

Geochemical Modeling of Groundwater in Granitic Terrain: the Yeongcheon Area

영천 화강암지역 지하수의 지화학적 모델링

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Abstract : We investigated the geochemistry and environmental isotopes of granite-bedrock groundwater in the Yeongcheon diversion tunnel which is located about 300 m below the land surface. The hydrochemistry of groundwaters belongs to the Ca-HCO₃ type, and is controlled by flow systems and water-rock interaction in the flow conduits (fractures). The deuterium and oxygen-18 data are clustered along the meteoric water line, indicating that the groundwater are commonly of meteoric water origin and are not affected by secondary isotope effects such as evaporation and isotope exchange. Tritium data show that the groundwaters were mostly recharged before pre-thermonuclear period and have been mixed with younger surface water flowing down rapidly into the tunnel 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, we have modeled the low-temperature hydrogeochemical evolution of groundwater in the area. The results of geochemical simulation show that the concentrations of Ca²⁺, Na⁺ and HCO₃⁻ and pH of waters increase progressively owing to the dissolution of reactive minerals in flow paths. The concentrations of Mg²⁺ and K⁺ first increase with the dissolution, but later decrease when montmorillonite and illitic material are precipitated respectively. The continuous adding of reactive minerals, namely the progressively larger degrees of water/rock interaction, causes the formation of secondary minerals with the following sequence: first hematite, then gibbsite, then kaolinite, then montmorillonite, then illitic material, and finally microcline. During the simulation all the gibbsite is consumed, kaolinite precipitates and then the continuous reaction converts the kaolinite to montmorillonite and illitic material. The reaction simulation results 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.

요 약 : 영천 도수터널 내 화강암 지역의 단열대를 따라 유출되는 지하수에 대하여 지화학 및 환경동위원소 연구를 수행하였다. Ca-HCO₃ 유형에 속하는 유출수의 화학 조성은 화강암을 구성하는 규산염 광물 및 열극 증진 방해석의 지화학적 용해 반응에 의해 설명되며, 그 수문지화학적 진화는 부분적 개방계에서 진행되었음을 보여준다. 환경동위원소 연구 결과, 유출수는 모두 강수 기원으로서 적어도 1953년 이전에 함양된(즉 체류 시간이 최소 45년 이상인) 지하수임을 지시해주며, 나아가 지표로부터의 거리와 단열대의 발달 상태에 따라 부분적으로 지표수의 혼입이 진행되고 있음을 지시한다. 지화학 반응 경로 모델인 CHILLER를 이용하여 본 지역 화강암 지하수의 수문지화학적 진화를 모델링 하였다. 그 결과, Ca²⁺, Na⁺, HCO₃⁻ 및 pH는 규산염 광물 및 방해석의 용해 작용과 더불어 점차 증가되는 반면, Mg²⁺ 및 K⁺는 각각 몬트모릴로나이트와 백운모의 2차 생성과 더불어 감소됨을 보여준다. 2차 광물의 생성 순서는 적철석, 깃사이트, 카올리나이트, 몬트모릴로나이트, 백운모, 장석의 순이다. 모델링 결과는 유출수의 물리화학적 분석값과 2차 광물의 동정 결과와도 잘 일치한다. 따라서, 이러한 물-암석 상호 반응 모델링을 비교적 복잡한 암반 지하수의 수문지화학적 진화 해석에 타당성 있게 적용할 수 있음을 보여준다.

Introduction

The groundwater chemistry is very important in the performance assessment of geological disposal for radioactive waste.

Crystalline rocks such as granite and gneiss have been considered as suitable sites of radioactive waste repository. A number of hydrogeochemical investigations in crystalline rocks have been performed to determine the suitability for radioactive waste disposal (Bottomley *et al.*, 1984; Frapce *et al.*, 1984; Nordstrom *et al.*, 1989; Grimaud *et al.*, 1990). The Korea Atomic Energy Research Institute (KAERI) is conducting hydrogeological and hydrogeochemical investigations of

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crystalline rocks as a part of Radioactive Waste Management Research Program. The granite area of the Yeongcheon diversion tunnel area was chosen as a research site for investigation of bedrock groundwater geochemistry. The Yeongcheon tunnel is now constructing after 1994 for water supply to the Yeongcheon area, and is about 40 km long between the Yeongcheon Dam and the Imha Dam of Andong area. The tunneling is done using Tunnel Boring Machine with a diameter of 2 m. Geology of the tunnel area is very diverse, consisting mainly of volcanic and sedimentary rocks in addition to granite. This area is adequate for systematic investigations of hydrogeology and hydrogeochemistry, as both the direct observation of fractures as groundwater flowing paths and the in-situ sampling of deep groundwater without sophisticated sampling device are possible.

The Yeongcheon diversion tunnel area in this study is located in the Kyeongsangbukdo province (Lat. $36^{\circ}7' - 36^{\circ}10'$ and Long. $128^{\circ}58' - 129^{\circ}5'$). Previous studies on groundwater of the Yeongcheon diversion tunnel area have been undertaken for the mineralogy of fracture-filling materials and hydrogeochemistry in the granite area (Lee *et al.*, 1996; Kim *et al.*, 1998a, b). In this paper, we interpret the groundwater geochemistry in more details by applying the multiphase geochemical modeling on water-rock (granite) interaction and explores 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 (Reed, 1982), SOLMINEQ.88 (Perkins *et al.*, 1990), PHREEQE (Parkhurst *et al.*, 1980) and EQ3/6 (Wolery and Daveler, 1992), 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 programs have been summarized and compared by Nordstrom *et al.* (1979) and Melchoir and Bassett (1990). 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.

Geology and Mineralogy

The topography and geology of the Yeongcheon diversion tunnel area have been described in detail in previous studies (Oh and Jeong, 1975; Chang *et al.*, 1977; Kim, 1992; Lee *et al.*, 1996). The geology of the tunnel area consists of sedimentary, volcanic, and plutonic rocks in the Cretaceous Kyeongsang basin (Figure 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. Biotite granite represents the youngest rock unit in the

