# In situ spectroscopic study of water intercalation into talc: New features of 10 Å phase formation

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#### ABSTRACT

The synthesis of 10 Å phase via the reaction of talc plus water at 8 GPa and 500 °C was studied by in situ Raman spectroscopy using a diamond-anvil cell. The initial fast (2 h) incorporation of interlayer  $H_2O$  molecules into the talc structure is traced by gradual growth of new OH stretching bands at 3592 and 3621 cm<sup>-1</sup> and the shift of several framework bands. Further monitoring at HP-HT conditions over 7 h reveals gradual weakening of the 3592 cm<sup>-1</sup> band, which can probably be related to the onset of the formation of "long-run" 10 Å phase through the appearance of silanol groups following the model proposed by Pawley et al. (2010), influencing the interlayer hydrogen bonding.

Keywords: 10 Å phase, talc, water transport, subduction

# INTRODUCTION

The Earth's mantle is considered to be an important  $H_2O$  reservoir in the global water cycle where water can be stored either in hydrous phases or as defects in nominally anhydrous phases (Jacobsen and van der Lee 2006; Kovacs et al. 2012). However, the mechanism of water transport from outer geospheres to the mantle is still debated. In cold subduction zones hydrous phases avoid dehydration and carry water to mantle depths. The serpentinized peridotite layer that lies just below the igneous oceanic crust constitutes an  $H_2O$  reservoir in the subducted lithosphere comparative in mass to the oceanic crust (Schmidt and Poli 2014). Although serpentine dehydrates at moderate temperatures (500–700 °C), it can be a precursor for dense hydrous magnesium silicates (DHMS) that are stable at mantle conditions. There are three main scenarios for water behavior in serpentinized peridotite depending on the position of the subduction geotherm (Fig. 1).

(1) During "hot" subduction, the release of water from the slab basement is controlled by serpentine and then chlorite breakdown into anhydrous phases and hydrous fluid. These processes lead to the formation of the lower part of so-called double seismic zones (Dorbath et al. 2008).

(2) During "cold" subduction a direct transformation of serpentine into *phase A*, Mg<sub>7</sub>Si<sub>2</sub>O<sub>8</sub>(OH)<sub>6</sub> (Ringwood and Major 1967), is possible with almost no water fluid production (Schmidt and Poli 2014). The retained water can then be transferred even to the lower mantle via the sequence of DHMS *phase A*  $\rightarrow$  *phase E*  $\rightarrow$  *superhydrous phase B*  $\rightarrow$  *phase D(G)* (Ohtani et al. 2004).

(3) As the "normal" subduction geotherm lies above the intersection of serpentine and phase A stability curves (Fig. 1), during "normal" subduction serpentine decomposes before phase A can be formed. However, experimental studies have shown that the so-called *10-angstrom phase* (TAP, 10 Å phase), nominally Mg<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>:xH<sub>2</sub>O, can exist in the low-temperature "dehydration gap" between the serpentine and phase A stability curves (Fig. 1). The corresponding succession of hydrous phases *serpentine*  $\rightarrow$  *10 Å phase*  $\rightarrow$  *phase A*, where 10 Å phase acts as an intermediate water carrier, can retain about 25% of the initially subducted H<sub>2</sub>O of the serpentinized peridotite even during "normal" subduction (Schmidt and Poli 2014).

The stability field of 10 Å phase is poorly understood. The position of the 10 Å phase dehydration curve, however, is particularly important because it limits the range of subduction geotherms where H<sub>2</sub>O can be retained in a slab via *serpentine*  $\rightarrow$  10 Å phase  $\rightarrow$  phase A transformations. According to equilibrium experiments of Pawley et al. (2011), the dehydration reaction 10 Å phase  $\rightarrow$  enstatite + coesite + H<sub>2</sub>O occurs at 690 °C at pressures below 7.5 GPa. In several studies 10 Å phase was obtained at higher temperatures of 700–750 °C (Yamamoto and Akimoto 1977; Pawley and Wood 1995; Dvir et al. 2011), see Figure 1. The latter studies, however, were synthesis experiments and can therefore not be considered as equilibrium. Most significantly, nanoinclusions of 10 Å phase have been found in mantle olivine (Khisina and Wirth 2008), which strongly supports the possibility of its occurrence in nature.

