

Dissolution Behavior of Plagioclase in HCl and KOH Solutions

염산과 수산화칼륨 수용액과의 반응에 의한 사장석의 용해 거동

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ABSTRACT : Dissolution experiments were conducted to understand chemical nature of weathering of anorthosite from the Hadong area. Anorthosite and plagioclase from it were reacted with HCl or KOH solutions under various conditions concerning such as grain size, initial pH of solutions, and shaking. Average composition of plagioclase used in the experiment was $\text{Na}_{0.32}\text{Ca}_{0.71}\text{Al}_{1.71}\text{Si}_{2.26}\text{O}_8$.

Under acidic conditions, solution pH increases rapidly in the initial stage and then gradually to reach plateau. Shaking agitates the reaction rate in the initial stage but does not affect after the system reached steady state. Ca and Si concentrations show rapid increase and then gradual increase. Al concentration increases rapidly in the early stage and then decreases. Later decrease was interpreted as the precipitation of an Al-bearing material. Different dissolution rates of different constituents of plagioclase together with precipitation of Al-bearing material might be responsible for the non-stoichiometric dissolution of plagioclase.

X-ray diffraction analyses on anorthosite before and after dissolution experiment show dissolution rates differ with different lattice planes of plagioclase. It suggests the crystallographic control on dissolution reaction. X-ray photoelectron spectroscopic result shows that the average composition of plagioclase surface reacted with HCl of initial pH 1.97 for 2000 hours is $\text{Na}_{0.20}\text{Ca}_{0.26}\text{Al}_{1.71}\text{Si}_{2.30}\text{O}_8$. It means that Na- and Ca-depleted H-feldspar is developed without Al-depleted layer on the surface of plagioclase by reaction with HCl and that dissolution reaction takes place sparsely on the surface of plagioclase.

Al and Si are dissolved preferentially over Ca from anorthosite powder in KOH solution. Reaction of acid-reacted anorthosite with KOH solution shows the same Si dissolution behavior as in the fresh anorthosite. This fact indicates that the Al-depleted and Si-enriched layer does not build up on the acid-reacted surface.

요약 : 하동 지역 회장암의 풍화 현상을 화학적으로 이해하기 위하여 회장암에 대한 용해 실험을 실시하였다. 입자 크기, 용액의 초기 pH, 그리고 교반 속도 등에 대해서 다양한 조건 하에서 하동 지역의 회장암과 사장석을 염산 혹은 수산화칼륨 수용액과 반응시켰다. 용해 실험에 사용된 사장석의 평균 조성은 $\text{Na}_{0.32}\text{Ca}_{0.71}\text{Al}_{1.71}\text{Si}_{2.26}\text{O}_8$ 이었다.

산성 조건에서 용액의 pH는 시간에 따라, 반응 초기에 급격히 증가한 후 증가 속도가 감소하여 대지(臺地)에 다다른다. 교반 속도는 반응 초기에는 반응 속도에 어느 정도의 영향을 주지만 계가 정상 상태에 도달한 후에는 영향을 주지 못한다. 칼슘과 규소의 농도는 반응 초기에 급격히 증가한 후 점차 증가 속도가 느려진다. 알루미늄의 농도는 초기에 증가한 후 감소한다. 이는 알루미늄을 포함하는 물질의 침전 반응이 있었던 것으로 해석된다. 각 구성분들의 용해 속도 차와 침전 반응이 사장석의 비화학양론적 용해 거동을 설명해 준다.

반응 전후 회장암에 대한 X-선 회절 분석 결과 용해 속도가 사장석의 격자면에 따라 서로 다르며, 이로부터 용해 반응이 결정학적인 제어를 받음을 알 수 있다. X-선 광전자 분광 분석법을 이용한 표면 화학 분석 결과, 초기 pH 1.97의 염산 용액과 2000 시간 동안 반응한 사장석 표면 (~60 Å)의 평균 조성은 $\text{Na}_{0.26}\text{Ca}_{0.26}\text{Al}_{1.7}\text{Si}_{2.3}\text{O}_8$ 이었다. 이는 염산 용액과의 반응에 의해서 사장석의 표면에 나트륨과 칼슘이 용탈된 수소-장석이 형성되나, 알루미늄이 용탈된 층은 형성되지 않았음을 의미한다. 또한 이 결과들은 용해 반응이 사장석 표면에서 불연속적으로 일어났음을 말해 준다.

회장암과 수산화칼륨 수용액의 반응에서 알루미늄과 규소의 용해 속도는 칼슘의 용해 속도보다 빠르다. 산성 용액과 반응했던 회장암 분말을 다시 수산화칼륨 수용액과 반응시킨 결과 신선한 회장암 분말과의 반응에서와 똑같은 규소의 용해 거동을 보여주었다. 이러한 결과는 사장석을 산성 용액과 반응시켰을 때 알루미늄은 용탈되고 규소만 부화된 층이 그 표면에 형성되지 않았음을 지시해 준다.

