

1 **In-situ infrared spectroscopic studies of hydroxyl in amphiboles at high pressure**

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4 **Revision 2**

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10 **Abstract**

11 Oceanic plates contain numerous hydrous phases including amphiboles, which are  
12 important carriers of water into subduction zones. The hydroxyl bound within the crystalline  
13 structure of hydrous minerals, as well as changes in hydrogen bond symmetry, can impact the  
14 bulk properties of these minerals. In this study, twelve natural amphibole samples spanning a  
15 range of ten compositions were probed with synchrotron infrared spectroscopy at room  
16 temperature and pressures up to 60 GPa. Infrared spectra were collected at atmospheric pressure  
17 and at regular intervals during compression, allowing for the collection of spectra centered on the  
18 typical O-H stretching region at 3600-3700 cm<sup>-1</sup> as they evolved with pressure for each  
19 composition. The number of O-H bands within each sample was found to vary with composition,  
20 but the pressure dependence of O-H frequency shifting more closely correlated with mode  
21 frequency at ambient pressure than with composition. Combined with earlier results, these data  
22 reveal a linear relationship between mode frequency at ambient pressure and pressure  
23 dependence of O-H stretching modes in amphiboles and sheet silicates.

24 Two sample preparation methods utilized in this study allowed for direct comparison  
25 between quasi-hydrostatic neon-loaded sample conditions and the conditions achieved with a  
26 KBr pressure medium. Samples loaded in neon preserved sharper peaks, allowing greater  
27 spectral resolution, especially at higher pressures when peaks are most likely to broaden or  
28 disappear due to crystalline disorder and pressure gradients across the sample. This new quasi-  
29 hydrostatic loading method proved valuable to tracing O-H stretching behavior in amphiboles to  
30 higher pressures than previously obtained and will lend itself to future study of O-H stretching  
31 pressure dependence in a wide range of hydrous minerals.

32 **Keywords:** infrared, high pressure, diamond anvil cell, hydroxyl, amphiboles

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## Introduction

35 Oceanic plates contain numerous hydrous phases, and since amphiboles contain ~2 wt.%  
36 H<sub>2</sub>O they are important carriers of water into subduction zones (Stern 2002). As amphiboles  
37 within the oceanic slab are subjected to increasing temperatures and pressures as the slab  
38 subducts along the cold slab geotherm, a dehydration reaction is initiated. The dehydration of  
39 amphiboles may extend to depths of 100 km, depending on local variations in the subducting  
40 slab's geotherm (Stern 2002). This reaction influences island arc volcanism, as 5-20% of the  
41 water released from subducting basaltic slabs into overlying mantle may originate from  
42 amphibole dehydration (Schmidt and Poli 1998). The accommodation and subsequent loss of this  
43 hydroxyl at elevated pressure has been predicted to vary with composition in response to the  
44 repulsive interactions between cations, as well as the influence on hydrogen bonding by next-to-  
45 nearest neighbors, in a chemically complex system which merits further study (Hawthorne and  
46 Della Ventura 2007). Hydrogen cycling in the Earth's interior is critical due to the influence of

47 hydroxyl on melting temperatures, rheology, electrical conductivity, and atomic diffusivity, as  
48 well as macro-scale phenomena including plate tectonics and volcanism (Hofmeister 2004;  
49 Hirschmann 2006). Lastly, hydrogen bond symmetrization in hydrous minerals may influence  
50 the response of bulk properties to pressure, for example increasing bulk modulus by as much as  
51 ~20% (Tsuchiya et al. 2005; Sano-Furukawa et al. 2009; Husher et al. 2011).

52 Amphiboles are a group of inosilicates that accommodate an extensive range of both  
53 cation and anion substitutions ( $AB_2C_5T_8O_{22}W_2$ ), resulting in classification into eight sub-groups  
54 (Hawthorne et al. 2012). In this generalized formula the large A site may contain a cation (e.g.,  
55 Na, Ca, etc.) but is often vacant, the B represents the cations of the M4 site which may be 6 or 8-  
56 fold coordinated, and the C represents the cations of the octahedral M1, M2, and M3 sites.  
57 Structurally, amphiboles are comprised of corner-linked double chains of silicate tetrahedra (T  
58 sites) that extend along the *c*-axis and bookend a single octahedral strip. Oxygens occupy two  
59 distinct planes; basal or bridging oxygen link adjacent  $(SiO_4)^{4-}$  tetrahedra along the *c*-axis and  
60 apical or non-bridging oxygen are coordinated to single tetrahedra. The A site between the  
61 octahedral and tetrahedral strips (also A in the generalized formula above) can host large alkali  
62 ions such as  $Na^+$  and  $K^+$  but often remains vacant. Three sites within the inner octahedral strip  
63 accommodate divalent and trivalent cations including Al, Ca, Fe, Mg, and Ti, and are  
64 represented by B and C in the generalized formula. The W site hosts  $OH^-$  or halogens. The  
65 amphibole family is divided into two symmetries; monoclinic and orthorhombic, and five  
66 structures; *C2/m*, *P2<sub>1</sub>/m*, *P2/a*, *Pnma*, *Pnmm*, of which the first four occur in natural samples.  
67 The natural specimens used in this study represent the four most common rock-forming  
68 compositional subgroups and both symmetry groups.

