Isotope Fingerprinting (Made Easy)

Can We Trace Conflict Diamonds ?

Yes We Can.... Sometimes

Case studies from Republic Democratic of Congo and Central African Republic

P. Cartigny - IPG-Paris
M. DeWit - AEON-Cape Town
S. Glider - Univ. München
E. Doucet - INPL
and many others

What is a conflict diamond?

Conflict diamonds are diamonds that originate from areas controlled by forces or factions opposed to legitimate and internationally recognized governments, and are used to fund military action in opposition to those governments, or in contravention of the decisions of the Security Council.

Source : United Nations

On 1 December 2000, the United Nations General Assembly adopted, unanimously, a resolution […] to break the link between the illicit transaction of rough diamonds and armed conflict […]

The main countries concerned by this resolution are/were :

Angola, Sierra Leone, Liberia,
Ivory Coast, Democratic Republic of Congo,
Republic of Congo
(so we are talking about diamonds
from Western and Central African cratons)

Among the different solutions listed/supported/applied

➡ The **industry** took steps to address the conflict diamond issue and created the **Kimberley Process Certification Scheme.**

➡ **Gouvernements want the Kimberley Process Certification Scheme to be monitored**

The question(s) asked to scientists is (are)

- Q1: How can a conflict diamond be distinguished from a legitimate diamond ?

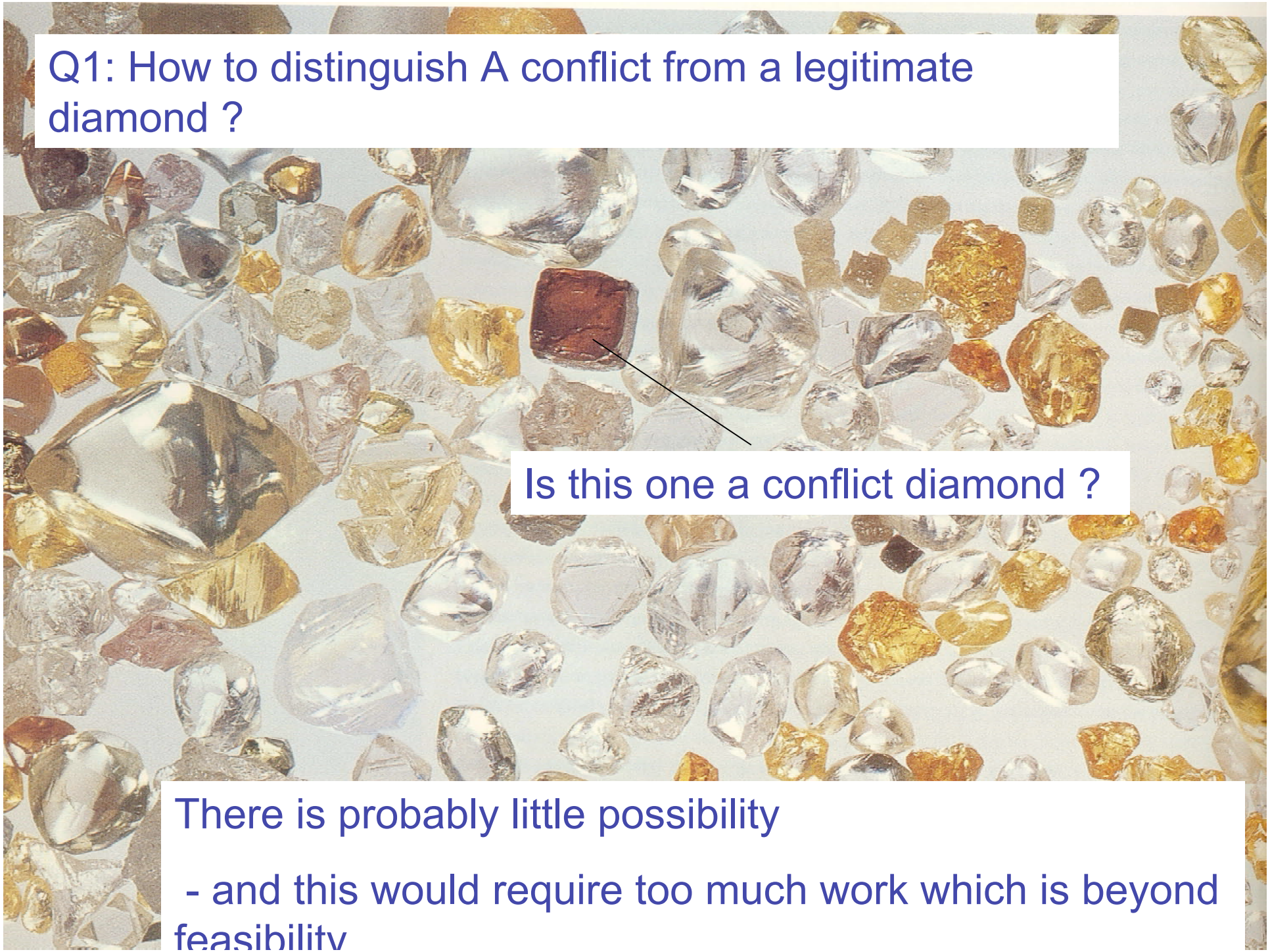
And/or (and this is not the same question)

- Q2 : How can conflict diamonds be distinguished from legitimate diamonds ?

Given that what is a “conflict/legitimate diamond” can change through time, the question is thus

“can we recognise the origin of diamonds ?”

[actually this is applied research]



Q1: How to distinguish A conflict from a legitimate diamond ?

Is this one a conflict diamond ?

There is probably little possibility

- and this would require too much work which is beyond feasibility

Q2 : How can conflict diamonds be distinguished from legitimate diamonds ?

Maybe

The(se) parameter(s) could be

- physical properties (size, shape, plastic deformation, surface features etc…)
- the types (eclogitic/peridotitic ratios), chemical/isotope composition of the inclusion,
- **C-isotopes, N-contents and N-aggregation state**, N-isotopes
- the trace element contents of diamond
- the magnetic properties (DeWit's talk)

- Better but not a prerequisite if the techniques are cheap, fast and not destructive

Thus to have diamonds from one location to differ from diamonds from another localition

the source of carbon
and or the process(es)

must be different

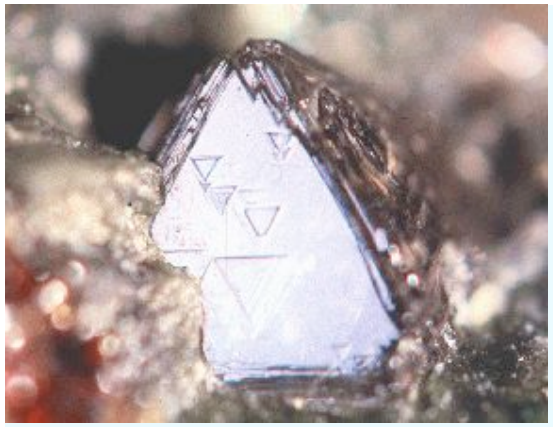
This can include : isotope composition of carbon, fluid-rock interaction, number and type of fluid(s), level of carbon surperstuartion, nitrogen content and isotope composition of the fluid(s), mantle residence time

Note that stable isotopes would not trace either eruption (e.g. resorption) or post-eruption (e.g. transport in rivers) processes.

Countries pointed to sale conflict diamonds
Is there any data available yet ?
Is there any available diamond collection to be studied ?

• Angola	No	No
• Sierra Leone	A few	No
• Liberia	No	No
• Ivory Coast	No	No
• Democratic Republic of Congo	A few	No
• Republic of Congo	n.a.	No

Q: “can we recognise conflict diamonds ?”
A : Maybe ! It requires conflict diamonds to be made available to research… nobody really appear to be motivated in supplying conflict diamonds

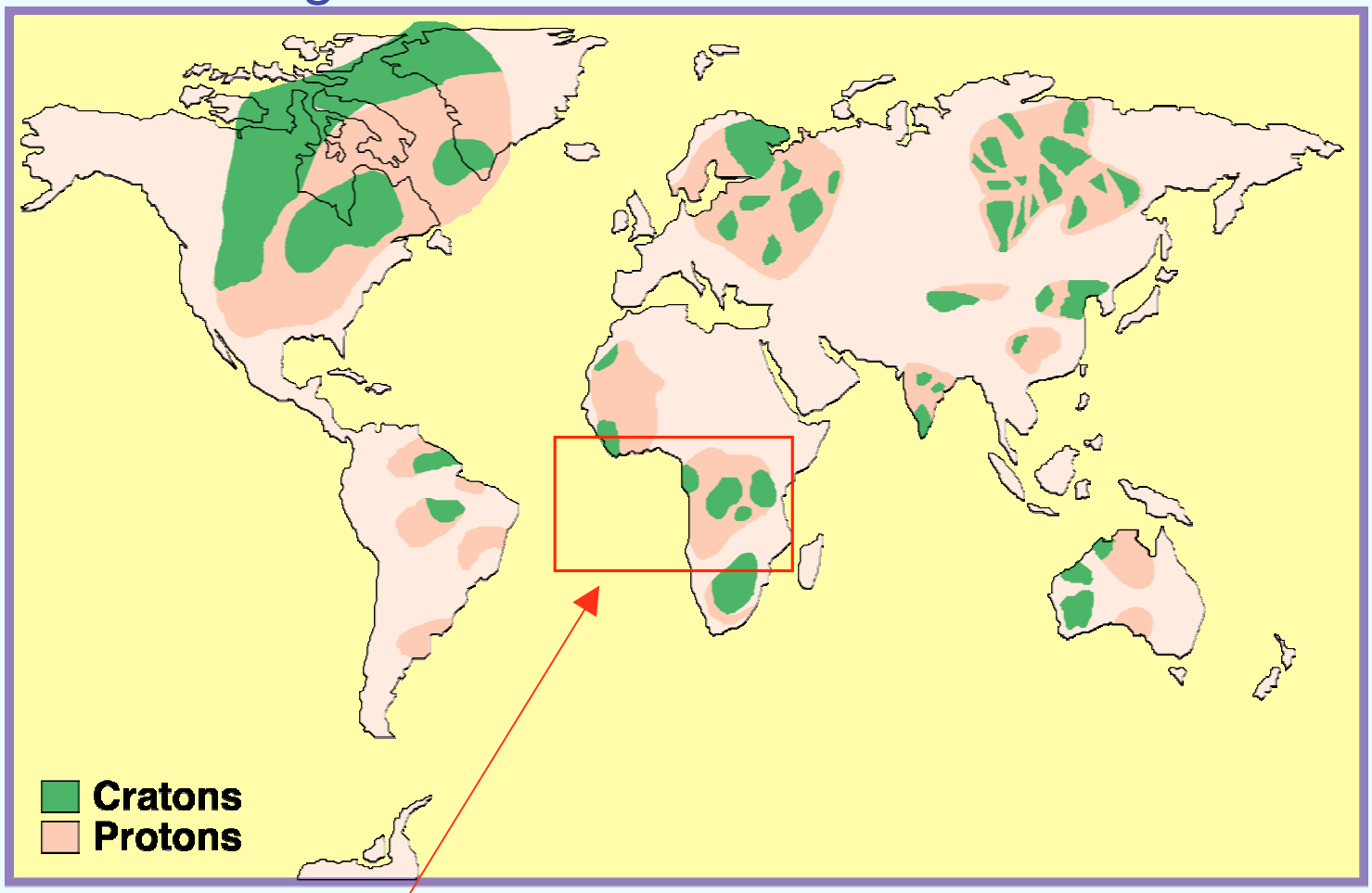


- So much research has been made on (legitimate) diamonds and deep-seated xenoliths