INTRODUCTION

It has been widely accepted that kaolin deposits in the Hadong area, Korea, have been formed by weathering of anorthosite (Lee et al., 1977; Kim et al., 1989; Jeong and Kim, 1993). They show that anorthosite is composed mostly of plagioclase (> 90 vol. %) with small amounts of hornblende, chlorite, and mica. Therefore the formation of kaolin minerals is attributed to the weathering of plagioclase. However most of previous studies are concentrated on the mineralogical characterization, utilization and genesis of the kaolin ores. So far no experimental study on the formation of kaolin has been made.

This paper aims to study the dissolution behavior of plagioclase by experimental method. Generally, dissolution of minerals in water is very slow under natural conditions. It is, however, accelerated by the aid of both acids and bases. Therefore the experiments were conducted under acidic and basic conditions using HCl and KOH solutions.

MATERIALS AND METHODS

Materials

Anorthosite from the Hadong area is composed mostly of medium- to coarse-grained plagioclase (>90 volume %) with small amounts of

chlorite, hornblende, and biotite. Microfractures are well developed by the cataclastic deformation during the regional metamorphism.

Plagioclase is subhedral to anhedral and shows albite or albite-Carlsbad twinning. It shows no compositional zoning. Microprobe analysis shows that mean composition of 20 points is $\text{Na}_{0.3}\text{Ca}_{0.7}\text{Al}_{1.7}\text{Si}_{2.3}\text{O}_8$ (Table 1). It exhibits abundant microfractures in several sets of directions due to cataclastic deformation. A complex combination of the microfractures, cleavages, and grain boundaries results in rhombic, rectangular, and irregular microfissure patterns (Jeong, 1992).

Sample Preparation

Anorthosite block. $1 \times 1 \times 1.5\text{cm}^3$ -sized block sample was obtained from a fresh anorthosite. The block was ultra-sonically cleaned in acetone to remove organic materials and ultrafine particles adhered to its surface.

Anorthosite powders. Fresh anorthosite was wet-ground in acetone using ceramic pestle to minimize the structural damages from heat and mechanical force that may be caused by grinding. The powder was dry-sieved to obtain size fractions of 62~44 μm and smaller than 44 μm in diameter. Each size fraction was repeatedly ultrasonified in reagent grade acetone until the clean supernatant was obtained. This process is

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Table 1. Electron microprobe analyses of plagioclase used in the experiment.

	1	2	3	4	5	6	7	8	9	10
SiO ₂	47.87	51.04	51.00	50.96	49.35	50.75	50.29	46.45	51.67	50.38
TiO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al ₂ O ₃	33.74	31.63	31.82	31.34	32.97	31.70	31.80	34.68	31.26	32.46
Cr ₂ O ₃	0.02	0.00	0.01	0.00	0.03	0.00	0.00	0.00	0.00	0.00
FeO	0.05	0.00	0.00	0.04	0.06	0.07	0.03	0.04	0.02	0.01
MnO	0.02	0.05	0.04	0.01	0.01	0.01	0.00	0.04	0.02	0.00
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	16.22	13.84	13.66	14.01	15.71	14.17	15.04	17.71	13.70	14.57
Na ₂ O	2.45	3.93	4.05	3.86	2.86	3.64	3.53	1.71	3.92	3.42
K ₂ O	0.03	0.11	0.09	0.08	0.05	0.09	0.07	0.04	0.10	0.09
Total	100.40	100.59	100.65	100.30	101.02	100.42	100.76	100.66	100.69	100.93
Cations on the basis of 32 O										
Si	8.74	9.24	9.23	9.26	8.94	9.21	9.12	8.50	9.33	9.10
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	7.26	6.75	6.78	6.71	7.04	6.78	6.80	7.48	6.66	6.91
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	0.01	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.00
Mn	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	3.17	2.68	2.65	2.73	3.05	2.76	2.92	3.47	2.65	2.82
Na	0.87	1.38	1.42	1.36	1.00	1.28	1.24	0.61	1.37	1.20
K	0.01	0.03	0.02	0.02	0.01	0.02	0.02	0.01	0.02	0.02

