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CLAY PROFILING: THE CLASSIFICATION OF MONTMORILLONITES

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Abstract—Montmorillonites, with the general composition $M_x^+(Si_{4-y}Al_y)[(Al,Fe^{3+})_{2-z}(Mg,Fe^{2+})_z]O_{10}(OH)_2$ where $x = \xi = 0.2-0.6$, $x = y+z$, and $y<<z$, vary widely in composition and structure. The commonly used classification into five montmorillonite and two beidellite groups for the solid-solution sequence does not allow an unambiguous classification with respect to structural features and the resulting properties.

The smectite structure reveals five features that allow an unambiguous description of a sample: (1) identification as either a dioctahedral or a trioctahedral smectite; (2) layer charge; (3) charge distribution between tetrahedral and octahedral sheets; (4) cation distribution within the octahedral sheet; and (5) Fe content. In addition, the nature of interlayer cations should be given as they influence certain properties of montmorillonites. Analytical methods are now available to measure and determine these structural features. Therefore, a precise classification for montmorillonites requires determination of layer charge and exchangeable cations, analysis of chemical composition, and thermal analysis (to determine the octahedral structure), in addition to X-ray diffraction analysis.

A comprehensive classification of montmorillonites based on these parameters is proposed. Ninety-six structural variations (expressed by systematic names) theoretically exist within the montmorillonite–beidellite series. Descriptive names can be used to elucidate the macroscopic properties of the montmorillonite samples in question.

Key Words—2:1 Layer Silicates, *Cis*-vacant, Classification, Dioctahedral, Layer Charge, Montmorillonite, Smectite, *Trans*-vacant

INTRODUCTION

A comprehensive characterization of smectites is of geologic and economic importance. Smectites are widespread in nature – as the main component of bentonites, they are used in a large number of technical and geotechnical applications. In civil engineering, bentonites are used in the construction of landfills, in the encapsulation of contaminated soils, as drilling fluids, and as slurry shields for tunneling processes. Technical applications are wide-ranging in industry and extend from cat litter, odor adsorbents, paint, paper industry, foundry industry, and waste-water treatment to bleaching agents in the food industry, as an additive in detergents, and in many more applications (Harvey and Lagaly, 2006). On the other hand, the smectite-to-illite transformation and expandability of mixed-layer illite-smectite in sandstones can be used as indicators of thermal maturity to check the potential of sandstones as potential sources of hydrocarbons.

Layered minerals such as smectites are usually characterized by a complex chemical composition due to various isomorphic substitutions within the tetrahedral and octahedral sheets (Drits, 2003; Drits *et al.*, 2006). In addition, they have broad particle-size distributions. Thus, structure and chemical composition not only vary with respect to different provenances but can also vary within a single sample due to changing geologic conditions during formation (Grim and Kulbicki, 1961; Drits, 2003). The transformation processes in geologic settings and in geotechnical and technical applications can change the compositions and structures of the smectites. Those pathways of transformation are not yet fully understood.

The term smectite is used for planar dioctahedral and trioctahedral 2:1 clay minerals with a layer charge between 0.2 and 0.6 per formula unit (f.u.) or per half unit cell (u.c.) and which contain hydrated exchangeable cations (Martin *et al.*, 1991; Guggenheim *et al.*, 2006). Smectites are swelling and turbostratically disordered minerals. Chemical and structural heterogeneity is typical for smectites. Even montmorillonite, which is regarded as a particular species of the smectite group, comprises a range of smectites differing mainly by the

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structure of the octahedral sheet. This is expressed by the general formula $M^{v+}_{x/v}(Si_{4-y}Al_y)[(Al,Fe^{3+})_{2-z}(Mg,Fe^{2+})_z]O_{10}(OH)_2$ with $x = \xi = 0.2-0.6$, $x = y+z$, and $y << z$. M^{v+} represents the interlayer cations such as Na^+, K^+, Ca^{2+}, or Mg^{2+}.

The amount and location of the layer charge results from isomorphic substitutions in the tetrahedral and octahedral sheets and strongly influences cation exchange capacity (CEC), intercalation, and swelling behavior (Grim and Kulbicki, 1961; Schultz, 1969; Maes *et al.*, 1979; Lagaly, 1994; Kaufhold *et al.*, 2002; Christidis and Eberl, 2003).

The type and number of octahedral cations also determine the chemical and thermal stability (Steudel *et al.*, 2007). The thermal stability of montmorillonites is strongly affected by the distribution of octahedral cations over *trans*- and *cis*-positions (Drits *et al.*, 1995). In addition, the Fe content and interlayer cations also influence the thermal stability (Mackenzie and Bishui, 1958; Köster and Schwertmann, 1993; Emmerich *et al.*, 1999).

The combination of various structural features therefore determines the macroscopic properties of montmorillonites. Quick screening of bentonite for industrial applications requires the development of index tests on the basis of only one or a few structural properties. This requires a comprehensive characterization and classification of montmorillonites that leads to an understanding of the impact of each structural feature on the macroscopic properties and which would result in a reduction in terms of the analytical effort required.

