

IDENTIFICATION OF KAOLIN MINERALS IN THE PRESENCE OF CHLORITE BY X-RAY DIFFRACTION AND INFRARED ABSORPTION SPECTRA

by

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ABSTRACT

Experimental data are presented to show that the current auxilliary procedures adopted for identification of kaolinite in the presence of chlorite are not generally valid because the procedures often fail to give an explicit condition for distinguishing both the minerals.

As the result of an examination of numerous infrared spectra in the OH region of clay minerals, obtained by using Nippon Bunko DS-401G Grating Spectrophotometer, it turned out that the absorption band at $3698 \pm 2 \text{ cm}^{-1}$ is effective for distinguishing kaolinite from other clay minerals without the use of any additional techniques. The absorption band seems to be less affected by variation of particle size and crystallinity than is the X-ray diffraction pattern. The band is detectable to a few weight percent of kaolinite in total amounts of clay minerals. Identification of kaolinite by its absorption spectrum in clay samples from sedimentary rocks was successful.

INTRODUCTION

In the course of studies on clay minerals in recent marine sediments and sedimentary rocks, we often encounter difficulty in identification of kaolinite in the presence of chlorite by X-ray powder diffraction methods. In such a case additional techniques such as critical heat treatment and hydrochloric acid treatment are frequently used. Though X-ray powder data obtained after these treatments provide valuable information for identifying kaolinite, it is often conditional because the treatments generally fail to give an explicit condition.

The infrared method has not yet been applied to the above problem. Recently the writers examined in detail features of absorption bands in the hydroxyl region for each clay mineral and noticed an effective absorption band for distinguishing kaolinite from the other clay minerals. Consequently they could easily develop their research on this problem.

The purpose of this paper is (1) to direct attention to the difficulty in obtaining useful differentiation by X-ray analysis involving additional

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techniques and (2) to propose the use of an infrared method for rapid, exact and sensitive recognition of kaolinite.

The writers wish to express their sincere thanks to Prof. Dr. Toshio Sudo of the Geological and Mineralogical Institute for his comments and also to Prof. Dr. Koji Nakanishi of the Chemical Institute for the use of spectrophotometers.

CRITICISM OF X-RAY IDENTIFICATION METHODS

Characteristic Reflections of Kaolinite

In principle, detection of kaolinite is possible by the presence of 003 reflection, $d = 2.383 \text{ \AA}$, and 060 reflection, $d = 1.490 \text{ \AA}$. However, since the 003 reflection is fairly weak and the 060 reflection is often modified by 060 reflections from other dioctahedral minerals, the exact detection of small amounts of kaolinite admixed with chlorite and other minerals is very difficult. In such cases the detection by the above reflections is indefinite. Thus, further analysis is necessary.

Thermal Technique

A combined thermal and X-ray method has been generally accepted as a method for distinguishing kaolinite and chlorite. However, as pointed out by Nelson and Roy (1953) (see also Brindley, 1961) there is a difficulty in this method in that a temperature (generally $600^\circ \sim 450^\circ\text{C}$) and a length of heating period (generally $\frac{1}{2} \sim 1 \text{ hr}$) used in the treatment, must be carefully chosen in accordance with particle size and degree of crystallinity. In addition, consideration must be given to variations in thermal behaviour of kaolin mineral varieties and chlorite mineral species. This statement is based on the following experimental results.

By using the oscillating-heating X-ray powder diffraction method, an experiment was made on detailed thermal change of 001 and 002 chlorite reflections and of 001 kaolinite reflection. The reference specimens used are sedimentary and hydrothermal kaolinites, dickite, ripidolite, leuchtenbergite and thuringite. They are well-crystallized materials except for sedimentary kaolinite with somewhat lower crystallinity. The intensity of each basal reflection was measured at intervals of 5° to 10°C . as the temperature was being raised 10°C per minute. Figures 1a and 1b are graphs of the change in intensity of the basal reflection against the change of temperature. In the experiments with the kaolin minerals, the 001 reflections disappeared entirely between 500° and 720°C . In the experiments with the chlorite minerals, the 002 reflections disappeared between 580° and 660°C , and the 001 reflections gave their maximum intensities between 610° and 710°C . Since these critical temperatures were measured in continuous heating experiment, the temperature at which the basal reflection disappears tends to be somewhat lower if thermal treatment is maintained over a longer period of time. It is noteworthy that these experiments have produced varied behaviour and overlap of critical

