

1 **High-pressure study of dravite tourmaline: Insights into the accommodating nature of the**
2 **tourmaline structure**

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10**Abstract**

11 The high-pressure behavior of dravite tourmaline [Na(Mg₃)Al₆(Si₆O₁₈)
12(BO₃)₃(OH)₃(OH)] has been studied using luminescence spectroscopy and synchrotron based
13single-crystal diffraction up to ~65 and ~23.6 GPa, respectively. Two emission bands associated
14with Cr³⁺/V²⁺ substitution are constant in energy up to ~9.0 GPa, and shift to longer wavelength
15at higher pressures, suggesting that a change in compressional mechanism could occur at this
16pressure. However, single-crystal diffraction data do not show evidence of any structural
17changes, nor any resolvable changes in the deformation mechanism at ~9.0 GPa. Near 15 GPa, a
18splitting of one of the emission bands is observed, suggesting that a phase transition occurs at
19this pressure and that two unique octahedral sites are present in the high-pressure phase.
20Hysteresis is not observed on decompression, which indicates that this is a second order
21transition, and the high-pressure structure appears to be metastable up to ~65 GPa. Single-
22crystal diffraction measurements show that a phase transition from rhombohedral *R3m* to
23rhombohedral *R3* occurs at pressures near 15.4 GPa. The high-pressure phase is characterized

24by a distorted Si_6O_{18} ring (e.g. the Si-Si-Si angles deviate from 120°), and the Si, Al, O6, O7, and
25O8 sites of the low-pressure phase split, implying that the high-pressure phase of tourmaline is
26a higher entropy phase. The large X-site exerts the primary control on compressibility, and the
27substitution of larger cations into this site will likely lower the pressure at which this transition
28occurs. Dravite tourmaline shows anisotropic compression with the c-axis being more
29compressible than the a-axis. The pressure volume data up to ~ 15.4 GPa were fit with 2nd and
303rd order Birch-Murnaghan equations of state. We obtain a bulk modulus, $K_0 = 109.0(2.9)$ GPa,
31and a pressure derivative $K_0' = 4.8(8)$ GPa, and with the pressure derivative set to 4, a bulk
32modulus of $112.2(9)$ GPa is derived.

33**Key Words:** dravite; High-pressure; Single-crystal diffraction, luminescence, phase transitions

34Introduction

35 Tourmaline is a supergroup of minerals that is chemically complex and is divided into
36different varieties based on chemical composition (Hawthorne and Henry 1999; Henry et al.
372011). This group of minerals is so complex and chemically variable that an entire subcommittee
38on tourmaline nomenclature exists. These minerals are categorized using the generalized
39tourmaline structural formula $\text{XY}_3\text{Z}_6(\text{T}_6\text{O}_{18})(\text{BO}_3)_3\text{V}_3\text{W}$ where $X = \text{Na, Ca, K}$; $Y = \text{Fe, Mg, Mn, Al, Li}$;
40 $Z = \text{Al, Fe, Mg, Cr}$; $T = \text{Si, Al}$; $B = \text{B}$; $V = (\text{OH}), \text{O}$; and $W = (\text{OH}), \text{O, F}$ (Hawthorne and Henry 1999;
41Henry et al. 2011). From a compositional perspective, most of the variability occurs in the X, Y,
42and Z sites; more information on the classification of tourmaline supergroup minerals can be
43found in Hawthorne and Henry (1999) and Henry et al. (2011). Tourmaline is also highly sought
44after as a gemstone due to its high hardness and wide range of colors.

45 Tourmaline typically crystallizes in the rhombohedral crystal system with $R3m$ symmetry
46(Hawthorne and Henry 1999; Henry et al. 2011), although other crystal systems have been
47reported (Akizuri et al. 2001; Shtukenberg et al. 2007). It is typically considered a ring-silicate
48with six corner-shared TO_4 tetrahedral sites that form a hexagonal ring, a nine-fold X -site, two
49six-fold octahedral Y - and Z -sites, and a trigonal planar B -site (Figure 1). Although the T -sites are
50dominantly occupied by Si , B and Li substitution into them has been reported (Rosenberg and
51Foit 1979; Hughes et al. 2000). Interestingly, the first reported structure of tourmaline
52presented the Si_6O_{18} ring as ditrigonal in symmetry (Hamburger and Buerger 1948). However, it
53was later shown to be hexagonal in symmetry (Ito and Sadanaga 1951), and all subsequent
54studies agree that the Si_6O_{18} ring is hexagonal at ambient conditions.

55 Tourmaline is the most widespread borosilicate mineral in natural rocks and the
56dominant carrier of B in many rock types (Henry and Dutrow, 1996), and is found in subduction
57zone environments (Nakano and Nakamura 2001; Bebout and Nakamura 2003; Ota et al. 2008).
58 B isotope systematics in tourmalines have been used to elucidate crust-mantle recycling
59processes in subduction zones (Nakano and Nakamura, 2001). Petrologic studies have shown
60that dravite tourmaline breaks down at ~ 7.0 GPa and ~ 900 °C (Werding and Schreyer 1996) and
61 ~ 3 - 5 GPa and ~ 1000 °C (Krosse 1995) and that breakdown pressures and temperatures are
62dependent on its precise composition (Ota et al. 2008). The decomposition products associated
63with tourmaline breakdown are complex, but one decomposition product, phengite, is
64important from a deep Earth boron and water cycling perspective; phengite could transport B to
65depths >300 km (Domanik and Holloway 1996; Marschall et al. 2007). Higher pressure studies
66(e.g. > 7.0 GPa) on tourmaline are scarce, and only two studies appear to have been reported: Li

67 et al., (2004) and Xu et al., (2016). Li et al. (2004) conducted high-pressure powder diffraction
68 experiments on schorl tourmaline $[\text{Na}(\text{Fe}_3)\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3(\text{OH})]$ up to 27.8 GPa, with no
69 phase transitions being reported. Xu et al. (2016) reported high-pressure and temperature
70 powder diffraction experiments on uvite tourmaline $[\text{Ca}(\text{Mg}_3)\text{MgAl}_5(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3(\text{OH})]$ up
71 to ~18.4 GPa and 723 K and again, no phase transitions were observed. These powder
72 diffraction studies provide insights into how the unit cell responds to compression, but they do
73 not elucidate the positional changes of the individual atoms in the unit cell (Li et al. 2004; Xu et
74 al. 2016).

75 This is in contrast to other ring-silicates such as cordierite $[(\text{Mg}, \text{Fe})_2\text{Al}_3(\text{AlSi}_5\text{O}_{18})]$ and
76 beryl $[\text{Be}_3\text{Al}_2(\text{Si}_6\text{O}_{18})]$ which each show extensive high-pressure polymorphism (Prencipe et al.
77 2011; Miletich et al. 2014; Scheidl et al. 2014; Finkelstein et al. 2015; O'Bannon and Williams
78 2016b). Both cordierite and beryl undergo high-pressure phase transitions that involve
79 distortion of the Si_6O_{18} ring. The main structural difference between tourmaline and these other
80 ring silicates is that tourmaline does not have open channels in its structure like cordierite and
81 beryl. Thus, it is possible that the denser-packed configuration of the Si_6O_{18} rings in tourmaline
82 produces a structure that is more stable under compression than open channel ring silicates like
83 cordierite or beryl.

84 Tourmaline is also both pyroelectric and piezoelectric, and has been used in industrial
85 applications such as pressure gauges and air and water purifiers (Fron del 1948; Lameiras et al.
86 2010). Growing synthetic tourmalines >1mm in diameter has not yet been achieved, and thus
87 industrial applications require natural tourmalines (Shekhar Pandey and Schreuer 2012). Thus,
88 despite its widespread use in industrial applications and as a geochemical probe, tourmaline's

89high-pressure stability/polymorphism is poorly understood. Hence, our experiments are
90oriented towards understanding the trace element behavior and the bulk structural response of
91dravite tourmaline to compression by combining the results of luminescence and single-crystal
92diffraction studies to provide an integrated picture of structural changes in dravite tourmaline
93under compression.

94**Methods**

952.1 *Sample characterization*

96 The natural light green gem quality tourmaline sample used in this study is from the
97Lengenbach Quarry, Switzerland. We characterized the sample with single-crystal X-ray
98diffraction, Raman, and luminescence spectroscopy, which all agree well with previous studies
99(Hawthorne et al. 1993; Gasharova et al. 1997; Gaft et al. 2005). Ambient pressure single-crystal
100X-ray measurements were conducted on Beamline 11.3.1 at the Advanced Light Source (ALS) at
101Lawrence Berkeley National Lab in Berkeley, CA. We modeled our tourmaline as an endmember
102dravite and our ambient structure refines with an R_1 of 1.85% when refined anisotropically and
1032.99% when refined isotropically. Its crystal system, spacegroup and unit cell parameters are:
104rhombohedral $R3m$, a -axis 15.9370(6) Å, c -axis 7.1749(3) Å, and volume 1578.19(14) Å³,
105respectively. For the ambient structure refinement, we fixed the O1-H1 and O3-H3 bond lengths
106to 0.958(8) and 0.972(2) Å, respectively. These bond lengths were determined from previous
107neutron diffraction results on tourmaline (Gatta et al. 2014). Trace element concentrations of
108dravite tourmaline were measured with a PhotonMachines Analyte 193H, which is a 193-nm
109ArF excimer laser system coupled with a ThermoScientific ElementXR single-collect or magnetic
110sector ICP-MS. The instrument was calibrated with a SRM 610 trace element glass from NIST,

111 and Al was used as the internal standard. The following trace elements were measured (in
112 ppm): Cr 215 (± 19), V 336 (± 32), Li 18 (± 4.0), Ti 474 (± 53), Ca 2183 (± 597), and K, Fe, and Mn are
113 below detection limits. The Subcommittee on Tourmaline Nomenclature (STN) of the IMA
114 Commission on New Minerals, Nomenclature and Classification recommends nomenclature of
115 tourmaline supergroup minerals (Novak et al., 2009; Henry et al., 2011; Hawthorne and Dirlam,
116 2011). Using our single-crystal X-ray results combined with our trace element results, and
117 following STN recommendations, we determined that this tourmaline is of the dravite variety.
118 Dravite variety tourmaline has an ideal chemical formula of $[\text{Na}(\text{Mg}_3)\text{Al}_6(\text{Si}_6\text{O}_{18})$
119 $(\text{BO}_3)_3(\text{OH})_3(\text{OH})]$. Hence, the structures were refined isotropically and modeled as
120 endmember dravite tourmaline: this allowed direct comparisons of the results obtained at each
121 pressure.

