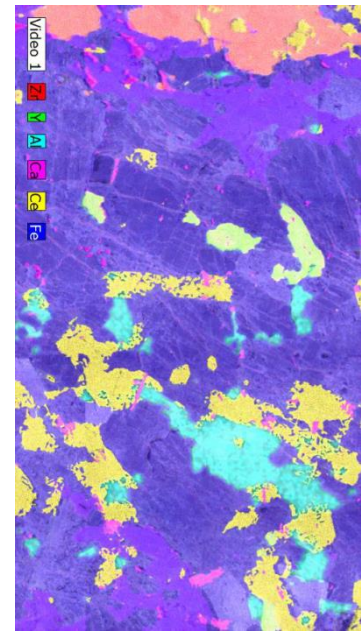
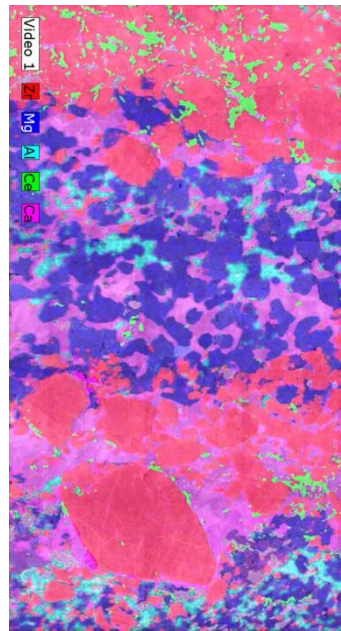


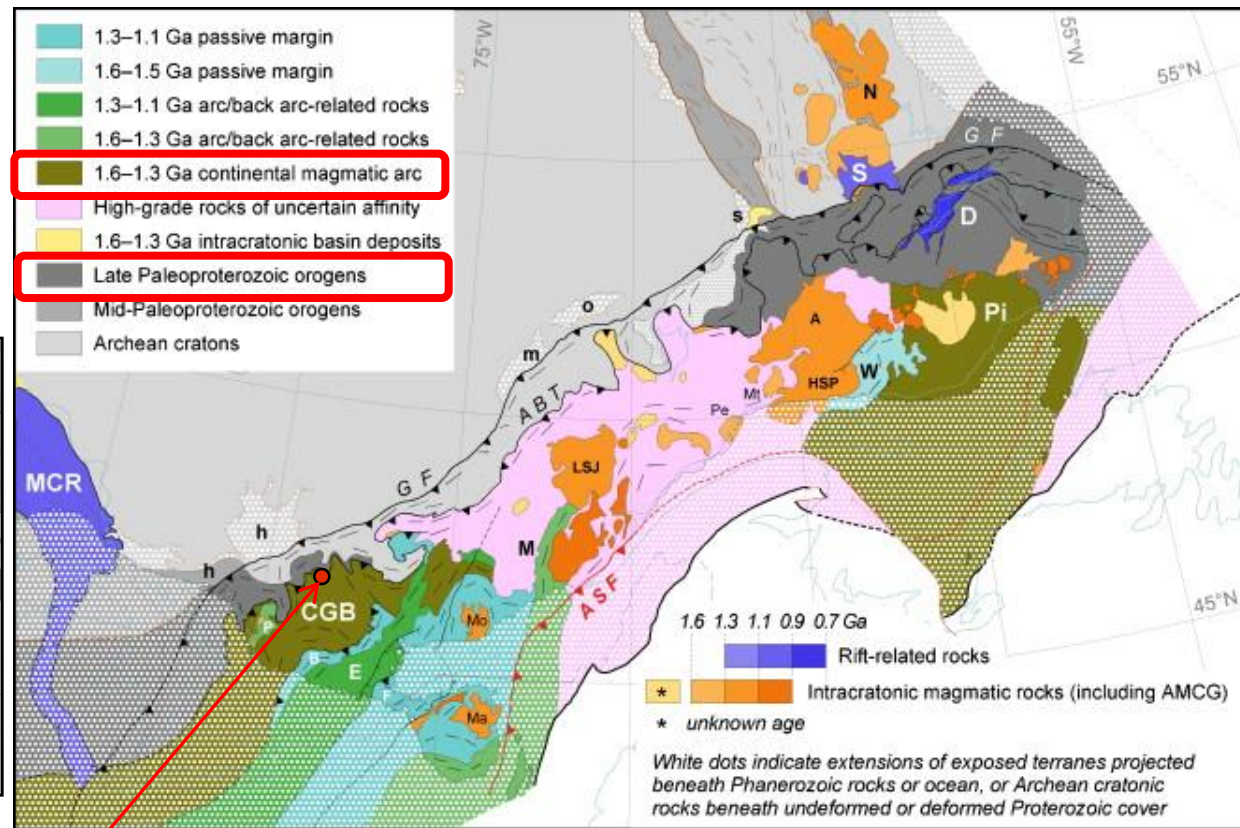
Le gisement de terres rares de Kipawa

Marc Constantin

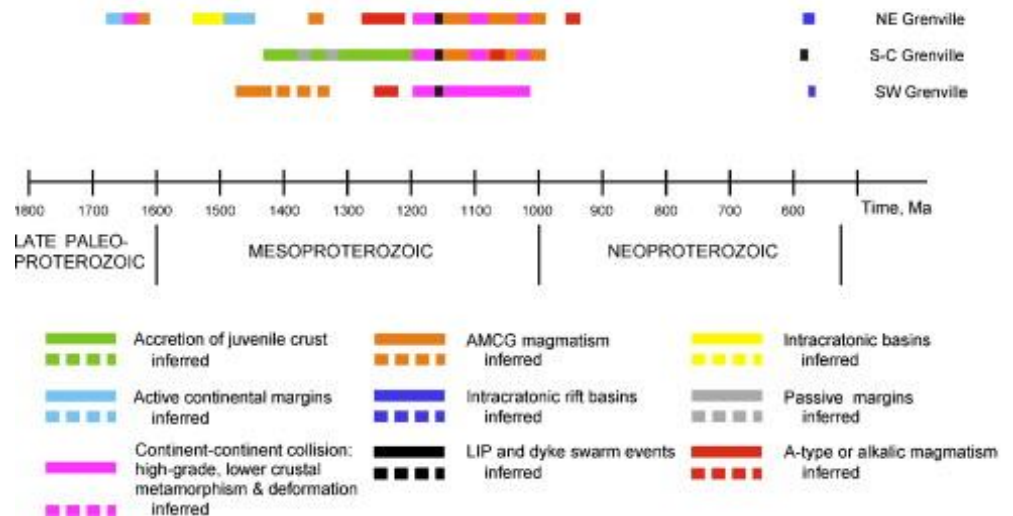
Université Laval



Paleotectonic characterization of terranes in the Grenville Province

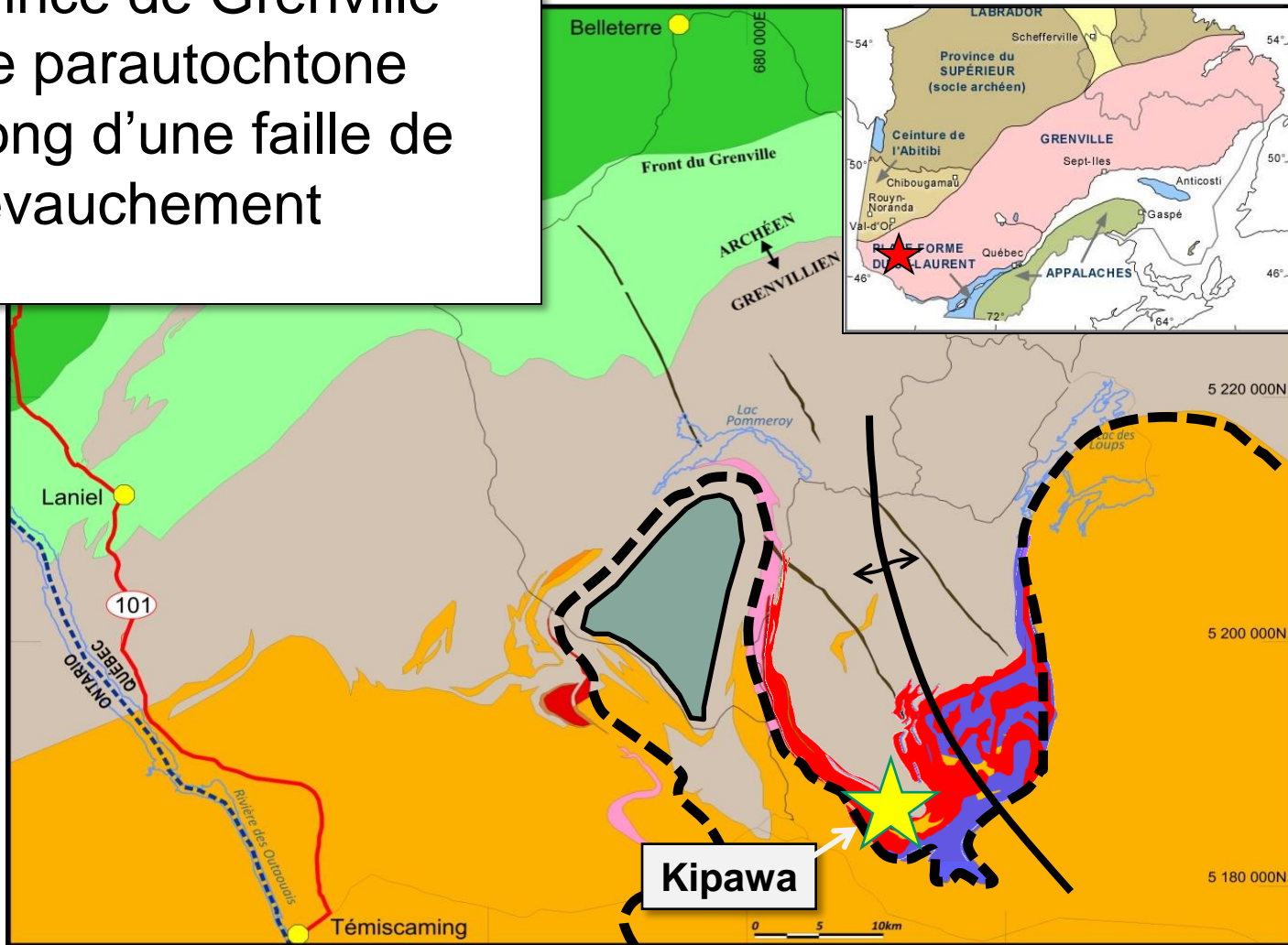


Kipawa syenite complex

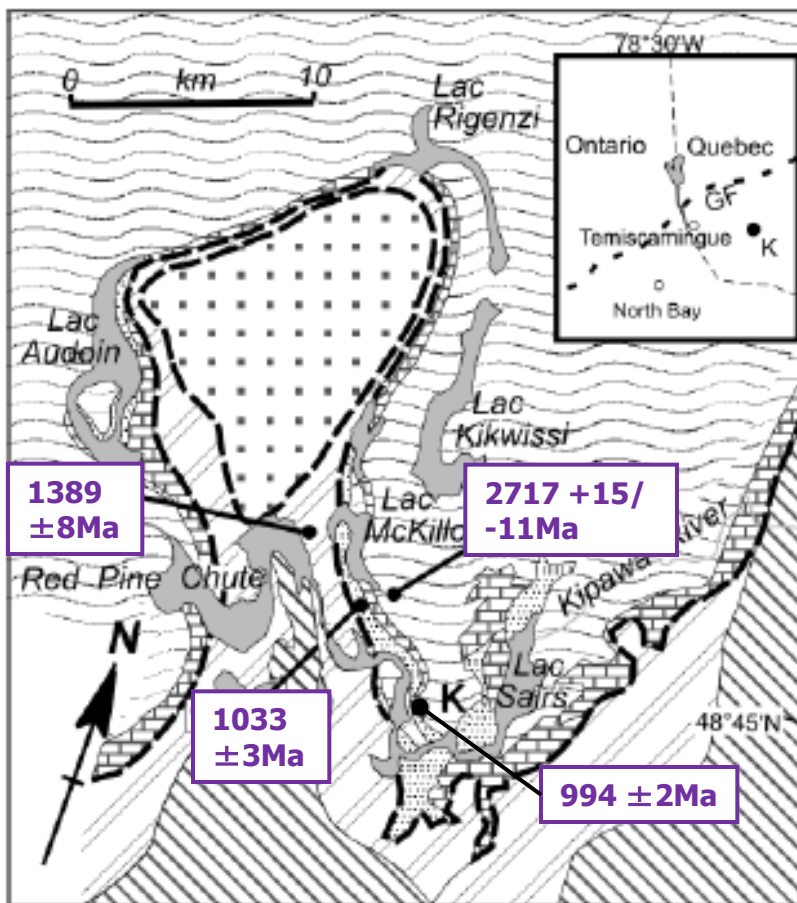


GISEMENT DE KIPAWA – Localisation

- Province de Grenville
- Zone parautochtone
- Le long d'une faille de chevauchement



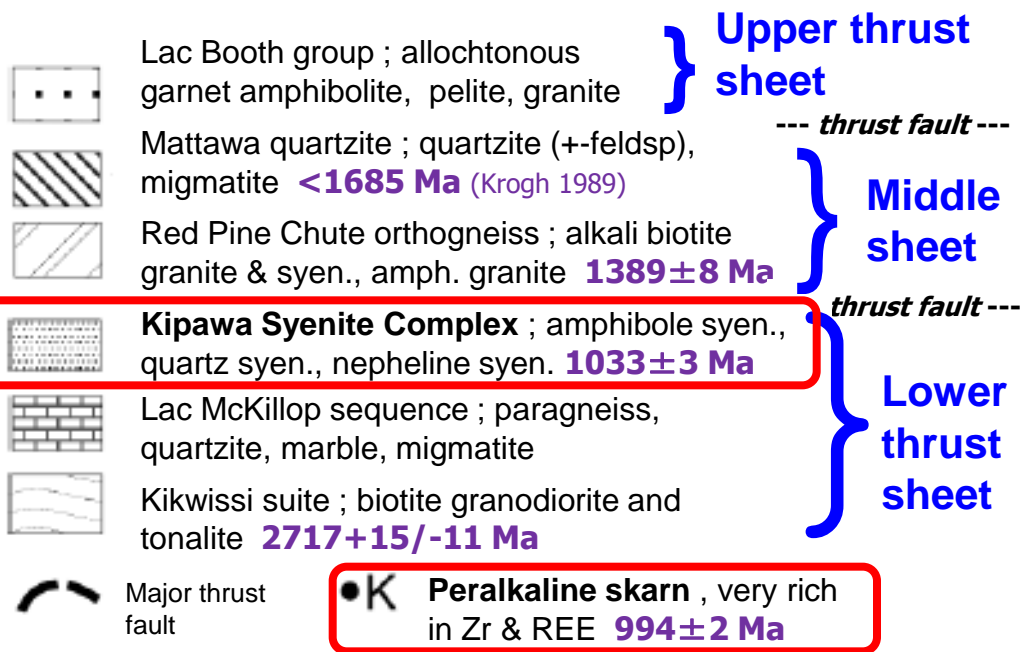
Simplified geological map of the Kipawa region



Location of U-Pb dating of zircon (TIMS and SHRIMP analyses)

Kipawa Syenite Complex ; amphibole syenite, quartz syenite, nepheline syenite, peralkaline granite.

Sheet-like body from ~200 m thick that can be traced along strike for a distance of ~ 100 km



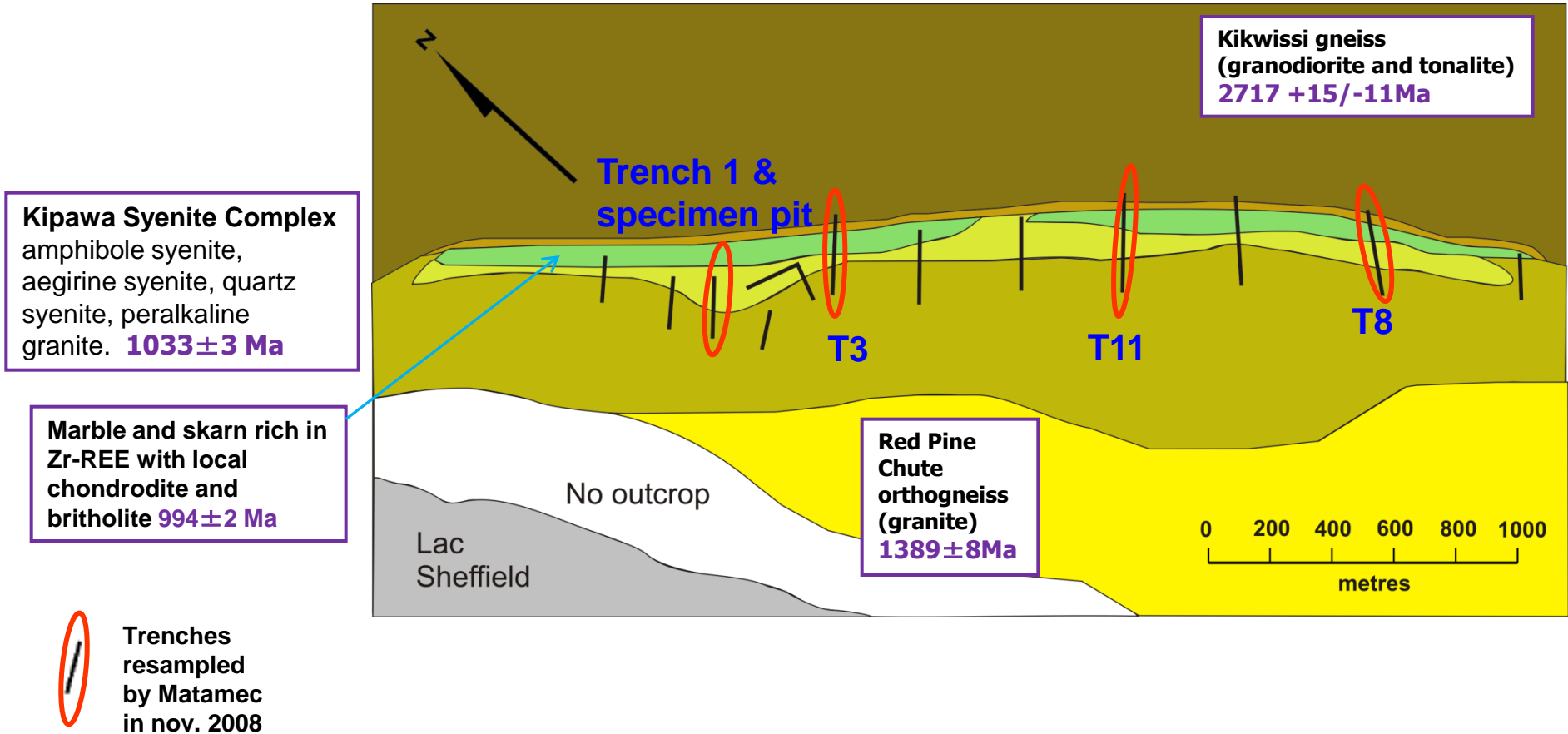
Metamorphic grade : upper amphibolite

Constantin and Fleury (2011, GAC-MAC ,Ottawa) adapted from van Breemen & Currie (2004 CJES, 41: 431-455) and Currie & van Breemen (1996, CanMin, 34: 435-451).

