INFRARED STUDIES OF Ni-BEARING CLAY MINERALS OF THE KEROLITE-PIMELITE SERIES

P. GERARD[1] AND A. J. HERBILLON[2]

[1] Ministère des Affaires Economiques, Laboratoire Central
rue de la Senne 17a, B-1000 Bruxelles, Belgium

[2] Section de Physico-chimie Minérale du Musée Royal de l'Afrique Centrale and
Université Catholique de Louvain, Place Croix du Sud 1
B-1348 Louvain-la-Neuve, Belgium

Abstract—Two kerolite and one garnierite samples were subjected to progressive heat treatments prior to their examination by infrared spectroscopy (IR) in the 1200–600-cm^{-1} and 3800–3000-cm^{-1} regions. The heat treatment of the garnierite (a mixture of nepouite and pimelite) selectively dehydroxylated the nepouite thus allowing an examination to be made of the OH-vibration bands due to the pimelite. Both the relative intensities of the 710–670-cm^{-1} doublet and of the different OH-stretching bands indicated the Ni content of this pimelite to be about 70%. The heat treatments did not modify the 1200–600-cm^{-1} region of the spectra of kerolites but caused a noticeable sharpening in the OH-stretching region. The relative intensities of the structural OH-stretching bands of dehydrated kerolites showed that they differ from Ni-talcs of similar composition in the distribution of Ni and Mg in the octahedral sites. These cations are randomly distributed in Ni-talc but are mainly segregated into Mg and Ni domains in kerolite. Changes in sharpness, intensity, and position of the structural OH-stretching bands of the kerolites as temperature increases and dehydration progresses are similar to those undergone by Mg- or Li-saturated trioctahedral smectites. Also thermal analysis curves of these minerals show similarities with those of Mg- and Ni-saturated smectites, and suggest that in kerolites too, the hydration water is associated with interlayer (though non-exchangeable) Ni and/or Mg cations.

Key Words—Dehydroxylation, Garnierite, Infrared spectroscopy, Kerolite, Nickel, Pimelite.

INTRODUCTION

During the last decade, several papers have provided a better understanding of the Mg-Ni hydrous silicates and have clarified their nomenclature (see Brindley, 1980, for a recent review). It is now generally agreed to restrict "garnierite" to a field term for all green, Ni-bearing, hydrous, phyllosilicates. Natural garnierites are generally mixtures of 1:1 and 2:1, nonswelling, trioctahedral layer silicates.

The 2:1 clay minerals in garnierite belong to the kerolite-pimelite series and differ from their homologues in the talc-willemseite series in their chemical, infrared spectroscopic, and thermal properties. Although kerolite-pimelite minerals have similar Mg/Ni ratios as talc-willemseites, they usually occur in much smaller particle sizes and have a higher degree of stacking disorder. Kerolite-pimelites also contain additional water (about $2H_2O$ per unit cell). The loss of this additional water at higher temperature than the normal hydration water present in most clay minerals is clearly indicated in the shape of the thermogravimetric curve (Brindley and Pham Thi Hang, 1973). In addition, the infrared spectrum (IR) in the OH-stretching region is also affected by this extra water making the IR spectra of kerolite-pimelites significantly different from those of talc-willemseites (Brindley *et al.*, 1979).

The present paper examines the IR spectra of kerolites and pimelites which have been subjected to progressive heat treatments to remove their additional water. Such heat treatments may also destroy any 1:1 clay mineral contaminating the samples. In addition, the location of the additional water in kerolites is deduced from their IR spectra and the proportion of Ni and Mg in the minerals of common garnierite is determined.

SAMPLES

Three natural clays and a synthetic Ni-willemseite were studied. Two kerolite samples were selected from a bulk sample from the Mont-Vert quarry, Népoui, New Caledonia. After grinding the original material, homogeneous grains between 1 and 2 mm were selected by hand picking using a binocular microscope. Two samples, labeled K_1 and K_2, were thus obtained having slightly different greenish colors. The other natural clay sample, labeled N-P, came from the Koungouahou quarry, Thio, New Caledonia. Although uniformly green and homogeneous under the microscope, this garnierite is a mixture of 1:1 and 2:1 clay minerals (Lemaître and Gérard, 1981; sample 37-1). The synthetic willemseite, labeled W, was prepared according to the hydrothermal procedure of Martin *et al.* (1970).

METHODS

After fluorhydric fusion (Voinovitch *et al.*, 1962), the natural samples were analyzed by atomic absorption spectros-
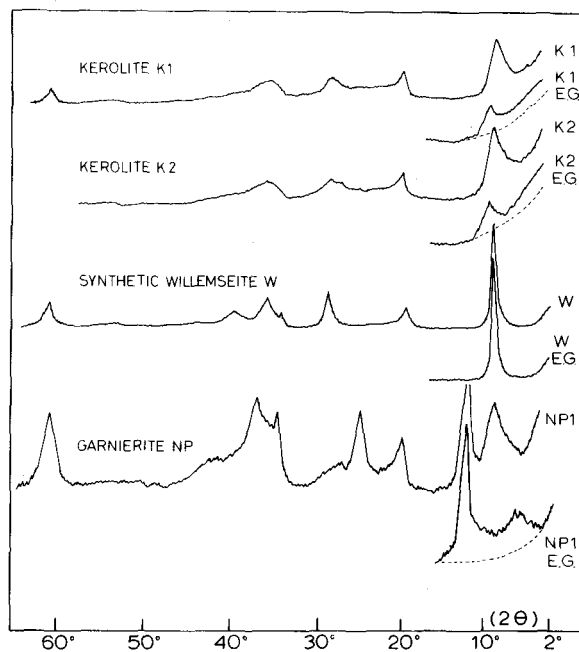
Figure 1.   X-ray powder diffraction traces of samples before and after saturation with ethylene glycol (CuKα radiation).

Table 1.   Chemical analyses and formulae of kerolites K_1 and K_2 (Népoui, New Caledonia) and garnierite N-P (Thio, New Caledonia).

	Kerolite K_1	Kerolite K_2	Garnierite N-P
Chemical analyses (wt. %)			
SiO_2	51.65	50.77[1]	38.54[1]
MgO	20.50	18.05	4.04
NiO	19.12	23.25	47.61
Fe_2O_3	—	—	0.43
CoO	—	—	0.27
H_2O+	8.45	7.93	8.95
	99.72	100.00	100.00
Cations and water (H_2O+)/½ u.c.			
Si	3.80	3.80	3.48
Mg	2.25 ⎤ 3.38	2.01 ⎤ 3.41	0.54 ⎤ 3.99
Ni	1.13 ⎦	1.40 ⎦	3.45 ⎦
H_2O+	2.08	1.98	2.70

[1] Obtained by difference.

copy for Ni, Mg, Al, Fe, Co, Cr, Na, K, and Ca. Their H_2O+ content was determined from the weight of the sample when heated overnight at 105°C minus the weight of the same sample after it had been heated to 1000°C for the same period of time. The thermogravimetric (TGA) curves were recorded using a SETARAM thermobalance programed at a heating rate of 10°C/min.

