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RHEOLOGY OF ICE II AND ICE III FROM HIGH-PRESSURE EXTRUSION

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Abstract. Rheological parameters for ice II and ice III, needed in tectonic models of the icy satellites of the major planets, are obtained from extrusion experiments and compared with the rheology of ice I at pressures ~2 kbar and temperatures ~240K. Ice II has a higher effective viscosity (by a factor ~10) than ice I at similar stress levels, whereas ice III has a lower viscosity (by a factor ~0.01). The rheological contrasts among the ice phases are related to differences in the dielectric relaxation behavior and state of proton order/disorder in the structures in a way that sheds light on the nature of dislocation motion in ice. A striking transformation plasticity accompanies the ice I-III transition and could have large tectonic effects.

Introduction

Because the interiors of several of the moons of the major planets consist to a large extent of ice in its high-pressure forms [Lupo and Lewis, 1979], the thermal and structural evolution of these moons (e.g., subsolidus convection) and its reflection in the morphology of their surfaces (e.g., impact crater relaxation) is dependent on the rheological properties of the dense ice phases [Poirier, 1982]. Additional interest in the rheology of these phases arises at a fundamental level with regard to general relationships between rheology and structure among polymorphs. Because proton disorder and the associated mechanism of proton rearrangement in the hydrogen-bonded structure of ice I are thought to have an important effect on the creep process [Glen, 1968], and because the other ice phases have different structures and proton order/disorder properties [Kamb, 1973], a comparison of their rheologies offers the possibility of obtaining new insight into the role of these structural features in creep.

Preliminary results of an ongoing experimental study of the creep properties of ice II and III by constant-strain-rate tests at high pressure have been reported by Kirby, Durham, and Heard [1985]. Because of the importance of the subject, we believe it of value to present briefly the results of an independent set of experiments we have carried out by a quite different method, namely, extrusion from high pressure. Our results agree in a general way with those of Kirby et al. [1985], and in addition reveal a flow runaway phenomenon that is a dramatic manifestation of transformation plasticity.

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Experimental Method

Extrusion experiments were carried out as follows. Approximately 2 cm^3 of distilled water was introduced into the 9.5-mm bore of a piston-cylinder apparatus, the upper piston of which was loaded by a hydraulic ram to pressurize the sample. Extrusion of the sample took place through a narrow cylindrical orifice along the axis of the lower piston, which was supported in fixed position in such a way that the extruded ice could escape at atmospheric pressure from the bottom. Orifices of diameter 1 to 2 mm, and of length 12.5 mm, were used in different experiments. The bomb was immersed in a cooling bath for temperature control to ±1°C. In each experiment, sample temperature and pressure were brought to desired values (Fig. 1), and the rate of extrusion was measured by monitoring the advance of the upper piston, detected with a displacement transducer and recorded on a strip-chart recorder along with the hydraulic-ram pressure.

Results and Analysis of Data

At sample pressures below the phase transition to ice II or III the extrusion rate is governed by the rheology of ice I, averaged over the pressure range from sample pressure to atmospheric and over the shear stress range across the orifice. If ice I obeys the non-linear flow law $\dot{\varepsilon} = A_1\tau^{n_1}$, where τ is shear stress, $\dot{\varepsilon}$ is shear strain rate, and A_1 and n_1 are rheological constants, whose variation with pressure is small enough to be neglected here [Weertman, 1983], and if there is no slip at the walls of the orifice in the extrusion, then the extrusion rate, expressed in terms of the speed of piston advance U, will be

$$U = A_1(P/L)^{n_1}\ a^{n_1+3}/[b^2(n_1+3)2^{n_1}] \qquad (1)$$

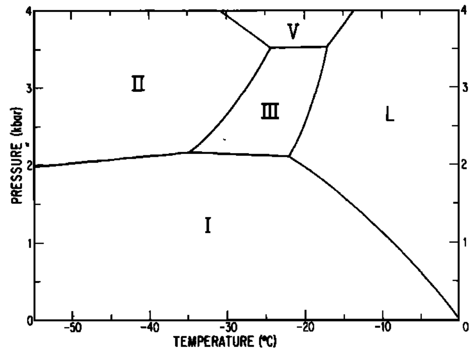

Fig. 1. Partial phase diagram of H_2O showing fields of ice I, II, III, and liquid water (L). Data from Bridgman [1912].

