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Methods for Determination of the Layer Charge of Smectites: A Critical Assessment of Existing Approaches

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Abstract Layer charge is an important property of 2:1 phyllosilicates originating from isomorphic substitutions in the structure, from vacancies in the octahedral sheet and from unsatisfied bonds at the edges of the crystals. It is of particular interest in the case of smectites because it affects important properties of this mineral. Several methods have been proposed for determining the layer charge of smectites, namely the structural formula method (SFM), the alkylammonium method (AAM), the NH_4-method, the K-saturation method, and the O-D method. Most of these methods have been used extensively in the past and they all have advantages and shortcomings. The SFM and the AAM are based on different principles and are considered as primary methods. They have been used for a long time but they are time consuming and they provide contrasting layer charge values, with the AAM yielding consistently lower layer charge values than the SFM, especially for low-charge smectites. The remaining methods have been developed more recently and have been calibrated over their primary counterparts. They are applied easily and are capable of producing a large amount of data within a short time. In this sense they can be used both for geological interpretations and for assessment of bentonite deposits at an industrial scale.

Introduction – General Considerations

Mineral surfaces generally possess a surface charge. In metal oxyhydroxides and primary minerals the surface charge results from ionizable groups often

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called "broken bonds" at the surface (Johnston & Tombacz, 2002). In 2:1 layer phyllosilicates, including clay minerals, and in zeolites, this charge stems from isomorphic substitutions in the structure or from vacancies in the octahedral sheet and to a lesser degree from 'broken bonds.' In aqueous media these surface sites may be protonated or deprotonated according to the pH of the media, depending on the amphoteric character of the surface. The charge of these surfaces, therefore, depends on the pH and is termed 'variable charge.' The charge from isomorphic substitutions cannot be balanced by protonation, because the pH would have to be below the pH-buffer range of water. These charges are, therefore, called 'permanent charges' and they are compensated by interlayer cations, which are usually hydrated and reside at the surface. The cations balancing the permanent and variable charge are largely exchangeable, contributing to the cation exchange capacity (CEC). However, in micas and high-charged smectites, the interlayer cations of low-hydration enthalpy are located deep inside the ditrigonal holes of the Si-tetrahedral sheet; they are not hydrated and cannot be exchanged easily. Layer charge is a main criterion for the classification of 2:1 layer phyllosilicates as described in most reference textbooks (Bailey, 1984; Bergaya & Lagaly, 2013; Newman & Brown, 1987). In the case of smectites, although the relative abundances of the two types of surface charge vary depending on the analytical method of determination (e.g. Anderson & Sposito, 1991; Sondi et al., 1997), the permanent charge predominates by far over the variable charge. Thus, the term layer charge refers to the permanent charge.

The layer charge of smectites is an intrinsic property that affects important physical water-clay properties such as swelling (MacEwan & Wilson, 1984; Güven, 1988; Christidis et al., 2006), cation exchange capacity and ion exchange selectivity (Laird et al., 1995; Maes & Cremers, 1977; Verbung & Baveye, 1994), as well as viscosity (Christidis et al., 2006). The characterization of smectite layer charge is, therefore, of economic and geologic importance. For this reason, various schemes to characterize smectites as low-, intermediate- and high-charged have been proposed, but the layer-charge boundaries are different in these classification schemes (Christidis et al., 2006; Emmerich et al., 2009). Still,

the layer charge is a property of the unit cell and does not refer to the charge of smectite particle surfaces (Christidis, 2011). The smectite properties result from particles consisting of hundreds or thousands of unit cells rather than single unit cells. In these cases, the term fundamental particle charge (Christidis, 2011) is more useful, the description of which is beyond the scope of this paper. Except for magnitude, an additional parameter that contributes to layer-charge complexity is charge heterogeneity. Smectites are commonly compositionally and structurally heterogeneous (Christidis, 2006; Christidis & Dunham, 1993, 1997; Decarreau et al., 1987; Lagaly, 1994; Lagaly & Weiss, 1975; Lim & Jackson, 1986; Stul & Mortier, 1974; Talibudeen & Goulding, 1983). This heterogeneity contributes significantly to layer-charge heterogeneity, both in terms of charge location (tetrahedral or beidellitic versus octahedral or montmorillonitic charge), cation ordering in the octahedral sheet, and *cis–trans* occupancy (Christidis & Dunham, 1993, 1997; Drits et al., 1998; Righi et al., 1998; Cuadros et al., 1999; Petit et al., 2002; Emmerich et al., 2009).

The layer charge is a property of minerals and as such is expressed as moles of charge per mole of formula unit ($mol_c \, mol_{fu}^{-1}$) or moles of charge per mole of unit cell ($mol_c \, mol_{uc}^{-1}$) (Laird, 1994; Laird & Fleming, 2007). Alternatively, it may be expressed as charge equivalents per formula unit (eq/fu), charge equivalents per unit cell (eq/uc), electrons per formula unit (e/fu), or electrons per unit cell (e/uc). Although layer charge refers only to the permanent charge of 2:1 phyllosilicates; in practice, it is not clear whether a reported value of layer charge represents the permanent charge or total charge (i.e. permanent and pH dependent charge) of minerals (Laird & Fleming, 2007). In addition, although both layer charge and CEC result from similar causes, they refer to different entities. The CEC is a measure of a sample's capacity to adsorb and retain exchangeable cations relative to sample mass, and as such there may be more than one phase of the sample contributing to the CEC, whereas layer charge is a property of a specific mineral phase. Also, as mentioned above, very often 2:1 phyllosilicates contain interlayer cations that are fixed, i.e. not exchangeable and the

charge deficit balanced by these cations is included in layer charge. Finally, the term 'surface charge density' is often used interchangeably with layer charge, although they describe different terms. Surface charge density, in fact, describes the layer charge per square meter and it is calculated by dividing the layer charge by surface area per unit cell (Laird & Fleming, 2007).

Several methods have been proposed for determining layer charge of smectites. They are based either on the calculation of the crystal chemical formula of smectites or on the use of a variety of X-ray diffraction (XRD) or vibrational spectroscopy results, usually after pretreatment of the smectite. These methods are, in terms of their chronological order of appearance, the structural formula method (Marshall, 1935, Ross & Hendricks, 1945), the alkylammonium method (Lagaly & Weiss, 1969), the NH_4-FTIR method (Petit et al., 1999), the K-saturation method (Christidis & Eberl, 2003), and the O-D method (Kuligiewicz et al., 2015b). The first two of these methods are considered primary, whereas the remaining methods have been calibrated relative to one of the primary methods and will be referred to hereafter as calibrated methods. The calibrated methods were developed mainly because of the complexity and time needed to perform analyses with their primary counterparts. Also, the primary methods are not suitable for the routine study of exploratory drill cores, nor for application in an industrial fast-turnaround laboratory environment. Finally, a method based on the ultraviolet–visible spectroscopy to determine layer charge was proposed by Bujdák et al. (2001), and Talibudeen and Goulding (1983) related the heat released during determination of an exchange isotherm to different types of exchange sites and hence to charge heterogeneity. However, both methods are qualitative/semiquantitative rather than quantitative and will not be considered further.

In the present review, an outline of the most widely used methods, both the primary and calibrated, for determining layer charge of smectites is presented. In each method, the outline of each approach is presented as well as the simplifications and limitations followed by refinement of the methods where available.

The Structural Formula Method (SFM)

General Considerations

The structural formula method (SFM) uses the chemical composition of minerals to express the chemical constituents as numbers of atoms in the crystallographic unit cell, or in a hypothetical unit cell when it is not known with certainty (Newman & Brown, 1987). It is the standard method to calculate the structural formulae of minerals forming large crystals, in which the unit-cell dimensions and crystal volumes are known. In most clay minerals this information is usually not known and calculations are made after comparison with layer silicates with well known structure (Newman & Brown, 1987). This is especially the case for smectites, the structure of which has not been refined yet. Due to these uncertainties, the SF of smectites is calculated from the chemical composition without knowing the unit cell and density with certainty.

The SFM is based on the electroneutrality principle, i.e. the total cation charge should equal the total anion charge. In this aspect, the SFM employs either a fixed number of anionic charges or a fixed number of cations in octahedral and tetrahedral sites of the structure (Grim & Güven, 1978; Newman & Brown, 1987; Karathanasis, 2007). In the former approach, the anionic charges are assumed to be O^{2-} and OH^-, although F^- may also contribute to anionic charge in trioctahedral smectites. Inasmuch as the O^{2-} is usually more stable than OH^- or F^-, the SF calculations are based on a fixed number of O^{2-} charges, while the OH^- occupancy is assumed to be ideal, or is calculated directly from thermogravimetric analysis (Karathanasis, 2007). This is also the case in SFs calculated from electron microprobe analysis (e.g. Christidis, 2006). The method of fixed numbers of cations in octahedral and tetrahedral sites assumes ideal octahedral and tetrahedral occupancy, with the positive charges being balanced by the ideal or determined anionic charges of the specific mineral group so as to maintain electroneutrality.

Assuming that the analyses are accurate, the two methods should produce almost identical structural formulae, and after that, layer charge can be calculated. The presence of impurities

in the analyzed sample may cause deviations between the two methods because it affects the calculated cation distribution in the structure (Karathanasis, 2007). In this case, it is necessary to quantify the abundance of the impurities and apply necessary corrections.

Description of the Two Approaches

The first step for calculation of a reliable SF of smectites is to obtain an accurate chemical analysis of the smectite clay fraction. Analysis of the <0.5 μm fraction is preferred because <2 μm fractions usually contain mineral impurities such as SiO_2-polymorphs (quartz and/or opal-CT), feldspars (both K-feldspar and plagioclase of variable composition), Ti-oxides (usually anatase), carbonates (calcite, dolomite/ankerite and/or siderite), zeolites (mostly clinoptilolite and/or mordenite), other clay minerals (usually kaolinite and/or illite), Fe oxides/oxyhydroxides, Fe sulfides (pyrite/marcasite), amorphous matter, and less often, organic matter. Usually Fe oxides/oxyhydroxides, sulfides, amorphous matter, and organic matter are removed by various pretreatments (Jackson, 1985) and the abundance of mineral impurities is estimated with quantitative XRD analysis, usually with the Rietveld approach (Bish & Howard, 1988; Ufer et al., 2008; Bish & Plötze, 2011). Then the abundances of element oxides attributed to mineral impurities are subtracted from the overall concentrations of the oxides. Finally, the abundances of TiO_2 and MnO are subtracted, because TiO_2 is bound in TiO_2 polymorphs and MnO in Mn oxides rather than the smectite (Christidis, 2006; Dolcater et al., 1970).

Fixed negative charge

This approach, proposed by Marshall (1935), considers that the formula has 22 anionic charges in the form of $O_{10}(OH,F)_2$. First the elemental oxide composition of smectite is normalized to 100% after subtraction of TiO_2, MnO, and loss on ignition. The approach calculates gram-equivalents of cationic constituents by dividing the percent oxide of the constituent by its molecular weight, and then multiplying by the cationic charges in the molecule. Then, the proportionality factor (R) is calculated by dividing the number of the fixed anionic charges in the structure of smectite (22) with the sum of charge

equivalents. The numbers of cations are calculated by setting the sum of gram-equivalents of cationic constituents equal to 22 anionic charges. Alternatively, the gram-equivalents of cationic constituents are multiplied by the number of oxygen atoms in the oxide concerned (Deer et al., 2013). In this case, the numbers of cations are calculated on the basis of 11 oxygen atoms corresponding to $O_{10}(OH,F)_2$. The assignment of cations to the structure follows the Pauling rules, namely, an amount of Al and, if necessary, Fe^{3+} is assigned in the vacant tetrahedral positions so as to make Si + Al $(+Fe^{3+}) = 4$. By default, the remaining Al, Fe, and Mg are assigned to octahedral sites, although this assignment is not accurate in the case of Mg (see next section). Unless the presence of Fe^{2+} is verified by an independent method, iron is assumed to be Fe^{3+}. Nevertheless, in dioctahedral and especially trioctahedral smectites i.e. saponites, Fe may also be present as Fe^{2+}, with the octahedral Fe^{2+} occupancy being very limited in dioctahedral smectites (e.g. Vogt & Köster, 1978; Güven, 1988; Treiman et al., 2014). Hence, Mössbauer spectroscopy is necessary for determination of the Fe^{3+}/Fe^{2+} ratio and accurate SF and subsequently layer charge, especially in trioctahedral smectites. Finally, Ca, Na, and K are assigned to interlayer sites. An example of determination of structural formula of a smectite from Cyprus (Christidis, 2006) and calculation of layer charge using the fixed negative charge approach is shown in Table 1.

