# Beidellite in tropical savanna soils

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## Introduction

Smectite is the one of most important 2:1 phyllosilicate group minerals in soils and sediments. Smectite is often the most abundant clay mineral in Vertisols and influences shrink-swell properties, causes high cation exchange capacity (CEC) and high specific surface area. These properties are due to the small crystal size of smectite and to negative surface charge so that smectite dominates the cation adsorption chemistry of these soils. Smectite formation in soil occurs when several of the following factors come together: basic parent rocks, poor drainage, low lying topography, high silica activity, high pH, and high concentrations of basic cations (Righi et al., 1998). High charge iron-rich beidellite has been reported as the major clay mineral in Vertisols (Chittamart et al., 2010). This study investigated properties of soil beidellite and the role of this clay mineral in some important tropical soils used for agriculture.

## Materials and Methods

Clay samples were obtained from several horizons of 12 representative Thai Vertisol profiles from lowland (Ban Mi, Bm; Lop Buri, Lb1, Lb2; Chong Khae, Ck) and upland sites (Buri Ram, Br; Chai Badan, Cd1, Cd2; Wang Chomphu Wc1, Wc2; Lop Buri, Lb3; Samo Thod, Sat1, Sat2). A summary of soil properties is given in Table 1. Mineral composition of silt and clay fractions was determined by X-ray diffraction (XRD) on oriented and random powder samples. Chemical composition and cation exchange capacity of clay were determined by X-ray fluorescence (XRF) and silver thiourea exchange (AgTU), respectively. Dehydration and dehydroxylation were determined by thermogravimetric analysis (TG/DTG).

## Results and Discussion

***Mineral composition.*** XRD analysis of 52 clay fractions from the Thai Vertisols showed that smectite is the dominant phyllosilicate in all soil profiles especially in Lb3, Br, and Cd1 profiles (Fig. 1). The Greene-Kelly test on oriented clay specimens demonstrated that the smectite in these soils is beidellite. Kaolinite occurs in all clay samples and is abundant in Ck, Sat1, Sat2 profiles. Illite occurs in Ck and vermiculite occurs in Sat (1, 2) and Cd2 profiles. Quartz occurs in all clay samples and is abundant in the silt fraction. Feldspar occurs in the silt fraction of all upland Vertisols.

***Beidellite formation and its role in soils.*** The octahedral occupancy of smectite was determined by measurement of the spacing of the $d_{060}$ peak in XRD patterns of random powder clay. Beidellite in these soils shows values ranging from 1.494-1.504 Å (Fig. 2a). The *b*-dimension thus ranged from 8.964-9.024 Å which reflects the occupancy by $Fe^{3+}$ of the octahedral sites (Fig. 2b).

Table 1. Summary of soil properties of 12 Thai Vertisols profiles.

| Soil Properties | Lowland Vertisols (n=30) | | | Upland Vertisols (n=52) | | |
|---|---|---|---|---|---|---|
| | Min | Mean | Max | Min | Mean | Max |
| pH ($H_2O$) | 5.0 | 7.5 | 8.4 | 5.6 | 7.7 | 8.7 |
| CEC ($NH_4OAc$ 7.0) | 17.91 | 43.37 | 69.75 | 22.33 | 49.71 | 96.80 |
| OC (%) | 0.09 | 0.62 | 2.79 | 0.11 | 0.61 | 1.76 |
| Bases (cmol $kg^{-1}$) | | | | | | |
| Ca | 20.4 | 43.9 | 67.0 | 14.5 | 45.5 | 132.4 |
| Mg | 0.03 | 2.71 | 5.51 | 1.57 | 10.4 | 24.9 |
| Na | 0.21 | 2.06 | 10.82 | 0.11 | 1.14 | 5.99 |
| K | 0.04 | 0.11 | 0.33 | 0.03 | 0.12 | 0.30 |
| Sand (g kg-1) | 18 | 100 | 322 | 27 | 212 | 502 |
| Silt (g kg-1) | 79 | 287 | 495 | 29 | 188 | 461 |
| Clay (g kg-1) | 363 | 613 | 878 | 215 | 599 | 910 |
| COLE | 0.08 | 0.22 | 0.34 | 0.03 | 0.22 | 0.32 |

