Melting, deep earth water and carbon

Marc Hirschmann
U. Minnesota
Oceans: 80%
Mantle: 20%

H$_2$O Concentration in Mantle
- Real Oceans: 88 ppm H$_2$O
- Real Oceans + 10%: 1400 ppm H$_2$O
- Real Oceans - 10%: 35% land, 28.5% land, 15% land

Mantle: 20%
- Oceans: 80%

Pie charts showing the distribution of water in the mantle and oceans.
DEEP EARTH CARBON CYCLE

Continental Sediments
5.88

weathering + metamorphism

Oceans
0.0033

accrmination

Oceanic Crust
1.2

pelagic sediments
basalt alteration

Subduction

ridges
1-2.5

Mantle
7-18

Reservoirs ($X \times 10^{21}$ mol/year)
Fluxes ($X \times 10^{12}$ mol/year)

Simplified after Sleep & Zahnle, 2001
Dasgupta and Hirschmann, 2010
Modern Deep Volatile Cycles

(diagram courtesy of J Phipps-Morgan)
Volatile gases in the mantle play a key role in maintenance of Earth’s climate.
Hydrogen in the Exosphere
(Exosphere = everything above the Moho)
(Lecuyer et al. 1998)

<table>
<thead>
<tr>
<th></th>
<th>Grams H₂O</th>
<th>Grams H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oceans</td>
<td>1.4 X 10^{24}</td>
<td>1.56 X 10^{23}</td>
</tr>
<tr>
<td>Other</td>
<td>2 X 10^{23}</td>
<td>2.22 X 10^{22}</td>
</tr>
<tr>
<td>Total</td>
<td>1.6 X 10^{24}</td>
<td>1.78 X 10^{23}</td>
</tr>
<tr>
<td>Exosphere Carbon</td>
<td>Moles (\text{CO}_2)</td>
<td>Grams C</td>
</tr>
<tr>
<td>--------------------------</td>
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<td>------------</td>
</tr>
<tr>
<td>Sleep&amp;Zahnle ‘02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sediments</td>
<td>(5.88 \times 10^{21})</td>
<td>(7.06 \times 10^{22})</td>
</tr>
<tr>
<td>Oceans</td>
<td>(3.31 \times 10^{18})</td>
<td>(3.97 \times 10^{19})</td>
</tr>
<tr>
<td>Oceanic Crust</td>
<td>(1.20 \times 10^{21})</td>
<td>(1.44 \times 10^{22})</td>
</tr>
<tr>
<td>Total</td>
<td>(7.08 \times 10^{21})</td>
<td>(8.50 \times 10^{22})</td>
</tr>
<tr>
<td>Hayes&amp;Waldbauer ‘06</td>
<td>(8.50 \times 10^{21})</td>
<td>(1.02 \times 10^{23})</td>
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<tr>
<td>Holser ‘89</td>
<td>(7.64 \times 10^{21})</td>
<td>(9.17 \times 10^{22})</td>
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<tr>
<td>Average</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(9.29 \pm 0.86 \times 10^{22})</td>
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</tbody>
</table>

H in Exosphere (grams) \(1.78 \times 10^{23}\)
C in Exosphere (grams) \(9.29 \pm 0.86 \times 10^{22}\)

H/C ratio of Exosphere \(1.95 \pm 0.15\)
H/C ratios of principal Geochemical and Cosmochemical Reservoirs

Hirschmann & Dasgupta, 2009
The H/C ratio of the exosphere is higher than the mantle H/C ratio.

H/C ratio of the Mantle: from undegassed basalts

H2O (wt. %)

CO₂/H₂O (mass ratio)

MORB
- Kolbeinsey (Macpherson05)
- Popping Rx (Pineau04)
- Siqueiros (Saal02)
- Axial Seamount JdF (Helo11)

OIB
- North Arch (Dixon97)
- Pitcairn (Aubaud06)
- Society (Aubaud05)
- Réunion (Bureau98)
(dashed lines show values used in Hirschmann & Dasgupta, 2009)
The exosphere carbon reservoir is dominated by continental sediments......

...and so the surface carbon reservoir grows with the continents.

Veizer and Mackenzie, 2004
Oceans 20%
Mantle 80%

H₂O Concentration in Mantle
88 ppm H₂O

Oceans 20%
Mantle 80%

H₂O Concentration in Mantle
1400 ppm H₂O
Asimow and Langmuir, 2003
Saal et al., 2002
MORB and seamount glasses
Easter Microplate

Kingsley et al. 2002
Hirschmann et al. 2009
(there are additional recent data, but they yield similar results)
MORB and seamount glasses
Easter Microplate

