Which constituent mineral is dominant in granite weathering? A solution-sided approach through a laboratory experiment

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ABSTRACT

To elucidate the influence of constituent minerals in weathering of whole rock granite under acidic conditions, an artificial weathering experiment was carried out in a closed system using uncrushed samples of a piece of granite and four single crystals (annite, albite, microcline, and quartz). Thermodynamic analysis of rock (mineral)–solution equilibria was performed using pH–Eh and stability diagrams. Based on the solution analytical viewpoint, dominant mineral which played a central role depended on the pH of solutions in the early stage of weathering: the mineral was plagioclase under a slightly acidic condition (pH 5), and biotite under more acidic conditions (pH 4–1). In near-neutral to slightly acidic conditions (pH $\geq$5), pH increased remarkably due to plagioclase dissolution. As a result, the solution characteristics made $Fe(OH)_3$ to precipitate easily. This H^+ consumption enhanced an acid buffer capacity of the aqueous solution with granite.

1. Introduction

Granite weathering has long been of interest to geoscientists. Many experiments concerning granite weathering have been focused on the reaction of specific constituent minerals and/or the release of some elements: plagioclase (Ganor et al., 2005; White and Brantley, 2003); biotite (Afifi et al., 1985; Kobayashi and Sakamoto, 2001); and calcite (White et al., 1999a). The leaching of elements has also been included in many studies (Savage et al., 1992; White et al., 1999b). It was observed that (1) biotite and plagioclase have higher reactivity than other granite-forming minerals (K-feldspar, muscovite, quartz and so on) except for calcite. The order of reactivity almost agrees with the stability series of minerals (e.g., Goldich, 1938; Lasaga, 1984), and thus will not be repeated here.

Although most researchers have been concerned with the whole rock reaction which involves finding out what role a constituent mineral plays in granite weathering, there have been no clear details on the matter due to the complexity of some minerals including their mixing effect and interaction. In a study discussing mineral to mineral interaction, Ganor et al. (2005) concluded that the coatings of iron mineral from biotite/chlorite inhibited feldspar dissolution. However, they did not consider the effect of pH on the reaction characteristics. The present study aims to clarify the specific reaction of whole granite including the interaction of minerals through a laboratory experiment at various pH

values using a common solution and analytical methods. The features of granite were determined by comparing a sample of it with single crystals of constituent minerals.

It has been noted that granite weathering and its minerals also produce (2) a weathering product, like clay and iron minerals, that is generated at an acid pH (e.g., Afifi et al., 1985; Murakami et al., 2003). The degree of saturation with secondary product in near surface region is said to be a reason of the gap between the field and the laboratory dissolution rates (e.g., Blum, 1994; Casey et al., 1993; Hellmann et al, 2012; Velbel, 1993; White and Brantley, 2003). The formation process of weathering products has been discussed through thermodynamic analysis using solution chemistry. Stability diagram shows the secondary mineral saturated with various natural water (e.g., Brookins, 1988; Garrels and Christ, 1965; Kinniburgh and Cooper, 2004; Zhu and Lu, 2009). In this study, a closed and batch system experiment was carried out under an acidic condition and in a near equilibrium condition. The reaction path and the formation of secondary minerals were analyzed thermodynamically using a pH–Eh diagram for the iron redox reaction and two stability diagrams in the system relating to Si and Al.

2. Experimental

2.1. Materials

The samples used in this study were single crystals of annite (Fe-rich end member of biotite), albite, microcline, and quartz, and a granite (see Table 1 for samples' places of origin). The granite, which is called "Aji-granite", was composed mainly of plagioclase (46.1%), quartz (31.4%),

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Table 1

Sampling location and bulk density of rock and mineral samples.

