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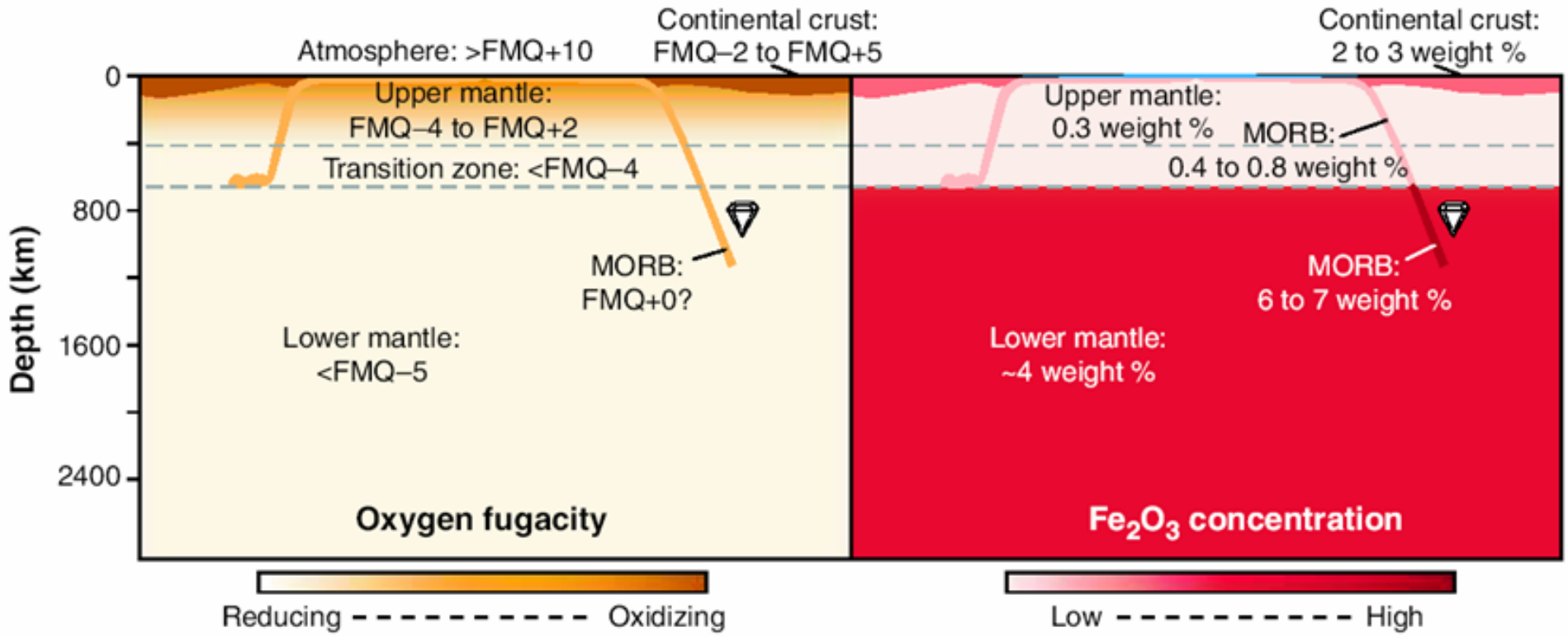
# The Paradox of Mantle Redox

Catherine McCammon




oxygen fugacity ? oxidation state

# oxidation state

| | |
|---|---|
| $Fe^{2+}$, $Fe^{3+}$, $Fe^{0}$ | $3d^6$, $3d^5$, $3d^6\ 4s^2$ |
| $Cr^{2+}$, $Cr^{3+}$ | $3d^4$, $3d^3$ |
| $V^{2+}$, $V^{3+}$, $V^{4+}$, $V^{5+}$ | $3d^3$, $3d^2$, $3d^1$, $3d^0$ |