Fig. 1. Simplified geological map of the Kipawa region, north-western Quebec (modified after Lyall (1958), Rive (1973), Tremblay-Clark and Kish (1978), and Currie (1998)). The inset location map shows the location of the Grenville Front (GF) in the Kipawa region. Numbers in boxes are U-Pb ages determined in this study and by Currie and van Breemen (1996).

The Sheffield deposit

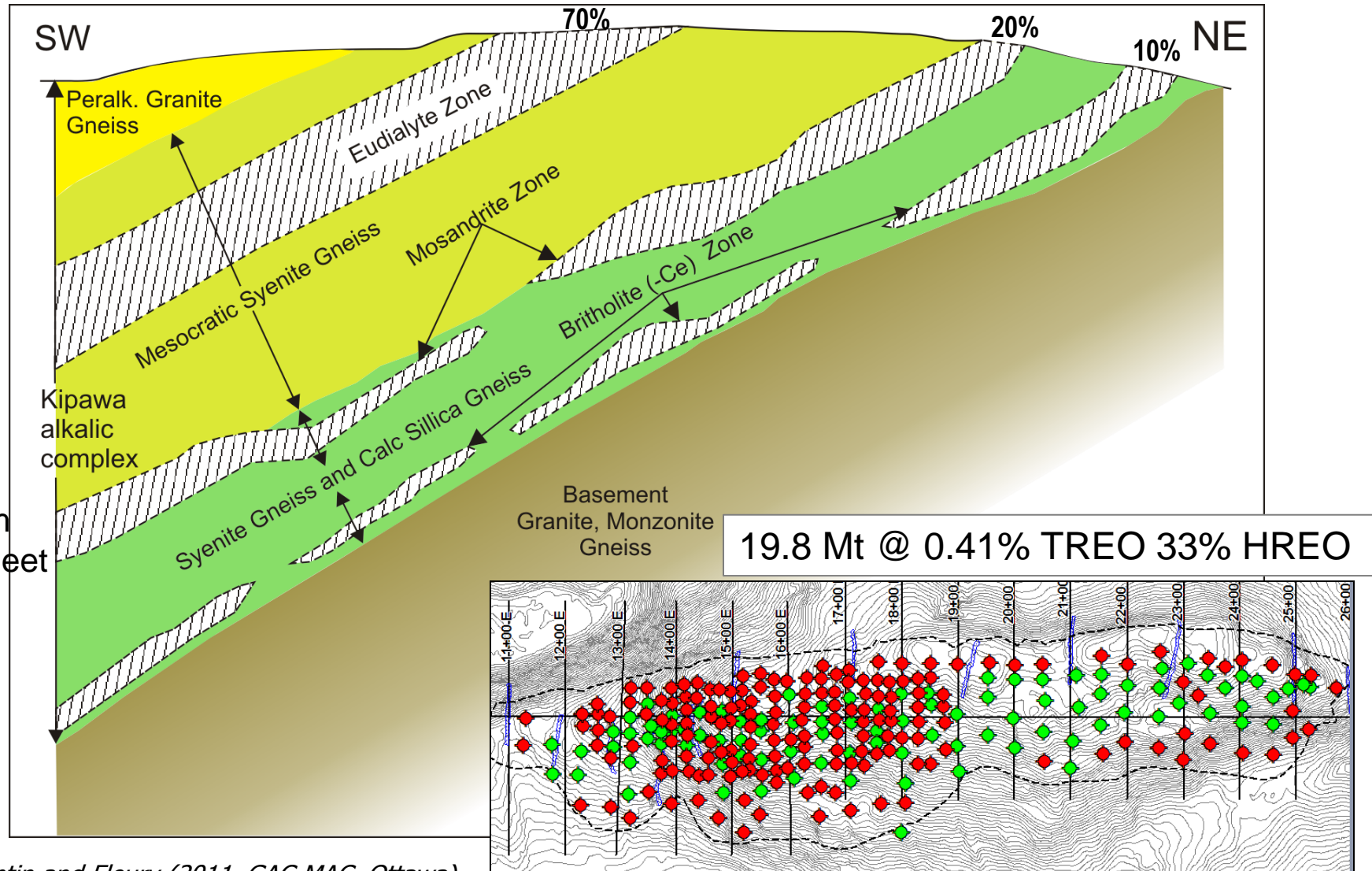
The rocks strike NW and dip gently (10-30°) to the SW.



Constantin and Fleury (2011, GAC-MAC, Ottawa) adapted from Currie & van Breemen (1996 CanMin, 34: 435-451) with addition from van Breemen & Currie (2004 CJES, 41: 431-455)

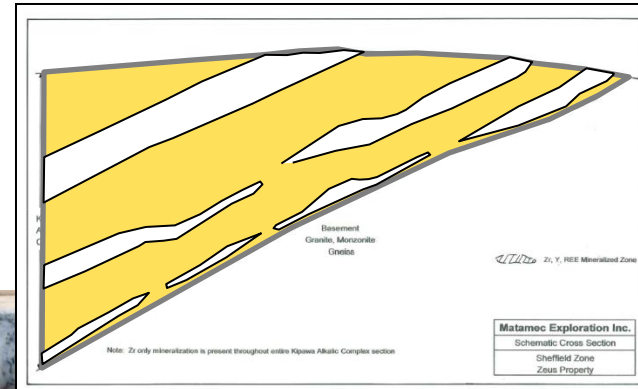
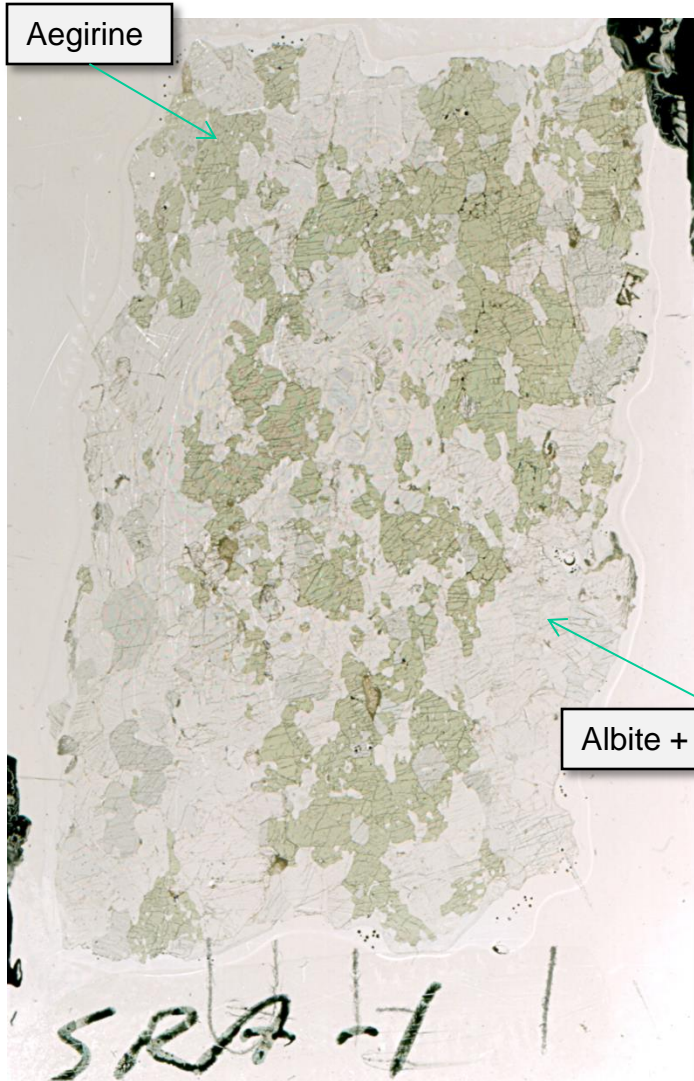
Four REE-Y-Zr zones identified at the Sheffield deposit

Eudialyte, Mosandrite, Britholite-(Ce), Zr-rich

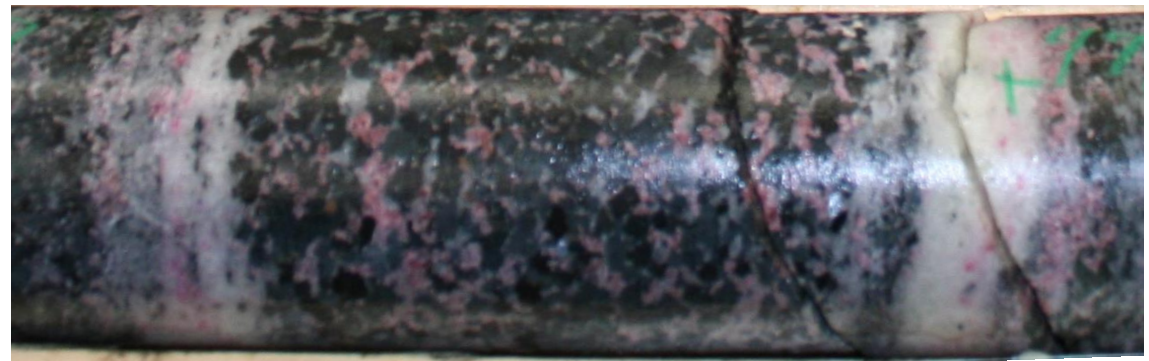
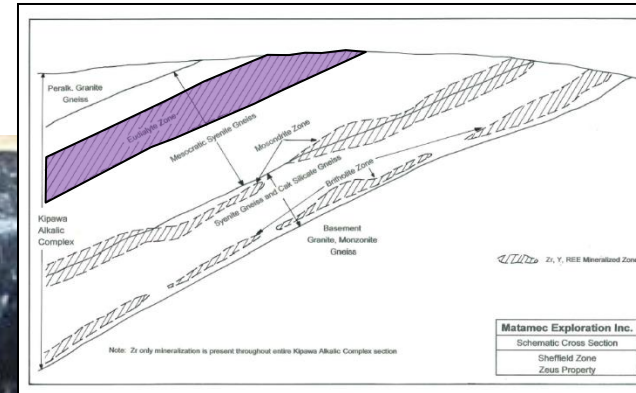
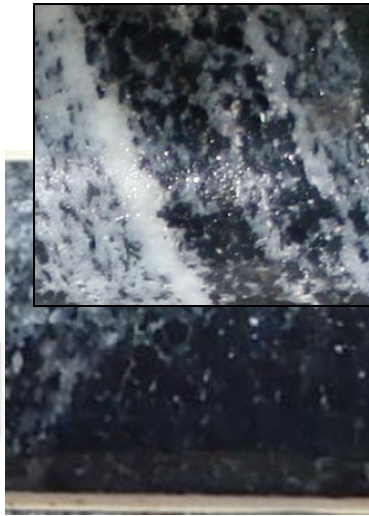


Pétrographie et minéralogie

Domaine A. Syénites et granites (70%)

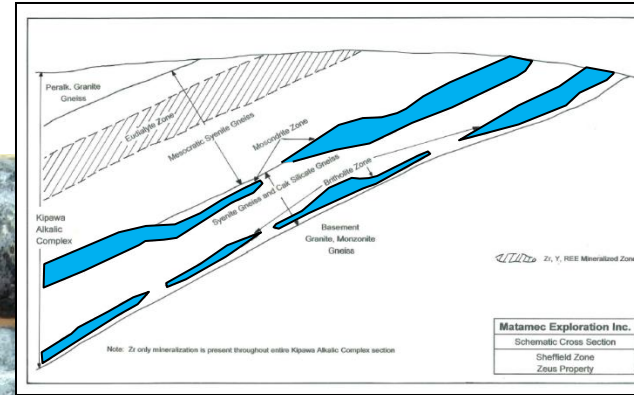
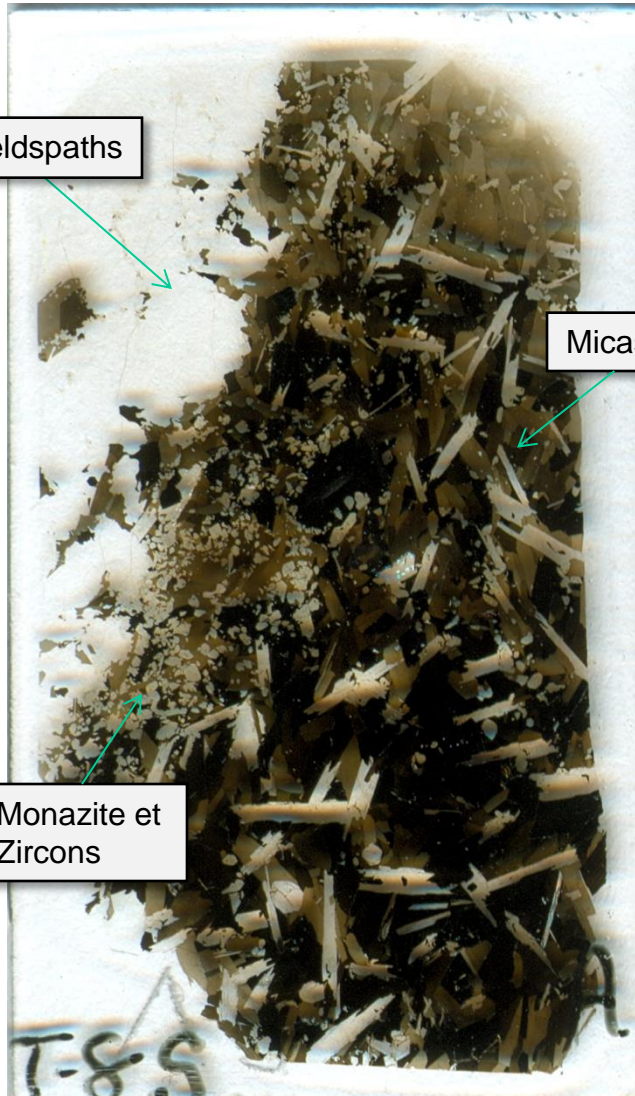


Domaine B. Amphibolites à richterite (10%)



- ▲ Grains grossiers à très grossiers
- ▲ Minces bandes ou intervalles métriques
- ▲ Souvent minéralisée

Domaine C. Roches calco-silicatées (15%)



- ▲ Roche à diopside-feldspath (zircon mineur)
- ▲ Phlogopitites

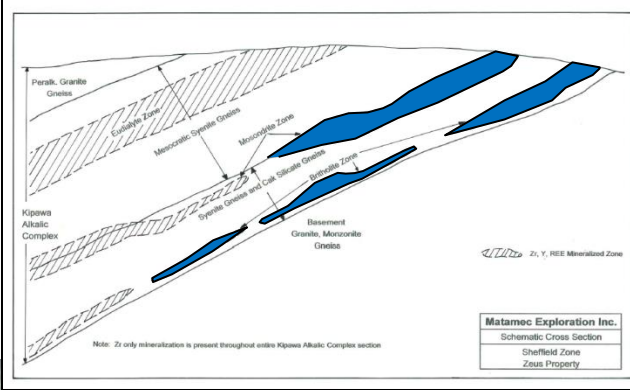
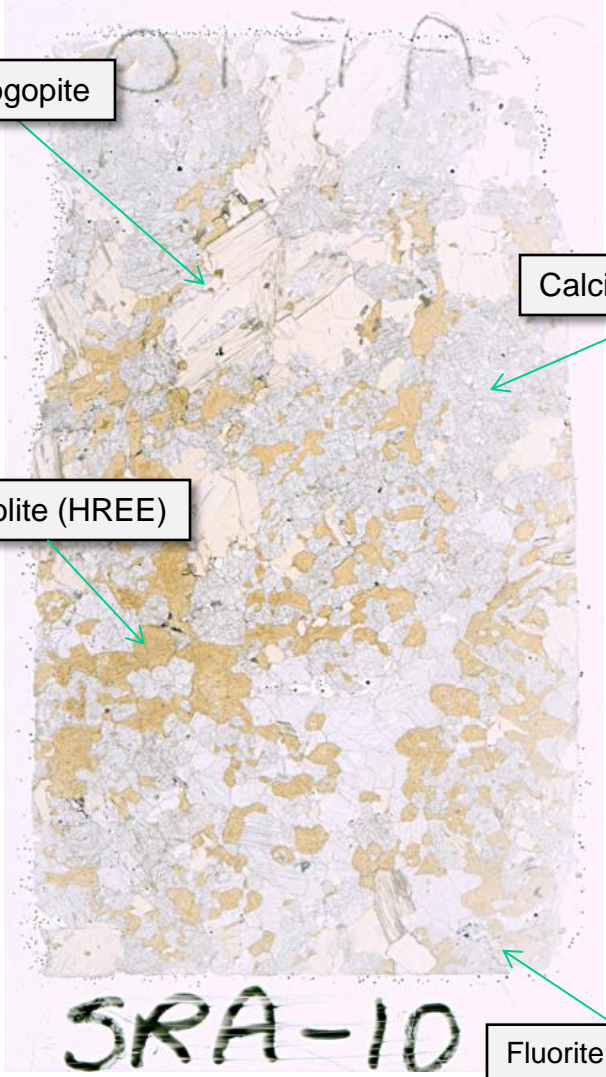
Domaine D. Skarns (5%)

Phlogopite

Britholite (HREE)

Calcite & Olivine

Fluorite en trace

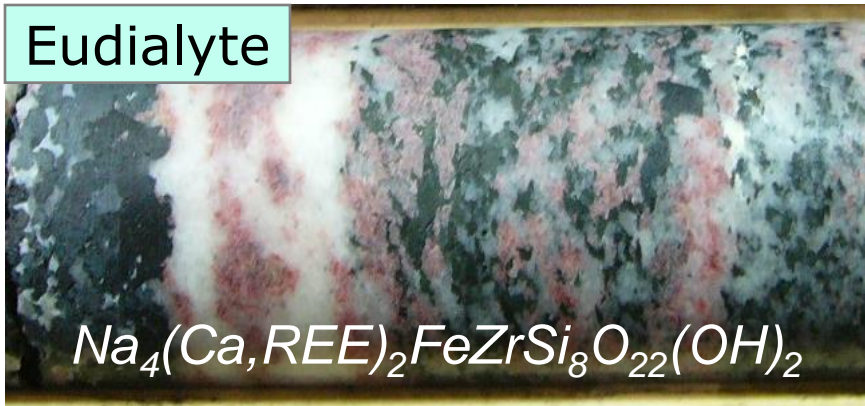


▲ Skarns à phlogopite, chondrodite, fluorite et diopside

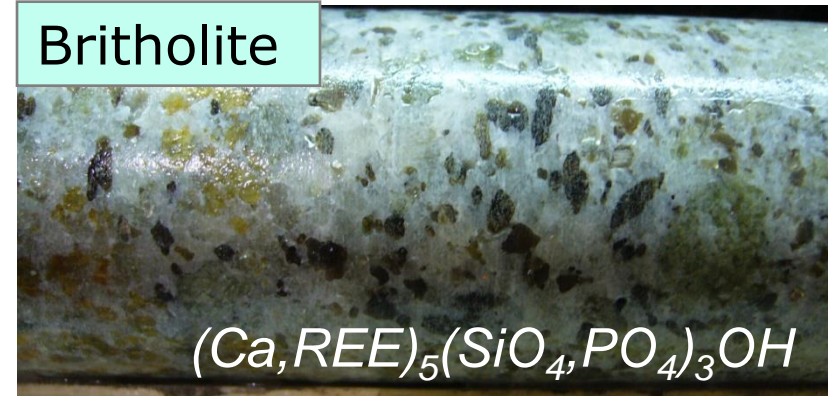
Fleury F. (2016) Séminaire de maîtrise. Université Laval.