Name	Location	Bulk density (g/cm³)
Annite (Ann)	Nellore, Andhra Pradesh, India	2.83
Albite (Ab)	Dunganon Township, Ontario, Canada	2.62
Microcline (Mc)	Nellore, Andhra Pradesh, India	2.56
Quartz (Qtz)	Minas Gerais, Brazil	2.64
Granite (Gr)	Aji-cho Takamatsu, Kagawa, Japan	2.65

alkali-feldspar (14.5%), biotite (7.6%), and other minerals (0.2%). The concentrations of major elements (SiO_2, TiO_2, Al_2O_3, $FeO + Fe_2O_3$, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5) were analyzed by using XRF (Rigaku, System 3270) and show compositions that are identical to previous reports (Ishihara, 1991; Kutsukake et al., 1979; Yuhara et al., 2004) (see Table 2). The chemical formulas of minerals are as follows: annite ($K_{1.08}$ $Mg_{0.45}$ $Fe_{2.10}$ $Na_{0.05}$ $Ca_{0.06}$ $Al_{1.69}$ $Si_{3.00}$ O_{12}); albite ($Na_{0.84}$ $K_{0.04}$ $Ca_{0.13}$ $Mg_{0.02}$ $Al_{1.07}$ $Si_{2.90}$ O_8); microcline ($Na_{0.30}$ $K_{0.64}$ $Ca_{0.03}$ $Mg_{0.02}$ $Al_{0.97}$ $Si_{3.01}$ O_8); quartz ($Na_{0.002}$ $Ca_{0.006}$ $Mg_{0.004}$ $Si_{0.995}$ O_2).

The samples were cut into specimens with the size of $10.0 \times 10.0 \times 3.0$ mm. Albite, microcline, and quartz were respectively sliced parallel to the planes (001) and (010), and prism. Granite was fine grained (several mm) as for surface analysis in micro region (will be reported at another paper). Except for annite, a side of the plane surfaces was polished with 0.25 μm diamond paste to attain surface uniformity. The specimens were then ultrasonically cleaned in ultra-pure acetone and pure water in turn, and stored in a desiccator with silica gel for at least 24 h. As for annite, cyano acrylate adhesive was applied to a pair of opposing edge surfaces. One fresh face was prepared by cleaving it with Scotch tape immediately prior to the experiment. Their dry bulk densities are shown in Table 1. Annite has the highest density (2.83 g/cm³), and microcline has the lowest (2.56 g/cm³).

2.2. Procedure and analysis

The weathering experiment was carried out in a closed system for 56 days at 25.0 °C. In each case, a specimen was placed centrally at the bottom of a polystyrene bottle containing 50.0 mL of a HCl solution, with the cleaved face pointing upwards. The solutions were made using ultra pure HCl and distilled water, and the initial pH values were chosen to be 5.0, 4.0, 3.0, and 1.0. Each specimen underwent reaction for a specified period, after which it was removed from the solution and stored in a desiccator with silica gel. To avoid the removal of secondary products, specimen cleaning was not done before analysis.

The pH and Eh values of the aqueous solutions in the bottles were measured after 7, 21 and 56 days using a pH meter (DKK-TOA, HM-60V and flow unit FAR-201A/GSU-202 with the precision of ± 0.01 for pH and ± 1 mV for Eh). Each solution sampled was then passed through a 0.45 μm filter. The elements Si, Al, Fe, Ca, Mg, Na, and K in these solutions were qualitatively analyzed by ICP-AES (Nippon Jarrell-Ash, ICAP-757V with the CV% < 5%).

Table 2

Chemical composition of rock and mineral samples (in wt.%).

	Ann	Ab	Mc	Qtz	Gr
SiO_2	33.12	65.09	66.83	97.48	72.14
TiO_2	2.17	n.d.	n.d	n.d.	0.31
Al_2O_3	15.83	20.24	18.30	n.d.	14.55
FeO[a]	27.75	n.d.	n.d.	n.d.	2.62
MnO	0.19	0.01	0.00	0.00	0.05
MgO	3.31	0.27	0.25	0.24	0.84
CaO	0.60	2.74	0.64	0.59	2.85
Na_2O	0.31	9.72	3.38	0.09	3.83
K_2O	9.32	0.75	11.17	n.d.	2.45
P_2O_5	0.01	n.d.	0.00	n.d.	0.07
Total	92.61	98.82	100.57	98.40	99.71

[a] Total Fe as FeO.

