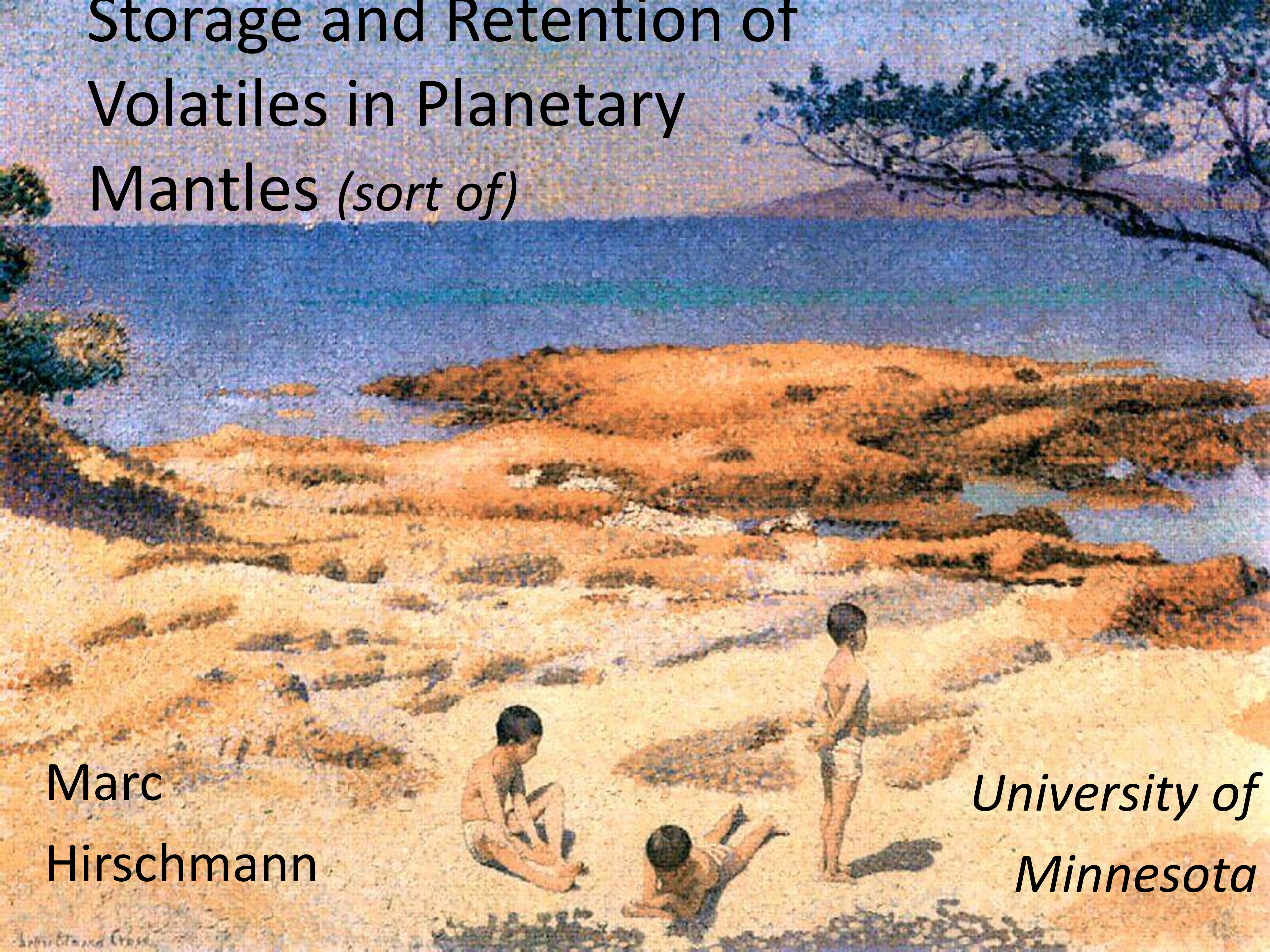
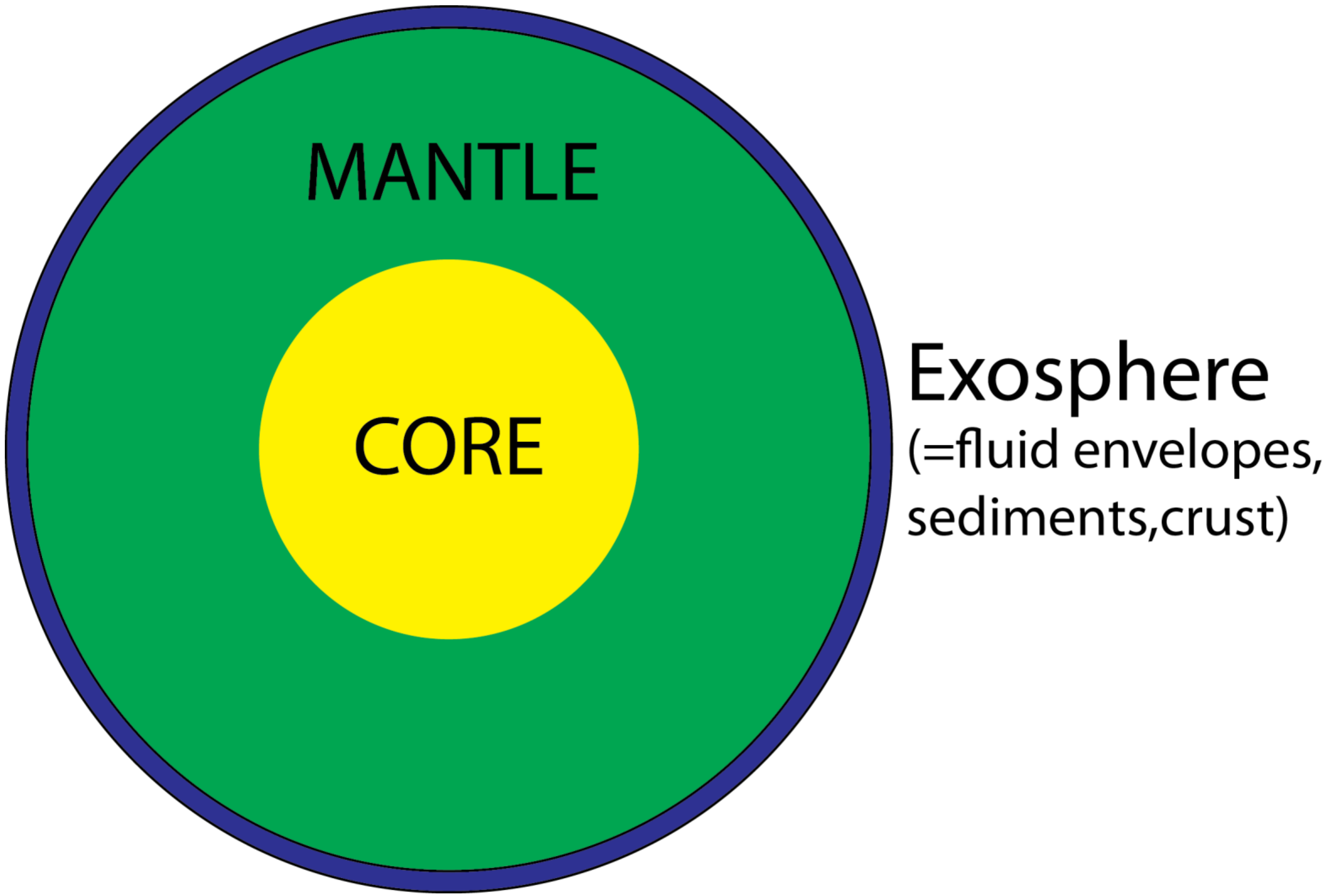
Storage and Retention of Volatiles in Planetary Mantles *(sort of)*



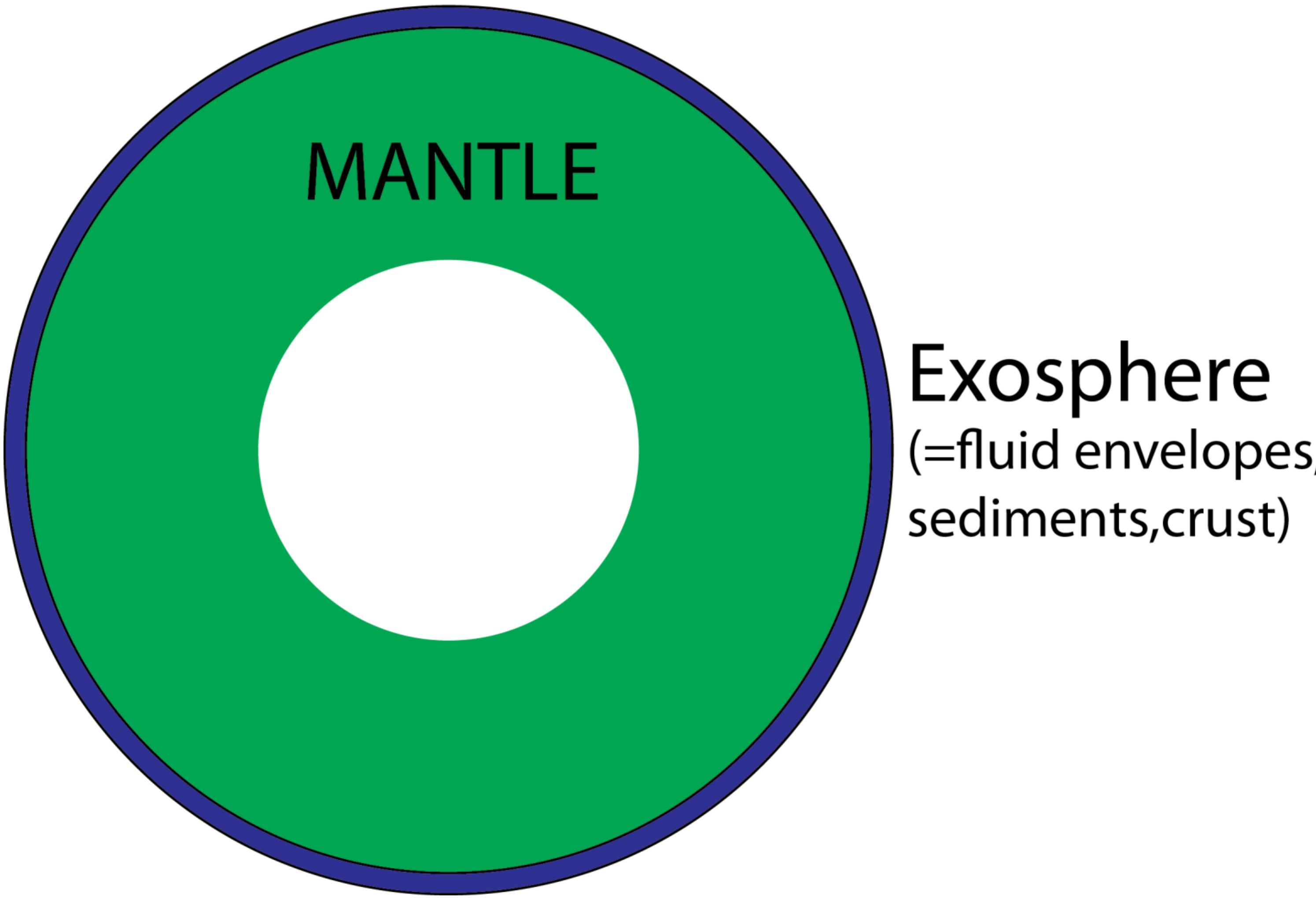
Marc Hirschmann

University of Minnesota

- What is the inventory of volatiles (H,C,N,S) in the bulk silicate Earth?
- How do these compare to potential cosmochemical sources?
- How does this constrain processes of volatile acquisition during accretion, differentiation, loss?


MANTLE
CORE
Exosphere
(=fluid envelopes,
sediments,crust)

“Bulk Silicate Earth” (BSE)

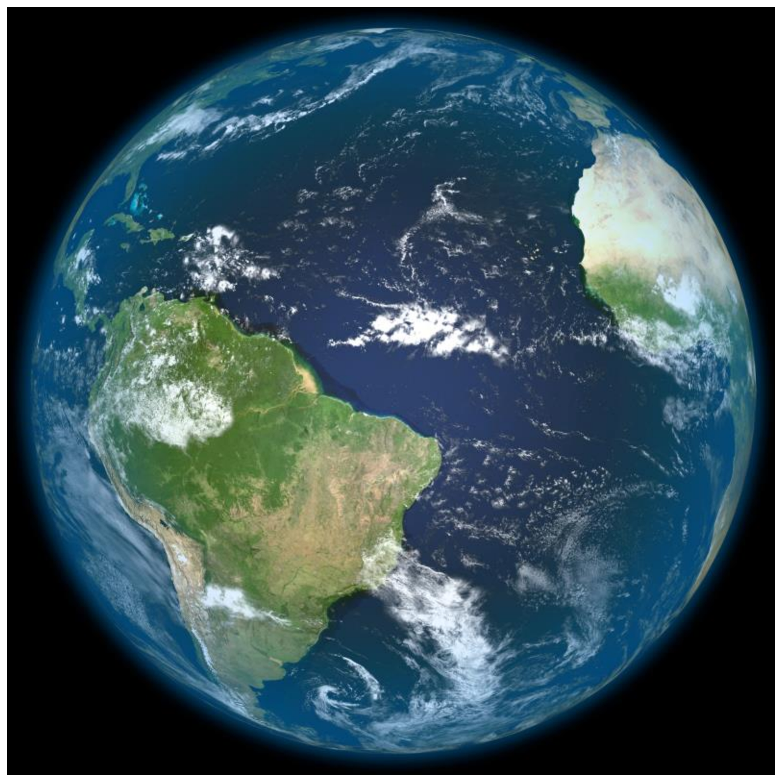


Hydrogen in the Exosphere

(Exosphere=everything above the Moho)

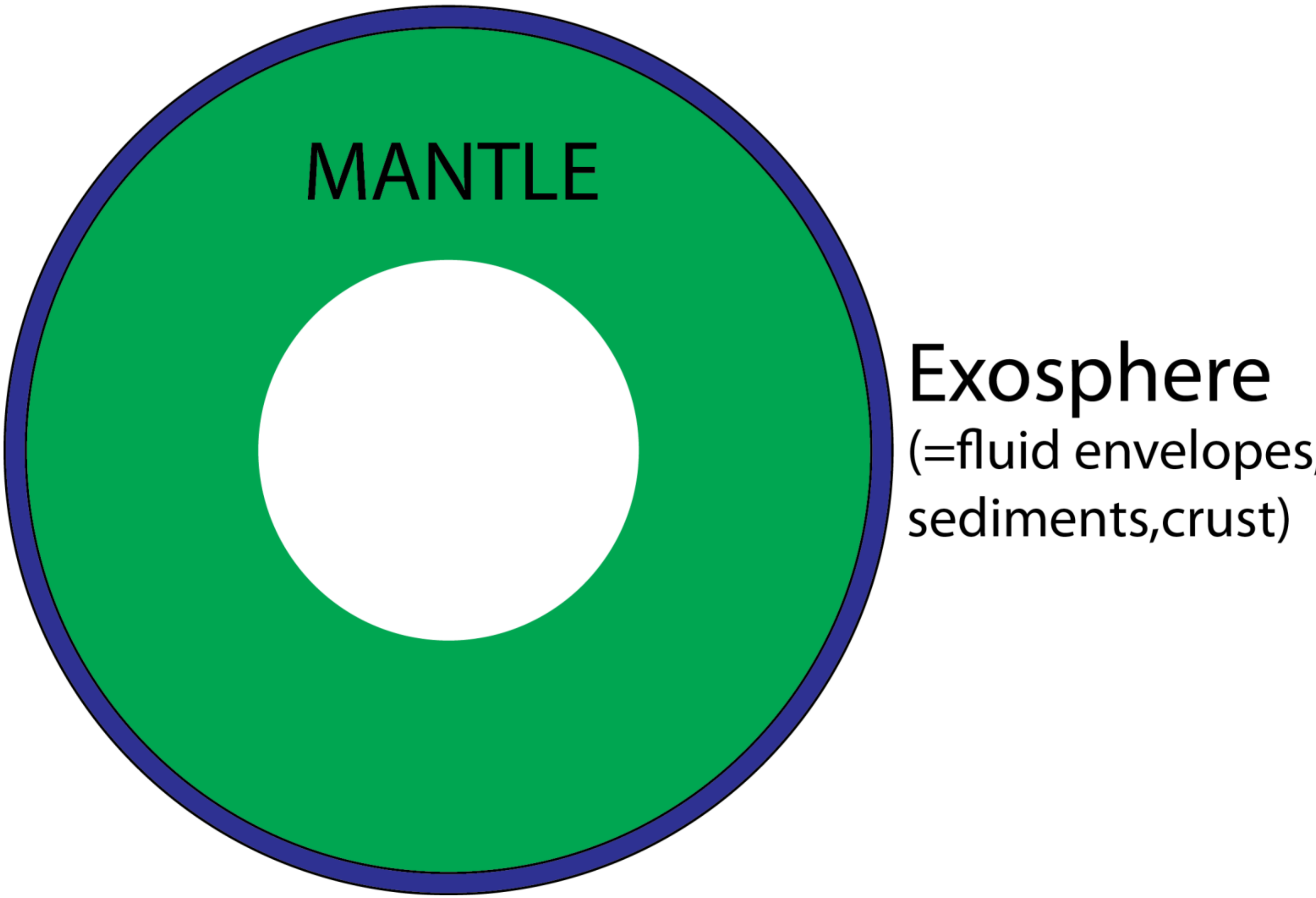
(Lecuyer et al. 1998)