69 Infrared (IR) spectroscopy allows direct detection of the O-H covalent bond stretching  
70 frequency within a hydrogen bond (O-H...O). Considering the stretching vibration as a simple  
71 harmonic oscillator it has been shown that the frequency of an idealized relaxed hydroxyl bond is  
72  $3600\text{ cm}^{-1}$  at ambient pressure, with deviations from this frequency as the result of changing the  
73 strength of the bond (Huggins and Pimental 1956). It has been observed that O-H stretching  
74 bands above a 1-bar frequency of  $\sim 3600\text{ cm}^{-1}$  are likely to increase in bond frequency with  
75 pressure while those below this set point are likely to decrease with pressure (Cynn and  
76 Hofmeister 1994). Yet, the hydroxyls within amphiboles are not isolated, therefore instead of a  
77 simple two mass harmonic problem, there is a potential for influence by nearest and next nearest  
78 neighbors. Additionally, the local environment of the hydroxyl site, including geometry, cation  
79 occupation, defect structure, and compression behavior influence O-H stretching pressure  
80 dependencies, potentially causing significant deviations from this trend (e.g., Koch-Müller et al.  
81 2003; Jahn et al. 2012). The wide range of amphibole compositions in this study was chosen to  
82 investigate whether composition has a primary influence on the pressure dependence of  
83 individual O-H stretching modes in amphiboles.

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### Experimental Methods

86 Twelve natural amphibole samples spanning ten distinct compositions were characterized  
87 using energy dispersive X-ray spectroscopy (EDS) as shown in Table 1. Subsequently, pieces of  
88 each amphibole composition were ground in an agate mortar and pestle, mixed in a 1:1 molar  
89 ratio with KBr, homogenized in a ball mill for 45 minutes at 20 Hz, and pressed into  $\sim 5\text{-}10\text{ }\mu\text{m}$   
90 thick platelets to load into symmetric-type diamond anvil cells (DACs). All sample powders  
91 were either kept in a desiccator prior to loading or were baked for 30-60 minutes at 375 K before

92 being compressed into pellets. Small ruby grains placed in the sample chamber enabled in situ  
93 pressure monitoring using the  $R_1$  luminescence line (Mao et al. 1978). Gaskets of stainless steel  
94 or rhenium were used, with sample chambers of 80  $\mu\text{m}$  or 50  $\mu\text{m}$  diameter, respectively.

95 The two sample geometries used in this study are shown in Figure 1b and 1c. The first  
96 sample set-up utilized 10  $\mu\text{m}$  thick platelets of KBr as non-hydrostatic pressure medium,  
97 surrounding the sample platelet of mixed amphibole + KBr following a methodology previously  
98 described by Robert et al. (1989). Mixing the sample material with dehydrated KBr mitigated the  
99 preferential orientation of amphibole grains during compression and limited the likelihood of  
100 saturated absorption peaks in the IR spectra. The second sample assembly also employed mixed  
101 amphibole + KBr platelets, but replaced the KBr pressure medium with a nearly hydrostatic neon  
102 pressure medium, which was loaded as a pressurized gas at the Advanced Photon Source using  
103 the COMPRES/GSECARS gas-loading system (Rivers et al. 2008). After loading the mixed KBr  
104 + amphibole platelets, but prior to closing the DACs, prepared sample assemblies were baked for  
105 an additional hour at 375 K to mitigate the effect of water vapor absorption (Jenkins et al. 2013),  
106 which can overwhelm the signal of structural hydroxyl.

107 Diamond anvils cells with 250  $\mu\text{m}$  culet sizes were used to pressurize the samples. All  
108 high-pressure synchrotron infrared spectra in this study were collected at the U2A beamline of  
109 the National Synchrotron Light Source at the Brookhaven National Laboratory using either a  
110 Bruker Vertex 80v FTIR spectrometer with Hyperion 2000 microscope, or a Bruker IFS/66v  
111 FTIR spectrometer with custom microscope, both with HgCdTe detectors. Different spectral  
112 resolutions of 1  $\text{cm}^{-1}$ , 2  $\text{cm}^{-1}$ , and 4  $\text{cm}^{-1}$  were tested for the lowest pressure spectra and no  
113 significant differences in the quality of data was found, therefore 4  $\text{cm}^{-1}$  resolution was applied to  
114 all spectra. The spectra presented here were recorded in 1024 or 512 scans. PeakFit (Systat

115 Software) was used for background subtraction and to obtain precise absorption peak positions  
116 using a least-squares refinement within the hydroxyl absorption region of interest following a  
117 previously published methodology (Hawthorne et al. 1997).

