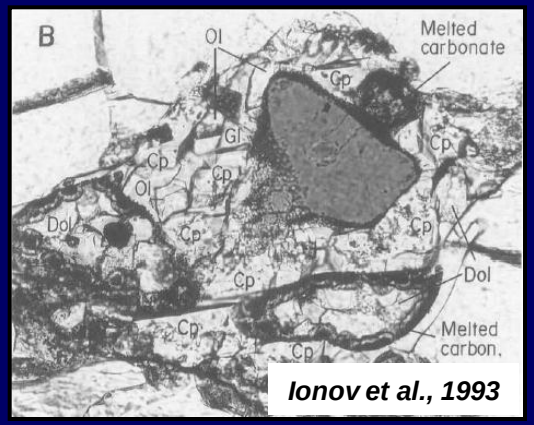
The stability of carbonate bearing minerals and melts with respect to diamond in the mantle

Dan Frost and Vincenzo Stagno

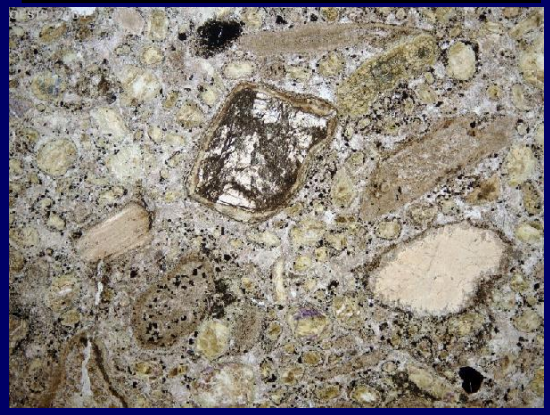
C
Graphite/Diamond

$+O_2=$

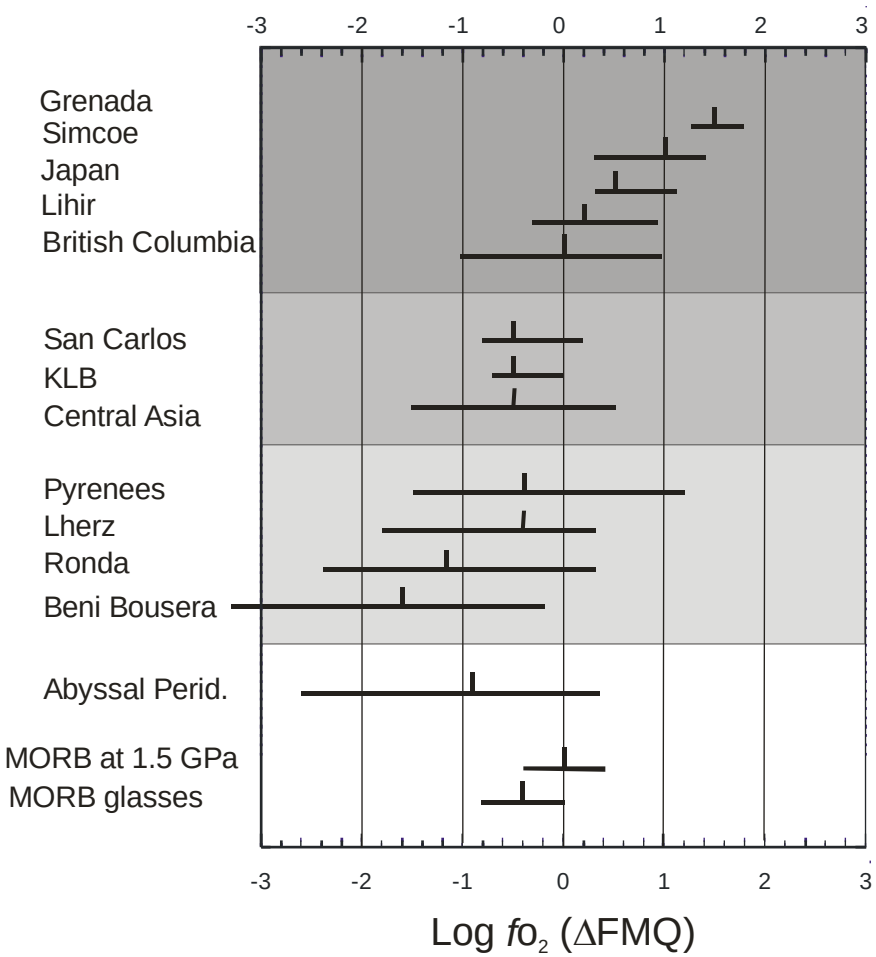
$(Mg,Ca)CO_3$
Carbonatite



Ionov et al., 1993



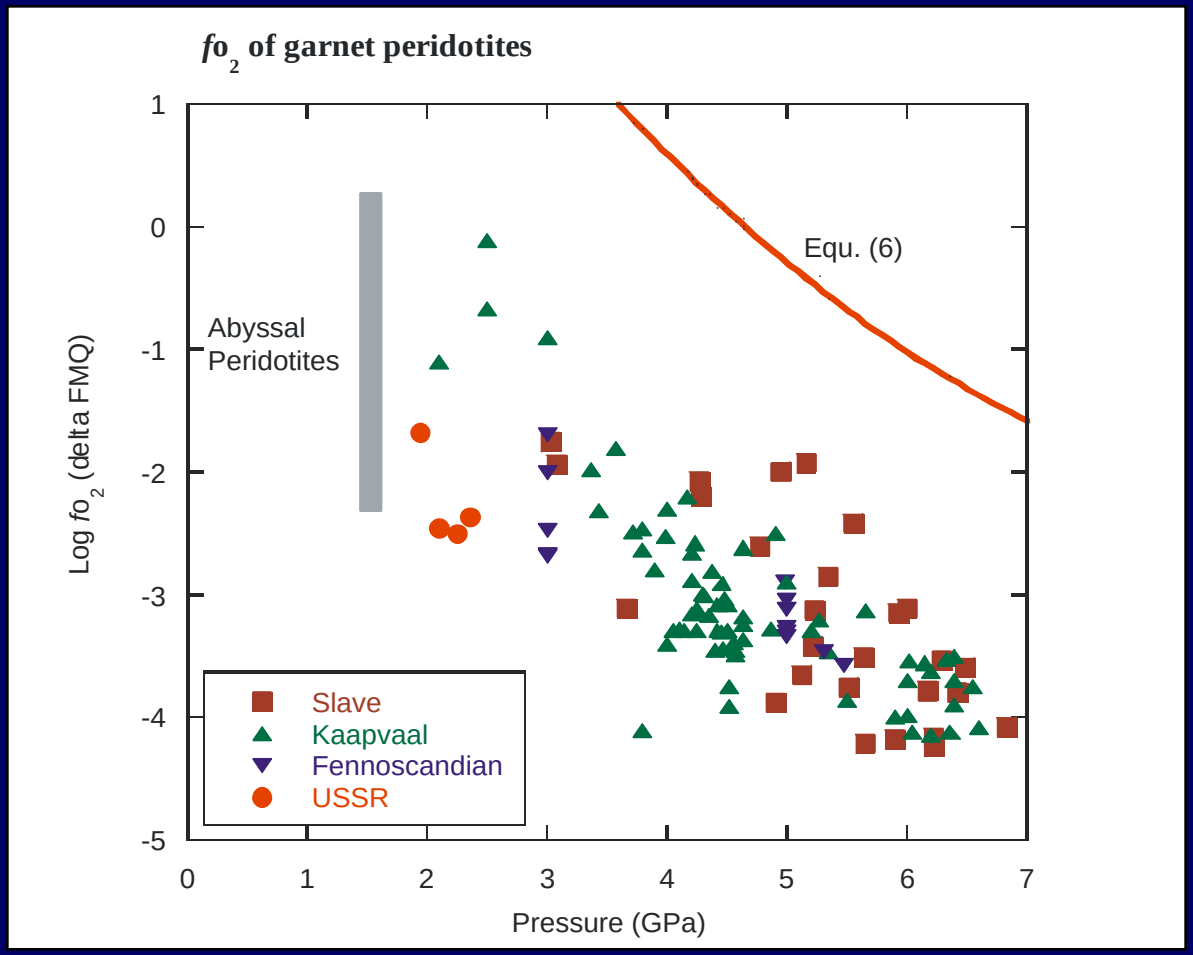
Oxygen fugacity of Spinel Peridotites



$3Fe_2SiO_4$ + **$2O_2$** = **$2Fe^{2+}Fe^{3+}{}_2O_4$** + **$3SiO_2$**

fayalite *magnetite* ***quartz***

Oxygen Fugacity of the Deep Mantle



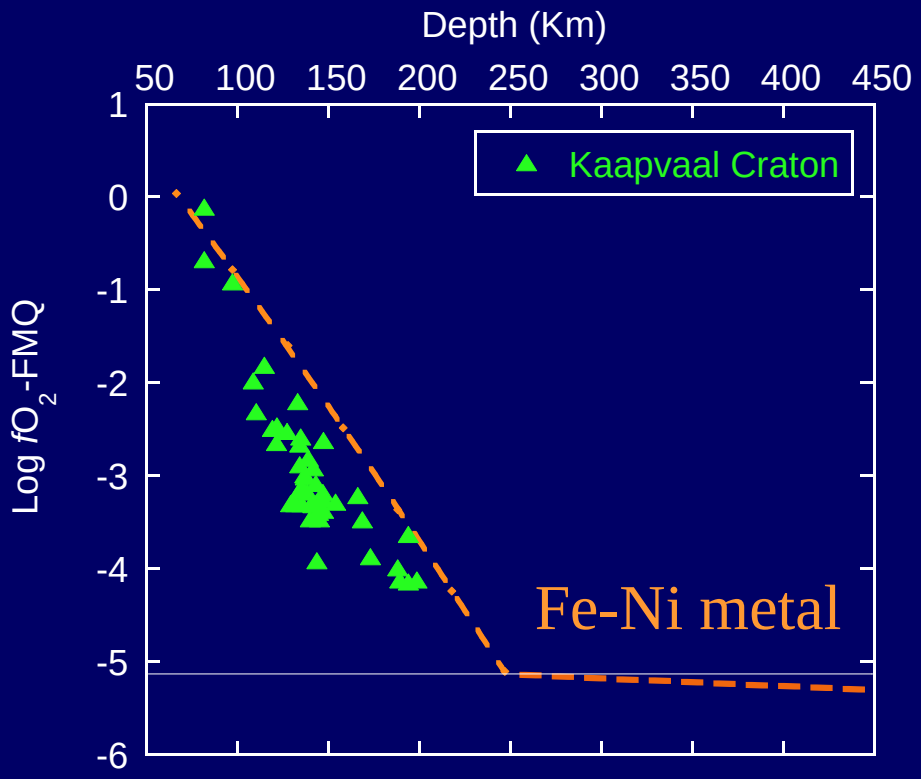
