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# Validity of the structural formula method for layer charge determination of smectites: A re-evaluation of published data

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## Abstract

The validity of the structural formula (SF) method for calculation of layer charge of smectites is examined through re-interpretation of published data, which suggest that the SF method overestimates layer charge. The overestimation of layer charge by SF is based on assumptions about the permanent CEC ( $CEC_{perm}$ ) of smectites i) on the association of the molar mass of half unit cell ( $M_{HUC}$ ) with the  $CEC_{perm}$  of the smectitic clay fraction and ii) on imbalanced SF calculated for a series of used smectites. The  $CEC_{perm}$  of smectites should not be determined at pH 4 because of competitive adsorption of  $H^+$  cations at exchangeable sites. This was verified by monitoring the pH of acidified smectite suspensions. Instead the pH at the isoelectric point (iep) should be used for determination of permanent charge of smectites. Moreover it is suggested that the equation of Lagaly [Lagaly, G., 1994. Layer charge determination by alkylammonium ions. In: Mermut, A.R. (Ed.), Layer Charge Characteristics of 2:1 Silicate Clay Minerals. CMS Workshop lectures, vol. 6. The Clay Minerals Society, Boulder Colorado, pp. 2–46] which relates the smectite content with layer charge may be used only if  $CEC_{perm}$  is calculated on a totally anhydrous basis, otherwise it may lead to significant underestimation either of smectite content or of layer charge.

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*Keywords:* Smectite; Structural formula; Layer charge; CEC due to permanent charge; Isoelectric point; Competitive adsorption

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## 1. Introduction

Layer charge is a fundamental property of 2:1 phyllosilicates, which stems from substitutions in the structure of minerals (permanent charge) and from ionizable groups on external surfaces of the minerals (variable charge). In some minerals this

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charge is balanced by fixed cations (e.g. micas), whereas in others it is balanced by the exchangeable cations (e.g. smectites and vermiculite). Layer charge affects many properties of smectites such as swelling (Laird, 2006), ion exchange capacity, ion exchange selectivity (Maes and Cremers, 1977; Shainberg et al., 1987), and rheological properties of bentonites (Christidis et al., 2006). Smectites contribute most cation exchange capacity (CEC) of bentonites and hence knowledge of layer charge may allow estimation of the smectite content of bentonites from measured CEC values (Lagaly, 1994).

A number of independent studies using different analytical methods have shown that distribution of layer charge in smectites is not homogeneous but may vary considerably (Talibudeen and Goulding, 1983; Nadeau et al., 1985; Lim and Jackson, 1986; Decarreau et al., 1987; Goodman et al., 1988; Iwazaki and Watanabe, 1988; Christidis and Dunham, 1993, 1997; Christidis 2001; Christidis and Eberl, 2003; Christidis, 2006). Similar conclusions have been drawn by the use of the alkylammonium method (Stul and Mortier 1974; Lagaly and Weiss, 1975; Lagaly, 1981, 1994). However the validity of charge heterogeneity calculated by the alkylammonium method has been challenged (Laird, 1994; Laird and Fleming, in press).

The layer charge of smectites can be estimated using a variety of analytical methods, which include i) the structural formula method (SF) (Weaver and Pollard, 1973; Grim and Güven, 1978; Bain and Smith, 1987; Newman and Brown, 1987; Laird, 1994; Laird and Fleming, in press), ii) the alkylammonium method (AAM) (Lagaly and Weiss, 1975; Lagaly, 1981, 1994) and iii) the investigation of XRD traces of K-saturated, ethylene glycol solvated smectites (Christidis and Eberl, 2003) (CE method). Additional methods, which however have not been used systematically, include i)  $\text{NH}_4^+$  saturation and examination by Infrared Spectroscopy (Petit et al., 2006) and ii) MB absorption and examination by UV spectroscopy (Budjak, 2006). From these methods only the CE method provides quantitative information about charge heterogeneity of smectites, since the validity of the AAM to quantify charge heterogeneity has been questioned as mentioned before (Laird, 1994; Laird and Fleming, in press). In contrast, the SF method provides information about charge localization (tetrahedral vs octahedral).

