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Thermal reactions of smectites—Relation of dehydroxylation temperature to octahedral structure

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Abstract

Montmorillonites are structural and chemical heterogenic with the octahedral sheet being the most distinguished structural feature. The occupancy of *cis*- and *trans*-positions of the dioctahedral smectites was investigated by simultaneous thermal analysis. *Cis*-Vacant (cv) phyllosilicates dehydroxylate between 650 and 700 °C and *trans*-vacant (tv) varieties between 500 and 550 °C. Calculation of peak areas from the peak fitted evolved water curves were used to estimate the ratio of *trans*- to *cis*-vacancies.

Limits for the proportion of *cis*- and *trans*-vacancies were defined resulting in four classes (cv; cv/tv; tv/cv; tv) for montmorillonites with respect to the distribution of the octahedral cations. Most common are mixed cv/tv montmorillonites with dominating amounts of cv 2:1 layers (74–50%). Pure cv montmorillonites occur in nature. Some montmorillonites classified as cv contain up to 25% tv layers. Pure tv montmorillonites were not found. All tv montmorillonites contain cv 2:1 layers (up to 24%).
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1. Introduction

Smectites are characterized by different forms of structural and chemical heterogeneity. Even montmorillonite, that is regarded as a certain mineral, presents a group of smectites, that is not homogeneous. This is expressed by a general formula of M_x^+ $(Si_{4-y}Al_y)$ $(Al, Fe_{2-z}^{3+}Mg_z)$ O_{10} $(OH)_2$ with $x = 0.2$, ..., 0.6; $x = y + z$ and $y \ll z$. The octahedral sheet is the most distinguished structural feature of montmorillonites. Therefore, a comprehensive classification of montmorillonites has to incorporate information on the structure of the octahedral sheet.

Montmorillonites are swellable dioctahedral 2:1 layer silicates. They consist of stacks of several so-called 2:1 layers. A layer is built of an octahedral sheet sandwiched between two tetrahedral sheets. The dioctahedral character of the montmorillonites leads to vacancies in the octahedral sheet. Only two of the three octahedral positions are occupied. The vacancies are of *cis*- or *trans*-vacant character.

Smectites show turbostratic disorder, which means their X-ray diffraction (XRD) patterns lack diagnostic $h\,k\,l$ reflections. Thus, their octahedral structure cannot be determined by XRD, as it is possible for other dioctahedral 2:1 layer silicates, e.g. illites.

Drits et al. [1] showed that the dehydroxylation behavior of aluminous dioctahedral 2:1 layer silicates is related to the distribution of the metal ions and vacancies in the octahedral sheet. They demonstrated that the dehydroxylation peak temperature (T_{DHX}) obtained by thermal analysis (TA) can be used to characterize the structure of the octahedral sheet. *Cis*-Vacant (cv) minerals dehydroxylate at about 650–700 °C and *trans*-vacant (tv) varieties dehydroxylate at about 500–550 °C. The boundary between *cis*-vacant and *trans*-vacant was found at about 600 °C (peak temperature) [2] under their chosen experimental conditions.

In the past a large quantity of thermal analysis data on clay minerals was collected [3,4] but interpretation was ambiguous. It was obvious, that dioctahedral 2:1 layer silicates are character-

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ized by a wide range of dehydroxylation temperatures between about 450 and 800 °C (or even higher). It was also found, that illites dehydroxylate more often at about 500–550 °C whereas the hydroxyl groups of montmorillonites are mostly released between about 650 and 700 °C. Hence, dehydroxylation of illites at 500 °C and dehydroxylation of montmorillonites at 700 °C was designated "normal" or "typical" or "ideal". A different behavior was called "abnormal", "untypical" or "non-ideal" [5–8]. This means "abnormal" illites dehydroxylate at 700 °C and "abnormal" smectites at 500 °C. In addition quite a few samples showed a dehydroxylation peak doublet.

The knowledge about the octahedral structure of montmorillonites is not only important for a comprehensive and unambiguous classification but is necessary to understand chemical reactions and mineral transformations of 2:1 layer silicates. Two examples shall stress the importance. First, smectites are used in a wide range of technical applications. Especially, in foundries the thermal stability determines the consumption of bentonite in foundry processes using molding sands. Second, smectites are precursors of illites during several geological (and geotechnical) processes like burial diagenesis or hydrothermal alteration. Therefore, the structure of smectites has to be known in detail to understand the smectite to illite transformation.

In this paper simultaneous TA (STA) (thermogravimetry (TG)/differential scanning calorimetry (DSC) linked with a quadrupol mass spectrometer for the analysis of evolved water) was used to study a random choice of 28 natural montmorillonites and to determine the amount of *trans*-vacant and *cis*-vacant 2:1 parts of each sample. First of all we focused on the reliability of the defined border of 600 °C for the dehydroxylation of tv and cv parts. Peak fitting and calculation of peak areas from the evolved water curves were then used to calculate the ratio of *trans*- to *cis*-vacancies for each sample. We were interested to investigate which octahedral structures are most common for montmorillonites. Before presenting the experimental data and our interpretations we want to give the reader some more information on the structure and thermal behavior of montmorillonites which we consider necessary to follow our contribution.

1.1. The thermal reactions of 2:1 layer silicates

2:1 layer silicates display four characteristic thermal reactions. These are dehydration, dehydroxylation, decomposition and recrystallization [9].

During dehydration adsorbed water from outer surface and interlayer water from inner surfaces and hydration shells of interlayer cations desorbs in an endothermic reaction between room temperature and 300 °C [8,10].

