

Supplementary material for:

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

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Space group determination of the high-pressure phase

Notably, there is no way to unambiguously distinguish between space groups *R3m* and *R3* by using systematic absences of reflections. Thus, caution is motivated when proposing that such a transition is occurring. This is especially true when dealing with high-pressure single-crystal data, which are often incomplete. For dravite, we believe this change in symmetry is robust for the following reasons: (1) structure solution of the complete room pressure data (and our data to 15.4 GPa) as rhombohedral *R3* results in an Si_6O_{18} ring that is hexagonal, (2) our luminescence data indicate that a subtle second order phase transition occurs near this pressure, (3) there are no indicators that suggest that the different Al or Si sites are highly correlated in our results above 15.4 GPa, implying that our structural models are not missing any symmetry elements, and (4) structure solution of the 15.4 GPa structure as rhombohedral *R3* results in a slightly distorted Si_6O_{18} ring, with an R_1 value that is similar to the *R3m* solution. However, the Al and Si sites show some correlations using the *R3* symmetry that indicate that we are likely missing a symmetry element at this pressure. Considering the incomplete nature of our high-pressure data, it is difficult to be certain if one solution is more correct than the other at this pressure. However, by 19.6 GPa, the structure can no longer be solved as *R3m*, and all attempts to refine the 19.6 and 23.6 GPa data sets as rhombohedral *R3m* failed. Hence, our luminescence and single-crystal results show that a subtle second order phase transition occurs near 15.4 GPa. The phase transition is characterized by a change in space group from *R3m* to *R3*.

Bond valence analysis details

Observed bond valence sums were calculated using the observed bond lengths and the following atom pair specific parameters for equation (1) $S_{ij} = \exp(R_o - R_{ij}/b)$.

<u>Atom pair</u>	R_o	b
Na-O	1.803	0.37
Si-O	1.624	0.37
Al-O	1.651	0.37
Mg-O	1.693	0.37
B-O	1.371	0.37

The solution of the network equations (eqs (2) $V_i = \sum_j S_{ij}$ Valence sum rule and (3) $0 = \sum_{\text{loop}} S_{ij}$ Equal valence rule is based on a given topology (i.e. atomic connectivity table). The calculations were performed with an in-house code written in Matlab. It follows the robust iterative approach originally described in Brown (1977). This method initially assigns to each bond starting bond valences which correspond to the average V_i/N for the two atoms terminating each bond, where V_i is the atomic valence and N is the coordination number. Since these initial average values do not obey equation (2) (valence sum rule) they are iteratively adjusted for all cations and anions until the valence sum rule is fulfilled at all atoms. The iterative adjustments ensure that equation (3) stays fulfilled. The number of iterative cycles

corresponds roughly to the number of bond valences to be determined.

Network equations intrinsically fail to predict the known asymmetry of the O-H \cdots O configuration. Although we do not attempt to compare network predicted O-H \cdots O configurations with our experimental ones, we still need to reproduce this asymmetry since mostly the strong O-H bonds have a ripple effect on the rest of the structure. As discussed by Kunz and Brown (1992), this can be accounted for by introducing weights into the network equations. We found that weights of 2.0 and 0.2 for O-H and O \cdots H, respectively, reproduce the observed configuration in a satisfactory way.

Mapping a given bond topology into 3-dimensional space leads in a general case to conflicting requirements due to mismatched dimensions of unstrained structural units. Therefore, comparing the bond valences predicted by the network equations with observed bond valences helps to understand where a given structure is strained due to steric mismatches and what limits its stability and thus drives observed phase transitions. We compare predicted bond valences with values observed at ambient conditions for all framework cations (Table S2). We do not include hydrogen atoms in this comparison because on the one hand their intrinsic asymmetry is not reproduced in the model and on the other hand, observed O-H \cdots O geometries determined with X-rays are not particularly accurate. However, they can be accounted for by introducing weights into the network equations [*Kunz and Brown, 1995*].

