

Noble Gas in Corundum : Interests in gemology

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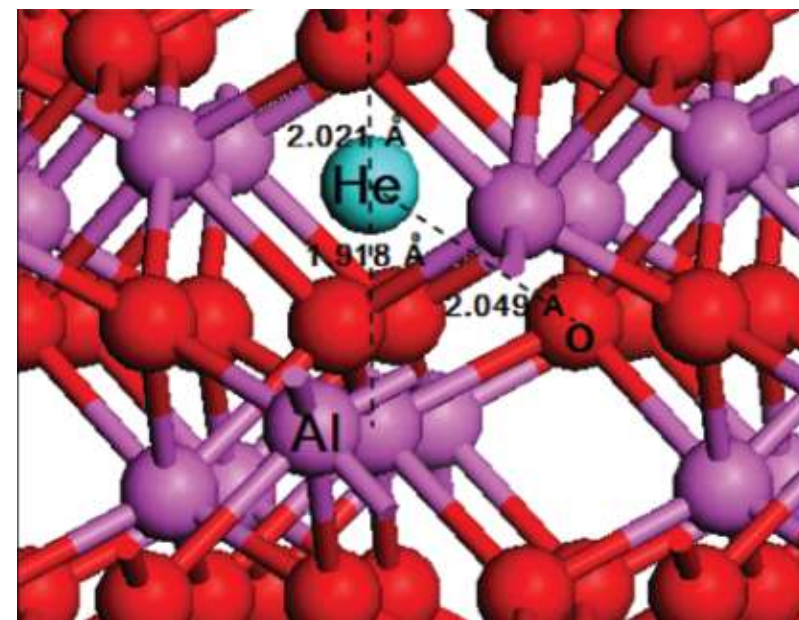
Noble Gas in Geology

- Elements with filled outer electrons shells, no chemical binding

Periodic Table of the Elements

Group 1												18						
Period 1	1																	2
	H																	He
	1.008 1.0129 Hydrogen																	4.0026 2032.9 Helium
Period 2	2											10						
	Li	Be											B	C	N	O	F	Ne
	6.94 7.016 Lithium	9.0122 9.0127 Beryllium											10.81 10.811 Boron	12.011 12.0107 Carbon	14.007 14.00643 Nitrogen	15.999 15.99903 Oxygen	18.998 18.99841 Fluorine	20.180 20.1797 Neon
Period 3	3											18						
	Na	Mg											Al	Si	P	S	Cl	Ar
	22.990 22.98977 Sodium	24.305 24.30409 Magnesium											26.982 26.981538 Aluminum	28.085 28.0855 Silicon	30.974 30.973762 Phosphorus	32.06 32.059 Sulfur	35.45 35.453 Chlorine	39.948 39.948163 Argon
Period 4	4											10						
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
	39.098 39.09831 Potassium	40.078 40.0783 Calcium	44.956 44.95591 Scandium	47.867 47.8671 Titanium	50.942 50.9415 Vanadium	51.996 51.9961 Chromium	54.938 54.93804 Manganese	55.845 55.845 Iron	58.933 58.9332 Cobalt	58.933 58.9332 Nickel	63.546 63.546 Copper	65.38 65.38 Zinc	69.723 69.7231 Gallium	72.630 72.6305 Germanium	74.922 74.9216 Arsenic	78.971 78.9718 Selenium	79.904 79.904 Bromine	83.798 83.798 Krypton
Period 5	5											10						
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
	85.468 85.4678 Rubidium	87.62 87.62 Strontium	88.906 88.90584 Yttrium	91.224 91.224 Zirconium	92.906 92.90638 Niobium	95.95 95.94 Molybdenum	(98) 98.906 Technetium	101.07 101.07 Ruthenium	102.91 102.9055 Rhodium	106.42 106.42 Palladium	107.87 107.8682 Silver	112.41 112.411 Cadmium	118.71 118.710 Indium	118.710 118.710 Tin	121.76 121.757 Antimony	127.60 127.603 Tellurium	126.905 126.90548 Iodine	131.29 131.294 Xenon
Period 6	6											10						
	Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
	132.91 132.90545 Caesium	137.33 137.327 Barium		178.49 178.49 Hafnium	180.95 180.9479 Tantalum	183.84 183.84 Tungsten	186.21 186.207 Rhenium	190.23 190.23 Osmium	192.22 192.222 Iridium	195.08 195.084 Platinum	196.97 196.96655 Gold	200.59 200.59 Mercury	204.38 204.377 Thallium	207.2 207.2 Lead	208.98 208.9804 Bismuth	(210) 210 Polonium	(210) 210 Astatine	(222) 222 Radon
Period 7	7											10						
	Fr	Ra	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
	(223) 223 Francium	(226) 226 Radium		(261) 261 Rutherfordium	(262) 262 Dubnium	(266) 266 Seaborgium	(264) 264 Bohrium	(277) 277 Hassium	(288) 288 Meitnerium	(271) 271 Darmstadtium	(110) 110 Roentgenium	(112) 112 Copernicium	(113) 113 Nihonium	(114) 114 Flerovium	(115) 115 Moscovium	(116) 116 Livermorium	(117) 117 Tennessine	(118) 118 Oganesson

Example of He in corundum structure



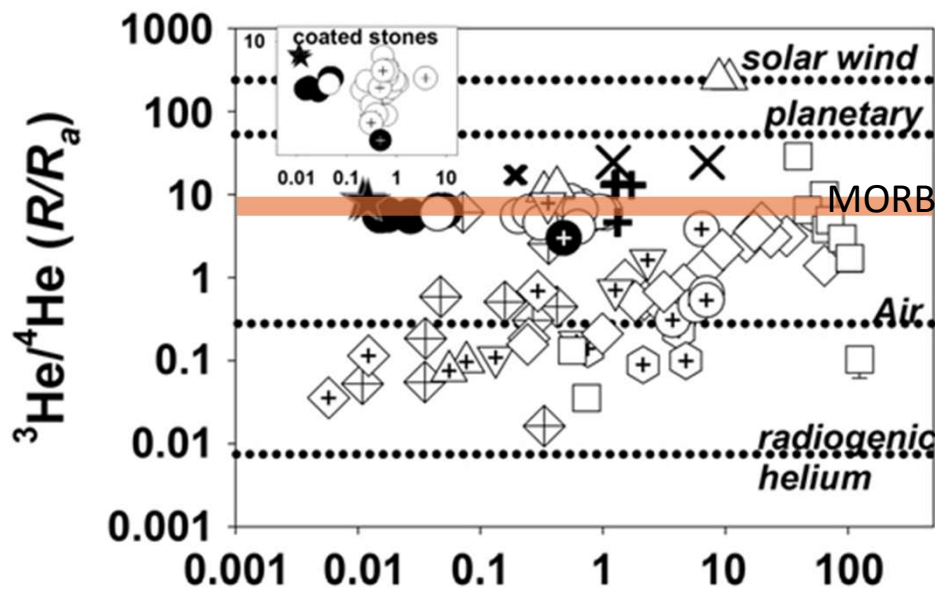
- alkali metals
- alkaline earth metals
- lanthanides
- transition metals
- unknown properties
- post-transition metals
- metalloids
- reactive nonmetals
- noble gases
- actinides



Noble Gas in Geology

- Elements with filled outer electrons shells, no chemical binding

Noble gases (He) in diamond : decipher geological environment



- coated stone - Zaire ⊕ coated stone - Jwaneng ● coated stone - Panda
- ⊕ resorbed coated stone - Panda ⊕ pipe diamond - Andhra Pradesh
- ◇ polycrystalline diamond - Jwaneng ◇ polycrystalline diamond - Orapa
- ⊕ framesite - Jwaneng □ metamorphic diamond - Kazakhstan
- △ alluvial - Argyle △ alluvial - Sierre Leone ▽ alluvial - Krishna gravel
- ★ Popping rock × Loihi × Iceland + Reunion

$1/4\text{He}$ (10^{-6} cc STP/g)

Basu et al. (2013)

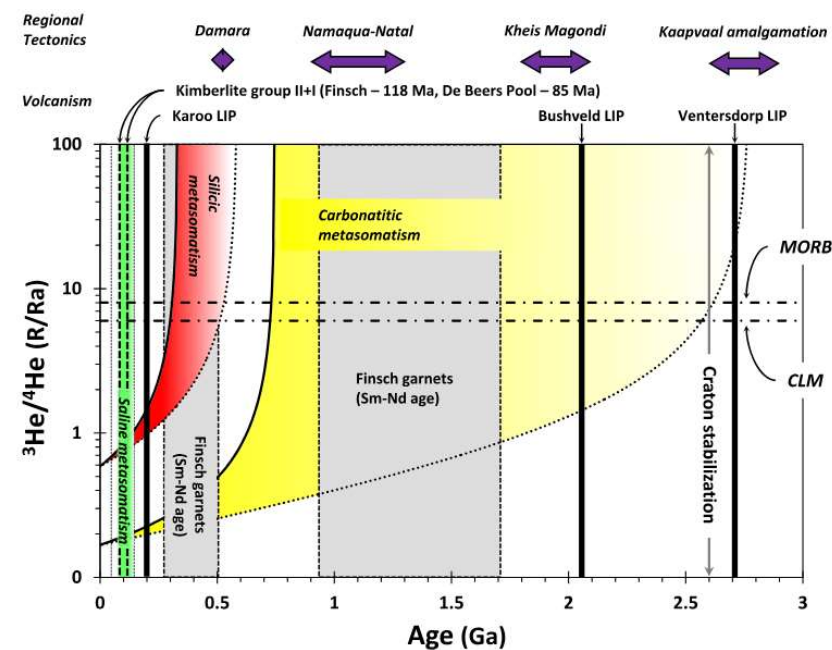


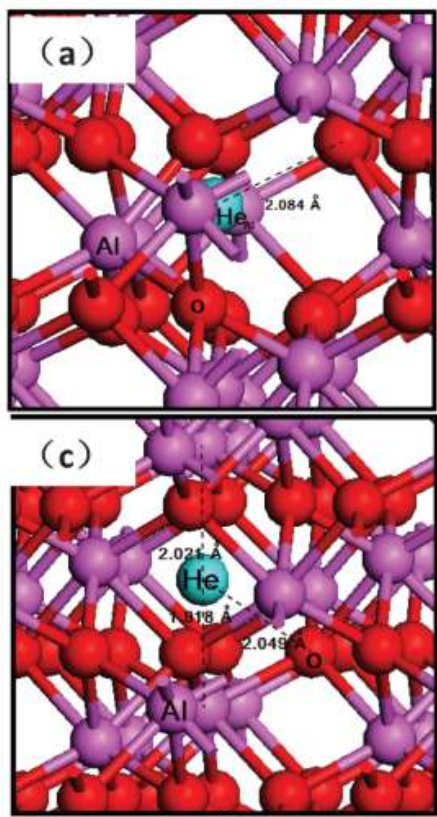
Fig. 6 Carbon- and water-rich (C-O-H) metasomatic events recorded by HDF-bearing diamonds in the southwest Kaapvaal cratonic lithosphere. U-Th-He geochronology of HDF-bearing diamonds from De Beers Pool and Finsch kimberlites reveal at least three episodes of different invading C-O-H fluid types affected 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 Finsch⁷⁴, 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 Myr⁷⁵, but a connection to older mantle metasomatic events and large surface deformational events are also possible.

