The deep mantle genesis of CLIPPIR and Type IIb diamonds

Evan M. Smith

Gemological Institute of America

12TH INTERNATIONAL KIMBERLITE CONFERENCE

30 YEARS OF DIAMONDS IN CANADA

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Primary Lecture for 12IKC Seminar II

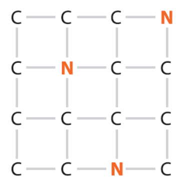
Large Irregular Type II diamonds: genesis and transport to surface

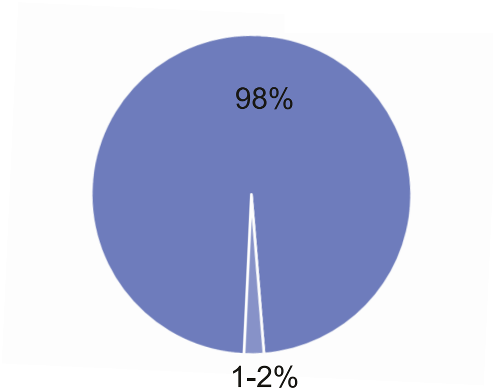
CARNEGIE SCIENCE | UNIVERSITÀ DEGLI STUDI DI PADOVA | UNIVERSITY OF CAPE TOWN IYUNIVESITHI YASEKAPA • UNIVERSITEIT VAN KAAPSTAD

Collaborators: Steven B. Shirey, Stephen H. Richardson, Fabrizio Nestola, Emma S. Bullock, Jianhua Wang, Wuyi Wang, Peng Ni, Anat Shahar

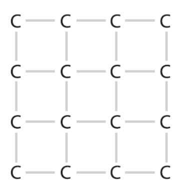
Diamond Type

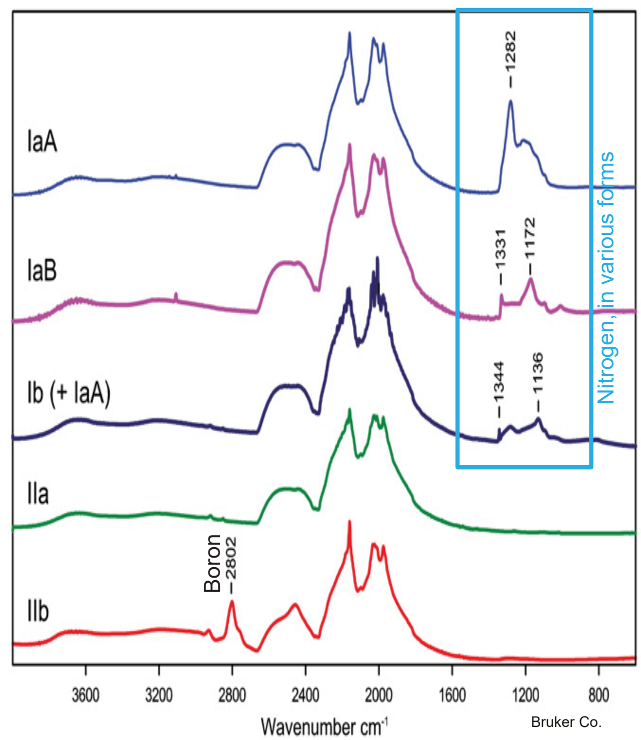
Type I
contains nitrogen





Type II
no nitrogen (<5 ppm)



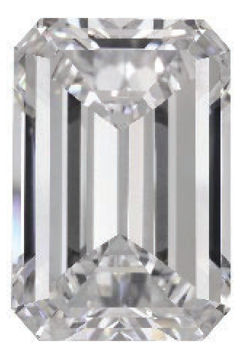


Bruker Co.

Do these diamonds form in a unique way?

It has long been recognized that CLIPPIR and Type IIb diamonds stand out as unusual, but it is only recently that we are beginning to understand why

“Ordinary” diamonds

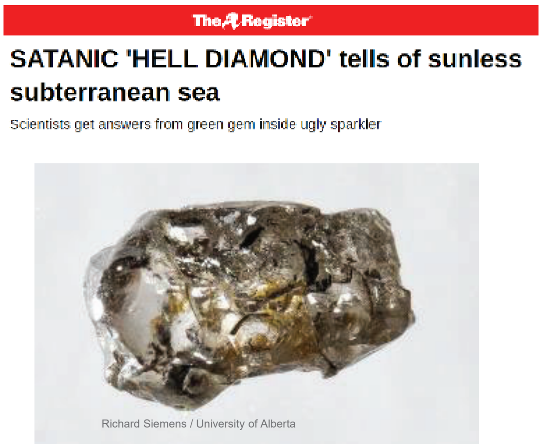


Large, irregular Type IIa (CLIPPIR)

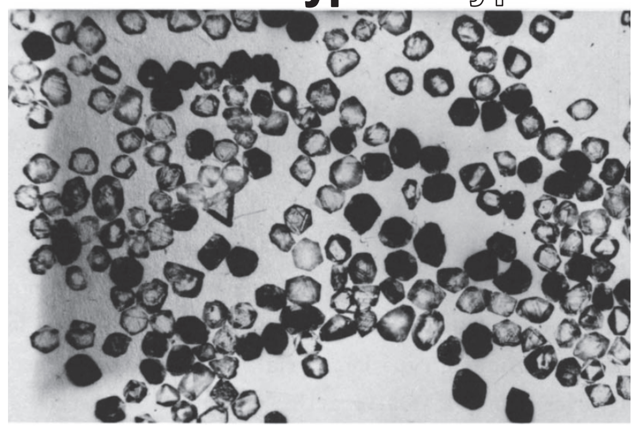
Type IIb

Type II is not a tidy geological category

- Boundary between Type I and Type II is fuzzy
- Several known processes can make nitrogen-poor diamonds
  - Lithospheric E- and P- type diamonds
  - Ordinary/Juina-type sublithospheric diamonds
  - Microdiamonds


The Register
SATANIC 'HELL DIAMOND' tells of sunless subterranean sea
Scientists get answers from green gem inside ugly sparkler

Microdiamonds **Type I** Type II



Tolansky, S., and M. Rawle-Cope (1969), Type 2 abundance in natural micro-diamonds, *Mater. Res. Bull.*, *4*(8), 555-562.

The "real" Type IIs

They are visually distinct, not just type II

10th International Kimberlite Conference, Bangalore - 2012

10IKC-123

TYPE IIA DIAMONDS AND THEIR ENHANCED ECONOMIC SIGNIFICANCE

J J Gurney[1], H H Helmstaedt[2]

"This population is visually recognizable on the basis of shape, colour and surface texture with more than 90% certainty."

Table 1
Accuracy of the visual recognition of Type IIa diamonds at Letšeng confirmed with a Bruker FTIR spectrometer.

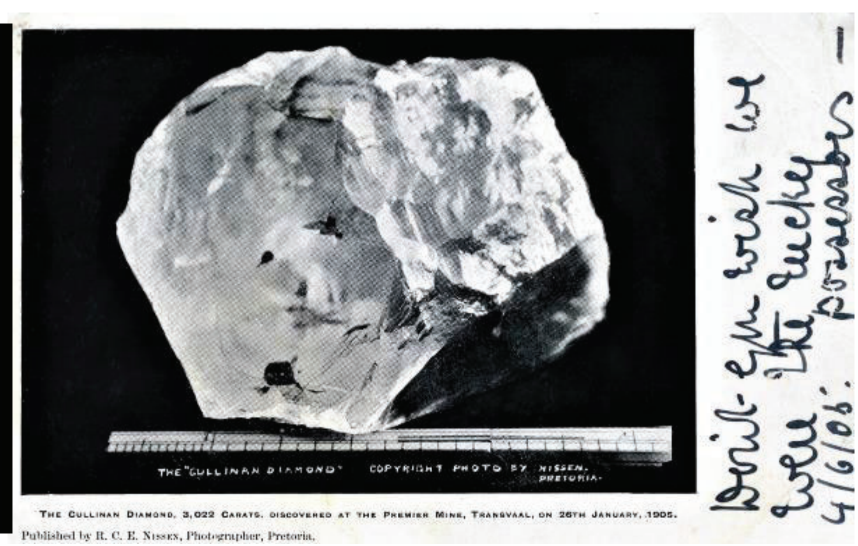
Visual identification of type IIa diamonds				FTIR confirmation by Bruker	
Size	Potential type IIA STONES	Total per size	% of size	Confirmed	Visual accuracy
2 ct	34	186	18.28%	33	97.06%
2.5 ct	13	54	24.07%	11	84.62%
3 ct	22	91	24.18%	21	95.45%
4 ct	12	56	21.43%	12	100.00%
5 ct	11	31	35.48%	11	100.00%
6 ct	3	14	21.43%	3	100.00%
7 ct	8	20	40.00%	8	100.00%
8 ct	3	6	50.00%	3	100.00%
9 ct	0	2	0.00%	0	0.00%
10 ct	2	5	40.00%	2	100.00%
+ 10.8 ct	13	19	68.42%	13	100.00%
TOTAL	121	484	25.00%	117	**96.69%**

Overall 96% accurate in a subset of 484 diamonds over 11 diamond size classes from 2 cts through to + 10.8 cts.

