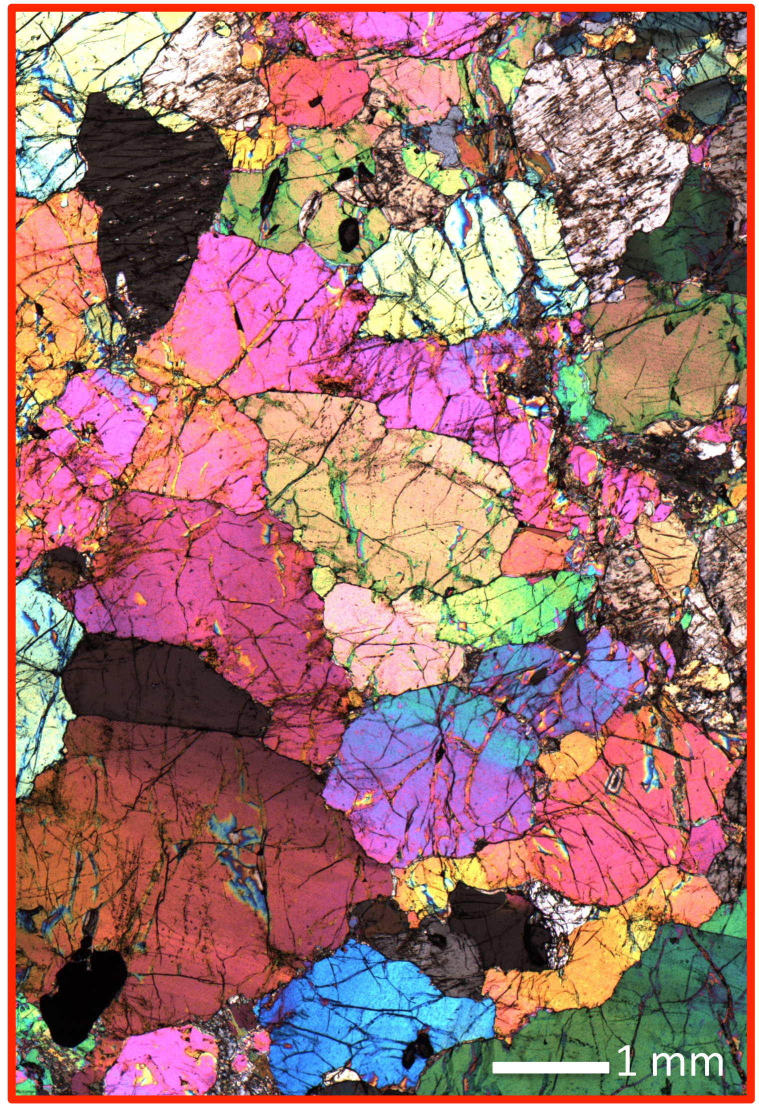
Planetary "Redox"

Liz Cottrell
National Museum of Natural History
Smithsonian Institution



Peridotite, Tonga Fore-Arc
Credit: S. Birner

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"geological activity is all about convection … and by the way, so is all of ocean and atmospheric science."

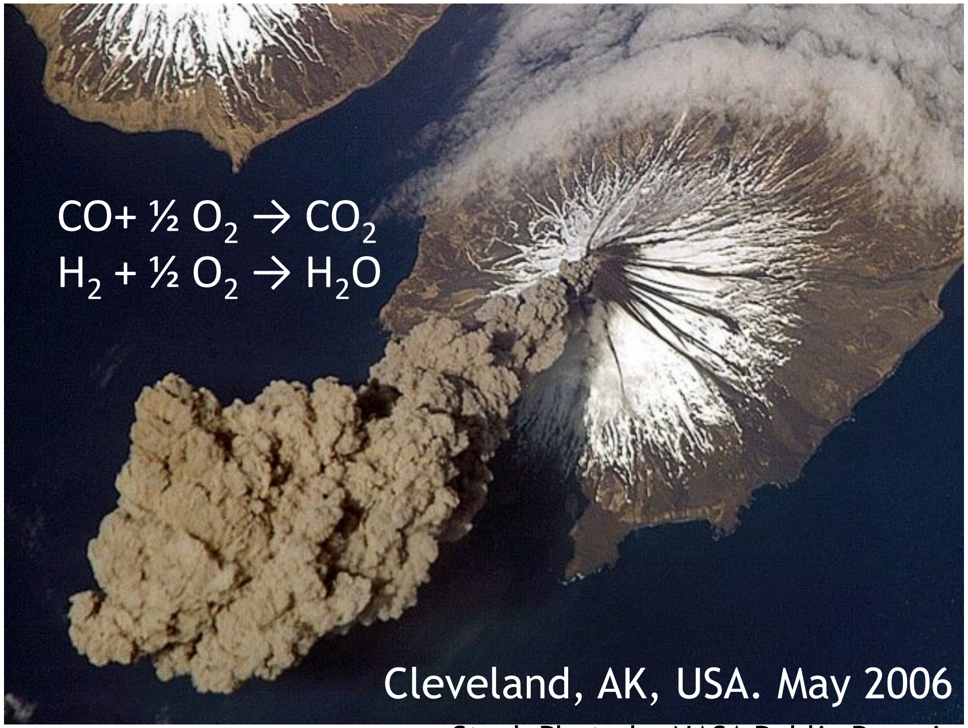
- Bruce Buffet, CIDER 2014

“geological activity is all about *redox* … and by the way, so is life.”

- Liz Cottrell, CIDER 2014

Redox, Oxygen, f_{O2}… Why to care.

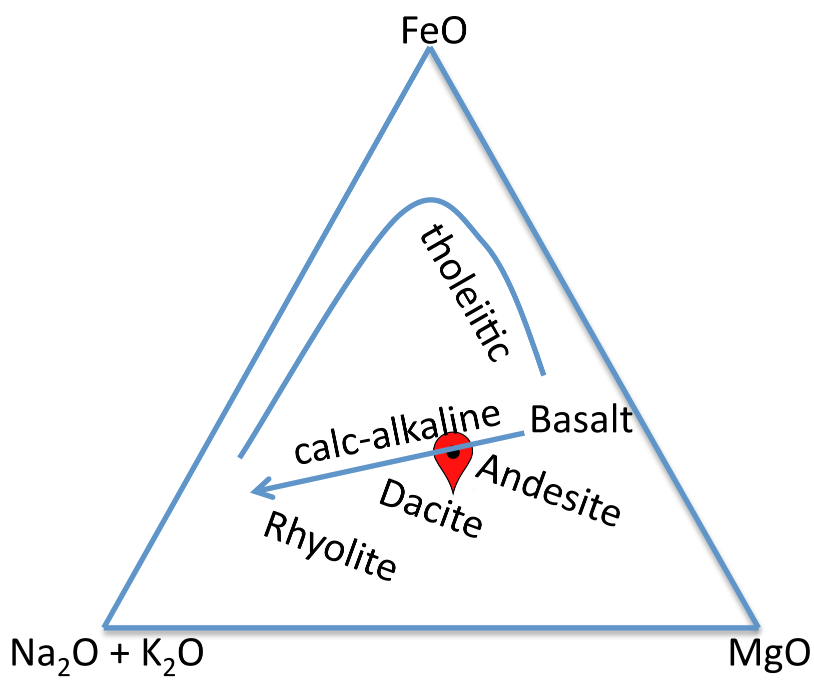
You breath oxygen. Enables a habitable planet.



Stock Photo by NASA Public Domain

Redox, Oxygen, f_{O2}… Why to care.

You live on land. Enables creation of continental crust.

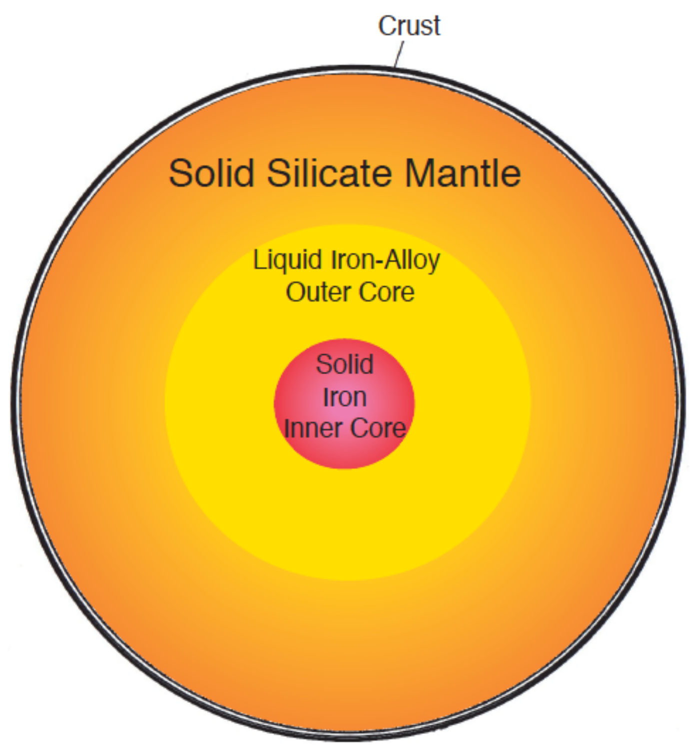


"With the hope of resolving the conflicting views of Bowen and Fenner, the present writer took to remelt and crystallize some natural basalts in laboratory crucibles. It became immediately apparent that the same basalt could be made to follow the Bowen trend … or the Fenner trend … depending on the partial pressure of oxygen…" – Kennedy, 1955

Kennedy, GSA Special Paper, 1955.

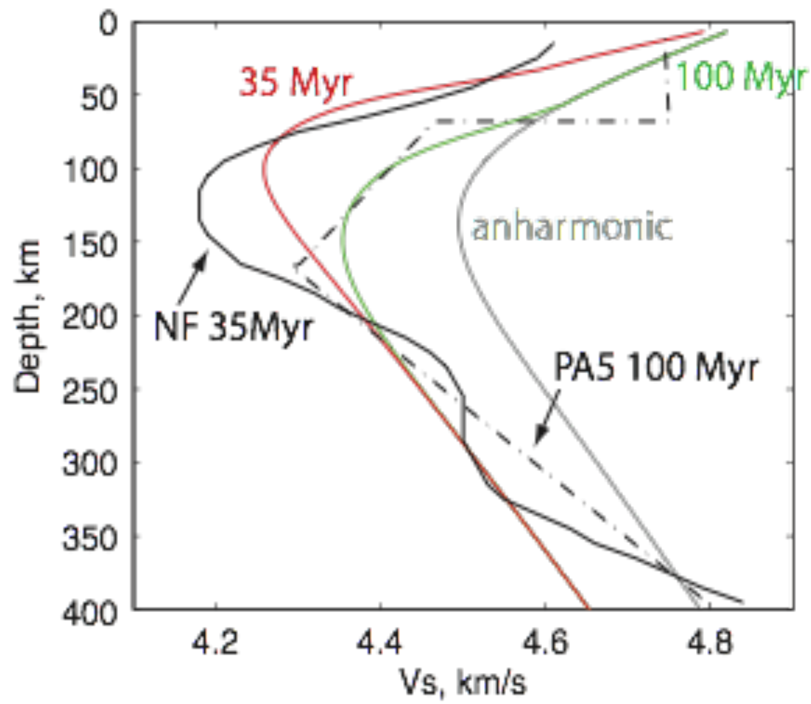
Redox, Oxygen, f_{O2}... Why to care.

You eschew cosmic rays. Enables a core.



Redox, Oxygen, f_{O2}… Why to care.

Interpretation of geophysical observations
of the upper mantle hinges on it.



Jackson & Faul, 2010

Getting things straight

Oxidation State

- hypothetical charge
- unrelated to oxygen

Fe^{3+} + e^{-} = Fe^{2+} (reduction)

$$K = \frac{[Fe^{2+}]}{[Fe^{3+}][e^{-}]} = 10^{13}$$

[e^{-}] = the activity of electrons, or pe

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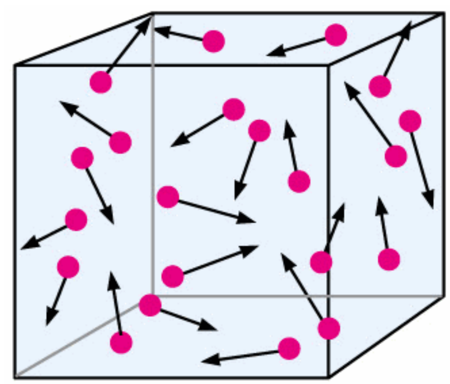
Fugacity (f_i)



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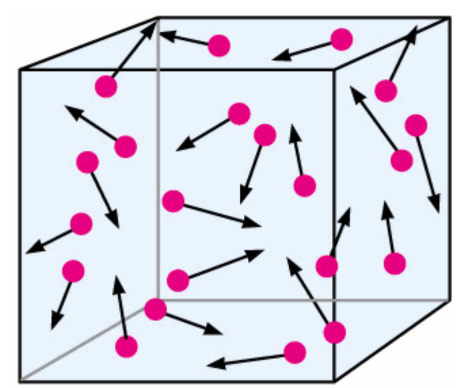
Fugacity (f_i)

- invented
- unrelated to oxygen
- the 'escaping tendency' (fugitive)
- $f_i = P_i$ when i is an ideal gas

$$\lim \frac{f}{P} \to 1, P \to 0$$



Fugacity, f

From the ideal gas law and

Gibbs free energy (energy to do non-PV work; combined 1st and 2nd laws)

of a gas at constant temperature

$$PV = nRT, V = \frac{nRT}{P}$$

$$dG = -SdT + VdP$$

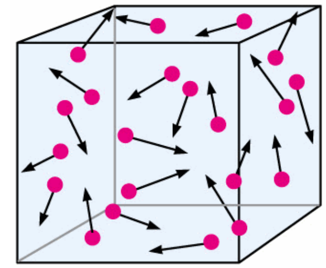
$$dG = VdP$$

$$G(P) - G(P_0) = \int_{P0}^{P} V\, dP = nRT \int_{P0}^{P} \frac{1}{P} dP$$

$$G(P) = G(P_0) + nRT \ln(\frac{P}{P_0})$$

$$\mu = \mu_i + RT \ln(\frac{P}{P_0})$$

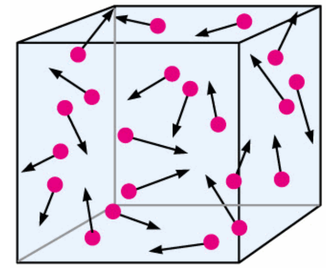
Fugacity, f



$$\mu = \mu_i + RT\ln(\frac{f}{f_0})$$

- But no gas is ideal so we make up a correction and replace the "p"s with "f"s (fudge factors).

Fugacity, f



$$\mu = \mu_i + RT\ln\left(\frac{f}{f_0}\right)$$

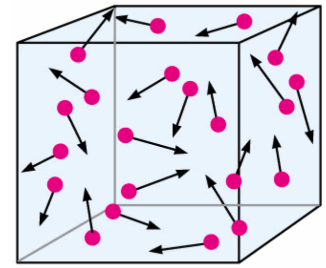
$$f = \gamma_i P_i$$

$$a_i = \gamma_i X_i$$

- But no gas is ideal so we make up a correction and replace the “p”s with “f”s (fudge factors).

- Fugacity is a corrected pressure and is closely related to the idea of ***activity (a)*** – a corrected concentration. *(*They are the same at 1 bar.)

Fugacity, f



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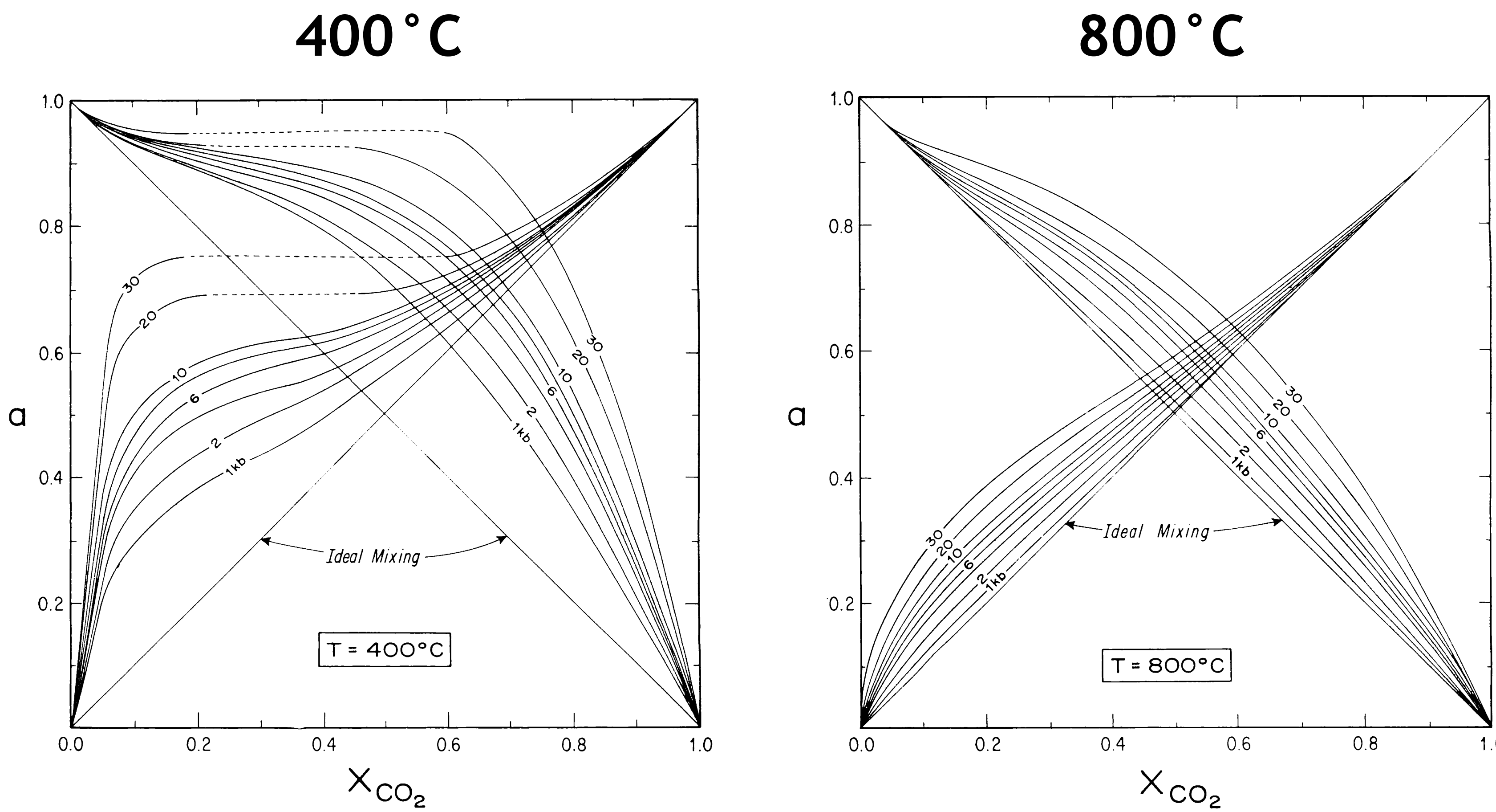
- But no gas is ideal so we make up a correction and replace the "p"s with "f"s (fudge factors).
- Fugacity is a corrected pressure and is closely related to the idea of ***activity (a)*** – a corrected concentration. *(*They are the same at 1 bar.)
- If rocks were an ideal gas, we'd just call it partial pressure!

forget rocks, even gases aren't ideal

activity-composition diagrams



Kerrick & Jacobs, 1981

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Oxygen Fugacity f_{O2}

$$Fe + \frac{1}{2}O_2 = FeO$$

$$M + \frac{x}{4}O_2 = MO_{x/2}$$

$$Keq = \frac{a_{MOx/2}}{a_M \cdot (f_{O2})^{x/4}} = \frac{\gamma_{MOx/2} \cdot X_{MOx/2}}{\gamma_M \cdot X_M \cdot (f_{O2})^{x/4}}$$

$$\log K = \log\frac{1}{D} + \log\frac{\gamma_{MOx/2}}{\gamma_M} - \frac{x}{4}\log f_{O2}$$

$$\log D = -\frac{x}{4}\log f_{O2} + const$$

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$$D = \frac{X_M^{metal}}{X_M^{silicate}}$$

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$$\frac{1}{D}$$

where D = met/sil partition coefficient

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ratio of activity coefficients = 1 (Henry's Law)

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Eqn of a line.
Valence state = 4 x slope

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ratio of activity coefficients = 1
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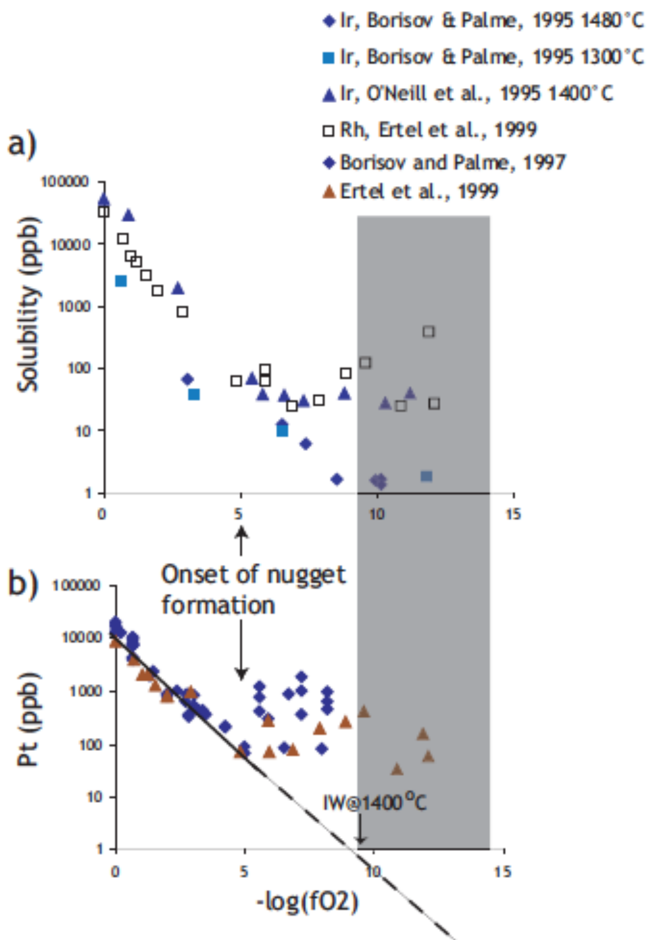
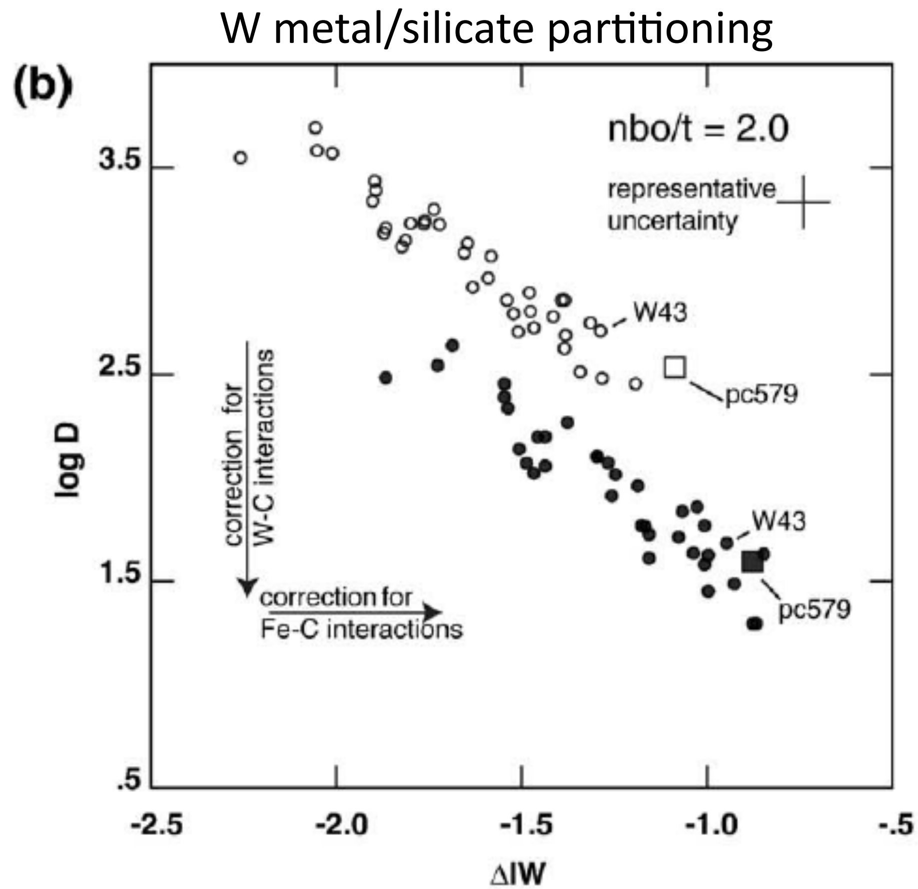
recall from Rich's talk





Cottrell et al., 2009

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For pure substances, activity is unity.

