Fluid inclusion and stable isotope evidence for mixing of magmatic – hydrothermal fluids with meteoric water in vein-type Cu-Au-Bi deposits, southern New Brunswick, Canada

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Abstract: Vein-type Cu-Au-Ag-Bi mineralization in the Caledonian Highlands, southern NB, Canada, is hosted within quartz-carbonate-rich shear zones cutting felsic lithic tuffs, intermediate intrusives and interbedded felsic and mafic flows of the Neoproterozoic Broad River Group. Mineralization in the veins consists of bornite-chalcocite-hematite, coprecipitated with electrum and bismuthinite; ore minerals post-date quartz and REE-rich carbonates in the veins, with later supergene oxidation and hydration of the ores to cuprite-malachite. Wall-rock alteration is characterized by albitization and paragonitization. Replacement of bornite by chalcocite- hematite indicates changes in fluid redox with mineralization progression.

Trails of secondary fluid inclusions in the quartz veins are two-phase liquid-vapour at room temperature. Homogenization occurs by vapour bubble disappearance between 150-270°C for all assemblages; individual assemblages show relatively narrow ranges (e.g., 173-191°C, n=22). Bulk salinities from final ice melting range from 4 to 13 wt% NaCl eq. with individual assemblages showing similarly narrow ranges.

Stable isotope data (bulk separates, and in-situ by secondary ion mass spectrometry [SIMS]) for vein-stage quartz ($\delta^{18}O_{bulk}$ = 13.7-15.1‰; $\delta^{18}O_{SIMS\text{-}qtz}$ = 10.8±1.5‰, 1ζ, n=32) and carbonate ($\delta^{13}C_{bulk}$ = -4.4 to -4.6 ‰) combined with microthermometric data rule out unmodified, heated seawater and meteoric water as the dominant fluid components, and suggest that the metal-bearing fluids were magmatic in origin or represented saline formation waters modified through fluid-rock interaction with the host volcanic rocks (calculated $\delta^{18}O_{fluid}$ ~ 6-7 ‰). However, significant variations in $\delta^{18}O_{SIMS\text{-}qtz}$ are observed within single quartz crystals across growth zones and in massive quartz texturally predating sulfides and gold (from as low as 8.2 ‰ to 14.8 ‰ in quartz enclosed entirely within bornite-chalcocite). This indicates either (i) localized mixing of the metal-bearing fluid with low latitude meteoric water (calculated $\delta^{18}O$ = -1.0 to 0 ‰), or (ii) fluctuations in fluid temperature during vein formation, with the lowest T portions of the vein associated with base metal-gold precipitation, or (iii) both. The isotopic composition of coeval quartz-carbonate predict a crystallization/final equilibration T of vein-stage at ~250- 270°C; if inclusions are primary, then a maximum $P_{trapping}$ = ~1.5 kbar, based on the lowest T assemblages, is estimated.

Significant fluctuations in fO_2, fluid temperature or fluid composition during vein precipitation highlight the importance of fluid mixing for mineralization. These characteristics, combined with the style of mineralization, link these deposits in NB genetically to much larger vein Cu deposits worldwide (e.g., Churchill, Davis-Keays, and Mamainse Point, Canada; Inyati, Zimbabwe; Copper Hills, Australia; Messina, South Africa; Cornwall, UK).

