

Dehydroxylation of muscovite: study of quenched samples

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Abstract Despite extensive research, many aspects of the changes that occur in muscovite on heating remain unclear. This study concentrated on quenched samples, to supplement data obtained in situ by previous investigators, which seemed to suggest that structural changes precede dehydroxylation. Samples of muscovite were heated to different temperatures at various heating rates and soaking times, rapidly quenched in air and cooled in a dry atmosphere. Infrared spectra (IR) and X-ray diffraction patterns (XRD) were recorded. Aliquots of a single flake, about 20–40 μm thick, were used for each set of experiments. Thermal changes in these flakes, heated at 10 $^{\circ}\text{C}/\text{min}$, were almost completely reversed at ≤ 780 $^{\circ}\text{C}$. Above that temperature, or on more prolonged heating, XRD showed two phases, residual muscovite and dehydroxylated muscovite, with basal spacings ranging between ~ 19.90 – 19.94 and ~ 20.06 – 20.14 \AA , respectively. As dehydroxylation progressed, the basal spacings of all residual muscovites were reduced relative to those of the original samples. The decreases were small, but consistent. The OH stretching bands in IR spectra of the muscovites showed four maxima. After partial dehydroxylation, the frequencies of these maxima remained almost unchanged, but the intensities of the two lower-frequency components were reduced more rapidly than those of the other two. Changes were also observed in the 900- to 600- cm^{-1} region of the spectra, reflecting changes in

the configuration of the tetrahedral sheets. The structure of the dehydroxylated phase changed with temperature. The trends are general, but the details are sample specific. The decrease in basal spacings of residual muscovite and the corresponding changes in the IR spectra, supported by results obtained in situ by previous investigators, indicate that dehydroxylation proceeds through one or more intermediate phases. This differs from dehydroxylation of other phyllosilicates reported in the literature, which do not form an intermediate phase.

Keywords Muscovite · Partial dehydroxylation · IR spectra · XRD · Reaction mechanism

Introduction

Changes that occur in phyllosilicates in general and in muscovite in particular have been studied extensively due to their importance in natural processes and in industrial applications. Muscovite is widely used for its electrical, mechanical and physical properties. On heating phyllosilicates, a temperature is reached where H_2O molecules are liberated. Phyllosilicates therefore play an important role in geochemical processes, particularly in low-grade metamorphism. Various studies have connected dehydration of hydrous minerals with seismic activity. Muscovite is used for $^{40}\text{Ar}/^{39}\text{Ar}$ dating; Ar is released in the course of dehydroxylation.

Chemically, the process of phyllosilicate dehydroxylation can be summarized as $2\text{OH}^- \rightarrow \text{H}_2\text{O} + \text{O}^{2-}$, but the mechanism and kinetics of the reaction are not yet completely understood. Different models have been proposed, most of which postulate the formation of water molecules by the condensation of two hydroxyl groups. Loss of water

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by diffusion is assumed to be the rate-limiting step (e.g. Tokiwa and Nakashima 2010a). Zhang et al. (2010a, b) raised doubts about these models, because they failed to detect H₂O molecules in high-precision in situ IR spectra of heated muscovite flakes. They concluded that dehydroxylation is a complex process that involves conversion of OH species.

Udagawa et al. (1974) determined the structure of dehydroxylated muscovite, where cations that were 6-coordinated by four oxygen atoms and two hydroxyl groups in muscovite became 5-coordinated by oxygen atoms only, similar to the structure of pyrophyllite dehydroxylate (Wardle and Brindley 1972). Mazzucato et al. (1999) found that muscovite and its dehydroxylated form always appear as two separate phases. Guggenheim et al. (1987) postulated that dehydroxylation of muscovite proceeds through a series of intermediate structures. Dehydroxylation of pyrophyllite, illite and other clay minerals was found to occur by a homogeneous mechanism, resulting in mixtures of unchanged and completely dehydroxylated layers in different proportions, without intermediate structures (Drits et al. 2011, 2012a, b).

Vedder and Wilkins (1969) noted small changes in shape of the broad OH stretching absorption band in a quenched sample of partially dehydroxylated muscovite, without further comments. Zhang et al. (2010a) observed a shift of the maximum of the band from about 3627 cm⁻¹ to near 3645 cm⁻¹ in muscovite that was quenched after annealing for about 23 h at 627 °C.

Fripiat et al. (1963) examined in situ changes in IR spectra of a muscovite flake on heating from RT to 700 °C. They regarded the decrease in the frequency of the OH absorption from 3640 to 3620 cm⁻¹ with increasing temperature as almost linear. However, the plot of frequency against temperature (Fig. 7 of Fripiat et al.) clearly shows a small decrease in slope above 600 °C.

Zhang et al. (2010a, b) studied thermal changes in the IR spectra of two muscovite flakes in considerable detail. Plots of band areas and of peak positions of the OH absorptions versus temperature recorded in situ show breaks in slope at 614 and 670 °C and values approaching zero at 665 and 770 °C for the two samples, respectively (Zhang et al. 2010a). The authors attributed changes in these temperature ranges to changes in local environment and loss of OH groups.

Tokiwa and Nakashima (2010b) also examined changes in OH absorption in IR spectra of a muscovite flake on heating. They observed a sharp decrease in the absorbance of the OH stretching band at about 650 °C, which, like Zhang et al. (2010a), they attributed to the onset of dehydroxylation. However, in contrast to Zhang et al., their spectra show that OH absorptions persisted in a sample heated to 900 °C.

Muscovite dehydroxylate does not contain hydroxyl groups. Changes in OH bands therefore indicate that modifications occurred in the structure of the remaining muscovite, either before dehydroxylation or in the course of partial dehydroxylation. Guggenheim et al. (1987) related the shift of the OH band on heating to weakening of the OH bond.

XRD studies of heated muscovite performed in situ also suggest that changes other than mere expansion of the structure may occur below the dehydroxylation temperature. Guggenheim et al. (1987) heated a muscovite flake of 30 μm thickness to 1000 °C for a minimum of 12 h at each temperature. Their plot of *c* versus temperature (Fig. 2c of Guggenheim et al. 1987) was regarded as linear up to about 850 °C, where a sudden break occurred, which was attributed to the onset of dehydroxylation. However, a slight downward inflection of the graph can actually be detected at about 650 °C.

