

## Intracrystalline expansion of the “10Å phase,” a high-pressure phyllosilicate in the system MgO–SiO<sub>2</sub>–H<sub>2</sub>O

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### Abstract

The “10Å phase” in the system MgO–SiO<sub>2</sub>–H<sub>2</sub>O is a high-pressure hydrous phyllosilicate with the proposed formula (H<sub>3</sub>O)<sub>2</sub>Mg<sub>6</sub>Si<sub>8</sub>O<sub>22</sub>(OH)<sub>2</sub>. Interaction of the 10Å phase with certain polar organic molecules results in a limited absorption and intercalation of these species with concomitant c-axis expansion of its lattice. This phase does not expand in the presence of water or non-polar organic species. These observations are consistent with the most recently proposed structural-chemical model for this phase (Bauer and Sclar, 1981) and serves to distinguish it from other similar phyllosilicates in this system.

### Introduction

Previous studies in the system MgO–SiO<sub>2</sub>–H<sub>2</sub>O at high pressures and temperatures have revealed the existence of a unique pressure-dependent hydrous 2:1 phyllosilicate (Sclar, et al., 1965a,b; Yamamoto and Akimoto, 1977; Bauer and Sclar, 1979, 1981), which is stable at pressures between 32 and 95 kbar and temperatures between 375 and 535°C (Sclar et al., 1965a,b; Bauer and Sclar, 1979). The composition and structure of this phase were recently re-defined by Bauer and Sclar (1981), who proposed the structural-chemical 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>. In this model, interlayer sites are occupied by 12-coordinated oxonium ions formed by the interaction of interlayer water molecules with octahedral-layer hydroxyls oriented normal to the a–b plane and projecting toward these sites. The resulting structure is, therefore, that of a fully trioctahedral 2:1 phyllosilicate, similar to talc but with a basal spacing of 9.96Å as compared with a basal spacing of 9.35Å for talc.

Although crystallographic and chemical similarities between the “10Å phase” and the trioctahedral mica family are obvious, its closest analogue appears to be the mineral kerolite. The latter has been characterized as a non-expanding, turbostratic, fine-grained “talc-hydrate” with the composition Mg<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>·n H<sub>2</sub>O (n = .75–1.2) and a basal spacing of 9.6Å (Brindley et al., 1977). The increase in *d*<sub>001</sub> in kerolite relative to that of talc was ascribed by Brindley et al. (1977) to the lack of close packing of adjacent layers and not necessarily to interlayer site occupancy by 12-coordinated H<sub>2</sub>O. Differences between kerolite and the “10Å phase” are observed in their respective X-ray powder diffraction patterns, their infrared absorption spectra, and the stoichiometry of kerolite and the “10Å phase,” the latter having a fixed total H<sub>2</sub>O content (cf. Bauer and Sclar, 1981; Brindley et al., 1977).

As an aid to further understanding the architecture of the “10Å phase,” a series of experiments was conducted to test the interlayer expandability of this material in the presence of various polar and non-polar media. Preliminary indications of the swelling behavior of this phase were forthcoming from the results of Sclar et al. (1965b) who reported some degree of expandability in the presence of ethylene glycol vapor; structural implications for the “10Å phase” however, were not discussed. To investigate this behavior further, the “10Å phase” was allowed to react with representative media from the following groups: alcohols, ketones, straight-chain aliphatic hydrocarbons, halogen-substituted hydrocarbons, aromatic hydrocarbons, and amines. In addition, expandability in the presence of water (vapor and liquid) was also examined. These groups of test media not only represented a wide range of molecular polarities, but also presented the opportunity for a variety of different bonding mechanisms to both the interlayer hydrous species and to the adjoining tetrahedral silicate network.

### Experimental

Two methods were used to characterize basal-plane expansion of the “10Å phase” in the presence of various polar and non-polar molecules. In both types of experiments, a 10–20 mg sample was allowed to imbibe a quantity of the test medium. After equilibration, each sample was analyzed immediately by X-ray powder diffractometry before the substance was released by the sample.