X-ray powder diffraction (XRD) patterns of samples deposited on glass slides were recorded with a Philips diffractometer (Ni-filtered CuKα radiation, rate = 1°2θ/min). The pattern of the synthetic willemseite was recorded after disorienting the sample by Niskanen's procedure (Niskanen, 1964).

The IR spectra were obtained at ambient temperature using KBr pellets made from samples which had been subjected to the heating for 2 hr at selected temperatures (see Figures 3, 4, and 6). The concentration of clay in the pellets was varied depending on the region of the spectrum to be examined and the thermal treatment used. For deuteration experiments, the sample, initially dried at 105°C and prepared as a self-sustaining film (30 mg/cm²), was placed in a cell allowing pumping, deuteration, and heating within the spectrometer itself. D_2O vapor at saturation value was introduced in the cell prior to the thermal rise up to the selected temperature (see Figure 5). After 30 min in this isothermal condition, the excess D_2O was pumped out and the sample cooled to 110°C before recording the spectrum.

RESULTS AND DISCUSSION

Samples identification

Figure 1 shows the XRD patterns of the starting samples. These diagrams indicate the structural disorder and the higher d(001) value of the two kerolite samples compared to the better crystallinity of the synthetic wil-

lemseite. Like other specimens of the kerolite-pimelite series (Brindley *et al.*, 1977, 1979), the kerolites partially expanded in the presence of ethylene glycol (K_1EG, K_2EG); however, in water, similar swelling was not observed.

In the XRD pattern of garnierite sample N-P (a mixture of 1:1 and 2:1 clay minerals), the intense basal reflection at 7.3 Å and the well-resolved peak at 2.63 Å indicate that the serpentine phase of the mixture belongs to the lizardite-nepouite series (Brindley and Wan, 1975). The platy, lizardite-like appearance of most of the particles of this garnierite under the electron microscope supports this identification. As in the kerolite samples, the 2:1 layer silicate present in garnierite N-P does not swell in water. In ethylene glycol (N-P-EG), however, it swells more than the kerolites.

The chemical analyses of the kerolite and garnierite samples (Table 1a) do not list Al_2O_3, Na_2O, K_2O, CaO, and Cr_2O_3 because less than 0.1% of these oxides was determined. The silica content of kerolite K_1 was determined by alkaline fusion of a separate aliquot of the sample. Becuase this value agreed with the silica content determined by difference, the silica contents in kerolite K_2 and garnierite N-P were also deduced by difference.

The structural formulae in Table 1b are based on an anionic composition $O_{10}(OH)_2$ and total cation charge of 22 per half unit cell. They show that the number of octahedral cations in kerolites ($\sim$3.4) largely exceeds the maximum permissible value for a talc-like layer. In contrast, the silicon content of the unit cell shows a deficit (3.8 instead of 4). Although discrepancies in the chemical composition of kerolites and talcs of similar Ni/Mg ratio have been noted elsewhere (Brindley *et al.*, 1979), the excess in octahedral cations and deficit in tet-
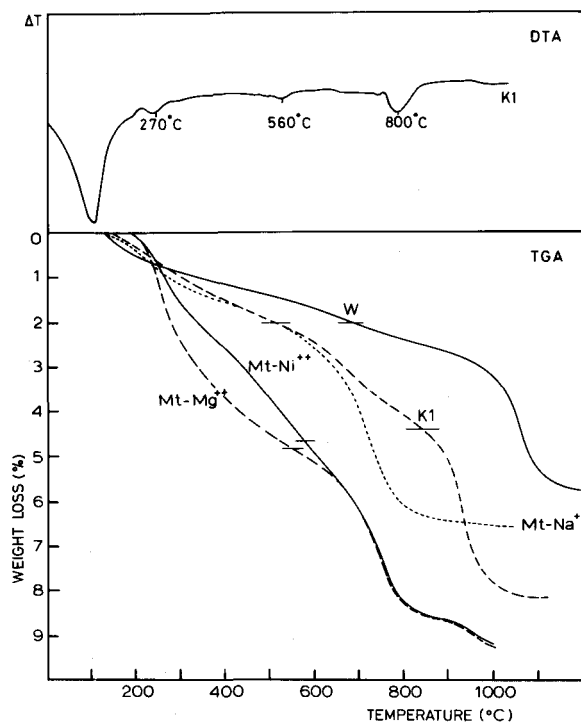
Figure 2. (a) Differential thermal analysis (DTA) pattern of kerolite K_1; (b) Thermogravimetric curves (TGA) of kerolite K_1 and willemseite W as compared with those of a Camp Berteau montmorillonite (Mt) saturated with different cations. The horizontal line on the curves indicates the theoretical limit between the adsorbed and structural water.

Although the presence of additional water is an important characteristic of kerolites and pimelites, it should be noted that this feature may also be exhibited by other 2:1 swelling layer silicates, the total weight loss and shape of the TGA curve being very dependent on the nature of their interlayer cation. This relationship is illustrated in Figure 2 where the TGA curve of a Na-montmorillonite is compared to those of Mg- and Ni-montmorillonites. For both the Mg- and Ni-smectites, the weight losses and curve shapes no longer agree with their hydroxyl contents and so the presence of additional water is suggested. As pointed out by Mackenzie (1970), in smectites saturated with cations with high hydration energy such as Mg^{2+} and Ni^{2+}, the dehydroxylation step may overlap with the last part of the dehydration. By analogy, the additional water in clay minerals such as kerolites and pimelites might be due to water tightly held by interlayer (though non-exchangeable) cations. This hypothesis is also supported by the DTA curve of kerolite K_1 (Figure 2) which, similarly to most of the DTA patterns of trioctahedral smectites illustrated by Mackenzie (1970, p. 512), exhibits a noticeable peak between 250° and 300°C. In this pattern, the small endothermic peak at about 560°C is probably due to minor contamination by a serpentine phase.

