Colloid Polym Sci 276:601–609 (1998)

ORIGINAL CONTRIBUTION

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# The mechanochemical reactions between CsF and kaolinite

Received: 4 February 1998
Accepted: 11 March 1998

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**Abstract** The grinding of a mixture containing kaolinite and CsF was carried out by three different techniques, short manual grinding, Fisher mechanical mortar and Retsch ball mill. In addition to different cesium aluminium silicates which were detected by X-ray powder diffraction, a new type of intercalation complex was identified by FTIR spectroscopy. The X-ray diffractogram of this complex did not show any basal spacing, which may characterize the complex but the 0.715 nm characteristic peak of the untreated kaolinite became very weak. The Retsch ball mill led to a slight destruction of the kaolinite and the formation of small amounts of the new intercalation complex. The delamination of book-like kaolinite assemblages was observed after the manual and Fisher mortar grindings. In the latter grinding techniques the kaolin-like layers persisted and served as the framework for the intercalation complexes.

**Key words** Kaolinite – cesium fluoride – intercalation complex – cesium aluminosilicates – FTIR spectra – X-ray diffractogram

## Introduction

Recently we studied the interaction of CsF with kaolinite through the evaporation of aqueous suspensions [1]. The X-ray diffractograms showed that the interaction resulted in a complex mixture of cesium silicates, cesium aluminium silicates, cesium aluminium fluoride and aluminium fluoride. Two types of intercalation complexes were also identified (labelled A and B), showing *d*-spacings of 0.984 and 0.830 nm, respectively. In complex B, water and HF (or probably $F^-$ together with $H_3O^+$) were intercalated. From the *d*-spacing it was concluded that in this complex the intercalated fluoride penetrated into the hexagonal hole of the oxygen plane (keying). Complex B showed an IR absorption band at 3518 $cm^{-1}$, attributed to a perturbed OH group. But at that time it was not clear which of the OH groups was perturbed, because the new band was weak and both the inner and the inner–surface OH bands remained intense. Intercalation complex B was obtained in non-rinsed mixtures which contained excess CsF. A very weak band was first detected after two months and its intensity increased with increasing ageing periods. Intercalation complex A was obtained in mixtures from which the excess CsF was removed by rinsing the solid phase after drying the aqueous CsF–kaolinite suspension. At that time its composition was not clear. Now we wish to study this intercalation reaction by mechanochemical treatments.

Mechanochemical technique was previously applied in the study of the intercalation of CsCl or CsBr together with water molecules into kaolinite [2–4]. In this

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technique mixtures containing kaolinite and cesium halides were ground by a mortar and pestle and drops of water were added during the grinding in order to keep the mixtures humid (wet grinding). The amounts of the intercalation complexes increased with the ageing of the ground mixtures. A kaolinite complex of CsCl was also obtained when the mixture was ground without adding water drops (dry grinding) but the amount of the complex was small compared with that obtained by wet grinding. In "dry grinding", water was adsorbed from the atmosphere. Intercalation complex of CsBr was not obtained by dry grinding whereas CsI was not intercalated either by wet or dry grinding.

Different intercalation complexes of CsCl and CsBr were obtained by drying an aqueous kaolinite-halide slurry and ageing the precipitate in a humid atmosphere [5, 6]. The former contained water whereas the latter were almost anhydrous. The OH stretching vibrations in the IR spectrum of kaolinite shifted after both treatments to lower wavenumbers due to hydrogen bonds which were formed between the hydrated cesium salts or the halide anions and the inner-surface hydroxyls of the mineral. The Al–OH and Al–O bands were also perturbed after both treatments. Furthermore, hydrogen-bonded water molecules were identified in the spectra of the complexes obtained by grinding and the Si–O bands were perturbed indicating that the oxygen planes were accepting protons from the intercalated water.

The intercalation of water was attributed to the effect of the large $Cs^+$ cation which acts as a structure breaker of water [7]. Monomeric water molecules in the presence of $Cs^+$ are active proton donors and acceptors and may react with oxygen and hydroxyl surfaces of kaolin-like layers.

XRD of complexes obtained by evaporating aqueous clay-salt slurries showed *d*-spacings of 1.06 and 1.10 nm due to the intercalation of CsCl and CsBr, respectively, in addition to the disappearance of the 0.715 nm peak, whereas those of complexes obtained by grinding showed only that the 0.715 nm peak of the kaolinite almost disappeared. The 0.715 nm peak was reobserved after washing the samples with water, indicating that the silicate layers did not become amorphous during the grinding but only the book-like crystals of kaolinite were delaminated [5].

By heating the ground samples to 250 °C, or by long ageing at humid atmosphere, the IR spectra and the X-ray diffractograms of the ground samples became similar to those of the intercalation complexes obtained by drying aqueous kaolinite-halide slurries, indicating that dehydration and reorganization of the kaolinite-halide system occurred [6].

The present communication is concerned with the effects of grinding kaolinite together with CsF by different techniques on the intercalation complexes. The present IR spectroscopy study enables us to gain a better understanding of the structures and compositions of intercalation complexes A and B. This will be shown in the Discussion section.

## Experimental

### Materials

Kaolinite and CsF used in the present study were previously described [1].

