

Low Differential Stress and Controlled Chemical Environment in Multianvil High-Pressure Experiments

D.C. Rubie¹, S. Karato², H. Yan², and H.St.C. O'Neill¹

¹ Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany

² Department of Geology and Geophysics, University of Minnesota, Minneapolis, MN 55455, USA

Received November 3, 1992 / Revised, accepted June 8, 1993

Abstract. Studies of mass transport and kinetics in minerals at high pressure often require a sample environment in which the stress is near-hydrostatic and the chemical environment is carefully controlled. We report here details of a multianvil sample assembly in which these requirements are fulfilled and which has been used to study the effect of pressure on the kinetics of dislocation recovery in olivine up to 10 GPa. Annealing experiments have been performed on single crystals of San Carlos olivine at 8.5 GPa and 1400° C in a 1200 tonne split-sphere multianvil apparatus. The sample assembly consists of an 18 mm MgO octahedron with a LaCrO₃ heater of variable wall thickness to give a small temperature variation (~20° C) along the 3 mm length of the sample capsule. To minimize the differential stress on the sample, the olivine single crystal is surrounded by NaCl and both pressurization and depressurization are performed slowly at a temperature of 600° C (to minimize the strength of the NaCl). The silica activity (a_{SiO_2}) is buffered by orthopyroxene powder in contact with the olivine and the oxygen fugacity is buffered by Ni + NiO within the sample capsule. The H₂O-content of the sample assembly is minimized by drying all components at 230° C under vacuum. Olivine single crystals recovered after annealing at 1400° C and 8.5 GPa show no evidence of deformation, either ductile or brittle. Dislocation densities of 10^9 – 10^{10} m⁻² are similar to those observed prior to high-pressure annealing and indicate differential stresses of <10 MPa. Infrared spectroscopy indicates that the hydrogen content of a sample annealed at 10 GPa, 1500° C for 21 h is ~13 H/10⁶Si, which, although low, is higher than that of the crystals prior to high-pressure annealing. Finally, the effectiveness of the fO₂ buffer has been verified by estimating the fO₂ at the surface of the sample from the solubility of Fe in Pt metal in equilibrium with the olivine and orthopyroxene.

Introduction

The kinetics of processes such as lattice diffusion, grain boundary diffusion, grain growth, high-temperature creep and dislocation recovery in minerals have been investigated extensively at moderate pressures (up to 2–3 GPa) using hydrothermal, gas-media and solid-media high-pressure apparatus. Because of the limited pressure range which has been used in these studies, the magnitudes of activation volumes and therefore the effects of pressure on the rates of mineralogical processes are still poorly understood. Consequently existing kinetic and creep data cannot be extrapolated reliably to mantle conditions. For example, the current uncertainty in the activation volume for dislocation creep in olivine (6–27 cm³ mol⁻¹; see Green and Borch 1987; Karato et al. 1993) results in an uncertainty in strain rate of ~8 orders of magnitude when olivine creep data are extrapolated to conditions of the base of the upper mantle (Fig. 6 in Kohlstedt et al. 1980). Such uncertainties in extrapolations of experimental creep data are a serious problem for understanding mantle convection.

Determinations of the effect of pressure on the kinetics of mineralogical processes will be more reliable when the pressure range over which the experiments are performed is large (e.g. 10 GPa). Although a large pressure range can be achieved easily using the multianvil apparatus, a number of additional parameters which significantly affect kinetics must be controlled carefully if useful data are to be obtained using this apparatus. These parameters include temperature, chemical environment (e.g. oxygen fugacity, fugacities of H₂O-related species, oxide activities), and differential stress.

In many kinetic studies, it is desirable that the sample is subjected to low differential stresses at all stages during the experiment. At high temperature, high stresses result in the generation and migration of dislocations which can significantly affect the rates of processes such as the nucleation of new phases (Rubie and Champness 1987) and atomic diffusion (Yund and Tullis 1980). During the compression and decompression stages of high

pressure experiments, significant fracturing frequently occurs because of high differential stresses (e.g. Fig. 3a in Rubie and Brearley 1990). Such fracturing would be a serious problem, for example, in diffusion studies (e.g., Kronenberg et al. 1986; Tingle 1988; Bertran-Alvaraz et al. 1992). In the synthesis of hot-pressed aggregates (for use in ultrasonic and grain boundary diffusion studies for example), it is also critical that samples are retrieved from high pressure without fracturing (Gwanmesia et al. 1990). High differential stresses result primarily from the use of a strong confining medium; the stress on the sample is likely to be particularly high when rates of compression/decompression and heating/cooling are fast compared with the relaxation rate of the pressure medium.

Here we discuss methods of minimizing differential stress and controlling and characterising the chemical environment in experiments designed specifically for studying the effect of pressure on the kinetics of dislocation recovery in olivine up to 10 GPa (Karato et al. 1993). Such experiments are performed by annealing olivine single crystals at high temperatures and pressures in a hydrostatic or near-hydrostatic stress environment and measuring the resulting decrease in dislocation density (Kohlstedt et al. 1980; Karato and Ogawa 1982; Karato et al. 1993). In addition to the near-hydrostatic stress requirement, a particular problem with such experiments is the choice of a sample container which maintains a controlled chemical environment within the olivine stability field (Nitsan 1974; Boland et al. 1986; Kohlstedt and Mackwell 1987; Jaoul et al. 1987).