Above 400 °C dehydroxylation takes place as endothermic reaction. Structural water from two hydroxyl groups per formula unit (half unit cell) migrates out of the mineral structure according to the reaction $2(OH) \rightarrow H_2O + O_r$ (r, residual). This dehydroxylation is influenced by three different structural features. (1) The nature of interlayer cation changes dehydroxylation temperature up to about 60 °C [11,12]. Therefore, homoionic samples with the same interlayer cations

must be used when relating dehydroxylation behavior to the structure of the octahedral sheet. (2) The nature of octahedral cations and their bonding strength affect the endothermic peak position. The dehydroxylation temperature increases as Fe–OH < Al–OH < Mg–OH [13]. Thus increasing layer charge of dioctahedral 2:1 layer silicates should increase T_{DHX} due to increasing Mg-content of the octahedral sheet. (3) *Trans*- and *cis*-vacancies lead for aluminous 2:1 clay minerals to different dehydroxylation temperatures which is the topic of the present investigation.

Decomposition and recrystallization reveal varying intensities and sometimes only one of the two reactions can be observed. Decomposition and recrystallization take place between 850 and 950 °C.

1.2. The structure of the octahedral sheet

To explain the different dehydroxylation behavior we need to understand the *cis*- and *trans*-isomers of the octahedra. The 2:1 layer silicates can either be di- or tri-octahedral. For the trioctahedral ones all three octahedra of a formula unit are occupied by divalent cations, commonly with magnesium. For the dioctahedral ones only two of the three sites are occupied by trivalent cations (e.g. by aluminum) and thus, vacancies remain in the octahedral sheet.

The octahedral sheet consists of *cis*- and *trans*-octahedra. A *cis*- or *trans*-position is defined by the position of the hydroxyl groups (Fig. 1). At the *trans*-octahedron the two hydroxyl groups are positioned at opposite corners. The *cis*-position is defined by two hydroxyl groups at one edge. There exist one *trans*- and two *cis*-positions in the octahedral sheet (Fig. 2a). In older literature M1 is used for *trans*-position and M2 for *cis*-position. Tsipursky and Drits [14] introduced the terms *cis*- and *trans*- in clay mineralogy.

Fig. 2(b) and (c) shows projections of the octahedral sheet of a *cis*- and a *trans*-vacant variety of a dioctahedral 2:1 layer silicates. Occupied positions are marked with M and vacancies are marked with V. For the dioctahedral 2:1 layer silicates one of the *cis*-positions or the *trans*-position is empty. In Fig. 2(b) the *trans*-position with opposite hydroxyl groups is filled. One
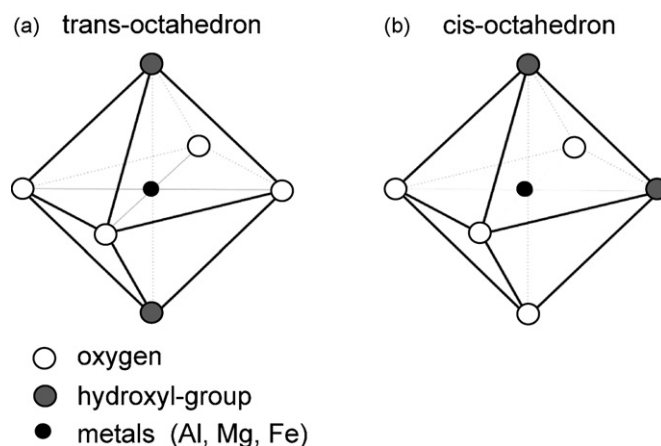

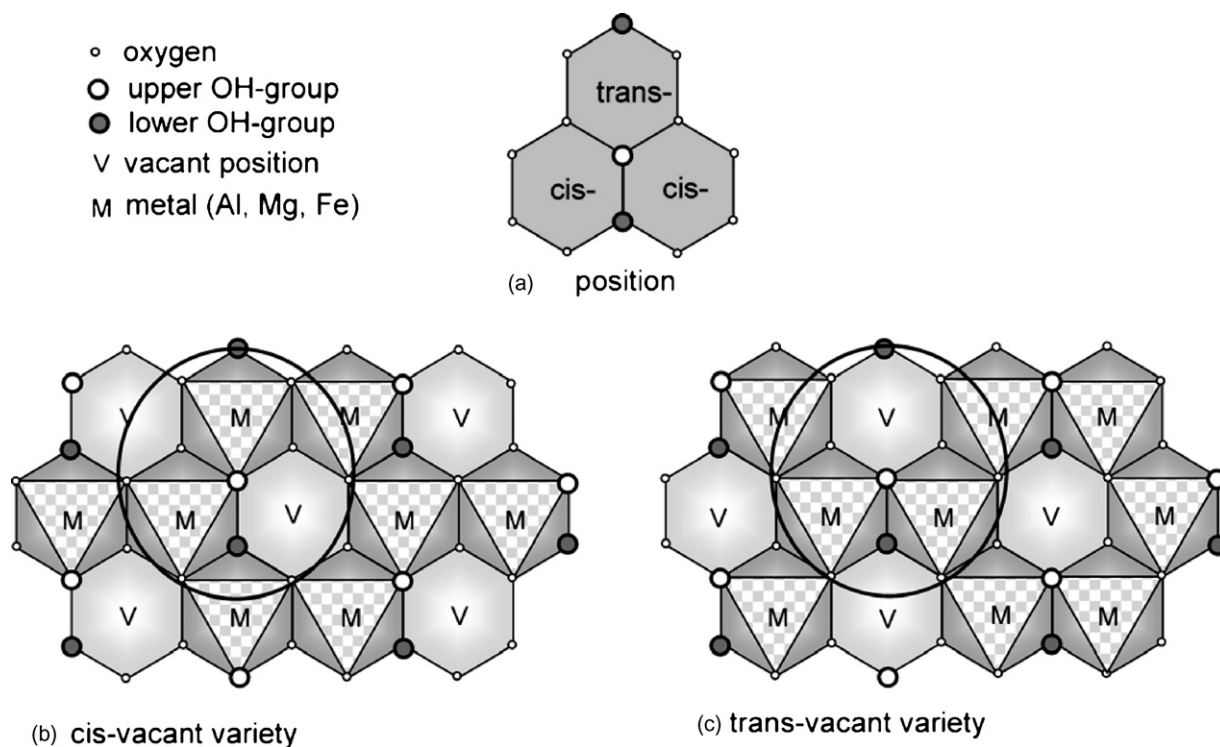Fig. 1. (a) *Trans*- and (b) *cis*-isomers of octahedral coordinated cations.