The structure of 10 Å phase is very similar to that of trioctahedral mica with 2:1 tetrahedral-octahedral layers parallel to (001), the interlayer space being occupied by H<sub>2</sub>O molecules (Comodi 2005). The H<sub>2</sub>O stoichiometry of 10 Å phase is not well constrained and varies, according to different estimations, from 0.6 to 2 H<sub>2</sub>O molecules per formula unit (Sclar and Carrison 1966; Yamamoto and Akimoto 1977; Bauer and Sclar 1981; Wunder and Schreyer 1992). However, recent structural and thermodynamic studies (Comodi 2005; Pawley et al. 2010, 2011) suggest 1 H<sub>2</sub>O

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**FIGURE 1.** Stability of low-temperature hydrous phases (*Serp* = serpentine, *Chl* = chlorite) in serpentinized peridotite after Schmidt and Poli (1998). The Moho geotherms in subducting slab for Antilles, New Zealand, and Kermadec after Syracuse et al. (2010) are shown as examples of "hot," "normal," and "cold" subduction, respectively. *P-T* conditions of experiments with 10 Å phase among run products are shown as diamonds (Yamamoto and Akimoto 1977; Welch et al. 2006; syntheses from oxides/hydroxides in pure MgO-SiO<sub>2</sub>-H<sub>2</sub>O system), triangles (Ulmer and Trommsdorff 1995; Khodyrev and Agoshkov 1986; syntheses from natural serpentine), "×" (Pawley and Wood 1995; syntheses from natural talc), and "+" (Fumagalli and Poli 2005; Dvir et al. 2011; syntheses from gel with peridotite composition).

molecule per formula unit as the most probable water content.

One of the most enigmatic features of 10 Å phase is the dependence of its properties on synthesis duration, first shown by Fumagalli et al. (2001). The first interpretation assumed a gradual hydration of 10 Å phase during synthesis (Fumagalli et al. 2001) which was not confirmed by the dehydration experiments of Pawley et al. (2011). Then a model of gradual accumulation of Si vacancies in the 10 Å phase via hydrogarnet-type substitution up to the composition Mg<sub>3</sub>[(Si<sub>3.83</sub>4H<sub>0.17</sub>)O<sub>10</sub>](OH)<sub>2</sub>·H<sub>2</sub>O was proposed (Welch et al. 2006; Phillips et al. 2007; Pawley et al. 2010). In the case of synthesis of 10 Å phase via interaction of talc with H<sub>2</sub>O (e.g., Chinnery et al. 1999), this model predicts a two-stage process. First, H<sub>2</sub>O molecules enter the interlayer space of talc, expanding  $d_{001}$ . This stage was monitored in situ by Chinnery et al. (1999) by measuring energy-dispersive X-ray diffraction from the sample  $d_{001}$ , and lasts tens of minutes. Then the expanded talc structure equilibrates via accumulation of hydrogarnet-type Si vacancies. This "maturation" process lasts hours and days and results in changes in stoichiometry, H-bonding scheme, and transformation of hydrophobic talc layers into hydrophilic layers of 10 Å phase. The understanding of the "maturation" of 10 Å phase is crucial for correct comparison of "short-" and "long-run" experimental data, and for correct estimation of 10 Å phase water content, important for petrological implications.

A detailed study of the complex two-stage formation of 10 Å phase requires application of in situ techniques instead of quenching experiments widely used in previous investigations. The only in situ study of 10 Å phase formation is the experiment

of Chinnery et al. (1999), where the shift of the basal diffraction peak indicating water intercalation into talc was measured. However, this method could not reveal the details of 10 Å phase "maturation" because the latter is not associated with significant changes in  $d_{001}$ . Since the structural model of 10 Å phase proposed by Phillips et al. (2007) implies that the changes in water bonding occur during "maturation," we have used the OH-stretching Raman bands to monitor in situ the reaction and follow both steps. Here we present the results of an in situ Raman study of 10 Å phase formation via the reaction of talc with water at 8 GPa and 500 °C and subsequent quenching using the diamond-anvil cell technique. Special emphasis is placed on the behavior of water constituents and possible role of Si vacancies.