Bowen et al., (2009) On the unusual characteristics of the diamonds from Letšeng-la-Terae kimberlites, Lesotho: *Lithos, Vol. 112, No. 0, p.p. 767-774.*

CLIPPIR diamonds

Cullinan-like, **L**arge, **I**nclusion **P**oor, **P**ure, **I**rregular, **R**esorbed



CLIPPIRs among 3.5 million diamonds

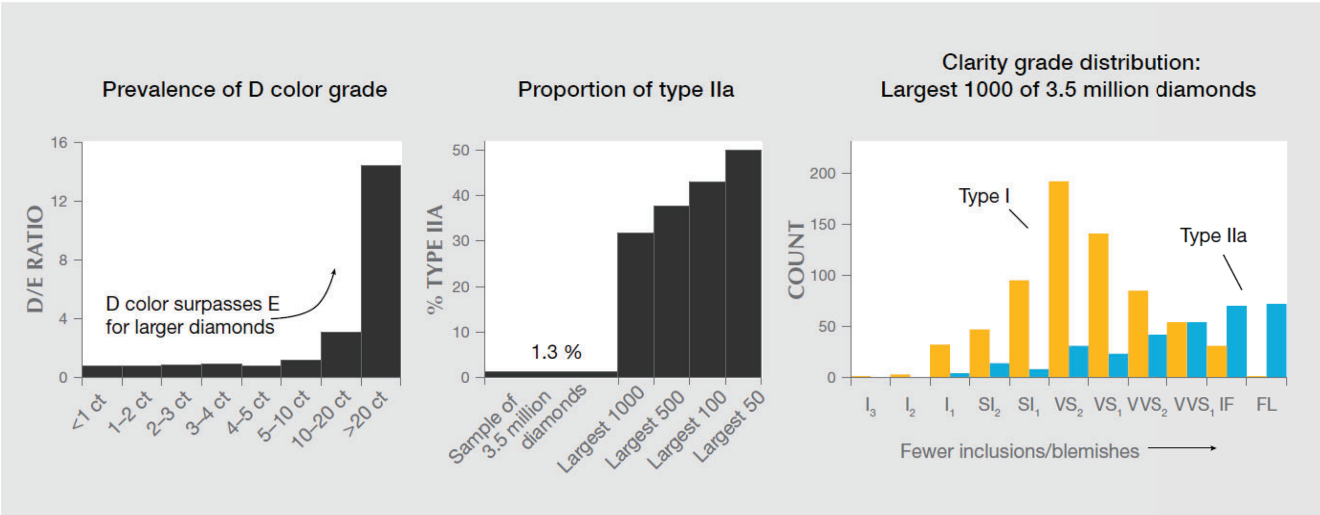
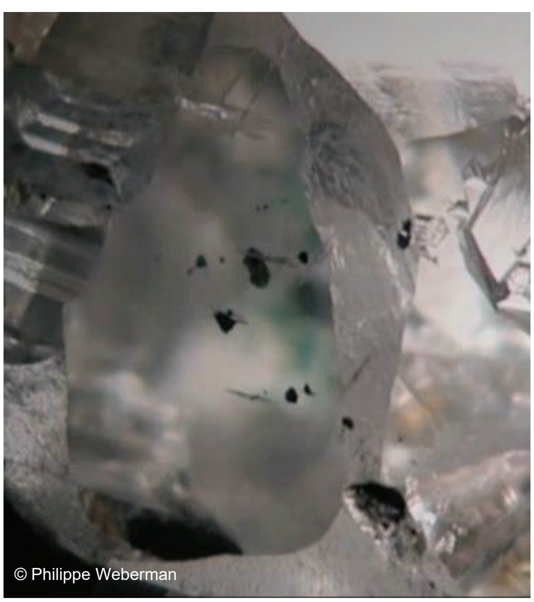


Figure 2. Systematic deviations of properties suggest that CLIPPIR diamonds become more prevalent among larger-sized diamonds. Left: Diamonds over 5 carats show an increasing incidence of D color grades in a random sample of 4.2 million diamonds graded by GIA; shown is the ratio of D color (colorless) to E color (not quite perfectly colorless) grades awarded. Center: In a similar dataset of 3.5 million samples, the proportion of type IIa diamonds (nitrogen-deficient, high-purity) also increases dramatically when considering only the larger diamonds. Right: Among a set of large diamonds, all over 15 carats, those qualifying as type IIa have markedly higher clarity and dominate the flawless grade category. (GIA clarity abbreviations: FL = flawless, IF = internally flawless, $VVS_{1/2}$ = very very slightly included 1/2, $VS_{1/2}$ = very slightly included 1/2, $SI_{1/2}$ = slightly included 1/2, and $I_{1/2/3}$ = included 1/2/3)

Smith et al. (2017). *Gems & Gemology* ***53, 388-403.***

Rounded, flaky "Graphite" inclusions

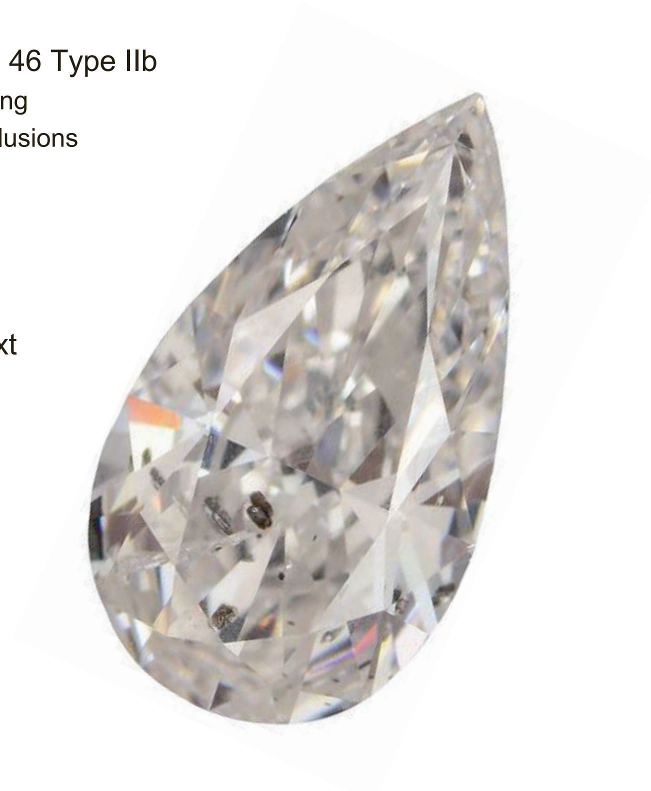
Lesotho Promise, 603 ct
(window showing inclusions)



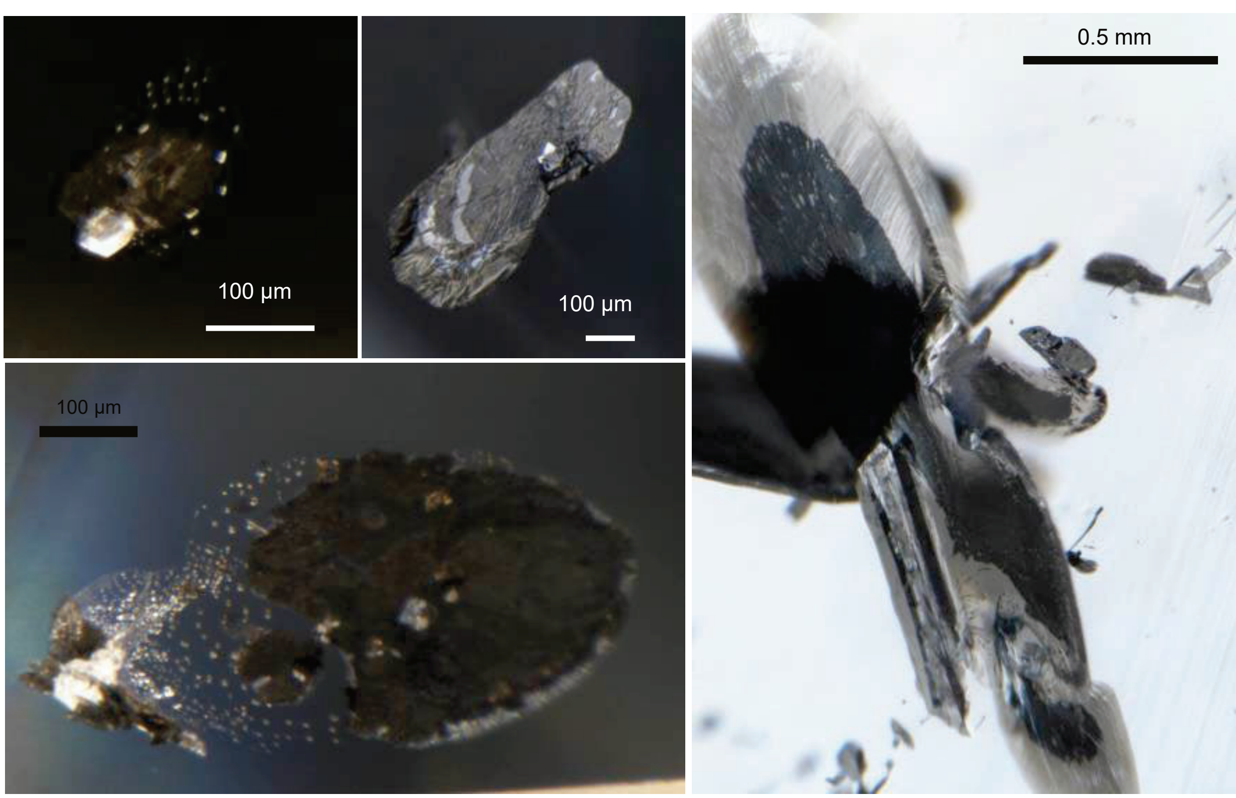
Flawless after cutting, 223 tcw

The Hunt for Inclusions

- Examined inclusions in 83 Type IIa and 46 Type IIb
  - Screened diamonds sent to GIA for grading
  - 1 in 10,000 is Type IIa diamonds with inclusions
  - Inclusion-bearing “offcuts”
- Raman spectroscopy
- X-ray diffraction
- Electron microprobe, SEM, EDS
- Inclusions reveal their geological context