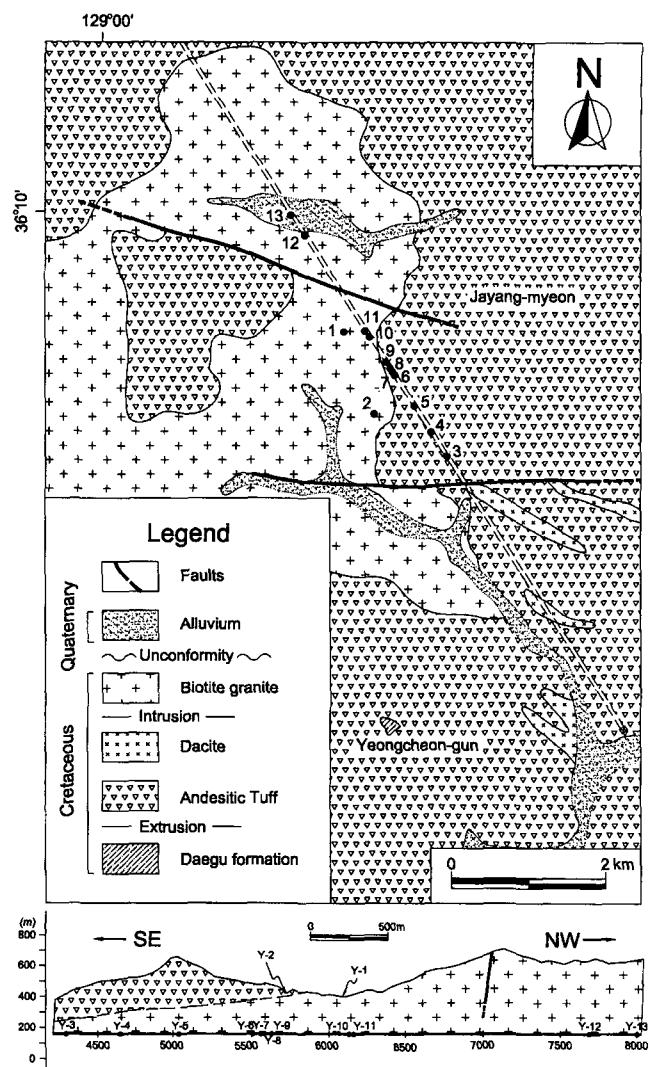


Figure 1. Geologic map and geologic section of the Yeongcheon diversion tunnel area, showing water sampling sites.

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). Basic dykes ubiquitously intrude the biotite granite.

This study is restricted in the area of biotite granite within the tunnel area. Calcite and pyrite occur as products of hydrothermal fracture filling in the granite. X-ray diffraction analyses of fracture materials by Lee *et al.* (1996) indicate the occurrence of illite, laumontite, stilbite, quartz, smectite and calcite. KAERI (1995) 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 (see WATER CHEMISTRY). It is also probable that the observed zeolites, including laumontite, stilbite and stellerite, are hydrothermal alteration products.

Water Chemistry

Sampling of waters including tunnel seepage waters and surface waters was carried out from totally thirteen localities between 1995 and 1996 (Figure 1). The pH, Eh, temperature, and electrical conductivity were measured in-situ with portable meters (Orion 290A and 190). Measurement of alkalinity was performed in the field by acid titration. After filtering with 0.45 μm cellulose membrane filters, the samples for cation analysis were acidified to pH of < 2.0 by adding few drops of 50% ultra-pure HNO_3 . 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 CO_2 equilibration method (at 25°C) and the reduction with Zn metal (at 450°C), respectively. Relative errors of analysis are $\pm 0.1\%$ for oxygen-18 and $\pm 1.0\%$ for deuterium. 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. The precision of tritium analysis is about 1.0 TU.

Physiochemical data of water samples are summarized in Table 1. 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^{2+} (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. Trilinear equivalence plots show that the waters are all of Ca ($\cdot\text{Na}$)- HCO_3 type (Figure 2).

The Na^+ and Ca^{2+} in natural waters are commonly derived

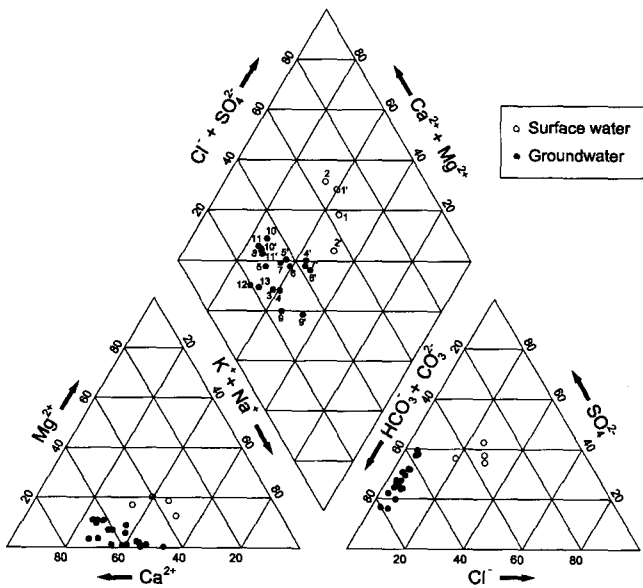


Figure 2. Trilinear compositional diagrams showing chemical compositions of water samples from the Yeongcheon diversion tunnel area.

from dissolution of plagioclase. The albite composition of plagioclase in granite of the Yeongcheon area ranges from Ab_{100} to Ab_{30} . The Na^+ concentration in groundwaters range from 0.4 to 0.7 mmole, and is similar to the Ca^{2+} concentrations (0.3~0.7 mmole). In order to explain the enhanced Ca^{2+} concentrations in waters, we consider the dissolution of calcite in addition to plagioclase (albite-oligoclase). In fact, hydrothermal fracture-filling calcites are ubiquitously observed along the groundwater flowing paths within the tunnel. Therefore, calcite dissolution acts as a main cause of Ca^{2+} enrichment in water. The K^+ and Mg^{2+} 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 (Figure 3). The Na^+ content tends to be increased with increasing pH, whereas no relationships of K^+ , Mg^{2+} and Ca^{2+} concentrations to pH are noticeable. Although the granite in the tunnel area contains abundant K-feldspar (30%) and biotite (6%), the K^+ and Mg^{2+} concentrations in waters are relatively low. This fact can be explained by considering the dissolution rates of silicate minerals. According to Walther and Wood (1986), 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^+

