Noble Gas in Corundum : Interests in gemology

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GEO GEMS

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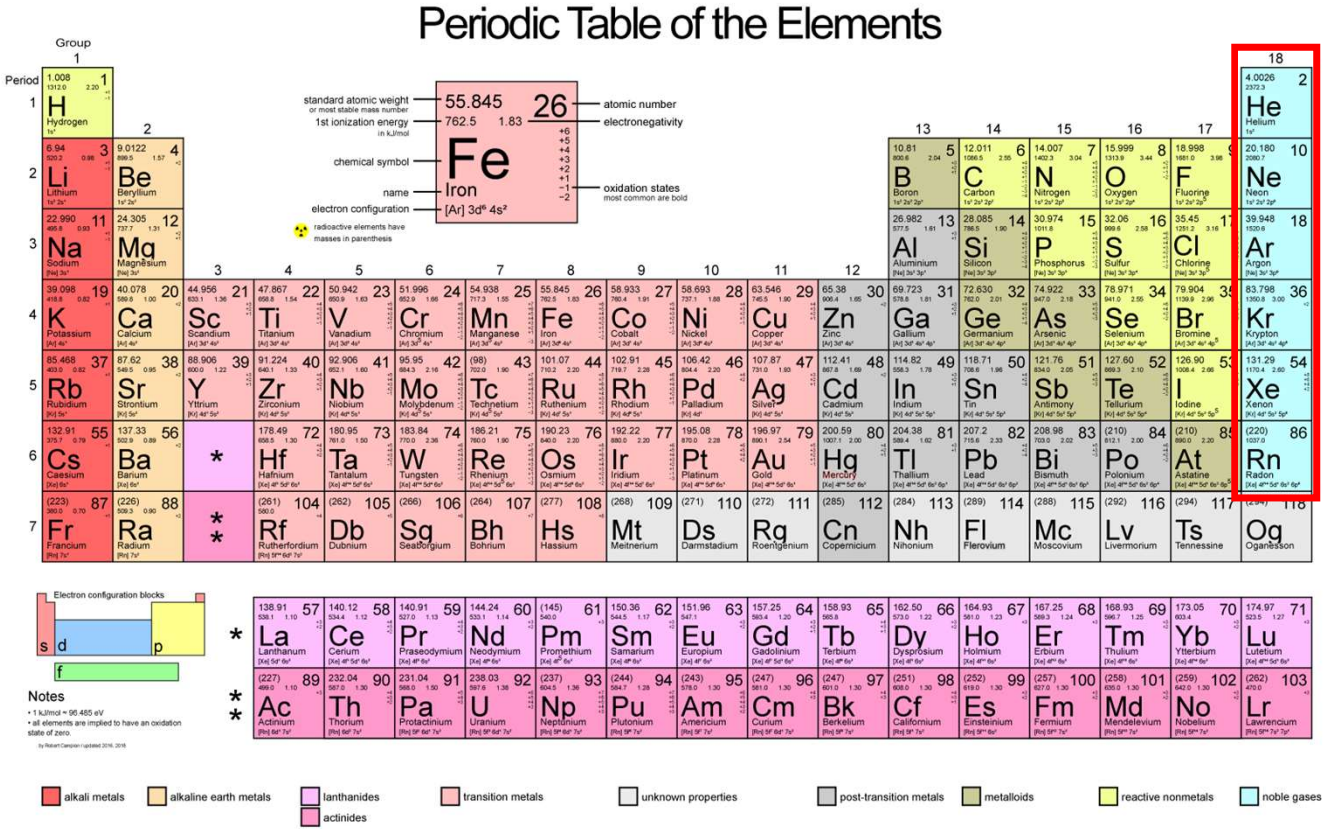
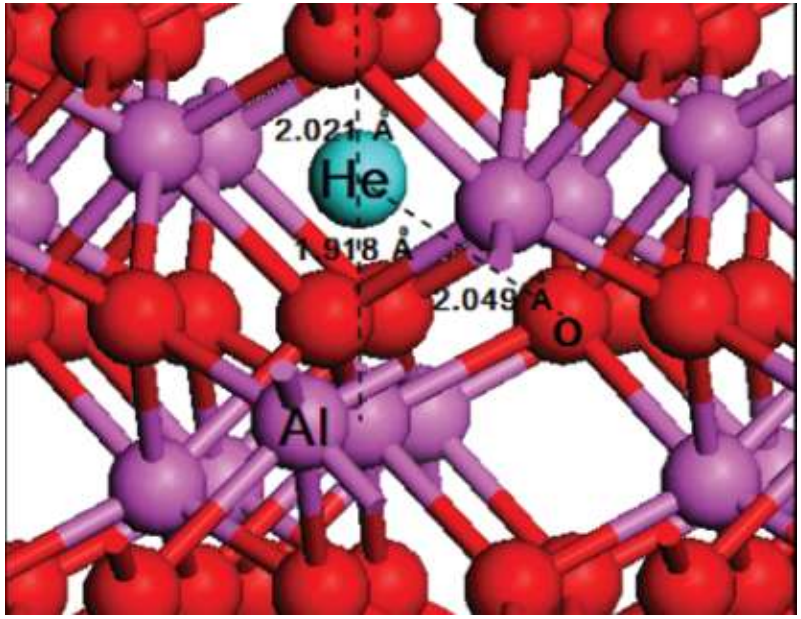
Noble Gas in Geology

- Elements with filled outer electrons shells, no chemical binding



Example of He in corundum structure

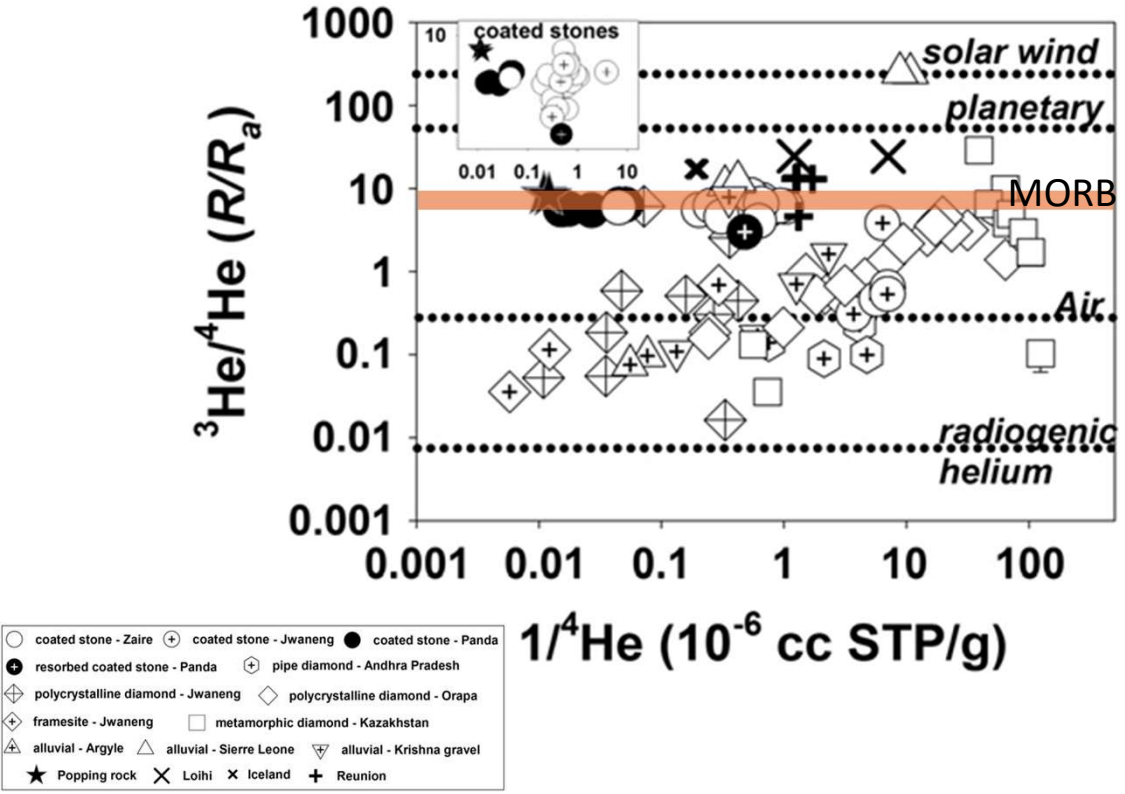


Zhang et al. 2016

Noble Gas in Geology

- Elements with filled outer electrons shells, no chemical binding

Noble gases (He) in diamond : decipher geological environment



Basu et al. (2013)

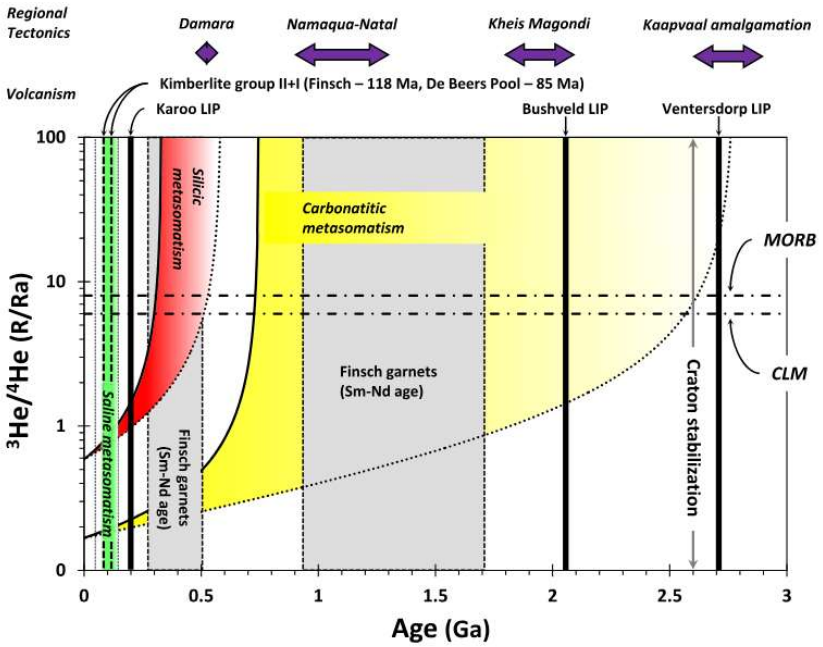
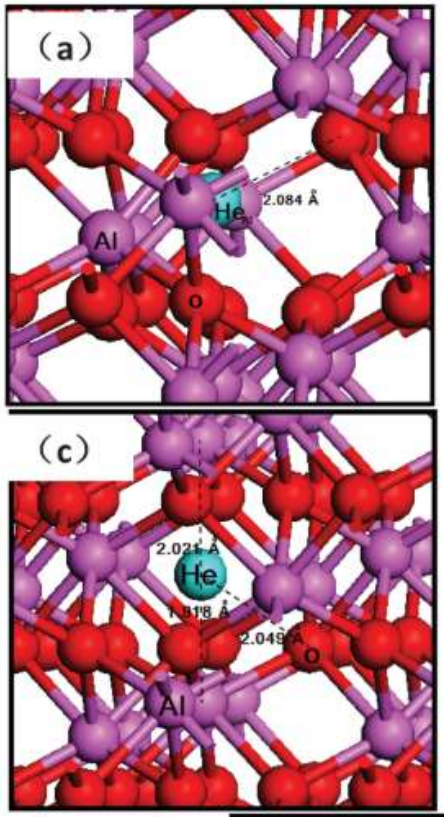


Fig. 6 Carbon- and water-rich (C-O-H) metasomatic events recorded by HDF-bearing diamonds in the southwest Kaapvaal cratonic lithosphere. U-Th-He geochronology of HDF-bearing diamonds from De Beers Pool and Finsch kimberlites reveal at least three episodes of different invading C-O-H fluid types affected the Kaapvaal continental lithospheric mantle (CLM) during the last ~2.6 Gyr. Saline fluids (green) controlled the metasomatism before/during late-Mesozoic kimberlite eruptions. An earlier silicic metasomatism (red) took place during the Paleozoic between 300–540 Myr; a time frame that coincides with CLM enrichment events at 391 ± 120 Ma as indicated by subcalcic garnets from Finsch[74], and overlaps the timing of the Damara orogeny (ca. 500 Ma)[76]. The oldest episode by carbonatite fluids (yellow) could take place throughout most of the Proterozoic, following craton stabilization at 2600 Ma and until 750 Ma. This event can be related to a mantle enrichment recorded in Finsch garnets (1720–940 Myr)[74] and the timing of the Namaqua–Natal Orogeny between 900 and 1250 Myr[75], but a connection to older mantle metasomatic events and large surface deformational events are also possible.

