LABORATORY DISSOLUTION OF PLAGIOCLASE FELDSPARS IN WATER AND ORGANIC ACIDS AT ROOM TEMPERATURE

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Abstract

Freshly fractured albite, oligoclase, labradorite, bytownite, anorthite, and a high–K variety of plagioclase in particle sizes between 44 μm and 150 μm were dissolved at room temperature in deionized water, 0.01 M acetic and aspartic acids (weakly complexing), and salicylic and citric acids (strongly complexing). Solutes of centrifuged solution were analyzed for pH, and for Si, Al, Fe, Mg, Ca, Na, and K.

Ca–rich plagioclases dissolved in organic acids more readily than did Na–rich plagioclases, whereas Na–rich plagioclases were the more soluble in deionized water. Al was preferentially dissolved over Si in particular from Ca–rich plagioclase in complexing acids. Ca was relatively more soluble than was Na in both organic acids and water.

The organic solvents, in order of increasing effect of dissolution, were acetic, aspartic, salicylic, and citric acids, which is the order of complexing capacities. Citric acid was more effective than other acids in extracting Al and Ca, particularly from Ca–rich plagioclases, presumably because of the formation of Al– and Ca– complexes.

Introduction

Organic materials and their associated organic acids are widely present, not only in humus and peat, but in groundwater. By forming soluble complexes particularly with polyvalent cations from minerals and rocks, organic acids play important roles in geochemical processes, such as the dissolution, transportation, and concentration of elements in the earth's surface and in the formation of resistate phases in the zone of weathering (Keller, 1964; Huang and Keller, 1970, 1971, 1972; Manskaya and Drozdova, 1968; Swain, 1970). Although some studies have been made on stabilities of plagioclase feldspars in inorganic aqueous solutions (Nash and Marshall, 1956; Correns, 1963; Keller *et al.*, 1963; Lagache, 1965; Burger, 1969), no prior systematic or quantitative laboratory study of them in organic acids has been reported.

Goldich (1938) noted that the susceptibility of primary rock–forming silicate minerals to weathering was in the order of Bowen's reaction series. By using the percentage of Ca released as an index of weatherability of three plagioclase minerals in sulfuric acid, Burger (1969) showed a sequence of decreasing weatherability as follows:

bytownite > labradorite > oligoclase. Huang and Keller (1970), however, found that primary rock–forming silicate minerals dissolved differently in organic acid solutions than they did in inorganic aqueous solutions, and concluded that weathering of silicate minerals by complexing acids may result in a different order of mineral stability than the traditional one of Goldich. Borovec and Neuzil (1966) working at 70°C found that in the dissolution of labradorite (An, 60-64) by water, Na was more mobile than Ca, and Si was about 15 to 30 times more mobile than Al at neutral pH.

In this paper we report the results of laboratory dissolution of a series of plagioclase minerals—albite, oligoclase, labradorite, bytownite, anorthite, and high–K plagioclase, in deionized water, and four organic acids at room temperature for periods up to 24 days.

<div align="center">EXPERIMENTAL</div>

Mineral Samples and Organic Solvents

Six plagioclase feldspars studied, albite, oligoclase, labradorite, bytownite, anorthite, and a high–K variety, were obtained from Ward's Natural Science Establishment. The minerals were relatively pure. A specimen purchased and labelled as "andesine" proved to be a high–K variety of plagioclase. It was included in the experiment as "andesine" before bulk chemical analyses revealing its composition were completed (Table 1). Results of its dissolution (Kiang, 1972), although non–sequential in the Na–Ca series, were consistent with responses found in an earlier experiment (Huang and Keller, 1970) embodying K–feldspar.

Large specimens of each mineral were broken with a hammer, and clean fragments from the interior were picked with tweezers. These were further crushed with an alumina mortar and pestle, rinsed with deionized water three times, dried, further pulverized with the alumina mortar and pestle, and sieved through a stainless steel screen, so as to recover the size fraction between 44 μm and 150 μm. These particles were soaked in deionized water, dried, and stored in plastic bottles. Aliquots of them were analyzed (Table 1).

Organic acids, at 0.01M concentration, whose functional groups are typically present in humic acids and other acids of geological environments (Saxby, 1969) were chosen; namely, weakly complexing acetic and aspartic acids, and strongly complexing salicylic and citric acids.

