

Diffusion in MgO at high pressures: Constraints on deformation mechanisms and chemical transport at the core-mantle boundary

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[1] High-pressure experiments on diffusion in MgO were performed to model the rheological and chemical transport properties of the lower mantle. Lattice and grain boundary diffusion coefficients for Mg, O and Al were determined at 2273 K and pressures up to 25 GPa. The results for pure MgO are in excellent agreement with first-principles calculations. In samples doped with Al₂O₃, cation vacancies were found to attach to Al impurities with a binding energy of ~ 0.7 eV. Our results predict that a transition from diffusion creep to dislocation creep will occur in the deep lower mantle if the shear stress exceeds ~ 1 –10 MPa, for a grain size of ~ 0.1 –1 mm. Diffusion through periclase is fast enough to allow substantial chemical exchange across the core-mantle boundary since core formation, with length scales of ~ 1 –10 km for lattice diffusion and 100 km for grain boundary diffusion. **INDEX TERMS:** 3902 Mineral Physics: Creep and deformation; 3904 Mineral Physics: Defects; 3924 Mineral Physics: High-pressure behavior; 5120 Physical Properties of Rocks: Plasticity, diffusion, and creep; 8162 Tectonophysics: Evolution of the Earth: Rheology—mantle. **Citation:** Van Orman, J. A., Y. Fei, E. H. Hauri, and J. Wang, Diffusion in MgO at high pressures: Constraints on deformation mechanisms and chemical transport at the core-mantle boundary, *Geophys. Res. Lett.*, 30(2), 1056, doi:10.1029/2002GL016343, 2003.

1. Introduction

[2] Diffusion is the rate-limiting step in many kinetic processes in Earth and planetary interiors, including solid-state creep (the process responsible for mantle convection), anelastic deformation (which contributes to seismic attenuation), phase transformations and chemical mass transfer reactions. Periclase, although a minor component of Earth's lower mantle ($\sim 20\%$), may have a strong influence on its physical and chemical properties, due to its large elastic anisotropy at high pressure and high ionic conductivity. Diffusion in periclase has been studied extensively in the materials science community, but the pressure dependence has not previously been measured. We have measured lattice and grain-boundary diffusion coefficients for cations and oxygen in periclase at pressures up to 25 GPa, allowing us to test both continuum [e.g. *Sammis et al.*, 1981] and first-principles methods [*Ita and Cohen*,

1997] for calculating diffusion coefficients at high pressures. We also studied the influence of grain boundaries (planar defects) and trivalent impurities (point defects) on diffusion in MgO, the presence of which must be taken into account when estimating diffusion rates in Earth's mantle.

2. Experiments

[3] Diffusion couples consisted of a single crystal of high-purity periclase (MgO) with natural isotopic abundances, surrounded by isotopically-enriched MgO powder (99% ²⁵Mg and 40% ¹⁸O) prepared by reacting ²⁵MgO with H₂¹⁸O to form brucite, then heating for several hours at 1000 K. The powder sintered to a dense polycrystal with 5–10 micron grain size during pressurization and heating. Each diffusion couple was inserted into an 8/3 octahedral assembly within a cylindrical Re resistance heater, with alumina rods bounding the couple at top and bottom. Experiments were performed with a 1500-ton multianvil apparatus [*Bertka and Fei*, 1997] at conditions of 15 to 25 GPa and 2273 K for times up to 9.5 hours (Table 1). Temperature was measured with an axially located W5%Re/W26%Re thermocouple and controlled within ± 2 K during each experiment. The difference in temperature between the thermocouple junction and the diffusion interface in this assembly is < 20 K (*van Westrenen et al.*, in review). The relative uncertainty in pressure is estimated to be ± 0.5 GPa. Following the isothermal diffusion anneal, each sample was ground and polished perpendicular to the diffusion interface. Isotopic concentration profiles were measured using a Cameca ims-6f ion microprobe with 0.1 nA Cs⁺ primary beam ~ 1 μ m in diameter. The negative ionic species

