

I.R. STUDIES OF SOME INTERSTRATIFIED MINERALS OF MICA AND MONTMORILLONITE*

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Abstract—I.R. band shifts in the 830, 750 and 530 cm^{-1} regions that occur in interstratified layer silicates on heating were used to characterize the nature of the component layers. Two specimens showed shifts characteristic of 1M illite and montmorillonite. Another specimen was similar to 2M illite even though the proportion of expanding layers was 0.4. The shifts for rectorite and allevardite resembled those of paragonite and 2M illite.

INTRODUCTION

INTERSTRATIFIED layer silicate minerals are described by the nature and properties of their elementary layers and by the statistical sequence of stacking of the layers. While X-ray methods have been used to determine the probability of the sequence of the elementary layers (Bradley, 1950; Brindley, 1956; Sato *et al.*, 1965), the nature of the elementary 2:1 layers in interstratified minerals is difficult to determine because of the variation within and between specimens. A variety of methods such as chemical analysis, C.E.C., unmixing of exchangeable cations, surface area, DTA and infra-red absorption have been used to describe the layers (Cole and Hosking, 1957; Oinuma and Hayashi, 1965, 1968; Kodama, 1966).

To clarify further the properties of the elementary layers of interstratified minerals, we made use of the fact that crystal distortion caused by heating is reflected in i.r. absorption patterns of such minerals. In this paper, thermally induced shifts in characteristic absorption bands of a variety of interstratified minerals and of monomineralic type clay specimens are discussed in relation to previously published data.

SPECIMENS

Specimen K. In tuff in the Noborikawa coal-bearing formation at Kamisunagawa, Hokkaido, Japan.

Specimen S. In the alteration area of the Shakanai mine, Akita Prefecture, Japan.

The mineralogical properties are very similar to each other.‡ They give a strong reflection at about 29 Å with higher orders, but there is an additional 11.8 Å reflection. When heated to 550°C, a 10.8 Å reflection appeared. From Fourier transform analysis these minerals are known to consist of three kinds of layers—a mica layer (10 Å in layer thickness), a 2:1 layer with a single water layer (12 Å) and an expandable 2:1 layer (15 Å).

Specimen Y. Associated with pyrophyllite at the Yonago mine, Nagano Prefecture, Japan.

This specimen gives strong reflections at 27.6 and 12.9 Å and a 10.1 Å peak at 550°C. The proportion of non-expandable layers is about 0.6 (Kodama *et al.*, 1969).

Allevardite. Allevard, France.

This specimen is a regular interstratified mineral of a mica-type structure with layers of water molecules separating double mica layers (Henin, Esquievin and Caillere, 1954; Brindley, 1956). It gives a 24.5 Å reflection with its higher orders and a 19.5 Å peak at 550°C.

Rectorite. Fort Sandman Dist., Pakistan.

Rectorite. North Little Rock, Arkansas.

Bradley (1950) showed that rectorite is a regular interstratification of pyrophyllite-like and vermiculite-like layers. Later, Brown and Weir (1963) described rectorite as a regular interstratified mineral of mica-like and montmorillonite-like minerals, and they also showed that rectorite and allevardite are similar. Recently, Kodama (1966) showed that the mica-like layers in rectorite are similar to paragonite and that the montmorillonite layers have a mixed montmorillonite-beidellite nature.

For comparison, the following (pure clay minerals) were also used in this study.

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- (a) 1M illite: Boulder Canyon (4-mile Creek) Colorado.
 (b) 2M illite: The Goto mine, Nagasaki Prefecture, Japan (Tomita and Sudo, 1968).
 (c) Paragonite: Monte Camione, Switzerland. Associated with kyanite and staurolite.
 (d) Pyrophyllite: Robbins, North Carolina (API sample H-49).
 (e) Montmorillonite: Polkville, Miss (API sample H-19).
 (f) Beidellite: Putnam, Missouri.

EXPERIMENTAL PROCEDURE

The < 2 micron fraction of each specimen was obtained by gravity sedimentation, flocculation of the suspensions with CaCl_2 , washing and freeze-drying. After the heat treatments in a muffle furnace at the appropriate temperatures for three hours, the specimens were cooled in a dessicator to prevent rehydration.

For the i.r. technique pellets containing 1mg specimen mixed with 400mg KBr were pressed under vacuum at 16,000 pounds/in² pressure and stored in a dessicator. A Beckman IR-12 spectrophotometer was used with the following operating conditions (Double beam against KBr; scan rate 80 $\text{cm}^{-1}/\text{min}$; gain 3 per cent; period 8).

