Potassium fixation is the entrapment of $K^+$ ions in between collapsed 2:1 phyllosilicate layers (Rich, 1968). In order for layer collapse to occur, interlayer spaces need to be dehydrated. Interlayer cations dehydrate when their attraction to interlayer surfaces exceeds their attraction to their hydration shell (Kittrick, 1966; Eberl, 1980). Potassium ions and other cations such as $NH_4^+$, $Cs^+$, and $Rb^+$ are readily fixed because they have relatively low energies of hydration. Thus, they can easily dehydrate. It should follow then that the greater the attraction of interlayer cations for interlayer surfaces, the greater the likelihood of cation fixation occurring. This study was conducted to test the hypothesis that increased negative interlayer charge caused by structural Fe reduction leads to increased $K^+$ fixation.

Vermiculites are defined as having greater negative layer charges than smectites, and they also tend to fix more $K^+$ ions than smectites (Rühlicke, 1985; Saha and Inoue, 1998). Furthermore, vermiculites with greater layer charge have been found to have greater cation fixation capacities than vermiculites with less layer charge, and smectites with greater layer charge have been found to have greater cation fixation capacities than smectites with less layer charge (Barshad, 1954; Weir, 1965; Inoue, 1983; Eberl et al., 1986; Douglas, 1989). Murashkina et al. (2007a,
2007b) speculated that K fixation in soils from California dominated by smectites may be due to high-charge smectites that are transitional to vermiculite.

Although micaceous minerals are generally characterized as having greater negative layer charges than both vermiculites and smectites, results have been mixed in terms of the relative K⁺ fixation capacities of micaceous minerals as compared with vermiculites and smectites (Fine et al., 1941; Stanford, 1947; Mordland and Gieseking, 1951; Wear and White, 1951; DeMumbrum and Hoover, 1958; Richards and McLean, 1963). This may be related to the fact that although micaceous minerals have a greater negative layer charge than vermiculites and smectites, much of this negative layer charge is already satisfied by structural K⁺ ions. Thus, depending on the extent to which the fixation capacity is already satisfied, micaceous minerals may fix more or less K⁺ than vermiculites and smectites.

One way to increase the negative layer charge of 2:1 layer silicates is to reduce structural Fe from Fe(III) to Fe(II) (Stucki et al., 1984a; Favre et al., 2002, 2006). Octahedral Fe reduction in smectites has been related to decreased layer spacing, decreased swelling pressure, decreased specific surface area, and more compact flocs (Lear and Stucki, 1989; Shen, 1994; Shen and Stucki, 1994; Gates et al., 1993; Kostka et al., 1999b; Stucki et al., 2000; Dong et al., 2003; Kim et al., 2003, 2005; Komadel et al., 2005; Stucki and Kostka, 2006). Relatedly, octahedral Fe reduction in smectites has also been associated with increases in cation fixation, with greater levels of reduction being associated with greater increases in fixation (Chen et al., 1987; Khaled and Stucki, 1991; Shen and Stucki, 1994; Lee, 2007). As negative charge increases, the Coulombic attraction between interlayer surfaces and cations also increases, leading to increased layer collapse and, if K⁺ ions are present, increased K⁺ fixation. Using soil samples as well as a vermiculite and an illite specimen, Seherer and Zhang (2002) found that NH₄⁺ fixation increased with octahedral Fe reduction and, additionally, the greater the reduction, the greater the increase in fixation. This is consistent with previous work on smectites.

Potassium fixation is in many ways analogous to the reversal of mica weathering. In natural environments, the weathering of micas has been associated with the oxidation of Fe, interlayer expansion, and the loss of K⁺ (Craw, 1981). Because mica weathering, interlayer expansion, and K⁺ loss can be facilitated by Fe oxidation, it is conceivable that interlayer collapse and K⁺ fixation can be facilitated by Fe reduction (Scott and Amonette, 1988).

Potassium fixation is affected not only by the total negative layer charge, but also the distribution of this charge over the layer silicate (Douglas, 1989). Negative charge originating from the tetrahedral sheet retains cations more strongly than equivalent negative charge originating from the octahedral sheet due to the proximity of the charges to the interlayer surface (Reid-Soukup and Ulery, 2002). In a study using 44 soil clays, three montmorillonites, and one vermiculite, K⁺ fixation capacity was found to be best correlated with total layer charge, well correlated with tetrahedral cation exchange capacity, and poorly correlated with octahedral cation exchange capacity (Bouabid et al., 1991). This is likely a function of interlayer cations being attracted to both tetrahedrally and octahedrally derived charge, but more so to tetrahedrally derived charge due to its proximity to the interlayer surface.

