

INFRARED EMISSION SPECTROSCOPY STUDY OF THE DEHYDROXYLATION OF 10 Å HALLOYSITE FROM A NEOGENE CRYPTOKARST OF SOUTH BELGIUM

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(5 figures and 1 table)

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ABSTRACT. The dehydroxylation of 10 Å halloysite from the Wellin (Weillen) cryptokarst (southern Belgium) was studied in situ by applying infrared emission spectroscopy. Dehydroxylation is evidenced by the loss of the OH-stretching modes between 3600 and 3700 cm^{-1} . A slow decrease of all intensities up to $\pm 500^\circ\text{C}$ is observed followed between 500° and 550°C by a rapid decrease to almost zero. The IES bands at 920 and 938 cm^{-1} , attributed to the accompanying inner and outer or inner sheet Al-OH libration modes, are removed on heating at the same rate and disappears at the same temperature as the OH-stretching bands. The low frequency bands that disappear upon heating are associated with OH-libration (920 and 938 cm^{-1}) or OH-translation modes (798, 754 and 693 cm^{-1}). At high temperatures only very broad bands around 800 cm^{-1} , a weak shoulder around 900 cm^{-1} and two broad bands around 1000 and 1175 cm^{-1} are observed. The first two are associated with newly formed Al-O bonds whereas the other two are associated with Si-O bonds in the dehydroxylated halloysite, an X-ray amorphous mullite-like phase.

KEYWORDS: halloysite, infrared emission spectroscopy, dehydroxylation, metahalloysite, hydrated kaolinite, cryptokarst, Belgium

SAMENVATTING. Infrarood emissie spectroscopische studie van de dehydroxylatie van 10 Å halloysiet uit een neogene cryptokarst in Zuid België. De dehydroxylatie van 10 Å halloysiet uit de Weillen (Wellin) cryptokarst (zuid België) is bestudeerd in situ met behulp van infrarood emissie spectroscopie. Dehydroxylatie is waarneembaar door het verdwijnen van de OH-stretching vibraties tussen 3600 and 3700 cm^{-1} . Een langzame afname in alle intensiteiten wordt waargenomen tot $\pm 500^\circ\text{C}$ gevolgd door een snelle afname tussen 500° en 550°C tot bijna nul. De IES banden rond 920 en 938 cm^{-1} , toegeschreven aan de bijbehorende inner en outer of inner sheet Al-OH libratie vibraties, verdwijnen met dezelfde snelheid en bij dezelfde temperatuur als de OH-stretching vibraties. De lage frequentie banden die verdwijnen bij verhitting zijn geassocieerd met de OH-libratie (920 en 938 cm^{-1}) of met de OH-translatie vibraties (798, 754, 693 cm^{-1}). Bij hoge temperaturen zijn alleen zeer brede banden rond 800 cm^{-1} , een zwakke schouder rond 900 cm^{-1} en twee brede banden rond 1000 en 1175 cm^{-1} waarneembaar. De eerste twee zijn geassocieerd met nieuwgevormde Al-O bindingen, terwijl de andere twee geassocieerd zijn met Si-O bindingen in de gedehydroxyleerde halloysiet, een röntgen amorfe op mulliet lijkende fase.

SLEUTELWOORDEN: halloysiet, infrarood emissie spectroscopie, dehydroxylatie, metahalloysiet, gehydrateerde kaolinite, cryptokarst

1. Introduction

Halloysite has a structure consisting of kaolinite-like layers interspersed in the fully hydrated state with a sheet of H_2O molecules (Newman, 1987), shown by an increase in the basal spacing from approximately

7.2 Å for a normal kaolinite to approximately 10 Å (Hofmann et al., 1934). This interlayer H_2O tends to be unstable and under ambient conditions, halloysite tends to dehydrate to metahalloysite (Mehmel, 1935). Halloysite contains, like kaolinite, two types of OH-groups: 1) the outer or inner surface OH-groups

(OuOH) located in the outer-upper unshared plane and 2) the inner OH-groups (InOH) located in the lower shared plane of the octahedral sheet.

