

# **GEOLOGICAL SURVEY OF CANADA OPEN FILE 7856**

# Targeted Geoscience Initiative 4: Canadian Nickel-Copper-Platinum Group Elements-Chromium Ore Systems — Fertility, Pathfinders, New and Revised Models

Recent advances in fluid and melt inclusion and applied mineralogical research in the Sudbury mining camp: improving ore genesis models and exploration success

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# **TABLE OF CONTENTS**

Abstract
Introduction
Analytical Methods
Optical and Scanning Electron Microscopy
Laser Ablation ICP-MS Analysis of Trace Elements in Garnet
Laser Ablation ICP-MS Analysis of Trace Elements in Apatite and
Melt Inclusions
Laser Ablation ICP-MS Analysis of Trace Elements in Biotite
Electron Microprobe Analysis
Fluid and Melt Inclusion Microthermometry
Secondary Ion Mass Spectrometry
Colour Cathodoluminescence Imaging
Bulk Oxygen Stable Isotope Analysis
Results and Data Analysis
Evolution of the Sudbury Igneous Complex Indicated from Silicate
Pathfinder Mineral Chemistry in the Sublayer Environment 220
Stable Isotone Alteration and Fluid Inclusion Fingerprints of
"Low-Sulphide" Mineralization in the Footwall
Discussion and Models 225
Evolution of the Sudbury Igneous Complex Indicated from Silicate
Melt Inclusions
Pathfinder Mineral Chemistry in the Sublayer Environment
Stable Isotope, Alteration, and Fluid Inclusion Fingerprints of "Low-Sulphide"Mineralization in the Footwall
Implications for Exploration
Melt Inclusion and Apatite Trace Element Chemistry in the Sudbury
Igneous Complex Main Mass and Sublayer
Biotite Chemistry in the Sublayer
Stable Isotope, Alteration, and Fluid Inclusion Fingerprints of
"Low-Sulphide"Mineralization in the Footwall
Forthcoming Releases
Acknowledgements
References
Figures
Figure 1. Microphotographs and thin section sketches showing the distribution of apatite in the Transition Zone Gabbro and Whistle offset dyke
Figure 2. Photographs of melt inclusions hosted in apatite from the
North Range Main Mass and offset dykes
Figure 3. Partial plot of the pseudo-ternary Grieg diagram showing the major element chemistry of apatite-hosted melt inclusions from the Main Mass Transition Zone Cobbre and Pale offset duke
Figure 4. Box and whicker plots of the Kd values between anotice and
melt inclusions in the Main Mass
Figure 5. Plot of Kd values between Si-rich and Fe-rich melt in the Pele
and Whistle offset dykes

Figure 6. Box-and-whisker plots of the(Ni) <sub>Bt</sub> , (Cu) <sub>Bt</sub> , (Cr) <sub>Bt</sub> , and	
(Ni/Cr) <sub>Bt</sub> in samples at different distances from the massive sulphide mineralization	1
Figure 7. Photomicrographs and compositional fields on a Ni-Cr-Cu ternary diagram for biotite populations	2
Figure 8. Mineralogical characteristics of the hydrothermal garnet- bearing "low-sulphide" assemblage	3
Figure 9. General fluid inclusion characteristics of hydrothermal garnet-bearing "low-sulphide" assemblages	4
Figure 10. δ <sup>18</sup> O in garnet and calcite from hydrothermal garnet- bearing "low-sulphide" mineralization	6

# Recent advances in fluid and melt inclusion and applied mineralogical research in the Sudbury mining camp: improving ore genesis models and exploration success

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#### ABSTRACT

A variety of microanalytical techniques (LA-ICP-MS, microthermometry, SIMS) were applied to resolve uncertainties about the chemical evolution of the Sudbury Igneous Complex (SIC) melt sheet and its associated hydrothermal systems. In the SIC sublayer and main mass, silicate melt inclusions in early apatite cumulate grains preserve evidence for high-temperature (>1100°C) immiscibility between Fe-rich and Sirich liquids. Melt inclusions record the base metal (Ni, Cu, Co) endowment of the melt sheet prior to and after sulphide saturation and allow quantification of trace element partitioning at various stages during meltsheet evolution, and prediction of the likelihood that an offset dyke contains or does not contain sulphide ore deposits locally. Melt inclusions were deemed unaffected by post-cumulus processes, providing an opportunity to characterize primary magmatic processes otherwise obscured by 1.85 Ga of metamorphism, deformation, and hydrothermal alteration. In the sublayer, analysis of the trace element chemistry of alteration, metamorphic and igneous biotite identified the chemical signature of biotites associated with the host inclusion-rich quartz diorite offset-style Ni-Cu-platinum-group element (PGE) sulphide orebodies, characterized by elevated Ni, Cu, and Ni/Cr ratios. Trace metal analysis of biotite allows differentiation between this key rock type and barren quartz diorite that is otherwise compositionally and texturally comparable. In footwall Cu-Ni-PGE ore deposits, alteration, fluid inclusion, and stable isotope studies provide a systematic description of "low-sulphide" deposit style. Hydrothermal sulphide precipitation, a process recorded in alteration vein styles, was associated with mixing of oxidized, <sup>18</sup>O-enriched, high salinity metal-rich fluids with cooler, reduced, <sup>18</sup>O-depleted, high-Ca groundwaters. Recognition of this mixing process through isotope mapping, fluid inclusion microthermometry, and alteration mineral chemistry provides a means to identify metal-precipitation fronts within the complex footwall environment.

#### INTRODUCTION

Improving exploration models for base metal and PGE deposits using advanced microanalytical research techniques aims to increase Canada's long-term resource base of these essential commodities. The research described here improves exploration models for deposits of Ni, Cu, and the platinum-group elements (PGE) in mafic-ultramafic igneous intrusions. The world-class Sudbury Igneous Complex (SIC) is one such intrusion associated with abundant magmatic-hydrothermal Ni-Cu-PGE sulphide deposits. Understanding the processes that led to the formation of these deposits is limited by significant knowledge gaps, some of which are outlined below, and addressed through the current research.

The study of melt inclusions (i.e. trapped Sudbury magma droplets hosted in minerals that grew from the

magma) is key in understanding the evolution of the SIC, the origin of its associated nickel and PGE deposits, and, defining robust criteria that can be used to discriminate between barren and mineralized regions of the Sudbury margin. Since its formation, the SIC has undergone intense deformation and hydrothermal alteration. These processes have modified the composition of the rocks, making it difficult to use the current chemical composition of the intrusion as a proxy for ore-forming processes that occurred 1.85 billion years ago when the deposits were forming. For example, a major limitation of mass balance exercises, which are focused at determining the amount of magma needed to generate the sulphide deposits, is knowledge of the metal and S content of the magma before the deposits formed and before the intrusion was subjected to deformation and alteration. Modelling the crystallization of

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the SIC melt evolution has been equally problematic; the controversy stems from conflicting models pertaining to the source of the melt sheet and its differentiation history (Peredery and Naldrett, 1975; Kuo and Crocket, 1979; Faggart et al., 1985; Grieve et al., 1991; Chai and Eckstrand 1994; Lightfoot et al., 1997a,b, 2001; Ariskin et al., 1999; Dicken et al., 1999; Ames et al., 2002; Therriault et al., 2002; Pope et al., 2004; Zieg and Marsh, 2005). In such environments where postmagmatic processes have reduced the effectiveness of routine whole rock geochemistry, the analysis of melt inclusion chemistry, could significantly enhance exploration success and address genetic uncertainties masked by post-cumulus processes.