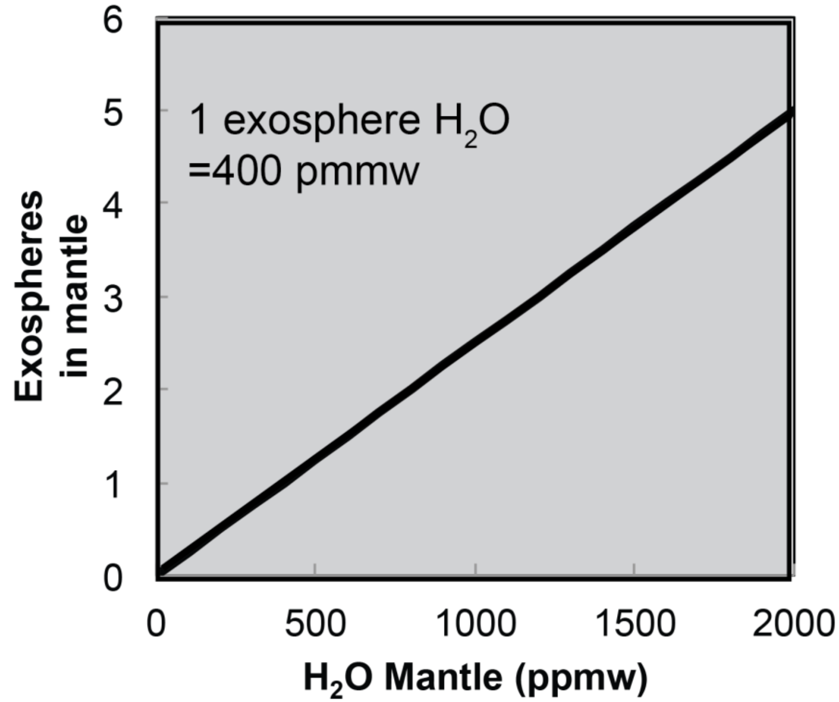
	Grams H_2O	Grams H
Oceans	1.4×10^{24}	1.56×10^{23}
Other	2×10^{23}	2.22×10^{22}
Total	1.6×10^{24}	1.78×10^{23}

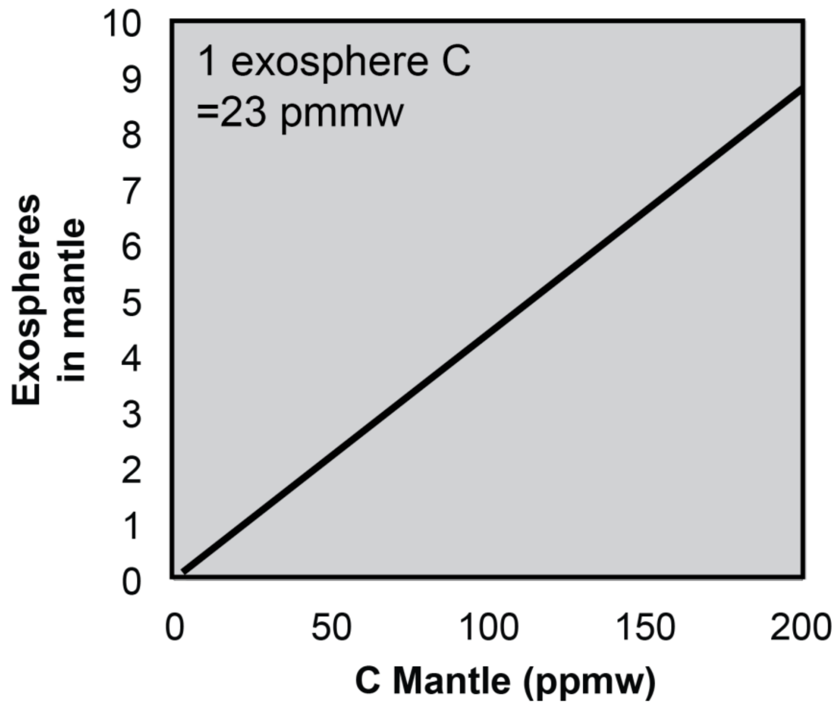


Exosphere Carbon	Moles CO_2	Grams C
Sleep&Zahnle '02		
Sediments	5.88×10^{21}	7.06×10^{22}
Oceans	3.31×10^{18}	3.97×10^{19}
Oceanic Crust	1.20×10^{21}	1.44×10^{22}
Total	$\mathbf{7.08 \times 10^{21}}$	$\mathbf{8.50 \times 10^{22}}$
Hayes&Waldbauer '06	$\mathbf{8.50 \times 10^{21}}$	$\mathbf{1.02 \times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

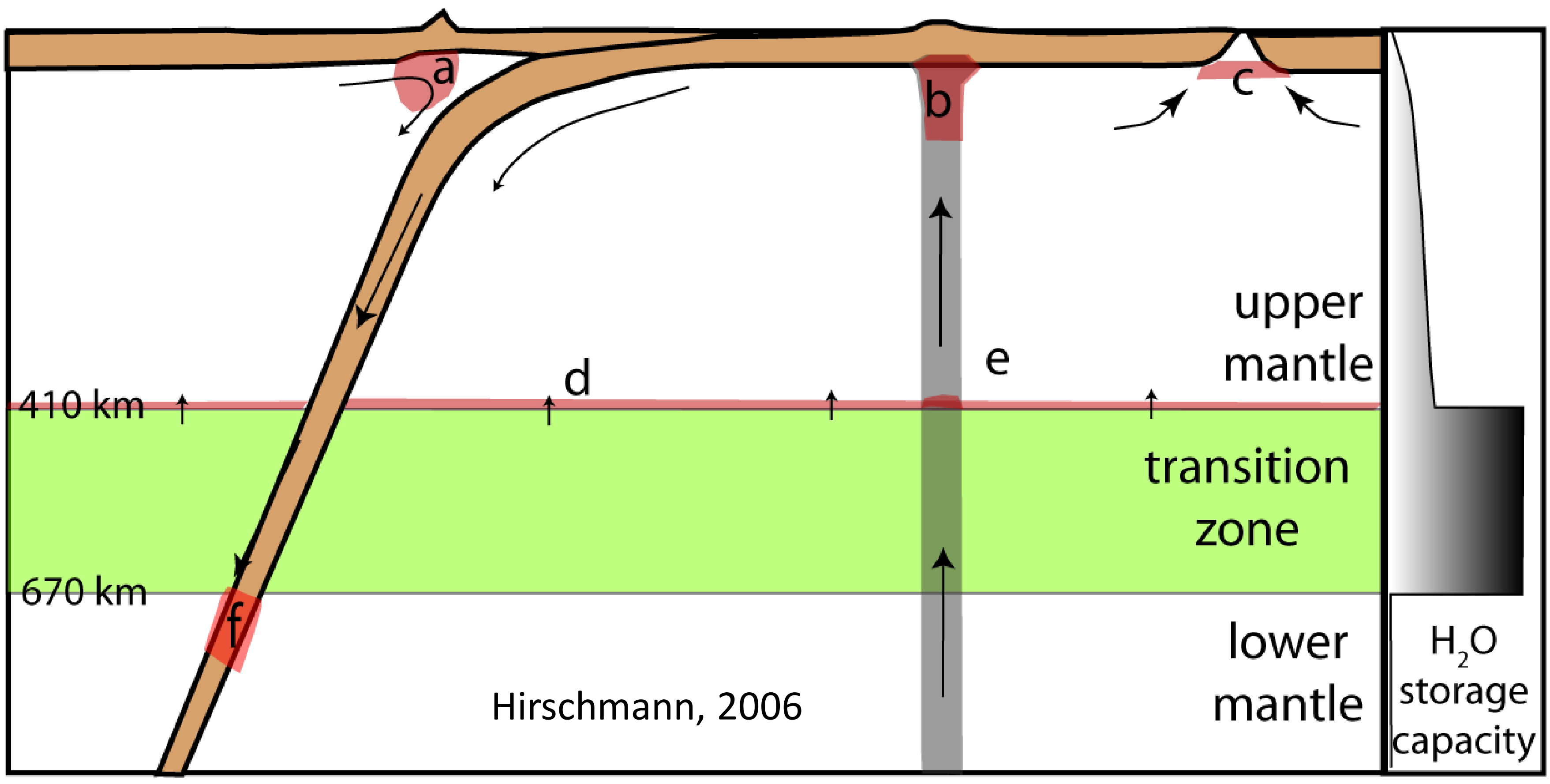
“Bulk Silicate Earth” (BSE)

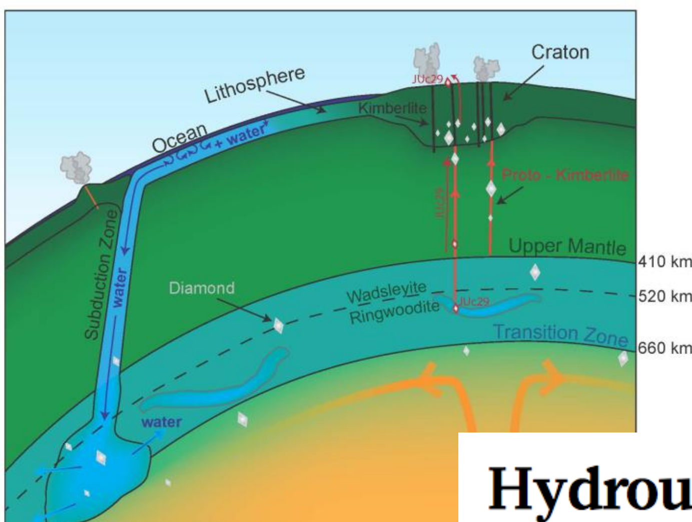


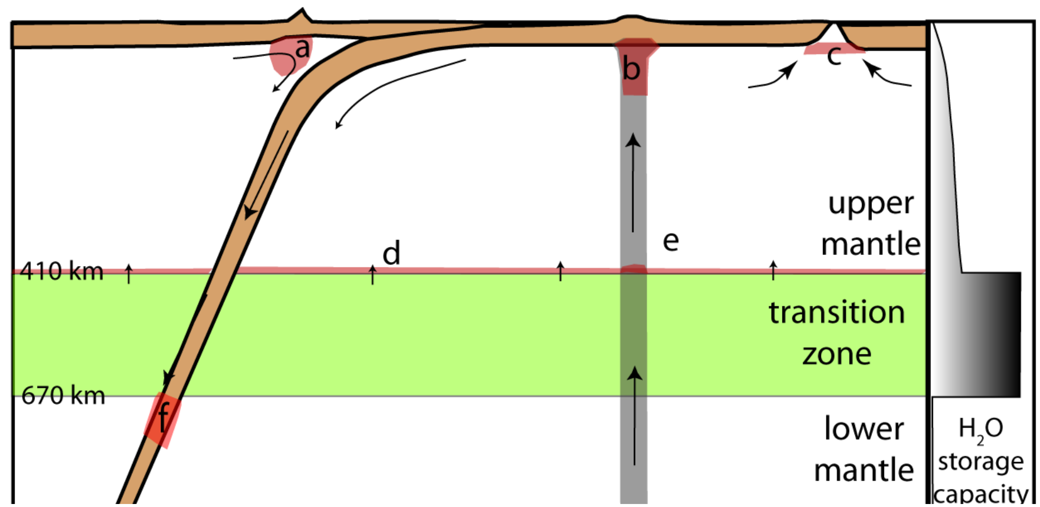

1 exosphere H_2O
=400 pmmw
Exospheres in mantle
0
1
2
3
4
5
6
0
500
1000
1500
2000
H_2O Mantle (ppmw)


1 exosphere C
=23 pmmw
Exospheres in mantle
0
1
2
3
4
5
6
7
8
9
10
0
50
100
150
200
C Mantle (ppmw)