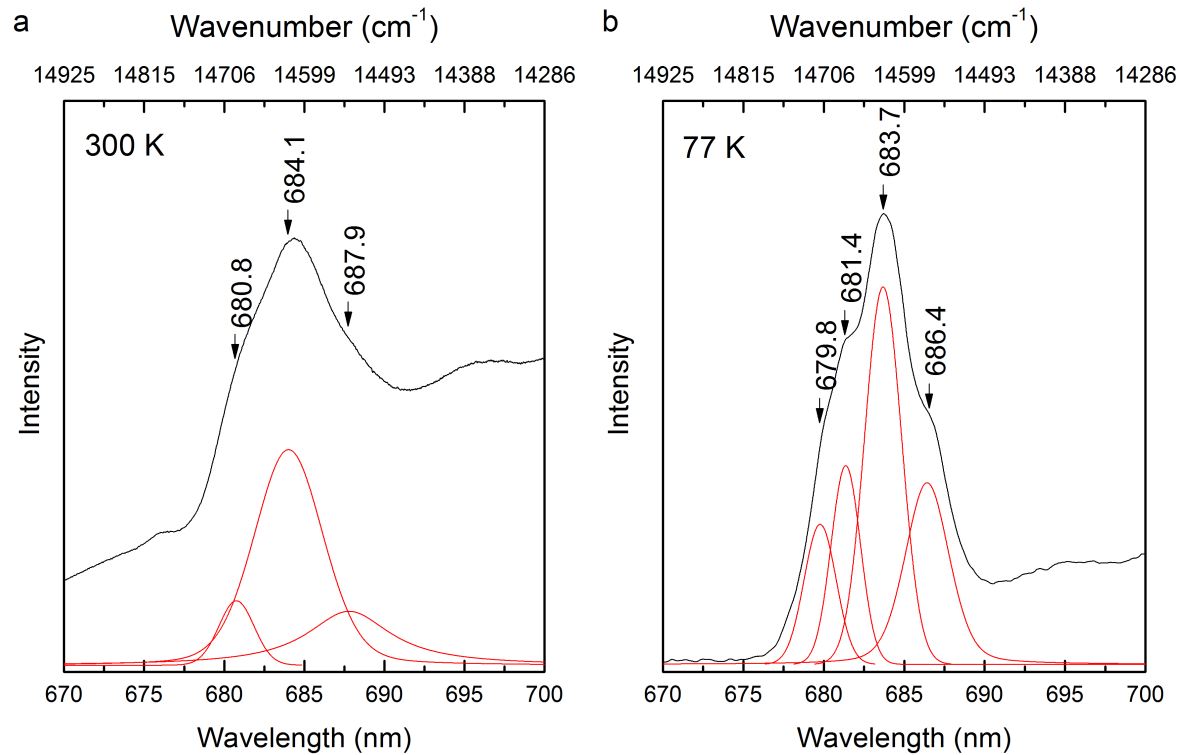


Figure S1. Fits to the ${}^2E \rightarrow {}^4A_2$ region of the luminescence spectra of dravite (a) 300 K and (b) 77 K.