Weiss et al. (2021)

Helium in corundum

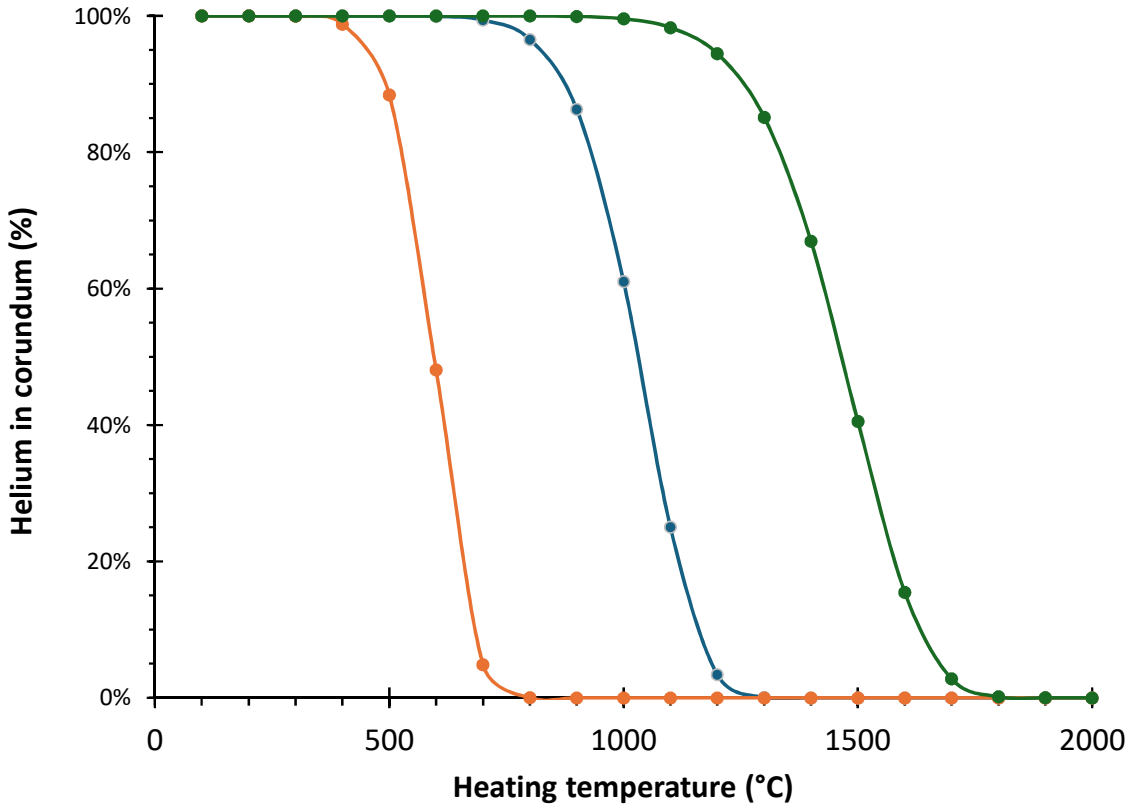
- Crystal defects in corundum could entrapped helium, released by heating.



He in Al vacancy

He in interstitial sites

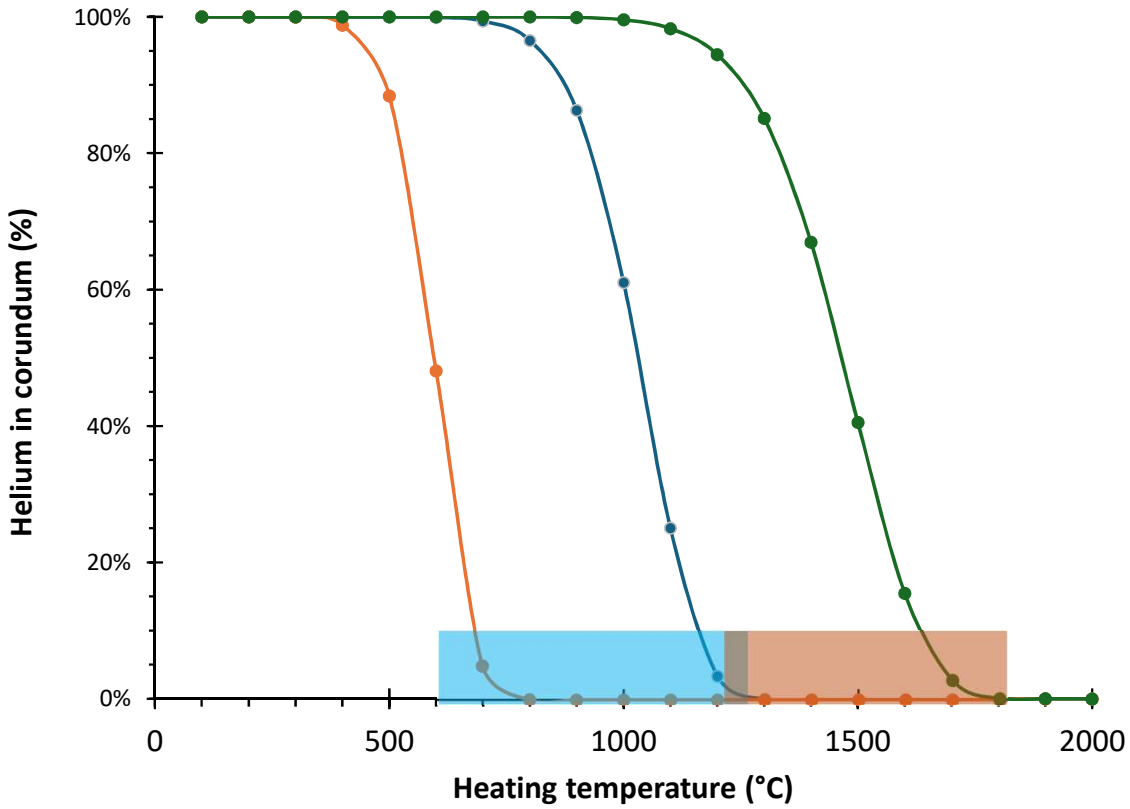
Zhang et al. (2016)



Calculation for 1 mm crystal from the equation from Fechtig and Kalbitzer (1966) with D_0 1.10^{-5} $m^2.s^{-1}$ and activation energy of 100 (orange), 150 (blue) and 200 (green) kJ/mol from Zhang et al. 2016.

Helium in corundum : insights on heat treatment ?

- Crystal defects in corundum could entrapped helium, released by heating.
- Is Helium a good indication of heating ?
- Traditionnal heating (≈600-1200°C)
- Modern heating (up to 1850°C)



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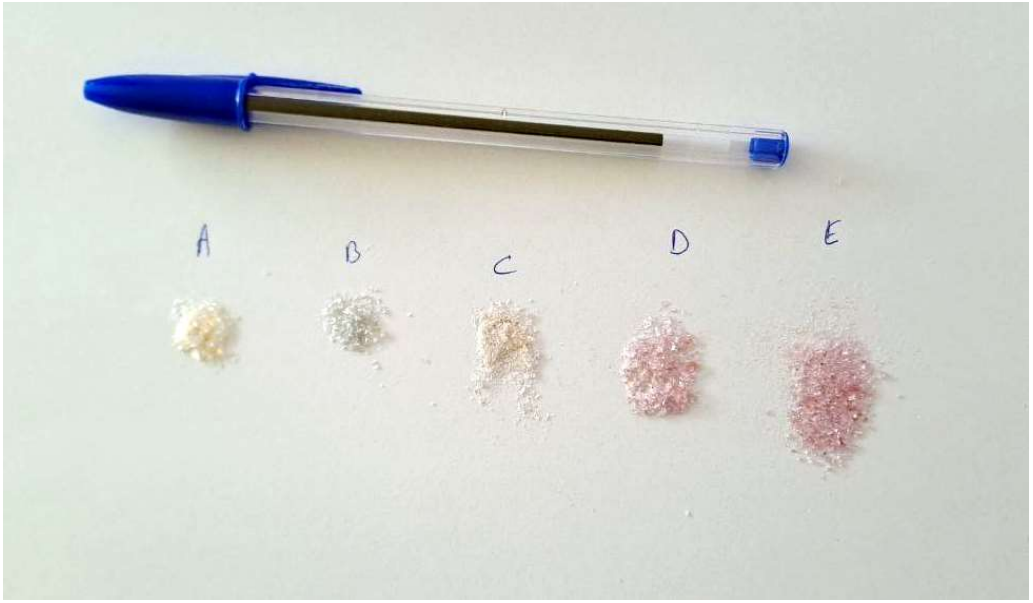
Helium in corundum : insights on heat treatment ?

- Is helium a good indication of heating ?

5 samples selected
(from Madagscar – collected on the field)

Crushed, and 12 pieces per samples selected

Each lot of 2 pieces are heated (2h)



Sample	Replica 1 Weight (mg)	Replica 2 Weight (mg)	Heating temperature (°C)
A0	5,18	3,42	No heating
A4	3,81	1,75	400
A5,5	4,09	2,85	550
A7	3,81	4,77	700
A8,5	2,62	2,99	850
A10	1,84	2,66	1000

Example of sample A

Helium in corundum : insights on heat treatment ?

- Is helium a good indication of heating ?

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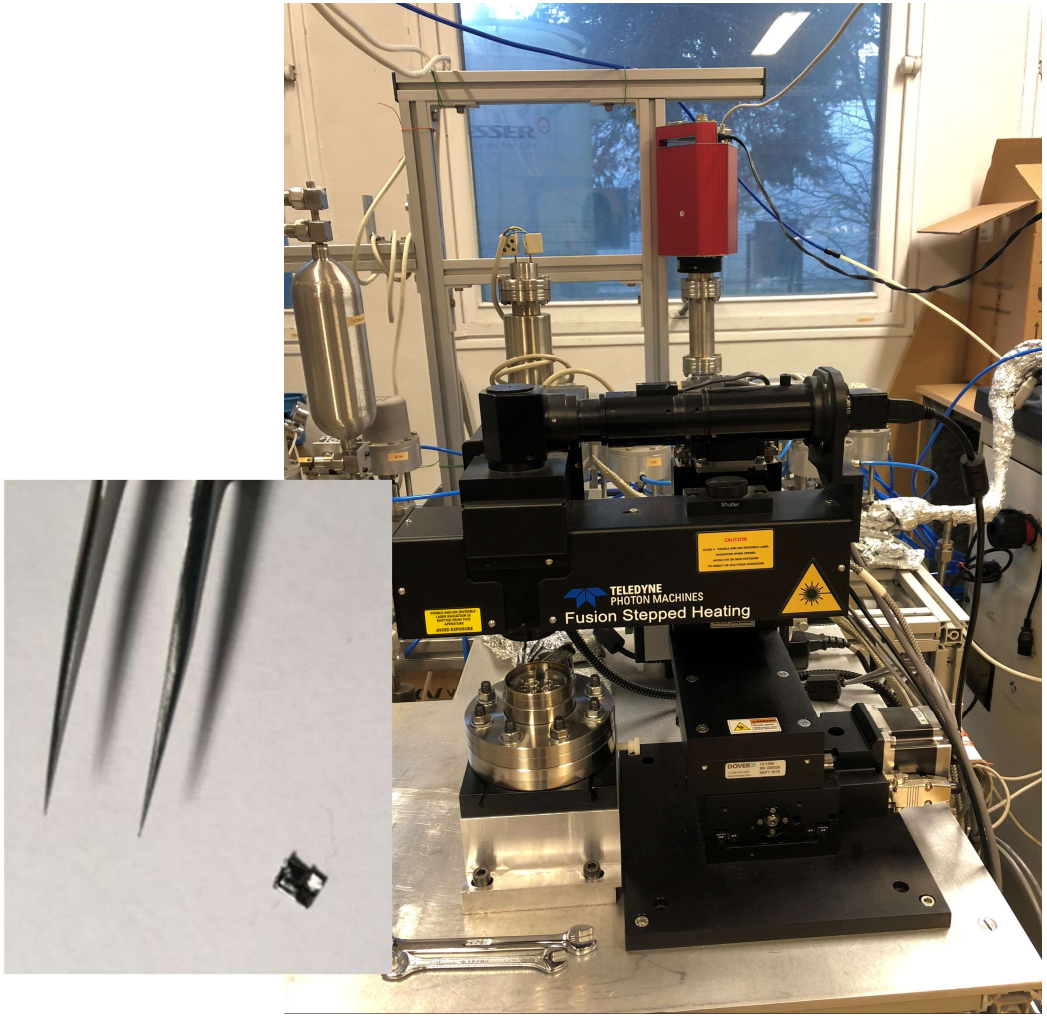
Crushed, and 12 pieces per samples selected

Each lot of 2 pieces are heated (2h)

Each pieces is weighted and
packed in niobium foils

Measurements with a Mass Spectrometer
specialized in noble gas (with purification)



He measurement in University Grenoble-Alpes

Helium in corundum : insights on heat treatment ?

