Reports

Activation Volume for Creep in the Upper Mantle

Abstract. The activation volume for creep, V*, of olivine-rich rocks has been determined in pressure-differential creep experiments on dunite at temperatures from 1100° to 1350°C and confining pressures from 5 to 15 kilobars. Values of V* range from 10.6 to 15.4 cubic centimeters per mole with a mean value of 13.4 cubic centimeters per mole, near that expected for oxygen ion self-diffusion. The quantity V* is incorporated into existing flow equations; in combination with observations on naturally deformed mantle xenoliths, estimates are given of the variation with depth of stress, strain rate, and viscosity.

It is generally conceded that thermal convection, of some form, in the earth's mantle either provides the driving force for or controls the nature of plate motions. Most recent models of mantle convection have been based on assumptions of Newtonian flow (1) or of constant stress distribution (2). These models predict different viscosity profiles, but both are likely to be physically unrealistic on the basis of experimental data which indicate that power law creep dominates upper mantle flow and that the stress state and strain rate vary with depth. Our approach to the problem of viscosity variation with depth has been based on application of experimentally determined flow data for olivine-rich rocks (the dominant constituents of the upper mantle), flow processes in the experiments and naturally deformed counterparts (3), pyroxene geothermometry and geobarometry (4, 5), and measurements of the stress versus recrystallized grain sizes (6-9). Although most of the creep parameters for the steady-state flow of olivine are reasonably well determined (3), the activation volume for creep has been elusive and is extremely important for estimates of variations of stress, viscosity, and strain rate (1, 10) at depths

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below those simulated by the experiments (about 50 km). This is so because one of the basic premises of flow, at least in the upper mantle, is that the creep rate is limited by intrinsic self-diffusion of oxygen ions or complexes, a premise for which there is ample empirical evidence. For these reasons we have sought to determine the value of the activation volume for creep of olivine, the preliminary results of which are reported here.

All of the steady-state experimental data obtained from both polycrystalline olivine (6, 11) and single crystals (12) are best fitted (3) by a power flow law of the form

$$\dot{\epsilon} = A \exp(-Q_{\rm c}/RT)\sigma^n \qquad (1)$$

where $\dot{\epsilon}$ is the steady-state strain rate during creep, A is a slightly temperaturesensitive material constant, Q_c is the activation energy for creep, σ is the stress difference, n is the stress exponent, R is the gas constant, and T is the temperature in degrees Kelvin. Steady-state flow in these experiments is accomplished by dislocation glide and climb (polygonization) and by dynamic recrystallization. The dominant flow process depends on the physical conditions of the experiments, but in all instances of steady-state creep it appears that diffusion controls the creep rate. The identity of the flow processes in these experiments and those that have operated in naturally deformed dunites and peridotites from the upper mantle has warranted attempts to extrapolate the mechanical data to depths below equivalent depths of the experiments and to the lower rates of natural deformations (about 10^{-14} sec⁻¹, on the average). In the absence of information on the activation volume for creep, the extrapolation most commonly used is based on the empirical relation (13)

$\dot{\epsilon} = Df(\sigma)b1 \ \ b_0 \exp(-aT_{\rm m}/T)f(\sigma) \quad (2)$

where D is the diffusion coefficient, $f(\sigma)$ is the stress function, D_0 is a constant, T_m is the melting temperature, and $a = Q_c/RT_m$. In Eq. 2 it is assumed, with some experimental justification (13), that the effect of pressure on D is given approximately by its effect on T_m . Our concern here is to develop a means for more accurate extrapolation of the laboratory



Fig. 1. Estimates of stress differences, as a function of depth, in the upper mantle beneath oceanic (a) and continental (b) regions; σ_1 is the maximum compressive stress, and σ_3 is the minimum compressive stress. The most recent pyroxene geotherms (4, 5) are used for temperature and depth estimates. Stresses indicated by the solid curves are determined from recrystallized grain sizes in olivine (9), and those indicated by the dashed curves are calculated from Eq. 9.

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Length Limit for Reports: The average length of individual Reports in Science has been steadily increasing. At the same time, the number of pages allotted to Reports has remained constant and cannot be increased. The net result has been that fewer Reports on fewer subjects are being published; many that receive excellent reviews are being rejected for lack of space. The overall rejection rate is more than 80 percent. In order to increase the acceptance rate for Reports in 1979 we plan to enforce the length rerequirements: one to seven double-spaced manuscript pages of text, including the references and notes, and two items of illustrative material (tables and figures) which together will occupy no more than half of a published page (30 square inches). After Reports are reviewed, those that are being considered for acceptance and that exceed the length limit will be sent back to the authors for shortening before a final decision is made. Reports that initially meet the length requirements will not be subject to this delay.

creep data to depth, and this requires a determination of the activation volume.

