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Effects of Water on the α-β Transformation Kinetics in San Carlos Olivine

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In experiments at 13.5 gigapascals and 1030°C, the growth rate of wadsleyite, which forms from transformation of olivine, was substantially enhanced by the presence of water. Wadsleyite had a low dislocation density and subgrain boundaries in wet runs. Water enhanced the dislocation recovery in wadsleyite and therefore caused inelastic relaxation of the localized pressure drop associated with the transformation, resulting in an increase of the growth rate in wet runs. These results imply that even a small amount of water of 0.05 weight percent can weaken wadsleyite in the mantle.

Water enhances the creep of many minerals, a process termed hydrolytic weakening or water weakening (*1*). To understand the dynamics of the mantle transition zone, it is important to know the effect of water on the plastic deformation of wadsleyite, a high-pressure polymorph of olivine and a major constituent in the mantle transition zone. Wadsleyite can contain a substantial amount of H_2O, up to about 3 weight % (*2*). Chen *et al.* (*3*) analyzed broadening of powder x-ray diffraction lines and suggested that water had little effect on deformation of wadsleyite up to 10 GPa at low temperature of ~600°C. Here we present evidence that water weakens wadsleyite, by examining transformation kinetics of olivine in wet and dry conditions.

We carried out high-pressure experiments using a 3000-ton multianvil (MA) press (*4*). The experiments were performed at 13.5 GPa and 1030°C, which is within the stability field of wadsleyite (*5*). Runs lasted from 0 to 1200 min. The starting material was single crystals of San Carlos olivine $(Mg_{0.89}Fe_{0.11})_2SiO_4$ that we cut into 1-mm^3 cubes. We used a stepped graphite heater, in which the central part is thicker than upper and lower parts. A sample was encased in a fine powder of NaCl in the central part of the heater in the dry runs. In the wet runs, the olivine was enclosed by a 10:1 or 500:1 mixture of NaCl and $Mg(OH)_2$ brucite by weight. We used a sealed platinum capsule in one of the wet runs. Temperature was measured between upper and center parts of heater with a Pt-Pt13%Rh thermocouple (*6*). Samples were first compressed at room temperature and then heated to the desired value. The heating rate, which was controlled to be same in all of experiments, was about 100°C per min. The sample was quenched to room temperature at high pressure, and then the pressure was released slowly over a period of several hours.

Fig. 1. Optical photomicrograph under crossed nichols of a thin section of an olivine single crystal partially transformed to wadsleyite at 13.5 GPa and 1030°C for 1200 min. The sample was enclosed by a mixture of NaCl and $Mg(OH)_2$ with a ratio of 500:1 by weight. The relict olivine is surrounded by the reaction rim consisted of elongated β-phase grains. Bar, 0.5 mm.

In the recovered samples, we observed a sharply defined rim of the product phase in both dry and wet [NaCl:$Mg(OH)_2$ = 500:1] runs (Fig. 1). X-ray diffraction analysis indicated that this phase was wadsleyite. Transmission electron microscope (TEM) observations (*7*) showed that the newly grown wadsleyite rim had no topotactic relations with the host olivine. This observation suggests that the wadsleyite nucleated randomly on the olivine surface. The only apparent compositional differences, on the basis of electron microprobe analysis, between relict olivine and the reaction rim was that the rims had a few tiny iron-rich grains (*8*). Thus, we conclude that the olivine transformed to wadsleyite by incoherent surface nucleation and interface-controlled growth. This result is consistent with previous studies with mantle olivine (*9*).

In the dry runs, wadsleyite growth was retarded with time and eventually ceased after 200 min (Fig. 2). In contrast, in the wet [NaCl:$Mg(OH)_2$ = 500:1] runs, the wadsleyite grew more rapidly than in the dry run, resulting in the large difference in the growth distance between the dry and wet conditions. When the ratio of NaCl and $Mg(OH)_2$ was 10:1, the transformation was completed within 180 min. These observations imply that the growth rate of the wadsleyite rim was enhanced by the presence of water in the