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## Results and Discussion

120 Room temperature infrared spectra were collected at atmospheric pressure and at regular  
121 intervals during compression until individual absorption bands were obscured by peak  
122 broadening consistent with non-hydrostatic stresses (Lager et al. 2005). Samples that contained  
123 peaks that were broad at atmospheric pressure, because of increased local cation substitution  
124 (Strens 1974; Noguchi et al. 2012), were monitored until all peaks became impossible to track.  
125 For most samples additional spectra were collected at regular intervals during DAC  
126 decompression. In all such cases the position of absorption bands returned to original  
127 atmospheric pressure conditions, although there were varying degrees of hysteresis in the  
128 decompression frequencies compared to the frequency at similar pressures on initial compression,  
129 as has been seen in a previous Raman study (Shim et al. 2006). The elapsed time between  
130 decompressing the sample and acquiring the spectra did not influence the degree of hysteresis.  
131 When determining the pressure dependence of individual stretching modes, only the frequencies  
132 measured during compression were used. The IR absorption peak positions are listed in  
133 Supplementary Table 1.

134 Although individual absorption peaks broadened at high pressures, no samples exhibited  
135 the gradual pressure-induced band-splitting that has been previously used to interpret symmetry  
136 changes (Yang et al. 1998). Depending on the composition and symmetry of each amphibole,  
137 samples exhibited between one and four distinct hydroxyl bands (Figure 2), identified here as

138 bands A, B, C, and D following the terminology of Hawthorne and Della Ventura (2007).  
139 Individual stretching bands are due not to a change in the location of the hydrogen, but rather  
140 nonequivalent bond lengths. Coexisting bands may exist due to variations in local M1 and M3  
141 occupancy, with additional fine structure due to variations in the M2 and A sites (Hawthorne and  
142 Della Ventura 2007). The number of observed bands may in fact be fewer than the actual number  
143 of absorption frequencies as closely overlapping absorption peaks may present as peak  
144 broadening (Hawthorne and Della Ventura 2007).

145         The frequency of each stretching band during compression is plotted against pressure for  
146 each of the twelve samples, spanning ten compositions, in Figure 3. Despite small offsets due to  
147 deviations in chemical composition (Oberti et al. 2007), it is quite possible to compare  
148 frequencies between different amphibole samples at similar pressures for all four hydroxyl bands  
149 (Figure 2). Two main features are evident; firstly peak positions are very comparable between  
150 compositions at similar pressures across all bands (within  $10\text{ cm}^{-1}$  at low pressure, with  
151 increasing spread at increased pressure), and secondly the pressure dependence of these bands is  
152 markedly consistent across a wide range of compositions (Figure 3). Considering that this data  
153 includes ten distinct compositions, nearest neighbor cations do not seem to have a primary  
154 influence on the pressure dependence of the O-H stretching modes in amphiboles. The change in  
155 pressure dependence of the anthophyllite (L31) A-band above 30 GPa may be due to a  
156 previously undetected symmetry change or developing deviatoric stresses within that sample.  
157 Similarly, a nonlinear trend appears in the pressure dependence of the arfvedsonite (L30) D-band  
158 at pressures exceeding 20 GPa.

159         Overall there was good agreement between samples loaded with both pressure media, but  
160 Ne-loaded samples exhibited sharper absorption peaks to higher pressure, indicating that the

161 greater hydrostaticity from this sample loading method minimized stress-induced peak  
162 broadening (Figure 4). Although the pressures achieved in this study greatly exceed the range of  
163 amphibole stability expected under geologic conditions, this method does enable the pressure  
164 dependence to be more precisely defined, providing greater insight into the physical mechanisms  
165 and systematics of pressure dependence in amphibole O-H stretching modes. Pressure  
166 dependences (Table 2) were determined by a linear fit to the pressure-frequency data of each O-  
167 H stretching band of each composition in the study up to 20 GPa.

168         These pressure dependences are plotted in Figure 5 against the initial 1-bar frequency of  
169 each band. Interestingly, there is a near-linear correlation between the 1-bar O-H stretching  
170 frequency and its pressure dependence in these amphiboles. The results of high-pressure IR  
171 absorption studies on other amphiboles (Yang et al. 1998; Iezzi et al. 2008) likewise follow the  
172 linear relationship found among the amphibole O-H stretching modes reported here. It has been  
173 observed previously that in certain minerals, higher 1-bar O-H stretching frequencies have  
174 positive pressure dependence and lower 1-bar O-H stretching frequencies have negative pressure  
175 dependence (Prewitt and Parise 2000; Yang et al. 2014). Similar to the findings of this study,  
176 Cynn and Hofmeister (1994) showed that the various O-H stretching modes within hydrous  
177 wadsleyite have pressure-dependences that are linearly related to their 1-bar frequencies. Based  
178 on our new data, we conclude that a similar correlation exists between 1-bar O-H frequencies  
179 and their pressure dependences are within the amphibole group. The 1-bar frequency from this  
180 study corresponding to the cut-off between positive and negative pressure dependence is  $\sim 3640$   
181  $\text{cm}^{-1}$ . This pressure-independent frequency is coincident with previous experimental results  
182 (Cynn and Hofmeister 1994) and the free oscillation parameter from the simple harmonic  
183 oscillator model.



