In Situ Observation of the Formation of 10 Å Phase from Talc + H_2O at Mantle Pressures and Temperatures

Nicholas J. Chinnery,[1]* Alison R. Pawley,[1]† Simon M. Clark[2]

Development of an x-ray–transparent capsule that is suitable for water-saturated experiments has allowed the high-pressure and high-temperature synthesis of 10 angstrom phase from talc + H_2O to be observed in situ in a multianvil apparatus with synchrotron radiation. The reaction talc + H_2O = 10 angstrom phase was observed within 20 minutes at 6 gigapascals and 500°C. The higher pressure vapor-absent reaction talc = 10 angstrom phase + enstatite + coesite was also observed. The 10 angstrom phase is therefore a good candidate for transporting water into Earth's mantle at subduction zones. The in situ technique may allow the hydration of other high-pressure mantle phases to be observed under dynamic conditions.

Dense hydrous magnesium silicates (DHMSs) are high-pressure hydrous phases that have been proposed as storage sites for H_2O in the mantle (*1*, *2*). They may form in subduction zones, where hydrothermally altered oceanic crust is recycled into the mantle and where dehydration reactions release the H_2O that is critical for the arc volcanism associated with subduction zones (*3*). Determining the stability of hydrous phases in subduction zones is therefore important for understanding the volcanic processes and for deducing the extent and history of H_2O storage and recycling in the upper mantle. Ten angstrom phase, $Mg_3Si_4O_{10}(OH)_2{\cdot}xH_2O$, is a DHMS formed by the reaction of talc with H_2O at pressures more than $\sim$5 GPa (*4*). Talc, $Mg_3Si_4O_{10}(OH)_2$, commonly occurs in hydrothermally altered ultramafic rock, where its formation is favored by metasomatism. It could therefore be present in subducting oceanic crust, which often contains a sizable component of hydrothermally altered ultramafic peridotite (*5*). It could also crystallize in mantle-wedge peridotite metasomatized by silica-rich fluids released from subducting slabs (*6*). After the high-pressure breakdown of talc, 10 Å phase could form (*4*), assuming that it is stable. However, its stability, as with the proposed stability of any DHMS in the mantle, depends on the results of experiments, because none of these phases have been found in nature. Most of the experiments to date have relied on the assumption that the sample recovered after quenching from high pressure and high temperature has not changed much, and this assumption may not be valid. For this reason, there has been some debate about whether 10 Å phase is a thermodynamically stable phase that can exist in the mantle or is an artifact of quenching experiments (*7*). The technique of synchrotron radiation has for several years allowed in situ high-pressure and high-temperature observations, which enable the stability of high-pressure phases to be determined directly. Until now, however, it has not been possible to apply this technique to encapsulated, fluid-saturated samples. Here, we report the development of a capsule that is suitable for H_2O-saturated synchrotron experiments and its use in synthesizing 10 Å phase from talc + H_2O.

The experiments were carried out on the energy-dispersive station 16.4 of the synchrotron radiation source at Daresbury Laboratory (*8*). A large-volume multianvil cell of the Walker design was used (*9*). In quench experiments with such an apparatus, samples may or may not be encapsulated. Capsules are unnecessary for investigating vapor-absent reactions, and reasonable positions of dehydration reactions may be obtained without encapsulation; but, for reactions that require excess H_2O (for example, the reaction talc + H_2O = 10 Å phase), encapsulation is required if a H_2O activity of 1 is to be maintained. In quench experiments, samples are typically contained in sealed noble metal capsules (for example, Au or Pt). However, these metals are unsuitable for synchrotron experiments because of their high x-ray absorbance. Previous synchrotron studies have therefore not used capsules, and although reactions involving H_2O have been investigated (*10*), these have been dehydration reactions. We used Ti for our capsules (Fig. 1), which has a much lower x-ray absorbance than Au and Pt but has the disadvantage of being difficult to weld shut. We overcame this problem by using Pt lids, which alloy with the Ti on pressurizing and heating (*11*). Titanium is highly reactive, but an oxidized layer between it and the sample limits reaction, and the relatively low temperatures of these experiments also prevented a sizable reaction (*12*). The pressure inside the capsule was calculated from the position of the talc (002) peak in the x-ray diffraction patterns (*13*, *14*).

