

TECHNICAL ARTICLES

HEATS OF K/CA AND K/Pb EXCHANGE IN TWO TROPICAL SOILS AS MEASURED BY FLOW CALORIMETRY¹

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Flow calorimetry can provide useful information about surface chemical reactions in soils that cannot be obtained readily by other methods. When flow calorimetry is conducted over a range of surface coverages, different sorption heats can be calculated to yield information about how binding energies vary with coverage, i.e., surface heterogeneity. The purpose of this study was to determine heats of exchange for K/Ca and K/Pb systems using flow calorimetry and to evaluate the degree of surface heterogeneity with respect to cation exchange. Surface horizon samples from a Typic Acrorthox and Typic Tropohumult from Puerto Rico were used. Lead was adsorbed specifically in both soils, but no adsorption heat was detected for this reaction in either soil. However, heats associated with reversible cation exchange between K and Pb were observed. Heats for K/Ca exchange were greater than those generated for K/Pb exchange in both soils. Heats of exchange were greater in the Ultisol than in the Oxisol. The differential heats of exchange were independent of exchange composition for both K/Pb and K/Ca exchange in the Oxisol, indicating that all cation exchange sites were similar energetically. In the Ultisol, the differential heats of exchange increased as exchangeable K decreased, indicating that the exchange sites were not similar energetically. These differences were attributed to the presence of smectite in the Ultisol, which was able, in part, to collapse when saturated with K. (Soil Science 2002;167:773-781)

Key words: Enthalpy, ion-exchange, surface heterogeneity.

FLOW calorimetry provides a direct and quantitative measure of the heat of a reaction at a soil surface (Rhue et al., 2002). Coupled with other macroscopic and spectroscopic techniques, flow calorimetry can provide useful information about surface chemical reactions in soils that cannot readily be obtained by other methods. For example, flow calorimetry combined with measure-

ments of surface coverage can yield information about how binding energies vary with saturation of reactive surface sites, i.e., surface heterogeneity. Thus, different types of exchange/sorption sites may be identified within a heterogeneous structure such as soil (Goulding, 1983).

To our knowledge, no research has measured the surface heterogeneity of soils using flow calorimetry, nor has anyone studied K/Pb and K/Ca systems using this technique. Lead was chosen because it is an important cationic contaminant in soils worldwide (Brown et al., 1999; Nriagu, 1998) and is known to undergo both specific and nonspecific adsorption reactions in soil. Calcium, on the other hand, does not adsorb specifically to soil surfaces and is commonly found in high relative concentrations on soil

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cation exchange sites (McBride, 1994; Sparks, 1995). Specific objectives of this study were (i) to measure integral heats of adsorption associated with K/Ca and K/Pb exchange using flow calorimetry and (ii) to derive information about the heterogeneity of cation exchange sites in these soils from the differential heats of adsorption.

METHODS AND MATERIALS

The surface horizons (0–15 cm) of two tropical soils from Puerto Rico were sampled between 1996 and 1998, air dried, and sieved to obtain aggregates between 0.25 and 0.50 mm. An Oxisol (clayey, oxidic, isohyperthermic Typic Acrorthox), sampled near Mayaguez on the west coast, and an Ultisol (clayey, mixed, isohyperthermic Typic Tropohumult), taken from the central mountainous area near Corozal, were used. Tropical soils were selected for study because, relative to their temperate region counterparts, much less is known about K/Ca and K/Pb exchange in these systems. Mineralogical and chemical properties of these soils reported by Appel and Ma (2002) are shown in Table 1.

Flow Calorimetry

The operation of the flow calorimeter has been described in a previous paper (Rhue et al., 2002). Approximately 50 mg of soil were placed inside a small column, and solutions containing K, Ca, or Pb as nitrates were forced through the column using a total pressure drop of about 100 cm of water. Flow rates were controlled with a precision needle valve at the outlet side of the calorimeter and were generally in the range of 0.25 to 0.35 mL min⁻¹. A pair of thermistors, one upstream and the other downstream from the soil column, formed one half of an electronic bridge and sensed temperature changes in the solution as it passed through the column. A change in solution temperature produced a differential output voltage from the bridge. This differential voltage was fed into an instrumentation amplifier, and the amplified signal was fed into a computer for processing.

