

A new method for identifying Wyoming bentonite by ATR-FTIR

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Abstract

Bentonites are important for numerous industrial applications. The properties of bentonite vary depending on their genesis. Wyoming bentonites often behave in a special way with respect to industrial applications; therefore, these bentonites are of special economic interest.

Bentonites of different origin differ in their mineralogical composition, chemical composition of individual minerals, surface properties, rheology, and texture. However, the analysis of these parameters is time-consuming. The aim of this study is to propose an accurate and fast analytical tool for the differentiation of bentonite products of unknown origin, particularly of Wyoming bentonites.

For this purpose infrared spectroscopy with the attenuated total reflection (ATR) technique is used which allows the fast and reproducible measurement of IR bands of octahedral sheets of smectites. The extinctions and positions of these bands are quantified by fitting procedures. The attention was focused on the OH-bending region, where the position of the AlMgOH band and also the intensity ratio $I_{(\text{AlMgOH}/(\text{AlAlOH} + \text{AlFeOH} + \text{AlMgOH}))}$ proved to be characteristic for Wyoming bentonites.

In total 60 bentonites were analysed as standards with known origin, 13 of which are from Wyoming while the remaining 47 are from 19 other districts. To eliminate disturbing bands of typical admixtures (carbonates and illite/mica), which can influence the intensity and the position of the octahedral bands of smectites, each sample was treated with HCl and smectites were enriched by centrifugation.

Applying this fast pre-treatment procedure, the AlMgOH band occurs at significantly higher wave numbers (10 cm^{-1}) in Wyoming bentonites than in other bentonites.

In order to verify this technique, 41 products of unknown origin were analysed. Six were identified as Wyoming bentonites. Analysis of the ratio of exchangeable cations $\text{Na}/(\text{Ca} + \text{Mg} + \text{Na})$, which is specifically high for Wyoming bentonites, confirms the IR identification.

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1. Introduction

According to their origin and genesis bentonites differ in their properties which are important with respect to

application and price. For industrial purposes the origin of bentonites is of economic importance. The aim of this study is the development of a fast analytical tool to distinguish smectites with the special colloidal properties of Wyoming bentonites from other bentonites.

Infrared spectroscopy in combination with CEC proved to be suitable for fast and accurate identification

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of bentonites. Our own preliminary investigations showed that bentonites from different deposits show characteristic middle infrared absorption bands which differ in their intensity. This is particularly valid for absorption bands related to the octahedral sheet. In this study the potential of these differences for the prediction of bentonite origin is assessed.

A summary of fundamental stretching and bending vibrations due to OH for phyllosilicates was given by Farmer (1974). OH bending vibrations are observed at $\approx 920\text{ cm}^{-1}$ for AlAlOH , $\approx 880\text{ cm}^{-1}$ for AlFeOH and $\approx 850\text{ cm}^{-1}$ for AlMgOH in montmorillonites (Farmer, 1974). Madejová and Komadel (2005) give an overview about information available from IR spectra of fine fractions of bentonites. Most of the studies available concentrate on the OH stretching region (Madejová et al., 1994). Slonimskaya et al. (1986) quantified the OH-stretching vibrations in glauconites. An improvement of this approach was given by Besson and Drits (1997a,b) for dioctahedral fine-grained mica minerals. Gates (2005) gives a review about the chemistry of dioctahedral smectites and their infrared spectra. Accordingly, there are several reasons which might determine the exact location of octahedral bands and the shifts which appear in the spectra of the different samples: 1) local order–disorder, 2) isomorphic substitution of octahedral cation and, 3) mass and valence of OH-sharing cations.

A quantification of the OH-bending region by deconvolution and correlation to cation abundance derived from chemical analysis was made by Vantelon et al. (2001). They observed a strong tendency of octahedral cation ordering in Wyoming bentonites, whereas other bentonites showed random distributions.

The Wyoming bentonites' characteristic bands of the central cations of the octahedral sheet (916 cm^{-1} (AlAlOH), 885 cm^{-1} (AlFeOH), and 846 cm^{-1} (AlMgOH)) are located at the flank of the SiO -stretching band (1003 cm^{-1}) (Madejová and Komadel, 2001). Therefore, the correct choice of the range and procedure of baseline corrections is important as will be shown. Admixtures of other minerals, especially carbonates and micas, can influence the intensity and the position of the respective bands. High amounts of these impurities prevent a correct deconvolution. Therefore a pre-treatment is necessary to eliminate the interfering minerals.

In this study a procedure for the fast and reliable measurement of OH-bending bands as well as an assessment of this data for the prediction of bentonite origin is presented.

2. Materials and methods

2.1. Samples

In total 60 bentonites with known origin were analysed in this study, 13 of which are from Wyoming while the remaining 47 are from 19 other districts (Table 1).

Among these are industrial products, unprocessed raw materials, and CMS Source Clays (Costanzo and Guggenheim, 2001).

In addition 41 industrial products with unknown origin were analysed (MKE1-36 and MKR1-5).

2.2. Characterization of bentonites

In addition to the IR measurements a bentonite characterization was carried out for the possible identification of properties which are characteristic with respect to their origin. The following parameters were investigated for the 41 unknown bentonite products and 9 standard materials (Ceramosil, Deponit CA, Calcigel, Calzonit N, MKBGR01, Volclay SPV, Mont. 25, Mont. 26, WB 90): mineralogical composition (XRD), chemical composition (XRF), CEC, and exchangeable cations by Cu-triene (Kahr and Meier, 1996), the content of carbonates (modified Scheibler method, Klosa, 1994) swelling-volume, and pH-value of the suspension (ratio solid/water=1 g/10 ml).