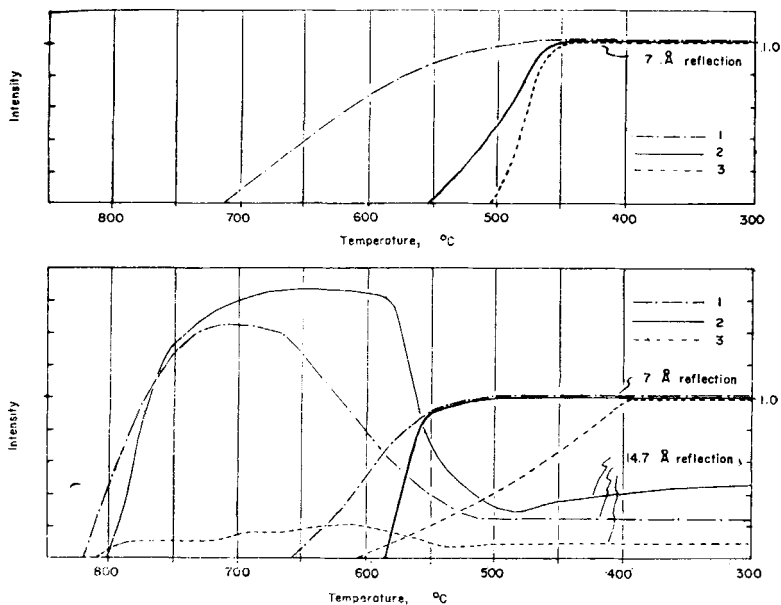


FIGURE 1.—(a) The change in intensities of the 001 reflections of some kaolinites against the change of temperature. 1, Dickite (Kasuga Mine). 2, Hydrothermal kaolinite (Kampaku Mine). 3, Sedimentary kaolinite (Hara, Gifu Pref.).—(b) The change in intensities of the 001 and 002 reflections of some chlorites against the change of temperature. 1, Ripidolite (Hitachi Mine). 2, Leuchtenbergite (Wanibuchi Mine). 3, Thuringite (Ichinokoshi, Toyama Pref.).

temperatures. Because of this, it is still more difficult to choose the best temperature for distinguishing kaolinite and chlorite.

Hydrochloric Acid Dissolution Technique

Hydrochloric acid treatment has often been used. In this treatment chlorite is decomposed, whereas kaolinite remains behind. This treatment is generally carried out with 6N hydrochloric acid in a boiling water bath. Though a poorly crystallized chlorite or iron-rich chlorite is easily decomposed by the treatment in a period of time as short as 10 min, generally treatment for 1 hr is required to achieve complete decomposition of most chlorites. However, according to Kobayashi and Oinuma (1961), experimental results suggest that it is difficult to choose with certainty the best period of time for treatment to differentiate between kaolinite and chlorite, regardless of variations of chemical composition and of crystallinity. Therefore, the following case frequently comes into question.

Figure 2 exemplifies X-ray diffraction patterns of four clay fractions from sedimentary rocks before and after hydrochloric acid treatment for one hour. All the patterns after treatment have no distinct 14.5 Å line, and have a

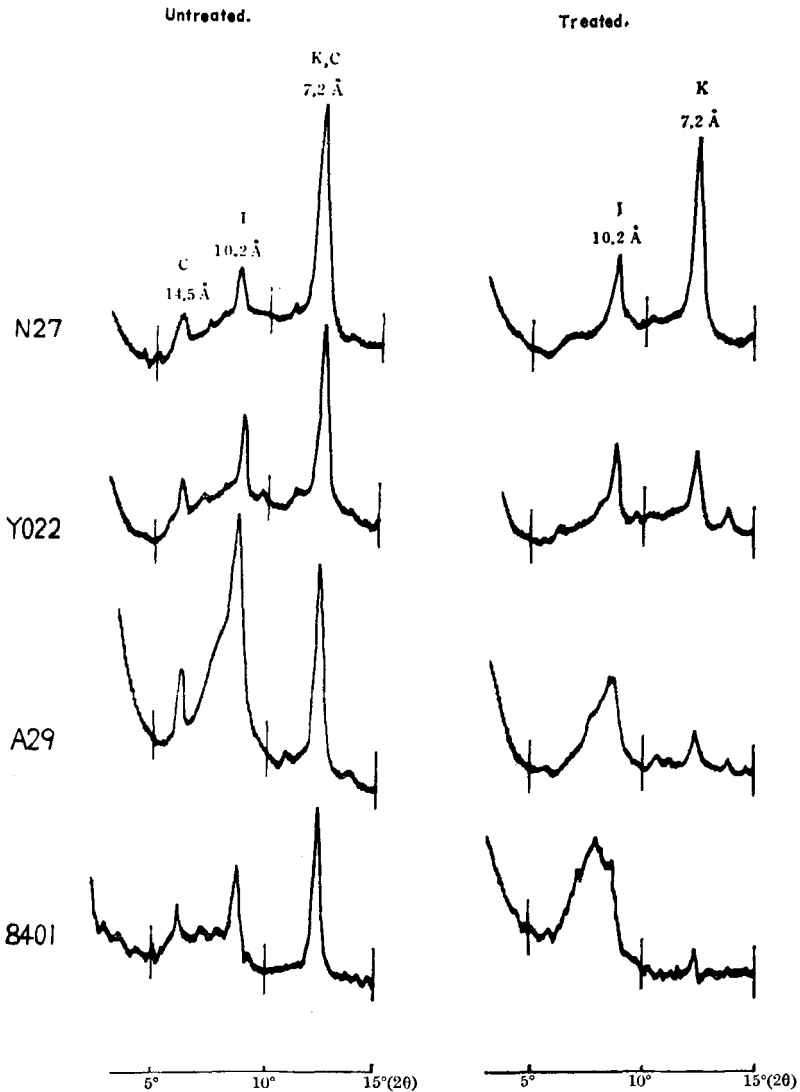


FIGURE 2.—X-ray diffraction patterns of four specimens before and after hydrochloric acid treatment for one hour. (Ni-filtered CuK_α radiation.)