Mazzucato et al. (1999) noted an abrupt decrease in expansion coefficient of *c* of a muscovite powder (<40 μm) at about 700 °C. The dehydroxylated phase appeared simultaneously. They suggested that the decrease in the coefficient may be caused by the activation of new vibration modes in the low-temperature phase during the transformation.

In a synchrotron study of muscovite heated in situ, Gemmi et al. (2008) distinguished three regions: a low-temperature region where the sample has a mica structure, a region where dehydroxylation is in progress and a region where dehydroxylation is complete. The dehydroxylation region is characterized by irregular changes in cell parameters.

Neutron diffraction patterns of phengite cell parameter evolution with temperature in situ (Mookherjee et al. 2001) showed a decrease in expansion coefficients between 500 and 600 °C, while the H-occupancy remained unity to 700 °C, the temperature limit of the experiments. The anisotropic vibrations of the O–H group increased with temperature, but the bonds were not disrupted.

The cell parameters of dehydroxylated muscovite are larger than those of the starting material (Eberhart 1963; Nicol 1964; Udagawa et al. 1974; Gemmi et al. 2008). A decrease in the slope of the graphs of *c* versus temperature cannot, therefore, be attributed to the formation of mixtures or intercalates of muscovite and the fully dehydroxylated form.

The decrease in the expansion coefficient of *c* beginning at about 650–700 °C and the changes in IR spectra at similar temperatures recorded in situ indicate that structural changes other than expansion occur in this temperature range. Differences in the IR spectra between those of the original muscovites and quenched samples after thermal treatment observed by Vedder and Wilkins (1969) and

Zhang et al. (2010a) suggest that some structural changes persist after cooling.

Interpretation of the experimental data frequently requires knowledge of the onset of dehydroxylation. The course of dehydroxylation depends on many factors. Grim et al. (1937) warned that dehydration curves should not be used as diagnostic characteristics of minerals unless particle size is considered. Kodama and Brydon (1968), using TG and DTA, clearly demonstrated that a decrease in particle size of muscovite reduced the dehydroxylation temperature. Gridi-Bennadji and Blanchart (2007) and Gridi-Bennadji et al. (2008) presented TG and DTA curves of a muscovite flake and of the same sample in powder form. Muscovite flakes heated at 10 °C/min showed no appreciable weight loss below about 750 °C, where an abrupt loss commences, as previously shown by Mackenzie et al. (1987). In contrast, thermal analysis curves of muscovite powder are bimodal and weight loss is observed over a wide temperature range. Thermal analysis of powders should, therefore, not be used as a basis for interpretation of the dehydroxylation process of single flakes, as sometimes appears in the literature (e.g. Guggenheim et al. 1987; Brigatti and Guggenheim 2002). The thickness of the flakes, crystal perfection, heterogeneity of the samples, heating rate and the surrounding atmosphere affect dehydroxylation kinetics.

The question arises: Which criterion can be used to determine the onset of dehydroxylation? The total area of absorption of OH stretching vibrations in IR spectra has been used to monitor dehydroxylation in quenched samples (Gaines and Vedder 1964; Vedder and Wilkins 1969; Rouxhet 1970). This presupposes that either no change in shape occurs on heating or that the absorption coefficients of vibrations in this region are independent of wavelength. In studies carried out, in situ effects of structural changes may overlap those due to dehydroxylation (Zhang et al. 2010a; Tokiwa and Nakashima 2010b). Moreover, an in situ study of sericite demonstrated that changes occurred in height and area of OH vibrations in IR spectra on cooling from 300 to 30 K (Zhang et al. 2007). Because changes in OH concentration can be ruled out at such low temperatures, the authors concluded that absorption coefficients calibrated at room temperature cannot be used for the determination of hydroxyl contents at other temperatures.

A decrease in the intensity of the XRD diffractions of muscovite or the appearance of diffractions attributable to the dehydroxylated form is also not entirely reliable criteria, due to possible structural changes in the starting material and poor crystallinity of the product.

The purpose of the present study is to obtain further information about different stages of the dehydroxylation

of muscovite from partially dehydroxylated, quenched samples. In particular, it addresses the question whether experimental evidence can be obtained for the formation of intermediate structures, which seemed to be indicated by studies of samples in situ and after quenching reported in the literature.

Materials and methods

Flakes from eight different samples of muscovite were studied. Sample MU3846 from Siberian pegmatites is from the collection of Koval and Kovalenko. All other samples are from the mineral collection of the Institute of Earth Sciences of the Hebrew University of Jerusalem. XRD analysis of powdered samples established that they are 2M₁ muscovite. Their chemical composition was determined at the Krueger Family Center for Nanoscience and Technology, The Hebrew University, on a Magellan XHR SEM, by EDS, method EDX (15 Kv), using a muscovite standard. Mean values were obtained from 3 to 5 different regions of each flake. The calculated cation composition of the samples is shown in Table 1.

Flakes of muscovite, about 20 × 30 mm in area and 20–40 μm thickness, were used for the experiments. These were sufficiently robust to endure repeated heating and cooling cycles. The flakes were subjected to various heat treatments, quenched rapidly in air and cooled in a dry atmosphere, unless otherwise stated.

Protocol A

Samples were heated at 10 °C/min up to 780 °C, and IR spectra and XRD patterns were recorded immediately. The samples were then stored over water vapour at room temperature and at 63 °C for various periods of time and re-examined.

