Diffusion Creep in the Earth's Mantle

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Abstract. By the process of diffusion creep polycrystalline materials can deform at slow strain rates with Newtonian viscosity. Creep mechanisms involving dislocations can result in more rapid, non-Newtonian flow, but the diffusion creep rate sets an upper limit to the resistance to nonhydrostatic stresses. It is shown that under the conditions of temperature and pressure expected in the earth's mantle, diffusion creep in close-packed oxide structures leads to a viscosity of the same magnitude as that determined from observations of crustal uplift after unloading. The results also show that it is reasonable to assume Newtonian viscosity in calculations of large-scale flow processes in the mantle.

In quantitative theories of nonelastic processes occurring in the earth's mantle it is often assumed that the materials constituting the mantle respond to nonhydrostatic stress as if they were characterized by Newtonian viscosity. Analysis of the post-glacial uplift in Fennoscandia [*Kääriäinen*, 1953] yields an effective viscosity, η, of about 10^{22} poises; η derived from isostatic loading of Pleistocene Lake Bonneville [*Crittenden*, 1963] is about 10^{21} poises. *Runcorn* [1964] has shown that if Newtonian viscosity is attributed to the mantle and laminar flow is assumed, tractions on the crust due to 'convection' currents in the mantle can be deduced from the nonhydrostatic harmonic terms for the earth's gravitational field. The tractions found are in general accord with those expected on the basis of geological evidence. *Orowan* [1964], however, has advanced the view that because the mantle is almost certainly crystalline its response to stress must be plastic rather than viscous. The purpose of this paper is to show that the mantle may be expected to display Newtonian viscosity under certain conditions. This viscous response to nonhydrostatic stress results from the phenomenon known as diffusion creep.

In the study of the creep of crystalline materials in the laboratory at high temperatures and under moderate to large stresses, *transient* and *steady-state* creep are observed [*McLean*, 1962]. Both are due to the motion of dislocations and the steady state is attained when the strain rate is limited by the rate of removal of barriers to dislocation motion by diffusion within the grains of the material. The theory of steady-state creep due to *Weertman* [1955] shows that the strain rate is

$$\dot{\epsilon} = B\sigma^n e^{-Q/kT}$$

where B and n are constants and Q is, when $T/T_m \gtrsim 0.5$, the activation energy for diffusion. T_m is the melting temperature. When n is large (it is usually of the order of 5), a material deforming by steady-state creep displays nearly ideal plasticity.

When the temperature is high but the applied stress relatively low, a different type of creep response is observed in polycrystalline materials. The strain rate is proportional to the stress; the material can be characterized by an effective viscosity coefficient. This creep response is not due to dislocation motion but to the thermally activated migration of atoms through the grains under the driving force of the applied stress. It is called *diffusion* or *Herring-Nabarro creep*. In materials with close-packed crystal structures the atomic migration responsible for diffusion creep occurs by the vacancy mechanism, the grain boundaries acting as the sources and sinks for the vacancies. The quantitative theory of diffusion creep is due to *Herring* [1950]. The creep rate is calculated for a monatomic solid under the conditions that there are no steady-state internal sources or sinks for vacancies within the grains, that surface free-energies at grain boundaries can be neglected in comparison with the effects of the externally applied forces, and that tangential stresses are relaxed at the grain boundaries. It is found that

$$\eta = 10kTR^2/DV_a \qquad (1)$$

where R is the grain radius, D the diffusion coefficient, and V_a the atomic volume. If tangential stresses are not relaxed at the grain boundaries, the numerical coefficient in (1) is changed but the equation retains the same form. In a material in which more than one atom species is present, the creep rate should be governed by the diffusion rate of the least mobile species.

Because the equilibrium vacancy concentration in a crystal cannot be suppressed, diffusion creep is expected to occur in all polycrystalline materials. Among the nonmetals, it has been observed in corundum [*Folweiler*, 1961; *Warshaw and Norton*, 1962], UO_2 [*Scott et al.*, 1959], and BeO [*Chang*, 1959]. The strain rate data for these materials exhibit the dependence on stress, grain size, and temperature predicted by (1). Diffusion coefficients calculated from the creep results agree with those measured directly for Al in corundum and Be in BeO. In corundum, diffusion of O ions is considerably slower than diffusion of the Al ions; the O-ion diffusion should be rate-limiting in diffusion creep. *Paladino and Coble* [1963] propose that it is not because of enhanced anion diffusion in the grain boundaries.