- So much progress has been made on understanding the age of diamond formation, the origin and the growth conditions of diamond

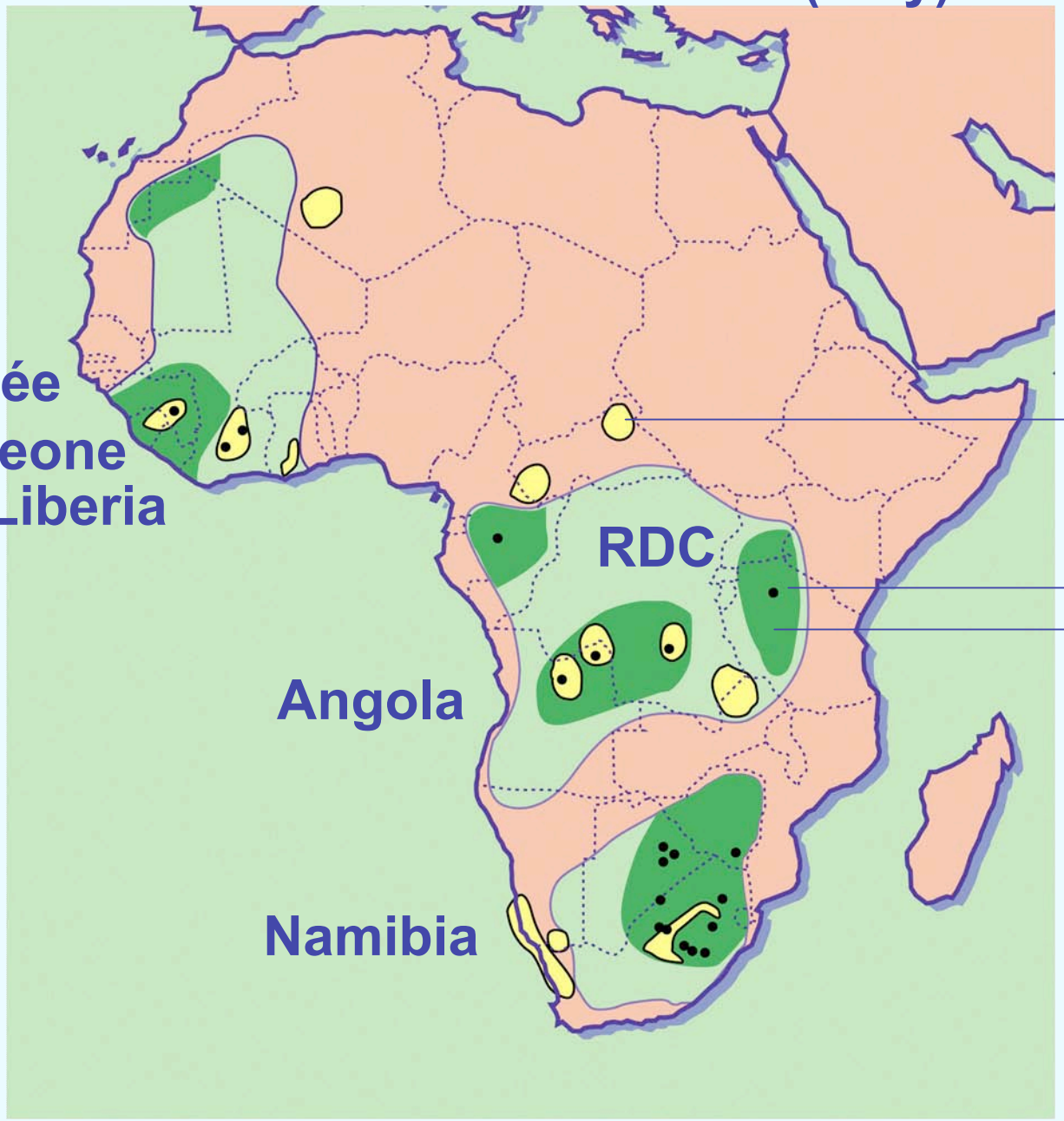
⇨ That one can (at least) approach the problem via "we can already distinguish diamonds from a legitimate diamond mine from another legitimate diamond mine"

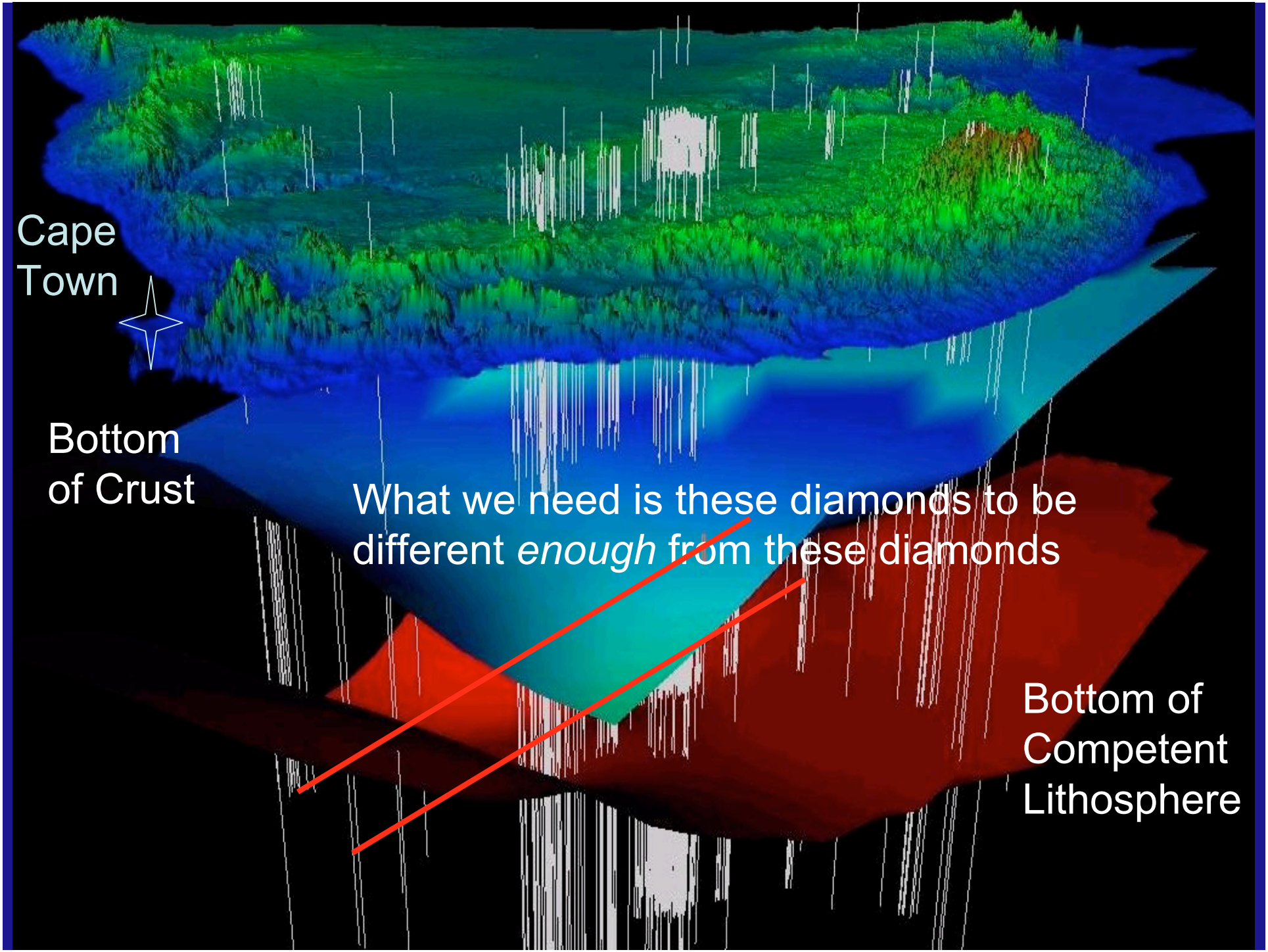
Back to basics :
Diamondiferous kimberlites are (almost) restricted to Archean continental settings.



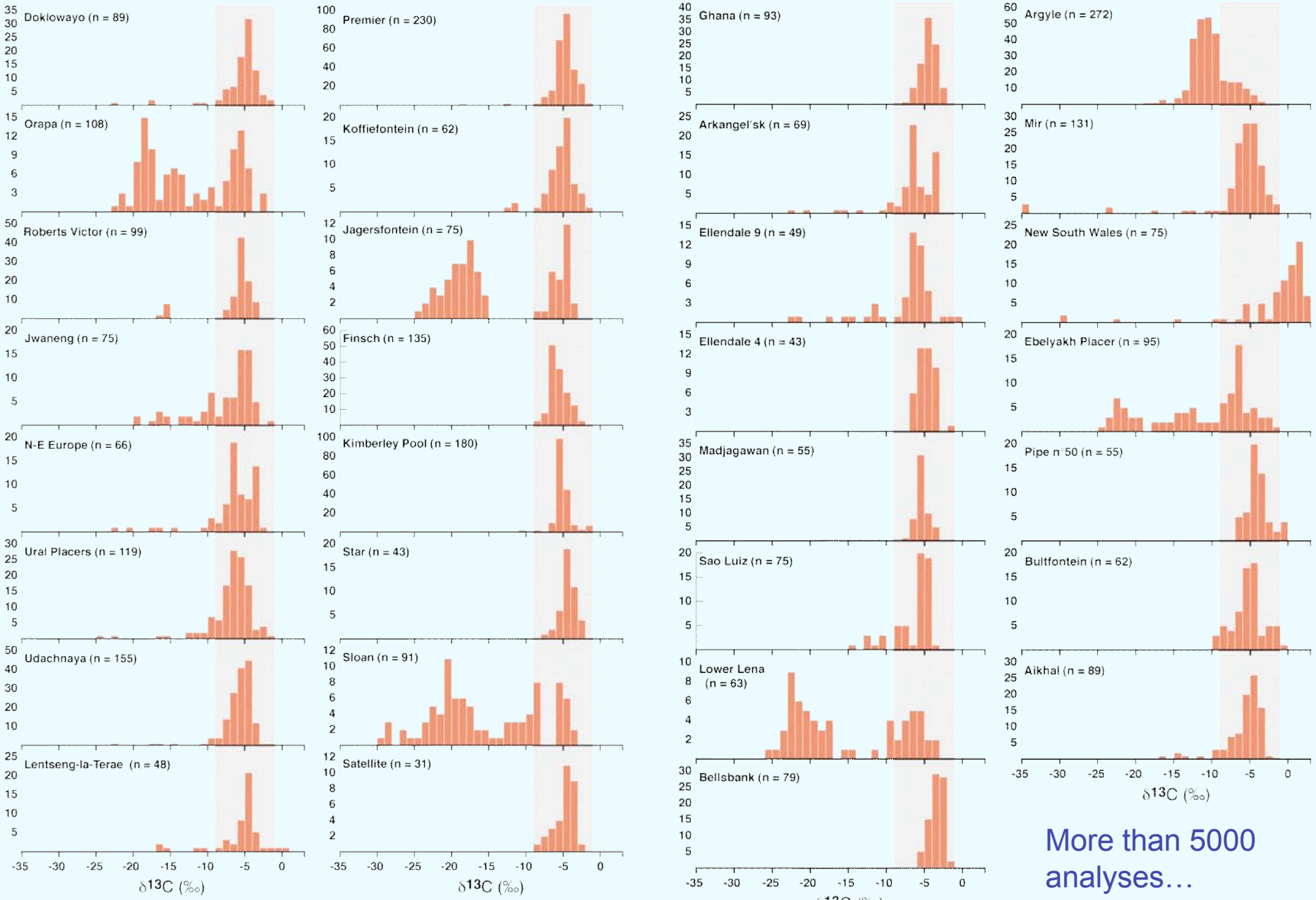
(So far) most conflict diamonds originate(d) from this area