Table 1 Cation composition of samples based on O₁₀(OH,F)₂

Sample	Formula	F (%)
Mu3846 ^a	K _{0.84} Na _{0.14} Ca _{0.02} (Al _{1.95} Fe _{0.08} Mg _{0.04})[Si _{2.97} Al _{1.03}]	0.08
Mu9169	K _{0.93} Na _{0.09} Ca _{0.03} (Al _{1.80} Fe _{0.12} Mg _{0.04})[Si _{2.90} Al _{1.10}]	0.18
Mu1183	K _{0.90} Na _{0.12} Ca _{0.01} (Al _{1.85} Fe _{0.08} Mg _{0.03})[Si _{2.90} Al _{1.09}]	0.07
Mu5594	K _{0.90} Na _{0.13} Ca _{0.00} (Al _{1.83} Fe _{0.08} Mg _{0.04})[Si _{2.94} Al _{1.06}]	0.09
Mu61928	K _{0.94} Na _{0.10} Ca _{0.02} (Al _{1.61} Fe _{0.25} Mg _{0.07})[Si _{2.94} Al _{1.06}]	0.17
Mu62913	K _{0.96} Na _{0.07} Ca _{0.02} (Al _{1.74} Fe _{0.15} Mg _{0.07})[Si _{2.94} Al _{1.02}]	0.09
Mu63112	K _{0.95} Na _{0.14} Ca _{0.01} (Al _{1.68} Fe _{0.18} Mg _{0.05})[Si _{2.91} Al _{1.09}]	0.13
Mu9061 ^b	K _{0.99} Na _{0.01} (Al _{1.85} Fe _{0.08} ³⁺ Fe _{0.02} ²⁺ Mg _{0.05})[Si _{3.05} Al _{0.95}]	n.d.

^a Lapides et al. (1977)

^b Heller-Kallai and Rozenson (1980)

Protocol B

Samples were heated stepwise at a rate of 10 °C/min.

Protocol C

Samples were heated to different temperatures and soaked for 2.5 h at each step.

In Protocols B and C, samples were quenched at various stages of the heat treatment. Aliquots of the same flakes were used throughout any one series of experiments. IR spectra were recorded immediately, fragments of the flakes, about $3 \times 5 \text{ mm}^2$, were reserved for XRD, and heating was resumed.

Protocol D

Samples were heated to 850 °C within about 70 min.

Additional samples were heated as specified in the text.

XRD patterns were recorded in Bragg–Brentano mode, using a Phillips automatic diffractometer (PW1710) with monochromated $\text{CuK}\alpha$ radiation, continuous scanning, step size $0.02^\circ/2\theta$, 0.5 s/step. Peak shapes were studied using the programme PC-APD, version 3.6. Aliquots of the flakes were mounted on vaseline-covered glass slides. Reproducibility of the measurements in the region studied in detail ($\sim 1.2\text{--}1.7 \text{ \AA}$), tested by repeated withdrawal and reinsertion of the slides in different positions, was $\pm 0.0003 \text{ \AA}$.

Transmission spectra of the flakes were obtained with a Bruker FTIR spectrophotometer (model Tensor 27), OPUS, DTGS detector, KBr beam splitter, ceramic source, nominal wavenumber resolution 4 cm^{-1} , 32 scans. Spectra were studied using the programme ORIGIN-7.

Results and interpretation

Thermal treatment A: When does dehydroxylation begin?

To establish the temperature at which flakes of muscovite of 20–40 μ thickness begin to dehydroxylate, samples were heated to 780 °C at 10 °C/min and quenched. This heating rate is standard procedure in thermal analysis and was adopted in previous studies of muscovite dehydroxylation by various physico-chemical methods, including in situ IR spectra (Zhang et al. 2010a, b; Tokiwai and Nakashima 2010a).

Comparison of the IR spectra of untreated samples (Mu9169, Mu5594, Mu63112, Mu62913, Mu1183, Mu61928) with those of the corresponding heated samples showed no differences. XRD of some of the samples showed very weak additional diffractions with basal

spacings of 20.14–20.17 \AA , corresponding to the dehydroxylated form. No changes were observed after exposure of these samples to water vapour at 63 °C for 8 days or to ambient conditions for 1 month.

It appears that under this thermal regime structural changes that had occurred on heating were almost completely reversed on quenching. It may be inferred that loss of hydroxyl groups from thin flakes of muscovite heated in air at 10 °C/min commences at $\sim 780 \text{ }^\circ\text{C}$.

Protocols B and C: partially dehydroxylated samples

Infrared spectra

Two regions of the IR spectra were studied, the OH stretching band between 3670 and 3620 cm^{-1} and absorptions ranging from 900 to 600 cm^{-1} . Thinner flakes are required for the analysis of Si–O vibrations in the 1100–900 cm^{-1} range, to avoid oversaturation of the detector. However, because the thickness of the flakes affects the rate of dehydroxylation, results obtained with flakes of different thickness are not directly comparable. We therefore used only a single flake, without manipulation, for each complete series. Thus, the study of the IR spectra was necessarily confined to two spectral regions.

All samples show a broad, asymmetric band due to OH stretching absorptions, with a maximum between 3627 and 3633 cm^{-1} . In addition to the maximum, the bands show two or three shoulders, with mean frequencies that fall within a narrow range: 3654–3660, 3647–3650 and 3620–3622 cm^{-1} . This is in agreement with data reported in the literature (e.g. Saksena 1964). Synthetic muscovite showed only three bands, at 3659, 3643 and 3625 cm^{-1} (Langer et al. 1981) or 3661, 3645 and 3626 cm^{-1} (Besson and Drits 1997). These are due to the effect of different Al/Si distribution in the tetrahedral sheets (Langer et al. 1981; Besson and Drits 1997) and to octahedral substitution (Farmer 1974). The presence of four bands in natural samples as opposed to three in synthetic ones must be attributed to the effect of octahedral substituents. The differences in position and the relative intensities of the four components in different samples are due to the combined effect of the composition of tetrahedral and octahedral sheets.

If muscovite were completely dehydroxylated in a single step, without structural modifications, a decrease in band area without a change in shape would be expected.

