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INFRARED STUDY OF MIXED-LAYER CLAY MINERALS

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ABSTRACT

The writers obtained the infrared absorption spectra of several specimens of mixed-layer clay minerals which were previously studied in detail by means of *x*-ray analysis, differential thermal analysis and chemical analysis. The specimens used in this study are, illite-montmorillonite or hydrated form of illite, pyrophyllite-montmorillonite, aluminian chlorite-montmorillonite, and kaolin-montmorillonite, occurring as respectively interstratified clay minerals. The results revealed that the infrared absorption spectra of these mixed-layer clay minerals overlap those of the respective constituents of each mixed-layer minerals; this fact agrees well with the results obtained through *x*-ray analysis and other methods. In particular, the infrared absorption spectra of the interstratified pyrophyllite-montmorillonite specimen clearly showed the absorptions of the two constituent clay minerals. In the spectra of the interstratified aluminian chlorite and montmorillonite, an absorption near 700 cm^{-1} tells that the chlorite, one of the major constituents of the specimen, is undoubtedly Al-rich chlorite, as is known by comparing the absorption spectra of Mg-rich chlorite and Al-rich chlorite. Also, in the case of the specimen of interstratified kaolin-montmorillonite, its infrared absorption spectra clearly showed the characteristics of the constituent minerals which would be hardly identified by the *x*-ray method. Thus, the infrared absorption spectra have justified the specific identification of the specimens.

INTRODUCTION

In the field of clay mineralogy, study of infrared absorption spectra has lately made a remarkable progress, as exemplified by numerous researches on the absorptions in the OH region, on the relationships between the chemical composition and the variation of position of absorption bands, and on the after-heating variation of absorption bands. Concerning the OH region a large number of researches have been made, particularly on absorption of kaolin minerals (Roy and Roy, 1957; Lyon and Tuddenham, 1960; Newnham, 1961; Serratosa *et al.*, 1962; Kodama and Oinuma, 1963). On mica there are the works of Serratosa and Bradley (1958) and Vedder (1964). Stubičan and Roy (1961a, c), in their study of synthetic clay minerals, reported on the assignment of absorption bands and the variation of absorption bands due to substitution. On chlorite Tuddenham and Lyon (1958) and Hayashi and Oinuma (1965) studied their chemical compositions and variation of their absorption bands. As for biotite, one of the latest studies is one by Liese (1963). After-heating changes of absorption bands of clay minerals have been studied by Stubičan (1957 and 1959), Stubičan and Roy (1961b), and

Hayashi and Oinuma (1963). Thus, many kinds of clay minerals are being studied from various angles by means of infrared absorption spectra. Since numerous kinds of mixed-layer clay minerals have become known lately, elucidation of such minerals is now one of the important problems of clay mineralogy. The present paper deals with the infrared absorption spectra of various kinds of mixed-layer clay minerals from Japan which were previously studied in detail by *x*-ray and other methods. The writers made a comparative study of these spectra and those of each constituent mineral, for purpose of supplementing the infrared study of clay minerals from a hitherto unattempted angle.

SPECIMENS

The specimens used in this study are mixed-layer clay minerals, namely, illite-montmorillonite or hydrated form of illite, pyrophyllite-montmorillonite, aluminian chlorite-montmorillonite, and kaolin-montmorillonite. Each of the specimens was already studied in detail by means of *x*-ray analysis, chemical analysis and differential thermal analysis. The specimens are enumerated below.

A) Non-regularly interstratified illite-montmorillonite

Specimen associated with metallic ore deposit (No. H3014)

Specimen H3014 from the Tsutsumizawa ore bodies of the Hanaoka mine, Akita Prefecture, occurs in a transition zone between the montmorillonite zone and the chlorite-1M type illite zone developed around sphalerite-galena ore bodies (Hayashi, 1961).

Specimen associated with coal-bearing sediments (No. N4)

Specimen N4 is tuff in the Noborikawa coal-bearing formation near Kamisunagawa in the Sorachi coal field, Hokkaido (Kobayashi and Oinuma, 1960).

The abundance ratio of montmorillonite and illite of these two specimens was calculated as about 3:7.

B) 26 Å mixed-layer minerals of illite and montmorillonite or hydrated form of illite

Specimen associated with metallic ore deposit (No. K49)

Specimen K49 from the Honko ore body, Kamikita mine, Aomori Prefecture, occurs in interspaces of pyrite crystals at the margin of the main ore body. The specimen was identified as a mineral of regularly interstratified layers of illite and montmorillonite (Hayashi, 1961).