The effect of pressure (depth) on the steady-state creep of olivine is given by

 $\dot{\epsilon} = A \exp -(Q + PV^*/RT)\sigma^n \quad (3)$

where Q is the activation energy of the rate-controlling process, P is the pressure, and V^* is the activation volume for creep. Thus, the activation energy for creep obtained empirically, Q_c , is the sum of Q and the product of P and V^* . The quantity V^* comprises the partial molar volume of mobile vacancies, $\Delta V_{\rm v}$, and the partial molar volume of activated complexes, $\Delta V_{\rm m}$ (13). The magnitude of $\Delta V_{\rm v}$ depends on the degree to which atoms surrounding a vacancy relax into it; for zero relaxation, $\Delta V_{\rm v}$ would be the partial molar volume of the diffusing species. Increases in pressure are accommodated by a loss of vacancies, which results in a decrease in diffusivity. The volume $\Delta V_{\rm m}$ involves a diffusing atom at a saddle point expanding a constriction of two neighboring atoms while the volume of the divided vacancy remains nearly unchanged. Thus $\Delta V_{\rm m}$ is a small positive volume, and an increase in P would also decrease the concentration of activated complexes and therefore the diffusivity.

Metallurgists have developed stress relaxation methods for estimating V^* (14). However, the values of V^* determined in those experiments relate to the dynamic aspects of dislocation glide and must be carefully distinguished from the activation volume for self-diffusion with which we are most concerned for extrapolations to depth. For plasticity, the mean velocity, \overline{V} , of mobile dislocations is a function of the effective stress, σ_e (15),

$$\overline{V} = \beta \sigma_{\rm e}{}^{m} = \beta (\sigma_{\rm a} - \sigma_{\rm i})^{m} \qquad (4)$$

Table 1. Activation volumes (in cubic centimeters per mole) for creep of olivine at confining pressures of 5 to 15 kbar.

1100°C	1165°C	1225°C	1350°C
12.2	11.9	12.4	14.2
14.3	14.4	14.7	13.1
12.5	14.4	15.4	10.6
14.0	13.8	13.2	
14.3	12.7	13.5	
	Me	an	
13.5	13.4	13.8	12.6

where β is a constant, σ_a is the applied stress, σ_i is the internal stress associated with mobile dislocations, and *m* is the stress sensitivity. It is assumed that dislocation motion is a thermally activated process controlled by a stress-dependent activation enthalpy

$$H = H_0 - b[Ad\sigma_a \tag{5}$$

where H_0 is the enthalpy in the absence of external stress, A is the area swept out by mobile dislocations, and b is the Burgers vector. If A is independent of σ_a , the velocity of a mobile dislocation then becomes

$$\overline{V} = V_0 \exp(-H/kT) = \overline{V}_1 \exp(bA \sigma_a/kT)$$
 (6a)

(where k is Boltzmann's constant, and V_0 and V_1 are constants) so that

$$kT\partial \ell n \overline{V} / \partial \sigma_{\rm a} = bA \tag{6b}$$

Hence, although bA has the dimensions of volume, the analysis involves only dynamic plasticity and not the partial volumes of vacancies and complexes of importance to our problem.

To estimate V^* in olivine, we have carried out 18 experiments on Mount Burnet and Balsam Gap dunites in a Griggs' solid pressure medium apparatus (16)



Fig. 2. Estimates of the variation of strain rate (a) and equivalent viscosity (b) with depth, based on Eq. 9 and on the assumption that the measured stresses (solid curves of Fig. 1) are correct.

with talc as the confining medium. The experiments were done at a constant differential stress of 5 kbar at temperatures of 1100° to 1350°C and confining pressures of 5 to 15 kbar. Each sample was first allowed to achieve a steady-state strain rate at a confining pressure of 5 kbar at the constant temperature used. The confining pressure was then raised rapidly to 15 kbar, and specimens were again allowed to creep to the steady state. Variations in the confining pressure were then converted to mean pressure were then converted to mean pressure, *P*, for the purpose of calculating V^* according to the relation

$$V^* = -RTd\ell n\dot{\epsilon}/dP =$$

$$RT(\ell n\dot{\epsilon}_2 - \ell n\dot{\epsilon}_1/P_2 - P_1)$$
(7)

The results of these experiments are presented in Table 1. Values for V^* range from 10.6 to 15.4 cm^3 /mole, with a mean value of 13.4 cm³/mole. Errors in the P values at these temperatures are probably about 10 percent (17), and errors in the strain rate as a result of temperature inaccuracies are approximately 5 percent (18), for a total error of about 30 percent. Thus the mean value of V^* is estimated to be 13.4 ± 4.0 cm³/mole. This value is greater than that measured for the simple cation diffusion of magnesium (5.3 cm³/mole) in olivine (19) and is close to that expected theoretically for the activation volume for the self-diffusion of oxygen ions (11.6 cm³/mole) by motions of simple point defects. Therefore, we believe that it is unlikely that mechanisms of bulk diffusion in olivine involve appreciable diffusion of groups of ions, as the energies of formation and motion of such defects (for example, 40 cm³/mole for SiO₄ complexes) are much higher than those for single oxygen defects.

