

## 原 著

# Artificial Chemical Weathering of Plagioclase by Acidic Hydrothermal Solutions — The Effect on Chemical Composition of Hot Spring Water —

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## 酸性熱水溶液による斜長石の風化変質に関する実験的研究 —温泉の化学成分への影響—

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## 要 旨

酸性熱水溶液による主造岩鉱物である斜長石(灰曹長石と曹灰長石)の人工風化実験を行い、岩石・鉱物の科学的風化作用の温泉水の化学組成への影響を調べるために以下の実験を行った。斜長石試料は切断後片面を研磨し用いた。開放系に改良したソックスレー抽出器を用い、pH 4 に調整した塩酸、硫酸、硝酸および蒸留水にて 50°C, 150 mL/day で、最長 600 日間の様々な期間晒すことを行った。溶脱元素は ICP-MS で検討し、結晶表面の化学組成、形態変化、生成物は偏光顕微鏡、SEM, EPMA, XRD, TEM によって検討した。実験時間の増加に伴って斜長石表面には不規則な割れ目などが、また  $(Ca + Na + K)/(Si + Al)$  比の減少が見られた。溶脱のしやすさを示すモル比(溶脱した各元素の量/未処理の斜長石中の各元素の量)は、Mg, Ba, La, Ce, Y が比較的高い値を示し、Fe, Mg, Zn, Mn および 3 価の希土類 (Ce, La, Nd, Sm) は反応の初期では高い値を示すが実験時間の増加によって減少することを、また構造中のフレームやその隙間を埋める斜長石の主成分 Si, Al, Na, Ca の溶脱は実験期間を通してほぼ一定であることを示した。灰曹長石および曹灰長石中から 525 日間に溶脱した主元素 Si, Al, Ca, Na の量は顕著である。以上の結果は、斜長石から溶脱したこれら元素は、温泉水の化学組成形成の一因である可能性を示した。

キーワード：泉質, 灰曹長石, 曹灰長石, 人工風化実験

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### Abstract

In order to predict the effects of chemical weathering of rocks and minerals by acidic hydrothermal solutions on chemical composition of surface water such as hot spring water, river water and seawater, artificial chemical weathering of plagioclases, which is the major constituent mineral of various rocks, has been conducted chemically and mineralogically. Oligoclase from Minas Gerais, Brazil and labradorite from Chihuahua, Mexico were exposed to HCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> solutions at pH 4, and distilled water at 50°C and 150 mL/day for various times up to 600 days in an open system using an improved Soxhlet extraction apparatus. The plagioclase plates with 10 mm×8 mm×5 mm in size were used for the experiment. The leached sample solutions were analyzed for major elements such as Si, Al, Fe, Ca, Mg, Mn and Na, and minor elements such as Ce, La using ICP-MS. Morphological and chemical changes on the mineral surfaces were studied by SEM, EPMA and microscopic techniques. Alteration products were examined using TEM and XRD.

The SEM images of the artificial weathered oligoclase and labradorite surfaces showed that many irregular fractures and etch pits developed on the minerals. The (Ca + Na + K)/(Si + Al) molar ratio for oligoclase and labradorite surfaces decreased with an increase in leaching time. Molar ratio, which is calculated by dividing the cumulative total mole of released each ion by the mole of the each element in the unaltered plagioclase, varied depending on the experimental period. The ratios of the elements such as Mg, Ba, La, Ce and Y were relatively high, whereas the ratios of Na and Ca of the major elements were low. At an early stage, after 6 days, the molar ratios of Fe, Mg, Zn and Mn, and trivalent Ce, La, Nd, and Sm are relative high. But at a later stage, after 525 days, the ratios are reduced significantly. The ratios of major elements in framework and cavity of plagioclase structure such as Si, Al, Na and Ca are almost constant in the early and later stage. The amount of leaching Si, Al, Ca and Na, which are major elements in both oligoclase and labradorite, shows the high value though the molar ratios of the elements are low. The dissolved ions from plagioclase by hydrothermal solution are likely to be one of the sources of ions in hot spring water.

Key words : spring quality, oligoclase, labradorite, artificial weathering

## 1. Introduction

Minerals and rocks are altered by chemical weathering in the Earth's crust near the surface. In the chemical weathering process, the mineralogical components are modified naturally by dissolution, oxidization, and hydration resulting from contact with geothermal water, rainwater, oxygen, and carbon dioxide. The alteration is controlled by temperature, chemical composition and pH of hydrothermal solution. Dissolved chemical compositions in hot spring waters by reaction between hydrothermal solution and rocks and minerals have been reported previously (e.g. Hurwitz *et al.*, 2010 ; Yoshiike, 1995).

In order to predict the effect of chemical weathering by acidic water on chemistry of ground water and seawater, the authors have conducted artificial chemical weathering of rocks in an open system using an improved Soxhlet extraction apparatus. In Kobayashi *et al.* (1993), the artificial chemical weathering of granitic rock was simulated chemically and mineralogically using HNO<sub>3</sub> solution at pH 4 for 189 days. As a follow-up study, Kobayashi and Sakamoto (2001) extended the reaction time to 780 or 824 days using HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HCl at pH 3 or 4, and also distilled water in an attempt to further simulate natural environmental conditions. In Kobayashi *et al.* (2005) the artificial chemical weathering of gabbroic rock was also reported. These

experiments were conducted on condition of acidic hydrothermal solution at 50°C. Hada (1999) used a circulating system of distilled water with carbon dioxide and air at pH 4.2-4.4 and 22°C to study the chemical weathering of granodiorite.

The chemical weathering process of the rock is extremely complex because of not only the degree of weathering of each constituent mineral is different but also the dissolved ions from weathered minerals react easily with weathered products and/or other unweathered constituent minerals. Moreover, both quantitative and qualitative data of dissolution ions from each constituent mineral in the works using granitic and gabbroic rocks could not be confirmed because it is difficult that the source of these dissolution ions could be specified accurately. Therefore, it is strongly important to examine the rock and its individual minerals separately to consider the reaction process for weathering of whole rocks by hydrothermal solution.

On the other hand, many experiments on weathering and dissolution experiments of rock-forming minerals, especially plagioclase, have been conducted. For example, the dissolution rate of minerals has been obtained experimentally (e.g. Holdren and Berner, 1979 ; Schott *et al.*, 1981). Lasaga (1984) evaluated the mean lifetime of  $10^{-3}$  m radius crystals of various minerals at 25°C and pH 5, based on the dissolution rate of the minerals. The weathering rates and related parameters of plagioclase are previously summarized in White and Brantley (2003). However, the experimental conditions in these studies differ greatly from those in natural weathering conditions, as many of them were operated using plagioclase of 38-1000  $\mu$ m in grain size at pH 3-7 under condition that is not open system.

