

# Synchrotron FTIR study of talc and 10-Å phase to 10 GPa

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## INTRODUCTION

Talc and 10-Å phase are potentially important H<sub>2</sub>O-bearing phases in the Earth's upper mantle. Talc, Mg<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>, is common in hydrothermally-altered and SiO<sub>2</sub>-metasomatised ultramafic rocks. It is stable to ~800°C at 3 GPa, decreasing to 700°C at 5 GPa [1]. Above ~4–5 GPa, and in the presence of excess H<sub>2</sub>O, it reacts to 10-Å phase, Mg<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>.xH<sub>2</sub>O. 10-Å phase is stable up to ~9 GPa [2]. Talc has a 2:1 layer structure, with sheets of edge-sharing octahedrally-coordinated Mg sandwiched between sheets of corner-sharing SiO<sub>4</sub> tetrahedra. Two OH groups form part of the octahedral coordination unit around each Mg, with the O-H bonds pointing towards the 6-fold rings in opposing tetrahedral sheets [perpendicular to (001)]. The 2:1 layer has monoclinic symmetry, but stacking arrangements typically reduce the symmetry to triclinic. Thus the space group is either  $C\bar{1}$  or C2/c. The structure of 10-Å phase is based on that of talc, but with the addition of H<sub>2</sub>O in the interlayer. However, both the amount of interlayer H<sub>2</sub>O, and its precise structural position, are uncertain.

The compressibility of talc and 10-Å phase have previously been measured using a powdered sample in a diamond-anvil cell with synchrotron radiation [3]. The talc data, measured up to 6 GPa, varied smoothly with pressure. The 10-Å phase data show a discontinuity at between 0.4 and 0.6 GPa, with the volume measured below this pressure being above the extrapolated curve through the higher-pressure points. However, the ambient-pressure 10-Å phase 00 $l$  diffraction peaks were broad, suggesting heterogeneity in the spacing between successive 2:1 layers (averaging ~10 Å). More recent high-pressure synchrotron XRD experiments on talc and 10-Å phase in a multi-anvil press at Daresbury Laboratory have, however, demonstrated that the peaks are as sharp as the talc peaks at high pressures and temperatures [4]. Thus it appears likely that the increased volume of 10-Å phase at ambient pressure is caused by the structural change responsible for the broadening of the diffraction peaks.

There have been several previous IR studies of talc at ambient pressure, focussing on the O-H stretching region. In pure talc there is a single sharp O-H stretching frequency of ~3677 cm<sup>-1</sup>. The high frequency of this vibration is characteristic of a strong O-H bond with little or no hydrogen bonding. There is only one band, since all OH groups are in identical environments, with 3 Mg as nearest neighbour cations in a pseudo-trigonal arrangement around the OH. Substitution of larger cations for Mg has the effect of lowering the vibrational frequency. The O-H stretching region of the spectrum of 10-Å phase is more complex than that of talc. An absorption has been observed at 3677 cm<sup>-1</sup>, as in talc, but with a lower intensity [5]. There were also three absorptions unique to 10-Å phase. They occurred at 3400 – 3440 cm<sup>-1</sup>, 3200 – 3250 cm<sup>-1</sup> and 2910 – 2930 cm<sup>-1</sup>. Two of these absorptions were assigned to vibrations involving H<sub>3</sub>O<sup>+</sup> ions, which were suggested to be formed by H<sup>+</sup> from OH groups in the octahedral layer being donated to interlayer H<sub>2</sub>O molecules. This was suggested to explain the reduced intensity of the OH group's stretching vibration. However, this interpretation was disputed in a differential thermal analysis study [6], in which the existence of interlayer O<sup>2-</sup> was proposed, stabilised by two resonating protons.

## EXPERIMENTAL

Samples used were a natural talc, with composition  $\text{Mg}_{2.93}\text{Fe}_{0.03}\text{Al}_{0.01}\text{Na}_{0.01}\text{Si}_{4.00}$ , and 10-Å phase synthesised from a mixture of  $\text{Mg}(\text{OH})_2$  and  $\text{SiO}_2$  at 6 GPa, 600 °C, 44 hours. XRD of the latter sample shows that it contains a few % talc.

