# *In situ* LA-ICP-MS of sulfide minerals in VMS deposits throughout the Bathurst Mining Camp, New Brunswick, Canada:
## volatile trace-element contents and distribution with implications for their syngenetic to polyphase metamorphic history


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## Abstract

The world-class massive sulfide deposits of Zn-Pb-Cu-Ag-Au type in the Bathurst Mining Camp, Eastern Canada are hosted within Middle Ordovician bimodal volcanic and sedimentary sequences. They have undergone complex polyphase deformation and associated regional greenschist and locally blueschist facies metamorphism during closure of the Tetagouche-Exploits back-arc basin in the Late Ordovician to Early Silurian (Salinic Orogeny) and again during the Late Silurian Acadian Orogeny. The mineralogy of massive sulfides consists of five minerals (pyrite, sphalerite, galena, pyrrhotite, and chalcopyrite) that comprise 95% of the mineralization, with minor amounts of arsenopyrite, marcasite, and sulfosalts.

*In situ* LA-ICP-MS analyses of the volatile trace-element suite (As, Cd, Hg, In, Sb, Tl, etc.) of the major sulfide minerals in some of the deposits in the BMC offer a lower detection limits than other micro-analytical methods. Data from the representative massive sulfide deposits of the BMC show that in addition to arsenopyrite, As is also concentrated in some pyrite porphyroclasts, galena, sphalerite, and chalcopyrite. Cadmium is enriched in galena and sphalerite. The most dominant carrier of Hg is sphalerite, followed by pyrite. Indium is enriched mostly in sphalerite and chalcopyrite. Antimony abundances are more variable, but it typically occurs in pyrite, and to a lesser degree in galena. Also, arsenopyrite exhibits a high content of Sb likely because of substitution of Sb and As in solid solutions. Thallium shows variable distribution, but it is mostly enriched in pyrite.

Abundances of volatile elements in Bathurst Mining Camp show that the contents of these elements varies in the various types of VMS deposits, which reflect the different conditions of massive sulfides formation, such as differences in the temperature of deposition, metal sources, and geochemical characters of the ore-bearing solutions and host rocks. Because of the primary variation of volatile trace elements in these sulfide facies, they can be used in enhancing our interpretation of the ore-forming environment, as well as potentially be used as a trace-element vectoring tool (volatile element halos dispersions) in the exploration for massive sulfide deposits.

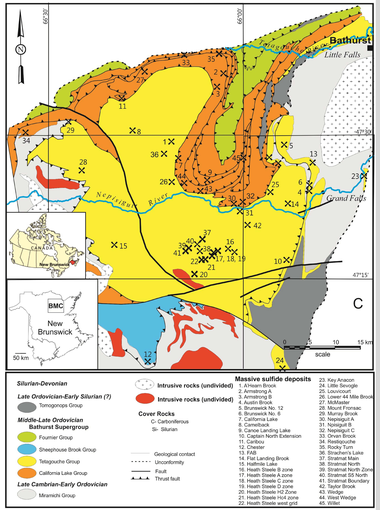

### Summary of the Bathurst Mining Camp Geology

The Bathurst massive sulfide deposits form part of a middle Ordovician arc and back-arc system that developed on the Gondwanan continental margin of the northern Appalachians (Goodfellow and McCutcheon, 2003).

Pre-Silurian rocks in the BMC can be divided into five groups, namely the Miramichi, Tetagouche, California Lake, Sheephouse Brook, and Fournier groups (van Staal, 1987; van Staal *et al.*, 2003a). The Miramichi Group, the oldest group (490-478 Ma), consists of a passive-margin continentally derived turbidite sequence. The Miramichi Group was succeeded by Bathurst Supergroup that constitutes Sheephouse Brook, Tetagouche, and California Lake groups, along with the Fournier Group. The first three groups mainly include ensialic volcanic and sedimentary rocks, which are dominated by two distinct cycles of felsic volcanism succeeded by mafic volcanism of the Fournier Group that is the youngest group (~ 465 Ma); it is defined by ocean-floor mafic volcanic and related sedimentary rocks that were obducted onto the para-autochthonous sequences.

