Dynamics of Potassium Release from Potassium-Bearing Minerals as Influenced by Oxalic and Citric Acids

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ABSTRACT

The effect of selected low molecular weight organic acids on release of K from K-bearing minerals was investigated by reacting biotite, muscovite, microcline and orthoclase (20–50 μm) with 0.01 mol L^{-1} oxalic and citric acids or water for 1 h to 30 d. The rates of the K release varied with the nature of organic acids and chemical composition, atomic bonding, crystal structure, and formation sequence of K-bearing minerals. The rate constants of K release from biotite in citric and oxalic acid solutions were 63 and 123 times, respectively, greater than those from muscovite. The K release from biotite in these two organic acid solutions was 14 to 18 times faster than that from K-feldspars. The rates of K release from these two K-feldspars were almost identical in the respective organic acid solution but were 4 to 7 times faster than those of muscovite. The renewal of organic acid solutions replenished the H ions and organic ligands as well as depleted the level of the structural cations released and thus enhanced the rate of dissolution of the minerals. The sequence of K release from these K-bearing minerals through the attack of the organic acids was biotite > microcline $\simeq$ orthoclase > muscovite, while that through the cation exchange process in the sodium tetraphenylboron systems was biotite > muscovite > microcline $\simeq$ orthoclase. The rates of release of structural cations from minerals by organic acids followed the order: Al(Fe, Mg) > K > Si. The nature of soluble products and surface features of selected minerals after reactions with oxalic acid was revealed by transmission and scanning electron microscopy. The present data indicate that the sequence of relative rates of K release from K-bearing minerals varies with the mechanisms of the release. The role of organic acids in affecting the K-supplying power of soils thus merits close attention.

Additional Index Words: K-reserves, Organic acids, Weathering, K-supplying power.

POTASSIUM IN SOILS mainly resides in K-bearing minerals. The K-supplying power of a soil depends not only on content and kind of K-bearing minerals in the soil but also on the rate at which structural and fixed K becomes available to plants. The nature of K reserves and rate of K release from minerals are even more important in forest soils where K fertilizers are usually not applied.

There are many factors which affect the rate of K release. The effect of the nature and particle size of K-bearing minerals and soil environments on the release of K has been reported (Reitemeier, 1951; Rich, 1968, 1972; Scott, 1968; Norrish, 1973; Fanning and Keramidas, 1977; Huang et al., 1968; Huang, 1977). The nature of K-bearing minerals, which plays a very important role in the release of K, includes crystal structure and chemical composition of the mineral, ori-

entation of structural OH, location of layer charge, degree of K depletion, and layer charge alterations in micaceous minerals. Among the surrounding environmental conditions, the nature and activity of various ions in soil solution, Eh and pH condition, temperature, wetting, and drying are important factors affecting the rate of K release (Fanning and Keramidas, 1977; Huang, 1977).

Organic acids can facilitate the weathering of minerals and rocks through the formation of metal-organic complexes (Kononova et al., 1964; Stevenson, 1967, 1982; Huang and Keller, 1970, 1971, 1972; Huang and Kiang, 1972; Schnitzer and Kodama, 1976; Tan, 1980; Kodama et al., 1983; Stumm et al., 1985). Organic acids are produced in soils in the decomposition of plant and animal residues and soil humic substances, microbial metabolism and rhizosphere activities (Stevenson, 1967; Wang et al., 1967; Stevenson and Ardakani, 1972; Rao and Mikkelsen, 1977), especially in forest soils which usually have a layer of forest litter on top of soil profiles. Besides humic and fulvic acids, many low molecular weight organic acids, e.g., oxalic, citric, tartaric, fumaric and glycollic acids, are present in forest litter and soil solutions (Schwartz et al., 1954; Kaurichev et al., 1963, 1969, 1977). Some of these organic acids were detected in the rhizosphere of several tree species (Spakhov and Spakhova, 1970). Among these acids, oxalic and citric acids are most common and present in a relatively large quantity (Kaurichev et al., 1963, 1969, 1977; Stevenson, 1967). These low molecular weight organic acids in forest soil solution would likely affect the movement and status of K in soils. However, the dynamics and mechanism of the release of K from soil minerals as influenced by various organic acids is still obscure.

The objectives of this paper were: (i) to examine the dynamics of K release from micas and K-feldspars as influenced by oxalic and citric acids, and (ii) to compare the sequences of K release from these K-bearing minerals through cation exchange reaction using sodium tetraphenylboron (NaTPB) and through the attack by the low molecular weight organic acids.

MATERIALS AND METHODS

Mineral Samples

Samples of biotite (Bancroft, Ontario), muscovite (Stoneham, Maine), microcline (Parry Sound, Ontario), and orthoclase (Belafa, Madagascar) from Ward's Natural Science Establishment, Inc., (New York) were used in the present study. The mica samples were ground in the presence of water in a Waring blender and then fractionated by wet-sieving and sedimentation (Jackson, 1979). The K-feldspars were ground in the presence of methanol in an agate mortar and then fractionated by dry-sieving and sedimentation. The 20 to 50 μm particle size fractions of micas and feldspars were used in this investigation. The determinations of total K, Si, Al, Fe and Mg were carried out by methods described by Jackson (1958). Iron(II) was determined by the method of Peters (1968). The results of elemental analyses are presented in Table 1.

