Case Study: Rocks in the outer solar system: Normal and Anomalous Properties of Water Ice

Water ice is one of the abundant minerals in the universe. The only form of ice that that we encounter naturally on Earth is that which is called ice I*h*. However, by changing the conditions of pressure and temperature, the atoms in the ice can be made to rearrange, and – as of 2021 – 19 different crystalline ice structures are now known; several of these high-pressure ices are thought to occur in the icy bodies of the outer solar system (e.g. Fig. 1). Ice I*h* has several unusual properties; in particular: (i) solid ice I*h* is less dense than liquid water – so ice floats, (ii) its thermal expansion is negative below 60 K – so the ice shrinks as you increase the temperature - and (iii) the molar volume of ice I*h* formed from D_2O ("heavy water") is greater than that of "ordinary" ice I*h* formed from H_2O; the origin of this "anomalous isotope effect" is, at present, not completely understood.

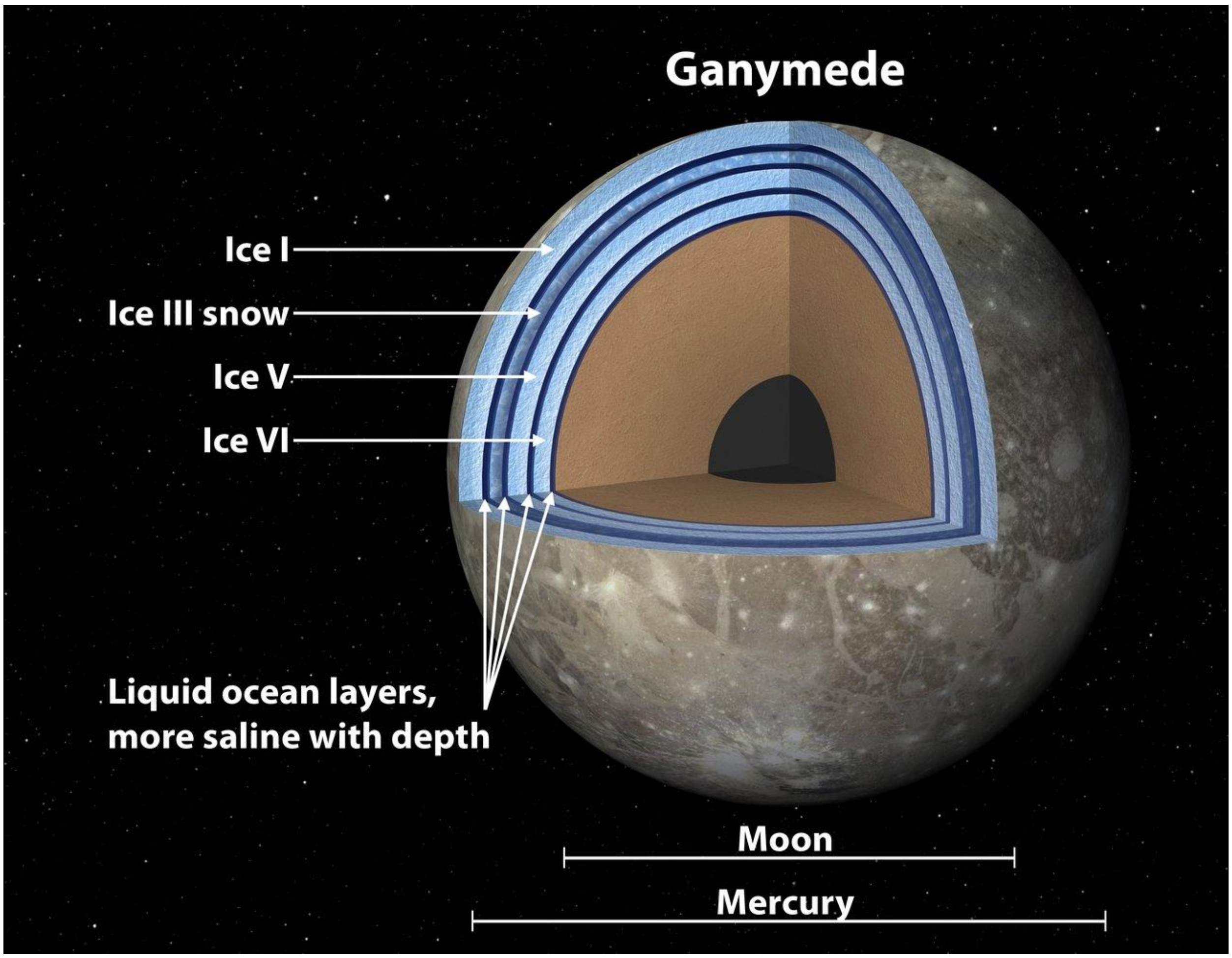

Fig. 1: A possible internal structure for the Jovian moon Ganymede, showing the layering of high-pressure ice phases (NASA).

