

## The "10Å phase" in the system MgO-SiO<sub>2</sub>-H<sub>2</sub>O

JON F. BAUER<sup>1</sup> AND CHARLES B. SCLAR

Department of Geological Sciences  
Lehigh University  
Bethlehem, Pennsylvania 18015

### Abstract

The 10Å phase is a unique pressure-dependent hydrous phyllosilicate in the system MgO-SiO<sub>2</sub>-H<sub>2</sub>O which is stable at pressures between 32 and 95 kbar and temperatures up to 535°C. Although it was previously characterized as a 2½-octahedral member of the mica family, re-examination of this phase has resulted in a new chemical and structural model represented by the formula [(H<sub>3</sub>O)<sub>2</sub><sup>XII</sup>Mg<sub>6</sub><sup>VI</sup>Si<sub>8</sub><sup>IV</sup>O<sub>22</sub>(OH)<sub>2</sub>]. The results of X-ray powder diffraction analysis, thermal analysis, and experiments in which the stoichiometry of oxide starting mixtures was carefully controlled indicate that the structure of the 10Å phase is that of a fully trioctahedral 2:1 phyllosilicate; it is similar to talc, but contains additional chemically-bound "water" in 12-coordinated sites [(H<sub>2</sub>O)<sub>2</sub><sup>XII</sup>Mg<sub>6</sub><sup>VI</sup>Si<sub>8</sub><sup>IV</sup>O<sub>20</sub>(OH)<sub>4</sub>]. The results of infrared spectroscopy, however, indicate that this "water" is best represented as oxonium ions (H<sub>3</sub>O<sup>+</sup>) formed by interaction of the 12-coordinated interlayer H<sub>2</sub>O molecules with certain octahedral-layer hydroxyl groups according to the relation:



or



The presence of the interlayer H<sub>3</sub>O<sup>+</sup> results in a basal spacing (*d*<sub>001</sub>) of 9.96Å as compared with 9.35Å for the corresponding basal spacing (*d*<sub>001</sub>) of talc. It also allows for stronger bonding between the 12-coordinated aqueous species and the silicate network, which accounts for the high thermal stability of the phase relative to other crystalline hydrates. Although the proposed structure of this phase is similar to that of a 10Å mica, the 10Å phase is not strictly isostructural with the mica family.

### Introduction

The existence of a new pressure-dependent hydrous magnesium silicate, which is stable at pressures between 32 and 95 kbar and temperatures between 375 and 535°C, was first reported by Sclar *et al.* (1965 a,b). Preliminary X-ray powder diffraction analysis of this phase showed that it was a 2:1 phyllosilicate crystallographically similar to talc, but with a 10Å basal-plane spacing analogous to that of mica. The deduced chemical formula for this phase was reported as [(H<sub>3</sub>O)<sub>2</sub><sup>XII</sup>(Mg<sub>6</sub>□<sub>1</sub>)<sup>VI</sup>Si<sub>8</sub><sup>IV</sup>O<sub>20</sub>(OH)<sub>4</sub>] where the Roman numeral superscripts indicate the coordination number with oxygen of each cation in

the lattice and the symbol □ denotes a vacant lattice site. Sclar *et al.* (1965 a,b) concluded that the structure and chemistry of this phase were indicative of a 2½-octahedral, alkali-free, non-aluminous mica.

Some support for this model was provided by the results of Seifert and Schreyer (1965) and Franz and Althaus (1974) who synthesized, respectively, what appeared to be the K<sup>+</sup>- and Na<sup>+</sup>-bearing analogues of this phase hydrothermally at pressures less than 3 kbar (Fig. 1). The potassium analogue was later found to be part of an extensive solid-solution series which included the aluminous mica phlogopite [K<sub>2</sub><sup>XII</sup>Mg<sub>6</sub><sup>VI</sup>(Al<sub>2</sub>Si<sub>6</sub>)<sup>IV</sup>O<sub>20</sub>(OH)<sub>4</sub>] (Seifert and Schreyer, 1971) and its ferrous iron analogue (Kwak, 1971). Both Seifert and Schreyer (1971) and Kwak (1971) found that there was continuous solid solution between the silicon-rich end member [K<sub>2</sub><sup>XII</sup>

<sup>1</sup> Present address: Johns-Manville Research and Development Center, P. O. Box 5108, Denver, Colorado 80217.