Kinetics of K Release from Minerals

Two hundred milligrams of each mineral sample (20–50 μm) was suspended in 20 mL of water or 0.01 mol L^{-1} oxalic or citric acid solution in a 100-mL centrifuge tube. Each tube was sealed with parafilm and agitated continuously at a speed of 132 ± 1 strokes per min at 298 ± 0.2 K in an oscillating shaker bath. After 1 h, 1, 2, 5, 10, 20, and 30 d, the mineral suspensions were centrifuged at 1150 × g for 10 min and 10 mL of supernatant was used for the determination of K concentration by flame emission spectrophotometry using a Pye Unicam Sp190 Atomic Absorption Spectrophotometer. The amounts of Si, Al, Fe, and Mg released from the minerals to the organic acid solutions or water at the end of a 30-d reaction period were also determined. Silicon was determined by the blue molybdosilicic acid method (Weaver et al., 1968), Al by the aluminon method (Hsu, 1963) with the addition of thioglycolic acid to eliminate the Fe interference (Huang and Liaw, 1977), Fe by the o-phenanthroline method (Jackson, 1958), and Mg by atomic absorption spectrophotometry.

The logarithm of the percent fraction of mineral K remaining was plotted vs. the reaction time in hours. The fittings of data into more than one straight line in the plottings indicate that K release obeyed multiple first-order kinetics. There were three stages of K release from the K-bearing minerals during the reaction period studied (first stage: 0 to 1 h; second stage: 1 to 48–120 h; third stage: 48–120 to 720 h). The first two stages were relatively rapid and could possibly be attributed to rapid dissolution of K from fine particles and/or mechanically disturbed material (Holdren and Berner, 1979; Petrovich, 1981). The third stage accounted for the bulk of the reaction period studied. Therefore, the rate constants of the K release, which were calculated from slopes of the straight lines obtained from regression analysis of the data at the third stage of the reaction, are presented in Table 2. The K release at the first stage was too fast to permit determination of rate constants. The sequence of the rates of K release from these minerals at the second stage of the reaction is identical to that at the third stage (not shown).

In addition to the first-order reaction, possible fittings of K release data to zero-order reaction and a number of other reaction orders up to the 40th order were examined. The data show that multiple straight lines were also obtained in these plottings. The conformity of K release data to both first-order and zero-order kinetics is illustrated in the plottings for a representative mineral orthoclase (Fig. 1). As indicated by the r and especially F values, however, the degrees of linear fittings of K release data at the third stage were higher when the first-order reaction model was used compared with zero-order plottings. Nevertheless, rate constants of K-release from these minerals calculated on the basis of the first-order and zero-order reactions followed the same sequence (not shown).

Potassium Release from Minerals in Renewal Solutions

To residues of the minerals that were treated for 20 d, 15 mL of water or 0.01 mol L^{-1} of oxalic or citric acid solution was added. The suspensions were then agitated at 298 ± 0.2 K in a shaker bath for 5 d. A 15-mL portion of supernatant was withdrawn after centrifugation at the end of the

5-d reaction period and 10 mL was used for determination of K concentration. This 5-d renewal treatment was repeated once more and then followed by two 10-d renewal treatments under the same condition.

Potassium Release in NaTPB Solution

A 20-mL portion of 1 mol L^{-1} NaCl–0.2 mol L^{-1} NaTPB–0.01 mol L^{-1} EDTA solution was added to 200 mg of biotite, muscovite, microcline or orthoclase (20–50 μm) in a centrifuge tube. The mineral suspensions in centrifuge tubes were sealed and shaken for 10 d at 298 ± 0.2 K. The K extracted by this solution was determined by the method developed by Scott and Reed (1962a,b), Scott and Smith (1966), Smith and Scott (1966) and Reed and Scott (1966) as modified by Wang (1981).

Electron Microscopic Examination

The minerals which had been subjected to treatment of the renewing extracting solution were dried on aluminum stubs at the end of the treatment and then given a gold coating to render their surfaces more conductive to the electron beam before they were viewed under the Cambridge scanning electron microscope Mark II.

The mineral–organic acid suspensions that had been agitated for 30 d were centrifuged at 1150 × g for 10 min. A small portion of the supernatant was dropped on carbon-coated formvar on a copper grid, air dried, viewed under a Philips 400 transmission electron microscope, and then examined by EDAX 707B energy dispersive analysis of x-rays. Another portion of the supernatant was taken and filtrated by Sartorius cellulose nitrate filter of 0.01-μm pore size. The ultrafilters were then air dried, given a gold coating, and viewed under the scanning electron microscope to observe any precipitation products formed in these mineral–organic acid suspensions during the reaction period.

X-ray Diffraction Analysis

The mineral samples that were used for the electron microscopic examinations were also examined by x-ray diffraction analysis. The samples were mounted on glass slides and then analyzed by x-ray diffraction using Ni filtered Cu-Kα radiation generated at 35 kV–16 mA.

RESULTS AND DISCUSSION

Rate Constants of K Release

The rate constants calculated (Table 2) are suitable for comparing the relative rate of K release from K-bearing minerals by oxalic and citric acid solutions. The rate constants of K release from biotite in citric and oxalic acid solutions were about 63 and 123 times, respectively, greater than those from muscovite; the rates of K release from biotite in these two organic acid solutions were about 14 to 18 times faster than those from K-feldspars. Data show that in the same organic acid solution, rate constants of K release from these two K-feldspars were almost the same and were

Table 1. Chemical composition of K-bearing primary minerals.