Weiss et al. (2021)



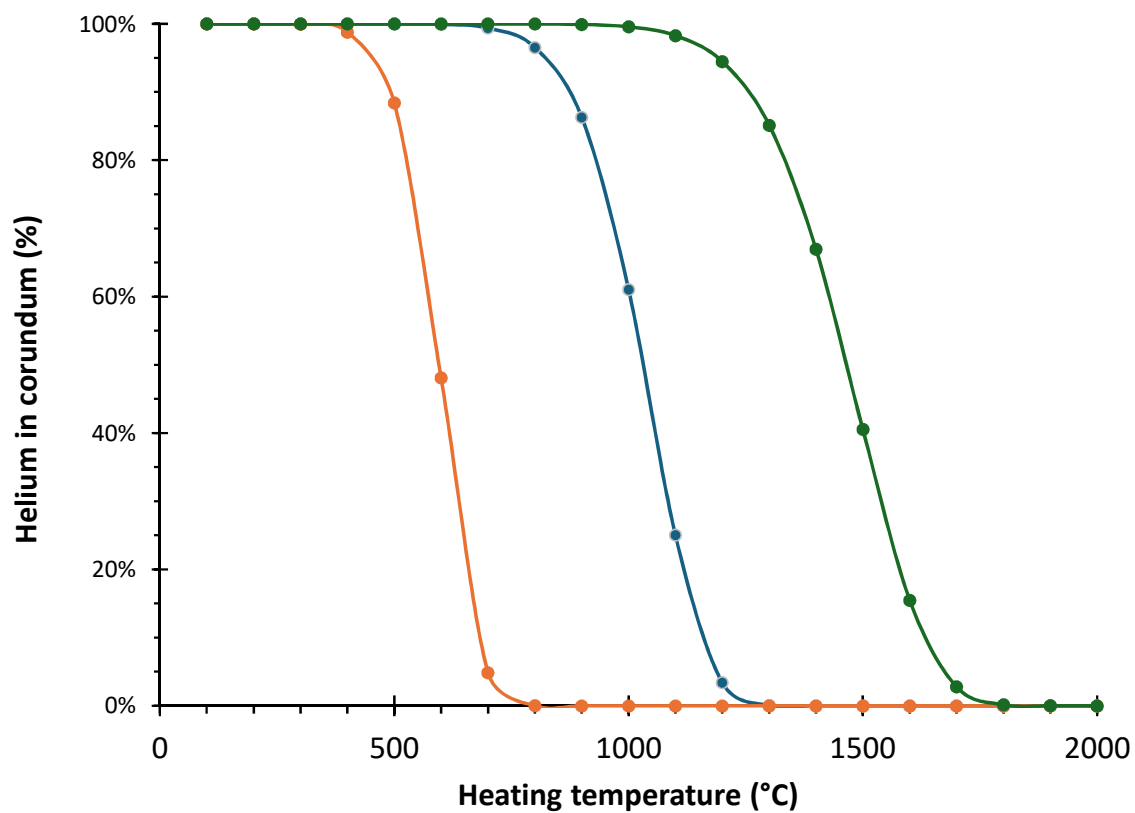
Helium in corundum

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



He in Al vacancy

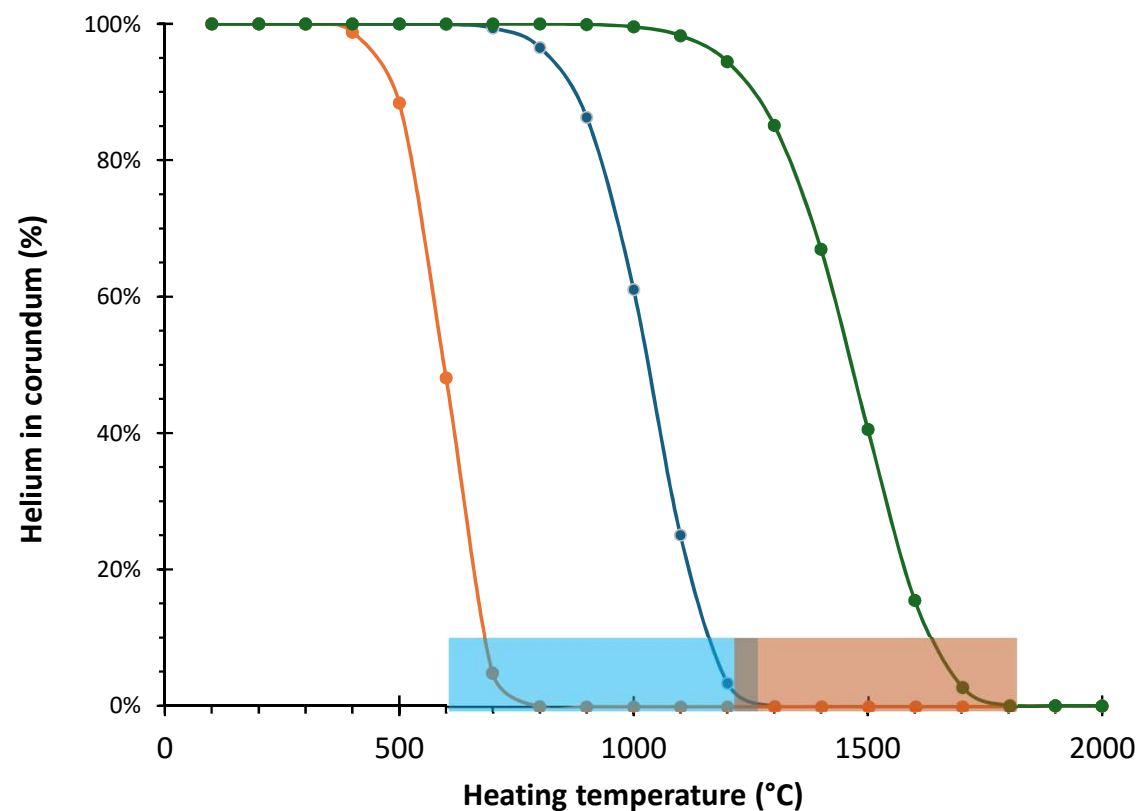
He in interstitial sites



Calculation for 1 mm crystal from the equation from Fechtig and Kalbitzer (1966) with D_0 $1.10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$ 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 ($\approx 600-1200^{\circ}\text{C}$)
- Modern heating (up to 1850°C)



Calculation for 1 mm crystal from the equation from Fechtig and Kalbitzer (1966) with D_0 $1.10^{-5} \text{ m}^2.\text{s}^{-1}$ 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 ?

- Is helium a good indication of heating ?

5 samples selected

(from Madagascar – 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 ?

5 samples selected

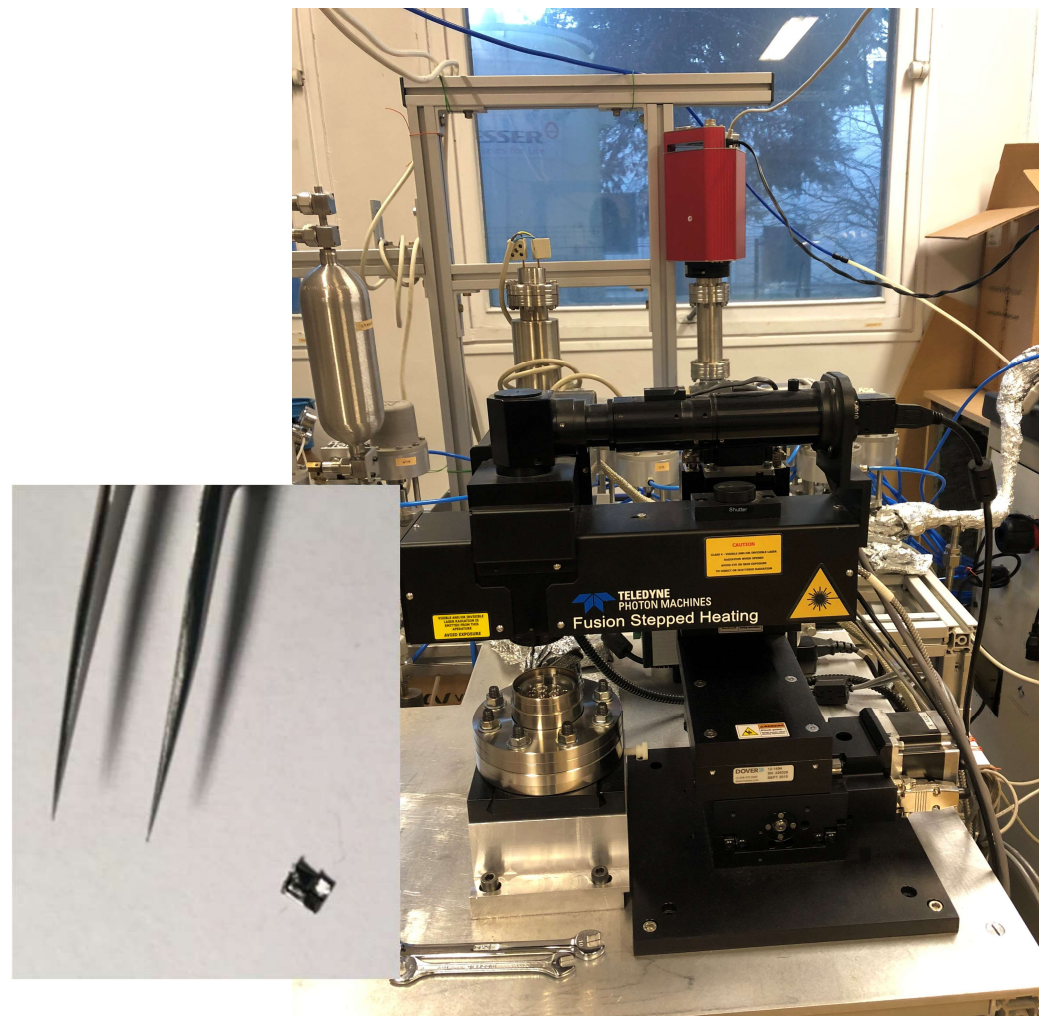
(from Madagascar – collected on the field)

