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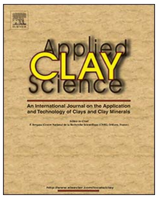

Research paper

Smectite in bentonite: Near infrared systematics and estimation of layer charge

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ABSTRACT

The facile and accurate measurement of the layer charge of dioctahedral smectite has been demonstrated recently by means of the O-D method, an infrared-based technique capable of recording the exact position of a dangling O-D (O—H) bond stretch of interlayer water. The present work attempts to transfer this know-how to the near-infrared (NIR) spectra of natural bentonites in anticipation of even higher throughput capabilities. For this reason, the NIR systematics of ~70 bentonites in both natural and Na-exchanged form have been analyzed against the mid-infrared-derived layer charges of the same samples. The as determined layer charges were not biased by the nature of the interlayer cations (Ca^{2+}, Mg^{2+}, Na^{+}). A linear correlation between the ($\nu + \delta$) combination modes of H_2O and Al_2OH at ~5250 and 4525 cm^{-1}, respectively, was established, confirmed on a broader collection of bentonite samples, and discussed in terms of interlayer and layer chemistry. The ($\nu + \delta$) H_2O wavenumber was found to correlate linearly with layer charge, but the slope was dependent on interlayer cation due to the cation-dependence of the bending δ H_2O fundamental mode. Additionally, PLS chemometric modeling of the NIR spectra was employed successfully to provide layer charge predictive algorithms, desensitized from the effect of interlayer cation (Ca^{2+}, Mg^{2+}, Na^{+}).

1. Introduction

Layer charge (*LC*) varying in the range of 0.2–0.6 electrons per $O_{10}(OH)_2$ formula unit is an important property of smectite. It is commonly estimated by fitting analytical data to the ideal formula (Structural Formula Method, SFM, e.g. Stevens, 1946), or by measuring the surface density of alkylammonium cations intercalated in the interlayer (Alkylammonium Method, AAM, e.g. Lagaly, 1981). The two methods yield different but correlated values of *LC* or layer charge density, *LCD* (Laird, 1994; Kaufhold, 2006). They are tedious to apply and unsuitable for high throughput application. For this reason, several alternative measurement techniques based either on SFM or on AAM charges have been proposed in the literature (for a recent review, see Kuligiewicz et al., 2015b).

One of these techniques involved the use of the vibrational spectrum of H_2O in smectite as an intrinsic probe of LC. The method was based on the systematics and fundamental understanding of an unusual, high-wavenumber, O-D_w (O-H_w) mode of interlayer H_2O (D_2O) in dioctahedral smectite measured by attenuated total reflectance (ATR) mid-infrared (Kuligiewicz et al., 2015a, 2015b; Szczerba et al., 2016). This fundamental mode was attributed to the localized stretching of dangling O—H (O-D) bonds that are decoupled from the strongly H-bonded network of H_2O (D_2O) in the interlayer and point towards the weakly charged siloxane layer. The exact wavenumber of this mode (νO-H_w, νO-D_w) was found to correlate linearly with permanent layer charge (*LC*), determined independently by either the structural formula or the alkylammonium methods (LC_{SFM} or LC_{AAM}, respectively), thereby providing an accurate, simple and fast method for performing routinely the otherwise tedious *LC* measurements. The ATR-based, O-D method of Kuligiewicz et al. (2015b) was found to be insensitive to interlayer chemistry for Na^{+}, Li^{+}, Ca^{2+}, Mg^{2+} and was independent of charge location (tetrahedral, octahedral).

The present work aimed at applying the O-D method to industrial, non-purified, samples, as well as at examining its possible transfer to the near-infrared (NIR) spectral range of combination and overtone modes. NIR spectroscopy in a diffuse reflectance acquisition mode presents several advantages in the study of clays, clay minerals and clay-based materials (e.g. Clark et al., 1990; Post and Noble, 1993; Bishop et al., 1994, 2002; Petit et al., 1999, 2015; Gionis et al., 2007): NIR requires no sample dilution, it is fast and yields high signal-to-noise spectra, suitable for 2nd derivative analysis and chemometric modeling (Chryssikos and Gates, 2017). NIR probes the OH— (also CH— and NH—) containing species present in the sample and is ideal for studying the clay fraction without interference from the silicate network,

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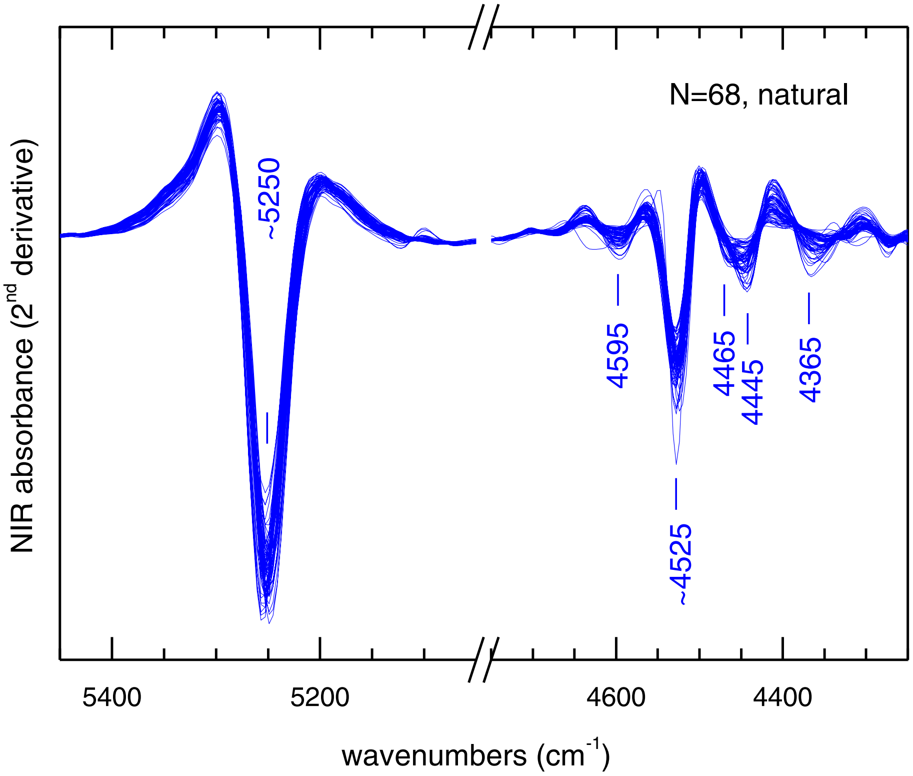