### Methods

Three different grinding techniques were employed in the present study, namely, (a) a short period manual grinding with a small agate mortar and pestle; (b) a Fisher mechanical porcelain mortar and pestle and (c) a ball mill (Retsch S1 with a 250 ml agate cell and seven agate balls). A mixture containing 0.5 g kaolinite and 0.5 or 1.0 g CsF (a weight ratio 1 : 1 or 1 : 2) was ground by one of these techniques for different time periods between 30 s and 60 min. The ground mixtures were examined by X-ray powder diffraction and by Infrared spectroscopy immediately after the treatment and after different ageing periods in which they were left in 100% humidity (in a desiccator which contained a beaker with water).

For the X-ray study, the ground powder was placed in glass sample holder and slightly pressed. The diffractograms were recorded by a Philips Automatic Powder Diffractometer (PW 1710) with a Cu tube anode. IR spectra were recorded by a Bruker IFS 113v FT-IR Spectrometer using KBr pellets or nujol.

## Results

The results obtained with a weight ratio 1 : 1 or 1 : 2 were in general very similar. Unless otherwise stated, the results presented in this paper are those obtained with a weight ratio kaolinite: CsF of 1 : 2.

### X-ray diffraction

Table 1 summarizes the spacings recorded after treatment of kaolinite with CsF in the different grinders and after different ageing periods. The table also shows spacings of untreated kaolinite and ground CsF. During grinding CsF

**Table 1** The *d*-spacings (in nm) of $CsF \cdot xH_2O$, untreated kaolinite and products of the interaction between CsF and kaolinite, (the numbers 1–9 in parenthesis show the relative intensity of the peak in the diffraction trace, x indicates the most intense peak)

| Phases | $CsF \cdot xH_2O$ | Kaolinite | a | b | c | d | e | f | g | h |
|---|---|---|---|---|---|---|---|---|---|---|
| 1, 8 | — | 0.715(x) | 0.715(x) | 0.712(x) | 0.713(1) | 0.710(1) | 0.711(x) | 0.712(3) | 0.714(x) | 0.713(x) |
| 3 | 0.683(x) | — | 0.681(2) | — | — | — | — | — | — | — |
| n.d. | — | — | — | — | — | 0.626(1) | — | — | — | 0.640(1) |
| n.d. | — | — | — | — | — | 0.575(1) | — | — | — | 0.590(1) |
| n.d. | — | — | 0.553(1) | — | — | — | — | — | — | 0.558(1) |
| n.d. | — | — | — | — | 0.532(1) | — | — | 0.530(1) | — | — |
| n.d. | — | — | — | 0.516(1) | — | — | — | — | — | 0.516(1) |
| 5, 8 | — | — | — | — | 0.507(1) | — | — | 0.507(1) | — | 0.504(1) |
| n.d. | — | — | — | — | 0.470(1) | 0.467(1) | — | 0.467(1) | — | 0.471(1) |
| 10 | — | — | — | — | 0.459(1) | — | — | — | — | — |
| 1 | — | 0.447(2) | 0.449(1) | — | 0.447(1) | — | 0.444(4) | 0.445(2) | 0.445(1) | 0.447(1) |
| 1 | — | 0.437(2) | 0.438(1) | — | — | — | — | — | — | 0.434(1) |
| n.d. | — | — | 0.424(1) | — | 0.429(1) | 0.426(4) | — | — | — | — |
| n.d. | — | — | — | — | 0.422(1) | 0.420(4) | — | — | — | — |