Schematic Features of Water Storage (and hydrous melting) the Mantle

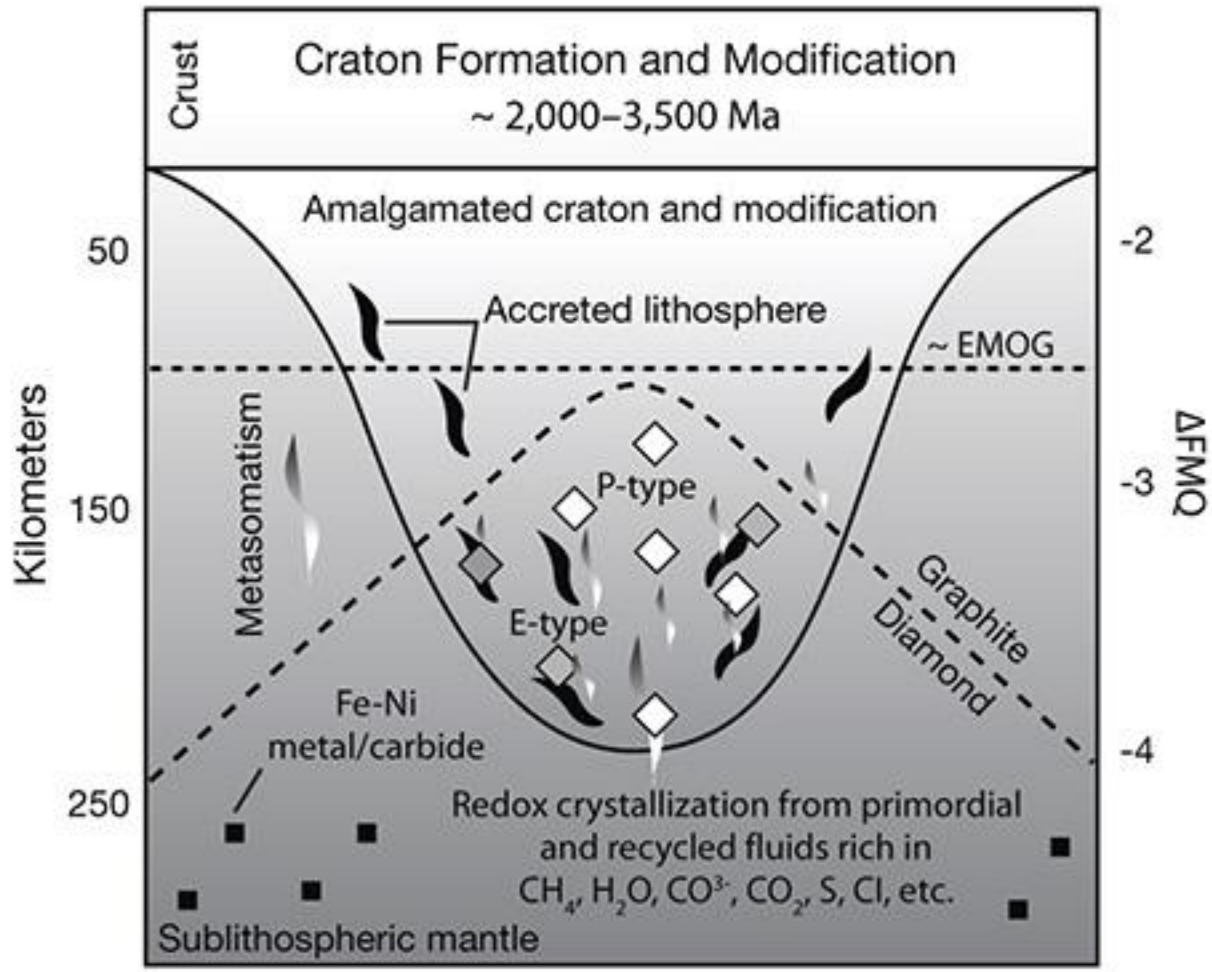






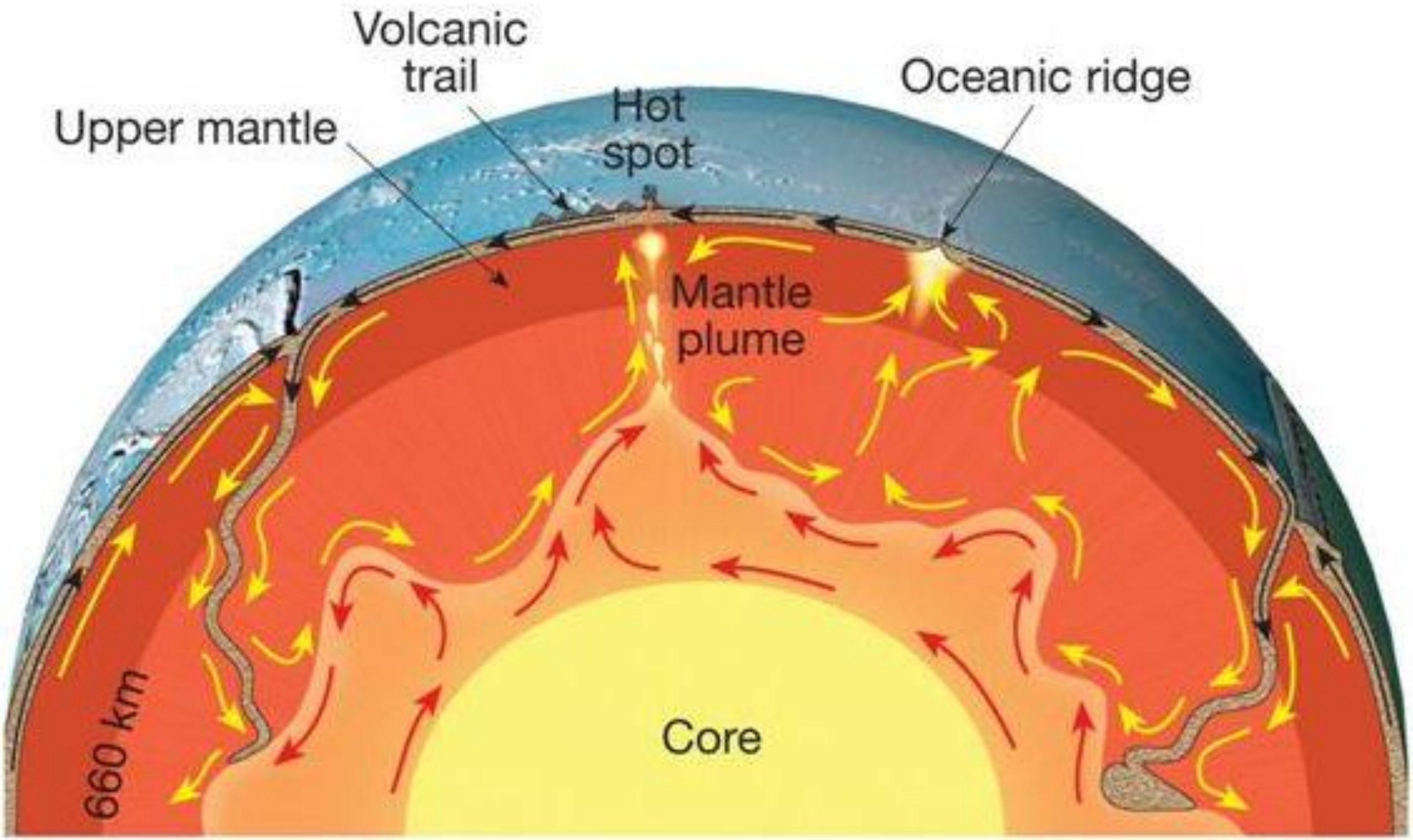
Hydrous mantle transition zone indicated by ringwoodite included within diamond

D. G. Pearson[1], F. E. Brenker[2], F. Nestola[3], J. McNeill[4], L. Nasdala[5], M. T. Hutchison[6], S. Matveev[1], K. Mather[4], G. Silversmit[7], S. Schmitz[2], B. Vekemans[7] & L. Vincze[7]

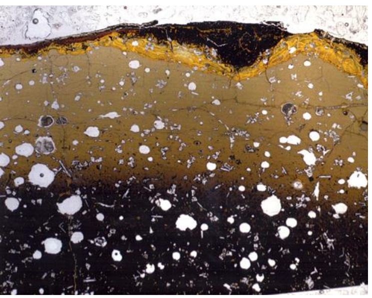


Crust
Craton Formation and Modification
~ 2,000–3,500 Ma
Amalgamated craton and modification
50
-2
Accreted lithosphere
~ EMOG
Kilometers
Metasomatism
ΔFMQ
P-type
150
-3
E-type
Graphite
Diamond
Fe-Ni
metal/carbide
-4
250
Redox crystallization from primordial
and recycled fluids rich in
CH_4, H_2O, CO^{3-}, CO_2, S, Cl, etc.
Sublithospheric mantle

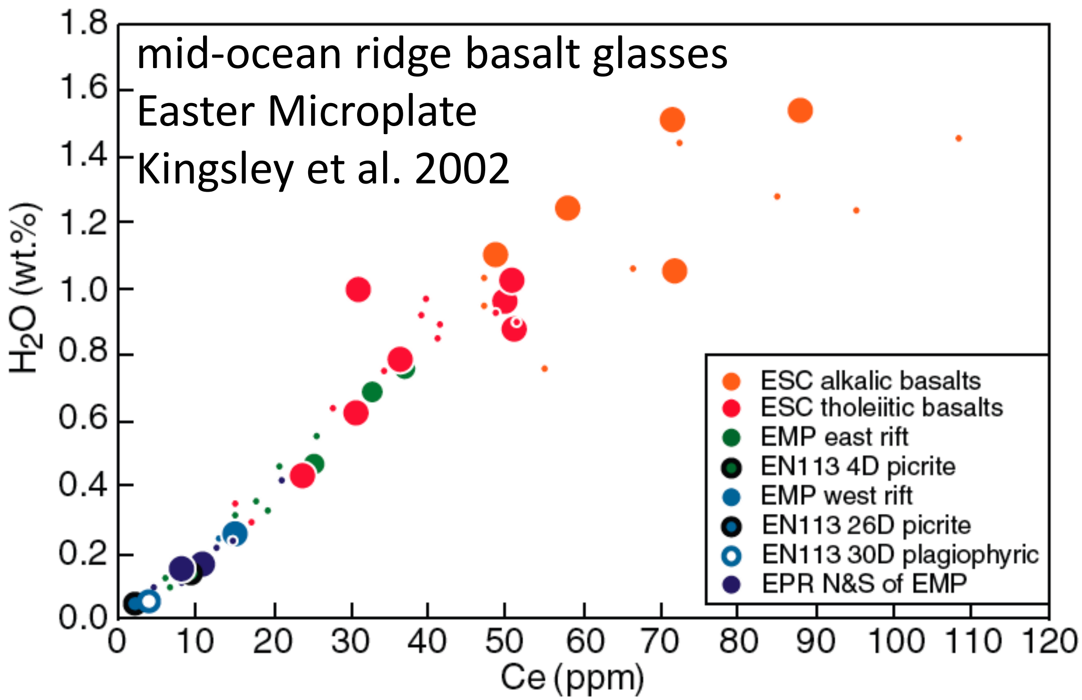
Shirey, 2013

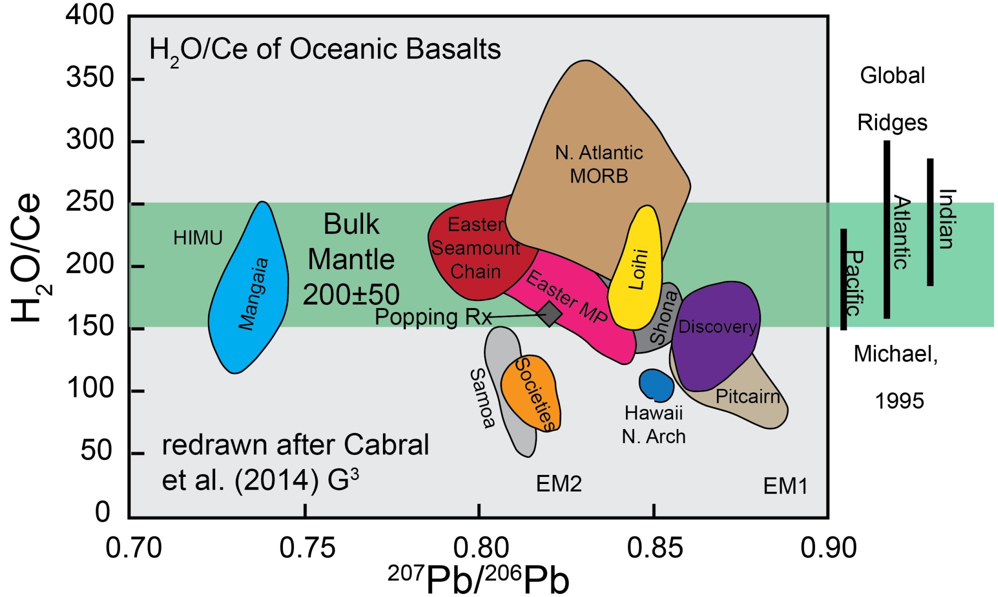

Volcanic trail
Oceanic ridge
Hot spot
Upper mantle
Mantle plume
660 km
Core

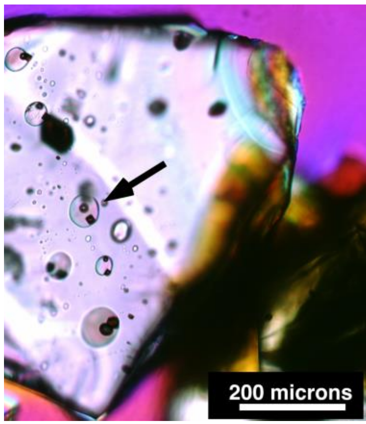
C.



