resents a new and exciting technique for geological dating which can be tested and developed with other examples. The example presented here indicates that the results obtained by this method complement the information obtained by the classical Rb-Sr, U-Th-Pb, and K-Ar methods and that fission xenon dating should prove to be especially valuable for samples that have been affected by a complex series of geological events.

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Supercooling of Water to -92°C Under Pressure

Abstract. *The temperature at which "clean" supercooled water freezes has been determined as a function of pressure up to 3 kilobars, using a differential thermal analysis technique on subdivided water samples. The supercooling limit of such samples, -38° C at normal pressure, is lowered by initial increase of pressure, reaching a minimum value of -92° C at 2.00 kilobars.*

Although water is the most intensively studied of all liquids, there remain important and accessible areas of experimentation in which its properties are quite unknown. The way in which the profoundly anomalous character of liquid water has been emphasized by the recent exploration of the supercooled liquid region at normal pressures (*1-6*) bears testimony to the importance of maximizing the range of pressure and temperature conditions in which measurements are made. Nothing is known of the range over which water can be supercooled under high pressure. To establish the extent of the unexplored pressure-volume-temperature (*PVT*) region for water, we have therefore determined the limit to supercooling at various pressures up to 3 kbar. Our results show that over a considerable range of pressures water can exist as a liquid at temperatures near -90°C, the extent of supercooling being nearly 30°C greater than at 1 atm.

The low temperature limit to supercooling, T_{H}, is imposed by the onset of homogeneous nucleation (crystal initiation by order fluctuations within the bulk water phase). We determined T_{H} by means of a simple thermocouple differential thermal analysis technique during cooling of small pressurized samples. The samples, in which heterogeneous nucleation was inhibited by emulsification (*7*), were isolated in thin-walled glass tubes at one end of a ¼-inch stainless steel high-pressure tube, and their thermal behavior was probed using a collinear sample and reference arrangement (*8*) in which the pressure-transmitting fluid served as the reference. To perform a measurement, oil pressure between 1 and 3000 bars was applied to the sample by means of a nonfreezing hydrocarbon fluid and the sample temperature was then lowered at ~3° per minute by inserting the pressure tube plus sample into a glass-jacketed aluminum cylinder 1 inch in diameter, and cooling the assembly in liquid nitrogen. After crystallization was observed the samples were reheated to observe the melting points, T_{m}, of the ices formed. Differential and total electromotive forces were recorded using a Honeywell two-pen recorder. Results were reproducible to within chart reading uncertainty except at high pressures, where crystallization apparently proceeds rather sluggishly, and some uncertainty in assigning the temperature at which it commences is encountered. Attempts to suppress the crystallization completely, and thus to obtain a vitreous phase of ice directly from the liquid, have not met with success despite the quenching rate of 180° per minute which our small thermal mass system permits.

Results are shown in Fig. 1 for emulsions of water in *n*-heptane and in a mixture of methylcyclohexane (MCH) plus methylcyclopentane (MCP), the latter dispersant phase being necessary for temperatures below the freezing point of *n*-heptane. Some earlier results obtained with a more massive pressure cell and larger samples are included (points denoted under "cell 1" in Fig. 1).

The most significant finding is the very wide region of additional *PTX* space in which properties, *X*, of water can be studied using techniques suitable for the dispersed nature of the sample. It will be possible to investigate somewhat less extensive regions with samples of fine-bore capillary tubes (*1-4*). Use of glass capillary tubing treated to withstand high internal pressure (~3 kbar) (*9*) should greatly simplify the exploration of this region.

The other striking feature of the results reported here is the similarity between the T_{H}-pressure function and the equilibrium melting curve. As the melting points of the samples show, the break in the T_{H}-pressure function is associated with a change in the polymorph of ice being nucleated. The similarity is interesting because homogeneous nucleation is intrinsically a kinetic phenomenon, whereas the triple point at 2.1 kbar and -22°C is determined only by the free energies of ice I, ice III, and water, which become identical at this point. Homogeneous nucleation theory (*10*) shows that the probability of occurrence of order fluctuations large enough to produce viable crystal nuclei in the supercooled liquid increases with increasing difference between the free energies of the solid and liquid. However (*10*) this dependence will lead to a break in T_{H} at the triple point pressure only if (i) the ice I-water and ice III-water surface free energies are the same and (ii) the probability of order fluctuations in the directions of the two crystal topologies (including fluctuation growth and decay constants) are also equivalent. In binary systems such coincidences are not common, because specific ordering in the liquid often favors fluctuations in the direction of one crystal type over more stable forms—in fact, highly metastable polymorphs may often be produced in this way. In such cases T_H will not mimic the equilibrium liquidus line.