Specimens associated with diaspore-pyrophyllite deposits (Sample Y, H, G)

Many specimens of this type occur in the pyrophyllite-diaspore deposits. Specimen Y; from Yonago mine (pyrophyllite-diaspore deposit), Nagano Prefecture (Shimoda and Sudo 1960), Specimen H; from Honami pyrophyllite deposit, Nagano Prefecture (Shimoda, 1960). Specimen G; from Goto mine, Nagasaki Prefecture (Sudo, Hayashi and Shimoda, 1962). These specimens were determined as a mineral having a 26 Å spacing due to complex combination of 10 Å mica clay mineral structure and its more hydrated form (Shimoda and Sudo, 1960; Sudo, Hayashi and Shimoda, 1962).

C) Regularly interstratified pyrophyllite-montmorillonite (H-5)

Specimen H-5 from the Honami mine, Nagano Prefecture, occurs in places along the marginal zone of pyrophyllite deposit. The specimen was determined as a regularly interstratified pyrophyllite-montmorillonite (Kodama, 1958).

D) Regularly interstratified aluminian chlorite-montmorillonite

Specimen associated with metallic ore deposit (A002H)

Specimen A002H from the Honko ore body of the Kamikita mine, Aomori Prefecture is the purest ever known in Japan (Sudo and Kodama, 1957). Many specimens of this type occur in the alteration zone of the Kuroko ore deposits.

Specimen associated with fire clay deposit (Kurata)

Kurata specimen from the Kurata fire clay deposit, Yamaguchi Prefecture, occurs in hydrothermal replacement bodies in liparite, and is associated with kaolinite and montmorillonite (Sudo *et al.* 1954).

The specimens were defined as a regularly interstratified chlorite-montmorillonite. The chemical analysis revealed that the specimen are poor in Mg but very rich in Al, which suggests that the chlorite, one of the constituents of this mixed-layer, is an aluminian dioctahedral chlorite (Sudo *et al.*, 1954; Sudo and Kodama, 1957). Engelhardt *et al.* (1962) have lately named this chlorite *sudoite,* and to this type of mixed-layer clay minerals Frank-Kamenetskii *et al.* (1963) has given the name *tosudite.*

E) Non-regularly interstratified kaolin-montmorillonite (Awazu, Wake and Raimaru)

Awazu specimen; from Awazu, Ishikawa Prefecture. Wake specimen; from Wake, Ishikawa Prefecture. Raimaru specimen; from Raimaru, Ishikawa Prefecture. These specimens are all alteration products of Tertiary tuff and taffaceous sediments. The specimens were identified as a randomly interstratified kaolin mineral-montmorillonite (Sudo and Hayashi, 1956).

For comparison, the following eight specimens among various clay minerals from Japan were used in this study:

1) Montmorillonite, Endani, Kurayoshi city, Tottori Prefecture (Yoshikawa and Sudo, 1961).
2) Illite (2M type); Yoji pass, Ozawa-mura, Gumma Prefecture (Kodama, 1957).
3) Illite (1M type); Kamikita mine, Aomori Prefecture (Kodama, 1962).
4) Kaolinite; Hara, Ena-gun, Gifu Prefecture.
5) Hydrated halloysite; Kusatsu-machi, Gumma Prefecture.
6) Pyrophyllite; Honami mine, Nagano Prefecture (Kodama, 1958).
7) Mg-chlorite; Wanibuchi mine, Shimane Prefecture (Sakamoto and Sudo, 1956).
8) Al-chlorite; Kamikita mine, Aomori Prefecture (Hayashi and Oinuma, 1964).

EXPERIMENTS

The sedimentation method was applied to all specimens of mixed-layer minerals and various clay minerals used in this study, and clay fractions smaller than 2μ were used in the infrared spectra analysis.

One to 3 mg powder of each specimen was mixed with 300 mg of KBr, and was pressed in vacuum by the oil press. The pressure exerted on the specimen was 10 tons per 1 cm^2. Thus, a disk of 10–13 mm in diameter and 1–2 mm in thickness was made. Vibrations of OH in clay minerals cannot be accurately identified, as water is absorbed by KBr in the OH region. Therefore, in several specimens the spectra of the OH region were obtained by the paste method using Nujol as the base. That is, about 5 mg of the specimen was placed in a small agate mortar, added with one drop of the base, and was kneaded well until it became pasty; then this paste-like mixture was sandwiched between two plates of sodium chloride, to be made into a uniformly thin film. Experiments were carried out with this thin film of the specimen.

The infrared spectrometers employed in the experiments were all Japan Spectroscopic spectrometers; namely, an IR-S type spectrometer was used in the range of 4000–700 cm^{-1}, and for precise examination of the OH region a grating DS-401-G type was used in the range of 3800 –3200 cm^{-1} and a DS-301 type in the range of 900–400 cm^{-1}.