Laboratory Dissolution and Analysis

Three grams (3.00 g) of each sample were added to 250 ml of 0.01 M organic acid solutions and deionized water in polyethylene bottles, and shaken slowly and continuously at room temperature for 1, 6, 12, and 24 days in closed systems. Reagent blank solutions were also run in the same procedure throughout the entire experiment. After each time interval, solutions were withdrawn and centrifuged (Sorval RC–2B supercentrifuge) at 25°C and 18,000 rpm for 30 minutes, which would throw down particles <250 Å (Huang and Keller, 1971). Twenty–five ml of the clear solution was pipetted and analyzed. The remaining contents of the centrifuged tube were returned, without any addition, to the

reaction bottle for continuing dissolution. The pH of the solution was immediately measured with a research model meter.

Si was determined colorimetrically following the procedure by Shapiro and Brannock (1952), which involved reduction of yellow silicomolybdate complex to molybdenum blue, measured at 780 nm with a Cary 14 spectrophotometer. Al was determined by nitrous oxide–acetylene flame emission (Perkin–Elmer 403 atomic absorption spectrophotometer) in a 4 ml aliquot to which 0.01 M of K–solution (40,000 ppm K) was added to enhance emission intensity. Mg was determined by atomic absorption in a 4 ml aliquot to which 0.01 ml of La–solution (40,000 ppm La) was added to correct interferences. Ca was de-

TABLE 1. CHEMICAL ANALYSES AND LOCALITIES OF MINERAL SAMPLES[a]

	Albite	Oligoclase	Labradorite*	Bytownite	Anorthite	High-K Plagioclase
SiO_2	65.63	58.81	52.40	46.40	42.24	64.40
Al_2O_3	22.37	27.16	33.12	34.14	37.68	20.78
Fe_2O_3	0.036	0.34	0.007	-----	0.36	0.044
FeO	0.026	0.217	0.27	0.49	0.37	0.336
MnO	0.005	0.012	0.009	0.01	0.009	0.006
MgO	0.016	0.073	0.10	0.33	0.39	0.033
CaO	0.166	3.61	9.00	13.99	17.04	0.042
P_2O_5	0.054	0.11	0.09	0.11	0.111	0.090
Na_2O	10.64	8.02	5.39	3.50	1.35	4.85
K_2O	0.71	1.07	0.78	0.55	0.27	9.06
H_2O^+	0.25	0.55	0.10	0.44	0.10	0.54
Ab[b]	95.0	75.0	49.5	30.0	12.4	44.8
An	0.8	18.6	45.8	66.8	86.1	0.2
Or	4.2	6.4	4.7	3.2	1.5	55.0

[a]Analyses by the Bruce Williams Laboratories, Joplin, Missouri
[b]Mol %

Albite:	Amelia Court House, Virginia
Oligoclase:	Bordam, Bamble, Norway
Labradorite:	Nain, Labrador
Bytownite:	Crystal Bay, Minnesota
Anorthite:	Japan
High-K plagioclase:	Near Judith Basin, Montana
("Andesine")	

*The analysis of this labradorite differs from the composition of labradorite reported in a previous experiment (Huang and Keller, 1970). The two specimens were purchased in 1968 and 1971, respectively -- presumably they were from different collections. The same laboratory analyzed both.
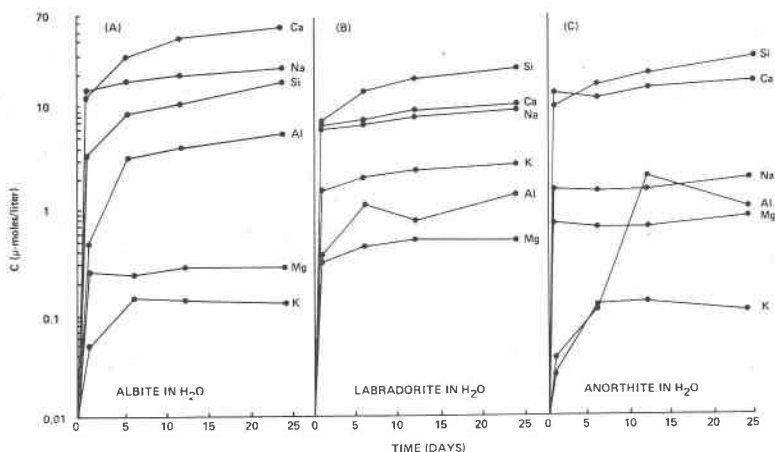
FIG. 1. Concentration of ions in μ-mol per liter dissolved from plagioclases in deionized water at room temperature after days indicated.

termined by atomic absorption using the aliquot for Mg after appropriate dilution, because concentrations of Ca were relatively high. Na and K were determined by air–acetylene emission flame, whereas Fe was determined by atomic absorption with air–acetylene flame (Huang and Keller, 1970, 1971).

