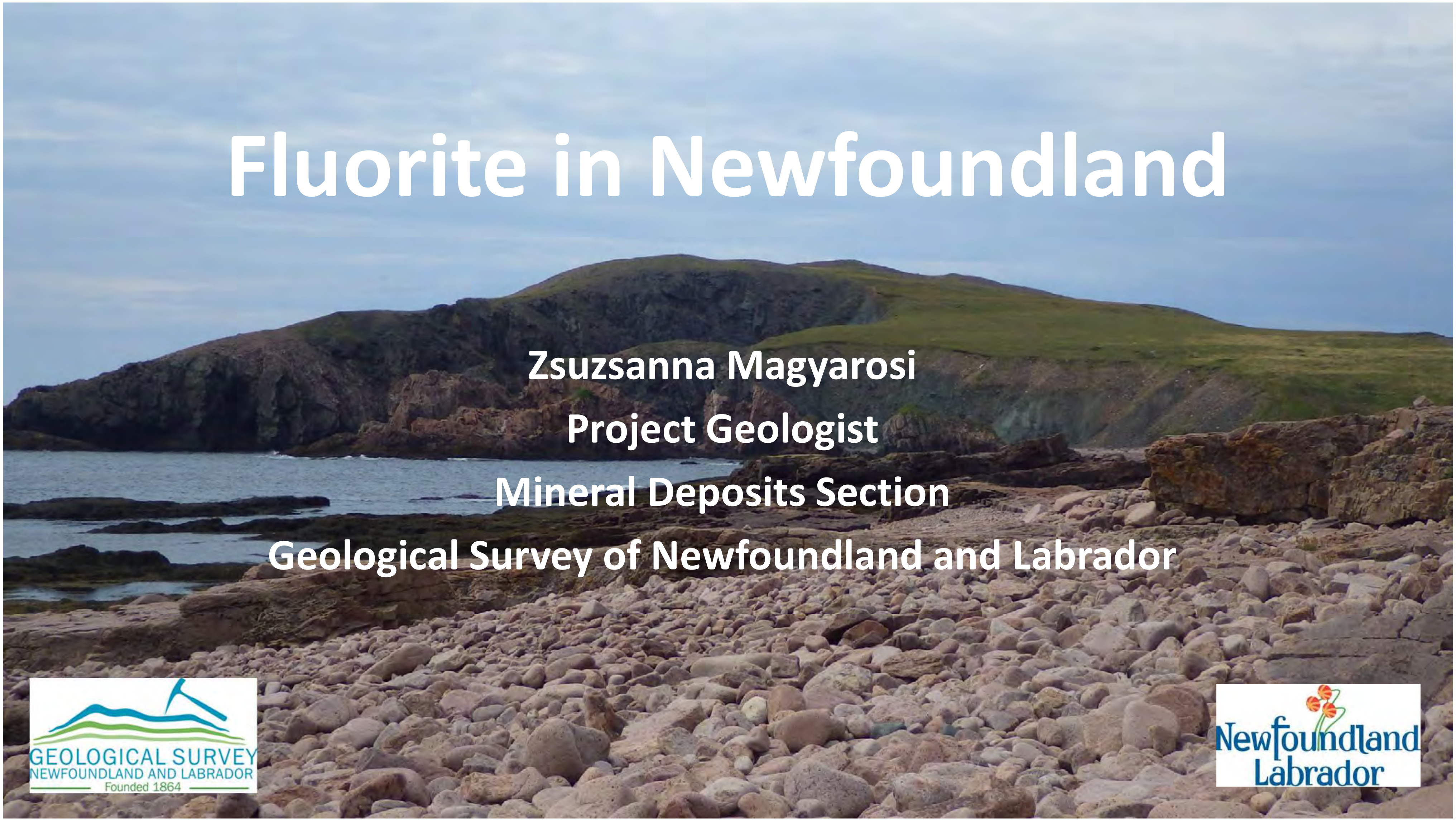

Fluorite in Newfoundland

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Mineral Deposits Section

Geological Survey of Newfoundland and Labrador

Outline

- Fluorite: mineralogy, uses and market, genesis

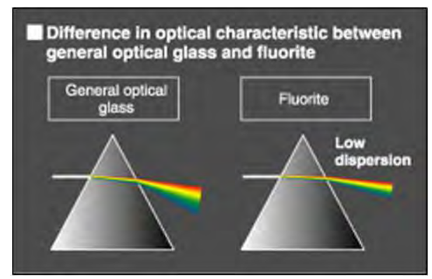
- Fluorite in the St. Lawrence area:
  - Fluorite veins (AGS deposit)
  - St. Lawrence Granite
  - Genesis
  - Implications of this study

- Other prospects/exploration in NL

Fluorite - CaF_2

It is a critical mineral (Canada, US, Europe): essential uses and cannot be recycled

- Cubic system (cubes, octahedra, dodecahedra, combinations)
- Very colourful, fluorescent under UV light, thermoluminescent
- Cause of colour variations: structural defects in fluorite crystal consisting REE, Ca, transition metals and/or O that substitute for F and/or Ca



Uses are based on grade of fluorite ore:

- Acid grade fluorite (>97% fluorite) – HF acid: chemicals, optical equipment
- Ceramic grade (85 to 97% fluorite): glass, ceramics
- Metallurgical grade (60 to 85% fluorite): iron, steel and other metal production

Leading producers in 2021: China, Mexico, Mongolia, South Africa, Vietnam, Canada

Nassau (1990) and references within, Dill and Weber (2010), https://www.earthmagazine.org/, USGS webpage: https://minerals.usgs.gov/minerals/, http://www.geologypage.com; https://geology.com/minerals/fluorite.shtml, https://single-market-economy.ec.europa.eu/sectors/raw-materials/areas-specific-interest/critical-raw-materials_en

Fluorite - Genesis

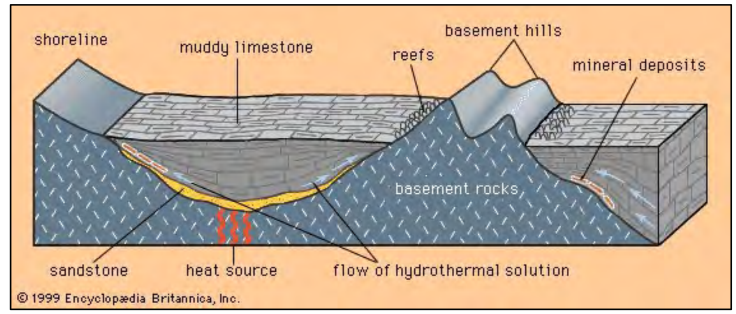
Three main genetic types of fluorite deposits (Strong et al., 1984):

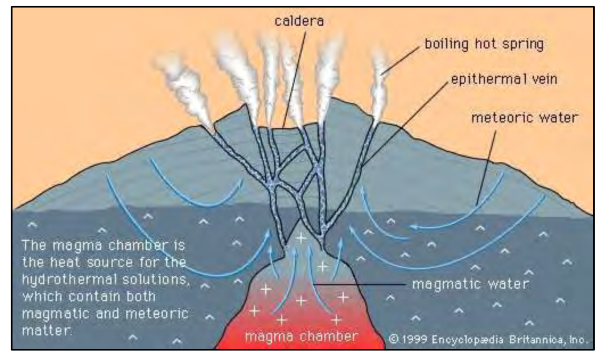
1. Sedimentary, dominantly carbonate hosted, similar to Mississippi Valley Type (MVT) deposits (Western US).

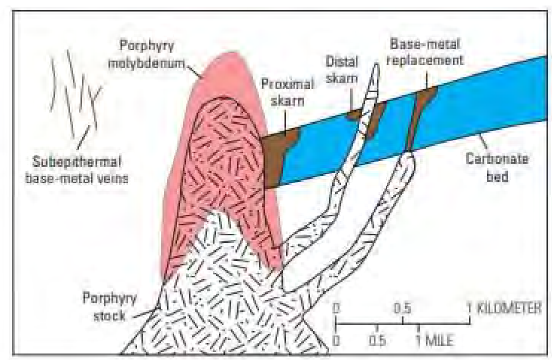
2. Magmatic-hydrothermal vein deposits associated with alkaline–peralkaline igneous rocks (St. Lawrence).

3. Intermediate type found at contacts between limestone and granitoid rocks similar to skarn (Japan, China, Alaska).

According to Dill (2010), most world-class fluorite deposits are associated with carbonates, inferred to be the source of Ca



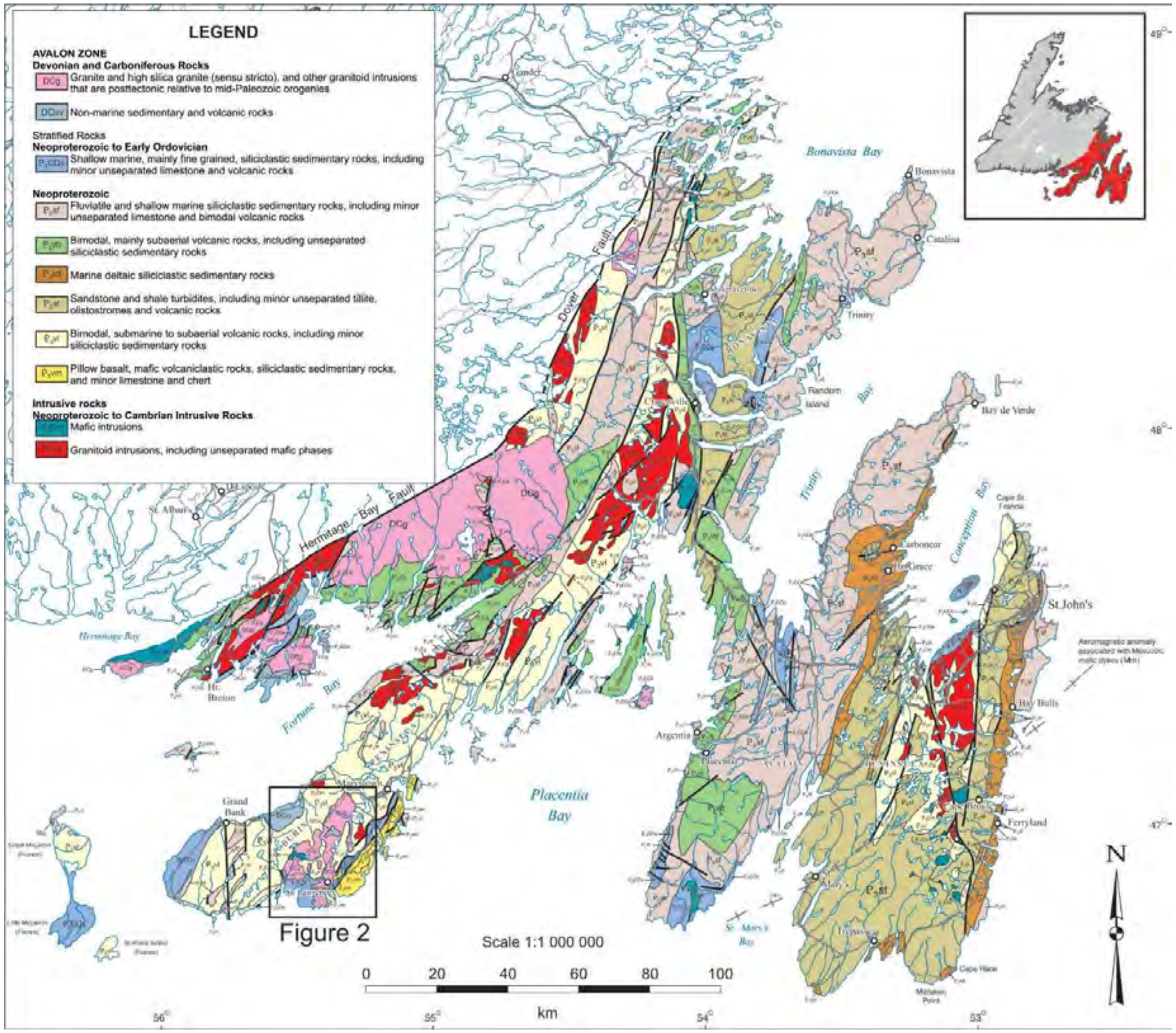




Strong et al. (1984), Dill (2010), https://geology.com, https://www.britannica.com

Fluorite in St. Lawrence

Fluorite mineralization is spatially associated with the St. Lawrence Granite (SLG) located on Burin Peninsula in Newfoundland, belongs to the Avalon Zone of the Appalachian Orogeny