weaker 7 Å line than untreated specimens. This fact suggests the presence of chlorite and kaolinite. Figure 3 shows X-ray diffraction patterns of two other clay samples before and after treatment for 10 min. The pattern of specimen A04 after treatment has no 14.5 Å and 7 Å lines, but that of specimen A03 has a weak 7 Å line. Therefore specimen A04 does not contain

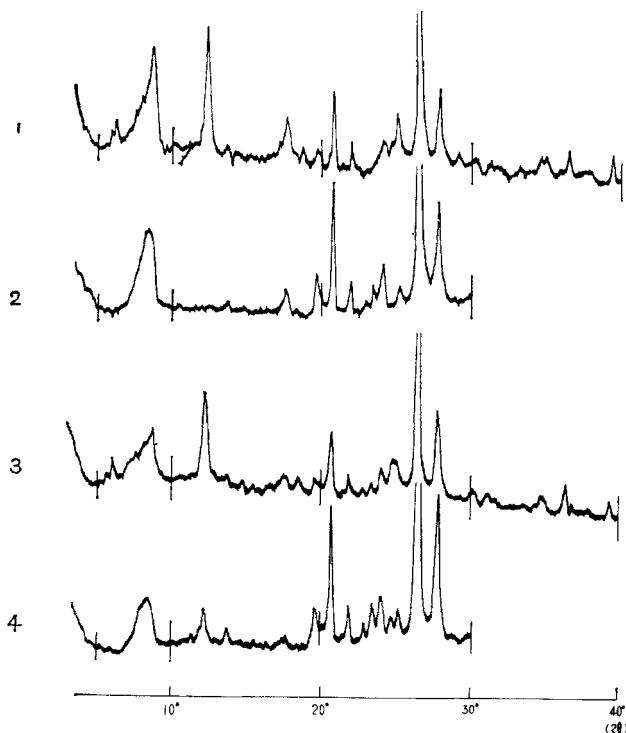


FIGURE 3.—X-ray diffraction patterns of two specimens before and after hydrochloric acid treatment for 10 min. (Ni-filtered $\text{CuK}\alpha$ radiation)
 1. A04 untreated, 2. A04 treated, 3. A03 untreated, 4. A03 treated.

kaolinite, but specimen A03 may contain both kaolinite and chlorite. As seen in the X-ray patterns of specimens A03, A29, and 8401, the presence of a weak 7 \AA line cannot give a clear definition of kaolinite. This is because it is ambiguous whether the weak line is caused by the presence of a small amount of kaolinite, or imperfect decomposition of chlorite. This is a serious weakness of the hydrochloric acid treatment method.

IDENTIFICATION BY INFRARED ABSORPTION ANALYSIS

Experimental

In their study on infrared absorption spectra of clay minerals, Oinuma and Kodama (1962) pointed out that kaolinite has a characteristic absorption band in the OH region, and that the band may be effective for distinguishing kaolin minerals from the other clay minerals. Recently the efficacy of the band to the identification has been reconfirmed on the basis of results of further

experiments. The experiments have been made using Nippon Bunko DS-401G Grating Spectrophotometer having excellent resolution power. Finely powdered specimens of typical clay minerals were prepared as mull in Nujol and mounted between sodium chloride cover slides. The region from 4000 cm^{-1} to 3200 cm^{-1} was scanned slowly. The frequency of each absorption band was calibrated with the absorption band of polystyrene at 3027 cm^{-1} .

Results

The infrared spectra obtained are reproduced in Figs 4 (a), (b), (c), (d), and (e). The wave numbers are listed in Table 1. Table 2 summarizes features of

TABLE 1.—LIST OF THE WAVE-NUMBER OF INFRARED ABSORPTION SPECTRA IN FIG. 4 (a), (b), (c), (d) AND (e).

