

## DISSOLUTION OF ROCK-FORMING SILICATE MINERALS IN ORGANIC ACIDS: SIMULATED FIRST-STAGE WEATHERING OF FRESH MINERAL SURFACES

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### ABSTRACT

Size fractions 149–297  $\mu\text{m}$  of olivine, augite, muscovite, labradorite, and microcline were dissolved in distilled water,  $\text{CO}_2$ -charged water, weakly complexing acids (0.01 M acetic or aspartic) or strongly complexing acids (salicylic or tartaric acid) for up to 21 days. Dissolved Si, Al, Fe, Mg, Ca, K, and Na, and pH and conductivity were determined in the centrifuged solutions.

Solubilities of Si, Al, Fe, Ca, and Mg were higher in organic acids than in  $\text{H}_2\text{O}$  or  $\text{CO}_2$ -charged water. Solubility of Al and Fe is enhanced presumably by complexing as respective salicylates and tartrates. Relatively high solubility of Al with respect to Si appears to be significant.

Congruency (or incongruency) of dissolution with respect to Si was estimated by comparing: (1) the ratio of the mole fraction of Si dissolved to the mole fraction of another ion (Al, Mg, for example) dissolved, with (2) the ratio of the Si to the other ion as contained in the solid mineral. Si and Al in augite dissolved essentially congruently in salicylic and tartaric acids; Al dissolved proportionately more than Si from microcline in all the organic acids. Calculated depths of dissolution ranged from 120 to 3000  $\text{\AA}$  inward from the surfaces of mineral particles.

Since the organic acids used are representative of components of humic acid and lignitic acids, they illustrate possible effects of organic acids in geological and pedological weathering. When Al is moved congruently with (or in excess of) Si in solution, field results such as podsolization, transfer of Al to Al-rich minerals (as bauxite under lignite in Arkansas), or recombination with Si to yield kaolin minerals (as in German kaolins via the Moorerwitterung process) may be attributed to dominant dissolution effects of organic acids.

### INTRODUCTION

Dissolution of minerals and rocks in aqueous solutions has been studied recently by Correns (1963), Keller *et al.* (1963), Marshall and McDowell (1965), Schalscha *et al.* (1967), Wollast (1967), Reesman and Keller (1968), but reports on controlled experiments on simulated weathering of minerals and rocks by organic acids are notably fewer. In this paper are reported the results of the laboratory dissolution of olivine, augite, muscovite, labradorite, and microcline, in deionized water,  $\text{CO}_2$ -charged water solution, and four organic acids at room temperature for periods of a few hours to 21 days.

### EXPERIMENTAL

*Mineral Specimens and Organic Acids.* Clean fragments of the minerals listed above were broken from the interior of newly fractured fresh specimens. After washing in deionized

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water, they were crushed and sieved in a Pitchford Grinder using bronze screens to avoid Fe contamination. Muscovite was reduced in a Waring Blender. Selected size-fractions, between 297 and 149  $\mu\text{m}$  (50–100 mesh sieve openings), were further washed in deionized water and dried at 60°C. Particles in that size range are fine enough to react rapidly with aqueous solutions but are coarse enough that the liquids may be clearly separated from them by gravity and centrifugation. X-ray diffraction and infrared spectroscopy showed the minerals to be relatively pure, except for the microcline which probably contained some albite. Chemical analyses of these samples are given in Table 1.

Organic acids selected for dissolution of the minerals were those whose representatives might be present in humic and other soil acids; namely, weakly complexing acetic and aspartic acids, and strongly complexing salicylic and tartaric acids. These acids likewise embody representative carboxyl groups, hydroxyl groups, or amines. Deionized water, CO<sub>2</sub>-charged water, and blank solutions were also used for comparative parallel dissolution.

*Experimental Procedures.* Ten grams of each mineral sample were added to 500 ml of 0.01 M organic acid reagent, including deionized water and CO<sub>2</sub>-charged water (ca. 0.01 M), in tightly-capped polyene bottles and shaken slowly and continuously at room temperature for 0.36, 1.2, 5 and 21 days. After each time interval, a 100 ml aliquot of centrifuged solution was withdrawn, and the pH and conductivity immediately measured. The solution was then acidified with 1.0 ml redistilled 6 N HCL.

Si in the solutions was determined colorimetrically using the formation of reduced silicomolybdate complex (Shapiro and Brannock, 1952). Total iron (Fe<sup>2+</sup> and Fe<sup>3+</sup>) was first extracted by 4, 7-Diphenyl-1, 10-phenanthroline and then determined colorimetrically (Sandell, 1959). The possible interference on Fe determination of organic acids used has been found to be insignificant. Al was determined by nitrous oxide-acetylene flame emission

TABLE 1. CHEMICAL ANALYSES AND LOCALITIES OF MINERAL SAMPLES<sup>a</sup>

	Olivine	Augite	Muscovite	Labradorite	Microcline
SiO <sub>2</sub>	39.10	51.10	44.70	52.60	63.30
Al <sub>2</sub> O <sub>3</sub>	2.13	2.38	38.45	29.07	21.30
Fe <sub>2</sub> O <sub>3</sub>	2.75	8.62	0.011	0.49	0.14
FeO	4.85	0.08	3.82	0.26	0.06
MnO	0.035	0.053	0.026	0.026	0.018
MgO	49.25	13.03	0.72	0.54	0.36
CaO	0.18	23.50	1.00	12.00	1.25
P <sub>2</sub> O <sub>5</sub>	0.06	0.08	0.06	0.06	0.06
Na <sub>2</sub> O	0.62	0.50	0.96	4.50	2.50
K <sub>2</sub> O	0.02	0.05	9.42	0.25	10.60
H <sub>2</sub> O <sup>+</sup>	0.10	0.66	0.40	0.20	0.40
	99.095	99.993	99.567	99.996	99.988

<sup>a</sup> Analyses by the Bruce Williams Laboratories, Joplin, Mo.

