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Original Paper

Enhanced quality control and smectite quantification for bentonites in the Bavarian mining district based on layer charge measurement with the O-D method

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Abstract

Bentonite is mined globally for use in commercial and industrial applications. In these applications, smectite content and composition are the paramount factors of the bentonite material and control its properties. As bentonite composition and properties can vary significantly over a large mining district or within a single mine, quality control is required including: mineral composition, especially smectite content; cation exchange capacity (CEC); exchangeable cation composition; and smectite crystallochemical features. Differences in bentonite composition locally or over a spatial area stem from the different geological settings present throughout bentonitization. The study aims were to: (1) determine the layer charge (LC) variation of dioctahedral smectite over the Bavarian mining district and within individual mines in the area; and (2) assess the error in smectite content calculations based on CEC data resulting from the actual range of experimentally determined LC values. This information has been missing in the scientific literature, as previous LC methods were laborious or subject to assumptions, making a comprehensive study over a large spatial area impractical. This study employed the use of the recently developed efficient and precise spectroscopic 'O-D method', which enabled the LC measurement of 40 samples from eight mines in the Bavarian bentonite mining district, covering an area of 250 km^2, within the North Alpine Foreland Basin. Results showed LC values calibrated against the alkylammonium method (LC (AAM)) generally ranged between 0.29 and 0.30 eq per formula unit (FU), with only 10% of samples showing LC values >0.31 eq/FU. This narrow LC range has positive implications for the accuracy of determining smectite content calculated from CEC data, during routine quality control of Bavarian and other bentonites. The average error of the CEC-based smectite contents resulting from LC variations was, on average, ±3 wt.%.

Keywords: bentonite; bentonite mining; cation exchange capacity; layer charge; smectite content

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Introduction

Bentonite is used for various applications (e.g. Harvey and Lagaly, 2006) and mined worldwide. The properties of bentonites from different mining districts, however, vary with the geological settings throughout bentonitization (Grim and Güven, 2011; Gilg et al., 2022). Significant variability of the bentonite materials can sometimes be observed within a single outcrop ranging from appearance to compositional variation. Bentonites from Wyoming (USA), for example, show similar mineralogical compositions but variable amounts of exchangeable Na^+ (Williams et al., 1953).

In Milos (Greece), both the type of dominating exchangeable cation and mineralogical composition show variability at least partly caused by post-formational alteration (Decher, 1996; Kaufhold, 2001; Kaufhold and Decher, 2003). The type of compositional variability of the different deposits translates directly into the required quality control. Despite the mineralogical compositions being significantly variable, most Milos bentonites have a high smectite content. In Milos, the most important parameter for quality control is the amount of naturally present exchangeable Na^+, as it determines the amount of Na_2CO_3 that has to be added technically during production (for most products). Conversely, in the Bavarian mining district, the exchangeable cation population was found to be quite constant (Kaufhold, 1998; Köster et al., 2019; Supplementary material) while the smectite content was observed to vary significantly (Kaufhold et al., 2003). In Bavarian deposits, therefore, the smectite content is an important quality-determining parameter while other technologically important compounds, e.g. carbonate content, are usually easier to measure accurately. Typically, it is sufficient to test the smectite content, e.g. by the traditional methylene blue (MB) method or by more

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straightforward cation exchange capacity (CEC) methods such as Cu-trien (Kaufhold and Dohrmann, 2003). For the calculation of the smectite content (S_{wt}, in wt.%) from CEC values, the molar weight (M_{FU}) of one formula unit (FU), and the smectite layer charge and the portion of variable charge, have to be known (Vogt and Köster, 1978; Lagaly, 1993; Kaufhold et al., 2002):

$$S_{wt} = \frac{CEC_{meas}}{CEC_S} \times 100, \quad (1)$$

where CEC_{meas} is the experimentally measured CEC value, whereas CEC_S is a theoretical CEC of pure smectite, assuming that smectite is the only compound contributing to bulk sample CEC:

$$CEC_S = \left(\frac{LC}{M_{FU}} + VC\right) \times 100{,}000. \quad (2)$$

In this study, layer charge (LC, given per FU) is used here as the charge generated only by substitution of heteroatoms in the 2:1 layer and neutralized by interlayer cations, which can then be measured by a probe specific to the interlayer space (Christidis et al., 2023). The variable charge (VC) occurring on the smectite crystallite edges, is pH dependent, and contributes to the CEC_S. The accuracy of CEC-based methods for the determination of the smectite content (Eqns 1 and 2) for bentonite mining quality control, therefore, depends heavily on the variability of the layer charge (Kaufhold, 2005). In smectites, LC varies from 0.2 to 0.6 eq/FU. Köster (1977) suggested use of the value 0.34 eq/FU for smectites if the LC was not determined analytically. With only a few exceptions (e.g. Christidis and Dunham, 1993; Christidis and Dunham, 1997; Christidis, 2006), a statistically sound study of the smectite LC distribution in a bentonite mine or even across a mining district, however, has not been conducted so far because both classical methods, the structural formula method (SFM) and the alkylammonium method (AAM), are laborious and/or erroneous (e.g. Laird, 1994; Christidis et al., 2023). One of few exceptions was provided by Christidis (2006) who used microprobe analysis to investigate Cyprus bentonites. Based on the chemical data, structural formulae were derived from which the LC was deduced. Those authors found significant variation of the LC even within different deposits (overall ranging from mean 0.38 to mean 0.59 eq/FU). Those authors, however, used a method that probes single smectite particles, in contrast to most other methods which provide a bulk-sample parameter. If considering the individual particle measurements, the LC variability is even broader (0.26–0.66 eq/FU). In contrast, Chiou et al. (2025) used AAM to investigate five bentonites from different quarries of the Milos deposit and found quite similar values (0.31–0.33 eq/FU). In the same study, five different Wyoming bentonites were additionally investigated, which are all low charged (as widely accepted for Wyoming bentonites) but still showed a large range of LC (0.18, 0.21, 0.25, 0.25, and 0.27 eq/FU). These results indicate that the LC can be more or less constant in a bentonite mining district or show comparatively large variation. The first comprehensive study on LC of Bavarian bentonites was published by Vogt and Köster (1978) who, based on 14 Bavarian samples, found low LC variability ranging from 0.36 to 0.39 eq/FU (determined by SFM) with one sample showing a lower LC accounting for 0.33 eq/FU.