Because (Archean) diamondiferous cratons overlap over different countries : the method must be (very) sensitive



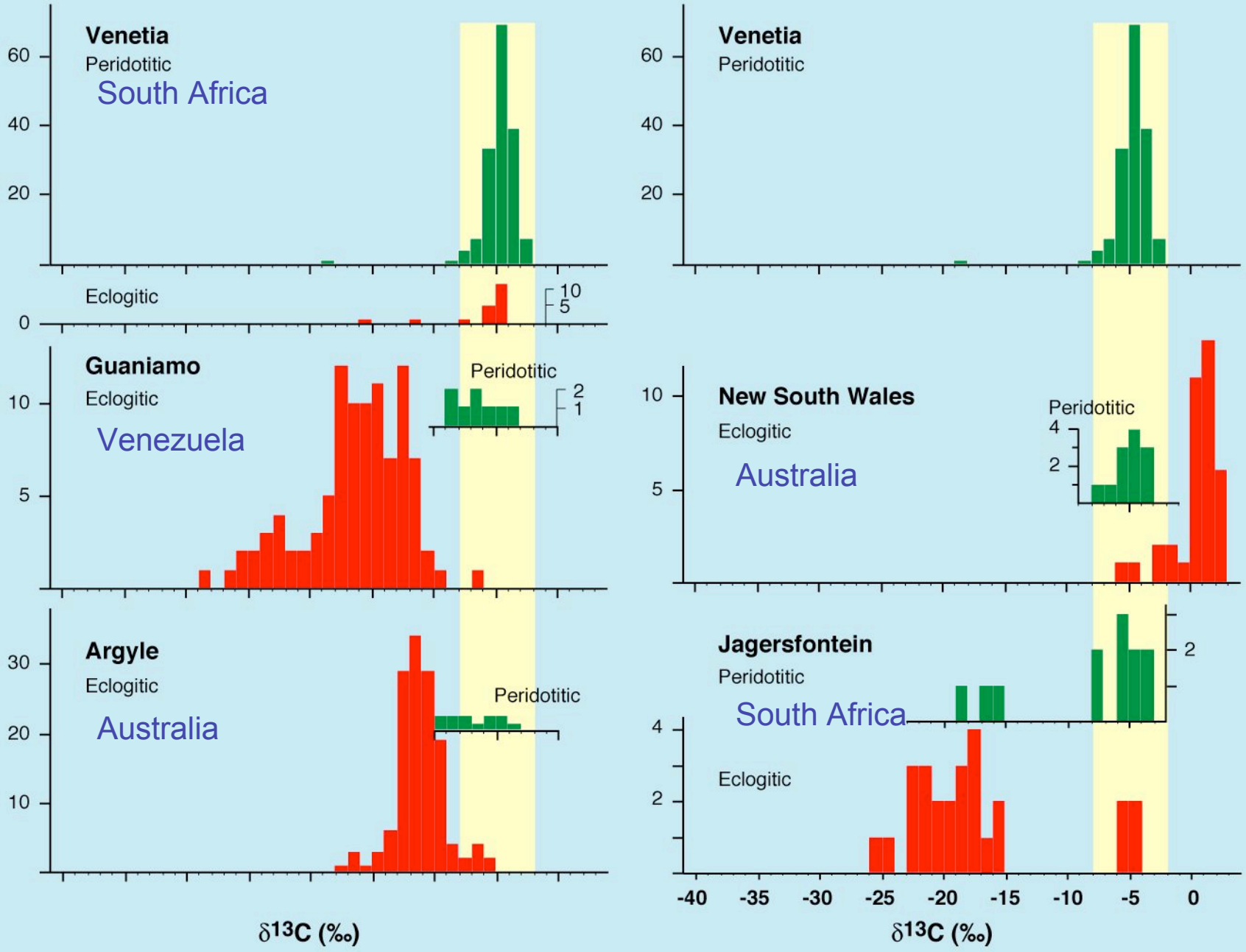

Cape
Town
Bottom
of Crust
What we need is these diamonds to be
different *enough* from these diamonds
Bottom of
Competent
Lithosphere

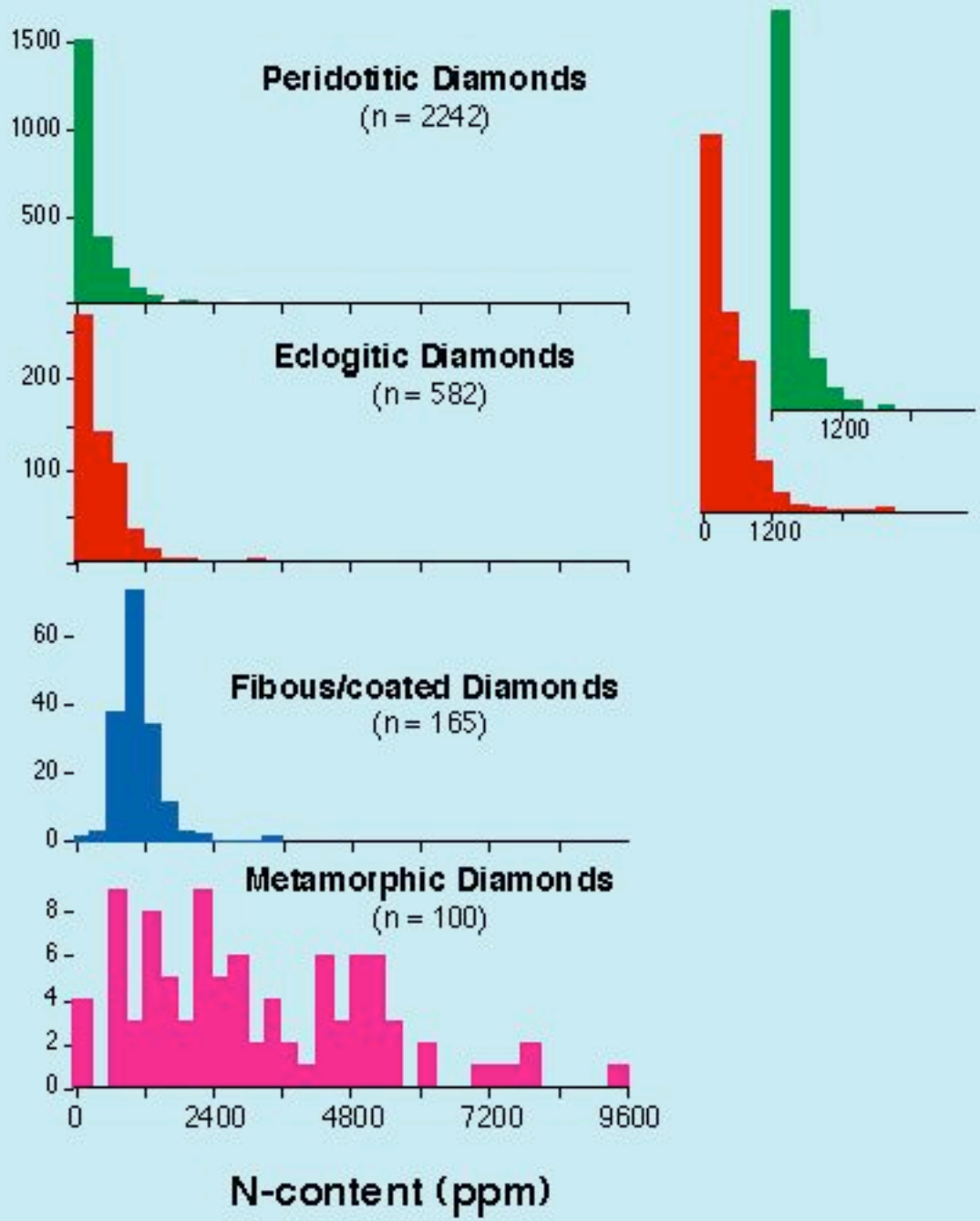
Often similar… sometimes distinct enough



More than 5000 analyses…
but still incomplete

An usual example (Venetia) and four easy to recognise exceptions

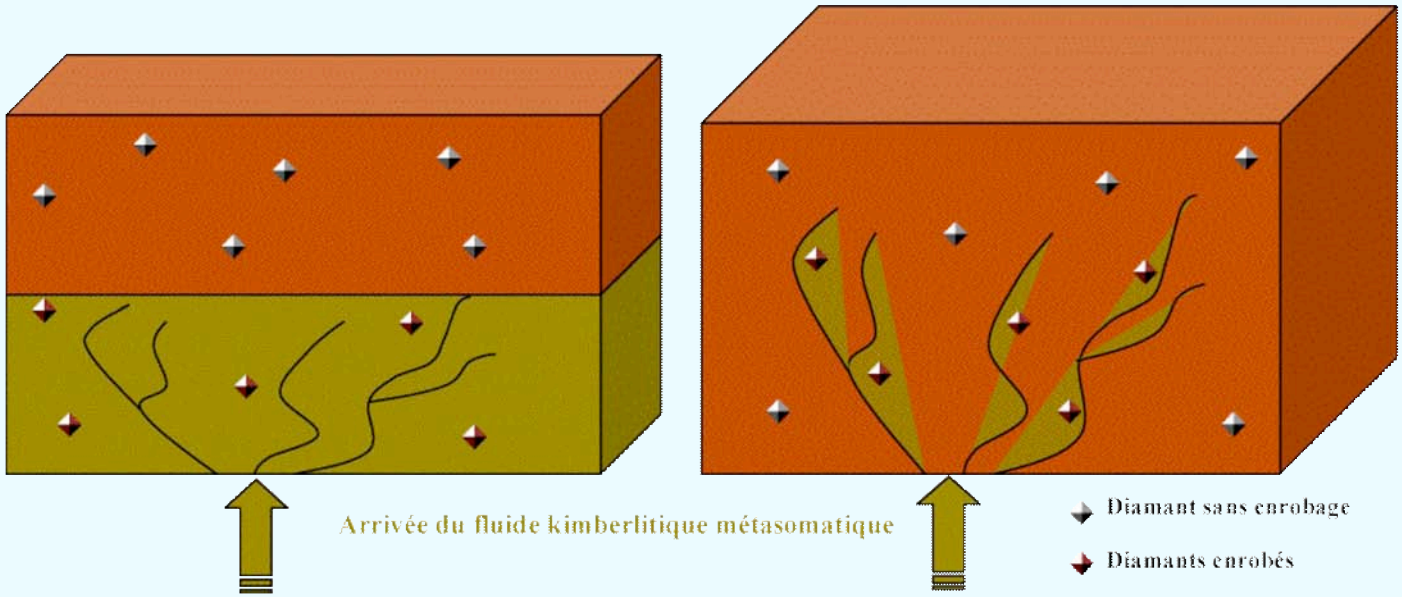



Peridotitic Diamonds
(n = 2242)
1500
1000
500
Eclogitic Diamonds
(n = 582)
200
100
1200
0
1200
Fibous/coated Diamonds
(n = 165)
60
40
20
0
Metamorphic Diamonds
(n = 100)
8
6
4
2
0
0
2400
4800
7200
9600
N-content (ppm)

A yet untested assumption : is a diamond production constant through time ?

= is the kimberlite vertically zoned (with respect to diamond characteristics) ?