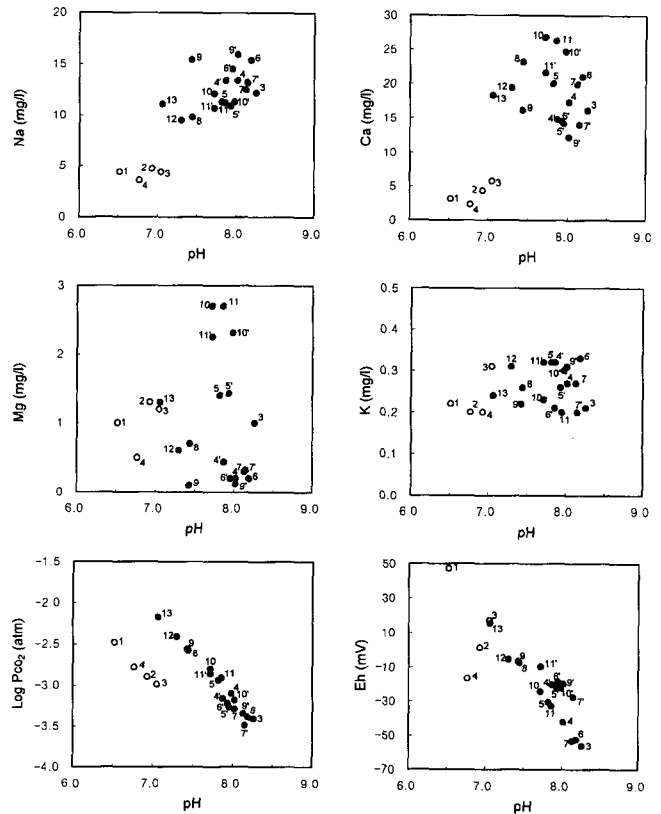


Figure 3. pH versus Na^+ , Mg^{2+} , Ca^{2+} , K^+ , Pco_2 , and Eh diagrams for water samples from the Yeongcheon diversion tunnel area. Symbols are the same as in Figure 2.

and Mg^{2+} may be explained by the removal through precipitation of clay minerals and/or illitic material. Similarly, the Ca^{2+} concentrations also may be controlled by the formation of Ca-bearing minerals such as Ca-montmorillonite.

Dissolved silica results 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 one of the less organized forms of silica rather than the direct precipitation of quartz (Hem, 1973). 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.* (1973), an amorphous clay mineral with the halloysite composition may be produced by the weathering of igneous minerals and may control the aluminum and silica concentrations in natural waters. Paces (1978) 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.

SO_4^{2-} 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 ($\delta^{34}S_{CDT} = +2.6 \pm 4.5\%$) in granite area indicates that sulfate is originated from hydrothermal fracture-filling pyrites ($\delta^{34}S_{CDT} = +4.2 \pm 5.3\%$; Yun *et al.*, in prep.). Compared with most fresh waters containing F^- of less than 1 mg/L (Hem, 1989), 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 (Savage *et al.*, 1987; 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^- .

Partial pressures of CO_2 (P_{CO_2}) in water were calculated from measured pH and alkalinity data using the program SOLVEQ (Reed, 1982) and are shown in Table 1 and Figure 3. Calculated log P_{CO_2} (atm) values range from -3.4 to -2.2 (Table 1). The origin of carbon in groundwaters includes: (1) atmospheric CO_2 , (2) dissolution of carbonate minerals, and (3) microbial oxidation of organic carbon and/or carbon dioxide from plant respiration. Relatively higher P_{CO_2} values (up to $10^{-2.2}$ atm) for Yeongcheon groundwaters possibly indicate the role of sources (2) or (3) in addition to atmospheric CO_2 (Plummer, 1977). 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 $\delta^{13}C_{PDB}$ values around -7‰ (Yun *et al.*, in prep.). These carbon isotope values are unlikely to form isotopically very light carbon in groundwater (-17.1 to -17.9‰; Yun *et al.*, in prep.). Therefore, we consider the contribution of carbon from either the microbial oxidation of organic matter or carbon dioxide from plant respiration. The $\delta^{13}C$ values of CO_2 generated by

Table 1. Physicochemical data of water samples collected from granite area within the Yeongcheon diversion tunnel

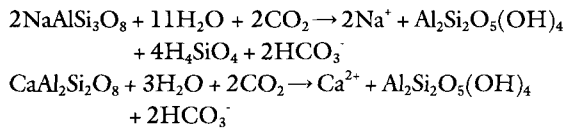
Sample no.	Water Type	Dis. from Portal (m)	Sampling Date	Temp. (°C)	pH	Eh (mV)	EC ($\mu S/cm$)	TDS (mg/L)	log $f_{CO_2}^*$ (atm)	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl	HCO ₃ [*] SO ₄ ²⁻	SiO ₂	NO	F ⁻	Al ^{**}	
																(mg/L)				
Y-1	S. W.	-	Feb-7-96	1.5	6.52	47.3	47.6	46	-2.48	4.4	0.22	3.1	1.0	5.0	10.5	8.0	12.0	1.4	0.11	0.0001
Y-1'	S. W.	-	Oct-10-95	20.3	6.93	1.2	46.5	53	-2.90	4.7	0.20	4.3	1.3	4.7	10.3	10.9	15.2	0.9	0.11	0.0002
Y-2	S. W.	-	Feb-7-96	1.5	7.05	17.1	55.6	52	-2.99	4.4	0.31	5.7	1.2	5.3	11.2	9.7	11.1	2.9	0.14	0.0004
Y-2'	S. W.	-	Oct-10-95	28.2	6.77	-16.7	48.1	44	-2.78	3.6	0.20	2.3	0.5	2.3	9.5	6.1	19.3	0.1	0.12	0.0001
Y-3	G. W.	4270	Feb-7-96	18.7	8.26	-56.2	145.3	135	-3.41	12.2	0.21	16.1	1.0	3.6	70.5	15.0	15.0	0.6	0.89	0.0047
Y-4	G. W.	4673	Feb-7-96	19.9	8.02	-42.3	149.5	139	-3.18	13.4	0.27	17.3	0.2	2.2	69.3	18.7	16.7	0.0	1.07	0.0024
Y-4'	G. W.	4673	Oct-10-95	15.7	7.87	-20.3	139.7	130	-3.16	13.4	0.32	14.8	0.4	2.2	50.3	27.7	19.9	0.0	1.42	0.0014
Y-5	G. W.	5040	Feb-7-96	19.6	7.82	-30.4	166.0	154	-2.94	11.3	0.32	20.0	1.4	2.4	75.4	20.7	20.3	0.0	1.88	0.0012
Y-5'	G. W.	5040	Oct-10-95	14.5	7.93	-21.7	135.3	124	-3.22	10.9	0.26	14.5	1.4	2.5	50.7	20.1	21.3	0.0	1.95	0.0015
Y-6	G. W.	5505	Feb-7-96	19.4	8.19	-52.3	167.5	150	-3.39	15.4	0.33	21.0	0.2	2.9	62.5	24.8	19.7	1.3	2.03	0.0030
Y-6'	G. W.	5505	Oct-10-95	15.3	7.95	-18.7	145.2	130	-3.27	14.5	0.20	14.2	0.2	2.5	47.2	24.8	25.0	0.0	1.07	0.0014
Y-7	G. W.	5560	Feb-7-96	19.6	8.13	-53.3	159.2	140	-3.35	12.5	0.27	19.9	0.3	1.9	60.7	22.3	21.2	0.0	1.37	0.0024
Y-7'	G. W.	5560	Oct-10-95	16.3	8.15	-27.5	123.1	124	-3.49	13.2	0.20	14.0	0.3	2.2	45.3	23.2	23.5	0.0	1.78	0.0023
Y-8	G. W.	5575	Feb-7-96	19.8	7.44	-7.4	167.8	150	-2.58	9.8	0.26	23.2	0.7	1.9	71.7	22.3	18.5	0.0	1.58	0.0006
Y-9	G. W.	5650	Feb-7-96	19.8	7.43	-6.8	169.2	149	-2.56	15.4	0.22	16.2	0.1	1.7	73.8	17.4	22.4	0.0	1.53	0.0005
Y-9'	G. W.	5650	Oct-10-95	15.2	8.02	-19.7	149.5	125	-3.29	15.9	0.31	12.2	0.1	2.1	52.7	16.6	23.8	0.0	1.81	0.0017
Y-10	G. W.	6140	Feb-7-96	18.1	7.72	-24.3	225.6	184	-2.80	12.1	0.23	26.8	2.7	3.6	82.7	29.3	23.2	2.2	1.59	0.0009
Y-10'	G. W.	6140	Oct-10-95	15.4	7.98	-22.3	159.3	168	-3.10	11.3	0.30	24.7	2.3	4.1	76.3	20.9	26.7	0.0	1.08	0.0014
Y-11	G. W.	6150	Feb-7-96	16.3	7.86	-32.8	190.4	184	-2.91	11.2	0.21	26.3	2.7	3.5	88.5	25.6	22.7	1.6	1.89	0.0012
Y-11'	G. W.	6150	Oct-10-95	17.9	7.72	-9.8	180.4	159	-2.86	10.7	0.32	21.6	2.3	3.7	71.5	19.4	27.7	0.0	1.92	0.0007
Y-12	G. W.	7700	Feb-7-96	19.1	7.30	-5.5	134.5	144	-2.41	9.5	0.31	19.4	0.6	1.7	75.8	12.3	21.3	0.0	2.62	0.0004
Y-13	G. W.	8000	Feb-7-96	20.9	7.06	15.4	145.8	151	-2.17	11.1	0.24	18.3	1.3	3.3	77.4	12.8	24.2	1.0	0.98	0.0002

