

Mixed-layer kaolinite-illite-vermiculite in North Sea shales

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ABSTRACT: The finest fractions of Upper Jurassic shales from the North Sea and onshore Denmark contain 80–90% of an illite-smectite-vermiculite (I-S-V) mixed-layer mineral and, in addition a phase which has X-ray diffraction (XRD) peaks at 7.20–7.26 Å and 3.56–3.58 Å in air-dried and glycolated specimens. This phase may be a fine kaolinite with a small thickness of coherent scattering domains (CSDs) or alternatively a mixed-layer mineral which has kaolinite as the dominant component. For one sample from the Norwegian well 9/4-3, these alternatives are investigated using the multi-specimen method by which agreement between the experimental pattern and the pattern calculated for one and the same structure is obtained for each of several specimens saturated with different cations and with/without glycolation. It is demonstrated that the modelled XRD patterns for a kaolinite-illite-vermiculite (K-I-V) structure having 0.94 kaolinite, 0.03 illite and 0.03 vermiculite layers and random alternation fit the experimental patterns.

Mixed-layer kaolinite-smectite (K-S) is very common in nature and occurs in different geological environments (Sudo & Hayashi, 1956; Shimoyama *et al.*, 1966; Schultz *et al.*, 1971; Wiewiora, 1971; Sakharov & Drits, 1973; Bogolyubova *et al.*, 1974; Djakonov & Kulikov, 1975; Drits & Sakharov, 1976; Brindley *et al.*, 1983; Hughes *et al.*, 1987). Structural and X-ray diffraction (XRD) characteristics of K-S determined by simulation of XRD patterns have been described by Wiewiora (1971), Cradwick & Wilson (1972), Sakharov & Drits (1973), Drits & Sakharov (1976), Reynolds (1980) and Drits & Tchoubar (1990). Furthermore, Drits & Sakharov (1976) calculated XRD patterns for mixed-layer kaolinite-illite-smectite (K-I-S) and demonstrated that a series of kaolinitic mixed-layers from the Yucatan in Mexico were actually K-I-S. Most of the well-documented kaolinitic mixed-layer minerals are randomly interstratified (Wiewiora, 1971; Drits & Sakharov, 1976; Hughes *et al.*, 1987; Drits & Tchoubar, 1990). Three-component kaolinite-smectite-swelling chlorite having ordered distribution of the inter-

stratified components has been described by Sakharov *et al.* (1981) and by Drits & Tchoubar (1990).

Kaolinitic phases with $d(001) > 7.15$ Å may be kaolinite with a small thickness of coherent scattering domains (CSD) or kaolinite which is mixed-layered. Randomly interstratified K-S is easily identified because glycolation results in easily distinguished changes in the XRD patterns compared to those of the air-dried specimens. However, kaolinite having thin coherent scattering domains (CSDs) may be difficult to distinguish from a mixed-layer structure containing predominantly kaolinite layers, especially when the non-kaolinite layers are illite or/and vermiculite. Characterization of a mixed-layer kaolinitic phase is even more difficult if this phase is present in small amounts in a multiphase sample and the characterization is further complicated when the main component of the sample has broad reflections close to the basal reflections of kaolinite or a kaolinite-containing mixed-layer phase. Due to partial overlapping of the reflections from the

different phases, different treatments of a sample may shift the basal reflection positions even for pure kaolinite. For such samples, a change of the $d(00l)$ after glycolation is not necessarily due to mixed-layering of the kaolinitic phase.

For investigation of the mixed-layer minerals in Upper Jurassic shales from the southern North Sea and onshore Denmark, we have applied a special fractionation technique and have obtained a very fine fraction from which the discrete minerals, such as kaolinite and illite, have been removed and which is dominated by mixed-layer minerals. For this fraction it is therefore possible to determine in detail the structure of the mixed-layer minerals. Previously, we found that a mixed-layer illite-smectite-vermiculite (I-S-V) constitutes 80–90% of this fraction (Drits *et al.*, 1997a). In addition, all studied samples contained a phase which was described as a mixed-layer kaolinite-illite-vermiculite (K-I-V). In the present, more detailed investigation, two additional techniques were applied in order to describe more completely the structure and the diffraction characteristics of the K-I-V phase. This kind of mineral may be more common in sediments than hitherto expected, since its diffraction characteristics are close to those of pure kaolinite and the peaks may thus be masked by those of pure kaolinite if present.

MATERIALS AND METHODS

Samples

Geological, mineralogical and structural characterization of the mixed-layer minerals in Upper Jurassic shales from the southern North Sea and onshore Denmark was carried out by Lindgreen & Hansen (1991), Lindgreen *et al.* (1991) and Drits *et al.* (1997a). Because the diffraction patterns of the kaolinitic phase were quite similar for all samples from this region (Drits *et al.*, 1997a), only one sample from the Norwegian well 9/4-3, 2435 m in depth (sample 92) will be studied in detail in this investigation.

Chemical pretreatment

The samples were pretreated to remove organic matter and Fe and Al oxides, and the mixed-layer fraction was isolated by centrifugation as described previously (Hansen & Lindgreen, 1989). The particles in this fraction are, according to scanning

probe microscopy, predominantly $<500 \text{ \AA}$ in diameter and $<100 \text{ \AA}$ in thickness (Lindgreen *et al.*, 1992). Furthermore, the fraction is dominated by the mixed-layer minerals, the other minerals having been removed.