Slight modifications of the fixed negative charge approach have been proposed by Ross and Hendricks (1945) and Köster (1977). Ross and Hendricks (1945) considered a constant value for exchangeable cations (0.33 per half unit cell) as an average value. Köster (1977) proposed that the layer charge (ξ) of the smectites should be subtracted from the total anionic charge and the exchangeable cation occupancy should be calculated separately. In this modified approach ξ is determined by the alkylammonium method described below. Apparently, the aforementioned modified approaches calculate a structural formula rather than an actual layer charge because they assume a fixed layer charge.

Fixed positive charge

This approach assumes that cations occupy certain positions in the smectite structure (Grim & Güven,

Table 1 Determination of a structural formulae using the fixed negative charge approach

(a) Use of number of cations and valence of cations in oxides

Oxide	Wt.%	Normalized wt.%	Mol. weight	Gram equivalents	No. of cations in oxide	Valence of cations	Mass equivalents	P.F. (R)	Cations per $O_{10}(OH)_2$	Structural formula	
SiO_2	53.55	61.91	60.08	1.0305	1	4	4.1220	3.7126	3.826	Si	3.826
Al_2O_3	15.17	17.54	101.94	0.1720	2	3	1.0322	3.7126	1.277	^{IV}Al	0.174
Fe_2O_3	11.51	13.31	159.7	0.0833	2	3	0.4998	3.7126	0.619	Octahedral cations	
MgO	2.95	3.41	40.32	0.0846	1	2	0.1692	3.7126	0.314	^{VI}Al	1.103
CaO	0.73	0.84	56.08	0.0150	1	2	0.0300	3.7126	0.056	Fe	0.619
Na_2O	0.71	0.82	61.98	0.0132	2	1	0.0264	3.7126	0.098	Mg	0.314
K_2O	1.88	2.17	94.2	0.0231	2	1	0.0461	3.7126	0.170	Total	2.036
										VI Cations	
Total	86.5	100					5.9257	3.7126		Interlayer cations	
						P.F (R)	3.7126			Ca	0.056
										Na	0.098
										K	0.17
										L. charge	0.380
										Int. charge	0.381

(b) Use of number of oxygens in oxides

Oxide	Wt.%	Normalized wt.%	Mol. weight	Gram equivalents	No. of oxygen atoms in oxide	Mass equivalents	P.F. (R)	Cations per $O_{10}(OH)_2$	Structural formula	
SiO_2	53.55	61.91	60.08	1.0305	2	2.061	3.7126	3.826	Si	3.826
Al_2O_3	15.17	17.54	101.94	0.1720	3	0.5161	3.7126	1.277	^{IV}Al	0.174
Fe_2O_3	11.51	13.31	159.7	0.0833	3	0.2498	3.7126	0.619	Octahedral cations	
MgO	2.95	3.41	40.32	0.0846	1	0.0846	3.7126	0.314	^{VI}Al	1.103
CaO	0.73	0.84	56.08	0.0150	1	0.0150	3.7126	0.056	Fe	0.619
Na_2O	0.71	0.82	61.98	0.0132	1	0.0132	3.7126	0.098	Mg	0.314
K_2O	1.88	2.17	94.2	0.0231	1	0.0231	3.7126	0.171	Total	2.036
									VI Cations	
Total	86.5	100				2.9628	3.7126		Interlayer cations	
					P.F. (R)	3.7126			Ca	0.056
									Na	0.098
									K	0.171
									L. charge	0.380
									Int. charge	0.381

P.F. (R) Proportionality factor; L. Layer charge; Int. Interlayer charge

1978; Karathanasis, 2007). Dioctahedral smectites contain six cations and their trioctahedral counterparts contain seven cations per $O_{10}(OH,F)_2$ structure. Similar to the fixed negative charge approach, the elemental oxide composition is normalized to 100% after subtraction of TiO_2, MnO, and loss on ignition. Then, the partial sum of mass equivalents for the oxides of those cations occupying the tetrahedral and octahedral sites is determined by dividing the percentage concentration of each oxide by its molecular weight and multiplying the quotient by the total number of metal cations in the oxide. The next step is to calculate the proportionality factor (R) by dividing the total number of structural cations with the partial sum of their mass equivalents. Then, cation occupancy in the structure is calculated by multiplying their respective mass equivalent with the proportionality factor (R) and dividing by their valence. Allocation of atoms in the structure is carried out assuming four tetrahedral atoms per $O_{10}(OH,F)_2$. Assignment of cations in the various sites follows the Pauling rules similar to the fixed negative charge approach. Finally, all remaining cations are interlayer cations (counter ions) balancing the layer charge. An example of determination of structural formula of a smectite from Cyprus (Christidis, 2006) and calculation of layer charge using the fixed positive charge approach is shown in Table 2.

Once the structural formula has been calculated, layer charges, both tetrahedral and octahedral, can be determined regardless of the approach. An ideal uncharged tetrahedral sheet has a positive charge of 16 per $O_{10}(OH,F)_2$ and an octahedral sheet has a positive charge of 6 per $O_{10}(OH,F)_2$. Ionic substitutions in the tetrahedral sheet (Al and/or Fe^{3+} for Si) and the octahedral sheet (Mg and/or $Fe2^+$ for Al and/or Fe^{3+}) create the layer charge (Bain & Smith, 1987). The abundance of tetrahedral Al and/or Fe^{3+} is the tetrahedral charge. Octahedral charge is calculated from the total amount of bivalent octahedral cations, namely Mg and Fe^{2+}, if the latter is present, minus the number of bivalent cations in excess of the ideal octahedral occupancy multiplied by 2 (the valence of Mg). The sum of charges of interlayer cations is the interlayer charge. If calculations are correct, the layer charge should equal interlayer charge. In correct analyses, deviations between layer and interlayer charge should not exceed ± 0.02 and are attributed to rounding of numbers.

Comparison of the Two Approaches and Interpretations

Normally, the two approaches should provide similar SFs if impurities are absent from the analyzed clay fraction (Grim & Güven, 1978; Karathanasis, 2007). Moreover, the layer charge and charge distribution in the SF of a Wyoming montmorillonite determined by both methods was identical (Karathanasis, 2007). In these analyses, an ideal octahedral occupancy was determined by the two methods, i.e. 4 octahedral cations per unit cell. Nevertheless, octahedral occupancy in dioctahedral smectites determined with the fixed negative charge approach usually exceeds 4 four cations, i.e. 4.14 cations per unit cell (Grim & Güven, 1978). In contrast, the fixed cation approach by definition assumes an ideal structural cation occupancy (Karathanasis, 2007). Actually, in SFs with octahedral occupancy significantly greater than 4 cations, deviations arise between the two methods that have been attributed to the presence of mineral impurities in the clay fraction (Grim & Güven, 1978). Still, the influence of excess octahedral occupancy on the two methods has not been considered in detail. For instance, Mg often resides also in exchangeable sites. Hence, assignment of Mg entirely to the octahedral sites may contribute to an excess octahedral occupancy, which is erroneous. The issue of exchangeable Mg may be resolved if the clay fraction is homoionic with a suitable index cation such as Ca or Sr (e.g. Eberl et al., 1986; Środoń & McCarty, 2008). Yet, preparation of homoionic forms of smectite is not possible in samples prepared for scanning electron microscope analysis coupled with energy dispersive spectrometry (SEM–EDS) or electron probe microanalysis (EPMA), such as polished blocks or polished thin sections. In addition, analyses of powder clay fractions are often performed without prior ion exchange with an index cation often yielding high octahedral occupancy.

The influence of octahedral occupancy on the SF and layer charge determined by the two approaches was resolved using published EPMA data on dioctahedral smectites present in bentonites (Christidis, 2001, 2006; Christidis & Dunham, 1993, 1997) and determined SFs with the two approaches. The data set included smectites formed from alteration of acidic, intermediate, and basic rocks. All but one SF calculated with the fixed anionic charge had

Table 2 Determination of a structural formula using the fixed positive charge approach

Oxide	Wt.%	Normalized wt.%	Mol. weight	Gram equivalents	No. of cations in oxide	Mass equivalents	P.F (R)	Cations per $O_{10}(OH)_2$	Structural formula	
SiO_2	53.55	61.91	60.08	1.0305	1	1.0305	3.6907	3.803	Si	3.803
Al_2O_3	15.17	17.54	101.94	0.1720	2	0.3440	3.6907	1.270	^{IV}Al	0.197
Fe_2O_3	11.51	13.31	159.7	0.0833	2	0.1666	3.6907	0.615	Octahedral cations	
MgO	2.95	3.41	40.32	0.0846	1	0.0846	3.6907	0.312	^{VI}Al	1.073
Partial sum						1.6257			Fe	0.615
					P.F. (R)	3.6907			Mg	0.312
CaO	0.73	0.84	56.08	0.0150	1	0.0150	3.6907	0.056	Total VI Cations	2.000
Na_2O	0.71	0.82	61.98	0.0132	2	0.0265	3.6907	0.098	Interlayer cations	
K_2O	1.88	2.17	94.2	0.0231	2	0.0461	3.6907	0.170	Ca	0.056
Total	86.5	100							Na	0.098
									K	0.17
									L. charge	0.509
									Int. charge	0.380

P.F. (R) Proportionality factor; L. Layer charge; Int. Interlayer charge

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excess octahedral occupancy ranging from 2.006 to 2.114 octahedral cations per half unit cell (phuc), and smaller tetrahedral charge and total layer charge than their counterparts calculated with the fixed cation charge. One smectite derived from acidic rocks had an octahedral occupancy of 1.978 cations phuc. In that smectite, the tetrahedral charge and the total layer charge calculated with the fixed anionic charge was greater than the tetrahedral charge calculated with the fixed cationic charge. Excess octahedral occupancies have also been reported in Ni,Cr-bearing, Fe-rich smectites derived from lateritic alteration of ultrabasic rocks (Gaudin et al., 2004). Although these smectites have been considered as intermediate di/trioctahedral smectites (Gaudin et al., 2004), mixtures of end-members are also common in such environments (e.g. Decarreau et al., 1987).

In addition, a nearly perfect linear trend ($R^2 = 0.998$) holds between the difference in layer charge determined by the two methods and the excess octahedral occupancy determined with the fixed anionic charge approach (Fig. 1a). A similar nearly perfect linear trend ($R^2 = 0.992$) is observed between the difference in layer charge determined by the two approaches and the difference in Si atoms calculated by the two approaches (Fig. 1b). The observed trends, which reflect differences in SFs determined by the two approaches, are due to differences in the main concepts of the two approaches and are not attributed to impurities. Indeed, the use of a focused electron beam (~1 μm in diameter) irradiates an area of 2.7 μm in diameter and allows selection of domains free of impurities (Christidis, 2006). Hence, by considering an ideal cation occupancy of 6 cations phuc corresponding to 4 tetrahedral and 2 octahedral cations, an assignment of Mg entirely to octahedral sites (although it may be partly exchangeable), will cause a decrease in the ^{VI}Al content whereas Fe^{3+} content will not be affected significantly due to its low abundance. Therefore, a larger amount of Al will be assigned to tetrahedral sites, causing a decrease in Si content and an increase in tetrahedral charge (Fig. 1b). Similarly, in fixed anionic charge, any exchangeable Mg is assigned to octahedral sites, increasing octahedral occupancy beyond the ideal value of 2, leading to a decrease in layer charge (Fig. 1a). The slight deviation of R^2 of the two linear trends from 1 is due to a systematic number of rounding errors.

Suggestions for Sample Treatment and Calculation of Structural Formulae of Smectites

The samples used for the calculation of SF of smectites can be classified in three types: powders of clay fractions for analysis with wet chemical methods, polished blocks or polished thin sections for EPMA or SEM/EDS analysis, and dilute suspensions deposited on grids for analysis with analytical transmission electron microscopy (ATEM). Powder clay fractions should be rendered homoionic with a suitable index cation (usually Na, Ca, Sr, or Ba) to remove exchangeable Mg. Inasmuch as Mg will be present only in octahedral sites, octahedral occupancy determined by the fixed anionic charge approach should approach the ideal value of 2 cations phuc in dioctahedral smectites and 3 cations phuc for trioctahedral smectites. In these cases, the two approaches should provide comparable SFs and layer charge, provided that no mineral impurities are present in the clay fraction. This approach is adequate for smectites in bentonites. In smectites from lateritic soils on basic/ultrabasic rocks, which after ion exchange with index cations and removal of Fe oxides/oxyhydroxides yield excess octahedral occupancy, the possibility for mixtures of dioctahedral and trioctahedral end members or existence of trioctahedral domains in dioctahedral structures and vice versa should be considered (Decarreau et al., 1987; Gaudin et al., 2004). In such complex cases, obtaining reliable SFs and, as a consequence, accurate layer charge is difficult.