A total of 1120 chemical analyses and pH determination (Table 2)[1] were made during the study. The results are summarized as follows.

RATES OF DISSOLUTION

Typical rates of dissolution of plagioclase minerals in the solutions are illustrated in Figures 1 to 3, which show the dissolution of albite (Na–rich plagioclase), labradorite (intermediate member), and anorthite (Ca–rich plagioclase) in deionized water, weakly complexing aspartic acid, and strongly complexing salicylic acid.

1. Two stages of equilibrium reactions

Two stages of reactions were significant in the dissolution of plagioclase minerals in all solvents used.

(a) Early stage of reaction (less than 6–days reaction)

In both deionized water and organic acid solutions, the dissolution of cations (Si, Al, Ca, and Na) from the plagioclase minerals increased

[1] Table 2, listing results of equilibrium runs, may be ordered as NAPS Document Number 01902. The present address is National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 866 Third Avenue, New York, New York 10022, and the price is $2.00 for microfiche or $5.00 for photocopies, payable in advance to CCMIC–NAPS. Check a recent issue of the journal for the current address and price.
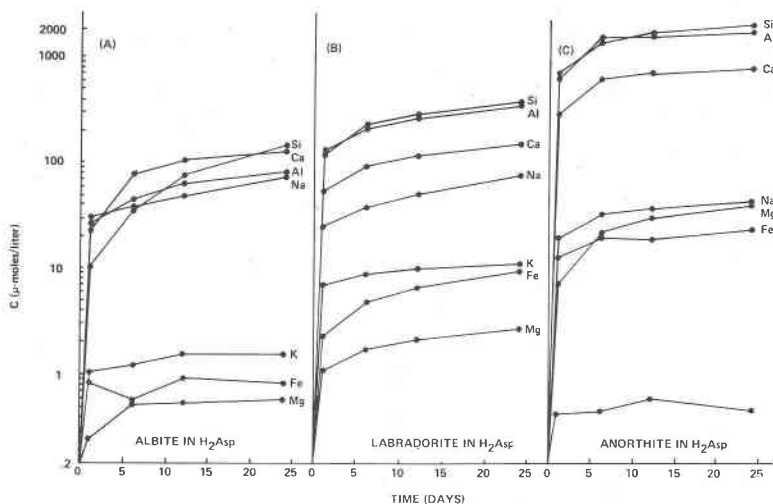
Fig. 2. Concentration of ions in μ–mol per liter dissolved from plagioclases in 0.01 M aspartic acid at room temperature after days indicated.
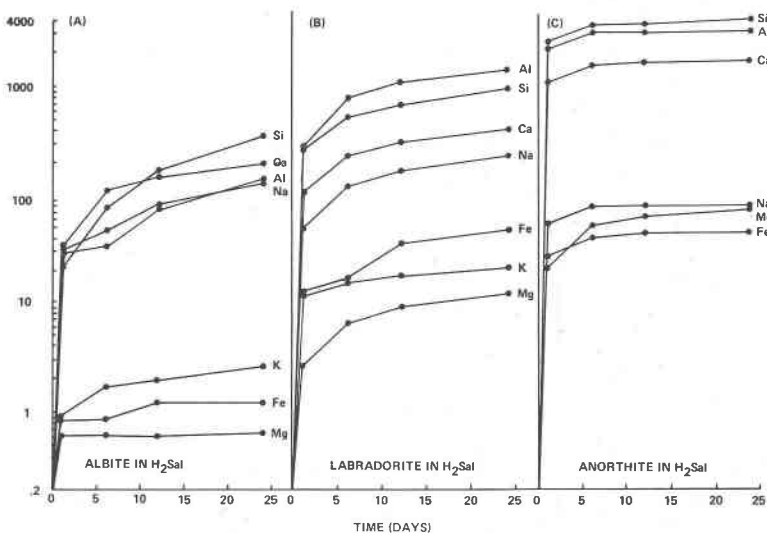

Fig. 3. Concentration of ions in μ–mol per liter dissolved from plagioclases in 0.01 M salicylic acid at room temperature after days indicated.

very rapidly within the first 24 hours, and then slowed down between the period of one day and six days. The rapid increase of dissolution in the early stage was due presumably to dissolution of cations from broken bonds, or from highly stained and disordered surfaces, possibly caused by crushing of the minerals, or due to diffusion from a thin altered layer (?).

