American Mineralogist, Volume 76, pages 106–112, 1991

The incorporation of "water" in a high-pressure 2:1 layer silicate: A high pressure differential thermal analysis of the 10 Å phase

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ABSTRACT

The 10 Å phase, a talc- and mica-like high-pressure phase with excess water relative to talc, was investigated using high-pressure differential thermal analysis at pressures to 5.2 kbar, in order to determine the enthalpy of bonding of the interlayer water species. The reaction involving the removal of the interlayer water species shows a monotonic variation with pressure, increasing from 454 °C at 1 atmosphere to 632 °C at 5.15 kbar. The enthalpy of dehydration ΔH_{dh} is equal to 200 ± 20 kJ/mol. This value is much higher than typical dehydration enthalpies of layer silicates but is similar to dehydroxylation enthalpies. It is proposed that O^{-2} occupies the 12-coordinated interlayer site and is stabilized by two resonating protons. This model is consistent with the enthalpy data and previously published infrared and thermogravimetric data. In contrast to an earlier model suggesting H_3O^+ occupancy of this site, the resonating proton model does not require the interaction of neighboring OH groups in the structure. The implication of this model is that, at high pressures, empty sites in a variety of mineral structures can be occupied by O, charge balanced by resonating protons. This model, therefore, provides a mechanism for the storage of "water" in the earth's mantle.

INTRODUCTION

Sclar et al. (1965) reported the synthesis of an unusual hydrous mica-like phase, chemically similar to talc but containing excess water, which they called the 10 Å phase. The phase is stable at pressures between 32 and 95 kbar at temperatures between 375 and 535 °C. They suggested that this phase contains either interlayer hydronium (= oxonium, H_3O^+) or H_2O. Yamamoto and Akimoto (1977) placed the minimum stability of the 10 Å phase at approximately 570 °C and 40 kbar, and they reported its composition as $Mg_3Si_4O_{10}(OH)_2 \cdot 2H_2O$. On the basis of thermogravimetric data and carefully controlled sample stoichiometry, Bauer and Sclar (1979, 1981) showed that the amount of H_2O in the structure is half of this and presented as a structural formula either $(H_3O)_2Mg_6Si_8O_{22}(OH)_2$, when assuming that hydronium is present, or $(H_2O)_2Mg_6Si_8O_2(OH)_4$, if the excess water relative to talc is H_2O. They suggested that this excess "water" is chemically bound in 12-coordinated sites, and noted that the existence of such a phase may be of importance with respect to storage of water in the earth's mantle.

The presence of hydronium in minerals is rare and difficult to document. Following a suggestion by Brown and Norrish (1952) that H_3O^+ may exist in micas, White and Burns (1963) used infrared (IR) techniques on a H-saturated and heat-treated muscovite after lithium nitrate extraction of K^+. They found an absorption band at 3470 cm^{-1}, which they attributed to H_3O^+. In studies with nonmica-like materials, other workers (e.g., Ratcliffe et al., 1985; Wilkins et al., 1974; Ferriso and Hornig, 1955) found additional absorption bands they attributed to H_3O^+ near 1100–1150 cm^{-1}, 1700–1740 cm^{-1}, 2600 cm^{-1}, and 3200 cm^{-1}. Ripmeester et al. (1986) used nuclear magnetic resonance (NMR) techniques to confirm the existence of H_3O^+ in the alunite-jarosite group. For the 10 Å phase, Bauer and Sclar (1981) suggested the presence of hydronium on the basis of a unique but poorly resolved band at 1700–1720 cm^{-1} and several additional bands that overlap with other absorptions that in part could be attributed to the presence of H_2O. In addition, they noted the presence of bands that are unique for H_2O. Thermogravimetric analysis conducted at 3.3 °C/min (Bauer and Sclar, 1981) showed two discrete weight-loss events. The first one occurred at 500–750 °C and is related to the interlayer. As a result of this water loss, the 10 Å phase transforms to talc. With further heating, the talc dehydroxylates at 750–875 °C, which results in the second weight-loss event. Additional thermogravimetric data, but with a 10 °C/min heating rate, reported in Evans and Guggenheim (1988) showed similar results, although a very small second dehydration event occurs at 550 °C in the derivative thermal gravimetry (DTG) data, representing about 5–10% of the interlayer weight loss. Because almost all of the interlayer water loss occurs in a single event, this weight loss predominantly involves one water species.