Infrared spectra in the 1200–600-cm⁻¹ region

Using the literature band assignments for talc, willemseite, and Ni-Mg serpentines, the 1200–600-cm⁻¹ region of the IR spectrum confirms and complements the identifications reported above. Where only 2:1 layer silicates were identified by XRD (Figure 1) in kerolites K_1 and K_2 (not shown) and in willemseite W, thermal treatment to 750°C did not modify the spectra in this region (Figure 3). Regardless of temperature, the strong symmetric band, assigned by Russell et al. (1970) to the $A_{1\nu1}$ tetrahedral vibration in talc, is present and, in agreement with their results, shifts slightly towards higher frequencies with increasing nickel content of the talc framework (i.e., ~1020 cm⁻¹ in kerolite K_1 and ~1035 cm⁻¹ in willemseite W) (Figure 3).

As noted by Stubican and Roy (1961) and Brindley et al. (1979), the part of the 1200–600-cm⁻¹ region most sensitive to composition differences is the doublet at 710 cm⁻¹ and 670 cm⁻¹. From the work of Russell et al. (1970), the assignment of the different vibrations contributing to this doublet is now well established and should be taken into account if the ratio of the intensities (measured by peak height above the base line) of the 710- and 670-cm⁻¹ doublet is to be used for composition estimates. Whereas the 710-cm⁻¹ peak may unambiguously be assigned to the δOH-bending vibration in a Ni-talc-like environment, the 670-cm⁻¹ region is composed of the superimposition of two phenomena, namely the δOH-bending vibration in a Mg-talc-like environment and a tetrahedral ($A_{1\nu2}$) vibration. Conse-
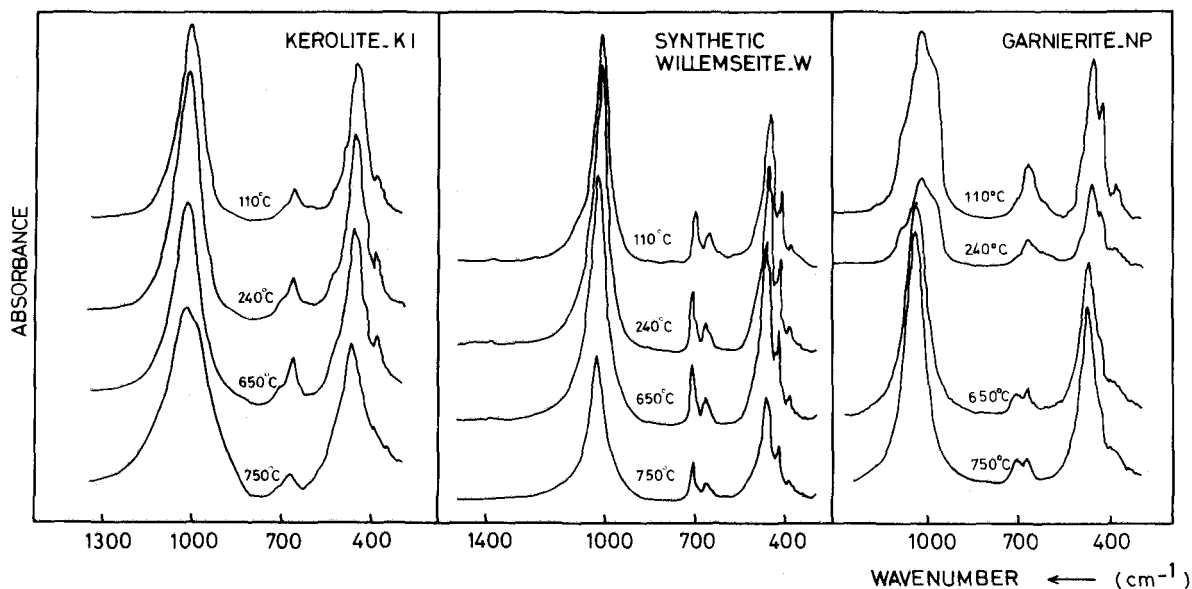
rahedral silicon observed here are significant. Previously, Brindley and Pham Thi Hang (1973) suggested that the Si/R²⁺ (R²⁺ = Ni²⁺ + Mg²⁺) of "garnierites" could be used to estimate their relative content of talc-like and serpentine phases. If applied to the chemical analysis of kerolites K_1 and K_2, the amount of serpentine in these samples should be as much as 30%, which is too high according to the XRD patterns (Figure 1) and the differential thermal analysis and IR results reported below. The same calculation applied to garnierite N-P indicates a serpentine content of 70%, in reasonable agreement with the results of Lemaître and Gérard (1981) and the XRD data (Figure 1). Further, the high Ni content of garnierite N-P (Table 1) indicates that this sample consists of a mixture of nepouite and pimelite.

The TGA curve illustrating the H_2O+ data of Table 1a for kerolite K_1 is presented in Figure 2. This clay has a structural formula showing an additional water content of 1.08 mole per half unit cell (Table 1b). The shape of its TGA curve is typical of a kerolite in that the water is released progressively between 100° and 840°C and then, more abruptly, up to about 1000°C. Further, the contribution of this last step is smaller than that expected for the weight loss due to the dehydroxylation of 2 OH per half unit cell.

Figure 3.   Infrared spectra in the 1200–600-cm^{-1} region.

quently, equal intensity of the 710- and 670-cm^{-1} bands does not indicate an equal amount of Ni and Mg in the octahedral sheet of the talc layer. This ratio for the willemseite W sample (Figure 3), as well as in similar willemseite spectra shown by Wilkins and Ito (1967) and Russell *et al.* (1970), is about 2.1. The spectra of Wilkins and Ito gives this ratio as zero for a Mg-talc, about 1 for a $Mg_{0.23}Ni_{0.77}$ willemseite, and about 0.5 for a $Mg_{0.52}Ni_{0.48}$ talc. Because this ratio does not vary linearly with composition, it is only accurate for samples in the willemseite (or pimelite) composition range. Further, where the Ni/Mg ratio is lower than 0.5, the 670-cm^{-1} band broadens considerably because the frequency of the tetrahedral $A_{1\nu 2}$ vibration is no longer exactly at 670 cm^{-1}. In a Mg-talc end member, this vibration is shifted by about 20 cm^{-1} towards higher frequencies and appears as a shoulder at 690 cm^{-1} (Russell *et al.*, 1970). In kerolites K_1 (Figure 3) and K_2 (not shown), as well as in Ni-talc of similar composition (Wilkins and Ito, 1967), the presence of Ni is indicated by a high frequency shoulder on the 670–690-cm^{-1} broad and complex band. In these spectra, however, a meaningful 710/670-cm^{-1} intensity ratio is no longer measurable.

