AN EMPIRICAL EQUATION OF STATE FOR ICE-VI WITH APPLICATION TO PLANETARY MODELLING AND IMPACT SIMULATIONS. A. D. Fortes[1], I. G. Wood[1], M. G. Tucker,[2] & W. G. Marshall.[2] [1]Department of Earth Sciences, University College London, Gower Street, London, WC1E 6BT, U.K. (andrew.fortes@ucl.ac.uk). [2]ISIS Facility, STFC Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Chilton, Didcot, Oxfordshire OX11 0QX, U.K.

Introduction: Ice-VI is a polymorph of water ice that is thermodynamically stable in the range $0.6 < P < 2.1$ GPa above 150 K (Fig. 1). Density measurements on ice-VI in its stability field have hitherto been sparse. Several efforts have been made to construct piece-meal or boot-strapped parameterisations of the ice-VI equation of state (EoS) or to obtain thermodynamic quantities from the available data, by combining the few published density values with elastic measurements made by ultrasonic or Brillouin scattering techniques. We have determined the unit-cell dimensions of D_2O ice-VI at seventy-six P,T points within its stability field (Fig. 1), and at a wide-range of metastable conditions below 150 K, using powder neutron diffraction. Whilst there are some subtle differences between D_2O and H_2O ice-VI (in, for example, the elastic anisotropy), the molar volumes, melting volumes and melting enthalpies are known to be substantially the same (see Figs. 2 & 3). Ice-VI is an attractive candidate ice phase for *in situ* determination of the P-V-T EoS, since its comparatively large stability field means that even weakly pressure- and temperature-dependent quantities may be obtained experimentally with reasonable precision; furthermore, the results have a broad applicability.
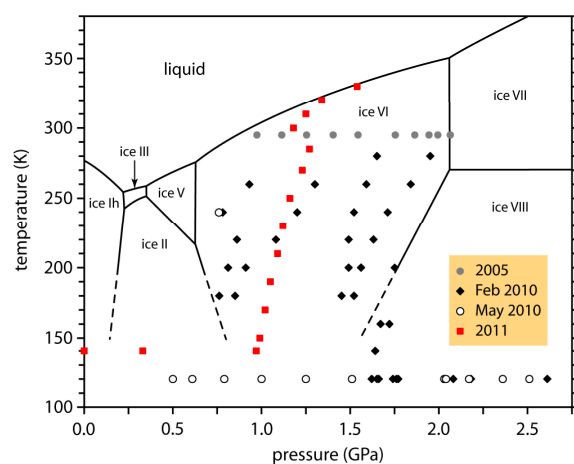

Figure 1. P,T phase diagram of ice, showing the loci of the various powder diffraction patterns collected from ice-VI in this study; symbols indicate each of the four sample loadings.

There is a strong impetus to obtain information on the properties of ice in the interior of the Earth and other planets; ice-VI is likely to be an important 'rock-forming' mineral in icy planetary bodies the size of Ganymede, Callisto or Titan [1]. The properties of this ice-VI layer will affect heat transport from the rocky cores of these bodies, hence playing an important role in their thermal evolution. Latent heat of crystallisation of high-pressure ices, released as subsurface oceans freeze over time, can buffer the overall heat loss, and the net volume change may produce lithospheric stresses sufficient to cause substantial extensional or compressional tectonics (depending on the sign of the volume change) such as rift valleys or mountains [2]. Moreover, the effect of ice phase transformations on the impact process may influence strongly the morphology of the resulting crater; pressure release of ice-VI has been implicated in the development of characteristic central-pit crater forms on Mars and on some icy satellites [3,4]. A thermal equation of state for ice-VI will improve the accuracy of both internal structure models for icy planetary bodies and simulations of the impact cratering process.

Experimental: A total of four experimental runs were carried out between 2005 and 2011, each involving an independent loading of a D_2O specimen into the Paris-Edinburgh (P-E) opposed-anvil press and measurements on the PEARL/HiPr beamline at the ISIS neutron spallation source. Liquid D_2O was soaked into a ball of silica wool situated in the cup of an encapsulated TiZr gasket [5], along with a ~50 mg ball of compacted Pb foil to aid in determination of the measurement pressure. Neutron powder diffraction data were collected over a period of several days for each loading, focused to a common scattering angle in the instrument software and then exported in a format suitable for analysis.

Results: Earlier parameterisations of the ice-VI equation of state have used up to eleven terms; we have adopted a straightforward 6-term parameterisation based upon the Murnaghan integrated linear EoS [8]:

$$V_{P,T} = V_{1.25,T} / [P^* (K' / K_{1.25,T}) + 1]^{(1/K')} \qquad \text{Eq. 1}$$
$$V_{1.25,T} = V_{1.25,225} + X1\ T^* + X2\ T^{*2} \qquad \text{Eq. 2}$$
$$K_{1.25,T} = K_{1.25,225} + (\partial K/\partial T)_P\ T^* \qquad \text{Eq. 3}$$

where the reference pressures and temperatures are, respectively, $P^* = P - 1.25$, and $T^* = T - 225$; the quantity K is the isothermal bulk modulus, and K' is the first pressure derivative of the bulk modulus, $(\partial K/\partial P)_T$. The reference P and T were chosen to fall in the middle of

the ice-VI stability field and thereby minimize the propagated errors around the boundaries of this phase field, particularly along the melting curve. This thermal EoS was fitted to the unit-cell volumes of ice-VI; the fit parameters are given in Table 1.