NON-REGULARLY INTERSTRATIFIED ILLITE AND MONTMORILLONITE

Figures 1(1,2) and 2(1,2) show the infrared absorption spectra of the specimens. The absorption spectra of the OH region presented the overlap of an absorption at 3630 cm^{-1} by illite and those at 3635 cm^{-1} and 3406 cm^{-1} by montmorillonite. In the range of 1700–850 cm^{-1} also, the absorptions seem to overlap. In specimen H3014 absorptions are noticed at 1480 cm^{-1} and 1580 cm^{-1}. In the range of 900–400 cm^{-1}, absorptions are found at about 820, 750, 520–540 and 470 cm^{-1}, which are known to occur in 1M polymorph of illite (Fig. 2 (I2)), except for the absorptions due to quartz in specimen N4. The absorptions at 835 cm^{-1} and 795 cm^{-1} which are characteristic of montmorillonite were not very clear in this case. This may be due to the small quantity of montmorillonite. The result of this infrared spectra analysis is not contradictory to the result *x*-ray and differential thermal analyses by which the specimens were identified as the non-regularly interstratified illite-montmorillonite.

26 Å MIXED-LAYER MINERALS OF ILLITE AND MONTMORILLONITE OR HYDRATED FORM OF ILLITE

As is seen in Figs. 1(3–6) and 2(3–6), the infrared absorption spectra of these specimens show absorptions similar to those of illite. Nevertheless, a board absorption is clearly noticed near 3400 cm^{-1} which is supposedly due to the absorption of interlayer water contained in montmorillonite or hydrous illite. Absorption in the range of 800–830 cm^{-1} occurs as a doublet. In Figs. 1(I1,I2) and 2(I1,I2) are also given the infrared absorption

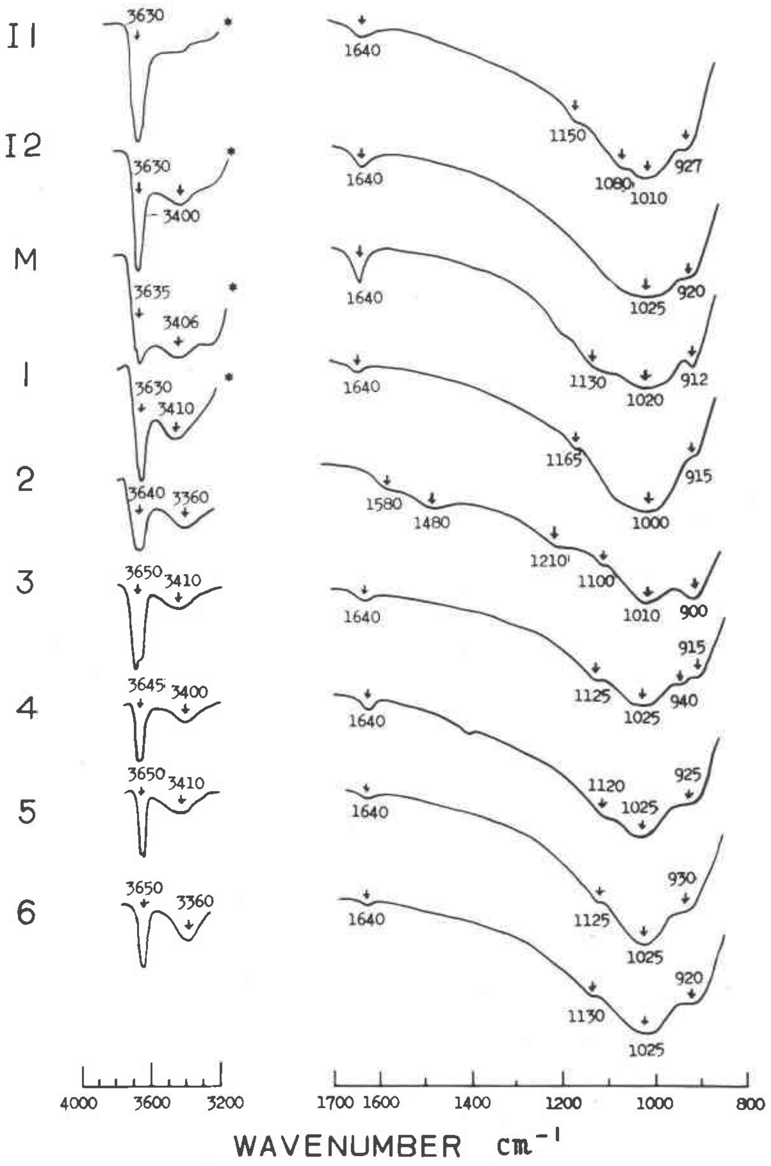

FIG. 1. Infrared spectra of illites, montmorillonite and mixed-layer minerals of illite and montmorillonite or hydrated form of illite in the region 800–1700 cm^{-1} and 3200–3800 cm^{-1}: (I1) 2M illite, (I2) 1M illite, (M) montmorillonite, (1) specimen N4, (2) specimen H3014, (3) specimen K49, (4) specimen Y, (5) specimen H, (6) specimen G, * Specimen was prepared in Nujol.

