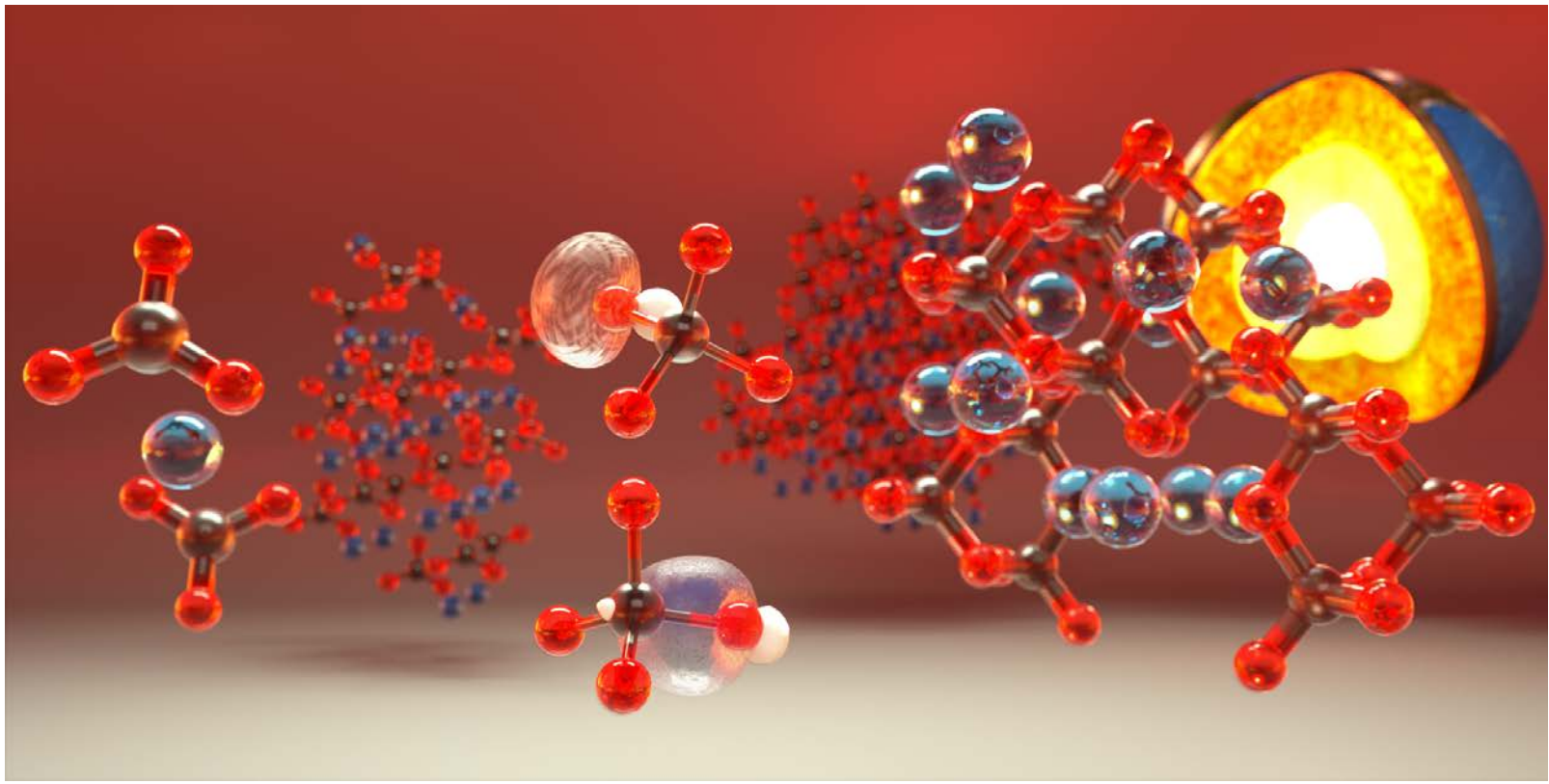
Investigating Carbon-Rich Phases at Mantle Conditions

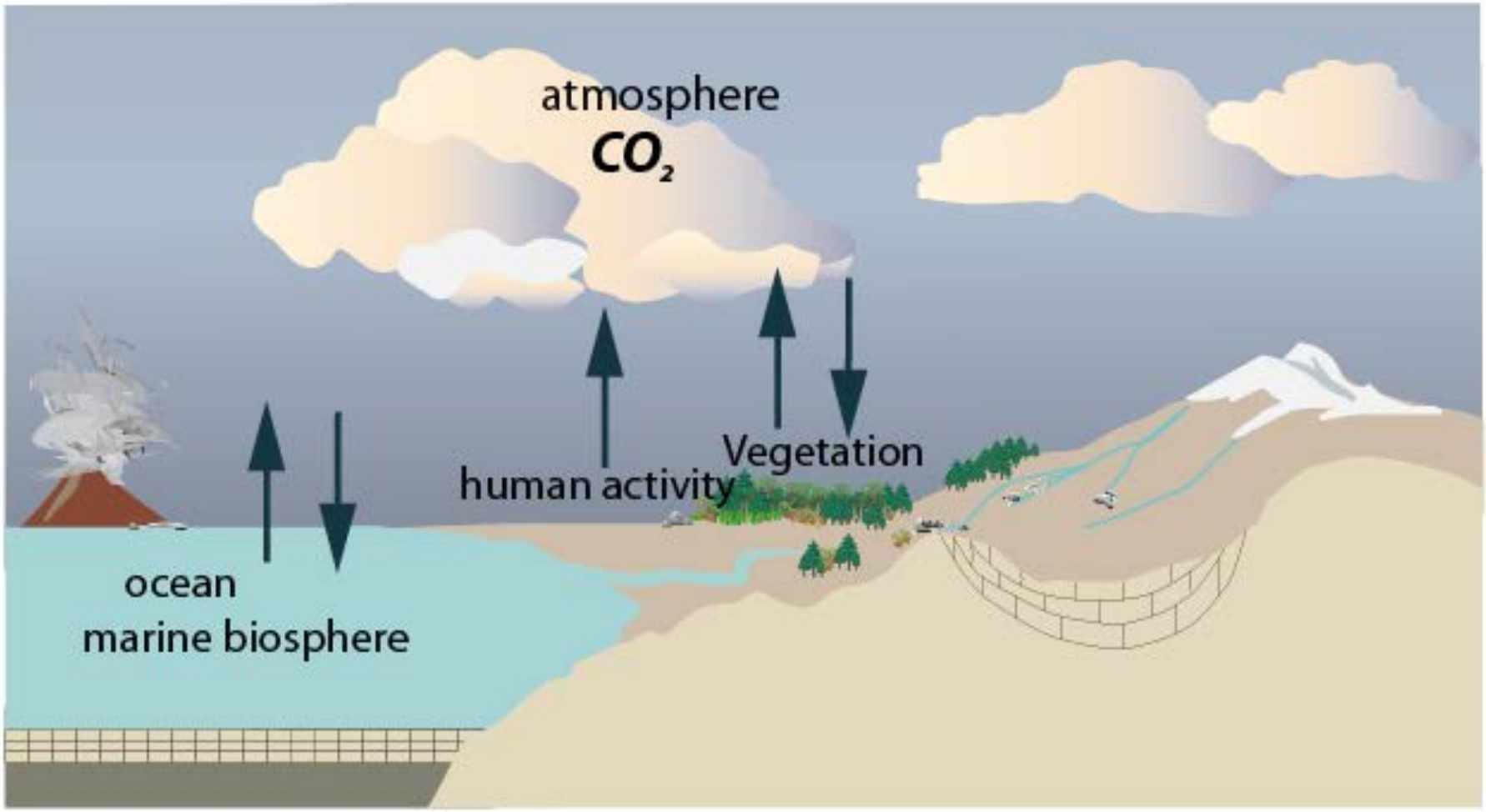
Eglantine Boulard



DEEP CARBON OBSERVATORY

Carbon External Cycle

Time scale : 1 to 10 000 years



Carbon in the Mantle

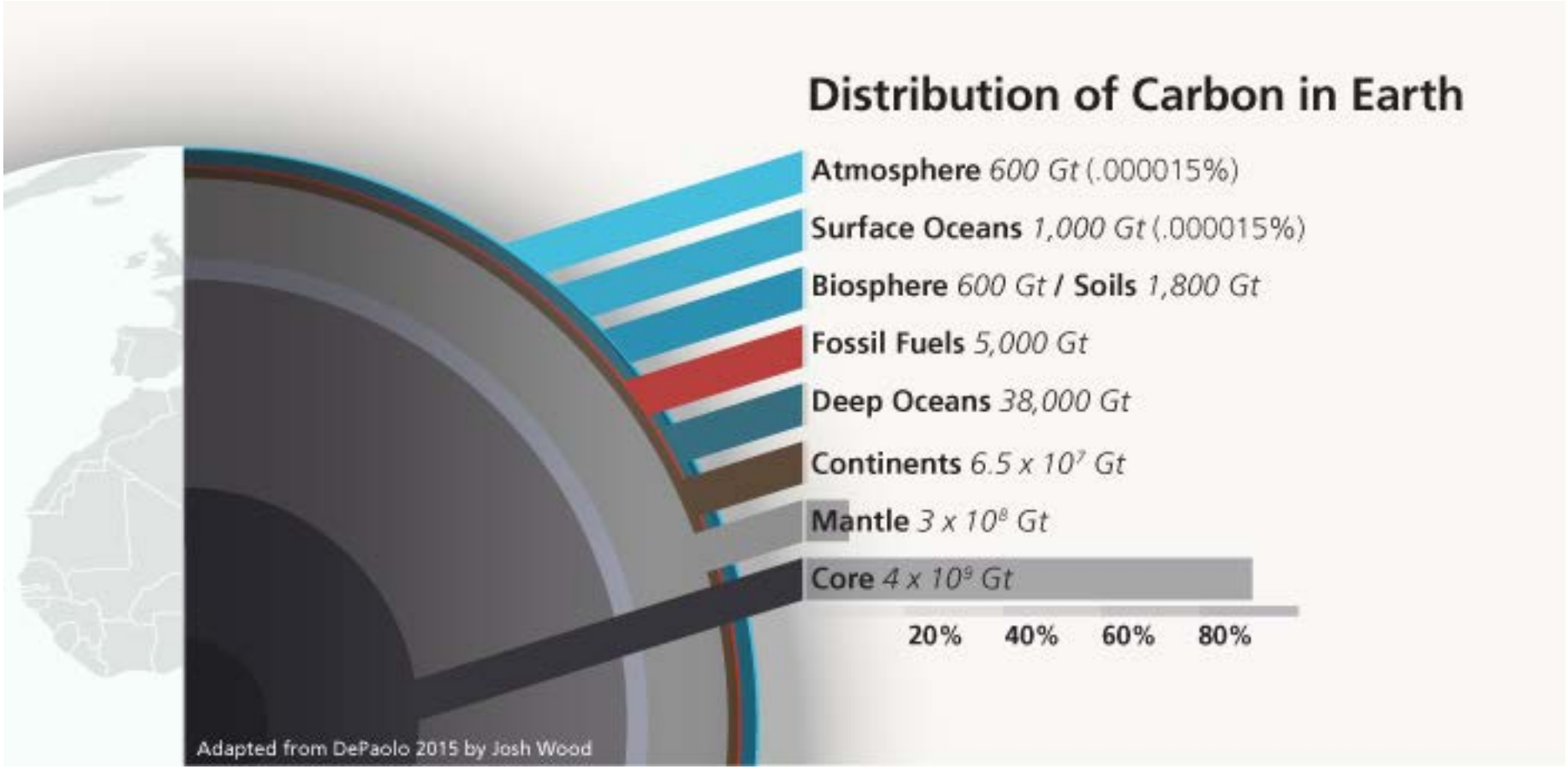
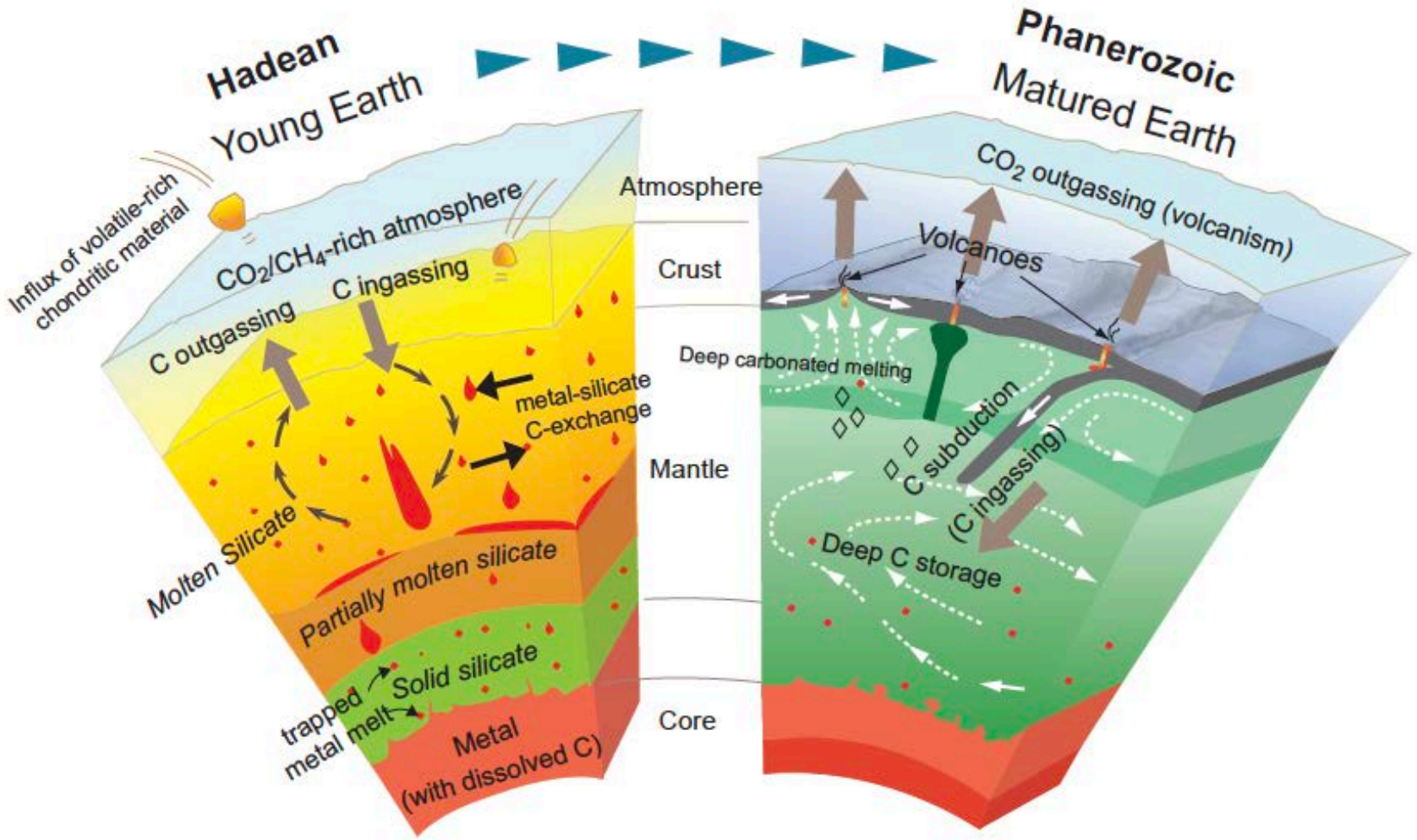


