Further complexities of the 10Å-phase revealed by infrared spectroscopy and X-ray diffraction

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ABSTRACT

Infrared spectroscopy, combined with the results of previous NMR studies, has been used to evaluate the OH and H₂O environments in 10Å-phase (“TAP”), nominally Mg₃Si₄O₁₀(OH)₂⋅H₂O. Two partially deuterated samples of TAP synthesized under different conditions have very similar IR spectra, indicating that the phase has a reproducible structural state. IR spectra were also collected of samples of fully Ni-substituted and partially deuterated TAP, and of samples heated for 1 – 2 h at 500 °C in order to remove structural H₂O/D₂O and leave behind bands due to OH/OD of the 2:1 layer. A high-pressure study of the Ni-TAP sample confirmed that the behavior of its H₂O and OH/OD bands was analogous to that observed in previous studies of Mg-TAP. Comparison of the IR spectra of unheated, heated and compressed samples has allowed three different types of Mg-OH (Mg-OD) stretching bands to be identified, two of which are further split, indicating subtle complexities in the TAP structure. The third band is identical to the band in talc. Two interlayer H₂O stretching bands have been identified. The presence of an absorption
feature that is broader than these interlayer H$_2$O bands suggests that there is a second type of more weakly bonded H$_2$O. On heating to 500 °C, the main interlayer H$_2$O bands are lost, the talc-like band is unchanged, and shifts in the other Mg-OH band frequencies indicate a change in environment following the loss of the interlayer H$_2$O. At the same time the signature of a silanol group is possibly revealed from the coincidence of band positions in the Mg-TAP and Ni-TAP spectra. The recognition of three distinct Mg-OH (Ni-OH) environments in Mg-TAP (Ni-TAP) is consistent with the structural model of TAP proposed by Welch et al. (2006) and Phillips et al. (2007), in which the transformation from talc to TAP involves a key change from hydrophobic to hydrophilic character that enables hydration of the interlayer. A final level of complexity is indicated by the identification of a 3c trigonal superstructure from single-crystal XRD, implying a structure analogous to that of the 3T phengite polytype, with interlayer H$_2$O fulfilling the role of K. The incorporation of interlayer H$_2$O through the formation of silanol groups has implications for the amount of water contained in 10-Å phase and related phyllosilicates in the Earth’s mantle. Moreover, the reproducibility of the key features of the IR spectra for different samples implies that this water content is fixed.

**INTRODUCTION**

The 10-Å phase ("TAP"), a high-pressure synthetic phyllosilicate related to talc, has been the subject of numerous experimental studies since the first report of its synthesis by Sclar et al. (1965), due to its potential significance as a host of water in subduction zones. TAP is stable at pressures above 5 GPa, where it forms from the reaction of talc, Mg$_3$Si$_4$O$_{10}$(OH)$_2$, with water (Pawley and Wood 1995). Above 700 °C it breaks down to...
enstatite + coesite + water (Pawley et al. 2011). Therefore any talc that is carried down into
the Earth’s mantle in subducting slabs will react to TAP at depths of around 200 km if the
temperature remains below 700 °C. Talc forms in subducting slabs from hydration of
mantle peridotite (e.g., Evans and Guggenheim 1988). Because of its mechanical weakness
and anisotropy, its presence in subduction zones is likely to have a significant effect on
rheological and seismic behavior (e.g., Hirauchi et al. 2013). TAP has similar physical
properties, and so it too would play an important role in the geophysical properties of
subducting slab, as well as delivering water to greater depths than is possible in talc.

The most obvious transformation in forming TAP from talc + H\textsubscript{2}O is the expansion of
the basal spacing as H\textsubscript{2}O is incorporated into the interlayer space between the 2:1 layers of
talc. However, the amount of H\textsubscript{2}O incorporation, and its variability with run conditions,
have been difficult to quantify. Attempts to measure the H\textsubscript{2}O content have yielded
concentrations ranging from 0.65 to 2 H\textsubscript{2}O per formula unit of talc (Bauer and Sclar 1981;
Wunder and Schreyer 1992; Yamamoto and Akimoto 1977). The structure reported by
Comodi et al. (2005) from single-crystal X-ray diffraction contains a single H\textsubscript{2}O molecule,
which is located at the (000) site of the interlayer. Attempts to use computer simulation (\textit{ab
initio} methods) to infer the state of hydration assume that TAP is simply a hydrated talc,
and have not provided good constraints on the likely H\textsubscript{2}O content, let alone plausible
structural mechanisms for hydration (e.g., Fumagalli and Stixrude 2007). Furthermore,
such studies ignore the problem that talc is hydrophobic.