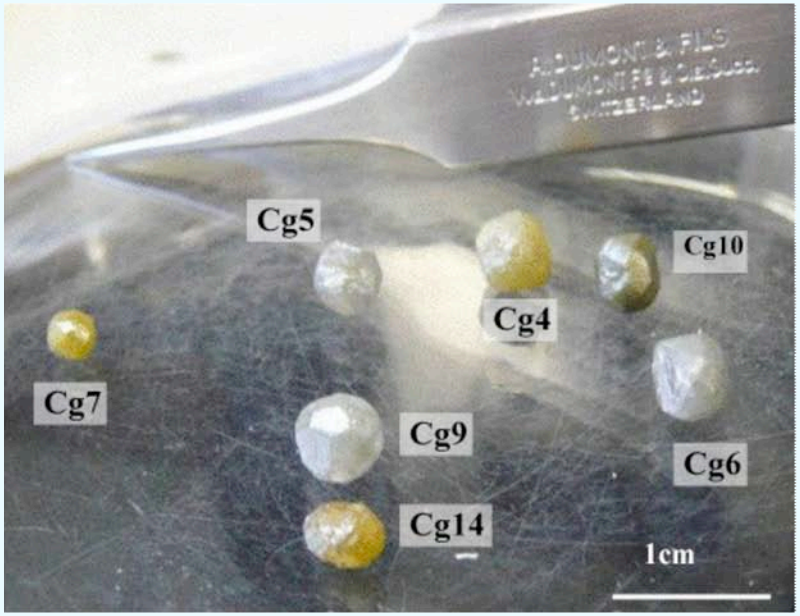
= are diamond characteristics zoned within the continental lithosphere ?



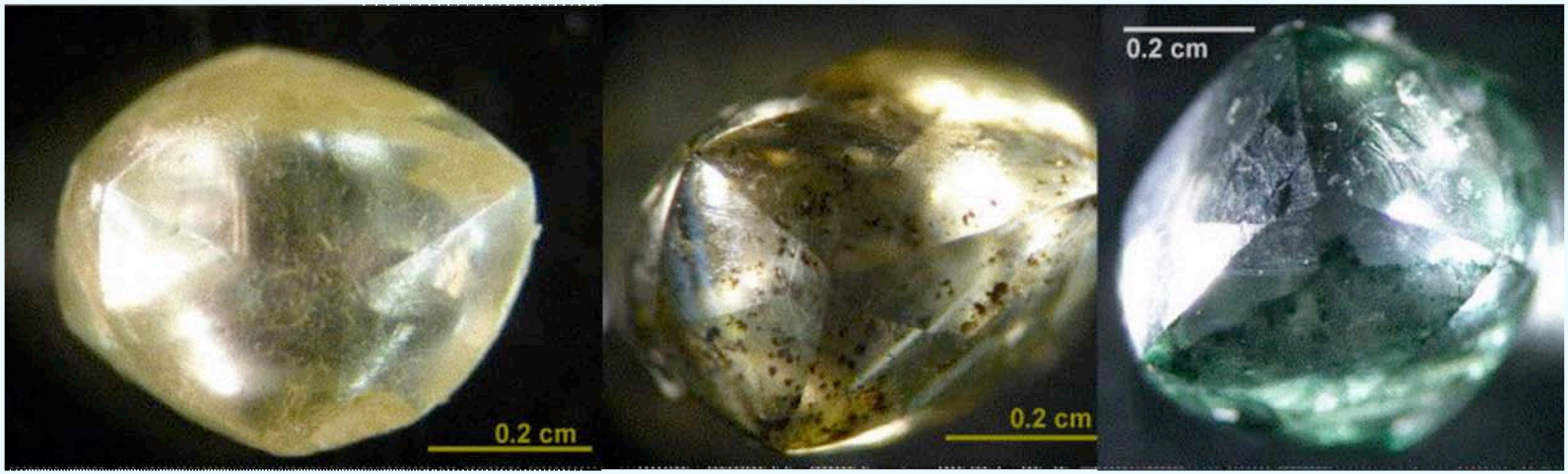
[actually this is basic research]

Fibrous vs gem diamonds from Central African Craton

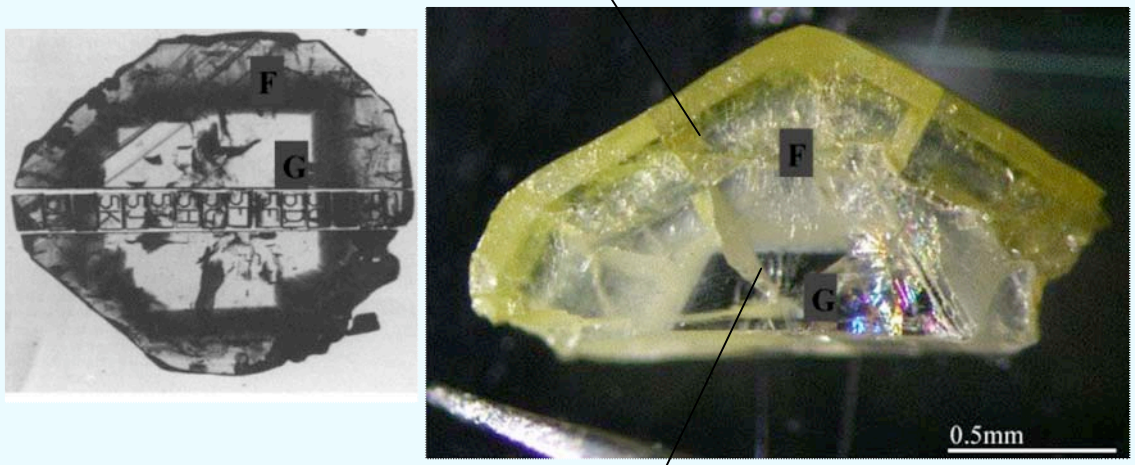
FIBROUS



GEMS



Fibrous coat = volatiles and age of the kimberlite (100 My)

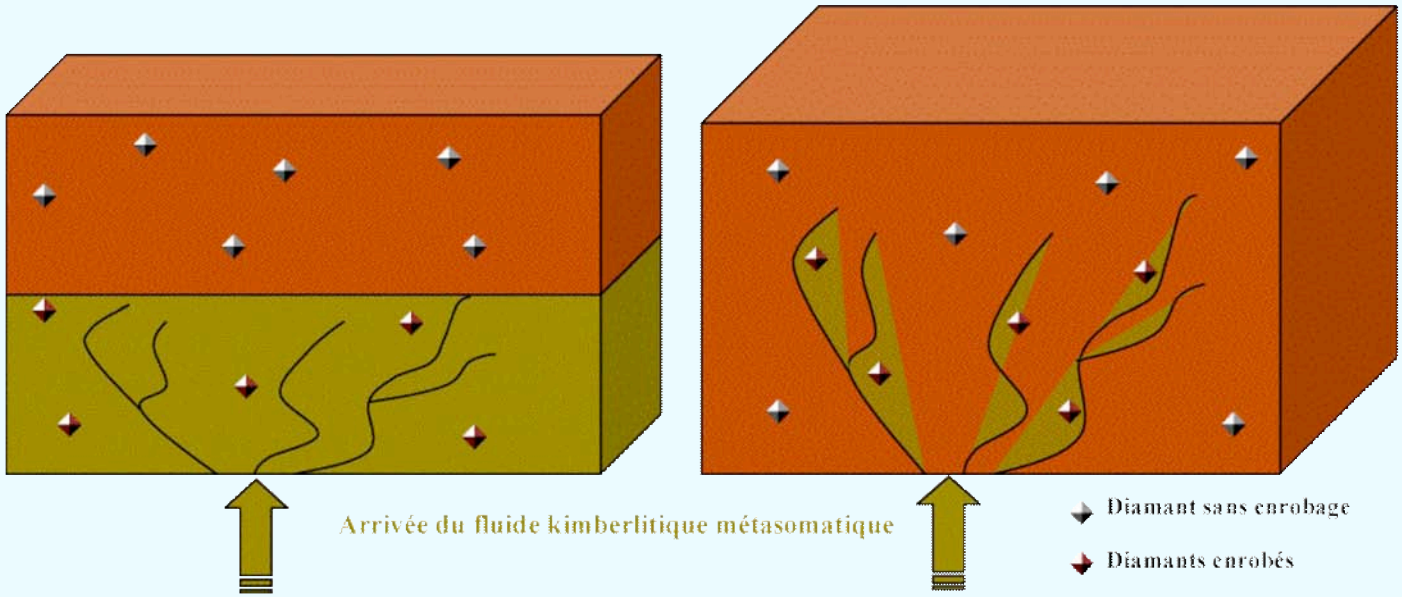


Gem diamond cores = much older
(usually Archean, > 2500 My)

Gem diamond cores are unusually N-rich.
What does this mean ?

Are diamond characteristics zoned within the continental lithosphere ? *(as discussed by Boyd et al. 94)*

An argument based on Central African fibrous diamonds only
no data available on gem diamonds from the same location