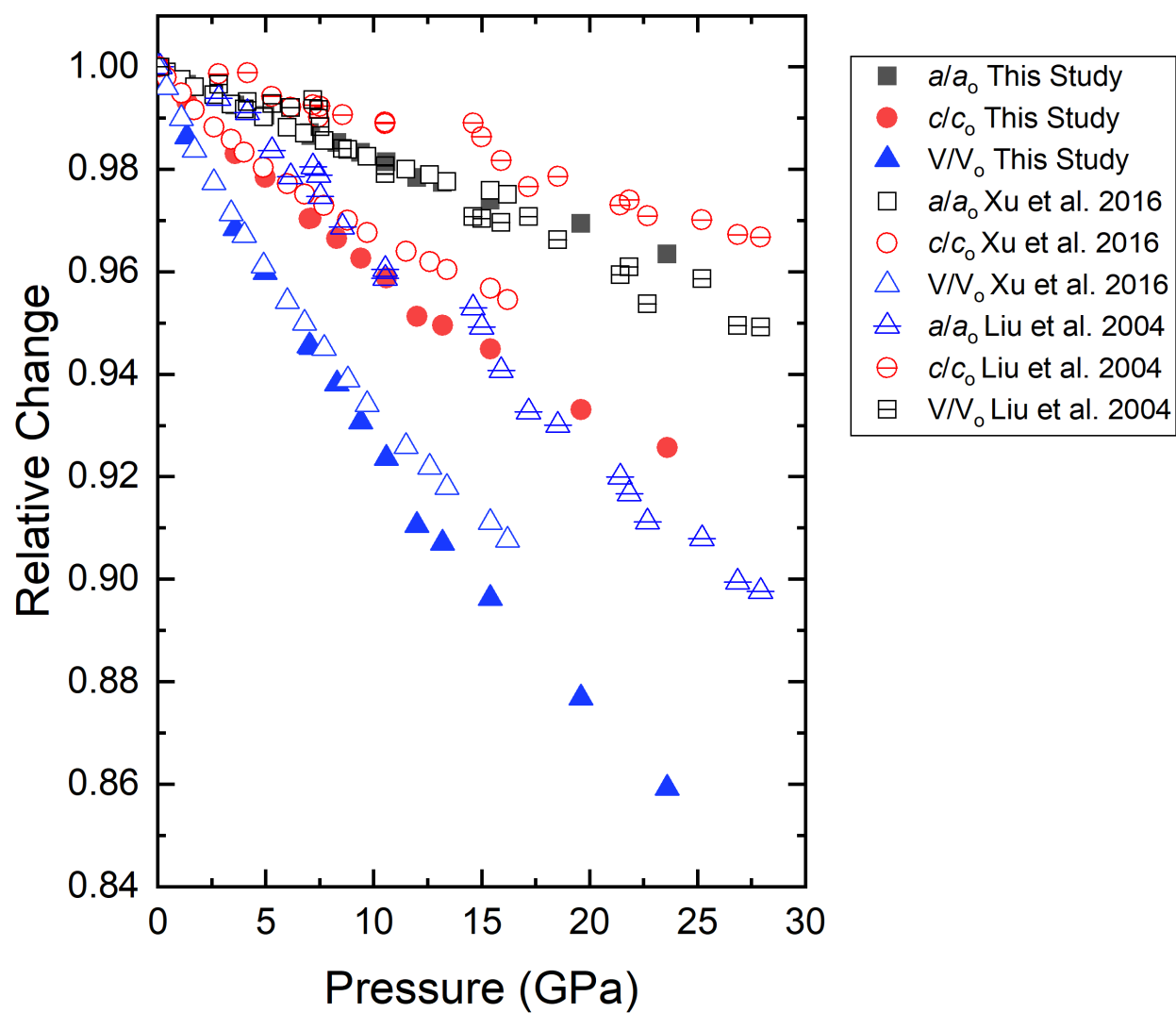


Figure S2. Comparison of lattice parameters as a function of pressure for dravite (this study), schorl (Liu et al. 2004), and uvite (Xu et al. 2016).