The purpose of this study was to further clarify the relationship among layer charge magnitude, layer charge origination, and K⁺ fixation by characterizing the effect of structural Fe reduction on K⁺ fixation for a variety of phyllosilicate types. Most of the prior work pertaining to Fe oxidation state and cation fixation was conducted using ferruginous smectites containing primarily octahedral Fe. Our investigation expands on this previous work by including specimen clays for kaolinites, illites, and vermiculites in addition to two smectites. We also included two soil clays. The reference clays selected represent a wide range in layer charges, charge distributions, Fe contents, and Fe distributions, with the vermiculite sample containing relatively large amounts of tetrahedral Fe.

Although it was not an original intent of the study, we also investigated how multiple sample washings might affect perceived K fixation values. Although there is not a standard procedure for measuring K⁺ fixation, it is generally measured by adding K to a sample and attempting to extract off solution and exchangeable K such that fixed K is all that remains in the sample. However, it is difficult to determine to what degree any extraction procedure truly removes solution and exchangeable K and leaves fixed K. Multiple washes recover more K than single washes (Pratt et al., 1956), but there is no consensus on how many washes are appropriate to use. One to five washes are typically used (Stanford, 1947; Mordland and Gieseking, 1951; Wear and White, 1951; Bouabid et al., 1991), but there is generally no rationale presented behind the use of any number of washes. We chose to use five with the thought that we did not want to mistakenly leave behind solution or exchangeable K and interpret it as fixed K. We also individually measured the K concentration of each wash. Hence, we determined that the washing process itself might be reoxidizing the samples and causing the samples to release their recently fixed K.

MATERIALS AND METHODS

Reference and Soil Clays

Five reference clays were used in this study—kaolinite (KGa-1b), illite (IMt-1), nontronite (NAu-2), montmorillonite (STx-1), and vermiculite (VTx-1). The first four reference clays were from the Source Clay Minerals Repository of the Clay Minerals Society in Chantilly, VA. Since VTx-1 reference clays were no longer available from the Source Clay Minerals Repository, we obtained our sample from Dr. Jerry Bigham. This sample was originally from the Source Clay Minerals Repository of the Clay Minerals Society in Columbia, MO. In addition, two soil clays were fractionated from soil samples of the upper 15 cm of the surface horizon of the Belvue series (coarse-silty, mixed,
superactive, nonacid, mesic Typic Udifluent) and the Cherokee series (fine, mixed, active, thermic Typic Albaqualf) in Kansas. Sampling locations, as well as physical and chemical properties of these soil samples, are given in Tran (2012). Soil clays were designated as BEL and CHE, respectively. All reference and soil clays were fractionated to <2 μm, Na saturated, and freeze dried following the methods of Jackson (1975). Additional details of the fractionation procedure are given in Tran (2012).

The BEL and CHE sites were selected for being similar in terms of physical and chemical characteristics but differing in terms of their K behavior. The CHE site had historically exhibited dramatic fluctuations in soil-test extractable K values between monthly and annual samplings, whereas the BEL site exhibited more predictable, stable K behavior. It was thought that perhaps that the fluctuations in extractable K at CHE were driven in part by fluctuations in soil redox conditions. Cherokee soils receive, on average, 255 mm more precipitation annually than BEL soils. Additionally, CHE soils are more poorly drained than BEL soils due to an underlying claypan that restricts water movement through the soil. Thus, regularly reducing conditions are more likely in CHE soils than BEL soils.

Kaolinite, illite, smectite, and vermiculite reference clays were selected because they reflect the diverse mineralogy of the soil clays selected, as well as the soil clays of temperate regions. KGA-1b, IMt-1, NAu-2, Stx-1b, and VTx-1 were selected specifically to reflect a wide range in layer charges, charge distributions, Fe contents, and Fe distributions (Van Olphen and Fripiat, 1979). Two types of smectite (Stx-1b and NAu-2) were included for their low and high iron contents—0.8 and 23%, respectively. Whereas most of the Fe in the reference clays is octahedral, NAu-2 has a small amount of tetrahedral Fe, and VTx-1 has only tetrahedral Fe (Van Olphen and Fripiat, 1979). With the exception of VTx-1, which is trioctahedral, all of the reference clays used were dioctahedral, typifying the clays likely to be found in soil environments. Although dioctahedral vermiculite would have been preferred for the sake of more accurately representing soil minerals, no pure samples of dioctahedral vermiculite were available. Although most of the layer charge for IMt-1, NAu-2, and VTx-1 is derived from the tetrahedral sheet, the layer charge for Stx-1b is derived wholly from the octahedral sheet. This spread in mineralogical characteristics allowed for evaluation of the effect of clay mineralogy, structural Fe redox state, layer charge magnitude, and layer charge location on K⁺ fixation.