Previous quench experiments on 10 Å phase have produced samples with structures similar to talc, as shown by powder x-ray diffraction (*2*, *7*, *15*). Talc is a sheet silicate with a basal spacing of 9.4 Å, which increases to $\sim$10 Å in 10 Å phase. The strongest peak in the diffraction patterns of both phases is the basal spacing peak [(001) or (002)] (*16*). Therefore, for the synchrotron experiments, a detector angle 2θ was chosen to maximize the intensity of these peaks. The strongest intensity of the peaks occurs for energies of $\sim$50 keV, and so a small detector angle was required to maximize the intensity of reflections corresponding to *d* spacings of 9 to 10 Å (*17*). A detector angle of

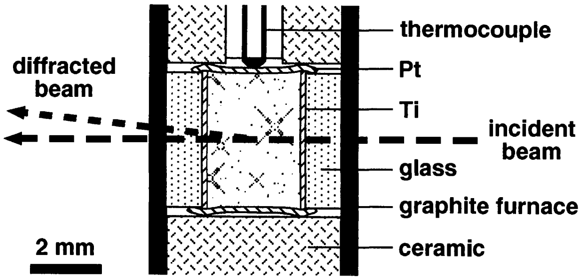

Fig. 1. Part of the sample assembly used for in situ H_2O-saturated experiments. About 25 to 30 mg of talc is pressed into the cylindrical Ti capsule (3-mm outer diameter, 0.1-mm wall thickness, $\sim$3-mm length), and 1 to 2 mg of H_2O is added. Discs of Pt foil of slightly larger diameter than the tubing are placed on either end. The capsule is surrounded by a glass sleeve, which, being amorphous, does not contribute any peaks to the x-ray diffraction pattern. The graphite furnace is 12 mm long and is contained in a hole drilled in the ceramic octahedral pressure medium. The tip of the Pt/Pt10Rh thermocouple is in direct contact with the Pt lid of the capsule. The x-ray beam passes through the central hottest part of the assembly. The thermal gradient, estimated in separate experiments with two thermocouples (*13*), is no more than 20°C over the 2-mm length between the center and the ends of the capsule. The diffracted beam is defined by collimating slits on the front of the detector, and the beam samples a volume that is $\sim$0.5 mm wide and 5 mm long.

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~1.6° 2θ was used in this study. Unfortunately, this precluded any other diffraction peaks from being visible in the diffraction patterns.

We performed three experiments to attempt to synthesize 10 Å phase from natural talc (*18*) + H_2O (Fig. 2). In the first experiment (10Å-1), we pressurized the sample to 6.3 GPa at room temperature and then slowly heated it, viewing the talc (002) peak continuously. Diffraction patterns were collected at room temperature and at 250°C (Fig. 3). At 470°C, a diffraction peak began to form at a lower energy than that of the talc peak, corresponding to an increase of 0.6 Å in the basal spacing. At 500°C, the growth of the new peak accelerated, and the talc peak shrank at the same rate, indicating that the new peak was indeed 10 Å phase forming at the expense of talc in the reaction talc + H_2O = 10 Å phase. The reaction went to completion in about 20 min (Fig. 3). An attempt to lower the pressure to reverse the reaction resulted in a blowout (a catastrophic pressure release). X-ray diffraction of the recovered sample showed it to be amorphous.

The aim of the second experiment (10Å-2) was to synthesize 10 Å phase in the same reaction but at a lower pressure, so that the reaction could then be reversed by increasing the temperature. The sample was pressurized at 500°C, and we expected that 10 Å phase would form as soon as the reaction boundary was crossed (Fig. 2). However, it became evident that there was no excess H_2O in the capsule, and this run was only able to produce 10 Å phase after it crossed the higher pressure vapor-absent reaction talc = 10 Å phase + enstatite + coesite and was heated to increase the reaction rate. Evidence that this reaction was occurring came from the fact that the rate at which the 10 Å phase peak grew was much slower than the rate at which the talc peak shrank (Fig. 3). This run was eventually heated until talc and then 10 Å phase disappeared, at 750° and 800°C, respectively. X-ray diffraction of the quenched run product revealed that it consisted of enstatite + coesite, the expected dehydration products of talc and 10 Å phase.

