

# Charge properties and potassium fixation by clay from Thai Vertisols

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## Abstract

Potassium fixation by soil clays dominated by smectite was examined in order to relate clay mineralogy and charge properties (total CEC and tetrahedral CEC) of clays from Thai Vertisols to K fixation capacity. Clays from representative Thai Vertisols were analysed for mineralogical properties including total CEC, tetrahedral CEC, and K fixation capacity by wet and dry procedures. The results show that beidellite is the dominant smectite species and has high total CEC. Tetrahedral CEC is poorly related to total CEC. Poor statistical relationships between both CEC values and K fixation are observed and reflect the uniformity of the soil clay mineralogy. Kaolinite, illite and vermiculite are associated clay minerals in the clay fraction. Vermiculite contributes to the K fixation by upland soil clays. K fixation by beidellite in Thai Vertisols is small with most K remaining exchangeable with  $\text{NH}_4^+$ , a little K being fixed. Potassium fixation by dry-wet cycles was more in soil clays from upland Vertisols than lowland Vertisols reflecting the presence of vermiculite.

## Key Words

Charge properties, potassium fixation, Thai Vertisols

## Introduction

Fixation and release of K by 2:1 layer silicates are very important processes influencing the availability of K to plants. Stage of weathering, types, and amounts of primary and secondary K-bearing minerals have been suggested as important factors affecting K equilibrium in soil. The magnitude of K-release and fixation appears to be directly related to the clay mineralogy. Illite is the source of K-released (Dowdy and Hutcheson 1963). Smectite in most Vertisols is Fe-rich, tetrahedrally high-charge beidellite. Beidellite and vermiculite are known to have more capacity to fix K than other clay minerals. Total charge and the distribution of the charge between the tetrahedral and octahedral sheets are also important properties that contribute to K fixation by 2:1 layer silicates. Vertisols are the important soils in Thailand being used for various field crops and they receive large K fertilizer applications. This study aimed at (i) determining charge properties of clays obtained from representative Thai Vertisols (ii) determining the effects of amount of added K and wetting-drying cycles on K fixation by soil clays and (iii) relating charge properties of soil clays to K-fixation by these soils.

## Methods

The clay fraction ( $< 2 \mu\text{m}$ ) which is dominated by smectite ( $> 60\%$ ) were extracted from representative Thai Vertisols which were categorized into lowland (Ban Mi (Bm1, Bm2), Wattana (Wa), Lop Buri (Lb1, Lb2), Chong Khae (Ck)) and upland ((Buri Ram (Br), Chai Badan (Cd1, Cd2), Wang Chomphu (Wc1, Wc2), Lop Buri (Lb3), Samo Thod (Sat1, Sat2)). Kaolinite, illite, and vermiculite are associated with smectite in these soils. The Greene-Kelly test was employed to identify the location of charge and species of smectite, which is beidellite (Chittamart *et al.* 2010). The chemical composition of the Ca-saturated clay fraction was determined by X-ray fluorescence (XRF) and used for calculation of structural formulae. Total CEC of Na-saturated clay was measured by the silver thiourea method (Rayment and Higginson 1992). Tetrahedral CEC was measured by the silver thiourea method after saturating the clay with 3 M LiCl and heating at 300°C overnight in order to neutralize octahedral charge (Lim and Jackson 1986). Potassium fixation was determined for soil clay following the method proposed by Bouabid *et al.* (1991). Four milliliters of KCl solutions containing three levels of K (K1 = 3.32 mg, K2 = 9.96 mg, K3 = 19.92 mg) were added to 500 mg of Na-saturated clay. The suspensions were shaken for 16 h at room temperature and exchangeable K was extracted three times with 10 ml of 1 M  $\text{NH}_4\text{OAc}$  at pH 7.0. The amount of K not displaced by  $\text{NH}_4$  was assumed to be fixed. To study the effects of wetting and drying in the presence of K, 250 mg Na-saturated clay were incubated three times with 20 ml of 1 M KCl solution and subjected to wetting in 20 ml of DI water and drying at 60 °C. Twenty five wetting and drying cycles were performed. After reaction, samples were washed several times with distilled water until chloride free, and then saturated with  $\text{Ca}^{2+}$  in 0.5 M  $\text{CaCl}_2$  solution. Oriented specimens were prepared, treated with glycerol and then analyzed by XRD.

## Results

### *Clay Mineralogy*

Clay fractions of these soils are dominated by smectite as indicated by the expansion after Mg-saturation and glycerol treatment. Kaolinite is present in small amounts in all clay fractions. Vermiculite occurs in small amounts (< 5-20 %) in the clay fraction of upland Vertisols which developed on residuum of andesite and basalt (Chai Badan (Cd2), Samo Thod (Sat1, Sat2)). Quartz occurs in all clay fractions and is dominant in the silt fraction of these soils. Results of the Greene-Kelly test indicate that all smectite behaved as beidellite indicated with re-expansion after Li-saturation, heating at 300 °C and glycerol solvation. The Greene-Kelly test also indicates that charge originates mainly in the tetrahedral sheet.