2.3. FTIR spectroscopy

The ATR technique was used for infrared measurements. For each sample 32 scans were recorded in the $4000\text{--}400\text{ cm}^{-1}$ spectral range with a resolution of 2 cm^{-1} . The measurements were carried out using a Nexus FT-IR of Thermo Nicolet.

The range from $950\text{ to }750\text{ cm}^{-1}$ was selected for the fitting procedure. The baseline in this range was corrected by the automatic algorithm of OMNIC-software (Fig. 1).

The spectra were deconvoluted using the Peakfit software. According to Strens (1974) and Zviagina et al. (2004) a symmetric Gaussian function with position and width as variables was chosen for deconvoluting the OH bands. The fit quality was controlled by the r^2 value (>0.98). Fig. 2 shows the deconvoluted spectra of a Morocco and a Wyoming bentonite.

Subsequently, the relative intensity ratios of all OH-bending bands of smectite were calculated from the peak heights (e.g. $I_{\text{AlMgOH}}: \text{Mg}^{**} = (I_{\text{AlMgOH}} / (I_{\text{AlAlOH}} + I_{\text{AlFeOH}} + I_{\text{AlMgOH}})) \cdot 100$). Peak areas were not used because they showed three to six times larger scatter. The precision of fitted bandpositions warrants a decimal number.

2.4. HCl treatment and enrichment of smectites

In order to eliminate the influence of interfering minerals (carbonates and micas) which affect both the position and intensity of octahedral bands of smectites, carbonates were

Table 1
Origin and sample names of 60 standards

Country/region	Sample name (location)	Source	Number
Argentina	SK-IB-22	Raw material	
Argentina	SK-IB-23	Raw material	2
Cyprus	R4091	Raw material	1
Czech Republic	Ceramosil	Industrial product	1
Georgia, Asia	SK-IB-17	Raw material	1
Germany, Bavaria	BK	Raw material	
Germany, Bavaria	GOG	Raw material	
Germany, Bavaria	M	Raw material	
Germany, Bavaria	Deponit CA	Industrial product	
Germany, Bavaria	Calcigel	Industrial product	
Germany, Bavaria	OG	Raw material	
Germany, Bavaria	OP	Raw material	
Germany, Bavaria	RAB	Raw material	
Germany, Bavaria	RAN	Raw material	
Germany, Bavaria	RB	Raw material	
Germany, Bavaria	SK-IB-16	Raw material	11
Greece, Milos	Calzonit N	Industrial product	
Greece, Milos	SP4	Raw material	
Greece, Milos	UA	Raw material	
Greece, Milos	SK-IB-3	Raw material	
Greece, Milos	SK-IB-4	Raw material	
Greece, Milos	SK-IB-5	Raw material	
Greece, Milos	SK-IB-6	Raw material	
Greece, Milos	SK-IB-7	Raw material	8
Hungary	SK-IB-13	Raw material	
Hungary	SK-IB-14	Raw material	
Hungary	SK-IB-15	Raw material	3
India	SK-IB-10	Raw material	
India	SK-IB-11	Raw material	
India	SK-IB-12	Raw material	3
Italy, Sardinia	SK-IB-1	Raw material	
Italy, Sardinia	SK-IB-2	Raw material	2
Morocco	MKBGR01	Industrial product	
Morocco	SK-IB-21	Raw material	2
Slovakia	FE	Raw material	1
Spain, Almeria	SK-IB-18	Raw material	
Spain, Almeria	SK-IB-19	Raw material	2
USA, Arizona	Mont 23 (Chambers)	CMS source clay	1
USA, California	Mont 24 (Otay)	CMS source clay	1
USA, Kentucky	Metabent 42 (High Bridge)	CMS source clay	1
USA, Mississippi	Mont 20 (Polkville, Husband Mine)	CMS source clay	
USA, Mississippi	Mont. 22B (Amory)	CMS source clay	
USA, Mississippi	(Polkville, Christholm Mine)	CMS source clay	3
USA, New Mexico	Mont 30 (Santa Rica)	CMS source clay	1
USA, South Dakota	Mont 27 (Belle Fourche)	CMS source clay	1
USA, Virginia	Metabent 38 (Catawba)	CMS source clay	
USA, Virginia	Metabent 41 (Tazewell)	CMS source clay	2
USA, Wyoming	Volclay SPV	Industrial product	
USA, Wyoming	Mont. 25 (John C. Lane Track, Upton) VK	CMS source clay	
USA, Wyoming	Mont. 26 (Clay Spur)	CMS source clay	
USA, Wyoming	WB 90	Industrial product	
USA, Wyoming	MKBGR 10	Industrial product	
USA, Wyoming	MKBGR 11	Industrial product	
USA, Wyoming	MX80	Industrial product	
USA, Wyoming	MX80 KM2	Industrial product	
USA, Wyoming	SK-IB-20	Industrial product	
USA, Wyoming	SK-IB-8	Raw material	

(continued on next page)

Table 1 (continued)

Country/region	Sample name (location)	Source	Number
USA, Wyoming	SK-1B-9	Raw material	
USA, Wyoming	SWy-2 (Crook County)	CMS source clay	
USA, Wyoming	Mont. 25 (Upton)	CMS source clay	13

dissolved and smectites enriched. For this purpose four methods were tested. They are based on the following assumptions:

1. The intensity of the acid-treatment used does not or only insignificantly damage the structure of the smectites.
2. The upper layer in the centrifuge tube is representative for the smectites in the bulk bentonite.

