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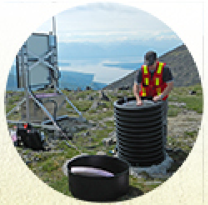


Geological Survey of Canada
Scientific Presentation 129

Mineralogical and geochemical characterization of the Kipawa syenite complex, Quebec: implications for rare-earth element deposits

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Abstract

The Kipawa rare-earth element (REE) deposit is located in the Parautochton zone of the Grenville Province 55 km south of the boundary with the Superior Province. The deposit is part of the Kipawa syenite complex of peralkaline syenites, gneisses, and amphibolites that are intercalated with calc-silicate rocks and marbles overlain by a peralkaline gneissic granite. The REE deposit is principally composed of eudialyte, mosandrite and britholite, and less abundant minerals such as xenotime, monazite or euxenite. The Kipawa Complex outcrops as a series of thin, folded sheet imbricates located between regional metasediments, suggesting a regional tectonic control. Several hypotheses for the origin of the complex have been suggested: crustal contamination of mantle-derived magmas, crustal melting, fluid alteration, metamorphism, and hydrothermal activity. Our objective is to characterize the mineralogical, geochemical, and isotopic composition of the Kipawa complex in order to improve our understanding of the formation and the post-formation processes, and the age of the complex.

The complex has been deformed and metamorphosed with evidence of melting-recrystallization textures among REE and Zr rich magmatic and post magmatic minerals. Major and trace element geochemistry obtained by ICP-MS suggest that syenites, granites and monzonite of the complex have within-plate A2 type anorogenic signatures, and our analyses indicate a strong crustal signature based on TIMS whole rock Nd isotopes. We have analyzed zircon grains by SEM, EPMA, ICP-MS and MC-ICP-MS coupled with laser ablation (Lu-Hf). Initial isotopic results also support a strong crustal signature. Taken together, these results suggest that alkaline magmas of the Kipawa complex/deposit could have formed by partial melting of the mantle followed by strong crustal contamination or by melting of metasomatized continental crust. These processes and origins strongly differ compare to most alkaline complexes in the world. Additional TIMS and LA-MC-ICP-MS analyses are planned to investigate whether all lithologies share the same strong crustal signature.

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Mineralogical and geochemical characterization of the Kipawa syenite complex, Quebec: implications for rare-earth element deposits

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Geological background : The Grenville orogen

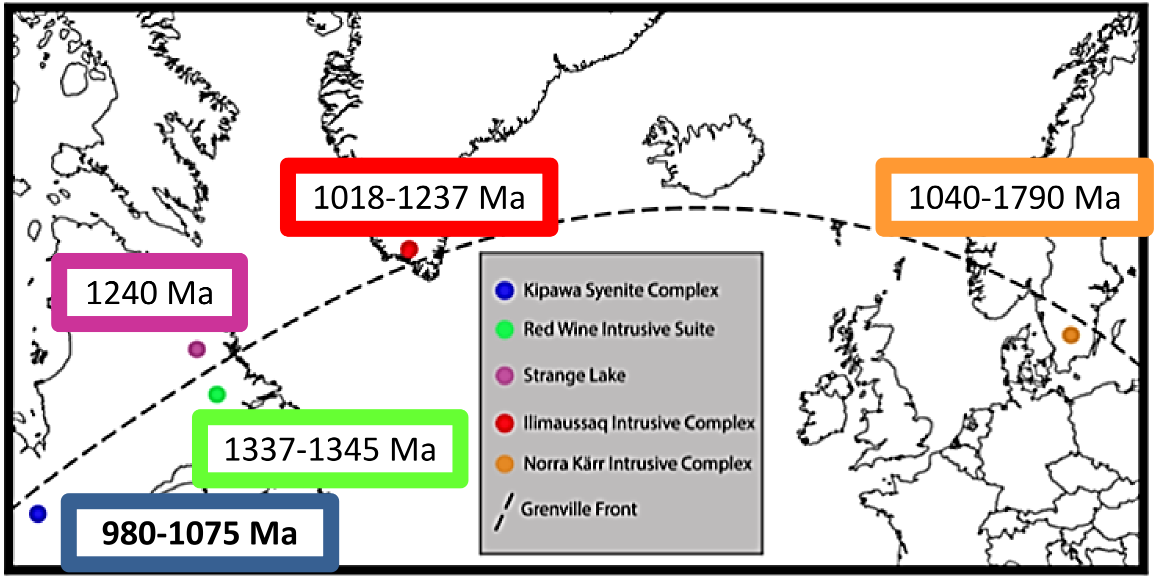
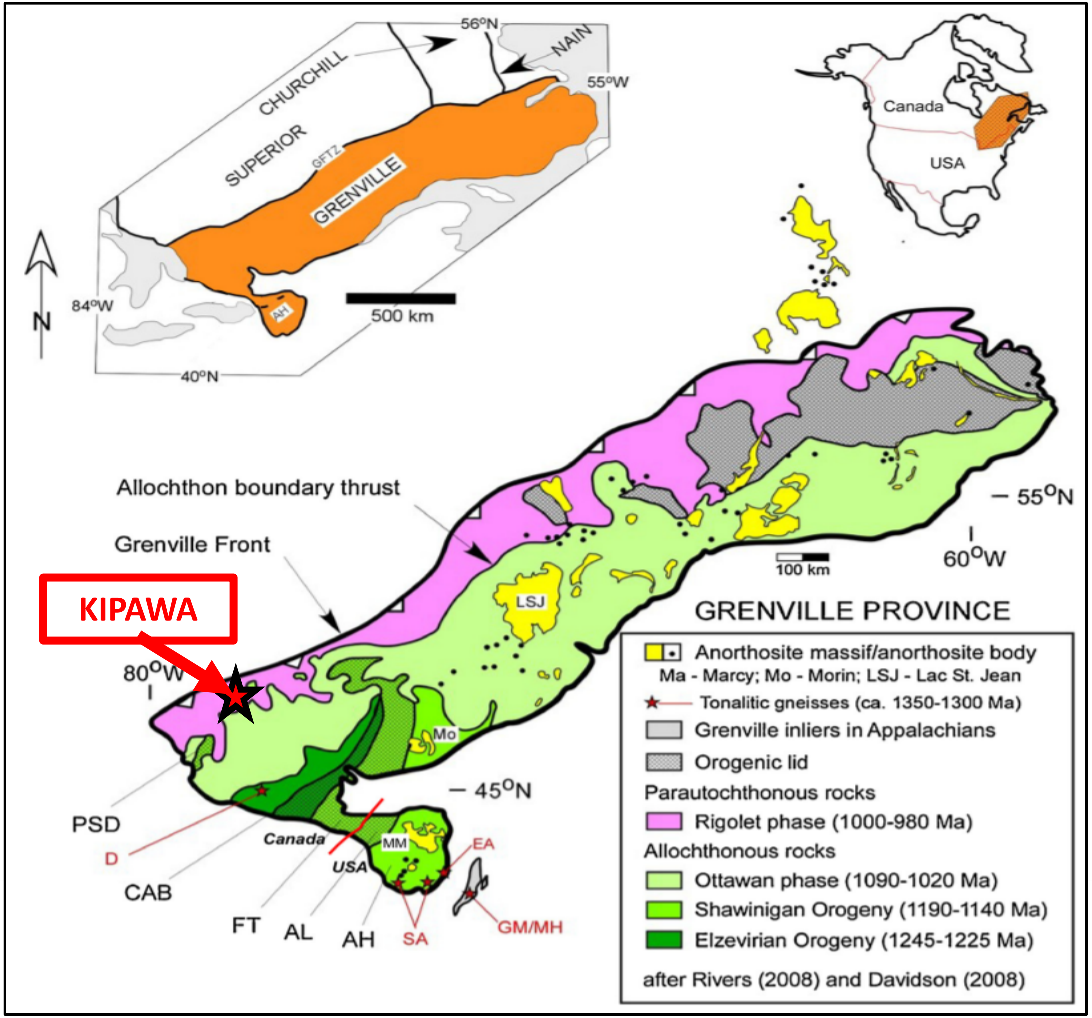


***Fig. 1 :** Location of Proterozoic peralkaline complexes in relation to the Grenville tectonic front (Leich, 2020, modified from Currie and Van Breemen, 1996). Ages: this study, Curtis and Currie (1981), Gandhi et al. (1988), Miller et al. (1997), Sjöqvist et al. (2017), Borst et al. (2018).*



- The Kipawa syenite complex (KSC) is located in the Parautochthonous zone of the Grenville province

Fig. 2 : *Location of the Grenville province with fundamental subdivisions (after Rivers, 2008, 2012) and anorthosite bodies (after Davidson, 2008). Figure from Valentino et al. (2019).*

