Mantle redox conditions

Carbonate related melting

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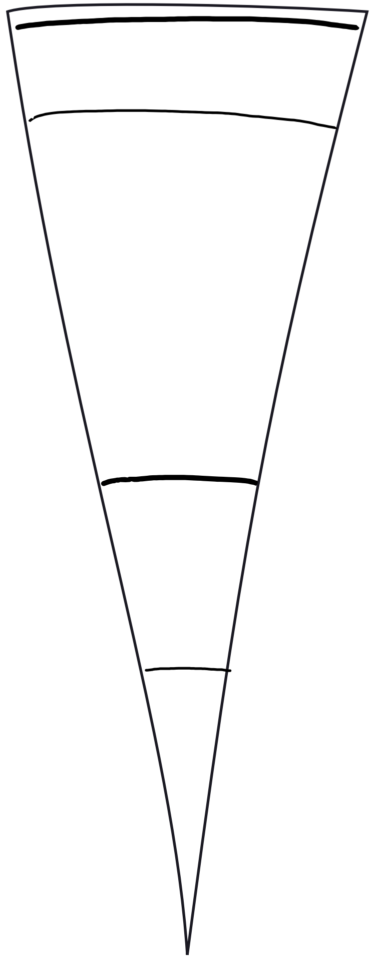
Introduction