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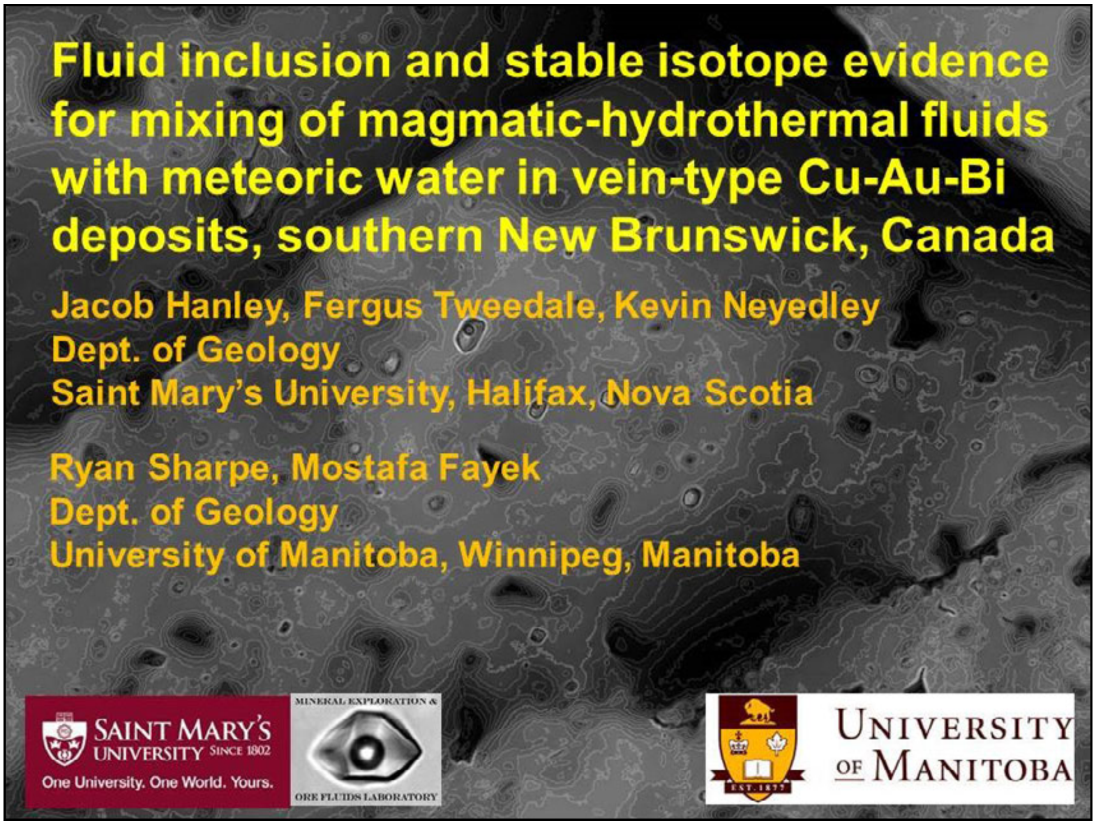
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MINERAL EXPLORATION &
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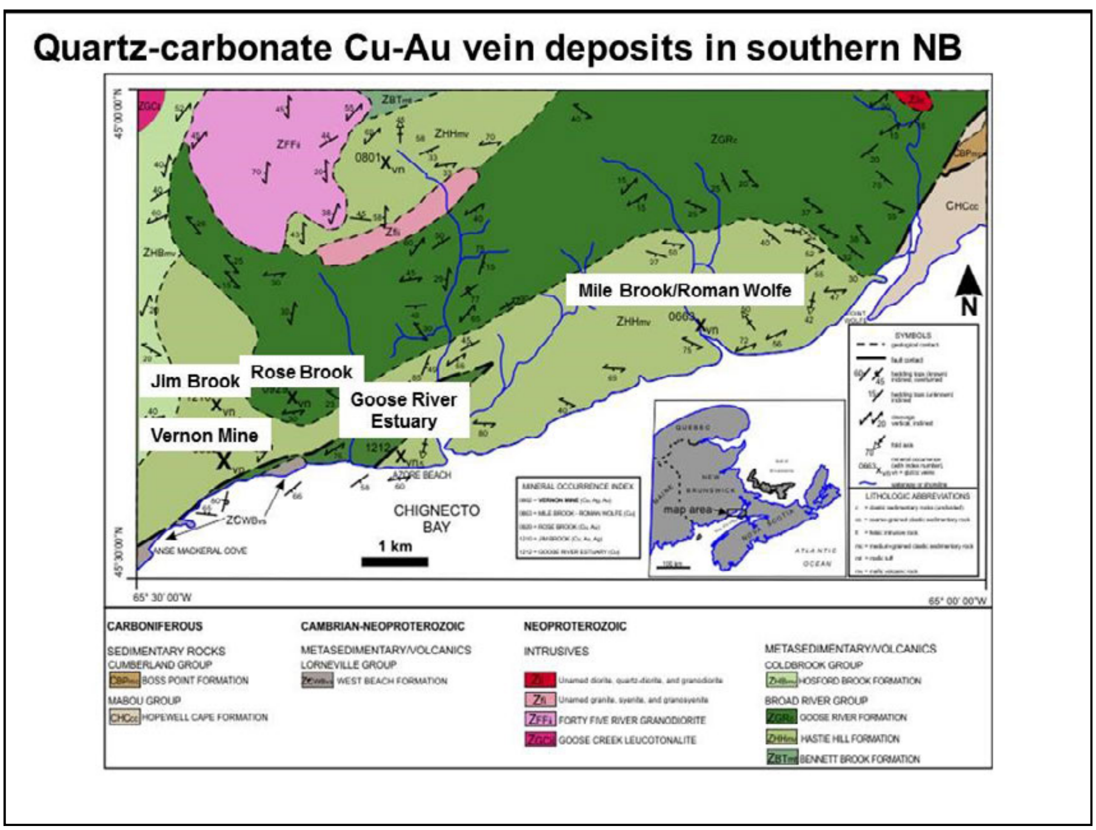
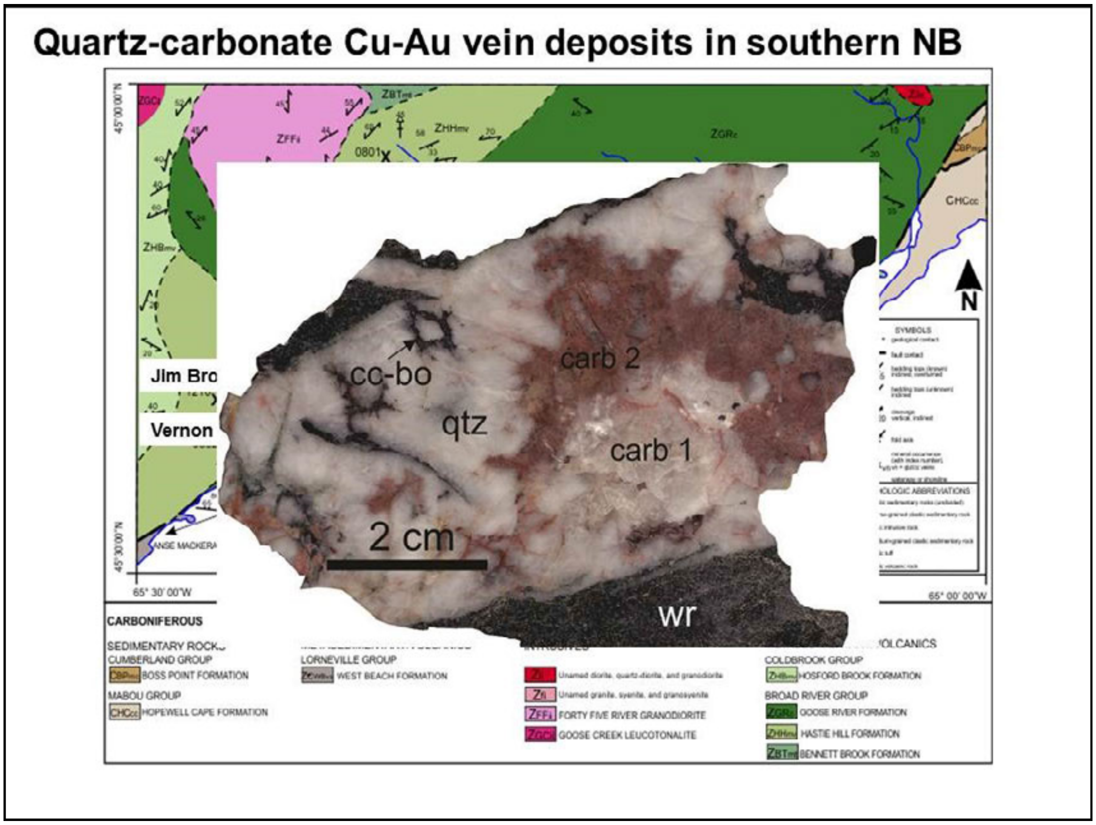