The possibility of the presence of impurities should be checked thoroughly. Therefore, at the second step, the separated clay fractions should be investigated by XRD to detect and quantify any impurities. Then, suitable corrections should be applied to the chemical analyses prior to calculation of the SF. Corrections are easily applied when the ancillary minerals are those with simple structural formula, such as SiO_2-polymorphs (quartz, opal-CT) or kaolin minerals (kaolinite, halloysite), but are more difficult when these phases have more complex compositions (e.g. plagioclase, K-feldspars, illite, chlorite, zeolites, etc.). In such cases an error might be introduced in the SF. The error can be minimized if a sufficiently fine-grained clay fraction is used for analysis (e.g. < 0.5 μm), because most of these phases are coarser.
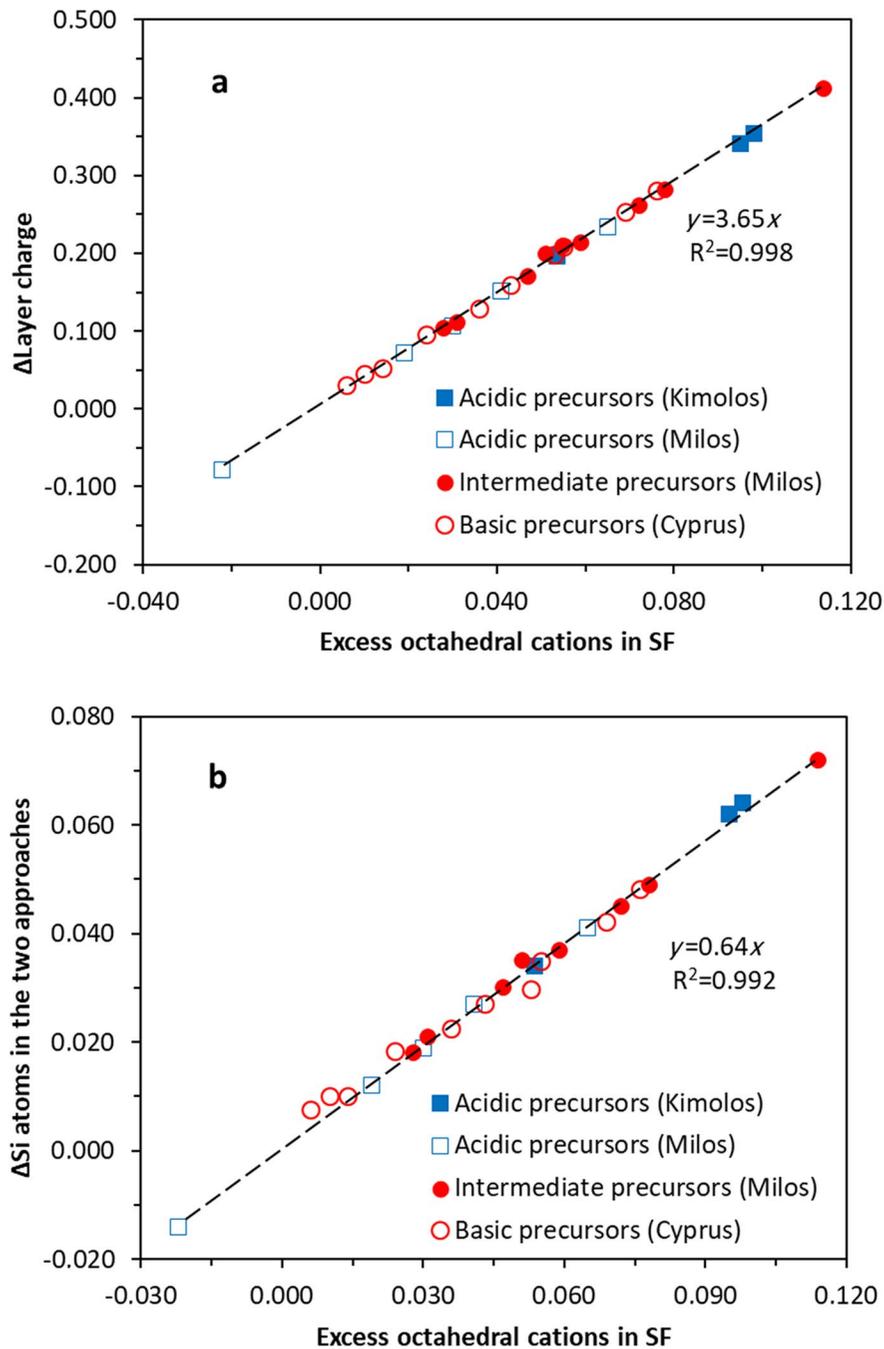
Fig. 1 Excess octahedral cations (e/huc) calculated with the fixed anionic charge approach vs **a** difference in layer charge calculated by the two approaches and **b** the difference in Si atoms calculated by the two approaches

Amorphous or crystalline Fe oxides/oxyhy-droxides or amorphous Si-Al gels can be removed with suitable treatments prior to analysis (Jackson, 1985). These treatments are pivotal for calculation of accurate SF and layer charge of Fe-rich smectites in lateritic soils. Carbonates (calcite, dolomite/

ankerite, and siderite) are common constituents of most bentonites and their presence will affect the accuracy of the SF, but they can be removed easily by dilute organic or inorganic acids prior to analysis (Jackson, 1985). Also, the oxidation state of octahedral Fe and the possible presence of free Fe oxides/oxyhydroxides might be determined using a suitable method (e.g. Mössbauer spectroscopy), although it is well established that octahedral Fe is present as Fe^{3+} in dioctahedral smectites in most cases (Grim & Güven, 1978; Karathanasis, 2007; Newman & Brown, 1987). Finally, it is possible that trace minerals, such as TiO_2-polymorphs, apatite, or Mn-oxides/oxyhydroxides, might be present although they are not detected by XRD. However, their presence will not affect the accuracy of the SF because Ti and Mn are not taken into account during calculation of SF. Also, apatite binds Ca but it is present in trace amounts in the clay fractions; hence its presence will not affect the SF considerably.

Calculation of SF with electron beam techniques is not affected by impurities, because the latter can be detected easily when analysis is performed in backscattered electron (BSE) mode (Christidis, 2006). Still, two main constraints may affect calculation of SF that should be taken into consideration. First, because preparing a homoionic clay is not possible, Mg can be present in both octahedral and exchangeable sites. Actually, most EPMA and SEM/EDS analyses yielded octahedral occupancies in excess of 2 cations in dioctahedral smectites (Christidis, 2001, 2006; Christidis & Dunham, 1993, 1997; Koutsopoulou et al., 2016) and relatively low layer charges. This suggests that the ideal number of 2 cations in dioctahedral smectites from bentonites should be considered and the excess Mg should be assigned as exchangeable (Christidis, 2006). Although such an assumption may increase uncertainty during calculation of SF, it is not far from reality because most smectites contain exchangeable Mg. Second, elemental loss, especially of Na, during analysis will affect the calculation of the SF (Christidis & Dunham, 1997). Nevertheless, elemental loss can be minimized by using suitable analytical conditions, namely, sample current, beam size, and time for analysis. Nominally, sample current of 1–2 nA, a beam size of 1 µm, and live time of 50–60 s for analysis will minimize alkali element loss due to evaporation (Christidis, 2006). The operator should experiment to determine optimum analytical

parameters prior to analysis, because the latter may change according to the type of sample (thin section/polished block vs suspension deposited on copper grids), the analytical setup (SEM–EDS vs EPMA or ATEM), the type of microscope, etc. Finally, microbeam analyses should be performed by EDS rather than by WDS because, although the latter method has greater accuracy, the overall time of analysis exceeds by far that of EDS, thereby increasing the possibility for elemental loss.

The Alkylammonium Method (AAM)

General Information

The intercalation of alkylammonium (AAM) cations in interlayer galleries of phyllosilicates was reported by the German Clay Scientist, Armin Weiss, at Darmstadt University starting in 1953 (Weiss, 1953, 1958, 1961). Later, Gerhard Lagaly, his PhD student in Heidelberg, developed the alkylammonium method (AAM) for determination of the layer charge (LC), sometimes referred to as layer charge density (LCD), with the unit eq/FU (equivalents per formulae unit) (Lagaly & Weiss, 1969; Weiss & Lagaly, 1967). The method is based on the intercalation of different alkylammonium (AA) ions consisting of a hydrophilic $-NH_3^+$ head connected to a hydrophobic zigzag-shaped alkylchain in the interlayer. The method uses a set of alkyl chains with different lengths.

The AAM yields systematically lower layer-charge values compared with the SFM (Maes et al., 1979; Senkayi et al., 1985; Laird et al., 1989, see also Laird (1994) for a review). The difference is particularly visible at high charge values (especially when >0.45 eq/fu), whereas at low charge values, differences between the two methods are smaller or absent. The deviation between the two methods has been attributed to particle size effects and occupancy of the interlayer space by the alkylammonium cations (Laird, 1994) and to the fixation of cations that are not replaced by alkylammonium (Kaufhold et al., 2011). According to the latter model, the amount of fixed cations increases with increasing layer charge (Kaufhold et al., 2011). Therefore, the two methods describe different parameters, namely, the SFM describes charges balanced by exchangeable and fixed

cations, whereas AAM describes charges balanced only by exchangeable cations.

Description of the Method

A set of various linear alkylammonium chloride solutions with various numbers of C atoms is prepared. The parameter "n_c" commonly indicates the numbers of C atoms within the alkyl chain. Their intercalation in the interlayer of smectite is based on cation exchange. The analytical challenge is to produce a homogeneous balance of the permanent charges by the alkylammonium ions for which it is important to first provide an excess of AAM, and secondly, even more importantly, to wash out the excess alkylammonium not used for layer-charge neutralization of smectite in the interlayer. The hydrophilic part of the molecule adsorbs to the permanent charge replacing the respective exchangeable cation. The analytical procedure has been described extensively. The most detailed descriptions of the method were published by Lagaly and Weiss (1969) and in The Clay Minerals Society Workshop lectures volume: *Layer Charge Characteristics of 2:1 Silicate Clay Minerals* (Lagaly, 1994). The analytical part starts with the preparation of the different alkylammonium solutions. The solutions should be freshly prepared because they cannot be stored over long times. The stabilities of the different solutions also differ. It is not possible, therefore, to propose a general storage recommendation. Some solutions with $nc > 14$ are heated to 60°C before use. A suitable option to test if the solutions can still be used is to include a reference material which has been investigated previously with the fresh solutions. In the present authors' experience, most of the solutions could be used for at least 3 months after which time

fresh solutions should be prepared. Preparation of the solutions is explained by Lagaly (1994). The different alkylammonium ions are available as chlorides, and chemical purity has to be checked carefully. These solutions are diluted and the pH has to be adjusted, which is challenging because titration has to be performed with concentrated acid. Once the solutions are prepared, the different smectite intercalations are produced. For the analysis of one sample, a set of different intercalations has to be prepared which means that the same starting sample should be treated with the various solutions. If only an estimation of the total layer charge is required, the method of Olis et al. (1990) with $n_c = 12$ may be used. Nevertheless, detailed information about charge characteristics are not available with this method.

