

A STUDY OF THE COMPOSITION, DISTRIBUTION, AND GENESIS OF PYRRHOTITE IN THE COPPER CLIFF OFFSET, SUDBURY, ONTARIO, CANADA

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ABSTRACT

Pyrrhotite (Po) from five orebodies (830, 865, 880, 890, and 100 OB) in the Copper Cliff Offset Dike (CCOD) at Sudbury, Ontario was studied using powder X-ray diffraction data and Rietveld analysis, SEM-EDS, magnetic colloid, optical petrographic techniques, and Laser Ablation-ICP-MS in order to: (1) quantify the distribution of NC (non-magnetic, symmetry higher than monoclinic) and 4C (magnetic, monoclinic in symmetry) Po; (2) characterize the major, minor, and trace-element chemistries of both polymorphs; and (3) determine the factors enhancing the stability of NC Po. Results confirm that both NC and 4C Po are present, with ratios varying between 0 to 0.97. In general, 4C Po is the dominant polymorph within the sampled OB, with the exception of the 100 OB, which is dominated by NC Po.

Mineral chemistry indicates that there is an almost complete compositional overlap between the major, minor, and trace-element compositions of NC and 4C Po from the CCOD. The data also show that both polymorphs are slightly metal-deficient relative to the ideal chemistry of 4C Po, Fe₇S₈. There were no significant differences found in the Ni contents of either polymorph. Data revealed that the main mineralogical difference between the five OB was the presence of ilmenite in the 830, 865, 880, and 890 OB, whereas magnetite dominates in the 100 OB.

Mineralization occurs along the eastern margin of the 830–890 OB, in contrast to the 100 OB, where mineralization occurs in the center of the dike. The increased abundance of NC Po in the 100 OB may be explained by this difference in the style of mineralization, specifically, the proximity of ore to the surrounding country rock. Therefore, *f*O₂ may have directly influenced the distribution and stabilization of NC Po, which would then impact the observed NC:4C Po ratios in the selected OB.

Keywords: monoclinic pyrrhotite, hexagonal pyrrhotite, Copper Cliff offset dike, Ni-Cu-PGE sulfide deposit, Rietveld analysis, Sudbury, Ontario, Canada.

INTRODUCTION

Pyrrhotite (Po) is a family of non-stoichiometric, metal-deficient iron sulfide minerals with the general formula Fe_{1-x}S ($0 \leq x \leq 0.125$) found in a variety of geologic environments, including magmatic Fe-Ni-Cu-PGE and VMS deposits, metamorphic and low-temperature diagenetic environments (Erd *et al.* 1957, Kissin & Scott 1982, Deer *et al.* 1992, Konty *et al.* 2000, Ferrow *et al.* 2006). While crystallizing with the relatively simple NiAs structure, the non-stoichiometry and various arrangements of Fe vacancies that are possible lead to a number of crystal-structure polymorphic variants, the predominant two of which are considered to be NC Po (nominally considered as being hexagonal in symmetry) and 4C

Po (monoclinic in symmetry) in most deposits. As each of these, beyond their symmetry, has distinct ranges in chemical composition, magnetic character, and thermal stability ranges, knowledge of the distribution of NC and 4C Po in nature has far-reaching implications, ranging from providing important clues as to the genesis of ore deposits, information regarding mineral exploration, implications for mineral processing, and the alteration character of Po in the natural environment.

To address these questions and to better understand the origin and evolution of sulfide ores present in the Copper Cliff Offset Dike (CCOD), Sudbury, Ontario, a study focused on (1) documentation and quantification of the distribution of NC and 4C Po in orebodies (OB); (2) investigation of variations in the major, minor, and

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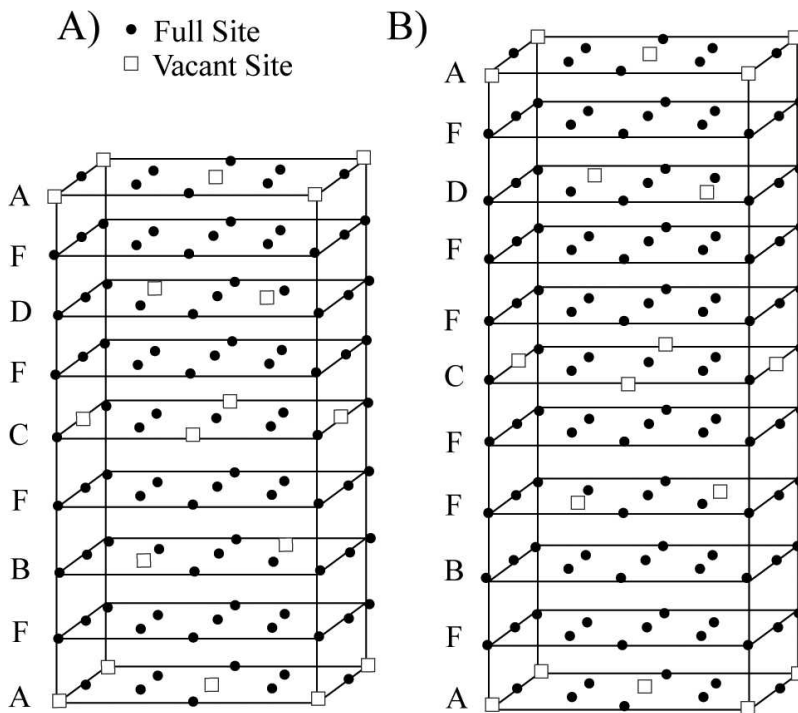


FIG. 1. Schematic representation of the vacancy distribution in (A) 4C Po and (B) NC Po; sulfur sites were omitted for clarity (modified from Becker 2009).

trace-element compositions of both polymorphs; and (3) determination of the physicochemical factors enhancing the stability of NC Po in the selected OB along the CCOD, was carried out, the results of which are summarized in this contribution.

BACKGROUND

Pyrrhotite: Crystal Structure and Composition

The Po crystal structure is based on that of nickeline (NiAs) and involves alternating layers of [6]-coordinated Fe and [5]-[6]-coordinated S along the *c* axis. It is stable over a wide range of temperatures, from the formation of monosulfide solid-solution at >900 °C, down to room temperature (Fig. 1; Vaughan & Craig 1974, Pratt *et al.* 1996). Above 350 °C, Po is considered to be the hexagonal NC polymorph, and below 254 °C, it transitions to the monoclinic 4C polymorph through a process involving the ordering of Fe and vacancies (Fig. 2; Kissin & Scott 1982). The type of polymorph present is not only a function of *T*, but also of composition: under *STP* conditions, stoichiometric troilite (FeS) contains 50 at.% Fe, NC Po between 46.63 and 47.37 at.% Fe, and 4C Po $\leq$ 46.63 at.% Fe (Kissin & Scott 1982). Such variations result in Po with varied magnetic, thermal, optical, and

electric properties and give rise to complicated phase-relationships involving members of the pyrrhotite family (Li & Franzen 1996, Wang & Salveson 2005). In this report, the designation 4C will be used for all Po considered to be monoclinic in symmetry, and the NC designation, for all Po that are not regarded as monoclinic, noting that there is still disagreement as to whether NC Po is in fact hexagonal, orthorhombic, or even monoclinic (de Villiers *et al.* 2009, Becker *et al.* 2010, de Villiers & Liles 2010, Elliot 2010, Liles & de Villiers 2012).

Pyrrhotite also has variable magnetic properties, with 4C Po considered to be ferrimagnetic while NC Po is considered antiferromagnetic. However, these end-member properties are simplistic, as Wang & Salveson (2005) determined that purely antiferromagnetic Po may only occur at the ideal compositions corresponding to 5C, 11C, and 6C Po, and ferromagnetic Po is strongly magnetic when occurring as 4C Po, with intermediate magnetism occurring between each of these compositions (Fig. 3).

As Po is a significant sulfide mineral in magmatic ore deposits, and relates to the formation and cooling histories of these deposits, it is important to understand its distribution and evolution. Using techniques described in the following sections, NC and 4C Po from

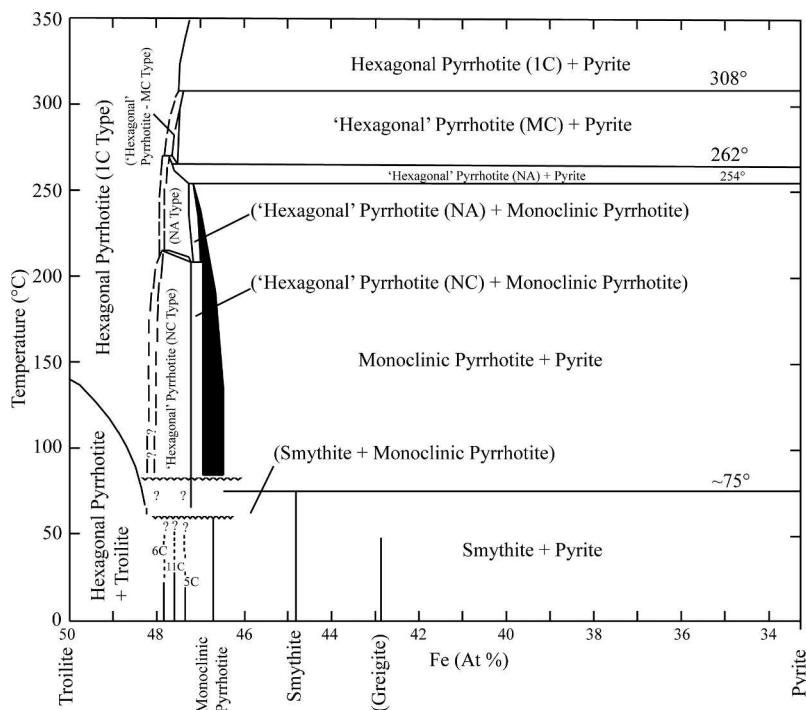


FIG. 2. Pyrrhotite stability graph showing the assemblages and polymorphs present below 350 °C and from 33 to 50 at.% Fe (Kissin & Scott 1982).

the CCOD will be characterized, and attempts will be made to ascribe a cause to the stabilization of NC Po.

Regional Geology

The Sudbury Structure, thought to have formed by a meteorite impact at 1850 Ma, can be found at the

intersection of the Superior, Southern, and Grenville Provinces of the Canadian Shield (Grant & Bite 1984, Krogh *et al.* 1984). The Sudbury Structure is divided into three parts, which include the Sudbury Basin, the Sudbury Igneous Complex (SIC), and footwall country rocks that were locally intruded by the Sudbury

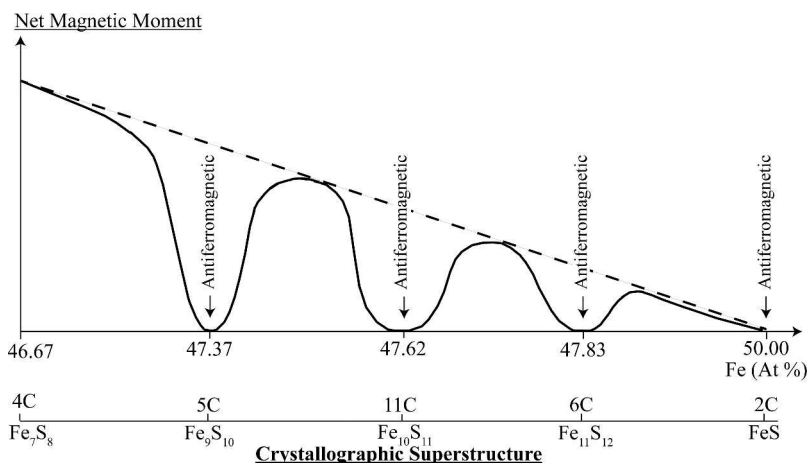


FIG. 3. Graph showing the net magnetic moment that occurs relative to the composition of Po (modified from Wang & Salveson 2005).