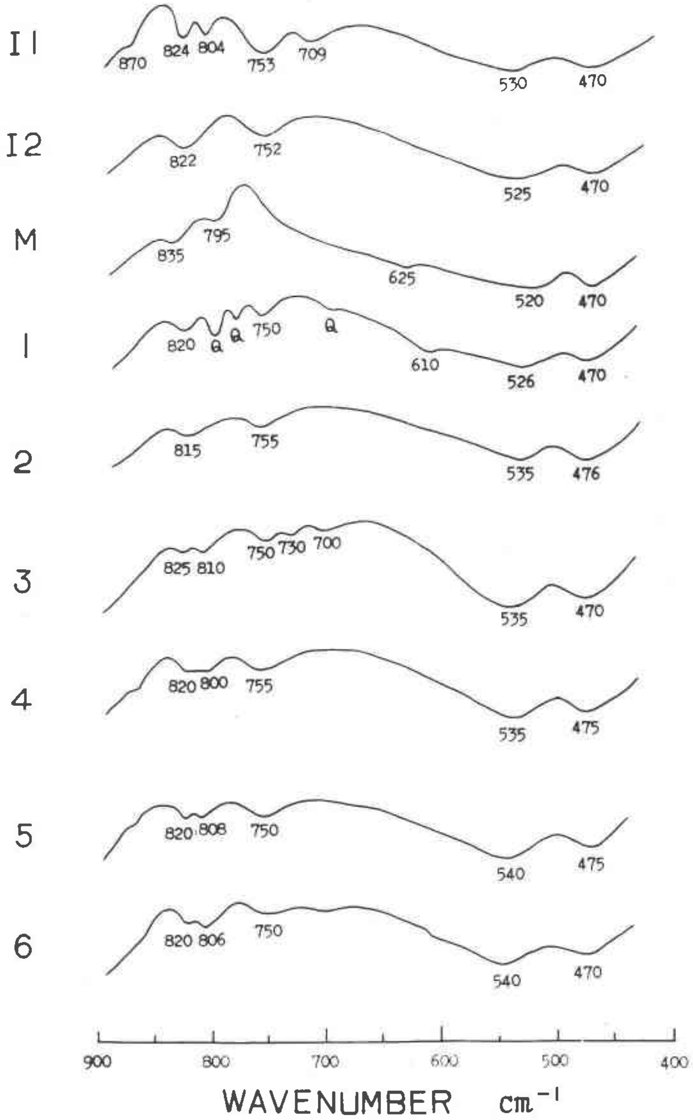

FIG. 2. Infrared spectra of illites, montmorillonite and mixed-layer minerals of illite and montmorillonite or hydrated form of illite in the region 400–900 cm^{-1}: (I1) 2M illite, (I2) 1M illite, (M) montmorillonite, (1) specimen N4, (2) specimen H3014, (3) specimen K49, (4) specimen Y, (5) specimen H, (6) specimen G. Q, Quartz.

spectra of illites whose types were determined as 2M and 1M after comparing them with the *x*-ray diffraction patterns of various polymorphs of mica reported by Yoder and Eugster (1955) and Smith and Yoder (1956). The 2M type illite shows doublets at 804 cm^{-1} and 824 cm^{-1}, while 1M type illite has only one broad absorption at 822 cm^{-1} of this range. Absorptions of the four specimens of mixed-layer clay minerals bear a close resemblance to those of 2M type illite. On the basis of the newly obtained data, as well as the previously known data, of infrared absorption, the four specimens are determined as the mixed-layer clay minerals of illite and montmorillonite or hydrated form of illite.