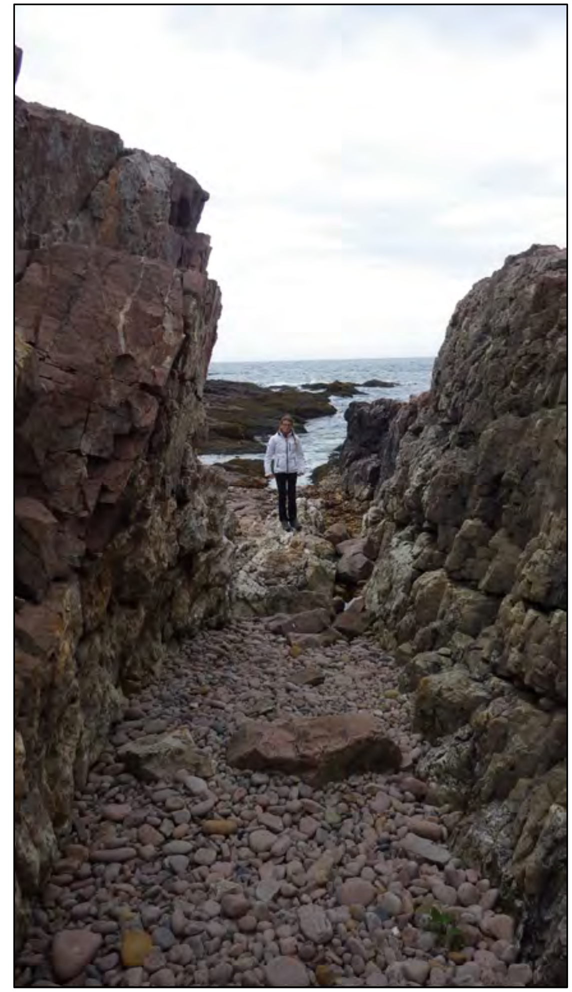
Colman-Sadd et al. (1990)

Newfoundland Labrador

St. Lawrence – History of exploration

- Discovered in 1800s by local residents
- Mined by French settlers before 1870
- 35 fluorite veins were discovered in early 1900s
- Intermittently mined between 1933 and 1990
- Fluorite in AGS area was discovered in 1940's (Grebes Nest), but no significant mineralization was found until 2013
- Canada Fluorspar Inc. (CFI) completed geophysical surveys, followed by drilling, which led to discovery of the AGS deposit that was mined until early 2022

Smith (1957), Edwards (1991), Sparkes and Reeves (2015)



Fluorite veins

Over 40 known fluorite veins, they are up to 30 m in width and 3 km in length

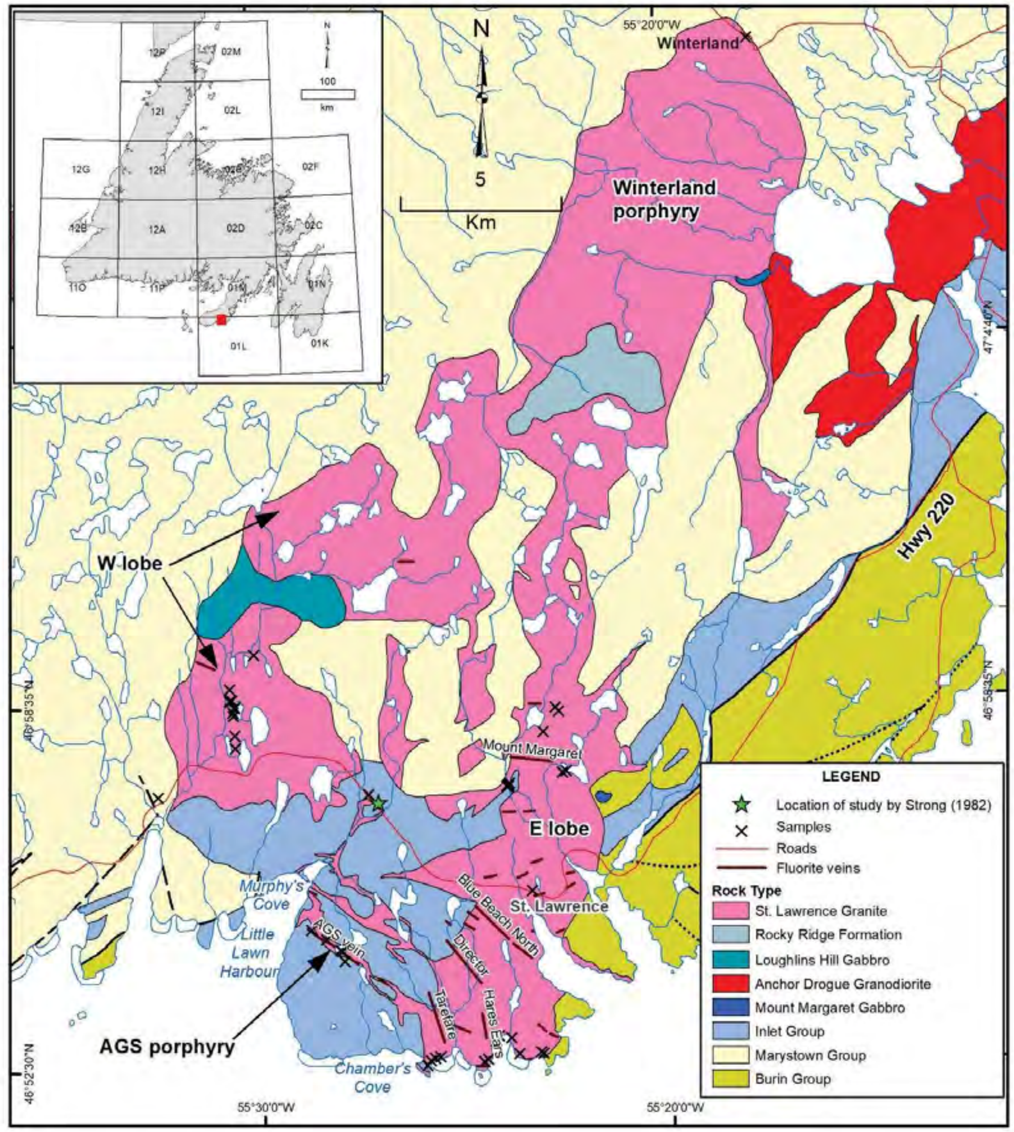
3 types based on orientation and grade:

- N-S trending low-grade veins
- E-W trending high-grade veins
- NW-SE trending veins

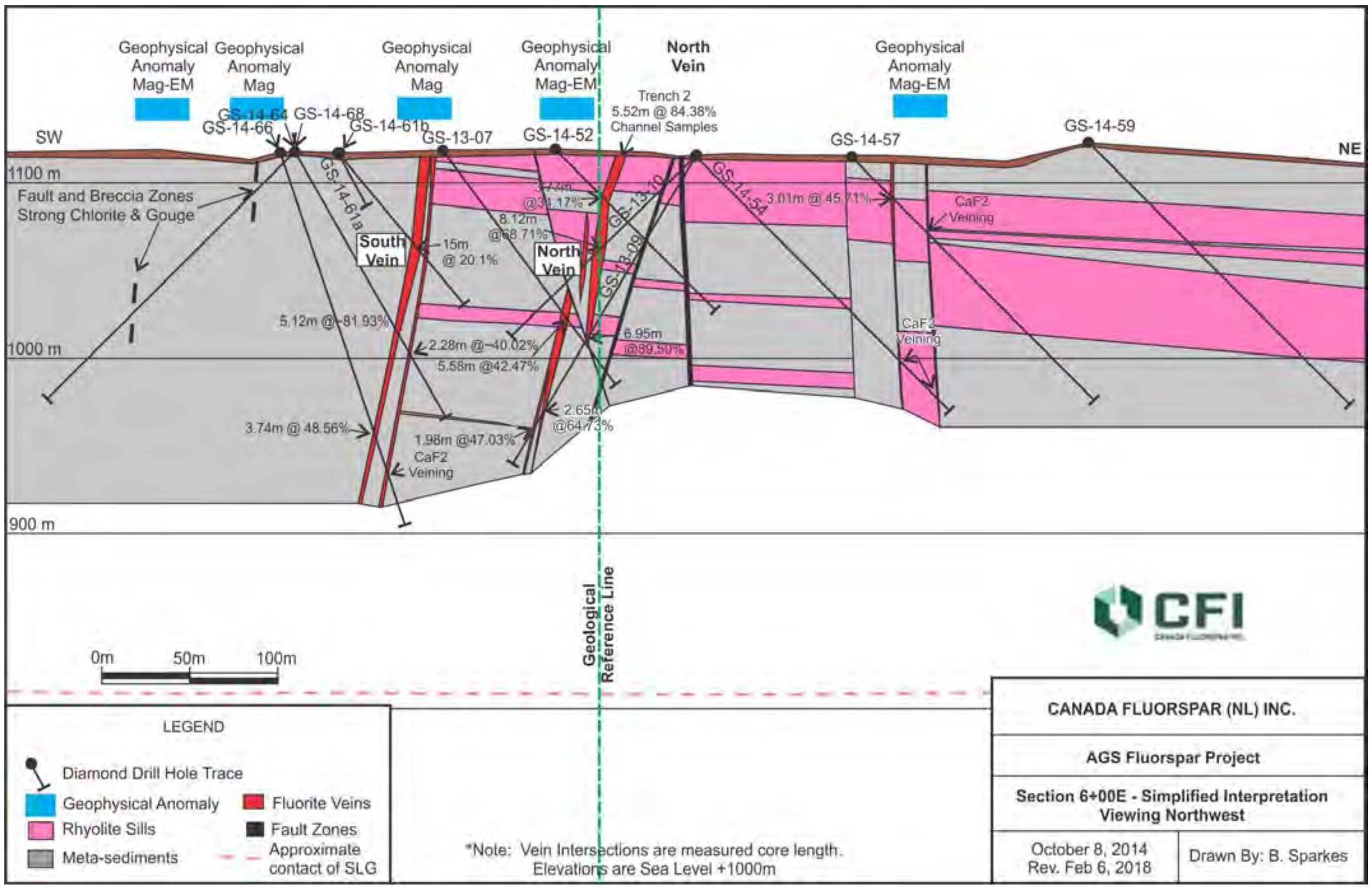
Most of them are hosted in the SLG.

AGS is the first economic deposit not entirely hosted in main granite, mining has been on hold since the early 2022, but large reserves still remain

Williamson (1956), O'Brien et al. (1977); Strong et al. (1978); Strong (1982), Wilson (2000); Reeves et al. (2016)



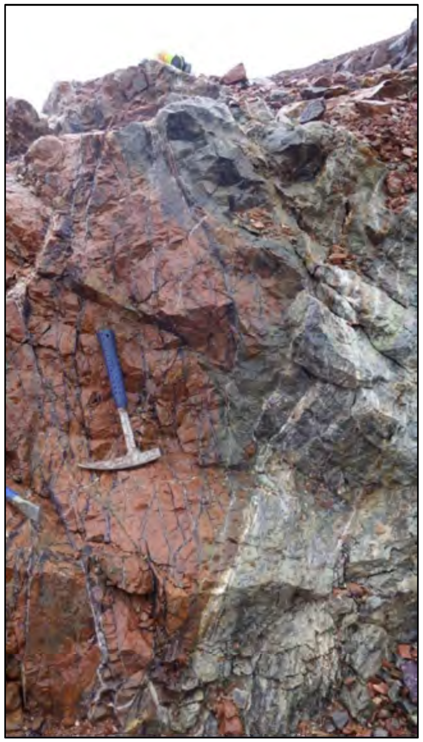
AGS Deposit

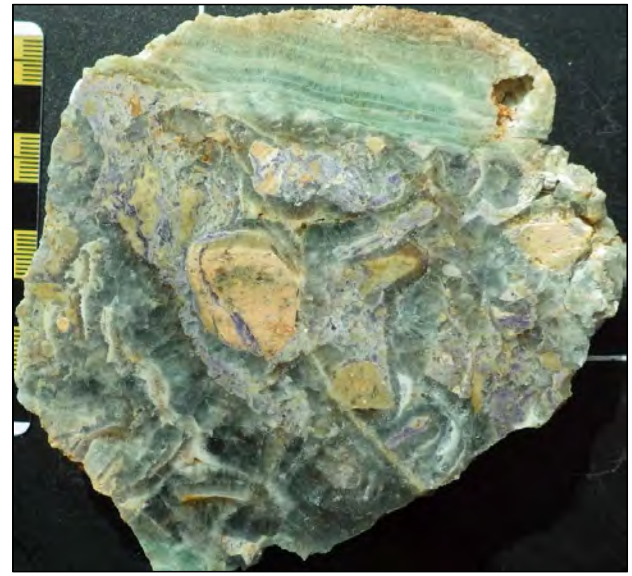


- Hosted in sedimentary rocks (Inlet Group) and AGS porphyry sills intruding them
- Main phase of SLG intersected at 250 to 300 m and veins continue into main phase (based on drilling)
- 1.85 km long
- Resource was ~9.4 M tonnes at ~33% fluorite (2014, NI 43-101 compliant)
- Similar to the granite-hosted fluorite veins, but there is:
  - More calcite
  - More sulphides
  - Green and blue fluorites (not found in granite-hosted veins)