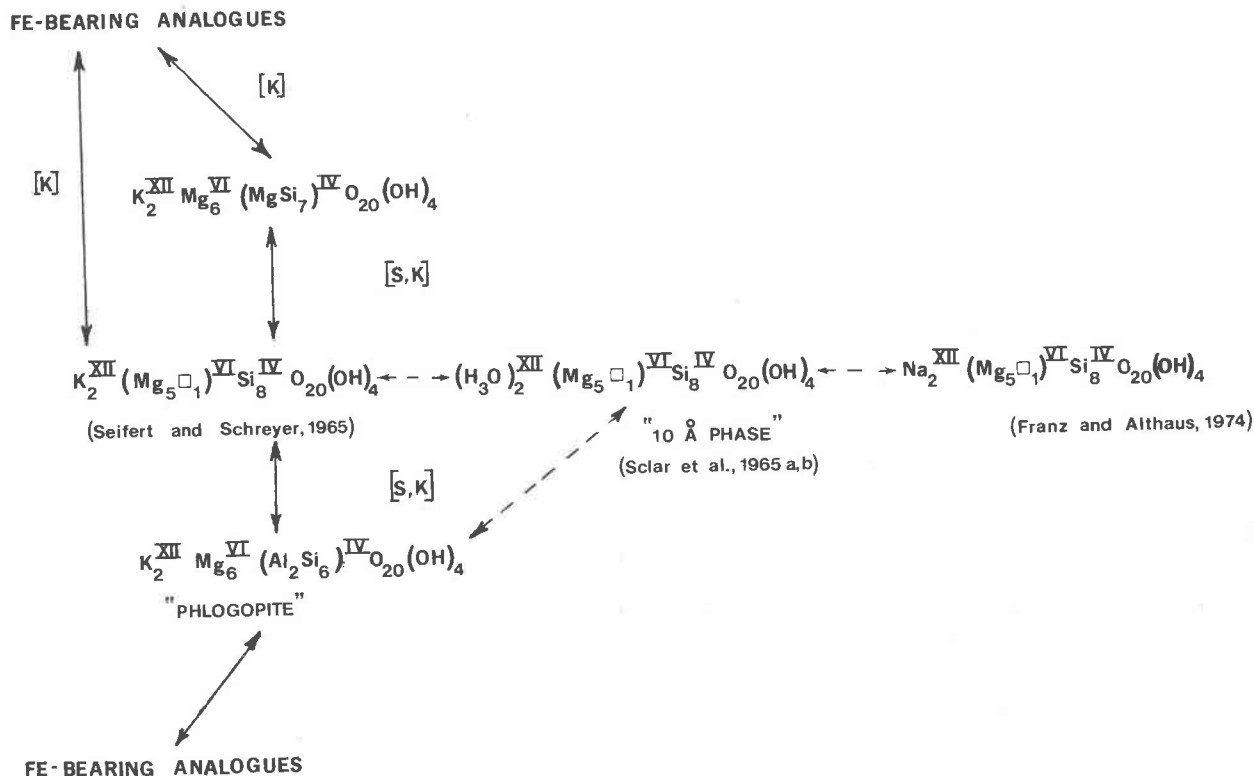


Fig. 1. Potential crystallo-chemical relationships of the 10Å phase to various alkali-bearing micas. Solid arrows represent experimentally verified solid solutions between the two indicated end members. Dashed arrows represent hypothetical solid solutions between mica end members and the 10Å phase mica based on the model of Sclar *et al.*, (1965a,b). [S] refers to Seifert and Schreyer, (1971); [K] refers to Kwak (1971).

$(Mg_5\Box_1)^{VI}Si_8^{IV}O_{20}(OH)_4$  and an ideal magnesium-rich end member  $[K_2^{XII}Mg_6^{VI}(MgSi_7)^{IV}O_{20}(OH)_4]$ . It appeared, therefore, that the 10Å hydrous magnesium silicate phase of Sclar *et al.* (hereafter referred to as the 10Å phase) might also be part of such a solid-solution series at very high pressures. The existence of such phases might be of great importance with respect to understanding (1) the storage and release of water in the earth's mantle and (2) the reaction of anhydrous silicate minerals with water at pressures in excess of 30 kbar.

Recent high-pressure studies in the system MgO-SiO<sub>2</sub>-H<sub>2</sub>O (Yamamoto and Akimoto, 1977) indicated that the chemical composition of the 10Å phase may be different from that initially reported by Sclar *et al.* Yamamoto and Akimoto gave the composition of the 10Å phase as  $(3MgO \cdot 4SiO_2 \cdot 2H_2O)$ , although this conclusion was not supported with crystallochemical data. Their results suggest that either (1) the 10Å phase is indeed an oxonium-bearing non-aluminous phlogopitic mica with the composition  $[(H_3O)_2^{XII}Mg_{5.364}\Box_{.636}^{VI}(Mg_{.364}Si_{7.363})^{IV}O_{20}(OH)_4]$ , which approaches that of the magnesium-rich end member

of the non-aluminous phlogopite series (Figure 1), or (2) the 10Å phase is a hydrated variety of talc  $[Mg_3^{VI}Si_4^{IV}O_{10}(OH)_2]$  whose detailed structure is as yet undefined. The experimental results of Bauer and Sclar (1979) indicate that the 10Å phase has a limited range of solid solution, which supports the latter model. In this paper, we report the results of a study of the composition and structure of the 10Å phase based on X-ray powder diffraction data, infrared absorption spectroscopy, and thermal analysis.

#### Experimental and analytical methods

All the high-pressure experiments in this study were carried out in a modified "belt" apparatus (Sclar *et al.*, 1963) at pressures between 35 and 60 kbar and temperatures between 425 and 500°C. The experimental *P-T* path employed was thermal quenching under pressure followed by pressure release. The reactants were sealed in welded gold capsules, and reaction times ranged from 1.5 to 24 hours; most experimental runs had a duration of 1-2 hours.

The reactants used in these experiments were high-purity MgO (periclase) and SiO<sub>2</sub> (dehydrated silicic

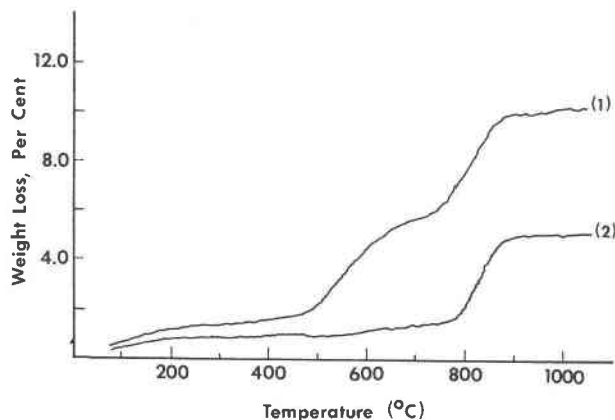


Fig. 2. Thermogravimetric curves showing progressive dehydration of the 10Å phase and of synthetic talc prepared from the same oxide components. Heating rate for all samples was 200°C per hour *in vacuo*. Curve (1) = 10Å phase; Curve (2) = synthetic talc.

acid) plus a fixed amount of high-purity water (45 mole % of the total oxide sum) which was previously distilled, deionized, and freshly boiled. With these starting materials, there was minimal contamination of the high-pressure products by magnesium carbonate which was present in experimental products obtained from mixtures of brucite and silicic acid and brucite and silica gel. The latter mixtures were used in earlier experimental studies (Sclar *et al.*, 1965a,b; Yamamoto and Akimoto, 1977).

The high-pressure products were analyzed by optical microscopy and by X-ray powder diffraction methods including both Debye-Scherrer techniques

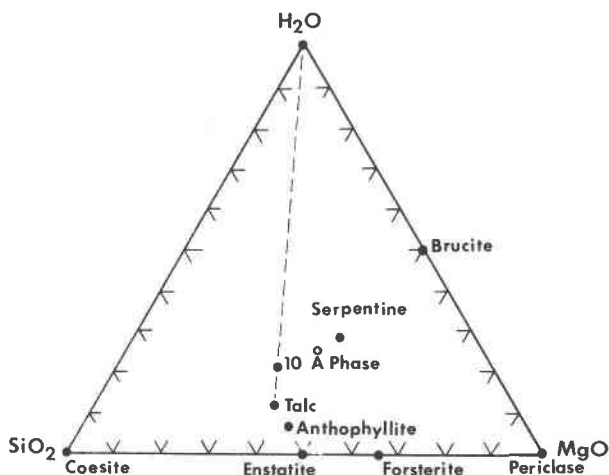


Fig. 3. The ternary system MgO-SiO<sub>2</sub>-H<sub>2</sub>O showing the composition of the 10Å phase, as proposed in this paper, and that of other selected phases. Note that the composition of the 10Å phase lies along the talc-H<sub>2</sub>O join (dashed line).

and diffractometry. Single-crystal X-ray diffraction analysis was precluded because the largest individual crystallites in the fine-grained platy aggregates of the 10Å phase were smaller than 5 μm. X-ray powder diffraction patterns of the 10Å phase were indexed and the corresponding lattice parameters calculated with the aid of the least-squares refinement program of Appleman and Evans (1973). Infrared absorption spectra were obtained in a dry N<sub>2</sub> atmosphere by means of the KBr pressed-pellet technique using a Perkin-Elmer 283 infrared spectrophotometer. Thermogravimetric analyses were obtained with a Sartorius microbalance in a vacuum of 5 × 10<sup>-4</sup> Torr using a heating rate of 200°C per hour.