Multianvil Experiments

Experiments were performed using a 1200 tonne uniaxial split-sphere multianvil apparatus in which both temperature and hydraulic oil pressure were computer controlled. Tungsten carbide anvils (Toshiba grade F) were used with octahedral sample assemblies fabricated from semi-sintered MgO (+5% Cr₂O₃) together with preformed pyrophyllite gaskets. The truncation edge length on the WC anvils was 11 mm, the edge length of the MgO octahedra was 18 mm and the gasket dimensions were 5 × 3 mm. The pressure at the sample was calibrat-

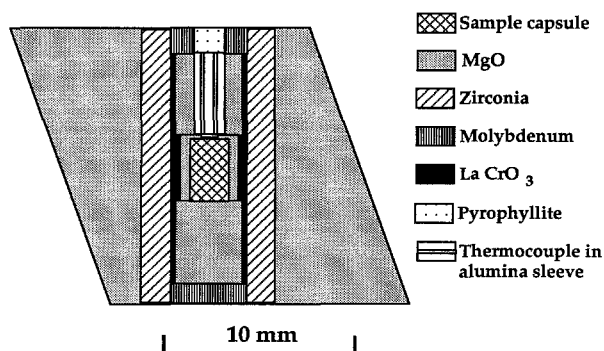


Fig. 1. Cross section of the pressure assembly used in multianvil experiments. A similar assembly in which the heater is graphite instead of LaCrO₃ has also been used

ed as a function of oil pressure using transitions in Bi at room temperature and by reversing the quartz/coesite, coesite/stishovite and Fe₂SiO₄ olivine/ γ -spinel equilibria at 1000° C (Fig. 1 in Rubie et al. 1993). An experiment at 1450° C using the Fe₂SiO₄ olivine/ γ -spinel equilibrium showed the calibration to be unaffected by temperature in the range 1000–1450° C. Uncertainties in pressure are estimated to be $\pm 5\%$. Details of the pressure assembly are shown in Fig. 1.

The use of a simple cylindrical graphite heater together with a thermocouple introduced diametrically through the heater wall in multianvil sample assemblies results in a temperature gradient across the sample of $\sim 200^\circ\text{C}/\text{mm}$ at 1500° C (e.g., Takahashi et al. 1982; see also Remsberg et al. 1988). In order to reduce this gradient to a level suitable for quantitative kinetic experiments, we have used stepped cylindrical heaters of variable wall thickness, consisting either of graphite or LaCrO₃, together with a thermocouple located along the axis of the heater (Fig. 1). In addition to the effect of the variable wall thickness of the heater, gradients are reduced using LaCrO₃ because the resistance of this material has a strong inverse relationship to temperature. The gradient is further reduced by eliminating the hot spot caused by introducing the thermocouple diametrically through the heater wall. Using two thermocouples, it has been determined that the heater geometry shown in Fig. 1 results in a temperature difference of $\sim 20^\circ\text{C}$ between the ends and the center of a 3 mm long sample capsule at 1400°–1500° C (Kanzaki 1987; Yasuda et al. 1990). Temperature was monitored using a W3%Re-W25%Re thermocouple, without any correction for the effect of pressure on thermocouple emf, and was controlled to $\pm 2^\circ\text{C}$.

Minimization of Differential Stress

The samples in the experiments described here were single crystals of San Carlos olivine with the approximate dimensions $1 \times 1 \times 1 \text{ mm}^3$ and with initial dislocation densities in the range 10^9 – 10^{10} m^{-2} (Fig. 4a). The corners and edges of the crystals were rounded to minimize possible stress concentrations. In order to investigate the differential stress during multianvil experiments, samples were annealed at 8.5 GPa and 1400° C for times ranging from 20–60 min (Table 1). Differential stresses during these experiments have been estimated from the resulting dislocation densities utilizing the technique of Karato and Ogawa (1982) and Wang et al. (1988) and the calibration of Kohlstedt et al. (1976a). Dislocation densities were observed by optical and scanning electron microscopy following dislocation decoration by oxidation in air at 900° C for 60 min (Kohlstedt et al. 1976b; Karato 1987).

In some previous high-pressure studies, the differential stress on the sample had been minimized by using either NaCl or graphite as a pressure medium (Karato and Ogawa 1982; Kronenberg et al. 1986; Tingle 1988; Wang et al. 1988; Gwanmesia et al. 1990). We have tested these two materials further using the capsule as-

Table 1. Observed dislocation densities (m^{-2}) in San Carlos olivine single crystals annealed at 8.5 GPa and 1400° C. "Center" and "edge" refer to locations on a cross section through the single crystal

Run #	Pressure medium	Capsule* Assembly	Time at 1400° C	Dislocation densities	
				Center	Edge
SCA-2	NaCl	(a)	50 min	$3-5 \times 10^9$	$\sim 10^{11}$
SCA-3	Graphite	(a)	30 min	$2-3 \times 10^9$	$\sim 10^{11}$
SCA-4	Opx	(b)	25 min	$10^{11}-10^{12}$	nd
SCA-5	NaCl (+Opx+NiO+Ni)	(c)	20 min	$\sim 10^{10}$	$\sim 10^{11}$
SCA-6	NaCl	(d)	60 min	$2-5 \times 10^9$	$\sim 10^{11}$
SCA-7	NaCl	(d)	55 min	$\sim 10^{10}$	$> 10^{10}$

Original dislocation density of San Carlos olivine = $10^9-10^{10} \text{ m}^{-2}$

* Refers to Fig. 2

nd - not determined

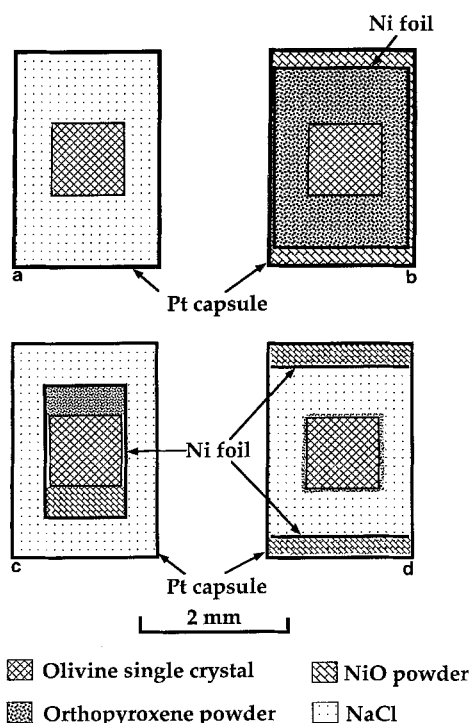


Fig. 2. Schematic drawings of the different capsule assemblies discussed in the text

sembly shown in Fig. 2a in which the olivine single crystal is surrounded by either NaCl or graphite within a Pt capsule. As in the earlier studies we used controlled slow rates of pressurization, depressurization, heating and cooling. At the start of each experiment, the uniaxial load on the hydraulic ram was increased at a rate of $100 \text{ tonnes h}^{-1}$ and, at the end of each experiment, the unloading rate was 85 tonnes h^{-1} (Fig. 3). These rates correspond to an increase and decrease in sample pressure of approximately 2.5 GPa h^{-1} and 2.1 GPa h^{-1} , respectively. Both compression and decompression were performed with the sample at elevated temperature (mostly 600° C, see Fig. 3) in order to minimize the strength of the pressure medium. Moderate rates of heating and cooling (as shown in Fig. 3) were used to avoid thermally shocking the sample.