REGULARLY INTERSTRATIFIED PYROPHYLLITE AND MONTMORILLONITE

Infrared absorption spectra of this specimen are illustrated in Figs. 3(1) and 4(1). For comparison, absorption spectra of montmorillonite (M) and pyrophyllite (P) are also shown in the figures. The pyrophyllite specimen which showed absorptions in the range of 900–400 cm^{-1} contains a small amount of quartz, so that the absorptions include that of quartz. Absorptions in the OH region are evidently the overlaps of those of montmorillonite and pyrophyllite. That is, an absorption at 3680 cm^{-1} due to pyrophyllite has a shoulder at about 3635 cm^{-1} which is due to montmorillonite, and an absorption due to interlayer water of montmorillonite appears at 3350 cm^{-1}. An absorption at 946 cm^{-1} is characteristic of pyrophyllite, and several separate absorptions due to Si-O are found in the range of 1000–1200 cm^{-1}. The absorption of pyrophyllite at 1050 cm^{-1} overlaps that of montmorillonite at 1020 cm^{-1}, and in this specimen the absorption appears in the position of 1030 cm^{-1}. Also, in the range of 900–400 cm^{-1}, all characteristic absorptions of pyrophyllite are found. Absorption spectra of pyrophyllite are characterized by several sharp bands, and these are especially remarkable in the infrared absorption spectra of the present specimen. When compared with pyrophyllite, montmorillonite shows less sharp absorptions; since they appear as broad bands they are difficult to recognize, and yet it is doubtless that absorptions due to montmorillonite occur as overlaps. With regard to the infrared absorption data the writers support Kodama's identification.

REGULARLY INTERSTRATIFIED ALUMINIAN CHLORITE AND MONTMORILLONITE

Figures 3(2,3) and 4(2,3) show the spectra of the present specimens; for comparison the spectra of Mg-chlorite (Cl), Al-chlorite (C2) and montmorillonite (M) are also given. Absorptions in the OH region of these specimens resemble those of Al-chlorite; absorptions in the range of

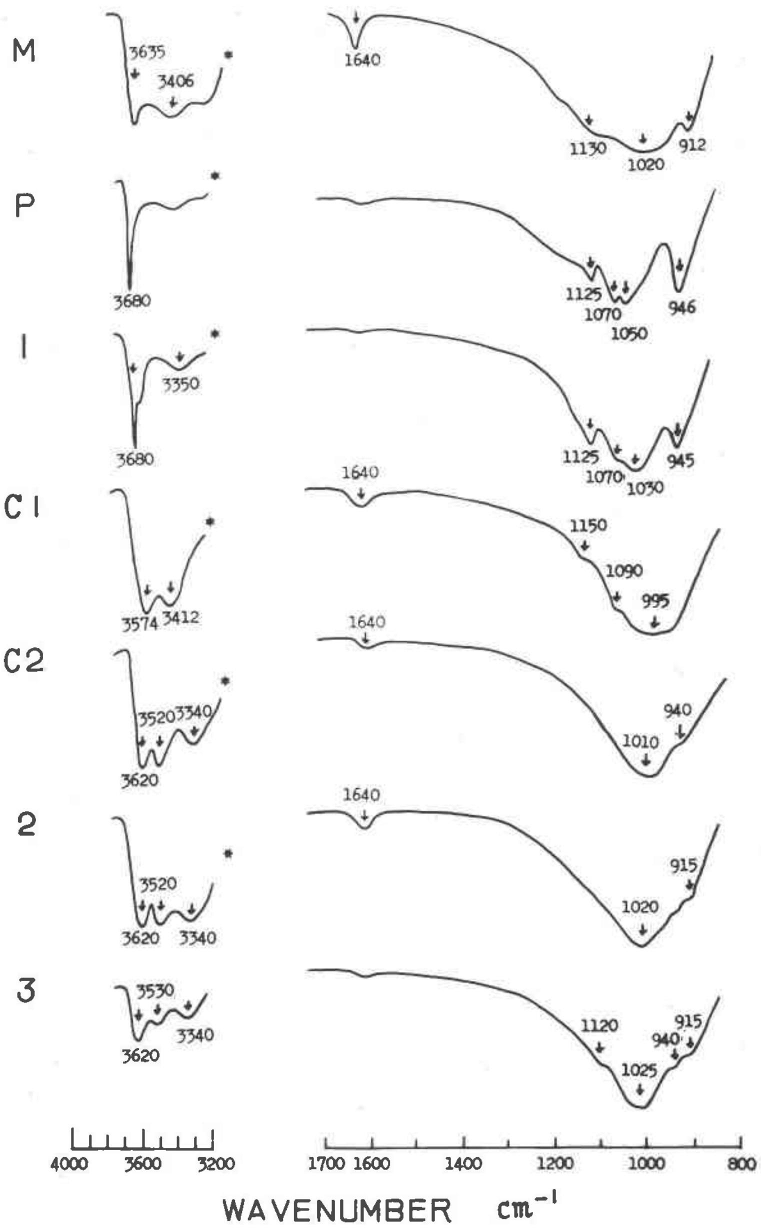

FIG. 3. Infrared spectra of montmorillonite, pyrophyllite, chlorites and mixed-layer minerals of pyrophyllite-montmorillonite and chlorite-montmorillonite in the region 800–1700 cm^{-1} and 3200–3800 cm^{-1}: (M) montmorillonite, (P) pyrophyllite, (1) specimen H5, (C1) Mg-chlorite, (C2) Al-chlorite, (2) specimen A002H, (3) Kurata specimen. * Specimen was prepared in Nujol.

