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LAYER CHARGE DENSITY OF SMECTITES – CLOSING THE GAP BETWEEN THE STRUCTURAL FORMULA METHOD AND THE ALKYL AMMONIUM METHOD

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Abstract—The layer charge density (LCD) of montmorillonite represents the permanent negative charge, its most important property. The LCD can be determined by two different methods, the structural formula method (SFM) and the alkylammonium method (AAM). Other methods of determining the LCD are calibrated against one or the other of these. The results of the two methods differ systematically: SFM values are larger than AAM values and the difference increases with increasing layer charge density.

In the present study, the critical parameters of both methods were considered quantitatively in order to identify the most likely reason for the systematic difference. One particularly important argument against the validity of the SFM is that typical SFM values correspond to unrealistically large CEC values that have never been reported. In addition, SFM does not consider the variable charge which causes cations to be adsorbed to the outer surface (at pH >4). In contrast to minor constituents, which can of course also affect SFM values, the variable charge can explain only part of the systematic difference. The exchange of pure smectite samples with both Cu-trien and alkylammonium revealed the presence of non-exchangeable, non-structural cations (Na, K, Ca). These cations, together with 10% (or more) variable charge, may explain the differences in LCD values. The non-exchangeable, non-structural cations could stem from undetected traces of feldspar or volcanic glass. The present samples indicated that the systematic difference in LCD values between the two methods is related to the amount of non-exchangeable, non-structural cations only, indicating that the two LCD methods probe different features of smectites. Using the SFM on pure smectite provides a value for the total number of charges (permanent with and without fixed (= non-exchangeable, non-structural) cations plus variable charge). The AAM, on the other hand, provides the charge density of the exchangeable cations (without variable charge).

Key Words—Alkylammonium Method, Layer Charge Density, Montmorillonite, Smectite, Structural Formula Method.

INTRODUCTION

The layer charge density (LCD), representing a proportion of permanent negative charge, is one of the most important properties of montmorillonites. Brindley and Pedro (1976) and later Emmerich *et al.* (2009) stressed its importance in smectite classification. Determination of the LCD, however, is still a subject of debate. In practice, two different methods and a variety of derived methods are used in the calculation of the LCD. (1) In the SFM, calculation of the structural formula (SF) is based on the chemical composition of the pure montmorillonite fraction (*e.g.* <0.2 μm). The layer charge density, LCD_{SFM}, is a by-product of SF calculation. (2) Calculation of the LCD using the AAM (LCD_{AAM}) is based on peak migration of the d_{001} reflection after intercalation of different *n*-alkylammonium ions (Lagaly, 1994). All other LCD methods are either erroneous (*e.g.* CEC and surface area, Kaufhold, 2006) or are calibrated against method 1 or 2.

LCD_{SFM}

Calculation of the SF is based on different assumptions which heavily influence the resulting LCD_{SFM} (Ross and Hendricks, 1945; Stevens, 1946; Grim and Güven, 1978; Newman and Brown, 1987; Laird, 1994). The SF methods differ with respect to the required assumptions. Two variables have to be considered for this formula. According to Čičel and Komadel (1994), a complete tetrahedral and octahedral sheet (4.0 and 2.0 cations, respectively) or a complete oxygen framework has to be assumed.

The tetrahedral sheet is generally believed to consist of 4.0 cations (^{IV}Si + ^{IV}Al) per formula unit (f.u.) whereas the octahedral sheet consists of 2–2.2 (Ross and Hendricks, 1945) cations per f.u. The sum of octahedral cations represents the first variable. The second unknown variable is the charge deficiency which is the LCD. One variable, the sum of octahedral cations, therefore, has to be assumed (or measured) in order to calculate the structural formula, or *vice versa*. As an example, Ross and Hendricks (1945) assumed a LCD of 0.33 eq/f.u. in order to calculate the structural formula. However, they stated that "of course a formula can be calculated in which the observed quantities of

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exchangeable bases, rather than assumed values, are used" which means that, for example, the CEC can be determined and used for the calculation. Köster (1977) suggested the use of $\mathrm{LCD_{AAM}}$ values for the calculation of the structural formula. If the SF is calculated to determine the $\mathrm{LCD_{SFM}}$, the sum of exchangeable cations (Na+Ca+Mg+K) is considered to be the LCD, which then allows determination of the sum of octahedral cations.

$\mathrm{LCD_{AAM}}$

The AAM is based on the determination of the *d* values of different *n*-alkylammonium montmorillonites (Lagaly and Weiss, 1969; Lagaly, 1994). This method has to be carried out with special care including attention to the quality of solutions, the intensity of washing, vacuum drying, preparation and storage of XRD mounts, and a dry atmosphere during XRD measurements. Many potential sources of error in the AAM have been identified and were re-summarized by Mermut (1994). Of particular importance is the particle-size correction, which should be performed routinely.

The $\mathrm{LCD_{AAM}}$ values can be used to calculate theoretical CEC values which correspond to experimentally determined CEC values, indicating the validity of the AAM (Lagaly, 1994). Recent criticism regarding this conversion (Środoń and McCarty, 2008) concerned the hydration state of the 105ºC-dried montmorillonite which affects the molar mass of one formula unit ($\mathrm{M_{f.u.}}$).

COMPARISON OF $\mathrm{LCD_{SFM}}$ AND $\mathrm{LCD_{AAM}}$

Values for $\mathrm{LCD_{SFM}}$ differ systematically from those for $\mathrm{LCD_{AAM}}$, a fact discussed in detail by Laird (1994) who summarized the data of Maes *et al.* (1979), Senkayi *et al.* (1985), and Laird *et al.* (1989). Kaufhold (2006) investigated ten bentonite samples (Bavaria, Milos, Slovakia) and confirmed the trend observed by Laird (1994). Wolters *et al.* (2009) also reported significant systematic differences. Clearly, SFM provides larger values than does the AAM and this is particularly obvious for high-charged montmorillonites.

The most important questions to be answered are: does any method provide correct LCD values and what is the reason for the differences?