	11	12	13	14	15	16	17	18	19	20
SiO ₂	50.22	51.28	51.14	49.81	48.50	50.86	50.91	50.88	52.22	51.31
TiO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al ₂ O ₃	32.10	31.73	31.09	32.45	33.10	31.29	31.64	31.65	30.09	31.18
Cr ₂ O ₃	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.02	0.00	0.00
FeO	0.00	0.00	0.04	0.08	0.04	0.04	0.03	0.00	0.05	0.00
MnO	0.00	0.05	0.06	0.06	0.00	0.02	0.00	0.05	0.00	0.00
MgO	0.00	0.00	0.01	0.00	0.01	0.02	0.00	0.00	0.00	0.00
CaO	14.77	13.77	13.68	14.64	16.30	13.75	14.10	14.03	12.63	13.81
Na ₂ O	3.55	4.01	3.97	3.49	2.66	3.87	3.93	3.89	4.67	4.34
K ₂ O	0.04	0.07	0.06	0.05	0.02	0.09	0.06	0.08	0.05	0.06
Total	100.68	100.91	100.05	100.56	101.63	99.91	100.67	100.60	99.69	100.70
Cations on the basis of 32 O										
Si	9.11	9.25	9.30	9.05	8.84	9.27	9.22	9.22	9.51	9.29
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	6.86	6.75	6.67	6.95	7.11	6.72	6.75	6.76	6.46	6.65
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.00
Mn	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.01	0.00	0.00
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	2.87	2.66	2.67	2.85	3.18	2.68	2.74	2.72	2.46	2.68
Na	1.25	1.40	1.40	1.23	0.94	1.37	1.38	1.37	1.65	1.52
K	0.01	0.02	0.01	0.01	0.00	0.02	0.02	0.02	0.01	0.01

Table 2. Experimental conditions of the dissolution experiments.

Experiment	Solid Material		Solution	Initial pH	Solid/Solution Ratio (gr/gr)	Temp. (°C)	Shaking
	Size (μm)	Material					
Run A	Block	Anorthosite	HCl	1.97	6.38/250	36 ± 1	No
Run B1	44~62	Anorthosite	HCl	1.97	3.62/250	36 ± 1	No
Run B2	<44	Anorthosite	HCl	1.97	3.62/250	36 ± 1	No
Run C1	44~62	Plagioclase	HCl	3.72	2.00/250	29 ± 2	Yes
Run C2	44~62	Plagioclase	HCl	3.72	2.00/250	29 ± 2	No
Run D1	<44	Anorthosite	KOH	12.02	0.80/250	29 ± 2	Yes
Run D2	Anorthosite After Run B2		KOH	12.02	0.80/250	29 ± 2	Yes

for the removal of the submicron-sized particles adhered to the surfaces of larger particles. It is a very important process in the sample preparation, since submicron particles are highly reactive because of their large specific surface area and can cause misinterpretation of the results.

Plagioclase powder. Plagioclase particles were hand-picked from the fresh anorthosite fragments under the stereo-microscope. 44~62 μm -sized plagioclase powder was prepared through the same procedure as that of anorthosite powder.

Dissolution Experiments

Anorthosite block, anorthosite powder, and plagioclase powder were reacted with acidic or basic solutions in polypropylene or high density polyethylene bottles. Each bottle was immersed in a water bath where temperature was kept constant and/or continuously shaken in a flask shaker. Experimental conditions are summarized in Table 2.

Solutions. Acidic solutions were prepared by adding reagent grade hydrochloric acid to the distilled-deionized water to pHs of 1.97 and 3.72 after equilibration with atmospheric CO_2 . Basic solution was prepared by dissolving reagent grade potassium hydroxide (KOH) in the distilled-deionized water to a pH of 12.02. It was immedi-

ately sealed so as not to have equilibrated with atmospheric CO_2 .

Five different sets of experimental runs were prepared to know the dissolution behavior of plagioclase.

Run A. Anorthosite block was reacted with HCl solution of initial pH 1.97 at $36 \pm 1^\circ\text{C}$.

Run B1 and B2. Anorthosite powders were reacted with HCl solution of initial pH 1.97 at $36 \pm 1^\circ\text{C}$. Powder used was 44~62 μm size fraction in run B1 and <44 μm size fraction in run B2 respectively.

Run C1 and C2. 44~62 μm plagioclase powder was reacted with HCl solution of initial pH 3.72 at $29 \pm 2^\circ\text{C}$. In run C1, system was continuously shaken and in run C2, it was not shaken.

Run D1 and D2. Anorthosite powders of <44 μm size fraction were reacted with KOH solution of initial pH 12.02 at $29 \pm 2^\circ\text{C}$. Powder used was fresh anorthosite in run D1 and anorthosite recovered after run B2 (after reaction with HCl solution of initial pH 1.97 for about 2000 hours) in run D2.

Solution sampling. In order to minimize the changes in the solution to solid ratios, sampling was conducted after enough shaking of the bottles. Three samples were collected for both so-

lution and solid from each bottle. One was for *in situ* pH measurement and other two for measurement of cation concentrations as duplicates. This way of sampling was employed to prevent possible contaminations from pH electrode.

Analytical Methods

pH measurement. An Orion EA 940 pH meter was used in the measurement of solution pH.

Chemical analyses. Chemical composition of plagioclase was analyzed using a JEOL Superprobe 733 electron microprobe. Analysis was carried out at an accelerating voltage of 15kV, sample current of 10nA and beam diameter of 10 μ m.

Cation concentrations of solutions were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using a Perkin-Elmer ICP emission spectrometer Plasma 40 at the Seoul Branch of the Korea Basic Science Institute. Concentrations of Ca, Al, and Si were measured.