Olivine: Jackson County, North Carolina (Geology Dept. Univ. of Missouri—Columbia).

Augite: Quebec (Ward's National Sci. Est. Inc. N. Y.).

Muscovite: Locality unknown (Geology Dept. UMC).

Labradorite: Nain, Labrador (Ward's National Sci. Est. Inc. N. Y.).

Microcline: Parry Sound, Ontario (Ward's National Sci. Est. Inc. N. Y.).

TABLE 2. THE PRECISION AND DETECTION LIMIT OF CHEMICAL ANALYSES

Element	Detection limit <sup>a</sup> (ppm)	Percent Error <sup>b</sup>
Si	—	~5%
Al	0.001	≤8%
Fe	~0.005 (est.)	~5%
Mg	0.0005 <sup>c</sup>	≤5%
Ca	0.0001	≤3%
Na	0.0001	≤3%
K	0.0001	≤3%

<sup>a</sup> "Detection limit" is the concentration in mg/l for which the emission or absorption intensity is about twice as great as the root mean square noise level at the wavelength of the line.

<sup>b</sup> Percent of amount determined.

<sup>c</sup> Slavin, W. (1966).

in a 10 ml aliquot to which 0.5 ml of K-solution (20,000 ppm K) was added to enhance emission intensity. Ca was also determined in the Al aliquot by the same flame-emission analysis at a different wavelength (Pickett and Koirtzohann, 1968, 1969). Mg was determined by atomic absorption. Because the Na and K concentrations were very low, they were determined by air-acetylene flame emission in a Jarrel-Ash 0.5 m Ebert Spectrometer. A conservative estimate of the overall precision of the analyses is given in Table 2.

## RESULTS AND DISCUSSION

*Dissolution of the Silicate Minerals.* A total of 144 solutions were analyzed for Si, Al, Fe, Mg, Ca, K, Na, pH, and conductivity. The data from 1080 analyses are reported as  $\mu\text{g/ml}$  of element dissolved as a function of time in hours (American Documentary Institute Auxiliary Publication Department, Document No. 01177).<sup>1</sup>

The data are summarized as follows.

### Similarities

The dissolution of cations, in particular of minor constituents of minerals, proceeded rapidly in the first 24 hours or so, and then slowed to give near-constant concentrations after 5 or 21 days in both types of solutions. These reactions are typically illustrated in Figures 1 to 3, which show the dissolution of microcline in deionized water, weakly complexing acid represented by acetic acid, and strongly complexing acid represented by salicylic acid.

The order of concentrations of cations dissolved from each mineral was

<sup>1</sup> To obtain a copy of this material, order NAPS Document Number 01177 from National Auxiliary Publications Service of the A.S.I.S.; c/o CCM Information Corporation, 909 Third Avenue, New York, N. Y., 10022; remitting \$2.00 for microfiche or \$5.00 for photocopies, in advance, payable to CCMIC NAPS.

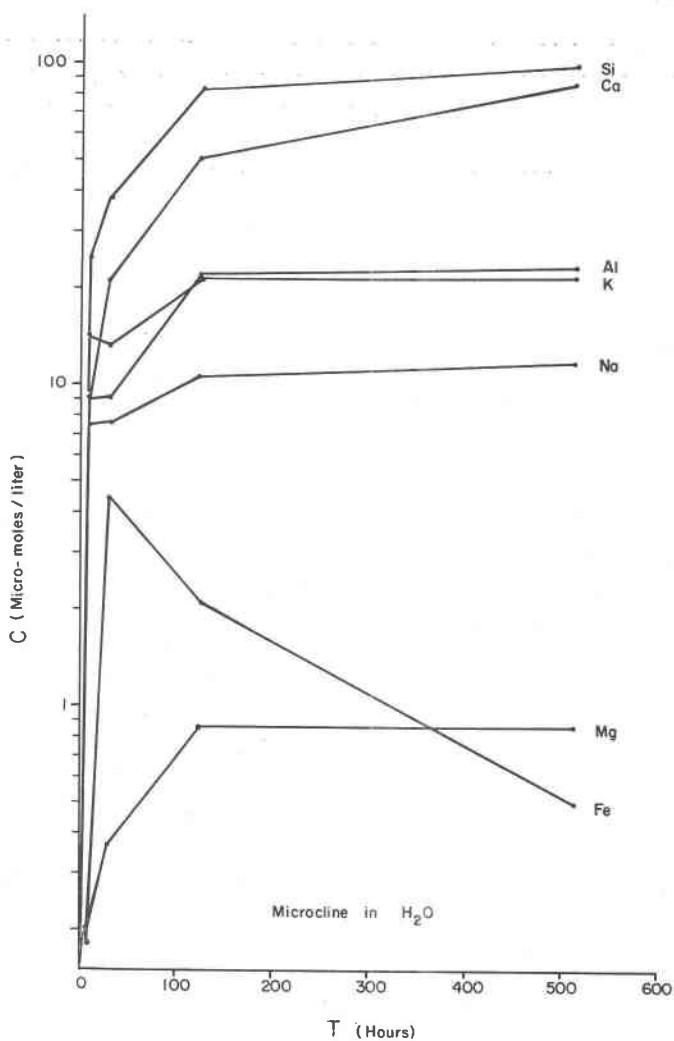


Fig. 1 Dissolution of cations from microcline in deionized water, closed system, as a function of time.

found to be much the same, independent of the kinds of acid solutions used.