122 2.2 Luminescence spectroscopy

123 Luminescence spectra were collected from 650-800 nm (15380 - 12500 cm^{-1}) with a
124 Horiba LabRAM HR Evolution Raman spectrometer with a spectrometer focal length of 800 mm.
125 Spectra were collected to a pressure of ~ 65 GPa and on decompression at 300 K using an
126 excitation wavelength of 532 nm. A symmetric type DAC with 200 μm type-Ia diamonds was
127 used in all high-pressure luminescence experiments, and single crystals of the sample and at
128 least two ruby spheres (Chervin et al. 2001) were loaded into the sample compartment. Either
129 4:1 methanol:ethanol mixtures or Ne was used as the pressure medium depending on the
130 target pressure range of the experiment. An Olympus BXF-ILHS microscope with a 50x long
131 working distance objective was used to focus the laser beam onto the sample. An 1800
132 lines/mm grating with a corresponding spectral resolution of ~ 1 cm^{-1} (or, equivalently, ~ 0.05 nm)

133 was utilized. Combinations of Gaussian and Lorentzian functions were fit to the luminescence
134 spectra with Horiba LabSpec6 software.

135 2.3 High-pressure single crystal diffraction

136 High-pressure single-crystal measurements were carried out using a (DESY) BX90 (Kantor
137 et al. 2012) type diamond anvil cell (DAC) equipped with type Ia 500 μm culet Boehler-Almax
138 geometry diamond anvils with 85° angular access (Boehler and De Hantsetters 2004). Rhenium
139 gaskets with a 300 μm hole were used to contain the samples. Gasket holes were cut using an
140 Oxford Instruments laser mill at the Advanced Light Source (ALS), Berkeley, CA. Single crystals of
141 dravite tourmaline and two ruby spheres were loaded into the sample compartment with neon
142 as the pressure medium. The standard ruby fluorescence gauge was used to determine pressure
143 (Mao et al. 1986). Neon was loaded using the gas loading apparatus at the ALS. Neon remains
144 hydrostatic up to ~ 15.0 GPa and above that pressure, the pressure gradients remain small (Klotz
145 et al. 2009).

146 High-pressure single-crystal X-ray diffraction measurements were conducted at Beamline
147 12.2.2 at the ALS. Measurements were taken at various pressures up to ~ 23.6 GPa at room
148 temperature. The DAC was mounted on a Huber sample stage, and shutterless single-crystal
149 diffraction data were collected on a Perkin Elmer amorphous silicon detector using synchrotron
150 radiation monochromated by silicon(111) to a wavelength of 0.49594 \AA (25 keV). Distance and
151 wavelength calibrations were done using a NIST single crystal ruby diffraction standard. Phi
152 scans were employed to measure across both diamonds with a 0.25° image width.

153 2.4 Data processing

154 Image masks, to avoid integrating signal from detector regions obscured by the DAC,

155 were created using the program ECLIPSE (Parsons 2010). The data were integrated using the
156 program SAINT v8.34A. A multi-scan correction for absorption was applied using the program
157 SADABS-2014/11. Structures were solved by dual space methods (SHELXS-97/ SHELXT) and
158 refined by full-matrix least-squares on F^2 (SHELXL-2014) (Sheldrick 2008) using the graphical
159 user interface *ShelXle* (Hübschle et al. 2011). All atoms in the room pressure structure and the
160 high-pressure structures were refined isotropically. Because of their small scattering cross-
161 sections, H atoms were not refined in the high-pressure structures. Complete crystallographic
162 information files (CIFs) for each structure can be found in supplementary material, as well as a
163 discussion on the selection of our unit cells.

164 Results and discussion

165 Ambient pressure luminescence spectra

166 The luminescence spectrum of dravite is characteristic of d^3 ions (e.g. Cr^{3+} , V^{2+}) in an
167 intermediate strength crystal field (Tanabe and Sugano 1954). Both sharp and broad emission
168 bands are observed at room temperature and 77 K at ambient pressures (Figure 2). Considering
169 the similar concentrations of Cr and V in our sample (e.g. Cr: 215 ± 19 ppm, V: 336 ± 32 ppm), it
170 is reasonable to assume that our steady state luminescence spectra contain overlapping bands
171 from the emission of both Cr and V. This is commonly observed in emerald, which is the Cr and
172 V rich variety of beryl (Ollier et al. 2015; O'Bannon and Williams 2016b). The intense and
173 relatively sharp emission bands are commonly referred to as the R-lines and are associated with
174 the spin-forbidden ${}^2\text{E}-{}^4\text{A}_2$ transition, with the ${}^4\text{A}_2$ state being the ground state and the ${}^2\text{E}$ state
175 being split in non-cubic environments (Syassen 2008), and the broad band emission is assigned
176 to the spin-allowed ${}^4\text{T}_2-{}^4\text{A}_2$ transition (Sugano and Tanabe 1958; Burns 1993; Gaft et al. 2005).

177 At 300 K, three bands can be fit under the sharp emission bands and two can be fit
178 under the broad portion of the spectrum at room temperature. At 77 K, the broad thermally
179 populated 4T_2 -associated bands are not entirely quenched, and four bands can be fit under the
180 sharp emission bands. A detailed deconvolution of these sharp line emission bands at both
181 room temperature and 77 K is given in the supplementary material (Figure S1). Dravite has two
182 crystallographically unique octahedral sites, Al and Mg, and emission bands from both sites
183 would likely be observed in steady state luminescence spectra. The simplest way for Cr^{3+} and V^{2+}
184 to substitute into dravite is through isovalent substitutions (e.g. Cr^{3+} into Al^{3+} site and V^{2+} into
185 Mg^{2+}). The four ~~deconvolved~~ deconvoluted components at 77 K thus can be attributed to two
186 sets of R-lines, one set from Cr^{3+} and one from V^{2+} . The Al site in dravite is less distorted than the
187 Mg site (Hawthorne et al. 1993, and this study), which would be expected to give rise to a
188 narrower R-line splitting. Given the likely relative intensities of R_1 and R_2 and the anticipated
189 relative splittings, we propose the following assignments: the Cr^{3+} R_1 band is likely located at
190 683.7 nm, with its R_2 band at 681.4 nm, and the V^{2+} R_1 band is at 686.4 nm and its associated R_2
191 band at 679.8 nm. This results in an R-line splitting of $\sim 50\text{ cm}^{-1}$ for Cr^{3+} and $\sim 143\text{ cm}^{-1}$ for V^{2+} . For
192 comparison, ruby [$Al_2O_3:Cr$] has an Al-site that is close to an ideal octahedron with a slight
193 trigonal distortion, and has an R-line splitting of $\sim 29\text{ cm}^{-1}$ (Syassen 2008), while zoisite
194 [$Ca_2Al_3Si_3O_{12}(OH)$] which has a highly distorted Al-site has an R-line splitting of $\sim 340\text{ cm}^{-1}$
195 (Kozarska et al. 1994). The distortions of the Al and Mg sites in dravite fall intermediate
196 between the distortions of the Al sites in ruby and zoisite, so these R-line splittings are plausible.
197 To confirm the assignments of these emission bands, luminescence lifetime measurements or
198 variably substituted samples would be required.

199 *High-pressure luminescence spectra*

200 High-pressure luminescence spectra are shown in Figure 3. Under compression the
201 intensity of the R-lines decreases: this is likely primarily associated with the transition metal
202 absorption bands migrating away from our excitation wavelength of 532 nm. Moreover, the
203 disappearance of the broad 4T_2 -associated band shows that a transition from an intermediate to
204 strong crystal field occurs in the first few GPa of compression, which is consistent with previous
205 observation in other Cr-bearing oxides (Dolan et al. 1986; de Viry et al. 1987; Hommerich and
206 Bray 1995; Grinberg and Suchocki 2007; O'Bannon and Williams 2016b). As at 300 K, it is
207 difficult to fit four bands under the 2E region under compression, so we fit the spectra with
208 three bands: based on our 77 K assignments, these are associated with the R_1 and R_2 peaks of
209 Cr^{3+} and the R_1 peak of V^{2+} . Near 6.0 GPa, the primary emission feature fit by three bands clearly
210 separates into individual peaks (Figure 3).

211 The pressure shift of two of the original three bands that were fit at ambient pressure
212 and temperature shift negligibly--essentially by 0 nm/GPa up to ~9 GPa, while the other band
213 shifts by 0.50 ± 0.02 nm/GPa ($-8.8 (\pm 0.3)$ cm^{-1}/GPa) up to the same pressure (Figure 4a). The
214 observation of effectively stationary emission bands under compression is without precedent
215 among Cr^{3+} emission in oxides (e.g., Dolan et al. 1986; Mao et al. 1986; de Viry et al. 1987;
216 Hommerich and Bray 1995; Grinberg and Suchocki 2007; O'Bannon and Williams 2016b). Above
217 ~9.0 GPa, the initially stationary bands begin to shift positively in wavelength, towards lower
218 energies (Figure 4b). The two bands that shift by 0 nm/GPa likely are associated with one
219 octahedral site while the other band is produced by substitution in the other octahedral site.

220 This is in accord with our assignment of the former two bands to emission from Cr^{3+} substituting
221 into the Al^{3+} site.

222 Four separate experiments were conducted in the ≤ 10.5 GPa range to assess the
223 reproducibility of the unusual negligible pressure shift. It is completely reproducible, and no
224 hysteresis is observed on decompression from ~ 10.5 GPa. The ~ 0 nm/GPa pressure shift
225 suggests one of three possibilities. First, the crystallographic site that this band is emitting from
226 may not be changing in volume under compression. Second, there may be a complex trade-off
227 between electron density and volumetric change within the site. Third, an admixture of
228 electronic states, rather than a pure ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transition, may generate the observed sharp-line
229 emission. As described in the single-crystal diffraction section below, there is no structural
230 “smoking gun” for this unusual pressure shift. Admixture of states (probably with the ${}^4\text{T}_2$ state)
231 is a possibility; however, the troubling aspect of this explanation is that a pressure-induced shift
232 in admixture must perfectly balance with the pressure shifts of the two states to produce a net
233 zero pressure shift. Stated another way, the separation of the two states, their resulting
234 admixture, and their pressure shifts must collectively sum to zero for ~ 9.0 GPa of compression.
235 This scenario is quite unlikely because of the dramatically different pressure-dependences of
236 the ${}^4\text{T}_2$ and ${}^2\text{E}$ states (e.g., O’Bannon and Williams 2016a), but could be testable with high-
237 pressure lifetime measurements. A trade-off between changes in electron density and
238 volumetric compaction is possible, but would require detailed insights into the bonding
239 environment/electron density within the octahedral site under compression.