X-ray diffraction analysis. Changes in crystallographic features of the anorthosite powders before and after dissolution reaction were investigated by X-ray diffraction using a Rigaku Geigerflex X-ray diffractometer. Analyses were conducted with Ni-filtered CuK α radiation at 40kV/30mA in a continuous scan-ning mode of scanning speed of 5° 2 θ /min.

Surface chemical analysis. Changes in the surface chemistry of plagioclase by reaction with acidic solution were studied with a VSW X-ray photoelectron spectrometer equipped with hemispherical-type analyzer. Both the fresh anorthosite and another anorthosite recovered after run B2 were analyzed after enough drying. ALK α radiation at 10kV/15mA was used for the X-ray

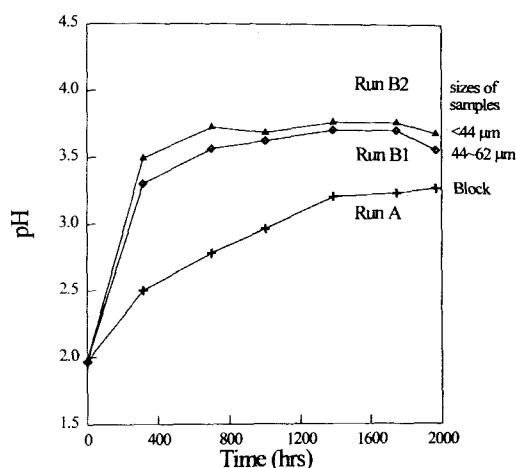


Fig. 1. pH variations with time in the reaction of anorthosite with HCl solution of initial pH 1.97. Note the reaction behavior with different sizes of samples.

source. To prevent possible contaminations from remnant gases and for the photoelectrons to have long mean free path, vacuum of high quality (10^{-9} ~ 10^{-8} mbar) in analyzer chamber was maintained during the whole process of analysis.

RESULTS AND DISCUSSION

pH Variations

In all the runs, pHs were not buffered and their variations with time were monitored. In the time-pH plot, run A (reaction of anorthosite block with HCl solution of initial pH 1.97) shows gradual increase with time. Run B1 (reaction of anorthosite powder of 44~62 μ m size fraction with HCl solution of initial pH 1.97) and B2 (reaction of anorthosite powder of <44 μ m size fraction with HCl solution of initial pH 1.97) show rapid increase at early stages followed by plateaus at about 3.7 after 700 hours from the start of the experiment (Fig. 1). The major difference among run A, B1 and B2 is grain size. The pH variation curves show that the rate of reaction increases with decreasing grain size.

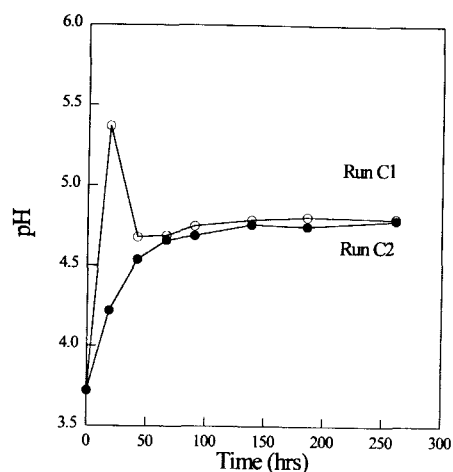


Fig. 2. pH variations with time in the reaction of plagioclase powder (44–62 μm) with HCl solution of initial pH 3.72. Reaction bottle was continuously shaken in ru62n C1 (open circle), but not shaken in run C2 (filled circle). Note the differences in the early stages.

In run C1 (reaction of 44~62 μm plagioclase powder with HCl solution of initial pH 3.72, in constant shaking), pH values show a rapid increase in the first measurement after 18 hours from the start of the experiment and then decrease to about 4.7. Run C2 (reaction of 44~62 μm plagioclase powder with HCl solution of initial pH 3.72, in no shaking) has no pH maximum at the early stage of experiment but shows rapid increase and reaches a plateau at about 4.7 in 66.5 hours (Fig. 2). The difference between two runs is shaking. Shaking has influences on the rates of diffusion of materials in solution. Therefore, the difference at the first measurement after 18 hours from the start of experiment can be interpreted as follows: cation exchange reaction between hydrogen (hydronium) ion and alkali and/or alkali earth ion determines pH of the system at the early stage of reaction. The adsorption of hydrogen ion to the surface of plagioclase, exchange of Na^+ and/or Ca^{2+} with H^+ , and desorption of Na^+ and Ca^{2+} from the surface of plagioclase resulting in the formation of