*Calculated from alkalinity and pH using SOLVEQ (Reed, 1982)

**Calculated values in equilibrium with kaolinite from SOLVEQ (Reed, 1982)

microorganisms generally range from -30 to -20‰ (Deines, 1980; Drever, 1988). The preliminary $\delta^{13}\text{C}$ values of groundwater (-17.1 to -17.9‰) also may reflect the important role of organic carbon in the groundwater in this area.

The mean annual evapotranspiration in Korea has been reported to be about 600 mm (540-647 mm; KWRC, 1993). According to Brook *et al.* (1983), mean log P_{CO_2} value in soil under the annual evapotranspiration (AET) of 600 mm is about -2.26. This log P_{CO_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^+ (15.4 mg/L) and 0.52 mmole Ca^{2+} (21.0 mg/L) for a water sample (No. 6 in Table 1) 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 relationship between Eh and pH data (Figure 3) shows that Eh is decreased with increasing pH. Although it is intrinsically difficult to measure accurate redox potential in the field (Stumm and Morgan, 1981), this relationship may indicate the progressive reduction of Fe^{2+} with deeper circulation and associated pH increase. Because there is no clear relationship between redox potential and iron concentrations (Table 2 in Lee *et al.*, 1996), however, it is possible that the iron contents in water are controlled by organic complexation.

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 (Figure 4). Groundwaters seem to be equilibrated with kaolinite and montmorillonite, indicating that silica and aluminum in water are largely conserved by the formation of kaolinite and montmorillonite through incongruent dissolution of silicate minerals. Figure 4 also shows that waters in the Yeongcheon tunnel area are undersaturated with respect to calcite.

Table 2. Isotopic compositions of water samples collected from granite area within the Yeongcheon diversion tunnel

Sample no.	Sampling Date	Dis. from Portal (m)	$\delta^{18}\text{O}$ (‰)	δD (‰)	Tritium (TU)
Y-1	Feb-7-96	-	-9.05	-62.2	9.6
Y-1'	Oct-10-95	-	-7.20	-46.0	8.5
Y-2	Feb-7-96	-	-8.88	-61.0	9.1
Y-2'	Oct-10-95	-	-7.35	-48.2	7.6
Y-3	Feb-7-96	4270	-9.59	-66.2	1.1
Y-3'	Oct-10-95	4270	-9.52	-66.2	0.9
Y-4	Feb-7-96	4673	-9.51	-62.3	1.4
Y-4'	Oct-10-95	4673	-9.54	-65.3	0.7
Y-5	Feb-7-96	5040	-9.50	-66.0	1.1
Y-5'	Oct-10-95	5040	-9.56	-67.8	0.2
Y-6	Feb-7-96	5505	-9.41	-63.8	1.6
Y-6'	Oct-10-95	5505	-9.44	-65.9	1.0
Y-7	Feb-7-96	5560	-9.44	-63.7	3.1
Y-7'	Oct-10-95	5560	-9.51	-65.9	2.4
Y-8	Feb-7-96	5575	-9.48	-63.7	4.1
Y-8'	Oct-10-95	5650	-9.59	-66.1	3.2
Y-9	Feb-7-96	5650	-9.66	-70.0	0.2
Y-9'	Oct-10-95	5650	-9.62	-66.5	0.9
Y-10	Feb-7-96	6140	-9.16	-62.5	3.0
Y-10'	Oct-10-95	6140	-9.30	-66.2	2.0
Y-11	Feb-7-96	6150	-9.18	-63.2	3.3
Y-11'	Oct-10-95	6150	-9.36	-65.5	1.6
Y-12	Feb-7-96	7700	-9.38	-66.1	4.5
Y-13	Feb-7-96	8000	-9.37	-64.8	1.7
Y-13'	Oct-10-95	8000	-	-	1.1

Environmental Isotopes

The environmental isotopic compositions of waters sampled twice between Oct. 1995 and Feb. 1996 are summarized in Table 2. 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. Relationships between oxygen and hydrogen isotope compositions are plotted in Figure 5. All samples studied closely follow the worldwide meteoric water line (Craig, 1961), indicating that groundwaters flowing into 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 tunnel 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 2. 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 tunnel groundwaters represent the old meteoric waters recharged during pre-thermonuclear periods before 1953 (IAEA, 1992).