Until recently, no mechanism for the incorporation of stoichiometric amounts of H\textsubscript{2}O
into TAP had been proposed. However, NMR studies by Welch et al. (2006) and Phillips et
al. (2007) provide clear evidence for the presence of Si vacancies in TAP, which must be
associated with Si-OH groups. These silanol groups confer a hydrophilic character upon the sheets of tetrahedra, which facilitates the incorporation of interlayer H$_2$O. The model developed by Phillips et al. (2007) is shown in Figure 1. The presence of vacant Si sites leads to triplets of Si-OH groups around each vacancy, along with a new Mg-OH group (type B) that is topologically distinct from the “normal” talc-like Mg-OH environment (type A). The creation of the Si vacancy also leads to a change in topology of the three nearest talc-like Mg-OH groups (type C). Thus, the model predicts three distinct types of Mg-OH groups in TAP. An H$_2$O group is hydrogen-bonded to each silanol OH. The hydrophilic tetrahedral sheet in TAP contrasts with the hydrophobic sheet of talc. Hence, when talc transforms to TAP at high pressure, this is due to the formation of Si vacancies, silanols and a resulting hydrophilic structure. The $^{29}$Si MAS NMR spectrum of sample DTAP3 reported by Welch et al. (2006) implies approximately 1 in 20 Si vacancies (5%). In talc there are 10 OH for every 20 Si. Therefore in TAP with 1 in 20 Si vacancies, the ratio of A-, B- and C-type Mg-OH and silanols is 7:1:3:3.

The structural mechanism for interlayer hydration proposed by Phillips et al. (2007), in which three H$_2$O groups are associated with each Si vacancy, allows considerable H$_2$O contents to be achieved with minor vacancy formation. A chemical formula corresponding to TAP with 5% Si vacancies is Mg$_3$Si$_{3.8}$O$_{9.2}$(OH)$_{2.8}$·0.6H$_2$O. With 8% Si vacancies, the formula is Mg$_3$Si$_{3.68}$O$_{8.72}$(OH)$_{3.28}$(OH)$_{2}$·H$_2$O. Just 2% Si vacancies (near the analytical uncertainty levels of Si for electron microprobe analysis) allows 0.25 H$_2$O per formula unit to be incorporated into the TAP structure.
In this paper we report the results of spectroscopic and diffraction experiments on partially deuterated TAP (Mg-TAP) and Ni-substituted TAP (Ni-TAP) that point to new levels of complexity in the structure of this beguilingly simple phase.

**EXPERIMENTAL METHODS**

**Sample synthesis**

Synthesis of the Mg-TAP is described in Welch et al. (2006). Samples from two different synthesis experiments were used in the present study. They were synthesized from a mixture of Mg(OD)$_2$ and SiO$_2$ at 6.5 GPa, 600 °C for 400 h (sample DTAP3) and 150 h (DTAP4). DTAP3 is the same sample as used for $^{29}$Si MAS NMR spectroscopy in Welch et al. (2006). The Ni-TAP was synthesized from synthetic Ni-talc [Ni$_3$Si$_4$O$_{10}$(OH)$_2$] + D$_2$O. The Ni-talc was synthesized hydrothermally from an oxide gel at 0.2 GPa, 500 °C (5 days). The Ni-TAP synthesis experiments used a multi-anvil apparatus at the University of Manchester. Samples were sealed in platinum capsules along with 10 – 15 wt % D$_2$O. The experimental procedure was the same as described in Welch et al. (2006). At the end of each experiment, capsule integrity was checked by measuring the weight before and after puncturing the capsule and placing in a drying oven for around an hour.

**X-ray powder diffraction (XRPD)**

All run products were studied by XRPD in order to check purity, identify product phases and to determine unit-cell parameters. The XRPD pattern of sample DTAP3 has already been reported by Welch et al. (2006). In order to minimize the effects of preferred orientation, which can be extreme for phyllosilicates, we prepared small spheres of a few
milligrams of powder bound in cow gum and mounted on a glass fibre. We used a Genix microsource X-ray generator equipped with CuKα radiation operated at 45 kV, 40 mA, and an Enraf-Nonius one-dimensional position-sensitive detector. A Gandolfi movement was used to maximize sample averaging and minimize preferred orientation. Samples diffracted out to ~80 °2θ, and preferred orientation effects were minimal.

**Single-crystal X-ray diffraction (SCXRD)**

All Ni-TAP products and sample DTAP4 were too fine-grained for analysis by SCXRD. However, the product of sample DTAP3 contained crystals of Mg-TAP that were large enough. Six crystals were studied. Each was mounted on a non-diffracting amorphous-carbon fibre (0.01 mm diameter), itself attached to a glass fibre base. Data were collected using an XcaliburE four-circle diffractometer equipped with an EoS 1K CCD detector (both Agilent Technologies) and MoKα radiation (50 kV, 45 mA). The data collection strategy was determined from a 30-min pre-experiment. Pure ω scans were used with a scan-width of 1° and frame-time of 60 s. The full data collection lasted 16 h. Unit-cell parameters were obtained using reflections with I > 7σ(I). Reflection intensities were corrected for Lorentz-polarization effects and absorption (Multiscan) and converted to structure factors using CrysalsPro (©Agilent Technologies). Structure solution by Direct Methods and structure refinement were carried out using SHELX (Sheldrick 2008) within the WinGX environment (Farrugia 1999).
Infrared (IR) spectroscopy

Powder IR spectra were collected using a Perkin Elmer Spectrum One FTIR spectrometer at the Natural History Museum. A resolution of 2 cm\(^{-1}\) was used, with a scan time of 16 s from 400 – 4000 cm\(^{-1}\). KBr was used as a reference standard. Before collecting the spectra, sample discs and the blank KBr disc were heated at 140 °C for 1 day. A set of spectra was collected for samples DTAP3, DTAP4, and all Ni-TAP samples. Some of the discs were then heated in a muffle furnace to 500 °C for 1 – 2 h, crushed, repressed and their spectra recollected as before. In a separate experiment a new disc of (unheated) DTAP4 was prepared and heated to 600 °C for 3 h and its spectrum collected. In addition, two spectra of sample DTAP3 were obtained using the IR microspectroscopy station at the Synchrotron Radiation Source, Daresbury Laboratory. The station set-up is described in Pawley and Jones (2011). The sample was placed on a BaF\(_2\) disc, and one spectrum collected of a single crystal, the other of a small clump of crystals.