## Results and discussion

### Composition

The chemical composition and stoichiometry of the 10Å phase was determined through a series of high-pressure experiments in which the atomic ratio of Mg/Si in the starting mixtures was carefully controlled. The purpose of these experiments was to synthesize the 10Å phase from mixtures representing a range of Mg/Si ratios and to determine the number and identity of the coexisting phases. By incrementally varying this ratio in successive runs, a unique bulk composition was found which yielded a single-phase product of the 10Å phase. This unique bulk composition has a Mg/Si ratio of 0.75 which is equivalent to that of talc. This Mg/Si ratio of the 10Å phase was also found to be independent of both temperature and pressure.

A Mg/Si ratio of 0.75 for the 10Å phase was also strongly suggested by the results of simple thermal dehydration experiments carried out at room pressure. Sclar (1967) showed that the 10Å phase may be partially dehydrated at temperatures of 500–600°C within 24 hours and reported that this resulted in the collapse of the basal-plane spacing from 10Å to 9.35Å which is equivalent to that of talc. These experiments were repeated in this study with the objective of carefully checking the thermal products for phases other than talc. X-ray powder diffraction analysis by the Debye-Scherrer method did not reveal any phases in the system MgO-SiO<sub>2</sub>-H<sub>2</sub>O other than talc which supports the conclusion that the Mg/Si ratio of the 10Å phase is 0.75. Additional support for this conclusion is forthcoming from the reaction talc + H<sub>2</sub>O → 10Å phase which was experimentally demonstrated at elevated temperature and pressure (Sclar *et al.*, 1965b; Sclar, 1967). Debye-Scherrer

Table 1. X-ray powder diffraction data for the 10Å phase

$d_{\text{obs}}$ (Å)	$I/I_0$	hkl	$d_{\text{calc}}$ (Å)
9.97	100	001	9.957
4.97	15	002	4.978
4.59	50	020	4.595
3.650*	10	$\bar{1}12$	3.650
3.320	80	003	3.319
2.903*	10	$\bar{1}13$	2.903
2.640	25	$\bar{1}30$	2.643
2.618	50	200	2.616
		$\bar{1}31$	2.614
2.502	15	113	2.503
		131	2.500
2.489	10	004	2.489
2.433	40	$\bar{1}32$	2.427
2.297	10	040	2.298
		$\bar{2}21$	2.295
2.168	10	$\bar{1}33$	2.165
1.996	20	005	1.992
		134	1.736
1.735	15	$\bar{2}41$	1.735
		$\bar{1}50$	1.734
		$\bar{1}52$	1.669
1.668	15	241	1.668
		$\bar{1}35$	1.665
1.532	40	060	1.532

\*obtained only from Debye-Scherrer powder patterns

patterns of products from these runs show that no crystalline phases other than talc and the 10Å phase are present. It thus appears that in both hydration and dehydration reactions involving the 10Å phase, the Mg/Si ratio remains constant.

The total water content of the 10Å phase was determined by (1) vacuum thermogravimetric analysis (TGA) of two 10 mg samples using pure alumina as a reference material (Fig. 2) and (2) simple dehydration experiments based on the difference in weight loss after 24 hrs at 110°C and 24 hrs at 1000°C on three discrete 15–20 mg samples. The total weight loss due to the release of structurally bound water was 9.0±0.2 percent (TGA) and 9.2±0.5 percent by simple dehydration methods. Thermogravimetric curves of nickelian talc and of nickelian 10Å phase (Ni<sup>2+</sup> in place of Mg<sup>2+</sup>) and of deuterated 10Å phase (prepared from D<sub>2</sub>O instead of H<sub>2</sub>O), all of which were synthesized at high pressure, are very

similar in shape to their magnesium- and hydrogen-bearing analogues; they showed weight losses due to structurally bound water that correspond exactly to those of their hydromagnesian counterparts.

The results of the high-pressure synthesis experiments and the thermogravimetric data indicate that the 10Å phase has a fixed composition within the system MgO-SiO<sub>2</sub>-H<sub>2</sub>O. In terms of oxide ratios, this composition may be expressed as 3MgO:4SiO<sub>2</sub>:2H<sub>2</sub>O which is equivalent to the composition inferred by Yamamoto and Akimoto (1977). The compositional relationship of the 10Å phase to other selected phases in this system is shown in Figure 3.

### Structure

The crystal structure of the 10Å phase was defined principally by X-ray powder diffraction analysis of high-pressure products. The  $d$ -values and relative intensities of the X-ray diffraction lines for this phase were constant regardless of the pressure or temperature of synthesis or of the bulk composition of the synthesis mix and the resulting presence or absence of other phases. This indicates that the fundamental crystal structure of the 10Å phase as well as its stoichiometry is not only unique, but very specific and non-variable in the system MgO-SiO<sub>2</sub>-H<sub>2</sub>O.

X-ray powder diffraction data for the 10Å phase are given in Table 1. Comparison of the unit-cell dimensions of the 10Å phase with those of synthetic phlogopite (Table 2) reveals the similarity of the structure of the 10Å phase with that of a 10Å mica. The unit-cell dimensions and chemical composition of the 10Å phase correlate well with a monoclinic 2:1 trioctahedral phyllosilicate structure (1M polytype). The  $b/a$  ratio of 1.731 is very close to the theo-

Table 2. Computed lattice parameters and densities for the 10Å phase and phlogopite

10Å Phase		Phlogopite*	
$\frac{a}{b}$	5.316 ± .010Å	$\frac{a}{b}$	5.314Å
$\frac{c}{b}$	9.191 ± .010Å	$\frac{c}{b}$	9.208Å
$\frac{c}{a}$	10.118 ± .015Å	$\frac{c}{a}$ **	10.314Å
$\beta$	100.25 ± .15°	$\beta$	99.9°
$D^\dagger$	2.712 g/cm <sup>3</sup>	$D$	2.785 g/cm <sup>3</sup>

\* Data from Hazen and Wones (1972).