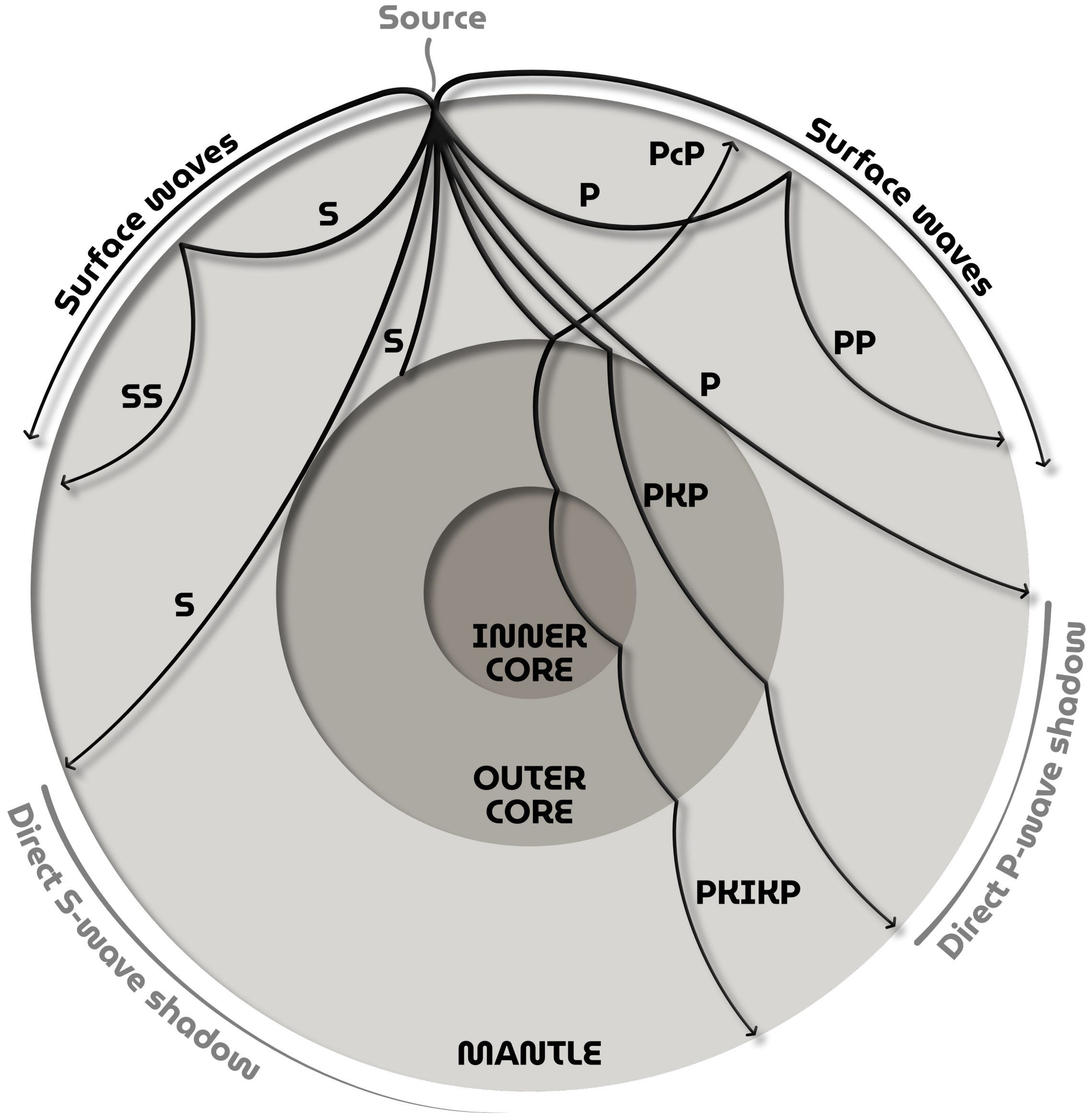
- Schematic cross section of the Earth

CRUST

MANTLE

CORE





Redox state

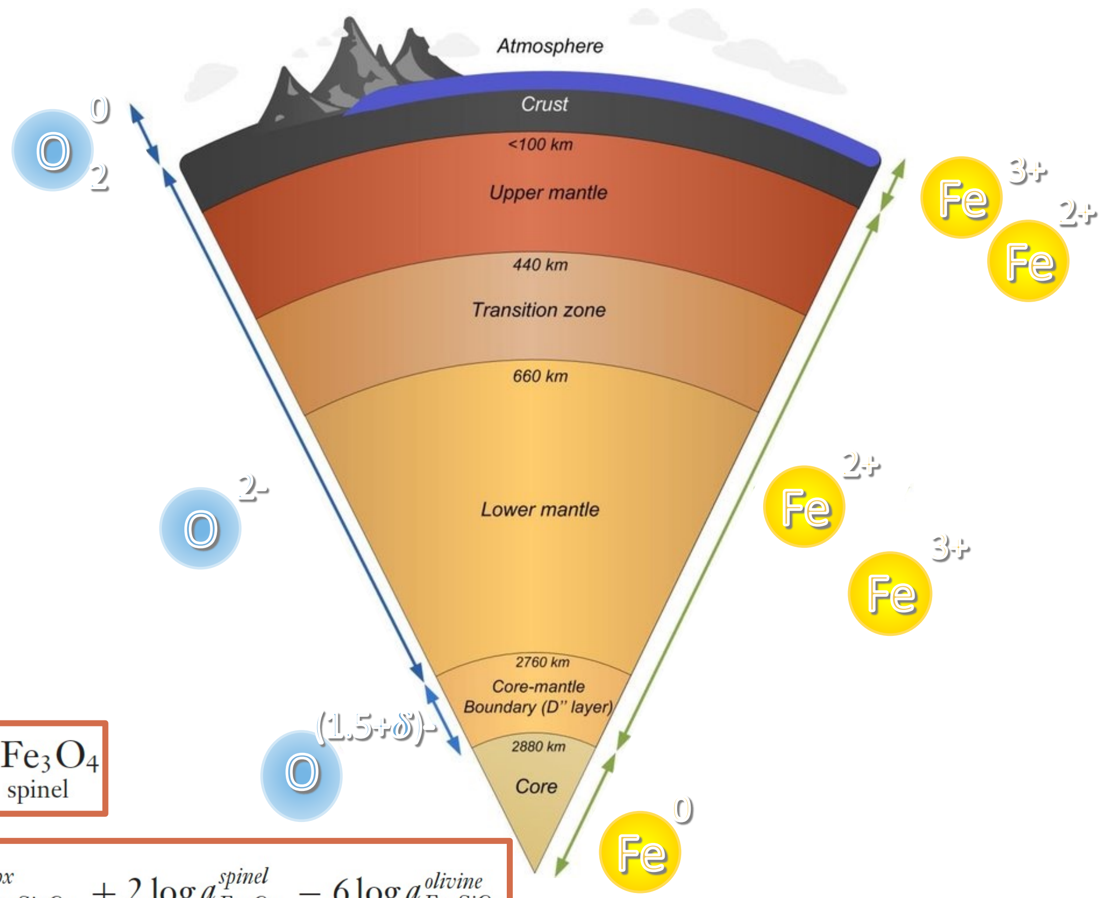
- **REDOX** = type of chemical reaction in which the OXIDATION STATE changes
- **Oxygen fugacity** (f_{O_2}) is a way to quantify the redox state
  partial pressure of oxygen
- **Redox buffer** = assemblage that constrains oxygen fugacity as a function of temperature
  it forces a certain oxygen fugacity
- iron-wüstite (IW) buffer