In order to establish if Ni-TAP behaves in a similar way to Mg-TAP, we compressed one of the Ni-TAP samples to 9 GPa. High-pressure synchrotron IR spectra were collected using a diamond-anvil cell at the Swiss Light Source (SLS). Details of the IR procedures and instrumentation used at the SLS are given in Jennings et al. (2010) and Welch et al. (2012). A sample chamber was created by filling the gasket hole (0.2 mm diameter) with dry CsI powder and then pressing a small clump of Ni-TAP powder into it with the top diamond. Pressure was determined using the ruby-fluorescence method (Mao et al. 1986). Two ruby fragments were loaded into the CsI plug along with the Ni-TAP powder.
RESULTS

Ni-TAP synthesis experiments

Four synthesis experiments were carried out using the synthetic Ni-talc + D₂O as starting material. An additional experiment used the Ni-talc gel + D₂O. The experimental conditions and run products are listed in Table 1, together with the conditions for the Mg-TAP synthesis experiments. All Ni-TAP synthesis experiments except NTAP3 showed visible fluid escape on puncturing the capsule after the run. For these four experiments, the amount of D₂O incorporated into the run product, which was the difference in weight between added D₂O and fluid released after puncturing, varied from 6 to 11 wt%. The maximum apparent incorporated D₂O is in the sample that did not transform to 10-Å phase (NTAP4), which means that these concentrations cannot be used to indicate the D₂O content of the run product. It is likely that some D₂O was lost during the capsule loading stage. Experiment NTAP3 showed only a small weight loss after puncturing and drying, suggesting water loss during the experiment.

Experiment NTAP1 suffered a short circuit after running for just 40 min, and NTAP2 also experienced heating problems. Nevertheless, both run products showed 100% transformation to TAP. After experiment NTAP2, a slight modification was made to the multi-anvil apparatus to keep the anvils apart and prevent another short circuit. Subsequent recalibration of pressure revealed a lower pressure than intended in experiments NTAP3 and NTAP4 (6.2 GPa instead of 6.5 GPa), which has led to the formation of talc. In NTAP4 there is also a minor amount of TAP, which means that the reaction Ni-talc + H₂O = Ni-10-Å phase must occur at close to 6.2 GPa at 600 °C. This is a considerably higher pressure than for the corresponding reaction of Mg-talc to Mg-10-Å
Experiment NTAP5 was run at a higher pressure and produced 100% TAP. As well as forming Ni-talc, XRPD of experiment NTAP3 showed the formation of an amphibole whose diffraction pattern most closely matches that of grunerite, implying an amphibole of composition Ni₇Si₈O₂₂(OH)₂.

Diffraction patterns of NTAP1 and NTAP4 are compared in Figure 2. The relationship between the talc and TAP structures is clear, with TAP showing an increased basal spacing with respect to talc. Unit-cell parameters of NTAP1 derived from XRPD (Le Bail refinement) are:

\[ a = 5.3189(5) \, \text{Å}, \quad b = 9.1797(6) \, \text{Å}, \quad c = 10.068(1) \, \text{Å}, \quad \beta = 100.33(1)^\circ, \quad V = 483.6(1) \, \text{Å}^3; \]

for NTAP5 they are:

\[ a = 5.3310(6) \, \text{Å}, \quad b = 9.174(1) \, \text{Å}, \quad c = 10.110(1) \, \text{Å}, \quad \beta = 100.39(1)^\circ, \quad V = 486.3(1) \, \text{Å}^3. \]

From a comparison of these parameters with those of DTAP3 measured by Welch et al. (2006) –

\[ a = 5.3297(9) \, \text{Å}, \quad b = 9.205(3) \, \text{Å}, \quad c = 10.202(3) \, \text{Å}, \quad \beta = 100.08(2)^\circ, \quad V = 492.8(2) \, \text{Å}^3 \]

– it can be seen that substitution of Ni for Mg in the TAP structure causes a small reduction in volume, which is mostly seen as a decrease in the basal spacing. The similarity of cell parameters for NTAP1 and NTAP5 suggests that the effect of different run durations (0.7 h for NTAP1 and 97 h for NTAP5) on the state of hydration is minor.

