Groundwater Chemistry in Granitic Rock Area Interpreted in Terms of a Coupled Fluid Flow-Dissolution and Precipitation Kinetics Model

Naotatsu Shikazono[1]* and Koichiro Fujimoto[2]

[1] Department of Applied Chemistry, Faculty of Science and Technology, Keio University
[2] Geological Survey of Japan, Ministry of Trade and Industry

Abstract

The chemical composition of shallow groundwater in the granitic rock area (Tsukuba-Kaba area, central Japan ; Kamaishi mine, northern Japan) was determined. Thermochemical calculations on the concentrations of Si, Na, K, Ca, H^+, and HCO_3^- in shallow groundwater (Tsukuba-Kaba area, central Japan) in equilibrium with silicate minerals in granitic rocks indicate that the equilibrium between shallow groundwater and silicate minerals (feldspars, kaolinite, amorphous silica) is not attained. Therefore, a coupled fluid flow-dissolution kinetics model was applied to interpret the chemical composition of shallow groundwater. Assuming reasonable values of residence time, solubilities (equilibrium concentration), and dissolution rate of Na·Ca feldspar, the ratio of the surface area of rock to the mass of water (A/M) for shallow groundwater was estimated to be 0.15~8.7. The width of a fracture in a granitic rock is estimated to be 0.2 mm~2 cm, considering estimated A/M and uncertainty of parameter values. The estimated value of the width is much wider than that obtained by pore sizes experimentally determined using the mercury intrusion method for a hand-specimen scale granitic sample, which is $n \times 10^{-1} \mu m$. It is suggested that the interaction of groundwater and country rocks takes place dominantly on the surface of a fracture with a width of ca. 2 mm and the chemical composition of groundwater is controlled by such interaction and fluid flow in the fracture.

Silica concentration of deep groundwater in the granitic rock area (Kamaishi, northern Japan) is in equilibrium with SiO_2 mineral (chalcedony). Based on a coupled fluid flow-dissolution-precipitation kinetics model the relationship between residence time of deep groundwater and A/M was derived, and the residence time for reasonable values of A/M (1) is estimated to be more than 40 years.

Key words : Groundwater, Dissolution rate of feldspar, Precipitation rate of SiO_2, Groundwater flow, Kinetics, Granite, Water-rock interaction

1. Introduction

A large number of studies on the chemical compositions of groundwater have been carried out from a thermochemical equilibrium point of view (e.g., Garrels, 1967 ; Drever, 1988, Appelo and Postma, 1993, Shikazono, 2001a). However, the rate of shallow groundwater interaction with country rocks is usually slow and the flow rate of shallow groundwater is high. These factors cause a chemical equilibrium between groundwater and minerals.

Recently, several studies intended to interpret hydrothermal alteration and chemistry of geothermal waters based on a coupled fluid flow-reaction kinetics model have been carried out (Rimstidt and Barnes, 1980). However, few studies on the interpretation of groundwater chemistry based on the fluid flow-reaction kinetics model have been done (Shikazono and Fujimoto, 1996 ; Shikazono, 2001b).

In this paper, an attempt is made to interpret the chemical composition of shallow and deep ground-

