Hydration of Olivine
and
Earth’s Deep Water Cycle
Olivine Hydration and Earth’s Deep Water Cycle

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Oceans cover 71% of the planet’s surface.
71% of the surface

But only 0.025% of the mass
• 0.15 percent \( H_2O \) by weight in the top 10 km of the descending slab is sufficient to recycle the entire ocean volume once over 4.5 billion years at current subduction rates.
H-cycling: Role of Nominally Anhydrous Phases

- **Synthesis Experiments**
  - Olivine
  - Wadsleyite (Spinellloid III)
  - Wadsleyite II (Spinellloid IV)
  - Ringwoodite (Spinel)
  - Pyroxene

- **Structure studies (X-ray, neutron):**
  - Protonation mechanisms
  - Volume of Hydration
H-cycling: Role of Nominally Anhydrous Phases

- Synthesis Experiments
- Effect of H on volume and density
- Effects of H on Transition Depths
- Effects of H on elastic properties:
  - Isothermal Bulk Modulus
  - P and S velocities
    - Brillouin
    - Ultrasonic
Nominally Hydrous
- Brucite
- Phase A
- Chondrodite
- Clinohumite

Nominally Anhydrous
- Periclase
- Olivine
- Clinoenstatite
- Stishovite
Olivine $\text{Fo}_{100}$: 12 GPa @ 1250°C (With Clinoenstatite)

$\sim$8000 ppmw $H_2O$
Hydration of Olivine

- Natural olivine contains less than ~0.03 wt % H$_2$O (300 ppm)

- H increases sharply with pressure

- 5000 to ~9000 ppm @ 12 GPa
Hydration of Forsterite@ 12GPa
FTIR results (ppmw H₂O)

<table>
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<th>1100°</th>
<th>1250°</th>
<th>1400°</th>
<th>1600°</th>
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<tr>
<td>Si-XS</td>
<td>5770</td>
<td>8000</td>
<td>3400</td>
<td>1000</td>
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<tr>
<td>Mg-XS</td>
<td>5560</td>
<td>8800</td>
<td>4400</td>
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Hydration of Olivine @ 12GPa

- We observe roughly equivalent amounts in equilibrium with enstatite or clinohumite.
- We observe ~20% more H at 1100°C than previous workers (Kohlstedt et al., 1996).
- We observe ~ 2.5 x more at 1250°C than previous workers at 1100°C.
Hydration of Olivine @ 12GPa

- We observe a measurable effect of hydration on unit cell volume.

- Structure refinements from X-ray single crystal data and FTIR spectra are consistent with M1 site vacancy as the principal hydration mechanism.

\[ 2H^+ \leftrightarrow Mg^{2+} \]
Cell Volume vs H content

Forsterite Vol vs H2O

Cell Volume Å\(^3\)

PPMW H2O
Cell Volume vs H content

Relative molar volume vs H2O

- Olivine
- Wadsleyite
- Ringwoodite

H2O (ppmw)

Relative molar volume

Linear (Wadsleyite)
Linear (Ringwoodite)
Linear (Olivine)
Hydration of Olivine @ 12GPa

- \( V (\text{Å}^3) = 290.107 + 5.5 \times 10^{-5} \times H_2O \)
  - \( (\partial V / \partial H) \)
  - \( H = \text{ppmw} \ H_2O \)

- 8000 ppmw \( H_2O \) in olivine has same effect on STP density as \( \sim 400^\circ C \) temperature rise.

- **Hydration is the third state variable in the equation of state of mantle minerals.**
Compression Experiment
Diamond Anvil Cell
Single-crystal X-ray Diffraction
2 Olivines with quartz in DAC @ 4.4 GPa
**Volume Compression**

- **Mg-Excess**
  - 8000 ppmw H₂O
  - $K_0 = 120$ GPa
  - $K' = 7.0$

- **Si-Excess**
  - 5000 ppmw H₂O
  - $K_0 = 122$ GPa
  - $K' = 5.8$

- **Dry Olivine**
  - $K_0 = 129$ GPa
  - $K' = \sim 5$
Isothermal Bulk Modulus vs H content

Effect of H on Bulk Modulus

- Ringwoodite
- Wadsleyite
- Olivine

Water Content: wt % H2O

Bulk Modulus: GPa
Hydration of Olivine

Effect of Temperature:
– Maximum $H$ at $\sim 1250^\circ C$
– decreases above $1250^\circ$ due to melting

• Effect of Pressure:
– Increases with pressure to 12 GPa (410km)

• Effect of Silica Activity:
– Minimal effect if any
Hydration of Olivine

- $H$ becomes compatible at $P > 10$ GPa
- Hydration causes increase in cell volume.
- Hydration causes decreased bulk modulus and seismic velocities.
Earth’s Deep Water Cycle

- Pressure strongly stabilizes H in cation vacancies.
- Decreases K and hence $-V_p$ and $V_s$ (no measurements on olivine).
- In ringwoodite, the effect of hydration on velocity is larger than effect of temperature!
- Hydration increases $V_p/V_s$
Below 200km $H$ is captured by olivine in the overlying mantle wedge.

$H$ softens the olivine allowing it to lubricate the descent of the cold slab.

$H$ is thus effectively entrained in the descending slab.
Interior Reservoir?

- Nominally Anhydrous Minerals (NAMs) can incorporate up to 9 times the total Ocean mass if saturated.
Water: The Third State Variable in Mantle Dynamics
A hydrous TZ should be thick and slow.
Lateral Velocity Variations in TZ May Reflect Hydration

- Red means Wet
- Blue means Dry
Hydration of Wadsleyite and Ringwoodite is more consistent with model shear velocity structure.
Upcoming Sessions on Water in the Deep Earth:

Fall AGU, San Francisco
“Effect of Hydration on Physical Properties of Mantle Minerals”

MSA Short Course
“Water in Nominally Anhydrous Minerals”

Verbania, Italy October, 2006
Reprints and preprints at

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