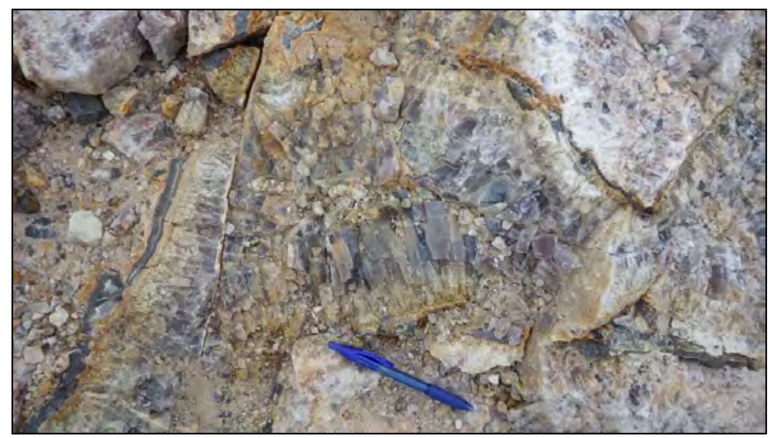
Sparkes and Reeves (2015), Reeves et al. (2016)

AGS deposit





- Hosted in a fault zone: faulted contacts with mineralization
- Several phases of fluorite, typically brecciated, with later phases cementing earlier phases
- Local extensional zones host high-grade mineralization
- Brittle conditions with high fluid pressure according "fault-valve" model (Sibson et al., 1988)

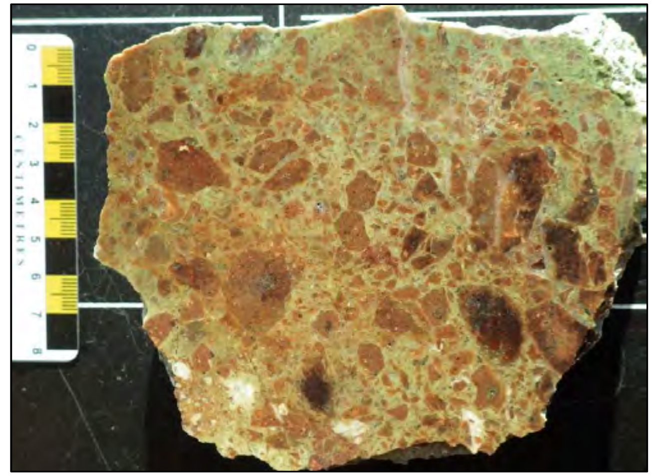


Paragenetic sequence

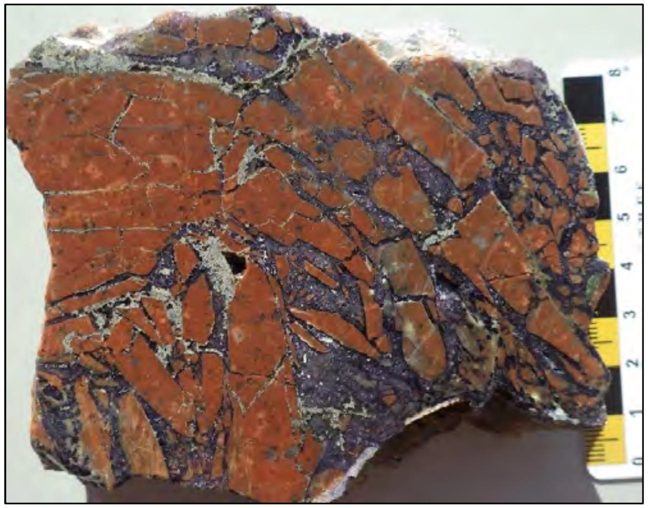
Stage	Phase		Description
Early stage	1	Brecciation of host rocks	Brecciated, weakly- to strongly-altered sedimentary rocks and rhyolite in a quartz-rich matrix.
	2	Purple fluorite stockwork and/or hydrothermal breccia	Purple fluorite and quartz forming stockwork veins and hydrothermal breccia with clasts of host rocks. *
	3a	Banded, fine-grained fluorite and/or yellow, coarse-grained fluorite	Finely banded, fine-grained fluorite and/or coarse-grained yellow fluorite.
	3b	Hematite-fluorite-quartz	Hematite with quartz and fluorite.
Main stage	4	Reddish grey fluorite	Massive, coarse-grained, grey, transparent fluorite, locally slightly reddish or pink.
	5	Fine-grained banded sulphides	Composed of sphalerite and galena.
	6	Grey elongated fluorite	Massive, grey fluorite with elongated crystals up to 20 cm in length.
Late stage	7	Green, blue and white, coarse-grained fluorite	Alternating layers of coarse-grained green, blue and white fluorite with disseminated sphalerite and galena.
	8	Clear or blue, cubic fluorite	Clear or blue cubic fluorite occurs filling vugs.
	9a	Blastonite	Breccia composed of fragments of previous phases in a matrix composed of quartz and fine-grained fluorite.
	9b	Late quartz	Quartz vein stockwork and vug filling.
	10	Pyrite and chalcopyrite	Pyrite and chalcopyrite crystals in quartz lined vugs.

*Variable amounts of calcite occur locally with fluorite in all phases.

Barren breccia:



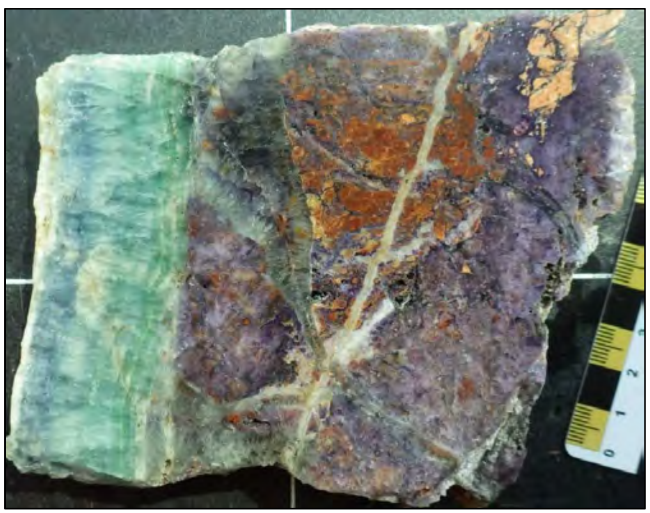
Early Stage



Purple fluorite (stockwork and fluorite-matrix supported breccia)

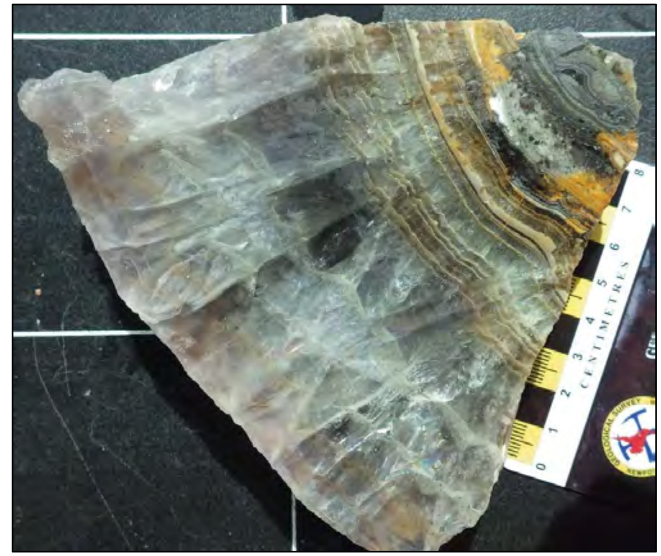
Banded fine-grained fluorite and yellow coarse-grained

Hematite-fluorite-quartz locally



Main Stage

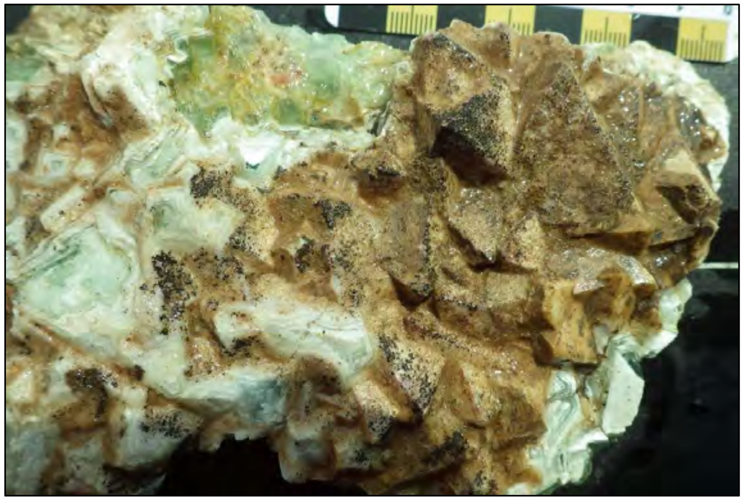
Fine-grained banded sulphides



Reddish grey fluorite

Elongated grey fluorite

Late Stage

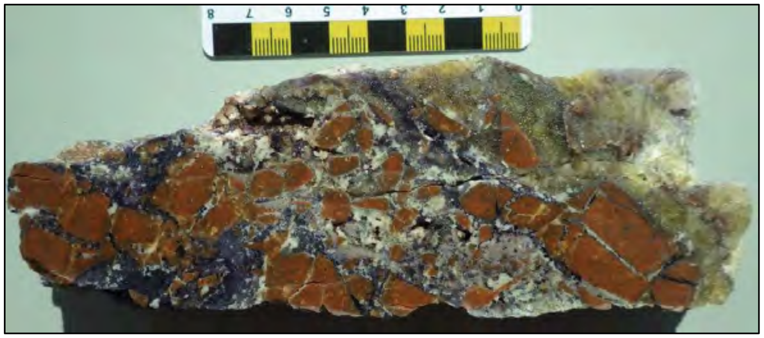
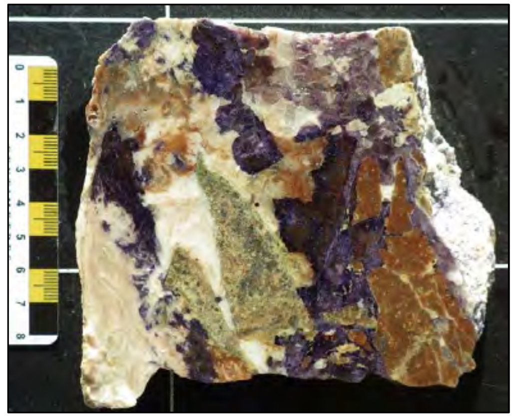


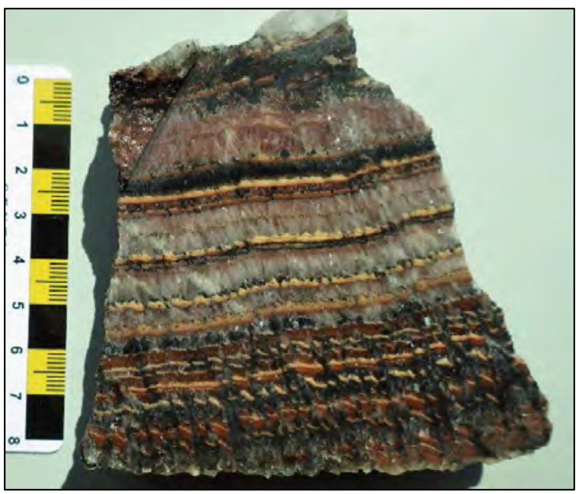
Green fluorite (octahedral)

