High-pressure, High-temperature Study of the Reaction of 10 Å Phase to 3.65 Å Phase

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Introduction

The 10 Å phase and 3.65 Å phase are dense hydrous magnesium silicates (DHMSs). These are phases that have been synthesized at high pressures in the system MgO-SiO_2-H_2O and proposed as storage sites for H_2O in the Earth's mantle. The 10 Å phase has been synthesized in a number of previous studies [e.g., 1-3]. It is readily formed from the reaction of talc with H_2O at pressures of more than 5 GPa and temperatures up to 700°C [2]. Its composition is similar to that of talc [$Mg_3Si_4O_{10}(OH)_2$], but it has extra H_2O [$Mg_3Si_4O_{10}(OH)_2 \cdot xH_2O$, where x is ~0.65]. The synthesis of 3.65 Å phase has been reported in only one previous study [4], at pressures above 9 GPa and temperatures below 500°C. At lower pressures, 10 Å phase was formed. The composition and structure of 3.65 Å phase have not been determined. It has been suggested [4] that 3.65 Å phase is much more H_2O-rich than 10 Å phase and, in fact, is more H_2O-rich than any other DHMS.

In preliminary quench experiments, we determined that the pressure-temperature (P-T) position of the reaction of 10 Å phase + H_2O to 3.65 Å phase occurs at pressures around 9.5 GPa and temperatures up to 500°C. We also expect 3.65 Å phase to break down at temperatures around 500°C and higher pressures, since this is the inferred breakdown temperature of 10 Å phase at its maximum pressure stability. However, none of our quench experiments produced a pure 3.65 Å phase, leading us to speculate that back-reactions may have occurred upon quenching the sample. The aim of the experiments at the APS was therefore to observe and characterize the synthesis of 3.65 Å phase *in situ.*

Methods and Materials

The experiments used the 2.5 MN large-volume press located on beamline 13-BM-D. The split-cylinder multi-anvil "T-cup" apparatus was used. Because we required the presence of excess H_2O in our experiments, some modifications to the usual sample assembly were made. Thus, instead of using a boron-epoxy capsule, we used BN, which we thought would be more water-tight yet still practical for these experiments. Thin MgO discs were used as lids to the capsule; they were cemented in place with ZrO_2 cement. We also could not have a thermocouple hole going through the capsule, which is normally done, since water would have leaked out through it. Our first experiment was therefore a calibration that used a dry sample in a BN capsule with a central thermocouple. We monitored the relationship of power consumption to temperature and used this as a calibration in subsequent experiments.

Another modification was to drill 1.25-mm holes in the pyrophyllite gaskets along the beam path and fill them with BN rod. This was done because we were using a small detector angle (~3° 2θ), which meant that the diffracting volume was >1-mm long, so considerable diffraction occurred from the pyrophyllite gaskets when the BN rod was not used.

The starting material for the experiments was a finely ground natural talc of close-to-end-member composition. This was placed in the capsule, and excess H_2O was added. In order not to lose H_2O by evaporation in the air-conditioned laboratory while capsules were being loaded and sealed, this procedure was carried out in a high-humidity glove bag containing pans of hot water. In the second experiment, we attempted to use the MgO capsule lid as a pressure standard, but we did not observe any diffraction from it. We thus concluded that it was too thin to be useful. Therefore, in experiment 3, we placed a pressed pellet of MgO in the capsule along with the talc.

A diffraction pattern of talc in the experimental apparatus is shown in Fig. 1. A low detector angle of 3° was chosen so that the (002) peak, normally talc's strongest diffraction peak, was within the usable energy
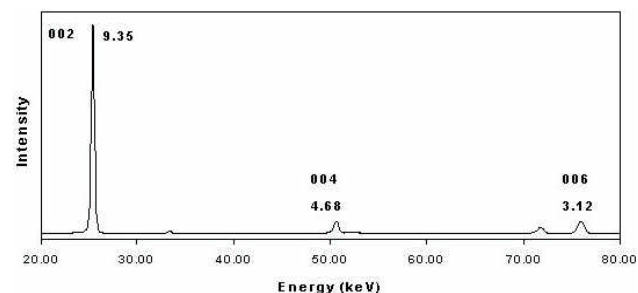

FIG. 1. Diffraction pattern of talc at ambient pressure and temperature in experiment 3.

range. This basal spacing diffraction peak corresponds to a d-spacing of 9.35 Å. On transformation to 10 Å phase, we expect this peak to disappear while a new peak appears at lower energy.