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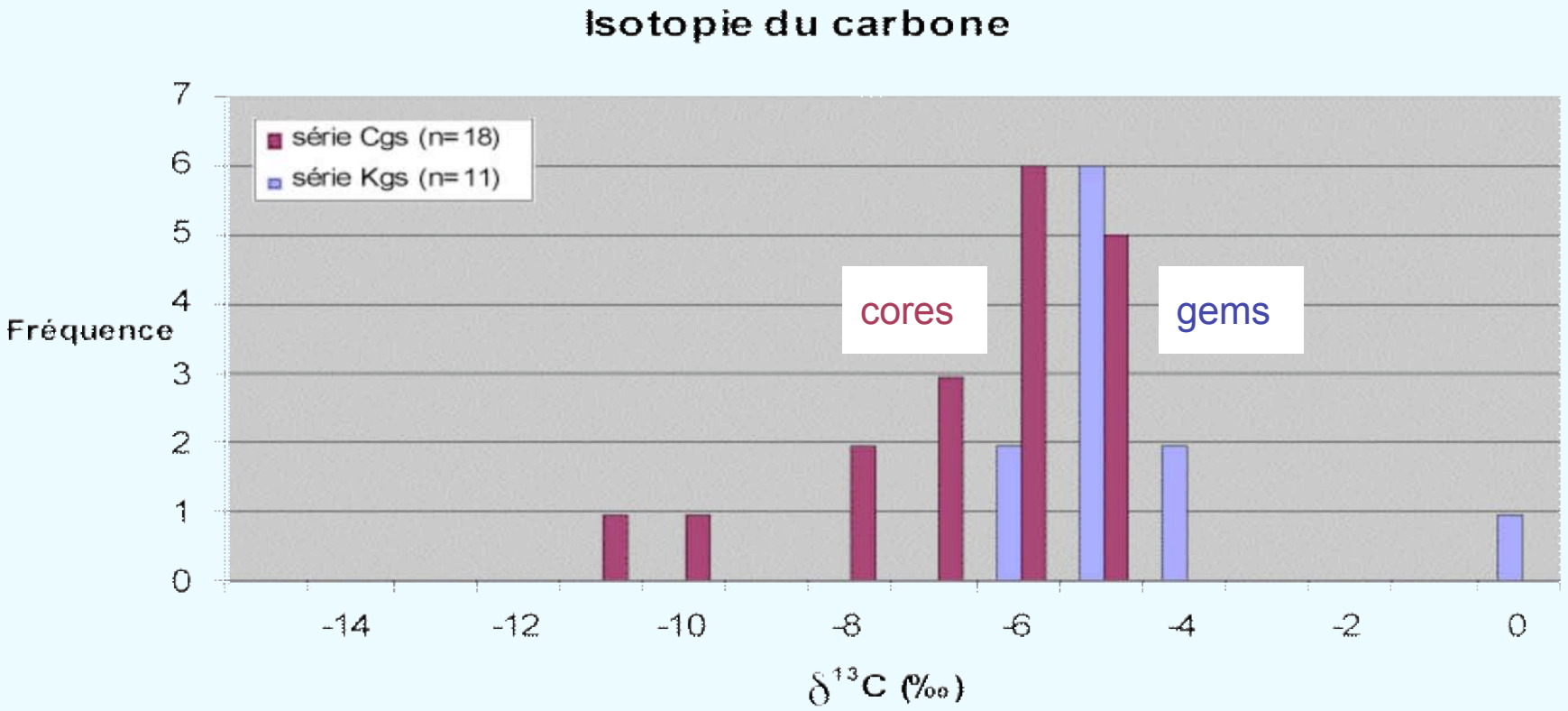
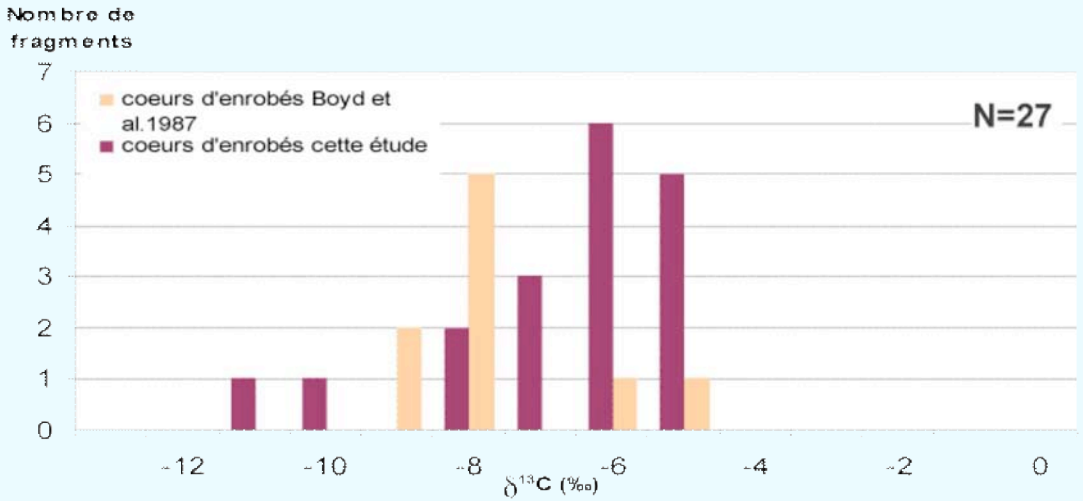
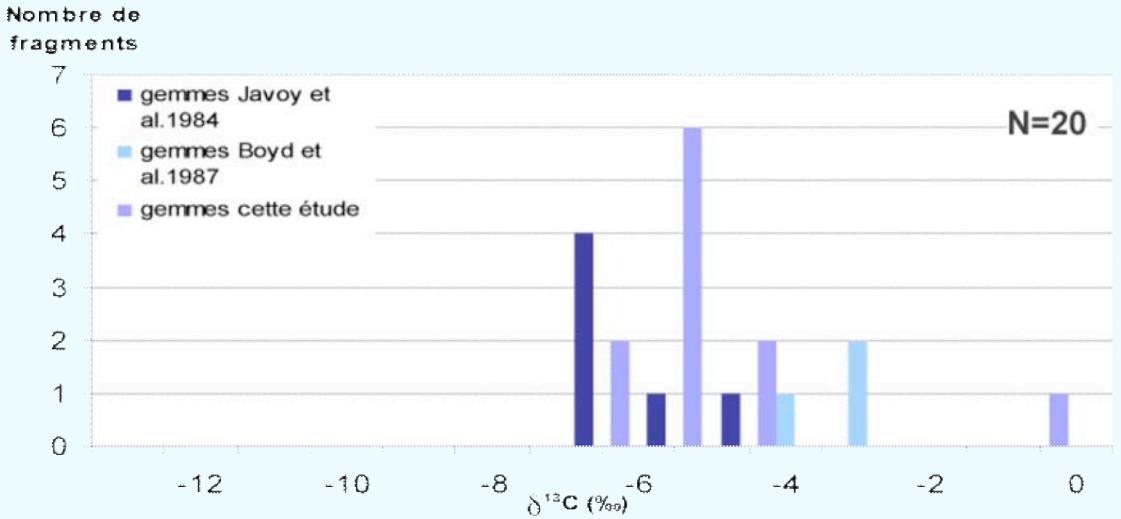
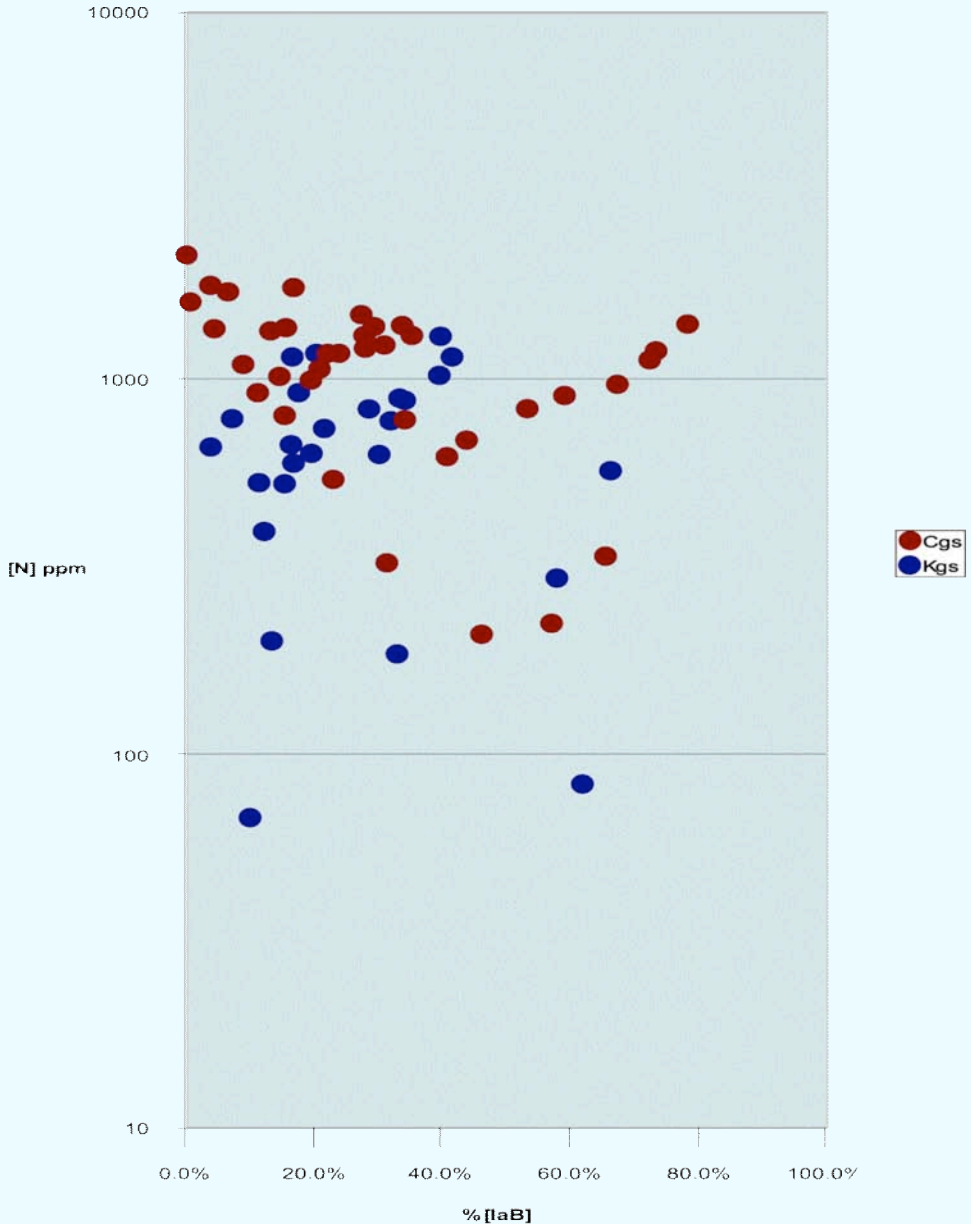
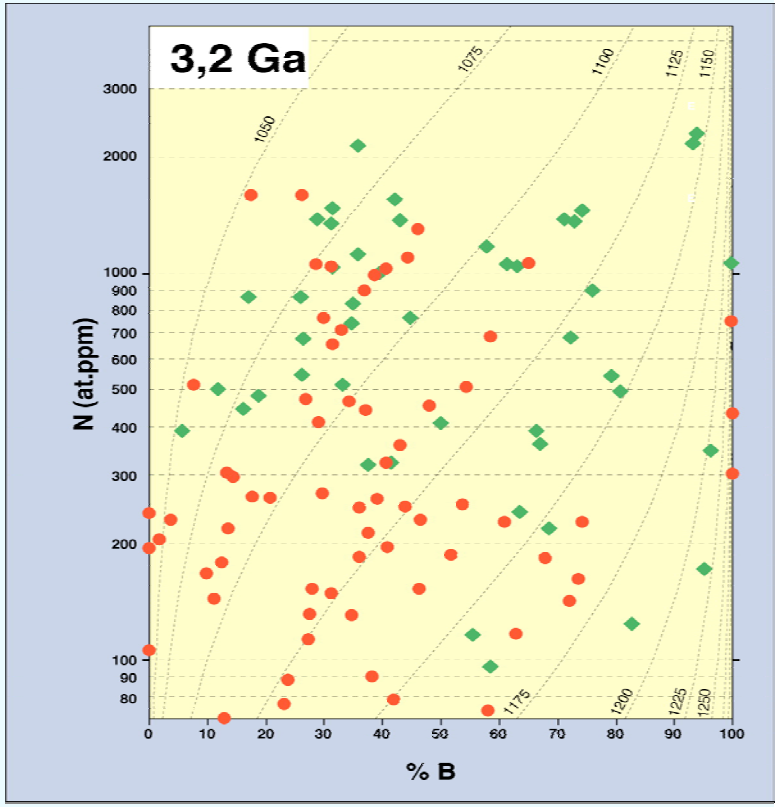
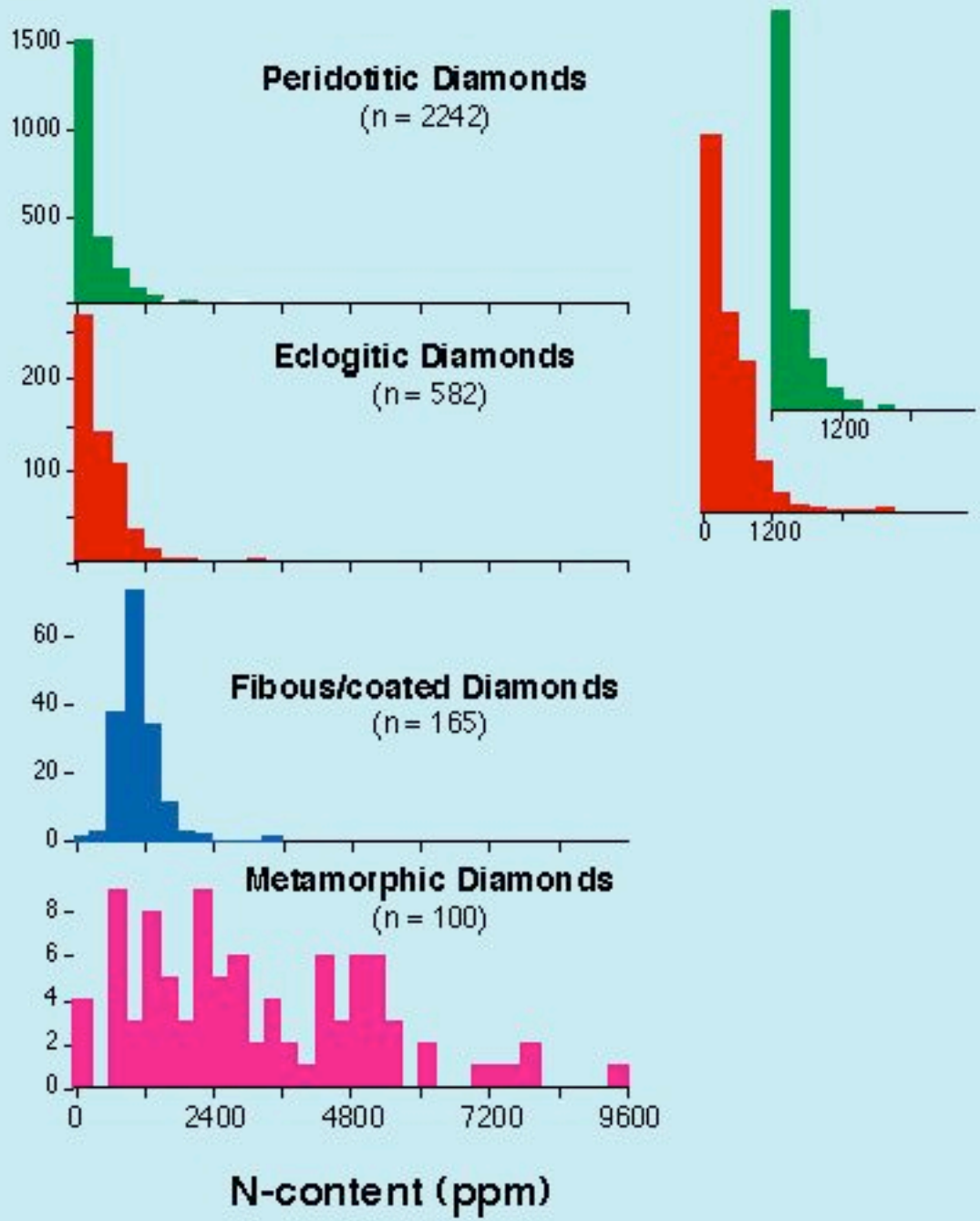