Geological background : Regional geology

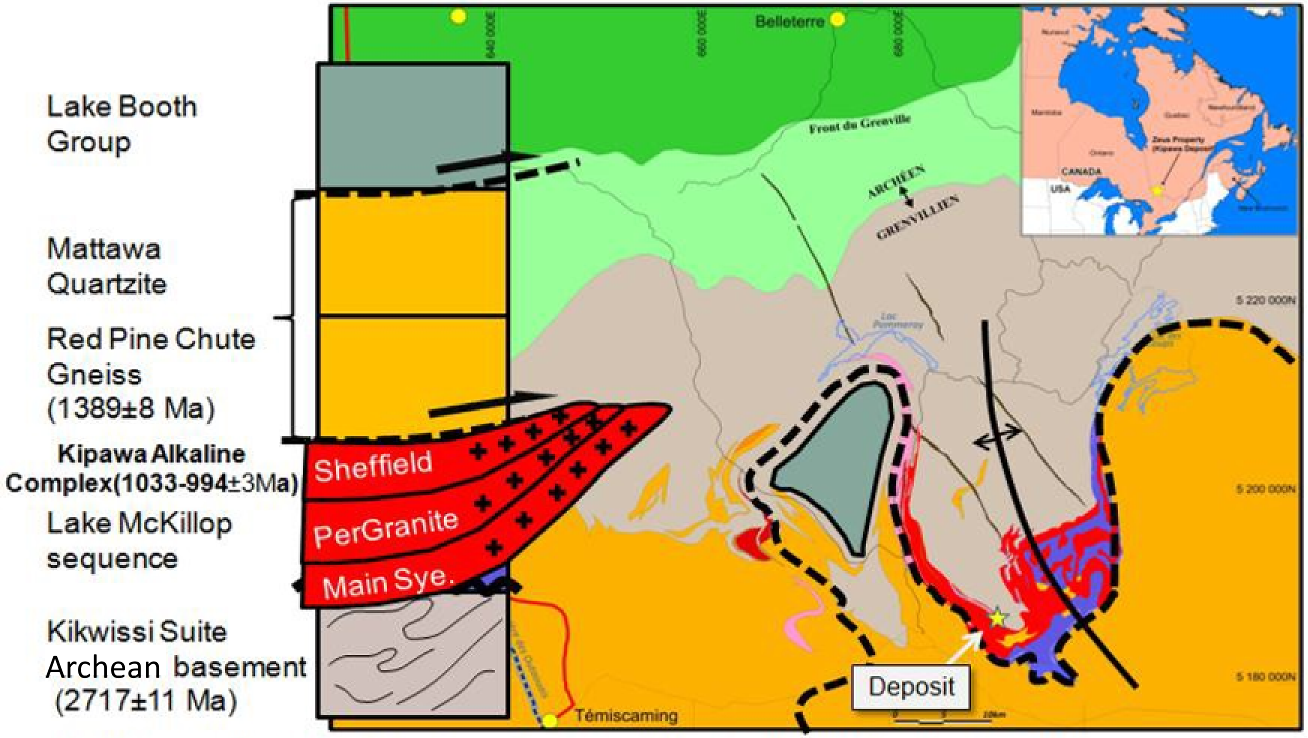
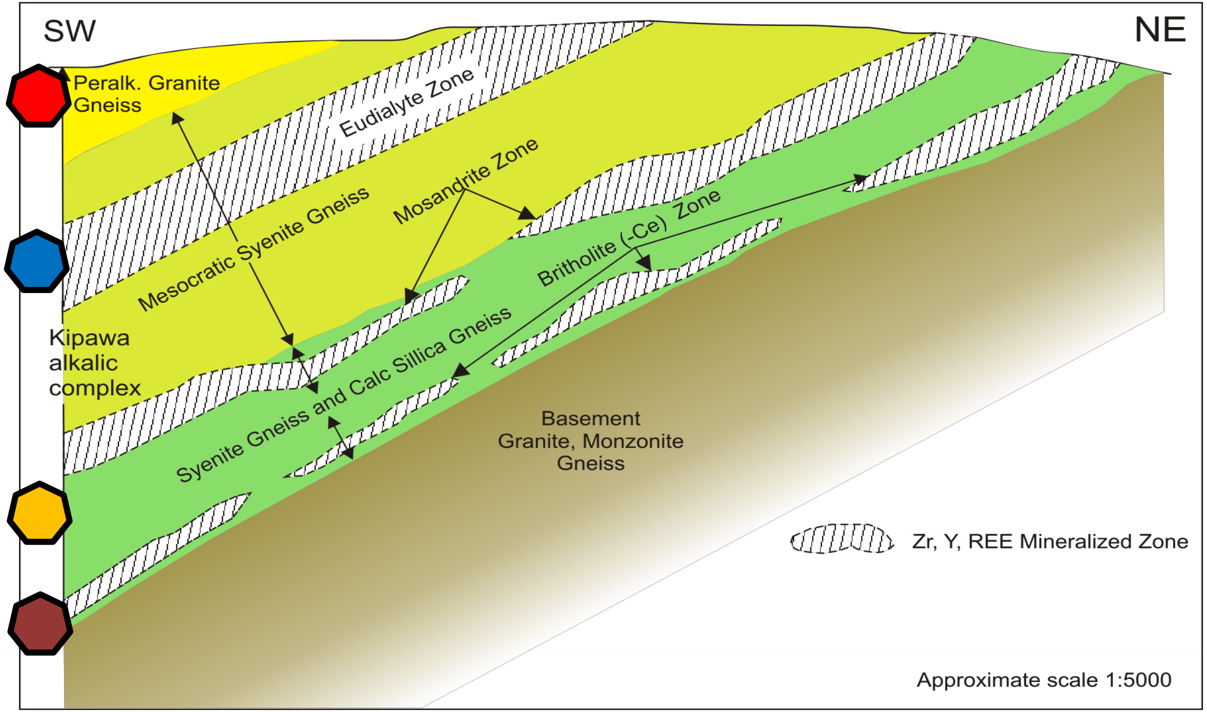


Fig. 3 : *Map of the kipawa Complex with the regional stratigraphic column (Saucier et al., 2013 after Allan, 1992; Van Breemen and Currie, 2004). U-Pb ages on zircon : Currie and Van Breemen (1996) and Van Breemen and Currie (2004).*

Geology of the Kipawa syenite complex REE-deposit



4 lithologic domains (heptagons)

3 mineralized zones : “Eudialyte zone”, “Mosandrite zone” and “Britholite zone”

The KSC is a peralkaline complex with the presence of eudialyte minerals, rinkite minerals, vlasovite = **Agpaitic rocks** (Marks and Markl, 2017).

Fig. 4 : *Schematic stratigraphic section southwest-northeast of the KSC with the three main mineralization zones.*

Granitoid lithologies (70 % of Kipawa rocks)

$Na_2O + K_2O$ versus SiO_2 for granitoid lithologies : see Appendix 1

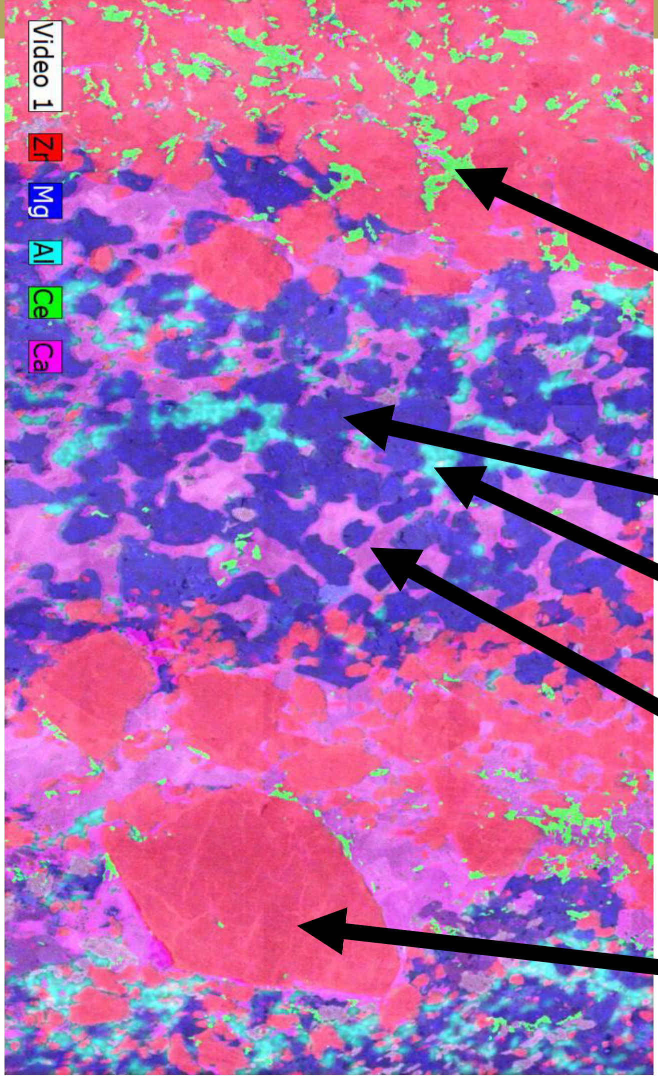
Hyperalcaline granites, pegmatites

Mesosyenites, leucosyenites, melanosyenites

Syenites (traces in calc-silicate domain), mafic syenites

Monzo-gneiss, Archean granites

Example of mesosyenite with REE-Zr mineralization (μ-XRF image, field of view is 2.6 cm x 4.6 cm)



Rinkite group minerals
(green minerals)

Aegirine and amphibole
(blue minerals)

K-feldspar
(cyan minerals)

Plagioclase
(pale pink minerals)

Eudialyte
(dark pink minerals)

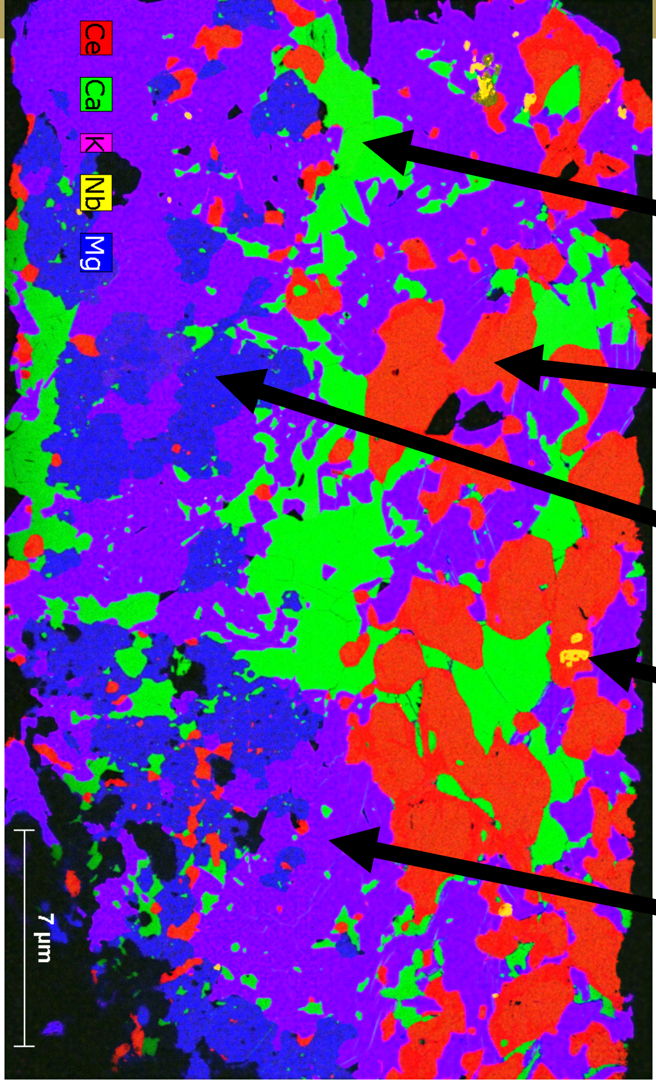
Calc-silicate rocks and carbonate lithologies (20%)

- Group of lithologies rich in Si-Ca, silicates-carbonates or only carbonates :

  - Rocks rich in diopside, feldspars and/or phlogopite
  - Rocks rich in calcite and feldspars, amphiboles or pyroxenes
  - Massive feldspar rocks
  - Marbles
  - Skarns
  - Veins of calcite, micas and fluorite

- Theses lithologies are intercalated with syenites.