**Single-crystal XRD**

Six crystals of DTAP3 were examined by SCXRD and all showed the same diffraction behavior, which was characterised by rows of superlattice reflections associated with a 3c superstructure. However, strong modulated diffuse scattering is superimposed upon these superlattice reflections, which did not allow their intensities to be integrated satisfactorily \( (R_{\text{int}} = 0.11 - 0.15) \), although peak positions were accurately determined for refinement of unit-cell parameters. For the best DTAP3 crystal studied, the unit-cell parameters of the
Trigonal 3T cell are: \(a = 5.3094(2) \text{ Å}, c = 30.073(2) \text{ Å}, V = 734.16(6) \text{ Å}^3\) \((1M \rightarrow 3T)\) transformation matrix = \(\frac{1}{2} -\frac{1}{2} 0 / \frac{1}{2} \frac{1}{2} 0 / 1 0 3\). In terms of the 3T cell, rows of superlattice reflections occur for \(h, k \neq 3n\), as shown in Figure 3. An attempt to refine the structure in the monoclinic subcell \((C2/m)\) confirmed the basic substructure reported by Comodi et al. (2005), but also revealed the presence of a minor second component in difference-Fourier maps that is rotated by 60° relative to the main component. After the SCXRD experiment, the crystal was heated in a muffle furnace to 500 °C for 1 h and studied again. However, the heated crystal did not diffract. It appeared to be delaminated, with obvious cracks and the flaky aspect of a damaged book. We interpret the non-diffracting nature of the heated crystal as being due to substantial loss of interlayer H₂O that removes hydrogen bonding across the interlayer and thereby renders the structure incoherent and effectively two-dimensional, with no periodicity along \(c\).

**Infrared spectra**

**IR spectra of Mg-TAP: unheated samples.** Powder and single-crystal IR spectra of unheated samples of DTAP3 and DTAP4 are shown in Figure 4, and stretching frequencies are listed in Table 2. The nominally pure D₂O synthesis environment evidently also contained H₂O, so that in addition to well-resolved spectral detail in the OD region, there are strong bands in the OH region. These are less intense in the DTAP4 spectrum than the DTAP3 spectra. The similarity of the powder spectra of DTAP3 and DTAP4 indicates little difference in the structural states of samples synthesised for 150 h (DTAP4) and 400 h (DTAP3). The spectra comprise three pairs of sharp bands at 3675/3665, 3643/3630 and 3588/3577 cm⁻¹, each having an OD counterpart at 2711/2704, 2683/2668 and...
2645/2626 cm\(^{-1}\), respectively. The \(\nu_{\text{OH}}/\nu_{\text{OD}}\) wavenumber ratios for these bands range from 1.355 to 1.362 and are very close to the theoretical value of 1.374, assuming that O-H and O-D bonds have the same force constant. Another sharp band in the OD region, at 2732 cm\(^{-1}\), with a shoulder at 2751 cm\(^{-1}\), does not at first sight appear to have an OH counterpart.

In addition to these sharp bands, there is a broad but well-defined band centred at 3268 cm\(^{-1}\), with a corresponding OD band at 2440 cm\(^{-1}\). The wavenumber ratio of this pair of bands is 1.339, which is lower than the values for the sharp bands. Between the set of sharp OH/OD bands and the broader 3628/2440 band is an ill-defined broad feature of variable intensity centred at \(\sim 3430\) cm\(^{-1}\), with a corresponding very weak OD feature centred at \(\sim 2555\) cm\(^{-1}\).

IR spectra of Ni-TAP: unheated samples. The powder-IR spectra of NTAP1, 2 and 5 (all 100% Ni-TAP) are very similar. Figure 5 shows the spectrum of NTAP5, together with that of NTAP4, which comprises talc + minor TAP. All Ni-TAP spectra consist of four well-defined OH bands at 3672, 3626, 3588 and 3532 cm\(^{-1}\), a sharp OD band at 2676 cm\(^{-1}\) and three small bands at 2731, 2648 and 2607 cm\(^{-1}\). The 3626/2676, 3588/2648 and 3532/2607 cm\(^{-1}\) bands are identified as OH/OD pairs since \(\nu_{\text{OH}}/\nu_{\text{OD}} = 1.355\) in each case.

Assuming that the 2731 cm\(^{-1}\) band is the OD counterpart of the 3672 cm\(^{-1}\) band, their \(\nu_{\text{OH}}/\nu_{\text{OD}} = 1.345\). In addition to these sharper bands, there is an intense broad band at 3256 cm\(^{-1}\) that has an OD counterpart at 2440 cm\(^{-1}\) (\(\nu_{\text{OH}}/\nu_{\text{OD}} = 1.334\)). Lastly, as with the DTAP samples, there is an ill-defined broad feature centred at \(\sim 3430\) cm\(^{-1}\). In this case there is no equivalent OD band. The NTAP4 spectrum contains strong sharp bands at 3626 and 2676 cm\(^{-1}\), with additional weak bands due to the presence of minor TAP.
IR spectra of Mg-TAP and Ni-TAP: heated samples. Figure 6 shows the unheated DTAP4 spectrum from Figure 4 together with spectra of three different heated discs of DTAP4, two that were heated at 500 °C for 2 h and the third that was heated at 600 °C for 3 h. After heat treatment at 500 °C, DTAP4 retains the OH/OD bands at 3675 and 2711 cm\(^{-1}\). A shoulder is evident on the high-frequency side of these bands, at 3686/2719 cm\(^{-1}\). The other sharp bands from the unheated spectrum are not retained, but instead there is a broader band at 3587/2651 cm\(^{-1}\), with a weak shoulder on the high-frequency side. Again there is an intermediate broad feature of variable intensity. It shows a small shift in frequency from the unheated spectrum, being centred at ~3445 cm\(^{-1}\). Its weaker OD equivalent is at ~2530 cm\(^{-1}\). The 600 °C spectrum is very similar to the 500 °C disc 2 spectrum, except that the shoulder on the high-frequency side of the 2651 cm\(^{-1}\) band is resolved into two bands at 2689 and 2677 cm\(^{-1}\), and there is no feature at 2530 cm\(^{-1}\).