Fig. 2. Projection of the octahedral sheet of a dioctahedral 2:1 clay mineral perpendicular to the *c*-axis. (a) *Trans* (M1)- and *cis* (M2)-positions with respect to the location of the hydroxyl groups, (b) the *cis*-vacant (cv) variety, and (c) the *trans*-vacant (tv) variety.

of the two *cis*-positions is occupied, but the other is vacant. This is the so-called *cis*-vacant (cv) variety. In Fig. 2(c) the *trans*-position is empty, and the two *cis*-positions are occupied. We call this the *trans*-vacant (tv) variety. Very important is that both variations occur in nature. There are cv and tv varieties and, in addition, mixtures of these two. It is also possible to transform a cv clay mineral into a tv one and vice versa [1,12,15]. Drits et al. [1] described the dehydroxylation as a two stage process. First, two adjacent OH-groups are replaced by a single residual oxygen. The Al^{3+}, which occupied *cis*- and *trans*-sites become five and six coordinated. Second, Al^{3+} migrate from a *trans*-site to a *cis*-site. Thus, cv becomes tv during the dehydroxylation of aluminous clay minerals. The distances of the hydroxyl groups are longer in cv montmorillonites (2.85–2.88 Å) than in tv varieties (2.40–2.50 Å) and require therefore a higher dehydroxylation energy than tv montmorillonites [1]. Emmerich et al. [12,15] converted a cv montmorillonite into a tv variety by dehydroxylation and rehydroxylation. The rehydroxylated sample showed a 190 °C lower dehydroxylation temperature than the initial material. The opposite behavior was detected for glauconite and celadonite. Ferrian 2:1 clay minerals were indirectly proved to be *trans*-vacant [16]. Dehydroxylation of celadonite and glauconite is accompanied by a migration of octahedral cations from *cis*- to *trans*-sites, thus, tv becomes cv. In glauconite with $Fe^{3+/2+}$ and Al^{3+} in the octahedral sheet a reverse cation migration occurs after rehydroxylation. Because of the low Al^{3+} content for most of the layers in celadonite reverse cation migration does not occur in the octahedral sheet after rehydroxylation. The authors concluded that during rehydroxylation, the layers with a higher Al^{3+} con-

tent are transformed into tv layers whereas layers with a lower Al^{3+} content preserve the cation distribution of the dehydroxylated form. Conclusively, the reverse migration of octahedral Al^{3+} cations to vacant *cis*-sites may provide a more stable configuration.

2. Experimental

2.1. Material specification

Twenty-eight smectite samples of various locations were investigated. All samples were identified by XRD to be dioctahedral smectites. Layer charge varied between 0.27 and 0.39 per formula unit [17]. Twenty-five samples were montmorillonites with less than 50% tetrahedral charge of the overall layer charge—five of these had less than 10% tetrahedral amounts of charge, which were regarded as plain montmorillonites. Twenty samples displayed 10–50% tetrahedral charge and therefore we call them beidellitic montmorillonites. Only three samples were montmorillonitic beidellites with more than 50 and less than 90% of tetrahedral charge (Table 3).

2.2. Sample treatment

All samples were purified by chemical pretreatment before separating the homoionic Na^+-saturated <0.2 μm fraction for STA.

The chemical pretreatment [18–21] included the removal of carbonates (mostly calcite, dolomite and siderite) with an acetic acetate buffer followed by the removal of iron oxides and

Table 1
Limits of the amount of *cis*- and *trans*-vacant octahedral sheets for classification of dioctahedral smectites

	cis-Vacant cv	*cis–trans*-Vacant cv/tv	*trans–cis*-Vacant tv/cv	*trans*-Vacant tv
Percentage area of MS curves ($m/e = 18$) of the evolved water during dehydroxylation	W_{cv} 100–75	W_{cv} 74–50	W_{cv} 49–25	W_{cv} 24–0
	W_{tv} 0–25	W_{tv} 26–50	W_{tv} 51–75	W_{tv} 76–100

aluminum hydroxides using sodium dithionite for iron reduction and citrate for complexion. Finally organic matter was destructed with hydrogen peroxide. A detailed description of the methods is given in [17].

From the purified samples the fraction <2 μm was obtained by sedimentation (Stokes Law). Thereafter the fraction <0.2 μm was obtained by centrifugation of <2 μm suspension.

All samples underwent the same pretreatment even if no or only some substances, that would prevent dispersion of the samples for grain size separation, were found.