The order was:

Olivine	Si~Mg>Ca~Fe>Al>Na>K
Augite	Ca>Si>Mg <sub>2</sub> Fe>Na>K~Al
Muscovite	Si>K>Al>Fe>Na>Mg>Ca
Labradorite	Si>Al <sub>2</sub> Ca>Na>Fe~K>Mg
Microcline	Ca>Si~K>Al <sub>2</sub> Fe>Na~Mg

## Differences

In organic acids the pH of solutions of minerals increased slightly (olivine in salicylic and tartaric acids, excepted). In deionized water or CO<sub>2</sub>-charged water the pH increased very rapidly in the early stages of dissolution. This increase in pH could be due, in addition to the effect of hydrolysis of silicates, to the introduction of ions of alkali and alkaline earths, and/or other ions dissolved from minerals.

Although the molarity of solution was the same for all acids used (0.01 M), in view of the difference in the dissociation constants ( $pK_1$

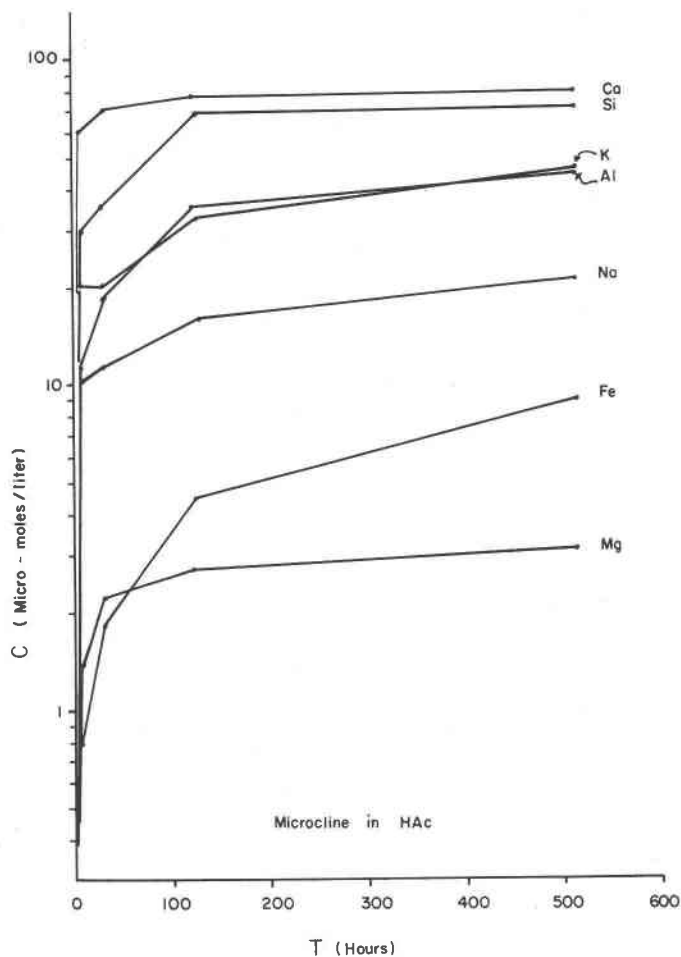


FIG. 2. Dissolution of cations from microcline in 0.01 M acetic acid, closed system, as a function of time.

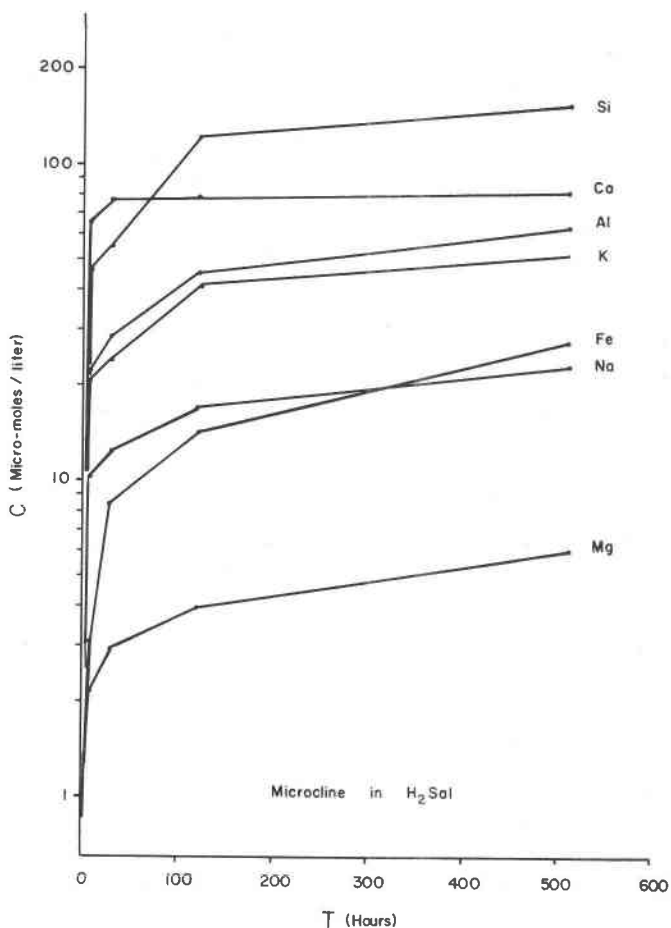


FIG. 3. Dissolution of cations from microcline in 0.01 M salicylic acid, closed system, as a function of time.