Figures 1, 2, 3 and 4 present spectra of samples at different stages of thermal treatments B and C, respectively. The absorption bands show maxima with two or more shoulders, with frequencies that remained almost constant throughout the heat treatments, while their relative intensities were changed. Attempts at resolving the spectra showed that the results were dependent on the

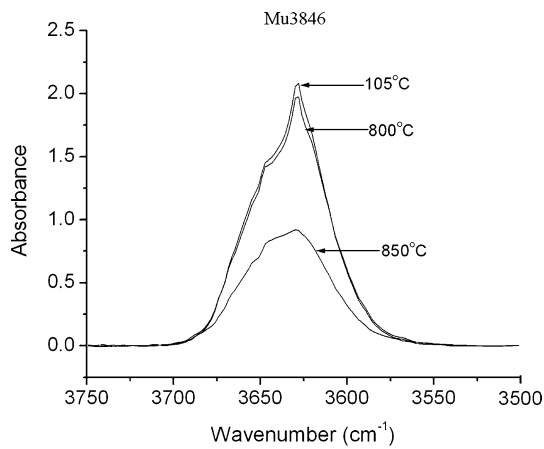


Fig. 1 Changes in OH stretching band after heating (Protocol B)

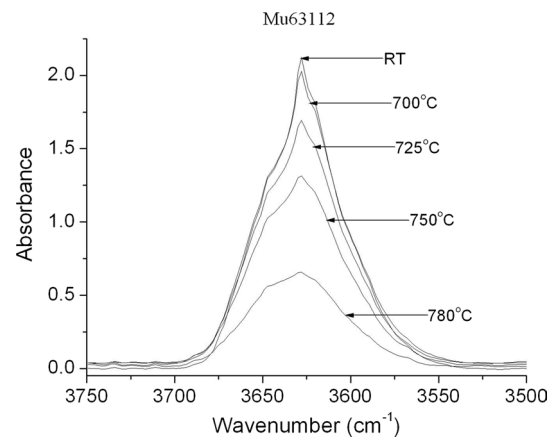


Fig. 4 Changes in OH stretching band after heating (Protocol C)

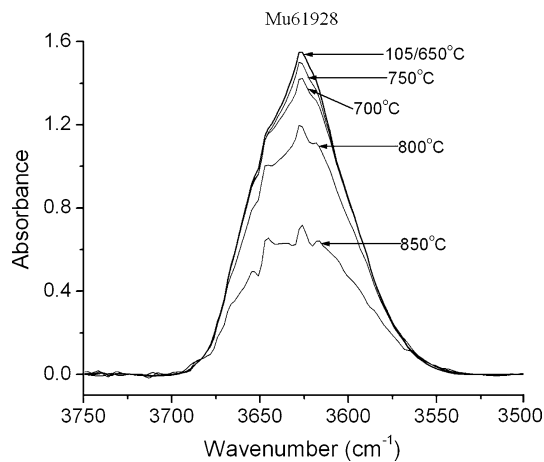


Fig. 2 Changes in OH stretching band after heating (Protocol B)

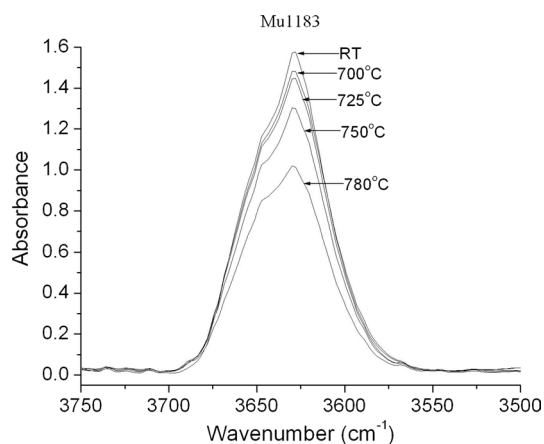


Fig. 3 Changes in OH stretching band after heating (Protocol C)

initial assumptions, such as shape and width of the bands and the distribution function. More consistent results were obtained by direct measurement of the absorption

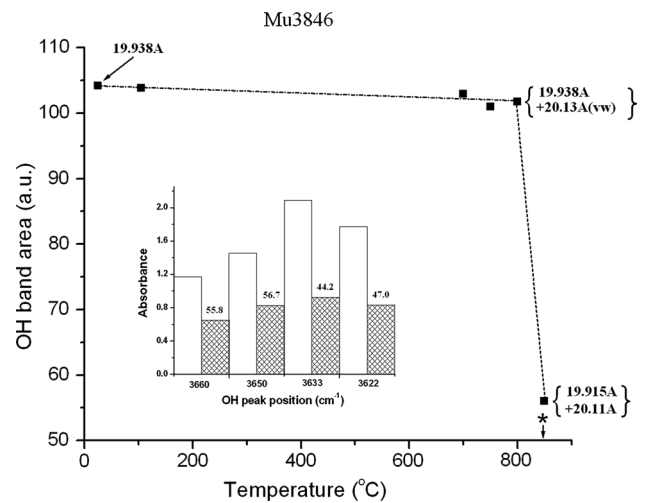


Fig. 5 OH band area after heating (Protocol B). Basal spacings (Å) of residual muscovite and dehydroxylate (where present) are shown on the right. Inset peak intensity of the four components: *blank*—original, *cross-hatched*—at the end of heat treatment. The % decrease is marked. The asterisk on the abscissa marks the temperature at which changes begin to occur in the 900- to 600-cm⁻¹ region

intensities of the maxima and of the shoulders at the observed frequencies.

Figures 5, 6, 7 and 8 correspond to Figs. 1, 2, 3 and 4, respectively. They present the decrease in the total area of the OH stretching bands of the samples on heating. The insets show the heights of the individual peaks of the original samples and those observed at the end of the thermal treatments, together with the % intensity of each remaining peak.