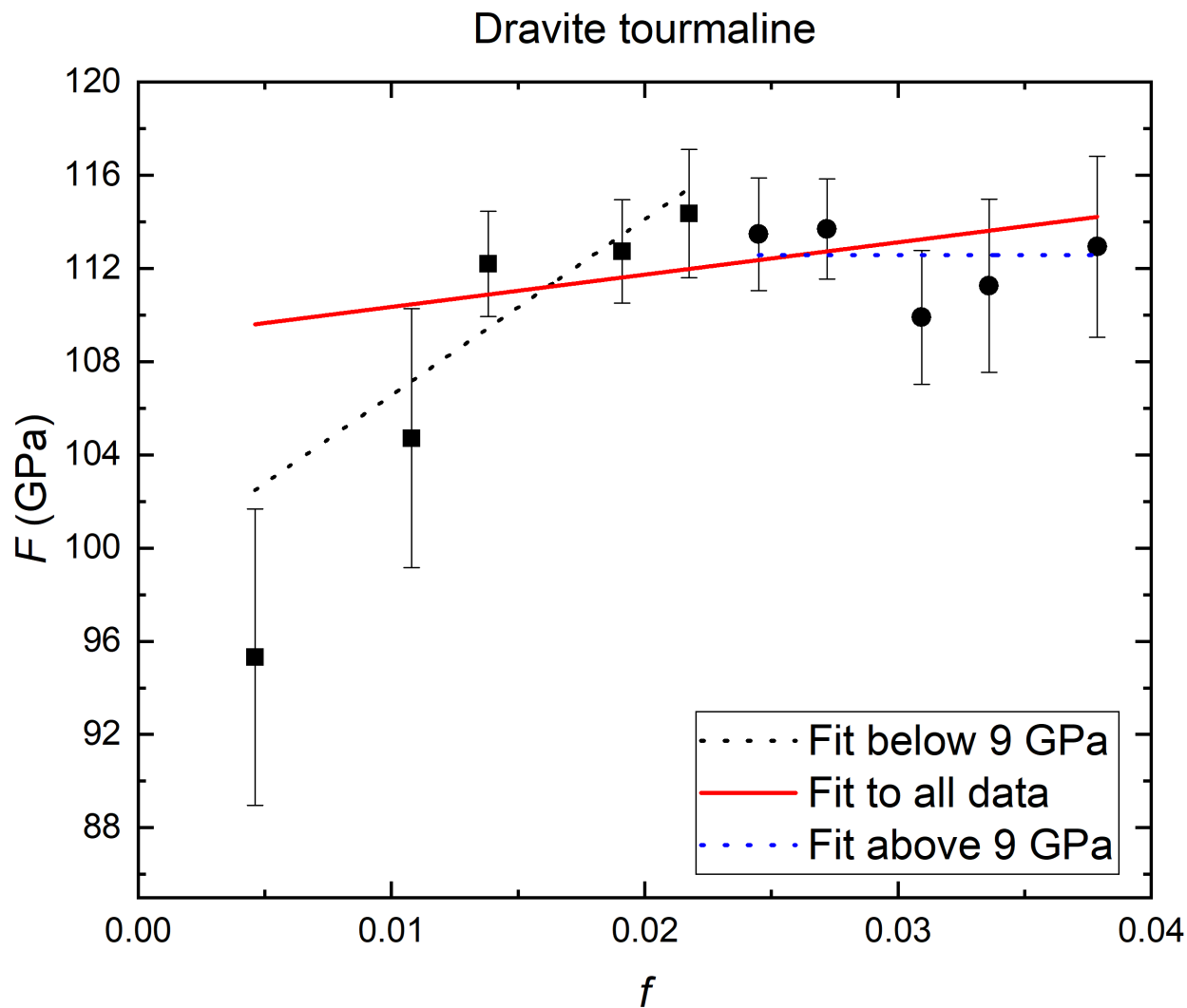


Figure S3. F - f plot based on the Birch-Murnaghan EoS fit of the pressure volume data. The solid red line is a weighted fit to all the data with $K_0 = 109(3)$ GPa and $K' = 4.8(8)$. The dashed black line is a weighted fit to the data below 9 GPa with $K_0 = 99(5)$ GPa and $K' = 9(2)$. The dotted blue line is a weighted fit to the data above 9 GPa with $K_0 = 112(1)$ with K' fixed to 4. In all cases V_0 was fixed to the value determined in our room pressure and temperature experiment.