Obtaining Integral Heats of Adsorption

The ionic strength (*I*) and pH of each solution were 15 mM and 4.7, respectively. Changes in soil solution pH and *I* can lead to changes in the surface charge of variably charged soil colloids and, thus, changes in cation sorption in these systems (Uehara and Gillman, 1981; van Olphen, 1977).

Approximately 50 mg of soil were placed in the calorimeter and equilibrated with 15 mM KNO₃ until a steady baseline was obtained. The input solution was then changed to 5 mM Ca(NO₃)₂, which resulted in an endothermic heat of exchange as Ca displaced exchangeable K. When the signal had returned to baseline, the solution was changed back to KNO₃, and the exothermic peak associated with the displacement of exchangeable Ca by K was recorded. Several K/Ca exchange cycles were recorded. The K and Ca peak areas were of equal and opposite magnitude, which was indicative of a reversible process.

Following the last 15 mM KNO₃ wash, the solution was changed to 5 mM Pb(NO₃)₂, and several K/Pb cycles were recorded as was done with K/Ca. After the last K/Pb cycle, several K/Ca cycles were repeated to determine if Pb treatment had affected changes in the heat of K/Ca exchange. After the last K/Ca cycle, the soil was removed from the calorimeter and analyzed for total Pb by digesting it in concentrated HNO₃ according to U.S. Environmental Protection Agency Method 3051 (USEPA, 1996). Lead extracted by this method was taken as a measure of specifically adsorbed Pb. The native soil Pb concentrations were 10 and 8 mg kg⁻¹ for the Oxisol and Ultisol, respectively, and were not used to correct values for specific adsorption.

Obtaining Differential Heats of Adsorption

Approximately 50 mg of soil were placed in the calorimeter and equilibrated with 15 mM KNO₃. When a baseline was obtained, the solution was changed to one containing both K⁺ and

TABLE 1
Physiochemical properties of soil (Appel and Ma, 2002)

Sample	Organic matter g kg ⁻¹	PZNC	pH	CEC mmol _c kg ⁻¹	Sum H + Al mmol _c kg ⁻¹	Total Fe + Al g kg ⁻¹	Clay mineralogy ¹	Texture ² g kg ⁻¹	Specific surface area m ² g ⁻¹
Oxisol	41	3.7	4.9	31	17	287	k>go>gi=q	100-340-560	41.9
Ultisol	19	2.3	4.7	110	71	86	k>q>s>go>m	120-290-590	37.8

¹k = kaolinite; gi = gibbsite; go = goethite; s = smectite; q = quartz; m = mica.

²sand - silt - clay.

M^{2+} ($M^{2+} = Ca^{2+}$ or Pb^{2+}) while keeping I constant at 15 mM and pH at 4.7. The solution compositions were as follows: 15 mM KNO_3 , 14.25 mM $KNO_3 + 0.25$ mM $M(NO_3)_2$, 13.5 mM $KNO_3 + 0.5$ mM $M(NO_3)_2$, 12 mM $KNO_3 + 1.0$ mM $M(NO_3)_2$, 9 mM $KNO_3 + 2$ mM $M(NO_3)_2$, 6 mM $KNO_3 + 3$ mM $M(NO_3)_2$, 3 mM $KNO_3 + 4$ mM $M(NO_3)_2$, and 5 mM $M(NO_3)_2$. Several cycles of heat measurements were obtained for each solution composition. The measured heats were plotted against the exchangeable divalent cation concentration and a smooth curve fitted through the data using a least squares procedure. The differential heat of exchange was obtained by differentiating this relationship with respect to exchangeable divalent cation concentration.