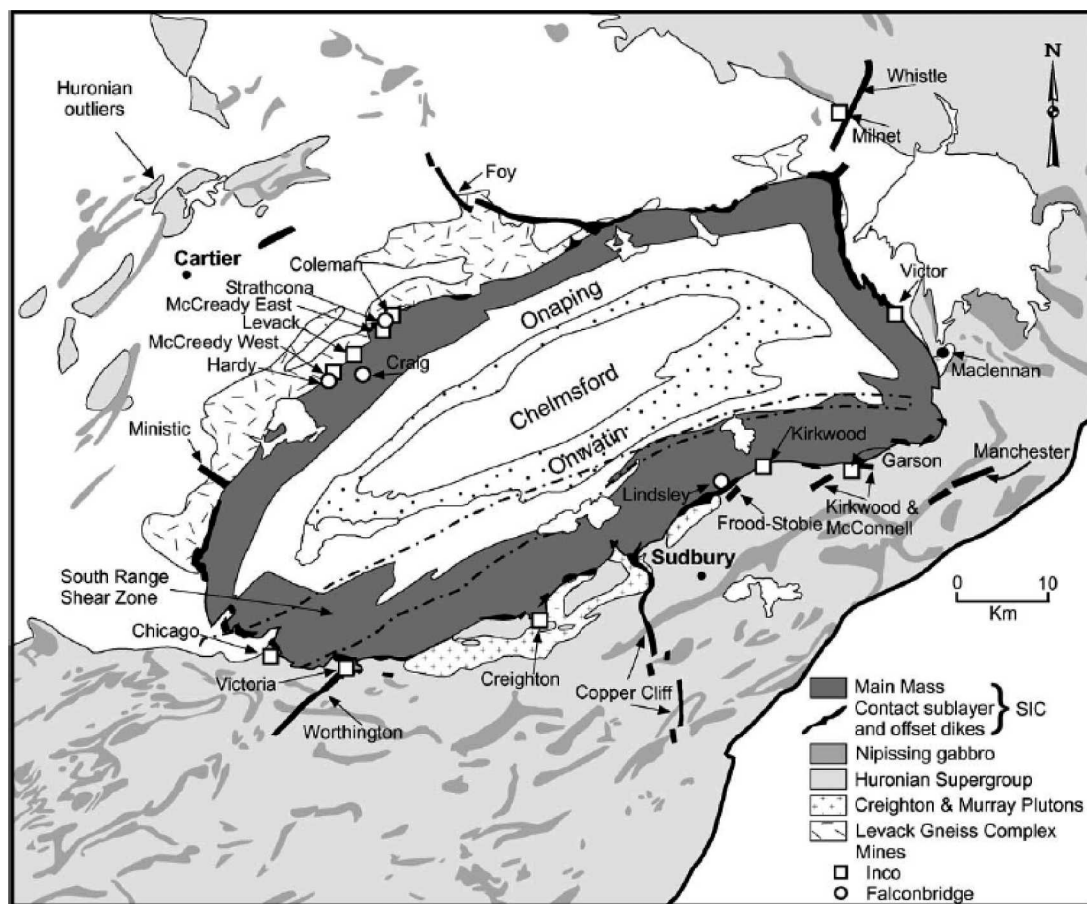


FIG. 4. Geologic map of the Sudbury area. The Copper Cliff Offset Dike (CCOD) is outlined in red (modified after Rousell *et al.* 2003).

Breccia (Fig. 4). It is elliptical in shape, measuring 60×40 km, this shape being attributed to a shortening event during the Penokean Orogeny at 1750 Ma, and it can be geographically subdivided into the North, East, and South Ranges (Grant & Bite 1984, Rousell 1984). The SIC comprises four major units which include, moving inwards and bottom to top, the contact sublayer, norite, quartz gabbro, and granophyre, with the last three units collectively termed the Main Mass (Naldrett 1984, Naldrett *et al.* 1984).

The Copper Cliff Offset Dike

Ore deposits of the SIC can be divided into one of four types based on the geologic setting: (1) SIC-Footwall contact deposits; (2) offset dike deposits; (3) footwall deposits; and (4) sheared deposits (Naldrett 1984, Morrison *et al.* 1994, Golightly & Rousell 2000, Farrow & Lightfoot 2002, Ames & Farrow 2007). The

Copper Cliff Offset Dike (CCOD), which is classified as an offset dike deposit, originates at an embayment in the Footwall contact of the Main Mass, extending perpendicularly away from the SIC, and is therefore considered to be a radial dike (Grant & Bite 1984, Mourre 2000). The embayment is 1.5 km wide and contains quartz-rich norite that grades over several meters into amphibole-biotite quartz diorite (QD). The CCOD narrows to a width of 20–75 m and extends ~19 km from the base of the SIC, with the most distal segment being less than 10 m wide (Fig. 5; Grant & Bite 1984). It is segmented by major E–W trending faults, including the Creighton and Murray faults, which are considered to be part of the same structural system (Fig. 5; Cochrane 1984). The CCOD was chosen as the area of study because the mine is positioned to become one of Vale's leading production mines, and because certain OB have been reported to possess anomalously

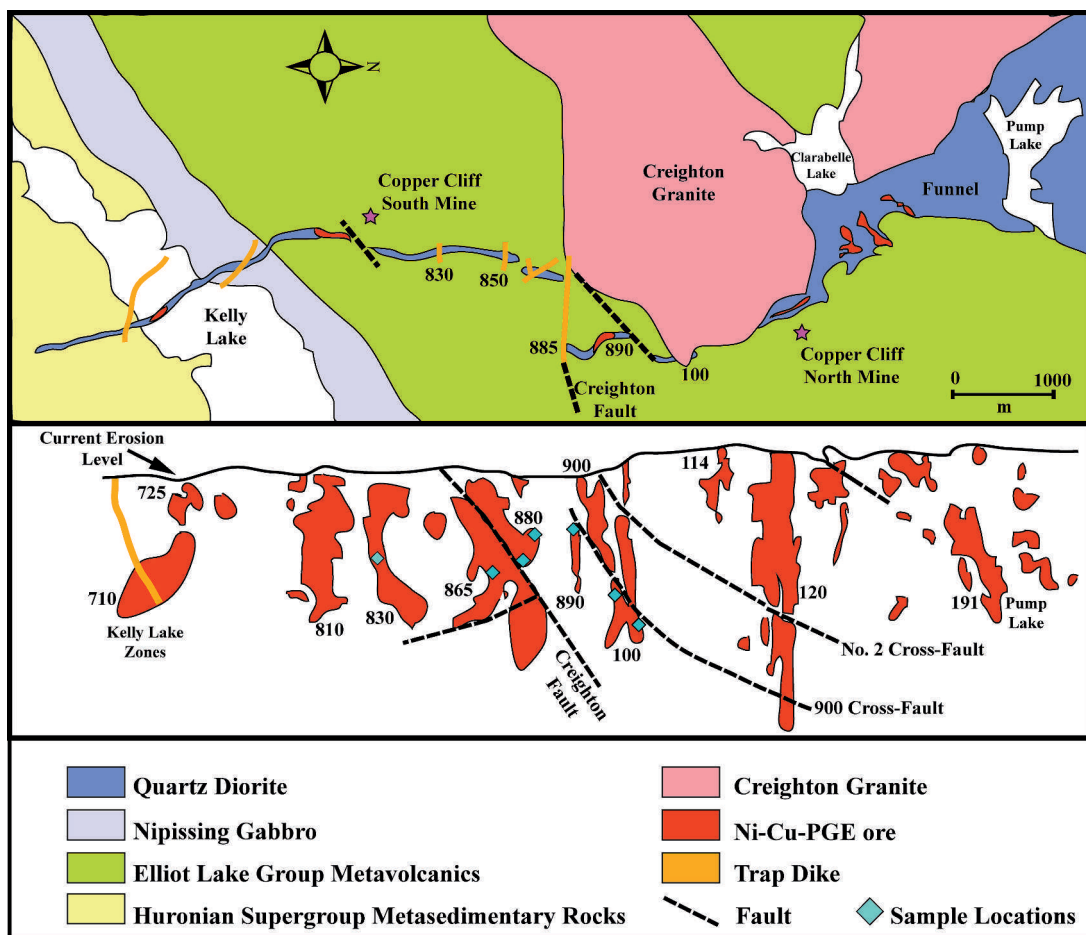


Fig. 5. Surface plan and cross-sectional view of the CCOD and its OB (modified after Cochrane 1984). Blue diamonds mark the locations in each OB from which samples were obtained.

high NC:4C Po ratios. It crosscuts a number of different country rocks; chilled margins are less evident near the embayment, but become more pronounced in the distal parts of the dike (Fig. 5; Cochrane 1984, Grant & Bite 1984).

To date, the prevailing model for emplacement of offset dikes involves QD magma that penetrated pre-existing, steeply dipping fracture zones that were opened owing to tensional stresses (Hawley 1962). Originally thought to have been emplaced by a single pulse of magma, recent work suggests that multiple pulses of magma were involved in forming the CCOD (Farrow & Lightfoot 2002). Its emplacement may have included an initial injection of sulfide-undersaturated magma that produced the marginal QD and a secondary magma pulse that was inclusion-bearing

and sulfide-saturated (Mourre 2000, Farrow & Lightfoot 2002).

Orebodies of the Copper Cliff Offset Dike

There are nine OB that constitute the CCOD, five of which were chosen for analysis during this study, including the 830, 865, 880, 890, and 100 OB. Some of these may have originally been part of the same ore zones, but were later dissected by faulting. For example, the 865 and 880 OB are separated by the Creighton fault, and the 900 and 100 OB are separated by the No. 2 Mine cross-fault (Cochrane 1984).

The OB of the CCOD can be divided into two types based on the position of mineralization within the dike: (1) *120-type* OB, where mineralization is located at the center of the dike, and (2) *810-type* OB, where

mineralization is located along the eastern contact of the dike with the surrounding country rocks (Cochrane 1984). The *120-type* OB are sub- to vertically dipping, which may have caused Ni-rich sulfide blebs to become concentrated at the center of the dike. Here, Po and pentlandite (Pn) first crystallized, with later Cu-Ni-PGE-enriched sulfides occurring along the margins of the ore zone (Cochrane 1984). In contrast, sulfide minerals that occur at the outermost footwall or eastern margin of the *810-type* OB are Ni-rich, massive Po and Pn, which modally decrease to the west as chalcopyrite (Cp) increases (Cochrane 1984). The Ni-Cu zoning is attributed to the attitude of the dike, which allowed for the earlier formed Po-rich monosulfide blebs to gravitationally settle toward the Footwall, leaving behind a Cu-Ni-PGE residual melt that formed Cu-rich sulfide minerals (Cochrane 1984). All of the sampled orebodies examined in this study fall into the *810-type* category, with the exception of the 100 OB, which is classed as a *120-type* OB. This difference in OB type is significant, as it may have impacted the cooling history of the sulfide minerals, which in turn would have influenced the resulting mineral assemblages.