The study of fluid inclusion, alteration, and stable isotope systematics of the footwall ore-forming systems contributes further to extensive fluid inclusion, O and H isotope, and petrographic evidence in high-sulphide systems, suggesting that high-salinity volatiles played a role in the precipitation and redistribution of base and precious metals, the compositional modification of the magmatic sulphides, and the generation of halogen-enriched haloes encompassing the orebodies (Li, 1992; Farrow, 1994; Jago et al., 1994; Farrow and Watkinson, 1997, Molnár et al., 2001; Hanley and Mungall, 2003; Hanley et al., 2004, 2005, 2011; Ames and Farrow 2007: Péntek et al., 2008: Hanley and Bray, 2009; Tuba et al., 2010). Evidence from these studies that lends support to a hydrothermal origin for low-sulphide footwall ore deposits include (i) the occurrence of ore metal-bearing, saline fluid inclusions in sulphide and silicate alteration minerals; (ii) the occurrence of co-precipitated metal halide minerals (e.g. Pd-Bi-chloride) in PGE-Au-rich sulphide vein assemblages; (iii) the occurrence of primary, low-temperature Pt- and Pdbearing minerals hosted in Cl-rich, hydroxysilicate mineral assemblages; and (iv) the presence of altered, oxidized, Cu-, Au-, and PGE-depleted ore zones, ("epidote zone") interpreted to be contact-style ores that were leached by hydrothermal fluids. Investigations of deposit-scale mineralogy and spatial relationships among different ore zones within the footwall (e.g. Farrow et al., 2005) show that low-sulphide footwallstyle deposits possess a largely fluid-derived metal component and were emplaced in the footwall prior to the emplacement of the sharp-walled high-sulphide deposits. Previous research has suggested that ore fluids associated with footwall-style deposits were mixtures of deeply sourced saline groundwaters and hightemperature "magmatic" fluids derived from the mineralized contact region or the main igneous mass of the SIC (Marshall et al., 1999; Hanley et al., 2005; Péntek et al., 2008; Tuba et al., 2010; Hanley et al., 2011). Areas of intense alteration and areas showing evidence of metal precipitation and/or remobilization appear to

be spatially associated with zones of partial melting within the footwall (Péntek et al., 2013) and injection of residual silicate liquids from the SIC into the surrounding footwall (Hanley et al., 2011). In addition to saline aqueous fluids in the North Range of the SIC, carbonic fluid phases (CO<sub>2</sub>, hydrocarbons) have also been reported (Farrow, 1994; Molnár et al., 2001; Hanley et al., 2005). Recent studies of the low-sulphide footwall deposits illustrate the importance of PGEenriched volatile phases and the existence of brittle structures in the Archean footwall as conduits for fluid migration and a chemical trap for metal precipitation (Tuba et al., 2014); however, the exact mechanism of metal precipitation and the source of volatiles remain unconstrained.

The study of metal chemistry of common alteration and igneous hydroxysilicate silicate minerals is justified based on the lack of such descriptions in unweathered, fresh, or hydrothermally altered (at non-surficial conditions) mafic-ultramafic settings. The majority of these studies have focused on magmatic Ni-Cu-PGE ore styles and associated alteration assemblages at Sudbury, Ontario, Canada where elevated concentrations of Ni (as structural substitutions) have been reported in biotite, amphibole, and chlorite in proximity to sulphide deposits (Li and Naldrett, 1993; Farrow, 1994; Magyarosi et al., 2002; Hanley and Mungall, 2003; Stewart, 2011; Tuba, 2012; Ames and Kjarsgaard, 2013 and references therein). Of these minerals, biotite is the most appropriate mineral for study as a pathfinder/indicator mineral because it is ubiquitous throughout both the SIC and all surrounding country rocks, having grown in association with specific and easily discernible magmatic, metamorphic, and hydrothermal events that are well documented in the literature (e.g. Coats and Snajdr, 1984; Thomson et al., 1985; Corfu and Andrews, 1986; Noble and Lightfoot, 1992; Li and Naldrett, 1993; Farrow, 1994; Farrow and Watkinson, 1997; Magyarosi, 1998; Magyarosi et al., 2002; Stewart, 2002; Hanley and Mungall 2003; Tuba, 2012; Ames and Kjarsgaard, 2013). However, there have been no robust evaluations of the factors controlling the Ni enrichment in biotite or its reliability as a routine exploration tool for Ni-Cu-PGE sulphide ore deposits at Sudbury, or any other mafic-ultramafic-associated sulphide deposit.

#### ANALYTICAL METHODS

#### **Optical and Scanning Electron Microscopy**

Optical petrography was completed using a Nikon Eclipse H550L microscope and major/minor element compositions for homogenized silicate melt inclusions, silicates, phosphates, carbonates, sulphides, and discrete metal-bearing phases were obtained using a LEO 1450VP scanning electron microscope (SEM) at Saint Mary's University, Halifax, Nova Scotia. An energy dispersive X-ray (EDS) Oxford INCA 80 mm<sup>2</sup> silicon drift detector (SDD; attached to the SEM) was operated at a working distance of 20 mm, beam current of 40  $\mu$ A, and accelerating voltage of 20–25 kV for analyses of all mineral types.

#### Laser Ablation ICP-MS Analysis of Trace Elements in Garnet

Trace element mapping and analysis of garnet was done at the University of New Brunswick, Fredericton, New Brunswick (quantified offline using *lolite* software) using a Resonetics S-155-LR 193 nm excimer laser coupled to an Agilent 7700x quadrupole inductively coupled plasma mass spectrometer (ICP-MS). The standards NIST 612 and BCR-2G were measured to calibrate analyte sensitivities as well as monitor instrumental bias and internal standardization was completed using Ca determined from microprobe and quantitative SEM-EDS analyses. The laser conditions used for all raster sequences were a spot size of 124  $\mu$ m, scan speed between 12 to 25  $\mu$ m/s, and pulse rate of 10 Hz.

