# Nanoscale structure of amorphous solid water: What determines the porosity in ASW?

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**Abstract.** The pore structure of vapour deposited ASW is poorly understood, despite its importance to fundamental processes such as grain chemistry, cooling of star forming regions, and planet formation. We studied structural changes of vapour deposited $D_2O$ on intra-molecular to 30 nm length scales at temperatures ranging from 18 to 180 K and observed enhanced mobility from 100 to 150 K. An Arrhenius type model describes the loss of surface area and porosity with a common set of kinetic parameters. The low activation energy (428 K) is commensurate with van der Waals forces between nm-scale substructures in the ice. Our findings imply that water porosity will always change with time, even at low temperatures.

**Keywords.** astrochemistry, methods: laboratory, planets and satellites: formation, comets: general, solar system: formation, ISM: kinematics and dynamics, ISM: evolution, dense matter

Vapour deposited amorphous solid water (ASW) is supposed to be the most common solid ice material in space. Low-temperature depositions are porous, suggesting that in space it may incorporate trace gases, influencing grain chemistry, Burke & Brown (2010), and grain collisions, Wang *et al.* (2005). However, the underlying structure of ASW is poorly understood. Laboratory experiments on interstellar ice analogues often yield seemingly contradictory results, as the porosity and ice phase are highly sensitive to the growth conditions employed. Moreover, the structures crystallise and lose porosity with temperature and potentially with time. This annealing process again depends on the ice's environmental conditions and thermal history. Building on earlier work by Hill *et al.* (2016), herein we attempt to quantify some structural aspects of ASW. We have grown vapour-deposited $D_2O$ ices in-situ, in a systematic and reproducible manner, and employed neutron scattering as a non-destructive probe of their structure from 18 to 180 K over intramolecular to nanometric length scales using the NIMROD instrument at STFC Rutherford Appleton Laboratory (beamtime allocations RB1610318 & RB1510246).

An Arrhenius-type model (Figure 1) is able to describe both the loss of surface area and the porosity over the temperature range studied. The activation energy for this process is (428 ± 104) K, which is in the range expected for van der Waals forces acting between ice structures of several nanometers in size, and over a distance of a few nanometers.
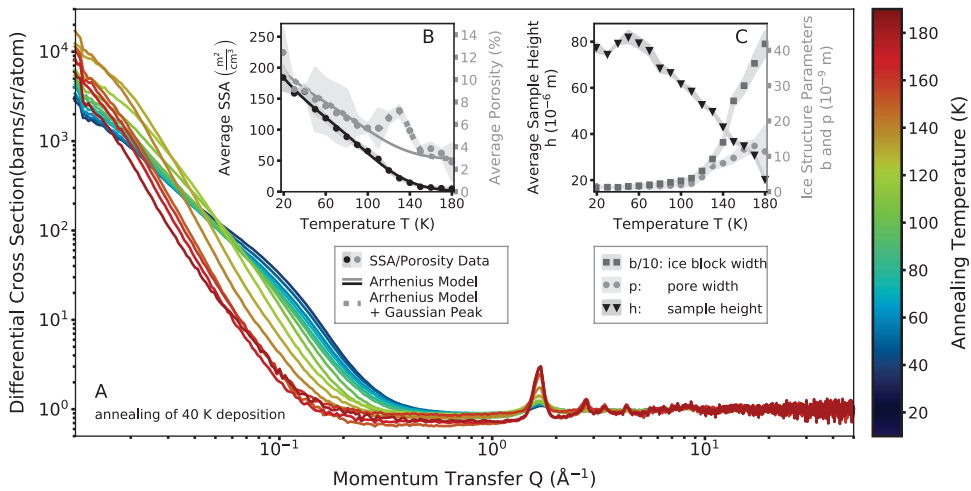
**Figure 1.** **A:** Examples of neutron scattering data: annealing of the 40 K deposition in 10 K steps. nm-scale sample structures cause features around 0.1 Å$^{-1}$. Their reduction with increasing temperatures indicates changes in pore structure. The 1 to 6 Å$^{-1}$ region shows increasingly cubic diffraction patterns with increasing temperature. **B:** Evolution of specific surface area, SSA, (left hand axis) and porosity (right hand axis) with annealing temperature. Solid lines show fits of the Arrhenius type model. The porosity data deviates from this model in the intermediate temperature range. In this range none of the available porosity models fully capture all features observed in the low $Q$ data, making interpretation of the data more difficult. To compensate for this effect, a Gaussian peak was added to the fit function (dotted line), which captures the observed deviations. **C:** Derived ice structure parameters across the whole temperature range investigated. Ice block width, $b$, is shown as $b/10$ to enable comparison with pore width, $p$.

Structural changes evidence enhanced mobility from 100 to 150 K and while derived structural descriptors such as the widths of pores and ice widths change by an order of magnitude, their effects on the kinetic parameters appear to cancel out. Both surface area and porosity may be described utilising a common set of kinetic parameters, but differing high-temperature equilibria. Despite the same mechanism driving both changes, this indicates that without known morphology, surface area is not a measure for porosity.

Our findings imply that models for ASW must include macroscopic effects and long-range, inter-molecular forces in order to reliably predict these structures in astrophysical environments. Furthermore, since changes in structure are well-described by an activation energy, these ices will always change over time, even at low temperatures, which demands critical reassessment of our picture of ice astrophysics.

## References

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