Woodland & Koch 2003
McCammon & Frost 2008

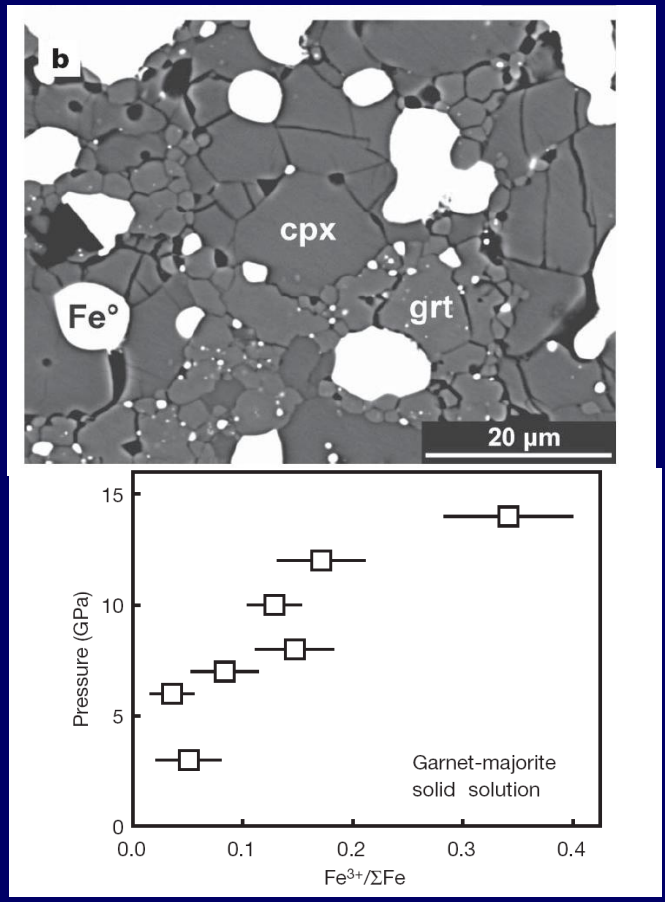
$$\underset{\text{olivine}}{4Fe_2SiO_4} + \underset{\text{opx}}{2FeSiO_3}+O_2 = \underset{\text{garnet}}{2\,Fe_3Fe_2^{3+}Si_3O_{12}} \quad \Delta=-8.6\text{cm}^3/\text{mol}$$

$$\log fo_2 = \frac{-\Delta G^{o}(6)}{\ln(10)RT} + 2\log a^{Gt}_{Fe_3Fe_2Si_3O_{12}} - 2\log a^{Opx}_{FeSiO_3} - 4\log a^{olivine}_{Fe_2SiO_4}$$

Gudmundsson & Wood 1995

Oxygen Fugacity of the Deep Mantle





Rohrbach et al. 2007

$$4Fe_2SiO_4 + 2FeSiO_3 + O_2 = 2Fe_3Fe_2^{3+}Si_3O_{12} \quad \Delta = -8.6 cm^3/mol$$