#### Laser Ablation ICP-MS Analysis of Trace Elements in Apatite and Melt Inclusions

Trace elements in apatite and homogenized and nonhomogenized melt inclusions were determined using a Resonetics RESOlution M50 laser probe (Ar-F Excimer laser) operated in dual detector mode at Laurentian University, Sudbury, Ontario, at a repetition rate of 5 Hz and a fluence of 6 J/cm<sup>2</sup>. Data reduction for melt inclusions analysed by LA-ICP-MS was done using SILLS (Guillong et al., 2008). Evaluation of analytical accuracy and precision for transient LA-ICP-MS signals is challenging since no certified synthetic melt inclusion reference standards are available. However, some statements can be made concerning the quality of the data. The accuracy of trace element analyses in melt inclusions, repeated analyses of synthetic glass standards at the Laurentian University laser ablation ICP-MS facility as secondary quality control (QC) standards (BHV02 from US Geological Survey; ATHO from MPI-DING), quantified using NIST610, routinely yield concentrations better than within 15% relative of expected concentrations (J. Petrus, pers. comm., 2013). Analytical precision cannot be readily evaluated since the method is destructive, however, two possible strategies are considered. First, when different integration windows through homogenized (glassy) melt inclusions are quantified, adjacent intervals of inclusion yield analytical reproducibility better than 5% relative. Similarly, when melt inclusion results from a single sample are compared (and assumed to contain the same liquid, for melt end-member compositions) reproducibility of melt compositions within single samples is high. However, these results are measures of melt homogeneity at various scales rather than true (external) precision. With respect to the accuracy of major element analyses in melt inclusions, comparison of analytical results yielded from SEM/EMP for homogenized inclusions with data from LA-ICP-MS shows that all major elements (with the exception of FeO, MgO, and MnO) yield concentrations within 25% (relative) of each respective method. For reasons that are unclear at this time, and likely related to the low concentrations in the standard NIST610 glass, FeO, MgO, and MnO are up to 70% higher in the LA-ICP-MS analyses of equivalent inclusions analysed by SEM/EMP. For these reasons, it is our preference to utilize the SEM/EMP data for major elements and the LA-ICP-MS data for trace elements. For precision of major element analyses, only a similar approach as that stated above for trace elements can be employed for the LA-ICP-MS method. For SEM/EMP analyses, repeated analyses of single points within homogenized melt inclusions yielded reproducibilities in the quantified EDS spectra of better than 2% relative. Analytical uncertainties in the SEM/EMP analyses (in the total wt% oxides excluding H<sub>2</sub>O, the CaO composition of the host apatite) and uncertainty introduced by assuming La to be the matrix-only tracer also impact the overall uncertainty in major and trace element analyses. Uncertainties in the host composition (which was selected for all data reduction as a constant value of CaO for each respective sample by SEM/EMP) are no larger than a few %, which would impact the resulting melt inclusion data reduced in SILLS proportionally. With respect to La as the matrixonly tracer, the actual ratio of Lahost/Lainclusion is on the order of ~100 (i.e. 0.2 wt% La in apatite versus 20 ppm expected for felsic liquids; not quantifiable). Uncertainties in melt composition resulting from this unmixing procedure will be larger for elements that show less compatibility in the melt phase.

#### Laser Ablation ICP-MS Analysis of Trace Elements in Biotite

Trace elements in biotite were determined by LA-ICP-MS at the Geological Survey of Canada, Ottawa using polished thick sections (200 um thick). The instrumentation used comprised a Photon Machines Analyte.193 Excimer laser for sample introduction and an Agilent 7700x quadrupole ICP-MS for isotope measurements. Details of the conditions for the analyses (including laser ablation parameters, ICP-MS settings, oxide production rates, etc.) are summarized in Warren et al. (2015). For single grain analyses, 1–3 spots per biotite grain and 4–20 grains per sample were obtained. Grain boundaries, cleavage planes, and grains that contained visible inclusions were avoided to reduce contamination. The isotopes <sup>42</sup>Ca (count rate increases when amphibole and plagioclase are encountered) and <sup>39</sup>K (count rate decreases when chlorite is encountered) were monitored visually and during data reduction to identify and avoid contamination from other hydroxvsilicate minerals. Data reduction was done using Glitter<sup>™</sup> software (Macquarie University), which allowed selection of portions of each signal that have consistent count rates, eliminating localized contamination in the signal (see discussion below). Calibration of analyte sensitivities was done using the standard basalt glass GSE-1G (USGS). Quality control standards BCR-2G (USGS), and SRM612 (NIST) were analyzed to evaluate the accuracy of results (which are in agreement with accept values to within ~10% relative for major and trace elements, with the exception of Cr, Zn, Ag, Cd, Sn, Sb, and Cu that were to within  $\sim 10-30\%$  relative). The internal standard used for quantification was the average wt% Al2O3 determined independently by quantitative SEM-EDS. The same population of grains was analyzed by SEM-EDS prior to LA-ICP-MS. Inter- and intra-grain variations in Al concentrations within single samples were very small and the results were comparable EMP analysis of biotite populations in the Worthington area by Magyarosi (1998). Uncertainties in determined trace element concentrations resulting from the use of average biotite Al<sub>2</sub>O<sub>3</sub> values in a single sample are  $\pm 2\%$ (relative; i.e. 400 ppm  $Cr \pm 8$  ppm). Element maps of biotite grains were also generated by LA-ICP-MS spot analyses over square gridded areas. The software Glitter<sup>TM</sup> was used for spot quantification and an inhouse (Geological Survey of Canada) program was used to generate logarithmic and percentile-scaled maps of major and trace element concentration. Concentrations were calculated using GSE-1G for external standardization and normalizing to 100% total element abundance; this approach does not account for the OH- content of biotite, and therefore, mapped element concentrations are overestimated by approximately 5% (relative). Minimum detection limits (MDL) for analytes are calculated by Glitter<sup>TM</sup> software at the 99% confidence level, based on Poisson counting statistics (MDL =  $2.3x\sqrt{2B}$ ; where B is the total counts in the background interval), converted to a concentration based on sensitivity determined using the external standard, and corrected for ablation yield.

#### **Electron Microprobe Analysis**

Electron microprobe analyses of silicate and phosphate minerals and homogenized silicate melt inclusions were obtained at Dalhousie University using a JEOL 8200 Superprobe. The operating conditions for all analyses were an accelerating voltage of 15.0 kV, beam diameter of 1 µm, and 20 seconds/10 seconds for mineral measurements/background measurements on each element, respectively. Standards and crystals used to measure each element of interest were K (Sanidine, PETJ), Cr (Cr\_metal\_CH2P, PETJ), Na (Jadeite\_Naonly, TAPH), Si (Sanidine, TAP), Mn (PyrolusiteCH5L, LIFH), Ca (K\_KaersCaTiMg, PETJ), Ti (K\_KaersCaTiMg, PETJ), Mg (K\_KaersCaTiMg, TAPH), Al (Sanidine, TAP), Fe (Garnet12442Fe5, LIFH), Ba (Barite\_BaCH2P, PETJ), Ni (Ni\_metal\_CH5L, LIFH), and Zn (Gahnite, LIFH).

#### Fluid and Melt Inclusion Microthermometry

Microthermometric analyses on fluid inclusions were carried out at Saint Mary's University using a Linkam FTIR 600 heating-freezing stage mounted on an Olympus BX51 microscope. Stage calibration was carried out using synthetic fluid inclusion standards containing pure CO<sub>2</sub> (melting at -56.6°C) and pure, critical density H<sub>2</sub>O (melting at 0°C and homogenizing at 374.1°C). Absolute uncertainties associated with the fluid inclusion measurements (based on measurement precision of the instrumentation and measurement reproducibility on standards) range from  $\pm 2-3^{\circ}$ C for output temperatures around the extremes of working conditions for the heating-freezing stages (-190°C and 560°C) to better than  $\pm 0.2$ °C for output temperatures near 0°C. Eutectic (first) ice-melting temperatures (T<sub>e</sub><sup>ice</sup>) were observed to help identify major cation compositions of the respective inclusions and final icemelting temperatures were used to calculate NaCl and CaCl<sub>2</sub> weight percent equivalency values (i.e. bulk salinity). Microthermometric determination of melt inclusion first melting, final melting, and bubble closure (providing minimum T<sub>trapping</sub>) was conducted using a Linkam TS1500 heating stage with sapphire plates for heating. The stage was mounted on a BX53 microscope with a O imaging colour video camera. Heating rates varied between 10 and 100°C/min, and a flow rate of 40 ml/min of argon gas was used to prevent oxidation of melt inclusions and their apatite host during heating. The error associated with the absolute temperature is  $\pm 2^{\circ}$ C, based on monitoring of fixed temperature stability. Pure Ag, Au, and Cu metals were used as standards to calibrate the stage by measuring their melting points and comparing them against accepted values.

