GeoRAMAN School for students and young scientists

SUBLITHOSPHERIC MINERAL ASSOCIATIONS OF INCLUSIONS IN SUPERDEEP DIAMONDS

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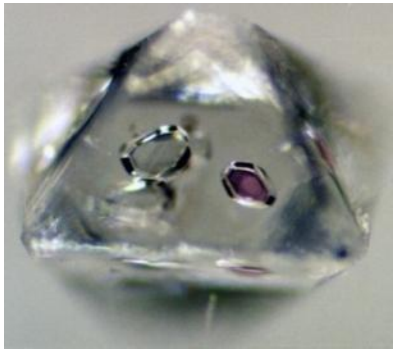
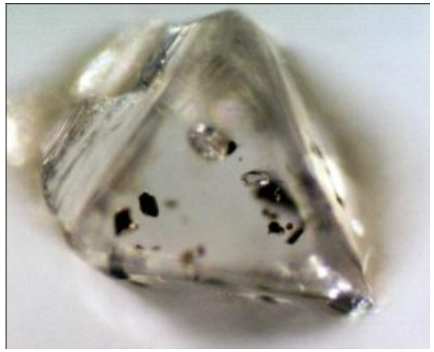
*THE REAL SCIENCE

Lithospheric diamonds





Crystalline inclusions in diamonds from the subcontinental lithospheric mantle (SCLM) testify that diamonds grow in a range of *peridotitic (P-type)* and *eclogitic (E-type)* host-rocks.

Diamond Inclusions

❖**P-type**

Ol, Grt, Opx,

CPx, Chr

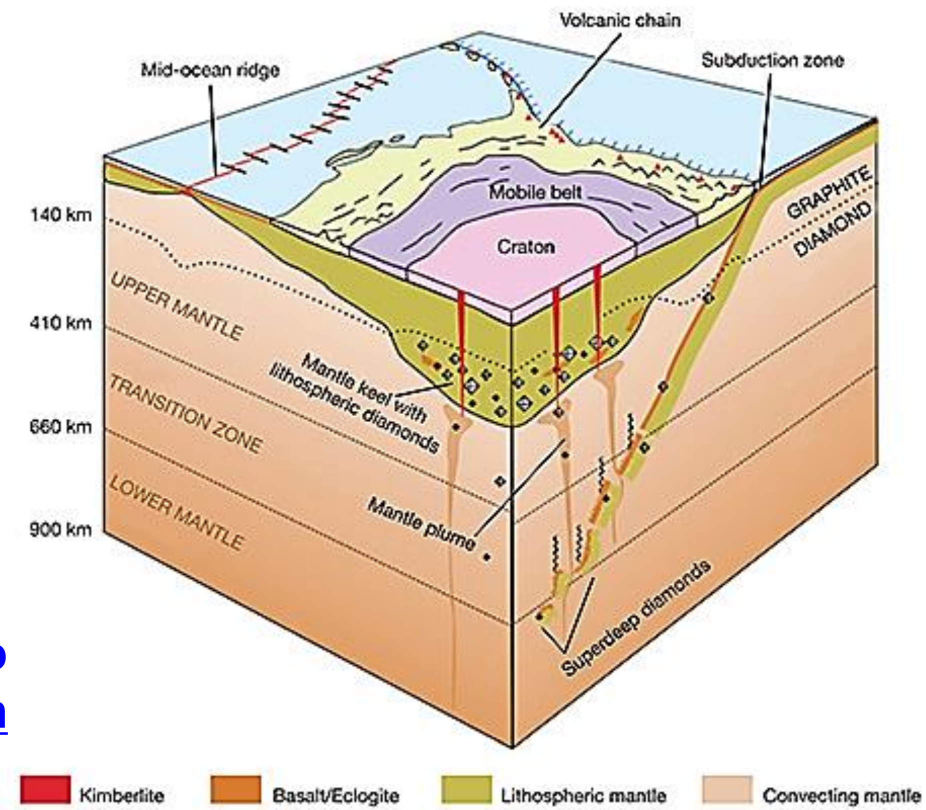
Phl, Ilm, Sph

❖**E-type**

CPx, Grt,

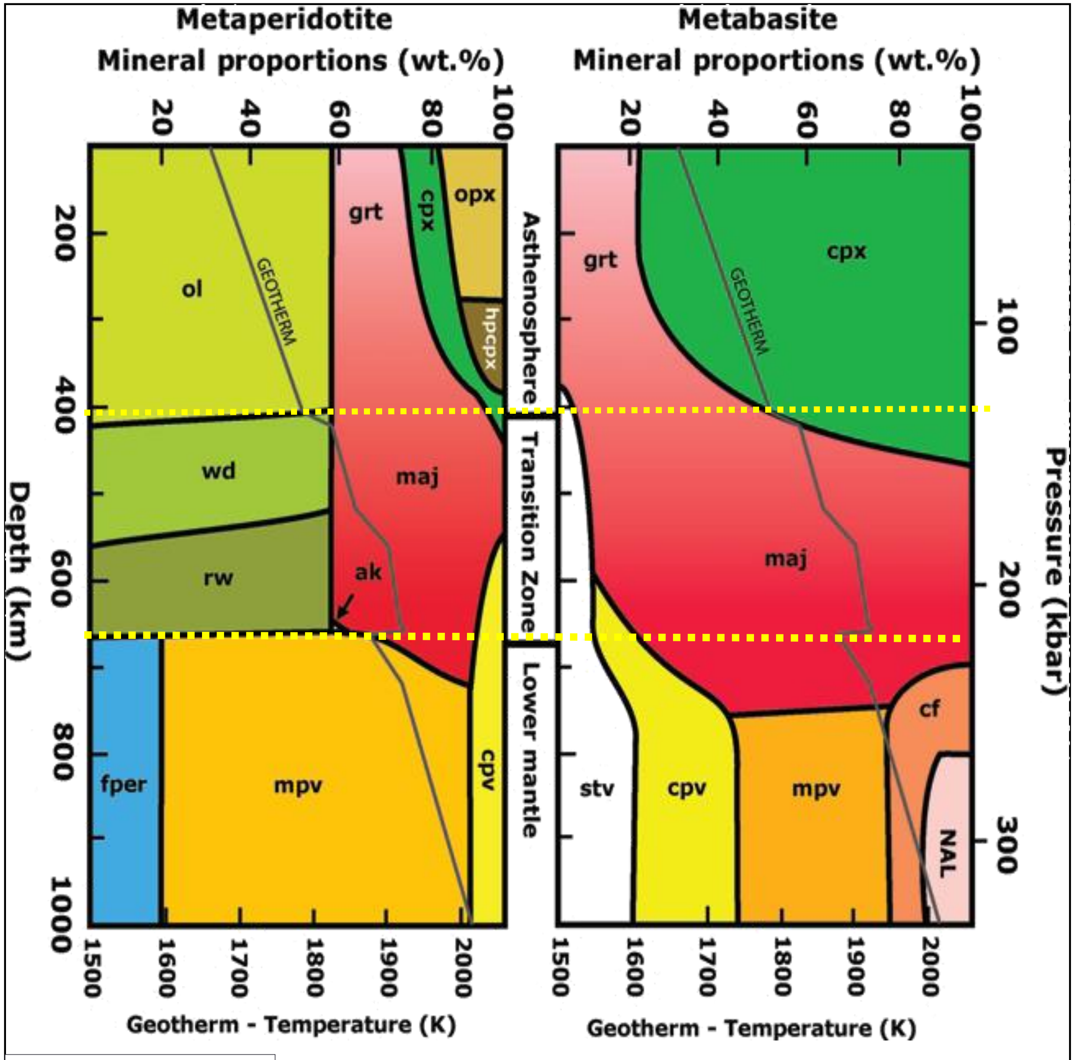
Coe, Ky, Rt, KFsp,

Cor, Ilm, Sph



Both associations commonly testify to diamond growth at depths 150÷250 km and at temperatures of 900÷1300°C.

Diamond Inclusions



Harte, 2010

Mantle Petrology: Field Observations and High Pressure Experimentation: A Tribute to Francis R. (Joe) Boyd
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Editors: Yingwei Fei, Constance M. Bertka, and Bjorn O. Mysen

Lower mantle mineral associations in diamonds from São Luiz, Brazil

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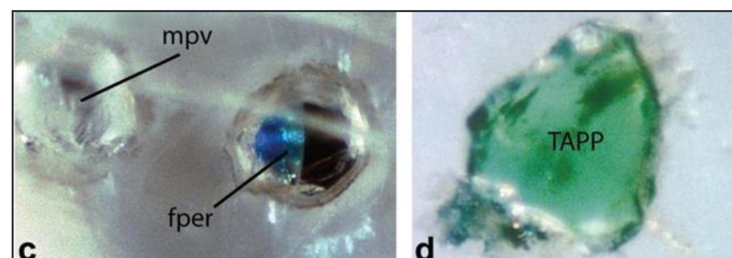
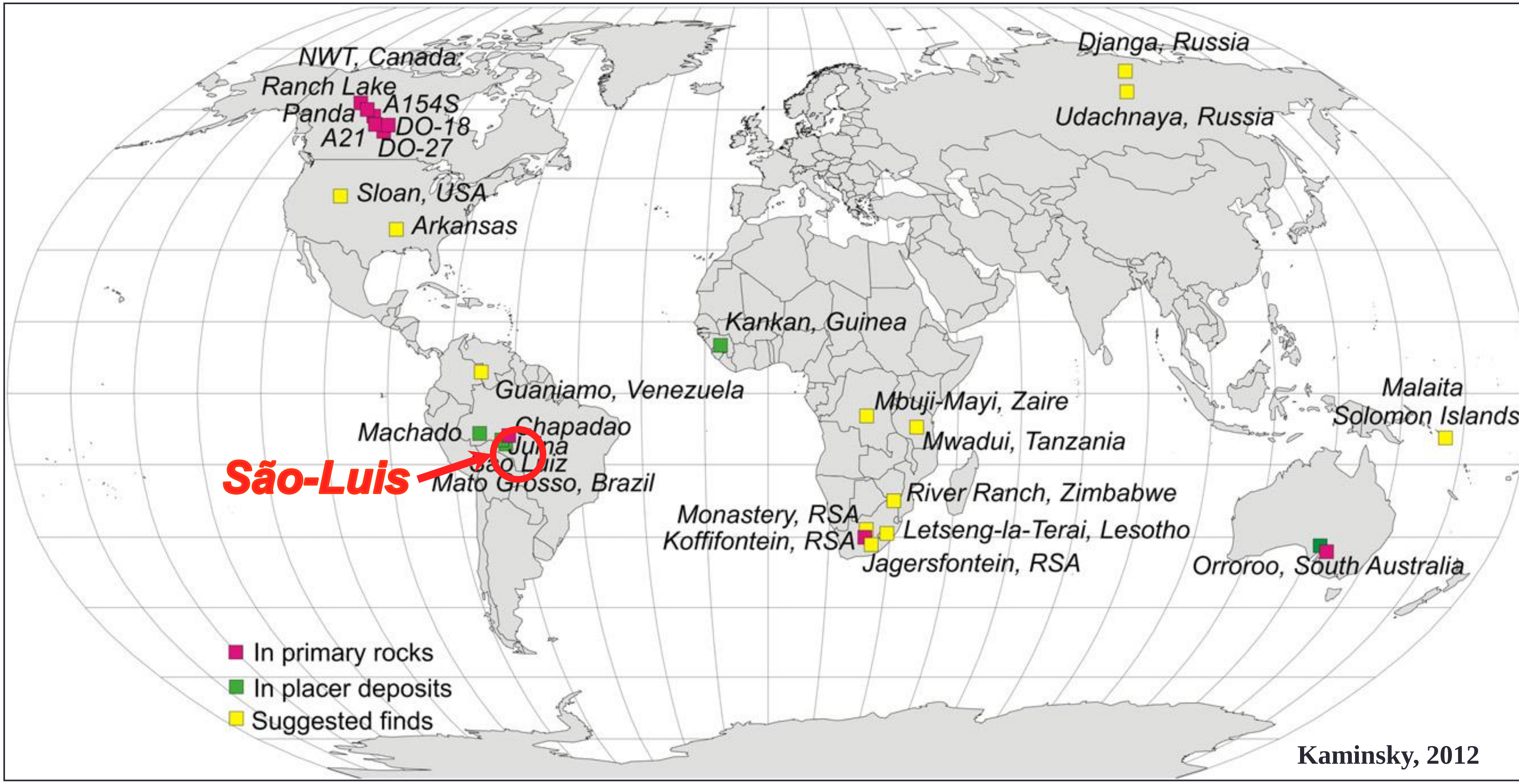
- MgSi-Pv, fPer, CaSi-Pv
- Maj-Grt, SiO_2 (Stv?)
- TAPP



Sublithospheric (Superdeep) Diamonds

Superdeep Diamonds

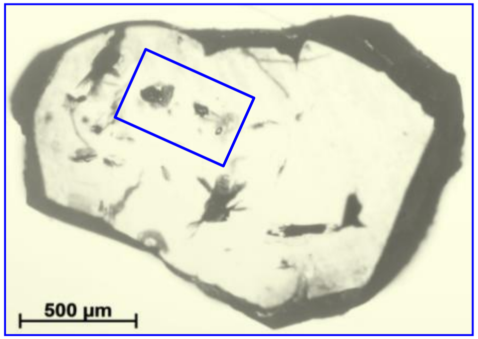


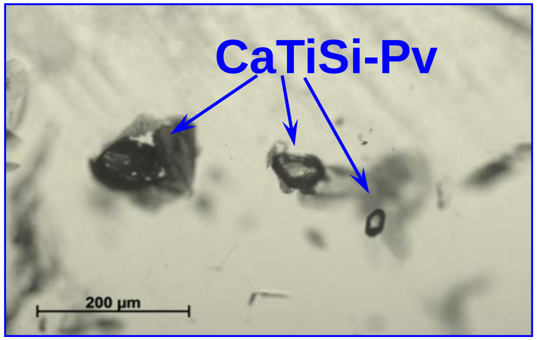
Kaminsky, 2012

Diamonds from <u>São-Luis</u> river deposits (Juina, Brazil) are known to have originated from the depths of the *Transition Zone* (TZ) and *Lower Mantle* (LM).