The influence of temperature and pressure on diffusion creep comes primarily through their influence on the diffusion coefficient. Diffusion occurring by interchange of atoms with vacancies, the dominant mechanism in crystals with close-packed structures, is given by

$$D = pa^2 \nu e^{-(G_v + G_m)/kT} \qquad (2)$$

where p is a constant that depends on the crystal structure, a is the lattice parameter, ν the atomic vibration frequency, and G_m and G_v the free energy of vacancy formation and free energy of activation for an atomic jump into a vacancy, respectively. The effect of pressure and temperature on a and ν is negligible in comparison with the effect on the exponential term. Each free energy may be expressed as the sum of three terms:

$$\begin{aligned} G_v &= E_v + PV_v - TS_v \\ G_m &= E_m + PV_m - TS_m \end{aligned} \qquad (3)$$

In these equations E_v is the energy of vacancy formation, V_v the partial molar volume of vacancies, and S_v the entropy change (other than the mixing entropy and primarily due to changes

in atomic vibrational frequencies near the vacancy) which accompanies vacancy formation. The corresponding terms for G_m are the energy, activation volume, and entropy change of the activated state of the diffusion process. Diffusion experiments made over a range of temperature and pressure permit evaluation of $E^* = E_v + E_m$, $V^* = V_v + V_m$, and $S^* = S_v + S_m$. Data of this kind are not available for the relatively complex minerals characteristic of the crust and the upper layers of the mantle. However, with increasing depth, increasing pressure is expected to favor the accommodation of the mantle's chemical constituents in mineral species having nearly close-packed crystal structures. Relevant evidence has been summarized by *MacDonald* [1962]. It indicates that the dominant olivine of the upper layers of the mantle transforms first to spinel and then to mineral species in which the oxygen atoms lie in closest packing, periclase and stishovite.

The temperature dependence of D has been measured for corundum and for periclase. Periclase is a convenient substance to choose for a first estimate of the influence of T and P on η in the mantle. For diffusion of Mg^{++} in periclase *Linder and Parfitt* [1957] find $E^* = 3.4$ ev. Electrolytic conductivity measurements by *Davies* [1963] show that in the intrinsic region E^* for Mg^{++} is 3.5 ev, and for O^{--} diffusion it is 5.2 ev. It is the intrinsic activation energies that must be considered for diffusion creep as intrinsic conductivity dominates at high temperature. The pre-exponential term

$$D_0 = pa^2 \nu e^{S^*/k}$$

was found to be 0.24 cm^2/sec in the experiments of Linder and Parfitt. The value of D_0 is not known for the O-ion diffusion in periclase; values appreciably less than unity or greater than about 10 cm^2/sec would, however, result in unreasonable entropies of activation.

Experimental determinations of the activation volumes for diffusion in nonmetallic crystals other than the alkali halides have not been made. For cation diffusion in halite $V^* = 12.8$ A^3 [*Pierce*, 1961] which, in terms of atomic volumes, is $3.55V_{Na}$ or $0.51V_{Cl}$. For metals with close-packed structures diffusion experiments under pressure show $V^* \approx 0.8V_a$. These experiments also show that the influence of P on D_0 is small in comparison with the effect on the ex-
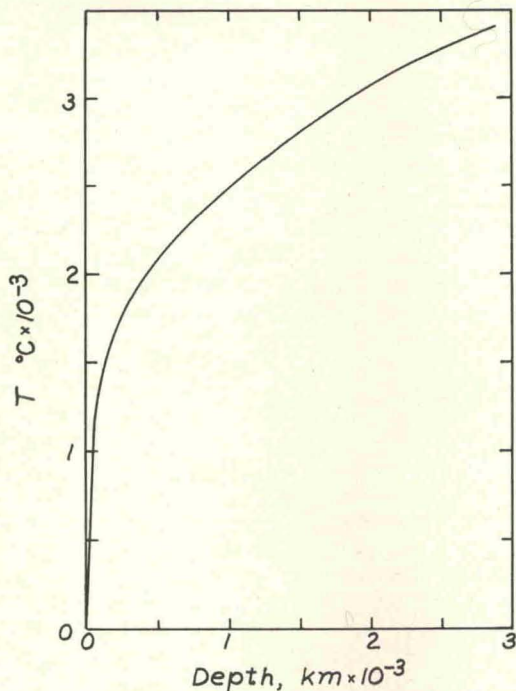
Fig. 1. Dependence of temperature on depth assumed for the calculation of effective viscosity shown in Figure 2.

rise in T at shallow depths where the pressure is relatively low. Beyond the depth corresponding to the minimum η, the direct effect of P on atomic mobility becomes large and pressure has an important influence not only on diffusion creep but on other processes dependent on atomic mobility, e.g., steady-state creep and recrystallization. The sensitivity of η to the choice of E^* and V^* is shown in the figure; the experimental evidence now available indicates that the best choice for these quantities is $E^* = 5.5$ ev and $V^* = 10$ A³. The effective viscosity is also sensitive to temperature, as shown in Figure 3. Here $E^* = 6$ ev and $V^* = 10$ A³, and the temperature distributions proposed by *Gutenberg* [1951] and *Lubimova* [1958] have been used.

