Geophysical and Mineralogical Constraints on H-Cycling in the Deep Interior

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How Much Water Is There?

- Oceans cover 71% of the planet’s surface.
- The mass of the oceans is only 0.025% of the planet.
H-cycling in the Deep Earth

• There has been running water (implying oceans) as far back as we can see in geologic time.
• Water fluxes melting at ridges.
  – MORBs contain 0.1 to 0.3 wt % H₂O
  – OIBs contain 0.6 to 1.0 wt % H₂O
H-cycling in the Deep Earth

- Water fluxes melting at ridges.
  - MORBs contain 0.1 to 0.3 wt % $\text{H}_2\text{O}$
  - OIBs contain 0.6 to 1.0 wt % $\text{H}_2\text{O}$
- Plates hydrate on ocean floor.
- Plates dehydrate on subduction.
  - Completely?
Dry Wadsleyite and Ringwoodite are too fast to be consistent with PREM model for olivine-rich upper mantle.
H-Cycling: Role of Nominally Anhydrous Phases

- Natural Samples
  - Eclogites and Peridotites
- Synthesis Experiments
  - Olivine, Wadsleyite, Wads II, Ringwoodite
- Effects on Transition Depths
- Effects on P and S velocities
- Isotope Effects
H-Cycling: Natural Samples: Eclogites

- Garnet: not much H
  - $\text{H}_4\text{O}_4$ tetrahedron large
  - Inhibited by pressure

- Clinopyroxene
  - $\text{HAlSi}_2\text{O}_6$ (hydro-jadeite)
  - 1000 ppm $\text{H}_2\text{O}$ by weight @ 4GPa
  - $>5000$ ppm at 10GPa
2 HAISi$_2$O$_6$ ->
H$_2$O + Al$_2$SiO$_5$ + SiO$_2$
H-Cycling: Natural Samples

- Nominally anhydrous minerals in eclogite can carry 2000 ppm or more
- Olivine can incorporate 2000 ppm
- 1000 ppm in crustal portion of slab can recycle the ocean volume in 4.5 Gy (at current subduction rates).
- Ocean volume may have exchanged more than once.
H-Cycling:
Natural Samples: Peridotites

- Olivine: natural samples typically < 200 ppm H$_2$O
- Olivine can incorporate > 2000 ppm H$_2$O @ P > 10GPa
- Loses H$_2$O quickly on decompression
Synthesis Experiments:
5000 ton Multi-anvil Press,
BGI Bayreuth
H-Cycling: Synthesis Experiments

- Synthesis
- Characterization
  - XRD single crystal
  - TEM
  - IR / Raman
  - Mössbauer
- Property Measurements
  - Isothermal Compression
  - Ultrasonic Vp and Vs

- Olivine
- Wadsleyite
- Wadsleyite II
- Ringwoodite
Dry Peridotite (after Zhang & Herzberg, 1994)

- Olivine
- Wadsleyite
- Wadsleyite II
- Ringwoodite
Hydration of Olivine: Summary

- Olivine accepts up to 0.2 wt % H$_2$O at 12GPa (Kohlstedt et al, 1996)
- Hydration causes measurable volume expansion
- Hydration appears to involve divalent cation vacancies principally at M2.
- Hydration may cause decreased bulk modulus and seismic velocities.
- H partitions strongly to wadsleyite.
Hydrous Wadsleyite

- $1.6[\text{MgO}] \cdot 0.2[\text{Mg(OH)}_2] \cdot 1[\text{SiO}_2]$
- Up to 0.4 H pfu
- H on non-silicate oxygens
- $\text{Si}/(\text{Mg+Fe}) = 0.5$
- $\rho = 3.36 \text{ g/cm}^3$
- 3.0% H$_2$O by weight
- 10 % H$_2$O by volume
Wadsleyite II (Spinelloid IV)

- 1.6[MgO]•0.2[Mg(OH)₂]•1[SiO₂]
- May occur between wadsleyite and ringwoodite (17.5 GPa @ 1400 °C)
- May require Fe³⁺, Cr or Al
- May obscure 520km discontinuity
Ringwoodite Composition

- \((\gamma\text{-Mg}_{1.63}\text{Fe}_{0.22}\text{H}_{0.4}\text{Si}_{0.95}\text{O}_4)\)
- ~10 % of Fe present as ferric (Mössbauer)
- Dark blue color
Ringwoodite with Quartz @ 11 Gpa
Ringwoodite Isothermal Compression to 11 GPa

Ringwoodite cell volume vs pressure

![Graph showing the relationship between unit cell volume (Å³) and pressure (GPa). The volume decreases as pressure increases, indicating compression.]
Ringwoodite Isothermal Compression to 11 GPa

- $F_{o_{90}}$ with 10,000 ppm $H_2O$
- $K_T = 169.0 \pm 3.4$ GPa
- $K' = 7.9 \pm 0.9$
- One Percent $H_2O$ in Ringwoodite
  - $= 600^\circ C$ on $K_T$
Ringwoodite Ultrasonics  
(Jacobsen et al BGI)

• P and S velocity measurements:
  – Ghz Interferometry in Single Xtls
  – $V_p = 9690 - 0.042 \, C_{H_2O} \, (m/s)$
  – $V_s = 5680 - 0.036 \, C_{H_2O} \, (m/s)$
  – $C_{H_2O} = \text{ppm (wt)} \, H_2O$

• One Percent $H_2O$ in Ringwoodite
  – = 600$^\circ$C on $V_p$ (at Low P) (~4%)
  – = 1000$^\circ$C on $V_s$ (at Low P) (~6%)
Hydration of Wadsleyite and Ringwoodite is more consistent with model shear velocity structure.
Lateral Velocity Variations in TZ May Reflect Hydration

- Red means Wet
- Blue means Dry
Blue = Dry;

Red = Wet

Dry

Wet

Cool

Hot
Deuterium/Hydrogen ratios in the Solar System

- Estimated protosolar: $\sim 2 \times 10^{-5}$
- Earth: $1.5 \times 10^{-4}$ (SMOW)
- Mars: $\sim 8 \times 10^{-4}$
- Venus: $\sim 2 \times 10^{-2}$
- Jupiter and Saturn: $\sim 2 - 2.5 \times 10^{-5}$
- Neptune: $\sim 6 \times 10^{-5}$
- Comets, asteroids, interstellar dust: $\text{???}$
D/H Fractionation of Mantle Minerals Relative to Phlogopite (after Bell and Ihinger, 2000). Fractionation increases with Pressure.
D-H fractionation increases with pressure

- High pressure phases prefer H
- Water returned to surface is D-enriched.
- The TZ nominally anhydrous silicates are big, but not sufficient to hold the missing light H.
- If Earth were Proto-solar in value there would be a huge reservoir of light H in the interior.
- Lower mantle or core
Are the oceans just the tip of the iceberg?