SUBLITHOSPHERIC MINERAL ASSOCIATIONS OF INCLUSIONS IN SUPERDEEP DIAMONDS

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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.
Sublithospheric (Superdeep) Diamonds

- MgSi-Pv, fPer, CaSi-Pv
- Maj-Grt, SiO₂ (Stv?)
- TAPP

Harte, 2010
Superdeep Diamonds

Diamonds from São-Luis 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

- Majoritic garnets (±Clinopyroxene)
- CaSi-perovskite (±CaTi-perovskite)
- Ferropericlase
- MgSi-perovskite (Bridgmanite)
- Olivine (Wadsleyite, Ringwoodite?)
- TAPP (Tetragonal Almandine-Pyrope Phase - Jeffbenite)
- SiO₂ (Coesite±kyanite=Stishovite?)
- Al-Si-phase
- K-feldspar (K-hollandite?)
- Cr-pyrope
- Grossular (CAS?)
- Merwinite
- Nepheline+Spinel (NAL?, CF?)
- Metallic Iron
- Fe-sulphides
- Carbonates (MgCO₃, CaCO₃)
Mineral inclusions

Ferropericlase

MgSi-perovskite

SiO₂ - phase

Majoritic garnet

CaTiSi-perovskite

No phase transition

Phase transition
**Ferropericlase (Mg,Fe)O**

**Associations**
- fPer+Ol
- fPer+MgSi-Pv

**Mineral inclusions**

- Júina
- São-Luis (Kaminsky et al., 2001)
- São-Luis (new data n=11)

**Graph**
- NiO, wt.% vs. Mg# (0.1÷0.8)
- Mg-ferrite (white)
- Plume-related (?)
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*) $\text{MgSiO}_3$

**Associations**
- $\text{MgSi-Pv} + \text{fPer}$
- $\text{MgSi-Pv} + \text{Ol} + \text{CaSi-Pv}$
- $\text{MgSi-Pv} + \text{TAPP} + \text{CaSiTi-Pv}$

![Graph showing Al₂O₃ wt.% vs Mg#]
Mineral inclusions

**Jeffbenite**

*TAPP – tetragonal almandine-pyrope phase* $(Mg,Fe)_{3}Al_{2}(SiO_{4})_{3}$

**Associations**

TAPP+MgSi-Pv+CaSiTi-Pv

(i) $(Ca,Mg,Fe)_{3}(Fe,Al,Si)_{2}(SiO_{4})_{3} \rightarrow (Mg,Fe)_{3}Al_{2}(SiO_{4})_{3} + CaSiO_{3}$

Maj-Gt \hspace{1cm} TAPP \hspace{1cm} CaSi-Pv

(ii) $Mg(Al,Si)O_{3} \rightarrow (Mg,Fe)_{3}Al_{2}(SiO_{4})_{3} + MgSiO_{3}$

Al-MgSi-Pv \hspace{1cm} TAPP \hspace{1cm} MgSi-Pv
Mineral Inclusions

‘Olivine’ (Mg,Fe)$_2$SiO$_4$

Associations
Ol+fPer
Ol+MgSi-Pv+CaSi-Pv
Ol+CaSi-Pv+Mrw
Ol+Cr-Prp

NiO, wt. %

Sao-Luis (new data)
Juina
Ol in Dia

Fo, mol. %

α – olivine (P <12 Gpa)
β – wadsleite (P >12 GPa)
γ – ringwoodite (P >17 Gpa)
Mineral Inclusions

‘Ringwoodite’ (Mg,Fe)$_2$SiO$_4$

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**

\[(\text{Ca,Mg,Fe})_3(\text{Fe,Al,Si})_2(\text{SiO}_4)_3\]

- ○ Eclogitic
- □ Pyroxenitic
- △ Peridotitic
- ★ Our new data

Most majoritic garnets in diamonds from Sao-Luis are of basitic affinity (eclogitic and pyroxenitic).
Majoritic Garnets
\((\text{Ca}, \text{Mg}, \text{Fe})_3(\text{Fe}, \text{Al}, \text{Si})_2(\text{SiO}_4)_3\)

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

- CaSi-Pv+Maj-Gt
- CaTiSi-Pv+Maj-Gt+SiO₂+FeS
- CaTiSi-Pv+Maj-Gt+SiO₂+Kya
- CaSi-Pv+SiO₂+AlSi-phase
- CaSi-Pv+AlSi-phase

- CaSi-Pv+CaSi₂O₅

*20 mol.% CaTiO₃*

*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-stishovite? (question mark)

Al solubility in stishovite increases with increasing pressure

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

[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

new aluminum silicate phase

(Na,K)AlSiO$_4$

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

CF

Ca-ferrite-structured phase

NaAlSiO$_4$

[Litason et al., 2007]
Association of CaAlSi- and SiAl-phases, K-hollandite, CF, NAL, Maj-garnets and SiO$_2$ correspond to experimentally founded associations of deeply subducted metasediments.
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).

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

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.

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

(Sao-Luis diamonds)
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**

\[(\text{Ca, Mg, Fe})_3(\text{Fe, Al, Si})_2(\text{SiO}_4)_3\]

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).
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)

FTIR spectroscopy:
Water, silicates and carbonates are NOT major components of these microinclusions.

\[ \delta^{13}C = -7.7 \div -5.1 \% \]

\[ H_2 \text{ or } C_nH_m? \]
\[ N_2 \text{ or } NH_3 \ (\text{Rudloff et al., 2014}) \]
Model

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)

❖ 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 metaperidotitic 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.