RESULTS

The pure clay minerals

The pure clay minerals gave different i.r. absorption patterns before and after heating (Fig. 1). On heating, the OH absorption bands disappeared as expected, and there were also changes in the absorption bands at 830, 750 and 530 cm^{-1} which are attributed to Si-O-Al bands (Farmer and Russell, 1964). These changes are related to the distortion of the silicate framework and seem to be specific for certain minerals. The shifts in the

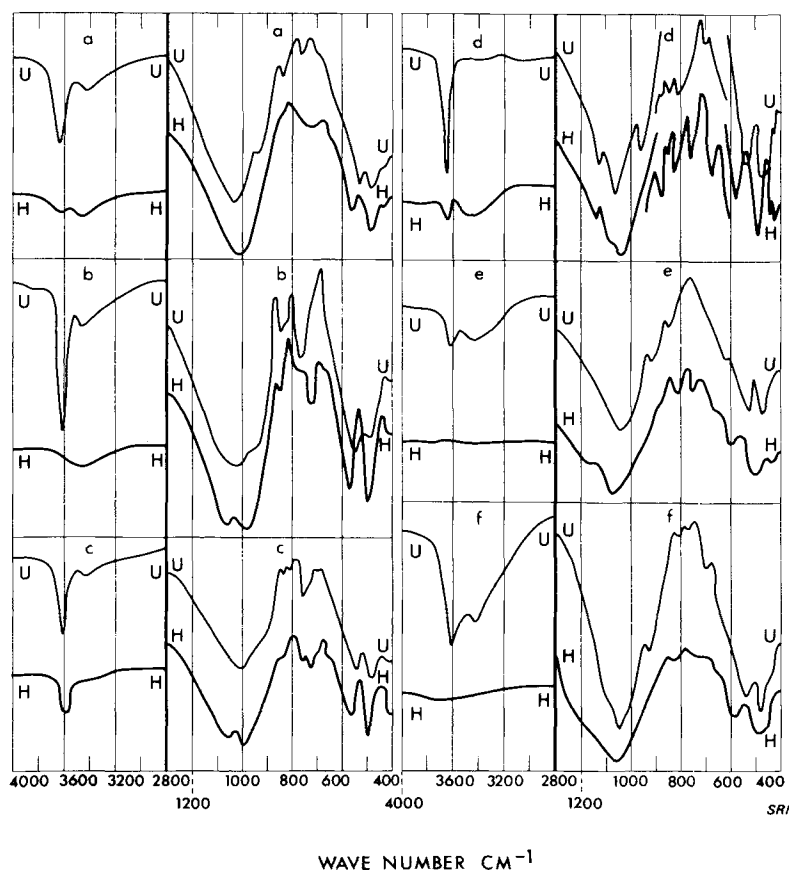


Fig. 1. I.R. spectra before and after heating at 700°C. (a) 1 M illite; (b) 2 M illite; (c) paragonite; (d) pyrophyllite; (e) montmorillonite; (f) beidellite.

bands on heating were distinctive with respect to the magnitude of the shift and the temperature at which it occurred.

The 830 cm^{-1} band in the three micas shifted to about 840 cm^{-1} at 700°C . The 1M illite showed a larger shift of the 830 cm^{-1} band than the 2M illite or paragonite. Pyrophyllite showed virtually no change of the 838 cm^{-1} band on heating and the band was absent from montmorillonite or beidellite.

In the three micas, the 750 cm^{-1} band appeared to shift to 725 cm^{-1} when heated to 700°C while a very weak absorption effect remained at 750 cm^{-1} . Pyrophyllite and montmorillonite showed an absorption band at 738 cm^{-1} on heating at 700°C which was not present in the unheated specimen.

In montmorillonite the shift of the 530 cm^{-1} band occurred on heating to 700°C whereas with the other minerals the shift occurred at 550°C . Presumably, the temperature of the shift is related to the temperature of dehydroxylation. The initial band position varied considerably (Table 1) among the minerals and the magnitude of the band shift on heating varied from 20 cm^{-1} for the 2M micas to 66 cm^{-1} for montmorillonite.