# oxygen fugacity

*Equilibrium configuration defined where G reaches a minimum, or dG = 0*

*For a gas at P,T:* $dG = -S\,dT + V\,dP$

$PV = n\,RT$

*at constant T:*

$dG = V\,dP = RT/P\,dP = RT\,d\ln P$

$\int dG = \int RT/P\,dP$

$\Delta G = \Delta G^\circ + RT \ln P$

*for an ideal gas*, $f = P$
*and for gases at low pressure*, $f \approx P$

*Fugacity is measured in units of pressure*

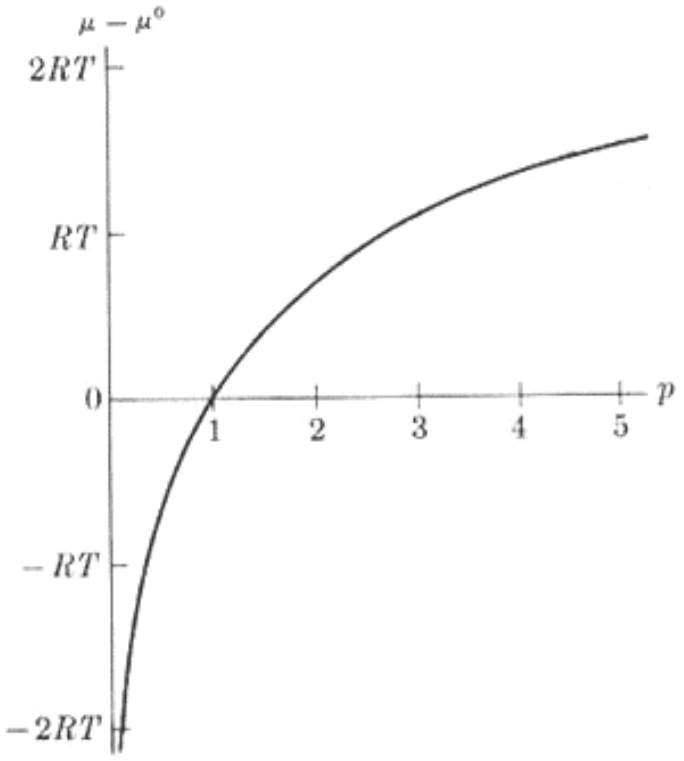



**Fig. 10–2** Free energy of ideal gas as a function of pressure.

*Castellan 1971*

# what is the oxygen fugacity of air?

At 1 bar assume ideal behaviour, so $f \approx P$ and $f_i \approx P_i = x_i P_{total}$

The sea-level composition of air (in percent by volume at the temperature of 15°C and the pressure of 101325 Pa) is given below.

| Name | Symbol | Percent by Volume |
|---|---|---|
| Nitrogen | $N_2$ | 78.084 % |
| Oxygen | $O_2$ | 20.9476 % |
| Argon | Ar | 0.934 % |
| Carbon Dioxide | $CO_2$ | 0.0314 % |
| Neon | Ne | 0.001818 % |
| Methane | $CH_4$ | 0.0002 % |
| Helium | He | 0.000524 % |
| Krypton | Kr | 0.000114 % |
| Hydrogen | $H_2$ | 0.00005 % |
| Xenon | Xe | 0.0000087 % |

CRC Handbook of Chemistry and Physics
by David R. Lide, Editor-in-Chief
1997 Edition

Hence $f_{O2} = x_{O2} \times P_{total} = 0.209476 \times 1$ bar

so $\log f_{O2} = -0.68$

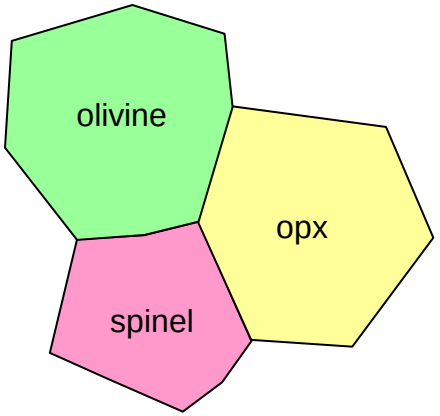
$x_{O2}$ of air is essentially constant with temperature, hence $\log f_{O2}$ (air) is also insensitive to temperature

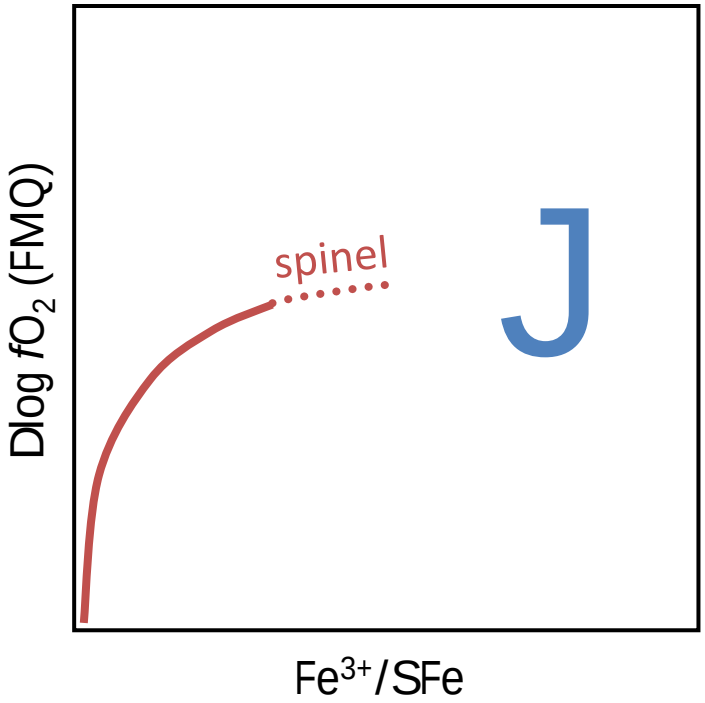
# what is the oxygen fugacity of spinel peridotite?