GISEMENT DE KIPAWA – Minéraux exotiques

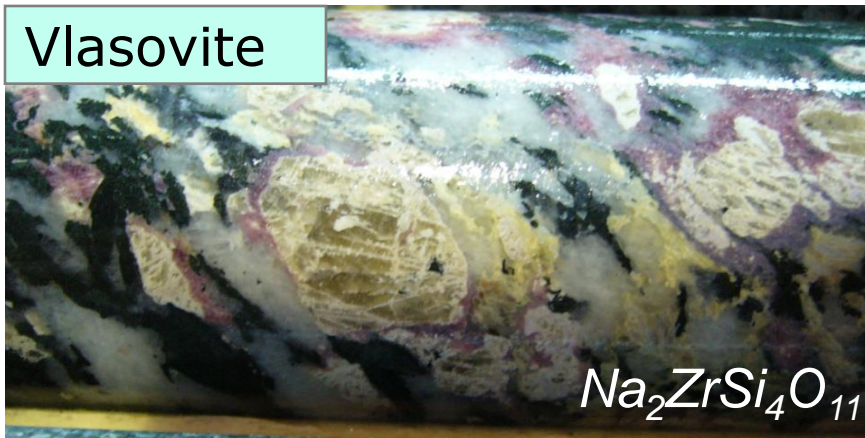
Eudialyte



Britholite



Vlasovite



Mosandrite



Minerals from the Kipawa deposit :

Mosandrite: $(\text{H}_3\text{O}^+, \text{Na}, \text{Ca})_3\text{Ca}_3\text{REE}(\text{Ti}, \text{Zr})(\text{Si}_2\text{O}_7)_2(\text{O}, \text{OH}, \text{F})_4$

Brown mosandrite with black magnesioferrikatophorite.



Scale: 4.5 x 3.7 cm

Mindat.org

Constantin and Fleury (2011, GAC-MAC, Ottawa)

Hiortdahlite:

$\text{Na}_2\text{Ca}_4\text{Zr}(\text{Y}, \text{Zr}, \text{Mn}, \text{Fe})(\text{Si}_2\text{O}_7)_2(\text{F}, \text{O})_4$

Yellowish brown hiortdahlite with black katophorite



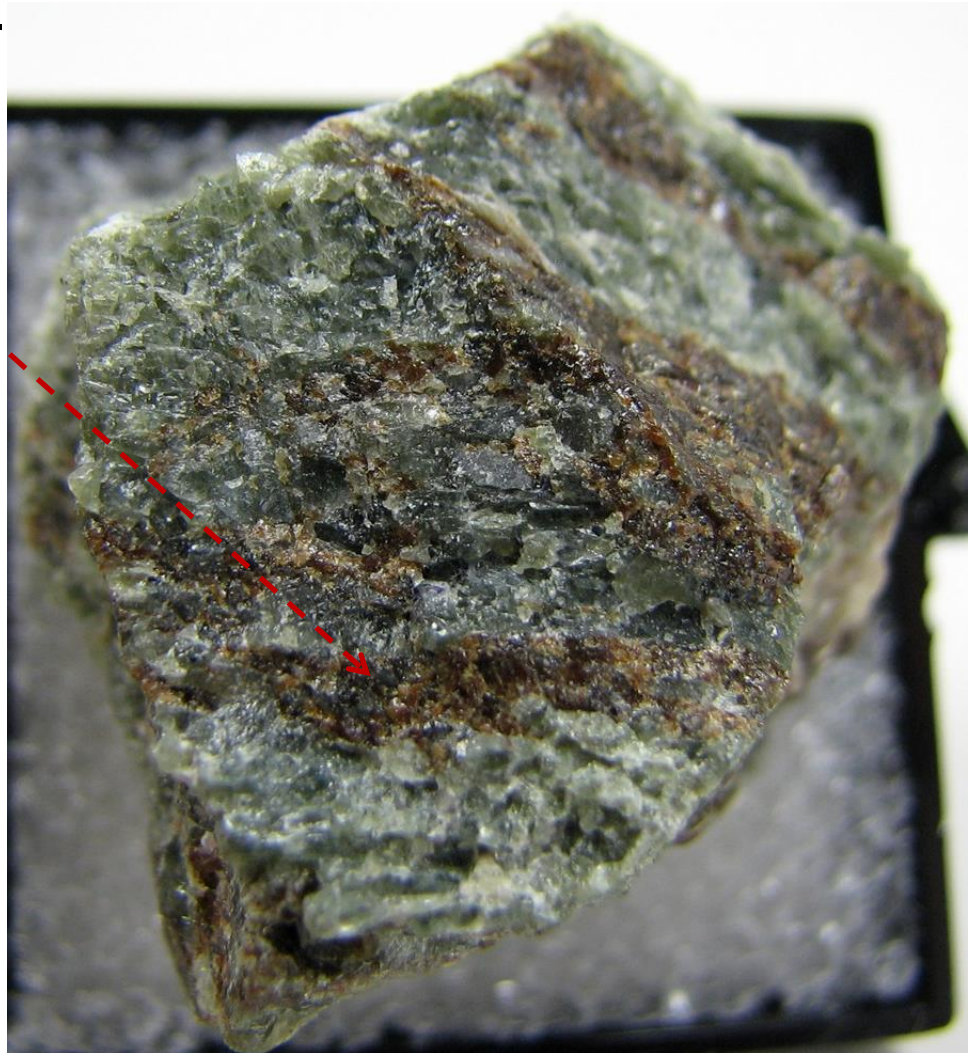
Scale: 2.5 x 2.0 x 1.5 cm *Mindat.org*

Minerals from the Kipawa deposit :

Britholite :



Massive brown britholite-(Ce).



Constantin and Fleury (2011, GAC-MAC, Ottawa)

Scale: 3.0 x 2.5 x 2.0 cm *Mindat.org*

Known rare minerals from the Kipawa region

- *Alkali and/or calcic zirconosilicates*

Eudialyte: $\text{Na}_4(\text{Ca}, \text{REE})_2(\text{Fe}, \text{Mn}, \text{Y})\text{ZrSi}_8\text{O}_{22}(\text{OH}, \text{Cl})_2$

Vlasovite: $\text{Na}_2\text{ZrSi}_4\text{O}_{11}$

Mosandrite: $(\text{H}_3\text{O}^+, \text{Na}, \text{Ca})_3\text{Ca}_3\text{REE}(\text{Ti}, \text{Zr})(\text{Si}_2\text{O}_7)_2(\text{O}, \text{OH}, \text{F})_4$

Gittinsite: $\text{CaZrSi}_2\text{O}_7$

Hiortdahlite: $\text{Na}_2\text{Ca}_4\text{Zr}(\text{Y}, \text{Zr}, \text{Mn}, \text{Fe})(\text{Si}_2\text{O}_7)_2(\text{F}, \text{O})_4$

- *Fluorocarbonates*

Britholite: $\text{Ca}_2(\text{Ca}, \text{REE})_3(\text{SiO}_4, \text{PO}_4)_3(\text{OH}, \text{F})$

Fluorite: $(\text{Ca}, \text{REE})\text{F}_2$

- *Other rare silicates*

Agrellite: $\text{Na}(\text{Ca}, \text{REE})_2\text{Si}_4\text{O}_{10}\text{F}$

Miserite: $\text{K}(\text{Ca}, \text{REE})_6\text{Si}_8\text{O}_{22}(\text{OH}, \text{F})_2$

Pectolite: $\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})$

Zircon: ZrSiO_4

Thorite: $(\text{Th}, \text{U})\text{SiO}_4$

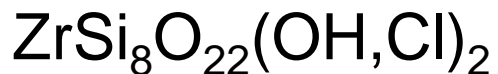
* *REE* = lanthanides + Y

Constantin and Fleury (2011, GAC-MAC, Ottawa)

Most mineral formulae from Back & Mandarino (2008) Fleischer's glossary of mineral species.

Syenite from the Kipawa deposit:

Eudialyte: $\text{Na}_4(\text{Ca}, \text{REE})_2(\text{Fe}, \text{Mn}, \text{Y})$



Vlasovite: $\text{Na}_2\text{ZrSi}_4\text{O}_{11}$

Gittinsite: $\text{CaZrSi}_2\text{O}_7$

Magnesiokatophorite: $\text{Na}[\text{CaNa}]$



Albite : $\text{NaAlSi}_3\text{O}_8$

Brown vlasovite with a halo of white gittinsite surrounded by pink eudialyte in a mixture of white albite, black magnesiokatophorite, and eudialyte.



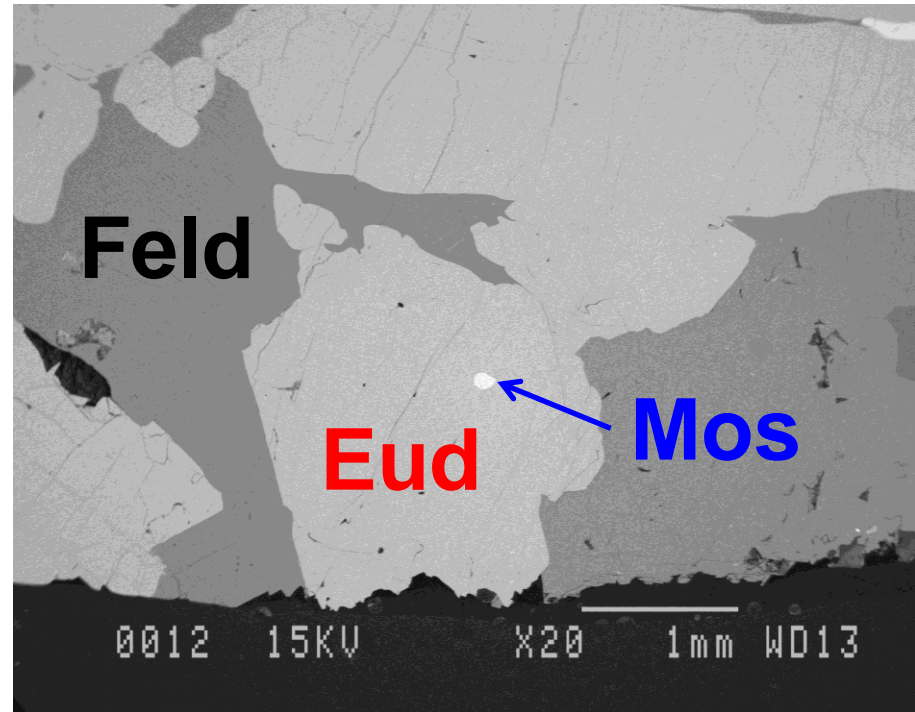
Scale: 4 x 4 x 3 cm.

Syenite from the Kipawa deposit

Feldspar + eudialyte + amphibole
+ pyroxene + mosandrite



Sample SRA-3



Minéral	Mode (%)	% Y ₂ O ₃	% ZrO ₂	% REO	% HREO	% HREO/REO tot.
Eudialyte	35%	2.0%	12.0%	5.1%	2.7-3.7%	38%
Mosandrite	Trace	5.7%	0.6%	19%	7.8%	40%

Leucosyénite à eudialyte, f.gr.

Photo macroscopie

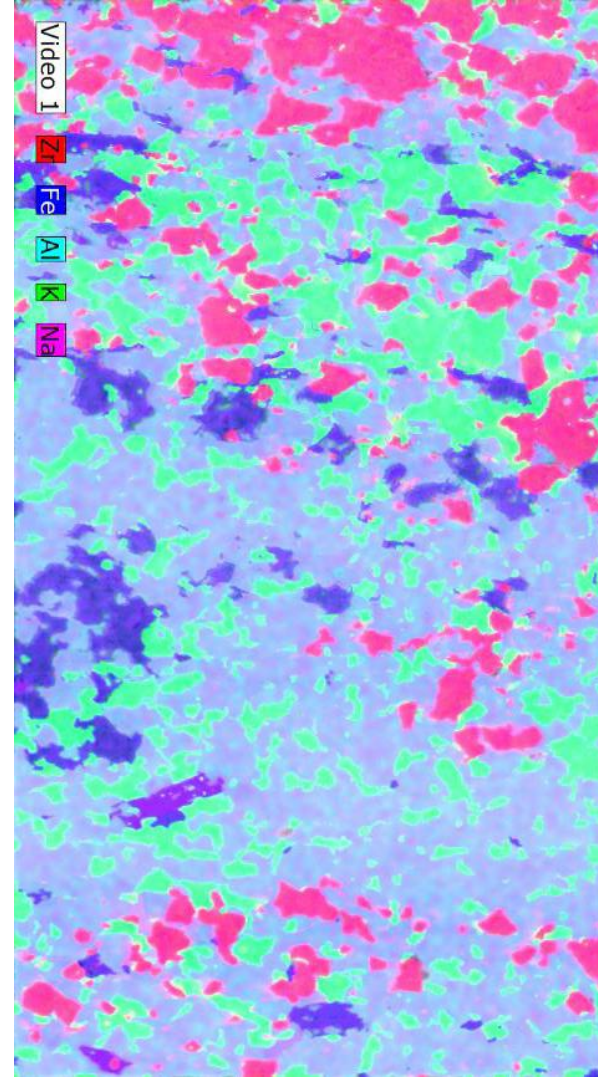
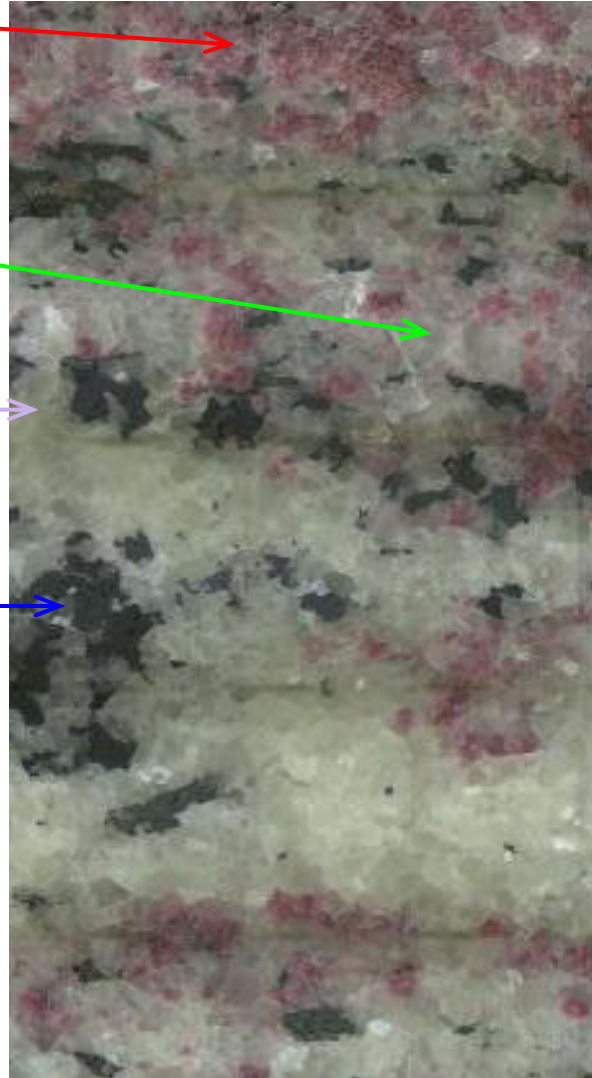
Carte élémentaire

Eudialyte
(rouge = Zr)

Feldspath-K
(vert pâle = K)

Plagioclase
(lavande = Al, Na)

**Aegyrine+
amphibole**
(bleu = Fe)



somet



Mélasyénite à cumulat d'eudialyte, m.-g. gr.

Photo macroscopie

Carte élémentaire

Inconnu ?

f.gr., interstitiel
(vert pâle = Ce)

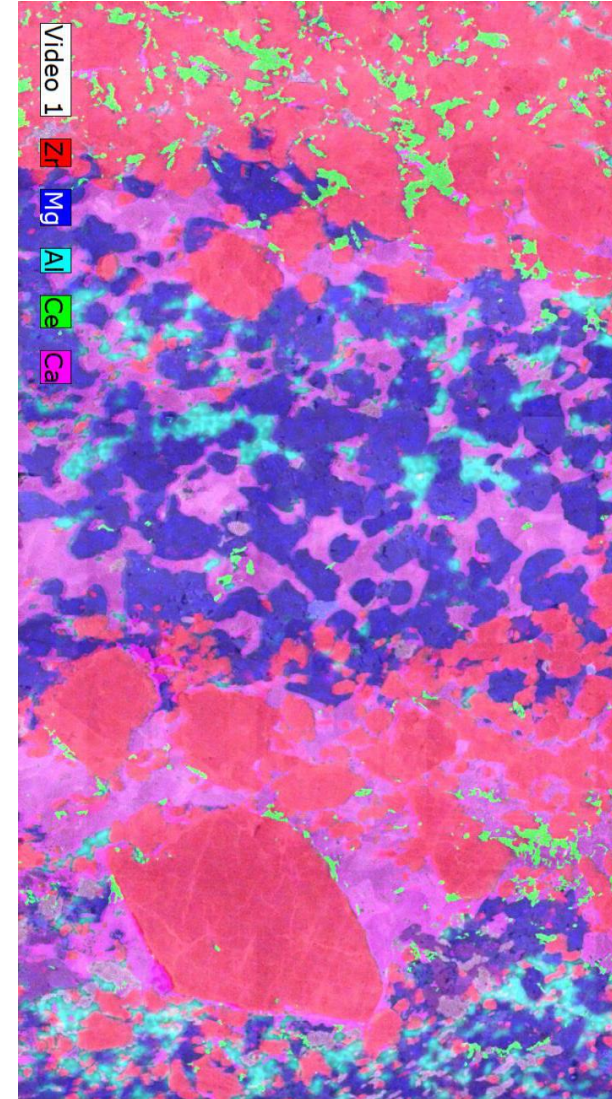
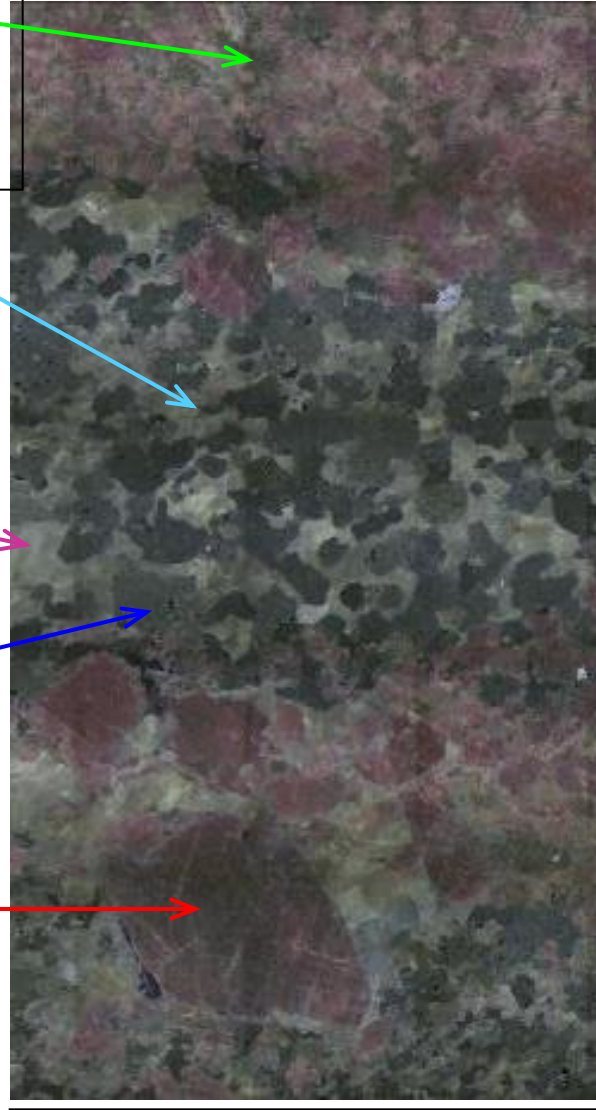
Feldspath-K
(bleu pâle = Al)