In the present investigation, mixed-layer samples have been saturated with K^+ , Na^+ , Mg^{2+} , and Ca^{2+} by five repeated washings using 1 M chloride solutions. Oriented specimens have been prepared by the pipette method using 2.5 mg/cm^2 of specimen and analysed in air-dry (60% humidity) and glycolated conditions, glycolation being carried out over three days at 60°C in glycol vapour.

X-ray diffraction

The XRD patterns were obtained using Cu- $K\alpha$ and Co- $K\alpha$ radiations with the DRON-4 and the Philips PW1050 diffractometers, respectively. The DRON-4 has a horizontal goniometer with a graphite monochromator having a set of fine antiscatter slits (0.1–0.25 mm) to limit the horizontal beam divergence and Söller slits (angular aperture 2.5°) to limit the vertical beam divergence. The intensities were measured for 100 s per $0.05^\circ 2\theta$ step. The Philips diffractometer has a vertical goniometer PW1050 with a thin Fe filter and pulse-height selection and $1/4^\circ$ fixed divergence and anti-scatter slits together with Söller slits. The intensities were measured for 10 s per $0.1^\circ 2\theta$ step.

Structural models, techniques and simulation of XRD patterns

Models of illite-containing 2:1 mixed-layer structures have 2:1 layers separated by different types of interlayers. For Na-, Mg- and Ca-saturated interlayers of air-dried 12.4–12.5 \AA , 14.0–14.2 \AA and 15.0–15.1 \AA smectite layers, fitting has demonstrated (Drits *et al.*, 1997a) that the structure and composition correspond to the one-dimensional structure of Moore & Reynolds (1989). For glycolated 17 \AA smectite layers, the z -coordinates of glycol molecules given by Moore & Reynolds (1989) have been used. The one-layer glycol complex of vermiculite interlayers has been modelled using 4.0 glycol molecules and the z -coordinates of Moore & Reynolds (1989). Illite interlayers have been modelled with 0.75 K per $\text{O}_{10}(\text{OH})_2$. For kaolinite-containing mixed-layer models, the structure and composition of smectite, vermiculite and illite layers are the same as those

for the 2:1 layer models, whereas for the kaolinite layers the z -coordinates and atomic occupancies determined by Bish (1993) have been used.

We have found that the most effective technique to reveal the mixed-layer nature of a phase having kaolinite as the main component is XRD analysis of the K-saturated sample heated at 300°C and computer-simulation of this pattern. To diminish the effect of partial overlapping of reflections, we have applied a decomposition technique (Drits *et al.*, 1993, 1996) in order to, firstly, separate these reflections and, secondly, subtract the contribution of the non-kaolinitic reflections from the experimental XRD pattern. Application of these two techniques in combination with fitting of the calculated and experimental XRD patterns for specimens saturated with Ca, Mg and Na and being air-dry or glycolated make it possible to determine the crystal structure of the kaolinitic phase.

Fitting of the XRD patterns within the 1.5–65°2 θ region has been carried out using the program designed by Drits & Sakharov (1976). Corrections for instrumental variables including horizontal and vertical beam divergences, goniometer radius,

dimensions and thickness of samples were made according to Reynolds (1986) and Drits *et al.* (1993). For the I-S-V models and the models of the kaolinitic phase, the value of the orientation function has been chosen to be the same (8°) as determined previously for the 2:1 I-S-V structure in the same sample (Drits *et al.*, 1997a). For the kaolinitic phase, as well as for the I-S-V structures, the models providing the best fit have a log-normal distribution of coherent scattering domain (CSD) thicknesses. Parameters describing the log-normal distribution of CSD thicknesses were determined using the mean thickness of CSD and the regression equations given by Drits *et al.* (1997b).

RESULTS AND DISCUSSION

Experimental XRD patterns

The XRD patterns of the kaolinitic phase have two strong basal reflections (Fig. 1). For air-dry specimens saturated with Na, Mg and Ca, the $d(001)$ of this phase are 7.21 Å, 7.22 Å and 7.22 Å, respectively, i.e. the position of the 001 reflection does not depend on the exchangeable cation.

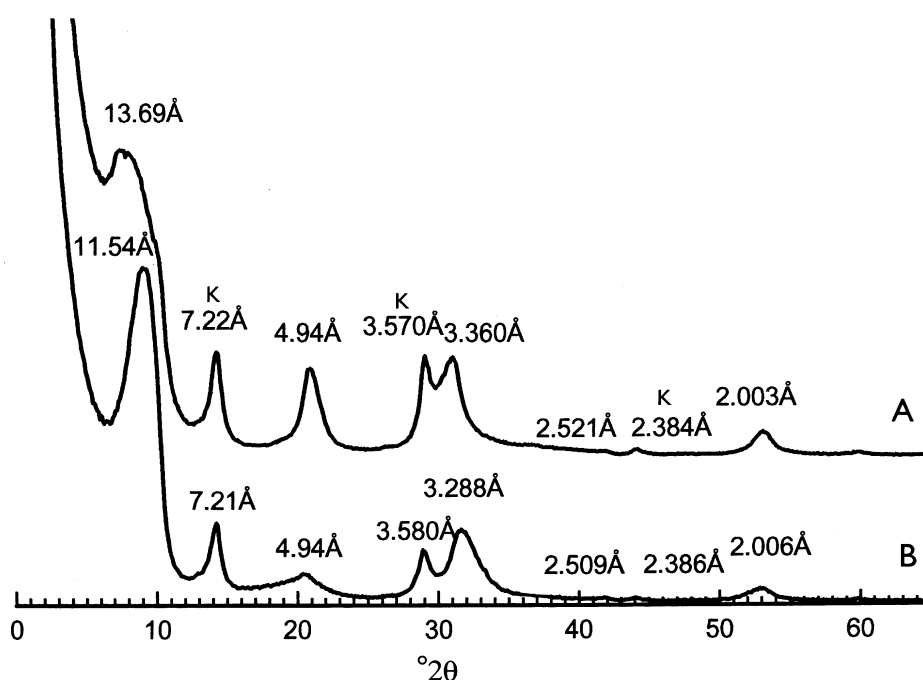


FIG. 1. Experimental XRD patterns for the air-dried specimens saturated with Mg (A) and Na (B). K = kaolinitic peaks. Co-K α radiation.