In agreement with the above data, the spectra of the moderately heated garnierite sample (Figure 3) indicates the presence of a Ni-rich serpentine phase. Here, the strong band near 1000 cm^{-1} is less symmetric than in talc and has shoulders at 1080 and 980 cm^{-1} where normally tetrahedral vibrations are resolved in different varieties of serpentines (Yariv and Heller, 1975). Further, the spectra are also characterized by a strong (but complex) band with a maximum at 670 cm^{-1}. In the synthetic Mg-Ni serpentines of Jasmund *et al.* (1976), this

frequency corresponds to the δOH vibration of serpentines rich in Ni.

From the observations of Pham Thi Hang and Brindley (1973) and Lemaître and Gérard (1981), it was expected that heating a garnierite consisting of a mixture of serpentine and talc-like phases at either 650° or 750°C should yield selective dehydroxylation of the serpentine without affecting the 2:1 layer silicates also present. This thermal treatment significantly modified the IR spectra (Figure 3) of our sample: the 1000-cm^{-1} region became similar to that of talc, and its maximum shifted slightly towards higher frequencies. Further, the 710–670-cm^{-1} doublet characteristic of a Ni-rich talc-like layer was resolved. From the calibration of this doublet (as above), the pimelite in the original, unheated garnierite N-P sample has an octahedral sheet containing about 70% Ni.

Infrared spectra in the 3800–3000-cm^{-1} region

Figure 4 presents the IR spectra of kerolites K_1 and K_2, and willemseite W in the spectral range containing the OH-stretching vibrations of both structural hydroxyl and water.

In the case of no or restricted heating treatment the spectra of kerolites resemble those shown by Brindley *et al.* (1979) for kerolites of similar Ni contents. Superimposed on the broad water band are peaks at about 3680 and 3625 cm^{-1} which are distorted on their left side by shoulders at ~3700 cm^{-1} and ~3640 cm^{-1}, respectively. The low temperature spectra of willemseite W are characterized by an unique sharp (~5 cm^{-1}) peak at 3625 cm^{-1} showing some tailing towards high fre-
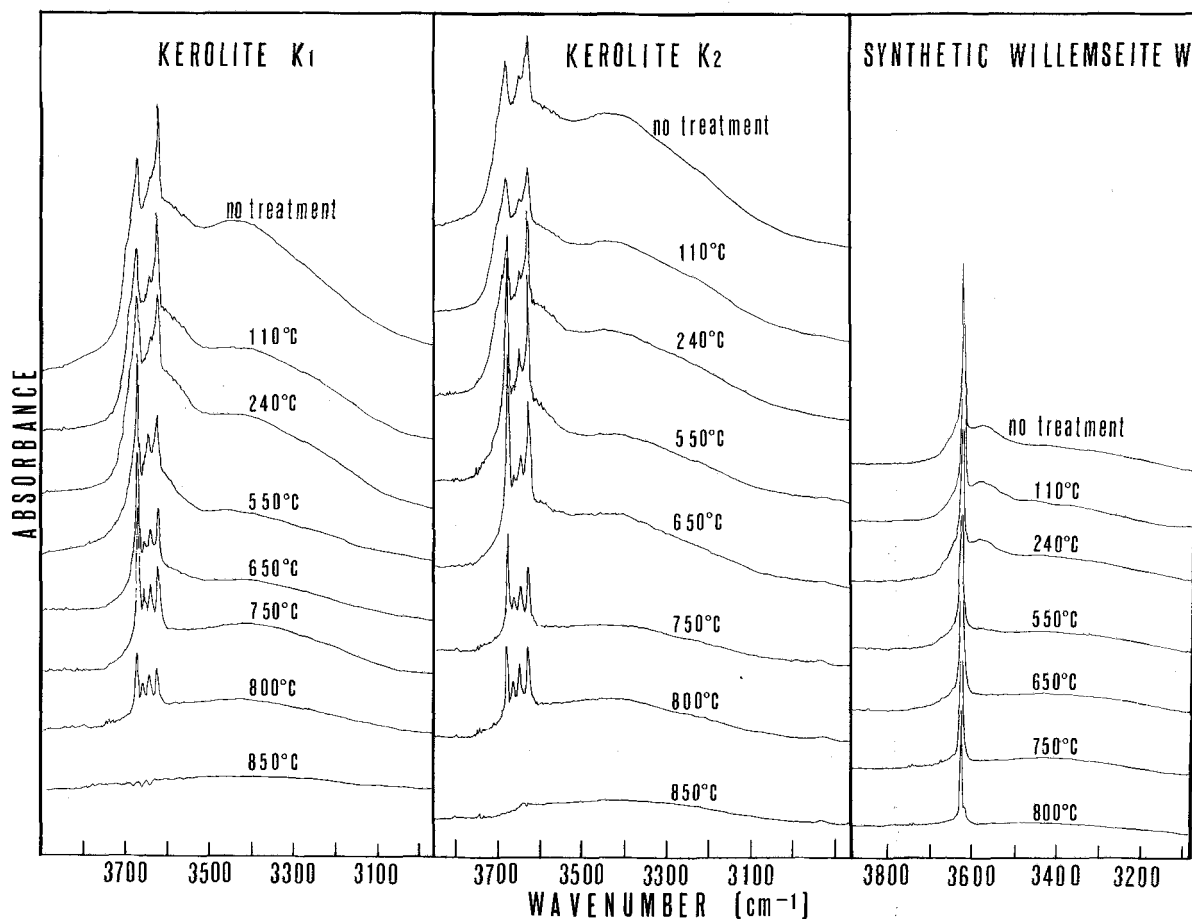
Figure 4.   Infrared spectra in the 3800–3000-cm^{-1} region.

Table 2.   Comparison of experimental (I_{obs}) and theoretical (I_{th}) relative intensities of OH-stretching bands in kerolites K_1 and K_2 and in the pimelite present in garnierite N-P.