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



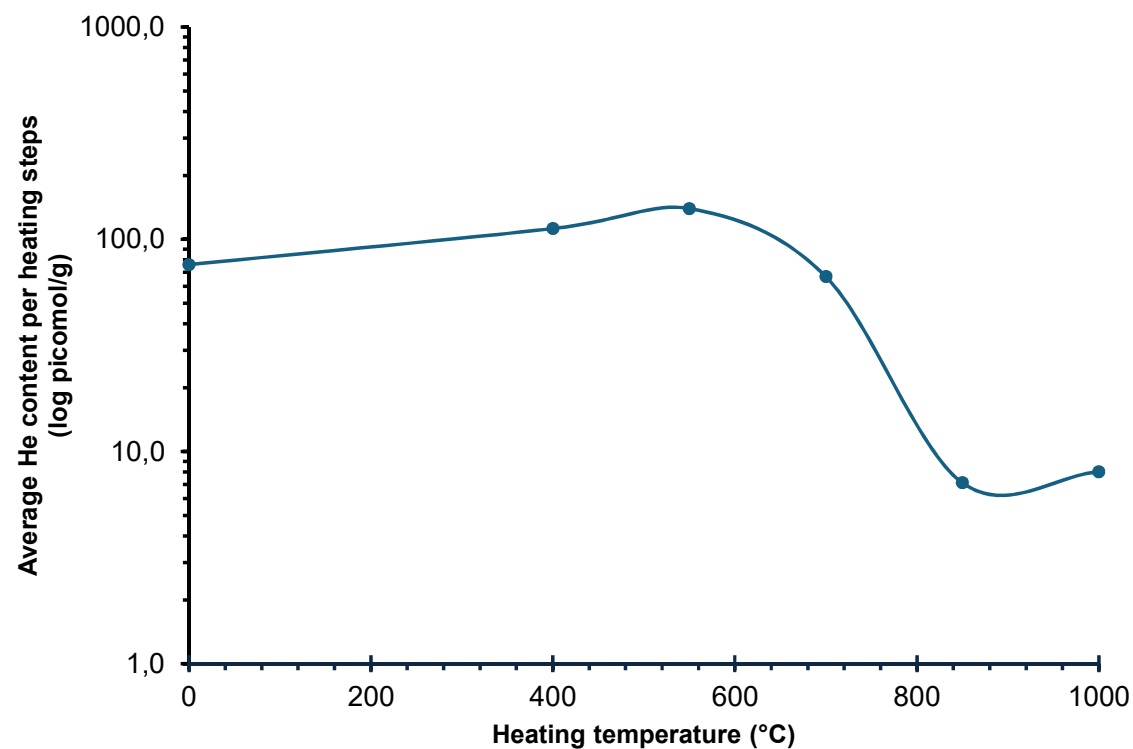
Helium in corundum : insights on heat treatment ?

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He diffused efficiently between 600-800 °C



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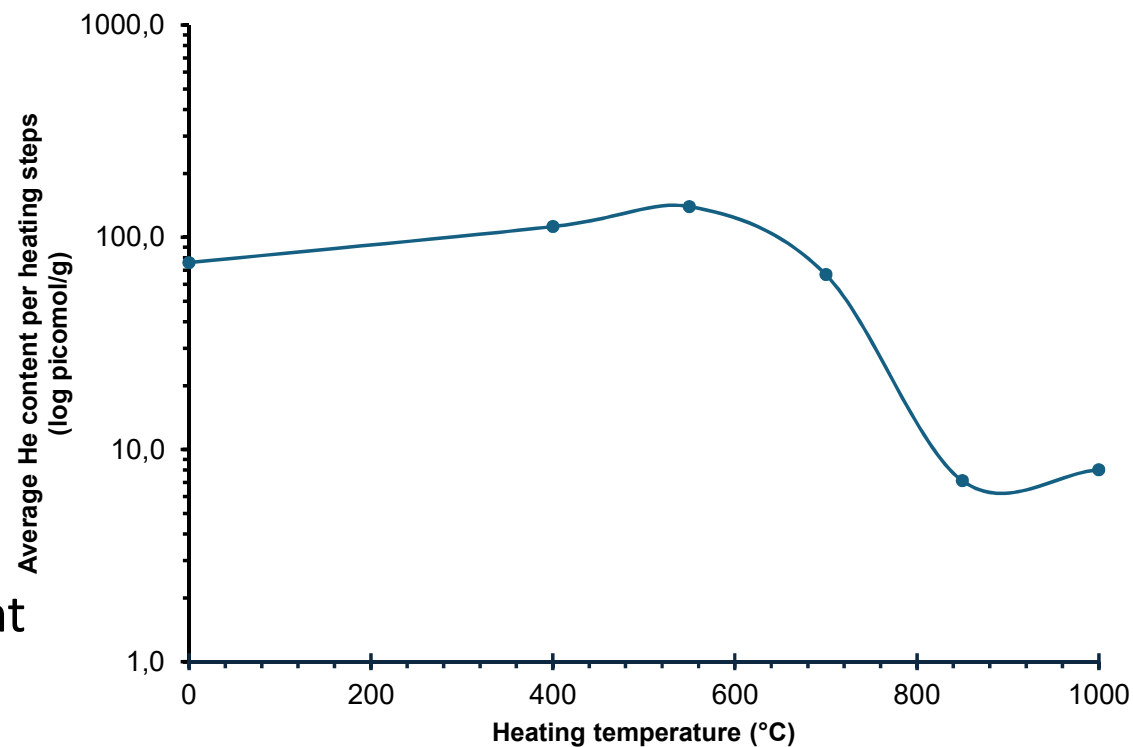
5 samples selected

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He diffused efficiently between 600-800 °C

But :

Heterogeneity of sample in term of He content



Helium content in unheated samples

Samples	A		B		C		D		E	
	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 ?

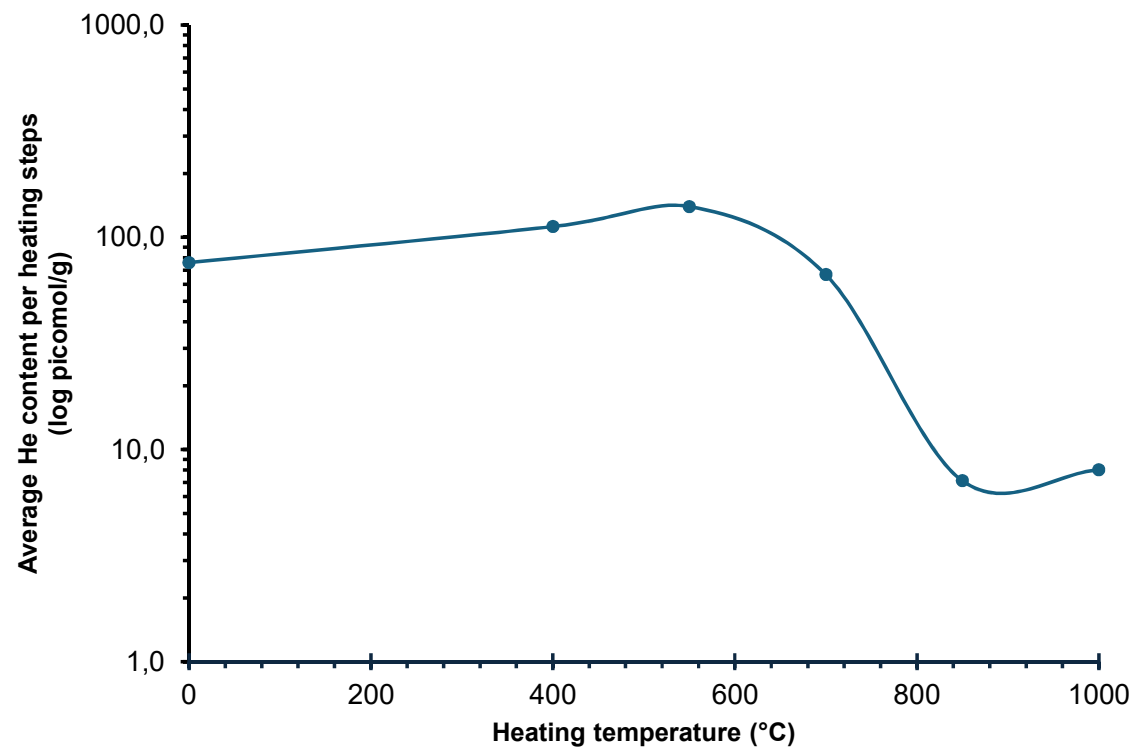
5 samples selected

(from Madagascar – collected on the field)

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

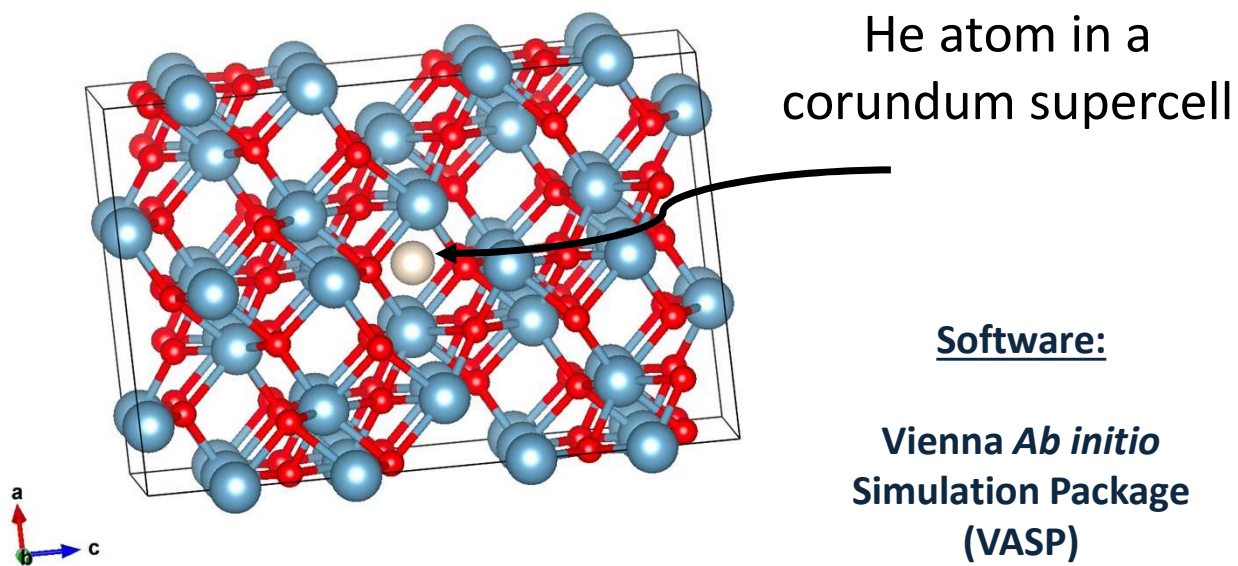
Helium in corundum : insights on heat treatment ?

- Is helium a good indication of heating ?