The present study further characterizes the 10 Å phase by delineating the reaction for the removal of the interlayer water species with respect to temperature and pressure by using high pressure differential thermal analysis

0003–004X/91/0102–0106$02.00

(HP-DTA). Furthermore, the enthalpy of the bonding of the interlayer species was determined in the expectation that it may provide insight into the nature of that species (hereafter referred to as "water") in the 10 Å phase. Because the product of the reaction involves water, the reaction studied is 10 Å phase = talc + H_2O, which is referred to as a dehydration reaction. Neither the term "water" nor dehydration as used here implies the nature of the interlayer species.

EXPERIMENTAL METHOD

Apparatus

The DTA apparatus used in this study was developed by Koster van Groos (1979). The apparatus allows experiments at pressures to 10 kbar at temperatures to 950 °C. It consists of a Cu sample holder with positions for two samples and a reference. The sample holder fits onto a $Pt/Pt_{90}Rh_{10}$ thermocouple assembly and is sealed inside an internally heated pressure vessel similar to that described by Holloway (1971). Samples and a reference, αAl_2O_3, are loaded into Au capsules, which may be left open or welded shut. The capsules are 0.07 mm in wall thickness, 7–8 mm in length, 3 mm in diameter, and have a reentry well 1 mm deep to accommodate the thermocouple; the latter allows the measurement of the temperature as close to the center of the sample as possible. Quartz was added to the sample as an internal temperature standard, using the high-low quartz inversion temperature at various pressures (Koster van Groos and ter Heege, 1973). Temperature corrections were typically 1–2 °C. Differential temperatures were recorded on the 20-μV or 50-μV range of a Kipp and Zonen recorder allowing a resolution of 0.02–0.05 °C. Experiments were made in the 30–800 °C range at a heating rate of 20 °C/min using a Honeywell programmable controller. Several experiments at low pressures were made at a heating rate of 10 °C/min for comparison. In the latter the peak became indistinguishable from the background. Pressure, using Ar gas as a pressure medium, was measured by calibrated high-precision Bourdon-type pressure gauges for low-, medium-, and high-pressure ranges. The pressure determinations of experiments at very low pressures are likely to be lower by as much as 0.5 bar compared with the actual pressures in the pressure vessel because of the pressure gradient between the gauge and vessel resulting from the thermal expansion of the Ar gas during an experiment. However, this pressure differential is only important in the low-pressure experiments.

Starting materials

Approximately 1 g of the 10 Å phase sample was obtained from C. B. Sclar. It was synthesized from MgO, SiO_2, and H_2O in a series of experiments at 450 °C and 50 kbar, using a belt-type apparatus (Sclar et al., 1987). The experimental products were examined by X-ray powder diffractometry for the phases present, after which they were combined. A partial Rietveld refinement showed that the products contain approximately 80 wt% 10 Å phase and 11 wt% coesite, with the remainder brucite (Bish and Guggenheim, unpublished data). These impurities in the samples did not interfere with data measurement because coesite does not exhibit a DTA peak in the 30–800 °C range and brucite, which may be regularly interstratified within the 10 Å phase (Sclar et al., 1987), is present in amounts too small to give a perceptible dehydration peak. The sample is a fine, pale gray powder in which the largest crystallites are probably smaller than 5 μm (Bauer and Sclar, 1981). The Debye-Scherrer X-ray powder patterns show fairly broad lines possibly caused by particle size variations or poor crystallinity. Preferred orientation effects were common.

