VARIATION OF PREFERRED ORIENTATION IN ORIENTED CLAY MOUNTS AS A RESULT OF SAMPLE PREPARATION AND COMPOSITION

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Abstract—In X-ray diffraction (XRD) analysis, preparation of oriented clay specimens enhances their 00l reflections by arranging basal surfaces parallel to the specimen surface. In one-dimensional modeling of XRD intensities, degree of preferred orientation is one of the variable parameters and a user may choose different σ^* values for different minerals. The usual assumption is, however, that the layers of all clay minerals that are present exhibit a similar degree of preferred orientation to that of the clay mineral flakes parallel to the basal plane. If the orientation of individual clay minerals is significantly different, and if this is not taken into account, the relative proportions of the constituent minerals cannot be modeled accurately. The actual or so-called 'preferred' orientation is a potentially large source of error in any attempt at quantitative XRD analysis because it cannot be assumed to be constant among different minerals and may also vary as a result of pretreatment. In the present study the influence of sample composition and sample pretreatment on the degree of preferred orientation was determined using the parameter σ^*. A statistical parameter was calculated to determine and ensure the reproducibility of σ^* measurements. The most important result was that, when mixed together, clay minerals influence each other in terms of the degree of preferred orientation. Among individual samples, the degree of preferred orientation can be different for each clay mineral. The power of sonication used in sample pretreatment of a pure kaolinite and a pure illite had no significant influence on the degree of preferred orientation. The changes in intensities upon variation of the tilting angle (χ) allowed for calculation of σ^* of smectites in pure samples, in admixtures, and in samples treated in two different ways (air-dried and glycerol-intercalated), which is reported here for the first time. Smectites are very fine grained with flexible morphology which is believed to be the reason for their tendency to exhibit poor orientation ($\sigma^* = 22°$); further research is required to establish whether this is a general feature of smectites. After glycerol treatment a soil smectite showed a slightly better orientation compared to the air-dried pattern. The results of the study illustrate the difficulty of predicting changes in preferred orientation of clay mineral admixtures, even if non-platy minerals such as clay-sized quartz are added. In general, σ^* decreased when non-platy minerals were added, which is explained by changes in geometry of the specimen. Not all clay minerals, however, showed simultaneous changes in their orientation behavior.

Key Words—Clay Minerals, Oriented Mounts, Preferred Orientation, Quantitative Phase Analysis, Sigma*, XRD.

INTRODUCTION

The preparation of oriented aggregates is a routine step in XRD analysis of clay-sized phyllosilicates. The procedure enhances their 00l reflections by orienting the crystallites parallel to the specimen surface.

Preferred orientation is one of the controls on the powder ring distribution factor (ψ), which in turn is part of the basic quantitative diffraction equation. "The orientation of crystallites in a powder is such that a Gaussian form describes the frequency of tilt angles about the plane defined by the sample surface. The function is completely described by the standard deviation, σ^*" (Reynolds, 1986). In modeling codes for XRD patterns of oriented aggregates, σ^* is used to describe "preferred orientation" (Reynolds, 1985, 1989).

Typical modes for the preparation of oriented aggregates produce σ^* values from 4° to 30° (Moore and Reynolds, 1997). In general, the degree of preferred orientation is poor when the σ^* parameter is large. With decreasing degree of preferred orientation, diffraction intensity is reduced because the amount of clay platelets oriented at diffraction conditions decreases.

Knowledge of σ^* is, therefore, essential to any kind of quantitative analysis that depends on the intensities of XRD maxima (Reynolds, 1986). Determination of σ^* is tedious and requires the use of sophisticated equipment, which is the main reason why Moore and Reynolds (1997, page 313) suggested that users assume σ^* to be

the same for all minerals in their derivation of a working form of the basic diffraction equation for quantitative analysis. Empirical considerations led Reynolds (1986) to propose a default value of $\sigma^* = 12°$ for such instances where recorded diffraction intensities suggested preferred orientation to be good. However, peak "intensity of a reflection at moderate values of 2θ (~25°) is proportional to $(1/\sigma^*)^2$" (Reynolds, 1986), so the estimated limiting values for the reported σ^* range from 4° to 30° (Moore and Reynolds, 1997) will produce a 56-fold difference in basal or 00l intensities. This potentially large error was the key motivation for the investigation of the effects of sample preparation and sample composition (different clay minerals, pure and in mixtures) on the variability of σ^*. A number of authors (Taylor and Norrish, 1966; Lippmann, 1970; Zevin and Viaene, 1990) reported preferred orientation in kaolinite samples to vary between $\sigma^* = 8°$ and 29°, depending on the method of preparation of the oriented specimen. The aim of the present study was, therefore, to provide the reader with a reassessment of the relative importance of major preparation steps for their potential to either enhance or reduce preferred orientation. Three procedural steps were identified with a potential to influence the numerical value of σ^*.