To illustrate the application to the earth of V^* so determined, we have made use of the flow equations for $\dot{\epsilon}$ of dunite of Post (P) (6) and of Carter and Ave'Lallemant (C & A) (3, 11) obtained near a confining pressure of 15 kbar:

= 4.3 ×

51×

$$10^8 \exp\left(-\frac{126}{RT \times 10^{-3}}\right)\sigma^{3.0}$$
 (P) (8a)

$$10^9 \exp\left(-\frac{111}{RT \times 10^{-3}}\right) \sigma^{3.3} (C \& A) (8b)$$

where V^* is expressed in kilocalories per mole and σ is in kilobars. Post's specimens and assemblies were dried carefully at high temperature, whereas Carter and Ave'Lallemant report 0.3 percent water (by weight) available in serpentine and hence their materials are damp. SCIENCE, VOL. 203 Using V^* , the values of O for these two flow laws are 121.2 and 106.2 kcal/mole for Post and for Carter and Ave'Lallemant, respectively. The equation for the extrapolation of these mechanical data is, following use of appropriate conversion factors,

$$\dot{\epsilon} = A \exp - \left(\frac{Q + 13.4 \times 2.39 \times 10^{-2}P}{RT \times 10^{-3}}\right) \sigma'' = A \exp - \left(\frac{Q + 0.32P}{RT \times 10^{-3}}\right) \sigma''$$
(9)

where Q is expressed in kilocalories per mole, P and σ are in kilobars, and the various material constants of Eq. 8, in addition to the new values of Q, are to be inserted appropriately.

Figure 1 shows the variation in differential stress at an assumed constant strain rate of 10^{-14} sec⁻¹ for both the dry and damp flow laws (dashed curves) under ocean basins (Fig. 1a) and continents (Fig. 1b). The geotherms used in the extrapolations are the most recent ones of Mercier (5), based on pyroxene geothermometry and geobarometry. The solid curves in Fig. 1 are also obtained from Mercier's geotherms and from determinations of recrystallized grain sizes, which are functions of stress only, in xenoliths based on the new data of Ross et al. (9). On the basis of the analysis of Ave'Lallemant et al. (20), the solid curves should be regarded as average estimates of variations of stress with depth under the continents and oceans. It is evident from Fig. 1A that extrapolation of Post's data to a strain rate of 10⁻¹⁴ sec^{-1} fits the measured oceanic stress data very well, whereas the results of Carter and Ave'Lallemant do not. However, under cratons (Fig. 1b), extrapolation of the latter flow equation provides the better fit, at least at depths above about 175 km. A similar observation by Mercier *et al*. (7) led them to suggest that the upper mantle beneath continents contains small but significant quantities of water, and more than beneath oceans, a suggestion supported by the presence of hydrous phases in many mantle xenoliths from beneath continents.

Following the procedure of Mercier et al. (7), we have attempted to estimate variations of strain rate and viscosity with depth, assuming that the measured stresses are correct and inserting these, as a function of depth, into Eq. 9. Strain rates and equivalent viscosities ($\eta =$ $\sigma/3\dot{\epsilon}$) are then calculated as a function of depth (Fig. 2). The mechanical results of Carter and Ave'Lallemant can be ignored for the upper mantle beneath SCIENCE, VOL. 203, 19 JANUARY 1979

ocean basins (solid lines), and only Post's results need be considered. These results indicate a rapid increase in $\dot{\epsilon}$ with depth to a value of $10^{-14.25}$ sec⁻¹ at 60 km (near the lid of the low-velocity zone) and then a slight decrease and leveling at about $10^{-14.75}$ sec⁻¹ at depths below 100 km. The value of η decreases to about 10^{21.5} poises at 60 km and remains nearly constant thereafter. Under continents, the values of $\dot{\epsilon}$ and η calculated from Carter and Ave'Lallemant's results seem more reasonable to depths of about 150 km, below which, perhaps because of dehydration, Post's data may be the more reliable.

The analysis given above indicates the importance of the determination of V^* for olivine. Stress generally decreases with depth in the depth interval for which observations are available, and the strain rate generally increases and viscosity decreases except under ocean basins. We believe that these conclusions are physically reasonable and should be incorporated as constraints into future attempts to model thermal convection and plate motions.

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Neutron Scattering of Solution-Grown Polymer Crystals: Molecular Dimensions Are Insensitive to Molecular Weight

Abstract. Neutron scattering gives information on molecular conformations in solid solutions of polymers of one isotope in another. Results on crystals of polyethylene grown from solution show a molecular dimension (in the form of a radius of gyration) that is almost invariant with the length of the chain. It is proposed that certain lengths of folded chains fold back onto themselves to form stacks of chain-folded ribbons ("superfolding").

The way in which long polymer chains accommodate themselves within crystal units has recently attracted renewed interest with the application of neutron scattering. This technique, with the use of isotopically labeled molecules, gives information on the trajectories of single molecules in the condensed state. Other techniques have established (1) that the crystal unit is characteristically lamellar, with the chain direction usually at an angle of 0° to 30° to the lamellar normals. The very existence of lamellae is now quite certain, but there is still lively discussion on precisely how the chains are folded into the crystallites. For crystal growth from dilute solution there has been considerable evidence that, for the most part, each chain tends to fold back on itself along the growth face of the crystal (1). Recent experiments have made it possible to put such models to more definitive tests.

The low-angle neutron scattering tech-

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