In the third experiment (10Å-3), the sample was heated and pressurized from room temperature at 4.1 GPa to 550°C at 5.0 GPa, where 10 Å phase started to form from talc + H_2O (Fig. 3). The reaction was, however, much slower than that in 10Å-1, perhaps because these lower pressure conditions were still within the vapor-absent talc stability field (Fig. 2). After some 10 Å phase had formed, the sample was heated to reverse the reaction. This occurred at 700°C, where the talc:10 Å phase peak intensity ratio increased, until 10 Å phase eventually disappeared. Cooling the sample then brought it back into the 10 Å phase stability field, after which it was heated and dehydrated in the same way that 10Å-2 was.

Our results demonstrate that 10 Å phase can be produced from talc in the reaction talc + H_2O = 10 Å phase, under vapor-saturated conditions (10Å-1 and 10Å-3), and in the reaction talc = 10 Å phase + enstatite + coesite, under vapor-absent conditions (10Å-2). These results contrast with the previously drawn conclusions (*7*) that 10 Å phase requires a considerable amount of H_2O for its synthesis (>30 weight %) and is metastable (*19*). The conclusion that 10 Å phase is metastable up to pressures of at least 7 GPa was later modified to allow for a lower pressure stability field, but only at temperatures of more than ~600°C (*20*). Considering that in our in situ experiments, 10 Å phase was consistently produced at pressures below 7 GPa and temperatures below 600°C, the conclusions drawn from the previous quench experiments must be incorrect. The reason for the apparent metastability of the 10 Å phase in those experiments is unclear, but the advantages of in situ experiments for investigating the stability of high-pressure and high-temperature phases are evident.

Our results also help to explain previous disagreements about the structure and H_2O con-

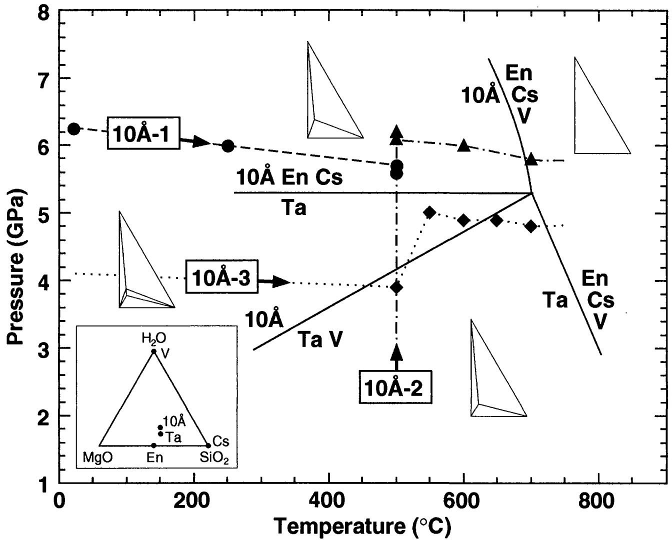

Fig. 2. The pressure and temperature paths followed by the three in situ experiments, indicating the conditions at which the diffraction patterns were collected, are shown as follows: dashed line with circles, 10Å-1; dashed-dotted line with triangles, 10Å-2; and dotted line with diamonds, 10Å-3. The final stages of experiments 10Å-2 and 10Å-3 are omitted for clarity. Also shown (solid lines) are the positions of 10 Å phase and talc reactions determined in quench experiments (*13*) and compatibility triangles representing the stable assemblages between reactions (the phases are shown in the inset). The reaction positions are not coincident with those suggested by the in situ experiments, in which reaction close to equilibrium boundaries was not always apparent, because of to the short run durations. Run durations were kept short because the purpose of the study was not to bracket reactions, but rather to demonstrate the feasibility of the technique and stability of 10 Å phase. 10Å, 10 Å phase; Cs, coesite; En, enstatite; Ta, talc; V, vapor.