Mineralogical Characterization

Mineralogical characterizations were performed via the use of X-ray diffractometry. All X-ray diffractometry work was done using a Phillips XRG-3100 generator, an APD 3520 X-ray diffractometer with Theta compensating slit, graphite monochromator, scintillation detector, and VisualXRD software (GBS Scientific Equipment, 2007). Copper Kα radiation was used at 35 kV and 20 mA. Step size for all scans was set at 0.02° with a time per step of 0.6 s.

Six parallel oriented mounts were made of each of the clay samples to characterize their mineralogy. Three of the preparations included K saturation of the clays, pipetting onto glass slides, and drying at 25, 350, and 550°C (treatments denoted as K-25, K-350, and K-550, respectively). Clay suspensions were saturated with K⁺ by washing three times with 1 mol L⁻¹ KCl solution and then with deionized water until dispersion.

The remaining three preparations included Mg saturation of the clays. Clay suspensions were saturated with Mg by washing three times with 1 mol L⁻¹ MgCl₂ solution and then with deionized water until the specimens dispersed. Two slides were made by pipetting the Mg-saturated clay onto a glass slide and drying at 25°C. One slide was allowed to remain, and the other was additionally heated to 60°C in a container of ethylene glycol (treatments denoted as Mg-25 and Mg-EG respectively). Another slide was made by using 1% (v/v) glycerol instead of deionized water to wash the Mg-saturated clays. This Mg-saturated and glycerol-solvated sample was pipetted onto a glass slide and dried at 25°C (treatment denoted as Mg-GLY). Each pipetting placed 2 mL of solution containing 30 mg of clay onto each glass slide.

All slides were scanned from 2 to 15°20 with the Mg-25 slides being scanned from 2 to 34°20. Semiquantitative estimates of the relative proportions of different clay minerals in the soil clays were made by comparing peak heights to pure sample peak heights. Silt samples were analyzed as randomly oriented powder mounts and scanned from 18 to 54°20.

Structural Fe Reduction

Fifty-milligram samples of freeze-dried, Na-saturated clay were placed into 50-mL centrifuge tubes with 50 mL of citrate-bicarbonate buffer. The citrate-bicarbonate buffer was made with one part 0.3 mol L⁻¹ sodium citrate (Na₃C₆H₅O₇) and eight parts 1 mol L⁻¹ sodium bicarbonate (NaHCO₃), and 36 parts deionized water. The clay was allowed to disperse in the reaction tube by shaking gently overnight.

After dispersion, an aqueous solution of sodium dithionite (Na₂S₂O₄) was made up such that a 5-mL aliquot contained 600 mg of sodium dithionite. Five-milliliter aliquots of this solution were then immediately added to the centrifuge tubes. The tubes were capped and placed into a water bath at 70°C for 4 h. Samples were then centrifuged for 5 min at 1800 rpm. If the supernatants were cloudy, the samples were centrifuged again for another 5 min. Once the supernatant became clear, it was decanted and discarded. Samples were then either transferred with deionized water into 125 mL amber high-density polyethylene (HDPE) bottles for Fe(II) and total Fe analysis or K saturated for the K⁺ fixation procedure. This reduction procedure was extensively modified and simplified from the procedure by Stucki et al. (1984b).