Fig. No.	Mineral	Origin	Wave-number (cm^{-1})					
			1	2	3	4	5	6
4(a)	1 Dickite	Nikkyo Mine	3700	3654	3626			
	2 Dickite	Kasuga Mine	3700	3660	3628			
	3 Nacrite	Nikkyo Mine	3696	3654	3624			
	4 Nacrite	Kasuga Mine	3700	3660	3628			
	5 Kaolinite	Kurata Mine	3696	3656	3626			
	6 Kaolinite	Kampaku Mine	3698	3662	3630			
	7 Kaolinite	Nikkyo Mine	3696	3658	3628			
	8 Kaolinite	Hara, Gifu Pref.	3696	3659	3624			
4(b)	1 Kaolinite	Sanage, Aichi Pref.	3698	3663	3630			
	2 Metahalloysite	Zao Mine	3696	3670	3630			
	3 Metahalloysite	Joshin Mine	3696		3632	3570	3420	
	4 Metahalloysite	Azuma Mine	3696		3624	3570	3410	
	5 Halloysite	Kusatsu, Gumma Pref.	3696		3624		3414	
	6 Halloysite	Chitose, Kanagawa P.	3698		3630	3575	3420	
4(c)	1 Leuchtenbergite	Wanibuchi Mine		3664		3574	3412	
	2 Mg-chlorite	Hanaoka Mine				3582	3414	
	3 Mg-chlorite	Hanaoka Mine				3584	3454	
	4 Ripidolite	Hitachi Mine				3560	3420	
	5 Chamosite	Arakawa Mine				3540	3380	
	6 Thuringite	Ichinokoshi, Toyama P.				3550	3390	
4(d)	1 Illite (2M-type)	Shiraishi Mine			3630			
	2 Illite (1M-type)	Abeshiro Mine			3642		3394	
	3 Montmorillonite	Endani Mine			3635		3406	
	4 Montmorillonite	Togo, Tottori Pref.			3644		3416	
	5 Montmorillonite	Hanaoka Mine			3641		3414	
	6 Montmorillonite	Aterazawa, Yamagata P.			3631		3416	
	7 Montmorillonite	Hojun, Gumma Pref.			3630		3424	
	8 Montmorillonite	Maeyama, Akita Pref.			3633		3428	
4(e)	1 Vermiculite	Uzumine, Fukushima P.					3360	
	2 Allophane	Kanuma, Tochigi Pref.					3410	
	3 Pyrophyllite	Honami Mine		3680				
	4 Talc	Manshu		3685				
	5 Serpentine	Haruyama, Fukushima P.		3674				
	6 Serpentine	Kamuikotan, Hokkaido						

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TABLE 2.—LIST OF FEATURES OF INFRARED ABSORPTION SPECTRA FOR EACH CLAY MINERALS

Mineral	Wave-number (cm^{-1})	Order of Relative Intensity	Remarks
Dickite, Nacrite	3696-3700	3 s	Shoulder-like peak in some cases.
	3654-3660	2 s	
	3624-3628	1 s	
Kaolinite	3696-3698	1 s	Indistinct shoulder-like peak in some cases.
	3656-3663	3 s	
Metahalloysite	3624-3630	2 s	In one case.
	3696	2 s	
	3670	(5) ind.	
	3624-3632	1 s	
	3570	3 s	
Halloysite	3410-3420	4 v br.	
	3696-3698	3 s	
	3624-3630	1 s	
Leuchtenbergite	3575	4 br. or ind.	
	3414-3420	2 v br.	
	3664	3 ind.	
Ripidolite	3574	1 br.	The richer the content of iron, the lower the frequency of the absorption bands.
	3412	2 br.	
Chamosite	3560	2 br.	The relative intensity of iron-rich chlorite is reverse to that of magnesium-rich chlorite.
	3420	1 br.	
Thuringite	3540	2 v br.	
	3380	1 v br.	
Illite	3550	2 br.	
	3390	1 v br.	
Montmorillonite (common)	3630-3642 (3394)	1 s v br.	Due to absorbed water.
	3630-3644	1 s	Similar to absorption bands of illite containing absorbed water.
Vermiculite	3406-3428	2 br.	Similar to absorption band of allophane.
Allophane	3360	1 v br.	
Pyrophyllite	3410	1 v br.	
Talc	3680	1 s	
Serpentine	3685	1 s	
	3674	1 s	

NOTE: S: sharp, br.: broad, v br.: very broad, ind.: indistinct.

spectra for each of the investigated mineral species or varieties. As easily seen in these data, a remarkable feature revealed in all spectra of kaolin minerals is the presence of the band at $3698 \pm 2 \text{ cm}^{-1}$, whereas none of the other clay minerals examined have such absorption band. The band is actually one member of the triplet in the range of $3700 \sim 3600 \text{ cm}^{-1}$ of kaolinite and of dickite, as reported in previous investigations (Roy and Roy, 1957), and is also characteristic of nacrite. The various hydrogenic stretching frequencies