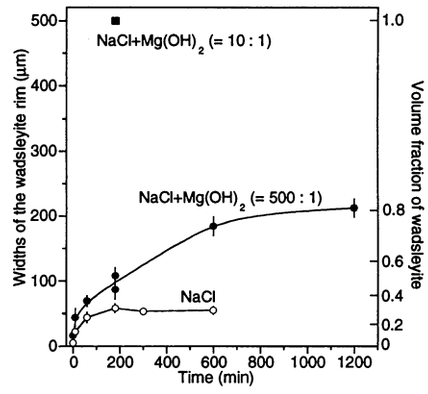

Fig. 2. Time dependence of the width and volume fraction of the wadsleyite rim in dry and wet runs at 13.5 GPa and 1030°C. The confining medium of the sample is also shown. The volume fraction of wadsleyite was estimated from widths of the wadsleyite rim. Time indicates the heating duration at the desired temperature.

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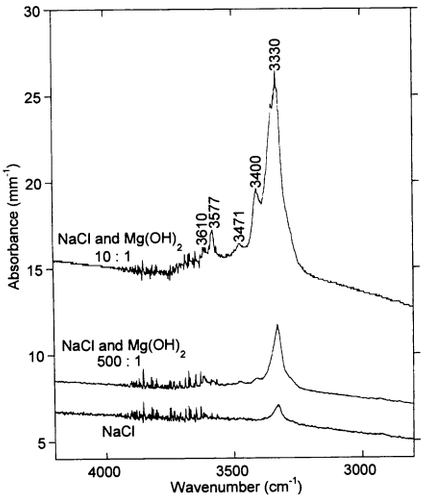

Fig. 3. FTIR spectra of wadsleyite recovered from the dry and wet runs. The confining medium of the sample is also shown. The water content of wadsleyite enclosed by NaCl, and NaCl and $Mg(OH)_2$ (500:1 and 10:1 in weight) confining medium was estimated to be 0.02 (±0.01), 0.05 (±0.02), and 0.21 (±0.01) weight % H_2O.

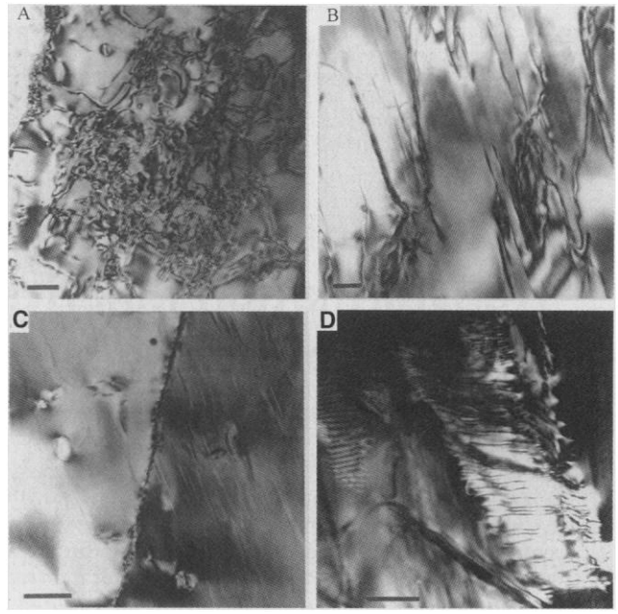

Fig. 5. TEM photomicrographs (bright field) showing dislocation microstructures in the wadsleyite rim. For the dry run (**A**), the tangled dislocations and high dislocation density imply the strain hardening of wadsleyite. For the wet [NaCl and $Mg(OH)_2$ = 500:1] runs, relatively low dislocation density (**B**), subgrain boundaries (**C**), and the dislocation network (**D**) imply the effective recovery in wadsleyite. Bars, 200 nm.

system. We measured the water content of the wadsleyite using a micro Fourier-transform infrared spectrometer (FTIR) (*10*) (Fig. 3). In samples enclosed by NaCl and $Mg(OH)_2$ of 500:1 and 10:1 in the wet runs, the water content of the wadsleyite was 0.05 (±0.02) and 0.21 (±0.01)% by weight, respectively. The water content in the dry run was estimated to be 0.02 (±0.01)%. We used a graphite capsule for dry runs, whereas we used both a graphite capsule and a platinum capsule for wet runs. We did not observe any substantial differences in the water content of wadsleyite between the wet runs using graphite and platinum capsules or with time (Fig. 4).