Kuligiewicz et al. (2015) introduced an efficient method for measuring the LC of smectite which is based on the determination of the position of a mid-infrared (MIR) band of OD stretching after a sample is saturated with D_2O. The D_2O saturation enables the use of water as an intrinsic probe of the wettable interlayer. The band position depends directly on the LC and hence the method can either be calibrated against SFM or AAM (LC (AAM) or (LC (SFM)). The systematic difference between values derived by both methods was previously discussed (see Kaufhold et al., 2011). However, in contrast to SFM, neither the O-D- nor the AAM-derived LC values are affected by the variable charge (Kuligiewicz et al., 2015). Determining the LC of one sample using the O-D method takes only ~40 min. Using this method, therefore, enables a significant set of bentonite samples to be measured quickly and precisely from one or several bentonite mines within a bentonite mining district. Hence the aim of the present study was based on the possibility of measuring the LC of large sample sets resulting from the recently established O-D method. None of the other laborious LC methods could facilitate the study of this quantity of samples. The aim of the present study was as follows: (1) use of the O-D method in a comprehensive investigation of the LC distribution over the Bavarian bentonite mining district; and (2) assess the error of smectite content calculations based on CEC data resulting from the actual range of LC values.

Geological setting

The Bavarian bentonite mining district is located within the eastern part of the Molasse basin also called the North Alpine Foreland Basin (NAFB; Schlunegger and Kissling, 2024). The NAFB is an asymmetric basin across the northern margin of the Alps and encompasses an area 1000 km long and 10–200 km wide (Rocholl et al., 2018). It was formed as a result of the Alpine orogenesis in the mid-Cenozoic and ranges from the Rhone valley to the alpine foothills of southern Germany and Austria (Homewood et al., 1986; Schlunegger et al., 1997). Significant uplift during the Alpine orogeny resulted in a lowering of the Molasse basin and the sedimentation regime changed from marine to terrigenous in the Upper Oligocene (Probst, 1986), then back to marine, and back again to terrigenous in the early Pannonian (Vogt, 1980). The Obere Süßwassermolasse (OSM) represents the end of the second marine to terrigenous clastic sedimentation cycle. The complete retreat of the Paratethys from the west side of the basin by the Middle Miocene (~16.3 Ma) (Reichenbacher et al., 2013) caused a transition to fluvial sedimentation at the axis of the basin and alluvial fan sedimentation in the southern rim (Kuhlemann and Kempf, 2002). Multiple methods which include litho-, magneto-, and bio-stratigraphic and isotopic dating (e.g. Dehm, 1951; Gubler et al., 1992; Bolliger, 1994; Heissig, 1997; Kälin and Kempf, 2009; Abdul Aziz et al., 2008; Gubler, 2009; Abdul Aziz et al., 2010) have been used to obtain stratigraphic subdivisions of the OSM sediments in order to overcome the lateral variability in sedimentation dynamics caused by the complex geometry of the basin (Reichenbacher et al., 2013). For a recent and detailed analysis of the OSM stratigraphic subdivisions the reader is referred to Abdul Aziz et al. (2008), Köster and Gilg (2015), Rocholl et al. (2018), and references within, as only the main subdivision features relevant for the context of this study are discussed below.

Briefly, the oldest sediments of the OSM are termed the Süßwasserschichten and consist of fine gravels, sand, and silt (Fig. 1). They are overlain by the thick (10–50 m) coarse gravel of the Nördlicher Vollschotter (NV) which in turn is overlain by the Sand-Mergel-Decke (SMD), an informal local lithostratigraphic unit ~15–40 m thick, consisting of fine fluvial to lacustrine gravel, sand, and carbonate-rich silts (sandy marls). The Brock horizon is an ejecta layer situated roughly between the NV and the SMD, containing up to 20 cm angular Jurassic limestone blocks that

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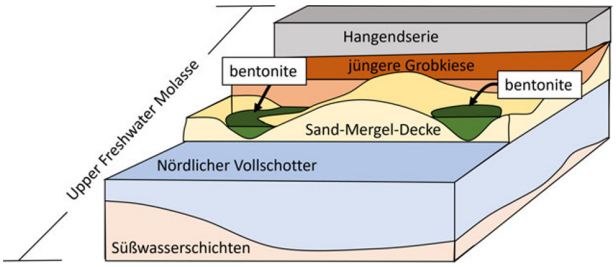


Figure 1. Schematic representation of the informal lithostratigraphy of the 'Obere Süßwassermolasse' (Upper Freshwater Molasse) near Mainburg-Landshut, modified after Ulbig (1994).

originated from the 'Nördlinger Ries' impact crater area ~100 km from the bentonite mining district (Unger et al., 1990; Ulbig, 1999; Abdul Aziz et al., 2008). The bentonite deposits are situated over the irregular erosional surface of the SMD. The bentonite deposits are covered by Miocene Hangend-Serie or Jüngere Grobkies coarse clastic sediments and are unconformably covered by Pleistocene loess.