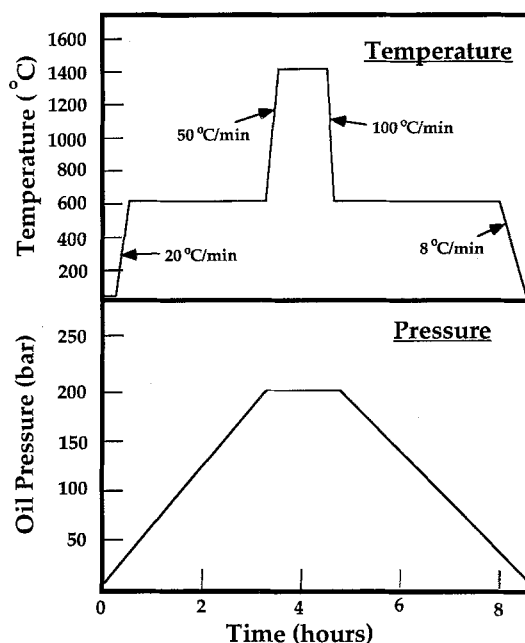


Fig. 3. Plots of temperature (top) and hydraulic oil pressure (bottom) against time for all annealing experiments at 8.5 GPa and 1400° C. The hydraulic oil pressure of 200 bar corresponds to a sample pressure of 8.5 GPa. During compression and decompression, the temperature was kept at 600° C in order to minimize the strength of the NaCl or graphite pressure medium surrounding the sample. Temperature and hydraulic oil pressure were computer controlled and were maintained within 1 bar and 2° C of the set-point values, respectively

Dislocation structures in olivine after annealing at 8.5 GPa, using both NaCl and graphite as the containing medium for the sample, are shown in Fig. 4b, c and the results of dislocation density measurements are summarized in Table 1 (# SCA-2 and # SCA-3). Except in a narrow zone 5–20 μm wide at the surface of the annealed crystals, dislocation densities are in the range $10^9-10^{10} \text{ m}^{-2}$ and are essentially identical to those of the starting material prior to the high pressure experiments. Dislocation densities of this magnitude are indicative of a differential stress of 3–10 MPa (Fig. 5), although the actual stress could be much lower because the kinetics of dislocation recovery are too slow at 8.5 GPa and 1400° C to observe any decrease in the disloca-