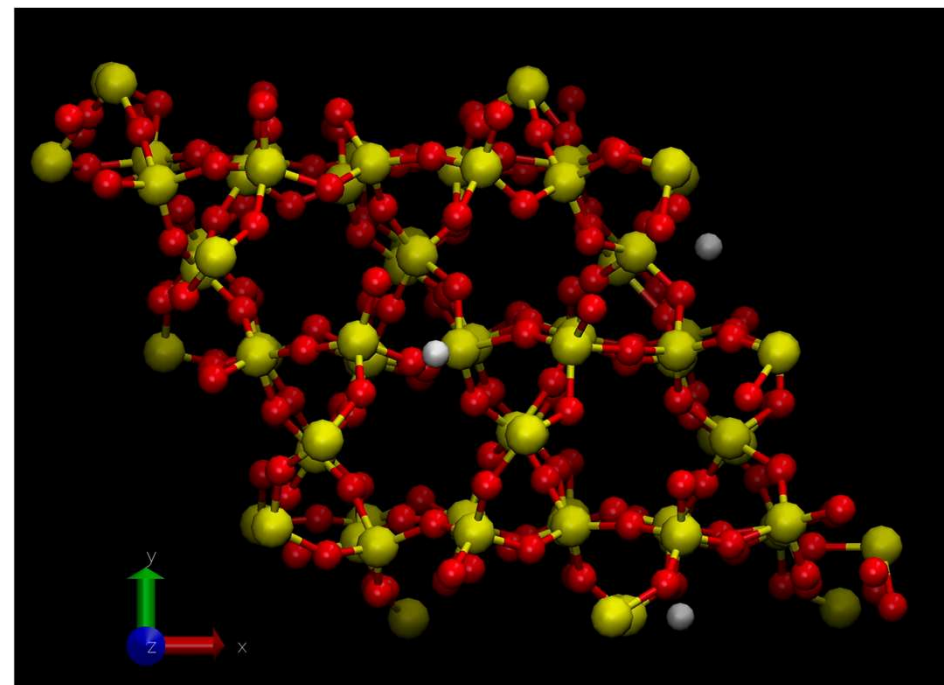
Next step: Measurements of He diffusivity in corundum from the same piece of sample (correcting intra-sample heterogeneity)

Modelling He diffusion in corundum

Collaboration with S. Figowy (Paris-Saclay University)



Example: He (interstitial point defect) in quartz



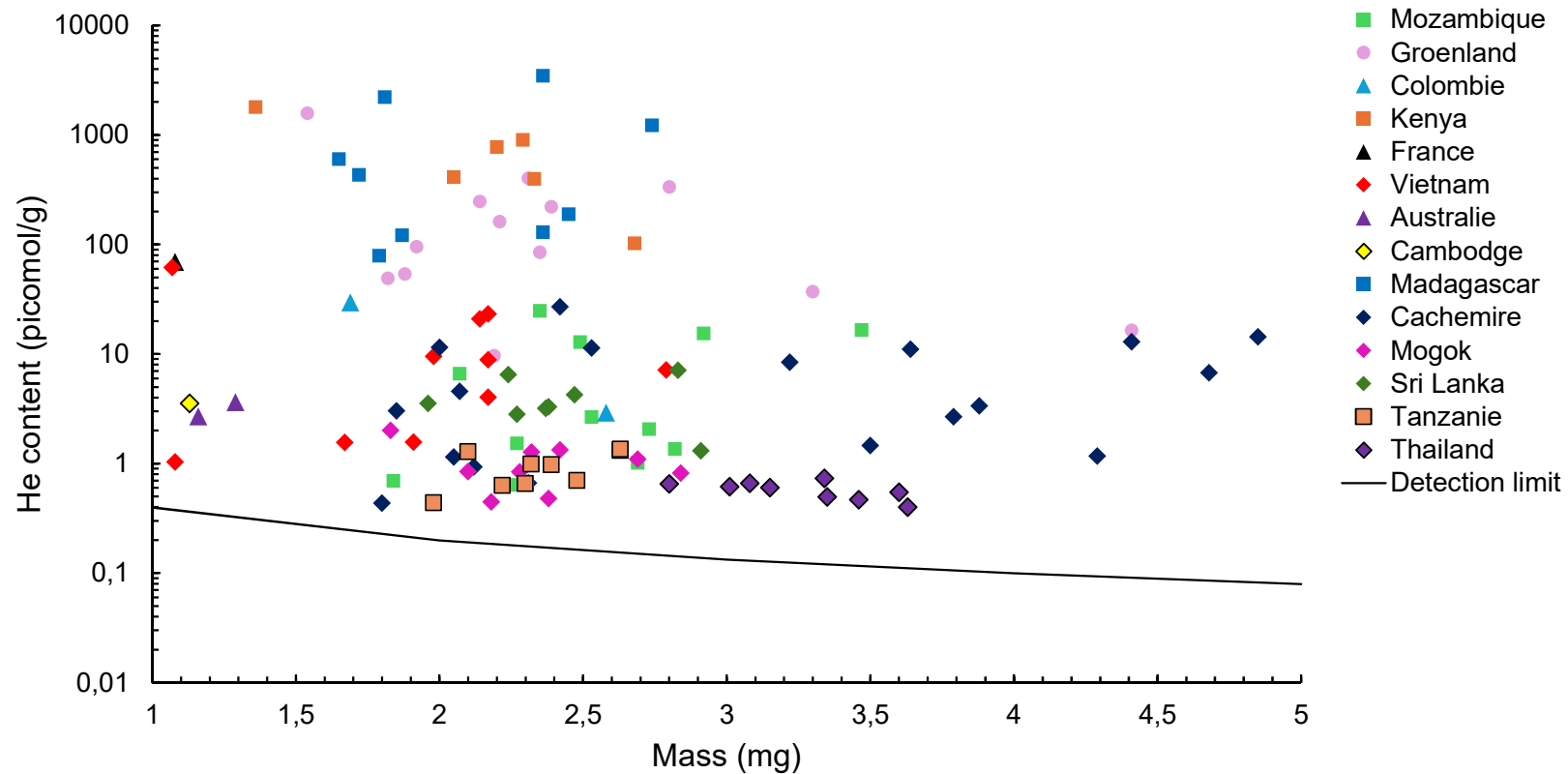


Helium in corundum : insights on formation ?

- Is helium could inform us about geology ?