It has long been known that there is significant discrepancy between the layer charge determined by the SF and the AAM methods (Maes et al., 1979; Laird et al., 1989). The magnitude of that discrepancy increases systematically with layer charge and may reach 40% for clays with high layer charge (Laird, 1994). Therefore corrections, which use empirical coefficients, have been proposed to the layer charge determined by AAM (Laird and Fleming, in press). Also it has been argued that local (nm scale) re-arrangement of interlayer alkylammonium cations will cause gradual mono-bilayer transitions even in smectites with a homogeneous layer charge and cause the AAM method to underestimate the layer charge (Laird et al., 1989; Laird, 1994). By contrast, Kaufhold (2006) suggested that the SF method may yield too high layer charge for smectites and that it cannot be used to obtain reasonable CEC due to permanent charge ( $\text{CEC}_{\text{perm}}$ ). Kaufhold (2006) further suggested that a layer charge of 0.5 equivalents per half unit cell (phuc) would result to unrealistically

low smectite contents in the bentonites he studied. This work was based on previous results, in which it was considered that  $\text{CEC}_{\text{perm}}$  can be measured at pH 4 and that the difference in CEC determined at pH 6 and pH 4 is a measure of the variable charge of smectites at pH 6 (Kaufhold et al., 2002). In this contribution we attempt to reexamine the validity of SF method and to reinterpret previous results presented in the literature.

## 2. The structural formula method

### 2.1. The traditional structural formula method

The SF method is a well-known procedure for calculation of the structural formulae of minerals (e.g. Deer et al., 1992) and is a standard method for determination of the layer charge of phyllosilicates. There are several ways of calculating the SF of phyllosilicates (Grim and Güven, 1978; Newman and Brown, 1987). In the case of smectites SF calculations are usually carried out on the basis of 44 anionic charges per unit cell (puc) or 22 anionic charges per half unit cell (phuc). Alternatively it is expressed in the form of 22 or 11 oxygen atoms puc or phuc respectively. Because of the fine-grained size of smectites, the  $<2 \mu\text{m}$  clay fraction (or finer clay fractions) is separated and chemically analyzed. Before chemical analysis the fine-grained minerals (Si-polymorphs, feldspars, zeolites other clay minerals), amorphous impurities (amorphous Al- and/or Si-oxides, organic matter) or Fe-oxyhydroxides are removed (Jackson, 1985). This will be denoted the traditional SF (TSF) method. Chemical analysis of clay minerals is given in terms of elemental oxides and allocation of the various cations in tetrahedral, octahedral and interlayer sites follows Pauling's rules (Pauling, 1960). Briefly, the empty sites in the tetrahedral positions are filled with Al to make  $\text{Si} + \text{Al} = 4$ . The remaining Al, Mg and Fe are assigned to octahedral sites. Iron is assumed to be ferric, unless the presence of  $\text{Fe}^{2+}$  is verified by independent wet chemical or Mössbauer spectroscopic methods. Finally Ca, Na and K are assigned to exchangeable sites. Application of the TSF method in smectites has shown that layer charge varies between 0.2 and 0.6 equivalents phuc. In fact, according to the AIPEA nomenclature, the upper layer charge limit separates smectites from vermiculite (Brigatti et al., 2006; Guggenheim et al., 2006). Detailed descriptions of the TSF method can be found in Bain and Smith (1987), Newman and Brown (1987) and Laird (1994).

The TSF method can determine the octahedral and tetrahedral charge of phyllosilicates including smectites, but it cannot determine layer charge heterogeneity within the analyzed clay fraction. Because the clay fractions may not be monomineralic the quality of the calculated formulae is affected by the presence of other minerals. Laird (1994) has shown that mineral impurities have little effect on values of total layer charge determined by the structural formula method, unless the contamination contributes excess index cations (for example  $\text{CaCO}_3$  contamination in a Ca-smectite). However, if impurities are present in the clay fractions it is difficult to determine accurately the tetrahedral octahedral, permanent and variable charge by this method (Laird, 1994). In this case the quality of

SF obtained by the traditional method may increase if quantitative determination of impurities is carried out, usually by means of X-ray diffraction (XRD). Hence the precision of the SF depends on the detection limit of XRD for these impurities, which can be very low for quartz and higher for minerals such as illite or kaolinite (Warren and Ransom, 1992). Moreover it is difficult to apply corrections for the presence of mineral impurities with more complex SF such as illite chlorite or feldspars. Contamination by fine-grained Si-polymorphs, which are very common impurities in smectite-rich clay fractions may be detected if tetrahedral Si exceeds 4 atoms phuc. To overcome the presence of impurities the <0.2  $\mu\text{m}$  fraction is often used. However this clay fraction may not be representative of the crystal chemistry of the smectites present (Nadeau et al., 1985).