The aforementioned five properties which allow unambiguous identification of montmorillonites were identified by Güven (1988) but not all of the properties could be measured. A comprehensive classification system for montmorillonites is proposed here, based on these five parameters. This will help to explore the structure-functionality (reactivity) relationship and to develop index tests for industrial applications. Descriptive names are proposed which elucidate the macroscopic properties of a montmorillonite sample.

The following classification takes into account the rules established by the International Mineralogical Association (IMA), the Association Internationale pour l'étude des Argiles (AIPEA), and The Clay Minerals Society (CMS) Nomenclature Committee (Guggenheim *et al.*, 2006), as well as common classifications established for clay science (Grim and Kulbicki, 1961; Schultz, 1969; Brigatti and Poppi, 1981).

The different methods required for the characterization of smectites are summarized and described in detail by Wolters *et al.* (2009). The focus, in the present study, is on montmorillonites and the montmorillonite–beidellite series but references relating to smectites, which have a large Fe content in the 2:1 layers, are made, and the proposed classification may be extended later to the montmorillonite–beidellite–nontronite series.

HISTORY OF CLAY-MINERAL NOMENCLATURE AND SMECTITE CLASSIFICATION

The development in classification of smectites since Ross and Hendricks (1945) is outlined briefly here. Early classifications of clay minerals were based mainly on chemical composition, with the structure largely ignored. Nomenclature was not uniform and not widely adopted. Later classifications have tended to overrate structure and underrate chemistry. Nowadays, clay scientists try to achieve a reliable classification with unambiguous nomenclature, based on both the chemical composition and the structure.

Some of the experimental methods required for a comprehensive characterization of smectites were not available at the time of the early attempts at classification. Although the structure of montmorillonite and its swelling behavior were described by Hofmann *et al.* (1933) from X-ray diffraction (XRD) analysis, a method to measure the layer charge was not available until Lagaly and Weiss (1970a, 1970b, 1970c, 1971) introduced the alkylammonium method. First, Stevens (1945) and later van Olphen (1963) described the calculation of the structural formula based on the chemical composition. An improved algorithm (Köster, 1977), taking into account the measured layer charge, has scarcely been used since publication. The relationship between the distribution of the octahedral cations in dioctahedral smectites and the dehydroxylation temperature was not known before the studies of Drits *et al.* (1995).

Ross and Hendricks (1945) published the first extensive and systematic study on the nomenclature of smectites. Smectites including not only dioctahedral but also trioctahedral 2:1 layer silicates were named 'montmorillonites' at that time. Mackenzie (1959) presented various classification schemes to encourage discussion of the nomenclature and classification of clay minerals. He stated that a sound nomenclature is necessarily based on a satisfactory classification scheme. However, it is equally true that classification requires sound nomenclature. Whereas nomenclature aims at unambiguous terms, the objective of classification is the sorting of different species into defined classes. Warshaw and Roy (1961), while attempting to establish a new classification, faced these uncertainties in nomenclature. Much work has been done since the 1960s in an effort to establish a general classification scheme for clay minerals.

The classification of clay minerals into layer type (1:1 or 2:1), groups (*e.g.* smectites), octahedral character (di- or trioctahedral), and species (*e.g.* montmorillonite or beidellite) is what pertains at present. More recently, layer charge was added as a criterion. The term 'smectite,' which was first proposed by the nomenclature subcommittee of the British Clay Minerals Group (Brown, 1955), was approved in 1980 by AIPEA (Bailey, 1982) as group name for swelling 2:1 layer

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silicates with a layer charge between 0.2 and 0.6. In 1972 the AIPEA nomenclature committee defined the terms single (atomic) plane, tetrahedral and octahedral sheets, 1:1 or 2:1 layers, and interlayers, and their combination into structural units that are characteristic for different clay minerals (Brindley and Pedro, 1972; Bailey, 1980).

A revised classification of clay minerals by the nomenclature committee of The Clay Minerals Society (Martin *et al.*, 1991) included information on the interlayer material (hydrated exchangeable cations in case of smectites). Recent developments in the nomenclature of clay minerals were summarized by Guggenheim *et al.* (2006).

Montmorillonites are defined as dioctahedral smectites and smectites are 2:1 clay minerals with a layer charge of between 0.2 and 0.6 and hydrated exchangeable interlayer cations. They are end-members of dioctahedral smectites with little or no tetrahedral charge. Layer charge is mainly generated by substitution of Al^{3+} by Mg^{2+} in the octahedral sheet. In contrast, beidellite is the end-member with mainly tetrahedral charge and low octahedral charge (Brindley and Brown, 1980; Moore and Reynolds, 1997; Güven, 1988). Nontronite is characterized by a large Fe content in the octahedral sheet and is regarded as the third end-member of dioctahedral smectites.

Even in early studies, montmorillonites from different sources obviously displayed different chemical and physical properties due to their different compositions and layer charges. This resulted in the classification of montmorillonites (Table 1) into Wyoming-type, Cheto-type, and two montmorillonite-types representing a chemical or a physical mixture of Wyoming and Cheto types (Grim and Kulbicki, 1961). This classification was extended by Schultz (1969) who defined five montmorillonite types and two beidellite types (Table 2). He renamed the Cheto-type montmorillonite as Otay-type, which he considered to be more representative. This extended classification has some unexplained exceptions. About 20% of the characterized samples could not be assigned unambiguously.