In Bavaria, bentonites have been mined for more than 100 years and over four different regions: Malgersdorf, Landshut, and East and West of Augsburg (Gilg and Ulbig, 2017). Samples investigated in the present study were all from the Landshut region.

The formation of the Bavarian bentonites was investigated by Unger and Niemeyer (1985), Unger et al. (1990), and Ulbig (1994). Bavarian bentonite mines are distributed over an area of about 400 km^2 (Köster, 2018). They consist of flat, lenticular clay bodies varying in thickness from 0.5 to 2 m (may reach 8 m). Beds with a thickness of up to 4 m are rare but of particular interest for mining. Occasionally, even thicker beds are observed in which incompletely altered tuffite, sandy clay, or silicified bentonite can be found ('Harte Platte' = 'hard plate') (Vogt and Köster, 1978; Köster and Gilg, 2015). Horizontal areas of the clay bodies range from 100 m^2 to 2 km^2. The tuffs/ash are considered a precursor of the bentonites (Ulbig, 1994, Abdul Aziz et al., 2008, Rocholl et al., 2018) and Köster et al. (2017) found the age of bentonitzation to be ~14.7±4.1 Ma. The thick bentonite beds formed within the braided river system of the upper fluviatile NV sand and gravel, and above the SMD floodplain sediments (Ulbig, 1994; Schmid, 2003; Maurer and Buchner, 2007) resulting in the formation of oxbow lakes into which ash accumulated and resedimented (Rocholl et al., 2018; Köster et al., 2017). The rhyolitic volcanic ash then altered *in situ* to smectitic clay minerals (Ulbig, 1994; Abdul Aziz et al., 2008; Abdul Aziz et al., 2010; Köster and Gilg 2015; Bauer et al., 2016). Vogt (1980) analyzed the chemical composition of the smectites from different locations and found that despite the spatial variability, the smectite samples had a typical montmorillonitic character with similar formulae. From a geochemical point of view and based on the current knowledge about the formation of Bavarian bentonites, this low variability can be explained by similar conditions throughout bentonitization and the absence of post-formational alteration. The protolith material of the Landshut bentonites is dominated by distal rhyolitic volcanic glassy ash from a single Plinian eruption, and a Ca-Mg-rich reduced meteoric water at low temperatures (Ulbig, 1994; Gilg and Ulbig, 2017; Bauer et al., 2016). Nevertheless, different carbonate contents and colors of the bentonite point towards locally different geochemical environments (including Eh) which in turn affects Fe mobility and charge in the octahedral sheet, which may also lead to different LC. The composition and, thus, LC of smectite from different locations are therefore expected to be similar. As such, any difference in the CEC between bentonite deposits would originate exclusively from the content of detrital material in the bentonite. The average temperature in this region is currently about 10°C with 1022 mm of annual precipitation. The soils of this region are used for livestock farming and growing hops.

Materials and methods

Materials

The Landshut region of the Bavarian bentonite mining district was selected for the investigation of the LC distribution as several samples from eight different mines were collected over several years, which is the reason for the different sample assignment in Fig. 2. These samples were probed to establish a new *in situ* quality control method that is based on measuring the water content and the specific electrical resistivity, which were correlated with methylene blue (MB) (Kaufhold et al., 1998) and CEC (Kaufhold and Penner, 2006; Kaufhold et al., 2014) values in different clay raw materials. An example for sampling in the Osterwaal deposit is given in Fig. 3.

Mineralogical and geochemical data were not available for all samples but CEC values were available. The LC values measured with AAM were available for five samples and were published in Kaufhold (2001). The latter were used for the comparison of the AAM and O-D method.

Layer-charge determination

The O-D method (Kuligiewicz et al., 2015) is based on a linear regression between the position of the sharp O-D stretching band (ν_{OD}) at ~2700 cm^{-1} and the layer charge. The O-D method is insensitive to interlayer chemistry as long as it is filled with Na^+, Li^+, Ca^{2+}, and/or Mg^{2+} cations which allow full interlayer expansion to two-water layers at high humidity (not suitable for use with K^+ or Cs^+ cations) and is independent of tetrahedral or octahedral charge locations. The best precision, however, is obtained when comparing samples with the same interlayer cation composition. As the O-D method measures only the wettable smectitic surfaces, it is not affected by bulk rock impurities or variable charge at crystallite edges. Therefore, no influence is observed from particle edges or the illitic interlayer charge as only the basal surface charges of fundamental particles are probed by the O-D method (Kuligiewicz et al., 2018). This means that the LC component is not measured for any 2:1 layers that are not fully expandable (only smectitic layers). In the case of partially collapsed interlayer and interstratified illite-smectite phase, the LC determined should be considered as the wettable surface charge.