Table 1. Conditions and Results of High-Pressure Diffusion Experiments at 2273 K

Expt.	P (Gpa)	t (hr)	Species	*D _v (m ² /s)	*δD _b (m ³ /s)
pcMgO2	15	9.50	²⁵ Mg	1.29×10^{-15}	—
			¹⁸ O	4.3×10^{-16}	—
			Al [•] _{Mg} - V'' _{Mg}	3.1×10^{-13}	—
pcMgO6	16	2.77	²⁵ Mg	2.6×10^{-15}	8.27×10^{-19}
			¹⁸ O	2.1×10^{-16}	3.80×10^{-18}
			²⁵ Mg	6.1×10^{-16}	7.61×10^{-20}
pcMgO3	25	8.87	¹⁸ O	5.7×10^{-17}	4.16×10^{-19}
			Al [•] _{Mg} - V'' _{Mg}	5.7×10^{-14}	—

*Formally propagated errors on the diffusion coefficients are $\sim 15\%$ for Mg volume diffusion, $\sim 20\%$ for Mg grain boundary diffusion, $\sim 25\%$ for O volume diffusion, 100–200% for O grain boundary diffusion, and $\sim 50\%$ for Al[•]_{Mg} - V''_{Mg} diffusion; actual errors may be larger.

† This diffusion coefficient corresponds to an Al concentration of 100 ppm, similar to the trivalent impurity content of the "pure" MgO used in the other experiments.

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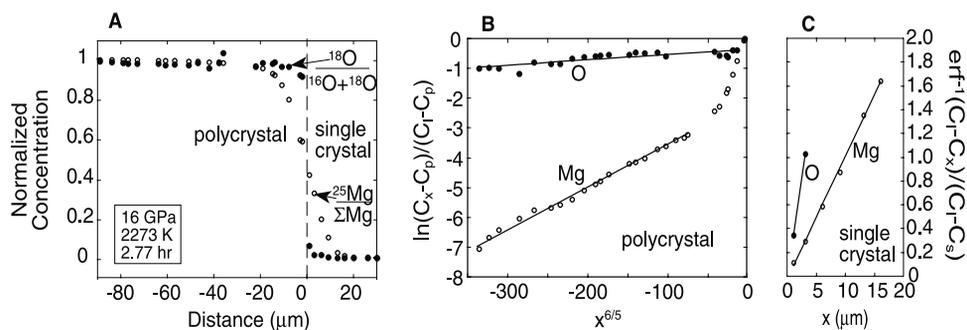


Figure 1. (a) Normalized Mg and O isotopic concentration profiles (run pcMgO6). The data are shown in linearized form for (b) the polycrystalline side and (c) the single-crystal side of the couple.

$^{16}\text{O}^-$, $^{18}\text{O}^-$, $^{24}\text{Mg}^{16}\text{O}^-$, $^{25}\text{Mg}^{16}\text{O}^-$, and $^{26}\text{Mg}^{16}\text{O}^-$ were counted at each spot.

3. Results

[4] In two experiments, Mg and O diffused through essentially pure periclase (<200 ppm impurities). In one of these experiments, thin Pt foil isolated the diffusion couple from the alumina end rods; in the other, Al diffusion was insufficient to intersect the Mg and O diffusion profiles. Simple diffusion equations were fit to the diffusion profiles to obtain volume and grain boundary diffusion coefficients for Mg and O (Figure 1). Each side of the diffusion couple was effectively semi-infinite, and it was assumed that constant isotopic ratios were maintained at the interface. Volume diffusion coefficients were obtained from the single-crystal side of each couple by fitting the isotopic concentration data to an error function solution, $(C - C_0)/(C_i - C_0) = \text{erf}[x/(2\sqrt{D_v t})]$, where C is the isotopic concentration ratio ($^{25}\text{Mg}/\Sigma\text{Mg}$ or $^{18}\text{O}/\Sigma\text{O}$) at a distance x from the single-crystal/polycrystal interface, C_0 is the concentration at the interface, C_i is the initial concentration in the crystal, D_v is the volume diffusion coefficient and t is the duration of the diffusion anneal (E-supplement 1). In the polycrystal, both volume and grain boundary diffusion were significant and the solution given by *LeClaire* [1963] was used to obtain the product of grain boundary width and diffusivity, $\delta D_b = 0.66(\partial \ln C'/\partial x^{6/5})^{-5/3}(4D_v/t)^{1/2}$. This equation strictly applies over a particular range of the dimensionless variable $\eta\beta^{-1/2}$ ($\sim 2-10$). For O $\eta\beta^{-1/2}$ was lower

($\sim 0.2-1$), but judging from *LeClaire's* Figure 6 the resulting error in D_b is probably less than a factor of 2.