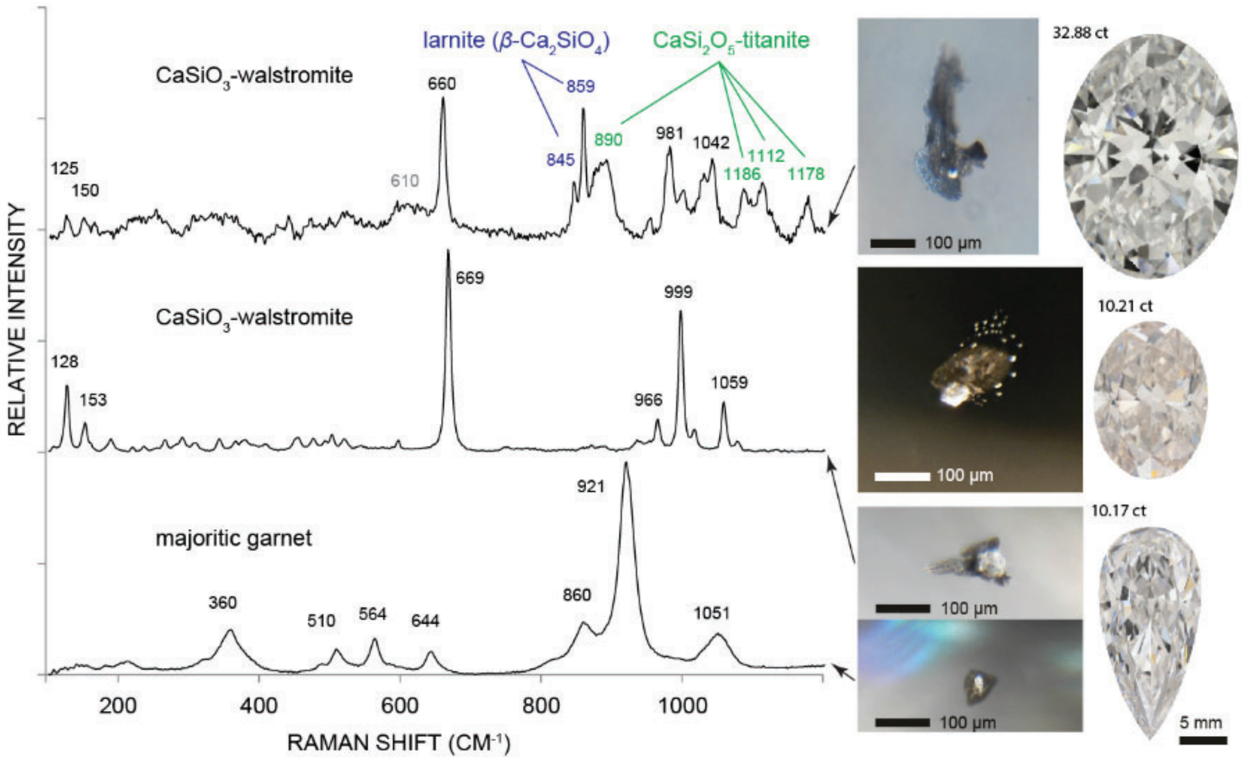


Rounded, flaky “Graphite” inclusions up close



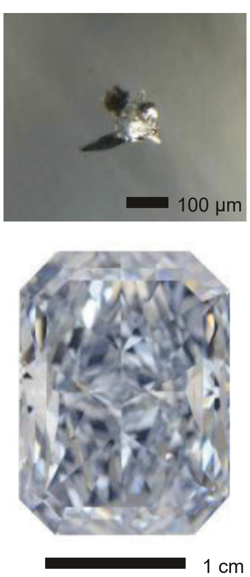
Photos: Evan M. Smith © GIA

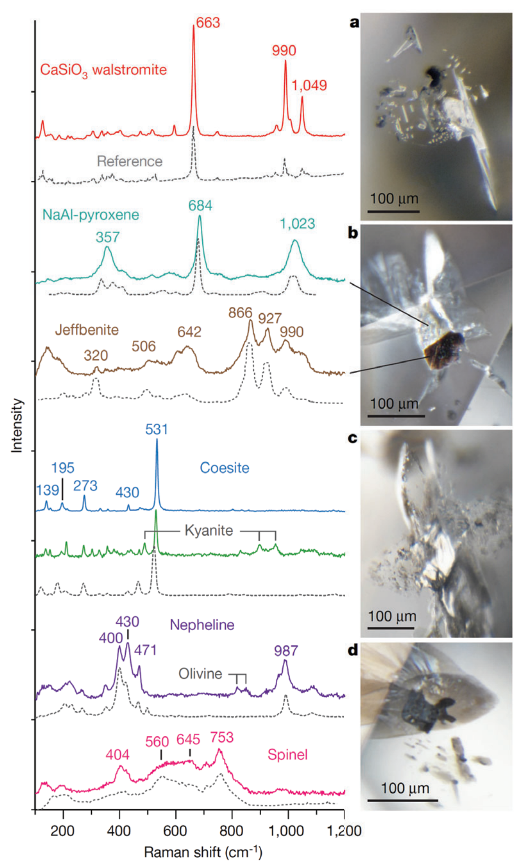
CLIPPIR silicate inclusions



Smith et al. (2017). *Gems & Gemology* ***53, 388-403.***

Type IIb inclusions

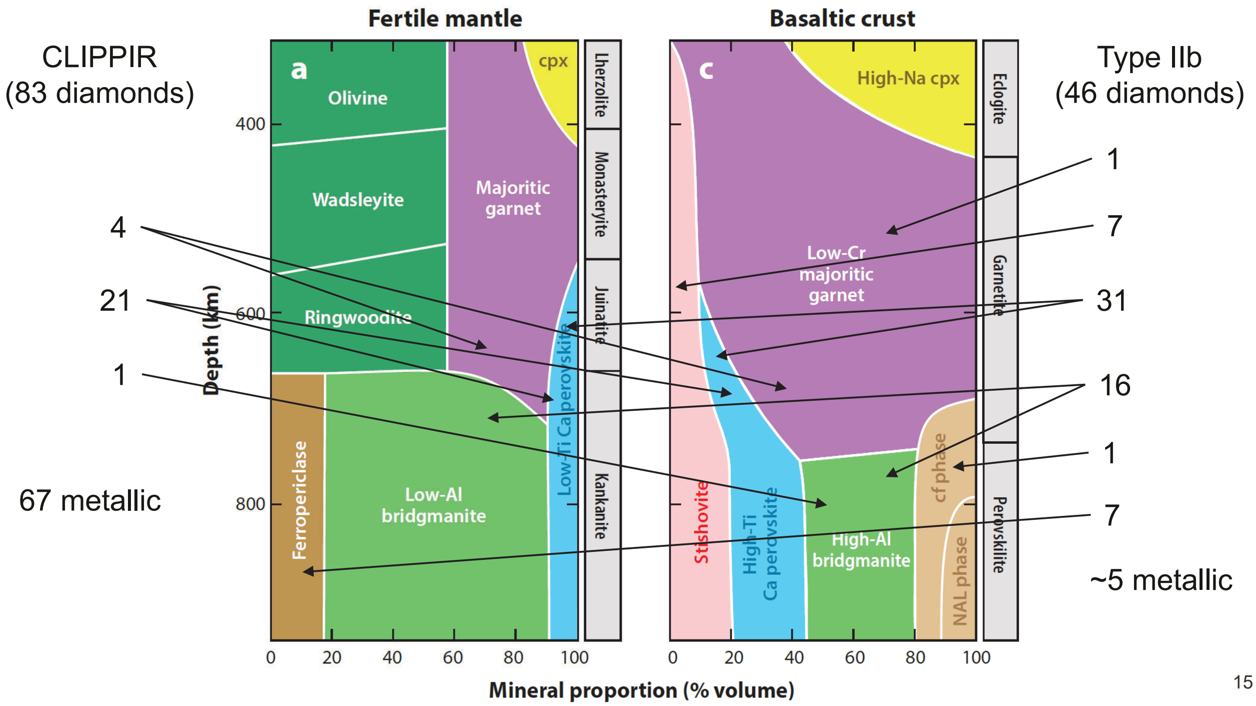




Smith et al. (2018). Blue boron-bearing diamonds from Earth's lower mantle. *Nature* ***560, 84-87.***