Quartz-carbonate Cu-Au vein deposits in southern NB
Mile Brook/Roman Wolfe
Jim Brook
Rose Brook
Goose River
Estuary
Vernon Mine
CHIGNECTO
BAY
1 km
N
map area
45° 30' 00"N
65° 30' 00"W
65° 00' 00"W
CARBONIFEROUS
SEDIMENTARY ROCKS
CUMBERLAND GROUP
BOSS POINT FORMATION
MABOU GROUP
HOPEWELL CAPE FORMATION
CAMBRIAN-NEOPROTEROZOIC
METASEDIMENTARY/VOLCANICS
LORNEVILLE GROUP
WEST BEACH FORMATION
NEOPROTEROZOIC
INTRUSIVES
Unamed diorite, quartz-diorite, and granodiorite
Unamed granite, syenite, and granosyenite
FORTY FIVE RIVER GRANODIORITE
GOOSE CREEK LEUCOTONALITE
METASEDIMENTARY/VOLCANICS
COLDBROOK GROUP
HOSFORD BROOK FORMATION
BROAD RIVER GROUP
GOOSE RIVER FORMATION
HASTIE HILL FORMATION
BENNETT BROOK FORMATION


Quartz-carbonate Cu-Au vein deposits in southern NB
cc-bo
qtz
carb 2
carb 1
2 cm
wr
Jim Bro
Vernon
N
65° 30' 00"W
65° 00' 00"W
CARBONIFEROUS
SEDIMENTARY ROCKS
CUMBERLAND GROUP
BOSS POINT FORMATION
MABOU GROUP
HOPEWELL CAPE FORMATION
LORNEVILLE GROUP
WEST BEACH FORMATION
Unamed diorite, quartz-diorite, and granodiorite
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FORTY FIVE RIVER GRANODIORITE
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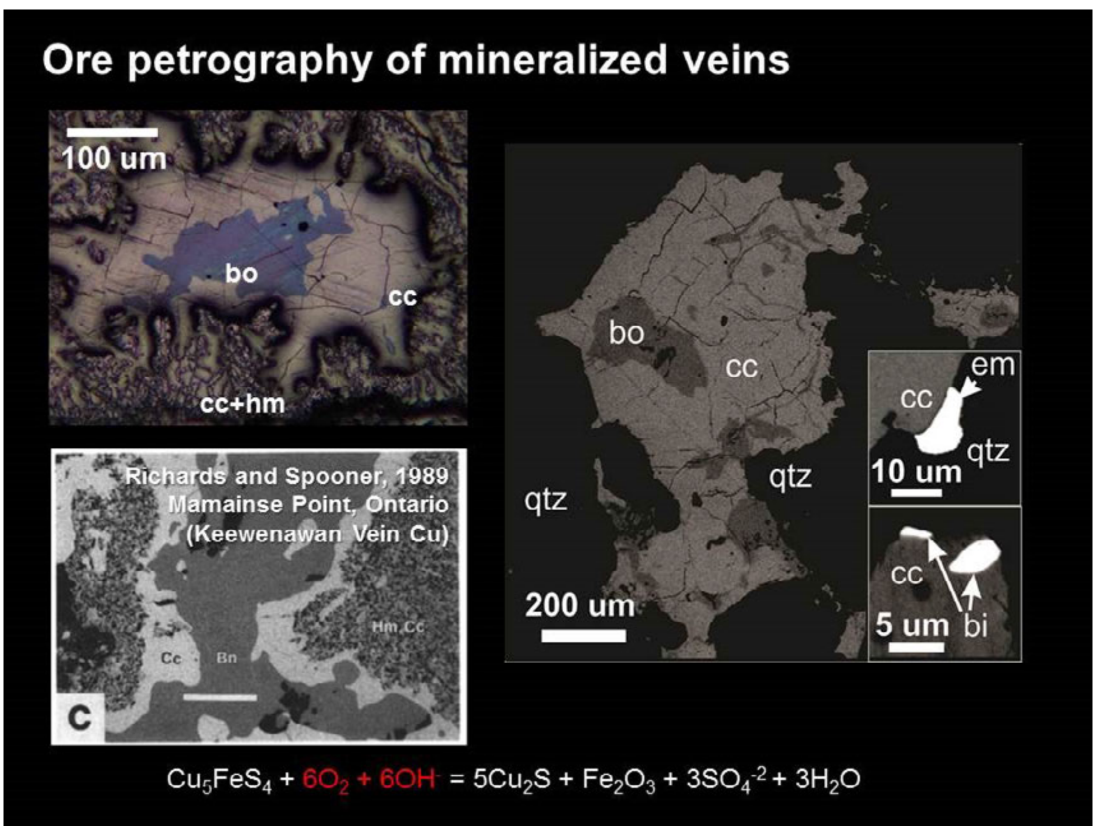
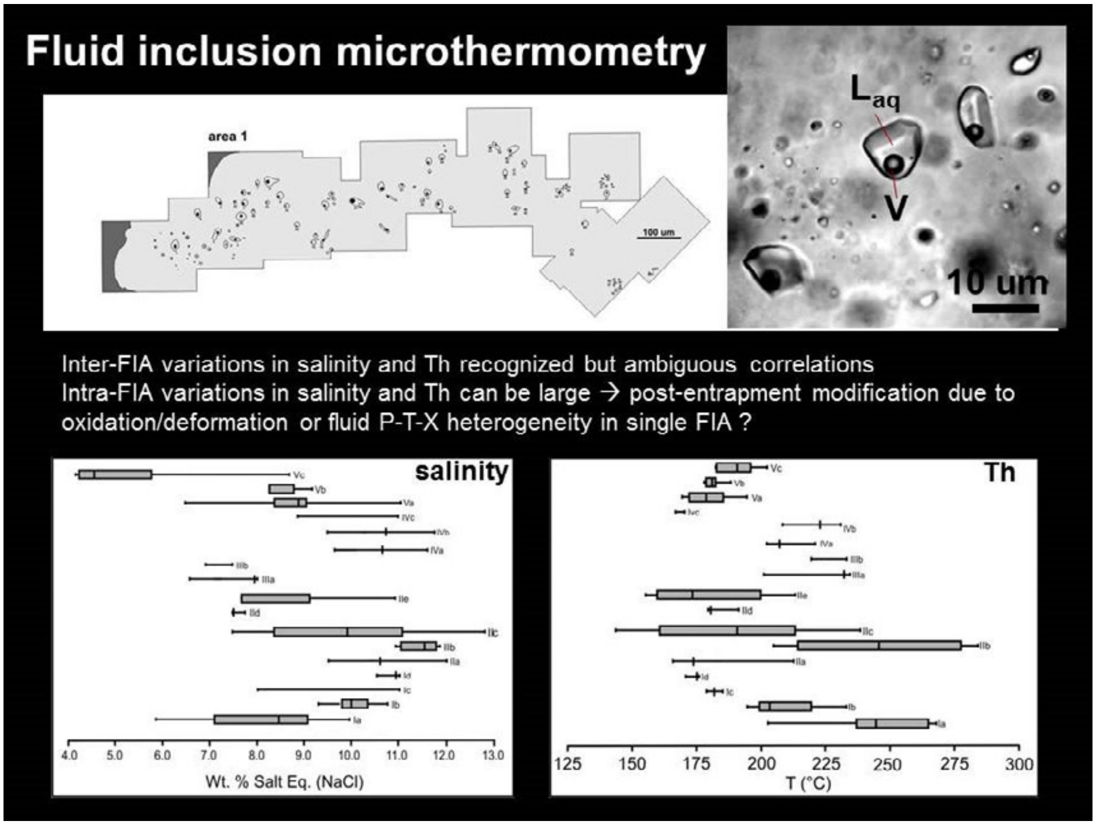
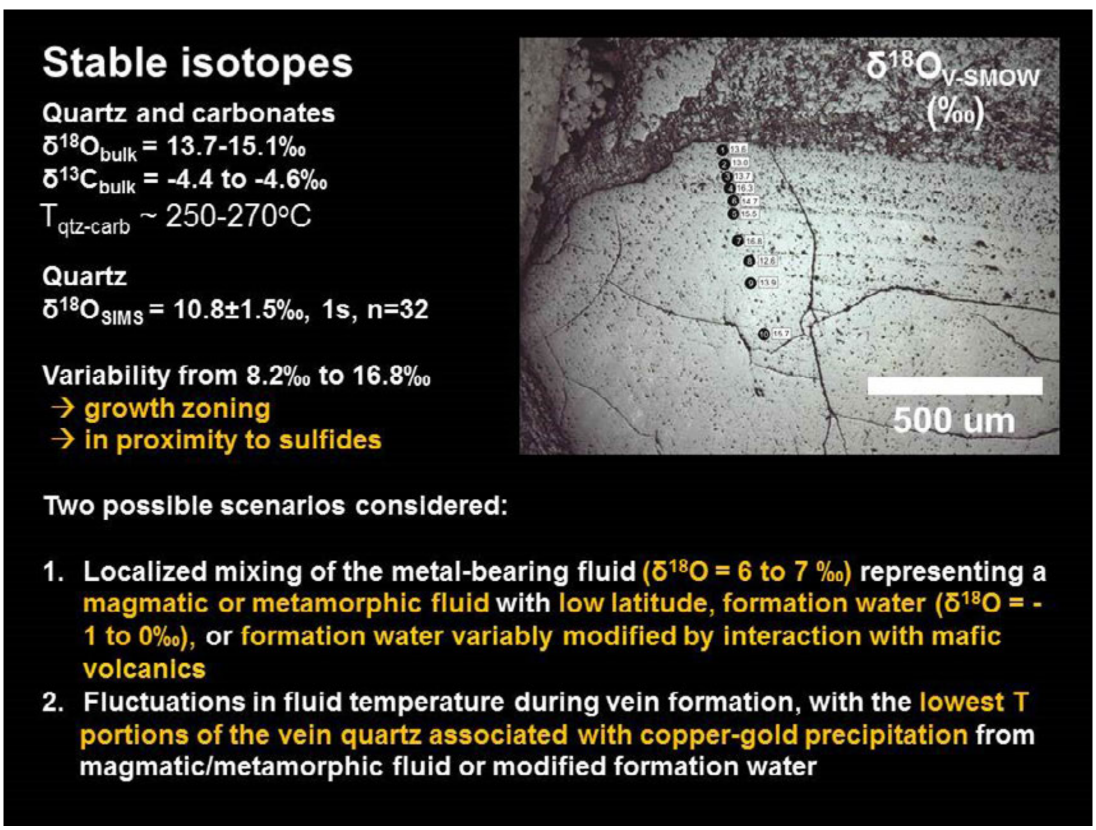