Sample	Octahedral sheet composition[1] (%)		N_A band[2] 3677 cm^{-1} MgMgMg		N_B band[2] 3662 cm^{-1} MgMgNi		N_C band[2] 3645 cm^{-1} MgNiNi		N_D band[2] 3625 cm^{-1} NiNiNi		$N_A + N_D$	
	$\frac{Mg}{Mg+Ni}$	$\frac{Ni}{Mg+Ni}$	I_{obs}	I_{th}[3]	I_{obs}	I_{th}[3]	I_{obs}	I_{th}[3]	I_{obs}	I_{th}[3]	I_{obs}	I_{th}[3]
K_1 at 650°C Figure 4	59	41	45	20.5	10.8	42.8	18.9	29.8	25.3	6.9	70.3	27.4
K_1 at 750°C Figure 4	61	39	43.3	22.8	17	43.5	18.3	27.8	21.3	5.9	64.7	28.7
K_2 at 650°C Figure 4	55	45	41	16.6	11	40.8	18.9	33.4	29.1	9.2	69.1	25.8
K_2 at 750°C Figure 4	56	44	39	17.6	16	41.4	18	32.5	27	8.5	66	26.1
N-P at 750°C Figure 6	30	70	18	2.7	11	18.9	20	44.1	51	34.3	62.1	46.2
K_1 at 560°C Figure 5			2708 cm^{-1}		2700 cm^{-1}		2688 cm^{-1}		2674 cm^{-1}			
	61	39	44.5	22.8	15.5	43.5	18.2	27.8	21.8	5.9	66.3	28.7

[1] Estimated from I_{obs}. Note for comparison that, from Table 1b, Mg/(Mg + Ni) = 66.6 in K_1 and 59.0 in K_2.
[2] Notation of OH-stretching bands according to Wilkins and Ito (1967).
[3] I_{th} is calculated assuming a random distribution of Mg and Ni (estimated from I_{obs}) within the octahedral sheet.

quencies and a well-resolved band centered at about 3580 cm^{-1}.

A comparison of the low-temperature spectra of kerolites (Figure 4 and Figure 4 in Brindley *et al.*, 1979) with those of synthetic Ni-talcs (Wilkins and Ito, 1967) or of a natural Mg-willemseite (De Waal, 1970) shows the differences in the 3800–3000-cm^{-1} region between the spectra. In Ni-talc and in Mg-willemseite, the structural OH-stretching vibrations give rise to four sharp peaks (labeled N_A, N_B, N_C, and N_D by Wilkins and Ito, 1967) corresponding to four different environments of the hydroxyl groups (Table 2). Because the specific absorption coefficient of these four bands is similar (Rousseaux *et al.*, 1973) and their width nearly the same, their intensity (I) provides a direct estimation of the composition of the octahedral sheet in terms of Mg and Ni contents. For example, if $\Sigma = I_{NA} + I_{NB} + I_{NC} + I_{ND}$, Mg/Mg + Ni (%) = $(I_{NA} + \frac{2}{3}I_{NB} + \frac{1}{3}N_C)/\Sigma$. Further, the intensity ratios of these bands indicate the partitioning of the two different cations within the octahedral sheet. For Ni-talcs and Mg-willemseites, Wilkins and Ito (1967) and De Waal (1970) showed that the octahedral Mg and Ni are almost perfectly randomly distributed. The low-temperature spectra of kerolites K_1 and K_2 (Figure 4) suggest an important segregation of Mg and Ni as deduced from the large predominance of the N_A (3 Mg) and N_D (3 Ni) bands over the N_B (Mg-MgNi) and the N_C (MgNiNi) bands. Below 550°C, however, part of the additional water may be reversibly regained by the sample during cooling (Brindley *et al.*, 1977), thus obscuring the spectra and making an accurate measurement of the intensity of the OH-stretching bands difficult. Above 550°C the bands are sharper and lend themselves to quantitative evaluation (Table 2).

The intensities of the N bands obtained for kerolites K_1 and K_2 pretreated at 650°C and 750°C (Table 2) yield an estimation of octahedral Mg and Ni in reasonable agreement with the results of the chemical analysis. The IR data, however, systematically yield overestimates of the Ni contents. Further, the data also suggest that both samples have much higher proportions of domains made of hydroxyls associated with either 3 Mg or 3 Ni (about 68%) than would be expected from a random distribution of the Mg and Ni (~27%). Thus, for the whole range of temperatures investigated and more precisely for those samples pretreated above 600°C, it is clear that kerolites differ from Ni-talcs of similar Ni/Mg ratio by the partition of the cations in their octahedral sheets, these cations being randomly distributed in talc and mainly segregated in kerolite.

Figure 4 shows also that below 550°C where some hydration water is present in kerolite, the width and the position of the N bands are not exactly the same as in Ni-talc. To investigate the modifications in the spectra with heating, Figures 4 and 5 (a deuterated K_1 sample)
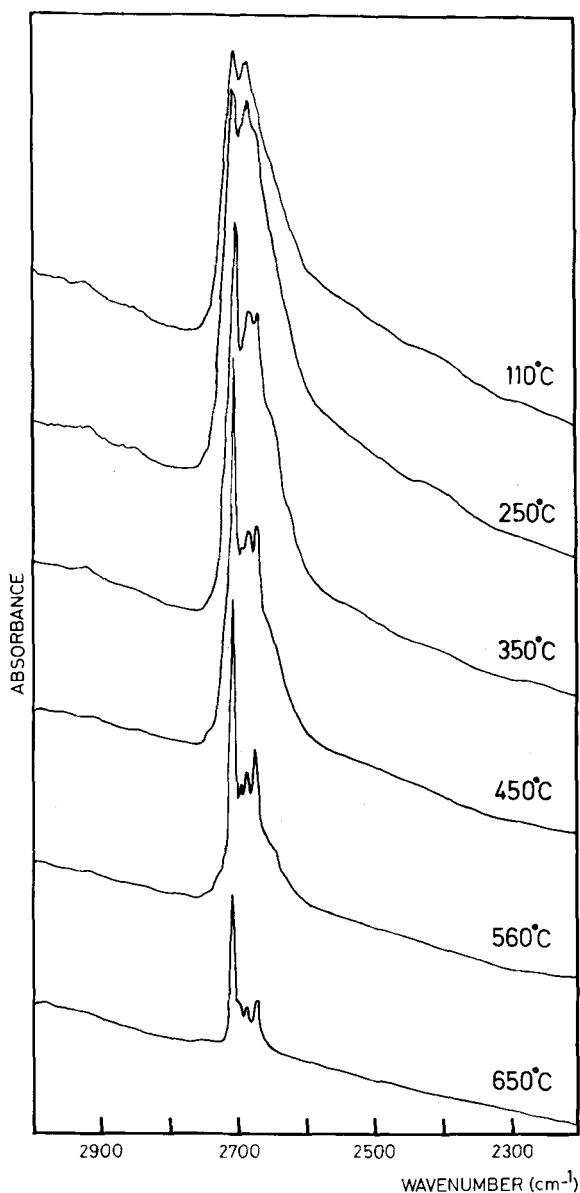

Figure 5.   Infrared spectra of kerolite K_1 after deuteration.

should be compared. However, it is important to note that the temperatures appearing in both figures do not have exactly the same meaning. In Figure 5, the sample was heated in the spectrometer itself and was never cooled to ambient temperature.