Experimental procedure

Samples weighing 16–20 mg and containing 20 wt% quartz (St. Peter sandstone ground to 200 mesh) were used in all experiments. At low pressures, experiments were made in open capsules because the large molar volume of H_2O results in the failure of closed capsules. In most experiments made with open capsules, approximately 10 wt% water was added in an attempt to maintain $P_{H_2O} = P_{total}$. Water was pipetted into the capsule before the sample was introduced. The sample was packed carefully to insure uniform sample density and the remaining space in the capsules was filled with silica wool. Closed-capsule experiments at low pressures were made without water added to avoid capsule failure, but in several experiments at higher pressures water was added to insure that $P_{H_2O} = P_{total}$. After loading the capsules, they were welded shut and checked for leaks. The closed capsules were weighed before and after the experiment. Approximately 70% of the closed capsule experiments showed a weight loss of >1% of the sample weight, indicating capsule failure. Data from these experiments provided minimum temperatures of dehydration, because they represent experiments with $P_{H_2O} < P_{total}$. Experimental products were analyzed by the Debye-Scherrer powder X-ray method.

RESULTS AND DISCUSSION

Results of the HP-DTA experiments for the 10 Å phase are listed in Table 1; successful closed capsule experiments, i.e., experiments that lost <1% of their sample weight, are indicated. DTA curves for open capsule experiments are shown in Figure 1. The curves of experiments at pressures below 10 bar show broad peaks compared with those at higher pressures. The breadth of these peaks is attributed to an increase in pressure in the apparatus during the experiment because of the increasing temperature and to the increase of P_{H_2O} in the capsule because of the release of H_2O by the dehydration reaction, which raises the dehydration temperature. As a result, the dehydration occurs over a pressure range and the peak may broaden. At higher pressures, the dehydration temperature is less sensitive to variations in pressure and the dehydration peaks are sharper. The peaks in experi-

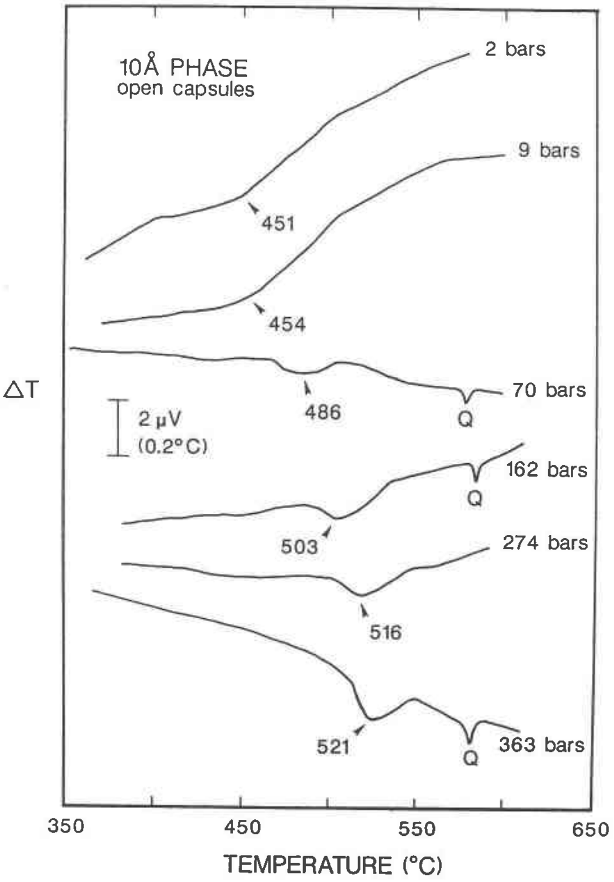

Fig. 1. High-pressure differential thermal analysis curves of the dehydration reaction of the 10 Å phase in open capsule experiments. Arrows indicate the peak temperatures. Q = low quartz–high quartz transition.