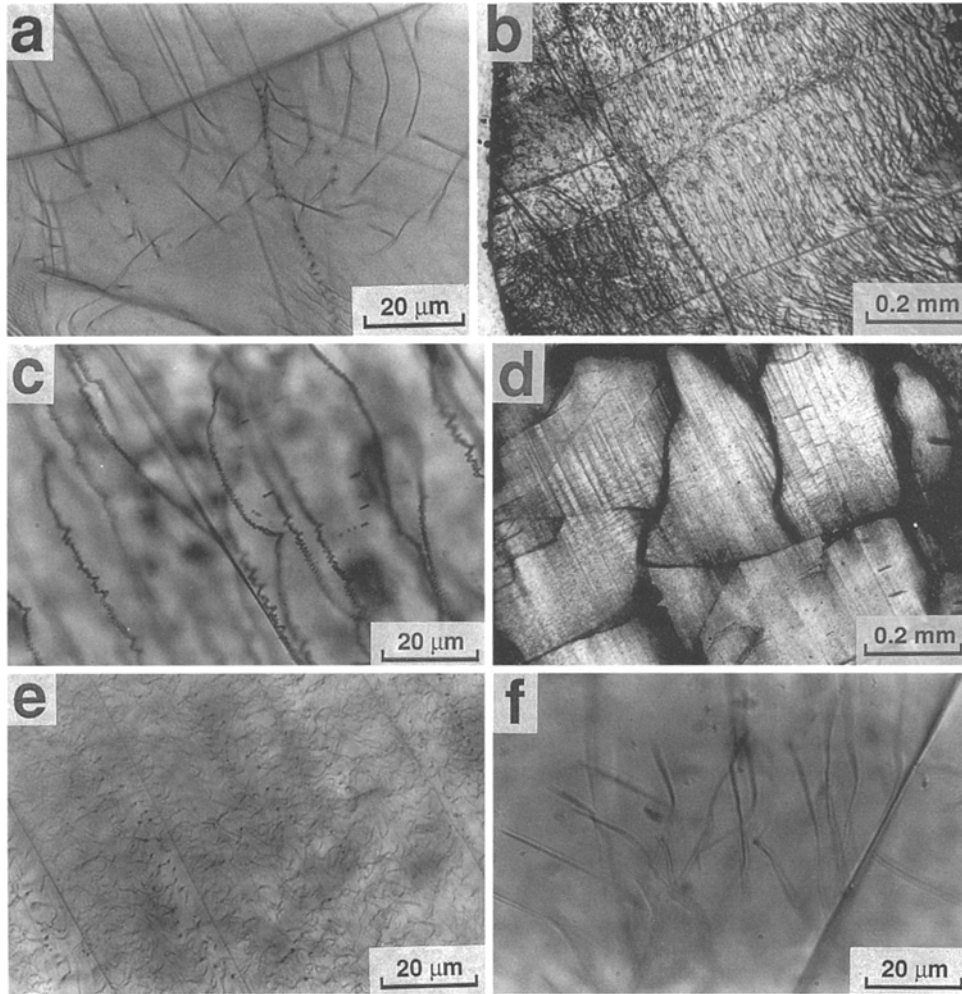


Fig. 4a–f. Photomicrographs showing dislocations in San Carlos olivine crystals before and after experiments at 1400° C and 8.5 GPa. **a** Typical dislocation density ($\sim 10^9 \text{ m}^{-2}$) in San Carlos olivine prior to high pressure experiments. **b** and **c** Sample (SCA-2) annealed using NaCl as the pressure medium. **b** Shows a large part of a cross section of the crystal with the edge on the left, and **c** is a higher magnification image from the center of the sample. The dislocation density in the bulk of the crystal is $2\text{--}3 \times 10^9 \text{ m}^{-2}$ but in a 10–20 μm wide zone at the surface the density is 10^{11} m^{-2} . **d** and **e** Sample (# SCA-4) annealed with orthopyroxene as the pressure medium using the capsule assembly of Fig. 2b. In addition to extensive fracturing seen in **d**, bulk dislocation densities are much higher than in samples annealed using NaCl or graphite as the pressure medium. **f** Sample (# SCA-7) annealed in the capsule assembly of Fig. 2d which showed a dislocation density similar to that of the starting material (Fig. 4a)

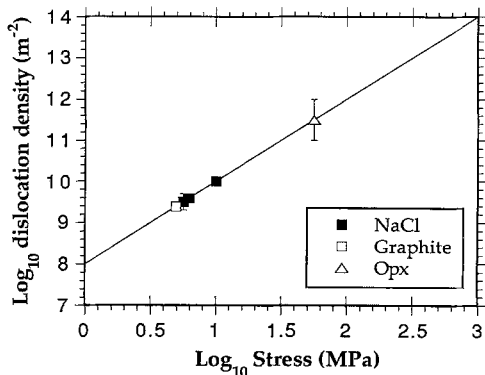


Fig. 5. Dislocation densities in olivine single crystals plotted on the differential stress-dislocation density correlation determined by Kohlstedt et al. (1976a). The dislocation densities were measured following annealing at 8.5 GPa and 1400° C in NaCl (filled squares), graphite (open square) and orthopyroxene (triangle) pressure media and give an estimate of the magnitude of the differential stress at high pressure. Using a pressure medium consisting of either NaCl or graphite the differential stress was low (<10 MPa or <0.1% of the confining pressure)

tion density on the time scale of these experiments (Karato et al. 1993). Dislocation densities in a 5–20 μm thick surface layer of the samples are often as high as 10^{11} m^{-2} (Fig. 4b). We have found that polishing and

grinding induces a high dislocation density in olivine within a few microns of the surface which indicates that sample preparation prior to high-pressure annealing may have caused these locally high dislocation densities. There is no evidence that the narrow surface layer with elevated dislocation densities broadens or that the locally high dislocation density decreases during high-pressure annealing on the time scale and temperature of these experiments.

The above results (Table 1, Fig. 5) suggest that NaCl and graphite are equally suitable pressure media for obtaining a low differential stress sample environment. Two potential problems with using graphite as a pressure medium are (1) the presence of this material in the sample capsule together with an oxygen buffer (see below) will complicate control of the oxygen fugacity and (2) transformation to diamond in multianvil experiments will cause the strength of the pressure medium to increase. In order to avoid these problems, we have used NaCl as a pressure medium in subsequent experiments.

Control of Chemical Environment

The sample environment was made as anhydrous as possible. The MgO octahedron and associated ceramic com-

ponents were fired at 1000° C for 1–2 h in air and were then stored at 230° C in a vacuum oven until ready for use. The olivine sample and NaCl pressure medium were loaded into the Pt capsule and were dried at 230° C in a vacuum oven for ≥ 12 h immediately prior to sealing the capsule by welding. Finally, the sample assembly was stored in the vacuum oven for at least 15 h immediately prior to starting the experiment.

The effectiveness of the above procedure was tested by measuring the OH content of an olivine single crystal which had been annealed at 10 GPa and 1500° C as part of a study of dislocation recovery kinetics (Yan 1992; Karato et al. 1993). Prior to the high-pressure annealing experiment, the olivine single crystal was deformed in the [011] orientation at 1400° C and 1 bar for 5 h under a controlled oxygen fugacity near the Ni-NiO buffer (obtained using a CO/CO₂ mixture). A polarized IR spectrum showed that this sample contained no detectable OH prior to high-pressure annealing. The OH content of the olivine crystal after annealing at 10 GPa and 1500° C for 21 h was estimated from a polarized IR spectrum (E parallel to [100]) by the method of Paterson (1982) (Fig. 6). Assuming an orientation factor $\gamma=1/3$, the spectrum yields a proton abundance of 90 parts per billion by weight, which corresponds to 13 H/10⁶Si. This concentration is comparable to the lowest OH contents in natural olivines reported by Miller et al. (1987). However, the result also demonstrates that the OH content of the olivine increased by a factor of at least 20 during the multianvil experiment. A change in OH content during the course of an experiment will obviously be a prob-