All the samples examined, whatever the thermal regime, display a common feature: the two lower-frequency absorptions decrease more rapidly than the higher-frequency components. The insets in Figs. 5, 6, 7 and 8 only show

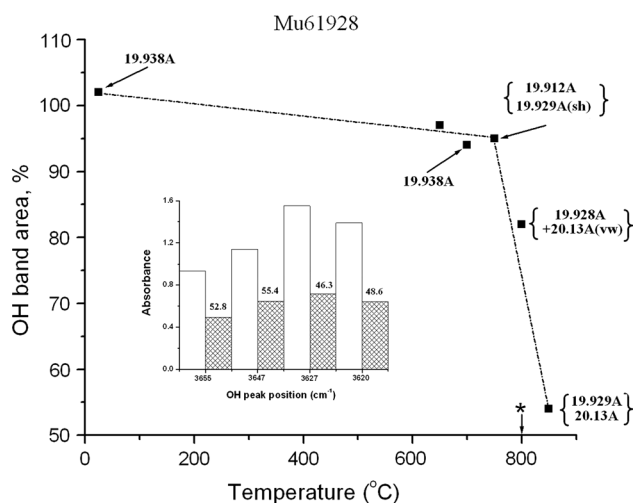


Fig. 6 Legend as for Fig. 5

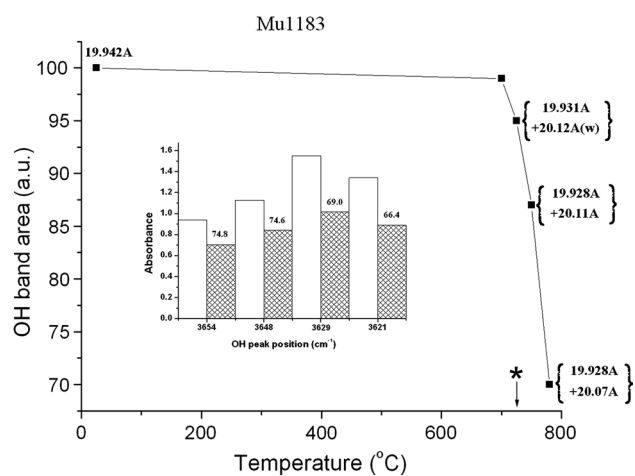


Fig. 7 OH band area after heating (Protocol C). Basal spacings (Å) of residual muscovite and dehydroxylate (where present) are shown on the right. Inset peak intensity of the four components: *blank*—original, *cross-hatched*—at the end of heat treatment. The % decrease is marked. The asterisk on the abscissa marks the temperature at which changes begin to occur in the 900- to 600-cm⁻¹ region

the changes observed at the end of the heating regimes, but throughout the dehydroxylation process, the lower-frequency components, which correspond to the more strongly hydrogen-bonded OH groups, decreased in preference to the higher-frequency ones.

Absorption bands between 900 and 600 cm⁻¹ have been assigned to various motions of the Al–O–Si tetrahedra (Farmer and Russell 1964; Vedder and Wilkins 1969; Zhang et al. 2010a). The most intense absorption, at about 751 cm⁻¹, was assigned to Al–O–Si in-plane vibrations (Farmer 1974). These absorptions are expected to be sensitive to structural changes in muscovite.

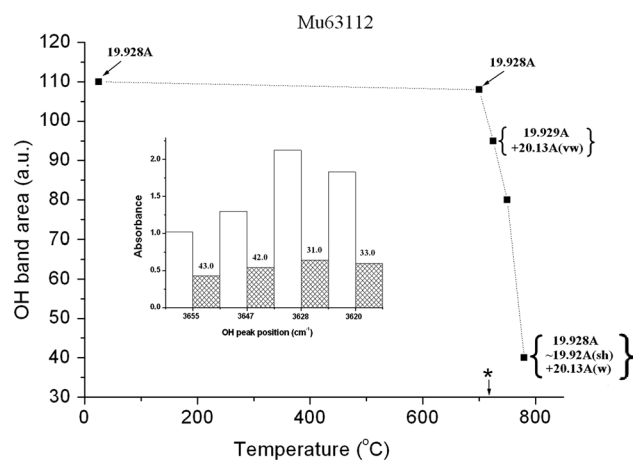


Fig. 8 Legend as for Fig. 7

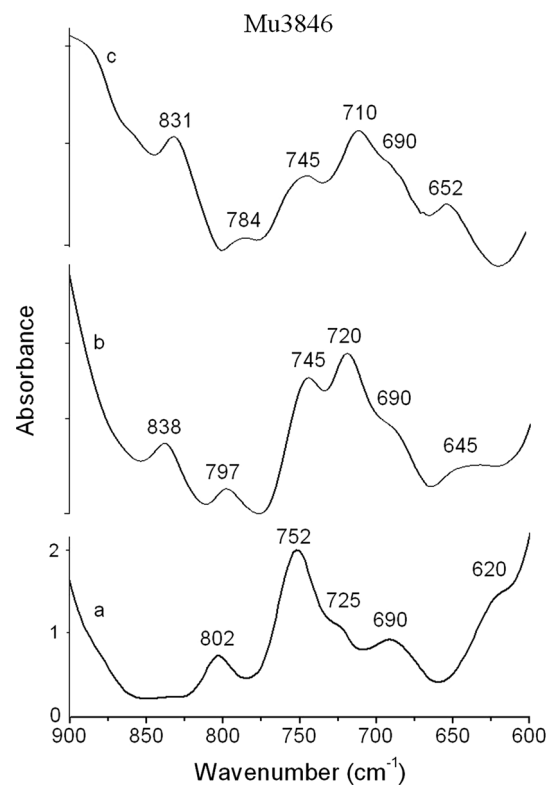


Fig. 9 Changes in 900- to 600-cm⁻¹ spectral region a original; b heated to 850 °C at 10 °C/min (partially dehydroxylated); and c heated at 850 °C for 2 h (fully dehydroxylated)

Absorptions due to the fully dehydroxylated form also occur in this region. Vedder and Wilkins (1969) observed a shift of the bands from 750 to 685 cm⁻¹ in muscovite to 715 and 655 cm⁻¹, respectively, in the fully dehydroxylated species. In addition, a new band appeared at 830 cm⁻¹, which they attributed to a change in tilt of the SiO₄ and AlO₄ tetrahedra.