Ore petrography of mineralized veins
100 um
bo
cc
cc+hm
Richards and Spooner, 1989
Mamainse Point, Ontario
(Keewenawan Vein Cu)
Cc
Bn
Hm Cc
C
bo
cc
qtz
qtz
200 um
cc
em
qtz
10 um
cc
5 um
bi
$Cu_5FeS_4 + 6O_2 + 6OH^- = 5Cu_2S + Fe_2O_3 + 3SO_4^{-2} + 3H_2O$


Fluid inclusion microthermometry
area 1
100 um
Laq
V
10 um
Inter-FIA variations in salinity and Th recognized but ambiguous correlations
Intra-FIA variations in salinity and Th can be large → post-entrapment modification due to oxidation/deformation or fluid P-T-X heterogeneity in single FIA ?
salinity
Th
4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0
Wt. % Salt Eq. (NaCl)
125 150 175 200 225 250 275 300
T (°C)

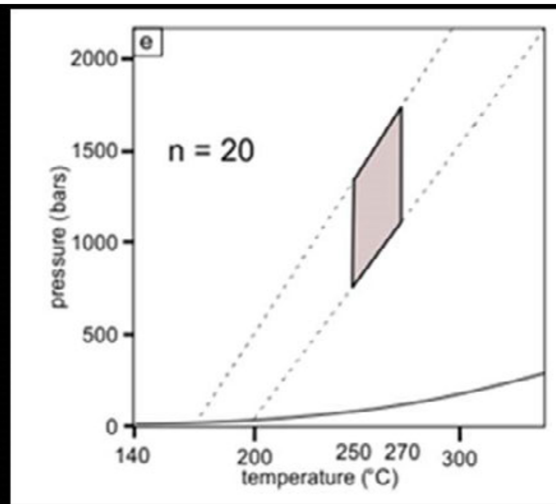

Stable isotopes
Quartz and carbonates
δ18Obulk = 13.7-15.1‰
δ13Cbulk = -4.4 to -4.6‰
Tqtz-carb ~ 250-270°C
Quartz
δ18OSIMS = 10.8±1.5‰, 1s, n=32
Variability from 8.2‰ to 16.8‰
→ growth zoning
→ in proximity to sulfides
δ18OV-SMOW (‰)
500 um
Two possible scenarios considered:
1. Localized mixing of the metal-bearing fluid (δ18O = 6 to 7 ‰) representing a magmatic or metamorphic fluid with low latitude, formation water (δ18O = -1 to 0‰), or formation water variably modified by interaction with mafic volcanics
2. Fluctuations in fluid temperature during vein formation, with the lowest T portions of the vein quartz associated with copper-gold precipitation from magmatic/metamorphic fluid or modified formation water

Stable isotopes

Quartz and carbonates
$\delta^{18}O_{bulk}$ = 13.7-15.1‰
$\delta^{13}C_{bulk}$ = -4.4 to -4.6‰
$T_{qtz\text{-}carb}$ ~ 250-270°C