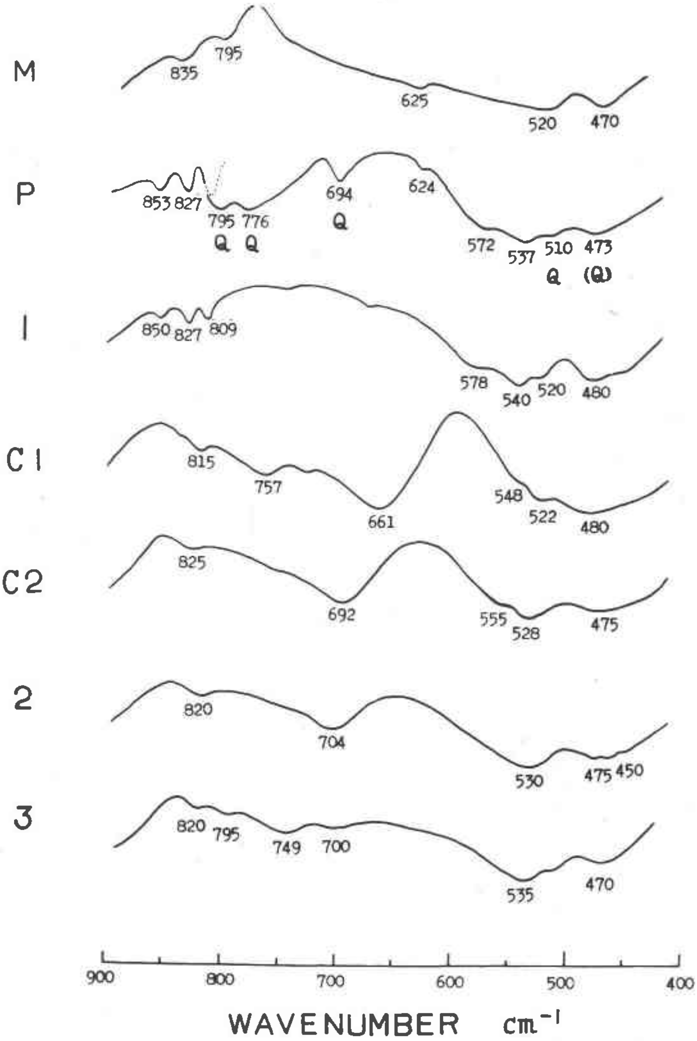

FIG. 4. Infrared spectra of montmorillonite, pyrophyllite, chlorites and mixed-layer minerals of pyrophyllite-montmorillonite and chlorite-montmorillonite in the region 400–900 cm^{-1}: (M) montmorillonite, (P) pyrophyllite, (1) specimen H5, (C1) Mg-chlorite, (C2) Al-chlorite, (2) specimen A002H, (3) Kurata specimen. Q; Quartz.

1200 – 900 cm^{-1} culminate at 1020 cm^{-1} which coincides with Si-O absorption of montmorillonite. In the present specimens the absorption near 915 cm^{-1} which is seen in montmorillonite occurs at 912 cm^{-1} as a shoulder of the strongest absorption at about 1020 cm^{-1}, and the absorptions at 940 and 1010 cm^{-1} as found in Al-chlorite seem to overlap there. In Mg- and Fe-rich chlorites, absorption due to Si-O vibration is found at 660–650 cm^{-1}, but in Al-rich chlorites this absorption appears at 690–700 cm^{-1} where the wave number is large (Hayashi and Oinuma, 1965). The present specimens show an absorption at 700 cm^{-1} or 704 cm^{-1}. Among clay minerals kaolinite is known to show an absorption at or near this position, but the results of *x*-ray analysis, DTA and examination of the OH region of infrared absorption spectra revealed that the present specimens do not contain kaolin minerals. Hence, it would be reasonable to conclude that the chlorite, one of the constituent minerals of this mixed-layer, is rich in Al. By means of *x*-ray analysis and chemical analysis, the specimens were identified as a mixed-layer of montmorillonite and Al-chlorite. The result of examination of the infrared absorption spectra evidently supports the above identification.