$$6\ Fe_2SiO_4(olivine) + O_2 = 3\ Fe_2Si_2O_6(opx) + 2\ Fe_3O_4(spinel)$$

$$\Delta G = \Delta G^\circ + 3\ RT\ \ln a_{Fe2Si2O6} + 2\ RT\ \ln a_{Fe3O4} - 6\ RT\ \ln a_{Fe2SiO4} - RT\ \ln f_{O2}$$

$$\log f_{O2} = -\log K + 3 \log a_{Fe2Si2O6} + 2 \log a_{Fe3O4} - 6 \log a_{Fe2SiO4}$$




intuitive relation between oxidation state and oxygen fugacity

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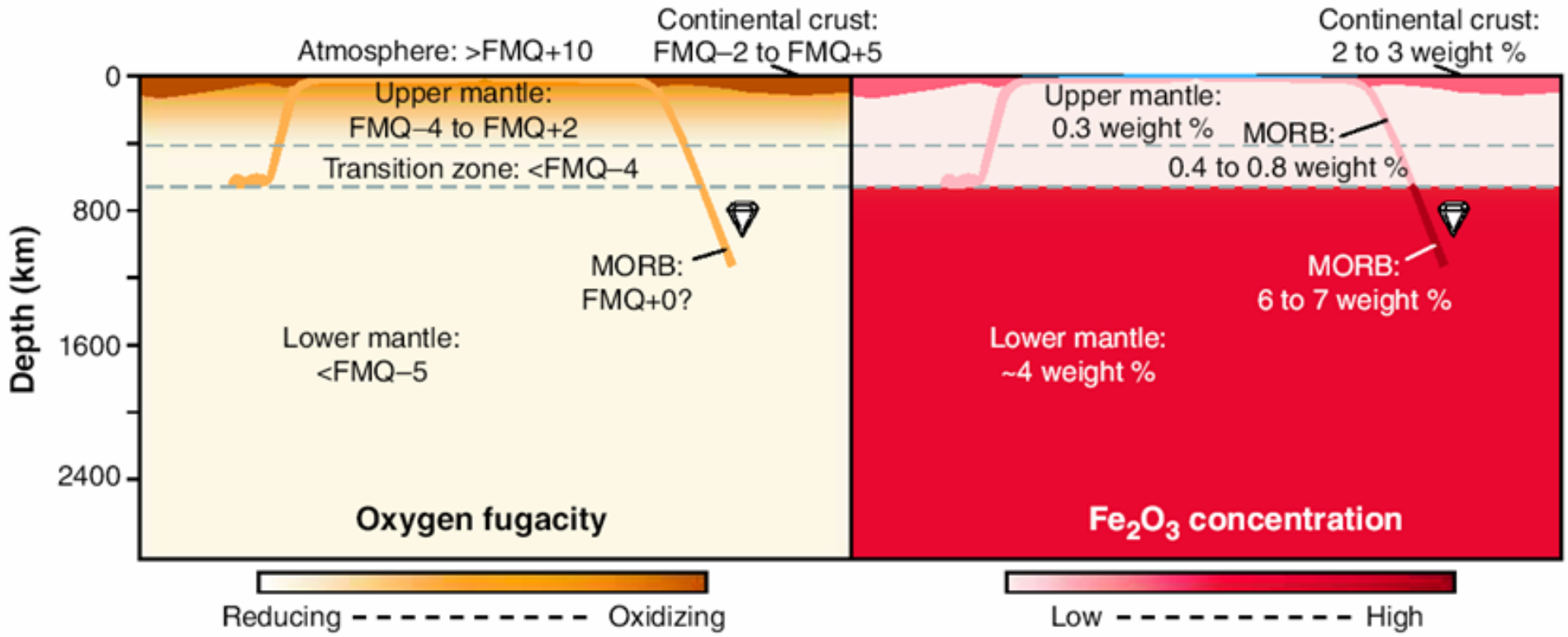