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5 samples selected
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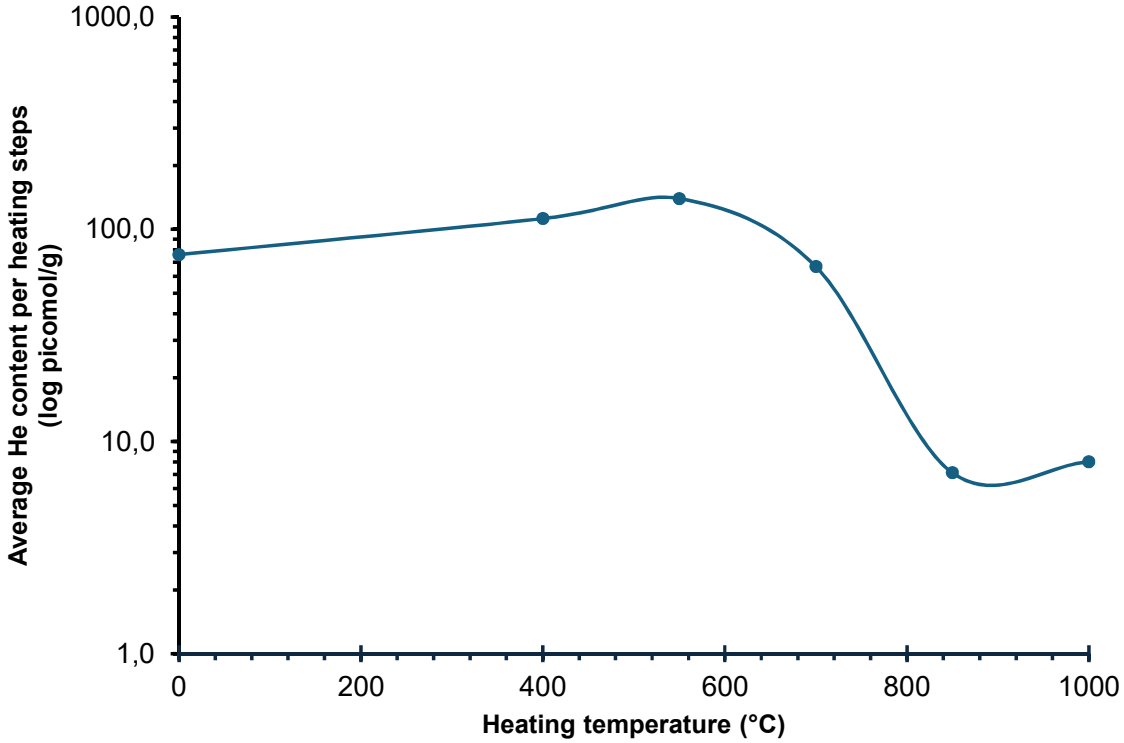
He diffused efficiently between 600-800 °C



Helium in corundum : insights on heat treatment ?

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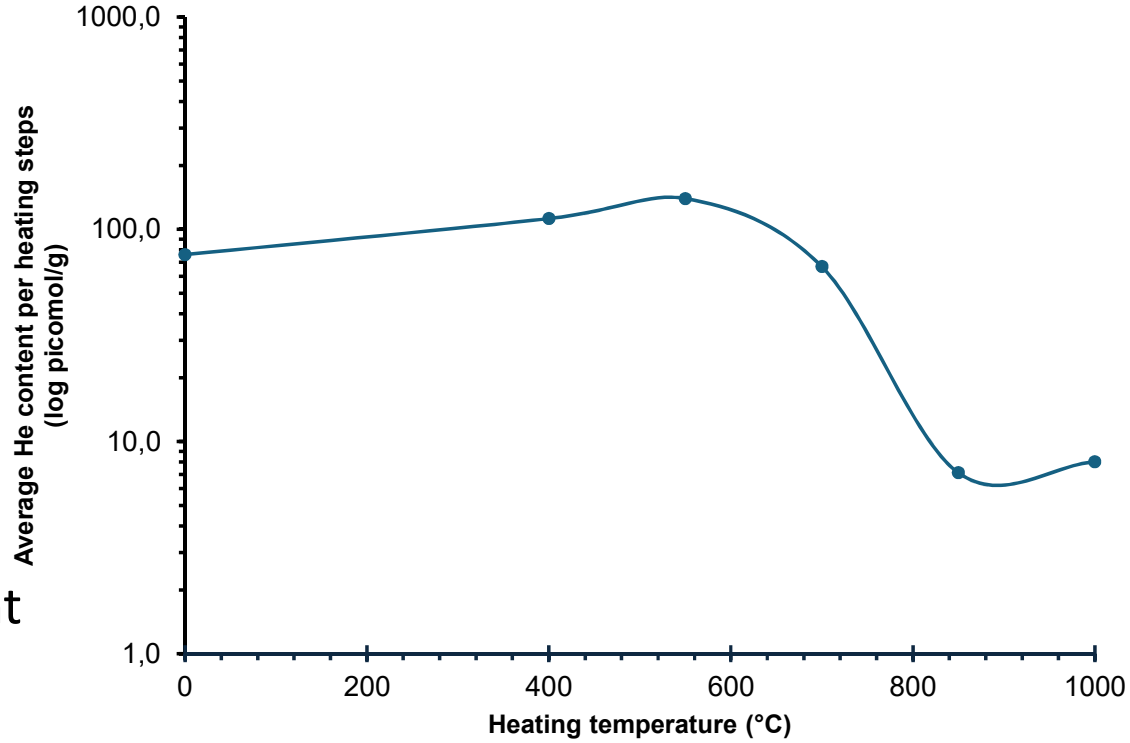
But :

Heterogeneity of sample in term of He content



Helium content in unheated samples

Samples	A		B		C		D		E	
Replica	AA	AB	BA	BB	CA	CB	DA	DB	EA	EB
He content (pmol/g)	268,96	173,40	3,29	3,93	21,19	37,76	148,91	4,12	0,26	98,53
% of difference	36		19		78		97		37197	

Helium in corundum : insights on heat treatment ?

- Is helium a good indication of heating ?

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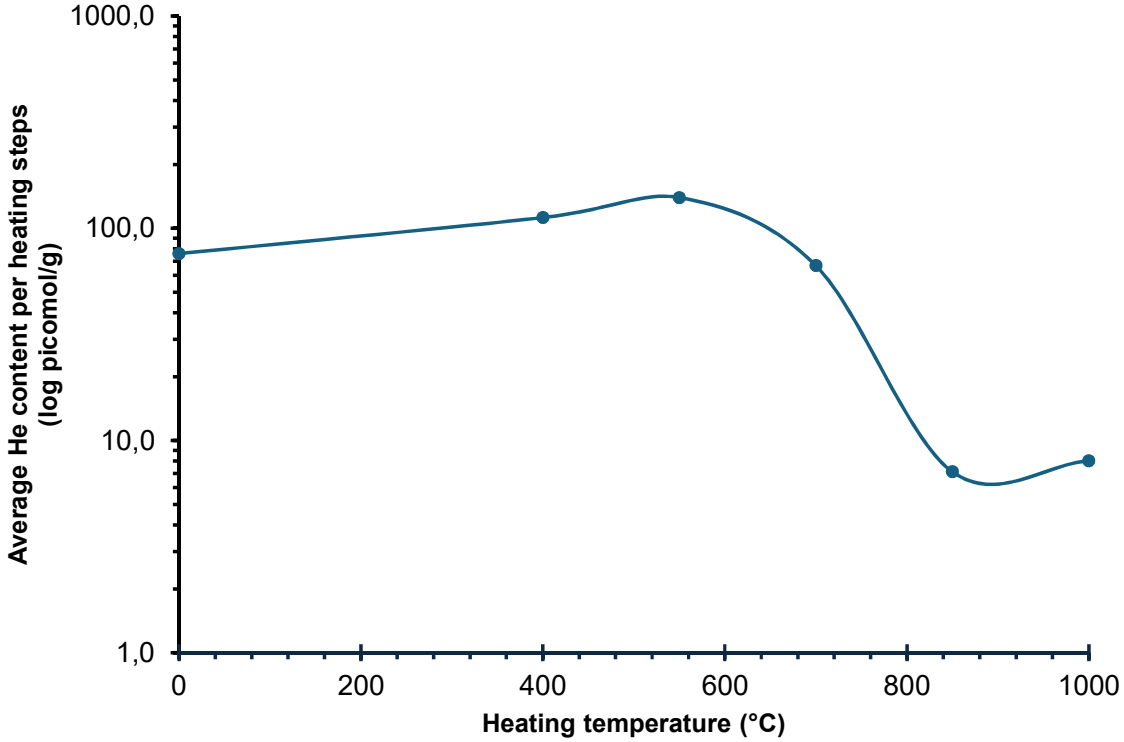
He diffused efficiently between 600-800 °C

But :

Helium remains retained after heating treatment (1000°C during 2 hours)



Samples	A		B		C		D		E	
Replica	AA	AB	BA	BB	CA	CB	DA	DB	EA	EB
He content (pmol/g)	0,92	2,56	0,30	0,40	0,90	3,71	1,25	67,81	1,47	1,04

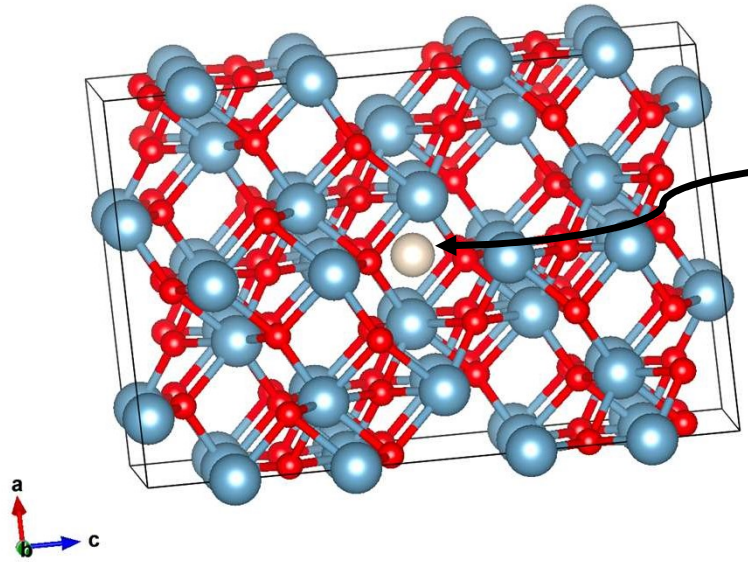
Helium in corundum : insights on heat treatment ?

- Is helium a good indication of heating ?