* e-mail: sikazono@applc.keio.ac.jp (3-14-1, Hiyoshi, Kohoku-ku, Yokohama 223-8521 Japan)
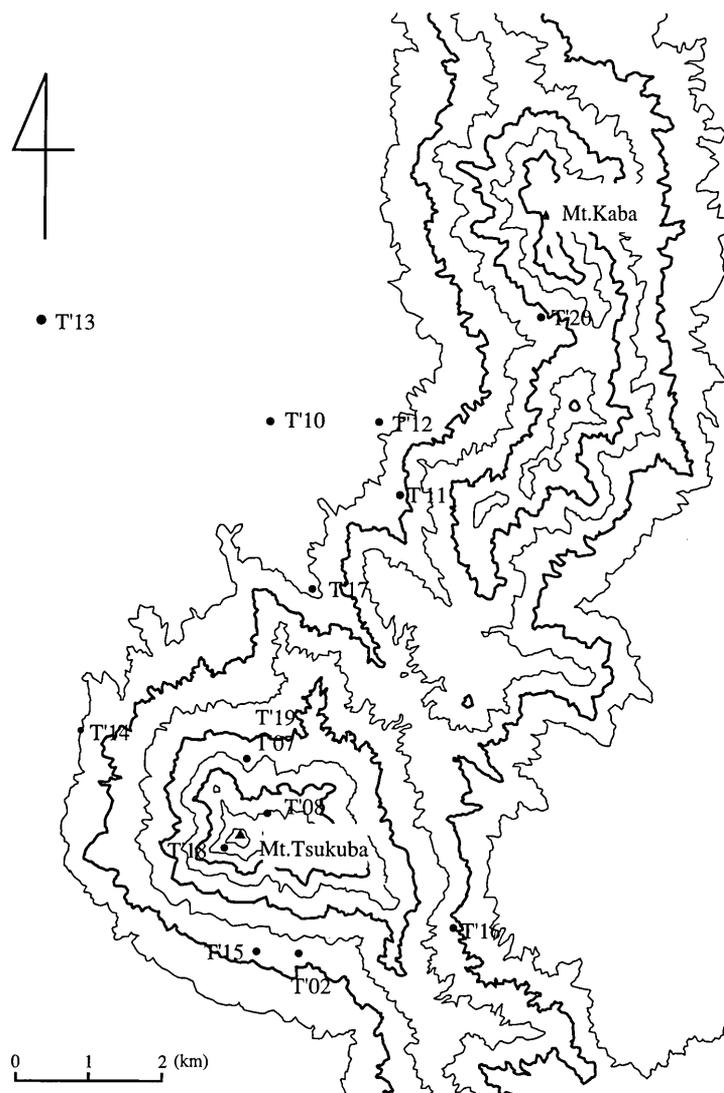
Fig. 1. Locality where samples were collected from the Tsukuba–Kaba granitic area. Elevation of samples collected is shown in Table 1.

waters in granitic rock areas (Tsukuba-Kaba, central Japan and Kamaishi, northern Japan) in terms of this model. Several parameters control the change of groundwater chemistry with time and degree of water-rock interaction. Among them A/M (the ratio of surface area of rock (A) to mass of water (M)) and residence time are considered to be the most uncertain parameters. Therefore, this ratio and residence time are estimated using the chemical composition of groundwater and assuming reasonable values for other parameters (rate of dissolution and precipitation, solubilities), which have been experimentally determined (e.g., Lasaga, 1997).

2. Chemical composition of shallow groundwater and interpretation; A case study on Tsukuba-kaba granitic rock area

2-1. Groundwater chemistry

The Tsukuba-Kaba area is located at a central part of Honshu, Japan. The area is mainly composed of late Cretaceous granitic rocks. The general geology of this area was studied by Takahashi (1980). Granitic rock is two mica granite. Dominant constituent minerals are feldspar, quartz, biotite, and muscovite. The surface of granitic rock is usually weathered.

Groundwater samples from the Tsukuba-Kaba mountain range were collected and analyzed. The locality of the sample analyzed is shown in Fig. 1. These analytical data together with the elevation of the samples collected are summarized in Table 1. Analytical data are plotted in $\log[Ca^{2+}]+2\,pH\text{-}\log[H_4SiO_4]$ diagram (Fig. 2). The data on the chemical compositions of groundwater are plotted for the kaolinite region, indicating that the groundwater is not

Table 1. Locality (elevation) and chemical composition of groundwater collected from the Tsukuba–Kaba granitic rock area.