## 2.2. Microbeam techniques for calculation of structural formula

More recently microbeam techniques such as Electron Microprobe Analysis (EMPA) and Analytical Electron Microanalysis (AEM) have been applied successfully to obtain reliable SF of smectites (Altaner and Grim, 1990; Banfield et al., 1991; Christidis and Dunham, 1993, 1997; Ddani et al., 2005; Christidis, 2006; Christidis and Mitsis, 2006). Note that, based on EMPA, Christidis and Mitsis (2006) reported the SF of the first natural Ni-stevensite i.e. a smectite, in which the layer charge stems from vacancies in the octahedral sheet (Brindley, 1980). The advantages of the microbeam techniques compared to the TSF method, which utilizes the whole clay fraction are a) the ability to calculate the SF of small domains a few microns in diameter, and thus, to estimate the compositional (and hence layer charge) heterogeneity of the mineral in question from a statistically significant number of microanalyses, b) it is not affected by coarser mineral impurities which can easily be recognized and analyzed separately, c) it is not affected by the presence of fine-grained Si-polymorphs and Fe-, Mn- and Ti-oxides, which are easily detected in the Back Scattered Electron (BSE) mode (Christidis, 2006) and d) the method allows investigation of the textural features of clay samples and hence the compositional heterogeneity of the clay minerals can be related to these features, if they exist. Similar to the TSF method, the layer charge of smectites determined by microbeam techniques can be as high as 0.62 equivalents phuc (Christidis, 2006).

The main drawbacks of the microbeam methods for analysis of smectites include: a) elemental loss due to volatilization especially of light elements such as alkalis due to beam damage which leads to underestimation of layer charge (Christidis and Dunham, 1997) b) uncertainty about the allocation of key elements such as Mg in octahedral or/and interlayer sites c) the presence of fine-grained impurities (mainly Fe-oxyhydroxides) below the surface and d) low totals owing to elemental loss, to inability to obtain analysis of structural and adsorbed water, to meso- and/or microporosity among the smectite particles and to inadequate sample preparation. The latter includes surface roughness and inappropriate carbon coating thickness. However most of these drawbacks can be overcome. Hence the use of Energy Dispersive Spectrometry (EDS) using low acceleration voltage (10 kV) and low sample current (1–2 nA) minimizes

elemental loss. Also sample preparation methods are well established even in the case of difficult (very soft) materials such as bentonites. The presence of fine-grained Fe-oxyhydroxides below the sample surface is limited by the limited beam excited area ( $\sim 5 \mu\text{m}^2$ ) and beam penetration depth (<1  $\mu\text{m}$ ) (e.g. Christidis, 2006). The most difficult question concerns allocation of Mg, which is assigned in octahedral sites although there are numerous reports for exchangeable Mg. In the TSF method, the clay fractions can be rendered homoionic using a suitable index cation; therefore Mg can be safely assigned in octahedral sites. In these cases the total number of octahedral cations is very close to the ideal dioctahedral occupancy, whereas in some cases it exceeds slightly 2 atoms (Schultz, 1969; Vogt and Köster, 1978; Newman and Brown, 1987). Similar data for octahedral occupancy were obtained by Christidis (2006) using EPMA. This information suggests that in EPMA it is relatively safe to consider that octahedral occupancy in dioctahedral smectites is 2 and that excess Mg can be assigned to interlayer sites.