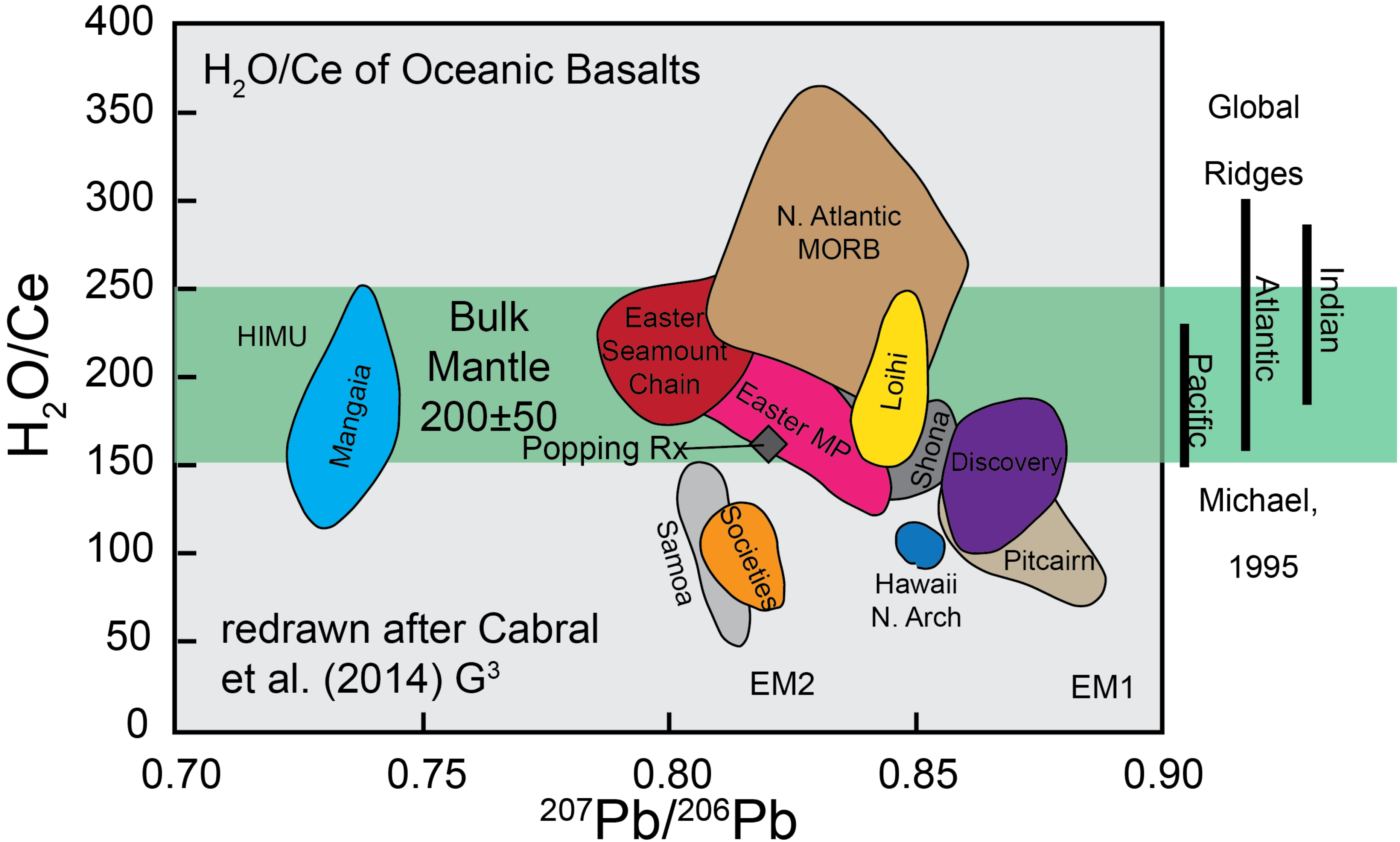
Mid-Ocean Ridge Quenched Pillow Glass

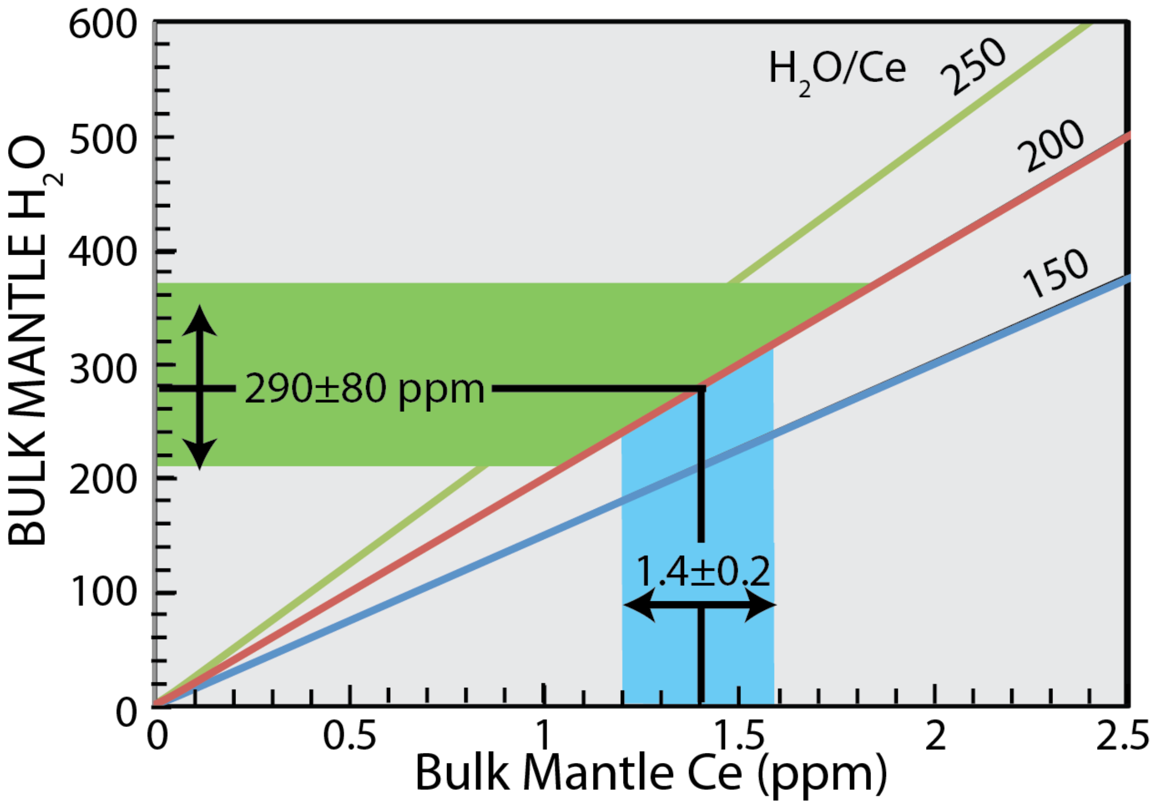




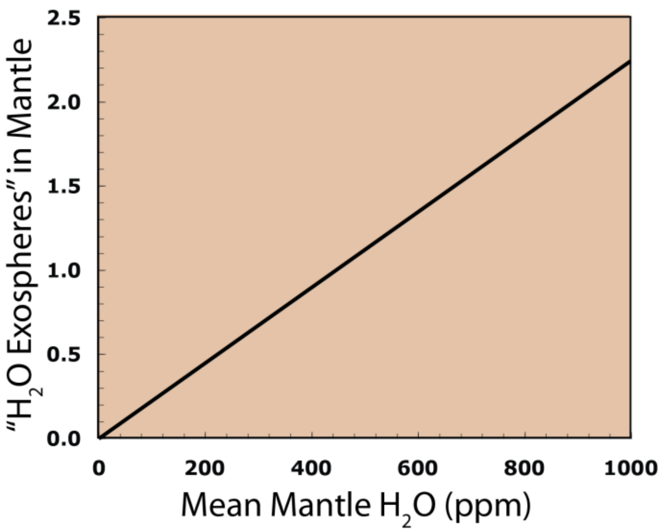


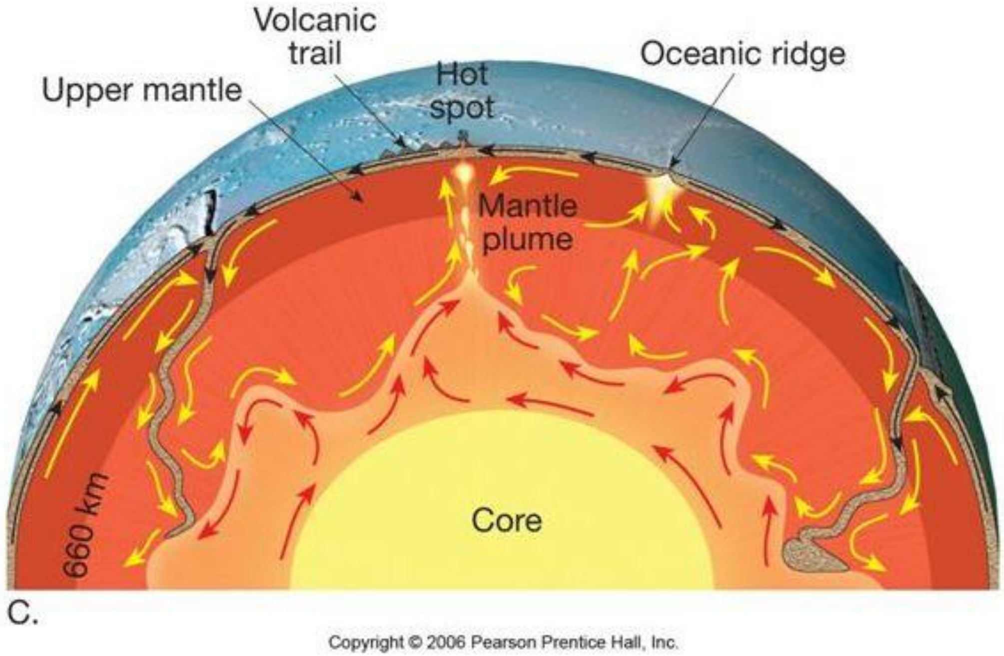
Olivine-hosted Melt Inclusions (in MORB or OIB)


H2O/Ce of Oceanic Basalts
400
350
300
250
200
150
100
50
0
H2O/Ce
0.70
0.75
0.80
0.85
0.90
207Pb/206Pb
HIMU
Mangaia
Bulk
Mantle
200±50
Popping Rx
Easter
Seamount
Chain
N. Atlantic
MORB
Easter MP
Loihi
Shona
Discovery
Samoa
Societies
Hawaii
N. Arch
Pitcairn
redrawn after Cabral
et al. (2014) G3
EM2
EM1
Global
Ridges
Pacific
Atlantic
Indian
Michael,
1995

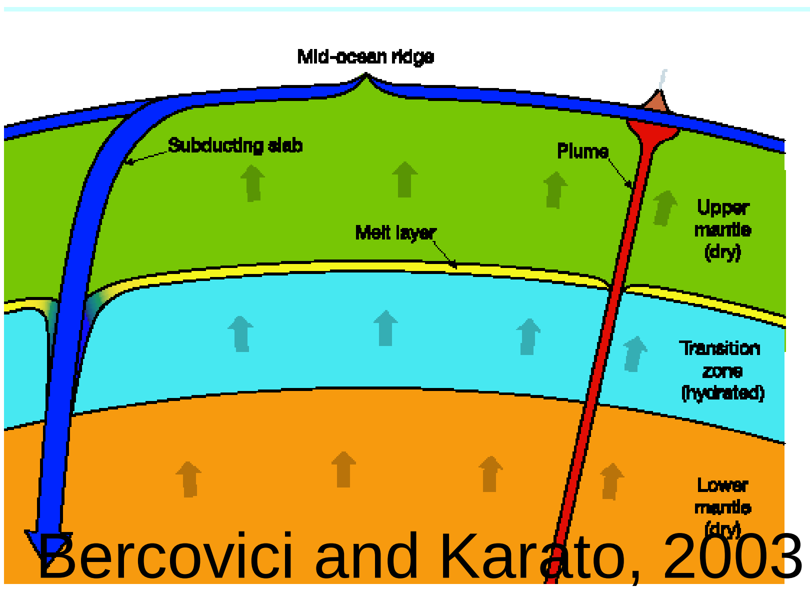


[McDonough&Sun, 1995, minus Continental Crust]

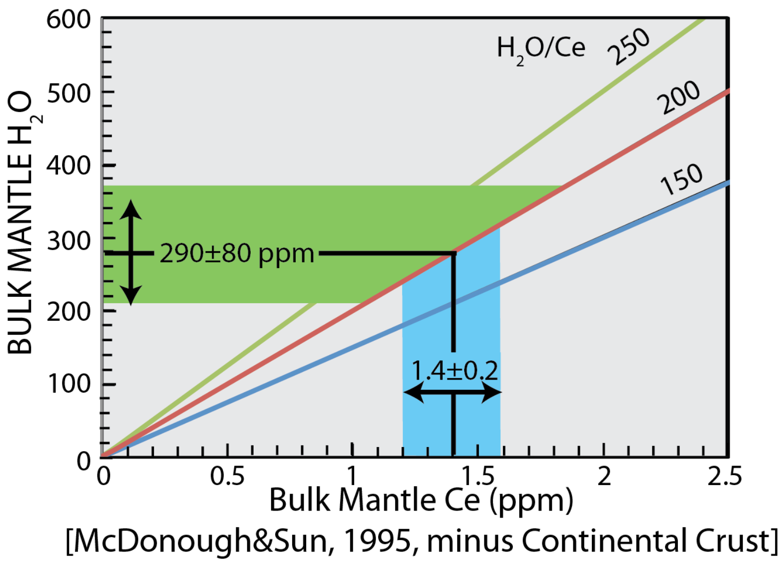




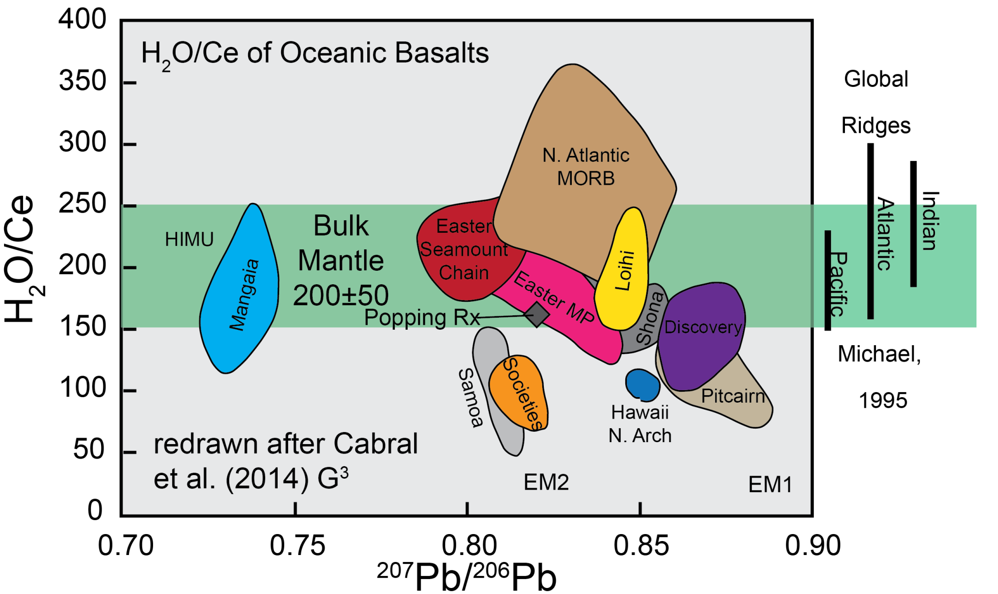
Volcanic trail
Upper mantle
Hot spot
Oceanic ridge
Mantle plume
660 km
Core
C.
Copyright © 2006 Pearson Prentice Hall, Inc.



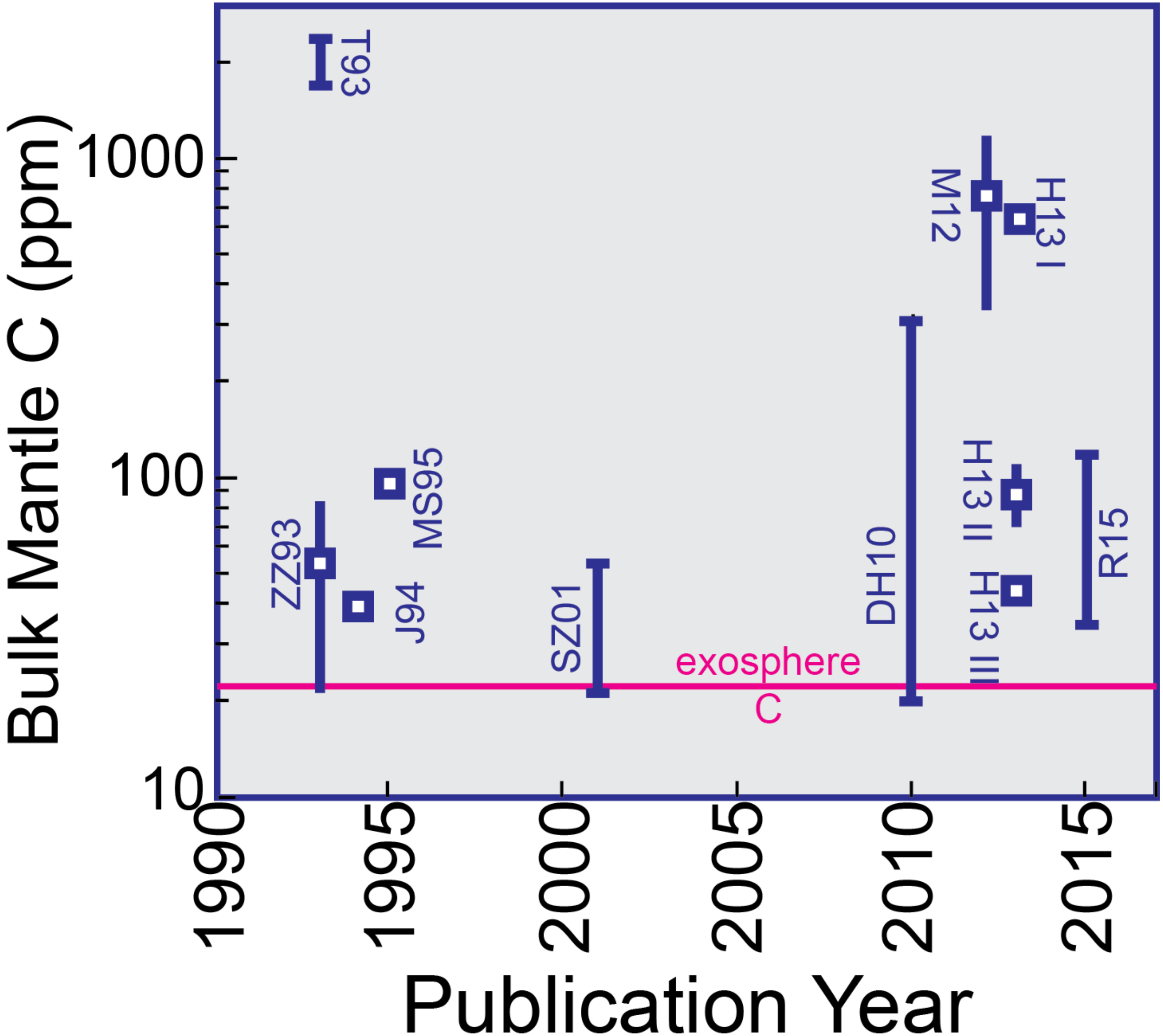
Mid-ocean ridge
Subducting slab
Plume
Upper mantle (dry)
Melt layer
Transition zone (hydrated)
Lower mantle (dry)
Bercovici and Karato, 2003



BULK MANTLE H_2O
H_2O/Ce
250
200
150
290±80 ppm
1.4±0.2
0 0.5 1 1.5 2 2.5
0 100 200 300 400 500 600
Bulk Mantle Ce (ppm)
[McDonough&Sun, 1995, minus Continental Crust]