| 1, 3 | 0.412(2) | 0.417(2) | — | — | — | 0.412(1) | — | 0.414(2) | 0.418(1) | 0.414(3) |
| 3, 9, 10 | 0.408(2) | — | 0.405(1) | — | — | — | — | 0.407(2) | — | 0.408(3) |
| 3, 8 | 0.396(9) | — | 0.400(1) | — | 0.398(1) | — | — | — | — | — |
| 1, 3, 5 | 0.386(8) | 0.384(1) | — | — | — | — | — | — | — | — |
| n.d. | — | — | — | — | — | — | — | 0.378(3) | — | 0.379(2) |
| 1 | — | 0.373(1) | — | — | — | — | — | — | — | — |
| 4, 7 | — | — | — | — | — | — | — | 0.365(1) | — | 0.366(2) |
| 1, 3, 8 | 0.358(8) | 0.358(x) | 0.358(5) | 0.356(x) | 0.357(1) | 0.356(1) | 0.358(x) | 0.357(1) | 0.357(9) | 0.357(8) |
| 1 | — | 0.351(1) | — | — | — | — | — | — | — | — |
| 2, 3 | 0.347(8) | — | — | — | — | — | — | 0.348(2) | — | 0.348(2) |
| 3, 7 | — | — | — | — | — | — | — | 0.344(x) | — | 0.344(4) |
| 3, 7 | 0.341(5) | — | 0.342(1) | — | — | — | — | — | — | 0.341(3) |
| 1 | — | 0.338(1) | — | — | — | 0.339(1) | — | 0.338(1) | — | — |
| 3, 5, 8 | 0.329(2) | — | — | — | — | 0.333(1) | — | 0.333(1) | — | — |
| 1, 3, 8 | — | 0.326(1) | 0.326(1) | — | 0.325(x) | — | — | 0.326(3) | 0.325(8) | — |
| 4, 5, 9 | — | — | 0.321(1) | — | — | — | — | 0.321(4) | — | 0.320(4) |
| 5, 6 | — | — | 0.318(1) | — | 0.317(1) | 0.316(5) | 0.318(3) | — | — | 0.317(2) |
| 1, 5, 8 | — | 0.312(1) | — | — | 0.314(3) | 0.313(x) | — | — | — | 0.314(1) |
| 3 | 0.309(x) | — | — | — | — | — | — | 0.308(1) | — | 0.309(1) |
| 2, 3, 8 | 0.305(9) | — | — | — | — | — | — | 0.303(1) | — | — |
| 3 | 0.300(x) | — | — | — | 0.300(2) | 0.300(6) | — | — | — | — |
| 3, 4 | 0.294(4) | — | — | — | — | — | — | 0.292(3) | — | 0.292(2) |
| 7, 9, 10 | — | — | — | — | — | 0.289(1) | — | — | — | 0.289(2) |
| 3, 8 | 0.285(7) | — | — | — | — | — | — | 0.285(1) | 0.286(1) | — |
| 3, 10 | 0.282(4) | — | — | — | — | — | — | 0.280(1) | 0.280(1) | — |
| 1, 10 | — | 0.276(1) | — | — | 0.277(1) | 0.274(1) | — | 0.276(1) | 0.277(1) | — |
| 8 | — | — | — | — | — | 0.269(1) | — | — | — | 0.271(1) |
| 3 | 0.264(8) | — | — | — | 0.265(1) | — | — | 0.265(3) | 0.266(1) | 0.265(1) |
| 3 | 0.260(5) | — | — | — | — | — | — | — | — | 0.263(1) |
| 1, 5, 6, 9 | — | 0.257(2) | 0.255(1) | 0.257(x) | 0.254(3) | 0.253(1) | 0.257(2) | 0.254(3) | 0.257(2) | 0.257(1) |
| 1, 3, 9 | 0.252(6) | 0.253(2) | — | — | 0.252(1) | 0.252(1) | — | 0.252(3) | — | 0.252(3) |
| 1 | — | 0.250(2) | — | — | — | — | 0.250(2) | — | 0.250(2) | 0.249(1) |
| n.d. | — | — | 0.248(1) | — | — | — | — | 0.248(3) | — | — |
| 3 | 0.246(2) | — | 0.245(1) | — | 0.246(1) | — | — | 0.245 (3) | — | — |
| 7 | — | — | — | — | — | — | — | — | — | 0.242(1) |
| 1 | — | 0.239(2) | — | 0.238(2) | 0.239(1) | — | 0.238(2) | 0.238(4) | 0.238(2) | 0.238(2) |
| 1, 3, 4 | 0.234(2) | 0.234(2) | — | 0.235(1) | 0.234(2) | 0.234(3) | 0.234(3) | 0.234(3) | 0.234(2) | 0.234(1) |
| 1 | — | 0.230(2) | — | 0.229(1) | 0.229(1) | 0.229(1) | 0.229(2) | 0.229(2) | 0.229(2) | 0.229(1) |

