

CHLORITE AND BIOTITE WEATHERING BY FULVIC ACID SOLUTIONS IN CLOSED AND OPEN SYSTEMS

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The dissolution by dilute fulvic acid (FA) solutions of elements constituting two chlorites and biotite was investigated in closed and open systems. In closed systems, dilute FA solution rapidly dissolved substantial amounts of Si, Al, Fe, Mg, and K (in the case of biotite only) from chamosite and biotite during the first 100 h of contact. Thereafter, the rate of dissolution decreased exponentially with increasing time. Maximal concentrations of elements dissolved were approximately proportional to FA concentrations when these were 0.1% (wt/vol) and lower. In the open systems, relatively fast dissolution rates of Fe-clinochlore and biotite were observed initially (up to 30–35 days). Following this, the rates slowed to near constancy. If the dissolutions had continued at the constant rates, it would have taken a 0.025% FA solution about 22 yr to dissolve 1 g of Fe-clinochlore and 7.2 yr to dissolve 1 g of biotite. Increases in flow rate from 1 to 3 mL/h increased the rates of dissolution of the elements by 2.5–3 times. Ratios of elements dissolved by FA in both systems differed from the elemental ratios of the minerals in being enriched in Fe and Mg, which indicates the preferential dissolution of elements in octahedral coordination.

Key words: Fe-clinochlore, Mn-Mg-chamosite, dissolution rate

[Désagrégation de la chlorite et de la biotite par l'acide fulvique en milieux clos et ouvert.]

Titre abrégé: Désagrégation des minéraux par l'acide fulvique.

On a étudié la dissolution des éléments constitutifs de deux chlorites et d'une biotite par de l'acide fulvique diluée en milieu clos et ouvert. En milieu clos, l'acide fulvique dissout rapidement une forte proportion de Si, Al, Fe, Mg et K (biotite seulement) au cours des 100 premières heures de contact avec la chamosite et la biotite. Par la suite, le taux de dissolution diminue de façon exponentielle avec le temps écoulé. La concentration maximum des éléments dissous est à peu près proportionnelle à celle de l'acide fulvique lorsqu'elle ne dépasse pas 0,1% (p/v). En milieu ouvert, on commence par observer une dissolution rapide du clinochlore ferreux et de la biotite (jusqu'à 30 à 35 jours) puis la dissolution ralentit pour devenir presque constante. Si la dissolution se poursuit effectivement à un taux constant, il faudrait environ 22 ans à l'acide fulvique (solution à 0,025%) pour dissoudre 1 g de clinochlore ferreux et 7,2 ans pour dissoudre 1 g de biotite. Lorsque le débit passe de 1 à 3 mL/h, le taux de dissolution des éléments augmente de 2,5 à 3 fois. La proportion des éléments dissous par l'acide fulvique dans les deux systèmes diffère des proportions relevées dans les minéraux en ce sens que la solution est plus riche en Fe et en Mg, signe qu'il y a dissolution préférentielle des éléments à construction octaédrique.

Mots clés: Clinochlore ferreux, chamosite à Mn et Mg, taux de dissolution

The weathering of minerals in soils and sediments is often enhanced by the action of naturally-occurring organic acids (Huang and Keller 1970). Among these, humic materials, especially water-soluble

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fulvic acids (FAs), are important because of their abundance, mobility and ability to complex or chelate metal ions and interact with silica. These interactions may increase the concentrations of metal ions and silica in aqueous solutions to levels that are far in excess of their normal solubilities. Thus, aqueous FA solutions may not only bring about the dissolution or degradation of existing minerals, but may also lead to the synthesis of new minerals by permitting the complexed and dissolved metals and silica to form new combinations (Schnitzer and Kodama 1977).

The dissolution of metal oxides, metal hydroxides and layer silicates by humic acids (HAs) and fulvic acids (FAs) has been described by several workers (Baker 1973; Evans and Russel 1959; Kodama and Schnitzer 1973; Schnitzer and Kodama 1976; Tan 1980).

Earlier investigations in this laboratory dealt with the dissolution of chlorites (Kodama and Schnitzer 1973) and micas (Schnitzer and Kodama 1976) by FA. Both types of minerals were attacked by FA solutions and substantial amounts of metals and Si were brought into solution. Minerals were shaken for up to 710 h with 0.2% (wt/vol) FA solutions in closed tubes. Although substantial amounts of elements (such as Fe, Mg, Al, Si, and K in the case of micas) were rapidly dissolved during the first 100 h, the rate of dissolution of metals was considerably reduced after 200 h of reaction time.