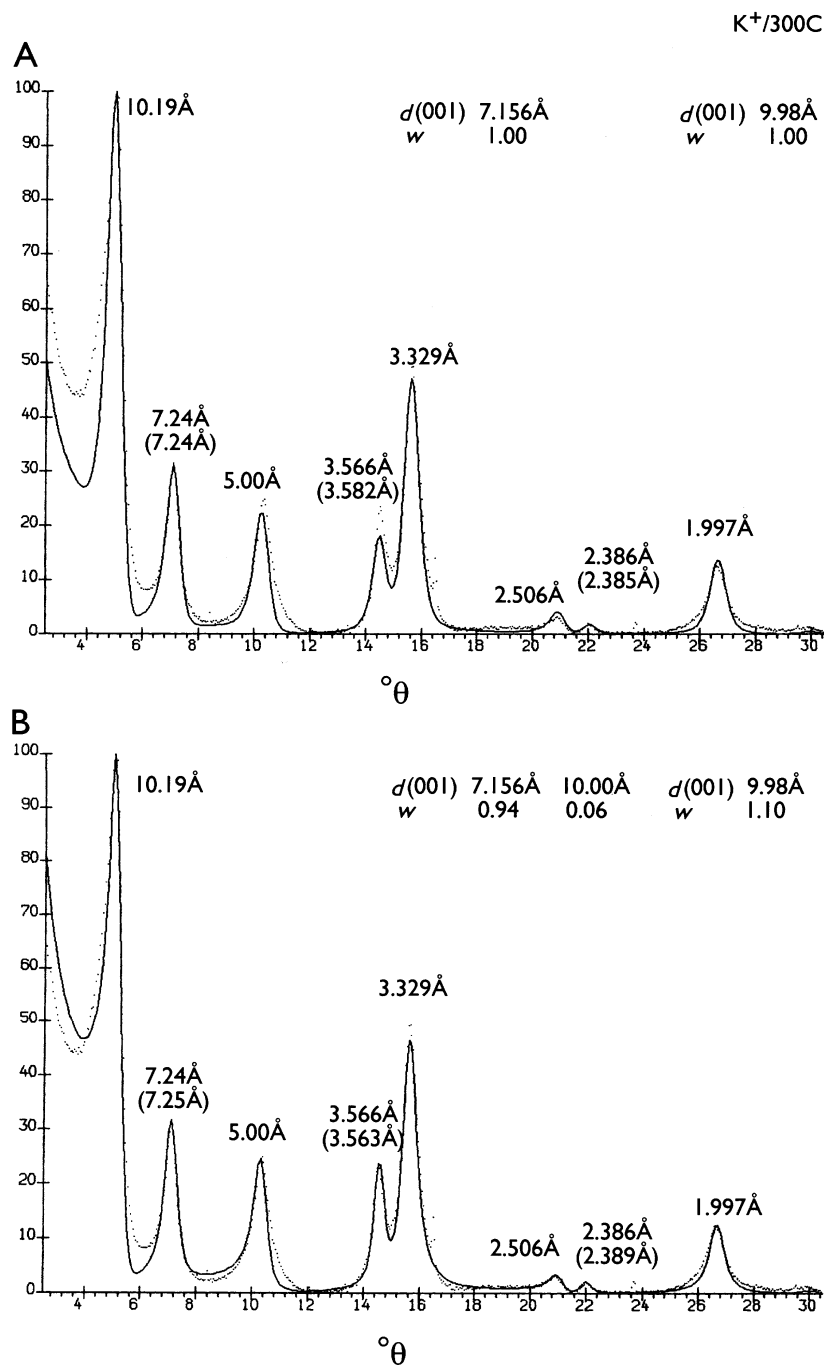


FIG. 2. Experimental XRD pattern (dotted line) and d -values for the specimen saturated with K and heated to 300°C. Co- $K\alpha$ radiation. (A) Modelled pattern (solid line, calculated d -values in parentheses) for a two-phase mixture of thin kaolinite and I-S-V. Thicknesses ($d(001)$) and amounts (w) of layer types are shown for each phase. (B) Modelled pattern (solid line, calculated d -values in parentheses) for a two-phase mixture of K-I and I-S-V. Thicknesses ($d(001)$) and amounts (w) of layer types are shown for each phase.