= 4.75 for acetic acid; 3.65 for aspartic acid; 2.98 for salicylic acid; and 3.00 for tartaric acid), concentration of given ions dissolved are not directly comparable in different solutions. Nevertheless, the relative mobilities of ions in different solutions may be compared by using the ratios of observed concentrations of cations in different solutions to the ions dissolved in deionized water. The data after 21.2-days dissolution, Table 3, show: (1) Generally, concentrations of alkaline earths and Si were relatively higher in organic acids than in deionized water and  $\text{CO}_2$ -charged water solutions. This increased dissolution is probably due to the formation of Al- and Fe-salicylic acid complexes, and Al- and Fe-

TABLE 3. RELATIVE MOBILITIES OF CATIONS FROM A  
GIVEN MINERAL IN DIFFERENT SOLVENTS

Olivine						
	H <sub>2</sub> O	CO <sub>2</sub> -H <sub>2</sub> O	HAc	H <sub>2</sub> Asp	H <sub>2</sub> Sal	H <sub>2</sub> Tart
Si	1.0	3.7	9.8	3.4	33.7	33.4
Al	1.0	1.5	1.0	5.8	135.2	4.8
Fe	1.0	1.4	5.3	6.6	34.2	34.2
Mg	1.0	2.9	6.6	3.0	21.2	19.5
Ca	1.0	3.7	7.8	7.6	8.1	8.1
Na	1.0	0.4	1.6	1.0	2.0	1.0
K	1.0	5	5	5	10	20
Augite						
Si	1.0	1.3	1.3	1.4	4.1	3.1
Al	1.0	0.6	1.7	3.0	13.5	8.2
Fe	1.0	0.3	2.6	4.5	14.0	10.0
Mg	1.0	1.1	1.5	1.2	4.0	3.0
Ca	1.0	7.4	9.3	10.0	10.0	10.5
Na	1.0	1.0	1.1	1.0	1.5	1.4
K	1.0	1.6	1.9	1.3	3.3	2.5
Muscovite						
Si	1.0	1.2	1.6	1.8	2.7	2.8
Al	1.0	0.03	1.0	1.3	2.4	2.3
Fe	1.0	0.2	1.3	2.1	3.8	3.8
Mg	1.0	1.0	1.8	1.4	2.3	2.1
Ca	1.0	3.0	3.0	7.0	5.0	6.0
Na	1.0	0.8	0.8	0.9	1.0	1.1
K	1.0	0.8	1.1	1.1	1.3	1.2
Labradorite						
Si	1.0	1.4	10.0	8.5	54.0	52.0
Al	1.0	1.5	19.3	6.8	94.5	86.0
Fe	1.0	2.6	21.5	20.2	216.0	225.0
Mg	1.0	2.0	7.6	4.9	22.8	22.2
Ca	1.0	1.6	4.7	4.2	22.0	19.4
Na	1.0	1.2	4.4	2.5	11.3	9.4
K	1.0	1.2	3.9	5.0	8.7	8.0
Microcline						
Si	1.0	0.38	0.71	0.55	1.6	1.4
Al	1.0	0.32	1.9	1.3	2.7	2.7
Fe	1.0	1.2	18.0	30.0	55.6	54.8
Mg	1.0	3.5	3.7	4.4	7.0	6.5
Ca	1.0	1.2	0.9	1.0	0.9	0.9
Na	1.0	1.1	1.8	1.3	1.9	1.9
K	1.0	1.1	2.1	1.2	2.4	2.0

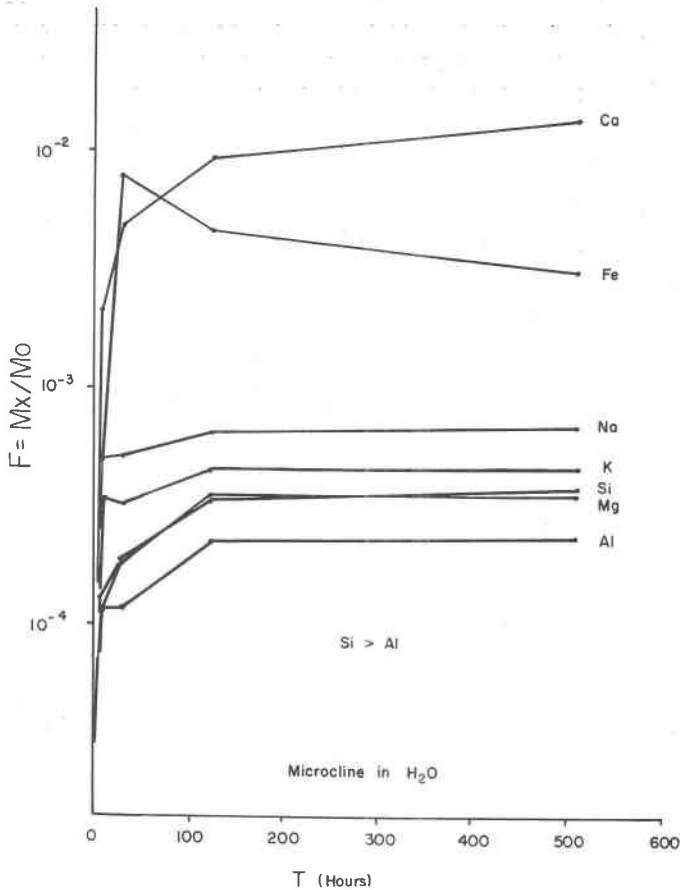


FIG. 4. Fraction of cations dissolved from microcline in deionized water, closed system, as a function of time.

tartrates. (2) Dissolution of alkali ions from microcline and muscovite in organic acids was found to be the same order of magnitude as in deionized water or  $CO_2$ -charged water solution. It is unlikely that monovalent cation chelates or complexes are formed during organic acid dissolution of the minerals.

