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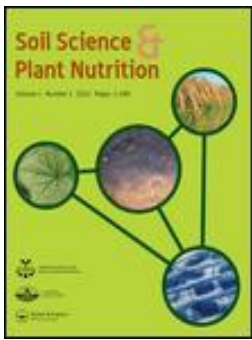
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# Mechanisms for high potassium selectivity of soils dominated by halloysite from northern California, USA

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## ABSTRACT

Mechanisms contributing to unusually high cation exchange capacity and potassium ion selectivity in several halloysite-rich soils remain a topic of intense debate. In spite of the large number of studies, a unifying mechanism to explain the high charge and K<sup>+</sup> selectivity has not been elucidated. High K<sup>+</sup> selectivity occurs in several soils from northern California whose clay fraction is dominated by hydrated tubular halloysite (1.0 nm) and abundant Fe (hydr)oxides. To investigate the mechanism(s), we measured K<sup>+</sup>/Ca<sup>2+</sup> selectivity and charge properties of the clay-size fraction of two California soils following various pretreatments, including organic matter removal by H<sub>2</sub>O<sub>2</sub>, Fe (hydr)oxide removal by citrate-dithionite (CD), and alteration of the basal spacing by dehydration (reduced-pressure drying). Transmission electron microscopy and X-ray diffraction indicated a predominance of tubular halloysite morphology with a 1.0-nm peak following Mg-saturation. In contrast, reduced pressure-dried samples showed a 0.7-nm peak without a 1.0-nm peak, indicating effective dehydration. The K<sup>+</sup> selectivity was strongly linked to the interlayer spacing (1.0 vs 0.7 nm) of halloysite and the presence of Fe (hydr)oxides. The 0.3 nm larger interlayer spacing in hydrated halloysite appears to contribute to K<sup>+</sup> selectivity as the weakly hydrated K<sup>+</sup> can readily dehydrate and enter into the interlayer space while the strongly hydrated Ca<sup>2+</sup> is too large to enter, a mechanism similar to K<sup>+</sup> selectivity of ion channels in human nerve and muscle tissue. The Fe (hydr)oxides may reduce the permanent negative charge and enhance K<sup>+</sup> selectivity via physically blocking interlayer exchange sites and repulsing cations, especially divalent cations, due to their positive charge. Results of this study suggest the occurrence of a high-charge, K<sup>+</sup>-selective halloysite for which hydration/dehydration and Fe (hydr)oxides strongly influence the charge and selectivity characteristics by altering ion access to interlayer exchange sites.

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## KEY WORDS

Dehydration; free iron oxides; hydrated tubular halloysite; permanent negative charge; potassium ion selectivity

## 1. Introduction

Mechanisms contributing to unusually high cation exchange capacity (CEC) and K<sup>+</sup>/Ca<sup>2+</sup> selectivity in several halloysite-rich soils remain a topic of intense debate (Joussein *et al.* 2005; Yang *et al.* 2016). Halloysite is a 1:1 aluminosilicate mineral, which is characterized by a diversity of morphologies, chemical composition, specific surface area, structural disorder, and physicochemical properties (e.g., CEC, ion selectivity) (Dahlgren *et al.* 2004; Joussein *et al.* 2005; Joussein 2016). Among the diversity of properties, CEC values for halloysite generally range between 2 and 10 cmol<sub>c</sub> kg<sup>-1</sup>, although values in excess 20 cmol<sub>c</sub> kg<sup>-1</sup> clay have been reported (Bailey 1990; Norrish 1995). The larger CEC values may originate from permanent negative charges derived from Al<sup>3+</sup> vacancies in the octahedral sheet, isomorphous substitution of Al<sup>3+</sup> for Si<sup>4+</sup> in the tetrahedral sheet, and/or isomorphous substitution of Fe<sup>2+</sup> for Al<sup>3+</sup> or nonstoichiometric substitution of Fe<sup>3+</sup> for Al<sup>3+</sup> (i.e., cation vacancies) in the octahedral sheet leading to a deficit of positive charge (Soma *et al.* 1992; Takahashi *et al.* 2001; Churchman *et al.* 2016; Joussein 2016; Yang *et al.* 2016).

There are several reports of soils dominated by halloysite in their clay fraction showing strong K<sup>+</sup> or NH<sub>4</sub><sup>+</sup> retention (e.g., Okamura and Wada 1984; Quantin *et al.* 1988; Delvaux *et al.* 1989; Delvaux *et al.* 1990a; Delvaux *et al.* 1990b; Delvaux *et al.* 1992; Fontaine *et al.* 1989; Espino-Mesa and Hernandez-Moreno 1994; Escudey and Galindo 1988; Escudey *et al.* 1997). The high K<sup>+</sup> (or NH<sub>4</sub><sup>+</sup>) selectivity has been explained in terms of (i) K<sup>+</sup>- or NH<sub>4</sub><sup>+</sup>-selective halloysite (Wada and Odahara 1993; Okamura and Wada 1984; Ndayiragije and Delvaux 2004), (ii) presence of a halloysite-smectite mixed-layer clay (Delvaux *et al.* 1990a; Delvaux *et al.* 1990b), (iii) presence of mica, vermiculite or zeolite impurities (Ming and Mumpton 1989; Parfitt 1992), (iv) preferential repulsion of divalent cations by Fe oxides surface coatings (Escudey and Galindo 1988; Escudey *et al.* 1997), and (v) whole salt (KCl) retention within halloysite tubes (Wada 1958; Wada 1959; Thomas 1960). However, no unique mechanism has been demonstrated to explain both the high charge and K<sup>+</sup> selectivity of halloysitic clays (reviewed by Joussein *et al.* 2005).

Takahashi *et al.* (2001) found high K<sup>+</sup> selectivity in the <2-mm fraction of subsurface horizons in soils derived from andesitic basalt flows in northern California. The clay fraction was dominated by hydrated tubular halloysite (1.0 nm) with abundant

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free iron oxides (70 – 100 g Fe kg<sup>-1</sup> by citrate-dithionite extraction). No detectable 2:1 layer silicates, 1:1–2:1 mixed-layer clays, or zeolites were identified in the clay-size fraction; however, trace levels of these constituents are very difficult to detect. The high K<sup>+</sup> selectivity in the fine-earth fraction (<2 mm) was attributed to the existence of a K<sup>+</sup>-selective halloysite phase and preferential repulsion of divalent cations by Fe oxide surface coatings, although the contribution of 2:1 minerals detected in the silt fraction could not be ignored (Takahashi *et al.* 2001). The <sup>27</sup>Al-NMR spectrum of the halloysite-rich clay indicated a poorly-ordered kaolin and a tetrahedral Al content of ~2% attributed to isomorphous substitution of Al<sup>3+</sup> for Si<sup>4+</sup> in the tetrahedral layer.