Mineral	Si	Al	K	Total Fe	Fe(II)	Mg
			— g kg^{-1} mineral —			
Biotite	180.3	55.6	74.7	132.7	132.0	76.8
Muscovite	213.8	151.2	82.8	18.2	3.6	1.9
Microcline	303.4	88.5	102.0	0.0	0.0	0.0
Orthoclase	296.7	83.7	125.7	0.8	0.0	0.0

Table 2. Rate constants of the release of structural K from K-bearing minerals by oxalic or citric acid at 298 K.

Mineral	Oxalic acid	Citric acid
	— h^{-1} —	
Biotite	8.7×10^{-3}	3.0×10^{-3}
Muscovite	7.1×10^{-5}	4.8×10^{-5}
Microcline	5.0×10^{-4}	2.1×10^{-4}
Orthoclase	4.8×10^{-4}	1.8×10^{-4}

(right margin, partial text)

Log Percent Fraction of K Remaining in Mineral
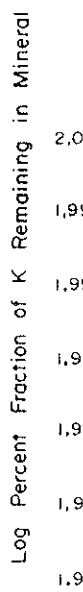
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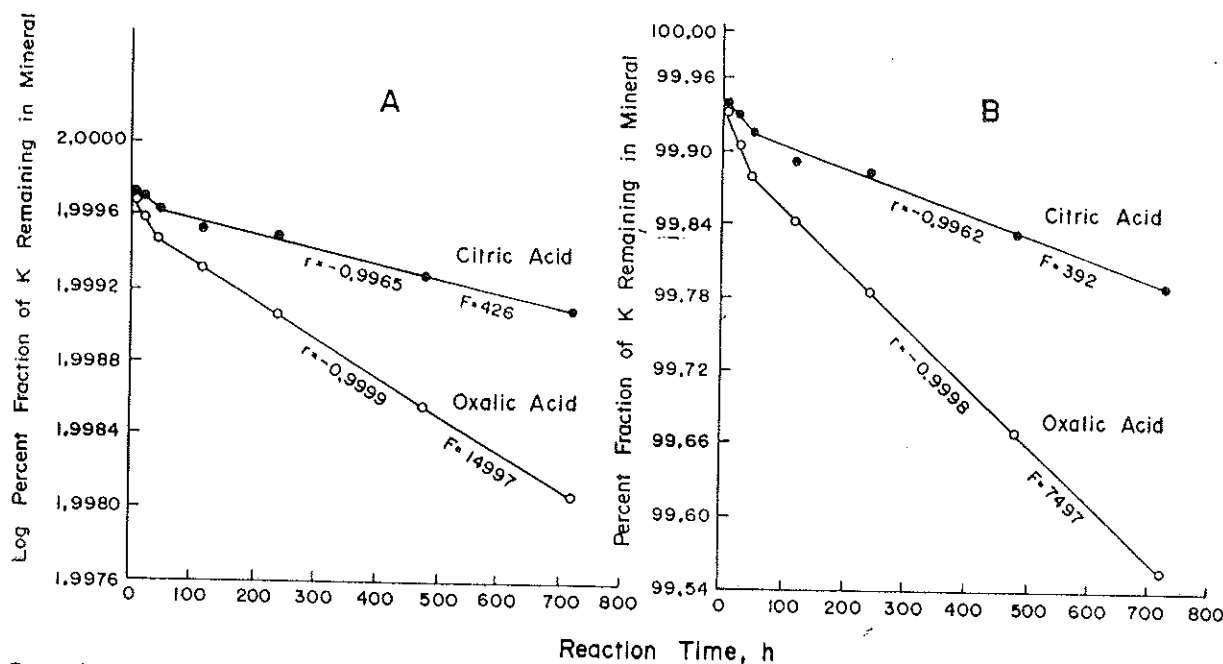The relea
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Fig. 1. Comparison of first-order and zero-order rate curves of K release from orthoclase in 0.01 mol L⁻¹ oxalic and citric acid solutions. A and B are first-order and zero-order plottings, respectively.

about four to seven times greater than those of muscovite.

The higher rate constants of K release from biotite than from muscovite in organic acids (Table 2) can be interpreted in terms of chemical composition and crystal structure of these minerals. The octahedral cations are mainly Fe(II) and Mg in biotite and Al in muscovite (Table 1). The dissolution of structural Fe(II) and Mg from biotite through the attack of hydronium ions followed by complexation reactions with oxalate or citrate ligands was evidently more extensive than that of structural Al from muscovite. These reactions apparently led to deterioration of biotite and release of K from the mineral structure. In the case of muscovite, the octahedral cation, Al, was more stable than Fe(II) and Mg of biotite in the organic acid solutions (Table 3). The amounts of K released from muscovite in organic acid solutions were lowest among K-bearing minerals studied. Besides chemical composition, the atomic bonding and crystal structure (Rich, 1968, 1972; Fanning and Keramidas, 1977; Sparks and Huang, 1985) may play a role in release of K from these minerals even in organic acid solutions. Potassium is held more tightly in muscovite than in biotite. The hydroxyl orientation in muscovite is oblique to silicate sheets; the distance between the proton and K is longer and the K is thus less repelled. In the case of biotite, the hydroxyl orientation is normal to the silicate sheets and the proton is closer to the interlayer K; the K is thus more repelled. Also, the degree of tetrahedral twisting and tilting to fit the octahedral sheet is greater in muscovite than in biotite. All these factors make the K ions more stable in muscovite than in biotite.