2.5. Method 1

0.5 g of sample were weighed into an 85 ml polycarbonate tube and mixed with 10 ml 0.2 N HCl. After a reaction time of 5 min 5 ml of HCl were added to check, whether dissolution of carbonates was complete. Completion was assumed when no more bubbles were observed. After 5 min centrifugation the surplus HCl was decanted and the sample was washed twice using 20 ml 1 M NaCl-solution and centrifuged at 4000 rpm. Washing was repeated using deionised water until turbidity of the supernatant was reached. Finally, centrifugation was repeated at 4000 rpm for 30 min and the clear supernatant was decanted. The surface layer of the obtained sediment (light colour) was carefully scraped off with a spatula. This material was dried at 60 °C and homogenized in an agate mortar.

2.6. Method 2

Carbonates were dissolved by 0.2 N HCl. 20 ml HCl were added to 1.2 g of sample. After a reaction time of 5 min 5 ml

HCl were added again in order to control if carbonate dissolution was completed. The sample was washed twice by ca. 20 ml 1 M NaCl-solution and after that washed with deionised water until turbidity of the supernatant. Then, the <2 µm fraction was separated by triple centrifugation. The suspension was dried at 60 °C, and homogenised.

2.7. Method 3

According to Tributh and Lagaly (1986), first, the carbonates were dissolved by a sodiumacetate–acetic acid buffer and iron oxides were dissolved by a mixture of sodiumcitrate–sodiumhydrogencarbonate buffer and sodiumdithionite. Then XRD amorphous SiO₂ was removed by a 5% Na₂CO₃-solution at 100 °C. The <2 µm-fraction was separated by sedimentation (Atterberg-principal). One part of the samples was dried at 60 °C and the other one was freeze-dried.

2.8. Method 4

Method 3 was repeated using only the carbonate dissolution step. SiO₂ and iron oxides remained in the sample. Further treatments were identical to method 3.

2.9. Comparison of expenditure of time

Method 1 is the fastest method for purification and enrichment of smectites. The total time required for sample

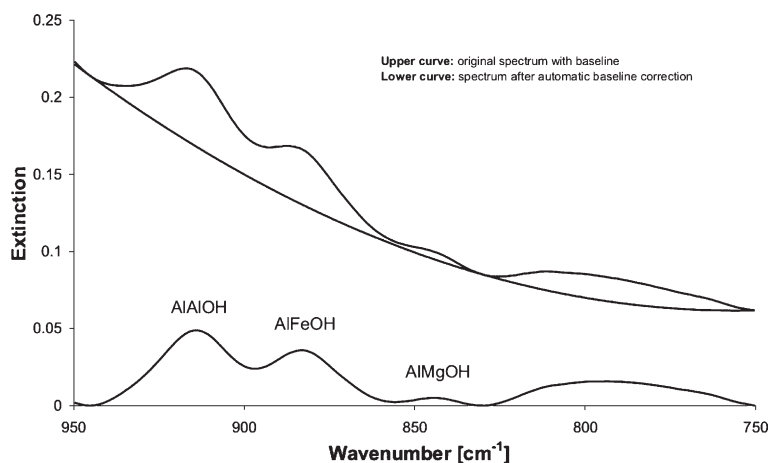


Fig. 1. Automatic baseline correction by OMNIC software for sample MKBGR01 (Morocco).