Brigatti and Poppi (1981) applied statistical analysis of chemical composition data collected from the literature. They tried to classify dioctahedral smectites within the montmorillonite–beidellite–nontronite solid-solution range and reported ranges for the composition of dioctahedral smectite types that partly overlapped. Brigatti and Poppi (1981) and Brigatti (1983) found that the so-called 'non-ideal' montmorillonites and beidellites were mostly Fe-rich minerals (Table 3).

Crystal-chemical factors, which are responsible for cation distribution (Drits *et al.*, 2006), and crystallochemical classifications of phyllosilicates (Wiewióra, 1990, 2000; Zvyagin, 2001) explain the occurrence of different structures of dioctahedral 2:1 layer silicates.

CLASSIFICATION: THE COMPLETE SET OF PARAMETERS

Identification by XRD

Smectites are identified by characteristic basal and 060 reflections (*e.g.* Moore and Reynolds, 1997). Oriented homo-ionic samples equilibrated at defined relative humidity (r.h.) and saturated with ethylene glycol (EG), glycerol, or propandiol (Plötze and Kahr, 2005) are best suited to observing the basal reflections. At moderate humidity (40–60% r.h.), Na^+-saturated smectites display $d_{001} \approx 12.4$ Å whereas samples with divalent interlayer cations such as Ca^{2+} show $d_{001} \approx 15$ Å (Ferrage *et al.*, 2005). Ethylene glycol solvation increases the basal spacing to 17 Å. Observation of higher orders of 00*l* reflections and calculation of the coefficient of variation (CV) (Bailey, 1982) allow identification of mixed-layer minerals with random interstratification. One should keep in mind that air-dry samples stored at undefined, moderate r.h. always represent interstratified smectites with 0, 1, and 2 water interlayers, depending on layer charge and

Table 1. Classification of montmorillonites according to Grim and Kulbicki (1961).

Type	Wyoming	Cheto (Otay)	Mixed[1]	Micellaneous[2]	Fe-rich
Al^{3+}/Si^{4+} substitution	Mostly <5%	<5%	Intermediate values		
Mg^{2+}/Al^{3+} substitution	5–10%	25–35%			
Octahedral Fe	5–15%	<5%			
Octahedral occupancy	<=2	>2			
Layer charge per f.u. from CEC_m[3]	0.33–0.41	0.42–0.49	0.38–0.44	0.30–0.43	n.a.
High-temperature phases[4]	CM	QCK	QCM, QCMK, CMK	QCM	C
K^+ test	Fully expandable	Restricted swelling			
Excess silica	Often	Seldom			

[1] can be separated by size fractionation
[2] cannot be separated by size fractionation
[3] based on measured CEC and an average molecular mass of 370 per f.u.
[4] H^+-saturated, 900–1400ºC; Q: β-quartz, C: β-cristobalite, K: cordierite, M: mullite.

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Table 2. Characteristics of the montmorillonite and beidellite types defined by Schultz (1969).

Type	Wyoming	Tatatilla	Otay	Chambers	Non-ideal mon-tmorillonite	Non-ideal beidellite	Ideal beidellite
Layer charge per f.u. (average)	0.31–0.54 (0.40)	0.45–0.53 (0.50)	0.38–0.60 (0.48)	0.43–0.64 (0.57)	0.35–0.50 (0.44)	0.46–0.68 (0.52)	synth. (0.33)
Tetrahedral charge (average) (%)	5–54 (27)	19–51 (30)	0–18 (7)	0–45 (24)	19–33 (27)	61–100 (84)	100
Al^{3+}/Si^{4+} substitution (%)[1]	4	3	<1	2	3	8	10
T_{DHX} (ºC)	700–725	700–735	650–690	660–690	550–590	550–600	720–760
Octahedral Fe (%)	4–12	0–3	2–7	0–12	14–32	1–25	0
Octahedral occupancy	1.97–2.04	2	1.98–2.05	1.97–2.05	1.98–2.03	1.96–2.05	2
High-temperature phases[2]	a (S)	M, KM, a	Q (S)	a, S, M, MS	a	a, M	M
K^+ test	Mostly fully expandable	Restricted swelling with basal spacings between 13 and 16 Å				Mostly fully expandable	

[1] based on layer charge of 0.4 mol/f.u.
[2] 1100ºC
a: amorphous, M: mullite, Q: β-quartz, S: spinel, K: cordierite; () in some cases

charge distribution (Ferrage *et al.*, 2005, 2007). Thus, calculation of CV and identification of mixed-layer minerals is more reliable when using EG- or glycerol-saturated samples (Moore and Reynolds, 1997). Mg^{2+}-saturated samples subjected to glycerol saturation reveal the smectitic or vermiculitic character of a sample (Walker, 1958; Schultz, 1969; Moore and Reynolds, 1997).

Homo-ionic K^+- and H^+-exchanged samples should be avoided, as suggested by Grim and Kulbicki (1961), as the use of K^+ leads to non-integral series of basal reflections after EG saturation of highly-charged montmorillonites (Christidis and Eberl, 2003; Wolters, 2005). Protons in the interlayer space cause autotransformation of smectites (Janek *et al.*, 1997).