Quartz
$\delta^{18}O_{SIMS}$ = 10.8±1.5‰, 1s, n=32

Variability from 8.2‰ to 16.8‰
→ growth zoning
→ in proximity to sulfides



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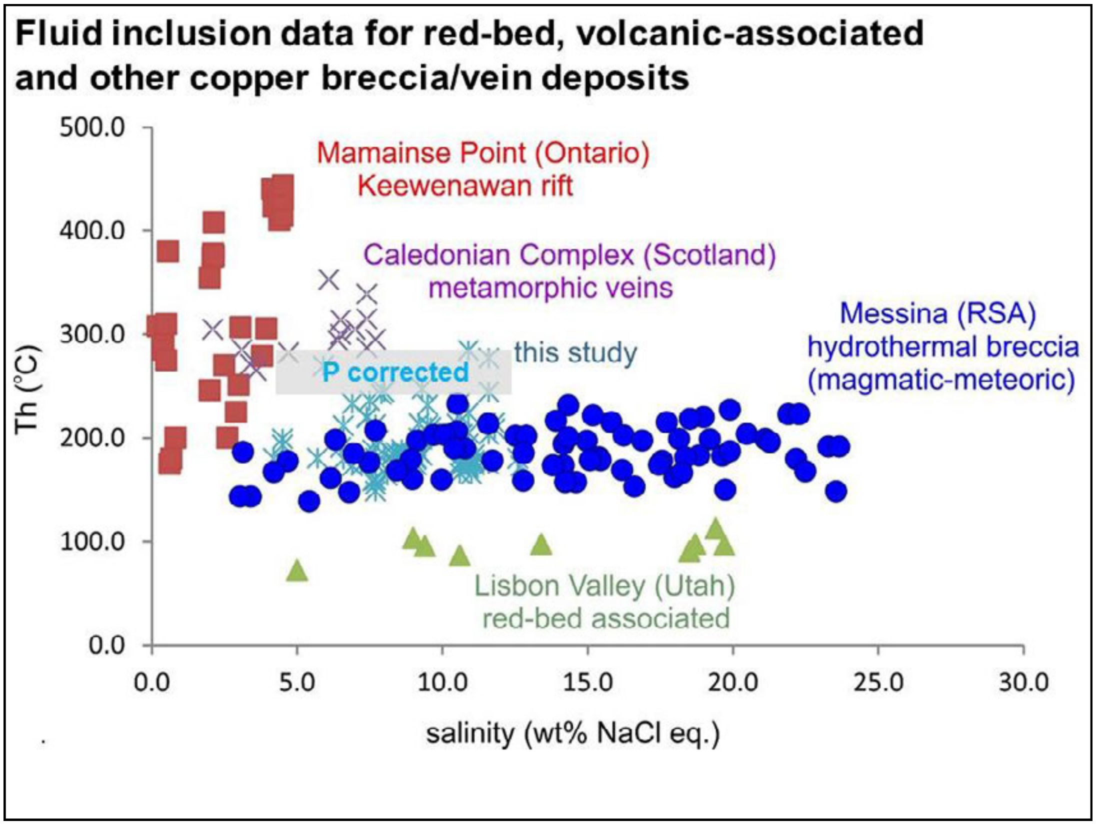
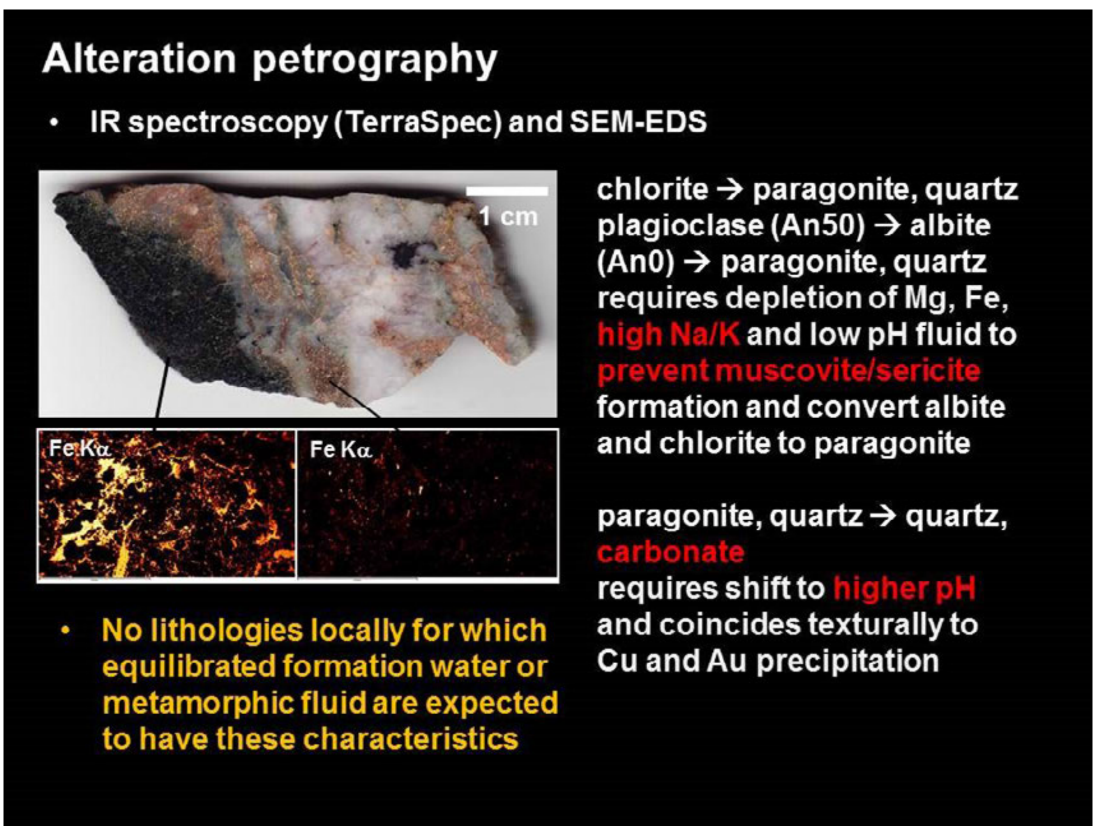
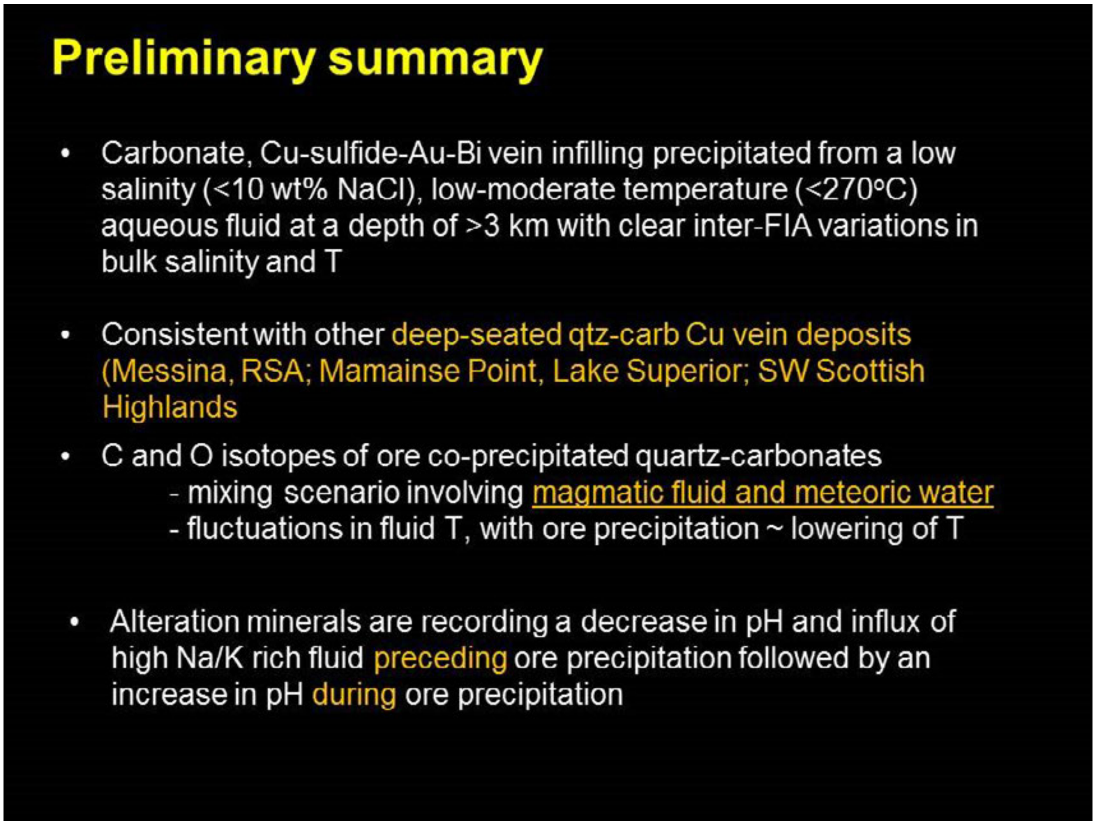
2. **Fluctuations in fluid temperature during vein formation, with the lowest T portions of the vein quartz associated with copper-gold precipitation from magmatic/metamorphic fluid or modified formation water**