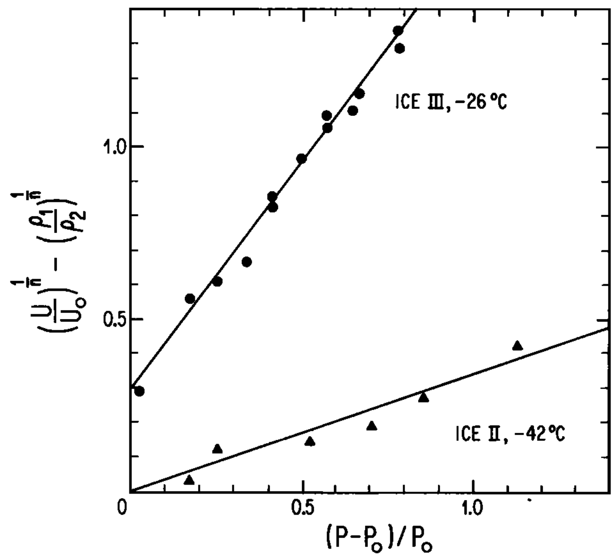

Fig. 2. Extrusion-rate data for ice II and ice III as a function of the excess of sample pressure P over the transition pressure P_o. The extrusion rate U is expressed in terms of the form suggested by (2), with n = 5.6. Orifice diameter 2.1 mm for ice-II extrusion tests, 1.0 mm for ice-III tests.

where P is the sample pressure, a the orifice radius, L the orifice length, and b the radius of the loading piston. Results of extrusion experiments of this type, evaluated in a log-log plot of U against P, give a straight-line relation as expected from (2), with slope $n_1 \approx 5.6$.

At sample pressures P above the phase transition, high-pressure ice fills the sample chamber and a length ℓ_2 of the orifice, to the point where the transition pressure P_o is reached and inversion to ice I occurs. In the length ℓ_1 of the orifice below this transition point, ice I is being extruded down a pressure gradient P_o/ℓ_1. The extrusion rate is controlled by an average of the effective viscosities of ice I and the high-pressure phase, weighted in relation to the filling lengths ℓ_1 and ℓ_2 in the orifice. The extrusion of the ice I in the length ℓ_1 follows (1) with P replaced by P_o, L by ℓ_1, and U by $U\,\rho_2/\rho_1$, where ρ_1 and ρ_2 are the densities of ice I and the high-pressure phase. If the high-pressure ice obeys a flow law similar to ice I, but with different parameters A_2 and n_2, then its flow is governed by (1) with A_1 and n_1 replaced by A_2 and n_2, and P/L by $(P-P_o)/\ell_2$. The resulting extrusion rate U can be expressed as follows under the simplifying assumption $n_2 = n_1 = n$:

$$(\frac{U}{U_o})^{\frac{1}{n}} - (\frac{\rho_1}{\rho_2})^{\frac{1}{n}} = (\frac{A_2}{A_1})^{\frac{1}{n}} (\frac{P - P_o}{P_o}) \qquad (2)$$

where U_o is the extrusion rate of ice I when the sample is at the transition pressure P_o, from (1).

Results of extrusion experiments for ice II and ice III are plotted in Fig. 2, following the form suggested by (2), with n = 5.6. The fact that the data points fall approximately on straight lines is an indication that the assumption $n_1 = n_2$ is consistent with the observed extrusion behavior. The non-zero intercept of the regression line for ice III, which departs from (2), is discussed later.

The slopes of the data lines in Fig. 2, < 1 for ice II and > 1 for ice III, indicate that ice II flows less readily than ice I, and ice III more readily than ice I. Interpreted on the basis of (2), with n = 5.6, the flow-law parameters for the high-pressure phases relative to ice I are as listed under entry (a) in Table 1.

Anomalous Extrusion

When a sample of ice I is taken at constant temperature up to the phase boundary with ice III by progressively increasing the sample pressure, a very rapid extrusion of ice takes place at or immediately above the transition pressure. By pumping rapidly on the ram it is sometimes possible to get through the transition and proceed to higher pressure, but in most attempts the ice sample is completely extruded before this can be accomplished. Extrusion experiments for ice III were done by first pressurizing the sample at low temperature and then warming into the field of ice III. Because of the anomalous extrusion at the ice I-III phase boundary, U_o (needed in (2)) could not be directly measured. It was obtained by extrapolation of extrusion-rate data from lower pressures.

Discussion

The relative viscosities of ice I, II, and III indicated by the extrusion experiments (Table 1) are qualitatively the same as reported by Kirby et al. [1985]. (Creep-viscosity values at a fixed strain rate are proportional to $A^{-1/n}$.) Quantitatively, however, there is not close agreement, as comparision between the two sets of $(A/A_I)^{1/n}$ values for entries (a) and (c) in Table 1 shows. The values in entry (c) are obtained from the results of Kirby et al. [1985, Fig. 7] by taking ratios of strength at constant strain rate, at the temperatures noted. Entry (a) indicates ice II to have a considerably higher viscosity relative to ice I than (c) does, and (c) indicates ice III to have a considerably lower viscosity relative to ice I than (a) does. The viscosity ratio of III to II is approximately the same for both (a) and (c).