184 The ability to correlate 1-bar hydroxyl vibration frequency with pressure dependence  
185 enables the prediction of either bond strengthening or softening. Bands with initial frequencies  
186 above the zero pressure-dependence threshold will shorten with increasing pressure, associated  
187 with greater force constant of the O-H bond. In amphiboles only bands that lie below the 3640  
188  $\text{cm}^{-1}$  threshold would plausibly symmetrize with pressure. In other words, only in the case of a  
189 band with negative frequency shift pressure-dependence can the double well potential of the H  
190 atom evolve with increased pressure to a single well potential minimum resulting in the H atom  
191 half way between the donor and acceptor oxygens (Prewitt and Parise 2000). In short, mode  
192 frequency at ambient pressure, rather than composition is the primary factor controlling the  
193 pressure dependence of individual stretching modes. Still, composition likely plays an important  
194 role, as 1-bar frequencies (i.e. presence of the A, B, C, and/or D bands) are a function of nearest  
195 neighbor and next-to-nearest neighbor occupancies.

196 Hydroxyl ions ( $\text{OH}^-$ ) within amphiboles are generally accommodated along the  
197 octahedral strip at the non-tetrahedral oxygen site, which is very similar to the  $\text{OH}^-$  site in *t-o-t*  
198 phyllosilicates (e.g. talc, micas). As shown in Figure 5, the O-H bonds within these comparable  
199 sites in amphiboles and *t-o-t* phyllosilicates largely exhibit the same linear relationship between  
200 pressure dependence and 1-bar frequency. This consistency in the high-pressure dependence of  
201 their O-H stretching frequencies is due to the similarity in the local environments of the hydroxyl  
202 in these minerals. Still, even within ino- and phyllosilicates, O-H stretching modes are not  
203 always so simply accommodated, as can be seen in the low frequency biotite datum from  
204 Williams et al. (2012), which the author attributed to an additional hydroxyl stretching mode  
205 juxtaposed with an octahedral vacancy. This may or may not be the case, as in Figure 5 the

206 datum for muscovite, whose octahedral strip contains systematic vacancies, clusters with the data  
207 for trioctahedral minerals (having fully-occupied octahedral sites).

208 Many other minerals incorporate hydroxyl on sites that are not equivalent to that in  
209 amphiboles (and *t-o-t* phyllosilicates), and in these minerals one should not expect that the  
210 pressure dependences of the O-H stretching modes would exhibit the same relationship to mode  
211 frequency at ambient pressure. Indeed, as shown in Figure 6, minerals such as wadsleyite,  
212 ringwoodite, superhydrous phase B (shy-B), and hydrous post-perovskite (hy-ppv) do not lie  
213 along the amphibole trends but exhibit different pressure dependence behavior because of the  
214 differences in the local environment of hydroxyl within their structures. Some minerals  
215 accommodate hydroxyl both in an amphibole-like site (i.e. at the non-tetrahedral oxygens within  
216 the *t-o* structure) and in one or more additional non-equivalent sites. In the example of the  
217 serpentine group (Figure 6), the observed pressure dependences of some O-H stretching modes  
218 cluster well within those of the amphiboles, and others lie slightly outside the range described by  
219 the amphiboles.

220 In Figure 6, the observed correlation between 1-bar O-H stretching frequencies and their  
221 pressure dependences in amphiboles is shown in the larger context of minerals that host  
222 hydrogen in a variety of crystallographic environments. Obviously the correlation among  
223 amphiboles (and in phyllosilicates) does not extend to all OH-bearing minerals. The correlation  
224 described here (and in Figure 5) was identifiable in amphiboles and *t-o-t* phyllosilicates because  
225 of the wide compositional range over which high pressure IR absorption data were obtained for  
226 these mineral groups. It is reasonable to anticipate that O-H stretching modes in other mineral  
227 structures might also exhibit systematics among their pressure dependences that have so far  
228 remained unrealized because of the limited data available.