The release of K from the interstices in a three-dimensional framework of linked SiO₄ and AlO₄ tetrahedra of a feldspar should be slower than that from the interlayers of a mica as in the case of biotite and K-feldspars (Table 2). The rate of K release from muscovite is even lower, however, than that from K-feldspars in the organic acid solutions. The slower release of K from muscovite than from K-feldspars in oxalic and citric acid solutions is coincident with the stability series of coarse-grained minerals (Goldich, 1938). This series has been interpreted by the differences between equilibrium conditions (e.g., composition, pressure, and temperature) at the time of mineral formation and those on the surface of earth. The greater the difference between these environmental conditions, the greater is the instability of the mineral. Muscovite crystallizes after K-feldspars, so it is more resistant to weathering than K-feldspars.

Renewal of Organic Acids and K Release

Organic acids were very effective in releasing K from the minerals (Fig. 2). The great effect of organic acids on releasing K and other structural cations (Table 3) is attributed to the dissociated H ions and complexing organic ligands in the organic acid solutions. The low molecular weight organic acids with OH and COOH groups in the ortho position tend to form metal-or-

Table 3. Amounts of structural cations of K-bearing minerals released to the 0.01 mol L⁻¹ oxalic or citric acid solution at the end of a 30-d reaction period.

Minerals and organic acids	Si	Al	K	Fe	Mg
			g kg⁻¹ mineral		
Biotite					
oxalic acid	9.86	3.62	5.14	9.50	5.38
citric acid	3.47	1.41	1.82	3.31	1.85
Muscovite					
oxalic acid	0.14	0.26	0.11	0.05	--
citric acid	0.09	0.13	0.10	0.03	--
Microcline					
oxalic acid	1.09	0.50	0.48	--	--
citric acid	0.42	0.25	0.24	--	--
Orthoclase					
oxalic acid	1.01	0.46	0.55	--	--
citric acid	0.41	0.25	0.26	--	--