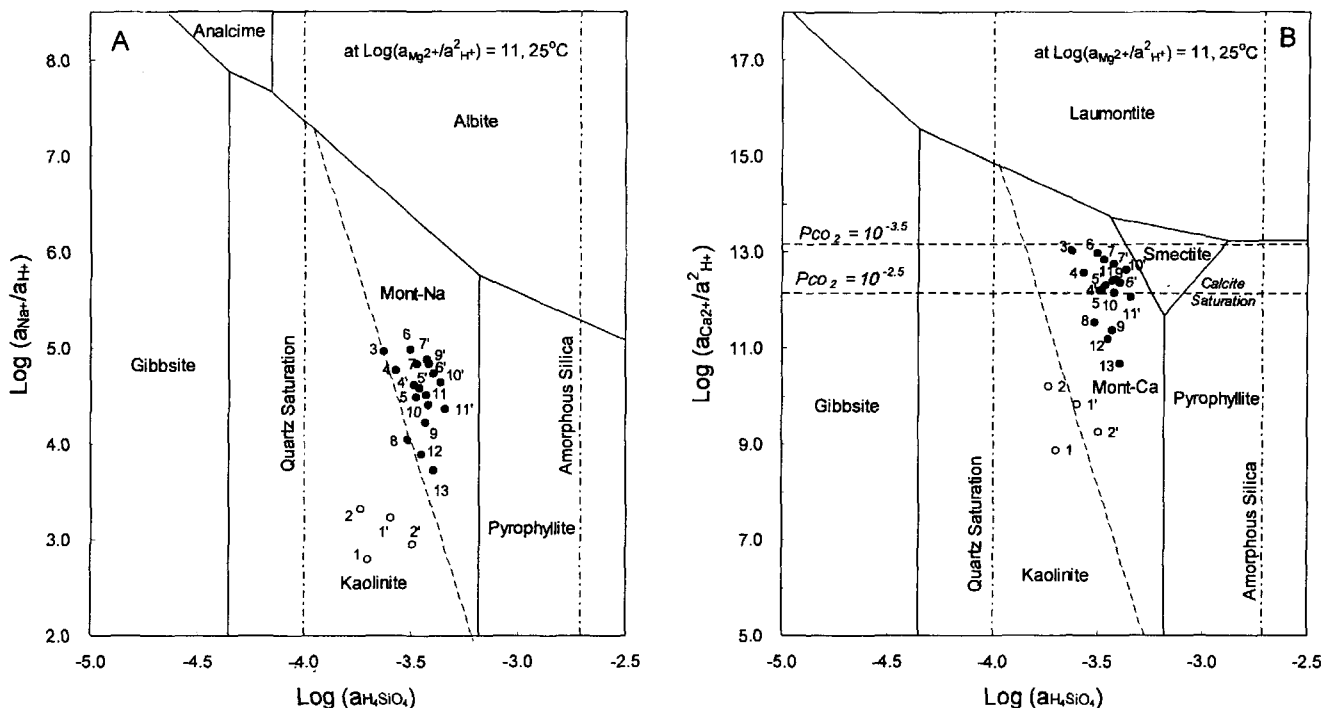


Figure 4. Stability diagrams for some minerals in the systems $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ (in A) and $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ (in B) at 25°C . Dashed lines represent the saturation of calcite at P_{CO_2} values of $10^{-3.5}$ and $10^{-2.5}$ atm. Thermodynamic data used are listed in Table 3. Solid circles = groundwaters discharged into tunnel; open circles = surface waters.

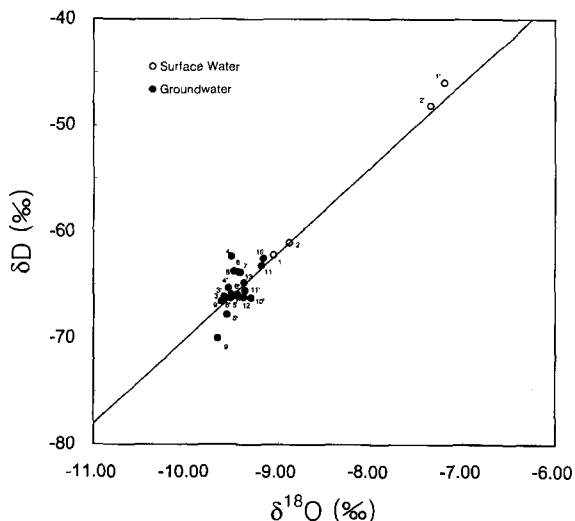


Figure 5. $\delta^{18}\text{O}$ versus δD diagram for water samples from the Yeongcheon diversion tunnel area. Meteoric water line from Craig (1961).

Some local tunnel 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 excavation 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 re-

present the mixing with rapidly downward flowing surface waters (about 10 TU).

Geochemical Simulation

Geochemical modeling for low-temperature groundwater-rock systems has been carried out by a number of geochemists (Grimaud *et al.*, 1990; Kenoyer and Bowser, 1992; Wolery and Daveler, 1992), in order to understand the water-rock interaction and related hydrogeochemical evolution.

In this study, we used the geochemical reaction program CHILLER (Reed, 1982) with adoption of thermodynamic data from EQ3/6 Version 7.2 (Wolery and Daveler, 1992). Table 3 summarizes the thermodynamic data for some minerals, which were used for the reaction simulation. The CHILLER is a Fortran program for computing multicomponent heterogeneous chemical equilibria among solids, gases and an aqueous phase (Reed, 1982), and applies a Newton-Raphson numerical method to solve a series of mass-balance and mass-action equations, together with a heat balance equation if needed (Reed, 1982; Reed and Spycher, 1984; Spycher and Reed, 1989). 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 repeated until the calculated assemblage is truly equilibrated. After this process, we can conduct particular model calculation includ-

Table 3. Dissociation-speciation reactions and corresponding equilibrium constants for some representative minerals and CO₂