\*\*Based on 1M polytype.

† Based on the composition [3MgO:4SiO<sub>2</sub>:2H<sub>2</sub>O].

retical value of  $(3)^{1/2}$  for an ideal monoclinic layer silicate, and all indexed reflections have even values of  $(h + k)$  in accord with the systematic extinction laws for a 1M polytype (space group  $C2/m$ ). Although the stacking sequence in the 10Å phase is clearly different from that in talc ( $2M_1$ ), it cannot be distinguished from a 3T stacking solely on the basis of X-ray powder data. 3T polytypes are encountered less frequently than their 1M counterparts in trioctahedral phyllosilicate structures, so it is probable that the latter stacking sequence is dominant in the 10Å phase.

The X-ray diffraction data for the 10Å phase given in Table 1 differ somewhat from those reported by Yamamoto and Akimoto (1977). Although the X-ray powder diffraction patterns given by the latter authors were not indexed and the corresponding cell parameters were not given, preliminary assignment of their reported reflections based on the indexing procedure used in this study indicates a unit cell which is approximately 3% larger in the  $c$ -axis direction and 0.5% larger in the  $b$ -axis direction than unit-cell dimensions of the 10Å phase given in Table 2. In addition, Yamamoto and Akimoto report a variable basal spacing for the 10Å phase ranging from 9.81Å to 10.23Å. The exact value for a given sample was somewhat dependent upon the bulk composition of the starting mix and apparently unrelated to the pressure or temperature of synthesis. No such variation in  $d_{001}$  was found in the present study. Apparent basal spacings of less than 9.96Å may be attributed to composite reflections resulting from talc-10Å phase random interstratifications, whereas those greater than 9.96Å may be due to the incorporation of weakly-bound excess H<sub>2</sub>O layers between some of the phyllosilicate sheets. Unfortunately, neither TGA nor other thermal dehydration data were provided by Yamamoto and Akimoto so that the distinction between relatively weakly-bound interlayer H<sub>2</sub>O and relatively strongly-bound H<sub>2</sub>O could not be made. In the present study, all synthesis experiments were carried out with a fixed mole fraction of water in the starting mixture of  $X_{H_2O} = .45$ ; however, the 10Å phase synthesized in twelve earlier experimental runs by C. B. Sclar in which  $X_{H_2O} \geq .45$  has a constant X-ray powder diffraction pattern with  $d$ -values and relative intensities in excellent agreement with those given in Table 1.

X-ray powder diffraction data were also obtained from samples which were heated at several temperatures between 100 and 1000°C in order to correlate structural changes with the thermogravimetric data. As shown by curve (1) in Figure 2, thermal dehy-

dration of the 10Å phase proceeds in two discrete steps, which occur at intervals of approximately 475–675° and 675–875°, respectively. The weight loss associated with each of these thermal intervals is the same, namely, 4.5% by weight. Both the nickelian and the deuterated isostructural analogues of the 10Å phase also show a well-resolved two-step thermal dehydration pattern involving weight losses of the same magnitude in the corresponding thermal intervals. X-ray powder diffraction data obtained from samples subjected to prolonged heat treatment at 500°C show that the first dehydration step corresponds to a collapse of the basal spacing of the 10Å phase from 9.96Å to 9.35Å and also results in a marked decrease in all observed  $d$ -values for reflections other than those from  $\{hk0\}$  planes. The  $d$ -values of  $\{hk0\}$  reflections show a relatively small decrease which is probably due to the small decrease in  $b$  from 9.191Å (10Å phase) to 9.171Å (talc). The resulting diffraction pattern is identical with that of pure magnesian talc. The additional 4.5 wt.% loss occurs only when the sample is dehydrated at temperatures greater than 650°. A comparison of curves (1) and (2) in Figure 2, shows that the second dehydration step is equivalent in temperature range and magnitude of weight loss to the single-step dehydration of talc. The high-temperature dehydration step of the 10Å phase, therefore, involves decomposition of the octahedral layer hydroxyl groups as in the simple dehydration of talc. This was confirmed by X-ray powder diffraction analysis of samples of both talc and the 10Å phase which were subjected to prolonged heat treatment at 1000°; both products were composed solely of clinoenstatite and cristobalite.

These results strongly indicate that the 10Å phase is a monohydrate with the structure of talc whose formula may be represented stoichiometrically as  $Mg_3Si_4O_{10}(OH)_2 \cdot H_2O$ . The marked effect of the "hydrate H<sub>2</sub>O" on the magnitude of the  $c$  parameter suggests a structural model in which H–O–H groups are stereochemically arranged parallel to (001) of the phyllosilicate structure. It also appears that the "hydrate H<sub>2</sub>O" is more weakly bound than the "hydroxyl H<sub>2</sub>O" of the octahedral layer, inasmuch as the former is released from the structure at lower temperatures.

The structural constraints imposed by the X-ray diffraction and thermogravimetric data can best be accounted for by assigning the "hydrate H<sub>2</sub>O", as individual H<sub>2</sub>O molecules, to quasi-hexagonal interlayer sites of 12-fold coordination within the opposing tetrahedral layers of a fully trioctahedral 2:1

phyllosilicate lattice. These 12-coordinated sites are structurally equivalent to those occupied by alkali ions in a 10Å mica. The characteristic "packing radius" of an H<sub>2</sub>O molecule is nearly identical with that of the K<sup>+</sup> ion (~1.35Å), so there appear to be no stereochemical restrictions on such an assignment. By analogy with the mica structure, a new structural-chemical formula for the 10Å phase can be written as [(H<sub>2</sub>O)<sup>xii</sup>Mg<sub>3</sub><sup>vi</sup>Si<sub>4</sub><sup>iv</sup>O<sub>10</sub>(OH)<sub>2</sub>]. In a strict sense, however, this talc-hydrate formula does not represent a true mica inasmuch as the octahedral-tetrahedral network carries no net charge.

The model for the 10Å phase presented above satisfies both the crystallographic and chemical constraints and is in reasonable accord with the results from thermogravimetric analysis. It does not, however, provide a mechanism by which the 12-coordinated H<sub>2</sub>O species can be chemically bound within the structure except for the possibility of hydrogen bonding to the oxygens of the tetrahedral (Si<sub>2</sub>O<sub>5</sub>)<sup>2-</sup> network. Such a simple model is not readily compatible with thermal experiments, which show that release of this H<sub>2</sub>O from the structure requires temperatures greater than about 400°C; this is much greater than the temperatures (100–200°C) which are normally required to dehydrate phases containing simple hydrogen-bonded water of hydration.