Fe(II) and Total Fe Determination

Iron(II) and total Fe contents were determined by a photometric method recommended by Amonette and Templeton (1998). Fifty-milligram samples were dissolved by 15 mL of
boiling acid matrix—containing 12 mL of 10% (w/w) \( \text{H}_2\text{SO}_4 \), 1 mL of 48% (w/w) HF, and 2 mL of a 10% (w/w) solution of 1,10-phenanthroline in 95% (v/v) ethanol—in 125-mL amber HDPE bottles. After allowing the sample to be digested in a boiling water bath for 30 min, 10 mL of 5% (w/w) \( \text{H}_2\text{BO}_3 \) and 90 mL of deionized water were added to the sample to stabilize and dilute the digestate. To determine the Fe(II) content of the digestate, 1-mL subsamples of the digestates were combined with 10 mL of 1% (w/w) sodium citrate (\( \text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \)) solution in 30-mL amber glass bottles. Absorbances of these solutions were measured at 510 nm in 1-cm path length quartz cells by a Genesys 20 spectrophotometer. To determine the total Fe content of the digestates, 1-mL subsamples were combined with 10 mL of 1% (w/w) \( \text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \), 1% (w/w) hydroxylamine (\( (\text{NH}_2\text{OH})_2\text{SO}_4 \)) solution. The hydroxylamine served to reduce any Fe(III) in the digestate, causing the measure of Fe(II) to be equivalent to a measure of total Fe. Absorbances of these solutions were measured in the same fashion as in the Fe(II) determination. A standard curve was constructed using ferrous ammonium sulfate [Fe (\( \text{NH}_4 \))\(_2\text{O}_7\text{SO}_4 \)\(_2\text{H}_2\text{O} \)].

**Relative K\(^+\) Fixation Capacity Determination**

Fifty-milligram samples of Na-saturated, freeze-dried clay, either unaltered or reduced, were K saturated by three washes with 50 mL of 1 mol L\(^{-1}\) KCl solution. Samples were then washed five times with 50 mL of 0.5 mol L\(^{-1}\) MgCl\(_2\) solution. Washes were weighed and saved. Washed samples were transferred into Teflon decomposition vessels using deionized water. Vessels were placed in an oven at 110°C until the samples were dry. This step was to ensure that there was enough space in the small vessels for the acid digestion to occur. After drying, 0.5 mL aqua regia and 5 mL of 48% (w/w) HF were pipetted into the vessels. Vessels were then capped and placed into Parr digestion bombs. Bombs were placed in the oven for 1 h at 110°C. Bombs were then removed and allowed to cool to ambient temperature. Once cool, bombs were opened, and the contents of the Teflon vessels were quantitatively transferred into 100-mL Nalgene volumetric flasks containing 2.80 g of \( \text{H}_2\text{BO}_3 \) powder using deionized water. Flasks were shaken to dissolve the powder and brought to volume using deionized water. Acid digestion K\(^+\) concentrations (K\(_\text{final}\)) were determined by a Varian model 720-ES inductively coupled plasma optical emission spectrometer. Initial mineral K contents (K\(_\text{initial}\)) were determined in the same manner as K\(_\text{final}\) but omitting the initial steps of K saturation and washing with MgCl\(_2\) solution. The amount of K\(^+\) fixed was calculated as: K\(_\text{fixed}\) = K\(_\text{final}\) – K\(_\text{initial}\). In addition to measuring the K\(^+\) concentration of the acid digestions, the K\(^+\) concentrations of each of the MgCl\(_2\) washes (K\(_\text{first wash}\), K\(_\text{second wash}\), etc.) were also determined.

**RESULTS**

**Mineralogical Characterization**

Reference clay minerals were characterized by X-ray diffractometry not only to confirm their identity, but also to reveal any crystalline impurities that might exist in the sample. X-ray diffractograms for the specimen and soil clays are available in Tran (2012). In response to the different treatments, KGa-1b demonstrated a classic kaolinitic response, and NAu-2 and STx-1b demonstrated classic smectitic responses. The diffraction patterns for IMt-1 indicated that the sample was mostly micaceous with small amounts of kaolinite. The K scans for VTx-1 were as to be expected for vermiculite, but the Mg scans were not. Although a strong and diagnostic 14.5-Å peak was present on all the Mg scans for VTx-1, so were a weak 24-Å and a strong 12-Å peak. These two peaks could be indicative of the presence of hydrobiotite, a trioctahedral layer silicate exhibiting a regular 1:1 interstratification of vermiculite and biotite layers (Sawhney, 1989).

The two soil clays both contained kaolinite, mica, smectite, and quartz. While not identified through X-ray diffraction, and based on selective dissolution studies (data available in Tran, 2012), it also appeared that both soil clays contained some iron oxides, most likely poorly crystalline. The CHE site appeared to be more weathered than BEL, containing relatively less of the 2:1 layer silicates and relatively more kaolinite and quartz. This observation was corroborated by the silt mineralogy of the two soil samples. Whereas the silt fraction associated with CHE was purely quartz, the silt fraction associated with BEL also contained substantial amounts of feldspars in addition to quartz, including orthoclase (Table 1).