*Congruency or Incongruency of Dissolution.* Incongruent dissolution of minerals is observed to occur more commonly than congruent dissolution in weathering environments. Likewise, most laboratory dissolution of silicate minerals and rocks in inorganic solutions has been incongruent (Correns, 1963; Keller *et al.*, 1963; Marshall and McDowell, 1965).

To evaluate the degree of congruency by which freshly fractured sur-



face of silicate minerals dissolve in organic acids, the fractional amounts of dissolved cations were divided by the fractional amounts present in the original bulk analyses, thereby yielding the fraction dissolved. As examples, Figures 4, 5, and 6 show the fractions dissolved from microcline in different solutions, as a function of time. In Figure 4, microcline in deionized water, alkalis and alkaline earths were more mobile than Si and Al, and Si was dissolved more rapidly than was Al. In Figure 5, microcline in weakly complexing acetic acid, Al was dissolved incongruently, slightly more rapidly than Si! In Figure 6, microcline in strongly complexing salicylic acid, Al was dissolved congruently with respect to Si.

In Table 4 are listed the calculated ratios of the molar fraction of each

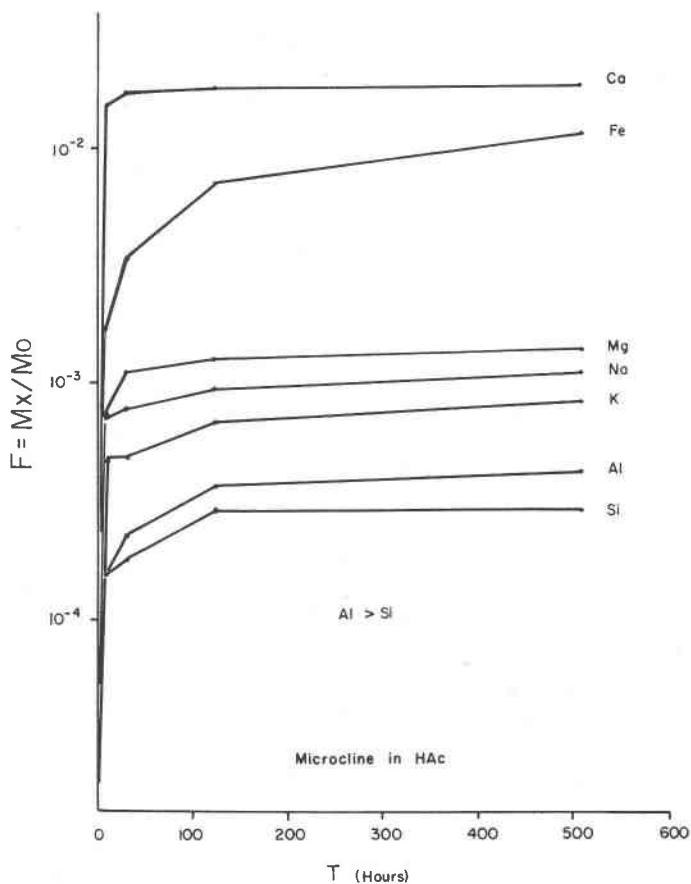


FIG. 5. Fraction of cations dissolved from microcline in 0.01 M acetic acid, closed system, as a function of time.

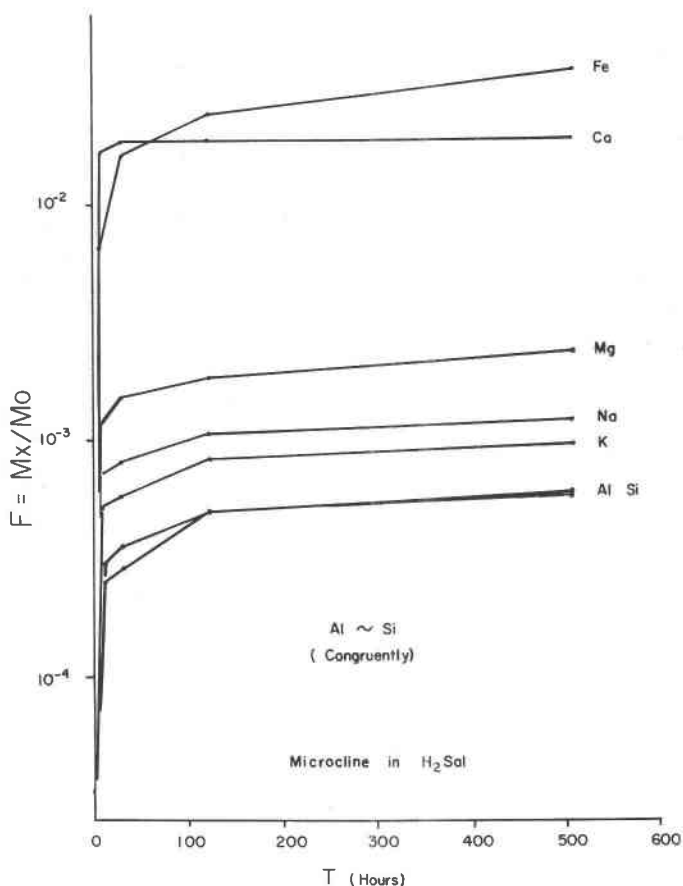


FIG. 6. Fraction of cations dissolved from microcline in 0.01 M salicylic acid, closed system, as a function of time.

cation dissolved with respect to the molar fraction of Si. Where the ratio is 1.0, the dissolution of a given cation and of Si was congruent with respect to the mineral formula. For those ratios greater, or less than 1.0, it means that the cation was dissolved either more readily, or less readily, respectively, than was Si from the formula. Responses of the individual minerals are summarized, as follows.