Dioctahedral smectites are characterized by d_{060} = 1.50 Å whereas trioctahedral smectites display d_{060} = 1.52 Å. The d_{060} value is derived from XRD patterns of randomly oriented powdered samples. These powdered samples also reveal crystalline impurities that cannot be separated from the smectite by size fractionation. The amount of associated and X-ray amorphous material has to be quantified in order to correct the chemical analysis when calculating the structural formula of the smectite (Číčel and Komadel, 1994). Quartz and cristobalite can be quantified by means of an external standard. Rietveld analysis can also be used to quantify them, as a structure model for turbostratic smectites is now available (Ufer *et al.*, 2004, 2008).

Layer charge

The total charge (ξ_T) of smectites combines the permanent negative layer charge (ξ_P) caused by structural cation substitutions and structural defects and the variable (pH-dependent) charge (ξ_V) at the edges, which becomes negative at pH> 5 (Lagaly, 2006; Bergaya *et al.*, 2006).

Determination of the layer charge is a difficult and time-consuming task. In most cases the layer charge is derived from the structural formula ($\xi_{P,c}$) which is calculated from chemical analysis. An independent method is the determination of the permanent layer charge ($\xi_{P,m}$) by intercalation of alkylammonium ions of different alkyl chain lengths (Lagaly, 1994). This layer charge should be used to calculate the structural formula (Köster, 1977).

Table 3. Compositional ranges of montmorillonites and beidellites by Brigatti and Poppi (1981).

Type	Wyoming	Otay (Cheto)	Chambers (mixed Cheto-Wyoming)	Tatatilla	Non-ideal (Fe-rich) montmorillonite	Beidellite	Non-ideal (Fe-rich) beidellite
Layer charge per f.u.	0.33–0.43	0.53–0.6	0.43–0.55	0.3–0.53	0.4–0.58	0.35–0.6	0.35–0.6
Tetrahedral charge (%)	20–50	5–25	15–35	10–40	20–50	50–100	50–100
Octahedral Fe (%)	8–15	3–8	5–12	0–3	15–31	0–15	15–25

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The numbers of cations balancing the variable (pH-dependent) negative charges at the edges are included in the chemical analysis. These numbers lead to errors in the calculation of structural formulae and in the determination of the permanent layer charge.

$CEC_{P,c}$, originating from ξ_P, can be derived by means of equation 1 in terms of the molecular weight of a formula unit (f.u.) or half unit cell (u.c.).

$$CEC_{P,c}[\text{meq}/100\ \text{g}] = \frac{\xi_P[\text{eq*mol}^{-1}]}{M[\text{g*mol}^{-1}]} * 100000 \quad (1)$$

Thus, the measured CEC, $CEC_{T,m}$, at pH 5−7 is greater than or equal to the CEC calculated from the permanent layer charge ($CEC_{P,c}$).

The $CEC_{P,c}$ values were derived from several hundred structural formulae of smectites reported in the literature and were compared with the measured $CEC_{T,m}$ values. The observed relationship: $CEC_{T,m}<CEC_{P,c}$ is inexplicable. When $\xi_{P,m}$ is used in the calculation of the structural formula, the condition $CEC_{T,m} \geqslant CEC_{P,c}$ is always fulfilled (Köster, 1977; Wolters *et al.*, 2009). The difference between $CEC_{T,m}$ and $CEC_{P,c}$ (from $\xi_{P,m}$) varies between 0 and 20% (Lagaly, 1981).

The total layer charge, ξ_T, is, on average, ~28% greater than $\xi_{P,m}$ (Wolters *et al.*, 2009). Although the controversial discrepancy between ξ_T and ξ_P is discussed by Laird *et al.* (1989), only the use of the measured layer charge $\xi_{P,m}$ in the calculation of the structural formula leads to reliable results (Köster, 1977; Vogt and Köster, 1978; Kaufhold *et al.*, 2002; Wolters *et al.*, 2009). In some cases, the amount of time required can be reduced by measuring a mean layer charge (according to Olis *et al.*, 1990). Layer-charge heterogeneity is explained as interstratification of layers with different permanent layer charges.

Structural formula and location of charges

The location of the charges is derived from the calculated structural formula. Index tests such as the Li^+ test (Hofmann and Klemen, 1950; Greene-Kelly; 1955, Schultz, 1969) can be used to prove the charge distribution determined.

Homo-ionic samples are used for chemical analysis by X-ray fluorescence (XRF) or chemical dissolution methods and subsequent element analysis (*e.g.* by atomic absorption spectroscopy). The original interlayer cation occupancy, in most cases a combination of Na^+, Ca^{2+}, and Mg^{2+}, and minor K^+, Al^{3+}, and H_3O^+, is unsuitable for chemical analysis and calculation of the structural formula because Mg^{2+} is also a main component of the octahedral sheet.