(b) Later stage of reaction (after 6–days reaction)

From albite (Na–rich plagioclase) cations continued to be dissolved in each solvent after six days, and apparently reached saturation after 24 days (Figs. 1a, 2a, and 3a). Anorthite (Ca–rich plagioclase), on the other hand, apparently reached near saturation after 12 days, as shown in Figures 1c, 2c, and 3c. Labradorite dissolved intermediately between albite and anorthite, as might have been expected (Figures 1b, 2b, and 3b).

2. Comparative dissolution at equilibrium (after 24 days)

(a) In deionized water, as shown in Figure 4a, Na–rich plagioclase dissolved more than did Ca–rich plagioclase.

(i) The concentration of Si dissolved was found to be much the same from all plagioclase minerals except oligoclase and bytownite, in which more Si was dissolved from oligoclase and bytownite than from the other minerals.

(ii) Dissolved Ca, Na, and Al, however, decreased from Na–rich to Ca–rich minerals.

(b) In organic acids, Figures 4b and 4c, to the contrary, Ca–rich plagioclase dissolved more than did Na–rich plagioclase. This finding agrees with the other of the susceptibility of plagioclase to weathering, proposed by Goldich (1938).

(i) The dissolution of framework cations (Si, Al, Ca, and Na) in organic acids generally increases from Na–rich to Ca–rich plagioclases.

(ii) Oligoclase yielded less Si, Al, and Na in acetic and aspartic acids than did albite, and likewise in salicylic acid, Ca, Si, and Na less than did albite.

3. Relative dissolution of Al/Si and Ca/Na

(a) In deionized water, Si from the minerals was always dissolved more than Al, and the molar ratios of Al/Si dissolved in the solutions were considerably lower than 1, as commonly recognized (Reesman and Keller, 1965; Reesman and Keller, 1968; Huang and Keller, 1970, 1971). In organic acids, to the contrary, the molar ratios of Al/Si dissolved in the solutions were significantly higher than those in deionized
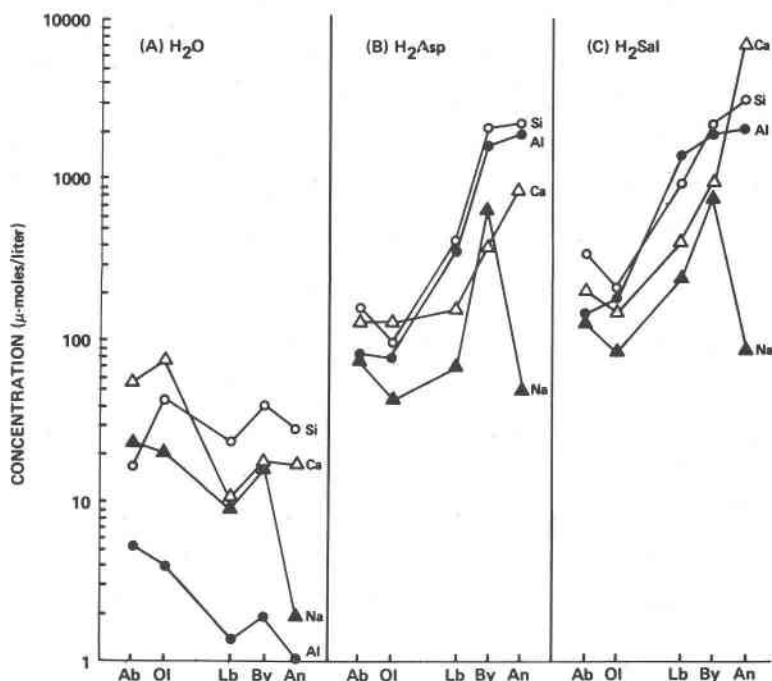
Fig. 4. Comparative dissolution of framework cations from a series of plagio-
clase minerals in (A) deionized water, (B) 0.01 M aspartic acid, and (C) 0.01
M salicylic acid at room temperature after 24 days. Ab, albite; Ol, oligoclase;
Lb, labradorite; By, bytownite; and An, anorthite.

water, nearly equal to 1, or even greater than 1 in the dissolution of
Ca–rich plagioclases in citric acid.