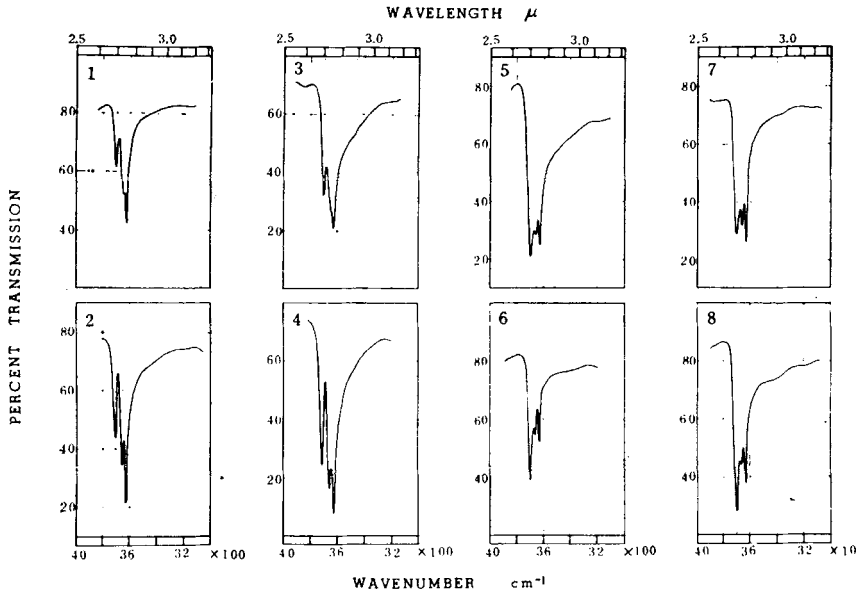


FIGURE 4 (a).—Infrared absorption spectra in the OH region of some kaolin minerals. Corresponding wave numbers are listed in Table I.

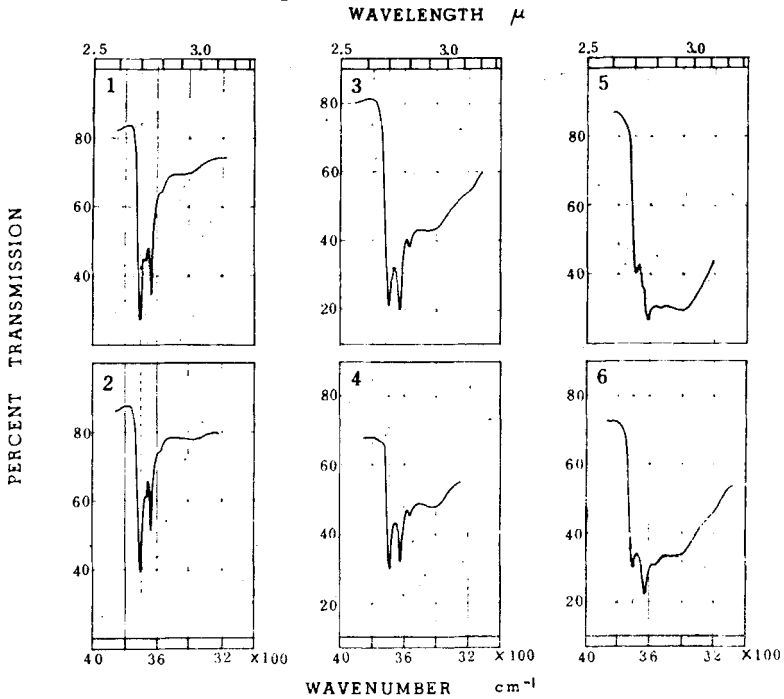


FIGURE 4 (b).—Infrared absorption spectra in the OH region of some kaolin minerals. Corresponding wave numbers are listed in Table I.

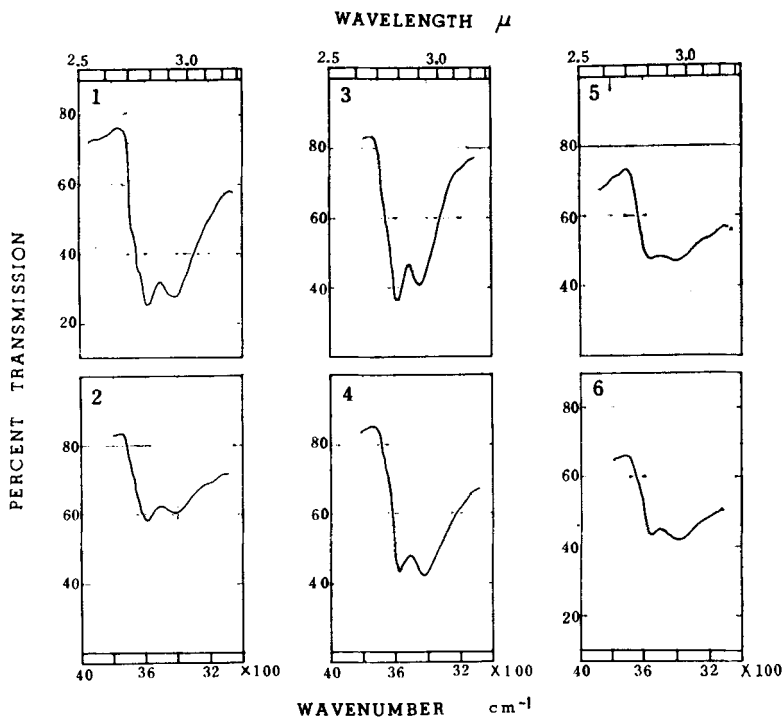


FIGURE 4 (c).—Infrared absorption spectra in the OH region of some chlorite minerals. Corresponding wave numbers are listed in Table 1.

observed in kaolin minerals can be tentatively assigned on the basis of Nakamoto, Margoshes and Rundle (1955) study as follows:

Frequency	Assignment	OH O Distance
3700 ~ 3696 cm^{-1}	Free OH	—
3670 ~ 3656 cm^{-1}	Associated OH*	3.2 (Å)
3632 ~ 3624 cm^{-1}	Associated OH*	3.1 (Å)
3575 ~ 3570 cm^{-1}	Associated OH*	3.0 (Å)
3420 ~ 3410 cm^{-1}	Associated OH†	2.8 (Å)

* Due to hydrogenic stretching between hydroxyl ion and its surrounding oxygen ions. The lower the frequency, the stronger the hydrogen bond.