The halloysite described in this paper is different from many other halloysites as it remains mostly in the hydrated state even after storage for two years without any precautions to prevent dehydration. Therefore, this halloysite is an excellent sample to study the hydrated 10 Å form of halloysite. Recently, the Raman spectra of this stable 10 Å halloysite have been described (Kloprogge & Frost, 1999). The OH-stretching region shows two antisymmetric inner surface OH-modes n_1 and n_2 (3703 and 3688 cm^{-1}) and inner OH-modes n_3 and n_4 (3642 and 3625 cm^{-1}) with additional broad, low intensity bands at 3556 and 3598 cm^{-1} . These bands are absent in dehydrated halloysite and are assigned to OH-stretching modes of adsorbed surface and interlayer H_2O . Comparison between the 10 Å halloysite and metahalloysite shows that almost all bands observed for the hydrated halloysite are also observed for the metahalloysite, however with small differences in their positions. These differences may indicate differences in crystal structure (interlayer H_2O) or folding of the layers. New bands are observed for the 10 Å halloysite at 359 and 332 cm^{-1} , which are absent in all other kaolin-minerals. Therefore, these vibrations are assigned to H-bonded H_2O modes of adsorbed and interlayer H_2O corresponding to the two OH-stretching modes around 3556 and 3598 cm^{-1} .

Infrared spectroscopy has proven to be useful in the study of the dehydroxylation of clay minerals (Stubican & Roy, 1961; Pampuch, 1973; Mackenzie, 1973; Han & Chen, 1982; Frost & Vassallo, 1996). The generally accepted concept of kaolinite dehydroxylation results from the interaction of two OH-groups in a two step process to form a H_2O molecule by proton transfer leaving a chemically bonded oxygen, as a superoxide anion, in the lattice (Pampuch, 1971; Maiti & Freund, 1981; Brindley & Lemaitre, 1987; Frost & Vassallo, 1996). Only a few studies have been carried out on the dehydroxylation of halloysite and it is generally assumed that the dehydroxylation is identical or at least similar to that of kaolinite (Holdridge & Vaughan, 1957).

The dehydroxylation behaviour of 10 Å halloysite has not been studied by *in situ* spectroscopic methods. The technique of measurement of discrete vibrational frequencies emitted by thermally excited molecules, known as Fourier Transform Infrared Emission Spectroscopy (FTIR ES, or IES) (Vassallo et al., 1992; Frost et al., 1995; Frost & Vassallo, 1996) has not been widely used for the study of minerals. The major advantages of IES are that the samples are measured *in situ* at elevated temperatures and IES requires no sam-

ple treatment other than making the sample of submicron particle size. Further the technique removes the difficulties of heating the sample to dehydroxylation temperatures and subsequent quenching prior to the measurement, as IES measures the dehydroxylation process as it actually is taking place. The aim of this paper is therefore to achieve a more detailed understanding of the dehydroxylation behaviour of 10 Å hydrated halloysite by applying infrared emission spectroscopy. This in contrast to most halloysites studied till now, which show mainly the 7 Å phase due to their unstable behaviour and subsequent dehydration when exposed to air.

2. Geological background

The sample studied was collected during the fieldtrip accompanying the Euroclay '95 conference in Leuven, Belgium, August 1995. The halloysite was collected in the Wellin (Weillen) karst located on the Entre-Sambre-et-Meuse plateau in southern Belgium. This area mainly consists of folded Upper Devonian shales and Lower Carboniferous limestones, which were initially uplifted during the Variscan Orogeny. During the Upper Cretaceous and the Cenozoic era the plateau went through alternating phases of continental conditions and southward regressions coming from the northern marine basins. A major relative sea level fall during the Neogene resulted in the deposits of continental sediments. The covered karsts (cryptokarsts) started to deepen during the Neogene due to progressive dissolution of the underlying limestones. They trapped pre-existing Eocene-Oligocene marine sands and clays as well as overlying continental sediments (Dupuis, 1992; Nicaise et al., 1995). The samples were collected from a breccia down the slope of the Weillen karst. The thickness of the breccia is variable and estimated to be several meters. This breccia is made up of silicified, sometimes partially transformed to halloysite, limestone blocks in a matrix of halloysite and kaolinite. This breccia is thought to be formed from the mechanical collapse of a stratiform deposit located higher in the karst during the deepening (Nicaise et al., 1995).