The primary objective of this paper was to further elucidate the mechanism(s) for high K<sup>+</sup>-selectivity of volcanic soils dominated by halloysite from northern California. Our previous study examined K<sup>+</sup>-selectivity in the fine-earth fraction (<2-mm fraction) of these soils (Takahashi *et al.* 2001). This study builds on our previous research by rigorously examining the charge and K<sup>+</sup>/Ca<sup>2+</sup> selectivity properties of the clay-size fraction (<2 μm) following various pretreatments. For high charge and K<sup>+</sup>-selective halloysite, it is considered that the halloysite should possess permanent negative charges that are selectively accessible to K<sup>+</sup>. Because permanent negative charge sites are considered to be located in interlayers, the basal spacing of halloysite (0.7 or 1.0 nm) was assessed (reviewed by Joussein *et al.* 2005; Joussein 2016). Thus, this study examined the permanent and variable charge characteristics and the changes in K<sup>+</sup>/Ca<sup>2+</sup> selectivity of the clay fraction upon selective removal of organic matter (by H<sub>2</sub>O<sub>2</sub>) and free iron oxides (by citrate-dithionite treatment) and alteration of the basal spacing by dehydration (reduced-pressure drying). In addition, the <2-mm fraction from a comparably weathered soil formed in andesitic lahar that was similarly dominated by tubular halloysite, but with detectable 2:1 clay minerals, was included to gain insights on the potential role of 2:1 layer silicates on charge and K<sup>+</sup>/Ca<sup>2+</sup> selectivity characteristics.

## 2. Material and methods

### 2.1. Experimental soils

Soils formed on extrusive volcanic materials were collected from two areas in northern California. Soils from two sites used in the

original study of K<sup>+</sup> selectivity (Takahashi *et al.* 2001) are located in the vicinity of Mt. Shasta volcano in the Cascade Range (LeTrab: 41°16'0"N, 121°48'10"W; Red Tank: 41°18'59"N, 121°46'46"W). These soils formed in andesitic basalt flows and were overlain by rhyolitic ash (25–40 cm) from Holocene eruptions (Takahashi *et al.* 1993; Takahashi *et al.* 2001). Based on Takahashi *et al.* (2001), we selected the 2Bt3 horizons from the LeTrab (fine-loamy, halloysitic, mesic, Andic Haploxeralf) and Red Tank (fine, halloysitic, mesic, Andic Haploxeralf) pedons for more intensive study. These horizons have clay mineralogy dominated by halloysite and display considerable weathering as evidenced by high clay (33 and 51%) and free Fe oxide (93 and 45 g Fe kg<sup>-1</sup>) concentrations (Table 1).

Soils from a second area located in the western Sierra Nevada (Aiken: 38°42'38.2"N, 120°33'04.0"W) were selected to include a soil whose clay mineralogy was dominated by tubular halloysite, but also contained detectable 2:1 layer silicates that may be expected to affect charge and K<sup>+</sup> selectivity (Rasmussen *et al.* 2007). The parent material of the Aiken soil consists of Miocene- to Pliocene-aged andesitic lahar with evidence of late-Pleistocene to early-Holocene volcanic ash inputs in the surface horizons. The Aiken pedon was classified as a fine, halloysitic, mesic Andic Palehumult. The Bt3 and Bt4 horizons selected for this study have a clay mineralogy dominated by halloysite with minor 2:1 layer silicates and display appreciable weathering as evidenced by the high clay (39 and 51%) and free Fe oxide (22 and 23 g Fe kg<sup>-1</sup>) concentrations.

### 2.2. Clay preparation for charge and k<sup>+</sup>/ca<sup>2+</sup> selectivity assessment

The clay-size fraction (<2 μm) from the LeTrab and Red Tank soils was isolated from air dry soil using the pipette method following dispersion with sonication (15 kHz, 150 W, 10 min) and pH adjustment to ~9 with NaOH. Five treatments were prepared from the collected clay specimens:

- (1) Air dried
- (2) Organic matter removal: Air-dried samples were treated with 5% H<sub>2</sub>O<sub>2</sub>.
- (3) Reduced-pressure drying: Air-dried clays were further dried under reduced pressure at about 15 Pa overnight.

**Table 1.** Selected physical and chemical properties of soil samples.

Soil sample	Particle size distribution				pH	pH	T-C	T-N	CEC	Exchangeable bases				Base
	Coarse sand	Fine sand	Silt	Clay	(H <sub>2</sub> O)	(KCl)				Ca	Mg	K	Na	Saturation
	--- % ---						-- g kg <sup>-1</sup> --			--- cmol <sub>c</sub> kg <sup>-1</sup> ---				%
LeTrab 2Bt3	4	26	37	33	5.9	4.4	3.0	0.2	24.7	3.8	0.8	4.0	0.2	36
Red Tank 2Bt3	2	12	35	51	6.2	5.1	2.0	0.2	23.7	4.8	0.6	4.7	0.1	43
Aiken Bt3	3	34	24	39	5.9	4.5	8.0	0.4	18.2	3.6	2.0	0.7	0.0	35
Aiken Bt4	3	24	22	51	5.8	4.2	5.0	0.4	12.6	1.9	2.0	0.8	0.0	37
Soil sample	Fe <sub>CD</sub>	Al <sub>o</sub>	Fe <sub>o</sub>	Si <sub>o</sub>	Al <sub>p</sub>	Fe <sub>p</sub>								
	--- g kg <sup>-1</sup> ---													
LeTrab 2Bt3	93	5.0	4.6	1.2	1.9	1.3								
Red Tank 2Bt3	45	6.5	5.3	2.6	3.9	2.3								
Aiken Bt3	22	4.6	3.0	1.0	1.9	0.8								
Aiken Bt4	23	3.3	3.3	0.9	1.7	0.5								

T-C: Total carbon; T-N: Total nitrogen; CEC: Cation exchange capacity; Fe<sub>CD</sub>: Citrate-dithionite extractable Fe (Holmgren 1967).

Al<sub>o</sub>, Fe<sub>o</sub> and Si<sub>o</sub>: Acid oxalate-extractable Al, Fe and Si (Blakemore *et al.* 1981).

Al<sub>p</sub> and Fe<sub>p</sub>: Sodium pyrophosphate- extractable Al and Fe (Blakemore *et al.* 1981).

**Table 2.** Permanent and variable negative charges of clay fractions after the treatments.

Sample treatment	Permanent charge		Variable charge		Total charge	
	LeTrab	Red Tank	LeTrab	Red Tank	LeTrab	Red Tank
	cmol <sub>c</sub> kg <sup>-1</sup>					
Air-dried	7.7	9.5	13.6 (5.4)*	10.4 (5.4)	21.3	19.9
Reduced pressure-dried	6.5	6.9	8.3 (5.4)	7.7 (5.4)	14.8	14.6
CD-air dried	12.6	17.1	11.6 (7.6)	12.0 (7.2)	24.2	29.1
CD-reduced pressure-dried	8.4	10.4	8.0 (7.5)	10.7 (7.2)	16.4	21.1

The values are reported based on the actual treated weight.