oxygen fugacity ? oxidation state


olivine

opx

cpx

spinel

*Rob Lavinsky, iRocks.com*


olivine

opx

cpx

spinel

*Rob Lavinsky, iRocks.com*


olivine

0.00

opx

0.10

cpx

0.11

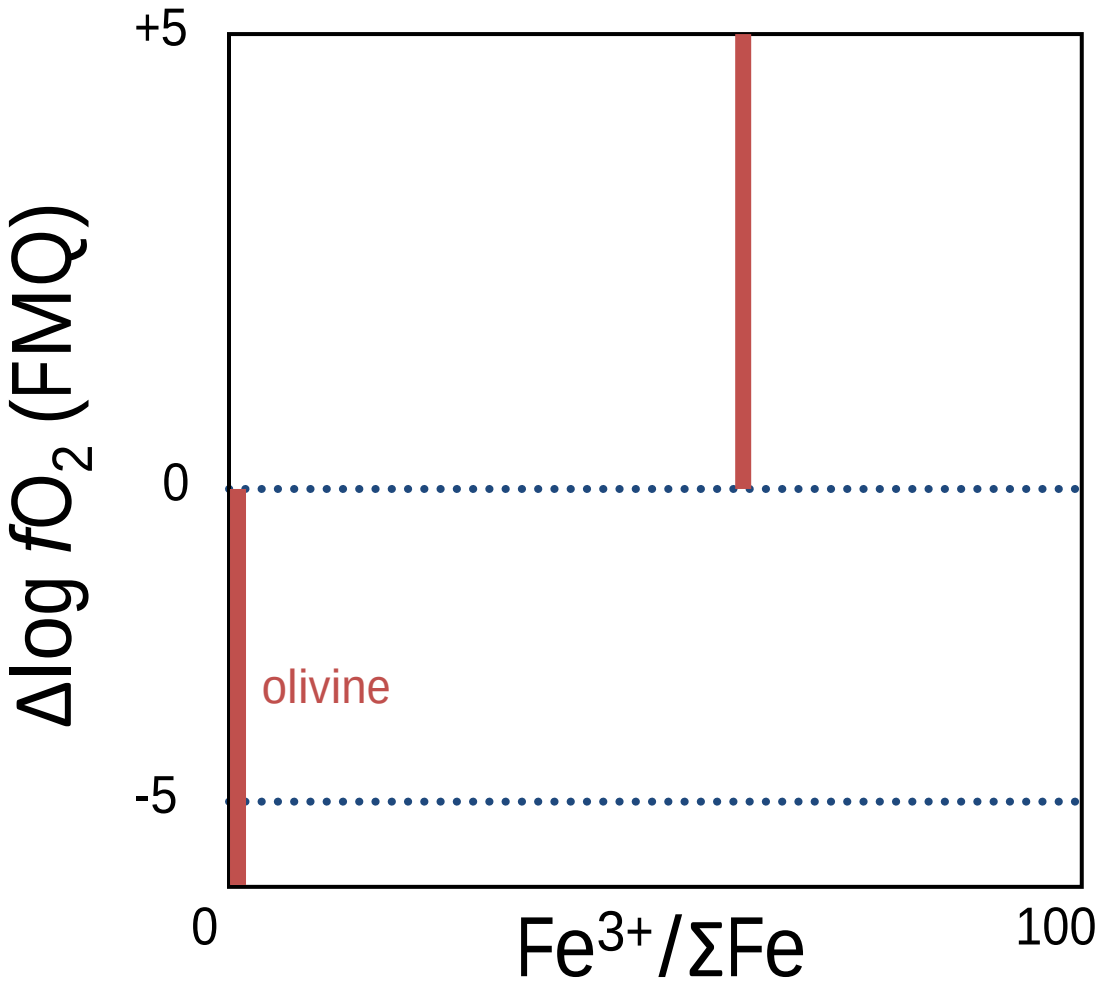