$$Fe + \frac{1}{2} O_2 \Leftrightarrow Fe_{1-y}O$$

metal wüstite

Redox state of the Earth's interior

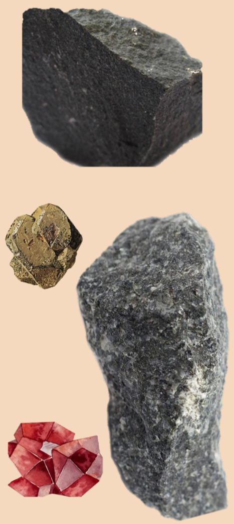
- Controls the speciation of multivalent elements such as carbon (C^0 or C^{4+}) and iron (Fe^0, Fe^{2+}, or Fe^{3+}) in minerals and melts
- Upper mantle – direct measurements of fO_2
- We analyze mantle-derived rocks whose minerals contain multivalent elements
- From the ratios of the oxidized and reduced forms of these elements we could infer redox conditions at which they formed



BASALTS (MORB)

SPINEL PERIDOTITES

GARNET PERIDOTITES

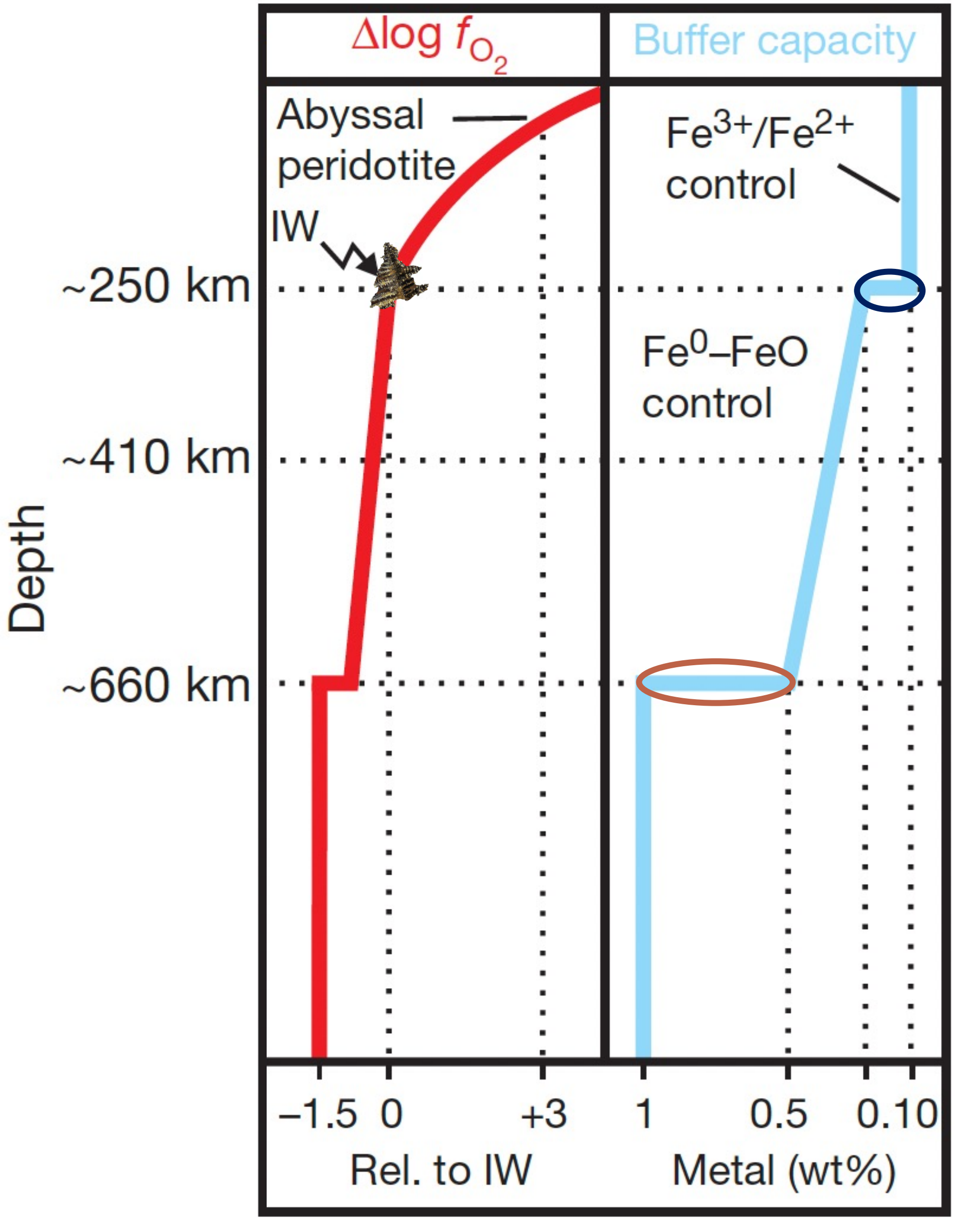


$$\underset{\text{olivine}}{6Fe_2SiO_4} + O_2 = \underset{\text{opx}}{3Fe_2Si_2O_6} + \underset{\text{spinel}}{2Fe_3O_4}$$

$$\log fO_2 = \frac{\Delta G^o_{(2)}}{\ln(10)RT} + 3\log a^{opx}_{Fe_2Si_2O_6} + 2\log a^{spinel}_{Fe_3O_4} - 6\log a^{olivine}_{Fe_2SiO_4}$$

$$\underset{\text{garnet}}{2Fe_3Fe_2^{3+}Si_3O_{12}} = \underset{\text{olivine}}{4Fe_2SiO_4} + \underset{\text{opx}}{2FeSiO_3} + O_2$$

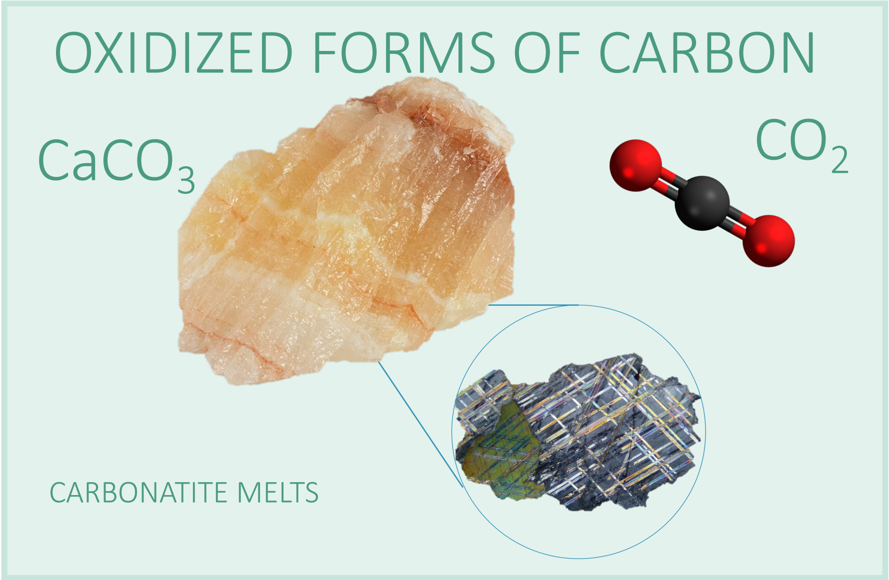
$$\log fO_2 = \frac{-\Delta G^o_{(6)}}{\ln(10)RT} + 2\log a^{gt}_{Fe_3Fe_2Si_3O_{12}} - 2\log a^{opx}_{FeSiO_3} - 4\log a^{olivine}_{Fe_2SiO_4}$$