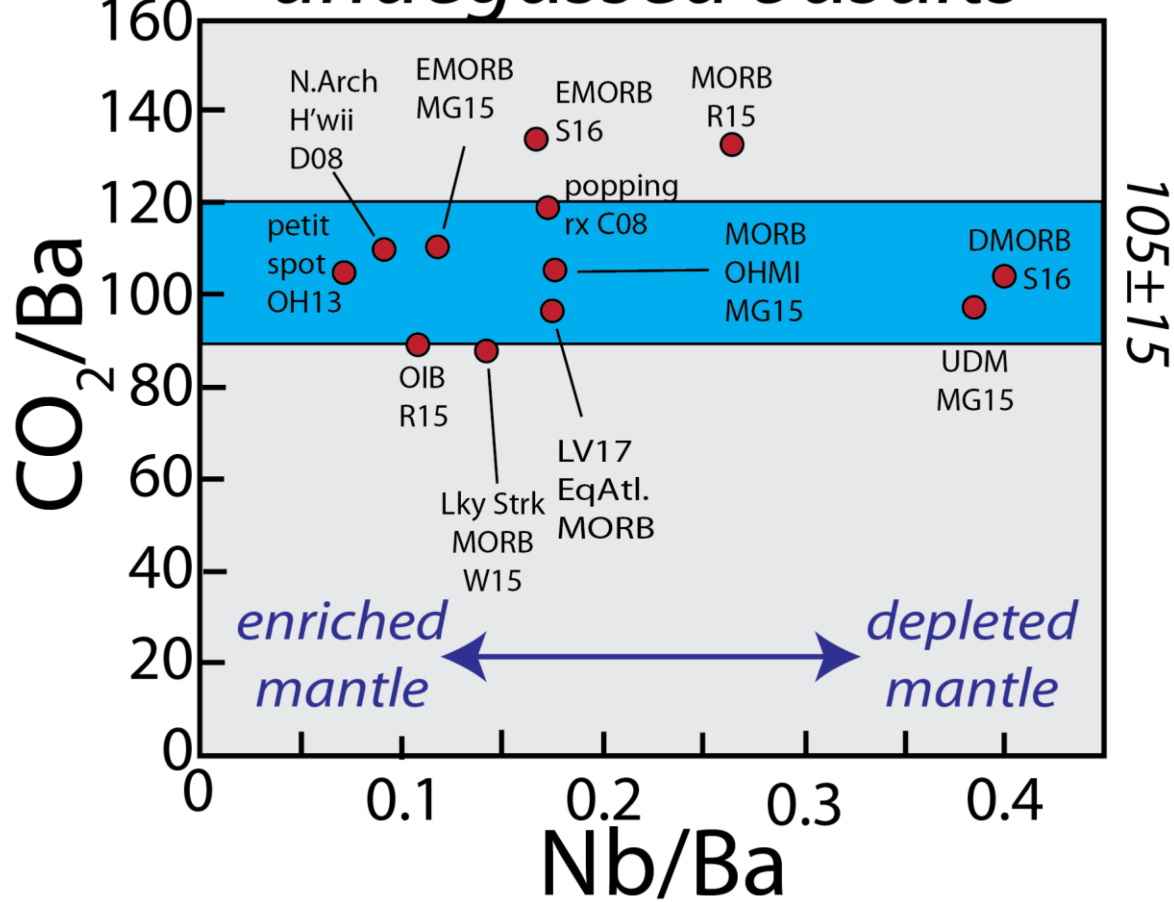


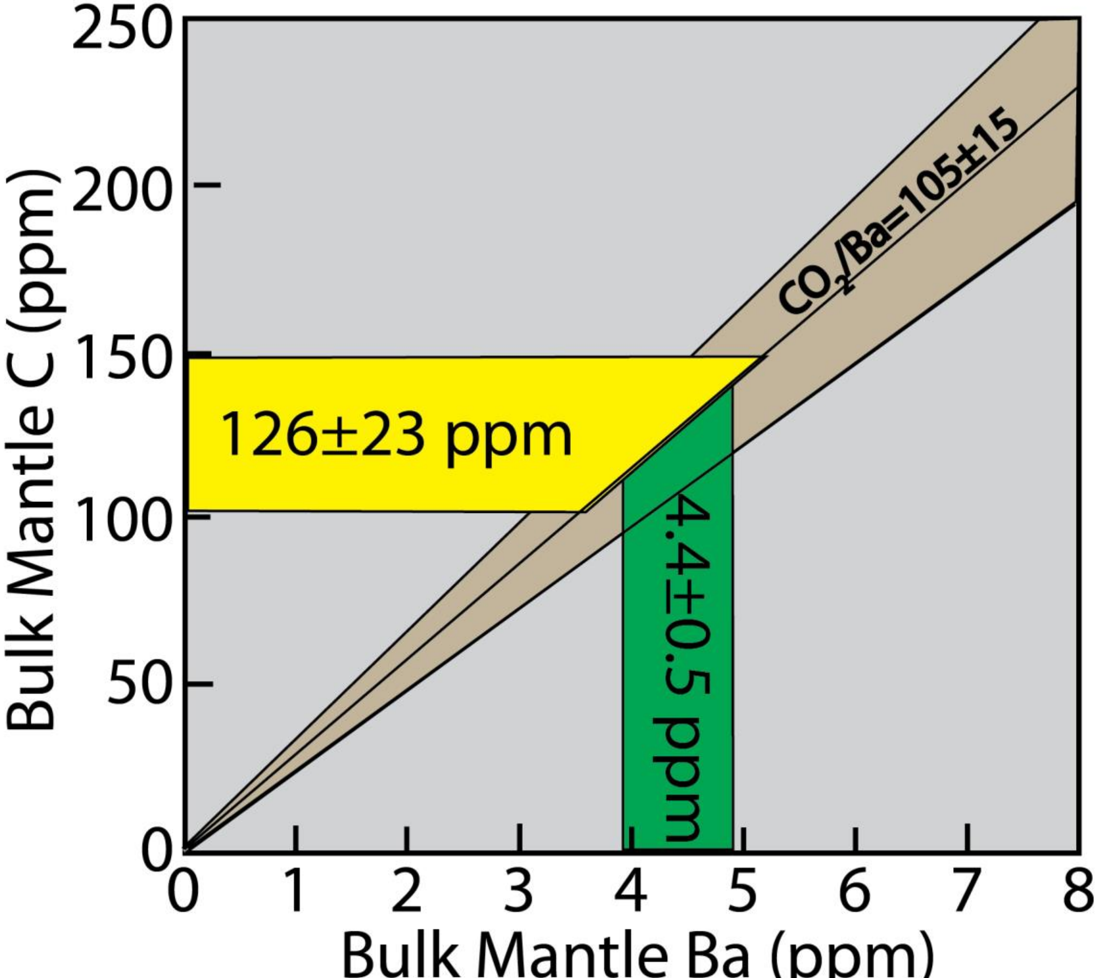
H_2O/Ce of Oceanic Basalts
H_2O/Ce
$^{207}Pb/^{206}Pb$
HIMU
Mangaia
Bulk Mantle 200±50
Easter Seamount Chain
N. Atlantic MORB
Easter MP
Loihi
Shona
Discovery
Popping Rx
Samoa
Societies
Hawaii N. Arch
Pitcairn
redrawn after Cabral et al. (2014) G³
EM2
EM1
Global Ridges
Pacific
Atlantic
Indian
Michael, 1995
0.70 0.75 0.80 0.85 0.90
0 50 100 150 200 250 300 350 400



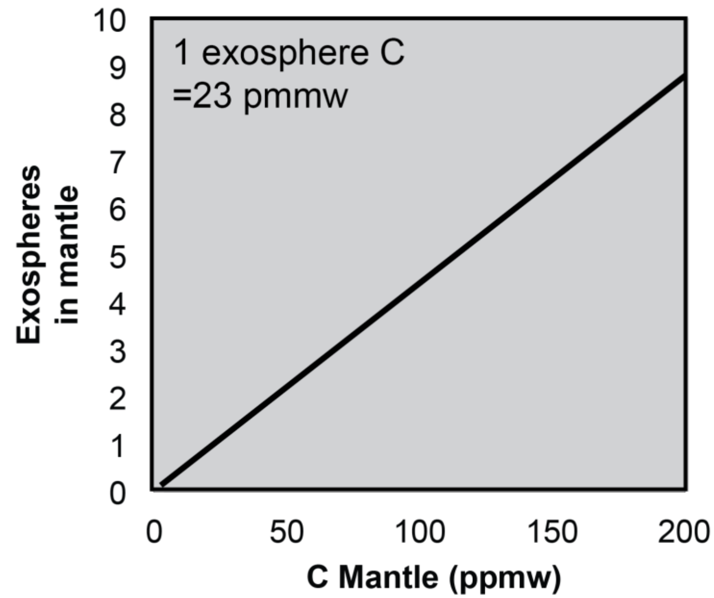
Bulk Mantle C (ppm)
1000
100
10
1990
1995
2000
2005
2010
2015
Publication Year
T93
ZZ93
J94
MS95
SZ01
DH10
M12
H13 I
H13 II
H13 III
R15
exosphere
C

CO_2/Ba of undegassed basalts

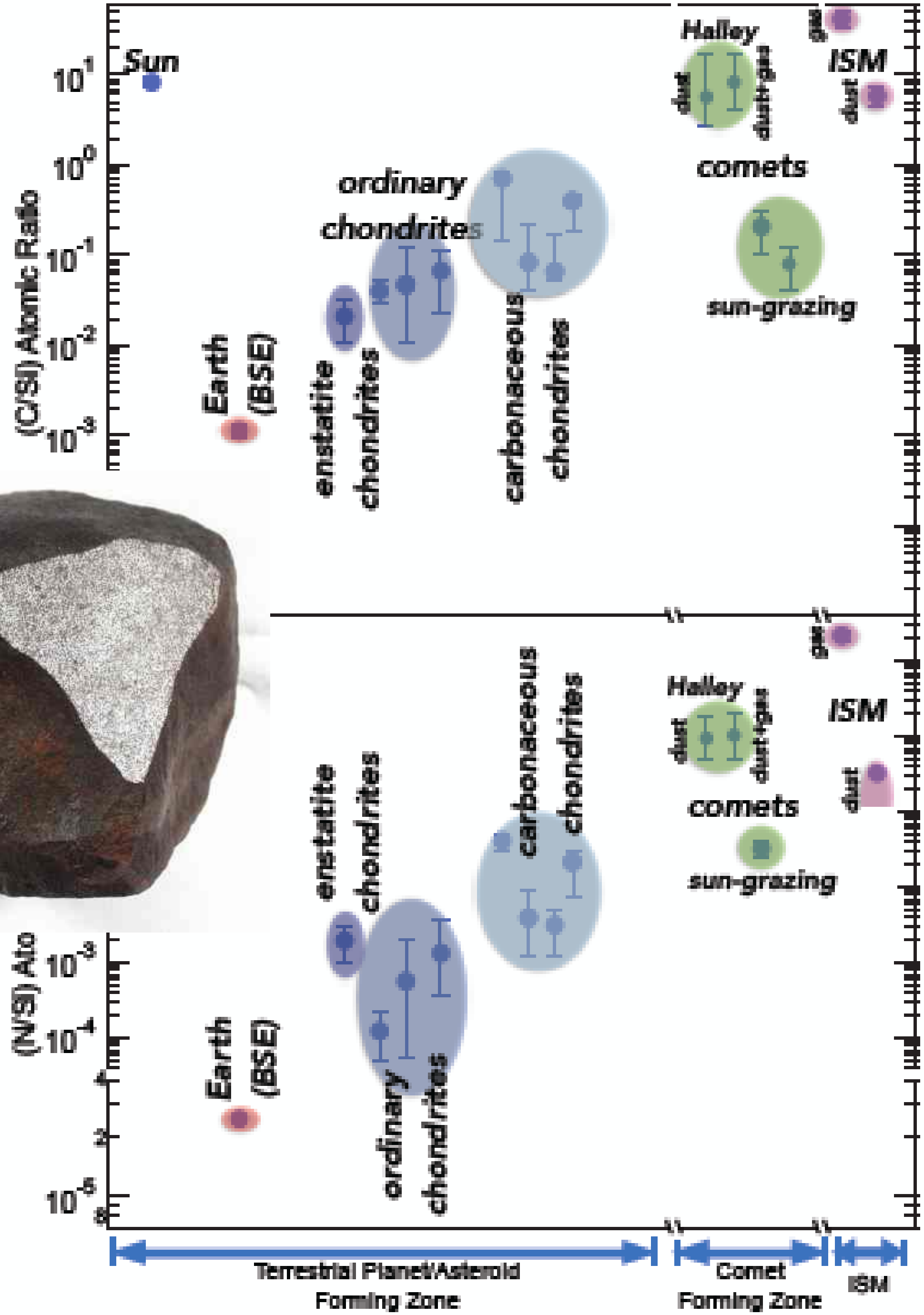


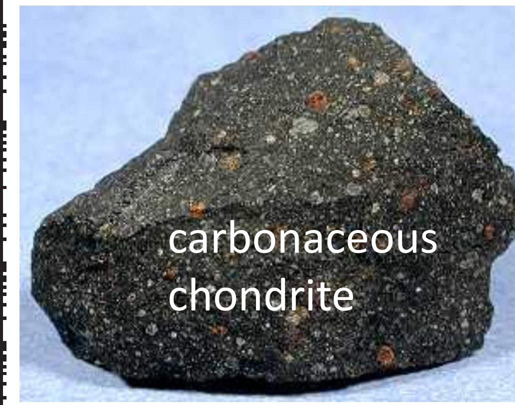


Bulk Mantle C (ppm)
250
200
150
100
50
0
0
1
2
3
4
5
6
7
8
Bulk Mantle Ba (ppm)
CO_2/Ba=105±15
126±23 ppm
4.4±0.5 ppm

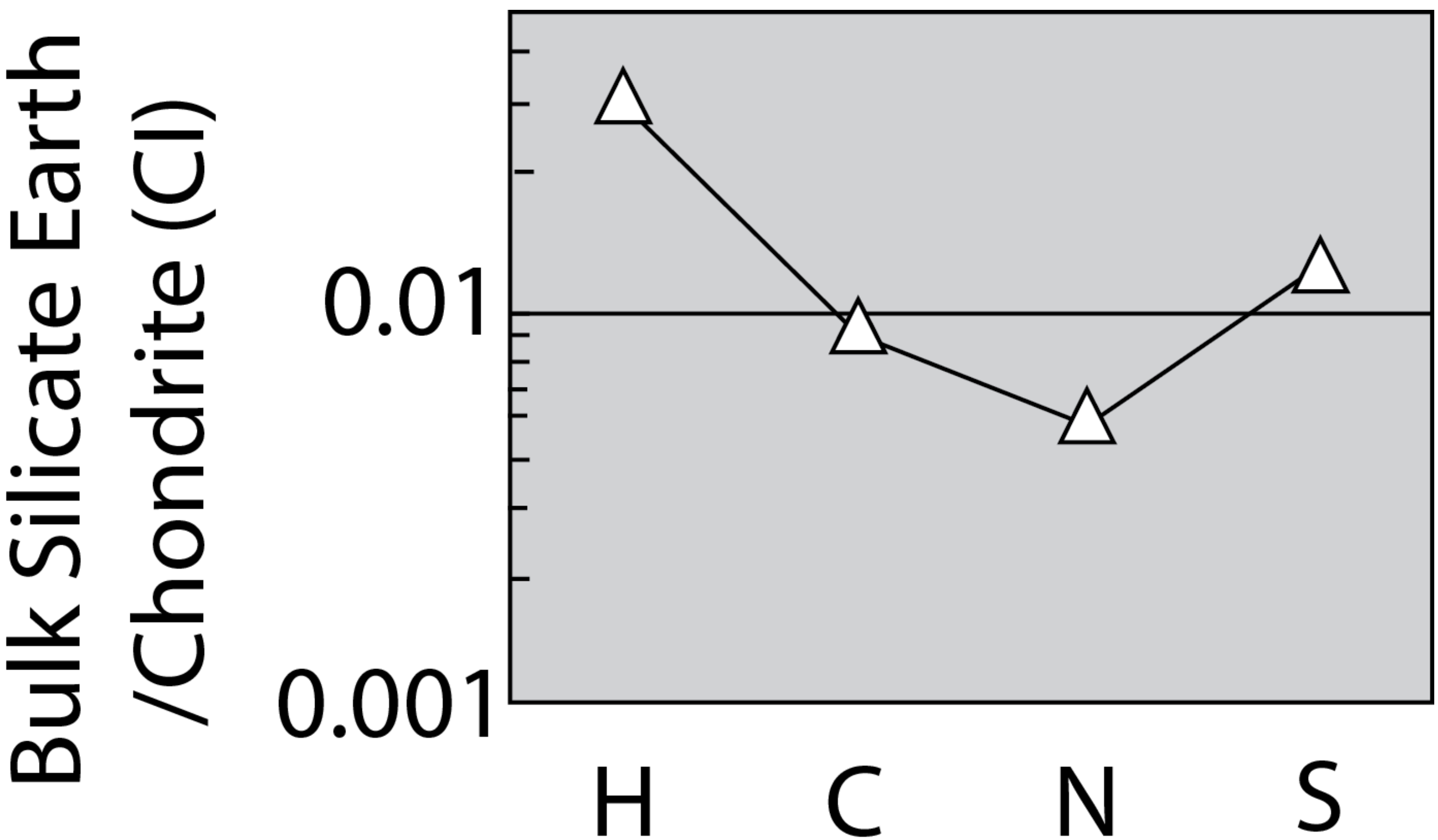


1 exosphere C
=23 pmmw
Exospheres in mantle
10
9
8
7
6
5
4
3
2
1
0
0
50
100
150
200
C Mantle (ppmw)



