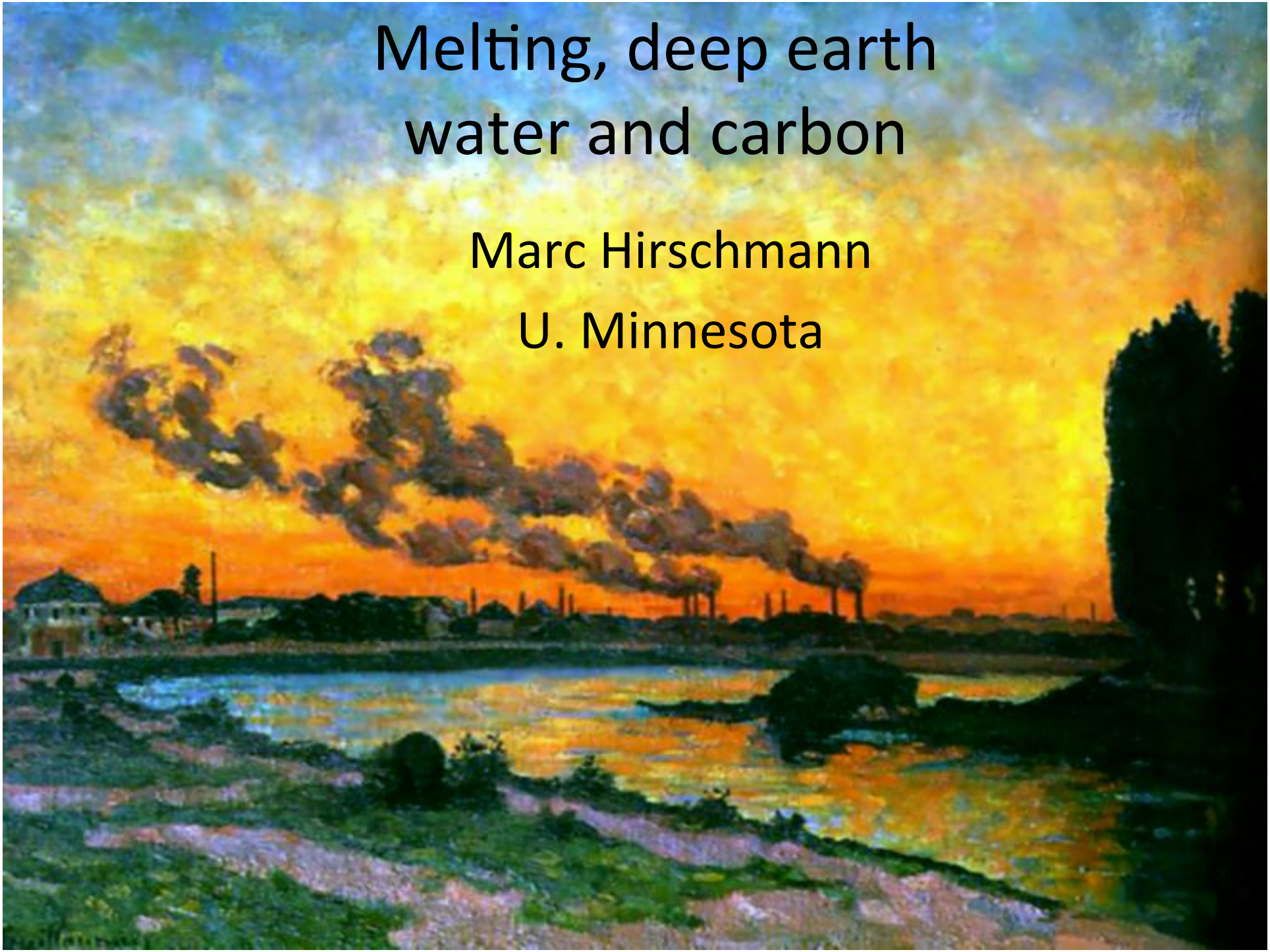
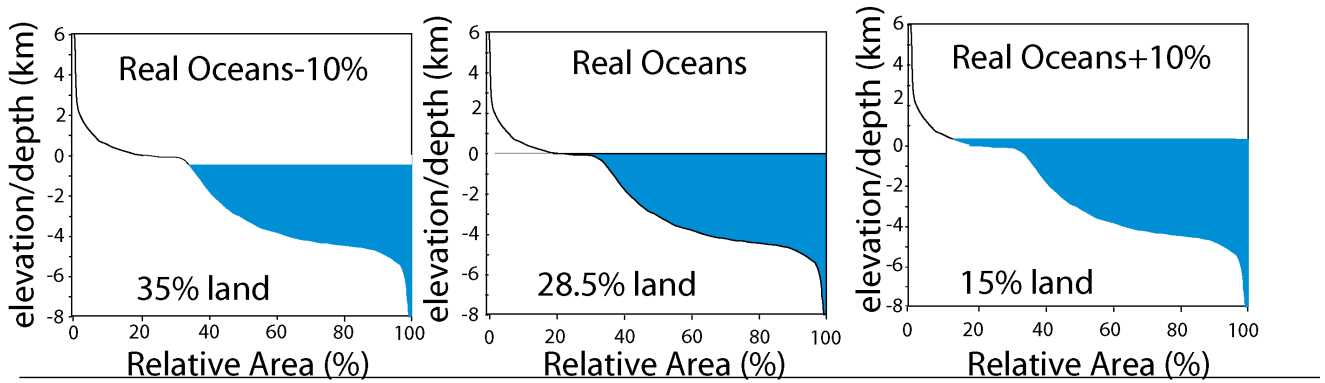
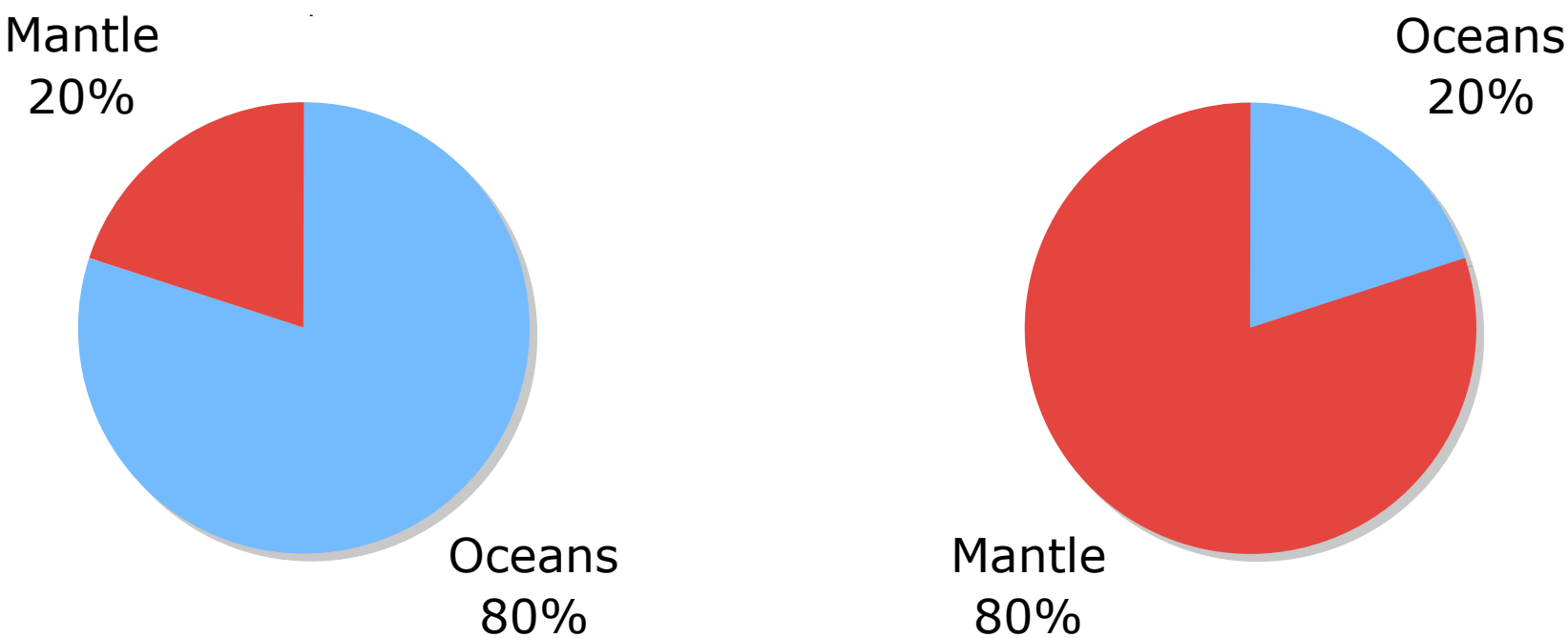
Melting, deep earth water and carbon

Marc Hirschmann

U. Minnesota



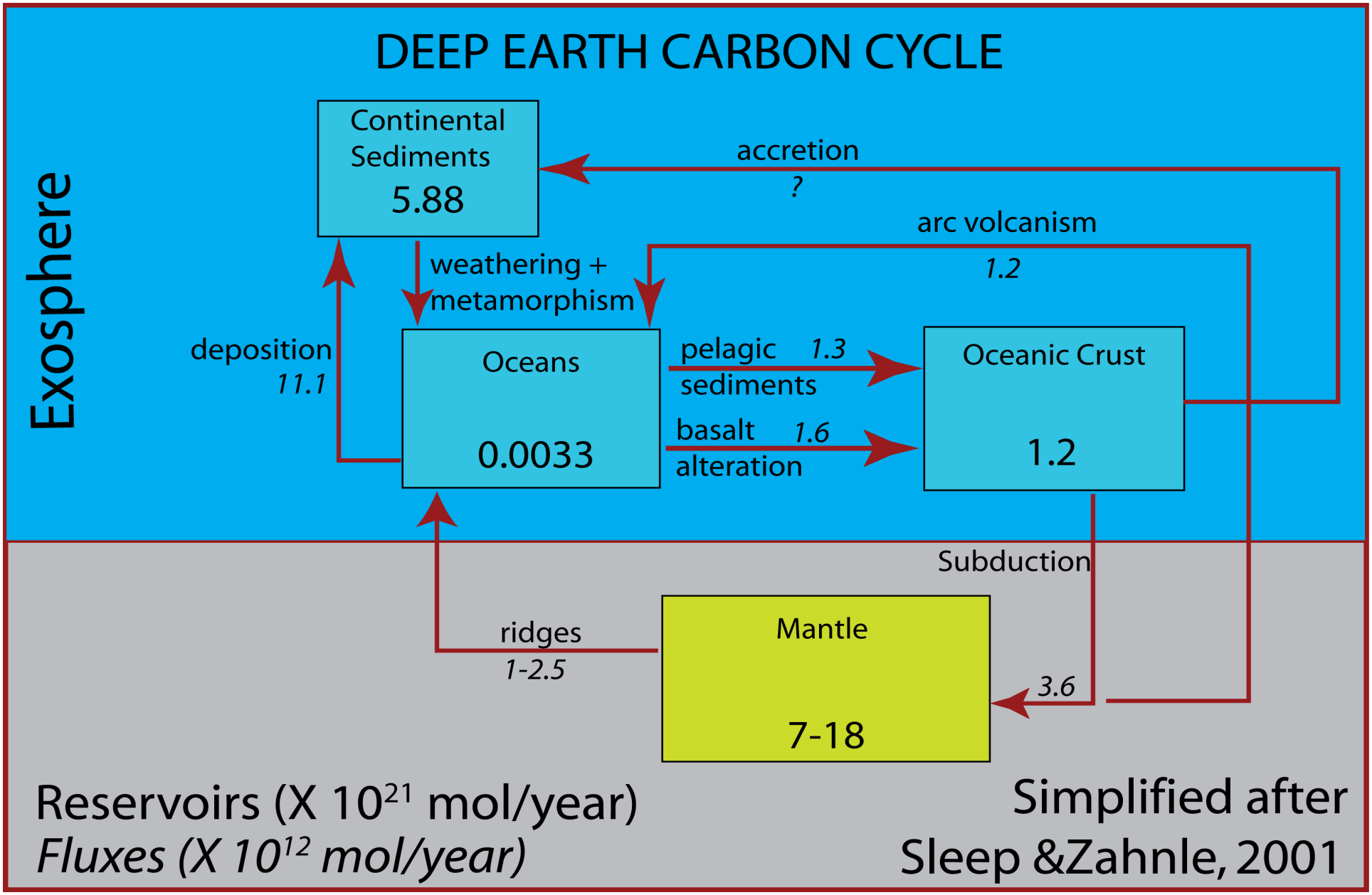


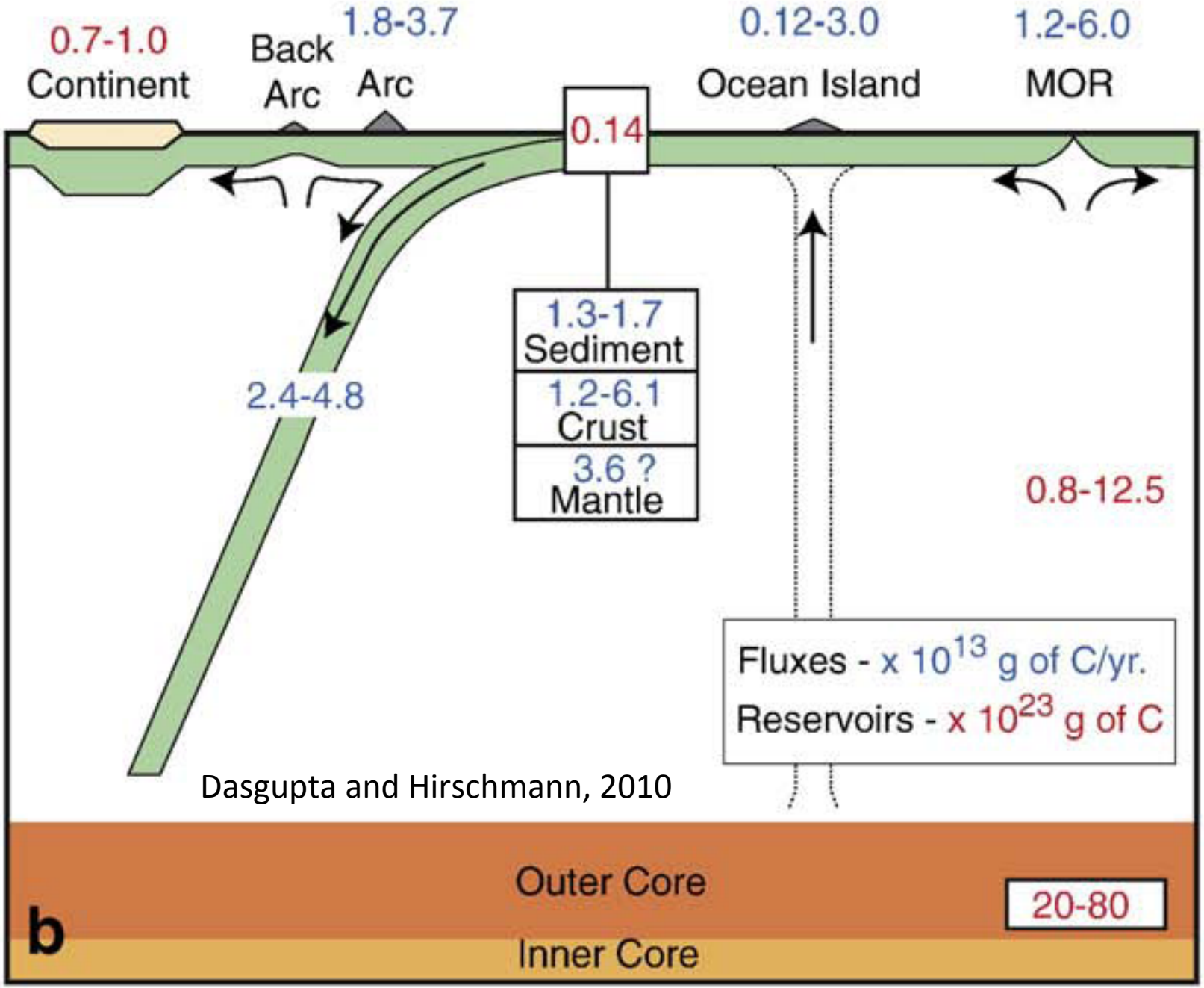


H_2O Concentration in Mantle

88 ppm H_2O

1400 ppm H_2O

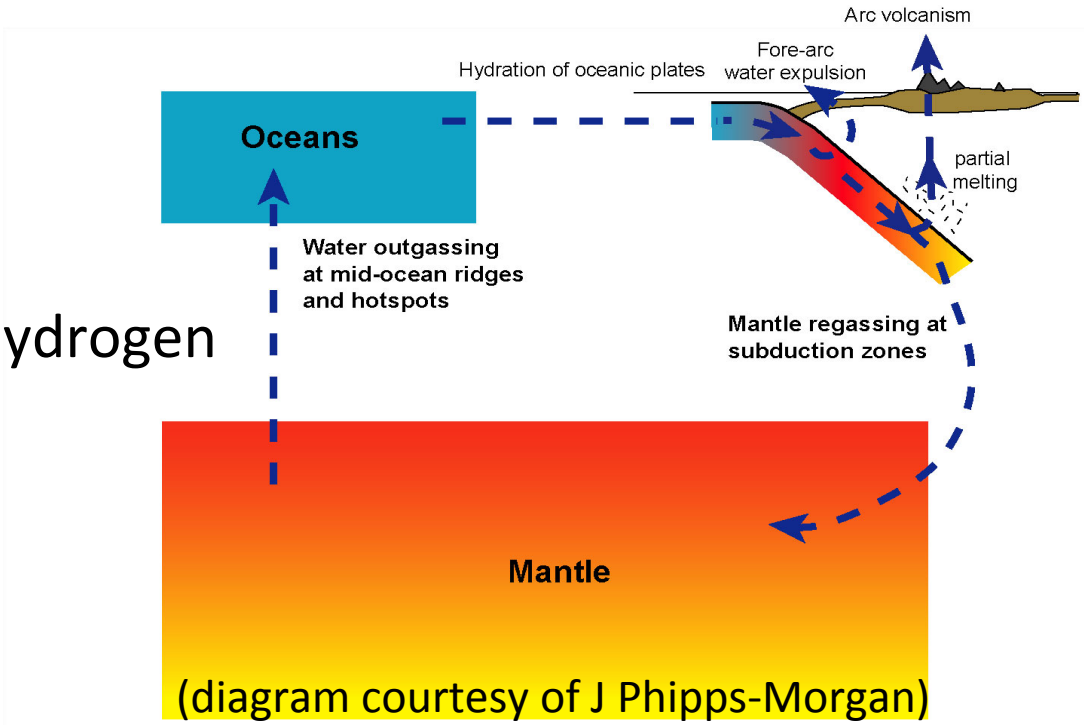

DEEP EARTH CARBON CYCLE
Exosphere
Continental Sediments
5.88
accretion
?
arc volcanism
1.2
weathering + metamorphism
deposition
11.1
Oceans
0.0033
pelagic sediments
1.3
basalt alteration
1.6
Oceanic Crust
1.2
Subduction
ridges
1-2.5
Mantle
7-18
3.6
Reservoirs (X 10^21 mol/year)
Fluxes (X 10^12 mol/year)
Simplified after Sleep &Zahnle, 2001



Dasgupta and Hirschmann, 2010

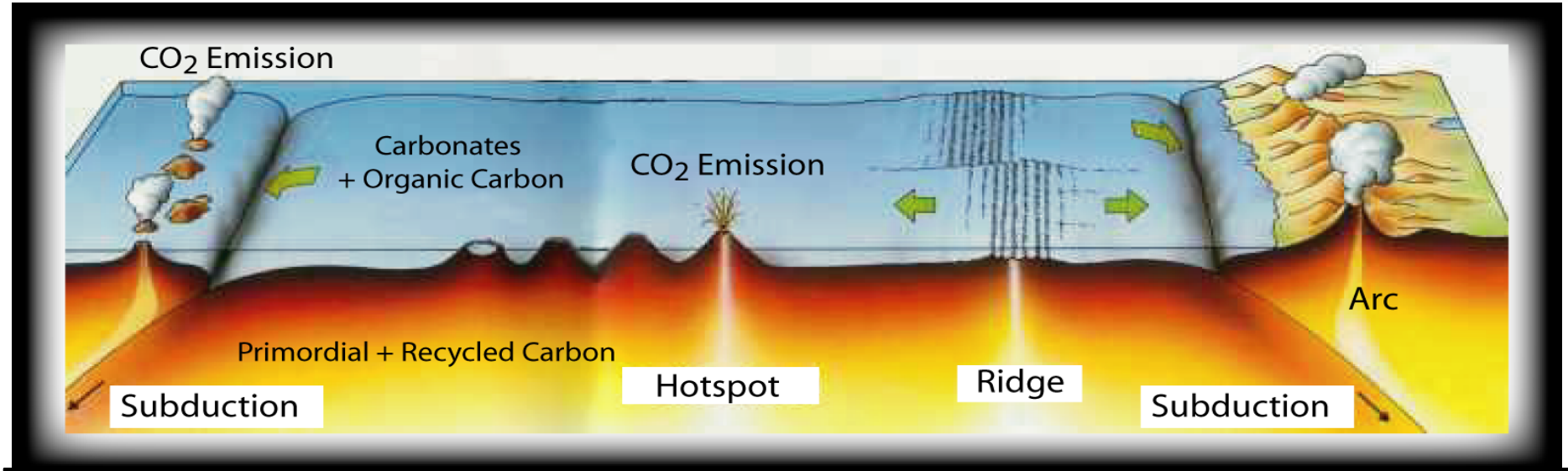
Modern Deep Volatile Cycles

Hydrogen

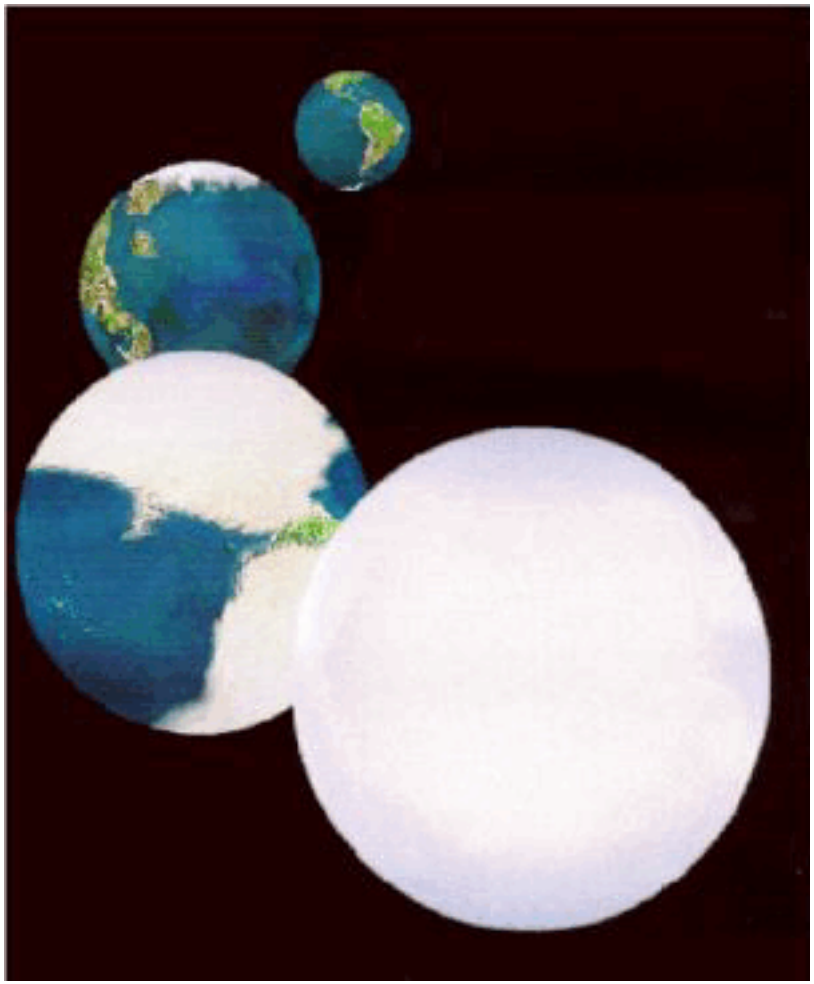


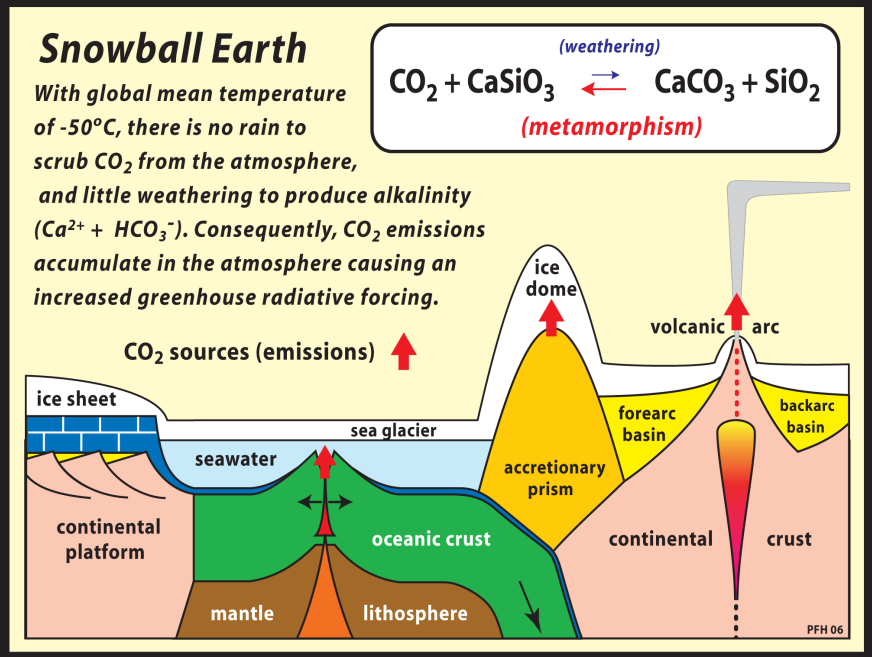
(diagram courtesy of J Phipps-Morgan)

Carbon



Volatiles in the mantle play a key role in maintenance of Earth's climate



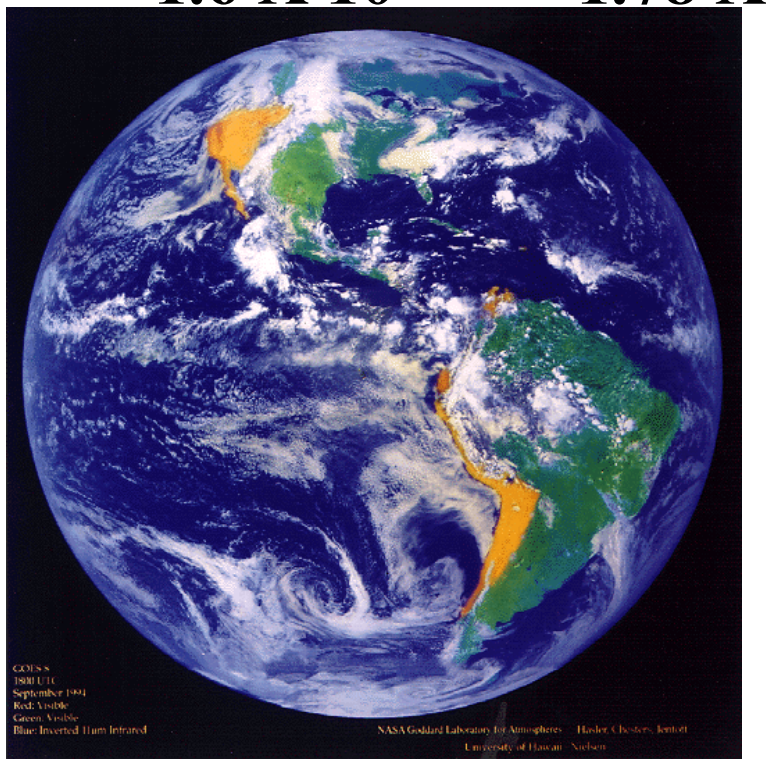


Hydrogen in the Exosphere

(Exosphere=everything above the Moho)

(Lecuyer et al. 1998)

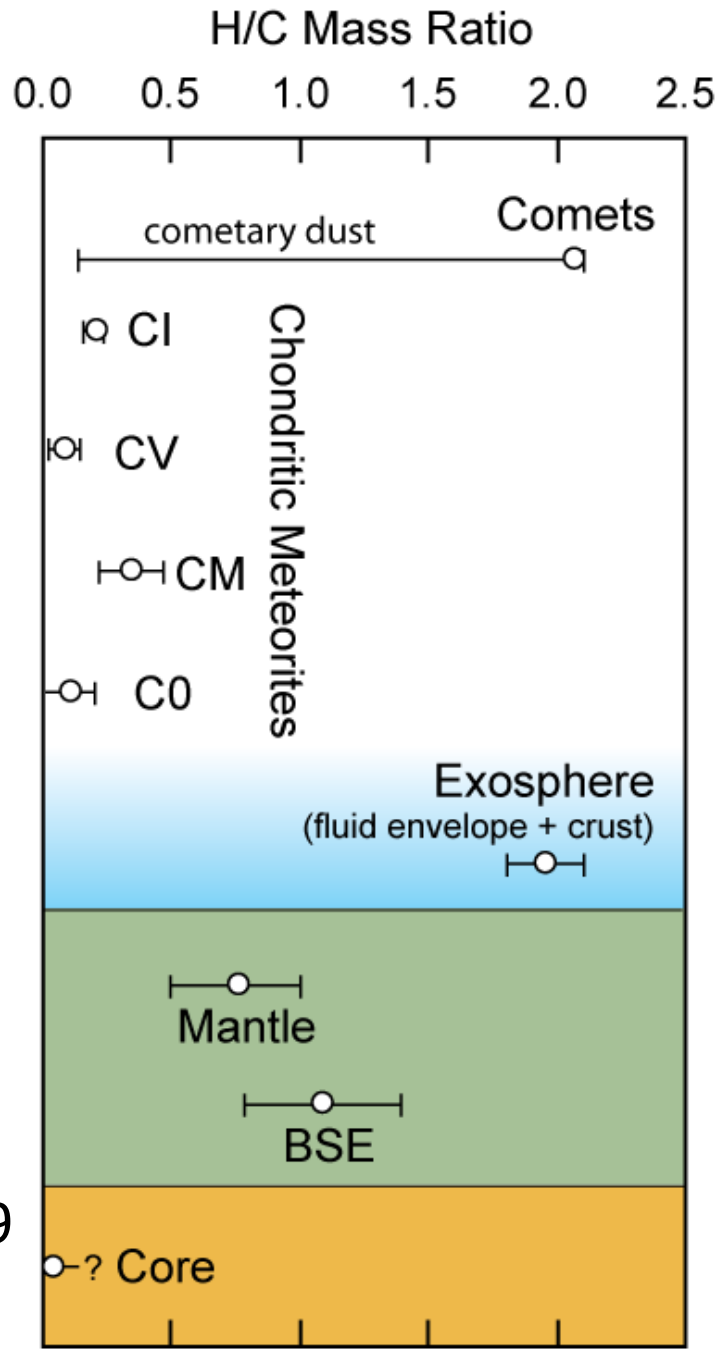
	Grams H_2O	Grams H
Oceans	1.4×10^{24}	1.56×10^{23}
Other	2×10^{23}	2.22×10^{22}
Total	1.6×10^{24}	1.78×10^{23}



Exosphere Carbon	Moles CO_2	Grams C
Sleep&Zahnle '02		
Sediments	5.88×10^{21}	7.06×10^{22}
Oceans	3.31×10^{18}	3.97×10^{19}
Oceanic Crust	1.20×10^{21}	1.44×10^{22}
Total	**7.08×10^{21}**	**8.50×10^{22}**
Hayes&Waldbauer '06	**8.50×10^{21}**	**1.02×10^{23}**
Holser '89	**7.64×10^{21}**	**9.17×10^{22}**
Average		**$9.29 \pm 0.86 \times 10^{22}$**

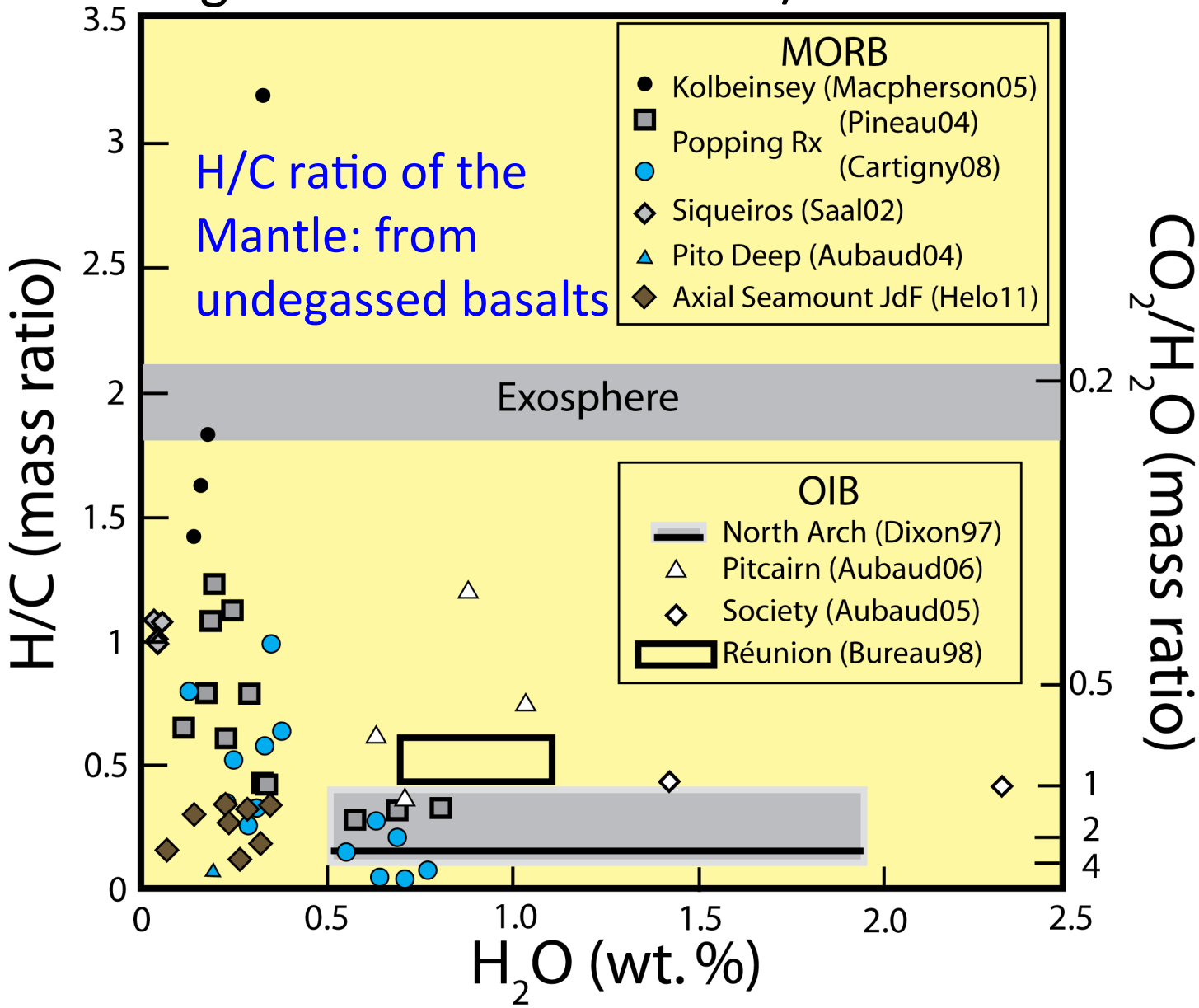
H in Exosphere (grams)	**1.78×10^{23}**
C in Exosphere (grams)	**$9.29 \pm 0.86 \times 10^{22}$**
H/C ratio of Exosphere	**1.95 ± 0.15**