**Iron Contents of Unaltered and Reduced Clays**

Total structural Fe present in the clay minerals ranged, as a weight percentage, from 0.29% for KGa-1b to a high of 23% for NAu-2 (Table 2). Initial amounts of Fe(II) were low for all clay minerals, ranging from 0% for KGa-1b to a high of 1.2% for IMt-1. This was to be expected, as many of the pretreatments steps used prior to iron assay were oxidizing (e.g., air drying, dry grinding, treatment with hydrogen peroxide, suspension in solutions containing dissolved oxygen, and freeze drying). Additionally, many of the reference minerals started in a fairly if not completely oxidized form. Our Fe(II) and total Fe content determinations largely matched source clay characterization data with one notable exception—the total Fe content for VTx-1. Source clay data show the total Fe contents for VTx-1 at <1.5%. Our assessment places this value closer to 8%. This elevated Fe content supports our suspicion that this sample is interstratified with biotite, which can be relatively Fe rich.

Upon reduction, Fe(II) content increases were observed across all samples. NAu-2 Fe(II) increased the most by far, from 0.12 to 15.4%. VTx-1 Fe(II) content increased the second most, from 0.8 to 1.65% (Table 2). Generally, reduction was associated with a loss in total structural Fe, which was most likely due to phyllosilicate dissolution caused by the chemical reduction process (Stucki and Kostka, 2006). In the soil clays, which experienced the most total loss in Fe, there was also likely some loss in Fe associated with Fe oxide dissolution. Whereas the X-ray diffraction patterns did not indicate the presence of iron oxides in either sample, it is difficult to detect poorly crystalline Fe oxides,
especially among crystalline materials, using conventional X-ray diffractometric techniques (Bigham et al., 2002).

**Potassium Fixation of Clay Minerals in Unaltered and Reduced State**

Prior to evaluation of clay mineral fixation capacity, baseline K contents were evaluated for each of the clay minerals being studied (Table 3). The results confirmed high amounts of K in IMt-1 and negligible amounts of K in KGa-1b, NAu-2, and STx-1b. These results were to be expected on the basis of characterization data from the Clay Minerals Society (Van Olphen and Fripiat, 1979). VTx-1, however, contained 20 mg K g⁻¹ clay, which exceeded the trace amounts of K it was supposed to have according to source clay characterization data. The vermiculite sample, unlike the rest of the reference clays, was not obtained directly from the Clay Minerals Society, but rather through an intermediate with some uncertainty about whether the sample had been previously processed in any manner other than grinding. The presence of increased amounts of K is consistent with the X-ray diffraction patterns and total Fe contents for VTx-1, which suggested the presence of biotite interstratified with vermiculite. Baseline results also indicated that BEL contained more K than CHE, which is consistent with the conclusion that BEL contained more mica than CHE (Table 3).

In the unaltered form, IMt-1 and STx-1b fixed an average of 3 mg K g⁻¹ clay, whereas CHE, KGa-1b, NAu-2, and VTx-1 fixed negligible amounts of K⁺ (Fig. 1). The BEL site actually released K⁺ as a result of K-saturation and washing with MgCl₂ solution. Upon reduction, only the amounts of K⁺ fixed by NAu-2 and VTx-1 were significantly affected. The amount of K⁺ fixed by NAu-2 and VTx-1 increased to 7 and 11 mg K g clay⁻¹, respectively, on reduction (Fig. 1).

**Effect of Sample Washing on Apparent K⁺ Fixation**

This study used five MgCl₂ washes on each sample with the K⁺ concentration determined for each individual wash. The intended purpose behind this was to see at what point we could reasonably assume to have washed off solution and exchangeable K. Our results suggest that most of the solution and exchangeable K was washed off by the second wash (Fig. 2). However, these values also led to some unanticipated insight into the relationship between Fe oxidation state and K⁺ fixation and release.