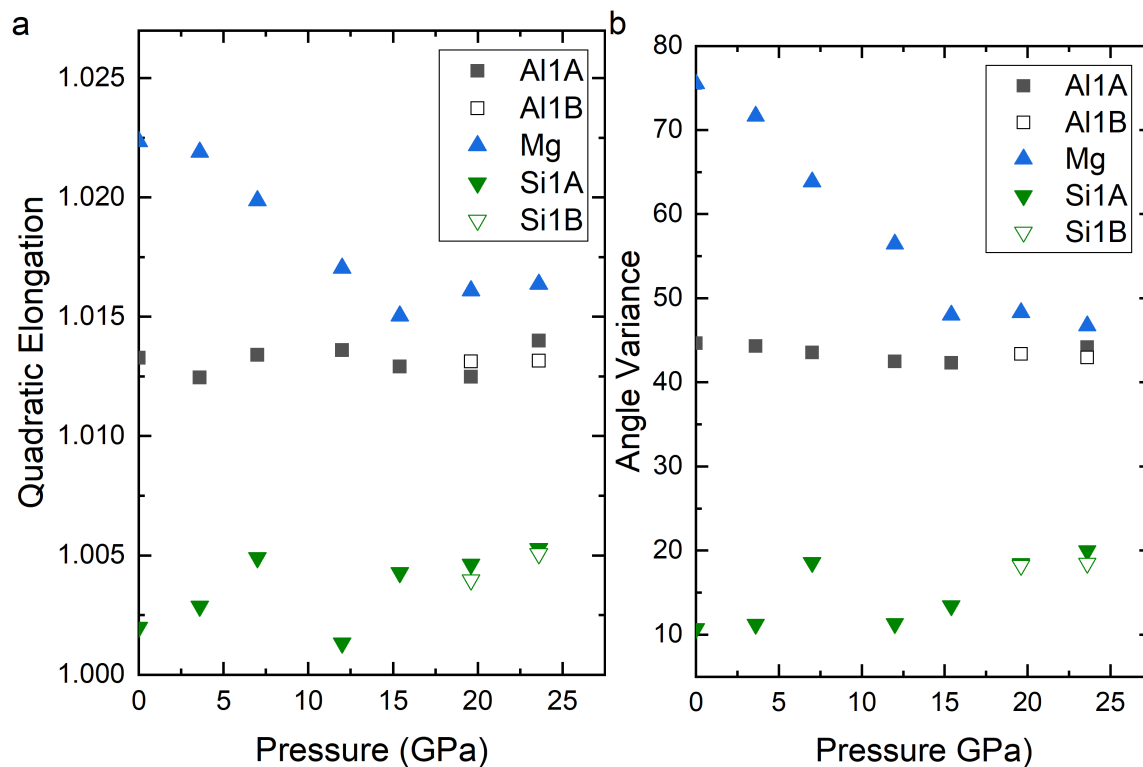


Figure S4. (a) Quadratic elongation (QE) and (b) angle variance (AV) of the Al, Mg, and Si sites in dravite tourmaline. An ideal octahedron or tetrahedron has a QE of 1 and an AV of 0. QE and AV are calculated using the equations below (Robinson et al. 1971). For QE $n=6$ for octahedrons and 4 for tetrahedrons. For AV $\theta_o = 90^\circ$ for octahedrons and 109.47° for tetrahedrons, and $n=12$ for octahedrons and 6 for tetrahedrons.