229 Using the high-resolution IR spectra available from this study, the relationship between  
230 frequency and pressure as a proxy for bond length within amphiboles was also investigated.  
231 Tremolite was singled out for this analysis, because as a near end-member composition it is  
232 particularly well-characterized even at high pressures. In this study three tremolite samples (L13,  
233 L14, L32), of two naturally occurring compositions, were compressed to pressures of 56, 37, and  
234 45.4 GPa respectively. O-H bond lengths were calculated using an isothermal bulk modulus ( $K_T$ )  
235 of 85 GPa from Comodi et al. (1991), a pressure derivative of the bulk modulus ( $K_T'$ ) fixed to 4,  
236 an estimated unit-cell volume of  $90 \text{ \AA}^3$ , and a 1-bar O-H bond length of  $0.957 \text{ \AA}$  (Hawthorne and  
237 Grundy, 1976) using a Vinet equation of state (Vinet et al. 1987) of the form:

$$P_{300}(V) = 3K_T \left( \frac{1 - \eta}{\eta^2} \right) e^{\frac{3}{2}(K_T' - 1)(1 - \eta)}$$

238 in which  $\eta = (V/V_0)^{1/3}$  and initial volume is  $V_0$ . The O-H bond length was assumed here to vary as  
239 the cube root of unit-cell volume, although it should be noted that tremolite does exhibit  
240 anisotropic compression (Comodi et al. 1991). Calculated pressures were matched to pressures  
241 obtained from the  $R_1$  luminescence line of ruby placed within the sample chamber of the  
242 diamond anvil cell. Badger (1934) proposed a general relationship between internuclear distance  
243 ( $r_e$ ) and force constant ( $k_0$ ) in binary molecules, as:

$$k_0(r_e - d_{ij})^3 = 1.86$$

244 in which  $k_0$  is given in N/cm,  $r_e$  is in Angstroms, and  $d_{ij}$  is a constant characteristic of a diatomic  
245 molecule with one element in the  $i$ th row and one element in the  $j$ th row. Oscillator frequency  
246 ( $\omega$ ) scales as  $k_0^2$ , so this equation suggests a linear relationship between  $\omega^{-2/3}$  and  $r_e$ . As shown in  
247 Figure 7, Badger's rule accurately describes the relationship between frequency and calculated  
248 bond length that we obtain from our tremolite data.

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## Implications

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Pressure induced hydrogen bond symmetrization, i.e. the shift from an asymmetric bonding configuration (O–H···O) to one in which the hydrogen is equidistant between two oxygens (O–H–O), has previously been detected in OH-bearing minerals (e.g., Xu et al. 2013). Our findings support and enhance previous observations that O-H bonds with high frequency stretching modes strengthen with pressure and are unlikely to participate in hydrogen bond symmetrization, whereas O-H bonds with low frequency stretching modes may soften with pressure. Furthermore, our findings demonstrate a relationship, linear over the range of minerals studied, between pressure shift and 1-bar frequency of the O-H modes in amphiboles. Neither composition nor symmetry plays a primary role in the pressure dependence of O-H stretching modes within this study. Additionally, a comparison of our findings to *t-o-t* phyllosilicate minerals (Figure 5), suggest that the stretching frequency at 1 bar is strongly associated with pressure dependence in O-H stretching in phyllosilicates as well. We propose that other structural groups of minerals might also show a clear relationship between 1 bar O-H stretching frequency and its pressure derivative, distinct from that shown for amphiboles. These relationships might be revealed through further systematic studies. Future high-pressure IR spectroscopy of hydrous minerals with improved spectral resolution, and especially single-crystal studies, would allow for a more refined understanding of the details of this relationship as a function of local hydroxyl environment.

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Our findings were in part enabled by our novel sample preparation technique, which improved the IR spectral resolution at higher pressures and enabled the simultaneous collection of well-defined Si-O and O-H stretching data at high pressure. Compared to the non-hydrostatic conditions achieved with a KBr pressure medium, the quasi-hydrostatic conditions of a neon-

273 loaded sample preserved much more sharply defined peaks, which proved essential to capturing  
274 the pressure dependence of O-H band frequency at high pressures (Figure 4). Technical  
275 advancements to preserve high spectroscopic resolution are increasingly important as increased  
276 pressures introduce complicating but unavoidable factors including structural disorder and  
277 pressure gradients within the measured sample. This new method will lend itself to the study of  
278 O-H stretching in a wide range of hydrous and nominally anhydrous minerals.

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## Figure Captions

412 **Figure 1.** Schematic of sample assemblies: **(a)** Previous studies which did not use a pressure  
413 medium or mix KBr with sample material were more likely to have preferred grain orientation,  
414 peak saturation, and larger pressure gradients; **(b)** Samples with KBr pressure medium and  
415 mixed KBr + sample platelets used in this study had reduced likelihood of grain orientation, peak  
416 saturation, and smaller pressure gradients; **(c)** Using mixed KBr + sample platelets while  
417 replacing KBr pressure medium with neon reduces deviatoric stresses, preserving sharper  
418 absorption peaks at high pressures.