From the spectra of deuterated and non-deuterated samples of the same material heated above 550°C (Figures 4 and 5), the wave shift due to deuteration corresponds to a mean ratio of 1.356. Thus, in the D_2O region, the N bands of the heated kerolite K_1 sample have the frequencies listed in Table 2. Further, the intensity of these bands indicates the same proportion and the same partition of Mg and Ni cations as those noted previously for the non-deuterated sample (Table 2).
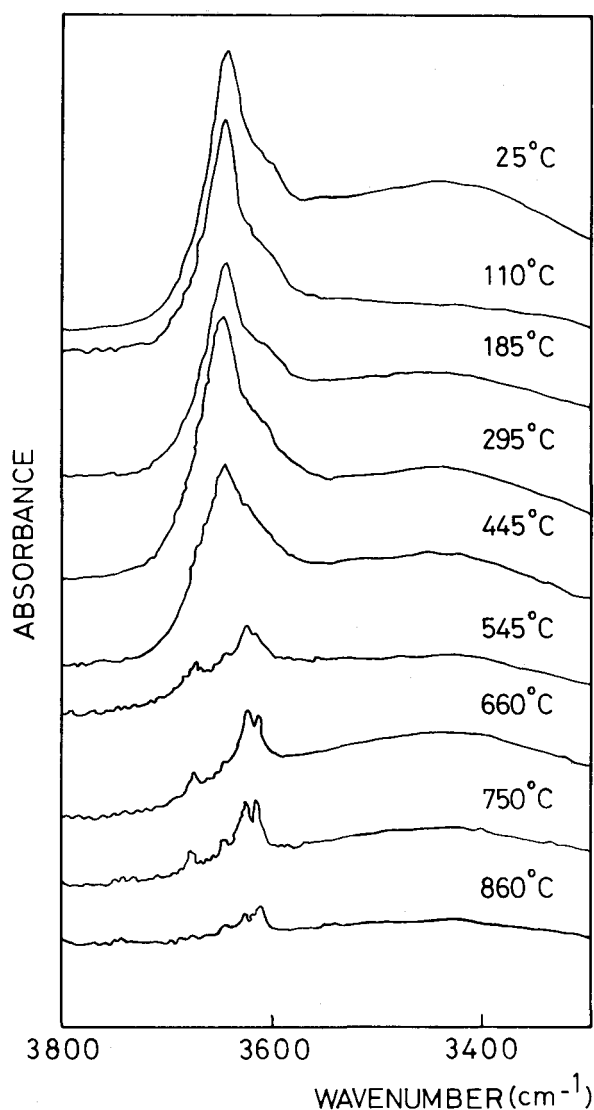
Figure 6. Infrared spectra of garnierite N-P in the 3800–3000-cm^{-1} region.

The same modifications due to thermal treatments (Figures 4 and 5), were noted for all kerolite samples. The structural vibrations sharpened not only on the low-frequency side (where, as discussed below, the stretching vibrations of strongly adsorbed water are expected to occur), but also on its high-frequency side. Also, the intensity of the N bands increased. As a whole, the modifications of the N bands in terms of position, sharpness, and intensity in Figures 4 and 5 are strikingly similar to those reported by Chaussidon (1970) and Suquet et al. (1982) for the OH-stretching bands of Mg- or Li-saturated trioctahedral smectites progressively dehydrated. Both studies demonstrated that the frequency of the OH-stretching vibrations is not a fixed value but depends on the nature and the hydration stage

of the interlayer cations. With Mg as the saturating cation, for example, the N$_A$ band in hectorite (Chaussidon, 1970, Figure 3) shifts progressively with dehydration from 3695 to 3677 cm^{-1} (i.e., the frequency of the N$_A$ band in talc). In a Li-saponite (Suquet et al., 1982, Figure 7) a similar, though slightly more restricted shift is present. In both cases, both bands are present at intermediate stage of hydration but their respective intensity decreases considerably, the former band eventually appearing as a shoulder in the 3690–3700-cm^{-1} region. In the present study (Figures 4 and 5), the N bands of kerolites behaved in the same manner. The 3700-cm^{-1} shoulder vanished as the N$_A$ band at 3677 cm^{-1} sharpened and increased in intensity (Figure 4). The low-temperature spectra showed no N$_D$ band at the expected frequency (2674 cm^{-1}) (Figure 5). This band resolved progressively at the expense of a peak at ~2690 cm^{-1} as the temperature pretreatment and resultant dehydration increased. Thus, in kerolite too, the frequency, sharpness, and intensity of the OH-stretching vibrations appeared to be affected by the hydration stage of interlayer cations trapped between the 2:1 layers. Figures 4 and 5 show also that, as the N bands sharpen, the broad shoulder between 3620 and 3550 cm^{-1} (2660 and 2620 cm^{-1} in Figure 5) which was resolved as a band at 3580 cm^{-1} in willemseite W progressively vanishes. In minerals of the kerolite-pimelite series, this band was previously assigned to the OH-stretching vibration of water forming weak H-bonds with surface oxygens (Brindley et al., 1977, 1979). However, in other swelling clay minerals, this range of frequencies has been attributed to stretching vibrations of the water molecules tightly held by interlayer cations (Prost, 1973; Suquet et al., 1982).

Figure 6 shows that important modifications appear in the 3800–3000-cm^{-1} region of the spectrum of garnierite N-P when it is heated. After moderate heating, the major band is at 3660 cm^{-1} and is probably due to the major OH-stretching vibration of the nepouite present, because the major OH-band in Mg-serpentine is located at 3690 cm^{-1} (Heller-Kallai et al., 1975) and the vibration of this type of hydroxyls is shifted by about 30 cm^{-1} towards lower frequency when Mg is substituted by Ni in amesite (Serna et al., 1977). As in Figure 3, heating the garnierite above the dehydroxylation temperature of the nepouite clearly revealed the pimelite phase also present. This pimelite is characterized by a strong N$_D$, weak N$_A$ and N$_C$, and very weak N$_B$ bands. It is to be noted that at both 660° and 750°C, the N$_D$ band is clearly a doublet with one component at the expected frequency (3625 cm^{-1}) and the second at 3615 cm^{-1}. At present, the assignment of this 3615-cm^{-1} component is uncertain. Although this band occurs in the frequency range of stretching vibrations due to water associated with interlayer cations, its thermal stability (up to 860°C, Figure 6) suggests that it could be due to the vibrations of structural OH located in an environ-

ment uncommon in a talc-like layer (e.g., $R^{2+}R^{2+}R^{3+}$ or $R^{2+}R^{2+}V$). When the contribution of the 3615-cm^{-1} peak is ignored and the intensity of the N bands is measured (Table 2), the estimated Ni content of the pimelite present in garnierite N-P is ~70%, and Ni and Mg appear to be segregated within the octahedral sheet.

