CESIUM SORPTION TO ILLITE AS AFFECTED BY OXALATE

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Abstract—Cesium uptake by plants depends on adsorption/desorption reactions in the soil, as well as root uptake processes controlled by the plant. In this study, sorption and desorption of Cs^+ on reference illite (IMt-1) was investigated in the presence of oxalate to gain understanding of mechanisms by which plant root exudates may influence Cs^+ bioavailability in micaceous soils. Cesium sorption on illite decreased significantly as oxalate concentration increased from 0.4 to 2 mM. Cesium desorption from illite increased significantly with increasing oxalate concentration. Desorption of Cs^+ by exchange with Na^+, Ca^{2+} and Mg^{2+} was significantly enhanced in the presence of oxalate as selectivity for Cs^+ decreased with respect to these ions in the presence of oxalate. On the other hand, oxalate had little effect on the Cs^+/K^+ selectivity coefficient. This suggests that oxalate treatments increase the relative proportion of exchange sites that are not highly selective for Cs^+ and K^+; *e.g.* 'planar' sites. The results indicate that oxalate plays an important role in Cs^+ binding on illite and, therefore, plant rhizosphere chemistry is likely to alter Cs^+ bioavailability in micaceous soils.

Key Words—Frayed-edge Sites, Phytoremediation, Rhizosphere, Weathering.

INTRODUCTION

Phytoremediation has been suggested as a cost-effective strategy for the removal of radionuclide and heavy-metal contamination on large tracts of land (Raskin and Ensley, 2000). In phytoextraction, contaminants are taken up by plant roots and accumulated in the above-ground portion of a plant followed by harvest and disposal of plant biomass. Phytoextraction can be applied to metal, radionuclide, metalloid, and non-metal contaminants that are not further degraded or transformed within the plant. One contaminant that is amenable to phytoextraction is cesium-137 ($^{137}Cs^+$), a radionuclide commonly found in shallow soil systems contaminated as a result of nuclear weapons testing, nuclear reactor accidents, and past waste-disposal practices at nuclear facilities.

Cesium contributes a major portion of the radio-activity at many sites associated with nuclear weapons production (Riley *et al.*, 1992), and as such is a key contaminant to be considered in ecosystem restoration strategies. Phytoextraction may be particularly suitable for Cs^+-contaminated soils because Cs^+ and the plant nutrient K^+ ions have similar ionic potentials and exhibit many similarities with respect to their behavior in plants (Gommers *et al.*, 2000; White and Broadley, 2000).

Cesium uptake by plants depends on adsorption/desorption and fixation/release reactions in the soil as well as root uptake processes controlled by the plant. The aqueous chemistry of Cs^+ in the environment is controlled by sorption reactions to mineral phases, particularly micaceous clay minerals (Francis and Brinkley, 1976). Phyllosilicate minerals comprise the bulk of the reactive solid phase in low-organic matter temperate soils. Interactions between Cs^+ and phyllosilicate mineral surfaces are relatively strong due to the formation of inner-sphere complexes, electrostatic interactions in which there are no intervening water molecules. Cesium bound to external planar surface sites can generally be exchanged by other cations, whereas that bound in interlayer sites or at frayed edges of an interlayer is more strongly sorbed and difficult to remove via ion exchange (Comans *et al.*, 1991).

Minerals in which interlayer sites are available for cation sorption have high cation exchange capacity (CEC) and high total uptake of Cs^+. The availability of interlayer sites for cation exchange depends on inter-layer spacing, which is influenced by the degree of hydration of the ions present in the interlayer. Cations with low hydration energy such as K^+, Rb^+, Cs^+ and NH_4^+ can shed their hydration shell in clay interlayers. Dehydration of these ions permits a close approach to the tetrahedral silicate sheets and formation of polar bonds with structural oxygen atoms. Cesium bound to dehydrated ('collapsed') interlayer sites is not readily exchanged by other cations and is usually considered 'fixed' (Comans *et al.*, 1991).

A strong surface association between Cs^+ and the soil solid phase occurs at frayed-edge sites (FES) of micaceous phyllosilicate minerals. Poorly hydrated alkali metal ions are selectively sorbed to FES when they dehydrate and cause partial collapse of the layers near the phyllosilicate edge. Frayed-edge sites form during mineral weathering when K^+ ions are replaced by hydrated cations such as Ca^{2+} and Na^+ through mass

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action. The hydration energy of an ion is the primary determinant of its affinity for the highly selective adsorption sites on the frayed edges of micaceous minerals. The FES of illite have a particularly high affinity for Cs^+ ions as compared to edge-interlayer sites of K^+-saturated vermiculite or montmorillonite (Sawhney, 1970; Staunton and Roubaud, 1997).