Strong evidence for the validity of the AAM can be deduced from comparing LCD values with the CEC, which results mainly from the permanent charge (Kaufhold, 2006). Of course the CEC is also influenced by variable charge which either can be assumed or estimated experimentally by CEC determination at pH 4, for example, as long as no significant amount of $\mathrm{Na^+}$ is present in the interlayer. In addition, a good estimate at least of the molar mass of one formula unit of the montmorillonite in question ($\mathrm{M_{f.u.}}$) is required to calculate the CEC from the $\mathrm{LCD_{AMM}}$ (Table 1). As an example, three theoretical montmorillonites with three different LCD values (0.3, 0.4, and 0.5 eq/f.u.) are considered. The LCD can also be expressed in moles of charge per formula unit (equal to eq/f.u.). Considering the mass of one formula unit and multiplying by 1000 results in a theoretical CEC (without variable charge) in mmole/g, the common unit being mmole/100 g. Assuming a variable charge of 10%, the montmorillonites should have a measurable CEC of 90, 120, and 150 meq/100 g, respectively (at least in this range).

A $\mathrm{LCD_{SFM}}$ of 0.5 eq/f.u., which corresponds to 0.35 eq/f.u. by AAM, is a common value for the European bentonites examined by Kaufhold (2006). On the other hand, 150 meq/100 g is an unrealistically large value for the CEC of common bentonites, even if the montmorillonite content is close to 100%. Kaufhold (2006) did not suggest any reasons for the observed differences between $\mathrm{LCD_{AAM}}$ and $\mathrm{LCD_{SFM}}$, however. The objective of the present study, therefore, was to identify the reason for the systematic difference between $\mathrm{LCD_{SFM}}$ and $\mathrm{LCD_{AAM}}$ values.

The AAM is known to have certain weaknesses, as discussed above, which have led to several improvements (Mermut, 1994). On the other hand, none of the weaknesses identified in the AAM explains the small measurable CEC values of montmorillonites with LCD = 0.5 eq/f.u. In the present study, therefore, conversion of the CEC to LCD (and *vice versa*), in particular, is assessed critically and compared with possible sources

Table 1. Example for calculation of the CEC from LCD values (based on the formula given by Lagaly, 1994, and Kaufhold, 2006).

Sample	Ref. *T*	LCD (eq/f.u.)	LCD (mol/f.u.)	$\mathrm{M_{f.u.}}$ (g/mol)	$\mathrm{LCD/M_{f.u.}}$*1000 (mmol/g)	*100 (mmol/100 g)	Var. charge (%)	CEC (meq/100 g)
$\mathrm{Bent_{LCD\ 0.30}}$	105ºC	0.30	0.30	370	0.81	81	10	89
$\mathrm{Bent_{LCD\ 0.40}}$	105ºC	0.40	0.40	370	1.08	108	10	119
$\mathrm{Bent_{LCD\ 0.50}}$	105ºC	0.50	0.50	370	1.35	135	10	149
$\mathrm{Bent_{LCD\ 0.50}}$	105ºC	0.50	0.50	380	1.32	132	10	145
$\mathrm{Bent_{LCD\ 0.50}}$	105ºC	0.50	0.50	404	1.24	124	10	136

of error in the SFM. With all the apparent possible sources of error in both methods, they must be assessed on a quantitative basis. An assessment of the methods based on qualitative arguments is insufficient.

MATERIALS AND METHODS

Thirty six different bentonites, dominated by dioctahedral smectites, were used in the present study. The <0.2 μm fractions were produced by chemical purification (Tributh and Lagaly, 1986), centrifugation, flocculation with NaCl, and dialysis. The $\mathrm{LCD}_{\mathrm{SFM}}$ was determined based on the chemical composition (X-ray fluorescence – XRF). The purity of the <0.2 μm fractions was investigated by X-ray diffraction (XRD) and infrared (IR) spectroscopy. The precursor materials were characterized by Kaufhold and Dohrmann (2008), Kaufhold *et al.* (2008), and Ufer *et al.* (2008). Samples B30 (= IB30) and B35 (= IB35) described by Kaufhold and Dohrmann (2008) and Kaufhold *et al.* (2008) were not considered in the present study because they contain illite/smectite mixed-layer minerals. The sample assignment was not changed. Ufer *et al.* (2008) did not consider these samples either, but changed the sample assignments: sample 31 was labeled 30 and sample 36 was labeled 34, because 30 and 35 were not used in the present study.

The chemical composition of the powdered <0.2 μm fractions were analyzed using a PANalytical Axios and a PW2400 XRF spectrometers. Samples were prepared by mixing with a flux material and melting into glass beads. The beads were analyzed by wavelength dispersive X-ray fluorescence spectrometry (WD-XRF). To determine loss on ignition (LOI), 1000 mg of sample material was heated to 1030ºC for 10 min. After mixing the residue with 5.0 g of lithium metaborate and 25 mg of lithium bromide, it was fused at 1200ºC for 20 min. The calibrations were validated regularly by analysis of 130 certified reference materials (CRM) used for the correction procedures.

The distribution of ferrous and ferric iron in the montmorillonites was calculated based on Mössbauer spectra (in order to differentiate different Fe minerals) and by the method reported by Komadel and Stucki (1988). In most cases, taking both sets of data into account led to a fairly complete and consistent characterization of the oxidation state and the type of Fe minerals in the bentonites. Variable-temperature Mössbauer spectra were obtained on the samples as received at liquid He temperature (nominally 4.2 to 6 K) and room temperature (nominally 298 K). The instrument was a custom-built device from Web Research, Inc. (Edina, Minnesota, USA) consisting of a constant acceleration drive system operating in the triangular waveform mode in conjunction with a Janis Model SHI-850-5 closed-cycle cryostat capable of cooling the sample from ambient temperature to liquid He temperature. The gamma-ray source was ^{57}Co dispersed as 10% in a thin Rh foil and spectra were calibrated relative to a 7 μm thick foil of α-Fe. Mössbauer hyperfine parameters, *i.e.* isomer shift (δ), quadrupole splitting (Δ), and magnetic hyperfine field (Bhf), were calculated by a least-squares fitting program, assuming Lorentzian line shapes.

The SFM was calculated according to the "fixed anion charge method" based on Stevens (1946) who used 22 negative charges plus the charge deficiency derived from the interlayer composition (Na+Ca+K). This method (fixed anion charge taking the interlayer composition into account) is regarded as the optimum structural formula method. Other algorithms such as the 'fixed cation method' (assumption: tetrahedral and octahedral sheets are complete; Grim and Güven, 1978) are known to be erroneous because the octahedral sheet could consist of 2.0–2.2 cations. The $\mathrm{LCD}_{\mathrm{AAM}}$ was determined according to Lagaly (1994).