On the whole, the rate of dissolution increased exponentially with time and was affected by the particle size of the mineral, the concentration of elements in solution, and differences in the reactivities of the functional groups of the FA. In general, the smaller mineral particles increase the rate of dissolution during the initial reaction period (cf. Holdren and Berner 1979) and the greater the concentration of elements in solution, the slower the rate of dissolution of elements from the minerals. The present authors believe that during the

initial reaction periods the most reactive functional groups interact, but as the reaction time lengthens, only less reactive functional groups are available for reaction so that the rate of dissolution slows.

While the experiments described above provided useful information on mineral weathering, they did not simulate what happens in nature where mineral weathering in soils occurs mainly in open systems. Therefore, we set up experiments in systems which more closely approximated natural conditions than had been the case in our earlier experiments.

The purposes of this paper were (1) to evaluate effects of different FA concentrations on the dissolution of minerals in closed systems; (2) to report results of metal and Si dissolution by FA in open systems; and (3) to compare data obtained with the two experimental systems.

MATERIALS AND METHODS

The FA was extracted from the Bh horizon (15- to 21-cm depth) of the Armadale soil, a poorly-drained Podzol with 4.2% C, a pH (H₂O) of 4.0 and sampled in Prince Edward Island. Methods of extraction, fractionation and purification of the FA were the same as those described earlier (Schnitzer and Skinner 1968). The purified FA contained (on a moisture- and ash-free basis) 50.9% C, 3.3% H, 0.7% N, 0.3% S and 44.7% O; 9.1 meq COOH, 3.3 meq phenolic OH, 3.6 meq alcoholic OH, 2.5 meq ketonic C=O, 0.6 meq quinonoid C=O and 0.1 meq OCH₃ per gram. Its ash content was 1.0% and it was completely soluble in water. Its number-average molecular weight (\bar{M}_n) measured by vapor pressure osmometry was 951.

The mineral samples used were Fe-bearing Mg-chlorite (Fe-clinocllore) from Chester, Vermont, Mn- and Mg-bearing Fe-chlorite (Mn-Mg-chamosite) from Ichinokoshi, Toyama, Japan, and biotite from Bancroft, Ontario. The chamosite sample was crushed and ground gently in an agate mortar under wet conditions, and then passed through a 325-mesh sieve (<45 μm). The clinocllore samples were crushed into small particles in a blender and then wet-sieved to obtain the following three fractions: <45 μm , 45–150 μm and 150–250 μm . Large biotite flakes were cut with scissors into small

pieces which were then macerated in a blender to form a fine suspension from which the desired fractions were collected by wet-sieving and sedimentation. One fraction of each of the minerals was analyzed chemically by methods described by Maxwell (1968), using HF-H₂SO₄-HNO₃ decomposition prior to the determination of Fe, Al, Mn, Mg, Ca, K and Na. Silicon was determined after Na₂CO₃ fusion. Variations in the chemical composition of a mineral due to particle-size are generally insignificant unless the particle-size is of a magnitude of a tenth of a micron (Kodama and Brydon 1968). In the samples investigated most particles were greater than 1.0 μ m.

For dissolution experiments in closed systems, duplicate 25.0-mg portions of each of Mn-Mg-chamosite (<45 μ m), and biotite (1–2 μ m) were weighed into 35-mL ground-glass-stoppered centrifuge tubes, to some of which 25.0-mL of 0.1% (wt/vol) FA solution (pH 2.80) were added, while 25.0 mL of 0.025% (wt/vol) FA solution (pH 3.25) were added to others. The tubes plus contents were agitated on a reciprocating shaker at room temperature (22 \pm 2°C) for up to 312 h. After completion of the reaction, pairs of tubes were removed from the shaker and centrifuged at 850 g for 1 h to collect the insoluble residues. The resulting clear supernatants were transferred to 25.0-mL

volumetric flasks and made to volume with distilled water. Suitable aliquots were digested on the steambath for 1/2 h with small volumes of 30% H₂O₂ until the color had disappeared. Fe, Al, Mg and K in these solutions were determined by atomic absorption spectrophotometry. Si was measured on untreated extracts on a Technicon Autoanalyzer by the method of Campbell and Thomas (1970). All results were corrected for amounts of each element in blanks, which consisted of FA solutions only, shaken for the same lengths of time as the FA-mineral systems. Coefficients of variations between replicate Si and metal analyses were <2.5%.