An independent test of the creep strength for ice III was obtained in an experiment by W.F. Brace and B. Kamb. A cylindrical sample of ice, jacketed in rubber, was end-loaded under fluid confining pressure near the transition pressure at -25°C. At a strain rate that required a stress difference of about 100 bar for ice I, the stress difference for ice III was below 10 bar, implying a creep strength for ice III lower than for ice I by a factor of $\lesssim 0.1$. Comparison with the results in Table 1 thus suggests that the extrusion tests appear to introduce a systematic bias toward higher viscosity for the high-pressure phases.

The bias may result from the rather high n value (5.6) used in the data analysis. The slopes of the lines in Fig. 2 are sensitive to the value

Table 1. Values of $(A_{II}/A_I)^{1/n}$ and $(A_{III}/A_I)^{1/n}$

	Source of data	ice II	ice III
(a)	Extrusion (n = 5.6)*	0.34	1.3
(b)	" (n = 4.0)*	0.50	2.3
(c)	Kirby et al. [1985]	0.82	3.0
	Temperature:	-42°C	-26°C

* n value assumed in extrusion data reduction

of n used in calculating the ordinate values for the data points. This is shown by entry (b) in Table 1, which gives $(A/A_I)^{1/n}$ values from reevaluating the extrusion data on the basis of n = 4. This shifts the bias toward lower viscosity for the high-pressure phases, and gives viscosities more nearly matching those of Kirby et al. [1985], who found n = 4 for ice I.

Interpretation of Flow Parameters

The low creep viscosity of ice III relative to ice I (at the same temperature and roughly the same pressure) is qualitatively what is expected from the concept that creep in a hydrogen-bonded, proton-disordered solid is controlled by the same point-defect-migration mechanism that controls dielectric relaxation in such solids, as first suggested for ice I by Glen [1968]. Detailed theories of dislocation motion in such solids give dislocation mobilities proportional to the dielectric relaxation rate [Whitworth, 1983; Frost et al., 1976]. The dielectric relaxation rate for ice III is about 100 times faster than that of ice I at about -30°C [Wilson et al., 1965]; hence if the creep rates at fixed stress behaved proportionally, the flow constant A_{III} would be about 100 times larger than A_I. In fact, Table 1 (b) and (c) give $A_{III}/A_I \approx 30$ to 80, which is of the expected order. Of course, creep rate and the underlying dislocation motion and density are affected by structural factors other than the dielectric relaxation rate, so that a close proportionality is not expected; the observed correspondence between creep and dielectric relaxation rate is thus remarkably good. A second example of this correspondence is ice VI, which has a dielectric relaxation rate similar to ice III [Wilson et al., 1965] and a creep viscosity that appears to be, again, much less than that of ice I, when extrapolated to comparable pressure and temperature [Poirier, 1983]. The probable reason why the dielectric relaxation rates are faster in these dense ice phases is that the hydrogen bonds are weakened by bending [Kamb, 1973, 1968], which reduces the energy barrier to migration of bond defects and thus increases their mobility.

The relationship between dielectric relaxation rate and creep rate also extends qualitatively to the observed behavior of ice II: the A values of the three ice phases (Table 1) are arrayed in the sequence of their dielectric relaxation rates, which are, at -30°C: ice III, $\sim 0.5 \times 10^6\ s^{-1}$; ice I, $\sim 0.5 \times 10^4\ s^{-1}$; ice II, $\sim 0\ s^{-1}$.

The creep of ice II poses a particularly interesting issue in relation to the nature of dislocation motion in hydrogen-bonded solids, because its structure is proton-ordered, unlike the proton-disordered structures of ice I and III [Kamb, 1973]. According to Glen's concept, "ice ought to be markedly softened if the hydrogen disorder can be destroyed" [1968, p. 50], because the interference to dislocation motion that proton disorder causes would be absent in a proton-ordered crystal. On this basis Glen [1968, unpublished] and later Poirier [1983] predicted that ice II would creep much more readily (i.e., have a higher A value) than either ice I or ice III. It is therefore particularly noteworthy that, according to the results in Table 1, the flow constant A for ice II is low compared to both ice I and III. The contrast would be increased if the A values were compared at the same homologous temperature, because the melting point of ice II (calculated from the entropies of ice II, III, and the liquid) is lower by 2°C than that of ice III.