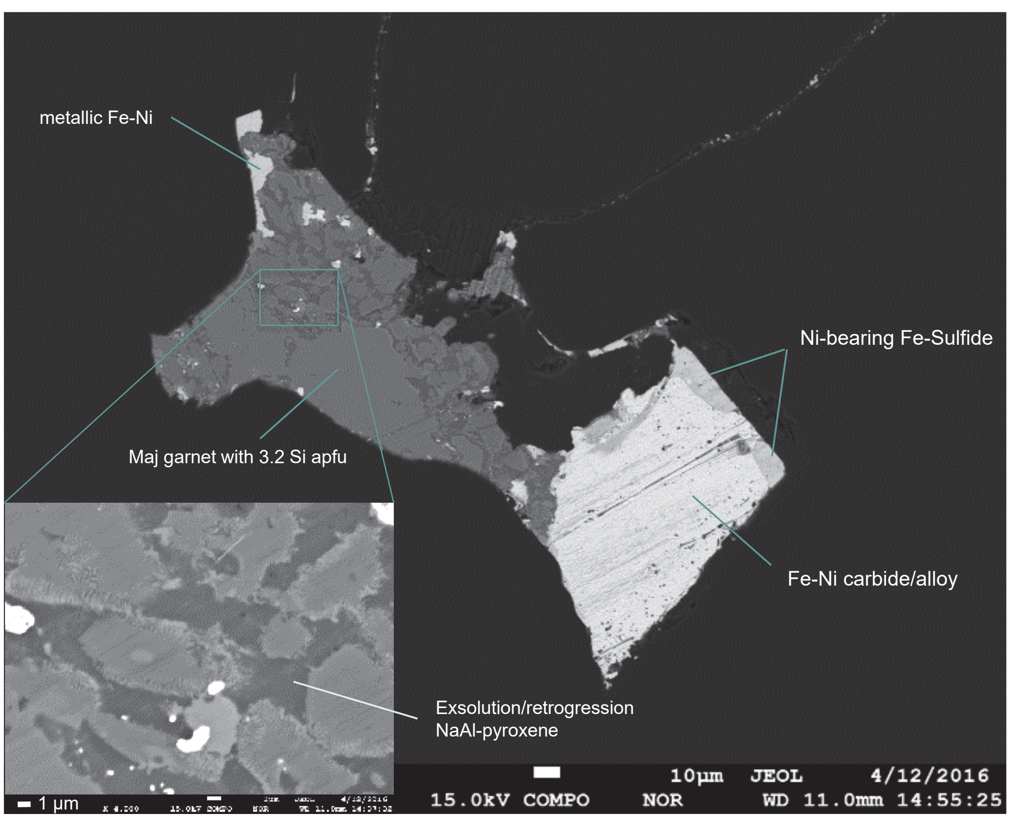
Inclusions & Mantle Mineralogy

- Resemble those reported in other sublithospheric diamonds
- Associated with subducted slab, 360–800 km



Shirey et al. (2024). Sublithospheric Diamonds: Plate Tectonics from Earth's Deepest Mantle Samples. *Annual Review of Earth and Planetary Sciences* **52.**

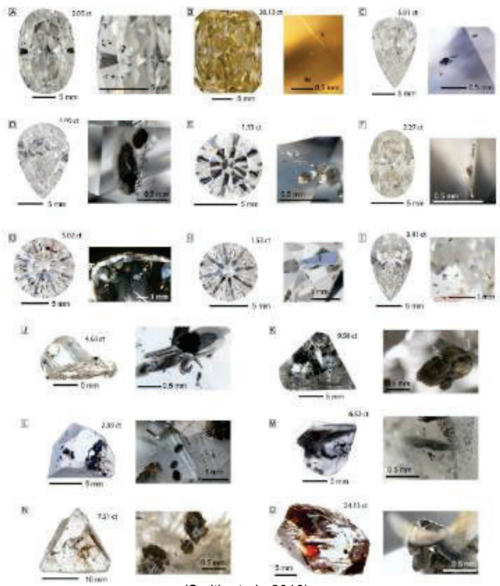
Majoritic garnet with metal



(Smith et al., 2016)

Metallic inclusions

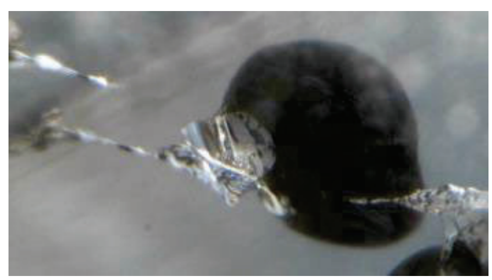
Account for 72% (n=83) of the inclusions in CLIPPIR diamonds



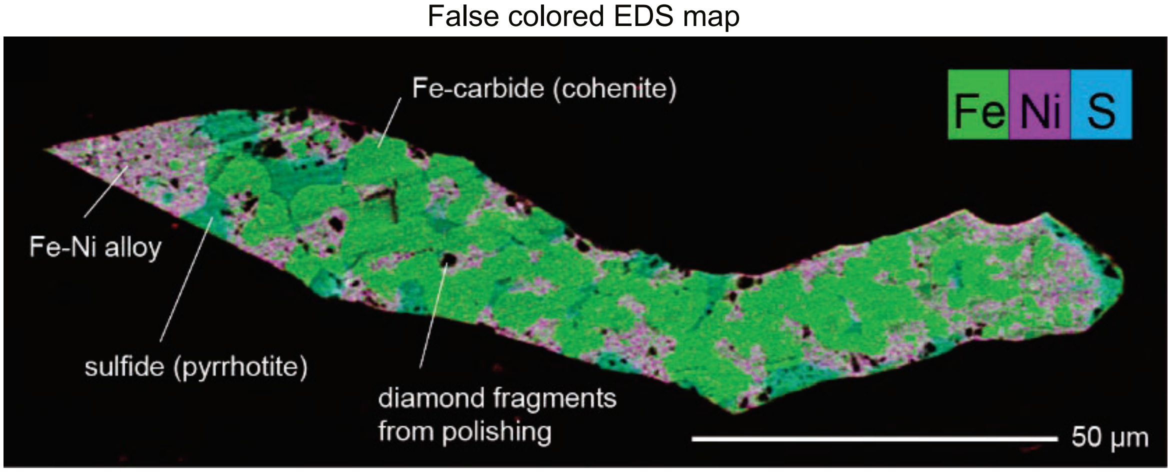
(Smith et al., 2016)

Metallic inclusions

- Metallic Fe-Ni-C-S melt inclusions
- $T_m \approx$ 1300–1400 °C (lower with H)
- Minor Fe-phosphate, Fe-Cr-oxide, Fe-oxide
- Estimated bulk composition: $Fe_{0.61\text{-}0.75}Ni_{0.10\text{-}0.13}C_{0.15\text{-}0.20}S_{0.05\text{-}0.12}$
- Served as diamond-forming medium



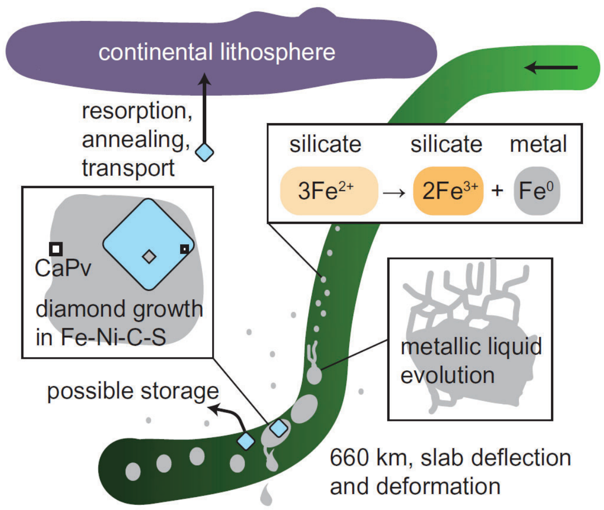
False colored EDS map



(Smith et al., 2016)