\*Value in parentheses shows the pH value associated with the measurement.

- (4) Free iron oxide removal: Air-dried samples were treated with sodium citrate and dithionite (CD treated) for 16 hr (Holmgren 1967). After washing with 80% acetone, the clay samples were air dried.
- (5) Iron oxide removal/reduced-pressure drying: Following free iron oxide removal by CD (Treatment 4), the iron oxide free clays were dried under reduced pressure overnight.

A preliminary study demonstrated no difference on charge and  $K^+/Ca^{2+}$  selectivity properties between field moist and air dried soils. Therefore, we elected to work with air-dried clays to maintain consistent moisture conditions among all treatments. We acknowledge that the clay pretreatment methods used in the present study may affect clay charge characteristics in several ways and therefore any conclusions must recognize the potential for artifacts.

### 2.3. Determination of permanent and variable charge characteristics

Permanent and variable charge characteristics of the pre-treated clay samples were determined by the CsCl method of Anderson and Sposito (1991). This method was developed for 2:1 type minerals that possess micaceous structure. Therefore, the values obtained in this study should be considered 'apparent' permanent negative charge because the clay samples did not possess any detectable micaceous minerals ( $K_2O < 0.1\%$ ). Briefly, samples were saturated with  $Cs^+$  using CsCl solutions (0.5 M and then 0.05 M) and washed with ethanol. Then, the Cs-saturated samples were dried at 65°C for 48 h. The  $Cs^+$  was extracted from the dried samples with 0.01 M LiCl (variable charge) and then 1 M  $NH_4OAc$  (permanent charge). Concentrations of  $Cs^+$  in the extracted solutions were measured by atomic absorption spectrophotometry (A-2000; Hitachi High Technologies Corp., Tokyo, Japan).

### 2.4. $K^+/ca^{2+}$ exchange equilibrium study

A  $K^+-Ca^{2+}$  exchange equilibrium study was performed using the method of Wada and Odahara (1993) on the five clay treatments from the LeTrab and Red Tank soils and also on the non-treated <2-mm fraction of the LeTrab, Red Tank and Aikens soils. Exchange equilibrium values were measured

across a range of K adsorption ratios ( $[K^+]/[Ca^{2+}]^{1/2}$ ) from 0.1 to 4.5  $mM^{1/2}$  (final values after equilibrium). Samples were washed five times with 0.5 M  $CaCl_2$  to saturate exchange sites with  $Ca^{2+}$ , then washed six times to equilibrate the exchange sites with mixed KCl- $CaCl_2$  solutions having a constant 0.02 M  $Cl^-$  concentration. After the final decantation, adsorbed  $K^+$  and  $Ca^{2+}$  were extracted five times using 1 M  $NH_4OAc$  solution. Concentrations of  $K^+$  and  $Ca^{2+}$  in the equilibrated and extracted solutions were measured by atomic absorption spectrophotometry. The equivalent fractions of adsorbed  $K^+$  ( $E_K$ ) and solution  $K^+$  ( $\bar{E}_K$ ) were compared using the Vanselow ( $K_V$ ) selectivity coefficient:

$$K_V = N_K^2(Ca^{2+})/N_{Ca}(K^+)^2$$

where  $N_K$  and  $N_{Ca}$  denote molar fractions of adsorbed  $K^+$  and  $Ca^{2+}$ , and  $(K^+)$  and  $(Ca^{2+})$  denote aqueous ion activities. Aqueous ion activities were calculated using activity coefficients computed from the Davies equation.

### 2.5. Transmission electron microscopy (TEM)

TEM observation was performed on the  $K^+$ -saturated clay specimens (CD-air-dried and CD-reduced pressure-dried) spotted onto C-coated collodion films using a Hitachi H-7650 operating at 100 kV (Hitachi High Technologies Corp., Tokyo, Japan). TEM observation was also performed on the CD-treated and  $K^+$ -saturated clay specimens isolated from the Akin soil horizons.

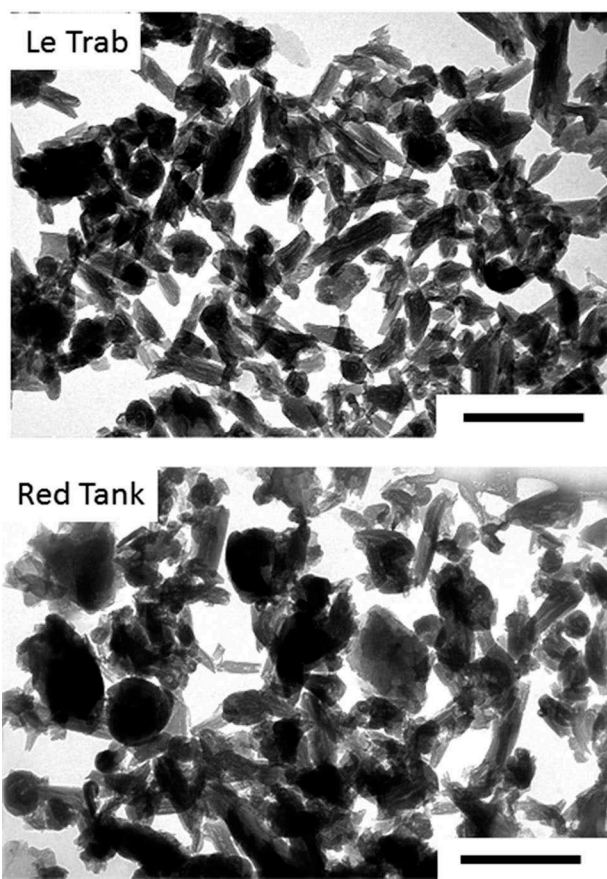
### 2.6. X-ray diffraction (XRD) analysis

The CD-air-dried samples and CD-reduced pressure-dried clay samples were saturated with  $Mg^{2+}$  (non-treated and solvated with formamide) and  $K^+$  (heated to 25, 300 and 550°C) for analysis with a MiniFlex XRD (Rigaku Corp., Tokyo, Japan) using Cu K $\alpha$  radiation generated with a 30 kV accelerating potential and a 15 mA tube current. Samples were step-scanned for 2 s at a 0.02° 2 $\theta$  step with the random orientation method. The CD-air-dried clay fraction (<2  $\mu m$ ) from the Aiken soil was also analyzed by XRD using the same XRD protocols.

## 3. Results

### 3.1. TEM and XRD analysis of LeTrab and Red Tank clay samples

Transmission electron microscopy showed a predominance of tubular morphology with lesser amounts of spheroidal morphology (Fig. 1), which are representative morphologies for halloysite (Joussein *et al.* 2005; Churchman *et al.* 2016; Yang *et al.* 2016). There were no morphological differences between the air-dried and reduced pressure-dried samples (data not shown). No identifiable 2:1 minerals, zeolites or allophane/imogolite phases were observed. We previously reported that concentrations of K (0.08–0.10%  $K_2O$ ), Fe (0.94–1.14%  $Fe_2O_3$ ), and Mg (0.06–0.09%  $MgO$ ) were low in the LeTrab and Red Tank CD-treated clay fractions indicating that they are only a minor structural component of the clay fraction (Takahashi *et al.* 2001).