| Loc.	A (m)	pH	Na (mol/l)	K (mol/l)	Ca (mol/l)	Mg (mol/l)	HCO_3^- (mol/l)	SiO_2 (mol/l)	SO_4 (mol/l)	Cl (mol/l)	NO_3 (mol/l)
T'13	-170	7.62	0.001018	0.000135	0.000245	0.000156	0.000488	0.000827	1.8E-05	0.000143	5.81E-07
T'10	-30	6.46	0.002436	0.000281	0.000414	0.000263	0.000629	0.00026	0.000279	0.001373	0.000359
T'12	60	7.44	0.000644	4.17E-05	0.000105	4.94E-05	0.000197	0.000538	3.52E-05	0.000171	7.15E-05
T'14	80	7.66	0.000766	6.88E-05	0.000255	8.23E-05	0.000285	0.000475	0.000127	0.000237	0.000177
T'11	90	5.93	0.000565	3.56E-05	4.49E-05	3.29E-05	0.000734	0.00052	3.89E-05	0.000204	2.34E-05
T'17	130	7.19	0.00531	5.88E-05	0.000185	8.23E-05	0.000318	0.000542	2.63E-05	0.000136	0.00014
T'16	230	7.51	0.0004	4.17E-05	8.98E-05	4.94E-05	0.000167	0.000375	3.7E-05	0.000211	0.000123
T'15	240	6.94	0.000713	5.27E-05	0.000409	0.000214	0.000472	0.00051	6.02E-05	0.000278	3.28E-05
T'02	250	6.11	0.000774	4.96E-05	0.000294	9.87E-05	0.000737	0.000575	9.68E-05	0.000307	
T'20	400	7.43	0.000383	6.78E-05	7.49E-05	3.29E-05	0.000279	0.000242	5.98E-05	7.01E-05	2.53E-05
T'19	460	7.62	0.000174	1.99E-05	8.98E-05	7.41E-05	0.000144	0.000207	2.22E-05	0.00011	7.1E-05
T'18	750	7.65	0.00027	5.88E-06	5.49E-05	4.94E-05	7.87E-05	0.000118	5.49E-05	0.000143	9.72E-05
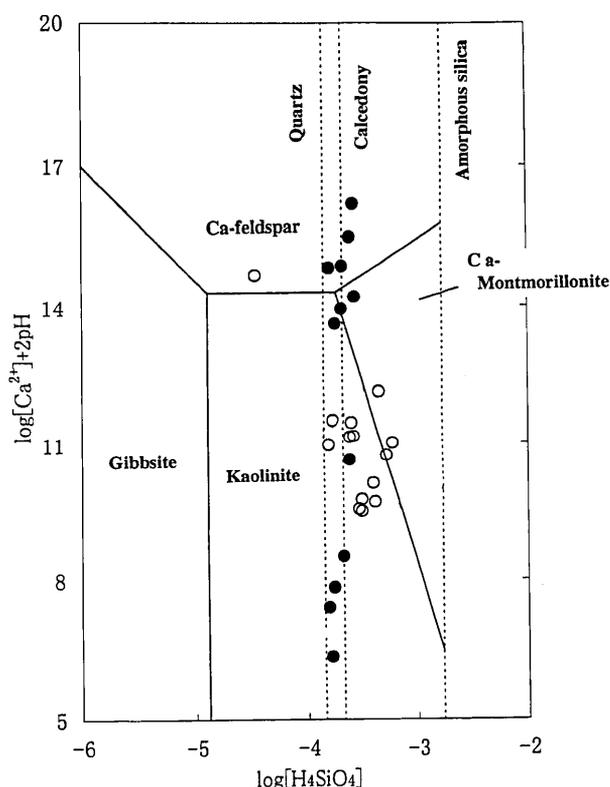
Fig. 2. Chemical compositions of groundwater from the Tsukuba–Kaba area (open circle) and underground in the Kamaishi mine (solid circle) plotted on $\log[Ca^{2+}]+2\,pH$-$\log[H_4SiO_4]$ diagram (Data sources: open circle, this study (Tsukuba–Kaba), solid circle, JNC (1999) (Kamaishi)).

in equilibrium with the common primary and secondary silicate minerals in granitic rocks (feldspars, quartz, amorphous silica, Ca-montmorillonite).

Fig. 3 shows the variation of groundwater chemistry with elevation (meters above sea level). There seems to be a tendency for cation (Na^+, Ca^{2+}, Mg^{2+}, K^+) and Si concentrations to increase towards a lower elevation. This relationship demonstrates that these concentrations are controlled dominantly by water-rock interaction (dissolution rate, precipitation rate, degree of water-rock interaction).

2-2. Estimate of A/M based on a coupled fluid flow-dissolution kinetics model

A coupled fluid flow-dissolution kinetics model was used to interpret the chemical composition of groundwater. It was assumed that a given mineral dissolves due to the interaction with flowing groundwater in a uniformly mixed reservoir. The change of concentration in groundwater in a reservoir with time is represented by the following equation (Shikazono and Fujimoto, 1996).

$$dC/dt = k\,(A/M)\,(C_{eq}-C)/C_{eq} + q/V\,(C_i-C) \qquad (1)$$

in which C : concentration (mole/kg·H_2O), t : time (sec), k : dissolution rate constant (mole m^{-2} s^{-1}), A/M : surface area of mineral/mass of water ratio (m^2/kg ·H_2O), q : volume flow rate of groundwater (m^{3}s^{-1}), C_{eq} : saturation concentration (mole/kg·H_2O), V : volume of reservoir (m^3), C_i : initial concentration of input water (mole/kg·H_2O).