Example of Skarn (image µ-XRF, field of view is 2.6 cm x 4.6 cm)



Calcite
(green minerals)

Britholite-(Ce)
(orange minerals)

Diopside
(blue minerals)

Pyrochlore, euxenite and aeschynite group minerals
(yellow minerals)

Phlogopite
(purple minerals)

Chemical classification : Whole rock major, minor and trace elements for Kipawa granitoids

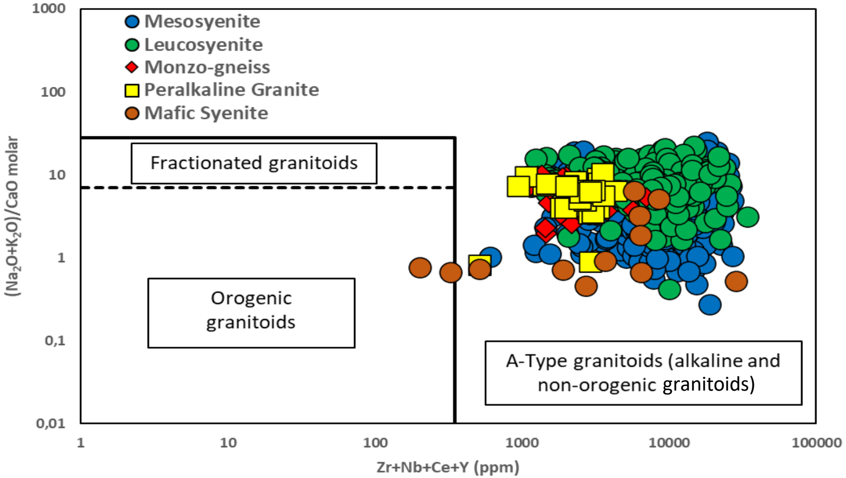


Fig. 5 : *$(Na_2O + K_2O)/CaO$ versus Zr + Nb + Ce + Y of A-Type granite with Kipawa granitoids (after Whalen et al., 1987).*

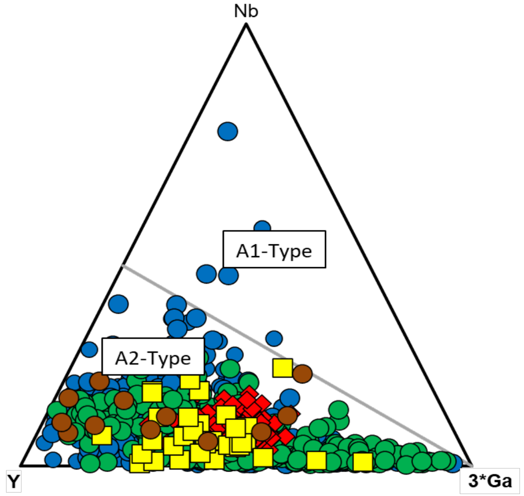
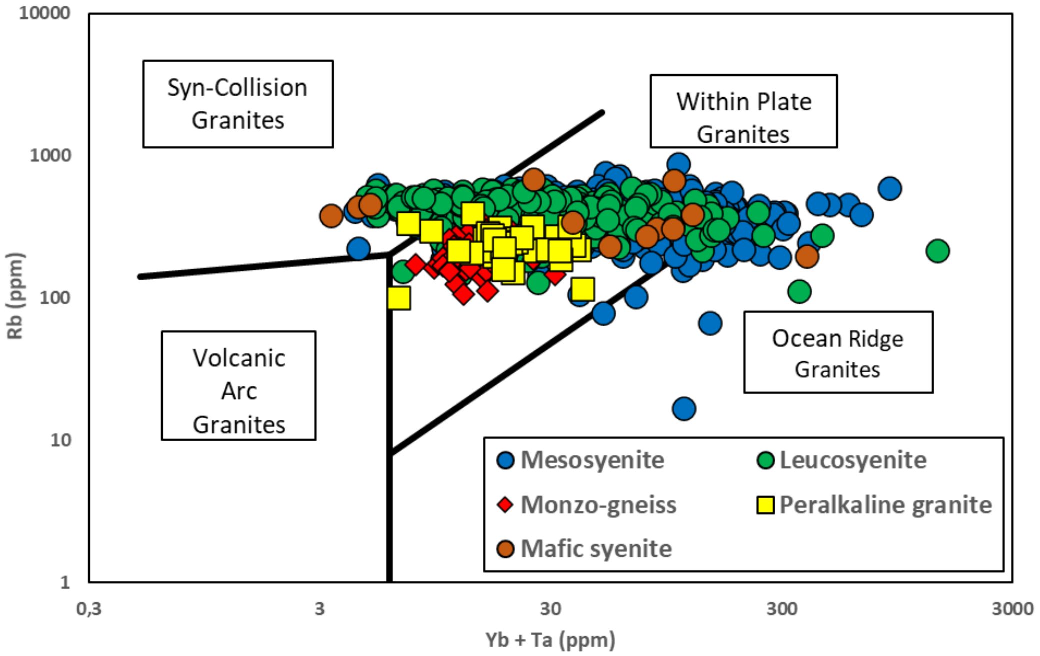
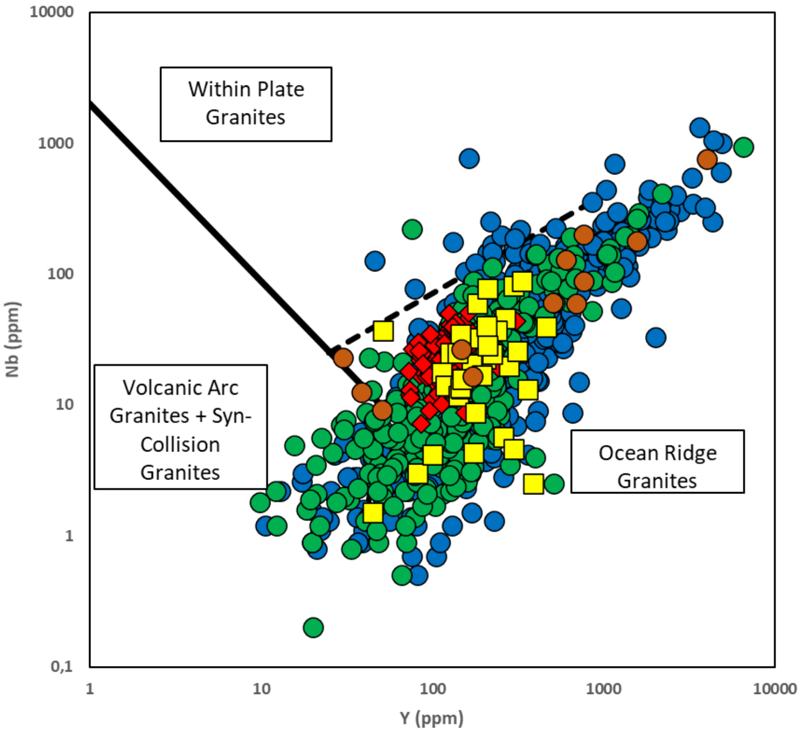


Fig. 6 : *Ternary diagram Y-Nb-Ga for A-type granitoids (after Eby, 1992).*

Granitoids and syenitoids of the Kipawa complex are A-type granitoids, anorogenic and/or alkaline, and A2-type granitoids. A2-type granites are derived by partial melting processes and are supposed to be related to average continental crust or arc type-sources (Eby, 1992).

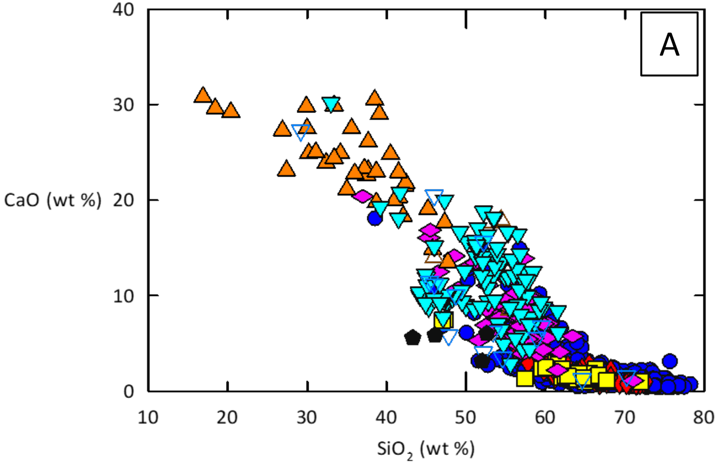




Trace elements compositions show KSC granitoids were emplaced in intraoceanic, intracontinental or attenuated continental lithosphere (Pearce et al., 1984).