Mineral inclusions

Mineral inclusions have been found in 61 diamonds





common

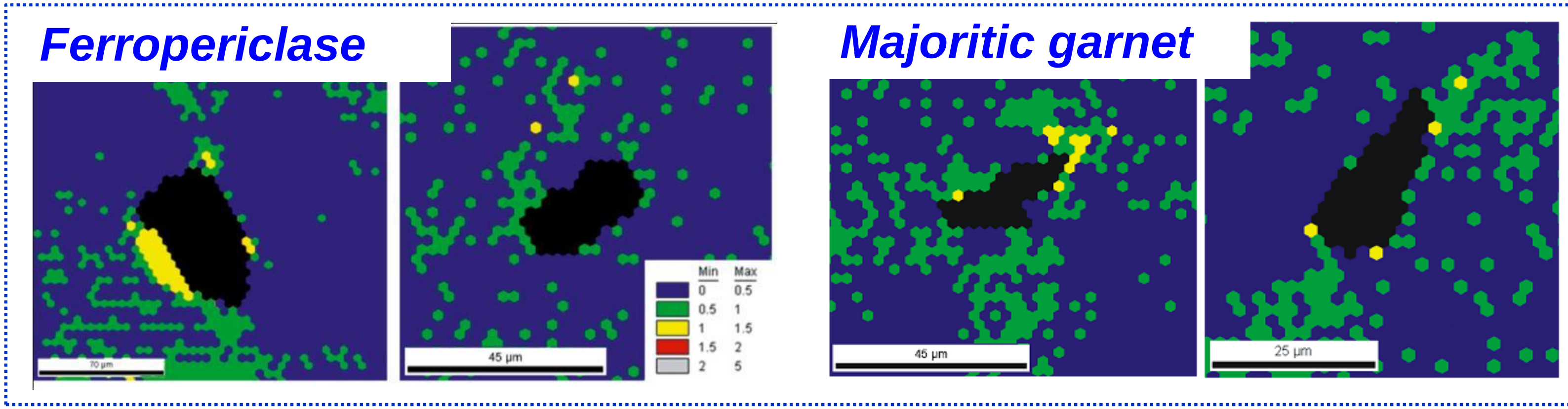
- ❑ Majoritic garnets (±Clinopyroxene)
- ❑ CaSi-perovskite (±CaTi-perovskite)
- ❑ Ferropericlase
- ❑ MgSi-perovskite (Bridgmanite)
- ❑ Olivine (Wadsleyite, Ringwoodite?)
- ❑ TAPP (Tetragonal Almandine-Pyrope Phase - Jeffbenite)
- ❑ SiO_2 (Coesite±kyanite=Stishovite?)
- ❑ Al-Si-phase

rare

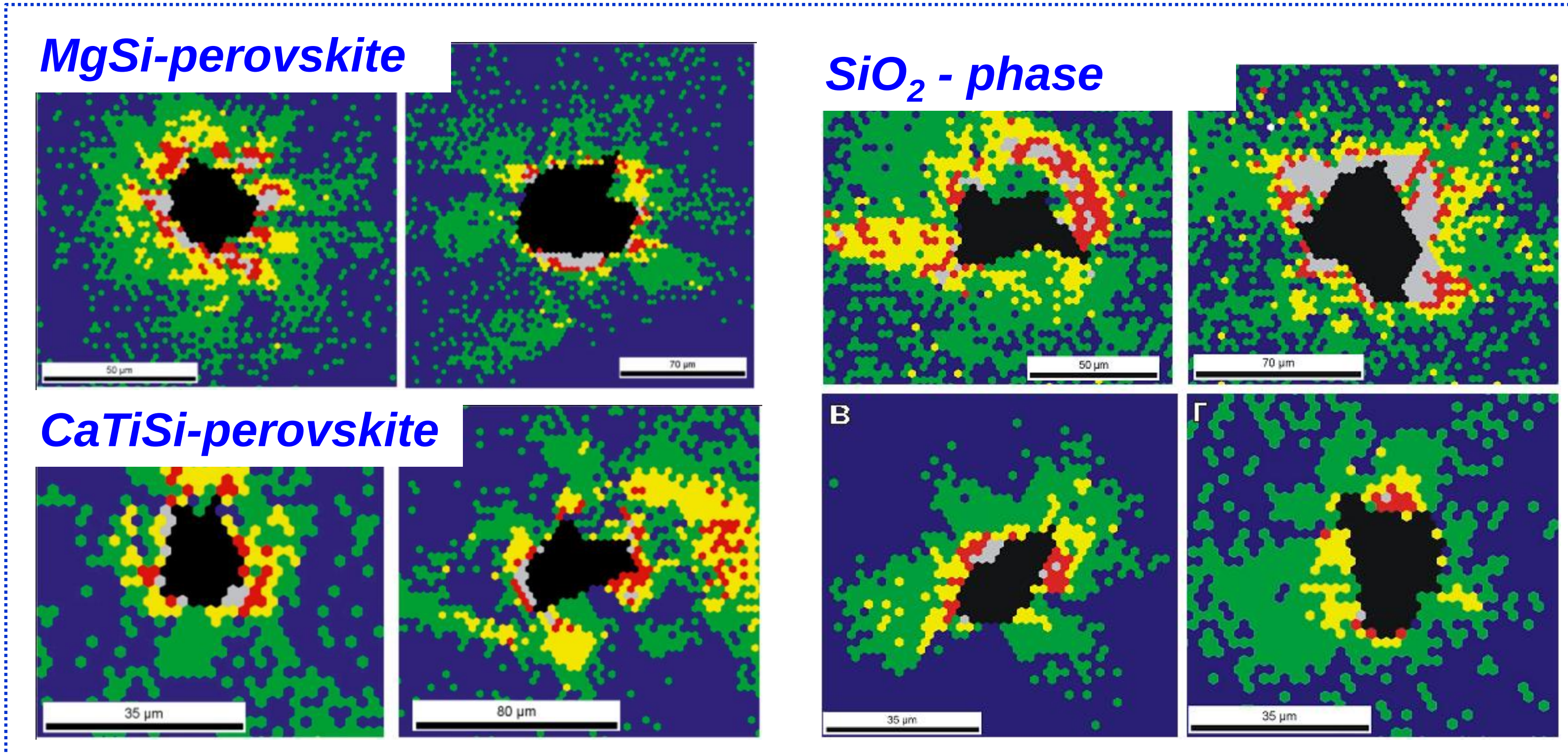
- ○ K-feldspar (K-hollandite?)
- ○ Cr-pyrope
- ○ Grossular (CAS?)
- ○ Merwinite
- ○ Nepheline+Spinel (NAL?, CF?)
- ○ Metallic Iron
- ○ Fe-sulphides
- ○ Carbonates ($MgCO_3$, $CaCO_3$)

Mineral inclusions

No phase transition



Phase transition



Mineral inclusions

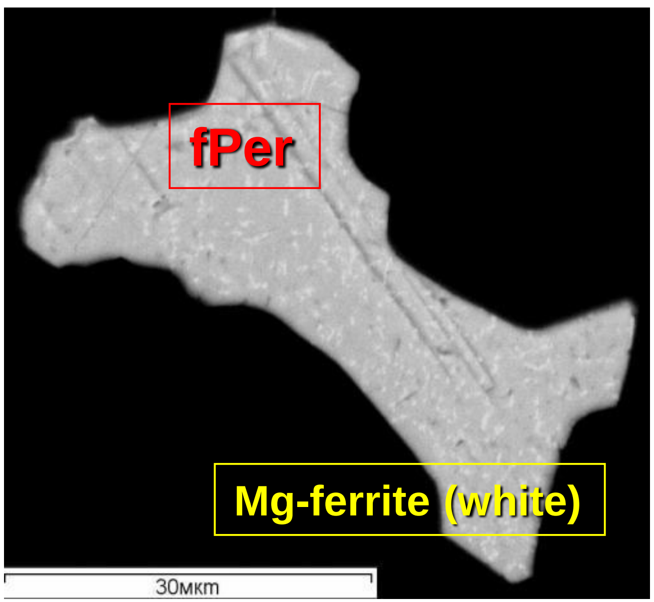
Ferropericlase (Mg,Fe)O

Mg# 0.1÷0.8

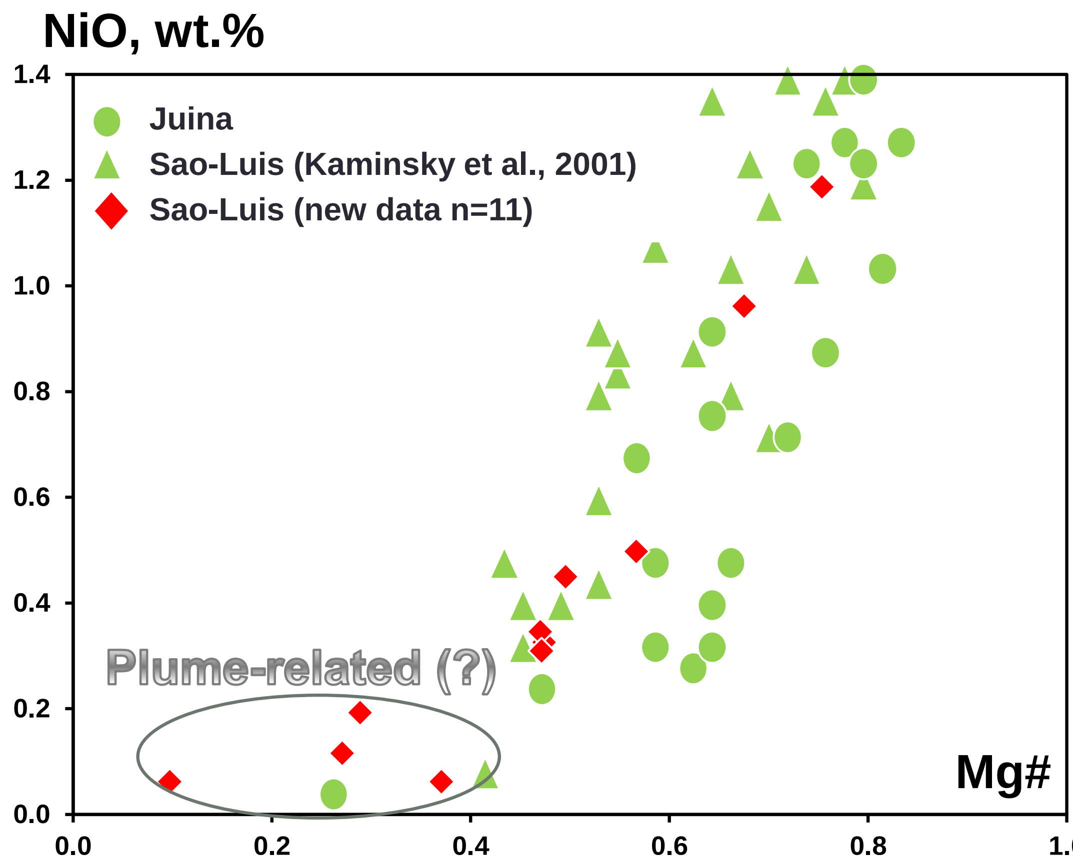
Associations

fPer+Ol

fPer+MgSi-Pv

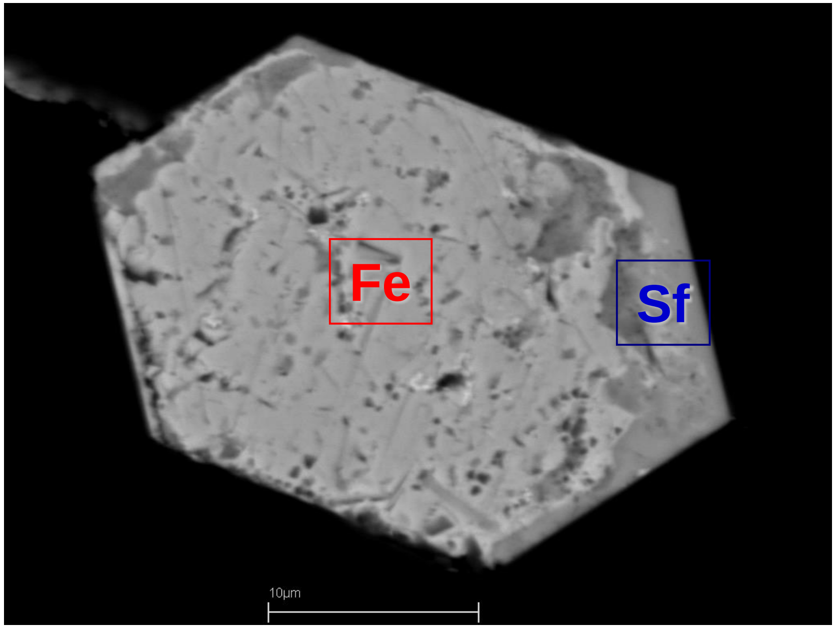


Mg-ferrite ($MgFe_2O_4$)



Mineral inclusions

Metallic Iron



Disproportionating of Fe^{2+} into Fe^{3+} strongly incorporated in MgSi-Pv and Fe^{0} results in the appearance of a metal phase (Ryabchikov, Kaminsky, 2014).

The formation of the metal phase as a result of FeO disproportionation should result in an increase of Mg# of both fPer and MgSi-Pv.