Rainwater is regarded as input water. Average concentrations of Japanese rainwater are negligible compared to groundwater. and it is assumed that C_i in equation (1) is zero. Therefore, equation (1) is converted into,
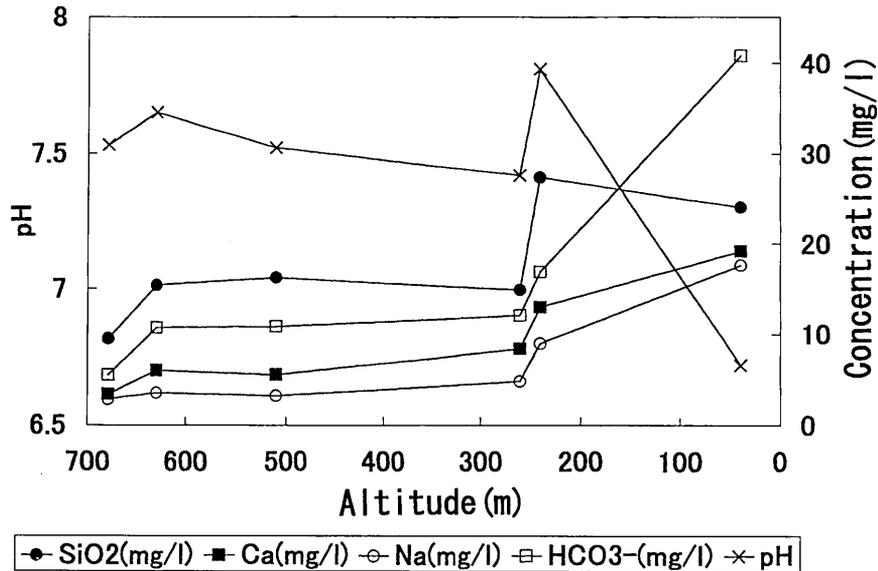
Fig. 3. Variations in chemical compositions of groundwater with elevation (meters above sea level) from the Tsukuba granitic rock area.

$$dC/dt = k(A/M)(C_{eq} - C)/C_{eq} - (q/V)C \qquad (2)$$

We can solve differential equation (2) for the initial concentration, $C(0) = 0$ as,

$$C/C_{eq} = (b/a)(e^{at} - 1) \qquad (3)$$

in which $a = [-k(A/M)/C_{eq} + q/V]$ and $b = k(A/M)$

Equation (3) implies that the concentration of groundwater is represented as a function of C_{eq}, k, A/M, t and q/V ($1/\tau$). In calculations it is possible to restrict the ranges of the above parameter values and it is assumed that τ is equal to t.

A/M : It is difficult to estimate A/M, but it is generally accepted that A/M is in the range of $10-10^4$ for a geothermal system (Rimstidt and Barnes, 1980).

q/V : V/q is equal to τ(residence time). That of shallow groundwater in a granitic rock area in Japan is estimated to be 1–10 years (Shimada, 1985).

k : A large volume of dissolution rate data on silicate minerals is available (e.g., Lasaga, 1984; Sverdrup, 1990). The dominant minerals in the Tsukuba-Kaba granitic rocks are feldspar, quartz, and mica (biotite and muscovite). Among these minerals, feldspar is the most abundant. Its dissolution rate is considerably higher than quartz and mica (Sverdrup, 1990). Therefore, the dissolution rate constant of feldspar was used for the calculation. Rate constant depends on pH. pH of groundwater in the Tsukuba-Kaba area is 6.5–7.5 (Table 1). The dissolution rate constants of Ca-feldspar, K-feldspar, and Na-feldspar in pH = 6.5–7.5 are 10^{-11}, 10^{-12} and 10^{-12}, respectively (Sverdrup, 1990). Based on the rate constant experimentally determined and the chemical composition of feldspar obtained by EPMA (Na : Ca = 6 : 4), k is assumed to be $10^{-11.5}$.

C_{eq} : The solubilities of feldspars in equilibrium with kaolinite can be calculated using the method of Stumm and Morgan (1970).