Using apparatus constructed at UCL (Fig. 2), we are investigating whether the negative thermal expansion and anomalous isotope effects seen in ice I*h* also occur in high-pressure water ices.

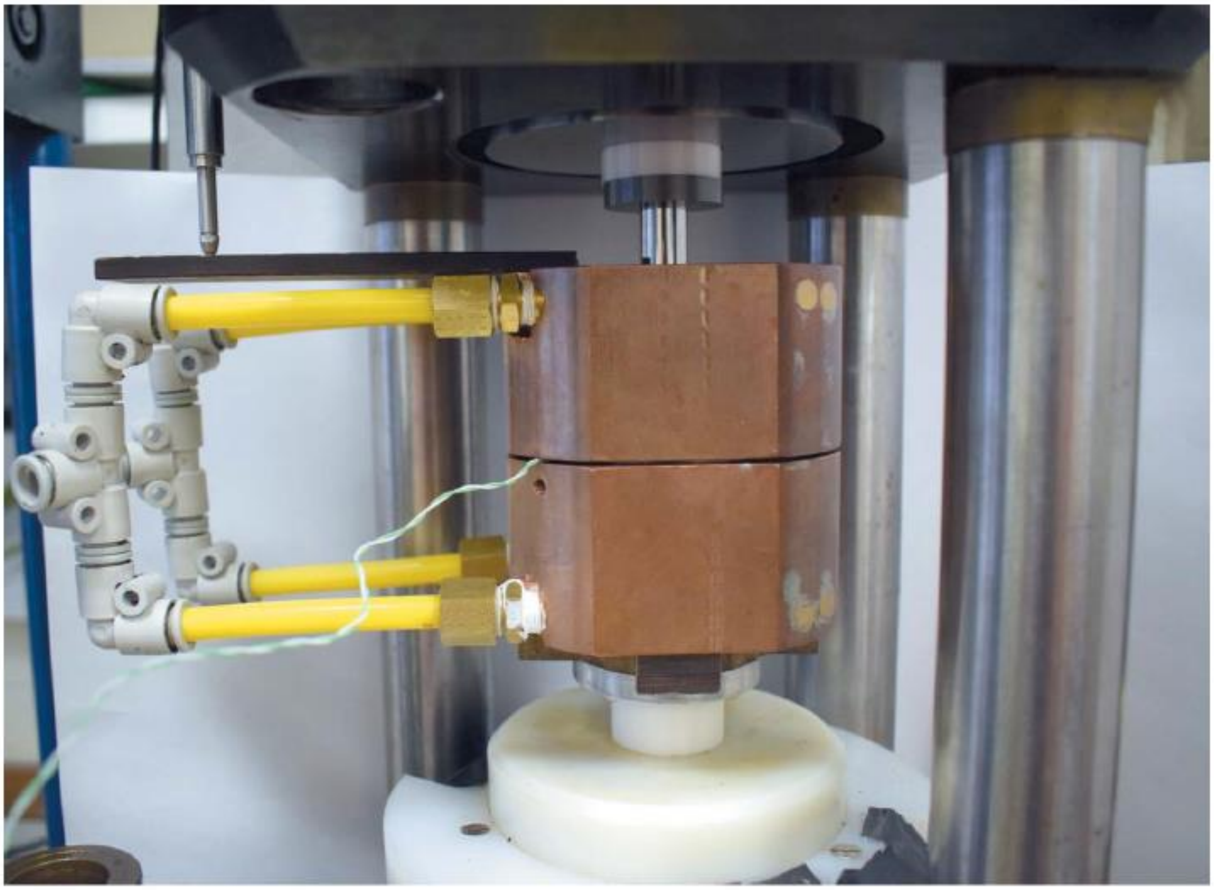

*Fig. 2: The UCL piston-cylinder cell (with insulating jackets removed) for preparation and cryo-recovery of high-pressure planetary ices (Wang et al., Journal of Applied Crystallography (2018), **51**, 692-705)*

We have done this by preparing samples of both H_2O and D_2O at high pressure in the ice II, V, VI, and ice IX structures, rapidly cooling these to 80 K, and then recovering them to atmospheric pressure under liquid nitrogen. Provided that the temperature is kept below about 140 K, these structures remain stable and can be examined by high-resolution X-ray and neutron powder diffraction. Our X-ray diffraction experiments are carried out at UCL; the neutron powder diffraction data are measured using the high-resolution powder diffractometer (HRPD) at the ISIS Facility, STFC Rutherford Appleton Laboratory in Oxfordshire.