Cesium sorption to soil minerals depends upon the concentration of Cs^+ in solution, the nature of the mineral surface, and the ionic strength, pH, temperature, and presence of competing ions in the solution phase (Cornell, 1993; Staunton and Roubaud, 1997). Cations with similar size and hydration energy can effectively compete with Cs^+ for binding sites on soil minerals. Both K^+ and NH_4^+ have been shown to replace Cs^+ on planar exchange sites and FES in phyllosilicate minerals (Comans *et al.*, 1991; Negri and Hinchman, 2000).

The biogeochemical processes occurring in the rhizosphere can affect the chemical reactions between contaminants and soil minerals. Release of organic substances from plant roots and the subsequent increase in microbial activity make the soil rhizosphere distinctly different from bulk soil, and organic acids such as those exuded by plant roots are significant components of mineral weathering processes in the soil environment (Bottomley, 1999; McBride, 1994). Numerous studies have provided evidence that the geochemistry of the soil environment influences Cs^+ binding, solubilization, mobility, and biological availability (Kruyts and Delvaux, 2002; Staunton *et al.*, 2002; Dumat *et al.*, 2000; Dumat and Staunton, 1999; Guivarch *et al.*, 1999; Shaban and Mikulaj, 1996). Plant-root exudates may enhance Cs^+ bioavailability by accelerating weathering at frayed edges of phyllosilicate minerals and releasing Cs^+ sorbed to frayed edge and interlayer sites, making the ion available for plant uptake. Alternatively, accelerated weathering may increase the quantity of FES and enhance Cs^+ binding to micaceous clays. The objective of this study was to examine Cs^+ sorption to, and desorption from, illite in the presence of oxalate to simulate plant root exudates.

MATERIALS AND METHODS

Recent surveys at the Idaho National Engineering and Environmental Laboratory (INEEL) in southeastern Idaho have shown $^{137}Cs^+$ levels in the top 30 cm of soil ranging from non-detectable to >100 pCi g^{-1} (Hamilton *et al.*, unpublished data). We chose crested wheatgrass (*Agropyron desertorum*) as the model plant species after field surveys of $^{137}Cs^+$ levels showed that >90% of the $^{137}Cs^+$ accumulation in above-ground biomass was associated with this species (Hamilton *et al.*, unpublished data). Laboratory investigations indicated that ~0.04 mM oxalate would adequately represent crested wheatgrass root exudates in the INEEL system (B. Bugbee, pers. comm., 2002).

The IMt-1 illite clay (Cambrian shale, Silver Hill, Montana) from The Source Clays Repository (Purdue University, Indiana) was selected as a surrogate for soil illite, the major clay mineral from the INEEL soil. The characterization of the clay was reported by Hower and Mowatt (1966). The 0.2–2 μm size fraction was isolated by gravity sedimentation and centrifugation after treating with $NaC_2H_3O_2$ at pH ~5 to remove carbonates. The illite was subsequently treated with KCl to saturate exchange sites with K^+ and washed several times with deionized water to remove excess salts. The K^+-saturated IMt-1 was oven dried to a constant mass at 60ºC and stored in an air-tight container prior to use.

Cs^+ sorption to illite

We measured Cs^+ sorption to IMt-1 both as a function of solution pH and Cs^+ and Na^+ concentration. The pH was varied from 6 to 10 in a 15 mM NaCl/0.00075 mM CsCl/20 mg L^{-1} illite suspension and pH was maintained with HCl and NaOH as needed. We added HCl or NaOH dropwise to maintain constant pH throughout the experiments. In this and all subsequent experiments, samples were passed through a 0.2 μm filter and analyzed for Cs^+ using ion chromatography (IC) or flame emission spectrometry. Cesium sorption was also determined as a function of pH at Cs^+ concentrations of 0.00075, 0.0015 or 0.003 mM. Finally, Cs^+ sorption at pH 8.0 was determined at NaCl concentrations of 15, 30, 45, 60 and 75 mM and with initial Cs^+ concentration of 0.04 mM. The pH experiments at low Cs^+ concentration were performed in 500 mL water-jacketed stir flasks maintained at 20ºC for 384 h and all others in 15 mL plastic centrifuge tubes using an end-over-end shaker for 96 h. We used 20 mg L^{-1} illite throughout.