3. Analytical techniques

3.1. X-Ray powder diffraction (XRD)

The nature of the clay (< 2 mm by sedimentation) was checked by X-ray powder diffraction (XRD). The XRD analyses were carried out on a Philips wide angle PW 1050/25 vertical goniometer equipped with a graphite diffracted beam monochromator. The d-values and intensity measurements were improved by application of an in-house developed computer aided divergence

slit system enabling constant sampling area irradiation (20 mm long) at any angle of incidence. The goniometer radius was enlarged from to 204 mm. The radiation applied was CuK_α from a long fine focus Cu tube operating at 40 kV and 40 mA. The samples were measured at 50 % relative humidity in stepscan mode with steps of $0.02^\circ 2\theta$ and a counting time of 2s.

3.2. Infrared emission spectroscopy (IES)

FTIR emission spectroscopy was carried out on a Digilab FTS-60A spectrometer, which was modified by replacing the IR source with an emission cell. A description of the cell and principles of the emission experiment have been published elsewhere (Vassallo et al., 1992; Frost et al., 1995; Frost & Vassallo, 1996). Approximately 0.2 mg of the halloysite sample was spread as a thin layer on a 6 mm diameter platinum surface and held in an inert atmosphere within a nitrogen-purged cell during heating. The infrared emission cell consists of a modified atomic absorption graphite rod furnace. A platinum disk acts as a hot plate to heat the sample and is placed on the graphite rod. An insulated 125-mm type R thermocouple was embedded inside the platinum plate in such a way that the thermocouple junction was <0.2 mm below the surface of the platinum. Temperature control of $\pm 2^\circ\text{C}$ at the operating temperature of the sample was achieved by using an Eurotherm Model 808 proportional temperature controller, coupled to the thermocouple.

The emission spectra were collected at intervals of 50°C over the range $200 - 800^\circ\text{C}$. The time between scans (while the temperature was raised to the next hold point) was approximately 100 seconds. It was considered that this was sufficient time for the heating block and the powdered sample to reach temperature equilibrium. The spectra were acquired by coaddition of 64 scans for the whole temperature range (approximate scanning time 45 seconds), with a nominal resolution of 4 cm^{-1} . Good quality spectra can be obtained providing the sample thickness is not too large. If too large a sample is used then the spectra become difficult to interpret because of the presence of combination and overtone bands and self-absorption. One has to bear in mind that as for normal infrared spectroscopical techniques the Beer-Lambert law is also valid for infrared emission spectroscopy and the emitted energy is therefore related to the sample mass. Spectral manipulation such as baseline adjustment, smoothing and normalisation was performed using the Spectralcalc software package (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package which enabled the type of fitting function to be selected and allows specific parameters to be fixed or

varied accordingly. Band fitting was done using a Lorentz-Gauss cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

4. Results and discussion

Figure 1 shows the XRD pattern of the halloysite sample from the Wellin (Weillen) karst after approximately two years storage under ambient conditions. Clearly two basal spacings can be distinguished around 9.93 and 8.02 \AA . The first basal spacing reflect the hydrated or 10 \AA halloysite whereas the 8 \AA phase represent the dehydrated halloysite or metahalloysite. No impurities of other minerals were observed. For comparison a completely dehydrated halloysite from New Zealand showing a basal spacing of 7.36 \AA has been added in Figure 1.

The hydroxyl-stretching region of the infrared emission spectra of the halloysite obtained at 50°C from 250° to 800°C is shown in Figure 2. The hydroxyl-stretching region is characterised by four bands as shown in Figure 3. The three higher frequency bands are assigned to (n_1 3693 cm^{-1} , n_2 3671 cm^{-1} and n_3 3647 cm^{-1}) to the three inner surface hydroxyls and the fourth (n_4 3625 cm^{-1}) is assigned to the inner hydroxyl (Johnston et al., 1990, Frost & Vassallo, 1996). The commonly accepted view is that the n_1 and n_2 are the coupled antisymmetric and symmetric vibrations (Brindley et al, 1986; Michaelian et al., 1987). These bands are in similar positions as observed for the New Zealand 7 \AA halloysite (3680 , 3670 , 3650 and 3628 cm^{-1} , Frost & Vassallo, 1996) as expected, because the hydrated interlayer will only have a minor effect on the hydroxyl groups as reflected in the slightly different band positions. Dehydroxylation is evidenced by the loss of signal intensity of the OH stretching modes between 3600 and 3700 cm^{-1} (Fig. 4). Below 300°C a strong decrease in intensity of the n_2 and n_4 is observed, in contrast to n_1 and n_3 which do not show a decrease within the experimental error, followed by a slow decrease of all intensities up to approximately 500°C . Between approximately 500° and 550°C a rapid decrease to almost zero is observed for all the bands and the bands can not be observed at temperatures above 600°C . This seems to suggest that the different hydroxyls of the halloysite are being removed at different temperatures or at different rates, in contrast to earlier IES observations of the dehydroxylation of kaolinite (Frost & Vassallo, 1996). It appears that the loss of the inner hydroxyl band is nearly linear over the temperature range between 300° and 500°C . The

