

GROUNDWATER EVOLUTION OF THE GRANITE AREA, KOREA

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Abstract

The geochemistry and environmental isotopes of groundwater in the Cretaceous granite of the Yeongcheon area has been investigated. The hydrochemistry of groundwater belongs to the Ca-HCO₃ type. The oxygen-18 and deuterium data are clustered along the meteoric water line, indicating that the groundwater is of meteoric water origin. Tritium data show that the groundwaters were mostly recharged before pre-thermonuclear period and have been mixed with younger surface water flowing rapidly along fractured zones. Based on the mass balance and reaction simulation approaches using both the hydrochemistry of groundwater and the secondary mineralogy of fracture-filling materials, the low-temperature hydrogeochemical evolution of groundwater in the area has been modeled. The results of geochemical simulation show that the concentrations of Ca, Na and HCO₃ and pH of waters increase progressively owing to the dissolution of reactive minerals in flow paths. The concentrations of Mg and K first increase with the dissolution of reactant minerals, but later decrease when montmorillonite and illitic material are precipitated respectively. The continuous adding of reactive minerals, i. e. the progressively larger degrees of water/rock interaction, causes the formation of secondary minerals with the following sequence: hematite > gibbsite > kaolinite > montmorillonite > illitic material > microcline. The results of reaction simulation agree well with the observed water chemistry and secondary mineralogy, indicating the successful applicability of this simulation technique to delineate the complex hydrogeochemistry of bedrock groundwaters.

1. INTRODUCTION

The groundwater chemistry is very important for the performance assessment of geological disposal for radioactive waste. Crystalline rocks such as granite and gneiss have been considered as suitable host rocks of radioactive waste repository. A number of hydrogeochemical investigations in crystalline rocks have been studied on the suitability for host rocks of a repository [1, 2, 3]. The Korea Atomic Energy Research Institute (KAERI) is conducting hydrogeological and hydrogeochemical investigations of crystalline rocks as a part of Radioactive Waste Management Research Program. The granite area of the Yeongcheon diversion tunnel was chosen as a research site for studying geochemical characteristics of bedrock groundwater. The Yeongcheon tunnel has been constructed since 1994 for water supply to the Yeongcheon area, and is about 40 km long between the Yeongcheon Dam and the Imha Dam of the Andong area. The tunnel is under construction using Tunnel Boring Machine with a diameter of 2 m. This area is adequate for the systematic investigations of hydrogeology and hydrogeochemistry, because of the direct observation of fractures for groundwater flow paths and the in-situ sampling of deep groundwater without sophisticated sampling device.

The Yeongcheon diversion tunnel is located in the Kyeongsangbukdo province (Lat. 36°7'-36°10' and Long. 128°58'-129°5'). Previous study on groundwater of the area has been undertaken for the mineralogy of fracture-filling materials and hydrogeochemistry in the granite area [4]. In this paper, we interpret the groundwater geochemistry in more details by applying the multiphase geochemical modeling on water-rock(granite) interaction and correlate the relationship between geochemical evolution of groundwater system and the formation of secondary minerals. Furthermore, the origin and residence time of groundwaters are inferred from environmental isotope compositions, including oxygen-18, deuterium and tritium. Several computer programs, including SOLVEQ and CHILLER [5], SOLMINEQ.88 [6], PHREEQE [7] and EQ3/6 [8], are available for predicting the

speciation of dissolved constituents, the determination of saturation states of water with respect to minerals, and the evolution of water owing to progressive water-rock interaction at a given temperature and pressure. Various available computer programs have been summarized and compared by Nordstrom et al. [9] and Melchior and Bassett [10]. In this study, we used the program CHILLER with a modification to simulate continuously the appropriate geochemical evolution path. The results of geochemical simulation were carefully compared with the data of in-situ measurements and of water chemistry.

2. GEOLOGIC SETTING

The topography and geology of the Yeongcheon diversion tunnel area have been described in detail in previous studies [4, 11, 12]. The geology of the tunnel area consists of sedimentary, volcanic, and plutonic rocks in the Cretaceous Kyeongsang basin (Fig. 1). The Daegu Formation forms the oldest unit in the study area, and consists mainly of shale, sandy shale and mudstone. Volcaniclastic rocks consist of tuff and andesitic to rhyolitic breccias, and were intruded by dacite.