Distribution map and the physical chemistry of Japanese spring waters are shown by Geological Survey of Japan, AIST (2005). Hot spring water is divided into acidic (<pH 3), weakly acidic (pH 3-6), neutral (pH 6-7.5), weak alkaline (pH 7.5-8.5) and alkaline (>pH 8.5) spring water by hydrogen ion concentration. According to the Standard Method of Analysis for Mineral Springs, they are categorized, based upon their temperature, into cold (<25°C), tepid hot (25-34°C), hot (34-42°C) and high-temperature (>42°C) springs. According to Geological Survey of Japan, AIST (2005), many of hot springs belongs to weak alkaline to alkaline. The most of these springs are cold or tepid hot types at 25 to 35 degrees. On the other hand, high temperature hot spring is limited to acidic or weakly acidic types because they distribute near the volcanoes. It is considered that the reaction of acidic hydrothermal solution and plagioclase is easy to proceed at higher temperature, and the effect on the hot spring water is high.

Consequently, in order to predict the effect of acidic hydrothermal solution on chemistry of surface water such as hot spring water, ground water and sea water, we have been conducted artificial chemical weathering for polished sample plates of several millimeters square of oligoclase and labradorite feldspars under an opened system. These minerals are a kind of plagioclase and the main rock-forming minerals. The artificial hydrothermal solutions are H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HCl at pH 4, and distilled water for reference. We have examined mineralogical and chemical changes on plagioclase surface and alteration process concerning dissolved ions.

## 2. Material and Experimental Methods

Oligoclase and labradorite from Gerais in Brazil and Chihuahua in Mexico were used in this

study, respectively. The chemical composition of the bulk of fresh oligoclase and labradorite was analyzed by X-ray fluorescence (XRF, Rigaku RIX-2100) and ICP-MS (Analyzed by Actlabs Co., LTD., Canada), and shown in Table 1. For example, since general formula of albite is shown as  $\text{NaAlSi}_3\text{O}_8$ , each analysis has been recalculated on the basis of the 8O (O : oxygen). The albite (Ab), anorthite (An) and orthoclase (Or) molecules of oligoclase and labradorite are  $\text{Ab}_{73.6}\text{An}_{22.3}\text{Or}_{4.1}$  and  $\text{Ab}_{39.0}\text{An}_{59.4}\text{Or}_{1.6}$ , respectively. Plagioclase compositions are usually expressed in terms of the two end-members albite and anorthite,  $\text{Ab}_x\text{An}_{100-x}$ . The series is divided into albite, oligoclase, andesine, labradorite, bytownite and anorthite at An mole percentages of 0–10, 10–30, 30–50, 50–70, 70–90, 90–100 respectively.

Hydrothermal solutions flow through opening of some rocks including plagioclase, but the flow rate is not only constant but also irregular such as a geyser. In this work, we assumed the solutions have flowed and stagnated. Therefore, an improved Soxhlet extraction apparatus was used in this study (see the details in report of Kobayashi and Sakamoto, 2001). Figure 1 shows a schematic illustration of the experimental apparatus. Oligoclase and labradorite plates were cut from a fresh block with a diamond blade and polished to provide specimens. The dimensions of each plate were about  $10 \times 8 \times 5$  mm. Forty plates weighing 33–40 g were put in the extraction chamber of four apparatus and four other apparatus without mineral specimens were used as control. The extraction chamber was heated with a mantle heater at  $50^\circ\text{C}$  during the experiment. HCl,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  solutions at pH 4, and distilled water for reference were prepared. Usually,  $\text{HNO}_3$  content in hydrothermal solution is very low ; it also was used for reference. The four fresh solutions, which were stocked in the reservoir tank, were dripped on a specimen covered by a Teflon sheet in each apparatus using a roller pump with the flow rate of 150 mL/day. The Teflon sheet is put so that the each solution is not directly exposed on the same

Table 1 Chemical composition of oligoclase and labradorite

wt%	Oligoclase	Labradorite	ppm	Oligoclase	Labradorite
$\text{SiO}_2$	62.56	53.21	Cr	20	20
$\text{Al}_2\text{O}_3$	22.82	29.10	Co	2	3
$\text{TiO}_2$	tr	tr	Ga	35	14
$\text{Cr}_2\text{O}_3$	tr	tr	Ni	20	20
$\text{Fe}_2\text{O}_3$	0.13	0.37	Zn	30	30
MgO	0.01	0.11	Rb	2	2
MnO	tr	tr	Sr	731	936
CaO	4.69	12.24	Y	1	1
$\text{Na}_2\text{O}$	8.50	4.44	Eu	1.17	0.43
$\text{K}_2\text{O}$	0.73	0.28	Nb	1	1
Total	99.42	99.75	Ba	79	129
(Numbers of ions on the basis of 8O)					
Si	2.785	2.411	La	0.4	1.6
Al	1.209	1.569	Ce	0.6	2.7
			Nd	0.1	0.9
Fe	0.004	0.013	Sm	0.1	0.2
			Gd	0.1	0.1
Mg	0.000	0.008	Tb	0.1	0.1
Mn	-	-	Yb	0.1	0.1
Na	0.734	0.390	Pb	26	5
Ca	0.223	0.594			
K	0.041	0.016			

\* Total Fe as  $\text{Fe}_2\text{O}_3$

sample. Each solution reacted with the platy specimen in the extraction chamber. The reactions ran until about 50 mL of solution could be collected in the extraction chamber of the apparatus. Then, the leached solution was collected by siphoning into a container. The leached solution was never return to the extraction chamber. The procedure was repeated three times a day. This can be compared to natural conditions where a sporadic gush of spring water such as a geyser could occur. Namely, the process is similar to combining flow method and batch method. The artificial chemical weathering was conducted for various times up to 600 days. Therefore, each total dripping of three kinds of acidic solutions and distilled water is about 90,000 mL for 600 days, respectively.

Artificially weathered sample plates were taken out of each apparatus and compared with the starting material using microscope, X-ray diffractometer (XRD ; Rigaku RINT-2500V). Chemical analyses of the plate surface were performed on an energy-dispersion spectrometer and scanning electron microscope with energy-dispersion spectrometer (SEM-EDS system ; JEOL JSM-5410LV SEM equipped with a JEOL JED-2140 EDS). Accelerating voltage and specimen current were kept at 15 kV and 0.15 nA on the Faraday cup, respectively. The beam diameter was 5  $\mu\text{m}$ . Standards used were quartz (Si), corundum (Al), rutile (Ti), eskolaite (Cr), hematite (Fe), periclase (Mg), manganosite (Mn), wollastonite (Ca), jadeite (Na), adularia (K). The ZAF method was used for corrections. Alteration products were picked by hand from the surfaces of each mineral and examined with transmittance electron microscope (TEM ; JEOL JEM-2010F).

Samples of the leached solution, which was stored in the container over a 3-day period, were collected every 3 days for the first 30 days, and then at 30-day intervals between 30 days and 150 days, and at 45- or 90-day intervals for the last 600 days. Major and minor ions in the leached sample solutions were determined using an inductively coupled plasma mass spectrometry (ICP-MS ; SII. SPQ-9700). The dissolution degree of each element is shown by molar ratios calculated from the cumulative total mole of released ions divided by the mole of individual elements in the starting materials of untreated oligoclase or labradorite (see appendix).