Specimen K and S

The two specimens showed similar absorption bands and only the data for specimen K are given in Table 1. The OH-stretching bands at 3640 cm^{-1} and 3445 cm^{-1} persisted up to 550°C . The Si-O vibration at 1035 cm^{-1} , with shoulders at 1100 and 995 cm^{-1} , shifted slightly to 1025 cm^{-1} and persisted on heating to 800°C . The 830 cm^{-1} band moved to 848 cm^{-1} at 550°C . The 760 cm^{-1} band weakened and broadened at 500°C and a new absorption band appeared at 730 cm^{-1} then shifted to 728 cm^{-1} at 700°C . The 535 cm^{-1} band broadened at 45°C . At 550°C , small peaks at 528 cm^{-1} and 566 cm^{-1} appeared, while a new band at 585 cm^{-1} appeared at 700°C , and the 566 cm^{-1} persisted to 800°C .

Fourier transform analysis of specimens K and S indicated three kinds of layers, mica (10Å in layer thickness), a mica layer with a single water layer (12Å) and an expandable layer (15Å). The DTA pattern showed two dehydroxylation endotherms at 550°C and 700°C . The 700°C endotherm and the presence of i.r. bands of 528 cm^{-1} at 550°C and at 585 cm^{-1} at 700°C are indicative of montmorillonite. The 500°C DTA endotherm and the shift of the 535 cm^{-1} band to 566 cm^{-1} at 550°C indicate 1M mica layers with the possibility of an overlapping beidellite band.

Specimen Y

The OH-stretching absorption band at 3650 cm^{-1}

was slightly higher than that of 2M illite. On heating, the intensity of it decreased and the wave number increased to 3660 cm^{-1} at 550°C . When heated at 800°C , the band completely disappeared but it reappeared after the heated specimen was immersed in water for 10 hr.

Although the 930 cm^{-1} OH-bending vibration disappeared at 450°C , the Si-O vibration at 1022 cm^{-1} persisted to 700°C and split into two bands at 1048 and 998 cm^{-1} at 800°C . Paragonite and 2M illite also showed this shift (Table 1).

The 820 cm^{-1} band with a shoulder at 810 cm^{-1} shifted to 840 cm^{-1} at 550°C . The strong 758 cm^{-1} band remained in the same position and decreased in intensity. The weak 728 cm^{-1} peak shifted to 722 cm^{-1} and increased in intensity. The strong 540 cm^{-1} band shifted to 568 cm^{-1} and increased in intensity. These changes are comparable with those in 2M illite and paragonite.

The results would indicate that the specimen is composed of one kind of silicate layer and corroborate DTA data which showed only one endothermic dehydroxylation reaction at 550°C (Shimoda *et al.*, 1969). Based upon these interpretations the expanding layers, the proportion of which were found previously to be 0.4 (Kodama *et al.*, 1969), must have been similar to 2M illite layers.

Allewardite and rectorite

The OH-stretching bands of the two specimens appeared at 3650 cm^{-1} . With rectorite, the 3650 cm^{-1} bend shifted to 3635 cm^{-1} and weakened at 550°C , but with allewardite it moved to 3660 cm^{-1} at 550°C . When heated at 700°C , the OH-stretching bands of the two minerals disappeared (Fig. 2). Rectorite shows a single DTA dehydroxylation peak whereas allewardite shows a doublet (Cole and Hosking, 1957) and this difference is reflected in the shifts of the OH-stretching i.r. bands on heating.

As seen in Fig. 2 in the range $400\text{--}1300\text{ cm}^{-1}$ the spectra of the untreated minerals are similar to each other and to the curve shown by Farmer and Russell (1964). The changes on heating did not match those of any of the pure minerals but resembled paragonite. The 547 cm^{-1} band, which has a higher wave number than any of the pure minerals, shifted to 570 cm^{-1} at 550°C . This 20 cm^{-1} band shift was similar to paragonite of 2M illite. Thus, even though rectorite and allewardite show differences in dehydroxylation and in the OH-stretching i.r. vibrations, the Si-O-Al absorption bands and the band shifts on heating were similar for the two minerals.