(b) In both deionized water and organic acids, Ca, however, was
more soluble than Na from the minerals except albite in citric acid.

EFFECTS OF ORGANIC ACIDS ON THE DISSOLUTION

The effects of organic acids on the dissolution of plagioclase minerals
were determined by the ratios of concentrations of cations dissolved
in organic acids to concentrations in deionized water after 24 days. The
results are illustrated in Figures 5 and 6, which indicate the ratios for
cations, Si and Al, and Ca and Na, respectively.

Generally the organic acids, in order of increasing extraction of
cations from the minerals by organic acids, with respect to deionized
water, were: acetic, aspartic, salicylic, and citric acids. An exception
is albite in citric acids, Figures 5 and 6. The order of extraction was
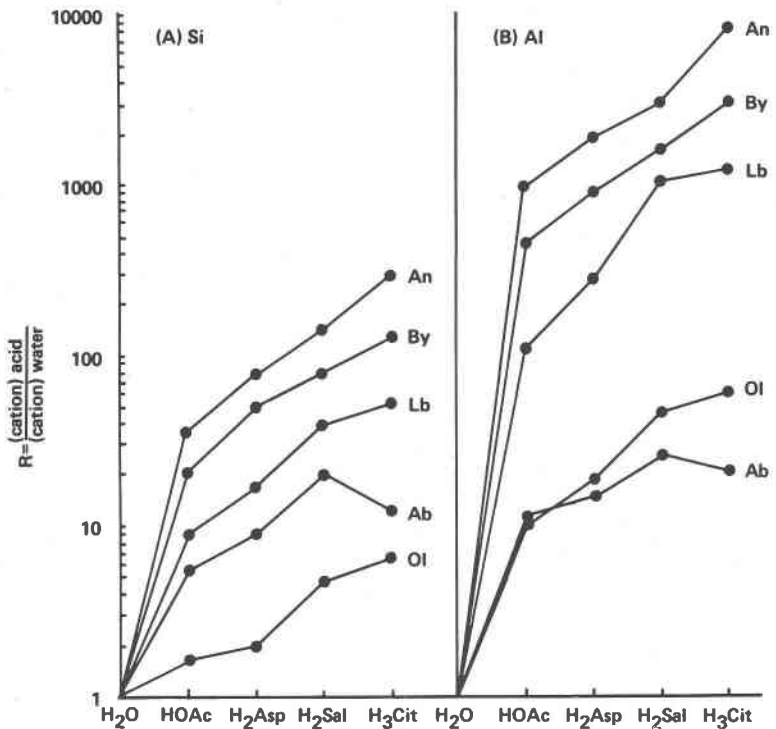not consistent with the order of dissociation constants of the acids

FIG. 5. The ratio of Si (A), or Al (B) dissolved in a given mineral–acid solution to that in mineral–water solution.
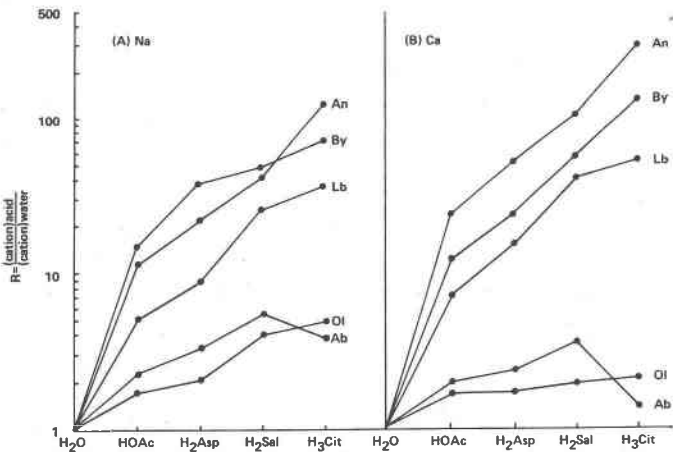

FIG. 6. The ratio of Na (A), or Ca (B) dissolved in a given mineral–acid solution to that in mineral–water solution.