We examined the effect of oxalate on Cs^+ sorption to IMt-1 at initial Cs^+ concentrations of 0.00075 and 0.0075 mM by preparing suspensions of illite in 0.08 mM NaCl and 0.04 mM $Na_2C_2O_4$. We also suspended illite in $Na_2C_2O_4$ solutions ranging in concentration from 0.000015 to 2 mM in which the Na^+ concentration was maintained at 4 mM with NaCl. These solutions were adjusted to pH 8 and had initial Cs^+ concentrations of 0.0075 mM.

Cs^+ desorption from illite

For these experiments, 0.2–2 μm IMt-1 was saturated with Cs^+ via treatment with CsCl. Illite was washed several times with deionized water to remove excess salts and supernatant solutions were analyzed for Cs^+ using flame emission spectrometry.

Cesium desorption from illite was determined in suspensions of Cs^+-saturated IMt-1 at oxalate concentrations from 0.000015 to 2 mM in a 4 mM total Na background. Samples were mixed on a reciprocal shaker for 168 h.

Exchange experiments were carried out with oxalate and chloride solutions of Na^+, K^+, Ca^{2+} and Mg^{2+} in

suspensions of Cs^+-saturated IMt-1. Solutions contained 0.04 mM Na, K, Ca, or Mg oxalate and were adjusted to 1 mM (K^+ and Na^+) or 0.5 mM (Ca^{2+} and Mg^{2+}) using the chloride ion of the cation present. All solutions were adjusted to pH 8 using the hydroxide salt of the cation present. Vanselow conditional exchange coefficients ($^cK_{ex}$) were calculated from the binary cation exchange reactions (Sposito, 1994). Concentrations of cations on the exchange sites were determined by difference from the initial and final solution concentrations. Activities of ions in solution were determined using the Davies equation (Sposito, 1994).

Measurement of frayed-edge site density

We estimated FES densities and Vanselow Cs^+/K^+ selectivity coefficients (K_c) on IMt-1 both prior to and after treatment with 0.04 mM oxalate using a modification of the method developed by Wauters *et al.* (1996). Illite was pre-treated with 100 mM $CaCl_2$/0.5 mM KCl mixed solution, then equilibrated with 100 mM $CaCl_2$/0.5 mM KCl/0.05 mM CsCl mixed solution. The clay was then equilibrated with 100 mM $CaCl_2$ followed by extraction with 1 M NH_4Cl. Frayed-edge sites were operationally defined as the sum of Cs^+ and K^+ extracted from the clay by NH_4Cl. Samples were analyzed using inductively-coupled plasma spectrophotometry-mass spectrometry (ICP-MS) and ICP-atomic emission spectrometry (AES).

Results of single-factor analysis of variance (ANOVA) and paired t-test statistical analyses were obtained using Statistix 7.1$^©$ for Windows (Analytical Software, Tallahassee, FL).

RESULTS AND DISCUSSION

Cs^+ sorption to illite

Figure 1 illustrates the relationship between solution pH and Cs^+ sorption to IMt-1. Solution pH had a significant effect on the extent of Cs^+ sorption to IMt-1, but no apparent effect on the time required for Cs^+ to reach equilibrium concentration on the illite. The most rapid sorption occurred within the first 24 h, followed by slower Cs^+ uptake that reached a maximum between 24 and 96 h (Figure 1). The results for the investigation of the effect of solution pH on Cs^+ sorption to IMt-1 are given in Figure 2. After 96 h, Cs^+ sorption to IMt-1 increased with increasing pH at all initial Cs^+ concentrations.