Next step: Measurements of He diffusivity in corundum from the same piece of sample (correcting intra-sample heterogeneity)

<u>Modelling He diffusion in corundum</u>

Collaboration with S. Figowy (Paris-Saclay University)

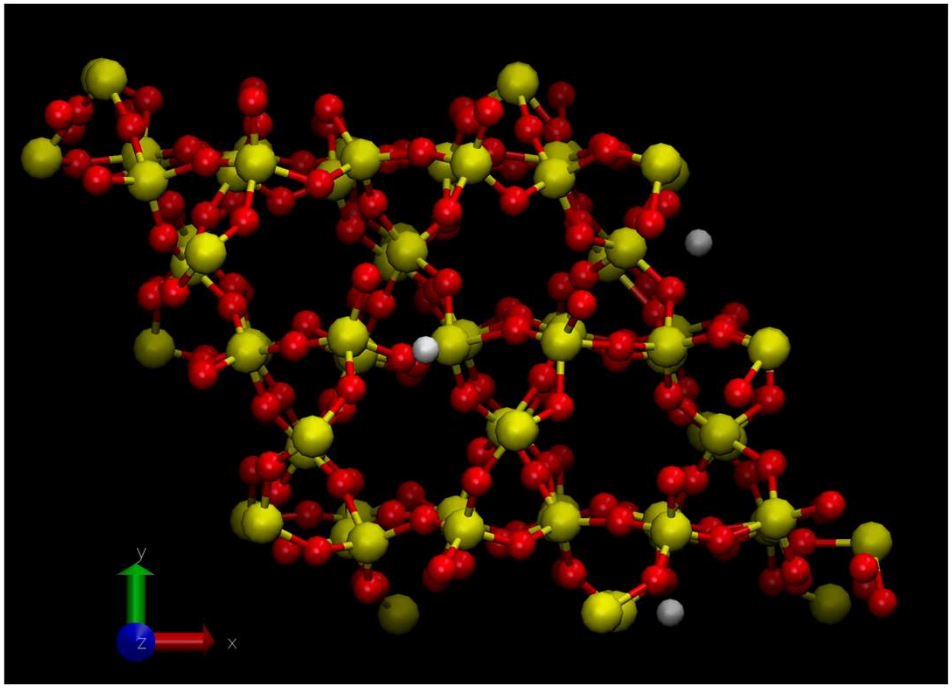


He atom in a corundum supercell

<u>Software:</u>

Vienna *Ab initio* Simulation Package (VASP)

Example: He (interstitial point defect) in quartz

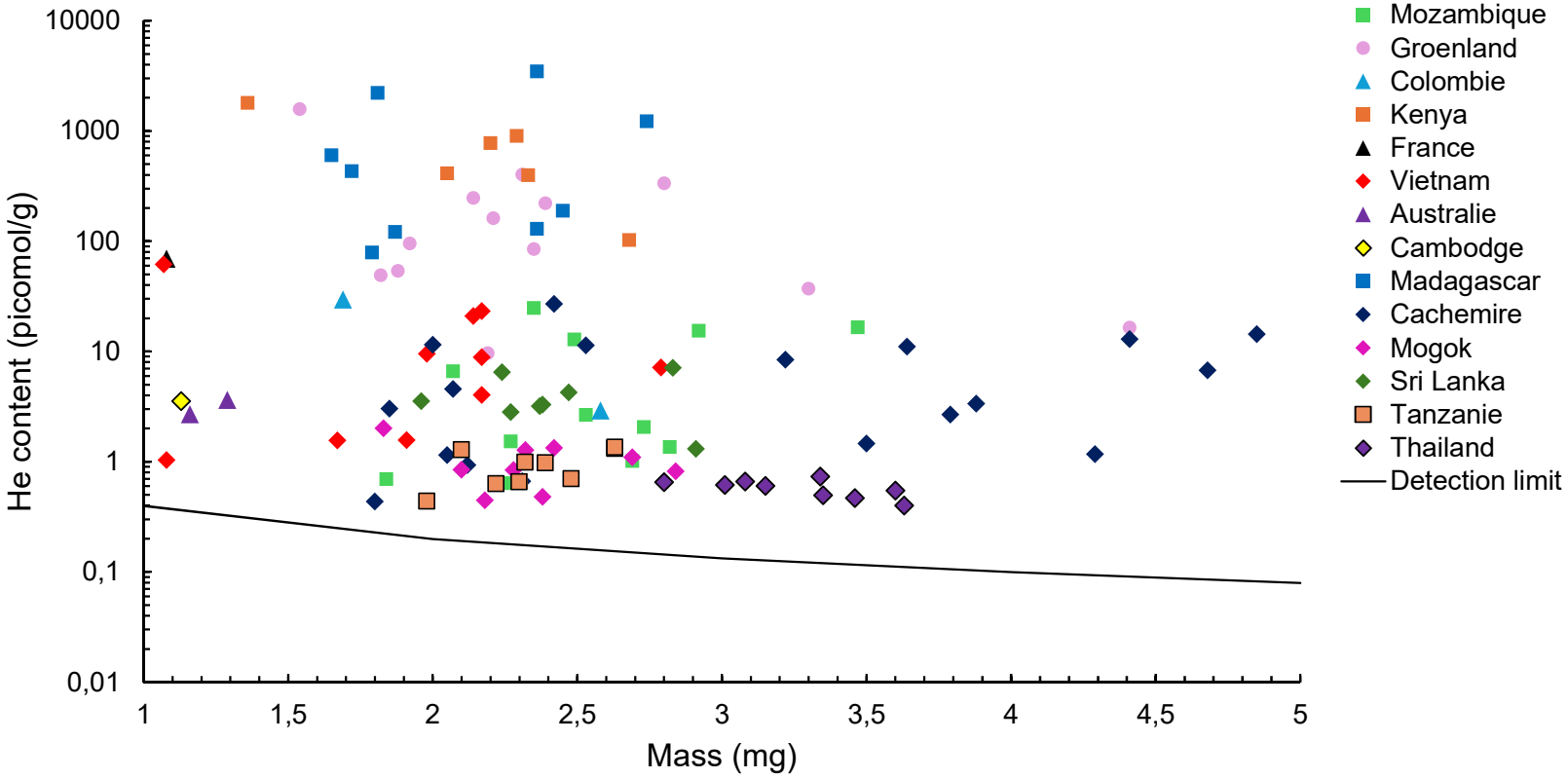


Helium in corundum : insights on formation ?

- Is helium could inform us about geology ?

117 analysis on 17 samples selected from 14 origins (collected from the field).

By origin



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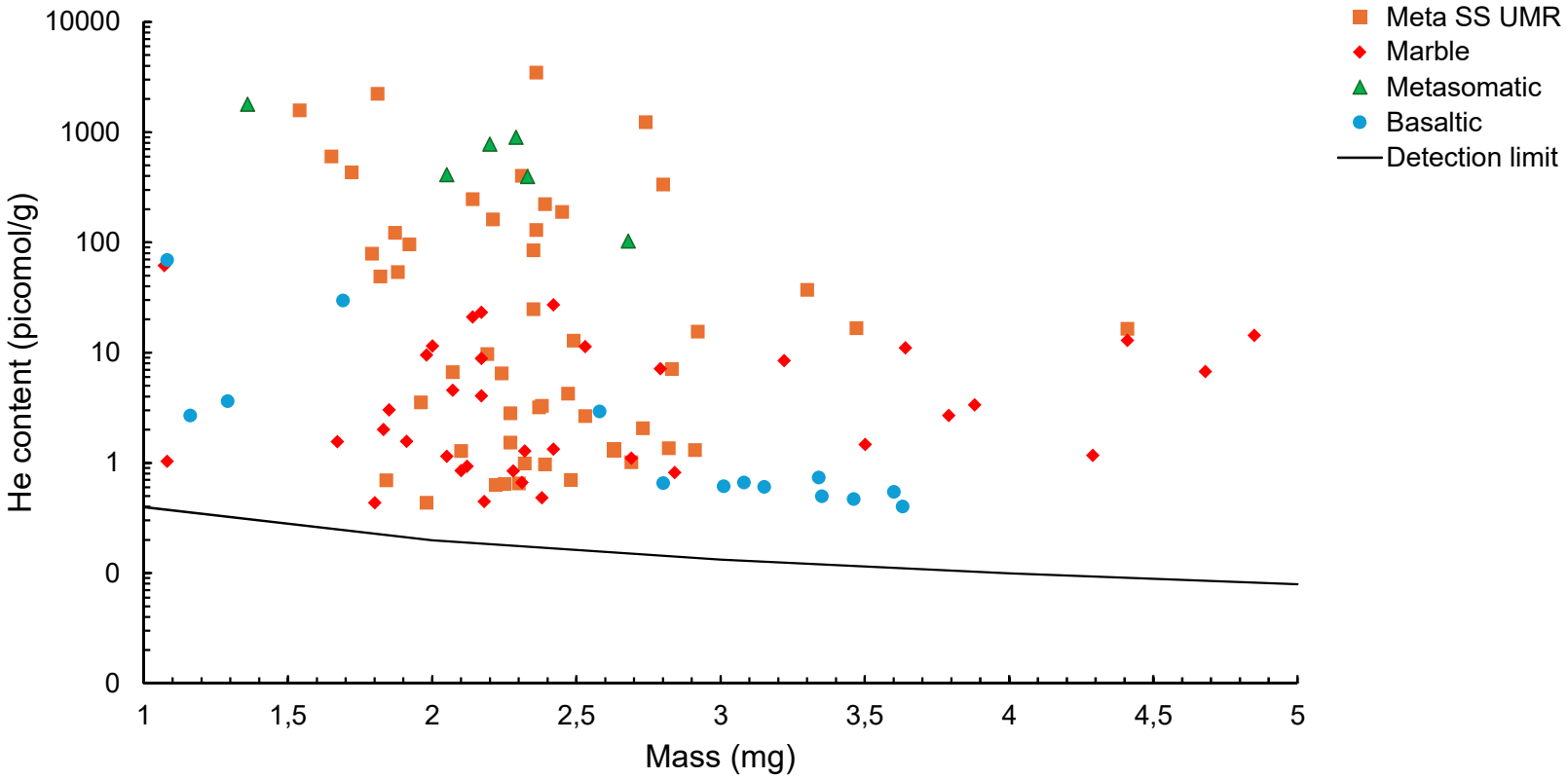
By geology



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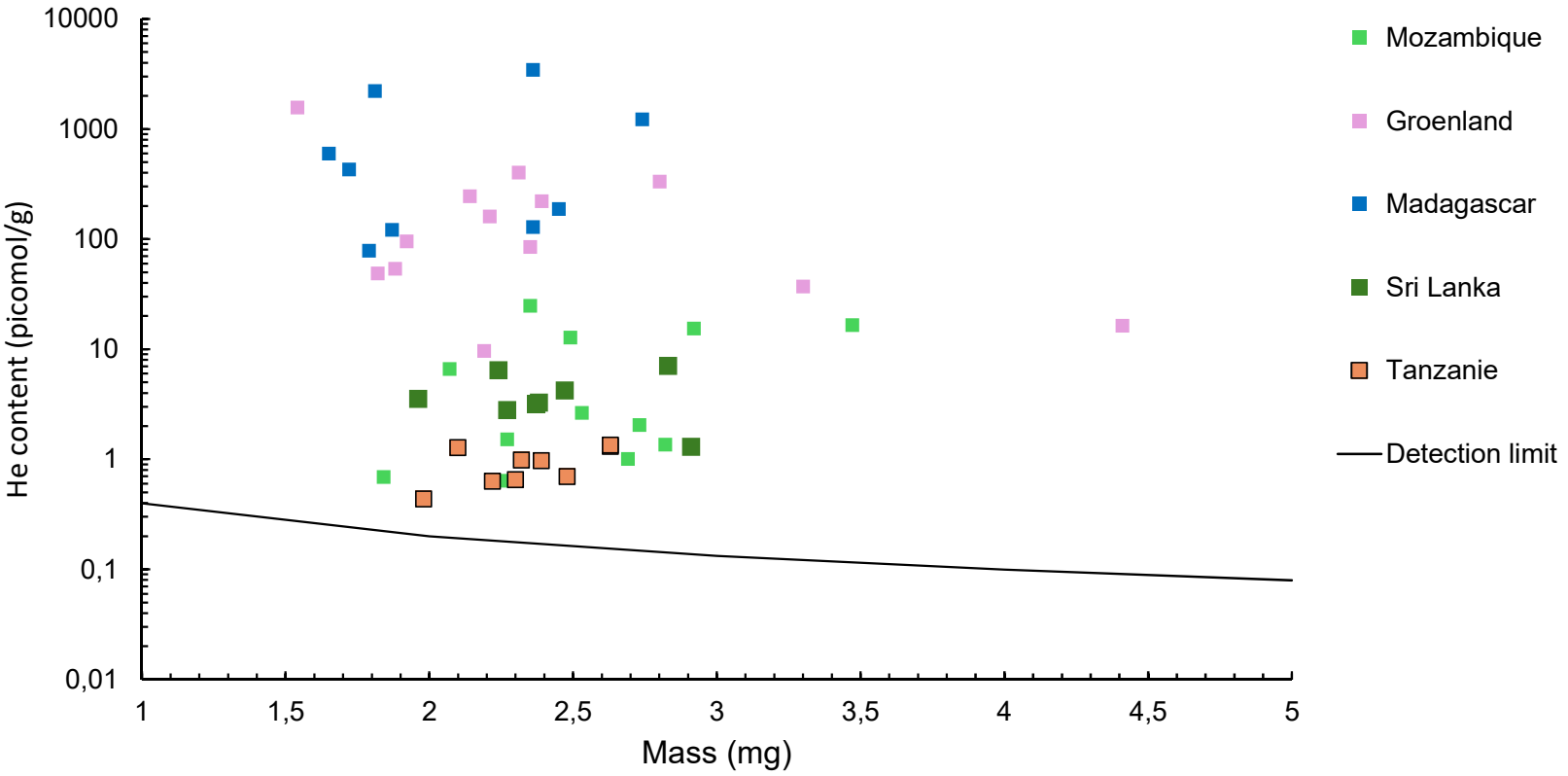
By origin
(Meta SS)