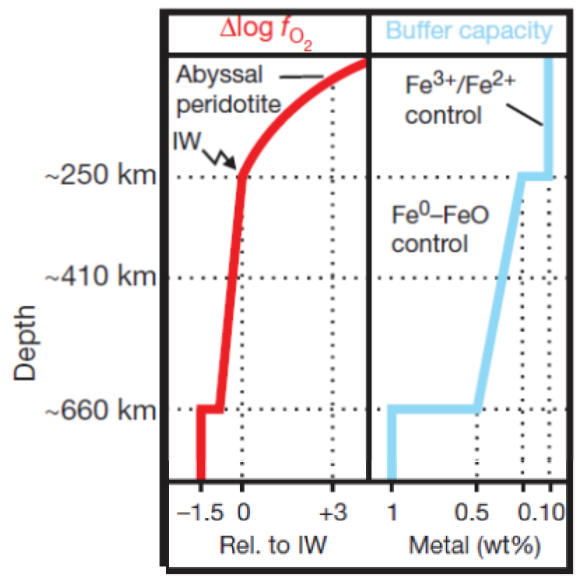
Disproportionation and Metallic Iron

Original 2016 CLIPPIR model, outdated



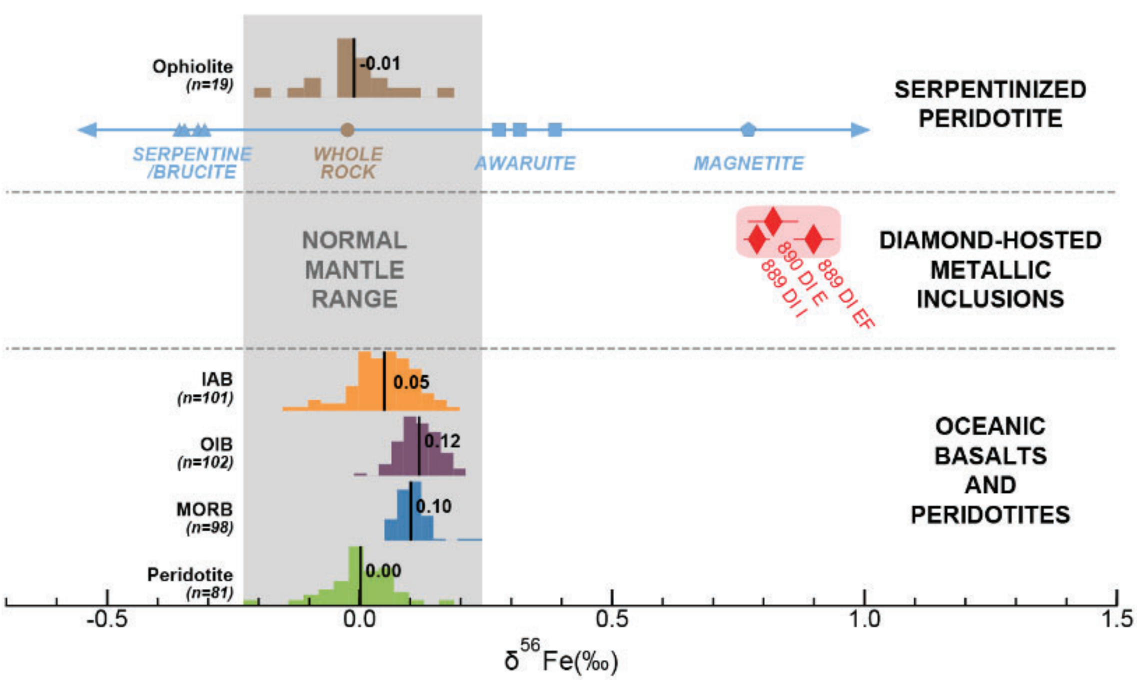
(Smith et al., 2016)

Below ~250 km, there should be metallic iron from disproportionation



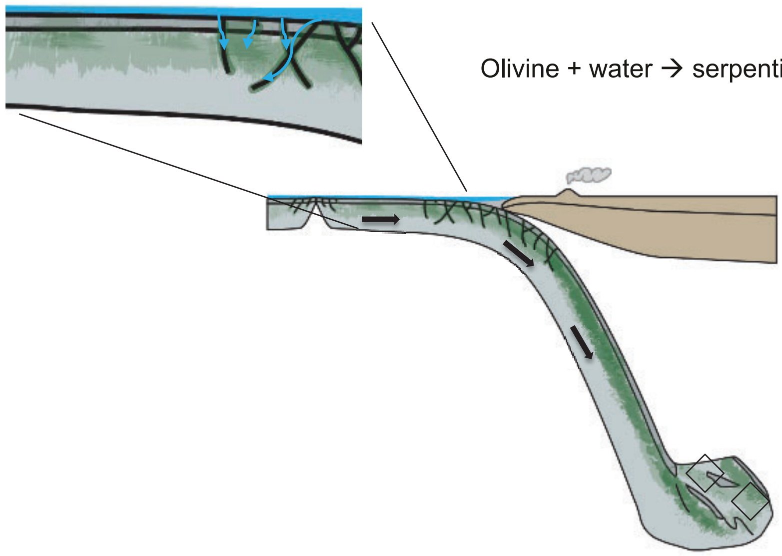
(Rohrbach and Schmidt, 2011)

Iron Isotopic Composition



Smith & Ni et al. 2021, *Science Advances*, *7*(14), eabe9773. DOI: 10.1126/sciadv.abe9773

Iron from Serpentinization



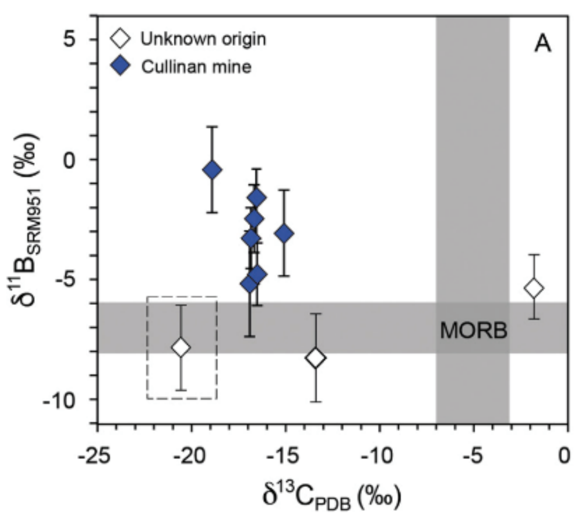
Olivine + water → serpentine + brucite + magnetite + H_2

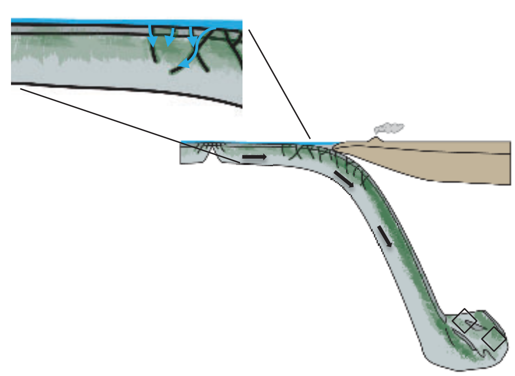
+ Fe-Ni alloys

These iron-rich phases contain heavy iron

Boron Isotopes in Type IIb diamonds

Boron also points to contribution from seawater-altered oceanic lithosphere

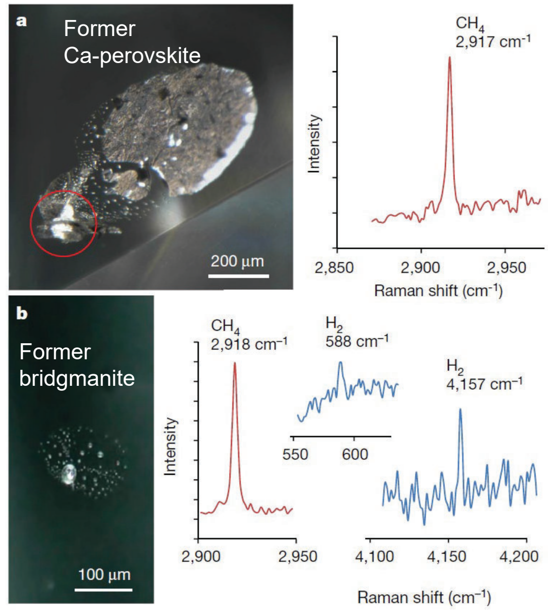




Regier et al., 2023. Boron isotopes in blue diamond record seawater-derived fluids in the lower mantle. EPSL. doi.org/10.1016/j.epsl.2022.117923

Hydrogen in silicate inclusions

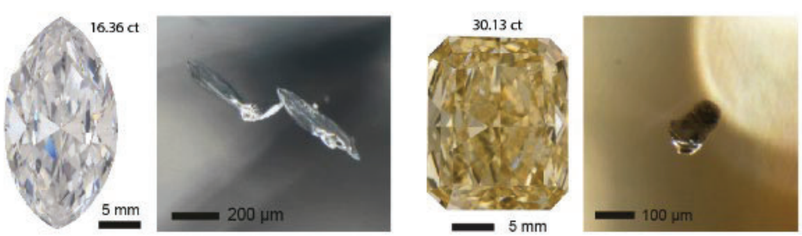
- 13 of 46 Type IIb diamonds have inclusions with $CH_4 \pm H_2$
- Hydrogen that exsolved and accumulated at inclusion interface
- Suggests a hydrous component in diamond formation

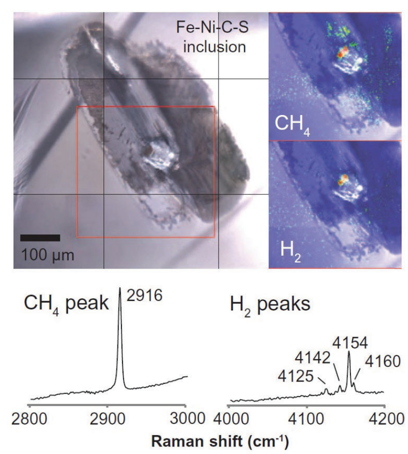


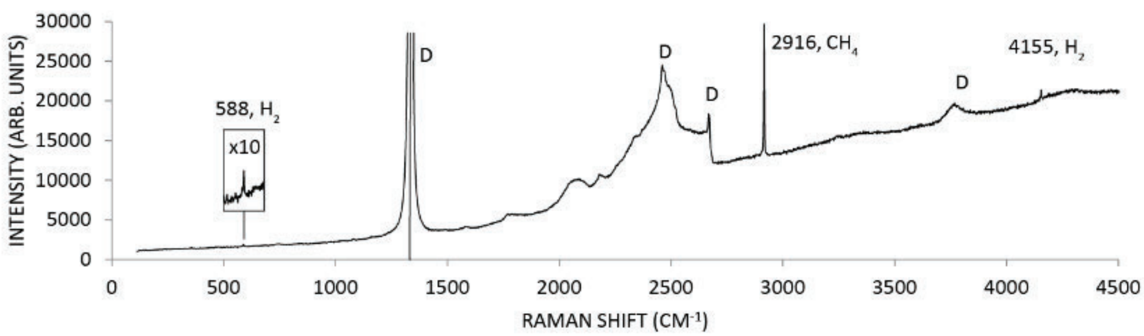
Smith et al. (2018). Blue boron-bearing diamonds from Earth's lower mantle. ***Nature* 560, 84-87.**