Glycolation of the Mg-saturated sample slightly changes the position of this reflection and $d(001) = 7.19 \text{ \AA}$. The $d(002)$ values vary within a very narrow interval ($\pm 0.002 \text{ \AA}$) around 3.578 \AA for the Na- and Ca-saturated, air-dried specimens and around 3.563 \AA for all glycolated specimens. Therefore, this phase may be a pure kaolinite consisting of very thin coherent scattering domains (CSDs), since the 001 reflection of such kaolinite is shifted towards small θ values and the observed $d(001)$ value thus is larger than the actual thickness of a kaolinite layer (7.156 \AA). In addition, d -values of the 002 reflection for the Na- and Ca-saturated and air-dried samples coincide with $d(002) = 3.578 \text{ \AA}$ of pure kaolinite. The shift of the 002 reflection by $\Delta\theta = 0.06^\circ$ observed after glycolation may be due to partial overlapping of this reflection with the nearest I-S-V reflection. Perhaps for the same reason, the $d(002)$ of the Mg-saturated, air-dried specimen (at 3.570 \AA) is different from the $d(002)$ of pure kaolinite (Fig. 1). Alternatively, the phase is a mixed-layer structure having kaolinite layers alternating at random with small amounts of illite, vermiculite, dioctahedral chlorite and/or smectite layers. To test these hypotheses, XRD patterns have been calculated for both models. For these calculations, the patterns calculated previously for the I-S-V phase (Drits *et al.*, 1997a) have been added to the patterns calculated for the kaolinitic phase, in order to obtain a fit of the whole diffraction profile.

Determination of the mixed-layer nature of the kaolinitic phase

For testing these alternatives, the specimen saturated with K and heated to 300°C was studied. In this specimen, smectite and vermiculite layers have approximately the same thickness as has illite; consequently, the I-S-V phase has a rational series of 00 l reflections with $d(001) \approx 9.98 \text{ \AA}$ (Fig. 2). A kaolinite mixed-layered with smectite, vermiculite or/and illite will have only 7.15 \AA and 9.98 \AA layers in this specimen. For the first model which has kaolinite with thin CSDs, the calculated curve in Fig. 2A is a sum of two XRD curves, one for the K-saturated and dehydrated I-S-V phase and the other for a pure kaolinite structure. The experimental XRD pattern has three basal reflections of the kaolinitic phase with d -values 7.24 \AA , 3.566 \AA and 2.386 \AA (Fig. 2). In the experimental and calculated patterns, positions,

intensities and profiles belonging to the 001 and 003 reflections of the kaolinitic phase are almost the same. However, a distinct discrepancy between the calculated and experimental intensities and profiles are observed for the 002 kaolinite reflection (Fig. 2A). This fit was obtained with mean and maximum CSD thicknesses for the kaolinite crystallites of 8 and 20 layers, respectively. Changing the mean thickness of the CSDs did not improve the agreement between the calculated and experimental intensities of the 00 l kaolinite reflections.

However, a random mixed-layer model which has 94% of 7.156 \AA kaolinite layers and 6% of 9.98 \AA illite-like layers results in good agreement between positions, intensities and profiles for all three basal reflections in the experimental and calculated XRD patterns (Fig. 2B). Mean and maximum thicknesses of CSD were equal to 14 and 25 layers, respectively, for the K-I-V, and 8 and 15 layers, respectively, for the I-S-V model. Thus, the kaolinitic phase has a mixed-layer structure.

Actual mixed-layer structure of the kaolinitic phase

In order to determine the number, nature and contents of interstratified non-kaolinite layers in the kaolinitic structures, it is important to measure precisely the positions of the basal reflections of this phase. As was mentioned, the 002 reflections of the kaolinitic phase partially overlap with the nearest peak of the I-S-V phase. Moreover, the degree of this overlapping depends on sample treatment. In order to minimize this overlap and to determine the actual position of the 002 peak, the experimental XRD patterns in the region $4.3\text{--}2.9 \text{ \AA}$ were decomposed into individual reflections according to the technique described by Drits *et al.* (1993, 1996). This procedure was applied to the patterns of the air-dried, Na, Mg and Ca-saturated specimens and of the glycolated, Mg-saturated specimens. Removal of the I-S-V peaks overlapping the 002 reflection of the kaolinitic phase resulted in the pattern in Figs. 3 and 4.

To obtain good agreement between calculated and experimental basal reflections for the kaolinitic phase subjected to different treatments, different models were tested. For the two-component systems K-I, K-S, kaolinite-chlorite (K-C) and K-V, the content of illite, smectite, dioctahedral chlorite and vermiculite layers was 6%, because the content of kaolinite layers was known to be 94% from the