#### Olivine

(1) Si dissolved preferentially, and more rapidly than other major cations in olivine, with the possible exception of Mg, as noted below. Thus the outer dissolved zone of the mineral surface of the particles

### Augite

(1) Al, Fe, Mg, and Ca were appreciably more soluble in organic acid solutions than in deionized water or CO<sub>2</sub>-charged water.

(2) In inorganic aqueous solution, the surface zone of augite was apparently enriched in Fe and Al, but in organic acids, it was depleted in Fe, Al (including also Mg, Ca) with respect to Si.

### Muscovite

(1) In virtually all cases K was the most mobile cation in the solution, followed by Na, and Mg.

(2) Mobilities of Al and Ca were lower than Si in both inorganic or organic acid solutions. Similar observations were found by Marshall and McDowell (1965) for inorganic aqueous, solution.

### Labradorite

(1) Labradorite, like most other minerals, yielded a surface zone enriched in Al in either organic acids or inorganic aqueous solutions.

(2) The relative mobility of Al with respect to Si remained much the same in either solutions.

(3) It would appear that the surface of labradorite was relatively enriched in Ca and Na in organic acid solution, whereas in deionized water or CO<sub>2</sub>-charged water, the surface was depleted of these two ions.

(4) Higher mobility of K relative to Si in CO<sub>2</sub>-charged water than other solutions was rather striking, but K is anomalous in the ideal formula of labradorite.

### Microcline

Microcline has long been found to dissolve incongruently in inorganic solutions. Likewise, it dissolved incongruently in entirety in organic acids, Figures 5 and 6, and Table 4, excepting, however, that in strongly complexing acids Si and Al dissolved congruently (from the freshly fractured mineral particles). Ca (scantly present) was most mobile, followed by Na, K, in organic acids, whereas Al and Si moved congruently in 0.01 M salicylic and tartaric acid solutions.

In summary, the dissolution of freshly fractured surfaces of silicate minerals was incongruent in deionized water, CO<sub>2</sub>-charged water, or organic acid solution, with three exceptions. From augite and microcline, Al and Si were dissolved congruently in salicylic and tartaric acids, and from olivine, Mg and Si dissolved congruently in aspartic acid or deionized water.

*Surface reactivity—Depths of dissolution below surface.* The approximate depths of dissolution of mineral particles from the original mineral surfaces may be calculated from the data available. Assuming a spherical shape (or cubical shape) for the particles for comparative purposes (except a disc-like model described for muscovite), and taking the mean diameter ( $R$ ) between the sizes of 297–149  $\mu\text{m}$  (sieves used), the total surface area of the mineral particles can be calculated from their volume, weight, and densities. The total weight of cations dissolved in 550 ml of reagents in 21.2 days has been found by analysis. The weight of each cation (*i.e.* element) statistically present to a depth of one Angstrom unit in each mineral particle can be calculated from the bulk analysis of the mineral. Assuming further that the cations were *completely* dissolved from the surface inward, the calculated *minimum* layer-thickness of dissolution for each cation is given in Table 5.

From these data, the following approximations may be made:

(1) With respect to olivine, Si and Mg were dissolved and removed in 21.2 days from freshly fractured particles to depths of approximately 300, 2500, 1100  $\text{\AA}$  in deionized water, acetic acid, and aspartic acid, re-

TABLE 5. THICKNESS OF LAYERS, IN ANGSTROM UNITS, DISSOLVED IN 550 ML REAGENT AFTER 21.2 DAYS

	H <sub>2</sub> O	CO <sub>2</sub> —H <sub>2</sub> O	HAc	H <sub>2</sub> Asp	H <sub>2</sub> Sal	H <sub>2</sub> Tart
Augite						
Si	395	485	417	433	1183	884
Al	125	80	194	309	1232	760
Muscovite						
Si	552	519	743	813	1277	1253
Al	283	34	314	413	729	641
Labradorite						
Si	90	114	664	670	3564	3356
Al	44	46	414	274	2034	1750
Microcline						
Si	141	73	110	83	217	199
Al	89	42	160	115	229	225
Olivine						
Si	308	1209	2862	1162	9106	9071
Mg	228	879	2103	1055	5911	5389

spectively. In CO<sub>2</sub>-charged water, salicylic acid, and tartaric acid solutions, Si was dissolved to far greater depth than Mg, by approximately 330, 3200, 3100 Å, respectively. The reason for higher solubility of Si in the latter case is not clear at this moment. In view of lower solubility of Fe in all cases, it may be conjectured that a Mg-silicate or a member of the serpentine group could possibly account for the reaction

(2) The composition of the dissolving surfaces of aluminum silicate minerals varies with the solutions used.

From freshly fractured augite particles, Si was removed to a greater depth than Al by approximately 270, 370, 220, 120 Å, in deionized water, CO<sub>2</sub>-charged water, acetic acid, and aspartic acid, respectively. In salicylic acid and tartaric acid solutions, it appears that augite dissolved congruently with respect to Si and Al. Relatively high solubility of Al may be due to its complexing by the organic compounds.

In the case of muscovite, Si was dissolved more readily than Al to depths of about 270 Å in deionized water, about 490 Å in CO<sub>2</sub>-charged water, about 430 Å in acetic acid, about 500 Å in aspartic acid, about 550 Å in salicylic acid, and about 610 Å in tartaric acid. These calculations imply that the surface of dissolving particles of muscovite was enriched in Al with respect to Si in virtually all cases of dissolution of muscovite.