The results in Figures 2 and 3 show that at the temperatures and pressures corresponding to depths of about 1000 to 1500 km, periclase
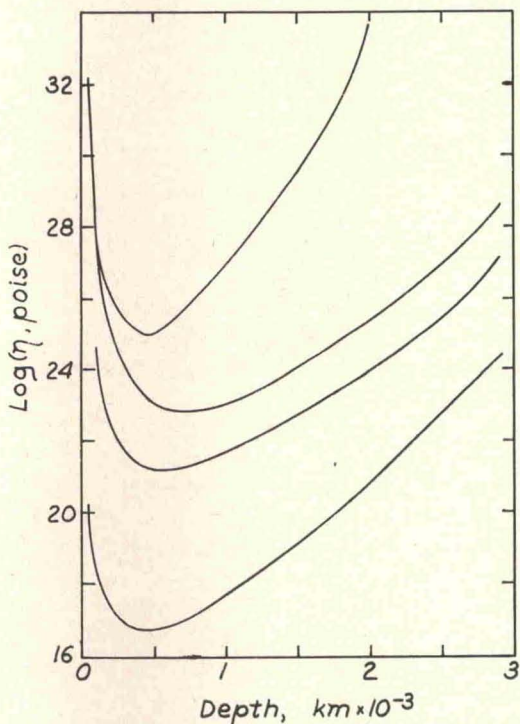
ponential term. To evaluate the effective viscosity of periclase at temperatures and pressures comparable to those in the mantle, allowance should be made for the possibility that either O-ion or Mg-ion diffusion may be rate-limiting. If $1 \leq D_0 \leq 10$, 3 ev $\leq E^* \leq 6$ ev, and $0.5V_a \leq V^* \leq 2V_a$ are considered, both possible mechanisms are encompassed. In periclase the atomic volume per O atom is 18 A³. The increase of pressure with depth is known accurately but the temperature gradient is uncertain. A smoothed temperature-depth curve which lies about midway of the extremes of the curves that have been proposed by various investigators is shown in Figure 1. The dependence of η on depth for this temperature distribution and for $R = 0.05$ cm and $D_0 = 5$ cm²/sec is shown in Figure 2 for several values of E^* and V^*. These curves are easily adjusted up or down for a different choice of R and D_0. V_a in (1) should be taken equal to V^* but, as η is not strongly sensitive to the exact choice, it suffices to take $V_a = 10$ A³.

The initial steep drop in η is due to the rapid

Fig. 2. The effective viscosity due to diffusion creep in a polycrystalline material with $D_0 = 5$ cm²/sec and $R = 0.05$ cm. Temperature as a function of depth is taken from Figure 1. From top to bottom the curves correspond to $E^* = 6$ ev, $V^* = 20$ A³; $E^* = 6$, $V^* = 10$; $E^* = 5$, $V^* = 10$; $E^* = 3$, $V^* = 10$, respectively.

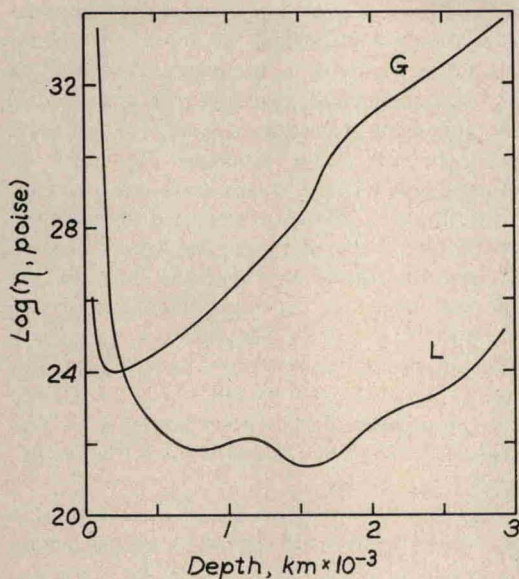Fig. 3. The effective viscosity as a function of depth for $D_0 = 5$ cm^2/sec, $R = 0.05$ cm, $E^* = 6$ ev, and $V^* = 10$ A^3. Curve G is for the *Gutenberg* [1951] temperature distribution and curve L is for the *Lubimova* [1958] distribution.