An independent method to evaluate the validity of structural formulae is the balance between the layer charge and the charge of the exchangeable cations. A considerably lower layer charge compared to the charge of the interlayer cations or vice versa, indicates an erroneous SF, which should be discarded. In fact, in correct analyses deviation between layer charge and charge of the exchangeable cations is attributed only to rounding errors during calculations (D. Laird written communication). Christidis and Dunham (1993, 1997) proposed maximum deviation of  $\pm 0.02$  equivalents phuc between layer charge and charge of exchangeable cations, because although the total cationic charge has to be equal to 11 positive charges possible contamination by impurities or elemental loss during analysis may yield an imbalanced structural formula. A high octahedral occupancy in a balanced SF obtained either by EPMA or by analysis of the bulk clay fraction, which has not been rendered homoionic using another index cation, may well indicate that some Mg must be assigned in interlayer sites. Several typical balanced smectite SF obtained by TSF have been published in the past (Schultz, 1969; Vogt and Köster, 1978; Newman and Brown, 1987). Assignment of a fixed octahedral occupancy at 2 atoms, by allocation of the appropriate Mg in interlayer sites increases the calculated layer charge of balanced SF.

## 3. Objections for the validity of SF method for calculation of layer charge of smectites

Lagaly (1994) attributed the difference in the layer charge obtained by the SF and the AAM method, to inconsistencies of the SF method. Recently Kaufhold (2006) questioned the validity of the SF method to calculate layer charge of smectites based on a series of smectites, mainly montmorillonites, from Bavaria, Germany (Kaufhold et al., 2002). Kaufhold (2006) proposed that the SF method overestimates layer charge and that the AAM method yields reliable layer charge estimates. The reasoning of these studies was that the layer charge calculated by SF, would yield too low smectite contents in high quality bentonites and that there is no agreement between the CEC and the layer charge determined by the TSF method. Kaufhold et al.

(2002) and Kaufhold (2006) used the procedure of Lagaly (1994) to calculate the smectite (montmorillonite) content:

$$\text{Mt}\% = \frac{\text{CEC}_{\text{perm}} M_{\text{HUC}}}{1000\text{LC}} \quad (1)$$

where  $\text{CEC}_{\text{perm}}$  is the CEC due to permanent charges (i.e. pH independent), LC is the layer charge phuc and  $M_{\text{HUC}}$  is the molar mass of half unit cell. The same authors proposed to use as  $\text{CEC}_{\text{perm}}$  the CEC obtained at pH 4, because they considered that at this pH smectite crystal edges will be positively charged and hence they will not bear cation exchange capacity. Kaufhold et al. (2002) also considered that the difference  $\text{CEC}_{\text{pH6}} - \text{CEC}_{\text{pH4}}$  corresponds to the CEC of smectites due to variable (i.e. pH dependent) charge at pH 6. It is not clear why they did not use the difference  $\text{CEC}_{\text{pH7}} - \text{CEC}_{\text{pH4}}$  (or  $\text{CEC}_{\text{pH6.5}} - \text{CEC}_{\text{pH4}}$ ) to calculate the variable charge. Kaufhold et al. (2002) calculated that at pH 6 on average 10% of the total layer charge of the smectites they examined is attributed to variable charges.

In order to substantiate his reasoning Kaufhold (2006) used the SF of 10 montmorillonites calculated by Kaufhold et al. (2002), according to Köster (1977), from chemical analyses of the  $<0.2 \mu\text{m}$  clay fractions of montmorillonite-rich bentonites. Before chemical analysis the clay fractions were treated so as to remove carbonates, Fe-oxyhydroxides and organic matter, and were rendered homoionic by saturation with  $\text{Na}^+$  (Kaufhold et al., 2002). With one exception, the layer charge obtained by the SF method was identical to that obtained by the AAM method, because the SF were obtained considering layer charge by AAM as the layer charge of the smectite. However the charge of exchangeable cations was at least by 45% greater than the layer charge (in some cases up to 67%), and the reason for this discrepancy was not addressed by the authors. Still the total number of octahedral cations varied between 2.05 and 2.07 phuc. According to the reasoning explained previously, such a large discrepancy indicates unreliable SF. Note that the observed difference between layer charge and charge of exchangeable cations cannot be attributed to the non-permanent charge, because, according to Kaufhold et al. (2002), the later accounts only for 10% of the total layer charge, as noted before. Rather it is due to inconsistencies in the chemical analyses as will be shown below.

