Kinetics and Mechanisms of Potassium Release from Sandy Middle Atlantic Coastal Plain Soils[1]

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ABSTRACT

Kinetics of K release were investigated on a Kenansville loamy sand (loamy, siliceous, thermic Arenic Hapludults), a Rumford loamy sand (coarse-loamy, siliceous, thermic Typic Hapludults), and a Sassafras fine sandy loam (fine-loamy, mixed, mesic Typic Hapludults) from the Delaware Coastal Plain. Previous field experiments had shown that corn (*Zea mays* L.) grown on these soils did not respond to K applications. The soils contained high levels of total K ranging from 22.5 to 46.5 cmol kg⁻¹. Most of the total K was in the mineral form, particularly feldspars, and was contained in the sand fractions of the soils. Kinetics of K release from the whole soils and from the coarse, medium, and fine sand fractions were studied using a H-saturated resin and 0.01 M oxalic acid. Potassium release from the whole soils, using the resin, ranged from 0.172 to 0.251 cmol kg⁻¹ over a 30-d period, and significantly more K was released with the resin than with oxalic acid. The K release that occurred from the sand fractions was attributed to the highly weathered nature of the K-feldspars in these soils as observed by electron microbeam analyses. The mechanism of K release from the soil feldspars appears to be a surface-controlled reaction.

Additional Index Words: nonexchangeable K, K-feldspars, physical chemistry of K.

DYNAMIC REACTIONS EXIST between solution, exchangeable, fixed, and mineral phases of soil K. These reactions markedly affect whether applied K is taken up by plants, leached into lower soil horizons, or converted into unavailable phases (Sparks and Huang, 1985; Sparks, 1987). Recently, Sparks and coworkers have investigated the kinetics of K exchange on soils and clay minerals (Sparks et al., 1980a, b; Sparks and Jardine, 1981; Jardine and Sparks, 1984; Sparks and Jardine, 1984; Carski and Sparks, 1985; Ogwada and Sparks, 1986a, b, c). These studies have clearly shown that the rate of exchange between solution and exchangeable K forms is diffusion-controlled and strongly dependent on clay mineralogy.

Numerous studies have appeared in the scientific literature on nonexchangeable K release from micas (Scott and Reed, 1962; Quirk and Chute, 1968; Malquori et al., 1975; Feigenbaum et al., 1981) and from soils (Talibudeen and Weir, 1972; Martin and Sparks, 1983; Havlin and Westfall, 1985; Havlin et al., 1985). Mengel (1985) has extensively reviewed the literature on plant uptake of nonexchangeable K, which indicates that many plants feed from this source of K, particularly monocots. Potassium release from speci-

men and soil feldspars has been studied by several workers (Huang et al., 1968; Berner and Holdren, 1979; Song and Huang, 1983). However, the weathering of feldspars and particularly the kinetics and mechanisms of K release from them is not well understood (Wollast, 1967; Berner, 1983) and needs further study.

In the past it was thought that only small amounts of K from feldspars and micas were released to plants over a growing season (Rasmussen, 1972). However, recently a number of reports have appeared in the scientific literature showing a remarkable lack of response by crops such as corn (*Zea mays* L.) to K applications on sandy soils of the Atlantic Coastal Plain Region (Liebhardt et al., 1976; Sparks et al., 1980a; Woodruff and Parks, 1980; Hendricks et al., 1985) and on sandy soils in Nebraska (Rehm and Sorensen, 1985). This lack of crop response is somewhat anomalous since these sandy soils often have low levels of water-soluble, exchangeable, and HNO₃-extractable K; thus one would expect yield responses to applied K. Additionally, the lack of crop response on Middle Atlantic Coastal Plain soils does not appear to be related to accumulations of K in subsoils that might be available for plant uptake. However, these sandy soils often contain copious quantities of K-feldspars. It has been hypothesized by several researchers (Rehm and Sorensen, 1985) that the lack of crop response on these soils may be attributed to K release from nonexchangeable soil K, particularly from K-feldspars.

Unfortunately, few reports have appeared in the literature on K release from sandy soils or on the role that the sand fractions, which often contain K-feldspars, play in the overall K supplying power of soils. Accordingly, the objectives of this study are to investigate the kinetics and mechanisms of nonexchangeable K release from sandy soils that have shown a lack of crop response to applied K, and to elucidate the mechanisms of K release from feldspars in these soils.