$$QE = \text{Quadratic Elongation} = \sum_{i=1}^n (l_i/l_o)^2 / n$$

$$AV = \text{Angle Variance} = \sum_{i=1}^n (\theta_i - \theta_o)^2 (n - 1)$$

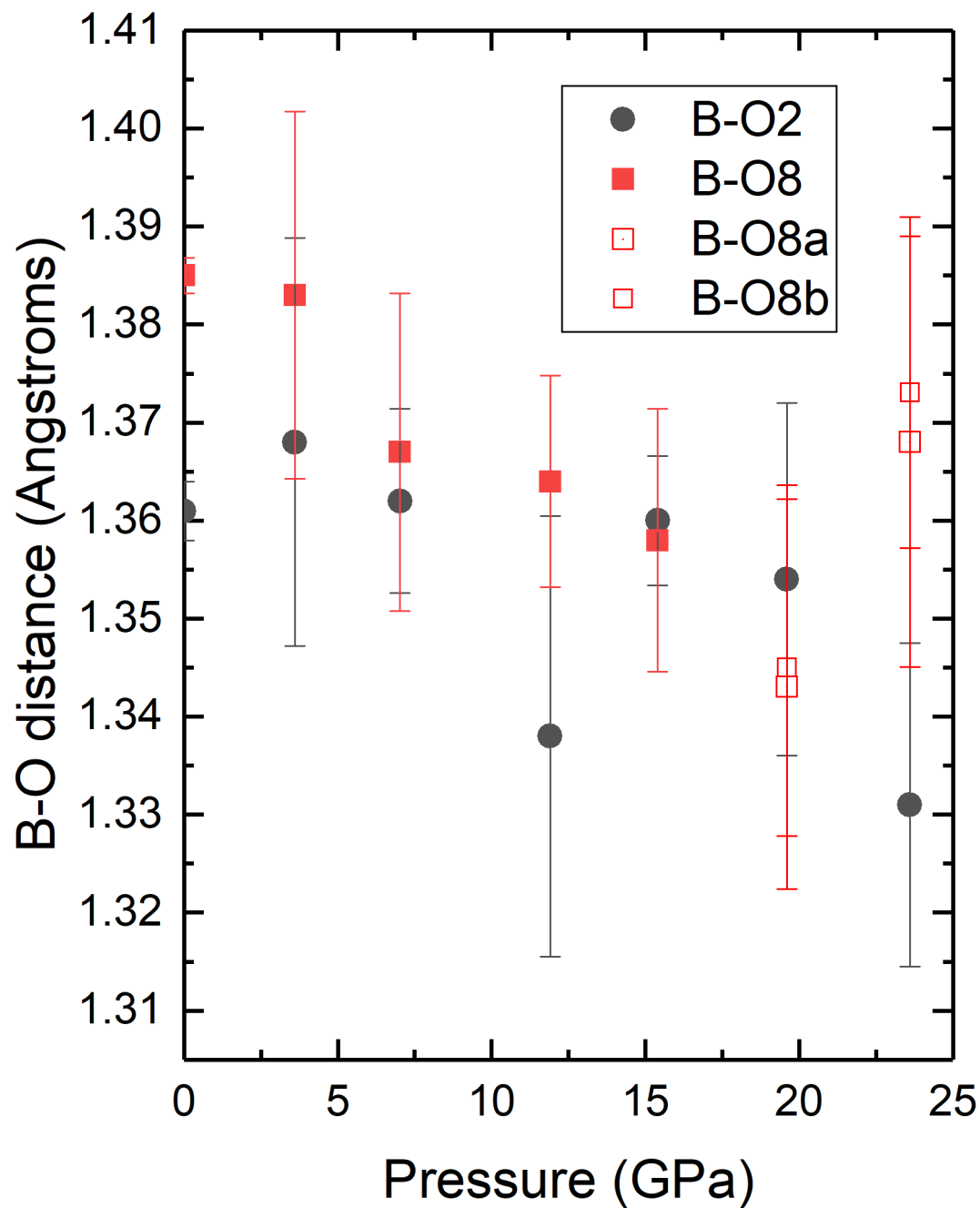


Figure S5. B-O bond lengths as a function of pressure. In the $R3m$ phase of dravite there are two O8 atoms. The error bars on the B-O distances are large; this is not surprising, considering the small scattering cross section of boron.