(1) Type of mount

Reynolds (1986) found σ^* values of chlorite to vary between 4.3° if centrifuged onto a porous plate, 6.1° if prepared by the Millipore filter-glass transfer method, and 12.8° if prepared by suction through a porous plate. Today, glass-slide mounts (Whitton and Churchman, 1987; Schulze, 1994) constitute the most commonly used routine method, but are believed to suffer from particle segregation effects leading to a redistribution of coarse minerals toward the bottom and fine-grained minerals toward the top of the clay film. Mounting techniques employing porous ceramic tiles seem to be more convenient because suction is much faster, within minutes, and does not allow demixing, as observed for sedimentation on glass slides, which may have drying times of several hours to days. Smear mounts were not considered as it is inconceivable that the maximum tilt angles could be parallel to the specimen surface as the force is introduced from the side and not from the bottom.

(2) Ultrasonic dispersion

Suspensions with known sediment concentrations per volume of liquid are commonly prepared by resuspending known amounts of (e.g. freeze-) dried clay in a given volume of H_2O by means of sonication. The efficiency of particle dispersion has been shown to depend on the ultrasound energy applied (Amelung and Zech, 1999; Schmidt et al., 1999), and might thus affect the ability of particles to settle in an oriented manner once the suspension has been transferred to the mount.

(3) Interactions with other mineral phases

Finally, the possibility also exists that platelets differing in average size and morphology may affect one another's preferred orientation if present in the same sample.

The central objective of the present study was, therefore, to determine how σ^* varies as a result of (1) the amount of ultrasonic energy used for sample dispersion, (2) the type of mount (glass slide vs. ceramic tile), and (3) the presence of accompanying mineral phases.

MATERIALS AND METHODS

Sample selection and pretreatment

Orientation measurements were performed using diverse samples, representing (1) fractions of clay deposits which are predominantly monomineralic, (2) artificial admixtures of these fractions, and (3) soil-clay fractions (Table 1). The illitic mineral in this study was identified as an illite-smectite showing R3 order. The illite:smectite ratio was calculated as 85:15−90:10 using the Rietveld code BGMN (Bergmann et al., 1998). This code is flexible enough to implement a recursive treatment of stacking disorder (Ufer et al., 2008), similar to that of the simulation software DIFFaX (Treacy et al., 1991). A comparison of XRD pattern and X-ray fluorescence (XRF) analyses of this illitic material with four samples from Füzérradvány revealed that all samples originated from the same deposit. Minor traces of quartz and kaolinite of ~2 wt.% were found, the latter estimated using infrared (IR) spectroscopy. Sample pretreatment included removal of carbonates, Fe oxides, and organic matter according to the method proposed by Tributh and Lagaly (1986), followed by repeated separation of the <2 μm fraction, and drying in an oven at 60°C.

Ultrasonic sample dispersion

Resuspension of dried clay in 20 mL of deionized water was done in two different ways. Treatment 1 encompassed sonication for 3 min using an ultrasonic homogenizer (Bandelin UW2200 at ultrasonic energy of 33, 42, and 82 J mL^{-1}). This first procedure was performed for selected samples to find out if the dispersion energy had an influence on the degree of preferred orientation. Treatment 2 was performed for all other samples as a typical procedure in a clay laboratory and consisted of sonication in an ultrasonic bath, usually for 10 min. The resulting suspensions were then transferred to either glass slides or ceramic tiles.

Preparation of oriented mounts

To achieve the condition of 'infinite thickness,' 15 mg cm^{-2} clay was used to record an XRD scan up to a value of 32°2θ (Moore and Reynolds, 1997). An

Table 1. Description of the samples used (<2 μm fractions) and σ* values of individual clay minerals on ceramic slides. All patterns were recorded from air-dry specimens.

Sample no.	Composition	Reference	Illite σ* (º)	Kaolinite σ* (º)	Smectite σ* (º)
<2 μm fractions of samples from clay deposits					
I	Kaolinite (Lamar Pit)	Dohrmann (1997)	–	19	–
II	Illite (R3 ordered illite-rich, mixed-layer illite/ smectite)	Unknown locality (probably Füzérradvány)	14	–	–
III	Smectite (Volclay) Na$^+$	Rüping (2007)	–	–	21
IV	Smectite (Morocco) Ca^{2+}	Dohrmann (1997)	–	–	22
<2 μm fractions of soils					
Va	Braunerde-Pararendzina (soil): Na$^+$ exchanged, air-dry, contains mainly smectite, ~5 wt.% illite + traces of kaolinite, quartz, anatase (all <<5 wt.%)	Soil description (Jahn and Kunold, 1997); mineralogy (Rüping, 2007)	–	–	18
Vb	Identical to sample Va after addition of glycerol		–	–	17
Vc	Identical to sample Va but Ca^{2+}-exchanged, air-dry		–	–	19
VI	Fossil Gley-Braunerde (soil): (concentrations: smectite = illite >> kaolinite > quartz)	Soil description (Brosche *et al.*, 1998); mineralogy (Rüping, 2007)	12	12	16
Mixtures of <2 μm fractions of samples from clay deposits					
VII	Kaolinite(50)Na$^+$-smectite(50) (wt.%)		–	14	20
VIII	Illite(80)-kaolinite(20) (wt.%)		14	11	–
IX	Illite(50)-Na$^+$-smectite(50) (wt.%)		14	–	16
X	Illite(50)-kaolinite(20)-Na$^+$-smectite-(30) (wt.%)		14	10	13
XI	Illite(50)-kaolinite(20)-Ca^{2+}-smectite-(30) (wt.%)		14	16	19