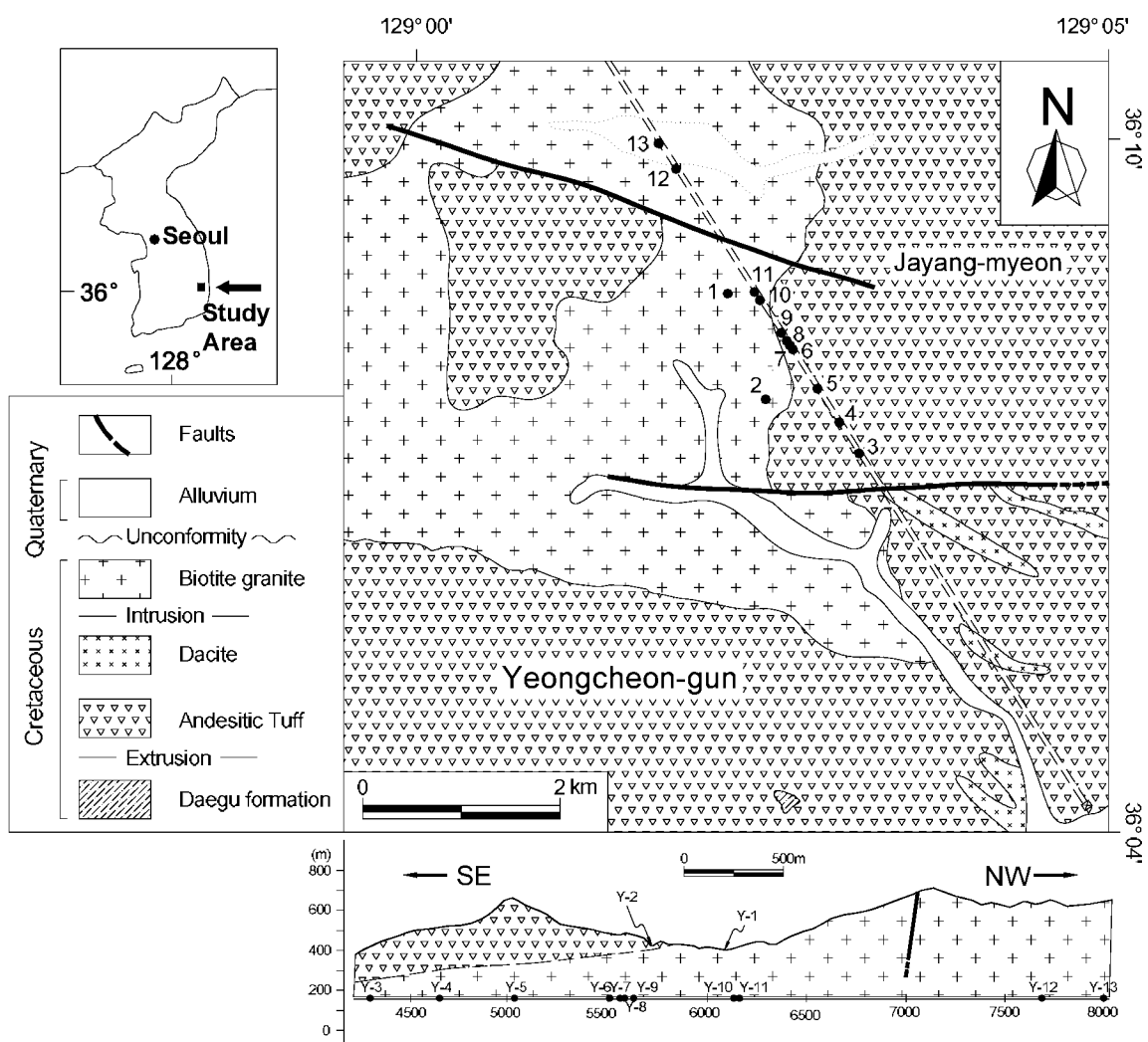


FIG. 1. Geologic map and cross section of the Yeongcheon area. Sampling locations and fault system are also shown.

TABLE I. GEOCHEMICAL AND ISOTOPIC DATA OF WATER SAMPLES WITHIN THE YEONGCHEON DIVERSION TUNNEL (UNIT: mg/L).

