Planetary
“Redox”

Liz Cottrell
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Peridotite, Tonga Fore-Arc
Credit: S. Birner
“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, $f_{O_2}$... Why to care.

You breathe oxygen. Enables a habitable planet.

CO + $\frac{1}{2}$ O$_2$ → CO$_2$
H$_2$ + $\frac{1}{2}$ O$_2$ → H$_2$O
Redox, Oxygen, $f_{O_2}$… 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

Redox, Oxygen, $f_{O_2}$... Why to care.

You eschew cosmic rays. Enables a core.
Redox, Oxygen, $f_{O_2}$... 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

\[ \text{Fe}^{3+} + e^- = \text{Fe}^{2+} \text{ (reduction)} \]

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

\[ [e^-] = \text{the activity of electrons, or } pe \]
Getting things straight

Oxidation State

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

Fugacity ($f_i$)

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

[e$^-$] = the activity of electrons, or pe
Getting things straight

**Oxidation State**
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\([e^-]\) = the activity of electrons, or \(p_e\)

**Fugacity \((f_i)\)**
- invented
- unrelated to oxygen
- the ‘escaping tendency’ (fugitive)
- \(f_i = P_i\) when \(i\) is an ideal gas

\[ \lim_{P \to 0} \frac{f}{P} \to 1, P \to 0 \]
Fugacity, $f$

From the ideal gas law and

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

of a gas at constant temperature

\[ PV = nRT, V = \frac{nRT}{P} \]

\[ dG = -SdT + VdP \]

\[ dG = VdP \]

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

\[ G(P) = G(P_0) + nRT \ln\left(\frac{P}{P_0}\right) \]

\[ \mu = \mu_i + RT \ln\left(\frac{P}{P_0}\right) \]
Fugacity, $f$

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

- 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
different-composition diagrams

Kerrick & Jacobs, 1981
Oxygen Fugacity $f_{O_2}$

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

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

$K_{eq} = \frac{a_{MO_{x/2}}}{a_M \cdot (f_{O_2})^{x/4}} = \frac{\gamma_{MO_{x/2}} \cdot X_{MO_{x/2}}}{\gamma_M \cdot X_M \cdot (f_{O_2})^{x/4}}$

$log K = log \frac{1}{D} + log \frac{\gamma_{MO_{x/2}}}{\gamma_M} - \frac{x}{4} log f_{O_2}$

$log D = -\frac{x}{4} log f_{O_2} + const$
Oxygen Fugacity $f_{O_2}$

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$$\log D = -\frac{x}{4} \log f_{O_2} + \text{const}$$

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

where $D = \text{met/sil}$ partition coefficient

ratio of activity coefficients $= 1$

(Henry’s Law)
Oxygen Fugacity $f_{O_2}$

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$$D = \frac{X^{\text{metal}}_M}{X^{\text{silicate}}_M}$$

where $D$ = met/sil partition coefficient

Eqn of a line.
Valence state = 4 x slope

ratio of activity coefficients = 1
(Henry’s Law)
recall from Rich’s talk

Cottrell et al., 2009
Oxygen Fugacity $f_{O_2}$

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Oxygen Fugacity $f_{O_2}$

\[ Fe + \frac{1}{2} O_2 = FeO \]

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For pure substances, activity is unity.

When Fe and FeO are in equilibrium, $f_{O_2}$ is fixed. This is the iron-wüstite buffer, IW

\[
Keq = \frac{a_{MOx/2}}{a_M \cdot (f_{O_2})^{1/4}} = \frac{\gamma_{MOx/2} \cdot X_{MOx/2}}{\gamma_M \cdot X_M \cdot (f_{O_2})^{x/4}}
\]

\[
\log K = \log \frac{1}{D} + \log \frac{\gamma_{MOx/2}}{\gamma_M} - \frac{x}{4} \log f_{O_2}
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\[ Fe + \frac{1}{2}O_2 = FeO \]

\[ M + \frac{1}{4}O_2 = MO_{x/2} \]

\[ K_{eq} = \frac{a_{MO_{x/2}}^{1}}{a_{M} \cdot (f_{O_2})^{1/4} } = \frac{\gamma_{MO_{x/2}} \cdot X_{MO_{x/2}}}{\gamma_{M} \cdot X_{M} \cdot (f_{O_2})^{x/4}} \]

\[ \log K = \log \frac{1}{D} + \log \frac{\gamma_{MO_{x/2}}}{\gamma_{M}} - \frac{x}{4} \log f_{O_2} \]

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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 $f_{O_2}$

If you were asleep and are now waking up...

If rocks were an ideal gas, we’d just call it partial pressure.
Oxygen Fugacity $f_{O_2}$ Buffers

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

Iron + oxygen $\rightarrow$ Wüstite
Oxygen Fugacity $f_{O_2}$ Buffers

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

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

Iron + oxygen $\rightarrow$ Wüstite

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

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Rookie Errors

• $f_{O_2}$ 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 $f_{O_2}$ 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; $f_{O_2}$ 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 $f_{O_2}$. 
Rock at >HM

hematite 1%
opx 50%
quartz 49%

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

Rock at QFM

fayalite 1%
magnetite 50%
quartz 49%

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 $f_{O_2}$

Measuring $O_2$ or its activity in rocks is important, but tricky.
Oxygen Fugacity $f_{O_2}$

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

Not all proxies work for all samples.