Hydrogen in metallic inclusions

- Thin $CH_4 \pm H_2$ fluid layer at inclusion/diamond interface of virtually all metallic inclusions
- Was originally dissolved H in the Fe-Ni-C-S melt



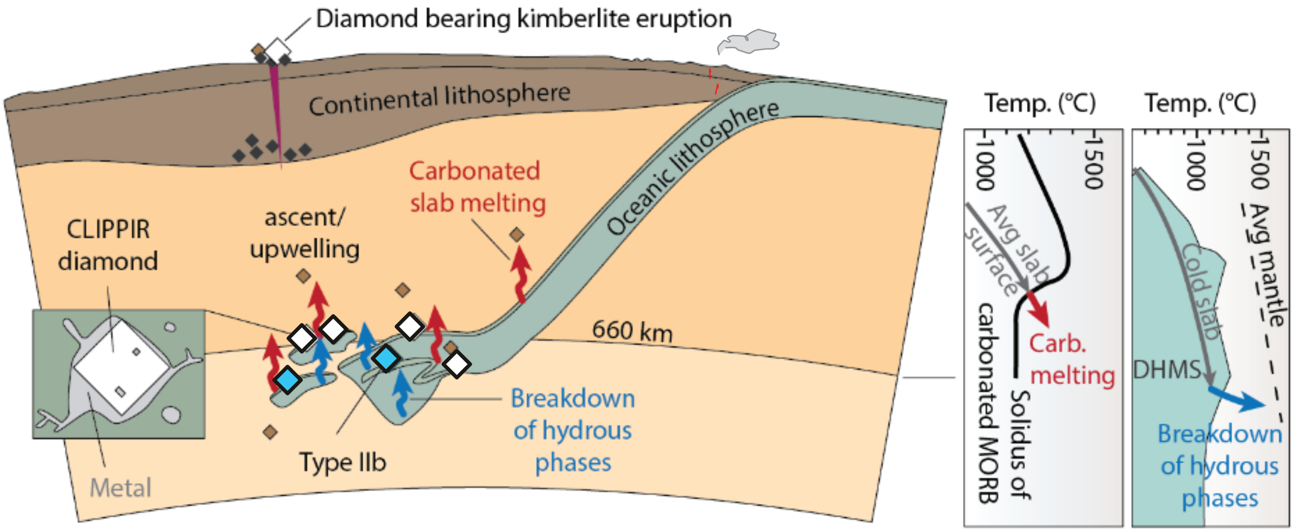




Smith et al. (2017).*Gems & Gemology* ***53*, 388-403.**

Diamond genesis

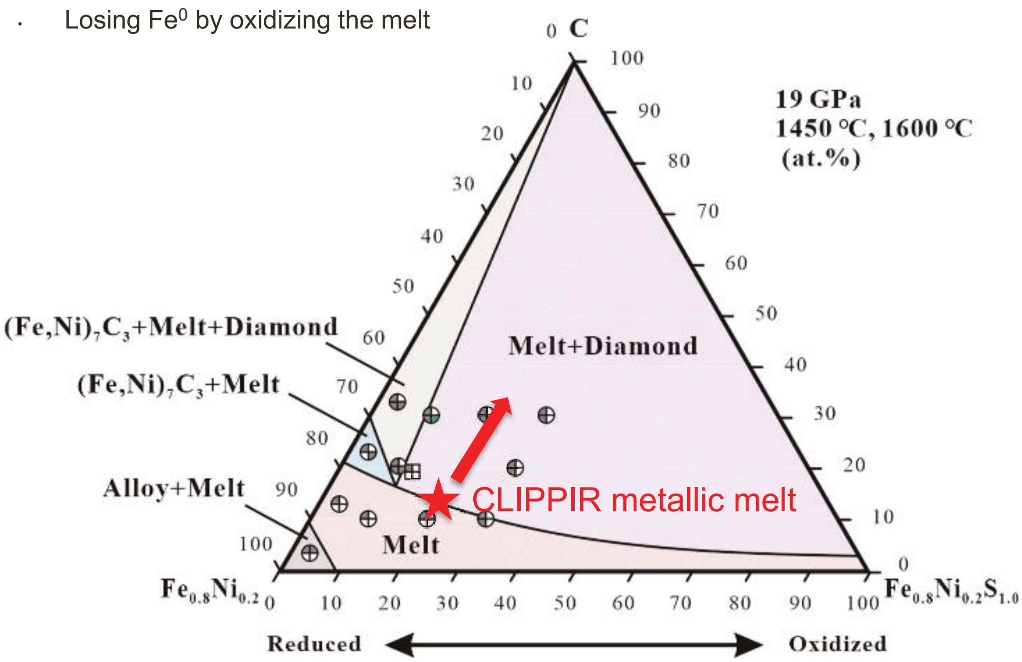
- CLIPPIR and Type IIb diamonds are related
- Altered oceanic lithosphere warming and deforming at MTZ/LM depths
- Fe-Ni-C-S melt evolution from meta-serpentinite is key for CLIPPIR
  - C precipitates from metallic melt
  - Interaction with hydrous/carbonatitic melt?



Smith, E. M., and Nestola, F., 2021, Super-Deep Diamonds: Emerging Deep Mantle Insights from the Past Decade, *in Marquardt, H., Ballmer, M., Cottaar, S., and Konter, J., eds., Mantle Convection and Surface Expressions, American Geophysical Union, p. 179-192.*

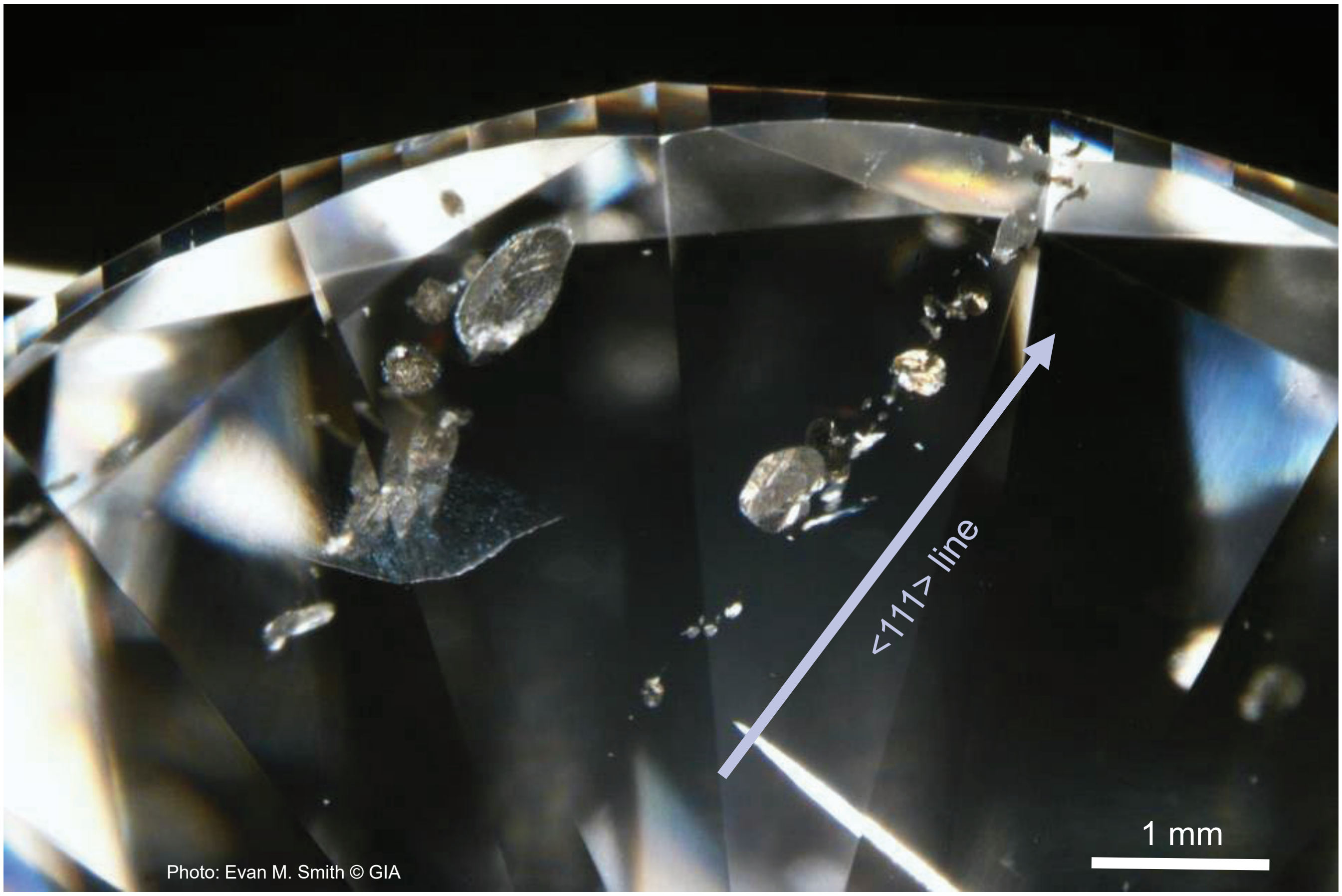
Diamond genesis

- C precipitates from Fe-Ni-C-S, possible melt by:
  - Adding C to the melt
  - Adding sulfur
  - Losing Fe^0 by oxidizing the melt