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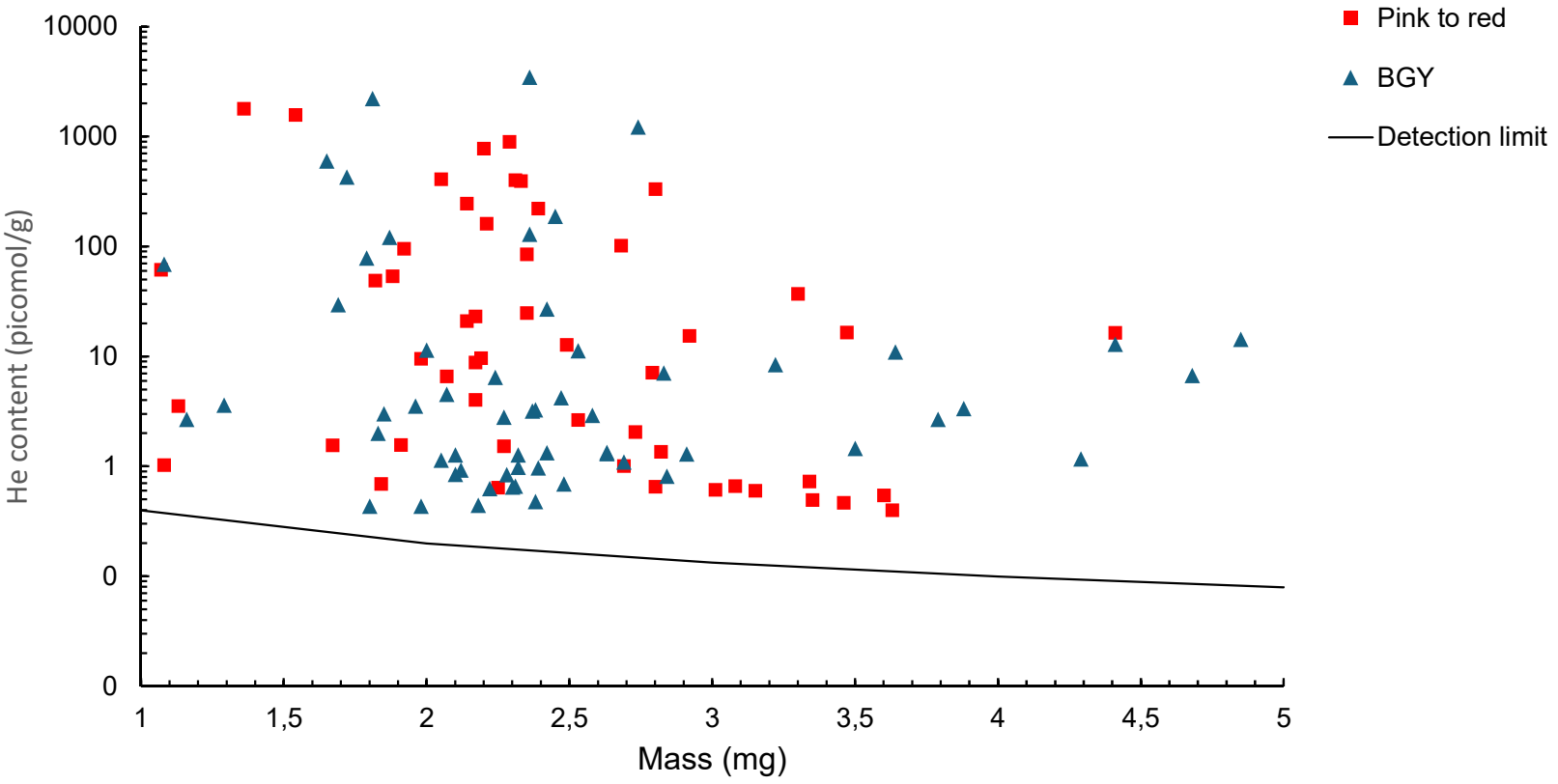
By color



Conclusions

- Helium has been measured in corundum for exploratory research
    - Detection of thermal treatment : He left after treatment, same range of natural samples
        - Compromised but modeling could help to assess the limit
    - For origin : interesting because no direct link with color and geology,
        - Could be coupled with other geochemistry.
- Still to explore, and could help to better understand geological aspect of corundum formation

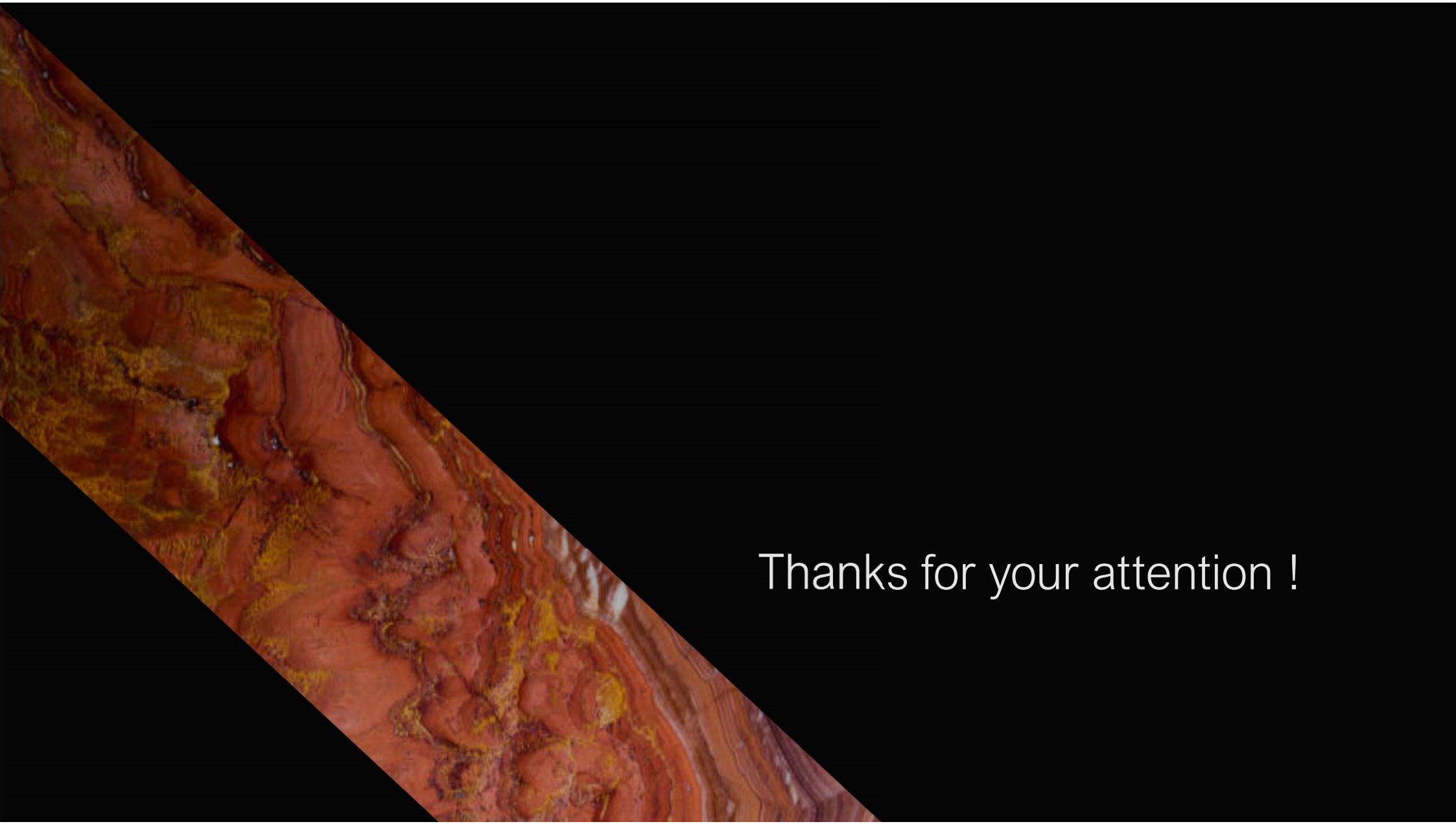
<u>Références</u>

Basu S, Jones AP, Verchovsky AB, Kelley SP, Stuart FM. An overview of noble gas (He, Ne, Ar, Xe) contents and isotope signals in terrestrial diamond. *Earth-Science Rev*. 2013;126:235-249. doi:10.1016/j.earscirev.2013.08.010

Moreira, M.A., Kurz, M.D. (2013). Noble Gases as Tracers of Mantle Processes and Magmatic Degassing. In: Burnard, P. (eds) The Noble Gases as Geochemical Tracers. Advances in Isotope Geochemistry. Springer, Berlin, Heidelberg. https://doi.org/10.1007/978-3-642-28836-4_12

Weiss Y, Kiro Y, Class C, Winckler G, Harris JW, Goldstein SL. Helium in diamonds unravels over a billion years of craton metasomatism. *Nat Commun*. 2021;12(1). doi:10.1038/s41467-021-22860-3

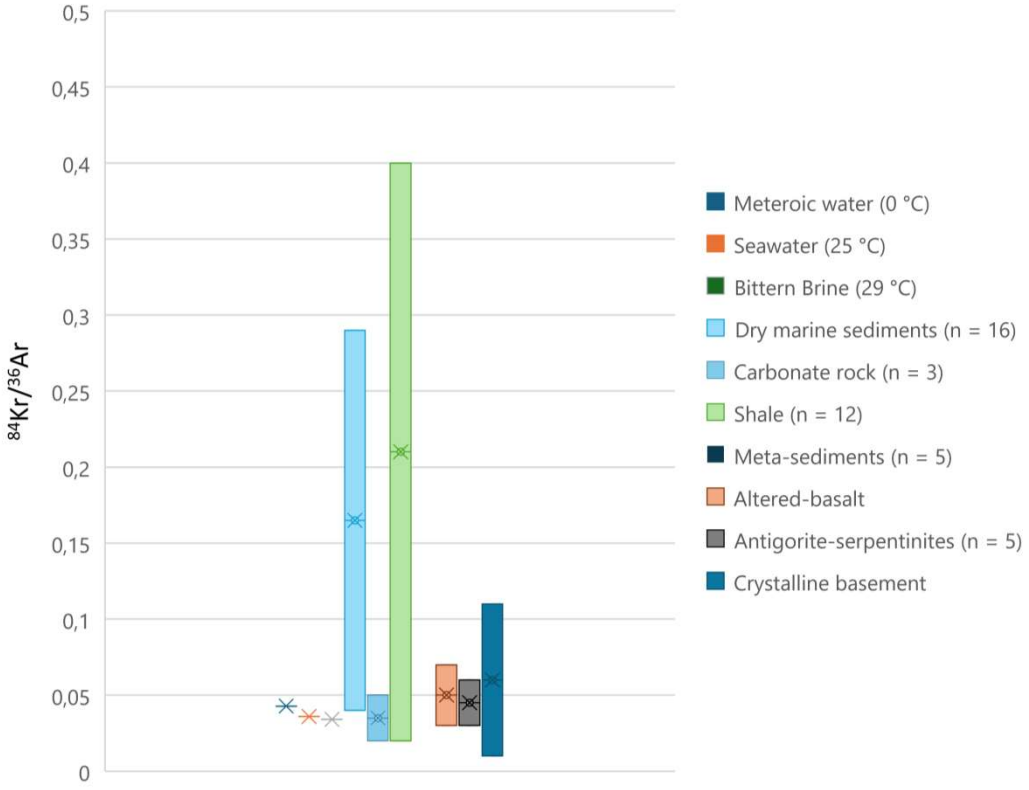
Zhang G, Xiang X, Yang F, et al. Helium stability and its interaction with H in α-Al2O3: A first-principles study. *Phys Chem Chem Phys*. 2016;18(3):1649-1656. doi:10.1039/c5cp06496a


Thanks for your attention !