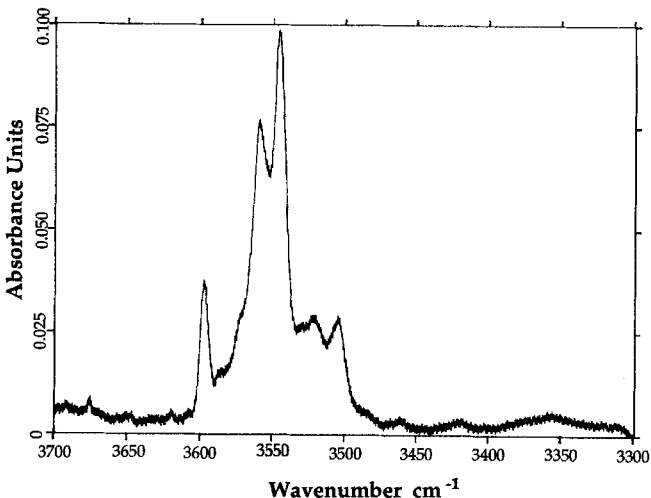


Fig. 6. Polarized IR spectrum (E parallel to [100]) of a single crystal of San Carlos olivine after annealing at 10 GPa, 1500° C for 21 h. The thickness of the crystal was 685 μm and the spectrum has been renormalized to a sample thickness of 10 mm. The measurement was done in the evacuated sample chamber of a Bruker IFS 120 FTIR spectrometer using a beam condenser. This spectrometer contains a Michelson-type interferometer. Experimental conditions: tungsten source, Si-coated CaF₂ beamsplitter, InSb detector, KRS-5 polarizer, spectral resolution 0.5 cm^{-1} , 1000 scans. An IR spectrum of the starting material for this experiment shows no detectable OH and indicates that the hydrogen content of the sample increased by a factor of at least 20 during high-pressure annealing

lem when kinetics are very sensitive to this parameter and could result in rates which are time-dependent. Whether or not the OH content stabilizes after a certain time in multianvil experiments remains to be determined.

In addition to hydrogen content, the high-temperature creep behavior of Fe-bearing olivine is sensitive to oxygen fugacity ($f\text{O}_2$) and oxide activity (e.g. Ricoult and Kohlstedt 1985; Bai et al. 1991). We have attempted to (1) buffer $f\text{O}_2$ by placing NiO in contact with a disk of Ni foil at each end of the sample capsule and (2) buffer the silica activity ($a\text{SiO}_2$) by placing orthopyroxene powder in contact with the olivine single crystal. The orthopyroxene consisted of San Carlos enstatite (Fe/(Fe+Mg)=0.085) which, after grinding, was dried by firing at 1200° C at an $f\text{O}_2$ equivalent to Ni/NiO for 10 h. Three different capsule assemblies, designed to maintain a controlled chemical environment, are shown in Fig. 2b–d. An assembly in which olivine is completely surrounded by orthopyroxene is most likely to produce a controlled and stable chemical environment. The differential stress on the olivine sample when surrounded by fine-grained orthopyroxene powder was estimated by annealing an olivine crystal at 8.5 GPa and 1400° C for 25 min (Table 1, # SCA-4) using the capsule assembly shown in Fig. 2b, with the capsule contained in an NaCl sleeve (instead of MgO as shown in Fig. 1). Compression and decompression were performed at 600° C as described above (Fig. 3). This experiment resulted in extensive fracturing of the olivine crystal and produced dislocation densities in the range 10^{11} – 10^{12} m^{-2} throughout the sample (Fig. 4d, e), indicating that differential stresses were relatively high (30–100 MPa). The containment of the olivine crystal in sintered orthopyroxene probably results in high stresses because of the anisotropic thermal expansion and compressibility of olivine combined with the high strength of orthopyroxene (in comparison with NaCl), as well as differences in these parameters for olivine and orthopyroxene. The differential strain which results from heating and compressing the olivine crystal must be easily accommodated by the surrounding material if differential stresses are to be low.

Because orthopyroxene is too strong to be used as a pressure medium, an alternative assembly was tested in which the olivine crystal was contained in Ni foil to isolate it from an NaCl pressure medium. Layers of NiO and orthopyroxene powder were placed adjacent to opposing faces of the olivine crystal, also within the Ni foil (Fig. 2c). After annealing, the bulk of the crystal was again extensively fractured, although in regions between the fractures the dislocation density remained relatively low (Table 1, # SCA-5). The fracturing is probably the result of different compressibilities and/or thermal expansivities for olivine and the sintered orthopyroxene layer. In addition, equilibrium with respect to oxide activity is unlikely to be achieved and cannot be constrained because at different faces of the olivine crystal there are metal-rich, metal oxide-rich and silica-rich environments, respectively.

Finally, experiments have been performed in which the surface of the olivine crystal was coated with a very thin orthopyroxene layer. This was applied as an alcohol-based slurry using a small brush. The crystal was

Table 2. Summary of thermodynamic data used to calculate fO_2 from olivine–orthopyroxene-metal equilibria.

	Reaction		References
$\Delta G_{(T, 1 \text{ bar})}^{\circ}$	(1)	$-564.8 + 0.1444 T$ kJ/mol	O'Neill (1987a)
$\Delta G_{(T, 1 \text{ bar})}^{\circ}$	(2)	$-485.7 + 0.1792 T$ kJ/mol	O'Neill (1987b)
$\Delta G_{(T, P)}^{\circ}$	(3)	$-6710 - 0.31 T - 0.375 P$ J/mol	O'Neill & Wall (1987)
$\Delta V_{s(298, 1 \text{ bar})}$	(1)	0.866 ^a J/bar	
$\Delta V_{s(298, 1 \text{ bar})}$	(2)	0.67 J/bar	
Activity coefficients:			
$\ln \gamma_{Fe}^{ol}$	$(1 - X_{Fe}^{ol})^2 (600 + 0.0013 P)/T$		O'Neill & Wall (1987)
$\ln \gamma_{Ni}^{ol}$	0		Seifert & O'Neill (1987)
$\ln \gamma_{Fe}^{met}$	$(1 - X_{Fe}^{met})^2 [-3.33 + 0.22 (4X_{Fe}^{met}) - 1]$		Heald (1967)
$\ln \gamma_{Ni}^{met, \infty}$	$-3450/T$		Walker & Darby (1970)

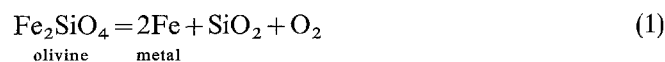
Units: temperature (T)–K; pressure (P)–bars

^a Includes a correction for the partial molar volume of Fe in Pt from Cabri & Feather (1975)

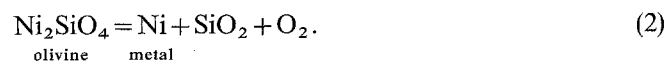
then loaded into the NaCl pressure medium which in turn was contained in the Pt capsule (Fig. 2d). As before, Ni + NiO were located at each end of the capsule. Dislocation densities after annealing at 8.5 GPa and 1400° C are similar to those of the starting material (Table 1, # SCA-6, Fig. 4f) indicating that differential stresses are ≤ 10 MPa. Usually samples were recovered completely unfractured using this assembly. However, in a few experiments, very localized fracturing of the sample did occur where the applied orthopyroxene layer was sufficiently thick to form a coherent sintered layer.