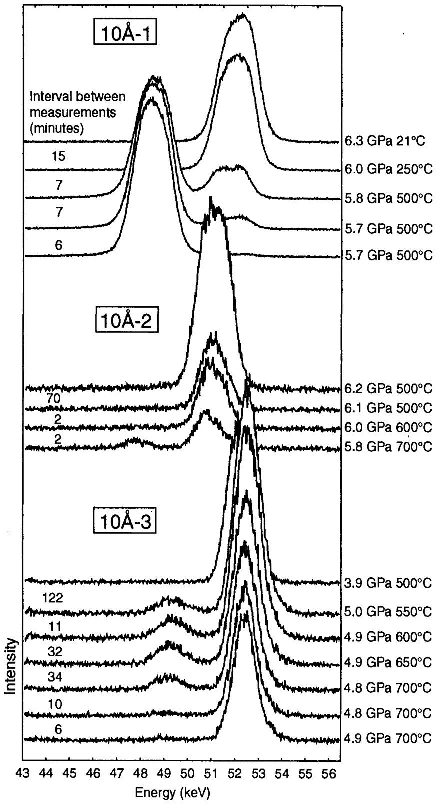

Fig. 3. Diffraction patterns collected for the three 10 Å phase synthesis experiments at the pressure and temperature conditions shown in Fig. 2. These conditions are shown at the right side of each pattern. Also shown are the approximate intervals between the start of the collection times for each diffraction pattern (left side). The peak on the right-hand side of each pattern is the (002) basal spacing talc reflection, and the peak on the left-hand side is the equivalent (001) basal spacing 10 Å phase reflection. Most diffraction patterns in each experiment were collected for the same length of time [5 min for 10Å-1 and all but the first pattern in 10Å-3, and 1 min for 10Å-2], but beam decay resulted in a decrease in peak intensity with time. The peak positions vary between experiments, because of small changes in detector angle. The detector angles (2θ) were 1.569°, 1.595°, and 1.534° for experiments 10Å-1, 10Å-2, and 10Å-3, respectively. We assume that the non-Gaussian peak shapes, sometimes giving the appearance of doublets, are artifacts of the detector electronics, as talc x-ray diffraction patterns collected with a different detector showed characteristically sharp reflections.

tent of 10 Å phase. In an earlier investigation (*2*), the composition was assumed to be $Mg_3Si_4O_{10}(OH)_2{\cdot}2H_2O$, but no direct compositional measurement was made. The Mg:Si ratio was later confirmed to be the same as in talc (*14*), but thermogravimetric analysis suggested a composition that was less rich in H_2O than previously suggested, $Mg_3Si_4O_{10}(OH)_2{\cdot}H_2O$. It was proposed that H_2O molecules occupied 12-fold coordinated interlayer sites between opposing tetrahedral layers in the talc structure and that the structure is stabilized through the interaction of each H_2O molecule with an octahedral-layer OH group to form H_3O^+ and O^{2-}. A subsequent study (*21*) argued against the necessity of neighboring OH groups to stabilize the interlayer H_2O and suggested that proton resonance between the interlayer O atoms and basal O atoms in the tetrahedral layers gives rise momentarily to OH^-, H_2O, H_3O^+, or a combination of these species. More recent weight-loss experiments (*7*) implied a composition that was even less rich in H_2O for 10 Å phase, $Mg_3Si_4O_{10}(OH)_2{\cdot}0.65H_2O$. Our thermogravimetric analysis has yielded the same H_2O content, $x = 0.65$ (*13*). These differences in previous values of measured H_2O content are accompanied by differences in measured position of the basal spacing diffraction peak, suggesting variable H_2O content depending on the pressure and temperature conditions of the synthesis or on the composition of the starting material. One feature that characterizes all previous studies is a broad basal spacing peak, in contrast to the sharpness of the talc peak. However, our in situ experiments, particularly 10Å-1, showed that, at high pressure and temperature, the 10 Å phase peak is identical in appearance to the talc peak (Fig. 3). It neither shows broadening, nor does it vary in position. Therefore, the variations seen in previous studies may be produced on quenching the sample, which might result in extra H_2O being incorporated in the interlayers, causing variable basal spacing. Our results therefore suggest that, within its stability field, 10 Å phase has a fixed structure. The difference in volume between talc and 10 Å phase is less than what would be expected if 10 Å phase contained two or three times as much H_2O as talc (*22*); instead, the difference is consistent with the composition $Mg_3Si_4O_{10}(OH)_2{\cdot}0.65H_2O$. The closeness of the extra $0.65H_2O$ to the value of two-thirds suggests a structural control on the interlayer H_2O content, filling two-thirds of the 12-fold coordinated interlayer sites.

Our results show that 10 Å phase could carry H_2O into the mantle in talc-bearing rocks in subduction zones beyond the depth at which talc breaks down. Our results are also important because the 10 Å phase problem is a tractable one whose conclusions may be applied to other, less accessible systems. We have shown that high-pressure and high-temperature hydration reactions can be observed in situ under dynamic conditions. This allows for the possibility of observing hydration reactions of other high-pressure mantle phases, perhaps revealing the stability of new phases, and also of observing reaction mechanisms and structural and volume relations between reactants and their hydrated products.