It is reasonable to suggest, on the basis of these considerations, that in the pressure range 0 to 2 kbar the local molecular order in water changes systematically with pressure in the direction of the ice III local structure. This is a multiple ring size (five-, six-, and eight-membered) arrangement of fully hydrogen bonded molecules in which the H–O–H angles are strongly distorted from the ideal tetrahedral value and the O–H···O bond angles are much less than 180° (*11*). Such a suggestion is quite consistent with the results of recent Raman spectral studies at high pressures (*12*) which show that volume decreases are not primarily associated with any increase in the proportion of broken hydrogen bonds, as two state models would suggest, but instead are accomplished by increased hydrogen bond distortion.

The fact that, above 2 kbar, T_H remains a constant 70° below the melting point shows that the low-pressure supercooling range of 38° is anomalously small. This premature termination of the supercooled state can be associated with the remarkable divergences in C_p, κ_T, and α (the heat capacity at constant pressure, compressibility, and expansivity) observed in low-pressure supercooled water (*2, 3, 6*) through the increase in nucleation probability which accompanies the implied increasing entropy and volume fluctuations ($\overline{\Delta S^2} = k_B C_p$, $\overline{\Delta V^2} = k_B T V \kappa_T$). The rapid increase in ($T_m - T_H$) with increasing pressure therefore implies that these interesting thermodynamic anomalies are also washed out by increasing pressure [as already suggested by the disappearance of the density maximum above 2 kbar (*13*)]. Since we inferred above that the same pressure increases are systematically favoring bent bond topologies, we can conclude that the water anomalies all derive from the possibility, at low pressures, of forming bonds which on average approach the ideal 180° O–H···O angle (within a single network as in ice VII). It is this unusually open disposition of linked tetrahedral units, rather than tetrahedral coordination per se, which is the unique feature of low-pressure water. In support of this we note that SiO_2, whose crystalline polymorph crystobalite (high-temperature form) has the ice Ic structure with linear "oxygen bonds" (Si–O–Si) averages Si–O–Si bond angles of only 144° in the liquid at normal pressures and low temperatures [judged from the vitreous structure frozen in at about 1300°C (*14*)]. Although this network liquid does exhibit a volume minimum (*15, 16*) it is only a shallow one on both absolute and reduced bases of comparison with water, and is only encountered at large (200°) supercooling. For GeO_2, in which the analogous oxygen bond angle (Ge–O–Ge) in the vitreous state has decreased to an average value of 133° (*17*), no volume minimum is observed anywhere in the liquid state.

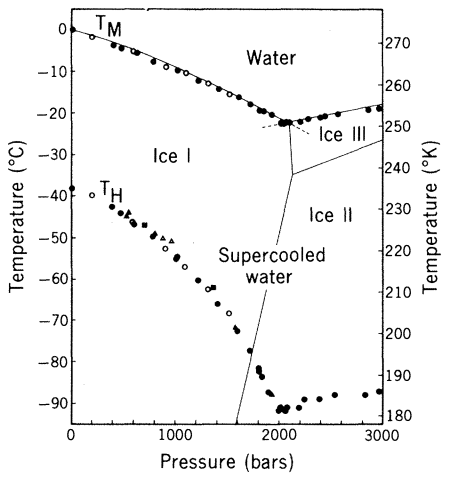

Fig. 1. Homogeneous nucleation and equilibrium melting temperatures for water in emulsion form as a function of pressure. Results obtained with different pressure cells and emulsion carrier fluids are distinguished as follows. Cell 1: (△) heptane, (■) pentane, (▲) methylcyclohexane. Cell 2: (○) heptane, (●) methylcyclopentane + methylcyclohexane. Solid lines are the accepted equilibrium phase boundaries.

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Muscle Activation: Effects of Small Length Changes on Calcium Release in Single Fibers

Abstract. *In single muscle fibers, small (1 percent) changes of length have a marked effect of both the calcium activation and the tension elicited by a constant current stimulus. The decrease in tension with shortening is accounted for almost entirely by a decrease in calcium release, rather than by changes in mechanical factors, such as filament geometry.*

It was well established by the work of Gordon *et al.* (*1*) and others (*2*) that the active force a muscle can develop depends on the length of the muscle. Typically, for striated muscles, a plot of length against maximum active tension (force per unit area) shows a maximum near in situ rest lengths. At muscle lengths shorter or longer than the rest length, active tension decreases. Much of this decrease may be due to mechanical factors involving filament geometry. At long lengths, the decreased amount of overlap between the thick and thin force generating filaments is probably a major factor. At short lengths, the major mechanical factors are less well understood. However, evidence is accumulating that factors other than filament geometry—for example, changes in calcium activation—operate, particularly at short lengths (*3*).

In this report we examine the hypothesis that length changes directly affect muscle calcium "activation" (that is, the amount of calcium released by a constant electrical stimulus). Since calcium ions activate the force generating cross-bridges in muscle (*4*), reduced calcium release at shorter muscle lengths would result in a reduced force output. This hypothesis is tested by