MATERIALS AND METHODS

The soils employed in this study were sampled from field experiments conducted by Parker et al. (unpublished data). The experiments were begun in 1982 on a Kenansville loamy sand (loamy, siliceous, thermic Arenic Hapludults), a Rumford loamy sand (coarse-loamy, siliceous, thermic Typic Hapludults), and a Sassafras fine sandy loam (fine-loamy, mixed, mesic Typic Hapludults) from Delaware. These are major soil types in Delaware and in the Middle Atlantic Coastal Plain Region.

Selected horizons from each of the soils were sampled, air-dried, and crushed to pass a 2-mm sieve in preparation for laboratory analyses. Some basic properties of the soils are reported in Table 1. Soil pH was measured on a 1:1 soil/water mixture using a glass electrode; cation exchange capacity (CEC) was determined by summation of exchangeable K, Ca, Mg, and Al using methods outlined by Rhoades (1982) and Barnhisel and Bertsch (1982); organic matter content was determined by wet oxidation with K₂Cr₂O₇ (Nelson and Sommers, 1982); and particle size distribution was determined by the pipet method (Gee and Bauder, 1986). The pH of the soils ranged from slightly acidic to neutral.

The soils contained high sand and low organic matter contents and had low CEC, which is typical for most Atlantic Coastal Plain soils (Sparks, 1980). The mineral suite of their <2-μm clay fraction, as determined by x-ray diffraction and differential scanning calorimetry analyses, was dominated by kaolinite and chloritized vermiculite.

Potassium Status of Soils

The K status of each soil horizon was determined. Exchangeable K was extracted using 0.5 M CaCl$_2$, boiling 1.0 M HNO$_3$ was used to give an index of nonexchangeable K (Knudsen et al., 1982), and total K was determined for the soils and sand fractions with HF digestion (Bernas, 1968; Buckley and Cranston, 1971). Potassium in each of the extracts was measured using a Perkin-Elmer 5000 atomic absorption spectrophotometer. Mineral K levels were estimated by subtracting the sum of CaCl$_2$-extractable and HNO$_3$-extractable K from total K. Although not shown, H$_2$O-soluble K was determined and found to be negligible. The soils were pretreated with NaOCl to remove organic matter (Anderson, 1963) and Na-citrate-dithionite-bicarbonate to remove oxide coatings (Mehra and Jackson, 1960). The sand fractions of the soils were then separated by wet sieving, and the K-feldspars were determined using a Zeiss petrographic microscope with attached 35-mm camera. The sand grains were prepared for optical study by mounting on glass slides in media of known refractive index.

Kinetics of K Release from Soils and Sand Fractions

The kinetics of K release from the three soils and from the coarse (0.50-1.00 mm), medium (0.25-0.50 mm), and fine (0.10-0.25 mm) sand fractions of the Kenansville loamy sand were investigated using a H-saturated resin and oxalic acid. A number of investigators have used H-saturated exchange resins to measure K release from soils (see, e.g., Martin and Sparks, 1985). These resins serve as a sink for released K, which prevents solution K from increasing to levels where further K release is inhibited (Rausell-Colom et al., 1965). Additionally, it has been shown that H-saturated resins do not effect decomposition of soil minerals (Martin and Sparks, 1985) and their pH can resemble the environment around plant roots (see, e.g., Blanchar and Lipton, 1986). Oxalic acid was chosen as an organic acid to also study K release rates. Soils contain numerous organic acids and they facilitate the weathering of minerals and rocks through formation of metal–organic complexes (Stevenson, 1982). Moreover, organic acids have been detected in the rhizosphere of several tree species (Spakhov and Sparkhova, 1970) and, thus, they may well affect weathering of nonexchangeable soil K.