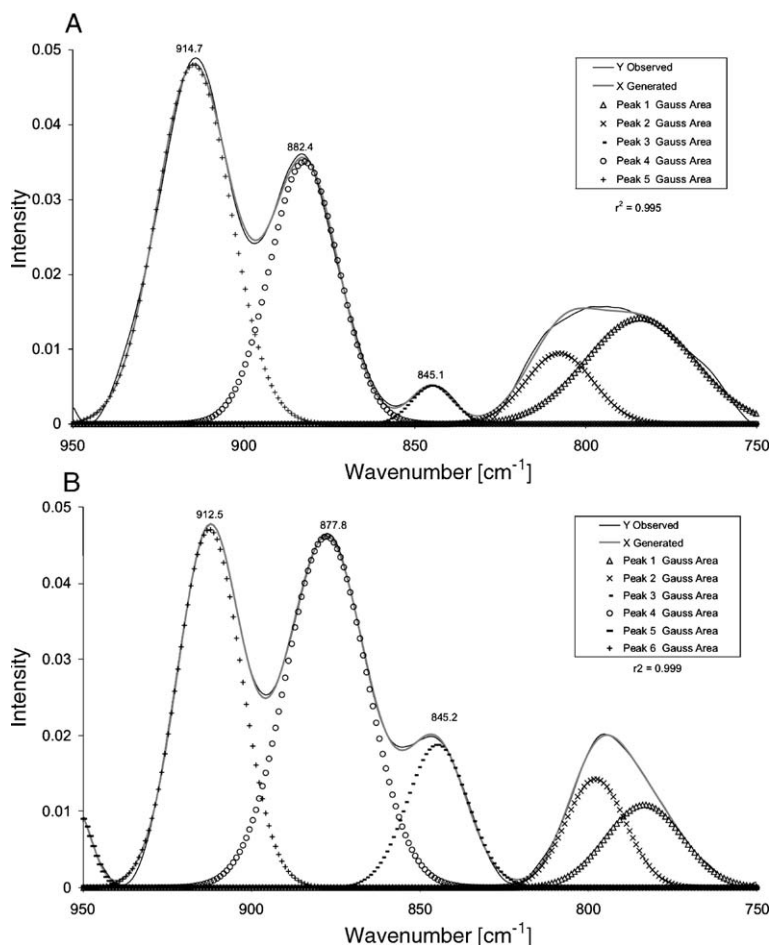


Fig. 2. A and B: Peak fitting results of the sample MKBGR01 (Morocco) (A) and Mont. 25 (Wyoming) (B).

pre-treatment according to method 1, ATR measurement, deconvolution, and interpretation is illustrated in Table 2 for different quantities of samples.

Comparing the ATR and KBr technique for IR measurements in the investigated range, the faster ATR-technique is advantageous.

The time required for method 2 is several days per sample because of centrifugation and drying.

Methods 3 and 4 (Tributh and Lagaly, 1986) are the most time consuming methods. These require several weeks because of the separation of the $<2 \mu\text{m}$ fraction by Atterberg, dialysis, and drying.

3. Results

3.1. Characterization of bentonites

XRD as well as XRF results did not provide information which was helpful for the identification of bentonite origin.

According to Grim and Güven (1978), Elzea and Murray (1990), Dohrmann (1997), and our own CEC analyses, the interlayer of Wyoming bentonites is occupied by at least 50% Na (mean value 69%, minimum 47%, Table 3). Lower values should therefore indicate a different origin (CEC-criterion). However, 23 of 41 bentonite products have $\text{Na} > 50\%$.

The swelling volume of all investigated Wyoming bentonites and of 12 bentonite products is $> 10 \text{ ml/g}$. The correlation between the swelling volume and the AlMgOH band position is not significant with $r^2 = 0.11$. Information about possible soda activation, which would influence the swelling volume, was not available, however.

The pH value is significantly determined by the presence of carbonates, particularly of Na_2CO_3 , which is frequently used for bentonite upgrading (alkaline activation). The pH values ranged between 6.5 and 10.0. Due to the missing information about the degree of

Table 2
Time required for several working steps for a different number of samples

Working steps	1 sample [min]	4 samples [min]	8 samples [min]	1–8 samples centrifugation [min]	1–8 samples drying [min]
Weighing of samples	2	8	16		
HCl-treatment	7	10	15	5	
2 × washing with NaCl	5	10	20	10	
2 × washing with H ₂ O	5	10	20	10	
Centrifugation				30	
Scrape off upper layer	5	20	40		
Drying (60 °C)					120
Scrape off and grinding	5	20	40		
ATR-measurement, deconvolution, interpretation	10	20	30		
Sum	37	90	165	55	120
Sum of working steps+centrifugation + drying [min]	212	265	340		
Hours	3.5	4.4	5.7		

Preparation (method 1), ATR-measurement, deconvolution, and interpretation.

alkaline activation as well as the non-characteristic occurrence of carbonates, pH does not provide unambiguous information about bentonite origin. Particularly high pH values indicate alkaline activation which in turn can explain high swelling volumes and/or a high amounts of exchangeable Na. In these cases the sum of exchangeable cations exceeds the CEC and the Na/(Na+Ca+Mg) parameter is not characteristic.

3.2. IR measurements

The reproducibility of the ATR measurements and the fitting routine was tested by 10 measurements of sample Mont. 25 representing 10 repeated preparations. For the AlMgOH band the mean position was

845.1 cm⁻¹ with a standard deviation of 0.2 (3σ), the mean intensity ratio was 15 with a standard deviation of 1.5 (3σ). To show the influence of baseline correction and peak fit operation on band positions of AlAlOH and AlMgOH, six samples with low Fe content were chosen. For the AlAlOH band an average decrease of 1.4 cm⁻¹ from 913.7 cm⁻¹ to 912.3 cm⁻¹ was calculated. For the AlMgOH band, the average difference was 2.2 cm⁻¹ from 839.8 cm⁻¹ to 837.6 cm⁻¹ (five samples). For unknown reasons, the band positions of the sixth sample could not be determined.

The variability of the IR band positions and intensity ratios is shown in Fig. 3 for the AlMgOH (Fig. 3A), AlFeOH (Fig. 3B) and AlAlOH bands (Fig. 3C) of naturally, non-calcareous bulk samples.