In the experiments reported here, electron microprobe investigations have shown no evidence of reaction as a result of direct contact between the olivine sample and the NaCl pressure medium. This is also the case in the majority of subsequent experiments at 1500° C and 7–10 GPa in which the effect of pressure on the kinetics of dislocation recovery in olivine has been studied (Karato et al. 1993). However, at conditions at which NaCl is molten, mass transport between the Ni/NiO buffer at the ends of the capsule and the sample is facilitated and reaction at the sample surface occurs, resulting in a Ni-rich layer. Karato and Ogawa (1982) also reported reaction zones ~ 100 μm wide around olivine crystals contained in a BN + NaCl pressure medium probably because the NaCl was in a molten state during high-pressure annealing.

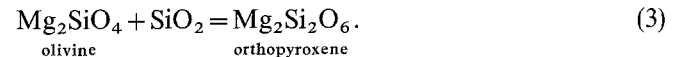
In order to determine the fO_2 at the surface of the olivine crystal in the capsule assembly by Fig. 2d, we performed an experiment at 1400° C and 8.5 GPa for 6 h in which a Pt wire (0.1 mm diameter) was wound once around the sample. During the course of the experiment Fe and Ni from the olivine diffused into the Pt wire, enabling the fO_2 at the sample surface to be evaluated from the two equilibria:



and



The presence of orthopyroxene buffer a_{SiO_2} via the reaction:



Therefore at equilibrium (using the usual notation):

$$\log fO_2 = \Delta G_{(T, 1)}^{\circ} / 2.303RT + 2 \log X_{Fe}^{ol} / X_{Fe}^{met} + 2 \log \gamma_{Fe}^{ol} - 2 \log \gamma_{Fe}^{met} - \log a_{\text{SiO}_2} + \Delta V_{s(298, 1)}^{\circ} P / 2.303 RT \quad (4)$$

for reaction (1), and likewise for reaction (2). The standard state is a pressure of 1 bar and the temperature of interest. We approximate the effect of pressure by neglecting thermal expansivities and compressibilities. The necessary thermodynamic data are summarized in Table 2.

Figure 7a shows a section through the contact between olivine and Pt wire after the high-pressure experiment. Electron microprobe analyses indicate the presence of Fe and Ni concentration gradients near the contact (Fig. 7b). At the interface, the metal composition is 1.9 ± 0.1 wt % Fe and 0.3 ± 0.02 wt % Ni (corresponding to $X_{Fe}^{met} = 0.063 \pm 0.003$ and $X_{Ni}^{met} = 0.009 \pm 0.001$) which coexists with olivine with $X_{Fe}^{ol} = 0.054 (\pm 0.006)$ and $X_{Ni}^{ol} = 0.0028 (\pm 0.0006)$. These values, which are reproducible at different points along the metal-olivine interface, give $\log fO_2 = -3.67 (\pm 0.2)$ and -2.01 (log-bar units) for the Fe and Ni reactions, respectively. The result from the Fe reaction is in good agreement with $\log fO_2 = -3.44$ log-bar units calculated for the Ni-NiO buffer at 1400° C and 8.5 GPa from the data of O'Neill (1987b). The quoted error for the Fe reaction depends mainly on uncertainties in the olivine composition at the interface; because of the steepness of the concentration gradients in the olivine, the errors are difficult to estimate reliably (see Fig. 7b). For this reason and because of an additional problem discussed below, we have not attempted to estimate the uncertainty in the fO_2 calculated from the Ni reaction.

The presence of Fe and Ni concentration gradients in both olivine and Pt indicates that reactions (1) and (2) did not go to completion. However, a state of local equilibrium for these reactions at the interface between

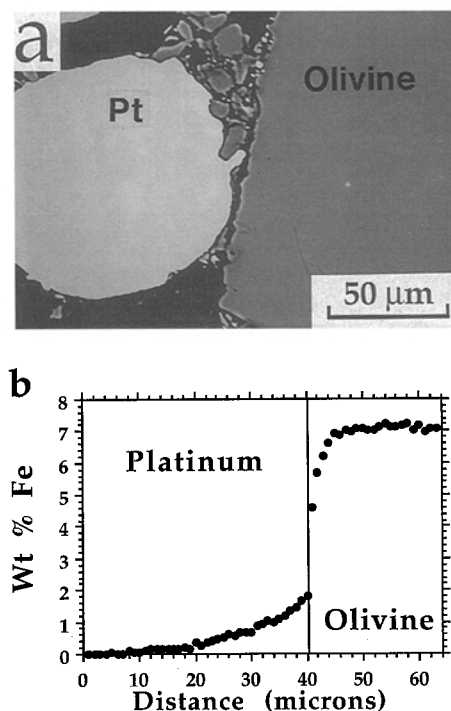


Fig. 7. **a** Back scattered electron image of the contact between Pt wire (seen in cross section) and an olivine single crystal annealed at 8.5 GPa and 1400° C for 6 h in the capsule assembly of Fig. 2d. The small grains are orthopyroxene. **b** Fe concentration in the platinum and olivine along a traverse perpendicular to the interface shown in **a**. Analyses along several parallel traverses gave consistent results. The profile for Ni concentration in the olivine close to the interface is steeper than for Fe, which makes the determination of the Ni content of the olivine in equilibrium with the metal difficult. Analyses close to the interface showed poor totals and were discarded; compositions at the interface were estimated by extrapolation of the concentration profiles

Pt and olivine (where the compositions were estimated) may be assumed. In addition, although the method only allows the fO_2 at the sample surface to be determined, the results suggest that the entire sample should have equilibrated to this fO_2 on the time scale of the experiment. This is because the equilibration kinetics with respect to fO_2 are controlled by the diffusion of vacancies and not by the diffusion of atoms and are much faster than the kinetics of chemical diffusion (Karato and Sato 1982; Mackwell et al. 1987). On the basis of these latter two studies, fO_2 equilibration at a scale of ~ 1 mm should be achieved when the chemical diffusion distance is ~ 10 μm .