NON-REGULARLY INTERSTRATIFIED KAOLIN AND MONTMORILLONITE

The infrared absorption spectra of the specimens show relatively broad absorptions, as seen in Figs. 5(1–3) and 6(1–3). These are not separate absorptions such as those found in kaolinite, but supposing the absorptions are overlapping those of montmorillonite they may not be necessarily represented by several clearly separate absorptions. In the present specimens of the mixed-layer the absorption near 910 cm^{-1} is stronger than that of montmorillonite. The absorption near 910 cm^{-1} due to Al-O-H vibrations is found in montmorillonite, too, but it is specially stronger in kaolinite. Considering this fact, the absorption near 910 cm^{-1} of these specimens may be closely related to kaolin minerals. As Fig. 6 indicates, an absorption occurs near 830 cm^{-1} which is characteristic to montmorillonite. However, hydrated halloysite also has a weak absorption at this position. In hydrated halloysite the absorption at 696 cm^{-1}, which is commonly found in kaolinite, appears as a broad absorption in the range of 660–690 cm^{-1}. In the present specimens no such broad absorptions are found, and only an absorption at 690 cm^{-1} is supposedly due to kaolinite. Absorptions at 790 cm^{-1} and 746 cm^{-1} are also attributable to kaolinite. In the *x*-ray analysis the identification of these specimens is very difficult since they do not show any sharp diffractions, but when supplemented with the data of infrared spectra the nature of the specimens would become clear. The infrared spectra of these specimens

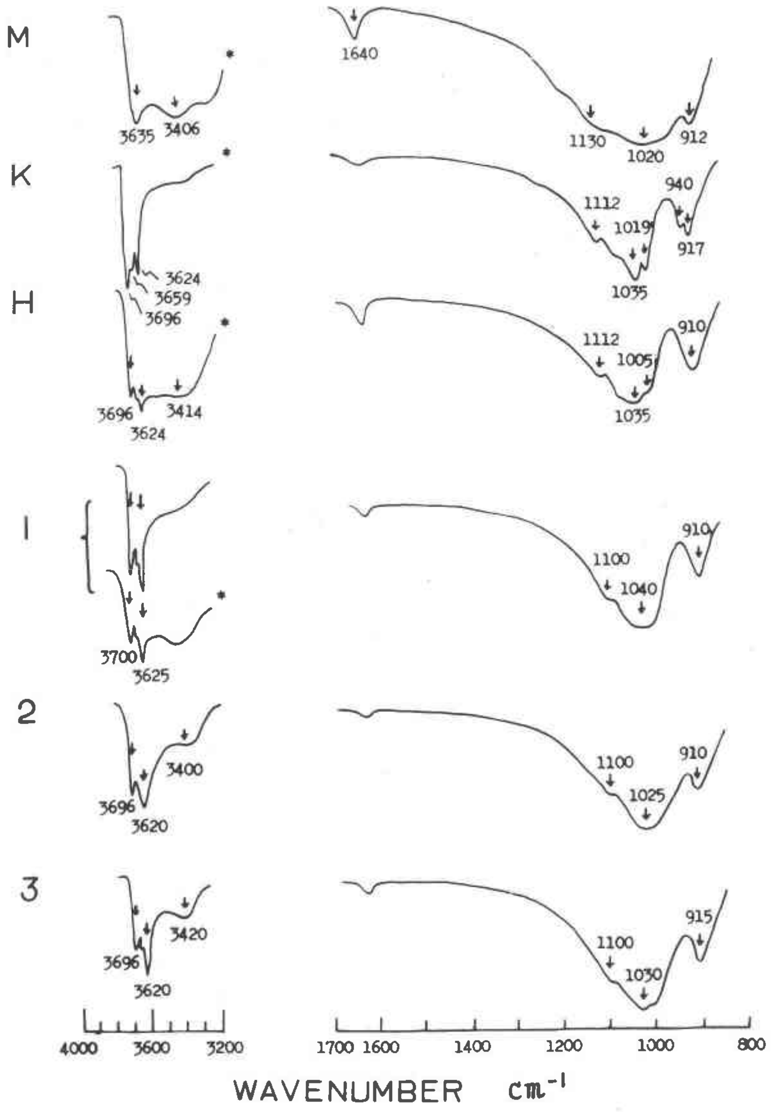

FIG. 5. Infrared spectra of montmorillonite, kaolinite, hydrated halloysite and mixed-layer minerals of kaolin-montmorillonite in the region 800–1700 cm^{-1} and 3200–3800 cm^{-1}: (M) montmorillonite, (K) kaolinite, (H) hydrated halloysite, (1) Awazu specimen, (2) Wake specimen, (3) Raimaru specimen. * Specimen was prepared in Nujol.