The concentrations of exchangeable cations corresponding to the above $K^+ + M^{2+}$ solutions were measured in a separate procedure. Five grams of soil were placed in 1.5 cm diameter columns (two replicates) and the exchange sites were initially saturated with K^+ using 15 mM KNO_3 (approximately 20 pore volumes). The columns were then drained under suction (20 cm) and weighed in order to correct for any residual nitrate salts left in the soil. The soil was then flushed five times using 5 mL of 0.5 M $Mg(ClO_4)_2$. The effluent was collected and refrigerated prior to analysis by flame atomic absorption spectrophotometry. Preliminary experiments indicated this amount of $Mg(ClO_4)_2$ desorbed all exchangeable cations satisfactorily. Following the last $Mg(ClO_4)_2$ extraction, the column was flushed with 20 pore volumes of 0.5 M KNO_3 , followed by 20 pore volumes of 15 mM KNO_3 to ensure that the soil was K saturated, and equilibrated at $I = 15$ mM, pH 4.7, before the next set of exchangeable cation measurements.

The soil was then saturated using one of the $K^+ + M^{2+}$ solutions, starting with the lowest M^{2+} concentration and proceeding to the highest, each time extracting with $Mg(ClO_4)_2$ and re-saturating with KNO_3 before proceeding with the next concentration step. The columns were flushed with $K^+ + M^{2+}$ solutions until the divalent cation concentrations in the column effluent were essentially the same as that in the input solution, which required as many as 100 pore volumes. Duplicate values of exchangeable cation concentration at each concentration step were averaged and standard deviations calculated.

Following the last $Mg(ClO_4)_2$ extraction of the Pb treated columns, the soil was removed from the column and analyzed for total Pb by di-

gesting it in concentrated HNO_3 according to USEPA Method 3051 (USEPA, 1996). This total Pb concentration was taken as a measure of specifically adsorbed Pb.

RESULTS AND DISCUSSION

Integral Heats of Adsorption

Because Pb is able to readily undergo specific adsorption reactions in a variety of soils, organic matter, and pure minerals (Bargar et al., 1998; Davis and Leckie, 1978; Eick et al., 1999; Pardo, 2000; Phillips, 1999; Strawn et al., 1998; Strawn and Sparks, 1999; Xia et al., 1997; Zhang et al., 1997), it was important to partition the calorimetric heat of sorption between reversible ion exchange and specific adsorption. The specific adsorption of Pb has been attributed to: (i) the relatively high affinity of Pb for most functional groups in organic matter, which are hard Lewis bases—carboxylic and phenolic groups (Pb^{2+} is a borderline hard Lewis acid); (ii) its electronegativity (2.10), enabling it to pull electron density away from soil surface functional groups during bond formation; and (iii) the relatively low pK_H (negative log of hydrolysis constant, 7.78) of Pb, which allows it to form chemical bonds with soil surfaces in hydrolyzed form (Bruemmer et al., 1986; Forbes et al., 1976; Huheey, 1983; McBride, 1994). In this study, sorbed Pb that was not exchangeable with a neutral salt such as $Mg(ClO_4)_2$ or KNO_3 was assumed to be specifically adsorbed. Specific adsorption is the proposed mechanism because speciation calculations performed by Visual Minteq (Gustafsson, 2002) showed that solutions were undersaturated with respect to solid phase $Pb(OH)_2$ and $Pb(CO_3)_2$.

The Oxisol soil specifically adsorbed 3000 to 3500 $mg\ kg^{-1}$ Pb, whereas the Ultisol specifically adsorbed 1900 $mg\ kg^{-1}$ (Table 2). The Oxisol had a greater abundance of both organic matter (4.1% and 1.9% for the Oxisol and Ultisol, re-

TABLE 2
Nonexchangeable Pb in column adsorption
versus calorimeter studies

Soil	Adsorption study	Calorimeter study
 $mg\ kg^{-1}$	
Oxisol	2975(694) ^{a1,2}	3469(1754) ^a
Ultisol	1848(472) ^b	1891(764) ^b

¹Numbers in parenthesis are standard deviations of the means.

²Means within a column or row with the same letter are not significantly different at $p < 0.05$.

spectively) and iron/aluminum oxides (28.7% and 8.6% for the Oxisol and Ultisol, respectively) compared with the Ultisol (Table 1). These components probably accounted for the greater specific adsorption of Pb in the Oxisol as both materials have been shown to be important in the specific adsorption of heavy metals, especially Pb (Bargar et al., 1997a and b; Gao et al., 1997; Gong and Donahoe, 1997; Jenne, 1968; Kinniburgh et al., 1976; Sauve et al., 1998, 2000).