The Bathurst Supergroup formed within an intra-crustal (continental) proto back-arc basin (similar to the Japan Sea) and is referred to as the Tetagouche–Exploits Basin (van Staal, 1987). Closure of the Tetagouche-Exploits back-arc basin from the Late Ordovician to Early Silurian has resulted in polyphase deformation and associated lower to upper grade greenschist facies and locally blueschist facies regional metamorphism during the Salinic Orogeny. Subsequent Acadian deformation (Late Silurian in this region) refolded pre-existing Salinic structures leading to complex re-folded fold structures. Peak metamorphism condition varies from 325° to 400°C and 6 to 7 kbars. The present distribution and shape of massive sulfide deposits and associated sulfide stringer zones are mainly controlled by D1 and D2 structures (Goodfellow and McCutcheon 2003).

Most deposits in the BMC are hosted by the Tetagouche Group (32 of 45) and California Lake Group (13 of 45), with the majority being associated with the Nepisiguit Falls and Spruce Lake formations, respectively. In addition, the Chester deposit belongs to the Sheephouse Brook Group the southern of Bathurst Mining Camp (Goodfellow and McCutcheon 2003).




*Simplified geological map of the Bathurst Mining Camp, Canada, showing the location of massive sulfide deposits.*

## Bathurst Mining Camp massive sulfide deposits (Goodfellow and McCutcheon, 2003)

Zn–Pb–Cu–Ag-Au type;

Pre-mining geologic resource of at least 349 Mt of massive sulfide grading 4.72% Zn, 1.78% Pb, 0.64% Cu, 51 g/t Ag, and 0.54 g/t Au;

45 deposits, 25 of which are in excess of 1Mt;

Supergiant Brunswick No.12 deposit, which was in excess of 290 Mt pre-mining massive sulfide resource;

Massive sulfide deposits of the BMC contain both syngenetic and epigenetic features;

Five distinct hydrothermal facies in the BMC:

(1) bedded or banded sulfide facies (layered Zn-Pb-rich sulfide facies: py+ sph + gn ± cpy, po, and td),

(2) bedded pyrite (py ± sph ± gn),

(3) vent complex or basal Cu zone or basal sulfide facies (Cu-rich sulfide facies; po + mt + py + cpy+ qtz ± sph ± gn),

(4) sulfide stringer zone (veins and impregnations of sulfide minerals (po and/or py with cpy, and traces of sph and gn) in hydrothermally altered sedimentary and volcanic rocks that underlie the vent complex), and

(5) carbonate-oxide-silicate iron formation

## Methodology

*In situ* LA-ICP-MS analyses of the volatile trace-element suite (As, Cd, Hg, In, Sb, Tl, etc.) of the major sulfide minerals in some of the deposits in the BMC offer lower detection limits than other micro-analytical methods (see Table).

Sulfide analyses were carried out at LA-ICP-MS lab at Department of Earth Sciences, University of New Brunswick , Fredericton on a Resonetics S-155-LR with laser wavelength 193nm excimer laser ablation system coupled to an Agilent 7700x quadrupole ICP-MS.

The technique can reveal whether the trace elements occur within the sulfide (as solid solution) or as micro- or submicroscopic inclusions of a different mineral that can be distinguished in the ablation profile.