Infrared absorption spectra of the 10Å phase were obtained in order to more fully characterize this hydrous species. Pure talc was used as a reference phase because it is structurally similar to the 10Å phase and its infrared absorption spectrum is well characterized (Wilkins and Ito, 1967; Russell *et al.*, 1970). Inasmuch as infrared absorption spectra provide qualitative information on bond strength, the coordination number of cations, and structural configurations within a phyllosilicate lattice, this analytical method was used as a check on several of the deduced features in the structural model presented above.

Representative IR absorption spectra of the 10Å phase and of synthetic talc are given in Figure 4 (a and b). As expected, the two patterns are very similar in accord with their close structural relationship. Correlation of observed absorption frequencies in the spectra of the 10Å phase and synthetic talc with those observed by Wilkins and Ito (1967) and by Russell *et al.* (1970) shows that all absorptions involving the tetrahedral layer and all absorptions involving interactions between the tetrahedral and octahedral layers (mixed vibrations) are virtually identical in position and have similar relative intensities (see Farmer, 1974, for a summary of as-

signed vibrational modes in the talc structure). This indicates that at least the tetrahedral layers in the 10Å phase structure do not deviate significantly from the relatively simple (Si<sub>2</sub>O<sub>5</sub>)<sub>n</sub><sup>2-</sup> network of talc. Absorptions involving the octahedral layer of talc are principally those of the hydroxyl group, which has three prominent vibrational modes. All three are infrared active and give rise to absorptions at 3677, 669, and 445 cm<sup>-1</sup>. These absorptions also appear in the spectrum of the 10Å phase; however, they have a much lower intensity than the corresponding absorptions in talc based on spectra obtained with the same concentration of each material in the beam path.

The only absorptions which are potentially assignable to the 12-coordinated hydrous species in the 10Å phase are given in Table 3. These are absorptions which are present in the spectra of the 10Å phase but are absent from the corresponding talc spectra. As shown in Table 3, three of these absorptions may be assigned to vibrational modes involving the oxonium (H<sub>3</sub>O<sup>+</sup>) ion as observed in solid acid hydrates (Ferriso and Hornig, 1955; Savoie and Giguere, 1964; Fournier *et al.*, 1969) and in various mineral phases (White and Burns, 1963; Wilkins *et al.*, 1974; Bokij and Arkhipenko, 1977). Of these, only one absorption frequency (1700–1720 cm<sup>-1</sup>) appears to be due solely to H<sub>3</sub>O<sup>+</sup>; the other two overlap absorptions which might arise from hydrocarbon contaminants, molecular H<sub>2</sub>O, or physically adsorbed hydrogen-bonded H<sub>2</sub>O networks. Additional evidence for the existence of H<sub>3</sub>O<sup>+</sup> in the 10Å phase was obtained from the infrared spectra of samples of the 10Å phase synthesized at high pressure from MgO-SiO<sub>2</sub>-D<sub>2</sub>O rather than MgO-SiO<sub>2</sub>-H<sub>2</sub>O mixtures. Spectra of these deuterated samples (Fig. 4c) show a predictable decrease in all octahedral layer hydroxyl absorption frequencies (see Russell *et al.*, 1970), and in addition, exhibit a new discrete absorption at 2445 cm<sup>-1</sup> which correlates well with one assigned fundamental frequency of the D<sub>3</sub>O<sup>+</sup> ion (Fournier *et al.*, 1969). Furthermore, this absorption band falls outside the reported range of absorptions attributable to surface adsorbed, hydrogen-bonded D<sub>2</sub>O groups (Yukhnovich, 1963).

The results obtained from infrared spectroscopy indicate that chemical bonding in the 10Å phase is somewhat more complex than would be predicted by the relatively simple talc-hydrate model. In particular, the possible presence of H<sub>3</sub>O<sup>+</sup> in this structure suggests a model which is more compatible with an oxonium-bearing mica (Figure 1). As noted above, the mica model cannot be rejected solely on the basis