For dissolution experiments in open systems, 0.5 g of mineral was placed in a plastic tube of 5.5-mm i.d. which was inserted into the leaching apparatus described in Fig. 1. The inlet of the apparatus was connected to a reservoir of 0.025% FA solution through a double syringe pump which pumped FA solution at a regulated flow rate through the reaction column. To prevent air bubbles entering the column, a small trap was installed between the pump and the column. The effluent from the sample column was collected in 25-mL aliquots with the aid of an automatic fraction collector. With the open system, all experiments were run at room temperature (25 \pm 3°C) using 0.025% FA solution; the 45- to 150- μ m fraction of biotite was

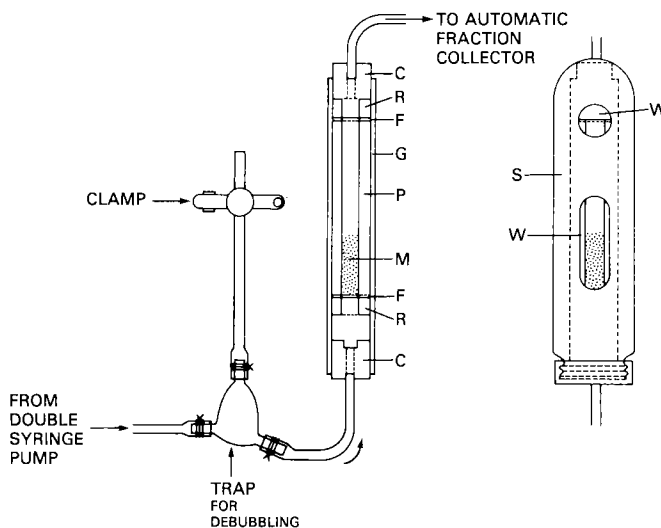


Fig. 1. Leaching apparatus. C, tubing connector; R, plastic ring; F, filter (paper); G, glass column; P, plastic tube housing sample; M, sample; S, shield for tightening the connectors to the column; W, observation window.

leached at flow rates of 1 mL/h and 3 mL/h, and the 45- to 150- μm fraction of Fe-clinocllore was leached at a flow rate of 1 mL/h. Coarser fractions of the minerals were used in the open system to prevent blockages or passage through the filter paper. Dissolved Si, Al, Fe, Mg and K, were determined by atomic absorption spectrophotometry in aliquots taken either directly from every 25 mL fraction collected or from concentrates of two or three fractions, depending on the concentrations of elements to be analyzed. All analyses were corrected for blanks.

X-ray diffraction analyses on leached biotite were done on a Philips diffractometer after treatment with glycerol.

RESULTS AND DISCUSSION

Closed Systems

Figure 2 shows the dissolution of Fe from Mn-Mg-chamosite ($<45\ \mu\text{m}$) by 0.025, 0.1 and 0.2% FA, respectively. The data obtained with 0.2% FA were taken from an earlier paper (Kodama and Schnitzer 1973) and are presented here for comparative purposes. Dissolution curves for other elements were omitted because their shapes resembled that of the dissolution curve for Fe. The concentration of FA affected the rate of dissolution of the metal ions and of Si. After 312 h of constant shaking (Table 2), 1 L of 0.025% FA dissolved 12.0 mg of Fe from 1 g of mineral, whereas 43.0 mg of Fe was brought into solution by 1 L of 0.1% FA, and 65.3 mg of Fe by 1 L of 0.2% FA under the same experimental conditions. Amounts of Fe dissolved were nearly proportional to FA concentrations at the 0.025 and 0.1% levels. However, the 0.2% FA solutions, which contained the highest concentration of FA that can be dissolved in 1 L of distilled water, dissolved proportionately less Fe than did the more dilute solutions. Similar trends were also observed with Al and Mg. The dissolving power of FA may be related to its metal-complexing capacity, which is to a large extent governed by the dissociation of the FA-COOH groups, with the dissociated protons dissolving metals from min-

erals and the dissolved metals being complexed by FA-COO⁻ groups (Schnitzer and Kodama 1977). Molar ratios of FA-COOH groups to metals dissolved (Table 2) for the three systems were 6.0, 6.0 and 7.8, respectively. Thus, in each system an excess of COOH groups in the FA over metals dissolved was apparent. Another explanation for our findings is that the reduced efficiency of more concentrated FA solutions to dissolve minerals was due to changes in the conformation of the FA. In dilute solutions, FA molecules are flexible linear molecules (Ghosh and Schnitzer 1980). In more concentrated solutions, the FA molecules adopt a coiled conformation that reduced the capacity of COOH and other functional groups to react with minerals.