olivine opx garnet

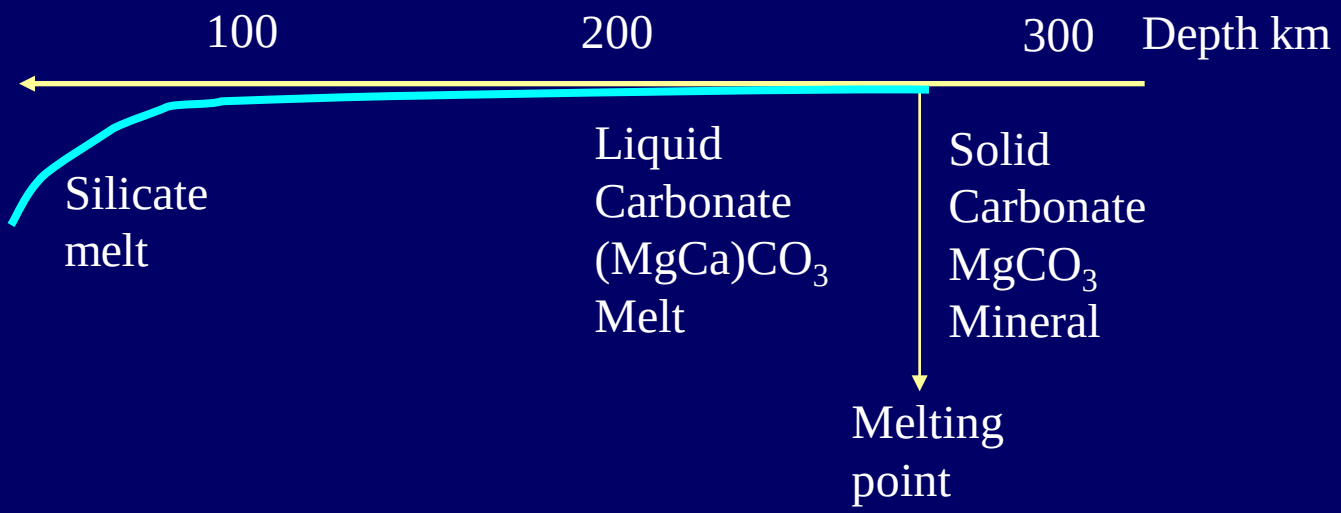
Carbonate Stability as a function of fo_2

- $MgSiO_3$ + $MgCO_3$ = Mg_2SiO_4 + C + O_2
  enstatite magnesite olivine graphite/diamond (EMOG/D)

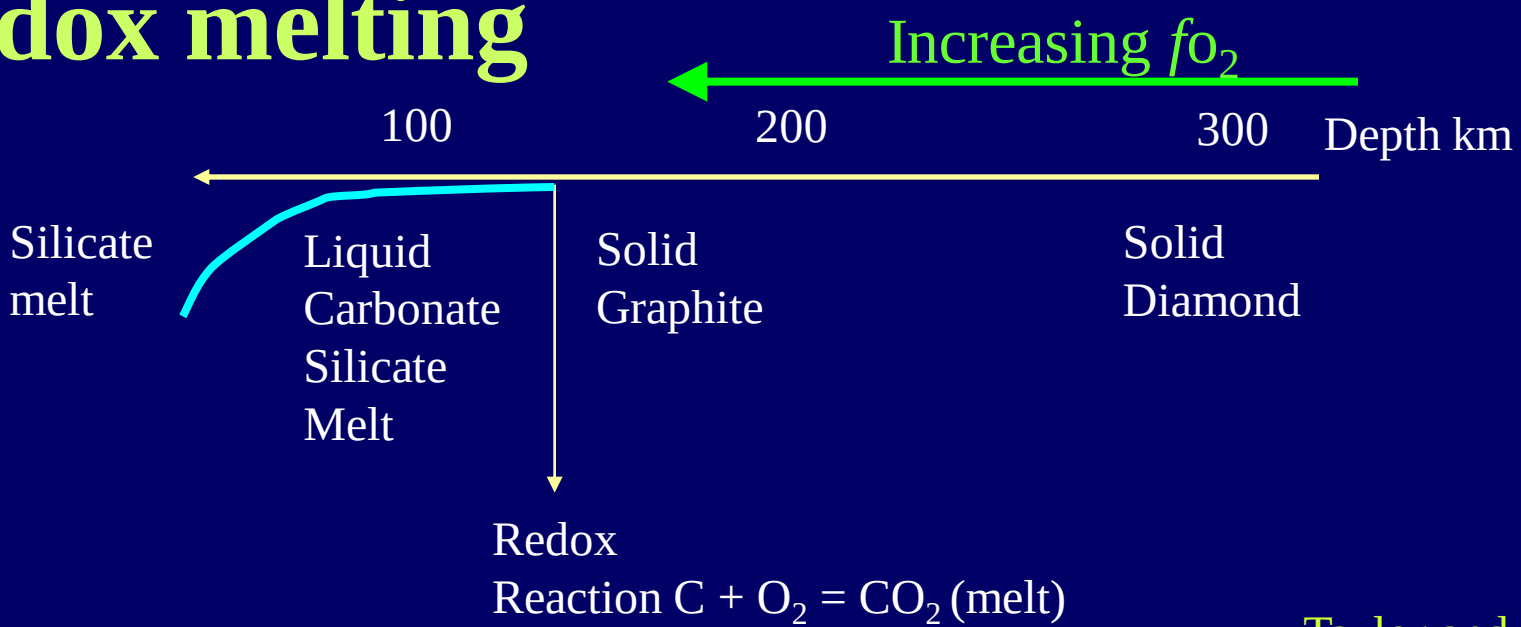
$$K_{P,T} = \frac{a_c a^{olivine}_{Mg_2SiO_4} fo_2}{a^{enstatite}_{MgSiO_3} a^{magnesite}_{MgCO_3}}$$

- $2Mg_2Si_2O_6$ + $CaMg(CO_3)_2$ = $2Mg_2SiO_4$ + $CaMgSi_2O_6$ + 2C + $2O_2$
  enstatite melt olivine diopside graphite/diamond

Carbonate melting



Redox melting

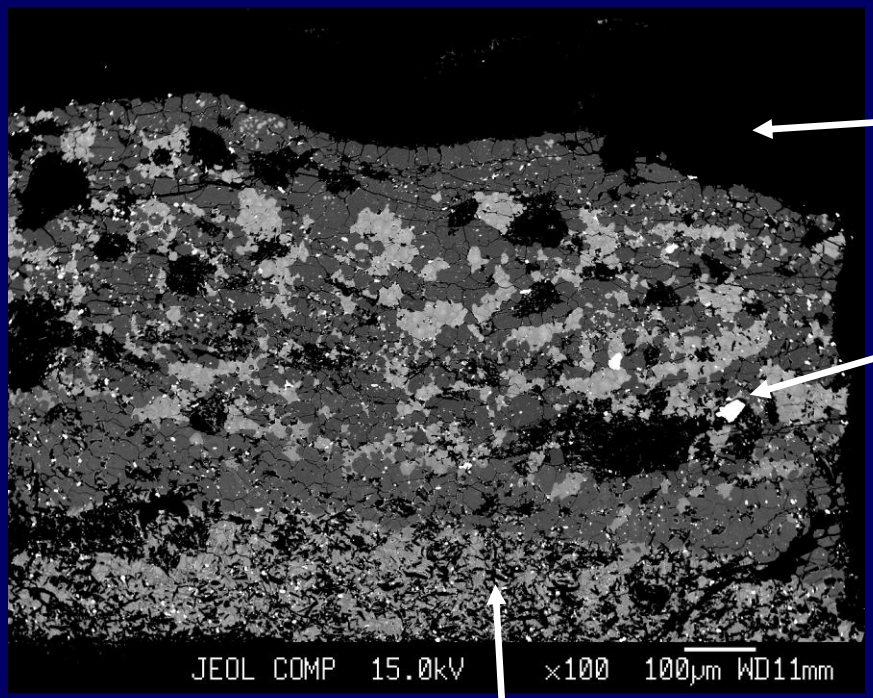


Taylor and Green 1988

Multianvil Run Products

$2(Mg,F)_2Si_2O_6$ + $CaMg(CO_3)_2$ = $2(Mg,Fe)_2SiO_4$ + $CaMgSi_2O_6$ + $2C$ + $2O_2$