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

By origin

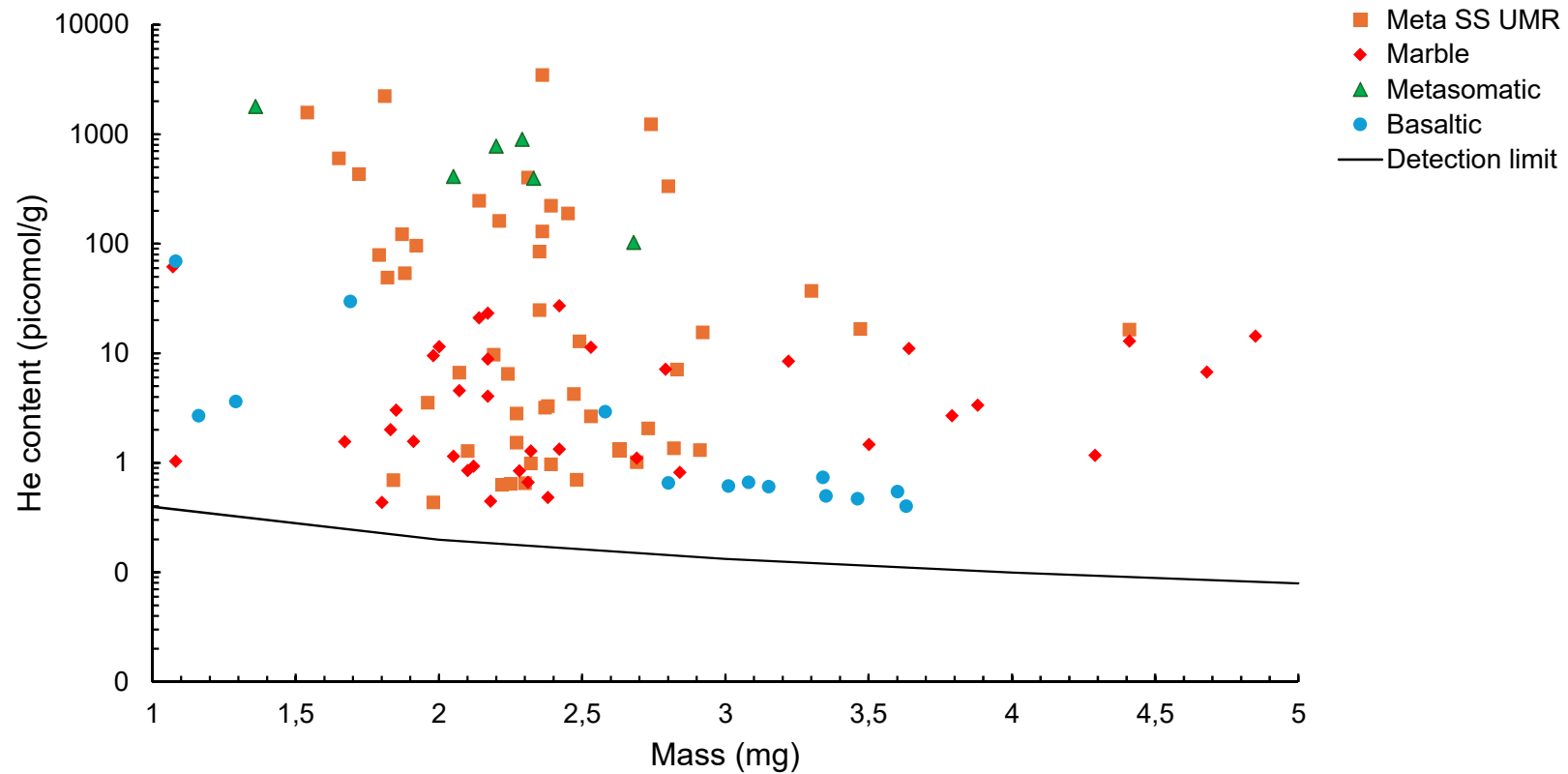


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By geology



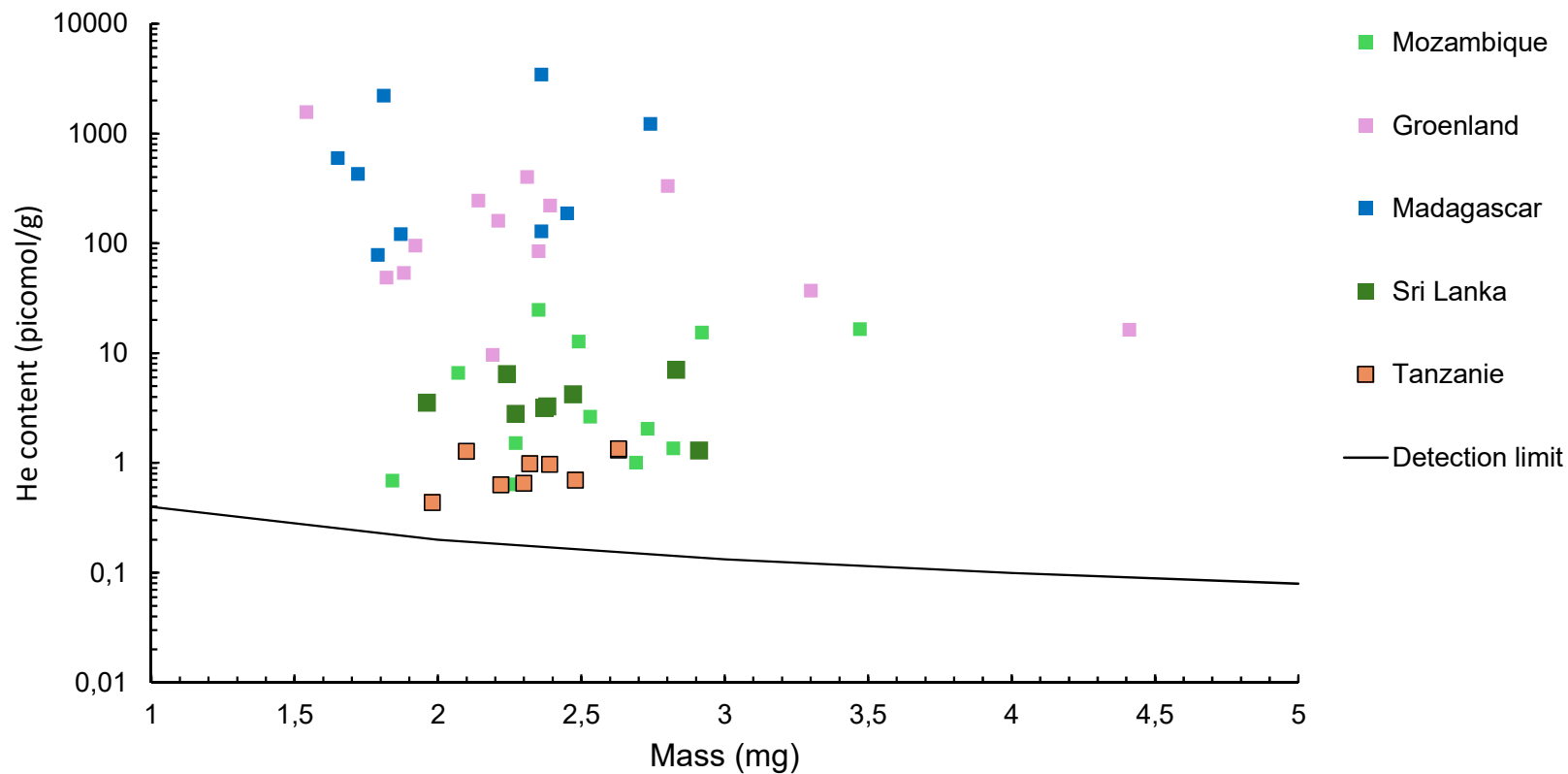


Helium in corundum : insights on formation ?

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

By origin
(Meta SS)

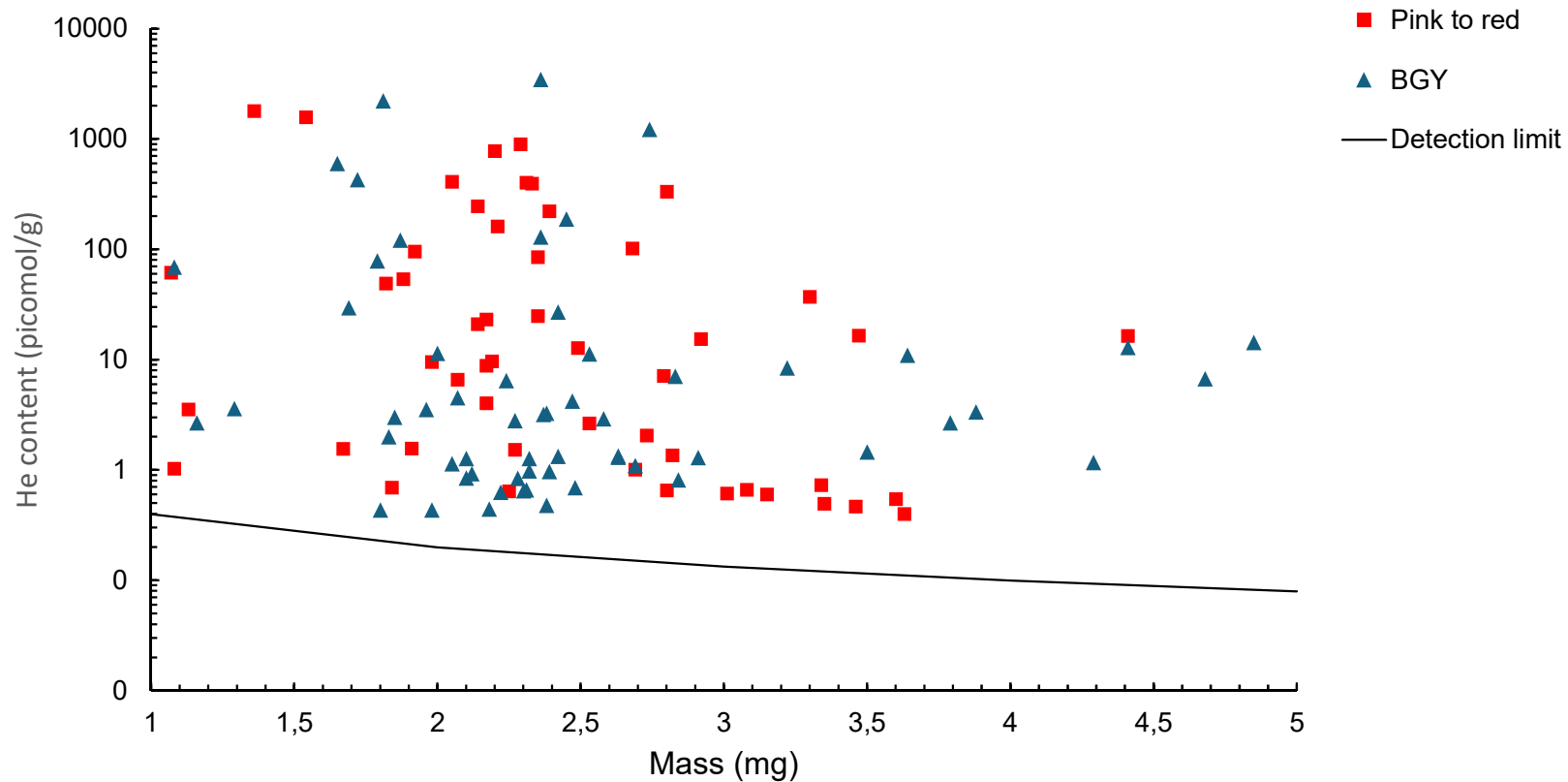


Helium in corundum : insights on formation ?

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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

Références

- 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



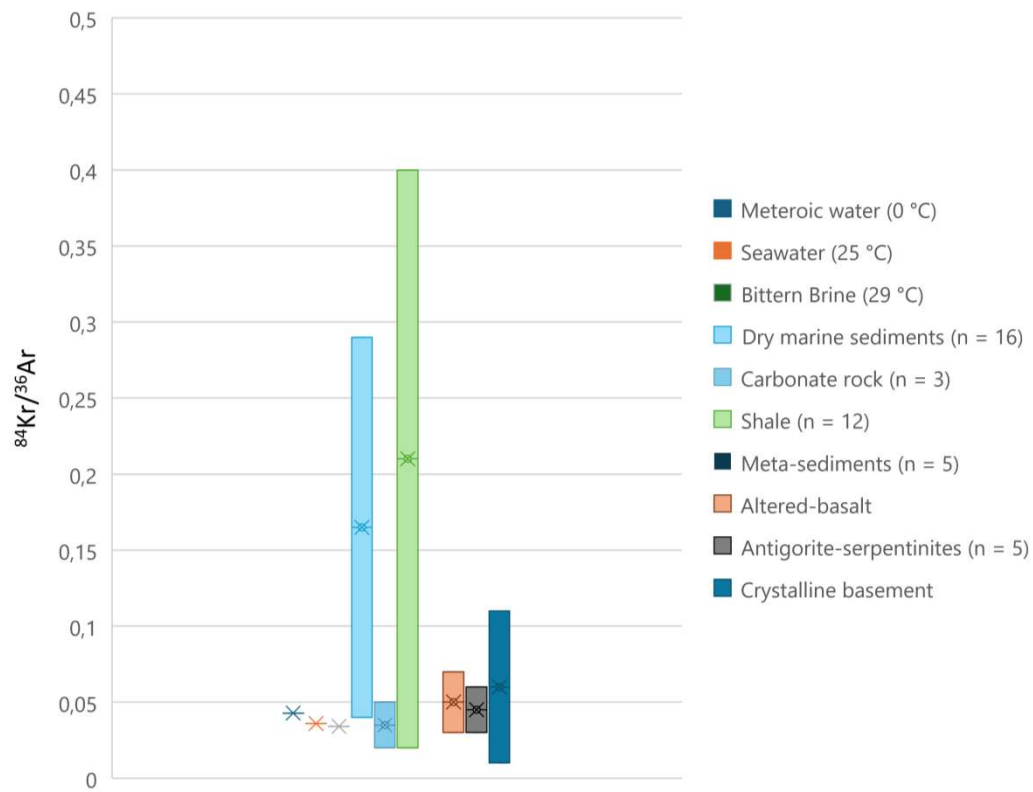
Thanks for your attention !



Noble Gas in Geology

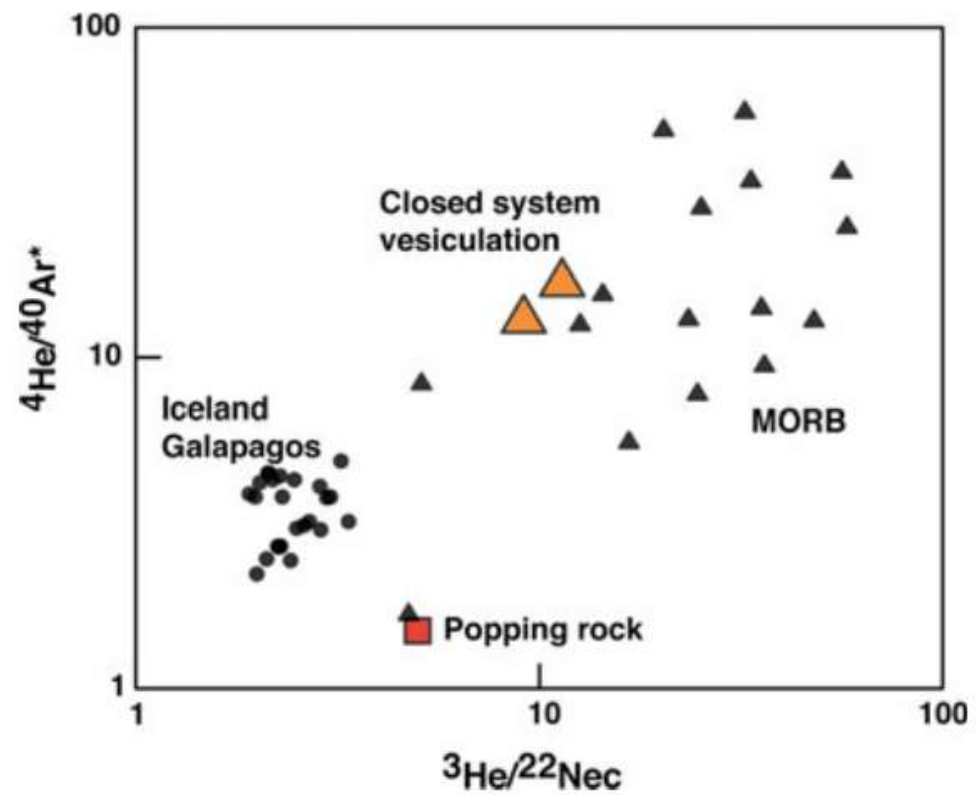
- Elements with filled outer electrons shells, no chemical binding