After heat treatment at 500 °C for 1 h, NTAP1 retains the sharp OH/OD bands at 3626 and 2676 cm\(^{-1}\), and again, a shoulder is evident on the high-frequency side of these bands, at 3637/2684 cm\(^{-1}\) (Fig. 5). The other sharp bands are replaced by a single band at 3578/2644 cm\(^{-1}\). The broad 3430 cm\(^{-1}\) band remains on heating, with a very weak OD equivalent, at ~2530 cm\(^{-1}\). Heat treatment of NTAP4 (Ni-talc) at 500 °C for 1 h has very little effect on its spectrum (Fig. 5).

IR spectra of Ni-TAP: high-pressure results. In the diamond-anvil cell, the only bands that are strong enough to be resolved above 0 GPa are those at 3672 and 3626 cm\(^{-1}\) (OH) and 2676 cm\(^{-1}\) (OD) (Fig. 7). The 3256 cm\(^{-1}\) band is visible, but interference fringes prevent its position from being measured. On compression to 9.0 GPa, the 3626 and 2676 cm\(^{-1}\) bands show a small positive $dv/dP$, moving to 3628 cm\(^{-1}\) (OH) and 2679 cm\(^{-1}\) (OD).
contrast, the 3672 cm\(^{-1}\) band shows a rapid decrease in frequency, shifting at a rate of -9
cm\(^{-1}/\text{GPa}\) over 3.5 GPa. At the same time, this band decreases in intensity so that by 5.3 GPa
it can no longer be resolved. Both bands return to their original position on decompression.

**DISCUSSION**

**Infrared band assignments**

The main motivation for producing Ni-substituted TAP was to aid in assigning bands
in IR spectra that previously have been the source of ambiguity. Substitution of 100% Ni
for Mg in talc results in a well-documented wavenumber shift from 3676 to 3626 cm\(^{-1}\), i.e.,
Ni for Mg causes a large (50 cm\(^{-1}\)) shift in OH vibrational frequency. If such shifts can be
identified, then bands can be assigned to Mg/Ni-OH. Unshifted bands can then be assigned
to H\(_2\)O or to Si-OH groups, which will be unaffected by Mg/Ni substitution as they are not
bonded to Mg or Ni.

Band assignments are summarized in Table 2. In both the Mg-TAP and Ni-TAP
spectra, there are sharp bands at the same frequencies as in Mg- and Ni-talc (highlighted by
asterisks in Figs 4 and 5). These bands are assigned to Mg/Ni-OH/OD in the same
environment as in talc. This is the same assignment as previously made (Parry et al. 2007;
Pawley and Jones 2011). The intensity of this talc-like band is much lower in the DTAP3
single crystal spectrum (Fig. 4) than in the powder spectra. This is because the orientation
of the single crystal was such that talc-like O-H bonds (parallel to [001]) would have been
nearly parallel to the incident direction of the IR beam. In contrast, powder spectra are
much more randomised and register all OH/OD bands.
If we compare the Mg-TAP and Ni-TAP spectra (Figs 4 and 5), we see that as well as the sharp talc-like band, the two pairs of OH bands at 3643/3630 and 3588/3577 cm\(^{-1}\) in the Mg-TAP spectra are related by 50 cm\(^{-1}\) shifts to the two OH bands at 3588 and 3532 cm\(^{-1}\), respectively, in Ni-TAP. We identify these two sets of bands as being due to distinct Mg-OH/Ni-OH groups in TAP that are different from the talc-like OH group, and are, therefore, new OH environments that only occur in TAP. The model of TAP proposed by Phillips et al. (2007), and shown schematically in Figure 1, has three different Mg-OH environments. We propose that the sharp talc-like band corresponds to type-A OH, with the other two sets of bands being types B and C. The fine structure of the Mg-TAP spectra, in which these pairs of Mg-OH (and Mg-OD) bands are resolved as doublets, implies that these new Mg-OH (Mg-OD) environments are further subdivided by subtle interactions with the surrounding structure. The separate bands are not resolvable in the Ni-TAP spectra because the sample is not as well crystallized as the Mg-TAP samples. The bands at 3665 and 2704 cm\(^{-1}\) may also be doublets with the talc-like bands at 3675 and 2711 cm\(^{-1}\). Their equivalents are not resolved in the Ni-TAP spectra.

