

MINERALOGICAL NOTES  
AMMONIUM IONS IN SERICITES

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INTRODUCTION

Disordered sericites from the western part of Japan were found to have ammonium ions which are believed to be located in the interlayer sites. Evidence for the presence of  $\text{NH}_4^+$  ions was obtained from chemical, infra-red, and weight-loss analyses. X-ray examination of a large number of sericites revealed that these minerals have basal spacings ranging from 10.0 Å to 10.5 Å, and that disordering in the layer-stacking increases with increasing basal spacing. The x-ray diffraction patterns of these minerals showed similarities to the  $2M_1$ -,  $1M$ -, and  $1Md$ -types, but detailed structural analyses have not been made, by which the polytype could be definitely identified. In this investigation a tentative classification has been made based on the average basal spacings; 10.0 Å ( $2M_1$ -type), 10.05 Å ( $1M$ ), 10.2 Å ( $1M$ ), and 10.5 Å ( $1Md$ ), respectively.

The chemical analyses indicate that an increase in the ratio, Si/Al, in the tetrahedral layers is associated with a decrease in the interlayer alkali content. However, decrease of the alkalis exceeds the Si/Al increase required for the electrical neutrality of the crystal, suggesting that some other cations are required to compensate the excess negative charges of the tetrahedral layers. In Table 1 the chemical and physical properties of these sericites are summarized.

EXPERIMENTAL RESULTS

Infrared spectra of a number of specimens were obtained by using a Shimadzu Sheisakusho Inc. IR-27 infrared spectrometer with either a NaCl or KBr prism. Figure 1 illustrates the room temperature spectra between  $5000\text{ cm}^{-1}$  and  $1250\text{ cm}^{-1}$  of some representative specimens. An absorption band around  $1410\text{ cm}^{-1}$  is seen clearly along with a  $1620\text{ cm}^{-1}$  band which represents the bending vibration of the interlayer water. Mortland *et al.* (1963) made a detailed examination of these bands in their study on an interaction between ammonia and montmorillonite, and assigned the  $1410\text{ cm}^{-1}$  as being the  $\nu_4$  vibration of the ammonium ion. Vedder (1965) has observed also an absorption band at around  $1430$

TABLE 1. PROPERTIES OF THE SERICITES OF FOUR DIFFERENT TYPES

Specimen No.	Crystallinity	Si/Al (3:1 in muscovite)	Inter-layer alkali	Inter-layer $\text{NH}_4^+$	Inter-layer water
301 (10.0Å type)	Ordered	Nearly 3:1		None	
304 (10.05Å)	Disordered ↓	Increase ↓	Decrease ↓	Increase ↓	Increase ↓
302 (10.2Å)					
323 (10.5Å)					

$\text{cm}^{-1}$  which represents  $\text{NH}_4^+$  ions located in the interlayer of muscovite substituting for potassium ions. With the  $\nu_4$  vibration of the ammonium ion at  $1410 \text{ cm}^{-1}$ , its stretching vibration should be observed at about  $3300 \text{ cm}^{-1}$ . In the present investigation, however, the latter was obscured in general by an overlap of the  $\text{H}_2\text{O}$  stretching band; but in the spectra of specimen 302 (10.2 Å type), with less interlayer water, the band is shown clearly along with the  $1410 \text{ cm}^{-1}$  band (Fig. 1). In the heated specimens which will be described below, these bands were observed also at  $300^\circ \text{ C.}$ , where the absorption bands of the interlayer water disappeared.

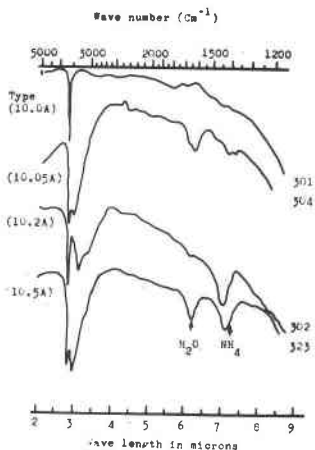


FIG. 1. Infrared absorption spectra between  $5000 \text{ cm}^{-1}$  and  $1250 \text{ cm}^{-1}$  of the four different types of sericites.