2.3. Measurements

Before STA measurements, the samples were stored in a desiccator over a saturated solution of $Mg(NO_3)_2$ (53% r.h.) at a minimum of 24 h to ensure equilibrated samples with respect to their hydration capacity. The measurements were performed in a Netzsch STA 449C Jupiter linked with a QMS 430C Aëolos (Netzsch, IPI), and used software was Proteus Netzsch and Peak-Fit (Jandel Scientific Software).

Sample amounts of 100 mg were heated at a rate of 10 K/min from 30 to 1000 °C using Pt80Rh20 thermocouples and Pt80Rh20 crucibles with lids. As reference an empty crucible with lid was used. The oven gas was streaming with 70 ml/min [20 ml/min protective gas: N_2 (quality 4.8), and 50 ml/min purge gas: synthetic air (20.5% O_2 in N_2)]. These are convenient conditions for the detection of gases by mass spectrometry (MS) with the DSC/TG measurements [9].

The temperatures given in this study are peak temperatures.

2.4. Proportions of trans- and cis-vacant layers

For the calculation of the *cis*- and *trans*-vacant proportions the boundary of the peak temperature between *cis*- and *trans*-varieties was set at 600 °C [2] under the chosen experimental conditions. No sample displayed a peak maximum exactly at 600 °C. The tv and cv proportions were determined by fitting the MS curves of evolved water ($m/e = 18$) and the integration of the identified peaks. The ratio between the areas of the peaks reflects the ratio between tv and cv layers [2]. According to the general 50% rule the boarders were set at 25, 50 and 75% (Table 1). For example, a variety containing 75–100% cv layers will be marked cv. An increasing amount of tv layers (above 25 and up to 50%) is indicated by a combined attribute like cv/tv montmorillonite. Thereby the dominating layer type (>50%) is listed first.

Before measuring and calculating proportions of tv and cv layers for the selected smectites defined mixtures of a tv and a cv sample were prepared. The <2 μm fractions of Valdol (sample 26, 27) and Volclay (sample 25) were mixed in ratios of 100/0; 80/20; 60/40; 40/60; 20/80 and 0/100 (in percent with respect to dry weight obtained at 375 °C from STA) with a total sample mass of 100 mg. The proportions of tv and cv layers were calculated by fitting the MS curves for evolved water ($m/e = 18$). First, peak positions were identified and second peak areas were integrated. The integrated area is computed from the minimum X of the fitted data to the maximum X of the fitted data. While fitting a MS curve of a sample several peaks are possible. Best fitting results were obtained with three to five peaks. Concerning the theoretical occurring bonding types of the cations and to the hydroxyl groups in smectites, up to 20 peak positions are reasonable. However, the sum of peak areas with peak maxima below and above 600 °C is most important for the investigation. Fitting with Gauss area or Gauss amplitude yields most reasonable results. This procedure was preferred as most of the curves are symmetrical. To find the optimum peak positions below curves with a shoulder near 600 °C, a peak position different from that of the program proposed has been tested as well as crosscheck. For example, the program recommends a peak at 610 °C, the peak has been then displaced first to 580 °C and second to 630 °C and the fitting procedure has been repeated. The result for both trials was a peak at 610 °C. Table 2 lists the parameters for the fitting procedure.

Prior to the measurements of the mixtures of Valdol and Volclay PA-curves [22] were recorded for both samples. PA-curves reveal the dependence of the peak temperature of a decomposition reaction on the sample amount [22]. Sample amounts of 20, 40, 60, 80 and 100 mg were measured. The sample mass was

Table 2
Parameters for the fitting procedure

| Parameter	Procedure
Baseline	Second derivative zero
Smoothing	Savitsky Golay
Curve fit	Individual maxima
Function	Gauss combination of visual peaks and using the residual procedure (add residuals and vary widths, minimization of the difference between measured and calculated EGA of water)
Coefficient of determination	Curve of residuals must result in a Gauss function
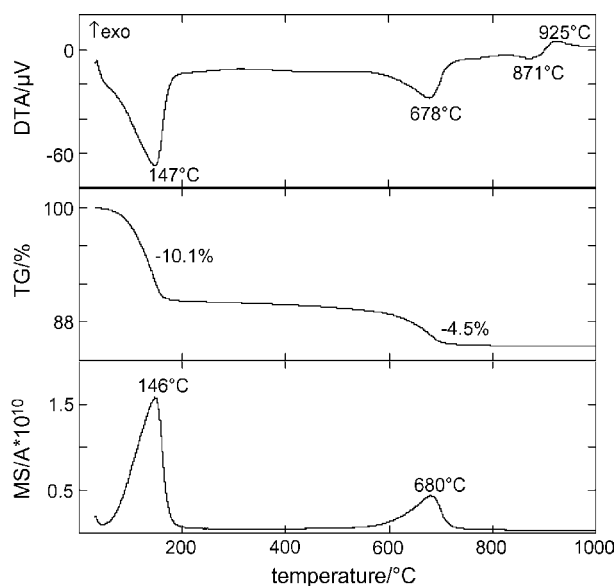
Fig. 3. Example for a cv smectite. Sample 2LP, <0.2 μm fraction. The lower curve displays the intensity of $m/e = 18$ for the evolved water.

corrected to the dry sample mass at 375 °C. At this temperature no hydration and no water evolved anymore.