In the schematic representation shown in Fig. 2, the sample was split into 12 aliquots and mixed with 12 different n-alkylammonium solutions. The aim of the quite laborious protocol is to obtain homogeneously intercalated samples. After mixing the solid sample and the solution, the samples should be stored in a shaking water bath at 60°C because the subsequent washing steps are much easier if the formation of a solid sediment is avoided by agitation. For washing, either water or ethanol or mixtures of both are suggested. Details about the washing procedure and recommended solutions were given by Lagaly (1994). Proper washing is crucial because excess alkylammonium can lead to inflated d_{001} values and extensive washing can lead to some desorption of saturating alkylammonium ions. To test the effect of washing, differently washed samples were investigated by XRD (Fig. 3). As an easy-to-handle control, a a drop of the solution after each washing step was dried on a glass slide lying on a sheet of black paper
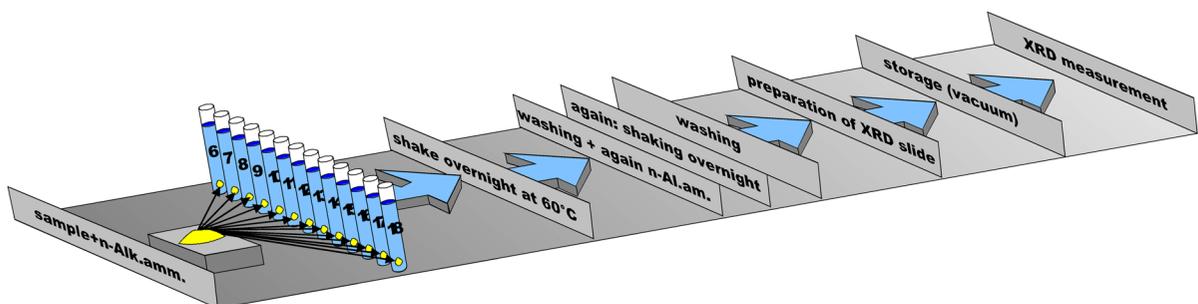
Fig. 2 Schematic representation of the AAM procedure

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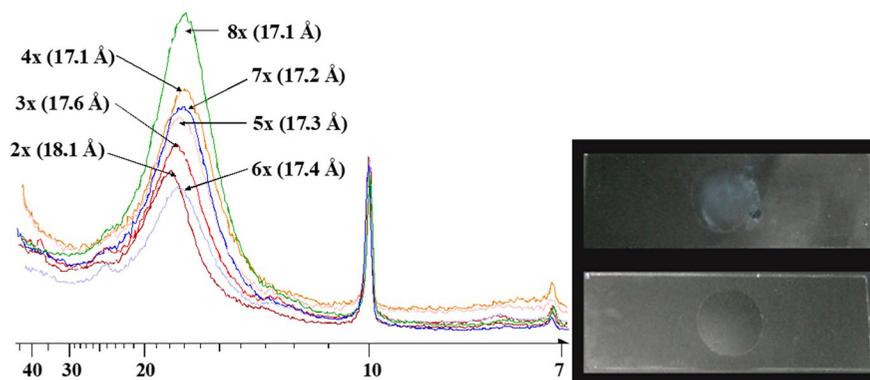
Fig. 3 Effects of various washing steps on the d_{001} spacing of a Bavarian bentonite ($n = 13$; left); right: photographs of glass slides with dried drops of various washing solutions (water/ethanol) in their respective centers. Upper: excess AA present with a cloudy, veil-like appearance; lower: sample after repeated washing, no excess AA is detectable

to test for remaining AA. If salt residues are still visible, the washing must be continued. Typically, d_{001} values were more or less constant after 4–10 washing steps (depending on the lengths of the chains) and the clear glass slide indicated a low concentration of excess alkylammonium. Then, an oriented XRD specimen should be prepared either by drying some of the slurry on glass mounts or by sucking the suspensions through a porous ceramic tile. The latter was preferred because the sediments often peeled off from the glass slides. Clay film peeling off may be avoided by roughening the surface of glass slides. If peeling occurs, preparation of new specimens with less sample mass may help. As such specimens are sometimes affected by displacement error ('sample height') caused by preparation and placement in the XRD apparatus not perfectly fitting on the Rowland circle geometry, erroneous shift of d values may occur. To overcome this problem, the current authors separated the < 2 μm fraction from talc powder and added it as an internal standard to each sample. After XRD analysis, the displacement error, if present, can be corrected based on the known peak position of talc by shifting the whole XRD diagram using the correct procedure given in the software (this should not be confused with zero point shift correction). According to Lagaly (1994), the AA-smectites are more hydrophobic than before but they can still take up some water, thus increasing the d_{001} value. Accordingly, the XRD mounts are dried in a vacuum (low pressure) at 60°C or in an XRD vacuum chamber at 60°C if available, and XRD measurements are performed in a closed chamber purged by dry nitrogen gas to prevent rehydration. Storage after vacuum prior to measurement may be performed in a desiccator to avoid such hydration.

The AAM method relates the chain length and the resulting geometry of the n-alkylammoniumion cations used with the d_{001} values of the respective smectite intercalations. The length and width of the 2-D dimensions of the various alkylammonium ions are known. Based on these, the space demand of a given alkylammonium-cation monolayer can be calculated and compared with resulting distances of the ammonium which is assumed to reside near the charges. The distance of the ammonium in turn corresponds to the layer charge density. As soon as the 2-D alkylammonium-cation density in the interlayer exceeds the layer charge density, a second layer of alkylammonium-cations starts to form leading to a 3-D arrangement. The calculation of LC values based on d_{001} spacings was described by Lagaly (1994). The background data were investigated recently by Lanson et al. (2022) who modeled the distance of various smectites with various alkylammonium cations. They found good correlation between the modeled data and the data provided by Lagaly (1994), indicating the validity of the geometric calculations provided by Lagaly (1994).

The interpretation of the XRD data is based on the peak migration curve which means that the d_{001} value of each smectite-alkylammonium complex is compared with the number of C atoms (n). The smallest chain length is $n_c = 6$, which in common smectites can
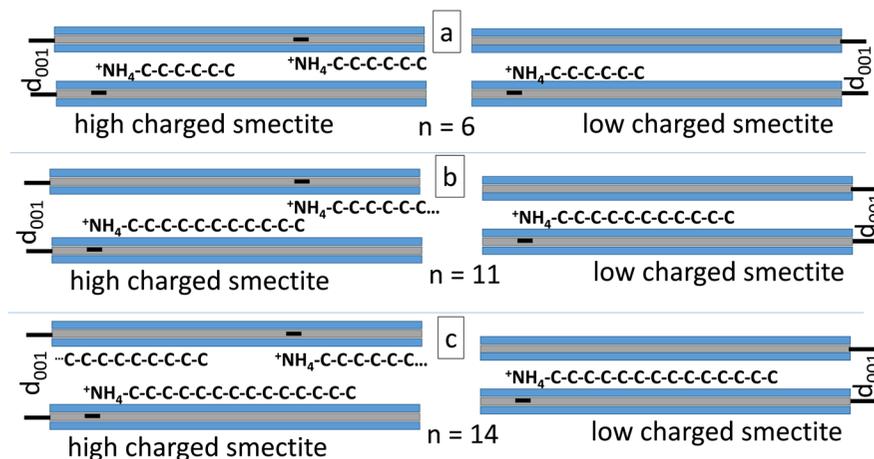
Fig. 4 Schematic representation of the basic concept for determination of the layer charge using the AAM method. The AAM-chains are shown as linear; they are, in fact, zigzag-shaped

be accommodated easily in a single-layer arrangement, leading to d_{001} values between 13 and 14 Å (Fig. 4a). These d_{001} values are also observed for alkylammonium ions with larger n_c until the distance to the next charge is attained. In the example in Fig. 4, this was reached at $n_c = 11$ in the case of the high-charge smectite but not in the case of the low-charge smectite (Fig. 4b). For chain length $n_c = 14$ a bilayer arrangement was reached in the case of the high-charge smectite ($d_{001} = 17$–18 Å) but the low-charge smectite remained in a monolayer state. Such a smectite would have an even lower charge compared to the Wyoming bentonite, as illustrated in Fig. 5, which shows two measured peak-migration curves of a high-charge smectite (Milos bentonite) and a low-charge smectite (Wyoming bentonite). In this example, the mono to bilayer transition of the smectites of the Wyoming bentonite began with a chain length of $n_c = 12$. The example also showed that using a chain length with $n_c < 6$ is not possible. In the Milos sample, increasing the chain length clearly increases d_{001} even beyond the bilayer arrangement (Fig. 5). This was explained by Lagaly (1994) by the formation of a pseudotrimolecular layer (~22 Å) and even by a paraffin-type arrangement of AA at higher d_{001} values.

The advantage of the AAM over the SFM and the AAM short version (Olis et al., 1990) is that it can calculate both average layer charge and layer-charge distribution (LCDD). Based on the results of AAM, classifying smectites into low- and high-charged as

well as homogeneously and heterogeneously charged ones is possible (Fig. 6, left). The calculation of LCDD is based on the probability of the existence of a certain LCD range depending on the d_{001} value of a given intercalation of alkylammonium ions. Details including particle-size correction have been explained by Lagaly (1994). An example based on measured values showing a more homogeneous and a more heterogeneous charge distribution is given in Fig. 6 (right). In the literature, this approach was discussed intensively and questioned (e.g. Laird, 1994; Laird et al., 1989).

The NH_4^+ Method

Introduction and Background

The method determines the layer charge of clay samples or pure clay phases based on the NH_4^+ infrared band from NH_4^+-saturated clays. The method is sensitive enough that it can be used even for very small samples and was described by Petit et al., (1998, 1999, 2006) and Joussein et al. (2001). The methodology is based on the quantification of the NH_4^+ infrared signal, which depends on the charge characteristics of the NH_4^+-saturated clay minerals. The NH_4^+ ion gives absorption bands at 3150, 3020, 2840, and 1400 cm^{-1} (Petit et al., 1998). The most intense bands are at 3150 and 1400 cm^{-1} and
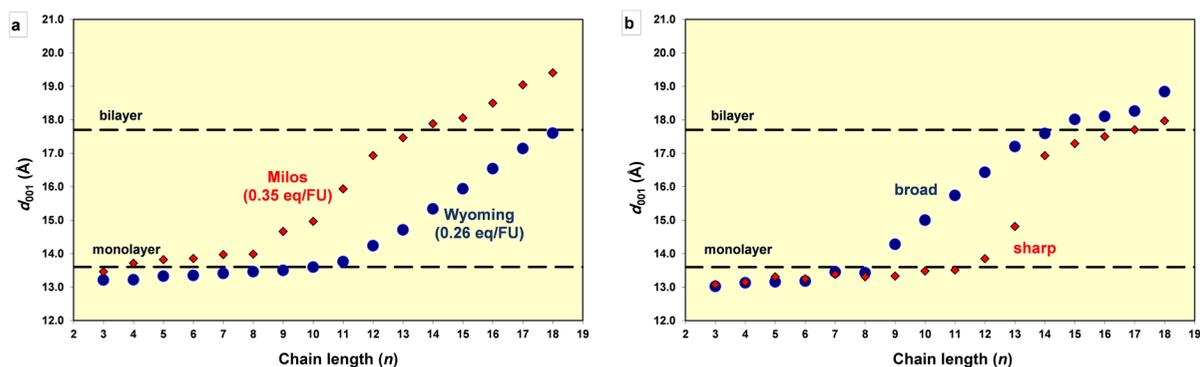
Fig. 5 Examples of peak migration curves in the AAM method: **a** low- and high-charge; **b** broad and sharp charge distributions

are attributed to the triply degenerate vibrations $\nu 3$ and $\nu 4$, corresponding to stretching and deformation modes, respectively. However, the stretching region of NH_4^+ at 3200–2800 cm^{-1} may partially overlap with the OH-stretching of clay minerals, rendering distinction difficult. The 1400–1440 cm^{-1} absorption band, therefore, has been selected to quantify the NH_4^+ because this region is not affected by the vibrations of OH and Si–O groups of clays (Chourabi & Fripiat, 1981), and displays good correlation between the absorbance and nitrogen content (e.g. Vedder, 1965). Briefly, using KBr pellets to obtain infrared spectra, the v4 deformation mode of the NH_4^+ signal can be decomposed into two components located at 1440 and 1400 cm^{-1}. The band at 1400 cm^{-1} is attributed to NH_4Br due to replacement of exchangeable NH_4^+ by K^+ from the KBr (Petit et al., 1999). In this case, the band indicates permanent low charge-density and/or variable charge for swelling clay minerals, as well as the presence of variable charge for kaolinite or the permanent charge balanced by non-exchangeable cations other than NH_4^+ (e.g. micas, etc.). Also, the band at 1440 cm^{-1} suggests that NH_4^+ balances only the permanent charge in the interlayer space, or part of the high charge in the interlayer space (Petit et al., 1999). Finally, to quantify the layer charge/CEC of clay minerals, the use of integrated intensity of the 1400–1440 cm^{-1} bands allows determination of proportions of the different types of charge (permanent vs non-permanent).

Sample Preparation and Methodology

An advantage of the NH_4^+-method lies in the speed of preparation of the clay samples. An aliquot of clay

(a few milligrams) is saturated with 1 M NH_4Cl solution and shaken for 1 h followed by centrifugation. This step is repeated three times for complete saturation. Then the sample is washed until NH_4^+-free (negative colorimetric test with Nessler reagent). For small quantities of starting material, it is preferable to carry out this operation by dialysis to avoid sample loss. The sample is then dried for analysis by infrared spectroscopy.