Phase number: 1 – Untreated kaolinite [1]; 2 – anhydrous CsF (PDF 15-759); 3 – $CsF \cdot x\,H_2O$ [1]; 4 – $Al_2SiO_4(F, OH)_2$, (PDF 12-765); 5 – $Cs_2Si_2O_5$, (PDF 19-317, 28-336); 6 – $Cs_2Si_4O_9$, (PDF 19-318); 7 – $CsAlSi_2O_6 \cdot xH_2O$, (PDF 25-194, 29-407); 8 – $CsAlSiO_4 \cdot x\,H_2O$, (PDF 39-131); 9 – $Cs_2AlF_5 \cdot H_2O$, (PDF 42-871); 10 – $Al(F,OH)_3 \cdot xH_2O$, (PDF 11-631, 24-1004); The symbols of the sample corresponds with that in Fig. 1.

is hydrated. The extent of hydration depends on the grinding conditions and on the relative humidity. Thus, different spacings were traced as due to residual CsF in the treated samples [1].

## Manual grinding

The X-ray diffractogram of a ground mixture of kaolinite and CsF in the ratio 1:2 recorded immediately after 30 s

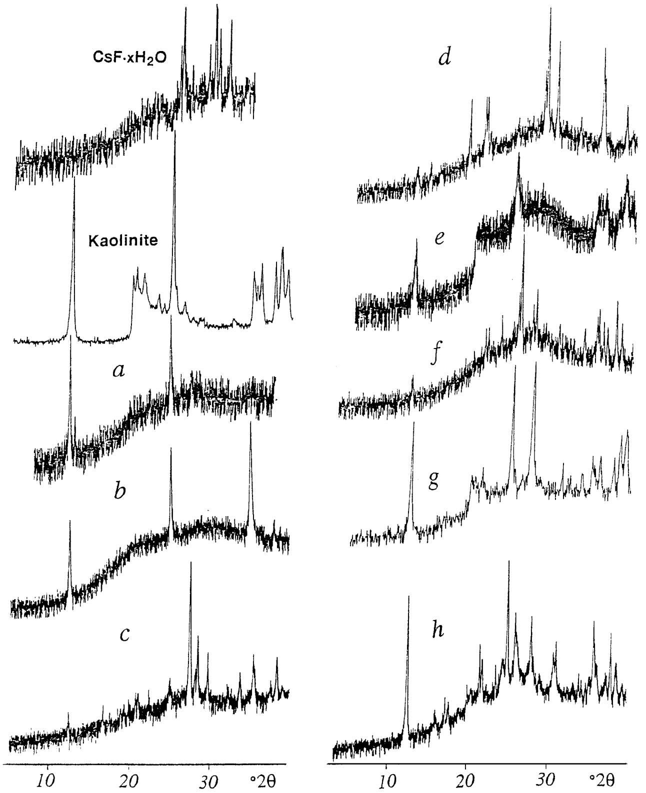

**Fig. 1** X-ray diffractograms of $CsF \cdot xH_2O$; untreated kaolinite; a mixture of kaolinite and CsF, recorded immediately after manual grinding and after one year ageing period (curves a and b, respectively); a mixture of kaolinite and CsF, recorded immediately after grinding in a mechanical Fisher mortar, after one year ageing period and after washing (curves c, d and e, respectively); a mixture of kaolinite and CsF, ground in mechanical Fisher mortar and recorded after two years (f); a mixture of kaolinite and CsF, ground in Retsch ball mill and recorded immediately and after two years (curves g and h, respectively)

grinding, shows that the 001 and 002 peaks (0.715 and 0.358 nm) persisted whereas all other peaks of kaolinite became very weak. Additional new, weak peaks of cesium silicates and aluminosilicates were observed (Fig. 1a, Table 1, column a). After one year the weak *hkl* peaks were not observed, but the 00*l* peaks persisted. A new strong peak appeared at 0.257 nm, probably of cesium silicate and/or cesium fluoro-aluminate (Fig. 1b, Table 1, column b.) The persistence of the 00*l* peaks and simultaneously the disappearance of most other peaks of kaolinite is an indication for a preferred orientation of the examined sample. Due to the original large size of the book-like assemblages of the well crystallized kaolinite, a preferred orientation is normally obtained to a very small extent by the standard procedure of preparing the kaolinite samples for X-ray analysis. A preferred orientation, as obtained in the latter case, is probably the result of the delamination of the kaolinite crystals which starts during the grinding process and continues during the ageing under the influence of water and CsF.

## Fisher mortar grinding

X-ray diffraction recorded immediately after 5 min grinding showed that the peaks which characterize kaolinite became very weak. However, 001 and 002 peaks, although weak, were intense relative to the *hkl* peaks, which is characteristic for delamination. A new strong peak appeared at 0.325 nm together with some other small peaks which are characteristic for cesium silicates and cesium aluminum silicates. These new peaks became more intense after grinding the mixture for 20 min (Fig. 1c, Table 1, column c). When the ground non-washed sample was aged for one year, the cesium silicates and cesium aluminum silicates peaks became more intense and additional peaks appeared, which indicate the formation of new phases of cesium aluminum silicates, probably in hydrated forms. The kaolinite peaks became very weak (Fig. 1d, Table 1, column d). After washing the fresh ground sample with distilled water the diffractogram showed the presence of most kaolinite peaks (Fig. 1e). However, they were weak and broad and Hinckley index of crystallinity became small (~1.0 and 0.2 before and after treatment, respectively). This is an indication that the grinding did not destroy the TO layers but only led to the delamination of the kaolinite crystals and that after removing the CsF, kaolinite assemblages were reformed, with a low degree of order.

X-ray diffraction recorded two years after the grinding showed peaks which characterize pollucite ($CsAlSiO_2O_6 \cdot xH_2O$) and other cesium aluminum silicates and cesium-fluoro-aluminate, $Cs_2AlF_5 \cdot xH_2O$ (Fig. 1f, Table 1, column f) in addition to very weak 00*l* peaks of kaolinite. The aged sample (sample f) was washed thoroughly. The XRD of the washed sample showed a significant increase of the kaolinite 00*l* peaks at 0.715 and 0.357 nm. Most of the reaction products (including pollucite) persisted the washing process. After ageing period (~2 yr) the sample was heated at 260 °C for 3 h. The diffractograms recorded after this thermal treatment were similar to those recorded before the treatment.

## Retsch ball mill grinding

The diffractogram recorded immediately after 60 min grinding showed most characteristic *hkl* peaks of kaolinite, indicating that the voluminous shape of the particles (with book-like crystals) were preserved during the grinding.

However, the area of the 0.715 nm peak became small relative to this area in the diffractogram of untreated kaolinite, indicating that some clay reacted with CsF. New phases were identified as cesium silicate and cesium aluminum silicates (Fig. 1g, Table 1, column g). After two years additional new phases were identified from the X-ray diffractogram. However, most kaolinite peaks persisted (Fig. 1h, Table 1, column h), indicating that the clay was not delaminated.