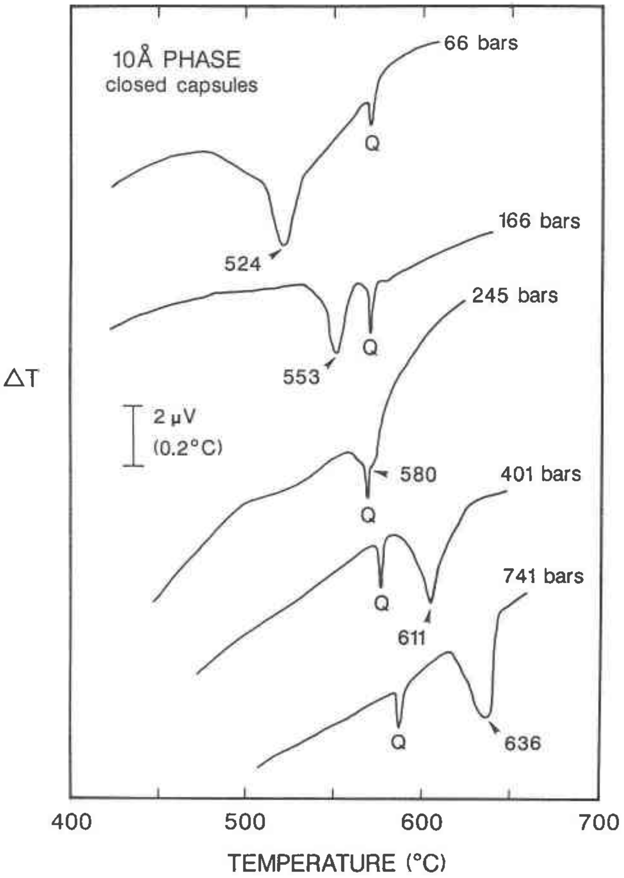

Fig. 2. High-pressure differential thermal analysis curves of the dehydration reaction of the 10 Å phase in closed capsule experiments. Arrows indicate the peak temperatures. Q = low quartz–high quartz transition.

ments with closed capsules are much sharper than those in experiments with open capsules (Fig. 2), confirming the effect of P_{H_2O} on the reaction temperature.

The P-T relations of the dehydration reaction are shown in Figure 3; the boiling curve of water is given for comparison. Note that peak temperatures (maximum deviation from the base line) of most of the failed closed capsule experiments fall between these two curves. Hence, the closed capsule data define the upper temperature limit of the dehydration reaction where $P_{H_2O} = P_{total}$. In the experiment at 1 bar the volume of water released during the experiment is probably sufficiently high to flush out the Ar gas pressure medium and $P_{H_2O} = P_{total}$. Therefore, the result of this experiment is considered compatible with the closed capsule data.

As noted by Bauer and Sclar (1981), the dehydration temperature of the interlayer "water" in the 10 Å phase is remarkably high when compared with the dehydration of most other hydrated layer silicates. Also unusual is that the dehydration reaction can be observed well above the critical point of water. This suggests that the interlayer "water" is relatively strongly bonded in the structure.

From the pressure and temperature data, the enthalpy of dehydration ΔH_{dh} for the 10 Å phase was determined, using the Clausius-Clapeyron equation, $d \ln P/dT = \Delta H_{dh}/RT^2$ and assuming that the fugacity coefficient $\Gamma_{H_2O} = 1$ and that the heat capacity ΔC_p of the participating solid phases is 0 (e.g., Anderson, 1977). It should be noted that the Clausius-Clapeyron equation can only be applied to stable and metastable equilibrium reactions. Considering that the 10 Å phase is not stable at the pressure range of this study, the dehydration observed in this study either represents a metastable equilibrium reaction or a kinetically controlled event. However, it is unlikely that at the high temperatures found for the dehydration reaction, small differences in pressure can delay a kinetically controlled reaction substantially. Equally important is the large difference between the reaction temperatures of the open- and closed-capsule experiments. This difference argues strongly against the possibility that the reaction is kinetically controlled and favors the conclusion that the f_{H_2O} is the determining factor. In contrast, the strong and regular (monotonic) increase of the dehydration reaction with pressure, which is similar to the pressure depen-