**Figure 1.** Transmission electron micrographs of the citrate-dithionite-treated clay fractions of LeTrab 2Bt3 and Red Tank 2Bt3 samples. Reference scales are 0.5  $\mu\text{m}$ .

The CD-air dried clay samples from both LeTrab and Red Tank soils showed a prominent 1.0-nm peak with Mg-saturation (Fig. 2). Upon K-saturation and heating to 300°C, the 1.0-nm peak collapsed to 0.7 nm, and the peak disappeared after heating to 550°C. The combined TEM images and XRD patterns confirmed the dominance of halloysite (1.0 nm) in the clay fraction. The CD-reduced pressure-dried samples showed a 0.7-nm peak without a 1.0 nm peak, indicating that the interlayer water was effectively dehydrated by reduced-pressure drying. The 0.7-nm peak largely expanded to 1.0-nm with formamide treatment indicating that the mineral retained the fundamental nature of halloysite.

### 3.2. Permanent and variable negative charge characteristics of LeTrab and Red Tank clay fractions

Permanent and variable negative charges determined by the method of Anderson and Sposito (1991) are shown in Table 2. The permanent negative charge for air-dried LeTrab and Red Tank clays decreased by 16% (from 7.7 to 6.5  $\text{cmol}_c \text{kg}^{-1}$ ) and 27% (from 9.5 to 6.9  $\text{cmol}_c \text{kg}^{-1}$ ) upon reduced-pressure drying, respectively. In contrast, free iron oxide removal with CD increased the permanent charge by 63% (from 7.7 to 12.6  $\text{cmol}_c \text{kg}^{-1}$ ) and 80% (from 9.5 to 17.1  $\text{cmol}_c \text{kg}^{-1}$ ) for the LeTrab and Red Tank clay fractions, respectively. Reduced pressure-drying of CD treated clays decreased the permanent charge of the LeTrab clays from 12.6 to 8.4  $\text{cmol}_c \text{kg}^{-1}$  and the Red Tank clays from 17.1 to 10.4  $\text{cmol}_c \text{kg}^{-1}$ .

The variable charge component of both clay samples was also decreased by reduced pressure drying; from 13.6 to 8.3  $\text{cmol}_c \text{kg}^{-1}$  for LeTrab and from 10.4 to 7.7  $\text{cmol}_c \text{kg}^{-1}$  for Red Tank. In contrast to the permanent charge, the difference in variable charge values between air dried and CD-air dried samples was small.

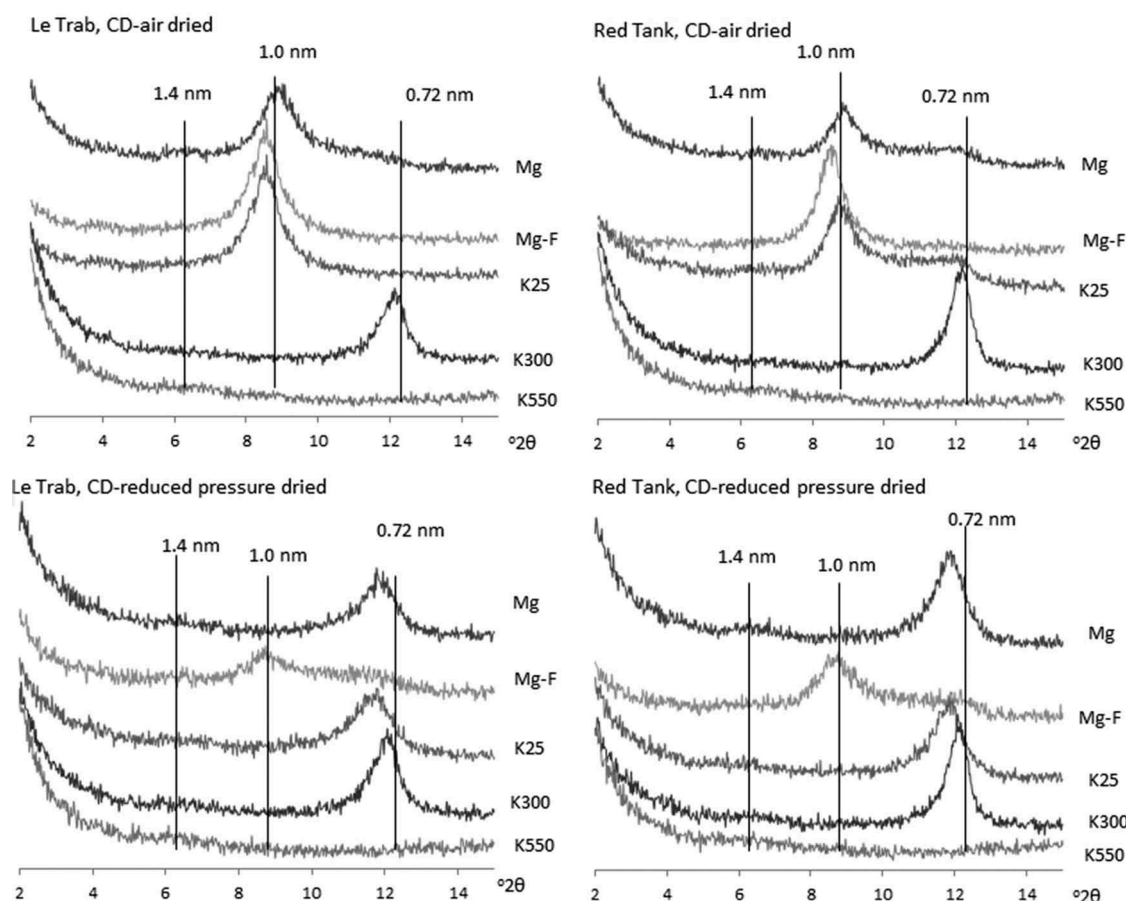
### 3.3. Potassium ion selectivity of LeTrab and Red Tank clay fractions

The variation in the sum of extracted  $\text{K}^+$  and  $\text{Ca}^{2+}$  in the  $\text{K}^+$ - $\text{Ca}^{2+}$  exchange equilibrium study was small (i.e., small SD values) for all treatments (Table 3). This indicates that the preferential adsorption of  $\text{CaCl}^+$  was negligible and  $\text{K}^+$  fixation was not an important factor (Takahashi *et al.* 2001) because the sum of extracted  $\text{K}^+$  and  $\text{Ca}^{2+}$  values is nearly constant across the entire  $\text{K}^+$  vs.  $\text{Ca}^{2+}$  saturation range (Supplementary Fig.1); adsorption of  $\text{CaCl}^+$  would increase the  $\text{K}^+ + \text{Ca}^{2+}$  values in the lower  $\text{K}^+$  saturation range and  $\text{K}^+$  fixation would decrease the  $\text{K}^+ + \text{Ca}^{2+}$  values in the higher  $\text{K}^+$  saturation range. The sums of exchangeable  $\text{K}^+ + \text{Ca}^{2+}$  were 11.7 and 13.3  $\text{cmol}_c \text{kg}^{-1}$  for air-dried LeTrab and Red Tank samples, respectively. These values were 1.4–1.5 times larger than the measured permanent charges, but 55–67% of the total negative charges (permanent + variable; Table 2). The trend for changes in the exchangeable  $\text{K}^+ + \text{Ca}^{2+}$  values across the various clay pretreatments was similar to changes in the permanent ( $r^2 = 0.69$  and 0.71 for LeTrab and Red Tank) and total negative charges ( $r^2 = 0.33$  and 0.83 for LeTrab and Red Tank) (Tables 2 & 3). Reduced pressure drying decreased the exchangeable  $\text{K}^+ + \text{Ca}^{2+}$  values while the CD treatment increased the values.