Approximately 2 mg of sample material was added to a 1.5 mL vial, saturated with ~1 mL 99.99% pure D_2O water (Sigma-Aldrich), and ultrasonicated for 4 s. A pipette was used to place a drop of the suspension onto the ATR crystal of a Nicolet 6700 by ThermoScientific (Waltham, MA, USA) FT-IR instrument (Bukas et al., 2013). A custom-made cap was used to cover the suspension during drying, to a thin film, by N_2 gas flowing through the cap. An N_2 gas and D_2O vapor mix, controlled at between 60 and 80% (±2%) relative humidity (RH), was delivered to the sample by a custom gas blending system. FT-IR spectra were collected in the range of 4000 to 580 cm^{-1} at RH values of 60, 65, 70, 75, and 80%. The LC for each of the RH values was calculated from the IR measurements with LC values reported as calibrated against the

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No.	Sample	Location	Color	LC OD-method [eq/FU] (*based on AAM)
1	B12A	Bergham	green	0.30
2	B12B	Bergham	green	0.30
3	B1A	Bergham	green	0.31
4	B1B	Bergham	green	0.31
5	B2A	Bergham	green	0.30
6	B3A	Bergham	green	0.30
7	B4A	Bergham	green	0.30
8	B5A	Bergham	green	0.29
9	O4A	Obergolzaberg	green	0.32
10	OG13A	Obergolzaberg	blue	0.31
11	OG14A	Obergolzaberg	blue	0.31
12	OG14B	Obergolzaberg	green	0.31
13	OG15A	Obergolzaberg	blue/green	0.30
14	OG16A	Obergolzaberg	blue/green	0.31
15	OG18A	Obergolzaberg	blue/green	0.30
16	OG19A	Obergolzaberg	green	0.30
17	OW2A	Osterwaal	yellow/brown	0.30
18	OW4B	Osterwaal	green	0.30
19	OW5A	Osterwaal	green	0.31
20	OW5B	Osterwaal	green	0.31
21	OW6A	Osterwaal	yellow/brown	0.30
22	OW6B	Osterwaal	yellow/brown	0.29
23	P2O W4C	Profil Osterwaal 2	green	0.29
24	P2O W7C	Profil Osterwaal 2	green	0.29
25	P2O W10C	Profil Osterwaal 2	blue	0.29
26	P2O W15C	Profil Osterwaal 2	green	0.29
27	P2O W18C	Profil Osterwaal 2	green	0.29
28	P2O W20C	Profil Osterwaal 2	green	0.30
29	P1	Priel	blue	0.29
30	P2	Priel	blue	0.30
31	P3	Priel	green	0.29
32	P5	Priel	green	0.29
33	P6	Priel	green	0.29
34	OPN1	Oberpriel neu	yellow/green	0.30
35	OPN2	Oberpriel neu	yellow/green	0.30
36	RB	Rehbach	green	0.30
37	BK	Berg	green	0.30
38	OP	Oberpriel	green	0.31
39	M	Martinszell	green	0.32
40	GOG	Obergolzaberg	blue	0.31

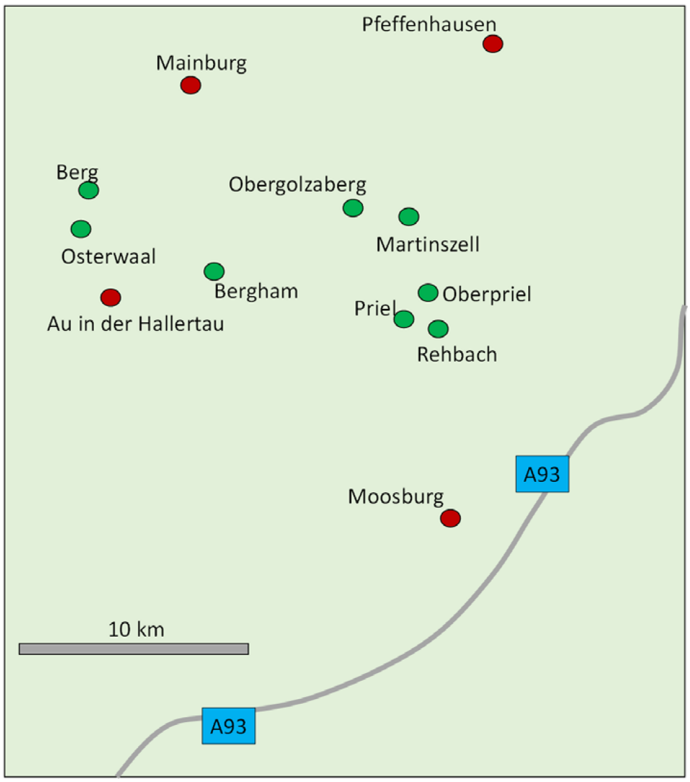


Figure 2. List of samples and locations of the mines (green circles) in the Landshut bentonite mining district. Larger towns are shown for orientation (red circles).