Late quartz

Cubic fluorite (clear or blue)

Locally abundant calcite and sulphides



Calcite and sulphides occur in most phases, but the amounts of both increase in later phases
Sulphides include sphalerite, galena, trace pyrite and chalcopyrite in last phase

Work completed on the AGS vein

Work on the fluorite veins included:

- Nd-Sm dating of fluorite (D. Kontak, R. Creaser)
- REE-Y patterns of fluorite
- Fluid inclusion analysis (J. Conliffe)
- C and O isotopes in calcite
- S isotopes in sphalerite
- Pb isotopes in galena (N. Pochereva)

→

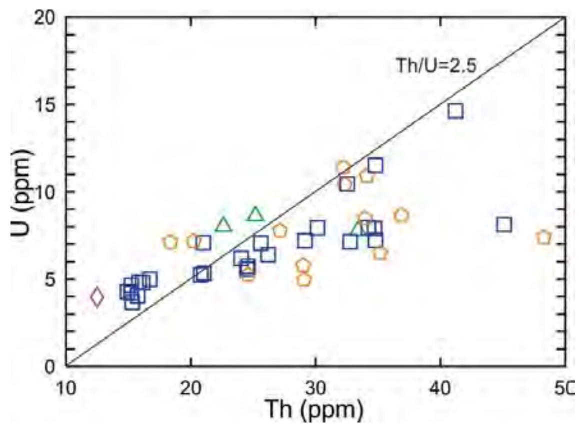
Source of fluorite is the SLG

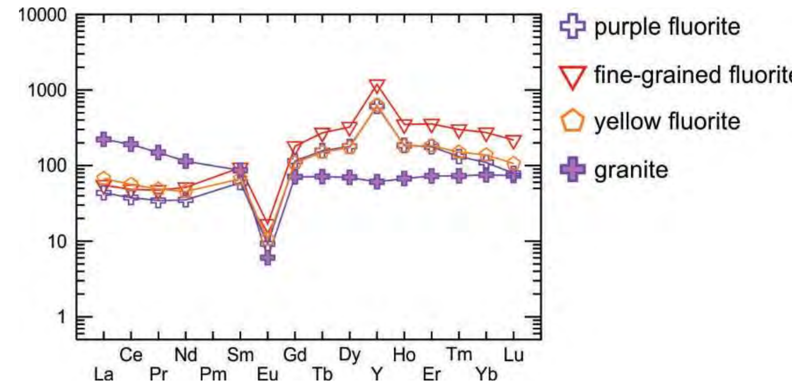
Increasing influence of sedimentary rocks in later stages due to increased circulation of fluids in the sedimentary rocks

AGS vein evolution

Nd-Sm data:

- ƐNd value suggests deep-seated origin for the fluorite (+2.691), similar to the SLG (+3.2)
- Age: 360 ± 14 Ma (SLG: 372-377 Ma)
- Extended hydrothermal activity due to SLG being "HHP" and/or origin from undated/uncovered phase of SLG (e.g. most likely the main phase SLG under the AGS deposit)

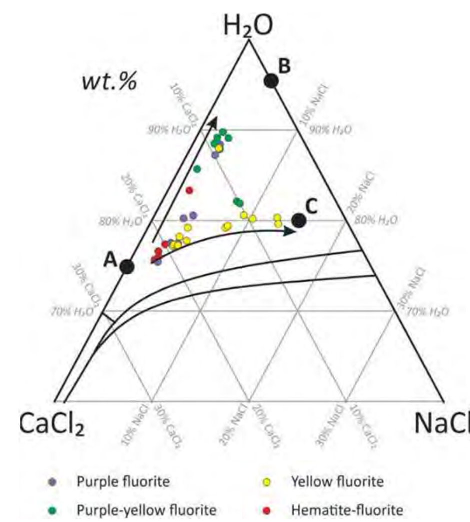




Early Stage

Magmatic signatures dominating, but there is mixing of fluids from other sources:

- C isotopes in calcite (-6.5 to -5.6 ‰) suggest deep-seated source
- REE-Y patterns in fluorite indicate origin from SLG
- Fluids (H_2O-NaCl-$CaCl_2$) are a mixture of magmatic and meteoric and, in yellow phase, basinal fluids
- O isotopes in calcite (8.6 and 19.3 ‰) also suggest fluid mixing



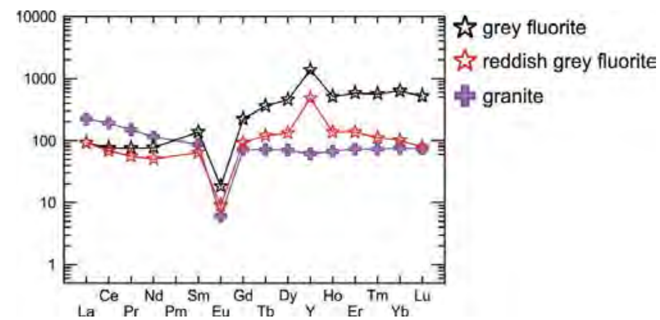
Zhao et al. (2004); Sharma et al. (2019); Magyarosi and Conliffe (2021); Magyarosi et al. (2022)

AGS vein evolution

Main Stage

Veins open up (extensional zones) and allow more circulation of fluids in surrounding rocks, resulting in increasing influence of the sedimentary rocks:

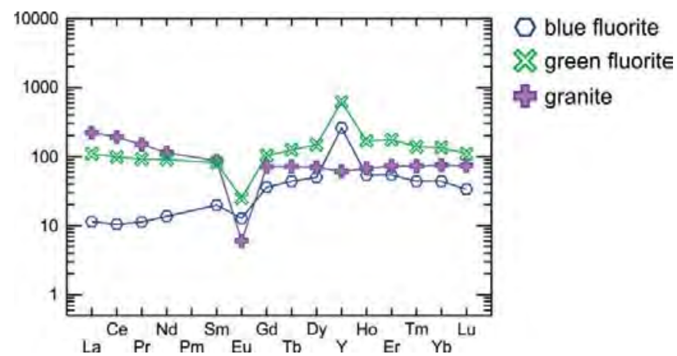
- Fluids are lower salinity and contain $MgCl_2$ and/or $FeCl_2$ in addition to NaCl and $CaCl_2$
- Sphalerite and galena appear, S ($\delta^{34}S$ =-33.36 to -31.41 ‰) and Pb from sedimentary source
- Oxidizing to reducing (hematite disappears, sulphides appear)



Late Stage

Further increasing influence of sedimentary rocks:

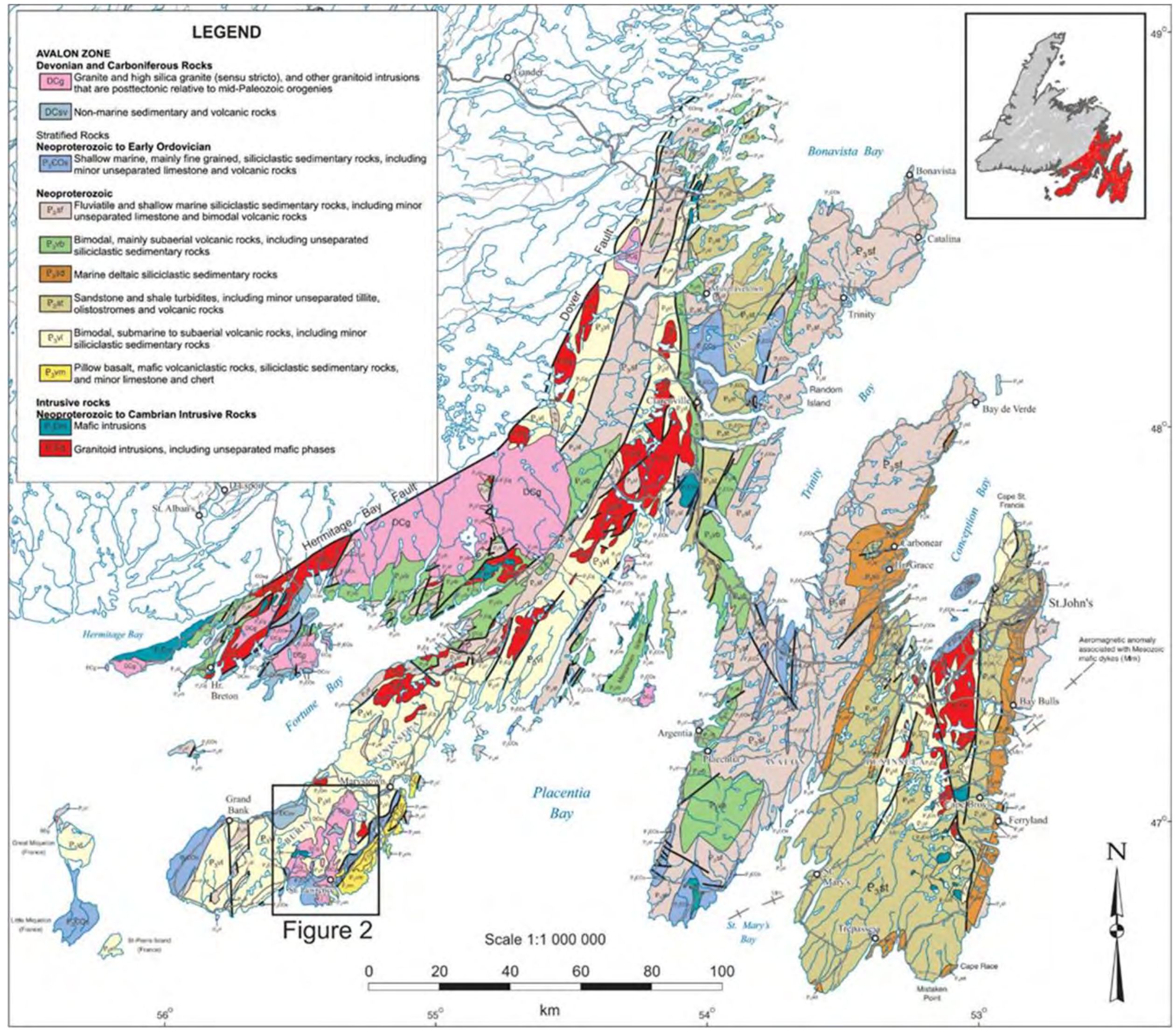
- Fluid becomes more reducing and/or less acidic ($\delta^{34}S$ in sphalerite =-1.57 to -1.02 ‰)
- Smaller Eu anomaly in late-stage fluorite (sedimentary rocks and more reducing)
- Blue fluorite representing remobilized earlier fluorites



Magyarosi and Conliffe (2021); Magyarosi et al. (2022)

SLG

- To understand some of the processes that led to the fluorite mineralization focus switched to the St. Lawrence Granite (SLG)
- SLG is one of the highly evolved Devonian granites in Newfoundland, which are associated with various types of mineralization (fluorite, Cu-Mo, Sn-W, Pb-Zn)
- These granites were emplaced during the late stages of Acadian Orogeny



After Colman-Sadd et al. (1990)

Work completed on the SLG

Problems with previous genetic models:

- No mineralization in country rocks (AGS deposit?)
- Source of Ca to form fluorite and locally abundant calcite is uncertain
- Lack of significant fluorite mineralization in the W lobe

Petrography

Whole-rock geochemistry

Geochronology

Scanning Electron Microprobe analysis

Electron Probe Micro-analyzer work

→

Fluorite mineralization (and alteration) are the results of devolatilization of the granite

Volatile phases included:

- F-rich vapour
  - Brecciation prior to mineralization
  - Created permeable zones above and allowed later mineralizing fluid to escape SLG
- F-rich acidic fluid
  - Main mineralizing fluid
  - Reacted with Ca-bearing minerals in the SLG and dissolved Ca
- CO_2-rich fluid

Van Alstine (1944, 1948); Williamson (1956); Strong et al. (1984); Collins (1984, 1992); Collins and Strong (1988); Magyarosi (2022)