Flow calorimetry allows multiple sorption/desorption cycles to be applied to the same sample, enabling reversible and irreversible processes to be distinguished (Rhue et al., 2002). For all soil samples subjected to Pb solutions during the calorimetry experiments, there were no significant differences between the heats of Pb sorption and desorption, and there were no significant changes in the heats associated with repetitive Pb sorption/desorption cycles. Thus, we conclude that the only reaction detectable calorimetrically was that associated with reversible K/Pb cation exchange. Since specific adsorption of Pb on these soils did not result in a detectable heat signal and was, therefore, a very low energy reaction, we also conclude that the driving force for the specific adsorption of Pb was predominantly entropic (i.e., driven by a positive ΔS). The loss of Pb from the solution phase and its replacement by H^+ , OH^- , and/or H_2O would result in an increase in entropy. Entropic reactions have been observed by others studying heterovalent cation adsorption in soils (Gast et al., 1969; Laudelot et al., 1968; Maes and Cremers, 1977; Sparks and Jardine, 1981).

Heat amounts associated with K/Ca exchange on soils before and after the specific adsorption of Pb were not significantly different. The specific adsorption of Pb must have occurred on sites other than cation exchange sites because the specific adsorption of Pb did not change the energetics of K/Ca exchange, nor did it change the CEC of our soils.

Table 3 shows the heats of K/Ca and K/Pb exchange, measured by flow calorimetry in the Oxisol and Ultisol. The adsorption of Ca and Pb was endothermic when replacing exchangeable K, which is consistent with literature for these cations (Deist and Talibudeen, 1967; Elkhatib et al., 1993; Laudelot et al., 1968; Maes and Cremers, 1977; Parida et al., 1996; Rodda et al., 1996; Scheinost et al., 2001; Udo, 1978). Furthermore, heats for K/Pb exchange were significantly smaller than those for K/Ca exchange in both soils ($P \leq 0.1$ for Oxisol K/Ca and Ultisol K/Pb)

TABLE 3
Heats of exchange (ΔH ; kJ mol_C^{-1}) for the Oxisol and the Ultisol

Soil	K/Ca	K/Pb
Oxisol	7.53(1.36) ^{a1,2}	5.61(0.51) ^a
Ultisol	10.63(1.17) ^b	7.72(0.28) ^c

¹Numbers in parenthesis are standard deviations of the means.

²Means within a column or row with the same letter are not significantly different at $p < 0.1$.

This means that more energy was absorbed from the surroundings when Ca replaced K than when Pb replaced K. This was most likely because Pb has a lower hydration energy and a higher hydrated charge density than Ca, facilitating the replacement of K.

Heats of exchange were significantly greater ($P \leq 0.1$) for the Ultisol than for the Oxisol. This indicates that both Ca and Pb required more energy to displace exchangeable K in the Ultisol than in the Oxisol. This was most likely caused by the presence of smectite in the Ultisol, which was not present in the Oxisol. This mineral tends to hold onto K tightly in its interlayer and most likely contributed to greater binding energy for K. In a thermodynamic study looking at K/Ca exchange in two soils, Sparks and Jardine (1981) found that the binding energy of K was greater in the soil having more interlayer surface charge.

The heats measured by calorimetry correspond to the enthalpy change for the experimental conditions used and not to standard state conditions. To convert the calorimetric ΔH to standard state conditions, ΔH° , requires correcting for the enthalpies associated with taking the clay/electrolyte systems to a state of infinite dilution (Goulding, 1983). However, differences between ΔH and ΔH° for ion exchange are usually small (<10%) (Barrer et al., 1963; Goulding, 1983; Laudelot et al., 1968).