AAM (Eqn 3; = LC (AAM)), although calibration for the SFM is also available (see Kuligiewicz et al., 2015). In the present study, however, all O-D derived LC values were calibrated against the alkylammonium method. Calculation of the final LC value and the standard deviation of the measurement for each sample was done by averaging the LC values collected at each step differing by 5% RH:

$$\mathrm{LC(AAM)} = 0.38 - 0.015\,(\nu\mathrm{OD} - 2686);\ \sigma = 0.02, R^2 = 0.96, \quad (3)$$

where LC is expressed in electrons per formula unit (FU) and νOD is the measured νO-D_w in cm^{-1}. The σ of 0.02 and R^2 of 0.96 were calculated from this study, as that reported by Kuligiewicz et al. (2015) are σ = 0.01 and R^2 = 0.92.

Spectra processing was done using OMNIC software following Kuligiewicz et al. (2015).

Results and Discussion

Layer-charge range and distribution

Examples of spectra for the samples with the highest and lowest LC values are shown in Fig. 4. The spectra at RH of 80 and 60% represent, respectively, the highest and lowest RHs of the five spectra collected for calculation of one LC value. The band intensity maximum between 2650 and 2700 cm^{-1} shows the position of the O-D stretching band correlated with LC and the inset depicts its second derivative (Fig. 4).

For five of the samples used in the present study, LC values determined previously by AAM were available (Kaufhold, 2001; Kaufhold et al., 2002). These values were compared with the results obtained by the O-D method in the present study (Table 1). The AAM values were slightly but systematically higher: 0.01 eq/FU for most of the samples. Although the sample from the Rehbach mine showed a slightly higher deviation of ~0.02 eq/FU, for other samples of the Rehbach deposit (RAB, RAN; Kaufhold et al., 2002) a value of 0.32 eq/FU was published, which would fit perfectly the trend shown by the others. Given that the analysis was done with different methods and by different operators, and also included a two-decade time difference between the analyses, the LC values measured for these samples are quite consistent.

All the measured LC values are summarized in Fig. 5. The lowest measured value was 0.29 eq/FU; however, most of the samples showed values between 0.29 and 0.30 eq/FU and only about 10% of the samples showed LC values above 0.31 eq/FU. The range of the measured values was surprisingly narrow but is in good agreement with the values published by Kaufhold et al. (2002) for eight Bavarian bentonites (0.29–0.33 eq/FU) and Wolters et al. (2009) for two Bavarian bentonites (AAM, 0.30 and 0.32 eq/FU). Based on AAM measurements, Vogt and Köster (1978) reported higher LC

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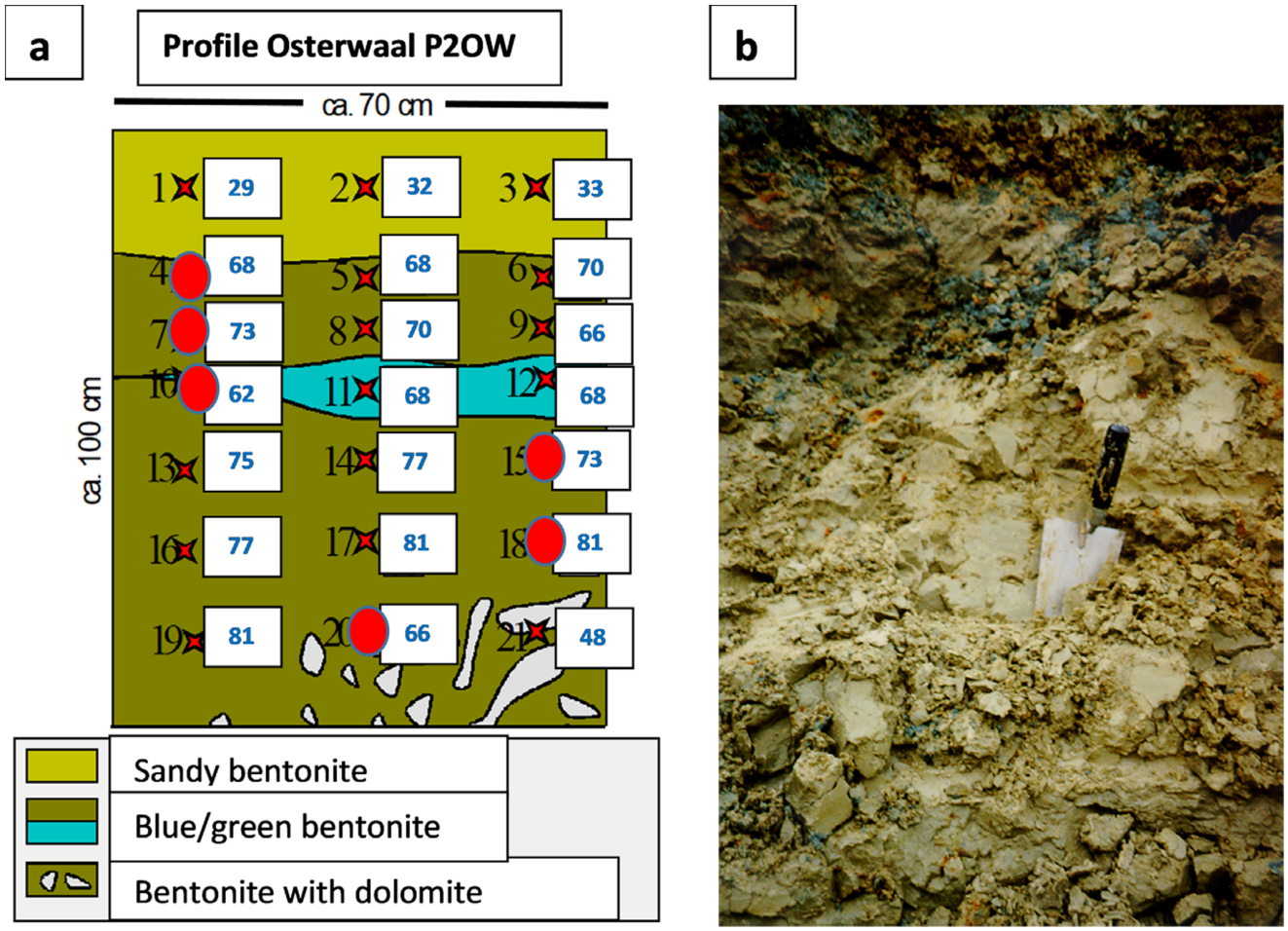