The CEC was determined by the Cu-triethylenetetramine method (Meier and Kahr, 1999; Ammann *et al.*, 2005) modified by Dohrmann and Kaufhold (2010) in such a way that correct values for exchangeable Ca could be determined.

Cu-trien-exchanged smectites were produced by reacting 600 mg of the <0.2 μm fraction of selected bentonites with the Cu-trien solution. The Cu-trien/CEC ratio was ~4 and the exchange was performed twice. Dispersions were shaken for 72 h each and finally washed, dialyzed, and dried at 60ºC.

Elemental analysis

The <0.2 μm fractions of six of the samples (B3, B5, B11, B15, B32, and B37) were saturated carefully with the Cu-trien molecule, then washed, dialyzed, dried, and subjected to elemental analysis. Owing to the expected demand for high-accuracy analysis of these samples, inductively coupled plasma-optical emission spectroscopy measurements were conducted on dissolved samples. In addition, three of the six samples were saturated with dodecylammonium (DDA) prior to elemental composition analysis (by Actlabs, Canada; www.actlabs.com) in order to compare the effects of Cu-trien and AAM (DDA) exchange.

XRD screening

The powder XRD patterns of Cu-trien-intercalated fractions were recorded using a PANalytical X'Pert PRO MPD θ-θ diffractometer (Cu*K*α radiation generated at 40 kV and 30 mA), equipped with a variable divergence slit (10 mm irradiated length), primary and secondary Soller slits, Scientific X′Celerator detector (active length of 0.59º), and a sample changer (sample diameter = 16 mm). The samples were investigated from 2º to 85º2θ with a step size of 0.0167º2θ and a measuring time of 10 s per step.

Sensitive XRD mode

The powder XRD patterns of Cu-trien-intercalated fractions of selected samples with only traces of impurities were recorded using a PANalytical X'Pert PRO MPD θ-θ diffractometer (CoKα radiation generated at 40 kV and 40 mA), equipped with a variable divergence slit (10 mm irradiated length), primary and secondary Soller slits, a graphite monochromator, a proportional counter, and a sample changer (sample diameter = 16 mm). The samples were investigated from 2º to 85º2θ with a step size of 0.03º2θ and a measuring time of 5 s per step. For specimen preparation, the top loading technique was used.

The powder XRD patterns of Na^+-intercalated fractions were recorded in the same way as the selected Cu-trien samples but with a step size of 0.02º2θ and a measuring time of 30 s per step. For specimen preparation of all samples, the top loading technique again was used.

The detection limit of XRD is widely variable depending on the sample and the setup of the diffractometer. The systems used in the present study and described above were tested with a pure smectite and a mixture of the same smectite sample plus 0.3 mass% feldspar (pure albite from Finland). The albite peaks were well resolved and, thus, the detection limit was supposedly lower, probably in the range 0.1−0.2 mass% (Figure 1).

RESULTS AND DISCUSSION

Possible errors in CEC-to-LCD$_{AAM}$ conversion

For the conversion of CEC to LCD (or *vice versa*), a value for the molar mass of a formula unit ($M_{f.u.}$) representing the mass of pure montmorillonite is required. Kaufhold (2005) showed that the $M_{f.u.}$ depends, particularly, on the Fe content which significantly affects the mass of the pure montmorillonite and, hence, affects parameters such as the specific surface area which can be calculated based on the dimension and mass of the formula unit. The $M_{f.u.}$ can be calculated from the chemical composition of a pure montmorillonite fraction or from the structural formula. The distribution of Al between the octahedral and tetrahedral sheets is not important with respect to the determination of the $M_{f.u.}$ because the mass of $^{IV}Al = {}^{VI}Al$.

One potential source of error of the LCD-to-CEC conversion is the hydration state of the montmorillonites and the influence of the hydration state on the $M_{f.u.}$ (Środoń and McCarty, 2008). The CEC is commonly referred to material dried at 105ºC and which still contains some water that was not considered in some $M_{f.u.}$ values given in the literature, *e.g.* by Kaufhold (2006). The hydration state of the 105ºC-dried Na^+-montmorillonite, therefore, must be taken into consideration for the calculation of the theoretical CEC based on measured LCD$_{AAM}$ data as suggested by Środoń and McCarty (2008).

The d_{001} spacing of 105ºC-dried Na-montmorillonite (rehydration prevented) ranges from 10 to 12.6 Å. A 12.6 Å peak with a pronounced 10 Å shoulder is often observed. The 10 Å domains represent fully dehydrated Na^+ cations ($0H_2O/Na^+$) and the 12.6 Å domains contain exchangeable Na^+ hydrated by up to two water molecules. Roughly estimated, the hydration state of Na^+ in montmorillonite at 105ºC is ~$1H_2O/Na^+$, meaning that ~1/3 of the mass of one water molecule must be added to the $M_{f.u.}$ of a montmorillonite which has a LCD of 0.33 eq/f.u. (= 0.33 Na^+/f.u.). In the case of a LCD of

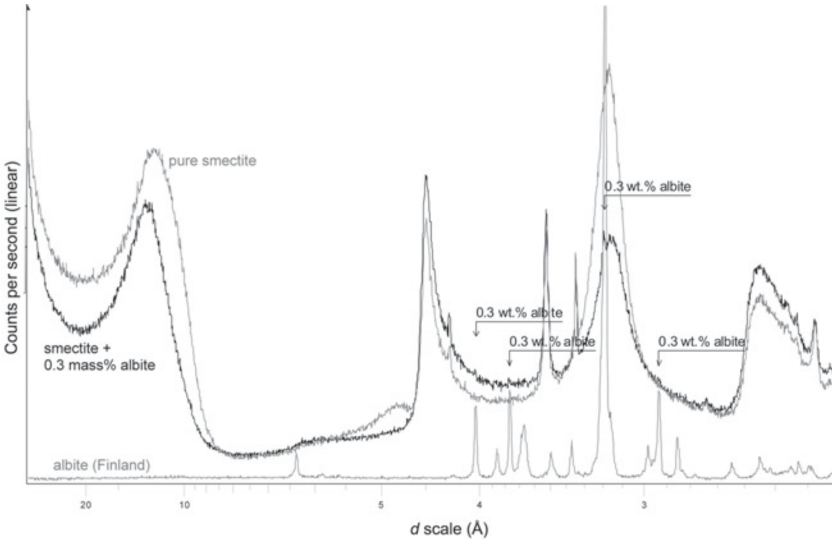

Figure 1. Comparison of the XRD patterns of pure albite, pure smectite, and pure smectite with 0.3 mass% albite. A hand mortar was used to achieve homogenization, which affected the hydration state of the smectite.