Minerals	Reactions	Log K (25°C)	References
Gibbsite	$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$	7.756	1
Kaolinite	$Al_2Si_2O_5(OH)_4 + 6H^+ = 2Al^{3+} + 2SiO_2(aq) + 5H_2O$	6.8101	1
Chalcedony	$SiO_2 = SiO_2(aq)$	-3.7281	1
Albite	$NaAlSi_3O_8 + 4H^+ = Na^+ + Al^{3+} + 3SiO_2(aq) + 2H_2O$	2.7645	1
K-feldspar	$KAlSi_3O_8 + 4H^+ = K^+ + Al^{3+} + 3SiO_2(aq) + 2H_2O$	-0.2753	1
Muscovite	$KAl_3Si_3O_{10}(OH)_2 + 10H^+ = K^+ + 3Al^{3+} + 3SiO_2(aq) + 6H_2O$	13.5858	1
Laumontite	$CaAl_2Si_4O_{12}(4H_2O) + 8H^+ = Ca^{2+} + 2Al^{3+} + 4SiO_2(aq) + 8H_2O$	13.6667	1
Pyrophyllite	$Al_2Si_4O_{10}(OH)_2 + 6H^+ = 2Al^{3+} + 4SiO_2(aq) + 4H_2O$	0.4397	1
Montmorillonite-Mg	$Mg_{0.495}Al_{1.67}Si_4O_{10}(OH)_2 + 6H^+ = 0.495 Mg^{2+} + 1.67Al^{3+} + 4SiO_2(aq) + 4H_2O$	2.3879	2
Montmorillonite-Ca	$Ca_{0.165}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2 + 6H^+ = 0.165 Ca^{2+} + 0.33 Mg^{2+} + 1.67Al^{3+} + 4SiO_2(aq) + 4H_2O$	2.4952	2
Montmorillonite-K	$K_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2 + 6H^+ = 0.33K^+ + 0.33Mg^{2+} + 1.67Al^{3+} + 4H_2O + 4SiO_2(aq)$	2.1423	2
Montmorillonite-Na	$Na_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2 + 6H^+ = 0.33Na^+ + 0.33Mg^{2+} + 1.67Al^{3+} + 4H_2O + 4SiO_2(aq)$	2.4844	2
Analcime	$Na_{0.96}Al_{0.96}Si_{2.04}O_6 \cdot H_2O + 3.84H^+ = 0.96Al^{3+} + 0.96Na^+ + 2.0406SiO_2(aq) + 2.92H_2O$	6.1396	3
Chlorite	$Mg_5Al_2Si_3O_{10}(OH)_8 + 16H^+ = 2Al^{3+} + 3SiO_2(aq) + 5Mg^{2+} + 12H_2O$	67.2391	1
Quartz	$SiO_2 = SiO_2(aq)$	-3.9993	1
Beidellite-K	$K_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 7.32H^+ = 0.33K^+ + 2.33Al^{3+} + 3.67SiO_2(aq) + 4.66H_2O$	5.3088	4
Beidellite-Mg	$Mg_{0.165}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 7.32H^+ = 0.165Mg^{2+} + 2.33Al^{3+} + 3.67SiO_2(aq) + 4.66H_2O$	5.5537	4
Beidellite-Na	$2^+ + 2.33Al^{3+} + 3.67SiO_2(aq) + 4.66H_2O$	5.6473	4
Beidellite-Ca	$Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 7.32H^+ = 0.33Na^+ + 2.33Al^{3+} + 3.67SiO_2(aq) + 4.66H_2O$	5.5914	4
Calcite	$Ca_{0.16}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 7.32H^+ = 0.165Ca^{2+} + 2.33Al^{3+} + 3.67SiO_2(aq) + 4.66H_2O$	1.8487	1
CO ₂ (g)	$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$	-7.8136	1

1) Johnson *et al.*, 1992; 2) Wolery and Daveler, 1992; 3) Johnson *et al.*, 1982; 4) Wolery, 1978

Table 4. Saturation indices of representative secondary minerals of water samples collected from granite area within the Yeongcheon diversion tunnel

Sample no.	albite	anorthite	calcite	chalce	clino	K-feld	gibbsite	illite	laumon	mont-Ca	mont-K	mont-Na	mont-Mg	musco	phlogo	quartz
Y-1	-3.97	-10.89	-3.27	0.03	-21.15	-2.46	-0.65	-2.73	-5.38	-1.13	-1.83	-1.07	-1.66	-2.11	-14.39	0.30
Y-1'	-3.33	-9.94	-2.74	0.13	-16.41	-1.89	-0.75	-2.16	-4.22	-0.43	-1.16	-0.37	-0.97	-1.75	-11.04	0.40
Y-2	-3.51	-9.58	-2.46	-0.01	-15.54	-1.86	-0.62	-2.08	-4.14	-0.62	-1.31	-0.59	-1.20	-1.44	-10.40	0.26
Y-2'	-3.39	-10.51	-3.18	0.23	-19.90	-1.84	-0.86	-2.31	-4.59	-0.52	-1.21	-0.48	-1.06	-1.90	-13.14	0.51
Y-3	-1.65	-6.75	-0.50	0.10	-3.91	-0.61	-0.72	-0.76	-1.09	0.86	0.04	0.80	0.36	-0.40	-2.24	0.37
Y-4	-1.74	-7.19	-0.26	0.16	-9.76	-0.62	-0.78	-1.07	-1.42	0.53	-0.26	0.35	0.03	-0.53	-5.79	0.43
Y-4'	-1.73	-7.56	-0.62	0.24	-9.69	-0.54	-0.86	-1.01	-1.63	0.65	-0.10	0.53	0.17	-0.61	-5.72	0.51
Y-5	-1.83	-7.54	-0.37	0.25	-7.47	-0.57	-0.87	-0.92	-1.59	0.82	0.05	0.78	0.30	-0.66	-4.42	0.52
Y-5'	-1.70	-7.44	-0.56	0.27	-6.30	-0.51	-0.89	-0.83	-1.46	0.96	0.18	0.93	0.45	-0.64	-3.68	0.54
Y-6	-1.38	-6.78	-0.07	0.22	-8.05	-0.24	-0.84	-0.75	-0.88	0.85	0.08	0.66	0.37	-0.28	-4.42	0.49
Y-6'	-1.42	-7.42	-0.58	0.33	-10.28	-0.47	-0.96	-1.01	-1.29	0.86	0.04	0.69	0.39	-0.73	-6.06	0.61
Y-7	-1.46	-6.92	-0.16	0.26	-7.70	-0.32	-0.88	-0.78	-0.95	0.93	0.14	0.77	0.42	-0.42	-4.31	0.53
Y-7'	-1.33	-7.02	-0.41	0.30	-7.42	-0.34	-0.92	-0.78	-0.97	1.03	0.22	0.90	0.55	-0.53	-4.19	0.57
Y-8	-2.35	-8.23	-0.71	0.21	-12.82	-1.11	-0.84	-1.51	-2.35	0.28	-0.53	0.17	-0.28	-1.13	-8.15	0.48
Y-9	-1.99	-8.40	-0.85	0.30	-17.01	-1.03	-0.92	-1.68	-2.35	0.16	-0.65	-0.06	-0.31	-1.21	-10.63	0.57
Y-9'	-1.35	-7.34	-0.53	0.31	-11.06	-0.25	-0.93	-0.92	-1.26	0.76	0.02	0.56	0.32	-0.47	-6.3	0.58
Y-10	-1.79	-7.62	-0.32	0.31	-7.07	-0.70	-0.93	-0.98	-1.55	0.97	0.13	0.95	0.44	-0.91	-4.34	0.58
Y-10'	-1.45	-7.13	-0.12	0.36	-4.70	-0.21	-0.99	-0.57	-0.95	1.33	0.54	1.31	0.79	-0.53	-2.47	0.63
Y-11	-1.71	-7.35	-0.16	0.29	-5.69	-0.62	-0.92	-0.87	-1.31	1.08	0.23	1.06	0.53	-0.81	-3.43	0.57
Y-11'	-1.68	-7.70	-0.46	0.38	-7.26	-0.40	-1.01	-0.82	-1.48	1.12	0.34	1.10	0.58	-0.76	-4.2	0.66
Y-12	-2.37	-8.58	-0.89	0.27	-14.43	-1.05	-0.90	-1.56	-2.57	0.26	-0.52	0.15	-0.30	-1.19	-9.09	0.55
Y-13	-2.43	-9.09	-1.15	0.33	-15.10	-1.29	-0.95	-1.74	-2.97	0.26	-0.55	0.21	-0.27	-1.54	-9.76	0.60