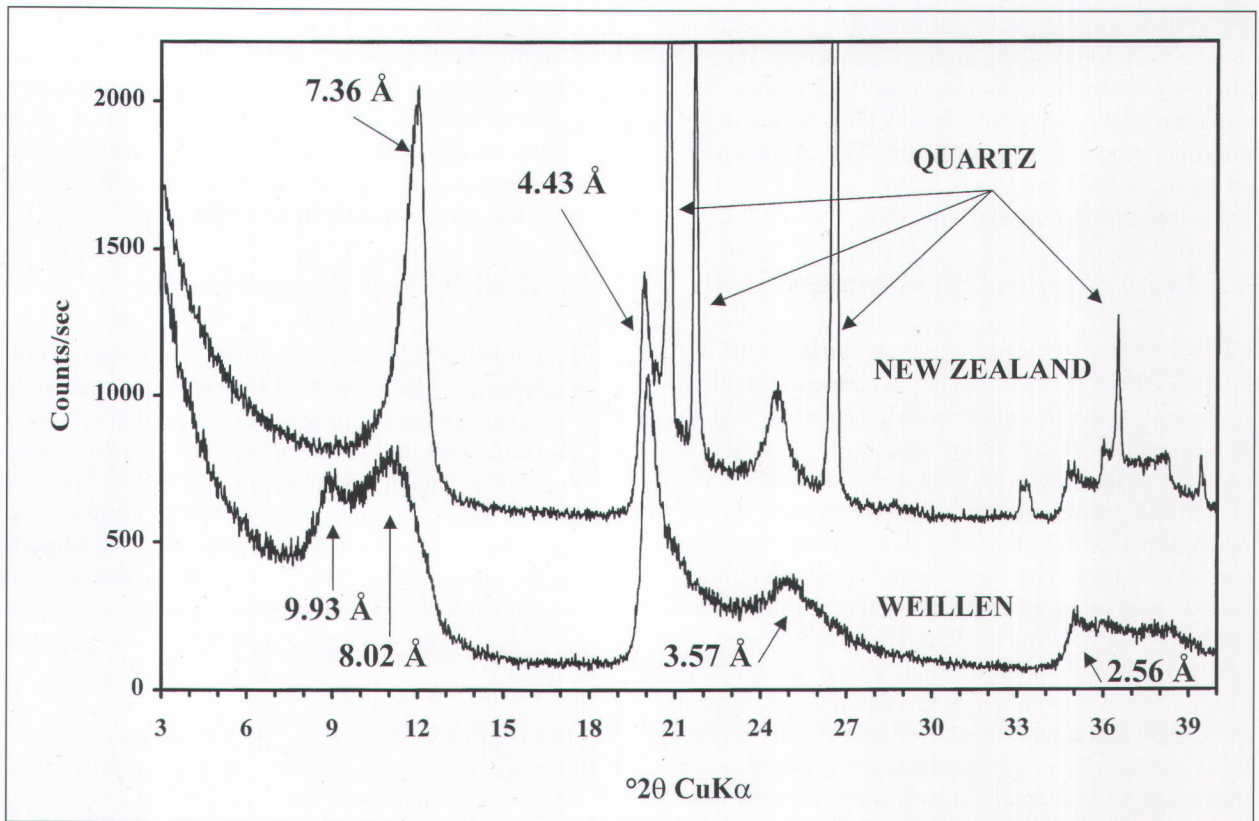


Figure 1. X-ray diffraction patterns of 10 \AA halloysite from the Weillen cryptokarst and 7 \AA halloysite from New Zealand. The sharp reflections in the New Zealand samples are due to quartz impurities.