#### **EXPERIMENTAL METHODS**

The most convenient way to obtain pure 10 Å phase is the reaction "talc +  $H_2O \rightarrow 10$  Å phase" (e.g., Chinnery et al. 1999). A natural sample of talc from Shabrovskoye deposit (Central Ural) with Mg2.94Fe0.05Al0.05Si3.97O10(OH)2 stoichiometry (by X-ray fluorescence analysis) was used as a starting material; similar samples with about 1% replacement of Mg by Fe and minor alumina content were used for 10 Å phase synthesis by Chinnery et al. (1999) and Pawley et al. (1995, 2011). A Diacell µScope diamond-anvil cell (EasyLab) with gas membrane and resistive heating was used for in situ Raman spectroscopy. Raman spectra were collected on a LabRAM HR800 spectrometer (HORIBA Jobin Yvon) with 1024 pixel CCD detector using the 514.5 nm argon laser (Melles Griot). An Olympus BX41 microscope with backscattering geometry was used with SLMPlan N 50× objective (18 mm working distance, 0.35 numerical aperture). The spectral resolution was set to ~3.0 cm-1 at a Raman shift of 1300 cm-1. This resolution was achieved by using a grating with 1800 grooves/mm and equivalent 150 µm slits and pinhole. Such resolution provides the accuracy of peak position determination of about 0.5 cm<sup>-1</sup>. The position, full-width at half maximum (FWHM), and integral intensity of Raman bands were fitted using Gaussian model in the Fityk 0.9.8 program (Wojdyr 2010).

Several flakes of talc up to 100 µm in diameter were placed in a 200 µm diameter hole in an Inconel gasket pre-indented to 100 µm thickness, then filled with distilled water. Two experiments were performed. In the first (calibration) experiment a chip of SrB4O7: Sm2+ pressure calibrant (Rashchenko et al. 2013, 2015) was also placed in the cell. Then the sample was pressurized to 8 GPa and heated to 500 °C. The temperature was measured using a type K thermocouple in contact with the gasket and diamond anvil. At these conditions, the positions of the main lattice bands of talc were recorded for future reference. The second experiment was performed without pressure calibrant to avoid dissolution of SrB4O7:Sm2+ in the fluid. The talc spectrum collected previously at 8 GPa/500 °C was used as a reference to reach the same high-pressure/high-temperature (HP-HT) conditions recorded with the pressure calibrant. The progress of the reaction  $talc + H_2O \rightarrow 10$ Å phase was then monitored in situ for about 3 h. After reaction completion (see Results), the spectrum of 10 Å phase was monitored at static HP-HT conditions for about 7 h. Raman spectra were collected every 15-25 min in both lattice-mode (below 1250 cm<sup>-1</sup>) and O-H stretching (3000-3900 cm<sup>-1</sup>) regions. The resulting duration of 10 Å phase synthesis in our experiment is about 10 h, and therefore our product can be regarded as "short-run" 10 Å phase, in contrast to "long-run" phase obtained after hundreds hours of synthesis (e.g., Fumagalli et al. 2001).

The quenching of synthesized 10 Å phase was performed in the following two steps. First, the sample was cooled from 500 °C to room temperature over four hours. Then the sample pressure was gradually decreased from 8 to ~6 GPa, followed by abrupt decompression to ambient conditions due to the hysteretic behavior of the gas membrane. The decompression stage lasted about 3 h. The pressure was estimated via interpolation of the O-H stretching frequencies between 8 GPa and room-pressure points.