3. Results and discussion

3.1. Thermal reactions of smectites

Figs. 3 and 4 present examples of the thermal reactions of mainly tv and cv montmorillonites. Both samples dehydrate at about 150 °C. The reaction is completed at 300 °C. Some of the purified <0.2 μm fraction samples displayed an exothermic reaction near 300 °C. Small amounts of CO_2 in MS curves (not shown) indicated organic matter, which was probably inherited from softener of plastic containers used during the purification of the smectites.
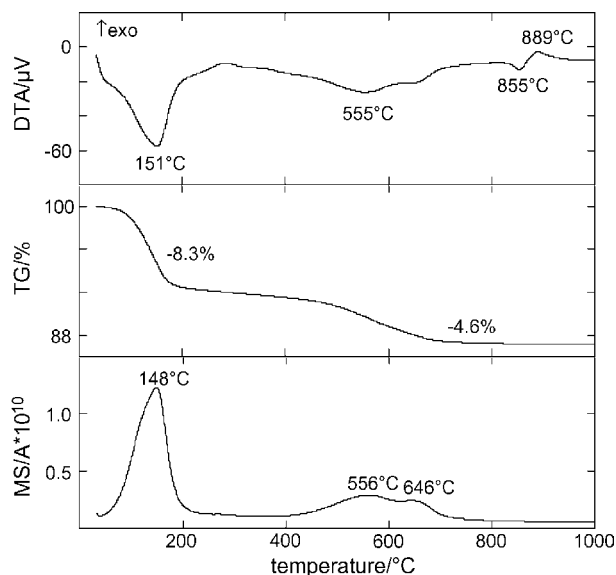

Fig. 4. Example for a tv smectite. Sample 41ValC18, <0.2 μm fraction. The lower curve displays the intensity of $m/e = 18$ for the evolved water.

In sample 2LP (Fig. 3), a *cis*-vacant variety, only two steps for mass loss due to dehydration and dehydroxylation are recorded whereas the *trans*-vacant sample 41ValC18 displays three distinct mass changes (Fig. 4). At about 600 °C the TG curve exhibits two levels of mass loss for the tv mineral with lower amounts of *cis*-vacancies. The dehydroxylation peak temperatures (T_{DHX}) determined from the DSC curve and MS curve for water ($m/e = 18$) showed a maximum difference of 2 K. Hence, the MS curves of evolved water were used within the region 300–900 °C to discriminate tv and cv types of the octahedral sheet.

In general, decomposition/recrystallization reactions were detected above 800 °C at varying temperatures. These reactions were not accompanied by further mass changes or release of gases.
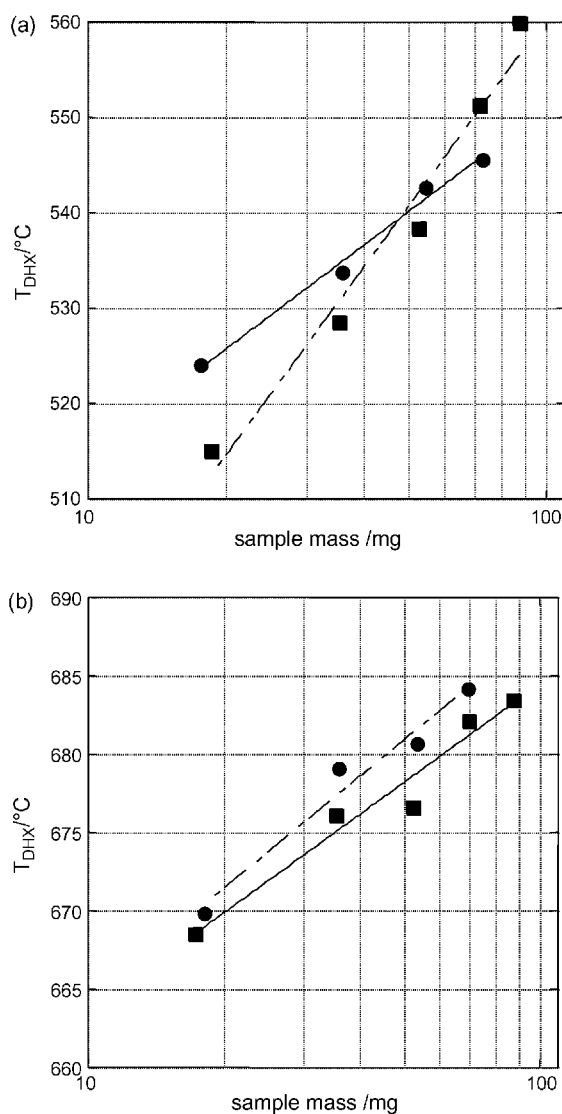

Fig. 5. PA-curves of T_{DHX} determined from MS curves of evolved water for tv 26/27ValdolC14 <2 μm fraction and cv 25Volclay <2 μm and mixtures of both. Pure samples and mixtures were measured after equilibration at 53% r.h. Sample weights were corrected to dry weight at 375 °C. (a) T_{DHX} of Valdol and (b) T_{DHX} of Volclay. (squares: pure samples, circles: sample in mixture).
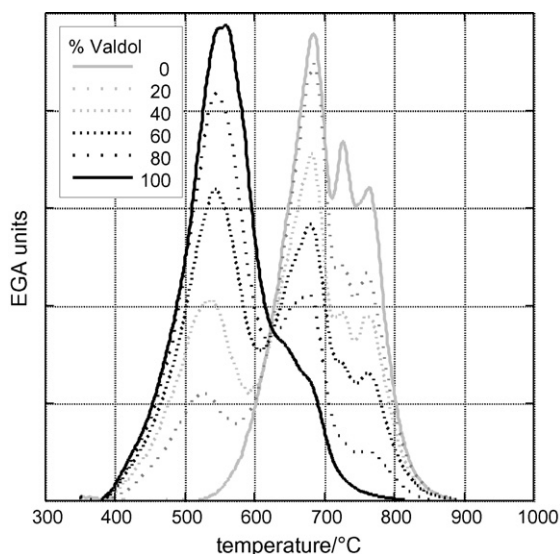
Fig. 6. MS curves of the evolved water during dehydroxylation of sample mixtures Valdol/Volclay.