Kingsley et al. 2002
**H₂O/Ce constrains the H₂O content of mantle reservoirs**

<table>
<thead>
<tr>
<th>Source</th>
<th>Mantle Reservoir</th>
<th>H₂O/Ce (ppm)</th>
<th>Ce (ppm)</th>
<th>H₂O (ppm)</th>
<th>Oceans/mantle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dixon et al. 2002</td>
<td>DMM</td>
<td>200</td>
<td>0.4</td>
<td>100</td>
<td>0.25</td>
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<tr>
<td>Dixon et al. 2002</td>
<td>Atlantic “FOZO”</td>
<td>250</td>
<td>3</td>
<td>750</td>
<td>2.00</td>
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<tr>
<td>Dixon et al. 2002</td>
<td>Pacific “FOZO”</td>
<td>200</td>
<td>3.8</td>
<td>750</td>
<td>2</td>
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<tr>
<td>Dixon et al. 2002</td>
<td>“Enriched” mantle</td>
<td>&lt;100</td>
<td>4</td>
<td>400</td>
<td>1</td>
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<tr>
<td>Dixon et al. 2001</td>
<td>Hawaiian</td>
<td>167</td>
<td>2.4</td>
<td>400</td>
<td>1</td>
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<tr>
<td>McDonough&amp;Sun 1995</td>
<td>Bulk Silicate Earth</td>
<td>250</td>
<td>1.68</td>
<td>420</td>
<td>1</td>
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<tr>
<td>Workman&amp;Hart, 2005</td>
<td>Avg. DMM</td>
<td>250</td>
<td>0.55</td>
<td>140</td>
<td>0.34</td>
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<tr>
<td>Workman&amp;Hart, 2005</td>
<td>Enriched DMM</td>
<td>250</td>
<td>0.726</td>
<td>180</td>
<td>0.45</td>
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<tr>
<td>Workman&amp;Hart, 2005</td>
<td>Depleted DMM</td>
<td>250</td>
<td>0.421</td>
<td>105</td>
<td>0.26</td>
</tr>
</tbody>
</table>
What is the right proxy for CO$_2$?

Siqueiros Fracture Zone

North Atlantic “popping rocks”

Cartigny et al. 2008
C partitioning experiments
Olivine tholeiite + 4 wt.% CO₂ olivine, cpx, opx, garnet
0.8-3 GPa, 1320-1500 °C
Silicate: $^{13}$C; graphite: $^{12}$C

Rosenthal et al. 2015
Tackley, 2000

Davies, 2002
Depleted Mantle Source:
120±40 ppm H₂O
75±25 ppm CO₂

OIB Mantle Source:
500±200 ppm H₂O
600±200 ppm CO₂
GEM DISCOVERY
POINTS TO SUBTERRANEAN OCEANS

RINGWOODITE
hidden within DIAMOND
FIRST TIME found in Earth

1.5% WEIGHT = WATER

BRAZIL

CRUST (100 km)
UPPER MANTLE (100-410 km)
TRANSITION ZONE (410-660 km)
LOWER MANTLE (660-2925 km)
Ohtani et al. 2014 GRL
Possible Loci of Hydrous Melting in the Mantle
Possible Evidence of Small Degree Melts in the Mantle

Conductive Anomaly at LAB

Naif et al. 2013

Small-volume oceanic seamounts
>16,000 seamounts <1 km high

Kim&Wessel, 2011; Conrad et al. DI33B-2242

Shear wave velocity anomaly at LAB

Kawakatsu et al. 2009

Inclusions in sublithospheric diamonds derived from carbonatite

Bulanova et al. 2010
Asimow and Langmuir, 2003
For a given bulk mantle H$_2$O content, how much H$_2$O can be in the melt?

*Answer: Mineral/Melt partition coefficients*

For a given melt H$_2$O content, how much is melt stabilized relative to dry conditions?

*Answer: Experiments defining the relationship between H$_2$O content and melt fraction*
\[ D_{\text{mantle/melt}} = 0.01 \]
Hirschmann et al. 2009


Sub-solidus Pyroxene $\text{Al}_2\text{O}_3$

Abundances along a ridge adiabat

For a given bulk mantle H$_2$O content, how much H$_2$O can be in the melt?

*Answer: Mineral/Melt partition coefficients*

For a given melt H$_2$O content, how much is melt stabilized relative to dry conditions?

*Answer: Experiments defining the relationship between H$_2$O content and melt fraction*
\[
T = \frac{T_{\text{fusion peridotite}}}{\left(1 - \frac{R}{\Delta S_{\text{fusion peridotite}}} \ln\left(1 - X_{\text{melt OH}^{-}}\right)\right)}
\]

H$_2$O Storage Capacity Experiments  
5-13 GPa

Tenner et al. 2012  
Ardia et al. 2013
Dasgupta+ Hirschmann, 2006
Experimental determination of enhanced peridotite melting owing to CO$_2$. 

Dasgupta et al. 2007
CO\textsubscript{2} has a smaller freezing-point effect than H\textsubscript{2}O...

...but is much more enriched in near-solidus melts.
At some depth, carbonate-rich melts become unstable and are replaced by reduced solid or liquid C-rich phases.
Lithospheric Age (Ma)
Plate Model (Stein&Stein, 1992)

No Melt Present

Carbonatite

Silicate Melt Present

Carbonatite Melt Present

Depleted Mantle

100 ppm H$_2$O

60 ppm CO$_2$

Hirschmann, 2010
This is based on the *assumption* that $H_2O$ stabilizes silicate melt relative to carbonatite. This needs to be tested experimentally.
If CO$_2$-rich melts are highly efficient at extracting H$_2$O from minerals
What if Peridotite+$\text{H}_2\text{O}+\text{CO}_2$ is not simply additive from Peridotite+$\text{H}_2\text{O}$ and peridotite+$\text{CO}_2$?
Effect of CO$_2$ on H$_2$O storage capacity in olivine:
6 GPa, 1400 °C, 1-4 hours

- Grow big olivines
- Mitigate H$_2$O, Fe Loss
- Control molar CO$_2$/(H$_2$O+CO$_2$) = $X$(CO$_2$)
Effect of CO$_2$ on H$_2$O storage capacity in olivine

$X$(CO$_2$) = 0

Olivine (Fo91), opx, grt, silicate melt

Olivine (Fo89), grt, carbonated silicate melt
• CO₂ reduces $f_{\text{H}_2\text{O}} \Rightarrow$ reduces $C_{\text{H}_2\text{O}}$ in olivine
• $D$ does not change as a function of $X(\text{CO}_2)$
• Models of Hirschmann (2010) won’t change much