Sample no.	Dis. from Portal(m)	pH	Eh (mV)	TDS	log fco ₂ *	Na	K	Ca	Mg	Cl	HCO ₃ *	SO ₄	SiO ₂	F	δ ¹⁸ O (‰)	δ ¹⁸ O (‰)	Tritium (TU)
<i>Surface water</i>																	
Y-1	-	6.52	47.3	46	-2.48	4.4	0.22	3.1	1.0	5.0	10.5	8.0	12.0	0.11	-9.05	-62.2	9.6
Y-1'	-	6.93	1.2	53	-2.90	4.7	0.20	4.3	1.3	4.7	10.3	10.9	15.2	0.11	-7.20	-46.0	8.5
Y-2	-	7.05	17.1	52	-2.99	4.4	0.31	5.7	1.2	5.3	11.2	9.7	11.1	0.14	-8.88	-61.0	9.1
Y-2'	-	6.77	-16.7	44	-2.78	3.6	0.20	2.3	0.5	2.3	9.5	6.1	19.3	0.12	-7.35	-48.2	7.6
<i>Groundwater</i>																	
Y-3	4270	8.26	-56.2	135	-3.41	12.2	0.21	16.1	1.0	3.6	70.5	15.0	15.0	0.89	-9.59	-66.2	1.1
Y-4	4673	8.02	-42.3	139	-3.18	13.4	0.27	17.3	0.2	2.2	69.3	18.7	16.7	1.07	-9.51	-62.3	1.4
Y-4'	4673	7.87	-20.3	130	-3.16	13.4	0.32	14.8	0.4	2.2	50.3	27.7	19.9	1.42	-9.54	-65.3	0.7
Y-5	5040	7.82	-30.4	154	-2.94	11.3	0.32	20.0	1.4	2.4	75.4	20.7	20.3	1.88	-9.50	-66.0	1.1
Y-5'	5040	7.93	-21.7	124	-3.22	10.9	0.26	14.5	1.4	2.5	50.7	20.1	21.3	1.95	-9.56	-67.8	0.2
Y-6	5505	8.19	-52.3	150	-3.39	15.4	0.33	21.0	0.2	2.9	62.5	24.8	19.7	2.03	-9.41	-63.8	1.6
Y-6'	5505	7.95	-18.7	130	-3.27	14.5	0.20	14.2	0.2	2.5	47.2	24.8	25.0	1.07	-9.44	-65.9	1.0
Y-7	5560	8.13	-53.3	140	-3.35	12.5	0.27	19.9	0.3	1.9	60.7	22.3	21.2	1.37	-9.44	-63.7	3.1
Y-7'	5560	8.15	-27.5	124	-3.49	13.2	0.20	14.0	0.3	2.2	45.3	23.2	23.5	1.78	-9.51	-65.9	2.4
Y-8	5575	7.44	-7.4	150	-2.58	9.8	0.26	23.2	0.7	1.9	71.7	22.3	18.5	1.58	-9.48	-63.7	4.1
Y-9	5650	7.43	-6.8	149	-2.56	15.4	0.22	16.2	0.1	1.7	73.8	17.4	22.4	1.53	-9.66	-70.0	0.2
Y-9'	5650	8.02	-19.7	125	-3.29	15.9	0.31	12.2	0.1	2.1	52.7	16.6	23.8	1.81	-9.62	-66.5	0.9
Y-10	6140	7.72	-24.3	184	-2.80	12.1	0.23	26.8	2.7	3.6	82.7	29.3	23.2	1.59	-9.16	-62.5	3.0
Y-10'	6140	7.98	-22.3	168	-3.10	11.3	0.30	24.7	2.3	4.1	76.3	20.9	26.7	1.08	-9.30	-66.2	2.0
Y-11	6150	7.86	-32.8	184	-2.91	11.2	0.21	26.3	2.7	3.5	88.5	25.6	22.7	1.89	-9.18	-63.2	3.3
Y-11'	6150	7.72	-9.8	159	-2.86	10.7	0.32	21.6	2.3	3.7	71.5	19.4	27.7	1.92	-9.36	-65.5	1.6
Y-12	7700	7.30	-5.5	144	-2.41	9.5	0.31	19.4	0.6	1.7	75.8	12.3	21.3	2.62	-9.38	-66.1	4.5
Y-13	8000	7.06	15.4	151	-2.17	11.1	0.24	18.3	1.3	3.3	77.4	12.8	24.2	0.98	-9.37	-64.8	1.71

* Calculated from alkalinity and pH using SOLVEQ [5]

Biotite granite represents the youngest rock unit in the area, and is composed mainly of quartz (25%), plagioclase (31%), K-feldspar (30%) and biotite (6%). Accessory minerals include hornblende, perthite, zircon, apatite and opaque minerals. The plagioclase belongs to albite-oligoclase (Oh and Jeong, 1975)[11]. Basic dykes ubiquitously intrude the biotite granite.

This study was carried out in the area of biotite granite within the tunnel area. Calcite and pyrite occur commonly as products of hydrothermal fracture filling in the granite. X-ray diffraction analyses of fracture materials by Lee et al. [4] indicate the occurrence of illite, laumontite, stilbite, quartz, smectite and calcite. KAERI [13] identified the presence of rectorite, laumontite, stellerite, calcite, smectite and quartz as fracture-filling minerals. However, the calcite is thought to be a hydrothermal origin (Section 3- Water Chemistry). It is also probable that the observed zeolites, including laumontite, stilbite and stellerite, are hydrothermal alteration products.

3. WATER CHEMISTRY

Sampling of waters including tunnel seepage waters and surface waters was carried out from totally thirteen localities between 1995 and 1996 (Fig. 1). The pH, Eh, temperature, and electrical conductivity were measured in-situ with portable meters (Orion 290A and 190). Concentrations of major cations were measured by the atomic absorption spectrometer (AAS) and inductively coupled plasma atomic emission spectrometer (ICP-AES). Anions were measured by ion chromatography (IC). Oxygen and hydrogen isotope compositions of water were determined through the conventional CO₂ equilibration method (at 25°C) and the reduction with Zn metal (at 450°C), respectively. Tritium

contents (TU) of water were measured by the liquid scintillation counting during 500 minutes after the electrolytic enrichment of the sample from 600 g to 20 g.