When Fe and FeO are in equilibrium, f_{O2} is fixed. This is the iron-wüstite buffer, IW

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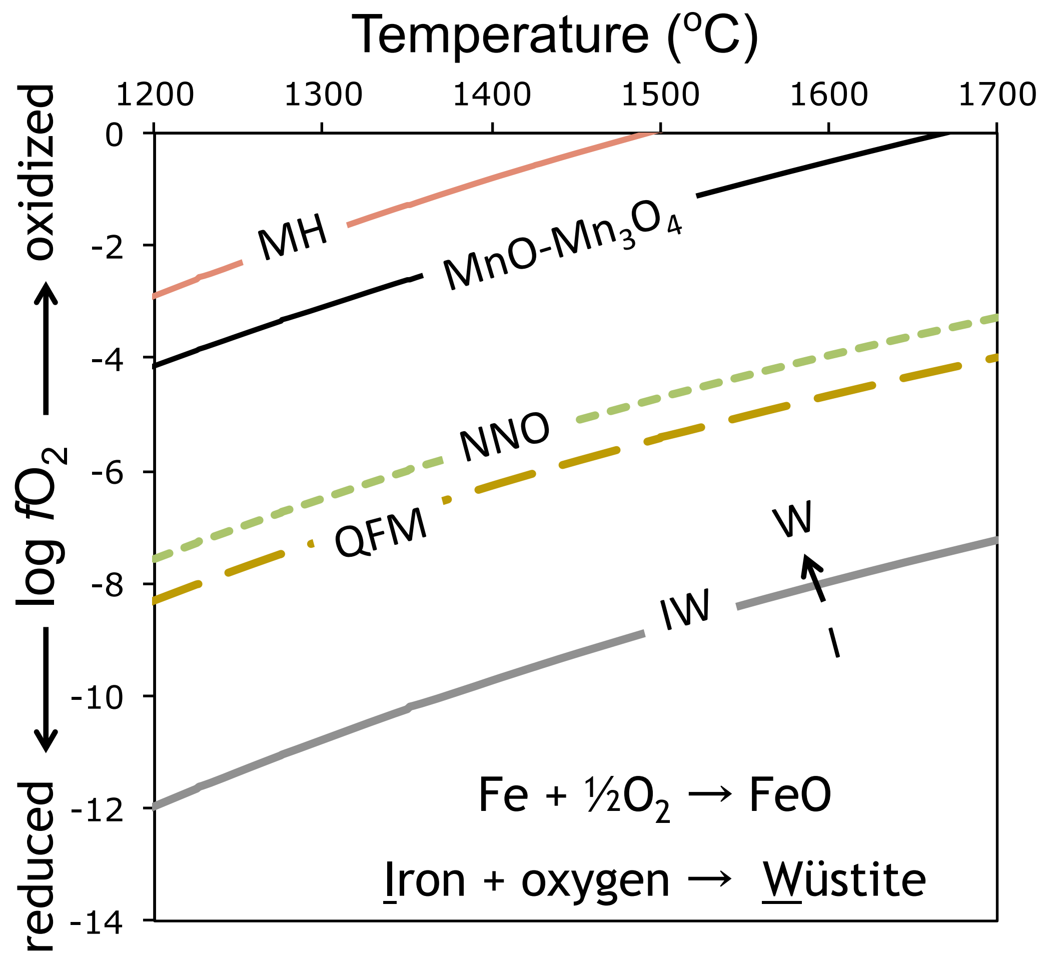
For fun… the core is 85 wt.%Fe and the mantle is 8 wt.% FeO. Convince yourself that core formation took place at IW-2.25.

Oxygen Fugacity f_{O2}

If you were asleep and are now waking up…

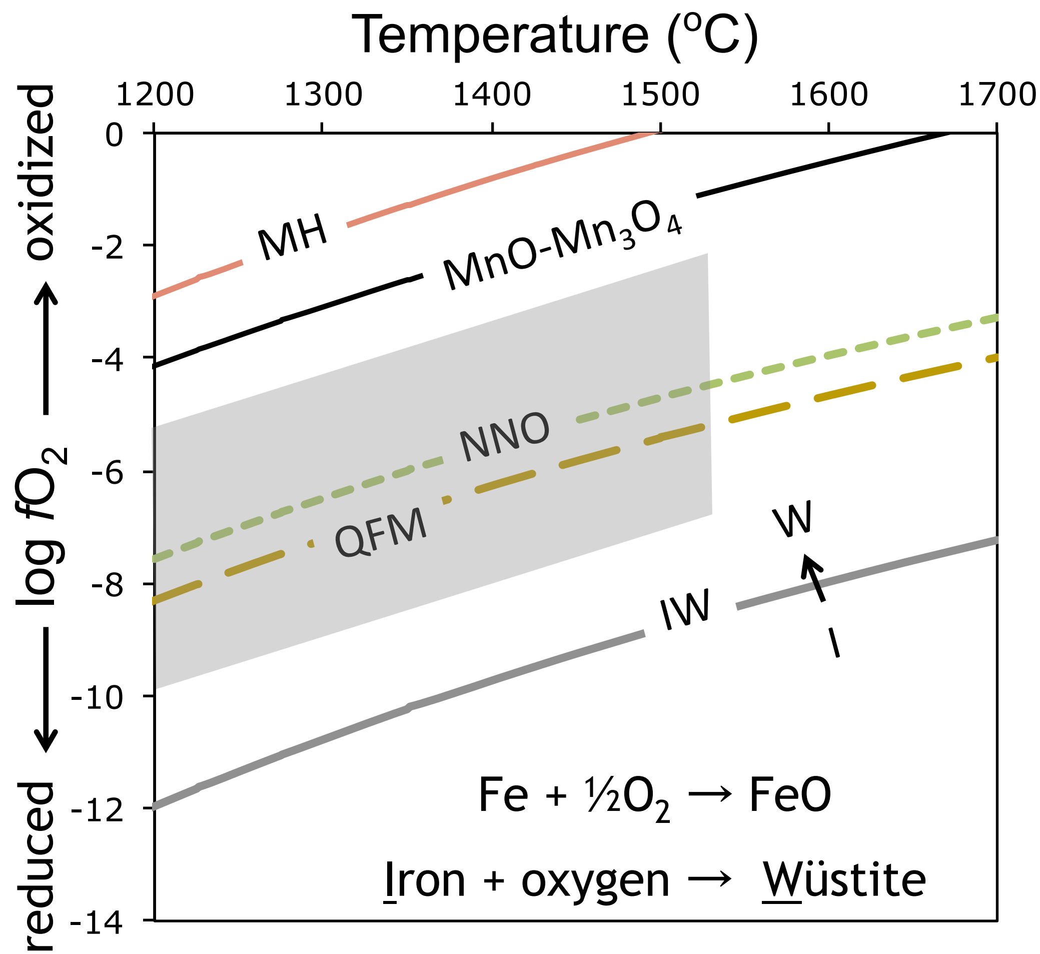
If rocks were an ideal gas, we'd just call it partial pressure.

Oxygen Fugacity f_{O2} Buffers



Oxygen Fugacity f_{O2} Buffers

Buffers, originating with Eugster in the 60s, are super-duper useful in experimental petrology.

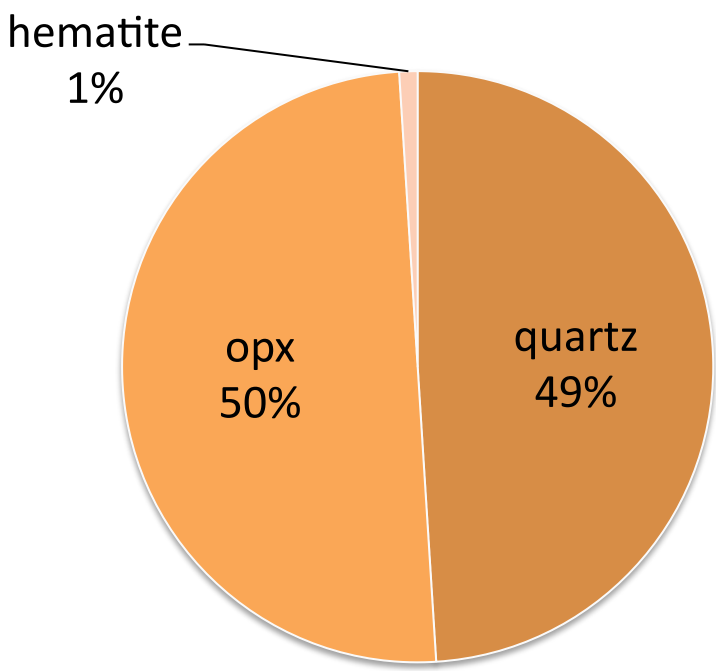


Piston cylinder charge: basalt within a Pt-jacketed olv capsule, with Ni and NiO. Cottrell et al., in prep

Rookie Errors

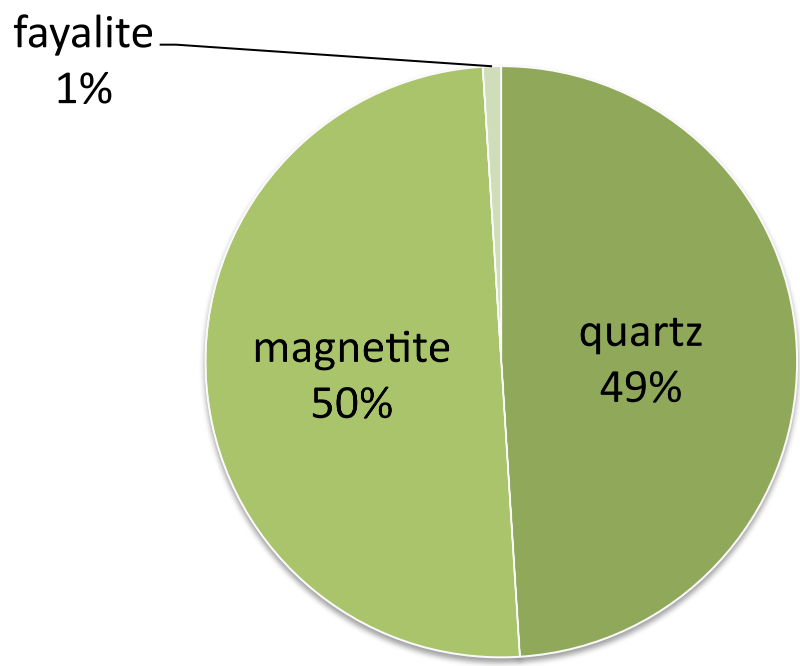
- f_{O2} without a temperature is meaningless.
- There is no free O_2 in condensed media (like the Earth!). Oxygen fugacity is actually "meaningless" in the deep Earth. We are talking about the f_{O2} the gas *would have* if it were in equilibrium with the rock.
- When we say that a magma is at the NNO buffer, it does not mean that those phases (Ni and NiO) are floating around in the magma.
- There is no needle valve in the mantle; f_{O2} is not imposed.
- Oxidation and reduction *of a system* requires someone to come or go. Otherwise electrons are just changing hands.
- Oxidation state can have a very opaque relationship with f_{O2}.

Rock at >HM



Fe^{2+}/Fe^{3+} = 6.3

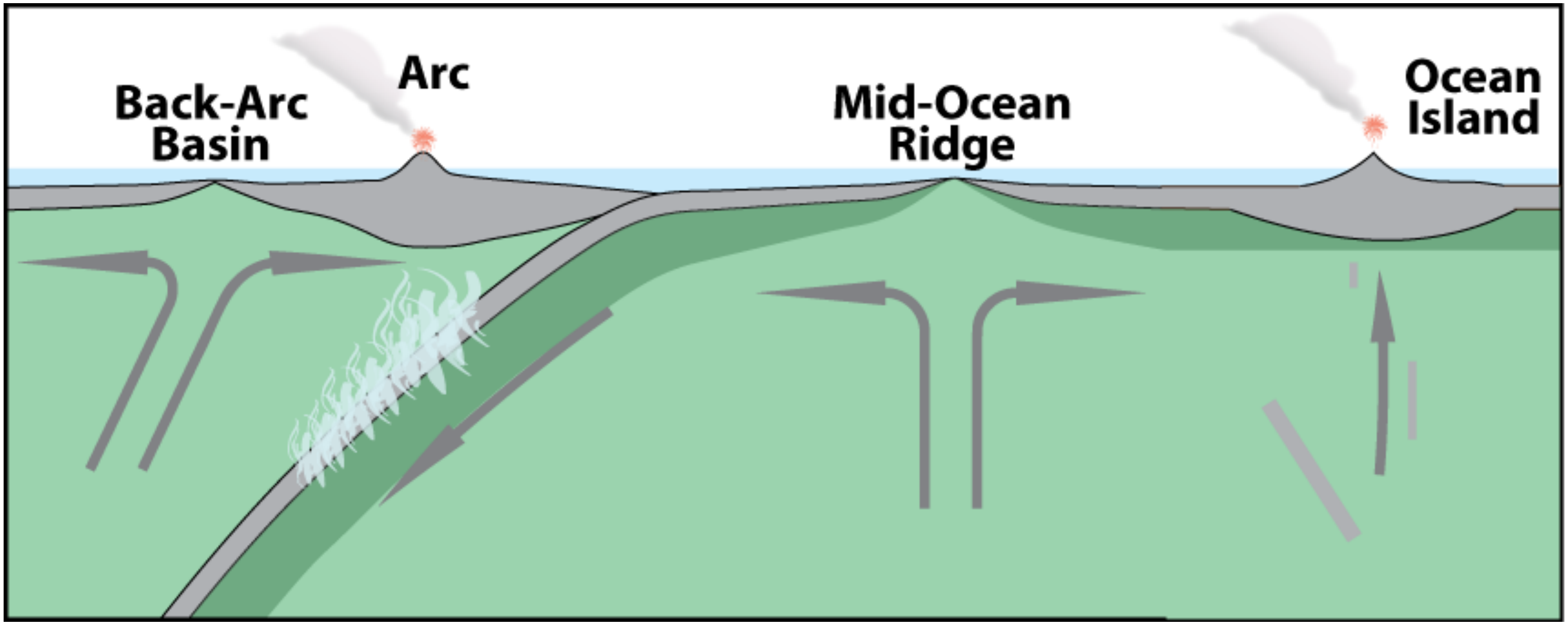
Rock at QFM



Fe^{2+}/Fe^{3+} = 0.47

Example from Frost, Rev. in Min, 1991

Free O_2 up here.

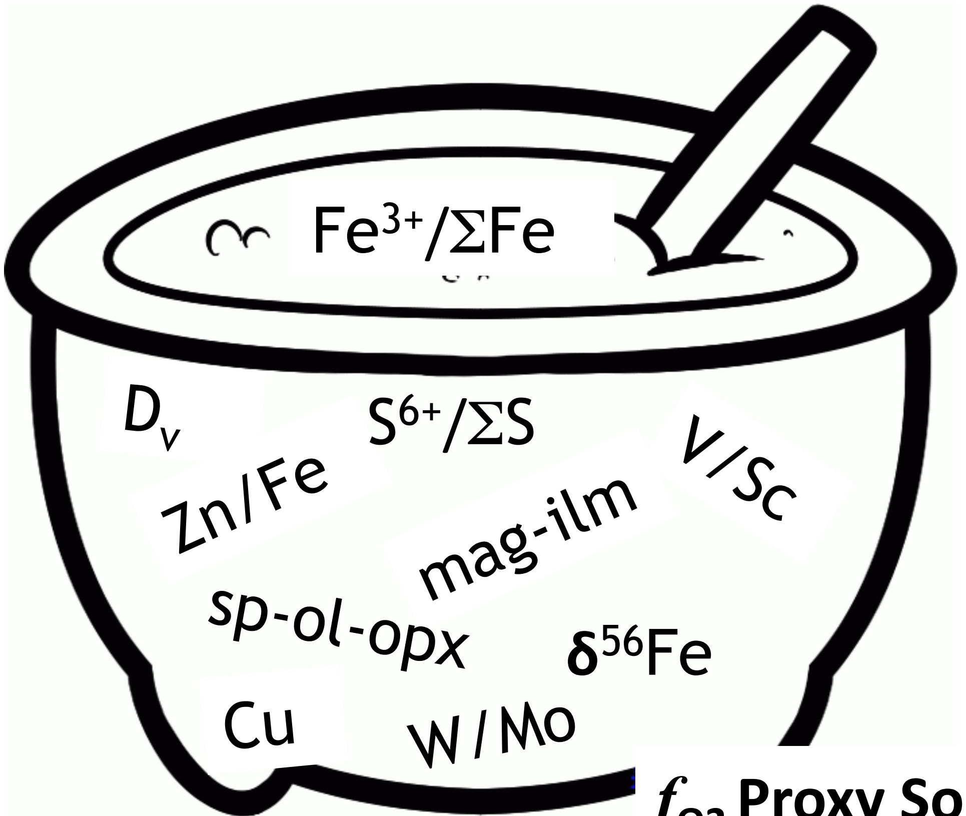


The core is down there ↓

Modified from Kelley & Cottrell, Science, 2009

Oxygen Fugacity f_{O2}

Measuring O_2 or its activity in rocks is important, but tricky.



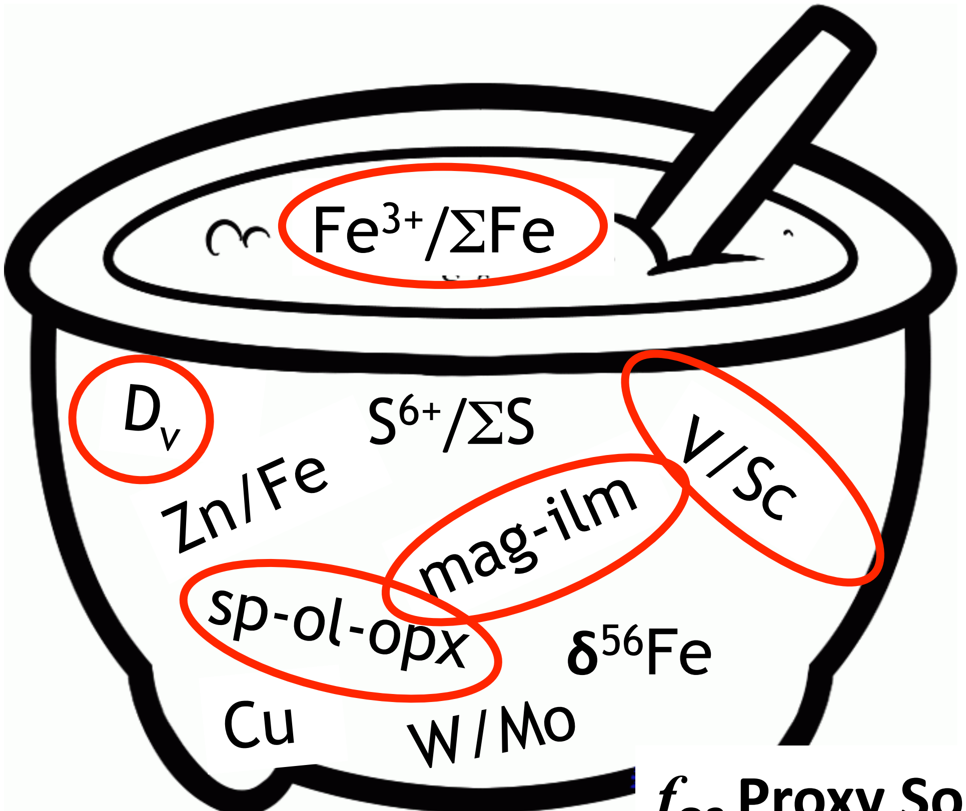
f_{O2} **Proxy Soup**

Oxygen Fugacity f_{O2}

Measuring O_2 or its activity in rocks is important, but tricky.

Not all proxies work for all samples.

Not all proxies agree.