Overall, it appeared that two washes removed the large bulk of solution and exchangeable K⁺, although trace amounts of K⁺ were still being removed from each sample by the fifth wash. Interestingly, the reduced samples usually yielded more K⁺ than the unaltered samples with each wash. This was especially pronounced for NAu-2, which had the greatest increase in Fe(II) associated with reduction (Fig. 2). We hypothesize that the additional amounts of K⁺ ions observed in the later washes of the reduced samples, particularly NAu-2, are a result of the reoxidizing effect of washing with MgCl₂ solution. Reoxidation of the samples would reverse the effects of reduction, which in the case of some of the samples causes them to yield up their recently fixed K⁺ ions. Thus, it may be that this study missed possible differences caused by Fe oxidation state changes on K⁺ fixation.

**Table 1. Semiquantitative mineralogical analysis of clay and silt fractions of studied soils.**

<table>
<thead>
<tr>
<th>ID</th>
<th>Clay fraction</th>
<th>Silt fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kaolinite</td>
<td>Mica</td>
</tr>
<tr>
<td>Belvue site</td>
<td>10</td>
<td>35</td>
</tr>
<tr>
<td>Cherokee site</td>
<td>25</td>
<td>30</td>
</tr>
</tbody>
</table>

**Table 2. Mean Fe(II) and total Fe contents of unaltered and reduced soil and reference clays as weight percentages. N = 3. Standard deviations are in parentheses.**

<table>
<thead>
<tr>
<th>ID</th>
<th>Fe(II) Unaltered</th>
<th>Reduced</th>
<th>Total Fe Unaltered</th>
<th>Reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belvue site</td>
<td>0.6 (0.1)</td>
<td>1.46 (0.08)</td>
<td>5.9 (0.3)</td>
<td>3.8 (0.2)</td>
</tr>
<tr>
<td>Cherokee site</td>
<td>0.55 (0.05)</td>
<td>1.23 (0.08)</td>
<td>4.6 (0.8)</td>
<td>2.3 (0.1)</td>
</tr>
<tr>
<td>IMt-1</td>
<td>1.2 (0.2)</td>
<td>1.7 (0.2)</td>
<td>5.6 (0.5)</td>
<td>4.77 (0.02)</td>
</tr>
<tr>
<td>KGa-1b</td>
<td>0.00 (0.01)</td>
<td>0.15 (0.03)</td>
<td>0.29 (0.05)</td>
<td>0.19 (0.03)</td>
</tr>
<tr>
<td>NAu-2</td>
<td>0.12 (0.01)</td>
<td>15.4 (0.2)</td>
<td>23 (2)</td>
<td>22.6 (0.3)</td>
</tr>
<tr>
<td>STx-1b</td>
<td>0.04 (0.01)</td>
<td>0.24 (0.05)</td>
<td>0.81 (0.01)</td>
<td>0.28 (0.02)</td>
</tr>
<tr>
<td>VTx-1</td>
<td>0.8 (0.6)</td>
<td>1.65 (0.03)</td>
<td>7.93 (0.3)</td>
<td>8 (1)</td>
</tr>
</tbody>
</table>

**Table 3. Mean potassium contents of clay minerals prior to K treatment (K_initial) and after K treatment (K_final) for both unaltered and reduced samples. Standard deviations are in parentheses.**

<table>
<thead>
<tr>
<th>ID</th>
<th>Baseline (K_initial, N = 2)</th>
<th>With fixed K—unaltered (K_final, N = 4)</th>
<th>With fixed K—reduced (K_final, N = 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline</td>
<td>mg K g⁻¹ clay</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Belvue site</td>
<td>20 (2)</td>
<td>17 (1)</td>
<td>17 (3)</td>
</tr>
<tr>
<td>Cherokee site</td>
<td>13 (2)</td>
<td>12.1 (0.6)</td>
<td>13 (1)</td>
</tr>
<tr>
<td>IMt-1</td>
<td>56.7 (0.3)</td>
<td>60 (3)</td>
<td>59 (3)</td>
</tr>
<tr>
<td>KGa-1b</td>
<td>0.0 (0.3)</td>
<td>1 (1)</td>
<td>0.2 (0.4)</td>
</tr>
<tr>
<td>NAu-2</td>
<td>0.2 (0.3)</td>
<td>1 (1)</td>
<td>7 (3)</td>
</tr>
<tr>
<td>STx-1b</td>
<td>0.2 (0.2)</td>
<td>3 (3)</td>
<td>3 (2)</td>
</tr>
<tr>
<td>VTx-1</td>
<td>20 (1)</td>
<td>21 (3)</td>
<td>31 (2)</td>
</tr>
</tbody>
</table>
DISCUSSION