ganic complexes in solution with some metal ions from mineral structure (Kononova et al., 1964), thus accelerating the decomposition of minerals (Huang and Kiang, 1972). The weakening of the metal–O bonds by the protonation of surface OH groups and the formation of inner sphere surface complexes with organic ligands (Stumm et al., 1985) certainly enhance the mineral dissolution. The release of K is thus affected by the kinds of organic acids. For instance, the rate of K release from biotite in oxalic acid solution was about three times as fast as that in citric acid solution (Table 2). The difference between the ability of these two organic acids in releasing K from minerals was considered to be due to differences in the amounts of organic ligands and H ions generated by organic acids and in the complexing ability of the ligands.
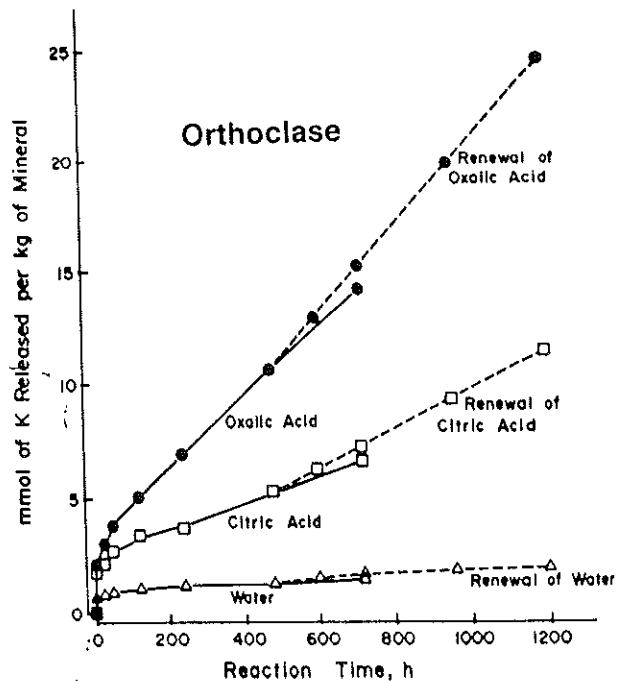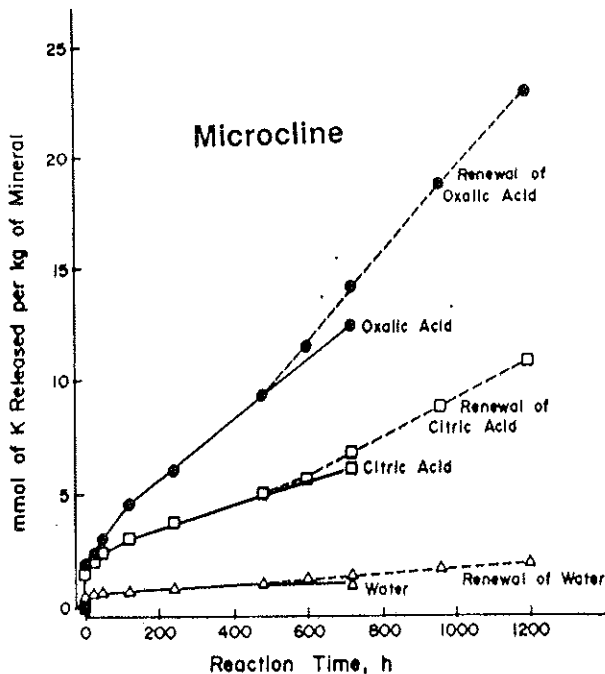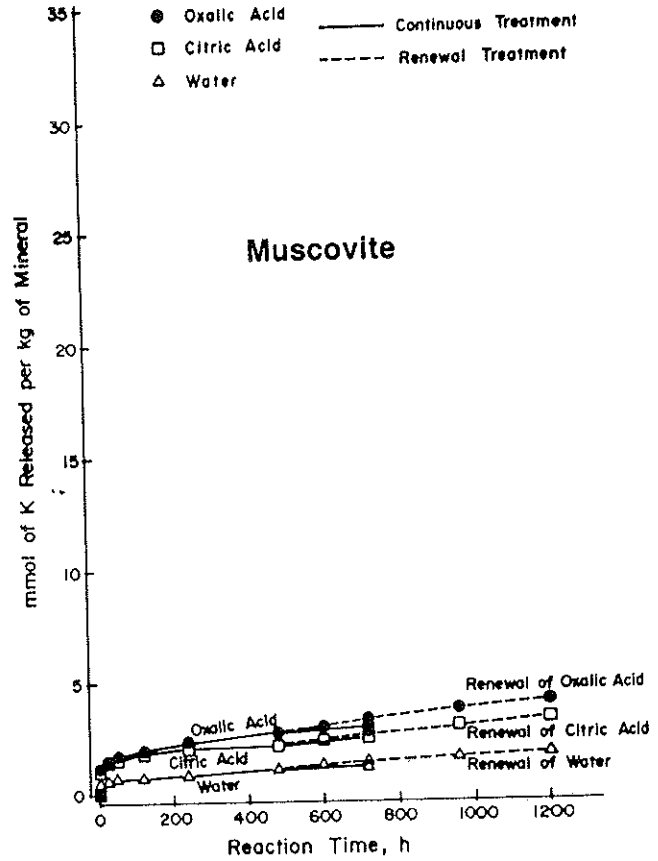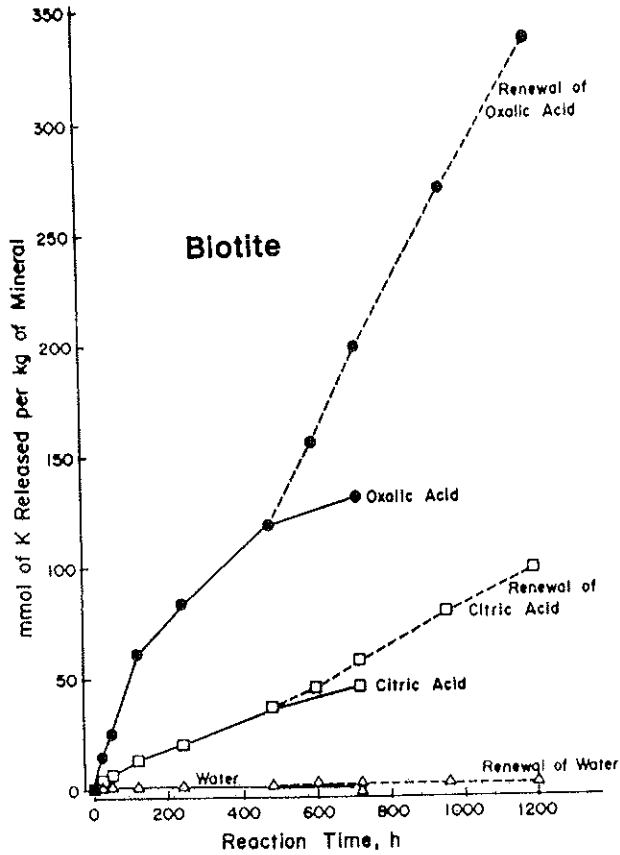

Fig. 2. Release of K from K-bearing minerals to water, 0.01 mol L^{-1} oxalic or citric acid solution during renewal treatments.

The pH values of 0.01 mol L^{-1} oxalic and citric acids were not adjusted so as to investigate the influence of the structure and functionality of these organic acids on the acidity and dissociation of organic ligands and the release of K from K-bearing minerals. Initial concentrations of dissociated organic ligands and H ions in both organic acid solutions were calculated on the basis of the pK_i's and the pHs of oxalic and citric acid solutions before reaction with the minerals. In citric acid solution, there were 2.2 $\times$ 10^{-3} mol L^{-1} of dissociated organic ligands and 2.5 $\times$ 10^{-3} mol L^{-1} of H ions, while in oxalic acid solution the concentration of dissociated organic ligands was 8.8 $\times$ 10^{-3} mol L^{-1} and H ions was 7.9 $\times$ 10^{-3} mol L^{-1}. Concentrations of dissociated organic ligands and H ions in oxalic acid solution were about four and three times, respectively, as high as those in citric acid solution. The more the H ions and dissociated organic ligands were in solution, the more extensively the mineral would be attacked by hydronium and complexing organic ligands. Therefore, at the same concentration, oxalic acid released much more K from the minerals than citric acid did.