The experimental plan involved pressurizing the sample of talc + H_2O to 8-9 GPa and heating it to 500°C. This temperature is known to be sufficient to produce 10 Å phase in a matter of minutes, as previously observed in *in situ* experiments at 6.5 GPa [3]. The plan was then to increase the pressure while maintaining a constant temperature, taking the sample into a 3.65 Å phase stability field. We would then heat the sample to observe the breakdown of 3.65 Å phase.

We conducted three experiments. The P-T paths followed are shown in Table 1. Experiment 2 was not heated because of pressure uncertainties due to the insufficient pressure standard. Attempts to pressurize experiment 3 beyond 9 GPa were unsuccessful because upon heating, the pyrophyllite gaskets became too soft to sustain any increase in pressure. Experiment 3 also suffered from the lack of adequate pressure standard because the MgO was inexplicably amorphous.

Table 1. P-T paths followed in the experiments.

Experiment	Procedure
1	Pressure and temperature calibration: Pressurized to 2000 psi oil pressure (~9 GPa), heated to 800K
2	Pressurized to 2000 psi oil pressure, not heated
3	Pressurized to 2000 psi oil pressure, heated to 700K

Results and Discussion

Before producing 3.65 Å phase, our experiments required the talc + H_2O starting material to react to 10 Å phase. The results are therefore discussed in two sections: 10 Å phase synthesis and 3.65 Å phase synthesis.

10 Å Phase Synthesis

Before our experiments, we assumed that 10 Å phase would be synthesized only when the sample of talc + H_2O was heated to a few hundred °C. However, when we looked at the diffraction pattern of the sample in experiment 2 after pressurizing to an oil pressure of 2000 psi, we observed much lower energies for the (00*l*) peaks than expected, suggesting that the talc had already transformed to 10 Å phase. Because there was no reliable pressure standard in this experiment, we could not confirm the sample pressure at this oil pressure. However, 10 Å phase has a similar compressibility to that of talc [5], so pressure could be estimated from 10 Å phase

peaks. The estimated pressure was 8 GPa, only slightly less than the pressure at the same load in experiment 1.

In experiment 3, we recorded this apparent room-temperature transformation as the sample was being compressed. It occurred at an oil pressure of ~1200 psi (Fig. 2). This corresponds to a sample pressure of ~2 GPa. The phase persisted to 2000 psi and also persisted during heating to 700K. In both experiments, upon decompression, the sample transformed back to talc, with a basal spacing of 9.3 Å.

Our observation of possible 10 Å phase synthesis at ~2 GPa at room temperature is surprising, given that in the previous *in situ* experiments, heating was required before the reaction took place. However, if our sample did indeed transform to 10 Å phase, it cannot have been the same 10 Å phase as that formed in the high-temperature experiments, since those samples did not transform back to talc upon quenching. Since our experiments were not designed to investigate the talc–10 Å phase reaction, and thus data coverage was poor, we are reluctant to draw any conclusions about this reaction. The fact that the pressure standard was not usable in either experiment 2 or experiment 3 is further reason for caution in interpreting our results. There is clearly a need for more work on this reaction.

3.65 Å Phase Synthesis

Because of the inability to pressurize our sample much beyond 9 GPa while it was being held at high temperature, our aim of reaching the stability field of 3.65 Å phase was not achieved. It was evident that to attain such P-T conditions, the sample should have been pressurized cold and then heated or an alternative gasket design and/or material should have been used.
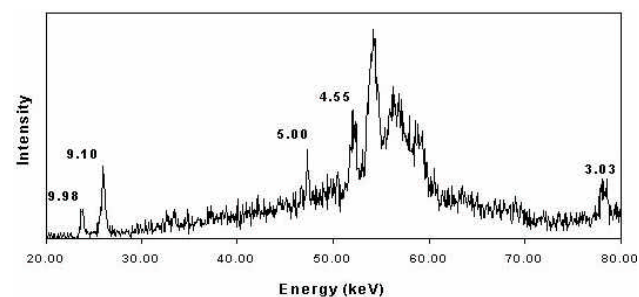
Acknowledgments

FIG. 2. *Diffraction pattern of talc and 10 Å phase at ~2 GPa in experiment 3. The diffraction pattern is of poor quality because press alignment had not been optimized when it was collected.*

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