Fig. 7. Calculated *cis*- and *trans*-vacant proportions of the Valdol/Volclay mixtures.

3.2. PA-curves and determination of proportions of tv and cv layers in mixtures of Valdol/Volclay

Fig. 5 shows that dehydroxylation temperatures of Valdol and Volclay decreased with lower sample amounts. This shift became less pronounced in the mixtures of Valdol and Volclay. Usually, mineral mixtures result in a different slope of the PA-curves for each component, reflecting the different peak temperature dependence on the amount of a mineral [22] in a certain matrix of other phases.

The different H_2O/OH content is also expected to influence the slope of the PA-curves because of the resulting partial pressure. As the amount of water in the clay minerals is nearly equal (mean difference of 0.8%) the PA-curves of the two smectites showed only small differences. In the mixtures the shift of the peak temperature occured only for small amounts.

The MS curves of evolved water ($m/e = 18$) during dehydroxylation of pure Valdol and Volclay as well as for their mixtures are presented in Fig. 6. The two samples have distinctly different dehydroxylation behavior. Valdol, the tv variety, dehydroxylates
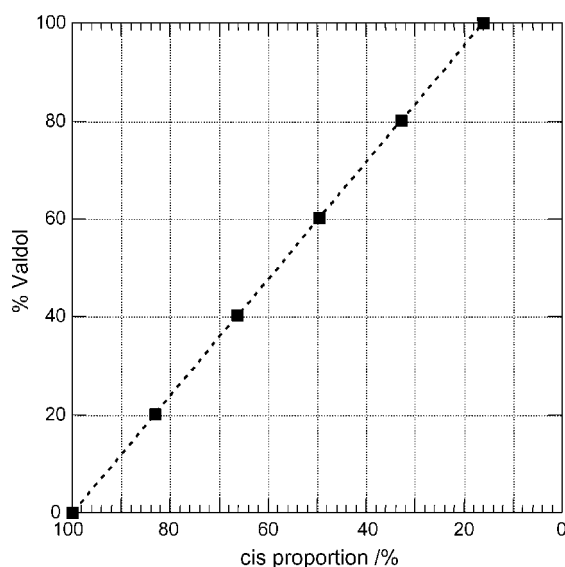
at 558 °C (100 mg). Some of the OH-groups are evolved above 600 °C. Hence, a cv proportion of 16% was calculated. With an increasing ratio Volclay/Valdol, the proportion of cv octahedral sheets increased. This is visualized by the height of the endothermic reactions due to the loss of hydroxyl groups at about 680 °C. Volclay reveals unusual peaks at 725 and 760 °C. Similar observations were made for samples 16GR01 and 17GR02. As these peaks were apparent only in the Na-saturated <2 μm and <0.2 μm fraction they are probably artifacts due to the pretreatment of the samples. Similar effects were reported for soda-activated bentonites [23]. Sodium might act as flux causing partial sintering and retardation of released hydroxyl groups. Trioctahedral domains are unlikely at these low contents of Mg in the octahedral sheet. In spite of this, Volclay can be regarded as pure cv variety. Even for small sample amounts peak temperatures below 600 °C were not detected for this smectite. The main endothermic reaction has its maximum at 684 °C (100 mg). Therefore, the limit of 600 °C is reliable.

Fig. 7 illustrates the relation between mass of Valdol/Volclay and calculated ratios of tv and cv layers. Calculating the theo-
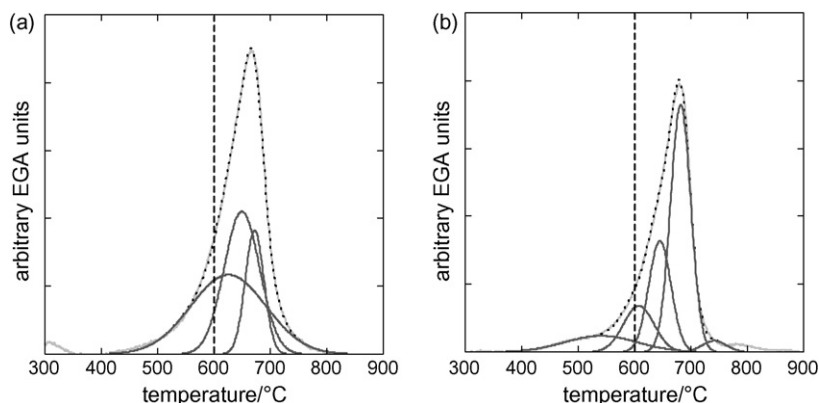

Fig. 8. MS curves of the evolved water during dehydroxylation of cv smectites. (a) Sample 8UAS < 0.2 μm with 100% cv parts. (b) Sample 2LP < 0.2 μm with 89% cv and 11% tv parts. Observed data: light grey; fitted curve: dotted black; fitted peaks: grey lines.