0.5 eq/f.u., half of the mass of one water molecule must be added to the $M_{f.u.}$ Assuming a $M_{f.u.}$ of 360 g/mole (totally anhydrous) and adding 1/3 or 1/2 of the mass of one water molecule leads to a correction of the $M_{f.u.}$ of 1.5−2.5% (366 or 369 g/mole, respectively).

Alternatively, the hydration state of 105ºC-dried Na^+ montmorillonite can be measured by determination of the mass loss between 105ºC and 200ºC (*e.g.* Środoń and McCarty, 2008). In order to obtain quantitative information about the mass loss (105−200ºC) of pure montmorillonites, raw bentonite samples (without any cation exchange) were used and the values corrected according to the montmorillonite content determined by Ufer *et al.* (2008).

This experimentally determined mass loss of the 36 bentonite samples between 105 and 200ºC ranged from 0 to 2.5 wt.% (Figure 2), which is in good agreement with the calculated values (1.5−2.5 wt.%).

The water content between 105 and 200ºC depends mainly on the type of exchangeable cation (Figure 2). Generally, Na^+-dominated montmorillonites contain less water than Ca^{2+}/Mg^{2+}-dominated montmorillonites (Figure 2a), which was expected because of the greater hydration energy of anhydrous Ca^{2+} and Mg^{2+} compared to anhydrous Na^+. The remaining scatter of the samples with Na^+ <2%/CEC (Figure 2a) suggests the influence of an additional parameter in determining the water content between 105 and 200ºC. As an exception, sample 28 contains 17 wt.% zeolite, which explains the larger hydration energy value for this sample. In addition, a good correlation of the water content with the amount of exchangeable Mg^{2+} of the Na^+-free samples was found, indicating that the water content of the Na-poor bentonites between 105 and 200ºC depends in particular on the amount of exchangeable Mg^{2+}.

Both experimental and calculated data suggest that the $M_{f.u.}$ in the case of Na^+-montmorillonites must be corrected by $\leqslant$1.5%. Accordingly, increasing the $M_{f.u.}$ by 6 g/mole is regarded as a suitable correction of the $M_{f.u.}$ with respect to the hydration of exchangeable cations. Considering the hydration state is important but a required correction of <2% does not explain the systematic difference of LCD_{AAM} and LCD_{SFM} accounting for up to 30% (*e.g.* between 0.50 and 0.35 eq/f.u.).

Purity of the montmorillonite fraction

The traditional SFM requires the production of pure montmorillonite fractions, unlike the AAM. To produce

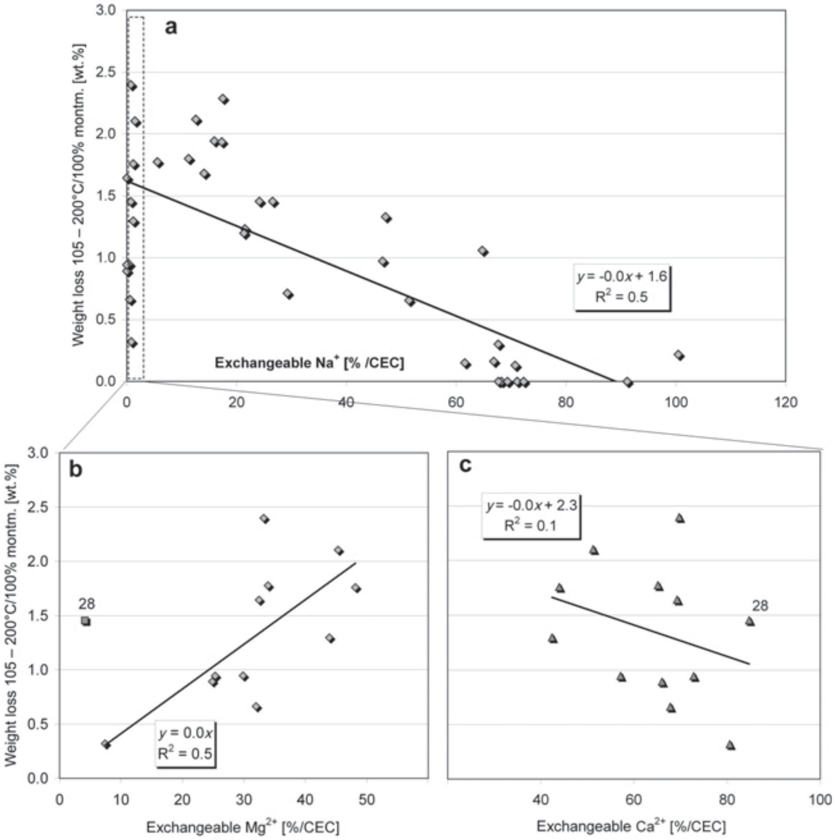

Figure 2. Experimentally determined weight loss of pure montmorillonite (bentonite samples were used and weight loss increased with increasing montmorillonite content) compared with the amount of exchangeable Na^+ (a), Mg^{2+} (b), and Ca^{2+} (c) in the case of Na-free samples. Sample 28 contains large amounts of zeolite.