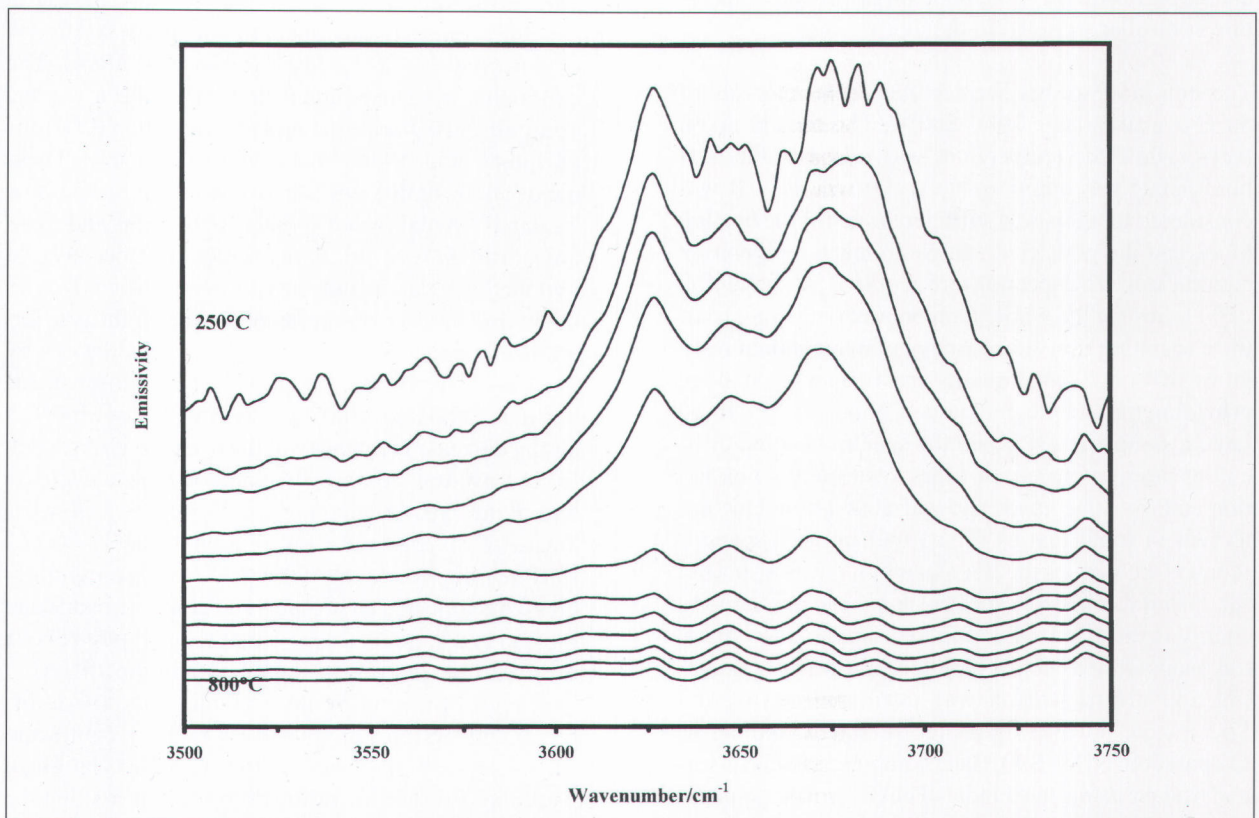


Figure 2. Infrared emission spectra in the hydroxyl-stretching region between 3500 and 3750 cm^{-1} of 10 \AA halloysite from 250° to 800°C at 50°C interval showing the decrease in intensities of the OH-stretching modes.