Abbreviations: chalce=chalcedony, clino=clinochlore, feld=feldspar, laumon=laumontite, mont=montmorillonite, musco=muscovite, phlogo=phlogopite

ing cooling, heating, boiling, condensation, mixing, water-rock titration, and evaporation under either open or closed system conditions.

Chemical speciation of groundwater samples was calculated using the aqueous speciation program SOLVEQ (Reed,

1982), in order to eliminate the reactions which are invalid thermodynamically. Table 4 shows the calculations of the degree of saturation of groundwater with respect to various minerals. Within the uncertainties of ±1 in log K values, it is clear that groundwater in the Yeongcheon tunnel area is

Table 5. Composition of the reactant minerals used for geochemical modeling of evolution of groundwater in granite area

Minerals	Compositions	Vol.%	Chemical Formula	Formula weight	Wt.%
Quartz/Biotite	SiO ₂	25.2	SiO ₂	60.08	3
K-feldsp	Ann ₅₀ Ph ₅₀	5.9	KMg _{1.5} Fe _{1.5} AlSi ₃ O ₁₀ (OH) ₂	464.59	7
Plagioclase	KAlSi ₃ O ₈	30.6	KAlSi ₃ O ₈	278.33	9
Opagues	Ab ₈₅ An ₁₅	30.7	NaAlSi ₃ O ₈	262.22	47
Accessory*	-	3.6	CaAl ₂ (SiO ₄) ₂	278.21	9
pyrite	-	4.0	-	-	-
calcite	FeS ₂	-	-	-	-
CO ₂ (aq)	CaCO ₃	-	FeS ₂	119.98	4

*Accessory minerals include chlorite, sphene, apatite, zircon, sericite and iron oxides

Table 6. Chemical composition of rainwater used as an initial solution of water/rock (granite) interaction (after Berner and Berner, 1987) (unit: mg/L)

pH*	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	SiO ₂ **	Al**	Cl ⁻	SO ₄ ²⁻	HCO ₃ ^{-*}
5.67	1.1	0.26	0.97	0.36	0.001	0.001	1.2	4.5	0.76

*Calculated values when water is in equilibrium with air

**Assumed values for geochemical modeling

undersaturated with respect to most igneous rock-forming minerals. Major rock-forming minerals in 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 the Ca²⁺ and SO₄²⁻ concentrations in groundwater (see WATER CHEMISTRY).

The dissolution of quartz is so slow that it shows little tendency for weathering (Garrels and Mackenzie, 1967; Cleaves *et al.*, 1970; Freeze and Cherry, 1979; Siegel and Pfannkuch, 1984). 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 (Gislason and Eugster, 1987; Schnoor, 1990; Velbel, 1992), the data are very inconsistent. Moreover, discrepancies of up to four orders of magnitude between field estimates and laboratory measurements have been documented (Brantley, 1992). In this study, we fitted the reactant minerals in the geochemical simulation (Table 5), based on considerations of mineral abundance, saturation states, and reaction kinetics.

In order to simulate the geochemical evolution of Yeongcheon groundwater, rain water (see Table 6 for the chemistry) was reacted with granite. In this calculation, the CO₂ concentration in reactant water was set to be 10^{-2.17} atm (see WATER CHEMISTRY). The results of simulation are plotted in Figures 6 and 7.

The continuous adding of granite (reactant minerals) to rain water causes precipitation of minerals in the following sequence: hematite, then gibbsite, then kaolinite, then montmorillonite, then illitic material, and then microcline (Figure 6). The solution first equilibrates with hematite and gibbsite, after only 10⁻⁴ grams of reactant minerals are added. By adding 10⁻² grams of reactant minerals, the solution

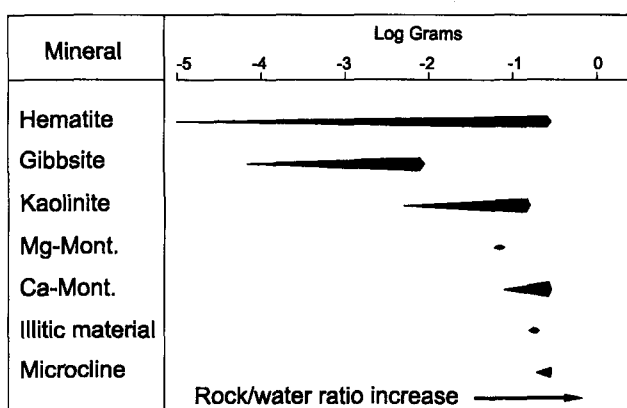


Figure 6. A diagram showing the formation sequence of secondary minerals in groundwater during progressive water/rock (granite) evolution. Line width correspond to relative abundance. See text for explanation.

becomes undersaturated with respect to gibbsite and is saturated with kaolinite. Then, the equilibrium phase is changed to illitic material if 10^{-1.5} grams of reactant minerals is added. It is noteworthy that the kinds of precipitating minerals correspond well with the observed mineralogy in fractures (Lee *et al.*, 1996).