aliquot of 1.5 mL of suspension was deposited on the circular (2.4 cm diameter) mounts. Repeated preparation was necessary to prevent peeling during drying; to avoid peeling, the glass slide was covered with a lid which kept the relative humidity high, though at the expense of long drying times. Drying time on glass slides varied from several hours to 2 days. The ceramic tiles were of identical diameter to the glass slides and were 3 mm thick. The suspension was filtered through the tile using a vacuum-filter apparatus. The suction time of the liquid varied between 1 and 30 minutes for the ceramic tiles; longer times were required for suspensions rich in expandable clay minerals.

Determination of preferred orientation (σ)*

X-ray diffraction was performed using a Seifert 3003 TT instrument configured with CuKα radiation, 250 mm goniometer radius, an open Eulerian cradle, and a position-sensitive MBraun detector, type PSD-50M (Figure 1). Unless indicated otherwise, scans were recorded using air-dried samples. A 0.2 mm primary beam collimator 135 mm long, with point focus, was installed to ensure that the illuminated area remained circular even at high χ angles. The variation of the diffracted integrated intensity, with changing χ, was recorded using the 'PSD Data Reduction' routine of the *ANALYZE* software (from Seifert). The samples were

rotated in increments of φ (phi) = 90º, while χ was varied in increments of 5º as long as the intensity of the platy minerals could be detected (up to 70º maximum). X-ray diffraction scans were obtained for every φ position, yielding a total of five scans (φ = 0º; 90º; 180º; 270º; 360º) per increment of χ. The five scans thus obtained overlap for a given χ angle and were added to yield a single scan per increment of χ. The counting time was 500 s per step, so that a typical pole figure was recorded within ~10 h. Quantification of peak intensity (area) was carried out for 001 and 002. Peak areas were obtained by integration of diffraction peaks after definition of left and right background. No correction of intensities to account for the geometric asymmetry was performed.

The pole figures were centrosymmetrical confirming the proposal by Taylor and Norrish (1966), which is important because it indicates that the platelets were oriented mainly parallel to the sample holder surface, and deviations can be described as being statistically tilted around this orientation.

The peak intensities at varying χ values followed a Gaussian-shaped curve. Such a function can be described by its standard deviation. Accordingly, the standard deviation of the tilt angles of the crystallites about the mean crystallite orientation yielded σ*. Test measurements showed that the intensities for negative χ values did not differ significantly
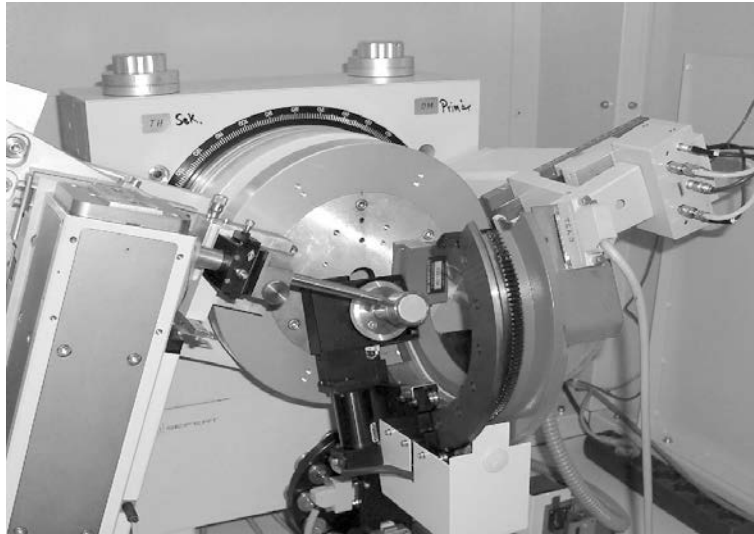
Figure 1. XRD configuration including point focus (CuKα radiation), 250 mm goniometer radius, primary beam collimator (0.2 mm), clay sample tilted at $\chi = 70°$ in an open Eulerian cradle, and a position-sensitive detector of MBraun, type PSD-50M.

from those for positive χ values (Figure 2). Because of this, only χ from 0° to 50°, and in the case of poorly oriented clay films, to 70°, was measured depending on the degree of preferred orientation.

