the tropical sea sediment (0 to 300,000 years old) and the result from the Greenland ice (100 to 300 years old) is what can reasonably be expected from the constancy of galactic cosmic rays in the last million years and from the fact that the $^{26}Al/^{10}Be$ ratios are compared: the ratio of the production rates $^{26}Al/^{10}Be$ in the atmosphere is practically independent of the geomagnetic latitude effect, and the two elements, aluminum and beryllium, show striking similarities in their chemical behaviors.

14. The earlier estimation of the ^{26}Al production in the atmosphere, 8×10^{-9} dpm cm^{-2} $year^{-1}$ (*5*), was based on the cross section calculated from an earlier formula of G. Rudstam [*Philos. Mag.* **46**, 344 (1955)], which is good only to about a factor of 3. By using a more elaborate formula [R. Silberberg and C. H. Tsao, *Astrophys. J. (Suppl. Ser. 220)* **25**, 315 (1973)], which generally shows an agreement with experimental results to within +30 percent and −25 percent, we obtained a ^{26}Al production rate of 5.3×10^{-9} dpm cm^{-2} $year^{-1}$. The ^{10}Be production rate was estimated at $(4.2 \pm 1.4) \times 10^{-7}$ dpm cm^{-2} $year^{-1}$ as an average of the estimation based on the use of radiochemically measured cross sections [B. S. Amin, S. Biswas, D. Lal, B. L. K. Somayajulu, *Nucl. Phys. A* **195**, 311 (1972)] and that based on the use of isotopically determined cross sections [G. M. Raisbeck and F. Yiou, *Phys. Rev. C* **9**, 1385 (1974)], 4.7×10^{-7} [B. S. Amin, D. Lal, B. L. K. Somayajulu, *Geochim. Cosmochim. Acta* **39**, 1187 (1975)] and 3.6×10^{-7} dpm cm^{-2} $year^{-1}$, respectively. From these results a $^{26}Al/^{10}Be$ ratio of 0.013 ± 0.006 was obtained for the production in the atmosphere.
15. Based on the cumulative meteroid flux determined by B. G. Cour-Palais [*NSAS Spec. Publ. 330* (1973), p. 22-1] from the Apollo window meteoroid experiment, we estimated a cosmic dust accretion rate of 35 ton/day and a saturation factor of about 50 percent. [For this estimate, we used the flux-mass curves in figure 21-4 of Cour-Palais: the solid line (NASA model curve) for particles of $> 10^{-8}$ g and the dashed line for smaller particles.] This meteoroid flux, in agreement with lunar sample microcrater data (F. Horz, D. A. Morrison, D. E. Gault, V. R. Oberbeck, W. L. Quaide, J. F. Vedder, paper presented at the Soviet-American Conference on the Cosmochemistry of the Moon and Planets, Moscow, 4–8 June 1974) may be uncertain by as much as a factor of 3. Assuming a solar proton flux of J (energy > 10 Mev) = 100 proton cm^{-2} sec^{-1} per 4π with a shape factor of R_0 = 100 Mv or J = 70 with R_0 = 150 Mv [Y. Yokoyama, J. Sato, J.-L. Reyss, F. Guichard, in *Proceedings of the Fourth Lunar Science Conference*, W. A. Gose, Ed. (Pergamon, New York, 1973), vol. 2, p. 2209], we obtained a saturated activity for ^{26}Al of 0.5 dpm per gram of cosmic dust. Combining these data, we estimated an influx of 0.6×10^{-9} dpm cm^{-2} $year^{-1}$, which is about 10 percent of the ^{26}Al production in the atmosphere.
16. We are grateful to Prof. J. Labeyrie for his constant encouragement and to Dr. F. Guichard for his valuable aid during the measurements. We thank Drs. K. Sakamoto and J. Takagi and Mrs. M. Tsuchimoto for their participation in the early part of this work.

12 January 1976; revised 22 March 1976

Density Maxima in High-Pressure Supercooled Water and Liquid Silicon Dioxide

Abstract. *With glass capillary pressure vessels it has been possible to study the effect of pressure on the temperature of maximum density (TMD) and on the "sharpness" of the density maximum in liquid H_2O and D_2O in the important but little-studied supercooled regime. A pressure of 1200 bars produces a 33°C depression of the TMD in these liquids and a considerable reduction in sharpness. Comparison with the rather flat density maximum for liquid SiO_2 supports the notion that the presence or absence of density anomalies in "tetrahedral" liquids depends on the average bridge-bond angle, which is evidently unusually large in water at normal pressure.*

The liquid states of H_2O and SiO_2 are unusual, although by no means unique, in their density-temperature relations insofar as both liquids exhibit density maxima (*1, 2*). In H_2O at a pressure of 1 atm the density maximum occurs in the stable liquid region, whereas in SiO_2 the maximum is observed only in the supercooled state. It has been common to assume in each case that the anomaly arises from the tendency of these liquids to establish an expanded tetrahedral network structure as the temperature decreases. The details of this structuring are clearly vital to an understanding of the properties of these important liquids.