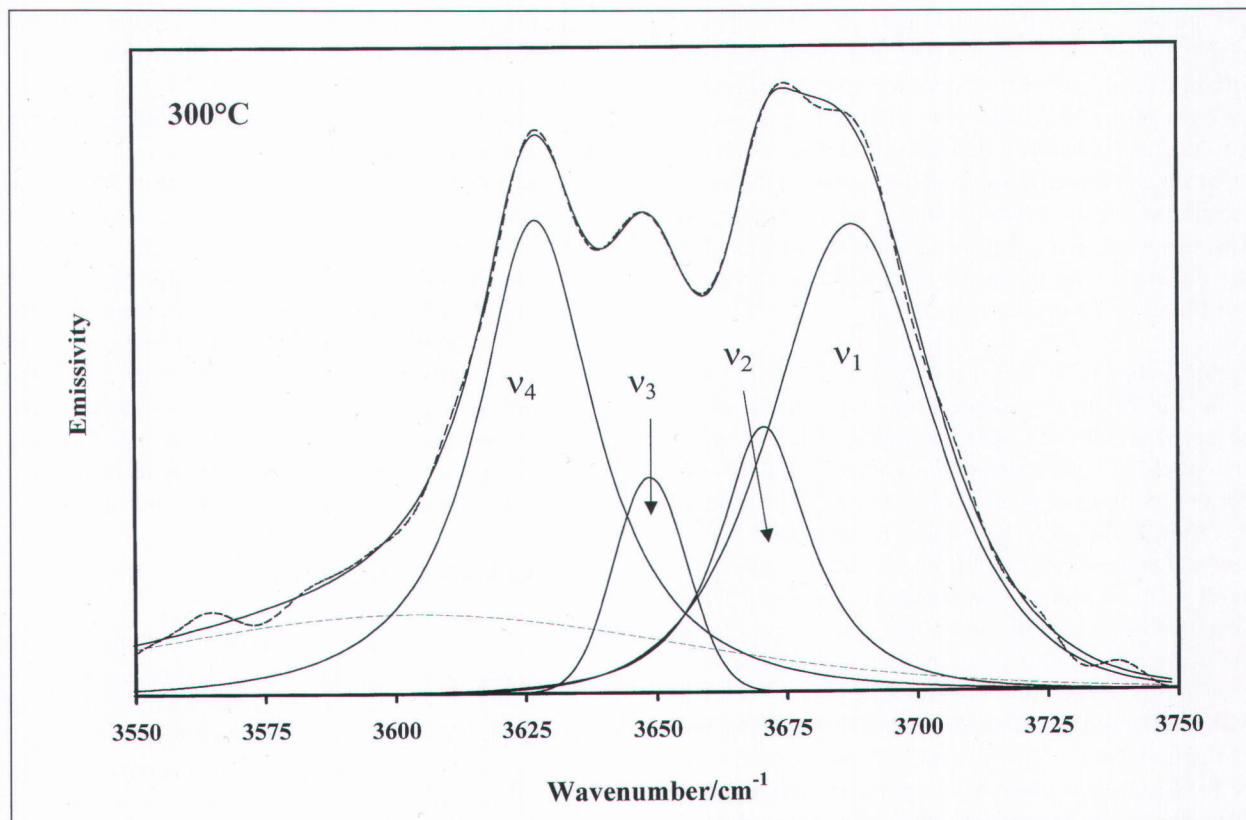


Figure 3. Band component analysis of the infrared emission spectrum in the hydroxyl stretching region between 3550 and 3750 cm^{-1} of 10 Å halloysite at 300°C showing the inner surface n_1 and n_2 and outer surface n_3 and n_4 OH-stretching modes.