Statistical parameters

The reproducibility of σ^* was estimated by the statistical parameter, S (Köster, 1979). S has the advantage that it does not depend on randomly distributed
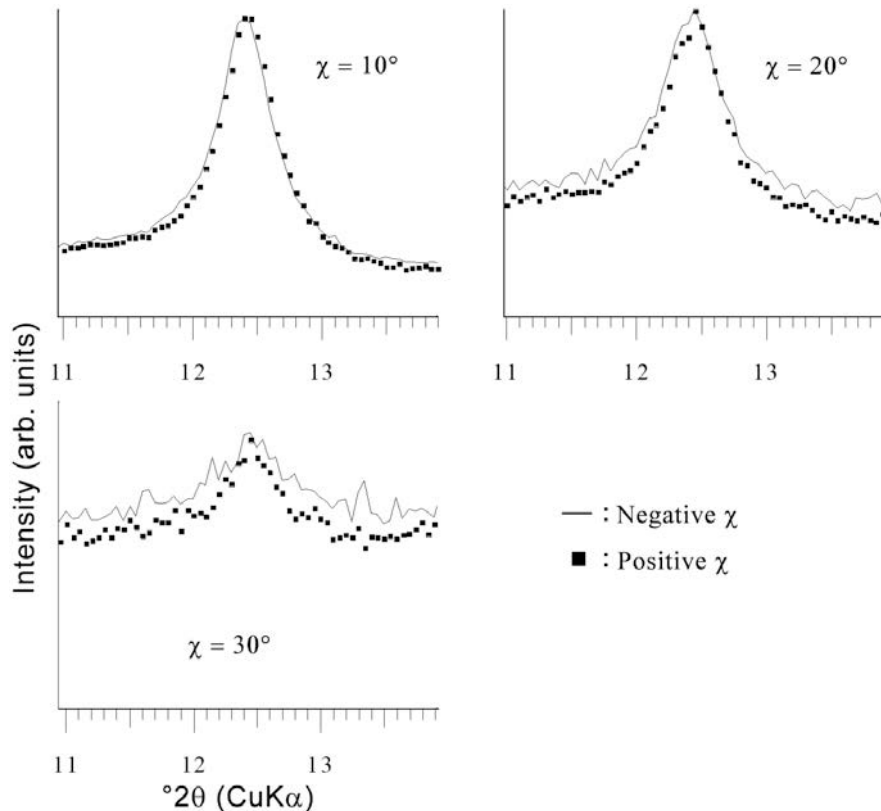

Figure 2. Congruence of the pole figures of kaolinite 001 obtained at $\varphi = 0°$ at different χ angles (±10°, ±20°, and ±30°).

differences resulting from the comparison of only one pair of data (duplicates). $S = ((\Sigma(X' - X'')^2)/2K)^{1/2}$ where X' and X'' are the 1st and 2nd measurements of duplicates, respectively. K = the number of similar objects. S, determined on paired data for a large set of similar samples (= similar objects), represents the standard deviation of the analytical procedure and can be applied to samples with similar properties.

RESULTS AND DISCUSSION

Preferred orientation of an expandable clay mineral compared to that of an illite

To the authors' knowledge, no other study has been reported on the XRD determination of preferred orientation of an expandable clay mineral mounted on a ceramic tile or a glass slide (with the samples air-dried and glycerol-intercalated). The XRD intensities of the Na^+ form of the fine fraction of a Wyoming bentonite material were found to be identical to the commonly shown patterns of oriented slides when $\chi = 0$, which represents the status with no tilting of the sample (Figure 3, lowest pattern). Tilting the specimen in the Eulerian cradle should cause a reduction in the recorded peak intensity because fewer crystallites are in preferred orientation. If the preferred orientation were perfect (*i.e.* no deviation from the parallel plane), the peak intensity should disappear quickly upon tilting the specimen by just a few degrees. The pattern of recorded intensities after the gradual tilting of the specimen (*i.e.* increasing the χ values, Figure 3) shows, however, that the
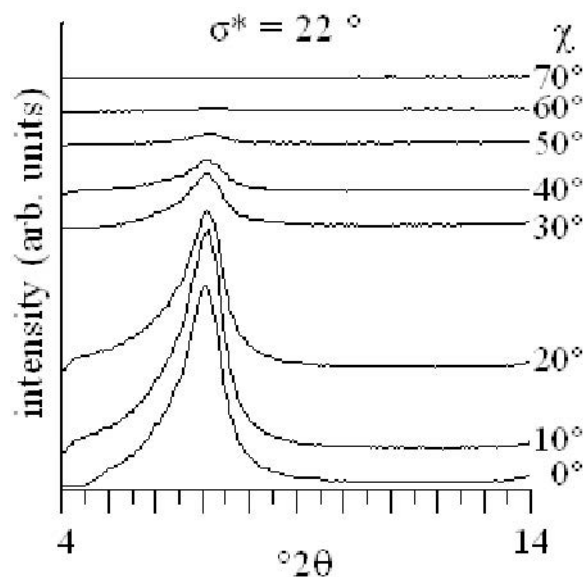

Figure 3. XRD intensity development with variation of χ of Na^+-smectite (Volclay, Wyoming bentonite, sample III) prepared on a ceramic tile.

preferred orientation was poor, because the 001 intensity was still visible at χ angles of 50°. The corresponding σ^* value was as much as 22°. Smectites are very fine-grained and frequently not planar (as observed using TEM, *e.g.* Fesharaki *et al.*, 2007), so these properties conceivably caused the small degree of preferred orientation observed in this oriented specimen.