Isotopie du carbone
série Cgs (n=18)
série Kgs (n=11)
cores
gems
Fréquence
0
1
2
3
4
5
6
7
-14
-12
-10
-8
-6
-4
-2
0
δ13C (‰)


Nombre de fragments
7
6
5
4
3
2
1
0
coeurs d'enrobés Boyd et al.1987
coeurs d'enrobés cette étude
N=27
-12
-10
-8
-6
-4
-2
0
δ13C (‰)


Nombre de fragments
7
6
5
4
3
2
1
0
gemmes Javoy et al.1984
gemmes Boyd et al.1987
gemmes cette étude
N=20
-12
-10
-8
-6
-4
-2
0
δ13C (‰)


10000
1000
100
10
[N] ppm
0.0%
20.0%
40.0%
60.0%
80.0%
100.0%
%[laB]
Cgs
Kgs


3,2 Ga
N (at.ppm)
% B
1050
1075
1100
1125
1150
1175
1200
1225
1250


Peridotitic Diamonds
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0
1200
Fibous/coated Diamonds
(n = 165)
60
40
20
0
Metamorphic Diamonds
(n = 100)
8
6
4
2
0
0
2400
4800
7200
9600
N-content (ppm)

Summary : gem cores and gem diamonds are both characterised by high N-contents

- Does not correspond to a vertical zonation of the continental lithosphere
- One way to easily identify diamonds from this area

Conclusions :

We can expect to be able recognising (at least) several conflict diamond productions...

...maybe all of them with increasing number of parameters (trace elements, inclusions chemistry, magnetic properties)

Need conflict diamonds : e.g. Sierra Leone, Angola, Liberia (not easy)

Probably need the support of diplomacy

Conclusions : If we want to (potentially) identify the origin of diamonds,

we need to get and study (> 50) samples from every conflict AND legitimate diamond mine

stable isotopes, N-contents are (only) sometimes symptomatic

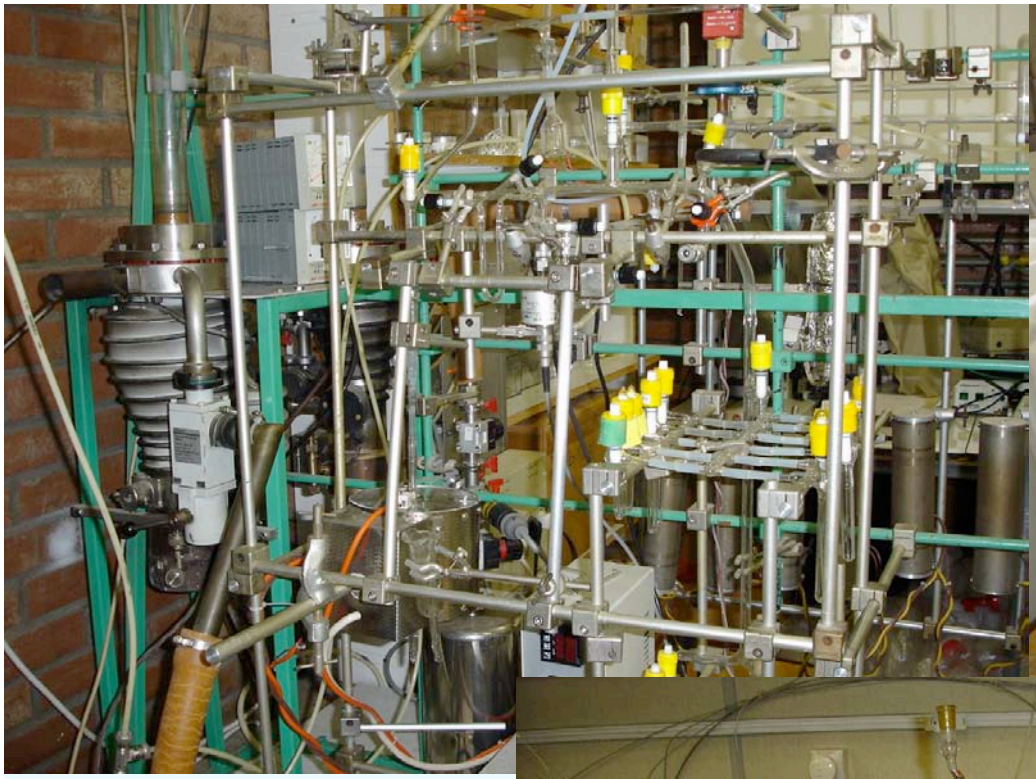
so fingerprinting must be rather seen through a multi-parameter study

Analytical Methods for $\delta^{13}C$-measurements

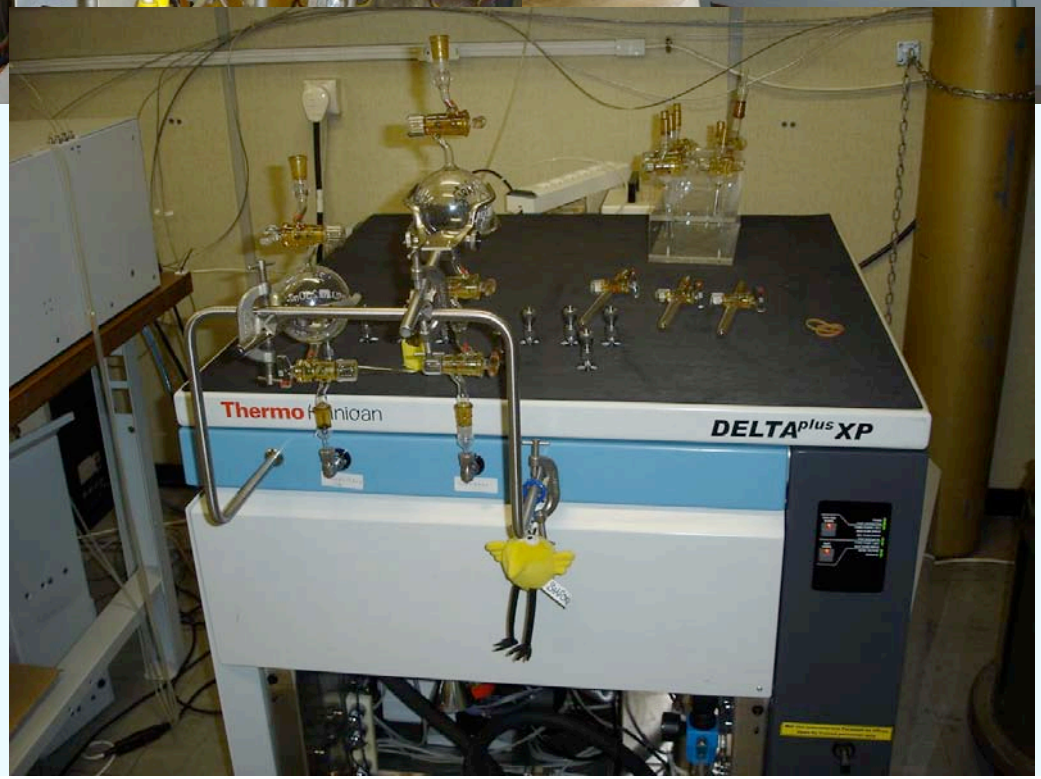
1) Online combustion - dual inlet IRMS
   - Very precise <0.02‰
   - 15 samples/day
   - sample size 0.05 to >> 3 mg
   - > 99.9 of published data

2) Online combustion - Flash EA IRMS
   - Precise <0.1‰
   - 100's samples/day
   - sample size <0.1 mg (1 paper)

3) Ion Probe
   - Relatively precise ≈0.3‰
   - XX samples/day (see Ben Harte's talk)
   - in situ




FlashEA


DELTAplus XP

Analytical techniques

- Infrared spectroscopy

Nitrogen concentration and speciation
(aggregation state)

- Mass spectrometry measurement after combustion

Isotopic compositions of carbon and nitrogen

- $$\delta^{13}C = \left(\frac{^{13}C/^{12}C_{\text{sample}}}{^{13}C/^{12}C_{\text{PDB}}} - 1 \right) \times 1000$$

$$\delta^{15}N = \left(\frac{^{15}N/^{14}N_{\text{sample}}}{^{15}N/^{14}N_{\text{Air}}} - 1 \right) \times 1000$$

N quantification and isotopic measurement

- Nitrogen: Small quantities in diamonds (average ~ 200 ppm)