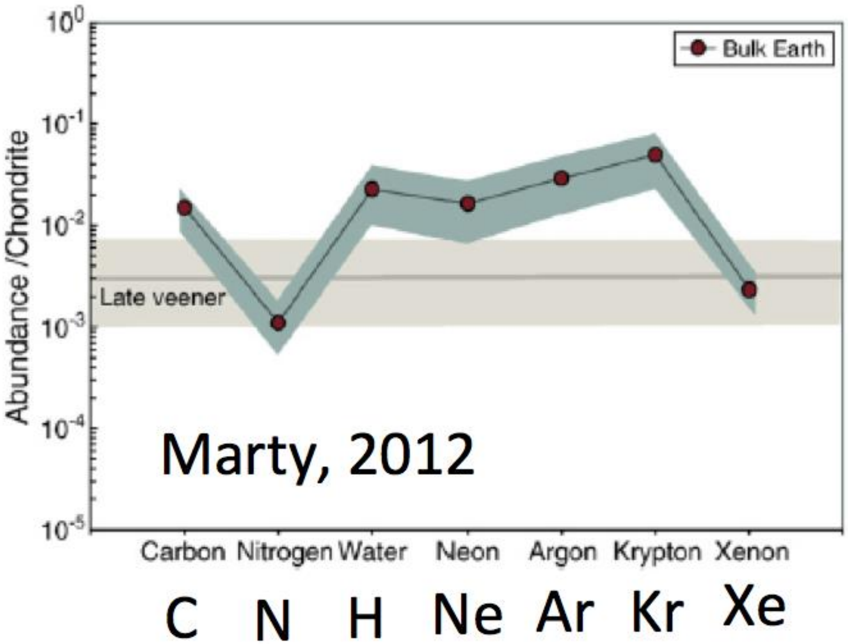


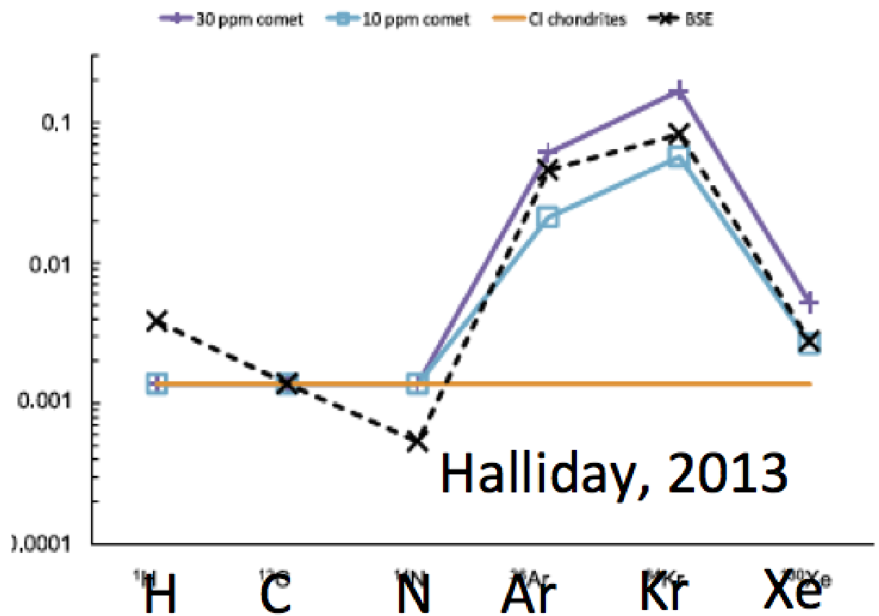
Bergin et al. 2015
PNAS

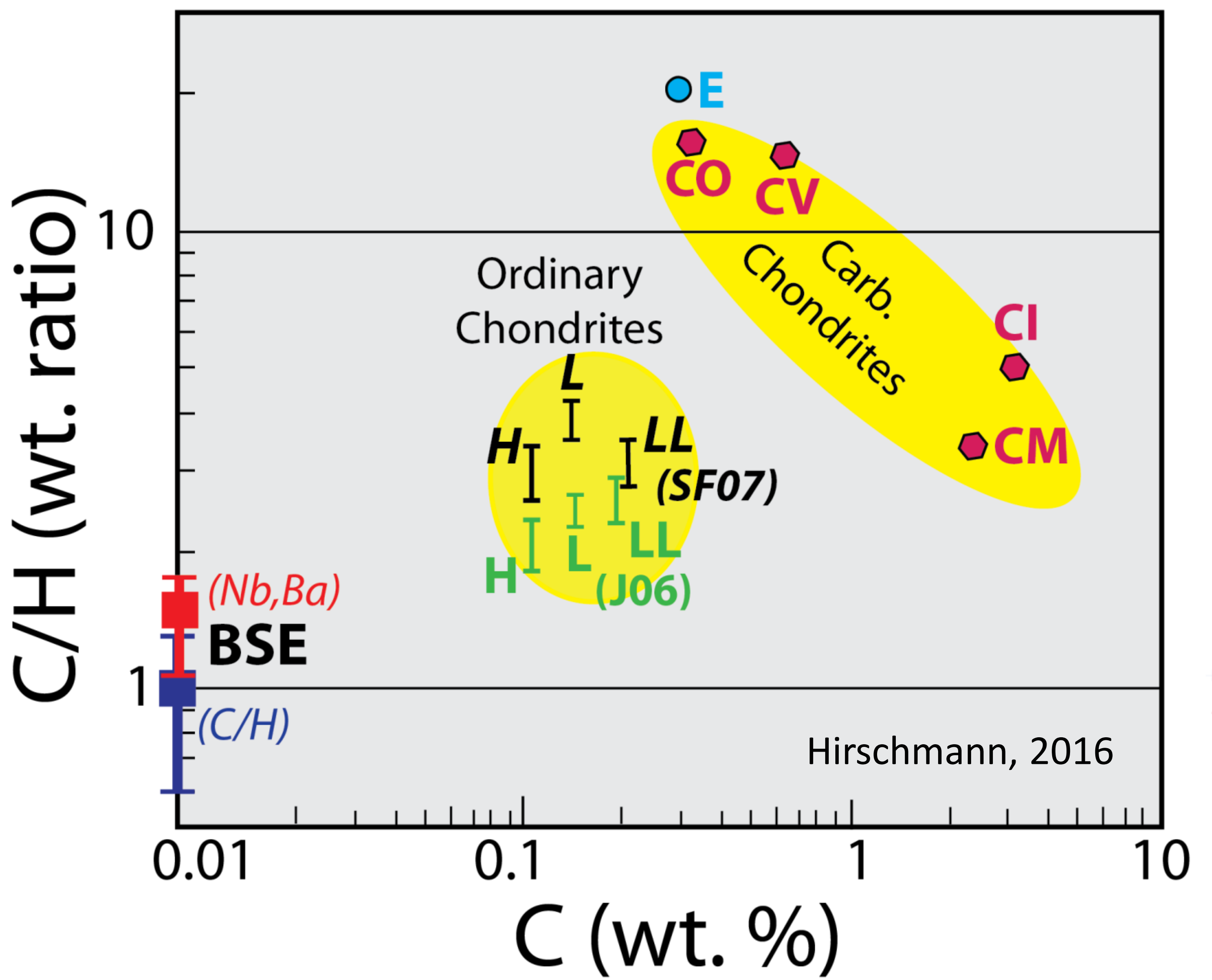


Bulk Silicate Earth
/Chondrite (CI)
0.01
0.001
H
C
N
S

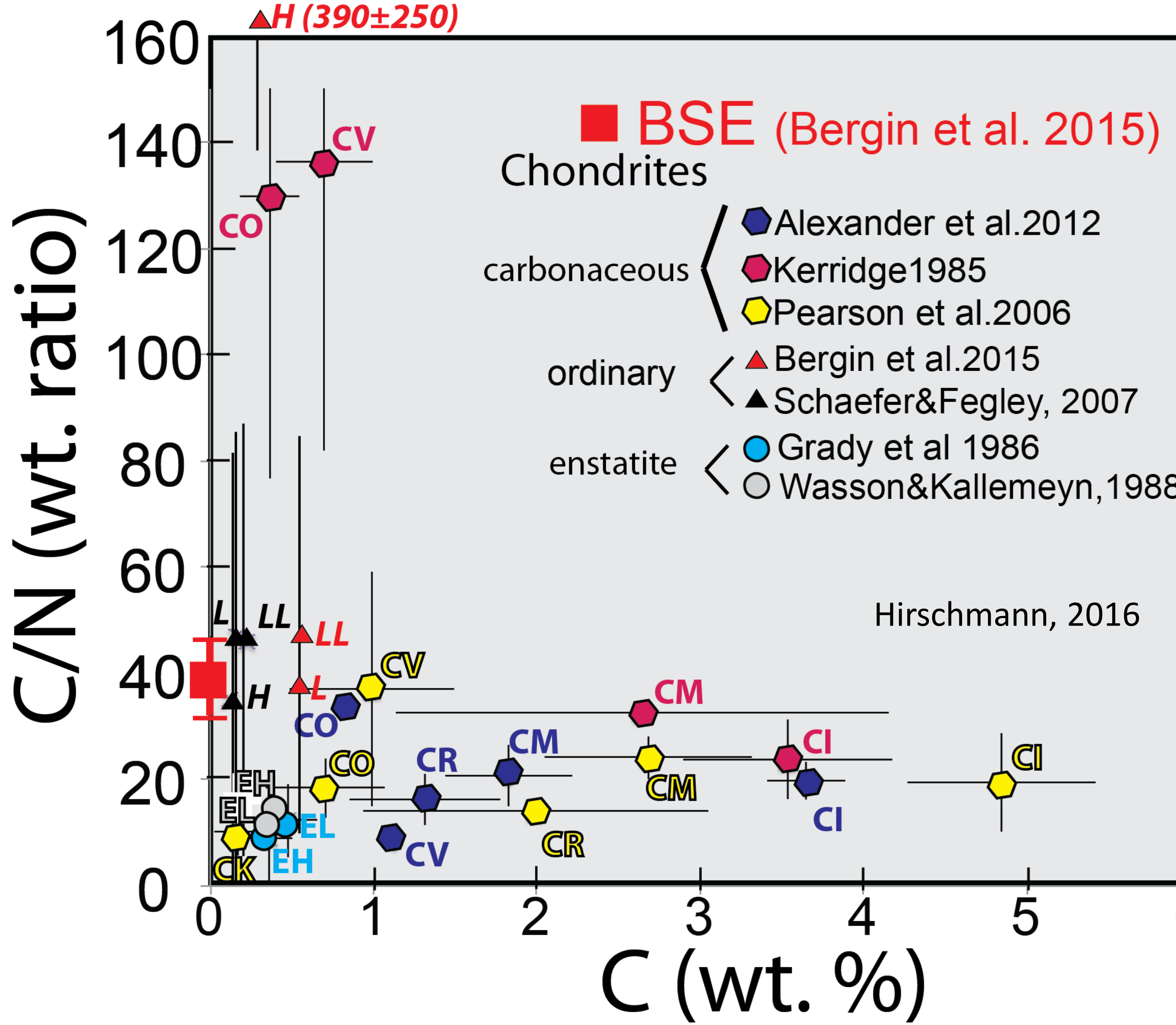
The Bulk Silicate Earth Abundances of Major Volatiles
Are FRACTIONATED compared to chondritic abundances



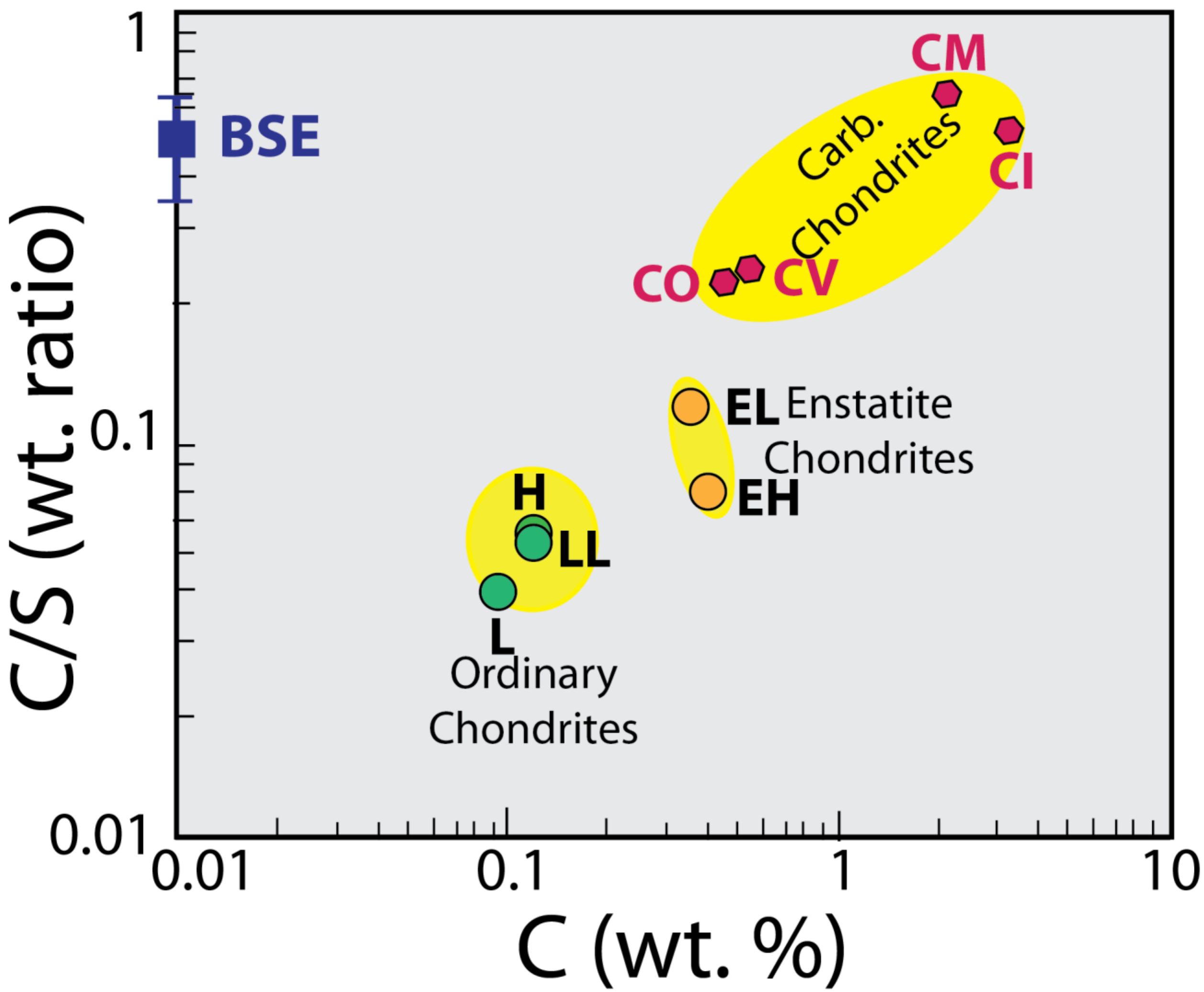




E
CO
CV
Carb. Chondrites
CI
CM
Ordinary Chondrites
L
H
LL
(SF07)
H
L
LL
(J06)
(Nb,Ba)
BSE
(C/H)
Hirschmann, 2016
10
1
0.01
0.1
1
10
C/H (wt. ratio)
C (wt. %)

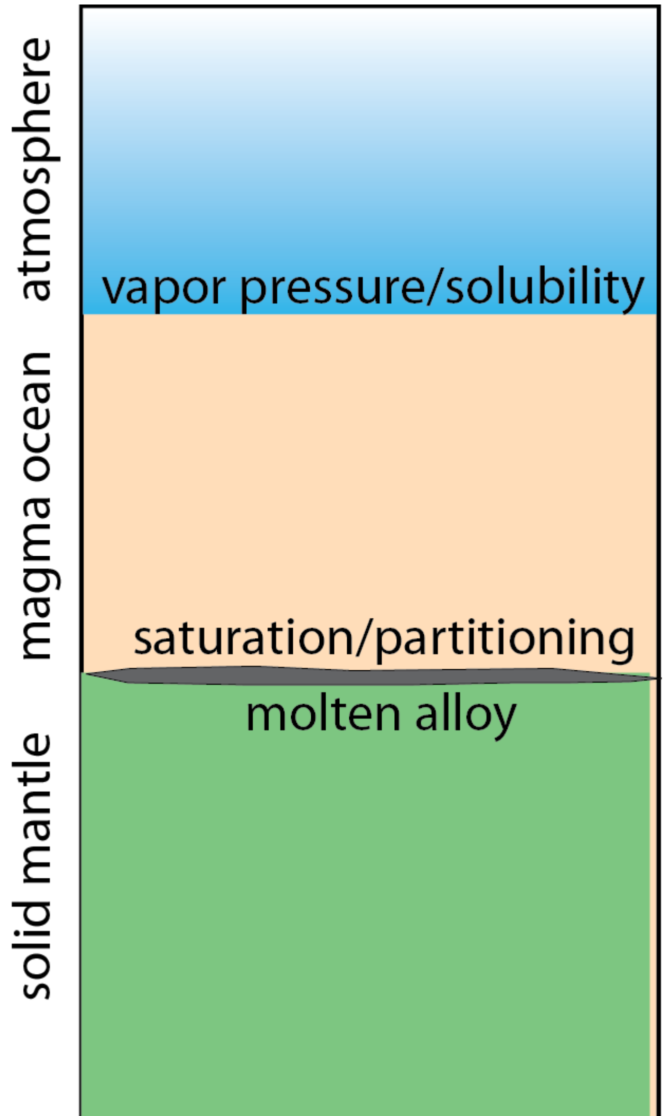


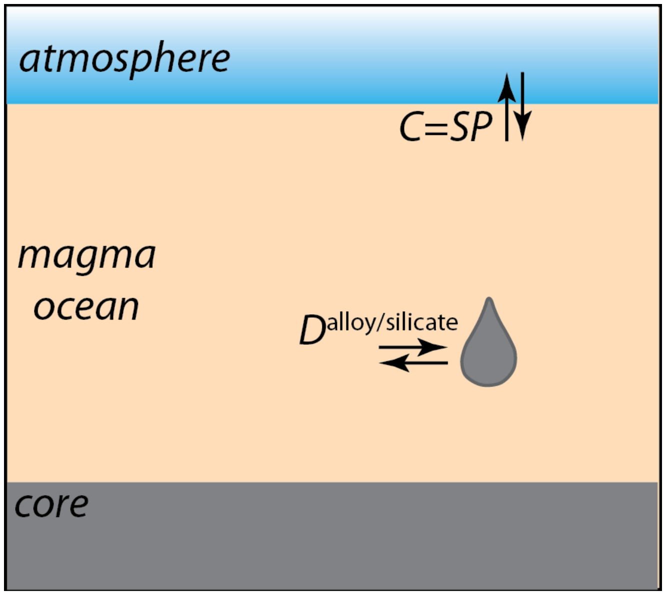
H (390±250)
BSE (Bergin et al. 2015)
Chondrites
carbonaceous
Alexander et al.2012
Kerridge1985
Pearson et al.2006
ordinary
Bergin et al.2015
Schaefer&Fegley, 2007
enstatite
Grady et al 1986
Wasson&Kallemeyn,1988
Hirschmann, 2016
CV
CO
L
LL
H
CM
CI
CR
EH
EL
CK
C/N (wt. ratio)
C (wt. %)
0
20
40
60
80
100
120
140
160
1
2
3
4
5
6



