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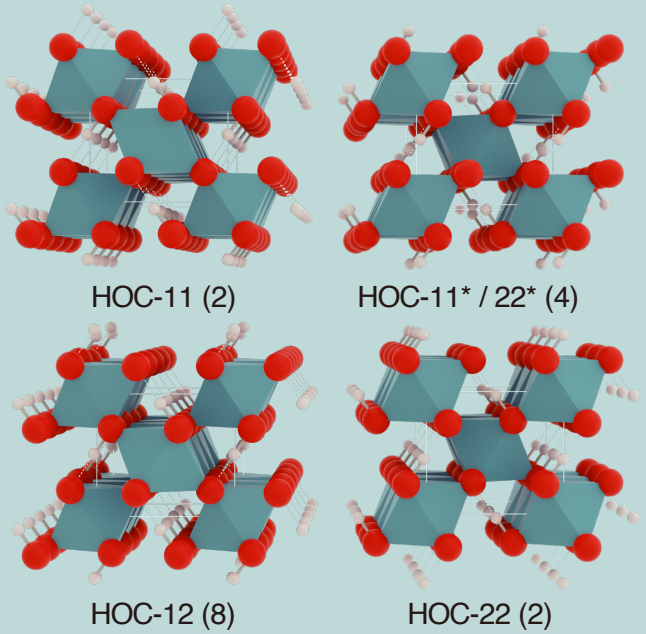
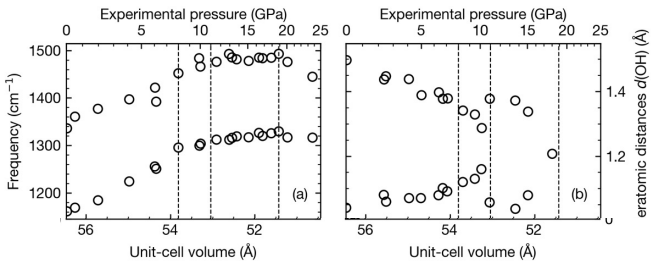
# Ab initio investigation of H-bond disordering in δ-AlOOH

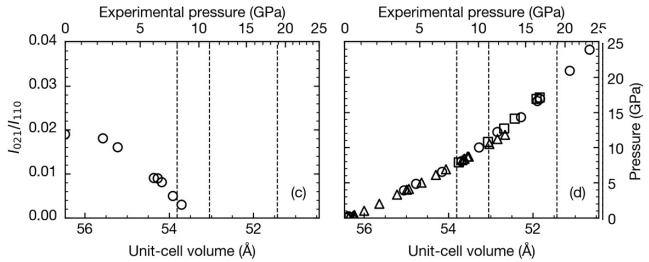



The H-bond disordering in δ was modeled with 1x1x2 supercells. Disordering is limited to 1D (*z*) and H-bond arrangements in (x,y) was restricted by "ice-rule"-like rules.

δ-AlOOH is an important hydrous phase that carries water into lower mantle via slab subduction. H-bonds (O—H···O) in δ is asymmetric at lower pressure. They undergoes symmetrization under compression and become degenerate ionic bonds (O—H—O) after the process.

H-bonds in δ are localized and independent from the Al-O-Al network which determine the structure. δ is an ideal example to study disordering and tunneling, the two process usually associates with the symmetrization because of the reduced energy barrier that facilitates the redistribution of protons.




**Acknowledgement**
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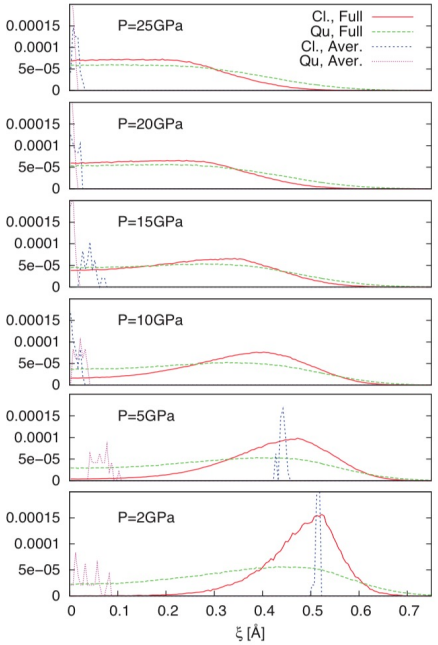
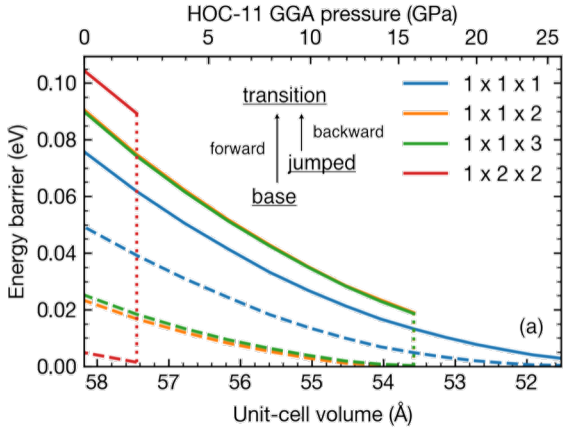
## Energy barrier