Table 3
Exchange cation population of Wyoming bentonites

Sample	Reference	Na ⁺ meq/100 g	Mg ²⁺ meq/100 g	Ca ²⁺ meq/100 g	Ratio Na/(Na+Mg+Ca)
B47	Dohrmann (1997)	59	6	26	0.64
B56	Dohrmann (1997)	76	4	8	0.87
VK25	Dohrmann (1997)	44	16	22	0.53
VK27	Dohrmann (1997)	68	14	22	0.66
1	Grim and Güven (1978)	85	16	6	0.79
2	Grim and Güven (1978)	66	5	22	0.71
3	Grim and Güven (1978)	94	10	95	0.47
4	Grim and Güven (1978)	67	14	12	0.72
5	Grim and Güven (1978)	106	17	25	0.72
6	Grim and Güven (1978)	70	5	22	0.72
7	Grim and Güven (1978)	67	14	12	0.72
Average	Elzea and Murray (1990)	106	7	21	0.79
Volclay SPV	Own measurements	66	6	31	0.65
Mont. 25	Own measurements	46	15	21	0.56
Mont. 26	Own measurements	66	8	6	0.83
WB 90	Own measurements	63	4	29	0.66
				Mean value	0.69

The AlMgOH band positions of Wyoming bentonites are up to 10 cm^{-1} higher than most of the other bentonites, which is not an artefact due to baseline

correction and fitting operation. This indicates that the AlMgOH band position could be used as a tool for the differentiation. Therefore, a field was defined based on

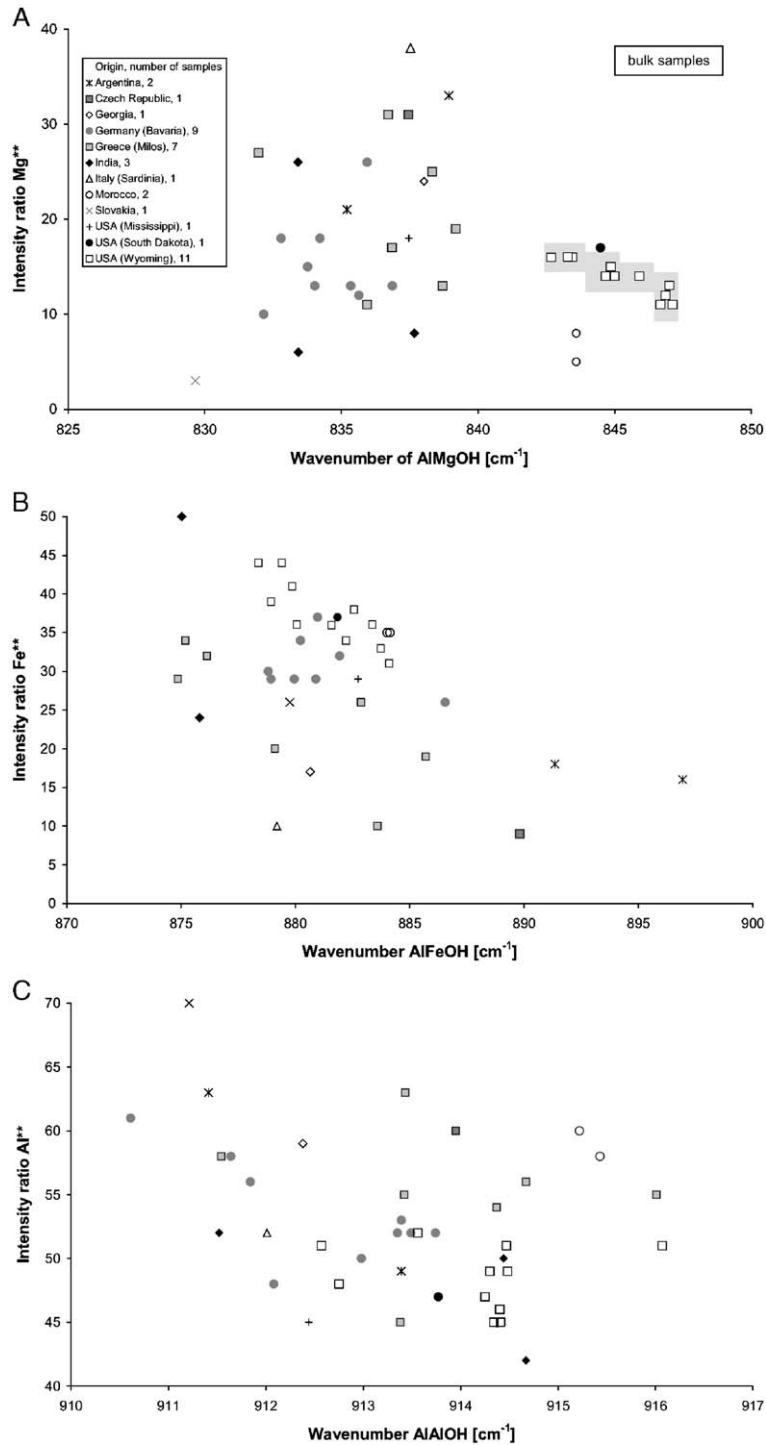


Fig. 3. A, B and C: Band positions versus intensity ratio of naturally non-calcareous bulk bentonites. A: AlMgOH-band, the grey field indicates the 3σ standard deviation of the measurement and fitting operation; B: AlFeOH-band; C: AlAlOH-band.

the data of Wyoming bentonites. The limitation of the grey field is based on 3σ standard deviation. One sample from South Dakota is occurring in this field which can be explained by its origin in the same geological environment. All other samples except for the Morocco bentonites are about 10 cm^{-1} lower than the Wyoming bentonites. The average position for Wyoming bentonites is 839.2 cm^{-1} and for the others it is 829.7 cm^{-1} . The band position of the two Morocco samples is close to that of the Wyoming bentonite at 843.6 cm^{-1} but the intensity ratios are much lower ($\text{Mg}^{**}=5$ and 8). Band positions and intensity ratios of AlFeOH (Fig. 3B) and AlAlOH (Fig. 3C) of Wyoming and other bentonites do not differ significantly. Particularly AlFeOH band positions of Bavarian and Morocco samples are overlapping with those of Wyoming.