[5] To examine the influence of trivalent impurities, Al from the end rods was allowed to diffuse simultaneously with Mg and O isotopes in one experiment (Figure 2). Aluminum diffusion profiles were measured using a JEOL 8900 electron microprobe with focused 50 nA beam and wavelength dispersive spectroscopy. Oxygen volume and grain boundary diffusion coefficients were similar to those in an experiment performed at similar pressure (pcMgO6). Diffusion of O thus appears to be unaffected by the presence of trivalent cations, in agreement with 1-atm O diffusion experiments [*Ando et al.*, 1983]. This suggests that O diffusion may take place via bound Mg-O vacancy pairs, since their concentration is insensitive to the presence of aliovalent cation impurities.

[6] In contrast to O, Mg and Al diffusion coefficients increase strongly with aluminum concentration. We used Boltzmann-Matano analysis to numerically evaluate the Mg self-diffusion coefficients and Mg-Al interdiffusion coefficients as functions of position along the concentration profiles. Aluminum increased cation lattice diffusion rates enough that grain boundary transport was indiscernable. Assuming ideal solution of $\text{AlO}_{1.5}$ the Al self-diffusion coefficient is $\sim 2/3$ the interdiffusion coefficient [*Whitney and Stubican*, 1971]. The asymptotic increase in D_{Al} with C_{Al} (Figure 2b) is consistent with diffusion by means of a defect pair consisting of an Al atom ($\text{Al}_{\text{Mg}}^\bullet$) and cation vacancy (V_{Mg}'') which are bound electrostatically. Impurity-vacancy binding enhances the diffusivity of the impurity by

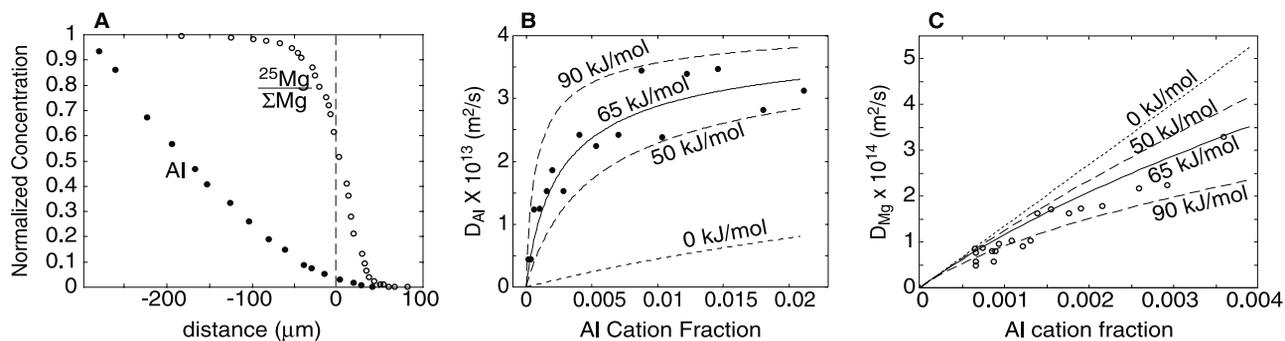


Figure 2. (a) Simultaneous diffusion of Al and ^{25}Mg in periclase (run pcMgO2). (b) Al diffusion coefficients (solid circles) as a function of Al cation fraction, with curves showing the predicted dependence for different values of the $\text{Al}_{\text{Mg}}^\bullet - V_{\text{Mg}}''$ binding energy. (c) D_{Mg} as a function of C_{Al} .