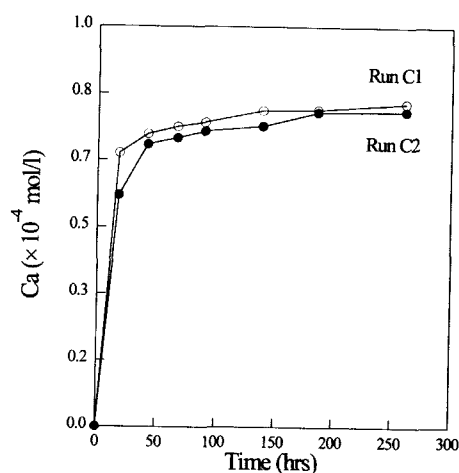


Fig. 3. Variations of total $[\text{Ca}^{2+}]$ with time in the reaction of plagioclase powder (44–62 μm) with HCl solution of initial pH 3.72. Reaction bottle was continuously shaken in run C1, but not shaken in run C2.

hydrogen-feldspar on the surface of dissolving plagioclase are faster than the diffusion of H^+ to the plagioclase-water interface and of Na^+ and Ca^{2+} from the interface to the far apart part of solution. The absence of any noticeable difference between two runs in the late reaction suggests that the rates of diffusion of chemical species in solution have no influences on the rate of dissolution of H-feldspar. Final pH plateau suggests that the rate of hydrogen release by the decomposition of hydrogen-feldspar in solution is similar to the rate of hydrogen consumption by the formation of hydrogen-feldspar in the late stage of dissolution.

The initial pH 3.72 in runs C1 and C2 is the steady state value in runs B1 and B2. Therefore if it were an equilibrium pH between plagioclase and solution, there would not have been pH changes in runs C1 and C2. However, there are evident changes in pH in runs C1 and C2. Therefore it can be concluded that it is not an equilibrium pH. The pH change is assumed to be controlled by the relative rates of H^+ consumption by H-feldspar formation and H^+ release by H-feld-

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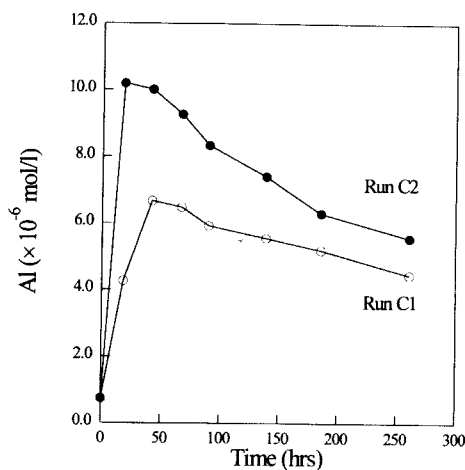


Fig. 4. Variation of total Al concentration with time in the reaction of plagioclase powder with HCl solution of initial pH 3.72 in shaking (run C1) and in no shaking (run C2). Later decrease suggests the precipitation of Al-mineral.

spar dissolution and some possible secondary precipitation.

Variations in Cation Concentrations with Time

Solutions from runs C1 (reaction of 44~62 μ m plagioclase powder with HCl solution of initial pH 3.72 in shaking) and C2 (reaction of 44~62 μ m plagioclase powder with HCl solution of initial pH 3.72 in no shaking) were analyzed for Ca, Al, and Si. In both runs, concentration of Ca^{2+} rapidly increased in the early stage, and then slowly increased in the later stage (Fig. 3). Concentration of Al rapidly increased in the early stage and then decreased in both runs (Fig. 4). Concentration of Si rapidly increased in the early stage and its release rate decreased in the later stage (Fig. 5). In both runs, solution compositions were different from those predicted from the stoichiometry of plagioclase.

Initial high release rate of Ca^{2+} suggests that active ion exchange between proton and Na^+ or

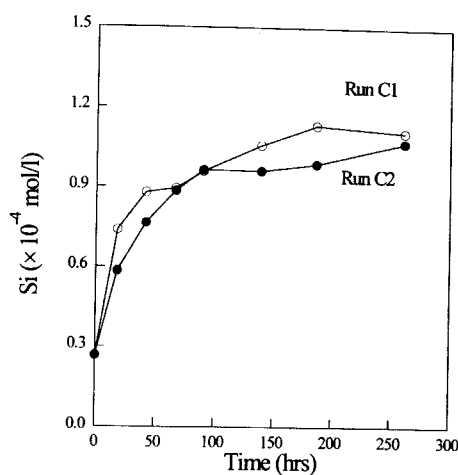


Fig. 5. Variation of total Si concentration with time in the reaction of plagioclase powder (44-62 μ m) with HCl solution of initial pH 3.72 in shaking (open circle; run C1) and in no shaking (filled circle; run C2).