In a recent report (*3*) we speculated, on the basis of the pressure dependence of the homogeneous nucleation temperature of water, that the difference in the temperature of maximum density (TMD) relative to the melting point, as well as a difference in the "sharpness" of the volume variations about the maximum in each case, was due to differences in the average "bridge-bond" angle, O···H–O or Si–O–Si. We present here some observations for D_2O on the pressure dependence of the TMD and of the density about the TMD, which tend to support the above suggestion. We report on D_2O rather than on H_2O because of the greater pressure range over which the TMD can be followed before the supercooling limit for our method is exceeded.

The new measurements cover the temperature (T) range from 30°C to −30°C and the pressure (P) range from 1 to 1200 bar. Because of the need to make the most important measurements at high pressures under conditions where the liquids were metastable, we found it necessary to develop an unusual though very simple high-pressure technique, which we describe briefly.

To avoid premature crystallization, small samples must be used (*4*). For the measurements described here we satisfied this condition by confining the samples in fine glass capillaries with a bore of ~ 90 μm. When freshly pulled from tubing 9 mm in outside diameter and 2 mm in inside diameter, these capillaries prove to be capable of withstanding internal pressures well in excess of 2 kbar without rupture. Thus the glass capillary can serve as the sample container, the crystallization inhibitor, and the pressure vessel at the same time. Because the pressure vessel is transparent, volume (V) measurements may be made by direct visual observation of the position of the mercury meniscus. With this capillary pressure vessel it is possible to extend a "see-through" volumetric technique for the study of supercooled water developed by Speedy and Angell (*5*) to the 2-kbar pressure range. Capillary tubes were selected for uniformity of diameter and calibrated. Triply distilled water was introduced and isolated by means of a mercury slug, and the filled capillary was sealed with epoxy resin into a steel connecting link to a hydraulic high-pressure system. We then monitored the position of the mercury meniscus relative to a series of fiducial marks on the capillary at various pressures and temperatures, using a cathetometer external to a thermostating bath.

Using capillaries of length 0.2 to 1.0 m, we could determine compressibilities (*6*)

$$-\frac{1}{V}\,(\partial V/\partial P)_T$$

to ± 1 percent. It was not possible to determine expansivities

$$\frac{1}{V}\,(\partial V/\partial T)_P$$

with as high a degree of accuracy, because the volume is very sensitive to pressure and the pressure on the Heise Bourdon gauge could not be read more accurately than ± 2 bars. However, the volume could be determined to ± 0.01 percent, sufficient to characterize the behavior of D_2O in the vicinity of the density maximum. Both compressibilities and expansivities could be studied down to temperatures in the range −20° to −30°C depending on pressure, before the measurements had to be terminated because of sample crystallization. This event tended to be destructive of calibrated capillaries and was therefore to be avoided as far as possible.

We determined the TMD for each pressure by computer-fitting the column length versus temperature data to a fourth-degree polynomial and finding the extremum. Corrections for the thermal expansivity of the glass are negligible, but it was necessary to correct for the dimensional changes of the capillary with pressure. We did this by calibrating each run, using the *PVT* data of Fine and Millero for water at ordinary temperatures (*7*).

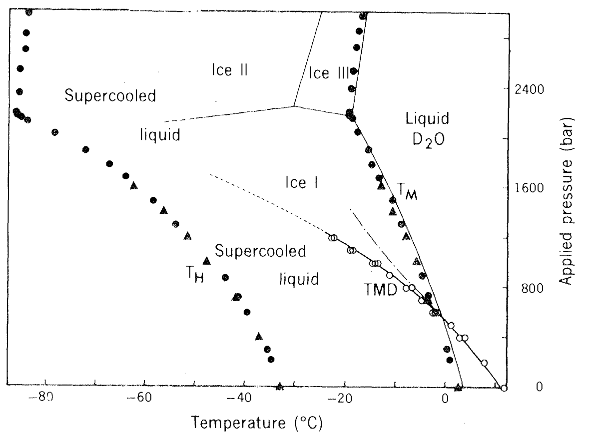
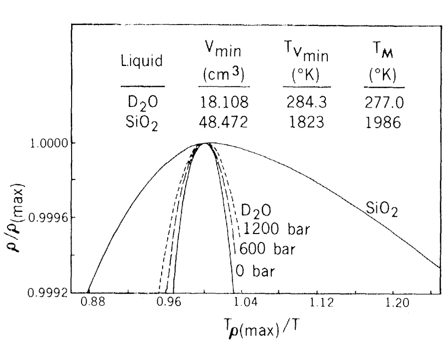