3.3. Reproducibility of HCl treatment and smectite enrichment methods

3.3.1. Method 1

The reproducibility was investigated by 8 measurements of sample Calzonit N which was selected because it contains an appreciable amount of calcite. The mean value of the band position of AlMgOH is $839.7 \pm 0.5\text{ cm}^{-1}$ (3σ), the mean intensity ratio Mg^{**} is 8.4 ± 2.1 (3σ). Different reaction times (5, 10, 15, 30, 45 and 60 min) were used to find out if the acid completely dissolved carbonates. This was checked FTIR. The maximum absorption of calcite is at 1450 cm^{-1} , but a further calcite band at 875 cm^{-1} overlaps with the diagnostic OH bending region of smectites. Spectra of the sample SK-IB-15 (Fig. 4) after the acid treatment show the disappearance of the carbonate band at 1450 cm^{-1} , which indicates complete dissolution of the carbonate.

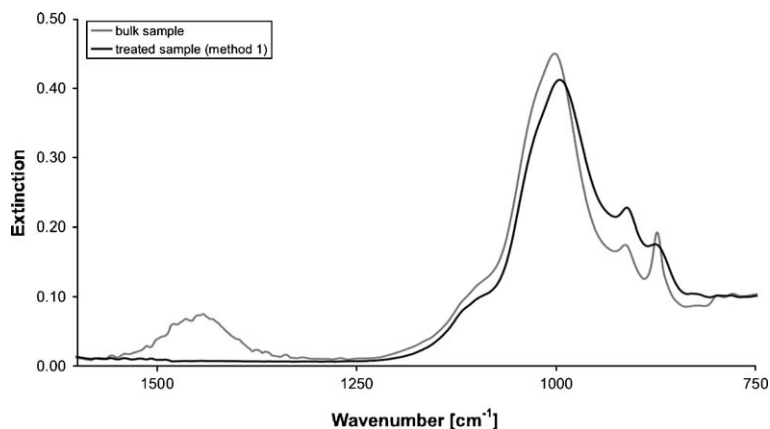


Fig. 4. Comparison of spectra (SK-IB-15) before and after treatment using method 1.

The AlMgOH band position is characteristic for each smectite, however independent on the starting position of the bulk sample and independent on the reaction time a shift of $2\text{--}4\text{ cm}^{-1}$ to higher wave numbers with a very low scattering was observed for each calcareous sample.

After 10 min no further changes of the IR spectrum could be found. Therefore, five minutes reaction time is considered as appropriate. Fig. 5 compares 11 spectra in the range 750 cm^{-1} to 950 cm^{-1} before (Fig. 5A) and after treatment (Fig. 5B). The samples from Hungary (SK-IB-13), and Arizona (Mont. 23) show a decrease of intensity of the band at 874 cm^{-1} due to carbonate dissolution. The decreasing quartz content is visible in the spectra of Hungary (SK-IB-13), India (SK-IB-10), and Wyoming (Mont. 25) SiO -bands at 798 cm^{-1} and 780 cm^{-1} .

3.3.2. Method 2

Five replicates of sample Calzonit N gave a mean band position of AlMgOH of $840.2 \pm 1.0\text{ cm}^{-1}$ (3σ) and an intensity ratio of 9.6 ± 2.4 (3σ).

3.3.3. Methods 3 and 4

In contrast to the bulk material samples that were pre-treated by methods 3 and 4 showed lower or equal intensity ratios Mg^{**} . The higher intensity ratio of the Calcigel is within the error range. The drying method does not to have an effect on the results of the IR measurements.

Table 4 compares band positions and intensity ratios for AlMgOH and AlFeOH for all methods.

After all four treatments, the average band positions of AlMgOH increased relative to positions of untreated samples, whereas the intensity ratios Mg^{**} decreased partly or remained constant. For the AlFeOH band a