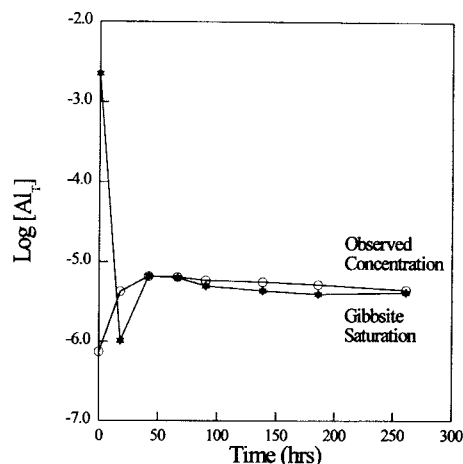


Fig. 6. Variation of total Al concentration (open circle) with time in the reaction of plagioclase powder (44-62 μ m) with HCl solution of initial pH 3.72 in shaking (run C1) compared with equivalent gibbsite saturation value (filled star). Solution is supersaturated with respect to gibbsite (Gibbsite saturation values from Smith and Martell, 1976).

Ca^{2+} occur in the early stage of the reaction. Decrease in Al concentration in the late stage of dissolution suggests the formation of some Al-bearing precipitates. Concentrations of Al in solution

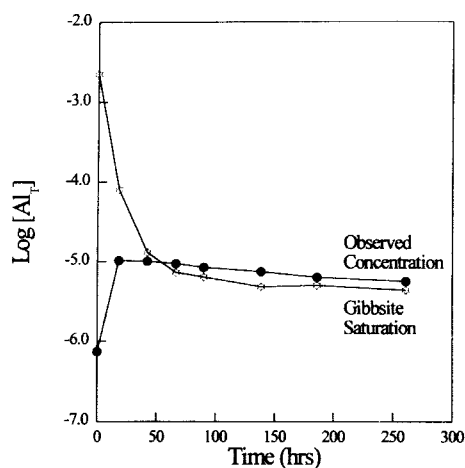


Fig. 7. Variation of total Al concentration with time (filled circle) in the reaction of plagioclase powder (44–62 μ m) with HCl solution of initial pH 3.72 in no shaking (run C2) compared with equivalent gibbsite saturation curve (open star). Solution is supersaturated with respect to gibbsite.

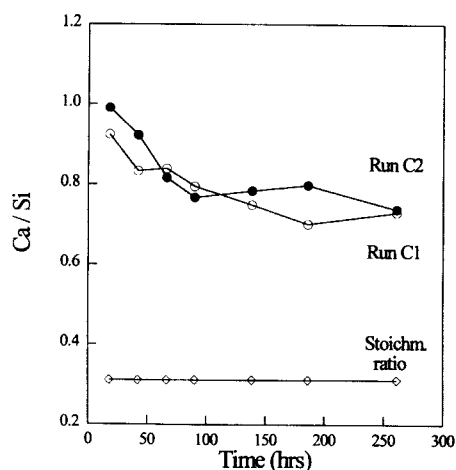


Fig. 8. Variation of Ca/Si values with time in the reaction of plagioclase powder (44–62 μ m) with HCl solution of initial pH 3.72 in shaking (open circle; run C1) and in no shaking (filled circle; run C2). Stoichiometric composition is also shown.

and equivalent gibbsite saturation values are plotted together in Figs. 6 and 7. Solutions are supersaturated with respect to gibbsite. The concentration of Al is determined by the rates of dis-

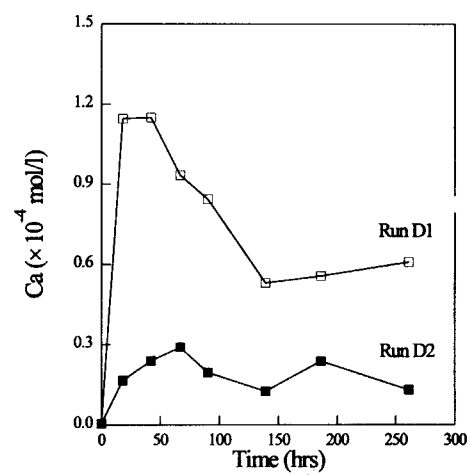


Fig. 9. Variation of total $[Ca^{2+}]$ with time in the reaction of KOH solution of initial pH 12.02 with fresh anorthosite (run D1) with acid-reacted anorthosite (run D2).

solution of hydrogen-feldspar and of precipitation of secondary Al-mineral. The precipitation of secondary mineral is also responsible for the non-stoichiometries of solution composition.

The release rate of Ca is faster than that of Si even after the solution reached steady state with respect to Al (Fig. 8). It suggests that Si-enriched layer that may remain on the dissolved surface cannot delay the release of Ca from the interior. In other words, even if Si-enriched layer is formed on the surface of the dissolving plagioclase, it might exist discontinuously or in porous forms on the surface of fresh plagioclase so that it cannot act as a diffusional barrier. Therefore it is likely that the dissolution reaction occurs sparsely. This matches well with the fact that many etch pits are found on the surfaces of feldspars from soils. It is important to mention that shaking has no effect on the dissolution rate. All these facts suggest that the dissolution of plagioclase follows a surface-controlled reaction mechanism in the experimental conditions.

