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Review article

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.

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) 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) rearrangement 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 (CEC_{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 CEC_{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 μm 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 Si+Al=4. The remaining Al, Mg and Fe are assigned to octahedral sites. Iron is assumed to be ferric, unless the presence of 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 $CaCO_3$ 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