TABLE 1. Pressure and temperature of the onset, peak, and termination of HP-DTA signals for the 10 Å phase

Pressure (bars)	Onset (°C)	Peak (°C)	Return (°C)
	Open capsule experiments		
2	403	454	504
9	410	454	502
30	435	452	474
70	467	486	503
162	480	503	520
274	496	516	546
363	505	521	544
	Closed capsule experiments		
66*	513	524	535
166*	534	553	563
245*	568	580	590
344	467	486	503
401*	480	603	620
427	496	516	546
466	505	521	544
475	549	563	571
547	574	582	594
603	562	585	591
632	513	535	553
741*	618	636	644
754	550	559	574
818	512	561	626
5157*	621	632	662

* Successful closed capsule experiments.

dence of stable and metastable dehydration and dehydroxylation reactions as observed in clay minerals (Koster van Groos and Guggenheim, 1987, 1989), indicates that the 10 Å phase dehydration represents a metastable equilibrium reaction.

Peak temperatures from closed capsule experiments and the 1 bar experiment (Table 1) are shown in a ln P − $1000/T$ diagram (Fig. 4). The first order regression of the data shows a high correlation ($r = 0.96$), which is further evidence that the dehydration represents a metastable equilibrium reaction. Using these data, a value of $\Delta H_{dh} = 200 \pm 20$ kJ/mol was obtained (the error is due mainly to the uncertainty in the actual P_{H_2O} of the experiment at approximately 1 bar). In these calculations the experiment at 5.12 kbar was not used, because at these high pressures the volume change in the solid phase assemblage cannot be ignored. This value is comparable although somewhat higher than the enthalpy of dehydroxylation of hydroxyl groups at the interlayer surface of 1:1 layers; e.g., 170 kJ/mol for halloysite and 160 kJ/mol for kaolinite (Weber and Roy, 1965), and substantially higher than the enthalpy of dehydration associated with interlayer water of montmorillonite, which shows a maximum of 31 kJ/mol for the inner hydration shell around Mg in a Mg-exchanged montmorillonite (Koster van Groos and Guggenheim, 1987). In contrast to the 10 Å phase, however, the interlayer water in montmorillonite is held primarily by its attraction to the interlayer cation; such a cation does not exist in the 10 Å phase.

The metastable reaction for dehydration of the 10 Å phase is shown in Figure 5 along with the high pressure reaction, 10 Å phase = talc + fluid, as determined by Bauer and Sclar (1979) and Yamamoto and Akimoto (1977). The mismatch of our data and the reaction given by Bauer and Sclar is very large and cannot be reconciled. However, the reaction was not reversed in their high pressure study and, therefore, the P-T conditions are not well defined. Yamamoto and Akimoto (1977) determined that the high-temperature stability of the 10 Å phase is bound by two reactions, 10 Å = talc + fluid at pressures below approximately 60 kbar, and 10 Å = orthoenstatite + coesite + fluid at higher pressures. Considering the temperature and pressure uncertainty of the experiments, ±50 °C and ±2 kbar, and that these experiments were generally made at 100 °C intervals, the slope of the reactions is not yet well defined (see Fig. 4). Liu (1986) concluded on the basis of a series of high pressure experiments on serpentine, that the temperatures may be slightly higher and that these reactions may be less temperature sensitive. Thus, it is likely that the slope of the first reaction is steeper with respect to pressure than shown by Yamamoto and Akimoto, and that the dehydration reaction as determined in our study is its metastable extension. The reaction limiting the stability of the 10 Å phase at some lower pressure is most likely 10 Å = serpentine + quartz/coesite [$Mg_3Si_4O_{10}(OH)_2 \cdot H_2O = Mg_3Si_2O_5(OH)_4 + 2(SiO_2)$]. The zero-pressure volume increase for this reaction is approximately 3% when quartz is produced and approximately 0.2% if coesite is pro-