## RESULTS

The starting spectrum of talc collected at ambient conditions (Fig. 2; Table 1) is similar to that reported by Fumagalli et al. (2001) for talc flakes with the (001) plane perpendicular to the optical axis. The changes in the talc spectrum upon pressure and temperature increase are shown in Figure 2. Note that the

contraction of the sample hole upon pressure increase from 6 to 8 GPa slightly changed the orientation of the talc flakes, which activated the band at 181 cm<sup>-1</sup> and decreased the intensity of the other bands below 250 cm<sup>-1</sup>.

Soon after the conditions of 8 GPa and 500 °C were achieved, the 10 Å phase began to form (Fig. 3). Since the main difference between talc and 10 Å phase is the presence of interlayer water molecules in the latter, the clearest evidence of the *talc* +  $H_2O \rightarrow$ 10 Å phase reaction progress was observed in the O-H stretching region. Two bands at 3590 and 3631 cm<sup>-1</sup>, corresponding to 10 Å phase, replaced the 3681 cm<sup>-1</sup> band of talc (Fig. 3b). Because of the similarity of the lattice spectra of talc and 10 Å phase, the corresponding transformation could be observed here only from the shift of the 376 cm<sup>-1</sup> talc band to a 364 cm<sup>-1</sup> 10 Å phase band (Fig. 3). The observed changes in the band intensities below 250 cm<sup>-1</sup> are mostly related to orientation change of newly formed 10 Å phase with respect to the initial talc flakes. According to the changes in both lattice and O-H stretching region, the reaction was complete after 120 min at 8 GPa/500 °C, in agreement with optical observation: talc flakes were substituted by a fine-grained mass of 10 Å phase (Fig. 4). A discrepancy with Chinnery et al. (1999) who observed *talc* +  $H_2O \rightarrow 10$  Å *phase* transformation in 15 min can be attributed to the fact that we used large talc flakes up to 100 µm in diameter, whereas Chinnery et al. (1999) used a more fine-grained powder, which could contribute to faster kinetics.

The post-formation treatment of the newly formed 10 Å phase at 8 GPa/500 °C over 7 h shows no changes in band intensities or widths in the lattice region (Fig. 5). In contrast, a progressive broadening and slow intensity decrease was observed for



**FIGURE 2.** Raman spectra of  $talc + H_2O$  sample in the lattice-mode region collected during pressure and temperature increase from ambient conditions to 8 GPa/500 °C.



**FIGURE 3.** Raman spectra demonstrating  $talc + H_2O \rightarrow 10$  Å phase reaction process in (**a**) lattice-mode region and (**b**) O-H stretching region. Timing start corresponds to the achievement of 8 GPa/500 °C conditions.

TABLE 1. Raman bands (cm<sup>-1</sup>) of talc and 10 Å phase

Talc		10 Å phase				Band assignment
0 GPa, 25 °C	8 GPa, 500 °C	8 GPa, 500 °C	0 GPa, 25 °C	dv/dP (cm <sup>-1</sup> /GPa) at 500 °C	dv/dT (cm <sup>-1</sup> / °C) at 8 GPa	
109ª		110ª	109 <sup>a</sup>	0.17	0.000	Mg-OH
	119					5
	146					
	182ª					
195ª	228ª	229 <sup>a</sup>	188ª	4.14	0.016	Mg-OH
	242ª					
292			289			
363ª	376 <sup>a</sup>	364ª	357ª			
433	449	434	432			Si-O-Si bending
452	476		451			2
469	490	479	466			Mg-OH
		542				
676 <sup>a</sup>	702ª	700 <sup>a</sup>	676ª	2.24	0.007	Si-O-Si bending
790	811	817	785			
1017	1030	1034	1000			Si-O-Si symmetric stretching
1052	1050	1094	1058			Si-O stretching
		3590 <sup>a</sup>	3592ª	-0.49	0.004	OH stretching of interlayer H <sub>2</sub> O
		3631ª	3621ª	1.07	0.004	OH stretching of interlayer H <sub>2</sub> O
			3646			
3677ª	3681ª		3667			OH stretching of structural hydroxyl
Notes: Band as	signments are giv	ven according to	the Raman stu	idy of talc (Bosasco and Blaha	1980), the most intense band	Is are marked with <sup>a</sup>



**FIGURE 4.** The sample at 8 GPa/500 °C before (**a**) and after (**b**) *talc*  $+ H_2O \rightarrow 10 \text{ Å phase transformation.}$ 

the 3590 cm<sup>-1</sup> band in the O-H stretching region (Fig. 6). This may indicate a slow gradual process affecting the arrangement of interlayer  $H_2O$  in the newly formed 10 Å phase.