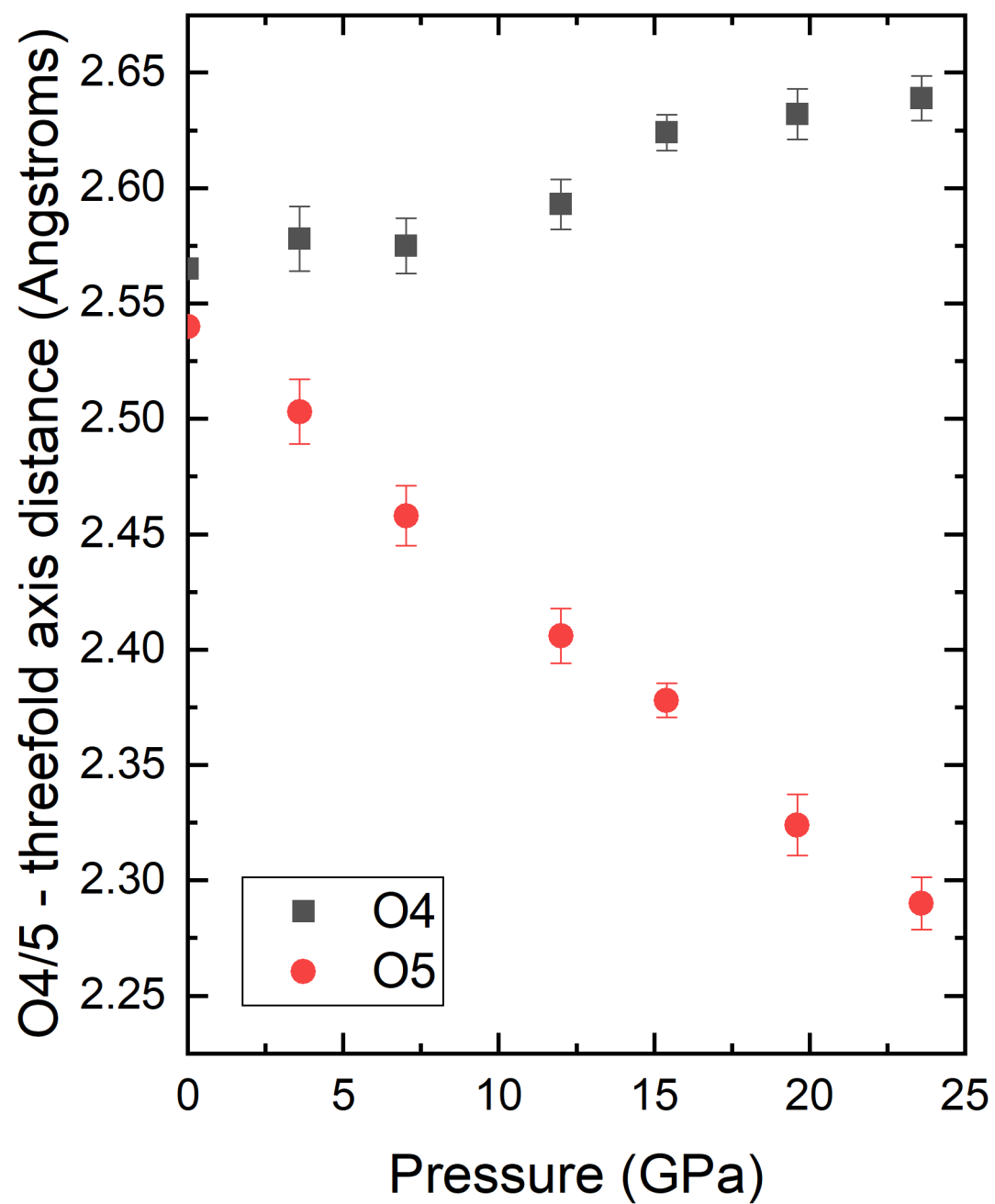


Figure S6. O4/O5 to threefold axis distance as a function of pressure. Note that the O4 to threefold axis distance increases above ~ 9.0 GPa.