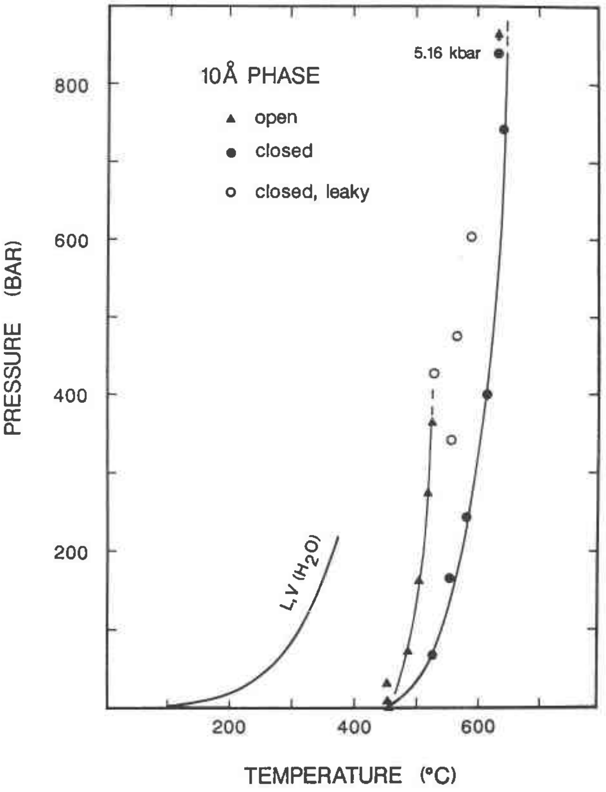

Fig. 3. P-T diagram for the dehydration reaction of the 10 Å phase. The boiling curve of water (derived from Keenan et al., 1978) is shown for comparison.

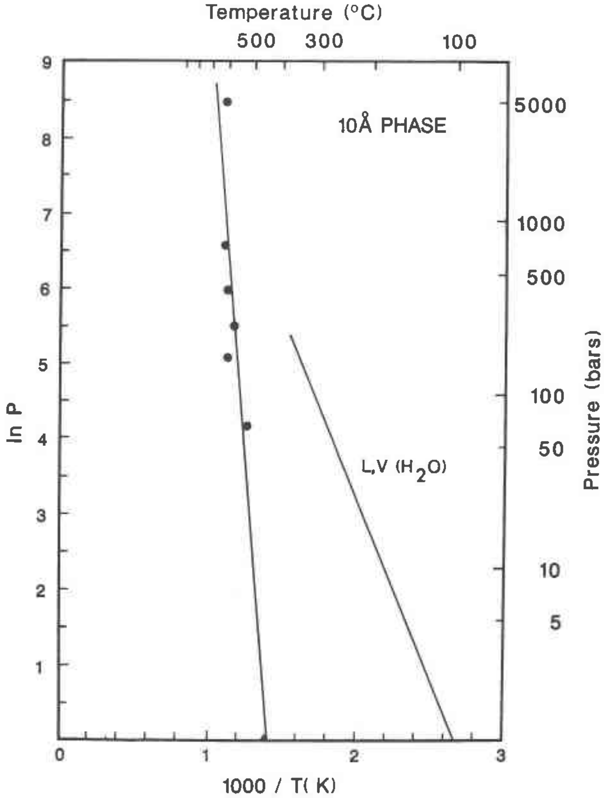

Fig. 4. Diagram of ln $P - 1/T$ for closed capsule experiments for the 10 Å phase. The boiling curve of water is shown for comparison.