419

420 **Figure 2.** Comparison of arfvedsonite (sample L30), anthophyllite (L31) and glaucophane (L24)  
421 peak occupations at ~12.5 GPa, with A, B, C, and D-bands corresponding to decreasing  
422 frequency. Circles indicate data points and dotted lines are the fitted peak shapes assigned based  
423 on that data.

424

425 **Figure 3.** High pressure, room temperature measurements of O-H frequencies within each  
426 sample composition in this study. Circles: individual peak positions. Different symbol colors are  
427 used for different compositions, and sample numbers appear in parenthesis. Compositional  
428 details available in Table 1. Error bars represent  $1\sigma$  uncertainties both in frequency and in  
429 pressure.

430

431 **Figure 4.** Comparison of spectral peak widths using a non-hydrostatic KBr pressure medium  
432 versus a quasi-hydrostatic Ne pressure medium. Both sets of measurements were made using the  
433 same mineral specimen (tremolite). Sample L13 (blue markers) was loaded in Ne and sample

19

434 L14 (red markers) was loaded using a KBr pressure medium. The same colors are used to  
435 identify samples within inset. Error bars represent  $1\sigma$  uncertainties.

436

437 **Figure 5.** Comparison of pressure dependence of O-H stretching frequency in amphiboles and  $t$ -  
438  $o$ - $t$  (talc and mica-like) phyllosilicates. Closed circles: this study; different shades of infill  
439 indicate the A, B, C, and D bands as identified in Figure 2 and Table 1. Open circles: other  
440 amphiboles, talc, and micas. All of these minerals containing analogous hydrogen bonding sites,  
441 at the non-tetrahedral oxygen in  $t$ - $o$ - $t$  layers. Error bars represent  $1\sigma$  uncertainties.

442

443 **Figure 6.** Comparison of pressure dependence of O-H stretching frequency in various minerals.  
444 Open circles: minerals containing only hydrogen bonding sites analogous to those in amphiboles.  
445 Cross symbols: minerals whose hydrogen accommodation mechanisms in the crystal structure  
446 are different from those in amphiboles. Open triangles: minerals containing both analogous and  
447 non-analogous hydrogen bonding sites. All literature data cited are from IR absorption studies,  
448 with the exception of Auzende et al. (2004), which used Raman spectroscopy.

449

450 **Figure 7.** Relationship between observed O-H frequency ( $\text{cm}^{-1}$ ) and O-H bond length calculated  
451 from amphibole compressibility using a Vinet equation of state. The vertical axis is in units of  
452 frequency<sup>(-2/3)</sup> to illustrate that the data conform to Badger's rule, which predicts a linear  
453 relationship between  $\omega^{-2/3}$  and  $r_e$ . Colors used here correspond to the same sample compositions  
454 as in Figure 3.

455

456

457

## Tables

458 Table 1. Compositions of samples from energy-dispersive spectrometry (EDS); presented as  
 459 cations per amphibole formula unit. All analyses are normalized to one hundred-oxide wt.% and  
 460 are averages of 5-10 point analyses within individual grains. Numbers in parentheses are  $1\sigma$   
 461 uncertainties on the last digit of each entry, and measured values smaller than  $1\sigma$  deviations have  
 462 been excluded from the table.

Sample	Na	Mg	Al	Si	Ca	Ti	Cr	Mn	Fe
L13, L14, tremolite	-	4.88(2)	0.06(2)	8.02(3)	1.76(2)	-	-	0.17(3)	-
L15, actinolite	-	4.35(2)	0.22(2)	7.91(3)	1.84(2)	-	0.05(2)	-	0.54(4)
L16, hornblende	-	4.34(2)	0.15(2)	7.96(3)	1.89(3)	-	0.03(2)	-	0.55(4)
L23, anthophyllite	0.15(2)	7.28(3)	3.41(3)	4.97(3)	-	-	-	-	0.56(4)
L24, glaucophane	1.75(2)	1.76(2)	1.10(2)	8.17(4)	0.06(1)	-	-	-	2.27(6)
R173, actinolite	0.21(2)	3.84(3)	0.33(2)	7.83(5)	2.02(4)	-	0.04(3)	-	0.78(6)
L26, L27, hornblende	0.72(2)	0.62(2)	6.04(4)	5.55(5)	0.03(2)	0.07(2)	-	-	1.66(8)
L30, arfvedsonite	2.77(2)	0.06(1)	0.23(1)	8.13(4)	0.04(1)	0.03(2)	-	0.16(3)	4.70(6)
L31, anthophyllite	0.10(2)	5.91(3)	-	8.44(3)	-	-	-	-	0.17(3)
L32, tremolite	0.32(2)	4.29(2)	0.19(2)	8.21(3)	1.77(3)	-	-	0.06(2)	-

463

464 Table 2. Pressure dependence of OH-frequencies within each sample. All values are in the units  
 465 of  $\text{cm}^{-1}\text{GPa}^{-1}$ . Numbers in parentheses are  $1\sigma$  uncertainties on the last digit of each entry.