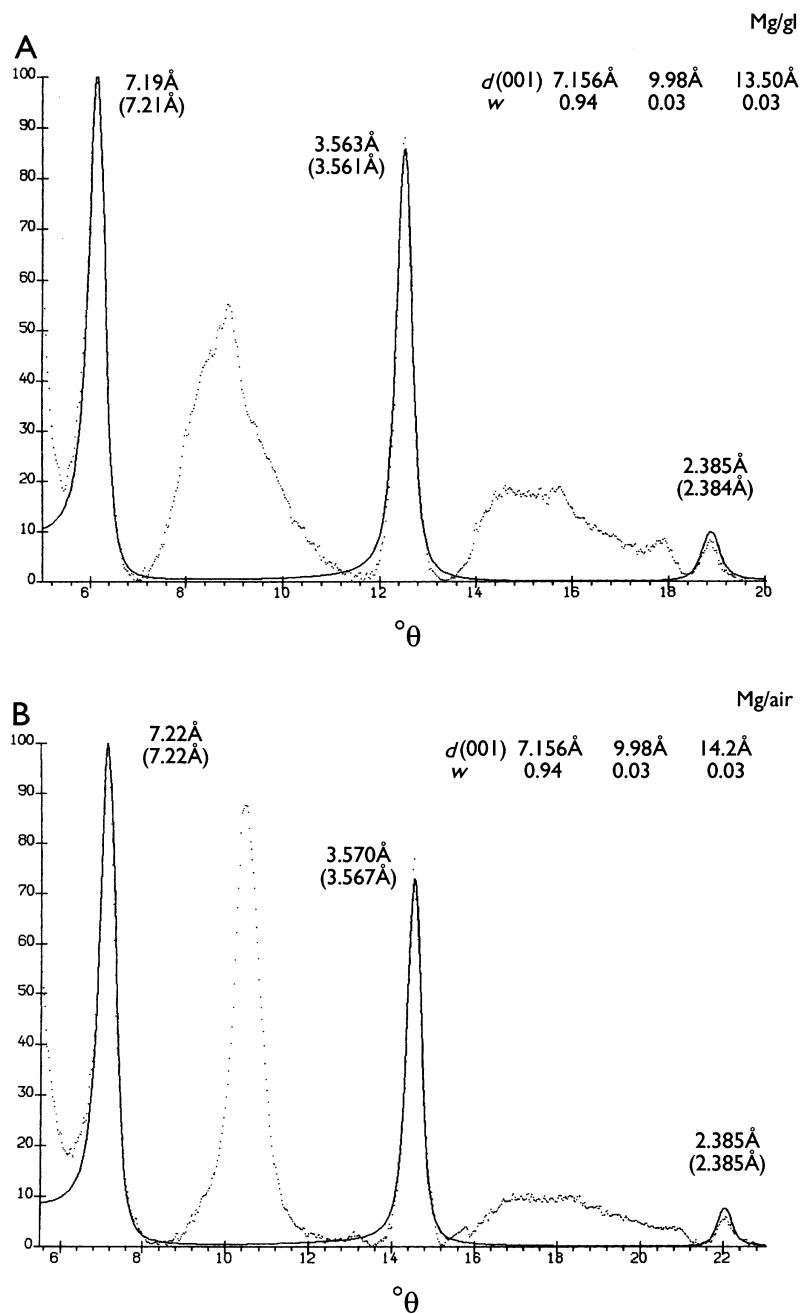


FIG. 3. Decomposed experimental XRD patterns (dotted line), from which the peaks of the I-S-V phase overlapping the kaolinitic phase have been removed, shown together with the patterns modelled for a K-I-V phase (solid line, calculated d -values in parentheses). The K-I-V phase composition is shown with thicknesses ($d(001)$) and amounts (w) of layer types. (A) Mg-saturated and glycolated specimen. Modelled pattern for a K-I-V phase. Cu- $K\alpha$ radiation. (B) Mg-saturated and air-dry specimen. Modelled pattern for a K-I-V phase. Co- $K\alpha$ radiation. (C) (*Opposite*) Detail of (B) showing experimental (dotted line) and calculated (solid line) profiles of the kaolinite 002 reflection. Co- $K\alpha$ radiation.

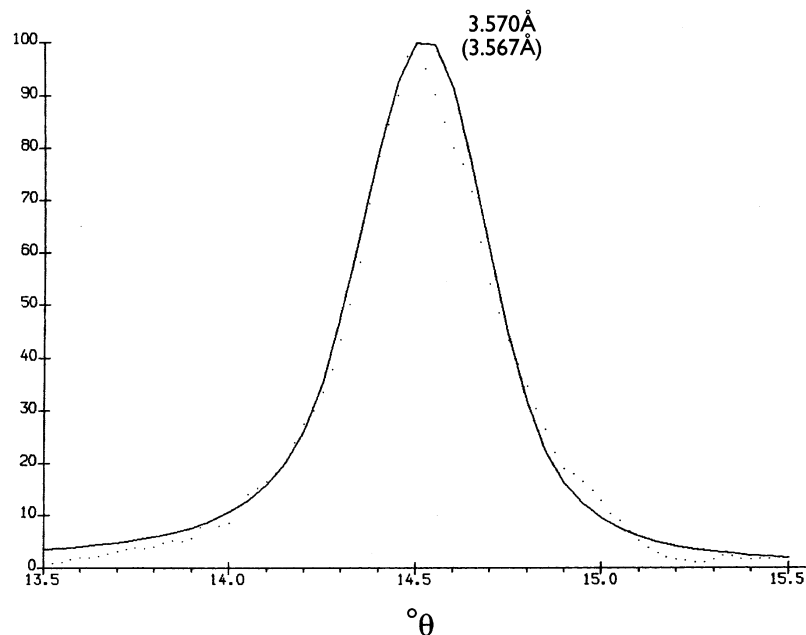


FIG. 3. (C).

analysis of the K-saturated and heated specimen. However, it was not possible to fit the experimental XRD patterns with patterns calculated for two-component models. On the other hand, a good fit between calculated and experimental positions, intensities and profiles of the three orders of basal reflections of the kaolinitic phase is obtained for a model in which 0.94 kaolinite, 0.03 illite and 0.03 swelling 2:1 layers are randomly interstratified. In Figs. 3A, 3B and 4A, experimental and calculated XRD patterns are compared for the Mg-saturated and glycolated and air-dried specimens and the Na-saturated and air-dry specimen. The thickness of the swelling 2:1 layers is equal to 15.0 Å, 14.2 Å and 14.2 Å for air-dried specimens saturated with Ca, Mg and Na, respectively, and to 13.5 Å for the Mg-saturated and glycolated specimen. For all specimens, the position of the kaolinitic 003 reflection in the calculated XRD patterns is sensitive to the thickness of vermiculitic layers and this thickness was therefore determined from coincidence of experimental and calculated 003 peak positions for each type of exchangeable cation and with/without glycolation.