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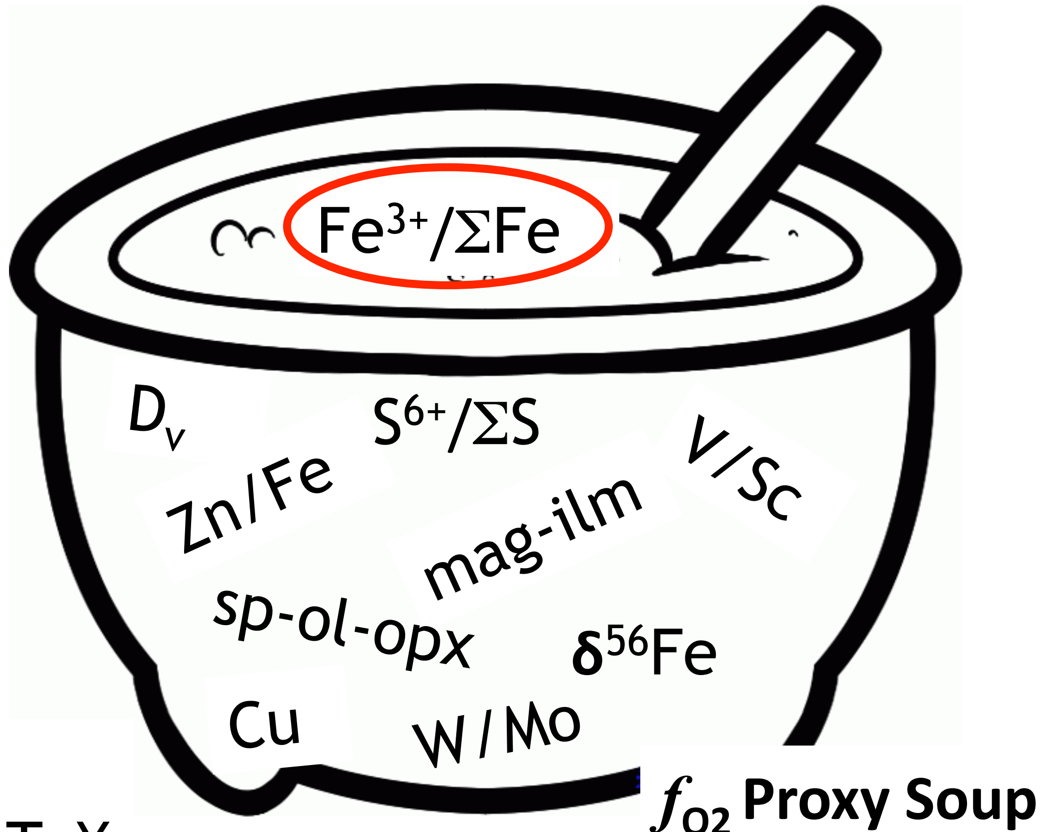

In silicate melts, $Fe^{3+}/\Sigma Fe$ varies as a function of f_{O2}, T, X

Micro-colorimetric determination of Fe speciation at NMNH
Credit: S. Grocke

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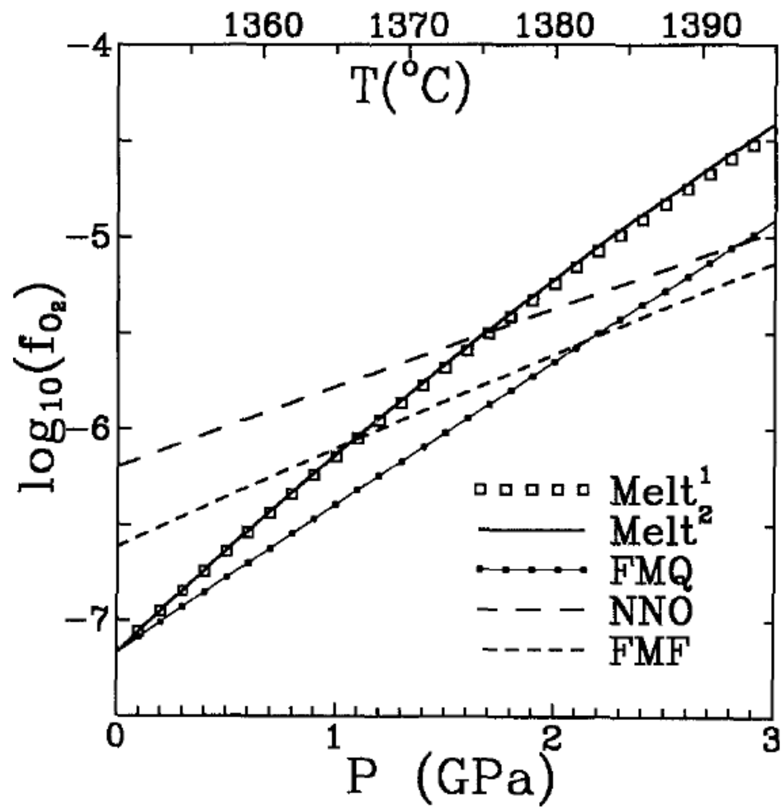
In <u>liquids</u>, there are no crystal-chemical controls, and the $Fe^{3+}/\Sigma Fe$ ratio *is* a function of f_{O2}

$$\ln\left(\boxed{\frac{X_{Fe_2O_3}}{X_{FeO}}}\right) = a\ln\boxed{(f_{O_2})} + \frac{b}{T} + c + \sum_i d_i X_i + e\left[1 - \frac{T_o}{T} - \ln\left(\frac{T}{T_o}\right)\right] + f\frac{P}{T} + g\frac{(T-T_o)P}{T} + h\frac{P^2}{T}.$$

The $Fe^{3+}/\Sigma Fe$ ratio of a basalt should tell us about the f_{O2} of the mantle



Kress and Carmichael, 1991; compressibility (P term) confirmed by O'Neill et al., 2006

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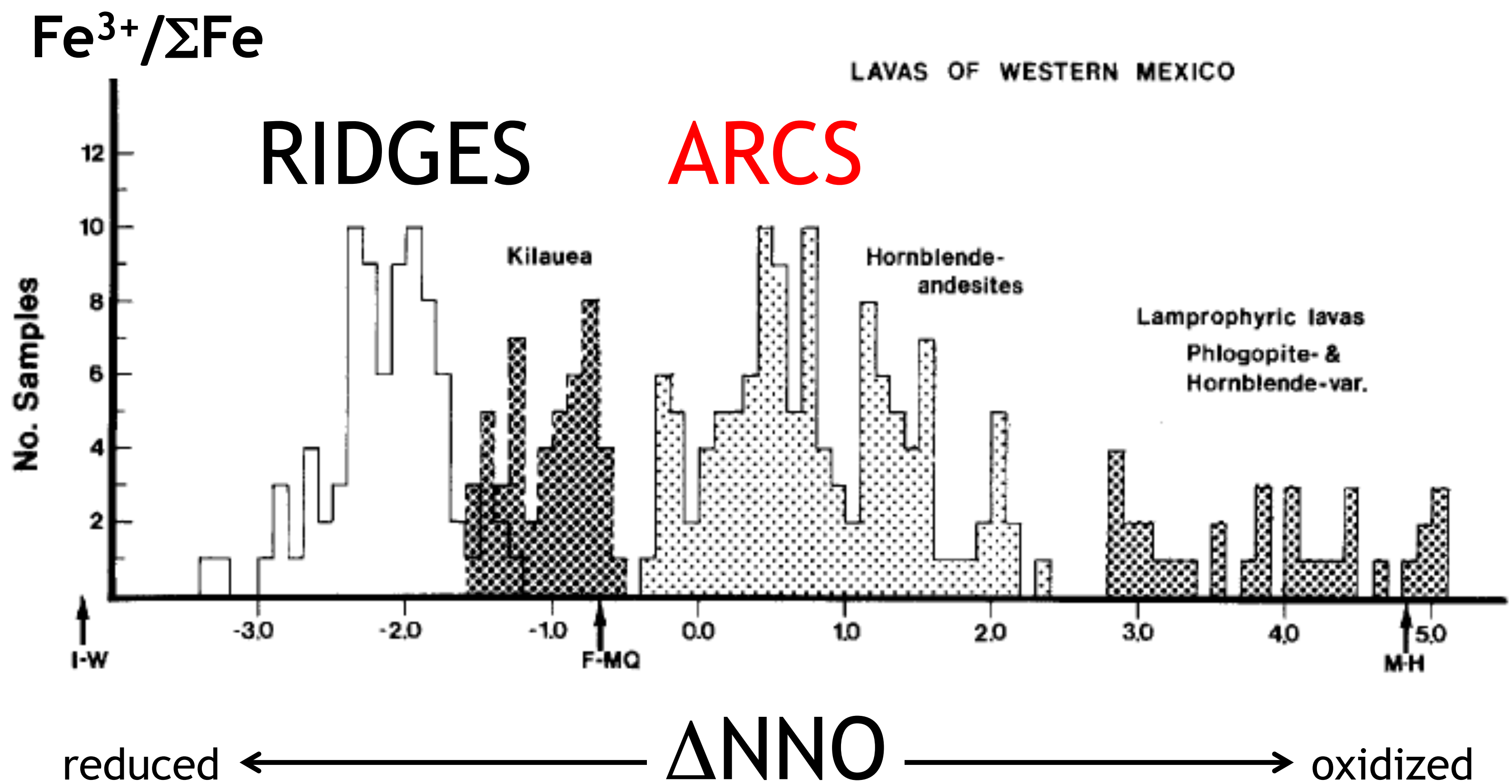
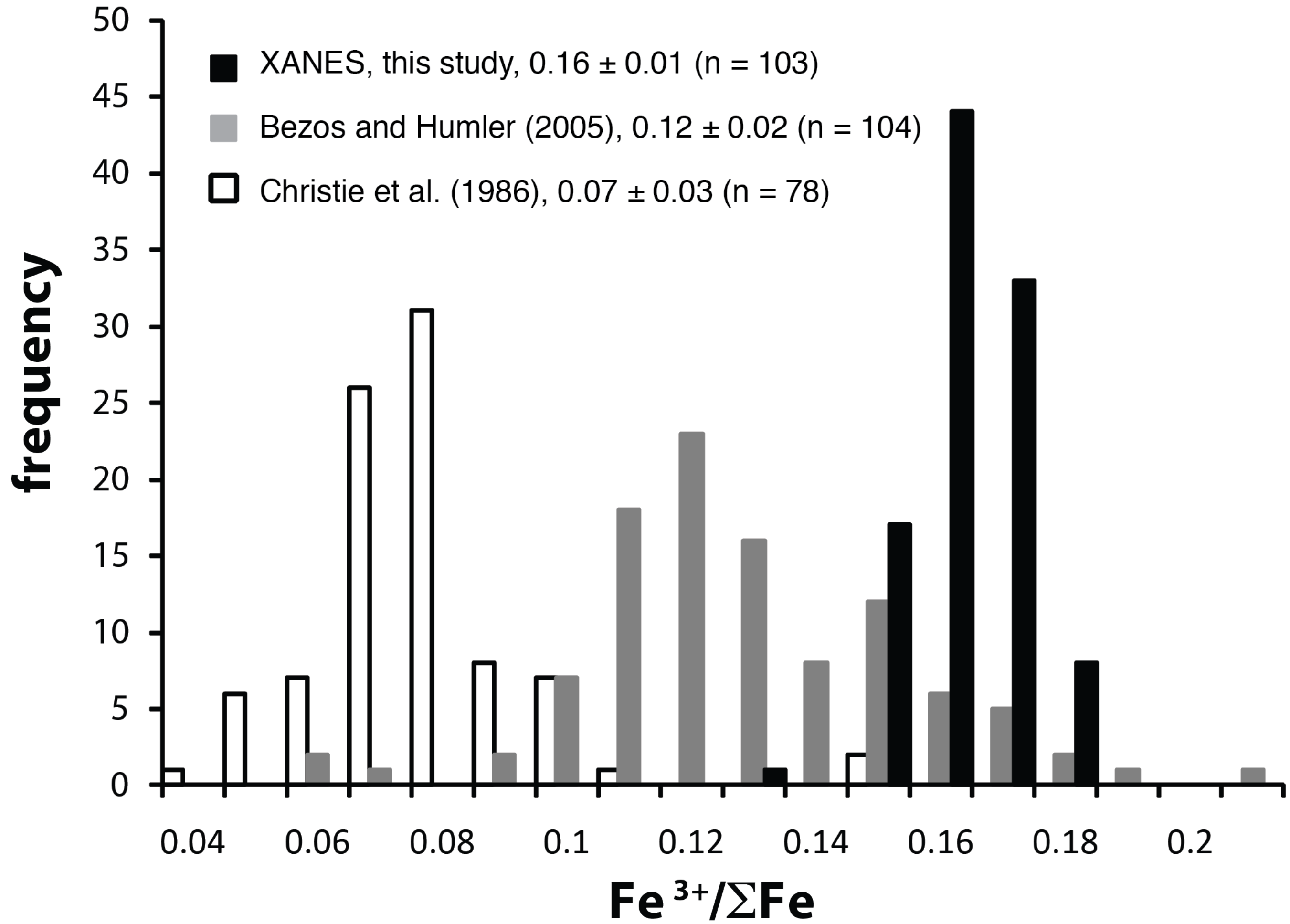
First order observations



Carmichael, CMP, 1991.

MORB



Cottrell and Kelley, EPSL, 2011

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Oxygen Fugacity f_{O2}

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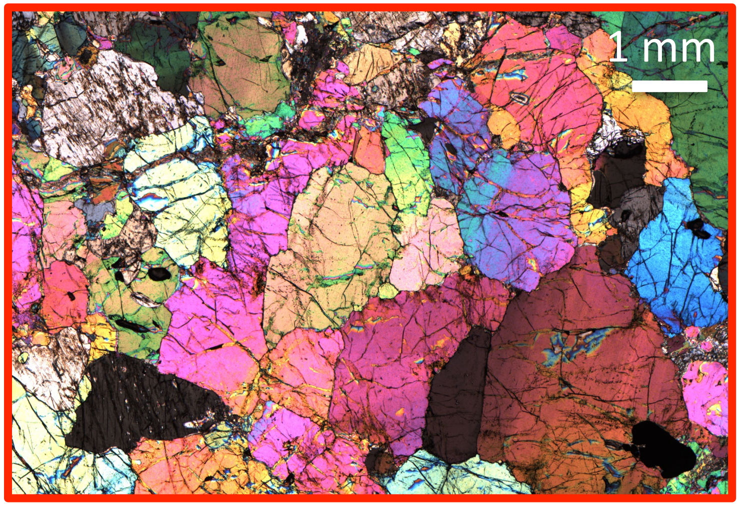
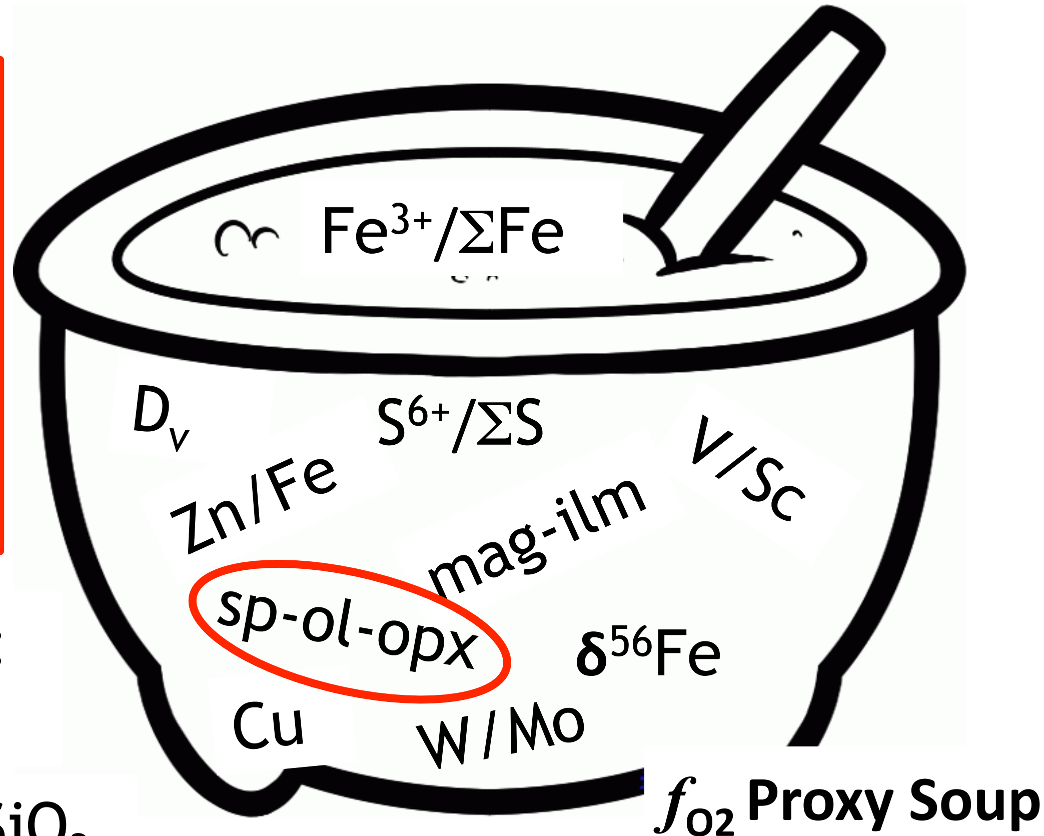


Upper mantle assemblage:
olv + spl + opx

$$6Fe_2SiO_4+O_2 \rightarrow 2Fe_3O_4+6FeSiO_3$$



Spinel peridotite oxygen barometry by EMPA at NMNH
Credit: S. Birner

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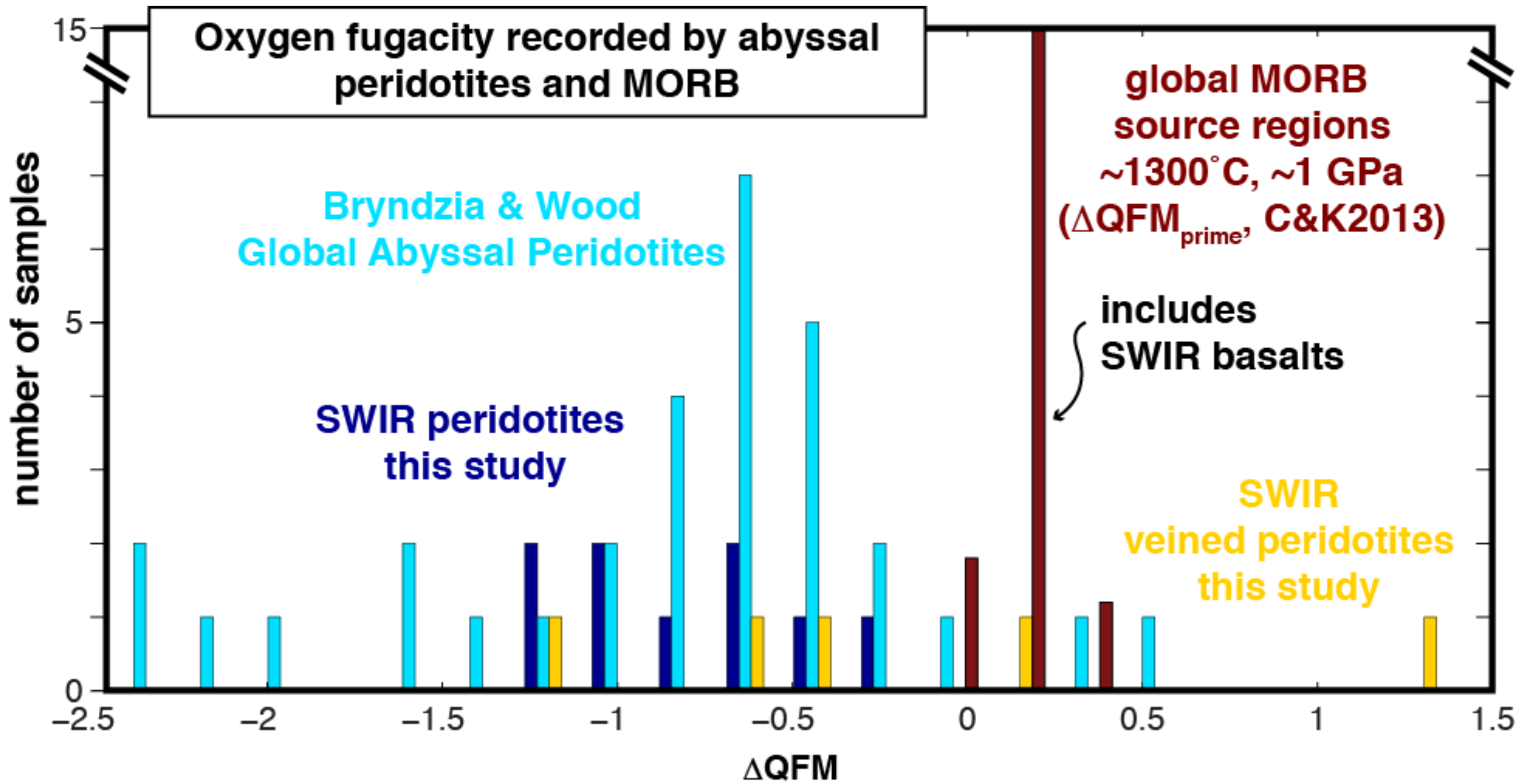

Birner, Cottrell, Warren, Davis, and Kelley, unpublished and in prep

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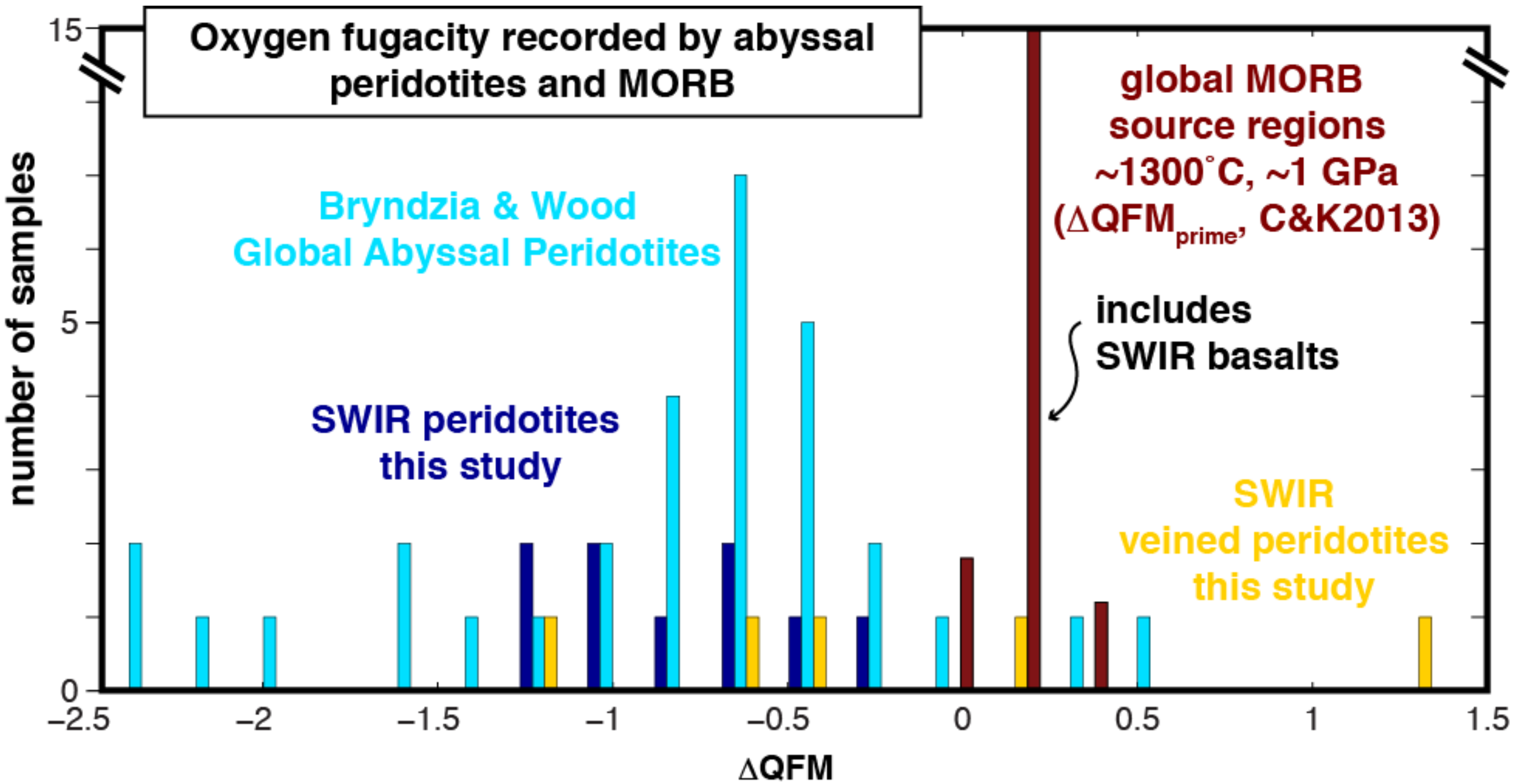

Didn’t we decide earlier that core formation took place at approx. IW-2?
That is 5 orders of magnitude lower than the modern mantle.
How did we get here? When?