#### **Secondary Ion Mass Spectrometry**

Oxygen isotope compositions in garnet and calcite were measured at the University of Manitoba, Winnipeg, Manitoba, using a Cameca IMS 7f secondary ion mass spectrometer (SIMS). Hand-picked garnet crystals were mounted in epoxy resin then polished using diamond paste to ensure even surfaces with exposed mineral grains. Samples were cleaned and coated with a thin layer of gold to provide a conductive surface (then held in SIMS sample holders and kept under vacuum overnight). During all analyses, a cesium (Cs<sup>+</sup>) primary beam with an  $\sim$ 2 nA current was accelerated at 8.75 kV towards the sample surface with a sputtering diameter of  $\sim 15-20 \,\mu\text{m}$  and the instrument was operated at a 250 V offset, -9 kV negative secondary accelerating voltage, and mass resolving power of 347. An intrinsic mass-dependent bias was introduced during SIMS analyses that favours the low-mass isotope and is known as "instrumental mass fractionation" (IMF). The ionization process is the most relevant contributor to IMF and depends most strongly on the chemical composition of the sample. IMF is also commonly referred to as "compositionally dependent fractionation" or "matrix effects" (e.g. Riciputi et al. 1998). Accurate SIMS isotope analyses require that IMF be corrected using mineral standards that are compositionally similar to the unknown. Isotopic measurements from the standard are compared against its accepted isotopic composition to calculate correction factors, which are applied to the unknowns that are measured during the same analysis session (e.g. Holliger and Cathelineau, 1988). The standard Joplin Calcite,  $(\delta^{18}O_{V-SMOW} = 5.7\%)$ ; where  $\delta^{18}O_{V-SMOW} =$  $1.03086*\delta^{18}O_{PDB} + 30.86$ ) was used for analyses of calcite; UWG-2 ( $\delta^{18}O_{V-SMOW} = 5.8\%$ ; Valley et al., 1995) was used for analyses of both garnet cores and garnet rims. However, the composition of UWG-2  $(Alm_{45}Prp_{40}Grs_{14}Sps_1)$  is not closely matched to the compositions of the cores or rims analyzed in this study. The most closely matched garnet standards reported in the literature for the cores and rims of the Sudbury footwall garnets are 92LEW7 (Adr<sub>89</sub>Grs<sub>6</sub>Alm<sub>4</sub>Prp<sub>1</sub>) and 92LEW10 (Adr<sub>50</sub>Grs<sub>42</sub>Alm<sub>4</sub>CaTi<sub>2</sub>Prp<sub>2</sub>), respectively. Page et al. (2010) reported average instrumental biases for 92LEW7 and 92LEW10 when corrected using UWG-2 of +6.69‰ and +5.64‰ and these additional errors are taken into consideration in the results section.

## **Colour Cathodoluminescence Imaging**

Cathodoluminescence images were obtained with a Reliotron-based hot cathode CL system at the Geological Survey of Canada (Ottawa). Sample photographs were taken with a vacuum gauge pressure that read between 57 and 82 millitorr, a beam current fluctuation between 40 and 70 microamps, a voltage of 12 kV, a beam focus of 28, and a current limit set at 2 ma. Photographs were taken using the Empix program and an Optronics camera.

## **Bulk Oxygen Stable Isotope Analysis**

Bulk oxygen isotope analysis of garnet was determined at Queen's University, Kingston, Ontario. Oxygen was extracted using a conventional bromine pentafluorine extraction line and the isotopes were measured on a Finnigan Mat 252 isotope ratio mass spectrometer with an analytical uncertainty of  $\pm 0.3\%$  (K. Klassen, pers. comm., 2011).

## **RESULTS AND DATA ANALYSIS** Evolution of the Sudbury Igneous Complex Indicated from Silicate Melt Inclusions

Analyses of primary melt inclusions hosted in cumulus apatite from the Transition Zone Gabbro (TZG), norite, and quartz diorite offset dykes of the SIC are used to decipher the thermochemical characteristics of the original melt sheet and trace element partitioning behaviour within the evolving melt sheet. Textural analyses of apatite in the SIC shows that apatite occurs as a cumulus phase in the Main Mass and quartz diorite offset dykes (Fig. 1). Early saturation of apatite in the SIC is supported by microthermometric data that yields melt inclusion minimum trapping temperatures in the TZG and quartz diorite offset dykes between ~1100 to 1200°C.

Apatite-hosted melt inclusions commonly display a negative crystal shape, occur parallel to the c-axis, and commonly occur within a central growth zone, which suggests a primary origin (Fig. 2). Coeval (coentrapped) melt inclusion compositions show two distinct types: (i) Si-rich liquids that range in composition from tonalitic to granodioritic (60–70 wt% SiO<sub>2</sub>,  $\leq$ 11 wt % FeO) and (ii) Fe-rich liquids that range in composition from syenogabbroic to essexitic to alkali gabbroic (27-49 wt% SiO<sub>2</sub>, 16-44 wt% FeO), determined by SEM-EDS and EMP analyses of opened, homogenized melt inclusions (apatite grains heated at 1100 to 1200°C for 3 hours in a box furnace). These contrasting melt pairs may represent the products of immiscibility by either simple cooling of the superheated melt sheet or fractional crystallization.

The position of the bulk liquid composition of the SIC, the equivalent of the chilled margin of the quartz diorite offset dykes and least altered vitric bombs and blocks of the Onaping Formation, falls between immiscible melt pairs and in close proximity to the two-liquid field in the system leucite-fayalite-silica (Fig. 3), which suggests that the onset of immiscibility in the SIC was a consequence of simple cooling of the superheated melt sheet (~1700°C) and not liquidus crystal-lization that has been indicated to occur in other well studied basaltic layered intrusions.

Trace element data, obtained by LA-ICP-MS analyses of single inclusions and surrounding host apatite, are used to infer Kd values (Fig. 4) between apatite and the two melt types, and between coexisting melt types (Fig. 5; KdFe-rich melt/Si-rich melt). The Kd values



**Figure 1.** Microphotographs (colour CL) and thin section sketches showing the distribution of apatite and trapped melt inclusions (MI) in the Transition Zone Gabbro and Whistle offset dyke. **a**, **b**) Apatite from the Transition Zone Gabbro and (**c**-**f**) apatite from the leucocratic quartz diorite Whistle offset dyke.



between immiscible melt pairs in this study show that the majority of trace elements partition evenly between Si- and Fe-rich liquid, with the incompatible elements (Hf, Zr, Nb, and Ta) showing a slight affinity for the Sirich liquid and V and Co showing a slight affinity for the Fe-rich liquid in the TZG. Immiscible melt pairs in the norite have Kd values closer to 1, with the exception of Co that prefers the Fe-rich melt. Kd values between immiscible Fe- and Si-rich liquid are also in close agreement to what has been found experimentally for melts with basaltic starting compositions. Kdapatite/melt values for both Si- and Fe-rich melt pairs show that REE, Sr, and Y are compatible in apatite, and As is weakly compatible or incompatible in apatite, whereas the following elements behaved incompatibly (in increasing order of incompatibility: Cr, Ni, Cu, Zr, Co, Cs, Ag, Nb, Hf, Ta, and Rb).