Most noteworthy among the minerals is the Al-Si dissolution from microcline. In deionized water and CO<sub>2</sub>-charged water, Si was removed to greater depth than Al by about 50 to 30 Å respectively; on the contrary, in acetic and aspartic acid solutions Al was removed further than Si by about 50-30 Å. In the dissolution of microcline by salicylic and tartaric acids, Si and Al apparently were dissolved and removed congruently from the surface of original particles.

In general, alkali ions were dissolved by organic acids to even greater depths than Si and Al from minerals in solution, with the exception of labradorite.

Although the preceding calculations were made on the assumption that the dissolved ions had been completely removed in a sharply bounded outer zone actually, and more realistically, the dissolution would be gradational, and therefore the partially depleted zones would be deeper than the calculations show for complete dissolution. In all minerals except olivine, the surface of dissolving silicate mineral remains rich in Al-Si relative to the unleached inner core.

After an envelope of residual weathered materials has thus been developed on Al silicate mineral particles, further dissolution weathering will proceed probably by diffusion through the envelope, accompanied by a certain amount of envelope removal. This is the condition under which

most rock and mineral weathering probably occurs in nature. The study reported in this paper is being continued on the residuum-coated particles, and will be reported as part II, Second-stage simulative weathering (in contrast to First-stage simulative weathering during development of the envelope on freshly fractured surfaces).

#### GEOLOGIC IMPLICATIONS

Reactions of organic acids with aluminum silicate minerals, especially labradorite, microcline, and augite have certain geologic implications relative to weathering and argillation. The behavior especially of Si and Al, also K in regard to phyllosilicates, is important to the solid phases (minerals) formed during weathering. Because Na and Ca are readily removed under natural conditions they may be considered completely mobile. If Al is concentrated in immobile positions during the reaction an aluminous mineral product may be favored, whereas if Si is concentrated on the surface of reacting mineral particles the daughter alteration mineral is likely to be Si rich.

*Influences of types of solvents.* Three types of solvent fluids in the laboratory experiment could yield correspondingly different mineral products, Table 6.

(1) Deionized water and CO<sub>2</sub>-charged water in which the pH of reaction ranged from 5.75 to 8.63. From both labradorite and microcline, Al was concentrated relative to Si on the surfaces of dissolving particles. Since Si was also present in the systems, halloysite might develop from labradorite. From microcline, to the contrary, K tends to be retained along with Al and Si relative to other cations, and hence, hydrous mica, illite, is more likely to form on the residues in the deionized water system. Furthermore, since the pH of the system was found to be 8.63 and  $\log (K^+)/[H^+]$  was 3.9, the formation of K-mica is clearly favored (kaolinite-mica stability diagram). In a solution of labradorite, at pH 5.75 the cation  $Al(OH)_2^+$  is likely to predominate, whereas from microcline at pH 8.63 the anion  $Al(OH)_4^-$  is likely to be dominant (Huang, 1969).

(2) Organic acids relatively weak in complexing properties, acetic acid and aspartic acid. From labradorite, Al was retained on the surface relative to Si, but in microcline, Si was retained relative to Al and K. These products might lead to halloysite from labradorite, but from microcline, both silica and clay might develop. In these solutions of low pH,  $Al^{3+}$  (in acetic acid, and  $Al(OH)_2^+$  (in aspartic acid) from labradorite, and  $Al^{3+}$  from microcline is more likely to predominate in the systems.

(3) Strongly complexing organic acids, salicylic acid and tartaric

TABLE 6. GEOCHEMISTRY OF ORGANO-CHEMICAL ALTERATION OF FELDSPARS IN DIFFERENT ENVIRONMENTS

	Labradorite		Microcline
	Residues <sup>a</sup>	Solutions	Solutions
1) Neutral water or CO <sub>2</sub> -solution	Al > Si	Al(OH) <sub>3</sub> <sup>+</sup> (87-98%); pH = 6 ±. Al(OH) <sub>2</sub> <sup>+</sup> , Al(OH) <sub>2</sub> <sup>+</sup> (2-13%) Na <sup>+</sup> , H <sub>2</sub> SiO <sub>4</sub> Ca <sup>++</sup>	Al(OH) <sub>4</sub> <sup>-</sup> (99%); pH = 6.3-8.6, (in H <sub>2</sub> O) Al(OH) <sub>3</sub> <sup>+</sup> (95%) Al(OH) <sub>2</sub> <sup>+</sup> (5%) (in CO <sub>2</sub> soln) Na <sup>+</sup> , H <sub>2</sub> SiO <sub>4</sub> Ca <sup>++</sup>
2) Weakly complexing organic acids (acetic or aspartic acid)	Al(Na, Ca) > Si	Al <sup>3+</sup> (92%); pH = 3.5-5.7. Al(OH) <sub>2</sub> <sup>+</sup> , Al(OH) <sub>3</sub> <sup>+</sup> (8%) (in HAc) Al(OH) <sub>2</sub> <sup>+</sup> (99%) (in H <sub>2</sub> Asp) Na <sup>+</sup> , H <sub>2</sub> SiO <sub>4</sub> Ca <sup>++</sup> FeAc <sup>+</sup> (50%), FeAsp <sup>+</sup> (85%)	Al <sup>3+</sup> (95%); pH = 3.4 ±. Al(OH) <sub>2</sub> <sup>+</sup> , Al(OH) <sub>3</sub> <sup>+</sup> (5%) K <sup>+</sup> , Na <sup>+</sup> , H <sub>2</sub> SiO <sub>4</sub> FeAc <sup>+</sup> (46%), FeAsp (96%)
3) Strongly complexing organic acids (salicylic or tartaric acid)	Al(Na, Ca) > Si	AlSal <sup>+</sup> (95%); pH = 4 ±. AlTart <sup>+</sup> (?) Al <sup>3+</sup> (5%) Na <sup>+</sup> , H <sub>2</sub> SiO <sub>4</sub> CaTart (33%), Ca <sup>++</sup> (67%) FeSal <sup>+</sup> , FeTart <sup>+</sup> (99%)	AlSal <sup>+</sup> (95%); pH = 2.7 ±. AlTart <sup>+</sup> (?) Al <sup>3+</sup> (5%) K <sup>+</sup> , Na <sup>+</sup> , H <sub>2</sub> SiO <sub>4</sub> FeSal <sup>+</sup> , FeTart <sup>+</sup> (99%)