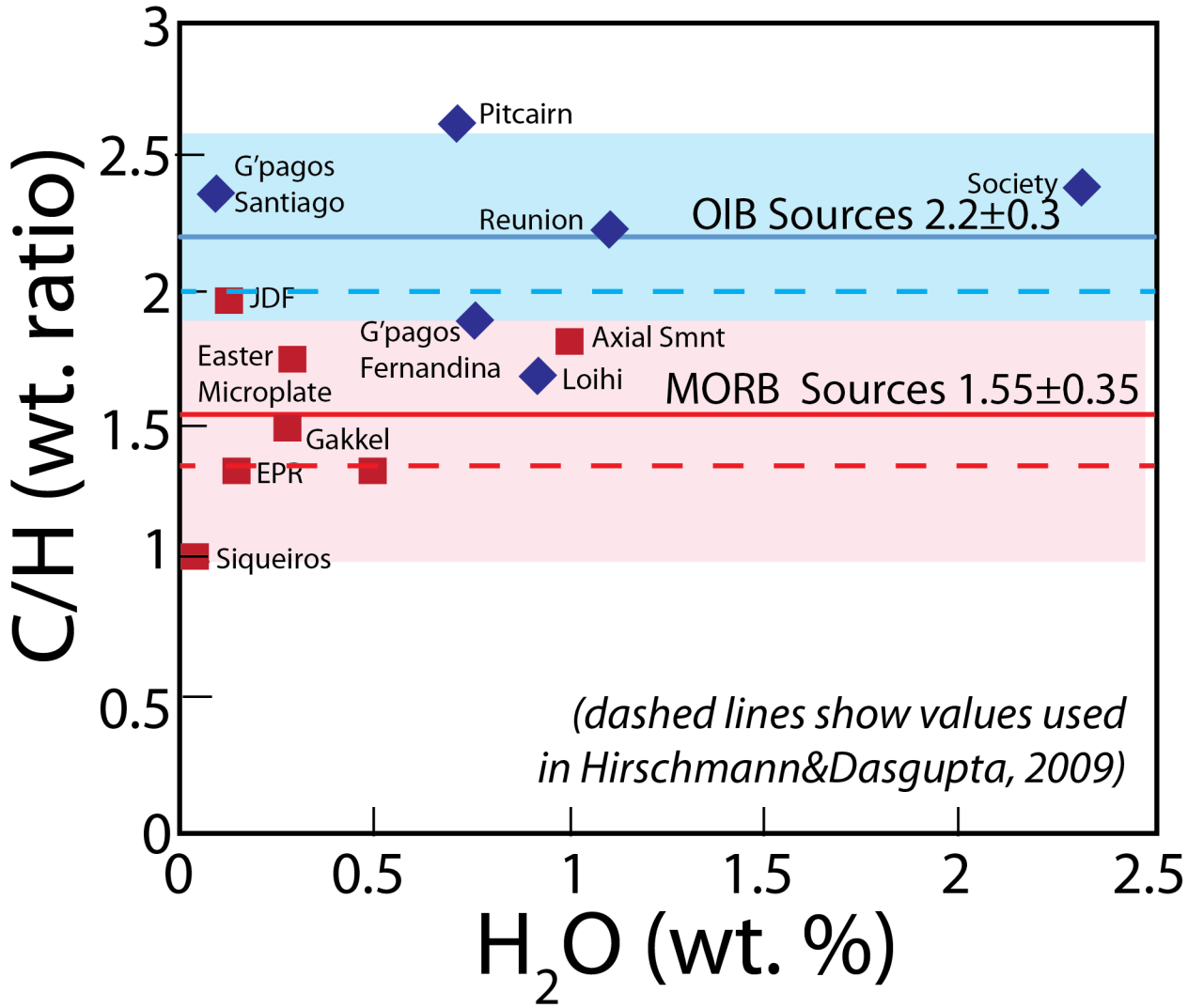
H/C ratios of principal Geochemical and Cosmochemical Reservoirs



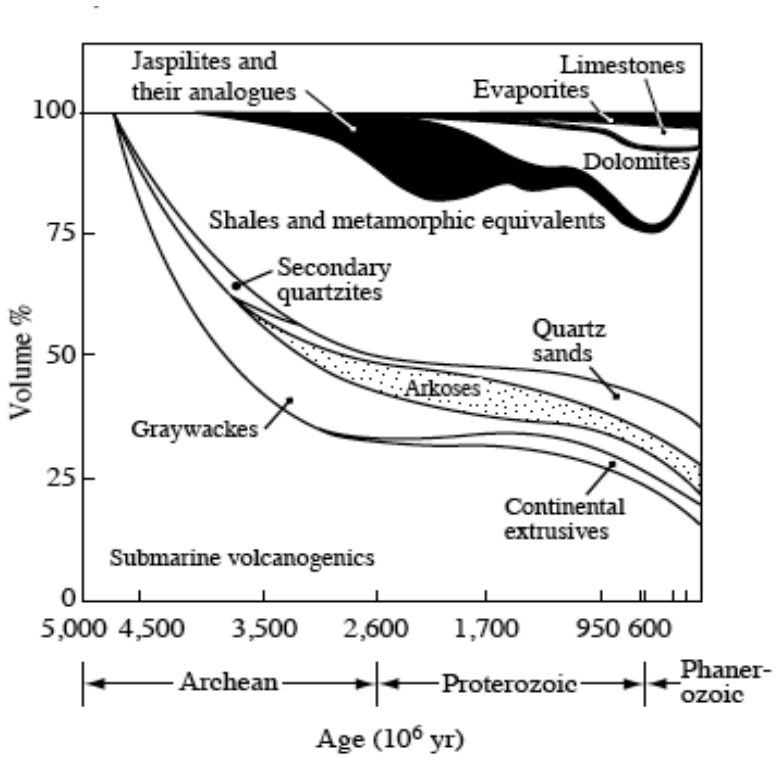
Hirschmann & Dasgupta, 2009

The H/C ratio of the exosphere is higher than the mantle H/C ratio.



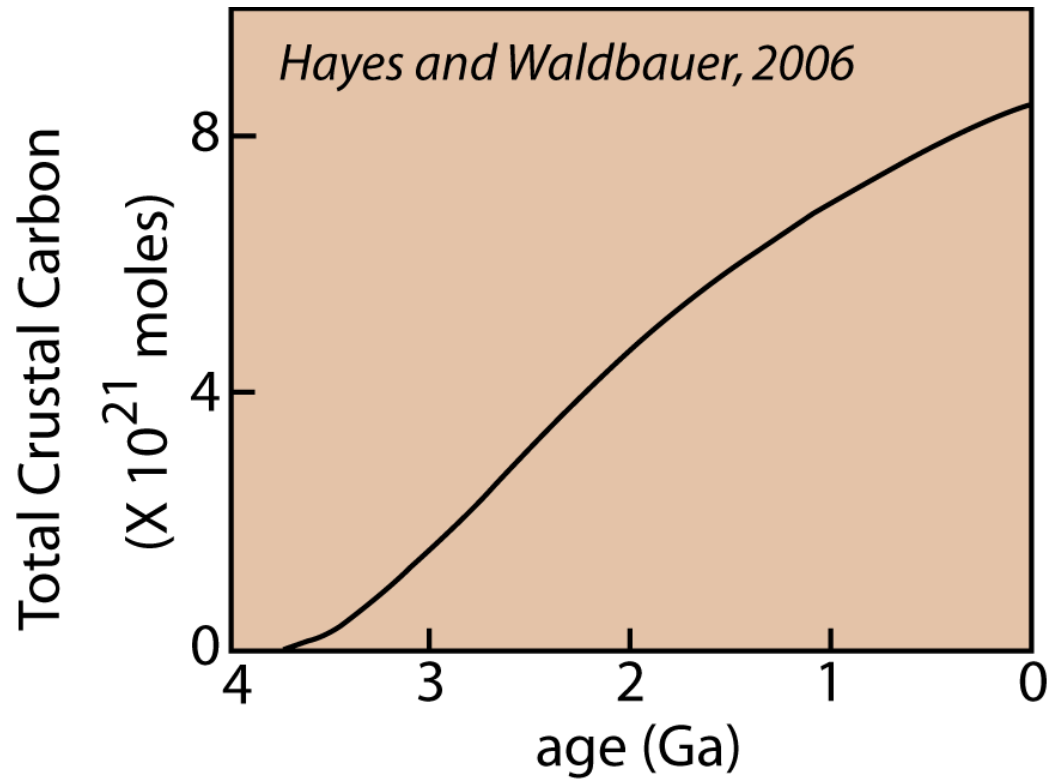

C/H (wt. ratio)
H2O (wt. %)
0
0.5
1
1.5
2
2.5
3
Pitcairn
G'pagos
Santiago
Society
Reunion
OIB Sources 2.2±0.3
JDF
G'pagos
Fernandina
Axial Smnt
Easter
Microplate
Loihi
MORB Sources 1.55±0.35
Gakkel
EPR
Siqueiros
(dashed lines show values used
in Hirschmann&Dasgupta, 2009)

The exosphere carbon reservoir is dominated by continental sediments……

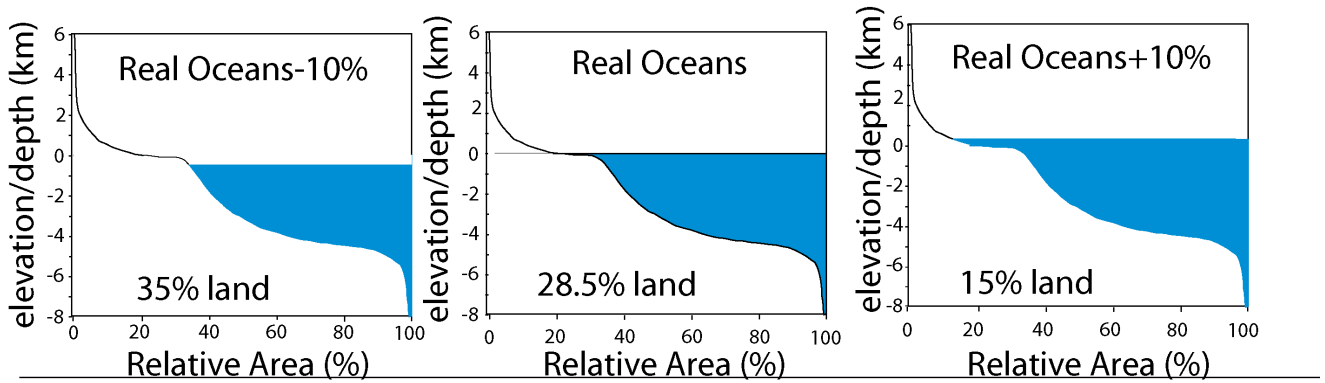


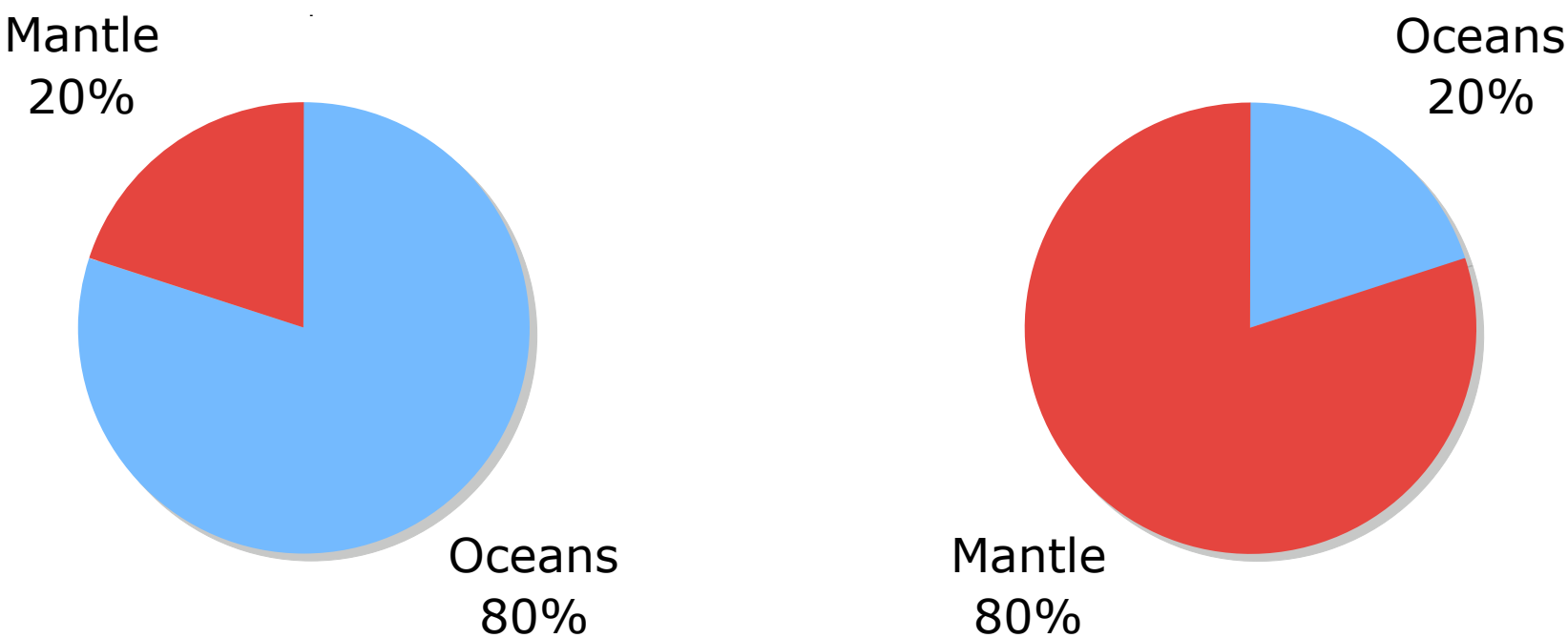
Age distribution of present-day continental sediments

Veizer and Mackenzie, 2004



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

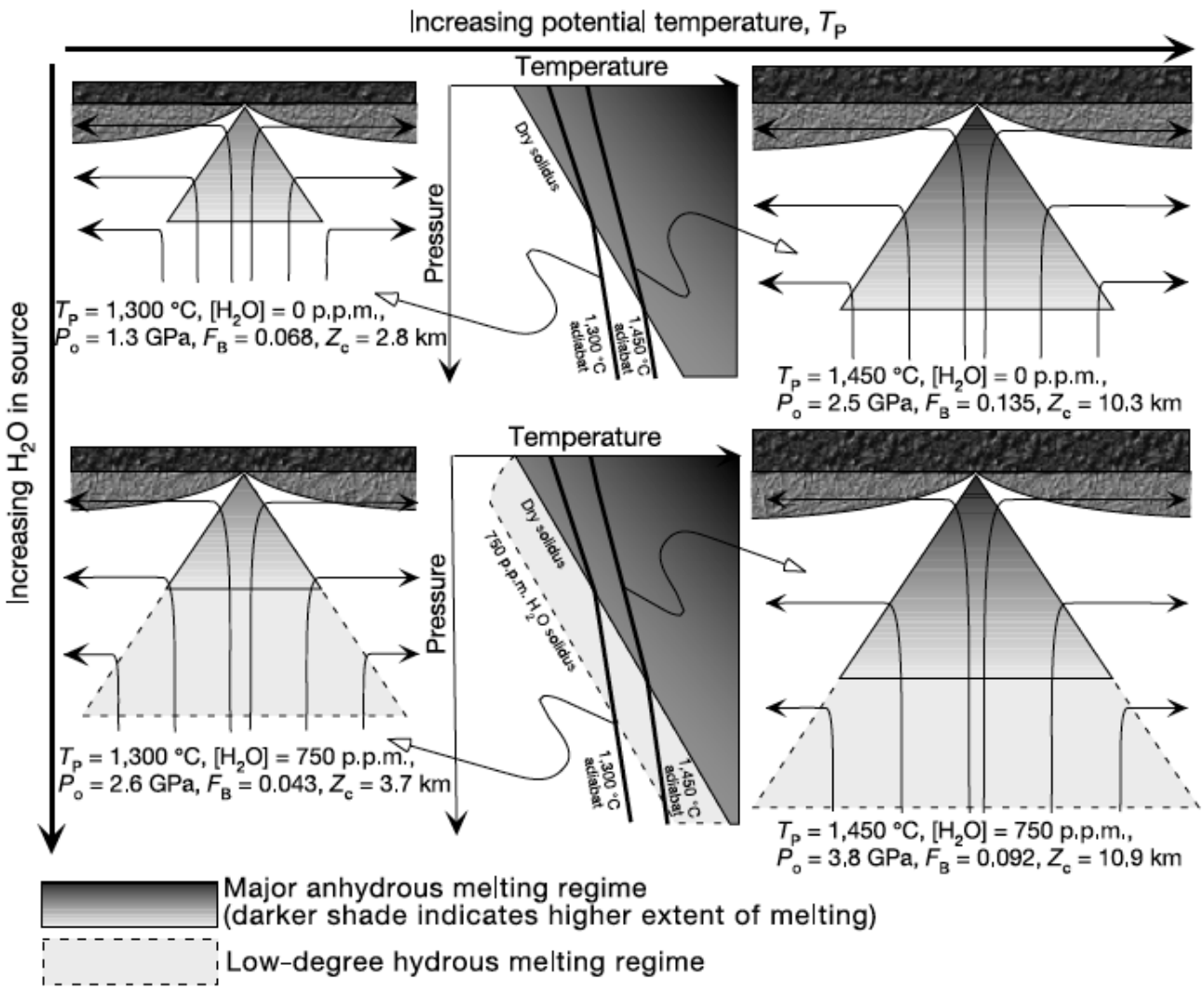




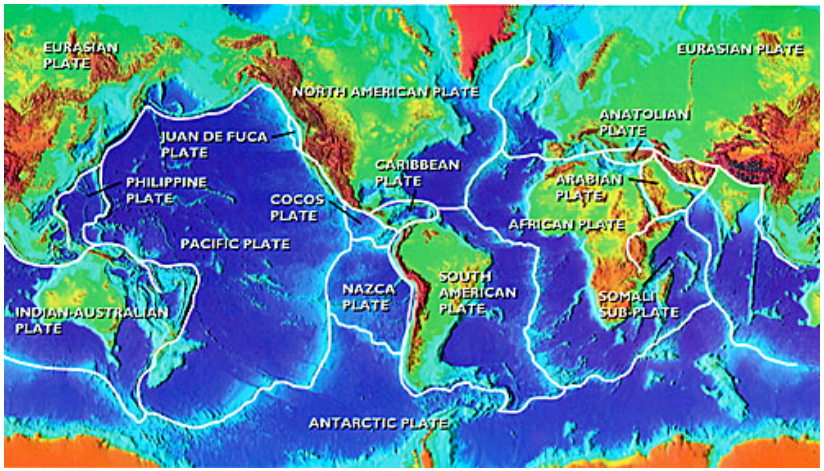
H_2O Concentration in Mantle

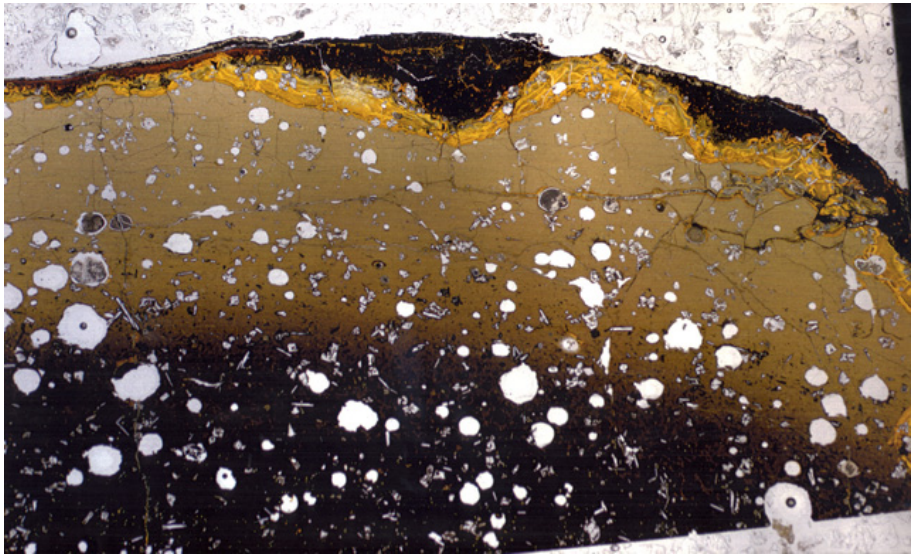
88 ppm H_2O

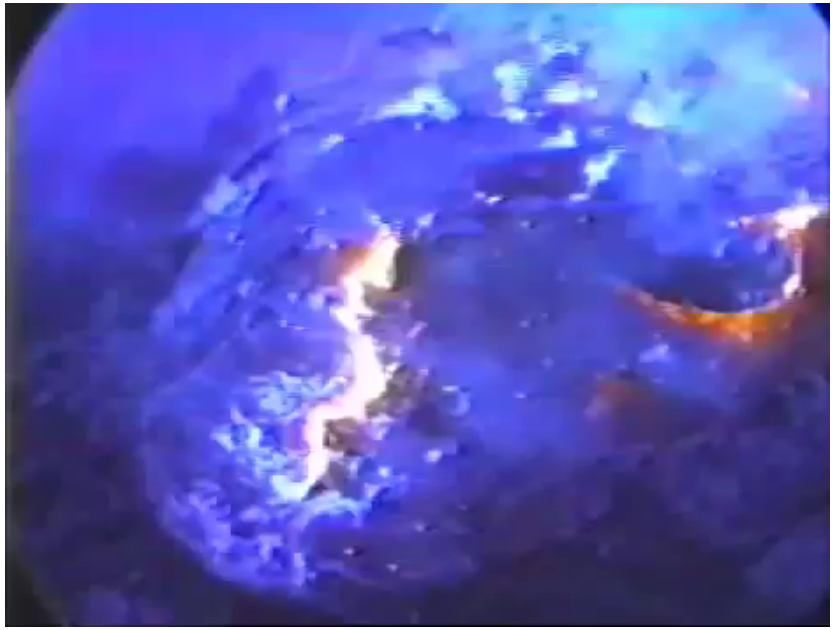
1400 ppm H_2O

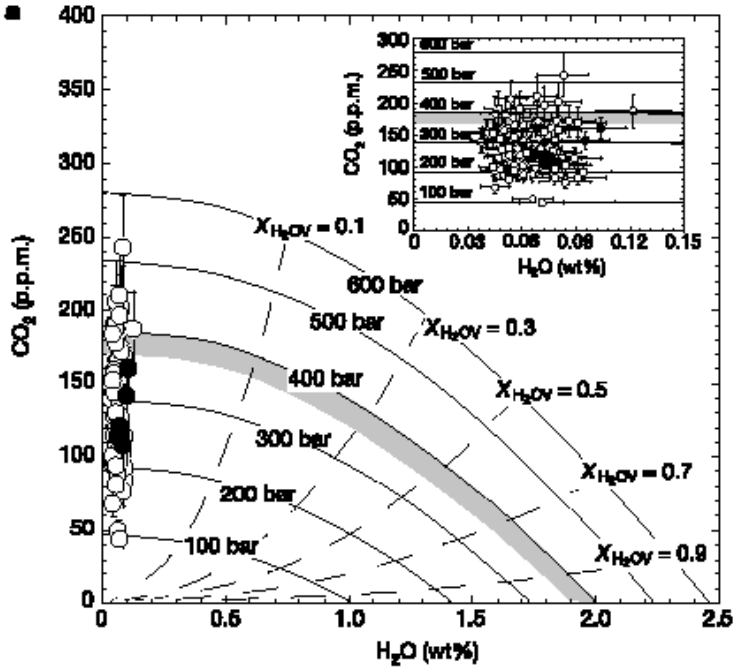


Asimow and Langmuir, 2003

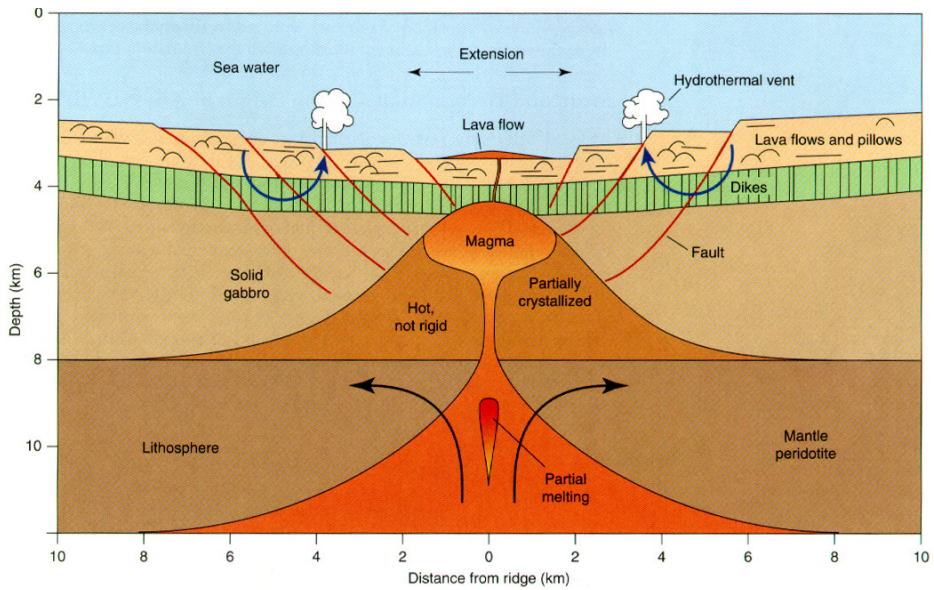




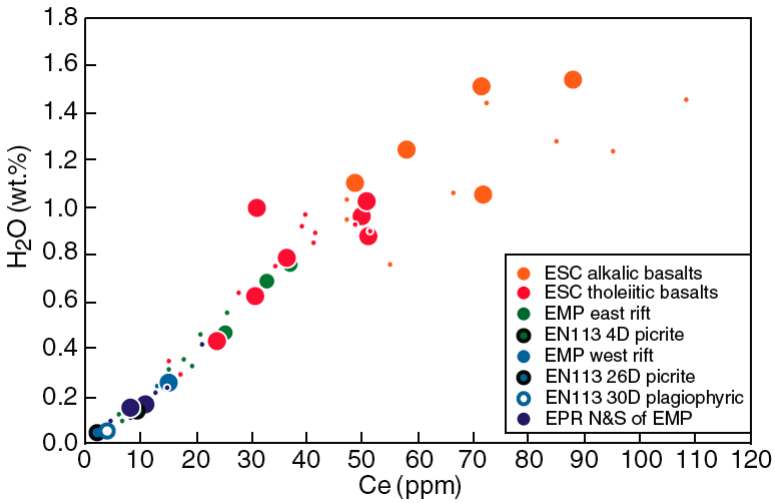




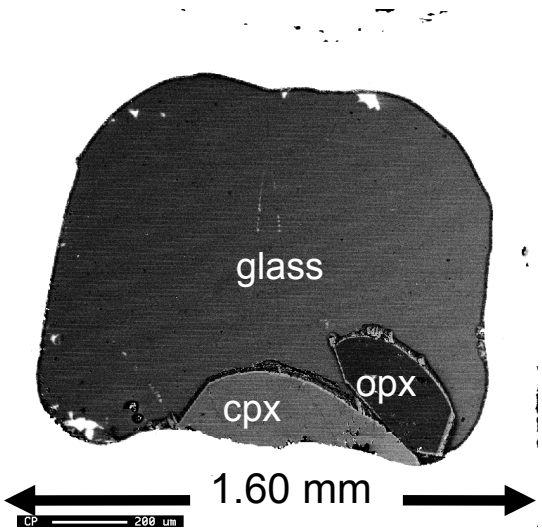
Saal et al., 2002

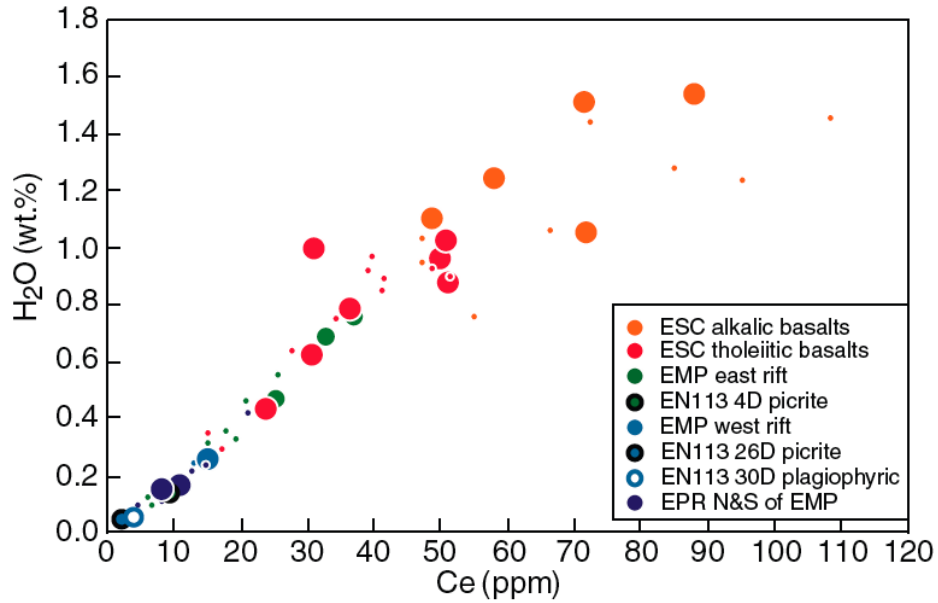


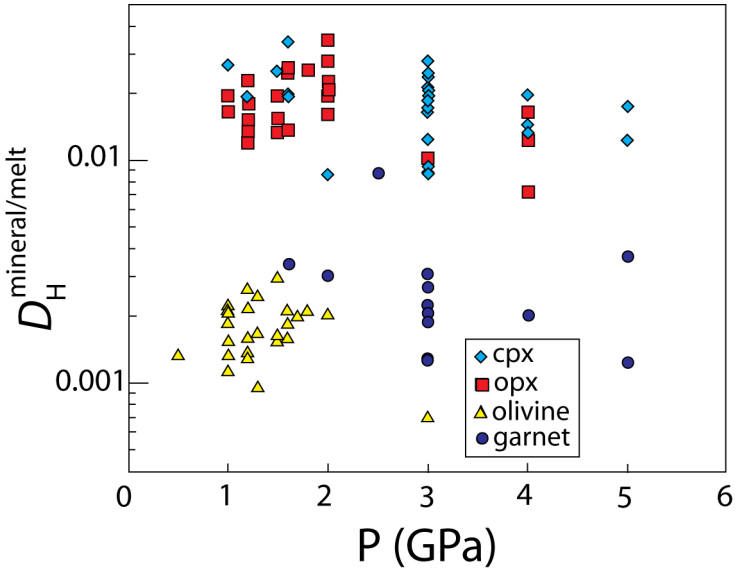
MORB and seamount glasses
Easter Microplate