# Pathfinder Mineral Chemistry in the Sublayer Environment

The chemistry of biotite in the Totten deposit (southeast corner of Sudbury Igneous Complex) and its surrounding country rocks was investigated. The deposit is a magmatic Ni-Cu-PGE sulphide system hosted within a radial offset dyke of multiphase quartz diorite. Despite evidence of complex interaction with its metasedimentary and metavolcanic country rocks, and overprinting by syn- to post-emplacement igneous, hydrothermal, and metamorphic events, the dyke remains a petrographically distinct unit comprising several phases of quartz dioritic rocks, with an inclusion-rich phase hosting discrete magmatic Ni-Cu-PGE sulphide orebodies (Zurbrigg et al., 1957; Cochrane, 1984; Grant and Bite, 1984; Lightfoot et al., 1997a,b; Lightfoot and Farrow, 2002; Murphy and Spray, 2002; Tuchscherer and Spray, 2002; Stewart, 2011).

LA-ICP-MS and quantitative SEM-EDS analyses of biotite were obtained from representative host rocks to, and igneous rocks of, the SIC in and surrounding the Worthington quartz diorite offset dyke at the Totten Mine (Vale Canada Ltd.). With the exception of Ni, Cr, and Cu, no systematic variations in dissolved trace elements concentrations were observed to be related to proximity to sulphide ore. Enrichment of Cu in biotite (up to two orders of magnitude higher than back-



Figure 3. Major element chemistry of apatite-hosted melt inclusions from the Main Mass Transition Zone Gabbro (TZG) and Pele offset dyke are plotted as shaded fields on an enlarged part of the pseudo-ternary Grieg diagram with the bimodal curve separating the one- and two-liquid fields. Major element compositions from the Main Mass TZG and Pele offset dyke are plotted along with the binodal curve that is drawn from a line of best-fit. The Sudbury Igneous Complex (SIC) bulk compositions are represented by the least altered vitric of the Onaping Formation (Ames et al., 2002), the chilled margin of the guartz diorite Offset dykes (Lightfoot et al., 2001), and the calculated by mixing endmember liquids from this study see discussion for how the calculation was done). The North Range quartz diorite bulk rock compositions are shown plotted (D.E. Ames, pers. comm. 2013) as well as the two-liquid field in the system leucite-favalite-silica (Roedder, 1979 after Jakobsen et al., 2011).

**Figure 2 (opposite page).** Melt inclusions hosted in apatite from the North Range Main Mass and offset dykes. Representative melt inclusion types in apatite in (a–g) the Transition Zone Gabbro, (h–l), leucocratic quartz diorite Whistle offset, and (m–o) quartz diorite, Pele offset. a) Unhomogenized melt inclusion. **b**, **c)** Homogenized melt inclusions that show a mixture of Fe- and Si-rich liquid. **d**, **e)** Homogenized Si-rich melt inclusions, as well as mixed melt inclusions. **f)** A single apatite grain that has trapped both pure end-member Fe-rich homogenized melt inclusions, as well as mixed. **g)** Homogenized Si-rich melt inclusion. **h**) Unhomogenized melt inclusion in a single apatite grain from the Whistle offset dyke. **I)** Heterogeneously trapped mixed melt inclusion and fluid inclusion in a single apatite grain from the Whistle offset dyke. **m)** Unhomogenized melt inclusion from the Pele offset dyke (PPL). **n**, **o)** Homogenized melt inclusion that is Fe-rich; SMI-Si = silicate melt inclusion that is Sirich; SMI-Si/Fe = silicate melt inclusion that has trapped both end-member types; XPL is cross polarized light.



**Figure 4.** Box-and-whisker plots of the Kd values between apatite and melt inclusions in the Main Mass. **a)** Kd values for the Si-rich melt of the Transition Zone Gabbro (TZG). **b)** Kd values for the Fe-rich melt inclusions of the TZG. **c)** Kd values for the Si-rich melt inclusions of the norite. **d)** Kd values corresponding to the Fe-rich melt of the norite.



**Figure 5.** Plot of Kd values between Si-rich and Fe-rich melt in the Pele and Whistle offset dykes. The Kd values for trace elements between Fe- and Si- rich melt inclusions for the Pele offset dykes are shown as box-and-whisker plots, which show that these values are close to 1 and compare favourably to what has been found experimentally (Veksler et al., 2006). The exceptions noted are Sr, the incompatible elements (Nb, Ta), and Sr, Cr, As, Ag, Pb, Sb, and Bi, which show slight affinities for the Fe-rich melt.



**Figure 6.** Box-and-whisker plots of the **(a)** (Ni)<sub>Bt</sub>, **(b)** (Cu)<sub>Bt</sub>, **(c)** (Cr)<sub>Bt</sub>, and **(d)** (Ni/Cr)<sub>Bt</sub> in samples at different distances from the massive sulphide mineralization hosted in IQD (traverse through Totten mine diamond drill hole 1265980 running perpendicular to the dyke trend; based showing lithologies logged from drill core and sample numbers at their positions downhole below collar. All samples contained only type III biotite with the exception of T137 and T143 (type I biotite) and T54, T62 and T69 (type II biotite). For each sample the maximum, minimum, first quartile (upper box), third quartile (lower box), and mean (separation between boxes) values are shown. For Cu, where some values were BDL, the data are shown for only those analyses that were above DL. Although sulphides are shown in both quartz diorite (QD) and inclusion-rich quartz diorite (IQD), the relative proportions of disseminated sulphide mineralization are not distinguished, and the occurrence of massive sulphides are restricted to IQD. Generally, biotite from the sulphide ore-associated IQD has elevated Ni relative to QD and the surrounding country rocks, however anomalously elevated Ni was measured in some country rock biotite. Variable and elevated concentrations of Cu were measured in biotite from QD and country rocks adjacent to IQD, correlating to an increase in the proportion of secondary chalcopyrite in the envelope of rock surrounding IQD. With the exception of Sudbury diabase dykes in which concentrations of Cr in biotite are consistently low relative to other lithologies, Cr concentrations are highly variable and show no systematic variations with distance to mineralization. The Ni/Cr in biotite increases east of a Sudbury diabase dyke hosted within the Huronian country rocks. After Warren et al. (2015).

ground) occurs within barren to weakly mineralized, sublayer quartz diorite and adjacent Huronian metasedimentary rocks within ~200 m of massive sulphide, whereas enrichment in Ni occurs only within the inclusion-rich quartz diorite (Fig. 6). Three distinct populations of Ni- and Cr-enriched biotite were distinguished based on textural and chemical criteria (Fig. 7): (i) type I — isolated, euhedral laths only within inclusion-rich sublayer quartz diorite (IQD; the main mineralized host lithology), and high Ni (>1400 ppm and up to ~2700 ppm) and variable Cr (up to ~2400 ppm) concentrations and variable Ni/Cr ratios (>2); (ii) type II — coarse-grained poikiloblasts (enclosing amphibole, chlorite, and type III biotite) within country rocks, and having moderate to high Ni (~500–1400 ppm) and high Cr ( $\leq$ 6000 ppm) concentrations but low Ni/Cr ratios



**Figure 7.** Photomicrographs (transmitted plane polarized light) and compositional fields on a Ni-Cr-Cu ternary diagram (ppmbasis) for biotite populations (by lithology). **a**) High-Ni, type I biotite from mineralized inclusion-rich quartz diorite (IQD). **b**) High-Cr, type II biotite from Huronian country rocks. **c–e**) Variable composition, type III biotite from barren QD, Huronian country rocks, and late Sudbury dykes. Abbreviations: Am = amphibole; Bt = biotite; Qtz = quartz. Analyses of biotite within the dashed circle represent a sample logged and identified (incorrectly) as IQD but with biotite composition characteristic of type II and III biotite, indicating a sample of country rock or barren QD (or inclusion or country rock or barren QD within IQD). After Warren et al. (2015).