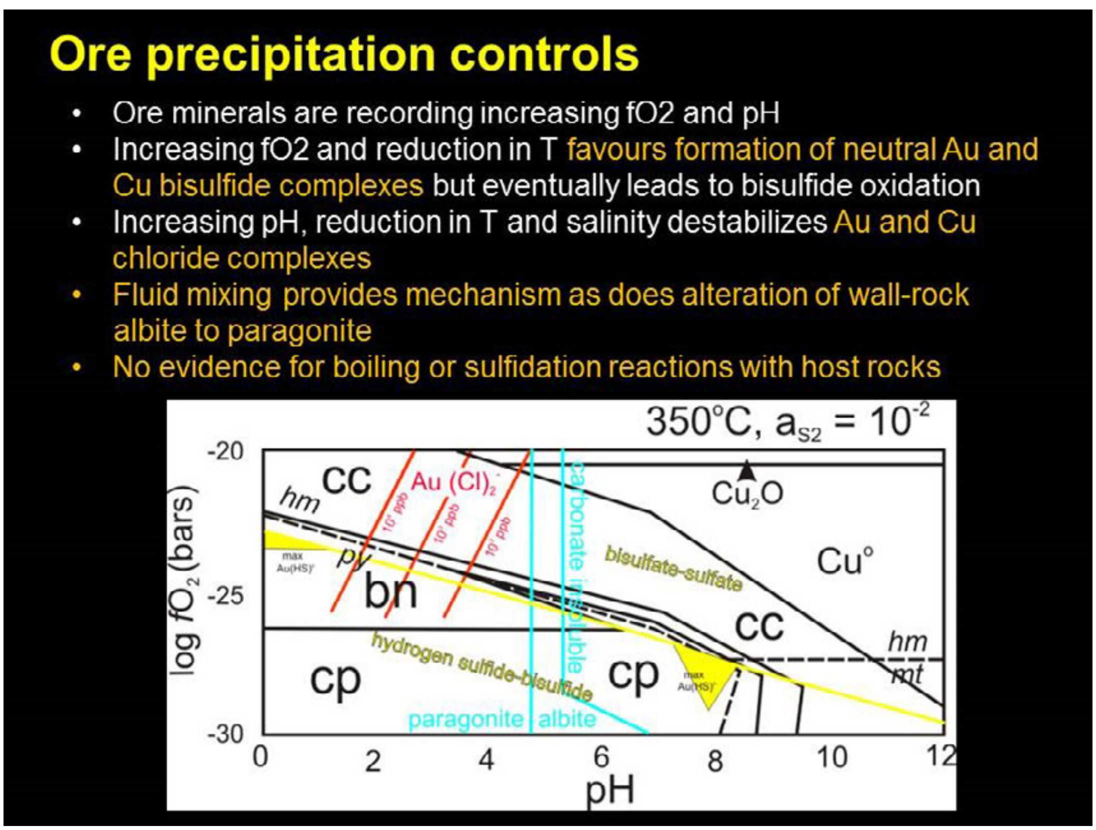
Comparison to other sediment and volcanic-associated Cu deposits