Fig. 1. Detail of the 2nd derivative NIR spectra of the 68 natural bentonite samples, over the H_2O (5300–5200 cm^{-1}) and ($\nu + \delta$) OH (4600–4300 cm^{-1}) ranges.

anhydrous accessory phases, or organics (Tsiantos et al., 2012; Madejová et al., 2016). It can be applied over different scales of sample size, from mg to tons, even remotely, and can be used to monitor time-dependent processes in situ (Bukas et al., 2013; Chryssikos, 2017). Anharmonicity operates as an important parameter for tuning the exact wavenumber and extinction coefficient of the NIR-active vibrational modes (Bokobza, 2002). Importantly, strong H-bonding reduces the intensity of the relevant NIR bands, thereby allowing for the relative strengthening of modes associated with weakly H-bonded dipoles (Siesler, 2002). Given the fact that the diagnostic νO-H$_w$ (actually, νO-D$_w$) mode of the ATR method is due to such weakly H-bonded dipoles (Kuligiewicz et al., 2015a; Szczerba et al., 2016), it was anticipated that NIR could offer an appealing high-throughput alternative for determining layer charge, in situ and without the need for sample deuteration.

2. Materials and methods

This study was based on a sample set of 68 bentonites from Milos, Greece, obtained from various exploratory drill cores, without any purification treatment. The set was provided in two matching series, one with natural interlayer composition, and the other subjected to an industrial "Na-activation" protocol involving the addition of 4 wt% Na_2CO_3 (c.f. Kaufhold et al., 2013). The samples (~20 g each) were available in ground form (< 200 μm) after long-term equilibration at ambient temperature and humidity and were studied without further treatment. The set of natural bentonite spanned a wide range of methylene blue adsorption (~80–160 cmol/kg) and contained up to 25% carbonates and up to 2.5% sulfur in sulphates and sulfides.

The aforementioned bentonite sample set was part of a company repository of ~950 powdered clays in natural form from various bentonite deposits representing all continents except Australia and Antarctica. No other information on these samples could be disclosed. A preliminary report about the near-infrared systematics of this "global" bentonite collection was presented in the 51st Annual Meeting of the CMS (A. Deligianni, V. Gionis, G. D. Chryssikos, 2014. Systematics of bentonite by near-infrared spectroscopy, Abstracts of the 51st CMS Annual Meeting, Houston, Texas, pp. 79–80).

Additionally, bulk powder montmorillonite SAz-1, SCa-3, STx-1 and SWy-2 were obtained from the Source Clays Repository of the Clay Minerals Society and studied as reference minerals in both their as-received and Na-activated forms.

All samples (~950 global, 2 × 68 Milos sets and reference montmorillonite) were measured in the near-infrared (NIR) on a Fourier transform instrument (Vector 22 by Bruker Optics) equipped with a NIR diode detector and a fiber optic bundle probe, suitable for the non-invasive measurement of powders in diffuse reflectance (e.g. Gionis et al., 2007; Chryssikos, 2017). The NIR spectra were measured over the 10,000–4000 cm^{-1} range (scanner velocity 10.0 kHz) against a Spectralon™ reflector (Labsphere Inc.) as averages of 100 scans at 8 cm^{-1} resolution. The position of NIR bands of interest was determined from the 2nd derivative minima of absorbance (Savitzky-Golay, 9-point smoothing for data spacing $\Delta\nu = 4$ cm^{-1}). In all cases, the precision in determining these positions was 0.1 cm^{-1} and the accuracy was better than ± 0.5 cm^{-1}.

Additionally, the layer charge of the smectite in the 2 × 68 bentonite series (natural and Na-activated) was determined by the O-D vibrational spectroscopic method of Kuligiewicz et al. (2015b). A Fourier transform mid-infrared spectrometer was employed (Equinox 55 by Bruker Optics) with KBr optics and a DLATGS detector, operating at 4 cm^{-1} resolution in the 6000–400 cm^{-1} range with 10.0 kHz scanner velocity. The spectrometer was equipped with a single-reflection diamond ATR accessory (DuraSampl IR2 by SensIR Technologies, currently Smiths Detection). Briefly, the measurement protocol (Kuligiewicz et al., 2015a) involved depositing a few drops of a sonicated clay in D_2O suspension (99.9 at.% D) on the ATR element fitted with a homemade environmental cup (Bukas et al., 2013), purge-drying with high-purity N_2 (< 5 ppm H_2O) to form a solid film in good contact with the diamond, equilibrating the film with D_2O vapor (60–80% RH D_2O) and measuring the ATR spectra in situ. The position of the sharp O-D stretching mode of D_2O in the ~2700–2685 cm^{-1} range (νO-D$_w$, cm^{-1}) was determined from the minima of the Savitzky-Golay 2nd