spinel

0.09

*whole rock $Fe_2O_3$ = 0.3 wt%*


high oxygen fugacity

low $Fe^{3+}$



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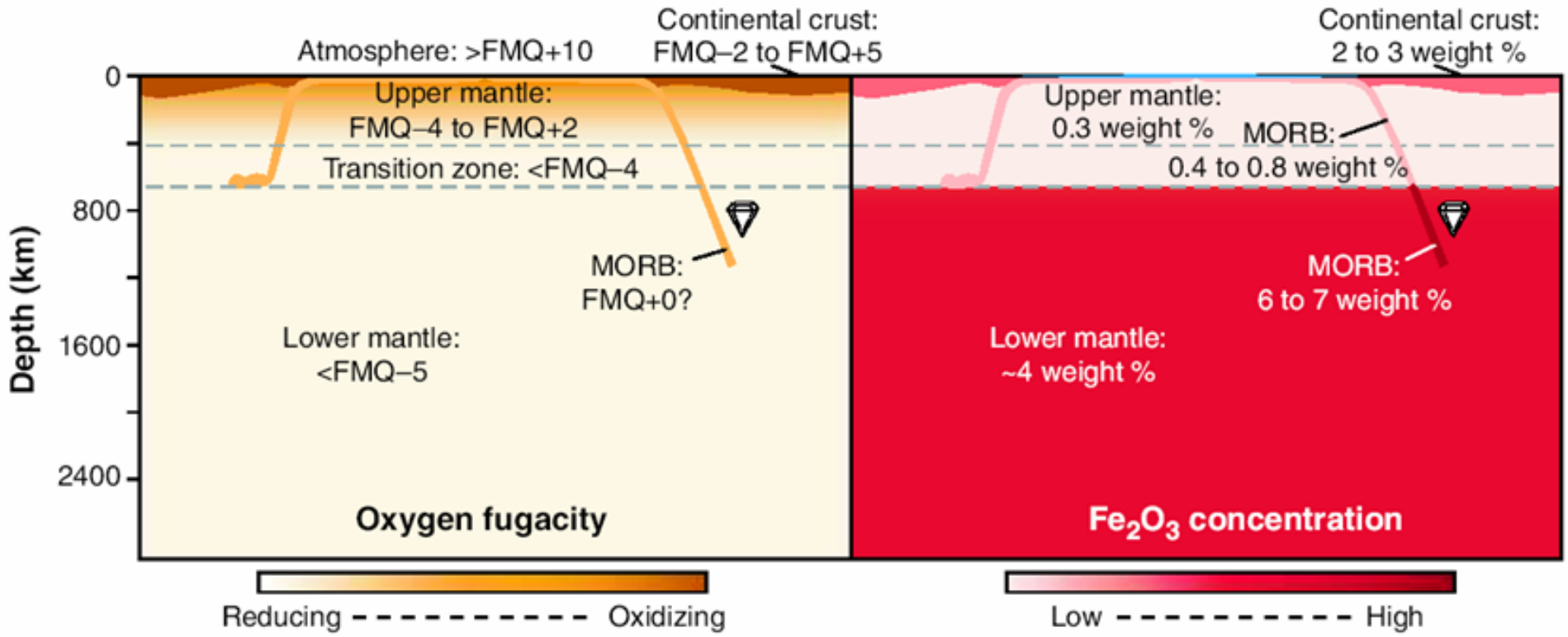
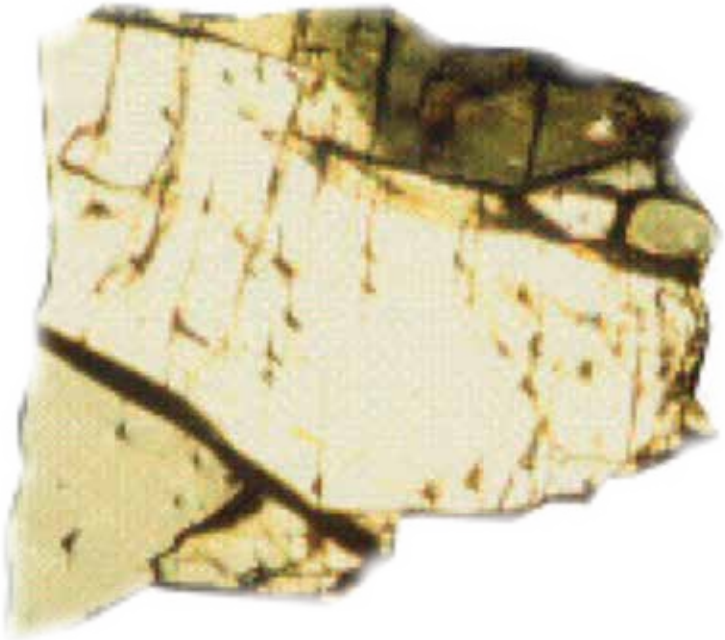