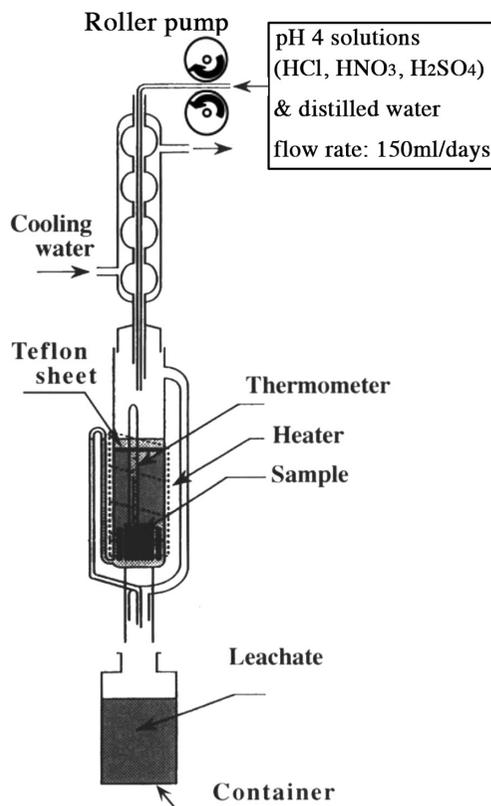


Fig. 1 Schematic illustration of experimental apparatus.

### 3. Results and Discussion

#### 3.1 Leached sample solution

The total amount of major and minor ions released from the oligoclase and labradorite as a function of leaching time up to 525 days are shown in Figures 2 and 3, respectively. The released ions are shown by molar ratios (see appendix) as mentioned above. The molar ratios of each ion in the leached solution from labradorite are relative high compared with that of oligoclase.

Figure 2 shows the molar ratios of major (a) and minor (b) ions in the leached solutions of  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{HCl}$  at pH 4 and distilled water for oligoclase as a function of leaching time. K, Mg and Fe, which are minor elements of plagioclase, are relatively high compared with Na, Ca, Al and Si, which are major elements in plagioclase. The ratios of Ba and Zn are also high compared to other ions. Figure 3 shows the ratios of major (a) and minor (b) ions after leaching with acid solutions and distilled water for labradorite. The ratios of Mg, Fe, K, Zn, Ba, Sm, and Tb are relatively high. On the other hand, the ratios of Na, Al, Ca and Si are relative low as well as these in oligoclase. Matsui *et al.* (1977) determined the partition coefficients between phenocryst and groundmass, and demonstrated partition coefficient versus six-fold coordinated ionic radius diagram of plagioclase. It is obvious from the diagram that the most suitable cation is Sr to fit the cavity, which is the space provided by the aluminum-silicate framework. The ionic radius of major cations in plagioclase, Na and Ca ions, are a little smaller than Sr, but the partition coefficient have considerable high. Therefore, it is consider that Na, Ca and Sr are easy to remain in the cavities within the framework. The molar ratio of Sr in Figure 3 is also relative low. Although the molar ratios of ions generally decrease gradually with increasing the duration, the major elements such as Na, Ca, Si and Al are dissolved at a nearly uniform rate. The dissolution degree of rare element (e.g. Mg and Fe) in the plagioclases extremely decreases after 350 days. Afifi *et al.* (1985) explain that dissolution of the various minerals, particularly those containing easily leachable cations such as Mg, are difficult to assess because of possible precipitation or incorporation of these cations in the alteration products. Thus, it is considered that the apparent dissolution degree becomes slow. It is also showed that the reactivity is different depending on a kind of the acid solutions. Its order for oligoclase seemed to be  $\text{HCl}$  and  $\text{HNO}_3 > \text{H}_2\text{SO}_4 >$  distilled water for minor elements though major elements as Na and Ca are not so clear (Fig. 2). It seemed that the order for labradorite is  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4 > \text{HCl} >$  distilled water in many elements (Fig. 3). The molar ratio of the each element in the acidic leached solutions is shown to be high compared with distilled water. It can be seen that the pH of the solution flowing in the earth's crust also is one of the factors in determining the spring quality. From the same experimental results of granite using  $\text{HNO}_3$  solution at pH 3 (Kobayashi and Sakamoto, 2001) and 4 (Kobayashi *et al.*, 1993), the influence of the leaching amount of plagioclase is estimated to increase as the pH is low.

Figure 4 shows the relation between the molar ratios of each ion resulting from dissolution of oligoclase and labradorite only after 6 ( $\text{RE}_{X \cdot 6}$ ) and 525 ( $\text{RE}_{X \cdot 525}$ ) days, and the ionic radius. Smith and Brown (1988) reported coordinations of Na and K in feldspars usually vary between five-fold and nine-fold. Moreover, Downs *et al.* (1996), and Megaw *et al.* (1962) indicated that Na,

