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Physics of the Earth and Planetary Interiors 166 (2008) 11–29

PHYSICS OF THE EARTH AND PLANETARY INTERIORS

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The effect of water on Si and O diffusion rates in olivine and implications for transport properties and processes in the upper mantle

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Received 27 April 2007; received in revised form 20 September 2007; accepted 15 October 2007

Abstract

We performed piston cylinder experiments (1200–1350 °C, 2 GPa) to determine the diffusion rates of Si and O in mantle olivine under water undersaturated (brucite absent, 45 ppm H_2O in olivine) as well as close to water-saturated (brucite present, ∼370 ppm H_2O in olivine) conditions. Diffusion couples consisted of oriented and polished San Carlos olivine cylinders coated with thin (∼few 100 nm) films of the same composition enriched in ^{29}Si and ^{18}O, with a protective coating of ZrO_2 on top. Relationships between water solubility in olivine and water fugacity, combined with thermodynamic equilibrium calculations, indicate fH_2O ∼1 GPa, fO_2 ∼IW buffer for brucite absent and fH_2O ∼9 GPa, fO_2 ∼QFM buffer for brucite present experiments. We find that under hydrous conditions $D_{Si} \approx D_O$ and diffusion anisotropy is weak to non-existent. Fitting the raw data at 2 GPa and fH_2O ∼0.93 GPa yields Arrhenius parameters [D_o and E_p in $D = D_o \exp(-E_p/RT)$] of: 1.68 (±3.52) × 10^{-7} $m^2\,s^{-1}$ and 358 ± 28 kJ mol^{-1} for Si, and 1.43 (±1.80) × 10^{-4} $m^2\,s^{-1}$ and 437 ± 17 kJ mol^{-1} for O, respectively (1 sigma errors). D (2 GPa, fH_2O = 0.97 GPa, 1200 °C): D (1 atm., dry, 1200 °C) is 1000 for Si and 10 for O, respectively. Equations incorporating explicitly the effect of water are discussed in the text.

Analysis of our data suggests that O diffuses by an interstitial mechanism whereas Si diffuses via vacancy complexes. The relation between the water fugacity and the Si diffusion rates seems to obey a power law with a water fugacity exponent of 0.2–1. The amount of H incorporated into olivine at the experimental conditions is orders of magnitude higher than the likely concentration of Si vacancies. Therefore, a small fraction (∼0.01%) of the total incorporated H in olivine suffices to considerably enhance the concentration of Si vacancies, and hence diffusion rates. Activation energies for O diffusion under dry and wet conditions are similar, indicating that the mechanism of this diffusion does not change in the presence of water. This inference is consistent with results of computer simulations.

Dislocation creep in olivine under wet conditions appears to be controlled by both, Si as well as O diffusion. Absolute creep rates can be calculated from the diffusion data if it is assumed that climb and glide of dislocations contribute equally to creep. Finally, analysis of the various transport properties indicate that <10 ppm of water in olivine is sufficient to cause a transition from "dry" to "wet" laws for most processes. As these water contents are even lower than the observed water contents in most mantle olivines (i.e. minimum values measured at the surface), we conclude that results of water present but undersaturated kinetic experiments are directly applicable to the mantle. Indeed, "wet" kinetic laws should be used for modeling geodynamic processes in the upper mantle, even if the mantle is thought to be undersaturated with respect to water.

Keywords: Diffusion; Water; Deformation; Olivine; Silicon; Oxygen; Creep; Mantle; Experiment; Nominally anhydrous mineral (NAM); Transport

1. Introduction

Water plays a crucial role in most biological, atmospheric, and surface geological processes. But it also has a large effect on the physical properties of materials and processes that occur deeper within the Earth. Experimental results in the last two decades show that even small amounts (<0.005 wt.%) of H in nominally anhydrous minerals (NAMs) such as olivine or pyroxenes decreases the melting temperature and viscosity of the mantle, and enhances electrical conductivity and chemical diffusivity in it (e.g., Mei and Kohlstedt, 2000; Bolfan-Casanova, 2005; Hier-Majumder et al., 2005; Hirschmann, 2006; Karato, 2006; Yoshino et al., 2006; Wang et al., 2006; Demouchy et al., 2007). Despite the information that already exists, one can identify three main areas where more work is required:

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doi:10.1016/j.pepi.2007.10.006

(1) A robust quantification of the relation between the H content and the different physical properties at the relevant conditions does not exist. Measuring the rheological behavior of mantle material in the presence of water at upper mantle pressures remains a daunting challenge, with only two data sets obtained above 300 MPa (e.g., Hirth and Kohlstedt, 2003; Karato and Jung, 2003). However, precise relations between the “wet” vs. “dry” flow of these materials at high pressures are necessary to understand the factors that determine the nature of plate tectonics (e.g., Lithgow-Bertelloni and Richards, 1995; Hirth and Kohlstedt, 1996; Billen and Gurnis, 2001; Bercovici and Karato, 2003; Regenauer-Lieb, 2006).