Plagioclase
(rose = Ca)

Aegyrine+
amphibole
(bleu = Fe)

Eudialyte

g.gr.
(rouge = Zr)



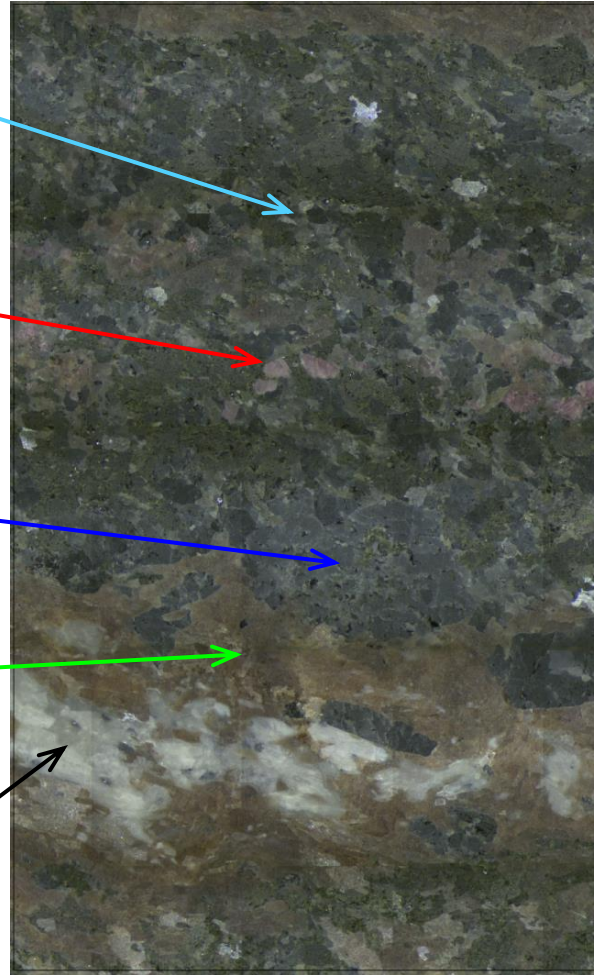
sommet

4 cm

Adapté de Plamondon (2017) Projet de fin d'études. Université Laval.

Roche calco-silicatée à lit pluri-centimétrique

Photo macroscopie



Feldspath
(bleu pâle = Al)

Eudialyte
(rouge = Zr)

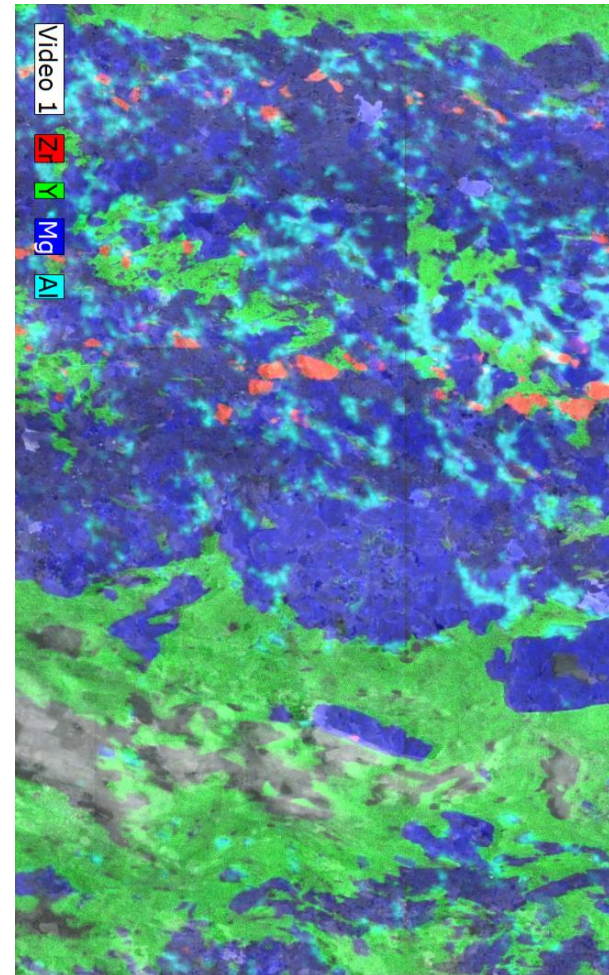
Diopside
(bleu = Fe)

Mosandrite
(vert = Y)

Carbonate
(blanc)

4 cm

Carte élémentaire



somet

*Adapté de Plamondon (2017)
Projet de fin d'études.
Université Laval.*

Syénite foliée et déformée

Photo macroscopie

Carte élémentaire

sommet

Feldspath
(bleu pâle = Al)

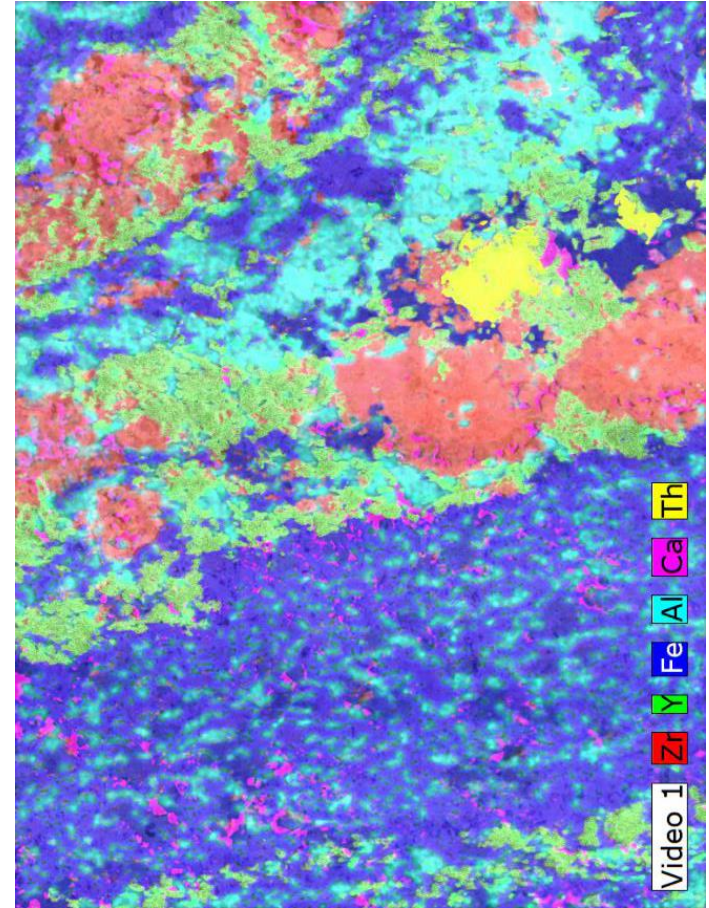
Thorite
(jaune = Th)

Mosandrite
(vert = Y)

Zircon
(orange = Zr)

Fluorite
(rose = Ca)

Aegyrine+
amphibole
(bleu = Fe)

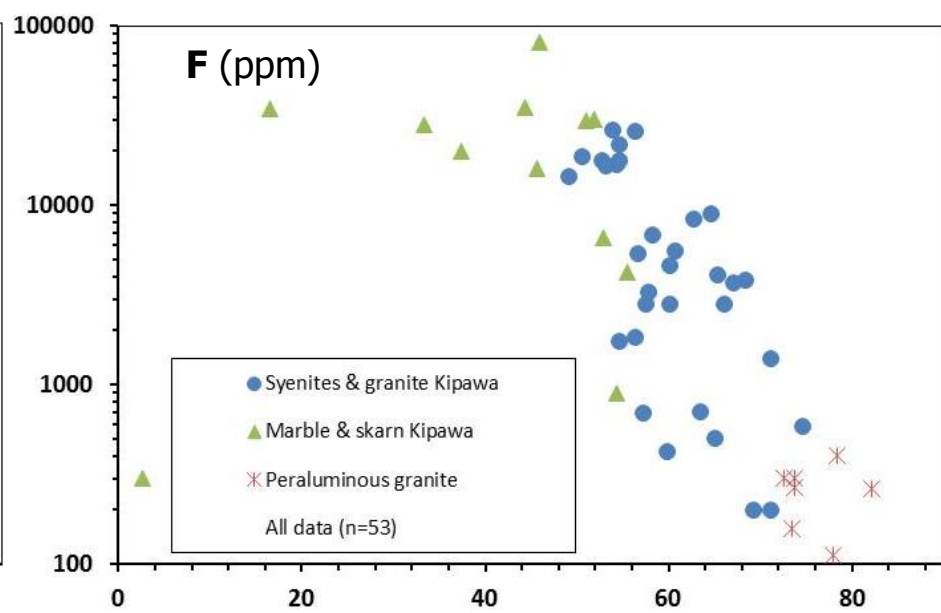
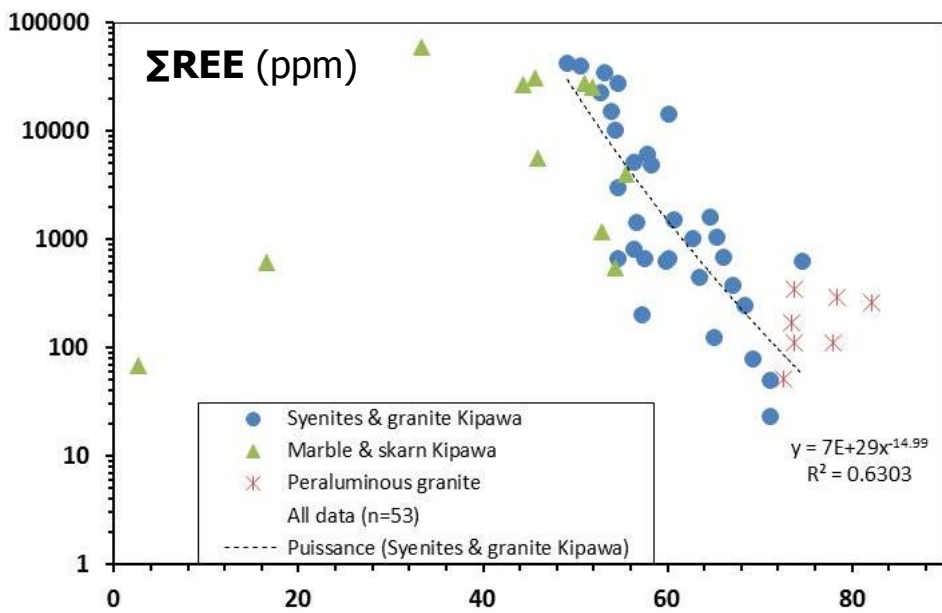
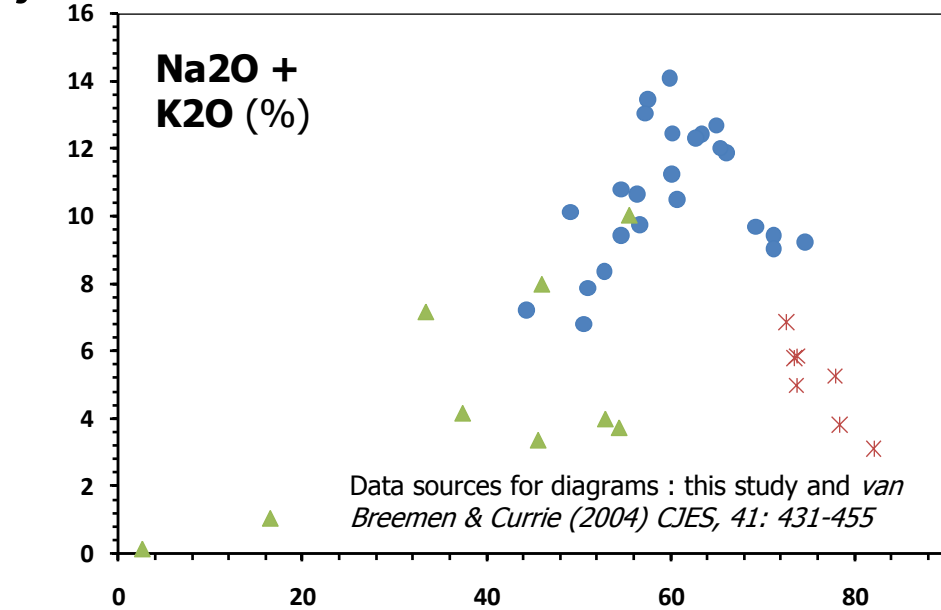
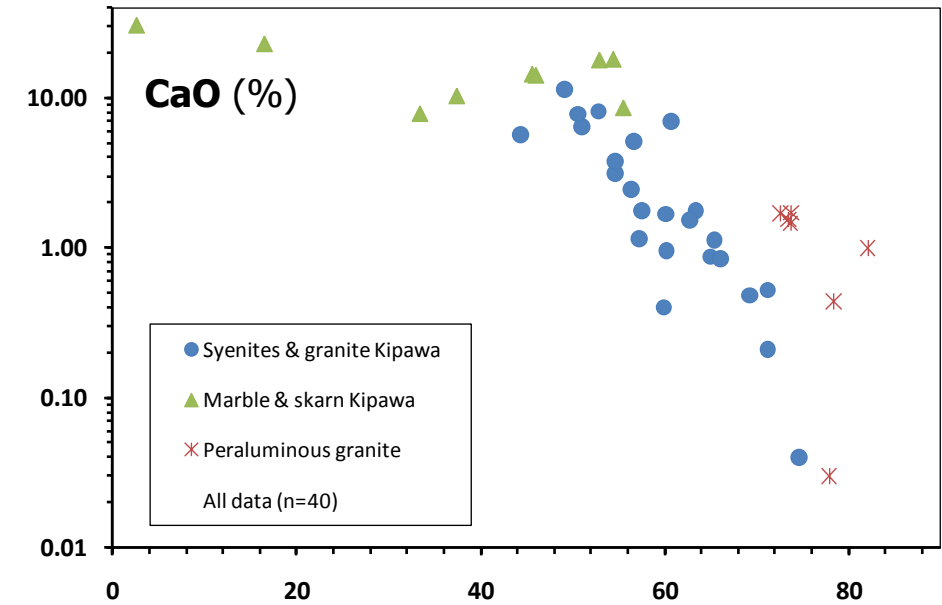


4 cm

Adapté de Plamondon (2017)
Projet de fin d'études.
Université Laval.

Géochimie des éléments majeurs et traces

Kipawa – whole rock major and minor elements

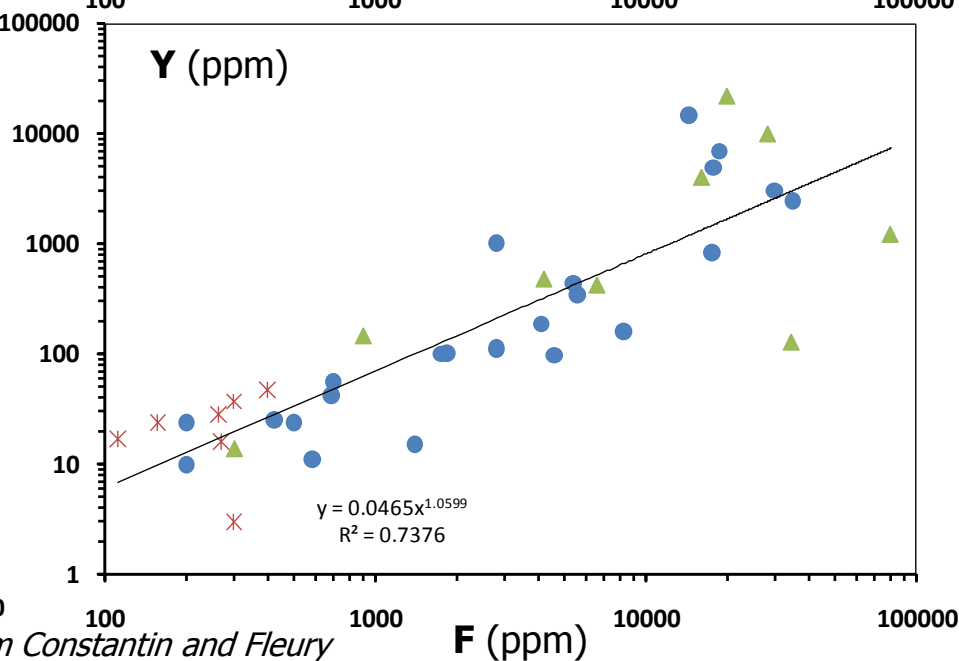
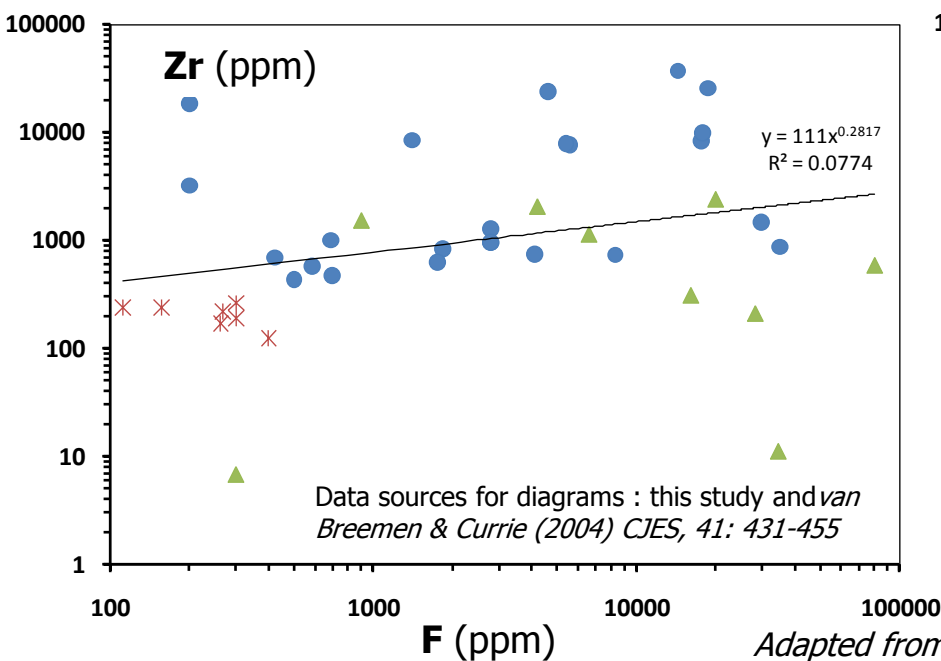
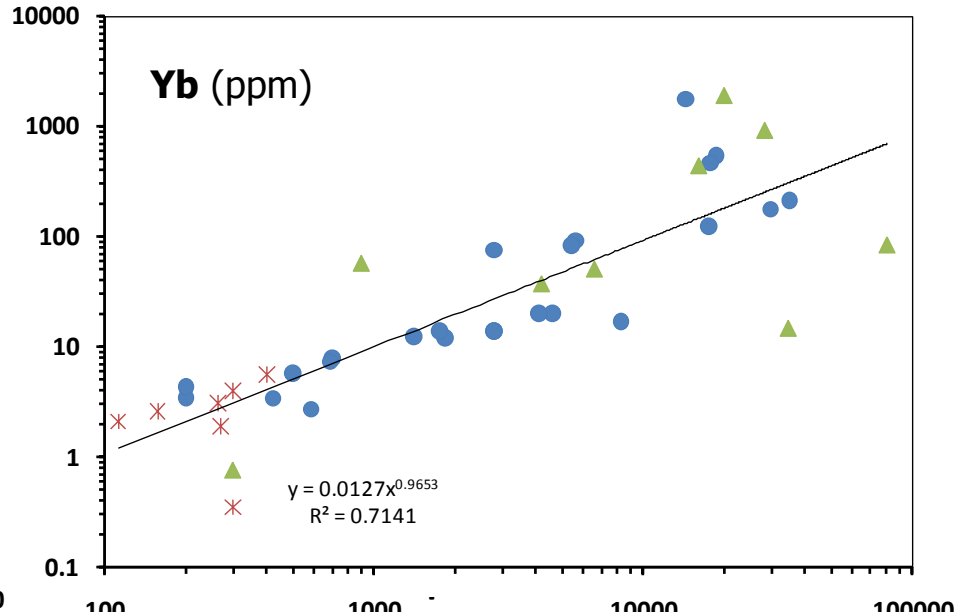
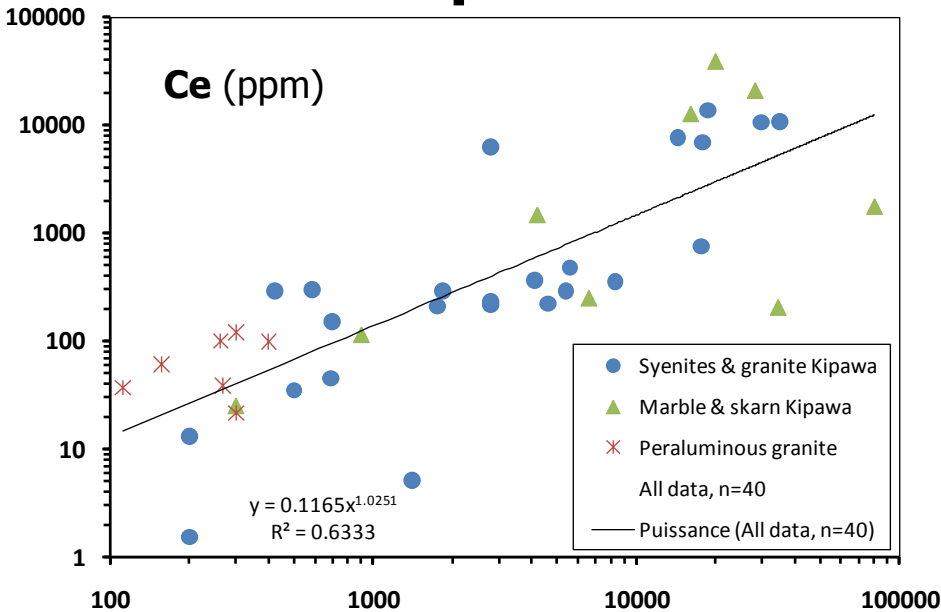