METHODS

Sampling and Magnetic Susceptibility

The samples used in this study were strategically chosen on the basis of preliminary data that suggested inherent problems relating to the NC:4C Po ratio, with sample locations shown in Figure 5. The sample suite is a combination of wallrock, grab, and drill-core samples taken from a variety of levels (1850–5020L). Samples were also chosen to investigate potential trends with increasing depth, a feature that has been observed in other deposits (*e.g.*, Konty *et al.* 2000).

Preliminary results from magnetic susceptibility measurements and Rietveld analyses were used to narrow the sample suite for further SEM-EDS and LA-ICP-MS analyses. Sample processing involved the preparation of polished thin sections (PTS) with the off-cuts subsequently being used for Powder X-Ray Diffraction (PXRD) analyses. This ensured that the chemical data obtained during SEM-EDS analysis of the PTS came from the same samples that were studied by Rietveld analyses of PXRD spectra.

Magnetic susceptibility measurements were obtained from hand samples using a KT-10 Magnetic Susceptibility Meter that is reported to have a sensitivity of S.I. times 1×10^{-6} and that was operated in Scan mode at a frequency of 10 kHz, taking 20 recordings/s. The data collected were subsequently processed using the accompanying software, GeoView version 2.1.3.

Petrographic Techniques

Petrographic analyses using transmitted and reflected light were carried out using an Olympus BX51 microscope in order to corroborate the modal mineralogy determined by Rietveld analysis and to investigate textures present, specifically in reference to those involving intergrowths of NC and 4C Po. The latter was facilitated by the use of magnetic colloid which preferentially adheres to the magnetic minerals present (Vaughan & Craig 1974).

Image analysis was used to quantify NC and 4C Po abundances to compare with the results from Rietveld analysis. This was conducted using high-resolution images (4800 dpi) collected with a HP Scanjet G4010 Series flat-bed scanner and then processed using ImageJ software (Abramoff *et al.* 2004). ImageJ does not generate errors associated with area fractions, and so a series of images were evaluated and averaged, which established an estimated relative error of 10%. Although the results from the scanned subsets reveal that there can be localized variations in the concentrations of NC and 4C Po, there is good agreement between the average modal abundances and those determined through Rietveld analysis.

Powder X-ray Diffraction and Rietveld Refinements

The modal abundances of major, minor, and trace minerals present in each sample, along with determination of NC:4C Po ratios, were quantified through PXRD and Rietveld analysis of the obtained diffractogram spectra. Samples were pulverized in a tungsten carbide ring mill for 60 s. Powdered material (1–2 g) was pressed into the wells of aluminum disks and then analyzed using an automated Philips PW1729 powder diffractometer employing Fe-filtered $\text{CoK}\alpha$ radiation operated at 40 kV and 30 mA. The PXRD data were collected over a range of $5\text{--}75^\circ$ with a step size of 0.02° and counting times of 6 s/step. The program HighScore Plus (version 3.0.5, Panalytical) was used for preliminary mineral identification and to quantitatively determine the modal mineralogy of each sample through Rietveld analysis. Starting models of high-quality crystal structures were pre-selected from the International Crystal Structure Database, for which the references can be found in Table 1.

While performing Rietveld analyses, it was important to establish the quality of refinements that resulted; this was accomplished by examining both the Weighted R (R_{wp}) and Goodness of Fit (GoF) with target values of approximately 15 and 10, respectively (Young 1993). For individual phase refinements, the R_{Bragg} , an estimate of how well a phase fits in the refinement, is quoted for each mineral. The R_{Bragg} was given because in some cases the overall R_{wp} and GoF

TABLE 1. REFERENCE LIST FOR THE .CIF FILES USED AS STARTING MODELS DURING RIETVELD ANALYSES

Mineral	Reference
4C Po	(Tokonami <i>et al.</i> 1972)
actinolite	(Urusov <i>et al.</i> 1987)
albite	(Prewitt <i>et al.</i> 1976)
almandine	(Armbruster <i>et al.</i> 1992)
apatite	(Mackie & Young 1974)
biotite	(Bohlen <i>et al.</i> 1980)
chlorite	(Zheng & Bailey 1989)
chalcopyrite	(Hall & Stewart 1973)
diopside	(Finger & Ohashi 1976)
epidote	(Kvick <i>et al.</i> 1988)
ilmenite	(Yamanaka <i>et al.</i> 2007)
microcline	(Blasi <i>et al.</i> 1987)
magnetite	(Fleet 1981)
muscovite	(Brigatti <i>et al.</i> 1998)
NC Po	(de Villiers <i>et al.</i> 2009)
olivine	(Heinemann <i>et al.</i> 2006)
pentlandite	(Tsukimura & Nakazawa 1984)
pyrite	(Finklea <i>et al.</i> 1976)
quartz	(Hazen <i>et al.</i> 1989)
stilpnomelane	(Guggenheim & Eggleton 1994)

were abnormally high due to complicated mineral assemblages, but the individual values were lower, suggesting that the data had been sufficiently refined.

Scanning Electron Microscope – Energy Dispersive Spectrometry (SEM-EDS)

The major and minor element composition of sulfide minerals was determined with a JEOL JSM-6400 Scanning Electron Microscope (SEM) equipped with an Oxford INCA Energy-Dispersive Spectrometer (EDS). Data were collected using a beam current of ~1 nA, an accelerating voltage of 20 kV, and a livetime of 180 s. Data were reduced using Ni and Co wire and natural chalcopyrite standards for Cu, Fe, and S. The *K*-series X-ray lines were analyzed for each element, so as to minimize possible elemental interferences. The selections of areas for quantitative analyses of NC and 4C Po were made using photomicrographs of the PTS after application of the magnetic colloid treatment, as the two polymorphs were indistinguishable in back-scattered electron (BSE) images. To provide for a statistical spread of data, a total of 19 polished thin sections were analyzed and 198 data points collected for each Po polymorph, with approximately 40 points for each polymorph per OB.

Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS)

Land (1980) found that the presence of trace elements can enhance the stability fields of some minerals (*e.g.*, aragonite and Mg-rich calcite), and so the PGE (Ru, Rh, Pd, Os, Ir, and Pt) and selected semimetals (As, Se, Sb, Te, Re, and Bi) in NC and 4C Po were sought by LA-ICP-MS (group VA or VIIA elements; Huminicki *et al.* 2005).

Analyses were obtained from representative samples from each OB of both NC and 4C Po along with associated Pn and Cp. A total of 10 samples with low, intermediate, and high NC:4C Po ratios were selected for data collection. Line scans were used to determine average PGE and semimetal concentrations and to search for possible core-to-rim variations. Integrations were carefully examined for platinum-group mineral (PGM) inclusions, however none were observed in the analyzed Po.

The instrument used in this study was a Resonetics RESOLUTION M-50 193 nm ArF Excimer laser with a 20 ns pulse duration that used He, later combined with Ar and N₂, as the carrier gas to transport the ions to a Thermo X-series II quadrupole mass spectrometer. The operating conditions include a fluence of 5–7 J/cm², an estimated spot size of 23–24 µm, lateral translation rate of 12 µm/s, and repetition rate of 5 Hz. Internal standardization was based on ³⁴S for Po, Pn, and Cp, using S concentrations as determined by SEM-EDS. The raw data were processed using the program Igor Pro (version 6.22A) along with Iolite (version 2.13), which uses the Trace Elements data reduction scheme (Woodhead *et al.* 2007).

Four different standards were used for the LA-ICP-MS data collection, including NIST 610, NIST 612 (Pearce *et al.* 1997), G-BHVO-2G Basaltic Glass (Jochum *et al.* 2005), and Po725 (Sylvester *et al.* 2005). The NIST 610 and 612 standards were used for the semimetal determinations, and Po725 was used for PGE standardization, with all standards being analyzed three to four times during a typical data collection.

When using this technique it is important to consider elemental interferences that may develop. Interferences of most concern to this study include ⁴⁰Ar⁶³Cu on ¹⁰³Rh and ⁴⁰Ar⁶⁵Cu on ¹⁰⁵Pd. The PGE content of Po was of interest in this study and it was determined that corrections were not required for interferences on Re, Os, Ir, Pt, and Au (Sylvester 2001). The interference corrections are minor for magmatic sulfides containing ppm levels of Ru, Rh, and Pd, although the errors can be significant when the PGE are present in phases with weight percent levels of Ni or Cu (Sylvester 2001). However, the Po examined in this study typically contained less than

1 wt.% Ni, with no Cu detected; therefore no corrections were carried out for interferences involving the PGE.

RESULTS

Petrography

The major opaque mineral assemblage present in the analyzed samples includes Po, Pn, and Cp, typical of all deposit styles present in Sudbury, and Ni-Cu-PGE deposits in general (Naldrett *et al.* 1999, Magyarosi *et al.* 2002, Bailey *et al.* 2006). Trace amounts of ilmenite (Ilm) and magnetite (Mgt) were also found, with Ilm occurring almost exclusively in the 830–890 OB and Mgt in the 100 OB, a noteworthy observation that will be discussed later. The non-opaque assemblage includes quartz, plagioclase, K-feldspar, biotite, amphibole, and rare pyroxene; these minerals, their abundances, and the textures observed are consistent with quartz monzodiorite to granodiorite lithologies. Alteration products of the felsic and mafic phases include chlorite, epidote, muscovite, and rare stilpnomelane. Accessory minerals found include trace apatite-, olivine-, and garnet-group minerals.

Pyrrhotite is the dominant sulfide mineral in all of the studied samples, with grains ranging in size from 40 μm to more than 1 mm. Using the classification scheme of Gu & Vokes (1996), three types of NC+4C Po intergrowth textures were observed: (1) crystallographically controlled lamellar intergrowths, (2) boxwork lamellae, and (3) irregular intergrowths.

Crystallographically controlled lamellar intergrowths consist of 4C Po as subparallel lamellae in a matrix of NC Po (Fig. 6A). The lamellae vary in thickness from 1 to 5 μm and terminate or change direction at grain boundaries. Boxwork and composite lamellae are caused by the coarsening and maturation of lamellae during annealing, which Gu & Vokes (1996) suggested could have been promoted by anisotropic stress. Zones of boxwork intergrowths were also observed, with lamellae either changing direction or closing in on themselves, creating irregularly shaped patterns (Fig. 6B). The relative proportions of NC to 4C Po lamellae vary greatly from sample to sample, and even from grain to grain. For example, within one grain, the 4C Po lamellae can represent >50 % of the grain, with adjacent grains being dominated by NC Po and nearly devoid of 4C Po lamellae (Fig. 6C). Both crystallographically controlled and boxwork intergrowths were observed in all samples from each of the OB. Most samples from the 100 OB were dominated by Po that was devoid of any 4C Po lamellae, suggesting that NC Po is the only polymorph present (Fig. 6D). However, some irregular intergrowths of 4C Po were found to occur as patches

along grain boundaries in some samples from the 100 OB (Fig. 7).

In general, all of the OB have very similar mineralogical compositions and modal distributions in terms of the sulfide minerals present (Table 2). The main mineralogical difference observed between the OB (other than the NC/4C Po ratio) is the type of oxide mineral that dominates: specifically, Ilm was found to be the dominant oxide mineral in all of the orebodies except the 100 OB, where Mgt dominates. In the 100 OB Mgt occurs as grey rounded blebs that are generally enclosed by Po, but are also found in contact with Pn (Fig. 6D). Magnetite was observed in only two samples from the 830–890 orebodies, occurring as rounded blebs at less than 2 modal percent in each case. In contrast, Ilm was found in several samples from the 830–890 OB, but was present in only one sample from the 100 OB.