In previous works, the ΔH° for K/Ca exchange on a variety of soils ranged from 3.3 to 16.3 kJ mol_C^{-1} (Deist and Talibudeen, 1967; Goulding and Talibudeen, 1984; Ogwada and Sparks, 1986; Sparks and Jardine, 1981), consistent with our values as measured by flow calorimetry. Most of these soils were dominated by 2:1 layer silicates, whereas the two soils used in this study were dominated by kaolinite and metal oxides. Reports of ΔH or ΔH° for exchange on highly weathered soils dominated by kaolinite and oxides are few. However, Udo (1978) reported a ΔH° of 54.5 kJ mol_C^{-1} for K/Ca exchange on a

kaolinitic soil clay that he derived from the temperature dependence of $\ln K$. Our Oxisol and Ultisol samples contained 56% and 59% clay, respectively, of which about half was kaolinite. On a per gram of clay basis, the ΔH for K/Ca exchange on the Oxisol and Ultisol was 13.4 and 18.0 kJ mol_c^{-1} , respectively, considerably below the value reported by Udo (1978). To our knowledge, Udo's value is considerably higher than any reported values for K/Ca exchange. After looking at Udo's data more carefully, however, we believe that an error may have been made when calculating ΔH° . We have reintegrated the $\ln K_c$ vs X'_K data in his Figure 2a, and then, using Udo's Equations (9) and (12), we calculated a ΔH° of about 15 kJ mol_c^{-1} , not the 54.5 kJ mol_c^{-1} originally reported. If our calculation is correct, Udo's enthalpy for K/Ca exchange is consistent with what we and others have found.

The thermodynamics of Pb reactions in soils and mineral specimen clay have been studied much less extensively than reactions involving Ca. In a Brazilian soil high in kaolinite and gibbsite, Airoldi and Critter (1997) found ΔH° for Pb adsorption was $-43.0 \text{ kJ mol}_c^{-1}$ (exothermic), based on the temperature dependence of the Langmuir isotherm. Lopez et al. (1995) and Lopez Delgado et al. (1998) suggested that Pb adsorption on blast furnace sludge, which was 47% and 34% Fe_2O_3 and carbon, respectively, occurred at least, in part, via the replacement of Ca (presumably cation exchange) and found ΔH° was endothermic. Their value of $26.1 \pm 3.1 \text{ kJ mol}_c^{-1}$ is about 10 times greater than our values for Pb/Ca exchange, which were on the order of 2 to 3 kJ mol_c^{-1} (Table 3). They did not partition the enthalpy change between ion exchange and specific adsorption. Rodda et al. (1996) determined that ΔH° for sorption of Pb on goethite at pH 5.5 was $8.2 \pm 5.5 \text{ kJ mol}_c^{-1}$ using the temperature dependence (10° to 70°C) of several sorption models (Langmuir two site, FDM surface precipitation, and BET models). The goethite surface would have been positively charged at that pH (ZPC = 8.3), suggesting that specific adsorption was a primary mechanism for Pb adsorption.

Differential Heats of Adsorption

The CEC of the Oxisol and Ultisol depended on the cation used to saturate the exchange sites (Table 4). The CEC followed the order Ca saturated > Pb saturated > K saturated. Deist and Talibudeen (1967), Maes and Cremers (1977), and Rhue and Mansell (1988) found higher measured CECs with divalent cations compared with

TABLE 4
CEC of the Oxisol and Ultisol as a function of the saturating cation

Soil	Ca	Pb	K
	mmol _c kg ⁻¹		
Oxisol	60.0(2.3) ¹	42.5(0.7)	28.1(4.0)
Ultisol	129.6(6.6)	112.3(2.4)	97.9(6.1)

¹Numbers in parenthesis are standard deviations of the means.

monovalent ones. Lower CEC is caused, at least in part, by a failure to take H^+ into account in the ion exchange process. pH changes that we have measured in column effluent during K/Ca exchange are consistent with a K/H/Ca ternary exchange reaction in these soils (data not shown). In addition, speciation calculations performed by Visual Minteq (Gustafsson, 2002) showed that 8% of the total Pb was present as PbNO_3^+ , whereas less than 2% of the total Ca was present as CaNO_3^+ . The higher amount of the monovalent PbNO_3^+ relative to CaNO_3^+ in the respective systems may also have contributed to the lower apparent CEC when comparing Pb with Ca.

By equilibrating soil with the various $\text{K}^+ + \text{M}^{2+}$ solutions, the concentration of exchangeable divalent cation was stepped incrementally from zero up to the values shown in Table 4 corresponding to 5 mM M^{2+} . Integral heats of exchange at each concentration step are plotted against the concentration of divalent cation on the exchanger in Figs. 1a and b and 2a and b. Smooth curves were fitted through the data points using a least squares analysis procedure.