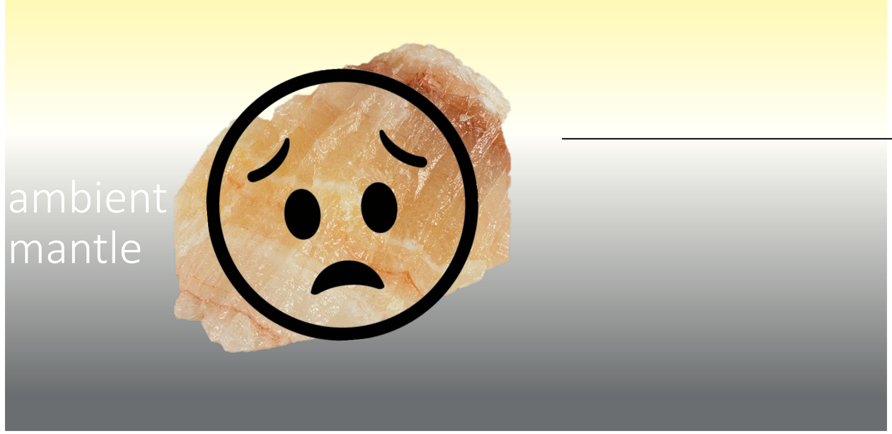
- change in redox control from Fe^{3+}/Fe^{2+} to Fe^0–FeO

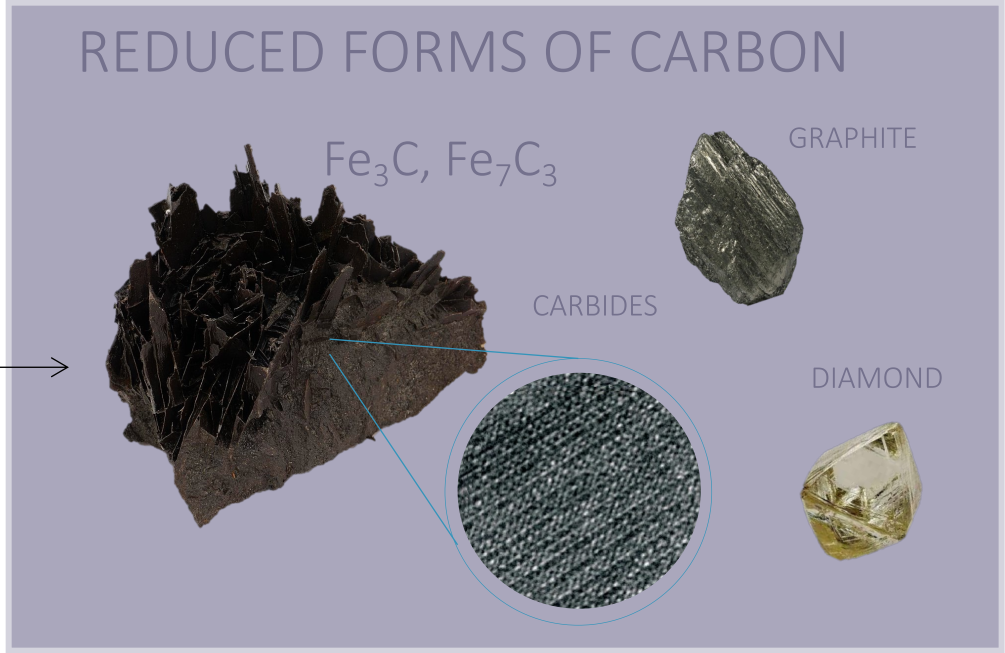
- MgSi–perovskite incorporates more Fe^{3+} at metal saturation fO_2 than majoritic garnet