Fig. 7 and 8 : *Rb versus Yb + Ta (Fig. 7, left) and Nb versus Y (Fig. 8, right) discriminant diagrams for granitoids, with KSC granitoids (after Pearce et al., 1984).*

Chemical classification: Whole rock major elements for all Kipawa rocks



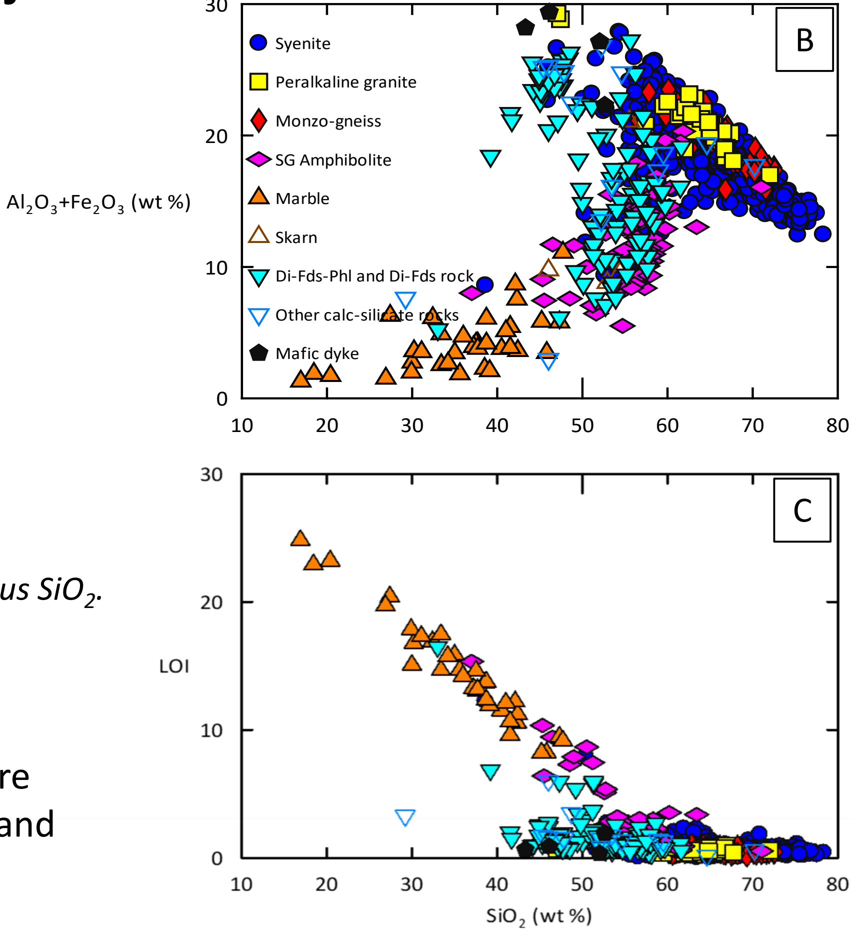


***Fig. 9 :** A) CaO versus SiO$_2$, B) Al$_2$O$_3$ + Fe$_2$O$_3$ versus SiO$_2$, and C) LOI versus SiO$_2$.*

Silver-grey (SG) amphibolites: Mix between syenites (or old syenites) and/or marbles or fluid's flux (deformation).

Diopside-, feldspars-, and/or phlogopite-rocks: Mix, but more importance of the marble pole, except fluids (melt down?) and rich in V (see Appendix 3), Ni, and Cr.

(See also Appendix 2 for additional diagrams).

Nd isotopes

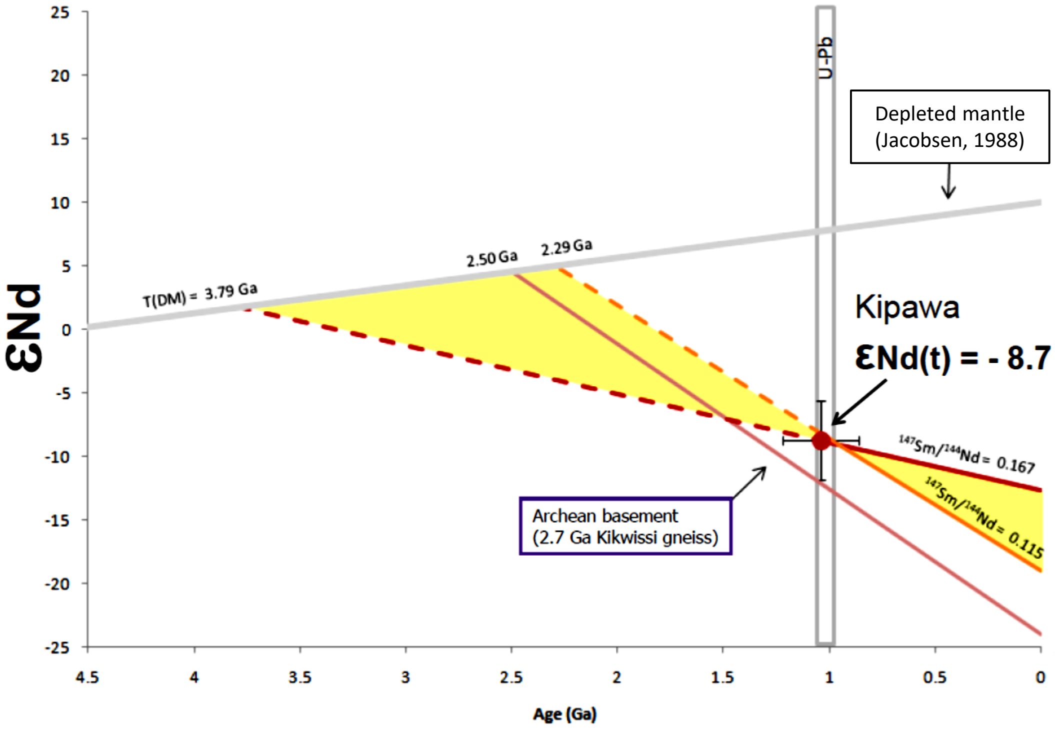
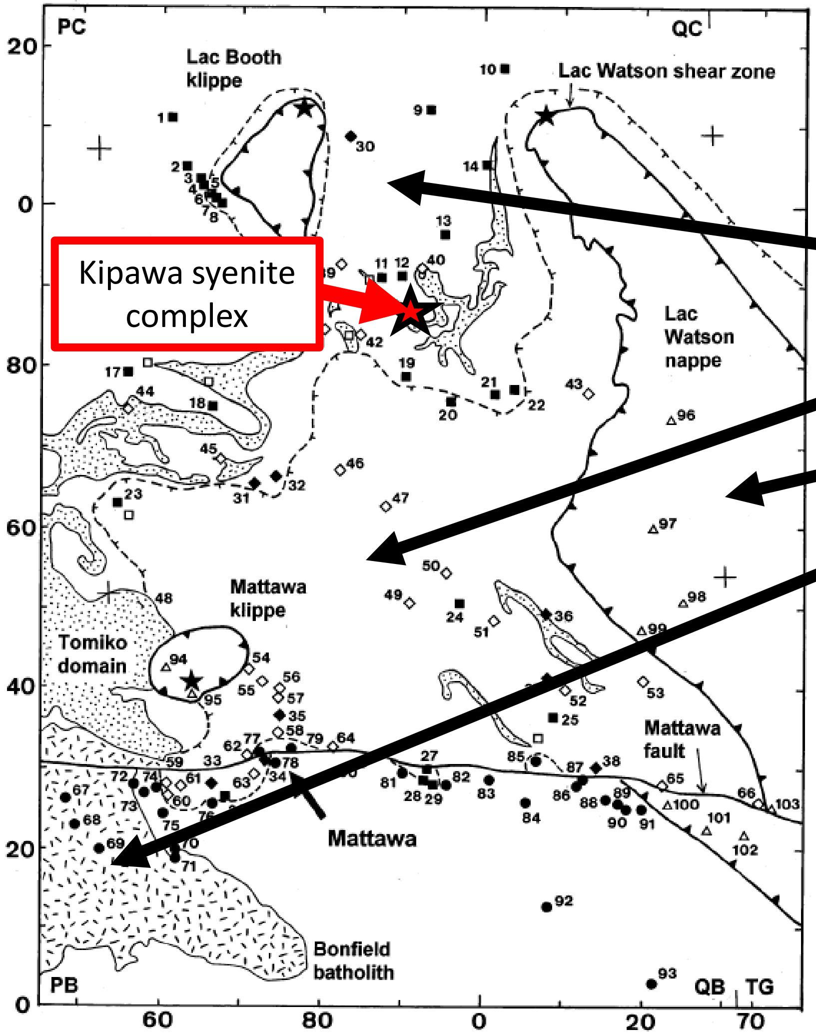


***Fig. 10 :** Nd isotopic signatures for KSC rocks.*

- 7 whole rock samples (syenites, granite, monzonite, marble, skarn) and 1 pyroxene concentrate
- Age of 1023 ± 36 Ma (not shown)
- εNd suggest a strong crustal signature

Nd model ages



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

Gneiss in the allochthon 1.5-1.8 Ga

Proterozoic intrusions 1.9-2.4 Ga

Proterozoic gneiss 1.8-1.95 Ga

Fig. 11 : *Nd model age map of the Mattawa area in the Grenville Province, with the location of the Kipawa syenite complex (after Dickin and Guo, 2001). Light stipple = quartzite–muscovite gneiss; coarse stipple = Bonfield batholith. Symbols: Black square = Archean grey gneiss; white square = quartzite-muscovite gneiss; black diamond = remelted Archean gneiss; white diamond = Proterozoic intrusions emplaced into Archean gneiss; black ring = Paleoproterozoic gneiss south of the Mattawa fault; white triangle = gneiss in the allochthon with TDM model ages < 1.8 Ga.*