The relationship between the heat of exchange and the concentration of exchangeable Ca or Pb for the Oxisol (Fig. 1a,b) was linear, with R^2 equal to 0.97 and 0.94, respectively. Differentiation of the linear equations in Figs. 1a and b provided the differential heats of exchange, which are plotted in Figs. 1c and d. The constant values for the differential heats of exchange for Pb and Ca indicate that as the exchange sites in the Oxisol became increasingly Ca or Pb saturated, the energy required to replace the remaining K did not change. Thus, the exchange sites were energetically homogeneous in the Oxisol. The main components capable of cation exchange at the pH of the experiment (pH = 4.7) were organic matter and kaolinite (ZPCs < 3 and 3 to 5, respectively; Braggs et al., 1994; Ferris and Jepson 1975; Sparks, 1995). Both materials have external cation ex

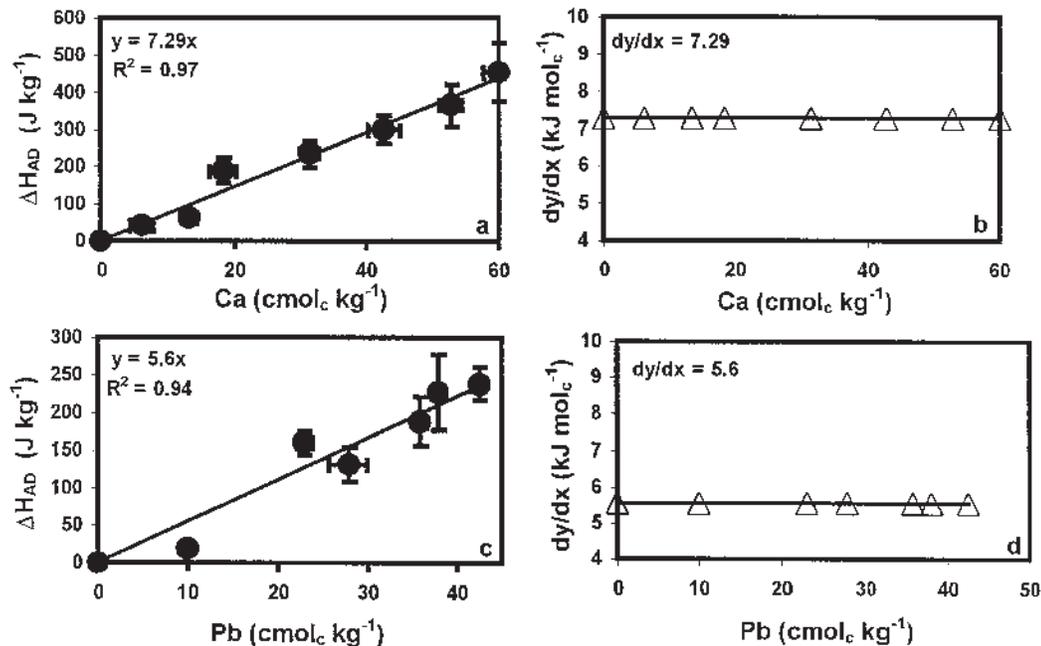


Fig. 1. Integral (a,b) and differential (c,d) heats of exchange for Ca and Pb on Oxisol.

change sites, which may exhibit constant affinities for K as exchangeable K content varies. The other major components capable of ion exchange in this soil were gibbsite, goethite, and amorphous Fe and Al oxides, which should have been positively charged at pH 4.7 and, thus, incapable of significant cation exchange (ZPCs of gibbsite and goethite 5.0 to 9.0 and 7.8 to 9.0, respectively; Sparks, 1995; Su and Suarez, 1997).

For the Ultisol, a quadratic equation best described the relation between the integral heats of exchange and concentration of exchangeable Ca or Pb (Fig. 2a and b) which, when differentiated, yielded the plots in Fig. 2c and d. The exchange sites in this soil showed evidence of heterogeneity in that an increasing amount of energy was required to remove exchangeable K as the amount of exchangeable K decreased.