PXRD and Rietveld Analysis

Rietveld analyses of PXRD spectra were conducted to (1) provide modal mineralogical data and (2) quantify NC:4C Po ratios of individual orebodies. To test the reproducibility of the Rietveld technique, select samples were separated into three aliquots, with PXRD data collected from each. The comparison indicates that a unique solution can be found with no significant difference between the three refinements (Table 3). When the Rietveld results are compared to those obtained from image analysis, a good correlation was also noted, although local variations in NC:4C Po ratios were observed in each sample studied.

The results from the Rietveld analyses produced NC:4C Po ratios (NC Po/NC Po + 4C Po) that were found to be consistent among the 830–890 OB, with average ratios ranging from 0.19 to 0.24, median values of 0.16–0.26, and minimum and maximum ratios of 0–0.05 and 0.36–0.48, respectively (Table 4). The NC:4C Po ratios for the 100 OB were found to deviate from this trend, with average values of 0.77, a median of 0.81, a minimum of 0.25, and a maximum ratio of 0.97.

Modal relationships among the silicate (*e.g.*, felsic and mafic minerals, chlorite, *etc.*) and sulfide mineralogies were also evaluated. However, no trends of any significance could be discerned. Therefore the stabilization and distribution of NC Po do not appear to be related to any component or components present in the associated mineralogy.

SEM-EDS – Mineral Chemistry

Major and minor element compositions of sulfide minerals present in each OB were determined using SEM-EDS. Although the two polymorphs can be

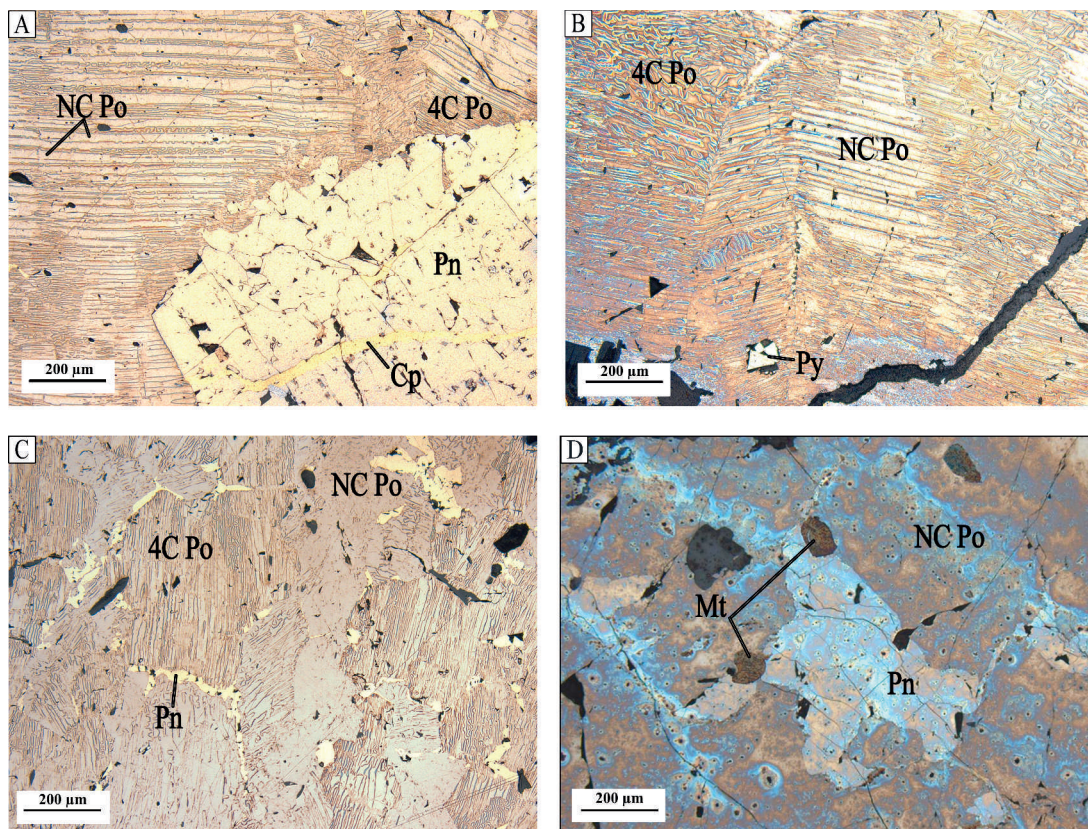


FIG. 6. Examples of the intergrowths and textures that can be found in the 830–890 OB include: (A) Coarse grain of Pn surrounded by Po with crystallographically controlled lamellae of 4C Po; (B) Lamellar zonation divided by a kink band in Po with varying degrees of boxwork lamellae in the surrounding grains; (C) Grains of NC and 4C Po, distinguished by the differing abundance of colloid and lamellae, with Pn stringers occurring along Po grain boundaries; from the 100 OB, (D) Po is almost entirely NC Po with a coarse grain of Pn in the center and several stringers present and grains of Mgt that have colloid adhering to them. The magnetic colloid treatment caused the Po to have a brown hue in the subsequent photomicrographs.

intergrown (on the basis of observations made of areas treated with magnetic colloid), care was taken to ensure that analyses were obtained from individual grains of either NC or 4C Po. However, before data collection was completed, a comparative study was done between data collected by SEM-EDS and a Cameca SX-100-WDS (Wavelength Dispersive Spectrometer) electron microprobe located at the Ontario Geoscience Labs, in order to evaluate the accuracy of the SEM-EDS data.

Results from the comparative studies show strong correlations for weight percent Ni and S data collected using different instruments (Fig. 8A and B). The correlation for weight percent Fe data is strong between the two SEM-EDS instruments. However, the correlation of that obtained from both SEM

instruments compared to that obtained by WDS methods with the SX-100 instrument is not as strong. In general, data obtained by WDS indicate greater Fe values, ranging from 59.6 to 60.5 wt.% Fe, compared to 58.8–60.0 wt.% Fe found by SEM-EDS. However, data for Fe collected by WDS using the SX-100 instrument have been found to overestimate the Fe content of Cp by 0.25 wt.% (D. Crabtree, *pers. commun.*). This provides a plausible explanation for the higher-than-expected Fe content measured for Po using the SX-100 instrument.

Once SEM-EDS was established as a viable method for collecting quantitative mineral-chemical data, experiments were conducted to investigate the nature of chemical differences between the NC and 4C Po. Results indicate that within all of the OB,

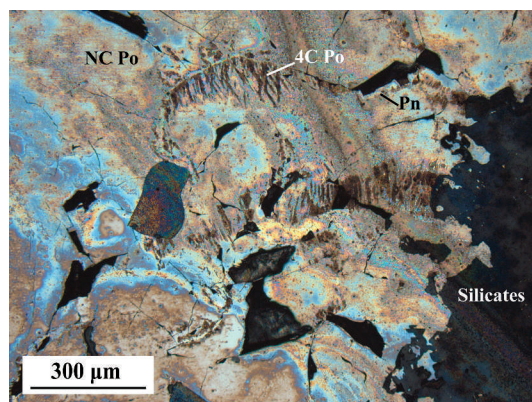


FIG. 7. Photomicrograph from the 100 OB showing irregular patches of 4C Po along the margins of NC Po; coloring is an effect of the colloid treatment.

regardless of the polymorph examined, the Po have remarkably similar mineral chemistries in terms of Fe, Ni, and S (Table 5). These observations are in contradiction to other studies that have suggested that NC Po is considered to have higher Fe and Ni contents than 4C Po (Batt 1972); they will be discussed in greater detail below.

The majority of the grains analyzed are slightly Fe-deficient (45.8–46.4 at.% Fe) relative to the ideal composition corresponding to 4C Po ($\sim\text{Fe}_7\text{S}_8$, which contains 46.63 at.% Fe), regardless of the Po polymorph analyzed (Fig. 9). Data from the 100 OB

TABLE 2. AVERAGE MODAL ABUNDANCES FOR EACH OB ALONG THE CCOD

Phase	OB				
	830	865	880	890	100
NC Po	18	17	12	17	45
4C Po	47	47	48	50	10
Pn	11	14	7	6	5
Cp	8	3	6	4	4
pyrite	0	0.5	0	0	0
magnetite	0	0	0	0	2
quartz	5	5	7	9	6
biotite	3	2	3	5	4
chlorite	2	4	2	4	2
amphibole	3	1	8	2	10
albite	4	3	6	3	11
almandine	0	1	0	0	0
olivine	0	1	0	0	0
epidote	0	1	0	0	0
Sum	100	99	99	100	99
NC:4C Po	0.28	0.26	0.20	0.25	0.81

TABLE 3. MODAL ABUNDANCES FROM THREE ALIQUOTS OF THE SAME SAMPLE, 06B FROM THE 865 OB

Phase	06B #1	06B #2	06B #3	Average
NC:4C Po	0.47	0.40	0.39	0.42
NC Po	33	29	28	30
4C Po	37	43	44	42
Pn	23	23	22	23
Cp	3	3	3	3
chlorite	2	2	2	2
muscovite	b.d.	b.d.	1	b.d.
Sum	99	100	100	100
Weighted R (R_{wp})	12.15	13.06	11.96	12.39
Goodness of Fit	7.44	5.93	5.63	6.33
Zero Shift	-0.042	-0.027	-0.175	-0.08

(b.d. = below detection)

show a range between 46.1 and 47.3 at.% Fe, which falls between the ideal composition for NC Po (specifically 5C Po) and 4C Po (*i.e.*, the two end-members of that stability field) and account for the points found above the 5C Po composition in Figure 9. Using the phase diagram of Kissin & Scott (1982) and plotting the data obtained in this study, results indicate that all Po, except for a few compositions of Po from the 100 OB, plot in the field corresponding to 4C Po, regardless of the polymorph inferred to be present. Analysis of adjacent grains of NC and 4C Po was done in order to evaluate local changes in chemistry, but there was no discernible difference between the Fe or Ni content, regardless of the polymorph inferred to be present after magnetic colloid treatment (Fig. 10). Therefore, within error, NC and 4C Po examined in this study are compositionally identical.