3. Results

The relationships between pH and Eh during the experiment are shown in Fig. 1. In granite at initial pH values of 4.0 and 5.0, Eh decreased linearly with the increase in pH. In annite at initial pH values of 4.0 and 5.0, a weak relationship was observed. In albite at initial pH values of 3.0, 4.0, and 5.0, Eh decreased at almost the same rate as in granite at initial pH values of 4.0 and 5.0. In the other cases, Eh tended to decrease with time. The variation of Eh was independent from pH.

Fig. 2 shows changes in cation concentrations with time during the experiment. Overall, the concentration of cations was greater in lower pH conditions. In granite at initial pH values of 5.0 and 4.0, the concentration of alkali elements was higher than that of Si and Al, in decreasing order: Ca, Na, and K. Concentrations of Fe, Si, and Al were higher than those of alkalis at initial pH values of 3.0 and 1.0. In annite, the leaching of Fe and K was recognized. At initial pH values of 3.0 and 1.0, the concentrations of all the elements increased with time. In albite, Ca leached to a remarkable extent. At initial pH values of 3.0 and 1.0, the leaching of Si and Al took place. In microcline, there was almost no leaching of Si, and Ca did not leached at initial pH values of 5.0, 4.0, and 3.0. The concentration of Al decreased after an increase at the initial stage. At an initial pH of 1.0, the concentration of Si increased with time. Quartz did almost not dissolve.

Relationship between initial pH values and cation concentration after 56 days is shown in Fig. 3; as a total cation (Si + Al + Fe + Ca + Mg + Na + K) concentration using the raw data (Fig. 3a), and the concentration using the normalized data by the mineral composition (%) in granite (Fig. 3b). Generally, the amount of dissolution depended on the initial pH of the solution, and the dissolution progressed remarkably at a lower pH in granite, annite, and albite (Fig. 3a, b). In microcline and quartz, there was almost no pH dependency. In the raw data at initial pH values of 5.0, 4.0, and 3.0, the descending order according to amount of dissolution was albite, granite, and annite (Fig. 3a). At an initial pH of 1.0, the concentration in annite was largest. In the normalized data, the concentration in albite was nearly equal to that in granite at initial pH values of 5.0, 4.0, and 3.0 (Fig. 3b). At an initial pH of 1.0, annite was dissolved slightly; the normalized value was below 1.0 mmol/L.

4. Discussion

This study performed the thermodynamic analyses of mineral–solution equilibria during primary mineral dissolution and secondary product precipitation. First, the saturation index for this experiment was calculated using a piece of software to determine whether the solution had been super-saturated or under-saturated with respect to some minerals. Next, two types of stability diagram were drawn up to illustrate the reaction path in the systems consisting of Fe, Al, and Si: (1) pH–Eh diagram in $Fe–O_2–H_2O$ system for annite and granite, and (2) theoretical and experimental stability diagrams in $Al_2O_3–SiO_2–H_2O$ system for annite, albite, microcline, and granite. As quartz showed no significant dissolution, it has been excluded from the list. The basic system was chosen in this study as Fe, Al, and S exist commonly in weathering products of iron minerals (goethite, hematite), alumina (gibbsite), aluminosilicates (halloysite, kaolinite) and silica. The following can be given as other systems (for various minerals): $MgO–SiO_2–H_2O$ (e.g., chlorite, smectite), $K_2O–Al_2O_3–SiO_2–H_2O$ (e.g., muscovite, K-feldspar); $NaO–Al_2O_3–SiO_2–H_2O$ (e.g., albite, analcite); $CaO–Al_2O_3–SiO_2–H_2O$ (e.g., laumontite, calcite) (Drever, 1997; Garrels and Christ, 1965; Helgeson et al., 1969; Kittrick, 1973, 1982; Nesbitt and Young, 1989).

4.1. Saturation index

The Saturation Index (SI) for phases assumed to be secondary products was calculated using PHREEQC version 2.16 with the database of