CONCLUSIONS

In garnierites consisting of mixtures of 1:1 and 2:1 layer silicates, the higher thermal stability of the 2:1 phase allows its selective examination by IR spectroscopy. For the Ni-rich garnierite sample examined here, both the 710–670-cm^{-1} doublet and the OH-stretching region provided a reasonable estimation of the octahedral composition of the pimelite present in the mixture. In general, and especially where the Ni content of the 2:1 clays is low, the OH-stretching region is likely to provide a more accurate estimate of composition than the 710–670-cm^{-1} doublet.

For minerals of the kerolite-pimelite series, whether they are mixed with serpentines or not, the OH-stretching band intensities suggest the presence of numerous domains made up of segregated Ni and Mg cations. In this respect, kerolites and pimelites differ clearly from their homologues of the talc-willemseite series where the octahedral cations are randomly distributed.

Additional water present in kerolite and pimelite can be considered as hydration water associated with trapped (and thus non-exchangeable) free cations of high hydration energy such as Mg^{2+} and Ni^{2+}. Such an interpretation is based on (1) the analogy of the TGA and DTA patterns of these clays with those of Mg- or Ni-saturated smectites, and (2) the similarity of the effects of dehydration on the position, sharpness, and intensity of their OH-stretching bands as compared with those observed for Mg- and Li-saturated trioctahedral smectites.

Finally, if one accepts that hydrated interlayer Mg and Ni cations are indeed trapped in kerolites and pimelites, the several features distinguishing these minerals from talcs and willemseite can be explained. These features include (1) higher d(001) spacings, (2) higher stacking disorder, (3) less perfect stoichiometry in terms of Si^{4+}/R^{2+} ratio, and (4) general capacity to swell irregularly in the presence of liquids more polar than water. It would therefore appear, especially considering this last characteristic, that kerolites and pimelites are minerals intermediate between talcs and smectites, somewhat like the highest charge-reduced montmorillonites prepared by Calvet and Prost (1971).

ACKNOWLEDGMENTS

REFERENCES

Brindley, G. W. (1980) Order-disorder in clay minerals structure: in *Crystal Structure of Clay Minerals and their X-ray Identification:* G. W. Brindley and G. Brown, eds, Mineralogical Society, London, 495 pp.

Brindley, G. W. and Pham Thi Hang (1973) The nature of garnierites. I. Structures, chemical compositions, and color characteristics: *Clays & Clay Minerals* **21**, 27–40.

Brindley, G. W. and Wan, H. M. (1975) Composition, structures, and thermal behavior of nickel-containing minerals in the lizardite-nepouite series: *Amer. Mineral.* **60**, 863–871.

Brindley, G. W., Bish, D. L., and Wan, H. M. (1977) The nature of kerolite, its relation to talc and stevensite: *Min. Mag.* **41**, 443–452.

Brindley, G. W., Bish, D. L., and Wan, H. M. (1979) Compositions, structures, and properties of nickel-containing minerals in the kerolite-pimelite series: *Amer. Mineral.* **64**, 615–625.

Calvet, R. and Prost, R. (1971) Cation migration into empty octahedral sites and surface properties of clays: *Clays & Clay Minerals* **19**, 175–186.

Chaussidon, J. (1970) Stretching frequencies of structural hydroxyls of hectorite and K-depleted phlogopite as influenced by interlayer cation and hydration: *Clays & Clay Minerals* **18**, 139–149.

De Waal, S. A. (1970) Nickel minerals from Baberton, South Africa: III. Willemseite, a nickel-rich talc: *Amer. Mineral.* **55**, 31–42.

Heller-Kallai, L., Yariv, S., and Gross, S. (1975) Hydroxyl stretching frequency of serpentine minerals: *Min. Mag.* **40**, 197–200.

Jasmund, K., Sylla, H. M., and Freund, F. (1976) Solid solution in synthetic serpentine phases: in *Proc. Intern. Clay Conf., 1975, Mexico City,* S. W. Bailey, ed., Applied Publishing, Wilmette, Illinois, 267–274.

Lemaître, J. and Gérard, P. (1981) Characterization of hydrous nickel-containing minerals by temperature programmed reduction: *Bull. Mineral.* **104**, 655–660.

Mackenzie, R. C. (1970) Simple phyllosilicates based on gibbsite-like and brucite-like sheets: in *Differential Thermal Analysis, Vol. I,* R. C. Mackenzie, ed., Academic Press, London, 775 pp.

Martin, G. A., Renouprez, A., Dalmai-Imelik, G., and Imelik, B. (1970) Synthèse du talc et de l'antigorite de nickel, étude de leur décomposition thermique et de leur réduction en vue d'obtenir des catalyseurs de nickel sur silice: *J. Phys. Physicochim. Biol.* **67**, 1149–1160.

Niskanen, E. (1964) Reduction of orientation effects in quantitative X-ray diffraction analysis of kaolin minerals: *Amer. Mineral.* **49**, 705–714.

Pham Thi Hang and Brindley, G. W. (1973) The nature of garnierites. III. Thermal transformations: *Clays & Clay Minerals* **21**, 51–57.

Prost, R. (1973) Spectre infrarouge de l'eau adsorbée sur l'hectorite saturée par différents cations à des teneurs en eau variables: in *Proc. Intern. Clay Conf., Madrid, 1972,* J. M. Serratosa, ed., Div. Ciencias, C.S.I.C., Madrid, 529–535.

Rousseaux, J. M., Gomez, C., Nathan, Y., and Rouxhet, P. G. (1973) Correlation between the hydroxyl stretching bands and the chemical composition of trioctahedral micas: in *Proc. Intern. Clay Conf., 1972, Madrid,* J. M. Serratosa, ed., Div. Ciencias, C.S.I.C., Madrid, 89–98.

Russell, J. D., Farmer, V. C., and Velde, B. (1970) Replacement of OH by OD in layer silicates and identification of the vibrations of these groups in infrared spectra: *Min. Mag.* **37**, 870–879.

Serna, C. J., Velde, B. D., and White, J. L. (1977) Infrared evidence of order-disorder in amesite: *Amer. Mineral.* **62**, 296–303.