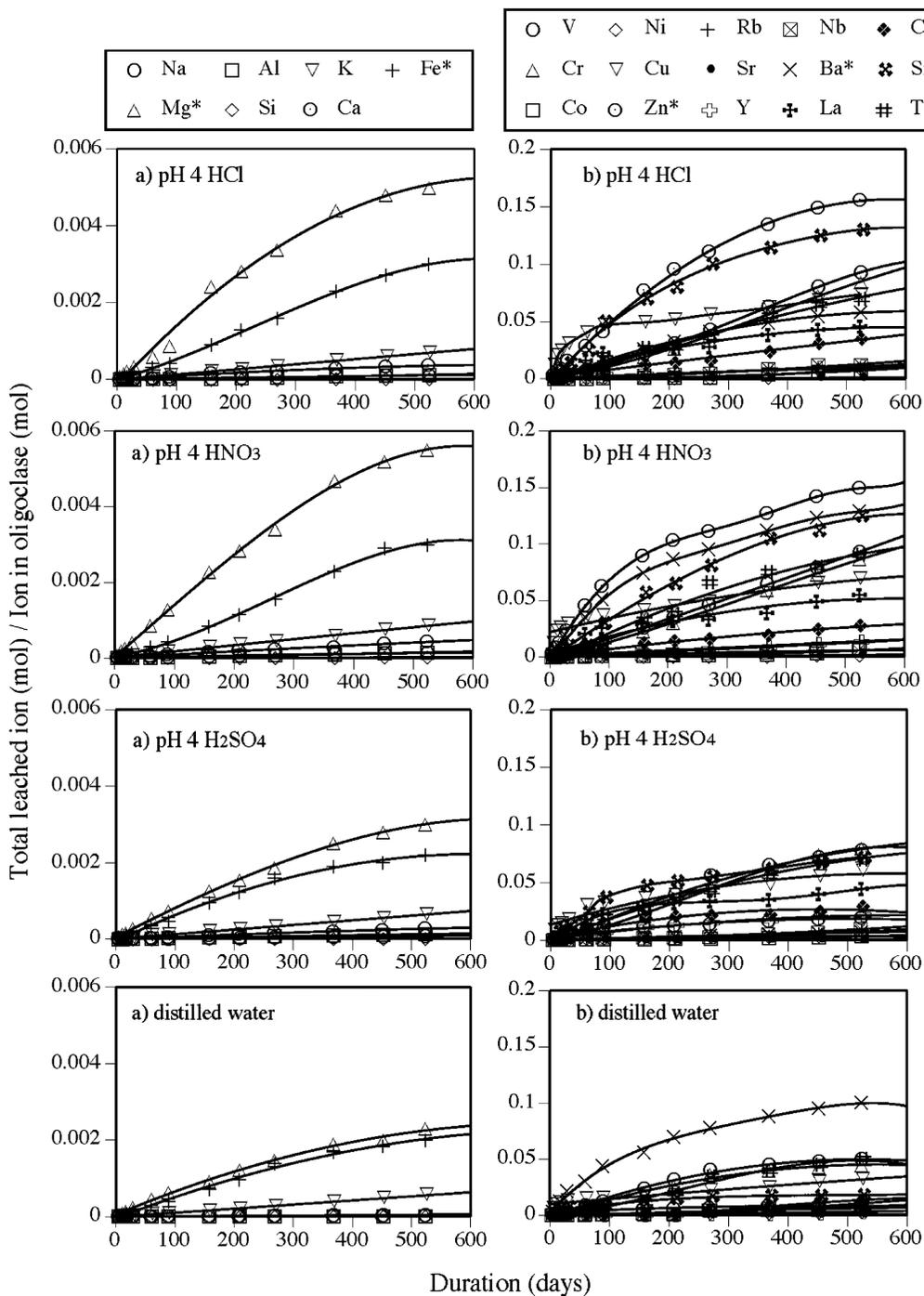


Fig. 2 Molar ratios of each ion in HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> leached solutions at pH 4, and distilled water to oligoclase versus duration. Molar ratio of Mg\* = Mg/10, Fe\* = Fe/10, Ba\* = Ba/2 and Zn = Zn/2. a) Major ions, b) minor ions.

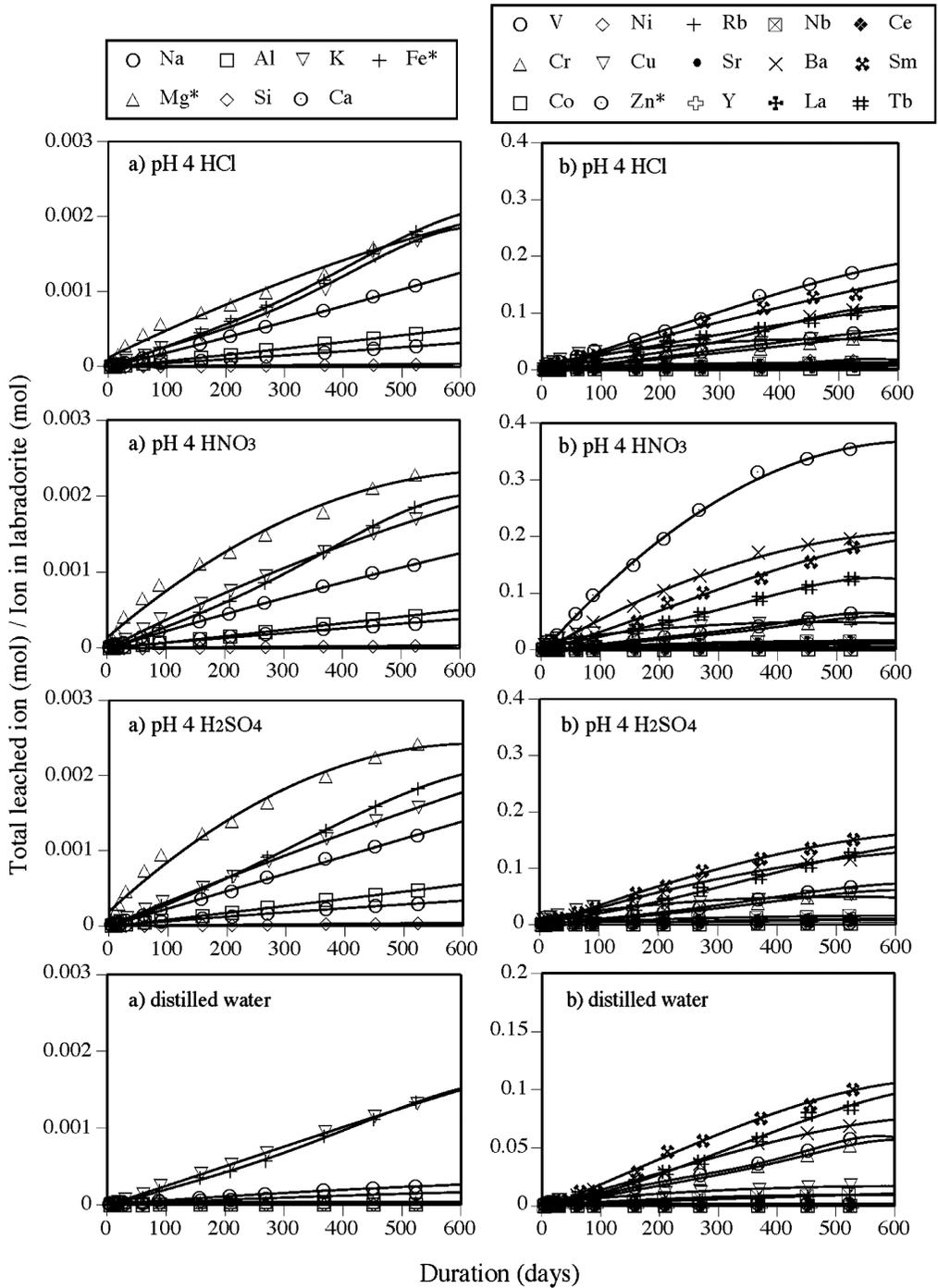


Fig. 3 Molar ratios of each ion in HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> leached solutions at pH 4, and distilled water to labradorite versus duration. Molar ratio of Mg\*=Mg/5, Fe\*=Fe/5 and Zn\*=Zn/2. a) Major ions, b) minor ions.