Before initiating kinetic studies, the soil and sand samples were Ca-saturated with 0.5 M CaCl$_2$ to remove any native exchangeable K. The samples were then washed with deionized water until a negative test for Cl$^-$ was obtained with 0.1 M AgNO$_3$. Duplicate 2-g samples of Ca-saturated soil or sand were added to 80-mL polypropylene centrifuge tubes with 4 g of moist Bio-Rad AG50 WX H-saturated resin (Bio Rad Lab., Richmond, CA) and 50 mL of 0.001 M HCl. The resin had a CEC of 54.1 mol$_c$(H$^+$) kg^{-1} and a 20 to 50 mesh size. Homoionic H-resin was prepared by leaching the resin with 1.0 M HCl solution and washing out excess salt with deionized water. The samples were equilibrated at 298 K for 10 min to 30 d on a reciprocating shaker placed in a temperature controlled chamber. Thirty days was chosen as the time when an apparent equilibrium in nonexchangeable K release was obtained from the soils and sand fractions. To reduce weathering and abrading of the soils and sand fractions, the shaker was turned off every other hour during the equilibration period. After equilibration, the soil or sand fractions were separated from the resin by sieving and the

Table 1. Basic chemical and physical properties of soils studied.

| Horizon | Depth | pH | CEC | Organic matter | Particle size analyses | | |
					Sand	Silt	Clay
	cm		cmol kg^{-1}	g kg^{-1}		%	
Kenansville loamy sand							
Ap	0–23	6.8	3.6	13.0	83.9	14.7	1.4
E	23–58	7.0	2.0	1.7	77.9	19.5	2.6
Bt2	85–118	7.0	4.0	0.4	77.3	12.1	10.6
C	≥140	7.1	2.0	--	89.5	8.2	2.3
Rumford loamy sand							
Ap	0–25	5.3	1.7	10.0	80.6	16.0	3.4
BC	89–109	6.4	2.2	1.0	66.0	24.9	9.1
Sassafras fine loamy sand							
Ap	0–20	6.0	2.4	20.	65.5	25.3	9.2
C1	84–99	5.2	2.3	<1.	76.6	7.6	15.8

resin was leached with 80 mL of 1 M NH$_4$Cl to remove the released K. Ten milliliters, of 1500 μg LiCl mL^{-1} was added to suppress ionization and the leachate was then brought to a 100-mL volume and analyzed for K using atomic absorption spectrophotometry.

The rate of nonexchangeable K release from the soil and sand samples was also determined using an organic acid, 0.01 M oxalic acid. The samples were equilibrated at 298 K using the same experimental conditions as used in the H-resin studies. After equilibration, the samples were centrifuged at 1118 × g for 10 min and a 10-mL aliquot was taken and analyzed for K as before.

Electron Microbeam Analyses of Soil K-feldspars

A number of feldspar grains were handpicked from the coarse sand fraction of the soils and these were analyzed before and after a 30-d equilibration with H-saturated resin using electron probe x-ray microanalysis. The soil feldspar grains were washed only with deionized water prior to examination with the electron probe. Electron probe x-ray microanalysis was done using a Camera MBX Electron Microprobe equipped with a Trecor Northern TN2000 EDAX and an Ortec Si(Li), Silly, detector. Electron micrographs of feldspar grains were used to assess the effects of the H-saturated resin on the surface of the grains. Additionally, thin sections of grains were made and secondary electron image maps were made to observe the distribution of K, Al, and Si from the core to the rim of the individual grains. These analyses were performed to assist in elucidating the mechanisms of K release from the soils and to assess the importance of the K-feldspars in releasing K that could be available for plant uptake.

RESULTS AND DISCUSSION

Potassium Status of Soils

All three of the soils contained high amounts of total K (Table 2). The bulk of the total K was in the mineral form, with only low levels of CaCl$_2$-extractable and HNO$_3$-extractable K present. This composition is typical for many of Delaware's sandy soils. The rather low amounts of exchangeable and HNO$_3$-extractable K might suggest that some crops might respond to applied K; however, as noted earlier, researchers have seen a lack of crop response to K fertilization on many Atlantic Coastal Plain soils.

A large amount of the total K is contained in the sand fractions of the soils. Taking into account the percentage of sand in each horizon (Table 1), the data in column 7 of Table 2 represent the amount of total K in the sand fractions based on a whole soil basis.