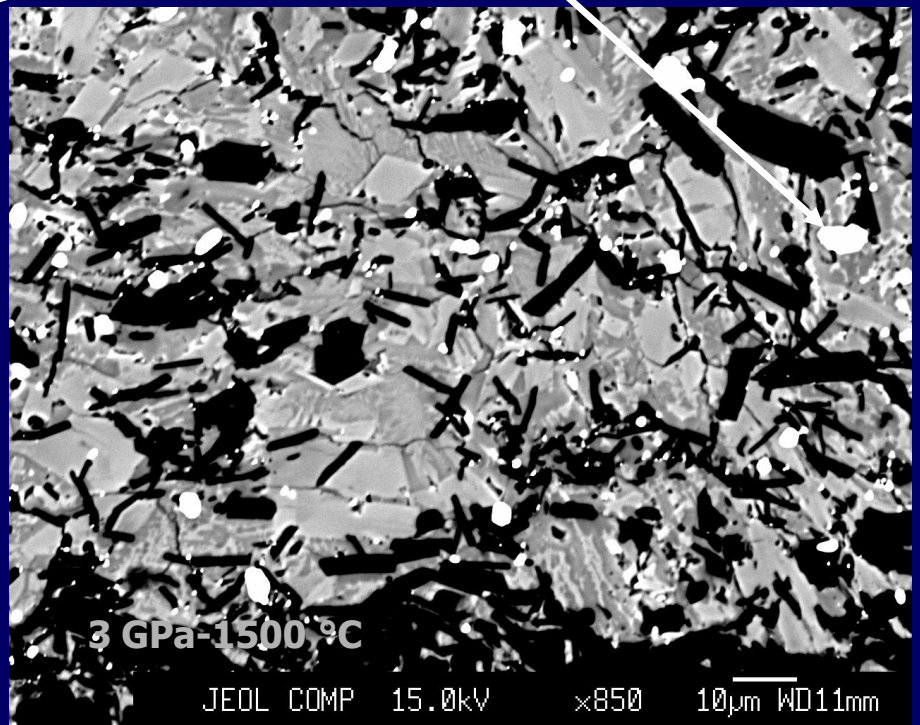
enstatite melt olivine diopside graphite/diamond



Graphite capsule

Fe-Ir Alloy

Carbonate melt



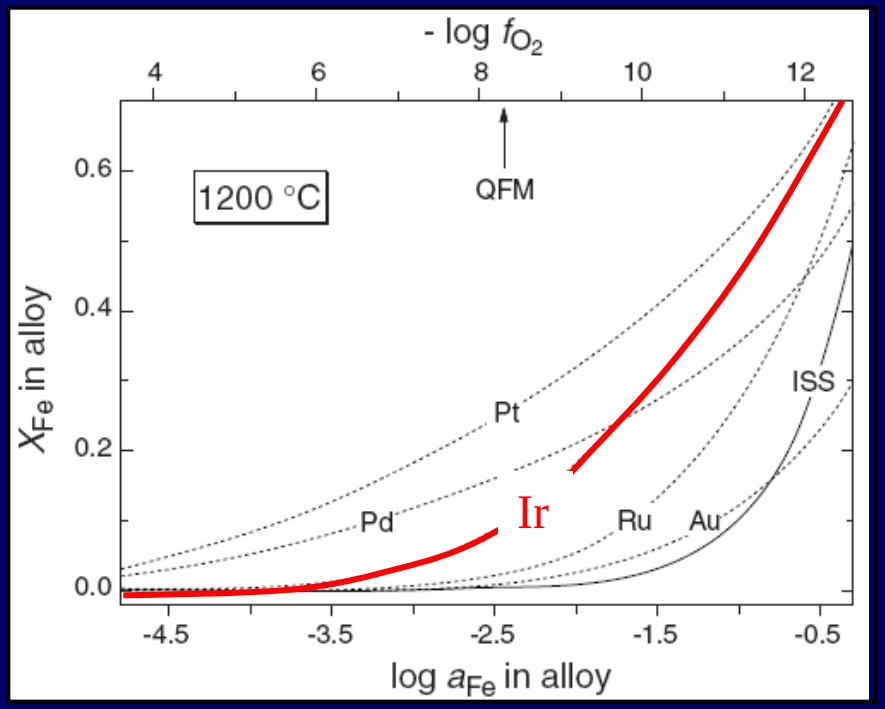
Experimental Measurement of fo_2

Fe-Ir Alloy

$2Fe_2SiO_4$ = $2FeSiO_3$ + $2Fe$ + O_2

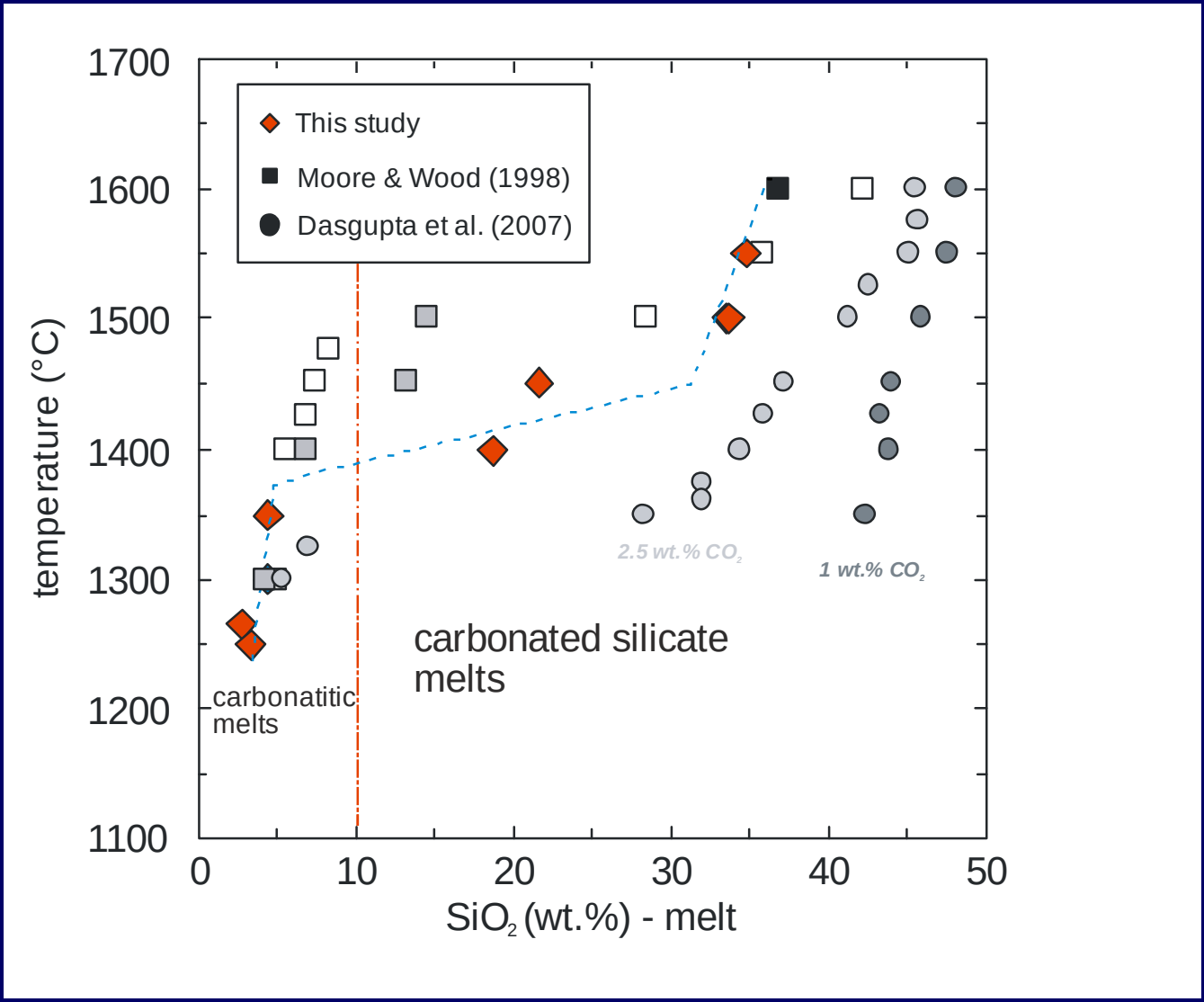
olivine *enstatite* *metal*

$$\log fo_2 = \frac{-\Delta G^{o}}{\ln(10)RT} + 2\log a^{Ol}_{Fe_2SiO_4} - 2\log a^{enstatite}_{FeSiO_3} - 2\log a^{metal}_{Fe}$$