SiO₂ (%)

Adapted from Constantin and Fleury (2011, GAC-Mac, Ottawa)

SiO₂ (%)

Kipawa – whole rock REE and Zr



Adapted from *Constantin and Fleury (2011, GAC-Mac, Ottawa)*

Méthodologie : 2 outils

I. Analyse par discriminants (ioGas)

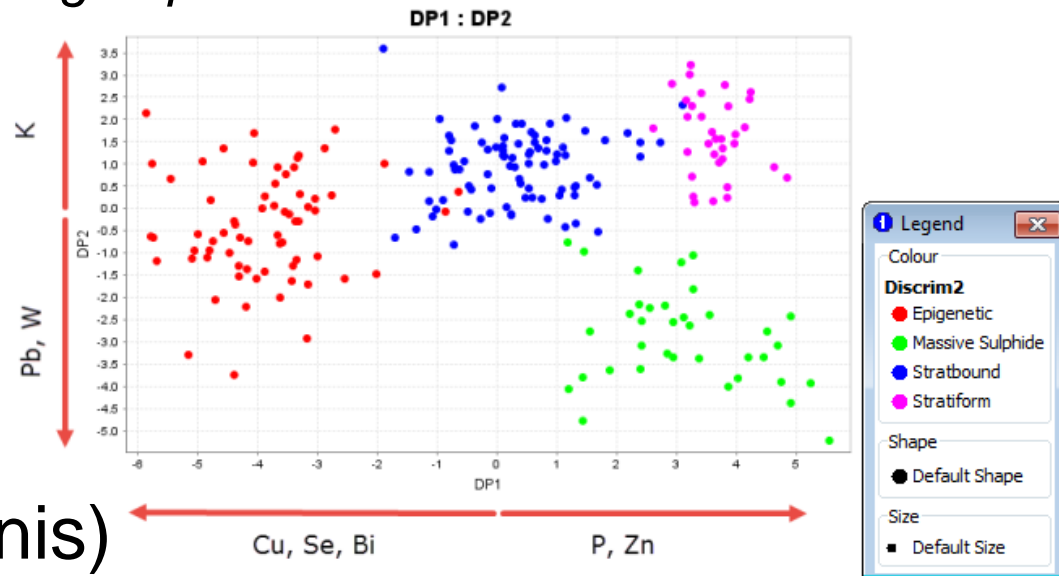
« Qu'est-ce qui différencie ces groupes? »

❖ ACP guidée

(groupes pré-définis)

❖ Maximise variance inter-groupe,
minimise variance intra-groupe

❖ Ne fonctionne pas avec RLC



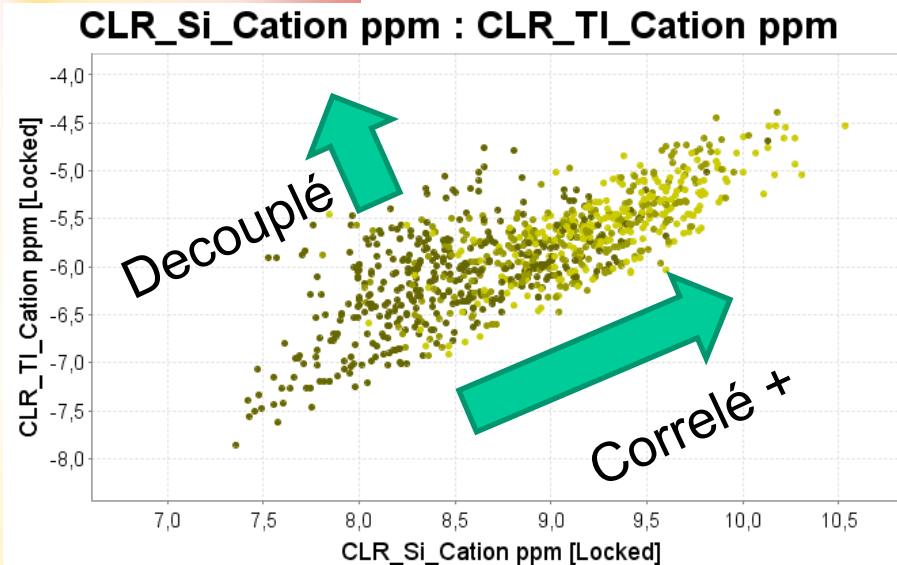
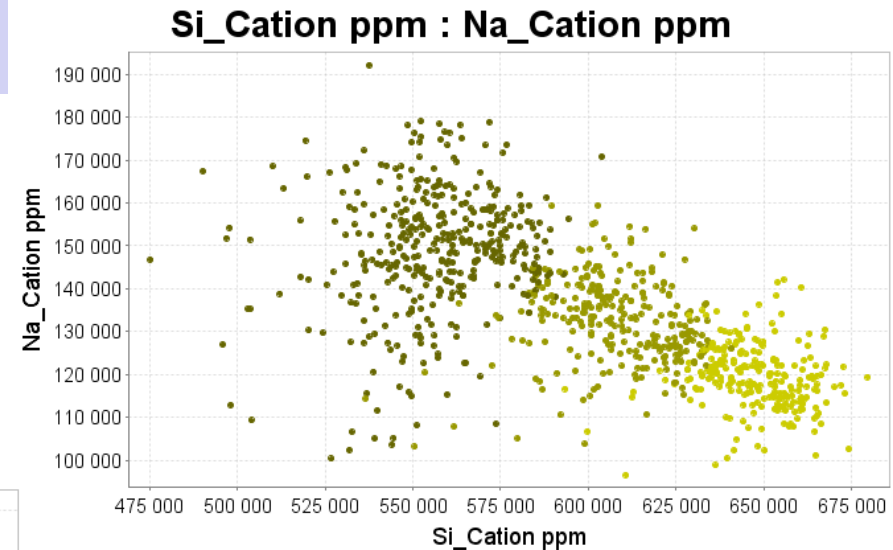
Site web d'ioGas

Méthodologie : 2 outils

II. Diagrammes bivariants

« Quelles sont les grandes tendances? »

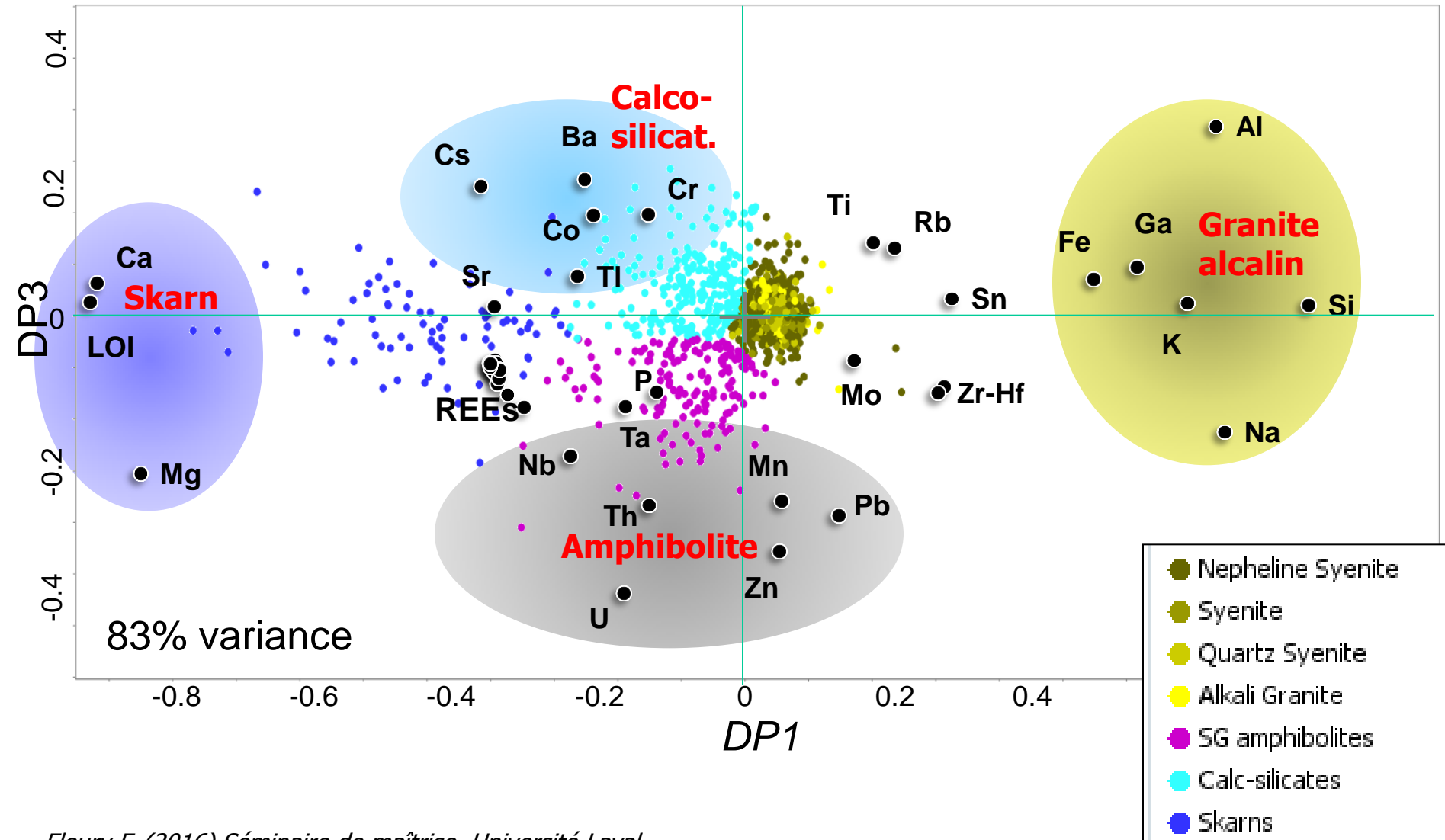
Classiques:



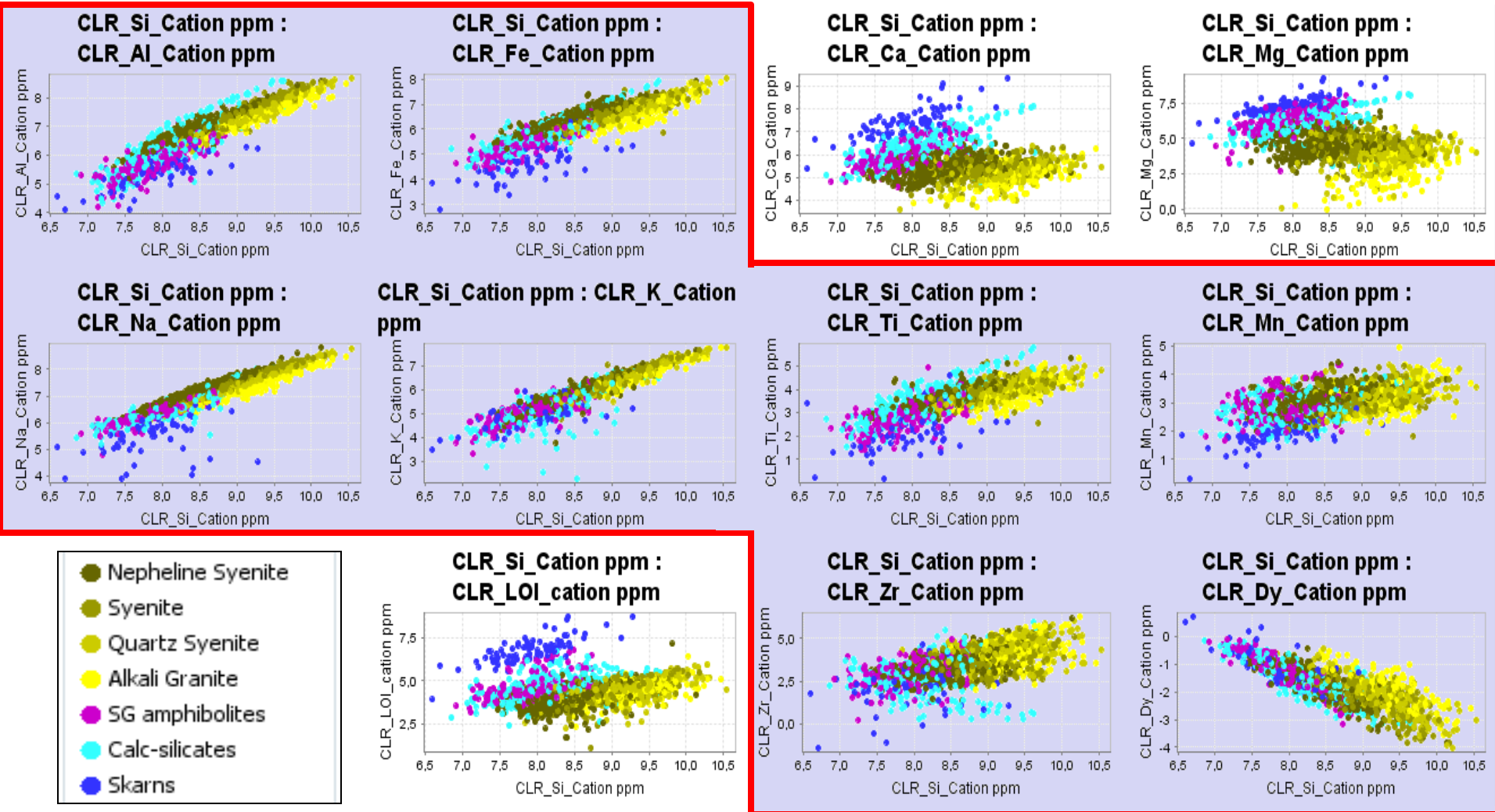
: Ratios log centrés (CLR)
= $\text{Log} (X / \text{Moy Géom})$
Élimine fermeture

Analyse par discriminants

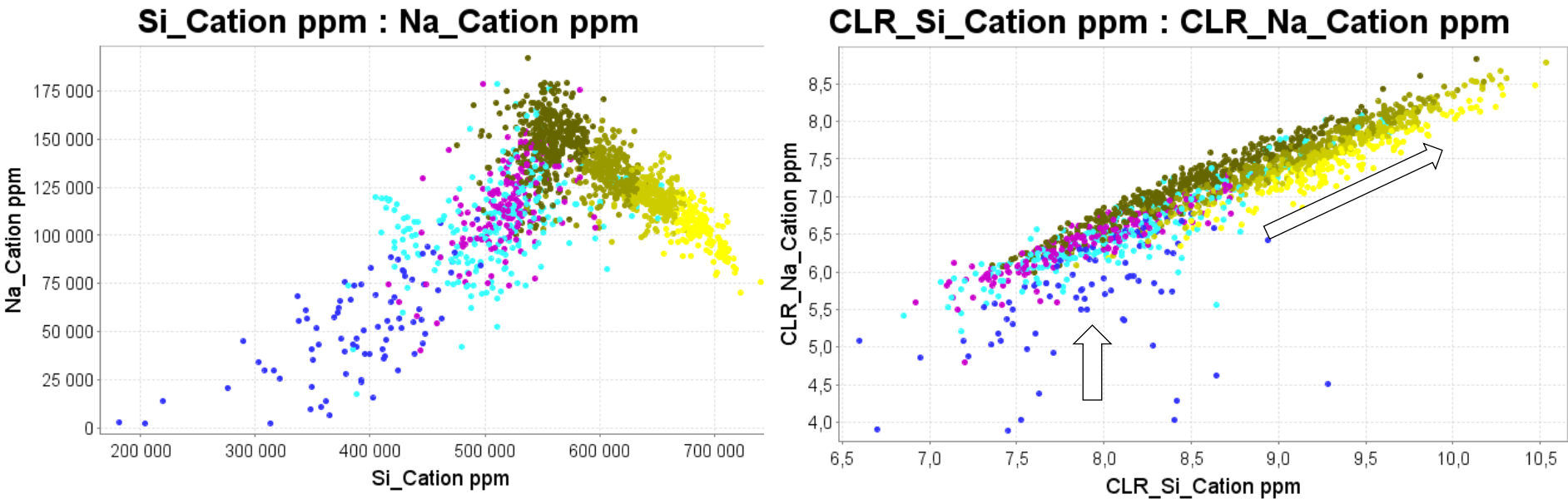
Chemical Litho for the Kipawa Complex



Diagrammes Bivariants (ratio-log centré): Tendance 1



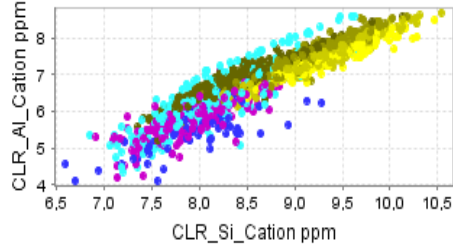
Diagrammes Bivariants (ratio-log centré) : Tendance 1