A similar degree of preferred orientation ($\sigma^* = 18°$ and 19°) was observed for a soil smectite (Table 1, sample Va, Na^+ form and sample Vc, Ca^{2+} form, respectively). After treatment of the Na^+ form with glycerol (sample V6), the degree of preferred orientation increased slightly ($\sigma^* = 17°$), though the deviation was less than reproducibility. The illite used in this study had a significantly better degree of preferred orientation ($\sigma^* = 14°$) than the smectites.

Reproducibility of σ^* determination

The results of the σ^* determination of a clay mineral prepared on a suitable specimen have to be independent of the order of the 00*l* peak chosen. In addition, the reproducibility of the σ^* determination should be good enough to distinguish actual differences in preferred orientation between different minerals. To evaluate if the differentiation of preferred orientation between different minerals is possible with the proposed method, kaolinite and illite were prepared in nine replicate specimens on technically equivalent ceramic tiles and glass slides, respectively. The specimens were measured as described above and σ^* was determined for 001 and 002 (Table 2). For kaolinite the average σ^* value was 19.1° (001) and 18.6° (002) on ceramic tiles and 18.3° (001) and 17.7° (002) on glass slides, whereas it turned out to be 15.1° (001) and 14.1° (002) for illite on ceramic tiles and 14.2° (001) and 13.4° (002) on glass slides ($n = 9$ in all cases). Integration of the illite 001 intensity was hampered by the different background levels because the left background was greater than the right background of this peak. The σ^* of 002 peak was more reliable in this case. σ^* values were slightly larger for 001 reflections than for 002 reflections and this trend was independent of the sample substrate (glass slide or ceramic tile); these differences were much smaller than absolute differences between σ^* values of the different minerals, however.

The S parameter yielded 3 S = 2.0° and 2.2° (confidence level of 99.7%) for kaolinite and illite, respectively (Table 2). For simplicity, the reproducibility of σ^* determination was approximated as ±2°. In the present study, therefore, σ^* values are reported without decimal digits with the exception of the data in Table 2.

In soil-clay samples, some 00*l* peaks belonging to different minerals are seen to overlap in several places. In such cases often only one basal reflection can be analyzed. Reproducibility tests led to the conclusion that the σ^* determination was mainly independent of the 00*l* peak chosen, although background levels hampered use of the first-order peak of illite.

Table 2. Reproducibility of σ* determination. All patterns were recorded from air-dry specimens.

Kaolinite (sample I)	001 σ* (°)	002 σ* (°)	Illite (sample II)	001 σ* (°)	002 σ* (°)
Preparation on ceramic tile					
Preparation 1	19.7	20.2	Ppreparation 1	14.1	13.4
Preparation 2	20.0	18.8	Preparation 2	14.3	12.4
Preparation 3	19.4	18.4	Preparation 3	13.6	12.9
Preparation 4	19.0	18.4	Preparation 4	15.9	15.4
Preparation 5	15.8	17.4	Preparation 5	15.0	13.9
Preparation 6	19.0	18.0	Preparation 6	15.3	14.6
Preparation 7	19.0	17.7	Preparation 7	15.8	14.0
Preparation 8	19.4	19.2	Preparation 8	15.9	15.3
Preparation 9	21.0	19.6	Preparation 9	15.6	14.7
Average (ceramic, $n = 9$)	19.1	18.6	Average (ceramic, $n = 9$)	15.1	14.1
Preparation on glass slide					
Preparation 1	18.8	18.2	Preparation 1	15.0	13.2
Preparation 2	18.5	18.0	Preparation 2	14.0	12.8
Preparation 3	18.0	17.3	Preparation 3	14.1	12.9
Preparation 4	18.6	17.7	Preparation 4	14.3	14.0
Preparation 5	17.7	17.4	Preparation 5	14.2	13.7
Preparation 6	18.8	17.3	Preparation 6	14.9	13.9
Preparation 7	18.1	18.2	Preparation 7	13.8	13.2
Preparation 8	18.2	17.6	Preparation 8	14.0	13.4
Preparation 9	18.2	17.4	Preparation 9	13.7	13.4
Average (glass, $n = 9$)	18.3	17.7	Average (glass, $n = 9$)	14.2	13.4
$S = 0.66°$ (1σ), $3\,S = 2.0°$ (3σ)			$S = 0.73°$ (1σ), $3\,S = 2.2°$ (3σ)		

Influence of sonication on preferred orientation

To evaluate the effect of sonication on the preferred orientation of kaolinite (<2 μm, sample I) and illite (<2 μm, sample II), the samples were subjected to different ultrasonic pretreatments. After preparation on ceramic tiles and glass slides, the 001 and 002 reflections of kaolinite and illite were measured and averaged for the calculation of σ* (Table 3).