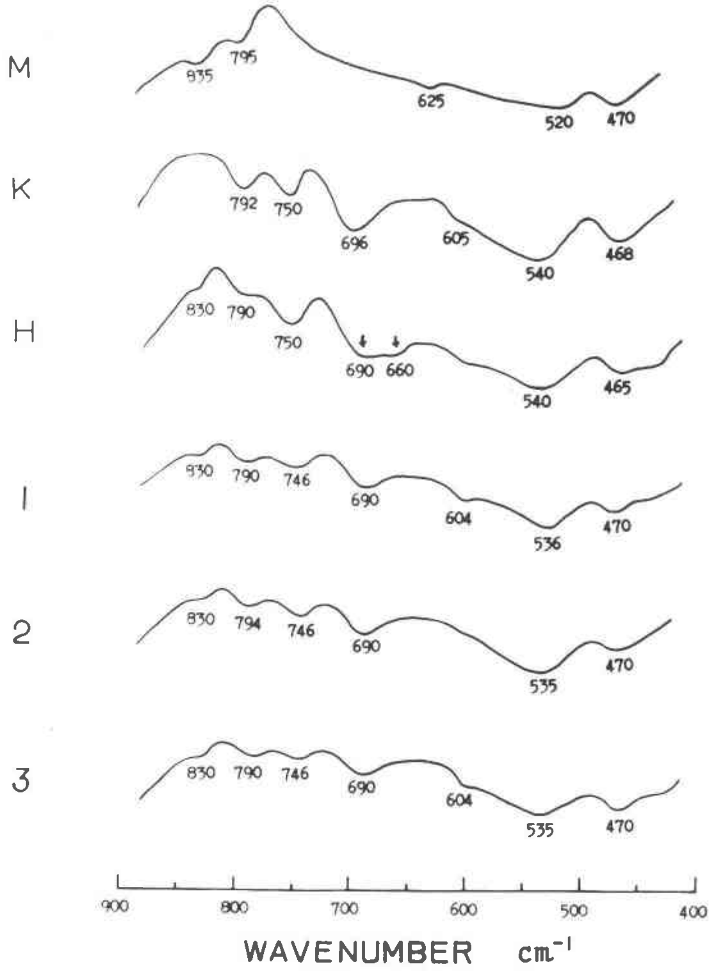

FIG. 6. Infrared spectra of montmorillonite, kaolinite, hydrated halloysite and mixed-layer minerals of kaolin-montmorillonite in the region 400–900 cm^{-1}: (M) montmorillonite, (K) kaolinite, (H) hydrated halloysite, (1) Awazu specimen, (2) Wake specimen, (3) Raimaru specimen.

disclosed undoubtedly the characteristics of both kaolinite and montmorillonite.

CONCLUSION

From the results of the infrared study of various kinds of mixed-layer clay minerals it has become clear that absorptions of the constituent minerals of a mixed-layer appear as overlapping spectra. For example, in a specimen of the mixed-layer of illite and montmorillonite, absorptions of illite were distinctly noticed and those of montmorillonite overlapped the former. In the specimens of non-regularly interstratified minerals, however, some showed a broad absorption near 820 cm^{-1}, whereas others having long spacing of 26 Å showed doublets at 800 cm^{-1} and 820 cm^{-1}. By comparing these spectra with those of illite in Fig. 2, it becomes clear that the broad absorption occurs in 1M type illite while the doublet is characteristic to 2M type illite. This fact may be related to the structure and origin of the mixed-layer minerals, but a reasonable interpretation would be a problem of future study. The absorption spectra of a mixed-layer of pyrophyllite and montmorillonite distinctly showed the absorptions ascribable to pyrophyllite and montmorillonite, thus verifying the existence of the two minerals. Comparison of absorption spectra of Mg-chlorite and Al-chlorite revealed that the specimen of chlorite-montmorillonite mixed-layer mineral used in the present study contains Al-chlorite as one of its constituents. In the interstratified kaolin-montmorillonite specimen which is hardly identified by the *x*-ray method, existence of kaolinite and montmorillonite was confirmed by the respective absorptions. Presence or absence of hydrated halloysite can be determined also by infrared absorption spectra. The study of infrared absorption spectra of mixed-layer minerals is thus useful in clarifying the nature of the constituents. In case the clay mineral has characteristic absorptions the identification becomes easier. By the infrared spectra analysis the mineral species in the mixed-layer specimens or mixtures of various kinds of clay minerals can be identified; however, the spectra usually show the mineral species as overlapping absorptions, so whether or not these species are true constituents of the mixed-layer clay minerals cannot be determined. In the study of mixed-layer clay minerals, the *x*-ray analysis, DTA and chemical analysis have been employed. If these methods were supplemented with the infrared spectra analysis, detailed study of the nature of minerals constituting the mixed-layer clay minerals would become possible.

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