The rectorite Si-O-Al band positions and shifts on heating differ from those of pyrophyllite, montmorillonite and beidellite but in a broad

Table 1. I.R. band frequencies of pure and interstratified minerals before and after heating at 700°C

1 M illite (a) Un.	2 M illite (b) 700°C		Paragonite (c) 700°C		Pyro. (d) 700°C		Mont. (e) 700°C		Beid. (f) 700°C		Y 700°C		R 700°C		A 700°C	
	Un.	700°C	Un.	700°C	Un.	700°C	Un.	700°C	Un.	700°C	Un.	700°C	Un.	700°C	Un.	700°C
				3682 S		3682 W										
3630 S	3650 sh	3655 sh	3655 sh		3630 S	3630 S	3630 S	3630 S	3640 S	3650 sh	3650 S	3650 S	3650 S	3650 S	3650 sh	3650 sh
3410 w	3636 S	3640 S	3640 S		3435 w	3440 SB	3440 w	3445 M	3445 M	3450 sh	3420 w	3420 w	3430 M	3450 M	3450 M	3450 M
1643 w	3450 w	3480 w	3450 w		1630 w	1640 M	1640 w	1645 w	1645 w	1645 M	1642 w	1642 w	1645 S	1640 S	1640 S	1640 S
1100 Inf	1110 sh	1110 sh	1110 sh		1190	1140 M	1120 M	1150 sh	1130 sh	1100 Inf	1100 Inf	1100 Inf	1125 sh	1120 sh	1120 sh	1120 sh
	1074 sh	1070 sh	1065 sh		1080 sh	1085 sh	1055 S	1055 SB	1080 sh	1083 sh	1080 sh	1080 sh	1083 sh	1080 sh	1080 sh	1080 sh
1030 SB	1037 S	1050 SB	1050 SB		1035 S	1035 S	1055 S	1040 SB	1035 SB	1035 S	1022 S	1015 S	1028 S	1040 S	1026 S	1050 S
	1012 S	990 SB	988 SB		951 S	738 M	750 sh	738 M	995 Inf	728 M	728 w	722 M	726 S	990 sh	970 sh	970 sh
	934 M	932 M	900 Inf		913 M	867 M	857 M	847 M	924 M	850 sh	930 M	916 sh	918 sh	918 sh	918 sh	918 sh
920 M	900 Inf	900 Inf	900 Inf		876 Inf	835 M	838 M	835 M	830 M	830 M	820 M	815 M	820 M	875 Inf	875 Inf	875 Inf
	863 Inf	837 M	837 M		868 M	807 M	813 M	803 M	798 w	800 w	820 M	815 M	820 M	850 w	850 w	850 w
828 M	832 M	831 w	837 M		847 M	800 sh	800 sh	803 M	830 M	830 M	810 Inf	815 M	810 M	800 w	802 w	802 w
	810 sh	803 w	802 w		800 sh	800 sh	800 sh	800 sh	760 M	760 M	758 M	755 w	750 Inf	800 w	802 w	802 w
753 M	782 sh	751 M	753 M		752 w	738 M	750 sh	738 M	760 M	728 M	728 w	722 M	726 S	750 Inf	750 Inf	750 Inf
	755 w	751 M	753 M		738 M	738 M	738 M	738 M	760 M	728 M	728 w	722 M	726 S	750 Inf	726 S	726 S
	716 S	726 sh	718 M		690 M	656 M	696 w	656 M	695 w	640 sh	640 sh	650 w	650 w	710 sh	710 sh	710 sh
	702 sh	695 w	650 sh		625 w	656 M	656 M	656 M	625 w	640 sh	640 sh	650 w	650 w	700 sh	700 sh	700 sh
682 sh	650 sh	650 Inf	650 sh		595 sh	573 S	575 sh	590 M	578 S	585 sh	564 S	568 S	570 S	645 sh	645 sh	650 w
	580 sh	560 S	562 S		575 sh	573 S	575 sh	590 M	560 Inf	564 S	564 S	568 S	570 S	650 w	650 w	650 w
	542 S	540 S	540 S		541 S	541 S	541 S	541 S	535 S	547 S	547 S	547 S	549 S	650 w	650 w	650 w
525 S	488 S	488 S	486 S		525 sh	490 S	525 sh	490 S	485 SB	487 S	487 S	483 S	495 S	568 S	568 S	568 S
477 M	478 S	475 S	475 S		483 S	477 S	483 S	477 S	482 S	482 S	477 S	477 S	483 S	570 S	570 S	570 S
	460 sh	460 sh	460 sh		460 sh	460 sh	460 sh	460 sh	450 sh	450 sh	450 sh	450 sh	483 S	547 S	547 S	549 S

S—strong; M—medium; w—weak; sh—shoulder; Inf—Inflection; B—broad; Un—unheated.