oxygen fugacity ? oxidation state


bridgmanite

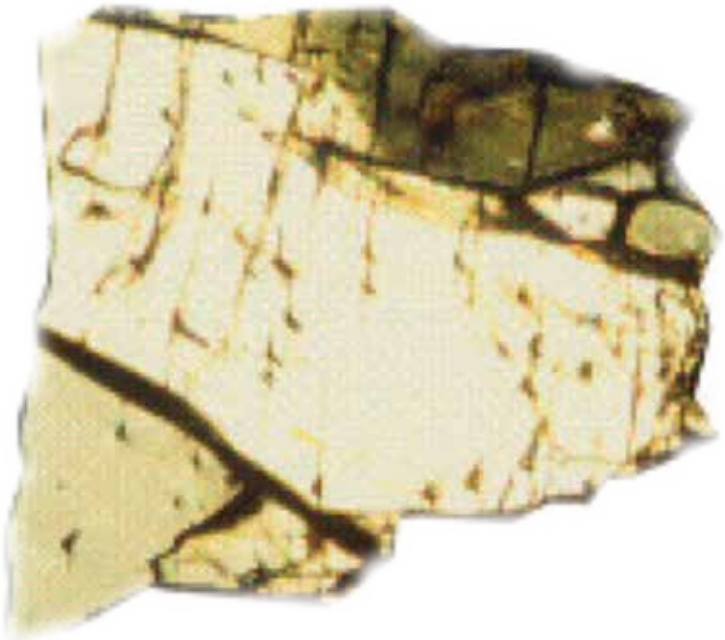
ferropericlase



*Dan Frost*

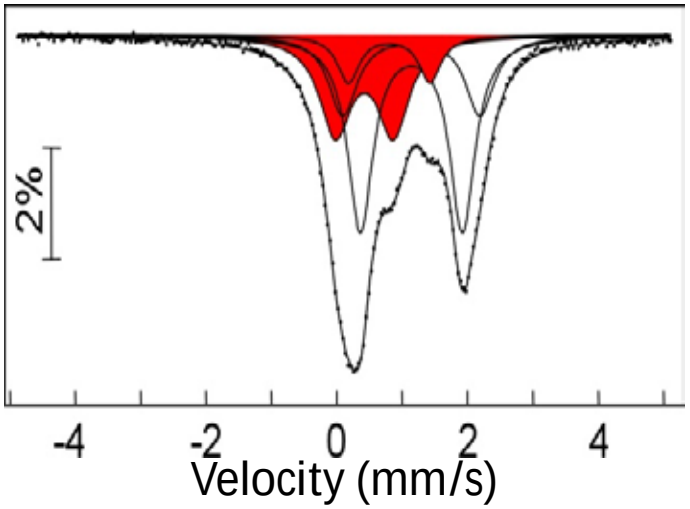

bridgmanite

ferropericlase

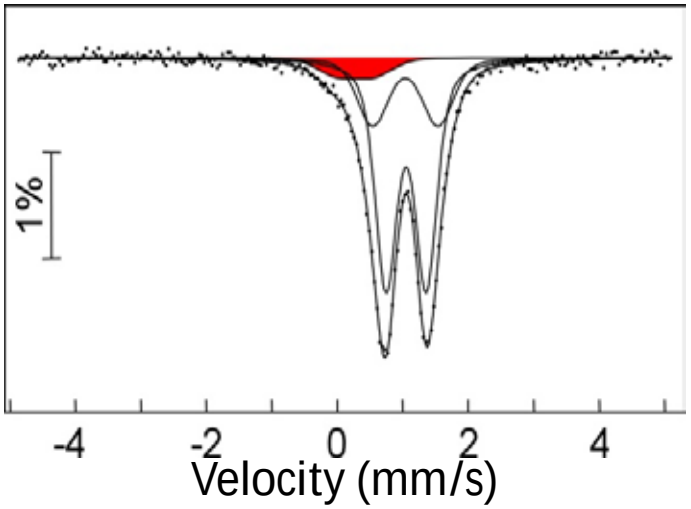


*Dan Frost*

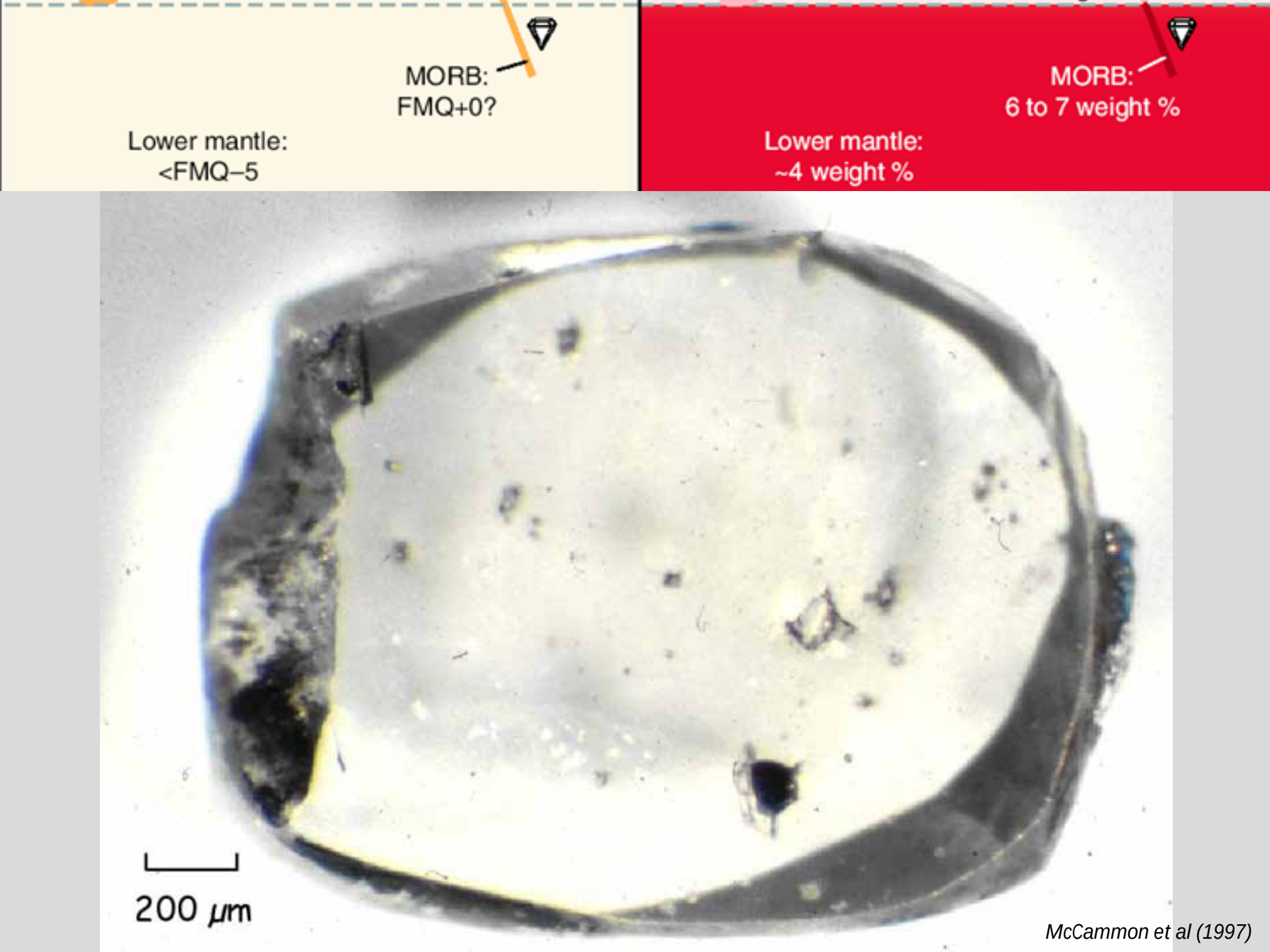

bridgmanite




ferropericlase

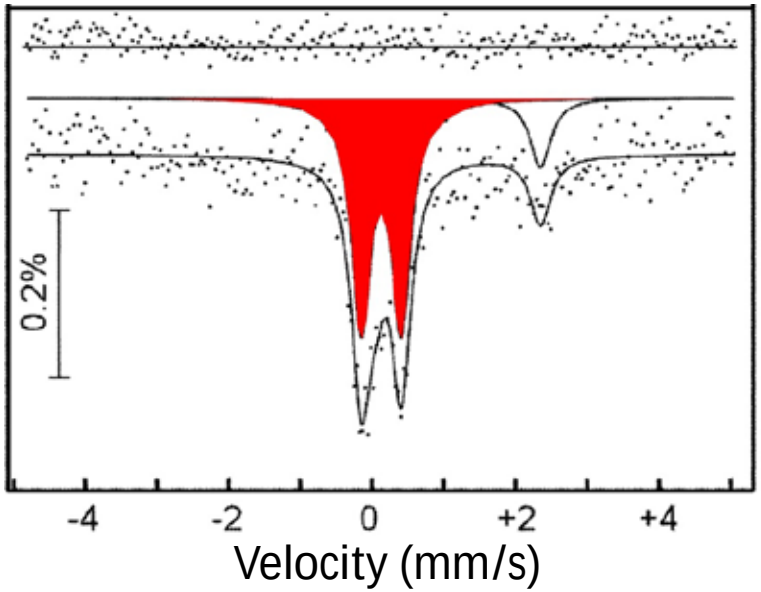



*McCammon (1997)*
*Lauterbach et al. (2001)*
*Frost et al. (2004)*