Fig. 1. Temperature of maximum density (TMD) and homogeneous nucleation temperature (T_H of D_2O as a function of pressure. Solid-solid and solid-liquid phase equilibrium lines are taken from (*13*). (—·—·—) TMD curve obtained by extrapolation of the *PVT* equation reported by Fine and Millero (*7*); in the pressure-temperature region in which it is considered reliable ($T > 2$°C, $P < 1000$ bars), the TMD plot in (*7*) is almost coincident with the data presented here; (-O-O-O-) experimental TMD values obtained in this work; (-●-●-●-) T_H and melting points (T_M) of D_2O emulsions in methylcyclohexane + methylcyclopentane (1 : 1); (-▲-▲-▲-) values of T_M and T_H of D_2O emulsions in *n*-heptane.

Values of the TMD for D_2O at various pressures are shown in Fig. 1 against the equilibrium freezing curve. Figure 1 includes data on the homogeneous nucleation temperature for D_2O obtained from emulsion studies companion to those recently published for water (*3*). Although our volumetric technique is rather crude by normal standards for water, it is sensitive enough to give TMD values in reasonable agreement with literature data over the common ranges of temperature and pressure (Fig. 1) and it also can be used to correct earlier estimates of the TMD at high pressures on the basis of extrapolations (*7*). In contrast to the original findings of Bridgman for H_2O (*8*), which have since been corrected (*9*) but are still being quoted (*1*, *3*), we find that the density maximum does not "wash out" via an intermediate maximum-plus-minimum stage but instead "drops out of sight" by progressive displacements to lower temperatures. Figure 1 suggests that a density maximum may be observable down to −85°C if a suitable technique for use with emulsified samples can be developed.

Of greater fundamental interest than the above is the manner in which the density varies about the maximum as a function of temperature. In our earlier report (*3*) we remarked that, when appropriate allowances are made for the differences in liquid temperatures, the density maximum in water appears very sharp by comparison with that in liquid SiO_2. This finding was taken as evidence that the average O···H–O bridge-bond angle in water is closer to 180° than the average Si–O–Si angle, 144°, determined for vitreous SiO_2 (*10*) (which has a structure characteristic of the supercooled liquid very close to the TMD). If this is the case, then the density variation for water about the TMD should become flatter and thus approach that of SiO_2, as increases in pressure force a decrease in the average O···H–O angle.

In Fig. 2 we show the data for these two substances at a pressure of 1 atm using the reciprocal temperature scale $1/T$ (in degrees Kelvin) reduced by the temperature of the density maximum, T_ρ (max), in order to best compensate for the difference in temperature at which the phenomena occur (the TMD for SiO_2 is 1500°C) (*2*). We also include in Fig. 2 our new data for D_2O at 600 and 1200 bars to show that the pressure effects are in the anticipated direction (*11*). It appears that pressures in excess of 2 kbar would be needed to obtain behavior for D_2O like that of SiO_2 and even greater pressures would be necessary to eliminate the possibility of a density maximum completely.



Liquid	V_{min} (cm^3)	$T_{V_{min}}$ (°K)	T_M (°K)
D_2O	18.108	284.3	277.0
SiO_2	48.472	1823	1986

Fig. 2. Reduced variables comparison of the variation of density ρ about the density maximum for liquid SiO_2 and liquid D_2O at various pressures; V_{min} is the minimum volume of SiO_2 or H_2O, that is, the molecular weight divided by the maximum density; $T_{V_{min}}$ is the temperature at which the volume minimum occurs.

At these high pressures the density maximum would occur at a greater relative supercooling in water than in SiO_2, raising the possibility that compressed water might, like SiO_2, tend to vitrify if quickly cooled. Unfortunately, however, even with the high quenching rates obtained on plunging our fine glass capillaries into liquid nitrogen, the vitreous state is not observed. Thus vapor deposition remains the most practical route to the vitreous state of water on which so much attention is currently being focused (*12*).

Note added in proof: We have largely overcome the accuracy limitation of the Bourdon gauge by the addition of a simple subsidiary pressure gauge, consisting of a mercury bead moving in a long fine capillary, which allows a given pressure to be reset to within ± 0.2 bar at any pressure up to the bursting pressure of the capillary (2.5 to 3 kbar). The capillary gauge is thermostated at room temperature and the bead position relative to a fiducial mark is monitored with a traveling microscope. The results shown in Figs. 1 and 2 are substantially confirmed. The 0.6°C error in the TMD due to the expansivity of Pyrex glass is now a significant correction and should be added to each TMD.

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14. Research supported by the National Science Foundation.

16 March 1976; revised 12 July 1976