Relatively less Si was dissolved from the mineral by 0.1% FA than by 0.025% FA solution (Table 2). Silicon was not determined in the 0.2% FA solutions. The pHs of all solutions increased with time (Table 2). Increases in pH with increasing metal extraction can be explained by assuming that, as a result of complexation, the FA displaced OH ligands from partly hydroxylated Fe and Al compounds and that OH groups were released. The dissolution of bases, such as Mg, would also increase the pH.

Another point of interest was to find out whether the attack of FA on the mineral was uniform. In FA solutions in contact with Mn-Mg-chamosite, molar Si:Al:Fe:Mg ratios were: (a) with 0.025% FA, 2.0:1.9:3.0:1.0 and (b) with 0.1% FA, 2.1:2.5:3.7:1.0. The same ratios for the initial mineral were 3.6:3.2:5.2:1.0 (Table 2). These ratios indicate that the release of the metal ions from the mineral was incongruent. Effects of different FA concentrations on the dissolution of biotite were similar to those observed on Mn-Mg-chamosite. The analysis of FA solution which had reacted with biotite for 720 h (Fig. 3) gave molar Si:Al:Fe:Mg:K ratios of 3.7:2.2:2.8:3.0:1.0. Molar ratios of the

same elements in untreated biotite (Table 2) were 3.3:1.2:1.5:1.8:1.0, so that the dissolution was incongruent. The pH of the 0.025% FA solution increased from 3.3 at the beginning, to 4.1 at the end of the experiment. The data indicate that octahedral elements in both chlorite and biotite such

as Fe and Mg were relatively easily dissolved by FA.

As shown in Figs. 2 and 3, the dissolution of the elements, with the exception of Si, from Mn-Mg-chamosite and biotite approached near-equilibrium conditions after 300 h of shaking. At that time about 4 and