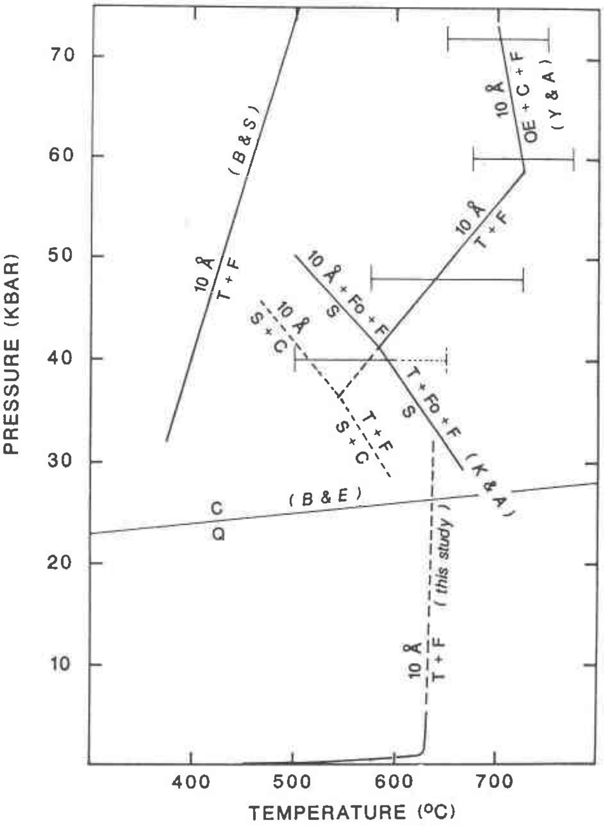

Fig. 5. *P-T* diagram of the stable and metastable reactions of the 10 Å phase. In addition, reactions involving serpentine, serpentine + coesite, and low quartz are shown. The error bars shown for the reactions 10 Å = OE + C + F and 10 Å = T + F are derived from Yamamoto and Akimoto (1977). The reactions shown with dashed lines are inferred, see text. Abbreviations: C = coesite; F = fluid; OE = orthoenstatite; Q = low quartz; S = serpentine; T = talc; B & E = Boyd and England, 1965; B & S = Bauer and Sclar, 1979; K & A = Khodyrev and Agoshkov, 1986; Y & A = Yamamoto and Akimoto, 1977.

duced, using the 10 Å unit-cell volume (Bauer and Sclar, 1981), the theoretical unit-cell volume of magnesium lizardite (Bailey, 1969), and the unit-cell volume of low quartz and coesite (Clark, 1966). Although the compressibility of the hydrated phases is not well known, the small volume change suggests that these reactions are not sensitive to pressure. The *P-T* conditions of this reaction are not known, although the stability of serpentine itself is limited at high pressures by the reaction serpentine = 10 Å + forsterite + fluid and serpentine = talc + forsterite + fluid (Khodyrev and Agoshkov, 1986). It is evident that more work is necessary to delineate the stability field of the 10 Å phase. However, the results of this study suggest that the stability of the 10 Å phase is probably limited to temperatures less than 700 °C. This is in agreement with the high-pressure experiments of Bauer and Sclar (1981) and Yamamoto and Akimoto (1977).

APPLICATIONS

Crystal chemical applications

Preliminary Rietveld refinement results of Bish, Guggenheim, and Joswig (unpublished data) indicate that the structure of the 10 Å phase is similar to a mica with *1M* stacking, as assumed by Bauer and Sclar (1981). In contrast, talc has adjacent 2:1 layers offset laterally across the interlayer. Mica stacking allows the formation of six- or 12-coordinated interlayer sites between adjacent silicate rings. This suggests that the "water" resides within the hexagonal rings in analogy to the interlayer cation in a mica structure. This interpretation is consistent with the transformation of the 10 Å phase to talc at high temperatures and with the assumption made previously by Bauer and Sclar (1981) that the "water" resides in 12-coordinated sites.