Previous studies have demonstrated that Cs^+ sorption to illite is characterized by initially rapid uptake followed by slower sorption processes, and is significantly affected by the nature of the competing cations in solution (Sawhney, 1966; Comans *et al.*, 1991; Comans and Hockley, 1992). Comans *et al.* (1991) suggest that the initial rapid Cs^+ sorption occurs on highly selective FES, followed by slow diffusion of Cs^+ into energetically favorable interlayer sites. The rate of Cs^+ movement into the clay interlayer is dependent on the competing cations and the fraction of sorbed Cs^+ occupying interlayer sites is practically non-exchangeable (Comans *et al.*, 1991; Comans and Hockley, 1992). The increase in sorption with increasing pH is probably due, in part, to increasing deprotonation of aluminol groups on clay edges. An increased attraction of Cs^+ to clay edges could have a positive effect on Cs^+ interaction with FES, which also occur at edges. Under alkaline conditions, silanol groups at the edges of tetrahedral sheets carry a net negative charge due to dissociation of >SiOH to form SiO^-, and under mildly acidic conditions (pH 4 to 6) the majority of surface silanol groups exist as the uncharged >SiOH (Clark and McBride, 1984; Stumm, 1992). Aluminol groups at edges of octahedral sheets in phyllosilicate minerals generally bear a net negative charge under alkaline conditions and a net positive charge under acidic conditions as their PZNPC is ~pH 7.5 (Hsu, 1989; Stumm, 1992).
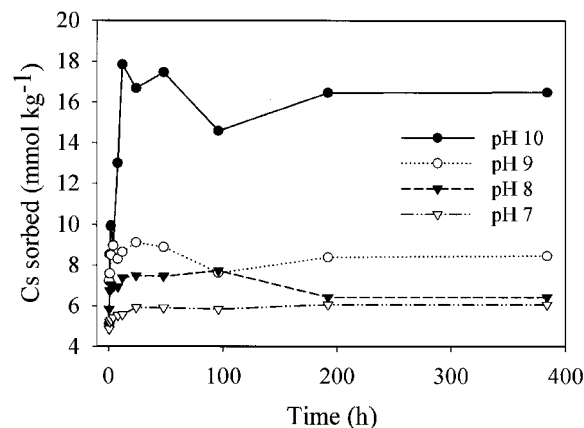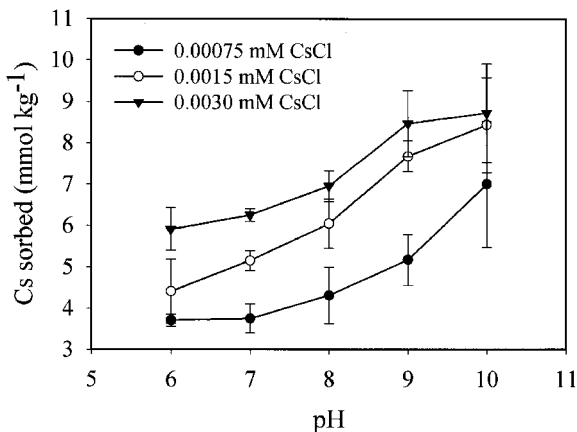

Figure 1. Cesium sorption to IMt-1 at pH 7, 8, 9 and 10 where initial Cs^+ concentration of 0.00075 mM and background NaCl concentration of 15 mM were held constant as pH was varied.

Figure 2. Cesium sorption to IMt-1 (mmol kg^{-1}) at solution pH between 6 and 10, and at initial Cs^+ concentrations of 0.00075, 0.0015 and 0.003 mM CsCl. Background NaCl concentration was 15 mM in all cases.
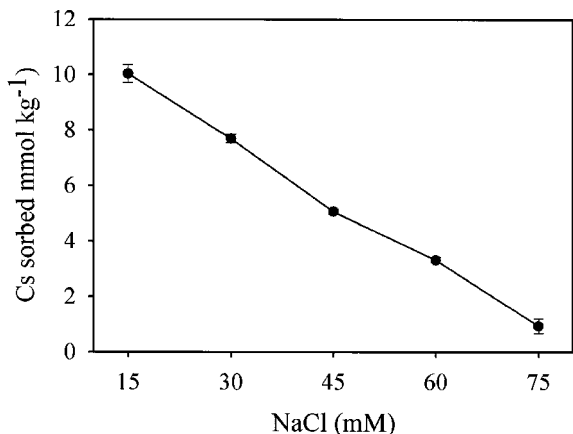
Figure 3. Cesium sorption (mmol kg^{-1}) to IMt-1 at NaCl solution concentrations between 15 and 75 mM. Initial Cs$^+$ concentration of 0.004 mM and solution pH of 8.0 were the same in all cases.