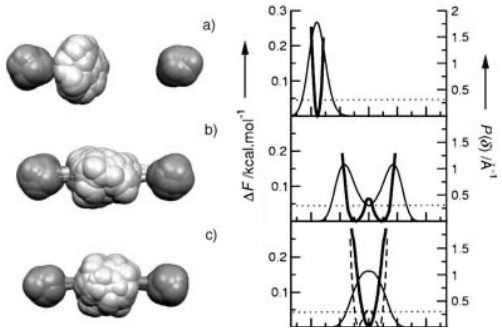
The energy barrier for a single proton jump from nudged-elastic band (NEB) calculation show barrier decreases vs. pressure before full symmetrization. Compared to $k_BT$ [4] at 300 K, shows tunneling could take place at ~10 GPa, agrees with MD simulation by Bronstein et al. [5].




Proton distribution from MD shows disordering at $P$ > 10 GPa [5].




Energy barrier vs. pressure / volume.

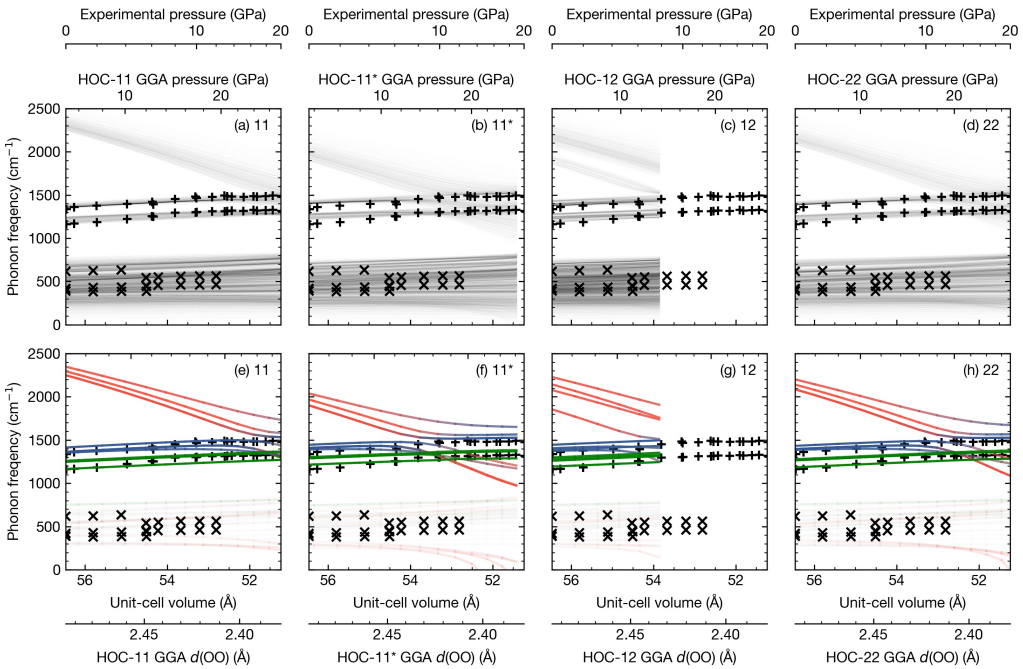



H-bond disordering roughly estimated by comparing energy barrier to $k_BT$ for ice [4].