Variation observed in the K+ fixation capacities of the clays in this study can be largely explained by variations in layer charge and charge location (Table 4). Greater negative charges were associated with greater levels of fixation because greater negative charges meant increased attraction for interlayer cations. NAu-2 and VTx-1 fixed little K+ (Fig. 1) in the unaltered form when they had little to no excess negative charge, but great amounts in the reduced form when electronic gains presumably led to increases in negative charge. Accounting for the preexisting interlayer K+ in NAu-2 and VTx-1, both actually had net positive layer charges (Table 4), which may have been the reason that they fixed virtually no K+ in the unaltered form. IMt-1 and STx-1b have greater negative layer charges than NAu-2 and VTx-1 (Table 4), which could explain their greater K+ fixation capacity in the unaltered form (Fig. 1). However, the K+ fixation capacities of IMt-1 and STx-1b were not significantly affected by Fe reduction in terms of their K+ fixation. This was unsurprising, as these two clay minerals experienced minimal gains in Fe(II) on reduction.

The relative responsiveness of different reference clays to reduction is likely in part due to the relative accessibility of the reducing agent to structural Fe. The Fe in IMt-1 was relatively resistant to reduction, which was probably due to the closed interlayer space of IMt-1. The Fe in micas can be particularly difficult to reduce due to the collapsed nature of the clay layers, which impedes electron transfer (Gilkes et al., 1972; Ross and Rich, 1974; Douglas, 1989). One caveat, however, when comparing the relative abilities of different phyllosilicates to be reduced, is that reduction rates are as much a function of particle size and surface area as clay mineralogy (Ernstsen et al., 1998; Kostka et al., 2002). The smaller the particle size, the more rapid and greater the extent of reduction is due to the increased surface area. Thus, what might appear to be one type of clay mineral being more responsive to reduction than another may really be a finer material being more responsive to reduction than a coarser material.

Although IMt-1 and STx-1b fixed comparable, intermediate amounts of K+ ions, they likely did so for different reasons. IMt-1 had the second most layer charge, but much of this negative charge is already satisfied by existing fixed K+, which means that not as many fixation sites are available as would be expected on the basis of layer charge alone. STx-1b has the most excess negative charge of all the reference clays and no existing fixed K+ ions. Thus, it might be expected that it would fix much more than IMt-1. However, STx-1’s charge is derived entirely from the octahedral sheet and therefore is not as effective at attracting interlayer cations as charge derived from the tetrahedral sheet (Table 4).

Charge origination may explain why the gains in fixation were greater for VTx-1 per unit increase in Fe(II) than for NAu-2. Since VTx-1 had all of its structural Fe in the tetrahedral sheet and NAu-2 had almost all of its Fe in the octahedral sheet, this observation is consistent with the fact that interlayer cations are more strongly attracted to negative charge derived from the tetrahedral sheet than from the octahedral sheet.

The effects of charge origination could also be observed with STx-1b and IMt-1. STx-1b had the most excess negative charge of all the reference clays and yet only fixed moderate amounts of K+. IMt-1 had less negative layer charge than STx-1b, some of which was already satisfied by preexisting K+, and yet fixed comparable amounts of K+ to STx-1b. Whereas all the negative charge in STx-1b is octahedrally derived, most of the negative charge in IMt-1 is tetrahedrally derived. Thus, we hypothesize that although IMt-1 may have had less total negative charge than STx-1b, because its charge was located closer to the clay layer surface, its charge was more attractive to interlayer cations.

KGa-1b fixed negligible amounts of K+. This was expected, considering that kaolinites are nonexpansible. It is worth noting that if we had used only one wash of MgCl2 solution, rather than five, to determine K fixation capacity, we would have accidentally concluded that KGa-1b fixed ~5 mg K g⁻¹ clay. This highlights the possibility of overstating K fixation capacity by inadequately washing off solution and exchangeable K. The problem with excessive washing where we are interested in the effect of Fe oxidation state on K fixation is that the washing process itself might oxidize the sample. One of the major limitations of this study is that minimal protections were made against reoxidation. Some workers in this area have used an apparatus called the Controlled Atmosphere Liquid Exchanger, which protects reduced samples from reoxidizing (Stucki et al., 1984b).