($pK_1 = 4.75$ for acetic acid, 3.65 for aspartic acid, 2.08 for salicylic acid, and 3.08 for citric acid), but instead was controlled by complexing capacities of the acids. That citric acid dissolved the plagioclase minerals more than the other acids was due, in addition to formation of Al–citric acid complex, to a Ca–citrate complex that would likely occur during dissolution, and which might accelerate the dissolution of the minerals (Huang and Conrad, in prep.) The structure of Ca–citrate complex is shown as follows:

$$
\begin{array}{c}
\text{structure diagram}
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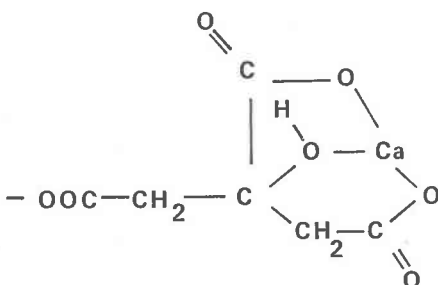
The great stability of Ca–citrate complex is the result of the formation of two chelate rings (one five–membered ring and one six–membered ring) involving two carboxyl groups and one hydroxyl group (Chaberek and Martell, 1959).

(a) In regard to Al and Si, strongly complexing citric and salicylic acids dissolved significantly more of both elements from the plagioclase minerals than did weakly complexing acetic and aspartic acids, or deionized water, Figure 5. Al was dissolved from Na–rich to Ca–rich plagioclases by factors of 10 to 970 in acetic acid more than in deionized water, 15 to 8260 in citric acid. Likewise, Si was also more soluble in acetic acid than in deionized water from oligoclase to anorthite by factors of 1.5 to 36, 2 to 80 in aspartic acid, 5 to 145 in salicylic acid, and 6 to 340 in citric acid.

An increase in concentrations of Al and Si dissolved from the plagioclase minerals in complexing salicylic and citric acids was due to the formation of soluble Al–organic acid complexes from Al on tetrahedral sites, which in turn caused partial or complete destruction of the tetrahedra, and accelerated the dissolution of Si in the solution (Huang and Keller, 1970, 1971).

(b) With respect to Ca and Na, strongly complexing acids likewise dissolved more of both elements than did weakly complexing acids or deionized water, from the Ca–rich plagioclase minerals but not from Na–rich plagioclase, Figure 6. From the Na–rich plagioclase minerals, however, no significant difference in the dissolution of Na

(and minor Ca) by different acids was found with respect to the amount of dissolution in deionized water.

APPLICATIONS TO GEOLOGIC SYSTEMS

Although macroscopic weathering processes in many geological environments have been considered to operate under open systems, the weathering reactions between minerals and aqueous solutions in many cases may be under microenvironments in essentially closed systems. These may approach new equilibia in accord with their specific geologic conditions.

Results of the dissolution of plagioclase in the laboratory by deionized water and organic acids in a closed system, however, indicate possible multiple products of weathering from plagioclase in some natural geologic environments.

Organic acids, representative of functional groups in soil humus, dissolved Ca–rich plagioclase more than Na–rich plagioclase, whereas deionized water ("rain water") dissolved more Na–rich plagioclase. Thus, the susceptibility of plagioclase to natural weathering differs significantly whether it be Na–rich or Ca–rich, and whether the leaching solutions are relatively pure water or contain humic compounds.

In strongly complexing acids, Al was dissolved equally or preferentially to Si, especially from Ca–rich plagioclase. Such weathering could yield a Si–rich residue, and an Al–rich solution. Such an Al–rich solution (Al/Si $\sim$ 1) might move to a new environment and deposit a kaolin mineral. Alternatively, it might replace other altering plagioclase with kaolin. In deionized water, however, because Si was dissolved more readily than Al, an Al–rich residue would be produced.

These diverse possibilities of dissolution observed in laboratory systems indicate a need for detailed inventory and knowledge of weathering solutions and altered products of plagioclase feldspars when studying existing natural weathering systems. Analysis of the weathering solutions for organic acid constituents, alternative to fresh water, becomes necessary to describe accurately the weathering processes involved and anticipation of weathered products.

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