Image credits : Deep Carbon Observatory

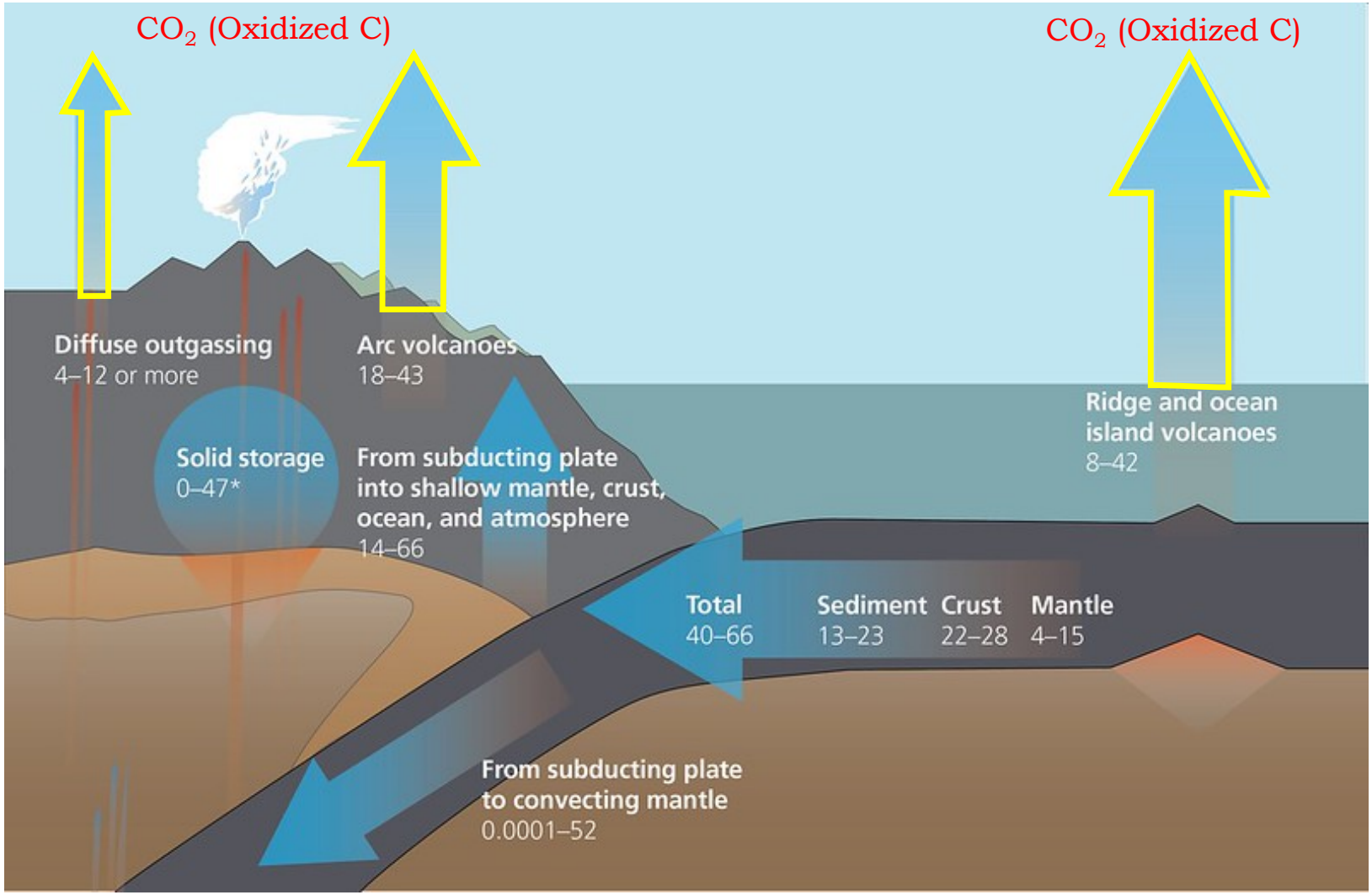
Carbon in the Mantle



Dasgupta, RiMG, 2013

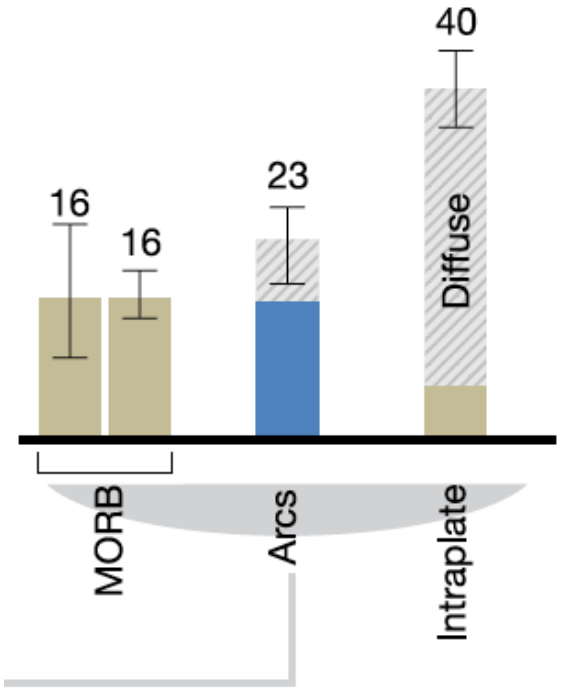
Deep Carbon Cycle

Carbon Fluxes in Mt/ year



Kelemen & Manning, PNAS, 2015
Image credits : Deep Carbon Observatory

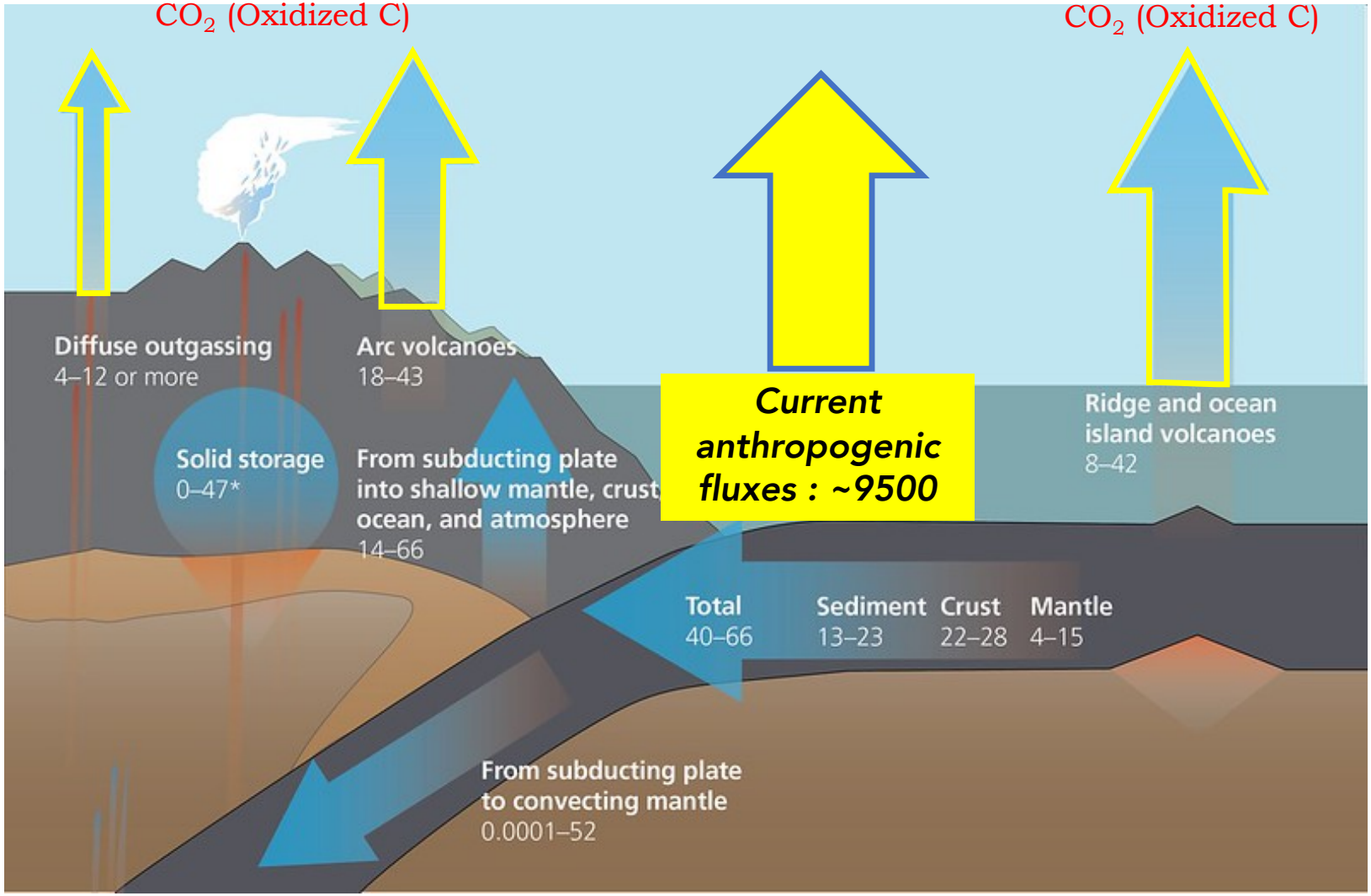
New Insight From Diffuse Carbon Output



Plank & Manning 2019

Deep Carbon Cycle

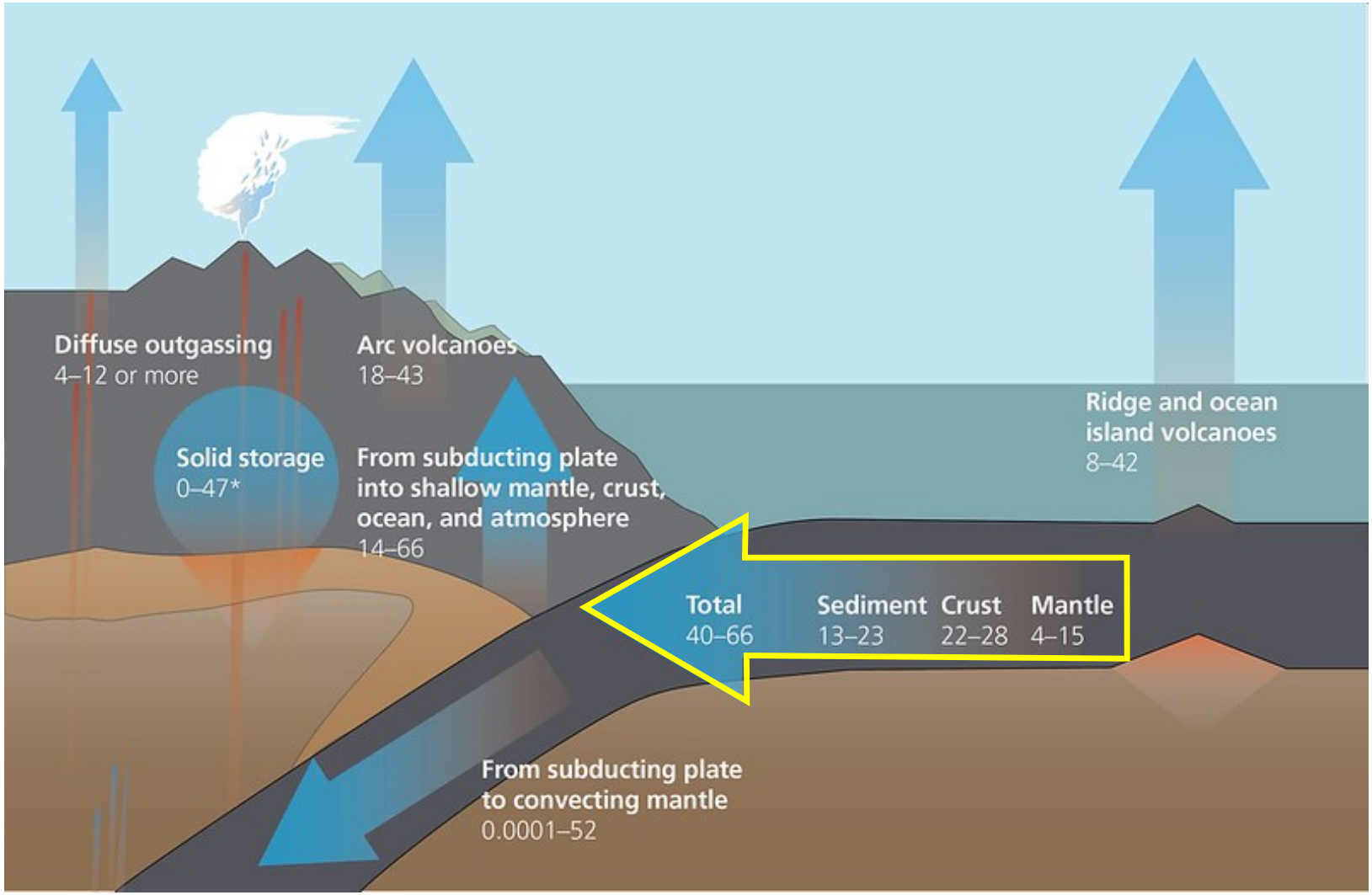
Carbon Fluxes in Mt/ year



Kelemen & Manning, PNAS, 2015
Image credits : Deep Carbon Observatory

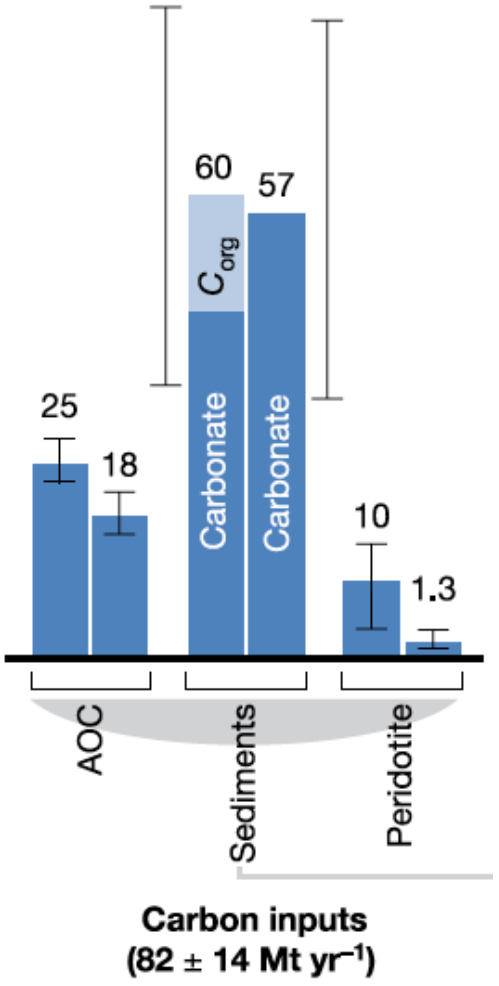
Deep Carbon Cycle

Carbon Fluxes in Mt/ year

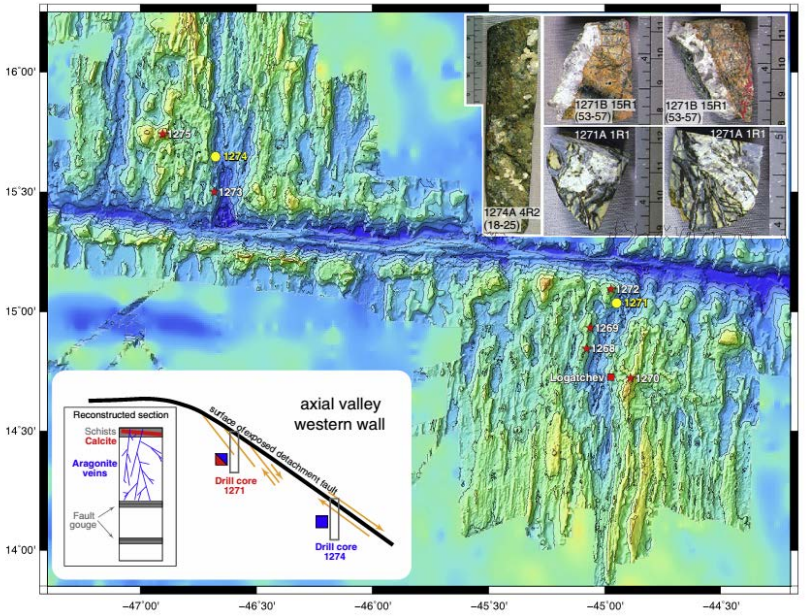


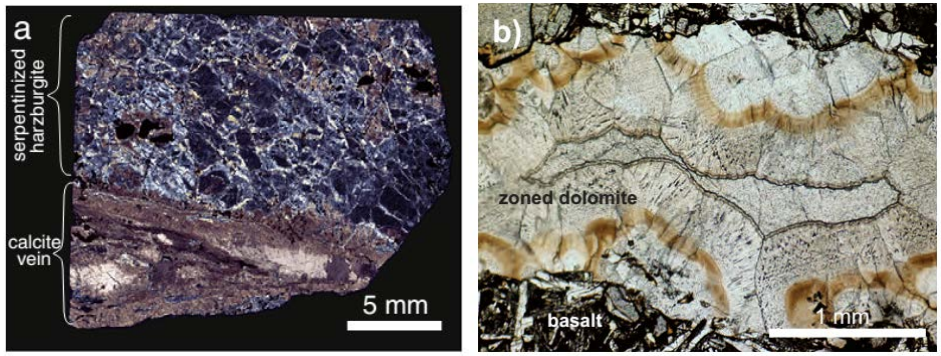
Kelemen & Manning, PNAS, 2015
Image credits : Deep Carbon Observatory

Deep Carbon Cycle



Plank & Manning 2019

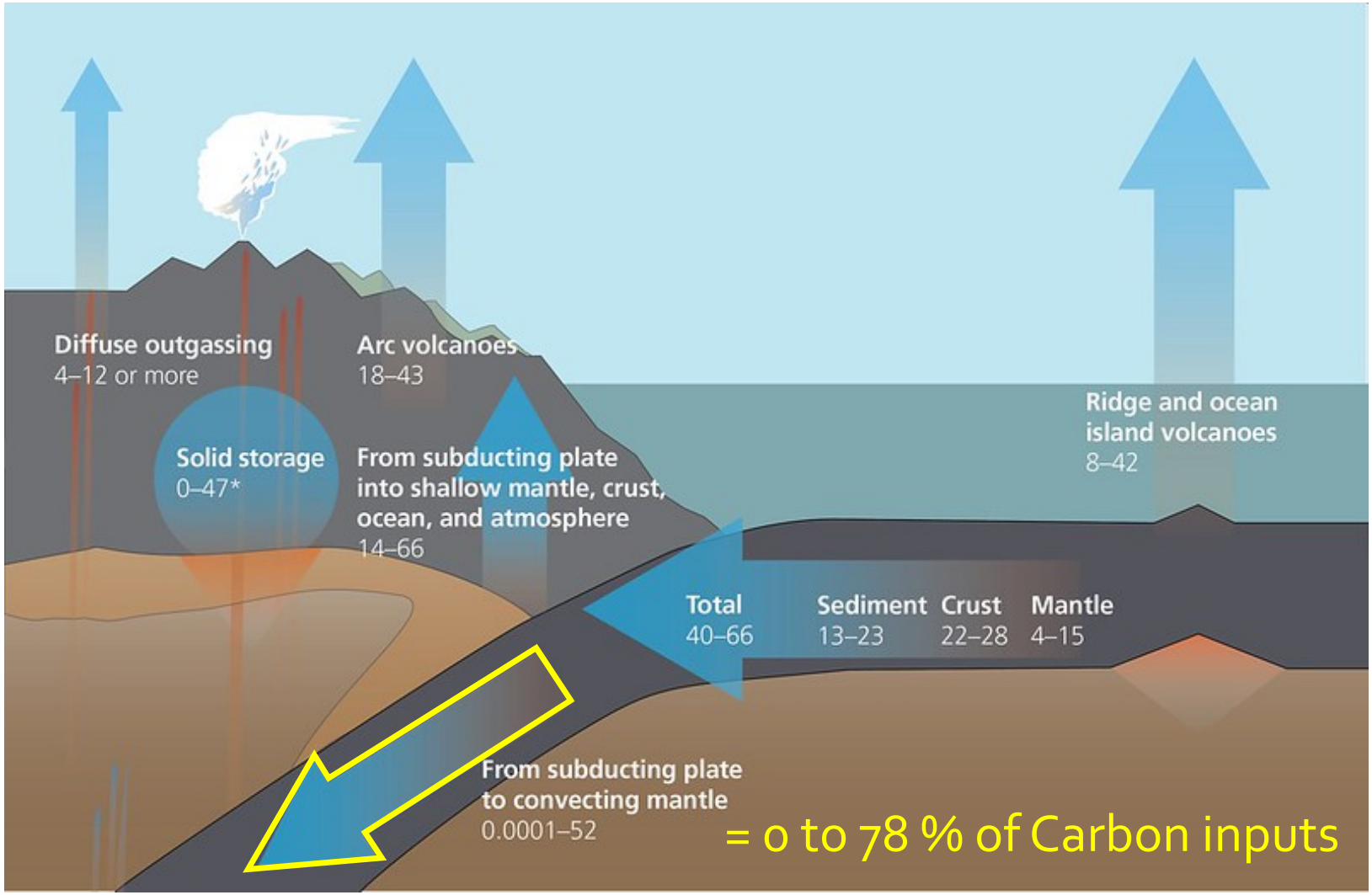




Bach et al., EPSL, 2011

Deep Carbon Cycle

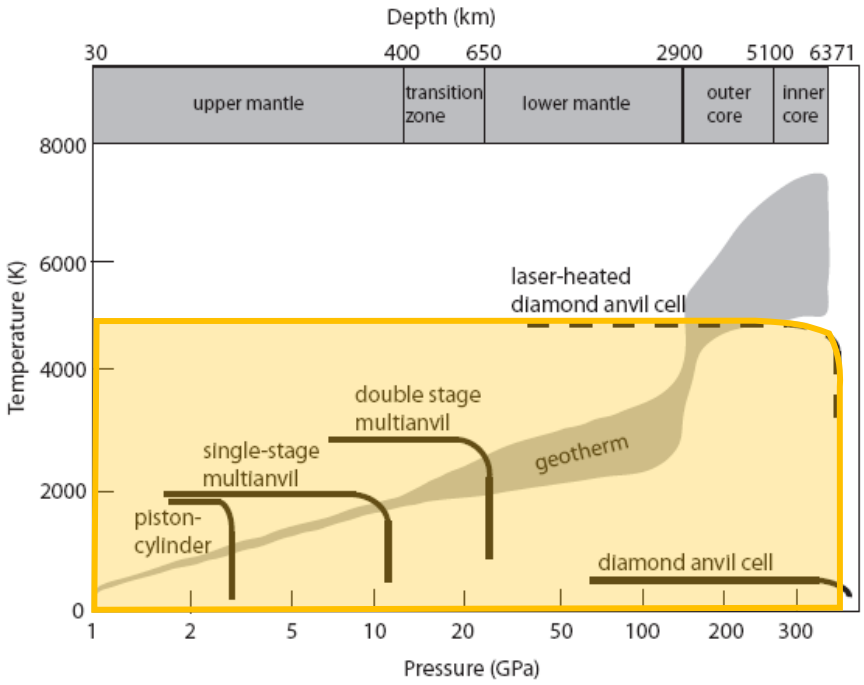
Carbon Fluxes in Mt/ year

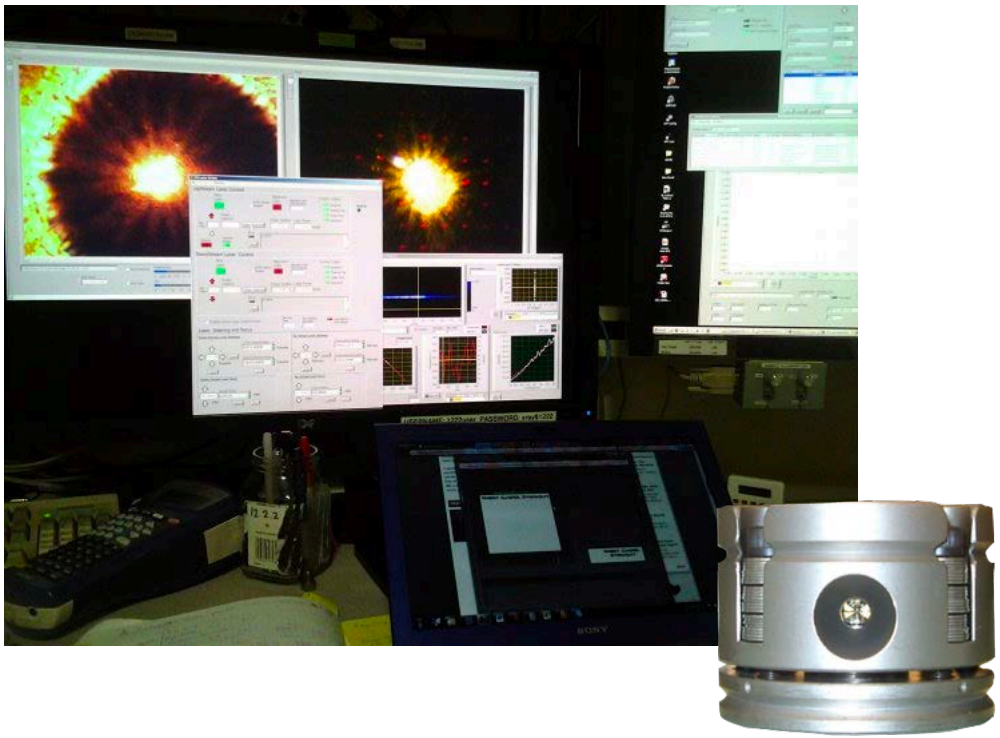


Kelemen & Manning, PNAS, 2015
Image credits : Deep Carbon Observatory

Experimental Approach

❖ Laser Heated Diamond Anvil Cell



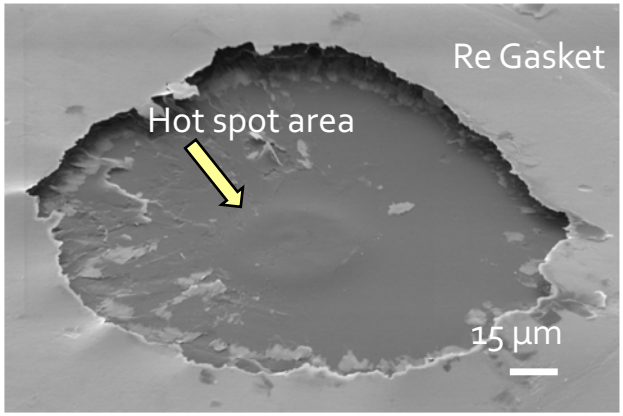


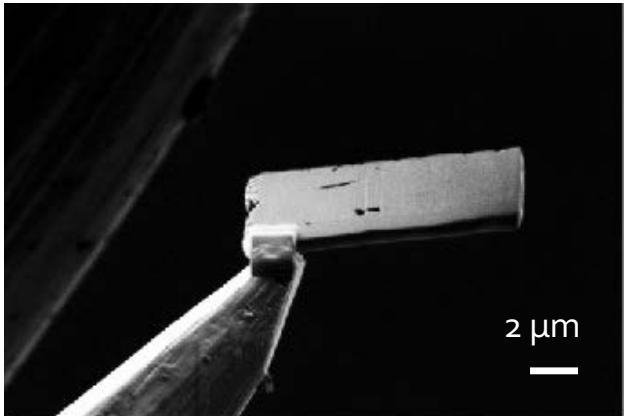
❖ In Situ analyses :

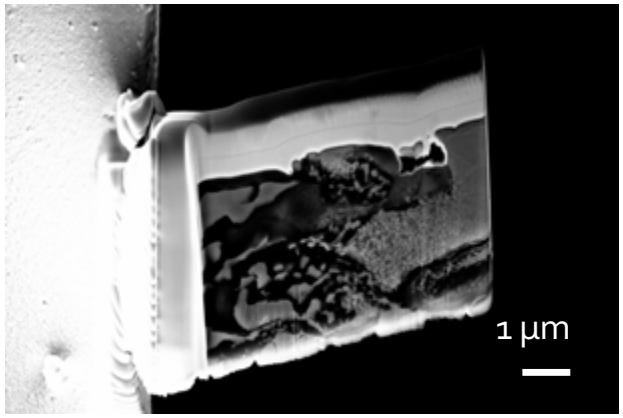
- Phase Identification, Structure Refinements : X-Ray Diffraction
- Bonding within the crystalline structure: IR spectroscopy
- Melt Percolation : X-ray Imaging

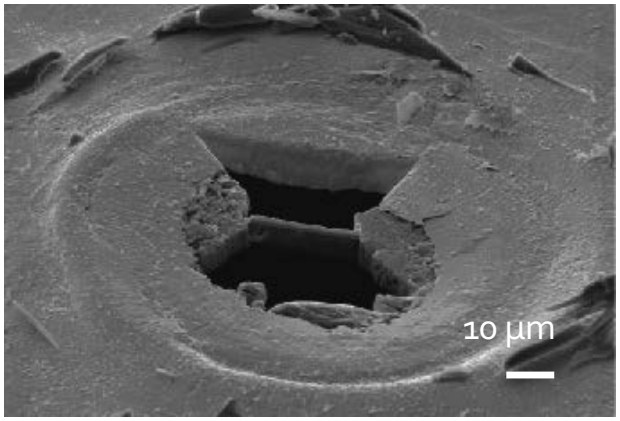
Experimental Approach

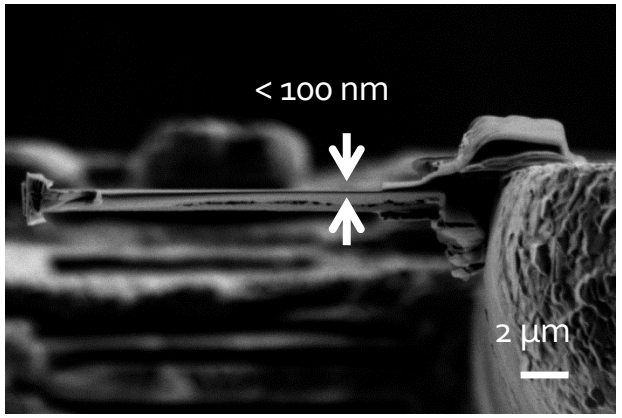
❖ Recovered Sample Preparation : Focused Ion Beam (FIB)