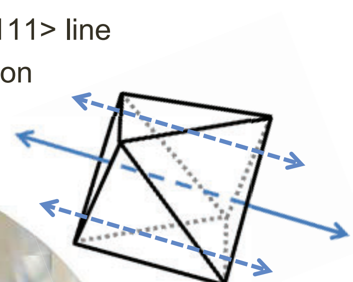
(Lei et al., Carbon in the deep upper mantle and transition zone under reduced conditions, GCA, 2022)

Metallic inclusion chains



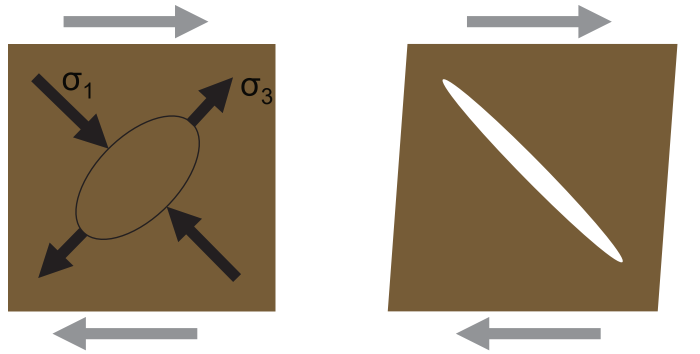
Metallic inclusion chains

- When present, multiple chains run sub-parallel along a single <111> line
- Define a pervasive fabric, possibly due to post-growth deformation



Like Tension Gashes

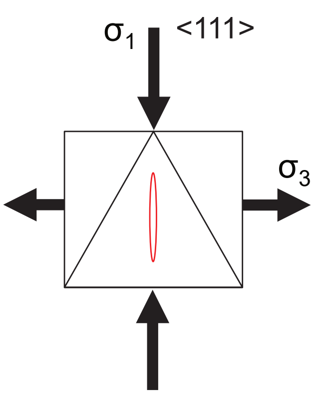
Fracture opens & fills
with mobile melt/fluids



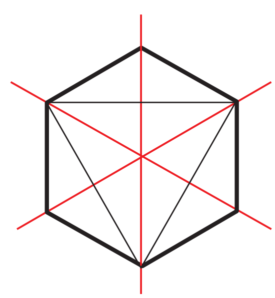
Rob Butler et al., University of Leeds, Teaching Resources in Structural Geology

Tension crack in diamond

Stress field inside the
diamond, resolved to
the crystal lattice



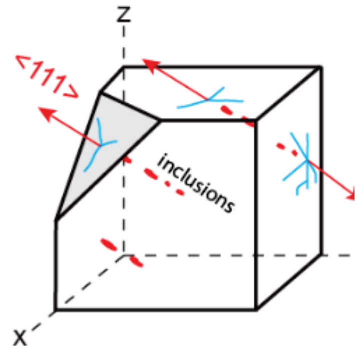
Top view

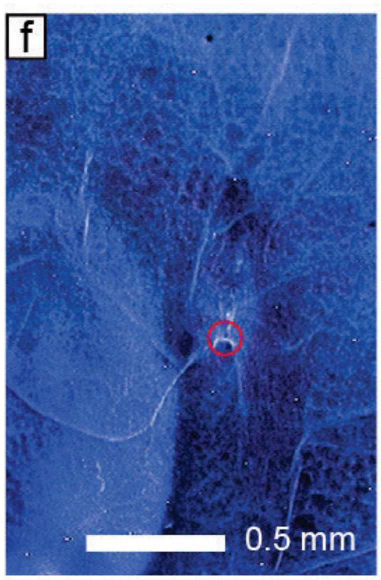


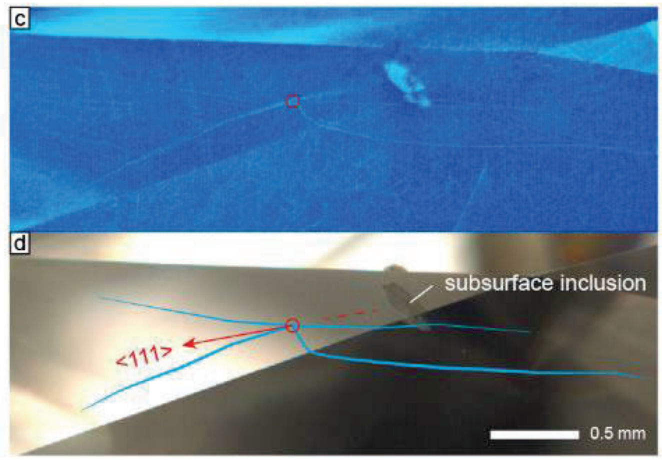
3 possible {110} cleavages

Metallic inclusion chains

Chains lie at intersection of curvi-planar features of {110} orientation, interpreted as healed fractures

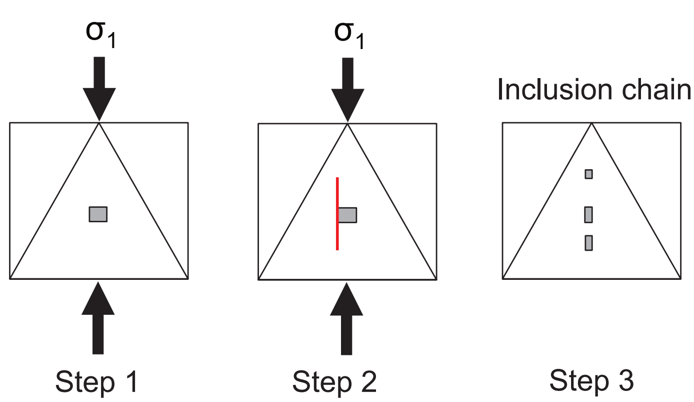






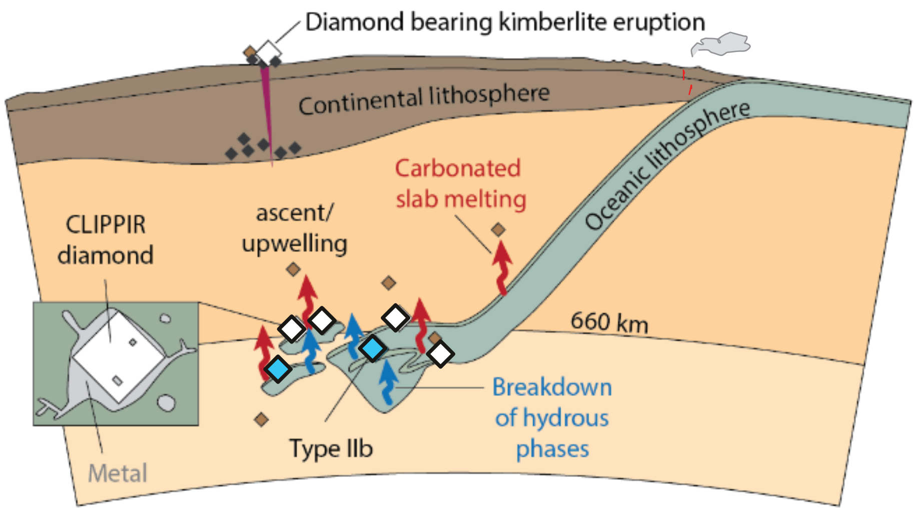
Smith, E. M., Shirey, S. B., and Wang, W. (2017) *Gems & Gemology, Vol. 53, No. 4, p.p. 388-403, http://dx.doi.org/10.5741/gems.53.4.388*

Chains by brittle-plastic deformation



Inclusion chain meaning

- Chains record a single high strain rate event
- Predates later deformation and annealing



Dislocation Networks

- CLIPPIR and Type IIb diamonds have high dislocation densities
- Dislocations have polygonised/annealed to form networks
- Deformation followed by annealing/polygonization
- Sometimes overprinted by renewed {111} slip