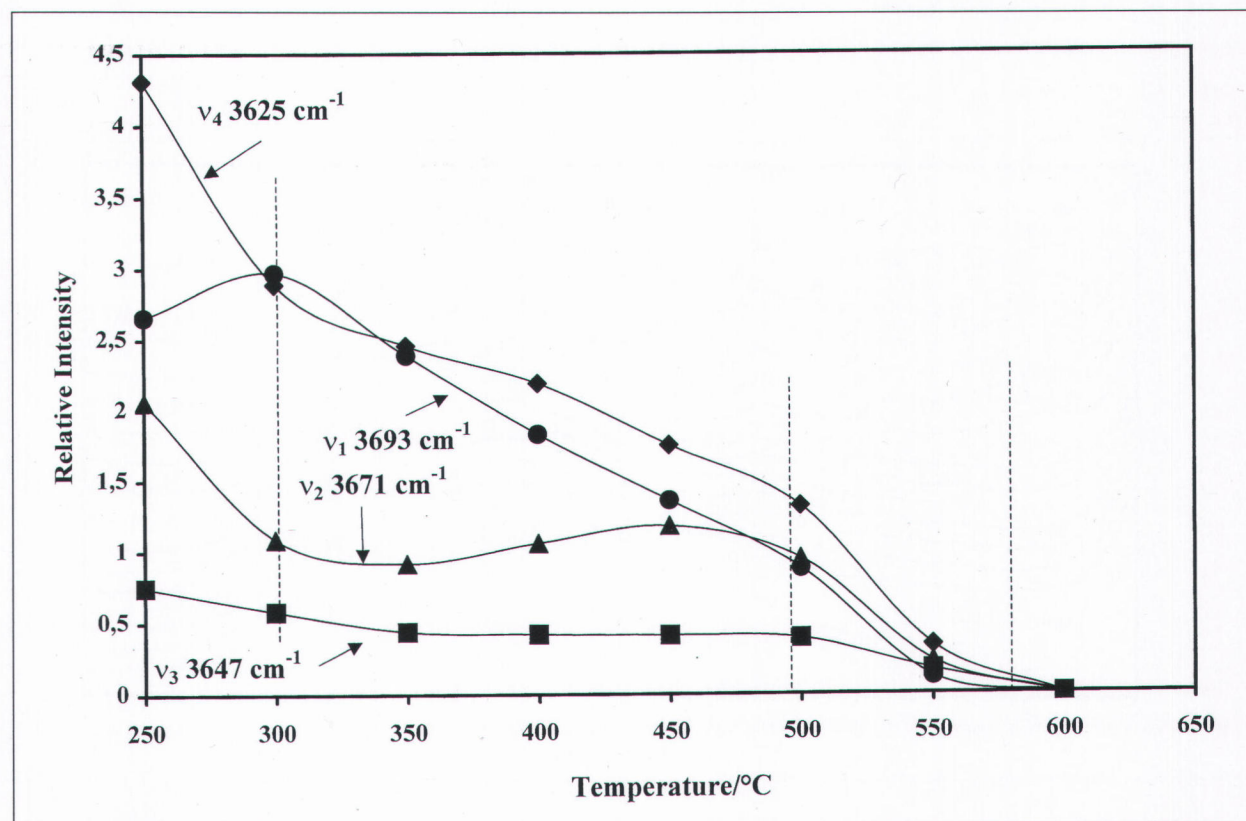


Figure 4. The variation of the relative intensities of the bands associated with the hydroxyl-stretching modes as function of the temperature based on the band component analysis data.

change in slopes of the temperature-relative intensity graph around 500°C support the hypothesis that two different mechanisms are working during the dehydroxylation of the 10 Å halloysite. It is further noteworthy that the IES bands at 920 and 938 cm⁻¹ are removed on heating at the same rate and disappears at the same temperature as the hydroxyl-stretching bands (Fig. 5). This is not unexpected as these bands are attributed to the accompanying inner and outer or inner sheet Al-OH libration modes (Farmer, 1974).

Figure 5 depicts the IES spectra of the 10 Å halloysite in the low frequency region. Prominent bands can be observed around 457, 472, 537, 693, 754, 798, 920, 1015 and 1117 cm⁻¹. These bands agree well with earlier observations of other kaolins and with the Raman spectrum of the 10 Å halloysite (Kloprogge & Frost, 1999). Table 1 reports the IES lattice modes and compares them with the Raman data. Strong changes are observed between 450° and 500°C as expected from the hydroxyl-stretching region. The bands that disappear in this temperature interval are either associated with OH libration (920 cm⁻¹) or translation modes (798, 754 and 693 cm⁻¹). The band at 537 cm⁻¹ is thought to be the Si-O-Al in plane bending mode similar to the 541 cm⁻¹ band observed for kaolinite (Frost et al., 1993). Upon heating and dehydroxylation this bond is altered and is lost above 500°C. At higher temperatures only very broad bands around 800 cm⁻¹, a weak shoulder

around 900 cm⁻¹ and two broad bands around 1000 and 1175 cm⁻¹ can be observed. The first two are associated with the formation of new Al-O type of bonds whereas the other two are associated with Si-O bonds in the dehydroxylated halloysite, an X-ray amorphous phase with a spectrum that starts to resemble that of mullite.

