows:

Deep (220 to 900 m from the surface) groundwaters from each of the areas are all saturated or supersaturated with respect to calcite, and are distinctly grouped into two main types, based on physicochemical characteristics: 1) the carbonate type water with lower pH (6.0 to 6.4) and higher Eh (34 to 58 mV) and TDS (1,210 to 3,310 mg/l) values; and 2) the alkali type water with higher pH (9.1 to 9.4) and lower Eh (-135 to -125 mV) and TDS (125 to 240 mg/l) values. The former type contains high amounts of dissolved CO₂, subsequently resulting in precipitation of abundant brown-colored (due to the coprecipitated Fe oxide) calcites after pumping-out, and has the chemical features of the calcium (-sodium)-bicarbonate (-sulfate) type which is relatively enriched in Ca²⁺, Na⁺,

Table 3. Estimates of groundwater recharge age, based on tritium concentrations (after Hendry, 1998).

Tritium (T.U.)	Age estimate
>100	average groundwater likely recharged during thermonuclear testing (between 1960 and 1965)
10~100	average groundwater less than 35 years old
2~10	average groundwater at least 20 years old
<2	average groundwater older than 30 years
<0.2	average groundwater younger than 50 years

Mg²⁺, HCO₃⁻ and SO₄²⁻, whereas the latter type shows the chemistry of the simple 'sodium-bicarbonate type' and characteristically contain high amounts of F⁻ (up to 14 ppm). Shallow (<60 m deep) cold groundwaters are all undersaturated with respect to calcite, and show the chemical features of the less-evolved, alkali type water or the mixture between the carbonate type water and surface water. Each type waters represent very similar hydrochemical compositions, regardless of the area (Jungwon and Munkyeong).

Compared to cold groundwaters and surface waters, the deep warm groundwaters show distinct environmental isotopic compositions as follows: 1) for deep warm groundwaters, δ³⁴S_{SO₄}=24.2 to 27.6‰ for the carbonate type waters from the Jungwon area, and 6.1‰ for the carbonate type water from the Munkyeong area, δ¹⁸O=-9.4 to -10.4‰, δD=-66.7 to -72.3‰, and tritium content=0.0 to 3.1 T.U.; 2) for cold groundwaters and surface waters, δ³⁴S_{SO₄}=3.6 to 7.6‰, δ¹⁸O=-7.9 to -8.6‰ (except those from the Munkyeong area), δD=-54.9 to -62.0‰ (except those from the Munkyeong area), and tritium content=6.5 to 9.2 T.U. These environmental isotope data are interpreted to indicate that two types of deep warm groundwaters were both derived from pre-thermonuclear (about more than 40 years old) meteoric waters (with lighter O and H isotope data than cold groundwaters and surface waters) which evolved through the longer duration of water-rock (mainly consisting of granites and gneisses, and minor amounts of metamorphosed sedimentary rocks including sandstone, shale and limestone for the Munkyeong area) interaction. Simple estimations of the percolating rates of groundwater flow, based on tritium data, are about 3.5 to 10 m/year mainly through faults and associated fractures in a crystalline granitic rock.

Combined with both the locations of groundwater wells and the hydrochemical data, the sulfur isotope data of dissolved sulfates indicate that the carbonate type waters were derived from the oxidation dissolution of pyrites in hydrothermal vein ores from the Daehwa and Donsan W-Mo mines (for the Jungwon water) or in anthracite coal beds (for the Munkyeong water).

Therefore, the carbonate type waters having high acidity could result in TDS-high groundwaters by larger degrees of dissolution of carbonates and silicates (possibly including calcite, plagioclase, muscovite, and Mg-bearing biotite and chlorite) around their pathways. If the deeply percolating meteoric water did not encounter the pyrites, the alkali type groundwaters simply formed through lesser degrees of chemical interaction (largely, accompanying the dissolution of calcite and plagioclase) with granitic rocks. Our hydrogeochemical genetic model as de-

scribed above may be successfully applied to the other carbonate type groundwaters in Korea.

ACKNOWLEDGEMENTS

This research was performed by the NON DIRECTED RESEARCH FUND, Korea Research Foundation. We also acknowledge the Center for Mineral Resources Research in Korea University for the support of stable isotope analysis. Prof. Jin, S.J. (Institute of Mineral Deposits, China) kindly performed the sulfur isotope analysis. We also thank Dr. Kim, C.S. (KAERI) for stimulation of this research project.

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Manuscript received 12 March 1998

한반도 지열수의 지화학적 연구: 환경동위원소 및 수문화학적 특성 II. 중원 및 문경 지역

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요약 : 탄산염형 지하수가 특징적으로 산출되고 있는 중원 및 문경 지역에서 유형별 자연수 (심부 지하수, 천부 지하수, 지표수)를 채취하고 (기간: 1996~1997년) 수문지구화학 및 환경동위원소(황산염의 황, 물의 산소 및 수소, 삼중수소) 연구를 수행하였다. 연구지역에는 지구화학적으로 뚜렷히 구분되는 두 유형의 자연수, 즉 탄산염형 및 알칼리형이 함께 산출된다. 탄산염형의 지하수는 수문화학적으로 $Ca(-Na)-HCO_3(-SO_4)$ 유형의 특성을 보이지만, 알칼리형 지하수는 $Na-HCO_3$ 유형의 특성을 나타낸다. 탄산염형 지하수는 특징적으로 보다 낮은 pH와 높은 Eh 및 높은 용존이온 (특히, Ca, Na, Mg, HCO_3 , SO_4) 함량을 갖는다. 두 유형의 지하수는 모두 방해석에 대하여 포화 또는 과포화 상태에 있다. 두 유형의 심부 지하수는 모두 핵실험 이전 (적어도 40년전)에 충전된 경우로부터 기원하여 오랜 수-암 반응에 의하여 진화하였다. 심부 지하수는 보다 젊은 시기에 충전된 물 (즉 천부 지하수 및 지표수)에 비하여 낮은 산소 및 수소 동위원소비를 갖는다. 그러나 지질 특성, 물의 화학성 및 환경동위원소 자료를 종합하여 보면, 두 유형의 심부 지하수는 각기 독특한 수문학적 및 수문지화학적 진화를 하였음을 알 수 있다. 탄산염형 지하수는 지역적으로 부화된 황화광물 (주로 황철석)의 용해에 의해 생성된 산성수의 혼합 결과로 형성되었는데, 황철석은 열수 광맥내 (중원 지역의 경우) 또는 무연탄층내 (문경 지역의 경우)에 존재하였다. 심부 순환하는 강우가 순환과 정중 황철석을 만나지 않았다면 알칼리형 지하수 만이 생성되었을 것이다. 이와 같은 수문학적 및 수문지화학적 모델은 한반도에 부존하는 기타 탄산염형 지하수에도 성공적으로 적용될 수 있을 것으로 사료된다.