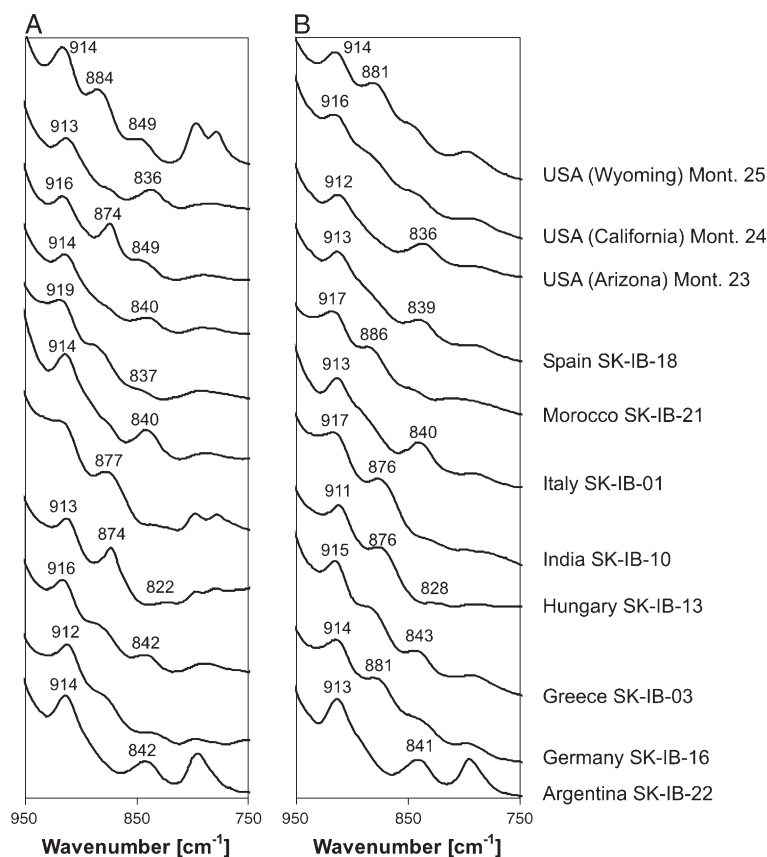


Fig. 5. A and B: Comparison of 11 different bentonites before (A) and after (B) treatment using method 1. Peak positions determined by OMNIC software.

decreasing band position and an increasing intensity ratio could be detected.

4. Discussion

4.1. Characterization of bentonites

Except for the CEC-analysis (CEC-criterion), the measured bentonite properties only provide limited information for the determination of the bentonite origin. However, it is well known that the trace element composition might be applicable. The amount of sample locations used for this study did not supply a sufficient base for a statistical evaluation of this method.

4.2. Removal of interfering minerals

The presence of carbonates results in an overestimation of the AlFeOH band intensity and a shift in position. Therefore, carbonates have to be removed.

Complete dissolution of carbonates does not significantly affect the positions and intensities of the smectite bands.

The presence of illite/muscovite results in a shift of the AlMgOH band towards lower wave numbers. Therefore, both minerals have to be removed, too. Centrifugation (method 2) resulted in a macroscopically visible enrichment of illite/muscovite in the $<2 \mu\text{m}$ fraction only in two samples out of four (Table 4). This method seems not suitable for the enrichment of smectite. Only method 1 proved suitable for the removal of illite/muscovite. To confirm this, the sample Calcigel was pre-treated according to method 1 and dried in the test tube. An enrichment of the micas on the bottom of the sediment was even macroscopically visible.

XRD results show that the coarse fraction (bottom) contains quartz, mica, and traces of chlorite, while the fine fraction (top) only contains smectite and a small amount of quartz. The infrared spectrum of the Calcigel sample shows that the coarse fraction contains a higher

Table 4
Comparison of the four different methods (M1–M4) for enrichment of smectite

Sample	Band position [cm^{-1}]						Intensity ratio					
	Initial	Average M1–M4	M1	M2	M3	M4	Initial	Average M1–M4	M1	M2	M3	M4
AlMgOH												
Calzonit N	838	839	840	841	838	837	12	10	8	9	12	10
Calcigel	831	832	834	828	832	832	7	8	8	9	8	7
Deponit CA	830	834	846	846	843	846	16	14	14	15	15	13
Volclay SPV	843	845	846	846	843	846	16	14	14	15	15	13
Average	836	837	838	836	838	838	11	10	9	10	11	10
Stab	5	5	5	8	4	5	4	3	3	2	3	2
AlFeOH												
Calzonit N	879	879	879	877	880	880	29	34	34	38	32	33
Deponit CA	879	877	877	877	877	878	29	33	34	33	32	31
Volclay SPV	884	880	878	879	883	879	33	37	37	38	34	38
Average	880	878	878	878	880	879	34	35	35	37	33	34
Stab	3	1	1	1	2	1	6	2	1	2	1	3

Stab=standard deviation

amount of quartz (798 cm^{-1} and 780 cm^{-1}) and a 6 cm^{-1} shift of the AlMgOH band to lower wave numbers compared to the fine fraction accounting.

At least the IR spectra gave no evidence that prolonged acid treatment ($>5 \text{ min}$) had damaged the clay minerals.

Summarizing, method 1 is particularly suitable for smectite enrichment. Additionally, this method is faster than the other ones. Therefore, this method was selected as the standard procedure for the sample pre-treatment of the 41 industrial products and the standards.

4.3. Application of the new method

4.3.1. Standard materials

After purification and enrichment of smectites by method 1 a shift to higher wave numbers was observed

resulting in a smaller “Wyoming-ATR-field” (width decreased from 5 to 3 cm^{-1}) (Fig. 6).

Compared to Fig. 3A AlMgOH-bands of smectites of Wyoming bentonites are in the range from 845.2 to 847.3 cm^{-1} with intensity ratios between 10 and 17. Their mean value of 846.0 cm^{-1} is on average 10 cm^{-1} higher than the positions of other smectites (mean value 136.2) except for the Morocco bentonites, which show the same position but a lower intensity ratio. One sample from Mississippi plots very near to the “Wyoming-ATR-field”. Both Morocco and Mississippi do not fulfill the CEC criterion (they contain less than 47% exchangeable Na).

