ISIS Experimental Report

Rutherford Appleton Laboratory

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Title of Experiment:	Proton ordering in Antarctic ice	**Local Contact:**	KS Knight
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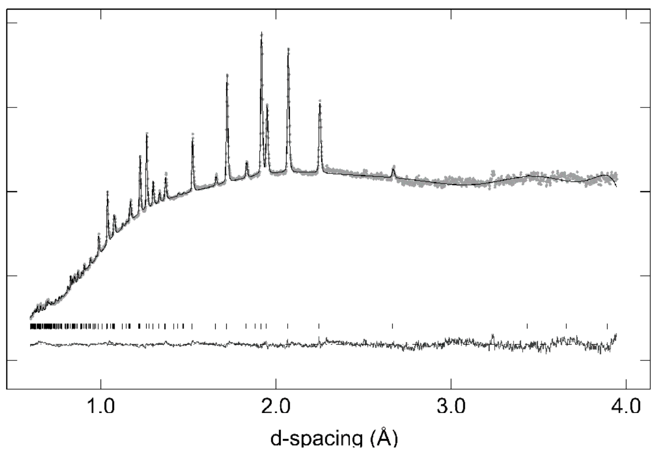
Introduction. Ice cores from the Dome-Fuji site in Antarctica have been examined by others using dielectric spectroscopy,[1] Raman spectroscopy, inelastic incoherent neutron scattering (IINS),[2,3] and neutron diffraction, both powder[4] and single crystal.[5] These experiments provided evidence for partial proton ordering of ice which had been kept below 237 K for many millennia in the Antarctic ice sheet. Determining whether or not Antarctic ice is proton ordered is important; the creep of ice is controlled by the abundance and mobility of defects in the crystal structure; in ice Ih, proton disorder provides abundant defects to ensure ready creep. However, if the ice were proton ordered, then one would expect it to flow differently. This could have consequences for models of ice sheet dynamics and, consequently, global climate change. Creep processes also control convection inside the icy moons of the outer solar system; altering the rate at which this occurs may have far-reaching effects on models of their thermal evolution. To examine the possibility that old Antarctic ice is partially proton ordered, we have carried out a powder neutron diffraction study of such a sample, exercising particular care to keep it below the proposed ordering temperature (237 K) from sample collection through to end-of-analysis. The diffraction experiment was carried out using the POLARIS powder diffractometer. The POLARIS 90° detector bank can easily resolve the diagnostic Bragg peaks of ice XI. Moreover, the high neutron flux on this station allows us to overcome the very strong incoherent contribution to the background of the diffraction pattern from the hydrogen atoms in the sample.

Sample collection and analysis. Two of our colleagues (Dimitri Grigoriev and Sepp Kipfstuhl) acquired a sample of Antarctic ice, estimated to be about 3000 years old, and returned it to the U.K. for analysis. The sample was collected from a shallow ice-core (B34) drilled at the Kohnen station (75°00' S, 00°04' E, Dronning Maud Land, Antarctica) as part of the European Project for Ice Coring in Antarctica (EPICA). At the sample acquisition depth (201.30m) the temperature was 228 K, which should result in ~20 % of the protons being ordered.[2-4] The sample was stored in a Taylor-Wharton XT10 dewar for transport back to the UK. The sample temperature was monitored continuously during transport with a Tinytalk®II miniature temperature logger, and was never observed to be warmer than 232.5 K. On the day of the neutron diffraction experiment, the sample was extracted from the dewar flask and transferred to an aluminium cup cooled in dry ice. The ice was powdered using a steel pestle and mortar, both cooled in a bath of liquid nitrogen. The powdered ice was spooned into a TiZr alloy sample canister held in liquid N_2, and then a cryostat centre stick was screwed to the top of the sample holder. The entire assembly was transported to the diffractometer immersed in liquid N_2 and rapidly placed in an aluminium-tailed cryostat that had been pre-cooled to 100 K. All of the tools used to manipulate the sample were cooled in either solid CO_2 or liquid N_2 and the entire sample preparation was carried out in the ISIS cold room at ~258 K. In situ temperatures were monitored with a thermocouple. We are confident that the temperature of our sample never exceeded 232.5 K from the moment it was collected until the last neutron was counted. Care was taken to exclude vanadium from the experimental setup since it introduces a Bragg peak at ~ 2.14 Å which might easily be confused with the diagnostic 131 peak of ice XI at 2.15 Å. A cadmium mask was constructed to collimate out any scattering which did not originate in the sample. Diffraction data were collected at 100 K in the 90° detector banks of the POLARIS diffractometer for ~ 36 hours (6134.3 μAhr).

Results. It is clear from the diffraction pattern (Fig. 1) that the 131 Bragg peak due to ice XI is absent. Indeed the pattern is fitted very well with a pure ice Ih model. In order to place an upper limit on the possible abundance of proton ordered ice in the sample, a two-phase refinement was tried, incorporating ice XI. Inclusion of the extra phase produced no real improvement in the fit (χ^2 drops only very minimally from 2.128 to 2.119). The refined phase fraction of ice XI is 2.3 ± 1.3 wt %, a value which is considerably less than the expected 20 % fraction of ice XI, and is not statistically significantly different from zero.

Conclusion. On the basis of this study, we conclude that it is unlikely that ice Ih becomes partially proton ordered at the temperatures encountered in the earth's ice sheets. This work is reported in detail in Fortes et al. (2004).[6]

Figure 1. The diffraction pattern of the Antarctic ice sample. Tic marks are for pure ice Ih.



[1]Matsuoka et al., *Geophys. Res. Lett.* **25**, 1573 (1998).
[2]Fukazawa et al., *Chem. Phys. Lett.* **294**, 554 (1998).
[3]Fukazawa et al., *Earth Planet. Sci. Lett.* **171**, 481 (1999).
[3]Fukazawa et al., *Ann. Glaciol.* **31**, 247 (2000).
[5]Mae and Fukazawa, *ISIS Experimental Report*, RB10625 (SXD).
[6]Fortes et al., *J. Chem. Phys.* **120**, 11376 (2004).