Fourier-transform infrared (FTIR) spectra are recorded on a classical FTIR spectrometer in transmission mode (reported in absorbance units) in the MIR 4000–400 cm^{-1} range. It is preferable to purge the sample continuously with dry air containing substantially less CO_2 than normal air. However, the use of other configurations may be possible (e.g. diffuse reflectance infrared Fourier-transform – DRIFT – spectroscopy, with or without KBr). Spectra are obtained from KBr pressed pellets mixing 1 mg samples with 150 mg of KBr, after dehydration of pellets at 110°C for 8 h.

Then, it is necessary to normalize the FTIR spectra to specific IR absorption bands, which act as an internal standard to compare samples quantitatively (Russell, 1965). Indeed, the IR beam scattering is a complex function of crystal size, aggregate size, and packing. Preparing samples that are strictly identical is difficult, and the intensity of an absorption band varies with the amount of absorbing units present in the sample (Schroeder, 2002). In terms of normalization, the OH-stretching bands are used as an internal standard, because, although the absorption coefficients of the OH-stretching bands differ slightly for different types of clays, they can be assumed to be equivalent in dioctahedral and trioctahedral smectites
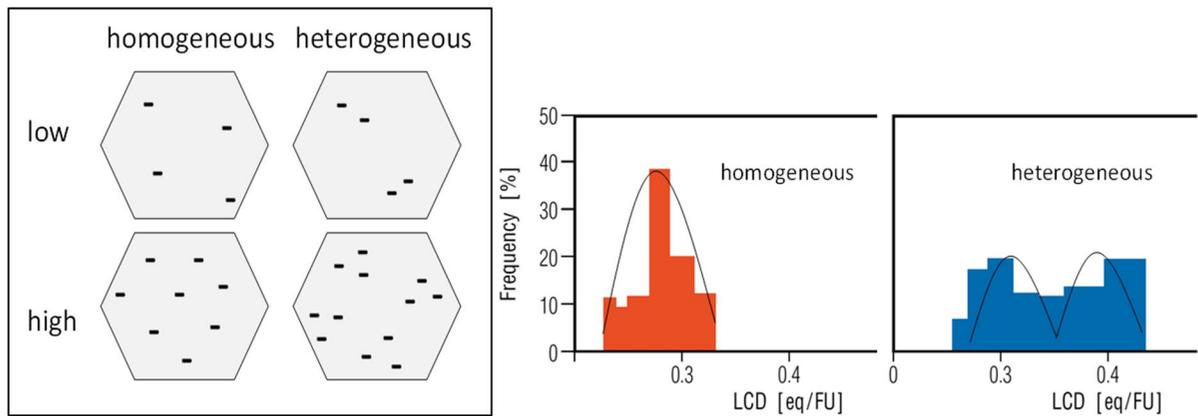
Fig. 6 Left: schematic representation of the option to classify smectites based on AAM results; right: measured data of a more homogeneously charged smectite (red) and a more heterogeneously (close to bimodally) charged smectite (blue)

(Petit et al., 2004). Finally, the total absorbance of OH-stretching bands is normalized over an arbitrarily chosen unit of integrated intensity S_{OH}. The normalization or correction factor, denoted f, which varies for each sample, is equal to:

$$f = S_{OH}/A_{OH} \qquad (1)$$

where A_{OH} is the measured integrated intensity of the OH stretching band. Then, the value for S_{NH4}, which is the normalized integrated intensity of the NH_4^+ band in arbitrary units, can be determined and corrected using the following relation:

$$S_{NH4} = f \times A_{NH_4} \qquad (2)$$

where A_{NH_4} is the integrated intensity of the NH_4^+ band.

The spectra can then be normalized relative to the Si–O band, which can be considered to be equivalent in different smectites. However, this is possible only for pure samples, i.e. free of quartz or feldspars which will affect this band. In this case, Eq. 1 can be written as:

$$f = S_{OH}/A_{OH} = S_{SiO}/A_{SiO} \qquad (3)$$

Similarly, S_{SiO} is expressed in arbitrary units of integrated intensity for the absorbance of Si–O, and A_{SiO} is the measured area of the Si–O band.

From these values obtained in arbitrary units, switch to units of interest is easy, i.e. layer charge or CEC, because the relationship between measured CEC and S_{NH4} is linear (Madejová, 2005; Petit et al.,

1998; Fig. 7). However, in order to determine a complete series or to compare samples, having a value of CEC or layer charge as a reference is necessary to calibrate the method.

This method is also applicable in the case of clay mixtures between 1:1 (kaolinite) and 2:1 smectite clays (Joussein et al., 2001). The method used is essentially the same as the previous one, i.e. it is necessary to normalize the spectra and then to determine the A_{NH4}/A_{OH} ratio in arbitrary units. However, because of the difference in absorbance of the OH-stretching of kaolinite and smectite, the resulting relationship is not linear. The weight ratio (x) of smectite in the mixture can be written in the following form:

$$y = (A_{NH4reference} \times x)/[(A_{OHsmectite} \times x) + (A_{OHsmectite} \times R(1 - x))] \qquad (4)$$

with $A_{NH4reference} = 8.113$ a.u., $A_{OHsmectite} = 9.6$ a.u., and R = 4.9 (ratio of measured absorbance of νOH for kaolinite relative to the measured absorbance of νOH for smectite, previously determined experimentally).

In this case, it is sufficient to measure the A_{NH4}/A_{OH} ratio of any mixture of discrete kaolinite/smectite (or even kaolinite/smectite interstratification) and to apply Eq. 4 to determine the smectite content (Fig. 8). Then, it is possible to switch to the unit of interest (CEC or layer charge) as before. Pironon et al. (2003) have used this approach to determine illite/smectite ratios in mixtures of discrete phases or interstratified phases.

Moreover, the proportion of tetrahedral/octahedral charge can be estimated by comparing the $v_4NH_4^+$

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bands before and after Li treatment. For this purpose, the Hofmann and Klemen effect is used (Greene-Kelly, 1953, 1955; Hofmann & Klemen, 1950), whereby Li^+ cations migrate into vacant octahedral sites and compensate the negative charge due to ionic substitutions in the octahedral sheet. Classically, measuring the CEC at each step is necessary, which is time consuming and costly in terms of sample quantity. Using infrared spectroscopy ($v_4 NH_4^+$ bands), the determination is much faster and requires only a very small amount of material (~4 mg). Thus, the charge distribution and the total charge in dioctahedral and trioctahedral 2:1 clays can be obtained from the integrated intensity of the $v_4 NH_4^+$ band. Before the Li treatment, the NH_4^+-content refers to the total charge (permanent plus variable charge), whereas after Li-treatment the NH_4^+ content is relative to the sum of the tetrahedral and variable charges. The difference between the NH_4^+ content before and after Li treatment can be attributed to the octahedral charge. Examples of charge distribution in a series of smectites have been reported by Madejová (2005) and Petit et al. (2006).

Advantages and Disadvantages of the Method

This method of layer-charge or/and CEC determination using infrared spectroscopy is very effective because:

(i)   of the rapid setup and measurement of a large series of swelling minerals with variable purity, and/or in mixture or interstratification;

(ii) it is sensitive; a detection limit of ~300 ppm of N can be expected (Pironon et al., 2003);

(iii) it requires only a small amount of sample, ~10 mg;

(iv) units can be easily switched from layer charge to CEC and vice versa;

(v)   exchangeable and fixed NH_4^+ in clay minerals can be distinguished based on the position and shape of the v4 NH_4^+ band near 1400 cm^{-1};

(vi) the tetrahedral/octahedral charge of smectite can be determined by comparing the v4 NH_4^+ bands before and after Li treatment.

The major disadvantage of the method is that the samples should not contain carbonate or organic matter as their bands may overlap with the v4 NH_4^+ bands. However, carbonates can be removed by treatment with dilute HCl.
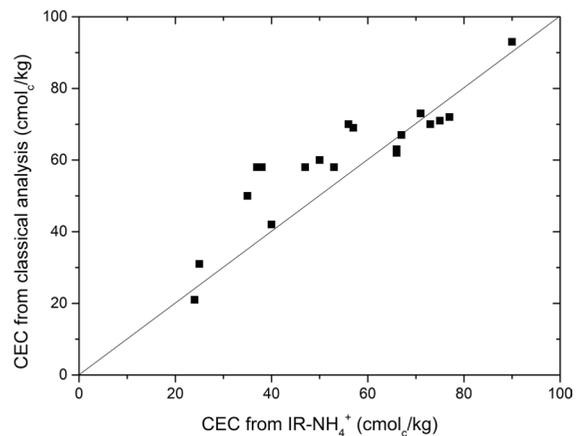
Fig. 7 Example of the relationship between the CEC calculated from NH_4^+ methods and the CEC measured by the classical method. The samples are from soil series and from various kaolinite-smectite mechanical mixtures. Data adapted and modified from Petit et al. (1998)

The K-saturation Method

General Characteristics

The K-saturation method uses X-ray diffraction (XRD) traces of oriented ethylene glycol (EG) -solvated clay fractions (Christidis & Eberl, 2003). It is particularly useful for bentonites, but it can also be used in any type of smectite-bearing clays, provided that a series of 00l basal reflections of smectites are present in the XRD traces of oriented clay samples. The method assumes that smectite is composed of random interstratification of 2:1 layers with different charges. Similar approaches had been proposed in the past and assumed that saturation with K yields three end-member layers with different d_{001} spacings of ~17, 14, and 10 Å (Tettenhorst & Johns, 1966; Machajdik and Čičel, 1981). These approaches either do not determine the layer charge (Tettenhorst & Johns, 1966) or they assign the layer charge to be 0.28, 0.6, or 1.0 electrons per half unit-cell (e/huc) for the three end members, attributed to smectite-like, vermiculite-like, and illite-type layers, respectively (Machajdik and Čičel, 1981). However, the end-members with layer charges 0.6 and 1.0 e/huc are not comparable to vermiculite and illite, respectively (Christidis & Eberl, 2003).

Random interstratification of smectite layers with variable swelling after K-saturation and
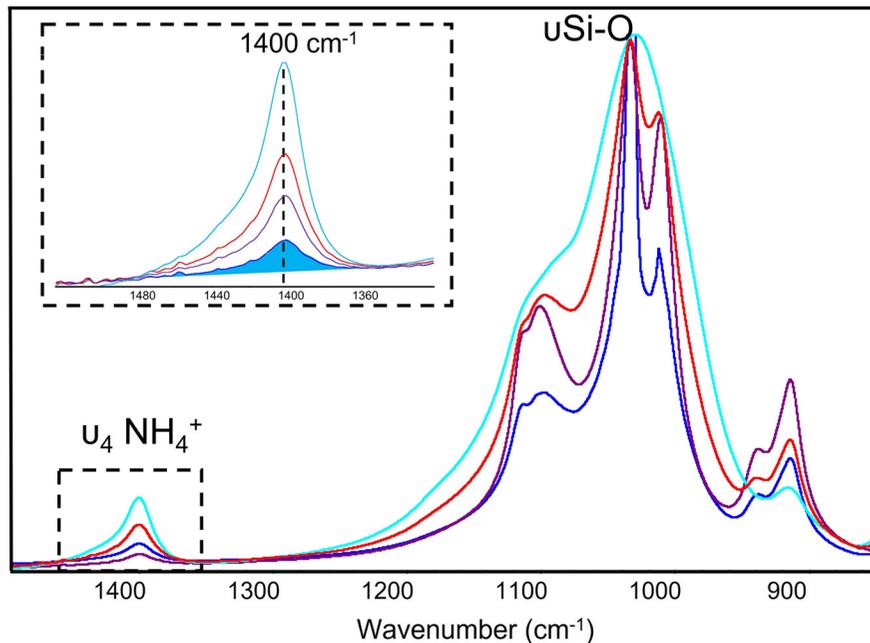
Fig. 8 Example of a normalized IR spectrum (see text) of smectite SAz-1 mixed with various weight percentages of kaolinite KGa-1 (0%, light blue line; 25%, red line; 50%, purple line; 75%, blue line) in the regions of the ν_4 NH_4^+ bands and νSi-O

EG solvation, yields XRD profiles with different characteristics (Fig. 9a) which can be quantified and assigned to different layer charge, by means of the *LayerCharge* computer program (Christidis & Eberl, 2003). The XRD profiles are characterized by migration of the main basal peaks relative to the counterparts of smectites saturated with cations of high hydration enthalpy, such as Na or Ca. In addition, the method calculates the proportions of fully, partially, and slightly swelling layers. Unlike their illite counterparts, smectite layers display peak migration of the basal peaks after back-saturation of the K-forms to Na- or Ca-equivalents (Fig. 9b).