<sup>a</sup> Although Na and Ca were held in the residues in the laboratory experiment, they would probably be completely removed in open, natural weathering—hence placed in parentheses in the "Residues" column.

acid. In labradorite, where Al was concentrated on the surface relative to Si, a kaolinitic clay mineral, possibly halloysite, is likely to develop. Microcline contains essential K, but since  $\log (K^+)/ (H^+)$  was  $-1.6$  to  $-1.5$ , and K and other cations were removed more rapidly than were Si and Al, the altered products are more likely to be kaolinite than K-mica or K-clay. In solutions in which the complexing effect of hydroxides is weak and insignificant, Al-chelates (Al-salicylate, or Al-tartrate?) are likely the predominant species in the solutions.

*Geologic Examples.* (1) According to German geologists, the large kaolin deposits of southern Germany and Czechoslovakia were the products of alteration of granite by organic acid solutions derived from the decomposition of overlying Tertiary lignites in the "Moor-Verwitterung" environment (Lilley, 1932, p. 156-162, quoted by Keller, 1967). Since some of the degradation products of lignins are strongly complexing organic acids, such as salicylic and tartaric acids, and the typical aluminum silicates in granite are microcline, muscovite, and Na-plagioclase, it follows that the laboratory experiments on the dissolution of microcline and muscovite by those two organic acids may describe the reactions that actually occurred in the areas. It was shown that Al and Si from microcline were dissolved congruently in those organic acids, but less readily than were K and other cations, whereas Al from muscovite was concentrated relative to Si and K. These products, therefore, might lead to kaolinite or high-alumina clay developed from the residues of altered minerals. Thus the field occurrences of those areas are consistent with what was found in the laboratory dissolution.

(2) Slatine and Heller (1961) proposed that high alumina clay from the Jurassic section in the Negev of Israel was formed by selective leaching of a weathered basalt flow in the presence of organic matter. Some of the representative acids present in soil organic matter are those weakly complexing organic acids, such as acetic acid and aspartic acid, and those strongly complexing organic acids, salicylic and tartaric acids. Since two aluminum silicates typically in a basalt are labradorite and augite, the laboratory dissolution of these two minerals by those organic acids may well explain what was actually altered in the Israel clay. In weakly complexing organic acids, it was shown that since Al was retained relative to Si, a silicate of high aluminum content, at the expense of primary labradorite or augite, would develop on the residues of altered minerals. On the contrary, in strongly complexing organic acids (*e.g.*, salicylic and tartaric acids), dissolution of Al behaved differently in labradorite and augite: from labradorite, Al was retained relative to Si, and hence a high-alumina silicate might develop from the residues, but from augite, Si



and Al were removed congruently but less readily than other cations, thereby halloysite might expect to form on the altered surface of augite. The consequences of these differences may well suggest the common association of kaolinite in bauxite or laterite deposits.

Although in the laboratory system, Na and Ca were concentrated with respect to Si on the surface of labradorite, these ions are expected to be leached out easily and preferentially in the natural environments.

(3) The bauxite deposits of Arkansas were formed by weathering of nepheline syenite in the presence of lignite-containing environment during the Eocene (Gordon *et al.*, 1958). The coarse-grained nepheline syenite contains more than 50 percent of tabular microcline crystals containing some albite, and 10–25 percent triangular or polygonal nepheline. In weakly complexing organic acids, such as acetic acid and aspartic acid, Si from microcline was concentrated relative to Al on the residues of dissolving particles—hence, not yielding bauxite. In strongly complexing organic acids, however, such as salicylic and tartaric acids, representative types of which occur in lignites, Si and Al from microcline were dissolved congruently, but less rapidly than other cations, and hence a kaolin, instead of a high-alumina clay, might expect to develop from the altered surface of the mineral. The Al-rich leaching solution, in the latter cases, might lead to the formation subsequently of a bauxite deposit in a place where the solution of low pH was buffered to pH of about 5 to 9 by rain water or ground water, thereby precipitating alumina directly from the solution. The dissolution of nepheline has not been studied experimentally.

#### CONCLUSIONS

(1) Weathering of silicate minerals by complexing acids, as commonly occur in soils and lignites may result in a different order or mineral stability than the traditional one of Goldich (the inverse of the Bowen Reaction series) which apparently applies more consistently to inorganic reagents.

(2) The nature of dissolution of Al from aluminum silicate minerals, either congruently or incongruently, was found to be strongly dependent on the solutions used. These laboratory differences, if followed logically, can explain the differences in weathering of these minerals as found in the field.

(3) Certain geologic examples, such kaolins of Central Europe and bauxite in Israel formed by the action of organic acids are consistent with the results of laboratory dissolution. The laboratory data also support bauxitization via kaolinization for the Arkansas bauxite deposits.

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