Figure 9 compares this spectral region of sample Mu3846 with that of the partially dehydroxylated sample obtained after heating to 850 °C (see Fig. 5) and of the fully dehydroxylated sample. An intense band appears at 752 cm⁻¹ in the spectrum of muscovite (Fig. 9a) and at 710 cm⁻¹ in that of the dehydroxylate (Fig. 9c), as was observed by Vedder and Wilkins (1969). The spectrum of partially dehydroxylated muscovite (Fig. 9b) differs appreciably from that of the original and of the completely dehydroxylated sample. Bands appear at 745 and 726 cm⁻¹, and the broad band at 620 cm⁻¹ observed in the spectrum of the original muscovite is absent. Other bands are shifted. On partial dehydroxylation, a weak absorption appears at 838 cm⁻¹, which increased in intensity with increasing dehydroxylation. After complete dehydroxylation, the frequency was reduced to 831 cm⁻¹. Similar spectral changes were observed in all the other samples studied. The temperatures at which changes were first observed in this spectral region are marked by an asterisk on the abscissa in Figs. 5, 6, 7 and 8. The frequencies of the absorption maxima differ slightly in different samples.

The absorptions at 710 and 651 cm⁻¹ observed in the spectrum of fully dehydroxylated muscovite are absent in that of the partially dehydroxylated sample. Overlap with the spectrum of unchanged muscovite cannot explain this, nor changes in other features of the spectrum. It appears that the configuration of the tetrahedral network changes with temperature.

All the absorption bands in this spectral region observed in the original muscovite were modified in the partially dehydroxylated form. Attempts to decompose the spectrum (Fig. 9b), and in particular, the band at 745 cm⁻¹ into two components, one of which corresponds to the 752 cm⁻¹ band of the original muscovite, failed with this and with other samples. Zhang et al. (2010a) observed a similar progressive decrease in frequency and intensity of the 750 cm⁻¹ band with temperature *in situ*. Although the evidence is not entirely conclusive, the changes in this spectral region indicate that the residual muscovite does not contain a completely unchanged muscovite component.

Basal spacings

The original muscovite samples show sharp basal diffractions with spacings ranging from ~19.93 to 19.95 Å. These remained unchanged on heating to 780 °C at 10 °C/min. After more intense heat treatment, two sets of broad basal diffractions appeared, attributed to muscovite dehydroxylate with an approximately 20.1 Å spacing, as found by previous investigators, and to residual muscovite, with basal spacings equal to or lower than those of the original samples. The diffractions due to dehydroxylate were very broad, but became much sharper after 3 h soaking

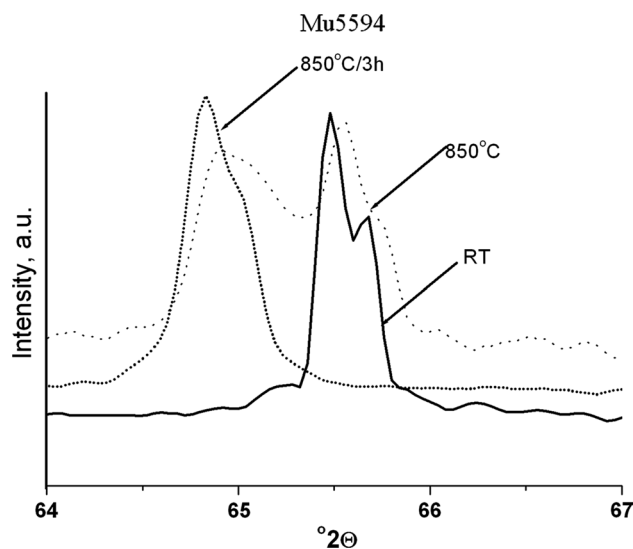


Fig. 10 (0014) diffraction ($K\alpha_1$, $K\alpha_2$) of muscovite flake: *full line*—original; *dashed line*—partially dehydroxylated; *dotted line*—fully dehydroxylated

at 850 °C, when diffractions of residual muscovite were absent (Fig. 10).

Accurate measurement of basal spacings of residual muscovite is difficult because of overlap with the very broad, temperature-dependent dehydroxylate diffractions. Precise measurements were therefore confined to the high-angle diffractions (0012)–(0016), and d_{001} was deduced from these. Table 2 presents the results obtained with a set of samples heated up to 850 °C (Protocol D). The small shifts in peak positions, which exceed the errors of measurement (± 0.0003 Å), were observed consistently with all eight samples. The precise basal spacings observed after heating are specific for each flake. Different flakes, or even different areas of the same flake, similarly treated, may give different results due to variations in sample thickness and perfection.

Basal spacings of residual muscovite and of the dehydroxylate at different stages of the thermal treatments are shown in Figs. 5, 6, 7 and 8. The decrease in basal spacings of residual muscovite occurred progressively, though not always monotonically.

The diffractions of residual muscovite are broader than those of the original samples and are frequently unsymmetrical (Fig. 10). That this is not an artefact caused by changes in geometry due to the delamination of the samples is shown by the high reproducibility of the measurements, which were independent of the orientation of the slides on the diffractometer stage. Moreover, the diffractions due to dehydroxylate became progressively sharper on heating. The asymmetry of some of the diffractions suggests that residual muscovite may be a composite phase.

Table 2 d_{001} (Å) of samples at room temperature and after heating to 850 °C

Sample	Mu3846	Mu5594	Mu62913	Mu1183	Mu9169	Mu63112	Mu9061	Mu61928
RT	19.938	19.943	19.929	19.942	19.948	19.928	19.939	19.938
850 °C								
M	19.904	19.914	19.914	19.916	19.937	19.921	19.911	19.929
D	20.10	20.11	20.11	20.10	20.06	20.14	20.13	20.13

M muscovite, *D* dehydroxylate

Due to the variability of peak position and shape of the diffractions with temperature, both of the partially and fully dehydroxylated muscovite, the quantity of each phase present could not be determined. A rough estimate of the relative degree of dehydroxylation of each sample is based on comparison of the intensities of the basal diffractions of the dehydroxylate with those of the residual muscovite. With samples soaked at 850 °C for 1 h under identical conditions, dehydroxylation decreased in the following order:

Mu61928 > Mu1183 > Mu9169 > Mu5594
> Mu3846 > Mu9061 > Mu63112.

However, this order varied with different thermal treatments. No correlation between these observations and the chemical composition of the samples could be detected.