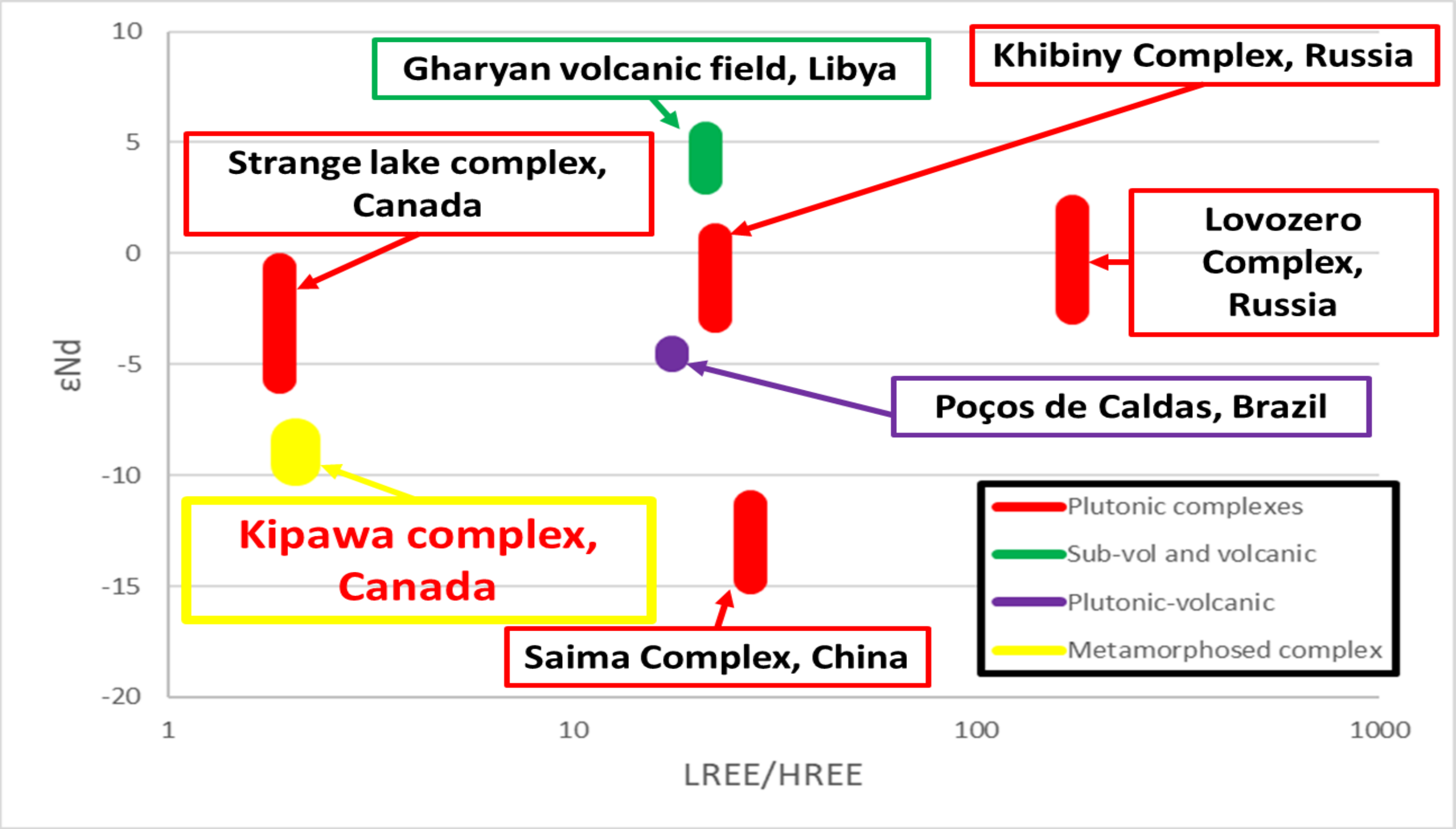


Fig. 12 : *εNd versus HREE enrichment for Kipawa complex and other peralkaline agpaitic complexes. Data from : Shea (1992), Ulbrich et al. (2003), Kramm and Kogarko (1994), Lustrino et al. (2012), Zhu et al. (2016), Siegel et al. (2017).*

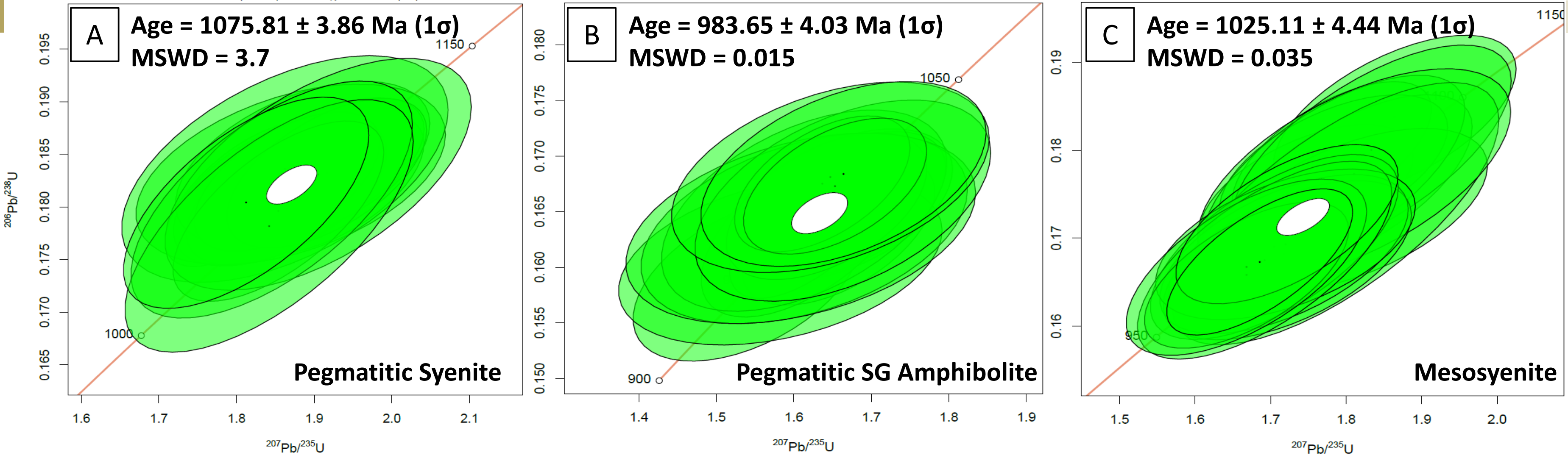


Fig. 13 : *Concordia age of crystals of zircon from Kipawa syenite complexe : (A) Two coarse crystals of a pegmatite sample from the specimen pit (n = 17), (B) one crystal of a pegmatitic silver-grey amphibolite in calc-silicate lens (n = 16) and (C) four crystals of a mesosyenite in contact with a calc-silicate lens.*

We obtained three more concordia ages from :

- Three fine crystals from the pegmatitic syenite : 1027.72 ± 4.20 Ma (1σ, MSWD = 0.15)
- Two coarse crystals from a diopside-feldspars-phlogopite rock in contact with a marble (n = 23) : 1035.13 ± 2.83 Ma (1σ, MSWD = 0.34)
- Six fine crystals from a mix between a felsic silver-grey amphibolite and a diopside-feldspars rock (n = 26) : 1025.83 ± 2.86 Ma (1σ, MSWD = 0.031)

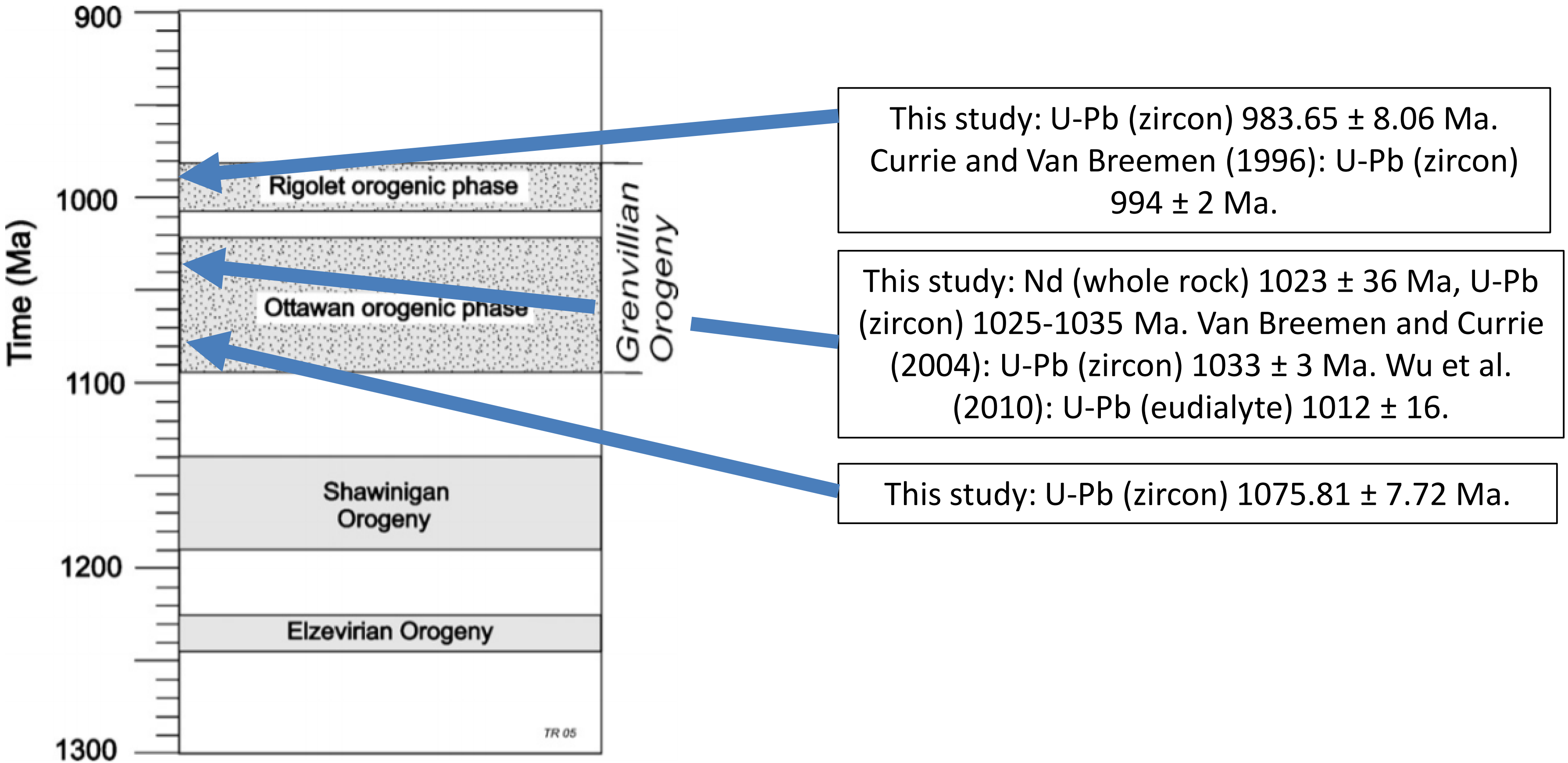


Fig. 14 : *Time scale showing middle to late Mesoproterozoic, pre-Grenvillian accretionary events and the late Mesoproterozoic to early Neoproterozoic, collisional Grenvillian Orogeny (Rivers, 2008), with Kipawa age (Currie and van Breemen, 1996; Van Breemen and Currie, 2004; Wu et al., 2010; and this study).*

Lu-Hf isotope in Kipawa zircon crystals

Table 1 : *εHf and Hf model age for Kipawa crystals of zircon, age model T(DM) and T(DM)^C calculated with f(Lu/Hf).*

Zircon (x = crystals, n = number of analysis)	εHf (2σ)	T(DM) in Ma (2σ)	T(DM)^C in Ma (2σ)
Pegmatitic syenite (x = 6, n = 80)	-28.22 ± 4.14	2091.13 ± 183.69	2767.25 ± 299.76
Pegmatitic silver-grey amphibolite (x = 2, n = 22)	-26.53 ± 2.73	1994.09 ± 185.67	2608.82 ±302.50
Mesosyenite (x = 12, n = 36)	-29.11 ± 2.57	2039.63 ± 116.03	2683.74 ± 189.49
Diopside-feldspars-phlogopite rock (x = 2, n = 28)	-27.06 ± 5.29	2065.36 ± 213.15	2725.18 ± 347.63
Mix silver-grey amphibolite and diopside-feldspars rock (x = 4, n = 21)	-26.21 ± 4.70	1972.06 ± 199.89	2572.71 ± 326.06

Summary

- Major and trace elements show that Kipawa syenite complex is an A2-granitoid complex, derived by partial melting processes, emplaced in intraplate field.
- Nd and Hf isotope signatures are strongly negative, indicating a crustal source and/or remelting of a precursor complex.
- Silver-grey amphibolites and calc-silicate rocks, which could be interpreted as a mix of between syenites and marbles, with differents processes.
- U-Pb analysis on zircon crystals show three ages. They could be interpreted as the formation of the complex (1075 to 1035-1025 Ma), followed by the Ottawan orogenic phase, and a metamorphic phase (980 Ma), the Rigolet orogenic phase.