Geochemical data of water samples are summarized in Table I. The measured pH and Eh values of groundwater range from 7.1 to 8.3 and from +15.4 to -56.2 mV, respectively. Major dissolved cations and anions are Na (9.5 to 15.4 mg/l) and Ca (12.2 to 26.8 mg/l) and HCO_3^- (45.3 to 88.5 mg/l) and SO_4^{2-} (12.3 to 29.3 mg/l), respectively. The waters in the Yeongcheon are all of Ca(-Na)- HCO_3^- type. Na and Ca in natural waters are commonly derived from dissolution of plagioclase. The composition of plagioclase in granite of the Yeongcheon area ranges from Ab_{100} to Ab_{30} . However, Na concentration in groundwaters range from 0.4 to 0.7 mmole, and is similar to Ca concentrations (0.3-0.7 mmole). In order to explain the enhanced Ca concentrations in waters, we consider the difference of dissolution rate between albite and anorthite. The dissolution of calcite may also contribute to Ca enrichment in the waters. In fact, hydrothermal fracture-filling calcites are ubiquitously observed along the groundwater flow paths within the tunnel. K and Mg contents are related to the incongruent dissolution of K-feldspar and biotite.

Chemical weathering of silicate minerals in granite to kaolinite consumes H^+ , resulting in gradual increase of pH of groundwater. The concentrations of major ions in waters are plotted with respect to pH (Fig. 2). Na and Ca content tends to be increased with increasing pH, whereas no relationships of K and Mg concentrations to pH are noticeable. Although the granite in the tunnel area contains abundant K-feldspar (30%) and biotite (6%), K and Mg concentrations in waters are relatively low. This fact can be explained by considering the dissolution rates of silicate minerals.

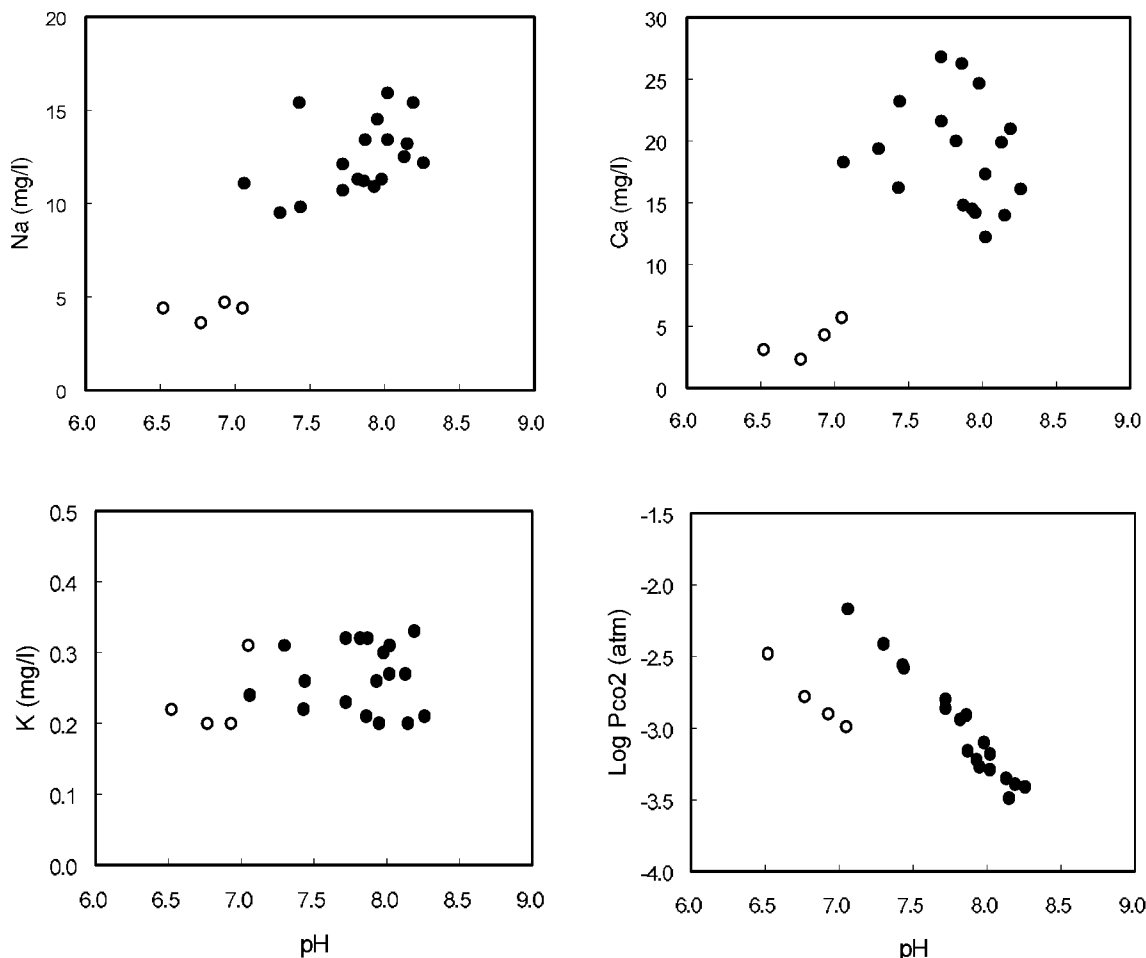


Fig. 2. pH versus Na, Ca, K and Pco_2 diagrams for water samples in the granite area. Open circles: surface water; solid circles: groundwater.