In the first series of experiments, 1–2 ml of the liquid were pipetted directly onto the sample surface and allowed to saturate the sample prior to X-ray analysis. Excess liquid was removed by blotting or “wicking” with a small bit of paper towel. Equilibration times were approximately 3 hrs.; in the case of highly volatile organic media, this procedure was repeated several times during the 3-hr. period to prevent complete “drying out” of the sample.

In the second series of experiments, the sample was allowed to contact only the vapor of the test substance. This was accomplished by placing the sample inside a desiccator partly filled with

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Table 1. Basal spacings ( $d_{001}$ ) of the "10Å phase" in the presence of water and of various organic molecules

Medium	Formula	$d_{001}$ (Å)
3 methyl-1 butanol	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{OH}$	14.2
t-butanol	$(\text{CH}_3)_3\text{COH}$	14.1
ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	13.1*
methanol	$\text{CH}_3\text{OH}$	13.1*
water	$\text{H}_2\text{O}$	9.96 (no expansion)
ethylene glycol	$\text{HOCH}_2\text{CH}_2\text{OH}$	13.3 (one molecular layer) 16.6 (two molecular layers)
acetone	$\text{CH}_3\text{COCH}_3$	13.6*
hexane	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	9.96 (no expansion)
pyridine	$\text{C}_5\text{H}_5\text{N}$	14.3
benzene	$\text{C}_6\text{H}_6$	9.96 (no expansion)
1,2-dichloroethane	$\text{ClCH}_2\text{CH}_2\text{Cl}$	9.96 (no expansion)
1,1,1-trichloroethane	$\text{CH}_3\text{CCl}_3$	9.96 (no expansion)
triethylenetetramine	$\text{H}_2\text{NCH}_2(\text{CH}_2\text{NHCH}_2)_2\text{CH}_2\text{NH}_2$	13.4

\*Obtained only by reaction of the "10Å Phase" with the liquid.

a reservoir of the test liquid. The sample was thereby exposed to the vapor at room temperature over a period of 24 hrs.

At least 3 X-ray diffractometer scans per sample were made between  $2^\circ$  and  $10^\circ 2\theta$  using  $\text{CuK}\alpha$  radiation at scan rates between 1/4 and 1 degree per minute, depending on the volatility of the test media. Average values of  $d_{001}$  were obtained from peak measurements from these scans; peak intensities were corrected for Lorentz-polarization prior to measurement.

### Results

Observed values of  $d_{001}$  for the "10Å phase" in the presence of water and various organic molecules are reported in Table 1. These results indicate that intracrystalline swelling of the "10Å phase" is possible in the presence of polar organic molecules containing O-H, C=O, or N-H (N-R) functional groups. Hydrocarbon molecules had no observed effect on the magnitude of the basal spacings of this phase. In addition, no swelling was observed in the presence of either liquid water or water vapor in agreement with the observation of Sclar et al. (1965b). This is unusual inasmuch as most expandable phyllosilicates will swell by physical incorporation of both polar organic molecules and water.

As expected, structurally "trapped" organic molecules can be released easily from the structure of the "10Å phase" by simple heat treatment. In all samples tested, drying at  $50^\circ\text{C}$  for 24 hrs. was sufficient to collapse the basal spacing of the "10Å phase" from its expanded value back to its original 9.96Å. The bonding of an organic molecule to the structure of the "10Å phase" is, therefore, quite weak and apparently does not involve a large displacement of the  $\text{H}_3\text{O}^+$  species from the 12-coordinated sites. The absence of a 9.35Å reflection<sup>2</sup> in X-ray powder diffraction patterns of expanded samples of the "10Å phase" suggests that the interlayer 12-coordinated hydrous species is more strongly

associated with the octahedral and tetrahedral layers than with the inter-lamellar organic molecules.