The σ* values of illite and kaolinite at different ultrasonic treatments were practically identical for the three ultrasonic steps and varied between 14−15° and 18−19°, respectively. These variations of the individual

minerals were too small to be identified as real differences. The energy employed to disperse the clay particles was, therefore, apparently unrelated to the preferred orientation. Secondly, a small tendency was noted for the preferred orientation of the clay minerals to be slightly better on glass slides than on ceramic tiles.

Influence of artificial mixing on preferred orientation

A pronounced difference was observed between the σ* value of pure kaolinite (σ* = 19°) and that for the same kaolinite in a mixture (σ* = 11°) of 80 wt.% illite (sample II) and 20 wt.% kaolinite (sample I). Due to the presence of the illite mineral, the kaolinite showed an enhanced preferred orientation. Scanning electron microscopy (SEM) images illustrate the XRD results. The SEM images (Figure 4) show a horizontal view of the deliberately broken ceramic tile, exposing the clay films of the illite/kaolinite mixture and the pure kaolinite standard.

In the illite(80)-kaolinite(20) mixture, an explicit parallel texture was visible (Figure 4a). Parts of the ceramic tile could be identified at the bottom of the image. The clay film of the kaolinite standard (Figure 4b) appeared massive and flocculated and ~2−3 times thicker than the clay film of the illite(80)-kaolinite(20) mixture (Figure 4a) although both were prepared using the same concentration of dispersed colloidal clay. Figure 4c shows in detail part of

Table 3. σ* values of illite, kaolinite, and illite/kaolinite mixture on glass and ceramic slides. All patterns were recorded from air-dry specimens.

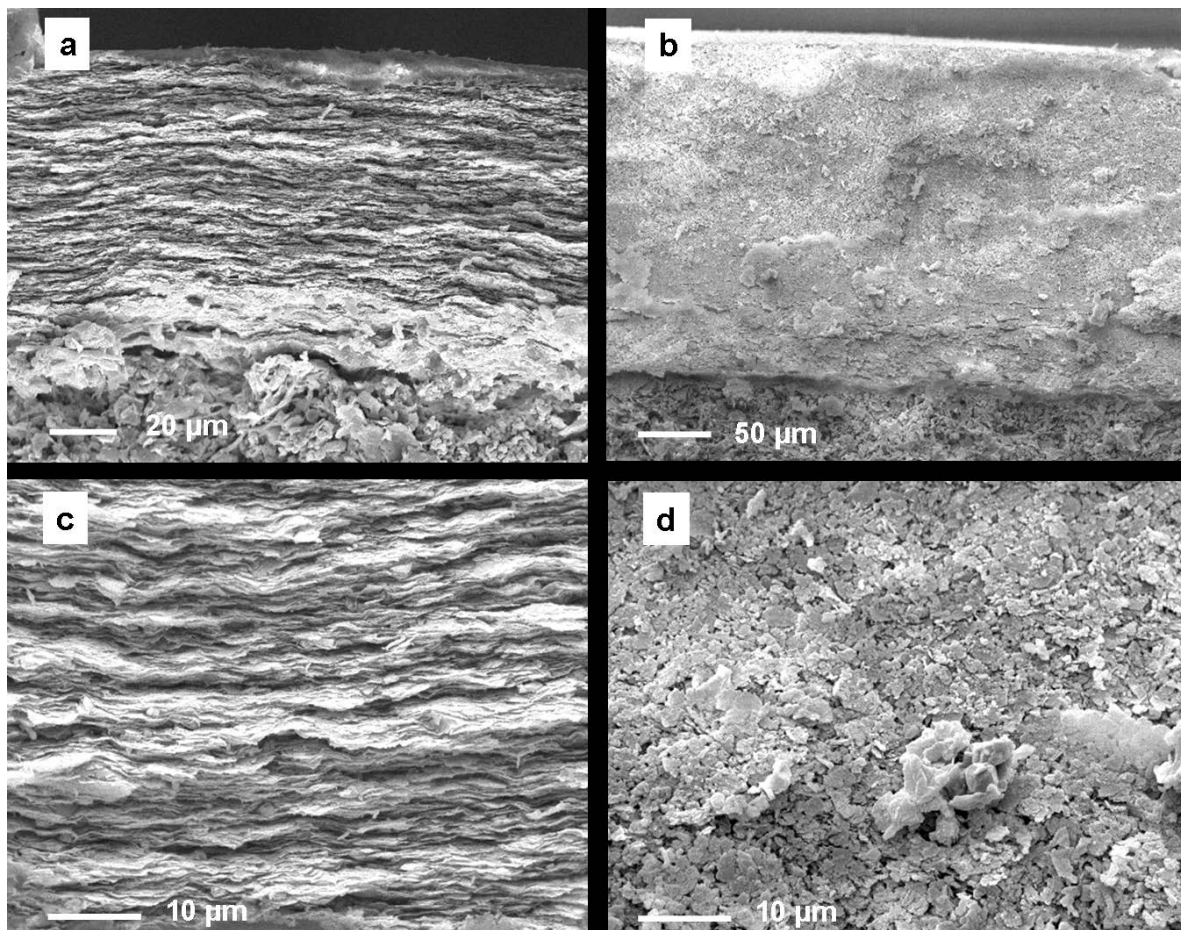| Preparation | Ultrasonic treatments | | |
	32 J s^{-1} σ* (°)	47 J s^{-1} σ* (°)	82 J s^{-1} σ* (°)
Illite (sample II)			
Glass slide	14	14	14
Ceramic tile	14	15	15
Kaolinite (sample I)			
Glass slide	18	18	18
Ceramic tile	19	19	19