Acknowledgments

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- M. Constantin acknowledges funding from le Fonds de Recherche Nature et Technologies du Québec - Programme de recherche en partenariat sur le développement durable du secteur minier (grant no. 2017-MI-202265)
- We would like to thank Dr. André Poirier (UQAM-Geotop) for his Assistance with the Lu-Hf and U-Th-Pb isotopic analysis
- Thanks are also extended to Dr. Anne-Aurélie Sappin (Geological Survey of Canada) for reviews that helped improve the final version of this contribution.

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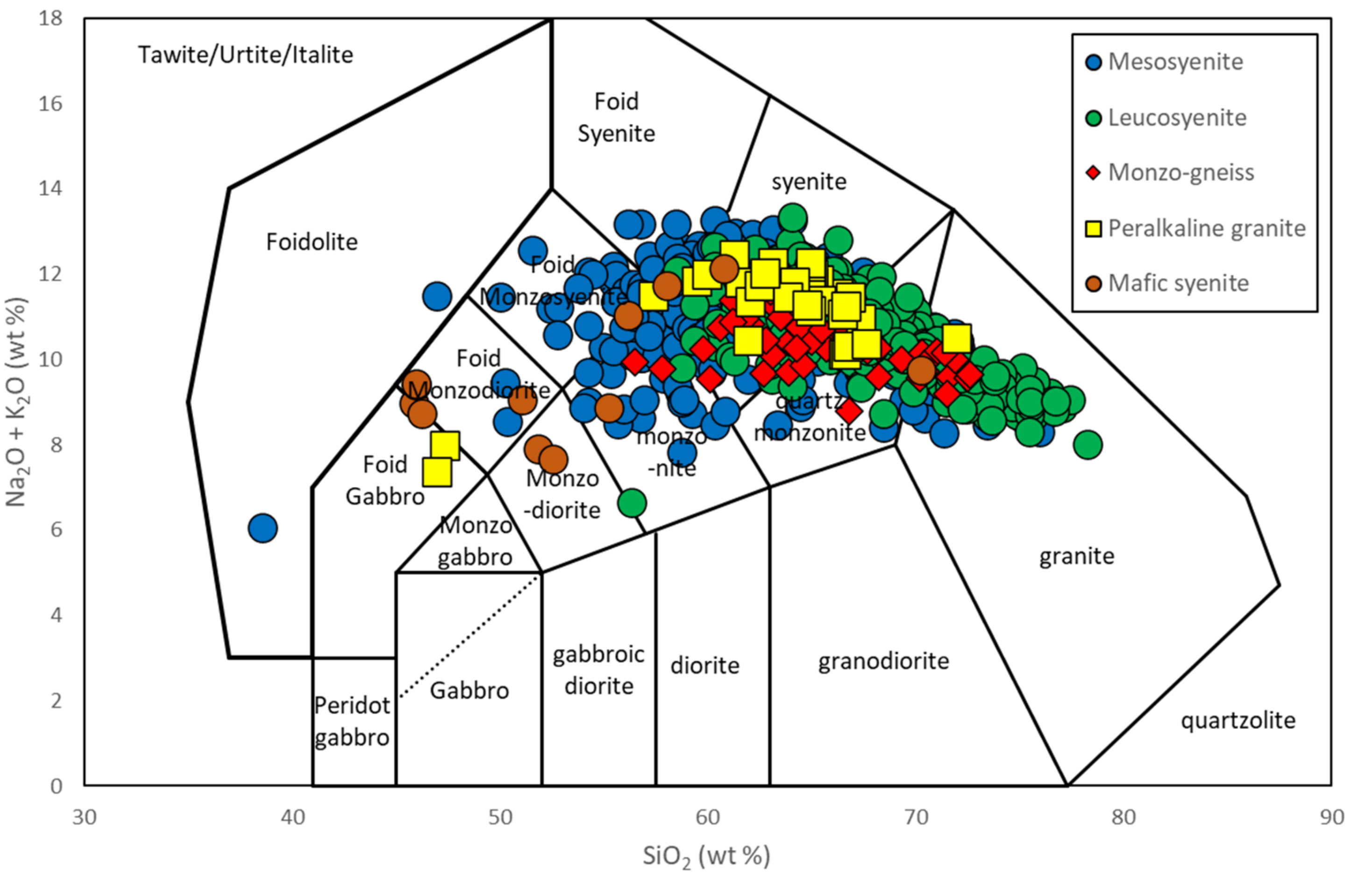
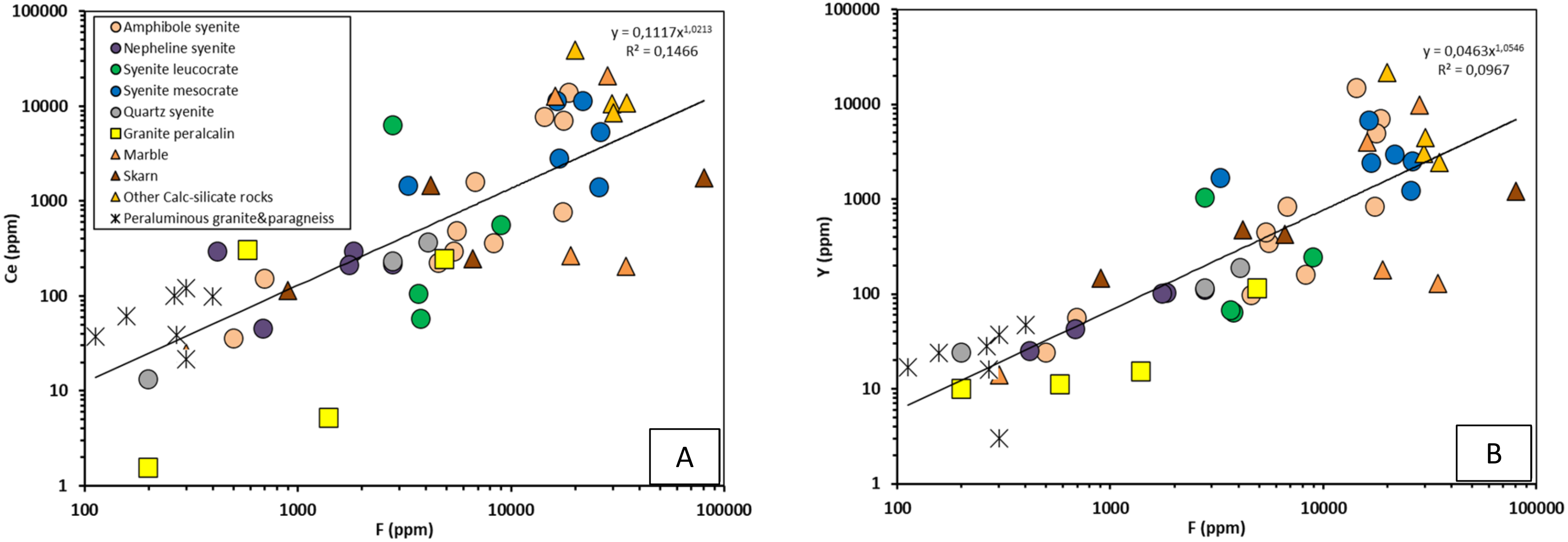
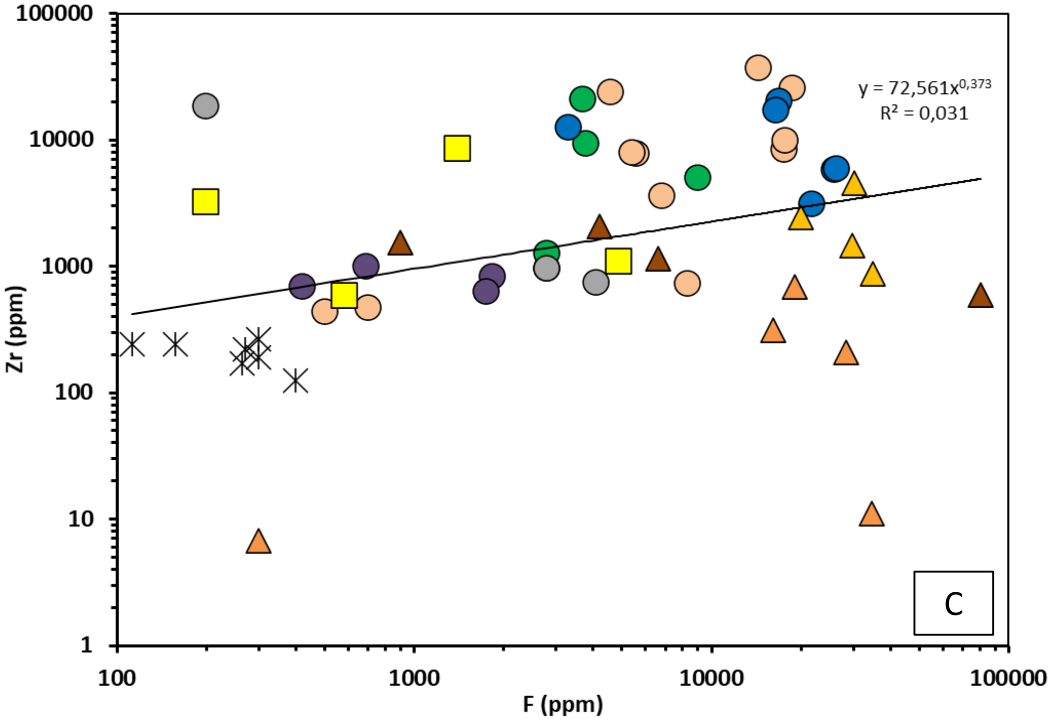
Annexes