Noble Gas in Geology

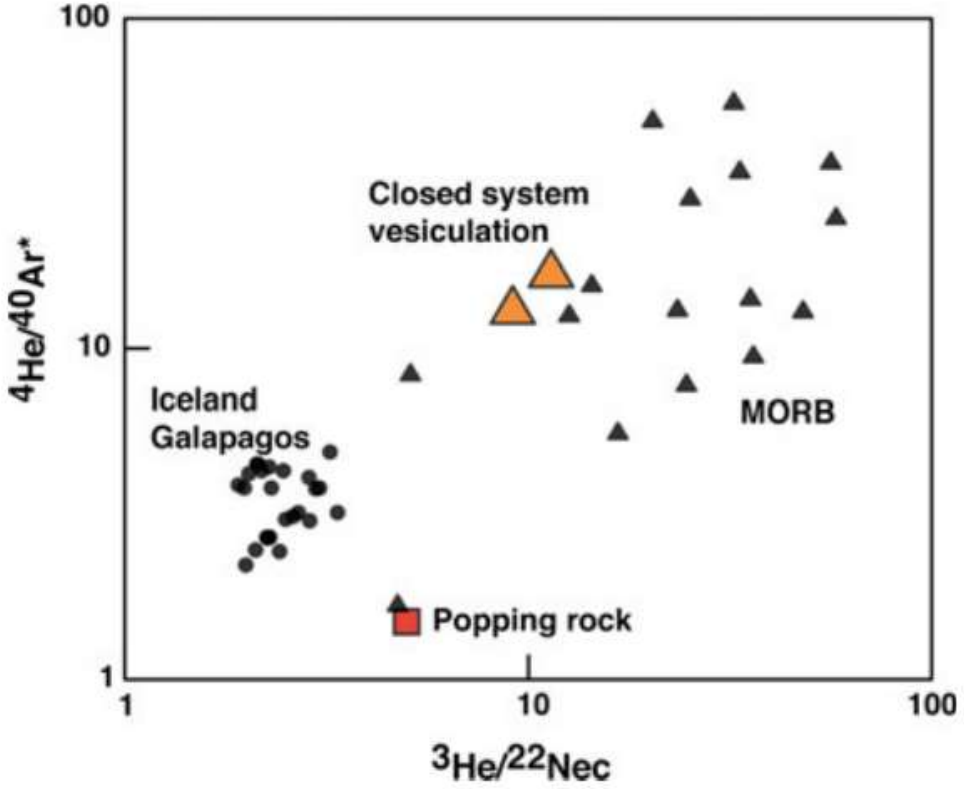
- Elements with filled outer electrons shells, no chemical binding

Noble gases in fluid inclusions as tracers of fluid origin



Data compiled from Burnard (2013)

Noble gases as tracers of magmatic processes



Moreira & Kurz (2013)

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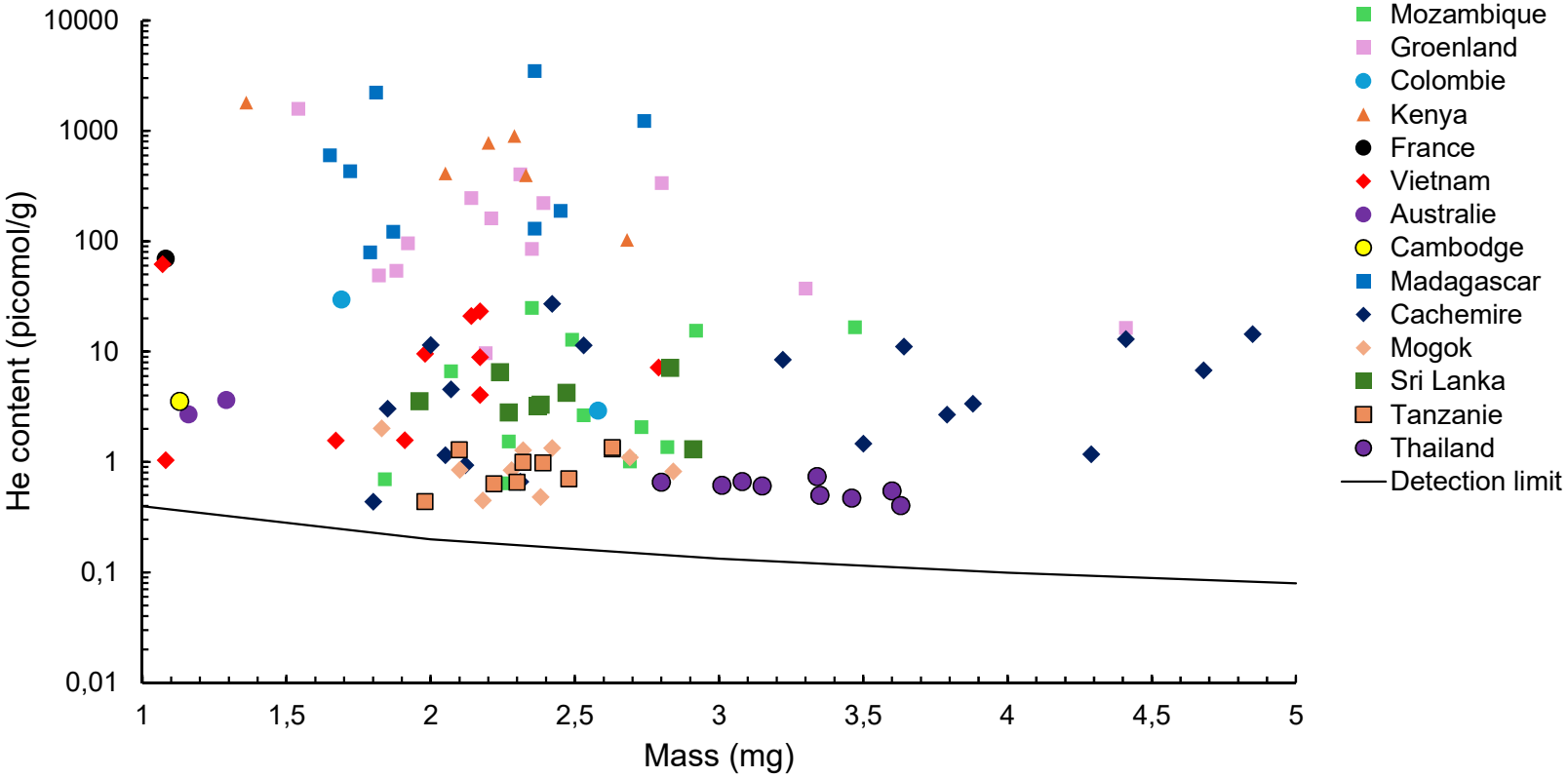
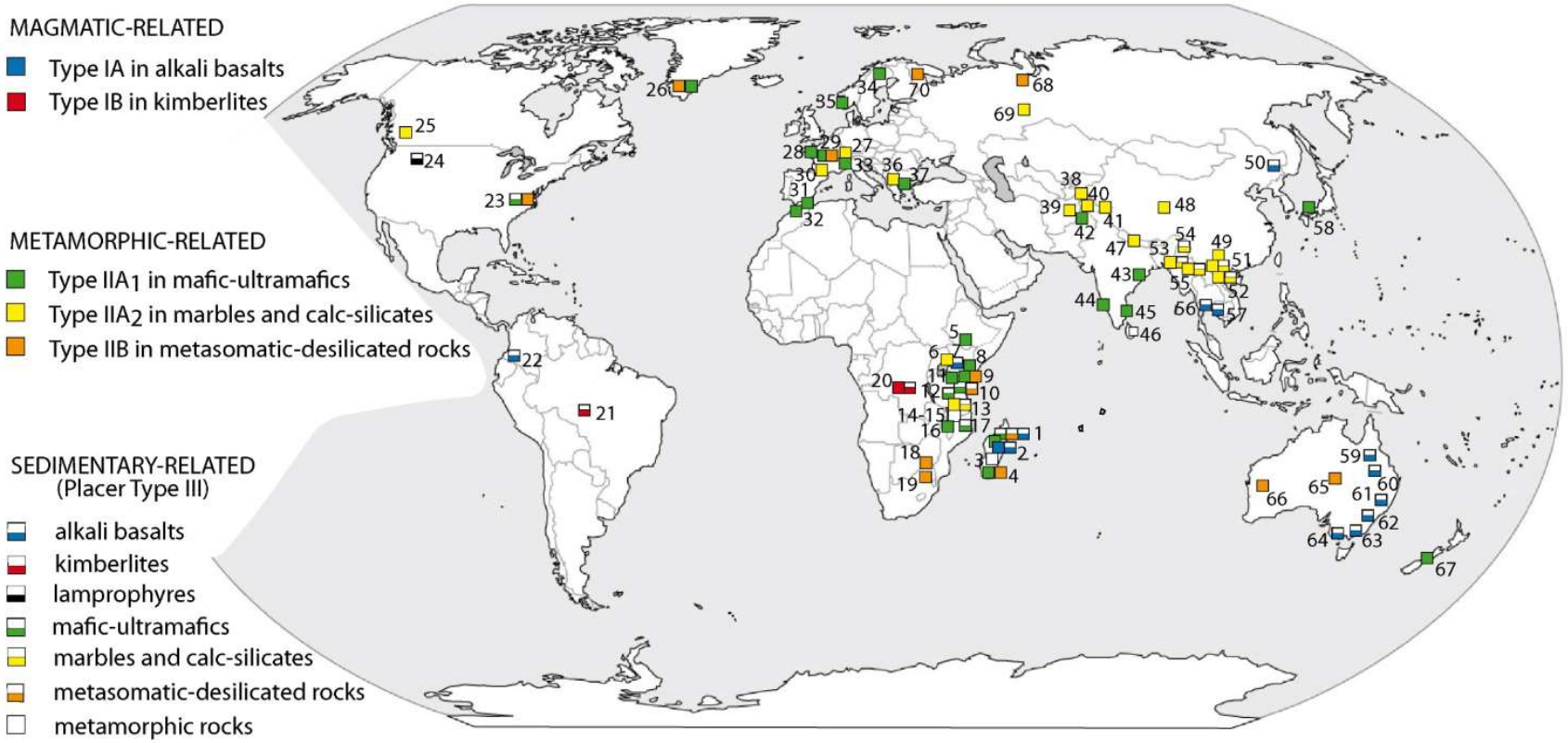
116 analysis on XX samples selected from 14 origins (collected from the field).