TEM observations indicated that many dislocations were created in wadsleyite for both dry and wet [NaCl:$Mg(OH)_2$ = 500:1] runs (Fig. 5). This plastic deformation in the wadsleyite rim is considered to be induced by the volumetric strain due to the transformation. The dislocation structures differed in the dry and wet runs. In the dry run (Fig. 5A), the dislocation density was high (~10^9 to 10^{10} cm^{-2}) and the dislocations were tangled, which implies strain hardening of the wadsleyite rim. In contrast, in the wet run, the dislocation density was low (~10^8 to 10^9 cm^{-2}) (Fig. 5B), and subgrain boundaries (Fig. 5C) and the dislocation network (Fig. 5D) were observed. These textures indicate that the dislocations recovered in the wet run. We found the Burgers vector **b** = [100] and 1/2{111} of the dislocations in wadsleyite in both the dry and wet runs using diffraction contrast analysis. This implies that water did not affect the slip system of wadsleyite.

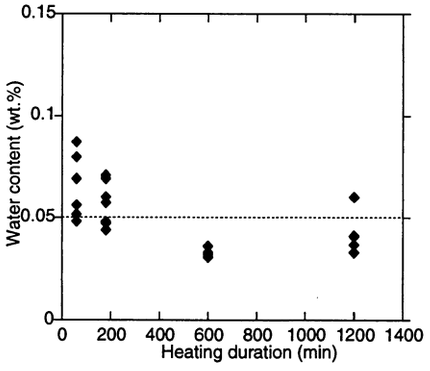

Fig. 4. Water content in the wadsleyite rim with time for the wet [NaCl:$Mg(OH)_2$] = 500:1 runs.

For solid-state first-order transformations, volume change accompanying transformation is often large, resulting in development of localized stress (*11*). In dry runs, a localized pressure drop in the relict olivine caused by a volume change during the transformation possibly caused a decrease in the free-energy change of reaction, resulting in a decrease in the growth rate (*12*) (Fig. 2). The plastic flow of the outer rim (Fig. 5) can relax the localized pressure drop and thus controls the growth rate of wadsleyite rim. Morris (*13*) proposed that growth is controlled by slip deformation of the outer rim in solid-state first-order transformations. Enhancement of the transformation rate by more than one order of magnitude in wet runs (Fig. 2) implies that the strain rate of the outer rim was enhanced by more than one order of magnitude by water; that is, the viscosity of the wadsleyite rim is reduced to less than one-tenth by existence of water of ~0.05 to 0.21 weight % H_2O. Our observations of enhancement of the growth rate and the dislocation texture showing effective recovery in the wet runs suggest that water weakens wadsleyite even when the water content is lower (about 0.05 weight % H_2O) than the solubility limit of water (3 weight % H_2O). This is not consistent with the results of Chen *et al.* (*3*). However, the inconsistency might be caused by a large difference in the experimental temperatures.

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6. The measured temperature is lower than that at the center of the heater by about 30°C at 1000°C based on measurements with two thermocouples. Therefore, we corrected the measured temperature of the sample by taking into account the effect of the temperature gradient in the furnace. The effect of pressure on the emf of the thermocouple was ignored in the present experiments.
7. Microstructures of the recovered samples and crystallographic orientation relations between the reactant

and product phases were examined with a 200-kV JEOL-2010 TEM.
8. Electron microprobe analysis of the recovered samples revealed that small, iron-rich grains (less than 10 μm) with olivine stoichiometry exist within the reaction rim especially near the surface. The Mg/(Mg + Fe) ratios in these iron-rich grains range from about 81 to 85. This suggests that the iron-rich grains are ringwoodite, and the transformation occurred in the coexisting field of wadsleyite and ringwoodite at lower temperature before the desired value was reached.
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10. FTIR measurements were carried out in air. Thickness of the sample was 80 to 140 μm, and aperture size ranged from 50 μm by 50 μm to 500 μm by 500 μm. Water content of wadsleyite was estimated from the integration of the infrared spectra using the calibration by Paterson [M. S. Paterson, *Bull. Mineral.* **105**, 20 (1982)].
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High-Temperature Silicate Volcanism on Jupiter's Moon Io

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Infrared wavelength observations of Io by the Galileo spacecraft show that at least 12 different vents are erupting lavas that are probably hotter than the highest temperature basaltic eruptions on Earth today. In at least one case, the eruption near Pillan Patera, two independent instruments on Galileo show that the lava temperature must have exceeded 1700 kelvin and may have reached 2000 kelvin. The most likely explanation is that these lavas are ultramafic (magnesium-rich) silicates, and this idea is supported by the tentative identification of magnesium-rich orthopyroxene in lava flows associated with these high-temperature hot spots.