The organic ligands and H ions were consumed during the reaction process. At the same time, the concentrations of cations released from mineral structure in the solution were increased. The renewal of the extracting solution replenished organic ligands and H ions as well as decreased the concentration of structural ions released in the solution. The rate of dissolution of residual minerals as controlled by a surface reaction at the solid-liquid interface (Chou and Wollast, 1984, 1985) would be enhanced by renewal of organic acid solutions. Therefore, the rate of K release was increased and sustained upon renewal of the extracting solution (Fig. 2). The modes of the attack of these minerals by organic acids studied in these systems appear to be similar to those of mineral dissolution by F$^-$ (Huang and Jackson, 1965).

Table 4. Potassium released from K-bearing primary minerals by oxalic or citric acid or NaTPB solution at the end of a 10-d reaction period.

Mineral	Organic acid†		NaTPB‡
	Oxalic	Citric	
	g of K released/kg of structural K		
Biotite	44.1	10.5	1000
Muscovite	1.1	0.9	83.0
Microcline	2.3	1.4	1.6
Orthoclase	2.2	1.2	1.3

†The concentration of organic acid solutions was 0.01 mol L^{-1}.
‡One mol L^{-1} NaCl-0.2 mol L^{-1} NaTPB-0.01 mol L^{-1} EDTA.

K Release by Organic Acids and NaTPB

The comparison between K released by organic acids and by NaTPB solution (Table 4) shows that the sequence of K release from K-bearing minerals in organic acid solutions was biotite > microcline $\simeq$ orthoclase > muscovite, while in the NaTPB solution it became biotite > muscovite > microcline $\simeq$ orthoclase. This indicates that the mechanism of K release by organic acids differs from that by the NaTPB solution. The NaTPB solution has been used to extract K from minerals and soils (Scott and Reed, 1962a,b; Reed and Scott, 1966; Scott, 1968; Smith et al., 1968; Kozak and Huang, 1971; Wang, 1981) and to examine the exchangeability of K in minerals and soils (Smith et al., 1968). The K in the mineral structure is replaced by Na in the NaTPB solution through a cation exchange reaction, while the TPB combines with released K and forms precipitates to ensure continuation of the exchange reaction. Except on particle surfaces, exchange of Na for K in the interlayers of micas is much easier than in the interstices of the three-dimensional framework structure of feldspars. More K is thus released through cation exchange from biotite and muscovite than from microcline and orthoclase (Table 4). In organic acid solutions, however, microcline and orthoclase released more K than muscovite did. Evidently, the K in microcline and orthoclase was more susceptible to the attack of organic acids than the K in muscovite. The sequence of minerals in releasing K in organic acid systems is in agreement with the stability series of minerals proposed by Goldich (1938), Jackson et al. (1948), Jackson and Sherman (1953) and Jackson (1968). Data obtained in the present study indicate that the sequence of rates of K release from K-bearing minerals varies with the mechanisms of release.

Molar Ratios of Released Cations

The calculation of molar ratios of Si to K or Al (Fe and Mg) to K in the structure of the original minerals and those released to organic acid solutions (Table 5) reveals that the extent of the release of K and that of the other structural cations are distinctly different. The molar ratios of Si to K released to solutions were significantly lower than those in the mineral structure. Except for muscovite in the citric acid system, molar ratios of Al (Fe and Mg) to K released in the solutions were either higher than or equal to those in the mineral structure. This exception is attributed to the relative resistance of muscovite to weathering by the citric acid solution. In the case of biotite, molar ratios

Table 5. The molar ratios of cations in the structure of K-bearing minerals and those released to 0.01 mol L^{-1} oxalic or citric acid solution at the end of a 30-d reaction period.

Mineral	Si/K			Al/K			Si/Al		
	Mineral	Oxalic acid	Citric acid	Mineral	Oxalic acid	Citric acid	Mineral	Oxalic acid	Citric acid
Microcline	4.1	3.3	2.6	1.3	1.6	1.5	3.3	2.1	1.6
Orthoclase	3.3	2.6	2.2	1.0	1.3	1.5	3.4	2.1	1.6
Muscovite	3.6	1.8	1.3	2.6	3.4	2.0†	1.4	0.5	0.7
Biotite	3.4	2.6	2.7	4.0‡	4.0‡	4.0‡	0.65§	0.67§	0.63§

†After the subtraction of the amounts of Al and K released to the citric acid solution at the end of the 1-h reaction period from those at the end of the 30-d reaction period, the molar ratio of Al to K in muscovite-citric acid system was 2.7.
‡The molar ratio of Al + Fe + Mg to K. The individual molar ratios of Al/K, Fe/K, and Mg/K in the mineral were 1.1, 1.2, and 1.7, respectively, and those released in the oxalic acid solution were 1.0, 1.3, and 1.7; while those released in the citric acid solution were 1.1, 1.2, and 1.6, respectively.
§The molar ratio of Si to Al ...