(<0.5); and (iii) type III — subhedral to euhedral laths, intergrown with amphibole in dense, foliated aggregates and having low Ni (<300 ppm) and low to moderate Cr (<1200 ppm) concentrations and high Ni/Cr ratios ( $\leq \sim 20$ ), found within Huronian country rocks,

sublayer quartz diorite (QD), and crosscutting diabase dykes (Sudbury dyke swarm). Two different controls on Ni and Cr cation substitution in biotite were identified: (i) biotite with low Ni+Cr concentrations (<1000 ppm) that show a positive correlation with  $X_{Mg}$ , indi-

cating crystallographic controls (e.g. avoidance and permissibility phenomena); (ii) biotite with high Ni+Cr concentrations (>1000 ppm) showing no correlation with XMg, suggesting another control (e.g. host-rock chemistry, proximity to sulphides, or availability of Ni and Cr in magmatic-hydrothermal volatiles) that influences biotite chemistry.

#### Stable Isotope, Alteration, and Fluid Inclusion Fingerprints of "Low-Sulphide" Mineralization in the Footwall

The North Range footwall of the Sudbury Igneous Complex (SIC) hosts numerous small-volume (relative to other SIC-associated deposits) Cu-Ni-PGE mineral deposits that have seen progressively increasing exploration interest within the last decade due to their high base metal (Cu, Ni) contents and precious metal (Pt, Pd, Ag, and Au) tenors. Farrow et al. (2005) separated footwall deposits at Sudbury into "high-sulphide" (sharp-walled vein) and "low-sulphide" (PGE-rich) systems based on their ore mineralogy, alteration mineralogy, and bulk rock chemistry. Both deposit types have significant representation in the literature and current models for their geneses attribute the formation of high-sulphide mineralization to magmatic/magmatichydrothermal mechanisms and/or remobilization by high-temperature volatiles Li et al., 1992; Naldrett et al., 1999; Péntek et al., 2008; Hanley et al., 2011, etc.) and the formation of low-sulphide mineralization to circulating (metal-loaded) hydrothermal fluids (e.g. Péntek et al., 2008; Nelles et al., 2010; Tuba et al., 2010, 2014; White, 2012; etc.). Crosscutting considerations indicate that the formation of low-sulphide mineralization occurred before the deposition of high-sulphide veins. However, at present there is no general characterization in the literature of many of the fluid conditions (fluid sources, transport mechanisms, ambient  $fO_2$  of fluids, fluid compositions, etc.) that resulted in the precipitation of low-sulphide high-PGE systems.

The variable types of low sulphide mineralization are most commonly distinguished on textural (i.e. veinlets, disseminations, blebs, stringers, etc.) and/or mineralogical (alteration phases, precious metal mineral assemblages) bases (Farrow et al. 2005; Gibson et al. 2010; Nelles et al., 2010; Tuba et al. 2010, 2014; White, 2012; Péntek et al., 2013) but general characteristics that encompass all low-sulphide subtypes are (i) <5 volume percent (%) Cu- and Ni-sulphide minerals (bornite, chalcopyrite, millerite), (ii) elevated (can be an order of magnitude higher) bulk rock PGE/S compared to high-sulphide veins, and (iii) hydrous alteration phases intergrown with the ore minerals (sulphide minerals, precious metal minerals). The most common alteration assemblage in low-sulphide environments consists of quartz+epidote+chlorite packages that enclose mineralization; however, more calcic alteration may be observed with the addition of calcite and calcic amphibole to the alteration assemblages.

Alteration assemblages containing hydrothermal garnet are reported for the first time associated with "low-sulphide" high-PGE footwall Cu-Ni-PGE mineralization in a calcite-quartz-garnet-epidote-chloriteamphibole-sulphide vein from Level 5080 of the Coleman 153 (Vale) orebody (Fig. 8). The garnet exhibits two different growth zones on the basis of their composition (and radite cores, grossular-rich rims) and the sulphides (bornite, chalcopyrite, millerite) are coeval with the grossular-rich rims on garnet as well as the surrounding calcite (~80 vol%) matrix. Calcitehosted fluid inclusions (Fig. 9) are two phase liquidvapour (L-V) and are separated into two populations: (1) 23.65 wt% eq. NaCl and (2) 8.26 wt% eq. NaCl. Homogenization temperatures recorded for all reported fluid inclusions have an average of 140.2°C and range from 90.1 to 210.0°C. Secondary ion mass spectrometry (SIMS) analyses were conducted on 10 (sulphidecoeval) calcite grains and the average  $\delta^{18}$ O value for these analyses is  $5.1 \pm 1.2\%$ , resulting in calculated  $\delta^{18}$ O values (O'Neil et al., 1969) of -11.5‰ and -0.02‰ at 100°C and 300°C, respectively, for the hydrothermal fluid at the time of sulphide precipitation.

#### DISCUSSION AND MODELS

#### **Evolution of the Sudbury Igneous Complex Indicated from Silicate Melt Inclusions**

The mass proportion of immiscible Fe-rich to Si-rich liquids (~1:4.5) predicted through melt-inclusion characterization is in close agreement with the volume of granophyric liquid predicted from experiments modelling the fractional crystallization of the SIC melt sheet. However, these experiments have shown that fractional crystallization alone does not account for the observed 1:3 ratio of norite to granophyre along the North Range. Importantly, trapped (immiscible?) Si-rich liquid lower in the SIC must be taken into consideration. If one considers immiscibility as a petrogenetic process for the SIC melt sheet, it may explain the large amount of granophyre in the SIC that has been so poorly understood in the past.

Apatite-hosted melt inclusions from the mineralized Whistle offset dyke are enriched in Ni by up to 4 orders of magnitude compared to melt inclusions trapped in units stratigraphically higher in the SIC, reflecting the loss of these metals to sulphide liquids prior to the crystallization of these units in the SIC. The absence of enrichment in Ni and Cu in melt inclusions from the unmineralized Pele offset dyke suggests that proximity of the trapped melt to the orebodies may influence their



**Figure 8.** Mineralogical characteristics of the hydrothermal garnet-bearing "low-sulphide" assemblage. **a)** Representative hand sample from a vein displaying a calcite-quartz matrix hosting garnet crystals and patches of epidote, amphibole, chlorite, and sulphides. **b)** Bornite disseminations and networks of chalcopyrite and millerite within a silicate host (plane polarized light). **c)** Garnet hosted in a calcite matrix and in equilibrium with granular epidote (cross-polarized light). **d)** Euhedral crystal of garnet (grossular-rich rim/andradite core) in equilibrium with granular epidote. **e)** Chalcopyrite inclusions hosted in the grossular-rich rim on a garnet crystal. The garnet is in contact with epidote along the outer edge of its rim. **f)** Calcite and chalcopyrite inclusions within the grossular-rich rim of a calcite-hosted garnet crystal. The garnet core is andraditic in composition. **g)** Inclusions of chalcopyrite hosted in grossular-rich patches within the andradite core of a garnet crystal. **h)** Chalcopyrite hosted in a grossular-rich patch within the andradite core of (calcite-hosted) garnet. Grossular-rich patches also occur along the edge of a crack that runs through the andradite core of garnet near the chalcopyrite inclusion (top left). Abbreviations: Act = actinolite; Adr = andradite; Bn = bornite; Cal = calcite; Ccp = chalcopyrite; Chl = chlorite; Ep = epidote; Grs = grossular; Grt = garnet; Mil = millerite; Qtz = quartz; Sil = silicates; Sul = sulphides.