† Due to a symmetrical stretching of interlayer water molecule.

Consideration of the variability of X-ray data on the kaolin minerals used in the writers' experiments leads to the conclusion that the absorption band at $3698 \pm 2 \text{ cm}^{-1}$ due to free hydroxyl stretching seems to be less affected by variation of crystallinity than is the X-ray diffraction pattern.*

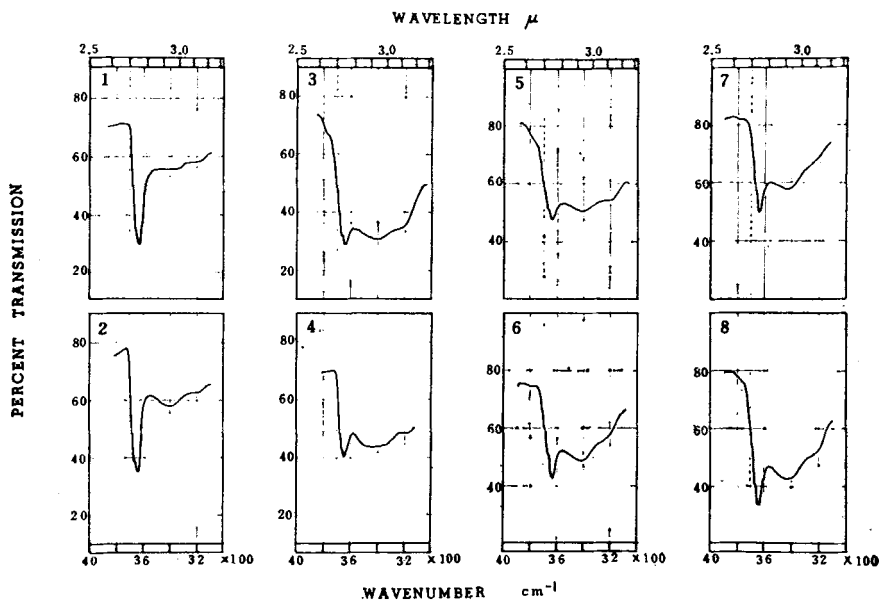


FIGURE 4 (d).—Infrared absorption spectra in the OH region of some illites and montmorillonite minerals. Corresponding wave numbers are listed in Table 1.

The absorption spectra for artificial mixtures of kaolinite and other clay minerals in various mixing ratios give information on the detection limit. (Fig. 5). Even in the spectra of a mixture of chlorite (1), illite (1), montmorillonite (1) and kaolinite (0.14), the band at $3968 \pm 2 \text{ cm}^{-1}$ is visible as a shoulder-like peak. Its approximate detection limit was estimated to be a few weight percent of kaolinite in the total amount of clay minerals. This seems to be about the same detection limit as in the X-ray method. However, infrared absorption analysis has an advantage in that there is no necessity for using any additional treatment.

Examples of Identification of Kaolin Minerals

The above-mentioned six hydrochloric acid treated specimens were re-examined by infrared absorption analysis. The results are shown in

* See also, for example, Hinckley in this volume.