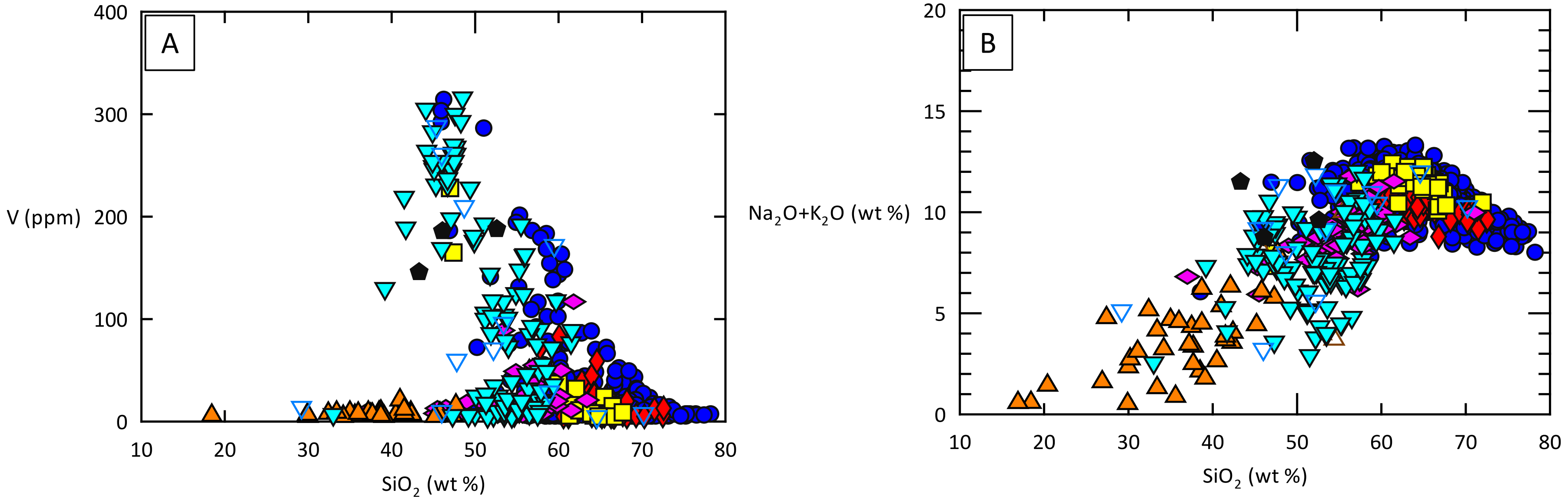
***Appendix 1 :** Chemical classification of plutonic rocks (after Middlemost, 1994). Database from Matamec.*



Appendix 2 : *A) Ce versus F and B) Y versus F for Kipawa rocks. Data from this study and van Breemen and Currie (2004).*

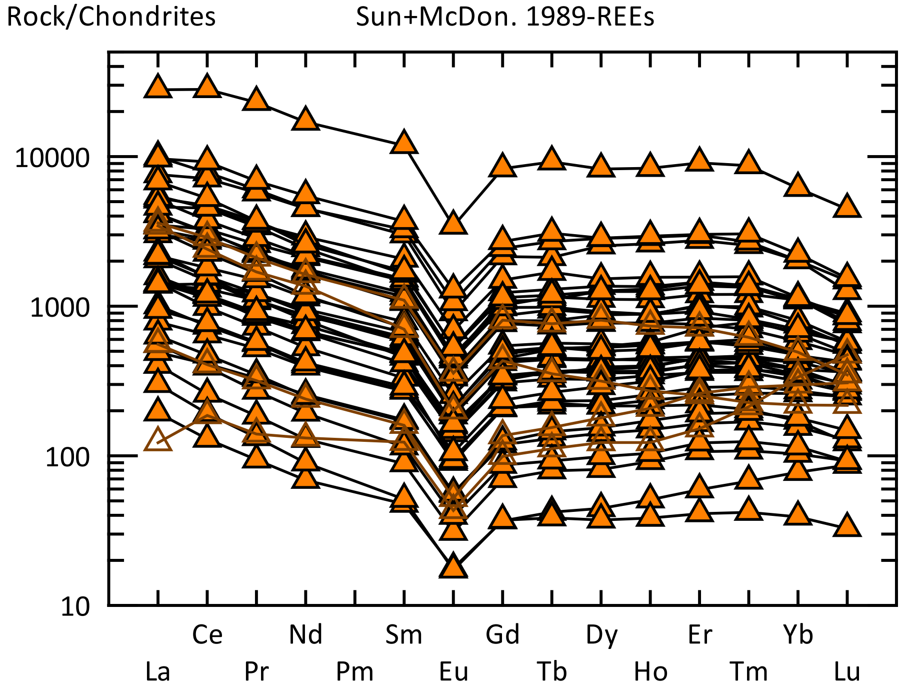


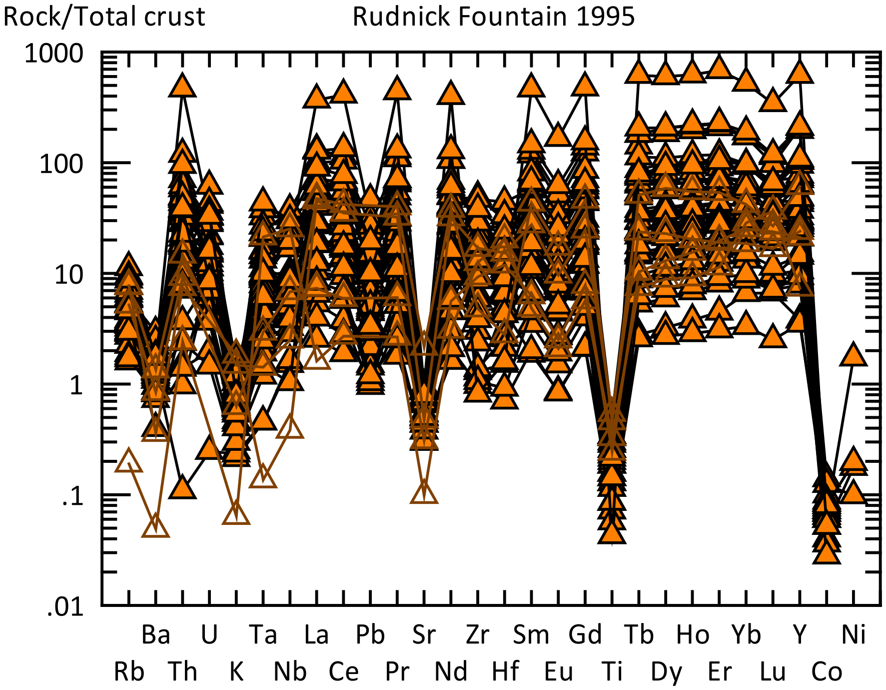
Appendix 2 : *C) Zr versus F for Kipawa rocks. Data from this study and van Breemen and Currie (2004).*



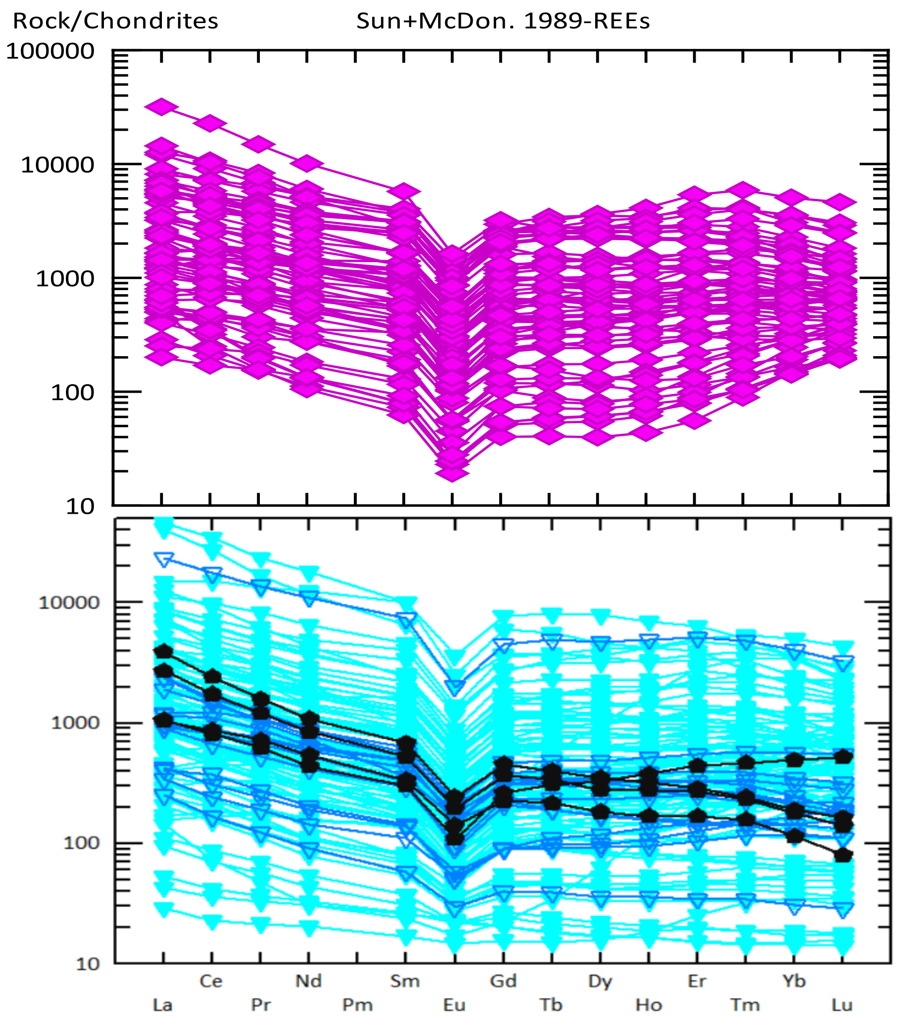
Appendix 3 : *A) V versus SiO_2 and B) $Na_2O + K_2O$ versus SiO_2.*
For the legend see Fig. 9