We have found that the volume isotope effect is normal (i.e. $V_{H2O} > V_{D2O}$) in all of these materials. However, this statement hides some interesting subtleties. Firstly, in ice IX, although the overall volumetric isotope effect is normal, the two axes of this tetragonal crystal's unit cell behave differently; the *a*-axis shows a normal isotope effect, whereas for the *c*-axis the isotope effect is anomalous (Fig. 3).

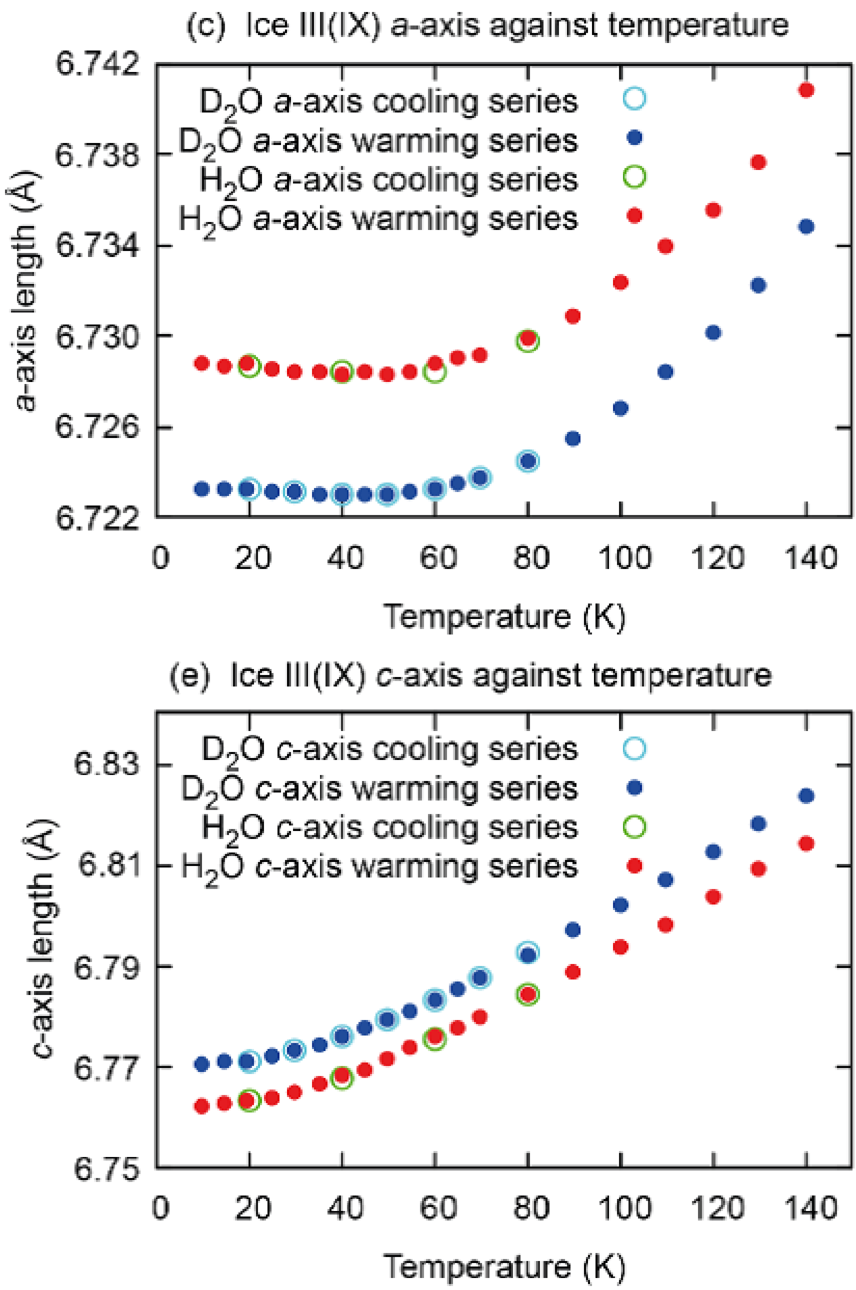

Fig. 3: Unusual isotope effects in the unit cell of ice IX. Ice IX crystals are composed of repeating units ("unit cells") that are shaped like square bricks, with two edges ("a-axis") equal in length and the third edge ("c-axis") about 0.5% longer. For the a-axis, the isotope effect is normal, i.e. the value is larger for H_2O (red dots) than for D2O (blue dots), whereas for the c-axis the effect is reversed (taken from G Baron, PhD thesis, UCL, 2022)

Secondly, in monoclinic ice V, in which the H (or D) atoms are disordered (i.e. distributed over more than one site in the structure) we have found that the *a*- and *b*-axes of the unit cell show significant changes in length (≈0.2%) on cycling the temperature between 10 K and 135 K; strangely, however, the unit-cell volume is not altered by this process.