The XRD patterns in Figs. 3A, 3B and 4A show some discrepancies between the experimental and the calculated d -values as determined from the

positions of the tips of the K-I-V reflections. However, these small discrepancies are of minor importance if the intensities and profiles of the experimental and calculated reflections coincide. For example, the experimental and calculated intensities and profiles of the K-I-V 002 reflection coincide even though a noticeable discrepancy is seen between the positions of the tips of the peaks (Figs. 3C, 4D).

In contrast to the K-I-V model, the kaolinite model resulted in distinct discrepancies, with respect to positions, intensities and profiles, between the experimental and calculated 002 reflections (Figs. 4B, 4C). In addition, for the Mg-saturated and glycolated specimen, a distinct difference is observed between positions of the experimental (3.563 Å) and calculated (3.581 Å) 002 reflections.

Using the parameters determined for the K-I-V phase and the I-S-V parameters obtained previously (Drits *et al.*, 1997a), a good fit was obtained between the experimental and calculated XRD pattern for the Na-saturated and air-dried specimen (Fig. 5B). However, the same statistical I-S-V model when applied to the glycolated state has not provided a good fit on high- and low-angle sides of the 3.56 Å and 3.35 Å reflections

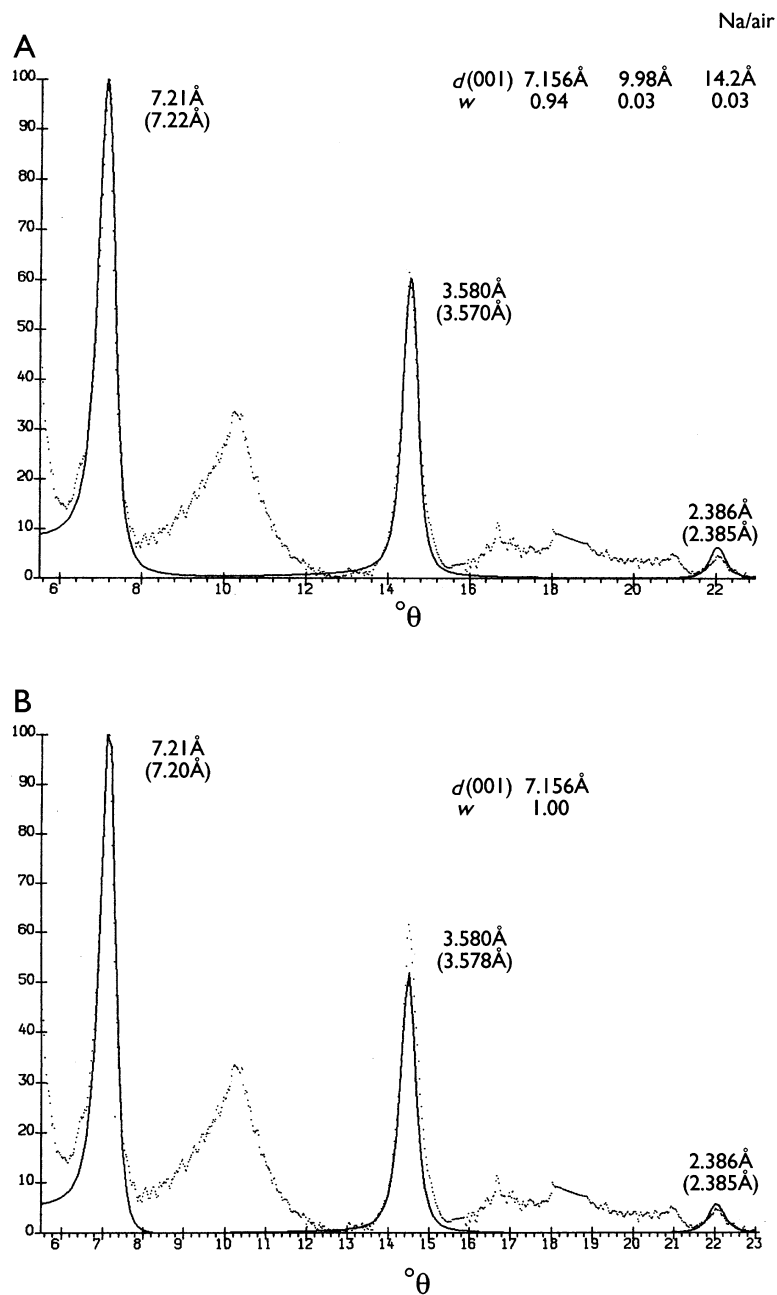


FIG. 4. Decomposed experimental XRD patterns (dotted line), from which the peaks of the I-S-V phase overlapping the kaolinitic phase have been removed, shown together with the patterns modelled for a K-I-V phase (solid line, calculated d -values in parentheses). For the K-I-V and K phase, thicknesses ($d(001)$) and amounts (w) of layer types are shown. (A) Na-saturated and air-dried specimen with a pattern modelled for a K-I-V phase. Co- $K\alpha$ radiation. (B) Na-saturated and air-dried specimen with a pattern modelled for a pure kaolinite. Co- $K\alpha$ radiation. (C) (*Opposite*) Mg-saturated and glycolated specimen with a pattern modelled for a pure kaolinite. Cu- $K\alpha$ radiation. (D) (*Opposite*) Detail of (A) showing experimental (dotted line) and calculated (solid line) profiles of the kaolinite 002 reflection. Co- $K\alpha$ radiation.