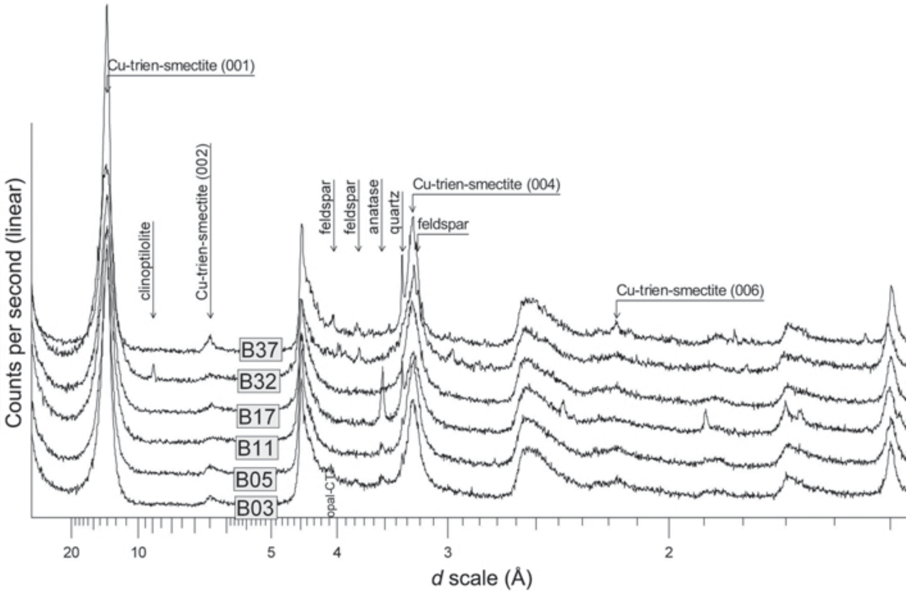

Figure 3. XRD pattern of the <0.2 µm fraction of six almost pure samples.

the pure fraction, the <0.2 µm fraction of a bentonite is commonly separated, *e.g.* by centrifugation. Some bentonites, however, contain minor impurities even in the <0.2 µm fraction. Note that, for the calculation of the LCD, impurities containing Na, K, or Ca are 'worse' than silica modifications (quartz, cristobalite, *etc.*) because Na, K, or Ca affect the permanent charge directly whereas increased Si mainly affects the ratio of tetrahedral/octahedral charge. Using the XRD screening mode proved that six of the 36 samples were almost pure (anatase is not important with respect to the calculation of the structural formula). Using the more sensitive XRD mode revealed some feldspar in two of these six samples (Figure 3). Unfortunately, quantification of these traces was difficult because of the small amount of sample. Comparing these results with those reported in Figure 1 suggests feldspar contents of <0.3 mass% and a little more in the case of sample B37. Sample B32 contains clinoptilolite rather than feldspar.

Impurities such as cristobalite, quartz, feldspar, clinoptilolite, and kaolinite affect the chemical composition and, hence, lead to unsystematic differences between $\mathrm{LCD}_{\mathrm{AAM}}$ and $\mathrm{LCD}_{\mathrm{SFM}}$ (Figure 4). In contrast, considering the pure montmorillonite samples only (B5, B11, B17) confirms the systematic difference between both methods as reported by Laird (1994) and Kaufhold (2006). The most important finding is that impurities, detectable or otherwise, do explain the LCD difference

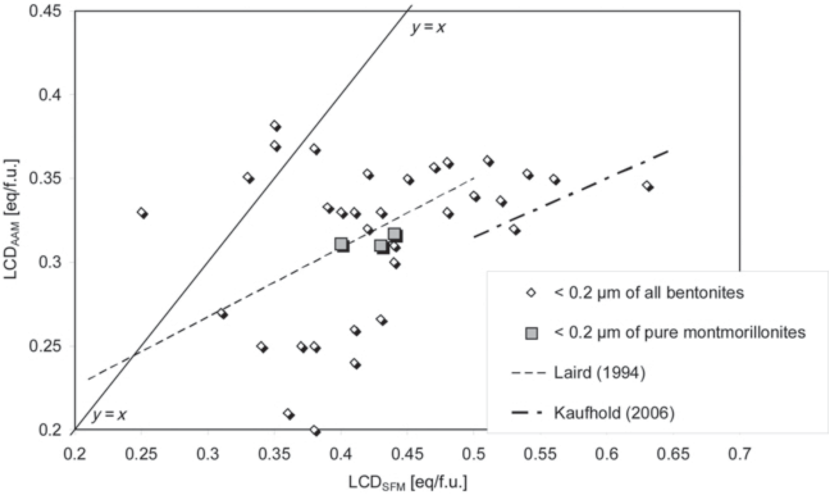

Figure 4. Comparison of LCD values obtained by AAM and SFM.

but do not explain why the deviation of LCD_{AAM} and LCD_{SFM} values is systematic, *i.e.* depends on the LCD.

Variable charge

The most accepted algorithm for the calculation of the SF is based on considering the exchangeable cations in order to calculate the charge deficiency. The pure montmorillonite fraction is commonly saturated with Na^+ and the amount of Na^+ is used to calculate the charge deficiency. Alternatively, the montmorillonite is Ca^{2+}-saturated before chemical analysis (Środoń and McCarty, 2008). Of course the Na^+ (or Ca^{2+}) value then represents the CEC. The CEC, in turn, is known to be the sum of variable and permanent charges. The variable charge (v.c.) can account for up to 20% of the CEC (Vogt and Köster, 1978). Nevertheless, the v.c. is rarely considered when calculating LCD_{SFM} values.

The Na^+ (Ca^{2+}) content is affected by the extent of dialysis which is commonly performed after the purification procedure (D. Laird, pers. comm.). In order to test this aspect, the conditions throughout the dialysis were varied. In the present study, standard dialysis was performed in a 5 L bath containing deionized water (electrical conductivity <0.7 μS/cm). The water was exchanged every 24 h until the electrical conductivity was <1 μS/cm (standard dialysis conditions: (A) In order to test the effect of dialysis, the conditions were varied: (B) one additional week (six additional changes of deionized water in the bath after conductivity reached <1 μS/cm); (C) using double-distilled water and 1 additional week after conductivity reached <1 μS/cm; and (D) using double-distilled water which was adjusted to pH 4 (addition of 1 mL of 1 N HCl/10 L) and 1 additional week after conductivity reached <1 μS/cm.

Changing the water in the dialysis bath repeatedly (variation B) and the quality of the water in the <0.7 μS/cm range (variation C) had only a minor effect on the chemical composition (Na^+ content) and hence on the LCD_{SFM} (Figure 5). Using double-distilled water adjusted to pH 4 (variation D) resulted in a pronounced decrease in the Na^+ content and, hence, in the LCD_{SFM} value. At pH 4, the edges of the montmorillonite, which carry the variable charge, should be proton saturated, in turn repelling excess cations. At the same time, pH 4 dialysis resulted in (1) cation exchange, and (2) even some montmorillonite decomposition as indicated by the large amount of structural elements such as Mg^{2+} and Al^{3+} (Table 2) in the CEC solutions. Clearly, protons entered the interlayer and exchanged for Na^+, which in turn was removed from the system by the next change of water in the dialysis bath. The resulting H^+-montmorillonite was unstable and turned into an H^+-Al^{3+}-montmorillonite according to the well known autotransformation (*e.g.* Janek and Komadel, 1999). The fast exchange of H^+ for Na^+ at low pH is also a well known process (Kamil and Shainberg, 1968; McBride, 1979). The <0.2 μm fraction of B17 was, therefore, saturated with Ca^{2+} after the purification procedure and finally dialyzed at different pH (pH 7 = A, pH 5 and pH 4 = D).