According to Walther and Wood [14], however, the dissolution rates of silicate minerals do not differ by one order of magnitude. Therefore, we consider that the observed low contents of K and Mg may be explained by the removal through precipitation of clay minerals and/or muscovite. Similarly, Ca concentrations also may be controlled by the formation of Ca-bearing minerals such as Ca-montmorillonite.

Dissolved silica is resulted from the chemical weathering of silicate minerals, and is controlled either by kinetic factors in the dissolution process or by precipitation of secondary minerals such as amorphous forms of silica rather than direct precipitation of quartz [15]. The measured silica concentrations of groundwater (15.0-27.7 mg/l) are higher than the solubility of quartz (6.0 mg/l at 25°C). According to Hem et al. [15], an amorphous matter with the halloysite composition may be produced by the weathering of igneous rock forming minerals and may control the aluminum and silica concentrations in natural waters. Paces [16] also suggested that aluminum and silica concentrations in groundwater are controlled by a metastable aluminosilicate mineral with a variable composition between gibbsite and kaolinite, which allows higher silica concentrations in water.

SO₄ in waters is likely to be deduced from oxidation of pyrite formed during hydrothermal alteration in fractures of granite. Preliminary sulfur isotope data of groundwaters ($\delta^{34}\text{S}_{\text{SO}_4} = +2.6$ - $+4.5\%$.) in the granite area indicates that sulfate is originated from hydrothermal fracture-filling pyrites ($\delta^{34}\text{S} = +4.2$ - $+5.3\%$.). Compared with most of the fresh waters containing F of less than 1 mg/l, the Yeongcheon groundwaters are relatively enriched in F (0.9-2.6 mg/l). Both F and Cl can be derived from dissolution of biotite and apatite [2]. According to Tsusue et al. [17], apatite and biotite from Korean Cretaceous granites typically contain appreciable amounts of F and Cl.

Partial pressures of CO₂ (Pco₂) in water were calculated from measured pH and alkalinity data using the program SOLVEQ [5] and are shown in Table I. Calculated log Pco₂ (atm) values range from -3.4 to -2.2. The origin of carbon in groundwaters includes: (1) atmospheric CO₂, (2) dissolution of carbonate minerals, and (3) microbial oxidation of organic carbon and/or carbon dioxide from plant respiration. Relatively higher Pco₂ values (up to $10^{-2.2\text{atm}}$) for Yeongcheon groundwaters possibly indicate the roles of sources (2) or (3) in addition to atmospheric CO₂.

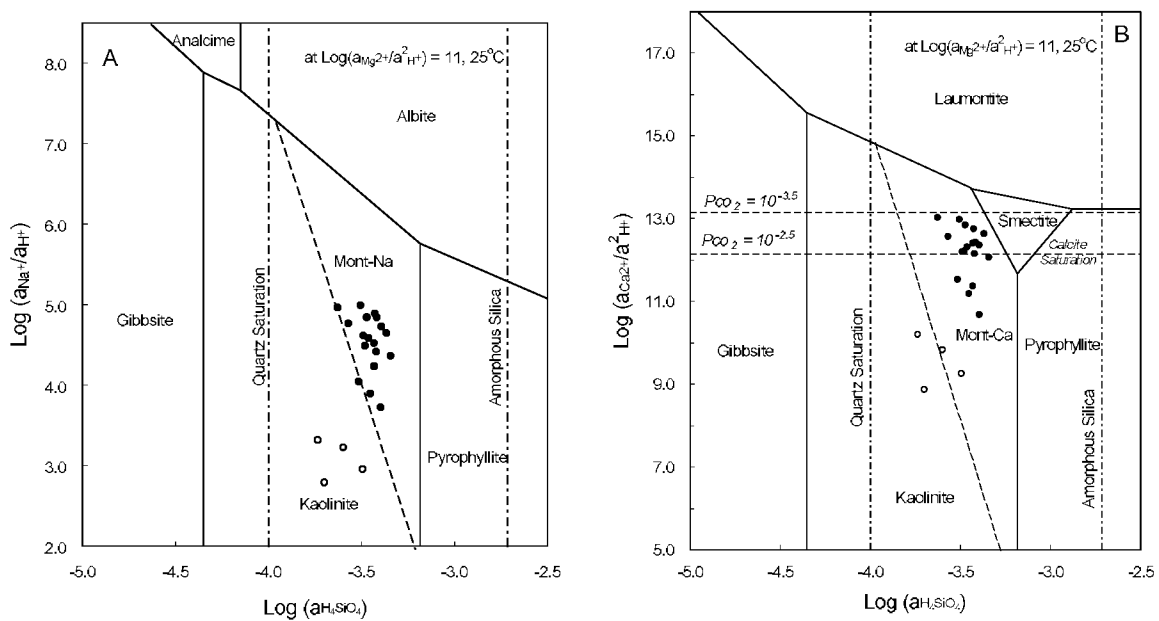
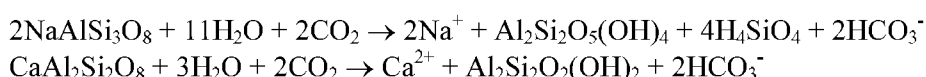


FIG 3. Stability diagrams for some minerals in the systems Na₂O-Al₂O₃-SiO₂-H₂O (in A) and CaO-Al₂O₃-SiO₂-H₂O (in B) at 25°C. Solid circles = groundwaters; open circles = surface waters.