Plots of adsorbed  $\text{K}^+$  saturation vs. solution  $\text{K}^+$  saturation and Vanselow ( $K_v$ ) selectivity vs. K-saturation are shown in Fig. 3 and Fig. 4, respectively. The air-dried LeTrab and Red Tank clays showed very high  $\text{K}^+$  selectivity as compared to the non-preferential  $\text{K}^+$ - $\text{Ca}^{2+}$  line. Following either reduced pressure drying or CD treatment, the  $\text{K}^+$  selectivity showed a large decrease for both clay samples. The decreased  $\text{K}^+$  selectivity was generally larger for the reduced pressure drying as compared to the CD treatment (Fig. 4). For example, at a given adsorbed  $\text{K}^+$  saturation level the  $\ln K_v$  for  $\text{K}^+$  selectivity decreased by 2–3, with reduced pressure drying being lower than the CD treatment by  $\sim 1$ , except for adsorbed  $\text{K}^+$  saturation levels greater than 0.3 for the Red Tank clays which had similar values between the reduced pressure drying and CD treatments (Fig. 4). Reduced pressure drying of the CD treatment further decreased the  $\text{K}^+$  selectivity, indicating a synergist effect of the combined treatments. The  $\text{H}_2\text{O}_2$  treatment slightly increased the  $\text{K}^+$  selectivity, possibly due to removal of organic matter (2–3 g C  $\text{kg}^{-1}$ ) that would exhibit a preferential affinity for divalent cations such as  $\text{Ca}^{2+}$ .

### 3.4. TEM images and XRD patterns for the clay fraction of Aiken soil

The TEM images of the clay fraction for the Aiken Bt3 and Bt4 horizons showed the predominance of tubular morphology similar to the clay fraction of the LeTrab and Red Tank samples (Fig. 5). The XRD patterns for the clay fractions of the Aiken soils showed distinct 0.7 nm- and 1.4 nm-peaks for Mg-saturation; there was no



**Figure 2.** X-ray diffractograms of CD-air dried and CD-reduced pressure dried clay fractions of LeTrab 2Bt3 and Red Tank 2Bt3 samples.

**Table 3.** Average and standard deviation values of adsorbed  $\text{Ca}^{2+}+\text{K}^{+}$  in  $\text{K}^{+}-\text{Ca}^{2+}$  exchange equilibrium study for clay fractions of LeTrab and Red Tank soils.

Sample	Treatment	Exch. $\text{Ca}^{2+}+\text{K}^{+}$	
		$\text{cmol}_c \text{ kg}^{-1}$	SD
LeTrab	Air-dried	11.7	0.41
	$\text{H}_2\text{O}_2$ -air dried	12.4	0.26
	Reduced pressure-dried	7.8	0.13
	CD-air-dried	17.7	0.07
	CD-reduced pressure-dried	16.4	0.14
Red Tank	Air-dried	13.3	0.20
	$\text{H}_2\text{O}_2$ -air dried	13.2	0.09
	Reduced pressure-dried	8.4	0.04
	CD-air-dried	15.1	0.13
	CD-reduced pressure-dried	12.8	0.16

The values are reported based on the actual treated weight.

distinct peak at 1.0 nm as observed in LeTrab and Red Tank soils (Fig. 6). With formamide solvation, the 0.7 nm-peak partially expanded to 1.0 nm and then disappeared with 550°C heating, indicating the existence of an *in situ* dehydrated halloysite phase. The 1.4 nm-peak collapsed to 1.0 nm with K-saturation and heating (Fig. 6). These characteristics indicate the presence of 2:1 type minerals with appreciable hydroxy-Al interlayering.

### 3.5. Potassium ion selectivity in the fine-earth fraction (<2 mm) of LeTrab, Red Tank and Aiken soils

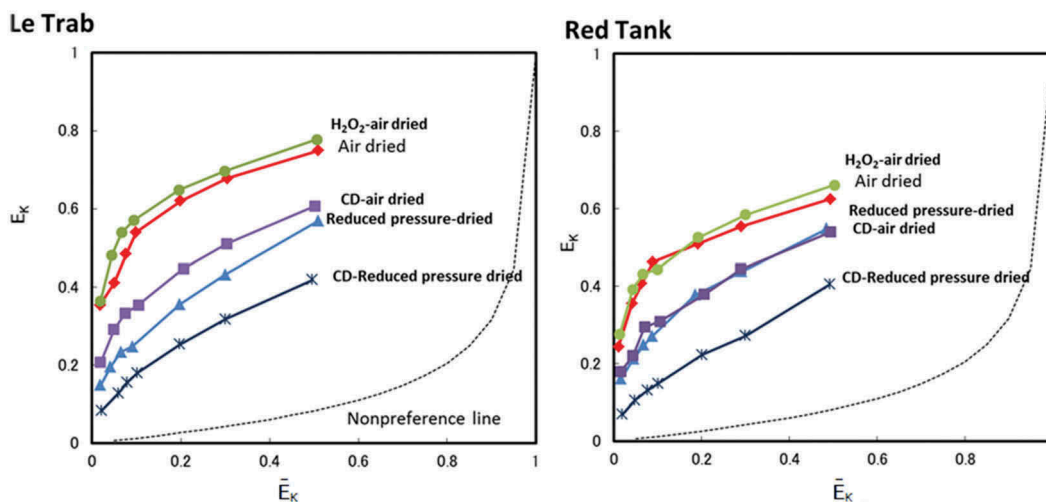
The average values for the sum of extracted  $\text{K}^{+}$  and  $\text{Ca}^{2+}$  in the  $\text{K}^{+}-\text{Ca}^{2+}$  exchange equilibrium study for the <2-mm fraction

were  $11.4 \text{ cmol}_c \text{ kg}^{-1}$  for LeTrab soil and  $10.6 \text{ cmol}_c \text{ kg}^{-1}$  for Red Tank soil (Table 4). In comparison, the values for the Aiken soils were substantially lower ( $7.5$  and  $7.0 \text{ cmol}_c \text{ kg}^{-1}$  for Bt3 and Bt4, respectively) in spite of their similar clay contents and dominance by tubular kaolin minerals. Plots of adsorbed  $\text{K}^{+}$  saturation vs. solution  $\text{K}^{+}$  saturation showed much higher  $\text{K}^{+}$  selectivity in the <2-mm fraction of the LeTrab and Red Tank soils in comparison to the Aiken soils (Fig. 7).