Figure 3. Example for sampling a small profile in the Osterwaal deposit. (A) Sketch of the different materials, sample numbers, and smectite contents based on MB (blue numbers), and samples included in the present study are marked with a red circle. (B) Example of a sampling spot which was used for geoelectrical investigation and sample collection (about 50 g wet state).

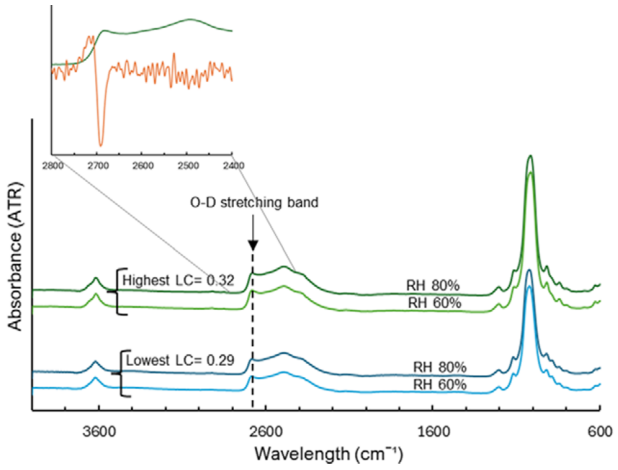


Figure 4. Spectra of the sample with the highest and lowest LC values of the 40 samples analyzed. Spectra taken at two of the five relative humidities (RHs) are shown for each sample. The inset shows the spectra of the sample measured with the O-D method and the highest LC at 80% RH along with its second derivative.

values for Bavarian montmorillonites ranging from 0.33 to 0.39 eq/FU; however, the reason for this deviation from other reported values remains unclear. Müller-Vonmoos and Kahr (1983) reported a LC for Montigel (a technical grade Bavarian bentonite from former Südchemie AG) of 0.28 eq/FU, which – based on the present study – is not representative of the average Bavarian bentonite but instead represents a low LC end member of Bavarian bentonite. The bentonite sample set described in Chiou et al. (2025) contained two Bavarian bentonites. Sample B25 has a LC of 0.30 eq/FU, which based on the present study can be considered typical for Bavarian bentonites. Sample B16, however, showed a LC value of 0.27 eq/FU which is comparatively low. This suggests that materials with LC values outside the range measured

Table 1. Comparison of LC values from five samples previously published by Kaufhold et al. (2002) with the LC values measured by the O-D (AAM) method (O-D calibrated against the alkylammonium method) two decades later (current study). Values for LC O-D (AAM) are shown here with 3 decimal places for ease of individual comparison but standard reporting is recognized to 2 decimal places, as the O-D methodological work of Kuligiewicz et al. (2015) reports a sigma value of 0.01 (AMM). As seen below, the precision of the O-D method for the bentonite samples here, was high.

Sample/region	LC from Kaufhold et al. (2002)	LC (O-D, AAM) current study
Rehbach	0.33	0.305 ± 0.002
Berg	0.31	0.298 ± 0.001
Oberpriel	0.32	0.308 ± 0.001
Martinszell	0.33	0.319 ± 0.002
Obergolzaberg	0.32	0.307 ± 0.001