Restriction of the method is the measurement of mixed bentonite samples. Using the peakfitting operation for determination of two band components the knowledge of the exact band positions of both

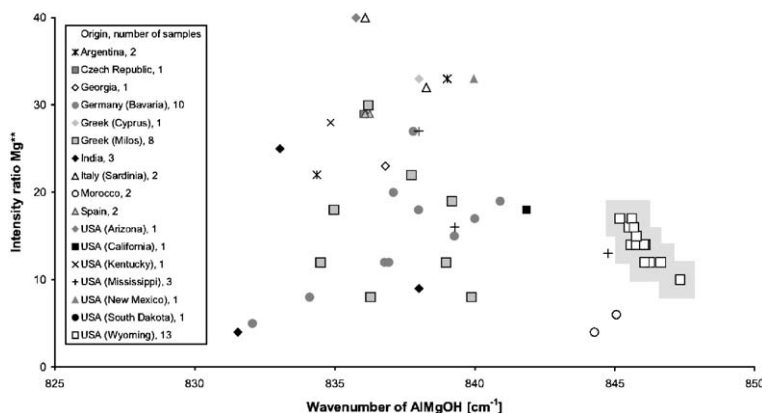


Fig. 6. Band position and intensity ratio of HCl treated and enriched smectites using method 1.

admixtures would be necessary. It is shown in the study that the band positions are quite variable. We conclude that a fitting procedure will not provide reliable information about the origin for mixed samples. It would also depend on the amounts of the admixtures. Theoretically, mixtures of a Wyoming smectite (band position AlMgOH at 847 cm^{-1} , CEC criterion 0.69) with, e.g. a Bavarian smectite (AlMgOH at 837 cm^{-1} , CEC criterion 0.02) would probably show the following if the position would shift in a linear way: Both criteria for Wyoming bentonite would be fulfilled for mixtures up to 20%, but above 30% the IR and above 40% both IR and CEC criteria would not be fulfilled.

4.4. Industrial bentonite products

Using the above procedure, the intensity ratio Mg** and the position of the AlMgOH band of 41 industrial bentonite products of unknown origin were measured. Five samples are within the “Wyoming-ATR-field” (Fig.

7A), one sample is close to this field. All other samples are clearly outside. Most likely, these samples do not originate from Wyoming.

The five samples of potential Wyoming bentonites lie also above the minimum sodium percentage of exchanged cations (dashed line in Fig. 7B). Furthermore, they plot around 0.69, which is the mean value for Wyoming bentonites.

Considering the CEC with 67% Na, it is likely that the sample close to the “Wyoming-ATR-field” also originates from Wyoming or is a mixture dominated by Wyoming bentonite. Finally, all six samples show swelling volumes $> 10\text{ ml/g}$.

5. Conclusions

After purification, a fast identification of Wyoming bentonites by FTIR in combination with the CEC criterion ($\text{Na} > 47\%$) is possible. The method is limited to non-activated bentonites. The new method can be

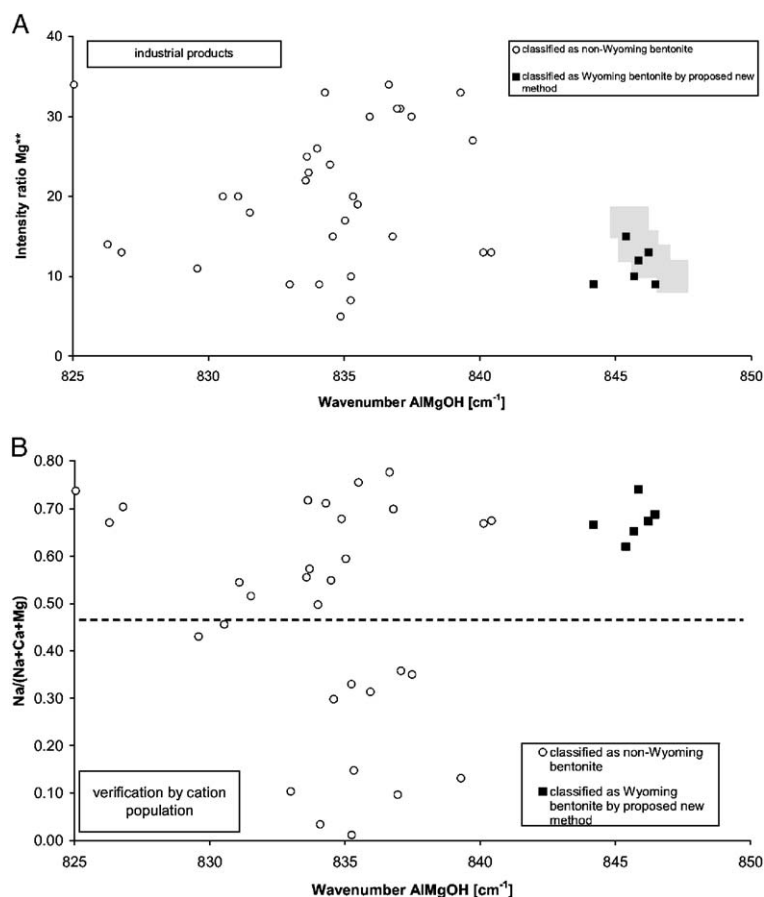


Fig. 7. A and B: A: band position and intensity ratio of 41 industrial products; B: band position and ratio of exchangeable cations of industrial bentonite products.

used for quality control in the bentonite industry. Other bentonite origins cannot be identified by this procedure. This approach will also fail for bentonites mixtures from different origins. Fast purification and enrichment procedures allow an identification within a few hours.

The AIMgOH band of Wyoming smectites occurs at significantly higher wave numbers (10 cm^{-1}) than in other bentonites. The reason for the shift is not yet clear but indicates the uniqueness of Wyoming smectites with regards to the octahedral sheet. Further investigations will concentrate on the quantification of IR bands and on a comparison with the chemical composition of the smectites and their layer charge.

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