Further indication that the 3675 cm\(^{-1}\) OH band in Mg-TAP (and equivalent OD and Ni-TAP bands) is due to OH in a talc-like environment comes from its behavior on compression. The small blue shift of the 3626 and 2676 cm\(^{-1}\) bands with compression of Ni-TAP is similar in direction and magnitude to the shift experienced by the 3675 and 2711 cm\(^{-1}\) bands in Mg-TAP (Pawley and Jones 2011), and by the 3676 cm\(^{-1}\) band in talc (e.g., Parry et al. 2007). The positive \(d\nu/dP\) indicates that there is no hydrogen bonding, either to oxygens of the silica ring or to interlayer H\(_2\)O. \(d\nu/dP\) is small because the 2:1 layers remain fairly rigid during compression, with most of the compression taken up by the interlayer
region. The persistence of the band in the spectra of DTAP4 heated to 500 and 600 °C is further evidence of its being due to vibration of strongly bonded OH/OD. In contrast, the interlayer water is driven off by 500 °C, as will be seen below. The invariance of the vibrational frequency as the interlayer water is removed is a further indication of an absence of hydrogen bonding between the talc-like OH and the interlayer H₂O.

The other band that is seen in the high-pressure Ni-TAP spectra, at ν₀ = 3672 cm⁻¹, experiences a large red shift on compression (Fig. 7). This behavior recalls that reported in Mg-TAP by Parry et al. (2007). In their Figure 3, a broad band emerges from the 3675 cm⁻¹ band at ~1 GPa and moves to ~3640 cm⁻¹ at 9.6 GPa. The behavior of these bands is similar in Mg-TAP and Ni-TAP samples, and the two bands can, therefore, be confidently assigned to the same stretching vibration. The similar values of ν₀ = 3672 cm⁻¹ in Ni-TAP and ν₀ = 3675 cm⁻¹ in Mg-TAP indicate that this band is not due to Mg/Ni-OH. The marked wavenumber shift on compression suggests that it is associated with the interlayer region, which has a high compressibility, rather than with the 2:1 layers. We therefore assign it to stretching of one of the O-H bonds of the interlayer water. In previous studies its assignment was uncertain (e.g., Pawley and Jones 2011), but comparison of Mg-TAP and Ni-TAP spectra removes any ambiguity, and shows that the 3675 cm⁻¹ band in Mg-TAP spectra is a near coincidence of H₂O and talc-like Mg-OH bands. The negative dν/dP of this H₂O band suggests increasing hydrogen bonding as the interlayer H₂O is brought closer to the neighbouring tetrahedral sheet.

Comparison of Figures 4 and 5 shows that the broad bands at 3268 and 2440 cm⁻¹ in the Mg-TAP spectra are equivalent to the 3256 and 2440 cm⁻¹ bands in the Ni-TAP spectrum. In this case there is only a small (OH), or no (OD), frequency shift with Mg-Ni
substitution. The bands can therefore be assigned to stretching of the other O-H/O-D bond of the interlayer water. This is the same assignment as made by Parry et al. (2007). The large bandwidth is interpreted as being due to a degree of orientational disorder. The low frequency indicates stronger hydrogen bonding than for the other O-H/O-D bonds.

The presence of an OD band at 2731-2732 cm\(^{-1}\) in the spectra of both samples needs further consideration. This band should have a corresponding OH band, but there are no OH bands with frequency higher than 3675 cm\(^{-1}\). However, it can be seen from Figure 4 that the intensity of this band (highlighted with a vertical dashed line) varies between spectra and roughly correlates with the intensity of the 2440 cm\(^{-1}\) band (also highlighted). These two bands are particularly strong in the DTAP3 single crystal spectrum. Both bands are weak in the Ni-TAP spectrum (Fig. 5). This correlation suggests that, like the 2440 cm\(^{-1}\) band, the 2732 cm\(^{-1}\) band can be assigned to stretching of OD in interlayer water, and is therefore the OD equivalent of the 3675 cm\(^{-1}\) interlayer H\(_2\)O band. That it has a different \(\nu_{OH}/\nu_{OD}\) from the 3675 cm\(^{-1}\) talc-like Mg-OH band (1.345 versus 1.356) is puzzling, but it should be noted that the lower-wavenumber H\(_2\)O band (3268 cm\(^{-1}\)) also has a low \(\nu_{OH}/\nu_{OD}\) (1.339). The 2751 cm\(^{-1}\) shoulder on the 2732 cm\(^{-1}\) band in the Mg-TAP spectra has no corresponding OH band, and remains an enigma.

The two bands assigned to OH/OD stretching of interlayer water are separated by around 400 cm\(^{-1}\) (OH). This degree of separation indicates that the two vibrations are not coupled, i.e. they are not symmetric and antisymmetric vibrations of H\(_2\)O. Instead, the two O-H bonds can be considered separately and each has its own stretching frequency. Assuming that in both Mg-TAP and Ni-TAP there are HOH, HOD and DOD molecules, the absence of coupling is also evident from the fact that there are only two \(\nu_{OH}\) and two \(\nu_{OD}\) in
both spectra, since coupling would lead to two frequencies for each of the HOH, HOD and DOD molecules. The large frequency difference between the two bands indicates a significant difference in hydrogen bonding, with a much shorter O$_w$-H⋯O for the band at 3268 cm$^{-1}$ than for the band at 3675 cm$^{-1}$ (~ 2.7 Å compared with > 3.0 Å, using the correlation of Libowitzky 1999). This difference suggests that either the H$_2$O molecule does not occupy a symmetric position with respect to the adjacent SiO$_4$ tetrahedra, or that there is dynamic disorder between two non-symmetric positions, as is the case for lawsonite (Libowitzky and Rossman 1996). On compression there is a strengthening of the hydrogen bonding for the weakly hydrogen-bonded O-H; the other band is not resolved on compression.