However, it is unlikely that source (2), a carbonate carbon, cannot be an adequate explanation in this area, because ion speciation calculations using the program SOLVEQ show that all of water samples examined are undersaturated with respect to calcite. Furthermore, hydrothermal calcites in the tunnel area have $\delta^{13}\text{C}_{\text{PDB}}$ values around -7‰. These carbon isotope values are unlikely to form isotopically very light carbon in groundwater (-17.1 to -17.9‰). Therefore, we consider the contribution of carbon from either the microbial oxidation of organic matter or carbon dioxide from plant respiration.

The mean annual evapotranspiration in Korea has been reported to be about 600 mm (540-647 mm) [18]. According to Brook et al. [19], the mean log Pco_2 value in soil under the annual evapotranspiration (AET) of 600 mm is about -2.26. This log Pco_2 value is equivalent to 0.17 mmole of aqueous CO_2 at 25°C. The dissolution of silicate minerals consumes large amounts of CO_2 and H^+ . If albite and anorthite were dissolved, 1 and 2 moles of CO_2 are consumed for unit mole of Na and Ca, respectively, through the following reactions.



As an example, the release of 0.67 mmole Na^+ (15.4mg/L) and 0.52 mmole Ca^{2+} (21.0mg/L) for a water sample (No. 6 in Table I) owing to the incongruent dissolution of albite and anorthite requires the consumption of CO_2 by about 1.71 mmole. This calculation indicates that if dissolution of albite and anorthite is proceeded under the CO_2 closed system, the amounts of CO_2 required for the dissolution is larger than the amounts of CO_2 generated from biological process. Therefore, we should consider the geochemical evolution of groundwater under partially open system in which CO_2 is supplied continuously.

The chemical compositions of surface water and groundwater in the Yeongcheon area are plotted in mineral stability diagrams for the systems of $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ and $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ at 25°C (Fig. 3). Groundwaters seem to be equilibrated with kaolinite and montmorillonite, indicating that silica and aluminum in water through incongruent dissolution of silicate minerals are largely conserved by the formation of kaolinite and montmorillonite. Figure 3 also shows that waters in the Yeongcheon tunnel area are undersaturated with respect to calcite.

4. ENVIRONMENTAL ISOTOPES

The environmental isotopic compositions of waters sampled twice between Oct. 1995 and Feb. 1996 are summarized in Table I. The $\delta^{18}\text{O}$ and δD values of surface waters range from -9.1 to -7.2‰ and -62.2 to -46.0‰, respectively. Groundwaters have $\delta^{18}\text{O}$ and δD values ranging from -9.7 to -9.2‰ and -70.0 to -62.3‰, respectively. All isotopic data closely follow the relation of the worldwide meteoric water line, indicating that groundwaters in the Yeongcheon tunnel have been recharged as local meteoric waters under present climate conditions. Surface waters also tend to show seasonal isotopic variation. It is noteworthy that isotopic compositions of groundwaters are lighter than those of surface waters. This likely indicates that groundwaters were recharged from the area of higher elevation than local land surface.

Tritium contents (TU) of water samples are listed in Table I. Based on tritium contents, groundwaters discharged into the tunnel can be grouped into two types: one with TU values near 0.0, and the other with TU values of 1.6 to 4.5. The former group with TU values of less than 1.6 is dominant. Based on the long-term monitored tritium contents of rain waters from Pohang and Taejon (IAEA, 1992; Koh et al., 1996), these remarkably low tritium contents suggest that most of groundwaters represent the old meteoric waters recharged during pre-thermonuclear periods before 1953 (IAEA, 1992). Some local groundwaters belonging to the second group possibly were recharged during the post-bomb age. In other words, these waters have the residence time of less than 45 years (likely 10 to 40 years). The construction of tunnel since 1994 would disturb the groundwater flow

system, resulting in fast groundwater flow toward the tunnel, especially at highly fractured zones. Therefore, it is reasonable that the second group groundwaters with higher tritium contents represent the mixing with rapidly downward flowing surface waters (about 10 TU).

5. GEOCHEMICAL EVOLUTION

Geochemical modeling for groundwater-rock systems under low-temperature has been carried out by a number of geochemists [3, 8, 20] in order to understand the water-rock interaction and related hydrogeochemical evolution. In this study we used the geochemical reaction program CHILLER [5]. The CHILLER provides stepwise incremental changes in temperature, pressure, enthalpy, or composition to a system. Following each step, both the equilibrium phase assemblage and the mineral and aqueous compositions are recalculated. This process is continued until the calculated assemblage is truly equilibrated. After this process, we can conduct the particular model calculation including cooling, heating, boiling, condensation, mixing, water-rock titration, and evaporation under either open or closed system conditions [5, 21].