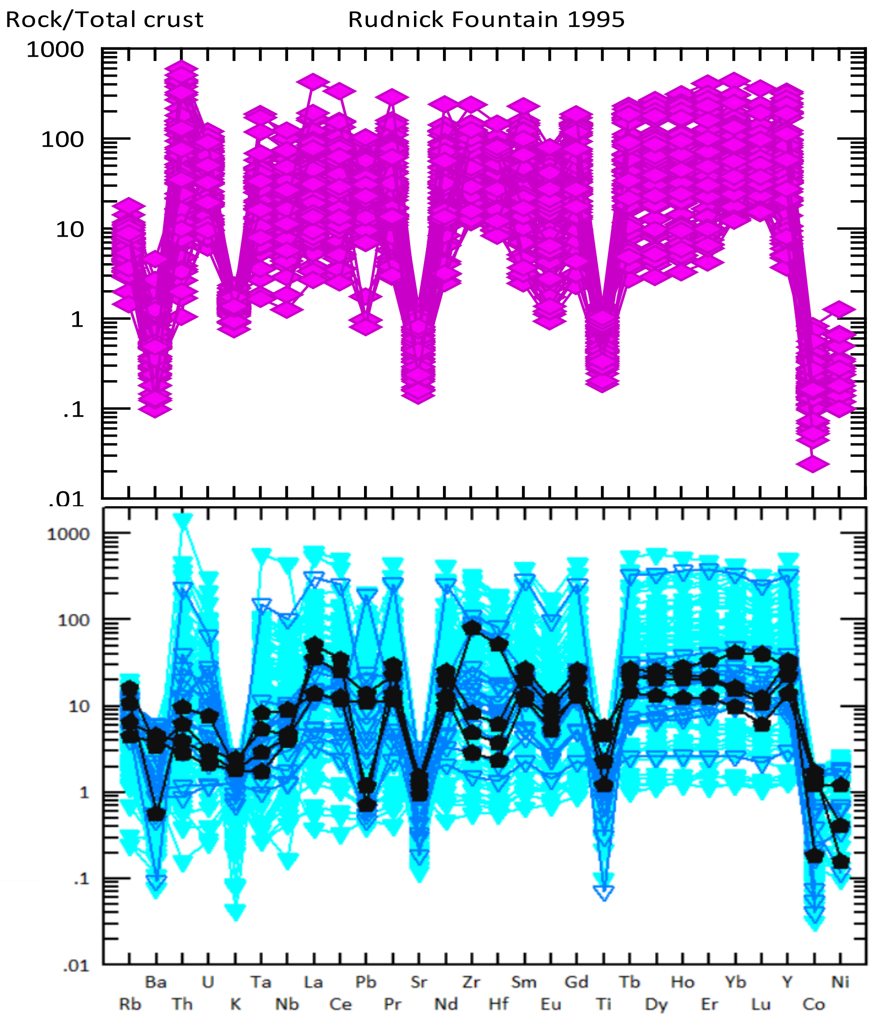
REE and incompatible element diagrams for other Kipawa lithologies

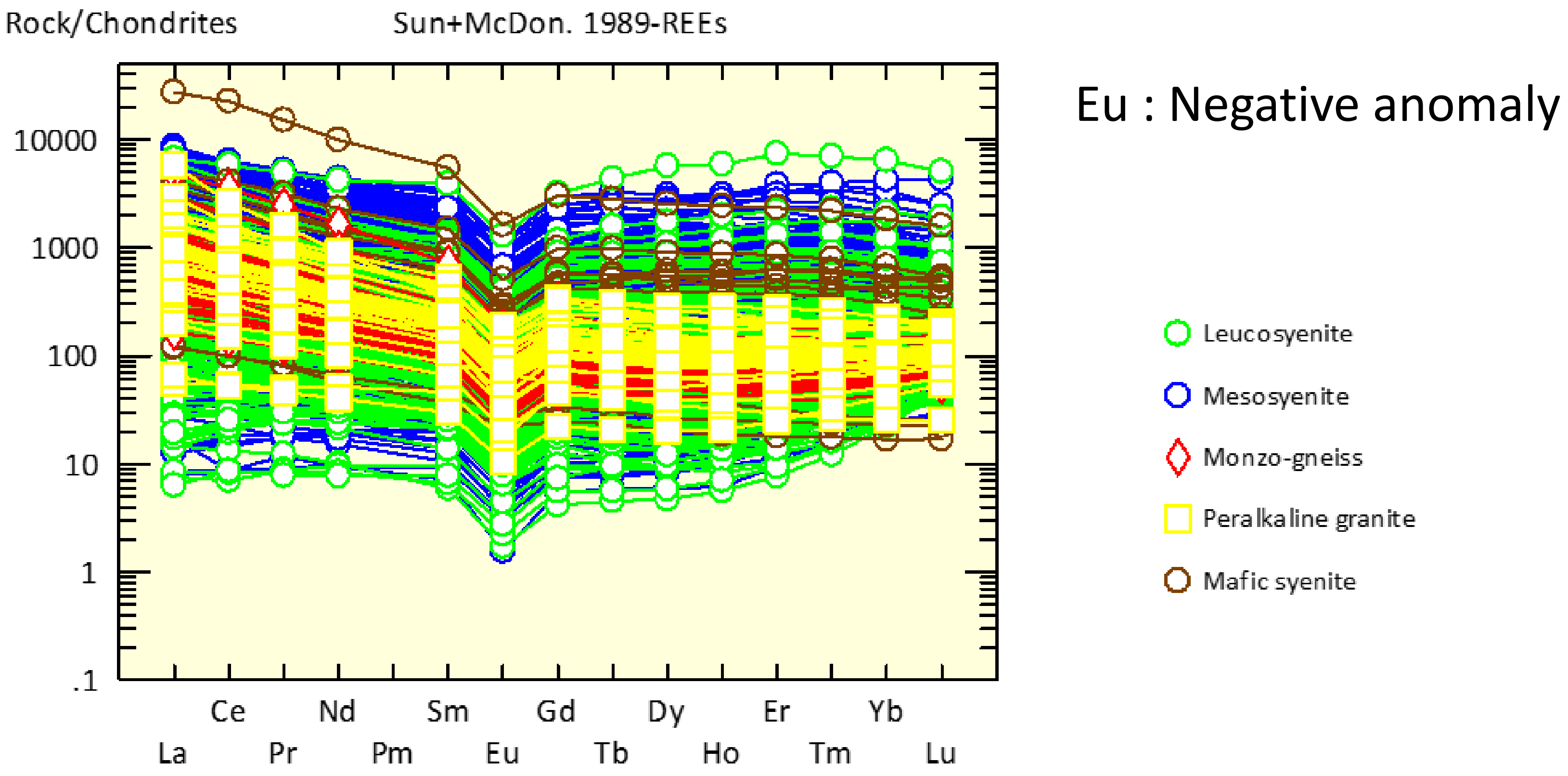




Appendix 4 : *REE and incompatible element diagrams for Kipawa marbles (orange triangle) and skarns (empty triangle), silver-grey amphibolites (purple diamond, next slide), diopside-, feldspars-, and/or phlogopite-rich calc-silicate rocks (spilled blue and empty triangle, next slide), and mafic dykes (black pentagone, next slide). Chrondrite normalization is from Sun and McDonough (1989). Total crust normalization is from Rudnick and Fontain (1995).*

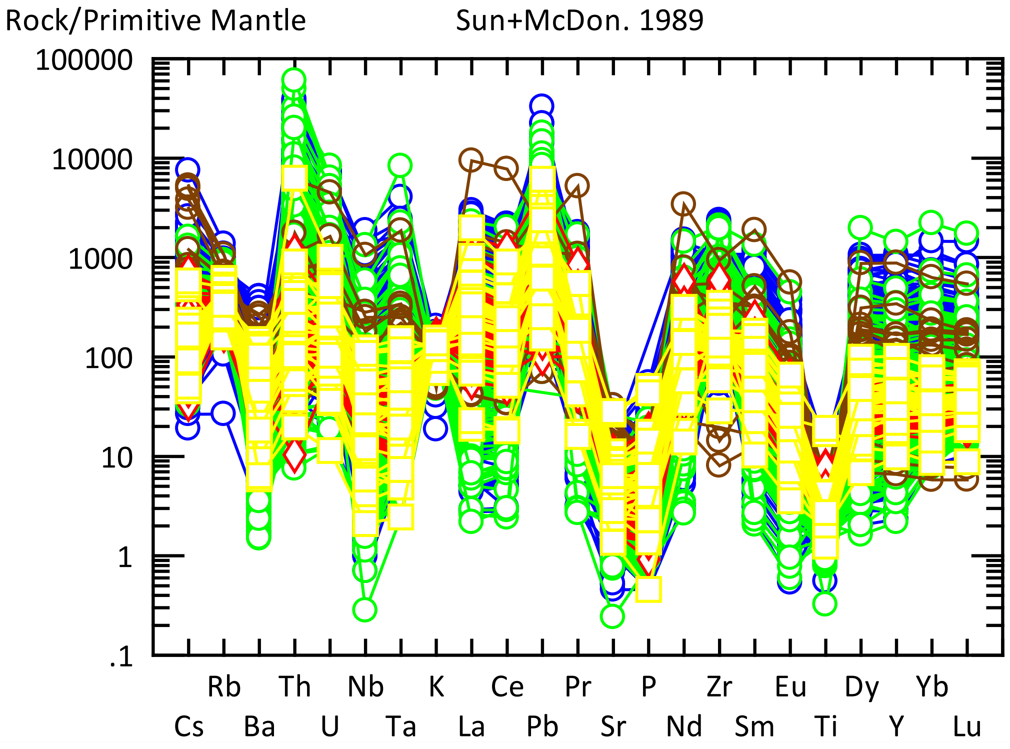

Rock/Chondrites
Sun+McDon. 1989-REEs
100000
10000
1000
100
10
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu


Rock/Total crust
Rudnick Fountain 1995
1000
100
10
1
.1
.01
Rb
Ba
Th
U
K
Ta
Nb
La
Ce
Pb
Pr
Sr
Nd
Zr
Hf
Sm
Eu
Gd
Ti
Tb
Dy
Ho
Er
Yb
Lu
Y
Co
Ni



Appendix 5 : *REE diagram for Kipawa granitoids, normalized to chrondrites (Sun and McDonough, 1989).*

Incompatible element diagrams for Kipawa granitoids



Appendix 6 : *Incompatible element diagram for Kipawa granitoids, normalized to primitive mantle (Sun and McDonough, 1989).*

Ba, K, Sr, P, and Ti : Negative anomaly. Same geochemical behaviour for all Kipawa rocks (Appendix 4)

REE diagram in Appendix 5 : Eu anomaly and rich in LREE and HREE