If Na-feldspar is in equilibrium with kaolinite, from the following reaction,

$$Na\text{-feldspar} + CO_2(gas) + 11/2H_2O$$
$$= Na^+ + HCO_3^- + 2H_4SiO_4 + 1/2kaolinite \qquad (4)$$
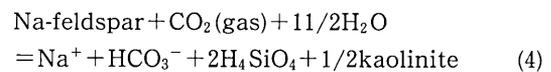
we obtain,

$$K_4 = (C_{Na^+} C_{HCO3^-} C^2_{H_4SiO_4})/(P_{CO_2} X_{Naf}) = 10^{-9.7}$$
$$(5)$$

in which K_4 : equilibrium constant of reaction (4), C : concentration (mole/kg·H_2O), P_{CO2} : partial pressure of CO_2 (atm) and X_{Naf} : mole fraction of Na-feldspar component in Na·Ca feldspar solid solution.

If dominant cation and anion are Na^+ and HCO_3^-, respectively, the electroneutrality relation can be approximated as,

$$C_{Na^+} = C_{HCO_3^-} \qquad (6)$$
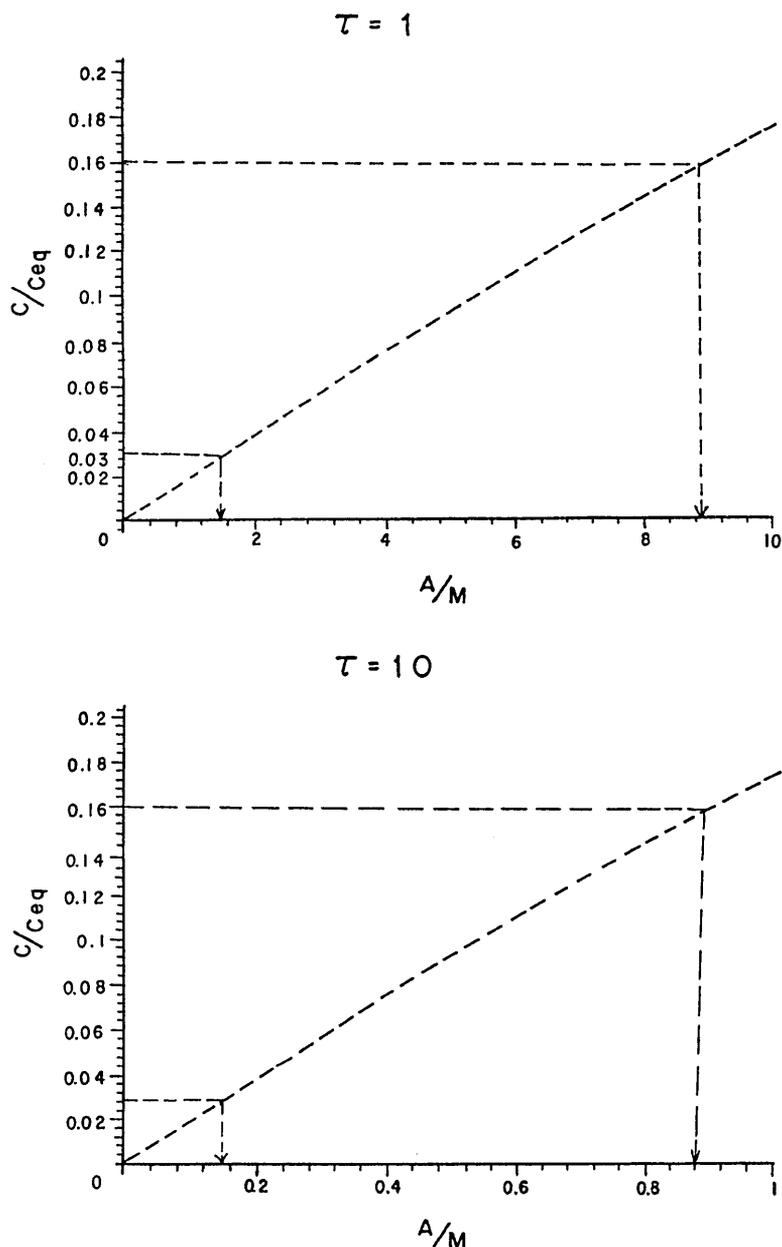
Stoichiometric relation for reaction (4) is written as,

$\tau = 1$

$\tau = 10$

Fig. 4. The relationship between C/C_{eq} and A/M based on the uniformly mixed flow-dissolution kinetics model. τ : residence time (in year).