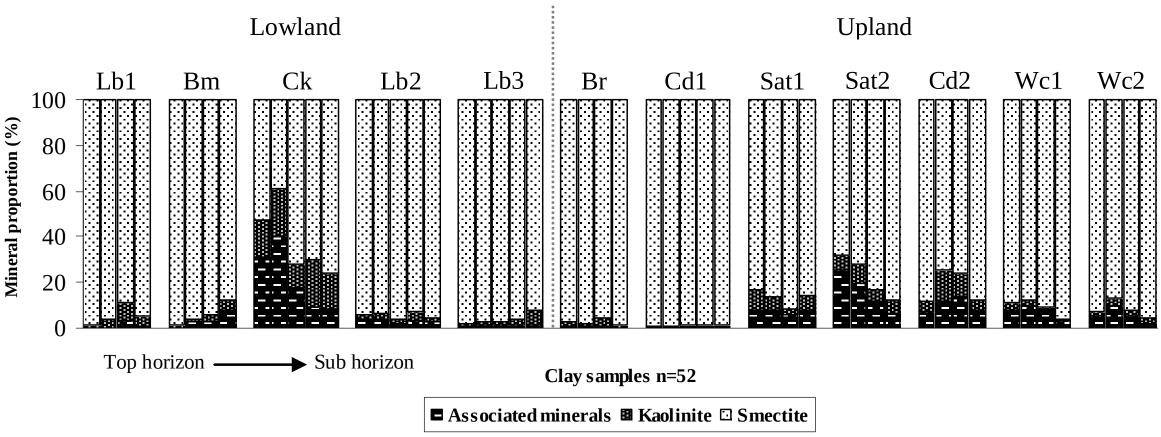


Fig. 1. Semi-quantitative mineral composition of 52 clay samples (< 0.2 μm) from Thai Vertisols.

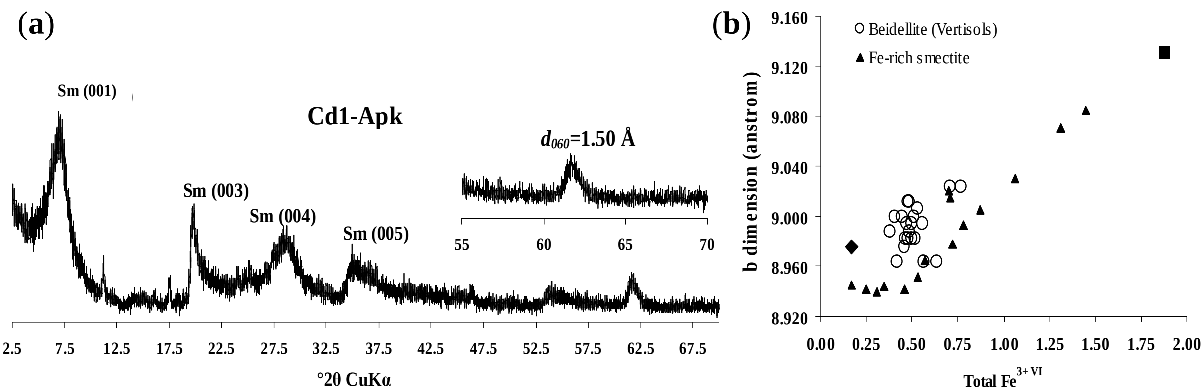


Fig. 2. (a) XRD pattern of an almost pure smectite sample (Cd1-Apk) and (b) relationship of *b*-dimension to Fe in the octahedral site: data for Fe-rich smectite (▲) from the literature (Brigatti, 1983), (◆) reference beidellite and (■) reference nontronite.

The chemical composition of beidellite was corrected for impurities determined by XRD and then the structural formula was calculated. Beidellite in Thai Vertisols has a narrow range of iron contents when compared to some Fe-rich smectites described in the literature. Aluminium is the major cation in the octahedral sheet and is substituted by Fe and Mg. Calcium, Na, and K are the major interlayer cations balancing negative charge. Iron content ranges from 0.38 to 0.76 (eq/f.u.) and has a positive relationship with tetrahedral $Al^{IV}$, in contrast Mg does not show a relationship (Fig. 3a ).

The structural stability determined by derivative themogravimetry (DTG) indicates that reduction of octahedral iron affected the dehydration and dehydroxylation of beidellite as seen in Figure 3b. The DCB-treated beidellite shows two dehydroxylation peaks near 312 °C and 447 °C with 3.55 and 5.49 % weight loss indicating that reduction of some $Fe^{3+}$ to $Fe^{2+}$ induced weaker bonding $Fe^{2+}$ to hydroxyl (Walters and Emmerich, 2007). Beidellite formation in Thai Vertisols reflects the mafic soil parent materials which contribute to neoformation of beidellite in an alkaline soil system. The semi-arid climate contributes to preservation of cations in the soil for beidellite formation.