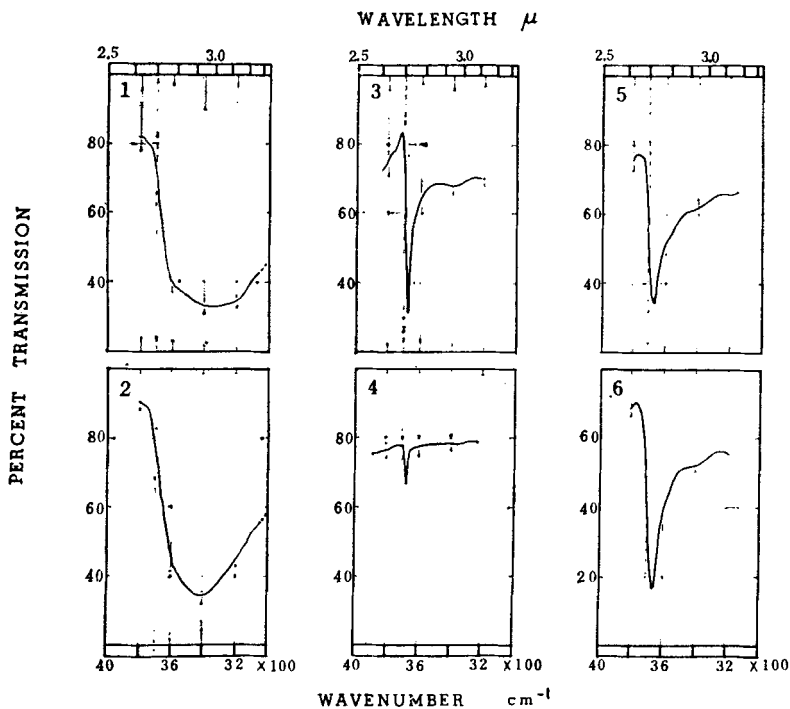


FIGURE 4 (e).—Infrared absorption spectra in the OH region of vermiculite, serpentine and some other minerals. Corresponding wave numbers are listed in Table I.

Figs 6 (a) and (b). Infrared spectra in the usual infrared region of $4000 \sim 650 \text{ cm}^{-1}$ were recorded by using a Nippon Bunko IR-S spectrophotometer. Results in the hydroxyl region were recorded with the DS-401G Grating Spectrophotometer. The spectrum of the specimen N27 shows other characteristic absorption bands of kaolinite in the range of $1100 \sim 900 \text{ cm}^{-1}$, but these bands can not be found when only a small amount of kaolinite is present ($< 15 \sim 20$ per cent) (Oinuma and Kodama (1962)). On the other hand, the absorption band at $3698 \pm 2 \text{ cm}^{-1}$ was clearly observed in the specimens N27 and Y022, and even in the specimens A29 and A03 showing a very weak 7 \AA X-ray diffraction line even after acid treatment. Thus, it can be concluded that the weak 7 \AA line is caused by the presence of a small amount of kaolinite. A very weak 7 \AA line in the specimen 8401 is still doubtful since the absorption band is very faint. Even if the specimen contains kaolinite, the amount might be less than a few weight percent. These results prove that infrared absorption analysis facilitates the identification of kaolinite, particularly in the presence of chlorite.

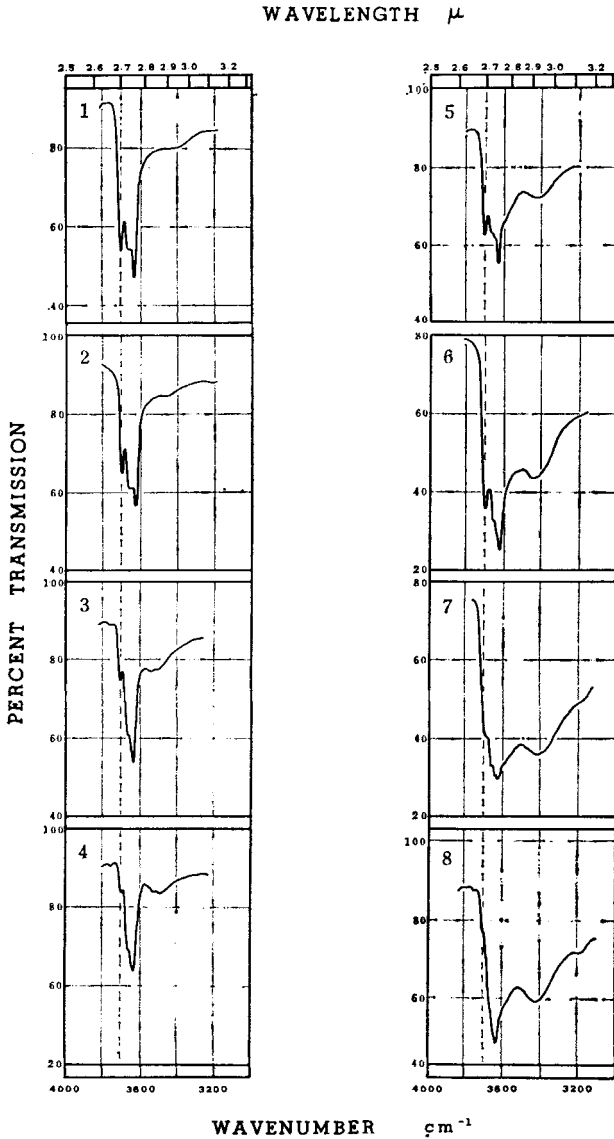


FIGURE 5.—Infrared absorption spectra of mixtures of standard clay minerals in the OH region.

1. I:K = 1:1, 2. I:K = 1:0.5, 3. I:K = 1:0.2, 4. I:K = 1:0.1, 5. Ch:I:K = 1:1:1, 6. Ch:I:M:K = 1:1:1:1, 7. Ch:I:M:K = 1:1:1:0.5, 8. Ch:I:M:K = 1:1:1:0.14. I . . . Illite (Shiraishi Mine), Ch . . . Chlorite (Wanibuchi Mine), M . . . Montmorillonite (Hojun, Gumma Pref.), K . . . Kaolinite (Hara, Gifu Pref.).