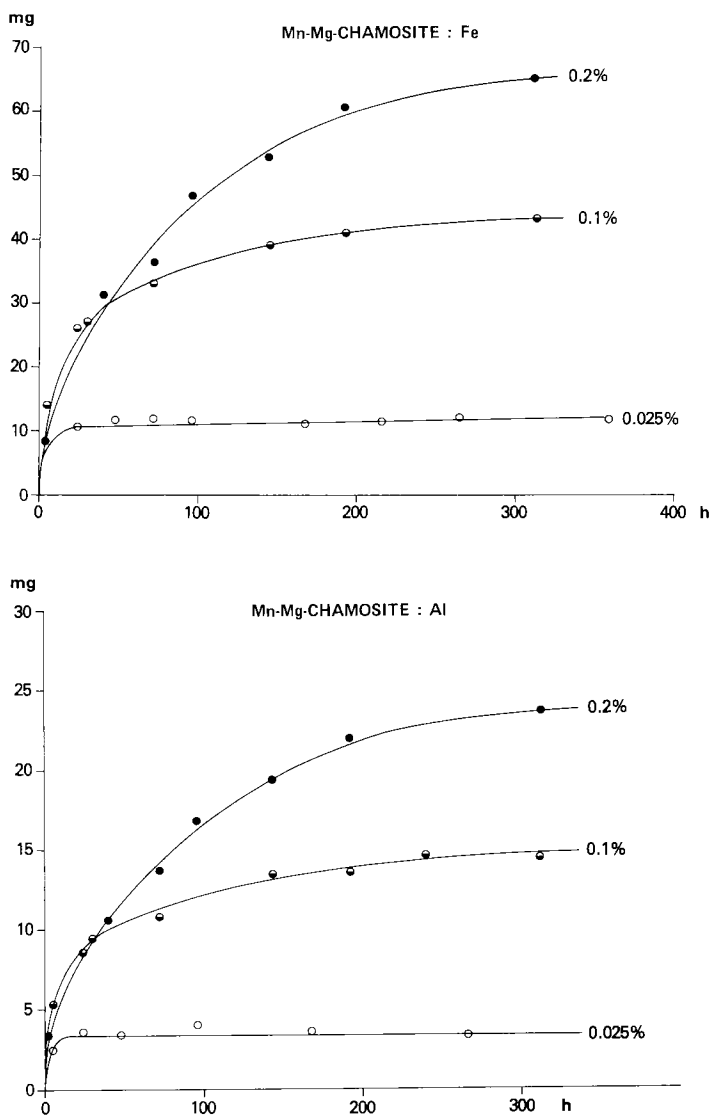


Fig. 2. Effect of FA concentration on the dissolution of Fe from Mn-Mg-chamosite in a closed system. Amounts of elements dissolved are expressed in milligrams per gram of mineral.

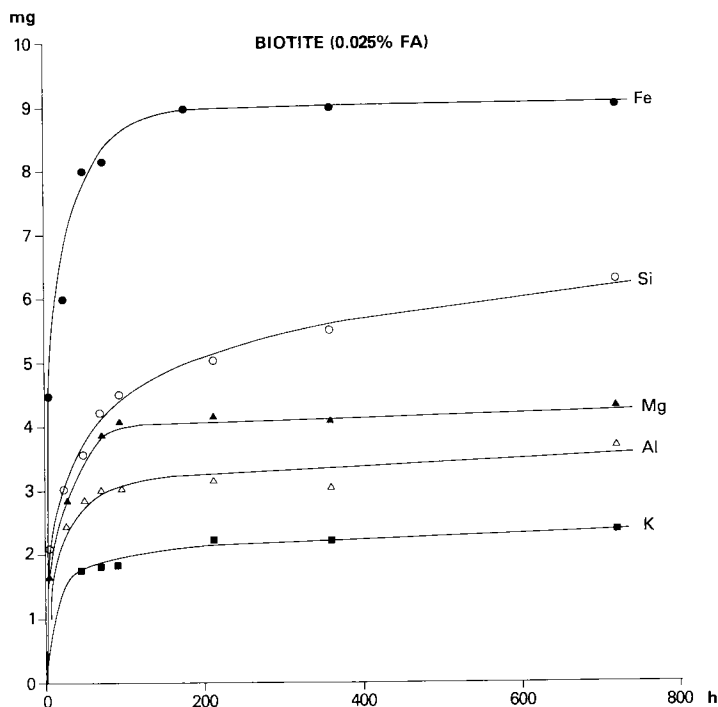


Fig. 3. The dissolution by 0.025% FA solution of Si, Fe, Al, Mg and K from biotite in a closed system. Amounts of elements dissolved are expressed in milligrams per gram of mineral.

5%, respectively, of the initial weights of the two minerals had been dissolved. Only small additional amounts of Si and metals were dissolved when shaking was continued beyond that time.

Open Systems

Figure 4 shows the cumulative release of Si, Al, Fe and Mg from Fe-clinocllore (45–150 μm) by 0.025% FA at a flow rate of 1 mL/h. The high initial reaction rates for the first 30–35 days are possibly due to the dissolution of finer particles. These initial reaction periods were followed by lengthy periods with slower but nearly constant reaction rates. After 90 days, the 0.025% FA solution had dissolved 1.6 mg Si, 2.2 mg Al, 2.0 mg Fe and 4.4 mg Mg from 1 g of Fe-clinocllore (Fig. 4). These gave molar ratios of 1.6:2.3:1.0:5.1 for Si:Al:Fe:Mg. The corresponding ratios in the original sample were 3.9:2.5:1.0:6.0,

which indicates that the dissolution of Si by FA was low. Based on the amount of Si released, approximately 1.1% of the original weight of Fe-clinocllore was dissolved after 90 days. If the mineral had continued to dissolve at a linear rate similar to the average rate of 0.017 mg/day found between 80 and 90 days of reaction, it would have taken about 22 yr to dissolve 1 g of the mineral.

In the case of biotite, 6.3 mg of Si were dissolved from 1 g of biotite after 90 days of reaction (Fig. 5), so that the rate of release of Si was faster than that from Fe-clinocllore. This indicates that the biotite structure was more readily attacked by FA than that of Fe-clinocllore. It would have taken only about 7.2 yr to decompose 1 g of biotite, judging from the high average rate of dissolution of 0.071 mg Si/day after 80 days of reaction (Fig. 5).

