Proton Magnetic Resonance Spectrum of Polywater

Abstract. *With the aid of a time-average computer, the proton magnetic resonance spectrum of anomalous water (polywater) is obtained. The spectrum consists of a single broad resonance shifted approximately 300 hertz downfield from the resonance of ordinary water.*

Anomalous water was first observed by Deryagin and his associates (*1*) who demonstrated that its physical properties differ from those of regular water. Lippincott *et al.* conclude (*2*) that the observed Raman and infrared spectroscopic data from water that condenses inside fused quartz capillaries is compatible with a highly ordered polymeric structure composed of H_2O monomer units. Lippincott *et al.* assume this to be the basic structural unit because of an extremely strong O–H–O three-center bond. One structure postulated by Lippincott involves the units being arranged in a plane to form regular interconnected hexagonal rings. These layers of rings tend to stack one on another to build a regular three-dimensional framework. In forming the hexagonal rings, oxygen atoms interact with the *s* orbital of the hydrogen atoms through sp^2 bonding. The network of rings has a negative charge (the number of rings minus one) which is presumably counterbalanced by hydrated protons. Such a structure implies extensive delocalization of the electrons throughout the network. Previous attempts to observe the proton magnetic resonance (pmr) spectrum of anomalous water [or polywater (*2*)] failed (*3*). It is postulated that the regular structure of the quartz surface and the small dimensions of the capillaries (inside diameter, commonly 10 to 50 μm) combine to produce the high degree of association of the water molecules. We decided to obtain a high-resolution pmr spectrum for polywater, in the hope of obtaining further information as to its structure.

Samples of polywater, prepared in the manner described by Lippincott (*2*) in capillaries of from 50 to 200 μm in diameter, are characterized by their Raman spectrum (*2*). High-resolution pmr spectra were obtained with a Varian A60A spectrometer equipped with a Varian C1024 time-average computer at ambient temperatures. Reference samples of water both in and out of quartz capillaries were observed and yielded only the normal resonance of water.

The polywater sample remained in the capillary tube during the pmr experiment; water was the external standard. The broad peak which occurs approximately 300 hz downfield from normal water has a line width at half height of approximately 120 hz (Fig. 1).

The spectrum observed may be due to a deshielding by the "ring current" from the delocalized π electrons of the oxygen atoms of the sample, combined with a high degree of hydrogen bonding between molecules, although other explanations are possible. This is in agreement with the hexagonal ring structure (*2*).

We postulate that the formation of polywater in quartz capillaries involves three steps. (i) Hydrogen bonds form between water molecules and the oxygen of the silicate framework. (ii) Further condensation of water brings the molecules close to each other and hydrogen bonds form between water molecules, combined with the release of a proton from one of the water molecules. If stability of electron delocalization is associated with a six-membered ring structure, then this type of structure will form, although the hexagonal structure of the quartz surface may also be a factor. (iii) A number of other layers of polywater form, and these stack on top of the first, possibly with further O–H–O hydrogen bonds forming between layers. These bonds might have a near-normal O–O distance of approximately 2.7 Å.

An attractive feature of this mechanism is that, should there be no hydrogen bond formation between the individual layers, the release of the proton provides the cation necessary to counterbalance the negative charge in the ring.

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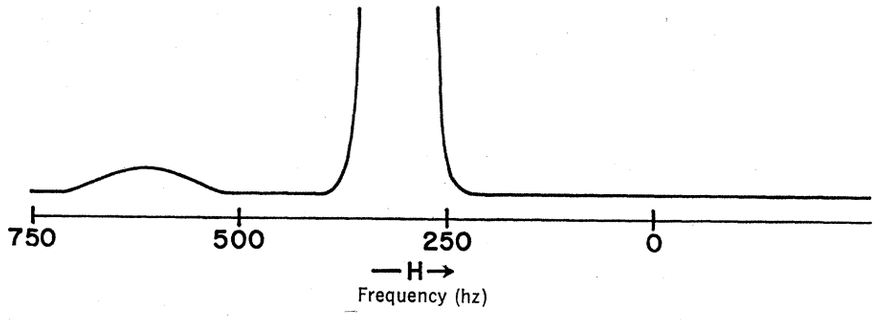

Fig. 1. The proton magnetic resonance spectrum of polywater. The small broad resonance is approximately 300 hz downfield from the resonance due to normal water. The spectrum was obtained with the aid of a time-average computer.

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Stalactite Growth beneath Sea Ice

Abstract. *Fresh ice stalactites were observed beneath sea ice in Antarctica. They are hollow, tapering, inverted cones having a base diameter between 10 and 20 centimeters and a tip diameter of 4 to 10 centimeters extending downward about 100 centimeters. The stalactites form when dense, chilled brine drains downward from the ice sheet into seawater of normal salinity and near-freezing temperature.*

A study of sea ice in McMurdo Sound, Antarctica, included the determination of seasonal changes in thickness. One problem in measuring the thickness of sea ice is that a large difference often occurs between measurements taken in the same small area at the same time. Observations made by scuba diving beneath the sea ice indicated that the differences were caused by the irregular skeleton layer at the bottom of the 1.5- to 2-m thick growing ice sheet. Other unusual features consisted of numerous stalactite-like growths extending downward as much as 1 m from the skeleton layer.