Noble gases in fluid inclusions as tracers of fluid origin



Data compiled from Burnard (2013)

Noble gases as tracers of magmatic processes



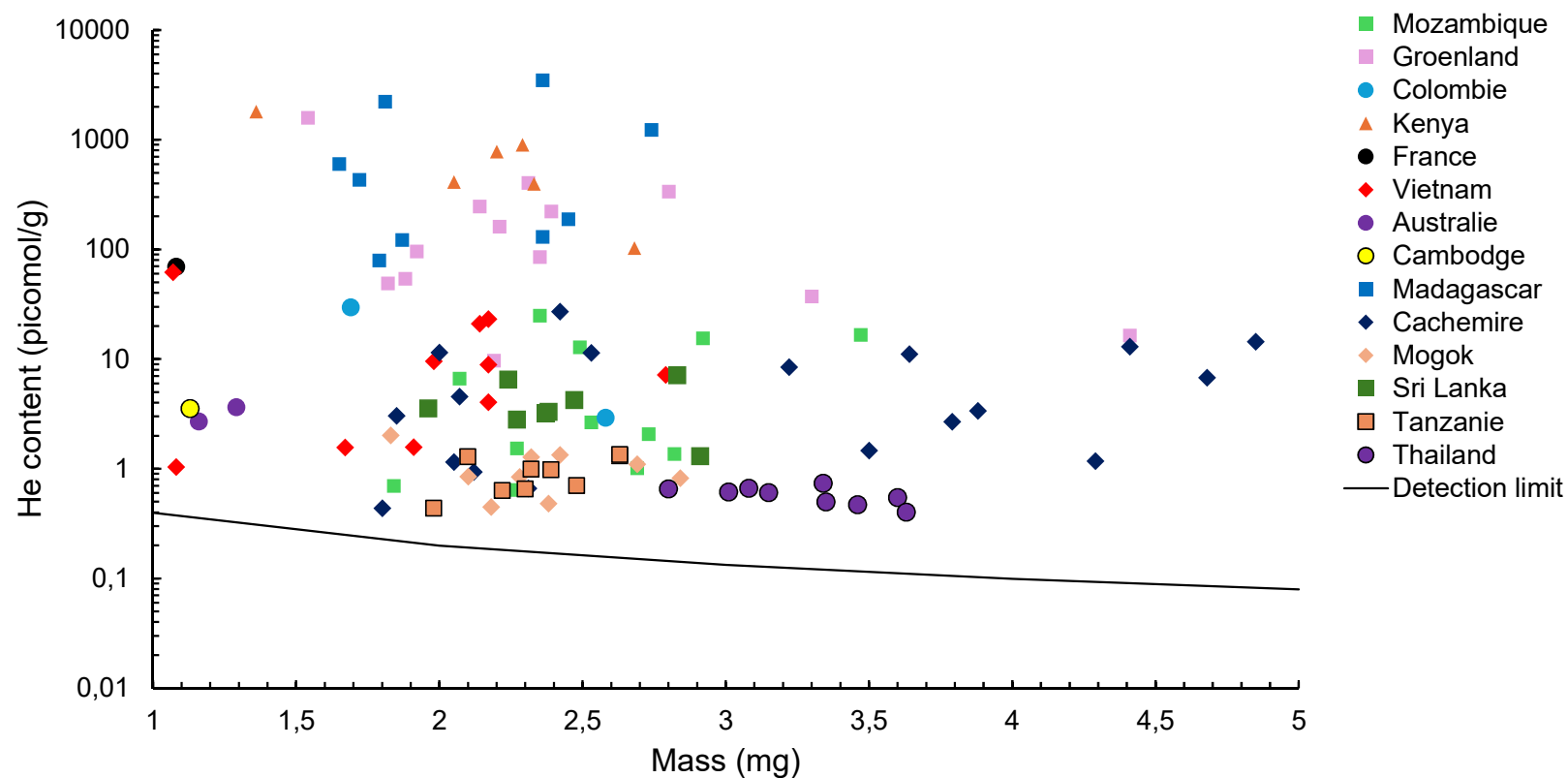
Moreira & Kurz (2013)



Helium in corundum : insights on formation ?

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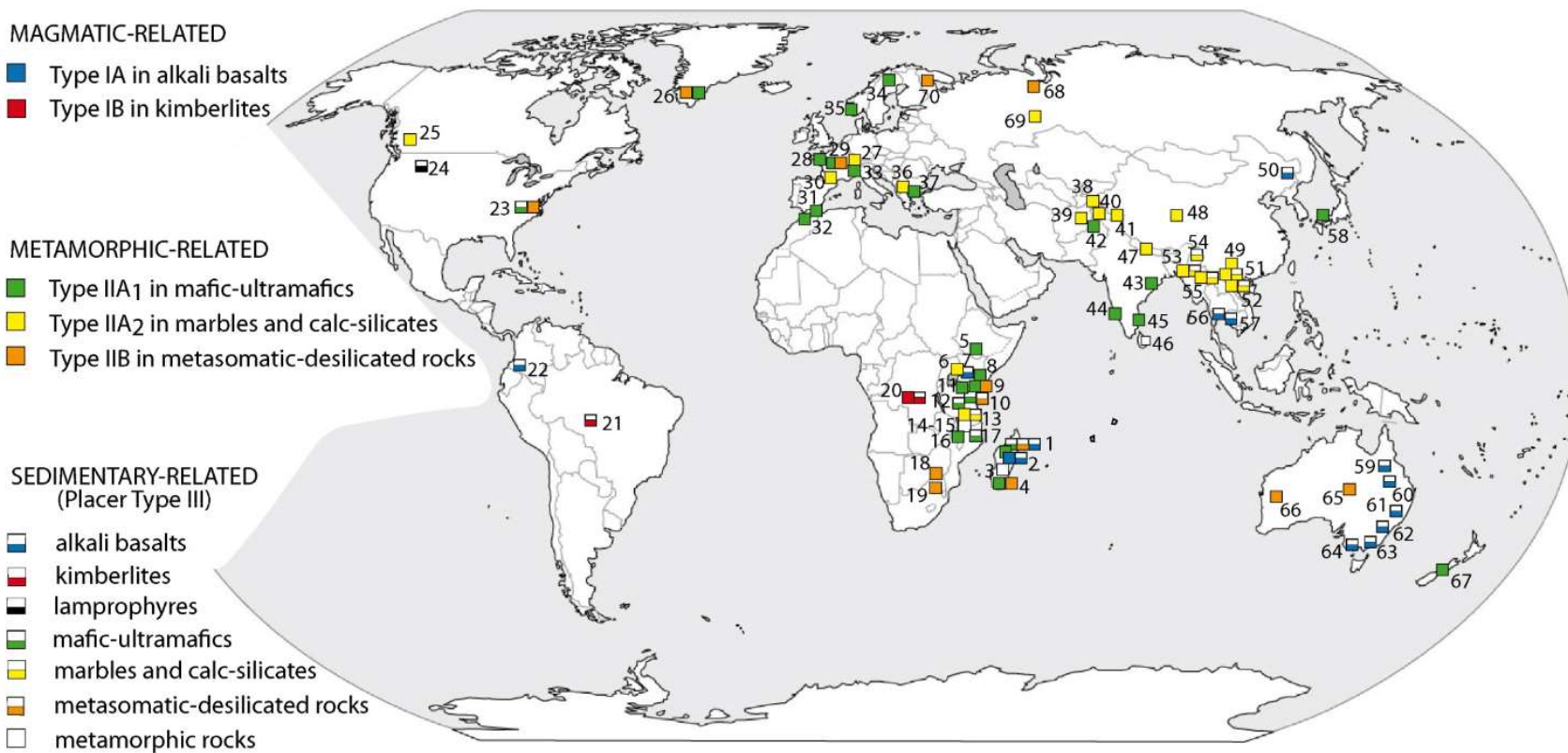
116 analysis on XX samples selected from 14 origins (collected from the field).





Géologie des corindons

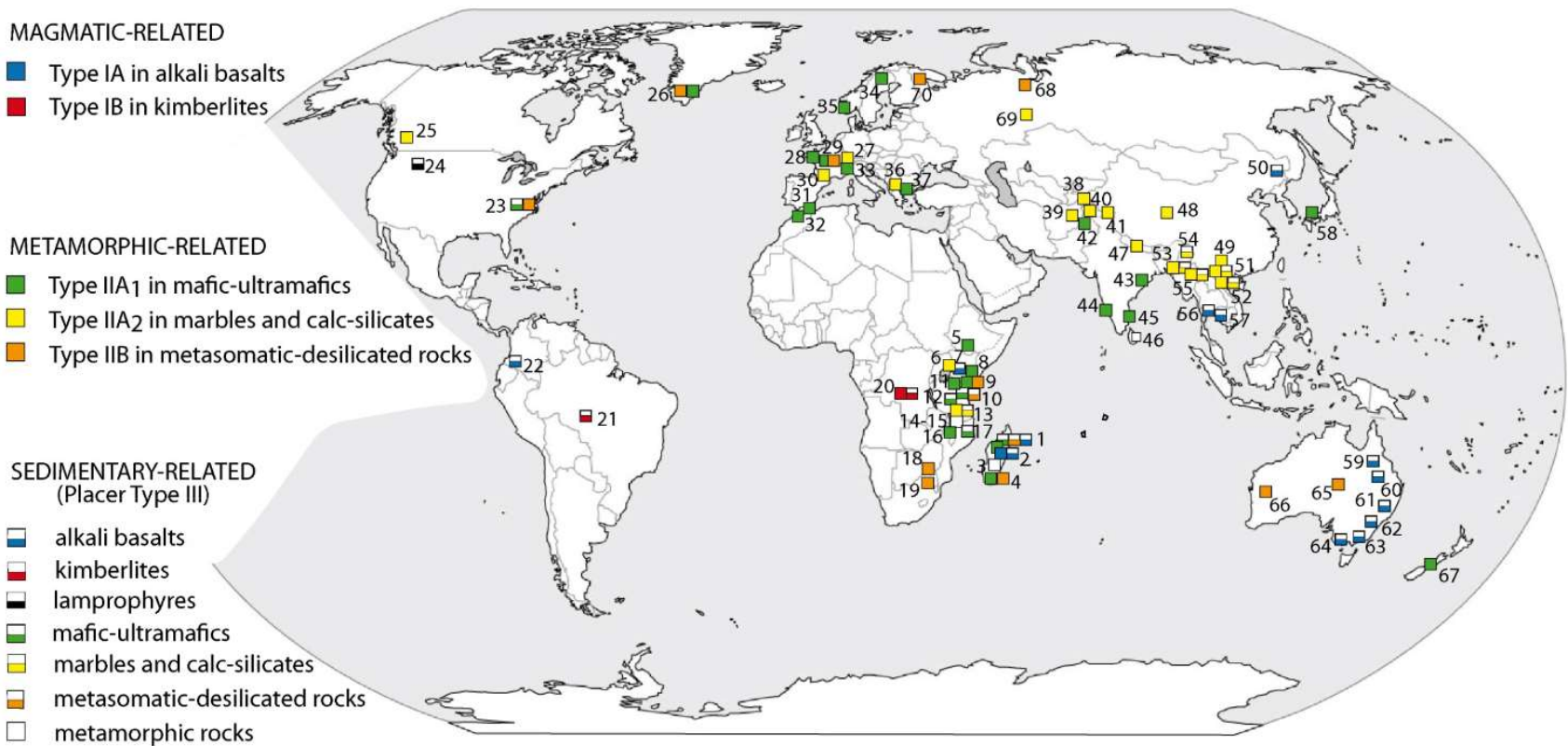
- Plusieurs classifications existent, sur les mêmes bases