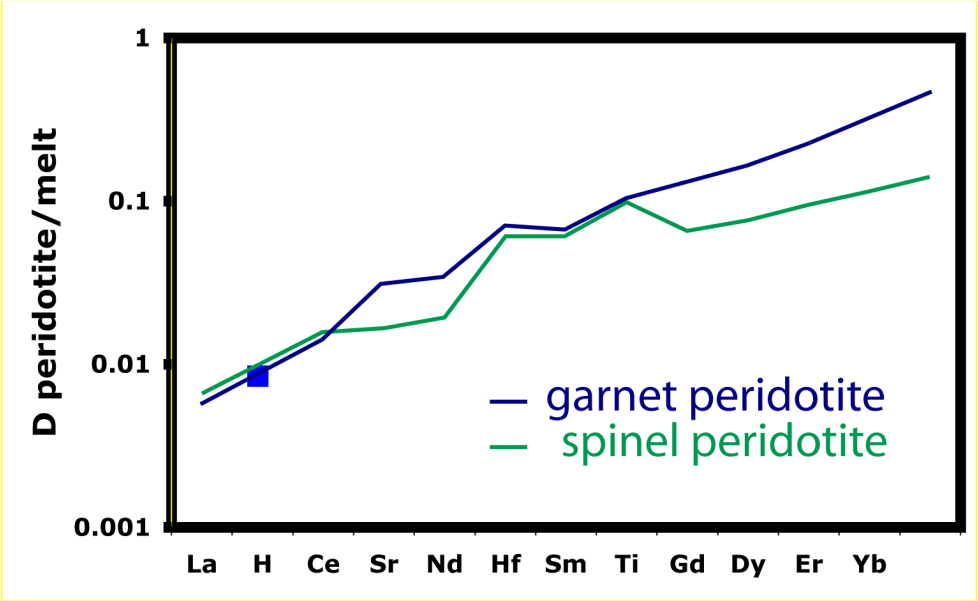
Kingsley et al. 2002



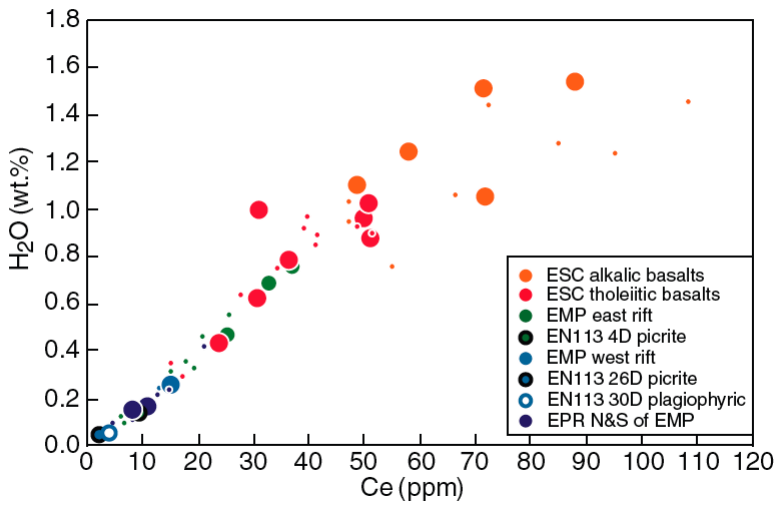




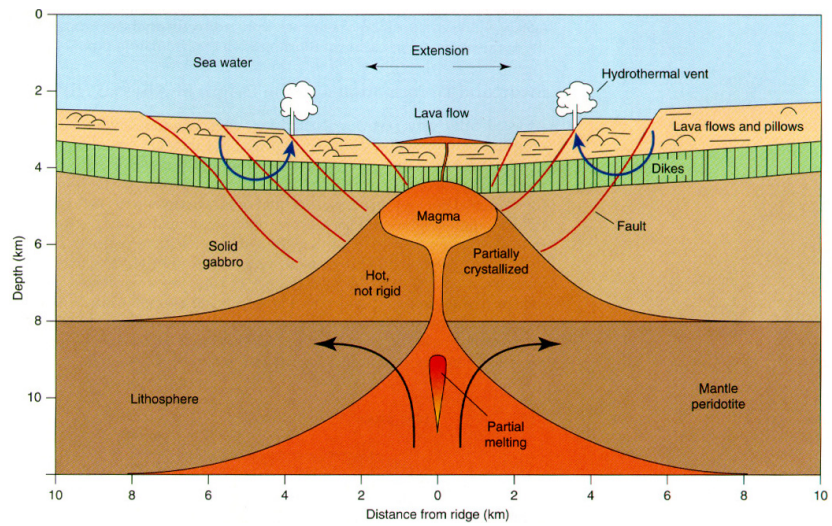
Hirschmann et al. 2009
(there are additional recent data, but they yield similar results)



MORB and seamount glasses
Easter Microplate



Kingsley et al. 2002

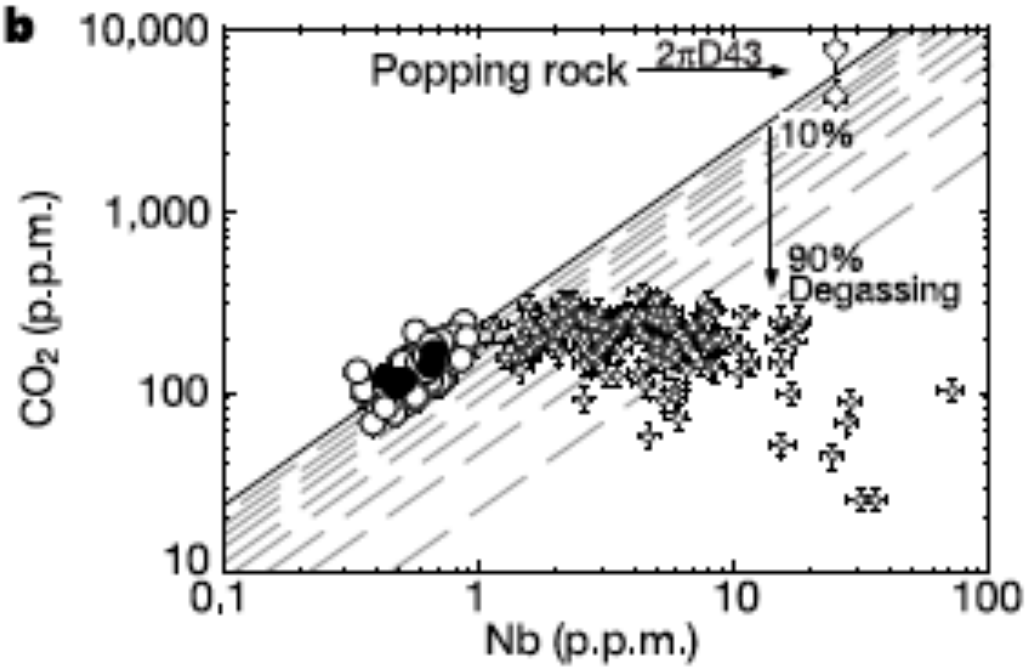


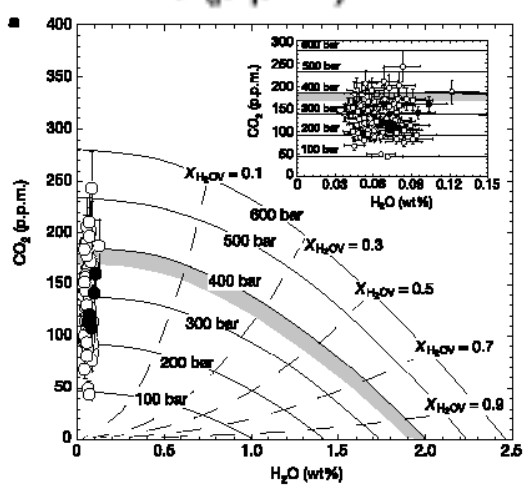
H_2O/Ce constrains the H_2O content of mantle reservoirs

Source	Mantle Reservoir	H_2O/Ce	Ce (ppm)	H_2O (ppm)	Oceans/ mantle
Dixon et al. 2002	DMM	200	0.4	100	0.25
Dixon et al. 2002	Atlantic "FOZO"	250	3	750	2.00
Dixon et al. 2002	Pacific "FOZO"	200	3.8	750	2
Dixon et al. 2002	"Enriched" mantle	<100	4	400	1
Dixon et al. 2001	Hawaiian	167	2.4	400	1
McDonough&Sun 1995	Bulk Silicate Earth	250	1.68	420	1
Workman&Hart, 2005	Avg. DMM	250	0.55	140	0.34
Workman&Hart, 2005	Enriched DMM	250	0.726	180	0.45
Workman&Hart, 2005	Depleted DMM	250	0.421	105	0.26

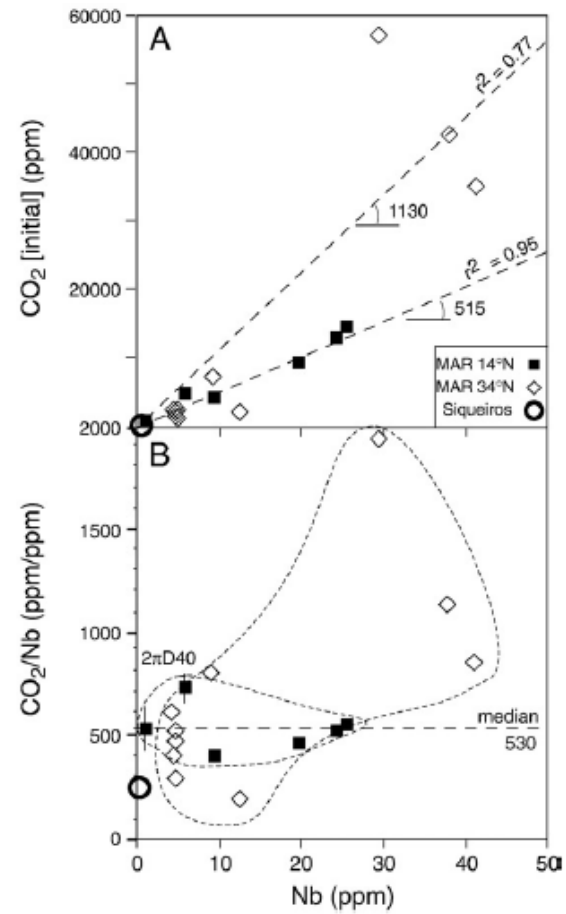
What is the right proxy for CO_2?

Siqueiros Fracture Zone





North Atlantic "popping rocks"



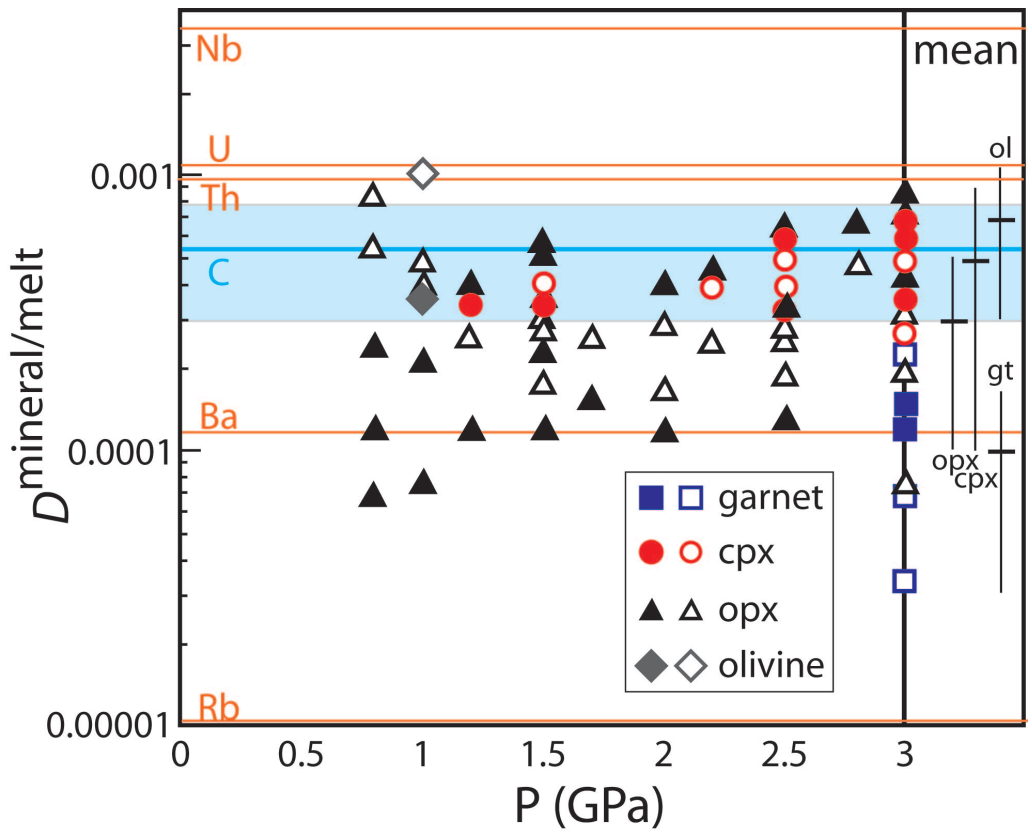
Cartigny et al. 2008

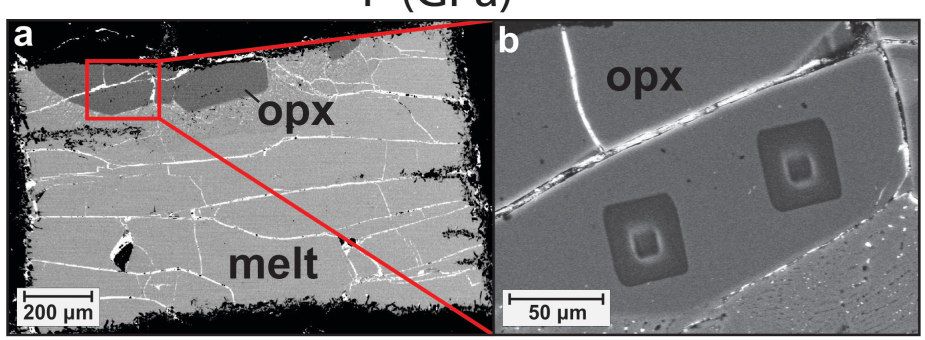
C partitioning experiments

Olivine tholeiite+ 4 wt.% CO_2 olivine, cpx, opx, garnet

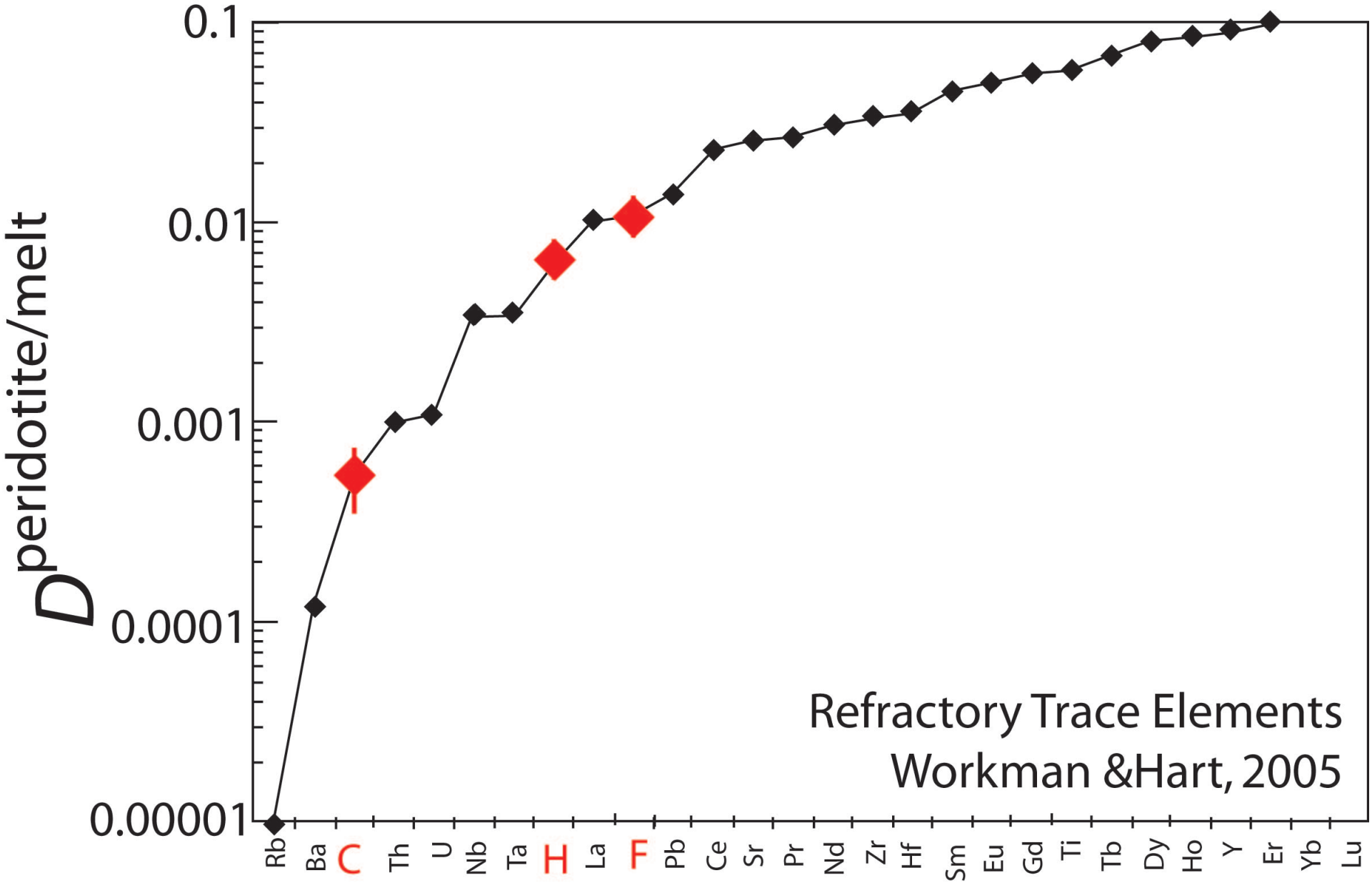
0.8-3 GPa, 1320-1500 °C

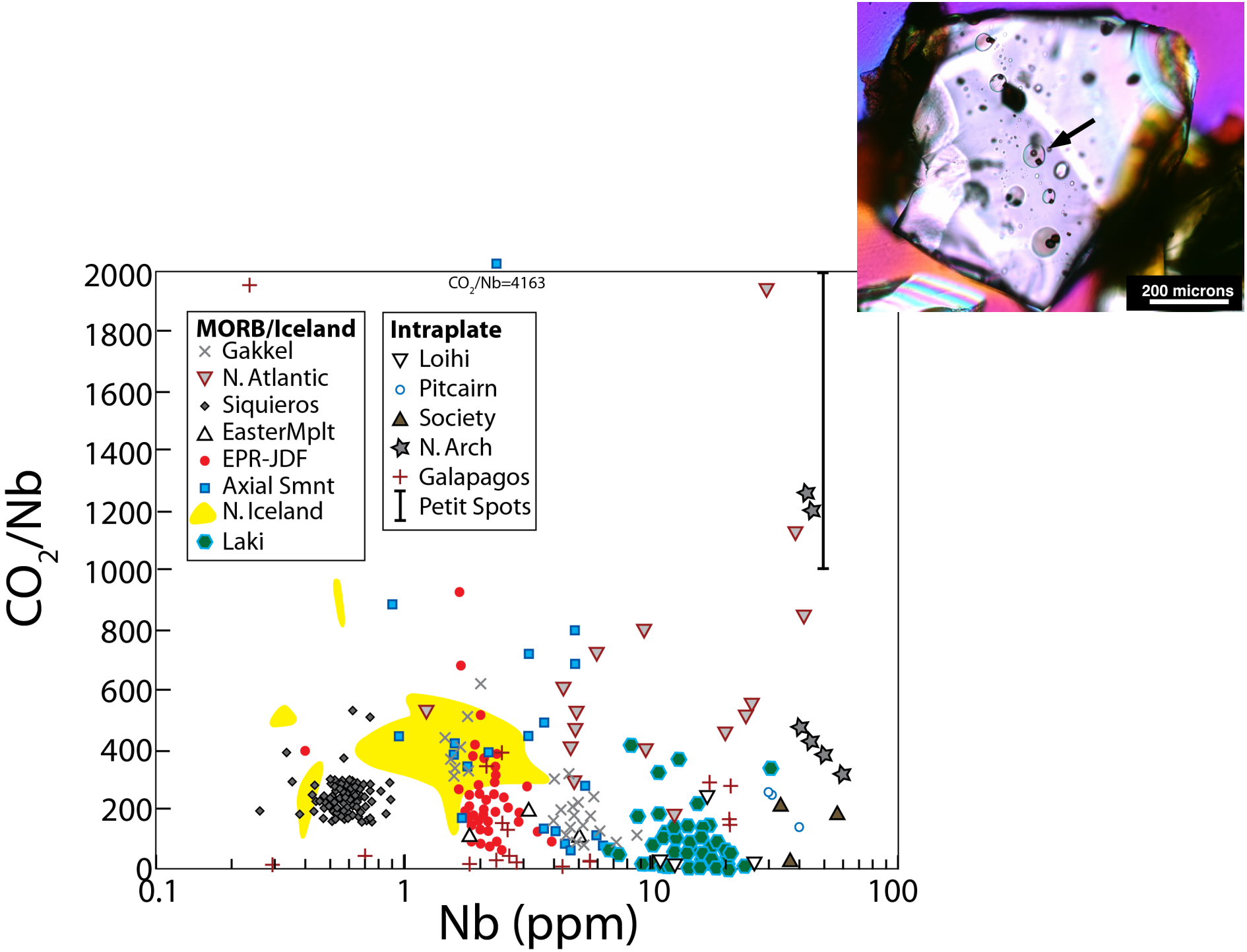
Silicate: ^{13}C; graphite: ^{12}C

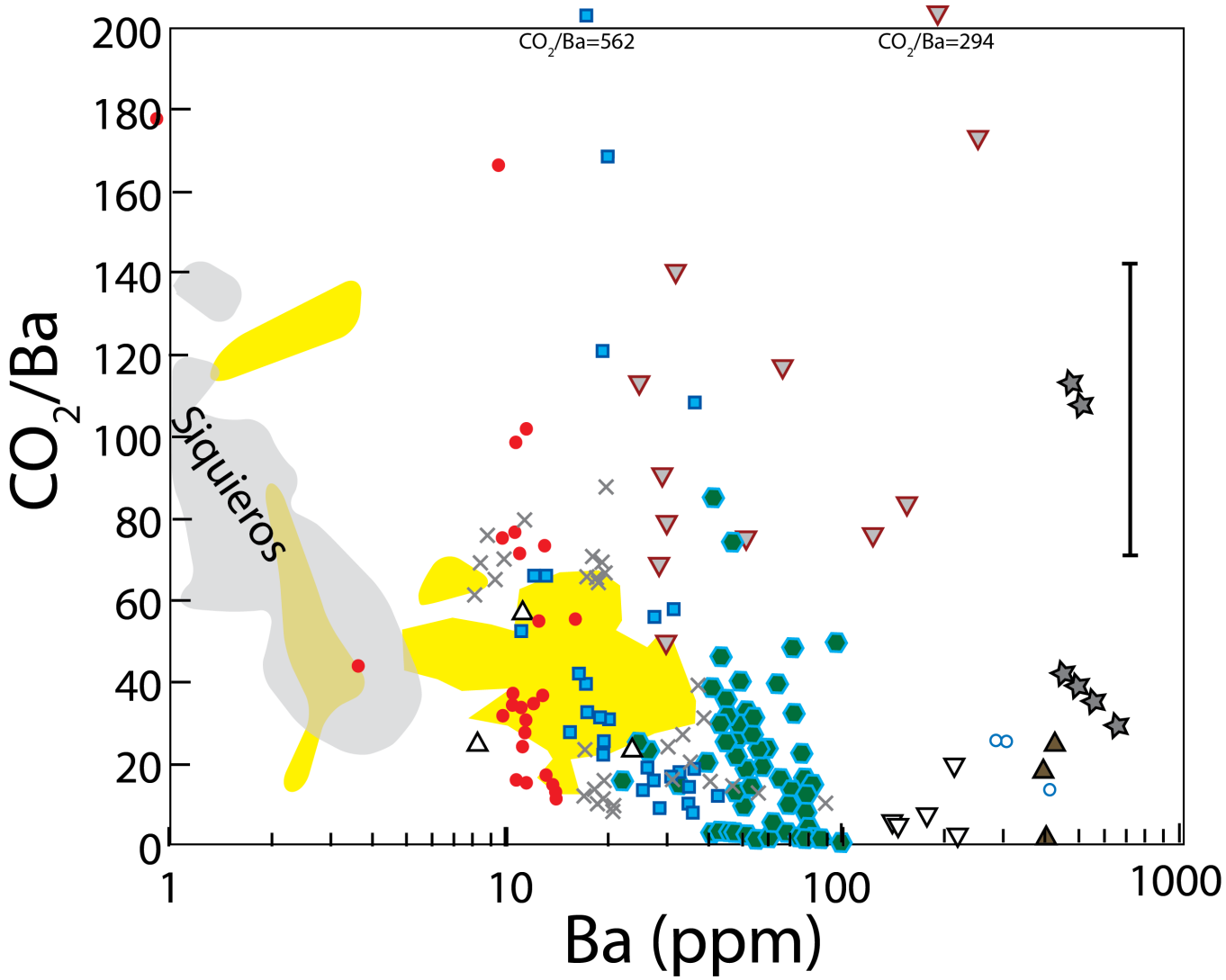


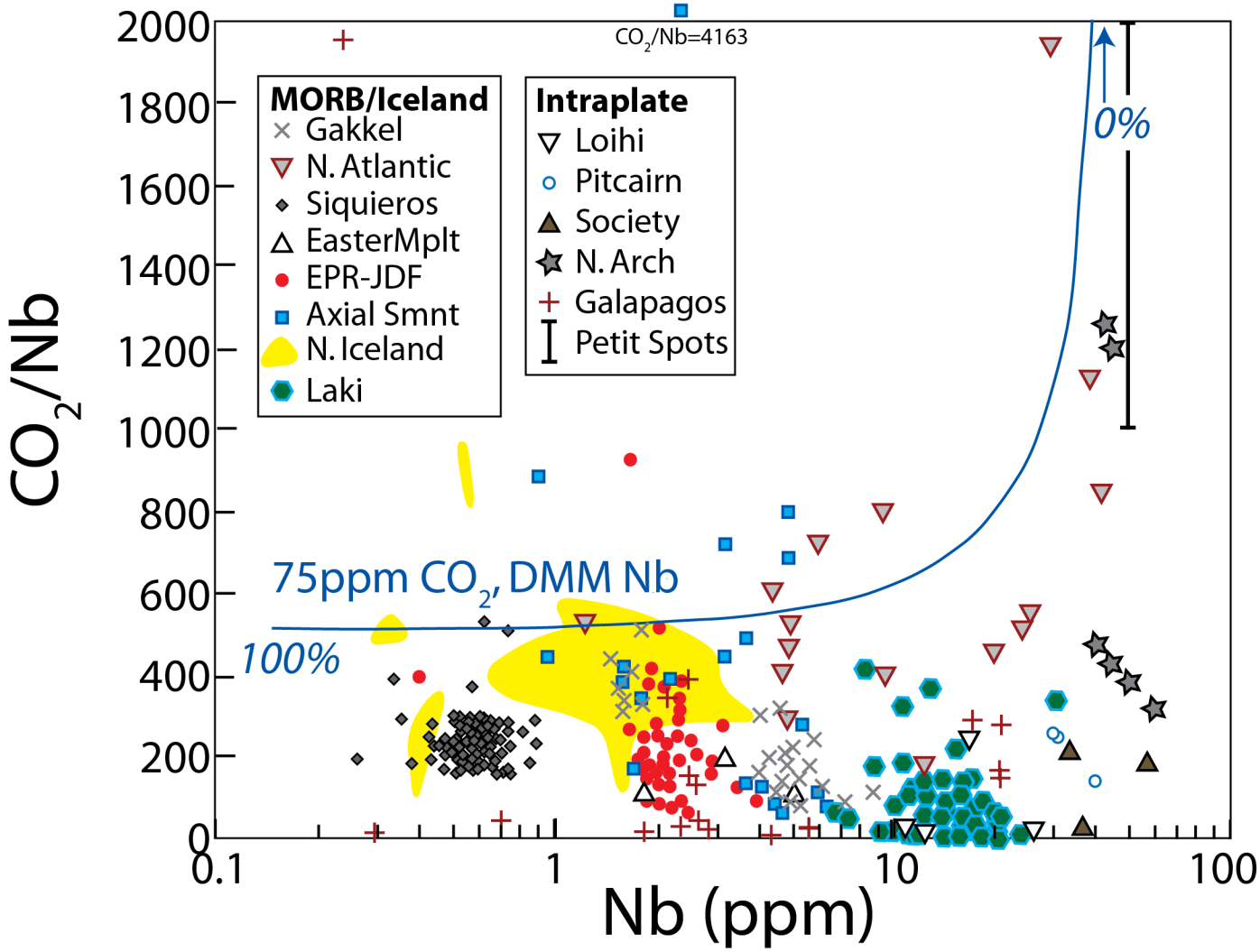


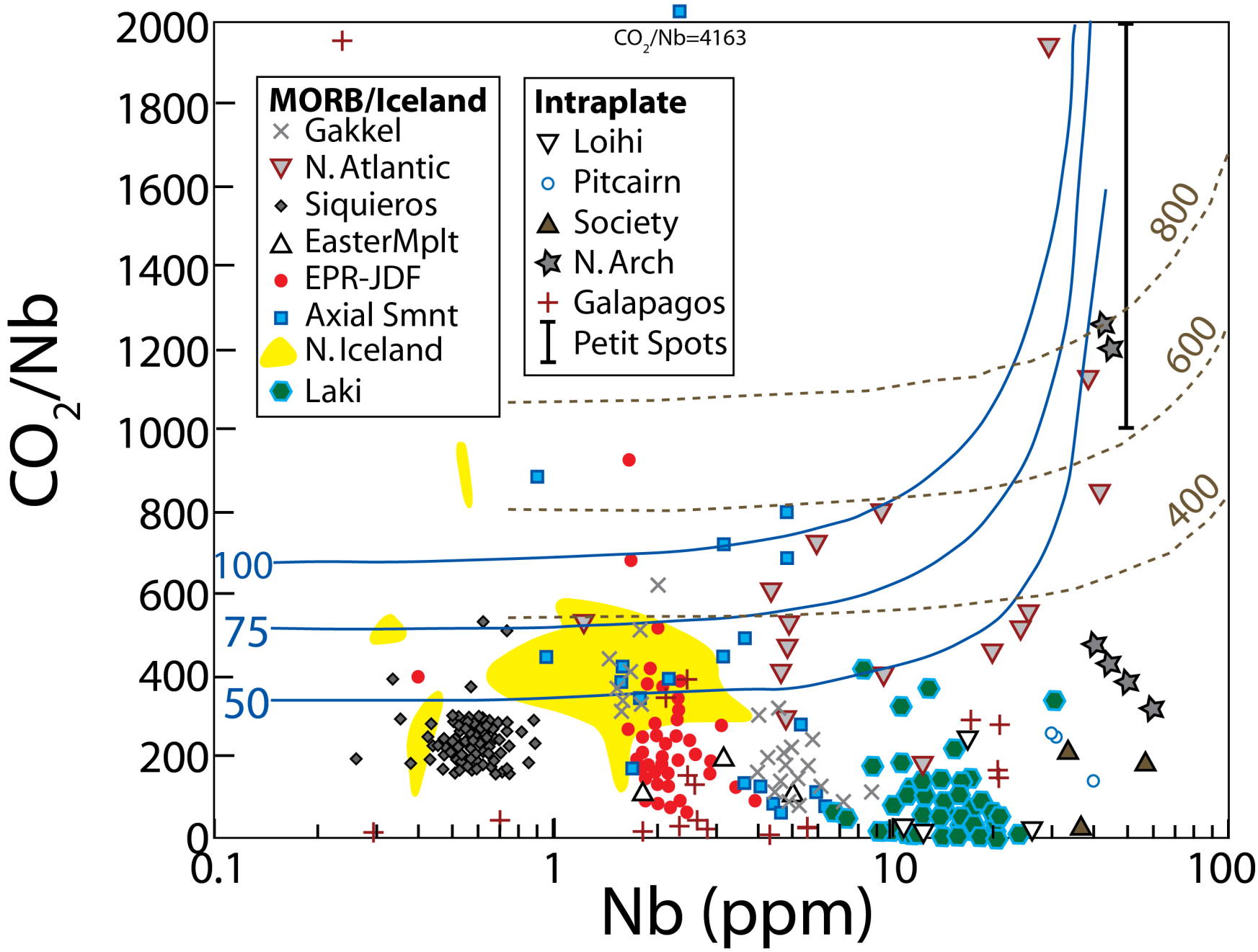
Rosenthal et al. 2015

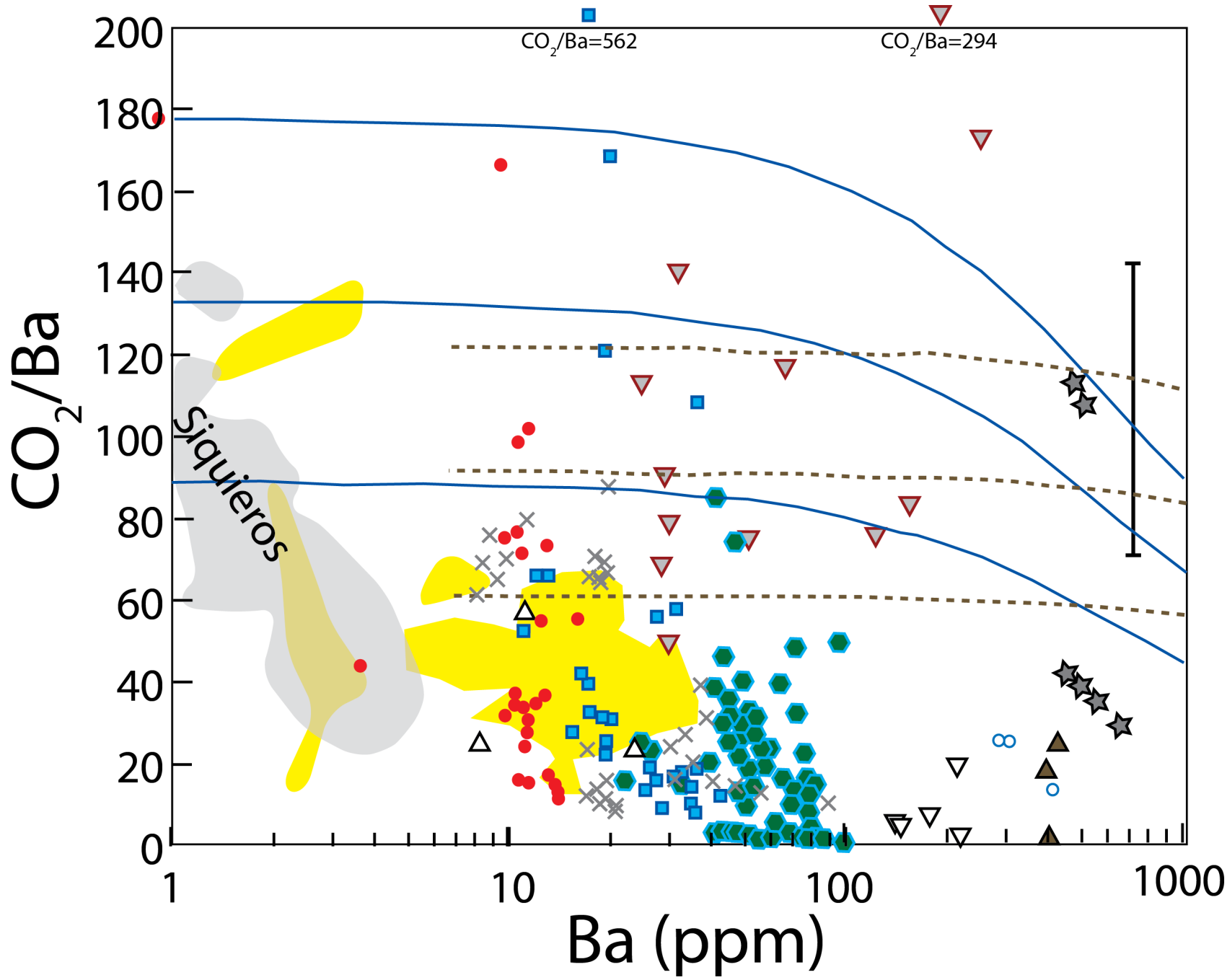

0.1
0.01
0.001
0.0001
0.00001
$D^{peridotite/melt}$
Rb
Ba
C
Th
U
Nb
Ta
H
La
F
Pb
Ce
Sr
Pr
Nd
Zr
Hf
Sm
Eu
Gd
Ti
Tb
Dy
Ho
Y
Er
Yb
Lu
Refractory Trace Elements
Workman &Hart, 2005