The Li^+ test is said to distinguish between smectites with different charge locations and can be used to verify the octahedral *vs*. tetrahedral charge distribution. Whereas homo-ionic Li^+-exchanged montmorillonite does not re-expand with glycerol after heating at 200ºC, homo-ionic Li^+-exchanged beidellite regains intercalation after treatment with glycerol. A good approximation of the proportion of expandable beidellitic layers can be determined using the shift in the *d* value of the 002/004 reflections (MacEwan *et al.*, 1961).

Representation of the structural formula has changed since Ross and Hendricks (1945) used two lines. The interlayer occupation was written above the silicate network composition showing first the octahedral, then the tetrahedral cations. The line ended with $O_{10}(OH)_2$. This notation was later reduced to one line reporting the cations in the interlayer space and the tetrahedral and octahedral sheets, again ending with $O_{10}(OH)_2$. Slightly different forms (varying in terms of the sequence of listing interlayer and tetrahedral and octahedral sheets) were used (*e.g.* Jasmund and Lagaly, 1993; Rieder *et al.*, 1998; Malfoy *et al.*, 2003). The IMA recommendations follow the systematic approach of Smith *et al*. (1998) to general and structure-type formulae for minerals and inorganic phases. Applying the specific structure-type formula of micas to dioctahedral smectites would require $DG_2[T_4O_{10}](OH)_2$ where *D* represents the interlayer cations; *G*, the octahedral cations, and *T*, the tetrahedral cations. However, the sequence interlayer-tetrahedral sheet-octahedral sheet allows the user to memorize the structural formulae of 2:1 layer silicates following the structural design.

Structure of the octahedral sheet

Cation distribution within the octahedral sheet was the final, missing piece of information to complete the structure of a dioctahedral smectite. Different octahedral sites, with respect to the position of the hydroxyl groups, have been known for some time. One *trans*- or *M*1-position and two *cis*- or *M*2-positions (Tsipurski and Drits, 1984; Güven, 1988) are distinguished. As smectites are turbostratically disordered, the octahedral occupancy cannot be determined by XRD techniques as is possible for illites (Drits, 2003), though oblique-texture electron diffraction might be applied to smectites, as demonstrated by Tsipurski and Drits (1984).

Montmorillonites usually dehydroxylate at ~650−700ºC but few montmorillonites dehydroxylate at 500−550ºC or show two dehydroxylation reactions. The samples, which dehydroxylated at high temperatures, are referred to as "normal, typical, or ideal," the others were referred to as "abnormal, untypical, or non-ideal" (Cole, 1955; Cole and Hosking, 1957; Heller *et al.*, 1962; Schultz, 1969). In contrast, most illites dehydroxylate at 500−550ºC and were referred to as "ideal." Illites with a high dehydroxylation temperature (T_{DHX}) were referred to as "non-ideal," which was confusing. Drits *et al*. (1995) showed that the dehydroxylation temperature is related to the octahedral occupancy of the dioctahedral 2:1 layer silicates. *Cis*-vacant (*cv*) 2:1 clay minerals dehydroxylate at >600ºC and *trans*-vacant varieties release their hydroxyl groups at

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<600ºC (Drits *et al.*, 1995; Wolters and Emmerich, 2007). Hence, thermal analysis provides the missing information on the octahedral structure. Peak deconvolution and integration of the mass-spectrometer curves of evolved water even allows determination of the number of *tv* and *cv* layers.

Fe content

In phyllosilicates, Fe^{2+} and Fe^{3+} can substitute for Al^{3+} in the octahedral sheet and Fe^{3+} can substitute for Si^{4+} in the tetrahedral sheet (Wagner and Wagner, 2004). Most chemical analyses only provide information on the total Fe content (Köster, 1979). Mössbauer spectroscopy enables the user to distinguish between Fe^{2+} and Fe^{3+} and their coordination, four or six, in clay minerals. The relative amounts of both Fe ions and their coordination can be detected by the center or isomer shift (IS) and quadrupole splitting (QS). In the present study, Mössbauer spectra of the bulk material and of the <0.2 μm fraction verified that no change in the oxidation state took place during the purification process of the samples (Wolters, 2005). The reliability of the structural formula based on chemical analysis, according to Köster (1977), was checked by the Mössbauer results. Fe^{2+} and Fe^{3+} ions were located only in octahedral sites. The montmorillonites contained <5% of Fe^{2+} of the total Fe content, *i.e.* $\leqslant$0.02 mol Fe^{2+}/f.u. Thus, determination of the Fe^{2+} content of montmorillonites with a small Fe content overall is not necessary in order to obtain reliable structural formulae (Wolters, 2005).

THE CLASSIFICATION

Prerequisites

Uniform pretreatment and sample preparation is imperative for reliable characterization of montmorillonites. Impurities should be removed as much as possible and homo-ionic samples must be prepared. The purification methods depend on the sample source and the paragenesis of the phases. The chemistry and structure of the montmorillonites might be slightly influenced by sample processing (possible changes in the Fe^{2+}/Fe^{3+} ratio and removal of very fine-grained (colloidal) material).