$$C_{Na^+} = 1/2 C_{H_4SiO_4} \tag{7}$$

From (5), (6), and (7), we obtain,

$$C_{H_4SiO_{4eq}} = 2(K_4 P_{CO_2} X_{Naf}/4)^{1/4} \tag{8}$$

It is likely that CO_2 is open to the atmosphere in a shallow groundwater system and P_{CO_2} is $10^{-3.5}$ atm, which is the atmospheric value. P_{CO_2} can be estimated from the equilibrium relation for the reaction,

$$HCO_3^- + H^+ = H_2O + CO_2 \tag{9}$$
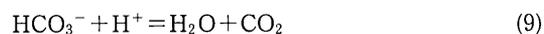
Equilibrium constant of reaction (9) (K_9) is,

$$K_9 = P_{CO_2}/C_{HCO_3^-} C_{H^+} = 10^{-7.8} \tag{10}$$

We measured $C_{HCO_3^-}$ and C_{H^+} (pH). Thus, putting these values, we obtain P_{CO_2}. Average P_{CO_2} is $10^{-3.5}$.

$C_{H_4SiO_{4eq}}$ estimated from equation (8) is $10^{-2.8}$. $C_{H_4SiO_{4eq}}$ can be also estimated from the saturation concentration for amorphons silica. This $C_{H_4SiO_{4eq}}$ is $10^{-2.5}$ (Drever, 1988).

The ratio, C/C_{eq}, for Si was calculated (Fig. 4) from the estimated $C_{H_4SiO_{4eq}}$ and the analytical data on H_4SiO_4 in groundwater given in Table 1. We can estimate A/M from these values and the relationship between A/M and C/C_{eq} theoretically derived. The

estimated A/M for $\tau=1$ year and 10 years are 0.15~8.7 and 0.15~0.87, respectively (Fig. 4). Using the relationship, $A/M=2\,V_{sp}/(1000\,W)$ in which V_{sp} : specific volume of water (cm³/gm), W : width of fracture in the rock (Rimstidt and Barnes, 1980 ; Phillips, 1991), and, for example, if we assume $A/M=1$ and $V_{sp}=1$, the width of a fracture is estimated to be 2 mm. This estimated value has an uncertainty of ± 1 in logarithmic units. Considering uncertainties of analytical, and thermochemical data and parameter values, and assumptions we have used for the calculations, the probable range of a width fracture is 2 cm $-$ 2×10^{-1} mm.

Hayashi *et al.* (1995) obtained the pore distribution size of Inada granitic rocks occuring near the Tsukuba-Kaba granitic rock area by a mercury intrusion method. Average pore size estimated by them is $n\times 10^{-1}\mu$m. This is much smaller than the value estimated by the present study. This inconsistency indicates that groundwater chemistry is not influenced by such microfractures with $n\times 10^{-1}\mu$m width, but a fracture with wider width of 10^{-1}~10 mm is important as the shallow groundwater pass media and the factor controlling the groundwater chemistry.

In previous studies, it has been cited that the experimentally determined dissolution rate of silicate minerals is inconsistent with field data (e.g., Paces, 1983 ; Velbel, 1985; Schnoor, 1990; Clow, 1992) (Table 2).

However, the present study suggests that one possible inconsistency is due to the uncertainty of the estimate of A/M for the groundwater-rock system in the field. This study indicates that if A/M is precisely estimated, laboratory data on the dissolution rate are consistent with field data. Groundwater flows in restricted parts of whole rock, namely, a fracture with a width of $n\times 10^{-1}\mu$m and most of the surface of granitic rocks do not contact with and interact with groundwater.

In previous field studies on the dissolution rate of feldspar, A/M has not been precisely estimated. Claasen and White (1979) mentioned that the dissolution rate of tuff estimated by a field study is slower that the laboratory data, and this discrepancy is considered to be due to the importance of fractures as pass media of groundwater flow. The present study is consistent with the study of Claasen and White (1979).

3. Chemical composition of deep groundwater and interpretation : a case study in Kamaishi area, northern Japan

Kamaishi mine is located in Kitakami, northern

Table 2. Dissolution rate of silicate minerals estimated from field and experimental studies (Si molm⁻²s⁻¹).