The average Ni content varies between 0.48 and 0.74 at.% Ni, regardless of the polymorph analyzed (Fig. 11). This range in data is fairly typical of Po from various deposit types in the SIC (0.40–0.60 at.% Ni; Vaughan *et al.* 1971, Gauld 1999, Szentpéteri *et al.* 2002, Huminicki 2003). However, the overlapping Ni content of NC and 4C Po is in contrast to other studies

TABLE 4. SUMMARY OF THE AVERAGE, MEDIAN, MINIMUM, AND MAXIMUM NC:4C PO RATIOS FOR EACH OB

OB	Average	Median	Min	Max	<i>n</i>
830	0.24	0.26	0	0.41	7
865	0.23	0.19	0	0.48	17
880	0.19	0.16	0.05	0.46	8
890	0.21	0.21	0	0.36	7
100	0.77	0.81	0.71	0.97	13

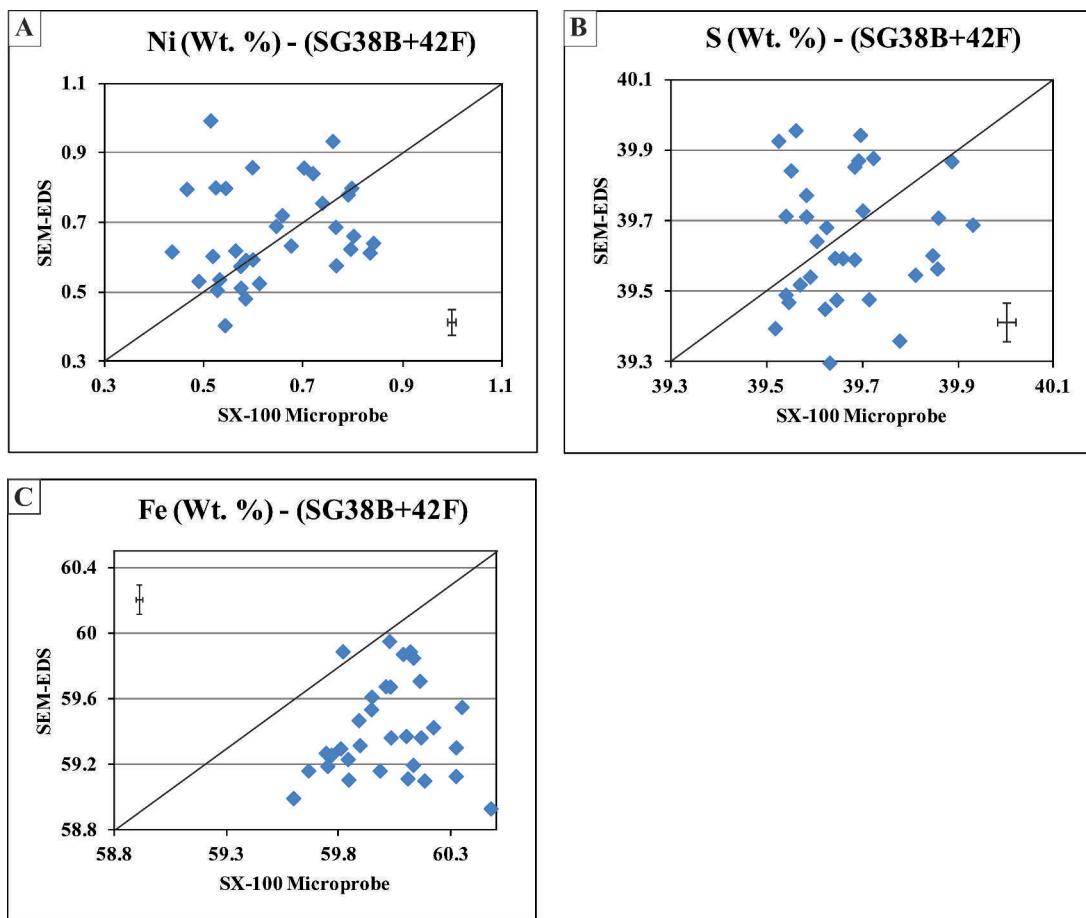


FIG. 8. Comparison between (A) Ni (wt.%), (B) S (wt.%), and (C) Fe (wt.%) data obtained through SEM-EDS and the SX-100 microprobe. Note: the 1:1 line is indicated and error bars represent a 2σ error.

within the SIC. For example, Batt (1972) analyzed 65 randomly selected grains of Po from composite samples from the Sudbury area and determined that NC Po contained 0.8–0.9 wt.% Ni and 4C Po contained 0.4–0.5 wt.% Ni, *i.e.*, a bimodal distribution of Ni content. Batt (1972) also etched specific samples and was able to correlate the two Ni populations with unetched NC Po and etched 4C Po.

Using the obtained mineral-chemical data and the normalized Fe:S, the average composition of NC Po is $\text{Fe}_{6.91}\text{S}_8$, whereas the average composition of 4C Po is $\text{Fe}_{6.88}\text{S}_8$. The two compositions are comparable and, most notably, both are slightly lower than the ideal Fe_7S_8 of 4C Po. When Ni is also taken into account, the average composition of NC Po is $(\text{Fe,Ni})_{7.00}\text{S}_8$, whereas 4C Po is $(\text{Fe,Ni})_{6.97}\text{S}_8$, *i.e.*, virtually the same for both NC and 4C Po. These results were unexpected if the magnetic character of the two polymorphs is

considered, in that both were found to be present upon magnetic colloid treatment of PTS and Rietveld results. These observations are not unique to the CCOD, and have been found in other OB from Sudbury (Szentpéteri *et al.* 2002).

There is a direct overlap in total metal (Fe+Ni):S ratios between NC and 4C Po, which was not predicted by empirical and experimental data from other studies. When analyses within a single grain of NC or 4C Po are compared, there do not seem to be any significant variations in the major or minor element chemistry. This is a significant finding, as it shows that regardless of the NC:4C Po ratio in an OB, all of the Po in the analyzed samples from the CCOD appear to have the same Ni content. As there is no significant difference between the mineral chemistry of NC and 4C Po, this cannot be the reason for the stabilization of the NC Po.

TABLE 5. SUMMARY OF THE AVERAGE CHEMICAL DATA FOR NC AND 4C PO FROM EACH OB

OB	4C Po (at.%)			NC Po (at.%)		
	S	Fe	Ni	S	Fe	Ni
830	53.4	46.1	0.50	53.4	46.1	0.48
865	53.6	45.7	0.73	53.5	45.7	0.74
880	53.5	45.9	0.62	53.4	46.0	0.63
890	53.4	46.1	0.51	53.4	46.1	0.52
100	53.3	46.0	0.73	53.0	46.4	0.59
Average	53.4	46.0	0.60	53.3	46.1	0.60
Error (2 σ)	0.27	0.27	0.15	0.27	0.27	0.15

LA-ICP-MS

Results of the LA-ICP-MS study indicate that only the PPGE Ru, Rh, and Pd are detected in the Po studied, with average concentrations of 0.33, 0.03, and 0.42 ppm in NC Po and 0.36, 0.22, and 0.62 ppm in 4C Po (Table 6). The IPGE (Os, Ir, Pt) were not detected in the sulfide minerals analyzed at the 3 σ level. Detection limits for the PGE are summarized in Table 7.

The majority of the semimetal data are below the 3 σ error levels, with the exception of rare elevations in As and Bi analyses. Arsenic and Bi were found to be heterogeneously distributed and can be attributed to micro-inclusions within the analyzed grains, which

were identified by sharp, intermittent peaks during data processing. This is in agreement with SEM-EDS analyses, which also indicated the presence of discrete grains of gersdorffite, Bi tellurides (tsumoite), and michenerite as inclusions in Po. As the average values for the PGE and semimetals in Po directly overlap for both NC and 4C Po, their presence cannot be invoked as a mechanism to explain the stabilization of NC Po.

DISCUSSION

Petrographic Characteristics

Varying proportions of 4C Po lamellae in NC Po were observed in all of the samples from the 830–890

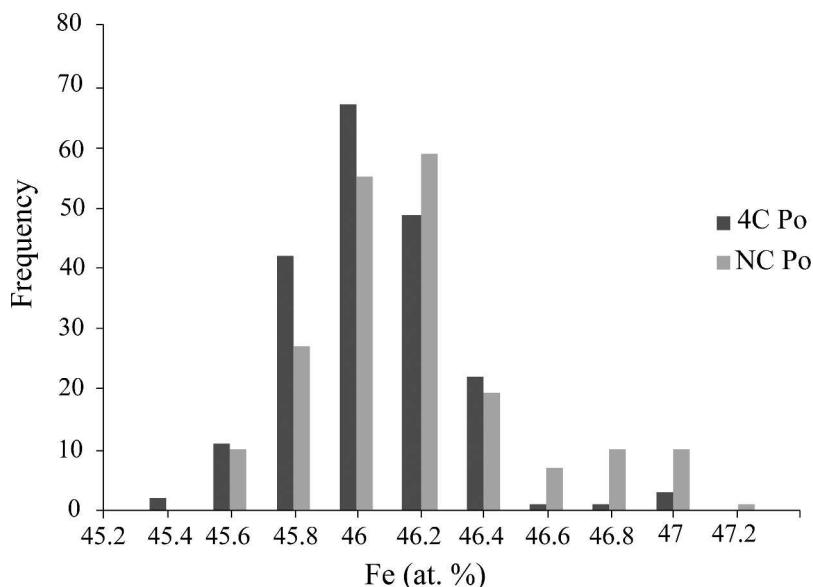


FIG. 9. Frequency histogram depicting the distribution of SEM-EDS data collected for NC and 4C Po with respect to their Fe contents.

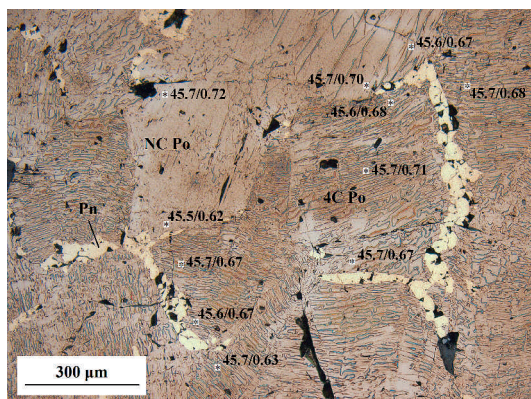


FIG. 10. Photomicrograph of a sample from the 865 OB after magnetic colloid treatment, with black asterisks marking SEM-EDS data collection points, with corresponding Fe/Ni (at.%) values labeled.

orebodies, along with lamellae of varying thickness. The lamellae may be the result of the transformation from NC to 4C Po, with 4C Po lamellae exsolving below temperatures of 254 °C (Arnold 1967, Yund & Hall 1969, Gu & Vokes 1996). The variable zones of 4C Po lamellae could also be attributed to strain variations across the Po grains, given that exsolution can be enhanced by strain (Stanton 1972, Gu & Vokes 1996).

Irregular patches, rather than distinct lamellae of 4C Po, were only found in the 100 OB samples and therein, only along the grain boundaries of NC Po.

Here, the lamellae of 4C Po appear to be oriented parallel to crystallographic planes of the host NC Po (Fig. 6A). It has been suggested that the lack of well-developed 4C Po lamellae may be a result of slow cooling (Lusk *et al.* 1993). It is noteworthy that the only place in the 100 OB that well-developed lamellae of 4C Po were found was in disseminated ore samples which also had the lowest NC:4C Po ratio (Fig. 7). These samples were taken from the margins of the 100 OB, where the degree of undercooling would be predicted to be greatest, thus enhancing development of 4C Po lamellae. Conversely, the development of 4C Po lamellae along NC Po grain boundaries may be related to the amount of oxidation that would be occurring near the margins of the OB.

The occurrence of Pn stringers along Po grain boundaries results in a net texture, which was initially of interest based on their potential relationship with the Po polymorphs (Fig. 6C). Gu & Vokes (1996) suggested that exsolution of 4C Po lamellae from a NC host could be enhanced by, or accompany, the exsolution of Pn, but this does not seem to be the case in the CCOD. The Pn stringers frequently occur between grains of NC and 4C Po, but can also be observed between grains of the same polymorph. Systematic analyses of both polymorphs in relation to Pn stringers indicated that the Fe and Ni contents of NC and 4C Po are within error of one another, regardless of whether the Pn stringers are present. There is no evidence to indicate that the associated Pn stringers are a product related to the conversion of NC to 4C Po.