**Figure 9.** General fluid inclusion characteristics of hydrothermal garnet-bearing "low-sulphide" assemblages. **a)** Photomicrograph displaying the area where fluid inclusion assemblages of interest were analyzed in this study (plane polarized light). **b)** Fluid inclusion map illustrating photomicrograph (a) and the relative locations of the 5 fluid inclusion assemblages (FIA) addressed in this section. **c)** Calcite-hosted trail of primary liquid-vapour (L-V) inclusions at FIA # 2a. **d)** Calcite-hosted trail of primary L-V inclusions at FIA # 2c. **e)** Calcite-hosted liquid-vapour-solid (L-V-S) inclusion of uncertain origin. Measure-ments were not taken on this inclusion and the compositions of the daughter minerals (S<sub>1</sub> and S<sub>2</sub>) are not known. This inclusion was not present within the field of view presented in (a, b). **f)** Garnet-core-hosted trails of primary (P) and secondary (S) L-V inclusions. These inclusions were situated outside of the field of view presented in (a, b). **g)** Magnified view of the garnet-core-hosted primary L-V inclusion outlined by the black square in photomicrograph (f). **h)** Segment of a garnet (left) – calcite (right) contact. Secondary fluid inclusion trails in garnet run perpendicular to garnet growth zones and exhibit abrupt terminations at garnet crystal edges (i.e. do not continue into calcite). Five of these trails are highlighted by black arrows. Abbreviations: Cal = calcite; Chl = chlorite; Grt = garnet.



Figure 10.  $\delta^{18}$ O in garnet and calcite from hydrothermal garnet-bearing "low-sulphide" mineralization. a)  $\delta^{18}$ O‰ V-SMOW results for core and rim spot analyses across 4 garnet grains. Standard deviations are reported at 1o and all analyses were calibrated using standard UWG-2. Additional positive error bars (dashed lines) account for the inherent instrumental bias in garnet relative to UWG-2, which varies as a function of garnet composition. The average core composition from 15 garnet grains analyzed in this study is Adr<sub>99,27</sub>Prp<sub>0.54</sub>Grs<sub>0.45</sub>Sps<sub>0.02</sub>, which closely matches garnet standard 92LEW7 (Adr<sub>89</sub>Grs<sub>6</sub>Alm<sub>4</sub>Prp<sub>1</sub>). Page et al. (2010) reported an average instrumental bias of +6.69% for 92LEW7 when calibrating analyses against UWG-2. The average rim composition from 38 garnet grains analyzed in this study is Adr<sub>53.73</sub>Grs<sub>44.92</sub>Sps<sub>0.60</sub>Prp<sub>0.14</sub>Uva<sub>0.02</sub>, which closely matches garnet standard 92LEW10 (Adr<sub>50</sub>Grs<sub>42</sub>Alm<sub>4</sub>CaTi<sub>2</sub>Prp<sub>2</sub>). Page et al. (2010) reported an average instrumental bias of +5.64‰ for 92LEW10 when calibrating analyses against UWG-2. The rim of one garnet (Grt 1) was also analyzed at Queen's University using a Finnigan Mat 252 isotope ratio mass spectrometer (IR-MS) and is represented by the dark blue band. Fields for magmatic waters (Marshall et al., 1999), North Range Canadian Shield groundwater (Kaufmann et al., 1987), SIC volatiles (scapolite; Hanley et al., 2011), footwall veins (sharp-walled vein-associated calcite and guartz; Farrow, 1994), and garnet from alteration assemblages (see text) at the Fraser Mine's "Epidote Zone" (Farrow, 1994) are also illustrated. b)  $\delta^{18}$ O‰ V-SMOW results for 10 spot analyses of calcite grains. Standard deviations are reported at 1 $\sigma$  and all analyses were calibrated using Jop-Cal. Average δ<sup>18</sup>O V-SMOW for the calcite-forming fluid were calculated at 100°C, 200°C, and 300°C using an equation from O'Neil et al. (1969) and are superimposed on this figure. "Minimum fluid composition for calcite-hosted inclusions" was calculated using the average fluid inclusion T<sub>h</sub> measured in calcite and the equation from O'Neil et al. (1969).

metal content. The results of this study have implications for our understanding of the petrogenesis of the SIC melt sheet and the potential effects of sulphide saturation in the presence of immiscible Si- and Fe-rich liquids. Melt inclusion compositions may provide an important proxy for distance to orebodies in the margin of the SIC. The study provides the first in-situ determination of actual ore metal concentrations from early trapped melt of the SIC and trace element partitioning behaviour between immiscible liquids in nature.

# Pathfinder Mineral Chemistry in the Sublayer Environment

Type I biotite within IOD is compositionally distinct from those observed in all other lithologies associated with the Sudbury Igneous Complex and its footwall rocks, and can be most readily discriminated in a Ni/Cr versus Ni binary diagram or in a Ni-Cr-Cu ternary diagram by anomalously high Ni content and a Ni/Cr ratio of >2. However, application of such diagrams requires caution. An examination of biotite chemistry in the Sudbury district shows that Ni (and likely Cr) concentrations in biotite vary greatly between different environments (both barren and ore-hosting), indicating the importance of establishing local "background" Ni concentrations in biotite in order to identify what is truly anomalous for that environment. Second, large ranges in Ni-in-biotite data reported previously from microprobe analyses result from analyses not representative of true dissolved concentrations. Introduction of falseanomalous Ni contents in biotite and a high degree of heterogeneity within sample sets may occur where biotite (i) contains discrete sulphide micro-inclusions that contaminate the analytical volume; (ii) occurs in direct contact with coeval sulphide minerals that caused localized changes in biotite composition; and (iii) was altered to chlorite, a process that modified primary metal abundances. Though routine microprobe analysis may be used to discriminate ore-diagnostic biotite using the Ni-Cr-Cu characteristics reported here, LA-ICPMS should be considered to allow identification/selective removal of sulphide inclusions and localized chemical zoning in biotite that is unrelated to lithology-pervasive, primary chemical composition.