The method was calibrated over 29 smectites with known structural formulae (Table 1 in Christidis & Eberl, 2003). Therefore, the layer charges determined with the K-saturation method were calibrated relative to the structural formula method. The smectites used for calibration covered the entire range of smectite compositions (Schultz, 1969; Newman & Brown, 1987) including montmorillonite, beidellite, nontronite, and hectorite, and layer charges, both with respect to location (beidellite and nontronite vs montmorillonite and hectorite) and magnitude (0.3–0.6 e/huc).

The *Layercharge* Program

The method is based on a comparison between XRD traces of K-saturated, ethylene glycol-solvated smectites and computer-simulated XRD traces calculated for three-component interstratification with the *LayerCharge* program and finding the computer-simulated traces that best fit the experimental traces (Christidis & Eberl, 2003). Sample preparation involves separation of the <2 μm clay fraction of the bentonites after settling and saturation twice with 1 N KCl, followed by repeated washing until chloride free and preparation of conventional oriented clay mounts on glass slides or (preferably) Si-wafers. K-saturation is followed by ethylene glycol (EG) solvation. The temperature for EG solvation should not exceed 60°C to avoid possible K-fixation in high-charge layers that would cause formation of illite-type layers. The XRD traces of EG solvated K-saturated smectites are inserted in the *LayerCharge* program.

The *LayerCharge* program determines total layer charges and layer-charge distributions for 100% expandable smectites from XRD patterns of K-saturated, ethylene glycol-solvated samples. Upon K saturation and glycol treatment, three types of layers may form in such smectites. Based

on computer modeling, these randomly inter-stratified layers have spacings of ~17.1, 13.5, and 9.98 Å. The *d* spacing values of the three types of layers are assumed to be related to at least three different values for layer charge, with the lowest-charged, 17.1 Å layers adsorbing two EG layers, the intermediately charged 13.5 Å layers adsorbing one EG layer, and the highest-charged 9.98 Å layers being completely collapsed. Calculated and measured patterns are matched either by matching peak positions for 00 *l* reflections, or by whole-pattern fitting. These matches are accomplished by finding the calculated pattern that minimizes the sum of the squared differences between either the experimental and calculated peak positions for the first six 00 *l* reflections, or for the whole-pattern fit of experimental and calculated intensities that are normalized to the intensity of the most intense peak. The program automatically selects the calculated pattern which best matches the experimental profile (Fig. 10). Once the calculated pattern is selected the relative proportions of the three types of layers are determined and the total layer charge is calculated. The precision of the method is better than 3.5% at a layer charge of 0.50 e/huc, thus providing a very good approximation for the layer charge of smectites. A detailed description of the *LayerCharge* program was given by Christidis and Eberl (2003).

Simplification of the K-saturation Method

The position of the first two basal reflections of K-saturated, EG-solvated smectites depends on the proportion of the low-charge layers (fig. 3 in Christidis & Eberl, 2003). More specifically, with increasing proportion of the low-charge layers, the 001 diffraction maximum migrates to higher 2θ angles (i.e. smaller *d* spacing values) whereas the 002 diffraction maximum migrates to lower 2θ angles (i.e. larger *d* spacing values). The peak migration of the 002 diffraction maximum resembles the peak migration of the (001) illite/(002) smectite peak of R0 mixed layer illite–smectite. However, the two phases can be distinguished by means of two features. Firstly, in smectite, the peak migration disappears after saturation with a cation of high hydration enthalpy (Li, Na, Ca, or Mg), whereas in R0 mixed-layer illite–smectite it is not affected by saturation with cations having high hydration

enthalpy. Secondly, the 001 diffraction maximum of R0 mixed layer illite–smectite remains constant at ~17 Å, whereas in K-saturated smectite the 001 diffraction maximum migrates to larger angles with increasing proportion of high-charge layers and thus with increasing layer charge. The d_{001} spacing of EG-solvated high-charge K-saturated smectites is ~14 Å. Therefore, high-charge smectites are clearly different from R0 mixed-layer illite–smectite.

Because the low-charge layers contribute to the total layer charge it follows that the position of the 001 maximum might be used to determine layer charge, without the use of the *LayerCharge* program. Based on the position of 001 diffraction maximum, layer charge may be determined by the following linear equation (Eq. 5) with Pearson r value = 0.93 (cf. Figure 7 by Christidis & Eberl, 2003):

$$\text{Layercharge(e/huc)} = (24.65 - d_{001}\text{spacing})/19.74 \tag{5}$$

Equation 5 is used in the *LayerCharge* program to provide an independent estimation of layer charge. Usually, the two methods provide similar layer-charge values that do not deviate more than 0.01 e/huc. By contrast, the 002 and 003 diffraction maxima cannot be used for independent estimation of layer charge, the former because it is either absent or almost constant in smectites with layer-charge > 0.48 e/huc.

Limitations and Refinement of the K-saturation Method

Although K-saturation was calibrated with a series of smectites with layer charge varying nearly over the entire range of layer charges typical of smectites, it became obvious that smectites with layer charge of < 0.39 e/huc display comparable XRD traces, due to lack of peak migration (Christidis & Eberl, 2003). Therefore, the method cannot be applied for smectites with layer charge < 0.39 e/huc. Nevertheless, this is not a major problem because the vast majority of natural smectites reported in the literature have layer charge > 0.39 e/huc.

A main observation during calibration of the K-saturation method was that the Glen Silver Pit, Black Jack, and #74 beidellites with high layer charge deviated from the overall trends; the calculated higher layer charge of these smectites was greater than the layer charge reported in the literature (Christidis &
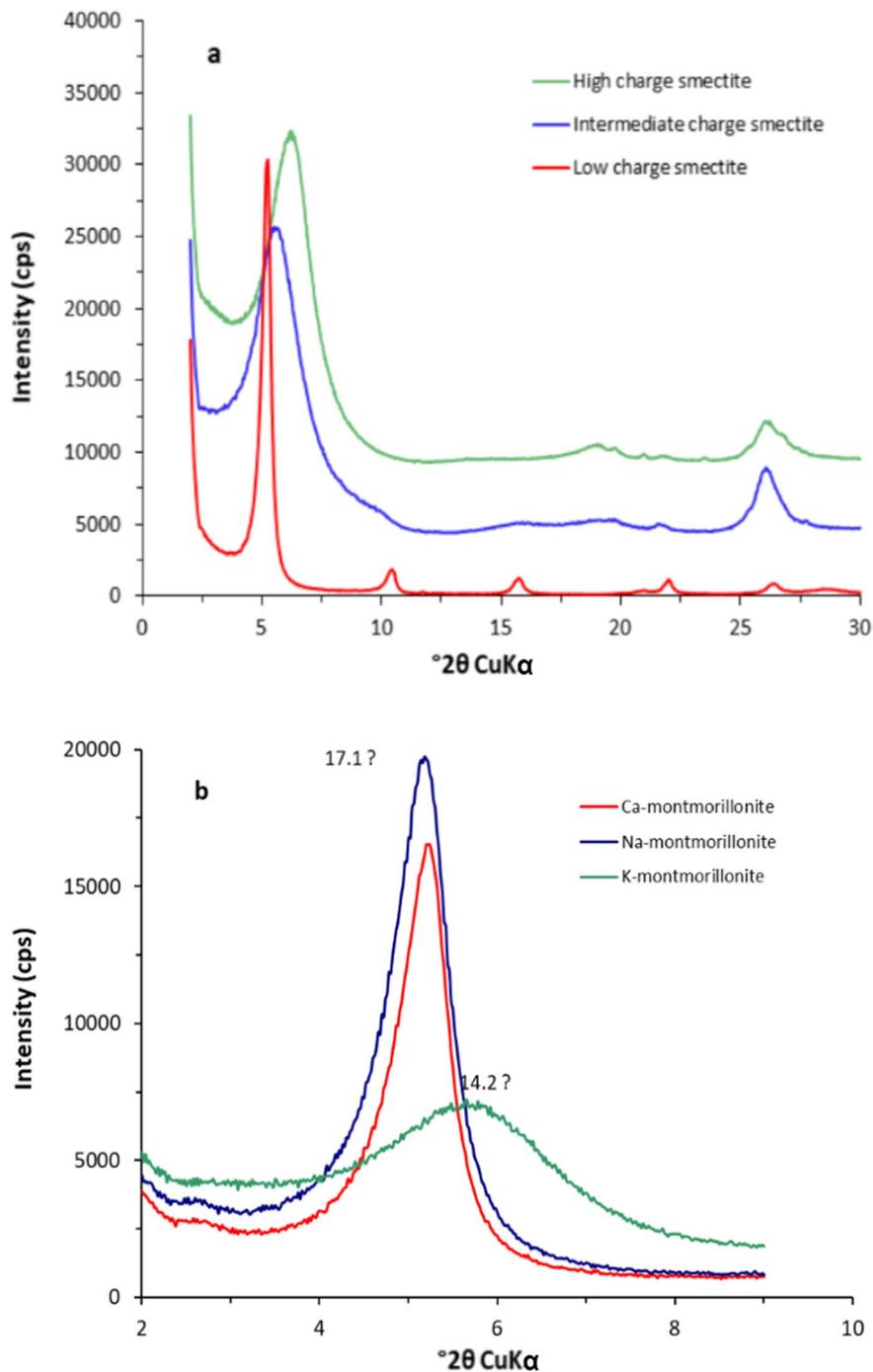
Fig. 9 **a** XRD patterns of K-saturated, EG-solvated smectites with low, intermediate, and high layer charge. **b** XRD traces of EG-solvated SAz-1 montmorillonite saturated with K, and back-saturated with Na and Ca ions

Eberl, 2003). A similar behavior was observed in nontronites and low-charge beidellites, suggesting that charge localization affects the method, because tetrahedral charge yields to the formation of a greater number of single-layer complexes or even to a lack of EG complexes in K-smectites. Therefore, a correction

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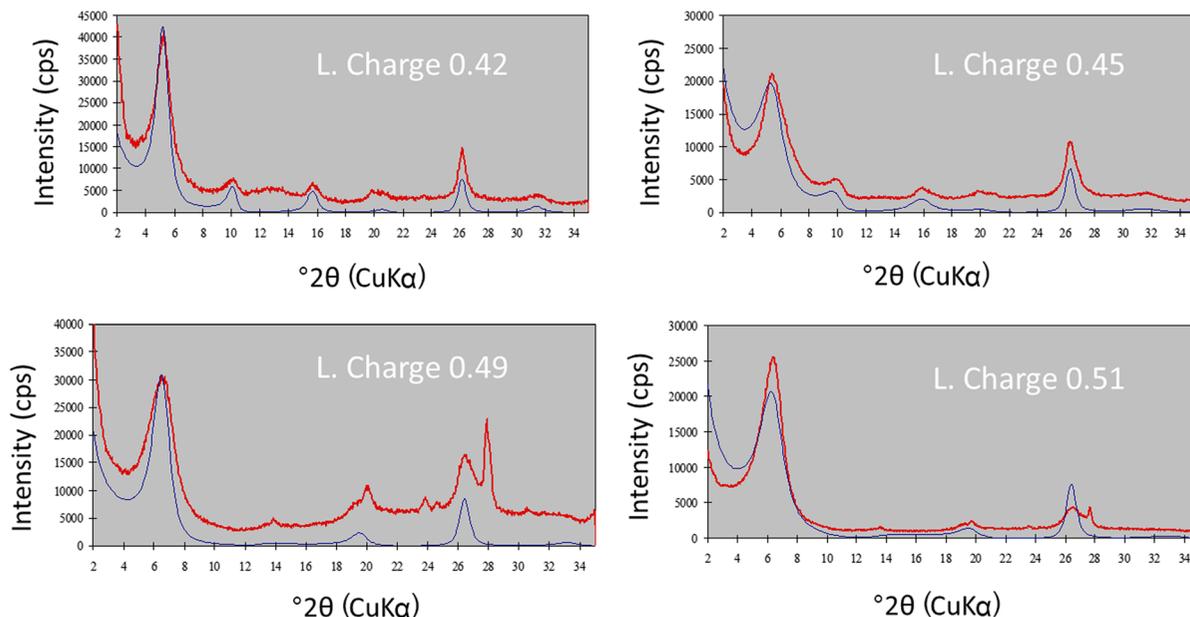
Fig. 10 Simulation of XRD traces of K-saturated and EG-solvated smectites using the *LayerCharge* program. Red = experimental XRD trace, blue = computed XRD trace (data from Makri, 2011)

needs to be applied for the overestimation of layer charge that would counteract this bias.