Figure 3 shows Cs$^+$ exchangeability by Na$^+$ on IMt-1. As NaCl concentration increased, Cs$^+$ sorption to illite approached zero, indicating that most of the Cs$^+$ sorbed to IMt-1 was not irreversibly sorbed and was readily exchanged by Na$^+$. When the illite interlayer contains only K$^+$ ions, such as in these experiments, edge sites are largely collapsed and exchange of Cs$^+$ for K$^+$ is difficult; therefore, most of the Cs$^+$ exchanges with ions at non-selective planar sites.

At concentrations of oxalate relevant to the rhizosphere of crested wheatgrass, Cs$^+$ sorption to IMt-1 was significantly greater than in the control as determined by paired t-tests (α = 0.05) (Figure 4). This result is consistent with results of Kruyts and Delvaux (2002) and Guivarch *et al.* (1999) showing enhanced Cs$^+$ sorption to rhizosphere soils as compared to non-rhizosphere soils.

Figure 5 illustrates the effect of oxalate concentration on Cs$^+$ sorption to IMt-1 across a range of oxalate concentrations from 0.000015 to 2 mM. A single factor ANOVA and paired t-tests indicated that Cs$^+$ sorption to IMt-1 was significantly inhibited at 0.4 mM and greater oxalate concentrations (α = 0.05). This observed reduction in Cs$^+$ sorption to illite with increasing oxalate concentration is consistent with observations of reduced Cs$^+$ sorption to minerals in the presence of greater concentrations of organic compounds (Staunton *et al.*, 2002; Dumat *et al.*, 2000; Dumat and Staunton, 1999; Shaban and Mikulaj, 1996). Because humic substances inhibit Cs$^+$ sorption on illite more than on montmorillonite, Dumat and Staunton (1999) concluded that this reduction resulted from a decrease in the affinity of the clay surfaces for Cs$^+$. When regular, or planar, sorption sites of illite were blocked with silver thiourea (AgTU), anionic polysaccharides lowered Cs$^+$ sorption, presumably by hindering the collapse of clay layers (Dumat *et al.*, 2000). This mechanism is less likely with
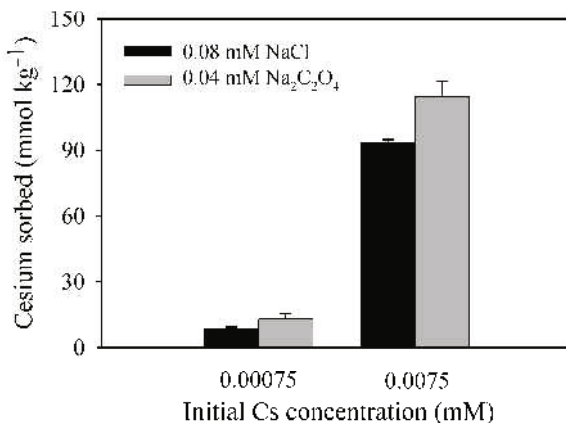

Figure 4. Cesium sorption (mmol kg^{-1}) to IMt-1 at pH 8 in the presence 0.08 mM NaCl and 0.04 mM Na$_2$C$_2$O$_4$ at initial Cs$^+$ concentrations of 0.00075 and 0.0075 mM.

a small molecule like oxalate. A more likely explanation is that oxalate led to significant dissolution of illite as discussed below.

Oxalate is not a strong complexant of Cs$^+$; therefore, we assume that the cause of the decrease in Cs$^+$ sorption to IMt-1 is due to Na$_2$C$_2$O$_4$ reaction with illite. Adsorption of oxalate to the mineral surface could alter surface-charge properties of illite; however, no effect of oxalate concentration on electrophoretic mobility was observed (data not shown), suggesting that oxalate does not impart significant negative charge on the illite surface through surface complexation.

Cs$^+$ desorption from illite

Figure 6 illustrates the effect of oxalate concentration on Cs$^+$ desorption from IMt-1 at pH 8.0 across a range of oxalate concentrations. A single-factor ANOVA and paired t-tests indicated that Cs$^+$ desorption from IMt-1 was significantly enhanced (α = 0.05) at 0.04 mM and
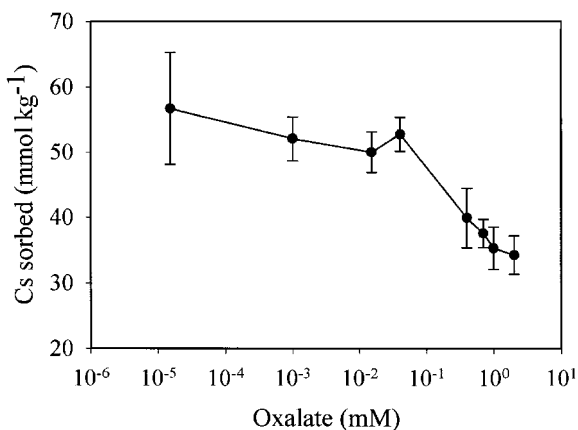