Chemical speciation of groundwater samples was obtained using the aqueous speciation program SOLVEQ [5], in order to eliminate the reactions which are invalid thermodynamically. According to the calculations of the degree of saturation of groundwater with respect to various minerals, it is clear that groundwater in the tunnel area is undersaturated with respect to most of the igneous rock-forming minerals. Major forming minerals of granite, such as quartz (25%), feldspar (30%), plagioclase (30%) and biotite (6%), are probable reactants in the reaction simulation. Additionally, we included calcite and pyrite in the model calculation, because they are commonly present as fracture-filling minerals and contribute significantly to Ca and SO_4 concentrations in groundwater (Section 3-Water Chemistry).

Although the mineralogy of granite is well documented, however, it is difficult to determine the exact reactant minerals owing to uncertainties in dissolution rates of silicate minerals. Though dissolution and precipitation rates of silicate minerals have been estimated by a number of scientists,

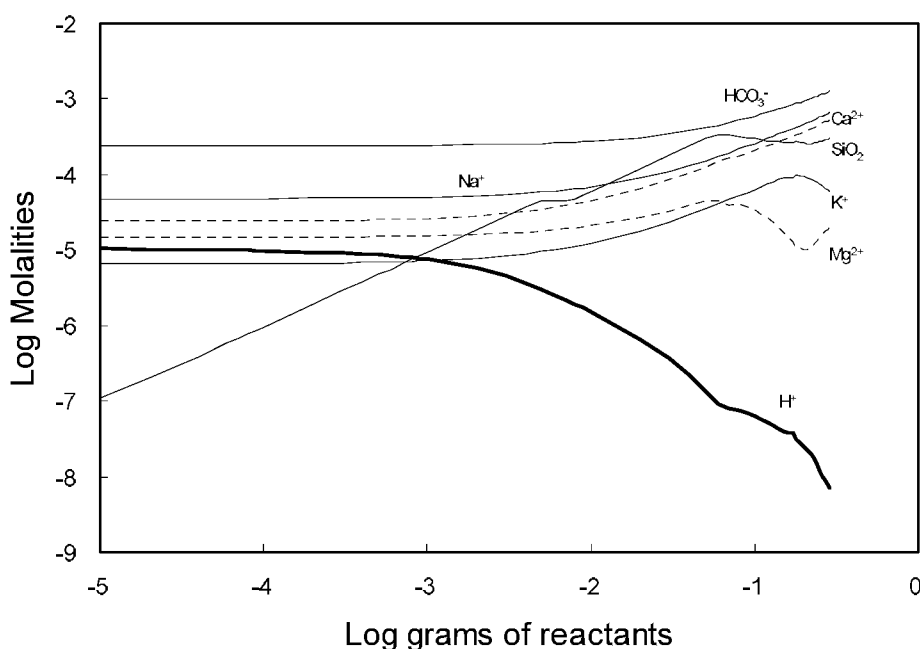


FIG.4. Results of geochemical simulation, showing compositional variation (in molalities) of major dissolved ions in groundwater during the progressive water/rock(granite) interaction.

the data are very inconsistent. Moreover, discrepancies of up to four orders of magnitude between field estimates and laboratory measurements have been documented [22, 23, 24]. In this study, we fitted the reactant minerals in the geochemical simulation, based on the considerations of mineral abundance, saturation states, and reaction kinetics.

In order to simulate the geochemical evolution of Yeongcheon groundwater, rain water was reacted with granite. In this calculation, the CO_2 concentration in reactant water was set to be $10^{2.17}$ atm (Section 3- Water Chemistry). The results of simulation are plotted in Figure 4. The continuous adding of granite (reactant minerals) to rain water causes precipitation of minerals in the following sequence: hematite > gibbsite > kaolinite > montmorillonite > illitic material > microcline. It is noteworthy that the types of precipitating minerals correspond well with the observed mineralogy in fractures [4]. Figure 4 shows the changes of dissolved ions with decreasing water/rock ratios. Progressive water/rock interaction, namely the decreasing water/rock ratios, results in progressive increase of Na, Ca and HCO_3^- in solution. The pH is constant (buffered) at initial stage of water/rock interaction, but increases steeply when about 10^{-3} grams of reactants are added. The alteration of albite to kaolinite and/or gibbsite consumes protons, whereas the alteration to montmorillonite consumes less acid. The increased aqueous silica causes the precipitation of kaolinite. The Mg and K concentrations in solution increase slowly with increasing water/rock interaction, but then decrease with precipitation of montmorillonite, muscovite and microcline. Dissolved silica increases as a whole due to the dissolution of silicate minerals, but decreases slightly in response to the successive precipitation of montmorillonite, muscovite and microcline. The results of simulation match well with measured geochemical data. However, computed potassium values are slightly higher than measured values. We consider that potassium smectite may precipitate from the solution (although the model calculations indicate the undersaturation with respect to any smectite; this may be related with the large uncertainty in thermodynamic data of smectites), resulting in actual lower concentrations of potassium.