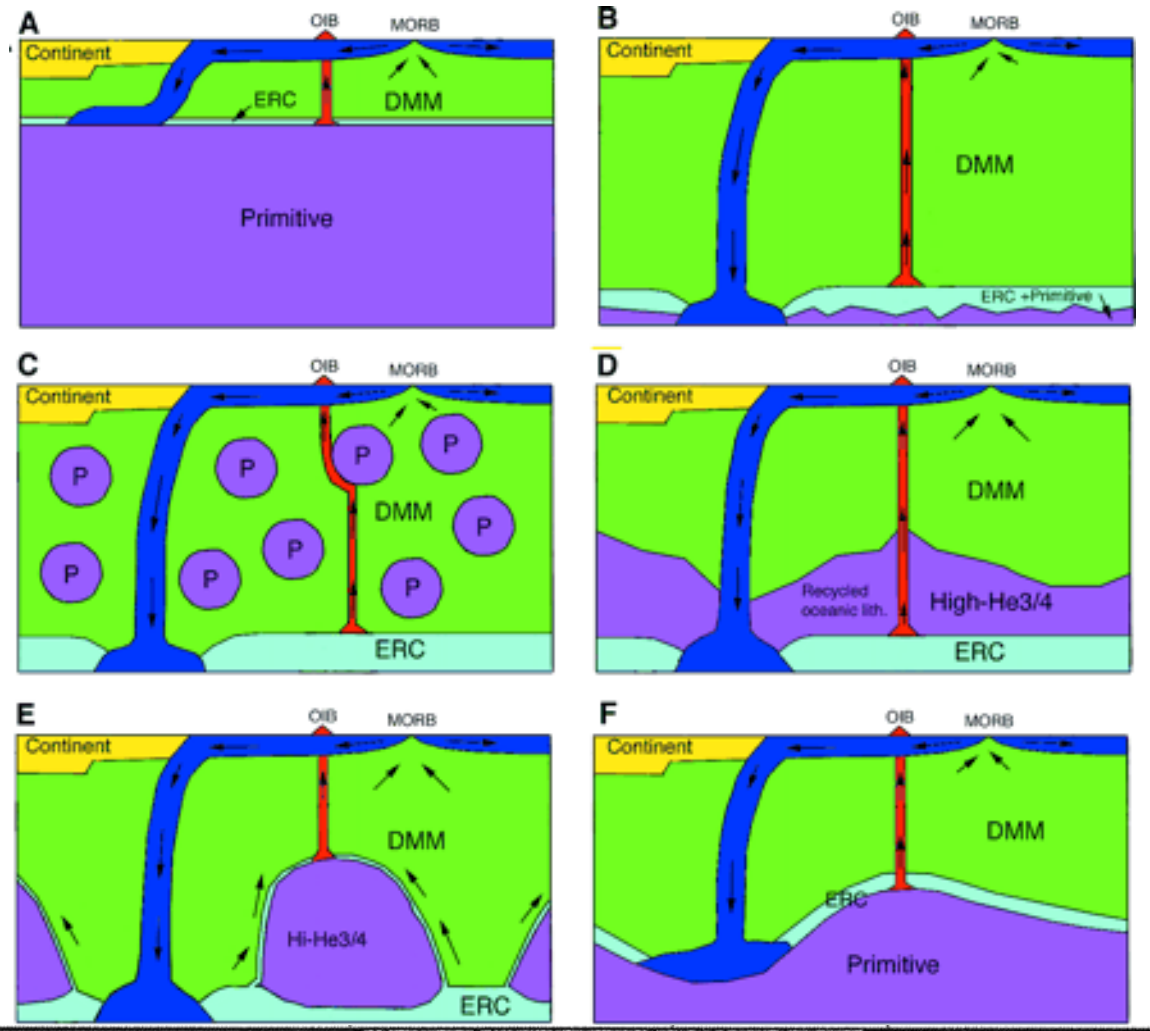

200 microns
CO2/Nb=4163
MORB/Iceland
Gakkel
N. Atlantic
Siquieros
EasterMplt
EPR-JDF
Axial Smnt
N. Iceland
Laki
Intraplate
Loihi
Pitcairn
Society
N. Arch
Galapagos
Petit Spots
CO2/Nb
Nb (ppm)
0
200
400
600
800
1000
1200
1400
1600
1800
2000
0.1
1
10
100


CO2/Ba=562
CO2/Ba=294
Siquieros
CO2/Ba
Ba (ppm)
200
180
160
140
120
100
80
60
40
20
0
1
10
100
1000


CO2/Nb=4163
MORB/Iceland
Gakkel
N. Atlantic
Siquieros
EasterMplt
EPR-JDF
Axial Smnt
N. Iceland
Laki
Intraplate
Loihi
Pitcairn
Society
N. Arch
Galapagos
Petit Spots
0%
75ppm CO2, DMM Nb
100%
CO2/Nb
Nb (ppm)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0.1
1
10
100

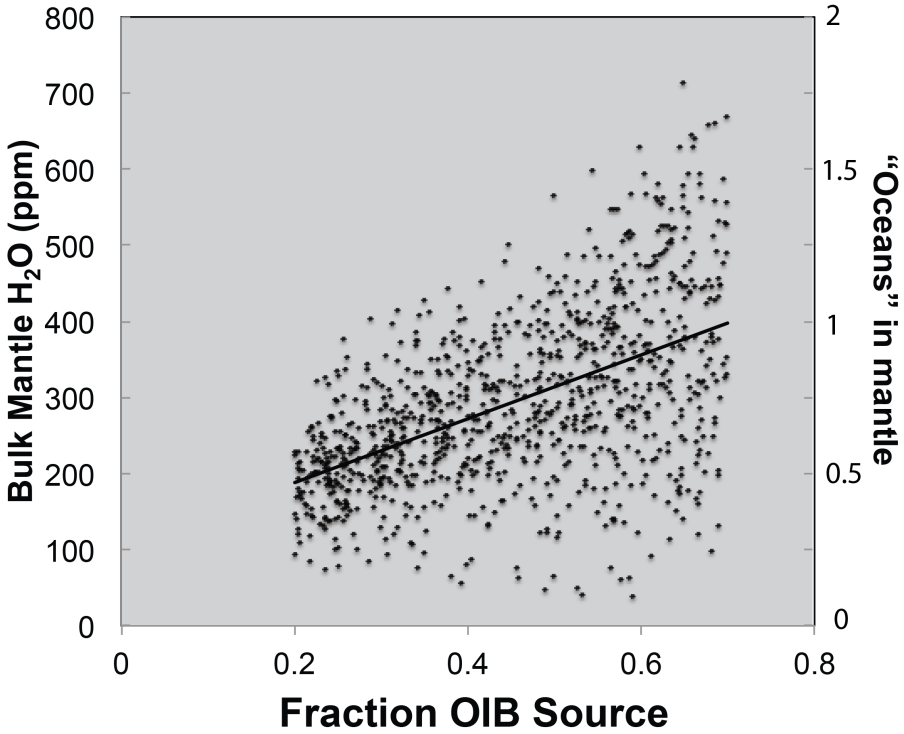

CO2/Nb=4163
MORB/Iceland
Gakkel
N. Atlantic
Siquieros
EasterMplt
EPR-JDF
Axial Smnt
N. Iceland
Laki
Intraplate
Loihi
Pitcairn
Society
N. Arch
Galapagos
Petit Spots
800
600
400
100
75
50
CO2/Nb
Nb (ppm)
0
200
400
600
800
1000
1200
1400
1600
1800
2000
0.1
1
10
100

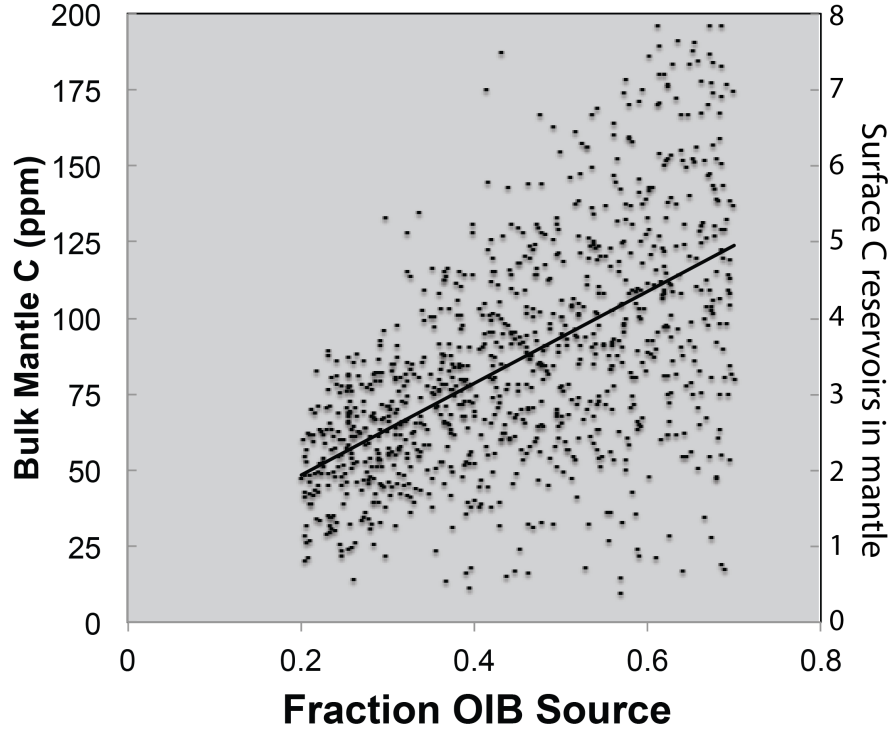

CO2/Ba=562
CO2/Ba=294
Siquieros
CO2/Ba
Ba (ppm)
200
180
160
140
120
100
80
60
40
20
0
1
10
100
1000



Tackley, 2000

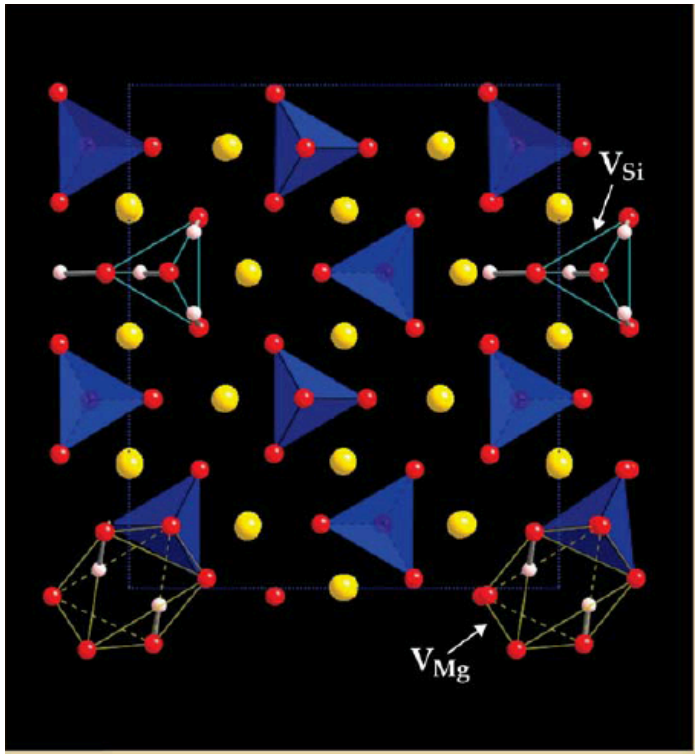
Davies, 2002



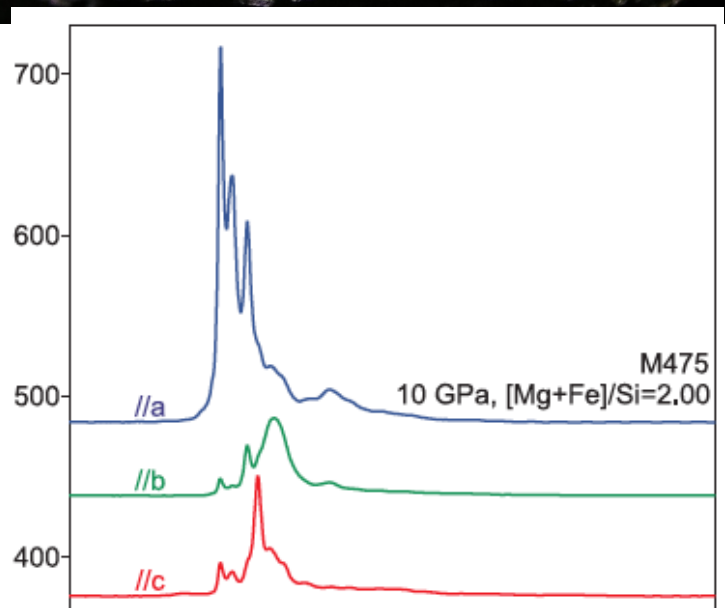


Depleted Mantle Source:
120±40 ppm H_2O
75±25 ppm CO_2

OIB Mantle Source:
500±200 ppm H_2O
600±200 ppm CO_2

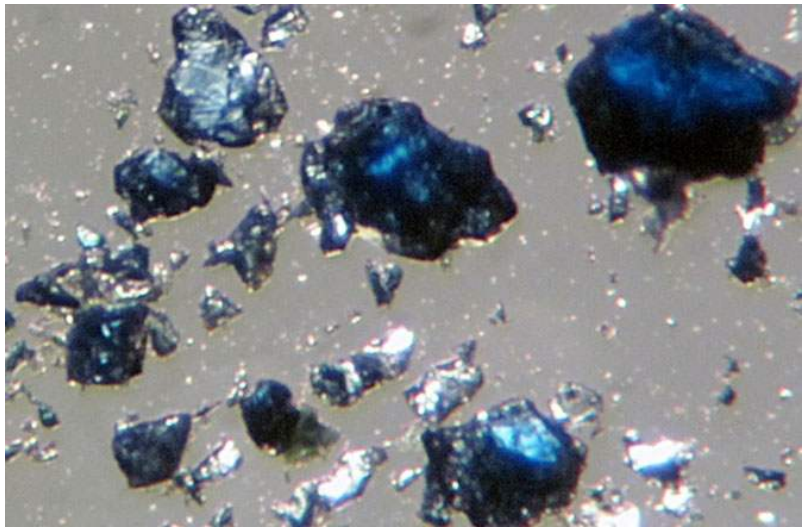


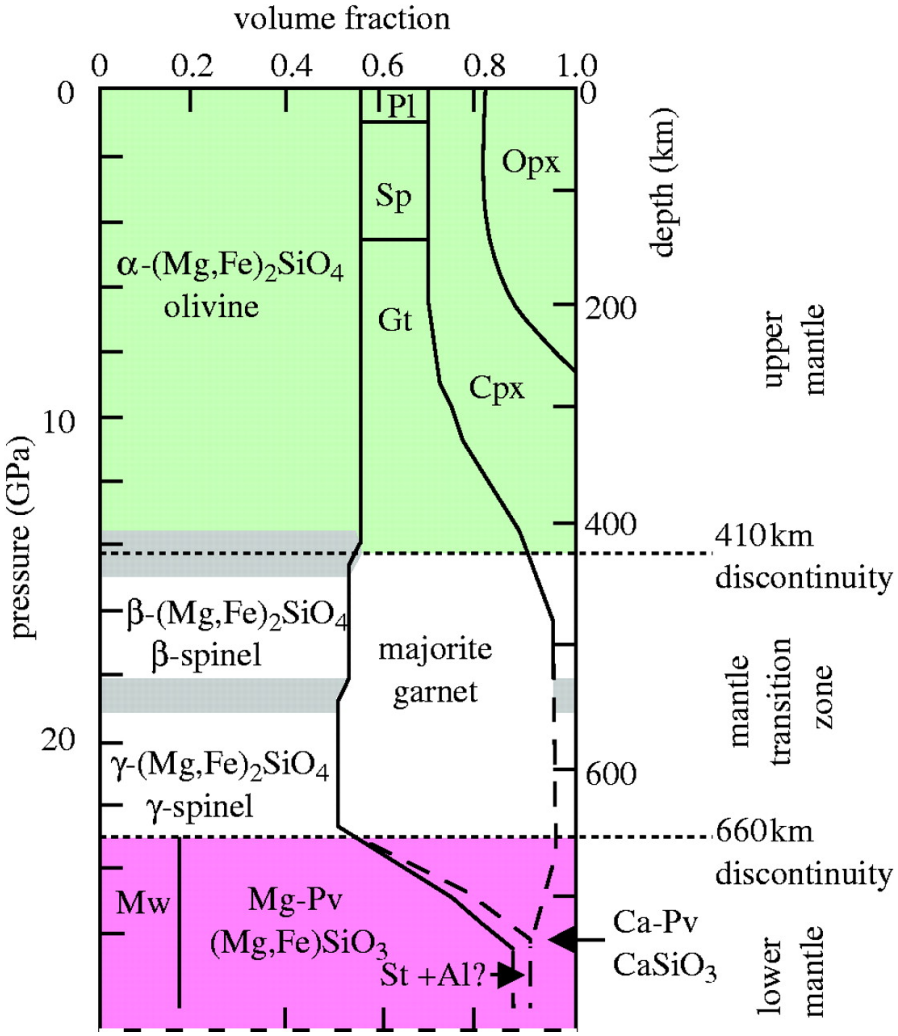
Umemoto et al. 2011

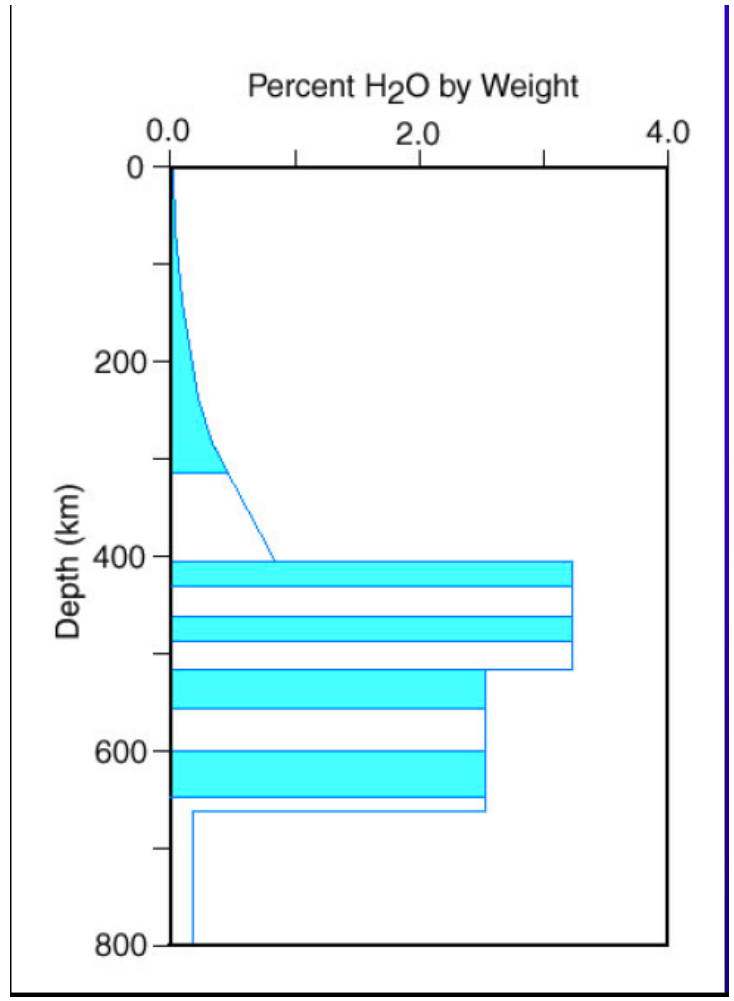


Withers et al. 2011

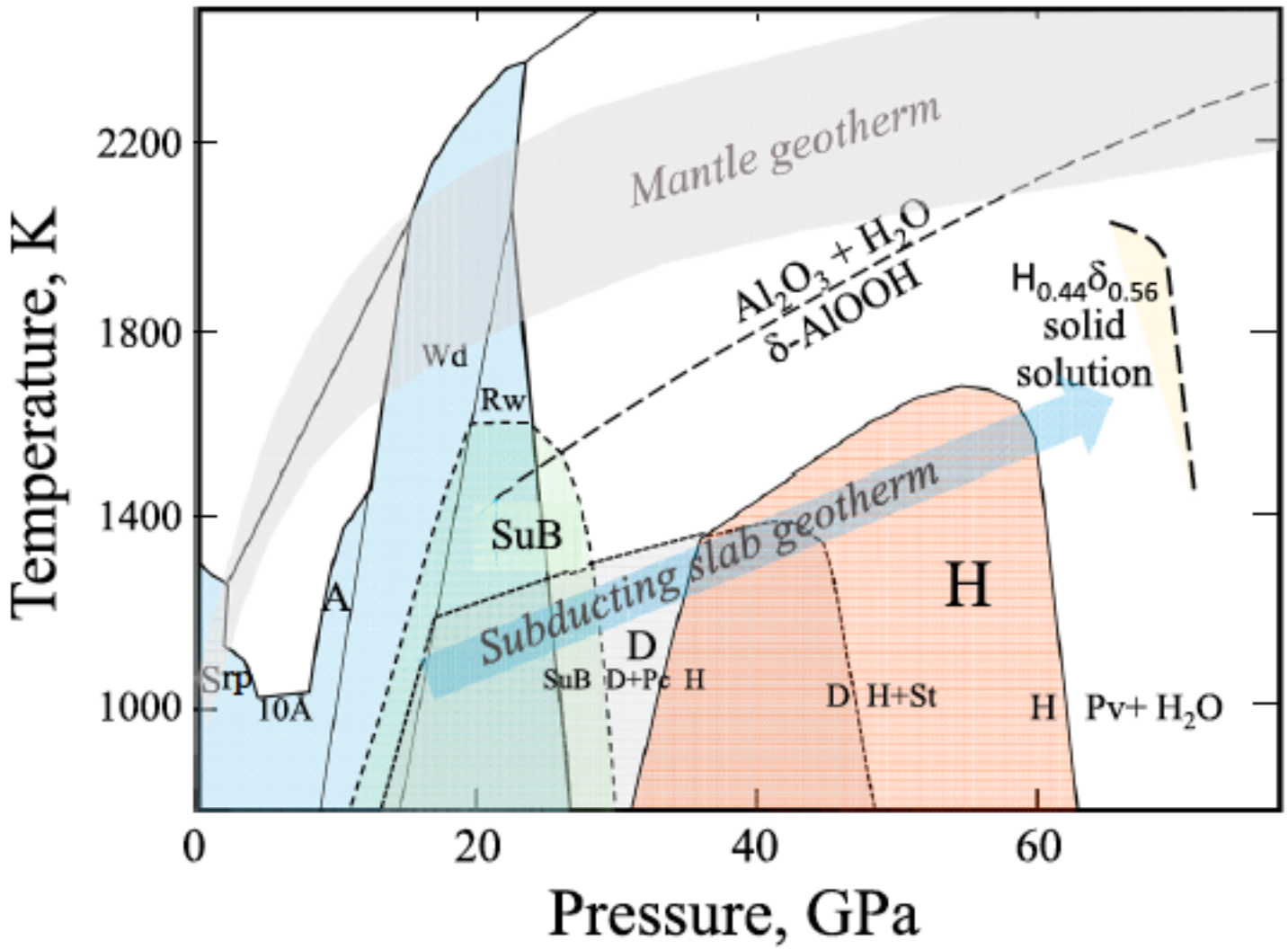

GEM DISCOVERY
POINTS TO SUBTERRANEAN OCEANS
BRAZIL
MINERAL:
RINGWOODITE
hidden within
DIAMOND
FIRST TIME
found in Earth
1.5 % WEIGHT
=WATER
CRUST (100 km)
UPPER
MANTLE
(100-410 km)
TRANSITION
ZONE
(410-660 km)
LOWER
MANTLE
(660-2925 km)




volume fraction
0
0.2
0.4
0.6
0.8
1.0
pressure (GPa)
0
10
20
depth (km)
0
200
400
600
Pl
Sp
Gt
Opx
Cpx
α-(Mg,Fe)2SiO4
olivine
β-(Mg,Fe)2SiO4
β-spinel
majorite
garnet
γ-(Mg,Fe)2SiO4
γ-spinel
Mw
Mg-Pv
(Mg,Fe)SiO3
St +Al?
Ca-Pv
CaSiO3
410km
discontinuity
660km
discontinuity
upper
mantle
mantle
transition
zone
lower
mantle