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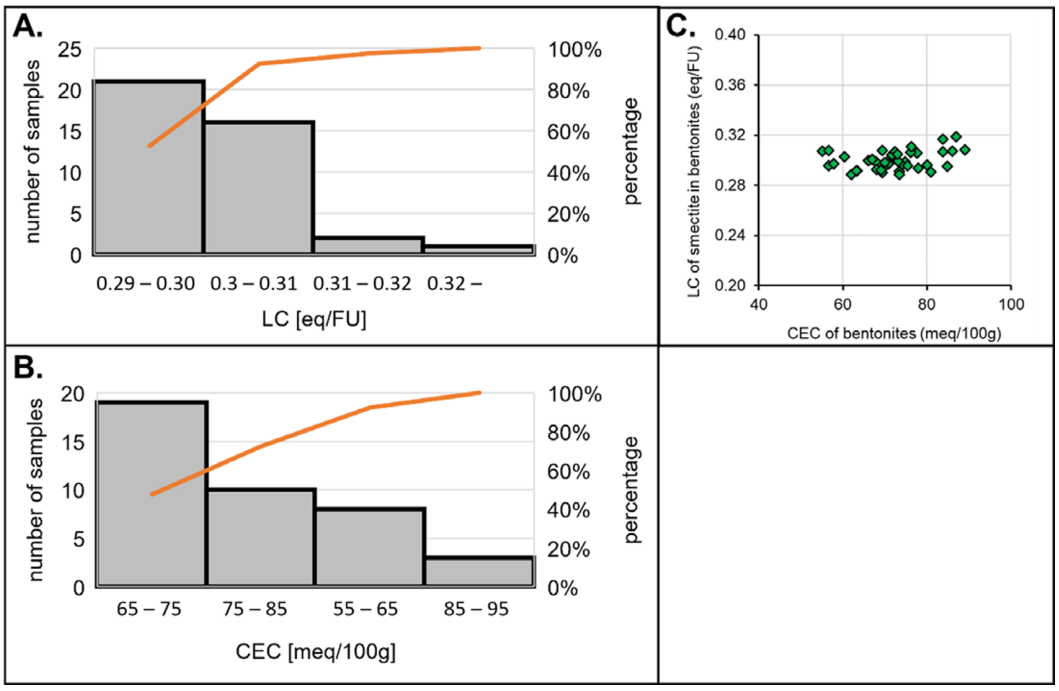


Figure 5. The distribution of smectite LC (calibrated against AAM) measured in the present study (A); compared with the CEC distribution in the same samples, from Kaufhold et al. (2002) (B); and the comparison of both the values on axes covering a typical range of LC and CEC values in bentonite (C).

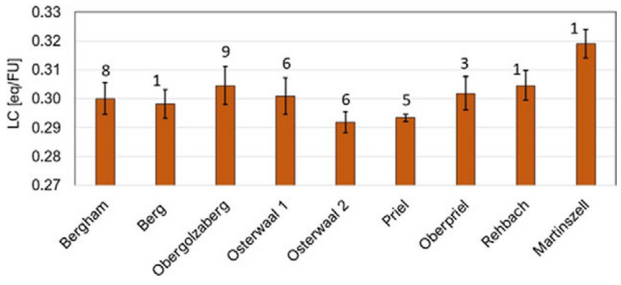


Figure 6. Comparison of LC values (O-D calibrated against AAM) from the different bentonite mines. The numbers above the bars denote the number of samples/measurements (*n*). Standard deviation of mines with *n*>4 was 0.005 eq/FU on average.

in this study may exist but should not be considered representative of the entire bentonite mining district.

In Fig. 6, all LC results are averaged according to the different bentonite mines (numbers represent the number of samples/measurements per mine). The hypothesis tested was that different mines could show different typical LC ranges. Most of the mines showed values of ~0.30 eq/FU (Bergham, Berg, Obergolzaberg, Osterwaal 1, Oberpriel, Rehbach). Two mines showed lower values, closer to 0.29 eq/FU (Osterwaal 2 and Priel) and only Martinszell showed a value closer to 0.32 eq/FU. The standard deviation over the samples analyzed ranged from 0.001 to 0.007 eq/FU. For the location which consisted of only a single sample analysis, the average standard deviation of 0.005 was assumed (Fig. 6). Overall, the differences among locations are minimal, and most of them overlap within the measurement range. Moreover, the highest value that was measured in the Martinszell deposit is based on only one sample and hence should not be interpreted further. The series Osterwaal 1 and Osterwaal 2, however, were both obtained in the same mine while the Osterwaal 2 sample series was collected several years later than the other. Although the differences between average values may represent different extents of bentonitization and possible post-formational overprints (Christidis, 2008), the overlapping measurement errors of LC for the two Osterwaal series indicate that LC differences within a single mine can be as significant as between different mines. In conclusion, no LC values or ranges can be given for a specific bentonite mine in the Bavarian mining district. Fortunately, the greater quantity of measurements possible with the use of the O-D method now enables the typical LC range of Bavarian bentonites to be determined based on solid statistics.

Smectite content calculation

In the Bavarian bentonite mining district, quality control is based mainly on estimation of the smectite content, which in turn is based on MB or CEC values (Kaufhold and Dohrmann, 2003) and reference samples of known composition. CEC values can, however, also be used for the calculation of absolute smectite content values without the need to use reference materials, in contrast to the procedure used to obtain MB values. The distribution of CEC values in Bavarian bentonites (Fig. 5B) compared with the variability of LC (Fig. 5C) implies that smectite crystallochemical composition varies far less than CEC; hence, it is not the smectitic LC but the smectite content which controls bulk rock CEC in the bentonites studied.