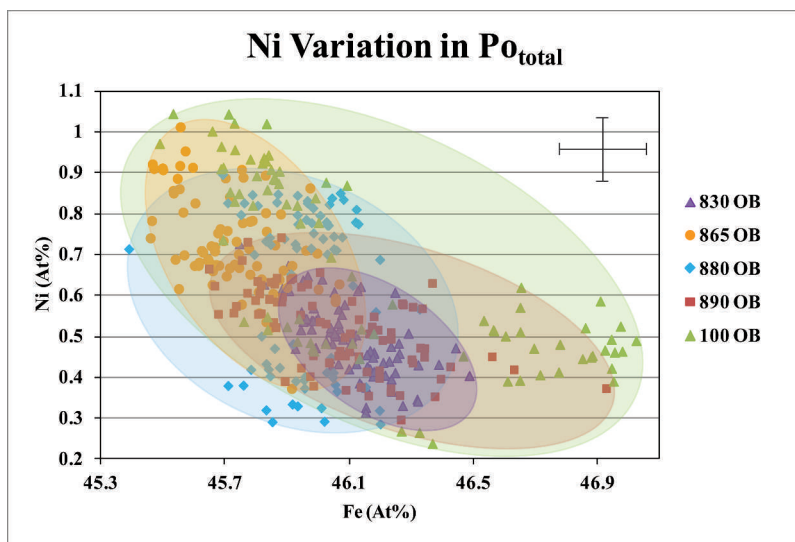


FIG. 11. Ni variation in total Po separated according to orebody. Note: error bars represent 2 σ error.

TABLE 6. AVERAGE AND MAXIMUM VALUES OF PGE DATA OBTAINED THROUGH LA-ICP-MS

	Average (ppm)			Maximum (ppm)		
	Ru	Rh	Pd	Ru	Rh	Pd
4C Po	0.37	0.22	0.63	0.58	0.95	0.97
NC Po	0.33	0.03	0.42	0.47	0.06	0.88

NC:4C Po Modal Mineralogy

The 830–890 OB have average NC:4C Po ratios of 0.19–0.24, while the 100 OB is significantly different, with an average ratio of 0.77. Based on the higher modal abundance of NC Po in the 100 OB, and considering differences in magnetic character between the NC and 4C Po, it was presumed that samples from this OB would generally exhibit lower magnetic susceptibility values. However, measurements show that this is observed only along the margins of the OB, and in fact exceptionally high magnetic susceptibility measurements were taken from the core of the 100 OB (Fig. 12). As was previously noted, Mgt was found in approximately half of the samples from the 100 OB, with concentrations ranging from 1 to 14% Mgt, but it is rare to non-existent in the remaining OB (*i.e.*, only in two samples from the 830–890 OB). The magnetic susceptibility measurements observed in Figure 12 suggest that the 100 OB has a magnetic core, with magnetism decreasing towards the margins of the dike.

TABLE 7. DETECTION LIMITS FOR THE ANALYZED PGE

	Ru	Rh	Pd	Os	Ir	Pt
Detection Limit (ppm)	2.1	0.12	0.11	0.21	0.26	0.09

Pyrrhotite has been established as a reactive mineral that is highly prone to oxidation (Belzile *et al.* 2004). While it is possible that certain areas of the 100 OB may have been preferentially oxidized, such as the margin in contact with the No. 2 cross-fault, there are no major structures occurring within the core of the 100 OB that would lead to a significant oxidation of the Po present, which in turn would lead to a pronounced increase in magnetic susceptibility. Trends in NC:4C Po ratios *versus* corresponding magnetic susceptibility measurements were evaluated, but none were observed in samples from the 830–890 OB; thus, changes in the magnetic susceptibility are more likely to be related to concentration of Mgt present and, to a lesser extent, Ilm. Although the data available are limited, a comparison of the modal abundance of Mgt and magnetic susceptibility suggests a positive correlation between the two.

Mineral Chemistry

When the average compositions of NC Po (46.1 at.% Fe) and 4C Po (46.0 at.% Fe) obtained in this study are considered in light of the experimentally determined phase diagram of Kissin & Scott (1982),

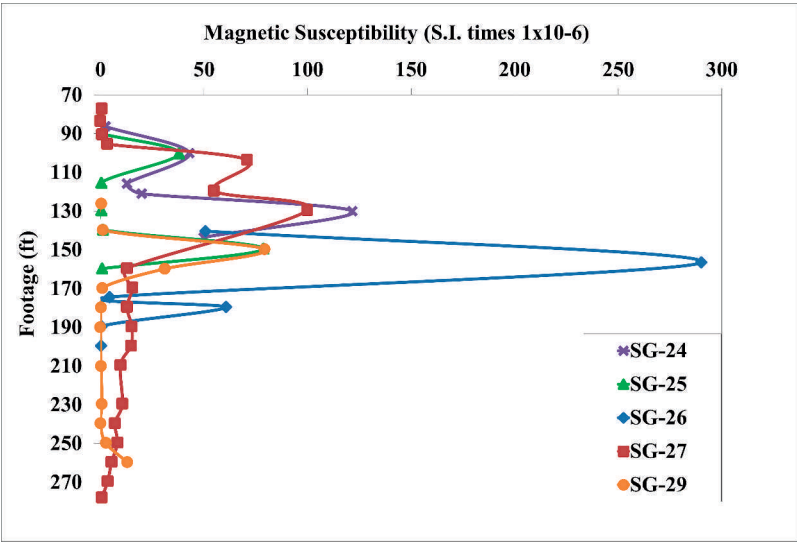


Fig. 12. Magnetic susceptibility trends taken from core that was drilled approximately across the 100 OB.

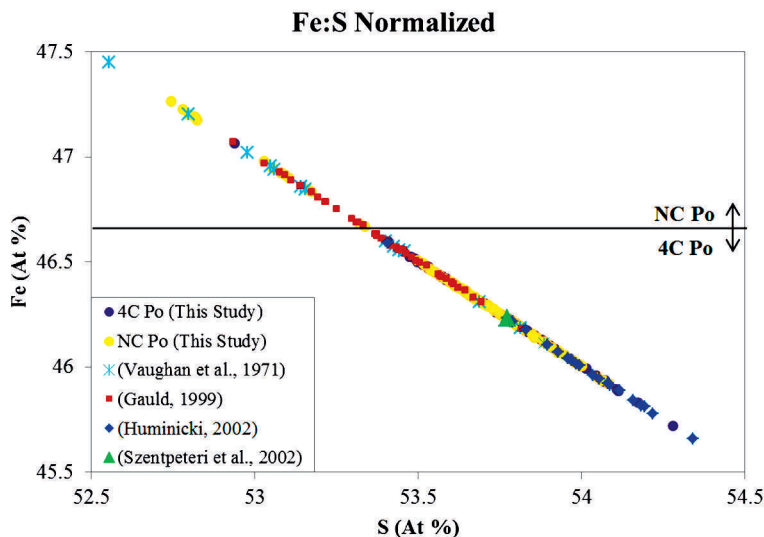


FIG. 13. A compilation of Po data from the SIC, Fe:S normalized, compared to the data obtained in this study. Note: the 1:1 line is indicated.

the observed Po should correspond to 4C Po. Grains that were initially considered to be NC Po, owing to their non-magnetic appearance after the application of magnetic colloid, were analyzed by SEM-EDS and were found to have the same average Fe values as 4C Po (Table 5). While there are a few analyses that plot within the NC Po field, the majority do not and the bulk of the data fall within the 4C Po field. Therefore, on a chemical basis, almost all of the NC Po should be classed as 4C Po, even though the physical properties are consistent with the non-magnetic NC Po form.

To establish whether similar trends exist at other deposits within the SIC, data were gathered and synthesized into a comparative graph (Fig. 13). The CCOD contains at least one anomalous OB with a high abundance of NC Po, and when compared with compositional data from the literature, there is an almost complete overlap in composition between the data sets (Fig. 13). Gauld (1999) collected data from a contact-style Ni-Cu ore deposit in the North Range of the SIC showing that more than 95% of the analyzed Po is 4C Po based on XRD results and etching. However, the chemical data actually plot on either side of the ideal 4C Po composition, indicating that some of the Po may be NC Po (Fig. 13). Szentpéteri *et al.* (2002) presented average chemical data from predominantly NC Po OB of the CCOD (*e.g.*, the 100 and 120 OB); these results, although they do not discriminate between NC and 4C Po, are represented by a single data point in Figure 13. Szentpéteri *et al.* (2002) found Po to have an average composition of 46.23 at.% Fe,

which overlaps with the data from both NC and 4C Po observed in this study (*i.e.*, 45.3–47.0 at.% Fe), *i.e.*, data from both studies are internally consistent. Finally, Vaughan *et al.* (1971) collected data on Po from the Strathcona mine, with the results indicating that Po from this area contains the highest Fe concentrations relative to the other data shown in Figure 13, although the data once again overlap with the compositions found in this study. It should be noted that in this study, each chemical analysis represents, strictly speaking, either NC or 4C Po; however, it is possible that the data from the literature represents Po of mixed compositions.

Considering the Fe:S normalized average formulae, $\text{Fe}_{6.88}\text{S}_8$ for 4C Po and $\text{Fe}_{6.91}\text{S}_8$ for NC Po, as determined in this study, the Po from the 100 OB observed in this study would be considered as 4C, in which case, it would be predicted to be ferromagnetic. This is inconsistent with the results from both the PXRD and colloid studies, which show that NC Po dominates, which in turn implies that it has not yet been converted to 4C Po, *i.e.*, it is existing metastably. While a portion of the NC and 4C Po could exist in equilibrium based on the phase-equilibria study of Kissin & Scott (1982), the chemical data obtained indicate that the majority of Po plot in the 4C Po field, *i.e.*, outside the field in which both may co-exist (Fig. 14). It is therefore possible that the NC Po present represents a high-temperature structure that was quenched from above the 254 °C conversion point

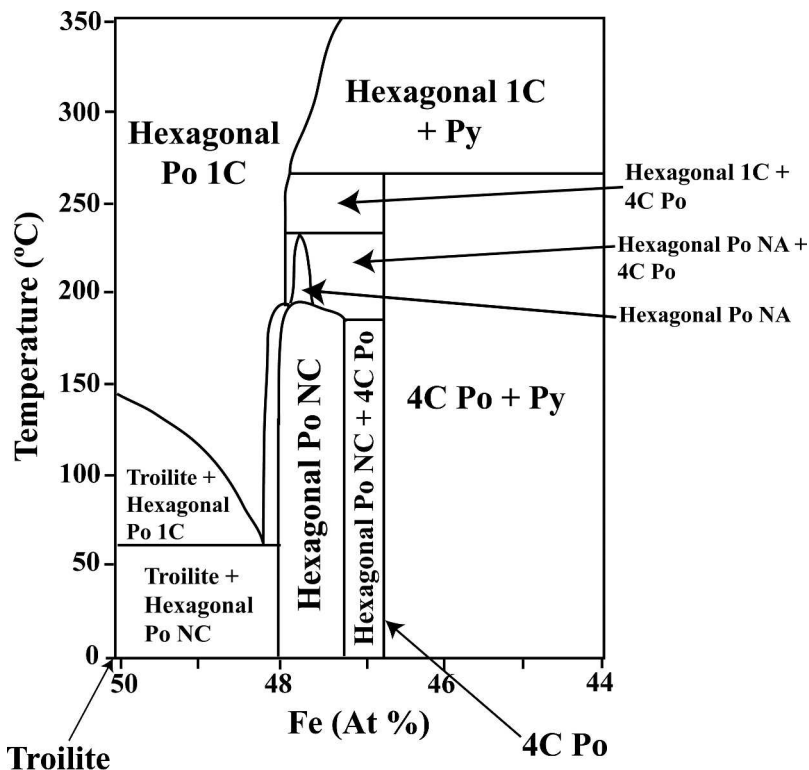


FIG. 14. Simplified phase diagram comparing temperature and normalized Fe (at.%) values for Po (modified from Kissin & Scott 1982).

and has not yet converted to 4C Po, as in the remaining orebodies.