Discussion

Changes caused by heating muscovite to 780 °C at the rate of 10 °C/min (Protocol A) were almost completely reversed on quenching. Minor amounts of fully dehydroxylated muscovite were detected in some samples. These results are in agreement with thermo-gravimetric analyses, which showed that, at this heating rate, dehydroxylation of thin flakes of muscovite commences at about 750–780 °C (Mackenzie et al. 1987; Gridi-Bennadji et al. 2008 and our unpublished data). The possibility of rehydroxylation of fully dehydroxylated muscovite on brief exposure to air may be discounted. Samples containing dehydroxylate remained unchanged after prolonged exposure to water vapour. Heller et al. (1962) reported that at atmospheric pressure, muscovite powder was not rehydroxylated on soaking in a stream of wet N₂ at 875 °C.

After more intense thermal treatment (Protocols B, C and D), XRD of the samples showed two sets of basal diffractions, ranging from 19.90 to 19.94 and from 20.06 to 20.14 Å, which were assigned to residual muscovite and to the fully dehydroxylated form, respectively. The basal spacings of residual muscovite were either unchanged after quenching or lower than those of the starting material. All the samples showed a decrease in basal spacings of the residual muscovite after sufficiently energetic heat treatment (Table 2). Because the basal spacings of

muscovite dehydroxylate are larger than those of muscovite (Eberhart 1963; Nicol 1964; Udagawa et al. 1974; Gemmi et al. 2008), the observed reduction in basal spacings cannot be attributed either to a mechanical mixture of the two phases or, according to Mering's first rule (Mering 1949), to interstratification of unchanged and dehydroxylated layers. Oxidation of Fe²⁺ may cause a decrease in basal spacings. However, sample Mu9061, which contains only a minor amount of Fe²⁺ (Table 1), showed a decrease in basal spacing after heating, similar to that of the other samples (Table 2). Moreover, Mössbauer studies revealed that iron oxidation occurs in the early stages of dehydroxylation (Heller-Kallai and Rozenson 1980; Mackenzie et al. 1987), whereas with some samples, a decrease in the basal spacings was observed only after appreciable dehydroxylation had occurred.

A decrease in expansion rates beginning at about 650–700 °C can be detected on plots of *c* versus temperature in experiments performed in situ by Guggenheim et al. (1987) and Mazzucato et al. (1999) (see "Introduction" section). This indicates that some structural changes begin to occur in this temperature range. Sletten and Onstott (1998) studied thermal changes of muscovite powder by XRD at 700 °C in situ under vacuum, both isothermally and incrementally. They observed a scatter of the data on incremental heating for <3 h, which, on the basis of the isothermal data, they attributed to transitory effects. Guggenheim et al. (1987) hypothesized that different transitional structures form as dehydroxylation proceeds. This is compatible with our observations on quenched samples, assuming that the reduced basal spacings of quenched samples correspond to transitional phases, not necessarily associated with the loss of OH groups from the structure. These structural changes may be partly reversed on quenching, before loss of OH groups occurs. The observation that basal spacings were not always reduced in the early stages of dehydroxylation can be explained by the instability and low concentration of the modified structures. At higher temperatures, as dehydroxylation proceeds, transitional structures become more stable. All the samples then show diffractions of residual muscovite with reduced basal spacings, together with those of a fully dehydroxylated phase.

The concept of one or more intermediate, modified structures formed on dehydroxylation of muscovite

receives support from the IR spectra. Changes in hydroxyl absorptions must be attributed entirely to changes in the residual muscovite. In all samples, whatever the heat treatment, when changes occurred in the spectra, the absorbance of bands with lower frequency was decreased preferentially (see insets of Figs. 5, 6, 7, 8). The changes in relative intensity of the components cause an apparent shift of the maximum of the entire absorption band towards higher frequencies, as previously observed by Vedder and Wilkins (1969) and Zhang et al. (2010a). The different rates at which OH groups are lost on dehydroxylation may be attributed to the differences in electric charge on the surrounding oxygen atoms due to the effect of different Al/Si distribution in the tetrahedral sheets and to octahedral substitution.

Inhomogeneous dehydroxylation due to the loss of Al–OH–Mg and Al–OH–Fe vibrations, which are of lower frequency, in preference to Al–OH–Al vibrations in the course of heating phyllosilicates was previously observed by Heller-Kallai and Rozenson (1980).

A decrease in the intensity of the low-frequency components of the OH stretching band in preference to high-frequency ones was also observed on heating muscovite flakes in situ. Zhang et al. (2010a) resolved the OH absorption bands of two samples of muscovite, heated under vacuum, into two components with frequencies at 3655 and 3627 cm^{-1} . They observed a sharp decrease in band area of both components with temperature of the samples at 615 and 680 °C, respectively, but the area of the lower-frequency component decreased more rapidly than that of the higher-frequency one. The decrease in band areas was attributed to both structural changes and dehydroxylation, although characteristic absorptions of H_2O were not detected. In similar in situ experiments performed in air, Tokiwai and Nakashima (2010b) resolved the OH absorption band into three components, with frequencies 3622, 3628 and 3650 cm^{-1} . Above 650 °C, the absorbance of the low-frequency components decreased more rapidly than that of the high-frequency component. Both studies show that species that give rise to the higher-frequency component are more heat stable than those producing the lower-frequency band. Tokiwai and Nakashima (2010b) found that changes that occurred up to 650 °C were reversed on cooling, but no information is given for samples heated to higher temperatures. The question of reversibility of the changes in spectra on cooling was not addressed by Zhang et al. (2010a). It is therefore difficult to differentiate between structural changes that occur with or without loss of OH groups. If no H_2O molecules were formed in these samples, as observed by Zhang et al. (2010a), it follows from thermodynamic considerations of the equation $2\text{OH}^- \rightarrow \text{H}_2\text{O} + \text{O}^{2-}$ that the changes in OH absorptions cannot be attributed to the loss of OH groups (Lapides 1997). This is in agreement with Mookherjee et al. (2001),

who found that the H-occupancy of phengite remained unchanged up to 700 °C. Whatever the cause, it appears that at temperatures above ~615–680 °C in situ the structure of part or all of the muscovite that was not completely dehydroxylated was modified.