of Si to Al + Fe + Mg released to the solution were comparable to the molar ratio in the mineral struc-
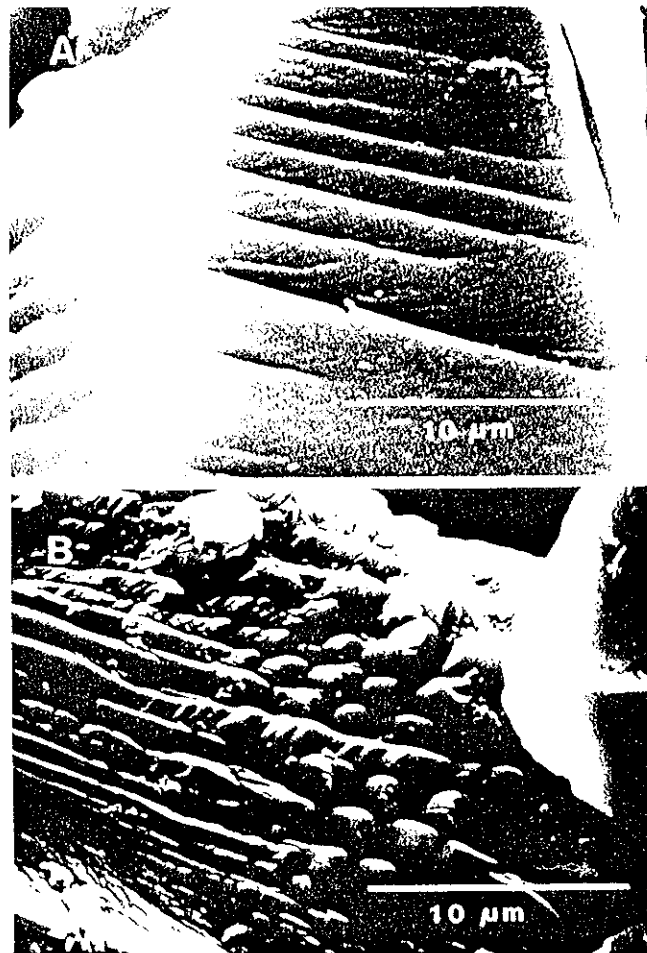

Fig. 3. Scanning electron micrographs of an orthoclase particle treated with water or 0.01 mol L⁻¹ oxalic acid at the end of renewal treatments. A was treated with water and B was treated with oxalic acid solution.

ture. In the muscovite, microcline, and orthoclase systems, molar ratios of Si to Al released to the solutions were all substantially lower than those in the mineral structure. This indicates that the rate of dissolution of the structural Al by organic acids was higher than that of tetrahedral Si, since the nonstoichiometric dissolution was observed at Si solution concentrations below the saturation level. The Si tetrahedra are evidently left behind as leached layers in organic acid weathering. Nonstoichiometric dissolution of aluminosilicates in inorganic weathering is an often observed phenomenon (Chou and Wollast, 1985; Holdren and Speyer, 1985).

When the mineral particles were suspended in organic acid solutions, a very fast K release was initially observed (Fig. 2). This phenomenon is attributed to the exposure of some K ions on the surface of the particles and to the possibility that the mineral structure could be damaged to some extent near the particle surface during the preparation of the sample. These damages would lead to more accessibility of the interlayers of micas and the interstices of K-feldspars to the surrounding solutions, thus releasing K ions at a faster rate. At this initial stage, the molar ratios of Al to K released from these minerals to the organic acid solutions could be very low; in the case of the muscovite–citric acid system it was 1.2 (1.37 mmol Al kg⁻¹ to 1.18 mmol K kg⁻¹) after a 1-h reaction period. As the reaction proceeded, organic acids progressively attacked the mineral structure and much more Al over K would be released. If the organic acid was very strong and/or the mineral was very susceptible to weathering, the portion of Al and K released at the initial stage would be negligible compared to the total Al and K released to the organic acid solution after a long reaction period. But in the case of the muscovite–citric acid system, muscovite is relatively more resistant to weathering and the citric acid solution at 0.01 mol L⁻¹ is not as effective as the oxalic acid solution in degrading the mineral. The total amount of Al and K released at the end of the reaction period was so small
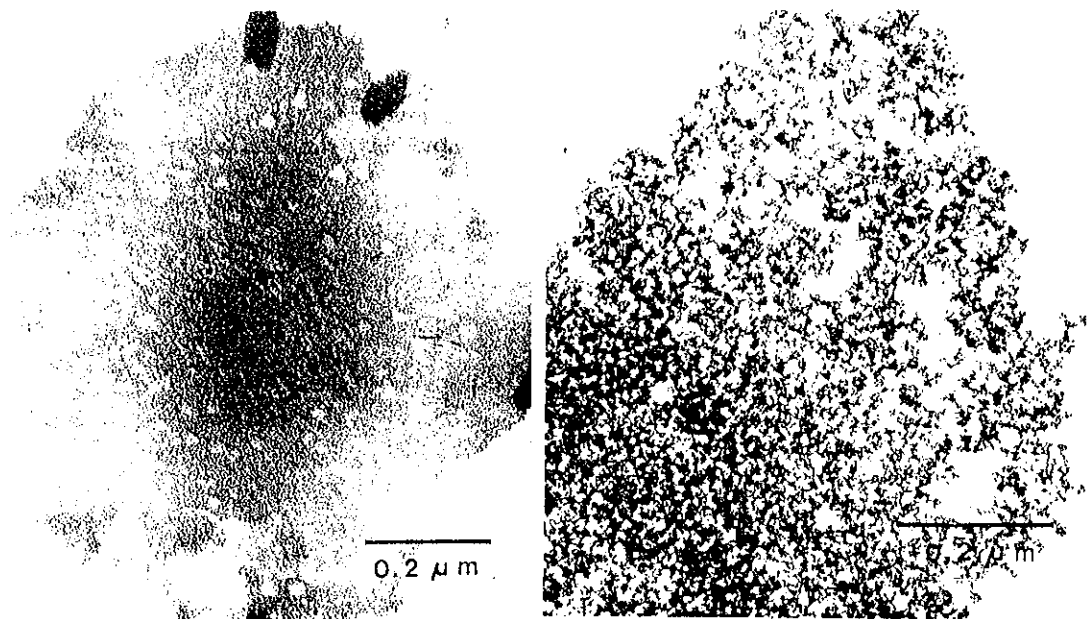