Géologie des corindons

- Plusieurs classifications existent, sur les mêmes bases





Géologie des corindons

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

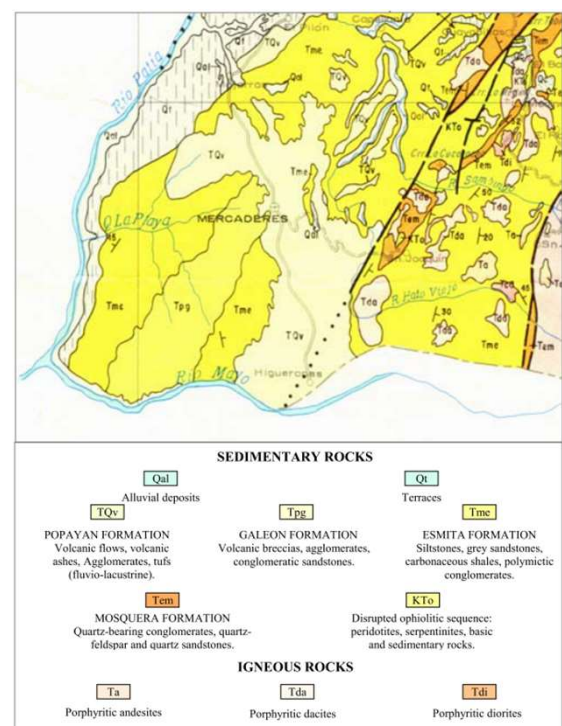
Géologie + Inclusions

=
Volcanique

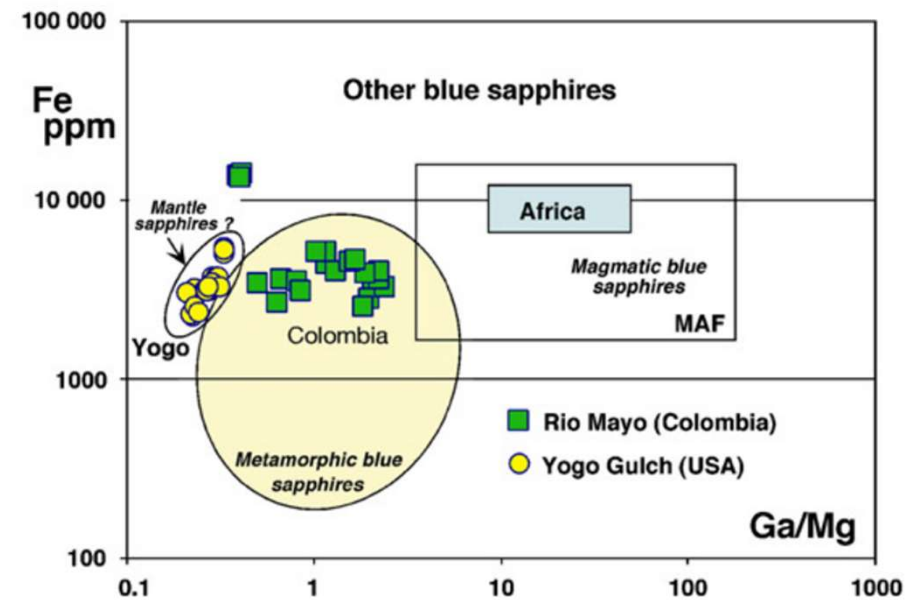
VS

Géochimie

=
Métamorphique



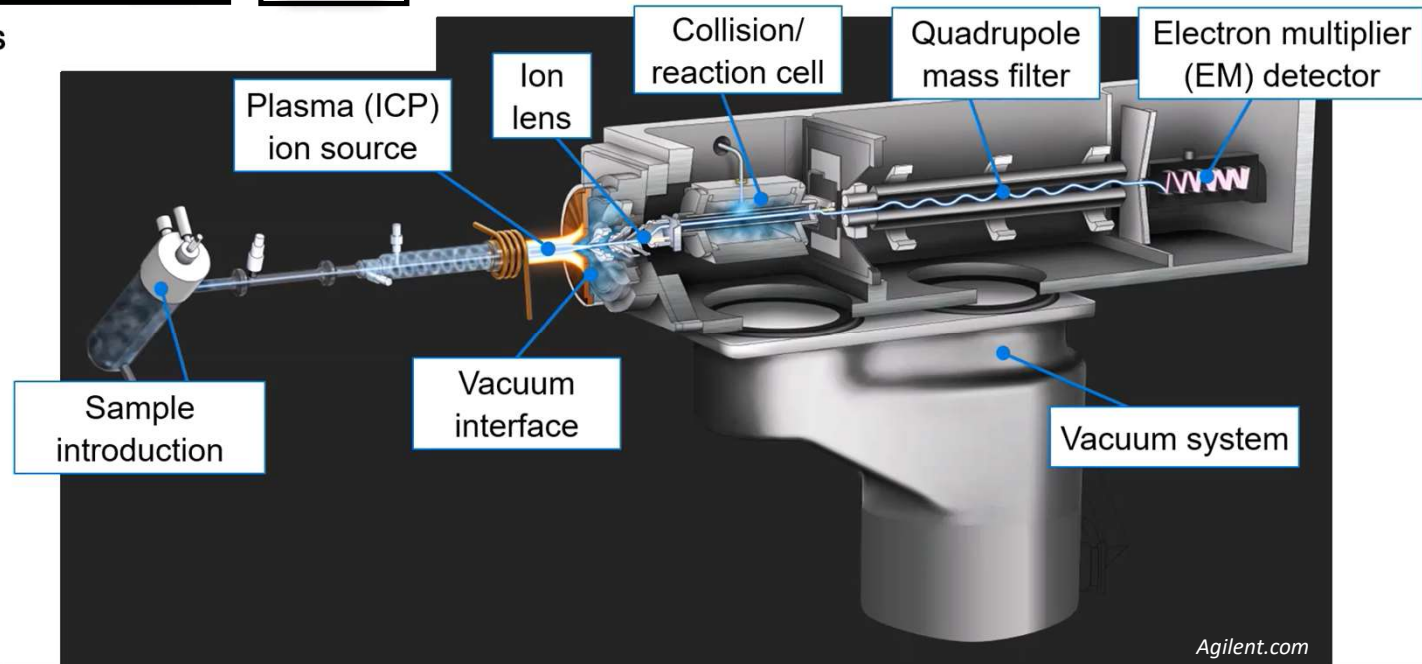
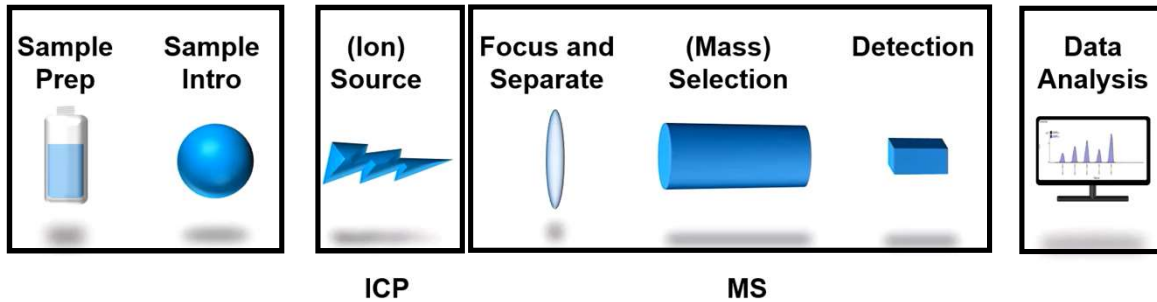
Marin et Paris (1979)



Peucat et al. (2007)