Changes in the 900- to 600- cm^{-1} spectral region with temperature (Fig. 9) show that the configuration of the tetrahedral sheets of residual muscovite differs from that of the original muscovite, confirming that structural changes other than loss of OH groups occurred.

The change in the configuration of the tetrahedral network in the course of dehydroxylation may be interpreted in light of figures presented by Gemmi et al. (2008). Figures 2, 6, 7 and 9 of their paper show, respectively, changes in cell parameters, average K–O distances, the tetrahedral rotation angle and average $\text{T}_1\text{–O}$, $\text{T}_2\text{–O}$ (T = tetrahedral cation) distances for a synthetic muscovite on heating in situ. Decreases in average K–O distances and rotation angle occurred below the onset of dehydroxylation that was indicated by changes in cell parameters, whereas T–O distances began to change at an appreciably higher temperature. It seems plausible that the spectrum shown in Fig. 9b corresponds to the intermediate stage, with a modified tetrahedral network, and the spectrum of the fully dehydroxylated form (Fig. 9c) corresponds to a structure with distorted tetrahedra.

Zhang et al. (2005) observed that incorporation of CO_2 in sericite is associated with or enhanced by the dehydroxylation process. They concluded that partially dehydroxylated sericite has a local configuration different from that of the original and of the dehydroxylated sample, in agreement with our observations on muscovite.

The decrease in basal spacings of residual muscovite with temperature is in contrast to the increase observed with partially dehydroxylated illite (Drits et al. 2012b) and pyrophyllite (Drits et al. 2011). On partial dehydroxylation, illite formed a single phase, composed of interstratified non-dehydroxylated and completely dehydroxylated layers with a strong tendency to separation. The basal spacing increased with increasing dehydroxylation. Pyrophyllite formed two phases, each a physical mixture of non-dehydroxylated and fully dehydroxylated layers, randomly interstratified in different proportions. The basal spacings of both phases increased with temperature. The detailed studies of illite and pyrophyllite dehydroxylation led to the conclusion that whereas illite dehydroxylation proceeds layer by layer, pyrophyllite dehydroxylates crystal by crystal. Both illite and pyrophyllite dehydroxylate by a homogeneous mechanism: individual layers are either unchanged or completely dehydroxylated. Possible causes cited for the difference between them are interstratification of smectite layers in illite, heterogeneity in crystal chemistry, the composition of the interlayers in illite and the effect

of different particle size. Illite crystallites are usually much thinner than pyrophyllite. Our results obtained for the much larger muscovite flakes are incompatible with a homogeneous dehydroxylation mechanism. Muscovite dehydroxylation apparently proceeds through one or more intermediate phases, which are sufficiently stable to persist, at least partially, on quenching.

The kinetics of muscovite dehydroxylation have been studied by different experimental and theoretical methods (Holt et al. 1958; Kodama and Brydon 1968; Rouxhet 1970; Lapidès 1997; Kalinichenko et al. 1997; Mazzucato et al. 1999; Gridi-Bennadji and Blanchart 2007; Tokiwai and Nakashima 2010a). The model generally adopted assumes formation of H₂O molecules in the octahedral sheets followed by diffusion of H₂O in the *c** direction and nucleation of the dehydroxylated phase. This requires an increase in size of the ditrigonal cavities, which occurs on heating, when the sheets expand and the rotation angle of the tetrahedra is decreased. The process is sluggish and is assumed to be the rate-limiting step. It is followed by diffusion of water through the interlayer space. This model cannot, however, be reconciled with the results of Zhang et al. (2010a, b), who failed to detect water molecules in the course of phyllosilicate dehydroxylation. No attempt seems to have been made to overcome these contradictions. The mechanism of muscovite dehydroxylation therefore still remains unclear.

Partially dehydroxylated dioctahedral 2:1 layer clay minerals rehydroxylate on cooling, if water is present in the system (Derkowski et al. 2012 and references therein). The presence of interlayer cations reduces the tendency to rehydroxylate. Intermediate structures formed by partial dehydroxylation of muscovite with its high interlayer K population would therefore be expected to be more stable than those of pyrophyllite or other clay minerals. Indeed, in contrast to pyrophyllite and smectites, completely dehydroxylated muscovite was not rehydroxylated under atmospheric pressure (Heller et al. 1962). Hence, partially dehydroxylated muscovite may also be expected to be more stable than intermediate phases of other phyllosilicates.

Conclusions

A synthesis of our results with data culled from the literature, mostly of experiments carried out in situ, leads to the following concept. On heating muscovite, the unit cell expands and changes occur in the structure. These are reversed on quenching, until the energy supplied suffices to break bonds and dehydroxylation commences. Due to the inhomogeneous distribution of charges on the oxygen atoms, this does not occur uniformly throughout the structure. On quenching partially dehydroxylated muscovite,

two phases are formed, residual and dehydroxylated muscovite. The structural changes that occurred on heating are no longer entirely reversed on quenching, and the partially dehydroxylated sample preserves some of the features observed in situ. Further heating leads to complete dehydroxylation. The structure tentatively proposed for residual muscovite is composed of inhomogeneously partially dehydroxylated octahedral sheets and tetrahedral networks that are less distorted than those in muscovite.

The formation of an intermediate phase on thermal decomposition of muscovite with layers different from those of the original and the completely dehydroxylated forms was hypothesized by Guggenheim et al. (1987). Drits et al. postulated that the homogeneous mechanism of dehydroxylation observed with pyrophyllite and illite applies to all phyllosilicates (Drits et al. 2011, 2012a, b). The dehydroxylation mechanism of muscovite may differ due to the stronger interlayer bonding and concomitant larger size of the crystals or crystallite packets and the relatively high concentration of K ions in the interlayers, all of which impede egress of the diffusing species.

To the best of our knowledge, our results present the first experimental evidence for the formation of an intermediate phase on dehydroxylation of a phyllosilicate. At this stage, the results provide fingerprints of this phase. Further study is required to establish its composition and structure.

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