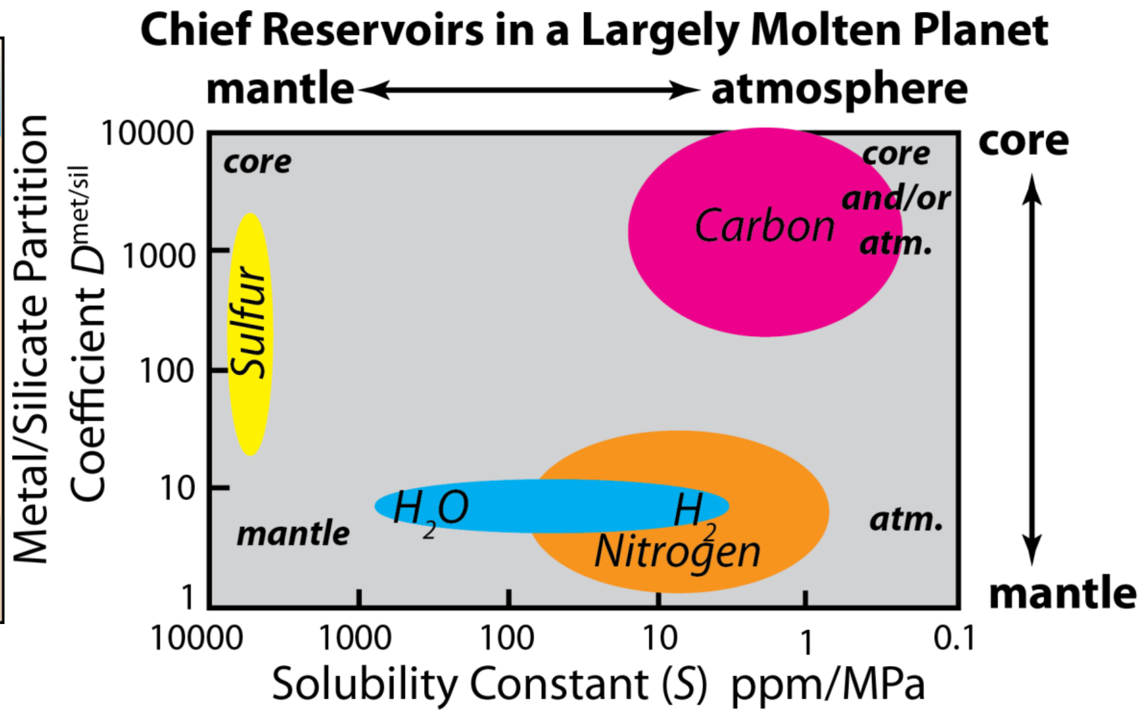
Hirschmann, 2016

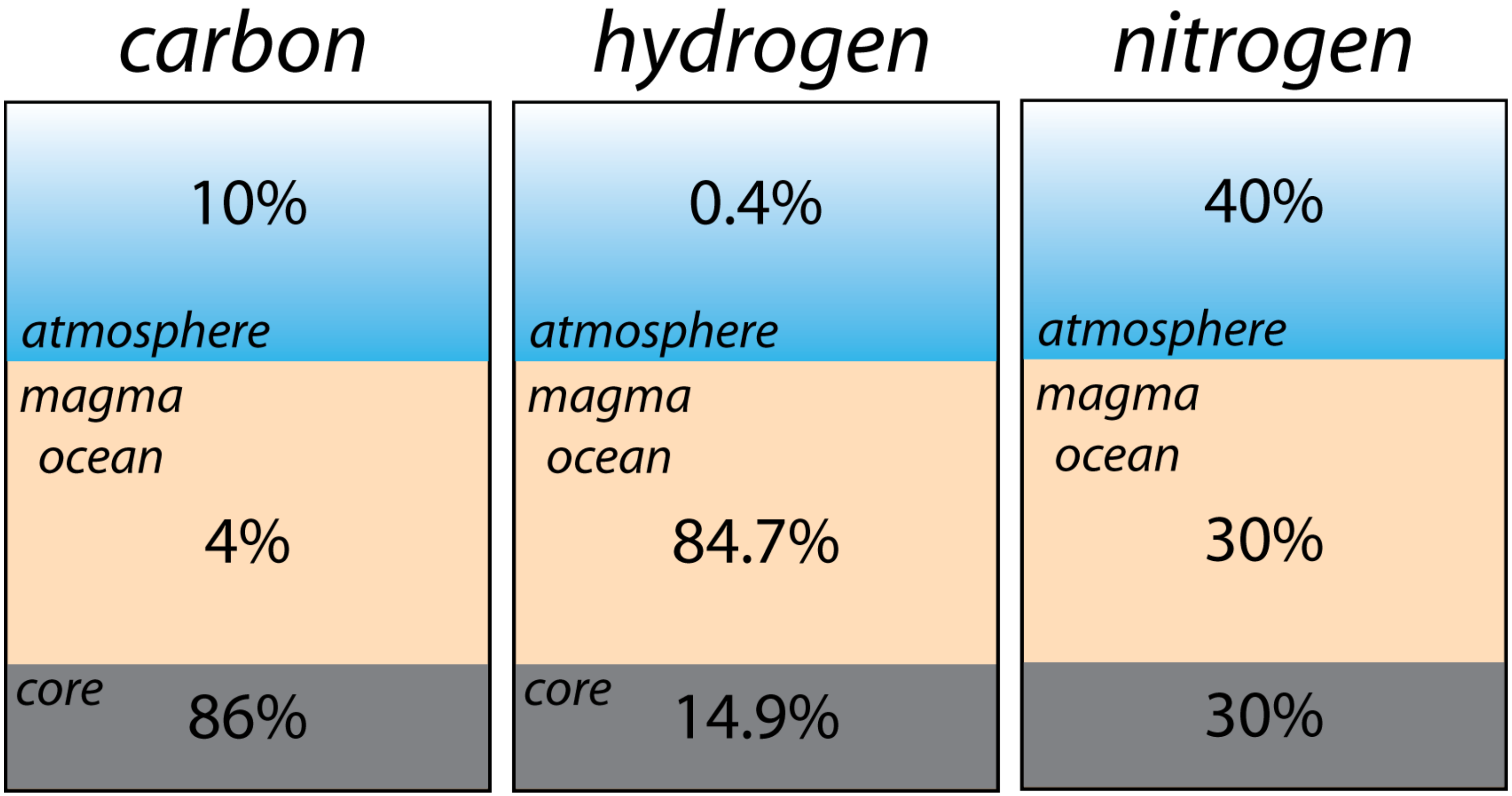
Consider a magma ocean: It produces (at least) 3 reservoirs
silicate, core, and atmosphere





Hirschmann, 2016

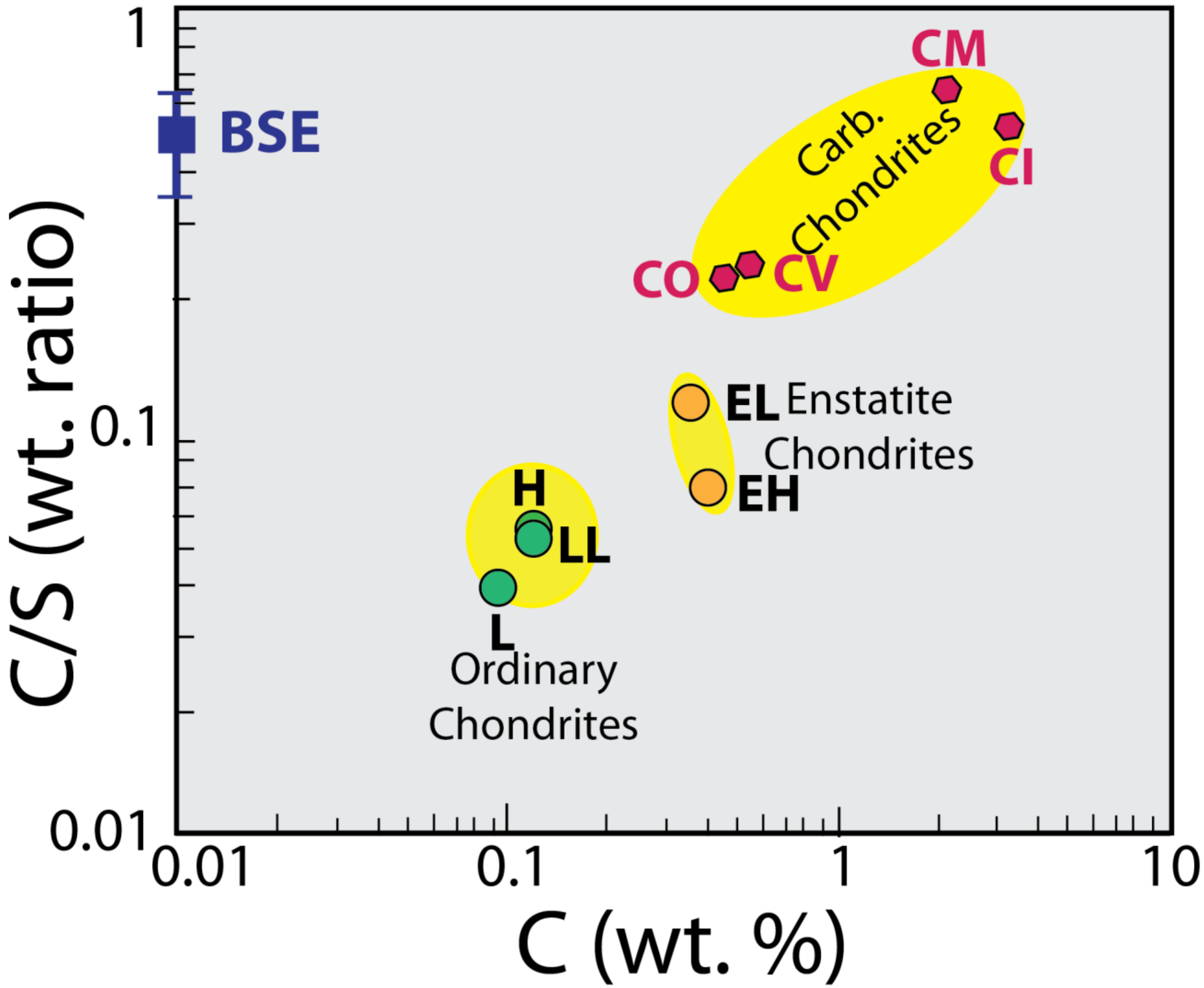




$D_C^{metal/silicate} = 200$ $D_H^{metal/silicate} = 14$ $D_N^{metal/silicate} = 10$

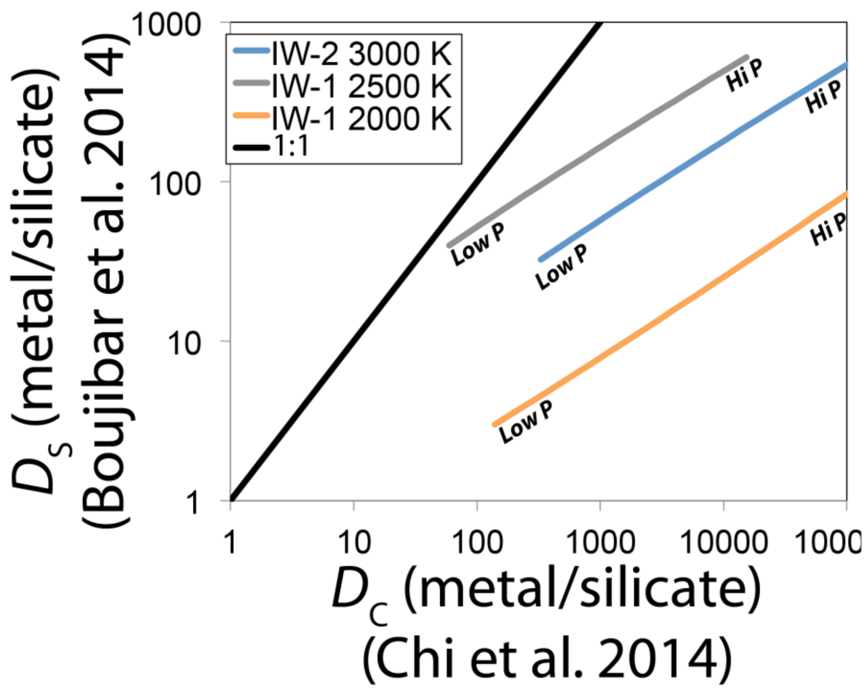
Partial Mantle/Core Equilibration
(mass metal/mass mantle=0.1)