Sample	D Band	C Band	B Band	A Band
L13, tremolite	-	-	-	1.43(04)
L14, tremolite	-	-	-	1.52(19)
L15, actinolite	-	-	1.03(17)	1.43(19)
L16, hornblende	-	-	0.92(13)	1.35(15)
L23, anthophyllite	-	-	-	2.32(19)
L24, glaucophane	0.26(08)	0.89(16)	1.33(16)	1.56(14)
R173, actinolite	-	0.07(06)	1.01(06)	1.63(03)
L26, hornblende	0.39(01)	0.37(05)	0.90(05)	1.34(04)
L27, hornblende	-0.30(04)	0.10(05)	1.08(14)	1.74(22)
L30, arfvedsonite	-0.33(01)	-0.04(04)	-	-
L31, anthophyllite	-	-	1.00(06)	1.43(08)
L32, tremolite	-	-	-	1.69(06)

466

467 Supplementary Table 1. Absorption peak positions, all values unless otherwise states in  $\text{cm}^{-1}$ .  
 468 Spectral resolution for all measurements is  $4\text{ cm}^{-1}$ . Pressure uncertainties on the last digit are in  
 469 parentheses.

Sample	A band	B band	C band	D band	Pressure (GPa)
L13 (tremolite)	3682(4)	-	-	-	2.7(03)
	3686(4)	-	-	-	4.7(05)
	3689(4)	-	-	-	7.1(1)
	3692(4)	-	-	-	9.9(1)

	3697(4)	-	-	-	13.0(1)
	3701(4)	-	-	-	15.0(2)
	3703(4)	-	-	-	17.5(2)
	3707(4)	-	-	-	21.0(2)
	3710(4)	-	-	-	25.0(3)
	3714(4)	-	-	-	27.0(3)
	3719(4)	-	-	-	31.5(3)
	3720(4)	-	-	-	34.0(3)
	3723(4)	-	-	-	37.0(4)
	3727(4)	-	-	-	41.0(4)
	3730(4)	-	-	-	43.1(4)
	3733(4)	-	-	-	45.1(5)
	3734(4)	-	-	-	48.0(5)
	3736(4)	-	-	-	51.2(5)
	3737(4)	-	-	-	54.0(5)
	3743(4)	-	-	-	56.0(6)
	3733(4)	-	-	-	58.1(6)
<b>L14 (tremolite)</b>	3674(4)	-	-	-	0.4(02)
	3677(4)	-	-	-	1.5(08)
	3683(4)	-	-	-	3.4(2)
	3693(4)	-	-	-	8.5(4)
	3698(4)	-	-	-	13.5(7)
	3701(4)	-	-	-	18.6(9)
	3709(4)	-	-	-	24.0(12)
	3715(4)	-	-	-	30.1(15)
	3719(4)	-	-	-	37.0(19)
<b>L15 (actinolite)</b>	3679(4)	3663(4)	-	-	3.1(2)
	3686(4)	3669(4)	-	-	6.0(3)
	3694(4)	3671(4)	-	-	11.2(6)
	3698(4)	3677(4)	-	-	14.0(7)
	3699(4)	3678(4)	-	-	17.5(9)
	3702(4)	3678(4)	-	-	21.5(11)
	3711(4)	3684(4)	-	-	28.5(14)
	3709(4)	3685(4)	-	-	32.5(16)
	3722(4)	3693(4)	-	-	39.5(20)
	3726(4)	3694(4)	-	-	43.0(22)
	3731(4)	3693(4)	-	-	48.0(24)
	3733(4)	3690(4)	-	-	52.5(26)
	3737(4)	3696(4)	-	-	56.5(28)
	3738(4)	3695(4)	-	-	60.5(30)
<b>L16 (hornblende)</b>	3695(4)	3663(4)	-	-	3.0(2)
	3686(4)	3670(4)	-	-	7.8(4)
	3694(4)	3671(4)	-	-	11.5(6)
	3702(4)	3679(4)	-	-	19.5(10)
	3718(4)	3687(4)	-	-	28.5(14)
	3729(4)	3697(4)	-	-	34.0(17)
	3726(4)	-	-	-	40.1(20)
<b>L23 (anthophyllite)</b>	3676(4)	-	-	-	0.7(01)
	3678(4)	-	-	-	1.8(02)
	3680(4)	-	-	-	3.2(03)
	3683(4)	-	-	-	4.8(05)
	3698(4)	-	-	-	10.0(1)
<b>L24 (glaucophane)</b>	-	3664(4)	3649(4)	3618(4)	1.1(01)
	-	3676(4)	3660(4)	3621(4)	7.0(07)
	-	3884(4)	3667(4)	3622(4)	12.7(1)
	-	-	3672(4)	3622(4)	17.8(2)
	-	-	3677(4)	3622(4)	20.6(2)
	-	-	3687(4)	-	30.7(3)
	-	-	3690(4)	-	38.0(4)
	-	-	3689(4)	-	42.2(4)
<b>R173 (actinolite)</b>	3678(4)	3663(4)	3648(4)	-	2.0(1)
	3680(4)	3666(4)	3649(4)	-	3.3(2)
	3682(4)	-	-	-	4.5(2)
	3691(4)	3672(4)	-	-	10.0(5)
	3694(4)	3674(4)	3648(4)	-	12.5(6)
	3697(4)	3675(4)	-	-	13.8(7)
	3701(4)	3679(4)	3649(4)	-	16.3(8)
	3711(4)	3676(4)	3649(4)	-	23.5(12)
	3719(4)	3687(4)	3656(4)	-	31.5(16)
	3720(4)	3689(4)	-	-	33.8(17)