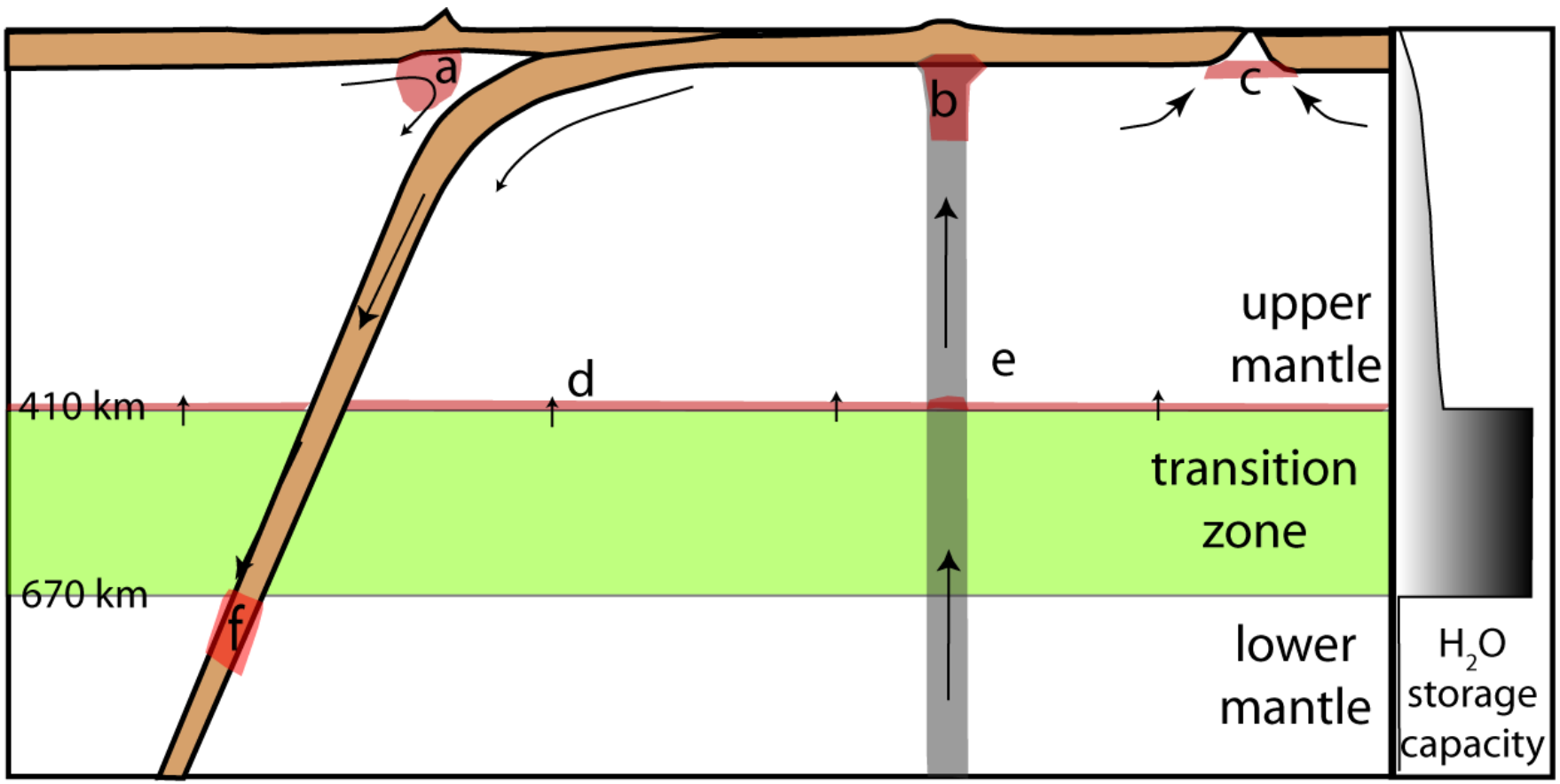

Percent H2O by Weight
0.0
2.0
4.0
Depth (km)
0
200
400
600
800

J. Smyth ~2005



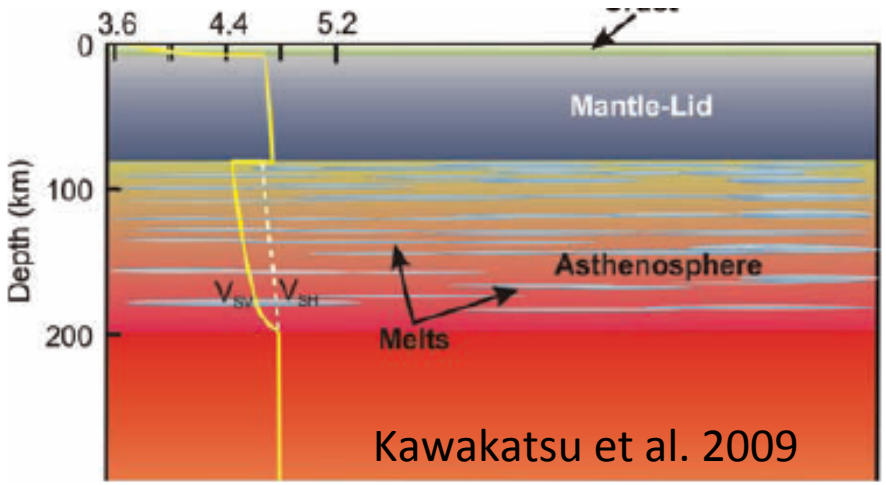
Ohtani et al. 2014 GRL

Possible Loci of Hydrous Melting in the Mantle

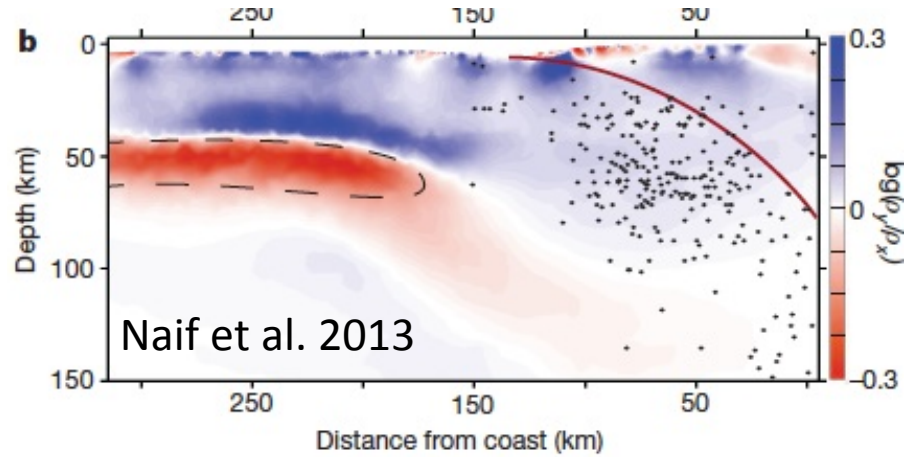


Possible Evidence of Small Degree Melts in the Mantle

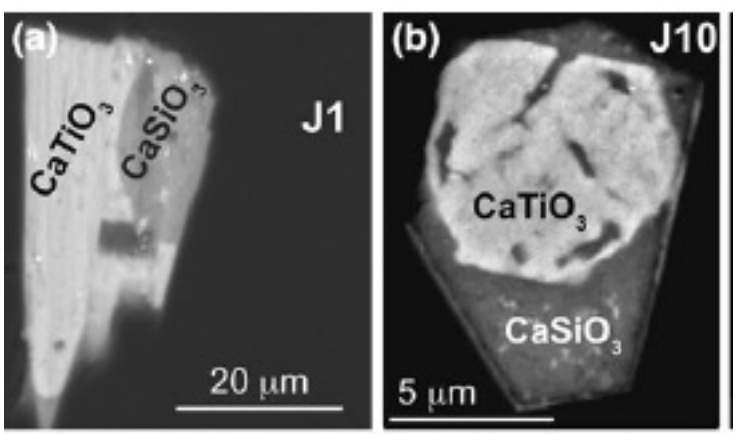
Shear wave velocity anomaly at LAB



Conductivity Anomaly at LAB

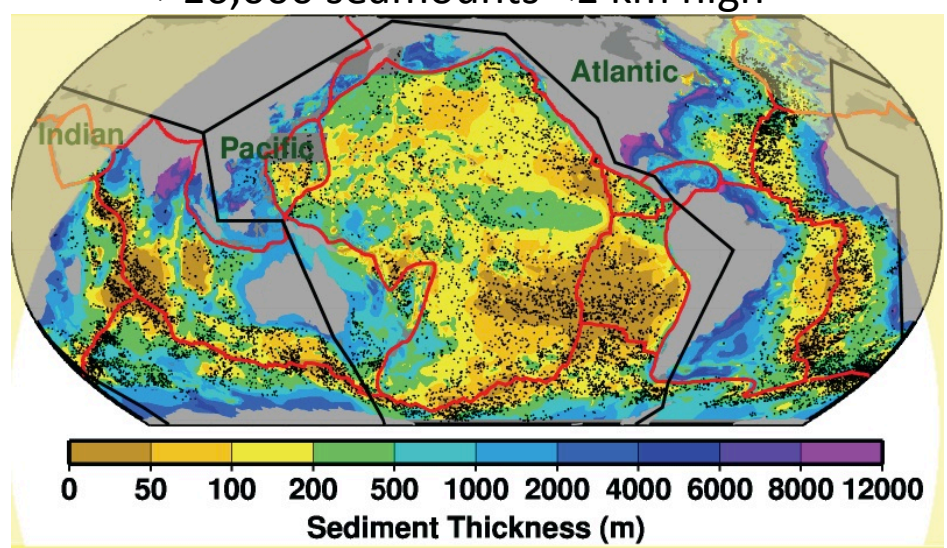


Inclusions in sublithospheric diamonds derived from carbonatite

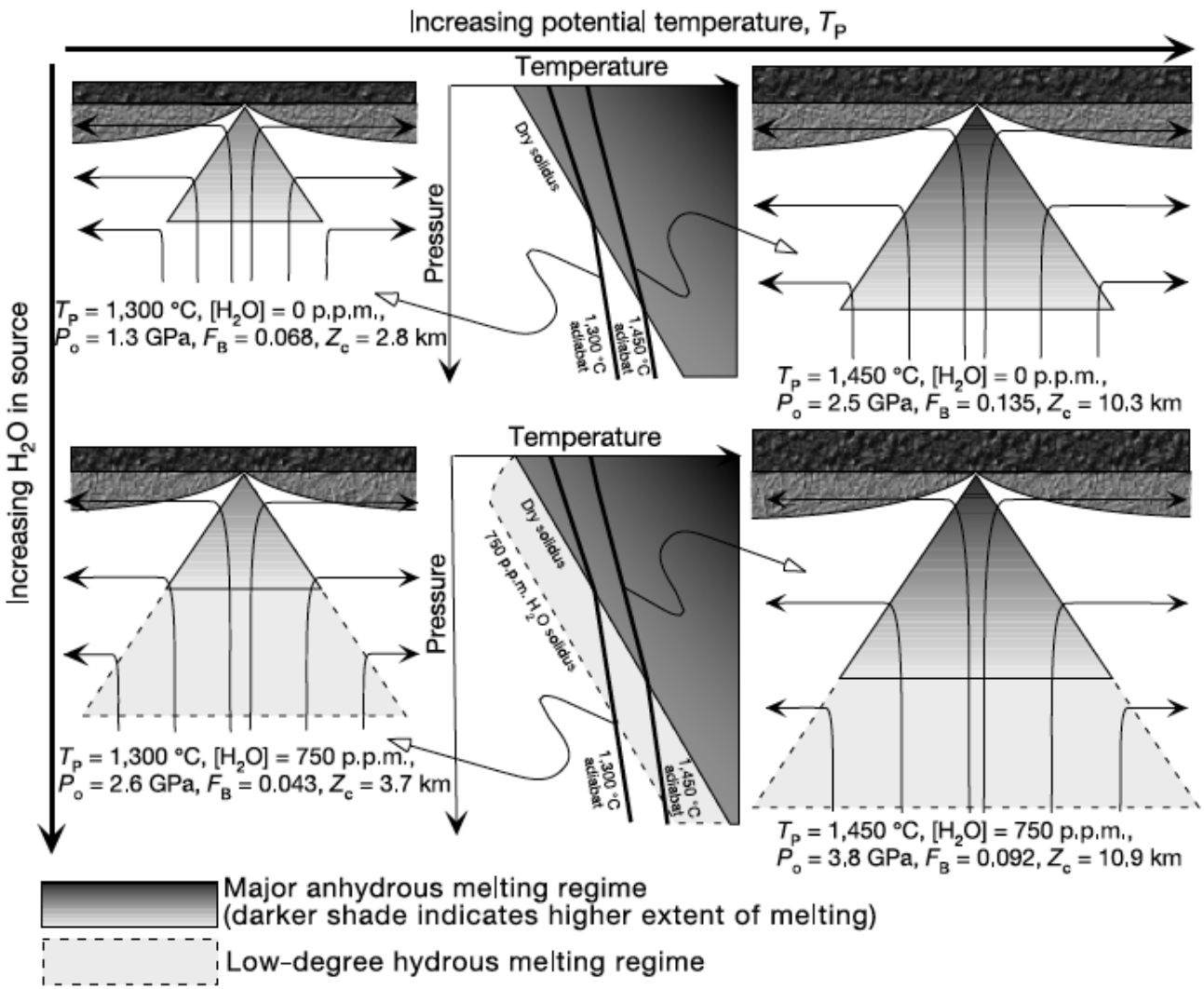


Bulanova et al. 2010

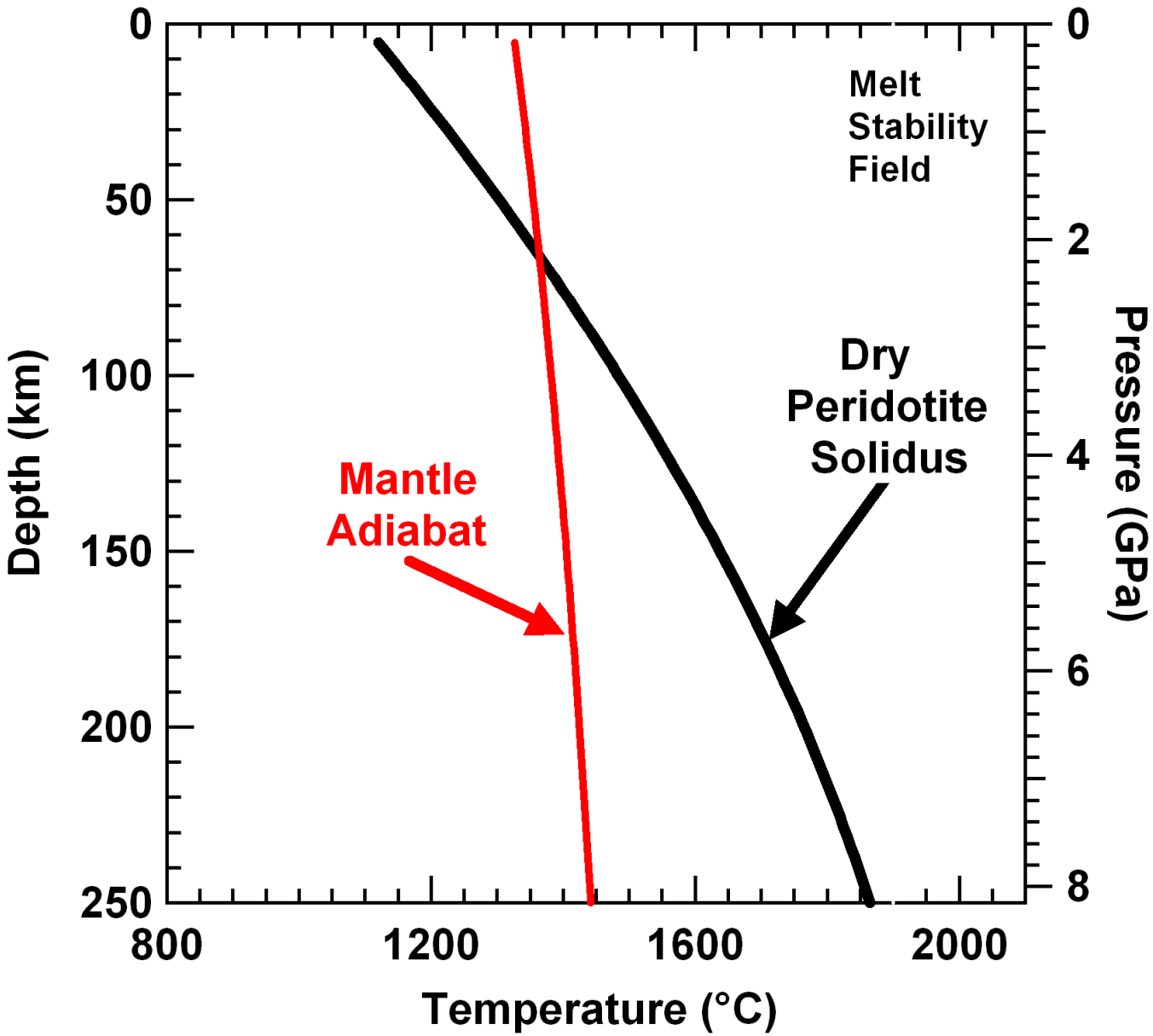
Small-volume oceanic seamounts
>16,000 seamounts <1 km high

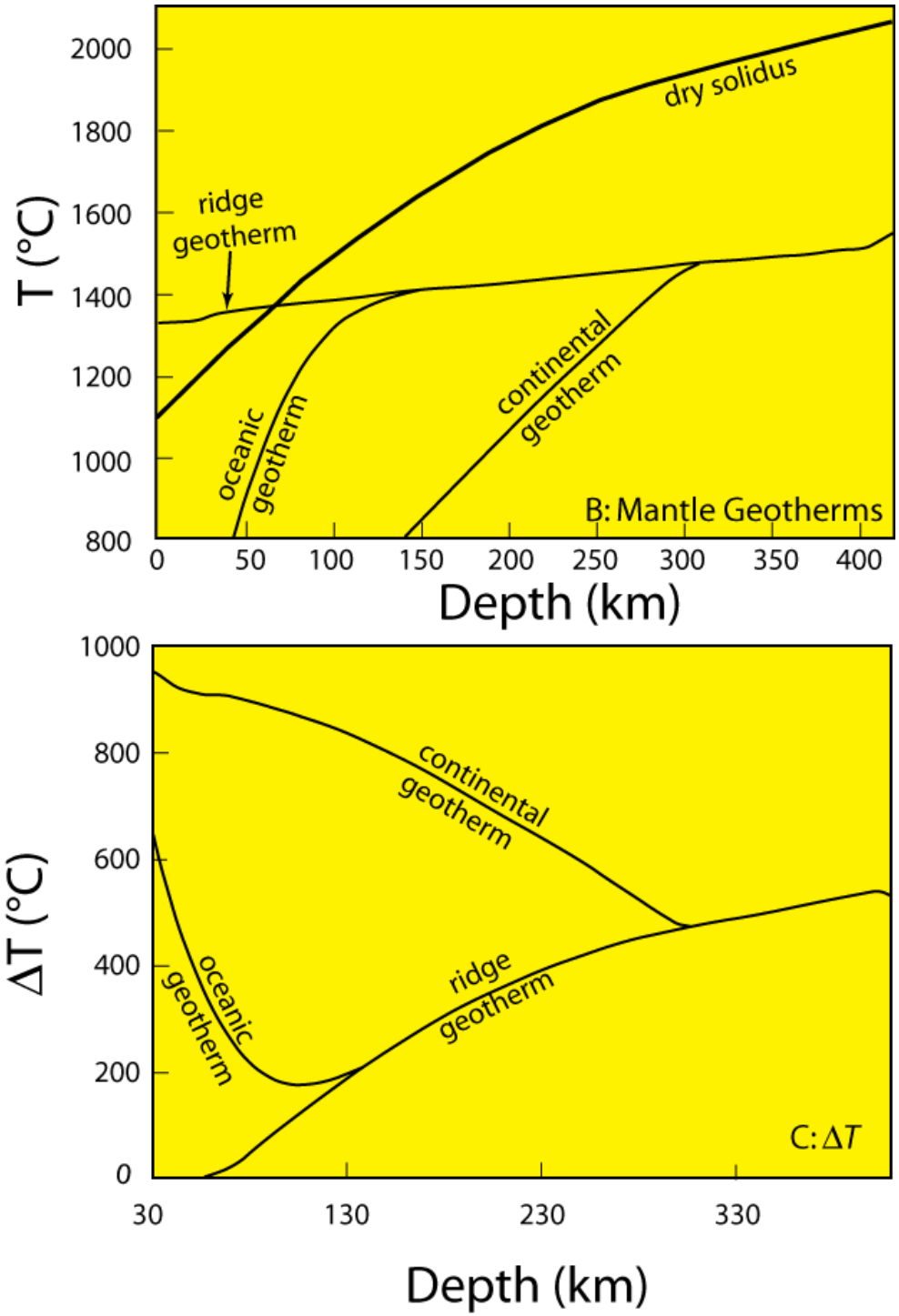


Kim&Wessel, 2011; Conrad et al. DI33B-2242



Asimow and Langmuir, 2003


Melt
Stability
Field
Dry
Peridotite
Solidus
Mantle
Adiabat
Depth (km)
Pressure (GPa)
Temperature (°C)
0
50
100
150
200
250
0
2
4
6
8
800
1200
1600
2000

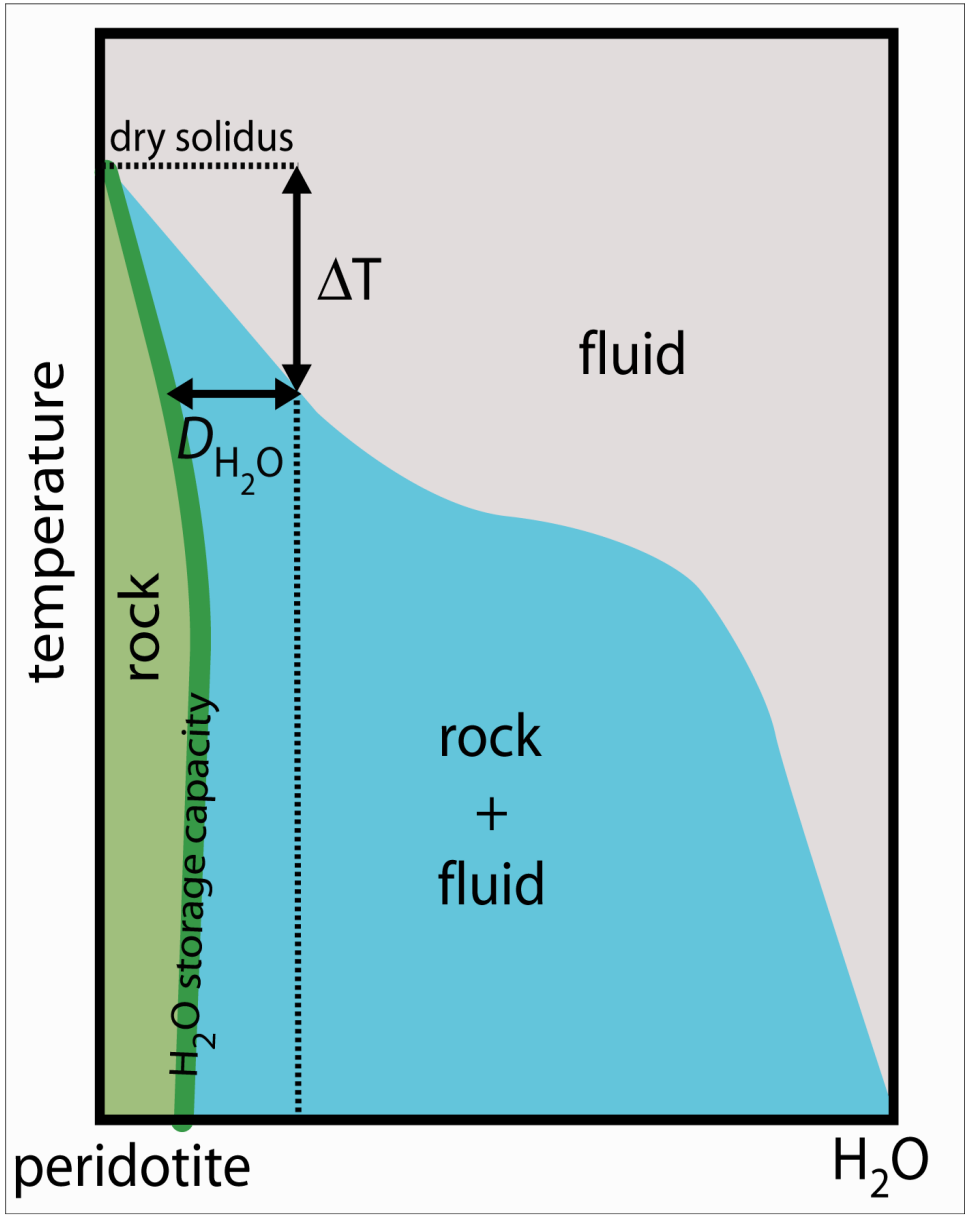

T (°C)
2000
1800
1600
1400
1200
1000
800
0
50
100
150
200
250
300
350
400
Depth (km)
dry solidus
ridge
geotherm
oceanic
geotherm
continental
geotherm
B: Mantle Geotherms
ΔT (°C)
1000
800
600
400
200
0
30
130
230
330
Depth (km)
continental
geotherm
oceanic
geotherm
ridge
geotherm
C: ΔT

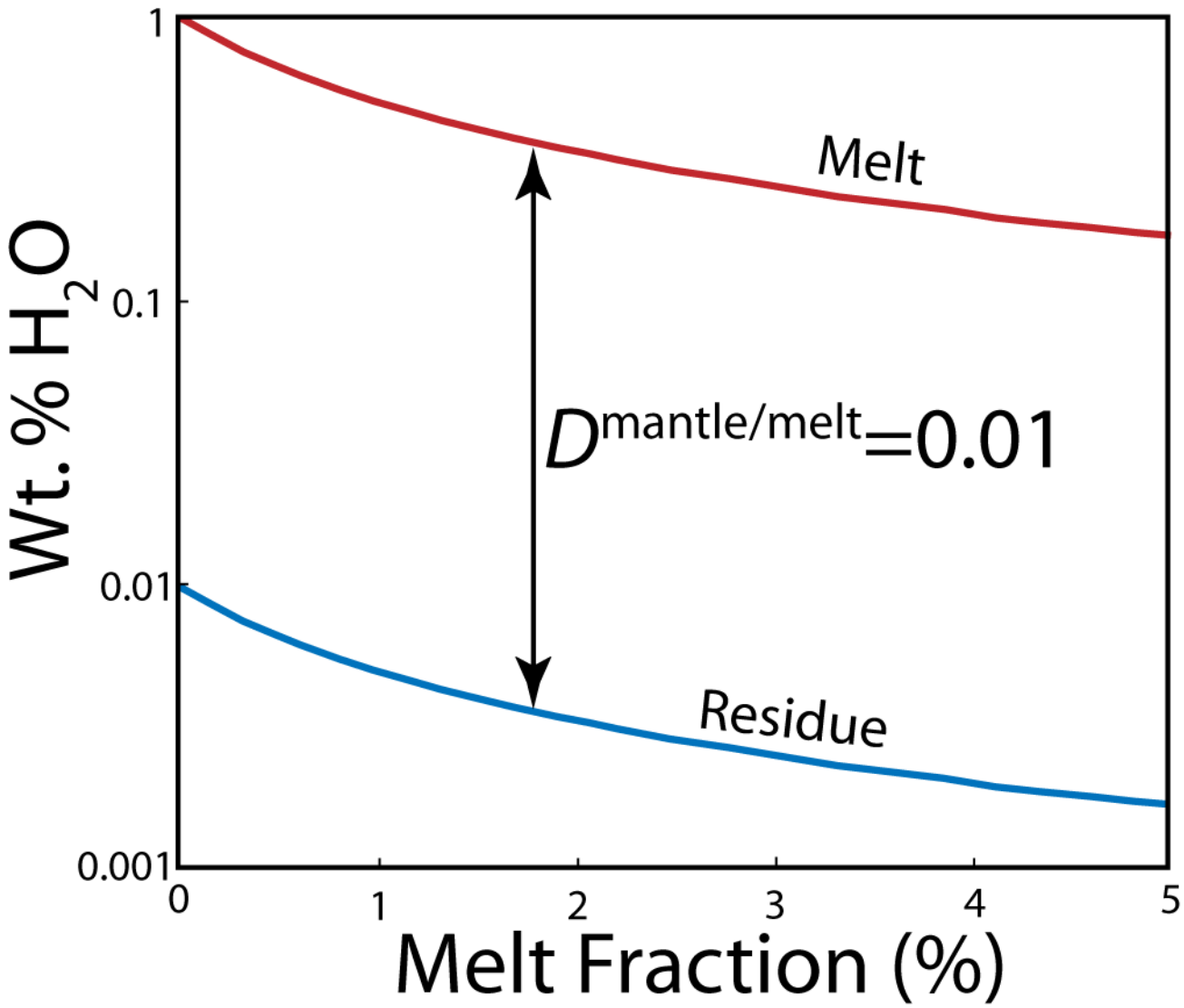
For a given bulk mantle H_2O content, how much H_2O can be in the melt?

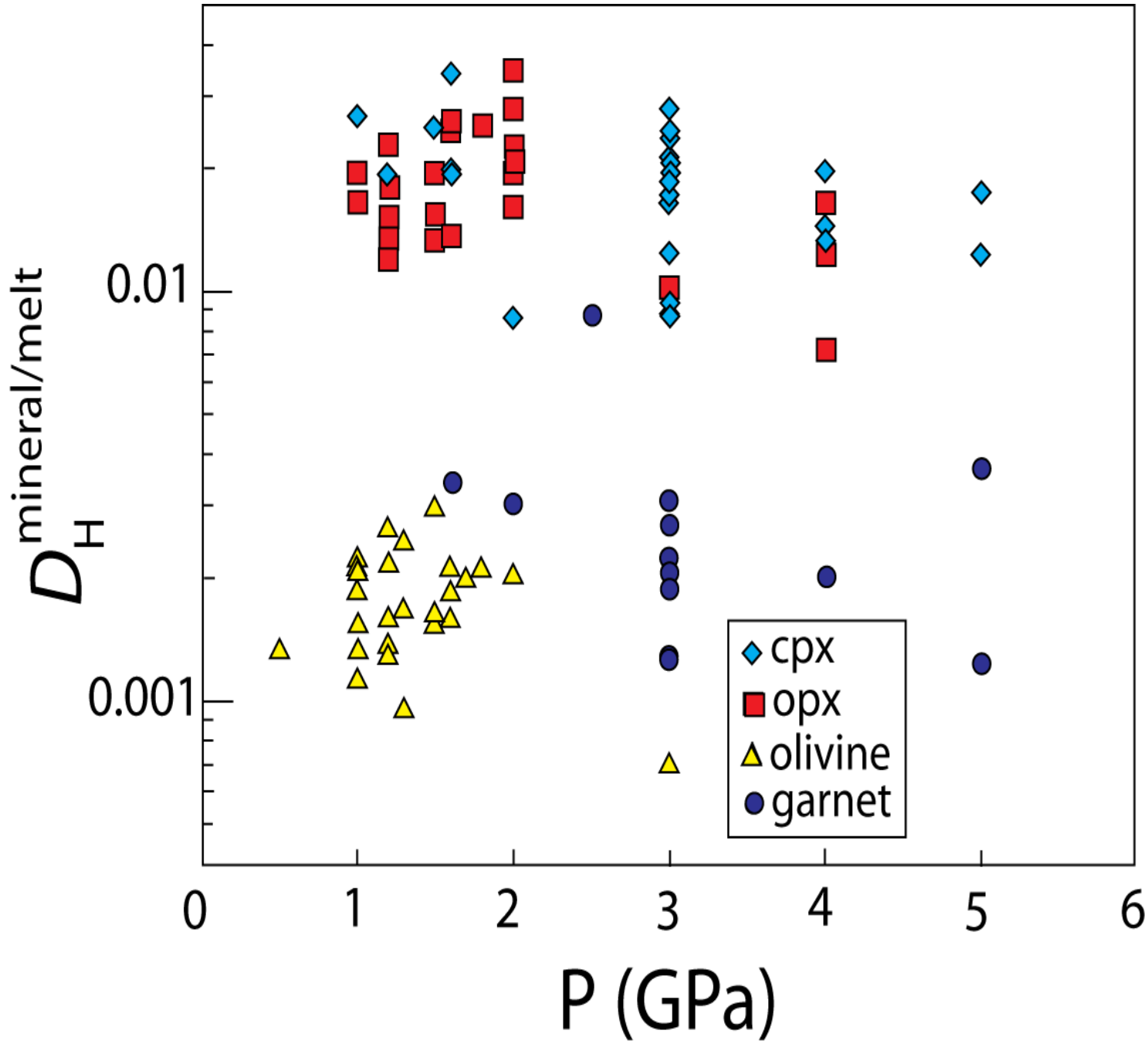
Answer: Mineral/Melt partition coefficients

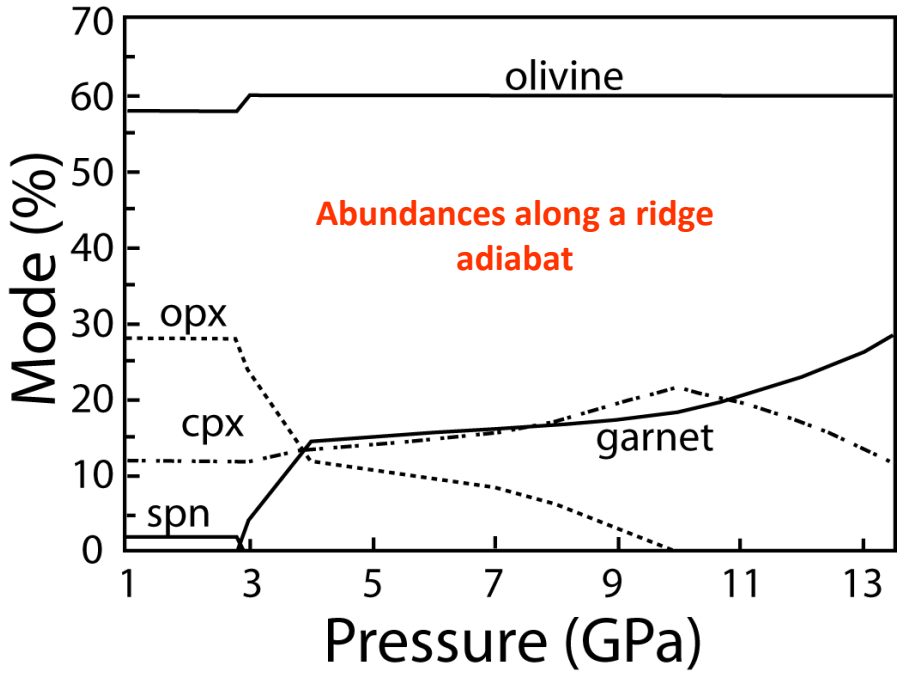
For a given melt H_2O content, how much is melt stabilized relative to dry conditions?

Answer: Experiments defining the relationship between H_2O content and melt fraction

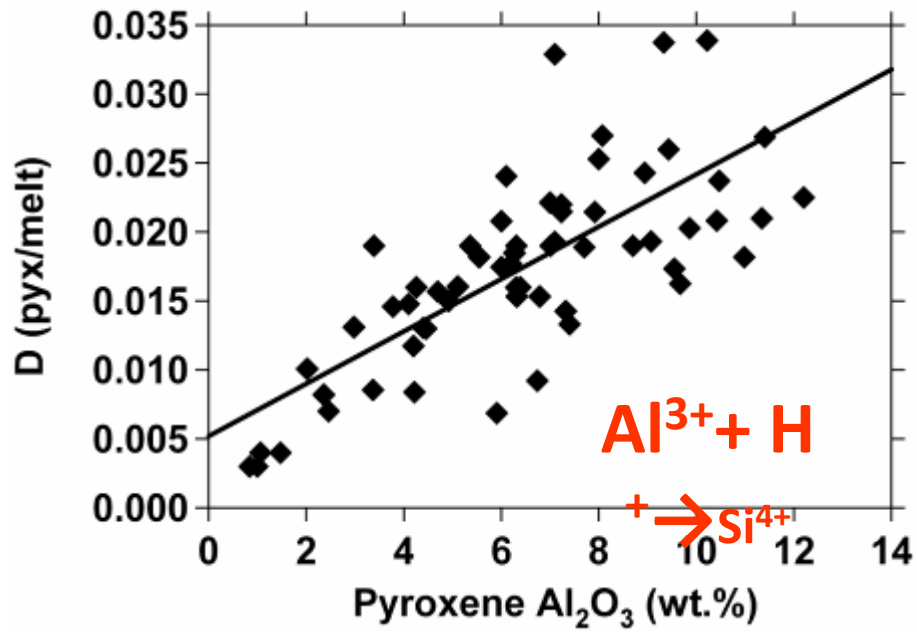



1
0.1
0.01
0.001
Wt. % H_2O
Melt
Residue
$D^{mantle/melt}$=0.01
0
1
2
3
4
5
Melt Fraction (%)

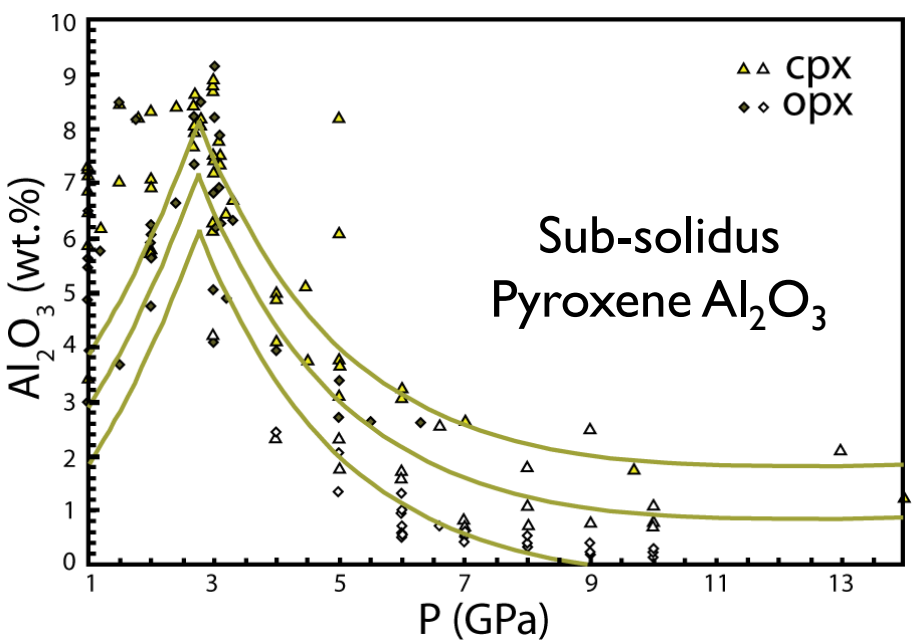

$D_H^{mineral/melt}$
0.01
0.001
0
1
2
3
4
5
6
P (GPa)
cpx
opx
olivine
garnet

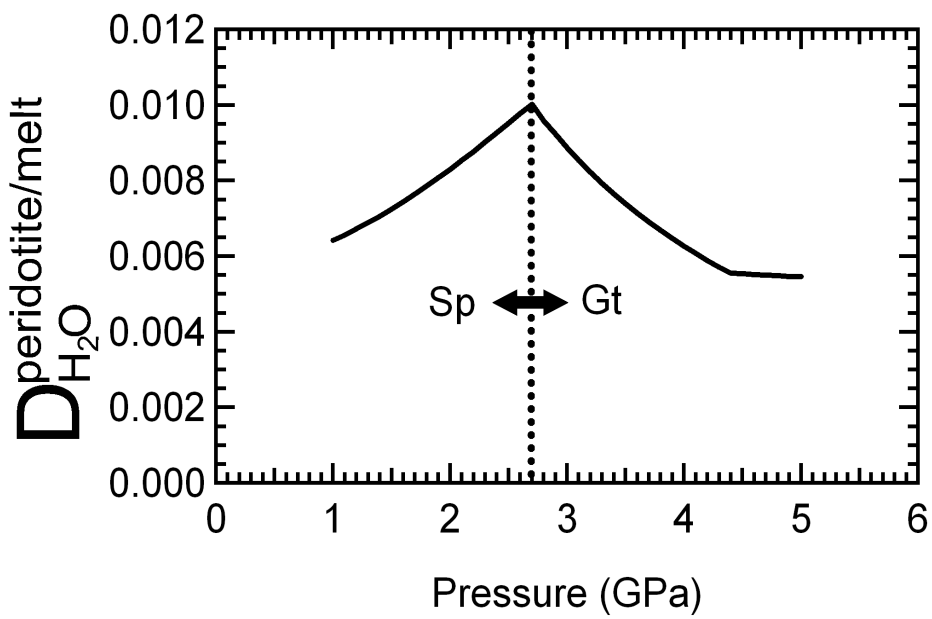


Hirschmann et al. 2009



Aubaud et al. (2004, 2008), Hauri et al. (2006), Tenner et al. (2009).



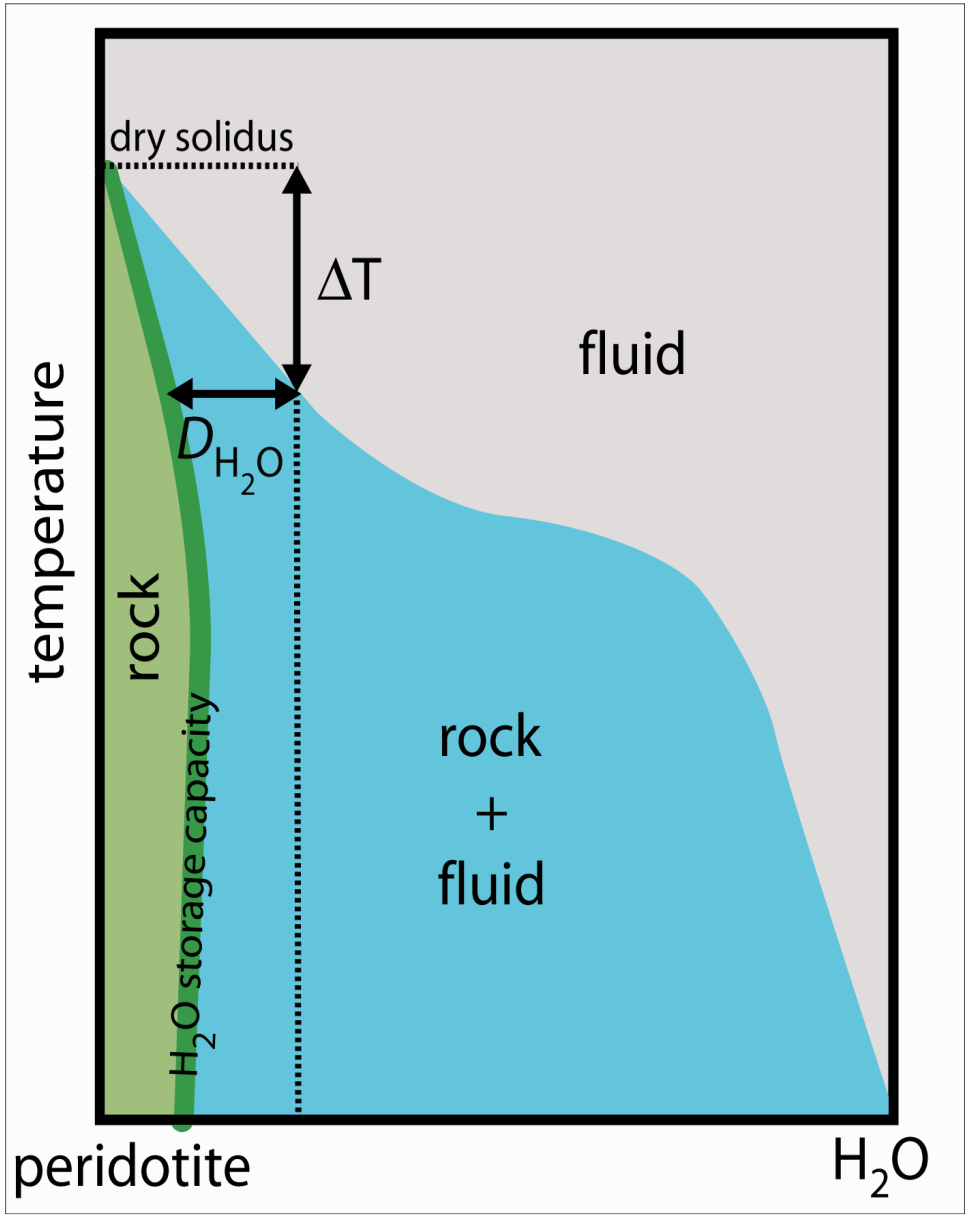


For a given bulk mantle H_2O content, how much H_2O can be in the melt?