	Richards 1985	Morrison & Parry, 1986	Richards *et al.*, 1988	Anderson *et al*, 2004	Greyling *et al.*, 2005	Bradshaw, 2008	El Desouky *et al.*, 2009
Geographic location	Mamainse Point (Canada)	Paradox basin, (SW USA)	Central African copper belt (Zaire and northern Zambia)	SW Scottish Highlands	Zambian Copperbelt (Africa)		Katanga Copperbelt (Africa)
Deposit (or group) name	Coppercorp mine	Lisbon Valley anticline	Musoshi Minet	Argyll Group	Chambishi deposit		Kamoto and Luiswishi Mines
Deposit type	Fissure/vein-hosted	Fault-related anticline	Stratiform	Vein	stratiform		hypogene strataform
Deposit age	Mesoprotererozoic (Keweenawan)	Post-Laramide (Cretaceous - Eocene)	> 550 m.y.	Carboniferous			
Host rock type	Volcanic/sedimentary (intra-continental)	Sedimentary	Sedimentary (shale) (intracontinental)	Metavolcanic/ Metasedimentary			
Host-rock age	Meso-proterozooic	Permian	1.3 Ga – 602 Ma	Neoproterozoic			
Major ore minerals	Cc	Cc	Ccp, Bn	n/a			
Trace ore minerals	Cp, Py, Hm, Cu, Ag, Bn	Ccp, Ca, Dol Ba-Sr(SO_4), Cv, Dg, Ag	Py	Ccp, Py, Sp, Gn			
FI- bearing mineral	Qtz	Calcite and dolomite	Qtz	Qtz	quartz		quartz
Timing of deposit	Syngenetic	Epigenetic	Epigenetic	Epigenetic	late-diagenetic		early-diagenetic
Fluid compositon (wt.% $NaCl_{equiv}$)	0 – 20	5.0 – 13.4 (vein) 18.5 – 19.7 (veinlets)	39 (high-temp group)* 28 (low temp.)*	4.0 – 12.7	11.9 - 23.1		11.3 - 20.9
T_H(°C)	100 – 450	72 – 113	397 ± 5[1] 275 ± 13[1]	223 – 360	86 - 160		115 - 220
P (bar)	X				480 - 800		
T (°C)	X				130 - 270		
O isotope data (SMOW ‰)	10.7 - -1.4	21.2 – 10.7	n/a	+11.7- +16.5 (Qtz) +17.1 - +24.5 (Dol)			
C isotope data (PDB)‰	-4.0 ± 0.9	-11.8 - -0.8	n/a	-3.0 - -0.8 (Dol)			
S isotope data		n/a	n/a	-13.6 - - 1.1 9 (excludes Brt = +7.1 - +8.1))			


Fluid inclusion data for red-bed, volcanic-associated and other copper breccia/vein deposits
Mamainse Point (Ontario)
Keewenawan rift
Caledonian Complex (Scotland)
metamorphic veins
this study
P corrected
Messina (RSA)
hydrothermal breccia
(magmatic-meteoric)
Lisbon Valley (Utah)
red-bed associated
Th (°C)
500.0
400.0
300.0
200.0
100.0
0.0
0.0
5.0
10.0
15.0
20.0
25.0
30.0
salinity (wt% NaCl eq.)


Alteration petrography
• IR spectroscopy (TerraSpec) and SEM-EDS
1 cm
Fe Kα
Fe Kα
chlorite → paragonite, quartz
plagioclase (An50) → albite (An0) → paragonite, quartz
requires depletion of Mg, Fe, high Na/K and low pH fluid to prevent muscovite/sericite formation and convert albite and chlorite to paragonite
paragonite, quartz → quartz, carbonate
requires shift to higher pH and coincides texturally to Cu and Au precipitation
• No lithologies locally for which equilibrated formation water or metamorphic fluid are expected to have these characteristics


Preliminary summary
• Carbonate, Cu-sulfide-Au-Bi vein infilling precipitated from a low salinity (<10 wt% NaCl), low-moderate temperature (<270°C) aqueous fluid at a depth of >3 km with clear inter-FIA variations in bulk salinity and T
• Consistent with other deep-seated qtz-carb Cu vein deposits (Messina, RSA; Mamainse Point, Lake Superior; SW Scottish Highlands
• C and O isotopes of ore co-precipitated quartz-carbonates
- mixing scenario involving magmatic fluid and meteoric water
- fluctuations in fluid T, with ore precipitation ~ lowering of T
• Alteration minerals are recording a decrease in pH and influx of high Na/K rich fluid preceding ore precipitation followed by an increase in pH during ore precipitation


Ore precipitation controls
• Ore minerals are recording increasing fO2 and pH
• Increasing fO2 and reduction in T favours formation of neutral Au and Cu bisulfide complexes but eventually leads to bisulfide oxidation
• Increasing pH, reduction in T and salinity destabilizes Au and Cu chloride complexes
• Fluid mixing provides mechanism as does alteration of wall-rock albite to paragonite
• No evidence for boiling or sulfidation reactions with host rocks
350°C, a_S2 = 10^-2
log fO2 (bars)
pH
-20
-25
-30
0
2
4
6
8
10
12
cc
hm
Au (Cl)2-
py
bn
cp
Cu2O
Cu°
carbonate insoluble
bisulfate-sulfate
hydrogen sulfide-bisulfide
paragonite
albite
max Au(HS)-
hm
mt

Connections to intrusive activity ?

Barr and White (1999), Park et al., (2008):

- W. Caledonian Highlands: 630-620 Ma dioritic to granitic plutons coeval with subduction-related volcanics in Broad River Group
- E. Caledonian Highlands: 560-550 Ma gabbroic to syenogranitic plutons coeval with extension-related volcanics in Cold Brook Group
- Many plutons show highly anomalous Cu contents (e.g., Point Wolfe River Pluton, Forty Five River Granodiorite near our study area)
- Initiated ~615 Ma regional deformation was prolonged, possibly up to Carboniferous and similar deposits to Mile Brook-Roman Wolfe are hosted in Carboniferous rocks (Mispeck Group), even cross cutting regional deformational fabrics (Ruitenberg, 1979)

→ Dating of monazite in qtz-carb-sulfide veins in progress
→ Regional structural study of deposits to clarify reported field relations
→ LA-ICPMS of fluid inclusions (is the fluid consistent with a contracted magmatic vapour phase ? Cs-B-As-Sb-Au-Cu)

Connections to intrusive activity ?

If so, which of these two suites are more productive for hydrothermal vein deposits at higher stratigraphic levels ? Are these “subepithermal” vein deposits spatially linked to hidden intrusion-related deposits in the Caledonian Highlands ?