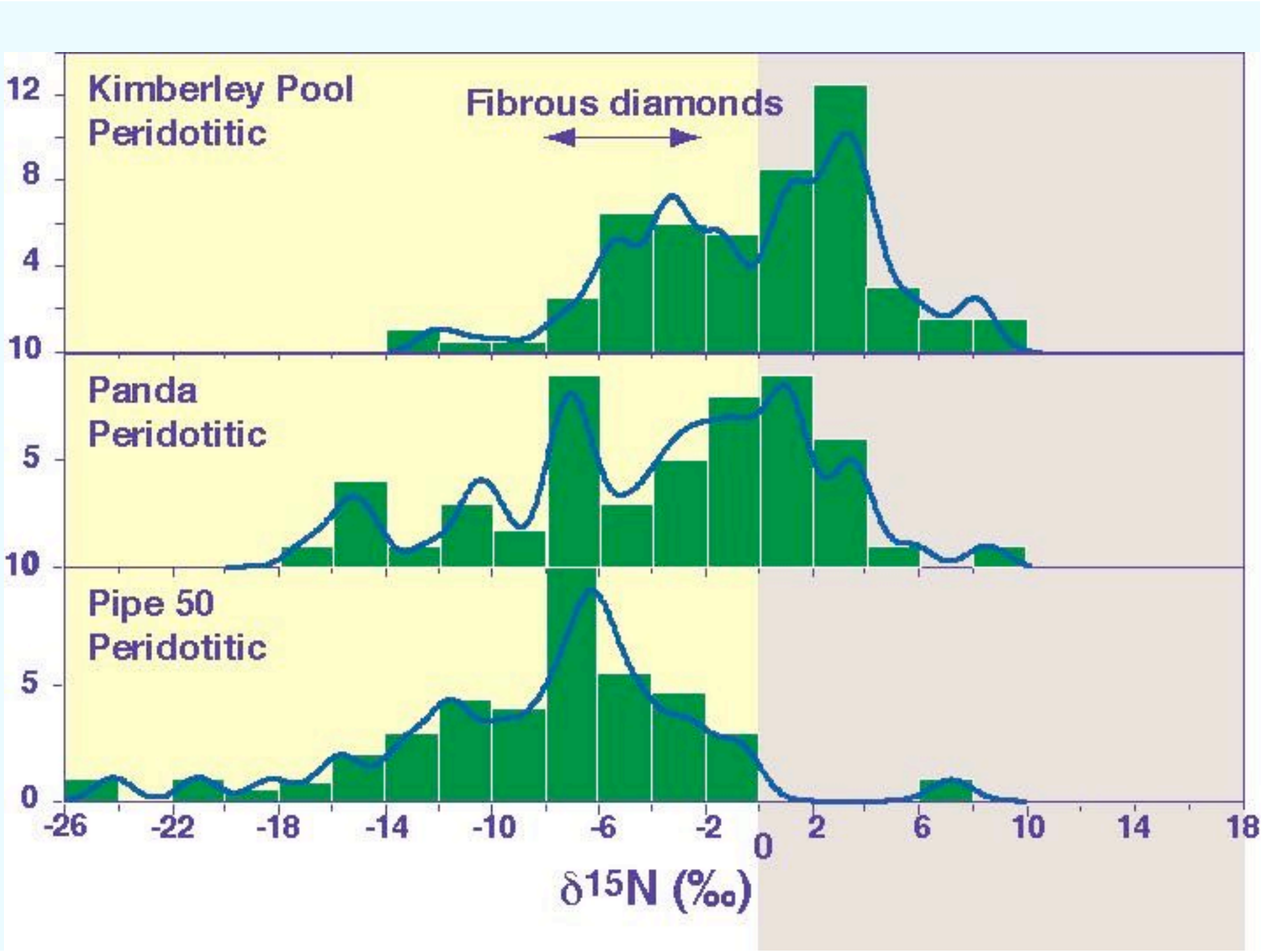
Extraction and analysis:
N_2 after combustion

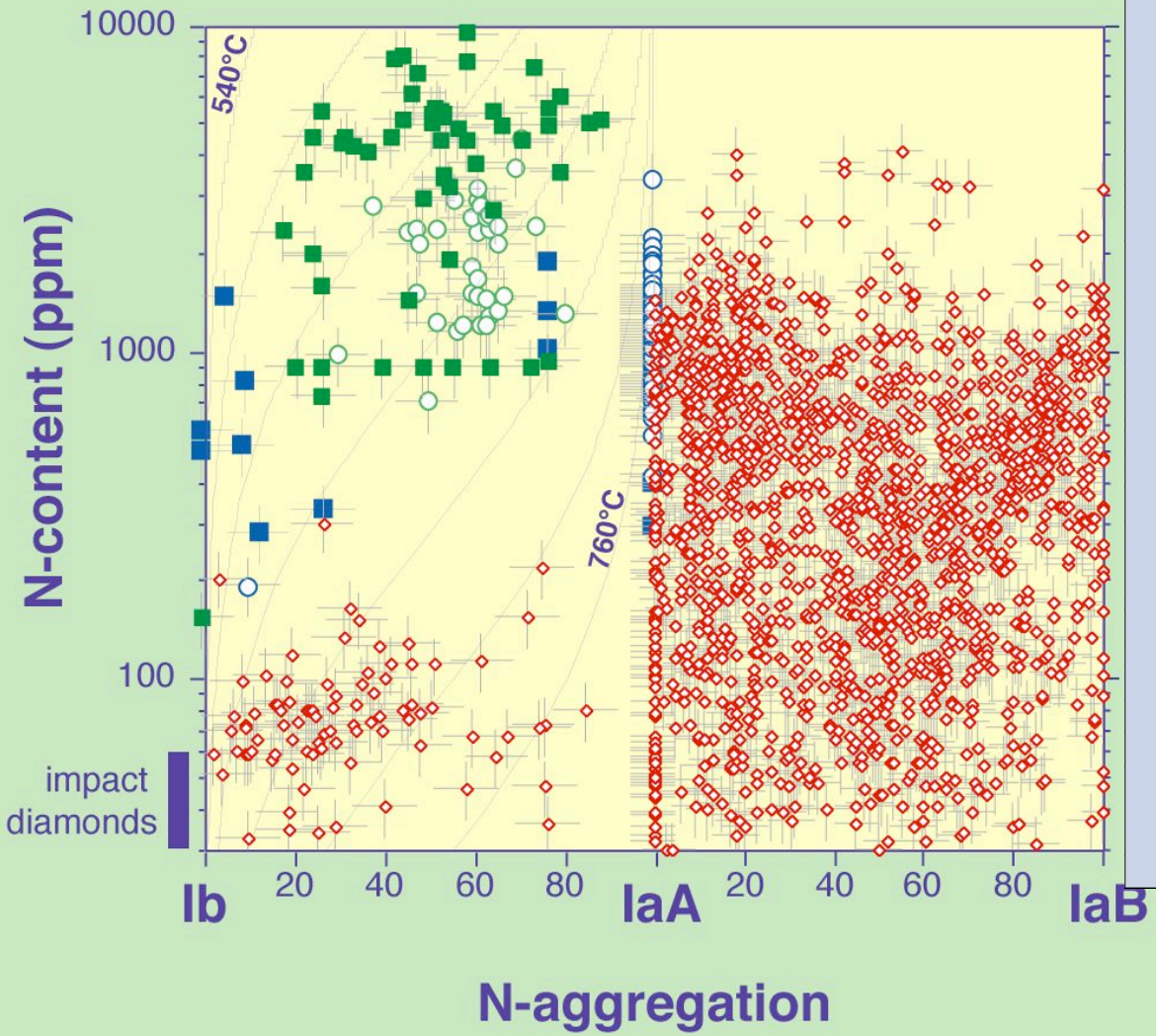
Quantification:
manometry
accuracy better than 8%

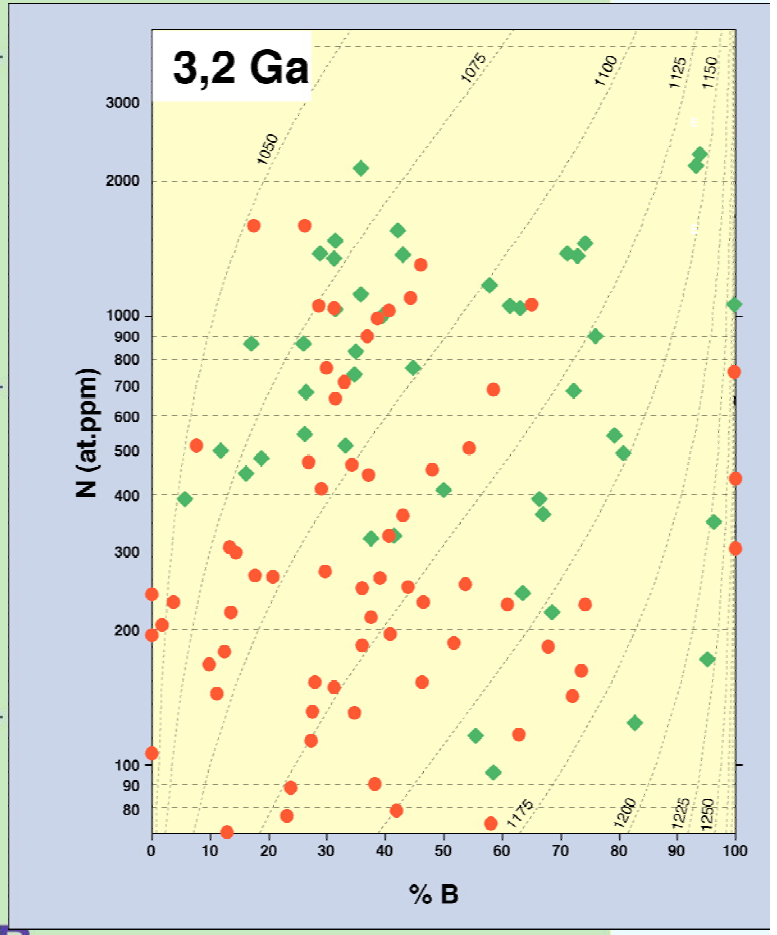
$\delta^{15}N$ measurement:
Static mass spectrometry
Precision ±0.5‰ (2σ)