Upon cooling, a slight low-frequency shift was observed for the 700 and 229 cm<sup>-1</sup> bands in the lattice region and for both the 3590 and 3631 cm<sup>-1</sup> O-H bands (Figs. 5 and 7). Subsequent pressure decrease caused a strong low-frequency shift of the 700, 364, and 229 cm<sup>-1</sup> lattice bands, whereas the band at 110 cm<sup>-1</sup> was found to be insensitive to both temperature and pressure. In the O-H stretching region, an opposite shift was observed for the 3590 and 3631 cm<sup>-1</sup> bands, which moved to higher and lower frequencies, respectively (Table 1).

The appearance of a band near 530 cm<sup>-1</sup> during quenching (Fig. 7a) is most probably related to an orientation effect, since this band was not observed after final decompression. A broad weak band near  $3650 \text{ cm}^{-1}$ , which also appears during quenching, correlates in intensity with the band at 530 cm<sup>-1</sup>, and therefore could be due to the orientation effect. However, the persistence of this band in the ambient spectrum, where it shifts to  $3667 \text{ cm}^{-1}$ , could also indicate some rearrangement of interlayer H<sub>2</sub>O during quenching.

The spectrum of quenched 10 Å phase at ambient conditions (Fig. 7) is identical to previously reported spectra (Fumagalli et al. 2001; Comodi et al. 2006, 2007) in both the lattice and O-H stretching regions. It is important to note an appreciable difference between the lattice spectrum of quenched and "in situ" 10 Å phase (Fig. 7a), obviously caused by different orientation of the grains. It is interesting that, in contrast to the lattice spectrum, the OH stretching bands are almost insensitive to orientation (Fig. 7b). This observation agrees with previous Raman measurements performed on oriented crystals (Fumagalli et al. 2001) and agregates of non-oriented crystals (Comodi et al. 2007), showing the same OH spectrum.

The Raman bands of talc and 10 Å phase observed at ambient conditions and at 8 GPa/500 °C are listed in Table 1. The assignments for lattice bands of 10 Å phase are given by analogy with the talc spectrum, according to Rosasco and Blaha (1980).

## DISCUSSION

The IR spectroscopic study of Parry et al. (2007) demonstrated that the talc band of structural hydroxyls near 3675 cm<sup>-1</sup> remains as the main band in the spectrum of 10 Å phase as well. It is consistent with the fact that interlayer  $H_2O$  molecules in the 10 Å phase are situated far from structural hydroxyls and can



**FIGURE 5.** The behavior of selected Raman bands of the newly formed 10 Å phase in the lattice-mode (up) and O-H stretching (down) regions at formation conditions (**a**), during temperature decrease (**b**), and during final decompression (**c**).



**FIGURE 6.** Evolution of selected band widths of newly formed 10 Å phase at synthesis conditions (**a**), during temperature decrease (**b**), and during final decompression (**c**) (frequencies in legend refer to 8 GPa/500 °C conditions).

hardly affect their stretching frequency. In contrast, in the Raman spectrum of 10 Å phase this band is hardly pronounced. The latter caused an erroneous assignment of another strong Raman band at 3621 cm<sup>-1</sup> to structural hydroxyls (Fumagalli et al. (2001). We suppose that both bands which appear in the O-H stretching region of the 10 Å phase (3590 and 3631 cm<sup>-1</sup> at 8 GPa/500 °C; 3592 and 3621 cm<sup>-1</sup> at ambient conditions) are related to the O-H stretching of interlayer water molecules. The latter implies



FIGURE 7. Raman spectra of the newly formed 10 Å phase during temperature and pressure decrease (a) the lattice-mode region and (b) the O-H stretching region.

an asymmetric environment of interlayer  $H_2O$  with one proton involved into a hydrogen bond with tetrahedral layer (the lower frequency band). Another proton can be involved into a weaker hydrogen bond or remain not bonded.