## Infrared spectroscopy

The labelling of the different IR absorption bands, which are used here, are similar to those which were previously used in the study of CsCl and CsBr intercalation complexes [2–4]. The spectrum recorded after grinding the mixture in a Fisher mortar grinder and after different ageing periods, up to two years showed that the characteristic absorption bands of the kaolinite framework, Si–O, persisted and did not shift from their original location. The hydroxyl band A also persisted, but band B disappeared after grinding, (Fig. 2e–h) indicating a lower degree of order [8]. This is in contrast to the persistence of band B in the spectra of samples obtained by drying aqueous CsF–kaolinite suspensions (Fig. 2a–c) or of samples after grinding by a Retsch ball mill (Fig. 2d). This is an indication that the original degree of order of the kaolinite is preserved in these treatments.

After grinding in the Fisher mortar the intensity of the hydroxyl band D decreased relative to that of band A (Fig. 2e). This trend became more pronounced after two years (Fig. 2f) and the intensity ratio of bands A/D, which in untreated kaolinite is 1.3, became 2.6–2.9. By rinsing the sample with a few drops of water, it adsorbed considerable amounts of water. After washing the sample with excess water or heating at 200–260 °C for three hours, the intensity ratio A/D became 1.5–1.6, similar to the ratio found in the spectrum of untreated kaolinite (Fig. 2g and h).

A new very weak absorption was observed at 3601 cm$^{-1}$. This band was not detected in the IR spectra of samples which were evaporated from aqueous suspensions [1]. This absorption did not increase even after an ageing period of three years. A broad absorption was observed in the range 3000–3700 cm$^{-1}$, with a maximum at ~3400 cm$^{-1}$ which is characteristic for hydrogen bonded water molecules (Fig. 2b–g).

The most striking effect of grinding was the appearance of a new weak band at 3518 cm$^{-1}$ which after an ageing period of two years intensified and became sharp (Fig. 2f). A similar weak band was previously shown in the spectrum of intercalation complex B [1].

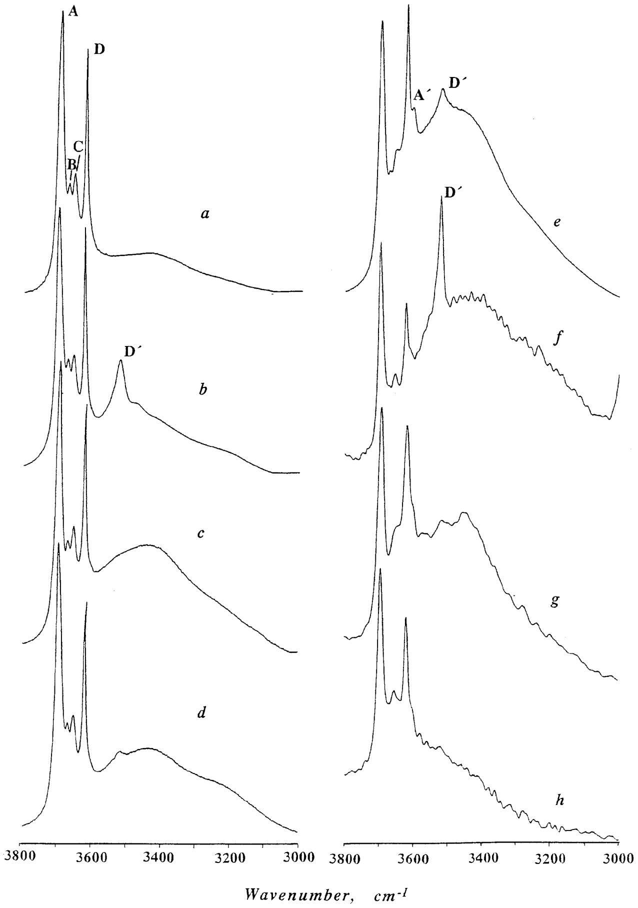

**Fig. 2** The OH stretching vibrations on region in the FTIR spectra of untreated kaolinite (a); a sample obtained by evaporating an aqueous suspension of kaolinite and CsF after one year ageing, unrinsed and rinsed with water (curves b and c, respectively); a mixture of kaolinite and CsF ground in a Retsch ball mill after one year ageing (d); a mixture of kaolinite and CsF ground in a mechanical Fisher mortar after one year ageing and two years ageing (curves e and f, respectively); sample (f) after heating at 200 and 260 °C (curves g and h, respectively)

A thermal treatment for 30 days at ~60 °C or 3 h at 200°C, or washing the ground kaolinite with water, resulted in the fading of the 3518 cm$^{-1}$ band (Fig. 2g). This band almost disappeared when the sample was heated for 3 h at ~260 °C (Fig. 2h). By these treatments the intercalated compound is evolved and the intercalation complex is decomposed.