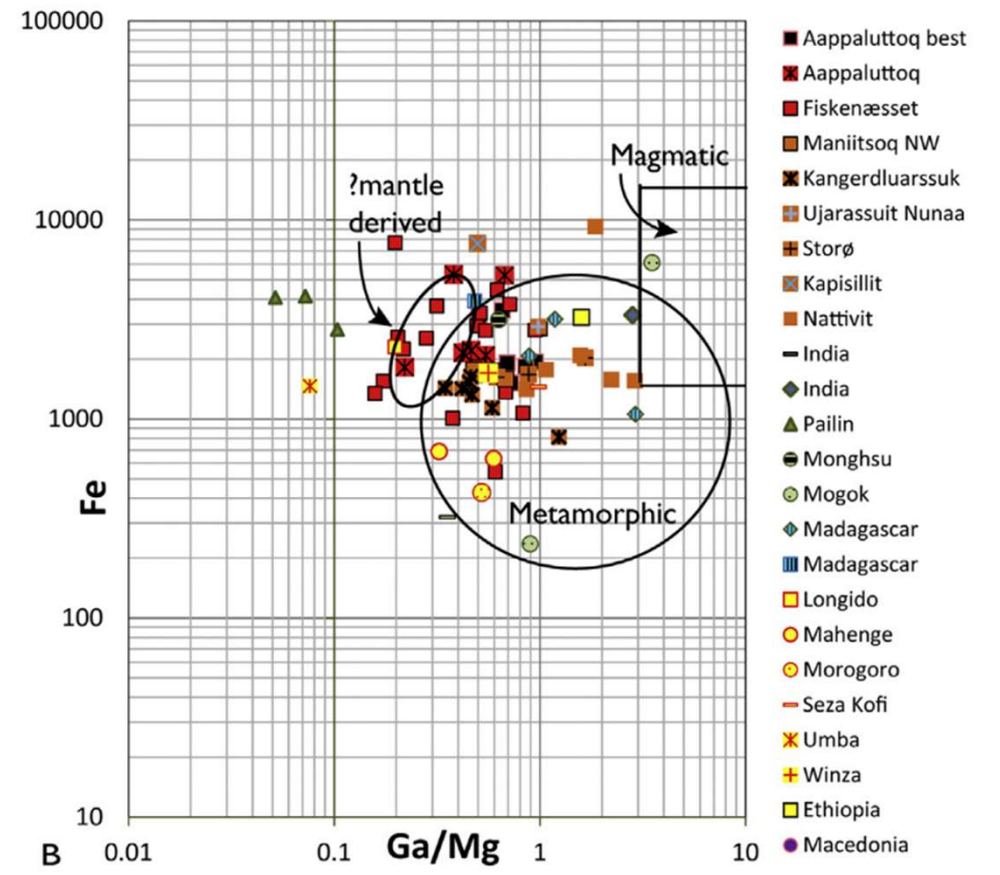
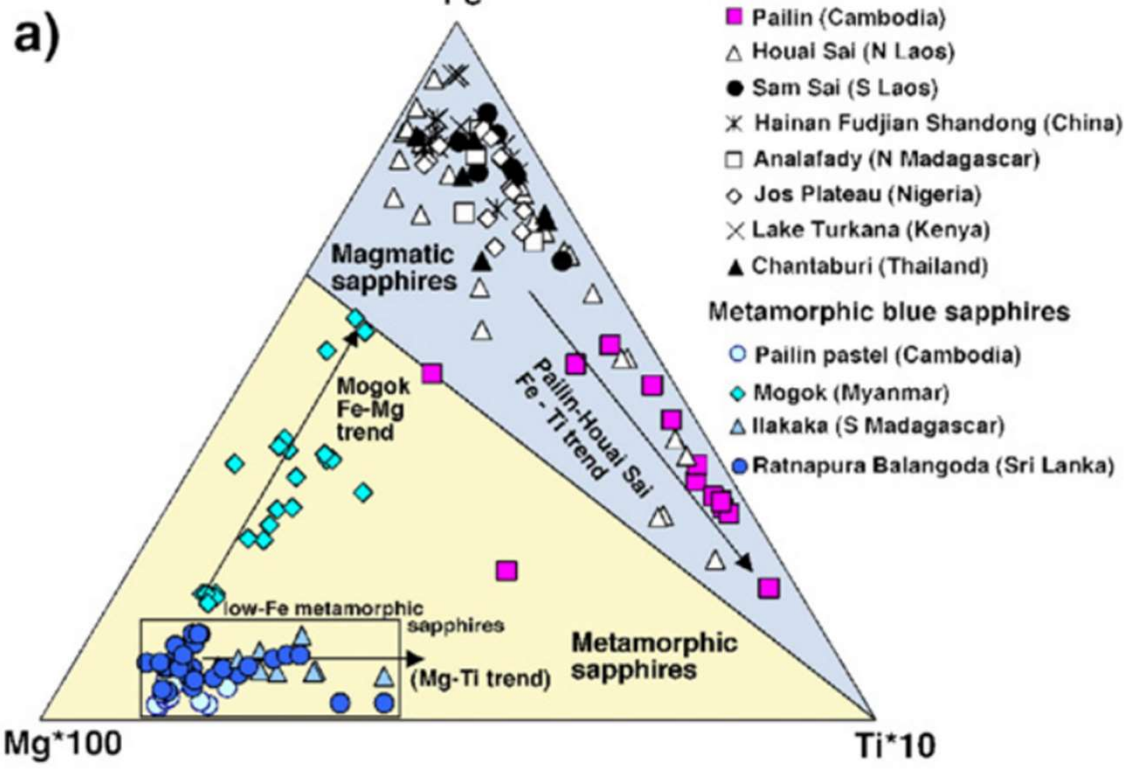
Géochimie des corindons

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



Géochimie des corindons

- Assez hétérogène

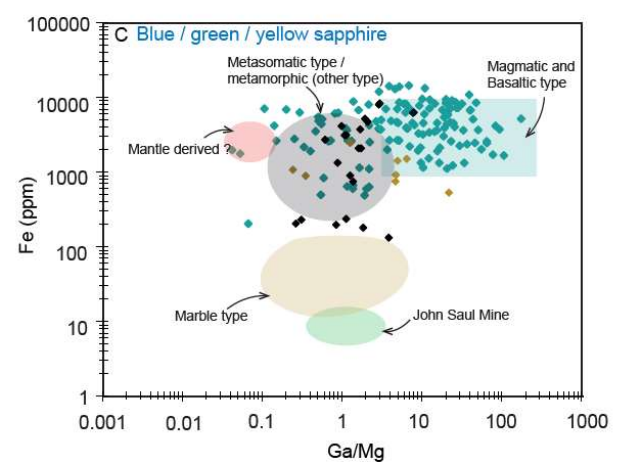
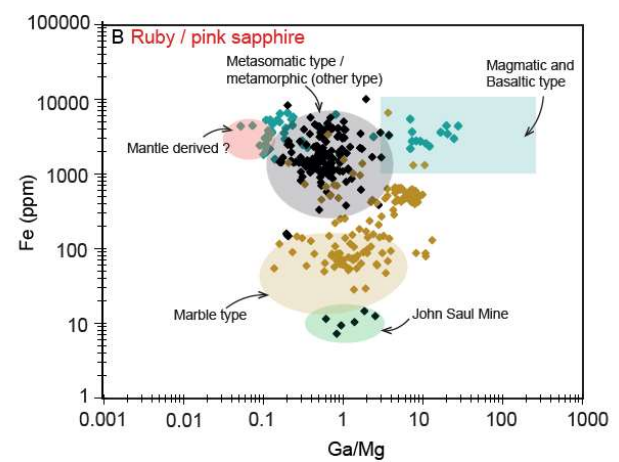
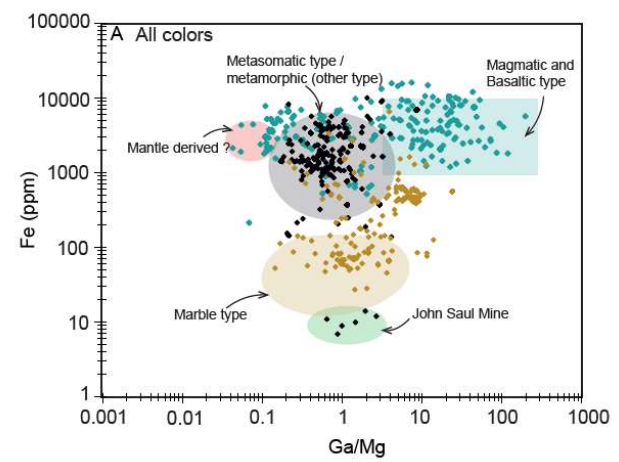
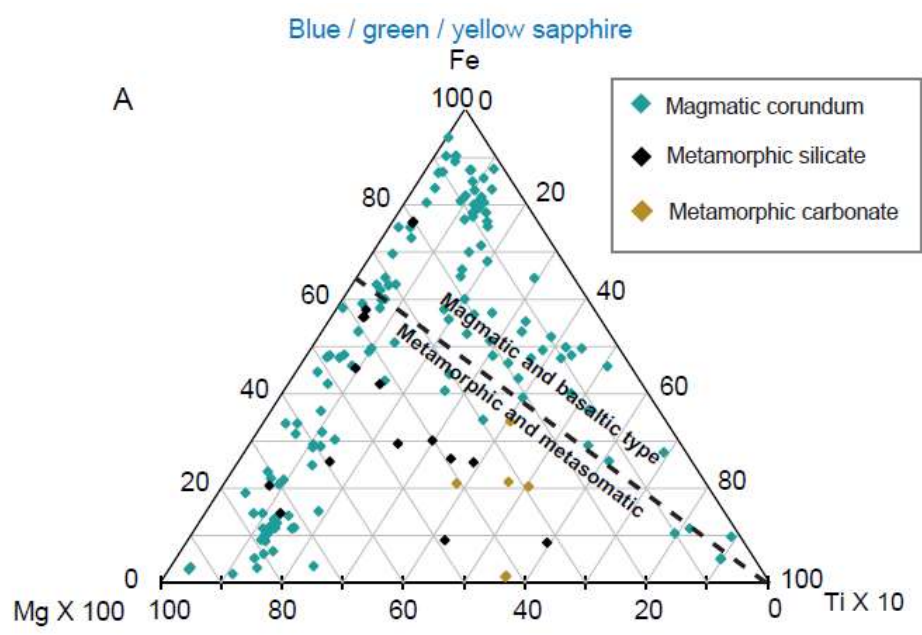


Peucat at al. (2007)

Keulen at al. (2020)

Géochimie des corindons

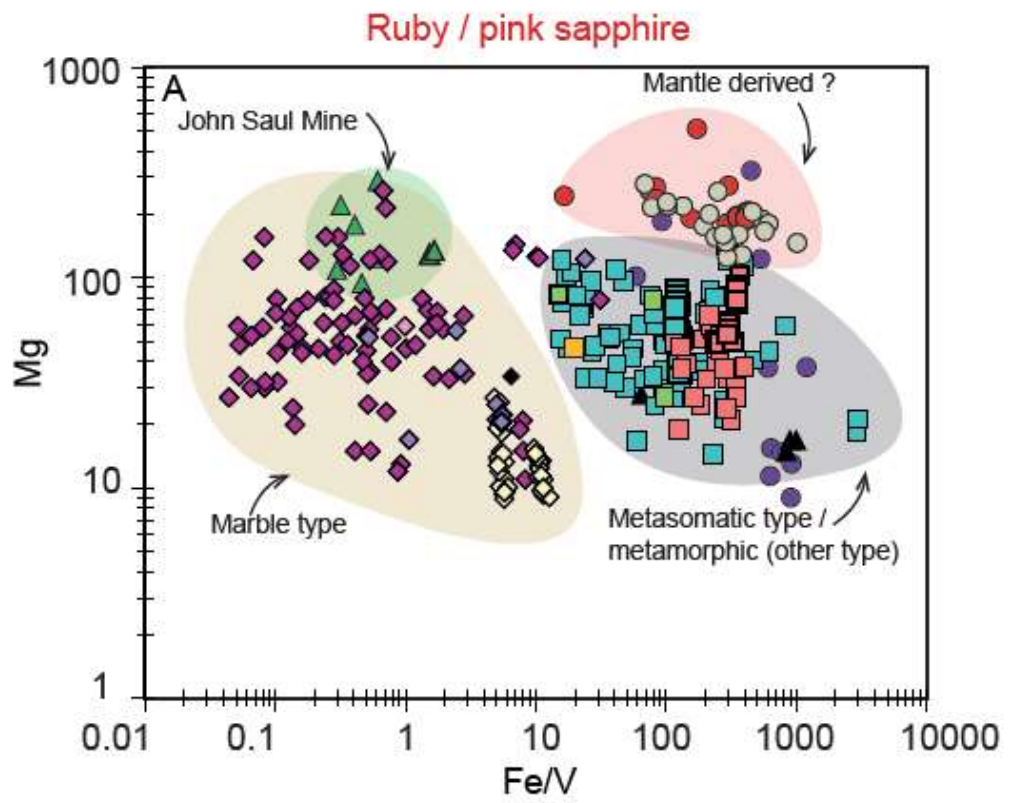
- Assez hétérogène



Corre at al. soumis

🧪 Géochimie des corindons

- Assez hétérogène



Geological Origin

- Xenocryst in basalt
- △ Metasomatic M-UMR
- Metamorphic ss M-UMR
- ◇ Metamorphic (marble type)

Geographical Origin

● Afghanistan	● Australia	● Cambodia
● Greece	● Greenland	● India
● Kenya	● Madagascar	● Mozambique
● Myanmar	● Tadjikistan	● Thailand
● Vietnam		

Corre et al. soumis