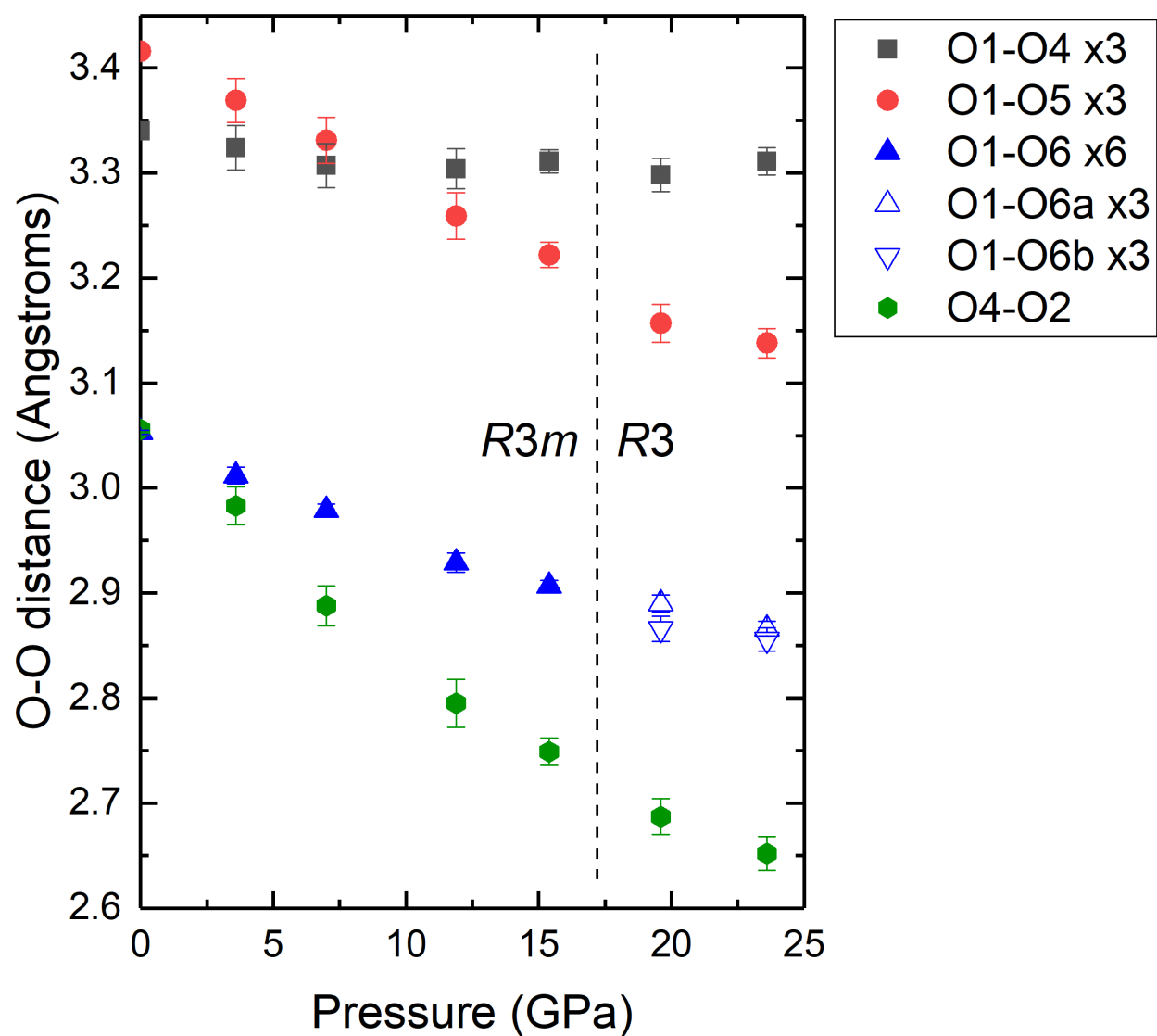


Figure S7. O-O distances around the X-site as a function of pressure. These observed trends do not suggest that O-O repulsion is markedly increasing across the pressure range of these measurements.