3724(4)	3693(4)	-	-	36.5(18)	
3726(4)	3693(4)	-	-	38.3(19)	
3727(4)	-	-	-	40.5(20)	
3728(4)	-	-	-	43.3(22)	
3730(4)	-	-	-	44.8(22)	
3732(4)	-	-	-	47.5(24)	
<b>L26 (hornblende)</b>	3673(4)	3659(4)	3647(4)	3622(4)	1.2(06)
	3676(4)	3661(4)	3648(4)	3623(4)	3.0(2)
	3681(4)	3665(4)	3650(4)	-	6.5(3)
	3684(4)	3666(4)	3651(4)	-	8.5(4)
	3692(4)	3672(4)	3653(4)	-	15.3(8)
	3696(4)	3674(4)	3653(4)	-	18.1(9)
	3702(4)	3675(4)	-	-	23.0(12)
	3710(4)	-	-	-	28.5(14)
<b>L27 (hornblende)</b>	3675(4)	3659(4)	3649(4)	3620(4)	2.3(1)
	3679(4)	3662(4)	3648(4)	3620(4)	3.0(2)
	3681(4)	3667(4)	3649(4)	3620(4)	6.3(3)
	3691(4)	3673(4)	3649(4)	3620(4)	13.1(7)
	-	-	3651(4)	3620(4)	16.8(8)
	3703(4)	3676(4)	3650(4)	3620(4)	22.9(11)
	3710(4)	-	3650(4)	3620(4)	27.8(14)
<b>L30 (arfvedsonite)</b>	-	-	3649(4)	3620(4)	9.2(5)
	-	-	3649(4)	3619(4)	12.9(6)
	-	-	-	3617(4)	16.1(8)
	-	-	3649(4)	3616(4)	20.0(10)
	-	-	3649(4)	3611(4)	24.5(12)
	-	-	3649(4)	3606(4)	28.4(14)
	-	-	3649(4)	3601(4)	32.6(16)
	-	-	3649(4)	3597(4)	36.2(18)
	-	-	3649(4)	3597(4)	38.3(19)
	-	-	3649(4)	3596(4)	40.6(20)
	-	-	3649(4)	3595(4)	43.0(22)
<b>L31 (anthophyllite)</b>	3683(4)	3665(4)	-	-	5.3(3)
	3684(4)	3665(4)	-	-	6.8(3)
	3687(4)	3667(4)	-	-	9.2(5)
	3690(4)	3670(4)	-	-	10.8(5)
	3693(4)	3672(4)	-	-	12.3(6)
	3696(4)	3674(4)	-	-	14.7(7)
	3703(4)	3678(4)	-	-	19.9(10)
	3714(4)	-	-	-	22.1(11)
	3732(4)	-	-	-	30.2(15)
	3741(4)	-	-	-	33.0(17)
	3761(4)	-	-	-	37.3(19)
	3776(4)	-	-	-	39.8(20)
	3788(4)	-	-	-	43.0(22)
	3799(4)	-	-	-	46.2(23)
	3809(4)	-	-	-	48.5(24)
	3823(4)	-	-	-	50.6(25)
<b>L32 (tremolite)</b>	3682(4)	-	-	-	4.4(2)
	3683(4)	-	-	-	6.4(3)
	3689(4)	-	-	-	8.9(4)
	3691(4)	-	-	-	10.2(5)
	3693(4)	-	-	-	11.5(6)
	3693(4)	-	-	-	12.7(6)
	3698(4)	-	-	-	14.1(7)
	3701(4)	-	-	-	15.7(8)
	3705(4)	-	-	-	18.4(9)
	3710(4)	-	-	-	22.9(11)
	3716(4)	-	-	-	28.9(14)
	3719(4)	-	-	-	32.3(16)
	3722(4)	-	-	-	35.5(18)
	3724(4)	-	-	-	37.8(19)
	3729(4)	-	-	-	42.8(21)
	3732(4)	-	-	-	45.4(23)