Figure 5. Cesium sorption (mmol kg^{-1}) to IMt-1 at pH 8 in Na$_2$C$_2$O$_4$ solution concentrations between 0.000015 and 2 mM. Initial Cs$^+$ concentration of 0.0075 mM was the same in all cases.

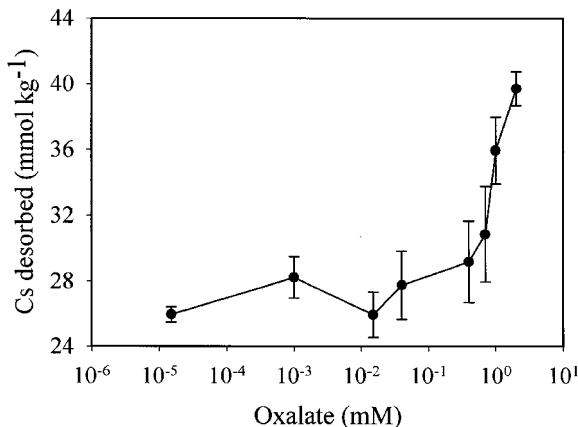Figure 6. Cesium desorption (mmol kg^{-1}) from IMt-1 at pH 8 in Na$_2$C$_2$O$_4$ solutions between 0.000015 and 2 mM. Initial concentration of Cs$^+$ on IMt-1 was ~75 mmol kg^{-1}.

Figure 7. Cesium desorption from IMt-1 at pH 8 in the presence of MgCl$_2$ and MgCl$_2$ + MgC$_2$O$_4$, CaCl$_2$ and CaCl$_2$ + CaC$_2$O$_4$, NaCl and NaCl + Na$_2$C$_2$O$_4$, and KCl and KCl + K$_2$C$_2$O$_4$. Initial concentration of Cs$^+$ on IMt-1 was ~75 mmol kg^{-1}.

greater oxalate concentrations. This is almost certainly due, in part, to dissolution of illite. Molar ratios of oxalate to Al range from 10^{-4} to 13.3; however, an increase in the total number of frayed-edge sites suggests that the surface properties of the illite have changed as well. Thus, the weathering reaction initiated by oxalate is altering the clay's ability to fix Cs$^+$ relative to the original material.

We measured Cs$^+$ desorption from IMt-1 in the presence of Na$^+$, K$^+$, Ca^{2+} and Mg^{2+} solutions with and without oxalate to examine the combined effects of oxalate and competition from the major cations in the INEEL system on Cs$^+$ desorption from illite. For the purposes of comparison, we used 1.0 mM KCl and NaCl and 0.5 mM CaCl$_2$ and MgCl$_2$ in these experiments. A single-factor ANOVA and paired t-tests indicated that Cs$^+$ desorption from IMt-1 in the presence of Mg^{2+}, Ca^{2+} and Na$^+$ was significantly enhanced (α = 0.05) by the addition of oxalate. Figure 7 shows the amount of Cs$^+$ desorbed from IMt-1 for different combinations of cations and oxalate. Of the cations examined, only the K$^+$ system exhibited no significant difference in Cs$^+$ desorption when in combination with oxalate (Figure 7). A significant lowering of the selectivity of Cs$^+$ relative to Na$^+$, Ca^{2+} and Mg^{2+} (Table 1) indicates that weathering has caused a relative increase in low-affinity sites – *i.e.* those that are accessible by hydrated cations.

We initially hypothesized that plant root exudates would affect Cs$^+$ interactions with micaceous minerals in the rhizosphere by accelerating weathering and altering the nature of frayed-edge sites. Measurement of FES on IMt-1 illite prior to and after treatment with oxalate indicated that the simulated root exudates significantly (α = 0.05) increased the quantity of FES on IMt-1 (Table 2). This result is consistent with observations by Boyle *et al.* (1967) that biotite treatment with 0.1 or 0.01 N oxalic acid resulted in a weathering edge that advanced inward with time. Nevertheless, there appears to be an even larger increase in the relative number of non-selective sites, as evidenced by the lowered Cs$^+$ selectivities.