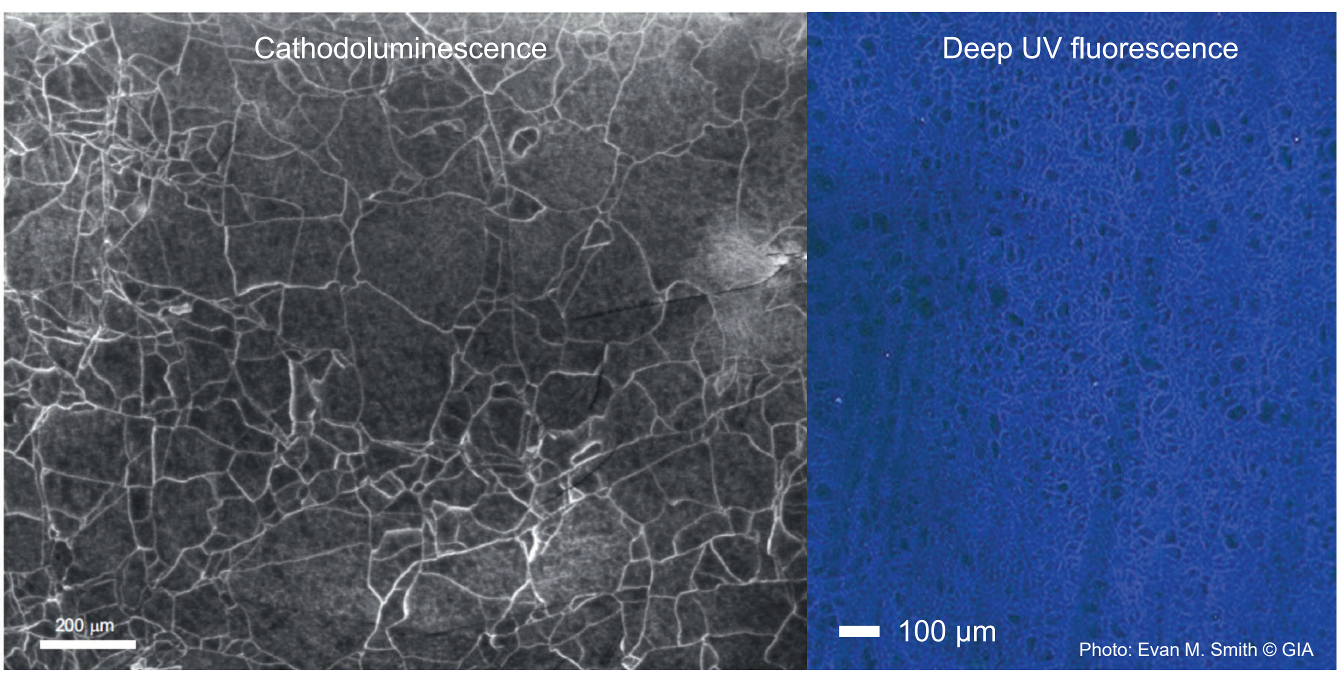
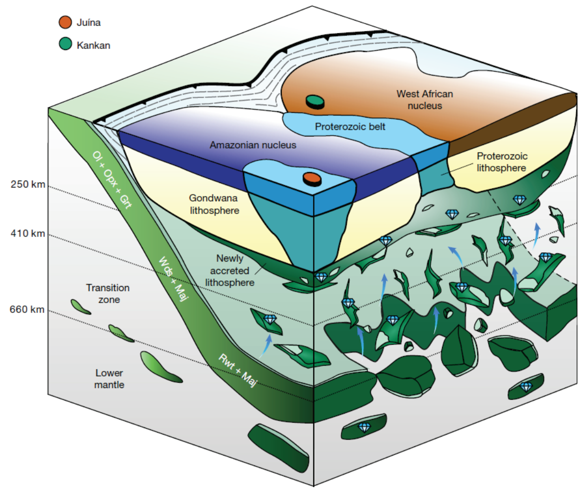
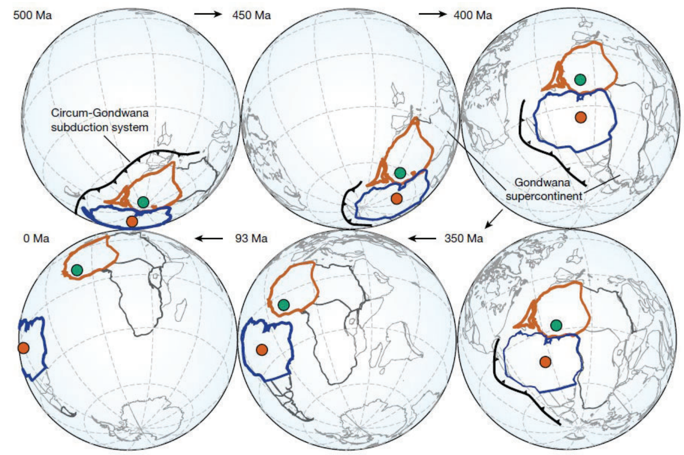


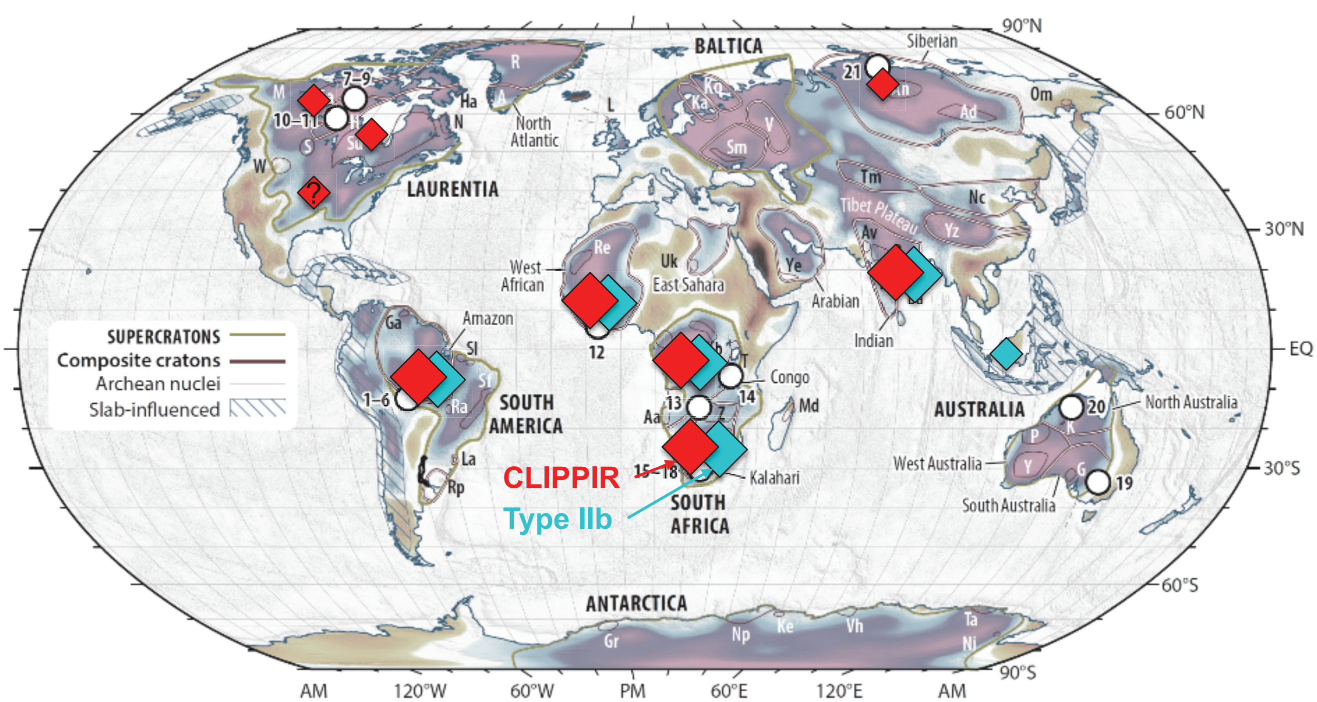
Plate deformation and fragmentation





Timmerman et al., (2023) Sublithospheric diamond ages and the supercontinent cycle: *Nature, Vol. 623, No. 7988, p.p. 752-756, http://dx.doi.org/10.1038/s41586-023-06662-9*

Approximate CLIPPIR/IIb Distribution



Localities (*modified craton)

A Atlantic	Ca Carajas	Ha Hall	Ks Kasai	Nc North China*	Re Reguibot	Sm Sarmatia	Uk Uweinat-Kamil
Aa Angola	D Dharwar	K Kimberley	La Lius Alves	Ni Nimrod	Rp Rio de la Plata	Su Superior	W Wyoming*
Ad Aldan	G Gawler	Ka Karelia	L Lewisian	Np Napier	S Sask	T Tanzania	Y Yilgarn
An Anabar	Ga Guiana	Kb Kibalia	M Mackenzie	Om Omolon*	Sa Slave	Ta Terra Adélie	Ye Yemen
Av Aravelli,	Gb Gabon	Ke Kemp Land	Md Madagascar	P Pilbara	Sf Sao Francisco	Tm Tarim Basin	Yz Yangtze*
B Bundelkand	Gr Grunehogna	Ko Kola	Mn Man	R Rae	Si Singhblum	V Volga-Uralia	Z Zimbabwe
Ba Bastar	H Hearne	Kp Kaapvaal	N Nain	Ra Rio Apa	Sl Sao Lucia	VH Vestfold Hills	

(Shirey et al. 2024)

Exploration Implications

- CLIPPIR & Type IIbs are sublithospheric
- *Any* sublithospheric diamond may be a positive sign
- Large-scale process, large geographic footprint
- Attention to CLIPPIR, not just Type IIa
- Inclusions: pay attention to paragenesis
- CLIPPIR’s are less prevalent among smaller size fractions

Conclusions

- CLIPPIR (~Type IIa) and Type IIb diamonds are related and have a distinct sublithospheric genesis
- Contain abundant Ca-silicates, like other sublithospheric diamonds
- Serpentinization, subduction, evolution of a Fe-Ni-C-S metallic melt
- It is plausible that there are superdeep xenoliths/xenocrysts or other indicators