It is curious that the OD bands of interlayer D$_2$O in Ni-TAP are much weaker than the corresponding OH bands. On the other hand, the talc-like OD band is relatively intense. This is seen even in the spectrum of the sample synthesized in < 1 h. Since the Ni-TAP samples were synthesized from Ni$_3$Si$_4$O$_{10}$(OH)$_2$ + D$_2$O, we might have expected the talc-like band to be stronger in the OH stretching region and the interlayer water bands to be stronger in the OD region. Instead, there appears to have been rapid exchange of the talc OH for OD, and preferential incorporation of H$_2$O in the interlayer.

All interlayer H$_2$O/D$_2$O bands in Mg-TAP and Ni-TAP spectra disappear after heating to 500 °C (Figs 5 and 6), an observation that is consistent with differential thermal analysis showing loss of interlayer water at around 450 °C at low pressure (Miller et al. 1991). Even after all the interlayer water has been removed, TAP still retains several structural differences from talc. The talc-like OH/OD band is the only band that is unchanged from the unheated spectra. The other bands are at different frequencies, indicating a structural
rearrangement, presumably caused by the removal of the interlayer H$_2$O. The new band that appears as a shoulder on the high-frequency side of the main talc-like band shows the same Mg-Ni frequency shift, indicating that it is also due to a Mg/Ni-OH/OD vibration. The similar frequencies of the 3587/2651 cm$^{-1}$ (Mg-TAP) and 3578/2644 cm$^{-1}$ (Ni-TAP) bands suggests that they include vibrations that are unaffected by Mg-Ni substitution, i.e., vibrations of silanol groups (see below). Their relative broadness suggests that they comprise more than one overlapping band. The shoulder on the 2651 cm$^{-1}$ band in the 500 °C DTAP4 spectra becomes resolved after heating at 600 °C into two bands at 2689 and 2677 cm$^{-1}$. The equivalent bands are too weak to be observed in the OH region.

The broad band at ~3430 cm$^{-1}$ in both Mg-TAP and Ni-TAP spectra is intriguing, as it is of variable intensity, and appears to persist after heating, albeit with a small shift in wavenumber. There is also a very weak OD equivalent, which is removed on heating Mg-TAP to 600 °C. This band is in the region of the spectrum where adsorbed H$_2$O can be expressed. We would expect much less adsorbed H$_2$O on single crystals than in powders, and indeed, the band intensity is reduced in the single-crystal spectrum of DTAP3. However, another possibility is that the band in the unheated samples’ spectra is due to additional H$_2$O in the interlayer. The NMR data of Phillips et al. (2007) suggest that as well as the strongly hydrogen-bonded interlayer H$_2$O, there could be additional, more weakly bonded interlayer H$_2$O, the amount of which could vary between samples. Variation of H$_2$O content is also suggested by the variable estimates of water content obtained in previous studies of TAP. We propose that the 3430 cm$^{-1}$ peak is due to these more weakly-bonded H$_2$O groups. These H$_2$O groups should be removed on heating to 500 °C, and so the
persistence of a feature at approximately the same wavenumber in the spectra of heated samples is puzzling.

Silanols?

The structural model for TAP proposed by Welch et al. (2006) and Phillips et al. (2007) has two important new features, both of which are associated with Si vacancies: (1) two new Mg-OH environments; (2) silanol groups. The presence of silanols is considered essential to providing hydrophilic character needed to incorporate interlayer H₂O, and stands in sharp contrast to the hydrophobic nature of talc. In the study reported here, we have identified three distinct Mg-OH (Ni-OH) environments in TAP, two of which appear to be unique to TAP. These two new Mg-OH sites may be further subdivided into pairs arising from more subtle interactions with the surrounding structure. However, we have not identified silanol groups spectroscopically. A search of the very limited literature on silanols in silicate minerals indicates that silanol vibrations occur over a wide wavenumber range from 3000 – 3700 cm⁻¹. It is possible that the 3587 cm⁻¹ (Mg-TAP) and 3578 cm⁻¹ (Ni-TAP) bands in the heated spectra are due to silanol groups, as their frequency is almost the same for both samples. Bands at these frequencies do not occur in the unheated samples’ spectra; however, we would not expect them to, since hydrogen bonding to the interlayer H₂O would cause a reduction in frequency. It may be that the silanol bands are not visible because they overlap with the low-frequency H₂O bands.
Reproducibility of TAP structure

The similarity of IR spectra and unit-cell parameters of samples of TAP synthesized under widely varying run durations (150 – 400 h for Mg-TAP, < 1 – 97 h for Ni-TAP) shows that the key features of their structural states are reproducible. Likewise, Ni-TAP is a good analogue of Mg-TAP, there being a close correspondence between their spectra and an analogous response to compression. If there is any variability, it is in the extent of weakly-bonded interlayer H$_2$O whose presence is implied by the broad spectral feature at ~3430 cm$^{-1}$.

The 3T superstructure

The presence of a 3$T$ superlattice in DTAP3 points to a further level of structural complexity beyond that of the monoclinic substructure reported by Comodi et al. (2005). The DTAP3 diffraction patterns are very similar to those of 3$T$ phengite (Schingaro et al. 2013), except for the presence of significant modulated non-Bragg intensity in the former. This similarity suggests that interlayer H$_2$O positions in TAP correlate with those of K in phengite. It may be possible to determine the crystal structure of this 3$T$ polytype using radiation with a wavelength longer than that of MoK$\alpha$, for example CuK$\alpha$. We are exploring this possibility.