Common chemical pretreatment consists of the removal of carbonates by means of an acetic acid buffer followed by the removal of Fe and Al (hydr)oxides and the decomposition of organic matter with hydrogen peroxide. Excess reactants are removed by washing with NaCl and finally by dialysis in deionized water. The purification process yields homo-ionic Na^{+}-saturated samples (for details see Mehra and Jackson (1960), Tributh and Lagaly (1986), Moore and Reynolds (1997), Dohrmann (1999), Emmerich (2000), and Carrado *et al.* (2006)).

Smectites are enriched by separation of the <2 μm fraction by gravitational sedimentation, and of the <0.2 μm fraction by sedimentation in a centrifugal field. Some samples might consist of a physical mixture of different varieties of montmorillonite, with different particle sizes (Grim and Kulbicki, 1961). In this case, the smectites in the different clay fractions have to be classified.

Homo-ionic samples with other interlayer cations such as Li^{+}, K^{+}, and Mg^{2+} are prepared by cation exchange with corresponding salt solutions and subsequent dialysis to remove excess salt (Emmerich *et al.*, 1999).

Associated phases besides the smectite have to be identified and quantified. Using conventional XRD, XRF, Simultaneous Thermal Analysis (STA), Mössbauer spectroscopy, CEC measurement, and layer-charge determination equipment, at least 6 g of purified clay-sized material is the amount of sample required in order to perform all of the necessary analyses. For each cation exchange experiment, additional amounts of 2 g are needed. The CEC measurement of the bulk sample allows estimation of the smectite content in the sample. This value can be used to estimate the amount of sample required for the purification procedure. The analysis of cations in the supernatant from CEC determination of the bulk material also reveals the type of original interlayer cations.

Limits of the parameters

The structural features of montmorillonites vary within defined ranges (Table 4). The limits for layer charge are derived from swelling properties and include results from the present study and from those by Schultz (1969) and Christidis and Eberl (2003). Swelling experiments with K^{+}-saturated samples indicate that the limits for low- and medium-charged montmorillonites are lower than indicated by data from the literature (Emmerich and Wolters, 2005; Wolters and Emmerich, 2007). Investigation of this phenomenon will be published later.

The limits for the transition from *cis*-vacant to *trans*-vacant montmorillonites were defined by applying the 50% rule (Wolters and Emmerich, 2007). No evidence has been found for discontinuous changes in the chemical and physical properties. Dehydroxylation seems to decrease continuously with increasing number of *tv* layers.

The limits for the Fe content correspond to the values defined by Brigatti and Poppi (1981), Brigatti (1983), and Güven (1988). The terminology relating to Fe-bearing smectites is still the subject of debate. At present, Fe^{2+}- or Fe^{3+}-rich smectite is preferred to ferroan (Fe^{2+}) or ferrian (Fe^{3+}) (Nickel and Grice, 1998; Guggenheim *et al.*, 2006). However, the term Fe^{2+}- or Fe^{3+}-rich interferes with the description of the interlayer occupancy, *e.g.* Ca-rich montmorillonite, making 'ferroan/ferrian' more attractive.

The lower limit for Fe-rich (ferrian) smectites was set at 0.3 mol/f.u. The upper limit for ferrian smectites was

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Table 4. Classification of smectites.

Structural feature	Limits	Designation
Layer charge (mol/f.u.)	0.2−0.374	Low-charged
	0.375−0.425	Medium-charged
	0.426−0.6	High-charged
Octahedral structure	w_{cv} 100−75%; w_{tv} 0−25%	*cv*
	w_{cv} 74−50%; w_{tv} 26−50%	*cv/tv*
	w_{cv} 49−25%; w_{tv} 51−75%	*tv/cv*
	w_{cv} 24−0%; w_{tv} 76−100%	*tv*
Fe content (mol/f.u.)	0−0.30 (0−15%)	–
(%Fe in octahedral cations)	0.31−1 (16−50%)	Ferrian
Charge location	*O* 100−90%, *T* 0−10%	Montmorillonite
	O 89−50%, *T* 11−50%	Beidellitic montmorillonite
	O 49−10%, *T* 51−90%	Montmorillonitic beidellite
	O 9−0%, *T* 91−100%	Beidellite

assigned differently. Brigatti (1983) documented samples with 15−30% octahedral Fe as Fe-rich montmorillonites and beidellites, whereas Güven (1988) proposed 15−50% octahedral Fe for Fe-rich smectites. Güven's (1988) upper limits are selected because the present results and the literature data do not show a miscibility gap in the octahedral Fe contents of montmorillonites, beidellites, and nontronites.

Tetrahedral substitution is often expressed by the term 'beidellitic.' In fact, no general rule for the use of this term exists. Therefore, proposed here is that the term 'beidellitic' be used for samples with a tetrahedral charge of 10−50% of the total charge, according to Greene-Kelly (1955), Güven (1988), and the IMA rules. Thus, samples with <10% tetrahedral charge are to be known as montmorillonites; samples with >90% tetrahedral charge are to be known as beidellites; intermediates will be considered as 'beidellitic montmorillonites' or 'montmorillonitic beidellites' (Table 4).