Mineral inclusions

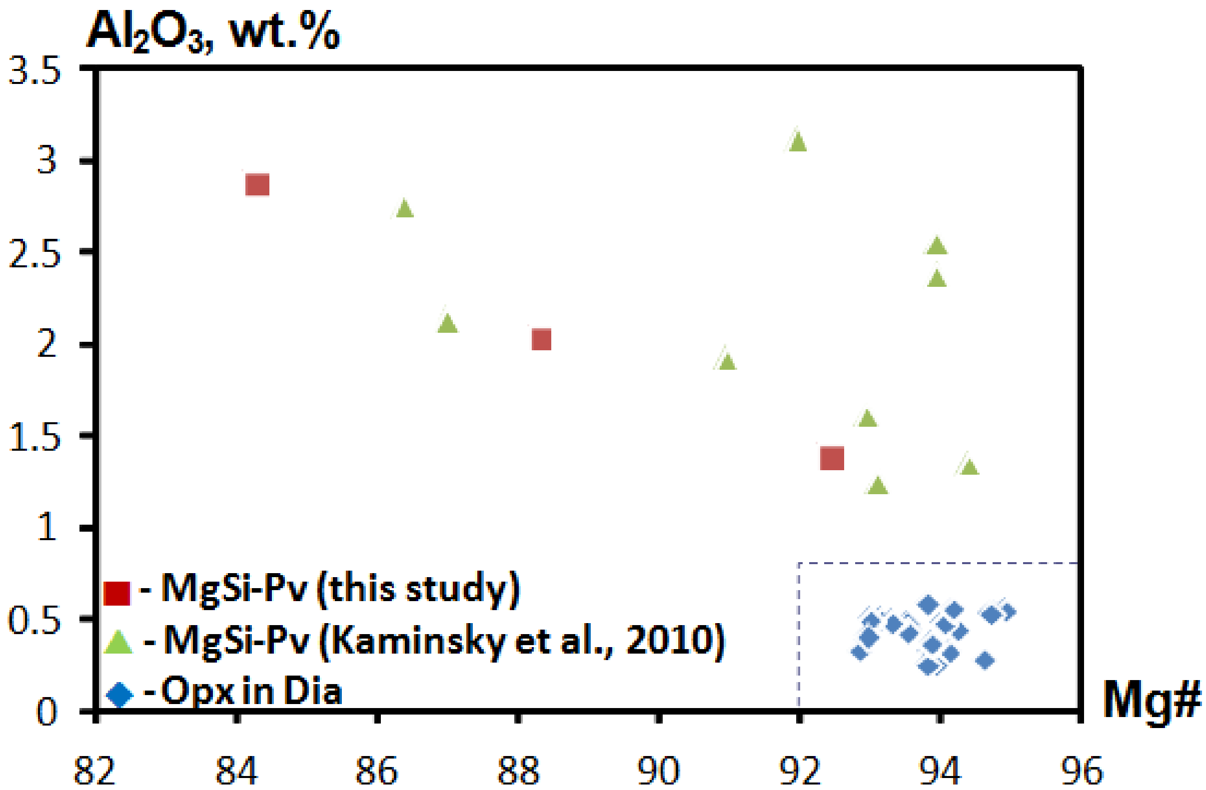
MgSi-perovskite (Bridgmanite) $MgSiO_3$

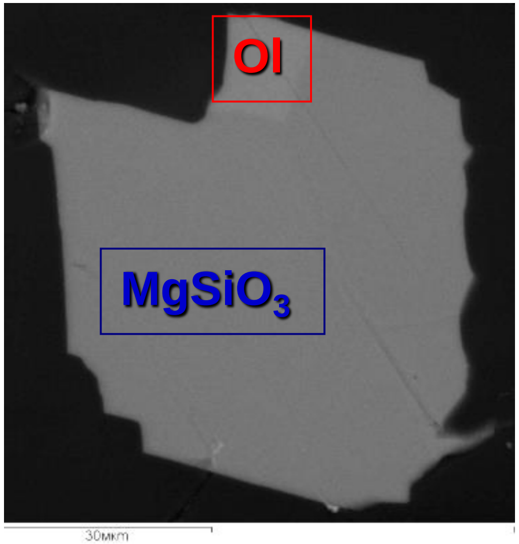
Associations

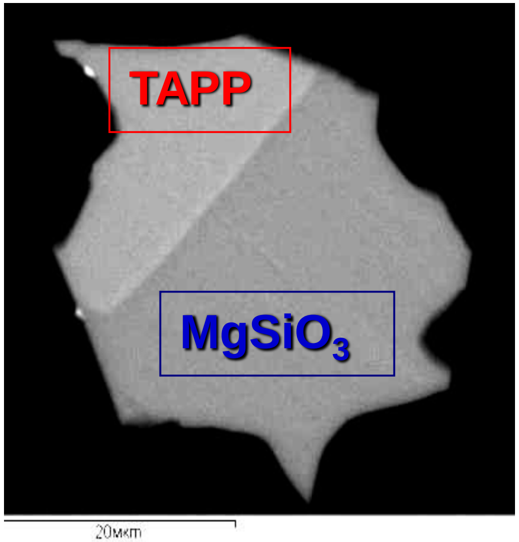
<u>MgSi-Pv+fPer</u>

MgSi-Pv+Ol+CaSi-Pv

MgSi-Pv+TAPP+CaSiTi-Pv







TAPP – tetragonal almandine-pyrope phase

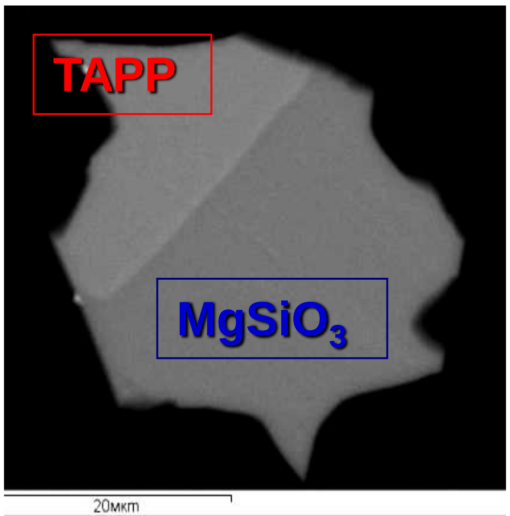
Mineral inclusions

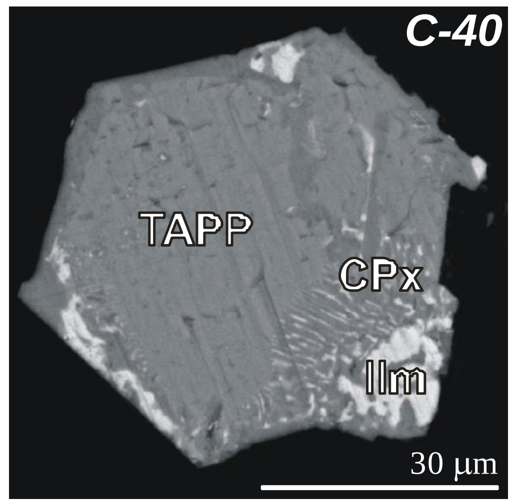
Jeffbenite

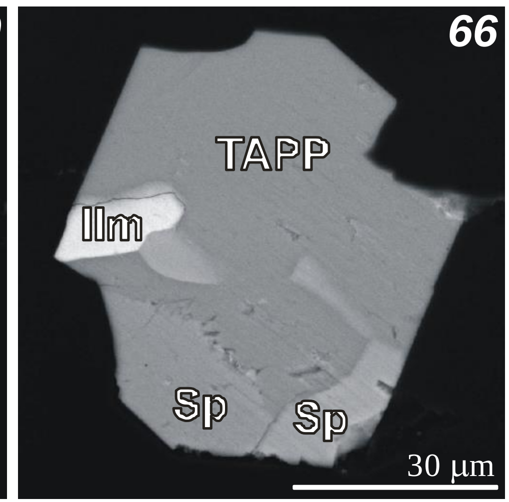
TAPP – tetragonal almandine-pyrope phase $(Mg,Fe)_3Al_2(SiO_4)_3$

Associations

TAPP+MgSi-Pv+CaSiTi-Pv







(i) $$\underset{\textit{Maj-Gt}}{(Ca,Mg,Fe)_3(Fe,Al,Si)_2(SiO_4)_3} \xrightarrow{P\uparrow} \underset{\textit{TAPP}}{(Mg,Fe)_3Al_2(SiO_4)_3} + \underset{\textit{CaSi-Pv}}{CaSiO_3}$$

(ii) $$\underset{\textit{Al-MgSi-Pv}}{Mg(Al,Si)O_3} \xrightarrow{P\downarrow} \underset{\textit{TAPP}}{(Mg,Fe)_3Al_2(SiO_4)_3} + \underset{\textit{MgSi-Pv}}{MgSiO_3}$$

Mineral Inclusions

'Olivine' $(Mg,Fe)_2SiO_4$

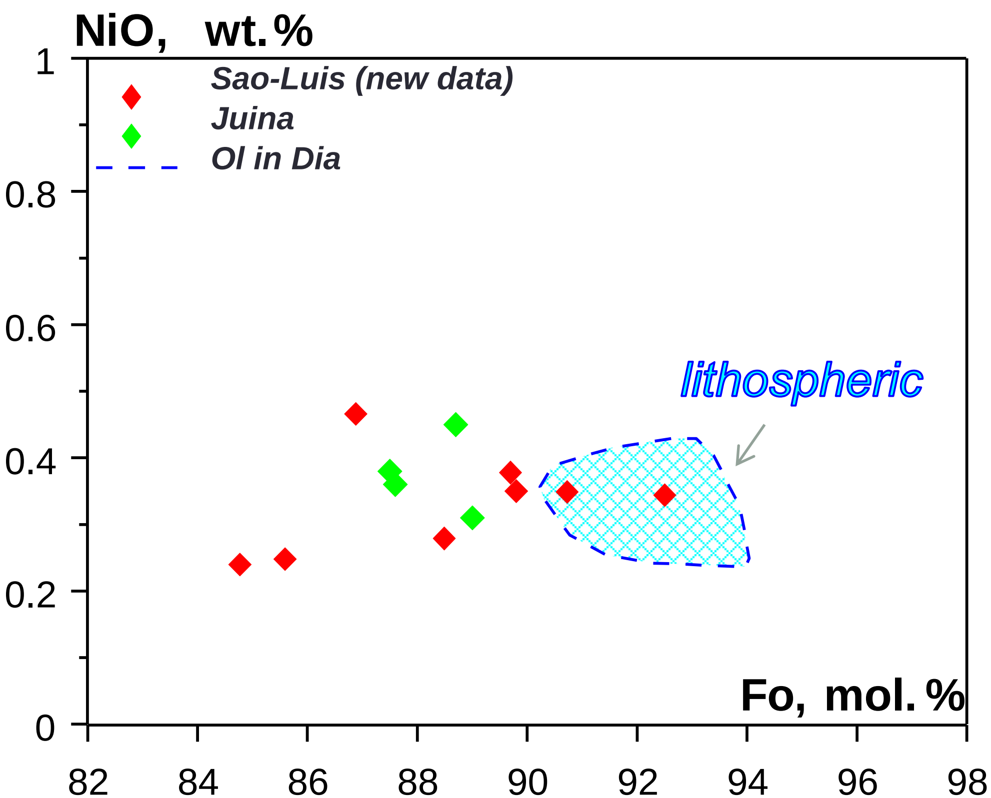
Associations

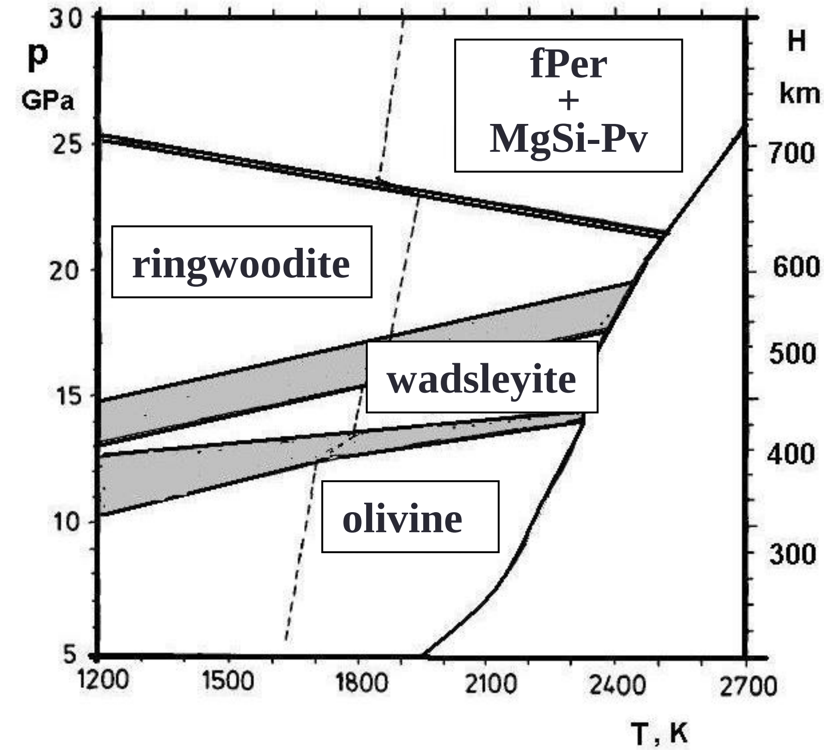
Ol+fPer

Ol+MgSi-Pv+CaSi-Pv

Ol+CaSi-Pv+Mrw

Ol+Cr-Prp





?

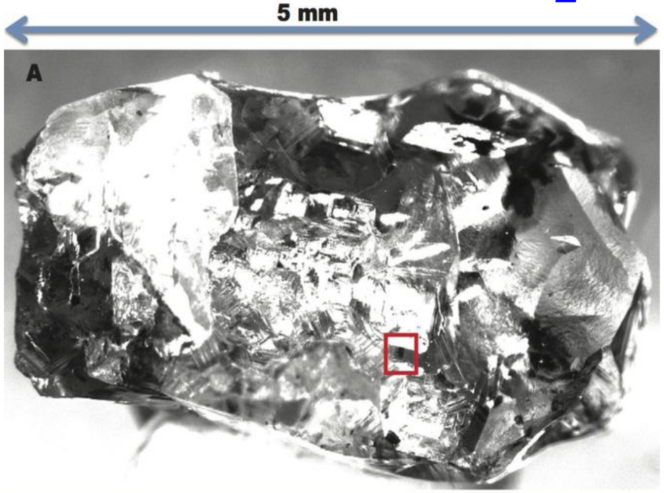
α – olivine (P <12 Gpa)

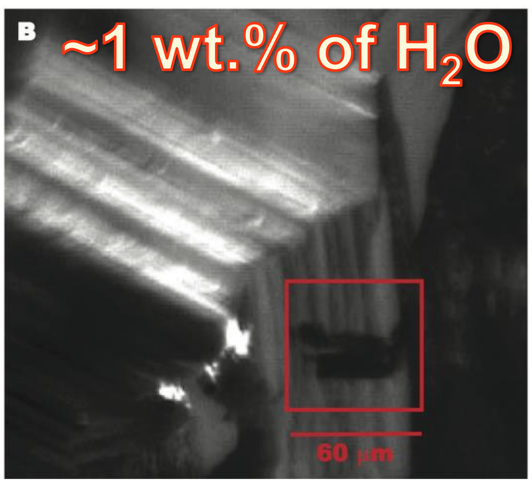
β – wadsleite (P >12 GPa)

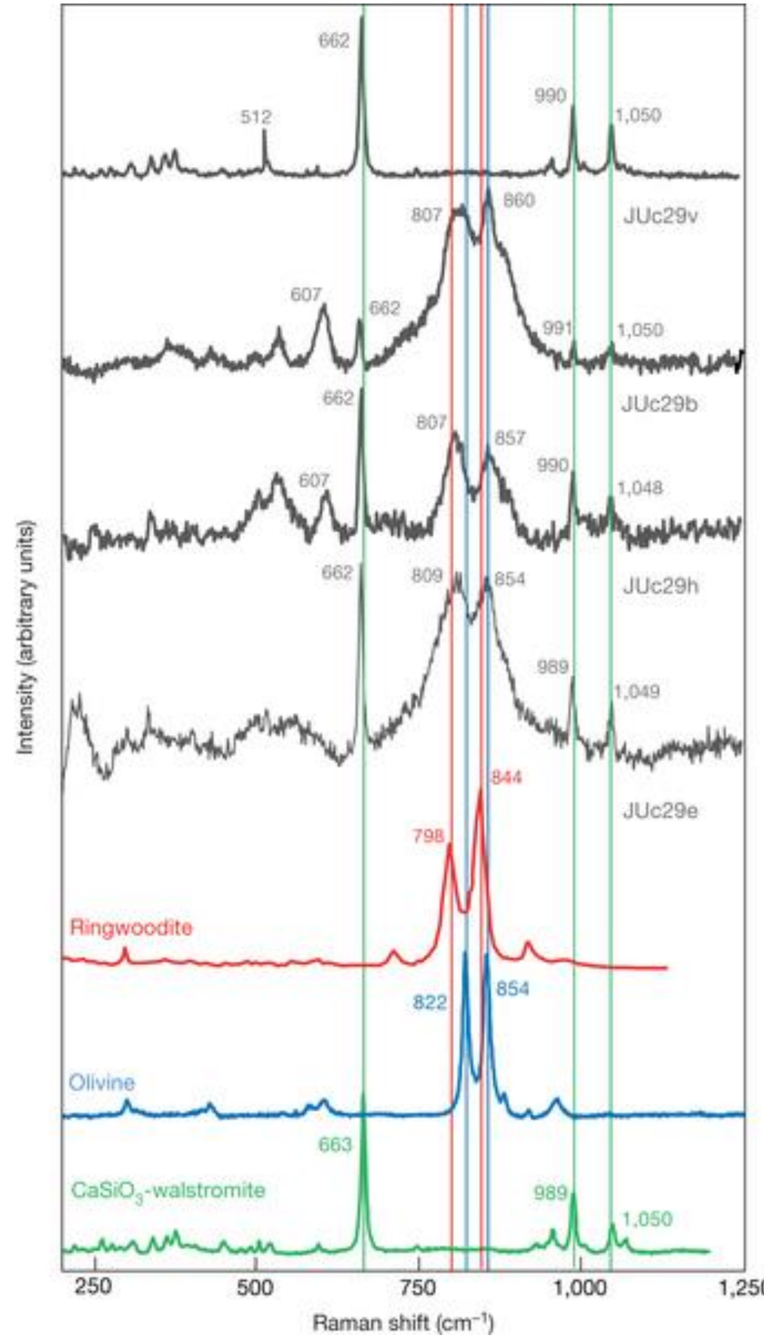
γ – ringwoodite (P >17 Gpa)