Figure 7 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⁺, Ca²⁺ and HCO₃⁻ 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 Mg²⁺ and K⁺ concentrations in solution increase slowly with increasing water/rock interaction, but then decrease with precipitation of montmorillonite,

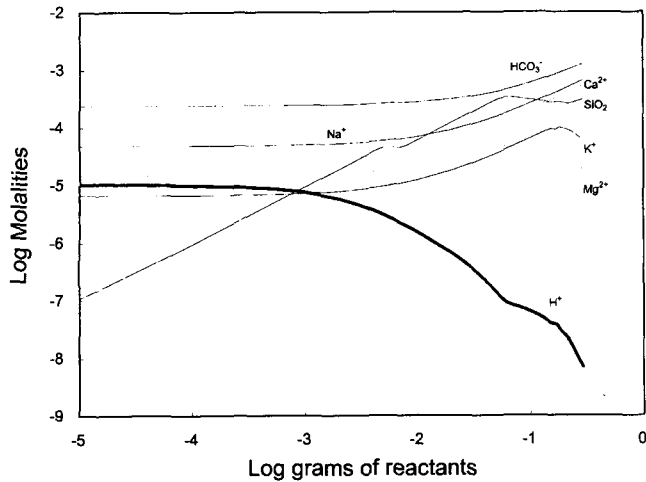


Figure 7. Results of geochemical simulation, showing compositional variations (in molalities) of major dissolved ions and SiO₂ in groundwater during the progressive water/rock (granite) interaction. See text for explanation.

illitic material and K-feldspar (Figure 7). Dissolved silica increases as a whole due to the dissolution of silicate minerals, but decreases slightly in response to the successive precipitation of montmorillonite, illitic material and microcline. The results of simulation match well with measured physicochemical data (as an example, see Table 7). 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.

In the simulation, chemical evolution of groundwater is modeled under both the closed CO₂ and the fully open CO₂ conditions (Table 7). Under closed CO₂ conditions, the pH rapidly rises far above the measured values, while P_{CO2} and ion concentrations are much lower. Under completely open CO₂ conditions, on the other hand, the simulated pH is too low and P_{CO2} high. Therefore, we consider that the evolution

Table 7. Comparison between actual physicochemical data (sample no. 6) and simulated data (unit: mg/L)

Compositions	Actual	Simulated data		
	Y-6	partially CO ₂	CO ₂ close	Fully CO ₂
pH	8.19	8.16	9.11	8.25
Temp. (°C)	19.4	25.0	25.0	25.0
Na ⁺	15.4	15.1	15.5	15.6
K ⁺	0.33	2.37	0.56	3.8
Ca ²⁺	21.0	21.4	7.8	22.1
Mg ²⁺	0.2	0.5	0.01	0.5
SiO ₂	19.7	18.2	1.54	19.0
HCO ₃ ⁻	62.5	76.8	23.7	96.3
SO ₄ ²⁻	24.8	24.5	25.1	25.1
P _{CO2}	10 ^{-3.39}	10 ^{-3.32}	10 ^{-4.81}	10 ^{-3.50}

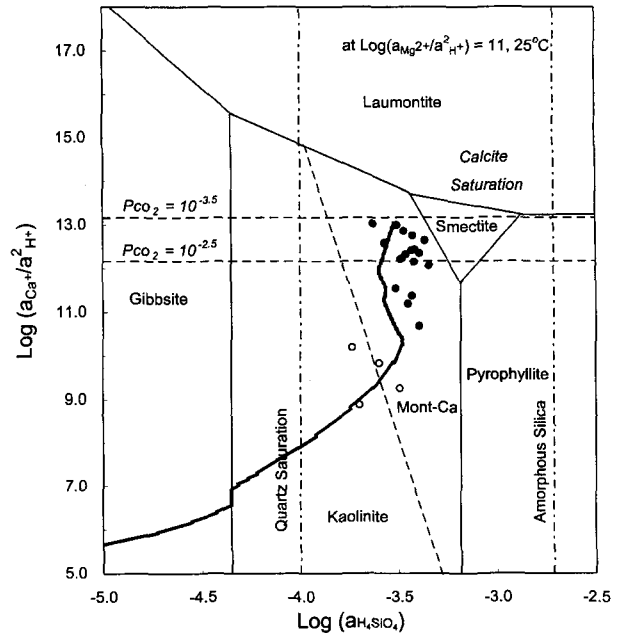


Figure 8. Stability diagrams for some minerals in the system CaO-Al₂O₃-SiO₂-H₂O at 25°C, showing the probable path (thick solid line) of groundwater evolution due to water/rock (granite) interaction. Solid circles=groundwaters discharged into tunnel; open circles=surface waters discharged into the tunnel.

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 (Figure 8). 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 8 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.

Conclusions

The bedrock groundwaters discharged into the Yeongcheon diversion tunnel in biotite granite chemically belong to Ca-HCO₃ type, and are controlled by the water/rock interaction. The hydrogeochemical evolution of groundwater occurs as a result of progressive reaction with the silicate minerals and hydrothermal fracture-filling calcite under partially CO₂ open conditions. 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 the waters have been recharged during pre-thermonuclear period (before 1953). However, some groundwaters with higher tritium contents (up to 4.5 TU) include the mixing of younger superficial water.

Geochemical reaction modeling using CHILLER is undertaken to identify the processes which control the chemical evolution of groundwater. The pH, Na⁺ and Ca²⁺ concentrations increase progressively due to the progressive dissolution of silicate minerals and calcite, whereas the K⁺ and Mg²⁺ concentrations first increase but decrease later through the precipitation of illitic material and microcline and Mg-bearing minerals such as clay. The results of modeling approximate to actual pH, alkalinity, and major ion concentrations of waters. By fitting some reactant minerals on the basis of mineral abundances, saturation states and dissolution kinetics, model calculations were conducted under partial CO₂ open conditions, and could trace the chemical evolution of groundwater. Under either fully open CO₂ or closed CO₂ conditions, on the other hand, the results do not match the measured pH and chemistry data.

Calcite and some zeolites have been reported to occur in fractures acting as conduits of groundwater flow, and are unlikely to have formed by water/rock interaction. Both the ion speciation calculation and the carbon isotope values indicate that calcite is not precipitated from groundwater and is of hydrothermal origin. Zeolites also have formed from ancient hydrothermal fluids, because the groundwaters are undersaturated with respect to zeolites.

Calculated K⁺ concentrations based on geochemical modeling of water/rock interaction are higher than actual analytical data. This discrepancy may be due to uncertainties of clay minerals such as montmorillonite. If K-bearing montmorillonite is equilibrated (precipitated from) in solution during the reaction, the potassium ion concentrations would be lowered, and its formation would prevent the precipitation of illitic material and microcline. Silica concentrations in groundwater are higher than the solubilities of quartz or chalcedony, indicating that silica concentrations are controlled by dissolution of metastable aluminosilicate minerals.

Under partially CO₂ open conditions, geochemical modeling on water/rock(granite) interaction and hydrogeochemical evolution was carried out with fitting of reactant minerals to match the water chemistry on the basis of mineral abundance and saturation states. Although this approach neglects the dissolution and precipitation kinetics of silicate minerals and, therefore, 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 reasonable 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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