### Discussion

There are many known and proposed mechanisms for phyllosilicate swelling and concomitant formation of inter-lamellar hydrous and organic complexes; extensive reviews on this subject are available (e.g., Weiss, 1958; Theng, 1974; MacEwan and Wilson, 1980). Most such mechanisms, however, require that the host phyllosilicate possesses (1) a finite layer charge which, in the case of 2:1 phyllosilicates like the "10Å phase," is associated with each tetrahedral-octahedral-tetrahedral unit ( $0 < \text{layer charge} < 2$  per formula unit) and (2) counter-balancing interlayer cations which may be "coordinatable," "complexable" or exchangeable with respect to the reactant hydrous or organic medium. The source of this layer charge may vary; however, it usually originates from charge imbalances generated in either the tetrahedral or octahedral layers resulting from heteroionic substitutions (e.g.,  $\text{Al}^{+3}$  for  $\text{Si}^{4+}$ ), vacancies, etc. Electron delocalization, largely through bridging oxygen networks, frequently allows this charge imbalance to be manifested as a net negative charge on the surface oxygens, thereby providing electrostatic attraction for counterbalancing interlayer cations or counterions.

The observed swelling behavior of the "10Å phase," almost certainly involves bonding to the interlayer hydrous species (" $\text{H}_3\text{O}^+$ "). However, it is not completely explainable on the basis of models developed for other expandable phyllosilicates, notably smectites and vermiculites. As reported previously, interlayer  $\text{H}_3\text{O}^+$  is not exchangeable (Bauer and Sclar, 1979; 1981), in accord with the structural model presented in the latter paper; it is formed, in part, by proton transfer from the octahedral layer hydroxyl groups to interlayer  $\text{H}_2\text{O}$  molecules occupying discrete 12-coordinated sites. This may explain why this species is not hydratable or the phase as a whole expandable with water, inasmuch as hydrogen bonds which might form between the water and the interlayer  $\text{H}_3\text{O}^+$  would be effectively counterbalanced by similar bonding to the octahedral layer (which also results in a net electrostatic attraction due to charge transfer). It may also explain the occurrence of interlayer "water" as a discrete site-bound hydrous species rather than as hydrogen bonded networks. In the presence of more polar molecules or molecules which are very effective Lewis bases, however, such bonds can form and the phase will expand by incorporation of one or two molecular layers. Similarly, non-polar molecules such as aromatic and aliphatic hydrocarbons do not produce any lattice expansion; bonds of the type  $\text{C-H}\cdots\text{O}$  apparently do not form between these substances and oxygens of the layer silicate surfaces (Greenland, 1965).

The above explains the swelling behavior of the "10Å phase" with respect to most of the organic species in Table 1. There is, however, an observed expandability of this phase in the presence of molecules with somewhat smaller dipole moments than water, notably the alcohols. In these

<sup>2</sup> 9.35 Å corresponds to the c-axis dimension of two tetrahedral units plus an octahedral unit as in the talc structure.

instances, there are certainly other controlling factors, such as steric specificity, which may be involved. The layer charge distributions on the surfaces of particles of the 10Å phase, for example, are unknown; they are expected to result largely from displacement of the hydroxyl protons along *c* to form interlayer  $H_3O^+$  species, thereby creating a charge imbalance primarily in the octahedral layer. However, as observed in octahedrally substituted smectites, this charge can be diffused and distributed over the network of surface oxygens. It is likely that such a phenomenon occurs in the case of the "10Å phase" resulting in partially localized and partially de-localized surface charge. Further work involving absorption spectroscopy and interlayer ion-exchange in expanded "10Å phase" complexes may provide a more detailed picture.

Finally, it should be noted that, although the "10Å phase" can be characterized as a structure of limited intracrystalline expansion, its swelling properties and propensity for inter-lamellar complexing appear to be somewhat different from those of other phyllosilicates in the primary system  $MgO-SiO_2-H_2O$ . Talc and kerolite are basically non-expanding phases whereas stevensite, saponites, and talc-saponites show strong tendencies to incorporate not only water but other molecules as well into their interlayer structure. This behavior supports the concept of a fundamental chemical and mineralogical distinction between the "10Å phase" and other phases in this chemical system.

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*Manuscript received, September 22, 1983;  
accepted for publication, October 26, 1984.*