240 The splitting between these two bands also does not change on compression, suggesting
241 that the site distortion is unchanged, as well. The change in slope at 9 GPa is, as described

242below, likely not an indicator of a phase transition, but may represent a change in the
243compression mechanism. Moreover, the other observed emission band shifts positively in
244wavelength, consistent with the volume of this site decreasing with increasing pressure. Since
245we cannot deconvolve the expected R_2 component of this band in this pressure range, it is
246difficult to know from the emission spectra if this site becomes more or less distorted. However,
247the peakwidth of the positively shifting band slightly narrows under compression to ~ 9.0 GPa,
248which is an indicator that its site becomes less distorted under compression.

249 In the pressure range above 10 GPa, peak splitting is observed near 15 GPa, with new
250emission bands observed; at pressures above 45 GPa, non-linear pressure shifts are observed
251(Figure 3, 4b). No hysteresis is observed in the emission on decompression from 65 GPa, and the
252Raman spectrum of the decompressed sample is identical to the starting material. Peak splitting
253of emission bands under compression has been shown to be an indicator of phase transitions
254(O'Bannon and Williams 2016a,b). This is particularly anticipated when multiple octahedral
255environments are produced by a decrease in symmetry associated with a phase transition. For
256example, in the ring silicate beryl, the Cr^{3+} R-lines split into two sets of R-lines near 14.7 GPa
257(O'Bannon and Williams, 2016b) which agrees well with a theoretically predicted ~ 15 GPa soft-
258mode transition (Prencipe et al. 2011), as well as high-pressure single crystal diffraction studies
259which show that the Al-site splits into two crystallographically unique sites near 15 GPa (M.
260Merlini, personal communication). The peak splitting observed in dravite tourmaline under
261compression provides clear evidence that one of the octahedral sites splits into two unique sites
262(Figure 5).

263 The additional new bands at longer wavelength that appear above 10 GPa (Figures 3, 4b)
264are likely neighbor lines that are due to paired Cr-Cr emission (e.g., O'Bannon and Williams,
2652017); vibronic lines may also lie at these wavelengths, but these typically do not dramatically
266exceed the zero-phonon lines in amplitude. The appearance of these new bands, and the
267progressive increase in their intensity with pressure may reflect: (1) the intensity of the broad
268 4T_2 transition has decreased substantially by this pressure and alternate mechanisms for
269emission are enhanced; (2) a change in the nearest neighbor configuration due to the splitting
270of one of the octahedral sites into two unique sites that produces configurations that favor
271energy transfer into and/or the magnetic interactions that generate emission from pairs; and/or
272(3) a pressure-induced shift in absorption that results in preferential excitation of pair-line
273emissions (e.g., O'Bannon and Williams 2017). Within the tourmaline structure, there are a
274wide range of possible prospective pair-wise magnetic interactions that could occur between
275substituents in the octahedral sites through an intervening anion, and it is well-known that the
276strength of such exchanges depends strongly on both the inter-ion distance and on the angle
277(e.g., McCarthy and Gudel 1988). Indeed, such pair-wise interactions between transition metals
278have long been recognized to be important within the optical spectrum of tourmalines (Mattson
279and Rossman 1987). Therefore, while the exact origin of the new bands and the shift in intensity
280above 10 GPa within the emission spectra remain unclear, it is probable that they can be
281attributed to pressure-enhanced pair-line emissions.

282 Thus, the major effects of compression on the luminescence spectrum are the change in
283pressure shift near 9.0 GPa and the peak splitting and increased intensities of new peaks
284observed at ~15 GPa. The lack of hysteresis on decompression from ~65 GPa indicates that any

285 phase transition associated with these changes is second order. We do not believe that the
286 change observed at 9.0 GPa is produced by a pressure-induced structural phase transition, but
287 is likely generated by either a change in compression mechanism or a progressive change in the
288 electron density associated with the site. The changes observed at ~15 GPa are, however,
289 consistent with a phase transition that involves a subtle distortion of the overall structure of
290 dravite tourmaline that splits the Al-site into two unique sites. By analogy to high-pressure
291 phase transitions in cordierite and beryl (Prencipe et al. 2011; Miletich et al. 2014; Finkelstein et
292 al. 2015; O'Bannon and Williams 2016b), the structural change likely involves a modest
293 distortion of the Si_6O_{18} ring away from hexagonal symmetry. Importantly, the overall topology of
294 the structure appears to be preserved, and a lowering of symmetry from rhombohedral is
295 unlikely. The presence of such a modest structural change implies that dravite tourmaline's
296 metastability under room temperature compression to ~65 GPa is generated by the topology of
297 the structure that stabilizes the Si_6O_{18} ring at high compressions. Moreover, a structural
298 transition that involves a modest distortion of the Si_6O_{18} ring with no change in crystal system
299 would be difficult to constrain with powder diffraction techniques (e.g., Li et al. 2004; Xu et al.
300 2016).

301 *High-pressure single-crystal diffraction*

302 To characterize the changes observed using luminescence spectroscopy, single crystal X-
303 ray diffraction measurements were done at various pressures up to ~23.6 GPa. Dravite
304 tourmaline indexes to a rhombohedral unit cell across the pressure range of the X-ray
305 measurements. Structures solved as rhombohedral $R3m$ up to ~15.4 GPa, and above this
306 pressure the space group changed to $R3$. In the following sections, we discuss the equation of

307state (EoS) for the low pressure phase of dravite tourmaline, and the high-pressure crystal
308structure of this material.

309*Dravite tourmaline EoS*

310 Dravite tourmaline shows highly anisotropic compression (Figure 6), with the *c*-axis
311being substantially more compressible than the *a*-axis, which is in good agreement with the
312previous study of uvite tourmaline reported by Xu et al. (2016). Interestingly, Liu et al. (2004)
313report that the *c*-axis of schorl tourmaline is less compressible than the *a*-axis, which is opposite
314of what is observed in dravite and uvite tourmaline. But, the lattice parameters and unit cell
315volumes reported by Liu et al. (2004) are quite scattered. For clarity, we do not include these
316results in Figure 6, but they are included in supplementary Figure S2. The reason for the scatter
317in their data, and the difference in compressibility of the *a*- and *c*-axes is not clear, but could be
318a result of non-hydrostatic conditions of methanol:ethanol mixtures above ~10.5 GPa. We fit
319our pressure volume data with both 2nd and 3rd order Birch-Murnaghan equations of state (Table
3201) using the EOSFit7GUI (Angel et al. 2014), and our results are shown in Table 2. An *F-f* plot
321based on the Birch-Murnaghan EoS fit of the volume data is shown in Figure S3. Our results
322indicate that dravite tourmaline is more compressible than uvite tourmaline. For comparison,
323the uvite sample measured by Xu et al. (2016) is not an endmember, but has ~10 % Na in the X-
324site, and pure uvite is likely less compressible than their measurements. The relatively large
325value for K_0 reported for schorl tourmaline by Li et al. (2004) does not appear compatible with
326our results, nor with those of Xu et al. (2016).

327*High-pressure crystal structures*

328 Structures were solved at various high pressures, and results of the structure
329refinements are shown in Table 3. The site volumes as a function of pressure show that the Na
330site is the most compressible (Figure 7). The Si site is the least compressible, while the two
331octahedral sites behave essentially identically to one another, and are intermediate in their
332compressibility between the Si and Na sites. Clearly, neither octahedral site volume is constant
333under compression. So, the unusual observation of a negligible pressure shift of two of the
334luminescence bands cannot be explained via a site volume argument alone. A more nuanced
335explanation for the shift of the energy levels, involving a shift in covalency/electron density of
336the site that counterbalances the volumetric compaction, appears necessary. The anisotropic
337compression of dravite tourmaline can be straightforwardly explained by the location of the Na
338site in the dravite structure and its large volume change under compression (Figure 7).
339Speculatively, the large volume change in the Na site could produce a pressure-induced
340reduction in the electron density around the Al-sites, such that their electron density remains
341fairly constant under compression up to ~9.0 GPa.

342 We calculate the distortion parameters for the octahedral and tetrahedral sites as a
343function of pressure (Supplementary Figure S4). Interestingly, the quadratic elongation (QE) and
344angle variance (AV) of the Mg site both decrease under compression, indicating that this site
345becomes less distorted under compression: this is in accord with our inference based on the
346width of the emission peak that we have assigned to this site. The Al site distortion changes by
347very little, and the Si site becomes slightly more distorted under compression. The Al-site
348distortion change is negligible, which also provides confirmation for our assignment of the two

349 emission bands with invariant positions that show no change in their splitting up to ~9.0 GPa to
350 this site.

351 The X-site in tourmaline (the Na site in dravite) is typically considered a 9-fold
352 coordinated site. Among the bond lengths associated with this site as a function of pressure
353 (Figure 8), there are two unique bonds between the Na and the Si_6O_{18} ring (O5 and O4), and
354 there is one unique bond between the Na and the Mg octahedra (O2). There is also a potential
355 10th coordinating oxygen atom (O1), and the distance to this oxygen atom is also shown in
356 Figure 8. The O1 atom is, however, one of the two proton sites in tourmaline, although the H1
357 site has a very low reported occupancy (Gatta et al. 2014). F substitution also occurs only at the
358 O1 site, and this site is influenced by cation occupancy of the X and Y sites (Henry and Dutrow
359 2011). Hence, O1 is not simply a simple oxygen site that appears to become bonded to the Na
360 atom at high-pressure: rather, it is a site that is partially occupied by O, OH, and F. Interestingly,
361 the two unique Na-O bonds to the Si_6O_{18} ring show different behaviors. Under compression to
362 ~15.4 GPa, the Na-O4 bonds change by ~0.05 Å while the Na-O5 bonds change by ~0.25 Å. Over
363 the same pressure range, the Na-O2 bonds change by ~0.11 Å. In this sense, the Na site appears
364 to undergo the bulk of its compaction through six neighbors: three bonds into the Si_6O_{18} ring
365 and three bonds into the Mg octahedra. This pseudo-six-fold behavior, with compacting
366 connections to both the Mg polyhedra and the Si-ring, also sets up a natural way to distort the
367 Si_6O_{18} ring away from hexagonal symmetry.

368 The B-O distances are less well-resolved, and change very little under compression but
369 show a trend towards being more equidistant up to ~15.4 GPa (Supplementary Figure S5). In the
370 high-pressure phase, B is surrounded by three crystallographically unique oxygen atoms (O8

371 splits into O8a and O8b). There is no indication that the BO_3 groups deviate from a planar
372 configuration up to at least 23.6 GPa, which is expected given the spacegroups of the low- and
373 high-pressure phases.