Birner, Cottrell, Warren, Davis, and Kelley,
unpublished and in prep

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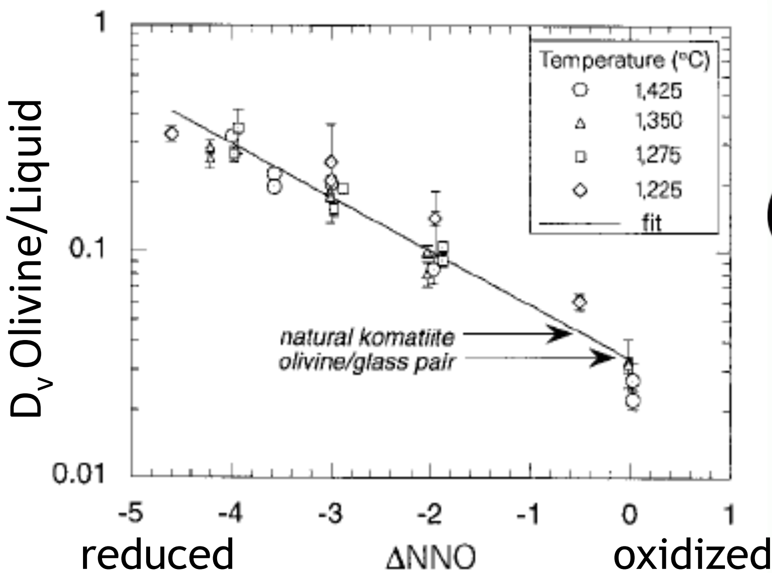
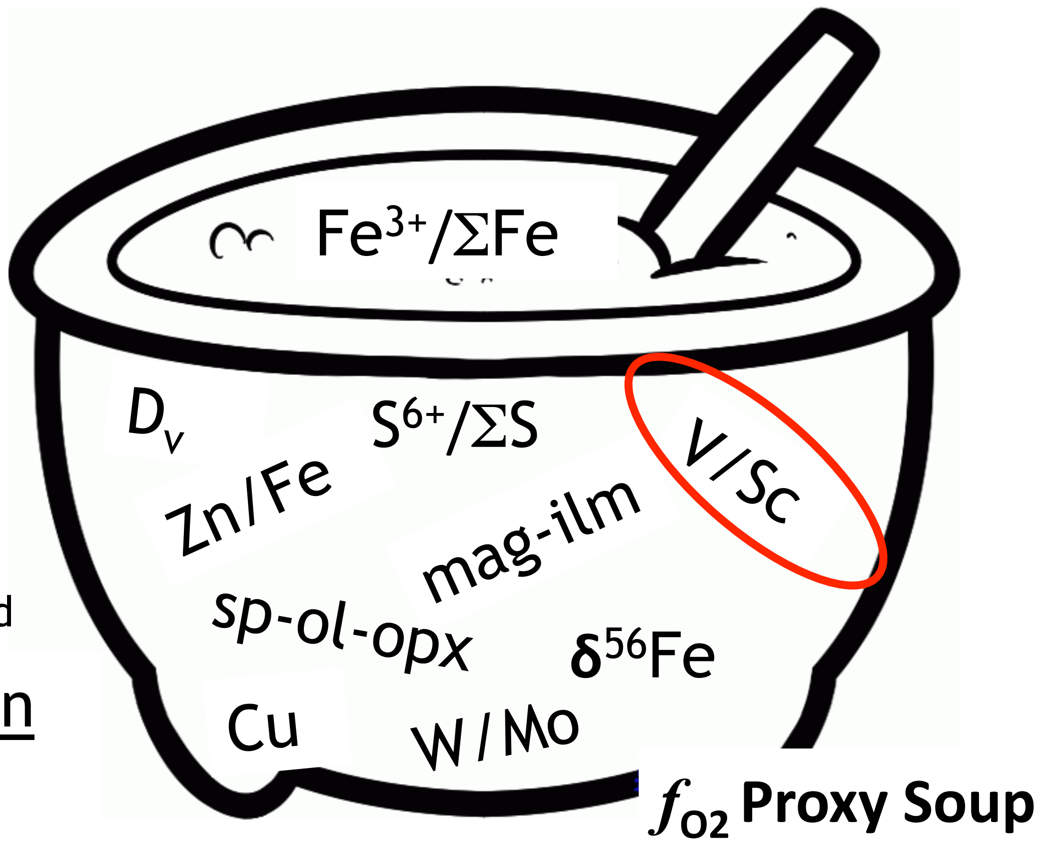
Oxygen Fugacity f_{O2}

Measuring O_2 or its activity in rocks is important, but tricky.

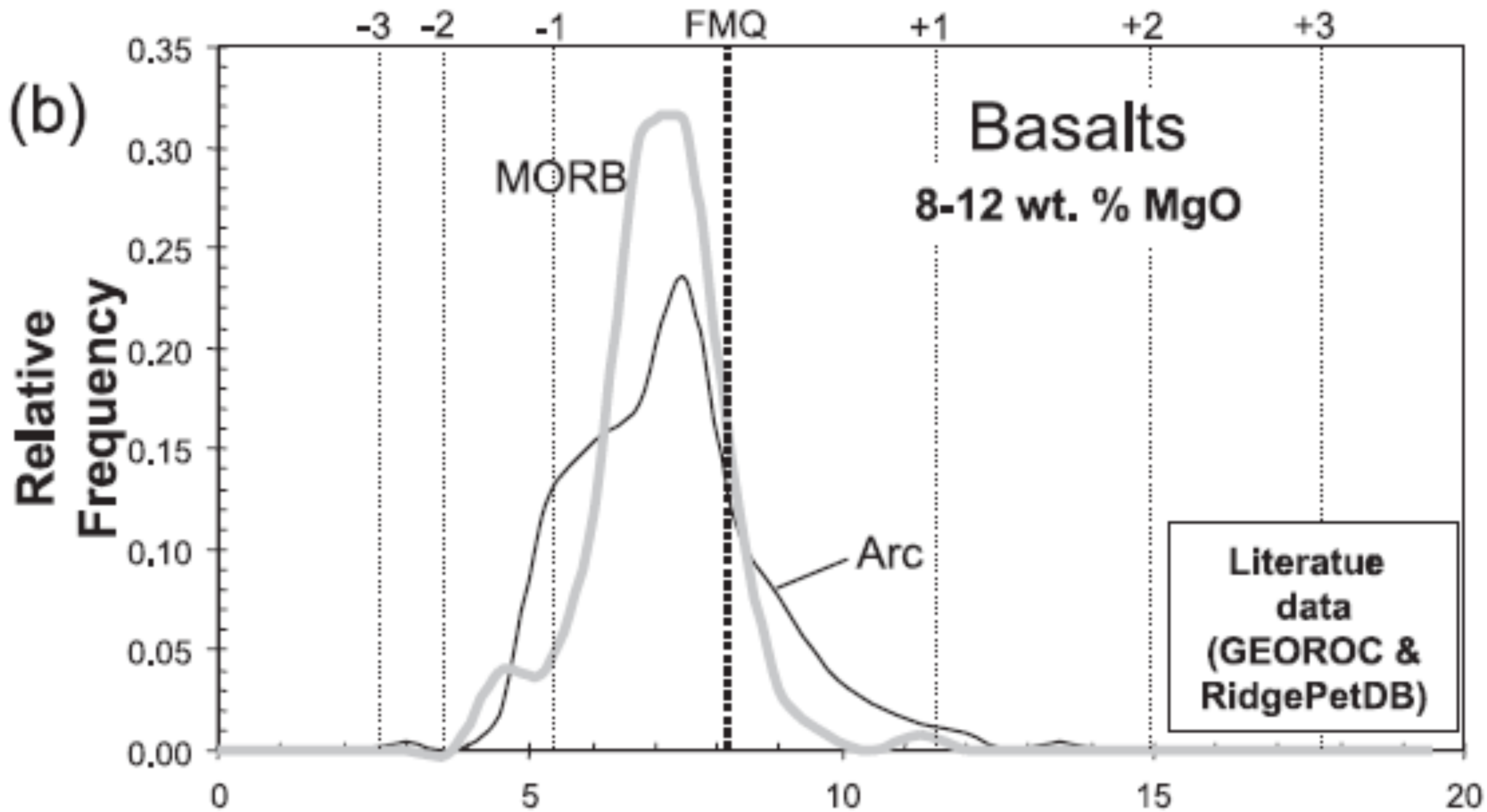


Whole rock V concentration may be set by f_{O2} during melting.



Canil, Nature, 1997

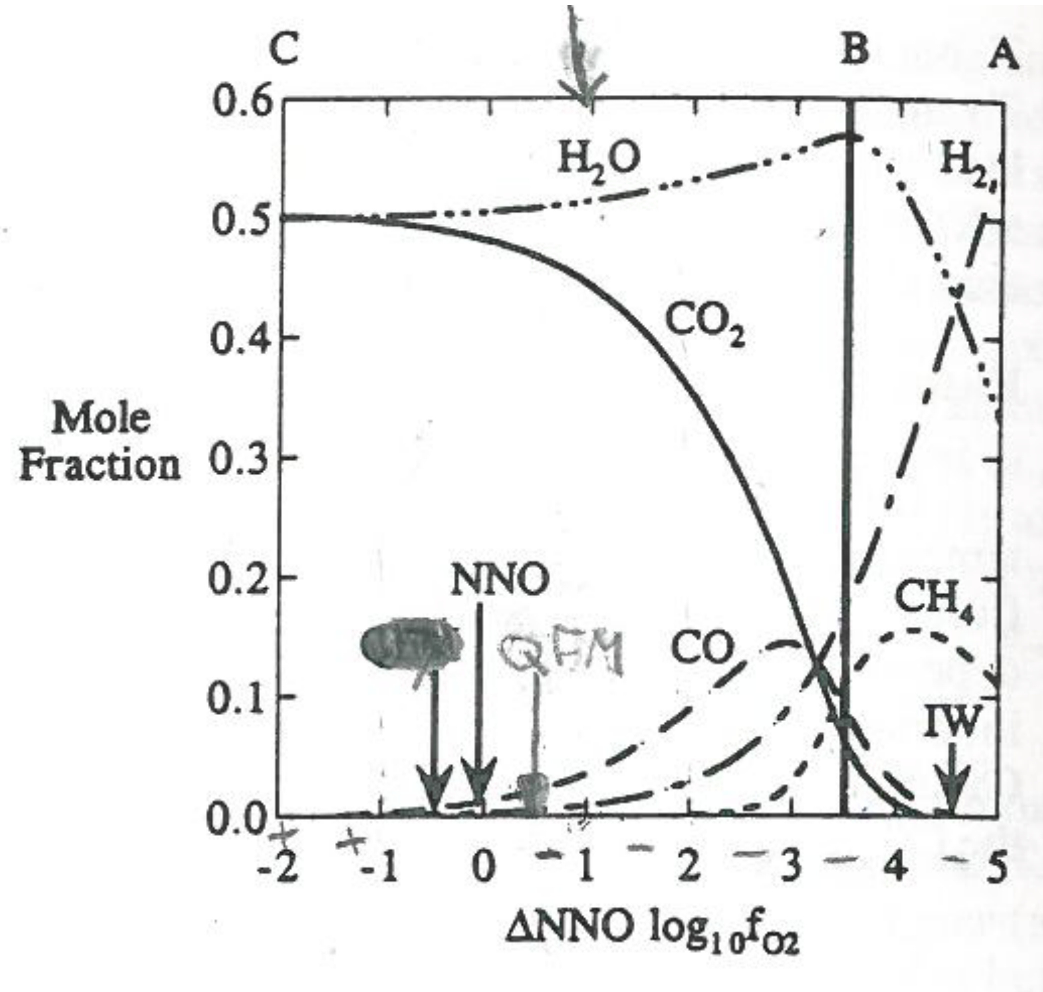
So what about trace element proxies?



reduced ← V/Sc (wt.%) → oxidized

Lee et al., EPSL, 2005

This whole business is pretty serious for the early life folks…



Holloway & Blank, Rev. Min., 1994

C. Lécuyer, Y. Ricard / Earth and Planetary Science Letters 165 (1999) 197–211 205

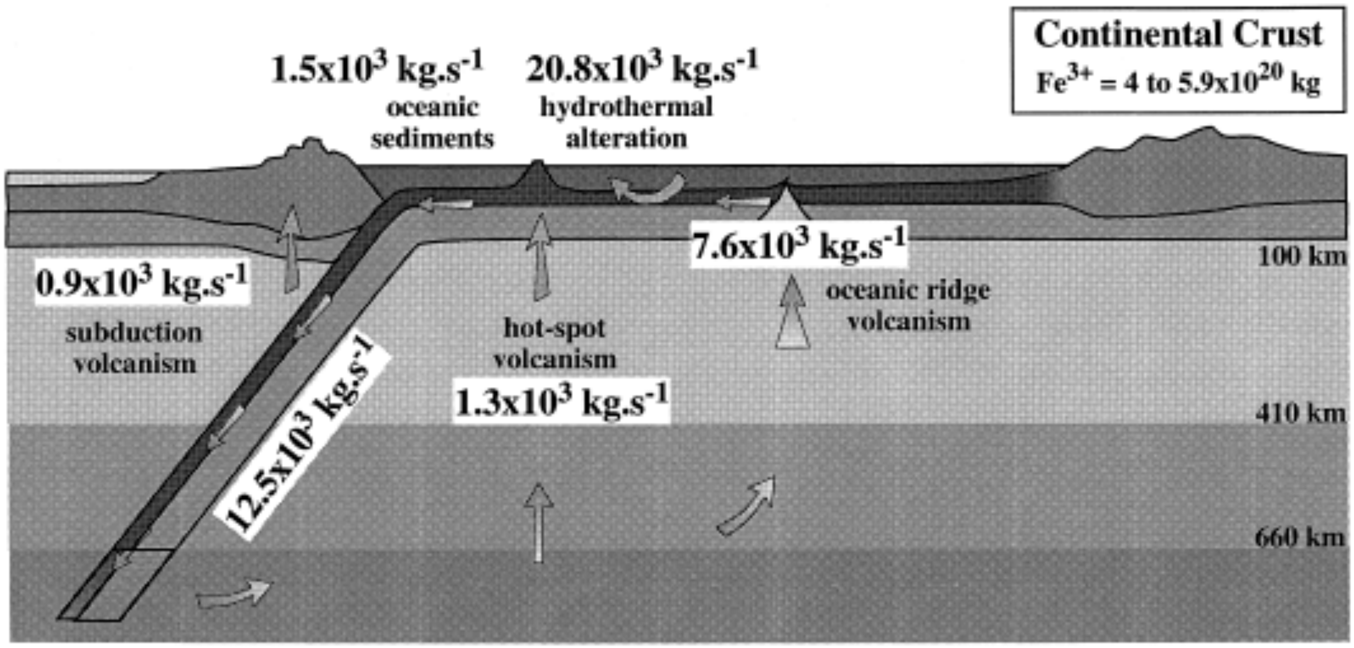


Fig. 5. Sketch summarizing the fluxes and amounts of Fe^{3+} for the main terrestrial reservoirs. A net flux of 12.5×10^3 kg s^{-1} of Fe^{3+} towards the mantle has been deduced using a mass balance equation (Eq. 3).

Net flux on order of 10,000 kg/s Fe^{3+} toward mantle.

Lecuyer and Ricard, 1999

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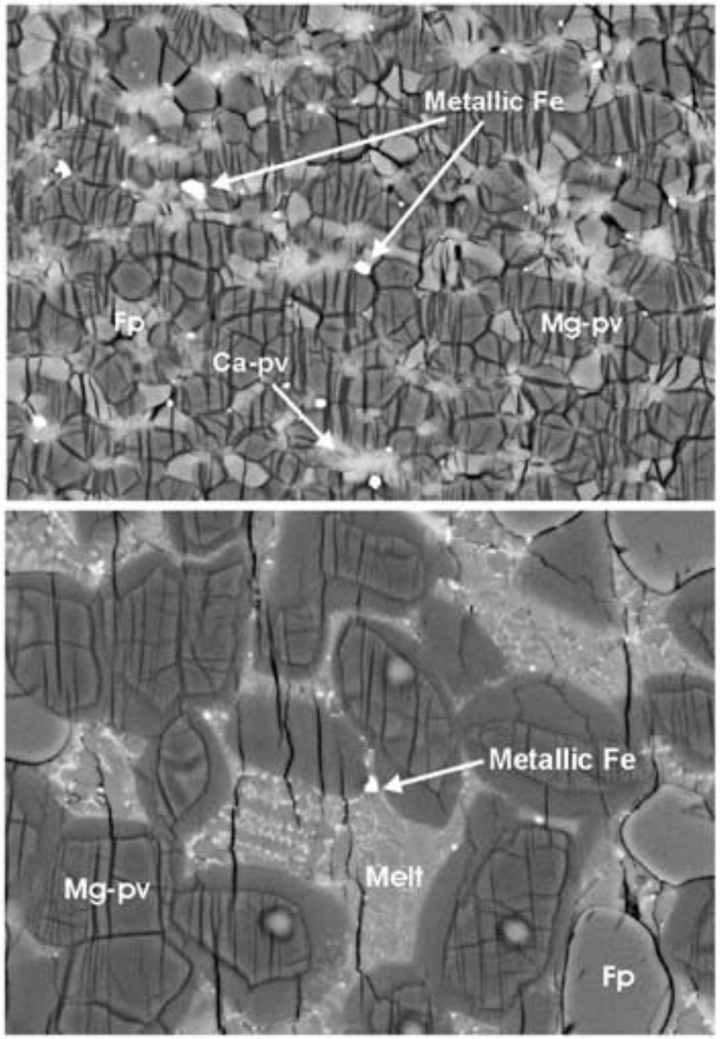
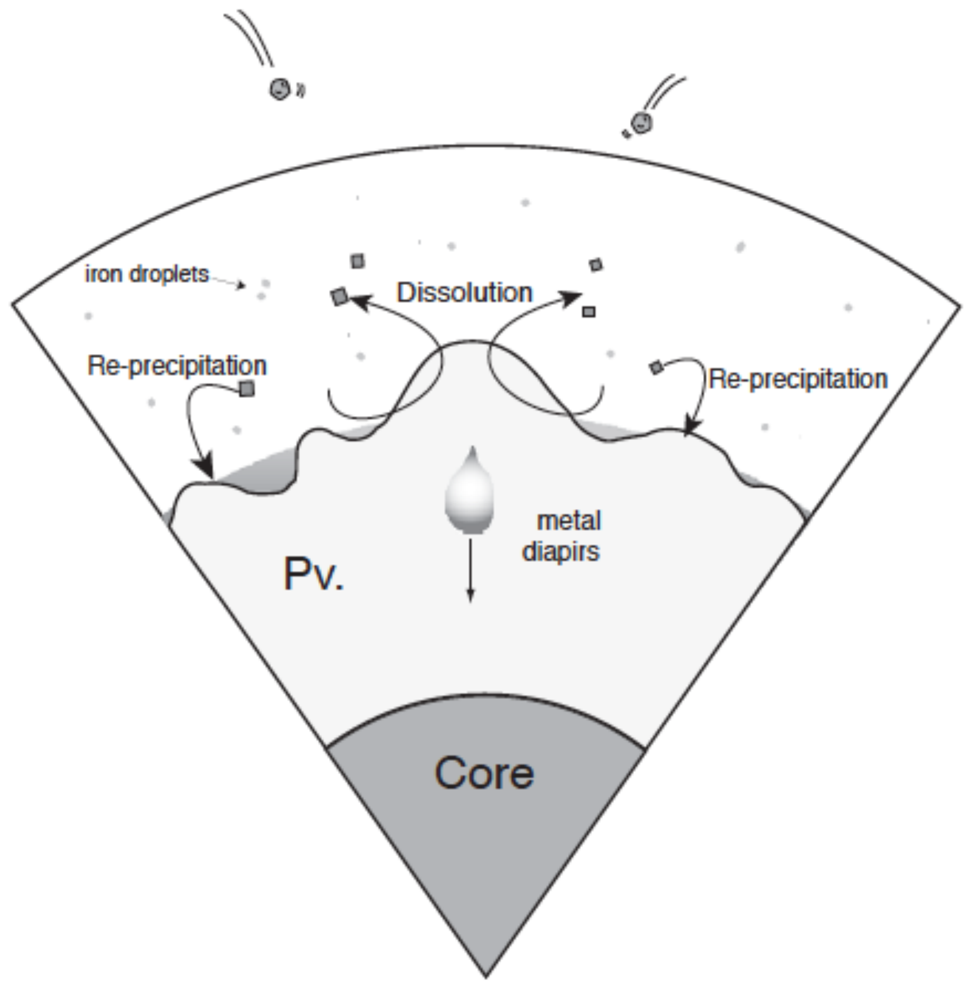
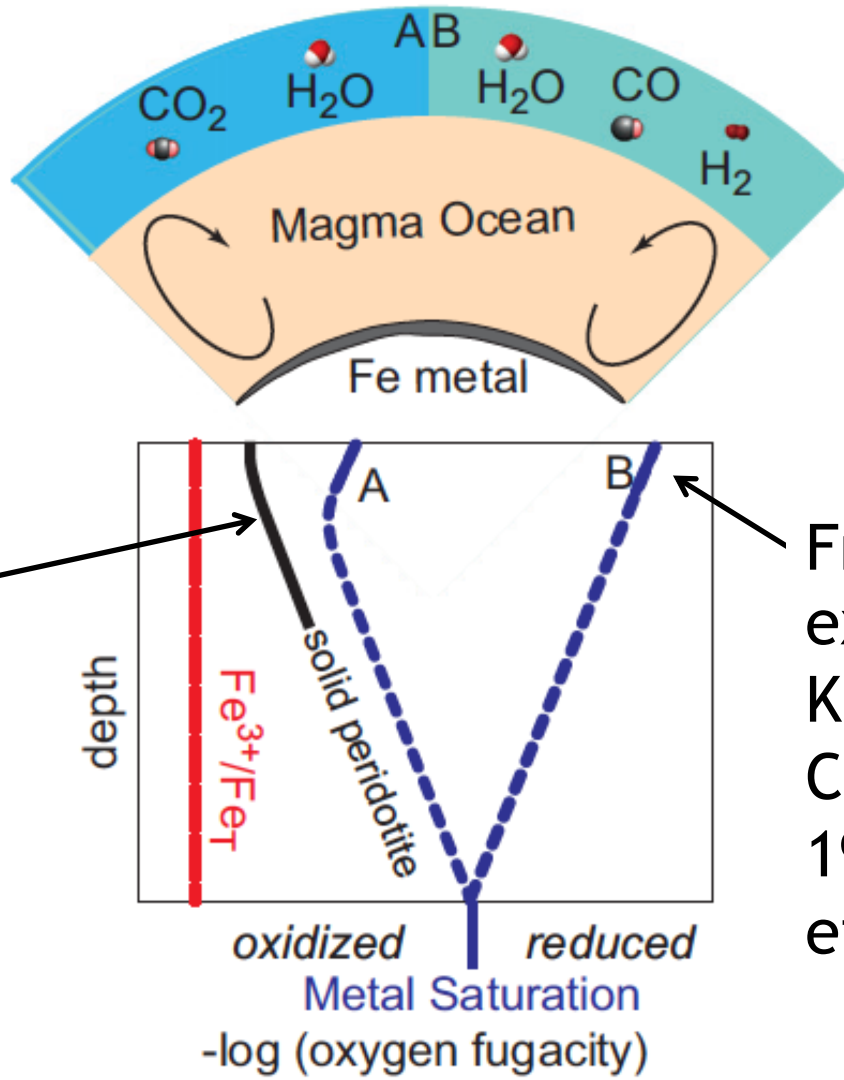


charge from a multi-anvil experiment
lower mantle: 70% pv with $Fe^{3+}/\Sigma Fe = 0.6$