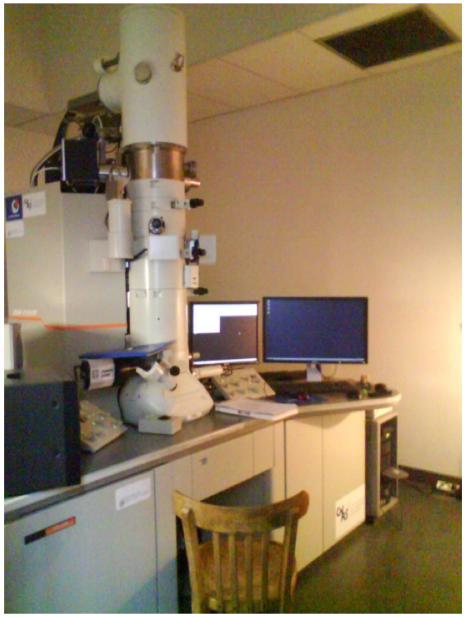


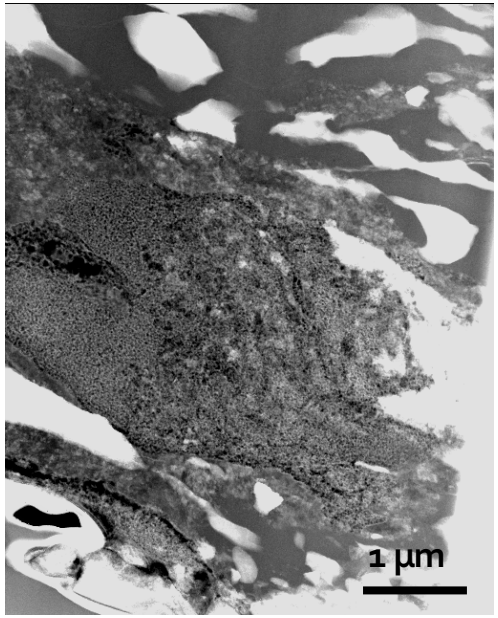




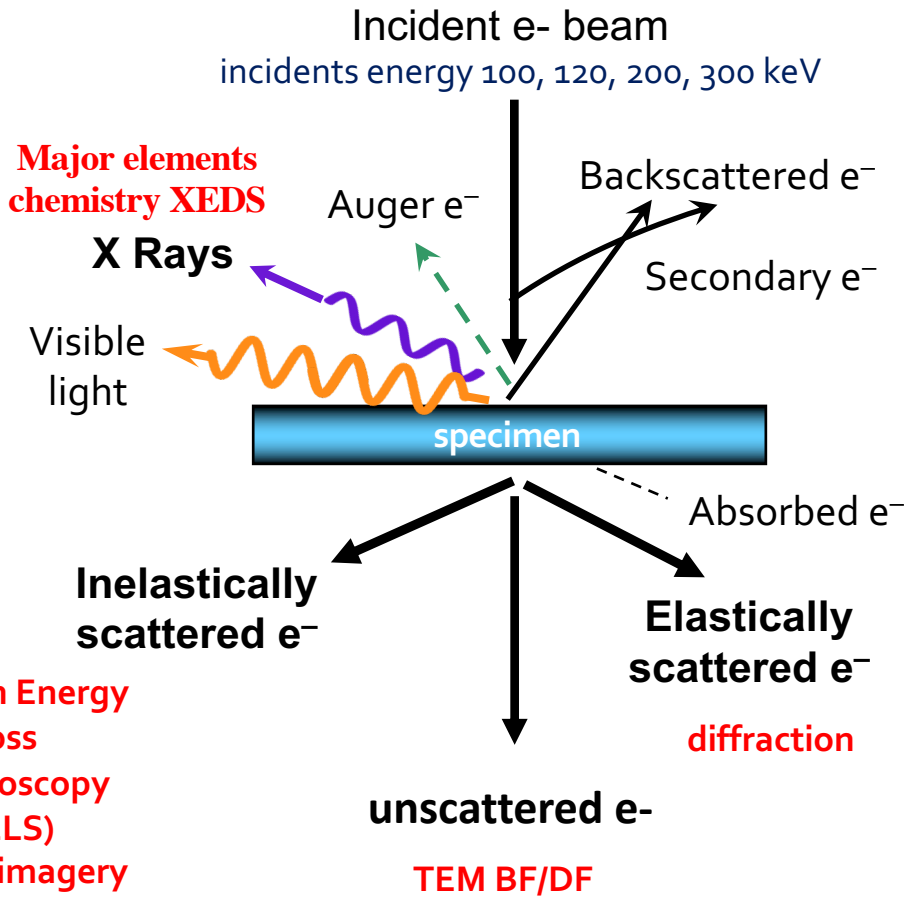
Experimental Approach

❖Ex Situ analyses : Transmission Electron Microscopy



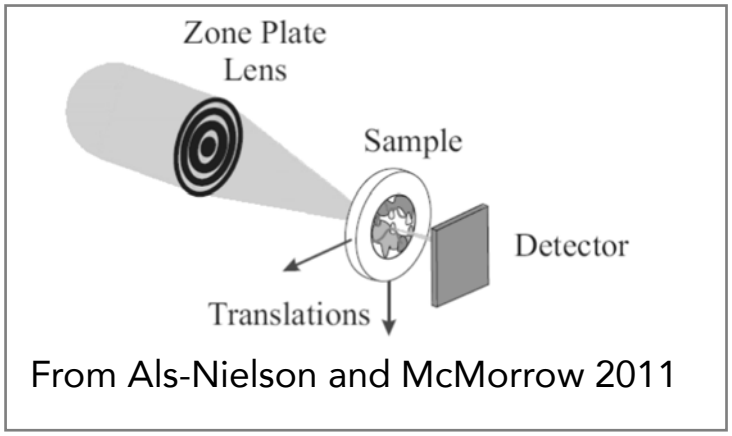


Electron – Matter Interaction:

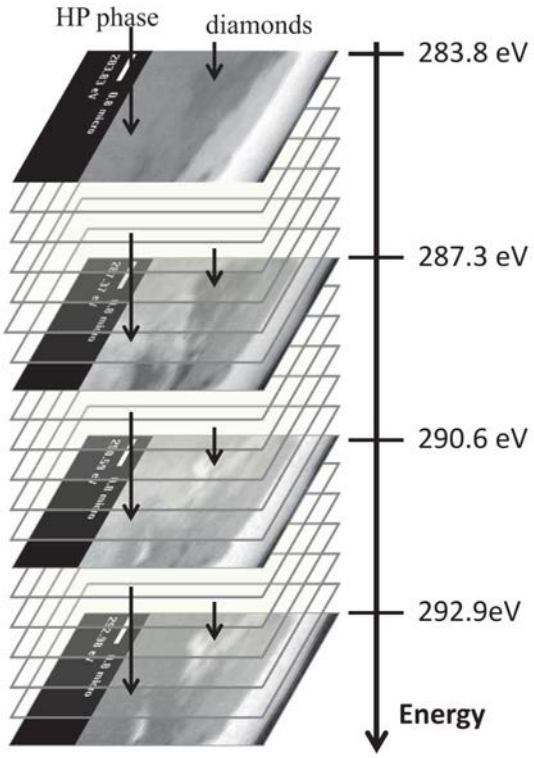


Experimental Approach

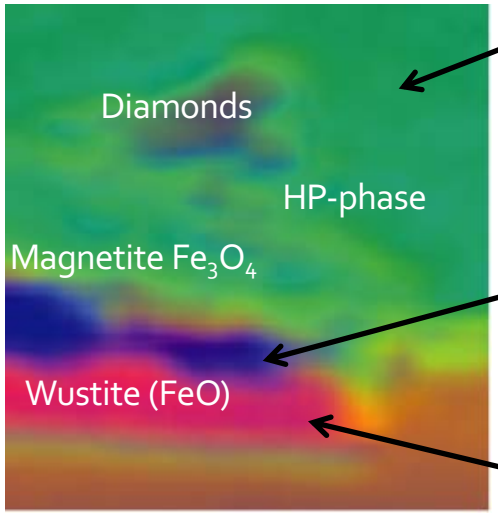
❖Ex Situ analyses : Scanning TransmissionX-Ray Microscopy

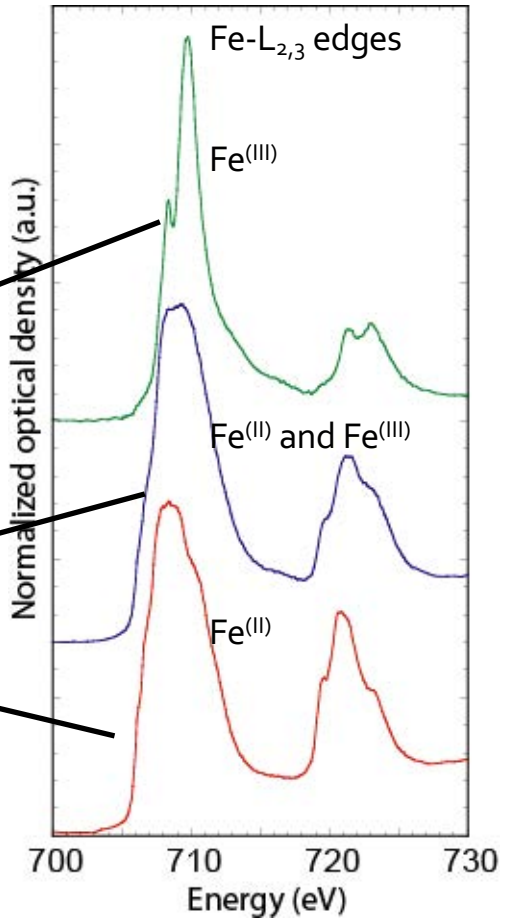


From Als-Nielson and McMorrow 2011



Mao and Boulard, 2013

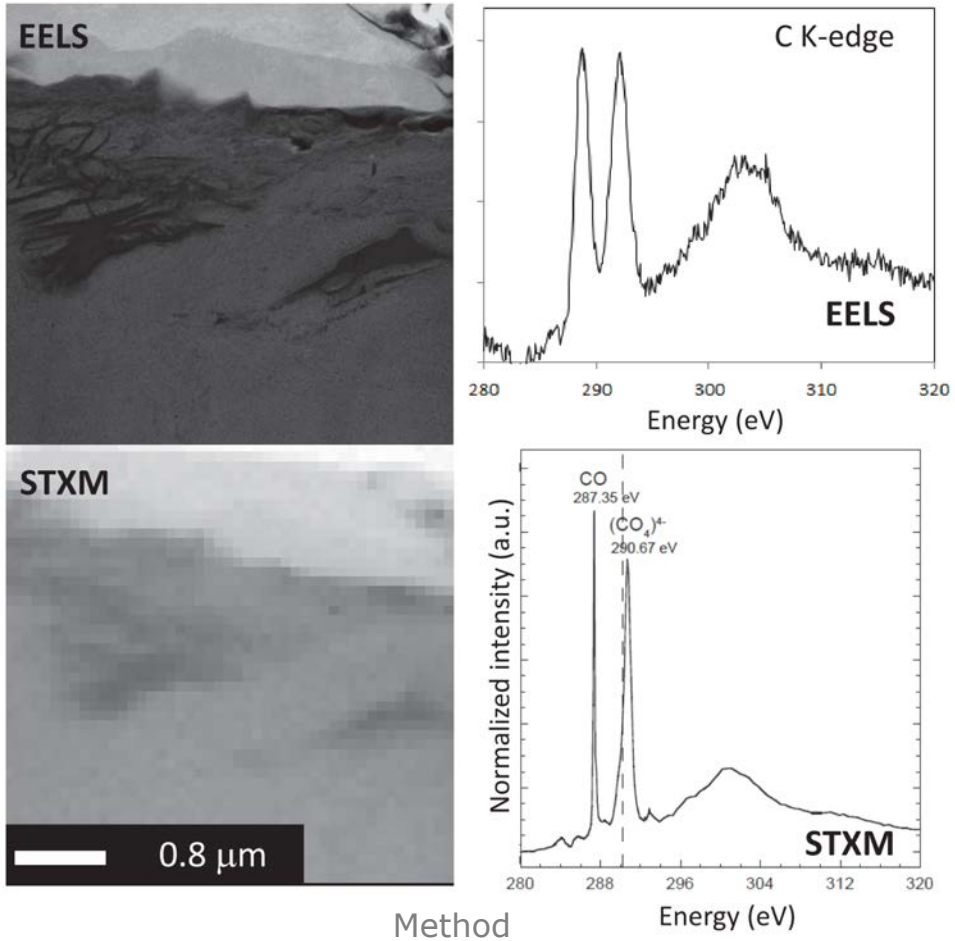




Experimental Approach

❖EELS versus STXM

	STXM	EELS
• Spatial resolution :	30 nm	1 nm
• Energy resolution :	0.1 eV	1 eV

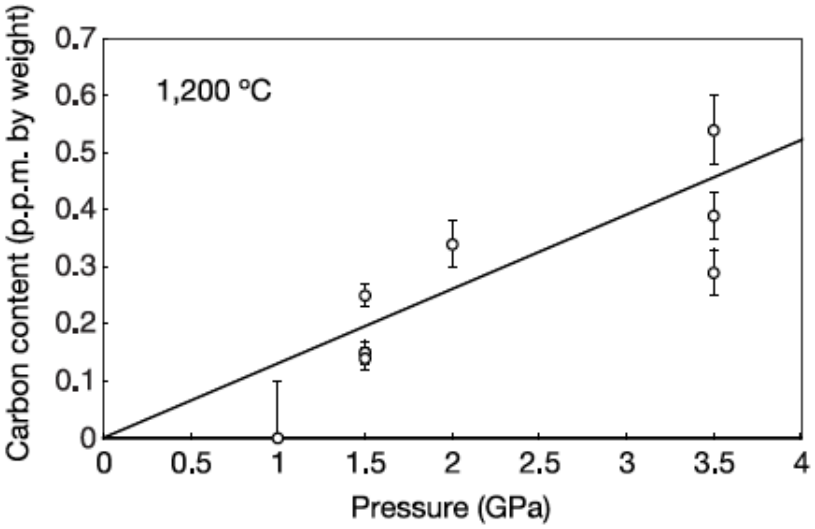


Mao and Boulard, 2013

Carbon Bearing Phases in the Mantle

- **Little solubility in major mantle minerals**:

Carbon solubility in olivine:



Keppler et al., Nature, 2003

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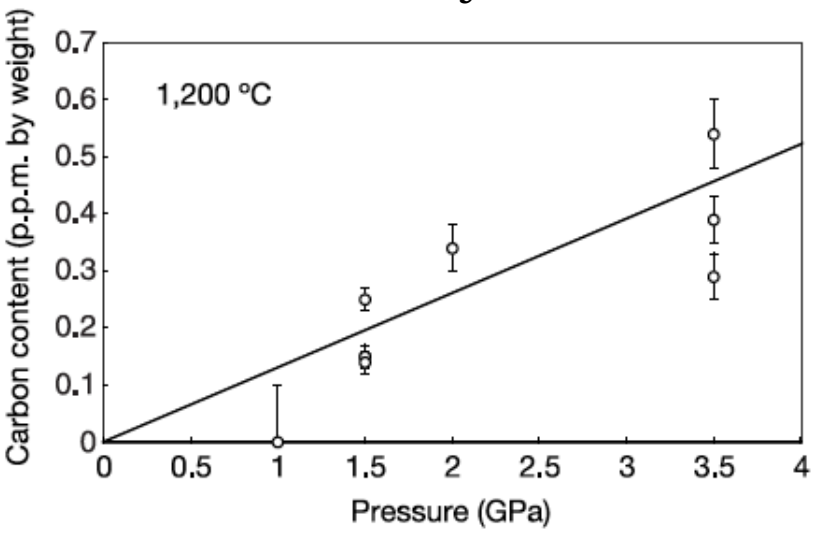
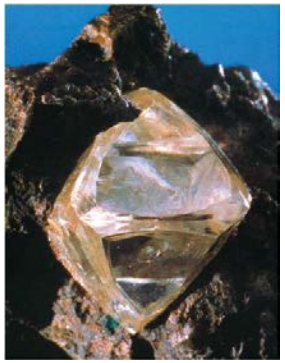


Keppler et al., Nature, 2003

- **Reduced Carbon**:



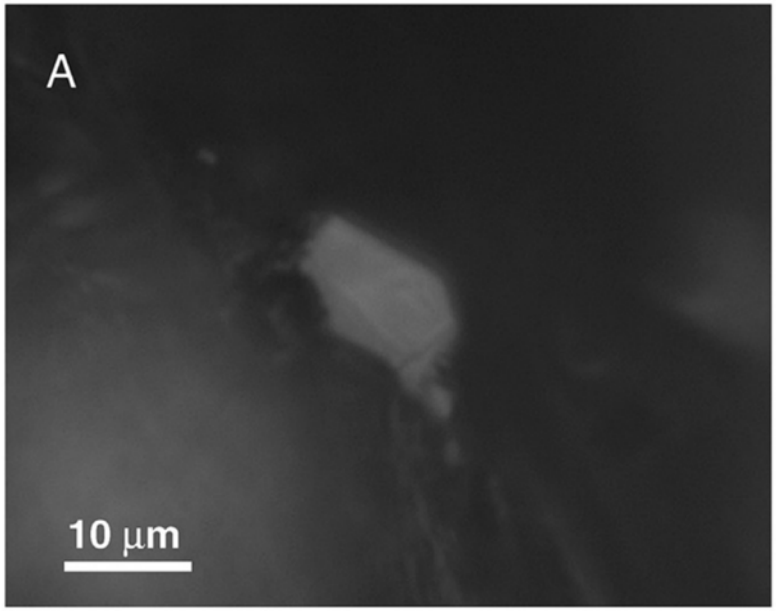
Diamond and alloys

- **Oxidized Carbon**:

Carbonates

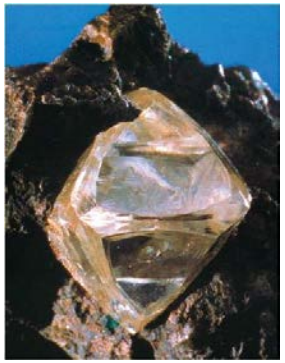
Carbon Bearing Phases in the Mantle

- Carbonate inclusions in lower mantle diamonds



Brenker et al., EPSL, 2007
Wang et al., EPSL, 1996
Kaminsky, Earth-Science Reviews, 2012

- **Reduced Carbon**:



Diamond and alloys

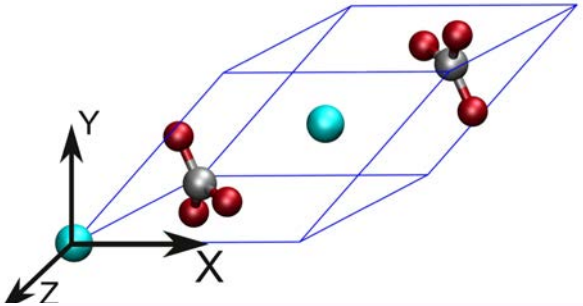
- **Oxidized Carbon**:

Carbonates

Carbonates

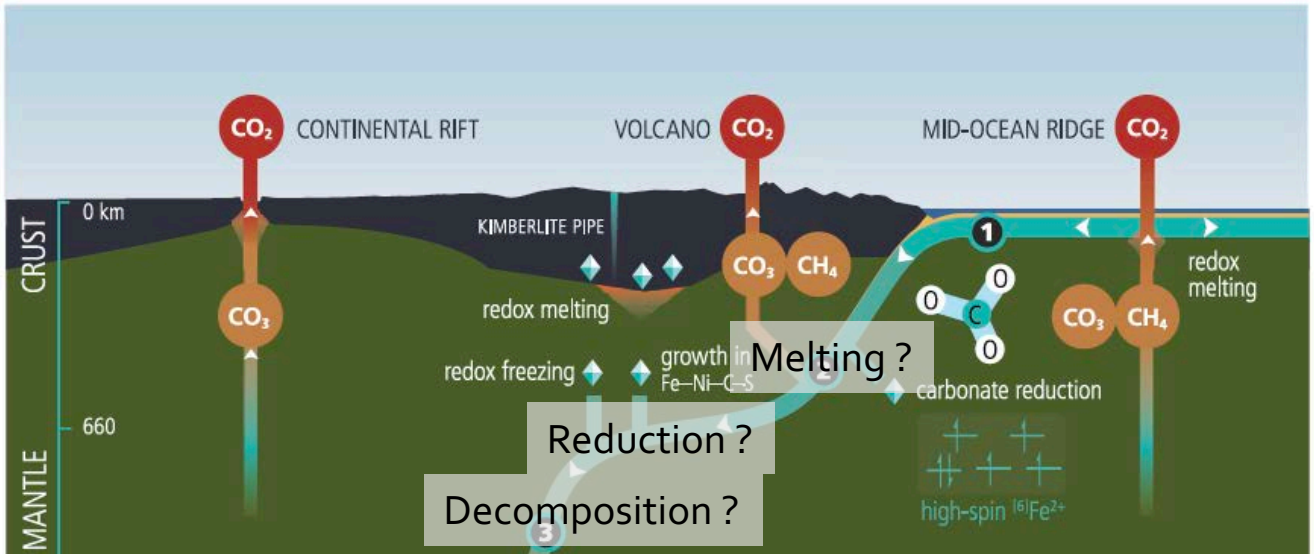
$CaCO_3$	$MgCa(CO_3)_2$	$MgCO_3$	$FeCO_3$	$MnCO_3$

Rhombohedral Structure
Space Group : R-3c



O
C

Ca, Mg, Fe, Mn ...