Table 2. Potassium status of soils and sand fractions.

| Horizon | Depth | Soils | | | | Sand fractions | |
		CaCl₂ ext.	HNO₃ ext.	Mineral K†	Total K‡	Total K	K-feld-spars§
	cm			cmol kg⁻¹			fre-quency %
			Kenansville loamy sand				
Ap	0-23	0.25	0.42	35.02	35.69	30.88	9.5
Bt2	85-118	0.25	0.49	45.30	46.04	33.86	12.0
			Rumford loamy sand				
Ap	0-25	0.33	0.49	21.67	22.51	18.62	6.7
BC	89-109	0.21	0.54	23.39	23.96	16.76	8.2
			Sassafras fine loamy sand				
Ap	0-20	0.35	0.56	43.54	44.45	28.95	16.0
C1	84-99	0.13	0.36	45.99	46.68	36.69	24.0

† Mineral K = [(total K) − (CaCl₂ ext. K + HNO₃ ext. K)].
‡ These data represent the amount of total K in the sand based on a whole soil basis.
§ Determined through petrographic analyses of the whole sand fractions and represents the percentage of total point counts in a given sample that were K-feldspars. The remaining minerals in the sand fractions were quartz, plagioclase, and opaques.

In the Kenansville loamy sand, for example, 87 and 74% of the total soil K in the Ap and Bt2 horizons, respectively, are contained in the sand fractions. This is also true for the Rumford soil (Table 2), which is very sandy (Table 1). In the Sassafras soil, which contains more clay, 65 and 79% of total soil K in the Ap and C1 horizons, respectively, are found in the sand fractions.

Most of the total K in the sand fractions can be directly attributed to the high frequency per cent of K-feldspars present (Table 2). Most of the mineral K in these soils is feldspars, and from electron micro-beam analyses, which will be discussed later, they appear to be highly weathered. The K-status data point out the sizable reservoir of K in the sand fractions of the soils.

Kinetics of K Release from Soils and Sand Fractions

Over a 30-d period, quantities of K ranging from 0.172 to 0.251 cmol kg⁻¹ were released from the soils using H-resin and 5.64×10^{-4} to 2.97×10^{-3} cmol kg⁻¹ were released using oxalic acid (Table 3, Fig. 1). Initially, K was released rapidly and then began to level off as an equilibrium was approached. More K was released in the subsoil horizons than in the Ap horizons of each soil, attributable to the higher clay

Table 3. Potassium release from soils using a H-resin and oxalic acid.†

Horizon	Depth	H-resin	Oxalic acid
	cm		cmol kg⁻¹
		Kenansville loamy sand	
Ap	0-23	0.199	1.97×10^{-3}
Bt2	89-118	0.251	2.97×10^{-3}
		Runford loamy sand	
Ap	0-25	0.172	1.41×10^{-3}
BC	89-109	0.231	1.97×10^{-3}
		Sassafras fine loamy sand	
Ap	0-20	0.235	5.64×10^{-4}
C1	84-99	0.246	1.69×10^{-3}

† These values represent amounts of K released at 30 d.

contents in the former, which are high in vermiculitic minerals.

The level of solution K markedly affects the release of nonexchangeable K from clays and soils (Martin and Sparks, 1983). The K concentration in the solution phase must be kept very low or K release will be inhibited (Rausell-Colom et al., 1965; Fanning and Keramidas, 1977). The concentration of soluble K in the soil-resin suspensions of this study ranged from 1.00 to 1.50×10^{-3} mmol L⁻¹. Feigenbaum et al. (1981) noted that concentrations of solution K up to 1.0 mmol L⁻¹ would not retard K release from trioctahedral micas, whereas concentrations >0.10 mmol L⁻¹ inhibited K release from muscovite. Thus, in this study, K release should not have been inhibited during extraction with the H-saturated resin.

Much smaller quantities of K were released from the soils using oxalic acid than with H-resin (Table 3). Potassium release may have been inhibited using oxalic acid. With the H-resin, a sink was provided for the released K, thus further release could occur. No such sink was present with the oxalic acid.

Potassium release from the coarse, medium, and fine sand fractions of the Kenansville soil to the H-resin is shown in Table 4 and Fig. 2; the fine fraction released the most K. This is important because the fine fraction comprises the bulk of the sand in these soils. If one averages the quantity of K released from the three sand fractions, multiplies by the percentage of sand in each soil horizon, and then divides this quantity by the total K released from the whole soil, some interesting data are obtained. One finds, for example, that in the Kenansville Ap and B2t horizons, 68 and 63%, respectively, of the total K released are coming from the sand fractions. These data again point to the immense importance of the sand fractions in the overall K balance and K-supplying power of these soils.