Frost et al., Nature, 2004; Wade & Wood, EPSL, 2005

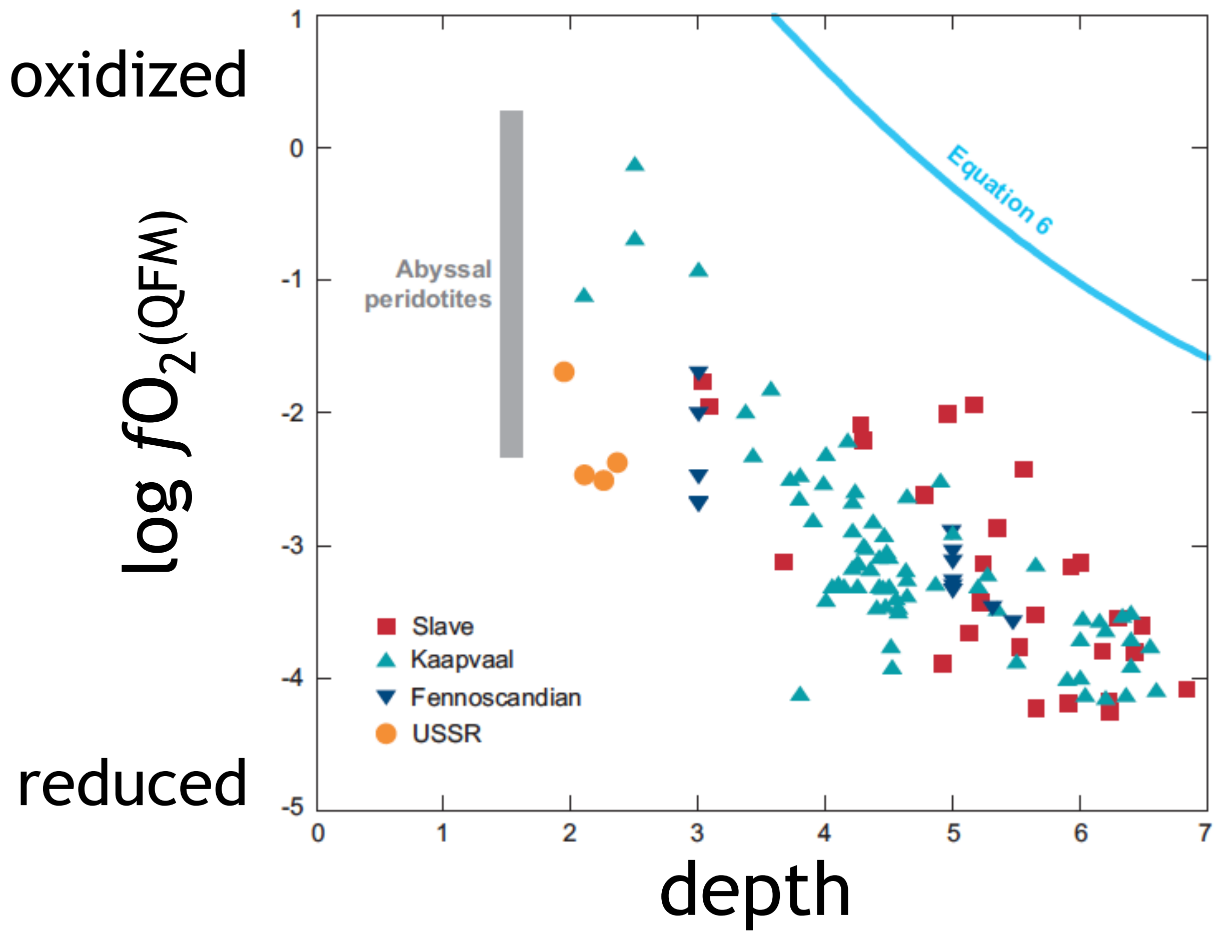
From mantle xenoliths: e.g. Frost & McCammon, 1998



From experiments: Kress & Carmichael, 1991 and O'Neill et al., 2006

Hirschmann, EPSL, 2012

Oxygen Fugacity (fO_2) decreases with depth (in continental cratons)



Frost & McCammon, 1998; Stagno et al., Nature, 2013

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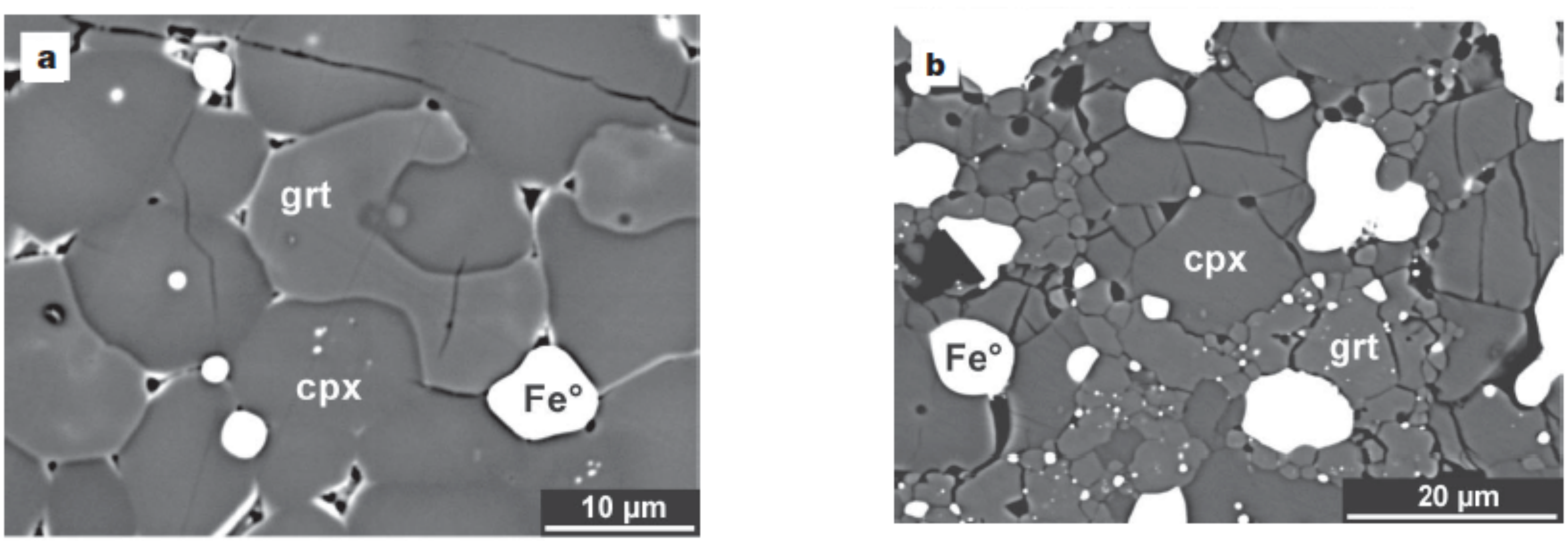
Change in oxygen activity can force changes in speciation:

$2Fe^{2+}O + 0.5\ O_2 \rightarrow Fe_2^{3+}O_3$

Change in speciation can force changes in oxygen activity:



Rohrbach et al., Nature, 2007
expts at 3 and 12 GPa

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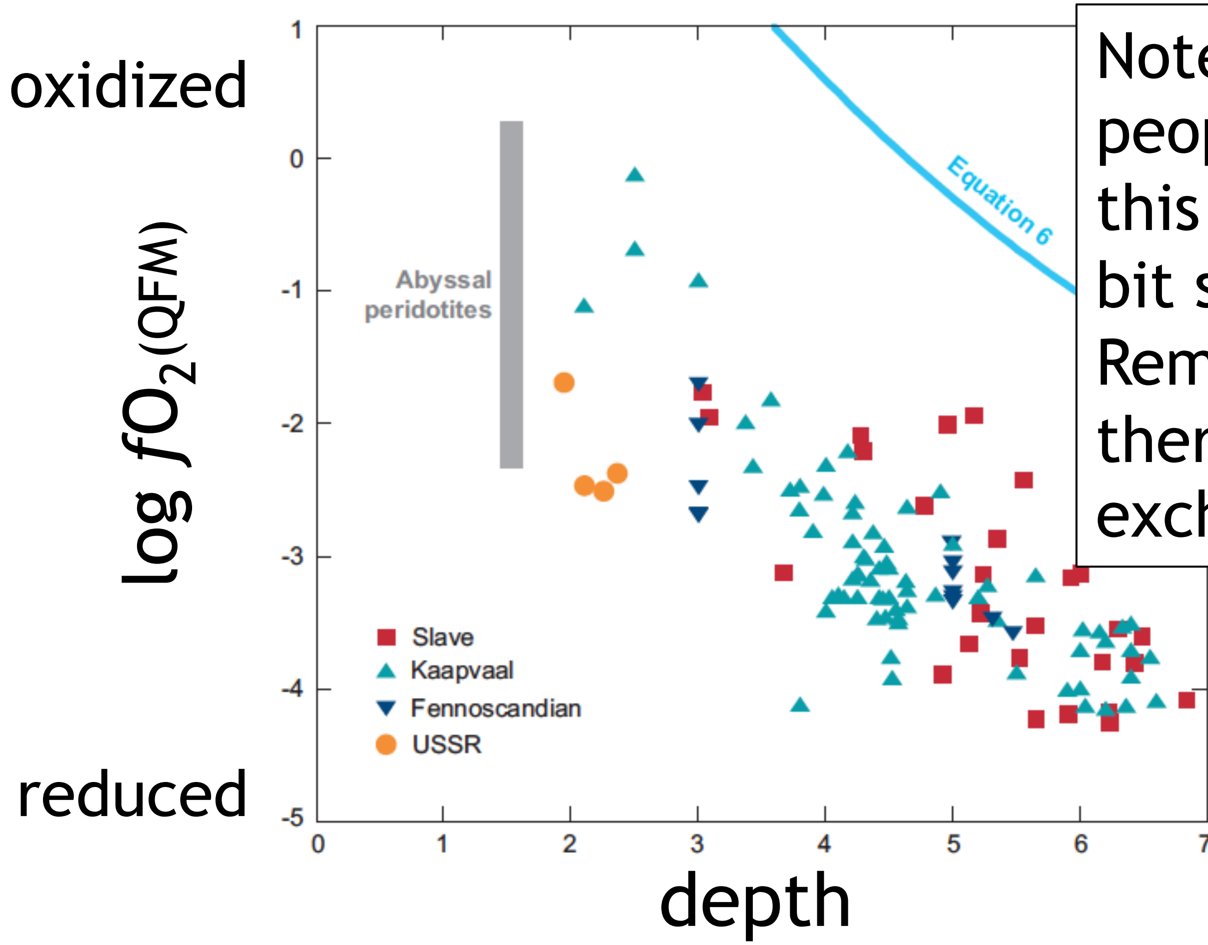
Oxygen Fugacity (fO_2) decreases with depth (in continental cratons)



Note: some people think this is a little bit silly. Remember, there is no mass exchange.

Frost & McCammon, 1998; Stagno et al., Nature, 2013

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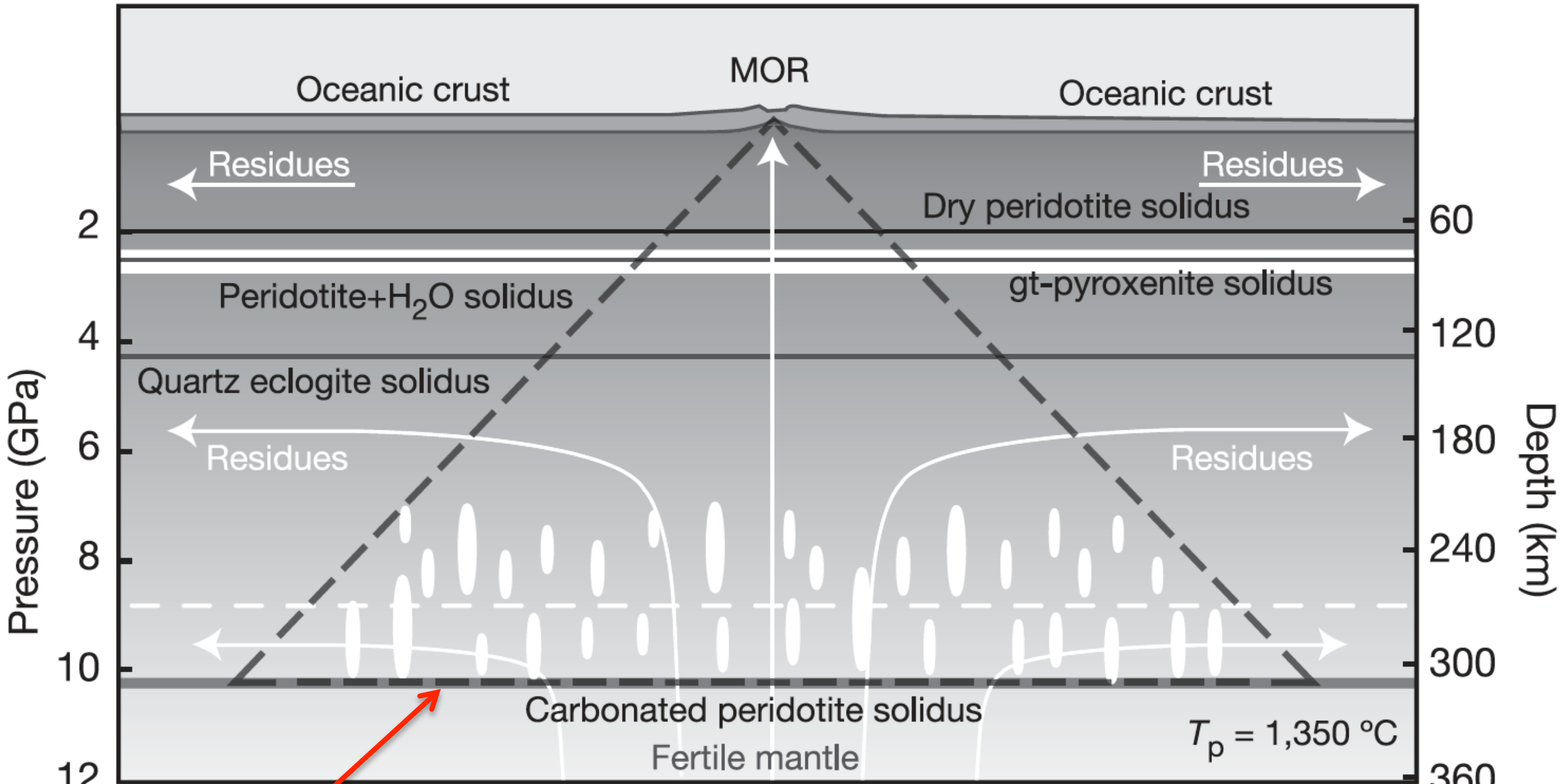
The depth of incipient mantle melting depends on f_{O2}



Requires carbonate, not carbon. fO_2 dependent.

Dasgupta and Hirschmann, Nature, 2006; EPSL 2010…

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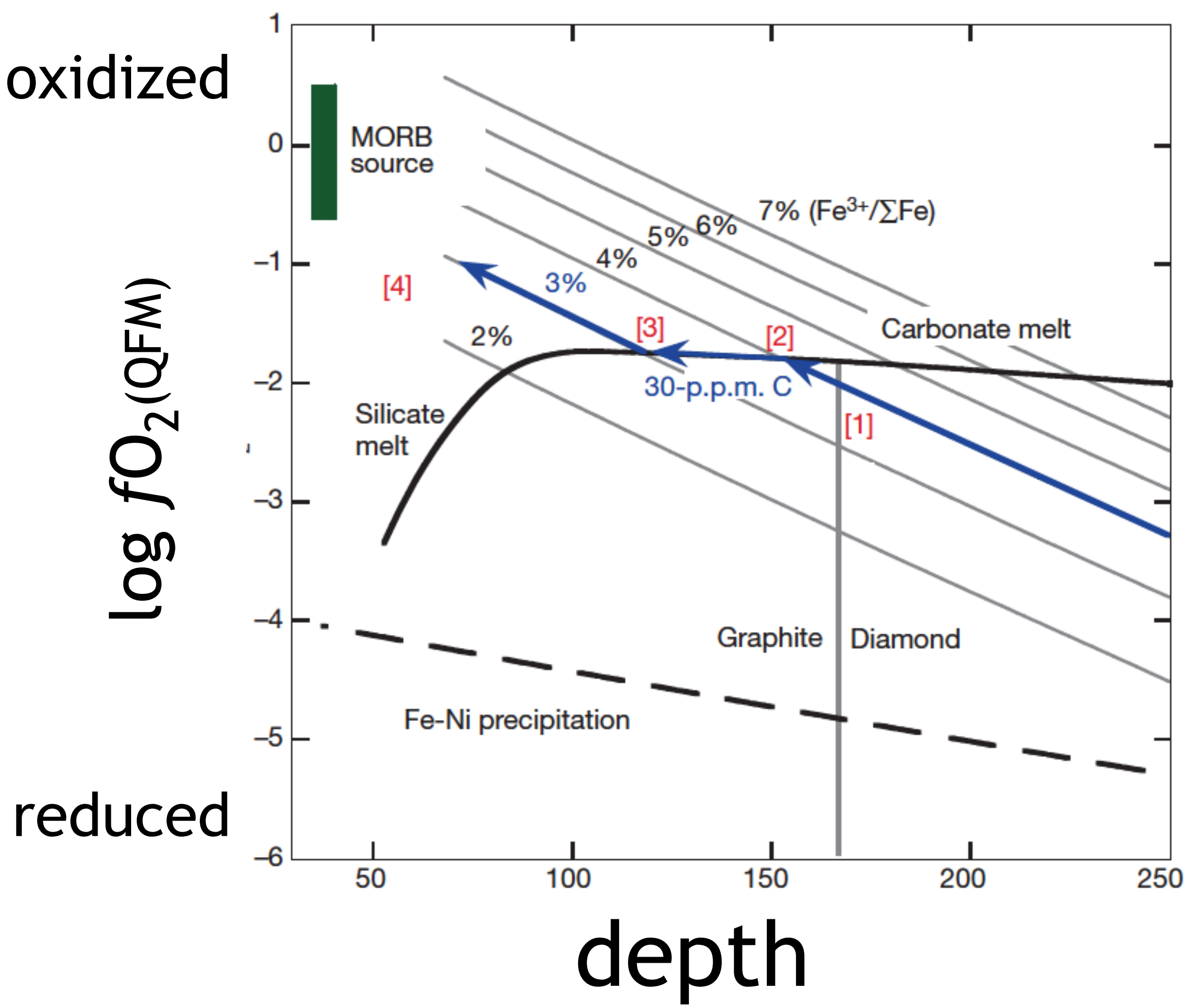

Stagno et al., EPSL, 2010 and Nature, 2013

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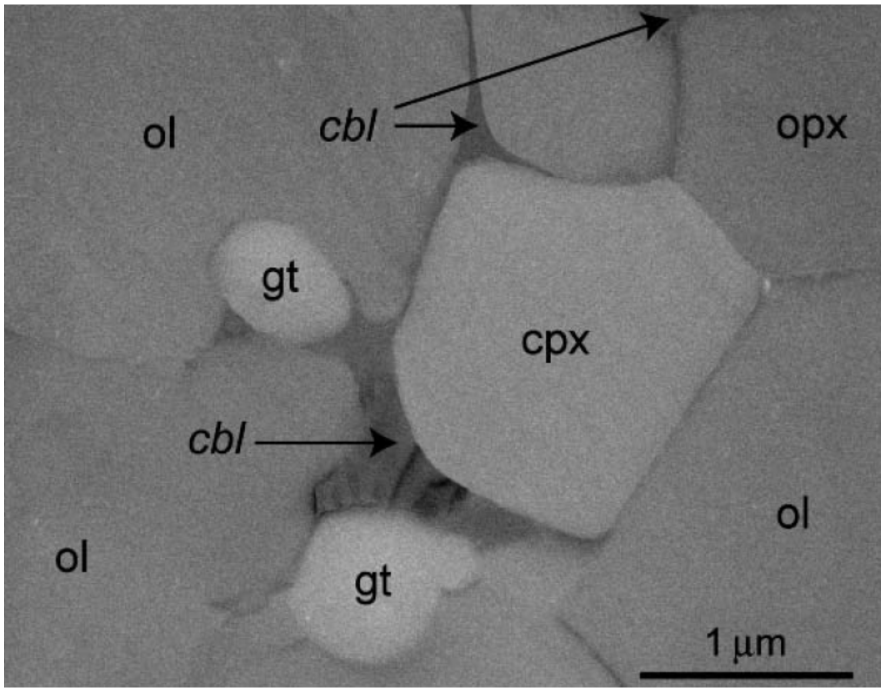
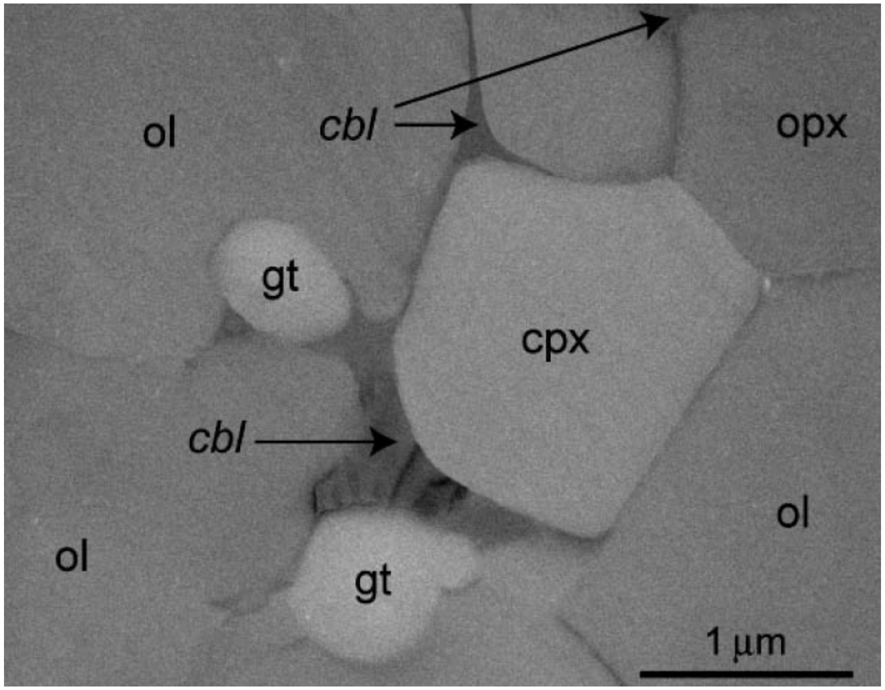
carbonate fluxes silicate melting



carbonate stability requires oxidizing conditions

Dasgupta and Hirschmann, Nature, 2006
Experiment M245: 6.6 GPa, 1220°C

carbonate fluxes silicate melting



carbonated (±damp) mantle:

melts 100-150km deeper

higher electrical conductivity

lower shear wave velocities

Dasgupta and Hirschmann, Nature, 2006
Experiment M245: 6.6 GPa, 1220°C

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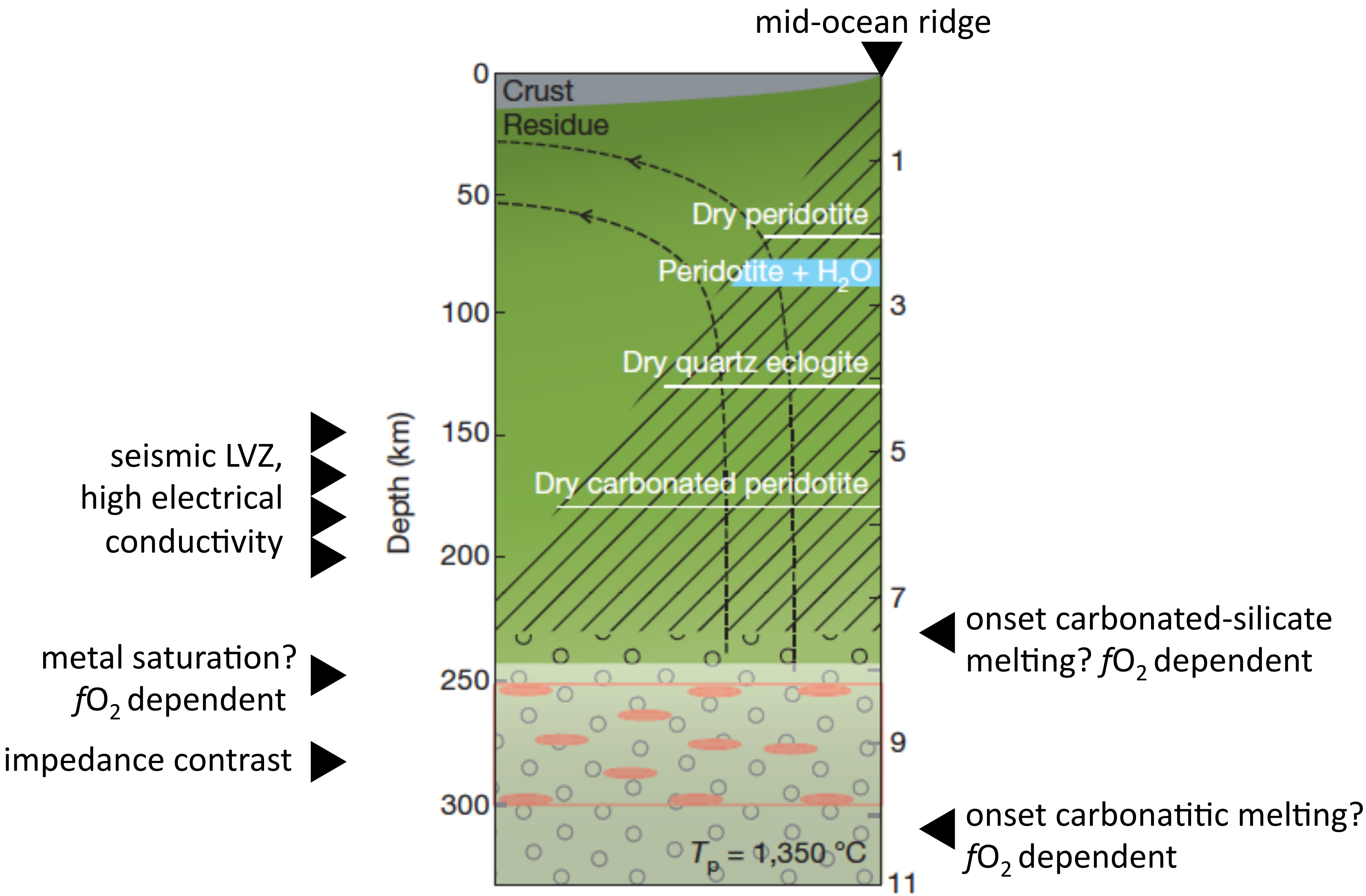
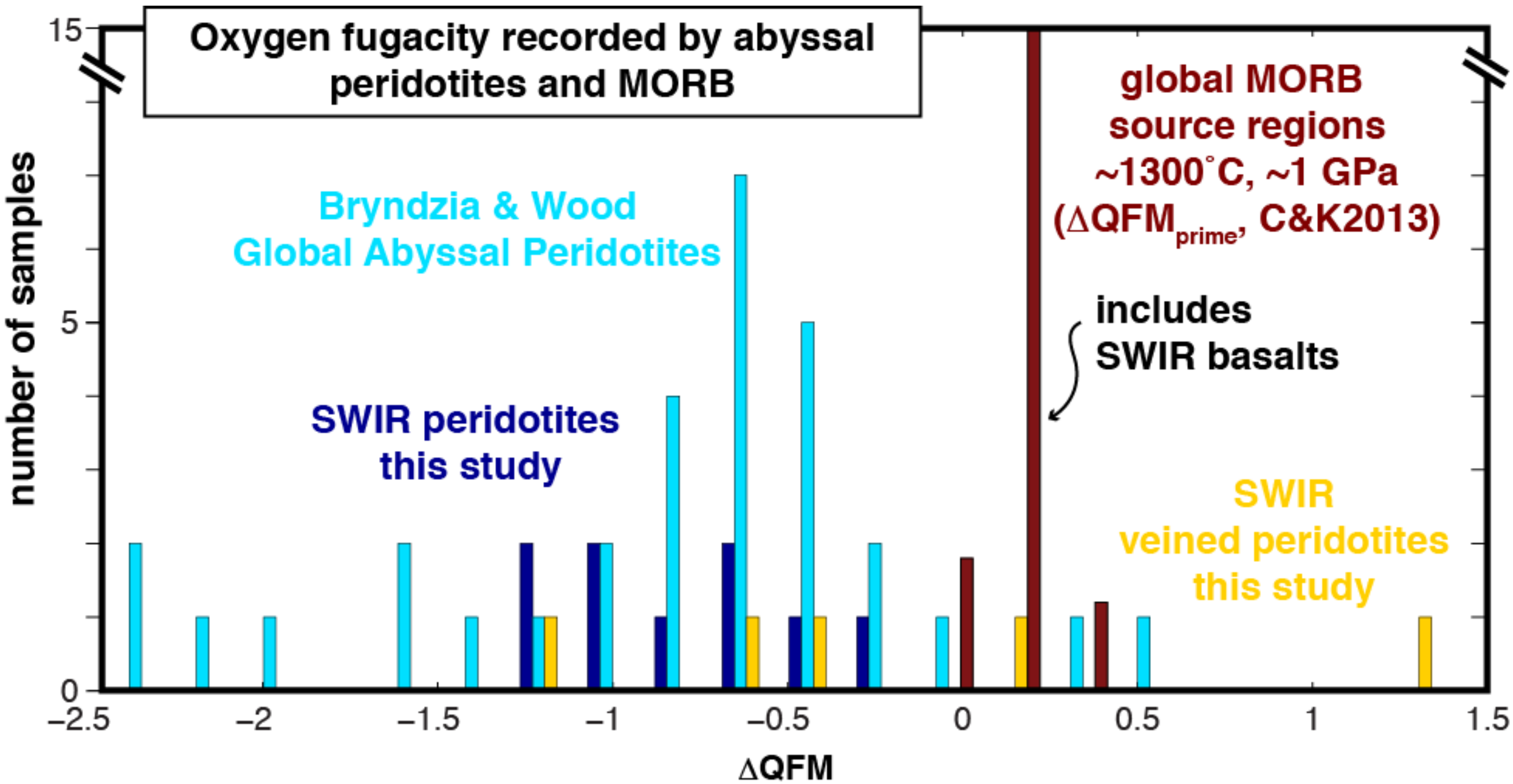


Dasgupta et al., Nature, 2013



Birner, Cottrell, Warren, Davis, and Kelley, unpublished and in prep

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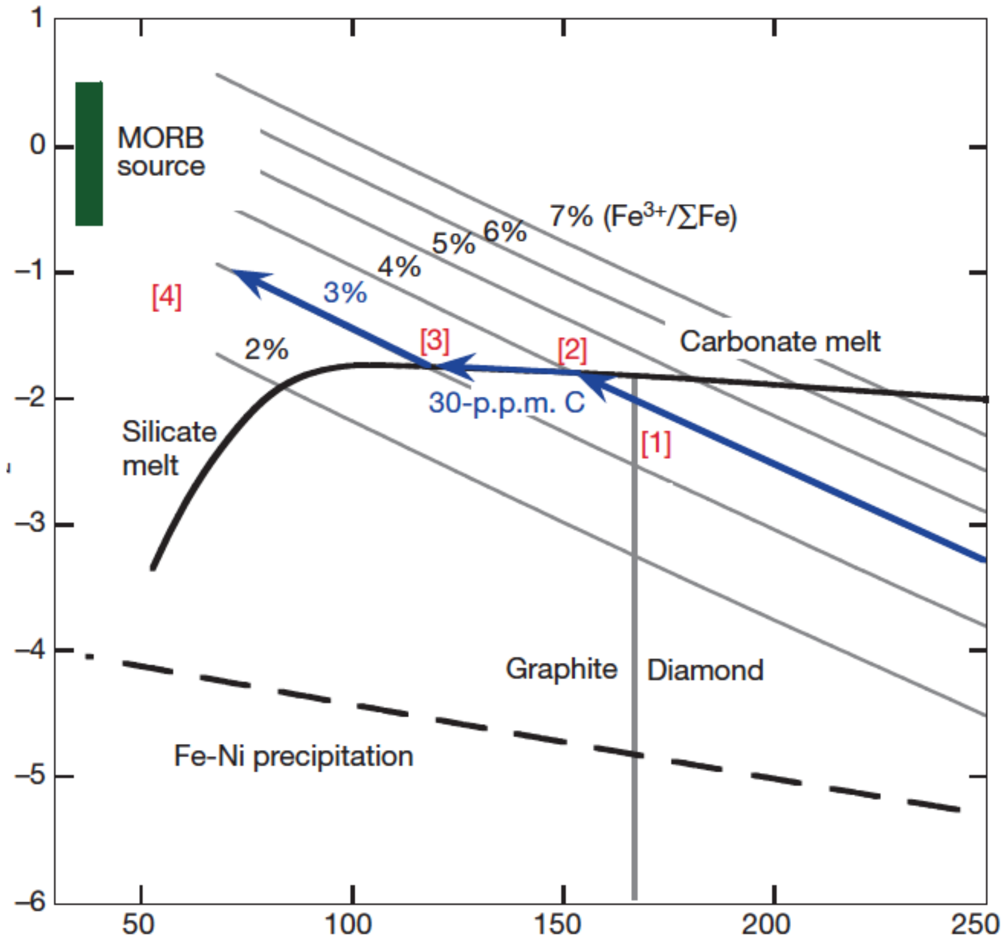
oxidized



log fO_2(QFM)

reduced

depth

Stagno et al., EPSL, 2010 and Nature, 2013

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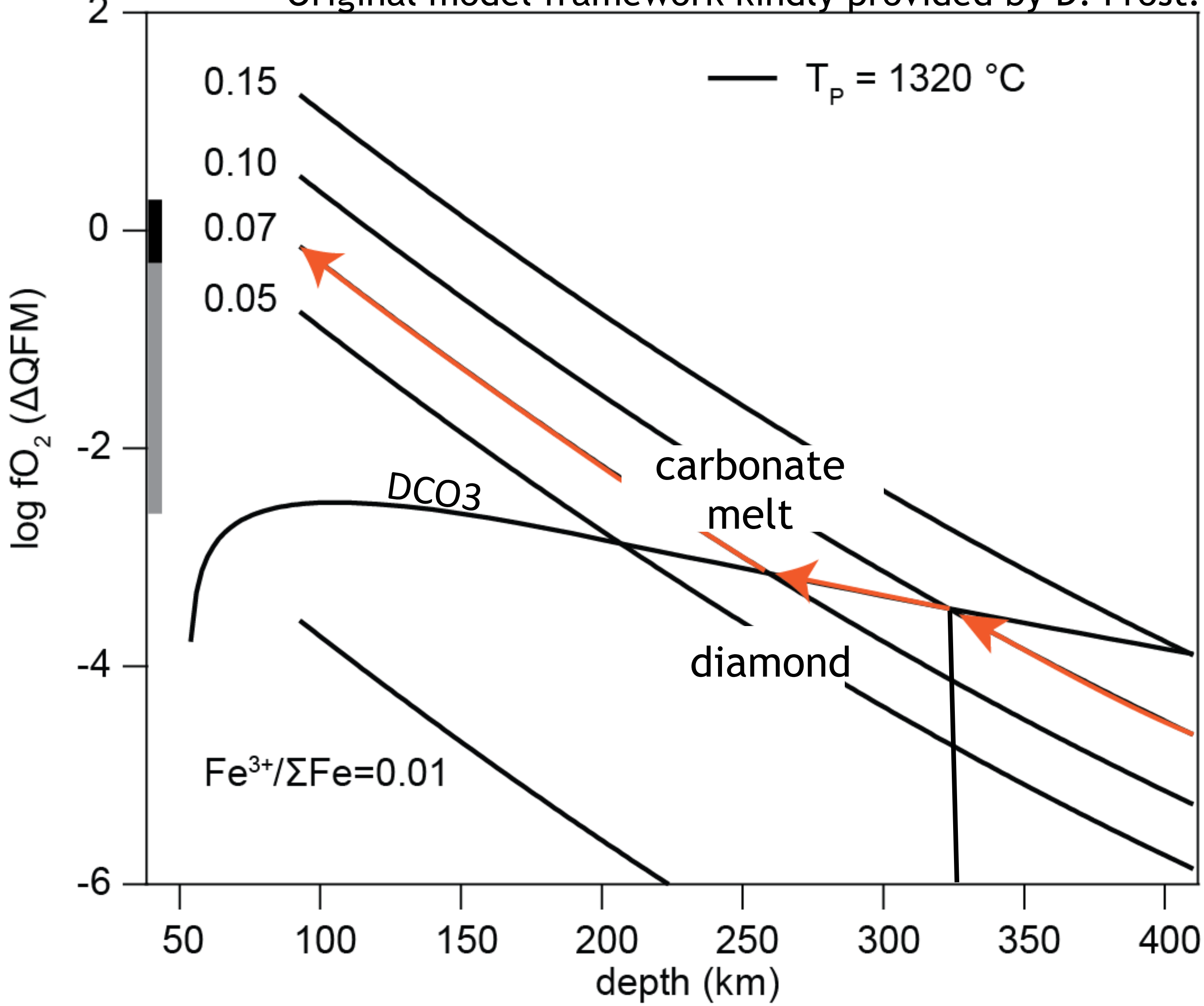
Original model framework kindly provided by D. Frost.



Davis et al., in prep

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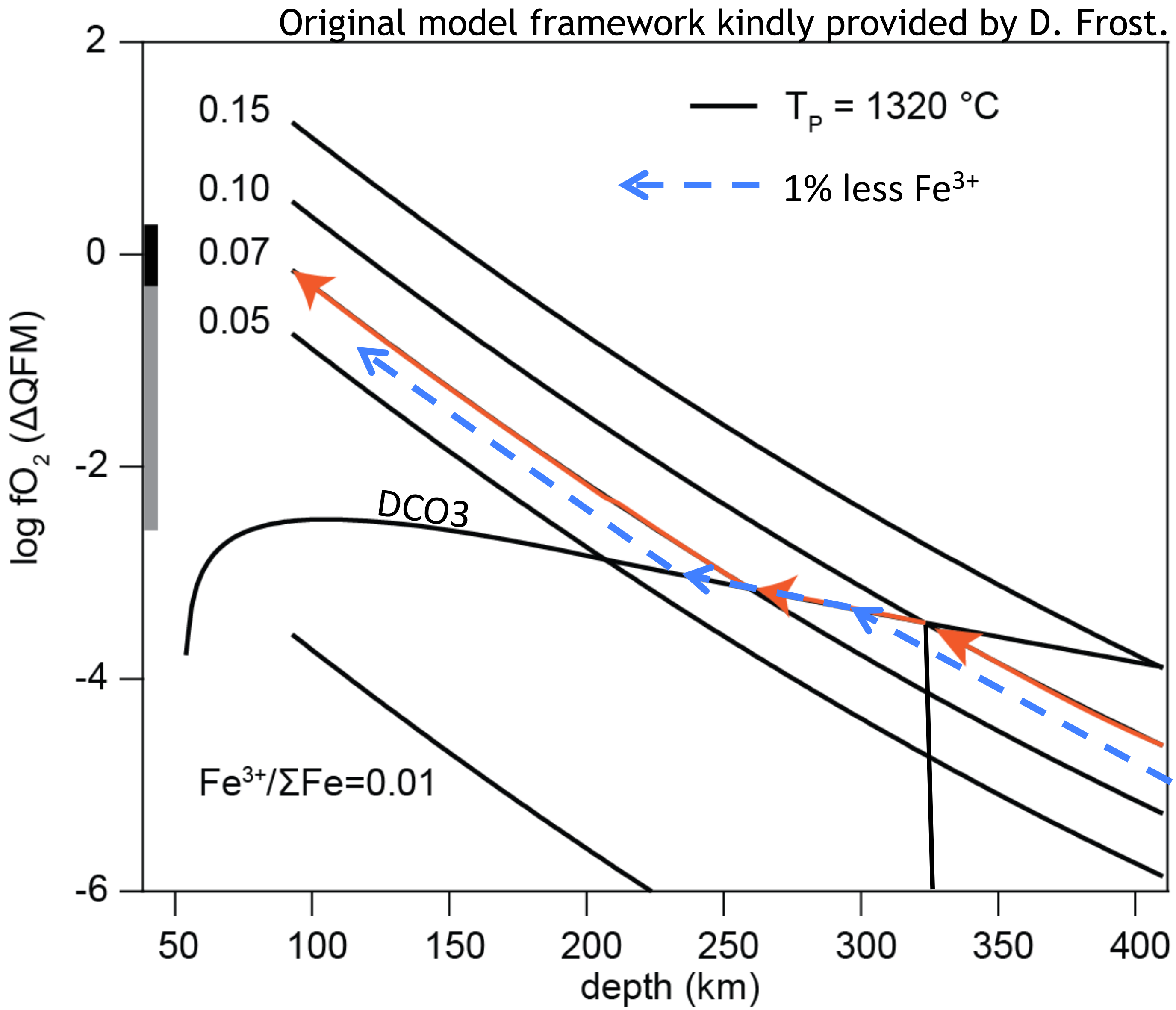

Davis et al., in prep

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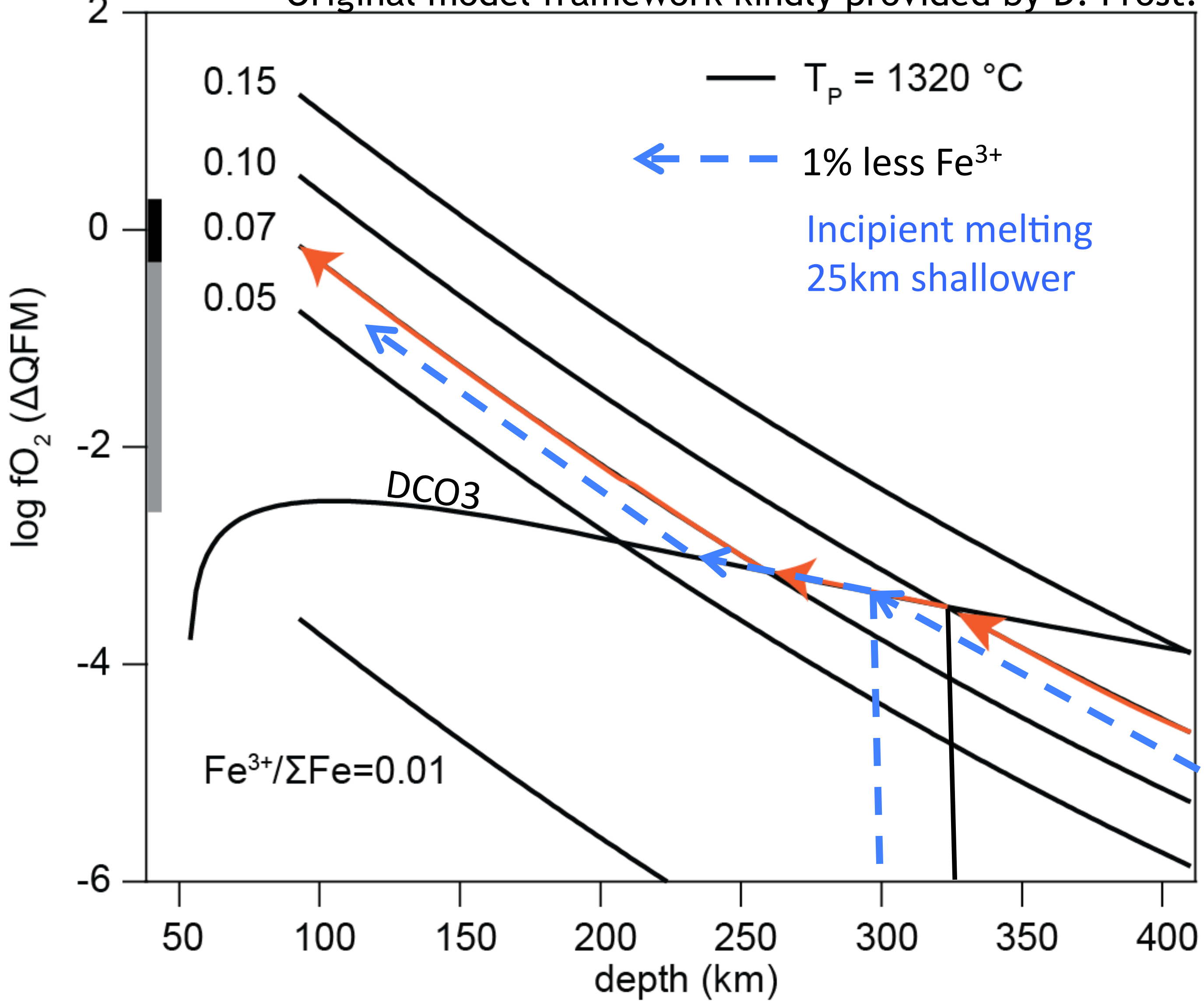
Original model framework kindly provided by D. Frost.



Davis et al., in prep

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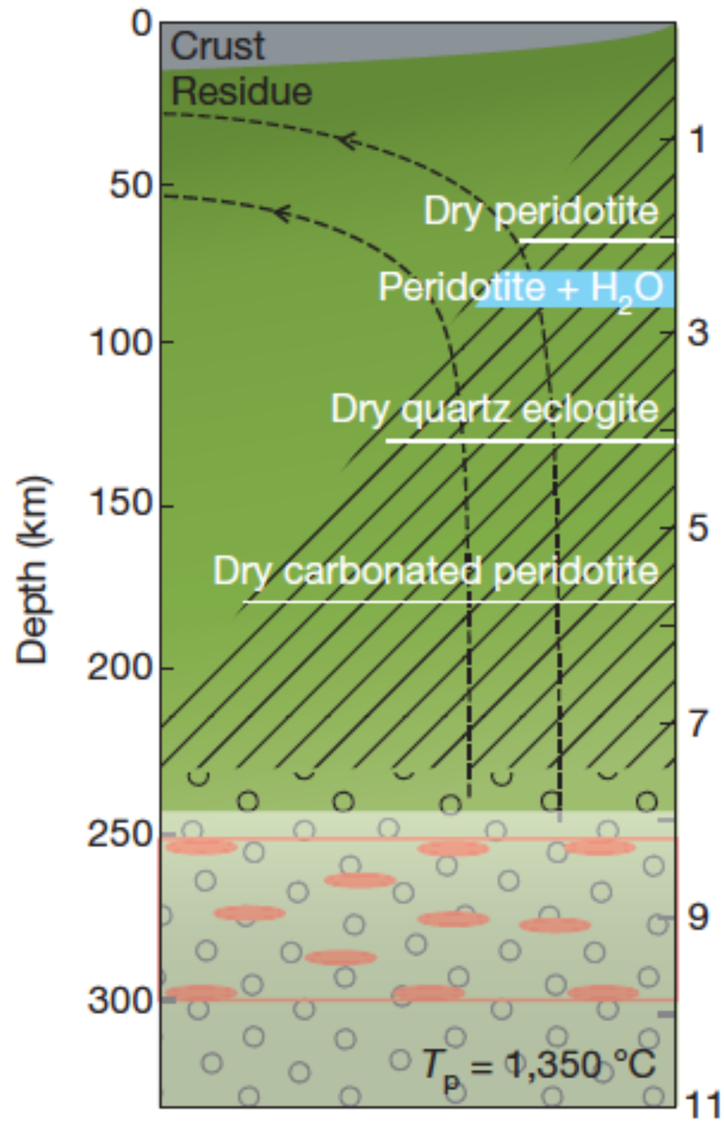
Open questions

- Are there domains oxidized enough to explain geophysical observations?