The spectra were collected on the infrared beamline 1.4.3 at the Advanced Light Source, Lawrence Berkeley National Laboratory, USA, using a Nicolet 760 FTIR bench and a Spectra-Tech Nic-Plan IR microscope. The microscope allows the synchrotron beam to be focussed to a spot size of around 6 by 10 microns. A Diacell microscope diamond-anvil cell was used to generate high pressures. The gasket was made of Inconel, pre-indented to a thickness of ~60  $\mu\text{m}$ , and with a 125  $\mu\text{m}$  sample hole. KBr was used as the pressure-transmitting medium, and pressure was measured using ruby fluorescence. Finely-ground sample was placed to one side of the sample hole, with the remainder of it filled with KBr, and a few ruby chips inserted. Spectra were collected at intervals of about 1 GPa during compression to 10 GPa, and at larger intervals during decompression. At each pressure, a background transmission spectrum was collected of KBr in the most transparent region, and sample spectra were collected at different places within the sample. Spectra were also contained at ambient pressure of samples pressed in a KBr pellet and mounted in the main bench, using the internal Globar IR source.

## RESULTS AND DISCUSSION

The 1-atmosphere spectrum of talc shows a strong vibration at 3677  $\text{cm}^{-1}$ , and a weak one at 3660  $\text{cm}^{-1}$ . These are interpreted as being due to O-H stretching of OH bonded to 3 Mg and 2 Mg + 1 Fe, respectively. The relative intensities of the two peaks are broadly consistent with 1 % of the octahedral sites being occupied by  $\text{Fe}^{2+}$ . Both stretching bands show linear shifts to higher frequencies on compression, the former at a rate of ~1.0  $\text{cm}^{-1}\text{GPa}^{-1}$  and the latter at a rate of ~0.6  $\text{cm}^{-1}\text{GPa}^{-1}$ . The decompression path followed the compressional path. The increase in frequency of the O-H stretching vibration with increasing pressure indicates that repulsion of the H by the cations in the adjacent tetrahedral layer increases as the structure is compressed. That this happens at a slower rate for the 3660  $\text{cm}^{-1}$  band than the 3677  $\text{cm}^{-1}$  band suggests that compression is less where a larger cation ( $\text{Fe}^{2+}$ ) occupies an octahedral site.

The 1-atmosphere spectrum of 10-Å phase shows a strong vibration at 3674  $\text{cm}^{-1}$ , which is assumed to be due to stretching of O-H in the same environment as in talc. The intensity of this band relative to the intensity of vibrations of the rest of the structure is similar to that in the talc spectrum, suggesting a similar concentration of talc-like OH in 10-Å phase. This observation disagrees with that of Bauer and Sclar (1981). As well as the talc-like O-H stretching band, there are prominent, but broad, bands at 3589 and 3246  $\text{cm}^{-1}$ , plus some less easily resolved bands between the other three. The talc band again shows an overall increase in frequency with pressure, with an average rate of ~0.9  $\text{cm}^{-1}\text{GPa}^{-1}$ . However, this time the behaviour is not smooth. Between 0 and 0.7 GPa the frequency decreases by ~0.4  $\text{cm}^{-1}$ , and between ~3.6 and 4.4 GPa the frequency increases by ~1  $\text{cm}^{-1}$  more than expected, and then by 4.6 GPa returns to a linear trend. On decompression, the frequency increases between 4.8 and 3.8 GPa, and at 1 GPa is above that observed during compression. On final pressure release, the frequency is the same as in the ambient spectrum of 10-Å phase pressed in a KBr pellet.

The first discontinuity in 10-Å phase's vibrational behaviour with pressure occurs at a similar pressure to that previously observed in its volume behaviour using XRD. However, in the latter case, the slope of volume change with pressure is negative on both sides of the discontinuity; here there is a reversal. Thus it appears that during the initial compression from ambient-pressure 10-Å phase with heterogeneous basal spacing to a better stacked structure, the O-H bond is not affected by increasing repulsion of tetrahedral cations. The discontinuity at ~4 GPa cannot at present be explained, since the previous volume data showed no anomalies at this

pressure. Further experiments are in progress to study 10-Å phase's compressional behaviour in smaller pressure steps over the pressure range 0 – 5 GPa.

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