The method is more accurate for the Fe reaction than for the Ni reaction, not only because the higher Fe contents reduce the effect of analytical uncertainty, but also because proportionally less Fe than Ni needs to diffuse out of the olivine and into the metal in order to achieve equilibrium (i.e. $D_{\text{Fe}}^{\text{ol}/\text{met}} \approx 2$ whereas $D_{\text{Ni}}^{\text{ol}/\text{met}} < 1$). This means that for Ni, the fO_2 calculation depends much more on an accurate estimation of the Ni content of the olivine at the olivine-Pt interface. An accurate estimate is difficult to make because the Ni diffusion profile in the olivine is very short and steep. This result is due to the slow diffusion rate of Ni in olivine; tracer diffu-

sion rates at 1 bar for Fe in olivine are about an order of magnitude slower than for Fe in Pt, while diffusion of Ni in olivine is another order of magnitude slower still (Berger and Schwartz 1978; Hermeling and Schmalzried 1984; Morioka and Nagasawa 1991). These considerations suggest that an obvious improvement of the method would be to reduce the diameter of the Pt wire, thereby minimizing the amounts of Fe and Ni which need to diffuse out of olivine.

There is no simple way to test the effectiveness of the oxide buffer. However, experimental studies of creep in olivine with different oxide buffers indicate that the equilibration kinetics are fast. For example, equilibration occurs within 1 h at 1300° C and 1 bar in samples with dimensions of several mm (Mackwell et al. 1987). It is therefore likely that equilibration is achieved in our small samples (~ 1 mm³) at 1400–1500° C and 8.5 GPa at an early stage provided the total duration of the experiment is reasonably long (e.g. 1–20 h).

Summary and Further Applications

This study demonstrates the feasibility of maintaining a low differential stress and a well-controlled chemical environment during multianvil experiments (although changes in the OH content of the sample at high P and T may still be a problem). Such developments make a variety of experimental kinetic studies possible at pressures up to at least 10 GPa. For example, in addition to studies of dislocation mobility in olivine (Karato et al. 1993), the same techniques are being used to study the effect of pressure on the self-diffusion of Mg in garnet (Chakraborty et al. 1992) and grain boundary diffusion in forsterite aggregates (Farver et al. 1993). These experiments involve a diffusion couple between a highly-polished sample surface and a precipitated layer of ²⁶MgO (see Cygan and Lasaga 1985). In this case, a low differential stress is critical in order to avoid mechanical damage to the polished surface because such damage would seriously affect the analysis of sub-micron diffusion profiles (see also the Fe–Mg diffusion experiments in olivine crystals by Bertran-Alvaraz et al. 1992).

Acknowledgements. We thank H. Keppler for obtaining FTIR spectra, S.L. Webb for orienting olivine single crystals, D.L. Kohlstedt and Q. Bai for discussions, R.C. Liebermann, S.J. Mackwell and an anonymous reviewer for helpful reviews and H. Kufner, H. Schulze and D. Krauße for technical assistance. This research was partially supported by NSF through grant EAR-9008984.

References

- Bai Q, Mackwell SJ, Kohlstedt DL (1991) High temperature creep of olivine single crystals 1. Mechanical results for buffered samples. *J Geophys Res* 96:2441–2463
- Berger D, Schwartz K (1978) Zur Fremddiffusion in Platin. *Neue Huette* 23:210–212
- Bertran-Alvaraz Y, Jaoul O, Liebermann RC (1992) Fe–Mg interdiffusion in single crystal olivine at very high pressure and controlled oxygen fugacity: technological advances and initial data at 7 GPa. *Phys Earth Planet Inter* 70:102–118