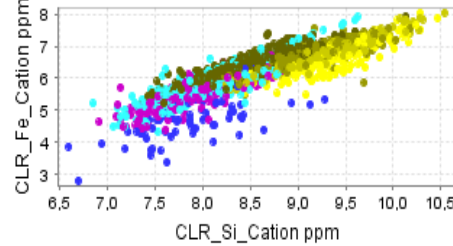
- Corrélation positive entre Si, Al, Fe, Na, K (LOI, Ti, Mn, Zr)
- Corrélation négative avec terres rares
- Affecte Syénites, Amphibolites et Calco-silicatés

Diagrammes Bivariants(ratio-log centré) : Tendance 2

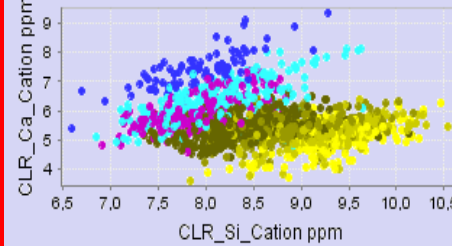
CLR_Si_Cation ppm :
CLR_Al_Cation ppm



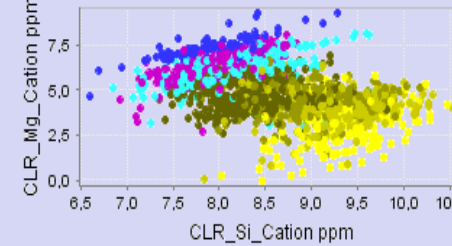
CLR_Si_Cation ppm :
CLR_Fe_Cation ppm



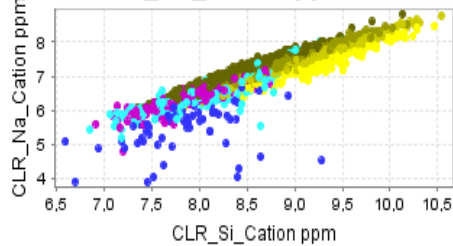
CLR_Si_Cation ppm :
CLR_Ca_Cation ppm



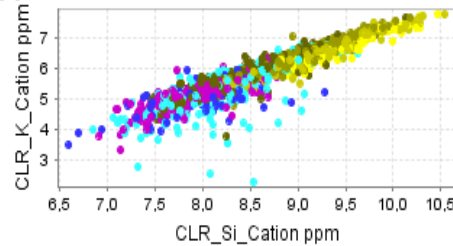
CLR_Si_Cation ppm :
CLR_Mg_Cation ppm



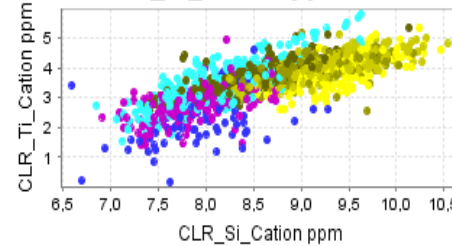
CLR_Si_Cation ppm :
CLR_Na_Cation ppm



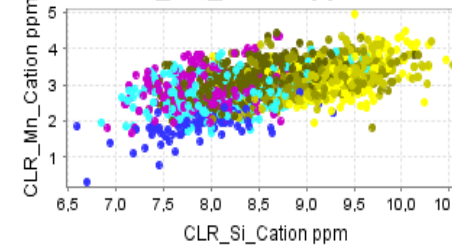
CLR_Si_Cation ppm : CLR_K_Cation ppm



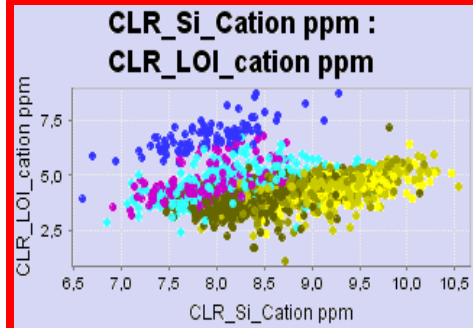
CLR_Si_Cation ppm :
CLR_Ti_Cation ppm



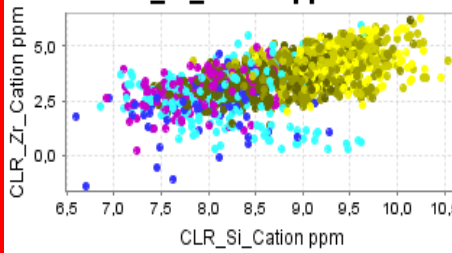
CLR_Si_Cation ppm :
CLR_Mn_Cation ppm



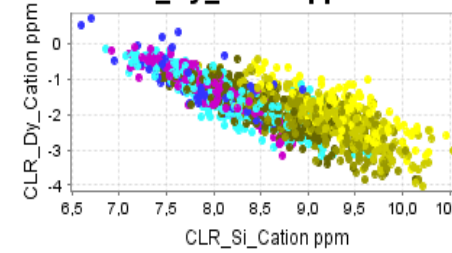
CLR_Si_Cation ppm :
CLR_LOI_cation ppm



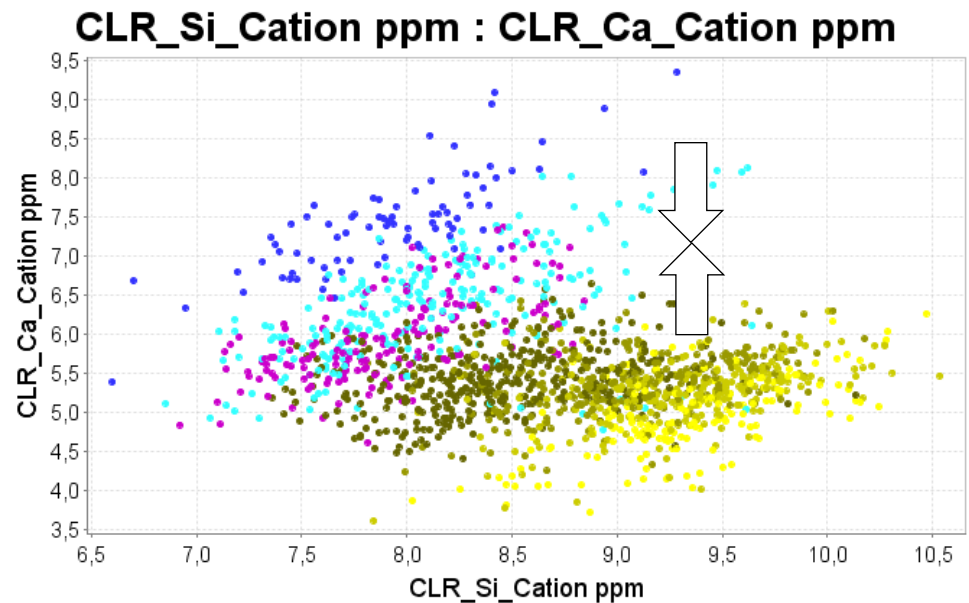
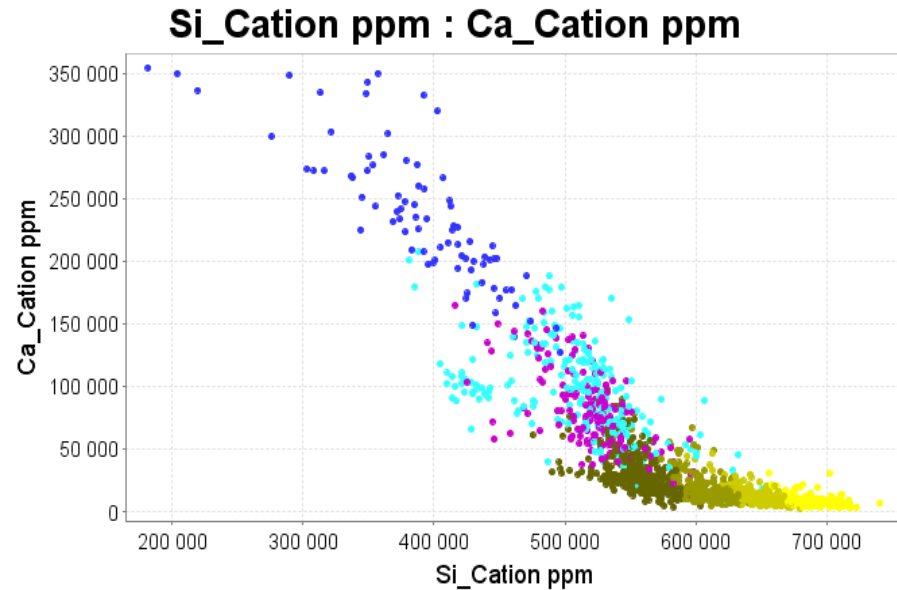
CLR_Si_Cation ppm :
CLR_Zr_Cation ppm



CLR_Si_Cation ppm :
CLR_Dy_Cation ppm



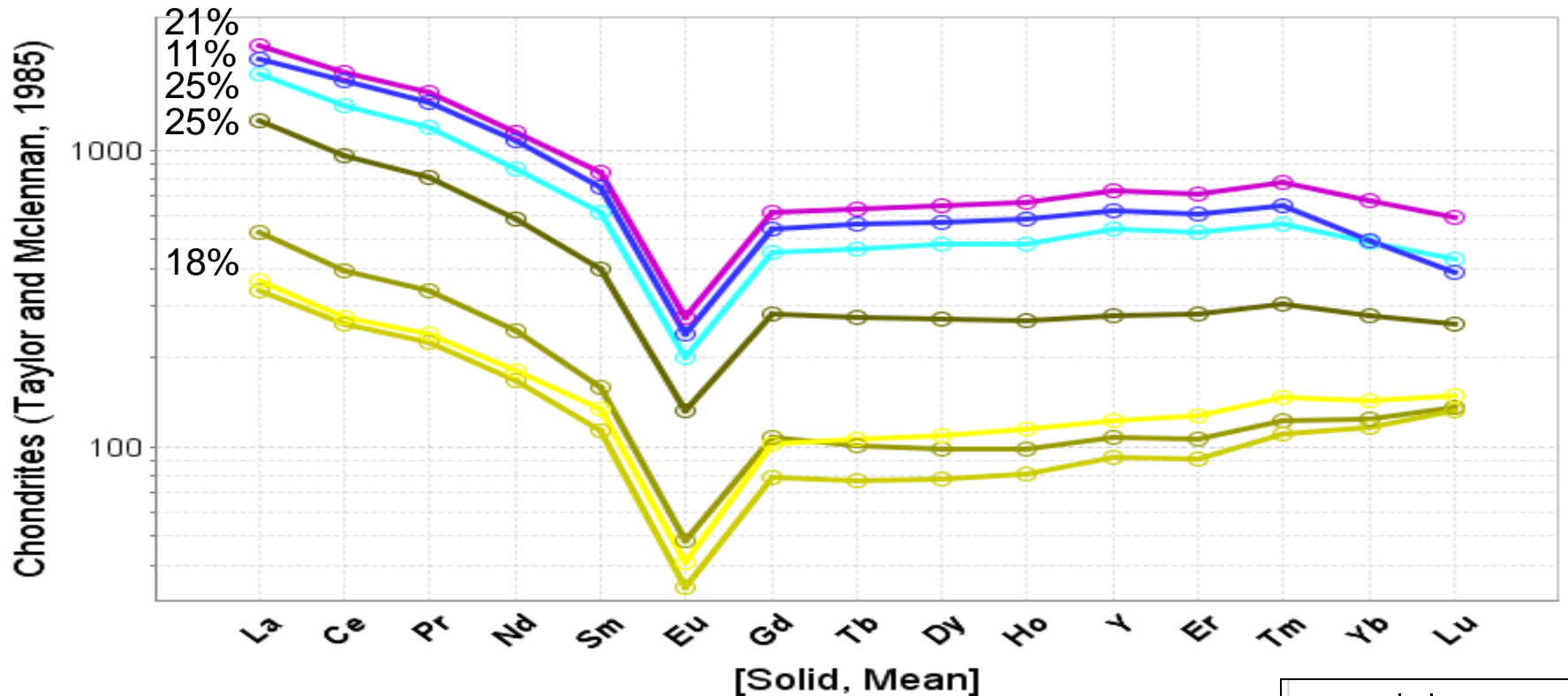
Diagrammes Bivariants (ratio-log centré) : Tendance 2



- Découplage de Si vs Ca, Mg et LOI
- Affecte amphibolites et calco-silicatées
- Une partie des syénites (Tendance 1 encore visible)

Patrons des terres rares (n=1670)

% metal Kipawa



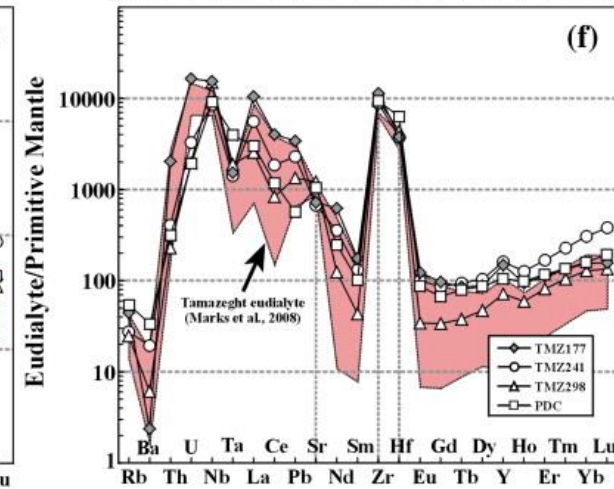
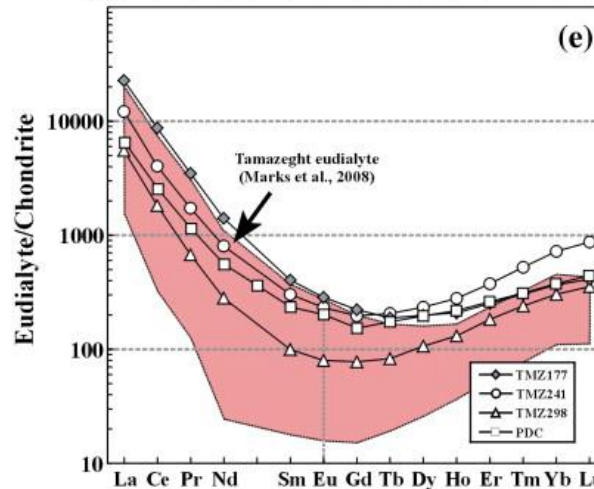
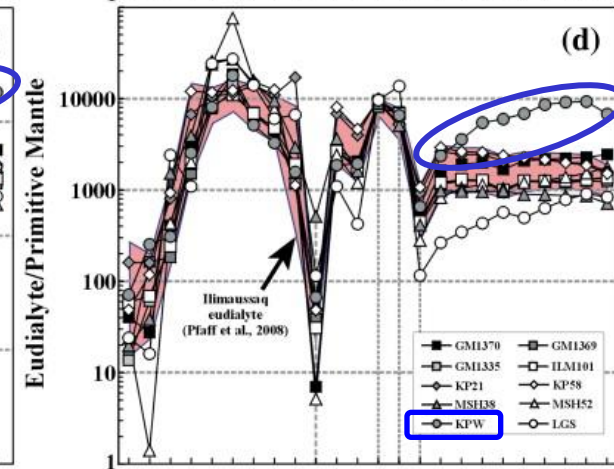
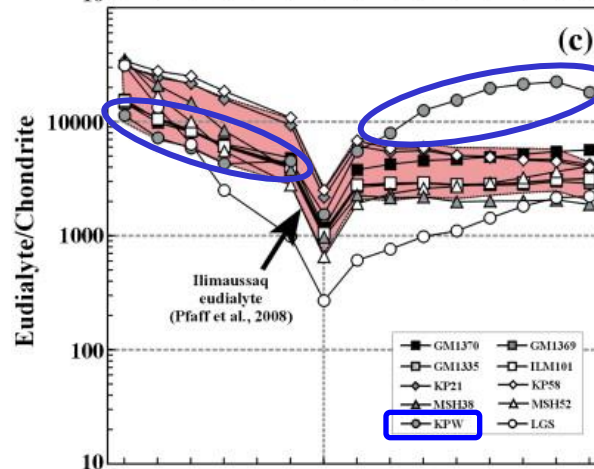
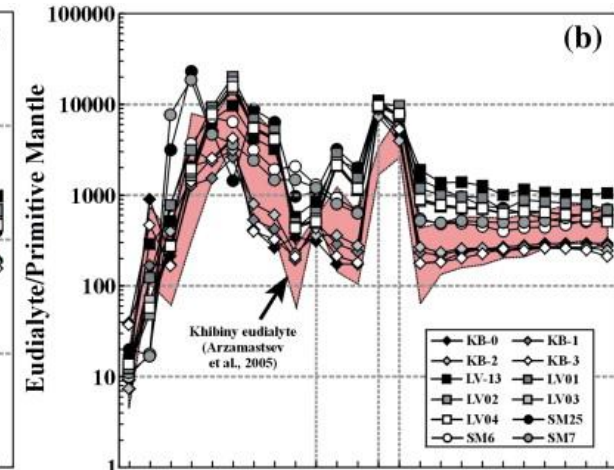
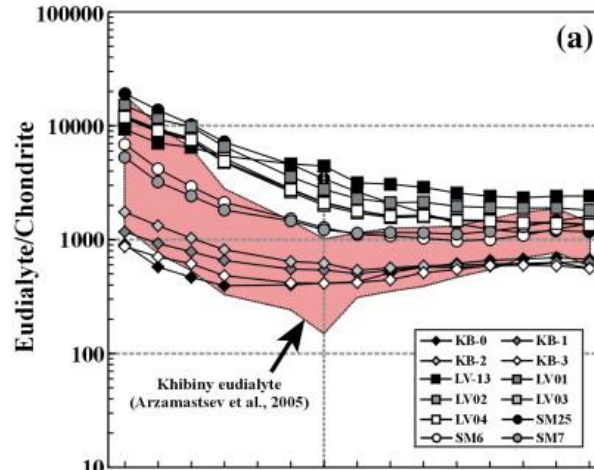
- Patrons parallèles, anom. négative Eu
- Teneurs croissantes vers skarns

Kipawa eudialyte

- Wu et al (2010) reported a comparative study of eudialyte composition in nepheline syenite from : Kipawa, Mt. St-Hilaire, Khibiny, Lovozero, Illimaussaq, Saima, Tamazeght, Poços de Caldas, Langesund Fjord.