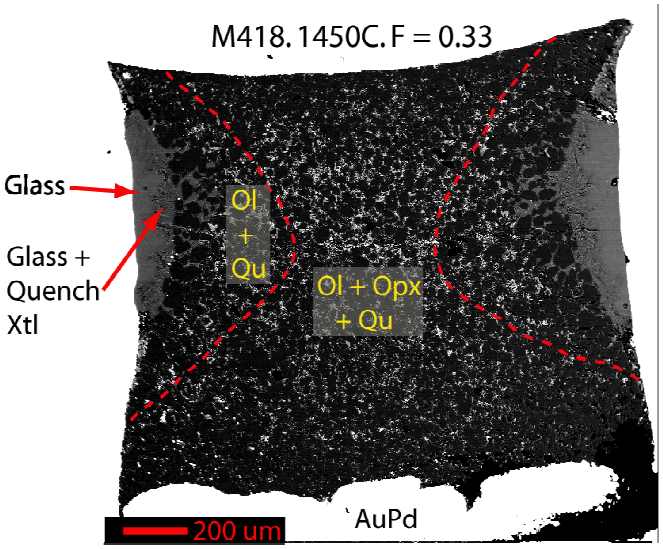
Answer: Mineral/Melt partition coefficients

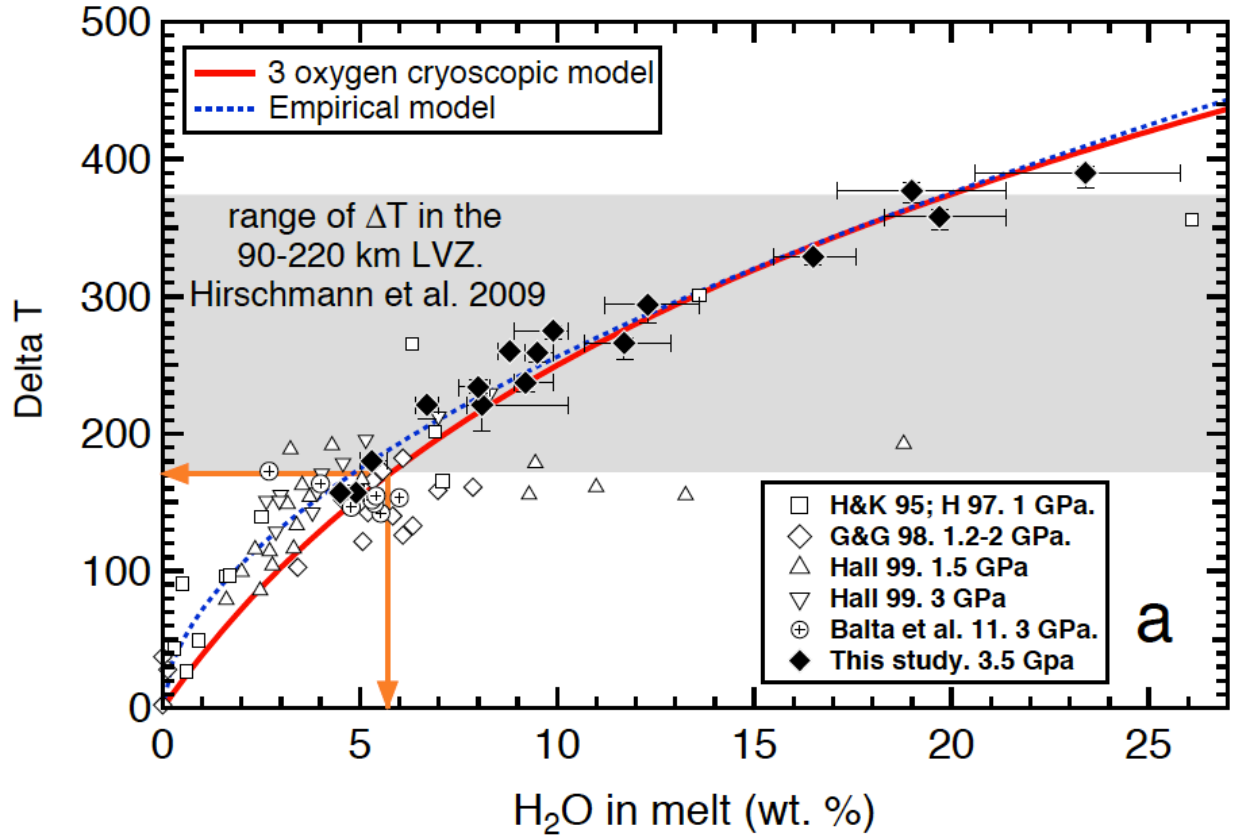
For a given melt H_2O content, how much is melt stabilized relative to dry conditions?

Answer: Experiments defining the relationship between H_2O content and melt fraction



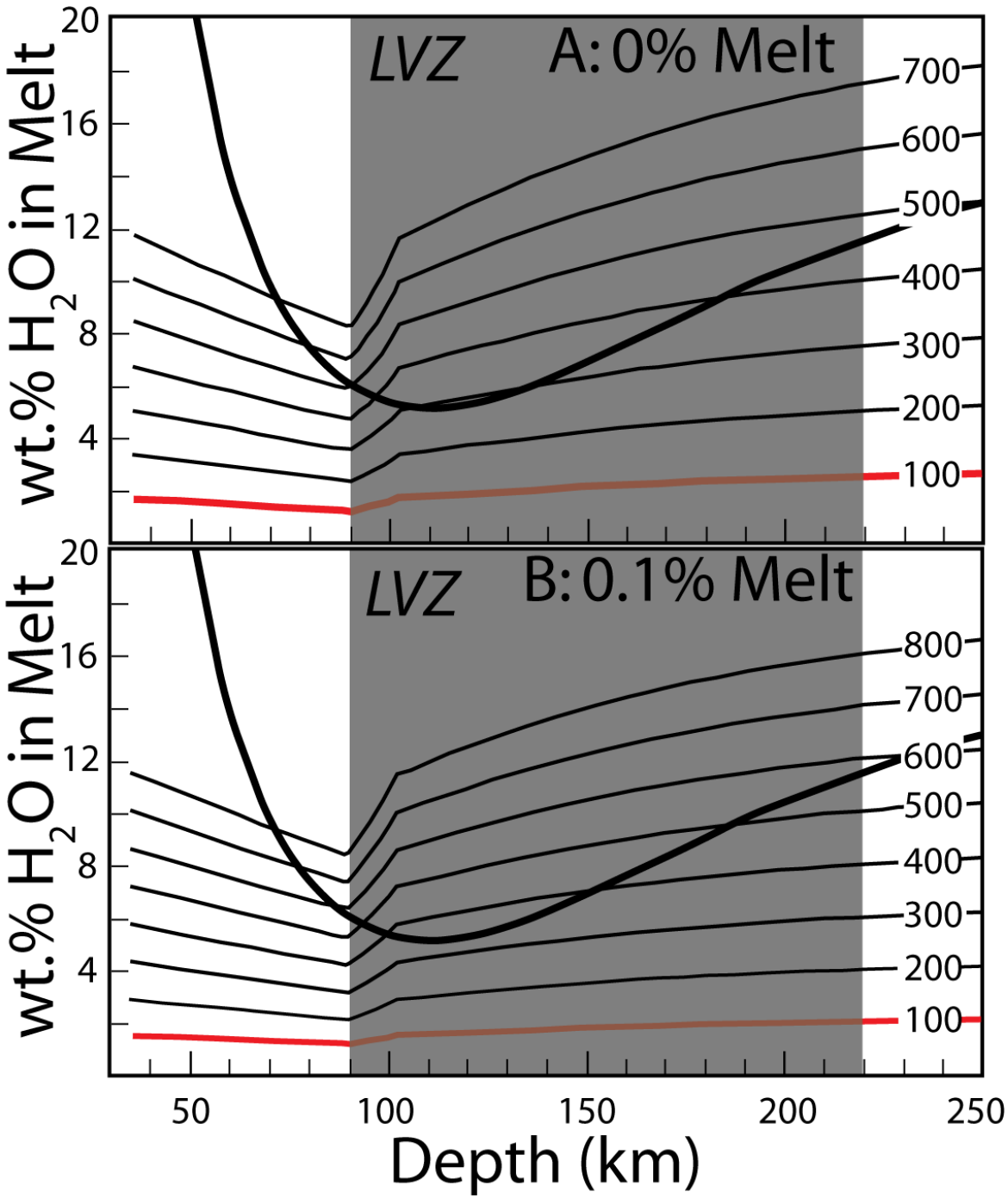
$$T = \frac{T^{\text{fusion}}_{\text{peridotite}}}{\left(1 - \frac{R}{\Delta S^{\text{fusion}}_{\text{peridotite}}} \ln\left(1 - X^{\text{melt}}_{OH^-}\right)\right)}$$



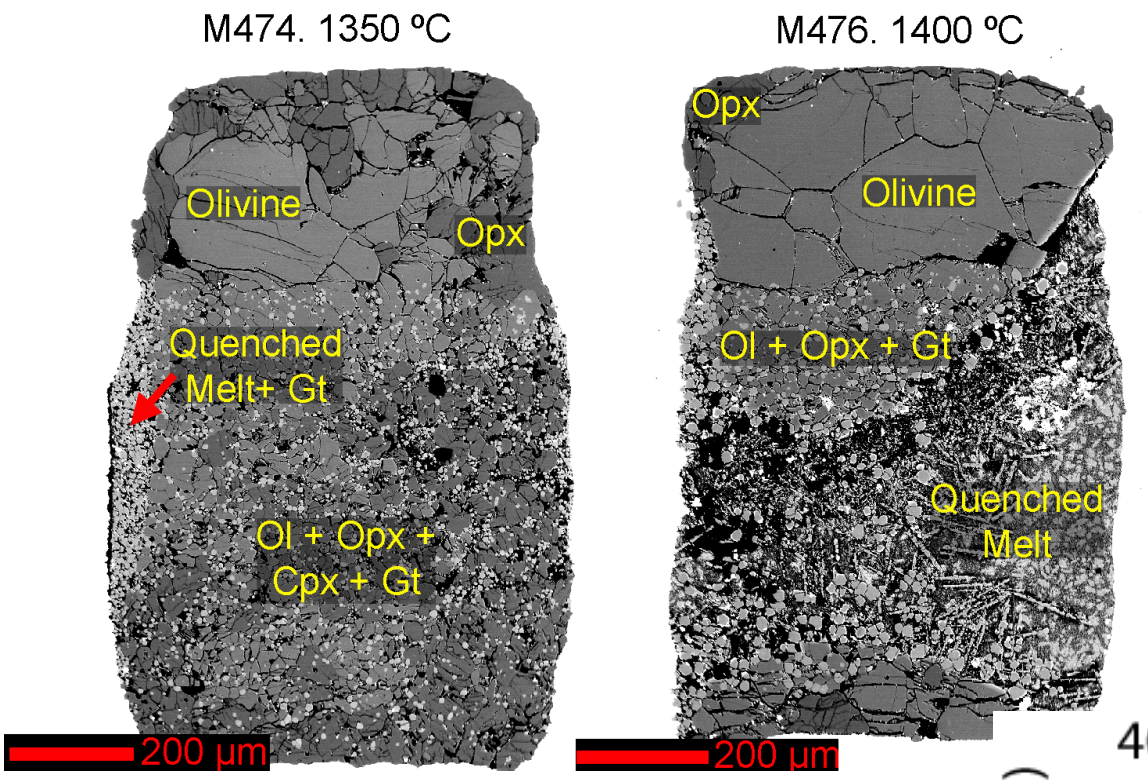


Tenner et al. 2012

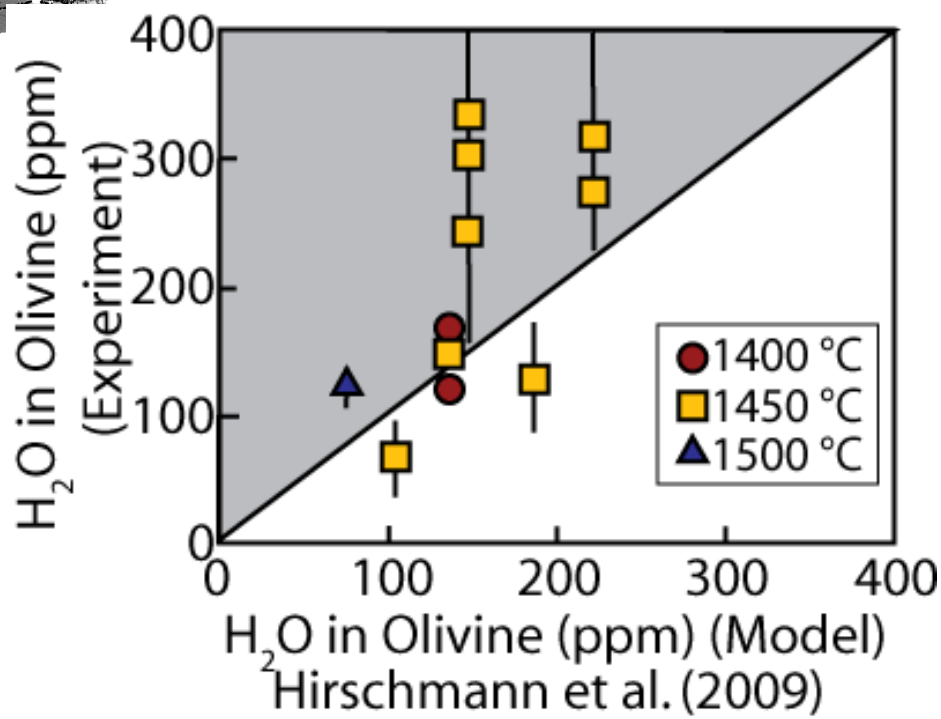
Hirose and Kawamoto 1995, Hirose 1997, Kawamoto and Holloway 1997, Gaetani and Grove 1998, Hall 1999, Balta et al. 2011

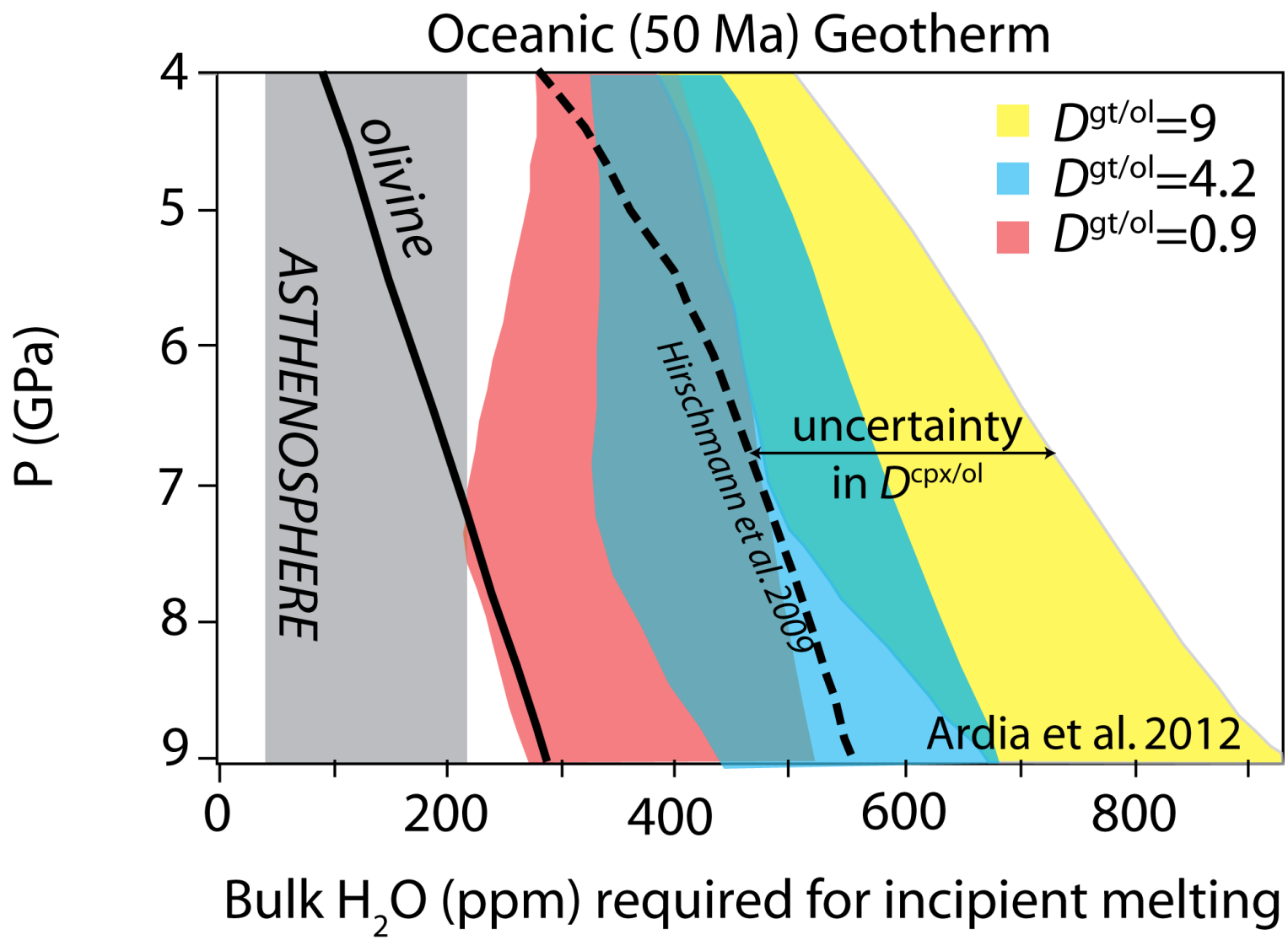

LVZ
A: 0% Melt
700
600
500
400
300
200
100
LVZ
B: 0.1% Melt
800
700
600
500
400
300
200
100
wt.% H_2O in Melt
20
16
12
8
4
50
100
150
200
250
Depth (km)

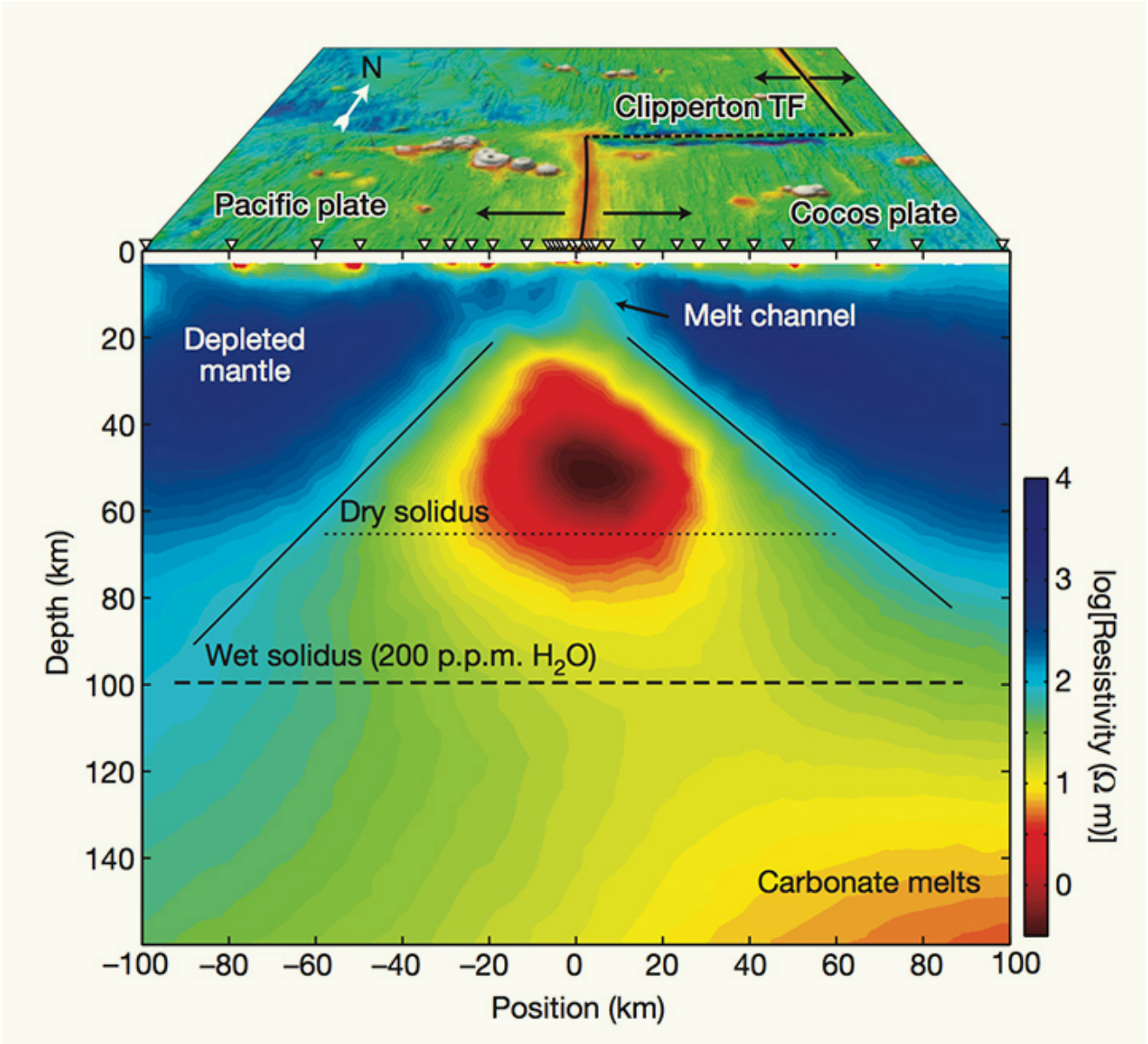
H_2O Storage Capacity Experiments 5-13 GPa



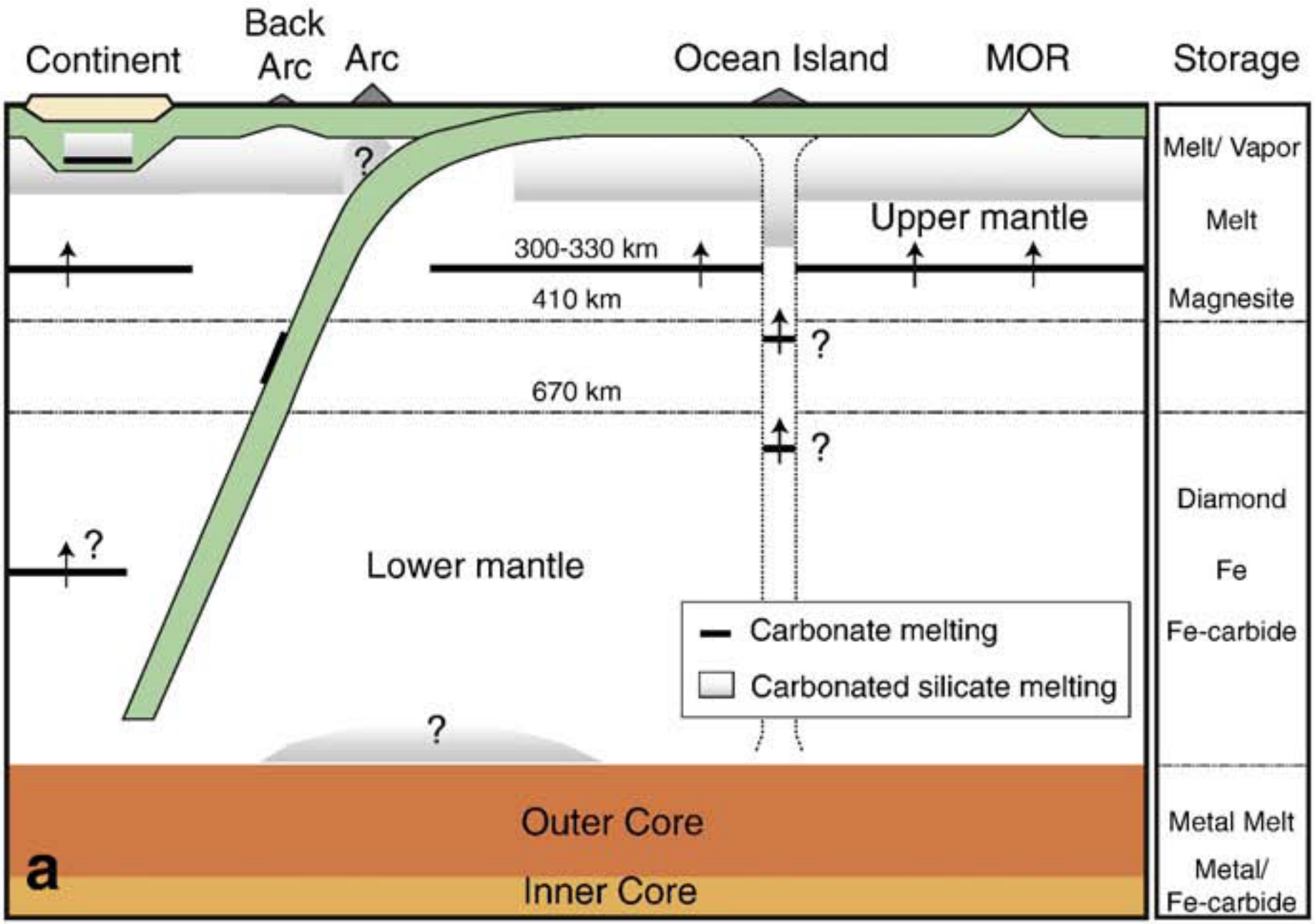
Tenner et al. 2012
Ardia et al. 2013

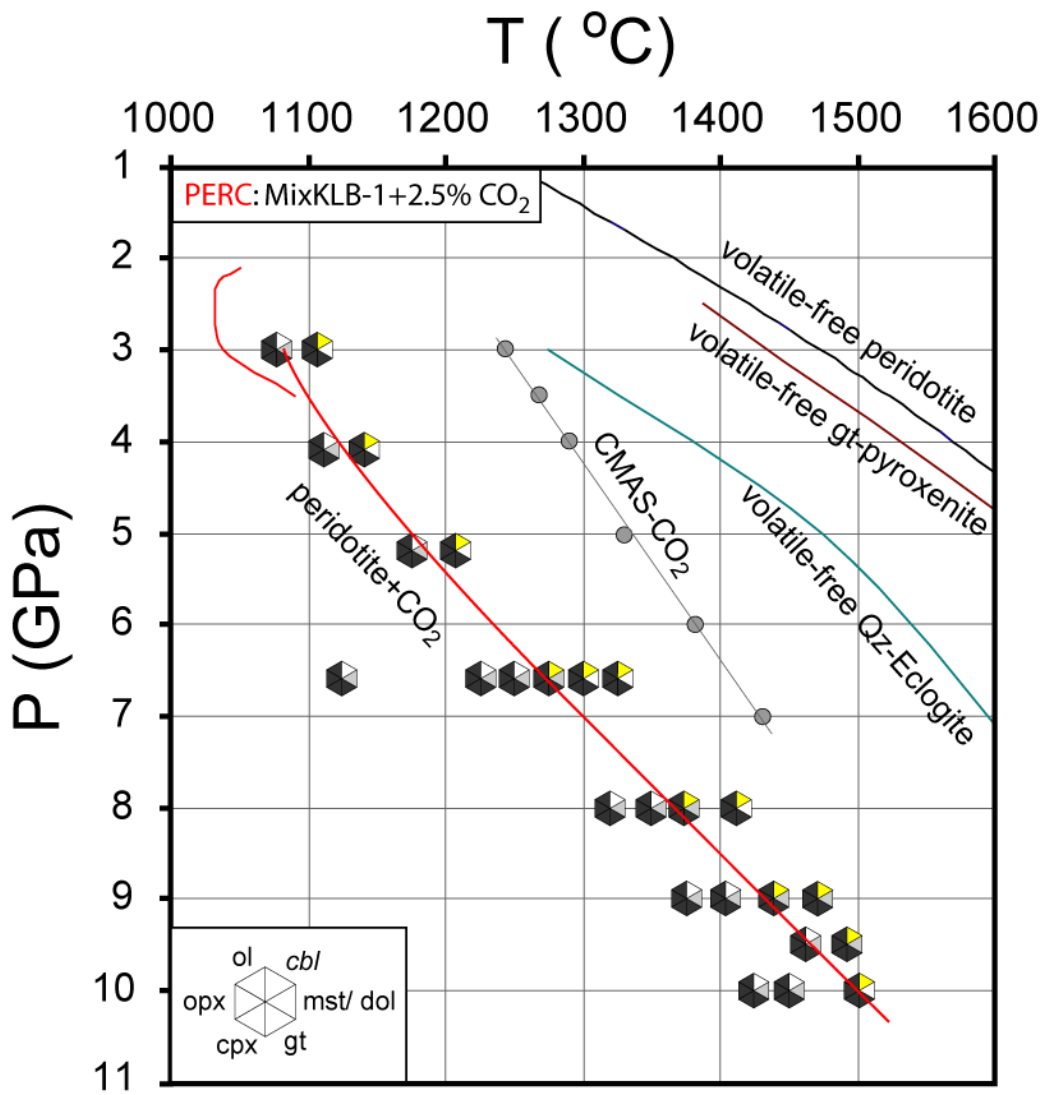


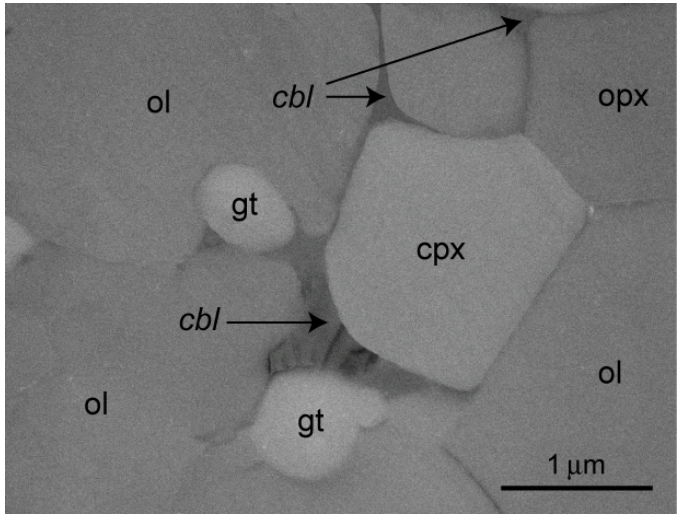

Oceanic (50 Ma) Geotherm
P (GPa)
4
5
6
7
8
9
0
200
400
600
800
Bulk H_2O (ppm) required for incipient melting
ASTHENOSPHERE
olivine
Hirschmann et al. 2009
uncertainty
in $D^{cpx/ol}$
Ardia et al. 2012
$D^{gt/ol}$=9
$D^{gt/ol}$=4.2
$D^{gt/ol}$=0.9