Similar observations were obtained in spectra of CsF-kaolinite mixtures ground by a Retsch grinder (Fig. 2d). However, the changes in the kaolinite spectrum were very slight and the new band at 3518 cm$^{-1}$ was weak even after an ageing period of one year and a band at 3601 cm$^{-1}$ was not observed at all. No significant changes were observed

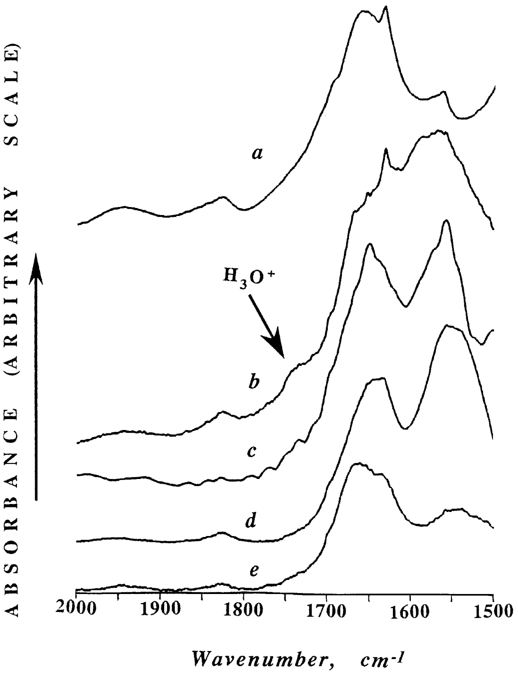

**Fig. 3** The water bending vibration region in the FTIR spectra of a sample obtained by evaporation of aqueous suspension of kaolinite and CsF after one year ageing, rinsed with water and unrinsed (curves a and b, respectively); a mixture of kaolinite and CsF ground in a mechanical Fisher mortar after two and one years ageing (curves c and d, respectively); a mixture of kaolinite and CsF ground in Retsch ball mill mortar after one year ageing (e)

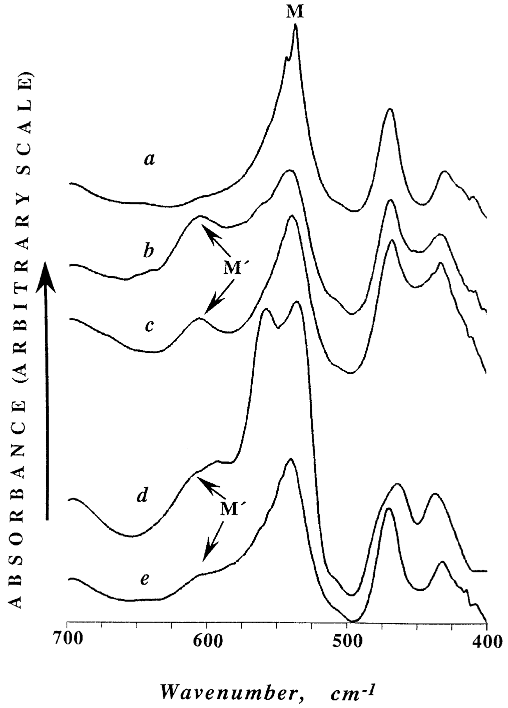

**Fig. 4** Deformation vibrations of Al–O and Si–O groups in the FTIR spectra of untreated kaolinite (a); a sample obtained by evaporating an aqueous suspension of kaolinite and CsF after one year ageing and after washing with water (curves b and c, respectively); a mixture of kaolinite and CsF ground in mechanical Fisher mortar after two years ageing (d); a mixture of kaolinite and CsF ground in Retsch ball mill after one year ageing (e)

in the spectrum of kaolinite after manual grinding with CsF.

In Fig. 3 the $H_2O$ deformation bands in the IR spectrum of an aged Fisher ground mixture is depicted. For comparison spectra of intercalation complex A and B are also shown. Figure 3d shows that the water band in the Fisher ground sample after one year ageing is very broad, extending between 1630 and 1650 $cm^{-1}$ and a shoulder at 1655 $cm^{-1}$. After longer ageing periods absorption at 1655 $cm^{-1}$ becomes the principal water band. Complexes A and B show a sharp band at 1630 $cm^{-1}$ (free water). Complex A shows a broad absorption at 1655–1670 $cm^{-1}$ (Fig. 3a) whereas complex B shows only trace absorptions in this region (Fig. 3b). The absorption at 1735 $cm^{-1}$ in the spectrum of complex B is due to $H_3O^+$ which is characteristic for this complex.

A sample ground by Retsch ball mill and aged one year showed $H_2O$ bands similar to those of the sample ground by Fisher mortar but the intensity of the bands was weak.

Al–OH deformation bands (H and I) in the region 900–940 $cm^{-1}$ were only slightly affected by the grinding process. They became broad but did not shift. Band J disappeared and band K at 756 $cm^{-1}$ almost disappeared.

Band M which is an Al–O deformation vibration with a contribution of Si–O, appears in the spectrum of kaolinite at 544 $cm^{-1}$ and is very intense (Fig. 4a). It is shifted to 537–540 $cm^{-1}$ and is weaker in the spectra of the ground samples by both grinder and of those obtained from the slurry. At the same time a new band appears at 606 $cm^{-1}$ (Fig. 4b–e). Upon washing the ground samples with distilled water, the band at 540 $cm^{-1}$ became more intense and that at 606 $cm^{-1}$ became very weak in comparison with band M (Fig. 4c). It is therefore suggested that this new band is a perturbed band M and is labelled here M′. This new band can be attributed to a vibration of an Al–F group which is formed by the replacement of surface OH by F.

The Fisher ground mixture showed weak absorption at 1410 –1450 and 1550 –1570 $cm^{-1}$, which are characteristic of carbonates. This indicated that $CO_2$ was absorbed by the basic system from the air to form a carbonate salt. As one would expect, these bands are weak in the spectrum of the mixture which was ground by the Retcsh ball mill.