In runs D1 and D2, there lies no noticeable difference in silica concentration (Fig. 11). Run D1

Dissolution Behavior of Plagioclase in HCl and KOH Solutions

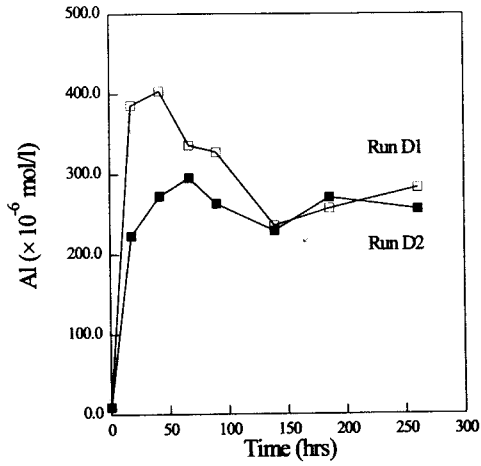


Fig. 10. Variation of total Al concentration with time in the reaction of KOH solution of initial pH 12.02 with fresh anorthosite (run D1) and with acid-reacted anorthosite (run D2).

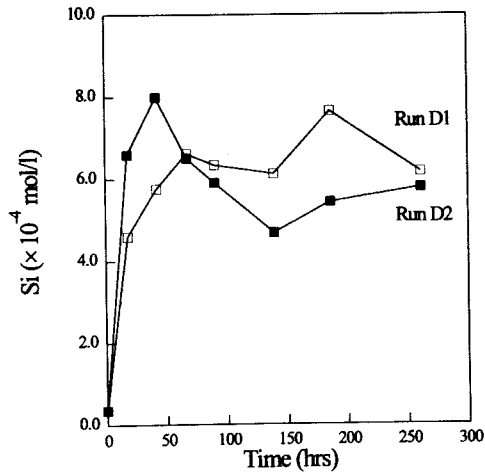


Fig. 11. Variation of total Si concentration with time in the reaction of KOH solution of initial pH 12.02 with fresh anorthosite (run D1) with acid-reacted anorthosite (run D2). The result suggests that no Si-enriched layer be developed by the reaction with acidic solution.

is a reaction of fresh anorthosite with KOH solution of initial pH 12.02. Run D2 is a reaction of anorthosite recovered after run B2 with KOH solution of initial pH 12.02, that is, anorthosite powder after the reaction with HCl solution of initial

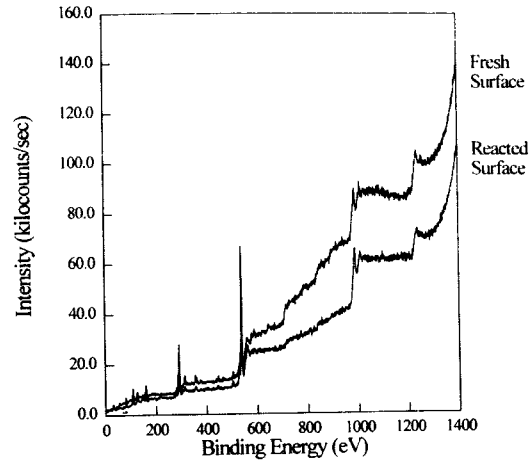


Fig. 12. X-ray photoelectron spectra of fresh and acid-reacted surfaces.

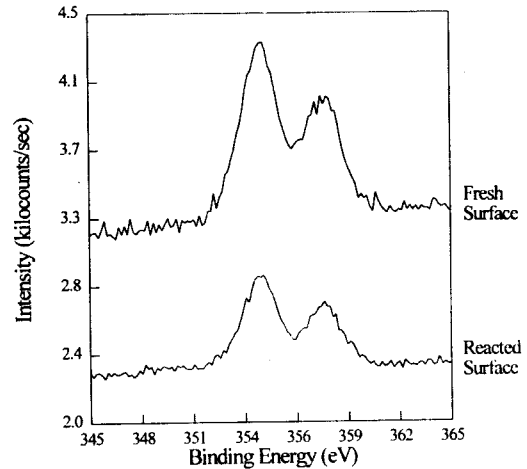


Fig. 13. Ca₂p peaks of fresh and acid-reacted surfaces. Peak intensity is notably weakened by the reaction with HCl solution.

pH 1.97 for 2000 hours was again reacted with KOH solution of initial pH 12.02. Considering the high solubility of silica in basic conditions (pH > ~9.3), we can expect that no Si-enriched layer thick enough to influence dissolution behavior of plagioclase builds up at the surface of plagioclase which has been reacted with acidic solution. The general trend of dissolution (Figs. 9, 10, and 11) shows that some aluminous material precipitated during dissolution of plagioclase.