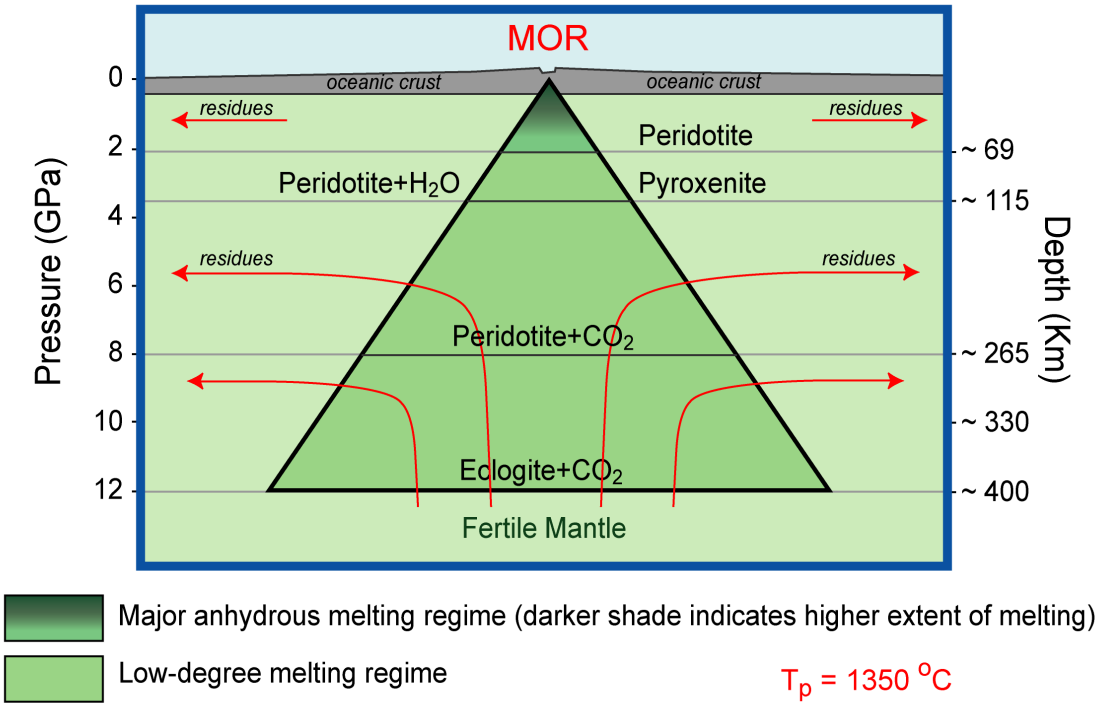
Key et al., 2013

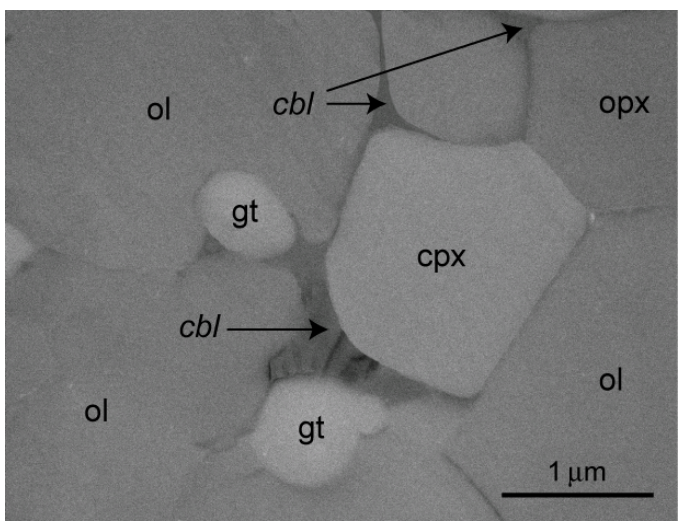

Continent
Back Arc
Arc
Ocean Island
MOR
Storage
Melt/ Vapor
Melt
Magnesite
Diamond
Fe
Fe-carbide
Metal Melt
Metal/ Fe-carbide
Upper mantle
300-330 km
410 km
670 km
Lower mantle
Carbonate melting
Carbonated silicate melting
Outer Core
Inner Core
a



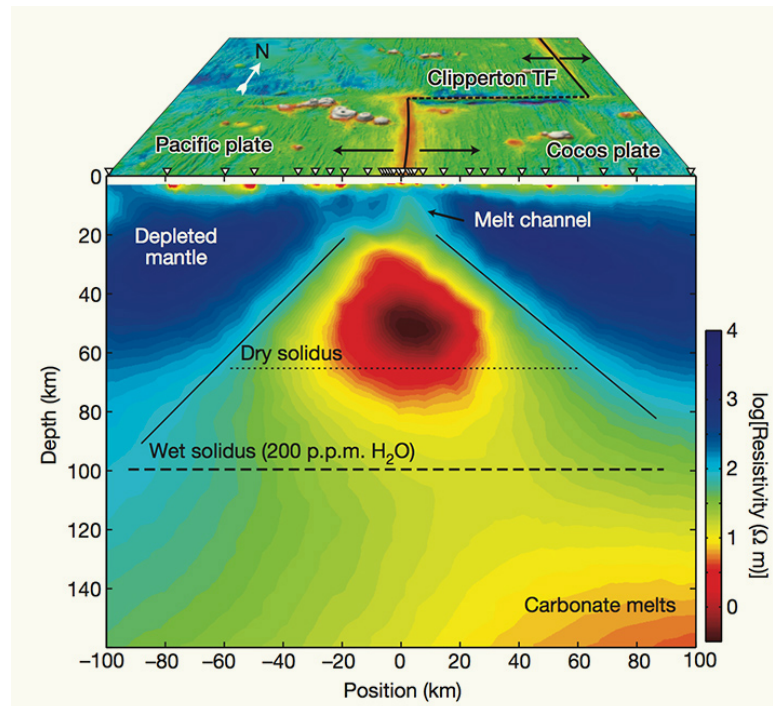


Dasgupta+
Hirschmann, 2006

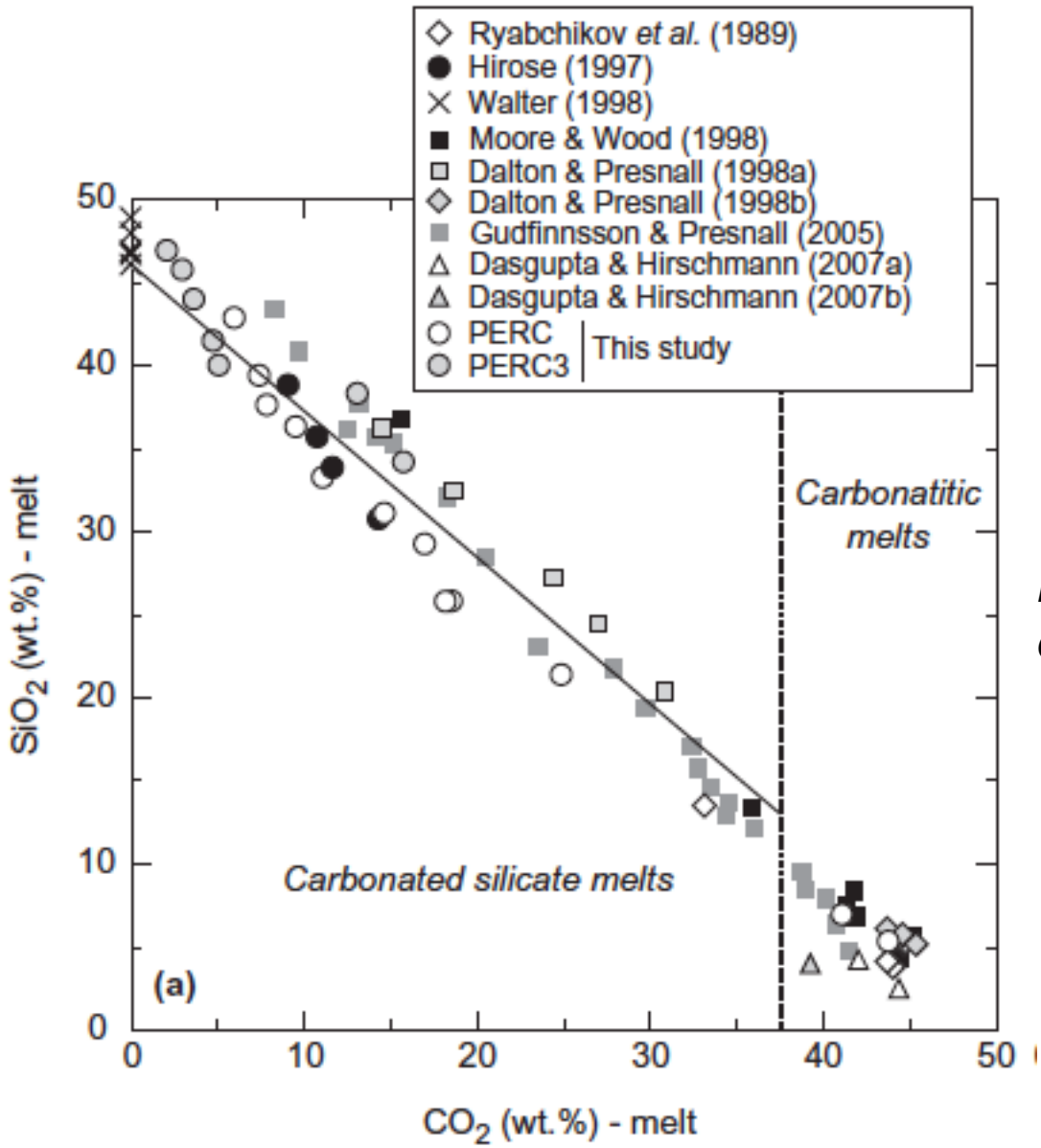




Dasgupta+Hirschmann, 2006

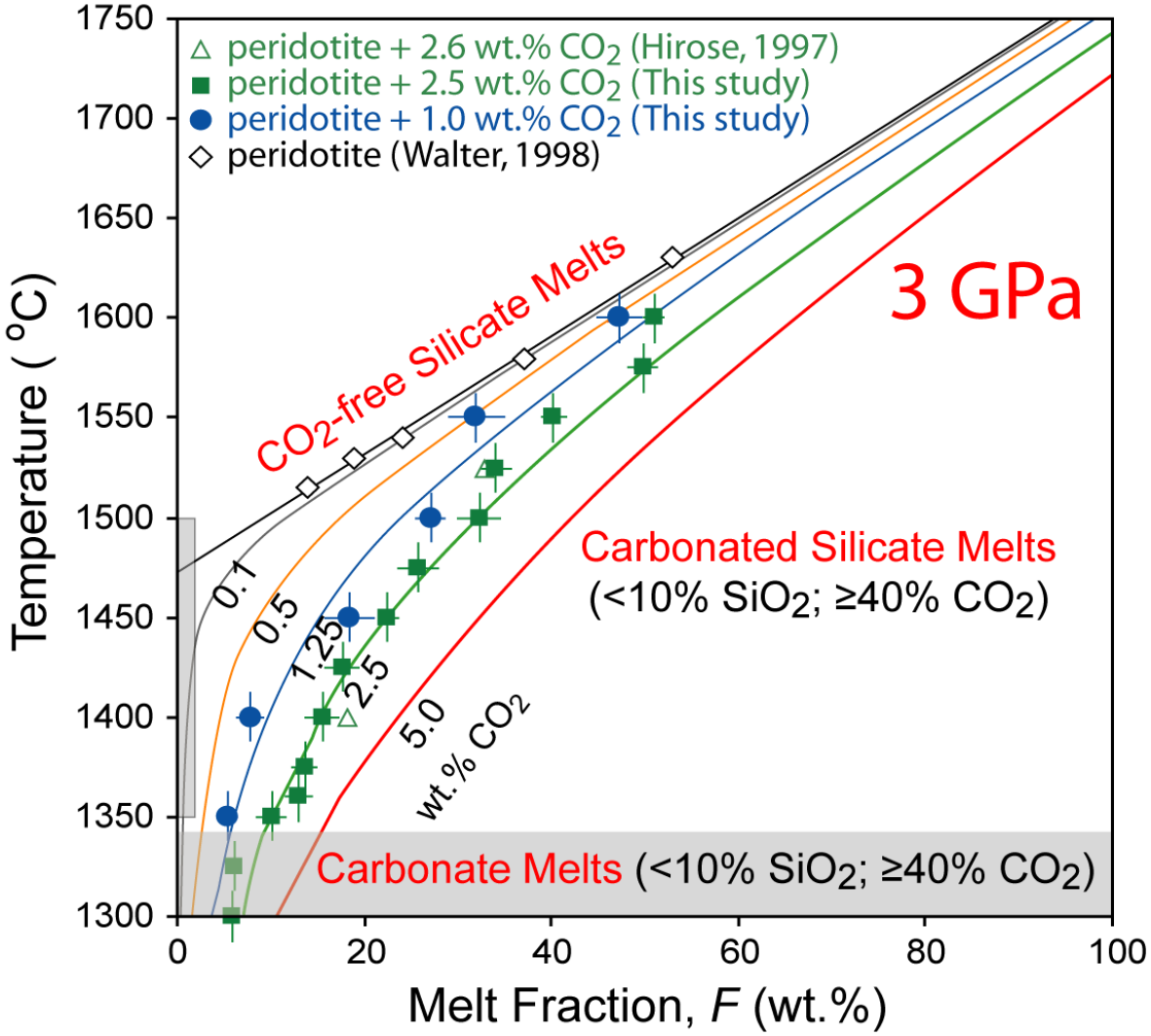


Key et al., 2013

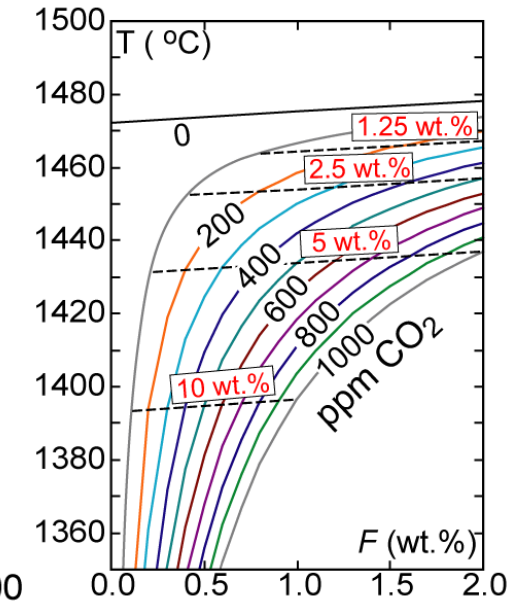


Dasgupta et al. 2007

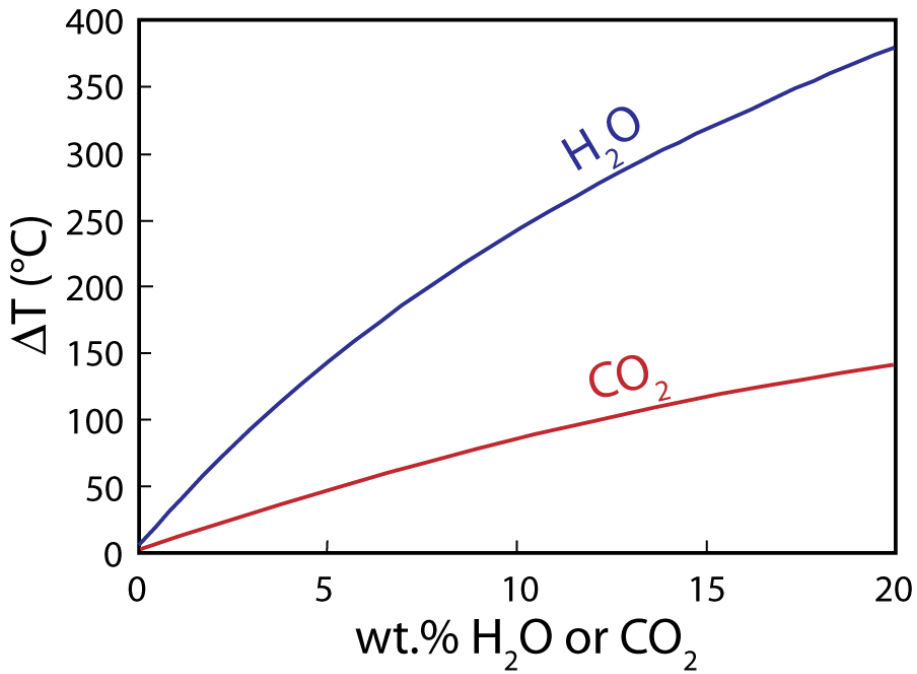
Experimental determination of enhanced peridotite melting owing to CO_2.



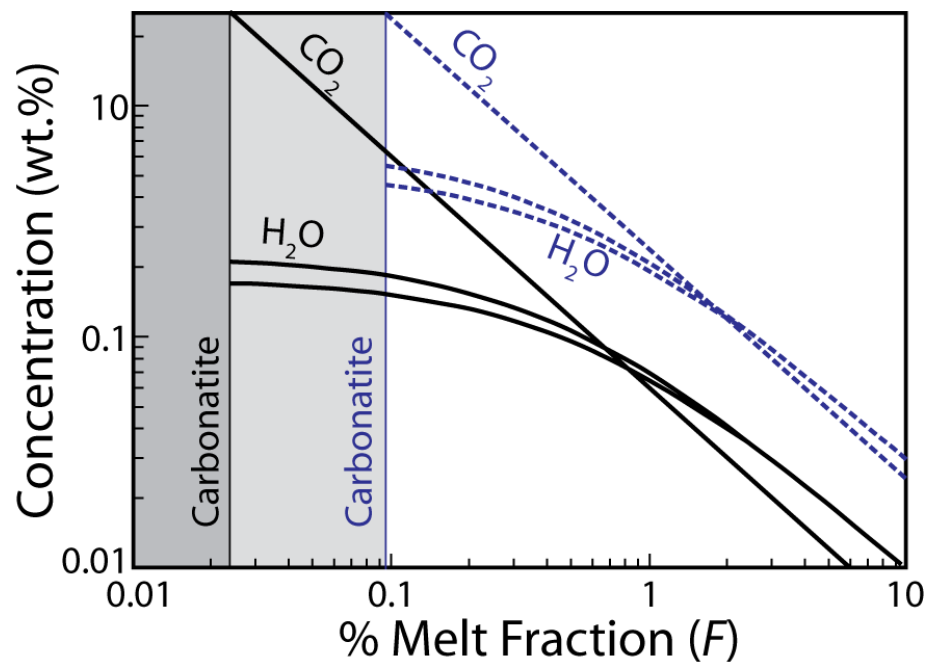
Dasgupta et al. 2007

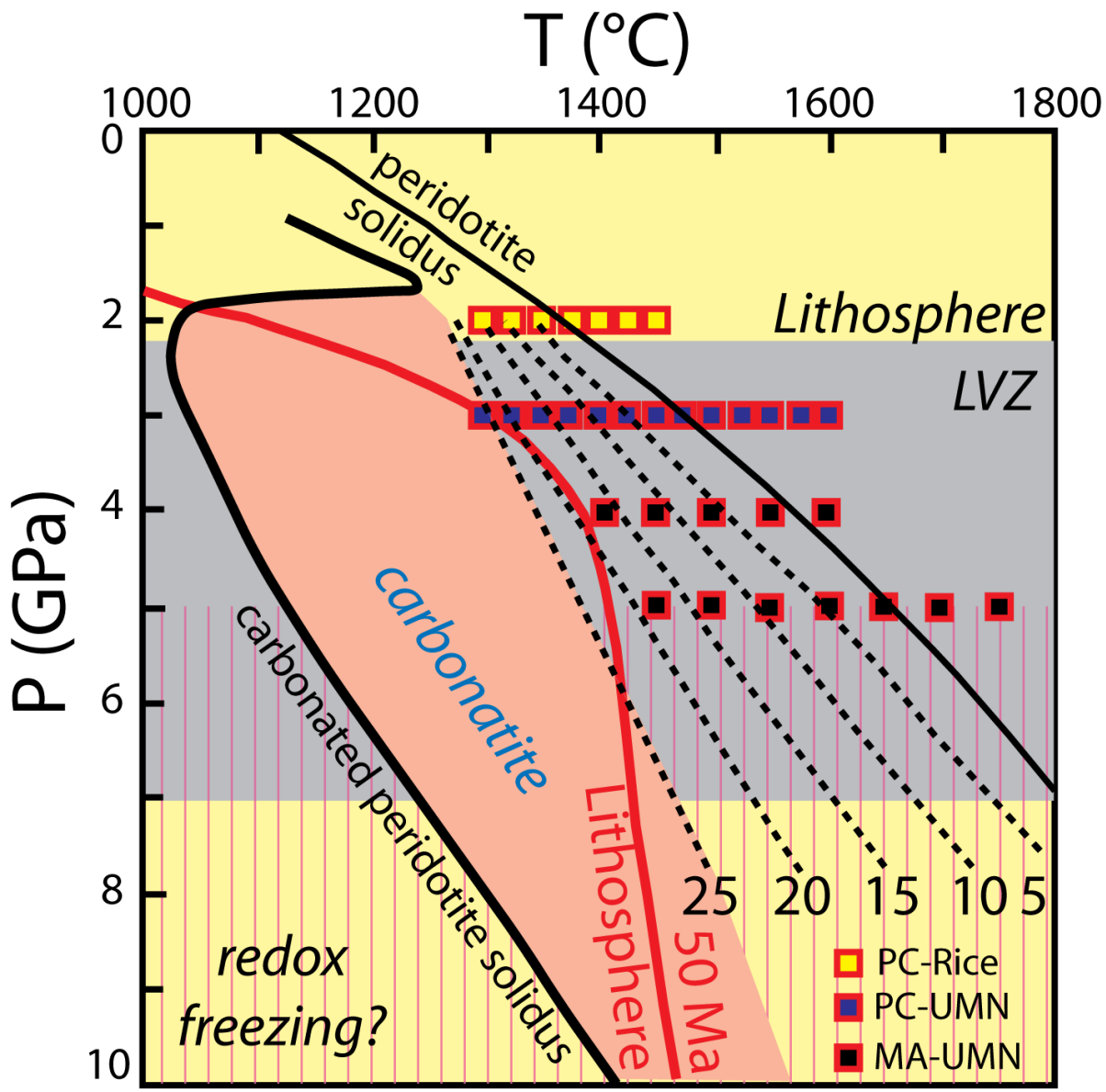


CO_2 has a smaller freezing-point effect than H_2O…



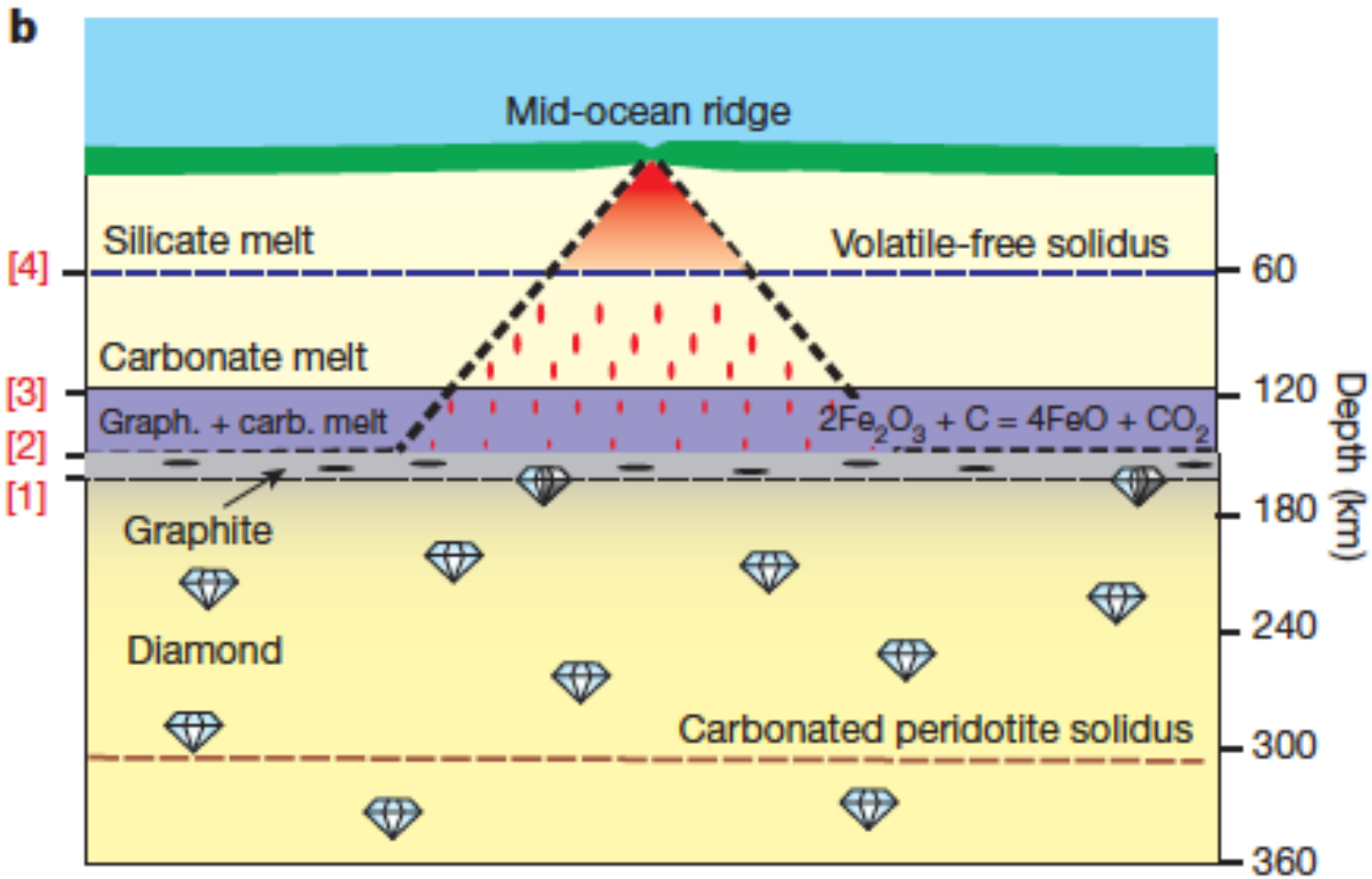
…but is much more enriched in near-solidus melts



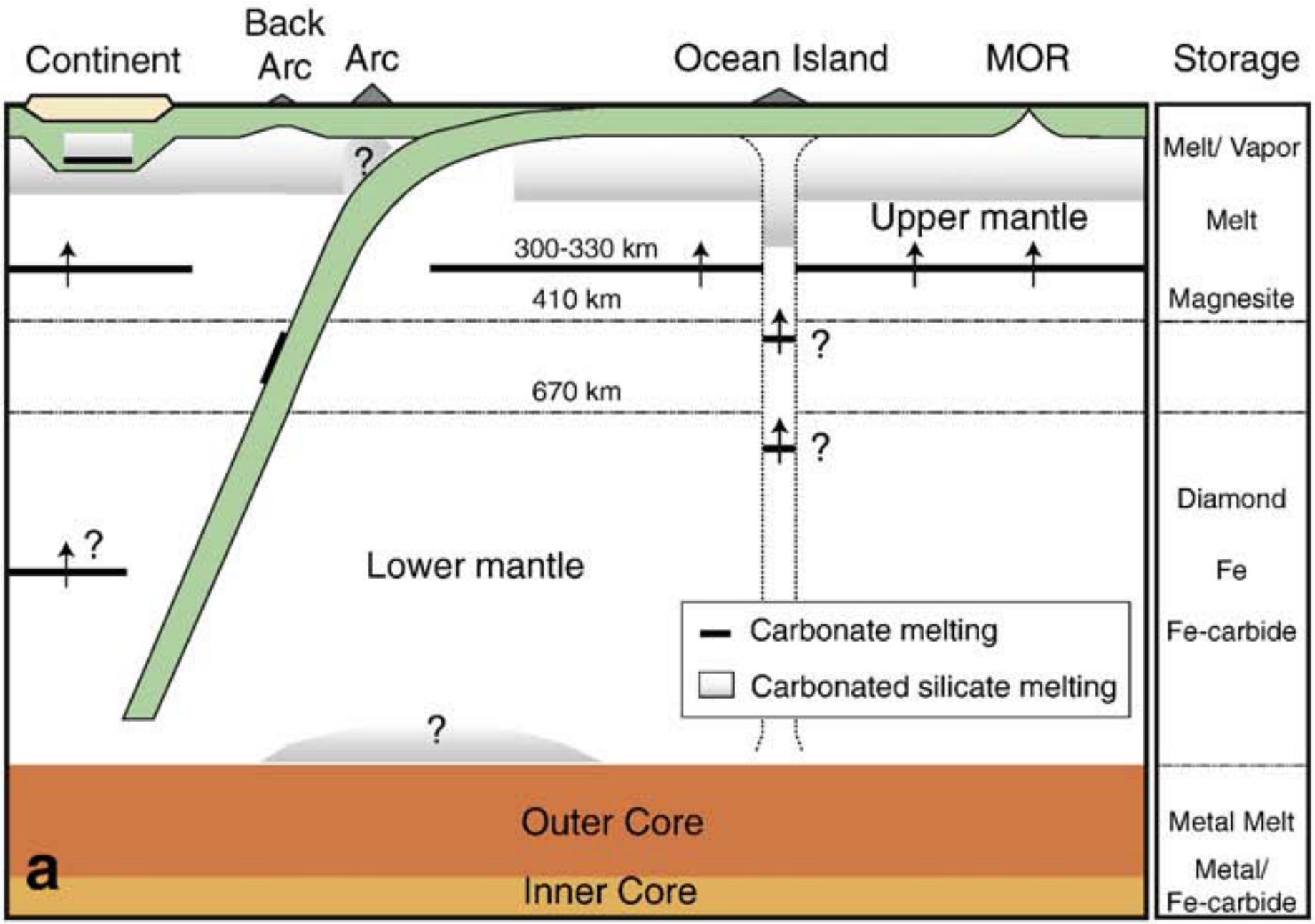


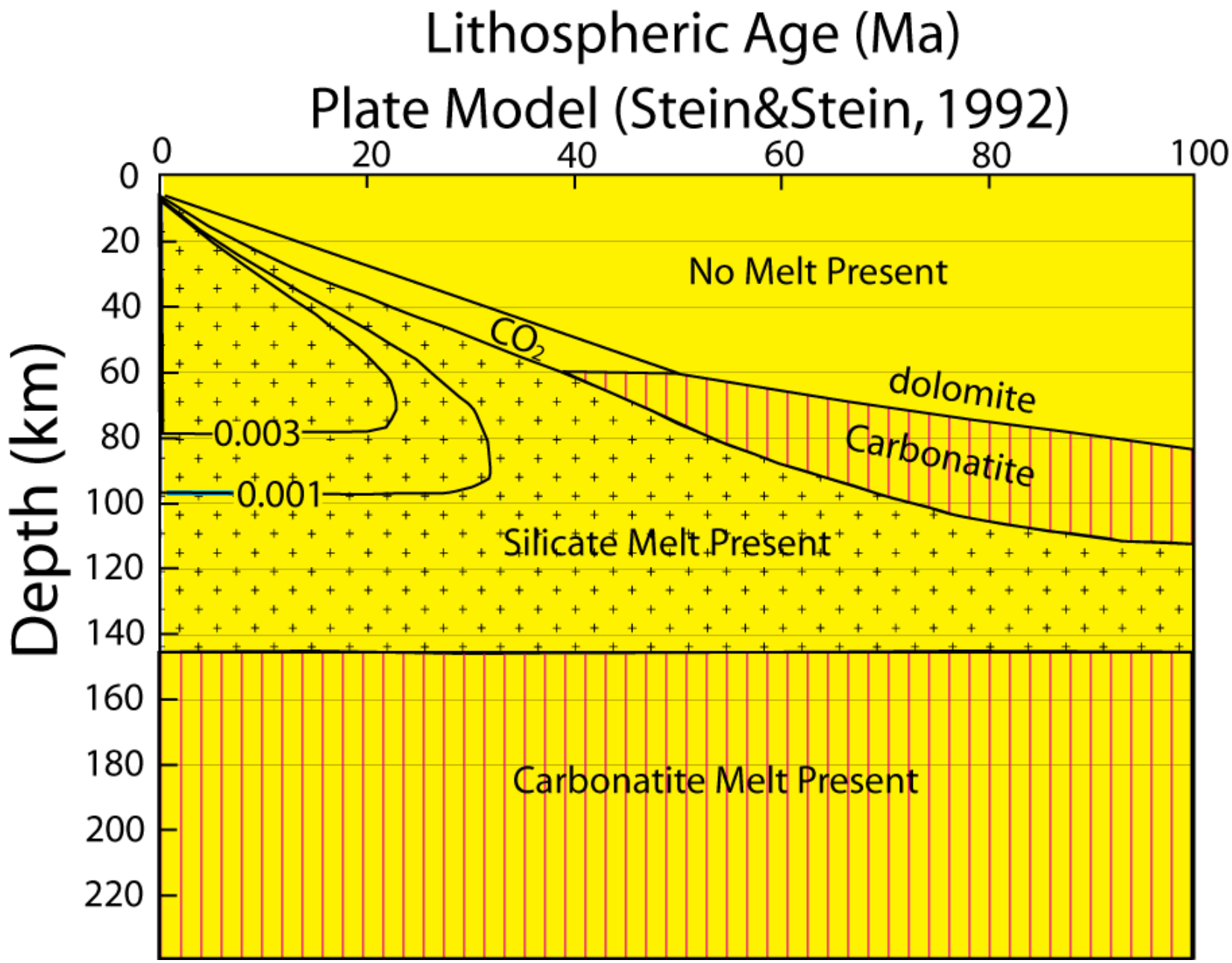
Dasgupta et al. 2007, 2013

At some depth, carbonate-rich melts become unstable and are replaced by reduced solid or liquid C-rich phases



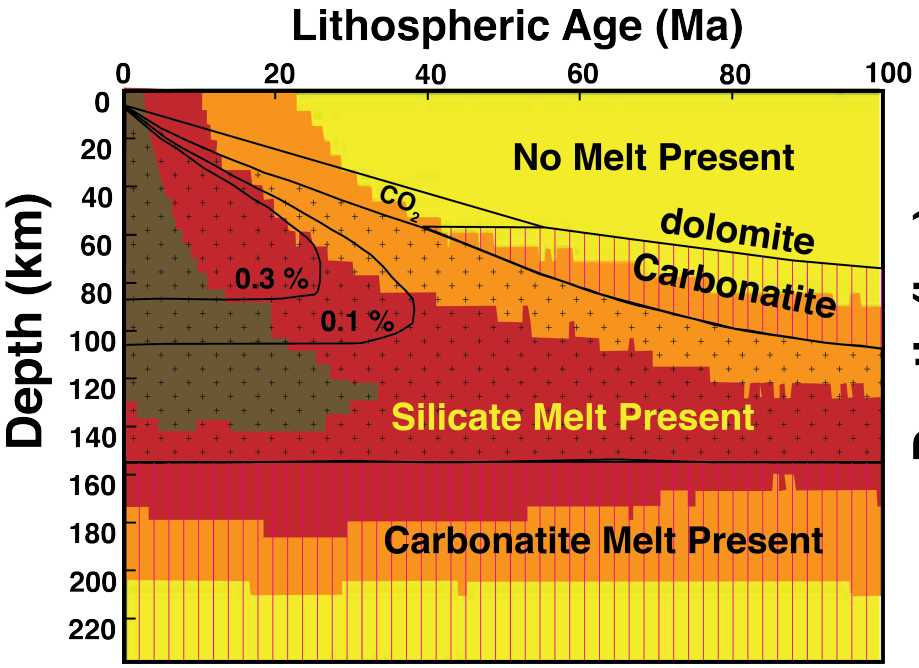
Stagno et al. 2013


Continent
Back Arc
Arc
Ocean Island
MOR
Storage
Melt/ Vapor
Melt
Magnesite
Diamond
Fe
Fe-carbide
Metal Melt
Metal/ Fe-carbide
Upper mantle
300-330 km
410 km
670 km
Lower mantle
Carbonate melting
Carbonated silicate melting
Outer Core
Inner Core
a