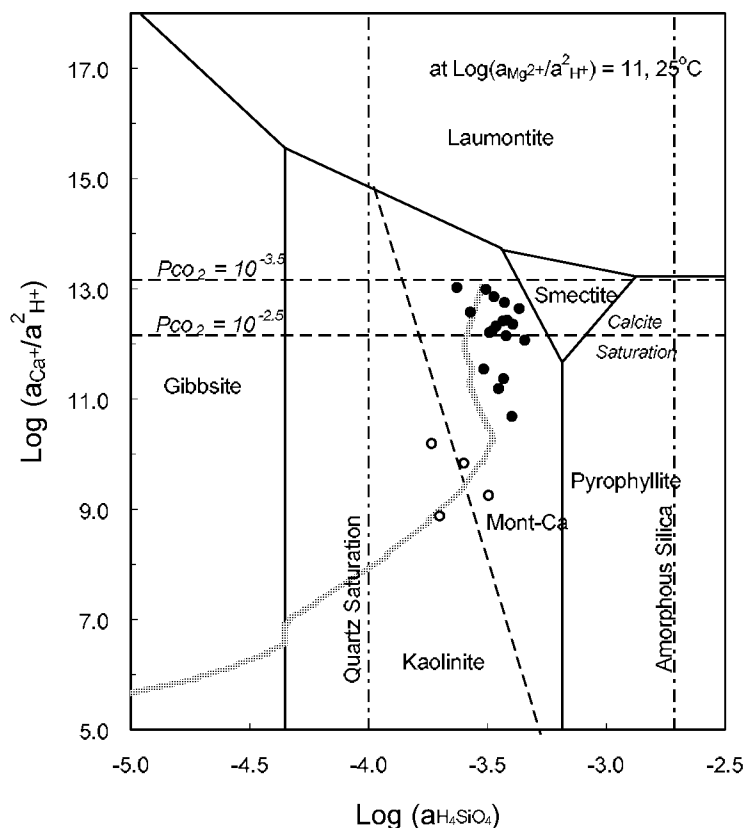


FIG.5. Stability diagrams for some minerals in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ at 25°C , showing the probable path (thick and solid line) of groundwater evolution due to water/rock interaction.

In the simulation, chemical evolution of groundwater is modeled under both the closed CO₂ and the fully open CO₂ conditions. Under the closed CO₂ conditions the pH rapidly rises far above the measured values, while Pco₂ and ion concentrations are much lower. Under the completely open CO₂ condition, on the other hand, the simulated pH is too low and Pco₂ high. Therefore, we consider that the evolution of groundwater in the Yeongcheon tunnel area occurs under the partially open CO₂ conditions.

The result of simulated geochemical reaction path is plotted on a mineral stability diagram in the system CaO-Al₂O₃-SiO₂-H₂O at 25°C (Fig. 5). Water in reaction with granite would first equilibrate with gibbsite and then kaolinite. In kaolinite field, the evolution path is accompanied with increasing silica concentration. Figure 5 shows that the evolution path of groundwater by the simulation is valid and reasonable geochemical process in the granite area, even though the complexities of natural processes could not be duplicated.

6. CONCLUSIONS

The bedrock groundwaters discharged into the Yeongcheon diversion tunnel in a biotite granite belong to Ca-HCO₃ type chemically and are controlled by the water/rock interaction. The hydrogeochemical evolution of groundwater occurs as a progressive reaction with the silicate minerals and hydrothermal fracture-filling calcite under partially CO₂ open condition. The δ¹⁸O and δD data of waters indicate their derivation from meteoric waters. Tritium contents of groundwaters are mostly very low (0.2-1.6 TU), indicating that waters have been recharged during the pre-thermonuclear period (before 1953). However, some groundwaters with higher tritium contents (up to 4.5 TU) results from the mixing of younger superficial water.

Geochemical reaction modeling using CHILLER is undertaken to identify the processes for the chemical evolution of groundwater. The pH, Na and Ca concentrations increase progressively due to the progressive dissolution of silicate minerals and calcite, whereas the K and Mg concentrations first increase but decrease later through the precipitation of illitic material, microcline and Mg-bearing clay minerals. The results of modeling approximate to actual pH, alkalinity, and major ion concentrations of waters. Model calculations were conducted under partial CO₂ open conditions, and could trace the chemical evolution of groundwater by fitting some reactant minerals based on mineral abundances, saturation states and dissolution kinetics. However, under fully open CO₂ or closed CO₂ conditions, the results do not match the measured pH and chemistry data. Although this approach neglects the dissolution and precipitation kinetics of silicate minerals and, in turn, does not trace hydrogeochemical evolution on time basis, the results of simulation in this study provide reasonable interpretation on groundwater evolution in granite area. In future, however, we should consider the dissolution rates of various reactant minerals. Such approach may be undertaken with considerations of water/rock ratio, particle size and effective surface area of reactant minerals, and precise groundwater age.

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