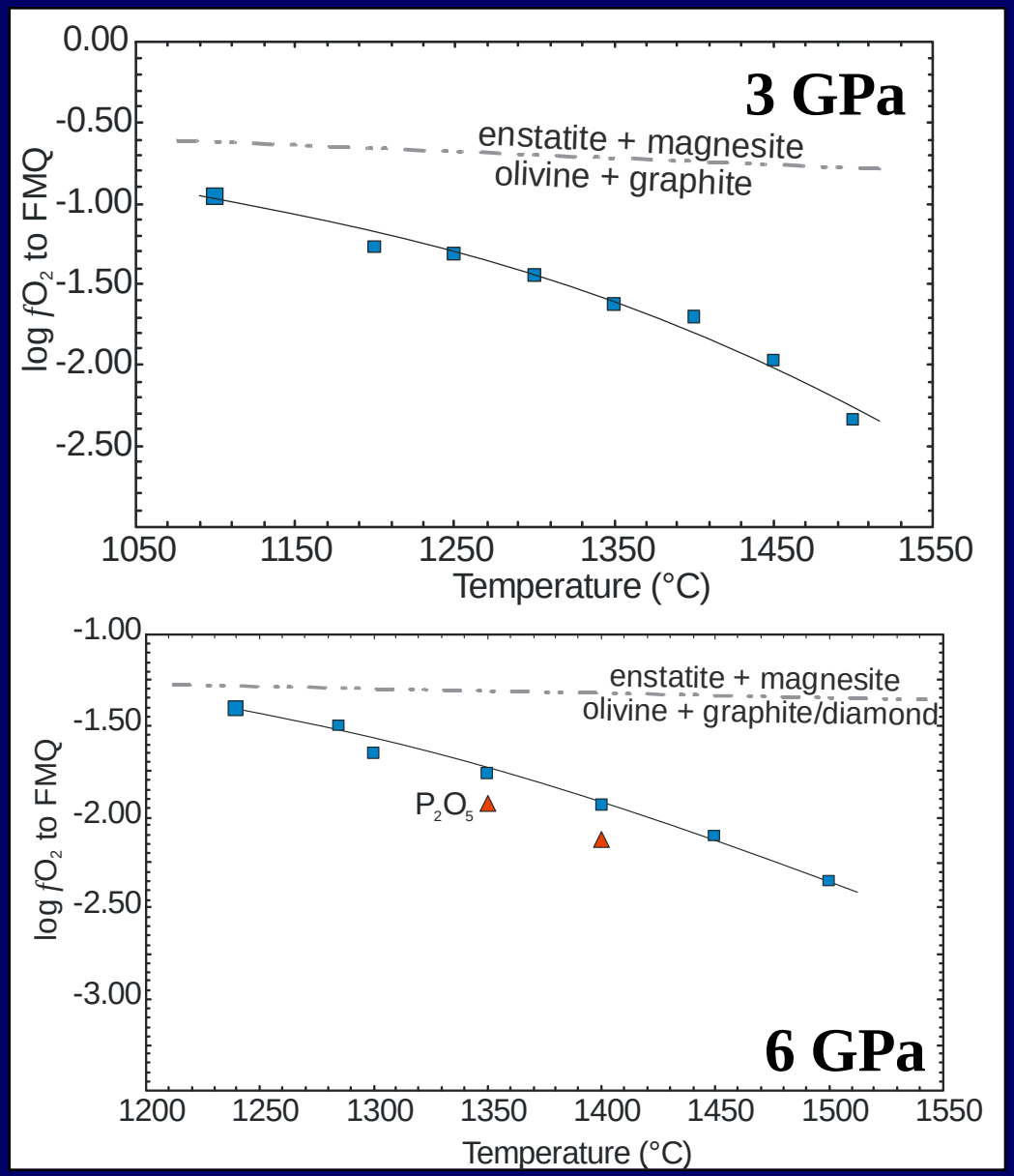


Borisov & Palme, 2000

Carbonate-Silicate Melts Evolution



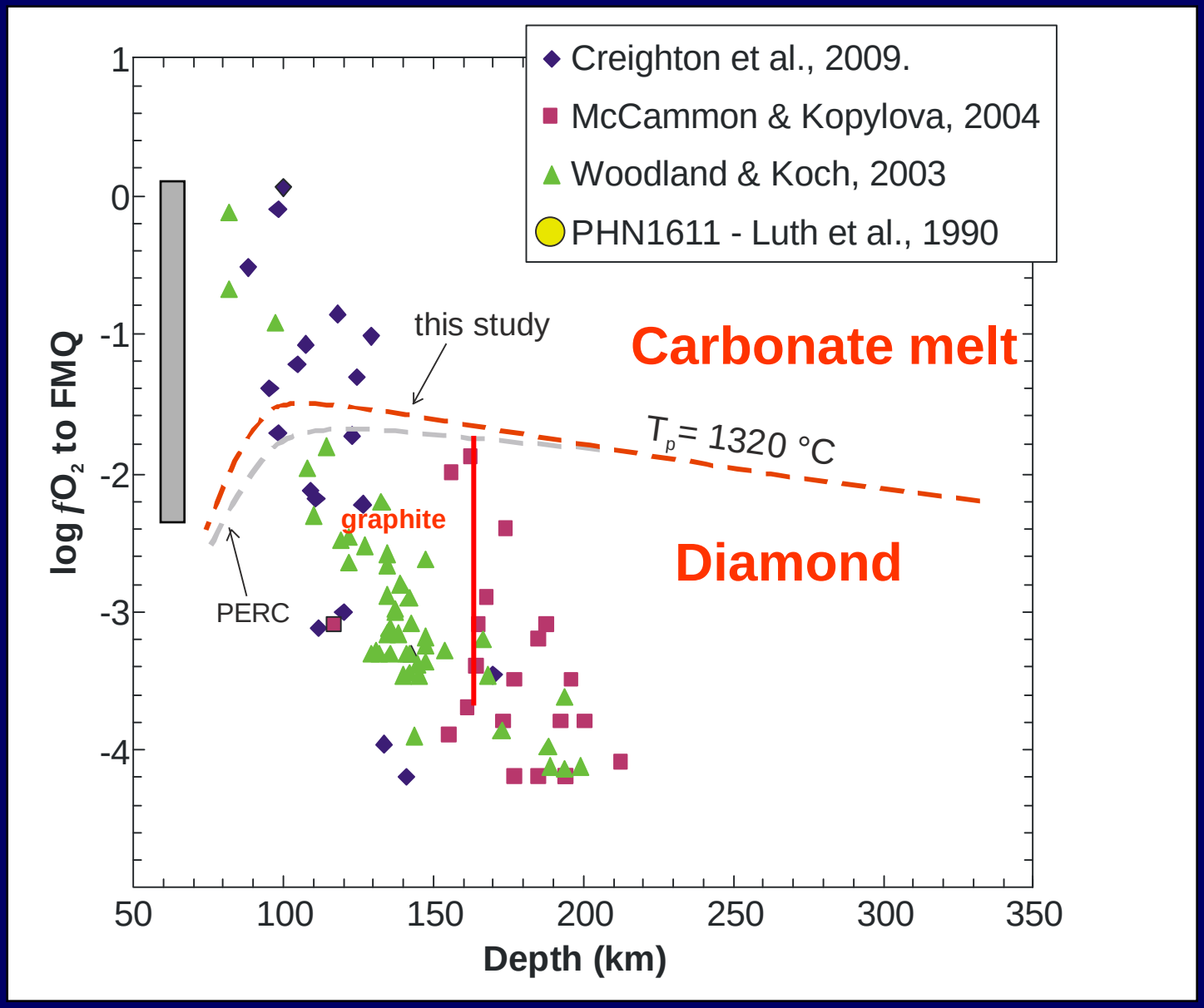
fo_2 of carbon-carbonate melt