### *Chemical composition*

The chemical composition of clay was corrected for relative percentages of mineral impurities determined by XRD and the structural formula of smectite was calculated. These data show that the beidellite has a quite constant chemical composition. Calcium, Na and K are allocated as exchangeable cations in calculated structural formulas (Laird 1994). Plot of major elements from tetrahedral and octahedral sheets  $[Al^{VI}/(Al^{VI}+Fe^{VI})]$  versus  $[Al^{IV}/(Al^{IV}+Mg^{VI})]$  (Figure 1.1) shows that all the samples have an iron rich beidellite composition. The structural formulas show that negative charges mostly originated in the tetrahedral sheet and thus confirm the result of the Greene-Kelly test. Beidellite in these Thai Vertisols has a high Fe content and low Mg content in the octahedral sheet. Therefore, the oxidation state of iron in the beidellite structure will affect fixation and release of interlayer  $K^+$  and  $NH_4^+$  (Barshad and Kishk 1970). This mechanism may be important for lowland Thai Vertisols which are used for paddy rice cultivation. Long waterlogging during rice cultivation practices may induce structural Fe reduction and the change in layer charge may increase K fixation capacity of these soils (Khaled and Stucki 1991).

### *Charge properties and K fixation*

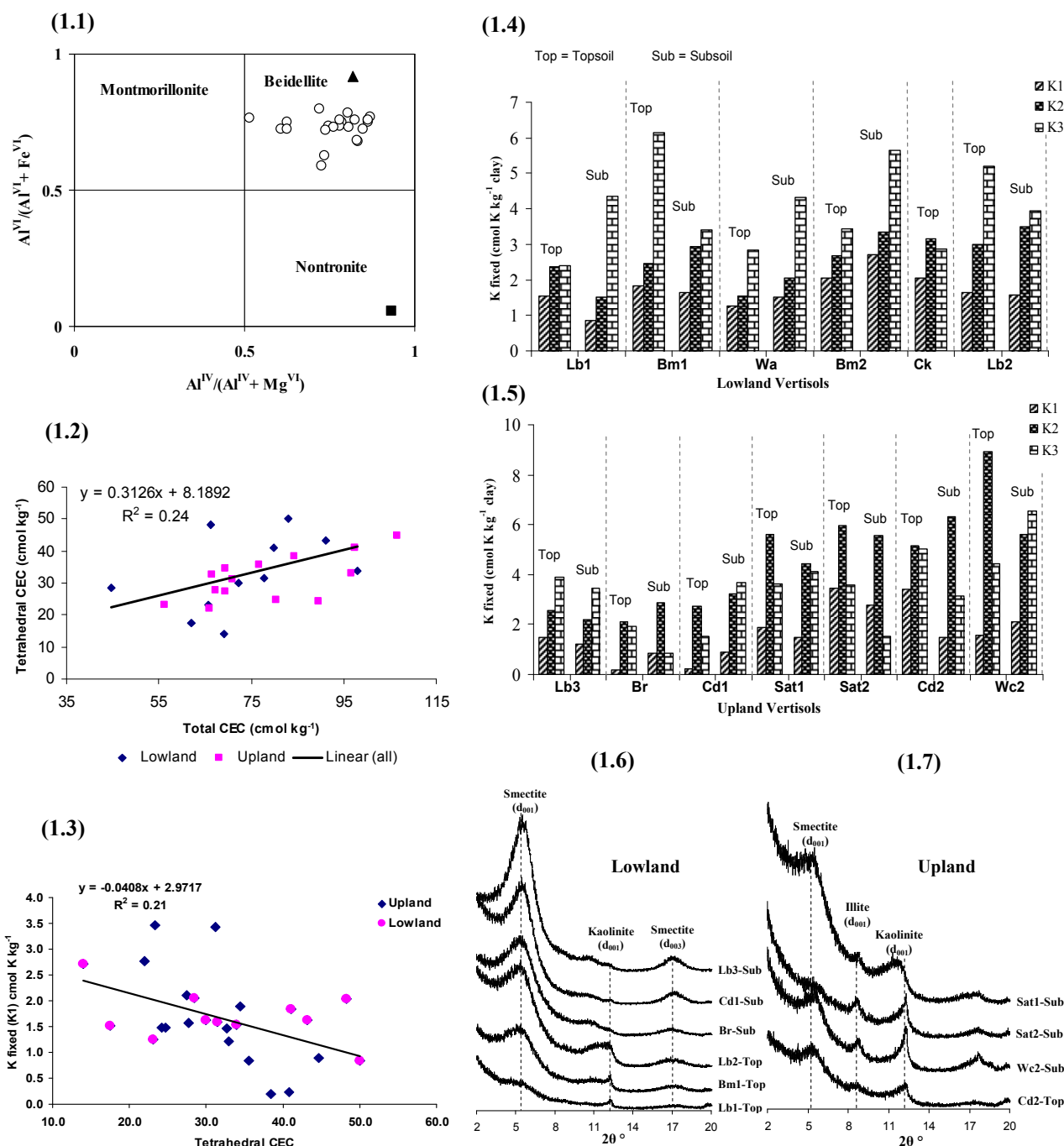
The total CEC refers to the total charge originating from interlayer, edge, and surface charged sites. The CEC values of these clay fractions are mostly very high (44.6-106.6 cmol/kg) reflecting high smectite content. Tetrahedral CEC values ranges from 14-50 cmol/kg based on the CEC of Li-treated and heated clays. The relationship between total CEC and tetrahedral CEC ( $R^2=0.24$ ) (Figure 1.2) is poor as the clays have a quite uniform composition. The variation of CEC values of these clay fractions partly reflects the presence of associated minerals. High proportions of kaolinite and illite which have lower CEC than smectite reduce CEC values (both total CEC and tetrahedral CEC) of clay samples. However the tetrahedral CEC tends to increase with increasing total CEC indicating that charge is mostly located in the tetrahedral layer of smectite structure that can be confirmed by Greene-Kelly test. In fact, ideal beidellite with tetrahedral charge > 50% is rarely found in soils. The determination of charge by CEC determination contributes error to the identification soil smectite species because of the effect of impurities. The combination of the Greene-Kelly test, layer charge measurement, CEC measurement and chemical analysis is recommended for detailed identification of soil smectite.