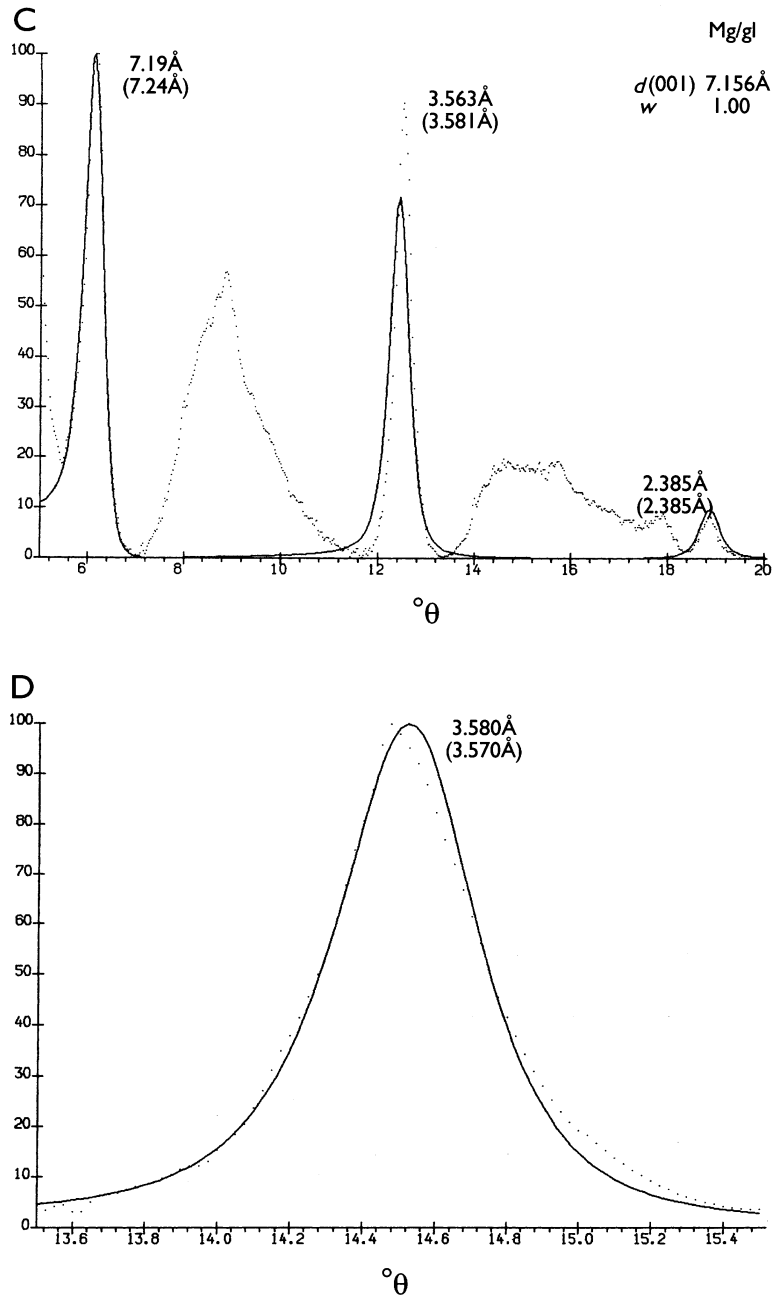


FIG. 4. (C & D).

(Fig. 5A). The observed lack of agreement is probably due to the fact that the I-S-V model does not describe properly the actual structure of this phase in the glycolated state because of

heterogeneous swelling of expandable interlayers. Because the decomposition procedure removed the experimental profile of the 3.35 Å reflection, its application eliminates diffraction effects of the