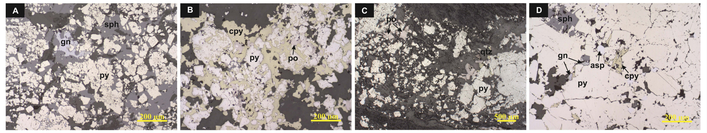
Detection limits of analysed sulfide grains in average (ppm)

| Analyte | Pyrite | Sphalerite | Galena | Chalcopyrite | Arsenopyrite | Pyrrhotite |
|---|---|---|---|---|---|---|
| $^{34}$S | 696.790 | 1052.087 | 905.450 | 2144.800 | 8551.050 | 5126.506 |
| $^{55}$Mn | 0.560 | 0.800 | 0.806 | 1.932 | 6.967 | 4.159 |
| $^{59}$Co | 0.030 | 7.671 | 2.723 | 0.047 | 0.000 | 0.017 |
| $^{60}$Ni | 0.144 | 0.908 | 0.072 | 0.468 | 1.502 | 0.980 |
| $^{63}$Cu | 0.084 | 0.201 | 0.111 | 0.361 | 0.017 | 0.036 |
| $^{66}$Zn | 0.800 | 0.109 | 0.104 | 3.056 | 9.262 | 8.451 |
| $^{75}$As | 0.632 | 1.032 | 2.047 | 2.291 | 84.286 | 5.259 |
| $^{78}$Se | 0.471 | 0.717 | 0.800 | 1.871 | 5.887 | 3.427 |
| $^{107}$Ag | 0.006 | 0.011 | 0.705 | 0.022 | 0.094 | 0.044 |
| $^{111}$Cd | 0.108 | 0.190 | 0.011 | 0.378 | 1.380 | 0.667 |
| $^{115}$In | 0.002 | 0.004 | 0.178 | 0.008 | 0.025 | 0.014 |
| $^{118}$Sn | 0.069 | 0.113 | 0.003 | 0.252 | 0.812 | 0.655 |
| $^{121}$Sb | 0.067 | 0.107 | 0.084 | 0.261 | 0.941 | 0.513 |
| $^{125}$Te | 0.101 | 0.171 | 0.080 | 0.360 | 1.204 | 0.670 |
| $^{197}$Au | 0.001 | 0.002 | 0.140 | 0.004 | 0.005 | 0.006 |
| $^{202}$Hg | 0.074 | 0.130 | 0.002 | 0.329 | 1.012 | 0.006 |
| $^{205}$Tl | 0.002 | 0.003 | 0.158 | 0.005 | 0.020 | 0.012 |
| $^{208}$Pb | 0.026 | 0.025 | 0.003 | 0.051 | 0.743 | 0.119 |
| $^{209}$Bi | 0.005 | 0.009 | 0.008 | 0.019 | 0.065 | 0.037 |

## Ore petrography

The massive sulfide ores are fine grained and commonly texturally complex, but typically contains predominately 95 percent of only five minerals (pyrite, sphalerite, galena, pyrrhotite, and chalcopyrite in order to abundance) and the minor amounts of arsenopyrite, marcasite, and sulfosalts.

primary textures are locally preserved and mostly have been overprinted by secondary textures, such as equilibrium textures, ductile and brittle deformation, intergrowth and replacement textures .




*Photomicrographs (plane-polarized reflected light) of representative massive sulfide samples of the BMC. A. Bedded sulfide facies (CP-39;161'; Restigouche deposit ), B. Replacement of pyrite by chalcopyrite and pyrrhotite ( 94 -DL-34; 423m; DDH 93-42, Key Anacon east zone), C. Chlorite-quatrz-pyrite-pyrrhotite vein hosted in altered, fine -grained crystal tuff (stringer zone) (LPA-025; 136.2 m; DDH A1, Brunswick No. 12), D. Cataclastic texture in pyrite with intergrowth of chalcopyrite, galena, and sphalerite and overgrowth of arsenopyrite (97-KM-30; 188'; DDH B-259, Brunswick No. 6).*

## Volatile element distribution at the mineral scale

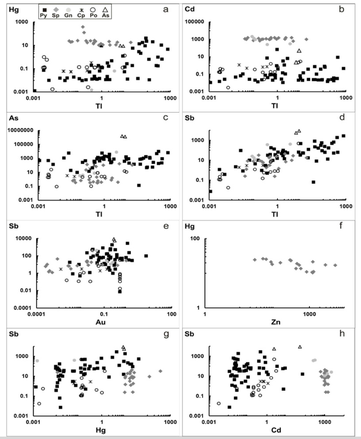
The occurrence of volatile elements between coexisting sulfide minerals is controlled mostly by lattice substitution (nonstoichiometric and stoichiometric) and also micro- to nano-scale mineral inclusions, which are detectable in the laser ablation profile.