374 *Compression mechanism*

375

376 The compression mechanism of tourmaline involves a complex interplay of bond length
377 shortening and oxygen atom displacement/rotation relative to its neighbors. Under
378 compression the Y-site (MgO_6) volume decreases through Mg-O bond shortening and the
379 distortion parameters of this site also decrease. As the volume of the Y-site decreases, the Si_6O_{18}
380 ring becomes more puckered due to the displacement of the O6 atom towards the threefold
381 rotation axis (Figure 9a). This increase in ring puckering has been observed in tourmaline when
382 smaller cations are substituted into the Y-site. Bosi and Lucchesi (2007) report that the
383 configuration of the six-membered ring is strongly affected by the average Y-O distance $\langle \text{Y-O} \rangle$
384 and, as $\langle \text{Y-O} \rangle$ decreases due to the substitution of smaller cations, the tetrahedra rotate around
385 the O4-O5 edge and the O6 atom is displaced towards the threefold axis which produces
386 puckering of the tetrahedral ring. Thus, chemical substitution of smaller cations into the Y-site
387 and pressure appear to have the same effect on ring puckering.

388 As ring puckering increases under compression the O7 atom rotates towards the Z-site
389 (AlO_6), which shortens the Al-O7 bond, and compresses the Z-site. This displacement of the O7
390 atom contributes to the increase in observed ring crimping under compression (Figure 9b), and
391 the increase in ring crimping changes the O7-O8 edge distance. Crimping is defined as $\Delta Z = [z_{\text{O5}} -$
392 $(z_{\text{O4}} + z_{\text{O7}})/2] * c$, where z is the coordinate of the oxygen atoms and c is the length of the c-axis
393 (Gorskaya et al. 1982). From a chemical substitution perspective, it has been shown that

394 substitution into the X-site primarily affects the crimping and ditrignality of the ring and
395 distortion of the tetrahedra, while substitution into the Y-site primarily affects ring puckering
396 (Foit, 1989). Ditrignality increases across the pressure range of this single-crystal study (Figure
397 9c). It is defined as $\delta = (r_1 - r_s)/r_s$, where r_1 and r_s are the distances from O4 and O5, respectively,
398 to the threefold axis (Barton 1969). Under compression, the Na site moves towards the ring,
399 which also contributes to the increase in ring crimping and ditrignality. Moreover, the overall
400 distortion of the Z-site is primarily controlled by the size of the Y-site cation (Foit 1989).
401 Therefore, it is not surprising that the distortion parameters of the Z-site show very little change
402 under compression. Above ~15.4 GPa, tetrahedral rotation and ring puckering continue to
403 increase while ring crimping decreases above the transition and then remains almost constant
404 to the highest pressure of this study.

405 *High-pressure phase transition*

406

407 At pressures above 15.4 GPa, the structure of dravite tourmaline is solved as
408 rhombohedral R3. The only difference in symmetry associated with this transition is the loss of a
409 mirror plane in the high-pressure structure. The net result is that the Si, Al, O6, O7, and O8 sites
410 all split into unique sites (Figure 10), which implies that the high-pressure phase of tourmaline is
411 likely a higher entropy phase. Since the 3-fold rotation axis is preserved across this phase
412 transition there is no change in the Mg, Na, or B sites. Importantly, this subtle crystallographic
413 change is completely consistent with our luminescence observations of a second order phase
414 transition occurring near ~15.4 GPa. Additionally, our assignment of the emission bands with an
415 initial ~0 nm/GPa pressure shift to the Al site is a robust assignment. Interestingly, the slight
416 distortion of the Si₆O₁₈ ring preserves the overall topology of the tourmaline structure, while

417 providing a new deformation mechanism for the high-pressure phase. A plot of the Si-Si-Si
418 angles shows that this angle deviates away from 120° above ~ 15.4 GPa and increases with
419 increasing pressure up to ~ 23.6 GPa (Figure 11a). There is also a discontinuous shift in
420 tetrahedral rotation, as well as a change in the pressure dependence of ring puckering and
421 crimping above ~ 15.4 GPa (Figures 9b, 11). The deformation mechanism of the high-pressure
422 phase primarily involves tetrahedral rotation and changes in the Si-Si-Si angles while ring
423 crimping and puckering play less of a role. These subtle changes in ring distortion demonstrate
424 the subtlety of this phase transition, and why it would be very difficult to resolve this type of
425 phase transition with high-pressure powder diffraction techniques. Our luminescence data
426 show that this high-pressure phase remains metastable under room temperature compression
427 up to at least 65 GPa.

428 Speculatively, the high-pressure transition appears to be driven by steric/geometric
429 effects caused by the decrease in volume of the Y-site and displacement of the X-site towards
430 the Si_6O_{18} ring. As the Y-site volume decreases, the O6 atom is displaced towards the threefold
431 axis causing ring puckering, which displaces the O7 atom towards the Z-site (Al), causing the Al-
432 O7 distance to shorten which increases ring crimping. This causes a change in the tetrahedral
433 rotation of the SiO_4 tetrahedra, which breaks the mirror plane symmetry for O6 and O7. This
434 change in rotation induces an additional twist on the MgO_6 and AlO_6 octahedra, which in turn
435 tilts the BO_3 plane out of the plane normal to the rotation axis, and breaks the mirror symmetry
436 of the O8 atom.

437 *Na site coordination change?*

438 The possible coordination change of the Na site merits discussion, as the topology of the
439tourmaline structure shows that the incipient Na1-O1 bond (Figure 8) provides the only
440straightforward means to further polymerize this structure. The distance to the potential 10th
441oxygen decreases by ~0.43 Å to 15.4 GPa, and the pressure dependence of its distance is
442constant above this pressure. Multiple phenomena could be at work here in changing the
443behavior of the Na-O bonds above the phase transition: (1) Na1 and O1 behave like they are
444bonded near the phase transition pressure (e.g. a coordination change of Na takes place); (2)
445repulsion increases between the O1 and O4, and O5 atoms; (3) an increase in repulsion
446between H1 and Na1 occurs near 15.4 GPa, which results in a shortening of the O1-H1 bond,
447and/or a change in H-bonding configuration; and/or (4) the compression mechanism of the
448high-pressure phase is different than the low pressure phase.

449 Considering the mixed occupancy of the O1 site (e.g. Gatta et al., 2014; Henry and
450Dutrow, 2011; Bosi, 2018), it is unlikely a bond is forming between Na and O1. A plot of O-O
451distances reveals that there are no systematic trends that would suggest that the change in
452pressure dependence of the Na-O1 distance is due to an increase in O-O repulsion
453(supplementary Figure S6). It has been reported that an increase in size of the X-site cation
454results in an expansion of the X-site coordination polyhedron, which impinges on the hydroxyl at
455the O1 site, leading to a shortening of the O1-H1 bond (Berryman et al., 2016). It is possible that
456above ~15.4 GPa, an increase in Na-H repulsion occurs that results in a shortening of the O-H
457bond which changes the pressure dependency of the Na1-O1 distance. However, due to the low
458reported occupancy of H1 this seems unlikely. As discussed above, ring puckering and crimping
459also behave differently in the high-pressure phase, indicating that compression mechanisms

460 shift in the high-pressure phase. Thus, a change in compression mechanism is the most
461 plausible explanation for the change in Na1-O1 pressure dependence that is observed above
462 ~15.4 GPa.

463 Bond Valence Analysis

464 We quantitatively analyze the stability of the dravite tourmaline structure using the
465 bond valence approach (Brown, 2002). The bond valence approach has been extensively
466 deployed to examine the structural changes in tourmalines due to chemical variability at
467 ambient conditions (Fortier and Donnay, 1975; Hawthorne et al., 1993; Hawthorne, 1996;
468 Hawthorne, 2002; Bosi and Lucchesi, 2007). We first use the relative deviation of the bond
469 valence sum from the ideal value ($(\sum(S_{ij}) - v_i)/v_i$) for all cations and anions to quantify the steric
470 stress of the structure at ambient condition. Here, S_{ij} is the bond valence between atoms i and j ,
471 and v_i is the absolute value of atom i 's valence. The bond valence sums are shown in Figure 12
472 on the ordinate (i.e. the zero-pressure values). It is striking that even at ambient conditions, the
473 Mg cation is overbonded by almost 20 %. This is due to the MgO_6 octahedron sharing two edges
474 in cis-conformation with the AlO_6 octahedron. The relaxed cation-oxygen distances for Al^{3+} and
475 Mg^{2+} differ by about 10% (1.9 vs 2.1 Å). Thus, each MgO_6 shares two edges with an AlO_6
476 octahedron, whereas each AlO_6 octahedron shares one edge with a MgO_6 octahedra. As a
477 consequence, Mg shows an almost 20% overbonding while AlO_6 is underbonded, albeit to a
478 smaller extent (~ 3%).

479 In terms of the bond valence sums as a function of pressure (Figure 12), two features
480 stand out: Na (which at ambient pressure is slightly underbonded) increases its overbonding by
481 a remarkable 70%. Mg, which starts out at almost 20% overbonded increases to about 40% by

48215 GPa, at which pressure it then levels out. Notably, Na and Mg are the two cations with the
483weakest individual bonds. All other cations show a shallow increase in overbonding, which
484increase moderately to a maximum of 20% at the highest pressures. The same general increase
485holds for the oxygen atoms, which are all tightly bunched together at values below 20 % (we
486disregard O1 and O3 here because the poorly constrained hydrogen positions make their bond
487valence sums ill defined).

488 The weakly bonded Na and Mg cations seem to be dramatically overbonded at high
489pressures, without affecting significantly ~~ly-effect on~~ the stability of the tourmaline structure
490(beyond the modest descent of symmetry near 15 GPa). This stability of the structure may be
491rooted in none of the oxygen atoms being overbonded by more than 20 % up to the highest
492pressure of ~24 GPa. Consequently, we hypothesize that this high-pressure stability of the
493tourmaline structure is closely tied to its extraordinary structural tolerance with respect to
494chemical substitutions on the X, Y, and Z sites. The bond network of tourmaline seems to have
495the ability to balance the modest overbonding of the oxygen atoms which hold the framework
496together, in spite of the significant overbonding on the most weakly bonded metal ions.

497 Indeed, the subtle mirror plane breaking phase transition observed above ~15.4 GPa is
498not reflected in the bond valence analysis. Instead, this phase transition is likely due to a
499steric/geometric effect caused by a complex interplay of bond length shortening and oxygen
500atom rotation/displacement which alter ring puckering, ring crimping, tetrahedral rotation, and
501ditrignality. As the ring distortion parameters change under compression, mirror plane
502symmetry is broken for O6, O7, and O8. Hence, there does not appear to be an obvious

503villain(s) that drives the transition from $R3m$ to $R3$; it is perhaps best viewed as a cooperative
504instability of the (initially) hexagonal ring configuration, via its interactions with the Y (Na)
505cation.