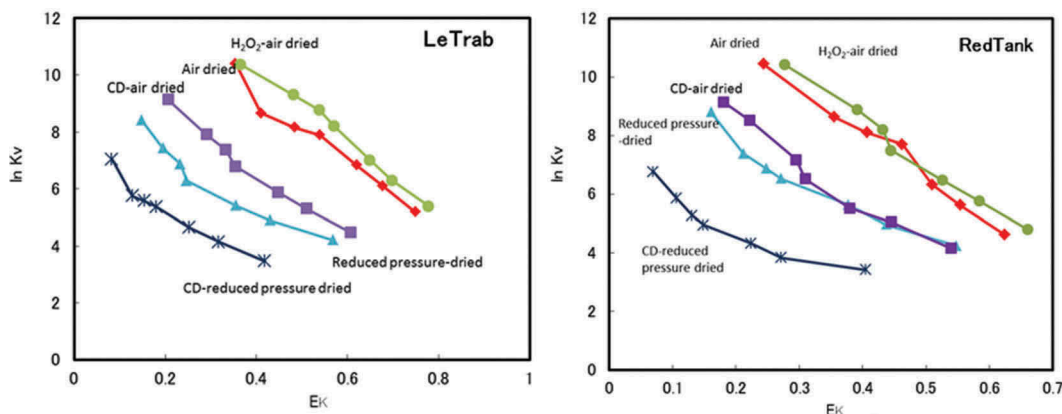
## 4. Discussion

To investigate possible mechanism(s) for the high  $\text{K}^{+}$  selectivity of halloysitic clays (1.0 nm) in the Bt horizons of the LeTrab and Red Tank pedons, we performed charge characterization and  $\text{K}^{+}-\text{Ca}^{2+}$  ion selectivity experiments on the clay fractions following several pretreatments. Previous studies indicated that there were no detectable 2:1 minerals, halloysite-2:1 mixed layer minerals or zeolites in the clay fractions of the LeTrab and Red Tank soils (Takahashi *et al.* 1993; Takahashi *et al.* 2001). We also compared the  $\text{K}^{+}$  selectivity of these soils to a soil (Aiken Bt horizons) dominated by dehydrated tubular halloysite (0.7 nm expandable to 1.0 nm with formamide treatment) and containing a minor component of 2:1 layer silicates.

In contrast to the idealized halloysite structure, permanent negative charge measurements following several clay pretreatments indicated the presence of considerable permanent



**Figure 3.** Equivalent fractions of adsorbed  $K^+$  ( $E_k$ ) vs. equivalent fraction of solution  $K^+$  ( $\bar{E}_k$ ) for clay fractions with the treatments. Non-preference line (dashed line) calculated following Sposito *et al.* (1983).



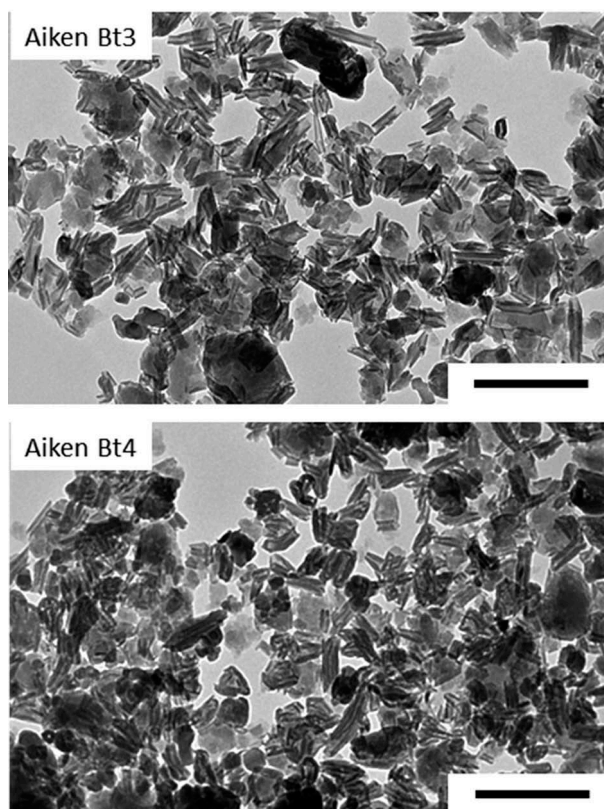
**Figure 4.** The Vanselow selectivity coefficient ( $\ln K_v$ ) as a function of the equivalent adsorbed fraction of  $K^+$  ( $E_k$ ) for clay fractions with the treatments.

charge ( $7\text{--}17\text{ cmol}_c\text{ kg}^{-1}$ ) on the LeTrab and Red Tank clay fractions (Table 2). A previous  $^{27}\text{Al}$ -NMR characterization of the Red Tank 2Bt3 clay fraction indicated a poorly ordered halloysite with a tetrahedral Al content of about 2% (i.e., 2%  $\text{Al}^{3+}$  and 98%  $\text{Si}^{4+}$  in tetrahedral sheet) (Takahashi *et al.* 2001). This level of isomorphous substitution could account for  $\sim 15\text{ cmol}_c\text{ kg}^{-1}$  of permanent negative charge (assuming substitution of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in the tetrahedral layer) and is consistent with the value of  $17.1\text{ cmol}_c\text{ kg}^{-1}$  measured in the CD-treated Red Tank Bt3 clay fraction in this study (Table 2). Similarly,  $\text{Fe}^{2+}$  substitution for  $\text{Al}^{3+}$  in the octahedral sheet (Churchman *et al.* 2016) could conceivably contribute 11.6 to  $13.5\text{ cmol}_c\text{ kg}^{-1}$  of permanent charge, assuming that the Fe was associated with isomorphous substitution rather than Fe contaminants from Fe (hydr)oxides. Therefore, permanent charge associated with isomorphous substitution in either the tetrahedral or octahedral sheets or  $\text{Al}^{3+}$  vacancies in the octahedral sheet could contribute to the permanent charge measured in the LeTrab and Red Tank clay fractions.