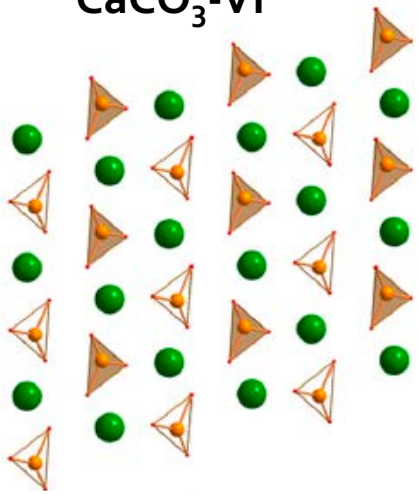


Carbon Bearing Phases in the Mantle

$CaCO_3$ & $MgCa(CO_3)_2$

At high pressure:
- no decomposition, no melting
- Adopt similar high pressure structure

$CaCO_3$-VI



Merlini et al., Min. Mag., 2014
Ono et al., Am. Min., 2007
Merlini al., PNAS, 2012

$$MgCa(CO_3)_2 + (Mg,Fe)SiO_3 \longrightarrow CaSiO_3 + (Mg,Fe)CO_3$$

Dolomite + Enstatite → Ca-perovskite + Ferromagnesite

$$CaCO_3 + MgSiO_3 \longrightarrow CaSiO_3 + MgCO_3$$

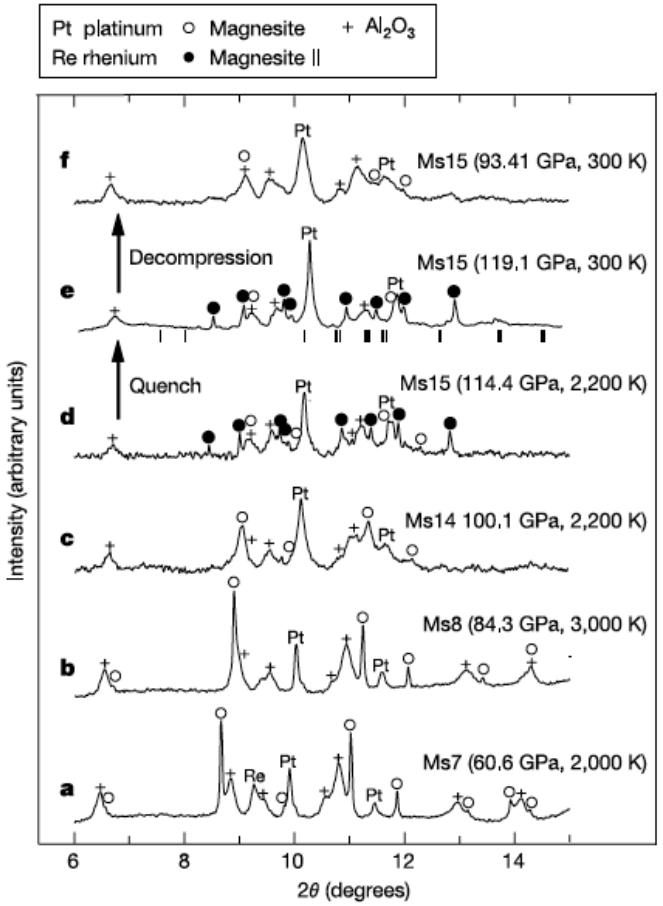
Calcite + Bridgmanite → Ca-perovskite + Magnesite

Biellmann et al., EPSL, 1993

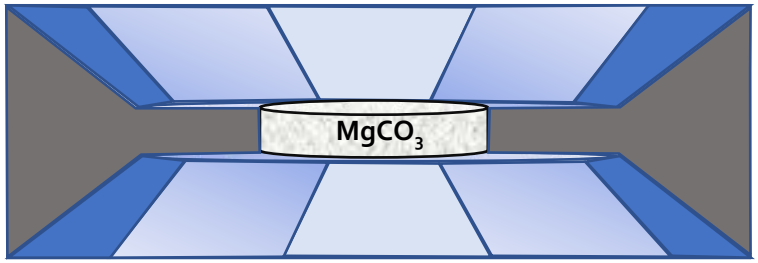
Stability of $MgCO_3$ at Extreme Conditions

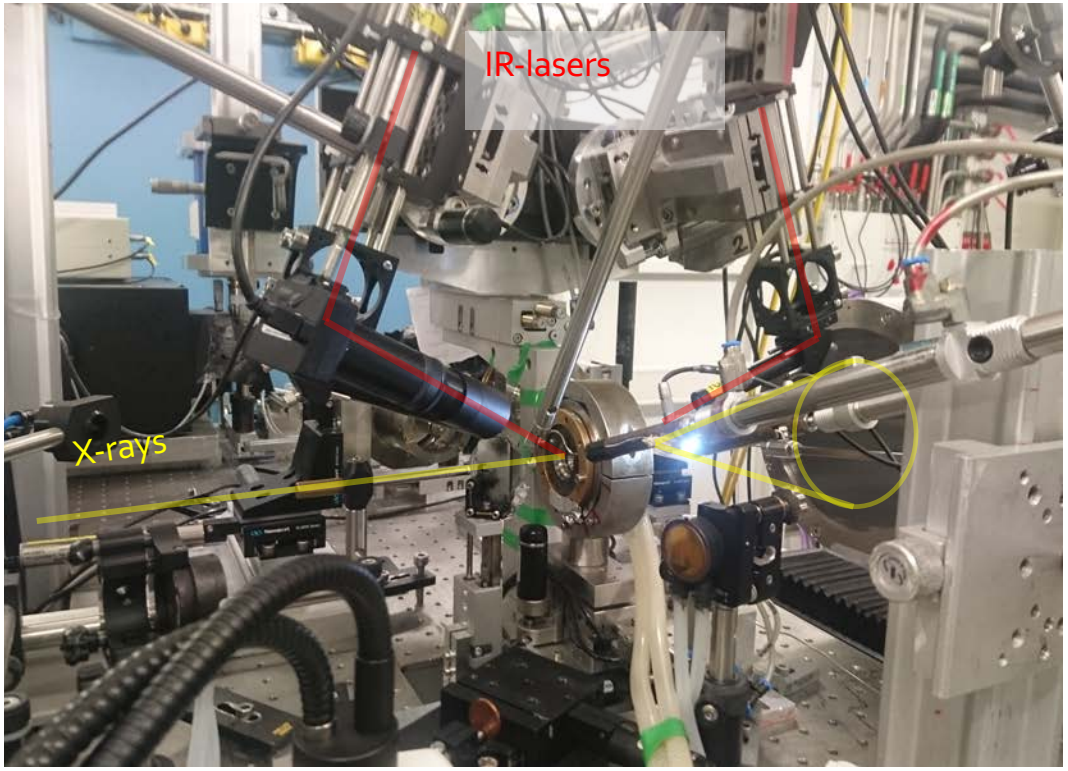
- First experimental evidence of a phase transition :

XRD: info on the crystalline structure



Isshiki et al., Nature, 2004





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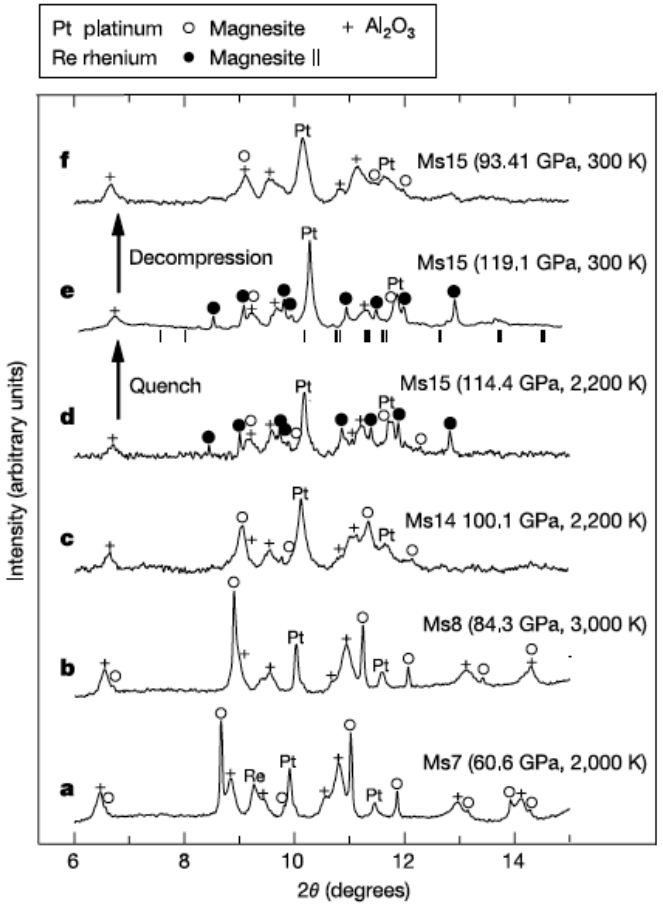
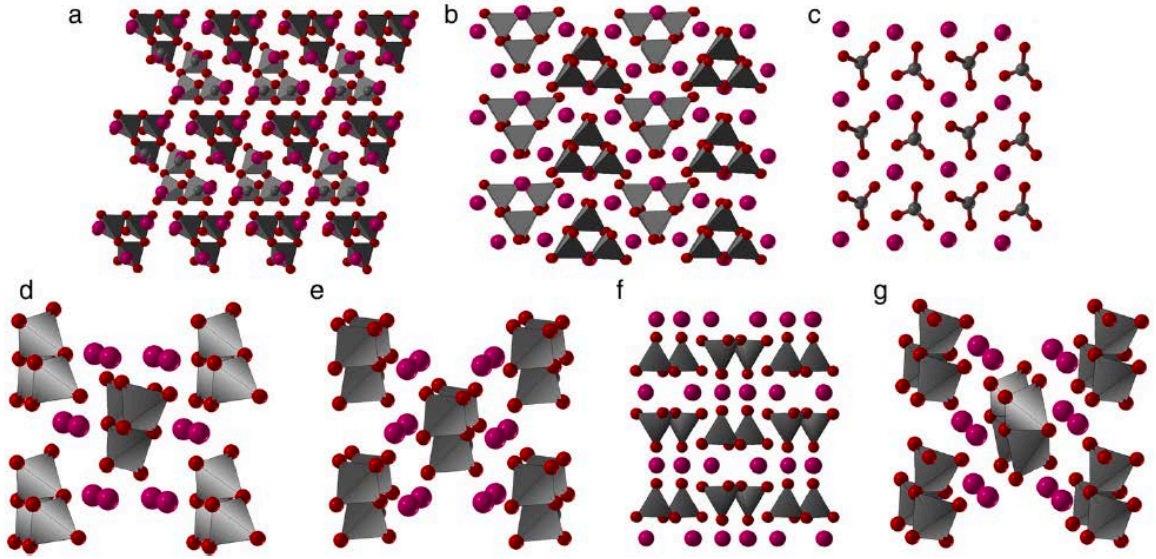


Isshiki et al., Nature, 2004

- Prediction of HP-Structures :

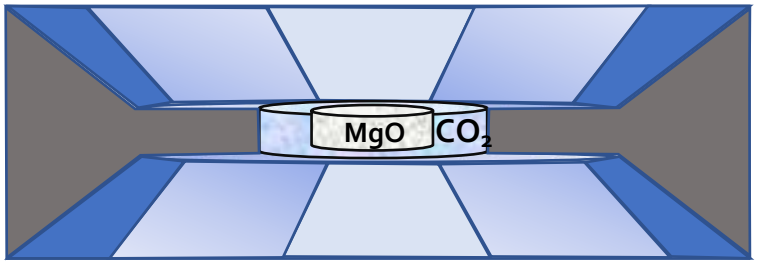
DFT theoretical calculations

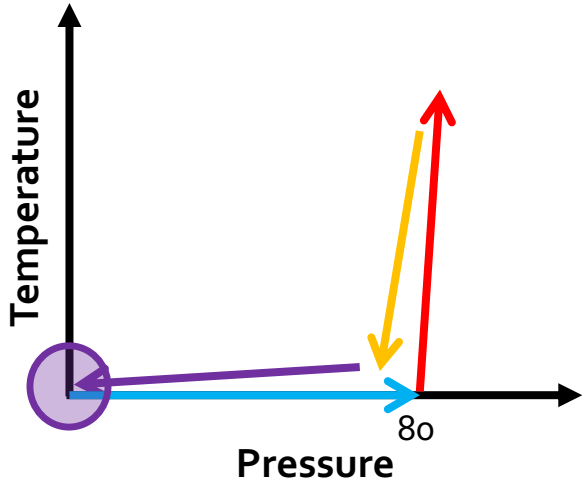


Oganov et al., EPSL, 2008
Skorodumova et al., Am. Min., 2005
Oganov et al., EPSL, 2006

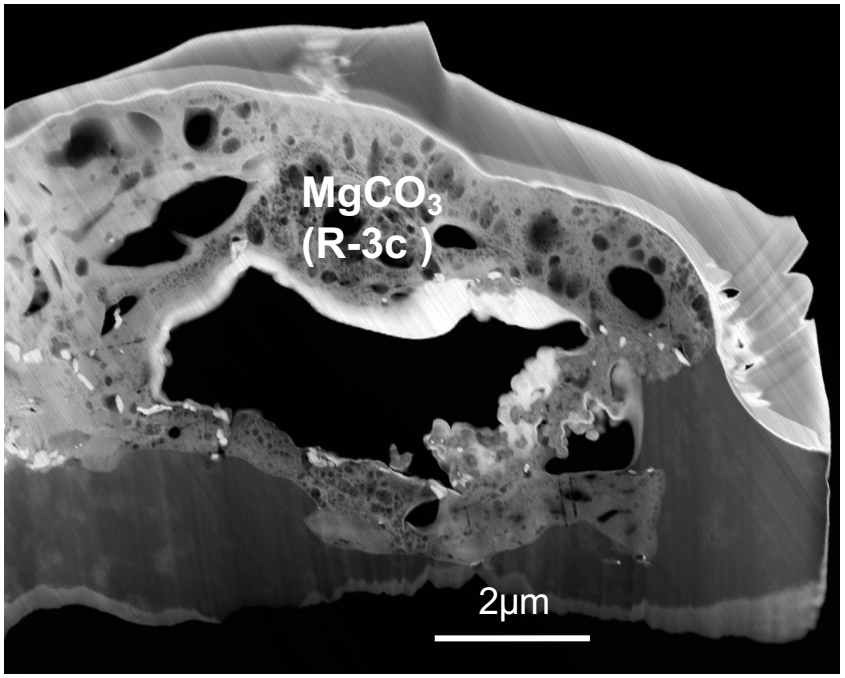
Stability of $MgCO_3$ at Extreme Conditions

MgO +CO_2 transformed at 85GPa-2300K (~1970 km)

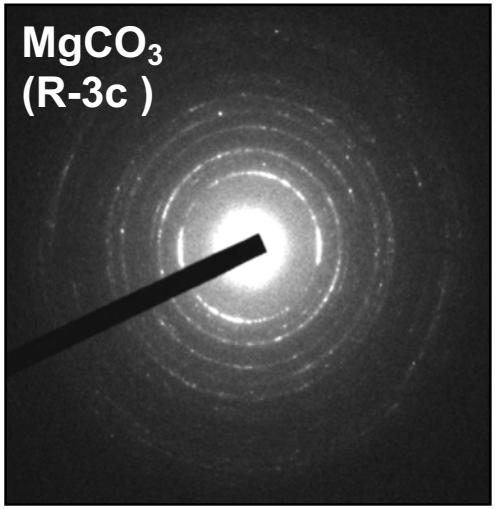




STEM image



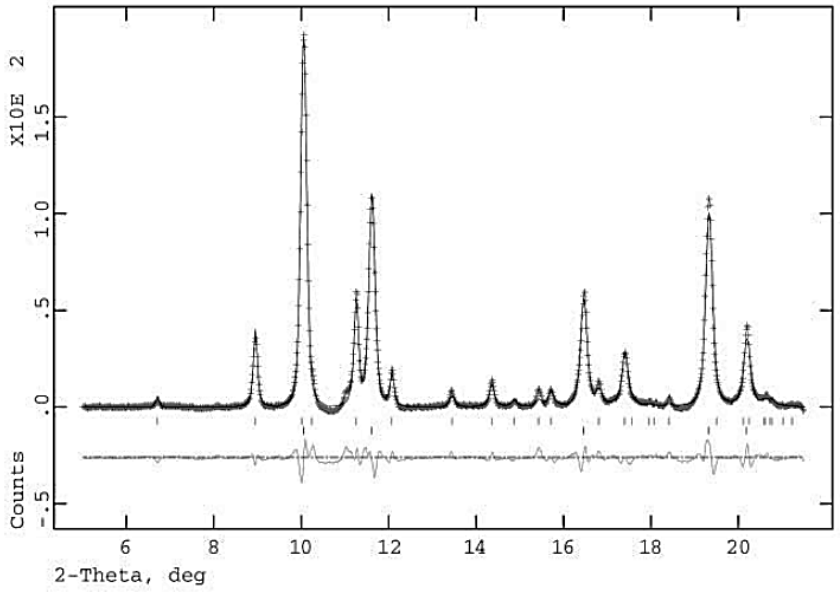
e⁻ Diffraction



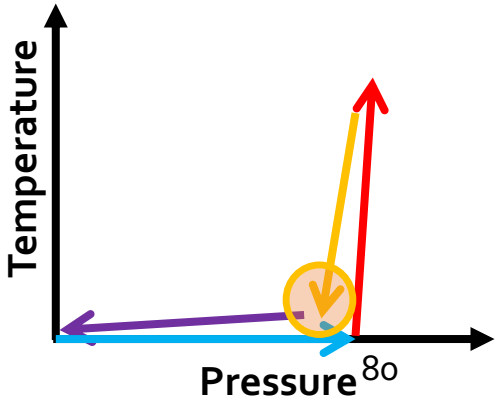
Stability of $MgCO_3$ at Extreme Conditions

(XRD: info on the crystalline structure)

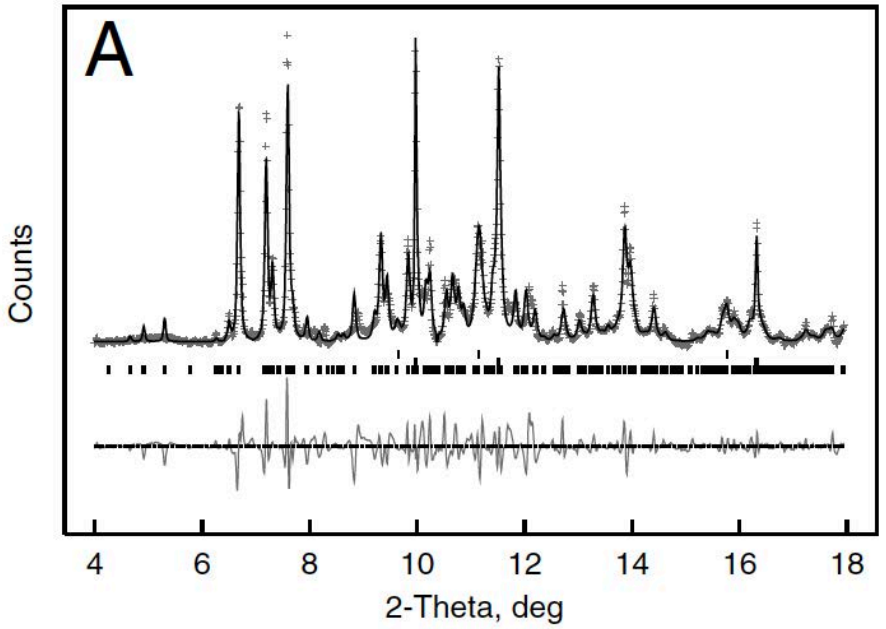
$MgCO_3$ + Pt at 82 Gpa – Room T°



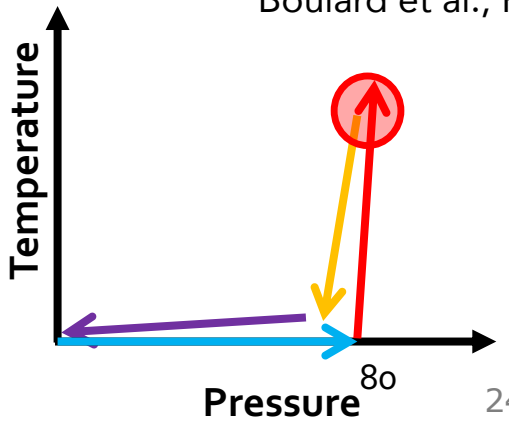
Fiquet et al., Am. Min., 2002



MgO + CO_2 at 85 GPa - 2300 K



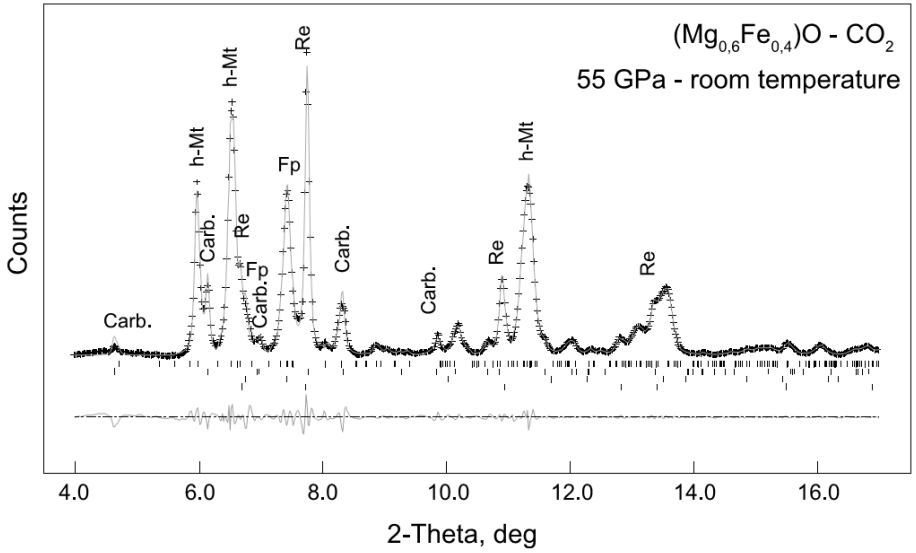
Boulard et al., PNAS, 2011



Stability of $(Fe,Mg)CO_3$ at Extreme Conditions

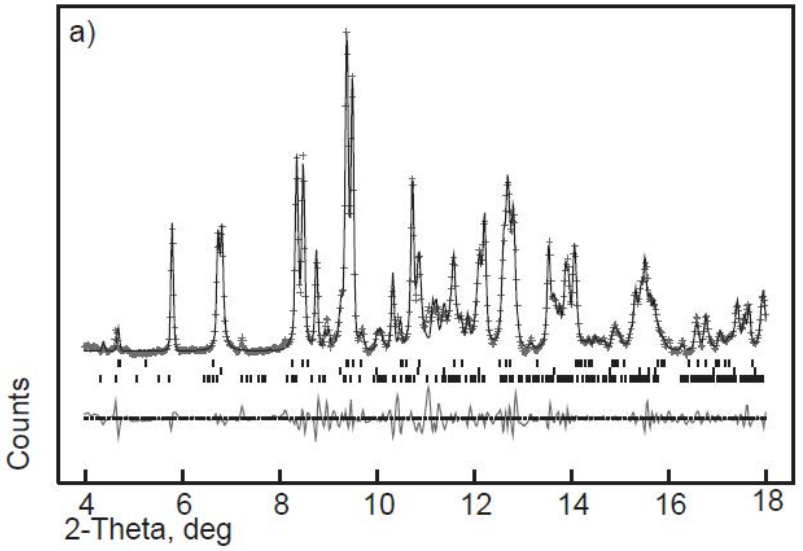
(XRD: info on the crystalline structure)

$Mg_{0,6}Fe_{0,4}O + CO_2$ at 55 GPa - RT

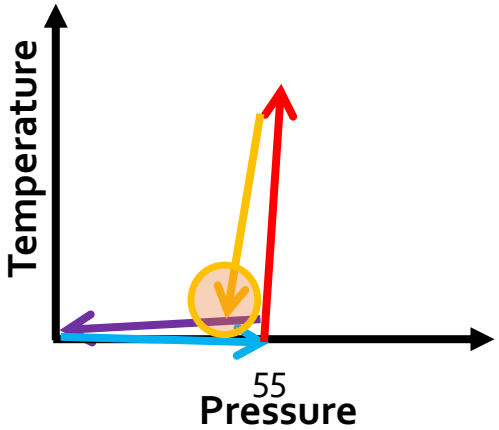


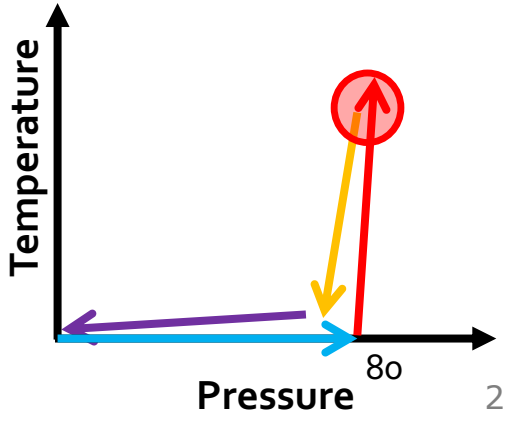
Boulard et al., JGR, 2012

$Mg_{0,25}Fe_{0,75}CO_3$ at 80 GPa - 2300 K



Boulard et al., PNAS, 2011

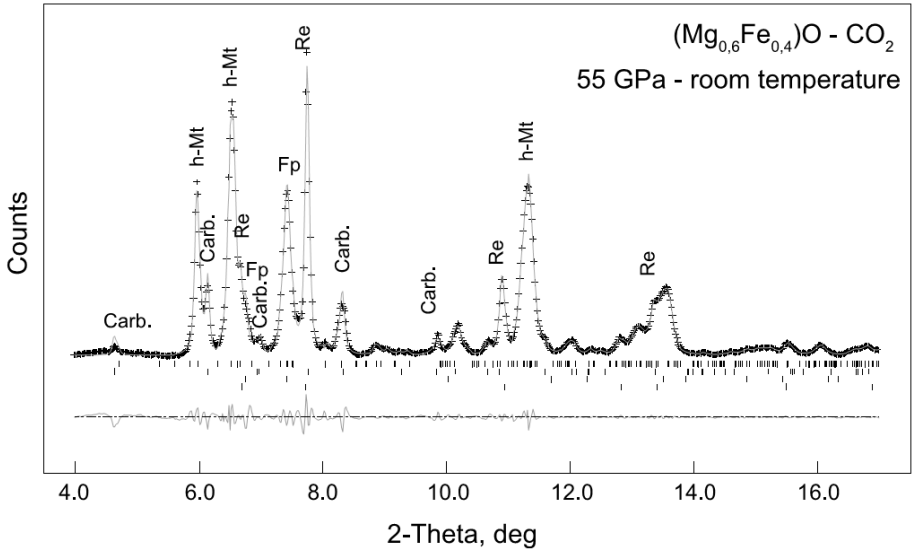




Stability of $(Fe,Mg)CO_3$ at Extreme Conditions

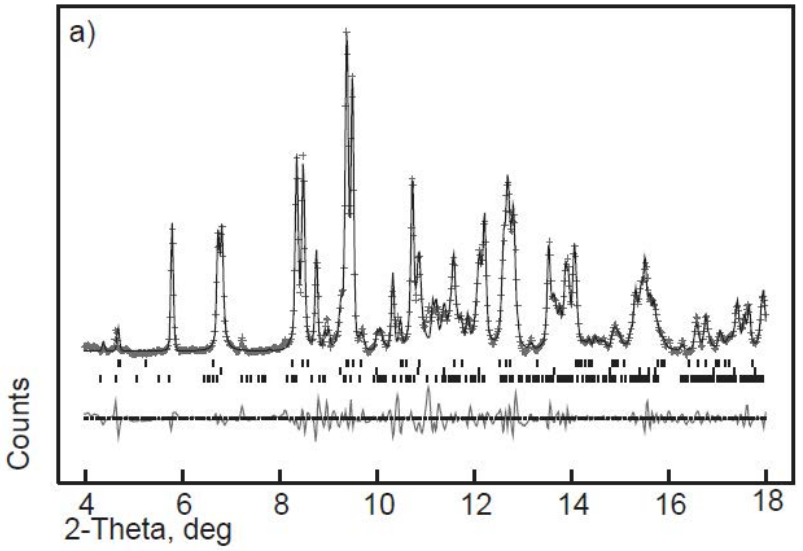
(XRD: info on the crystalline structure)

$Mg_{0,6}Fe_{0,4}O + CO_2$ at 55 Gpa - RT



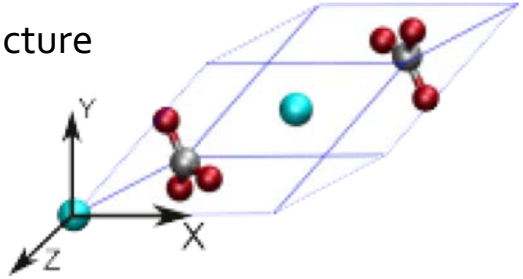
Boulard et al., JGR, 2012

$Mg_{0,25}Fe_{0,75}CO_3$ at 80 GPa - 2300 K



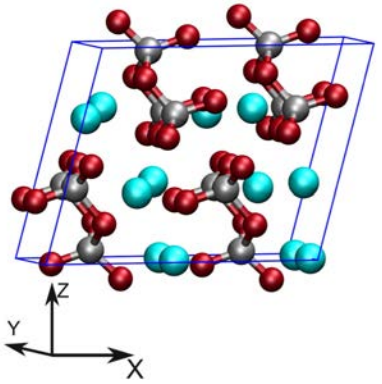
Boulard et al., PNAS, 2011

Calcite-type structure
Rhombohedral
R-3c



Structure predicted by Oganov et al., EPSL, 2008

?