St. Lawrence Granite

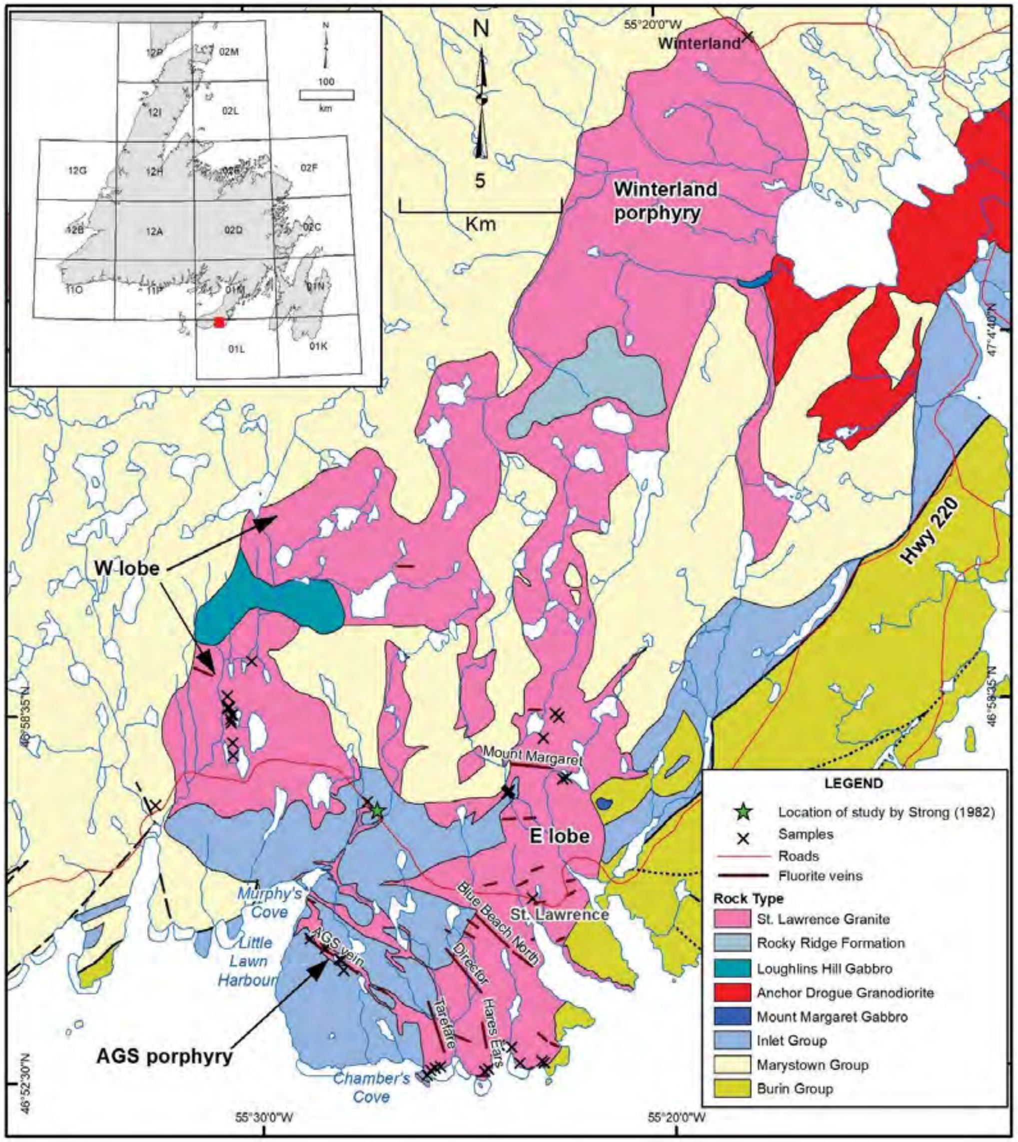
Composed of E and W lobes, pophyritic sills and dikes, Winterland porphyry

E lobe is peralkaline (molar (Na+K)/Al > 1), W lobe, sills and dikes are metaluminous **=>** peralkaline complex

Most of the fluorite veins are associated with E lobe

Geochronology with U/Pb in zircon

- S lobe: 374 ± 2 Ma
- AGS porphyry is slightly older: 377.2 ± 1.3 Ma

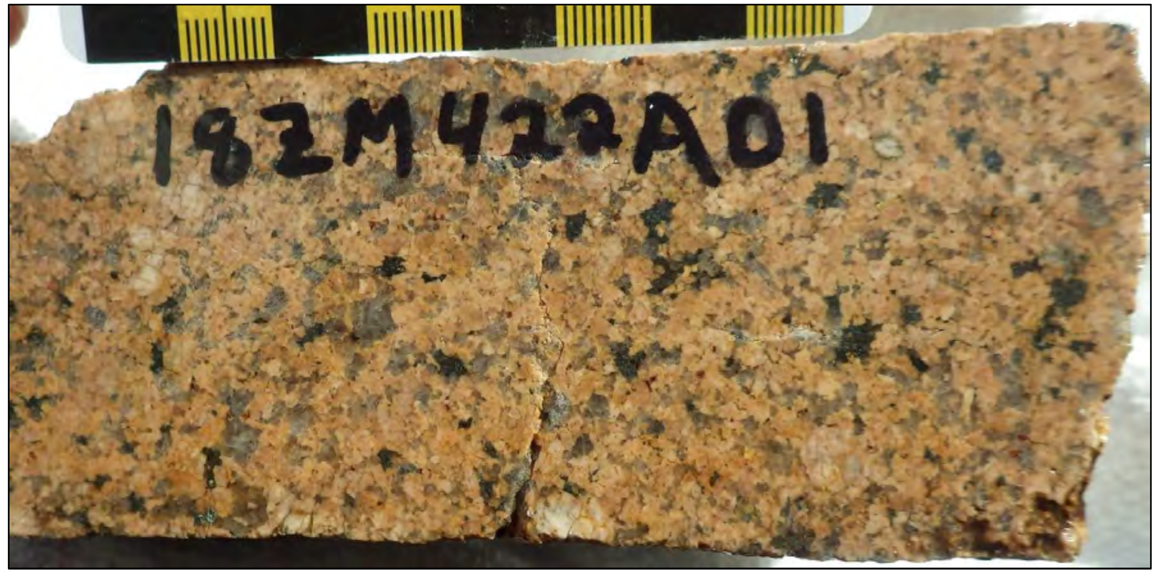


O'Brien et al. (1977); Strong et al. (1978); Kerr et al. (1993); Wilson (2000); Magyarosi et al. (2019)

W lobe

Main minerals:

- Quartz
- Perthitic feldspar
- Biotite



Alteration:

- Albitization
- Biotite altered to chlorite

Magyarosi (2022)

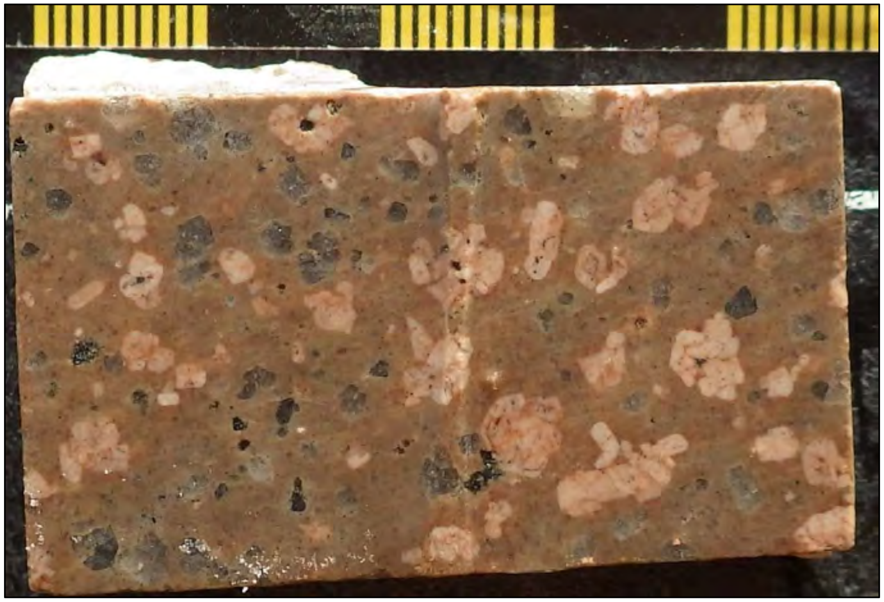
AGS porphyry

Main minerals:

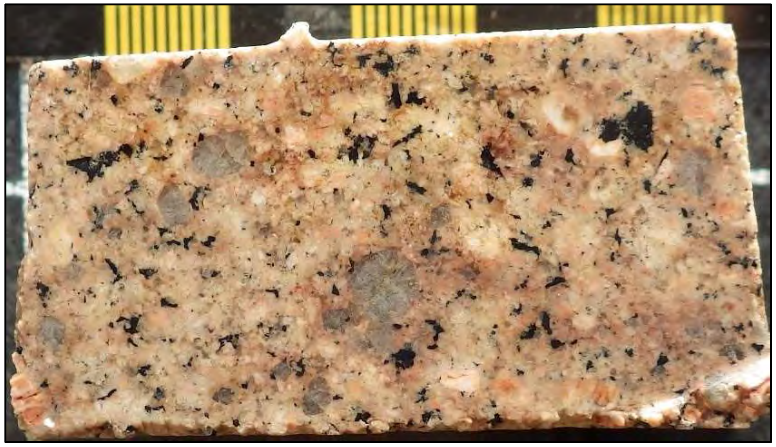
- Quartz
- K-feldspar
- Albite
- Chlorite (alteration)

Alteration:

- Chloritization
- Greisenization: sericite

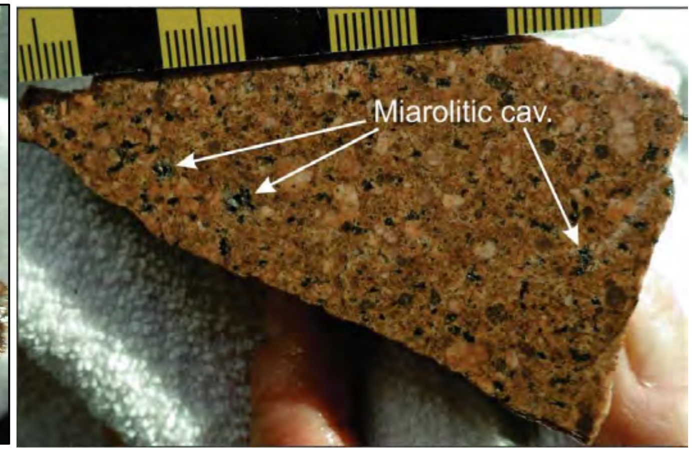


E lobe



Weakly altered granite

Tuffisite



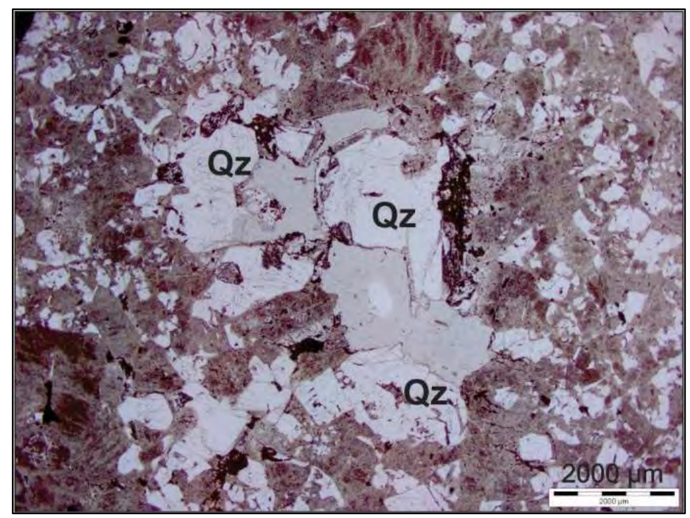
Miarolitic cavities

Main minerals:

- Quartz
- Perthitic feldspar
- Arfvedsonite
- Aegirine

Top of granite to the S in the E lobe:

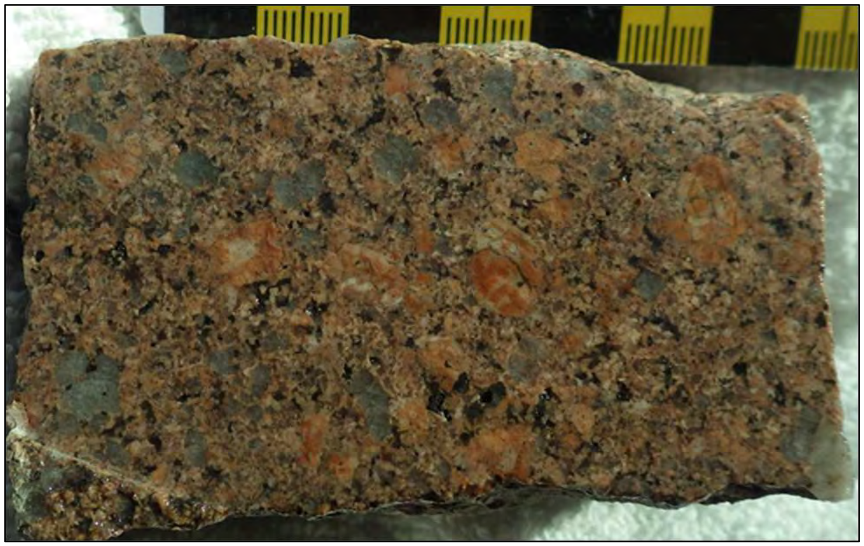
- Tuffisites (gas breccia)
- Miarolitic cavities
- Porphyritic phases



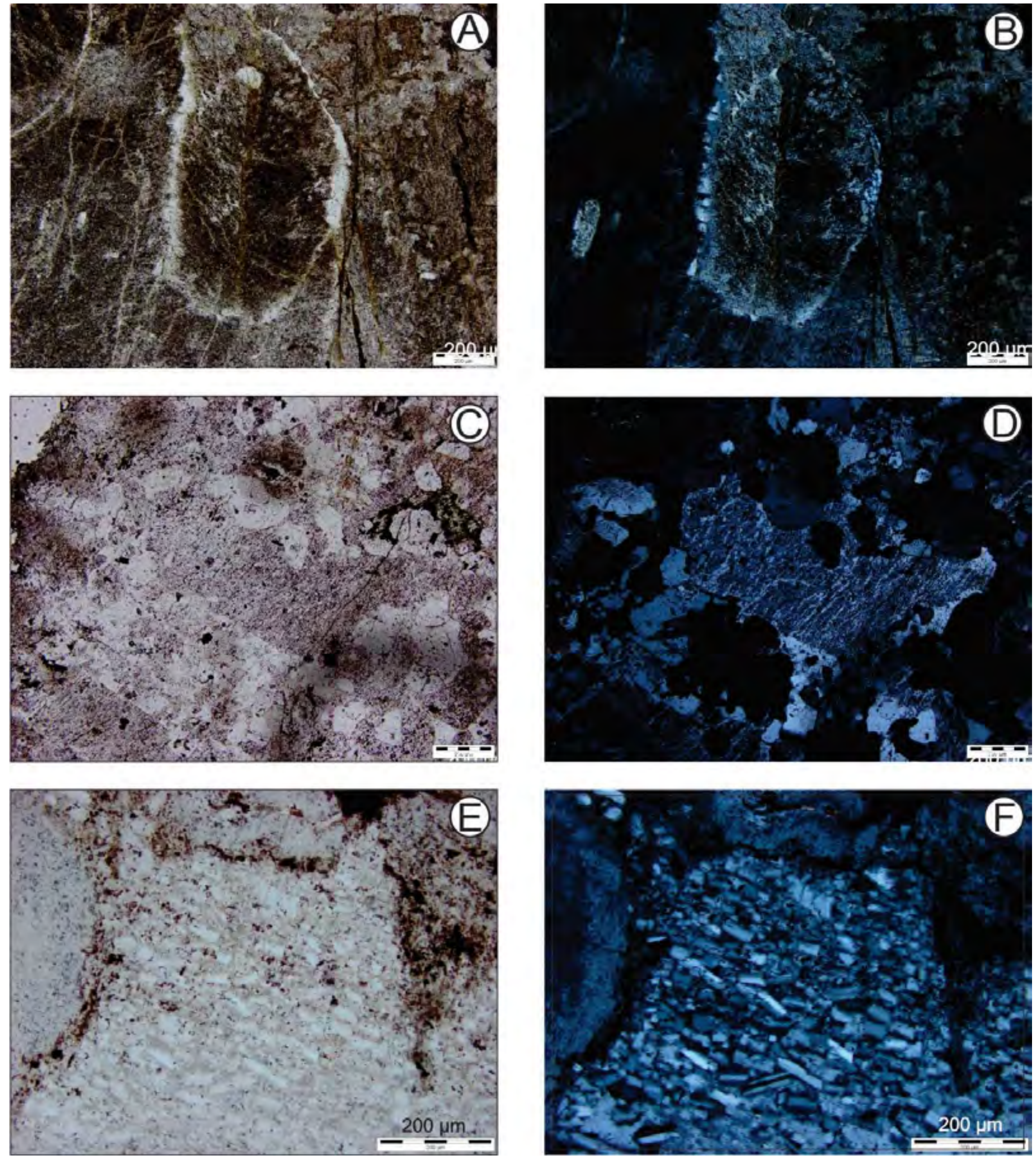
(Williamson (1956); Teng and Strong (1976); Kerr et al. (1993b)

E lobe alteration

Intensity of all alteration types increases towards the south



Increasing degree of albitization



Albitization:

- Albitization of K-feldspar and primary plagioclase
- Ca (and K) enters the fluid

Magyarosi (2022)

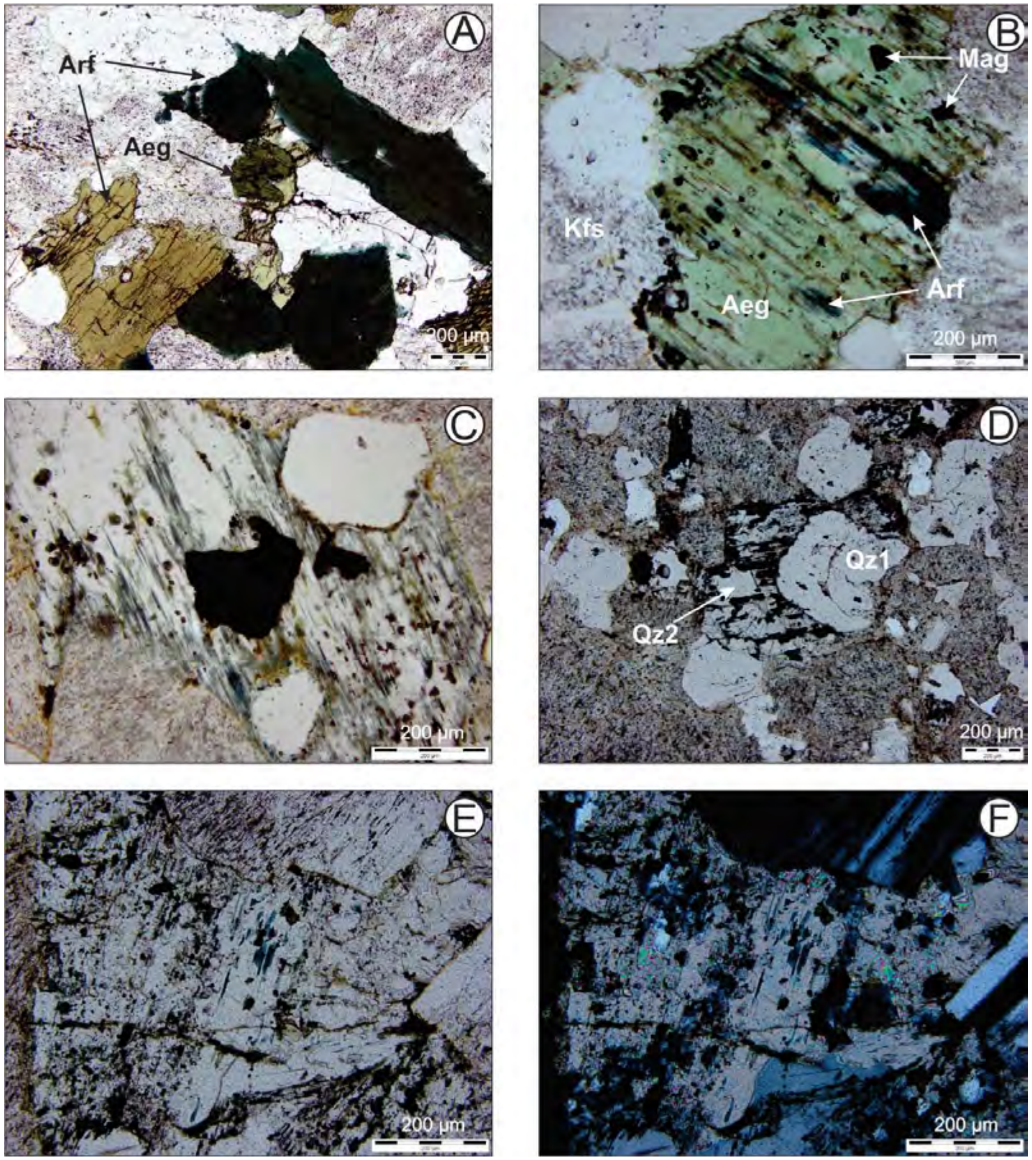
E lobe alteration

Alteration of arfvedsonite

- Arf => Aeg
- Arf => Hem + Q
- Arf => Hem + Chl + Q

Na and Ca (1.5 wt%) enters the fluid

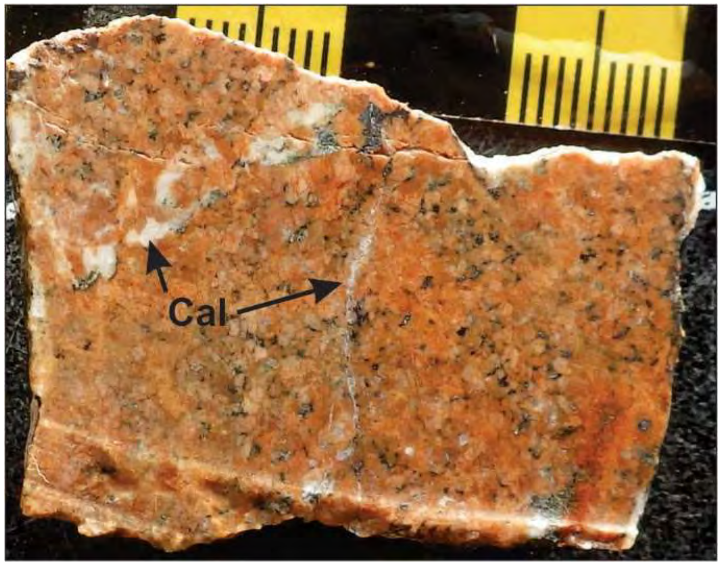
Calcite replacing quartz after breakdown of arfvedsonite => carbonatization was later

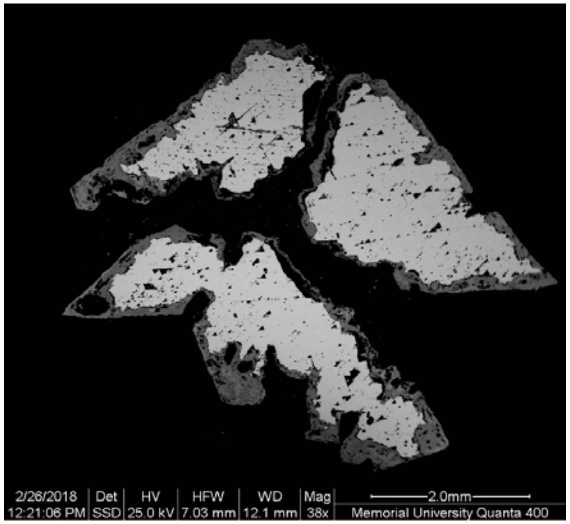


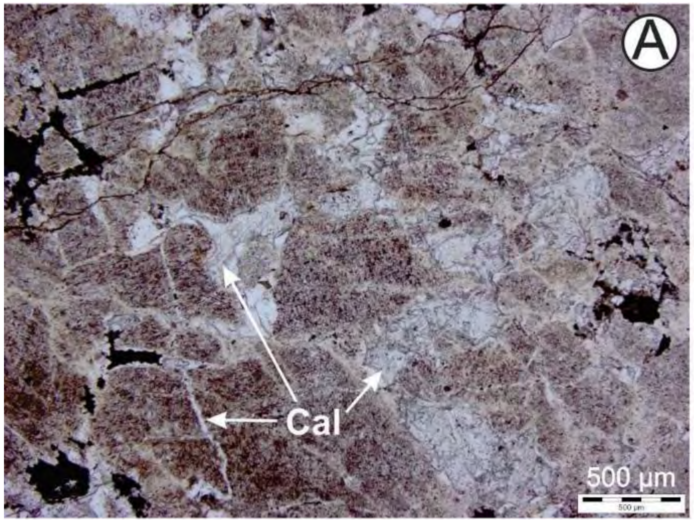
E lobe alteration

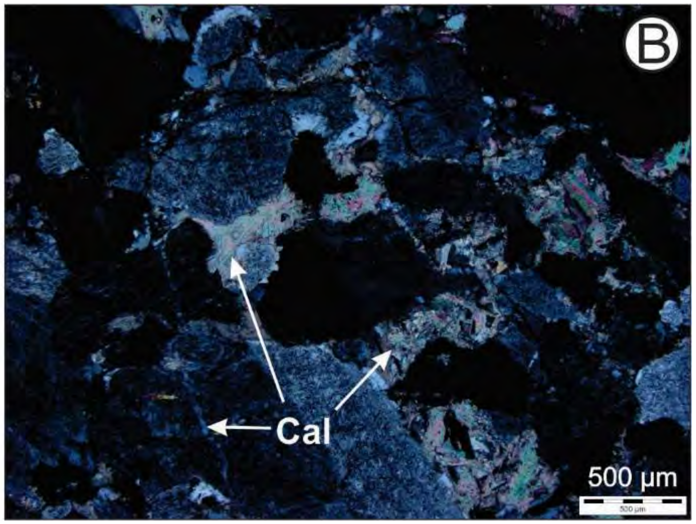
Carbonatization

- Late (postdates the breakdown of arfvedsonite)
- Calcite replaces quartz
- Strongest in cupolas (highest point) of granite (e.g. Chamber's Cove)
- Postdates fluorite mineralization: galena altered to cerrusite (PbCO3) in the fluorite vein at Chamber's Cove