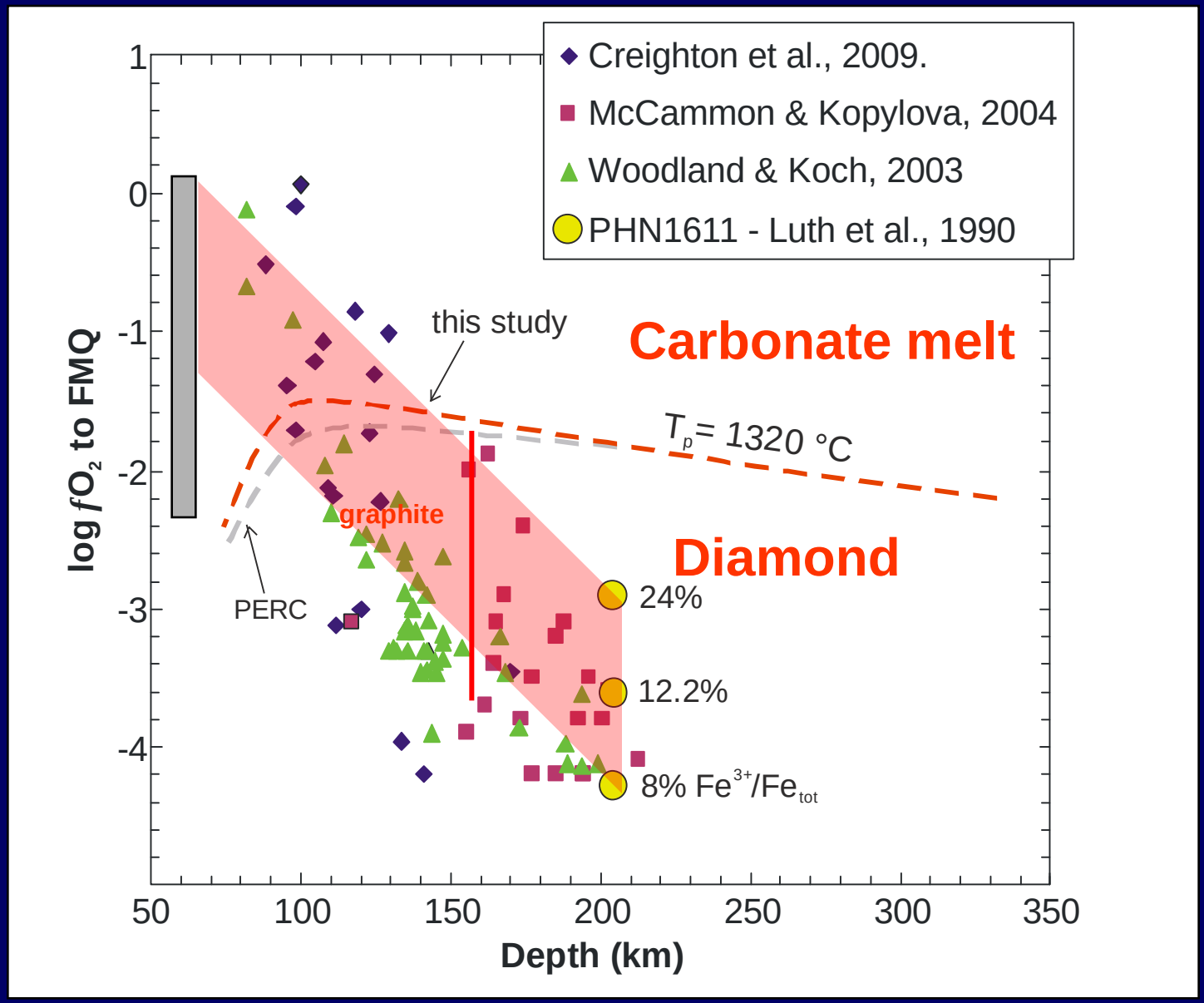
C + O_2 = CO_2
(grph/dia) (melt)

$$\log fo_2 = \frac{\Delta H^o + T\Delta S^o + P(V-1)}{\ln(10)RT} + \log X_{CO_2}$$