On the other hand, the Vanselow conditional exchange coefficient for Cs$^+$-K$^+$ exchange did not change significantly in the presence of Na$_2$C$_2$O$_4$, because Cs$^+$ and K$^+$ have similar affinities for non-selective (planar) exchange sites and K$^+$ is also able to compete with Cs$^+$ for FES. The selectivity coefficient for Cs$^+$-K$^+$ exchange calculated for FES alone decreased, indicating a decreased selectivity for Cs$^+$ on illite FES following oxalate treatment (Table 2); however Cs$^+$ is still preferred over K$^+$ at FES.

Boyle *et al.* (1967) suggested that organic-acid treatment of biotite removes cations from the octahedral sheet, leaving an amorphous matrix; however, using scanning electron microscopy (SEM), we did not

Table 1. Calculated Vanselow conditional exchange coefficients ($^cK_{ex}$) between Cs$^+$ and major cations in INEEL vadose zone water on IMt-1 in the presence and absence of 0.04 mM oxalate.

Cation	Conc. (mM)	$^cK_{ex}$ (Cs/X) IMt-1	$^cK_{ex}$ (Cs/X) IMt-1 + oxalate
Mg^{2+}	0.5	898	610
Ca^{2+}	0.5	767	580
Na$^+$	1.0	889	591
K$^+$	1.0	19.3	19.7

Table 2. Frayed-edge site (FES) concentration and calculated Cs$^+$/K$^+$ Vanselow selectivity coefficients (K$_c$) for frayed edges of IMt-1 prior to and following treatment with 0.04 mM oxalate.

Sample	FES (mmol$_c$ kg^{-1})	K$_c$ FES (Cs/K)
IMt-1	2.9	5.19
IMt-1 + oxalate	4.1	2.73

observe any differences in surface morphology of IMt-1 following treatment with 0.04 mM oxalate. This is probably due to the dilute oxalate concentration we used. Following infrared (IR) spectral studies, Varadachari *et al.* (1994) reported evidence for the formation of a new silica phase as a result of biotite treatment with oxalic acid. Scanning electron microscopy analyses did not indicate the presence of a neoformed silicate at the biotite surface, either because the new crystal phase was too small or dispersed to be observed (Varadachari *et al.*, 1994). However, observation of oxalic acid-treated biotite using SEM clearly showed fraying of biotite edges (Varadachari *et al.*, 1994). There is some evidence that treatment of biotite mica with oxalic acid results in the formation of crystalline Fe^{2+} oxalates which adhere to the mineral surface, although the primary effects are fraying of biotite edges, mineral fragmentation, and reduction in sheet thickness (Varadachari *et al.*, 1994).

As a result of oxalate weathering of illite, the relative number of less selective sites is increased and the availability of Cs^+ to plants is likely to be enhanced in the rhizosphere where oxalate is present in the soil solution. Conflicting results of weathering experiments on biotite and vermiculite suggest the possibility of the formation of neoformed silicates at mineral edges as well as the fraying of mineral edges as a result of treatment with oxalic acid. Additional work is necessary to determine whether the less selective sites formed as a result of oxalate weathering of illite are due to the formation of neoformed silicates at illite edges or to the fraying of mineral edges alone.

CONCLUSIONS

The results of this study indicate that oxalate plays an important role in Cs^+ interactions with illite and, therefore, the plant rhizosphere is likely to alter Cs^+ availability in micaceous soils. The majority of Cs^+ sorption to IMt-1 is on exchange sites accessible to Na^+ and other strongly hydrated cations. These sites appear to include aluminol groups at pH >8. The addition of oxalate significantly increases the quantity of sorption sites and the ability of Ca^{2+}, Mg^{2+}, and Na^+ to desorb Cs^+ from accessible exchange sites. Cesium exchange selectivity with respect to K^+ does not change when the illite is treated with oxalate but decreases with respect to Ca^{2+}, Mg^{2+} and Na^+. These results indicate that oxalate treatment increases the number of sites accessible to ion exchange; however, the mechanism for the increase in exchange sites is not known. The results strongly suggest that, in the short term, Cs^+ will become more available to plants that exude oxalate into the rhizosphere.

ACKNOWLEDGMENTS

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