Amounts of the other elements released

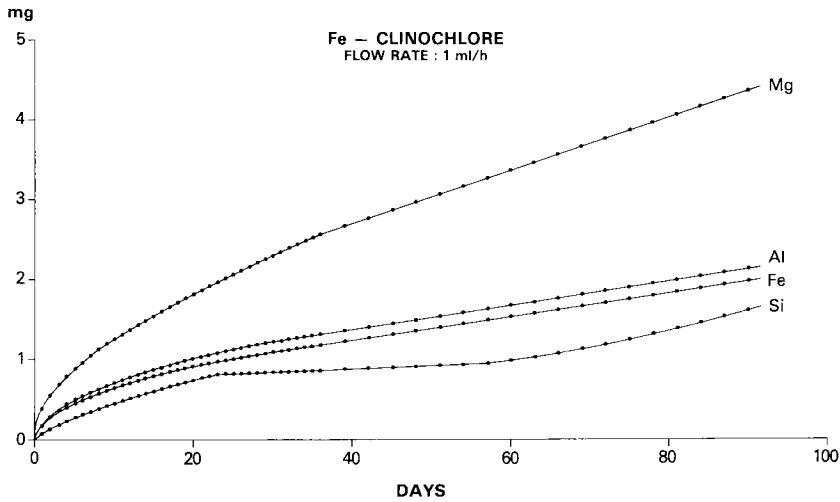


Fig. 4. The dissolution by 0.025% FA solution of Si, Fe, Al and Mg from Fe-clinocllore in an open system; flow rate: 1 mL/h. Amounts of elements dissolved are expressed in milligrams per gram of mineral

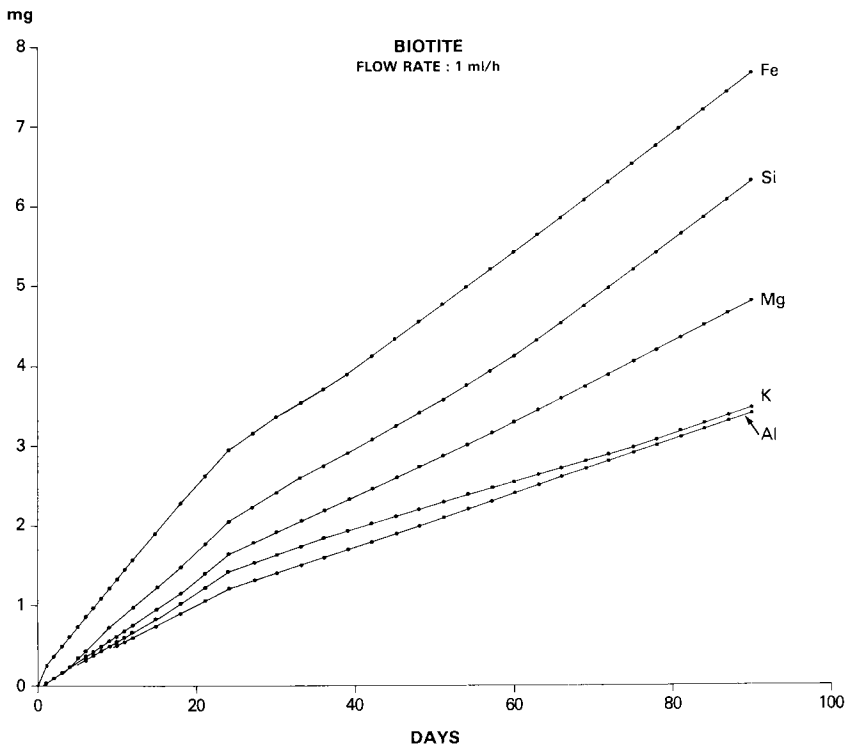


Fig. 5. The dissolution by 0.025% FA solution of Si, Fe, Al, Mg and K from biotite in an open system; flow rate: 1 mL/h. Amounts of elements dissolved are expressed in milligrams per gram of mineral.