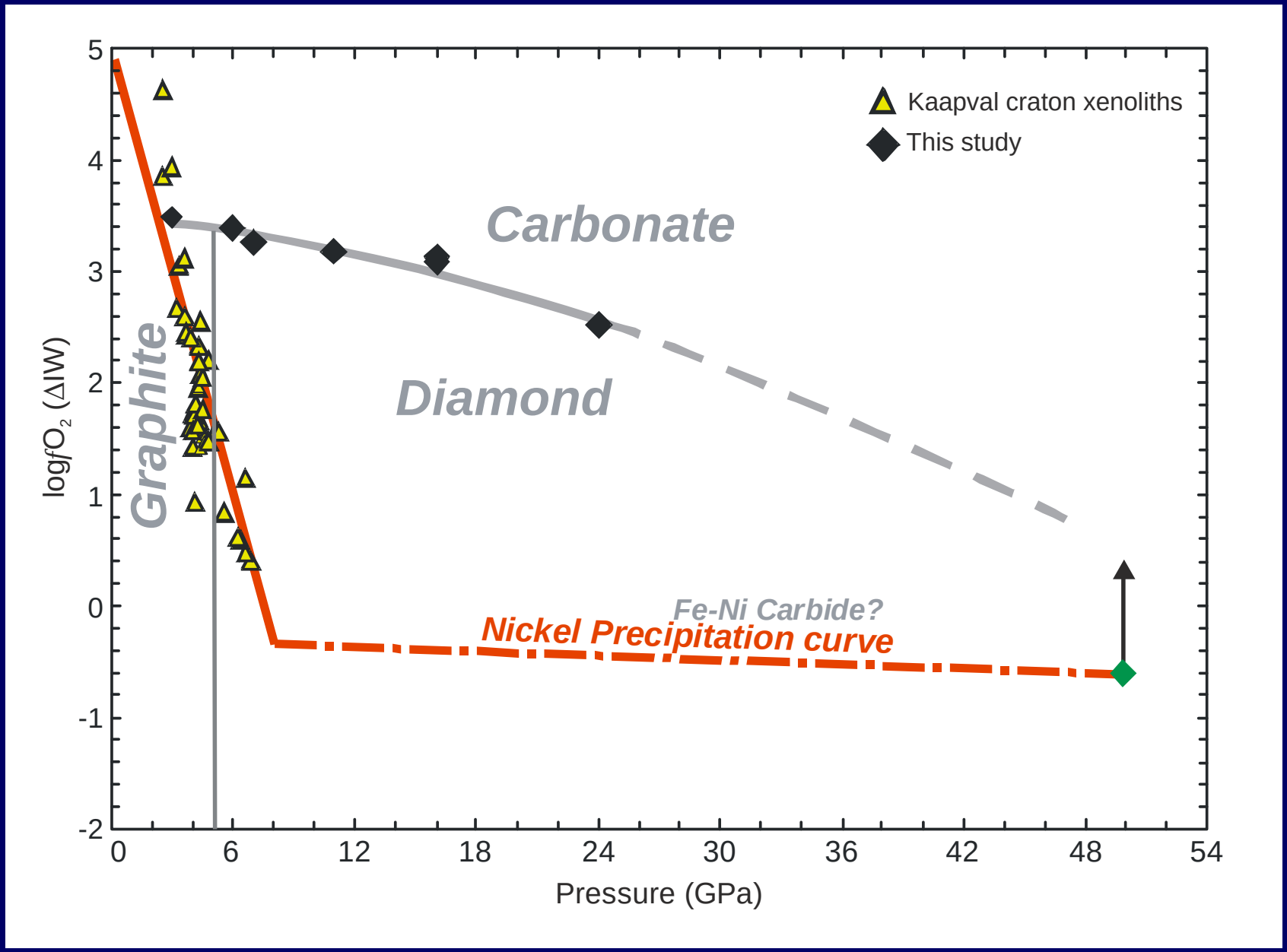
Onset of adiabatic melting



Onset of adiabatic melting



Carbonate Stability in the Mantle



Conclusions

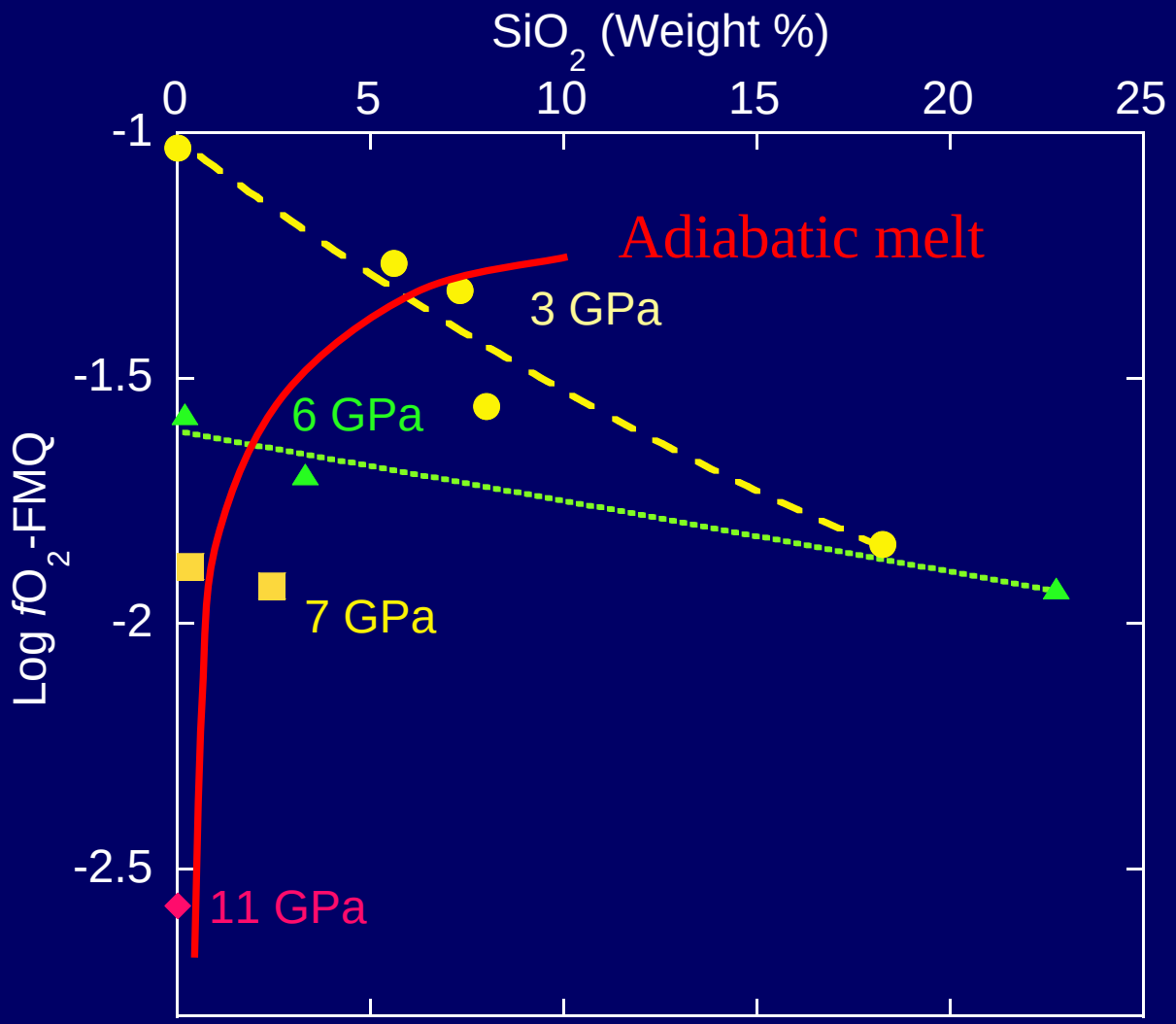
Carbonate bearing melts are unstable with respect to the oxygen fugacity of average mantle deeper than 150 km

Deep mantle melting could only be caused by carbonates if the region had an unusually high $Fe^{3+}/\sum Fe$ ratio (kimberlites).

The negative slope of the carbonate/diamond buffer with depth may result in carbonates being the stable host of C in the deep lower mantle but at pressure >50GPa (1200 km)

Opposite possess of carbonate reduction by Fe^{2+} oxidation may occur with increasing pressure in subduction zone.

Effect of Pressure & SiO_2 content on fO_2



Oxygen Fugacity

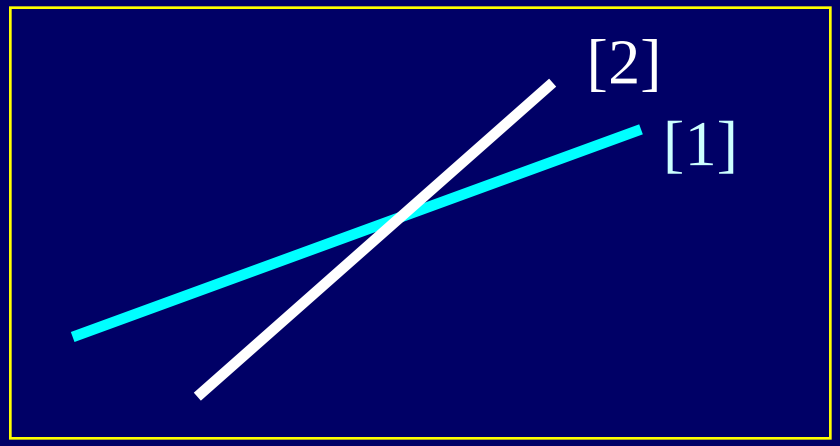
[1] **$Fe^{2+}Fe^{3+}_2O_4$ + $3FeSiO_3$ = $3Fe_2SiO_4$ + O_2**
spinel *enstatite* *olivine*