Nonstoichiometric substitution in pyrite:
$(AsS)^{3-}$ for $(S_2)^{2-}$

Stoichiometric substitution in pyrite:
$Co^{2+}$, $Ni^{2+}$ for $Fe^{2+}$
$SeS^{2-}$, $Se^{2-}$ $TeS^{2-}$, $Te^{2-}$ for S

Mercury and cadmium in sphalerite:
$Fe^{2+}$, $Cd^{2+}$, $Hg^{2+}$, … for $Zn^{2+}$

Indium in sphalerite:
$(Cu^{+} + In^{3+})$ for $2Zn^{2+}$




*Binary plots of representative volatile and other trace elements (in ppm) from representative massive sulfide deposits in the BMC.*

Sphalerite is the most dominant carrier of Hg (10 to 376 ppm), followed by pyrite (0.001 to 22 ppm).

Cadmium is enriched in galena (259 to 2192 ppm) and sphalerite (686 to 1569 ppm).

In addition to arsenopyrite, As is also concentrated in some pyrite porphyroclasts (0.25 to 10140 ppm), galena (2.7 to 7700 ppm), sphalerite (0.1 to 130 ppm), and chalcopyrite (2.4 to 113 ppm).

Antimony abundances are more variable, but it typically occurs in pyrite (0.002-2770 ppm), and lesser degree in galena (10-407 ppm). Arsenopyrite exhibits high content of Sb (5660-8800 ppm) likely because of substitution of Sb and As in solid solutions.

## Volatile element distributions in VMS sulfide minerals: Implications for their syngenetic to polyphase metamorphic history

There is vast variation of volatile trace-element contents in different pyrite grains

Elevated contents of volatile elements in pseudo-primary pyrite are signature of their syngenetic origin. Metamorphism and deformation processes cause the depletion trends in recrystallized pyrite.

The variation of volatile trace-elements, such as Hg, Cd, and In is higher in remobilized sulfide phases (sphalerite, galena, and chalcopyrite).

## Future work

Comprehensive study of distribution of volatile trace-element suite in the major deposits in the BMC in different sulfide facies;

Elucidation of inter- and intra-deposit variation of volatile trace-elements and its implication in genesis related processes;

Determination of the volatile element halos in the Bathurst Mining Camp will reveal the vertical and extensive lateral distributions of volatile elements in this area and introduce effective exploration tools for the locating concealed deposits that might be undetected by other explorations methods.

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**Acknowledgements** This project is supported by funding from the NRCan Targeted Geoscience Initiative IV program allocating to Azam Soltani Dehnavi's PhD research project. We appreciate advices from Dr. Jan Peter (Geological Survey of Canada, Team leader VMS project) and Dr. Patrick Mercier-Langevin for critical revision of this publication. We are also thankful colleagues at New Brunswick Department of Energy and Mines in Bathurst, especially Jim Walker for assistance in locating previous dataset and samples.

Office Mapping Inc Queen in Right of Canada 2014

doi:10.4095/295690

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**Recommended citation**
Soltani Dehnavi, A., McFarlane, C.R.M., McClenaghan, S.H., and Lentz, D.R., 2014, In situ LA-ICP-MS of sulfide minerals in VMS deposits throughout the Bathurst Mining Camp, New Brunswick, Canada: volatile trace-element contents and distribution with implications for their syngenetic to polyphase metamorphic history; Geological Survey of Canada, Open File 7537, doi:10.4095/295690

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7537
2014