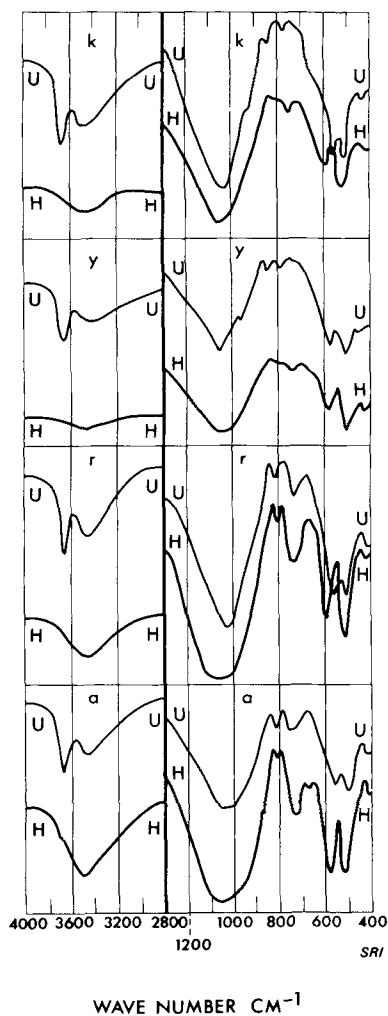


Fig. 2. I.R. spectra of interstratified minerals K and Y, rectorite (R), and allevardite (A), before and after heating at 700°C.

sense the i.r. absorption characteristics are similar to those of paragonite or 2M illite. The slight differences between rectorite and mica were explained by Farmer and Russell 1964 as related to differences in the substitution of Al for Si in the tetrahedral layer. Kodama (1966) showed that rectorite had a net octahedral positive charge of +0.63 per unit cell and it is possible that the i.r. band shifts of rectorite are related to the high content of octahedral layer cations also.

CONCLUSION

The shifts of the Si-O-Al i.r. absorption bands on heating give both positive and negative clues as

to the nature of the component layers of interstratified minerals. Specimens K and S showed 1M illite and montmorillonite bands and band shifts. Specimen Y gave bands characteristic of 2M illite only, even though it had been previously shown (Kodama *et al.*, 1969) that the proportion of expanding layers was 0.4. Rectorite and allevardite showed i.r. absorption characteristics similar to paragonite and 2M illite. They showed no similarity to montmorillonite or beidellite even though the 0.5 expanding layers showed X-ray diffraction characteristics of a 3:1 mixture of beidellite and montmorillonite.

The i.r. absorption characteristics corroborate the separation of interstratified minerals into the two groups proposed by Shimoda *et al.* (1969). Specimens K and S may be called interstratified mica and montmorillonite. For specimen Y, the name of hydrous mica complex (Shimoda and Sudo, 1960; Kodama *et al.*, 1969) seems to be more descriptive. Rectorite fits the first group on the basis of its X-ray characteristics and fits the second group on the basis of its i.r. absorption band shifts on heating.

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Résumé—Les déplacements des bandes infra-rouges dans les zones 830, 750 et 530 cm^{-1} qui se produisent pendant le chauffage de silicates à couches interstratifiées, ont été utilisés pour caractériser la nature des couches composantes. Deux spécimens ont montré des déplacements caractéristiques de 1M illite et montmorillonite. Un autre spécimen était similaire à 2M illite, bien que la proportion des couches en expansion était de 0,4. Les déplacements pour la rectorite et l'allévardite ressemblaient à ceux de la paragonite et de l'illite 2M.

Kurzreferat—Es wurden Verschiebungen der Ultrarotbänder in den 830, 750 und 530 cm^{-1} Bereichen, die in zwischengeschichteten Silikaten bei der Erwärmung vorkommen, verwendet um das Wesen der Einzelschichten zu charakterisieren. Zwei Proben wiesen Verschiebungen auf, die für 1M Illit und Montmorillonit charakteristisch sind. Eine weitere Probe war ähnlich 2M Illit obwohl der Anteil an ausdehnbaren Schichten 0,4 war. Die Verschiebungen für Rektorit und Allevardit waren ähnlich denjenigen von Paragonit und 2M Illit.

Резюме — Смещение ИК-полос смешаннослойных силикатов при 830, 750 и 530 cm^{-1} вследствие нагревания использовано для характеристики природы составляющих слоев. Два образца обнаружили смещения, характерные для иллита 1М и монтмориллонита. Один образец аналогичен иллиту 2М несмотря на то, что доля разбухающего компонента в нем составляет 0,4. Смещения полос для ректорита и аллевардита аналогичны смещениям полос для паргонита и иллита 2М.