In November 1968 it was possible

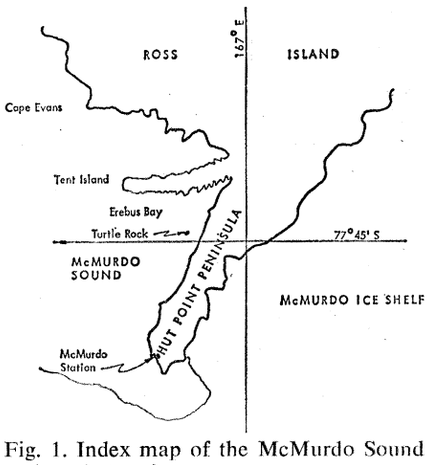

Fig. 1. Index map of the McMurdo Sound region, Antarctica.

to arrange a scuba dive beneath sea ice about 1.8 m thick near Turtle Rock in Erebus Bay (Fig. 1). Stalactites were abundant in this area and were observed closely; however, no exact measurements were made nor were samples collected.

The bottom of a growing sea ice sheet is characterized by an irregular surface with numerous disconnected ice platelets protruding downward. This layer has been termed the skeleton layer by Assur (*1*) and results from the separation and growth of pure ice platelets freezing from seawater (*2*).

The thickness of the skeleton layer beneath Arctic Sea ice has been described as being 1 to 2 cm (*3*), up to 2 cm (*4*), and 2.4 to 2.8 cm (*5*). However, direct observations beneath sea ice in Antarctica revealed that the skeleton layer was at least 10 to 15 cm thick and up to 60 cm or more in many locations. The bottom surface was extremely irregular with a relief of 30 to 60 cm (*6*). Part of the irregular bottom topography caused by uneven platelet growth consisted of ice (freshwater) stalactites extending downward from the growing sea ice.

Ice stalactites consist of freshwater ice frozen from seawater with the concurrent expulsion of brine. They occur singly or in groups and extend downward from 15 or 20 cm to 100 cm or more below the skeleton layer. They are sparse, averaging no more than three or four in an area of about 25 m^2. Two forms were observed within the same area and were growing under the same conditions; these forms are designated as the platelet-growth type and the ice-shell type.

The platelet-growth stalactite consists of ice platelets meshed together to form a hollow, slightly tapering, inverted cone hanging from the skeleton layer. Individual platelets are 1 to 2 mm thick with vertical or slightly inclined *c*-axis orientation predominating. The maximum base diameter appeared to be about 20 cm, tapering to a tip diameter of 6 to 10 cm over a length of about 100 cm.

All of the platelet-growth stalactites observed were hollow, and some contained brine of higher density than the surrounding seawater. Under ideal conditions of light, this brine could be seen draining downward from the tip of the stalactite. The stalactites are fragile but flexible enough to bend slightly with the gentle tidal currents; however, strong currents probably destroy the longer growths.

Ice-shell stalactities consist of a shell, 1 to 2 mm thick, that also forms an irregular hollow cylinder or cone tapering downward and having dimensions similar to the platelet-growth type. Platelet growth is poorly developed or absent along the sides of the stalactite, although a normal skeleton layer usually occurs around the base. These stalactites commonly occur singly or occasionally in groups. One stalactite consisted of three concentric hollow cones. The inner cone was about one-third the length and diameter of the outer cone, which was about 15 cm in diameter at the base and 80 cm long. The ice-shell stalactites are much more fragile than the platelet-growth type and are quite brittle; it is unlikely that they survive much disturbance and their existence is probably brief.

The ice stalactites probably result from a concentrated flow of dense, highly saline, cold brine draining into seawater of normal salinity (34 to 35 parts per thousand in McMurdo Sound). During the growth of sea ice, brine is expelled from seawater and becomes trapped as vertical, elongated cells at interplatelet boundaries. When growth occurs during the coldest part of the winter, most brine features are small and closely spaced except for occasional drainage channels that may become several millimeters in diameter. Occasionally, high-density brine may collect in several coalescing drainage channels that conduct it downward toward the bottom of the ice sheet. In addition to high salinity and density, brine trapped and draining from a thick ice sheet could also be quite cold. For example, at a depth of 1.5 m in sea ice 2 m thick, the ice temperature was −14°C early in November 1968.

When a large quantity of chilled, dense brine collects and begins to drain downward, stalactite growth is probably initiated as soon as the cold brine encounters seawater of normal salinity and near-freezing temperature. As platelets begin to grow around the periphery of the brine column, they in turn may add to the process of brine concentration. The platelet-growth stalactite is probably formed when a large amount of brine drains slowly during a long time period that allows for peripheral platelet growth. The ice-shell stalactite forms when a mass of cold, dense brine drains rapidly downward from the ice sheet and through the seawater. Ice continues to form until the density current gains heat from the surrounding seawater or until it dissipates.

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Scanning Electron Microscopy of Fresh Leaves of Pinguicula

Abstract. *Moist surfaces of leaves of* Pinguicula grandiflora *Lamck. can be observed directly by scanning electron microscopy, without metal coating. Samples dry out rapidly in the instrument, but during the first few minutes images can be obtained which must represent the natural state of the leaf surface.*

It has been commonly accepted that the biological applications of scanning electron microscopy are limited by the fact that samples have to be examined at very low pressures of the order of 10^{-5} torr and by the need to coat non-