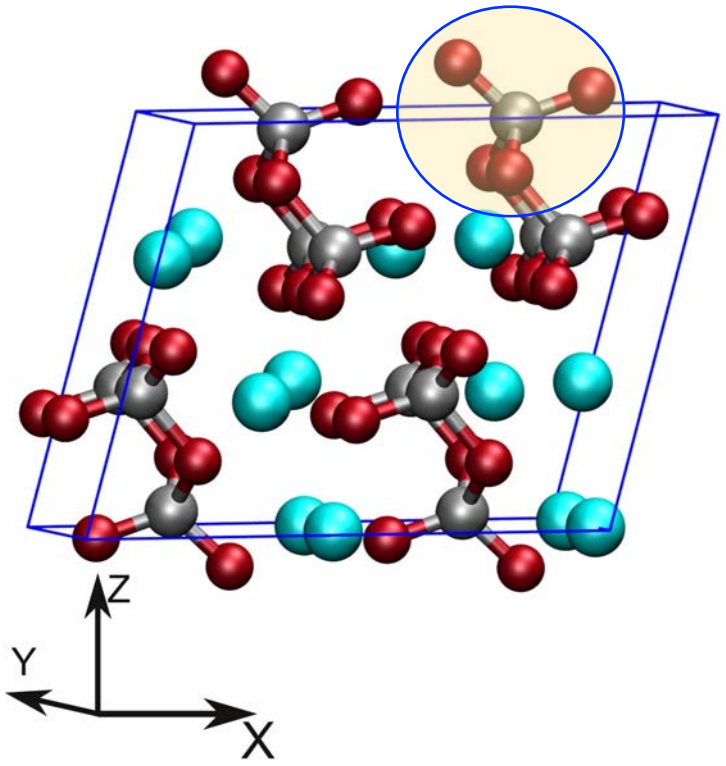


Mg-Fe Carbonates Structure at High Pressure

Monoclinic Structure
Space group P21/c

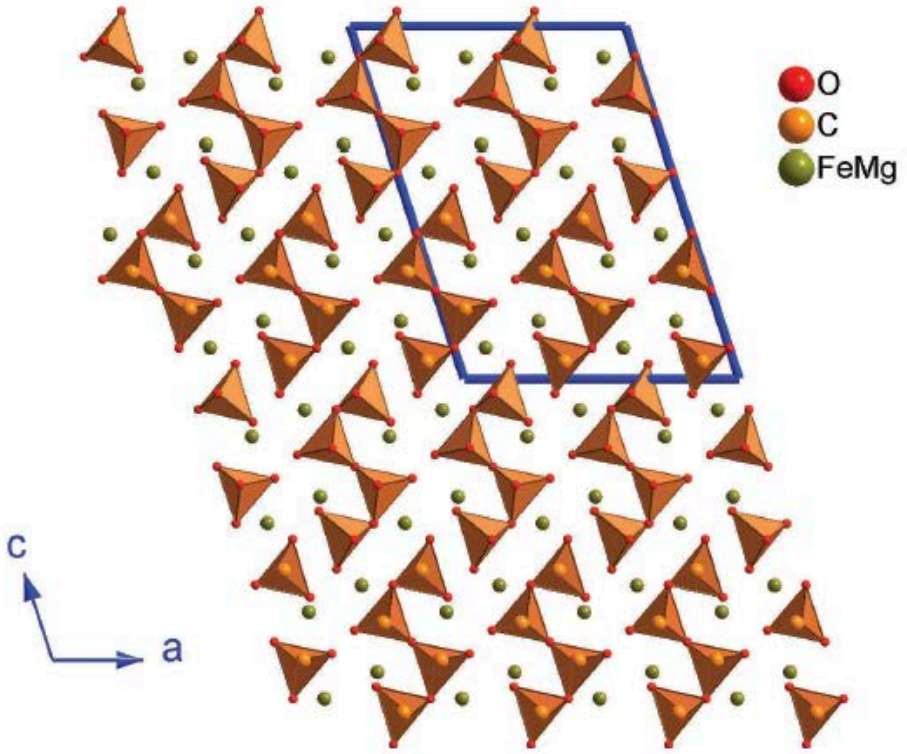
$Mg_{0.25}Fe^{III}_{0.3}(C_3O_9)_{0.233}$

Tetrahedral Groups CO_4^{4-}



1) Crystalline Structure Refinements

XRD on Monocrystal

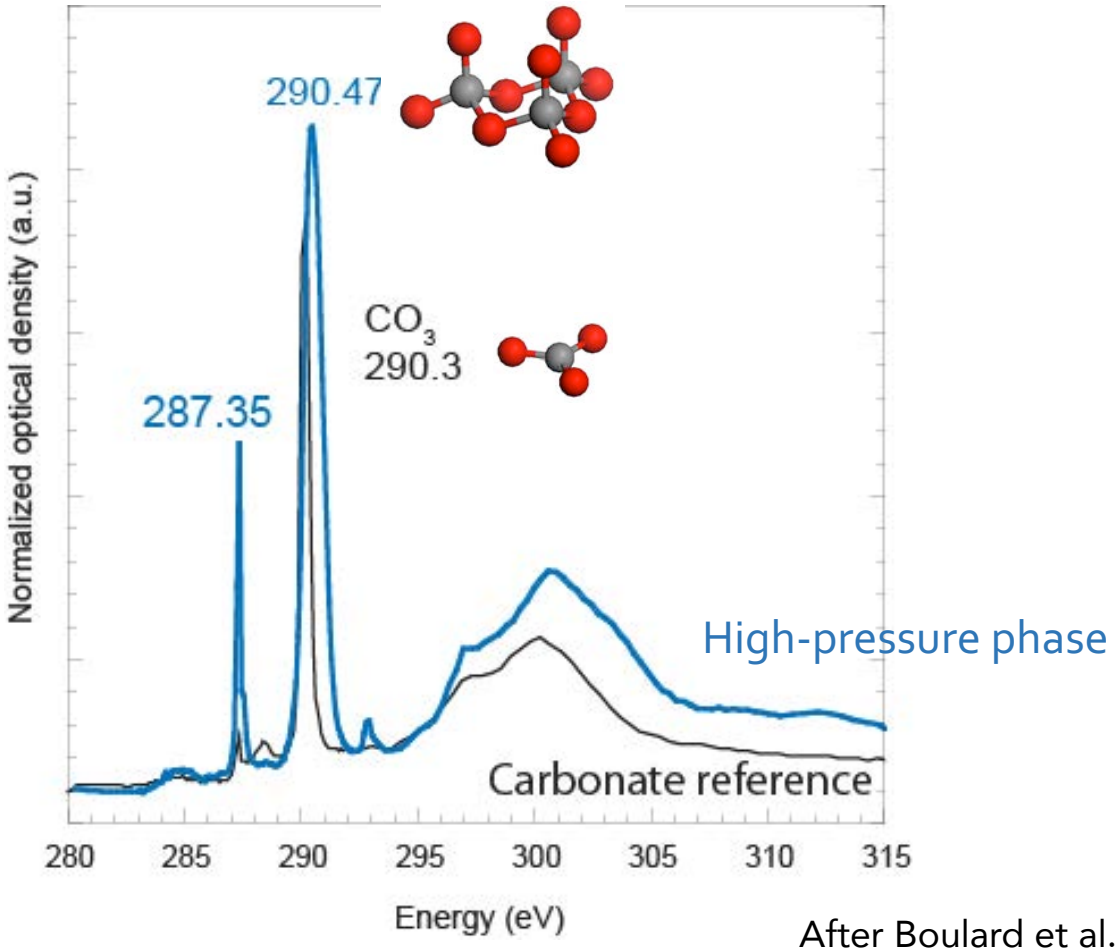


$Mg_2Fe^{III}_2(C_4O_{13})$ at 135 GPa – 2650 K (2900 km)

Merlini et al., Am. Min., 2015
Cerantola et al., Nat. Com., 2017

2) New Spectroscopic Signature at the C K-edge

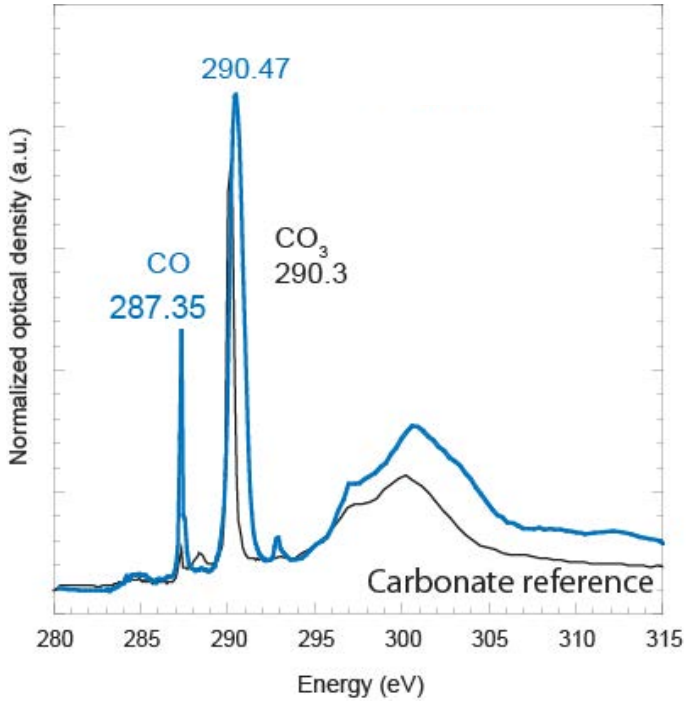
Ex situ Analyses STXM at the C K-edge : determine the electronic structure and local environement of carbon



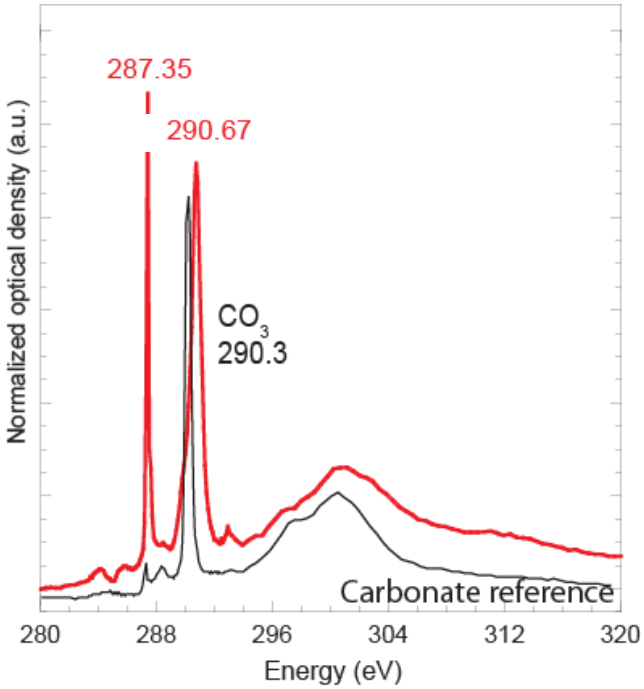
After Boulard et al., JGR, 2012

2) New Spectroscopic Signature at the C K-edge

Mg-Fe composition



Fe end-member



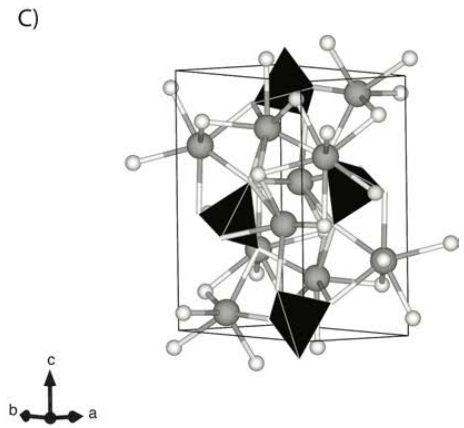
Boulard et al., JGR, 2012

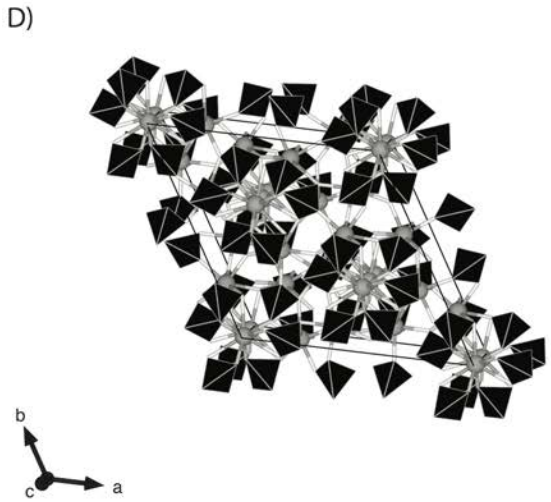
2) New Spectroscopic Signature at the C K-edge

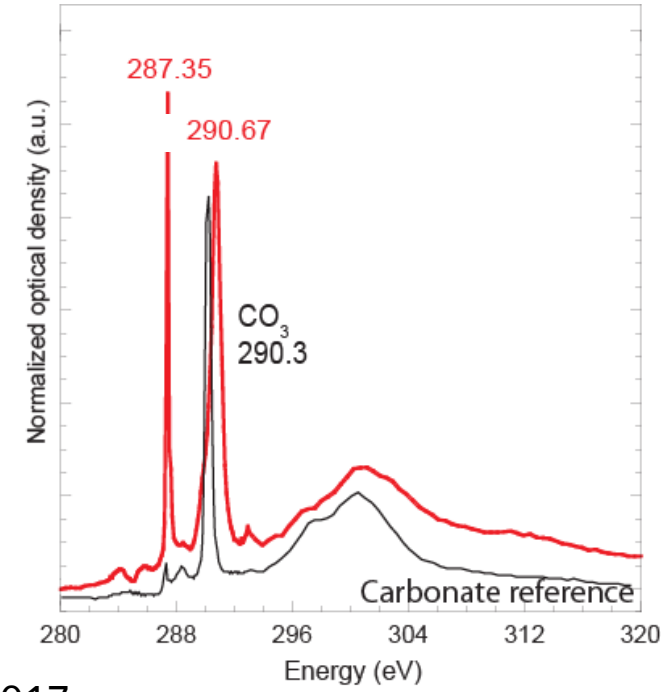
$FeO + CO_2$

$FeCO_3$

Fe end-member







Boulard et al., JGR, 2012

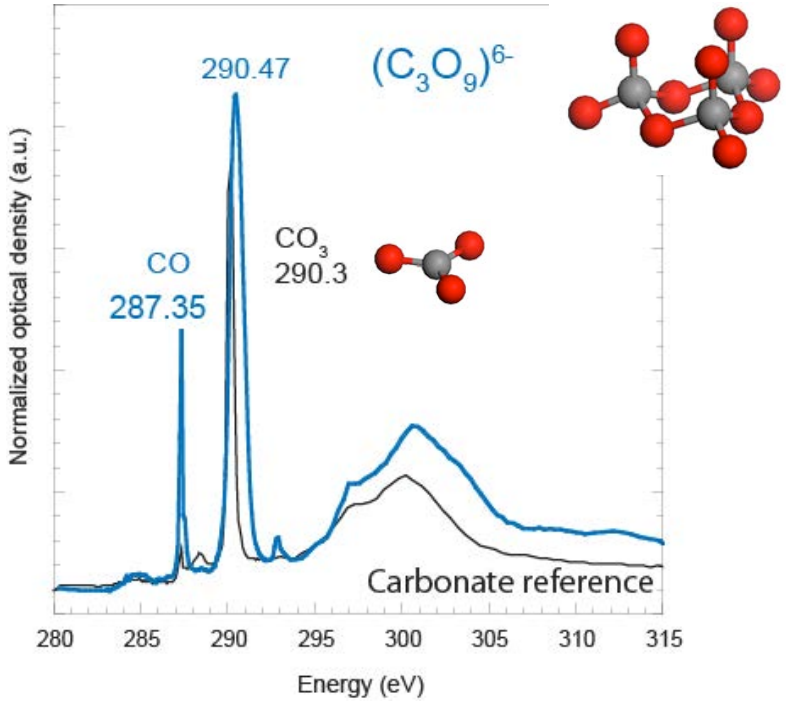
Cerantola et al., Nat. Com., 2017

$Fe_4C_3O_{12}$

isolated CO_4 groups

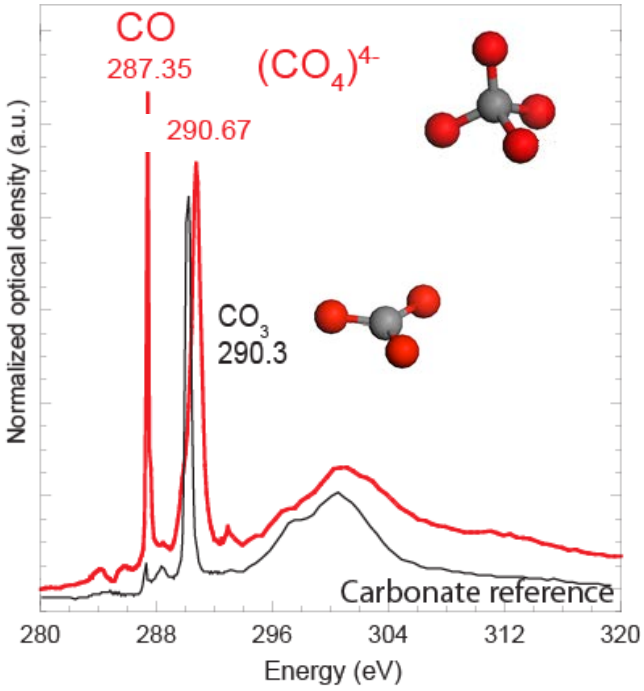
2) New Spectroscopic Signature at the C K-edge

Mg-Fe composition



$Mg_{0.25}Fe^{III}_{0.3}(C_3O_9)_{0.233}$

Fe end-member



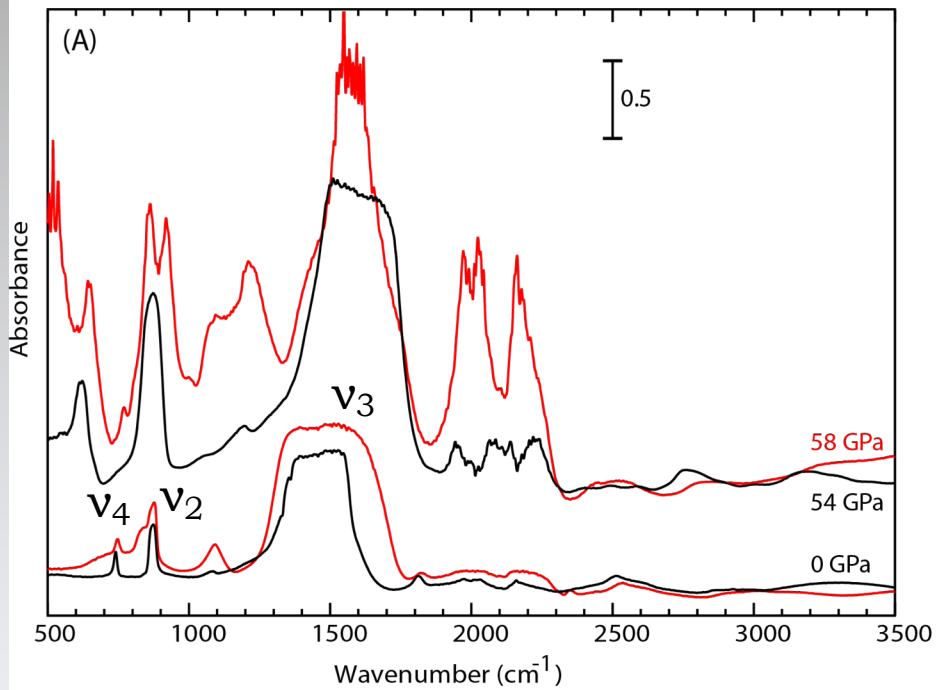
$Fe^{III}_4C_3O_{12}$

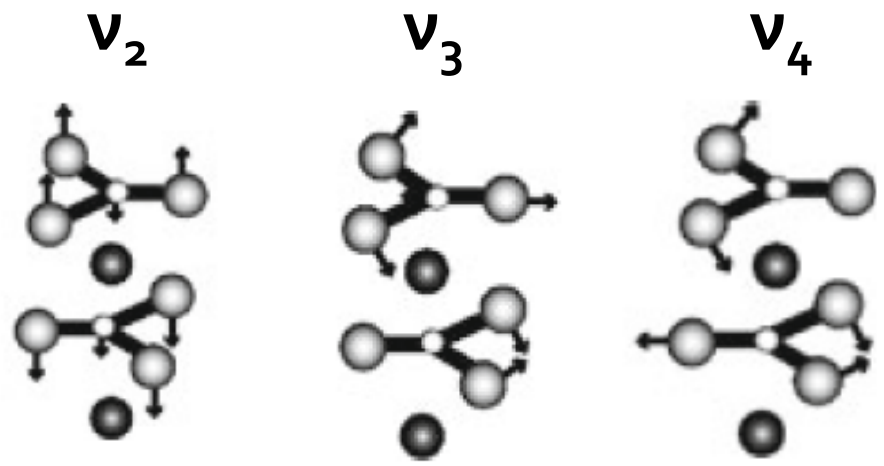
- Different polymerizations for different Mg content?