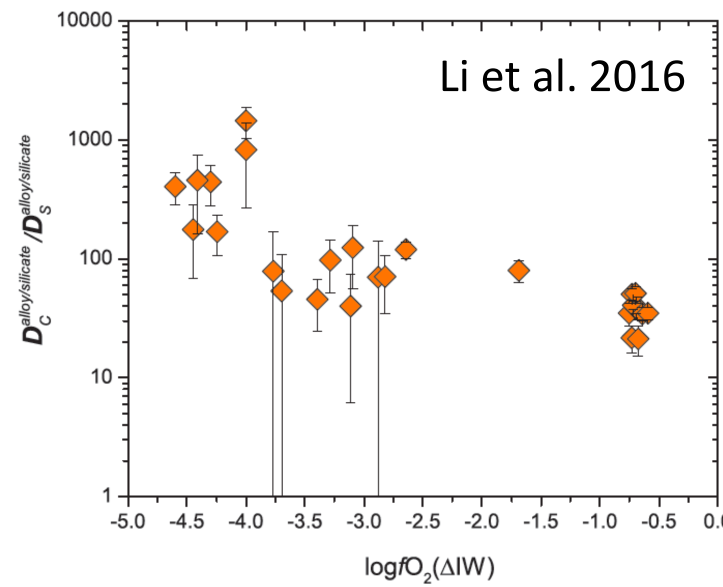
Hirschmann, 2016

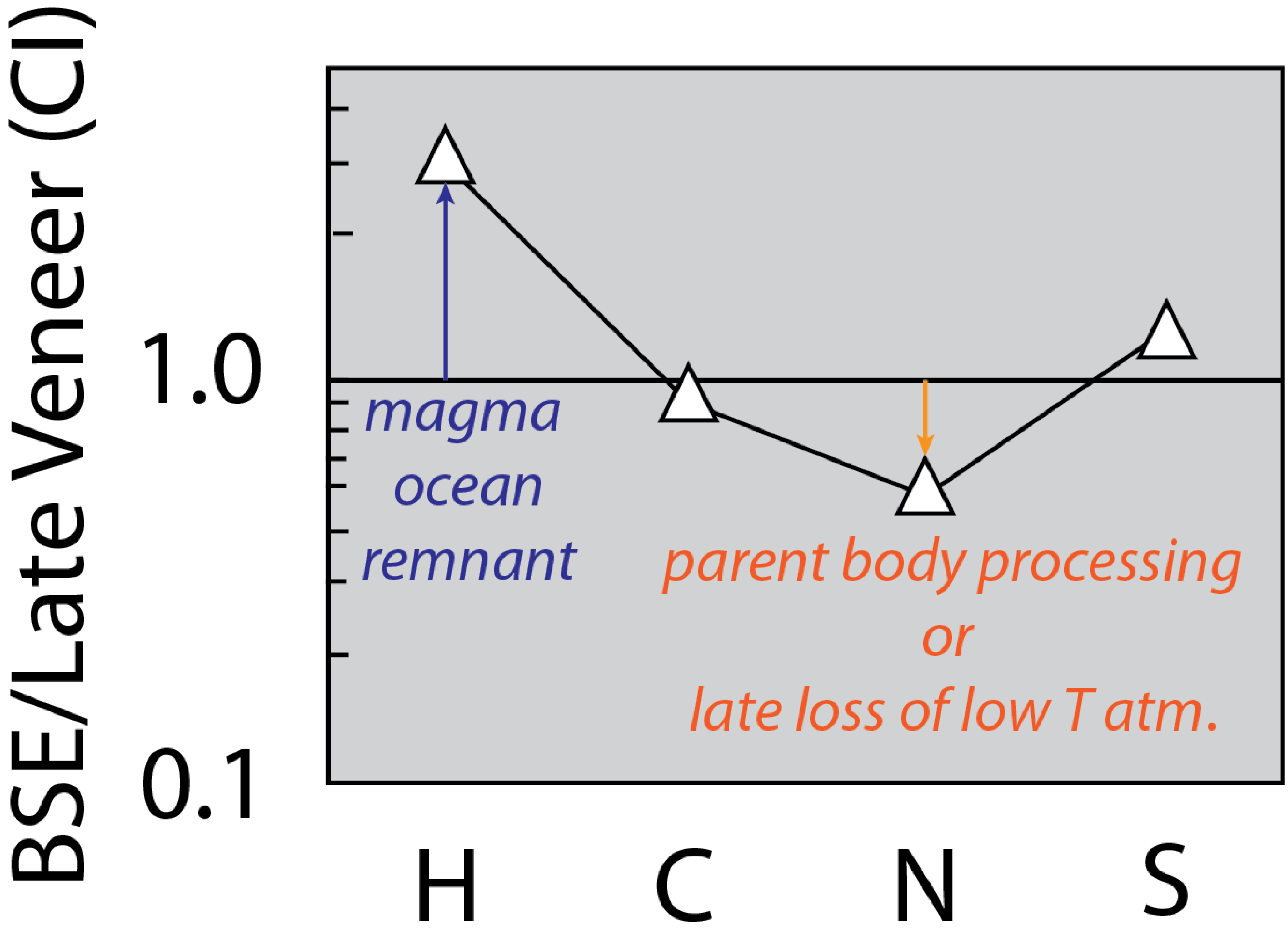


Hirschmann, 2016

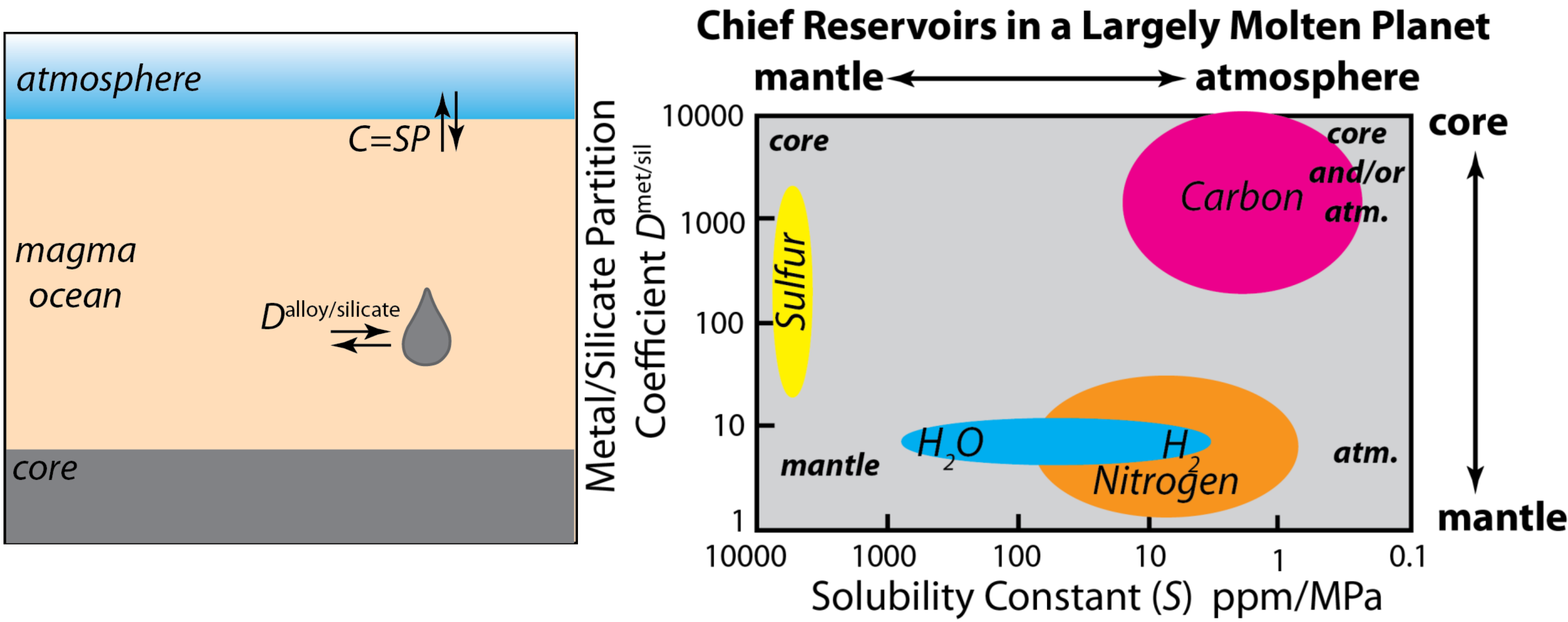
Siderophile Tendency (Preference for the core)
C>>S



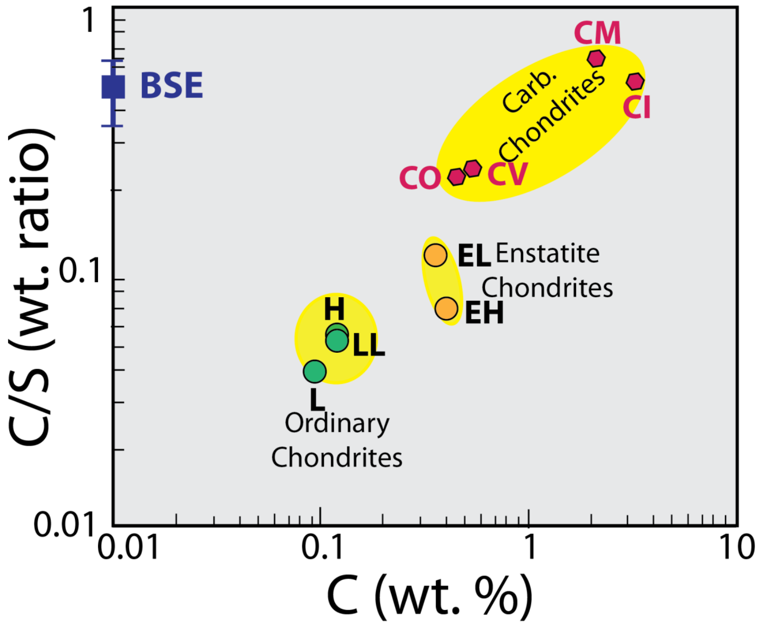


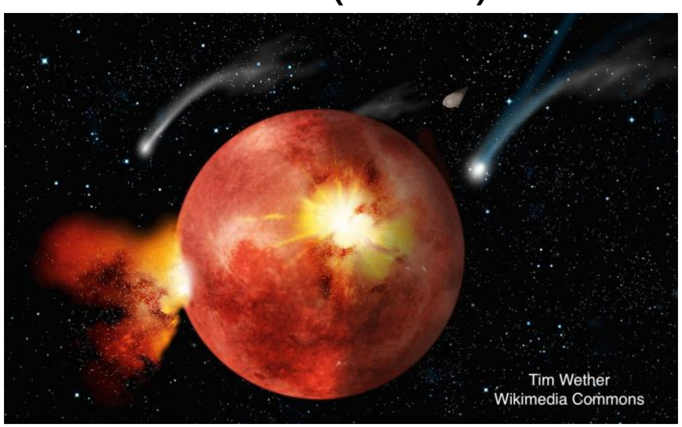


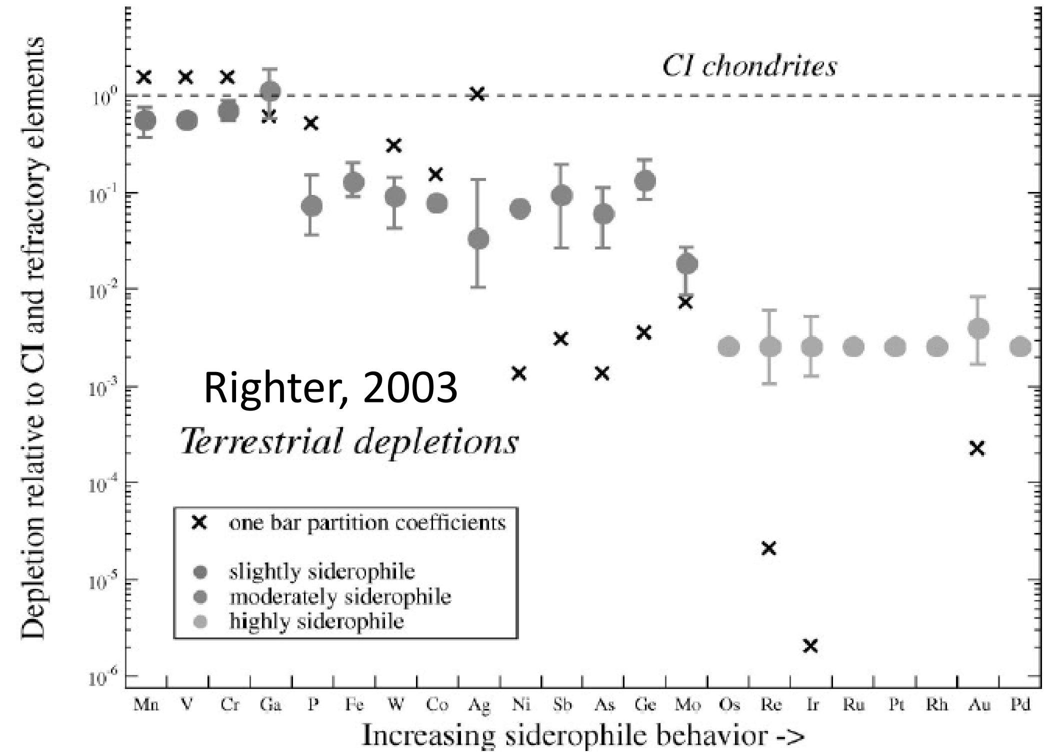
BSE/Late Veneer (CI)
1.0
0.1
magma
ocean
remnant
parent body processing
or
late loss of low T atm.
H
C
N
S

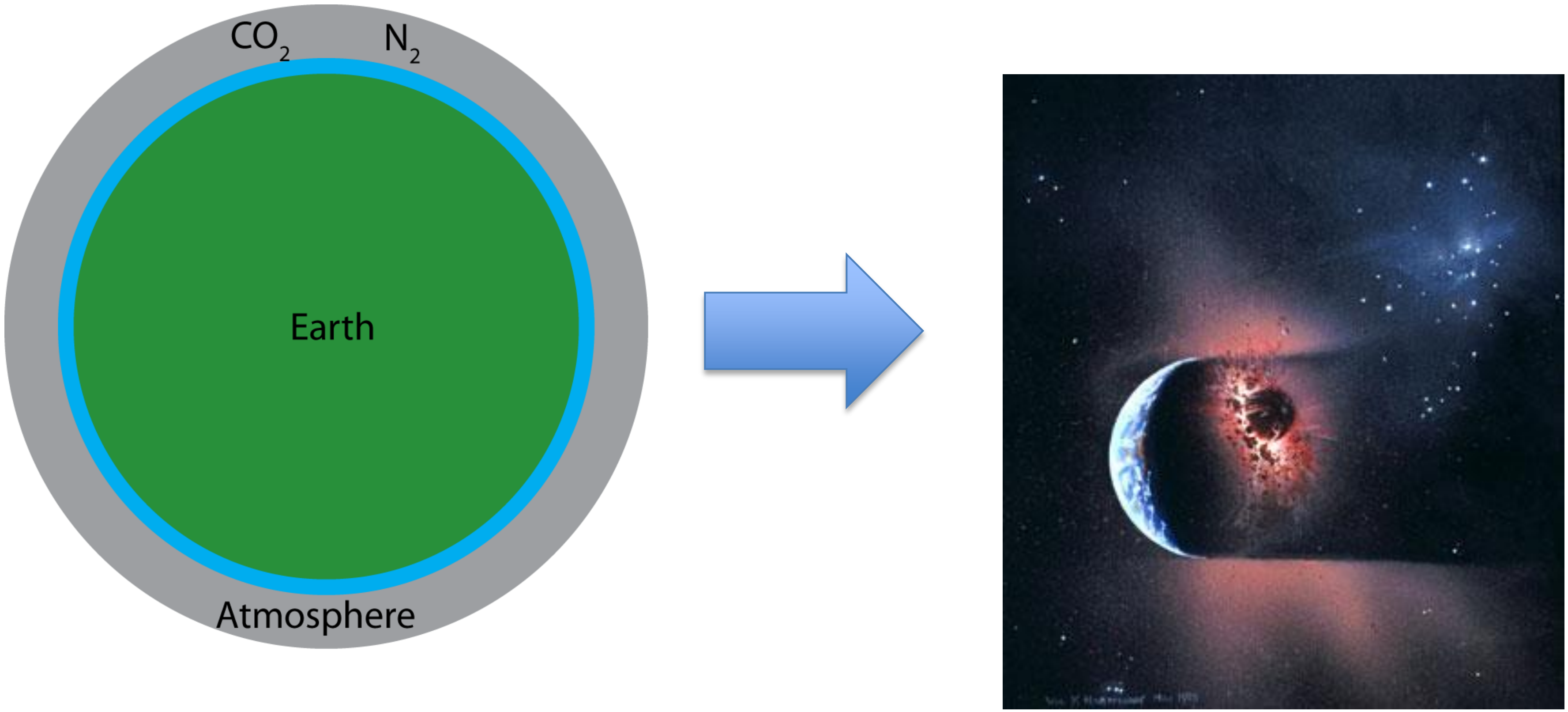

atmosphere
C=SP
magma
ocean
Dalloy/silicate
core
Chief Reservoirs in a Largely Molten Planet
mantle
atmosphere
core
mantle
Metal/Silicate Partition
Coefficient Dmet/sil
10000
1000
100
10
1
core
Sulfur
Carbon
core
and/or
atm.
H2O
H2
Nitrogen
mantle
atm.
10000
1000
100
10
1
0.1
Solubility Constant (S) ppm/MPa

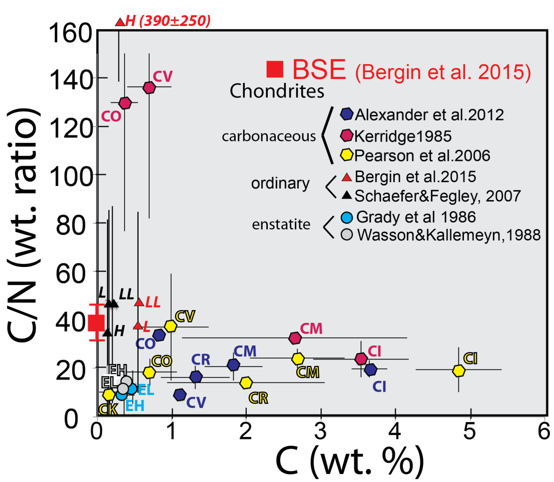
C/S ratio has echoes of the "Late Veneer"

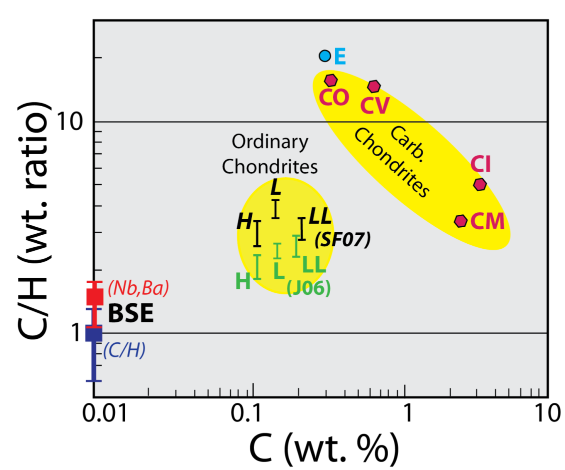


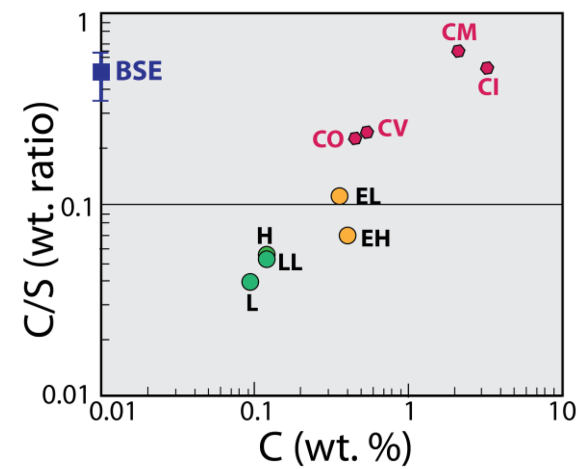





CO2
N2
Earth
Atmosphere


H (390±250)
BSE (Bergin et al. 2015)
Chondrites
carbonaceous
Alexander et al.2012
Kerridge1985
Pearson et al.2006
ordinary
Bergin et al.2015
Schaefer&Fegley, 2007
enstatite
Grady et al 1986
Wasson&Kallemeyn,1988
C/N (wt. ratio)
C (wt. %)


E
CO
CV
Carb. Chondrites
CI
CM
Ordinary Chondrites
(SF07)
(J06)
(Nb,Ba)
BSE
(C/H)
C/H (wt. ratio)
C (wt. %)


BSE
CM
CI
CO
CV
EL
EH
H
LL
L
C/S (wt. ratio)
C (wt. %)

Summary

- The BSE budgets of C and H are well-constrained by ratios to refractory lithophile elements (Ba, Ce)
- BSE volatiles are low, but there are plenty of loss mechanisms (to core, to space)
- BSE volatiles are fractionated relative to chondrites. Either volatiles were delivered by differentiated bodies or there were selective loss mechanisms during differentiation. Probably both.