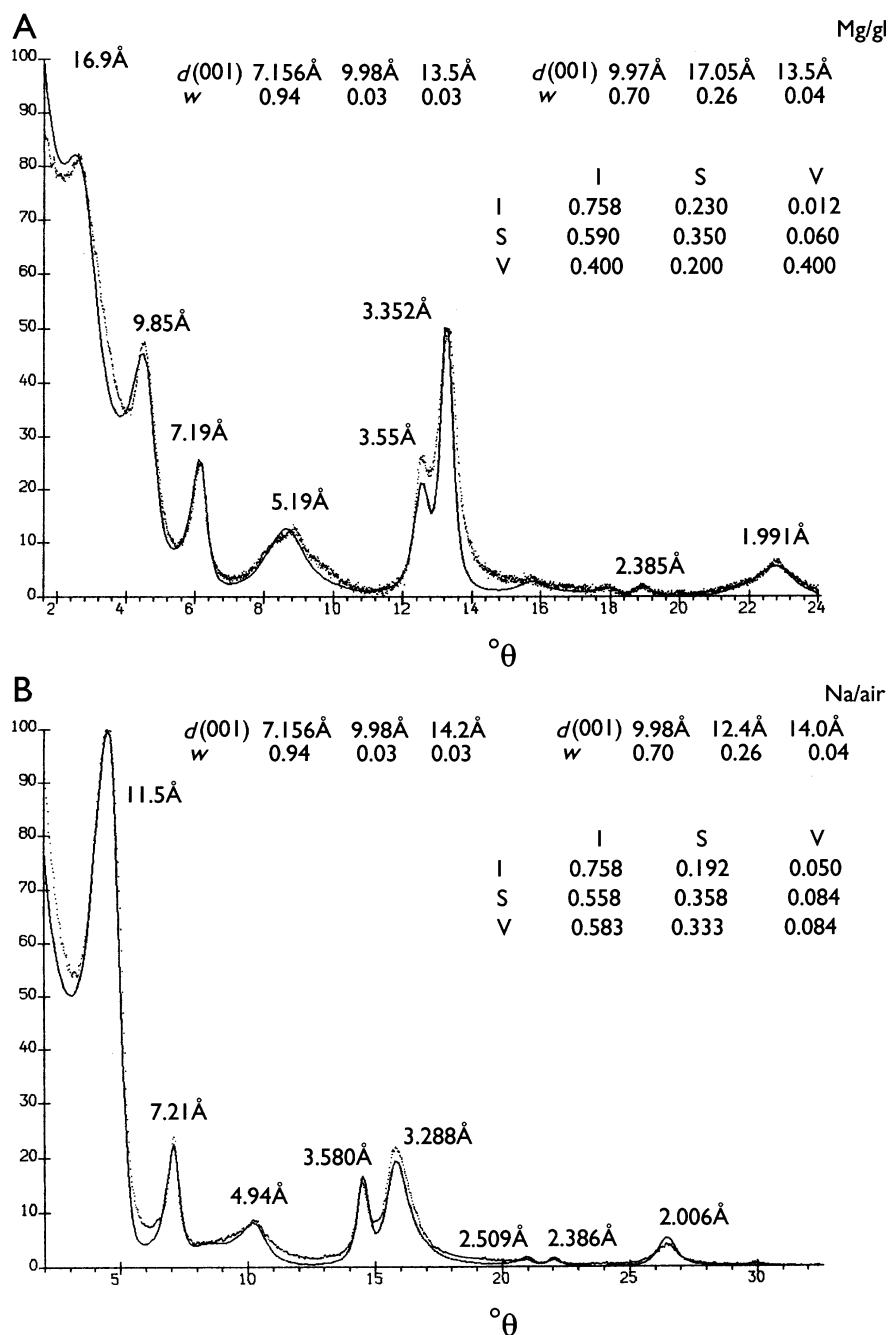


FIG. 5. (A) Experimental pattern (dotted line) and d -values for the specimen saturated with Mg and glycolated. Cu- $K\alpha$ radiation. Modelled pattern (solid line) for a two-phase mixture of K-I-V and I-S-V. Thicknesses ($d(001)$) and amounts (w) of layer types are shown for each phase. (B) Experimental pattern (dotted line) for the air-dry specimen saturated with Na. Co- $K\alpha$ radiation. Modelled pattern (solid line) for a two-phase mixture of K-I-V and I-S-V. Thicknesses ($d(001)$) and amounts (w) of layer types are shown for each phase.

actual structure of the I-S-V phase. Therefore, the decomposed XRD pattern of the Mg-saturated and glycolated specimen provided an opportunity to choose a structural model for the kaolinitic phase.

The results obtained demonstrate that the experimental XRD patterns for the different specimens saturated with different cations and with/without glycol can be reproduced with models having identical numbers and proportions of components. Furthermore, the swelling component of the kaolinitic phase has one glycol interlayer in the Mg-saturated and glycolated specimen and two water interlayers in the air-dry specimens. Accordingly, the swelling component is vermiculite, and the kaolinitic phase is a random mixed-layer having kaolinite, illite and vermiculite layers in the proportions 0.94:0.03:0.03. A three-component kaolinite-illite-dioctahedral chlorite model has been considered but rejected because, for this structure, the positions of the basal reflections do not change with different treatments. For this model, however, it should be noted that, in spite of discrepancies between the calculated and experimental patterns with respect to reflection positions and profiles, there is general agreement between the reflection intensities.

The K-I-V phase in the North Sea shales

Previously, we found that the K-I-V is always present in small amounts in the North Sea and Danish Upper Jurassic shale samples (Drits *et al.*, 1997a). In this paper, the new results confirm the actual structure of this phase. It is remarkable that the K-I-V phase in all samples has quite similar diffraction features, i.e. quite similar structural characteristics. This result indicates that minor phases previously being reported as kaolinite in other investigations from this region may in fact be kaolinitic mixed-layer minerals. This possibility can, however, be tested if the multispecimen fitting method in combination with the decomposition technique is applied to study the samples in question. The fact that the kaolinitic phase present in the finest fraction of the Jurassic samples is actually a K-I-V indicates that this phase has been derived from weathering and that it is detrital, like we found previously for the I-S-V in some of the most shallow samples investigated. Furthermore, the finding that the K-I-V does not change in composition but only decreases in amount during the diagenetic stages investigated, indicates that

unlike the I-S-V it is not transformed during diagenesis but instead it is gradually dissolving. This fact may be considered as additional evidence for the detrital origin of the K-I-V phase.

CONCLUSIONS

When a kaolinitic phase is present in the sample in small amounts, computer modelling of the XRD pattern of the K-saturated and heated specimen is essential for distinguishing between kaolinite with small CSD thicknesses and kaolinite mixed-layered with small amounts of illite and/or swelling 2:1 layers. Fitting of peak positions alone is not sufficient since the intensity and the profile of the peaks of the kaolinitic phase depend strongly on mixed-layering also. The multi-specimen fitting procedure, supplemented by decomposition of partially overlapping peaks, accurately reveals the nature and proportions of the non-kaolinitic interstratified components.

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