Stubican, V. and Roy, R. (1961) A new approach to assignment of infrared absorption in layer-structure silicates: *Z. Kristallogr.* **115**, 200–214.

Suquet, H., Prost, R., and Pezerat, H. (1982) Etude par spectroscopie infrarouge et diffraction X des interactions eau-cation-feuillet dans les phases à 14.6, 12.2 et 10.1 Å d'une saponite-Li de synthèse: *Clay Miner.* **17**, 231–241.

Voinovitch, I. A., Debras-Gueldon, J., and Louvrier, J. (1962) *L'Analyse des Silicates:* Hermann, Paris, 510 pp.

Wilkins, R. W. T. and Ito, J. (1967) Infrared spectra of some synthetic talcs: *Amer. Mineral.* **52**, 1649–1661.

Yariv, S. and Heller-Kallai, L. (1975) The relationships between the IR spectra of serpentines and their structures: *Clays & Clay Minerals* **23**, 145–152.

Резюме—Два образцы керолита и один образец гарниерита были подвержены постепенной термической обработке перед исследованием путем инфракрасной спектроскопии (ИС) в спектральных областях от 1200 до 600 см⁻¹ и от 3800 до 3000 см⁻¹. Термическая обработка гарниерита (смесь непуита и пимелита) селективно дегидроксилировала непуит, таким образом допуская возможность исследования колебательных полос OH вследствие присутствия пимелита. Как относительные интенсивности двойной полосы 710–670 см⁻¹, так и различные валентные полосы OH указывали на то, что содержание Ni в этом пимелите было около 70%. Термические обработки не изменяли область 1200–600 см⁻¹ спектра керолитов, но вызывали заметные сужения полос в области валентных колебаний OH. Относительные интенсивности структурных валентных полос OH обезвоженных керолитов показали, что они отличаются по распределению катионов Ni и Mg в октаэдрических местах от Ni-nn mrjd gjlj4yjuj cjcnfdf. Эти катионы беспорядочно распределены в Ni-тальке, но, в основном, находятся в отдельных областях Ni и Mg в керолите. С увеличением температуры и прогрессом дегидратации изменения формы (остроты), интенсивности и положения структурных валентных полос OH керолитов похожи на изменения, которые происходили с Mg- или Ni-насыщенными трехоктаэдрическими смектитами. Кривые этих минералов по термическому анализу также являются подобными кривым для Mg- или Ni-насыщенных смектитов, и наводят на мысль, что также в керолитах гидратационная вода связана с межслойными (хотя необменными) катионами Ni и/или Mg. [E.C.]

Resümee—Zwei Kerolit- und eine Garnierit-Probe wurden auf ansteigende Temperaturen erhitzt bevor sie mittels Infrarotspektroskopie (IR) im Bereich von 1200 bis 600 cm⁻¹ und 3800 bis 3000 cm⁻¹ untersucht wurden. Das Erhitzen von Garnierit (ein Gemenge aus Nepouit und Pimelit) führte zu einer selektiven Dehydroxylierung von Nepouit, wodurch eine Untersuchung der OH-Schwingungsbanden von Pimelit möglich wurde. Die relativen Intensitäten des 710 bis 670 cm⁻¹ Dubletts und der verschiedenen OH-Streckschwingungsbanden deuten darauf hin, daß der Ni-Gehalt des untersuchten Pimelit bei etwa 70% liegt. Die Erhitzungsversuche veränderten den Bereich von 1200 bis 600 cm⁻¹ der Kerolitspektren nicht. Sie bewirkten jedoch eine beachtliche Verschärfung im Bereich der OH-Streckschwingung. Die relativen Intensitäten der strukturellen OH-Streckschwingungsbanden der dehydratisierten Kerolite zeigten, daß sie anders sind als die von Ni-Talk-Proben, die eine ähnliche Zusammensetzung im Hinblick auf die Verteilung von Ni und Mg auf den Oktaederplätzen haben. Diese Kationen sind im Ni-Talk statistisch verteilt, während sie in Kerolit in Mg- und Ni-Domänen auftreten. Die Veränderungen in der Schärfe, der Intensität und in der Lage der strukturellen OH-Streckschwingungsbanden der Kerolite mit zunehmender Temperatur und zunehmenden Dehydratationsprozessen sind ähnlich denen, die bei Mg- oder Li-gesättigten trioktaedrischen Smektiten auftreten. Auch die Kurven der Differentialthermoanalyse dieser Minerale zeigen Ähnlichkeiten mit denen von Mg- und Ni-gesättigten Smektiten. Dies deutet darauf hin, daß das Hydrationswasser auch in den Keroliten an die Zwischenschichtkationen Ni und/oder Mg gebunden ist (die jedoch nicht austauschbar sind). [U.W.]

Résumé—Deux kérolites et une garniérite ont été soumises à des traitements thermiques progressifs avant d'être examinées par spectroscopie infrarouge dans les régions spectrales 1200–600-cm⁻¹ et 3800–3000-cm⁻¹. Le chauffage de la garniérite (qui était un mélange de népouite et de pimélite) provoque la déshydroxylation sélective de la népouite et permet d'examiner les bandes de vibration des hydroxyles structuraux de la pimélite. Tant les intensités relatives des bandes formant un doublet à 710 et 670 cm⁻¹ que celles des vibrations de valence des hydroxyles structuraux permettent d'estimer que le contenu en nickel de cette pimélite est proche de 70%. Les traitements thermiques n'affectent guère la région spectrale 1200–600-cm⁻¹ des kérolites mais ils provoquent un affinement notable de la région où sont localisées les vibrations de valence des hydroxyles structuraux. L'intensité relative des différentes vibrations dues à ces hydroxyles permettent d'établir que la répartition des cations octaédriques Ni et Mg dans les kérolites déshydratées est très différente de celle des talcs nickelifères de même composition. Les cations octaédriques sont répartis au hasard dans les talcs et répartis en domaines magnésiens et nickelifères dans les kérolites. Les modifications de position, d'intensité et de largeur qui affectent les bandes de vibration des hydroxyles structuraux des kérolites au fur et à mesure que progresse leur déshydratation, sont semblables à celles de smectites trioctaédriques saturées par Mg ou Li. De même, les kérolites montrent des courbes thermogravimétriques et des diagrammes ATD qui ressemblent à ceux de smectites saturées par Mg²⁺ et/ou par Ni²⁺. Ces analogies suggèrent que, dans les kérolites aussi, l'eau d'hydratation est liée à des cations interfoliaires. Cependant, dans les kérolites, ces cations ne sont pas échangeables.