506Implications

507 Other compositions of tourmaline that are rhombohedral $R3m$ at room temperature and
508pressure will likely behave similarly, and undergo a similar transition, under compression. The
509main difference is likely to be the pressure at which the $R3m$ to $R3$ transition occurs. Tourmaline
510is a complex mineral group, and the high-pressure behavior of tourmalines with extensive Li, Cr,
511or V substitution into the Y and Z sites, Pb substitution into the X-site, or Al, Li substitution into
512the T-sites could be quite different than that of tourmalines with predominantly Al and Mg in
513their Y and Z sites. Nevertheless, the main chemical control over the pressure at which this
514transition occurs is likely the identity of the cation in the X-site. Here, simple systematics would
515indicate that a larger cation would generate this distortion at lower pressure conditions. Thus,
516the pressures of this transition in uvite tourmaline $[\text{Ca}(\text{Mg}_3)\text{MgAl}_5(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3(\text{OH})]$ and
517maruyamaite tourmaline $[\text{K}(\text{MgAl}_2)(\text{Al}_5\text{Mg})(\text{BO}_3)_3(\text{Si}_6\text{O}_{18})(\text{OH})_3\text{O}]$ are expected to be higher
518and lower than in dravite tourmaline, respectively. Moreover, our high-pressure results show
519that massive overbonding of the X and Y sites can be accommodated by the tourmaline
520structure. This unexpected result may explain the extraordinary structural tolerance with
521respect to chemical substitution on the X, Y, and Z sites. Hence, any over/underbonding due to
522chemical substitutions is balanced by the topology of the tourmaline structure, and perhaps in
523particular the oxygen atoms.

524 The crystallization conditions of metamorphic tourmaline are complex, but one means of
525 crystallization involves consuming B that is released during clay and mica mineral dehydration
526 reactions (Ota et al. 2007). Hence, tourmaline is likely present in subduction zones where
527 sedimentary rocks are being subducted. Petrologic studies have shown that dravite tourmaline
528 breaks down at ~7.0 GPa and ~900 °C (Werding and Schreyer 1996) and ~3-5 GPa and ~1000 °C
529 (Krosse 1995). However, tourmaline stability is highly dependent on compositional variations
530 (e.g. its Mg/[Fe+Mg] ratio, Na, Al and B contents), coexisting fluids and the host rock (Henry and
531 Dutrow, 1996; Dutrow et al., 1999; Schreyer, 2000; Ota et al. 2008). The higher pressure/lower
532 temperature stability of dravite tourmaline is not well constrained (see figure 2b in Ota et al.
533 2007). Moreover, tourmaline has a greatly diminished stability range in SiO₂ saturated systems
534 with common pelitic compositions, and even in relatively cold subduction zones, tourmaline
535 breaks down by ~150 km depth (Ota et al. 2008). Hence, the commonly invoked “cold
536 subduction zone” argument for the stability of tourmaline appears to be invalid. A complete
537 understanding of the host rock chemistry, redox conditions, and pressure and temperature
538 conditions are required to truly constrain the stability field of tourmaline supergroup minerals in
539 subduction zones. The stability fields of dravite tourmaline and other varieties of tourmaline
540 are not well constrained, and neither the onset pressure of the symmetry-lowering transition in
541 other varieties of tourmaline, nor its temperature-dependence is known. Thus, it is unclear
542 whether the high-pressure phase of dravite or other compositions of tourmaline would be
543 found at depth within subduction zones.

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545

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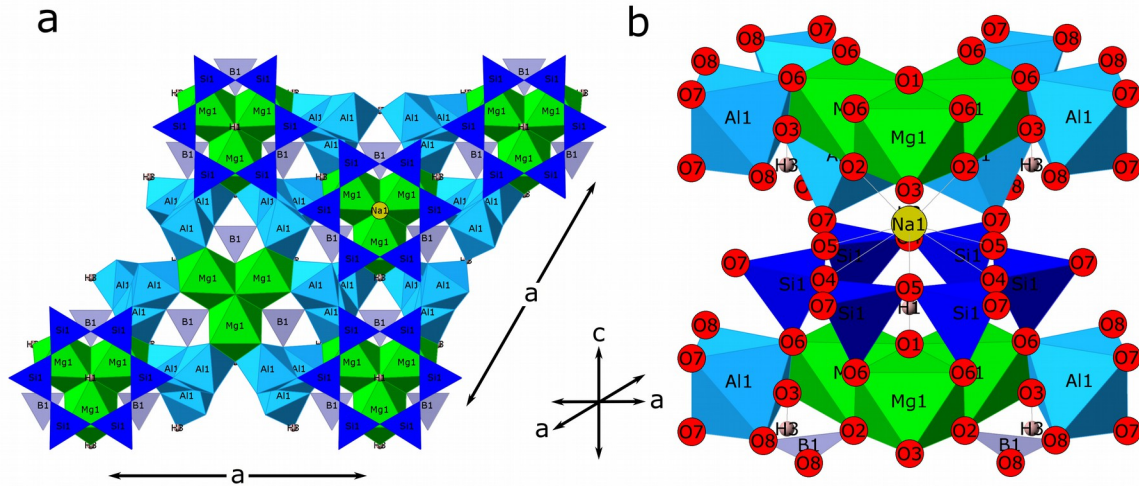
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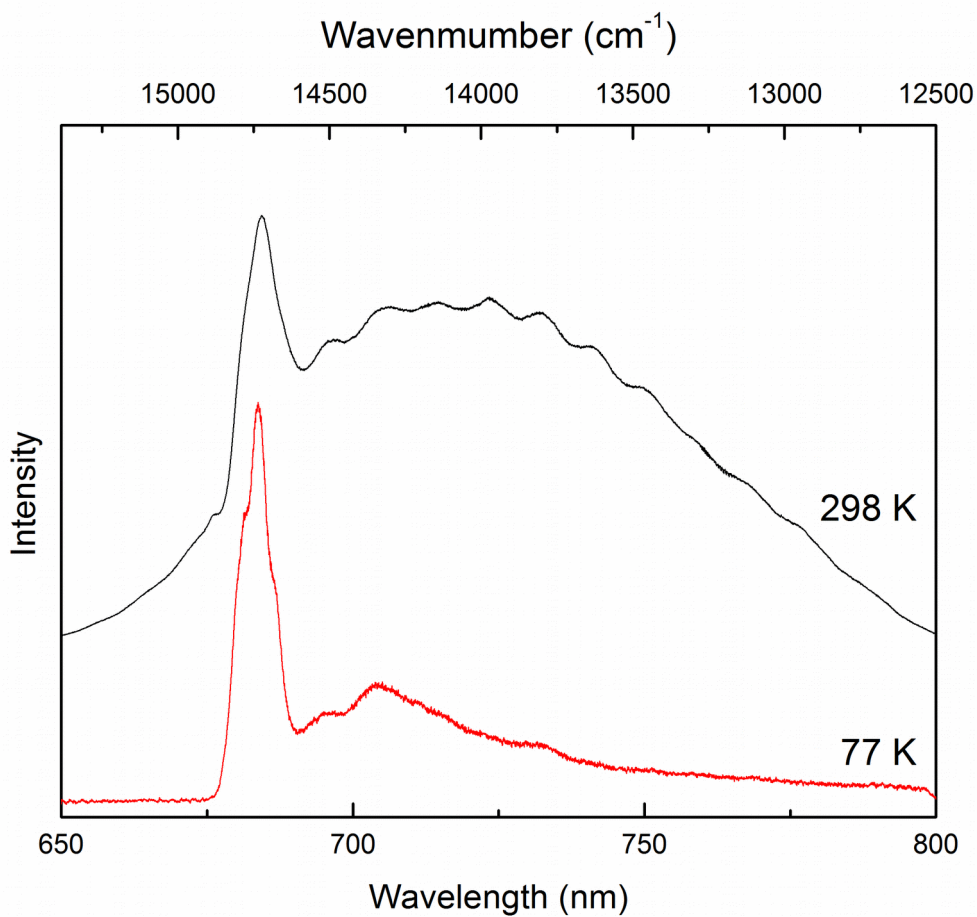
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727Figure 1. Our room pressure crystal structure diagram of dravite tourmaline. (a) looking down
 728the c-axis with oxygens removed for clarity. (b) oblique view showing the configuration of the X-
 729site within the Si₆O₁₈ ring. Modified after Hawthorne and Dirlam (2011). Diagrams were
 730generated in CrystalMaker® v8.7.6.

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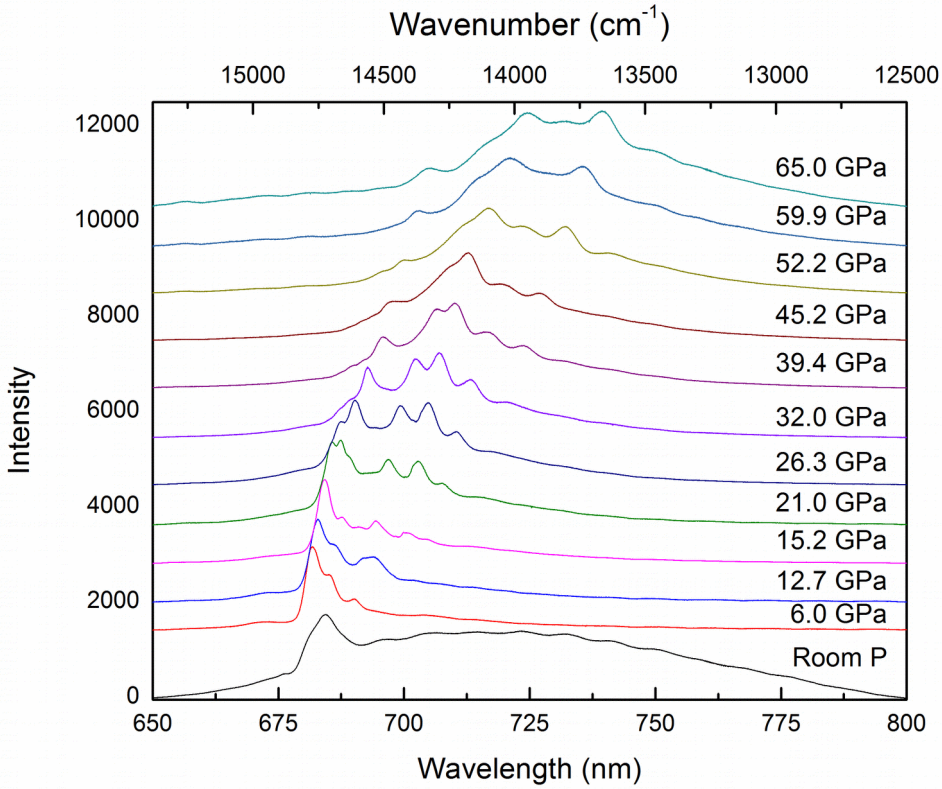
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734 Figure 2. Steady state luminescence spectra of dravite tourmaline at 300 and 77 K using 532nm
735 excitation. Note that the thermally populated 4T_2 bands are not entirely quenched at 77K. The
736 modulation in the broad band emission band at 300 K is an artifact.