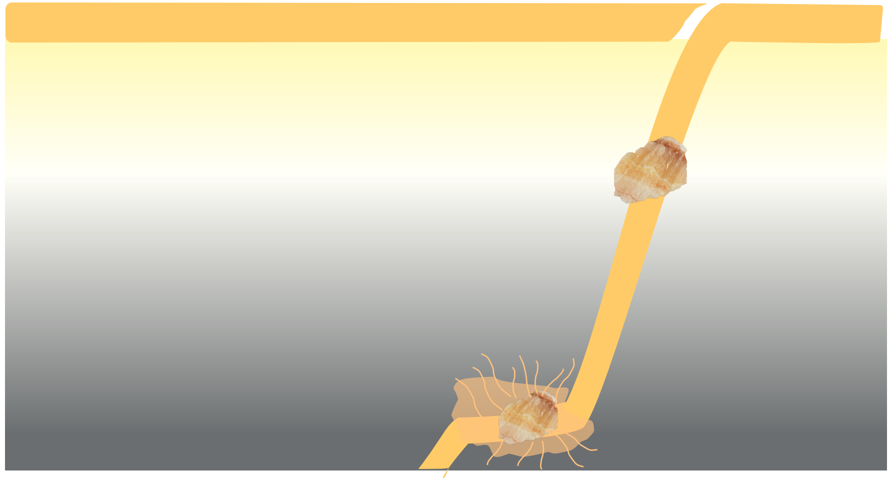
The story of oxidized carbon



- Carbonate remixed into the mantle at > 150 km depth is unstable and would dissolve in the metal phase or form iron carbides depending on the Fe-C ration and P-T conditions
- **Carbonate related melting** is unlikely to occur in lower mantle