Table 3
Peak temperatures and integrated peak areas from fitted dehydroxylation MS curves ($m/e = 18$); proportions of *trans*-vacant (W_{tv}) and *cis*-vacant (W_{cv}) parts and classification

Sample (<0.2 μm)	Dehydroxylation peaks (°C) <600°C			>600°C					Peak areas (%) <600°C			>600°C					W_{tv} (%)	W_{cv} (%)	Classification
2LP[a]	541			608	645	682	742		11			14	24	49	2		11	89	cv
3 7th Mayo[a]	533			627	648				52			28	20				52	48	tv/cv
4JUP[b]	460	522		647	669				8	36		47	9				44	56	cv/tv
5MC[a]	563			640	663	728			52			36	9	3			52	48	tv/cv
6GPC[a]	533	575		660	707				54	28		14	4				82	18	tv
7EMC[a]				661	684	702						52	29	19			0	100	cv
8UAS[c]				626	650	672						45	38	17			0	100	cv
12TR02[a]	498	582		648	679	713			16	23		37	18	6			39	61	cv/tv
13TR02[c]	564			614	652	733	833		41			27	22	8	2		41	59	cv/tv
14TR03[c]	586			631	656	731	818		32			44	17	5	2		32	68	cv/tv
16GR01[c]				652	684	707	780	807				29	31	17	15	8	0	100	cv
17GR02[a]	509			628	669	703			5			22	25	48			5	95	cv
18UA01[a]	598			660	688	774			29			45	24	2			29	71	cv/tv
19UA02[a]	567			653	676	695	778		28			41	19	10	2		28	72	cv/tv
21D01[a]	530			639	665	731			44			44	10	2			44	56	cv/tv
24Beid[b]				642	673	699	795					32	37	25	6		0	100	cv
25 Volclay[d,a]				649	687	727	760					33	28	4	35		0	100	cv
26, 27 Valdol C14[d,a]	473	556		640	677				14	70		6	10				84	16	tv
28SB[a]	497	591		652	753				13	44		38	5				57	43	tv/cv
31BAR3[*]	552			620	655	712			40			33	22	5			40	60	cv/tv
32Volclay[a]				669	700	798						58	38	4			0	100	cv
33CA[a]	517			633	662				33			52	15				33	67	cv/tv
36M650[b]	494	522	561	641					28	17	29	26					74	26	tv/cv
37BB[a]	536	561		614					65	13		22					78	22	tv
38MW[a]	506	576		650	668				24	52		13	11				76	24	tv
39GQ_I[a]	538			629	662	734			24			48	22	6			24	76	cv
41ValC18[a]	549			655	711				80			16	4				80	20	tv
42Linden[a]	583			650	673				34			51	15				34	66	cv/tv

[a] 10–50% tetrahedral charge.
[b] 51–89% tetrahedral charge of the overall layer charge.
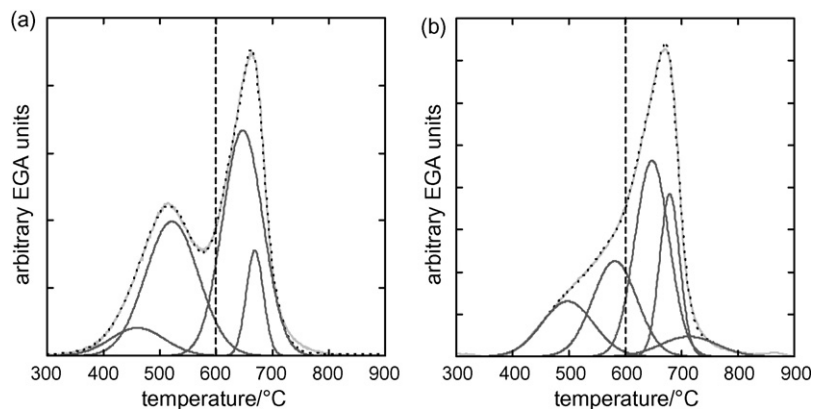[c] <10% tetrahedral charge.
[d] <2 μm.

Fig. 9. MS curves of the evolved water during dehydroxylation of cv/tv smectites. (a) Sample 4JUP <0.2 μm with 56% cv proportions. (b) Sample 12TR01 <0.2 μm with 61% cv proportions. Observed data: light grey; fitted curve: dotted black; fitted peaks: grey lines.
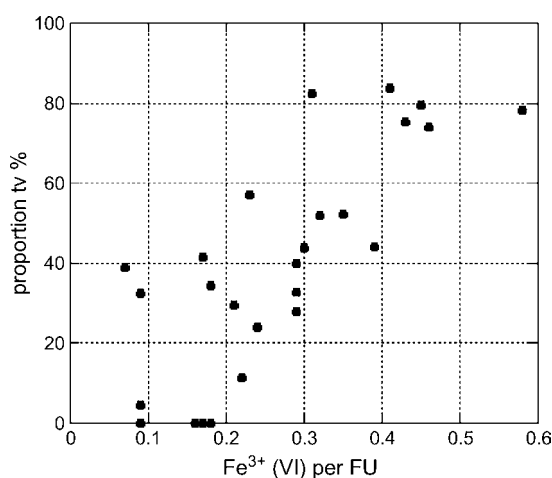

Fig. 10. Amount of tv layers vs. octahedral iron content.

retical *trans*- and *cis*-proportions of both components that can be expected from their content (related to their dry mass) in the mixture served as a crosscheck. The difference to the peak area calculation is smaller than 1%. The results described above indicate that STA is the tool to quantify tv/cv proportions in smectites.