The high ΔH_{dh} value for the 10 Å phase implies that "water" does not reside in the interlayer site as a discrete molecule. Instead, considerable interaction with its neighbors is necessary to achieve the high bond energies as determined in this study. Such interactions probably include H resonance between basal O atoms and the O located in the interlayer site. If protons are sufficiently mobile, several exchanges may occur which allow the momentary formation of OH, H_2O, and H_3O^+. Such a complex H configuration is consistent with the ambiguous nature of the infrared data of Bauer and Sclar (1981) with regard to the nature of the interlayer species. Furthermore, unlike a model involving discrete molecules, this model is consistent with the thermogravimetric data (Bauer and Sclar, 1981; Evans and Guggenheim, 1988) and the data presented here, which show essentially a single interlayer "water"-loss event. This interpretation is also more satisfying in that isomorphous K-bearing analogues could not be prepared (Bauer and Sclar, 1979), which may be the result of the 2:1 layer of the 10 Å phase not having a residual charge, in contrast to the -1 charge of true micas which require a univalent interlayer cation. The 10 Å phase, therefore, does not require a charged interlayer cation (or discrete molecule) located in the interlayer site. Because it is unclear whether the *2/m* site symmetry of the interlayer site of the *1M* structure is maintained, it is difficult to constrain the H configuration further.

The nature of the interlayer species in 2:1 layer silicates is an important parameter to consider in developing solution and activity models. For example, substitution site models of the type $(K^+,Na^+) = H_3O^+$, which involve the interlayer site only, produce different results from models that balance substitutions between the interlayer and octahedral sites. The possible incorporation of vacancies in either model involves further complications.

The 10 Å phase may be considered an approximate analogue structure to the micas, although this conclusion should be considered tentative without additional structural data. Because the nature of the interlayer material remains imperfectly characterized, the data presented here do not directly support a unique interlayer substitution for micas. It is, therefore, possible that H_2O, H_3O^+, or more strongly bound water (i.e., the H-resonance model) may be appropriate in thermodynamic formulations. In this context, progressive dehydration upon heating as observed commonly in thermal analysis studies of micas and, presumably, in metamorphic reactions, may reflect various interlayer forms.

Geological applications

The presence of H_2O in the mantle is unequivocal. More to the point are questions concerning the quantity present, and where and how it is stored. The results of this study contribute to the evaluation of the storage mechanism. In most of the water-bearing phases that are thought to be present in the mantle, e.g., brucite, phlogopite, serpentine, minerals of the humite group, as well as a series of phases not yet found in nature, such as phase A, phase B, and the 10 Å phase (Yamamoto and Akimoto, 1977; Benimoff and Sclar, 1984, 1985; Khodyrev and Agoshkon, 1986; Ahrens, 1989; Finger and Prewitt, 1989), water appears to be stored as OH. In the 10 Å phase, however, additional water may be incorporated in 12-coordinated sites as O ions, charge balanced by two resonating protons. Such a storage mechanism suggests that water may be stored in the earth's mantle in minerals that incorporate additional O ions within the structure and charge balance these ions with moderately mobile protons. The consequence of this mechanism is fundamentally different than that proposed by Bauer and Sclar (1981) involving H_3O^+ because, in that model, the H_3O^+ present in the 12-coordinated site requires OH interaction. Such interaction is not a prerequisite in the proton resonance model proposed here.

In this study, the concept of the incorporation of O stabilized by resonant protons was limited to the fixation of "water" in the 10 Å phase. However, this concept has a universal application in that a variety of minerals may be amenable to incorporating H and O in their structures. This indicates a need for the careful evaluation of other high-pressure mineral phases which have structural imperfections suggesting a propensity for excess "water."

ACKNOWLEDGMENTS

We thank A. Begley, A.I. Benimoff, and C.B. Sclar (Lehigh University, Bethlehem, Pennsylvania), for synthesizing and providing the starting material. This work was supported in part by the Petroleum Research Fund of the American Chemical Society under grants 17263-AC2, 21974-AC8-C, and 20016-AC2, and by the National Science Foundation under grants EAR-8704681 and EAR-8816898. In addition, we thank J.F. Bauer (Johns Manville, Denver), D.L. Bish (Los Alamos National Laboratory), and C.B. Sclar for helpful reviews of this paper.

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Manuscript received March 21, 1990
Manuscript accepted November 10, 1990