- Among the 10 localities, Kipawa display unique REE patterns :
 - **Highest HREE** values (e.g. Yb = 4500 ppm, n=1)
 - Much lower LREE/HREE ratios
 - Negative Eu, Sr anomalies

Constantin and Fleury (2011, GAC-MAC, Ottawa) adapted from Wu et al. (2010)



Géochimie isotopique

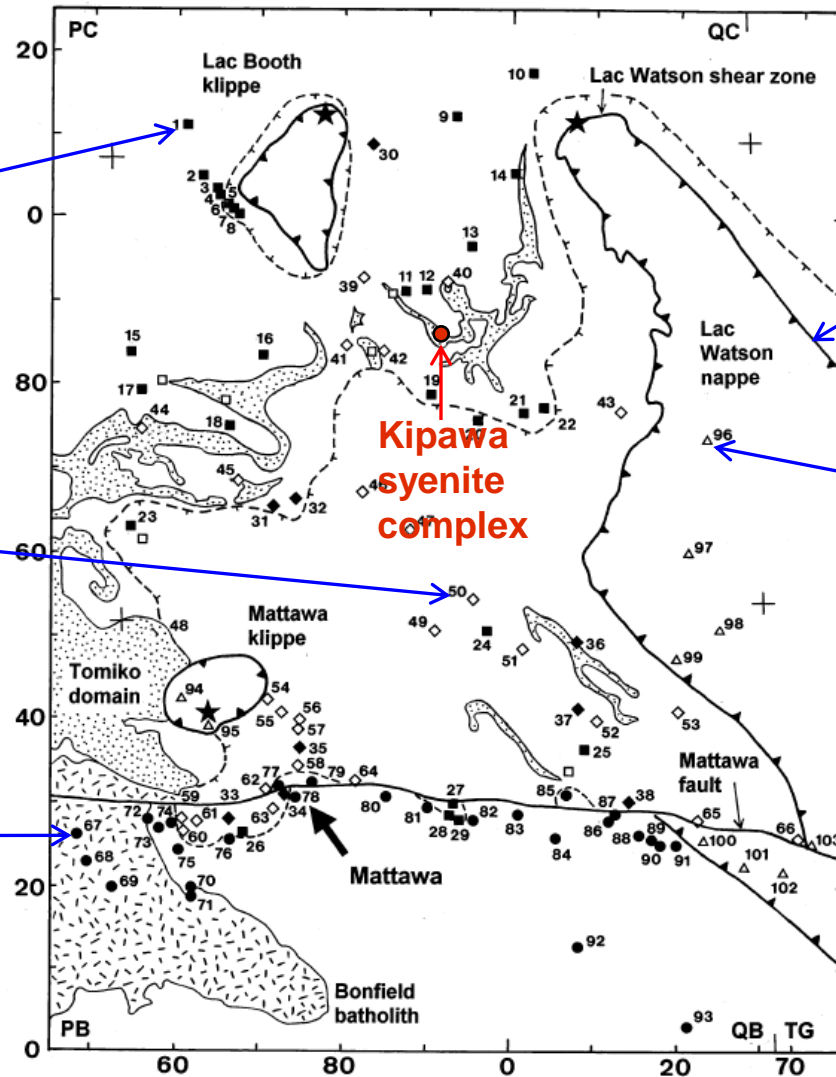
Sm-Nd

Nd model ages

Mostly Archean parautochthon
2.6-2.9 Ga, with some remelted
Archean gneiss 2.3-2.66 Ga

Proterozoic intrusions
1.9-2.4 Ga

Proterozoic gneiss
1.8-1.95 Ga



ABT
Northwest
directed
thrusts

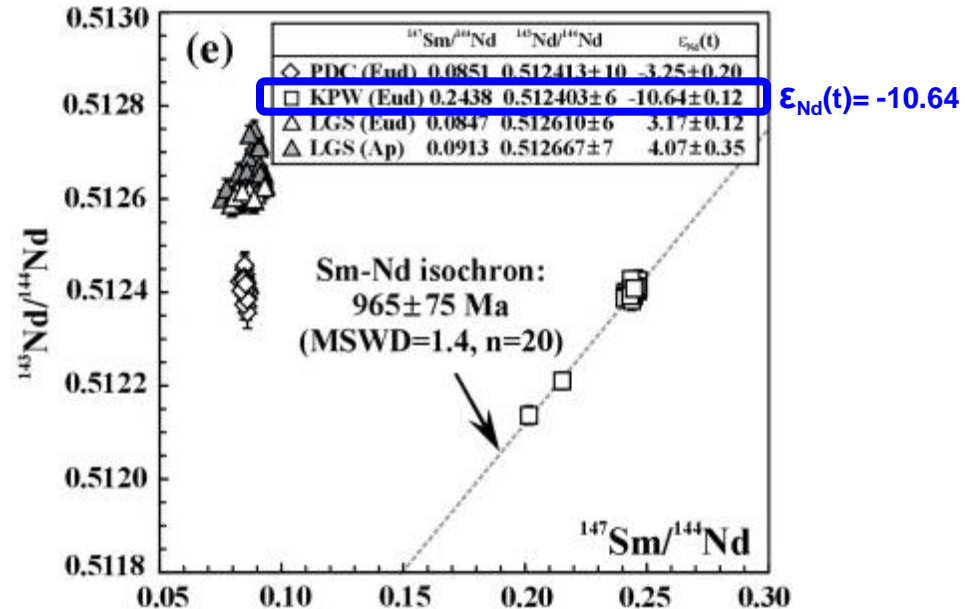
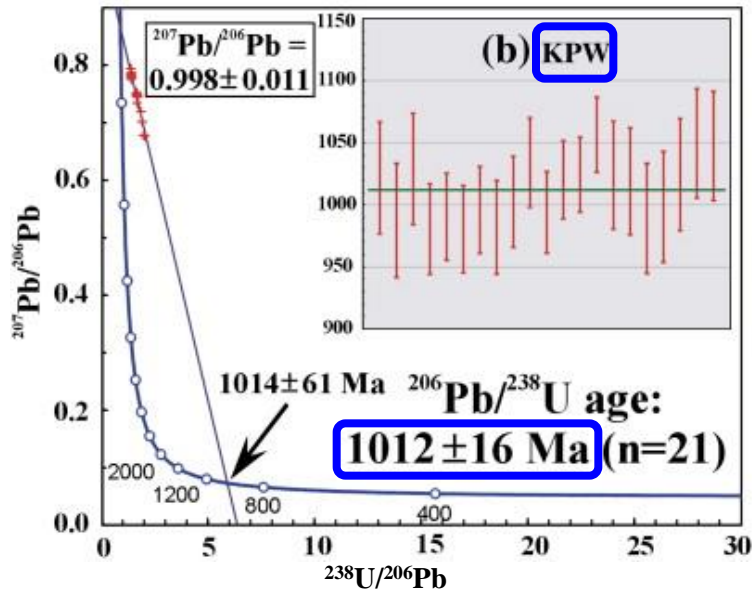
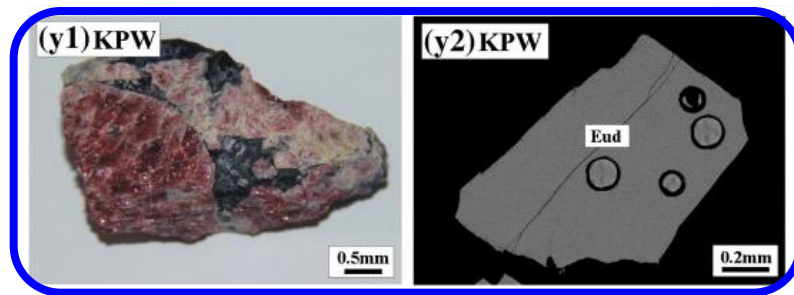
Gneiss in the
allochthon
1.5-1.8 Ga

Fig. 2. Map of the study area showing localities of analysed samples relative to 10 km UTM grid lines, overlain on a geological base map. Light stipple = quartzite-muscovite gneiss; coarse stipple = Bonfield batholith. Symbols: (■) = Archean grey gneisses; (□) = quartzite-muscovite gneiss; (◆) = remelted Archean gneiss; (◇) = Proterozoic intrusions emplaced into Archean gneiss; (●) = Paleoproterozoic gneiss south of Mattawa fault; (△) = gneisses in the allochthon with TDM model ages < 1.8 Ga. Stars indicate areas of retrogressed eclogite or dated coronitic metagabbro. Heavy lines with ticks indicate the location of the ABT proposed in the present study. Dashed lines with ticks indicates the location of the ABT proposed by Davidson (1998a,b) and Ketchum and Davidson (2000). Simple dashed line indicates proposed Archean-Proterozoic suture. Note that this map overlaps parts of several 100 km UTM grid squares; the boundary between the QB and TG squares is at 78°W longitude, where two major grid sections are juxtaposed.

Constantin and Fleury (2011, GAC-MAC, Ottawa) adapted from Dickin & Guo (2001) Prec Res 107: 31-43

Kipawa eudialyte

Dated by laser MC-ICP-MS at **1012 ± 16 Ma** (Wu et al 2010)

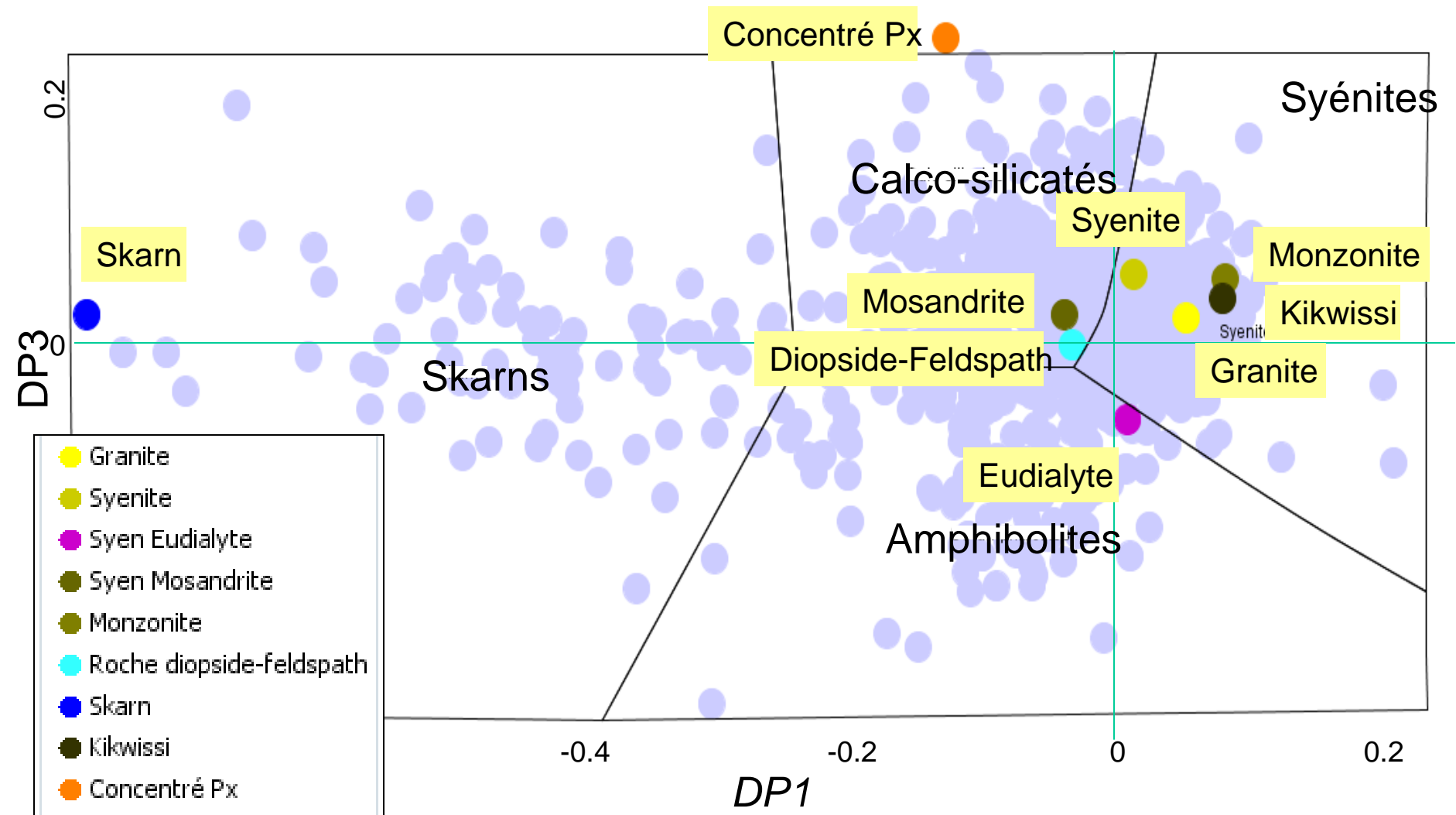


Similar, within error, to zircon from peralkaline skarn dated at **994 ± 2 Ma** (Currie & van Breemen 1996)

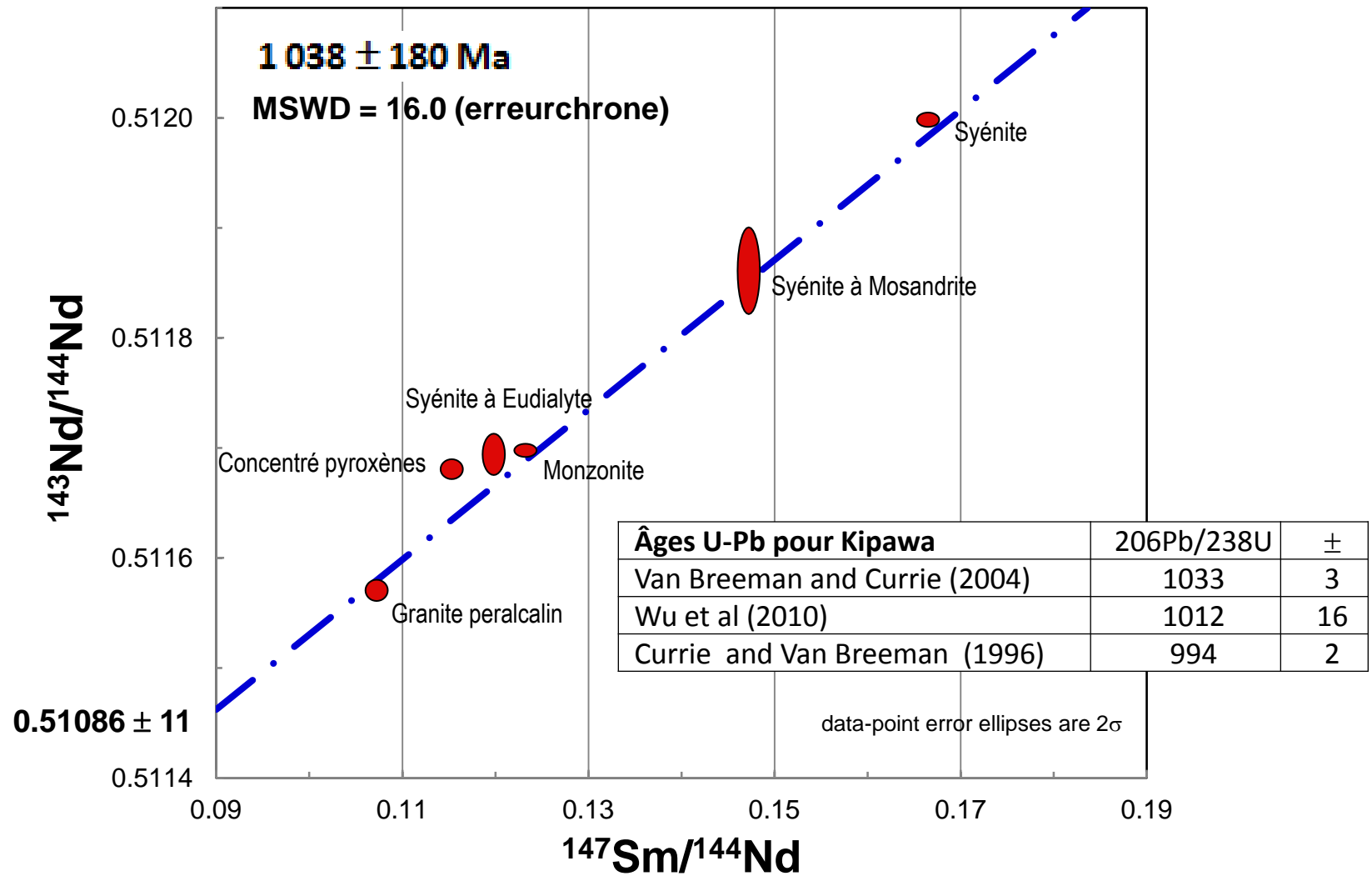


Zircon from Kipawa
Mindat.org

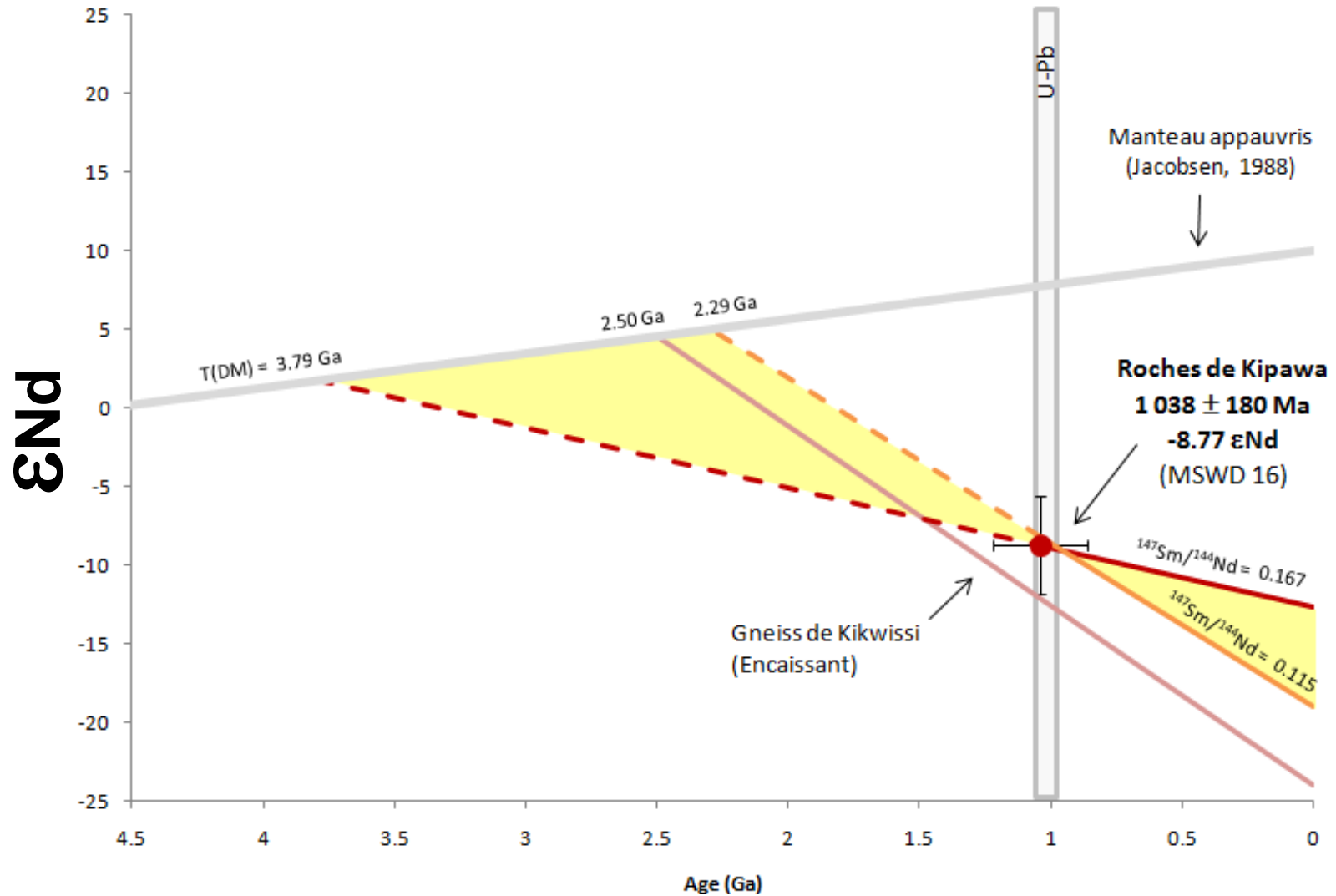
Représentativité des échantillons pour isotopes Sm-Nd