Boulard et al., JGR, 2012
Merlini et al., Am. Min., 2015
Cerantola et al., Nat. Com., 2017

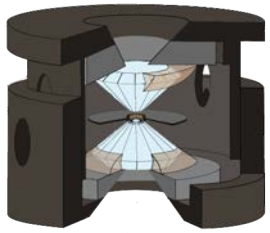
3) New Infrared Spectroscopic Signature

in situ Infrared Spectroscopy (synchrotron radiation) : probe molecular bonds



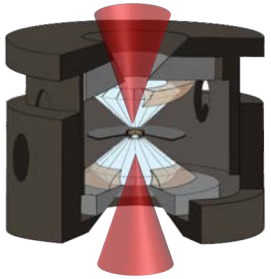


Untransformed carbonate



Compression at room Temp.

Transformed carbonate



Decompression after LH

Boulard et al., Nat. Com., 2015

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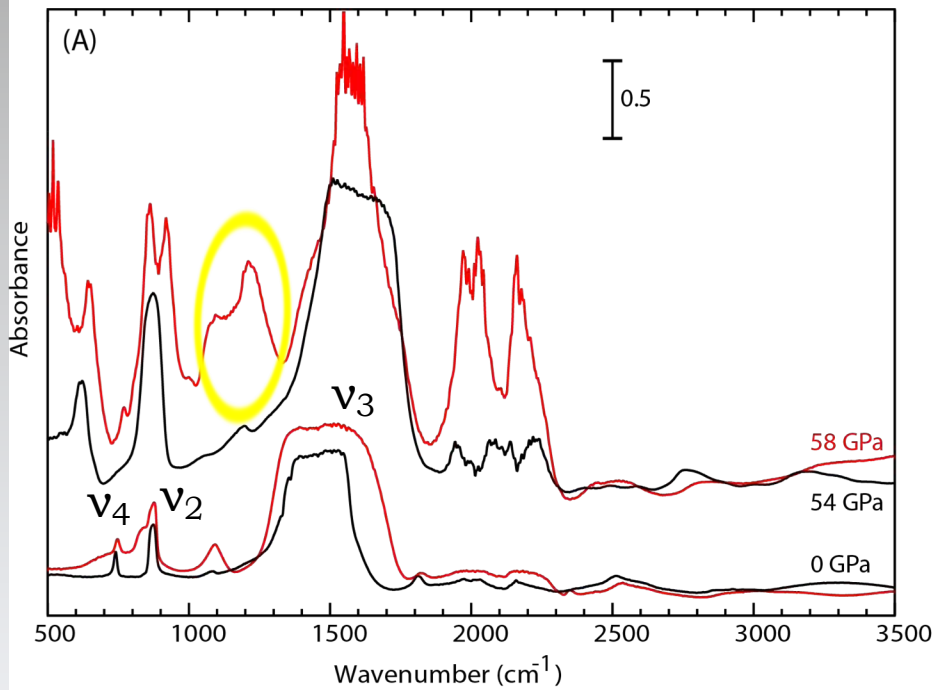
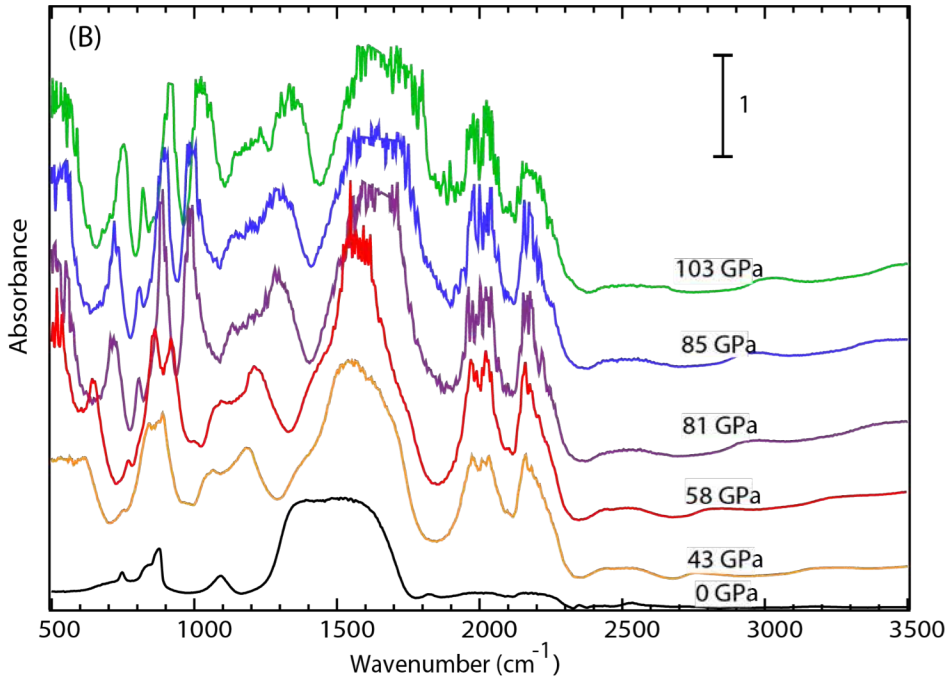
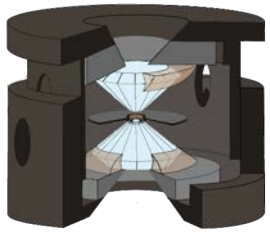




Untransformed carbonate



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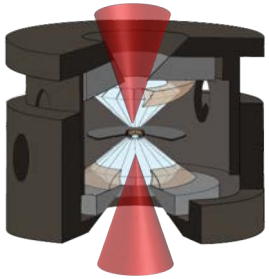

Decompression after LH

Boulard et al., Nat. Com., 2015

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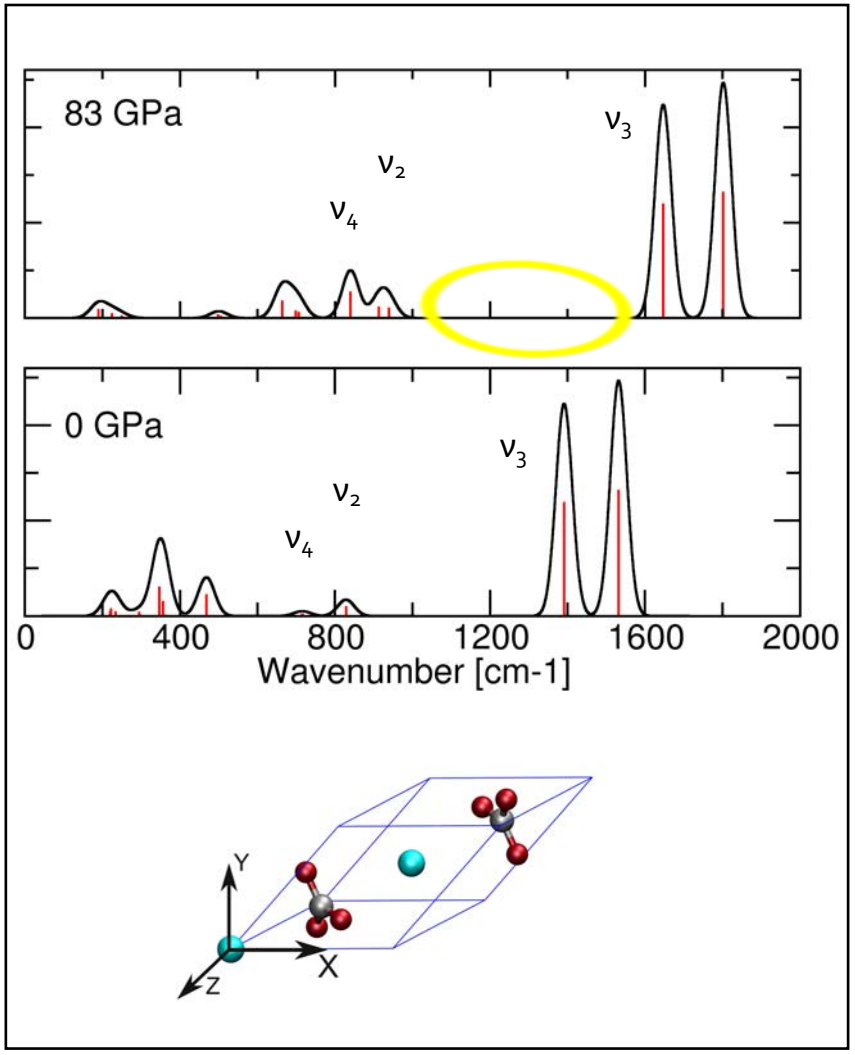
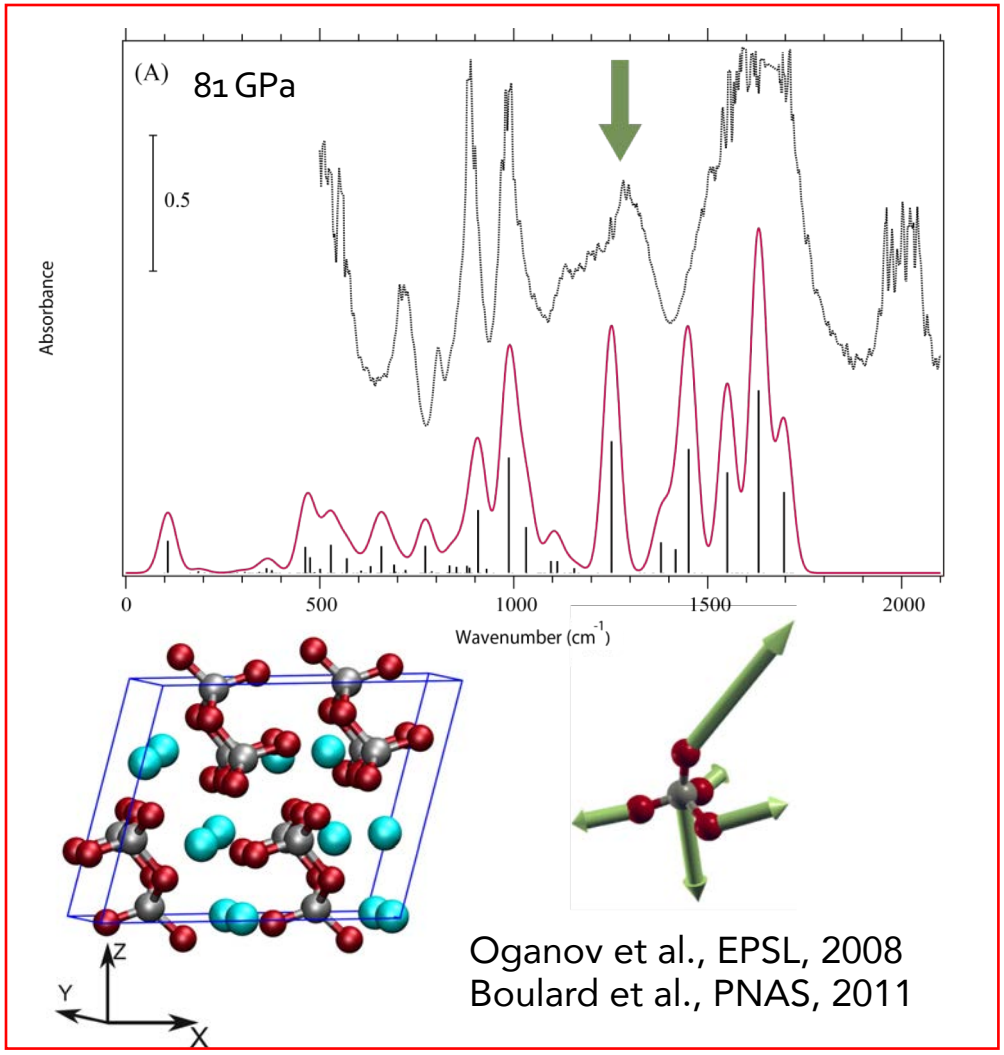




Oganov et al., EPSL, 2008
Boulard et al., PNAS, 2011

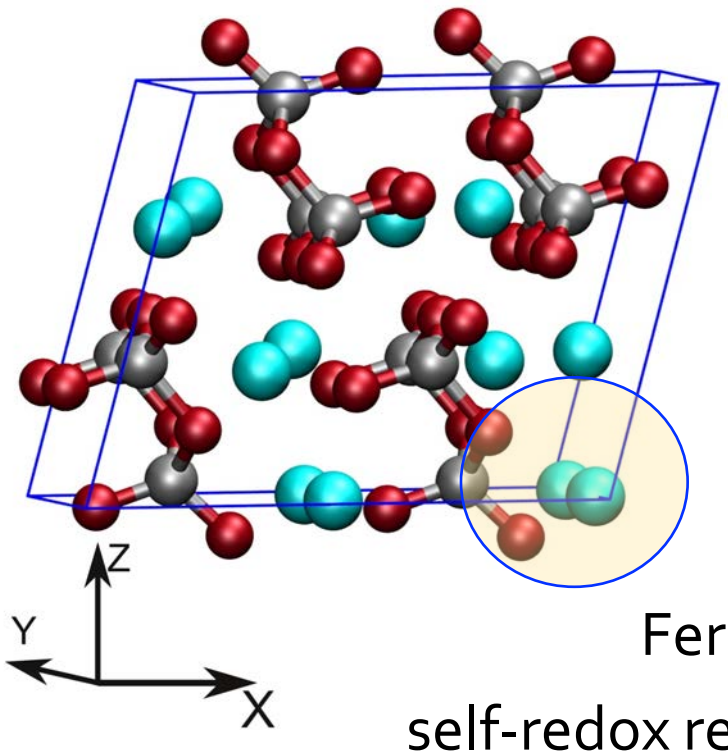
Boulard et al., Nat. Com., 2015

Mg-Fe Carbonates Structure at High Pressure

Monoclinic Structure
Space group P21/c

$Mg_{0.25}Fe^{III}_{0.3}(C_3O_9)_{0.233}$

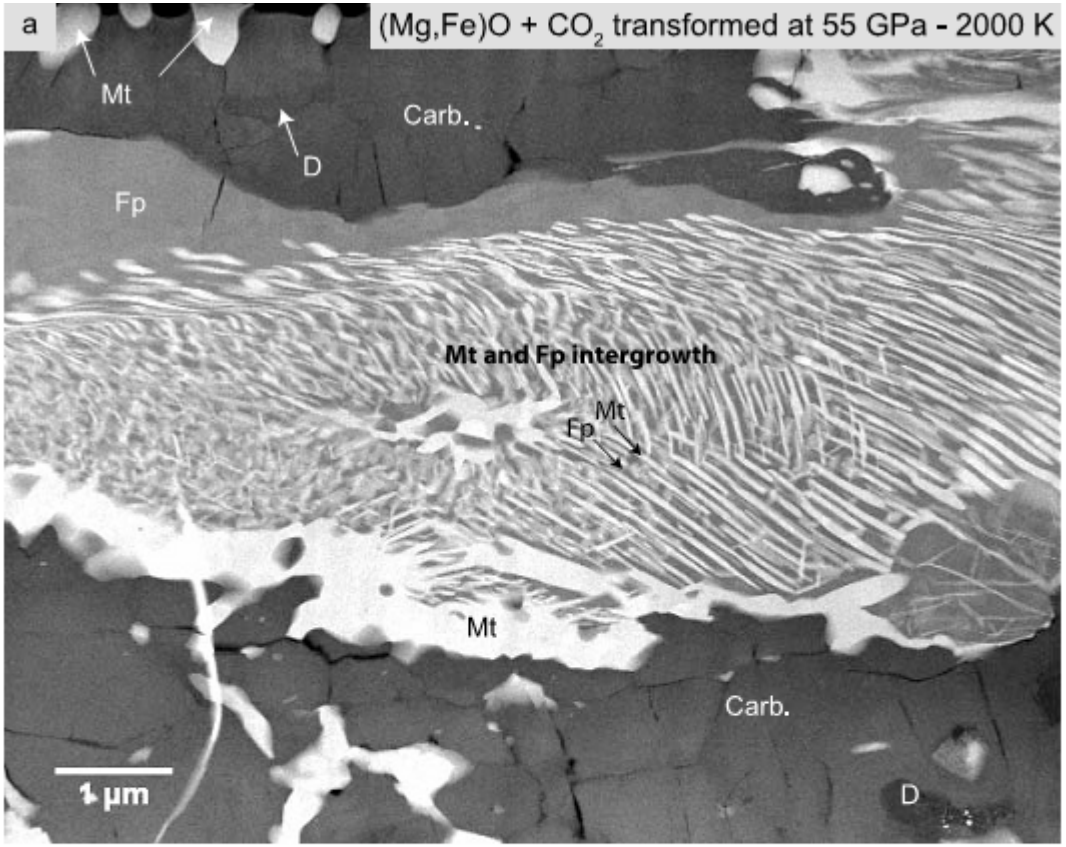
Tetrahedral Groups CO_4^{4-}



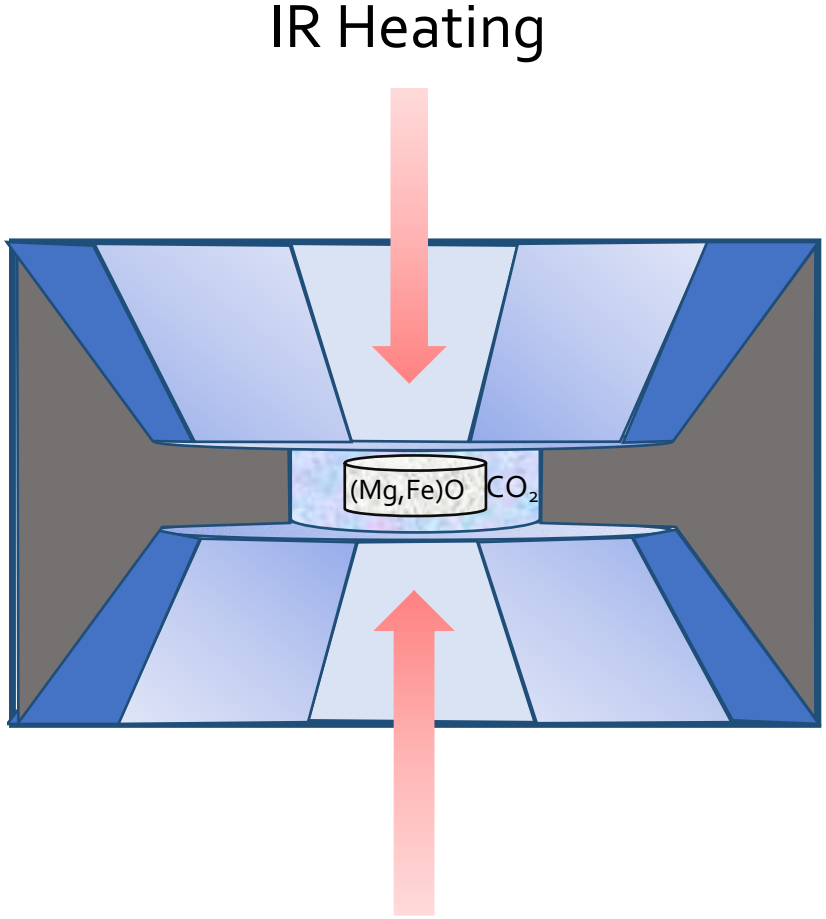
Ferric iron Fe^{3+}

self-redox reactions

1) Coexistence of Carbonates with Iron Oxides



STEM image



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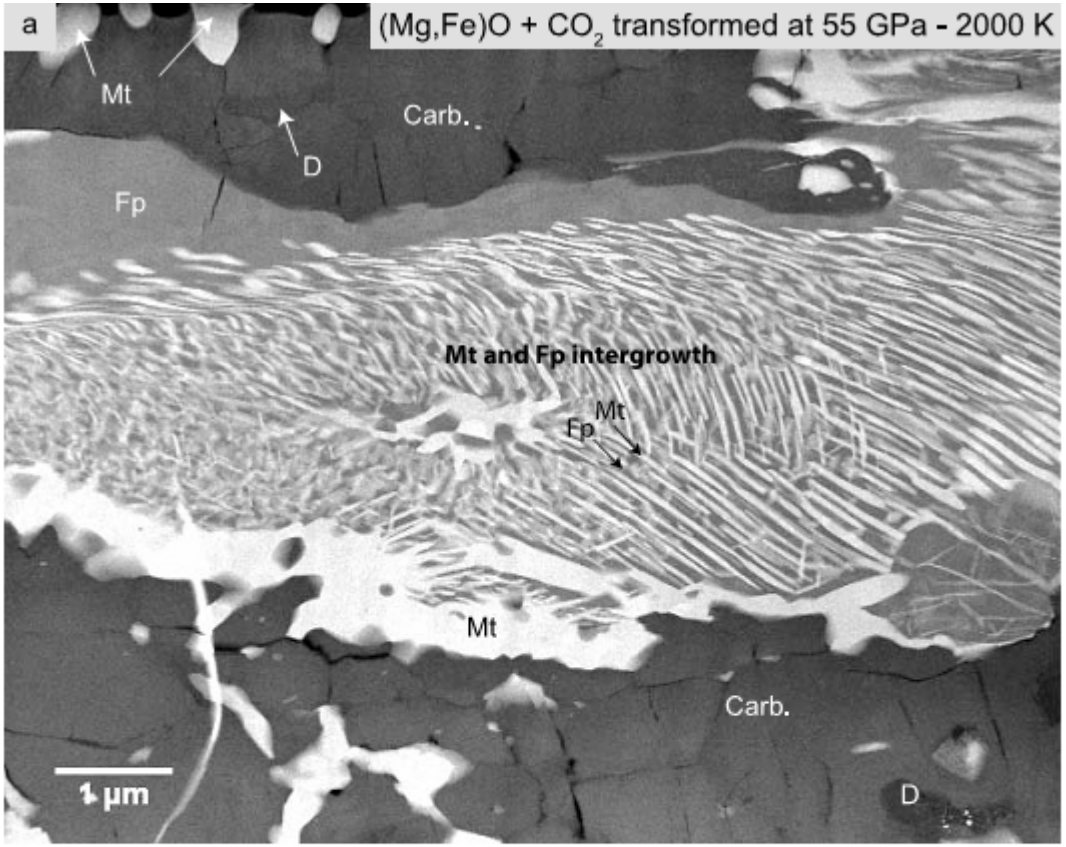
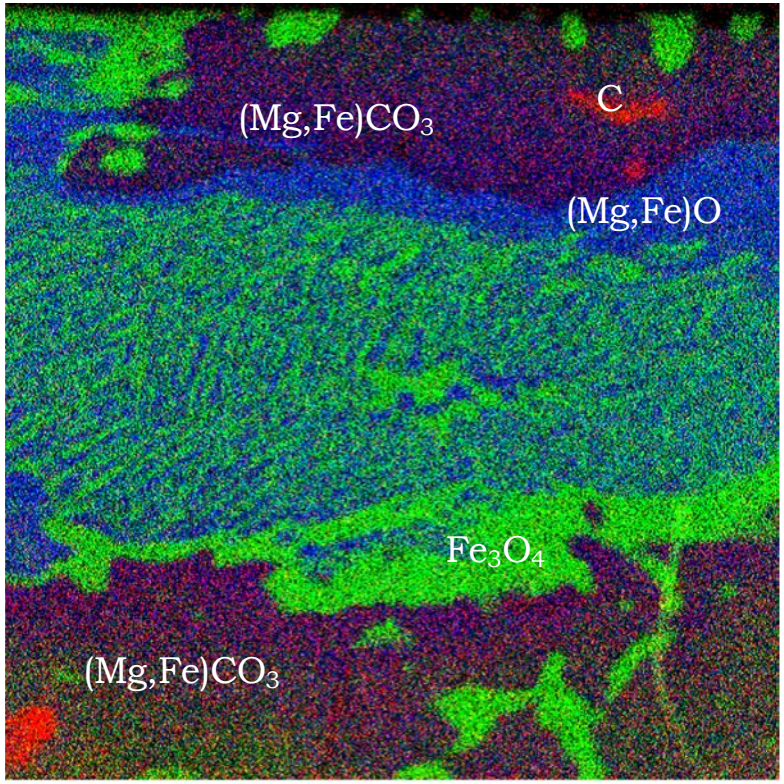
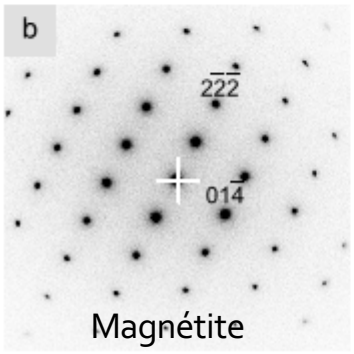
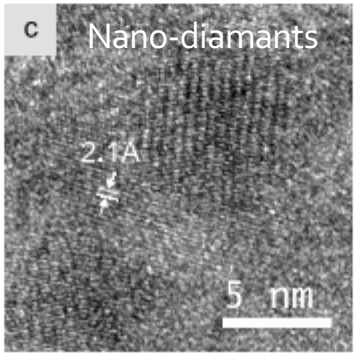
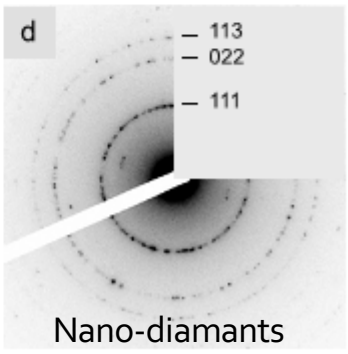