After the Voyager spacecraft flybys of the Jupiter system in 1979, many investigators thought that the active volcanism on Io was dominated by sulfur-rich lavas, although silicate magmas at depth may have initially melted these lavas (*1*). The highest temperatures estimated from Voyager were ~650 K (*2*), consistent with sulfur volcanism, but Voyager could not detect small areas at higher temperatures because of limitations in sensitivity and wavelength coverage. Ground-based telescopic observations in 1986 provided observations of a temperature exceeding 900 K, suggesting at least occasional eruptions of silicate lavas (*3*). Recent Earth-based and Galileo observations have shown that such high-temperature hot spots are actually common on Io (*4*, *5*). Thirty locations with temperatures higher than 700 K were identified during the Galileo tour in 1996 to 1997; most of these probably include areas with temperatures higher than 1000 K (*6*). These temperatures are well above the boiling point for elemental S in a near vacuum (*7*), so silicate eruptions are now thought to be a fundamental part of Io's active volcanism (*8*).

We report principally on observations of Io in eclipse (in Jupiter's shadow; see Fig. 1) by the Galileo Solid State Imaging (SSI) experiment (*9*). SSI has observed Io during 11 eclipses in the first 11 orbits, including observations through the broadband clear filter and six color filters with effective wavelengths from 0.42 to 0.99 μm. These images revealed (i) small bright spots in the clear and 1MC (~0.99 μm) bandpasses that are due to high-temperature hot spots and (ii) faint diffuse glows due to electronic excitation of gases around the limb and near active vents in the clear and visible bandpasses (*5*, *6*, *10*). The actual area of each hot spot (typically

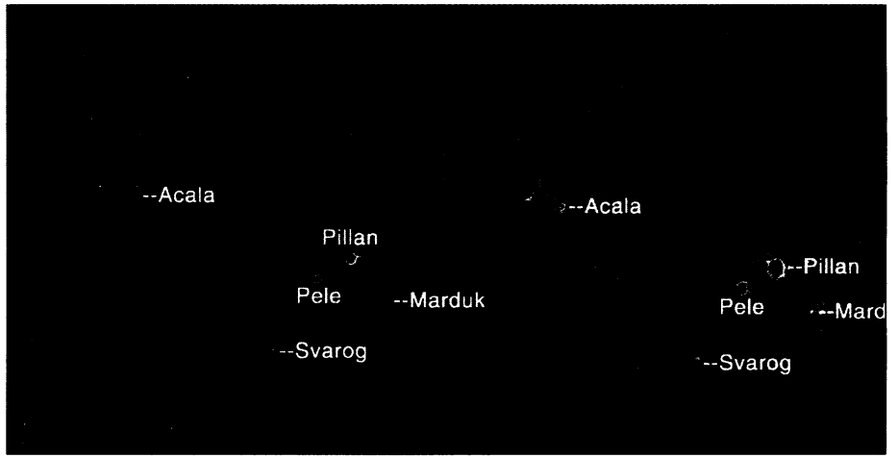

Fig. 1. SSI image showing Io in eclipse (PICNOs C9I0025-26). Image is color coded with blue-yellow-red representing increasing brightness. This image is a "raw" spacecraft frame, with no processing other than color coding and labels, to illustrate several characteristics of the data. The left-hand image was acquired through the 1MC bandpass and the right-hand image is dominated by the clear-filter exposure (plus 1MC exposure). The scale is 14.6 km/pixel, but each hot spot is smeared over an area about nine pixels in diameter. Temperature-area modeling (Table 2) indicates that the actual hot areas are much smaller than the pixels. Diffuse glows from electronic excitation of gases highlight Io's limb and active plumes such as Marduk in the clear-filter image. Small bright pixels and clusters of pixels are noise from radiation hits. The horizontal line between Pillan positions is due to 1MC exposure during scan platform motion. The bright vertical lines are due to column blemishes, and the blockiness at low brightness levels is due to data compression (*9*).

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