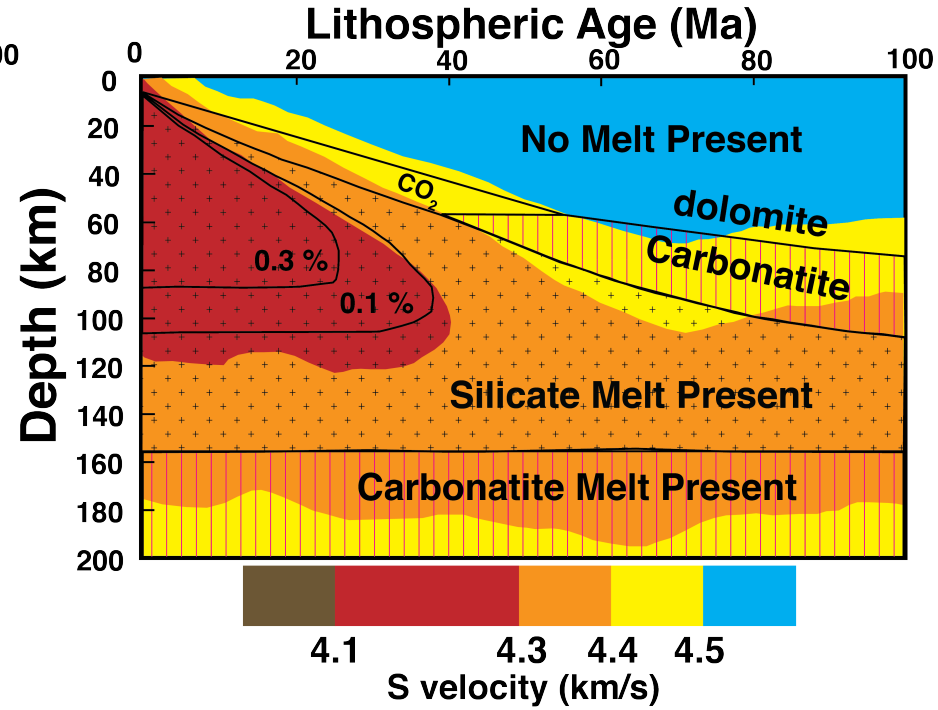


Depleted Mantle 100 ppm H_2O
60 ppm CO_2

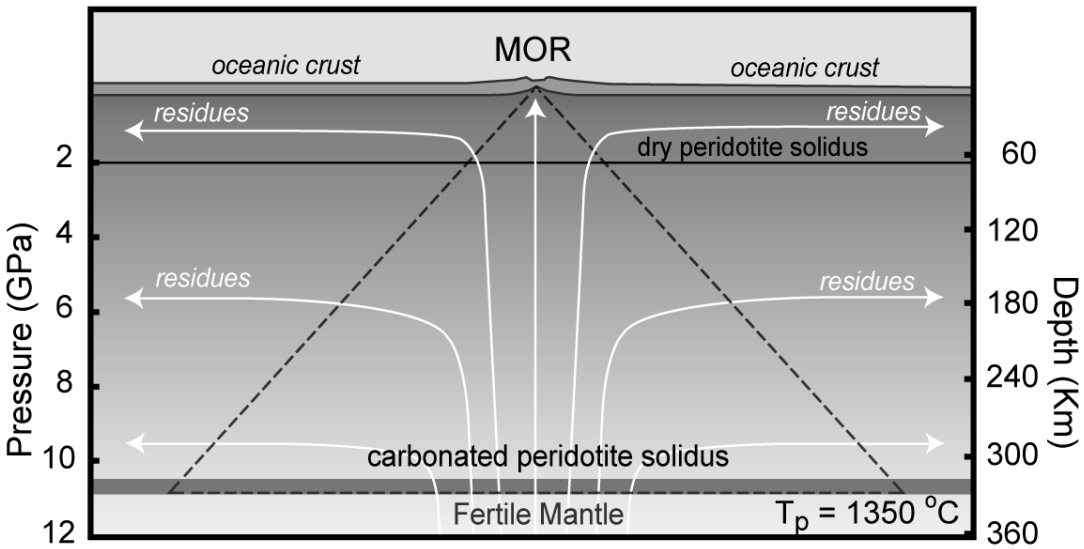
Hirschmann, 2010

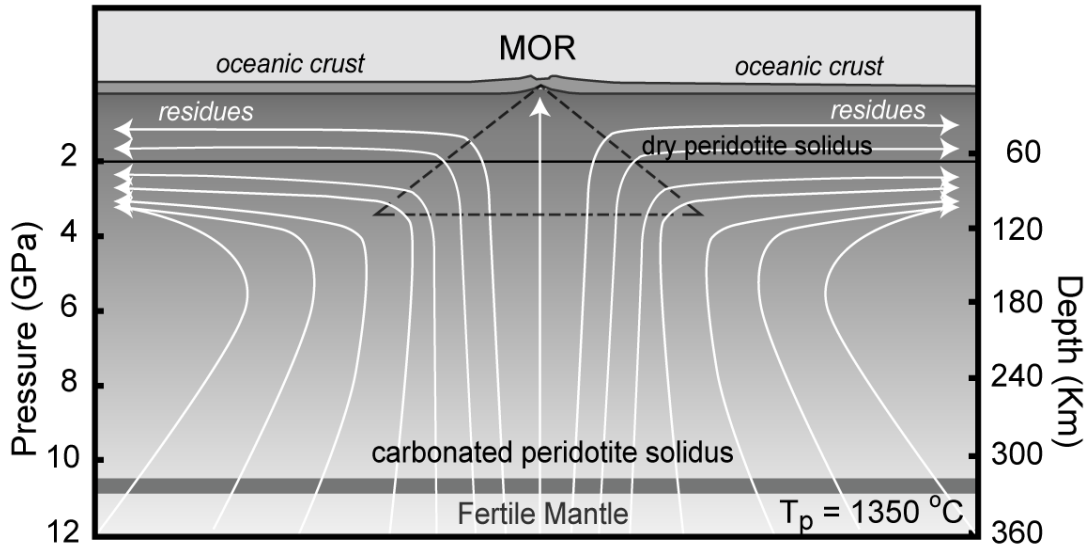


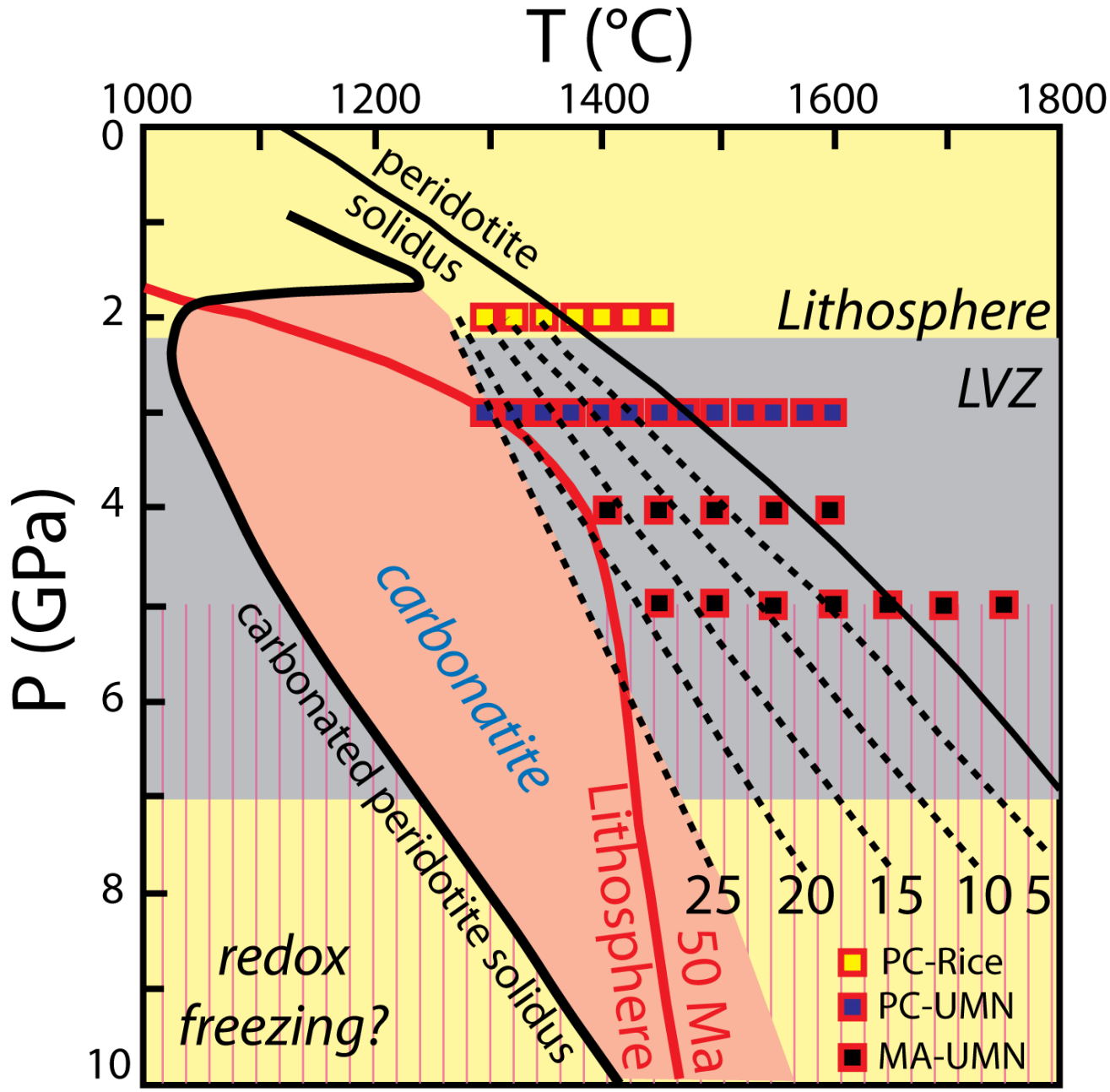
Priestly and McKenzie, 2006



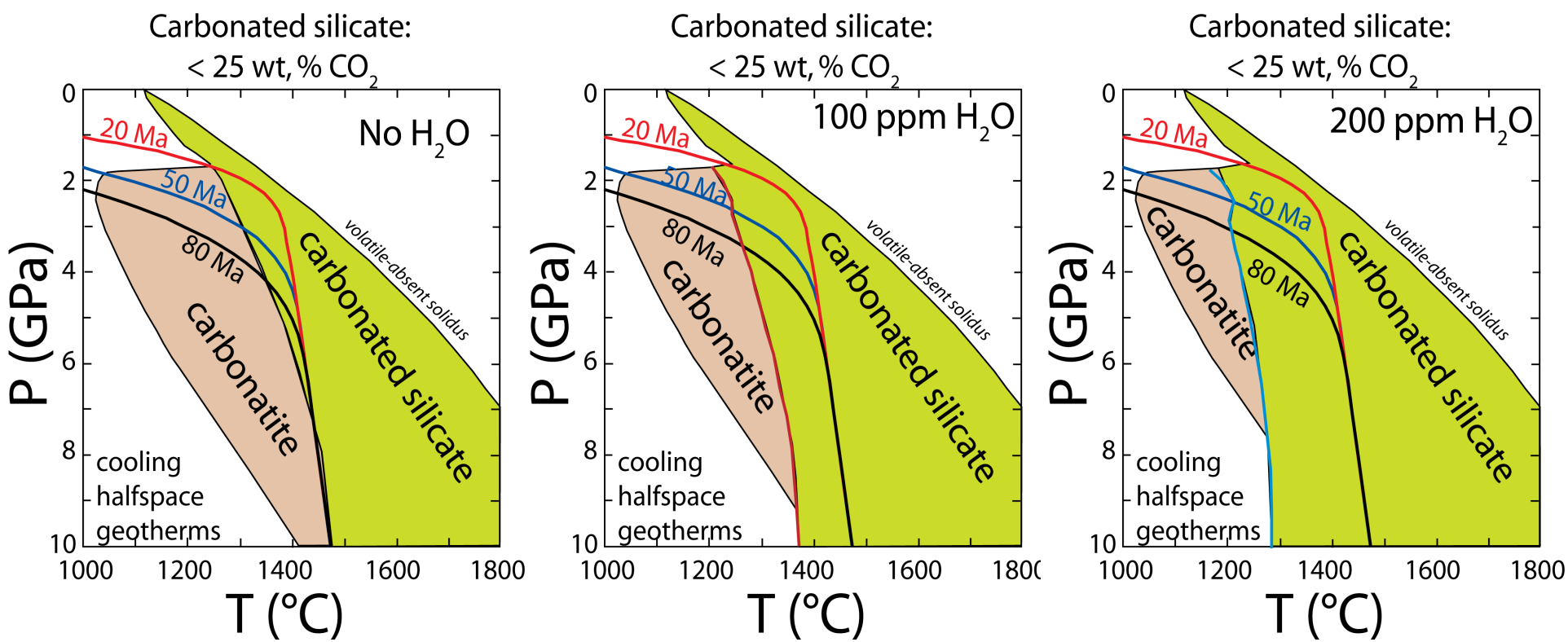
Ritzwoller et al. 2004


MOR
oceanic crust
oceanic crust
residues
residues
dry peridotite solidus
residues
residues
carbonated peridotite solidus
Fertile Mantle
T_p = 1350 °C
Pressure (GPa)
2
4
6
8
10
12
Depth (Km)
60
120
180
240
300
360


MOR
oceanic crust
oceanic crust
residues
residues
dry peridotite solidus
carbonated peridotite solidus
Fertile Mantle
T_p = 1350 °C
Pressure (GPa)
2
4
6
8
10
12
Depth (Km)
60
120
180
240
300
360

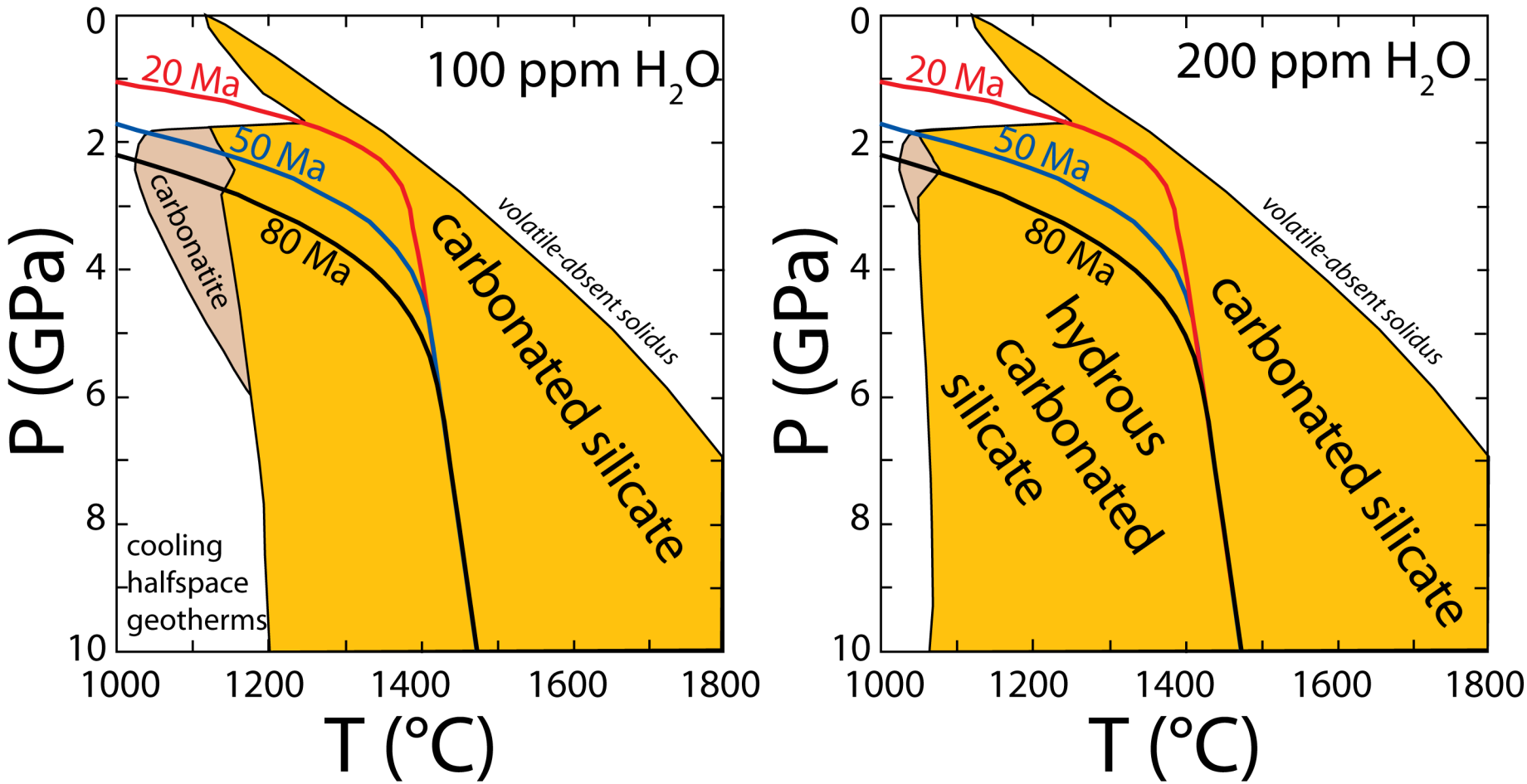


Dasgupta et al. 2007, 2013

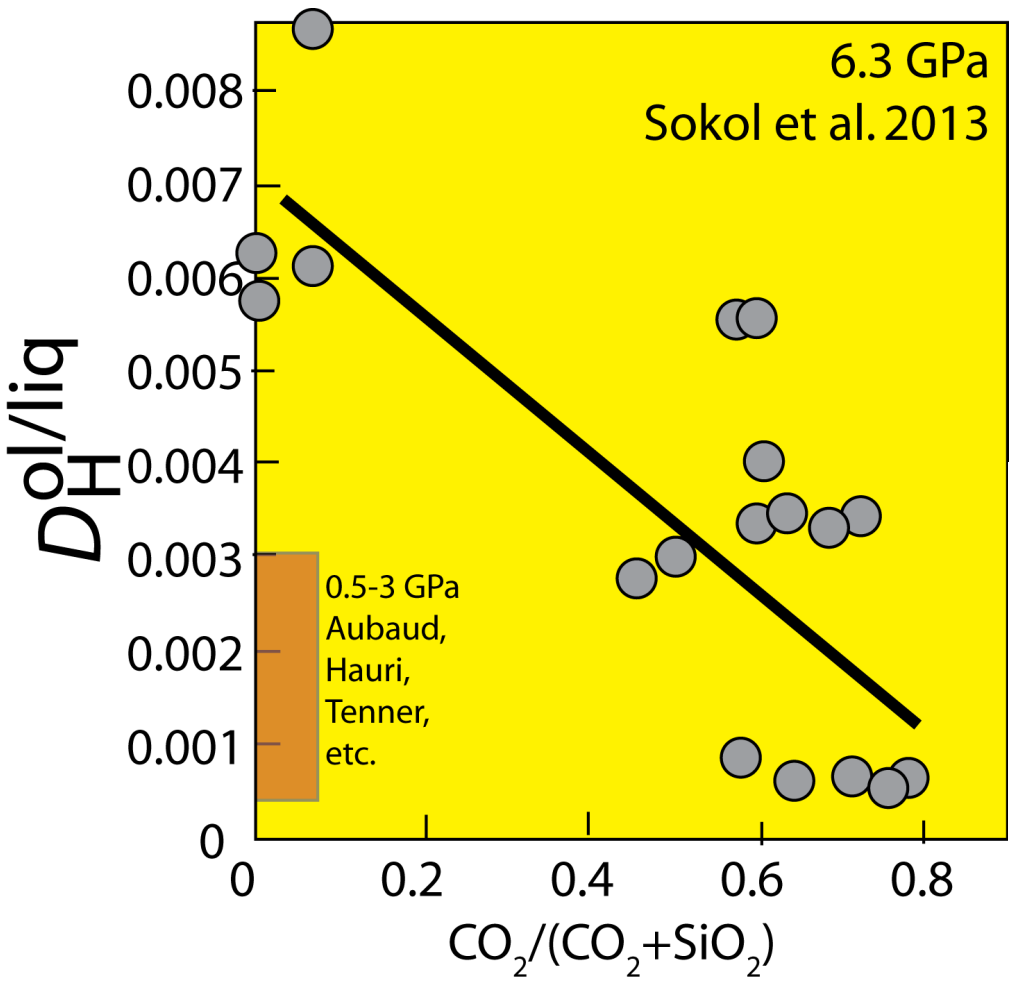


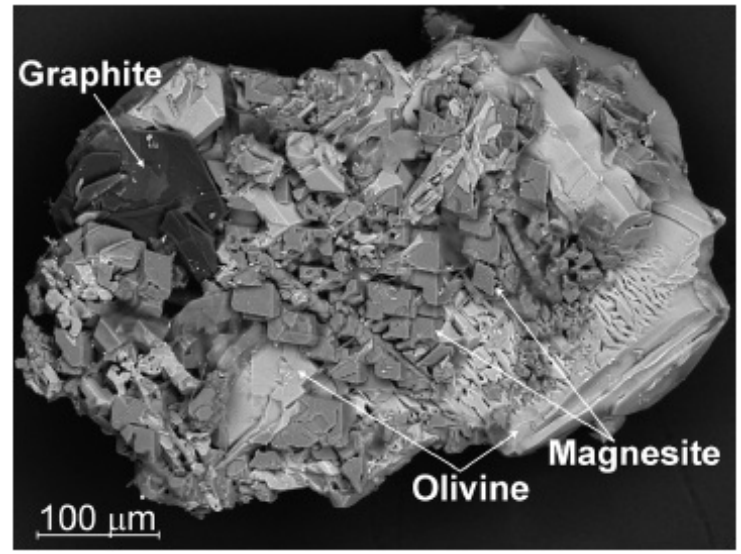
*This is based on the *assumption* that H_2O stabilizes silicate melt relative to carbonatite. This needs to be tested experimentally.*

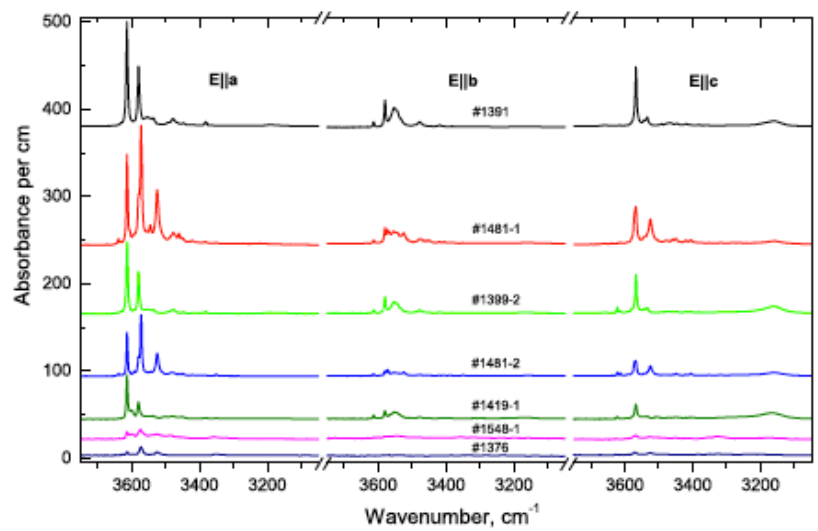
If CO_2-rich melts are highly efficient at extracting H_2O from minerals



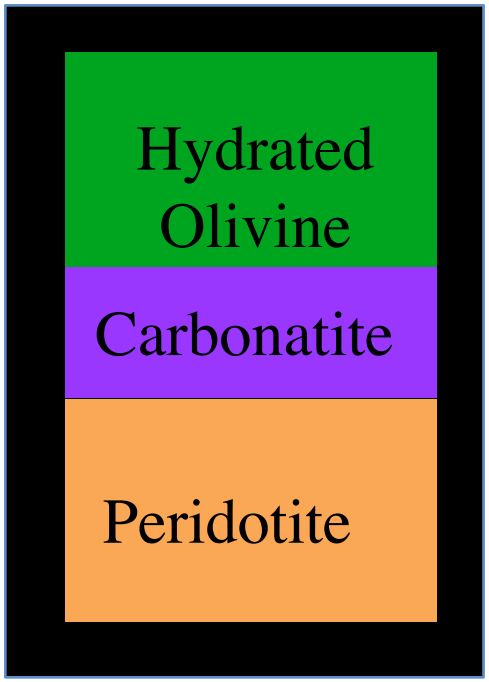
What if Peridotite+H_2O+CO_2 is not simply additive from Peridotite+H_2O and peridotite+CO_2?







Effect of CO_2 on H_2O storage capacity in olivine:
6 GPa, 1400 °C, 1-4 hours



Fo89.6 + 15 wt% H_2O

Dasgupta et al. (2007)
6.6 GPa composition

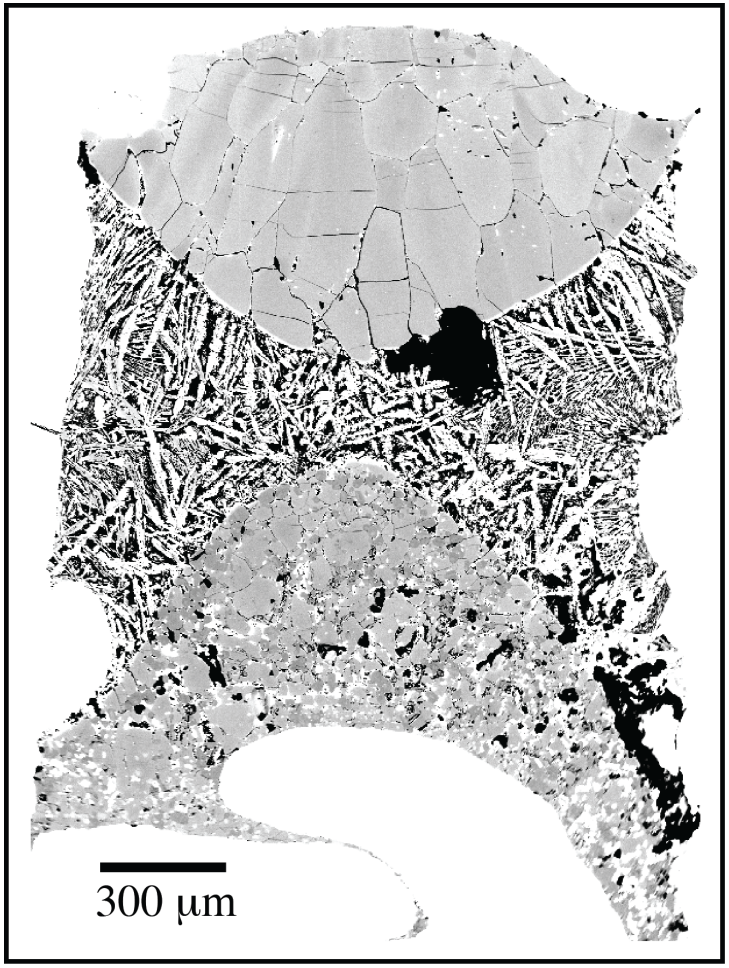
KLB-1 oxide mix
(nominally dry)

Fe-doped $Au_{75}Pd_{25}$

- Grow big olivines
- Mitigate H_2O, Fe Loss
- Control molar $CO_2/(H_2O+CO_2) = X(CO_2)$

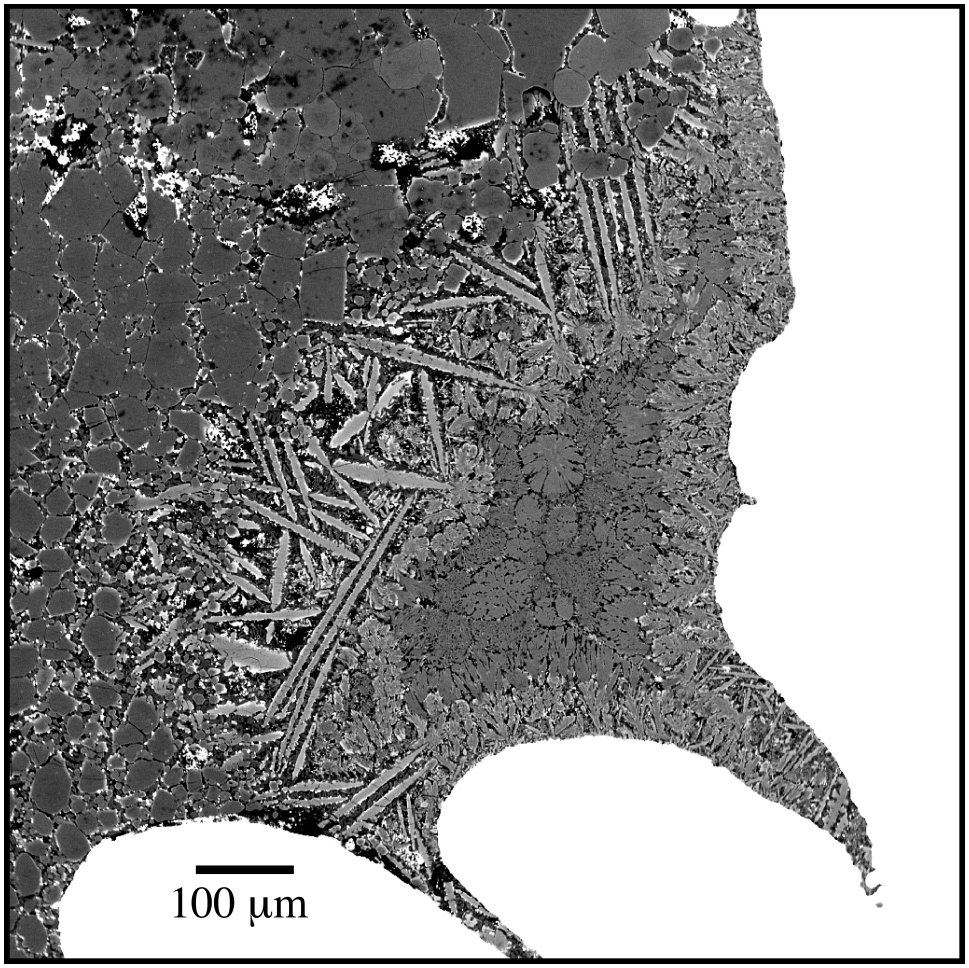
Effect of CO_2 on H_2O storage capacity in olivine

$X(CO_2) = 0$



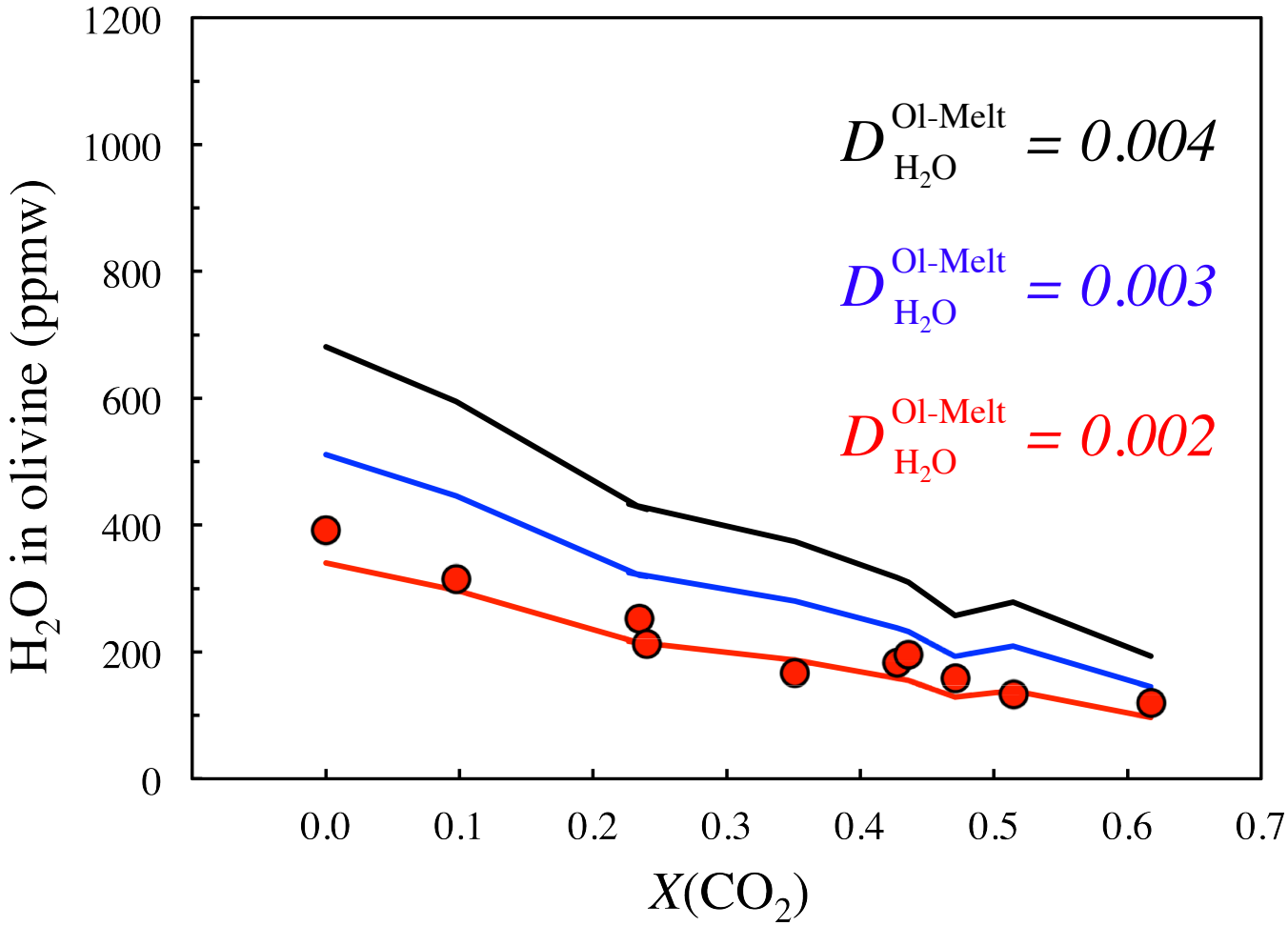
Olivine (Fo91), opx,
grt, silicate melt

$X(CO_2) = 0.436$



Olivine (Fo89),
grt, carbonated silicate melt

Modeling/Conclusions



- CO_2 reduces fH_2O ➔ reduces C_{H2O} in olivine
- *D* does not change as a function of $X(CO_2)$
- Models of Hirschmann (2010) won't change much