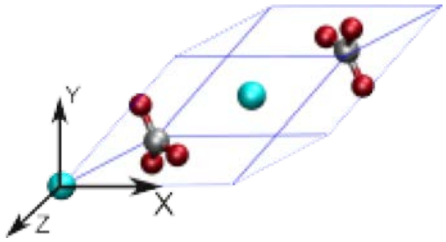
EDX map : C Fe Mg











Boulard et al., JGR, 2012

e⁻ diffraction

High Resolution Imaging

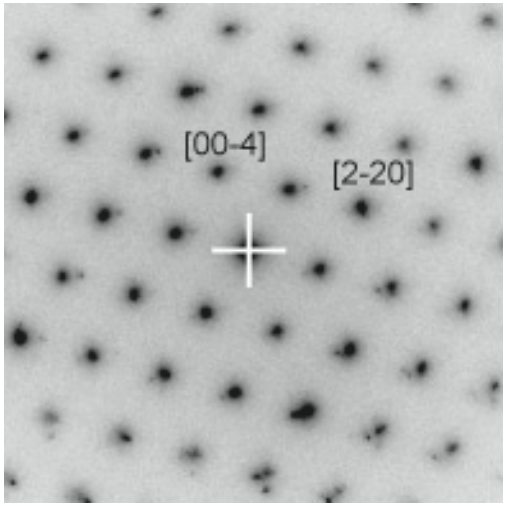
1) Coexistence of Carbonates with Iron Oxides

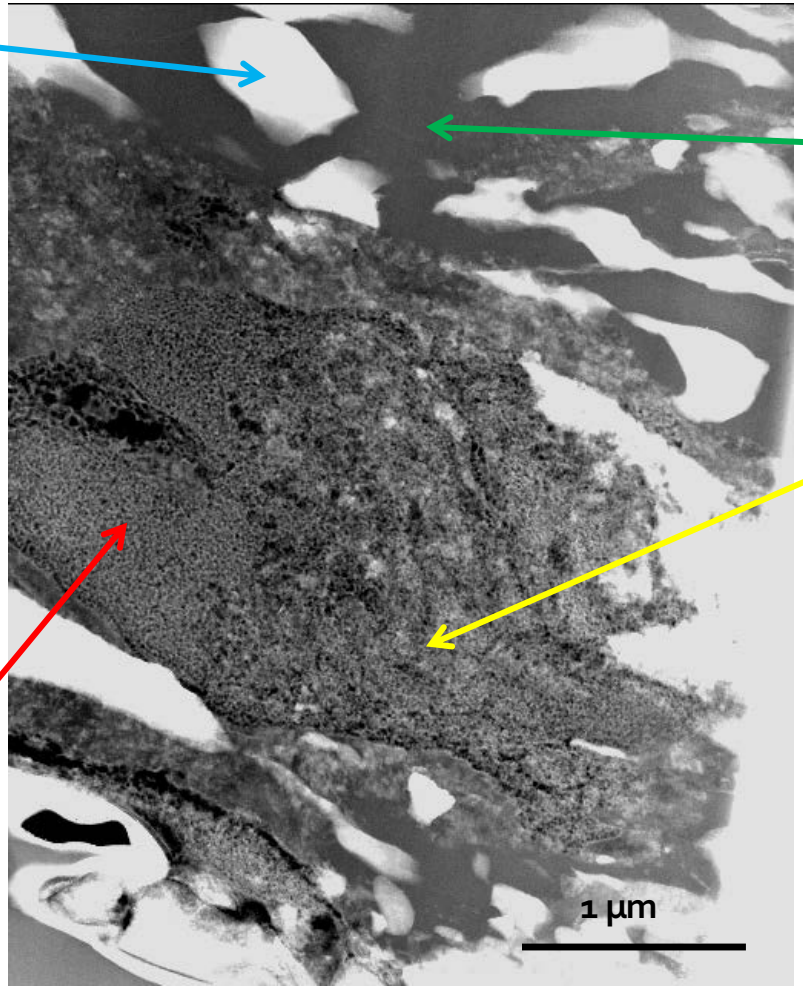
(Mg,Fe)O + CO_2 transformed at 103 GPa- 2700 K (~2300 km)

STEM image

Magnetite
Fe_3O_4

e⁻ diffraction

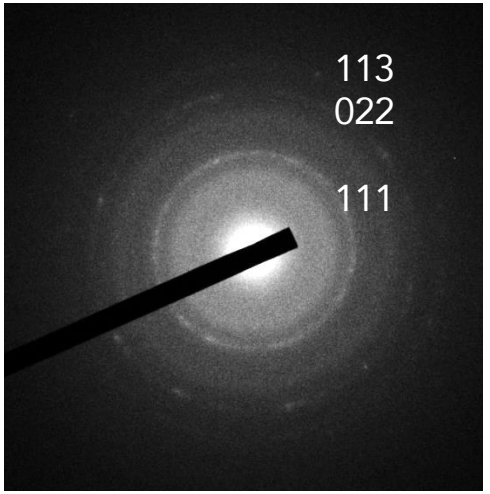




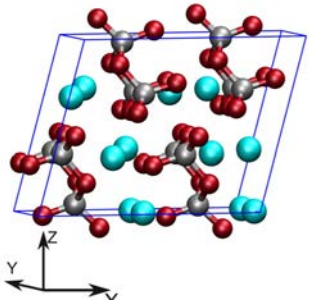
Ferropericlase
(Mg,Fe)O

Nano-diamonds
C

e⁻ diffraction

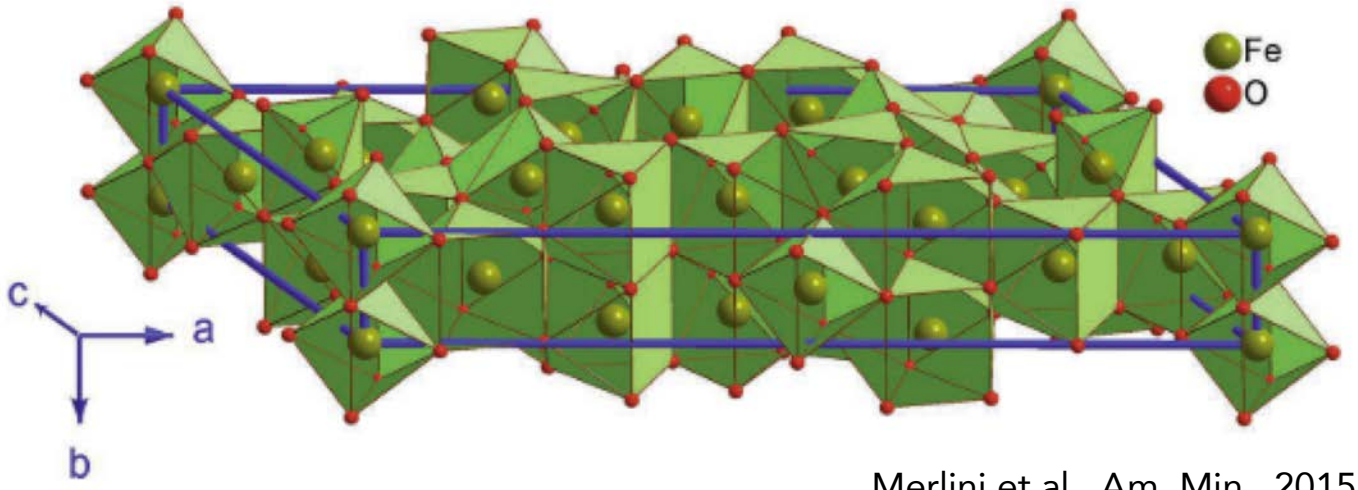


HPHT-(Mg,Fe)CO_3



1) Coexistence of Carbonates with Iron Oxides

$Fe_{13}O_{19}$ at 135 GPa – 2650 K

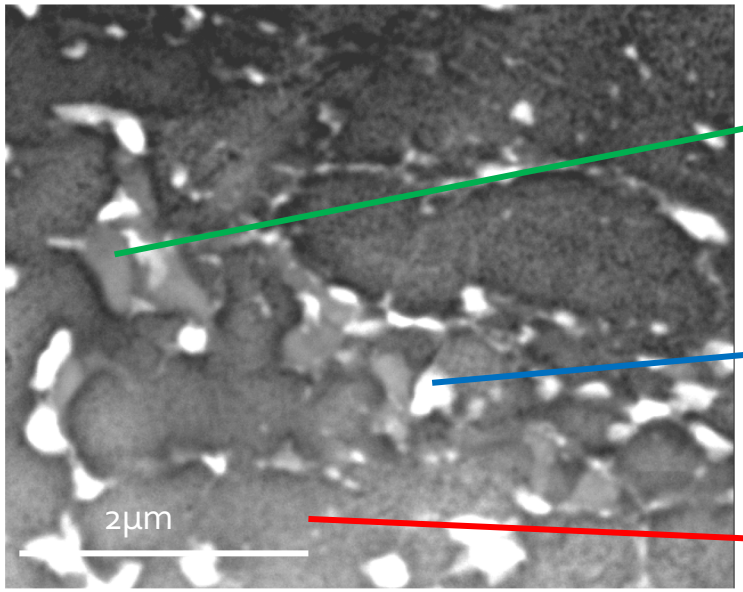


Merlini et al., Am. Min., 2015

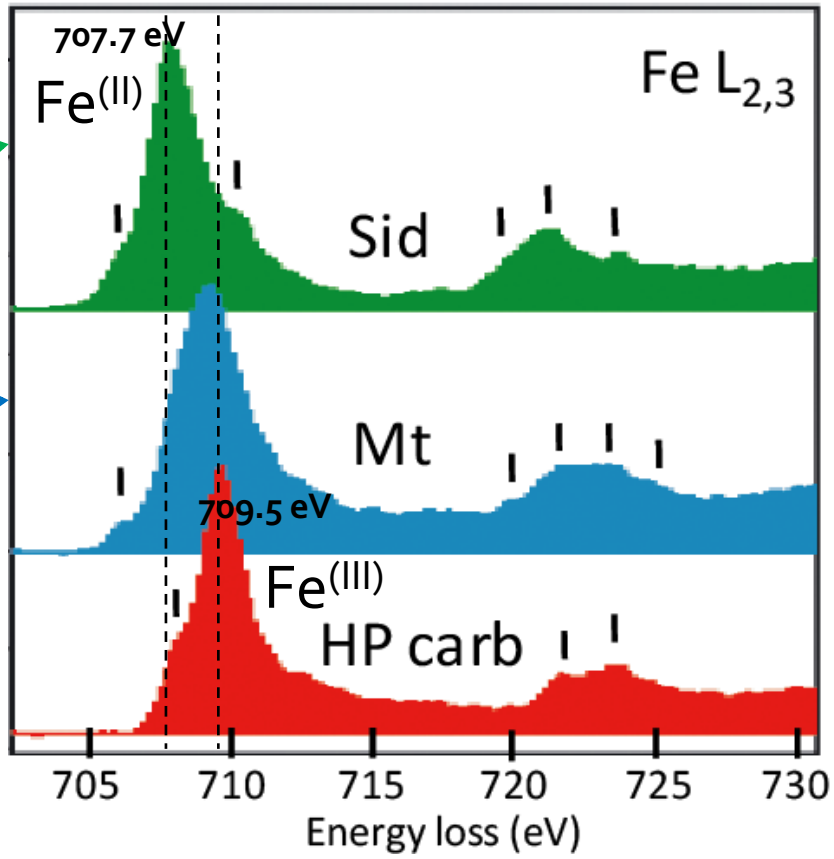
2) Fe^{3+} - rich « Carbonates »

$Mg_{0,25}Fe_{0,75}CO_3$ transformed at 80 GPa - 2300 K (~1870 km)

STEM picture



Electron Energy Loss Spectroscopy (EELS)



Boulard et al., PNAS, 2011

Self Redox Reactions

Iron Oxidation:

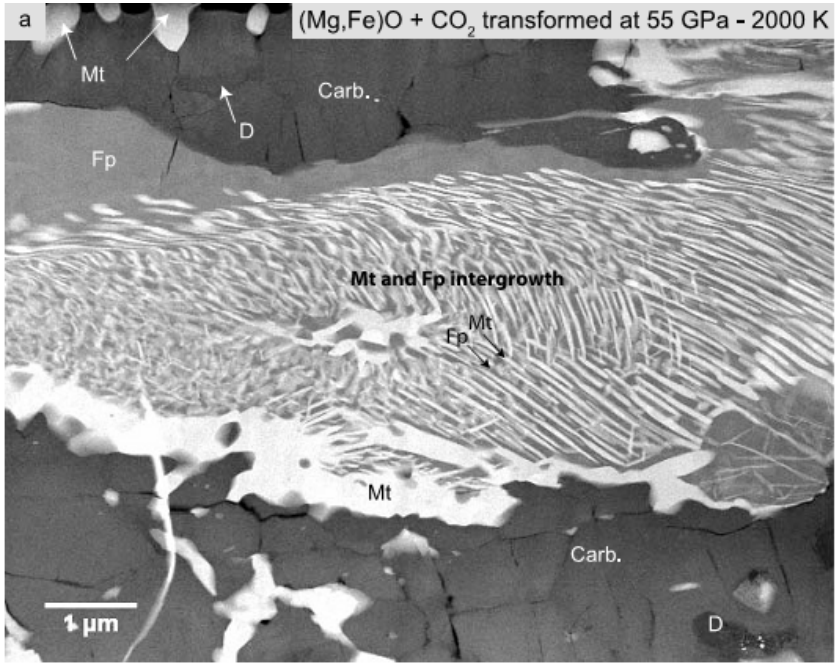
$Fe^{(II)} \longrightarrow Fe^{(III)}$

Carbon Reduction:

$CO_2 \rightarrow C$

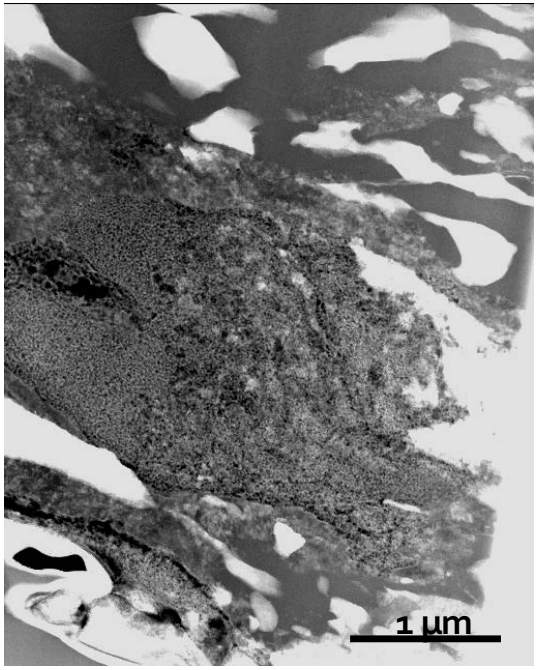
At low pressure :

Carbonate Fe^{2+} + magnetite (Fe_3O_4) + diamant (C)

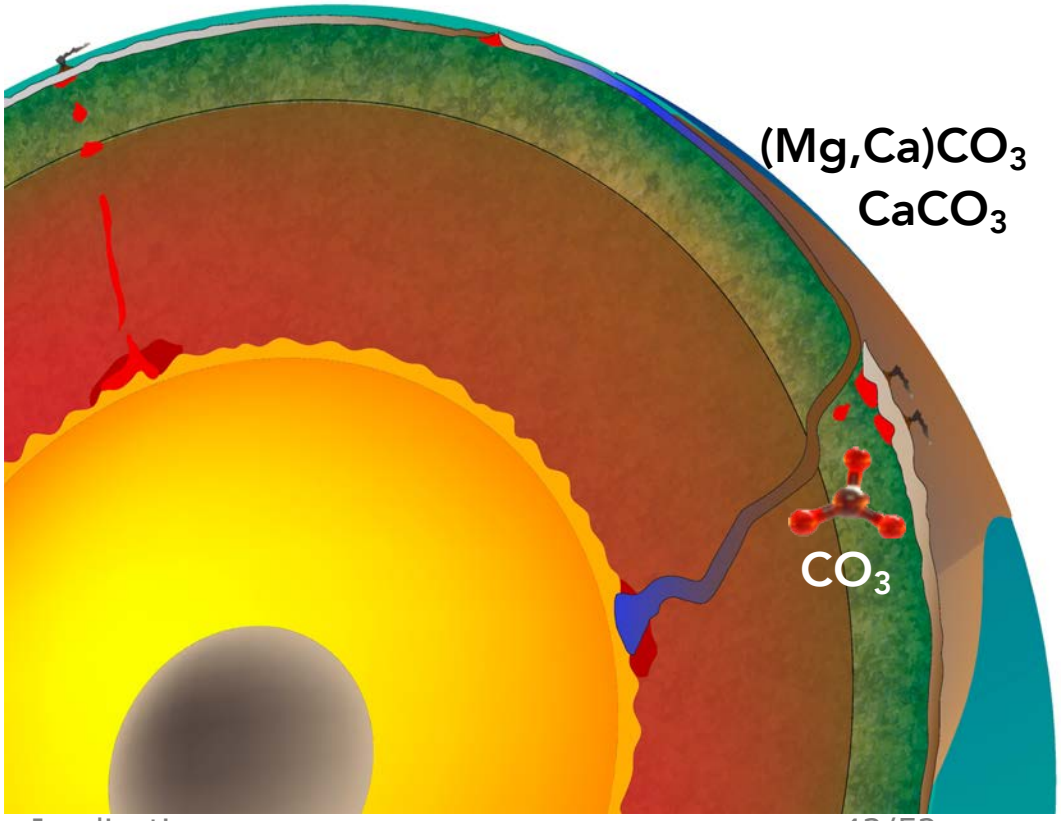


At high pressure :

Carbonate Fe^{3+} + magnetite (Fe_3O_4) + diamant (C)