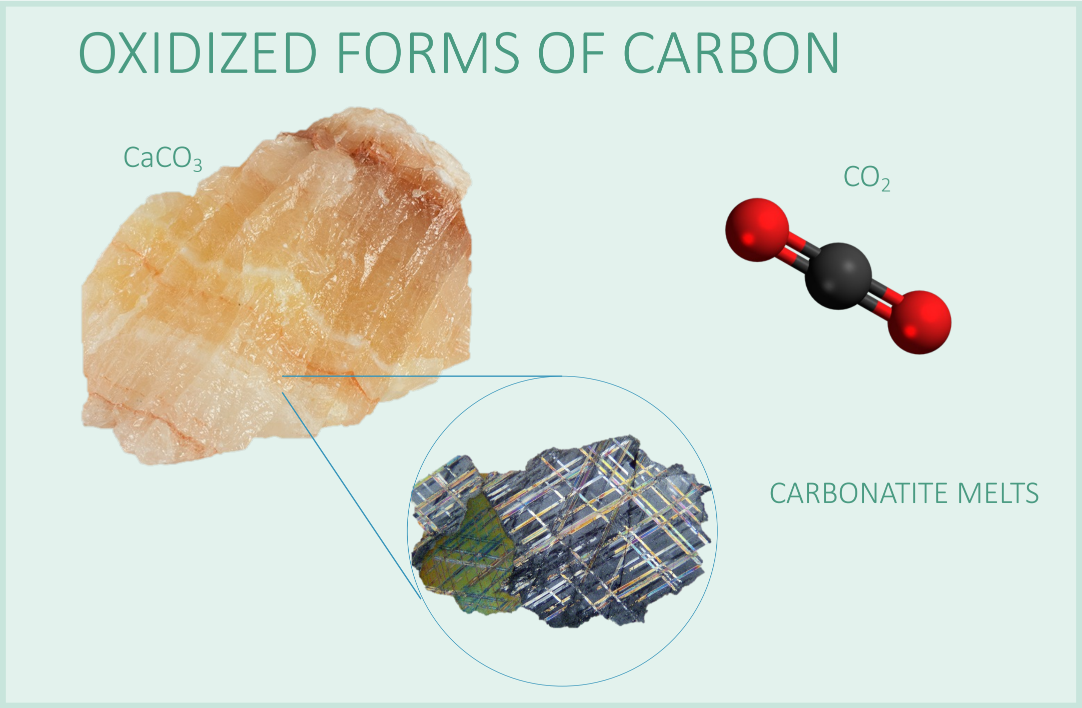




Subduction

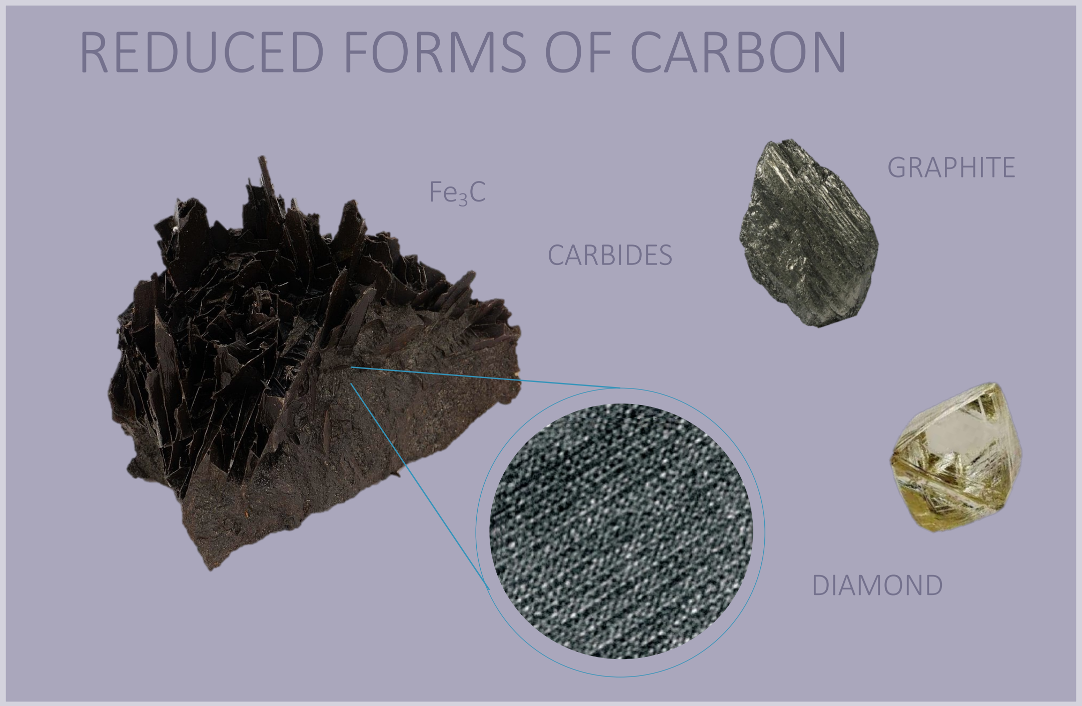
- Addition of subducted carbonate changes relative buffer capacity in the mantle

What happens with oxidized carbon at transition zone depth?