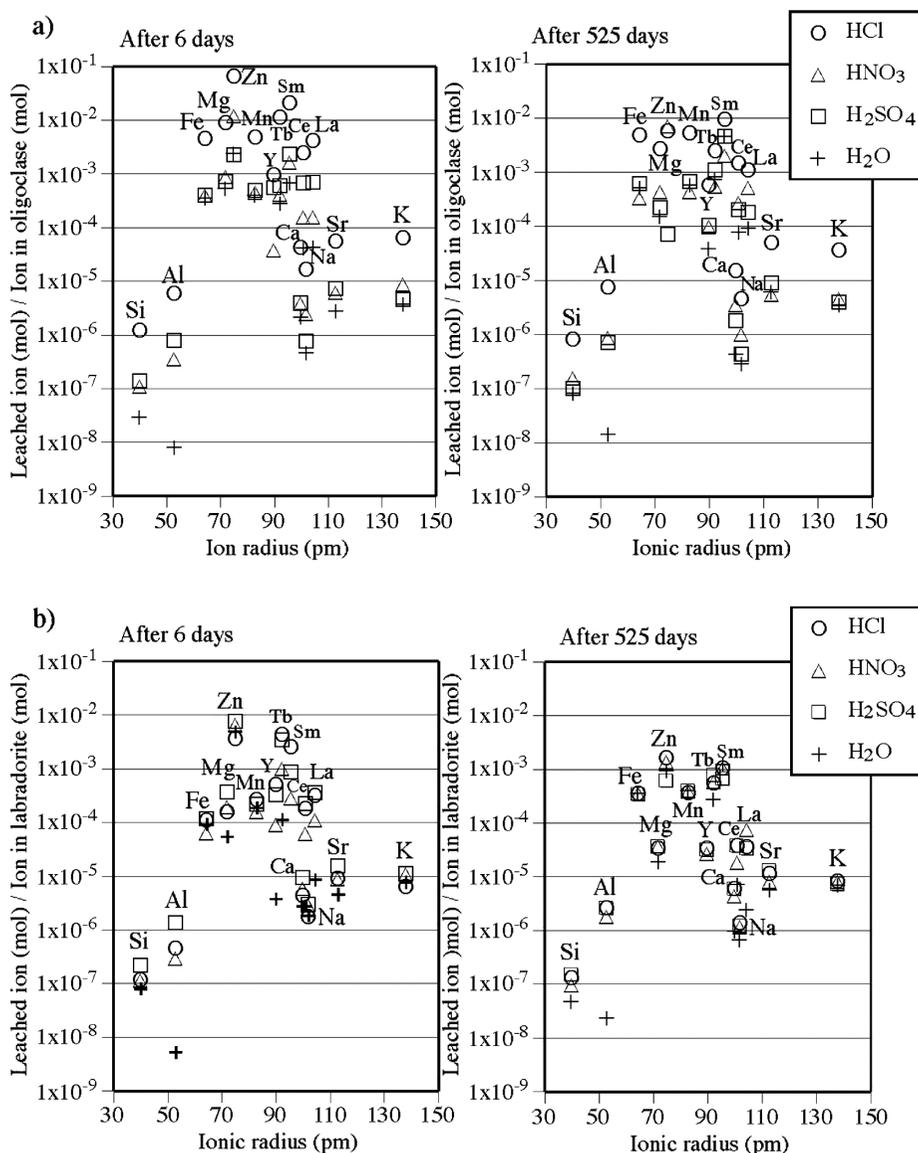


Fig. 4 Molar ratios of the elements released at 6 ( $RE_{X \cdot 6}$ ) and 525 ( $RE_{X \cdot 525}$ ) days of oligoclase (a) and labradorite (b) against ionic radius.

Ca and K are five-fold, six- or seven-fold and nine-fold coordination, respectively. K having large ionic radius is an appropriate element in the cavity of alkali feldspar rather than plagioclase. On the other hand, the ionic radius was changed by a coordination number. In this figure, the ionic radius expediently used the value of six-fold coordination number that had been indicated by Shannon and Prewitt (1969). The molar ratios clearly vary with the ions. At an early stage, after 6 days, the ratios of trivalent ions such as Ce, La and Sm having an ionic radii near 100 pm, which occupied cavities within the framework, are relative high. But at a later stage, after 525

days, the ratios are reduced significantly. The ionic radii of these ions are similar to Na and Ca, which are typical elements in the cavity of plagioclase. In addition, some small size ions of around 70 pm such as Fe, Mg, Zn and Mn, which occupied cavities within the framework, also showed a similar change. The ratios of Na, Ca and Sr having the most appropriate ionic radius to the size of cavity as indicated by Matsui *et al.* (1977) are almost constant in the early and later stage. Moreover, it seems that the ratio of trivalent Al ion in labradorite, which is one of the constituent elements of the framework, is increased in the ratio of 525 days. From the above results, it is concluded that the dissolution of elements from plagioclase proceeds rapidly from trivalent ions and small size ions in the cavities within the framework by an exchange reaction with  $H_3O^+$  ions in the early stages, and then the dissolution of divalent and monovalent ions which occupy commonly such as Na, Ca and Sr in the cavities are generated successively, and finally the dissolution of Al from the framework is occurred in the later stages of the reaction.

### 3.2 Artificially weathered sample plates

#### 3.2.1 Surface morphology

The surface of labradorite plates became cloudy after 120 days and a part of them disintegrated into small fragments during the experiments. The most altered parts of the

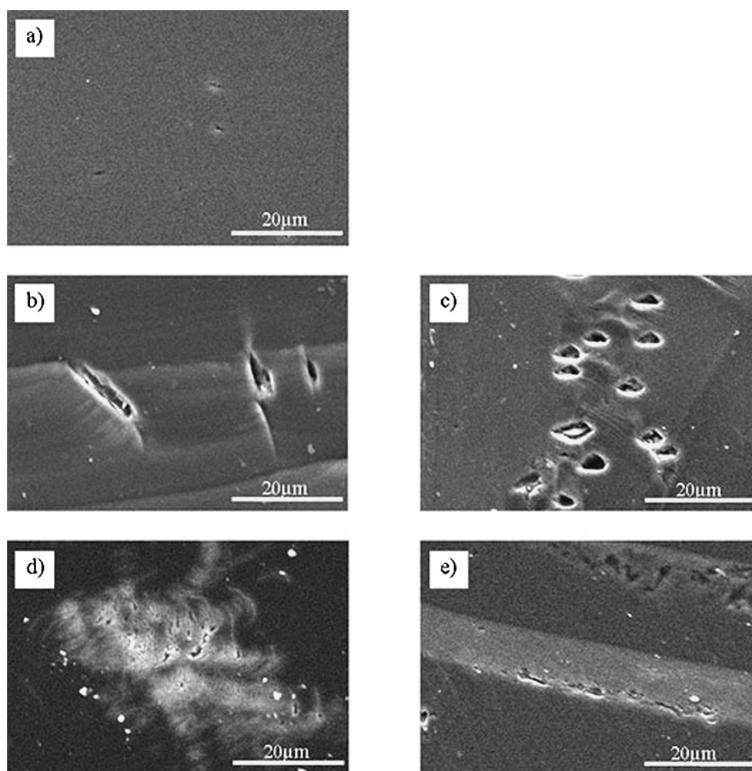


Fig. 5 SEM images of untreated oligoclase (a), and artificial weathered oligoclase after 581 days by artificial weathering using HCl (b),  $HNO_3$  (c) and  $H_2SO_4$  (d) solutions of pH 4, and distilled water (e).

labradorite exfoliate by scratching with fingernail after 600 days. The alteration increased with an increase in reaction time. In contrast, the oligoclase surface showed almost no change.

Figures 5 and 6 show SEM images of surfaces for oligoclase and labradorite before and after (581 days) the experiments, respectively. Numerous irregular fractures formed in the labradorite crystal reacted with  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ . Dissolution proceeded along cleavages and cracks in the crystals. The dissolution of labradorite by the  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  solutions is remarkable when compared with the  $\text{HCl}$  and distilled water. The surface of oligoclase is not readily altered by the acid solutions although etch pits were confirmed on the surface by  $\text{HNO}_3$  solution.