from biotite after 90 days of leaching were 2.4 mg Al, 7.7 mg Fe, 4.8 mg Mg and 3.5 mg K (Fig. 5). The resulting molar ratios, including Si, were 2.5:1.0:1.6:2.3:1.0 for Si:Al:Fe:Mg:K. Since the corresponding ratios calculated for the original biotite (Table 1) were 2.9:1.0:1.3:1.6:0.9, the dissolution of Si by 0.025% FA appeared to be slightly suppressed while Mg and Fe were dissolved preferentially. These data also indicate that octahedral sheets of biotite were attacked by FA, so that preferential dissolution of interlayer K was not noticeable. Similar results were observed in a previous dissolution study in a closed system in which shaking with FA solution of biotite and phlogopite (in contrast to muscovite) failed to show preferential dissolution of K (Schnitzer and Kodama 1976). It is noteworthy that X-ray diffraction data of the residual biotite after 90 days of reaction showed the presence of a minor 11A phase mineral (partially hydrated biotite) in addition to unaltered biotite, suggesting that the dissolution mechanism included a hydration stage.

The same biotite sample was further

used to study the effect of flow rate on the rate of release of constituent elements. Data obtained with a flow rate of 3 mL/h are presented in Fig. 6. The dissolution of Al was an almost perfect example of linearity with time and proportionality to flow rate (see Figs. 5 and 6). The rate of release of K was linear with time at a flow rate of 3 mL/h (Fig. 6), but exhibited a relatively fast rate in the initial period (up to ~ 25 days), followed by a linear reaction with a flow rate of 1 mL/h (Fig. 5). If these rates are taken as representative, the rate of K dissolution from biotite at a flow rate of 3 mL/h is nearly three times as fast as that at a flow rate of 1 mL/h, indicating that the dissolution of K was directly proportional to the flow rate.

The dissolution of Fe and Mg resembled that of K, except that the rate of dissolution did not increase proportionally, but increased approximately 2.5 times with an increase in the flow rate from 1 mL/h to 3 mL/h. For the release of Si, more complicated dissolution behaviour was observed. With a flow rate of 1 mL/h there were three stages in the rate of release: an initial one

Table 1. Chemical composition of the primary minerals

	Fe-clinocllore (Chester, Vermont) <45 μm	Mn-Mg-chamosite (Ichinokoshi, Toyama) <45 μm	Biotite (Bancroft, Ontario) <2-45 μm
	%		
SiO ₂	30.14	22.24	39.32
Al ₂ O ₃	16.74	17.05	11.58
Fe ₂ O ₃	0.56	13.38	4.73
FeO	8.81	26.26	17.42
MnO	0.03	5.42	1.13
MgO	30.83	4.10	14.08
CaO	0.01	tr	0.01
Na ₂ O	-	-	0.62
K ₂ O	-	-	9.50
Ign. † loss	11.88	11.03	0.49
	99.00	99.48	98.88
	mg/g		
Si	140.89	103.96	183.80
Al	88.60	90.24	61.29
Fe	72.40	297.70	168.49
Mg	185.94	24.73	84.92
K	-	-	78.87

*Ignition.

Table 2. Dissolution of Si and metal ions after 312 h of shaking from Mn-Mg-chamosite by 0.025, 0.1 and 0.2% FA solutions (expressed as milligrams and mmol per 1 g of sample and 1 L of FA solution)

	FA concentration											
	0.025%				0.1%				0.2%			
	Si	Al	Fe	Mg	Si	Al	Fe	Mg	Si	Al	Fe	Mg
mg	3.8	2.8	12.0	1.6	12.4	14.3	43.0	5.0	ND	23.7	65.3	6.7
mmol	0.14	0.10	0.21	0.07	0.44	0.53	0.77	0.21	ND	0.88	1.17	0.28
CO ₂ H metals (mol:ratio)												
pH initial/final				6.0			6.0					7.8
				3.3/4.2			2.8/3.4					2.5/3.2

ND = not determined.

(up to 20 days), a relatively slow intermediate one (up to 60 days), and a steady state (after 60 days) (Fig. 5). Compared with this, a flow rate of 3 mL/h (Fig. 6) produced a relatively slow initial reaction (up to 4~12 days), followed by a relatively fast and steady reaction period. The rates of the steady reaction at flow rates of 1 mL/h and 3 mL/h were not exactly proportional to flow rates but increased as the flow rate increased.