Assignment and occurrence of different montmorillonite/beidellite varieties

The classification of smectites (Table 4) leads to 96 varieties within the montmorillonite−beidellite series. If all are thermodynamically stable, this should be shown by molecular modeling. Extensive screening of natural samples from various locations and of different origins will reveal the natural abundance. For illites and micas, crystal-chemical factors were identified that are responsible for the distribution of the octahedral cations over *trans*- and *cis*-vacant sites (Sainz-Díaz *et al.*, 2004; Drits *et al.*, 2006). Micas rich in octahedral Fe^{3+} and Mg occur only as *tv* varieties. Pure *cv* illites were poor in Fe and Mg. Information on the occurrence of *cv* or *tv* smectites is very limited although large Al contents in the tetrahedral sheet (beidellites) and large Fe contents (nontronites) seem to favor *tv* smectites but *cv* beidellites are also known. In the case of montmorillonites, several octahedral structures from pure *cv* to nearly pure *tv* are known (Drits *et al.*, 1995, 1998, 2004; Wolters and Emmerich, 2007). The formation of *tv* and *cv* layers in dioctahedral smectites seems to be related to local order-disorder in the distribution of isomorphous cations (Drits *et al.*, 2006).

As recently as the late 1990s, many characterizations of montmorillonites and beidellites were incomplete, because one or more of the range of analytical methods required was missing. Data from 300 samples from the literature were considered in the present study (not listed because of the large number). Fewer than 65% of the samples assigned as smectites (mainly montmorillonites) fulfilled the definitions with respect to layer charge and the number of substitutions. Some data sets must be considered with more than the usual skepticism because the structural formulae were not charge balanced. Reported layer charges were <0.2 or >0.6 per f.u. or the CEC_T value was less than that for CEC_P. In addition, the sample-preparation techniques were often poorly documented.

Only seven types of montmorillonite and beidellite were distinguished in the literature. When applying the reported criteria to the 28 samples investigated, an assignment was in some cases ambiguous, confusing (ideal *vs*. non-ideal), or even impossible (Table 5). One reason is that the reported classifications were based on questionable layer charges and classifications as low- or high-charged montmorillonite were insufficient. Many of those samples showed characteristic attributes of two types of montmorillonites such as small layer charge combined with small tetrahedral charge (sample 16: Wyoming/Otay) or small layer charge combined with intermediate tetrahedral charge and intermediate octahedral Fe content (sample 32: Wyoming/Tatatilla).

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Table 5. Classification and descriptive names of 28 smectites (Na-saturated, <0.2 μm) and assignment to trivial names according to known classifications (samples and analytical data see Wolters *et al.* (2009)).**The names listed in bold type are the descriptive names**.

Sample		Layer charge mol/f.u.		Octahedral structure w_{tv}/w_{cv} (%)		Fe in % of octahedral cations		Tetrahedral charge in % of total charge		Mineral	Schultz (1969)	Brigatti and Poppi (1981)	New trivial name
16	GR01	**low**	0.32	***cv***	0/100	–	4	–	9	**montmorillonite**	Wyoming	Tatatilla	Tatatilla
8	UAS	**low**	0.37	***cv***	0/100	–	8	–	3	**montmorillonite**	Wyoming/Otay	Tatatilla/Otay	ditto
7	EMC	**low**	0.21	***cv***	0/100	–	8	**beidellitic**	40	**montmorillonite**	Wyoming	Wyoming	Wyoming I
32	Volclay	**low**	0.21	***cv***	0/100	–	9	**beidellitic**	11	**montmorillonite**	Wyoming	Wyoming/Tatatilla	ditto
25	Volclay	**low**	0.26	***cv***	0/100	–	9	**beidellitic**	12	**montmorillonite**	Wyoming	Wyoming/Tatatilla	ditto
2	LP	**low**	0.29	***cv***	11/89	–	11	**beidellitic**	24	**montmorillonite**	Wyoming	Wyoming	Wyoming II
17	GR02	**low**	0.3	***cv***	5/95	–	4	**beidellitic**	33	**montmorillonite**	Wyoming	Wyoming/Tatatilla/ Otay	ditto
39	GQ-I	**low**	0.39	***cv***	24/76	–	12	**beidellitic**	15	**montmorillonite**	Wyoming	Wyoming/Tatatilla	ditto
31	BAR3	**low**	0.3	***cv/tv***	40/60	–	14	–	3	**montmorillonite**	Wyoming/Otay	Wyoming/Otay	Otay I
13	TR02	**low**	0.35	***cv/tv***	41/59	–	8	–	6	**montmorillonite**	Wyoming/Otay	Wyoming/Otay	
14	TR03	**low**	0.36	***cv/tv***	32/68	–	4	–	3	**montmorillonite**	Wyoming/Otay	Wyoming/Otay	
18	USA01	**low**	0.26	***cv/tv***	29/71	–	10	**beidellitic**	15	**montmorillonite**	Wyoming	Wyoming/Chambers/Tatilla	Wyoming III
19	USA02	**low**	0.3	***cv/tv***	28/72	–	14	**beidellitic**	17	**montmorillonite**	Wyomimg/non-ideal	ditto	ditto
33	CA	**low**	0.31	***cv/tv***	33/67	–	15	**beidellitic**	23	**montmorillonite**	Wyomimg/non-ideal	ditto	ditto
21	D01	**low**	0.31	***cv/tv***	44/56	–	15	**beidellitic**	29	**montmorillonite**	Wyomimg/non-ideal	ditto	ditto
42	Linden	**low**	0.35	***cv/tv***	34/66	–	9	**beidellitic**	14	**montmorillonite**	Wyomimg	Wyoming/Otay/ Chambers	ditto
12	TR01	**low**	0.35	***cv/tv***	39/61	–	3	**beidellitic**	17	**montmorillonite**	Wyoming/Otay	Tatatilla/Otay	
28	SB	**low**	0.36	***tv/cv***	57/43	–	11	**beidellitic**	19	**montmorillonite**	non-ideal	non-ideal	y.t.b.d.
37	BB	**low**	0.25	***tv/cv***	78/22	**ferrian**	28	**beidellitic**	48	**montmorillonite**	non-ideal	non-ideal	y.t.b.d.
3	7th Mayo	**low**	0.31	***tv/cv***	52/48	**ferrian**	17	**beidellitic**	29	**montmorillonite**	non-ideal	non-ideal	ditto
5	MC	**low**	0.32	***tv/cv***	52/48	**ferrian**	16	**beidellitic**	13	**montmorillonite**	non-ideal	non-ideal	ditto
6	GPC	**low**	0.34	***tv***	82/18	–	15	**beidellitic**	38	**montmorillonite**	non-ideal	non-ideal	y.t.b.d.
38	MW	**low**	0.26	***tv***	76/24	**ferrian**	21	**beidellitic**	50	**montmorillonite**	non-ideal	non-ideal	Valdol
26-27	Valdol C14	**low**	0.27	***tv***	84/16	**ferrian**	20	**beidellitic**	37	**montmorillonite**	non-ideal	non-ideal	ditto
41	Val C18	**low**	0.3	***tv***	80/20	**ferrian**	21	**beidellitic**	47	**montmorillonite**	non-ideal	non-ideal	ditto
24	Beid	**medium**	0.38	***cv***	0/100	–	<1	**montmorillonitic**	77	**beidellite**	beidellite	beidellite	y.t.b.d.
4	JUP	**low**	0.26	***cv/tv***	44/56	**ferrian**	19	**montmorillonitic**	62	**beidellite**	beidellite	Fe-rich beidellite	y.t.b.d.
36	M650	**low**	0.27	***tv/cv***	74/26	**ferrian**	22	**montmorillonitic**	70	**beidellite**	non-ideal beidellite	Fe-rich beidellite	y.t.b.d.