Geochemistry

A-type granite

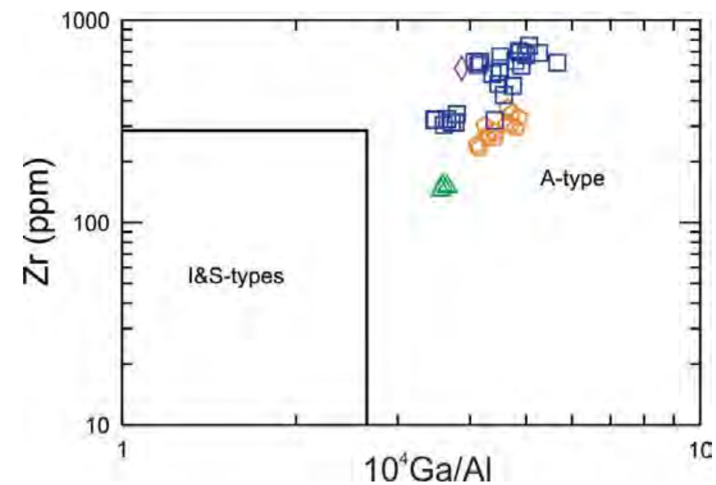
W lobe is A1 type and E lobe is A2 type, unusual

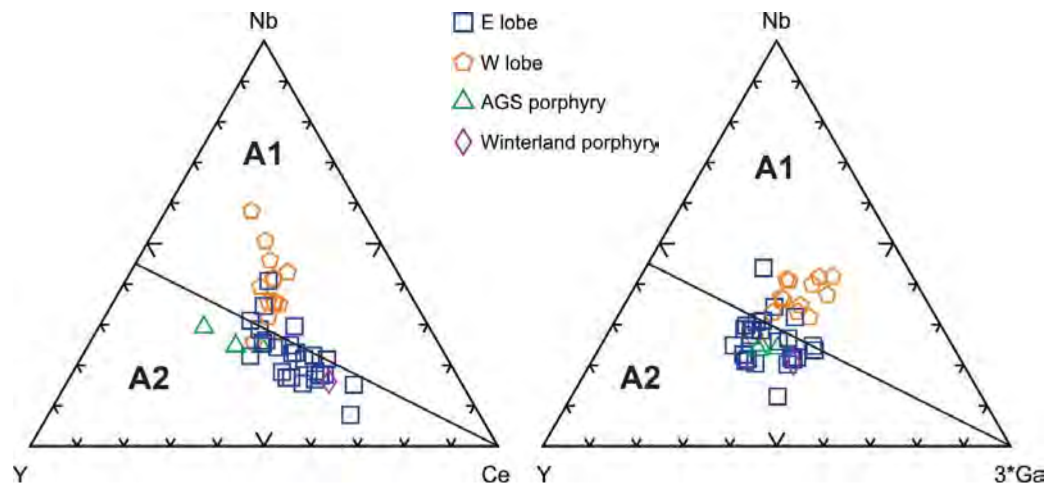
Most likely reason is crustal contamination of E lobe (introduce Ca?)

Conditions of crystallization (typical of peralkaline granite):

P ~ 0.61 kbar

T ~ 954 °C





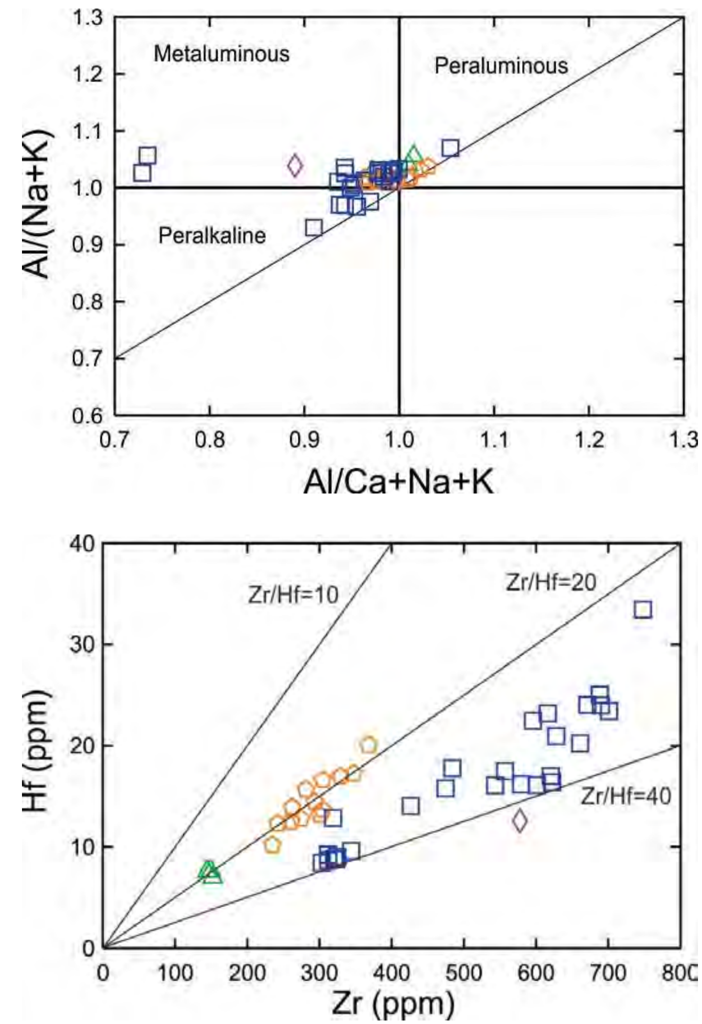
Whalen et al. (1997); Eby (1990, 1992); Yang et al. (2021); Magyarosi (2022)

Geochemistry

Peralkaline to metaluminous

Altered peralkaline plots into metaluminous or peraluminous (greisenized)

Hf vs. Zr plot indicates all E lobe is peralkaline: solubility of Zr and Hf depends on the alkalinity of the melt (in peraluminous and metaluminous melts Hf is enriched in the melt)



Shand (1922); Linnen and Keppler (2002); Zaraisky et al. (2009); Magyarosi (2022)

Volatile exsolution

Alteration and fluorite mineralization were the results of devolatilization of the granite:

- Increasing degree of alteration toward the top
- Increasing amount of volatiles (F - fluorite, CO_2 - calcite)

Volatiles included: F, Cl, CO_2 and water (fluid inclusion analysis, mineralogy)

Volatiles are incompatible => stayed in the melt, then entered a fluid phase, which moved towards the top of the granite (E lobe)

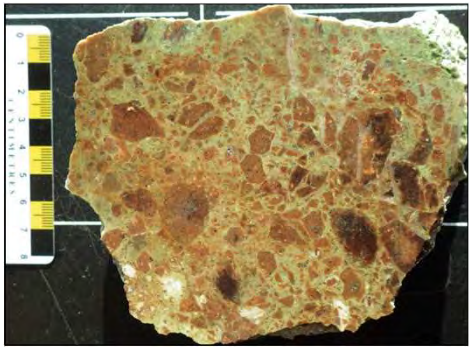
The fluid(s) altered the granite above (autometasomatism)

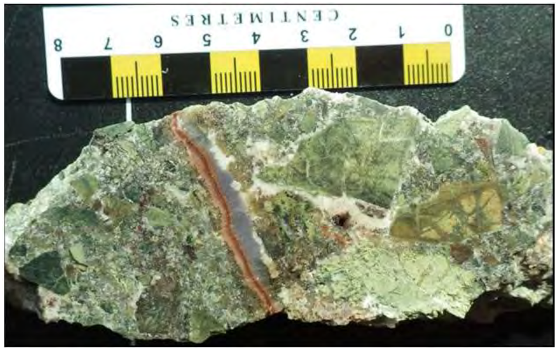
Magyarosi (2022)

Fluorite mineralization

F-rich vapour: vapourization of F as mostly SiF_4 gas in peralkaline melts between 600-1000 °C:

- Tuffisites
- Miarolitic cavities with quartz
- Barren breccia (q rich, no Ca)
- Brecciation creating highly permeable zones above





F-rich acidic fluid:

- Main mineralizing fluid
- Needed F and Ca to form fluorite
- Cooling led to the rest of F partitioning into a hydrothermal fluid
- Acidic fluid reacted to Ca-bearing minerals (arf, plag) dissolving Ca
- Fluorite-rich fluid moved upwards and accumulated in the upper parts of the granite, released episodically
- Fluorite precipitation (<260 °C) is controlled by fluorite solubility, happened due to change in pH, salinity

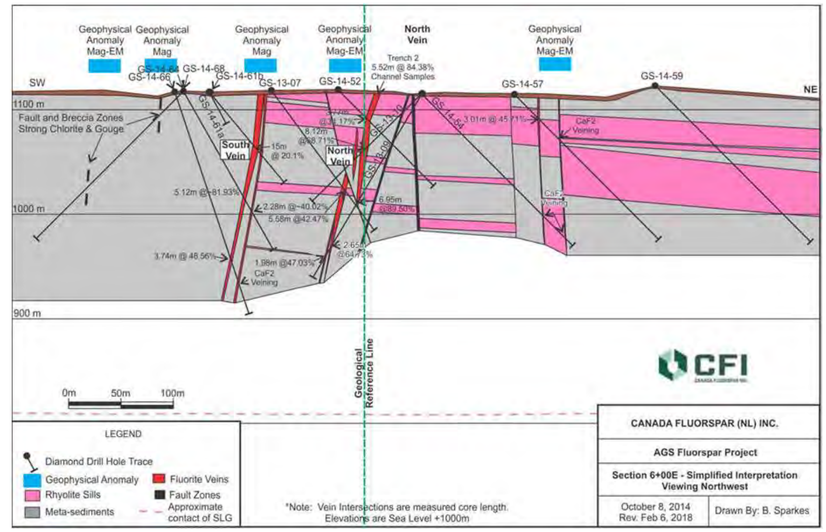
CO_2-rich fluid:

- Late carbonatization, fluid was less volatile, no F left

Bailey (1977); Sibson (1977); Richardson and Holland (1979a and b); Manning and Exley (1984); Strong et al. (1984); White et al. (2005); Topper and Manning (2007); Dolejs and Baker (2004, 2007); Magyarosi (2022)

Implications

- Significant fluorite mineralization associated only with the peralkaline phase
  - Most likely due to lack of Ca in metaluminous phase
  - Peralkaline granites are richer in Ca and there is no Ca in country rocks
  - Metaluminous/peraluminous granites may need Ca from country rocks for significant fluorite mineralization
  - Winterland porphyry (along same trend as E lobe) is richer in Ca
  - Source of Ca may have been early crustal assimilation at depth (A2 type)?
  - No F-rich vapour in metaluminous phase
  - AGS deposit probably underlain by peralkaline phase (source of mineralization)