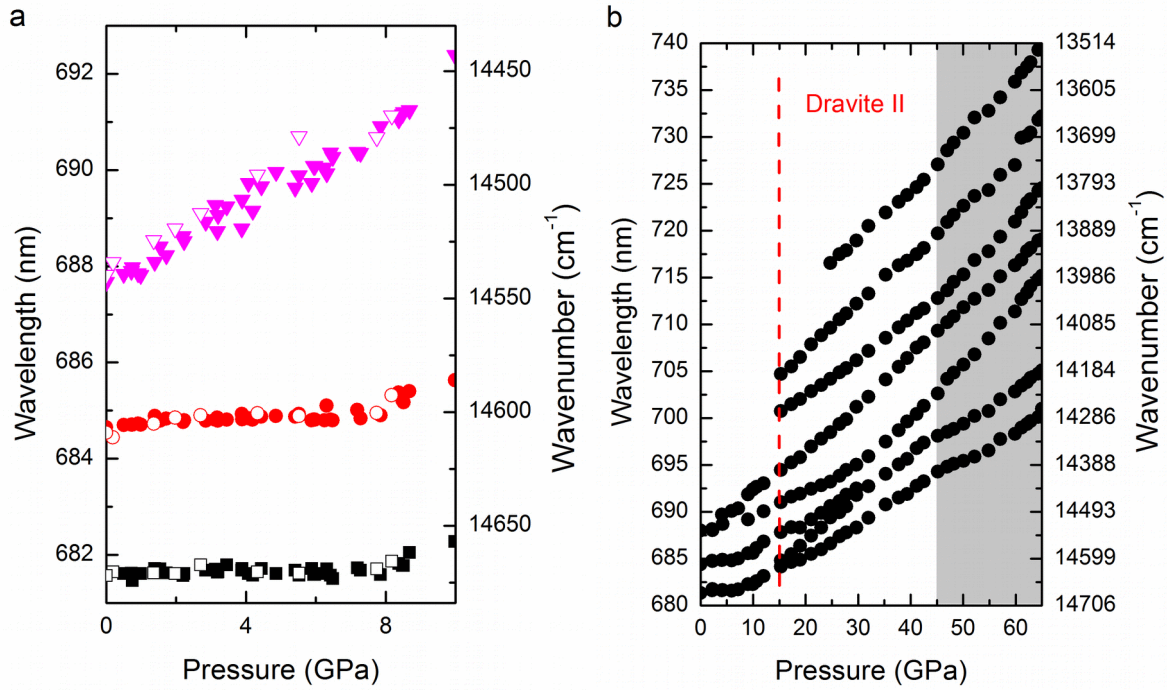
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739 Figure 3. High-pressure luminescence spectra of dravite tourmaline up to 65 GPa in a Ne
 740 pressure medium. The transition from intermediate to strong crystal field occurs between room
 741 pressure and ~6.0 GPa, as manifested by the decline in intensity of the broad-band 4T_2 emission
 742 centered near 725 nm.

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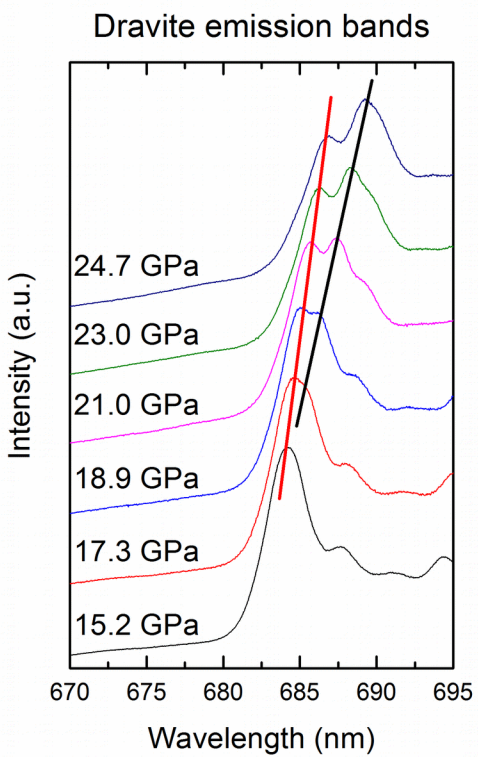


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745 Figure 4. Pressure shift of the observed luminescence bands in dravite (a) low pressure region,
 746 showing the essentially 0 nm/GPa pressure shift of two of the emission bands; and (b) up to 65
 747 GPa. The grey region indicates a possible change in compression mechanism. Closed symbols
 748 are data collected on compression, and open symbols are on decompression (for clarity, these
 749 are not included in b). Error bars are smaller than the symbols.

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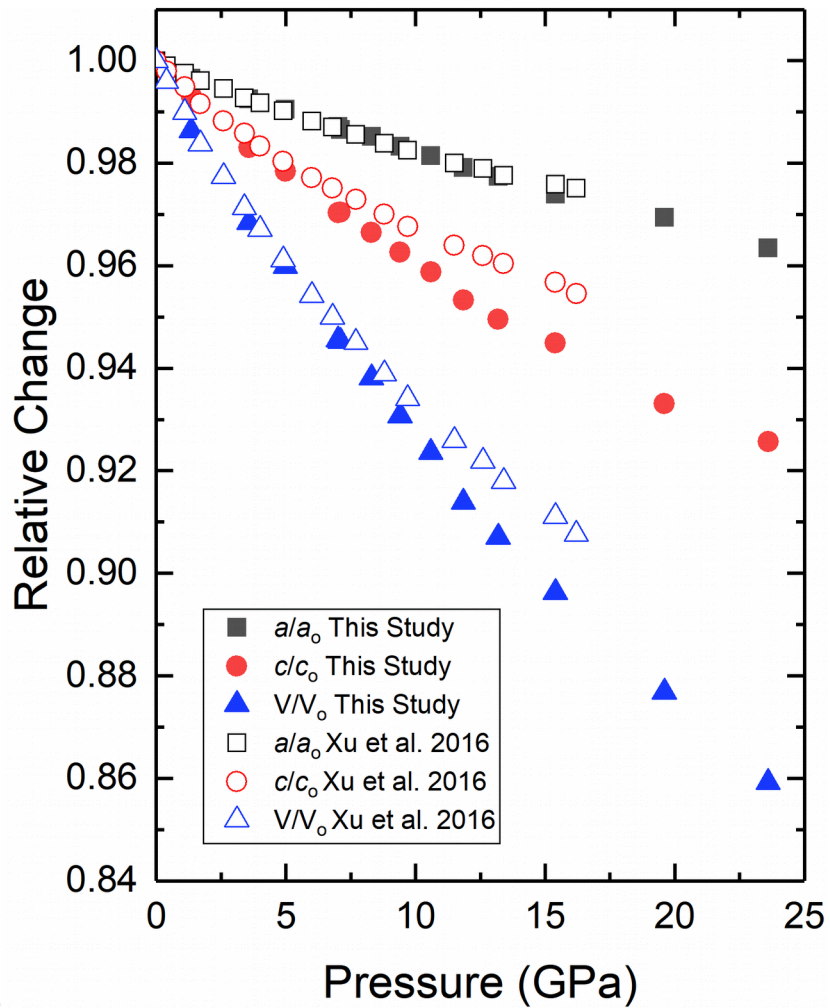
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753 Figure 5. Detail of dravite R-related emission band illustrating the splitting observed under
754 compression.