Figure 4. Side view of broken specimen showing the clay films observed using SEM: (a, c) illite/kaolinite mixture; and (b, d) pure kaolinite. In the lower part of (a) and (b) the substrate (ceramic tile) is visible.

Figure 4a and emphasizes the good preferred orientation of the clay minerals in the illite(80)-kaolinite(20) mixture, whereas the amplified image (Figure 4d) confirms the more random orientation of the kaolinite mineral.

The XRD and SEM results showed that the clay minerals illite and kaolinite did not have the same degree of preferred orientation when they were mixed together. When mixed with illite, kaolinite achieved better orientation compared to its orientation as a pure phase. This means that phyllosilicate clay minerals influenced each others' orientation in mixtures.

Experimental results of σ^* measurements of pure illite, kaolinite, smectite, and their admixtures revealed that artificial mixing had a strong influence on the preferred orientation of the individual clay minerals (Table 1). The illite (50−80 wt.%) had the same degree of preferred orientation when occurring as pure material and when present in a mixture. In three admixtures with 20 wt.% of kaolinite each, kaolinite showed an enhanced preferred orientation in the presence of other clay minerals when compared to the pure standard material

($\sigma^* = 10-16°$ instead of $19°$). At a 50:50 ratio of kaolinite:smectite, the preferred orientation of the kaolinite increased from $\sigma^* = 19°$ to $14°$. This is remarkable because the Na^+ smectite (Volclay) itself had nearly the same relatively poor preferred orientation when examined as a pure mineral ($\sigma^* = 21°$) and in the mixture with kaolinite ($\sigma^* = 20°$). The σ^* value of the Na^+-smectite (Volclay) studied decreased further to $16°$ when mixed with illite (50:50), and even more, to $13°$, upon addition of both minerals simultaneously (illite(50)-smectite(30)-kaolinite(20)). When exchanging the Na^+-smectite in that last mixture for a Ca^{2+}-smectite (Morocco), the preferred orientation of the illite remained unchanged though the preferred orientation of smectite ($19°$) and of kaolinite (from $10°$ to $16°$) deteriorated compared to the mixture containing the Na^+-smectite. In colloid chemistry Me^{2+} cations are well known to cause flocculation of clay suspensions, which of course affects the quality of preferred orientation. This requires further study.

In all artificial mixtures using the four clay fractions tested, the illite always had the same degree of preferred

orientation. The question arises if this phenomenon might indicate the existence of a 'material constant' property typical for at least this particular illite. To test this hypothesis, several pure clay fractions and admixtures of these clay fractions (Table 1, samples I−IV) were mixed with quartz (<2 μm) which was separated in the same way as the clay minerals (clay size of quartz grains confirmed by SEM).

Development of the degree of preferred orientation upon stepwise addition of 2, 5, and 10 wt.% of quartz (<2 μm) to the monomineralic fractions (Figure 5a) showed no pronounced change in σ*. Only after addition of 10 wt.% of quartz did the σ* value of the illite increase from 14º to 17º.

A change in the degree of preferred orientation was observed for kaolinite in the illite(80)-kaolinite(20) mixture (Figure 5b), where σ* increased slightly from 11º to 12−13º after addition of 1−20 wt.% quartz, and then strongly to 18º after addition of 50 wt.% quartz. The σ* value of illite remained unchanged (in the range of the analytical error) as long as 20 wt.% or less quartz was added. The σ* value increased, however, from 14º to 18º when 50 wt.% quartz was added. Such large quartz concentrations are unrealistic for clay separates though the experiments were helpful in showing the principle of geometrical influence (here the addition of non-platy minerals) on the degree of preferred orientation.