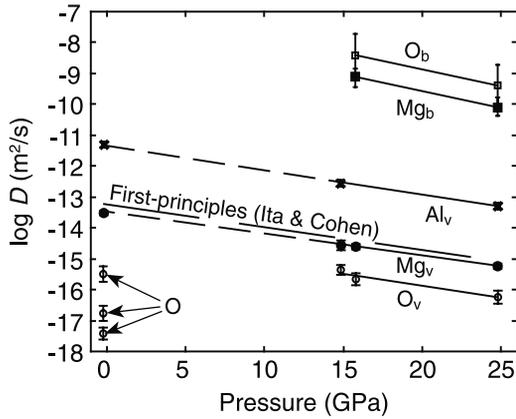


Figure 3. Diffusion results for Mg, Al and O in periclase at 2273 K. Volume diffusion data at atmospheric pressure are from *Whitney and Stubican* [1971], *Wuensch et al.* [1973], *Ando et al.* [1983], *Yoo et al.* [1981], and *Yang and Flynn* [1994]. A grain boundary width of 1 nm was assumed in calculating O_b and Mg_b .

increasing the probability that a vacancy and impurity atom will be on adjacent cation sites. On the other hand it decreases the diffusivity of unbound cations (such as neutrally charged Mg) because it removes free vacancies from the lattice, thereby reducing the probability that a vacancy will be adjacent to an unbound cation. The theoretical dependence of diffusivity on concentration, in the presence of trivalent-impurity/cation-vacancy binding, is [*Lidiard*, 1955]:

$$D_{Al} = D_{Al,sat} \{ -[1 + 24C_{Al} \exp(\Delta G_b/RT)] \}^{-1/2},$$

where ΔG_b is the $Al_{Mg}^{\bullet} - V_{Mg}''$ pair binding energy and C_{Al} is the fraction of cation sites occupied by Al. The Al diffusion coefficient increases with the proportion of vacancies that are bound to Al atoms, which in turn increases with the concentration of Al and with the binding energy. At sufficiently high concentration (~ 0.01) nearly all of the vacancies are bound to Al impurities and the Al diffusion coefficient approaches a saturation value.

[7] The Mg diffusion coefficient is proportional to the concentration of free cation vacancies, which is given by $24 \exp(\Delta G_b/RT) [V_{Mg}'']^2 + 2[V_{Mg}''] = C_{Al}$. Both the Al and Mg diffusion profiles are consistent with a binding energy of approximately 65 kJ/mol, or ~ 0.7 eV (Figures 2b and 2c), in good agreement with theoretical estimates [*Hirsch and Shankland*, 1991] and ionic conductivity studies [*Sem-polinski and Kingery*, 1980]. Similar association with vacancies is expected for Fe^{3+} and Cr^{3+} , which along with Al^{3+} are the most abundant trivalent impurities in the Earth's mantle.

[8] The effect of pressure is to decrease the diffusion rates of all species along all paths (Figure 3). Diffusion studies on Mg and Al volume diffusion at atmospheric pressure [*Whitney and Stubican*, 1971; *Wuensch et al.*, 1973] agree well with the high-pressure data, and together give activation volumes of 3.0 ± 0.4 (2σ) cm^3/mol for Mg and 3.5 ± 0.5 cm^3/mol for Al. These are interpreted as volumes of migration for Mg and $Al_{Mg}^{\bullet} - V_{Mg}''$ defect pairs, respectively.

[9] First-principles calculations [*Ita and Cohen*, 1997] give a migration volume for Mg (3.1 cm^3/mol) which is indistinguishable from our experimental value. Moreover, the absolute values of Mg diffusion coefficients calculated by Ita and Cohen (Figure 3) are within a factor of two of our experimental data at a similar cation vacancy concentration 100 ppm. Elastic strain models are also in reasonable agreement with our results. The model for cubic crystals described in *Sammis et al.* [1981] predicts an activation volume for Mg migration of ~ 2.7 cm^3/mol , which is within the uncertainty of our measurement. Similar estimates have been made by *Karato* [1981] and *Yamazaki and Karato* [2001]. A useful prediction of elastic strain models is that the ratio of migration volume to migration energy should be the same for all ions. This is supported by the data for Mg and Al in periclase, both of which have $V_m/H_m^o \approx 1.1 \times 10^{-11}$ m^3/J .

[10] Our high-pressure O volume diffusion data give an activation volume of 3.3 ± 2.4 cm^3/mol , consistent with the theoretical migration volume of 2.8 cm^3/mol calculated by *Ita and Cohen* [1997]. Our data are higher than O diffusivities measured at 1 bar (which themselves are widely scattered). It is possible that O diffusion in our experiments was enhanced by the presence of dislocations formed during compression, although dislocations do not appear to have affected the transport of Mg or Al. A dislocation density on the order of 10^{16} m^{-2} would be required to account for the discrepancy, based on the measured diffusivity of O in dislocation cores [*Narayan and Washburn*, 1972]. Extrapolating from the stress/dislocation-density relationship determined for MgO by *Takeuchi and Argon* [1976], this would imply a shear stress in our samples of approximately 1–2 GPa.