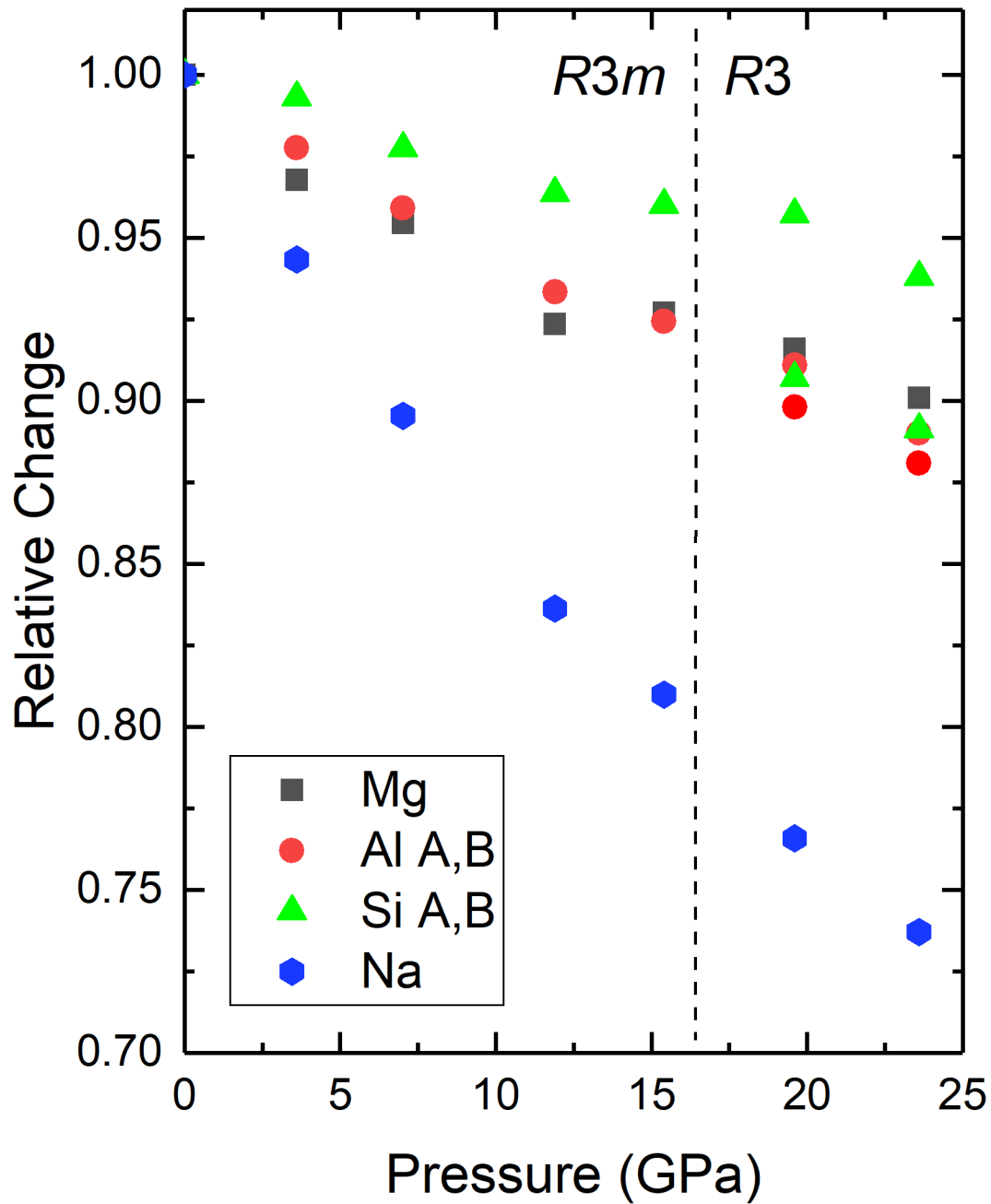
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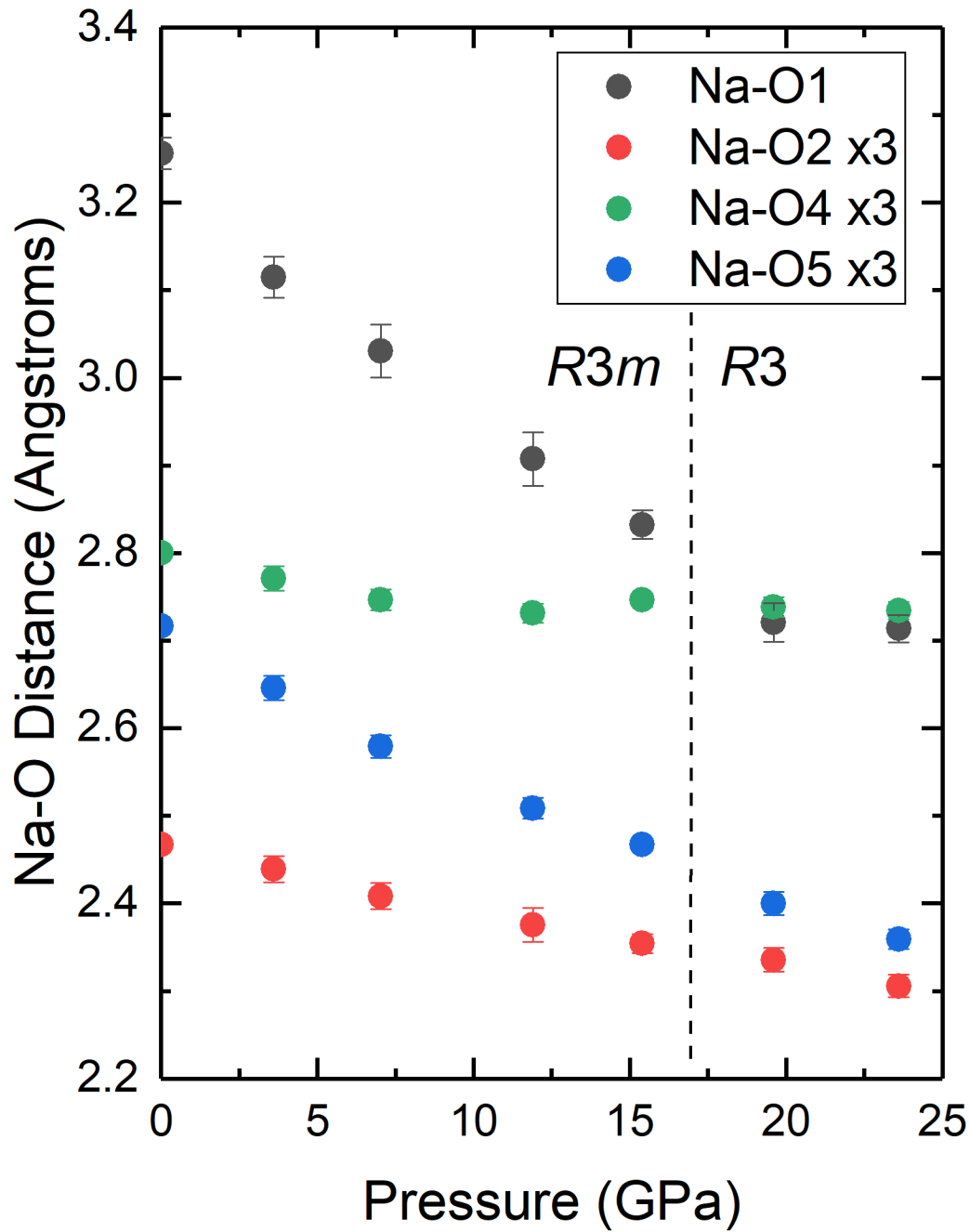
758 Figure 6. Relative change of lattice parameters and unit cell volume for uvite (Xu et al. 2016),
 759 and dravite (this study). The results of Li et al. (2004) are not plotted for clarity (see
 760 Supplementary Information). Error bars for our study are smaller than the symbols.
 761



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764 Figure 7. Site volumes in dravite tourmaline as a function of pressure. There is a large difference
765 in compressibility between the Na site and the Si, Al, and Mg sites. Note that the Na site is
766 considered 9-fold across the pressure range of these measurements.

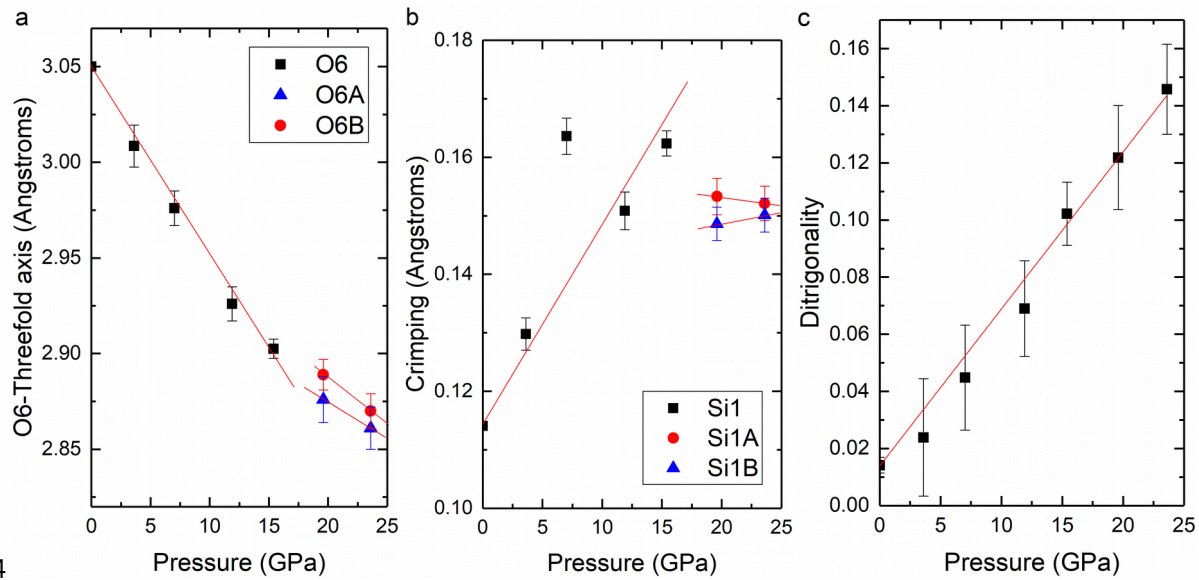
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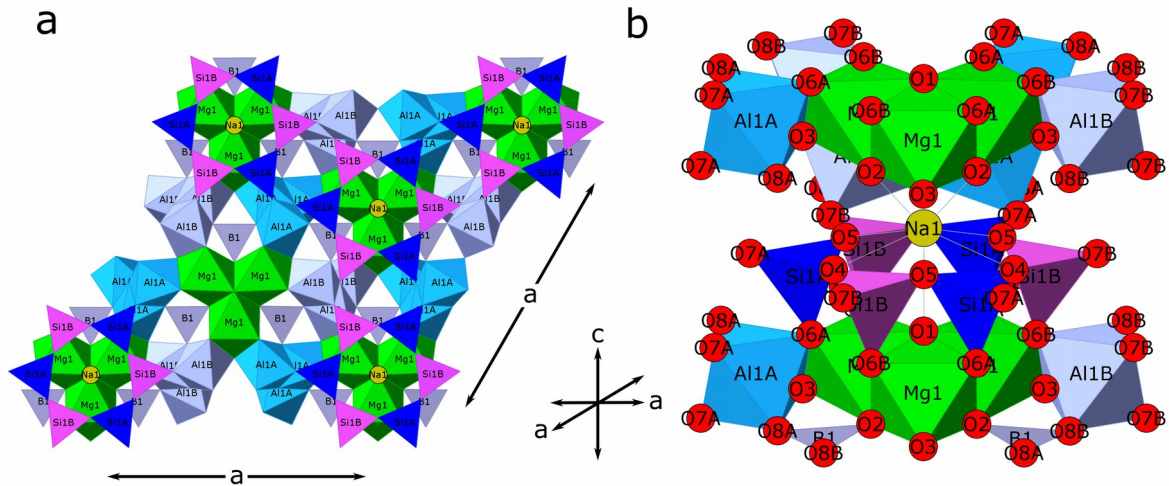
770Figure 8. Na-O bond lengths of dravite tourmaline as a function of pressure. Note the different
 771behavior of the two sets of three Na-O-Si bonds, and the change in slope of the Na-O1 distance
 772above ~15.4 GPa.