Fig. 4. Transmission electron micrographs of A, air dried pure oxalic acid after the solution evaporated on the stub and B, air-dried solid products of reaction of biotite with 0.01 mol L⁻¹ oxalic acid at the end of a 30-d reaction period.

po...ion of Al and K released at the initial
s substantial enough to influence the final ra-
to K released to the solution. This reasoning
ubstantiated by subtracting the moles of Al
eleased from muscovite in the citric acid at
al stage from those at the end of a 30-d re-
eriod. After the subtraction, the molar ratio
K released to the citric acid solution is ap-
tely equal to that in the muscovite structure
). Based on Table 5 and the above discussion,
us be deduced that the rates of release of oc-
cations from micas and the Al ions from the
rk of feldspars by the organic acids were ap-
tely equal to or higher than those of the re-
K from the interlayers of micas and the in-
of feldspars. In contrast, the molar ratios of
ased to solutions were substantially lower than
mineral structure (Table 5), indicating that
hering of the K-minerals by organic acids lost
proportion of K than Si.

Ray and Electron Microscopic Analyses

diffraction patterns of the minerals after their
with the oxalic or citric acid solutions showed
eable changes from those of the original min-
amination of the mineral residues by scan-
tron microscopy provides evidence for mod-
of r face features of weathering products of
, by   e organic acids. In the case of ortho-
dges on the cleavage surface (Fig. 3A) were
y preferentially attacked by oxalic acid and
ormed (Fig. 3B). Weathered surfaces of ortho-
oxalic acid look much like those of naturally
d K-feldspar (Parham, 1969). Under the at-
oxalic acid, outer layers of biotite particles
and formed ridges on the surface; with fur-
thering, cracks developed in the middle of the
ot shown).

4 shows the transmission electron micro-
f dried pure oxalic acid and the dried soluble
s of the reaction of oxalic acid with biotite at
of a 30-d reaction period. The scanning elec-
rograph of the ultrafilter after filtrating the
ant (not shown) reveals the absence of col-
rticles retained, indicating that the soluble re-
roducts passed right through an ultrafilter of
pore size. The transmission electron micro-
the soluble reaction products (Fig. 4B), how-
eals the presence of shapeless aggregates in
r of 20 nm in size upon air drying. These
s seem to be formed by small agglomerates
of submicroscopic particles and may contain
es of metal-oxalates and silica gels. The spec-
the soluble reaction products determined by
ispersive analysis of x-rays reveals that the
l cations of the shapeless colloids are Si, Al,
lg, M   and Ti.

CONCLUSIONS

n up, the dynamics of K release from K-bear-
rals is greatly influenced by the nature of the
cids such as oxalic and citric acids, which are
in soil environments, especially in localized

zones where biological activity is intense, such as in
the rhizosphere and near decomposing plant residues.
The sequence of K released from the K-bearing min-
erals through the attack of organic acids differs from
that through a cation exchange process using the
NaTPB solution. The data obtained in this study in-
dicate that the sequence of the rates of K release from
K-bearing minerals varies with the mechanisms of the
release. The role of organic acids in affecting the K-
supplying power of soils thus merits close attention.

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The Feasibility of Using Sequential Extraction Techniques for Arsenic and Selenium in Soils and Sediments

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ABSTRACT

Laboratory experiments were conducted with well-characterized minerals to test the applicability of selective extraction schemes for Se and As partitioning in soils and sediments. Two specific steps were tested: the reductive dissolution of amorphous iron oxides and the oxidation of organic material. Selenium and As associated with amorphous iron oxides were usually not found in solution after reductive dissolution, due to readsorption onto other minerals unaffected by the extractant. Oxidants intended to dissolve organic material also oxidized Se(IV) adsorbed on a mineral to Se(VI), causing the release of Se(VI) to the extractant solution. The selective extraction schemes which are currently available do not appear to produce reliable results for Se and As partitioning among sediment components.

Additional Index Words: Selenite, Selenate, Hydrous iron oxides, Selective extraction, Adsorption.

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SELENIUM AND ARSENIC are toxic to animals and humans at low concentrations. Elevated concentrations of As and Se are associated with some soils and agricultural drainage, (e.g., Deverel et al., 1984; Presser and Barnes, 1984, 1985; Tidball et al., 1986), coal and petroleum by-products including coal fly-ash wastes (e.g., Campbell et al., 1978; White et al., 1984), metal refining operations (e.g., Lakin and Davidson, 1973) and mine tailings (e.g., Thomson and Heggen, 1982). Arsenic is also a component of pesticides, herbicides, and fungicides (Moore and Ramamoorthy, 1984). The rate and extent to which these elements can be mobilized and released to surface and ground water depends on their chemical speciation and partitioning in soils and sediments. Various sequential extraction techniques have been proposed to estimate the partitioning of trace elements among broad chemical classes of solid phases in sediments and soils, (e.g., carbonates, manganese oxides, organic matter, amorphous iron oxides, crystalline iron oxides, and silicates). This study examines the applicability of the commonly used extraction steps for the determination of Se and As partitioning in sediments and soils.