Table 1. Values obtained by fitting Eq. 1-3 to our data.

$V_{1.25,225}$ (Å^3)	214.94(5)
$X1$	3.47(6) x10^{-2}
$X2$	6.1(9) x10^{-5}
$K_{1.25,225}$ (GPa)	21.7(2)
$\partial K/\partial T$ (GPa K^{-1})	-0.015(2)
$K_0{}'$	4.4(4)
R^2	99.790
Min residual (%)	-0.2577
Max residual (%)	+0.2451

Because of their importance to modelling of planetary structures and dynamics, we wished to determine if the ice-VI EoS could be used to obtain accurate values for other thermodynamic quantities of interest, such as the volume change and enthalpy of melting, ΔV_m and ΔH_m, respectively. Using a newly derived EoS for D_2O liquid [9] and ice-VI, we calculated their specific volumes along the D_2O-ice-VI melting curve [10] to obtain the variation of ΔV_m with temperature, shown in Fig. 2. The difference between our result and Bridgman [11,12,13] varies from +2.2 % at 0.49 GPa (i.e., on the metastable extension of the ice-VI liquidus into the field of ice V) to +7.2 % at 0.83 GPa, although it appears likely that these are close to being within the experimental error.

The enthalpy of melting, ΔH_m, is determined from the slope of the melting curve, dP/dT, and the volume of melting, ΔV_m, using the Clausius-Clapeyron relation, $\Delta H_m = (dP/dT)\cdot T\cdot\Delta V_m$. Fig. 3 shows our calculated ΔH_m along with data from Bridgman's experimental studies of D_2O and H_2O. At lower pressures (0.6—0.8 GPa) the agreement is very good, and the trend towards higher pressures exhibited by Bridgman's D_2O data suggests that our result is valid. Above 0.8 GPa, our calculated enthalpy of melting is considerably higher than Bridgman's values for H_2O-ice-VI, and we cannot presently rule out the possibility that this – at least in part – reflects a true difference between H_2O and D_2O ice. Measurements of ΔV_m for D_2O ice are required to higher pressures, and determination of the molar volume of liquid D_2O above 1.2 GPa is desirable.

The value of ΔH_m = 5296.5 J mol^{-1} employed widely for modelling the thermal evolution of icy planetary bodies [14-16] is a fair approximation for the lowermost portion of the ice-VI melting curve, but the experimental results and our work suggest that this value may increase by between 30 and 80 % up to the L–VI–VII triple point near 2.1 GPa. Therefore, studies

of larger icy bodies will need to account for the substantially larger ΔH_m at higher pressures.

Figure 2. Volume of melting calculated from our EoS. The dashed extension to the line reflects an extrapolation beyond the region of available data for liquid D_2O.
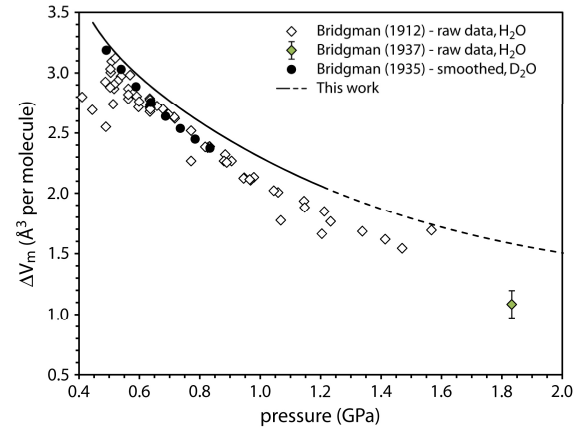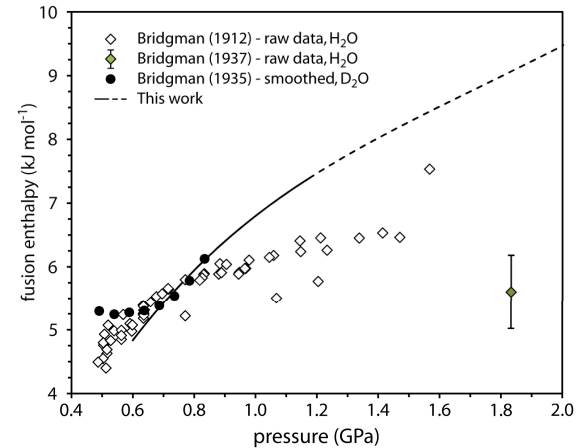

Figure 3. Enthalpy of melting calculated from our EoS. The meaning of the solid and dashed line is the same as Fig. 2.

Conclusions: For the first time, a coherent set of data have been obtained for ice-VI covering its field of stability and a large region of metastability. A thermal EoS containing only six parameters reproduces the observed P-T dependence of the unit-cell volume to within 0.25 %, which is a substantial improvement over all previous computational or empirical ice-VI EoS parameterisations.

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