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11. In a study by Ayers *et al.* [J. C. Ayers *et al.*, *Am. Mineral.* **77**, 1080 (1992)] and in ours, a watertight seal was formed when the sample was pressurized at low temperature during the experiment, and then the Pt alloyed with the Ti on heating. Leakage of some of the H_2O out of the capsule before pressurization resulted in a variable H_2O content during our experiments.
12. The Ti content of a sample run at 6.5 GPa and 700°C for 4 hours was determined by electron microprobe analysis. At a distance of 10 μm from the Ti wall, the Ti content was 0.25 weight %, and at a distance of 90 μm, it was <0.01 weight %.
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14. The volume behavior of talc at pressure and temperature conditions within the 10 Å phase stability field was measured in (*13*). The talc sample was mixed with NaCl, and diffraction patterns were collected at 4 to 6 GPa and 25° to 600°C. The pressure was determined with equation of state data for NaCl [D. L. Decker, *J. Appl. Phys.* **42**, 3239 (1971)]. Sodium chloride could not be mixed with the talc in this study because it would have dissolved in the H_2O in the capsule.
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16. The convention that the repeat length of the unit cell along the *z* crystallographic axis in 10 Å phase is half that in talc results in (001) in 10 Å phase being equivalent to (002) in talc.
17. The relation between energy *E*, *d* spacing, and detector angle θ is given by the equation $d = 6.199/(E \sin \theta)$.
18. The composition of the talc, as analyzed by electron microprobe, is $Mg_{2.93}Fe_{0.03}Al_{0.01}Na_{0.01}Si_{4.00}$.
19. Experiments at 3 to 7 GPa and 200° to 700°C (*7*) suggested that 10 Å phase should break down to talc + H_2O at these conditions.
20. The position of the reaction talc + H_2O = 10 Å phase was found to extend from 730°C at 5.3 GPa to 580°C at 7 GPa [B. Wunder and W. Schreyer, *Lithos* **41**, 213 (1997)].
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22. Quench experiments on the 10 Å phase dehydration reaction, 10 Å phase = enstatite + coesite + H_2O, have shown it to have a negative value for dP/dT (the derivative of pressure with respect to temperature) (*13*). Applying the Clausius-Clapeyron equation, $dP/dT = \Delta S/\Delta V$, and assuming that the entropy change, ΔS, for this dehydration reaction is positive, we infer that the volume change, ΔV, is negative. Using estimated volumes of 10 Å phase from (*13*) and from A. R. Pawley, S. A. T. Redfern, B. J. Wood [*Contrib. Mineral. Petrol.* **122**, 301 (1995)] and volumes of enstatite, coesite, and H_2O from T. J. B. Holland and R. Powell [*J. Metamorph. Geol.* **16**, 309 (1998)], we calculated that ΔV can only be negative if less than $\sim 1.8H_2O$ per formula unit of 10 Å phase is released in the reaction.
23. This work was supported by Natural Environment Research Council (NERC) studentship GT4/95/223/E to N.J.C. and NERC grants GR3/10308 and GR3/11181 to A.R.P. We thank M. Henderson for helpful discussions and R. Jones for technical assistance.

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Field-Effect Flow Control for Microfabricated Fluidic Networks

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The magnitude and direction of the electro-osmotic flow (EOF) inside a microfabricated fluid channel can be controlled by a perpendicular electric field of 1.5 megavolts per centimeter generated by a voltage of only 50 volts. A microdevice called a "flowFET," with functionality comparable to that of a field-effect transistor (FET) in microelectronics, has been realized. Two flowFETs integrated with a channel junction have been used to generate opposite flows inside a single EOF-pumped channel, thus illustrating the potential of the flowFET as a controlling and switching element in microfluidic networks.

Integrated microfluidic (μfluidic) devices are being used to automate the generation and analysis of chemical compounds (*1–6*). Chemical analyses on μfluidic devices can be highly automated and can reduce the consumption of reagents by several orders of magnitude (*7–9*). Miniaturized analysis systems depend on the precise control of fluids through the network. One approach is to use pressure-driven flows delivered by off-chip pressure

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