The Ca^{2+}-montmorillonite was more or less stable at pH 4 ('exchangeable Al^{3+}' = 0 meq/100 g; Table 2). The CEC at pH 4 should derive from the permanent charge only. By adjusting the pH to 4, the LCD_{SFM} decreased by 0.05 eq/f.u. (from 0.48 to 0.43 eq/f.u.) which is a change of ~10% and, hence, appears to be a good estimate of the variable charge of at least this Ca^{2+}-smectite (Kaufhold *et al.*, 2002). Typically, Na^+ montmorillonites are more alkaline than Ca^{2+} montmorillonites (Kaufhold *et al.*, 2008). Na^+-montmorillonites, therefore, have a greater

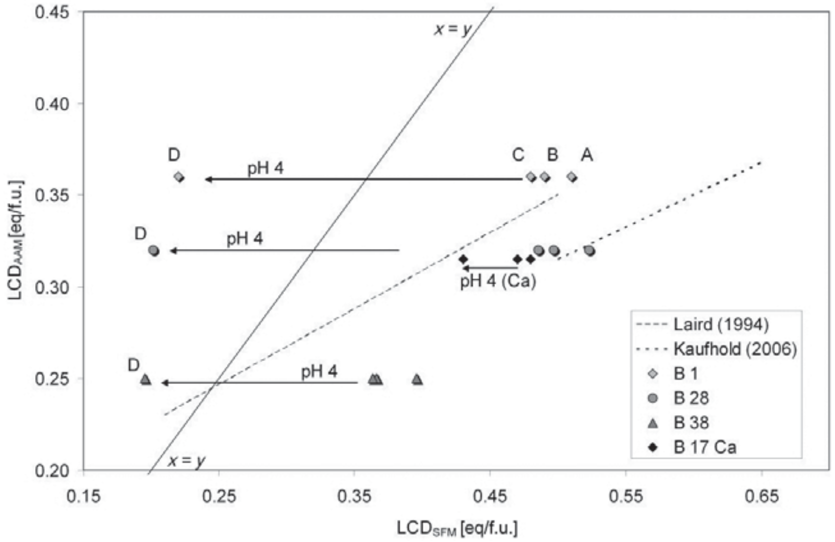

Figure 5. Effect of varying the dialysis conditions on the LCD_{SFM} of three Na^+ montmorillonites and one Ca^{2+} montmorillonite (purified from a Na^+ bentonite and subsequently saturated with Ca^{2+}).

Table 2. Effect of changing the dialysis conditions on the CEC of three bentonites (meq/100 g).

	Dialysis procedure	Na^+	K^+	Mg^{2+}	Ca^{2+}	Al^{3+}	Fe^{3+}	Sum of cations	CEC	Sum CEC
B1	A	88	1	7	1	0	0	97	93	4
B1	C	84	1	8	1	0	0	93	92	2
B1	D	4	1	15	1	36	2	60	76	−16
B28	A	57	0	2	0	0	0	59	50	9
B28	C	53	0	3	0	0	0	56	51	5
B28	D	13	0	4	0	21	0	39	40	−1
B38	A	55	1	2	2	0	0	60	57	3
B38	C	43	1	5	2	0	1	51	52	−1
B38	D	1	1	8	3	22	6	41	50	−10
B17 Ca	A	0	2	4	95	0	0	101	100	1
B17 Ca	pH5	0	2	4	94	0	0	101	99	2
B17 Ca	D pH4	0	2	7	87	0	0	96	97	−1

proportion of variable charge than Ca^{2+}-montmorillonites, as long as the pH of the respective dispersion is not controlled.

The variable charge was found to be important with respect to the calculation of the SF because it results in a ~10% (or even more when Na^+ is the interlayer cation) reduction in the LCD_{SFM}. Unfortunately, systematic studies concerning the variable charge depending on the interlayer cation are not yet available. However, variable charge can only explain part of the systematic deviation of the two LCD methods. In addition, as in the case of the impurities, the variable charge does not explain the fact that the LCD deviation is systematic, although often expressed in %/CEC. The variable charge does not depend on the LCD but only on the number of exposed-edge aluminol groups and, hence, on the particle diameter determining the edge surface area, neither of which depends on CEC nor on LCD.

FERROUS AND/OR FERRIC IRON

Determination of the chemical composition of the <0.2 μm fraction rarely consists of the differentiation of ferrous and ferric iron. The Fe content is often determined as Fe_2O_3. Some montmorillonites are known to contain at least a small amount of Fe^{2+} which of course affects the LCD_{SFM} calculation based on the SF. Each Fe^{2+} in an octahedral position creates one permanent charge. According to Laird (1994), this has only a minor effect on the LCD_{SFM} because Fe normally exists in the trivalent (ferric) state, with a much smaller proportion being in the divalent (ferrous) state.

The average Fe^{2+}/Fe^{3+} ratio of the 36 bentonites in the present study was 0.06, as determined by the relative area of Mössbauer spectra and confirmed by the method of Komadel and Stucki (1988).

Among the pure montmorillonite samples (gray squares in Figure 3), the 0.2 μm fraction of sample B11 had the largest Fe_2O_3 content at 9.3 wt.%. The Fe^{2+} content of this sample was virtually 0. If this sample were assumed to have an Fe^{2+}/Fe^{3+} ratio of 0.06 (the average of the 36 bentonites), its LCD_{SFM} would increase by only 0.001 eq/f.u. from 0.396 to 0.397 eq/f.u., which is insignificant. The same holds true for the Fe^{2+}-rich samples because the total Fe content is small. As an example, ~20% of the Fe in sample B17 is ferrous, but considering that the total Fe content is only 3.1 wt.% Fe_2O_3 the Fe^{2+} content would increase LCD_{SFM} by 0.001 eq/f.u. (from 0.471 to 0.472 eq/f.u.). Accordingly, the Fe^{2+}/Fe^{3+} ratio is generally not included in the calculation of the SF, based on chemical data, for montmorillonites of common bentonites (as reported by Laird, 1994).