Dasgupta et al., Nature, 2013

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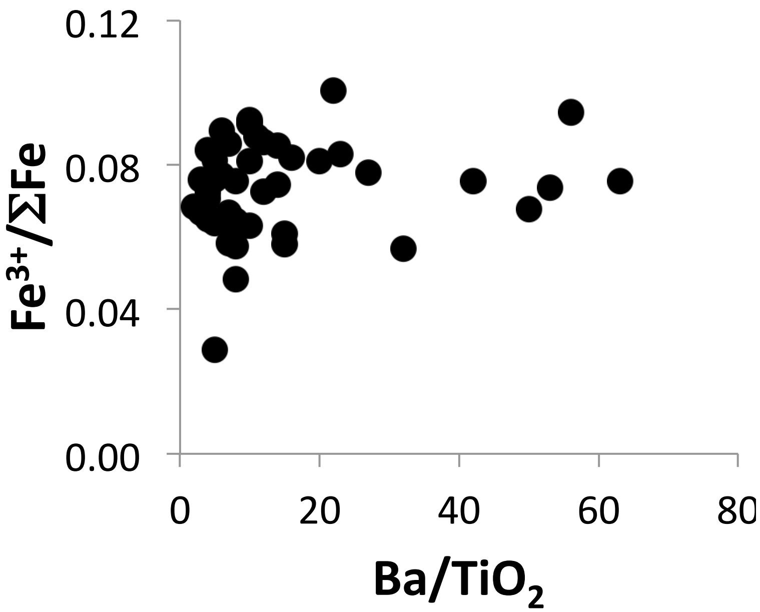
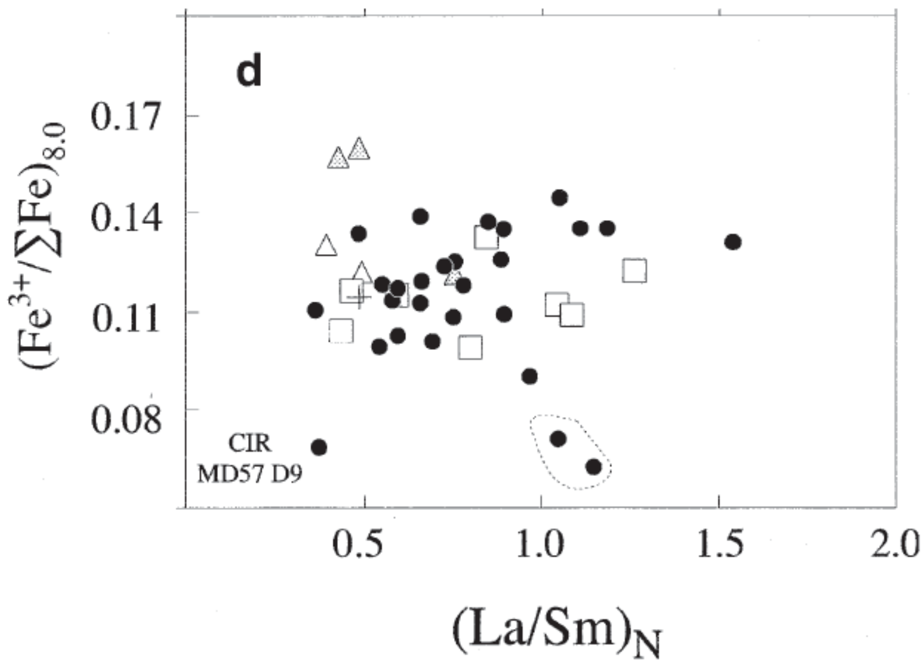
Prior study of MORB $Fe^{3+}/\Sigma Fe$





"These results indicate that the oxidation state of MORB glasses is not sensitive to mantle geochemical anomalies."

Christie, Carmichael, & Langmuir, EPSL, 1986 (left)
Bézos and Humler, EPSL, 2005 (right)

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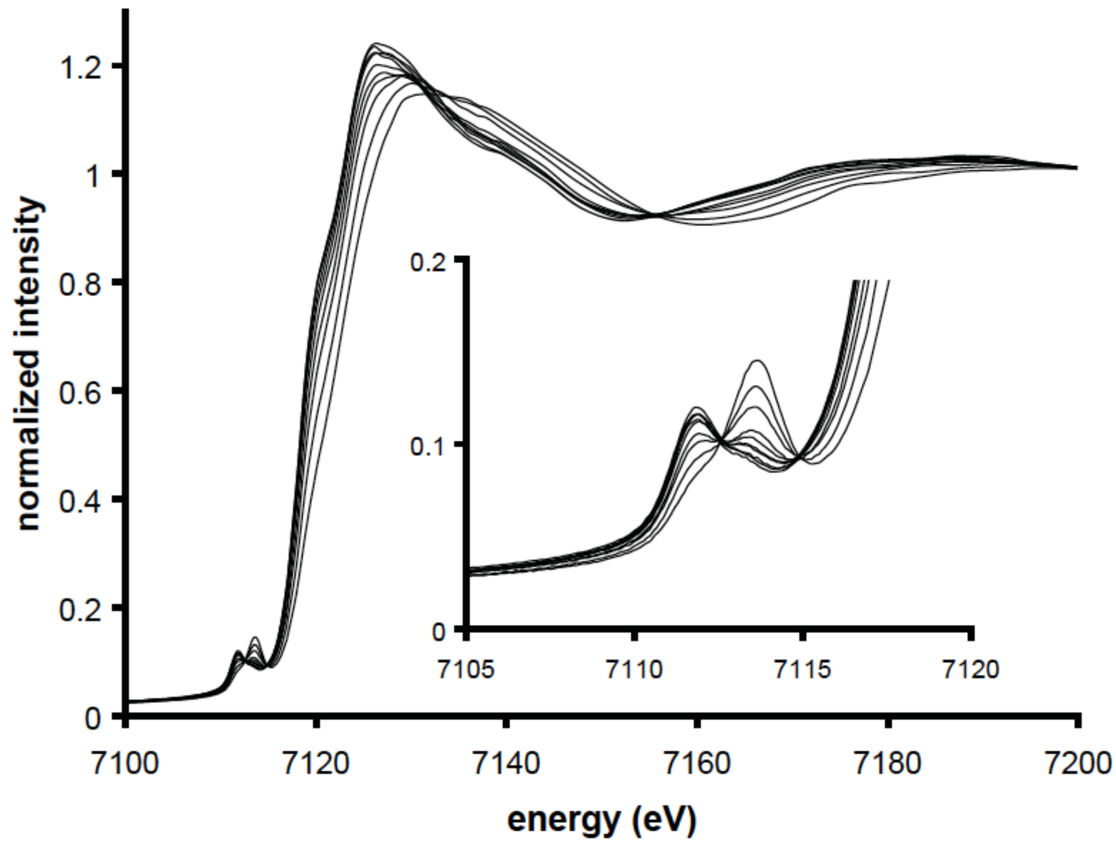
$Fe^{3+}/\Sigma Fe$ by XANES

National Synchrotron Light Source, BNL

basalts equilibrated at known *f*O2 (1 atm)

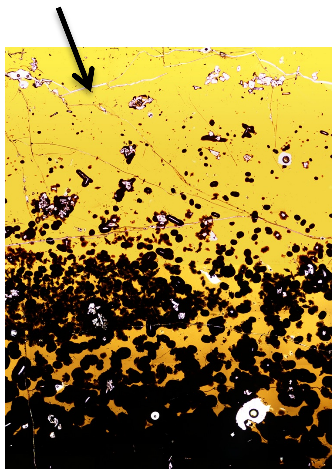
$Fe^{3+}/\Sigma Fe$ determined by Mössbauer spectroscopy and wet chemistry.

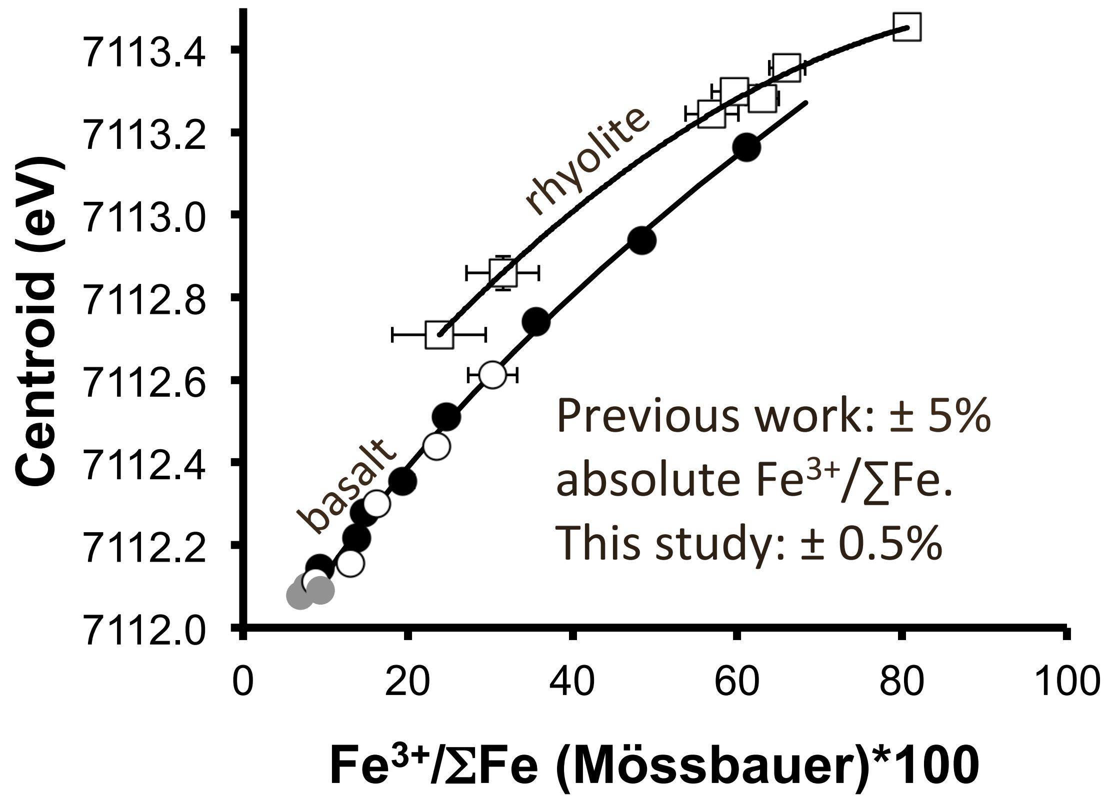


Cottrell et al., Chem Geol., 2009

$Fe^{3+}/\Sigma Fe$ by XANES

10µm X-ray spot in a MORB pillow glass

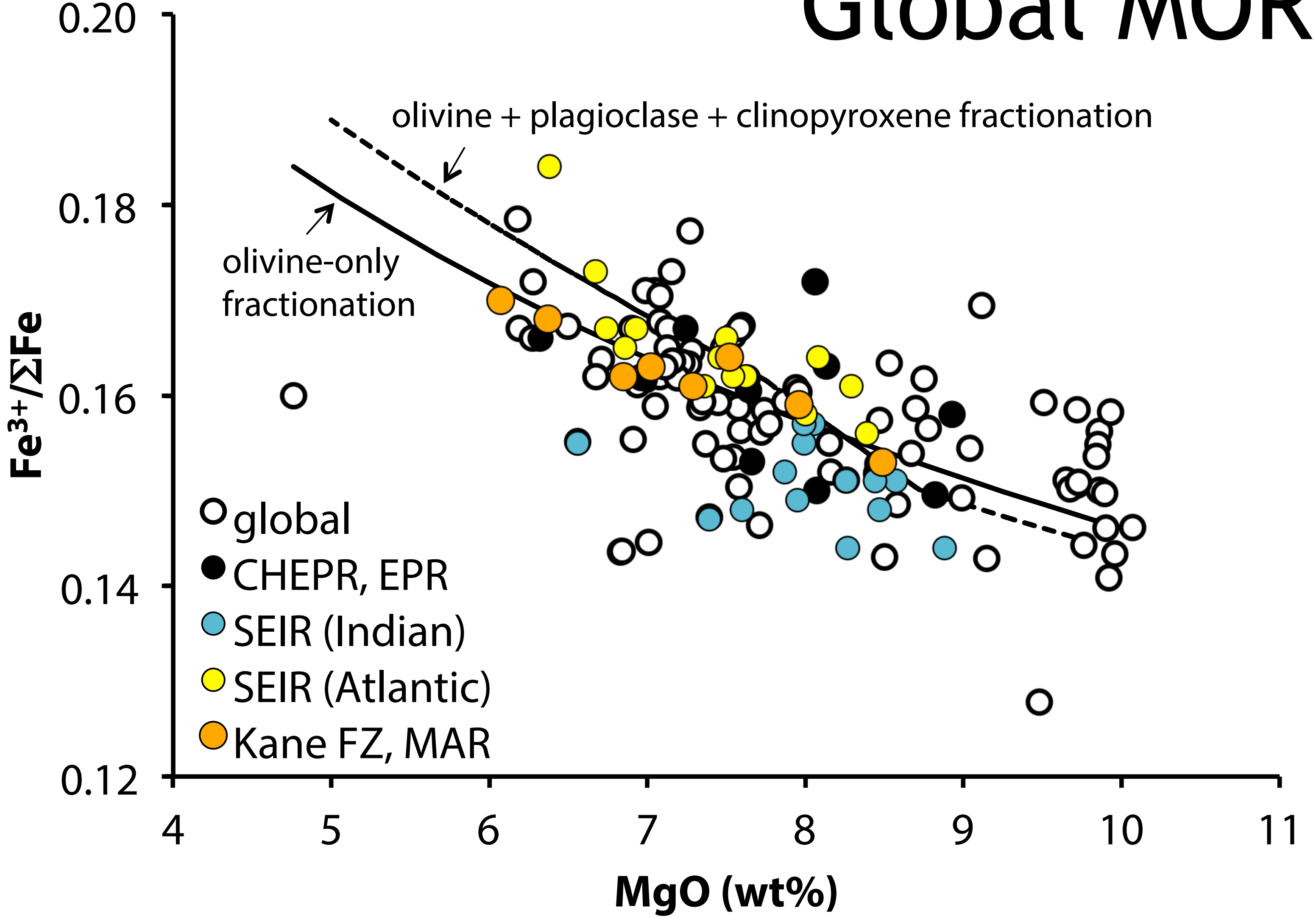




reduced ⟷ oxidized

Cottrell et al., Chem Geol., 2009

Global MORB



Cottrell and Kelley, EPSL, 2011 & unpub.

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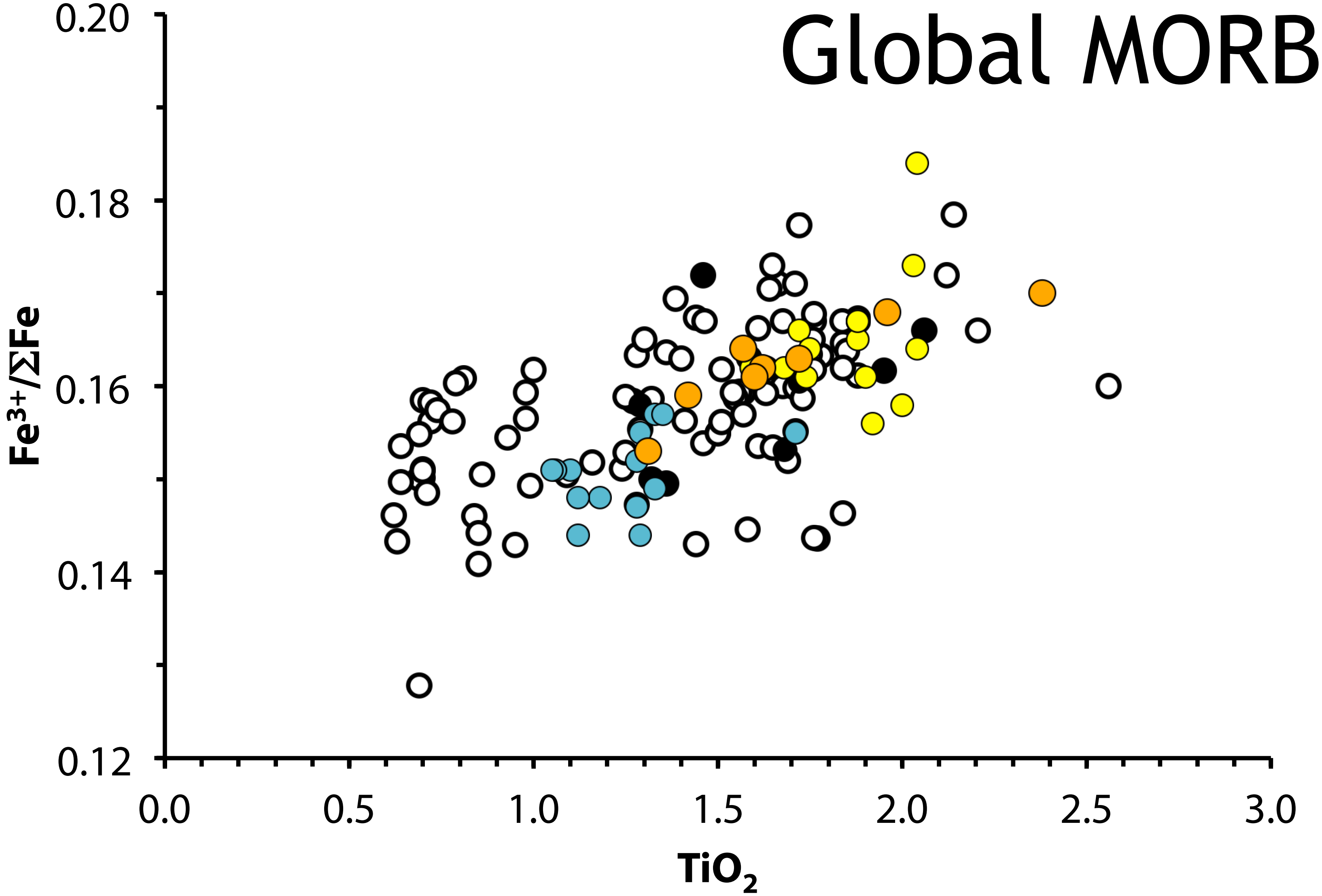

Cottrell and Kelley, EPSL, 2011 & unpub.

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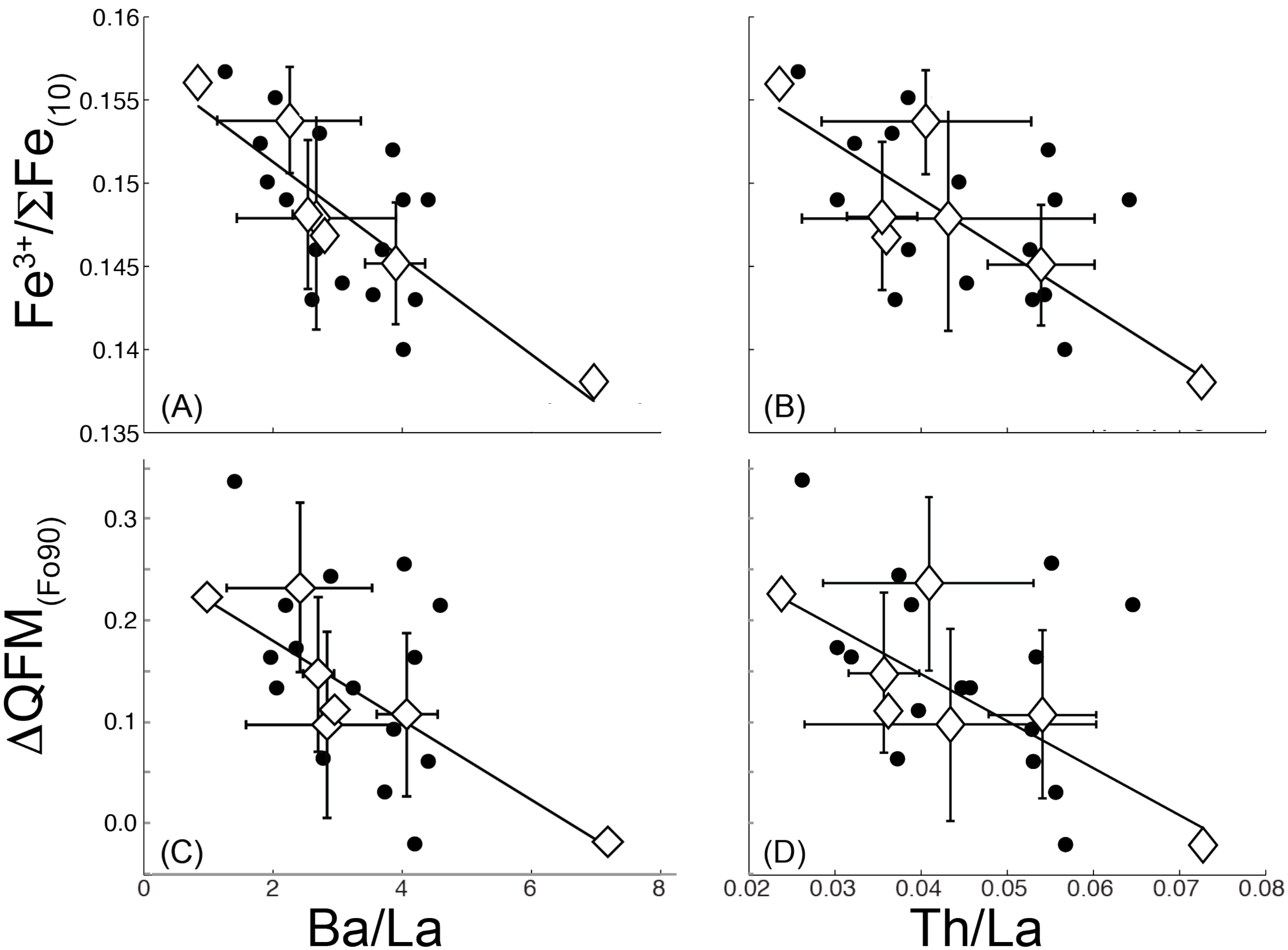

Cottrell and Kelley, Science, 2013

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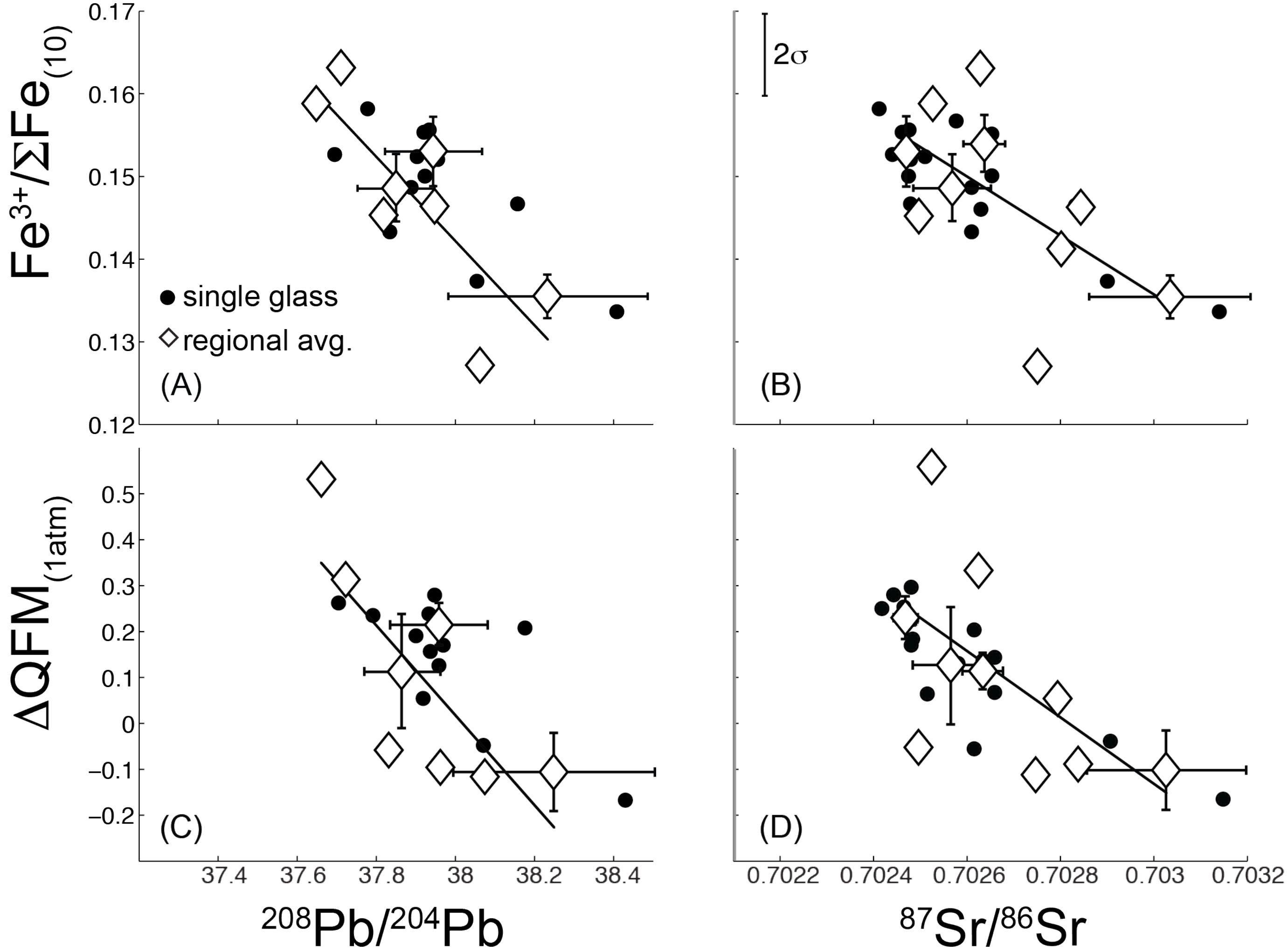