REDOX FREEZING

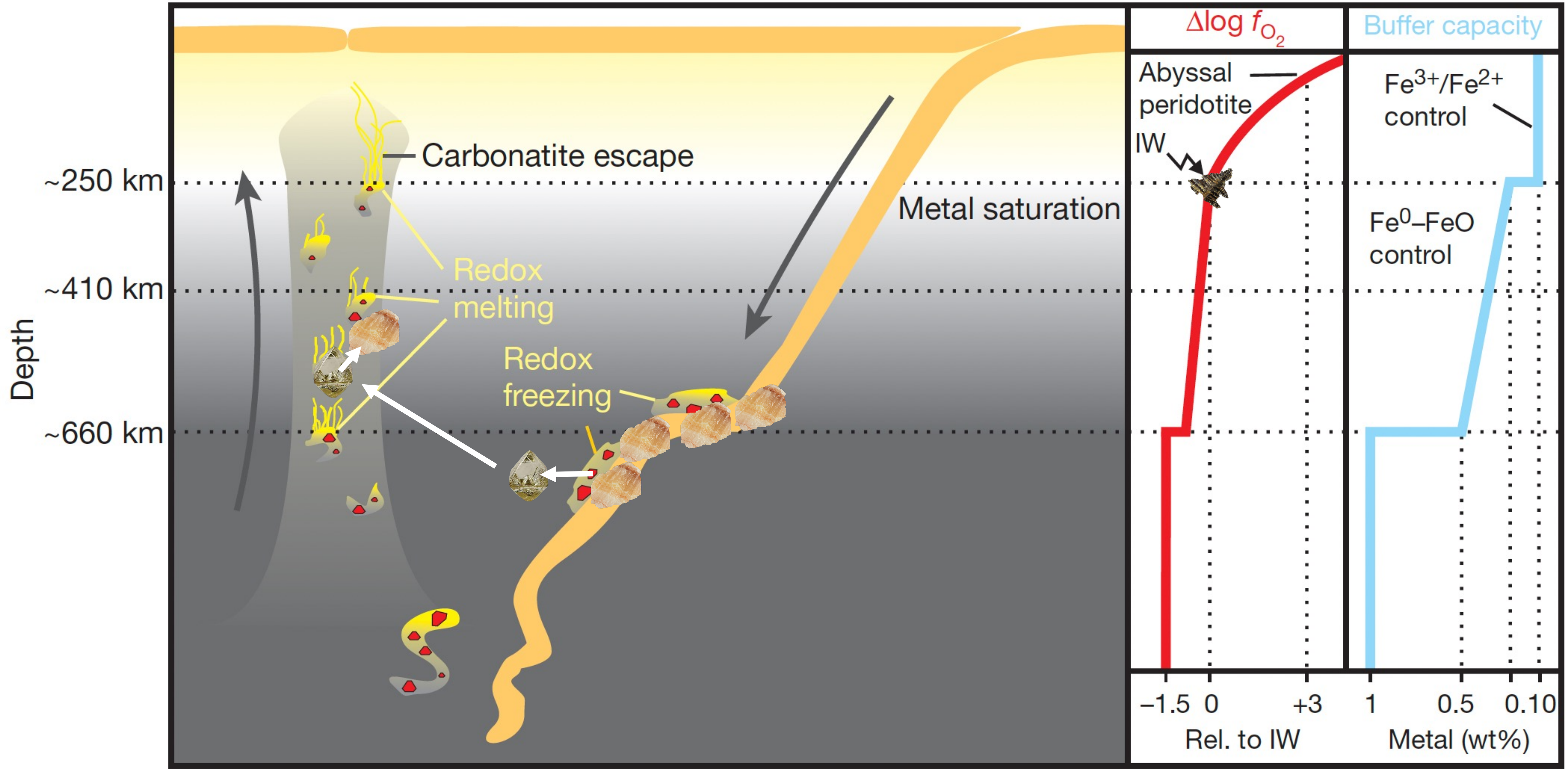
- Reduction of carbonatites to diamond
- Immobilization of carbonatite melts

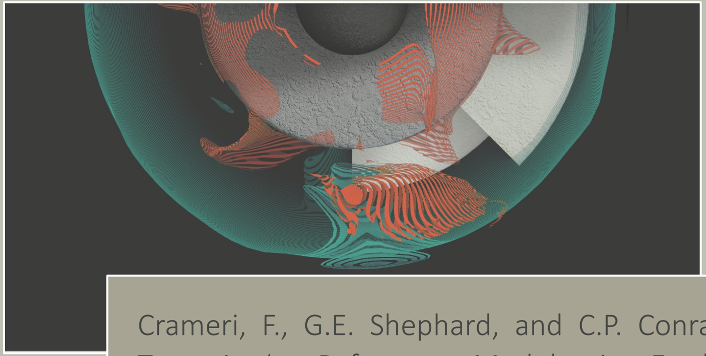


REDOX MELTING

- Oxidation of diamond to carbonatite melts
- Remobilization of carbon
- Potentially controls the onset of ultra-deep melting

Redox freezing and melting





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Stefan Scherrer: BSc Thesis, ZHDK – image Dynamic Mantle

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HRTEM picture of a cementite particle in steel (https://www.tf.unikiel.de/matwis/amat/iss/kap_5/illustr/i5_3_3.html)

Calcite crystals in a marble. XPL image (https://www.alexstrekeisen.it/english/meta/calcite.php)

Iron carbide cementite image (https://en.wikipedia.org/wiki/Cementite#/media/File:Iron_carbide.jpg)