Mineral Inclusions

'Ringwoodite' $(Mg,Fe)_2SiO_4$







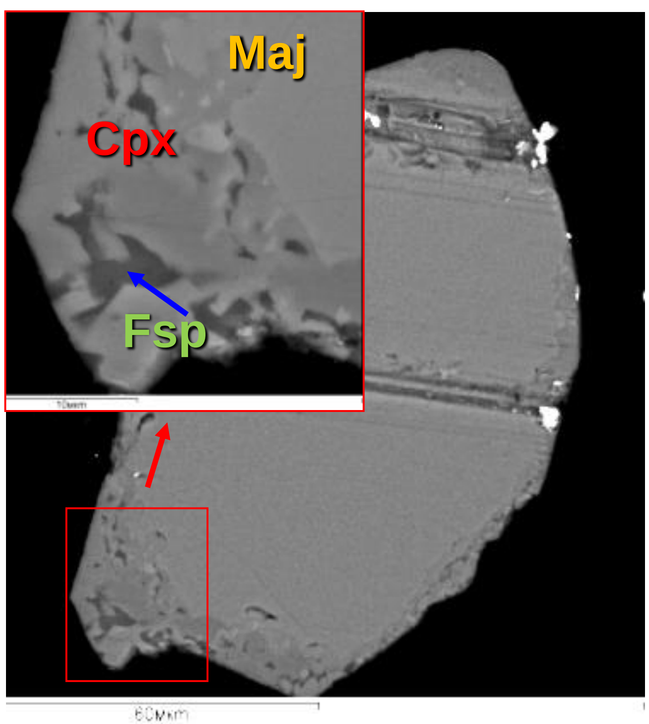
Pearson et al., 2014, Nature

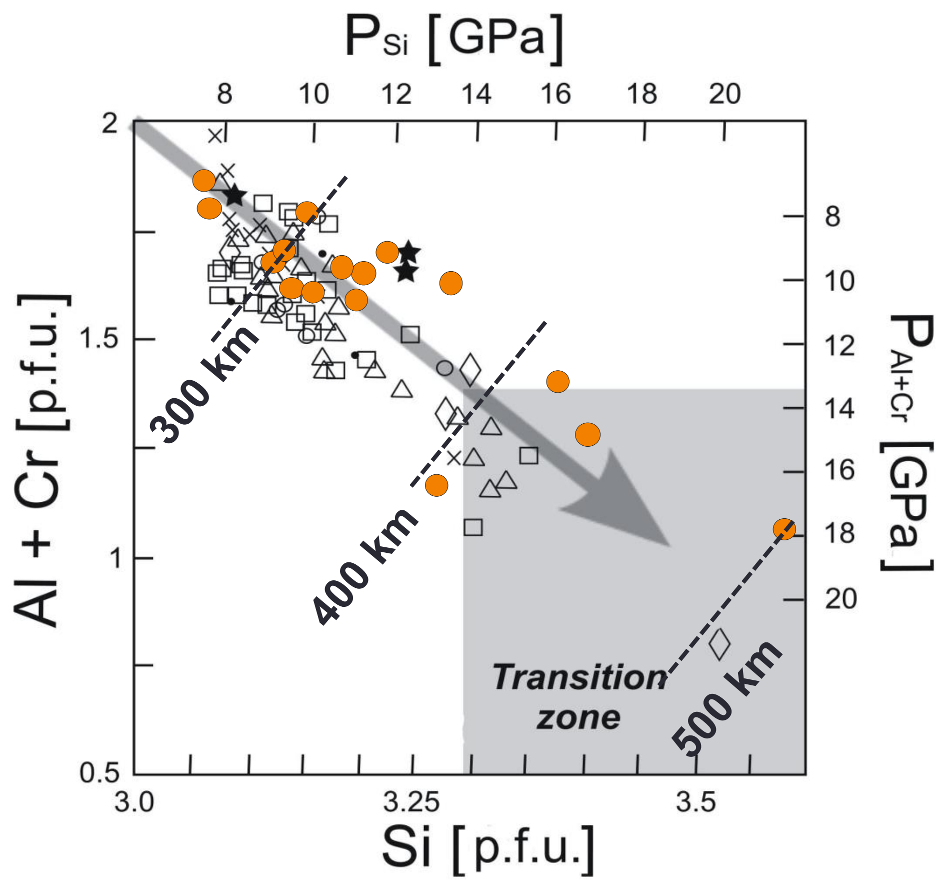
Mineral inclusions

Majoritic Garnets $(Ca,Mg,Fe)_3(Fe,Al,Si)_2(SiO_4)_3$

Associations

Maj-Gt+CaTiSi-Pv+SiO_2+Kya
Maj-Gt+SiO_2
Maj-Gt+CPx
Maj-Gt+Neph



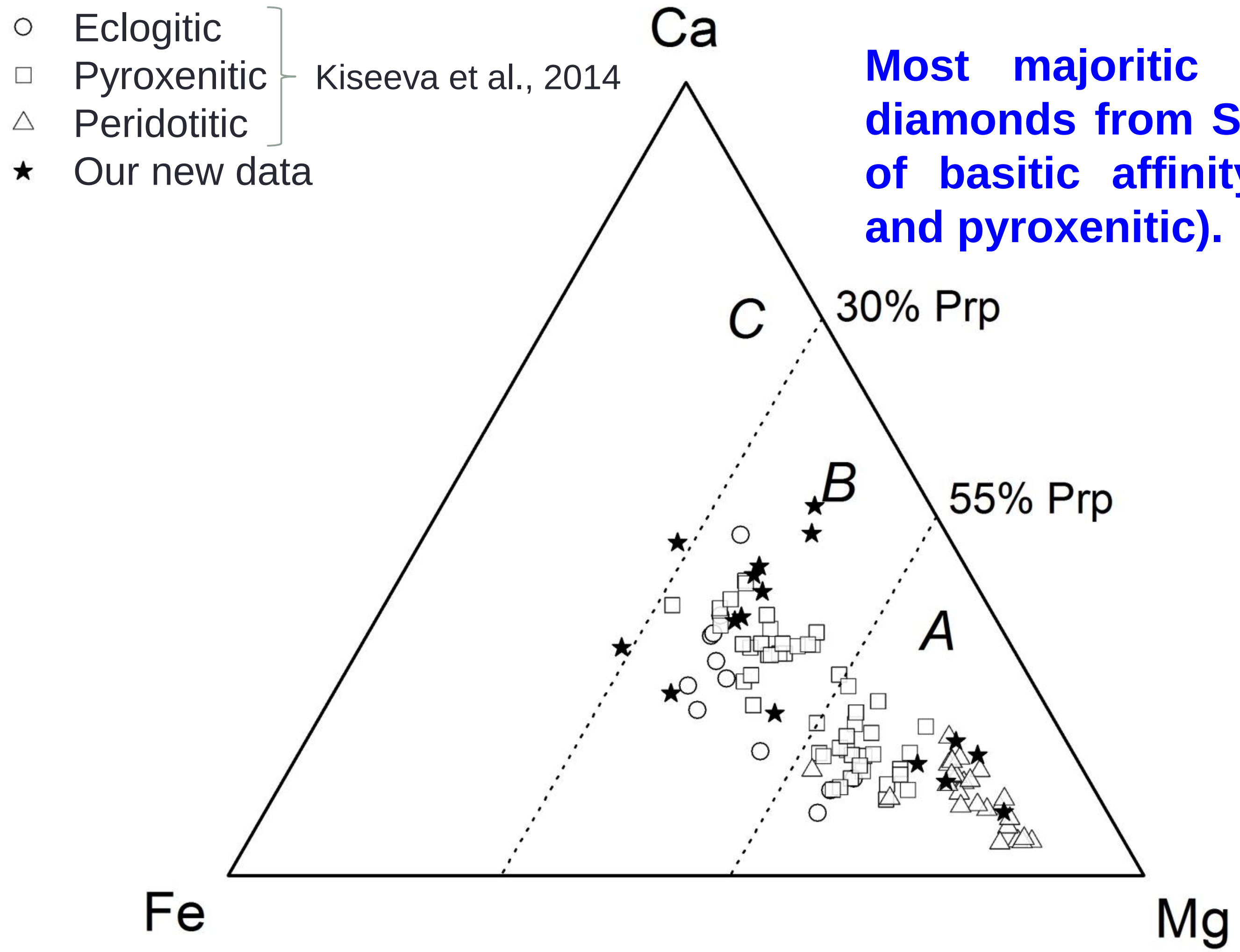


The formation of diamonds with majoritic garnets relates to the different levels of lowermost Upper Mantle and Transition Zone.

Mineral Inclusions

Majoritic Garnets

$(Ca,Mg,Fe)_3(Fe,Al,Si)_2(SiO_4)_3$



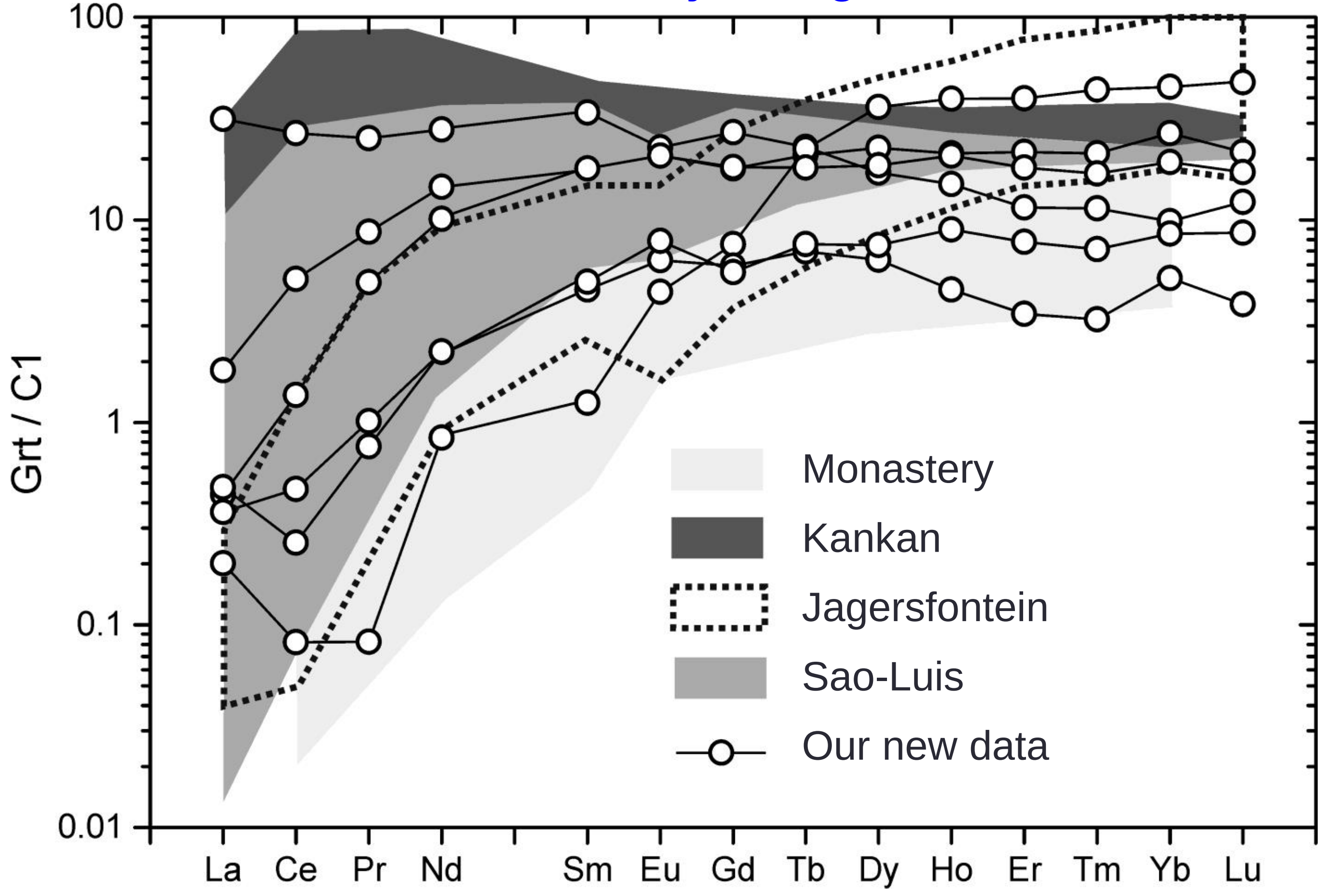
Most majoritic garnets in diamonds from Sao-Luis are of basitic affinity (eclogitic and pyroxenitic).

Mineral Inclusions

Majoritic Garnets

$(Ca,Mg,Fe)_3(Fe,Al,Si)_2(SiO_4)_3$

Majoritic garnets show wide range of REE.



Mineral inclusions

CaSi-perovskite (±CaTi-perovskite)

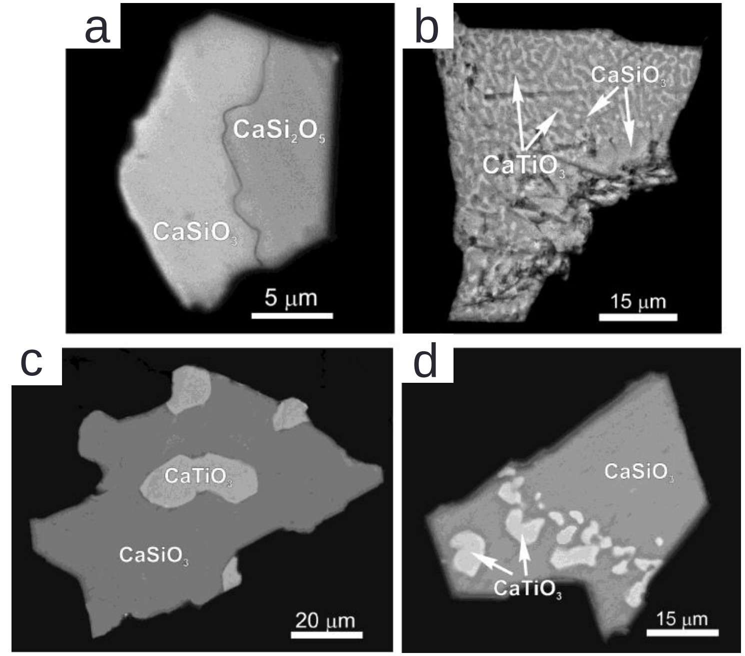
Associations

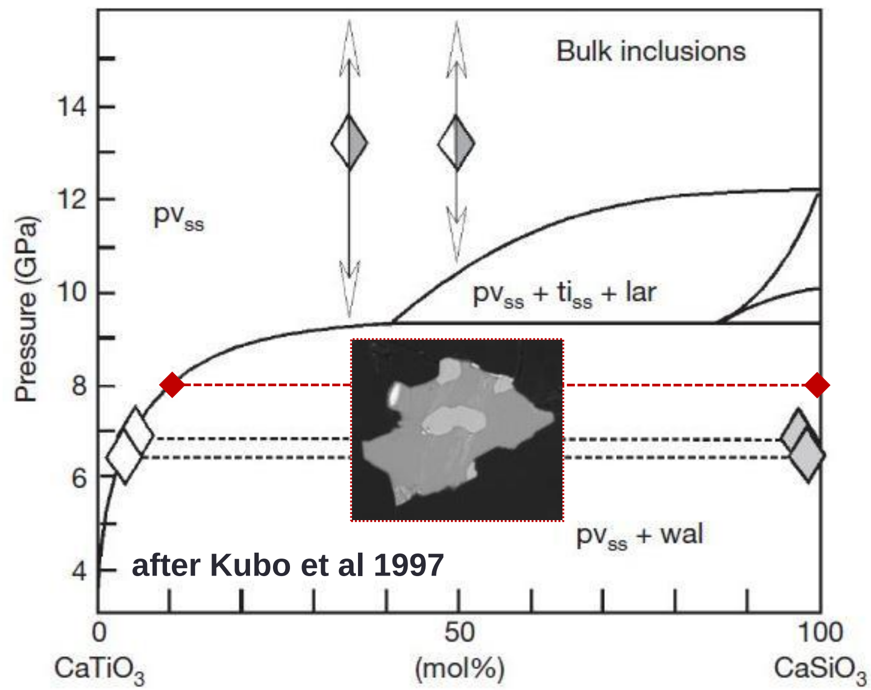
CaSi-Pv+Mrw+Ol
CaSi-Pv+MgSi-Pv+Ol
CaSiTi-Pv+TAPP+MgSi-Pv
} ***Metaperidotic***

CaSi-Pv+Maj-Gt
CaTiSi-Pv+Maj-Gt+SiO_2+FeS
CaTiSi-Pv+Maj-Gt+SiO_2+Kya
CaSi-Pv+SiO_2+AlSi-phase
CaSi-Pv+AlSi-phase
} ***Metabasitic***