Not all proxies agree.
Oxygen Fugacity $f_{O_2}$

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

In silicate melts, Fe$^{3+}/\Sigma$Fe varies as a function of $f_{O_2}$, T, X

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

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In liquids, there are no crystal-chemical controls, and the Fe\textsuperscript{3+}/ΣFe ratio is a function of $f_{O_2}$

$$\ln \left( \frac{X_{Fe_2O_3}}{X_{FeO}} \right) = a \ln (f_{O_2}) + \frac{b}{T} + c + \sum_i d_i X_i + e$$

$$\left[ 1 - \frac{T_0}{T} - \ln \left( \frac{T}{T_0} \right) \right] + \frac{f}{T} + g \frac{(T-T_0)P}{T} + h \frac{P^2}{T}.$$

The Fe\textsuperscript{3+}/ΣFe ratio of a basalt should tell us about the $f_{O_2}$ of the mantle

Kress and Carmichael, 1991; compressibility (P term) confirmed by O’Neill et al., 2006
First order observations

Fe$^{3+}$/ΣFe

Ridges     ARCS

reduced   ΔNNO   oxidized


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MORB

- XANES, this study, $0.16 \pm 0.01$ (n = 103)
- Bezos and Humler (2005), $0.12 \pm 0.02$ (n = 104)
- Christie et al. (1986), $0.07 \pm 0.03$ (n = 78)
Oxygen Fugacity $f_{O_2}$

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

Upper mantle assemblage: olv + spl + opx

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

Proxy Soup

Spinel peridotite oxygen barometry by EMPA at NMNH
Credit: S. Birner
Oxygen fugacity recorded by abyssal peridotites and MORB

Bryndzia & Wood
Global Abyssal Peridotites

SWIR peridotites
this study

global MORB source regions
\( \sim 1300^\circ C, \sim 1 \text{ GPa} \)
(\( \Delta QFM_{\text{prim}} \), C&K2013)

includes
SWIR basalts

SWIR veined peridotites
this study

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
Oxygen Fugacity \( f_{O_2} \)

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

Whole rock V concentration may be set by \( f_{O_2} \) during melting.

So what about trace element proxies?
This whole business is pretty serious for the early life folks…

Holloway & Blank, Rev. Min., 1994

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Net flux on order of 10,000 kg/s Fe$^{3+}$ toward mantle.
charge from a multi-anvil experiment
lower mantle: 70% pv with Fe$^{3+}$/ΣFe = 0.6
From mantle xenoliths: e.g. Frost & McCammon, 1998

From experiments: Kress & Carmichael, 1991 and O’Neill et al., 2006
Oxygen Fugacity ($fO_2$) decreases with depth (in continental cratons)

Change in oxygen activity can force changes in speciation:

\[2\text{Fe}^{2+}\text{O} + 0.5\ \text{O}_2 \rightarrow \text{Fe}_2^{3+}\text{O}_3\]

Change in speciation can force changes in oxygen activity:

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

The depth of incipient mantle melting depends on $f_{O_2}$

Requires carbonate, not carbon. $f_{O_2}$ dependent.

Dasgupta and Hirschmann, Nature, 2006; EPSL 2010...
Stagno et al., EPSL, 2010 and Nature, 2013
carbonate fluxes silicate melting

carbonate stability requires oxidizing conditions

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

Experiment M245: 6.6 GPa, 1220°C
Oxygen fugacity recorded by abyssal peridotites and MORB

Bryndzia & Wood
Global Abyssal Peridotites

SWIR peridotites
this study

global MORB
source regions
~1300°C, ~1 GPa
($\Delta$QFM$_{prime}$, C&K2013)

includes
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veined peridotites
this study

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

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Stagno et al., EPSL, 2010 and Nature, 2013
Original model framework kindly provided by D. Frost.

\[ T_p = 1320 \, ^\circ\text{C} \]

- \( \log f_{\text{O}_2} (\Delta \text{AQFM}) \)
- \( \text{Fe}^{3+}/\Sigma \text{Fe} = 0.01 \)
- \( \text{DCO}_3 \)
- \( \text{carbonate melt} \)
- \( \text{diamond} \)
Original model framework kindly provided by D. Frost.

\[ T_p = 1320 \, ^\circ \text{C} \]

\[ \text{DCO}_3 \]

\[ \text{Fe}^{3+}/\Sigma \text{Fe} = 0.01 \]
Original model framework kindly provided by D. Frost.
Open questions

- Are there domains oxidized enough to explain geophysical observations?

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

basalts equilibrated at known $f_{O_2}$ (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

Cottrell et al., Chem Geol., 2009

Previous work: ± 5% absolute Fe$^{3+}/\Sigma$Fe.
This study: ± 0.5%

Cottrell et al., Chem Geol., 2009

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Global MORB

Implications

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

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Smithsonian

GSO

Deep Carbon Observatory

Reservoirs and Fluxes

NSF

Margins

Advanced Photon Source

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Extra Slides
Oxygen Fugacity $f_{O_2}$

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

In magmas, minerals may record $f_{O_2}$.

Fe-Ti oxide thermobarometry by EMPA at NMNH
Credit: S. Grocke
Papike, 2005