In addition, Fe^{3+} is also known to occur in a tetrahedral position where it creates 1 permanent charge by substitution for tetravalent Si^{4+}. Based on chemical data alone, however, the accurate distribution of both Al and Fe into tetrahedral and octahedral positions is impossible. Recent results suggest, however, that Fe-rich montmorillonites have a larger proportion of tetrahedral charge than Fe-poor montmorillonites (Kaufhold *et al.*, 2011), which complicates the calculation of the structural formula. This observation, however, although interesting, does not explain why LCD_{SFM} and LCD_{AAM} differ systematically. The Fe^{2+}/Fe^{3+} ratio plays no role in this respect.

Fixed cations

As discussed above, Ca-, K-, and Na-containing ancillary minerals as impurities affect the determination of LCD_{SFM} (Laird, 1994). These elements may be present in X-ray amorphous phases (*e.g.* Čičel and

Komadel, 1994) and as fixed cations (Verburg *et al.*, 1995; Środoń and McCarty, 2008) in the montmorillonite. In the present study, the <0.2 μm fraction of all 36 bentonites was collected but only six of these were considered further. The XRD patterns of the <0.2 μm fraction of samples B5, B11, and B17 (Figure 2) revealed pure smectite. XRD patterns of the other samples, B3, B32, and B37, showed traces of feldspar and clinoptilolite which were difficult to quantify. Based on the investigation of an artificial mixture of sample B17 with 0.3 mass% albite suggests that the feldspar content is <0.3 mass% (*cf.* Figure 1).

Elemental analysis (Table 3) of the six selected <0.2 μm fractions (samples B3, B5, B11, B15, B32, and B37) revealed that the elemental composition of the Cu-trien and DDA-exchanged samples were comparable, even though measured in different laboratories, indicating that both Cu-trien and DDA possess comparable selectivity, leaving the same elements in the sample. Particularly interesting, of course, are those cations which directly affect the LCD, *i.e.* Ca^{2+}, K^+, and Na^+. The exchange of these cations by Cu-trien was robust (shaken and washed twice with four-fold excess) so any remaining Ca^{2+}, K^+, and Na^+ was considered to be non-exchangeable. Because these cations are also unlikely to exist in either the tetrahedral or octahedral sites, they are also referred to as 'non-exchangeable, non-structural' cations. In samples B3, B32, and B37, traces of Ca, K, and Na could have also been in feldspars or clinoptilolite ancillary phases.

The Ca, K, and Na could also stem from impurities such as volcanic glass, though samples with larger differences between the two LCD methods were noted to contain more non-exchangeable, non-structural cations (Figure 6). The same trend held true even when samples containing traces of feldspar were not considered.

Of the parameters investigated in the present study, the amount of non-exchangeable, non-structural cations was the only one which explained the systematic difference between the two methods.

The attempt to quantify the effect of the different amounts of non-exchangeable, non-structural cations on the LCD_{SFM} (Figure 6b) found that it depends on the overall composition. The effect of changing 0.1% of the element oxide (based on the actual composition) on the LCD was, therefore, determined empirically for each of the six samples. Increasing the Na_2O content by 0.1 wt.% led to an increase in the LCD of 0.014 eq/f.u.; increasing the K_2O content by 0.1 wt.% gave + 0.01 eq/f.u.; and increasing the CaO content by 0.1 wt.% increased the LCD by 0.015 eq/f.u. (on average). The values listed were used to calculate the total theoretical effect of the measured non-exchangeable, non-structural cations on the LCD. Approximately 1 mass% of Na_2O+K_2O+CaO results in an increase in the LCD of 0.16 eq/f.u. The amount of non-exchangeable, non-structural cations of the pure Cu-trien-exchanged smectites measured explains why the two methods vary systematically but does not explain the total difference between them.

SUMMARY AND CONCLUSIONS

The systematic deviation of the AAM and SFM in the determination of the LCD as reported by Laird (1994), Kaufhold (2006), and Wolters *et al.* (2009) was confirmed by the investigation of additional samples. Strong evidence was shown for the validity of the AAM results from the comparison of the CEC and the LCD_{AAM} (Lagaly, 1977, 1994; Kaufhold, 2006). The comparison does not explain the systematic deviation which was investigated here. Various possibilities were considered.

Recent criticism regarding the CEC-to-LCD conversion concerned the hydration state of the 105ºC-dried montmorillonite (Środoń and McCarty, 2008). The

Table 3. Elemental composition of the Cu-trien and AAM-exchanged (DDA cation) <0.2 μm fractions and calculated effect on the LCD_{SFM}.

Sample <0.2 μm of B	LCD AAM (eq/f.u.)	LCD SFM (eq/f.u.)	ΔLCD SFM-AAM (eq/f.u.)	K (wt.%)	K_2O (wt.%)	Na (wt.%)	Na_2O (wt.%)	Ca (wt.%)	CaO (wt.%)	Sum oxides (wt.%)	Calculated effect on LCD (eq/f.u.)
Cu_{trien} exch.											
3	0.33	0.41	0.08	0.15	0.18	0.08	0.11	0.05	0.07	0.36	0.04
5	0.31	0.43	0.12	0.26	0.31	0.10	0.13	0.04	0.06	0.50	0.06
11	0.31	0.40	0.09	0.02	0.02	0.07	0.09	0.03	0.04	0.16	0.02
17	0.32	0.44	0.12	0.40	0.48	0.11	0.15	0.06	0.08	0.71	0.08
32	0.26	0.41	0.15	0.14	0.17	0.11	0.15	0.06	0.08	0.40	0.05
37	0.30	0.44	0.14	0.22	0.27	0.14	0.19	0.21	0.29	0.75	0.09
AAM exch.											
5	0.31	0.43	0.12	0.29	0.35	0.10	0.14	0.01	0.02	0.51	0.06
17	0.32	0.44	0.12	0.42	0.50	0.10	0.14	0.03	0.04	0.68	0.08
32	0.26	0.41	0.15	0.23	0.28	0.25	0.34	0.06	0.08	0.70	0.09