Experimental evidences related to the 300 K multistage transition: (a) IR peaks [1] (b) OH-bond lengths [2] (c) neutron diffraction 021 peak intensity [2] (d) compression curve [3]

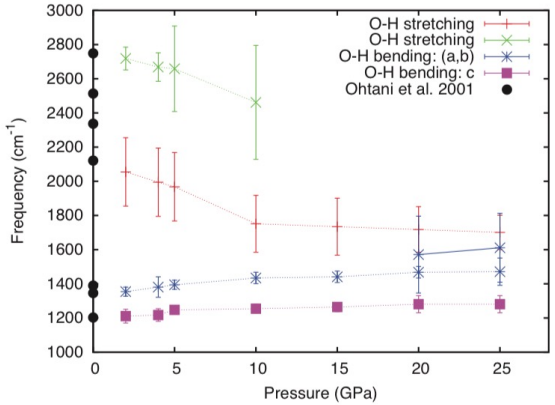
1. H. Kagi *et al.*, *J. Phys.: Conf. Ser.* **215**, 012052 (2010).
2. A. Sano-Furukawa *et al.*, *Scientific Reports.* **8**, 15520 (2018).
3. A. Sano-Furukawa *et al.*, *American Mineralogist.* **94**, 1255–1261 (2009).
4. M. Benoit, D. Marx, *ChemPhysChem.* **6**, 1738–1741 (2005).
5. Y. Bronstein, P. Depondt, F. Finocchi, *ejm.* **29**, 385–395 (2017).

# Phonon properties




(a-d) Phonon VDoS vs. pressure; (e-h) :Γ-point OH stretching (red), in-plane bending (blue) and out-of-plane bending (green). Higher frequency band corresponds to H-aligned in z; lower frequency band corresponds to H-not aligned.

Phonon modes vs. pressure from supercell MD [1]. Two OH-stretching modes observed in MD at 0-10 GPa; one observed after 10 GPa. Disappearance of high-frequency mode corresponds to disappearance of H-aligned (HOC-11, 22) configuration.



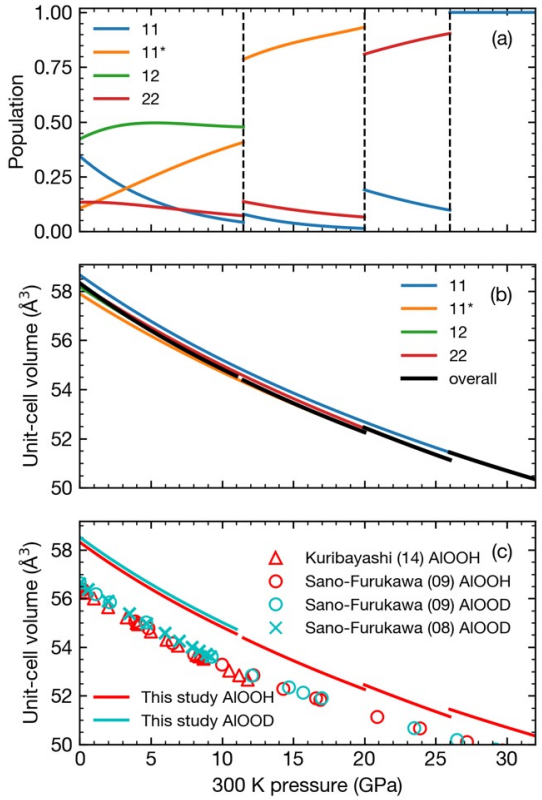

# Thermodynamic properties

We perform a multiconfiguration QHA to calculate thermodynamic properties of δ. The compression curve from mc-QHA shows that disordering explains well the greater compressibility at ~0-8 GPa.

**mc-QHA formalism**

$$n_m(V,T) = \frac{Z_m}{Z_{\mathrm{QHA}}} = \frac{g_m \exp\left[-\frac{F_m(V,T)}{kT}\right]}{\sum_m g_m \exp\left[-\frac{F_m(V,T)}{kT}\right]}$$

$$F_{\mathrm{QHA}}(V,T) = k_B T \ln Z_{\mathrm{QHA}}(V,T)$$




(a) Pressure evolution of HOC-11, 11*, 12, and 22 population from mc-QHA at 300 K. (b) Comparison between HOC-11, 11*, 12, and 22 EoS and the multi-configuration overall EoS; (c) Comparison of δ-AlOOH (red) and δ-AlOOD (blue) at 300 K. Curve represent overall EoS from mc-QHA.

# Neutron diffraction intensity & bond length