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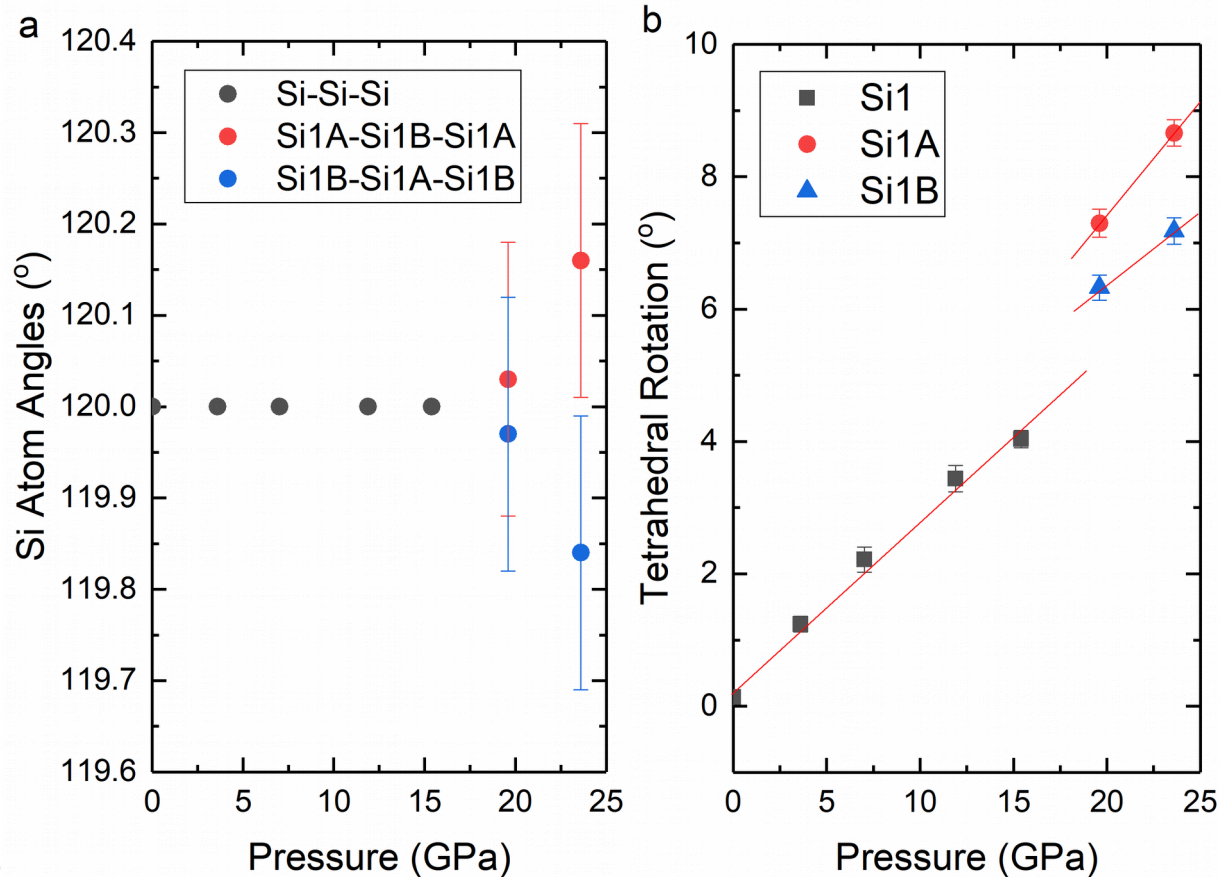
775 Figure 9. Ring distortion parameters as a function of pressure: (a) O6-threefold axis distance as a
 776 function of pressure (e.g. ring puckering). This distance decreases as pressure increases,
 777 indicating that ring puckering increases as pressure increases. (b) Ring crimping (see text for
 778 definition), showing the change in ring crimping in the high-pressure phase. (c) Ditrignality (see
 779 text). The change in puckering and crimping in the high-pressure phase indicate that the
 780 compression mechanism changes in the high-pressure phase.



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783 Figure 10. Our 23.6 GPa R3 structure of dravite tourmaline. (a) looking down the c-axis with
784 oxygens removed for clarity. (b) oblique view showing the configuration of the X-site within the
785 Si₆O₁₈ ring. Note that Al, Si, O₆, O₇, and O₈ all split into unique sites in the high-pressure phase.
786 Diagrams were generated in CrystalMaker[®] v8.7.6.

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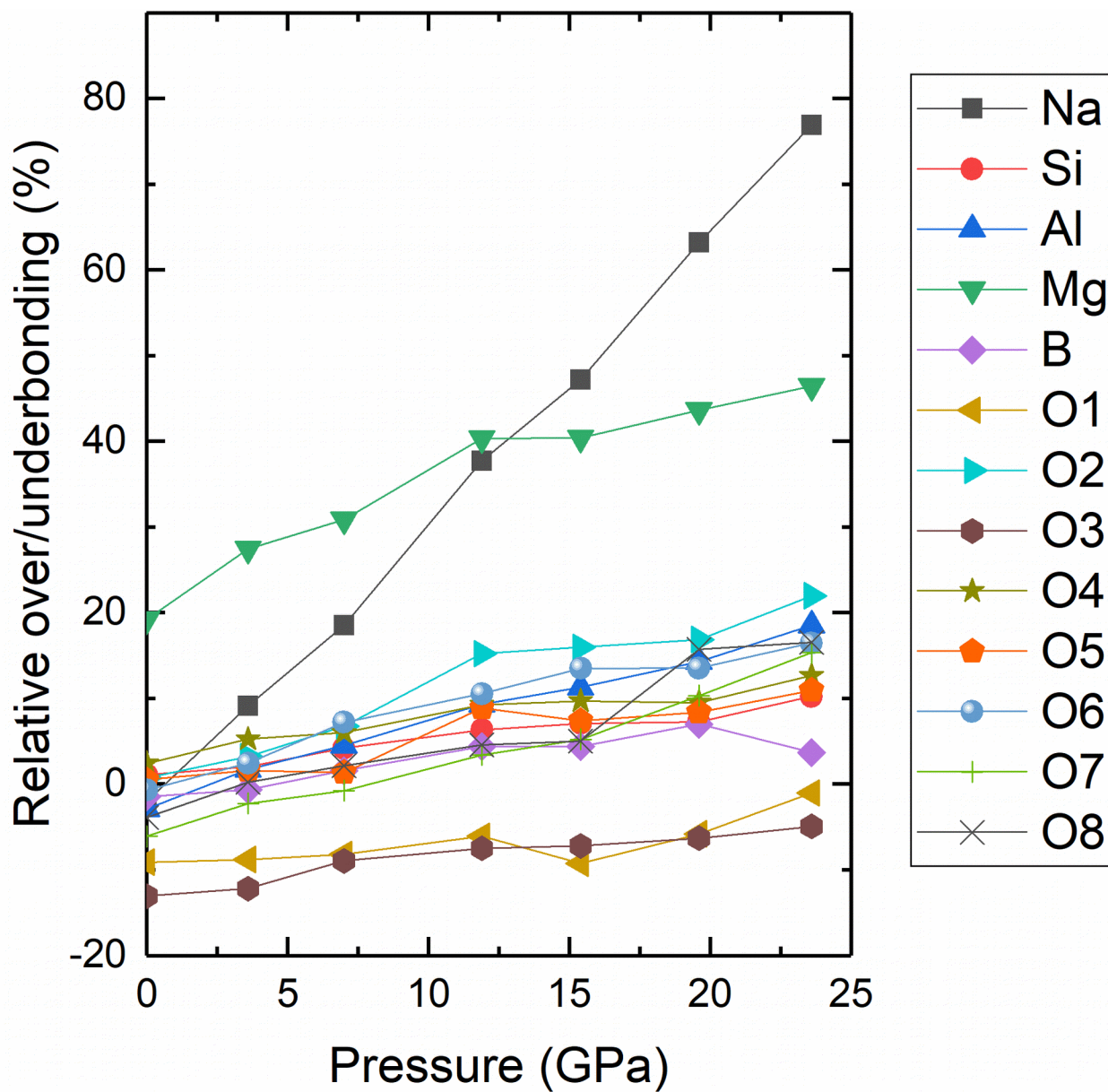


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791 Figure 11. (a) Si-Si-Si atom angles and (b) tetrahedral rotation as a function of pressure. Note
792 that the errors on bond angles are typically quite large; however, by ~23.6 GPa the deviation
793 away from 120° is larger than the errors. The discontinuous shift in tetrahedral rotation near
794 15.4 GPa shows that the phase transition occurs near this pressure, but the pressure
795 dependence of rotation is only slightly altered in the high-pressure phase.
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800Figure 12. Bond valence calculations for different ions within the dravite tourmaline structure as
801a function of pressure.

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Pressure (GPa)	<i>a</i> -axis (Å)	<i>c</i> -axis (Å)	Volume (Å ³)
*0.0001	15.9370(6)	7.1749(4)	1578.19(14)
1.4(1)	15.8820(8)	7.1258(4)	1556.60(22)
*3.6(2)	15.8180(7)	7.0534(3)	1528.38(22)
5.0(1)	15.7860(7)	7.0198(3)	1514.95(20)
*7.0(1)	15.7323(7)	6.9617(4)	1492.20(20)
7.1(1)	15.7219(8)	6.9628(4)	1491.83(22)
8.3(2)	15.7015(8)	6.9344(4)	1480.55(23)
9.4(2)	15.6711(7)	6.9066(4)	1468.91(21)
10.6(2)	15.6418(10)	6.8794(5)	1457.66(29)
*11.9(2)	15.6040(4)	6.8401(17)	1442.30(70)
13.2(3)	15.5765(14)	6.8127(7)	1431.53(40)
*15.4(4)	15.5214(21)	6.7796(11)	1414.48(58)
*19.6(4)	15.4491(13)	6.6948(6)	1383.80(32)
*23.6(5)	15.3537(15)	6.6419(6)	1355.97(37)

804

805Table 1. Unit cell parameters of dravite tourmaline at various pressures. *Crystal structures
806solved at these pressures
807

Sample	V_0 (Å ³)	K_0 (GPa)	K'_0 (GPa)	Method	Reference
Schorl	1595.52(1.98)	183.5(4.2)	4(fixed)	Powder XRD	Li et al. (2004)
Uvite	1537.1(11)	96.6(9)	12.5(4)	Powder XRD	Xu et al. (2016)
		120(2)	4(fixed)	Powder XRD	Xu et al. (2016)
Dravite	1578.19(14)	109.0(2.9)	4.8(8)	Single crystal	This study
		112.2(9)	4(fixed)	Single crystal	This study

808

809Table 2. Pressure-volume data fit up to ~15.4 GPa using both 2nd and 3rd order Birch-
810Murnaghan equations of state.

811

Pressure (GPa)	0.0001	3.6(2)	7.0(1)	11.9(2)	15.4(4)
Temperature (K)	298(2)	298(2)	298(2)	298(2)	298(2)
Crystal System, space group	rhombohedral <i>R3m</i>	rhombohedral <i>R3m</i>	rhombohedral <i>R3m</i>	rhombohedral <i>R3m</i>	rhombohedral <i>R3m</i>
<i>a</i> (Å)	15.9370(6)	15.8180(7)	15.7323(7)	15.6040(4)	15.5214(21)
<i>c</i> (Å)	7.1749(3)	7.0534(3)	6.9617(4)	6.8401(17)	6.7796(11)
Volume (Å ³)	1578.19(14)	1528.38(22)	1492.20(20)	1442.30(70)	1414.48(58)
<i>R</i> ₁ (%)	2.99	6.57	4.89	4.07	3.07
w <i>R</i> ₂ (%)	7.35	16.23	11.86	9.83	8.33
Goodness-of-fit	1.079	1.158	1.238	1.267	1.193
No. refined parameters	44	44	44	44	44

812

19.6(4)	23.6(5)
298(2)	298(2)
rhombohedral <i>R3</i>	rhombohedral <i>R3</i>
15.4491(13)	15.3537(15)
6.6948(6)	6.6419(6)
1383.80(32)	1355.97(37)
6.95	7.35
17.60	18.50
1.050	1.056
70	70

813

814 Table 3. Crystal structure refinement details for dravite tourmaline at various pressures.

815 Complete CIFs can be found in the supplementary material.

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