Géologie des corindons

- Plusieurs classifications existent,
  sur les mêmes bases



Giuliani et al. (2020)

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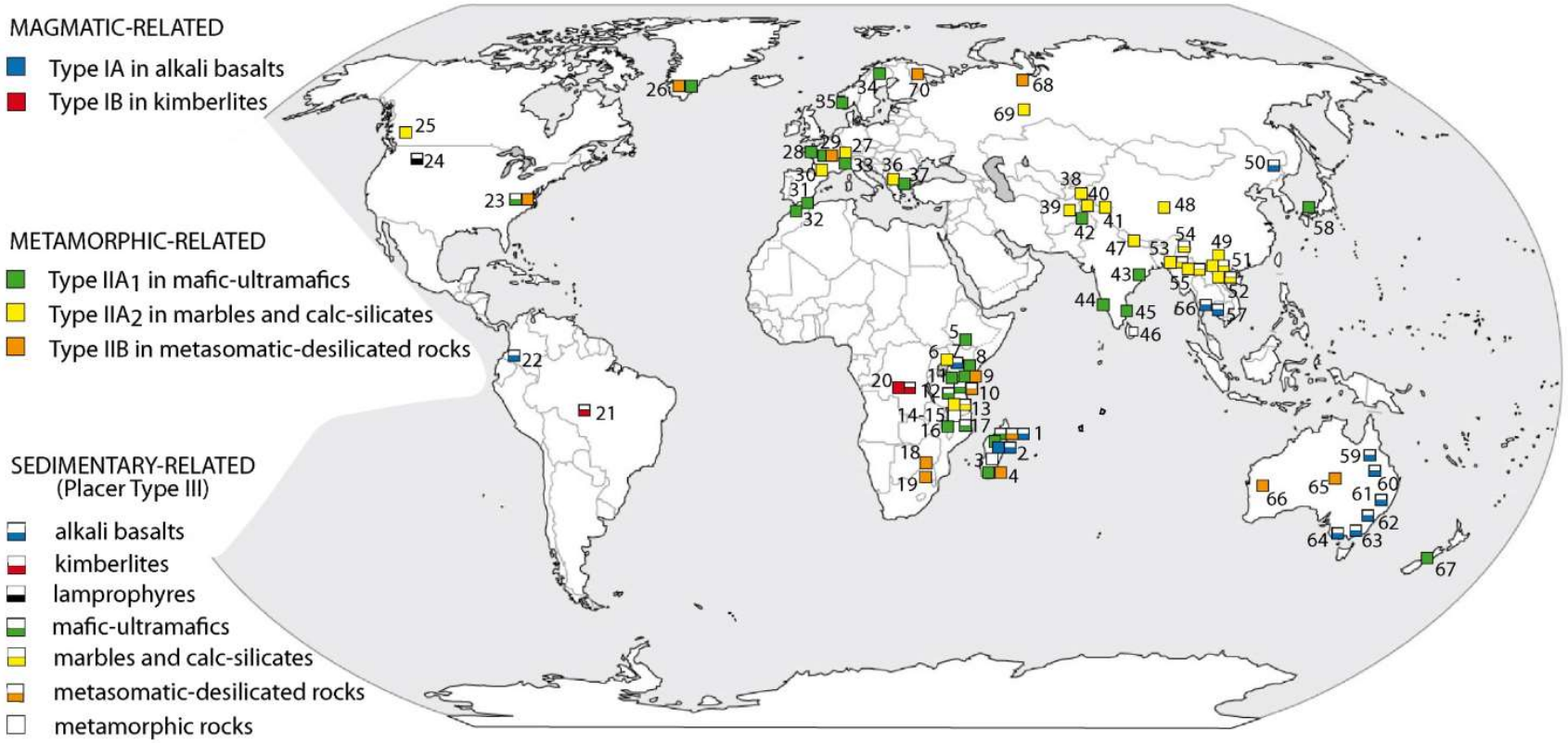


Giuliani et al. (2020)

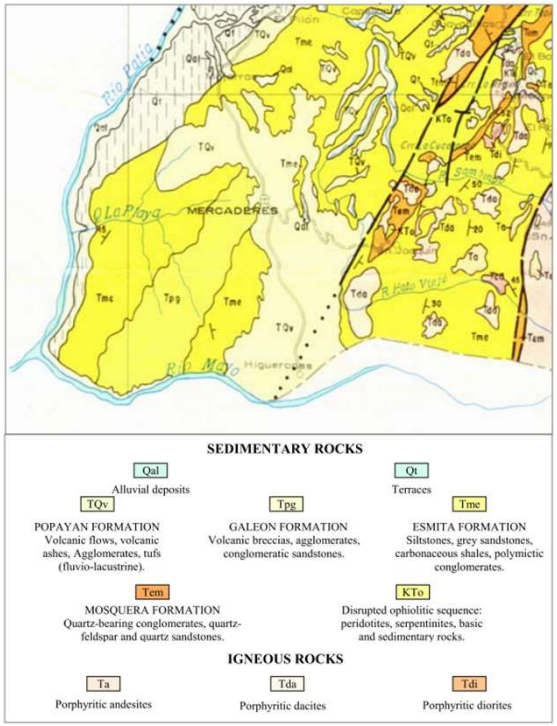
Géologie des corindons

- Mais, comme toujours, la nature n'est pas si simple
- Exemple des corindons de Mercaderes-Mayo (Colombie)

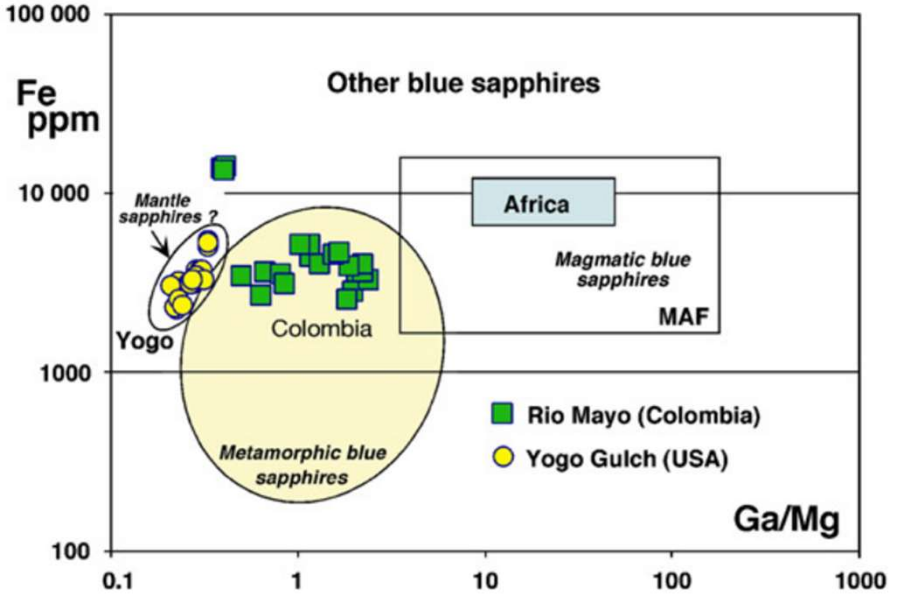
Géologie + Inclusions
=
Volcanique

vs

Géochimie
=
Métamorphique



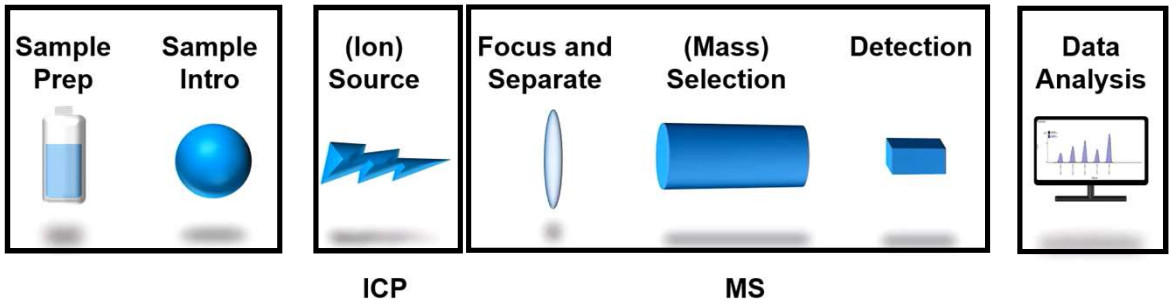
Marin et Paris (1979)

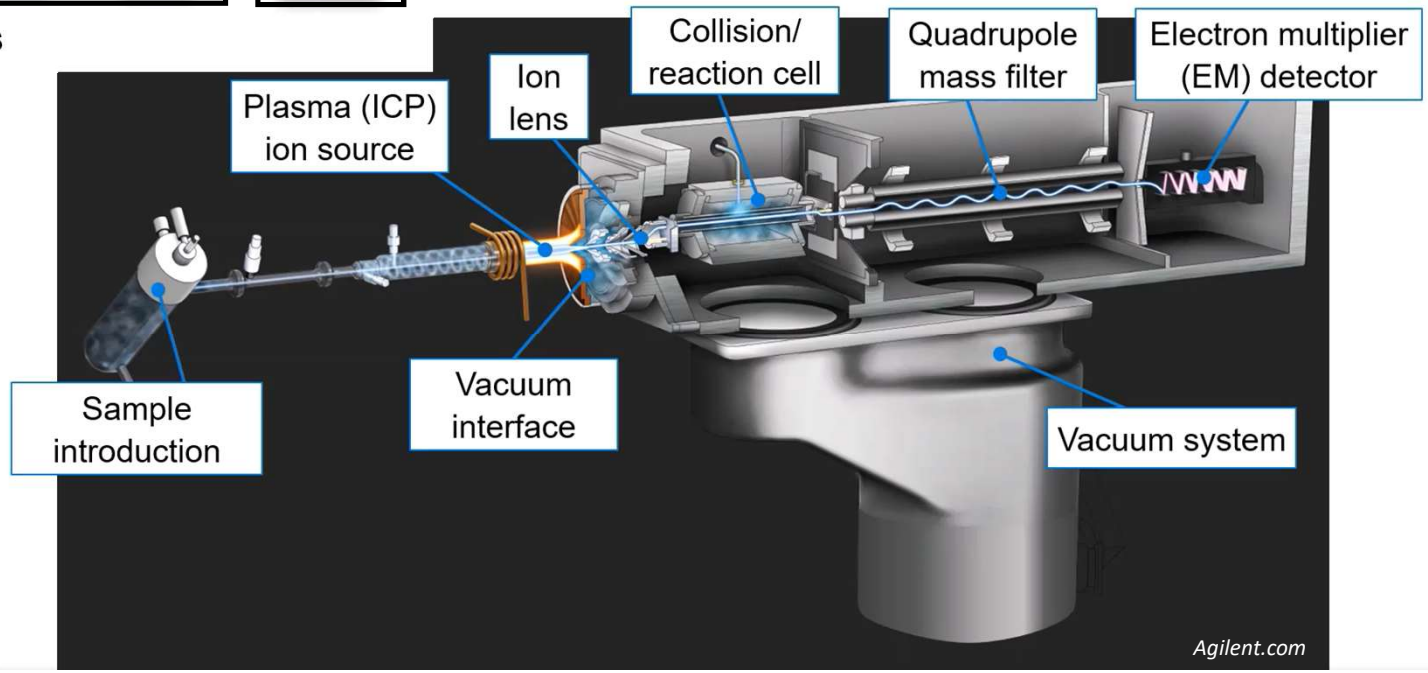


Peucat et al. (2007)

Géochimie des corindons

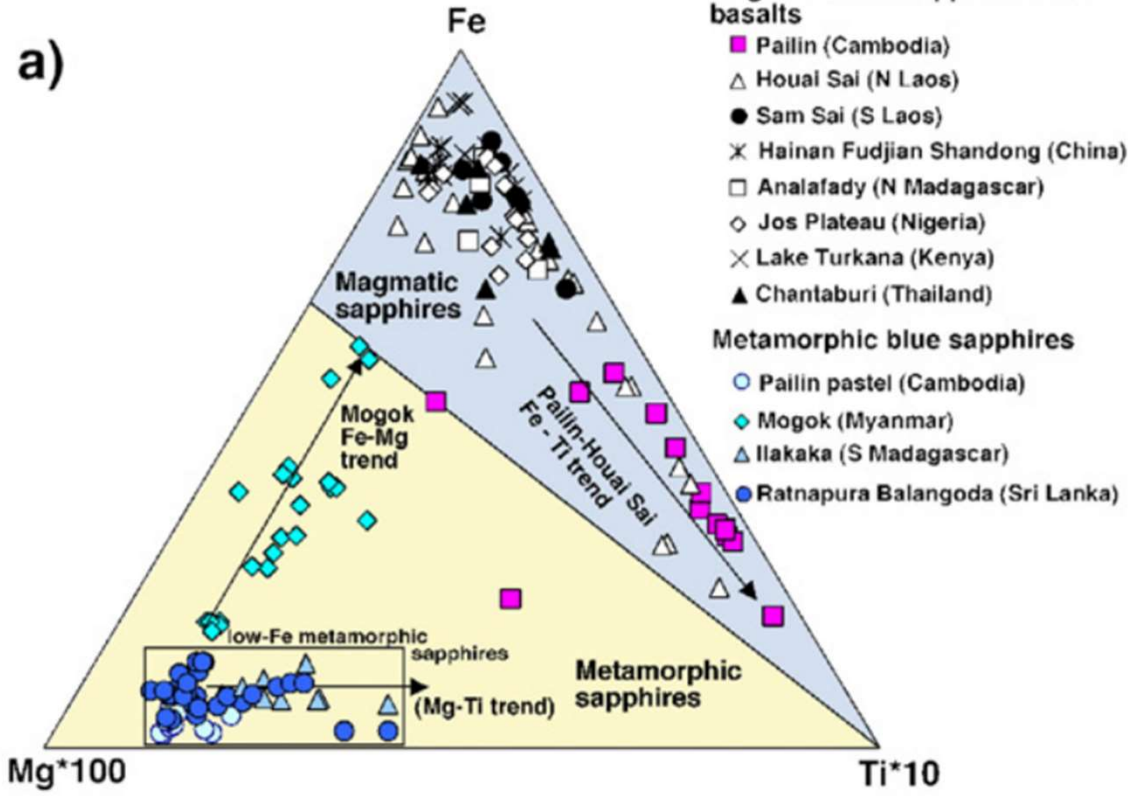
- Technique utilisé : spectrométrie de masse (plus commun, ICP-MS)