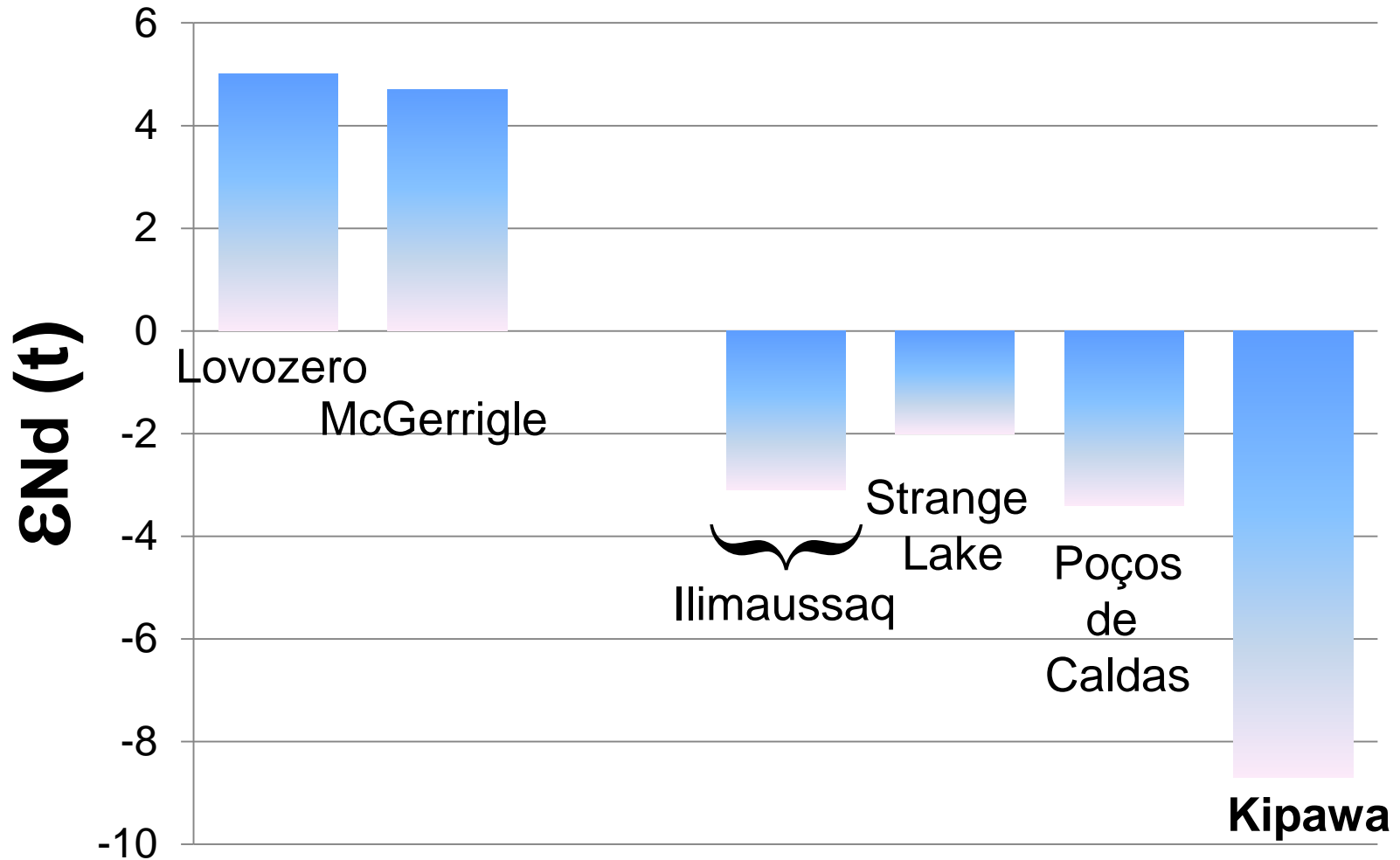
Isochrone



Isochrone



Comparaison avec d'autres complexes



Synthèse et modèle métallogénique préliminaire

Synthèse des travaux de maîtrise Frédéric Fleury

I. Analyse par discriminants

- 4 pôles chimiques
- Calco-silicatés et Amphibolites entre Syénites et Skarns
- Terres rares tirent vers le pôle skarnifère

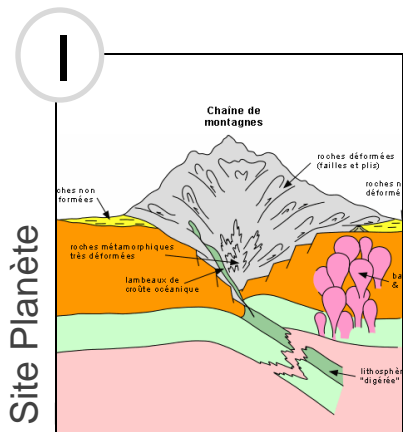
II. Diagrammes bivariants

- Tendance 1. “Syénitique” affecte tous les domaines sauf skarn
- Tendance 2. “Calcique” affecte Amphibolites + Calco-silicatés

III. Isotopes Sm-Nd

- Contamination crustale importante ($\epsilon Nd_t -8.7$)
- Âge d'uniformisation Sm-Nd correspond aux âges U-Pb sur zircon

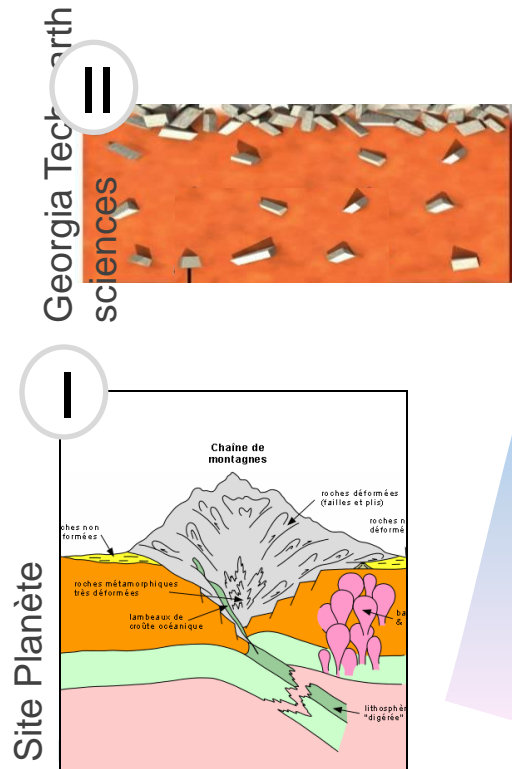
Modèle proposé



I. Fonte partielle

- ❖ Manteau métasomatisé (Na)
- ❖ Faible %*f*

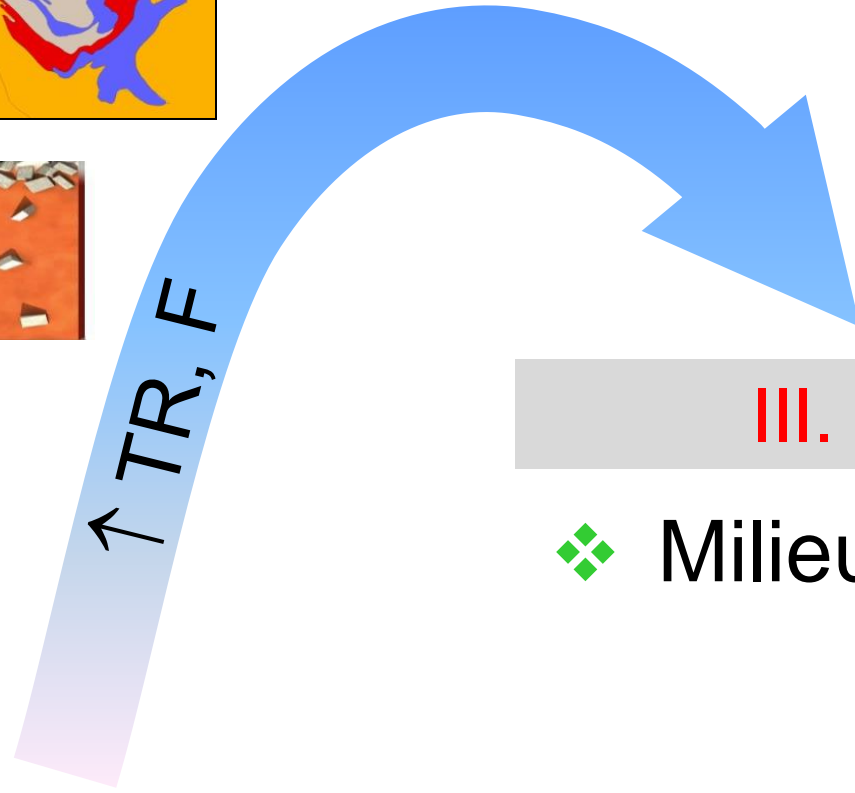
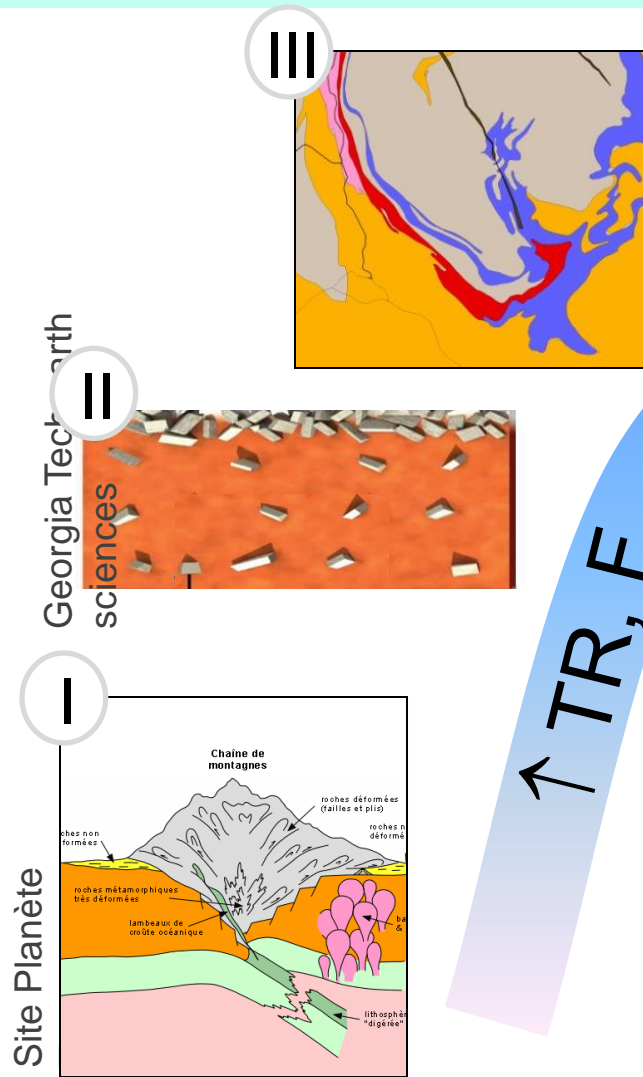
Modèle proposé



II. Cristallisation

- ❖ Enrichissement du liquide en TR

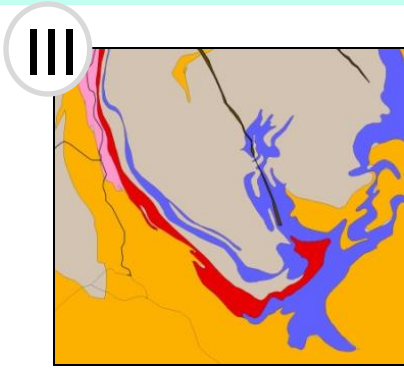
Modèle proposé



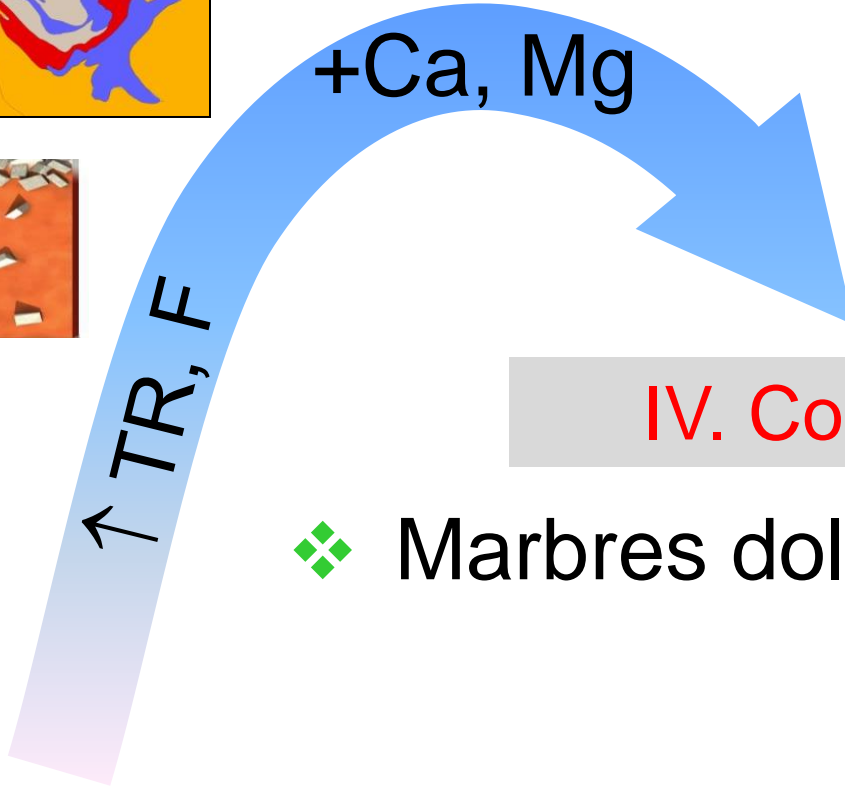
III. Injection

❖ Milieu dynamique

Modèle proposé



+Ca, Mg

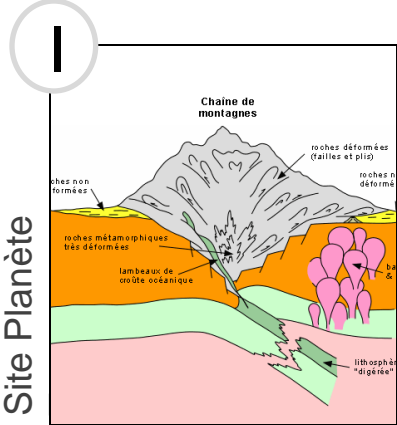


IV. Contamination

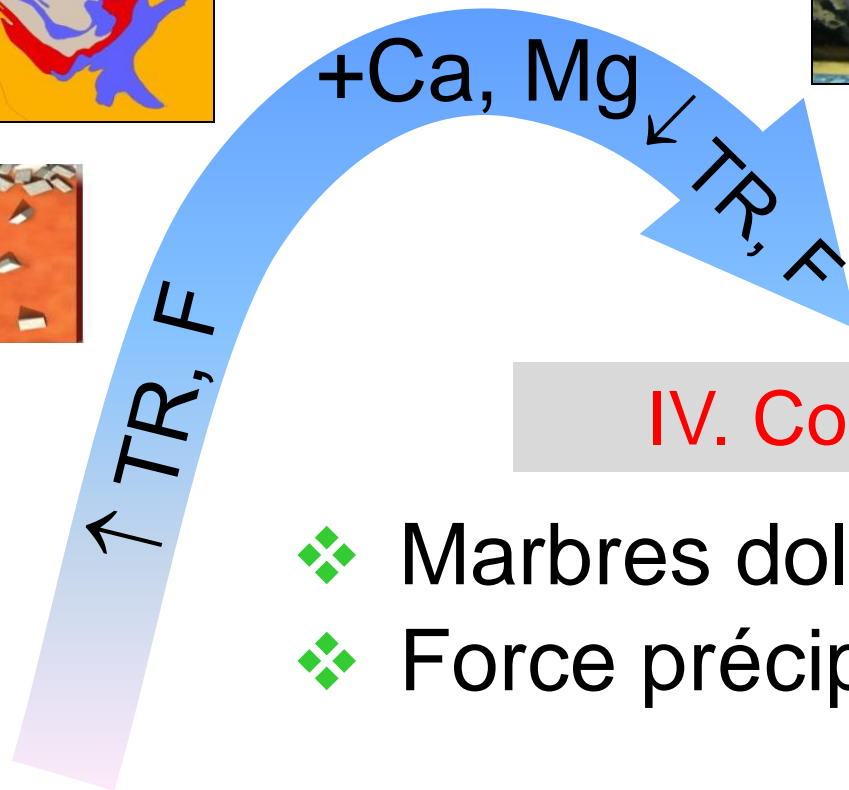
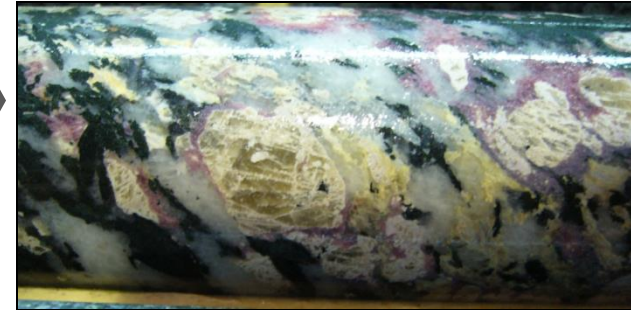
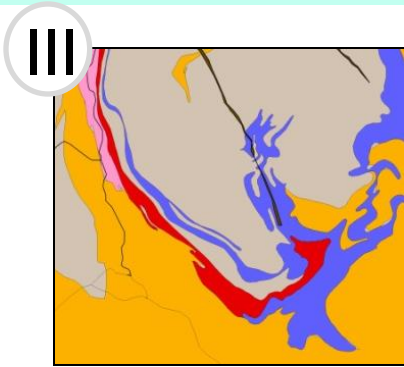


Marbres dolomitiques

Georgia Tech Earth sciences



Modèle proposé



IV. Contamination

- ❖ Marbres dolomitiques
- ❖ Force précipitation des TR