Cottrell and Kelley, Science, 2013

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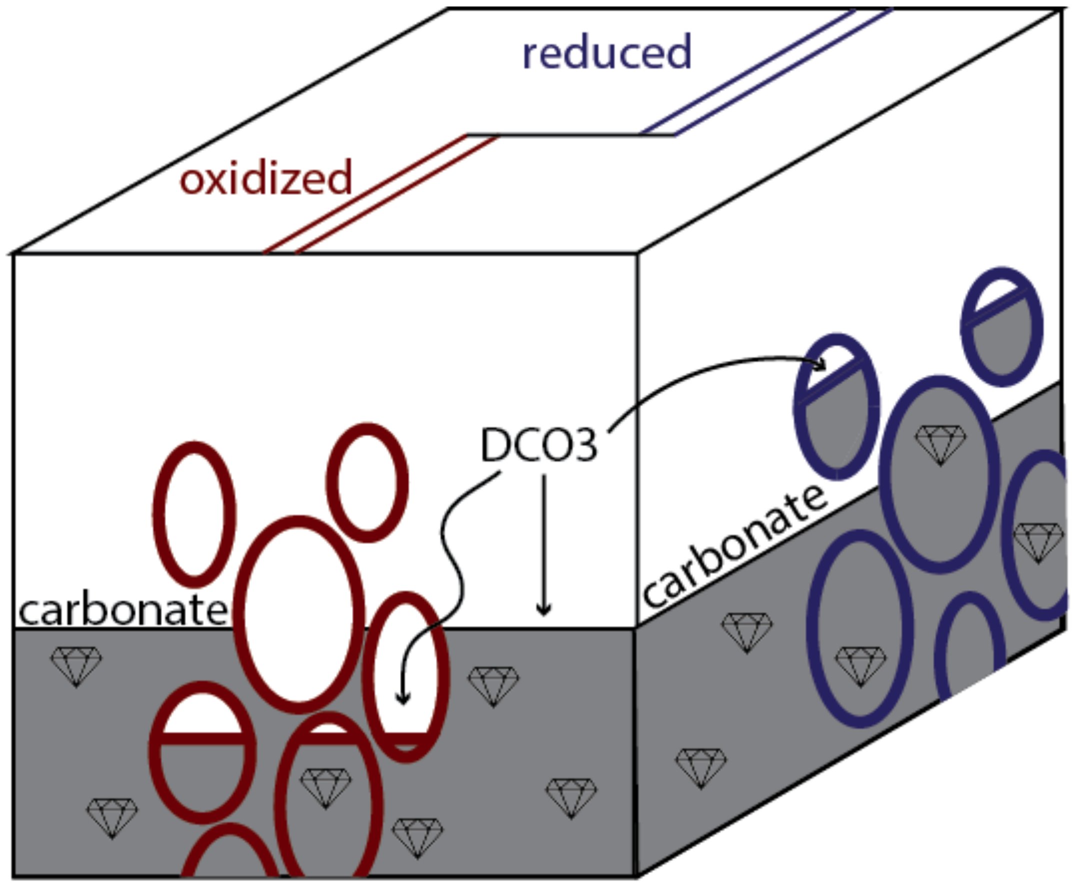
Implications



Cottrell, Lekic et al., in prep and Davis et al, in prep

thank you

Katie Kelley University of Rhode Island, Graduate School of Oceanography

Maryjo Brounce URI & Smithsonian; Antonio Lanzirotti University of Chicago, CARS; Bjorn Mysen Geophysical Lab, Carnegie; Becky Lange U. of Michigan; **Christa Jackson**, **Stephanie Grocke**, **Marion Le Voyer, and Fred Davis**
Rebecca Fischer Smithsonian Institution

Those who generously provided samples: D. Christie, T. Plank, V. Kress, L. Cooper, M. Zimmer, E. Hauri, D. Clague, M. Jackson; C. Langmuir, M. Rutherford, and G. Moore

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GSO

DEEP CARBON OBSERVATORY
RESERVOIRS AND FLUXES

NSF

COMPRES

MARGINS

nsls
IR UV X

ADVANCED PHOTON SOURCE

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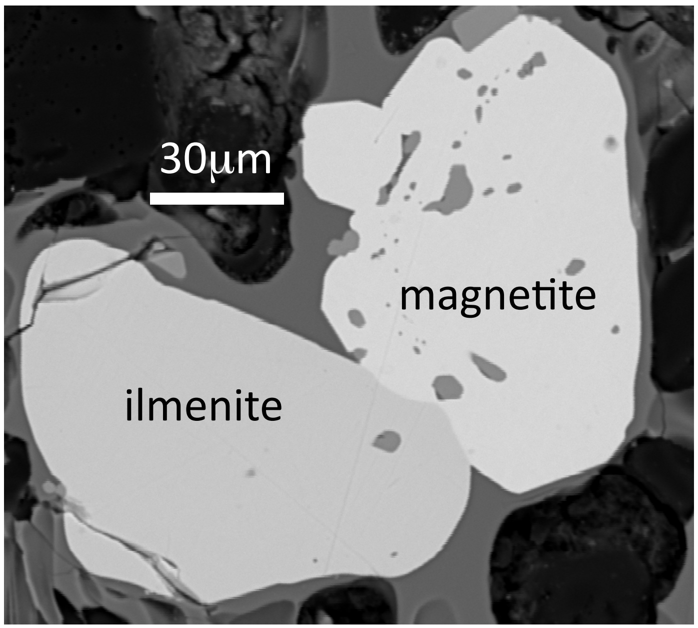
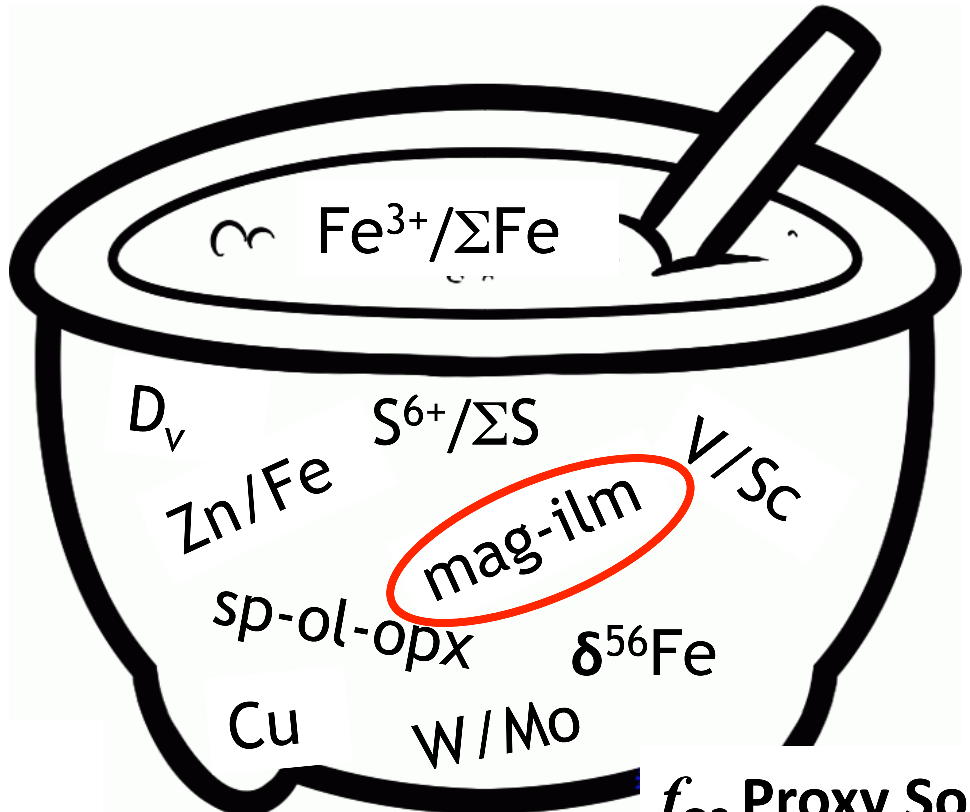
Extra Slides

Oxygen Fugacity f_{O2}

Measuring O_2 or its activity in rocks is important, but tricky.



In magmas, minerals may record f_{O2}.



f_{O2} Proxy Soup

Fe-Ti oxide thermobarometry by EMPA at NMNH
Credit: S. Grocke

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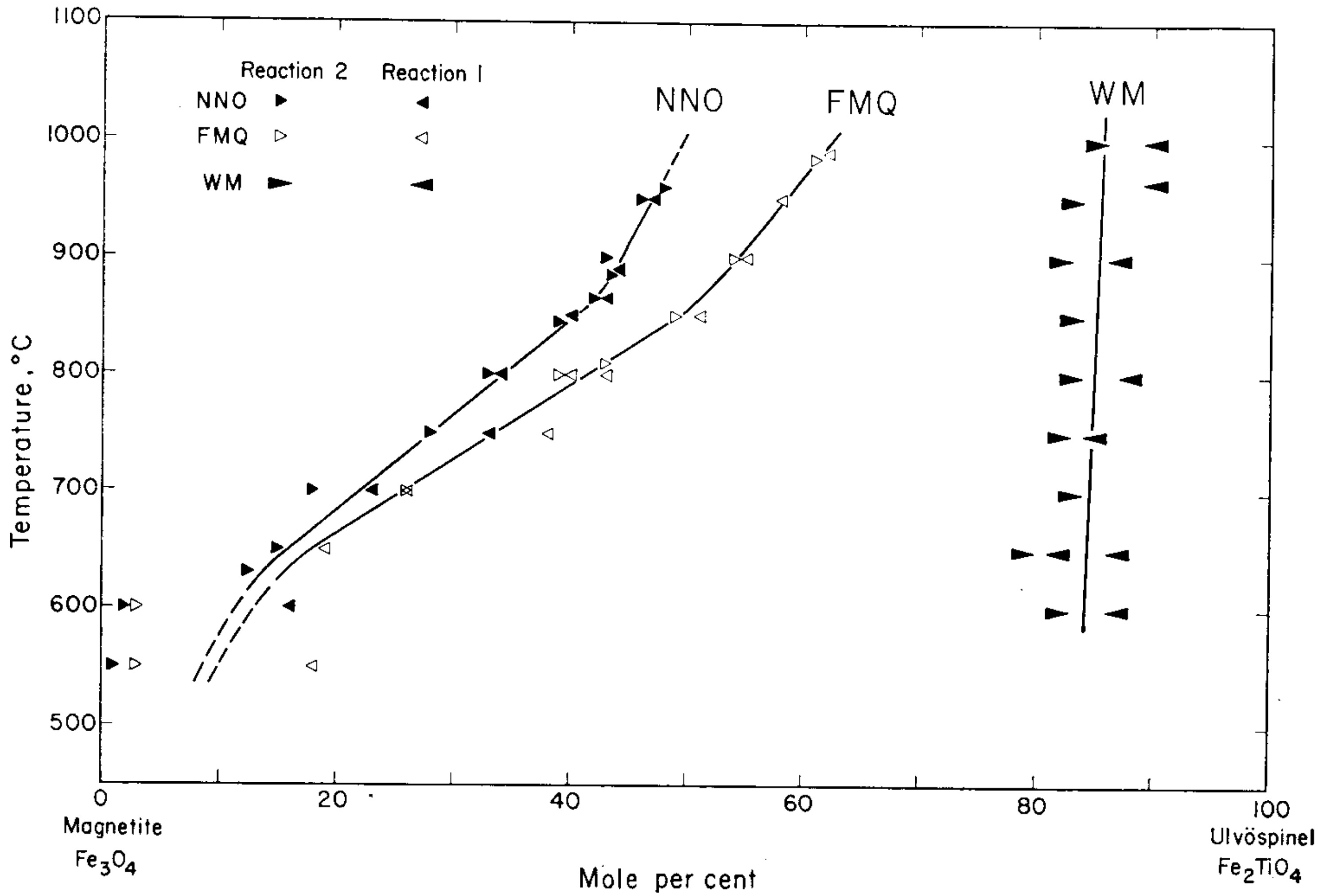
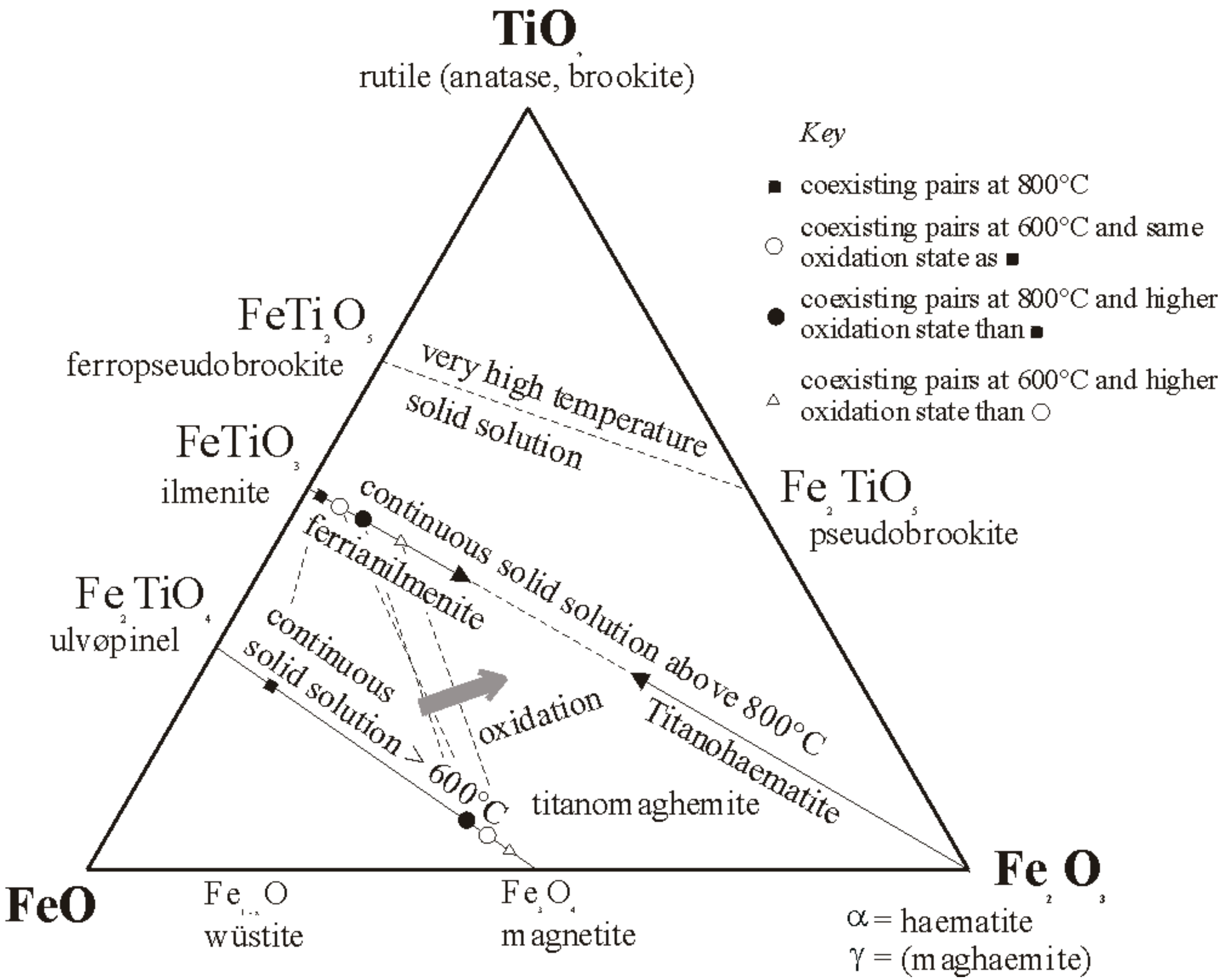


Buddington and Lindsley, 1964 (Classic!)



http://www.ngu.no/prosjekter/Geode/TiN/images/TIN%20Fig%2003.gif

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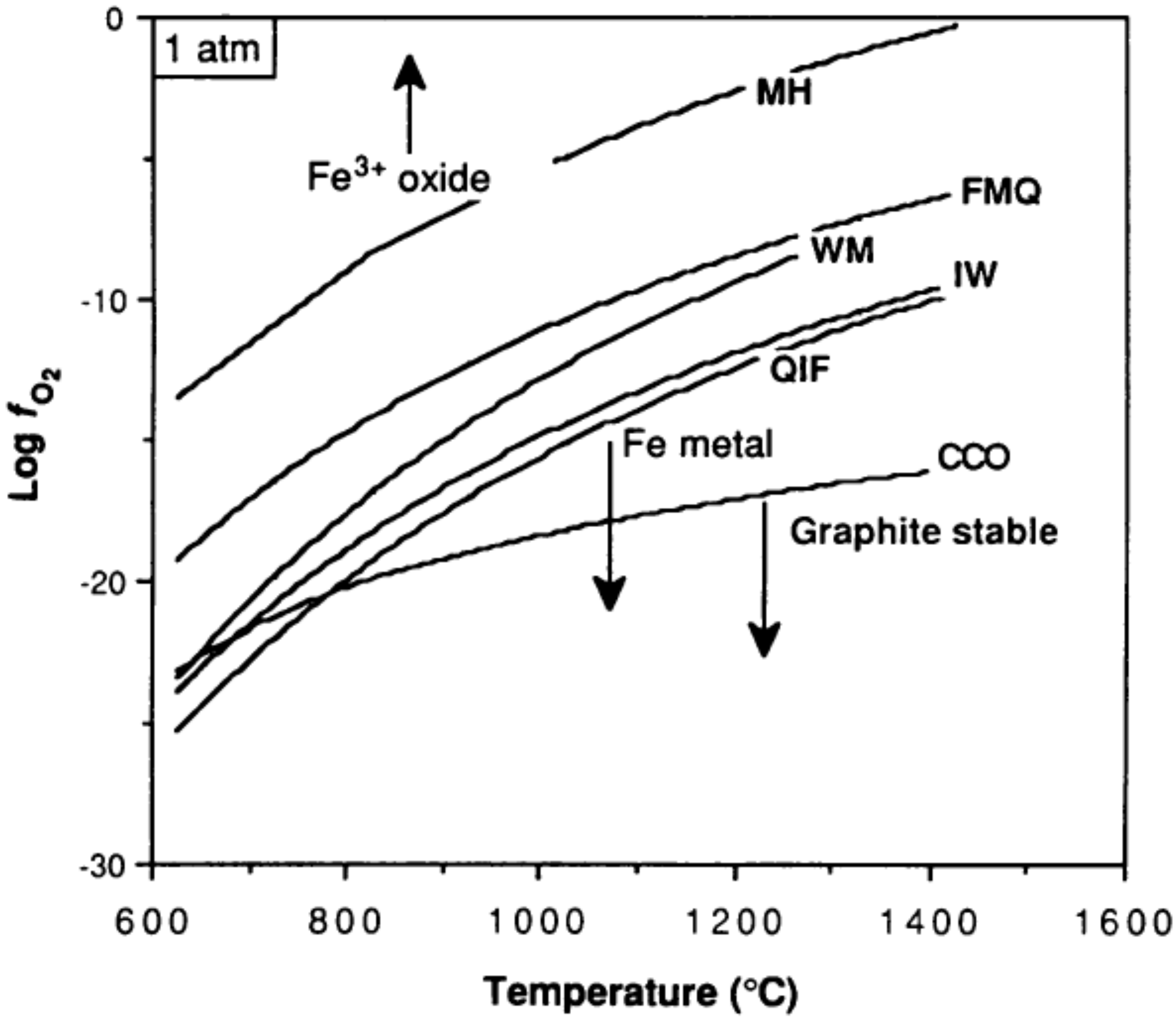

Wood et al., Science, 1990

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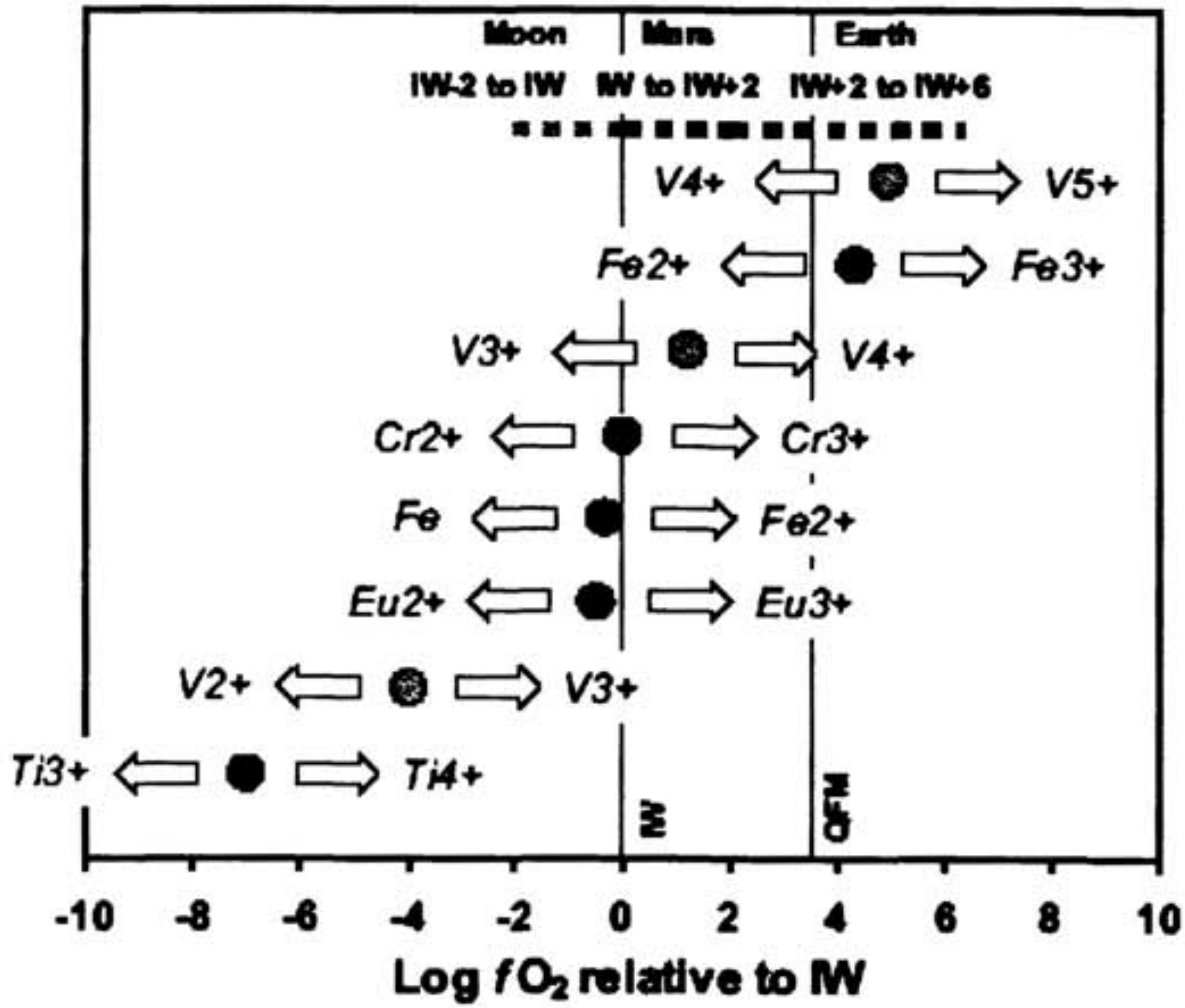
Moon
Mars
Earth
IW-2 to IW
IW to IW+2
IW+2 to IW+6
V4+
V5+
Fe2+
Fe3+
V3+
V4+
Cr2+
Cr3+
Fe
Fe2+
Eu2+
Eu3+
V2+
V3+
Ti3+
Ti4+
IW
QFM
-10
-8
-6
-4
-2
0
2
4
6
8
10
Log fO_2 relative to IW

Papike, 2005