### 3.2.2 Chemistry of mineral surface

The chemical change on oligoclase and labradorite surfaces was examined by EDS. Figure 7 shows the change in  $(\text{Ca} + \text{Na} + \text{K})/(\text{Si} + \text{Al})$  molar ratio for plagioclase surface as a function of leaching time. The results suggest that the main elements constituting labradorite are easily released by  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  and distilled water at an early stage up to 200 days. After this time, the change in ratio with an increase in leaching time gradually becomes smaller. These data suggest that the leaching of Ca, K, Na proceeded at the initial stage of the weathering on the original mineral surfaces, and these were controlled by secondary formed products. In Figure 7b, the  $(\text{Ca} + \text{Na} + \text{K})/(\text{Si} + \text{Al})$  molar ratios of labradorite for three kinds of acidic solutions

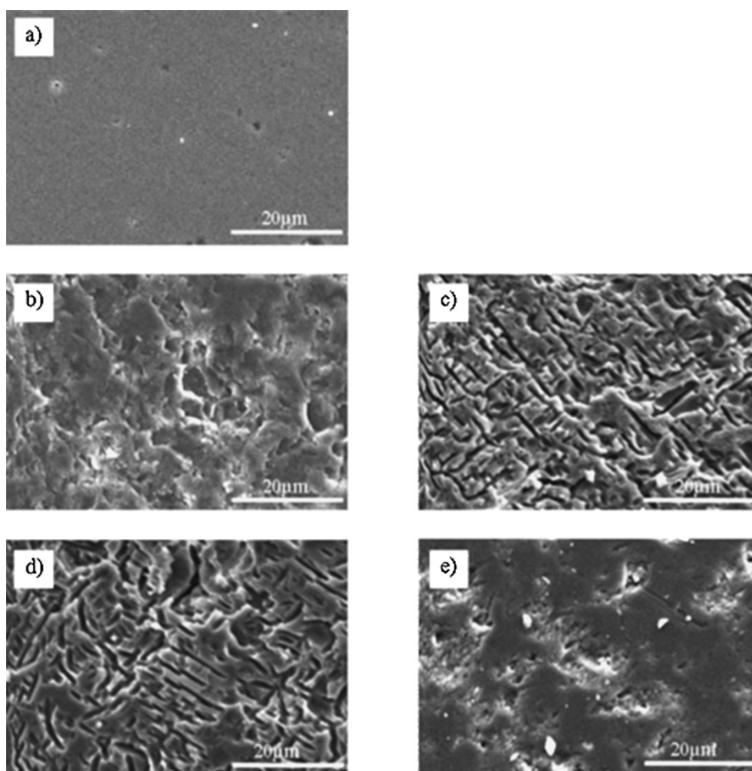


Fig. 6 SEM images of untreated labradorite (a), and artificial weathered labradorite after 581 days by artificial weathering using  $\text{HCl}$  (b),  $\text{HNO}_3$  (c) and  $\text{H}_2\text{SO}_4$  (d) solutions of pH 4, and distilled water (e).

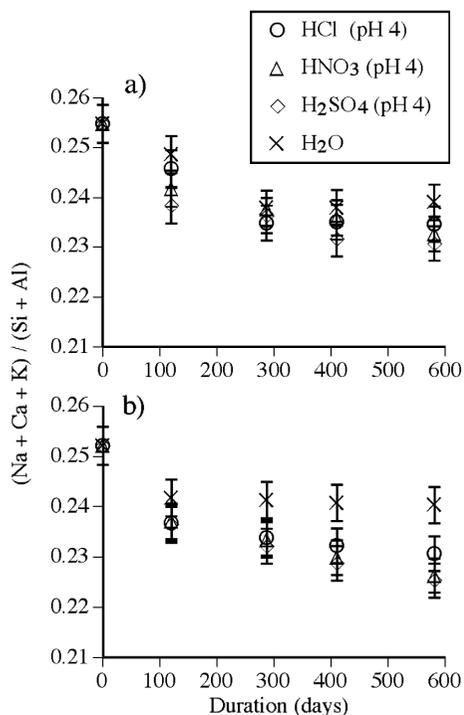


Fig. 7 Changes in  $(\text{Ca} + \text{Na} + \text{K}) / (\text{Si} + \text{Al})$  molar ratio for oligoclase (a) and labradorite (b) surfaces during artificial weathering by acid solutions. Each bar shows the distribution range of data.

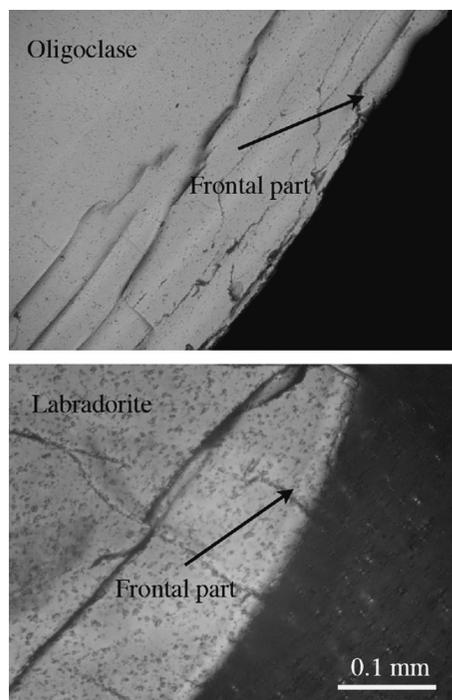
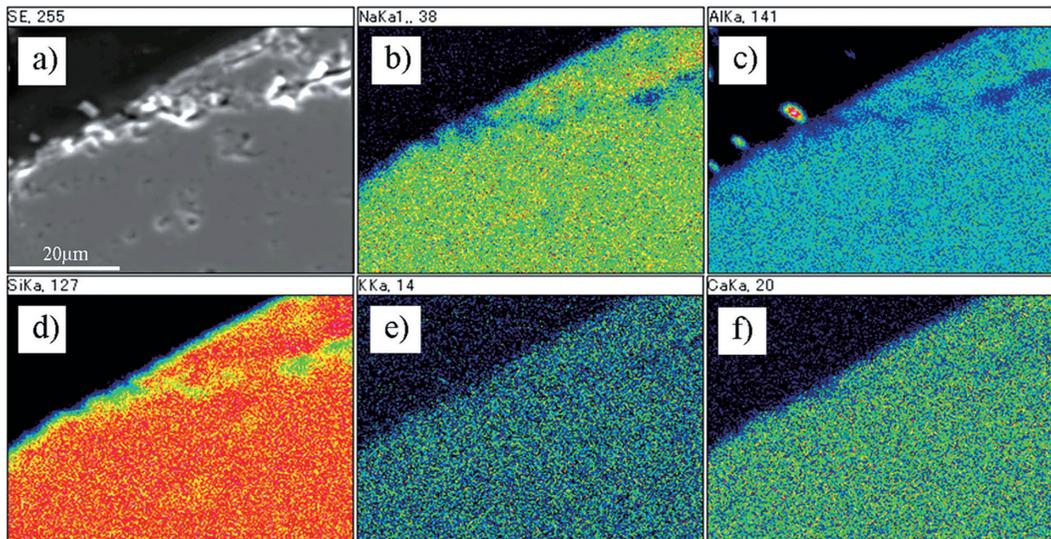


Fig. 8 Photomicrograph showing the frontal part of the oligoclase (a) and labradorite (b), which is in direct contact with pH 4 HNO<sub>3</sub>. Cross-polarized light.

are similar up to 120 days, but after then, it is seemed that the ratios by HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> treatment are smaller than one of HCl. Therefore, the reactivity order, which estimated by the ratio at 581 days of three kinds of the solutions and distilled water, was HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> > HCl > distilled water. On the other hand, there was only a little change shown in the chemistries of the oligoclase surface by the three acidic solutions and distilled water (Fig. 7a). The orders of chemical changes on oligoclase surface for kinds of the solutions were H<sub>2</sub>SO<sub>4</sub> > HCl and HNO<sub>3</sub> > distilled water.