Stabilization of NC Po

The primary goal of this study was to determine the distribution of NC and 4C Po along the CCOD, followed by broadly determining potential explanations for variations in the observed NC:4C Po ratios and those factors enhancing the stabilization of NC Po. While a robust methodology involving PXRD and Rietveld analyses has been developed to quantify the NC:4C Po ratios, results from this study show that there are no significant differences in the major, minor, and trace-element compositions of NC and 4C Po, nor any discernible trends with respect to these variations and changes in modal mineralogy.

One significant difference that was observed relates to the geologic setting of the OB (*120- versus 810-type*), and the potential effect this may have had on the observed mineral assemblages. The crystallization of Po from an Fe-S-O liquid coincides with a rise in the fO_2 of the Po + liquid mixture, with O being lost and

subsequently incorporated into surrounding silicate minerals (Naldrett 1969). As previously noted, all the 830–890 OB occur along the margins of the offset in contact with the surrounding country rock (*810-type*), while the 100 OB occurs in the center of the offset (*120-type*; Cochrane 1984). Thus, the high modal content of Mgt in the 100 OB and its near-absence in the 830–890 OB may be related to their proximity to the country rock, which could have removed oxygen from the cooling sulfide melt and inhibited the crystallization of Mgt. While the presence of Mag is an important indicator of changes to the fO_2 conditions during cooling, these conditions become relevant when considering the effect that O may have had on the Po that was forming.

In an attempt to resolve conflicts in the literature regarding the occurrence of natural Po, the accepted phase diagram for the Fe-S system, and to characterize a specific OB, Graham *et al.* (1987) performed a series of experiments to determine whether O could be present in Po. Using data obtained by nuclear microprobe, these authors concluded that it could be present, with concentrations up to 0.35% in NC Po and

up to 1.6% in 4C Po (Graham & McKenzie 1987). These authors also suggested that the presence of O in Po could inhibit the kinetic conversion of NC to 4C Po by inhibiting the ordering of Fe and vacancies within the Po structure (Graham *et al.* 1987). The important implication of this suggestion is that the presence of O could play an important role in stabilizing NC Po beyond its normal range.

Whereas the analysis of minerals for O by standard means (*e.g.*, electron microprobe analysis) is neither routine nor straightforward, evidence for elevated O in the environment of formation can be alluded to through an examination of the associated mineral assemblage. While the silicate mineral assemblage in all the orebodies examined in this study is relatively similar and constant, the oxide mineral component is not. If one considers the elevated concentration of Mgt *versus* Ilm in the 100 OB, then it suggests that the 100 OB may have developed under conditions of higher f_{O_2} than the other OB. In light of the results presented by Graham *et al.* (1987), the implication is that the elevated NC:4C Po ratio in the 100 OB is a function of an enhanced f_{O_2} at the time of formation. Further work is necessary to test this hypothesis, both in terms of determination of the O concentration present in both NC and 4C Po and whether other OB within the CCOD and other related environments show evidence for the same trends.

CONCLUSIONS

Rietveld analysis of PXRD data is shown to be a viable method for determining the modal abundances of NC and 4C Po. Results from Rietveld analyses agree well with those from image analysis techniques. Rietveld data from multiple aliquots of the same sample imply a high accuracy in the reproducibility of the technique. It should therefore be considered as a methodology to augment geochemical whole-rock data or textural data collected *via* optical or scanning electron microscopy for the CCOD.

Results from Rietveld analyses give average NC:4C Po ratios for the 830–890 OB of 0.19–0.24, whereas for the 100 OB, an average ratio of 0.77 was determined. The 100 OB was found to have the highest NC:4C Po ratios.

The NC:4C Po ratio is independent of depth for the levels sampled at the CCOD.

There were virtually no trends observed between the abundance, textures, or composition of associated mineralogy and the observed NC:4C Po ratio, with the exception of the presence of Mag in the 100 OB, which also contains the highest abundance of NC Po.

Micro-analytical SEM-EDS and LA-ICP-MS chemical analyses indicate a complete overlap in

compositions between NC and 4C Po in terms of their major, minor, and trace element data. Thus differences in these components cannot explain the stabilization of NC Po.

Both polymorphs are slightly metal-deficient relative to the ideal 4C Po formula of Fe_7S_8 , with the average Fe:S normalized composition being $Fe_{6.88}S_8$ for 4C Po and $Fe_{6.91}S_8$ for NC Po.

The data show that there is no significant difference in Ni content between NC and 4C Po (0.80 and 0.84 wt.% Ni, respectively), and so it was concluded that Ni is not a factor in the stabilization of NC Po. To date, phase diagrams relating to the polymorphs of Po are based on experiments within the Fe–S system. While this gives a general idea of the polymorphs that can occur together, along with their temperature and chemical characteristics, these diagrams are inadequate when evaluating Po with Ni in solid-solution with Fe.

There is a higher abundance of Mgt present in the 100 OB relative to the 830–890 OB. This may be related to differences involving the *120-* and *810-type* OB settings and the proximity of the ore relative to the intruded country rocks. The increased magnetic susceptibility in the core of the 100 OB is most likely associated with increased abundances of Mgt.

The NC Po may have been stabilized from higher temperatures because of the presence of low concentrations of oxygen. This could have inhibited the atomic movements of Fe and the ordering of vacancies during cooling, stabilizing NC Po and preventing the conversion to 4C Po in the 100 OB. The presence of oxygen in the system is indicated by the presence of Mag and lack of Ilm in the 100 OB, compared to the opposite pairing that has been observed in the 830–890 OB.

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This paper is dedicated to the memory of the late, great Dr. John Jambor, an inspirational researcher who saw the merits and strengths of applying mineralogy to solve real-world, geologically based problems. His approach to applied mineralogy, which to a certain extent provided the framework for this particular contribution, will inspire generations of mineralogists to come.

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REFERENCES

- ABRAMOFF, M.D., MAGALHÃES, P.J., & RAM, S.J. (2004) Image Processing with Image. *Biophotonics International* **11**(7), 36–42.
- AMES, D.E. & FARROW, C.E.G. (2007) Metallogeny of the Sudbury mining camp, Ontario. In *Mineral Deposits of Canada: A Synthesis of Major Deposit-Types, District Metallogeny, the Evolution of Geological Provinces, and Exploration Methods* (W.D. Goodfellow, ed.). *Geological Association of Canada, Mineral Deposits Division, Special Publication* **5**, 329–350.
- ARMBRUSTER, T., GEIGER, C.A., & LAGER, G.A. (1992) Single-crystal X-ray structure study of synthetic pyrope almandine garnets at 100 and 293K. *American Mineralogist* **77**, 512–521.
- ARNOLD, R.G. (1967) Range in composition and structure of 82 natural terrestrial pyrrhotites. *Canadian Mineralogist* **9**, 31–50.
- BAILEY, J., McDONALD, A.M., & LAFRANCE, B. (2006) Variations in Ni content in sheared magmatic sulfide ore at the Thayer Lindsley mine, Sudbury, Ontario. *Canadian Mineralogist* **44**, 1063–1077.
- BATT, A.P. (1972) Nickel distribution in hexagonal and monoclinic pyrrhotite. *Canadian Mineralogist* **11**, 892–897.
- BECKER, M. (2009) *The mineralogy and crystallography of pyrrhotite from selected nickel and PGE ore deposits and its effect on flotation performance*. Ph.D. Thesis, University of Pretoria, Pretoria, South Africa.
- BECKER, M., DE VILLIERS, J., & BRADSHAW, D. (2010) The mineralogy and crystallography of pyrrhotite from selected nickel and PGE ore deposits. *Economic Geology* **105**, 1025–1037.
- BELZILE, N., CHEN, Y.W., CAI, M.F., & LI, Y. (2004) A review of pyrrhotite oxidation. *Journal of Geochemical Exploration* **84**, 65–76.
- BLASI, A., DE POL BLASI, C., & ZANAZZI, P.F. (1987) A re-examination of the Pellotsalo microcline: Mineralogical implications and genetic considerations. *Canadian Mineralogist* **25**, 527–537.
- BOHLEN, S.R., PEACOR, D.R., & ESSENE, E.J. (1980) Crystal chemistry of a metamorphic biotite and its significance in water barometry. *American Mineralogist* **65**, 55–62.
- BRIGATTI, M.F., FRIGIERI, P., & POPPI, L. (1998) Crystal chemistry of Mg-, Fe-bearing muscovites – 2M1. *American Mineralogist* **83**, 775–785.
- COCHRANE, L.B. (1984) Ore deposits of the Copper Cliff Offset Dike. *Ontario Geological Survey Special Volume* **1**, 347–359.
- DEER, W.A., HOWIE, R.A., & ZUSSMAN, J. (1992) *An introduction to rock-forming minerals* (2nd ed.). Addison Wesley Longman Limited, Essex, England, 696 pp.
- DE VILLIERS, J.P.R. & LILES, D.C. (2010) The crystal-structure and vacancy distribution in 6C pyrrhotite. *American Mineralogist* **95**, 148–152.
- DE VILLIERS, J.P.R., LILES, D.C., & BECKER, M. (2009) The crystal structure of a naturally occurring 5C pyrrhotite from Sudbury, its chemistry and vacancy distribution. *American Mineralogist* **94**, 1405–1410.
- ELLIOT, A.D. (2010) Structure of pyrrhotite 5C (Fe₉S₁₀). *Acta Crystallographica* **66**, 271–279.
- ERD, R.C., EVANS, H.T., JR., & RICHTER, D.H. (1957) Smythite, a new iron sulfide, and associated pyrrhotite from Indiana. *American Mineralogist* **42**, 309–333.
- FARROW, C.E.G. & LIGHTFOOT, P.C. (2002) Sudbury PGE revisited: Toward an integrated model. In *The geology, geochemistry, mineralogy and mineral beneficiation of Platinum-Group Elements* (L.J. Cabri, ed.). Canadian Institute of Mining and Metallurgy and Petroleum Special Volume **54**, Montreal, Quebec, Canada (273–297).
- FERROW, E., ADETUNJI, J., & NKOMA, J.S. (2006) Characterization of pyrrhotite in Cu-Ni-ore bodies from mines in Botswana by Mössbauer spectroscopy, X-Ray diffraction, and thermomagnetometry. *European Journal of Mineralogy* **18**, 653–664.
- FINGER, L.W. & OHASHI, Y. (1976) The thermal expansion of diopside to 800°C and a refinement of the crystal structure at 700°C. *American Mineralogist* **61**, 303–310.
- FINKLEA, S.L., CATHEY, L., & AMMA, E.L. (1976) Investigation of the bonding mechanism in pyrite using the Mössbauer effect and X-ray crystallography. *Acta Crystallographica* **32**, 529–537.
- FLEET, M.E. (1981) The structure of magnetite. *Acta Crystallographica* **37**, 917–920.
- GAULD, C.M.B. (1999) *Characterisation of sulphides from the Inco WD-16 Ni-Cu sulphide deposit, Wisner township, District of Sudbury, Ontario, Canada*. M.Sc. Thesis, Laurentian University, Sudbury, Canada.
- GOLIGHTLY, J.P. & ROUSELL, D.H. (2000) Nature and origin of the Sudbury Structure, Canada and the Ni-Cu-PGE ores. In *Symposium Proceedings, Geology and Ore Deposits 2000: The Great Basin and Beyond*. Geological Survey of Nevada, Reno/Sparks, Nevada, United States (37–60).
- GRAHAM, J. & MCKENZIE, A.D. (1987) Oxygen in pyrrhotite: 2. Determination of oxygen in natural pyrrhotites. *American Mineralogist* **72**, 605–609.
- GRAHAM, J., BENNETT, C.E.G., & VAN RIESSEN, A. (1987) Oxygen in pyrrhotite: 1. Thermomagnetic behaviours and