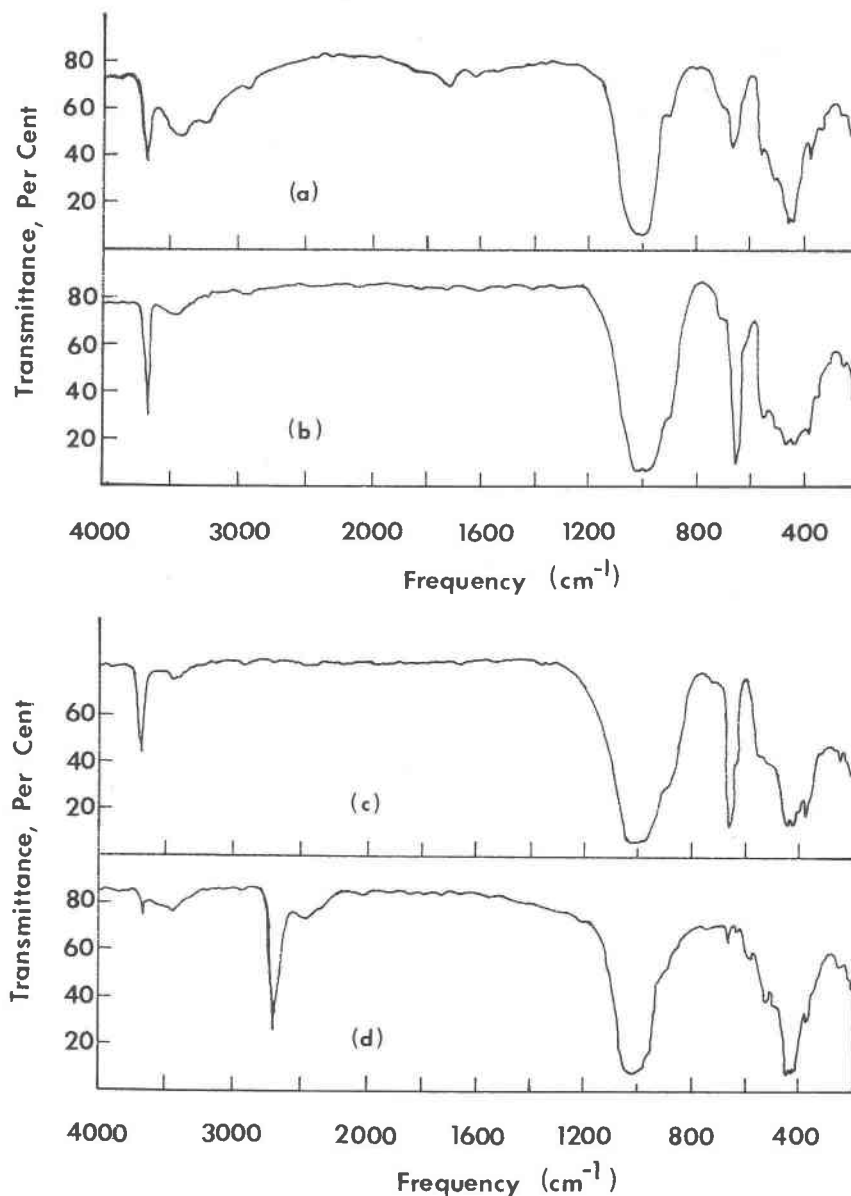


Fig. 4. Representative infrared absorption spectra of experimental products. Spectra were obtained in a dry N<sub>2</sub> atmosphere from samples dispersed in KBr pressed pellets: (a) 10Å phase; (b) Synthetic talc; (c) 10Å phase heated in air at 550°C for 24 hours; (d) Deuterated 10Å phase.

of the Mg/Si ratio. It does, however, have the following shortcomings:

(1) The H<sub>2</sub>O content of a mica phase with the composition  $[(H_3O)_2^{XII} (Mg_{5.364} \square_{.636})^{VI} (Mg_{.364} Si_{7.636})^{IV} O_{20} (OH)_4]$  is not equivalent to that observed for the 10Å phase; complete dehydration of the 10Å phase results in a weight loss of 9.0%, not 11.5% as predicted by this model.

(2) Dehydration of the 10Å phase results solely in the formation of talc plus free H<sub>2</sub>O; dehydration of the

corresponding mica phase to talc plus H<sub>2</sub>O would result in the production of free protons, which would create a charge imbalance in either of the product phases, and would, therefore, present a chemical problem which is not easily resolved.

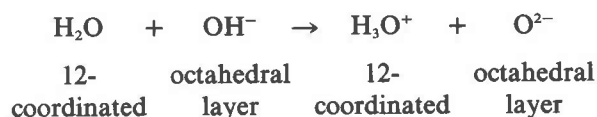
(3) The presence of octahedral vacancies, as required by the mica model, would result in different chemical environments for the individual octahedral layer hydroxyl groups which should thus give rise to unique well-defined IR absorption bands satellite to and at

slightly lower frequencies than the principal O-H stretching frequency (3675 cm<sup>-1</sup>) (see Kodama *et al.*, 1974); no evidence for such bands was found in the spectrum of the 10Å phase.

The structural model for the 10Å phase which best fits the sum of the analytical data is illustrated in Figure 5. Chemically, this model may be represented as follows:



Note that this is stoichiometrically equivalent to the talc hydrate formula presented above; however, allowance has been made for the following interaction:



Such an interaction appears likely if the octahedral layer hydroxyl groups are oriented normal to the *a-b* plane and lie directly beneath the 12-fold sites as they do in other trioctahedral phyllosilicates such as micas (Serratos and Bradley, 1958). Because of this unique orientation of the O-H groups, the K-H distance in phlogopite, for example, is close to the K-O distance in the 12-coordination "sphere," namely, 3.10Å vs. 2.96Å, respectively (Rayner, 1974). However, the K-H distance in phlogopite is largely controlled by repulsive forces between the positively charged potassium ion and the positive end of the hydroxyl dipole (Bassett, 1960), which results in both a larger *c* and a larger *b* (due to shortening of the OH-OH shared edges) than would be expected if there were either an attractive interaction or no inter-

Table 3. Unique infrared absorptions characteristic of the 10Å phase

Frequency (cm <sup>-1</sup> )	Possible Assignment
3400-3440	O-H stretch (H <sub>2</sub> O·····HOH) O-H stretch (HOH·····O-Si) 2ν <sub>4</sub> (H <sub>3</sub> O <sup>+</sup> )
3200-3250	2ν <sub>2</sub> (H <sub>2</sub> O)
2910-2930	C-H stretch (contamination) ν <sub>1</sub> , ν <sub>3</sub> (H <sub>3</sub> O <sup>+</sup> )
1700-1720	ν <sub>4</sub> (H <sub>3</sub> O <sup>+</sup> )
1600-1640	ν <sub>2</sub> (H <sub>2</sub> O)

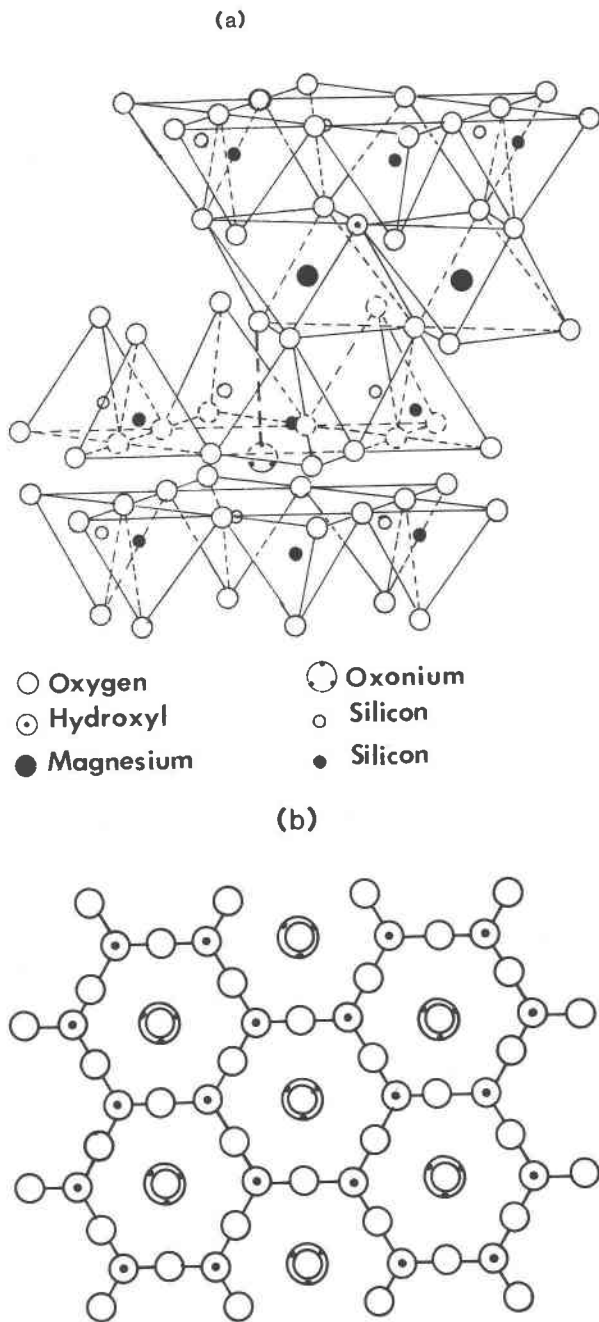


Fig. 5. Idealized crystallographic model of the 10Å phase showing the arrangement of the tetrahedral and octahedral layers and the position of the interlayer 12-coordinated H<sub>3</sub>O<sup>+</sup> species: (a) (100) projection (modified from Grim, 1968); (b) (001) projection (modified from Bailey, 1967).