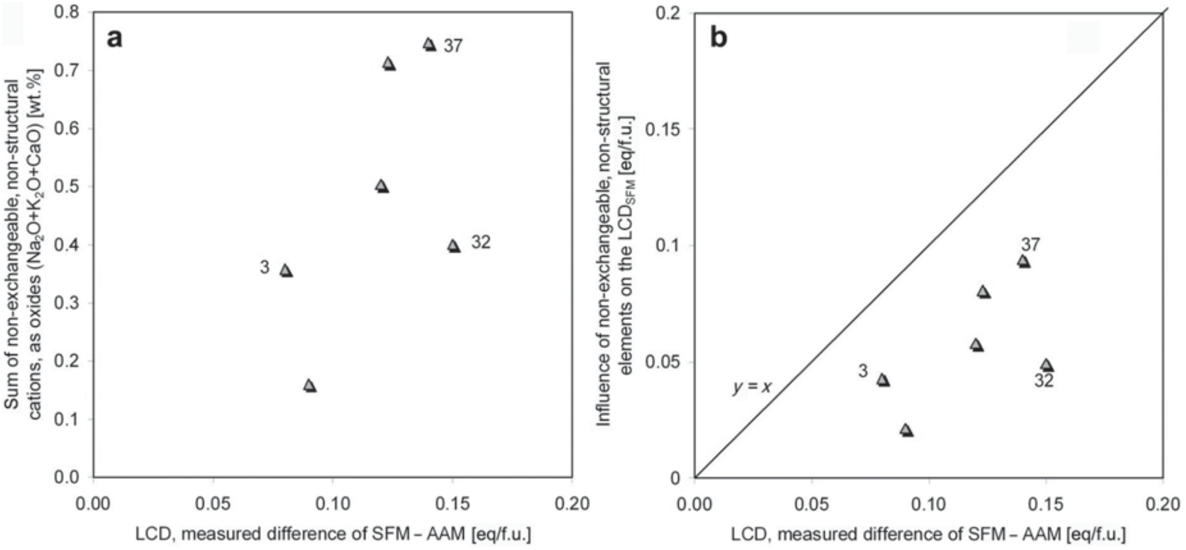

Figure 6. Comparison of difference between two LCD methods: (a) measured non-exchangeable, non-structural cations, expressed as the sum of oxides; and (b) the calculated effect of the non-exchangeable, non-structural cations on the LCD_{SFM}.

present study proved that the hydration state accounts for 0–3% water (depending on the type of exchangeable cation). The effect of the hydration state ($\leqslant 3\%$) is, therefore, insignificant with respect to the typical differences between the two methods.

The variable charge was found to be important. In spite of excessive dialysis performed on the purified montmorillonite fractions, Na^+ (or other cations) still covers permanent and variable-charge sites, which affects LCD_{SFM} values directly. This effect is of particular importance for Na^+-montmorillonites, because Na^+-montmorillonite suspensions are more alkaline than Ca^{2+}-montmorillonite suspensions (Kaufhold *et al.*, 2008). Depending on the pH of the dispersion, the analysis must account for ~10–20% variable charges.

Mineral impurities, detected by XRD and/or IR, cause non-systematic deviations and pose a significant challenge in the determination of the structural formula. The impurities provide no explanation of why the deviation is systematic. Almost all <0.2 μm fractions (Na form) of the 36 samples investigated in the present study contained larger amounts of K_2O and CaO than expected from CEC results. The possible role of fixed cations, defined here as the 'non-exchangeable, non-structural' elements, were investigated further: six different Cu-trien-saturated smectite fractions were analyzed with respect to Ca+K+Na. Unexpectedly large Ca, K, and Na contents were detected and the sum of these elements could be related to the difference between the LCD values, even though traces of feldspar

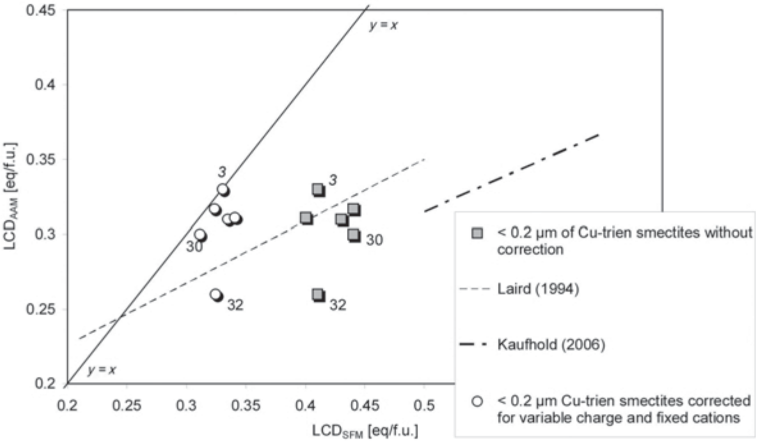

Figure 7. Comparison of the LCD values (both methods) of the six almost pure smectites with and without correction of LCD_{SFM} values for the non-exchangeable, non-structural elements and variable charge.

and clinoptilolite were found in three of the six samples. The LCD_{SFM} values were corrected based on the elemental composition and the assumption of 10% variable charge (Figure 7). Except for sample B32 (LCD_{AAM} = 0.26 eq/f.u.), a satisfactory result was obtained. One may speculate whether the unique fibrous morphology of the smectite in sample B32 resulted in a larger proportion of variable charge or if this was caused by the clinoptilolite. The non-exchangeable, non-structural cations together with the variable-charge estimation explain quantitatively the difference between LCD_{AAM} and LCD_{SFM} (Figure 7).

Regardless of the mechanism of binding of the non-exchangeable, non-structural cations, the present study proves that both methods, LCD_{SFM} and LCD_{AAM}, provide reasonable values for the characterization of smectites and that the conversion of CEC to LCD_{AAM} is more or less correct. The present study indicates that the two methods provide different information about the smectites. The hypothesis is that LCD_{SFM} provides a value for the total number of permanent charges which includes the permanent charges with fixed cations, which is the sum of exchangeable and non-exchangeable, non-structural cations. LCD_{AAM}, on the other hand, provides the charge density of the sites which are actually exchangeable (without variable charge). Using both methods together, at least in the case of samples with pure <0.2 μm fractions, a more complete picture can be obtained, *i.e.* the ratio of negative charges with fixed cations to the sites which are actually exchangeable.

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