Bailey (1990) proposed that the interlayer water in halloysite (1.0 nm) is associated with exchangeable cations that

balance the layer charge. The decrease in permanent charge following reduced pressure drying (of both the air dried and CD-air dried treatments) may be attributed to a decrease of ion accessibility to some ion-exchange sites because of inter-layer collapse ( $1.0 \rightarrow 0.7\text{ nm}$ ). This is consistent with the findings that hydrated halloysite (1.0 nm) generally has a larger CEC than dehydrated forms (0.7 nm) (Grim 1968; Norrish 1995). In contrast, the near doubling of permanent charge upon free iron oxide removal was ascribed to an increase of ion accessibility to the interlayer by removal of prominent iron (hydr)oxide coatings that hinder ion diffusion to and from the interlayer (Shao and Wang 1991). Variable charge negative sites were not strongly affected by iron oxide removal, but did demonstrate a large reduction following reduced pressure drying. These variable charge sites are associated with broken bonds at particle edges. Changes in charge characteristics following strong soil drying are commonly reported and attributed to irreversible changes in the chemical (e.g., change in surface coordination) and physical (e.g., decrease in surface area and aggregation) surface properties (Dowling *et al.* 2005).





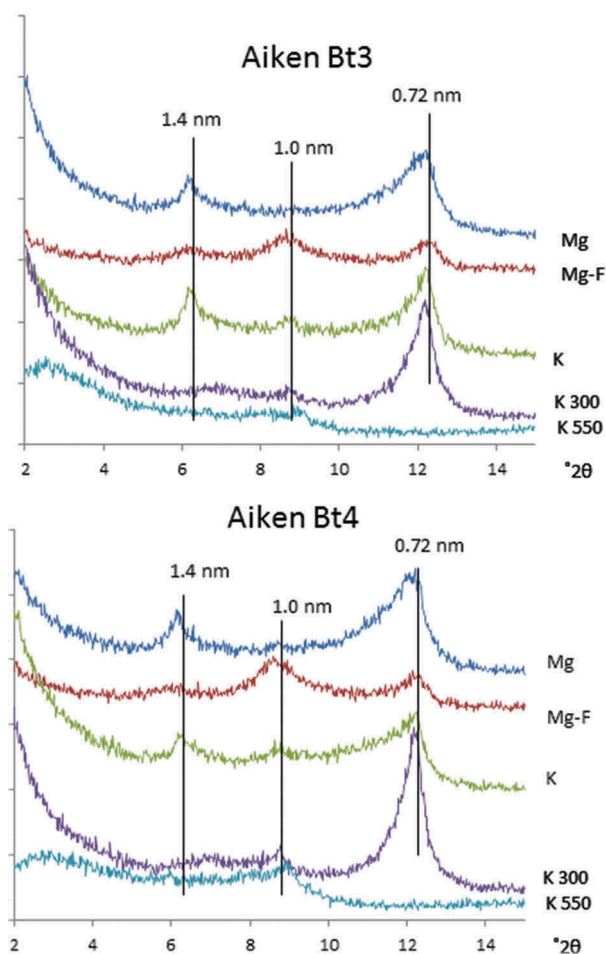
**Figure 5.** Transmission electron micrographs of the citrate-dithionite-treated clay fractions of Aiken Bt3 and Aiken Bt4 soils.

There are several studies of  $K^+$ - $Ca^{2+}$  selectivity for 2:1 clay minerals reported in the literature (Robbins and Carter 1983; Ogwada and Sparks 1986; Feigenbaum *et al.* 1991; Wada and Seki 1994; Bond 1995). In general, when the  $E_K$  is 0.4 in the  $E_K$  vs.  $\ln K_V$  diagram (Fig. 4), the  $\ln K_V$  values are in the range of 2–6 as shown in the literature cited above. In sharp contrast, the clay fractions of the LeTrab and Red Tank samples were much higher, about 11 for LeTrab and 9 for Red Tank (Fig. 4). This literature comparison is also consistent with the differences measured in the <2-mm fraction between the LeTrab/Red Tank soils and the Aiken soils that contained dehydrated halloysite and a minor 2:1 layer silicate component. However, the hydroxy-Al interlayering of the 2:1 layer silicates in the Aiken soil may change the  $K^+$ - $Ca^{2+}$  selectivity dynamics compared to 2:1 layer silicates having no hydroxy-Al interlayers. Given that the pH range of the LeTrab/Red Tank soils (5.9–6.2) were similar to the Aiken soil horizons (5.8–5.9), it may be expected that any 2:1 layer silicates present in the LeTrab/Red Tank soils would also contain hydroxy-Al interlayers as in the Aiken soil horizons. Thus, we interpret these results to suggest that the mechanism for high  $K^+$  selectivity in the LeTrab and Red Tank clay fractions is not solely due to 2:1 clay mineral impurities.

If the halloysite is the source of the high  $K^+$  selectivity, the halloysite should possess permanent negative charge and the basal spacing (0.7 nm or 1.0 nm) should be a key factor affecting the accessibility of  $K^+$  to the permanent charge sites. The evidence obtained in this study suggests the presence of permanent negative charge that increases following

removal of free iron oxides. Following CD treatment,  $K^+$  selectivity decreased (Figs. 3 and 4) and the sum of exchangeable  $Ca^{2+}+K^+$  increased. This indicates that the iron minerals may physically block the exchange sites of halloysite and repulse cations, especially divalent cations, due to their positive charges (Escudey and Galindo 1988; Takahashi *et al.* 2001). Iron (hydr)oxides, which possess a zero point of charge (ZPC) of  $\sim 8.8$  (Sverjensky and Sahai 1996), have a net positive surface charge at the ambient pH of our soils (Table 1). Thus, charge-to-charge repulsion could make access of divalent cations (e.g.,  $Ca^{2+}$ ) to the internal negative surface charge sites more difficult than for monovalent cations (e.g.,  $K^+$ ).

With reduced-pressure drying and dehydration of interlayer waters, the  $K^+$  selectivity showed a large decrease (Figs. 3 and 4). The selectivity for Aiken soils, whose halloysite was naturally dehydrated, was far lower compared to those of LeTrab and Red Tank soils, but similar to that of the reduced pressure-dried LeTrab and Red Tank clay fractions. These results provide strong evidence that the hydrated form of halloysite (1.0 nm-basal space) was an important factor affecting the high  $K^+$  selectivity in this study. The potassium ion has a comparatively lower hydration energy and easily dehydrates to monatomic  $K^+$  that can selectively enter the interlayer of halloysite (1.0 nm) relative to hydrated  $Ca^{2+}$ . With the dehydration of the halloysite and the collapse of the interlayer,  $K^+$  appears to have a more difficult time accessing the permanent charge sites in the interlayer and the selectivity of  $K^+$  is correspondingly decreased. This mechanism contributing to  $K^+$  selectivity in hydrated halloysite has potential similarities to the  $K^+$  selectivity associated with ion channels in