Mineral	Laboratory dissolution (mol Si m⁻²s⁻¹)	Fieldestimate dissolution rate (mol Si m⁻²s⁻¹)	Cations	Notes	References
Plagioclase (oligoclase)	5×10^{-12} [a]	3×10^{-14}	Na^+	Trnavka River Basin(CZ)	Paces (1983)
Plagioclase (oligoclase)	5×10^{-12} [a]	8.9×10^{-13}	Na^+, Ca^{2+}	Coweeta Watershed, NC(USA)	Velbel (1985)
Almandine		3.8×10^{-12}	Mg^{2+} Ca^{2+}		
Biotite		1.2×10^{-13}	K^+, Mg^{2+}		
Plagioclase (bytownite)	5×10^{-12}	5×10^{-15}	Ca^{2+}, Na^+	Filson Creek, MN (USA)	Siegel and Pfannkuch(1984)
Olivine	7×10^{-12} [b]	1×10^{-13}	Mg^{2+}		
Plagioclase, epidote, biotite		6×10^{-14}	Ca^{2+}, Na^+, K^+	Cristallina, Switzerland	Giovanoli et al. (1989)
Plagioclase, biotite	6×10^{-12}	9×10^{-15}	Ca^{2+}, Na^+, Mg^{2+}	Bear Brooks Watershed, Maine(USA)	Schnoor (1990)

a : Rate determined in the laboratory by Busenberg and Clemency (1976) and Mast and Drever (1987) at pH 4.

b : Rate determined in the laboratory on beach sand by Grandstaff (1986) at pH 4.5.

Japan. Cretaceous granitic rocks and associated metallic ore deposits (skarn and vein-type Fe, Cu, Au and W) are distributed in Kitakami. The Kamaishi skarn-type Fe-Cu deposits are thought to have formed due to Cretaceous granitic activities.

The undergroundwater samples collected from the Ohmine 550 m level drift and borehole (KH-1) on the Kamaishi mine were analyzed by JNC (1999). The data are plotted on a $\log[Ca^{2+}]+2\,pH\text{-}\log[H_4SiO_4]$ diagram (Fig. 2). These data are plotted near SiO_2 (chalcedony) saturation.

Based on this equilibrium condition and a coupled fluid flow-precipitation kinetics model represented by the following equation, we can derive the relationship between A/M and residence time.

$$dC/dt = -k(A/M)(C-C_{eq})/C_{eq}+(q/V)(C_i-C) \quad (8)$$

If we take A/M value=1, residence time is estimated to be more than 30 years. As noted already, it is reasonable to assume that it takes at least $1\sim10$ years for the A/M=1 that the solution becomes to be oversaturated with respect to SiO_2 (chalcedony), which is caused by the dissolution of silicates.

Therefore, the total time to reach equilibrium between SiO_2 (chalcedony) and deep groundwater is more than 40 years if A/M=1. However, it is clearly required to estimate A/M based on an investigation of fractures through which groundwater flows.

4. Conclusions

The important conclusions obtained by this study are summarized below.

(1) Chemical compositions of major elements (Si, Ca, Na, K, Mg, H^+, HCO_3^-) of shallow groundwater in granitic rock area (Tsukuba-Kaba, central Japan) were analyzed. Analytical data and thermochemical calculations indicate that chemical equilibrium between shallow groundwater and granitic rock is not attained.

(2) A coupled fluid flow-dissolution kinetics model for uniformly mixed system was applied to the interpretation of chemical compositions of shallow groundwater in the Tsukuba-Kaba area. Using this model and assuming reasonable parameters values for residence time, k (dissolution rate constant for feldspar) and H_4SiO_4 concentration of groundwater, A/M was estimated to be $0.15\sim8.7$. This implies that the width of a fracture through which ground-

water flows is in range of $0.2\,mm\sim2\,cm$.

(3) It is evident, although a large uncertainty (±1 in logarithmic unit) over calculated results exists, that the estimated fracture width is inconsistent with the laboratory data on the granite sample of the hand-specimen scale obtained using the mercury intrusion method, which has a much smaller width ($n\times10^{-1}\mu m$). This inconsistency suggests that the flow of groundwater in fracture with wide open space ($n\times10^0\sim n\times10^{-1}\,mm$) is dominant compared to the flow through microfractures within the width of $n\times10^{-1}\mu m$.

(4) H_4SiO_4 concentration in deep groundwater from underground in the Kamaishi mine is nearly in equilibrium with SiO_2 mineral (chalcedony).

(5) This suggests that the residence time of groundwater from Kamaishi mine was more than 40 years.

References

Appelo, C.A.J. and D. Postma, 1993, Geochemistry, Groundwater and Pollution. Rotterdam: A.A. Balkema

Busenberg, E. and C.V. Clemency, 1976, The dissolution of feldspars at 25℃ and at 1atm CO_2 partial pressure. *Geochim. Cosmochim. Acta*, **40**, 41-46.