$$K_{P,T} = \frac{a_{ol}^3 \, fo_2}{a_{opx}^3 a_{sp}}$$

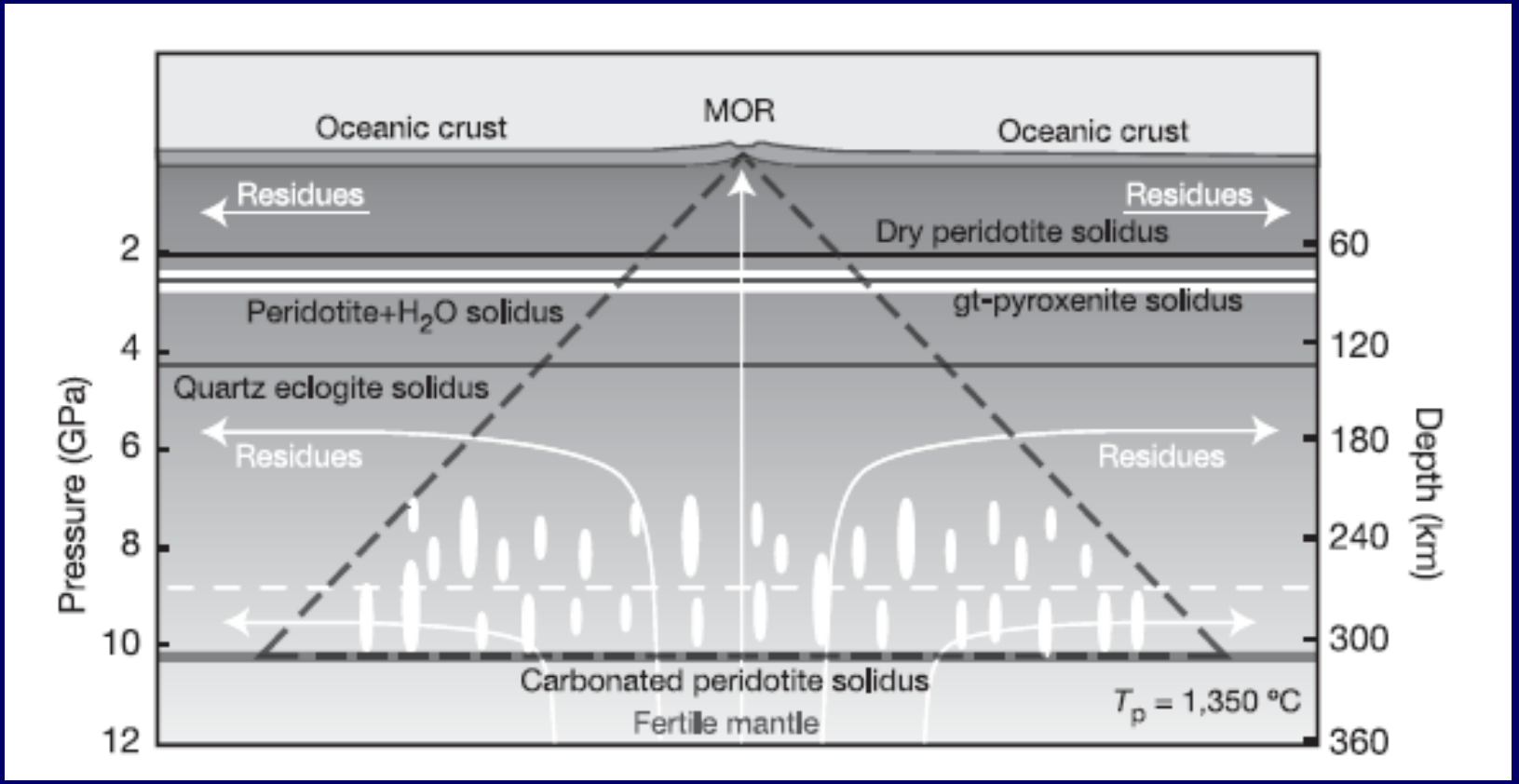
[2] **C + O_2 = CO_2**
graphite *gas*

$$K_{P,T} = \frac{CO_2}{a_{graph} \, fo_2}$$

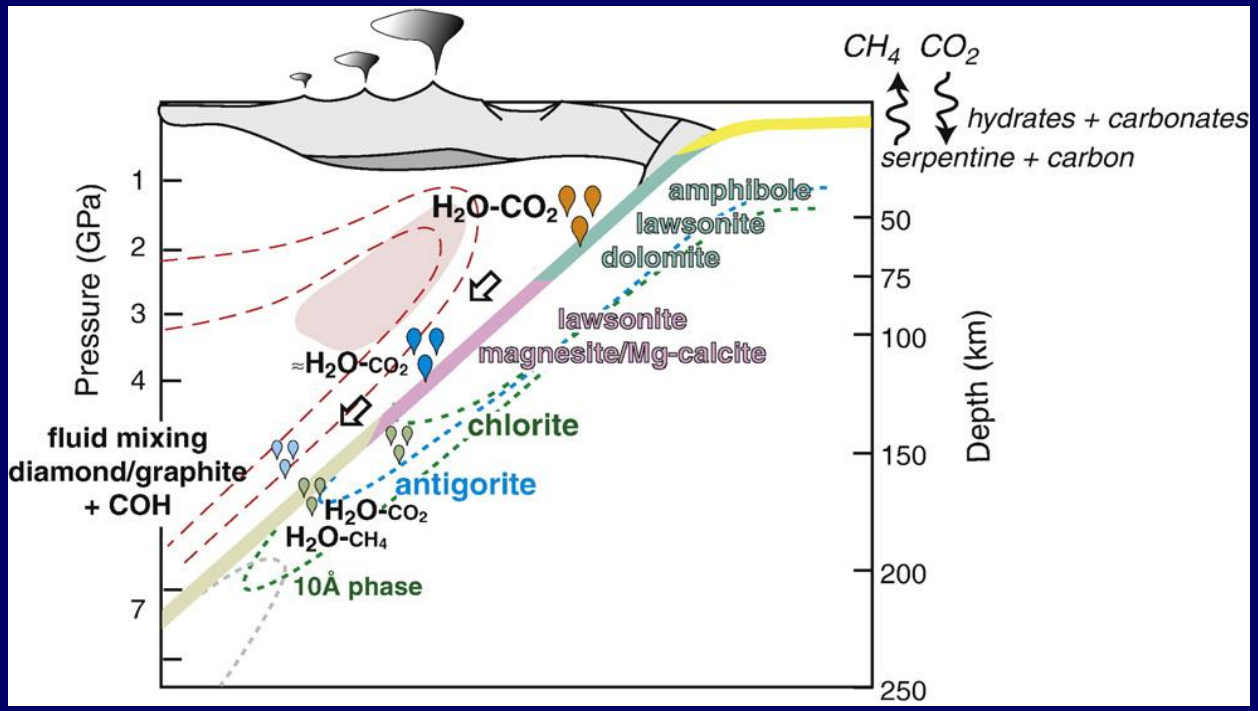
$Fe^{2+}Fe^{3+}_2O_4$ + $3FeSiO_3$ + C = $3Fe_2SiO_4$ + CO_2
spinel *enstatite* *graphite* *olivine* *gas*



Deep Melting of Carbonates



Dasgupta & Hirschmann (2006) – Nature 440, 659.



Poli et al. “The transport of carbon and hydrogen in subducted oceanic crust” EPSL 278 (2009) 350