#### 4. Comparison of the two approaches—Interpretation and discussion

##### 4.1. Published structural formulae and CEC values revisited

Using Eq. (1), Kaufhold (2006) suggested that the layer charge obtained by the TSF method yields a low montmorillonite content in samples containing almost pure montmorillonite and proposed that in order to obtain a rational montmorillonite content the CEC has to be considerably higher than that obtained at pH 7. The problem in this reasoning is that in Eq. (1)  $M_{\text{HUC}}$  was calculated from SF of Na-smectites on an anhydrous basis (i.e. only crystalline water was considered in calculations), whereas during calculation of the  $\text{CEC}_{\text{perm}}$  from Ca-smectites, (method C of Kaufhold et al., 2002) a considerable amount of adsorbed water

was present which however is not known. In fact this is a common procedure, because the exact experimental conditions under which CEC is determined are not always specified (Bergaya et al., 2006). The two parameters would be comparable if CEC was calculated from the SF i.e. from the  $\text{Na}_2\text{O}$ ,  $\text{CaO}$  and  $\text{K}_2\text{O}$  contents, on an anhydrous basis. This procedure is common in other mineral species with CEC like zeolites (c.f. Moraetis et al., 2007). However the chemical composition of montmorillonites was not available (Kaufhold et al., 2002). Due to the  $(\text{OH})_2$  component, smectites contain ~4% crystalline water, whereas the adsorbed water content depends on the preparation method and the type of exchangeable cation (Ca-smectites adsorb greater amounts of water). Ca-smectites contain 15–20% adsorbed water when dried at 105 °C (e.g. Table 8 in Vogt and Köster, 1978 among many others), and more than 25% when dried at lower temperatures. This is the first test of evidence suggesting a) the CEC obtained by Kaufhold (2006) were underestimated by at least 15–20% relative to the structural formula and b) the layer charge obtained by AMM method was underestimated by a similar proportion (c.f. Eq. (1)).

There are two additional questions about the assumption of Kaufhold (2006). The first concerns the validity of the SF obtained for the smectites examined. As it was already mentioned, the SF of the montmorillonites (Table 2 in Kaufhold et al., 2002) are imbalanced. Most important, using the layer charge obtained from the SF and which is comparable to that obtained by the AAM method, 7 out of 10 of the SF given correspond to beidellite (i.e.  $\geq 50\%$  of the layer charge stems from substitutions in tetrahedral sites) and in 2 SF the smectites are almost beidellites (tetrahedral charge is  $\geq 45\%$  of the total charge). The SF provided by Kaufhold et al. (2002) have very high Fe contents. In fact all but one montmorillonites can be characterized as Fe-rich smectites (mainly Fe-rich beidellites) because they have  $\geq 0.3 \text{ Fe}^{3+}$  atoms phuc (Güven, 1988). Such  $\text{Fe}^{3+}$  contents are too high both for Bavarian smectites (Vogt and Köster, 1978) and for Milano smectites (Christidis and Dunham, 1993, 1997). The high  $\text{Fe}^{3+}$ -content leads to high octahedral occupancy observed in all SF. If an octahedral occupancy of 2 atoms phuc is considered for all SF, and all Mg is considered octahedral, then the layer charge is comparable to the charge of exchangeable cations and a positive

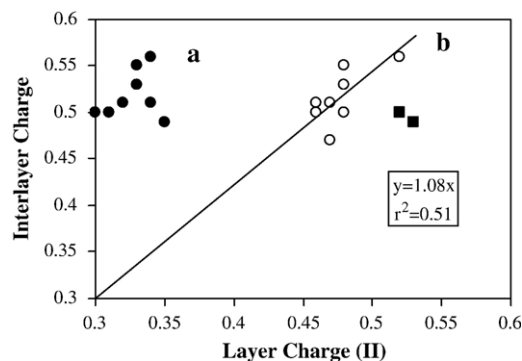


Fig. 1. Relationship between layer charge and interlayer charge in the SF of Kaufhold et al. (2002). a) Raw data b) recalculation of SF by assuming that all Mg is octahedral and that total number of octahedral ions is 2. The full squares belong to two SF which do not follow the overall trend.

trend is observed (Fig. 1). Also in all but two smectites (full squares in Fig. 1) the charge of exchangeable cations is greater than the layer charge by ca. 7%. This difference could be attributed to variable charge. With the existing data the reason for high Fe contents in the SF provided by Kaufhold et al. (2002) is not known. Three possible reasons may be considered, the incomplete removal of free Fe-oxides from the analyzed clay fractions the existence of part of Fe as  $\text{Fe}^{2+}$  (c.f. Vogt and Köster, 1978) and systematic analytical errors.