There is no relationship between K-fixed and total CEC or tetrahedral CEC because K was almost completely exchanged by  $NH_4^+$  (Figure 1.3). Potassium fixation capacity by clays is quite different for lowland and upland Vertisols. Clays from lowland Vertisols shows the amount of K fixed increased with increasing of quantity of K added ( $K1 < K2 < K3$ ). Similar results were found by Bouabid *et al.* (1991) using clay minerals from soils of Morocco in which smectitic soil clays and vermiculitic soil clays fixed much more K than soil clays with mixed mineralogy and clays from Thai Vertisols. Lowland Vertisols have average fixed-K values of 1.69, 2.60, and 4.05 cmol K/kg for K1, K2, and K3 levels of added K respectively (Figure 1.4). For upland Vertisols, clays have average fixed-K values of 1.64, 4.52, and 3.39 cmol K/kg for K1, K2, and K3 treatments respectively. The differences in amount and K fixation capacity between lowland and upland Vertisols reflect the differences in mineral assemblage. Most sorbed K could be exchanged by  $NH_4^+$  indicating that the smectites do not extensively fix K.

In nature, the presence of highly hydrated cations like Ca, Mg competes and would further reduce fixation of K in these soils. Clays from upland Vertisols have higher fixed-K values than clays from lowland Vertisols, reflecting the presence of vermiculite especially in Sat1, Sat2, Cd2 and Wc2 soils along with the soils developed under drier condition (Figure 1.5).

The effect of wetting and drying cycles on K-fixation as indicated by XRD shows that for lowland soil smectite reflections do not collapse to 10 Å (Figure 1.6) after wash with  $CaCl_2$  solution indicating that K was exchanged by Ca and not fixed. This behavior indicates that beidellite in these soils does not fix K. In contrast, beidellite in upland soil clays associated with vermiculite shows 10 Å peak after wetting-drying

cycles, washing with CaCl<sub>2</sub> and solvating with glycol. Wet-dry cycles may have altered smectite to illite (Figure 1.7).



**Figure (1.1)** Plot of major elements calculated from structural formula in tetrahedral and octahedral sheets showing beidellite composition, **(1.2)** Relationship between tetrahedral CEC and total CEC, **(1.3)** Relationship of K fixation and tetrahedral CEC, **(1.4, 1.5)** K fixed for the three levels of K added (K1, K2, K3) of lowland soil clays and upland soil clays respectively, **(1.6, 1.7)** XRD pattern showing effect of wetting and drying on K fixation by smectite from lowland and upland Vertisols respectively, (Ca and glycerol saturated samples).

## Conclusion

Clay in Thai Vertisols is dominated by beidellite. Beidellite in these soils has a high capacity to retain and exchange cations but does not fix substantial amount of K. The magnitude and location of charge may affect K fixation in smectite, but this study shows that total CEC and tetrahedral CEC have no relationship with K fixation.

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