The chemical analysis of ammonium ions was made by a method described by Erd *et al.* (1964), and the results also indicated the presence of ammonium ions in these sericites, amounting to 0.44% ( $(\text{NH}_4)_2\text{O}$ ) for the specimen 304 (10.05 Å type), 1.77% for 302 (10.2 Å type), and 1.57% for 323 (10.5 Å type), respectively. This correlates fairly well with the infrared data.

A further confirmation for the presence of  $\text{NH}_4^+$  ions was obtained by heating the specimens at 300° C. and 650° C., respectively. Following the quenching of the specimen to room temperature, infrared absorption bands were examined for each specimen with the result that the 1620  $\text{cm}^{-1}$  band disappeared at 300° C. whereas the 1410  $\text{cm}^{-1}$  band was still

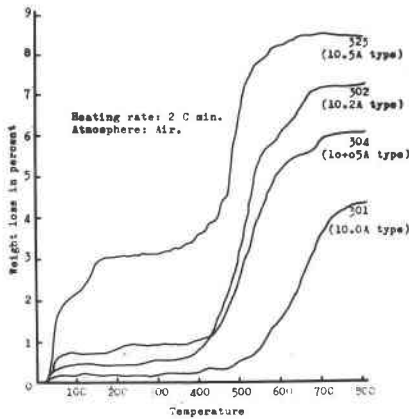


FIG. 2. Weight-loss curves of the four different types of sericites.

present. Heating at 650° C. resulted in a disappearance of the 1410  $\text{cm}^{-1}$ . In these experiments, care was taken not to rehydrate the specimens.

Inasmuch as the decomposition of the structure was observed at about 800° C. for almost all the specimens, measurements of the weight-loss upon heating were made of the specimens of the four different types at a heating rate of 2° C./min in air up to 800° C.; some of the curves are illustrated in Fig. 2. The curves can be divided into two regions, below and above 400° C. In comparison with the infrared observations, the weight-loss below 400° C. can be attributed to the dehydration of the interlayer water. A subtraction of this water from the total ignition loss gives 4.6% for 301 (10.0 Å type), 5.0% for 304 (10.05 Å type), 7.0% for 302 (10.2 Å type), and 6.4% for 323 (10.5 Å type), respectively. In the range above 400° C., a further subtraction of the amount of ammonium ions in these specimens results in 4.5% for 301, 4.6% for 304, 5.2% for 302, and 4.8% for 323, respectively. The resulting ignition losses are

nearly equal to the amount of the structural hydroxyl ions in an ideal muscovite layer, suggesting that the weight-loss above 400° C. involves the liberation of both the interlayer ammonium ions and the structural water.

#### DISCUSSION

In sericites or so-called illites, the presence of hydronium ions ( $H_3O^+$ ) has been frequently suggested. These suggestions are based mainly on either weight-loss studies which seem to suggest a presence of strongly chemisorbed interlayer water, or on charge balance requirements throughout the crystal, but no direct evidence has yet been obtained. At an early stage of the present investigation, the presence of hydronium ions was assumed in order to interpret the excess decrease of alkali ions over the increase of the ratio, Si/Al, in the tetrahedral layers, and also the abnormal weight-loss characteristics of the disordered sericites (Fig. 2). As described above, however, the interlayer ammonium ions can account for these abnormalities without assuming the presence of hydronium ions, except that the specimen 302 still retains a little excess of the ignition loss (about 0.7%) after the subtraction of ammonium ions, which may indicate the presence of  $H_3O^+$ . Without direct evidence, however, presence of the hydronium ion is still open to question. Details of the present investigation will be reported in the near future.

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#### VARIATIONS OF THE BASAL SPACINGS OF MUSCOVITE IN SILLIMANITE-BEARING PELITIC SCHISTS OF NORTHWESTERN MAINE

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#### INTRODUCTION

During a detailed petrologic study of the pelitic schists of N.W. Maine (for location see Fig. 1, Guidotti, 1963) it became apparent that the basal spacings of muscovite in sillimanite-bearing rocks fall into dis-