**Figure 6.** X-ray diffractograms of CD-air dried clay fractions of Aiken Bt3 and Aiken Bt4 soils.

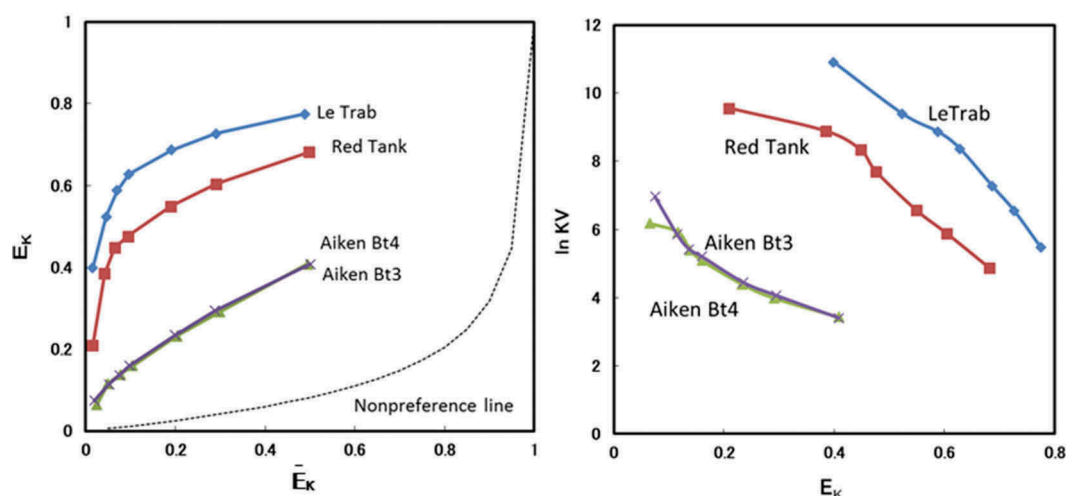
**Table 4.** Average and standard deviation values of adsorbed  $\text{Ca}^{2+}+\text{K}^{+}$  in  $\text{K}^{+}-\text{Ca}^{2+}$  exchange equilibrium study for fine earth fractions (<2 mm) of LeTrab, Red Tank and Aiken soils.

Soil Sample	Exch. $\text{Ca}^{2+}+\text{K}^{+}$ $\text{cmol}_c \text{ kg}^{-1}$	SD
LeTrab 2Bt3	11.4	0.27
Red Tank 2Bt3	10.6	0.12
Aiken Bt3	7.5	0.05
Aiken Bt4	7.0	0.09

human nerve and muscle tissues (Degrève *et al.* 1996). The selectivity of these channels was related to the hydration structure of ions with the weakly hydrated  $\text{K}^{+}$  being selectively transported (as opposed to the larger strongly hydrated  $\text{Na}^{+}$ ) through ion channels with diameters of 0.3 nm. The diameter of these  $\text{K}^{+}$ -selective ion channels is equivalent to the 0.3 nm difference in the interlayer distance between hydrated (1.0 nm) and dehydrated (0.7 nm) halloysite/kaolin phases. Thus, the ionic diameter of  $\text{K}^{+}$  relative to the hydrated halloysite interlayer spacing may play an important role in its preferential selectivity versus the much larger hydrated  $\text{Ca}^{2+}$ .

TEM observation showed that the clay fractions of LeTrab and Red Tank soils were dominated by tubular halloysite. Tubular halloysite has the structure of several concentric

layers of 1:1 aluminosilicates in a rolled internal configuration when viewed in cross-section (e.g., similar to a roll of paper). When the tubular halloysite (1.0 nm) dehydrates upon drying, parts of the layer structure may become disordered resulting in an irregular interlayer spacing. Dehydration was shown to expand the diameter of individual halloysite tubes, and layers within the rolls comprising the tubes became separated to form large voids between the individual sheets and slit-shaped pores along the tube axis (Kohyama *et al.* 1978; Kohyama *et al.* 1982; Churchman *et al.* 1995). Thus, some parts of the dehydrated halloysite interlayer may expand allowing access to hydrated  $\text{Ca}^{2+}$ , and therefore result in a decrease in  $\text{K}^{+}$  selectivity. Similarly, some parts of the interlayer may become blocked due to the collapsed interlayer resulting in the loss of preferential access to  $\text{K}^{+}$  and also to the loss of accessible permanent charge to all ions. The much lower sum of extracted  $\text{K}^{+}$  and  $\text{Ca}^{2+}$  measured for the naturally dehydrated halloysite in the Aiken soil compared to the LeTrab/Red Tank soils (Table 4) may also result in part from *in situ* dehydration and lack of access of cations to interlayer permanent charge sites. Thus, the concomitant decrease of  $\text{K}^{+}$  selectivity and permanent charge by the reduced-pressure drying is consistent with a high-charge,  $\text{K}^{+}$ -selective halloysite (1.0 nm).



**Figure 7.** Equivalent fractions of adsorbed K<sup>+</sup> (E<sub>K</sub>) vs. equivalent fraction of solution K<sup>+</sup> (E<sub>K</sub>-bar) (left) and the Vanselow selectivity coefficient (ln K<sub>V</sub>) as a function of the equivalent adsorbed fractions of K<sup>+</sup> (E<sub>K</sub>) (right) for fine earth fractions (<2 mm). Non-preference line (dashed line) calculated following Sposito *et al.* (1983).

There have been previous reports indicating that halloysite with a basal spacing of 1.0 nm was responsible for high K<sup>+</sup> selectivity of soils. Delvaux *et al.* (1990a), (1990b) and Ndayiragije and Delvaux (2004) showed a close correlation between the amounts of halloysite and K<sub>V</sub> values and considered that the selectivity was derived from hydrated halloysite (1.0 nm). Some other studies have reported that soils with dehydrated halloysite (0.7 nm) also showed high K<sup>+</sup> selectivity (Fontaine *et al.* 1989; Wada and Odahara 1993). However, in the study of Fontaine *et al.* (1989), the existence of halloysite-smectite mixed layer clays was suggested and may contribute to the high K<sup>+</sup> selectivity. Overall, there is paucity of evidence for high K<sup>+</sup> selectivity in soils dominated by dehydrated halloysite (0.7 nm).

## 5. Conclusions

The results obtained in this study indicate the presence of a K<sup>+</sup>-selective halloysite phase having considerable permanent negative charge. The K<sup>+</sup> selectivity of the halloysite was strongly linked to its interlayer spacing (1.0 vs. 0.7 nm). The 0.3 nm larger interlayer spacing in hydrated halloysite appears to contribute to K<sup>+</sup> selectivity as the weakly hydrated K<sup>+</sup> can readily dehydrate and enter into channels with a 0.3 nm diameter while the strongly hydrated Ca<sup>2+</sup> is too large to enter, as has been demonstrated for K<sup>+</sup> selective ionic channels in human muscle and nerve tissues. Thus, ion hydration energy plays an important role as the ions must lose their hydration shell to enter the halloysite interlayer space. The role of Fe (hydr)oxides was also shown to strongly affect the permanent charge and K<sup>+</sup> selectivity. The Fe (hydr)oxides appear to physically block the exchange sites of halloysite and repulse cations, especially divalent cations, due to their positive charge. Verification of these mechanisms to explain high K<sup>+</sup> selectivity for halloysite is required for a variety of other halloysite-rich soils experiencing high K<sup>+</sup> selectivity.

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