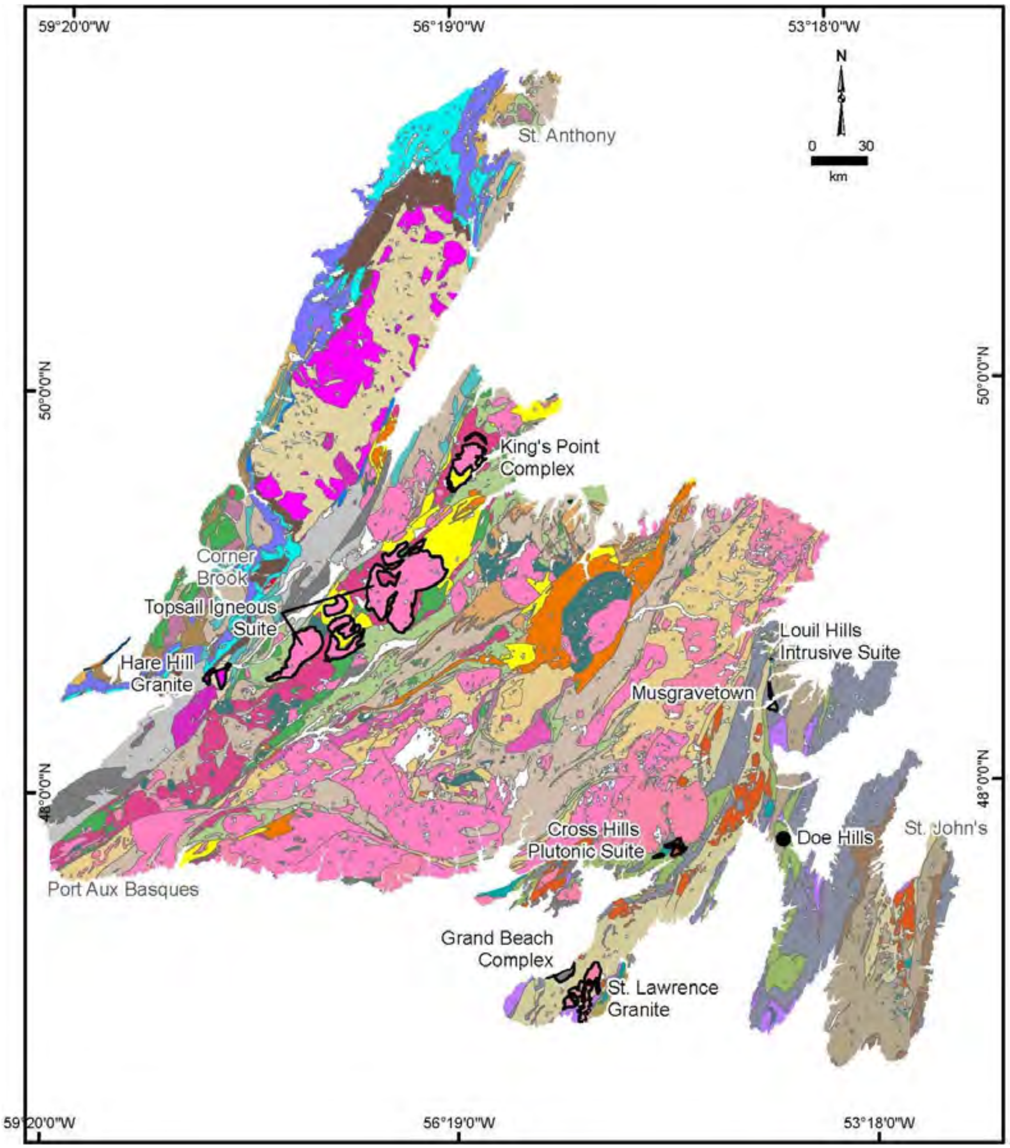
- Fluorite mineralization occurs in country rocks, due to volatile F-rich vapour being able to escape the granite (e.g. AGS deposit)
  - Contrary to previous studies (Strong, 1982; Williamson, 1956)
  - Encourages further exploration in the country rocks

- No need for Ca-rich country rocks since granite is source of Ca

Dolejs and Baker (2006); Dill (2010); Magyarosi (2022)

Fluorite potential in Newfoundland

Other peralkaline complexes, although may be associated with other type of granites as well, if there is a Ca source



Ackley Granite

Concentration of fluorite occurrences that are hosted in felsic volcanic rocks of the Long Harbour Group, but likely underlain by Ackley Granite (similar to AGS):

- Geophysics
- Mo mineralization identified further W also part of Ackley
- Few analysis of felsic volcanic rocks returned F <319 ppm

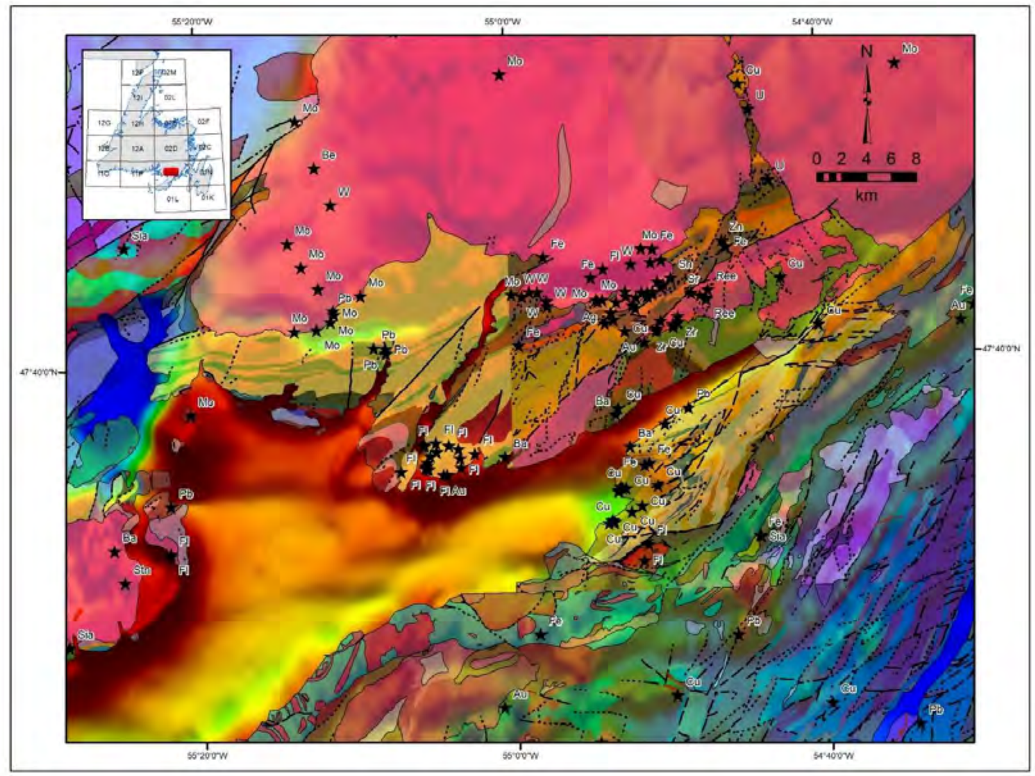
Similar age as St. Lawrence Granite (Devonian)

It is a composite pluton, but contains A-type, highly fractionated parts with high F content

Shallow granite

Hydrothermally altered roof zones identified in southern part

Associated with fluorite occurrences in addition to Mo, W and Sn



Kerr et al. (2009) and references within

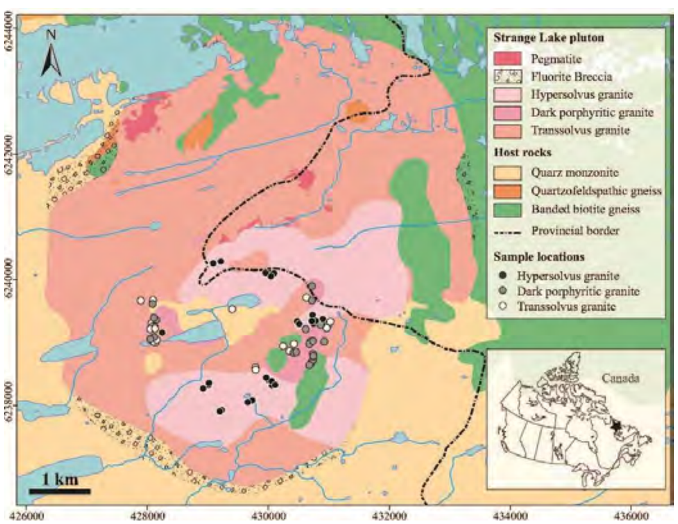
Labrador

Peralkaline complexes

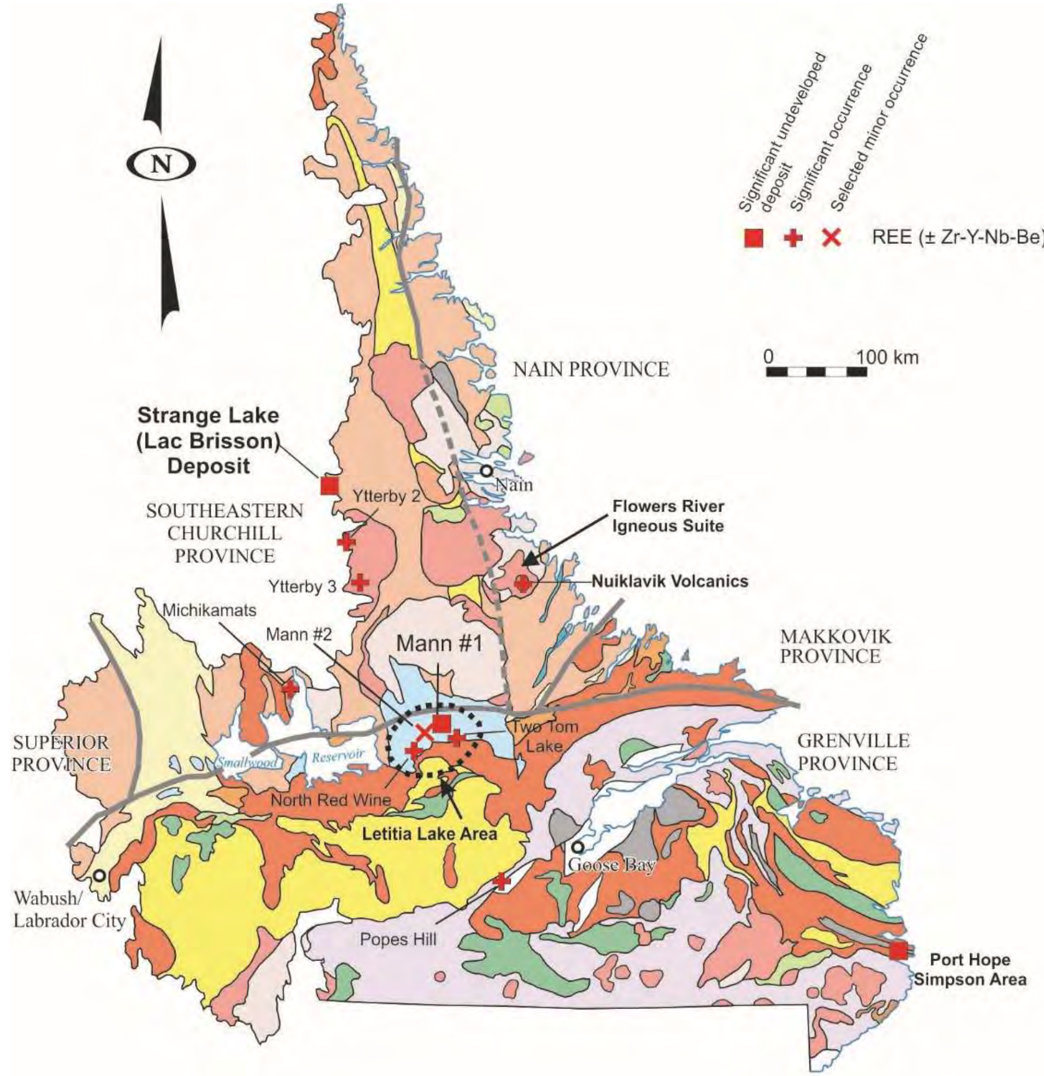
All associated with fluorite

Strange Lake: fluorite breccia

PHS area: fluorite in peralkaline rocks, fluorite occurrences



Siegel et al., 2018



Modified after Kerr et al., 2011

Thank you!

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