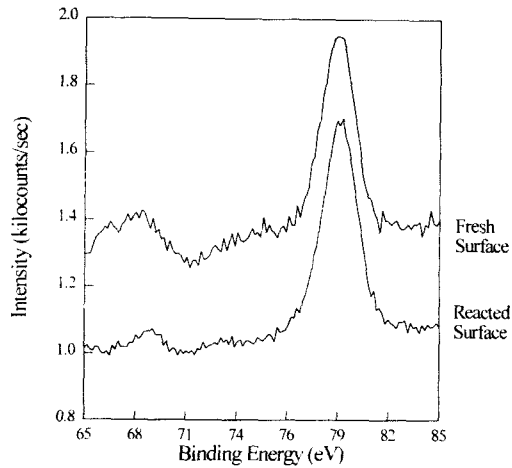


Fig. 14. Al₂p peaks of fresh and acid-reacted surfaces. No noticeable difference is observed.

Table 3. Peak areas obtained from XPS. Each peak area is obtained by repeated scanning over small ranges of binding energy around the peak position. Units are arbitrary.

Peak	Area	Fresh Plagioclase	Reacted Plagioclase
Ca 2p		4.661	2.198
Na 1s		2.022	1.117
Al 2p		1.435	1.621
Si 2s		4.186	4.296
O 1s		44.279	48.194

Changes in Surface Chemistry

Fresh anorthosite as well as anorthosite recovered after run B2 (reaction with HCl solution of initial pH 1.97 for 2000 hours) were analyzed by XPS (Figs. 12, 13, and 14). The peak intensities are given in Table 3. From these data, average formula of the reacted surface ($\sim 60\text{\AA}$) is calculated as $\text{Na}_{0.2}\text{Ca}_{0.3}\text{Al}_1\text{Si}_2\text{O}_8$.

The fact that no significant chemical shift in the peak positions of cations and oxygen exists suggests that the surface structure of plagioclase is not significantly disturbed by the reaction with acidic solution. Considering the rise of pH of solution in the dissolution reaction, it can be con-

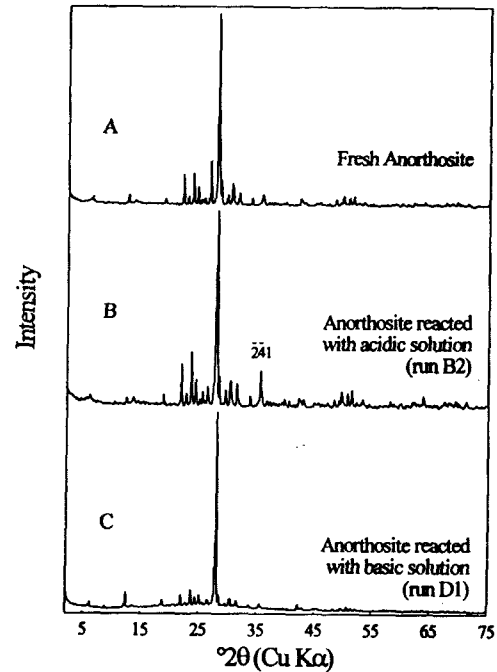


Fig. 15. X-ray diffraction pattern of fresh anorthosite (A), its reacted sample with HCl solution of initial pH 1.97 (B), and its reacted sample with KOH solution of initial pH 12.02 (C).

cluded that hydrogen occupies the empty Na^+ and Ca^{2+} sites to maintain basic plagioclase structure.

Crystallographic Control of Dissolution Reaction

X-ray diffraction patterns of original anorthosite, another sample treated in run B2 (reaction with HCl solution of initial pH 1.97) and the other sample treated in run D1 (reaction with KOH solution of initial pH 12.02) were compared after normalization with respect to their (002) peaks of plagioclase (Fig. 15).

X-ray diffraction peaks of plagioclase reacted with acidic solution are generally weak and the intensity ratios are also changed, but intensities of (241) and (331) peaks became stronger compared with untreated one. Peaks of plagioclase reacted

with basic solution are also generally weakened.

It can be concluded that the dissolution rates vary with the lattice plane, especially in acidic solution, since the densities of the reactive sites vary with lattice plane. Information on the crystallographic features of the mineral, rather than its mere specific surface area, is needed for a quantitative work in the mineral water reaction. Reactive sites can also be created during the process of sample preparation.

XRD identification of secondary precipitates was difficult because of too small quantity and poor crystallinity.

CONCLUSIONS

Hydrolysis of plagioclase in HCl solution seems to follow the sequence; 1) rapid adsorption of hydrogen (hydronium) ion on the reactive surface sites of plagioclase, 2) ion exchange between hydrogen and Na or Ca, 3) desorption of Na and Ca, 4) formation of hydrogen-feldspar, 5) release of Al and Si from the hydrogen-feldspar at comparable rates.

Dissolution reaction occurs sparsely on the surface of plagioclase without thick leached layer in acidic conditions. The coupled dissolution-pre-

cipitation reaction and different release rates of different cations are responsible for the non-stoichiometric dissolution of plagioclase.

In basic solution, release rates of Al and Si are faster than that of Ca.

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