(2) The mechanistic connection between H incorporation and changes in the different transport properties such as ionic diffusion, deformation, and electrical conductivity remains unclear. Diffusion data in water-bearing olivine is limited to Fe–Mg (Hier-Majumder et al., 2005) and it is not directly related to deformation or electrical conductivity. Computer simulations (e.g., Brodholt and Refson, 2000; Walker et al., 2003; Wright, 2006), water solubility measurements (e.g., Bai and Kohlstedt, 1992; Kohlstedt et al., 1996; Keppler and Bolfan-Casanova, 2006), and spectroscopic studies of NAMs (e.g., Beran and Putnis, 1983; Beran and Libowitzky, 2006; Kohn, 2006) have contributed much to indicate the possible location of H in the olivine structure, but the results are far from conclusive.

(3) It is necessary to quantify at what H concentration the physical and chemical behavior of mantle materials change from the dry to the water-bearing mechanisms/rates, and if such concentrations are likely to be present in the upper mantle. Studies of mantle xenoliths indicate that NAMs contain significant but very variable amounts of H (a few to a few hundred ppm; e.g., Bell and Rossman, 1992; Ingrin and Skogby, 2000). These water contents are typically lower than those at which the experimental data on physical properties are acquired. Nonetheless, evidence from modeling the mantle flow under the western U.S. seems to require a ’wet’ rheological law (Dixon et al., 2004; Freed and Bürgmann, 2004).

Here we present experimental data on Si and O diffusion rates in mantle olivine in the presence of H, and use these results to address some of the points above. We first explain in some detail the experimental and analytical strategy we have used. Next, the diffusion data are presented and the influence of the different intensive variables on the kinetic parameters are disentangled. The results are then discussed within the context of existing point defect thermodynamic models of olivine and related to Fe–Mg diffusion and dislocation creep rates of mantle olivine.

2. Experimental and analytical approach

One the of the main challenges of the experiments was to ensure mechanical as well as chemical stability of olivine and of the diffusion couple (crystal plus thin film) during the water-bearing, high pressure and temperature annealing conditions. Thus, we describe below in some detail the problems encountered before reaching the final working configuration.

2.1. Starting materials and diffusion couples

San Carlos olivine crystals free of cracks or inclusions were selected and oriented parallel to one of the crystallographic axes using optical methods on a spindle stage. The orientations of some of these crystals were determined *a posteriori* using the EBSD technique (electron backscatter diffraction) on a scanning electron microscope and differences between the two methods were <10°. The oriented crystals were cut into 1–2 mm thick slices and polished using diamond compounds followed by the combined mechano-chemical action of a highly alkaline colloidal silica solution (OP-S of Struers). We used cylinders that were drilled out of the olivine slices with a diameter of ∼2.5 mm and thickness of 1–2 mm.

The polished surfaces of the olivine cylinders were deposited with thin films (200–1000 nm thick) of the same olivine major element composition but doped with ^{18}O and ^{29}Si using the pulsed laser deposition facility available at the Institute of Geology, Mineralogy and Geophysics at Ruhr-Universitat Bochum (Dohmen et al., 2002a, 2007). It was found that recrystallization, grain growth or dissolution during annealing destroyed the olivine thin film. This was overcome by depositing a second protective layer that would act inertly; after several tests a film of ZrO_2 was found to be ideal for this purpose (Fig. 1a). Moreover, to minimize surficial effects and reaction with the environment, two such doubly coated crystals were placed on top of each other

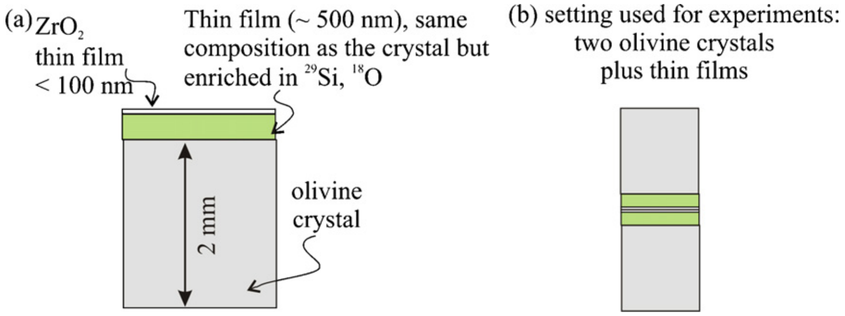

Fig. 1. (a) Olivine crystal plus thin films of olivine enriched in ^{18}O and ^{29}Si plus a protective thin film of ZrO_2. (b) A sandwich of two olivine crystals was used in the experiments. This setting prevented olivine thin films from reacting with the environment and yielded two crystals per anneal, providing a check for reproducibility of data.