The behavior of the O-H stretching bands during the experiment allows to divide the formation of the 10 Å phase into two steps. The first step is accompanied by the appearance and growth of the bands at 3590 and 3631 cm<sup>-1</sup> (at 8 GPa/500 °C) and lasts about 120 min (Fig. 3b). We interpret this step as intercalation of water molecules into the interlayer space of talc with formation of the "short synthesis" 10 Å phase (Fumagalli et al. 2001).

The next step ("maturation") of the 10 Å phase is much slower and can be observed in situ as gradual broadening and extinction of the band at 3631 cm<sup>-1</sup> (at 8 GPa/500 °C). We observed this process only for the first 10 h (Figs. 3b and 6), but, extrapolating it for a longer time, we suppose that after few hundreds of hours at 8 GPa and 500 °C the band at 3631 cm<sup>-1</sup> should completely disappear from the Raman spectrum of the 10 Å phase. The latter is consistent with previous observations, which demonstrated that (1) the "short synthesis" 10 Å phase can be synthesized in few hours, whereas its transformation into the "long synthesis" phase ("maturation") requires hundreds of hours (Fumagalli et al. 2001), and (2) the "long synthesis" 10 Å phase is characterized by the absence of the band at 3631 cm<sup>-1</sup> at 8 GPa and 500 °C (Comodi et al. 2007).

The observed extinction of the band at 3631 cm<sup>-1</sup> can be interpreted as a result of gradual reorientation of the interlayer H<sub>2</sub>O molecules. Assuming that this band is associated with H<sub>2</sub>O bonded to O-atoms of tetrahedral layer, we suppose that during "maturation" of the 10 Å phase this H-bond becomes unfavorable. The latter is consistent with the model of gradual accumulation of Si vacancies during the "maturation" of the 10 Å phase (Welch et al. 2006; Phillips et al. 2007; Pawley et al. 2010) with each vacancy compensated by four OH groups: one Mg-OH and three Si-OH silanol groups. The Si-OH groups in the tetrahedral layer are: (1) less favorable as proton acceptors than ordinary O-atoms, and (2) can serve as proton donors for interlayer H<sub>2</sub>O. Herewith, the accumulation of the silanol groups associated with Si vacancies in the tetrahedral layer should change the role of interlayer H<sub>2</sub>O from proton donors to proton acceptors, leading to the extinction of the band at 3631 cm<sup>-1</sup>. The fact that we did not observe any new bands related to the O-H stretching of silanol groups is probably caused by very intense Raman signal of water fluid present in DAC, hiding the range between 3100 and 3500 cm<sup>-1</sup>.

The proposed model agrees well with the previous observations of the "maturation" process of 10 Å phase (Fumagalli et al. 2001) and the model of Si vacancies accumulation (Pawley et al. 2010); however, several further experiments using NMR and in situ Raman and IR techniques are needed to constrain the details of 10 Å phase "maturation" and differences between "short" and "long" synthesis samples.

# IMPLICATIONS

The 10 Å phase plays a crucial role if the succession of hydrous phases *serpentine*  $\rightarrow 10$  Å *phase*  $\rightarrow$  *phase* A is considered as a mechanism of water transport to the deep mantle. However, a wide consideration of the 10 Å phase in petrological models was hampered by several disputable issues concerning its possible metastability, vague water content, and dependence of properties on the synthesis duration. Our results give a new insight into the latter issue, showing that the orientation of interlayer H<sub>2</sub>O molecules in water-intercalated talc ("short-synthesis" 10 Å phase) does change upon subsequent HP-HT treatment. The latter convincingly agrees with a model of gradual accumulation of Si vacancies during synthesis of the 10 Å phase, proposed by Pawley et al. (2010).

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