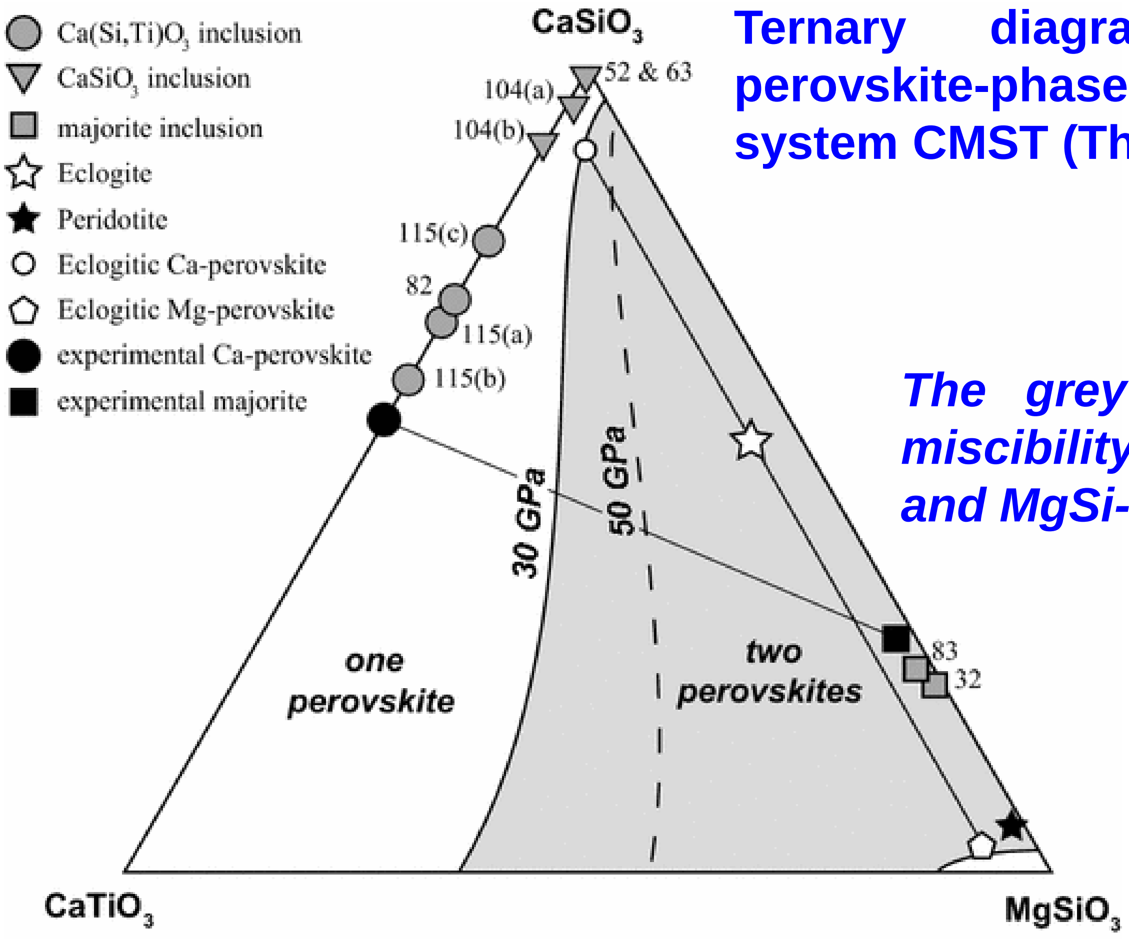
CaSi-Pv+$CaSi_2O_5$

20 mol.% $CaTiO_3$
Estimated unmixing pressure ~ 9 GPa





Mineral inclusions



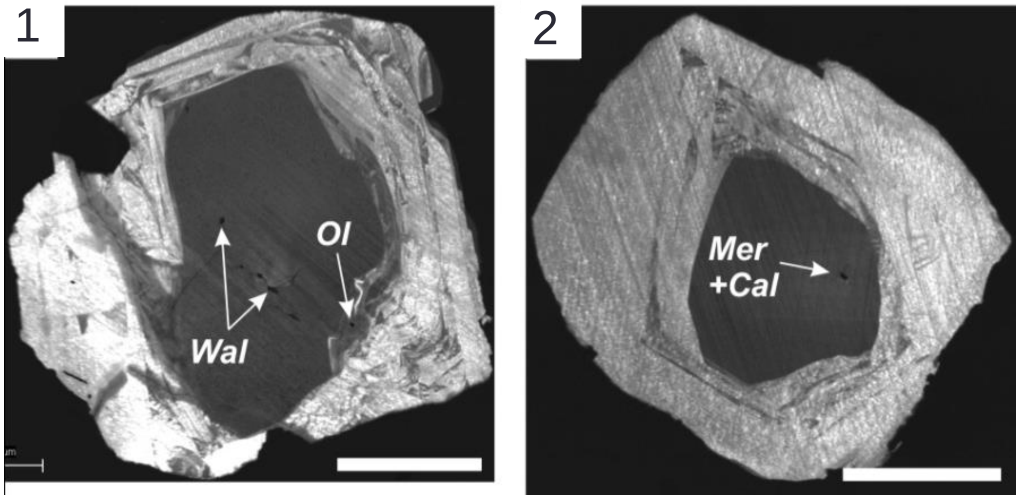
Ternary diagram showing the perovskite-phase relations in the system CMST (Thompson et al., 2014).

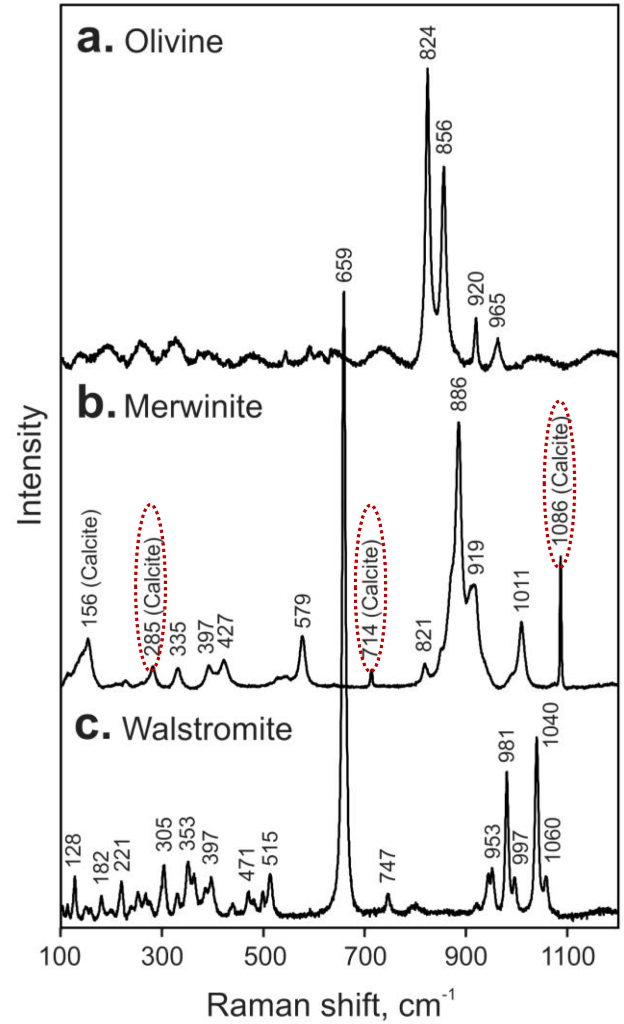
The grey field represents the miscibility gap between CaSi-Pv and MgSi-Pv at 30 GPa

Any bulk composition lying in this field, i.e. peridotite (black star) or eclogite (white star), will contain two perovskite phases with compositions lying on the edge of this field (e.g. small white symbols).

Mineral inclusions

Merwinite $Ca_3MgSi_2O_8$





Merwinite could be an apparent evidence of Ca-carbonatite metasomatism in the deep mantle.

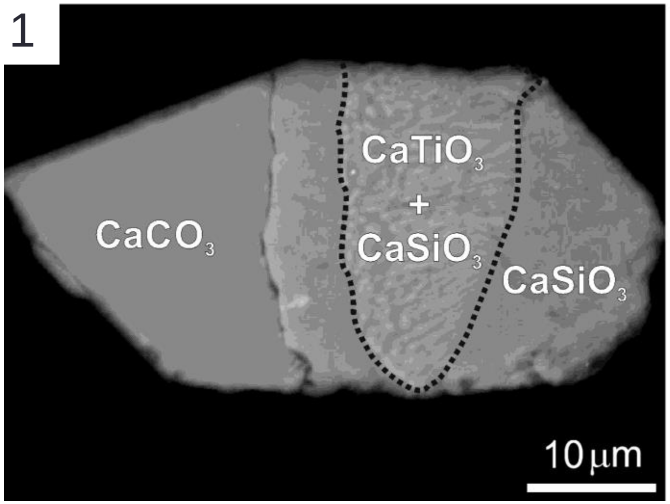
(i) **$4Mg_2Si_2O_6$ (OPx) + $8CaCO_3$ (Liq) = Mg_2SiO_4 (Ol) + $CaMgSi_2O_6$ (CPx) + $Ca_3MgSi_2O_8$ (Mer) + $3SiO_2$ (Liq) + $4CaMg(CO_3)_2$ (Liq)**

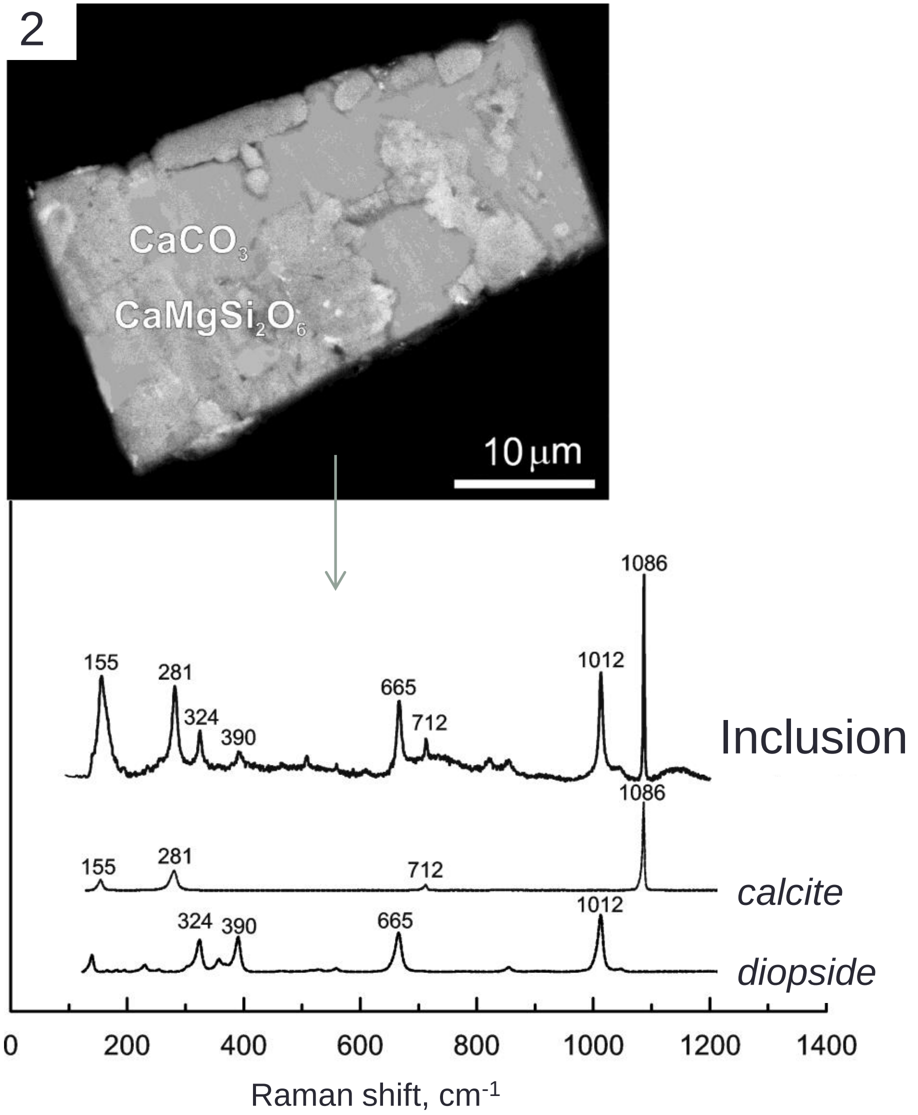
(ii) **$2Mg_2SiO_4$ (Ol) + $6CaCO_3$ (Liq) = $Ca_3MgSi_2O_8$ (Mer) + $3CaMg(CO_3)_2$ (Liq)**

Sharygin et al. 2014

Mineral inclusions

Carbonates





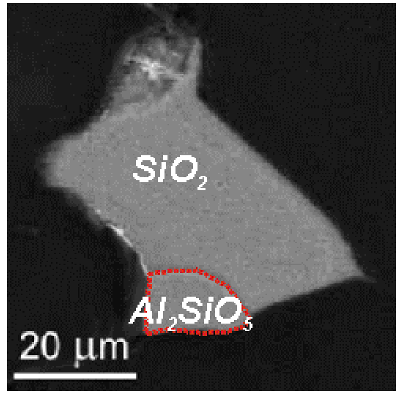
[Brenker et al., 2007]

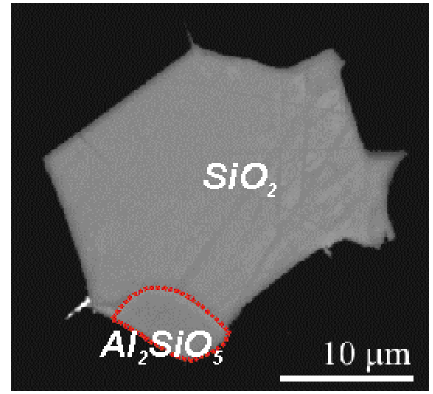
Applying several in situ analytical techniques on inclusions in diamonds from Juina (Brazil) originating from the lower part of the TZ (>580 km) or even the LM (>670 km), reveal the existence of *deep Earth carbonates*.

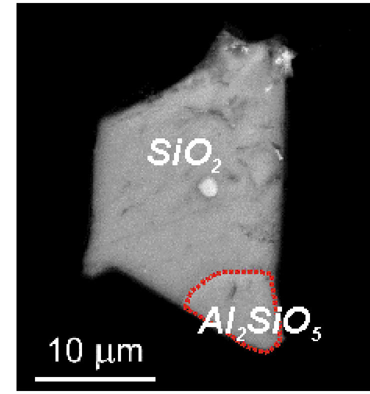
Mineral inclusions

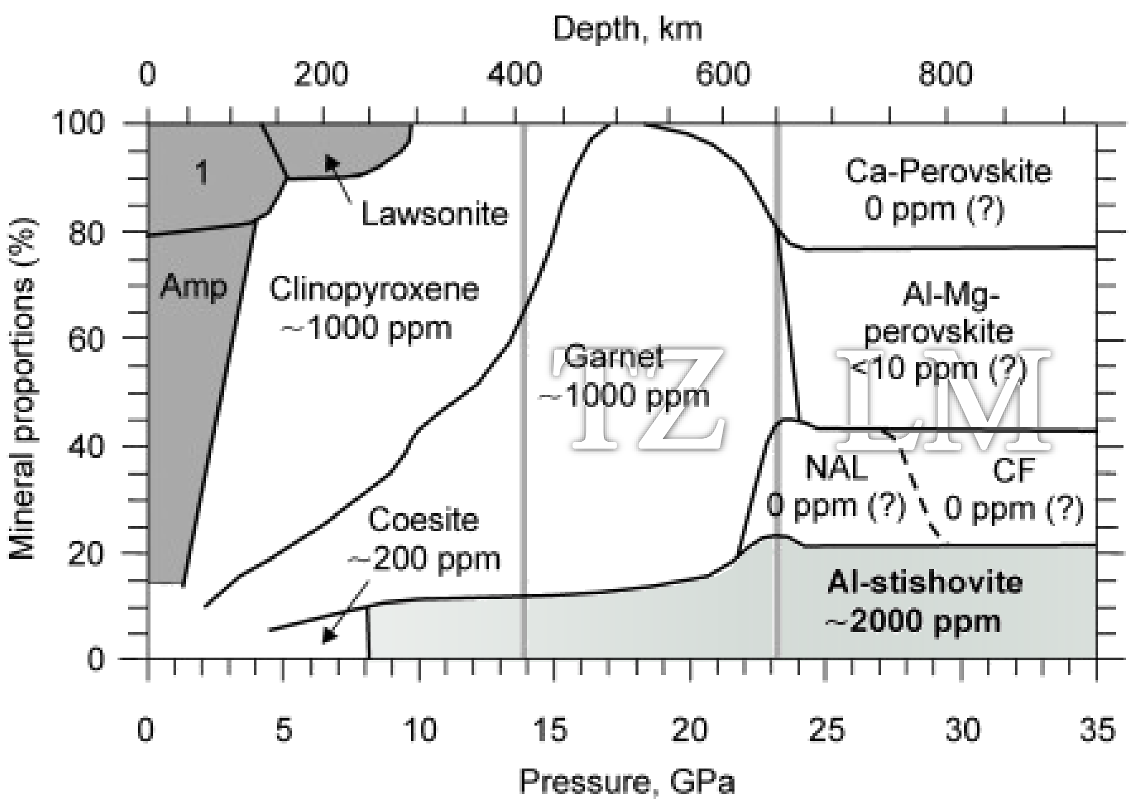
SiO_2-phase

Al-stishovite ?