- Boland JN, Duba AG (1986) An electron microscope study of the stability field and degree of nonstoichiometry in olivine. *J Geophys Res* 91:4711–4722
- Green II HW, Borch RS (1987) The pressure dependence of creep. *Acta Metall* 35:1301–1305
- Cabri LJ, Feather CE (1975) Platinum-iron alloys: A nomenclature based on a study of natural and synthetic alloys. *Can Mineral* 13:117–126
- Chakraborty S, Rubie DC, Elphick SC (1992) Mg tracer diffusion in aluminosilicate garnets at 800° C, 1 atm. and 1300° C, 8.5 GPa. *EOS, Trans Am Geophys Union* 73, Fall Meeting Supplement, 567
- Cygan RT, Lasaga AC (1985) Self-diffusion of magnesium in garnet at 750° C to 900° C. *Am J Sci* 285:328–350
- Farver JR, Yund RA, Rubie DC (1993) Magnesium grain boundary diffusion in fine-grained forsterite aggregates. *EOS, Trans Am Geophys Union* 74, Spring Meeting Supplement, 315
- Gwanmesia GD, Liebermann RC, Guyot F (1990) Hot-pressing and characterization of polycrystals of β - Mg_2SiO_4 for acoustic velocity measurements. *Geophys Res Lett* 17:1331–1334
- Heald EF (1967) Thermodynamics of iron-platinum alloys. *Trans Metal Soc AIME* 239:1337–1340
- Hermeling J, Schmalzried H (1984) Tracer diffusion in olivine ($\text{Fe}_x\text{Mg}_{1-x}$)₂SiO₄ (III). *Phys Chem Minerals* 11:161–166
- Jaoul O, Houlier B, Cheraghmakani M, Pichon R, Liebermann RC (1987) Surface destabilization and laboratory-induced nonstoichiometry in San Carlos olivine. *Phys Chem Minerals* 15:41–53
- Kanzaki M (1987) Physical properties of silicate melts at high pressures. PhD thesis, Geophysical Institute, University of Tokyo
- Karato S (1987) Scanning electron microscope observation of dislocations in olivine. *Phys Chem Minerals* 14:245–248
- Karato S, Ogawa M (1982) High-pressure recovery of olivine: implications for creep mechanisms and creep activation volume. *Phys Earth Planet Inter* 28:102–117
- Karato S, Sato H (1982) Effect of oxygen partial pressure on the dislocation recovery in olivine: a new constraint on creep mechanisms. *Phys Earth Planet Inter* 28:312–319
- Karato S, Rubie DC, Yan H (1993) Dislocation mobility in olivine under deep upper mantle conditions: implications for creep and diffusion. *J Geophys Res* 98:9761–9768
- Kohlstedt DL, Goetze C, Durham WB (1976a) Experimental deformation of single crystal olivine with application to flow in the mantle. In: Strens RG (ed) *The Physics and Chemistry of Minerals and Rocks*. Wiley, New York, pp 35–49
- Kohlstedt DL, Goetze C, Durham WB, Van der Sande JB (1976b) A new technique for decorating dislocations in olivine. *Science* 191:1045–1046
- Kohlstedt DL, Mackwell SJ (1987) High-temperature stability of San Carlos olivine. *Contrib Mineral Petrol* 95:226–230
- Kohlstedt DL, Nichols HPK, Hornack P (1980) The effect of pressure on the rate of dislocation recovery in olivine. *J Geophys Res* 85:3122–3130
- Kronenberg AK, Kirby SH, Aines RD, Rossman GR (1986) Solubility and diffusional uptake of hydrogen in quartz at high water pressures: Implications for hydrolytic weakening. *J Geophys Res* 91:12723–12744
- Mackwell SJ, Dimos D, Kohlstedt DL (1987) Transient creep of olivine: point defect relaxation times. *Philos Mag* A57:779–789
- Miller GH, Rossman GR, Harlow GE (1987) The natural occurrence of hydroxide in olivine. *Phys Chem Minerals* 14:461–472
- Morioka M, Nagasawa H (1991) Ionic diffusion in olivine. In: Ganguly J (ed) *Diffusion, Atomic Ordering, and Mass Transport, Advances in Physical Geochemistry*, Vol 8, Springer, Berlin Heidelberg New York, pp 176–197
- O'Neill HStC (1987a) The quartz–fayalite-iron and quartz–fayalite–magnetite equilibria and the free energies of formation of fayalite (Fe_2SiO_4) and magnetite (Fe_3O_4). *Am Mineral* 72:67–75
- O'Neill HStC (1987b) The free energies of formation of NiO, CoO, Ni₂SiO₄ and Co₂SiO₄. *Am Mineral* 72:280–291
- O'Neill HStC, Wall VJ (1987) The olivine–orthopyroxene–spinel oxygen geobarometer, the nickel precipitation curve, and the oxygen fugacity of the Earth's upper mantle. *J Petrol* 28:1169–1191
- Nitsan U (1974) Stability field of olivine with respect to oxidation and reduction. *J Geophys Res* 79:706–711
- Paterson MS (1982) The determination of hydroxyl by infrared absorption in quartz, silicate glasses and similar materials. *Bull Minéral* 105:20–29
- Remsberg AR, Boland JN, Gasparik T, Liebermann RC (1988) Mechanism of the olivine-spinel transformation in Co₂SiO₄. *Phys Chem Mineral* 15:498–506
- Ricoult DL, Kohlstedt DL (1985) Experimental evidence for the effect of chemical environment upon the creep rate of olivine. In: Schock RN (ed) *Point Defects in Minerals*, Geophys Monograph Ser 31, AGU, Washington, pp 171–184
- Rubie DC, Champness PE (1987) The evolution of microstructure during the transformation of Mg₂GeO₄ olivine to spinel. *Bull Minéral* 110:471–480
- Rubie DC, Brearley AJ (1990) Mechanism of the γ – β phase transformation of Mg₂SiO₄ at high temperature and pressure. *Nature* 348:628–631
- Rubie DC, Ross II CR, Carroll MR, Elphick SC (1993) Oxygen self-diffusion in Na₂Si₄O₉ liquid up to 10 GPa and estimation of high-pressure melt viscosities. *Am Mineral* 78:574–582
- Seifert S, O'Neill HStC (1987) Experimental determination of activity-composition relations in Ni₂SiO₄–Mg₂SiO₄ and Co₂SiO₄–Mg₂SiO₄ olivine solid solutions at 1200 K and 0.1 MPa and 1573 K and 0.5 GPa. *Geochim Cosmochim Acta* 51:97–104
- Takahashi E, Yamada H, Ito E (1982) An ultrahigh-pressure furnace assembly to 100 kbar and 1500° C with minimum temperature uncertainty. *Geophys Res Lett* 9:805–807
- Tingle TN (1988) Retrieval of uncracked single crystals from high pressure in piston-cylinder apparatus. *Am Mineral* 73:1195–1197
- Walker RA, Darby JB Jr (1970) Thermodynamic properties of solid nickel-platinum alloys. *Acta Metall* 18:1261–1266
- Wang Y, Liebermann RC, Boland JN (1988) Olivine as an in situ piezometer in high pressure apparatus. *Phys Chem Minerals* 15:493–497
- Yan H (1992) Dislocation recovery in olivine. MSc. Thesis, University of Minnesota
- Yasuda A, Fujii T, Kurita K (1990) Melting relations of anhydrous abyssal basalt at high pressures. In: Marumo F (ed) *Dynamic processes of material transport in the earth's interior*. Kluwer, Dordrecht, pp 327–337
- Yund RA, Tullis J (1980) The effect of water, pressure, and strain on Al/Si order-disorder kinetics in feldspar. *Contrib Mineral Petrol* 72:297–302