In order to calculate the smectite content from CEC data, information or assumptions about the LC, the molar mass of a formula unit, and the portion of variable charge are required (Eqns (1) and (2); Lagaly, 1993). In a test shown in Table 2, these parameters were varied systematically in order to assess the error of smectite content calculations based on the CEC data from Bavarian bentonites. Based on the results of the present study, one can assume smectites of most Bavarian bentonites to be represented

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Table 2. Effect of relevant parameter variation on the smectite content as calculated based on CEC values

Row #	Sample	LC AAM [eq/FU]	CEC [meq/100g]	Var. charge [%/CEC]	M_{FU} [g/mol]	sme content [mass%]	difference [Δmass%]
1	lower LC values	0.31	70	10	370	75	2.5
2	average LC value	0.30	70	10	370	78	
3	higher LC values	0.29	70	10	370	80	2.7
4	lower LC values	0.31	90	10	370	97	3.2
5	average LC value	0.30	90	10	370	100	
6	higher LC values	0.29	90	10	370	103	3.4
7	average LC value	0.30	70	10	360	76	2.1
8	average LC value	0.30	70	10	370	78	
9	average LC value	0.30	70	10	380	80	2.1
10	average LC value	0.30	70	5	370	82	4.3
11	average LC value	0.30	70	10	370	78	
12	average LC value	0.30	70	15	370	73	4.3

The values do not correspond to specific samples but were selected in order to represent the realistic range.

by a LC range from 0.29 to 0.31 eq/FU. The CEC of Bavarian bentonites typically ranges from 60 to 80 meq 100 g^{-1} (Fig. 5B,C), which corresponds to the reported average of 70 meq 100 g^{-1} in the first rows of Table 2. The molar mass of a formula unit (M_{FU}) depends largely on the Fe content (Środoń and McCarty, 2008) but also some single remaining water molecules after 105°C drying in an oven for 4 days (which is the reference state of the CEC measurements) must also be considered. Based on the moderate Fe content in the Bavarian bentonites and, thus, low Fe in the montmorillonite, structure M_{FU} results in about 370 g mol^{-1} and is considered to be a suitable reference value for Bavarian bentonites (Kaufhold, 2005). To be able to compare the CEC with LC values that represent permanent charge sites only, the CEC has to be reduced by the amount of CEC index cation adsorbed to variable charge sites (Eqn 2). This amount depends on the pH throughout the CEC measurements, which is discussed in detail by Kaufhold and Dohrmann (2013). Based on the present study in Table 2, a 10% variable charge was used as a reference value. Based on the reference values and using Eqns 1 and 3, a variation of the resulting smectite content of ±3 mass% was calculated. In the case of higher CEC values (90 meq 100 g^{-1}, rows 4–6 in Table 2), this value may increase to 3.2–3.4%. In rows 7–9 of Table 2, the M_{FU} was varied and the calculations based on the average LC of 0.30 eq/FU. Varying Fe content and/or amount of relict water may cause some variation of the M_{FU}. The effect of lower and higher M_{FU} on the smectite content resulted in an error of ±2 mass%. The M_{FU} range of 360–380 g mol^{-1}, however, is large compared with the actual variability. More detailed discussions on the variability of M_{FU} can be found elsewhere (Kaufhold et al., 2002; Kaufhold et al., 2013). The effect of variable M_{FU} on the calculated smectite content is considered to be low. On the other hand, a significant effect of the variable charge on the calculated smectite content was observed (±4 mass%) which shows the importance of considering the pH throughout CEC measurements. Overall, the surprisingly narrow range of LC values can be considered beneficial with respect to the accuracy of smectite content calculations for the Bavarian bentonites based on CEC values. The error in smectite content obtained based on the narrow LC range measured and realistically assumed from the other components of Eqn 2 is no greater than the error observed in the best analytical approaches for smectite quantification in clay-bearing rocks (Omotoso et al., 2006).

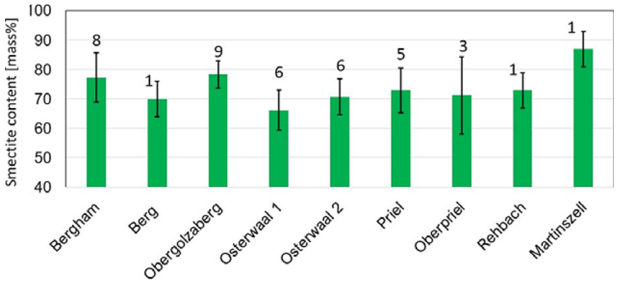


Figure 7. Comparison of calculated per cent smectite content for samples from the different locations. The numbers above the bars denote the number of samples (*n*).

The assumed 10% of variable charge and 370 M_{FU} value were used to calculate the smectite content in all the samples analyzed, taking their individually measured LC (this study) and CEC from Kaufhold et al. (2002). With one exception (Oberpriel), all other samples showed standard deviation of smectite content in 5–8% range (Fig. 7). The deposits with only one sample analyzed were assumed to have a standard deviation of 6%.

Conclusions

The new O-D method can be used for comprehensive characterizations of LC distribution in bentonite mining districts and was demonstrated in this study based on the Bavarian bentonites mined in eight different open pits or parts of mines. The O-D-LC values showed low variation (0.29–0.32 eq/FU) and the values are in agreement with published data of single Bavarian bentonite samples. While the previously reported range was slightly larger, it should be noted that these values were analyzed by AAM in different laboratories and the measurement itself is very laborious (Janek and Smrčok, 1999). The narrow LC range has positive implications for the accuracy of determining smectite content calculated from CEC data, as routinely done for quality control of Bavarian bentonites. The remaining error of the CEC based smectite contents resulting from LC

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variations accounts for, on average, ±3 wt.%, which is as good or better than smectite quantification using structural analysis methods. The similarity of LC among the deposits implies a similar origin, i.e. tephra composition and formation conditions of smectite, regardless of the smectite content (Vogt, 1980).

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Competing interests. The authors declare none.

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