Al solubility in stishovite increases with increasing pressure

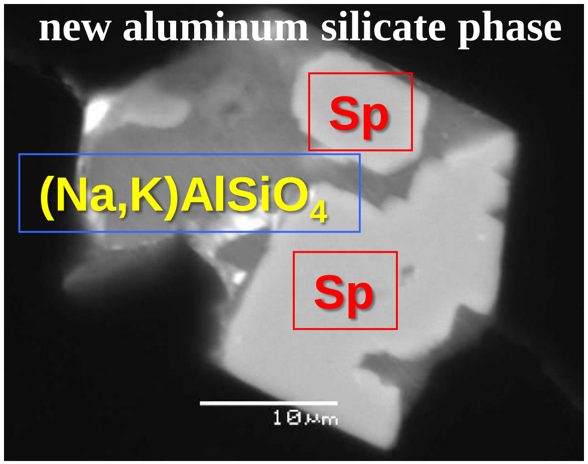
$$Si^{4+} \rightarrow Al^{3+} + H^{+}$$

[e.g. Pawley et al. 1993; Smyth et al. 1995; Panero et al. 2003, 2004]

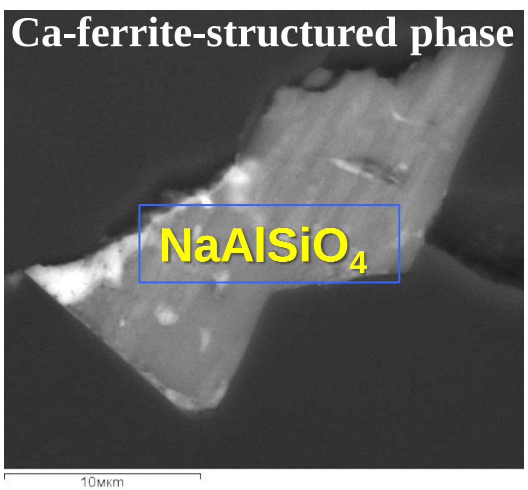
Al-stishovite is a potential “container (carrier)” of water in metabasite affinity into LM [Litasov et al., 2007]

Mineral inclusions

NAL

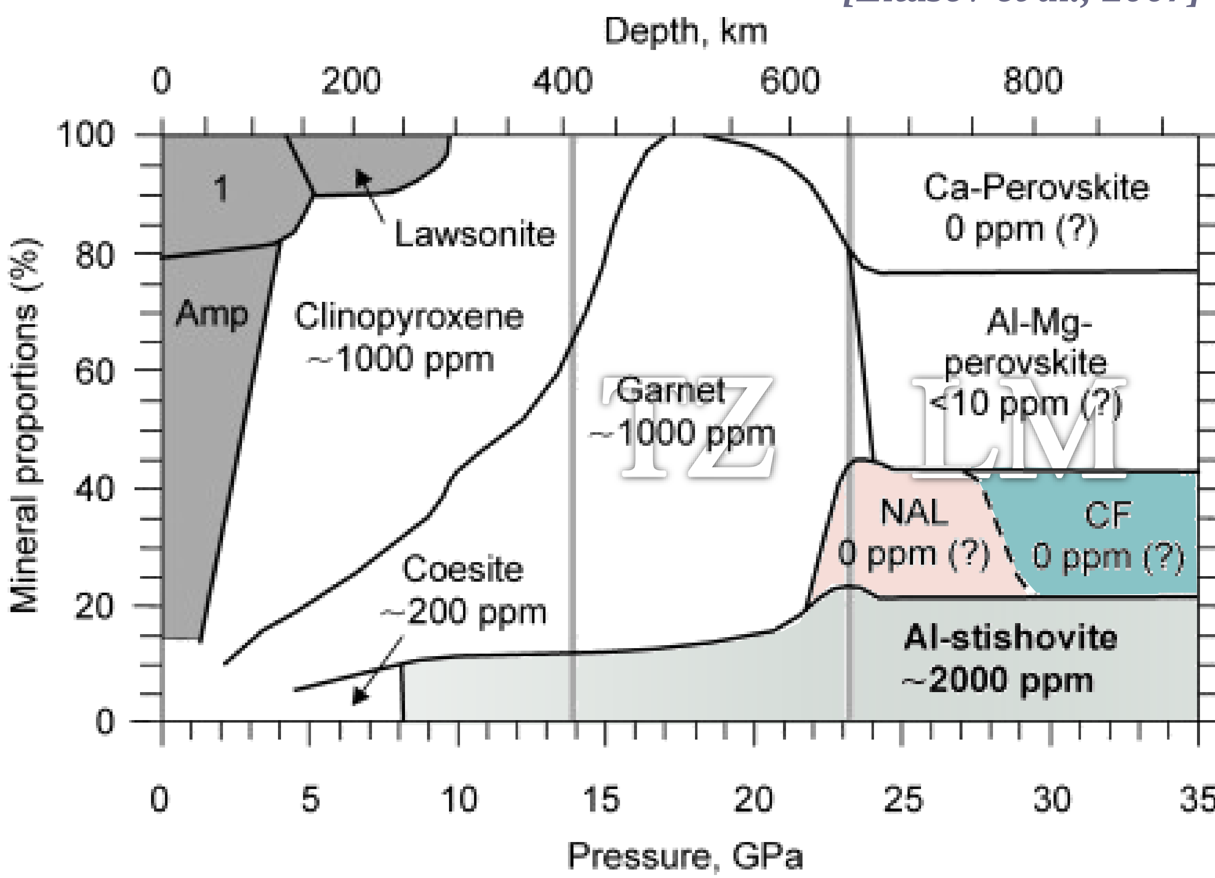


CF



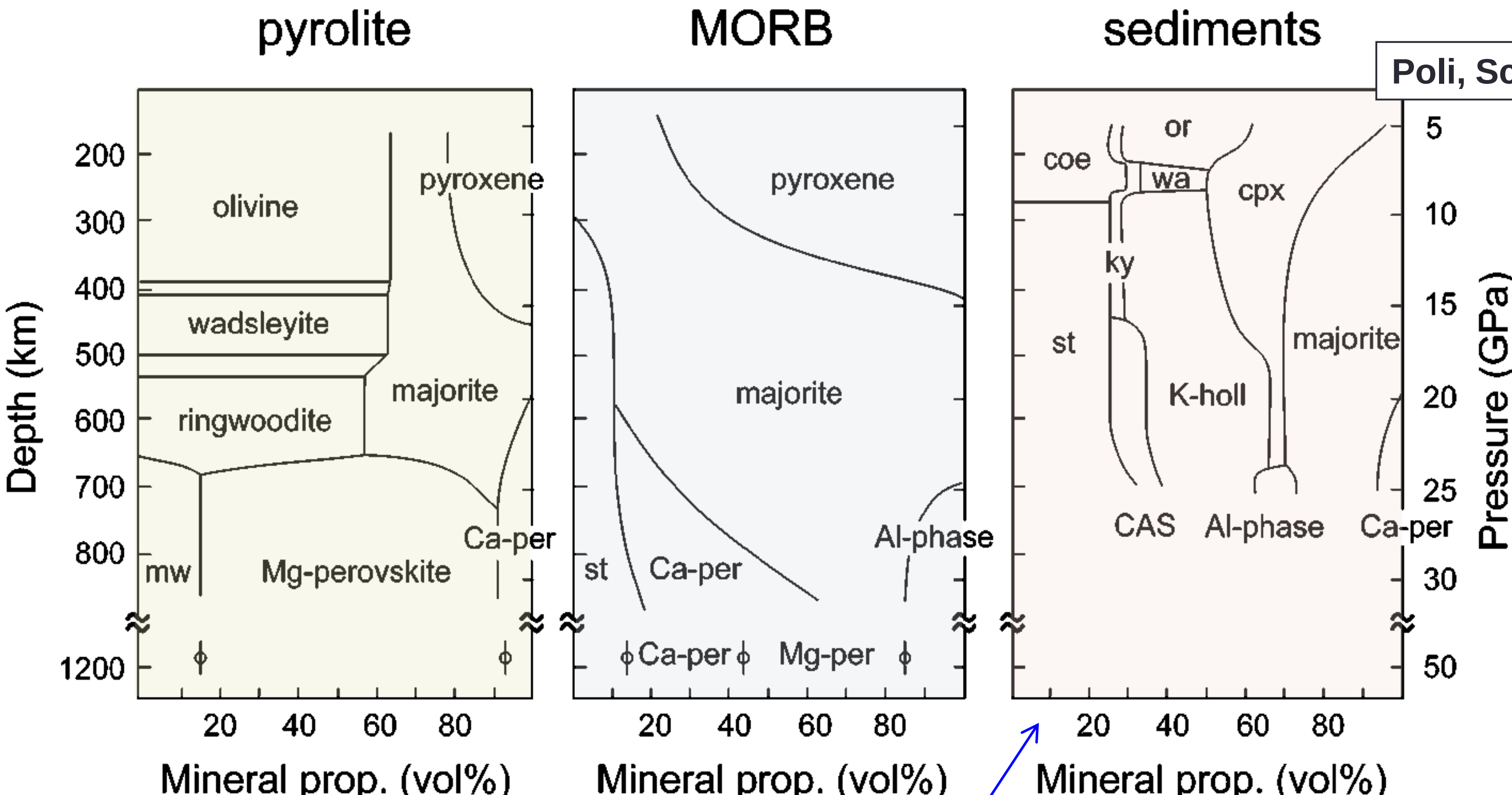
Phases of CF and NAL may be formed only in oceanic crustal rocks subducted into the LM [Walter et al., 2010]

[Litasov et al., 2007]



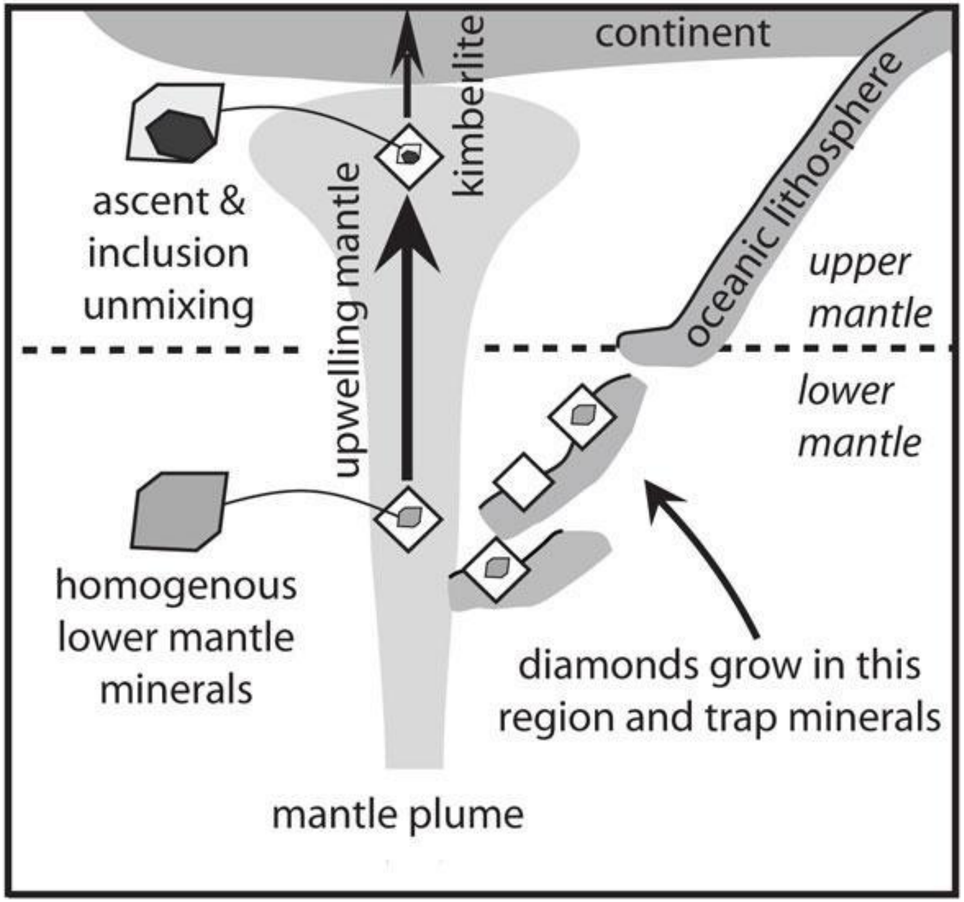
Mineral inclusions

Ol (Wd, Rw?), fPer, MgSi-Pv, CaSi-Pv, TAPP	Maj-Grt, Omph-CPx, CaSi-Pv, SiO_2 (St?), AlSi-phase	K-holl, CAS, CF, NAL, CaSi-Pv, SiO_2 (St?), AlSi-phase



Association of CaAlSi- and SiAl-phases, K-hollandite, CF, NAL, Maj-garnets and SiO_2 correspond to experimentally founded associations of deeply subducted *metasediments*.

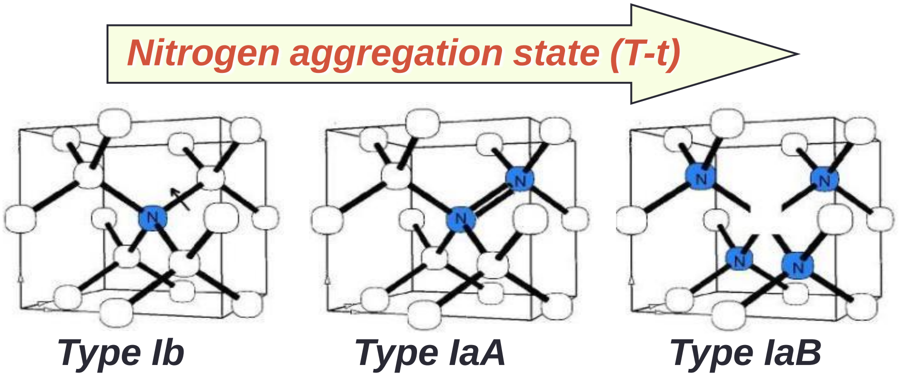
Mineral inclusions

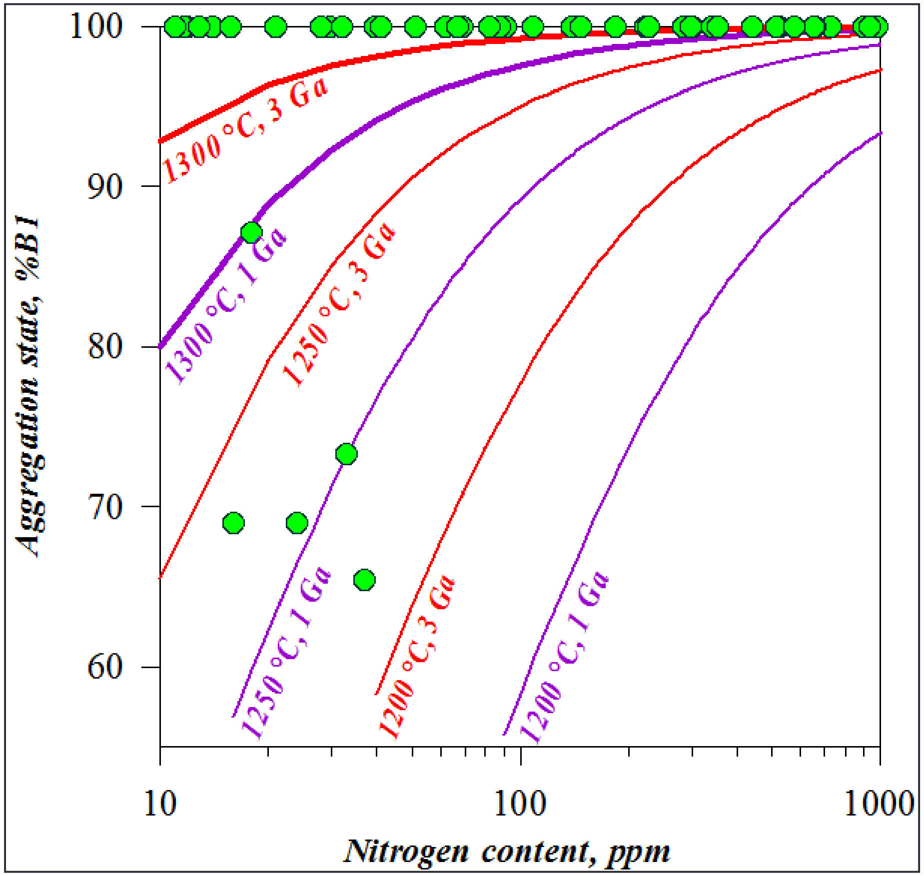


A conceptual model showing that the diamonds and inclusions form in the lower mantle in subducted oceanic crust, are then transported by mantle flow to the upper mantle, and finally to the surface in a kimberlite magma.

Nitrogen content and aggregation state

- Most superdeep diamonds from Sao-Luis are nitrogen-free (type IIa).
- A specific feature of superdeep diamonds from Sao-Luis is extremely high nitrogen aggregation state (65-100 %B1).