The observed creep behavior of ice II thus shows that the role of proton order/disorder in the rheological behavior of ice needs to be reevaluated. Instead of thinking of the proton-disordered structure as posing a barrier to dislocation motion, which can be overcome only by intervention of the mobile bond defects, we should instead think of the disordered structure and its associated molecular-reorientation mobility as a mechanism that promotes dislocation motion, perhaps by a process of breaking bonds immediately ahead of the moving dislocation, reducing the local Peierls barrier. Such a mechanism would link creep rate with dielectric relaxation rate; in a proton-ordered crystal, in which there is no dielectric relaxation, the mechanism would not assist the creep, and the Peierls barrier would have its normal height appropriate to the strength of the bonds that must be broken in dislocation motion.

Transformation Plasticity

The anomalously accelerated extrusion that occurs at the ice I-III transition is very likely a manifestation of transformation plasticity, which is promoted by the large volume change in the transition (23%), according to theoretical concepts of the transformation-plasticity phenomenon [Poirier, 1985]. The high anomalous extrusion rates suggest that the effective viscosity of the "mixed phase" ice is very low.

In the extrusion of ice III, a zone of mixed ice I and III can be expected to intervene between ice III in the upper part of the orifice and ice I in the lower part. If the effective viscosity is low in this zone, because of transformation plasticity, the pressure gradient along it will be low, and the pressure gradient in the remainder of the orifice will be increased, causing an increased extrusion rate. Model calculations similar to (2), taking this effect into consideration, show as expected that the curve of $(U/U_0)^{1/n}$ vs. $(P-P_0)$ will be shifted to higher U. This explains why the data line for the extrusion of ice III in Fig. 2 has a non-zero ordinate intercept.

As an effect of transformation plasticity the non-zero intercept does not seem to imply as drastic a lowering of the "mixed phase" viscosity as does the anomalous extrusion. A possible explanation may be in the following concept of what is happening in anomalous extrusion. On raising the sample pressure P to the transition pressure P_0 and a little beyond, the sample normally remains at first as ice I because some pressure overshoot ($P - P_0 \sim 100$ bars) is necessary before the transition will nucleate. It is possible that under the high shear stresses in the orifice, where the extrusion is taking place, the transition nucleates more readily. In this case, ice I at pressure $P > P_0$ enters the orifice and there begins to transform to ice III. As the ice flows down the orifice, the content of ice III increases until P has dropped to P_0; beyond that, back-transformation to ice I occurs until all the ice III is gone. As a result, the transition zone can be much longer, and the extrusion rate correspondingly greater, than in the one-way transformation III→I that occurs in extrusion of ice III. Model calculations based on the assumption that the "transformation viscosity" is Newtonian (n = 1)

[Poirier, 1985] and that the transformation rate is proportional to $P-P_o$ indicate that the apparent viscosity, manifested by the slope of the U vs. P curve, will be 2n times the actual effective viscosity of the transformation zone; if n ≈ 5, the factor 2n is a tenfold enhancement.

The experiments give no indication of transformation plasticity associated with the ice I-II transition. The contrast with the large effect for ice III is at first sight surprising, because the volume changes at the two transitions are similar. A possible reason for the difference in behavior is that transformation plasticity lowers the effective viscosity from something like the mean of the high- and low-pressure phases, so that when the high-pressure phase has a low viscosity (ice III), the overall weakening effect is large, whereas when the high-pressure phase has high viscosity (ice II), the overall weakening is little if any.

Conclusions

The contrast in rheology among ice I, II, and III, which is already noteworthy when expressed as in Table 1, becomes striking when expressed in terms of the tectonically more relevant measure, viscosity at a given stress level: ice III is ~100 times less viscous than ice I, and ice II is ~10 times more viscous than ice I. In terms of tectonic processes in the icy satellites it must therefore make a great difference whether the "geotherm" in these bodies passes through the field of ice II or ice III. The creep viscosity will be particularly small on passing into the ice III field because of the notable effect of transformation plasticity. Examples of tectonic effects that could result from transformation plasticity have been pointed out by Parmentier [1981] and Ruff and Kanamori [1983]. The effect of transformation plasticity in subduction [op. cit.] is essentially the inverse of the effect in extrusion. Its effects in "subduction" of an ice I "crust" could be particularly drastic.

The fact that the flow rates (under fixed stress) of ice I, II, and III are ordered in the same way as their dielectric relaxation rates is important for the mechanism of dislocation motion in the ice structures and its relation to the phenomena of proton order/disorder. The behavior of the proton-ordered phase ice II, which is contrary to what is predicted by the current concept of the controlling mechanism for dislocation motion [Glen, 1968], requires a rethinking of this concept.

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