The depth dimension of the sections of altered oligoclase and labradorite sample plates, which were cut and polished in the direction of the right angle to the surface, were observed using a microscope, SEM, and EDS. The frontal part of plagioclases after 581 days treatment with the HNO<sub>3</sub> solution did not show birefringence clearly (Fig. 8) and showed a weak contrast in the SEM image (Fig. 9a). The altered part of labradorite is slightly thick compared with it of oligoclase. The element distribution maps of Na, Al, Si, K and Ca in crystals of oligoclase and labradorite show that the decrease of these elements were observed in near the front (Fig. 9b-f). From the photomicrograph and SEM image, it can be seen that plagioclase is changed to alteration products of up to 5  $\mu\text{m}$  in thickness, such as a leached layer or hydration layer by the acid solution at an early stage of weathering.

## Oligoclase



## Labradorite

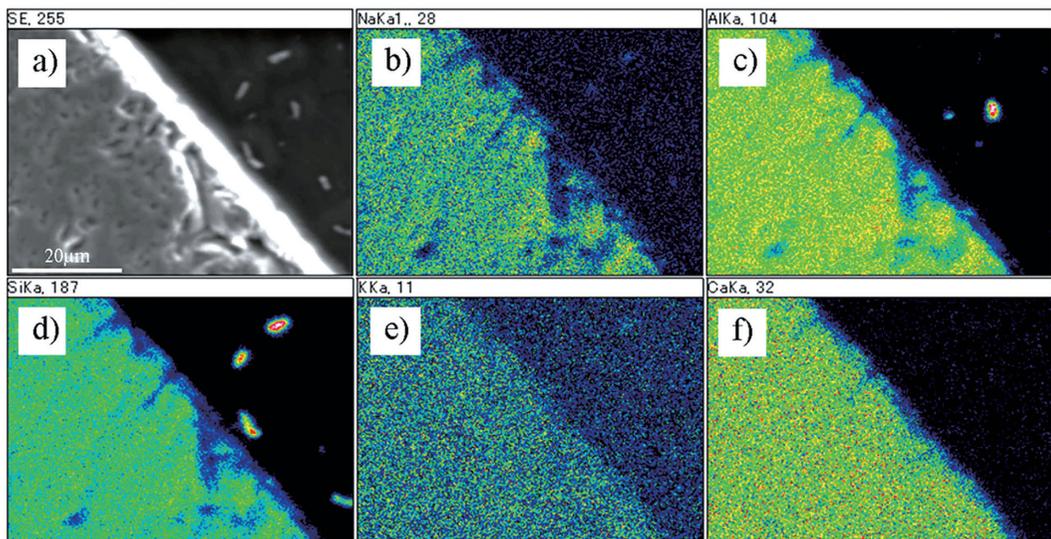


Fig. 9 SEM and X-ray images of element distribution in oligoclase and labradorite.  
a) SEM image, and b) Na, c) Al, d) Si, e) K and f) Ca images.

### 3.2.3 Altered products

TEM image of the altered products from the labradorite surface is shown in Figure 10. The morphology of the products shows a typical two-dimensional flake of 100–200 nm in length. EDS detected mainly Si, Al and Ca in the altered products, but Na was hardly detected (Fig. 10b). On the other hand, the relative intensities of Al and Ca are considerably lower than those in unaltered labradorite (Fig. 10c). The formation of smectite from plagioclase is often observed in natural

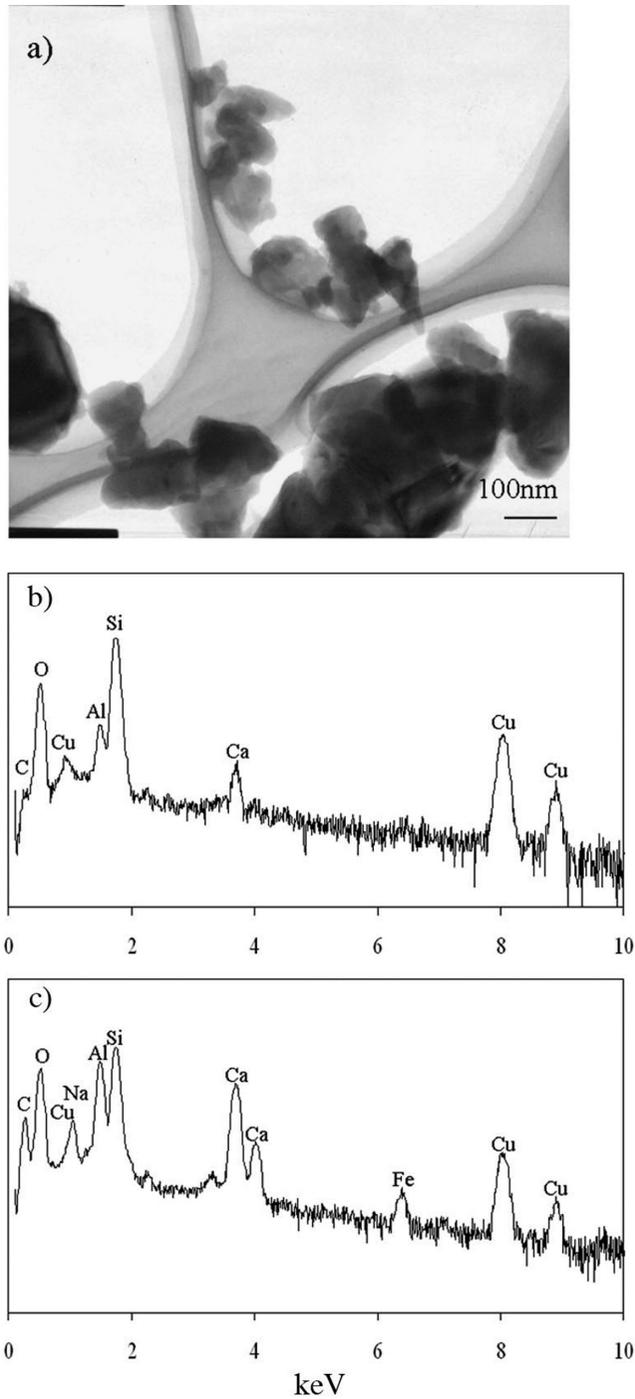


Fig. 10 TEM image (a) and EDX spectra of the weathered products of labradorite by pH 4  $H_2SO_4$  solution after 410 days (b), and EDX spectrum of unweathered labradorite (c).

weathering (e.g. Sakamoto and Kobayashi, 1997 and 1998). Therefore, from the TEM and EDS information, the alteration product is likely to be Ca-smectite. Because altered product is extremely small amount, it could not be identified by XRD.

In the present study, the formation of altered products was not so remarkable in this work using individual mineral of oligoclase and labradorite though a little altered product on labradorite surface was detected. However, no altered product was detected from the oligoclase. In contrast to this, previous studies (e.g. Kobayashi and Sakamoto, 2001) have reported the existence of altered products on the surface of oligoclase in granite. From this it may be inferred that the altered product such as smectite was formed by addition of elements (e.g. Mg and Fe), which dissolved from coexisting biotite in granite.