#### Stable Isotope, Alteration, and Fluid Inclusion Fingerprints of "Low-Sulphide" Mineralization in the Footwall

Shifts towards lighter  $\delta^{18}$ O values from the paragenetically-early garnet cores (10.0‰) to the synsulphide precipitation rims (4.7‰) track progressive interaction with and dilution by (CaCl<sub>2</sub>-rich) isotopically-light North Range groundwater (Kaufmann et al., 1987): -10.8 to -10.5‰ (Fig. 10). Recent studies (Hanley et al., 2005; Kerr and Hanley, 2013) have shown that the fluid associated with low-sulphide mineralization was hydrocarbon-rich and numerous observations in this study (sulphide/gangue relationships, garnet trace element zoning, garnet-epidote equilibria chemistry, presence of primary sulpho-bismuthide minerals) indicate that this fluid became more reducing over its evolution. Progressive mixing of meteoric groundwater with hydrocarbon/metal-rich aqueous fluids can achieve both carbonate and sulphide precipitation as well as lower the ambient oxygen fugacity of the mineralizing system. Calcium-rich alteration (calcite, garnet, epidote, calcic amphibole) within the low-sulphide assemblage, which is the focus of this study, represents an apparent end-member to the low-sulphide continuum; where the mineralizing fluid has experienced the most interaction with CaCl<sub>2</sub> groundwater. Low Pt+Pd grades and the absence of Pt- and Pd-PGM in this calcium mineral-rich vein suggests that the mineralizing hydrothermal fluid lost the majority of its PGE load at an earlier point in its evolution. Anomalously high Au grades coupled with the presence of primary electrum suggest Au deposition was not temporally linked with the precipitation of the PGM and persisted to the extremities of low-sulphide footwall systems.

# IMPLICATIONS FOR EXPLORATION Melt Inclusion and Apatite Trace Element Chemistry in the Sudbury Igneous Complex Main Mass and Sublayer

Variations in melt composition of different units of the SIC, and in different areas of the SIC, near and distal to sulphide orebodies in the footwall-contact area enables the identification of spatial differences in interstitial melt composition resulting from sulphide separation, indicating melt chemistry (and host apatite chemistry, by association) is an appropriate exploration tool in delineating "metal-depleted" versus "metal-fertile" regions of the SIC sublayer. The immiscible melts found in the SIC Main Mass are devoid of metals compared to melt inclusions from the mineralized quartz diorite in the Whistle offset dyke. The absence of Ni and Cu in melt inclusions from the unmineralized Pele offset and Main Mass of the SIC may reflect loss of these metals to early sulphide liquids, however, if the differentiation of immiscible liquids resulted in a density-stratified melt prior to in situ crystallization processes, the most basal layers in the density-stratified melt sheet would be more mafic and may crystallize the Ni- and Cu-rich sulphide (Lightfoot et al., 2001). The Ni-rich apatite-hosted melt inclusions from the Whistle offset are, therefore, likely a result of trapped immiscible liquid that was in equilibrium with sulphide liquid. Apatite-hosted melt inclusions that were compared between mineralized (Whistle) and unmineralized (Pele) offset dykes revealed that melt inclusions in close proximity to mineralization contain high (>400 ppm) amounts of Ni. In addition, apatite from the Whistle offset contained the highest amounts of Cu and As. These findings are comparable to what is found in apatite from the mineralized footwall and may be applicable to exploration in the SIC. The conclusions of this study suggest that apatite-hosted melt inclusions from the Whistle offset dyke were in equilibrium with sulphide liquids at the time of their entrapment. Therefore, the metal content of apatite-hosted melt inclusions (and by partitioning association, the apatite host phase itself) in the basal portions of the SIC may serve as a proxy for distance to orebodies within the SIC sublayer, including offset dyke settings.

## **Biotite Chemistry in the Sublayer**

There are two potential applications of the biotite chemistry to exploration. First, in drill core (or surface mapping involving outcrop or till/rubble surveying), differentiation between QD and IQD can be confirmed through analysis of [Ni]Bt, provided that the identity of the rock type in question has been confirmed as quartz diorite. The threshold for Nibiotite in inclusion-rich versus inclusion-free phases is proposed tentatively at  $\sim$ 1500 ppm, a concentration level that can be readily identified using LA-ICP-MS, electron microprobe, or even SEM-EDS, provided adequate counting times are utilized during spectrum collection. Textural scrutiny and determination of the absolute concentration of Nibiotite are not essential in this case since inclusionrich QD contains only a single, high-Ni variety of biotite and inclusion-poor OD biotite is consistently very low in Ni (<300 ppm). Textural analysis can be used to confirm that high-Ni biotite is of the magmatic, "type III" variety described here. Generally, this application may encourage more careful delineation of the two phases of QD in offsets and, although bulk rock assays may be ambiguous, especially at low-sulphide abundances in IQD, biotite compositions consistently show enrichment in Ni and elevated Ni/Cr ratios. The results may be extended to other mafic-ultramafic systems where sulphide-saturated or metal-enriched intrusive phases grew metal-enriched biotite during primary crystallization or through secondary processes of metasomatic enrichment involving remobilization of base metals by magmatic-hydrothermal fluids.

Second, a broader reaching application to surface exploration in uncharacterized and variably covered areas is proposed that involves the analysis of biotite and its weathering products in regolith. In this scenario, the target material is grains of fresh biotite, or secondary hydrobiotite or vermiculite liberated from sulphide-associated mafic lithologies through erosion and weathering. Micaceous grain populations with the characteristically high Ni (> ~1400 ppm) and elevated

Ni/Cr ratio (>2) should be suspected as having been liberated from inclusion-rich guartz diorite hidden at depth (if soil formation had been in situ) or distally in cases where micaceous sediment transport by wind or water has occurred. Biotite readily alters at surface conditions and, depending on the "strength" of chemical weathering, it may generate a variety of alteration products (e.g. vermiculite, chlorite, clay minerals, and Fe-oxide minerals; Wilson, 2004, and references therein). The weathering of biotite may begin with vermiculation through the replacement of K by other cations (which may be controlled by the amount of K contained within external solutions; Martin and Sparks, 1985) as well as the loss of octahedral Fe through oxidation (Barshad 1948; Walker, 1949; Rausell-Colom et al., 1964; Newman and Brown, 1966). Despite these structural changes, Gilkes and Suddhiprakarn (1979) have shown in saprolite and pallid zones of lateritic profiles that primary Ni and Cr are largely retained during soil formation, remaining in the most advanced alteration products of biotite (vermiculite, clays) at concentrations equivalent to their primary levels in the protolith. Therefore, the criteria here may be applicable to exploration in a diversity of environments, even those showing advanced stages of chemical weathering. However, the importance must be stressed of establishing bulk compositional or textural criteria to discriminate different types of biotite recovered from regolith, and where possible, establishing "background" levels of Ni and Cu enrichment in representative basement lithologies in a prospective study area.

#### Stable Isotope, Alteration, and Fluid Inclusion Fingerprints of "Low-Sulphide" Mineralization in the Footwall

Changes in fluid chemistry (reduction, dilution, neutralization, cooling) associated with early mixing events in the footwall are recognizable through systematic mapping of alteration mineralogy and stable isotopes. These changes were responsible for the dissociation of metal complexes leading to the precipitation of base and precious metals. In particular, identification of zones where mixing between calcic, high-salinity brines and oxidized metal-rich fluids (possibly derived from the SIC contact region) took place should be a priority for exploration. Identification of the original fluid pathways (from contact to footwall) within complex structural zones linking the footwall and contact environments is stressed.

## FORTHCOMING RELEASES

The study of melt-inclusion chemistry and its applications to understanding SIC evolution and ore formation will be submitted to *Journal of Petrology* in 2015. The study of fluid chemistry, alteration, and stable isotope systematics of low-sulphide systems will be submitted to *Mineralium Deposita*, in 2015. An article outlining the trace element chemistry of biotite and its application to routine exploration will be published in the *Journal of Geochemical Exploration* in June, 2015 (Warren et al., 2015).

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