Mechanisms of K Release from Soils and Feldspars of Sand Fractions

Although the calculations are not shown, a number of simple kinetic models including zero- and first-order equations (Sparks, 1985, 1986) were applied to the K release data. All these equations described the data rather well, and it was difficult to conclude whether a simple zero- or first-order equation best described the
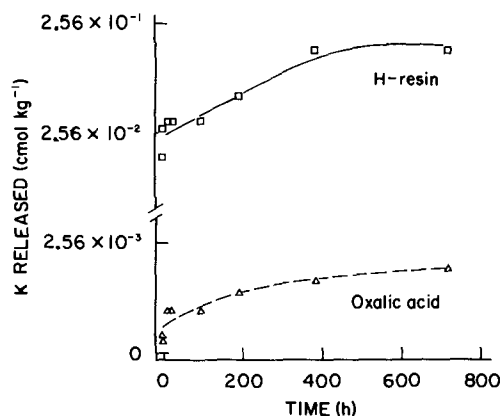

Fig. 1. Kinetics of nonexchangeable K release from the Ap horizon of a Kenansville loamy sand using H-resin and oxalic acid.

K release data from the soils. However, overall K release from the sand fractions was best described by the zero-order equation.

The first-order equation has successfully described K exchange kinetics (Jardine and Sparks, 1984; Ogwada and Sparks, 1986b) and zero-order kinetics was found to describe nonexchangeable K release (Mortland and Ellis, 1959). Recently, Havlin and Westfall (1985) and Havlin et al. (1985) found that a power function equation best explained K release rates from Nebraska soils; however, their study involved reactions occurring over a 7000-h period.

Yet, as Sparks (1987) has recently pointed out, conformity of rate data to a certain kinetic model does not yield mechanistic information, nor can one definitely conclude that it is the best model. Perhaps the best way to glean mechanistic information about K release from minerals and soils is to study their surface chemistries in conjunction with rate experiments using spectroscopic techniques (Sparks, 1987). This was done in the present study by using electron microbeam analyses.

Figure 3 is a scanning electron micrograph (SEM) of a feldspar grain before treatment with H-resin. The "fuzzy" areas in the center and the upper right of the photograph are secondary precipitates of hydroxy-Al and Al-silicate material. This occurs on the surface of the grain, which acts as a site for nucleation. Petrović (1976) suggests that this material has a very low density and ion diffusion rates through it are within one order of magnitude of diffusion rates in water. The light patches within this probably amorphous mass may be crystals of kaolinite forming.

The remainder of the surface of the grain (Fig. 3) is a K-feldspar. The surface features are very similar to those described by Holdren and Berner (1979) and Berner (1983). First, one sees small submicron to micron linear or curvilinear cracks forming on the flat surfaces, best exhibited in the right center of the micrograph. One can also see a widening of the cracks and the formation of oval-shaped etch pits. These are often obscured by large prismatic etch pits (upper-right corner of SEM). This is the most important stage of weathering as chemical weathering may lead to enhanced mechanical weathering by the abrasion and subsequent removal or "plucking" of loose pieces of the surface. The etch pits may align along structural and crystallographic axes forming saw-tooth patterns (lower-right corner of SEM). Finally, the coalescence of the prismatic etch pits produces an angular, highly irregular surface. The SEM photographs clearly show the highly weathered nature of the feldspars in these soils, which could be sources for K release to plants.
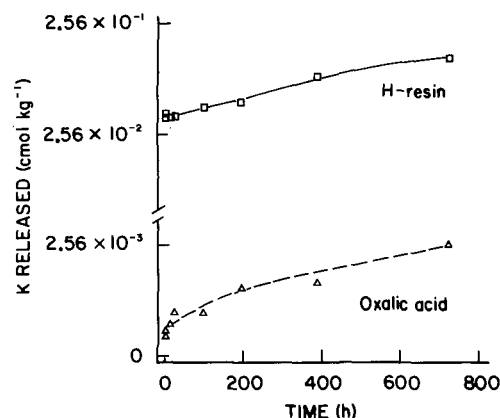

Fig. 2. Kinetics of nonexchangeable K release from the fine sand fraction (0.10–0.25 mm) of the Ap horizon of a Kenansville loamy sand using H-resin and oxalic acid.