### 3.3 Effect of plagioclase-acidic water interaction on chemistry of spring water

Geological Survey of Japan, AIST (2005) summarized 4,536 hot and mineral springs in Japan. The data for each spring was compiled into tables consisting of name, location, temperature, amount of discharge, spring quality and pH. Generally, it is considered that hot springs are divided into 4 types of neutral type, acidic type, carbonate type and alkaline simple type. Among them, weakly acidic springs which is conducted in this work, are over 250 such as Appi spring in Akita prefecture, Ubako spring in Kanagawa Prefecture, Shinyu spring in Kagoshima Prefecture, and so on. Springs are seen under various geological environments such as plutonic rock, volcanic rock, sedimentary rock and metamorphic rock areas. On the other hand, plagioclase such as oligoclase and labradorite, which consist mainly of Na, Ca, Al and Si, is one of the essential minerals in these rocks. For example, plagioclase is included 25 to 60% in the modal value in igneous rocks. According to Geological Survey of Japan, AIST (2005), Na, Ca, Al and Si as cation are included in all types of the hot spring water, as well as acidic type.

Although the dissolution degree of each element was shown by molar ratios as mentioned above, in order to know the actual leaching amount from plagioclase, the amount of dissolved major and rare earth ions (REE) during 525 days is shown in relation to the ionic radius (Fig. 11). Si, Al, Ca and Na, which are major elements in both oligoclase and labradorite (Table 1), are shown the high value though the molar ratio of the ions are low as shown as Figures 2 and 3. The values of REE showing high molar ratio at an early stage is also low because REE content in plagioclase is originally low. These elements, especially Na and Ca, are major elements in plagioclase though pyroxene, amphibole and biotite are also slightly included. Al is also major element in plagioclase though it is included in amphibole and mica of rock-forming mineral. Si is contained in all of rock-forming minerals. Therefore, major elements in the cavity and framework of plagioclase are one of the important sources for the hot spring water in chemical weathering by acidic water under the earth surface.

## 4. Conclusions

In order to predict the effects of interaction between acidic hydrothermal solution and rocks and minerals on spring quality, artificial chemical weathering of plagioclases composed in almost rocks in earth crust has been investigated chemically and mineralogically. The mineralogical

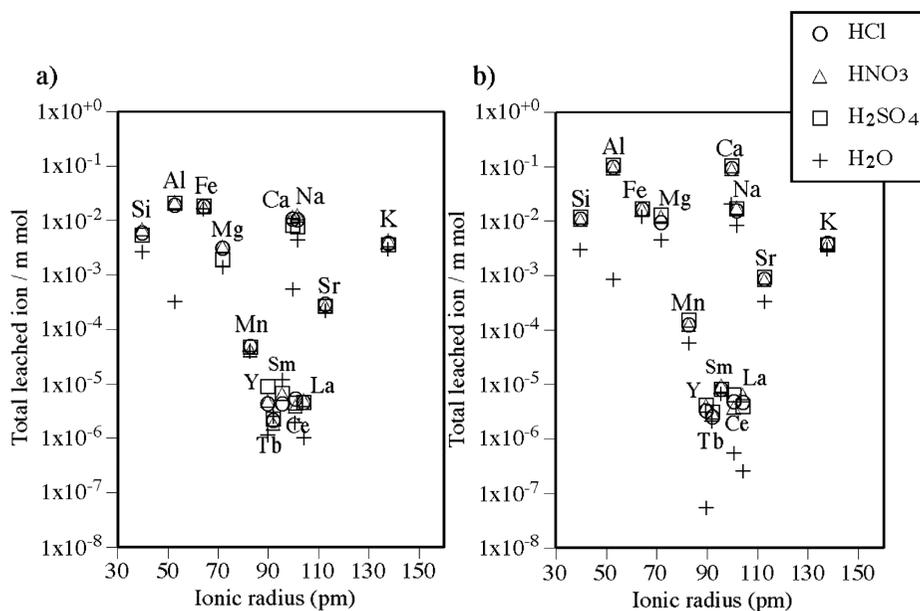


Fig. 11 Amount of dissolved major and rare earth elements during 525 days of oligoclase (a) and labradorite (b) against ionic radius.

and chemical changes of oligoclase and labradorite surfaces, and the molar ratio of ions released from the each plagioclase by the pH 4 acidic leached solutions differed from the reaction with distilled water. At an early stage, the molar ratios of Fe, Mg, Zn, Mn, Ce, La, and Sm in leached sample solution, which occupied cavities within the framework, are relative high. But at a later stage, the ratios are reduced significantly. The ratios of major elements in framework and cavity, such as Si, Al, Na, Ca, K, and Sr, are almost constant in the early and later stage. The amount of leached Si, Al, Ca and Na having the most appropriate ionic radius to the size of cavity, which are major elements in both oligoclase and labradorite, are shown the high value though the molar ratios are low. The SEM images of plagioclases surface showed that many irregular fractures formed by dissolution developed on the minerals.  $(Ca + Na + K)/(Si + Al)$  molar ratios for oligoclase and labradorite surfaces decreased with an increase in leached time.

The dissolved ions from plagioclase by acidic hydrothermal solution are likely to be one of the sources of ions in hot spring water of the acidic or weakly acidic types. The results obtained are expected to give the fundamental chemical information that is useful in consideration of the spring quality, source and the path of the hot spring water.

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**Appendix** : The molars of released elements ( $RE_{X \cdot d}$ ) in the leached solution calculated from

$$RE_{X \cdot d} = (V \cdot C_{X \cdot d}) / A_X,$$

where  $d$ ,  $V$ ,  $C_X$  and  $A_X$  are experimental period, volume of leached solution, ion concentration of  $x$  and atomic weight of  $x$ , respectively.  $V$  is 450 mL because samples of the leached solution, which was stored in the container over a 3-day period, were collected every 3 days. For instance,  $RE_{X \cdot d}$  of Na ion at the first 3 days in the leached solution is

$$RE_{Na \cdot d} = (450 \cdot C_{Na \cdot 3}) / A_{Na}.$$

The cumulative total mole ( $CTM_{X \cdot D}$  :  $D$  = total reached time) for the first 30 days is calculated from  $C_{X \cdot d}$  ( $d = 3, 6, 9, 12, 15, 18, 21, 24, 27, 30$ ) as follows :

$$CTM_{X \cdot 30} = RE_{X \cdot 3} + RE_{X \cdot 6} + \dots + RE_{X \cdot 30}.$$

After then, leached solution was collected at 30-day intervals between 30 days and 150 days, and at 45- or 90-day intervals for the last 525 days. For instance, the  $CTM_{60}$  of Na after 60 days is calculated using ion concentration in the leached solution of 60 days, it is assumed that leached ion concentrations from 30 days to 60 days are the same as them at 60 days as follows :

$$CTM_{Na \cdot 60} = CTM_{Na \cdot 30} + (450 \cdot C_{Na \cdot 60}) \cdot (60-30) / 3 / A_{Na}.$$

The molar ratio which means the dissolution degree of each element was calculated from the  $CTM_{X \cdot D}$  divided by the mole of individual elements in the unaltered plagioclase.