y.t.b.d.: yet to be defined

Thus, a classification, based on descriptive names for montmorillonites which include all relevant information on the crystal chemistry and the structure in combination with trivial names that are already well established (Table 5), is proposed. The advantage of descriptive names is the indication of macroscopic properties such as CEC and surface-charge density, thermal stability (from the kind of octahedral substitutions and the distribution of octahedral cations), or swelling properties (from layer charge, charge distribution, and interlayer cations).

Although the interlayer cations are not considered for classification, the descriptive name of a montmorillonite can be extended with respect to the original or exchanged interlayer cations, which, on one hand indicate conditions during smectite formation, and on the other, are responsible for macroscopic properties (*e.g.* rheological behavior and thermal reactions).

As an example, Volclay (sample 25) has the formula

$$Na^{+}_{0.26}(Si_{3.93}Al_{0.07})(Al_{1.59}Fe^{3+}_{0.18}Mg_{0.23})O_{10}(OH)_2$$

based on the measured layer charge of 0.26. The tetrahedral charge is 12% of the total charge and 9% of the octahedral cations are Fe ions, *i.e.* <0.3 mol/f.u. The octahedral sheet is 100% *cis*-vacant (Wolters and Emmerich, 2007; Wolters *et al.*, 2009) and so the sample is described as Na-exchanged, low-charged *cv* beidellitic montmorillonite. The descriptive name indicates low CEC, the high thermal stability of the sample, and partial swelling of the heated, K-exchanged material after EG saturation. The Na-rich montmorillonite will fully delaminate into single 2:1 layers in water.

The Wyoming-type montmorillonites are low-charged beidellitic montmorillonites with three different octahedral structures. Pure *cv* varieties are type I; type II samples display certain amounts of *trans*-vacant octahedral sheets; and type III are *cv/tv* varieties (26–50% *tv*, Table 4). The trivial name of the sample above is therefore Na-rich Wyoming type I (montmorillonite).

CONCLUSION

A comprehensive and reliable classification of smectites requires knowledge of the chemical composition (tetrahedral/octahedral charge distribution), the layer charge and exchangeable cations, the di- and trioctahedral character, and the Fe content, but also the structure of the octahedral sheets (*cis*-, *trans*-vacancy). Today, these properties can be measured so that a new classification is based on these distinctive properties. Descriptive names provide the structure-property relationship. For instance, the name of a Wyoming-I montmorillonite is 'low-charged *cv* beidellitic montmorillonite' and indicates low CEC, high thermal stability of the sample, and partial swelling of the heated, K-exchanged material after EG saturation. The Na-rich montmorillonite delaminates into single 2:1 layers in water. The classification thus allows for quick industrial screening of bentonites.

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