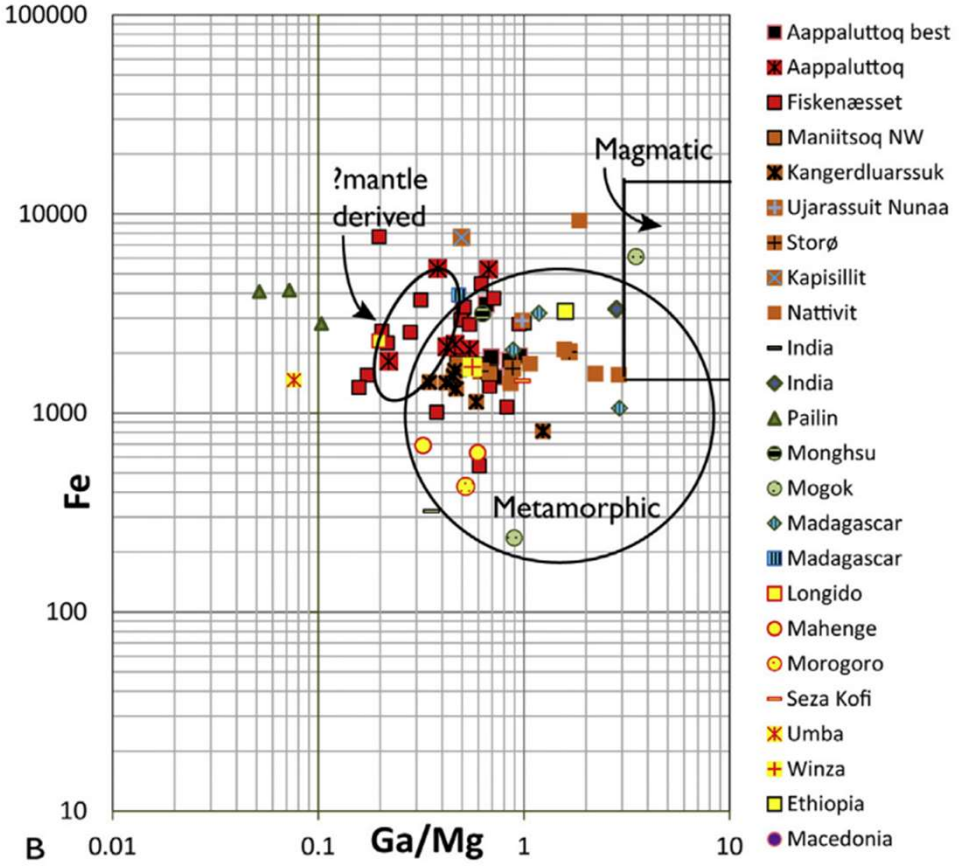


Géochimie des corindons

- Assez hétérogène



Peucat at al. (2007)



Keulen at al. (2020)

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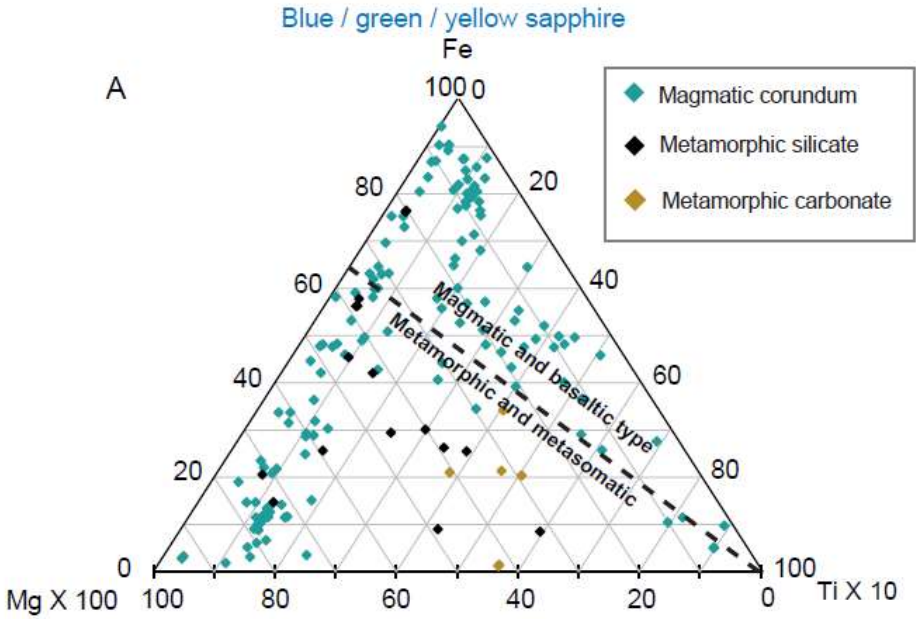

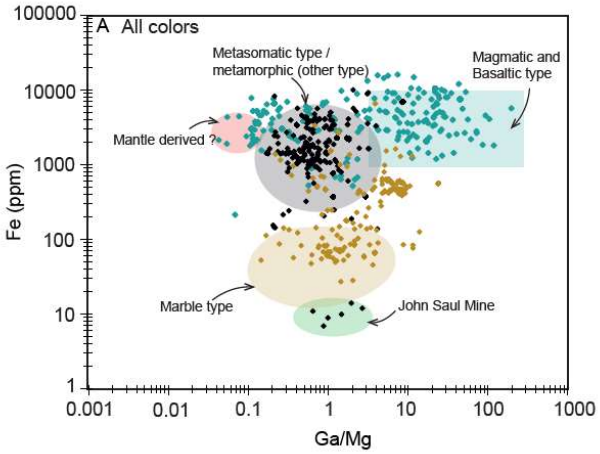

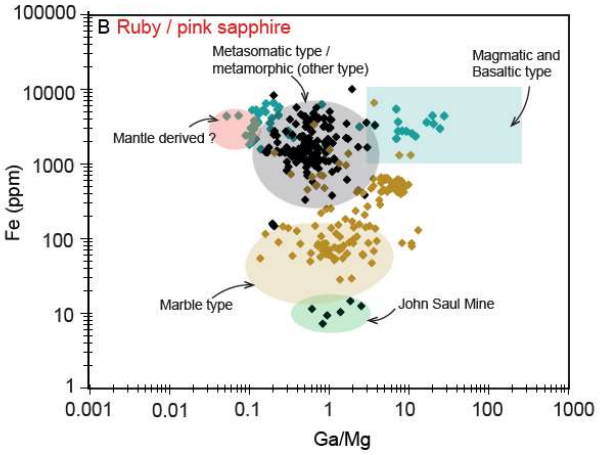

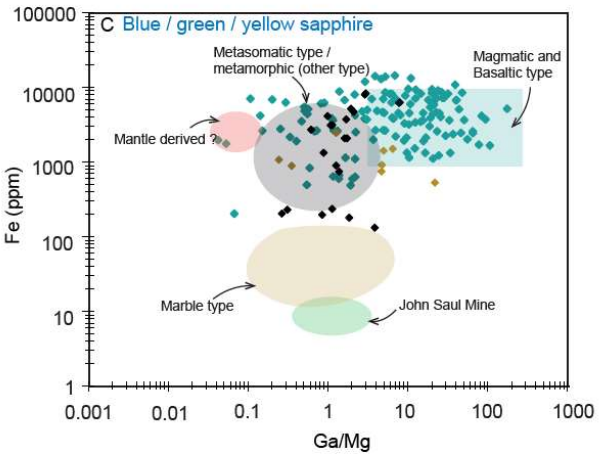

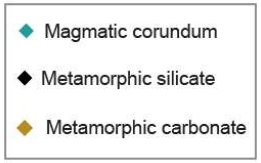

Corre at al. soumis

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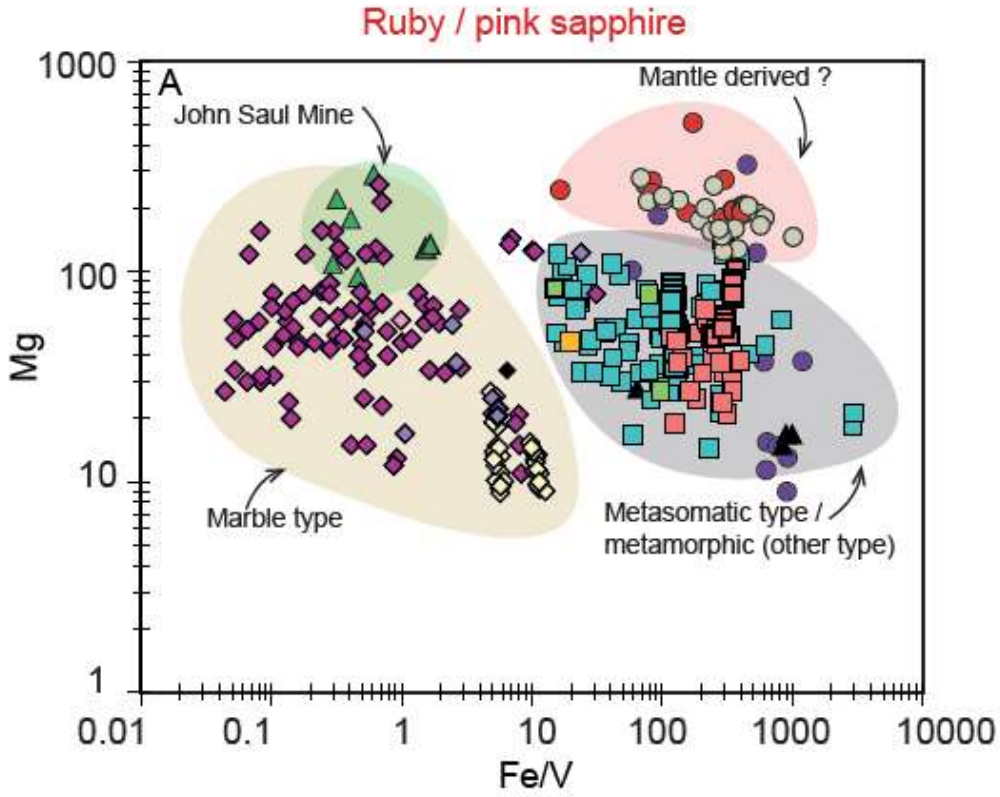

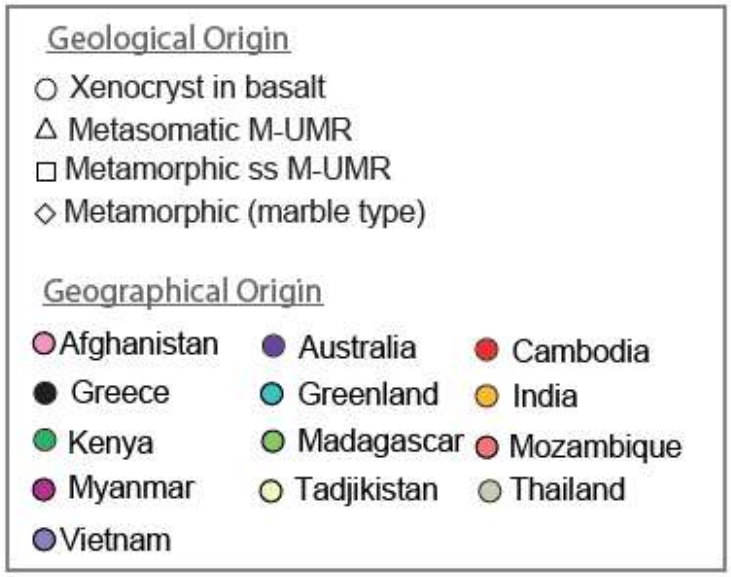

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