# Strategies to obtain highly-ordered deuterated ices presented on the example of ice XIV

**SUPPLEMENTARY INFORMATION**

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## Supplementary Figures:

**Figure S1:** Blind experiment for isothermal annealing at 0.81 GPa done the same way as described for Fig. 1, but without the 600 mg of ice XII sample. Please note that the volume change of the metal pistons alone is negative, whereas the volume change inferred from Fig. 1 is positive.

**Figure S2:** Depiction of the calorimetric signature of a typical ice XIV to ice XII order-to-disorder transition. The onset/offset temperature ($T_{onset}$ / $T_{offset}$) is defined by the intersection of tangents along the peak flank (red) and the baseline before/after the endothermic peak (purple). The limits for the peak integration, *i.e.*, initial/final temperature $T_{init}$/$T_{final}$, are set at the temperature where the calorimetric signal (i) starts to deviate from the baseline before the peak ($T_{init}$) and (ii) where it returns to baseline level ($T_{final}$).

**Figure S3:** Calorimetric heating scans (recorded at 30 K min$^{-1}$) for highly-ordered ice XIV samples as prepared through the isothermal annealing protocol (110 min at 94 K and 0.81 GPa). The respective degrees of order (quantified by % $\Delta S_P$) extracted from the area under these endotherms are summarized in Fig. 3 of the main manuscript.

**Figure S4:** Same as Fig. 3 in the main manuscript, but enthalpy values of the XII→XIV transition endotherm (seen in Fig. S3) were obtained from the comparison with the literature value of the melting endotherm, before entropies were calculated. However, this method is sometimes afflicted with unwanted evaporation of small droplets from outside the crucible during heating above the melting temperature. Therefore, the data shown in Fig. 3 is derived from enthalpies that were calculated relative to the literature value of the ice XII →$I_{sd}$ transition exotherm.

**Figure S5:** Dielectric loss spectra for highly-ordered ice XIV samples prepared from the proposed annealing protocol, all recorded at 102 K, just before the transition to ice XII takes place.