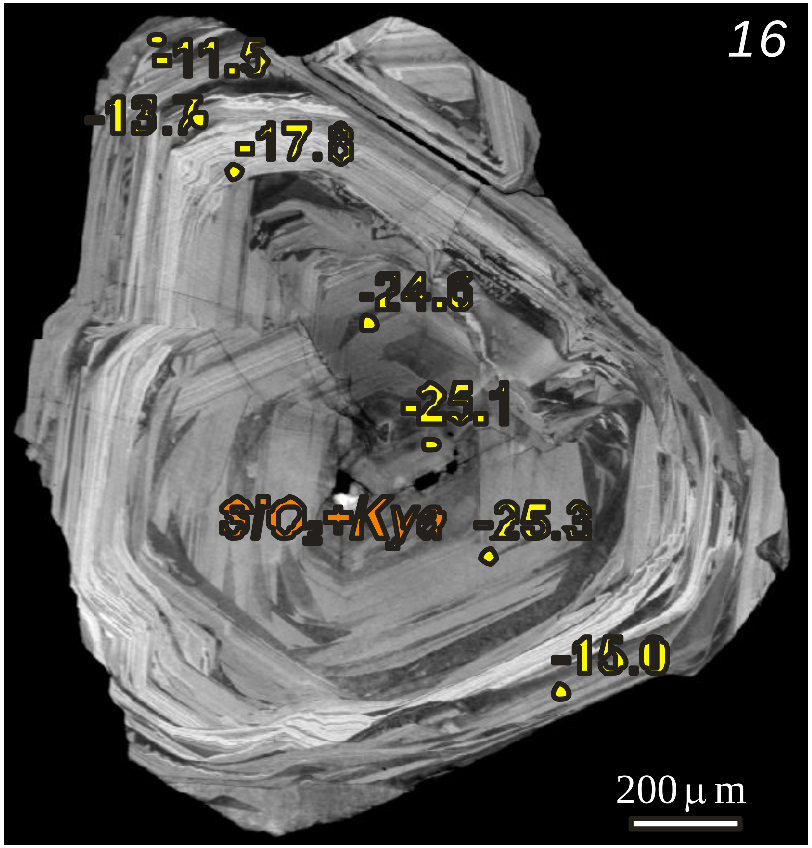


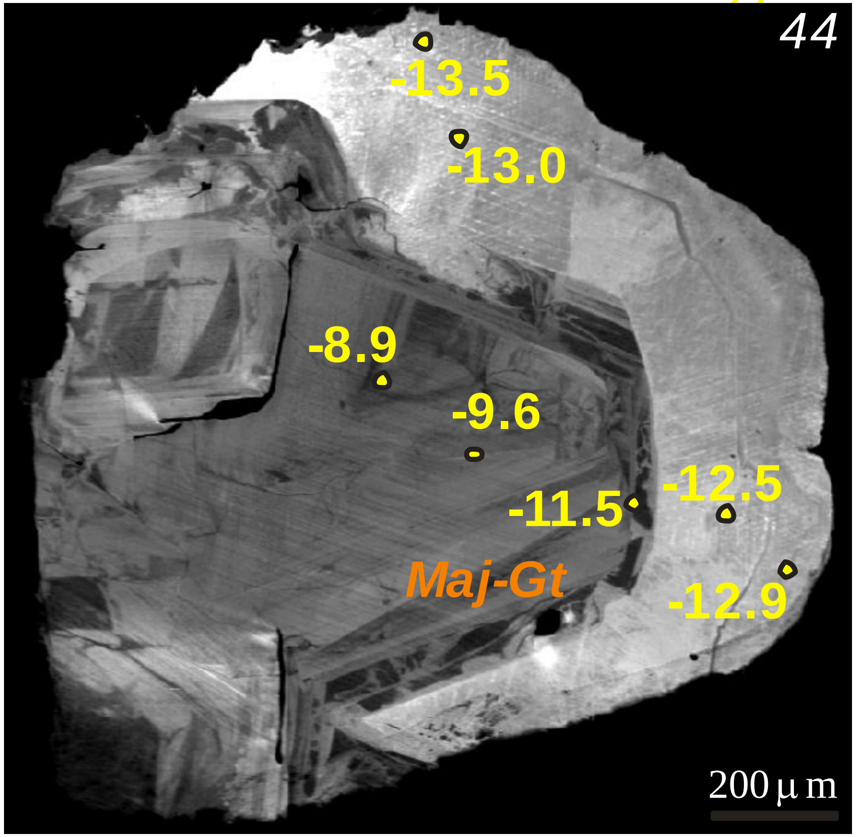
Extremely high nitrogen aggregation state suggest high temperature.

100%B1 (N>100 ppm)
T=1300°C – time>3 Ga (?)
T=1500°C – time>0.1 Ma

Carbon isotope composition

CL imaging has revealed the complex growth history for most diamonds, reflecting their formation in several stages.

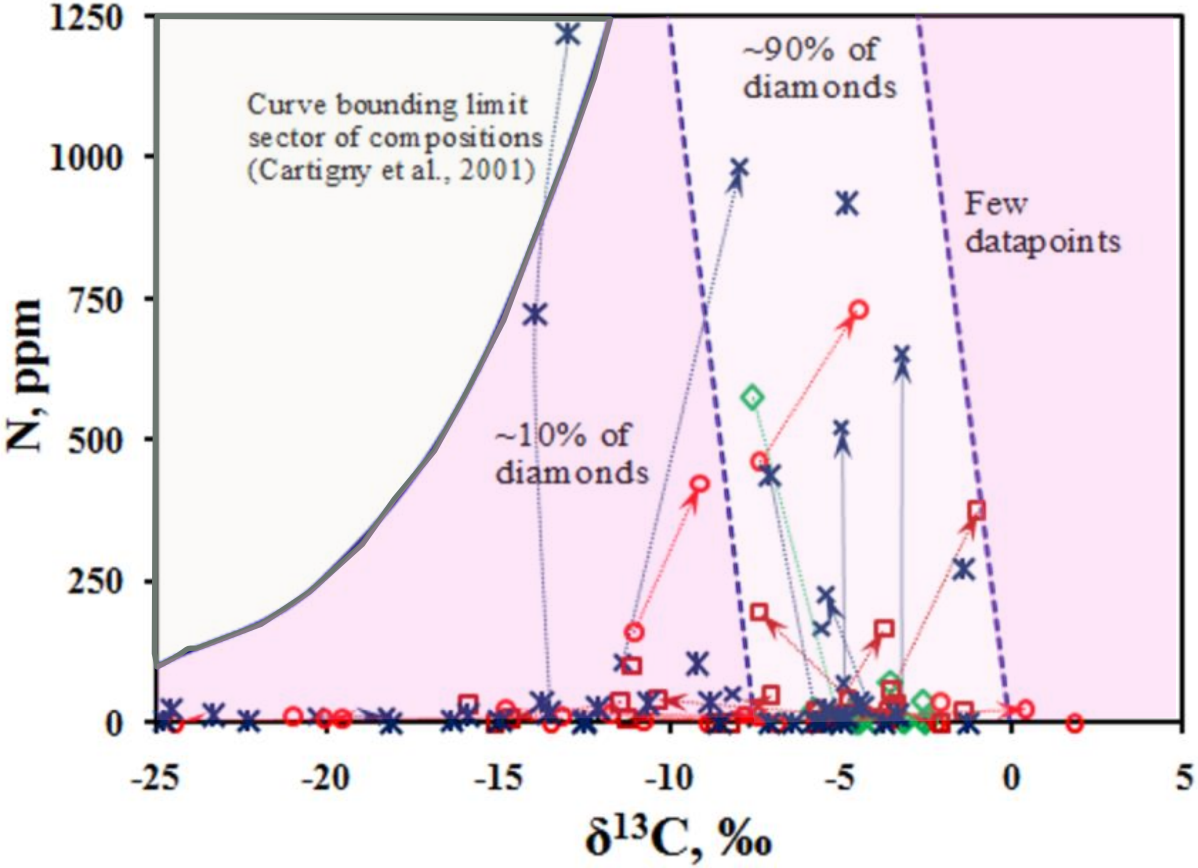




The $\delta^{13}C$ measurements in core–rim traverses within some individual crystals varied substantially, indicating multi-stage growth histories.

Carbon isotope composition

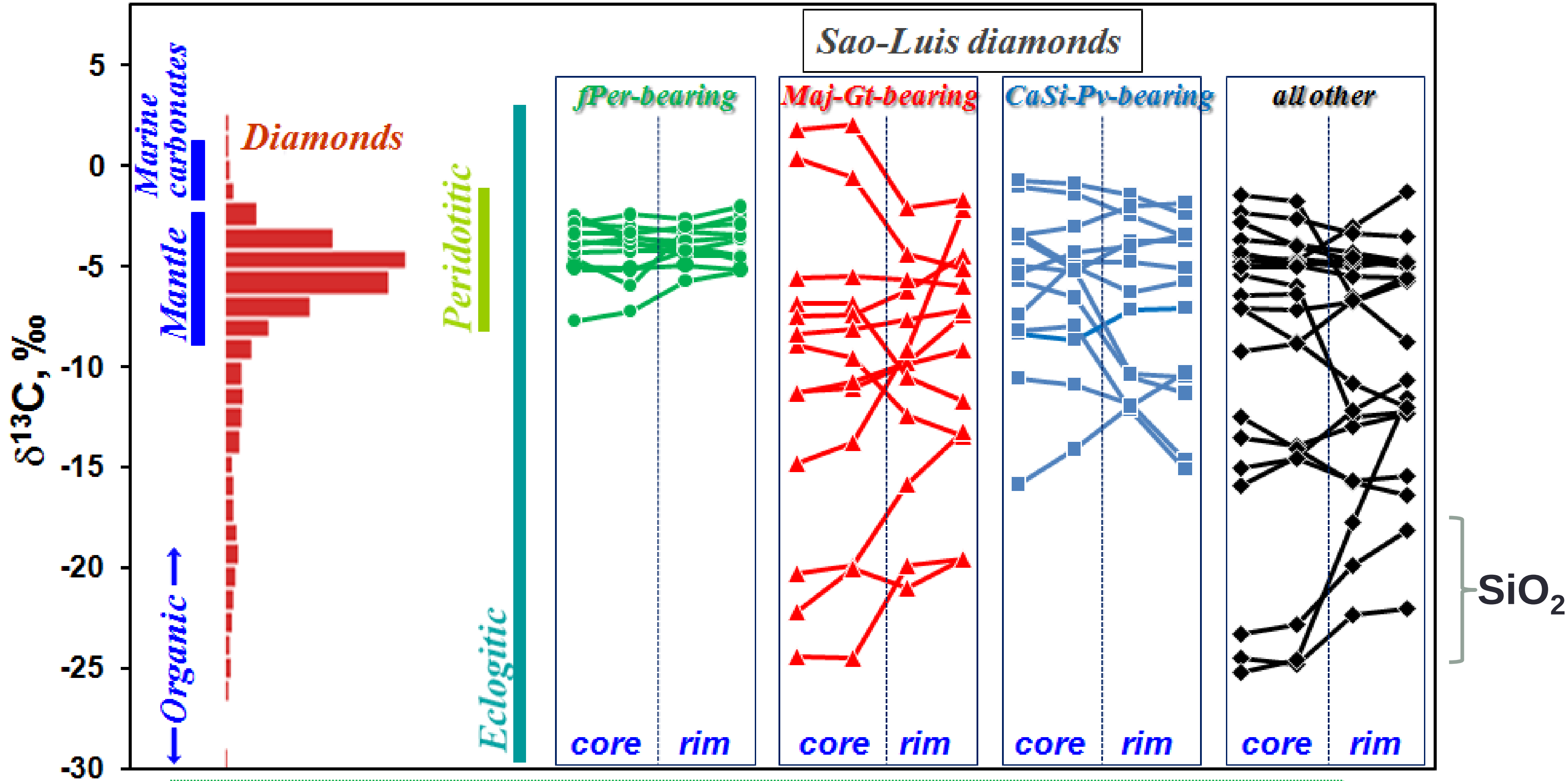
No correlation of carbon isotope composition and nitrogen content has been found in an individual diamonds.



The cores and rims of the São-Luis diamonds precipitated from *different fluids/melts* with variable N/C ratios and/or under *different growth conditions*.

Carbon isotope composition

The diamonds from Sao-Luis display wide variations of carbon isotope compositions ($\delta^{13}C$) from +2.7 to -25.3 ‰.



- ○Diamonds with inclusions of fPer ($\delta^{13}C$ -2÷-6‰)
- ○Diamonds with inclusions of Maj-garnets ($\delta^{13}C$ 2÷-25‰)
- ○Diamonds with inclusions of CaSi-pv ($\delta^{13}C$ -1÷-16‰)

Carbon isotope composition

Remarks

- ✓ The variations in $\delta^{13}C$ within individual diamonds may be attributed to either different source of carbon or fractionation effect during diamond growth.

- ✓ The highly negative $\delta^{13}C$ values in the core of some diamonds(-20÷-25 ‰) potentially represent *organic* matter in sediments or altered basalts, and the higher $\delta^{13}C$ values may represent mixing trends towards “normal” mantle compositions.

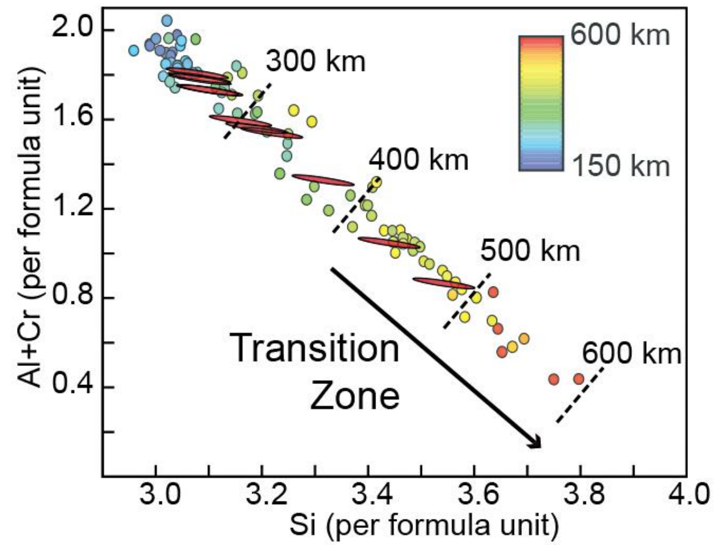
- ✓ There are also a series of diamond which show opposite trend of change carbon source from primordial mantle to subducted/crustal (either biotic or abiotic carbon).

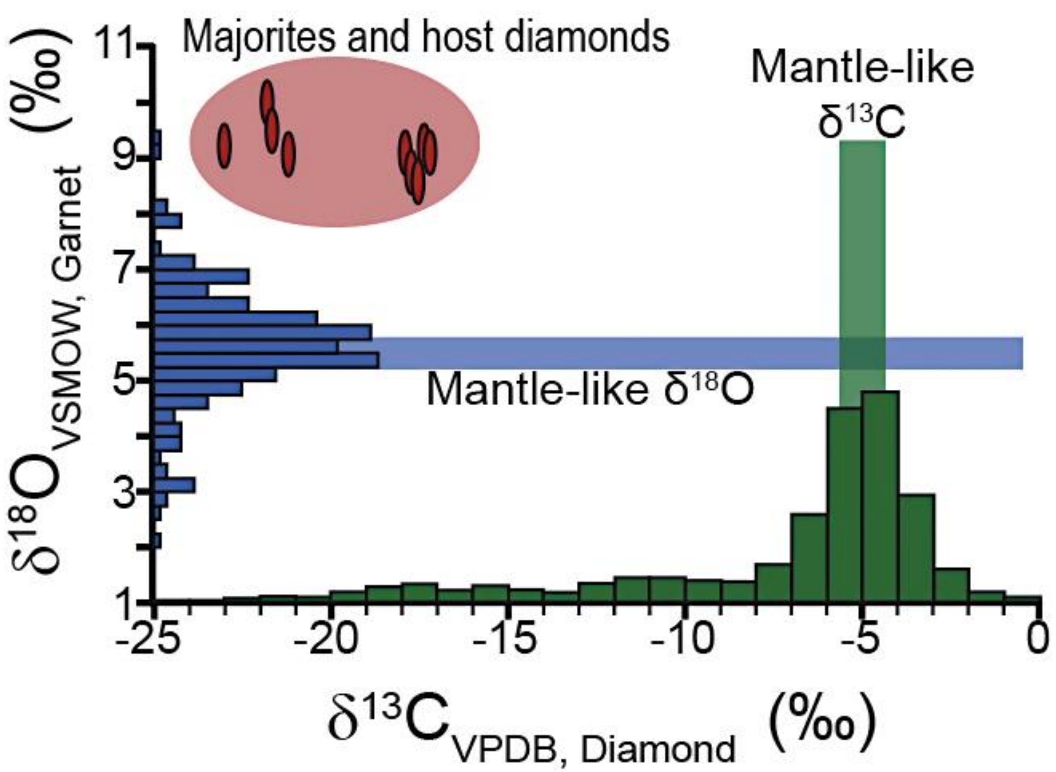
Mineral inclusions

Majoritic Garnets

$(Ca,Mg,Fe)_3(Fe,Al,Si)_2(SiO_4)_3$

Ickert et al., 2015





The majoritic garnets and their diamond hosts plot well away from the mantle field.