3.3. The tv and cv character of natural smectites

A wide range of tv and cv proportions was detected for all investigated <0.2 μm fractions. The amounts of tv and cv octahedral sheets found by fitting the MS curves for evolved water ($m/e = 18$) and its integrated peak areas prove that pure cv samples (100% cv layers) can be found in nature (six out of nine cv samples). Other samples comprise small amounts of tv layers indicated by a peak broadening at lower temperatures (Fig. 8). In this sample collection most abundant were mixtures of *trans*- and *cis*-vacancies with dominating amounts of *cis*-vacancies (10 samples). Four samples are tv/cv varieties. Five samples can be classified as tv and none of them is pure tv (Table 3).

According to the proposed classification system (Table 1) examples for each group (cv, cv/tv, tv/cv and tv) with well and poorly resolved peaks are indicated (Figs. 8, 9, 11, 12). To determine quantitatively the relative proportions of the different layer types each sample was fitted until the coefficient of determination R^2 was better than 0.999. The cv/tv samples can be divided into two subgroups. Samples with well resolved peaks in the tv and cv region (Fig. 9a) and samples with a broad shoulder below 600 °C (Fig. 9b). For samples with a content of Fe > 0.3 mol/FU a distinct peak in the tv region was determined. With increasing amount of Fe, the proportions of the tv layers increased (Fig. 10).
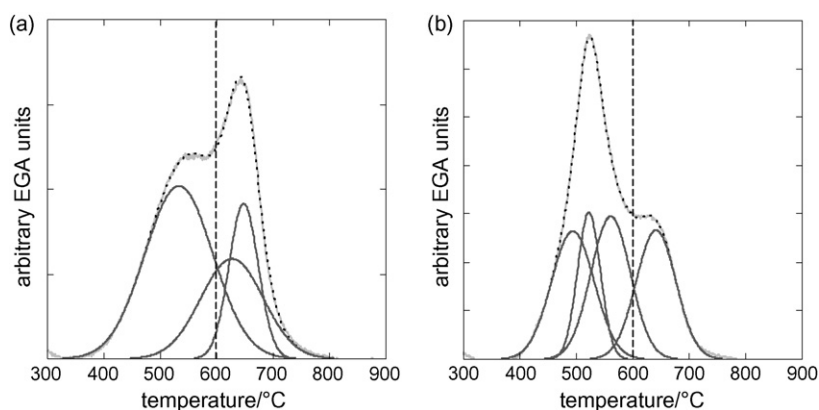

Fig. 11. MS curves of the evolved water during dehydroxylation of tv/cv smectites. (a) Sample 3 7th Mayo < 0.2 μm with 48% cv proportions. (b) Sample 36M650 < 0.2 μm with 26% cv proportions. Observed data: light grey; fitted curve: dotted black; fitted peaks: grey lines.
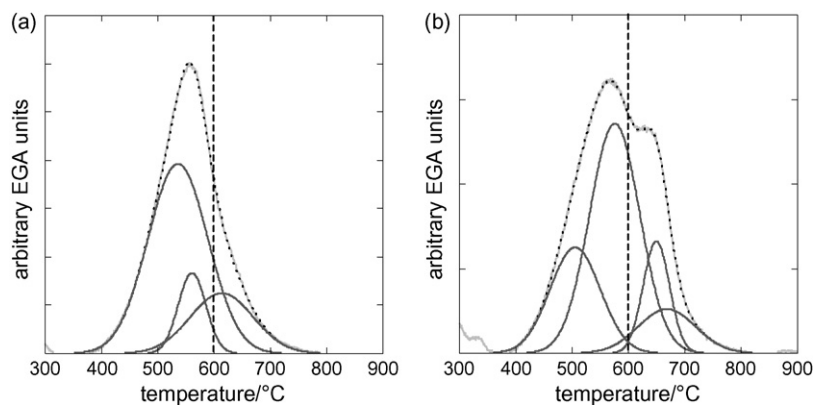
Fig. 12. MS curves of the evolved water during dehydroxylation of tv smectites. (a) Sample 37BB < 0.2 μm with 22% cv proportions. (b) Sample 38MW < 0.2 μm with 25% cv proportions. Observed data: light grey; fitted curve: dotted black; fitted peaks: grey lines.

Examples for tv/cv varieties are presented in Fig. 11. Varieties with a main peak in the region above 600 °C and a broad shoulder (Fig. 11a) at lower temperatures were found in this group. Continuous heating during STA measurements may lead to a broadened dehydroxylation peak and asymmetry [2,24]. This example illustrates that the cv proportions can be overestimated without fitting the dehydroxylation curves.

This can also be the reason for missing pure tv varieties. On the other hand, pure tv smectites should have at least 1.0 Fe mol/FU concerning a theoretical calculation of the chemical composition. In addition, the influence of Fe on the thermal stability of clay minerals has to be considered. Iron ions reduce the thermal stability of 2:1 clay minerals according to the reduced bond energy Mg–OH > Al–OH > Fe–OH [13]. Five samples can be assigned to tv varieties with minor cv proportions (Fig. 12).

Sample 37BB is the only one with a contribution to a peak in the 600 °C region indicated by a merely visible shoulder (Fig. 12a). The other samples of this group have two rather good resolved peaks like displayed for sample 38MW (Fig. 12b).

4. Conclusion

The data obtained confirm that STA is a powerful method to calculate the ratio of *cis*- and *trans*-vacancies in smectites by integrating MS curves of evolved water. Still uncertain is whether the *cis*- and *trans*-vacancies are varying within an octahedral sheet (clustering) or whether some kind of mixed layer minerals with alternating cv and tv layers developed.

Until now, STA is the best method to determine the structure of the octahedral sheet. Structural insight into the octahedral sheet cannot be obtained by XRD as smectites are turbostratically disordered so that the diagnostic ($h\,k\,l$)-reflections are absent.

Acknowledgements

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