Claasen, H.C. and A.F. White, 1979, Application of geochemical kinetic data to groundwater systems, In : Chemical Modeling in Aqueous Systems, edited by E.A. Jenne, pp. 771-793.

Clow. D.W., 1992, Weathering rates from field and laboratory experiments on naturally weathered soills, Unpub. Ph.D. Dissertation, Univ. Wyoming.

Drever. J.I., 1988, The Geochemistry of Natural Waters. Second ed. Prentice Hall.

Garrels. R.M., 1967, Genesis of some groundwaters from igneous rocks, In : Researches in Geochemistry, v.2, edited by P.H. Abelson, pp. 405-420. John Wiley & Sons.

Giovanoli. R., J. Schnoor, L. Sigg, W. Stumm and J. Zohrist, 1989, Chemical weathering of crystalline rocks in the catchment area of acidic Tiona Lakes, Switzerland. *Clays Clay Miner.*, **36**, 521-529.

Grandstaff, D.E., 1986, The dissolution rate of forsteritic olivine from hawaiian beach sand. In : Rates of chemical weathering of rocks and minerals (ed. S. Cloeman and D. Dethien), 41-59, Academy Press.

Hayashi, N., M. Takahashi and N. Sugita, 1995, Microcrack width of Inada granitic rocks, *Applied Geology*, **36**, 300-304 (in Japanese).

JNC, 1999, Summary report on Kamaishi mine, JNCTN7410 -99-001.

Lasaga, A.C., 1984, Chemical kinetics of water-rock interaction. *J. Geophys. Res.*, B6, 4009-4025.

Lasaga, A.C., 1997, Kinetic Theory in the Earth Sciences, Princeton University.

Mast, M.A. and J.I. Drever, 1987, The effect of oxalate on the dissolution rates of oligoclase and tremolite. *Geochim.*

Cosmochim. Acta, **51**, 2559-2568.

Paces, T., 1983, Rate constants of dissolution derived from the measurements of mass balance in hydrological catchments, *Geochim. Cosmochim.Acta*, **47**, 1855-1863.

Phillips, O.M., 1991, Flow and reactions in permeable rocks, Cambridge, Cambridge University Press, 277 p.

Rimstidt, J.D. and H.L. Barnes, 1980 The kinetics of silica-water reactions. *Geochim, Csmochim, Acta*, **44**, 1683-1699.

Schnoor, J.L., 1990, Kinetics of chemical weathering : a comparison of laboratory and field weathering rates. In : Aquatic Chemical Kinetics, edited by W.Stumm), pp. 475-504, John Wiley and Sons, New York.

Shikazono, N. and K. Fujimoto, 1996, Dissolution rates of silicate minerals in aqueous solution- a comparison of experimental and field results and interpretation of groundwater chemistry by a coupled fluid flow-dissolution kinetics model, Chikyukagaku (*Geochemistry*), **30**, 91-97 (in Japanese).

Shikazono, N., 2001a, Compositional variation of major elements in groundwater caused by water-rock interaction (I)-Chemical equilibrium and mass balance-. *Jour. Groundwater Geochemistry (Chikasui Gakkaishi)* (in press) (in Japanese).

Shikazono, N., 2001b, Compositional variation of major elements in groundwater caused by water-rock interaction (II)-Influence of reaction kinetics and fluid flow-, *Jour. Groundwater Geochemistry (Chikasui Gakkaishi)* (in press) (in Japanese)

Shimada, J., 1985, Changes in a groundwater regime in the crystalline bedrock caused by the construction influence on the water chemistry. *Hydrology*, **15**, 42-54 (in Japanese).

Siegel, D.F. and H.O. Pfannkuch, 1984, Silicate dissolution influence in Filson Creek chemistry, Northeastern Minnesota. *Geol. Soc. Am. Bull.*, **95**, 1446-1453.

Stumm, W. and J.J. Morgan, 1970, Aquatic Chemistry, John Wiley & Sons, New York.

Sverdrup, H., 1990, The kinetics of base cation relaease due to chemical weathering, Lund Univ. Press, 240p.

Takahashi, Y., 1980, Geology of the granitic rocks in the Tsukuba area, *Jour. Geol. Soc. Japan*, **88**, 177-184 (in Japanese).

Velbel, M.A., 1985, Geochemical mass balances and weathering rates in Forested watersheds of the southern blue ridge, *Am.Jour. Sci.*, **285**, 904-930.