#### 4.2. Influence of pH on determination of CEC

The second question concerns the validity of the assumption that  $\text{CEC}_{\text{perm}}$  is measured in pH 4 (Kaufhold et al., 2002; Kaufhold, 2006). Although it is true that at such a low pH smectite particle edges would be positively charged and, thus, would not contribute to the CEC, it is also true that at such pH there would be competitive adsorption of  $\text{H}^+$  ions during CEC measurements and thus the CEC would be underestimated. (Maes et al., 1975; Amman et al., 2005). Moreover at such a low pH, the Al released through hydrolysis of the clay will compete with  $\text{Cu}_{\text{trien}}$  (Amman et al., 2005; Laird and Fleming, in press). According to Amman et al. (2005) the  $\text{Cu}_{\text{trien}}$  complex is strongly preferred to uncomplexed cations including  $\text{H}^+$ ; in this sense CEC should not depend on pH. However selectivity coefficients of  $\text{Cu}_{\text{trien}}$  exchange with various inorganic cations, obtained from ion exchange experiments, are not available at any pH. Moreover, the observed evolution of CEC with pH using  $\text{Cu}_{\text{trien}}$  as index cation (Kaufhold et al., 2002), resembles closely to the evolution of CEC of smectites using typical metal index cations (Maes et al., 1975; Christidis, unpublished data), suggesting that competitive adsorption of  $\text{H}^+$  or other cations and/or hydrolysis of smectite occurs also during  $\text{Cu}_{\text{trien}}$  exchange.

The possibility for competitive adsorption of  $\text{H}^+$  ions and/or hydrolysis of smectite during CEC measurements was tested by recording the pH of a set of Milos bentonite suspensions, with the solid:liquid ratios used in the determination of CEC with  $\text{Cu}_{\text{trien}}$  (Meier and Kahr, 1999) and aqueous blank suspensions as follows. The pH of the original bentonite suspensions varied between 8 and 8.45. Then the pH was adjusted to  $4 \pm 0.1$  by adding dilute HCl (1:50 v/v) and the volumes of added acid were recorded. Subsequently the same volume of dilute HCl acid was added to the distilled water (blank suspensions). The pH of the aqueous suspensions varied between 2.78 and 2.95. The observed differences in pH between the bentonite suspensions and the blank suspension after addition of the same volume of HCl, are due to the amount of  $\text{H}^+$  ions, which was adsorbed by bentonite mainly in exchangeable sites or consumed in hydrolysis of smectite. The contribution of the edge sites on the total surface charge is minimal according to recent electrokinetic experiments (Sondi et al., 1997; Saka and Güler, 2006). Using the data obtained from adsorption of  $\text{H}^+$  ions, the amount of  $\text{H}^+$  ions, which were adsorbed by bentonite was calculated, by assuming an average final pH of 2.9 for the blank suspension. It was found that on average 16 meq  $\text{H}^+$ /100 g was adsorbed. This value is comparable to the difference  $\text{CEC}_{\text{pH6}} - \text{CEC}_{\text{pH4}}$  obtained by Kaufhold et al. (2002) for their bentonite from Milos.

Moreover in Fig. 1 of Kaufhold et al. (2002) it can be observed that the CEC increases by more than 20% between pH 4 and  $\sim$ pH 6.5, i.e. in the pH range that the smectite particle edges are positively charged. The most appropriate pH at which the  $\text{CEC}_{\text{perm}}$  must be measured so that the effect of pH-dependent charge is minimal is the pH at the isoelectric point (iep) of the edges. In this case the CEC is attributed solely to the permanent charge provided that there is no competitive adsorption of hydronium ions. The CEC should increase at pH higher than the iep up to a point, due to CEC at particle edges. Several independent studies on different smectites have shown that the iep of the edges varies between 6.1 and 7 (Wanner et al., 1994; Duran et al., 2000; Ramos-Tejada et al., 2001; Tombacz and Szekeres, 2004). If pH 6.5 is taken as an indicative average iep of smectites in Kaufhold et al. (2002) then from Fig. 1 in their study, it follows that the CEC due to variable charge will be less than 5% of the total CEC. Moreover, in two samples used by Kaufhold et al. (2002), (their samples UA and BK) the iep at edges seems to be between pH 6 and pH 6.5. In any case the variable charge in these smectites is very small compared to the permanent charge, in accordance with other independent studies (Sondi et al., 1997; Saka and Güler, 2006).