The relationship between the calculated and measured layer charge is shown in Fig. 11. Equation 6 is proposed for correction of the calculated layer charge of unknown smectites, dominated by tetrahedral charge.

$$LC_{corr} = 1.087(LC_{meas} - 0.11) \tag{6}$$

where LC_{corr} is the actual LC determined after correction for charge localization and LC_{meas} is the layer charge determined by the K-saturation method. It is suggested, therefore, that the layer-charge method be accompanied by the Greene-Kelly (1953) test and application of a correction where necessary.

Implications of the K-saturation Method-Classification of Smectites According to Layer Charge

The K-saturation method has been useful: (1) in the classification of smectites according to the layer charge; (2) in assessing the influence of layer charge on smectite-water properties; (3) in separating high-charge smectite from vermiculite; (4) in understanding the influence of layer-charge distribution of smectites on illitization; and (5) in determining

the distribution of layer charge in bentonite deposits (Christidis & Eberl, 2003; Christidis & Huff, 2009; Christidis et al., 2006). The classification of smectites according to layer charge is of particular importance. Christidis et al. (2006) classified smectites according to their layer charge, based on their behavior after K-saturation and EG solvation, as this was demonstrated in the oriented XRD traces of clay fractions. According to this classification scheme, low-charge smectites have a layer charge of < 0.425 e/huc and are characterized by a d_{001} spacing > 16.6 Å and rational higher-order basal reflections, suggesting that K-saturation does not affect swelling of the interlayer. The high-charge smectites have a layer charge of > 0.475 e/huc and display the largest number of high-charge, non-swelling layers, with d_{001} spacing < 15.5 Å (usually ~ 14 Å) and d_{003} spacing ~ 4.60–4.65 Å, with the 002 basal reflection being absent. Finally, Christidis et al. (2006) introduced the term "intermediate layer charge" to describe smectites with layer charge between 0.425 and 0.475 e/huc, having d_{001} spacing between 16.6 and 15.5 Å and irrational higher-order basal reflections. This was the first attempt to classify smectites according to the layer charge and to define and use the term intermediate layer charge. Furthermore, the layer-charge limits were correlated with swelling and rheological properties of bentonites

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(Christidis et al., 2006). In this classification scheme, low-charge smectites can be considered as "real smectites" because they display maximum swelling after EG solvation (i.e. formation of two layer EG complexes), regardless of the type of exchangeable cation.

This classification scheme has two characteristics. Firstly, the layer-charge boundaries are not distributed symmetrically in the layer-charge range of smectites (e.g. 0.2–0.6 e/huc). Secondly, because charge localization affects the K-saturation method, the layer-charge boundaries are different for the smectites dominated by tetrahedral charge, suggesting that the terms low-, intermediate-, and high-charge are not defined by fixed layer-charge boundaries. Hence, the low-charge smectites with predominantly tetrahedral charge should have layer charge < 0.365 e/huc, high-charge smectites with predominantly tetrahedral charge should have layer charge > 0.415 e/huc, and intermediate-charge smectites with predominantly tetrahedral charge should have layer charge between 0.365 and 0.415 e/huc.

Emmerich et al. (2009) used similar terms to classify smectites according to layer charge but applied different charge boundaries. Hence, low-charge smectites have layer charge of < 0.375 e/huc, medium-charge smectites have layer charge of between 0.375 and 0.425 e/huc, and high-charge smectites have layer charge of > 0.426 e/huc (Emmerich et al., 2009). The problem with this scheme is that the selection of layer-charge boundaries for classification of smectites was not based on specific criteria. Also, none of the smectites examined in this scheme were classified as high-charge smectites (e.g. Wolters et al., 2009).

In conclusion, the K-saturation method is a fast and reliable method for determination of layer charge of dioctahedral smectites with precision of ± 0.02 e/huc. It has been applied to determine the distribution of layer charge in bentonite profiles (Christidis & Huff, 2009) and may contribute to the understanding of the mechanism of bentonite formation. The main limitations of the method are the detection limit (it determines layer charge > 0.39 e/huc) and the influence of charge localization (octahedral vs tetrahedral) on the method. While the detection limit is an intrinsic limitation, the issue with charge localization can be resolved by applying the Greene-Kelly test and using Eq. 6 to correct for the influence of tetrahedral charge. The correction should be applied
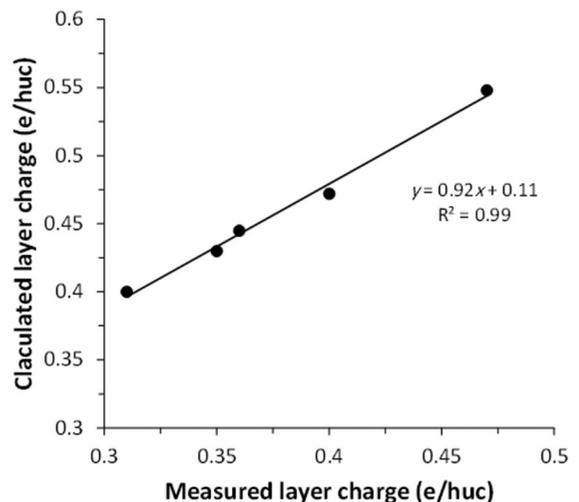
Fig. 11 Correction of the layer charge for smectites with a predominantly tetrahedral charge

when tetrahedral charge exceeds 50% of total layer charge, i.e. the smectites are beidellites, nontronites, or saponites. The method can be applied to both dioctahedral and trioctahedral smectites.

The O-D Method

Theoretical Background of the Method

The so-called O-D method is the most recent attempt toward a simple LC measurement protocol. The method exploits the ubiquitous existence and unique properties of interlayer water in smectite, namely, the presence of H_2O species on the surface of the interlayer with one dangling O–H bond pointing toward the weakly charged siloxane surface, whereas the second O–H bond is part of the H-bonded 'bulk' interlayer (Fig. 12). A sharp high-frequency O–H (or O–D, in D_2O-saturated samples) infrared band was assigned to the stretching of the dangling bond νO–H$_w$ / νO–D$_w$ (Russell & Farmer & Russell, 1964; Farmer & Russell, 1971; Suquet et al., 1977; Sposito & Prost, 1982).

In this context, Kuligiewicz et al., (2015a, b) and Szczerba et al. (2016) tested the hypothesis that the weak H-bonding between the dangling O–H (O–D) and the siloxane surface would depend on LC and produce a measurable proportional
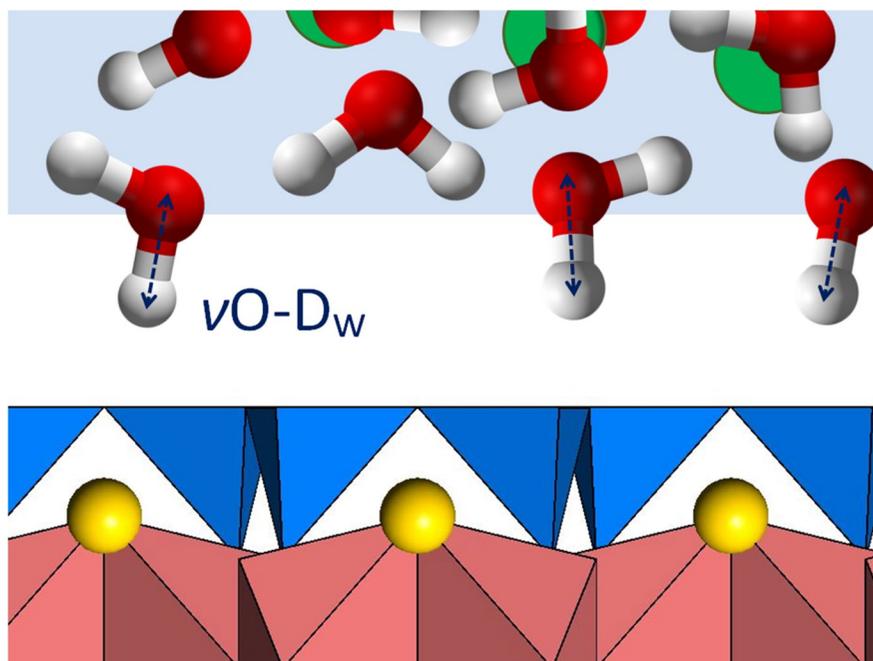
Fig. 12. Schematic representation of the dangling O–H$_w$/O–D$_w$ bonds in the interlayer of smectite (drawing not to scale). For details, see text

wavenumber change of νO–H$_w$ (νO–D$_w$) mode in the mid-infrared.

The dangling νO–H$_w$ mode of smectites is active at ~3630 cm^{-1} and, in common dioctahedral smectites, it is often masked by the dominant bands of the structural OH-stretching units in the octahedral sheet. Consequently, the interlayer H$_2$O had to be exchanged by D$_2$O at ambient temperature in order to separate the spectrum of the non-exchangeable structural OH from that of the accessible interlayer (Fig. 13) (Kuligiewicz et al., 2015a). In smectites, the sharp dangling νO–D$_w$ mode was observed within a narrow wavenumber range (~2695–2685 cm^{-1}) and its position could be determined accurately (typically to less than ± 0.3 cm^{-1}) by the sharp minimum in the 2nd derivative spectra (Fig. 14) because the neighboring bands of liquid-like, 'bulk' interlayer water (at ~2500 and 2375 cm^{-1}) were much broader. Theoretical simulations confirmed that the νO–H$_w$ / νO–D$_w$ mode originates from (mostly) monodentate interactions of interlayer H$_2$O/D$_2$O with the siloxane surface and is sensitive to the total charge generated by both the octahedral and tetrahedral-sheets (Szczerba et al., 2016).

Importantly, common high-hydration enthalpy cations (Na$^+$, Li$^+$, Ca^{2+}, Mg^{2+}) which affect significantly the position of the bands of liquid-like interlayer H$_2$O or D$_2$O had a negligible effect on the position of the sharp νO–D$_w$ mode (Kuligiewicz et al., 2015a). At or above the 2W interlayer hydration level, the peak position was unaffected by hydration. Surprisingly, despite having measured a large collection of smectite samples of different crystallochemical composition, no effect of charge location (octahedral, tetrahedral) was found on the position of νO–D$_w$ (Kuligiewicz et al., 2015b). This is attributed to the fact that the method aims at LC at full interlayer expansion (at least two water layers equivalent), at which conditions the charge becomes homogeneous across the interlayer.

Sample Preparation – Instrumentation

The instrumentation requirements of the measurement of νO–D$_w$ are modest. They are based on a single-reflection diamond ATR cell fitted to a routine FTIR spectrometer (capable of optical resolution of 4 cm^{-1}). A removable cup with gas input and output is clamped
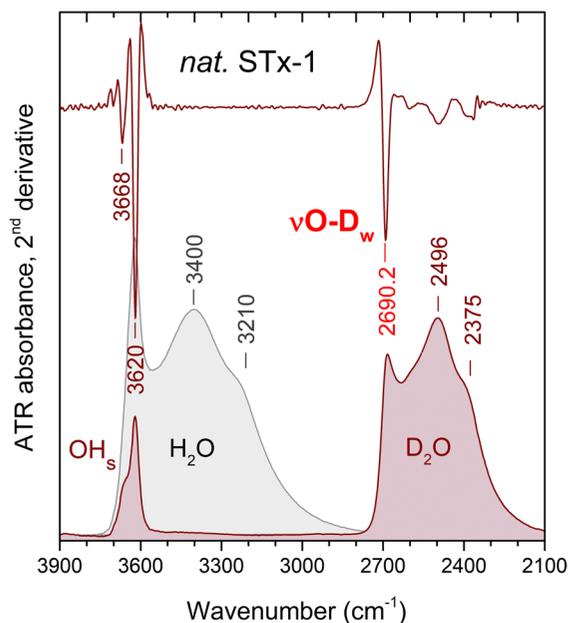
Fig. 13 Separation of structural OH (OH$_s$) and H$_2$O (as D$_2$O) absorbance spectra of STx-1 montmorillonite (in as-received interlayer cation form) by in situ deuteration at ambient temperature. The position of the sharp νO–D$_w$ mode (highlighted red) is determined by the 2nd derivative minima (4 cm^{-1} resolution, $\Delta\nu = 2$ cm.$^{-1}$, Savitzky-Golay 13 pt smoothing, as in Kuligiewicz et al., 2015b). The ATR spectrum of the sample prior to deuteration is included for comparison (shaded gray)

Fig. 14 Position of the νO–D$_w$ 2.nd derivative minima of SWy-2, STx-1, SAz-1, and SCa-3 montmorillonites in their as-received cation forms (cf. Figure 13)

on the cell, rendering it suitable for real-time measurements during purge-drying or hydration, depending on the composition of input gas (Chryssikos, 2017). A few drops of a dilute clay suspension, well dispersed in water, are deposited on the diamond element and purged briefly with dry N$_2$ (other gases can be used as well) to produce a thin dry film adhering to the diamond. The gas input is then switched to pass through a D$_2$O bubbler, to obtain the gas with D$_2$O relative humidity of at least 60%, to ensure the interlayer 2W full development. The H$_2$O/D$_2$O exchange of the interlayer is fast due to the small mass of the sample and 5–10 spectra (typically at 100 scans each) are collected in situ under the saturated D$_2$O atmosphere. No H/D exchange of the structural OH occurs under these conditions.