## Discussion

### Intercalation complex type C

The peaks of kaolinite in the X-ray diffractograms of a sample which was ground by the Fisher mechanical mortar grinder became very weak and new peaks which characterize several cesium silicates and cesium aluminum silicates were detected. IR spectroscopy is not enough sensitive to detect these trace products and did not show new bands which could be attributed to the new products. After grinding and a two years ageing period most characteristic IR absorption bands of kaolinite persisted. This, together with the weakening of the 00*l* peaks in the XRD indicate that the kaolinite was delaminated but the TO layers were not destructed during this period. Some features of the IR spectrum which increase with ageing, are characteristic for an intercalation complex (type C). This complex differs from types A and B which were previously obtained through the evaporation of a kaolinite–CsF suspension. In contrast to complexes A and B no $d(0\,0\,1)$ spacing was determined in the XRD of complex C and it is therefore concluded that each particle is composed of non-oriented layers (Fig. 5).

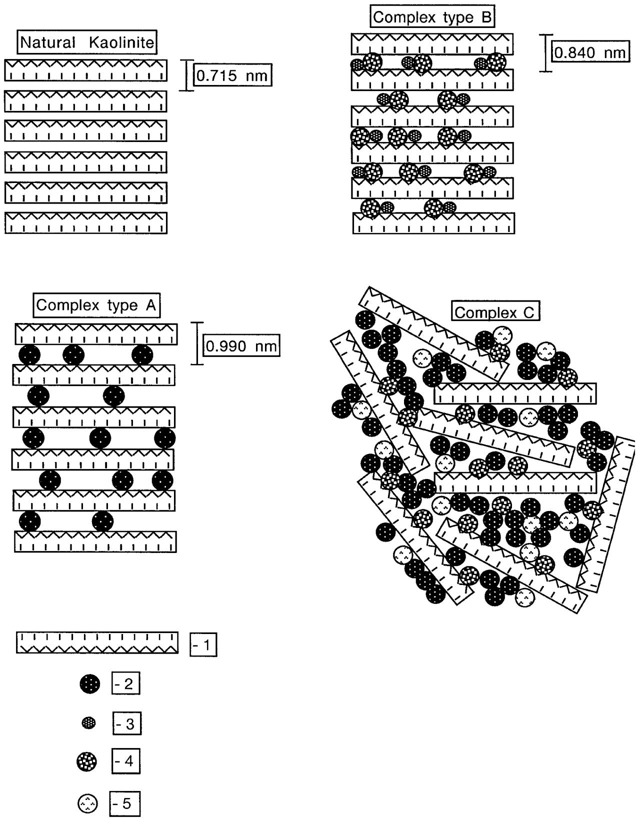

**Fig. 5** Models of the three complex structures: 1 – TO layers; 2 – $H_2O$ molecule; 3 – $H_3O^+$ cation; 4 – $F^-$ anion; 5 – $Cs^+$ cation

Cesium fluoride is hygroscopic and the mixture kaolinite–CsF adsorbed water from the atmosphere during grinding. Consequently, the grinding process can be regarded as a wet grinding. In the presence of excess $Cs^+$, which is a water structure breaker [7], the adsorbed water is non-structured and water molecules may form hydrogen bonds with active sites on the layers of delaminated kaolinite. This was previously observed during the intercalation of CsCl or CsBr into kaolinite [2, 7, 9]. The appearance of a new band at $\sim 3600\,\text{cm}^{-1}$ was attributed to the perturbation of band A, the stretching vibration of the inner-surface hydroxyls originally located at $3695\,\text{cm}^{-1}$. The extinction of band A and the appearance of the new band provided evidence for the interaction of water with exposed inner-surface hydroxyls. Furthermore, band H disappeared and band I shifted to lower frequencies; both are Al–OH deformation vibrations. In the present study a very weak absorption was observed at $3601\,\text{cm}^{-1}$ which can be attributed to perturbed band A, i.e. hydrogen bonded inner-surface hydroxyls, probably with intercalated water. However, this band is weak and may indicate that this water–clay mineral interaction takes place to a small extent only. In agreement with this conclusion bands H and I are not shifted but are only slightly broadened compared with the spectrum of untreated kaolinite.

Band D which represents the stretching vibration of inner hydroxyls slightly decreases immediately after grinding. This band further decreases with ageing. The extinction of band D, which was previously observed during the grinding of kaolinite with different alkali chlorides and bromides [9, 10], was supposed to be due to prototropy, which occurs as soon as the grinding process begins. However, in the present study the decrease of band D is accompanied by the appearance of a new band at $3518\,\text{cm}^{-1}$ which increases with ageing. Furthermore, the intensity of the $3518\,\text{cm}^{-1}$ band decreases and that of band D increases by removing CsF either by washing with water or by heating the sample at 260 °C. We assume that the new band at $3518\,\text{cm}^{-1}$ is a perturbed band D and that the perturbation results from hydrogen bonds which are formed between fluoride ions and inner OH groups. Since these OH groups are located in the plane which is common to the tetrahedral and octahedral sheets, hydrogen bonds between inner hydroxyls and fluorides may be formed only if the fluoride ions penetrated into the ditrigonal holes of the oxygen planes. The penetration of atoms into the tetrahedral sheets is known as keying.