In the artificial mixture illite(50)-kaolinite(20)-Na+-smectite(30) (Figure 5c) the trend was clearly toward decreasing degree of preferred orientation with increasing addition of quartz. In general, the σ* values of all

clay minerals increased, though the increase was not simultaneous for all minerals. Once a few wt.% of quartz was added, σ* increased for kaolinite and smectite. This orientation was more or less unchanged until as much as 20 wt.% and 50 wt.%, respectively, of quartz was added. The σ* development of illite in the same specimen was different. Here the first increase in σ* could be recorded for the addition of 5 wt.% of quartz (no changes for 1 and 2 wt.%) followed by a continuous increase with every quartz addition.

When the same series of experiments was performed and only the type of smectite (Ca^{2+}-smectite from Morocco, illite(50)-kaolinite(20)-Ca^{2+}-smectite(30) mixture, Figure 5d) was varied, the trend was completely different from that in Figure 5c. As soon as >1 wt.% of quartz was added, the degree of preferred orientation increased markedly, a phenomenon which cannot be explained by typical geometrical considerations. σ* of kaolinite and Ca^{2+}-smectite increased again and reached the starting values after the largest amount of quartz (50 wt.%) was added. The starting values of σ* (14º) were exceeded only for the illite, and only after the largest amount of quartz (50%) was added (16º).

Variation of preferred orientation in soil clay

The orientation of individual clay minerals was shown to vary in artificial admixtures. The question arises whether this is transferable to real samples, e.g. clay fractions from soils. Therefore, a soil clay-fraction with three different clay minerals was studied (sample VI, Table 1). The orientation of smectite (σ* = 16º) in
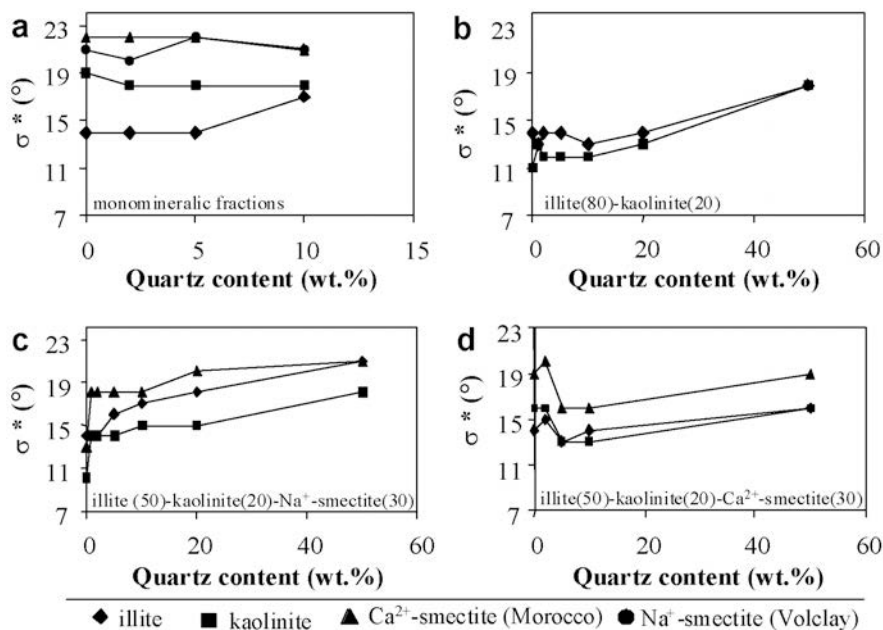

Figure 5. Development of the degree of preferred orientation upon addition of quartz (<2 μm) to (a) monomineralic fractions, (b) an illite(80)-kaolinite(20) mixture, (c) an illite(50)-kaolinite(20)-Na+-smectite(30) mixture, and (d) an illite(50)-kaolinite(20)-Ca^{2+}-smectite(30) mixture.

this sample showed pronounced differences from the orientation of illite and kaolinite (both $\sigma^* = 12º$), although smectite and illite were present in approximately equal amounts.

CONCLUSIONS

The results clearly showed that clay minerals have different degrees of preferred orientation when present as pure minerals compared to being part of an artificial mixture. Kaolinite and smectite achieved better preferred orientation when mixed with other clay minerals, particularly with illite, than as a single phase. The conclusion from these results is that the clay minerals influenced each other in terms of their orientation in mixtures. These influences were also detectable when non-clay minerals such as quartz (<2 μm) were present. Not all clay minerals showed the same change in orientation, or at the same rate, when different amounts of quartz were added. This complicates any attempts to predict the degree of preferred orientation for quantitative XRD analysis of oriented specimens.

Only a few pure clay minerals were studied, but the results are probably transferable to clay minerals from other localities because they will all differ in size and particle geometry. In the case of smectites and expandable mixed layers the cation population is also believed to play an important role. A significant result of this study is the observation that the assumption of some 'rule of thumb' value for σ^* in quantitative XRD analyses of oriented specimens of soils, as has been a standard laboratory practice for decades, appears to constitute a major analytical flaw. More research is necessary to reconcile these findings into robust and practical protocols for the quantification of phyllosilicate minerals in soils and sediments.

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