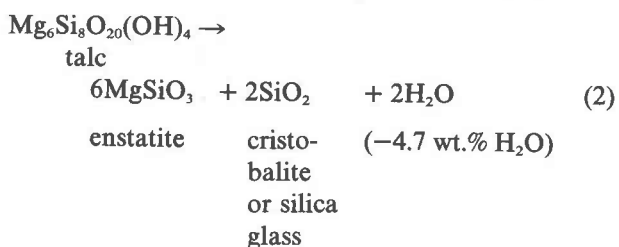
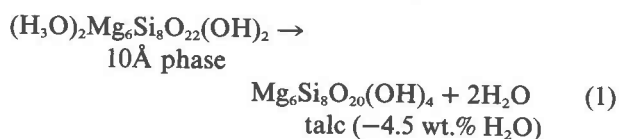
action between the 12-coordinated species and the hydroxyl hydrogens. Inasmuch as H<sub>2</sub>O, H<sub>3</sub>O<sup>+</sup>, and K<sup>+</sup> are nearly the same size, the smaller *c* and *b* parameters of the 10Å phase relative to those of phlogopite suggests that the (hydrous species)<sup>XII</sup>-OH



bond in the 10Å phase involves a net attractive interaction. Correspondingly, this supports the view that the 12-coordinated hydrous species in the 10Å phase is (H<sub>3</sub>O)<sup>+</sup>.

This new model is in accord with the existence in the 10Å phase of two types of structurally bound site-specific hydrous species, namely, oxonium ions and hydroxyl ions, both of which can be recognized in the infrared absorption spectrum. It also accounts for the observed reduction in intensity of all absorptions assigned to vibrations of the octahedral layer hydroxyl groups relative to those in talc, which has twice as many hydroxyl groups per formula unit. In addition, this model helps to explain the relatively high thermal stability of the 10Å phase as compared to other crystalline hydrates by allowing for (a) electrostatic attraction between the 12-coordinated hydrous species (H<sub>3</sub>O<sup>+</sup>) and the octahedral-tetrahedral network and (b) hydrogen bonding between this species and the oxygens of the surfaces of the adjoining tetrahedral layers.

Thermal dehydration of the 10Å phase is thus considered to proceed as follows:



Note that the theoretical weight loss values shown above are in excellent agreement with the results of thermogravimetric analysis (Fig. 2). Because the first step in this process initially involves re-protonation of oxygen ions in the octahedral layer, it does not require that, upon initial loss of water (oxonium ion destruction), residual protons remain in the interlayer site (or anywhere else in the lattice).

This model also provides an explanation for the lack of incorporation of (K<sup>+</sup>)<sup>XII</sup> or (Al<sup>3+</sup>)<sup>IV or VI</sup> into the lattice of the 10Å phase in high-pressure synthesis runs (Bauer and Sclar, 1979); that is, neither potassium- nor aluminum-bearing analogues of this phase could be prepared. It appears that the ability

of the 12-coordinated hydrous species to form bonds with the octahedral layer oxygens provides definite restrictions on ion interchangeability in the 12-fold site. Inasmuch as micas readily accept Al<sup>3+</sup> into their structure whereas talc accepts only a few weight per cent (see Fawcett and Yoder, 1966), the lack of solid solubility of aluminum in the 10Å phase is more consistent with a structural model based on a talc-like lattice rather than on a mica lattice. The earlier conclusion of Bauer and Sclar (1979) that solid solubility in the 10Å phase appears to be limited to substitutions in the octahedral layer of ions similar in size and charge to Mg<sup>2+</sup>, such as Co<sup>2+</sup> and Ni<sup>2+</sup>, is, therefore, completely compatible with this model.

### Conclusions

The 10Å phase is a unique high-pressure phyllosilicate phase in the ternary system MgO-SiO<sub>2</sub>-H<sub>2</sub>O. It has a specific fixed composition, independent of the temperature and pressure of synthesis which may be expressed stoichiometrically as 3MgO : 4SO<sub>2</sub> : 2H<sub>2</sub>O. The crystal structure of the 10Å phase is that of a fully trioctahedral 2:1 phyllosilicate with a 9.96Å basal spacing. The octahedral and tetrahedral network of this phase is similar to that of talc; however, in the 10Å phase a discrete H<sub>2</sub>O molecule occupies each 12-coordinated interlayer site. Infrared absorption spectroscopy and thermogravimetric analysis indicate that each 12-coordinated H<sub>2</sub>O molecule is extensively bonded to both the tetrahedral and the underlying octahedral layer of the structure. Interaction of each H<sub>2</sub>O molecule with the octahedral layer hydroxyl group results in the formation of H<sub>3</sub>O<sup>+</sup> and O<sup>2-</sup> from the H<sub>2</sub>O and OH<sup>-</sup>. It is concluded that the preferred formula for the 10Å phase is [(H<sub>3</sub>O)<sup>XII</sup>Mg<sub>3</sub><sup>VI</sup>Si<sub>4</sub><sup>IV</sup>O<sub>11</sub>(OH)]. Although they are structurally similar, the 10Å phase is not a true isostructural member of the mica family and does not appear to form solid solutions with the isostructural series [KMg<sub>3</sub>AlSi<sub>3</sub>O<sub>10</sub>(OH)<sub>2</sub> - KMg<sub>2.5</sub>□<sub>0.5</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>].

### Acknowledgments

This paper is based on a doctoral dissertation presented to the faculty of the Department of Geological Sciences at Lehigh University by Jon F. Bauer in partial fulfillment of the requirements for the Ph.D. degree.