As expected, the major difference between the results obtained in closed and open systems was that in the closed system the rate of the release of constituent elements decreased exponentially with increasing extraction time, while in the open system the rate was steady and nearly constant after the initial reaction period. It is likely that the fast initial reactions observed in both systems indicated the dissolution of small particles in the minerals. In open systems, metal and Si concentrations in solutions around the mineral surfaces were relatively low, so that nearly constant dissolution rates were observed after the initial reaction periods. These constant rates can be used to extrapolate from laboratory experimental data to mineral dissolutions in nature. Naturally occurring mineral weathering reactions in Podzolic soils are more closely simulated by our reactions in open systems. Reported values for organic matter concentrations in soil solutions and surface waters range from about 4×10^{-2} to 1.2 g/L (Holzhay 1975; Schnitzer and Desjardins 1969) The 0.025% FA solution that we employed contained 0.25 g FA/L, which was well within the range reported for organic matter concentrations in natural solutions. The following example shows how our laboratory data for open systems can be used to calculate mineral dissolutions in soils. If we assume that a volume of water, corresponding to an annual precipitation of 100 cm, penetrates a surface horizon of soil, then its average flow rate in the soil would be about 0.01 cm/h. Since the cross-section

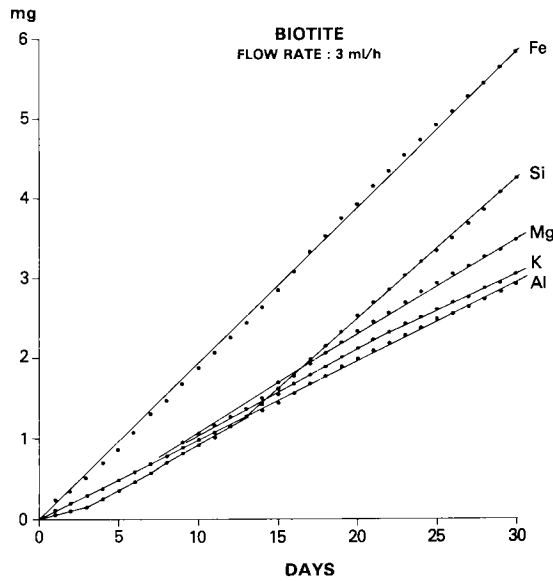


Fig. 6. The dissolution by 0.025% FA solution of Si, Fe, Al, Mg and K from biotite in an open system; flow rate: 3 mL/h. Amounts of elements dissolved are expressed in milligrams per gram of mineral.

tional area of the reaction column was 0.238 cm², the flow rates of 1 and 3 mL/h convert to 4.2 and 12.6 cm/h, respectively. Therefore, under conditions prevailing in nature, a 0.025% FA solution would dissolve Fe-clinocllore in 9240 yr whereas biotite would be dissolved in 3024 yr, which reflects the susceptibility of biotite to weathering. In fact, it is very rare to find biotite or chlorite in Ae horizons of Podzolic soils even if these minerals are present in subsoils of the same soils. Of course, the periods of time calculated above may vary with precipitation, evaporation, uptake by plants, temperature and soil structure, concentrations of organic matter in soil solutions and leachates, and also with particle-sizes of minerals. As mentioned before, the dissolution of elements was nearly proportional to the flow rate and the FA concentration. Therefore, if the flow rate and the FA concentration are known, the near-constant dissolution rate data reported for the open systems can be applied to computing the dissolution of minerals by dilute FA solutions in soils.

SUMMARY

The dissolution by dilute FA solutions of Fe-clinocllore, Mn-Mg-chamosite and biotite was investigated in closed and open systems. In closed systems, the rate of dissolution of the elements decreased exponentially with increasing reaction time. With FA concentrations of 0.1% (wt/vol) and lower, the concentrations of elements dissolved were approximately proportional to the FA concentrations. Higher FA concentrations were relatively less effective in this regard than were lower ones.

In open systems, fast dissolution rates were observed during the initial 30–35 days. Following this, the dissolution rates slowed to near constancy. If the dissolution had continued at the constant rates, it would have taken a 0.025% FA solution about 22 yr to dissolve 1 g of Fe-clinocllore and 7.2 yr to dissolve 1 g of biotite.

The data indicated the preferential dissolution of octahedral elements but no dissolution of interlayer K from biotite was observed.

An increase in flow rate from 1 to 3 mL/h increased the dissolution of the elements by 2.5–3 times.

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