A SEM of the feldspar particles after the 30-d treatment with the H-resin is shown in Fig. 4. This micrograph shows the same weathering patterns and etch pits as found and described above. One will note the general absence of the fuzzy precipitate, which was found in the feldspar grain not reacted with H-resin (Fig. 3). This is likely a result of the agitation of the grains that would inhibit nucleation of the precipitate on the feldspar grains. However, one can see (Fig. 4) that the extent and depth of weathering, as exhibited by the etch pits, are much more drastic after weathering with H-resin than before (Fig. 3).

Two theories have been advanced to explain the dynamics of feldspar weathering. Results from studies on specimen feldspar weathering (Lagache, 1976; Petrović, 1976; Holdren and Berner, 1979) suggest that during dissolution the rate-limiting step is a surface-controlled reaction resulting in a constant rate of dissolution. On the other hand, some workers (Wollast, 1967; Busenberg and Clemency, 1976) suggest that weathering of feldspars proceeds incongruently, with the consequent formation of a residual protective layer of altered composition on the surface of the mineral. As a result, so-called parabolic kinetics are found whereby the rate of dissolution decreases with time due to the growth in thickness of such surface layers (Schott and Berner, 1985; Wollast and Chou, 1985).

The data collected in this study suggest that the surface-controlled kinetics mechanism is operable for soil feldspar weathering. The presence of etch pits on the weathered feldspar grains would suggest a surface-controlled reaction (Berner, 1983). The etch pits indicate selective attack of the feldspar surface by soil acids (Fig. 3), which is enhanced by weathering (Fig. 4).

Table 4. Potassium release from sand fractions of a Kenansville loamy sand using H-resin and oxalic acid.

Soil horizon	Depth	K released from sand fractions[†]					
		Coarse (0.50–1.00 mm)		Medium (0.25–0.50 mm)		Fine (0.10–0.25 mm)	
		H-resin	Oxalic acid	H-resin	Oxalic acid	H-resin	Oxalic acid
	cm	cmol kg⁻¹					
A	0–23	0.137	1.28×10^{-3}	0.167	1.85×10^{-3}	0.183	2.69×10^{-3}
E	23–58	0.137	1.41×10^{-3}	0.149	1.85×10^{-3}	0.224	2.54×10^{-3}
Bt2	85–118	0.195	2.72×10^{-3}	0.178	2.69×10^{-3}	0.255	2.82×10^{-3}
C	≥140	0.224	3.26×10^{-3}	0.227	3.26×10^{-3}	0.255	4.51×10^{-3}

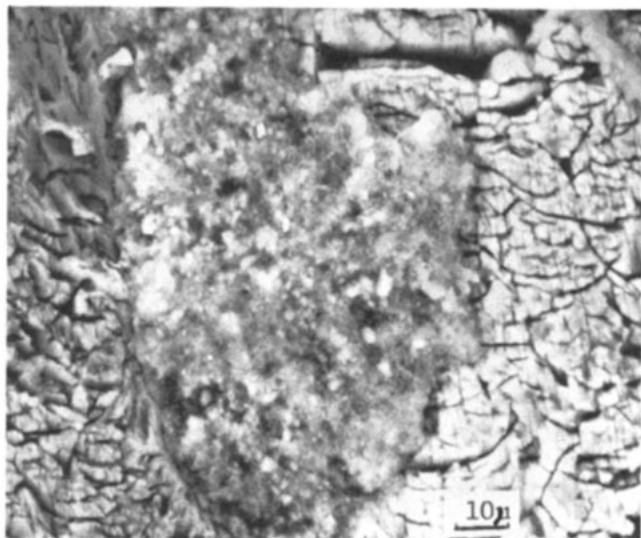† These values represent amounts of K released at 30 d.