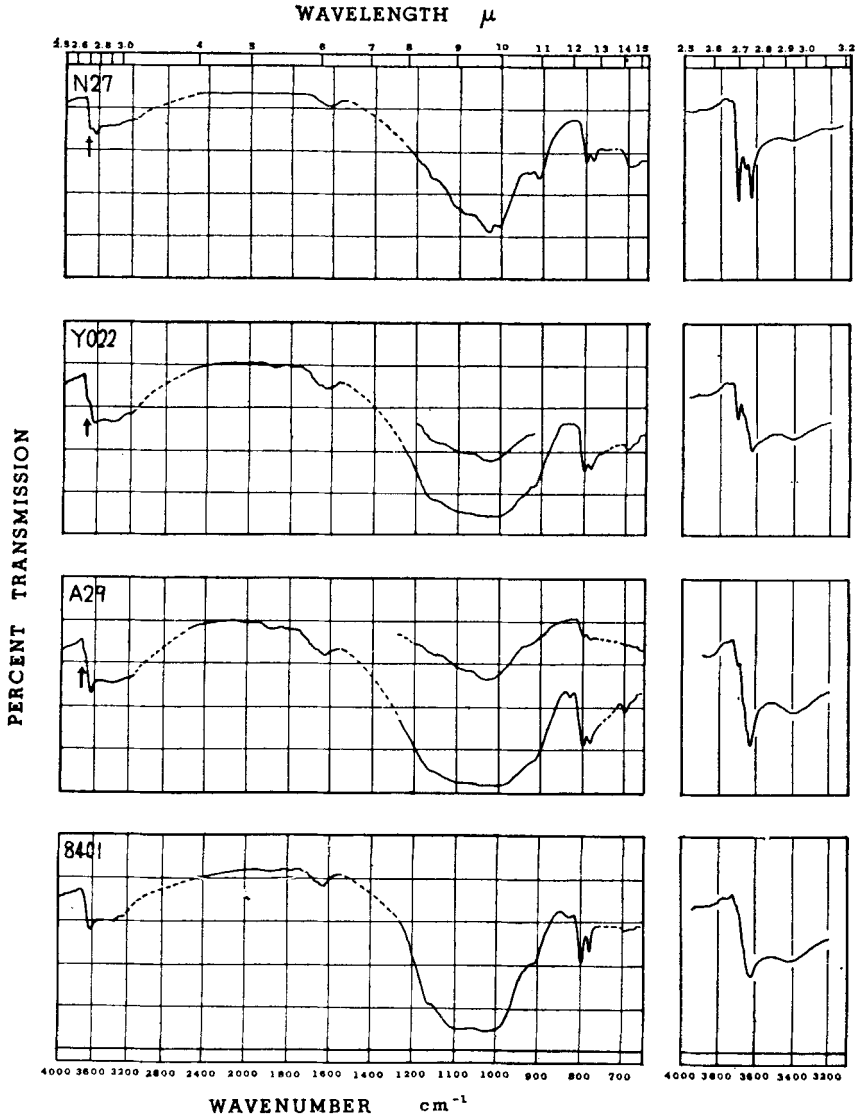


FIGURE 6 (a).—Infrared absorption spectra of four specimens from sediments and sedimentary rocks.

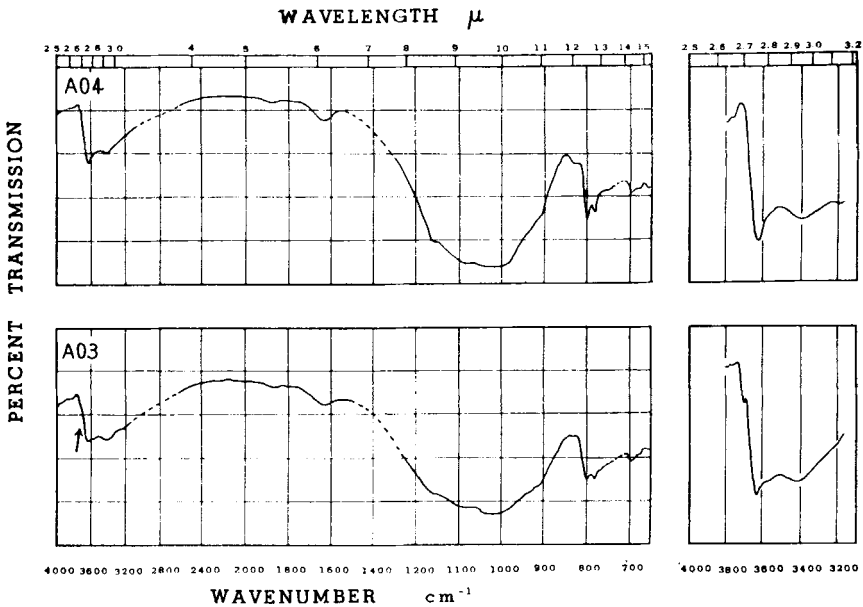


FIGURE 6 (b).—Infrared absorption spectra of two specimens from sedimentary rocks.

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