Two reasons may account for the small extent of the H-bonds between inner-surface hydroxyls and intercalated water. (1) Some of the OH groups are substituted by

F groups during the treatment with CsF [11], leading to the fading of band M (Al–O plus Si–O vibration) and the appearance of a new band M′. Residual OH groups may form intralayer H-bonds with F groups and thus they do not form H-bonds with intercalated water molecules. (2) Fluoride ions which have penetrated into the ditrigonal holes and are H-bonded to inner hydroxyls have a strong inductive effect on the inner-surface hydroxyls and consequently the acid strength of the latter becomes too weak to form H-bonds with intercalated water.

Intercalation complex C is also formed in a Retsch grinder, but in relative small amounts. In this grinder kaolinite is only the slightly delaminated and only the delaminated fraction of the clay is ready to form complex type C. Manual grinding, although it leads to delamination, does not lead to the formation of an intercalation complex of type C.

## Intercalation complex type A

This complex can be identified by XRD. It has been detected in fresh evaporates of kaolinite–CsF suspensions after rinsing the treated kaolinite with a few drops of water. In our previous study a very weak peak at 0.99 nm was observed together with a very intense peak at 0.715 nm, indicating that only a small fraction of the kaolinite was intercalated. This complex was not detected in any of the diffractograms recorded after the different grinding techniques applied in the present study.

According to the IR spectrum this complex is hydrated. The characteristic bands of kaolinite, either the OH, the Al–OH or the Si–O, are not perturbed, indicating that there are no interactions between functional surface groups of the kaolinite (OH or Si–O groups) and adsorbed water molecules. The adsorbed water molecules form intermolecular H-bonds between themselves. Intercalation complex A should be similar to the 1.0 nm hydrated kaolinite which has been previously synthesized by Constanzo et al. [11, 12] by washing the DMSO intercalation complex with aqueous $NH_4F$. According to the calculations of Wolfe and Giese [13] the substituion of F for OH groups dramatically weakens the interlayer bonding of kaolinite. Each particle of the intercalated complex is composed of oriented layers with a $d(001)$ spacing of 0.99 nm (Fig. 5).

## Intercalation complex type B

This complex can be identified by XRD. It has been detected in evaporates of kaolinite–CsF suspensions which were not rinsed from excess salt. In our previous publication we showed by X-ray study that very short after the beginning of the interaction between kaolinite and CsF the 0.715 nm peak became weak. After two months a new peak appeared at 0.830 nm which characterizes the intercalation complex B [1]. The intensity of the 0.830 nm peak relative to that of the 0.715 nm peak increases with time. The 0.830 nm peak disappeared when the sample was washed with water indicating that the intercalated compound was water soluble. Furthermore, this peak also disappeared when the sample was heated at 260 °C, indicating that the intercalated compounds was volatile. With a $d$-spacing of 0.830 nm the keying of $F^-$ is obvious but $Cs^+$ cannot be located in the interlayer space. We therefore suggested that HF (or $[H(H_2O)_x]$ F) was the intercalated compound [1]. Indeed, the infrared spectrum of this complex recorded either of freshly prepared samples or after different ageing periods showed a weak broad absorption at 1730 –1740 $cm^{-1}$. This band disappeared when the sample was heated at 260 °C or washed with water, indicating that HF was evolved.

In our previous study we showed that a sharp band at 3518 $cm^{-1}$ appeared in the spectrum of complex B. In the present study it has been demonstrated that this band is a perturbed stretching vibration of inner hydroxyls (band D) and was therefore labelled by D′. This perturbation occurs as a result of the keying of intercalated $F^-$ and the formation of the hydrogen bonds between the inner hydroxyls and the fluoride ions. Each particle of the intercalation complex is composed of oriented layers with a $d(001)$ spacing of 0.830 nm (Fig. 5).

## The mechanochemical interactions of kaolinite and CsF

In the present study different products were identified by IR and X-ray methods after treating the kaolinite–CsF mixture by the different grinding techniques. The Retsch ball mill almost did not delaminate the clay crystal in contrast to the manual or Fisher mortar grinding techniques. It seems that the reason for the different results are the different active forces in the grinding processes. The delamination of the voluminous book-like crystals was observed after the manual and the Fisher mortar grindings because the direction of forces in these techniques are normal and tangential simultaneously [14]. Increasing shearing stress and treatment time in the Fisher grinder resulted in decreasing particle size and increasing crystal and surface defects. After long ageing period very intensive reaction between small particles of kaolinite and CsF or $CsF \cdot xH_2O$, resulted in the formation of intercalation complex C as well as the formation of cesium silicates and cesium aluminum silicates. This was not the case in the manual grinding.

In contrast to these techniques, the direction of the forces in the Retsch ball mill is mainly normal. Due to the impact of the balls there is almost no delamination of the kaolinite crystals in this grinder and the intercalation process is very slow and small. There is only a weak band D′ at 3518 $\text{cm}^{-1}$ (complex C) in the IR spectrum after a long ageing period. Some medium peaks of cesium silicates and cesium aluminum silicates were observed in the XRD.

**Acknowledgement** Partial financial support of the Internal Funds of the Hebrew University of Jerusalem is acknowledged. I.L. is also grateful to the Ministry of Absorption of the Government of Israel for financial support.

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