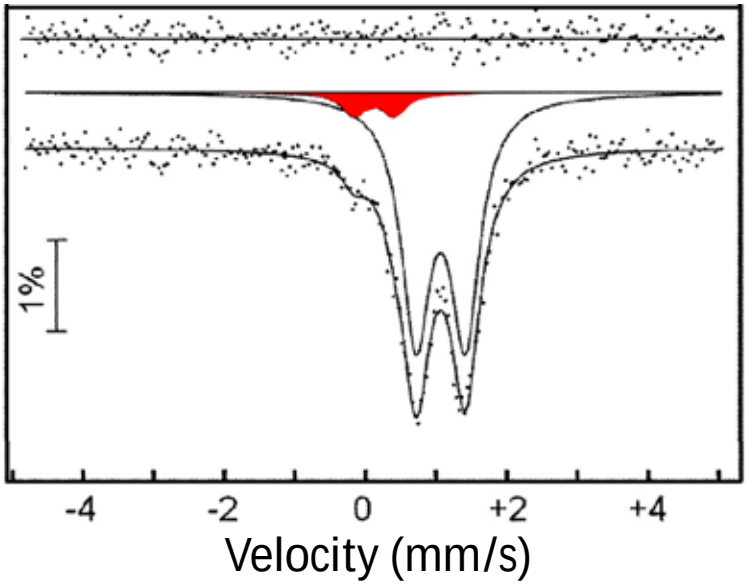



*McCammon et al (1997)*


former bridgmanite




ferropericlase




*McCammon et al (1997)*


bridgmanite

ferropericlase

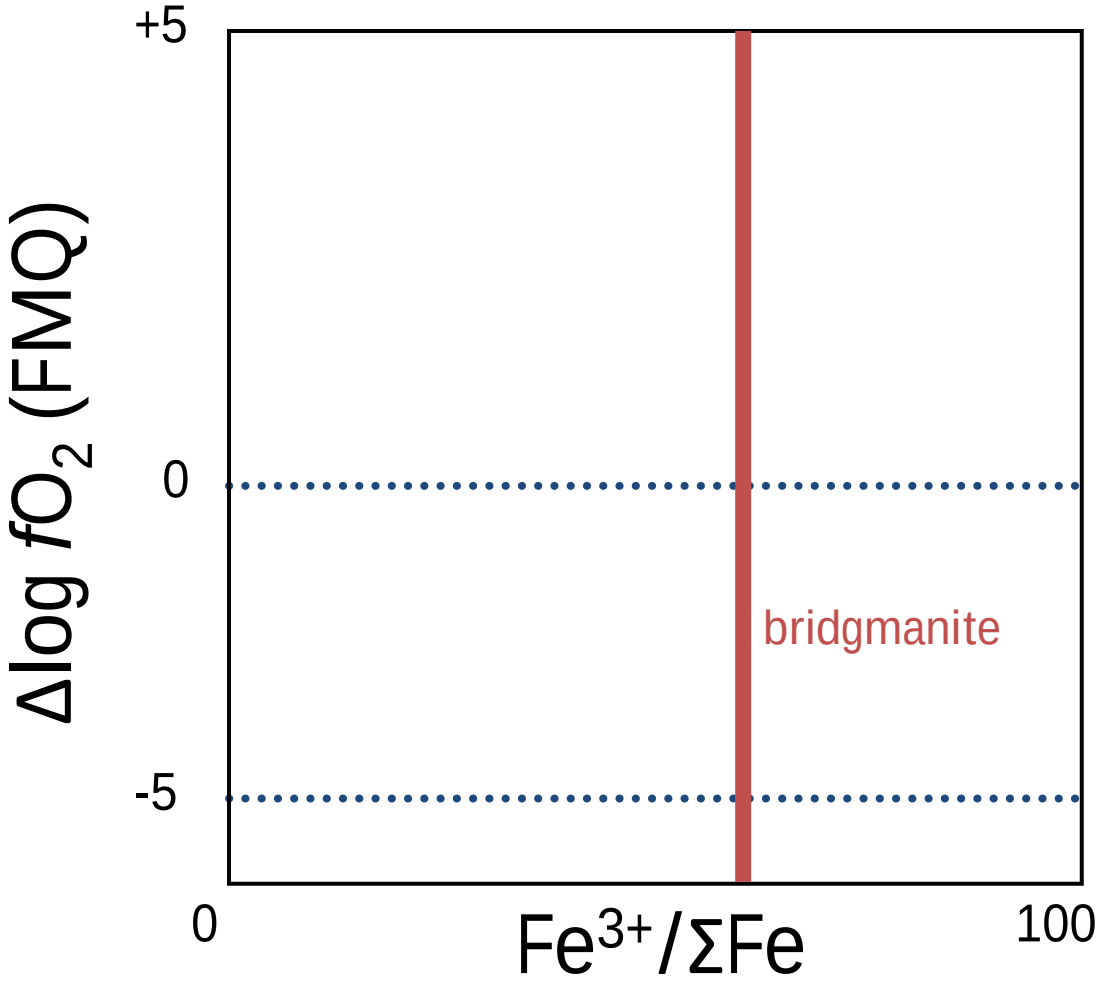
3.9

0.02

*whole rock $Fe_2O_3$ = 3.9 wt%*


low oxygen fugacity

high $Fe^{3+}$



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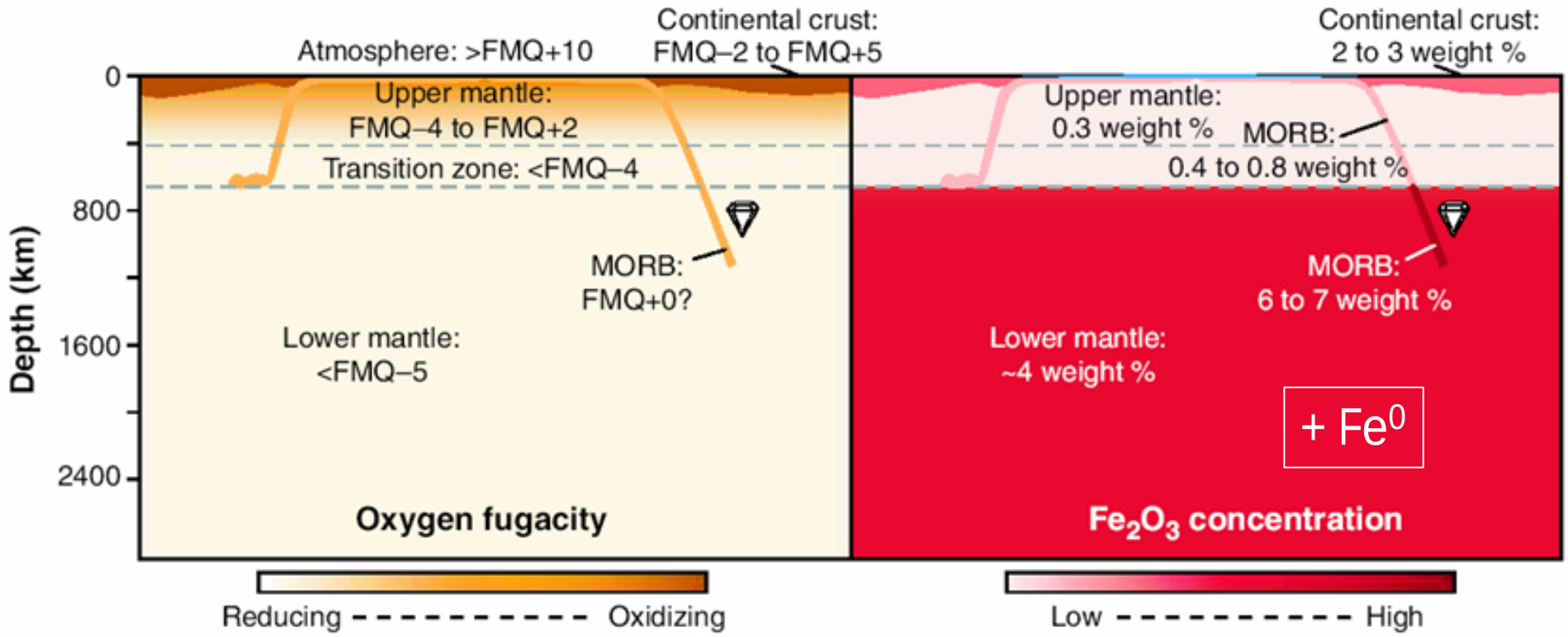


oxygen fugacity J oxidation state

# why should you care?

## oxidation state

physical properties
*elasticity, electrical conductivity, thermal diffusivity, rheology, viscosity, …*
→ LLSVPs, plumes, MiMOSAs, lithosphere

chemical properties
*melting, element partitioning, …*

## oxygen fugacity

volatile speciation
*carbon, hydrogen, nitrogen, …*
→ slab processes

Earth differentiation including core formation

evolution of Earth's atmosphere