Implications

The complexity of the IR spectra of Mg-TAP and Ni-TAP is evidence for a structural modification of the talc-like 2:1 layer building block of 10-Å phase that stabilizes the incorporation of interlayer H$_2$O. Following Phillips et al. (2007), we propose that Si
vacancies and silanol groups are formed when talc transforms to 10-Å phase, making the 2:1 layer hydrophilic and enabling the incorporation of interlayer H₂O. The presence of silanol groups means that 10-Å phase can incorporate more water than proposed for structural models in which water is only present as interlayer H₂O. It also means that if another phyllosilicate shows solid solution or lamellar intergrowths with 10-Å phase at high pressure, such as has been proposed for phlogopite (Fumagalli et al. 2009), it too is likely to contain silanol groups.

The reproducibility in detail of the main structural features of 10-Å phase implies that the concentration of Si vacancies and silanol groups is essentially constant. A well-defined H₂O content may imply ordered arrangement of Si vacancies and silanol groups, in turn producing an ordered arrangement of interlayer H₂O that defines a characteristic stoichiometry. The presence of a 3T-superstructure may be associated with such ordering. An ordered structure means that any variation in measured H₂O content of 10-Å phase samples is likely to be due to weakly bonded interlayer H₂O. This H₂O is assumed to be incorporated during quenching and decompression, as inferred from phase equilibrium experiments on two apparently different samples of 10-Å phase, which suggested no difference in water content at high pressures and temperatures (Pawley et al. 2011). Therefore, in the Earth's mantle, 10-Å phase should have a fixed composition and H₂O content.

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REFERENCES CITED


Table 1. Synthesis conditions and run products of Ni-TAP (this study) and Mg-TAP (Welch et al. 2006). Abbreviations: TAP = 10-Å phase, amph = amphibole, en = clino-enstatite.

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Table 2. Summary of OH and OD stretching frequencies and their assignments for Mg-TAP, Ni-TAP and samples heated at 500 °C for 1 – 2 h. Figures in parentheses are the pressure dependence (cm⁻¹/GPa) for the strongest Ni-TAP bands, measured up to 9 GPa (3626 and 2676 cm⁻¹ bands) and up to 3.5 GPa (3672 cm⁻¹ band). Assignments described as “New Mg-OH” are Mg/Ni-OH/OD environments that are not present in talc.

<table>
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<th>ν\text{OD} (cm⁻¹)</th>
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Figure captions

**Figure 1.** The 2:1 layer OH sites in TAP based upon the model proposed by Phillips et al. (2007). The structure of a 2:1 layer is shown projected onto (001) with $^{[6]}$Mg octahedra (yellow), SiO$_4$ tetrahedra (blue), O and H atoms (grey and teal-green, respectively) of OH and H$_2$O groups. Other O atoms are omitted for clarity. Three different OH environments labelled A, B and C are shown. A sites are normal talc-like OH; B and C sites are new OH groups that arise from the presence of Si vacancies in the sheet of tetrahedra. One such Si vacancy and its associated OH groups is shown.

**Figure 2.** X-ray diffraction patterns of Ni-TAP (sample NTAP1) and Ni-talc (sample NTAP4). The bands marked with asterisks are the (001), (003) and (004) basal spacing reflections.

**Figure 3.** (a) An $a^*-c^*$ diffraction pattern of TAP indexed for the 3T supercell (trigonal) and showing the rows of superlattice reflections that occur for $h, k \neq 3n$, as is also seen in 3T phengite (Schingaro et al. 2013). (b) Two-dimensional diffraction profile along part of the 10$l$ row of superlattice reflections indicated by the area in (a) defined by the dashed box. Although most peaks are easily located, the considerable peak overlap prevented successful integration of intensity.

**Figure 4.** IR spectra of Mg-TAP in the OH and OD stretching regions. The DTAP3 spectra were collected at Daresbury Laboratory, the DTAP4 spectrum at the Natural History Museum. The region of the spectra between 2800 and 3050 cm$^{-1}$ contains vibrations of
organic compounds which have been omitted for clarity. Vertical dashed lines = positions of the stretching vibrations of the interlayer H$_2$O/D$_2$O, * = talc-like OH/OD stretching vibrations (only shown above the top spectrum). See text for further discussion.

**Figure 5.** IR spectra of Ni-TAP and Ni-talc in the OH and OD stretching regions. The talc sample contains a small amount of TAP. Also shown are spectra of Ni-TAP and Ni-talc heated at 500 °C for 1 hour. The dashed lines and asterisks represent the same features as in Figure 4.

**Figure 6.** IR spectra of Mg-TAP in the OH and OD stretching regions after heating at 500 and 600 °C. The spectra represent three separate heating experiments. Also shown is the unheated spectrum of disc 1. The dashed lines and asterisks represent the same features as in Figure 4.

**Figure 7.** IR spectra of Ni-TAP (NTAP1) under compression in the diamond-anvil cell. The upper three spectra were collected during decompression.