An important difference between the Ultisol and the Oxisol is the presence of smectite in the former (Table 1). As indicated previously, 2:1 layer silicates generally exhibit high selectivity for K relative to Ca in the interlayer. The observed surface heterogeneity can be explained if initially Ca and Pb replaced K adsorbed to external exchange sites (i.e., organic matter, kaolinite, edges and planar smectitic surfaces) and then proceeded

to replace K from the smectite interlayers, the latter requiring more energy (Gast, 1972; Sparks and Jardine, 1981). Results obtained from X ray diffraction analysis support this hypothesis since the smectite in the Ultisol was able to collapse, in part, when K saturated but re expanded on Ca saturation. The d spacings for the Ca saturated smectite were 1.472 nm both before and after K saturation; the d spacing for the K saturated smectite was 1.404 nm.

SUMMARY AND CONCLUSIONS

Lead was adsorbed specifically in both soils. The Oxisol had between 3000 and 3500 mg kg^{-1} nonexchangeable Pb whereas that value for the Ultisol was about 1900 mg kg^{-1} . Specific adsorption of Pb was found to be driven predominantly by a change in entropy inasmuch as there was no detectable heat associated with this reaction.

Flow calorimetry was used to measure the heat associated with K/Ca and K/Pb exchange in these two soils. The heat of reaction provided information about the binding strength of these cations to soil surfaces. The adsorption of Ca and Pb, when replacing exchangeable K, was endothermic. The heats of exchange were smaller for Pb than for Ca on both soils, indicating that

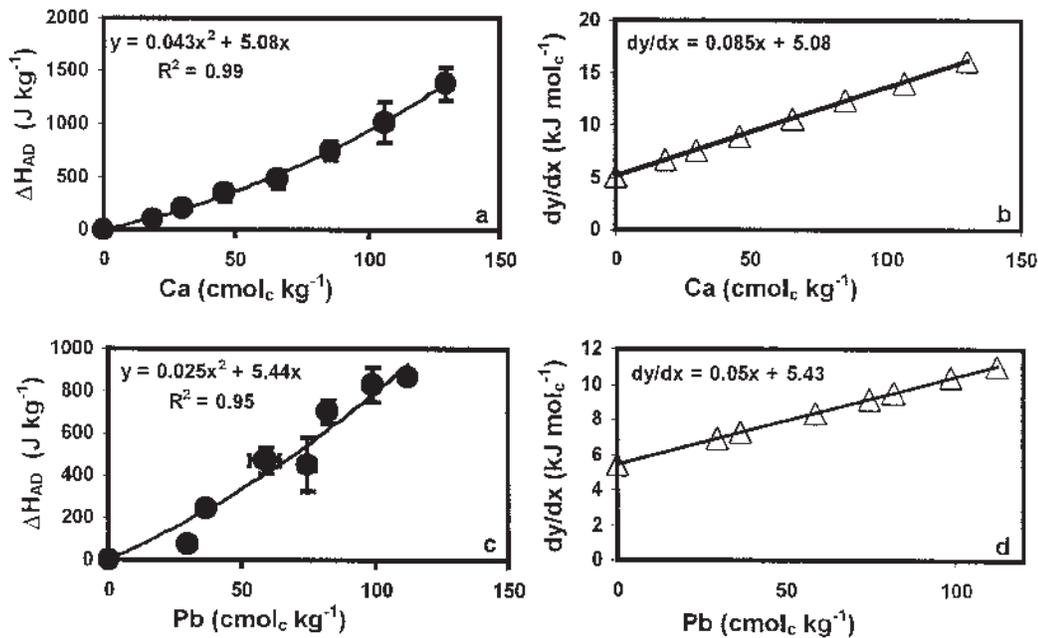


Fig. 2. Integral (a,b) and differential (c,d) heats of exchange for Ca and Pb on Ultisol.

more energy was required for Ca to replace K than for Pb to replace K from soil surfaces. As divalent cation saturation of the Oxisol increased, there was no change in the amount of heat required to replace the remaining K, indicating that exchange sites were energetically similar in this soil. However, it took an increasing amount of energy to remove exchangeable K as the amount of exchangeable K decreased in the Ultisol. Differences between the two soils were attributed to smectite, which was present in the clay fraction of the Ultisol but not in the Oxisol.

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