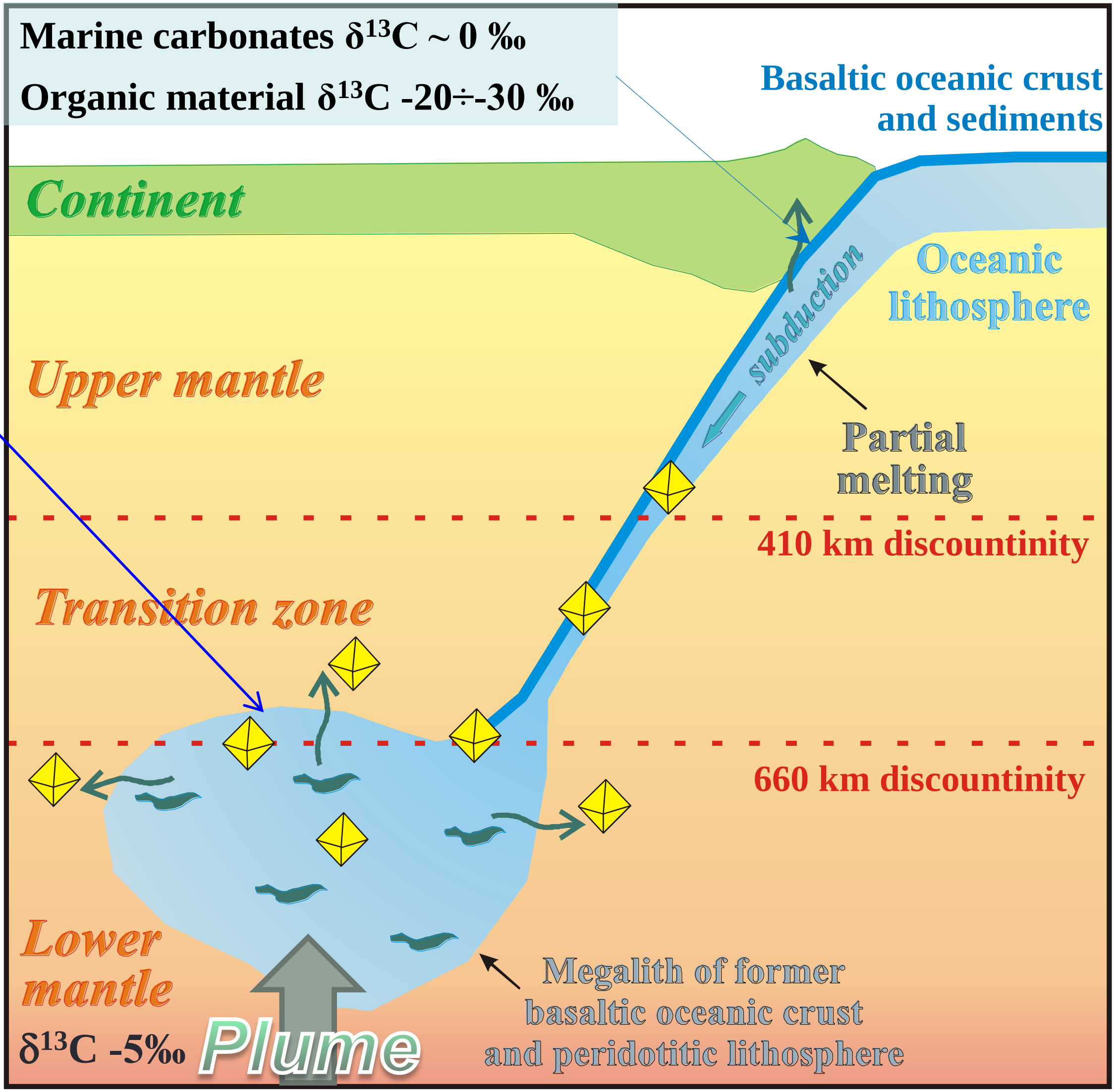
The histogram on the Y-axis is of garnets from eclogite xenoliths (compilation of Ickert et al., 2013), the histogram on the X-axis is of cratonic diamonds (Stachel et al., 2009).

Superdeep Diamonds

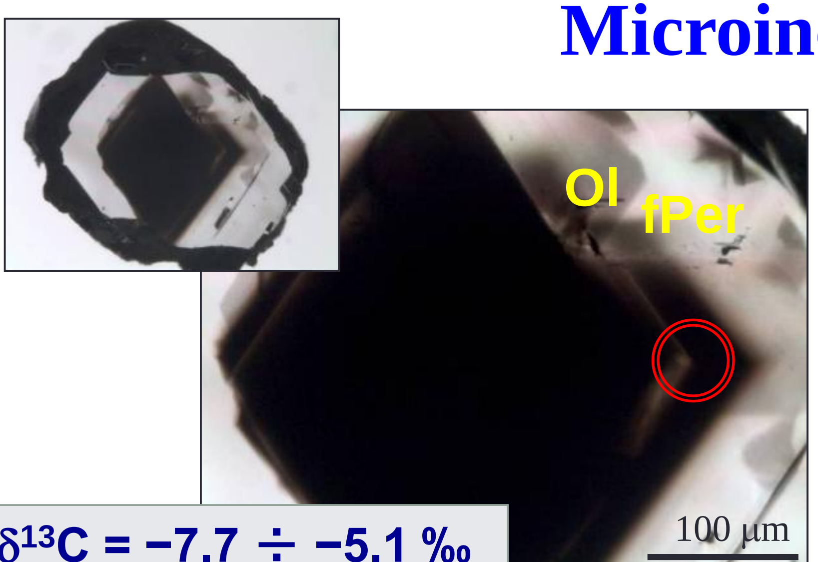
There are some evidences that *superdeep diamonds* were not derived from primitive mantle but from former oceanic slabs that accumulated at the top of the lower mantle (the "megalith model" of Ringwood, 1991).

Growth media of *superdeep diamonds* are not well constrained (?)

- Carbonate melts
  (Walter et al., 2008; Bulanova et al., 2010)
- Reduced C-O-H fluids
  (Davies et al., 1999; Kaminsky et al., 2001)
- Both
  (Harte et al., 1999; Stachel et al., 2002)



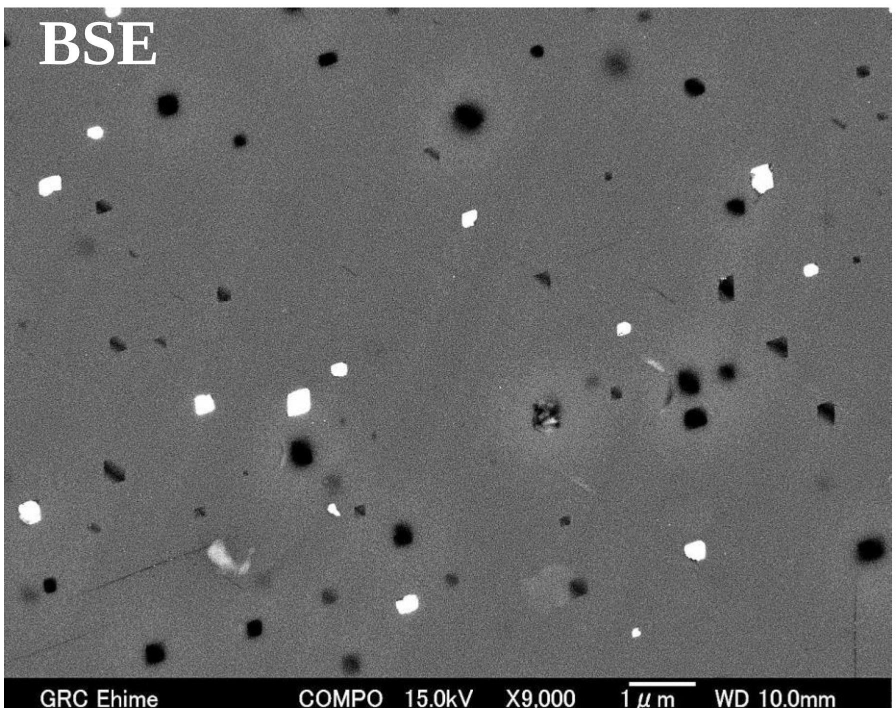
Microinclusions (fluid/melt)

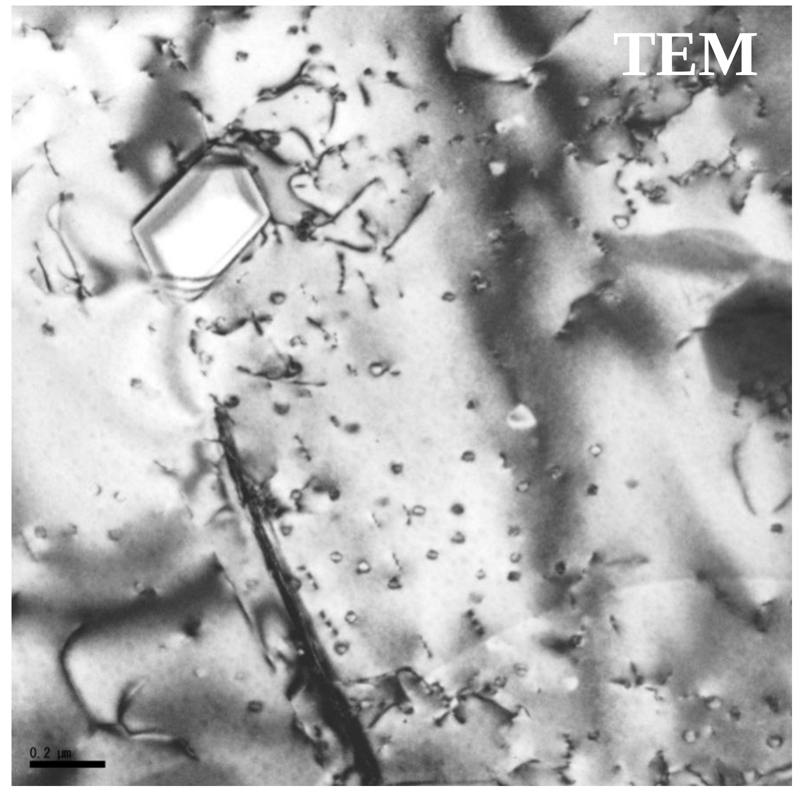


$\delta^{13}C = -7.7 \div -5.1$ ‰

FTIR spectroscopy:

***Water**, **silicates** and **carbonates** are NOT major components of these microinclusions.*

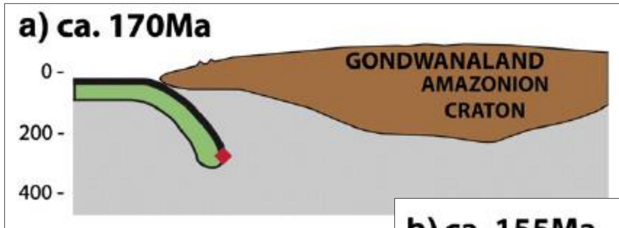


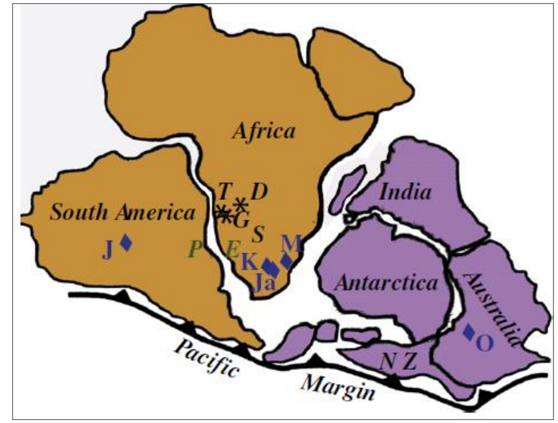


H_2 or C_nH_m?

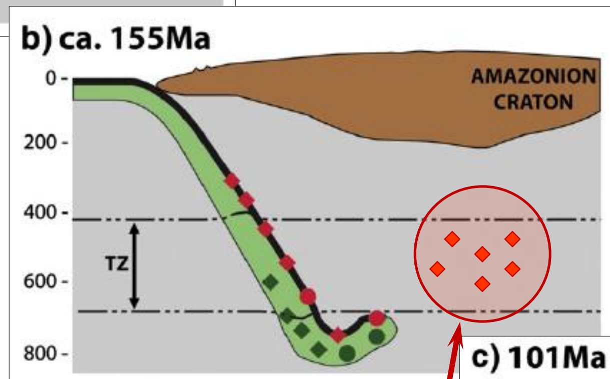
N_2 or NH_3 (Rudloff et al., 2014)

Model





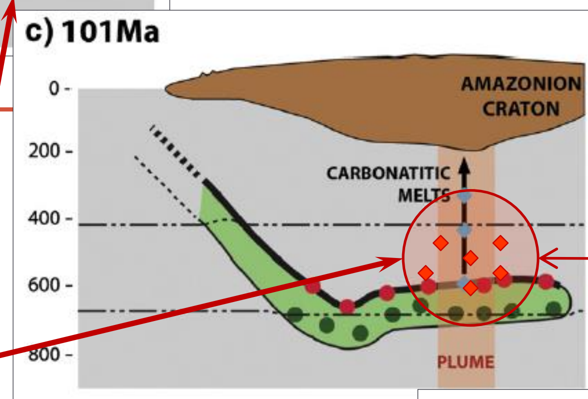
Harte&Richardson, 2011



Timing

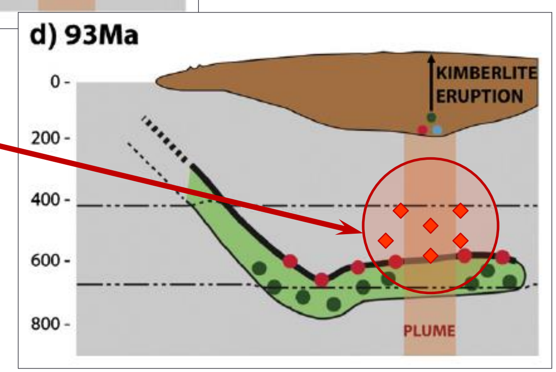
► Grt Nd/Sm 180-200 Ma – São-Luiz (Harte&Richardson, 2011)

► CaTiSi-Pv Pb/U 101 Ma – Collier 4 pipe (Bulanova et al., 2009)



Remnants of Cambrian slab

☺Zrn Pb/U 460-465 Ma;
Rt Pb/U 418-512 Ma (this study)



✓Most probable source for *Ca-silicate environments* might be carbonatitic melts/fluids from deeply subducted oceanic lithosphere.

✓*Fe-rich reduced environments* might be formed in the uplifted in plume originated from D″ layer at the CMB.

Conclusions

❖Superdeep (sublithospheric) diamonds from São-Luis were formed at different mantle levels (lowermost UM, TZ and LM) over a long period of time.

❖The mineral assemblages described in this study reveal metabasitic and metaperidotitc lithologies as a major (but not only) source of superdeep (sublithospheric) diamonds from São-Luis.

❖Superdeep (sublithospheric) diamonds from São-Luis often have complex growth histories, reflecting several separate growth events. The range of carbon isotope composition is from +2.7 to -25.3 ‰ ($\delta^{13}C$):

(i) The lowest values potentially represent organic matter in sediments or altered basalts subducted to the TZ and LM, and the higher values may represent mixing trends towards normal mantle compositions.

(ii) Some superdeep diamonds have initiated their growth in the LM and following slow uplift in a convective mantle have equilibrated in the TZ, and in doing so show another evolution in carbon isotopic composition.