As for the soil clays, it was expected that CHE would fix more than BEL, having the more unpredictable K+ behavior in the field. However, CHE did not fix significant amounts of K+ under our K

![Graph showing potassium fixed (± SEM) from K fixation treatment for different clay minerals unaltered and reduced. BEL, Belvue site; CHE, Cherokee site.](Image)
fixation protocol in either its unaltered or reduced form. The BEL site, in contrast, actually released K⁺. This latter observation is consistent with the mineralogical observations indicating that the BEL soil was less weathered than the CHE soil and thus may have had more reserve K⁺. It is possible that these soil clays might have fixed K in their reduced form, but our multiple washings caused the samples to reoxidize and release their fixed K.

Potassium fixation and release phenomena are often used to explain fluctuations in soil exchangeable K⁺. While it is possible that redox driven changes in K⁺ fixation are partly responsible for temporal fluctuations in soil exchangeable K⁺, more work needs to be done to further test that possibility. However, it seems clear that certain sites are less susceptible to fluctuations in soil exchangeable K⁺ than others due to their higher K buffering capacity. The BEL soil most likely did not experience dramatic oscillations in soil exchangeable K⁺ due to its relatively large amounts of reserve K in the form of K-bearing feldspars and micas, which would have buffered decreases in soil exchangeable K⁺.
K⁺. Contrast this with the CHE soil, which had relatively low amounts of reserve K and would have not been able to rapidly buffer losses in soil exchangeable K⁺.

SUMMARY AND CONCLUSIONS

Structural Fe reduction of NAu-2 and VTx-1 significantly increased their K⁺ fixation capacities. It seems likely that this increase was due to increased negative interlayer charge. Furthermore, Fe reduction in the tetrahedral layer appeared to promote K⁺ fixation more so than Fe reduction in the octahedral layer. Tetrahedrally derived charge would be expected to exert a greater attractive force on interlayer K⁺ than octahedrally derived charge due to its proximity to the interlayer surface.

The remaining specimen clays tested were not responsive to our reduction procedures, and consequently their K⁺ fixation capacities were not significantly affected by them. In the case of KGa-1b and STx-1b, they simply had such low Fe contents (<1%) that there wasn’t much Fe to reduce. In the case of IMt-1, collapsed clay layers probably impeded the process of electron transfer.

Neither BEL nor CHE demonstrated K⁺ fixation in either their unaltered or reduced forms. We speculate that these soil clays might have fixed K⁺ in their reduced form, but that our use of multiple MgCl₂ washes reoxidized the sample and caused them to release their fixed K⁺. With regard to whether soil redox conditions might affect soil K⁺ fixation through their effects on structural Fe oxidation state in clay minerals, it certainly seems possible, although more work would have to be done paying special care to the issue of sample reoxidation.

This study highlighted the difficulty in both fully removing exchangeable and solution K⁺ but not reoxidizing the samples. To those studying K⁺ fixation where oxidation is not an issue, we would like to draw attention to how solution and exchangeable K⁺ can still remain after five washes and how a single wash could cause an overestimation of the fixation capacities. To those studying Fe redox state in clay minerals, we would like to underscore how a simple solution wash might rapidly affect Fe oxidation state.

ACKNOWLEDGMENTS

We thank Dr. Jerry Bigham, The Ohio State University, for generously sending a sample of VTx-1.

Table 4. Theoretical charge magnitudes and distributions of 2:1 reference clays based on structural formulas. Charges calculated from structural formulas minus exchangeable and fixed cations. Additional adjustments were made for IMt-1 and VTx-1 to account for the large amounts of K⁺ in the structures neutralizing the negative charge of the tetrahedral sheet.

<table>
<thead>
<tr>
<th>ID</th>
<th>Octahedral</th>
<th>Tetrahedral</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMt-1</td>
<td>−0.43</td>
<td>−1.23</td>
<td>−1.66</td>
</tr>
<tr>
<td>IMt-1 (with initial interlayer K)</td>
<td>−0.43</td>
<td>−0.07</td>
<td>−0.50</td>
</tr>
<tr>
<td>NAu-2</td>
<td>+0.92</td>
<td>−0.43</td>
<td>+0.49</td>
</tr>
<tr>
<td>STx-1b</td>
<td>−2.96</td>
<td>−0.00</td>
<td>−2.96</td>
</tr>
<tr>
<td>VTx-1</td>
<td>+0.02</td>
<td>−0.29</td>
<td>−0.27</td>
</tr>
<tr>
<td>VTx-1 (with initial interlayer K)</td>
<td>+0.02</td>
<td>+0.12</td>
<td>+0.14</td>
</tr>
</tbody>
</table>

REFERENCES


