

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

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

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; Warsaw 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

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

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:

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

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 $0.24 \text{ cm}^2/\text{sec}$ 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 $10 \text{ cm}^2/\text{sec}$ 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 $V^* = 12.8 \text{ \AA}^3$ [Pierce, 1961] which, in terms of atomic volumes, is $3.55V_{\text{Na}}$ or $0.51V_{\text{Cl}}$. 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-