Calibration of the Method

Method calibration was performed by measuring dioctahedral smectites which were previously and independently evaluated by other LC measurement techniques: 15 samples from the study of Wolters et al. (2009), eight samples from the Christidis collection including six from the Christidis and Eberl (2003) study, 13 reduced-charge Li-SAz-1 montmorillonites (Skoubris et al., 2013), and six smectites from the Source Clays Repository of The Clay Minerals Society (SAz-2, SCa-3, SWy-2, SbCa-1, SbId-1, SWa-1). Two independent calibrations were derived in this manner:

$$LC(SFM) = 0.60 + 0.030(v - 2686); \sigma = 0.02, R^2 = 0.96 \tag{7}$$

and

$$LC(AAM) = 0.38 - 0.015(v - 2686); \sigma = 0.01, R^2 = 0.92 \tag{8}$$

where LC is expressed in e/huc (per formula unit) and $\nu = \nu$O–D$_w$ in cm^{-1}. The methods were based on Li- and Na-saturated smectites, respectively, but can be applied with negligible bias to smectites with common natural cations (Tsiantos et al., 2018). SFM- or AAM-corresponding charges can, therefore, be obtained

Table 3 LC(SFM) and LC(AAM) measured by the OD method (Eqs. 1 and 2, respectively), independent AAM data (full method, Kaufhold et al., 2018; Olis et al., 1990; Kaufhold et al. unpublished data), and their residuals for 38 bentonites from the Kaufhold collection

	νO-D (e/huc)		AAM (e/huc)		Resid. AAM-LC(AAM)	
	LC(SFM)	LC(AAM)	Full	Olis	Full	Olis
B01	0.55	0.35	0.36	0.35	0.01	0.00
B02	0.54	0.35	0.35	0.36	0.00	0.01
B03	0.48	0.32	0.33	0.33	0.01	0.01
B04	0.50	0.33	0.31	0.38	-0.02	0.05
B05	0.48	0.32	0.31	0.35	-0.01	0.03
B06	0.48	0.32	0.33	0.33	0.01	0.01
B07	0.50	0.33	0.33	0.33	0.00	0.00
B08	0.37	0.26	0.27	0.27	0.01	0.01
B09	0.33	0.25	0.18	0.26	-0.07	0.01
B10	0.47	0.32	0.33	0.34	0.01	0.02
B11	0.46	0.31	0.31	0.31	0.00	0.00
B12	0.53	0.34	0.35	0.35	0.01	0.01
B13	0.54	0.35	0.37	0.37	0.02	0.02
B14	0.49	0.32	0.33	0.34	0.01	0.02
B15	0.53	0.35	0.38	0.38	0.03	0.03
B16	0.39	0.28	0.27	0.27	-0.01	-0.01
B17	0.48	0.32	0.32	0.32	-0.00	0.00
B18	0.57	0.36	0.36	0.36	0.00	0.00
B19	0.55	0.35	0.35	0.36	0.00	0.01
B20	0.37	0.27	0.25	0.27	-0.02	0.00
B21	0.50	0.33	0.34	0.34	0.01	0.01
B22	0.53	0.35	0.35	0.35	0.00	0.00
B23	0.54	0.35	0.36	0.35	0.01	0.00
B24	0.47	0.31	0.34	0.34	0.03	0.03
B25	0.43	0.30	0.30	0.30	0.00	0.00
B26	0.53	0.34	0.35	0.35	0.01	0.01
B27	0.38	0.27	0.21	0.27	-0.06	0.00
B28	0.49	0.32	0.32	0.31	0.00	-0.01
B29	0.47	0.31	0.33	0.31	0.02	0.00
B30	0.35	0.26	0.25	0.25	-0.01	-0.01
B31	0.46	0.31	0.32	0.32	0.01	0.01
B32	0.41	0.29	0.26	0.26	-0.03	-0.03
B33	0.37	0.26	0.25	0.26	-0.01	0.00
B34	0.55	0.36	0.37	0.37	0.01	0.01
B35	0.47	0.32	0.35	0.36	0.03	0.04
B36	0.40	0.28	0.20	0.26	-0.08	-0.02
B37	0.48	0.32	0.30	0.30	-0.02	-0.02
B38	0.40	0.28	0.24	0.26	-0.04	-0.02
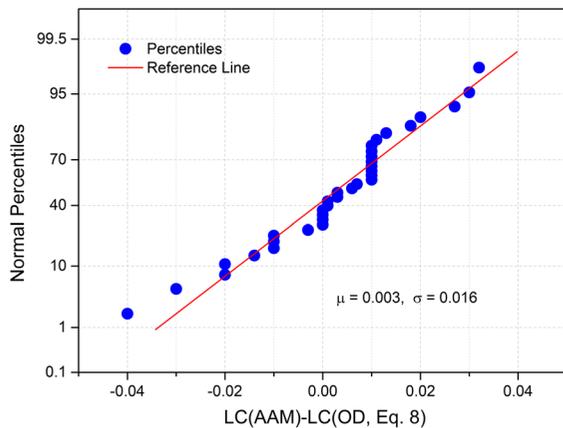
Fig. 15 Validation of the νO–D$_w$ AAM predictions against the independent reference values of bentonite samples from the Kaufhold collection. The normal probability plot of the residuals indicates $\sigma = 0.016$ and $\mu = 0.003$ e/huc, in excellent agreement with the original calibration (Kuligiewicz et al., 2015b)

easily from a single νO–D$_w$ measurement. The measurement takes about half an hour and requires <5 mg of sample. The common forms of Eqs. 7 and 8 confirm that the LC(SMF) and LC(AAM) are linearly correlated: LC(AAM) = 0.5LC(SFM) + 0.08 (c.f. Kaufhold, 2006; Laird, 1994).

Within the LC(SFM) range of the smectite definition (0.6–0.2 e/huc, translated to 0.38–0.18 e/huc in the AAM formalism), natural smectite calibrants exhibited νO–D$_w$ ranging between ~2686.0 and 2694.5 cm^{-1} and covered the range between ~0.6 and 0.35 e/huc, respectively (Kuligiewicz et al., 2015b). Lower LC(SFM) values (as low as ~0.25 e/huc) were represented only by charge-reduced Li-samples. As a result of the reduced hydration accompanying Li-fixation, the νO–D spectra of these samples underwent a rapidly decreasing intensity of the νO–D spectrum below LC(SFM) $\approx$ 0.3 e/huc, which determined the low-LC limit for the O-D technique. No such limit was found at the high LC(SFM) end (i.e. for νO–D < 2686 cm^{-1}) and the method may be suitable for measuring vermiculite with LC(SFM) > 0.6 e/huc as long as the surfaces are fully wettable. Some band broadening toward low wavenumbers may be an early sign of a progressive loss of νO–D definition upon increasing LC (Tsiantos et al., 2018).

A new independent external validation of the O-D method against AAM data, performed since the original calibration of Kuligiewicz et al. (2015b), is

presented here. The layer charges of 38 bentonites from the Kaufhold collection were measured by the O-D method (Table 3) and compared to the AAM charges originally determined by both the full method and the Olis shortcut (Kaufhold et al., 2018). The samples were in Na-form, had variable % tetrahedral charge, and contained typically <20 mass% accessory phases (exceptionally up to 60%), depending on locality (Kaufhold et al., 2012).

Five samples had LC values by the full AAM and Olis et al. (1990) methods differing by more than 0.03 e/huc (IB-4, -5, -9, -27, and -36) and were left out of the comparison with the OD data. The agreement between the AAM and O-D layer charges for the remaining samples yielded a normal distribution of residuals LC(AAM)-LC(OD) with $\sigma = 0.016$ (essentially identical to $\sigma = 0.013$ in the original calibration of Kuligiewicz et al., 2015b) and a very small bias, $\mu = 0.003$ e/huc (Fig. 15). Comparing the O-D charges to the Olis et al. (1990) data on the same samples (Table 3) yielded a similar standard deviation, $\sigma = 0.015$, and a slightly higher bias, $\mu = 0.006$ e/huc.

Besides accuracy and convenience in application, the O-D method combines uniquely a number of advantages. First, it is specific to the interlayer because surface OH or H$_2$O attached to the edges by strong H-bonds may be exchangeable by D$_2$O but do not contribute to the sharp, high-frequency νO–D$_w$. Unlike the AAM or the NH$_4^+$ exchange methods, the O-D method relies on accessibility by an intrinsic probe, H$_2$O/D$_2$O, which is linked to the definition of smectite, its hydration properties, and its layer charge. To be measured, the interlayer H$_2$O must be wettable, thus accessible for H$_2$O/D$_2$O exchange. If the sample contains collapsed, non-accessible interlayers (either because their charge is outside the smectite range, or because the interlayer cations have low hydration enthalpy), these will not be measured (Kuligiewicz et al., 2015a). For example, the OD method has been applied to determine specifically the surface charge of the smectitic interlayers and surfaces in illite–smectite (Kuligiewicz et al., 2018). However, in this case, the illitic interlayers are not accessible to D$_2$O, their surface charge is not measured, hence the total layer charge of the 2:1 layer remains unknown.

Second, the shift of νO–D$_w$ is an intensive and not extensive property of the sample. Peak positions are determined more accurately than peak

intensities and the measurement does not need to be corrected for the smectite content of the sample. Non-hydrous accessory phases as well as clay minerals with non-accessible interlayers have no contribution to the sharp νO–D_w. As a result, there is no need for sample purification for measuring the average smectitic LC of the sample unless the nature or quantity of the impurities prevents thin-film preparation. Readers are reminded that the independent validation in Table 3 represents measurements on non-purified samples. Together with the insensitivity of νO–D_w on the nature of the interlayer cations commonly found in nature (Na^+, Ca^{2+}, Mg^{2+}), this property has enabled the routine characterization of geological or industrial samples, essentially without pretreatment (Kanik et al., 2022; Kaufhold et al., 2019; Tsiantos et al., 2018).

Last, although the calibration of νO–D_w against other LC-measuring procedures has been based on dioctahedral smectites, its physical foundations are applicable equally to their trioctahedral analogs (Kuligiewicz et al., 2015a). A recent study of Laponites® and synthetic hectorites (including fluorinated compositions) revealed the existence of well defined νO–D_w bands corresponding to 'apparent' (due to the absence of proper calibration) LC(SFM) in the range 0.35–0.65 e/huc and permitted the identification and evaluation of a charge-reduction, stevensite-to-hectorite Li-fixation process (Christidis et al., 2018).

Concluding Remarks

Extensive work on the crystal chemistry of smectites over the past 75 years has yielded a variety of analytical methods that are capable of determining the layer charge. All of these methods have advantages and limitations. The primary methods (SFM and AAM) are time-consuming and yield different results. The calibrated methods (NH_4-method, K-saturation method, and O-D method) are easier to apply and yield results quickly, within their limitations. A simplified version of the AAM is available, thus rendering the method more attractive than it has been in the past. Similarly, the K-saturation method has been simplified so that determination of layer charge is feasible from measurement of the 001 diffraction maximum of smectite only. Still, the present authors suggest that the calibrated methods be accompanied

by the Greene-Kelly test for complete characterization of the LC and application of corrections where necessary, i.e. in the NH_4^+-method and the K-saturation method. The most recent methods can be used to obtain results that might be used for geological and pedogenic interpretations regarding soil profiles and bentonite genesis and applications in industrial practice based on smectite properties.

Declarations

Not Applicable.

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