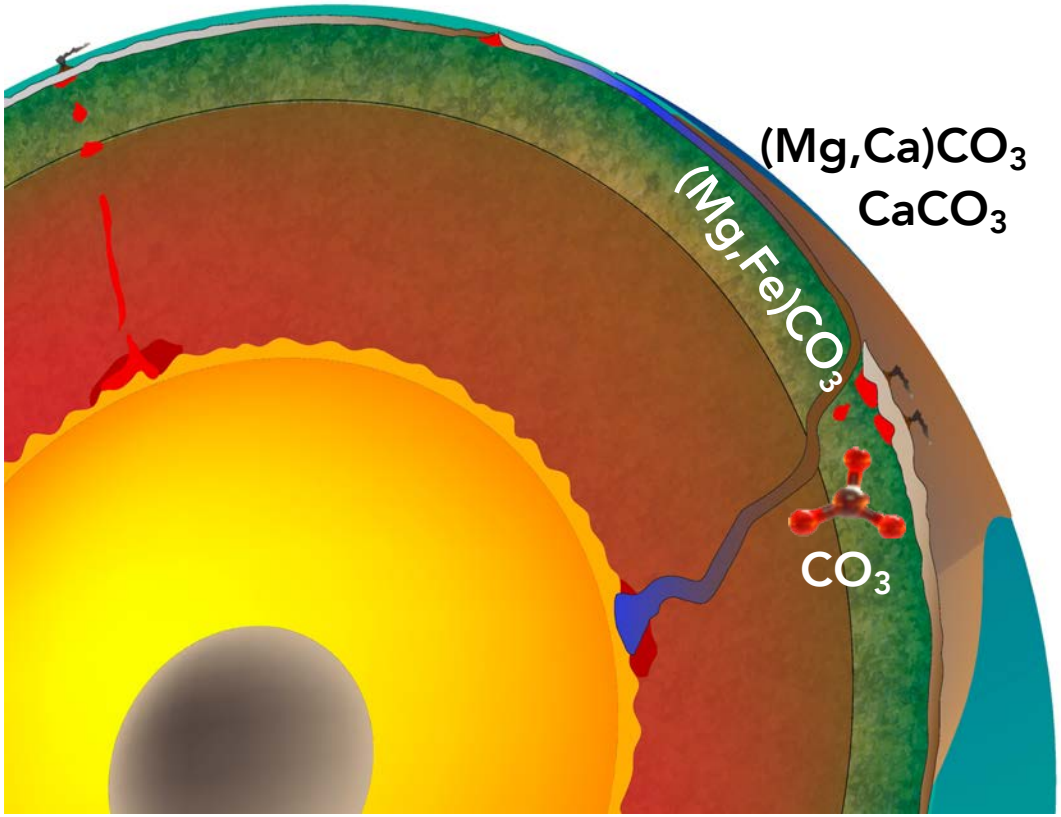


The Deep Carbon Cycle



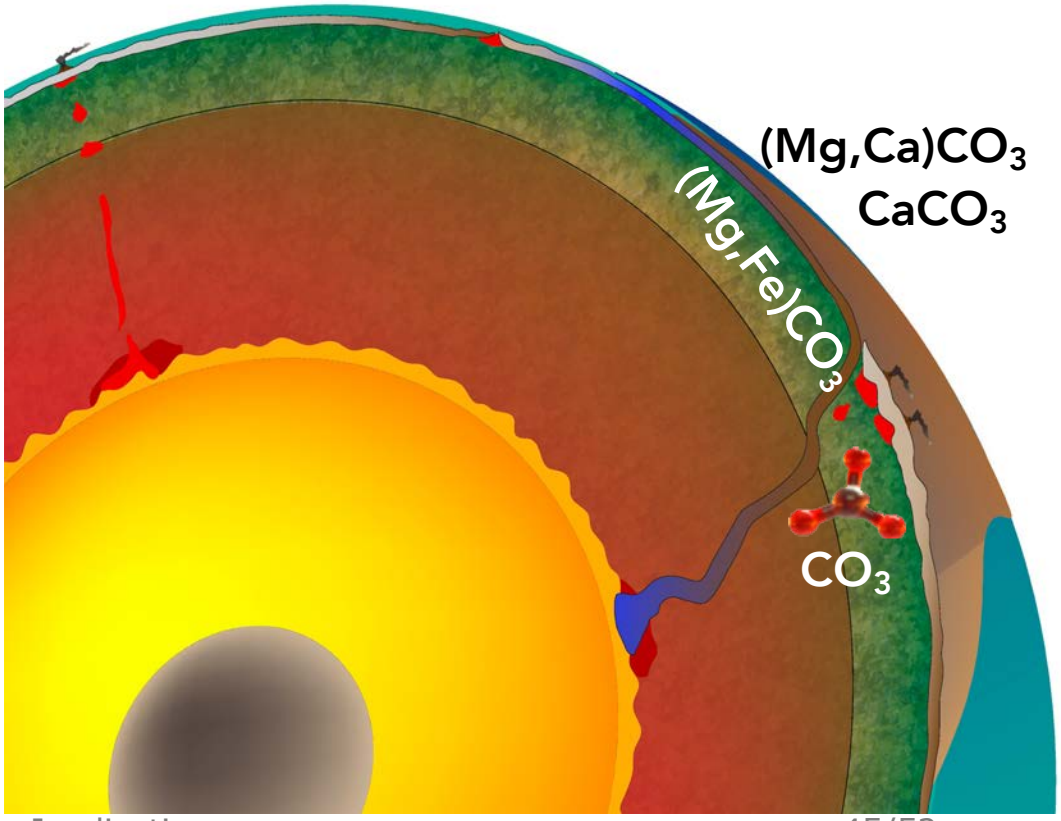
The Deep Carbon Cycle

- Reactions with ferromagnesian silicates : carbonates change their composition



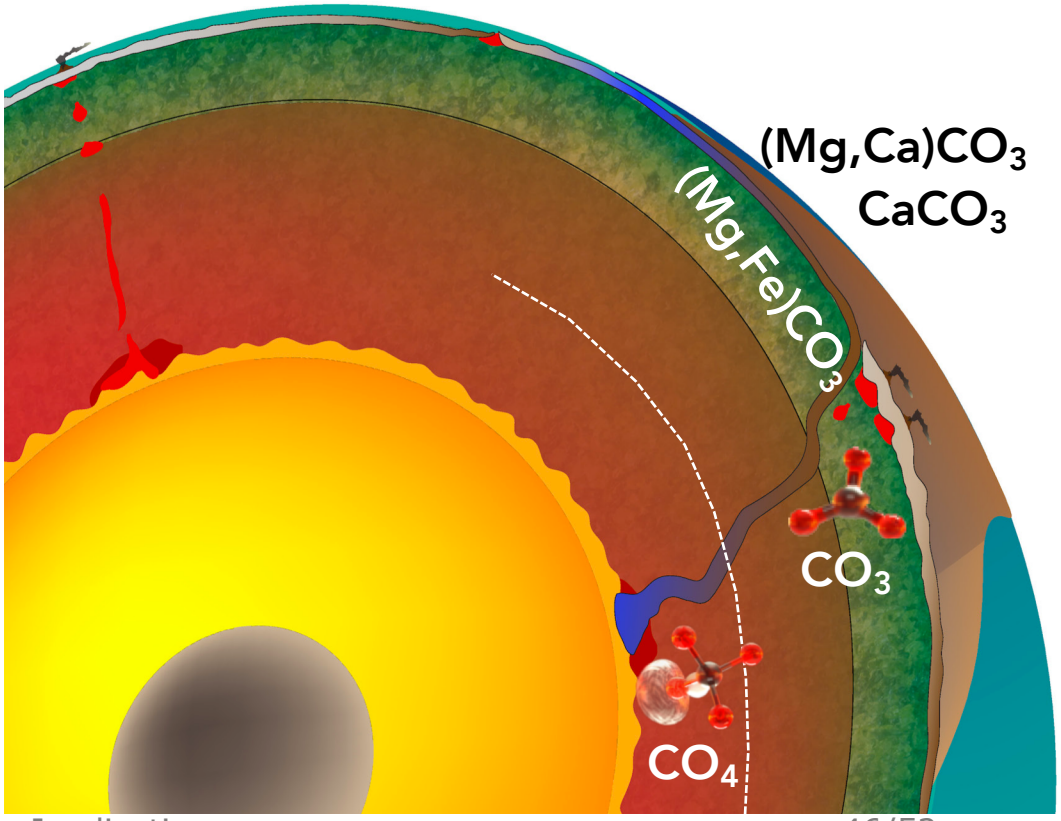
The Deep Carbon Cycle

- Reactions with ferromagnesian silicates : carbonates change their composition
- Mg-Fe carbonate phases can host and transport carbon in the deep mantle



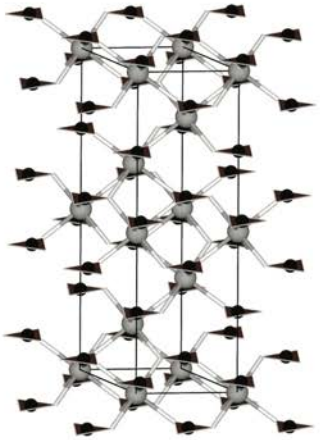
The Deep Carbon Cycle

- Reactions with ferromagnesian silicates : carbonates change their composition
- Mg-Fe carbonate phases can host and transport carbon in the deep mantle
- Below 1500 – 2000 km deep: structural changes with a new carbon coordination



High Pressure Structures of Mg-Fe Carbonates

A)

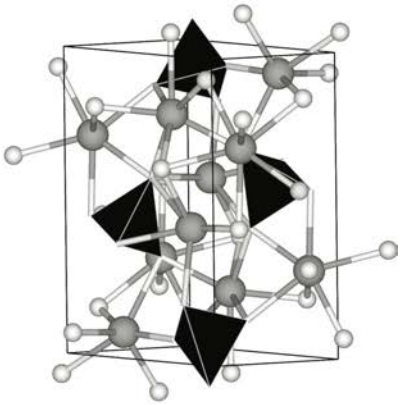


$(Mg,Fe)CO_3$ (RP-RT)

B)

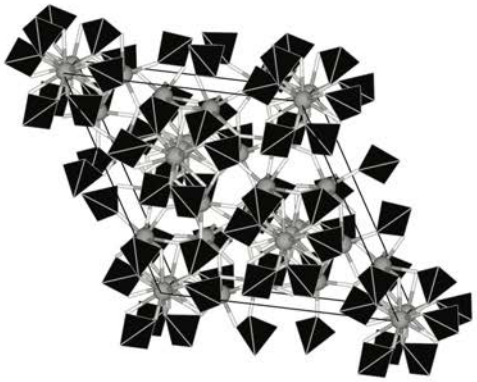
$Mg_{0.25}Fe^{III}_{0.3}(C_3O_9)_{0.233}$
Boulard et al., 2011

C)



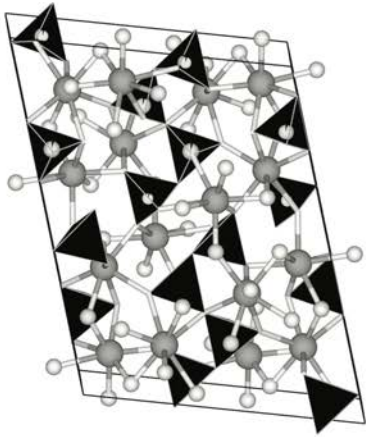
$Fe^{III}_4C_3O_{12}$
Boulard et al., 2012

D)



$Fe^{III}_4C_3O_{12}$
Cerantola et al., 2017

E)

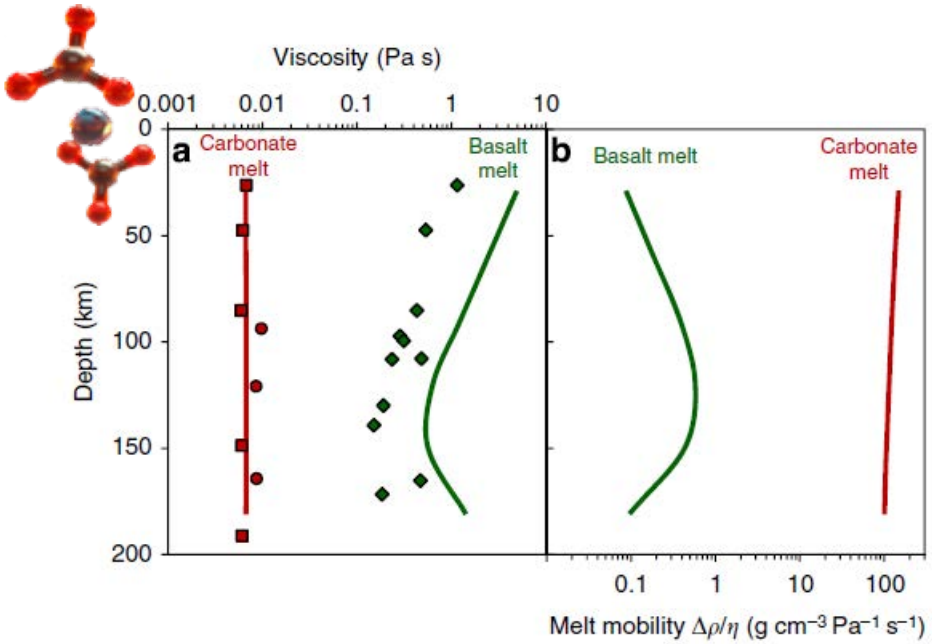


$(Mg,Fe^{III})_2Fe^{III}_2C_3O_{12}$
Merlini et al., 2015; Cerantola et al., 2017

+ Isshiki et al., 2004
Liu et al., 2015
...

Boulard et al., AGU monograph "Carbon in Earth's Interior", 2020

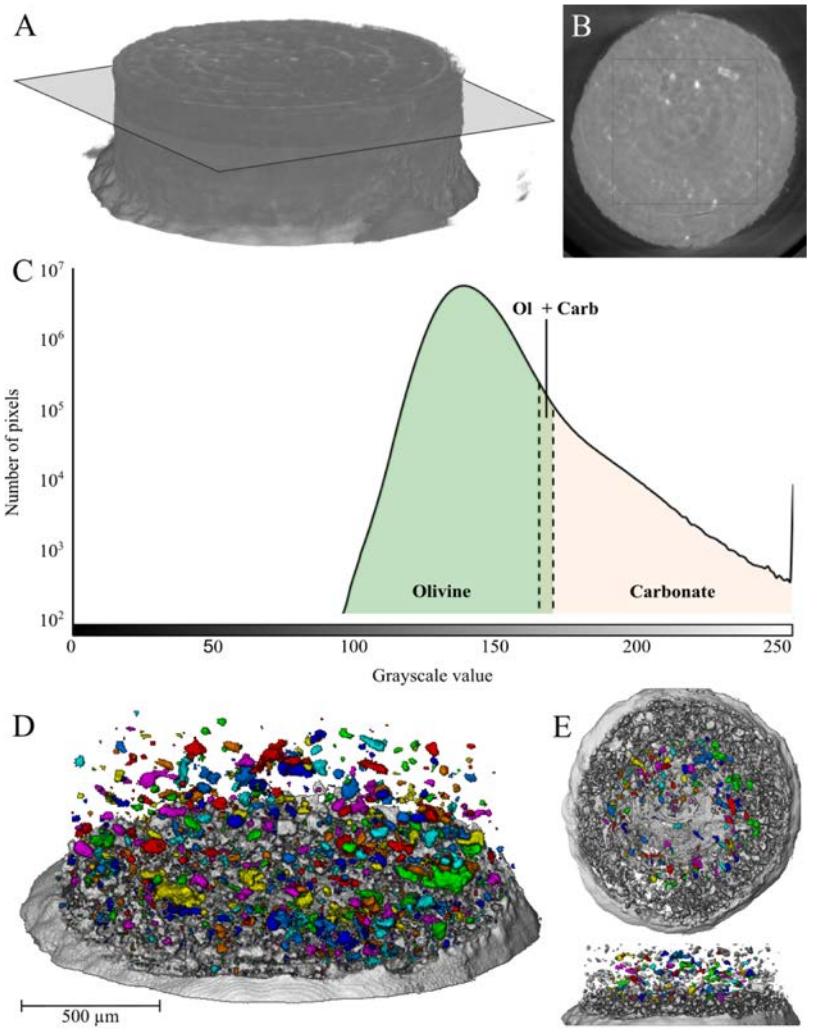
New Carbon Coordination



Kono et al., Nat. Com., 2014

Very low viscosity of carbonate melt at "low" pressure

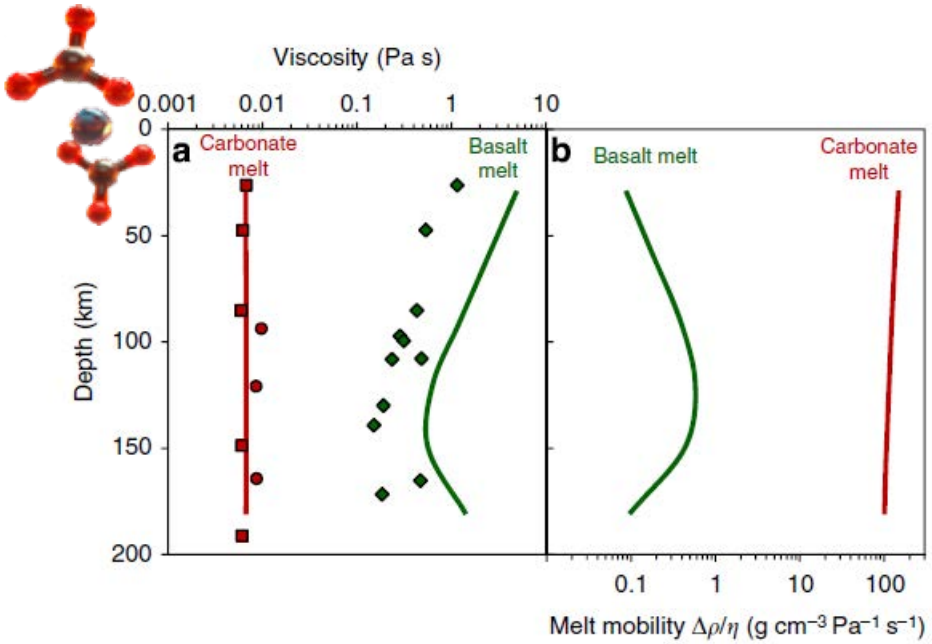
In situ 3D Imagery at high pressure and temperature



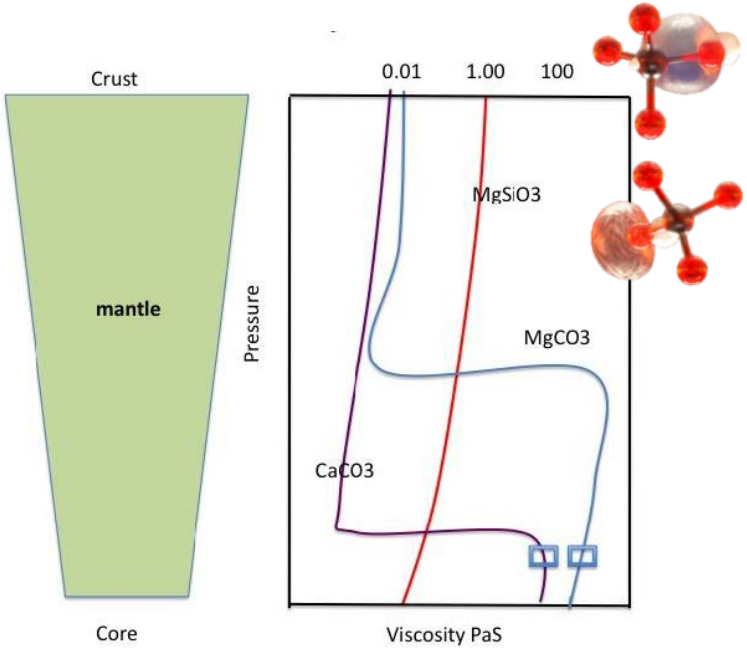
Giovenco et al., 2022

New Carbon Coordination

Sanloup et al., Front. Earth Sci., 2019



Kono et al., Nat. Com., 2014



Jones and Oganov, 2010

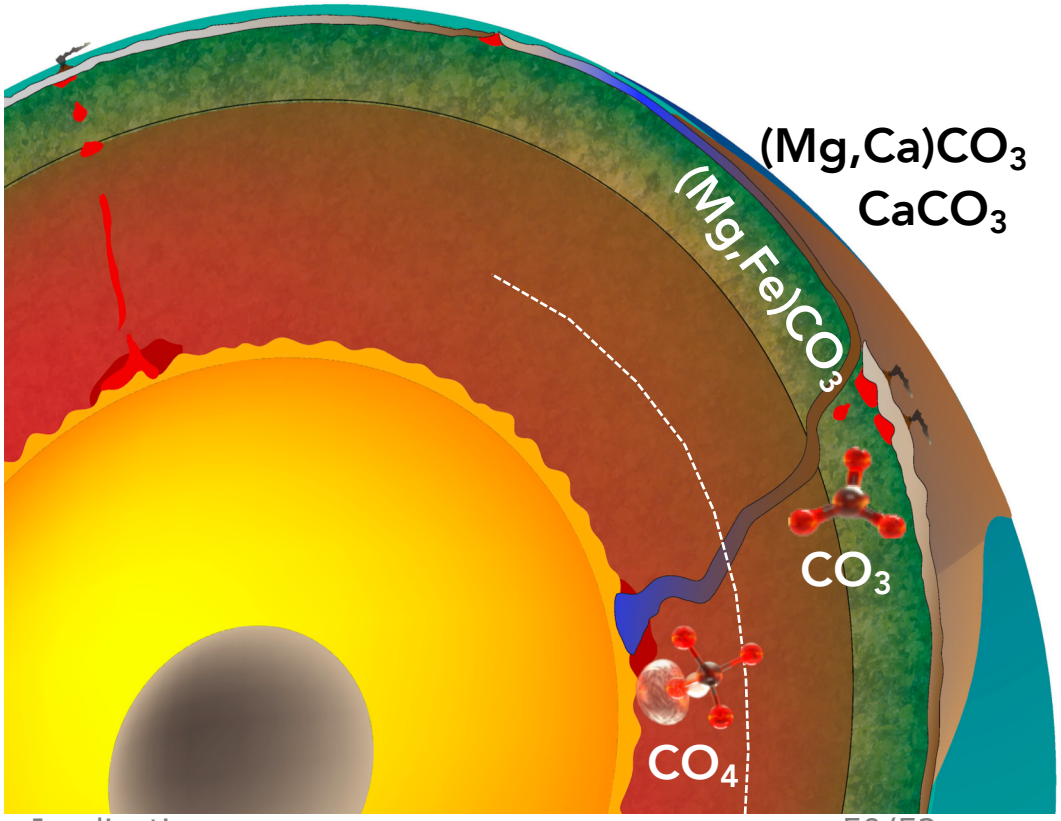
High viscosity at high pressure

Effect of the Composition Mg, Fe VS Fe ?

The Deep Carbon Cycle

- Reactions with ferromagnesian silicates : carbonates change their composition
- Mg-Fe carbonate phases can host and transport carbon in the deep mantle
- Below 1500 – 2000 km deep: structural changes with a new carbon coordination

➢ Possible deep carbon reservoir?



The Deep Carbon Cycle

- Reactions with ferromagnesian silicates : carbonates change their composition
- Mg-Fe carbonate phases can host and transport carbon in the deep mantle
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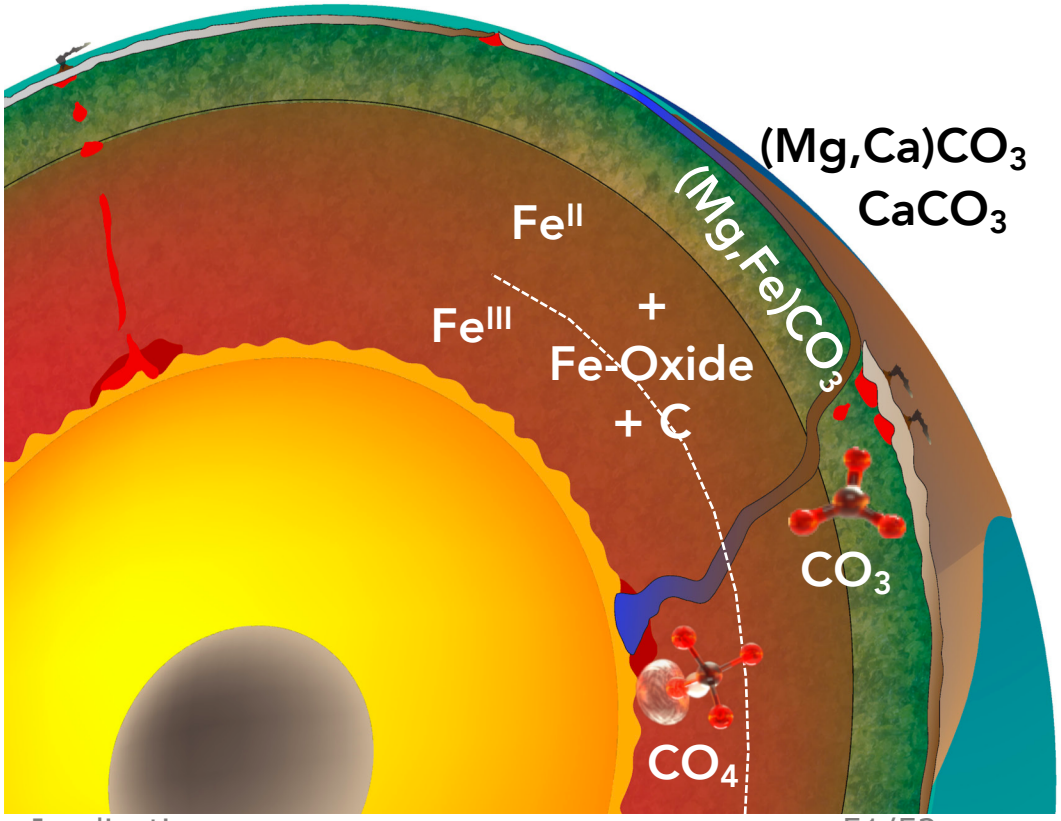
  - Possible deep carbon reservoir?

- Self Redox reactions of Fe-rich carbonates : partial reduction of carbon et oxidation of iron

  - Possible Al-rich phases in the deep mantle?



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