(or any other polycrystalline material of comparable atomic mobility) is expected to display diffusion creep leading to an effective viscosity of the same order of magnitude as that indicated for the upper mantle by geological evidence. Before it is decided that this viscous behavior is or is not representative of diffusion creep in the earth's mantle, these factors must be considered:

1. *Activation energies.* The activation energies 3 ev $\leq E^* \leq$ 6 ev bracket the observed values for periclase, a supposedly important constituent of the mantle. It is expected that E^* nearer to 6 ev than to 3 ev will be appropriate for the mantle. The low E^* is expected only if there is enhanced anion diffusion in the grain boundaries. Because of the relatively open structure of a grain boundary, even low pressure should rapidly suppress such enhanced diffusion. The observed E^* for O-ion diffusion in corundum is 6.6 ev [*Oishi and Kingery*, 1960]. Since stishovite has a close-packed oxygen structure, it is expected to have $E^* \approx 6$ ev. To make a major change in the η versus depth curves, E would have to be different from the value used above by an unreasonably large amount.

2. *Activation volumes.* Experiments on metals with close-packed structures are consistent in showing $V_v + V_m \approx 0.8V_a$. However, these results are based on experiments over a limited range of pressure ($<$10 kb). They are consistent with the model used in the absolute reaction rate theory of diffusion but as yet there have been no predictions of activation volumes on the basis of this theory. According to the semiempirical theory of *Keyes* [1963], the activation volume is related to the activation free energy by

$$V^* = 2G^*(\gamma - 1/2)\beta$$

where γ is Grüneisen's constant and β is the isothermal compressibility. V^* is expected, then, to decrease only slowly with increasing P. Variation of V^* with depth by an amount large enough to make a major alteration of the curves of Figures 2 and 3 is not expected.

3. *Grain size.* By equation 1, $\eta \propto R^2$. At room pressure and at high temperature where atomic mobility is large, large grains grow in high-purity materials; the grain growth is arrested when the boundaries form a geometrically stable network (like a stable soap bubble foam). Unusual conditions are required to generate grain sizes larger than about 1 mm diameter. When two or more phases are present in the microstructure (almost certainly the case throughout the mantle), grain growth is inhibited by the tendency of grain boundaries to be held up by second-phase particles. If there are internal steady-state sources or sinks for vacancies, R is reduced [*Freidel*, 1964]. Thus, it is not expected that variation in grain size could alter η from the values shown in Figures 2 and 3 by more than about a factor of 100 at most.

4. *Grain boundary properties.* Internal friction experiments show that grains slide past each other with a liquid-like viscosity [*Kê*, 1947]. It is expected, therefore, that tangential stresses at the grain boundaries will always be relaxed at any temperature where diffusion creep may occur. If applied pressure were to strongly decrease the atomic mobility in the boundaries relative to that in the grains, the numerical coefficient in (1) would have to be changed but the curves in Figures 2 and 3 would hardly be altered.

I conclude that diffusion creep can reasonably be expected to be a significant flow process in the mantle. In fact, the most probable values of E^*, V^*, D_0, and R lead to a predicted effective viscosity, for depths to 1500 km and for all except the lowest of the various proposed temperature distributions, which is about equal to that deduced from the observed uplift of unloaded sections of the earth's crust. Diffusion creep is a consequence of the thermally activated mobility of atoms in crystals and so occurs quite generally in polycrystalline materials. It is not dependent on the presence of any type of specialized structure (e.g., particular dislocation arrays or obstacles to dislocation motion), and the mechanism is established by both theory and experiment beyond any reasonable doubt. In contrast, the calculations of viscosity in the earth by *Cook* [1963] are based on a model whose applicability to close-packed crystalline structures is not established, and they lead to activation energies that are much too low by any reasonable physical standards.

The occurrence of diffusion creep fixes a definite minimum for the resistance of a material to creep deformation. For the effective viscosity of an appreciable part of the mantle to be greater than 10^{25} poises, the amount required for the current figure of the earth to have been retained from an earlier equilibrium shape [*MacDonald, 1963*], either E^* and V^* would have to be unreasonably large or the temperatures at depths below 1000 km would have to be as low as those proposed by Gutenberg.

The occurrence of diffusion creep in the mantle does not rule out creep deformation at a more rapid rate due to motion of dislocations. Such deformation is expected, for example, in regions of orogenic and earthquake activity. However, the occurrence of diffusion creep at significant rates indicates that the assumption of Newtonian viscosity usually made in calculations of large-scale flow processes in the mantle is a reasonable one.

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