4. Discussion

[11] The absence of seismic anisotropy in most of Earth's lower mantle has led to the suggestion that diffusion creep is the dominant deformation mechanism [*Karato et al.*, 1995], while patchy anisotropy just above the core-mantle boundary (CMB) may indicate a transition to dislocation creep [*Karato*, 1998; *McNamara et al.*, 2002]. Dislocation creep is a power-law function of shear stress and leads to strong preferred crystal orientation at large strains. The rate law is $\dot{\epsilon} = A\sigma^n \exp[-(E + PV)/RT]$, with $n = 4.0$, $E = 327$ kJ/mol and $A = 2.4 \times 10^{-24}$ $Pa^{-3} s^{-1}$ for ferropericlase at low pressure [*Stretton et al.*, 2001]. The activation energy for dislocation creep is consistent with the activation energy for O migration [*Yoo et al.*, 1981; *Ita and Cohen*, 1997], the rate-limiting step in dislocation climb. Because the diffusion coefficient is the only parameter in the rate law that is sensitive to pressure, the pressure dependence of dislocation creep should be the same as that for O diffusion.

[12] Diffusion creep is grain-size sensitive, involves diffusion of all species along all available paths, and does not lead to significant crystal preferred orientation. The rate equation is $\dot{\epsilon} = (13.3\sigma\Omega D_{eff}/RTd^2)$ where d is the grain size, Ω is the molar volume and D_{eff} is a weighted mean of the bulk diffusivities of Mg and O, with $D_{bulk} = D_v + \pi\delta D_b/d$. Where lattice diffusion dominates the creep rate scales as D_v/d^2 , and where grain boundary diffusion dominates the

creep rate scales as D_b/d^3 . Our results indicate that Mg boundary diffusion will limit creep at grain sizes below ~ 500 microns, and O boundary diffusion at grain sizes above ~ 3 mm. Oxygen volume diffusion contributes only when the grain size is $\gg 1$ cm, so is unlikely to be important in Earth's lower mantle.

[13] A transition in creep mechanisms may result from changes in shear stress (or grain size). We extrapolated the dislocation creep and diffusion creep flow laws to core-mantle boundary conditions (140 GPa, ~ 4500 K) using the high-pressure migration enthalpies for Mg and O calculated by *Ita and Cohen* [1997]. We assumed that the ratio of grain boundary migration enthalpy to volume migration enthalpy remained constant with increasing pressure, and used 1-atm values of 230 kJ/mol for O boundary diffusion and 200 kJ/mol for Mg [Frost and Ashby, 1982]. At grain sizes of 0.1–1 mm [Solomatov et al., 2002], the transition stress is calculated to be 1–10 MPa. This is similar to shear stresses thought to be associated with convection in the Earth's mantle and may be exceeded within the D'' boundary layer, where stress and strain associated with mantle convection are concentrated. Although there are significant uncertainties in grain size and other parameters within the CMB region, a transition to dislocation creep is certainly plausible and other mechanisms for generating seismic anisotropy may not be required.

[14] Experimental [Knittle and Jeanloz, 1991; Goarant et al., 1992] and geochemical observations [e.g. Walker et al., 1995] suggest that there may be significant chemical exchange across the core-mantle boundary. The length scale of such interactions is probably determined by diffusion. We calculated the upper bound [Hashin and Shtrikman, 1962] on bulk diffusivity through solid lower mantle at CMB conditions, assuming negligibly slow diffusion in perovskite [Yamazaki et al., 2000]. This upper bound will be approached if periclase grains link up to form an interconnected network. In the time since core formation (~ 4.5 Ga), the diffusion length scale may be up to ~ 1 – 10 km if controlled by volume diffusion and up to ~ 100 km if controlled by boundary diffusion. The grain boundary flux will be highest for elements that are partitioned into these defective regions in preference to silicate and oxide crystals. Osmium and other highly siderophile elements may fit into this category, and grain boundary diffusion could provide an effective means for exchange of these elements between core and mantle.

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