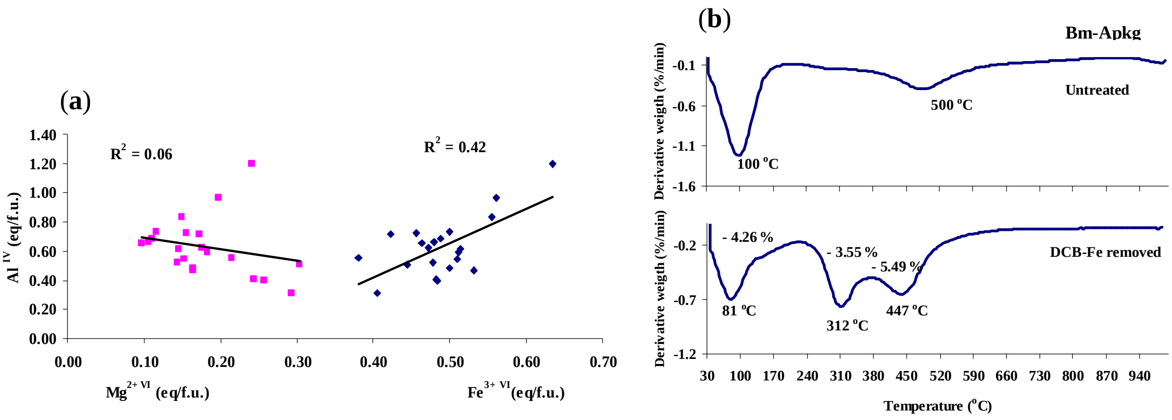


Fig. 3. (a) Relationships of Fe and Mg in the octahedral site with tetrahedral charge ($Al^{IV}$), (b) DTG curves showing the effect of reduction of Fe by dithionite citrate-bicarbonate on the thermal stability of beidellite in Bm-Apkg.

***Role of beidellitic clay in soils.*** Clay fractions in these soils have high CEC values ranging from 34.3 up to 115.9 cmol $kg^{-1}$, which is very high. Clay content has a positive relationships to CEC, coefficient of linear extensibility (COLE) and basic cations (sum bases) (Fig. 4). High charge beidellite can take up much water in the interlayer (see Fig. 3b for water lost at low temperature) contributing to the high shrink-swell property and also leads to some practical agronomic problems because of the development of very hard structure and stickiness, so the soils may be difficult to plow or can only be tilled when at a narrow range of moisture contents (Dixon, 1991).

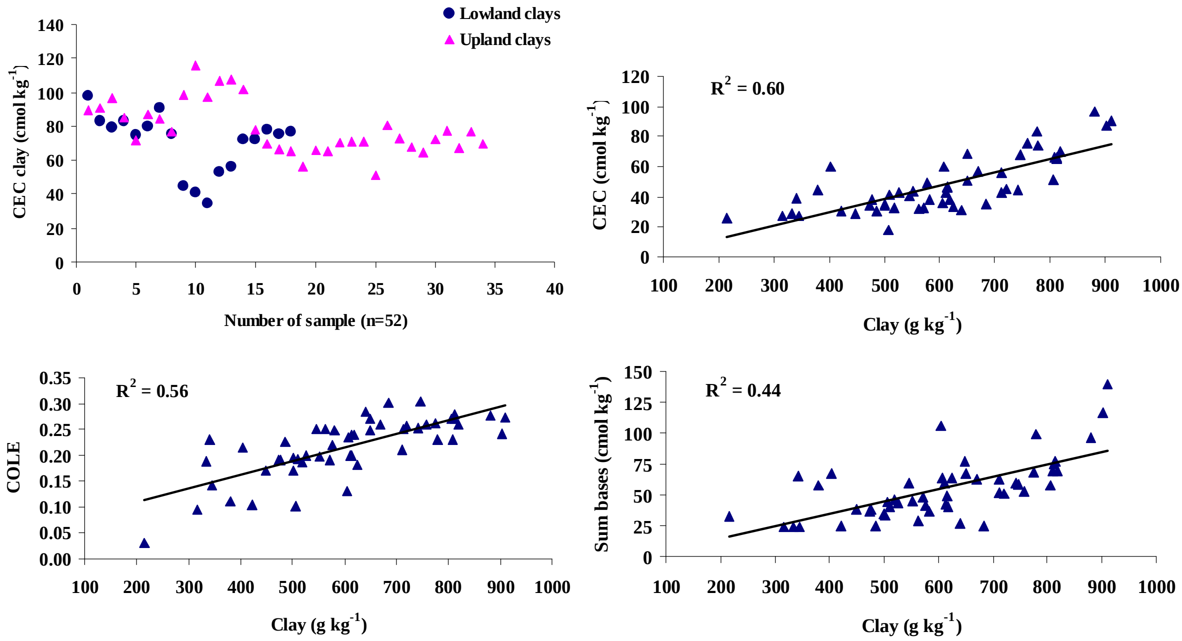


Fig. 4. Cation exchange capacity of samples and relationships between clay content and some important soil properties.

## Conclusions

The important formation factors of beidellite in Thai Vertisols are mafic soil parent materials which contribute high Si, Al, Fe, Mg and Ca for neoformation and the stability of high charge beidellite in alkaline soils with restricted drainage. The high cation exchange capacity is an important property for retaining plant nutrients (e.g. $NH_4^+$ $K^+$, $Ca^{2+}$ $Mg^{2+}$) and other metals. These distinctive positive fertility properties make these soils a valuable resource in tropical agriculture production systems.

## Acknowledgement

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