Fig. 3. Scanning electron micrograph of a Kenansville soil feldspar before treatment with H-resin.
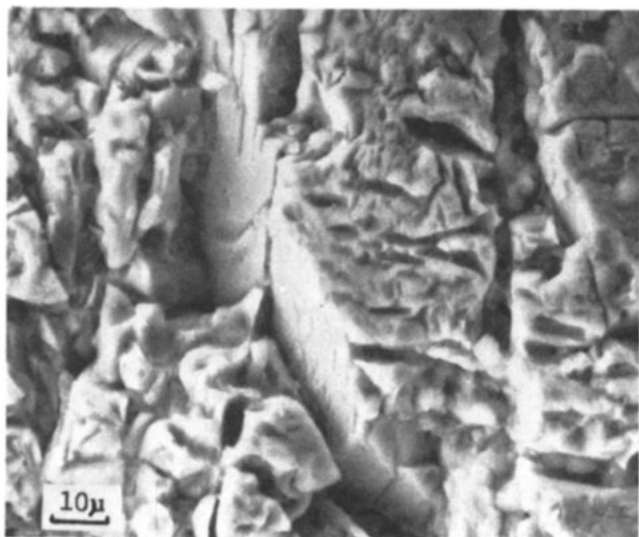

Fig. 4. Scanning electron micrograph of a Kenansville soil feldspar after 30-d treatment with H-resin.
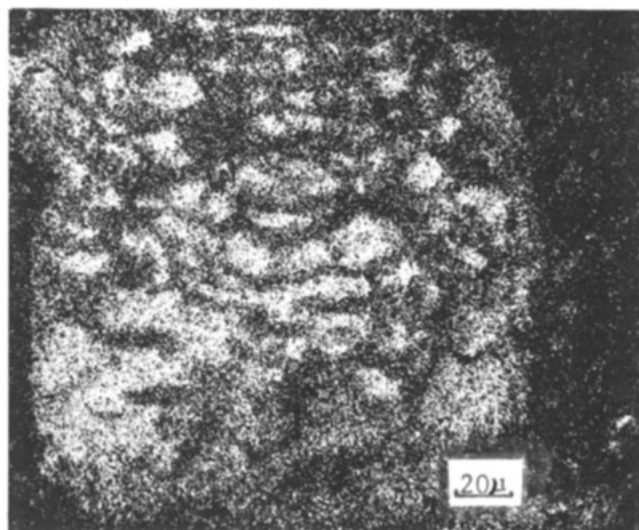

Fig. 5. Electron beam scanning image of $K_{K\alpha}$ from a thin section of a Kenansville soil feldspar.

Figure 5 shows the $K_{K\alpha}$ secondary electron image for a feldspar grain from the Kenansville soil and would also support a surface-controlled mechanism for K release from soil feldspars. The grain was cut and polished so that one could see a cross section of the grain from core to rim. Much of the grain in Fig. 5 has been leached of K as shown by the darker areas. This is a cross section of a feldspar grain, however, and not a surface that has been exposed to weathering. The leaching of K from the internal part of the feldspar grain we studied would seem to exclude the hypothesis of K-feldspar weathering as first promoted by Wollast (1967). This suggests that a tightly bound aluminosilicate rind forms uniformly about the grain and limits further weathering to a strongly diffusion-controlled reaction whereby further leaching of K must proceed by ionic diffusion through this aluminosilicate layer. The pattern exhibited in the $K_{K\alpha}$ secondary electron image (Fig. 5) for the K-feldspars in this study is similar to the fragile honeycomb-like shell described by Berner and Holdren (1979), who concluded that the mechanism for K-feldspar weathering was surface controlled.

An additional piece of evidence that would suggest a surface-controlled rate of K release from the soil K-feldspars in this study is the linear rate of K release from the sand fractions with H-resin (Fig. 2). If parabolic kinetics were occuring, nonlinear plots would have been observed (Berner, 1983).

CONCLUSIONS

The sandy soils examined in this study exhibit a remarkable ability to release K. Much of this release occurs from the sand fractions, which are high in K-feldspars. The feldspars, as examined by electron microbeam techniques, are very weathered and exhibit pronounced etch pits. The mechanism of K release from the K-feldspars appears to proceed via a surface-controlled mechanism. The lack of crop response that has been observed on these soils following K applications can be explained by the large amounts of K that are being released from the sand fractions, which are very weathered. These data vividly demonstrate the importance of sands in supplying K to plants grown on Atlantic Coastal Plain soils.

ACKNOWLEDGMENT

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