- annealing of pyrrhotites containing small quantities of oxygen. *American Mineralogist* **72**, 599–604.
- GRANT, R.W. & BITE, A. (1984) Sudbury quartz diorite offset dikes. *Ontario Geological Survey, Special Volume* **1**, 275–301.
- GU, LIANXING & VOKES, F.M. (1996) Intergrowths of hexagonal and monoclinic pyrrhotites in some sulphide ores from Norway. *Mineralogical Magazine* **60**, 303–316.
- GUGGENHEIM, S. & EGGLETON, R.A. (1994) Stilpnomelane and parsettensite: A distance least squares (DLS) study. *American Mineralogist* **79**, 438–442.
- HALL, S.R. & STEWART, J.M. (1973) The crystal structure refinement of chalcopyrite, CuFeS_2 . *Acta Crystallographica* **29**, 579–585.
- HAWLEY, J.E. (1962) The Sudbury ores: Their mineralogy and origin. *Canadian Mineralogist* **7**, 146–207.
- HAZEN, R.M., FINGER, L.W., HEMLEY, R.J., & MAO, H.K. (1989) High-pressure crystal chemistry and amorphization of alpha quartz. *Solid State Communications* **72**, 507–511.
- HEINEMANN, R., KROLL, H., KIRFEL, A., & BARBIER, B. (2006) Order and anti-order in olivine I: Structural response to temperature. *European Journal of Mineralogy* **18**, 673–689.
- HUMINICKI, M.A.E. (2003) *Geology, mineralogy, and geochemistry of the Kelly Lake Ni-Cu-PGE deposit, Sudbury, Ontario*. M.Sc. Thesis, Sudbury, Canada, Laurentian University.
- HUMINICKI, M.A.E., SYLVESTER, P.J., CABRI, L.J., LESHER, C.M., & TUBRETT, M. (2005) Quantitative mass balance of Platinum Group Elements in the Kelly Lake Ni-Cu-PGE deposit, Copper Cliff Offset Dike, Sudbury. *Economic Geology* **100**, 1631–1646.
- JOCHUM, K.P., WILLBOLD, M., RACZEK, I., STOLL, B., & HERWIG, K. (2005) Chemical Characterisation of the USGS Reference Glasses GSA-1G, GSC-1G, GSD-1G, GSE-1G, BCR-2G, BHVO-2G and BIR-1G Using EPMA, ID-TIMS, ID-ICP-MS and LA-ICP-MS. *Geostandards and Geanalytical Research* **29**, 285–302.
- KISSIN, S.A. & SCOTT, S.D. (1982) Phase relations involving pyrrhotite below 350°C. *Economic Geology* **77**, 1739–1754.
- KONTY, A., DE WALL, H., SHARP, T.G., & POSFAI, M. (2000) Mineralogy and magnetic behavior of pyrrhotite from a 260 °C section at the KTB drilling site, Germany. *American Mineralogist* **85**, 1416–1427.
- KROGH, T.E., DAVIS, D.W., & CORFU, F. (1984) Precise U-Pb zircon and baddeleyite ages for the Sudbury area. *Ontario Geological Survey, Special Volume* **1**, 431–446.
- KVICK, Å., PLUTH, J.J., RICHARDSON, J.W., JR., & SMITH, J.V. (1988) The ferric ion distribution and hydrogen bonding in epidote: A neutron diffraction study at 15K. *Acta Crystallographica* **44**, 351–355.
- LAND, L.S. (1980) The isotopic and trace element geochemistry of dolomite: The state of the art. *SEPM Special Publication* **28**, 87–110.
- LI, F. & FRANZEN, H.F. (1996) Ordering, incommensuration, and phase transitions in pyrrhotite: Part 2: A high-temperature X-Ray powder diffraction and thermomagnetic study. *Journal of Solid State Chemistry* **126**, 108–120.
- LILES, D.C. & DE VILLIERS, J.P.R. (2012) Redetermination of the structure of 5C pyrrhotite at low temperature and at room temperature. *American Mineralogist* **97**, 257–261.
- LUSK, J., SCOTT, S.D., & FORD, C.E. (1993) Phase relations in the Fe-Zn-S system to 5 kbars and temperature between 325°C and 150°C. *Economic Geology* **88**, 1880–1903.
- MACKIE, P.E. & YOUNG, R.A. (1974) Fluorine-chlorine interaction in fluor-chlorapatite. *Journal of Solid State Chemistry* **11**, 319–329.
- MAGYAROSI, Z., WATKINSON, D.H., & JONES, P.C. (2002) Mineralogy of Ni-Cu-platinum-group element sulfide ore in the 800 and 810 orebodies, Copper Cliff South Mine, and P-T-X conditions during the formation of platinum-group minerals. *Economic Geology* **97**, 1471–1486.
- MORRISON, G.G., JAGO, B.C., & WHITE, T.L. (1994) Footwall mineralization of the Sudbury Igneous Complex. *Ontario Geological Survey, Special Volume* **5**, 57–64.
- MOURRE, G.A. (2000) *Geological relationships at discontinuities in the Copper Cliff quartz diorite offset: An investigation into offset dikes and their relationship to the Sudbury Igneous Complex, Ontario*. M.Sc. Thesis, Laurentian University, Sudbury, Canada.
- NALDRETT, A.J. (1969) A portion of the system Fe-S-O between 900 and 1080°C and its application to ore magmas. *Journal of Petrology* **10**, 171–201.
- NALDRETT, A.J. (1984) Mineralogy and composition of the Sudbury ores. *Ontario Geological Survey, Special Volume* **1**, 309–325.
- NALDRETT, A.J., HEWINS, R.H., DRESSLER, B.O., & RAO, B.V. (1984) The contact sublayer of the Sudbury Igneous Complex. *Ontario Geological Survey, Special Volume* **1**, 253–274.
- NALDRETT, A.J., ASIF, M., SCHANDL, E., SEARCY, T., MORRISON, G.G., BINNEY, W.P., & MOORE, C. (1999) Platinum-group elements in the Sudbury ores: Significance with respect to the origin of different ore zones and to the exploration for footwall ores. *Economic Geology* **94**, 185–210.
- PEARCE, N.J.G., PERKINS, W.T., WESTGATE, J.A., GORTON, M.P., JACKSON, S.E., NEAL, C.R., & CHENERY, S.P. (1997) A compilation of new and published major and trace element data for NIST SRM 610 and NIST SRM 612

- glass reference materials. *Geostandards Newsletter* **21**, 115–144.
- PRATT, A.R., NEBITT, H.W., & MYCROFT, J.R. (1996) The increased reactivity of pyrrhotite and magnetite phases in sulphide mine tailings. *Journal of Geochemical Exploration* **56**, 1–11.
- PREWITT, C.T., SUENO, S., & PAPIKE, J. (1976) The crystal structures of high albite and monalbite at high temperatures. *American Mineralogist* **61**, 1213–1225.
- ROUSELL, D.H. (1984) Onwatin and Chelmsford Formations. *Ontario Geological Survey, Special Volume 1*, 211–219.
- ROUSELL, D.H., FEDOROWICH, J.S., & DRESSLER, B.O. (2003) Sudbury Breccia (Canada): a product of the 1850 Ma Sudbury Event and host to footwall Cu-Ni-PGE deposits. *Earth Science Reviews* **60**, 147–174.
- STANTON, R.L. (1972) *Ore Petrology*. McGraw-Hill, New York, New York, United States, 713 pp.
- SYLVESTER, P.J. (2001) A practical guide to platinum-group element analysis of sulphides by laser ablation ICPMS. In *Laser-Ablation – ICPMS in the Earth Sciences: Principles and Applications* (P. Sylvester, ed.). *Mineralogical Association of Canada, Short Course* **29**, 203–211.
- SYLVESTER, P.J., CABRI, L.J., TUBRETT, M.N., McMAHON, G., LAFLAMME, J.H.G., & PEREGOEDOVA, A. (2005) Synthesis and evaluation of a fused pyrrhotite standard reference material for platinum group element and gold analysis by laser ablation-ICPMS. In *10th International Platinum Symposium, Extended Abstracts* (T.O. Tormanen & T.T. Alapieti, eds.). Geological Survey of Finland, Finland (16–20).
- SZENTPÉTERI, K., WATKINSON, D.H., MOLNÁR, F., & JONES, P.C. (2002) Platinum-Group Elements-Co-Ni-Fe sulfarsenides and mineral paragenesis in Cu-Ni-Platinum-Group Element deposits, Copper Cliff North area, Sudbury, Canada. *Economic Geology* **97**, 1459–1470.
- TOKONAMI, M., NISHIGUCHI, K., & MORIMOTO, N. (1972) Crystal structure of a monoclinic pyrrhotite (Fe₇S₈). *American Mineralogist* **57**, 1066–1080.
- TSUKIMURA, K. & NAKAZAWA, H. (1984) Determination of Fe/Ni distribution in pentlandites. *Acta Crystallographica* **40**, 364–367.
- URUSOV, V.S., ZVER'KOVA, O.N., YAMNOVA, N.A., & POLOSIN, A.V. (1987) Complex refinement of the structure of actinolite. *Vestnik Moskovskogo Universiteta Geologiya* **42**, 43–53.
- VAUGHAN, D.J. & CRAIG, J.R. (1974) The crystal structure and magnetic properties of iron in the monosulfide solid solution of the Fe-Ni-S system. *American Mineralogist* **59**, 926–933.
- VAUGHAN, D.J., SCHWARZ, E.J., & OWENS, D.R. (1971) Pyrrhotites from the Strathcona Mine, Sudbury, Canada: A thermomagnetic and mineralogical study. *Economic Geology* **66**, 1131–1144.
- WANG, H. & SALVESON, I. (2005) A review on the mineral chemistry of the non-stoichiometric iron sulphide, Fe_{1-x}S (0 ≤ x ≤ 0.125): Polymorphs, phase relations and transitions, electronic and magnetic structures. *Phase Transitions* **78**, 547–567.
- WOODHEAD, J., HELLSTROM, J., HERGT, J., GREIG, A., & MAAS, R. (2007) Isotopic and elemental imaging of geological materials by laser ablation inductively coupled plasma mass spectrometry. *Journal of Geostandards and Geo-analytical Research* **31**, 331–343.
- YAMANAKA, T., KOMATSU, Y., & NOMORI, H. (2007) Electron density distribution of FeTiO₃ ilmenite under high pressure analyzed by MEM using single crystal diffraction intensities. *Physics and Chemistry of Minerals* **34**, 307–318.
- YOUNG, R.A. (1993) *The Rietveld Method*. International Union of Crystallography Monographs on Crystallography (Book 5). Oxford University Press, New York, New York, USA, 298 pp.
- YUND, R.A. & HALL, H.T. (1969) Hexagonal and monoclinic pyrrhotites. *Economic Geology* **64**, 420–423.
- ZHENG, H. & BAILEY, S.W. (1989) Structures of intergrowth triclinic and monoclinic IIb chlorites from Kenya. *Clays and Clay Minerals* **37**, 308–316.

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