In conclusion it can be said that infrared emission spectroscopy is a very powerful tool in the study of dehydroxylation mechanisms of halloysite. The IES spectra clearly show the temperatures at which the dehydroxylation starts and when it is complete. The spectra clearly show that the vibrations that involve OH groups undergo dramatic changes upon heating, whereas the Si-O bands remain large unchanged.

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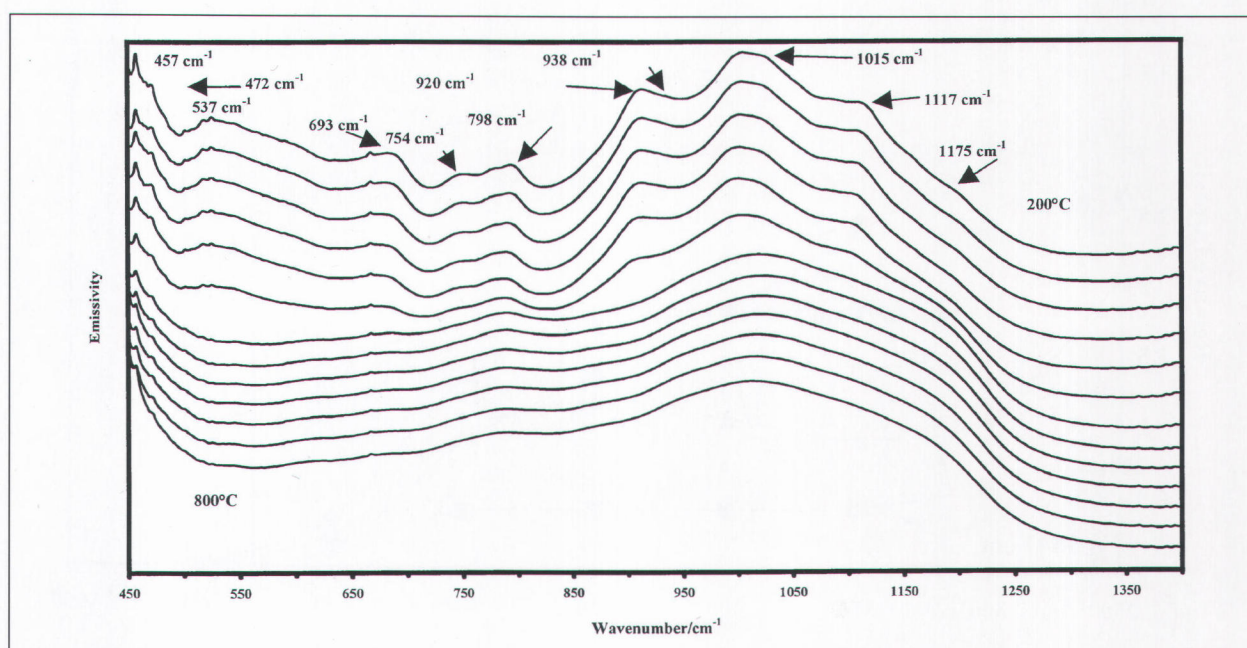


Figure 5. Infrared emission spectra in the low frequency region between 450 and 1400 cm⁻¹ of 10 Å halloysite from 200° to 800°C at 50°C interval showing the changes in the OH-libration modes due to dehydroxylation and the formation of a new X-ray amorphous phase with broad bands above approximately 500-550°C.

	10 Å halloysite IES this study (cm ⁻¹)	10 Å halloysite Raman (Kloprogge and Frost, 1999) (cm ⁻¹)	Dehydrated halloysite (Frost and Shurvell, 1997) (cm ⁻¹)	Assignment
V ₁	1117		1100	Si-O stretch
V ₂	1015			Si-O stretch
V ₃	938	944		Al-OH libration
V ₄	920	910	910	Al-OH libration
V ₅		826	844	Si-O-Al deformation
V ₆	798	794	779	OH translation
V ₇	754	748	728	OH translation
V ₈	693	710	693	OH translation
V ₉	537	548	540	Si-O bend
V ₁₀		503	510	Si-O bend
V ₁₁	472	465		Si-O bend
V ₁₂	457	430	442	Al-O stretch

Table 1. Band positions in the IES low frequency region of 10 Å halloysite and comparison to the Raman spectrum of 10 Å halloysite and to dehydrated halloysite.

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