This research was supported in part by Grant No. 1975-75 to JFB from the Geological Society of America and a Grant-in-Aid to JFB from Sigma Xi. Thermogravimetric analyses were obtained at Bat-

telle-Columbus Laboratories under Grant No. DA-ARO-D-31-124-G673 to CBS.

### References

- Appleman, D. E. and Evans, H. T., Jr. (1973) Indexing and least-squares refinement of powder diffraction data. U. S. National Technical Information Service, PB-216-188.
- Bailey, S. W. (1967) Polytypism in layer silicates. In Layer Silicates, AGI Short Course Lecture Notes. American Geological Institute, Washington.
- Bassett, W. A. (1960) Role of hydroxyl orientation in mica alteration. *Bulletin Geological Society of America*, 71, 449-456.
- Bauer, J. F. and Sclar, C. B. (1979) Crystal chemistry and stability of a high-pressure hydrous 10Å layer silicate in the system MgO-SiO<sub>2</sub>-H<sub>2</sub>O. In K. D. Timmerhaus and M. S. Barber, Eds., *High-Pressure Science and Technology (Proceedings Sixth AIRAPT Conference)*, Vol. 2, p. 144-152. Plenum Press, New York.
- Bokij, G. B. and Arkhipenko, D. K. (1977) Infrared spectra of oxonium and ammonium ions in layer aluminosilicates. *Physics and Chemistry of Minerals*, 1, 233-242.
- Farmer, V. C. (1974) The layer silicates. In V. C. Farmer, Ed., *The Infrared Spectra of Minerals*. Mineralogical Society Monograph 4, 331-364, London.
- Fawcett, J. J. and Yoder, H. S. (1966) Phase relationships of chlorites. *American Mineralogist*, 51, 353-380.
- Ferriso, C. and Hornig, P. (1955) The infrared spectra of oxonium halides and the structure of the oxonium ion. *Journal of Chemical Physics*, 23, 1464-1468.
- Fournier, M. G., Mascherpa, G., Rousselet, D., and Potier, J. (1969) Assignment of oxonium ion vibrational frequencies. *C. R. Acad. Sci. Ser. C*, 269, 279-282.
- Franz, G. and Althaus, E. (1974) Synthesis and thermal stability of 2½-octahedral sodium mica, NaMg<sub>2.5</sub>(Si<sub>4</sub>O<sub>10</sub>)(OH)<sub>2</sub>. *Contributions to Mineralogy and Petrology*, 46, 227-232.
- Grim, R. E. (1968) *Clay Mineralogy*. Second Edition. McGraw-Hill, New York.
- Hazen, R. M. and Wones, D. R. (1972) The effect of cationic substitutions on the physical properties of trioctahedral micas. *American Mineralogist*, 57, 103-129.
- Kodama, H., Ross, J. G., Iyami, J. T., and Robert, J. L. (1974) Effect of layer charge location on potassium exchange and hydration of micas. *American Mineralogist*, 59, 491-495.
- Kwak, T. A. (1971) An experimental study on Fe-Mg micas transitional between dioctahedral and trioctahedral compositions. *Neues Jahrbuch Mineralogie, Monatshefte*, 1971, 326-335.
- Rayner, J. H. (1974) The crystal structure of phlogopite. *Mineralogical Magazine*, 39, 850-856.
- 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 infra-red spectra. *Mineralogical Magazine*, 37, 869-879.
- Savoie, R. and Giguere, P. A. (1964) Infrared study of the crystalline monohydrates of nitric, perchloric, and sulphuric acids. *Journal of Chemical Physics*, 41, 2698-2705.
- Sclar, C. B. (1967) High pressure silicate chemistry: synthesis, stability, and transitions of crystalline phases in the system MgO-SiO<sub>2</sub>-H<sub>2</sub>O. *Proceedings USARO-Durham Conference on New Materials from High Pressure High Temperature Processes*, Watervliet, N.Y., 135-150.
- Sclar, C. B., Carrison, L. C., and Schwartz, C. M. (1963) The calcite-aragonite transition and the calibration of a "belt-type apparatus" between 15 and 25 kb, 700°C-1400°C. In A. A. Giardini and E. C. Lloyd, Eds., *High Pressure Measurement*, Butterworths, Washington, 286-300.
- Sclar, C. B., Carrison, L. C., and Schwartz, C. M. (1965a) High-pressure synthesis and stability of a new hydronium-bearing layer silicate in the system MgO-SiO<sub>2</sub>-H<sub>2</sub>O (abstr.) *Transactions of the American Geophysical Union*, 46, 184.
- Sclar, C. B., Carrison, L. C., and Schwartz, C. M. (1965b) The system MgO-SiO<sub>2</sub>-H<sub>2</sub>O at high pressures, 25-130 kb. and 375-1000°C (extended abstr.), *Basic Science Division, American Ceramic Society Fall Meeting*, Paper 2-b-65 F.
- Seifert, F. and Schreyer, W. (1965) Synthesis of a new mica, KMg<sub>2.5</sub>(Si<sub>4</sub>O<sub>10</sub>)(OH)<sub>2</sub>. *American Mineralogist*, 50, 1114-1118.
- Seifert, F. and Schreyer, W. (1971) Synthesis and stability of micas in the system K<sub>2</sub>O-MgO-SiO<sub>2</sub>-H<sub>2</sub>O and their relations to phlogopite. *Contributions to Mineralogy and Petrology*, 30, 196-215.
- Serratos, J. M. and Bradley, W. F. (1958) Determination of the orientation of OH bond axes in layer silicates by infrared absorption. *Journal of Physical Chemistry*, 62, 1164-1167.
- White, J. L. and Burns, A. F. (1963) Infrared spectra of hydronium ion in micaceous minerals. *Science*, 141, 800-801.
- Wilkins, R. W. T. and Ito, J. (1967) Infrared spectra of some synthetic talcs. *American Mineralogist*, 52, 1649-1661.
- Wilkins, R. W. T., Mateen, A., and West, G. W. (1974) The spectroscopic study of oxonium ions in minerals. *American Mineralogist*, 59, 811-819.
- Yamamoto, K. and Akimoto, S. (1977) The system MgO-SiO<sub>2</sub>-H<sub>2</sub>O at high pressures and temperatures—stability field for hydroxyl chondrodite, hydroxyl clinohumite, and 10Å phase. *American Journal of Science*, 277, 288-312.
- Yukhnovich, G. V. (1963) Advances in the use of infrared spectroscopy for the characterization of O-H bonds. *Russian Chemical Reviews*, 32, 619-633.

*Manuscript received, September 17, 1980;  
accepted for publication, January 6, 1981.*