The fact that the  $\text{CEC}_{\text{pH4}}$  considered as  $\text{CEC}_{\text{perm}}$  and used in Eq. (1) is lower than the real  $\text{CEC}_{\text{perm}}$  by at least 20% due to competitive adsorption of hydronium ions, provides the second independent test of evidence that the alkylammonium method underestimates significantly the layer charge, in accordance with previous studies which were based on different experimental setup (e.g. Laird et al., 1989; Laird 1994). Therefore the structural formulae calculated by Kaufhold et al. (2002) according to Köster (1977) and used by Kaufhold (2006), which were based on the AAM yield low layer charge values.

SF have been used for a long time to calculate the chemical composition and layer charge of minerals, including clay minerals, according to Pauling's rules (Pauling, 1960). What have changed with time are the analytical procedures; chemical methods (wet chemical which involve sample digestion with concentrated acids, or XRF) have been gradually replaced by microbeam techniques. For instance using the SF method, it is well established that the layer charge of micas is 1.0 eq/phuc, and that serpentine, kaolinite, talc and pyrophyllite do not possess layer charge (e.g. Newman and Brown, 1987; Brigatti et al., 2006; Guggenheim et al., 2006). There is no rational reason to accept that the SF method yields erroneous layer charge calculations in smectites provided that the sample has undergone suitable pre-treatment to remove fine-grained impurities from the smectite-bearing clay fractions (Warren and Ransom, 1992; Laird, 1994; Laird and Fleming, in press). Therefore the question for reliable layer charge calculations is transferred to the reliability of analytical methods. Once the impurities are removed, a reliable structural formula can be obtained. The increasing use of microbeam techniques (Altaner and Grim, 1990; Christidis and Dunham, 1993; 1997; Ddani et al., 2005; Christidis, 2006; Christidis and Mitsis, 2006) has confirmed previous results with TSF that the layer charge of smectites varies within the limits established by AIPEA i.e. 0.2–0.6 equivalents phuc.

Finally it has been shown that, although Eq. (1) (Lagaly, 1994) may be very useful, it may lead to erroneous interpretations if it is not used properly. In order to obtain a correct relationship between smectite content and layer charge, the CEC has to be determined correctly. The CEC must be determined on a totally anhydrous basis to be used in Eq. (1). This can be achieved by simultaneous DTA–TG analysis of the same clay fraction and normalization of sample weight to an anhydrous basis i.e. only with structural water. Alternatively the SF has to be calculated with the appropriate number of water molecules expressed as  $n\text{H}_2\text{O}$  in the SF, which will be distinguished from structural water. In this case the CEC will be related to the  $M_{\text{HUC}}$  and the smectite content or the layer charge calculated from Eq. (1) will be valid.

## 5. Conclusions

The SF method is indeed a reliable method for the calculation of layer charge of smectites within its limitations. A series of independent studies using a variety of analytical methods have shown that the layer charge of smectites varies between 0.2 and 0.6 as already accepted by AIPEA (Guggenheim et al., 2006) and not between 0.3 and 0.39 (Kaufhold, 2006). Hence the SF method does not overestimate the layer charge. In contrast the AAM underestimates layer charge significantly as has been determined by several independent studies which used different reasoning including this one (e.g. Maes et al., 1979; Laird et al., 1989). The equation of Lagaly (1994) may be useful to calculate the layer charge from smectite content and *vice versa* provided that the CEC of the smectitic clay fraction is calculated on an anhydrous basis. Finally the CEC due to permanent charge should not be calculated at pH 4 due to competitive adsorption of hydronium ions and/or hydrolysis of the smectite particles.

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