- ~1 mg of diamond required for $\delta^{15}N$ analysis

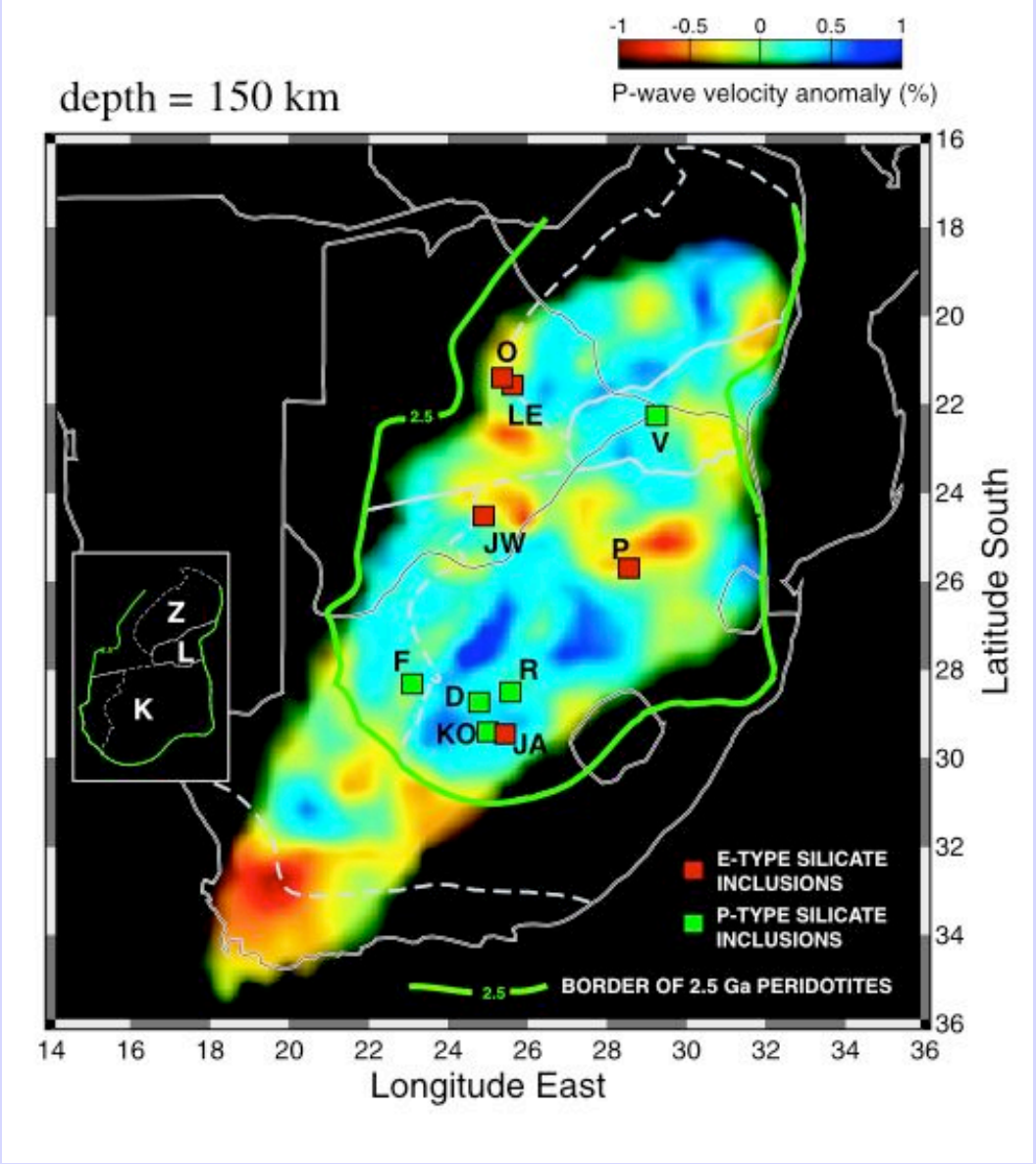
Boyd et al., 1995, Meas. Sci. Technol

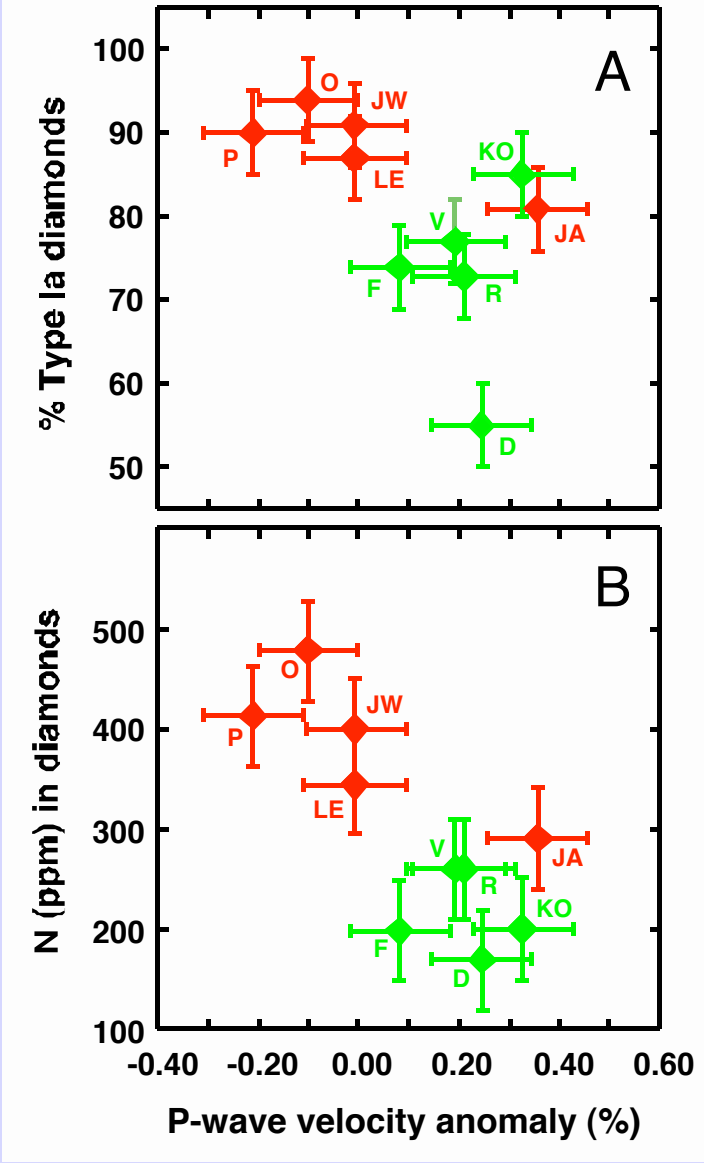

Kimberley Pool
Peridotitic
Fibrous diamonds
Panda
Peridotitic
Pipe 50
Peridotitic
12
8
4
10
5
10
5
0
-26
-22
-18
-14
-10
-6
-2
0
2
6
10
14
18
δ15N (‰)


10000
1000
100
N-content (ppm)
540°C
760°C
impact
diamonds
Ib
20
40
60
80
IaA
20
40
60
80
IaB
N-aggregation


3,2 Ga
1050
1075
1100
1125
1150
1175
1200
1225
1250
3000
2000
1000
900
800
700
600
500
400
300
200
100
90
80
N (at.ppm)
0
10
20
30
40
50
60
70
80
90
100
% B

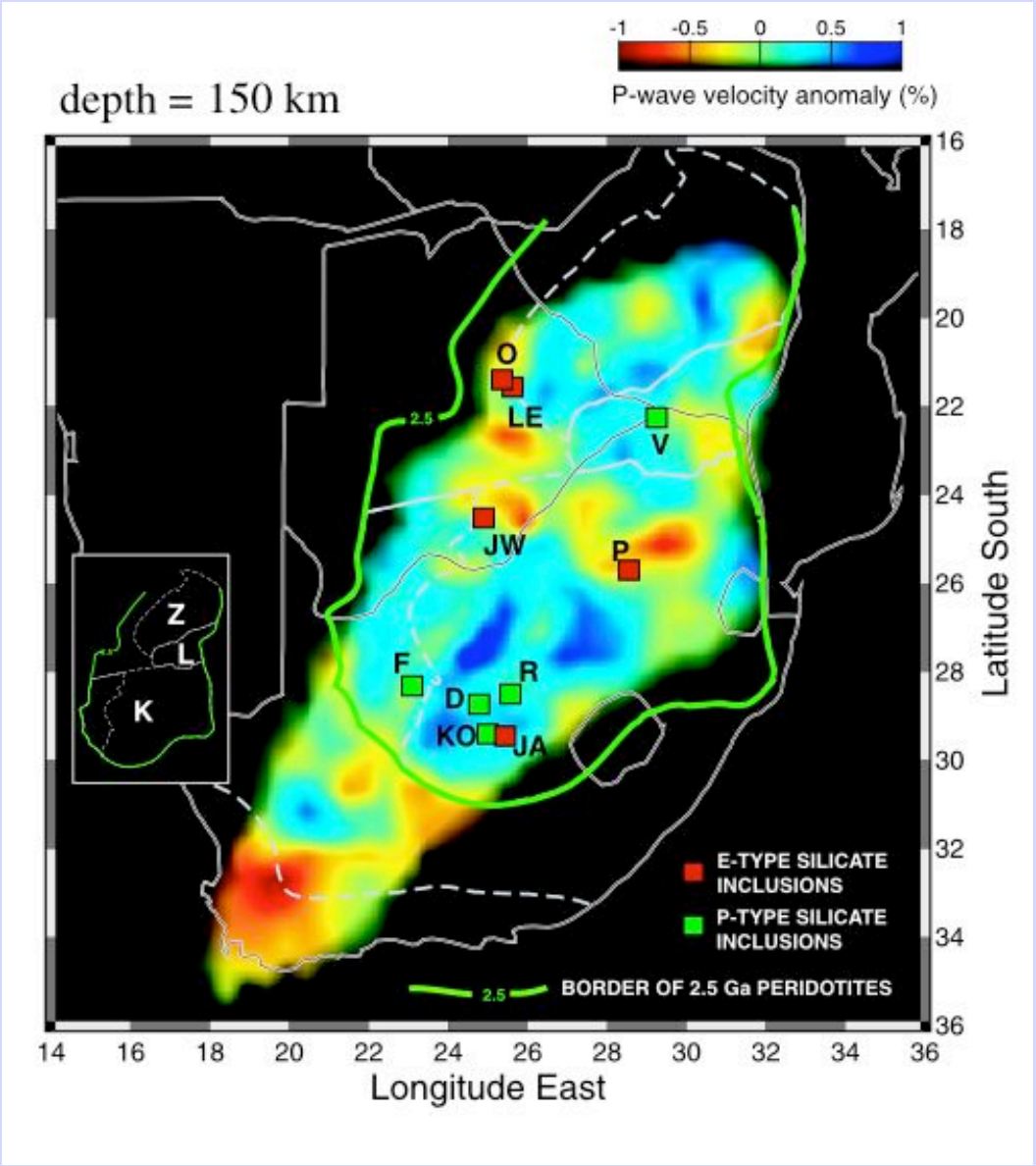
Diamond composition & inclusion paragenesis of the silicate inclusion suite correlates with lithospheric mantle composition

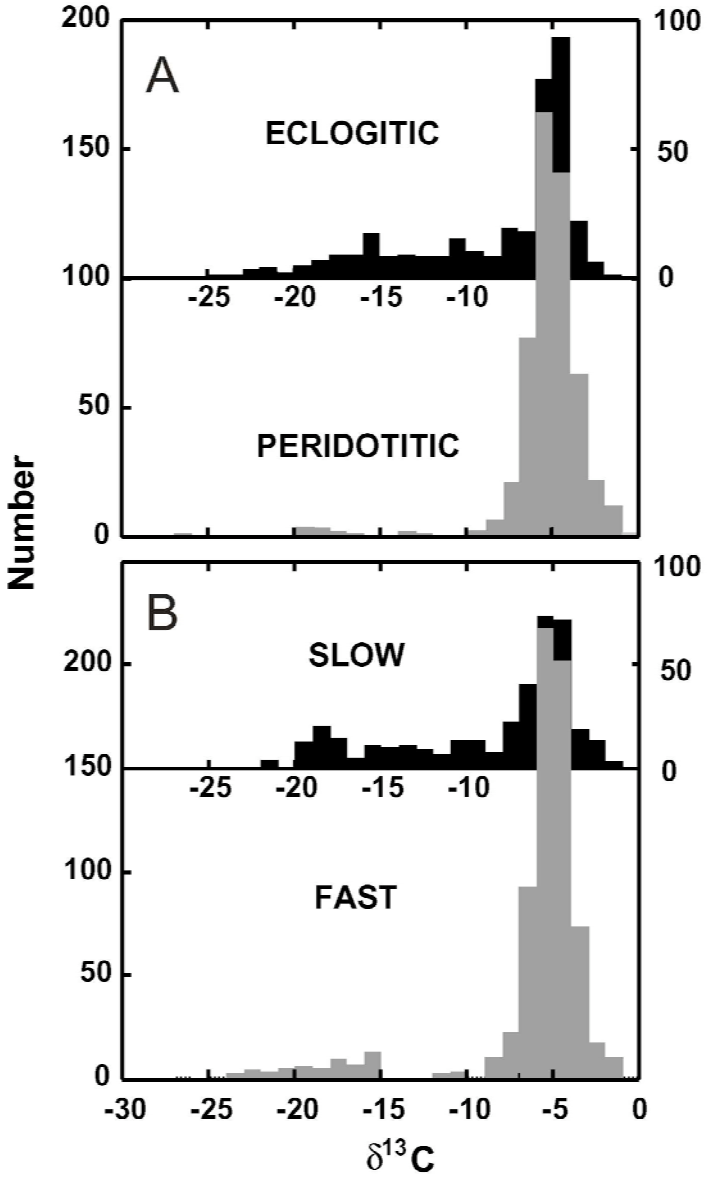




Shirey et al., (2002, 2004)

Diamond composition & inclusion paragenesis of the silicate inclusion suite correlates with lithospheric mantle composition





Shirey et al., (2002, 2004)