Fluid-inclusion characteristics of hydrothermal Cu–Ni–PGE veins in granitic and metavolcanic rocks at the contact of the Little Stobie deposit, Sudbury, Canada

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Abstract

Cu- and precious-metal-enriched massive ore and veins occur at contacts of two Fe–Ni–Cu sulfide orebodies of the Little Stobie Mine, Sudbury, with metavolcanic rocks of the Elsie Mountain Formation, and the Murray granite. Veins contain chalcopyrite, pyrrhotite, pentlandite, platinum-group minerals, quartz, carbonate, chlorite, amphibole and other minerals. A granitic dike, resulting from partial re-melting of the Murray Granite, cuts back into the Sudbury Igneous Complex near Little Stobie Mine, and contains barren veinlets with similar mineralogy but no sulfides. Quartz from ore veins contains fluid inclusions that were trapped during several stages. Early high-temperature fluids (at least 180–270°C in orebody 1 and 280–350°C in orebody 2) were extremely saline and occur as polyphase, isolated and fracture-controlled inclusions with halite, sylvite, Fe–Mn-, as well as Pb–Ba-chloride daughter minerals and other unknown solids. Late secondary aqueous inclusions are not chloride-saturated; they were trapped at a minimum of 80–150°C. Their microthermometric behavior may be modeled in the CaCl₂–NaCl–H₂O system with salinity of 21–27 CaCl₂ equiv. wt.%. Very late secondary inclusions have either Ca-rich saline, or very dilute (about 1 equiv. wt.% NaCl) compositions and homogenization temperatures of 200–300°C. With the exception of these very late secondary inclusions, the association of CO₂–(CH₄)-rich inclusions with aqueous ones was usually observed. The density of these carbonic fluids decreased from early to late stages. Microthermometric data from barren veins are fundamentally different from those of early inclusions from orebodies; this implies that these heavy-metal-rich fluids were responsible for ore deposition in veins. The minimum pressure of entrapment for early fluids was 1800–2200 bars. Late Ca-rich brines were trapped at lower minimum pressure (200–900 bars). High-pressure data are in agreement with the estimated minimum paleodepth of crystallization of South Range ores. Later fluids were probably trapped during the uplift of orebodies and their host rocks. Comparison of data to other Cu–PGE–Au-rich ore of the Sudbury Structure suggests that the presence of CO₂-rich fluids in South Range deposits and their absence in North Range deposits may be related to different metamorphic histories. The high-temperature hydrothermal fluids were driven by the heat of the Sudbury Igneous Complex; these very saline fluids interacted with primary magmatic ores, remobilized metals and redeposited them along convenient structures such as fracture zones and breccias in and along various units near the footwall contact. The identification of such highly saline fluid inclusions with high heavy-metal content may be useful in
the exploration for Cu–PGE–Au-enriched, footwall vein-type ores in the Sudbury Structure. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Sudbury; Hydrothermal Ni–Cu–PGE ores; Heavy-metal rich fluid inclusions

1. Introduction

Magmatic Ni–Cu–platinum group element (PGE) ores result from liquid immiscibility between sulfide and silicate magmas (Naldrett, 1989); however, it is clear that hydrothermal processes also play a role in PGE and base-metal (especially Cu) enrichment in some magmatic ore deposits (Ballhaus and Stumpfl, 1986; Johan and Watkinson, 1987; Nyman et al., 1990; Watkinson, 1990; Farrow, 1994; Molnár et al., 1997).

The Sudbury Igneous Complex (SIC) in northern Ontario contains many Fe–Ni–Cu sulfide deposits along the contact of the layered magmatic body with footwall rocks. The magmatic-segregation origin of these massive sulfide orebodies in the Sublayer and Footwall Breccia to the Sudbury Igneous Complex is clear (Naldrett, 1989). Some deposits, enriched in Cu and precious metals near the footwall contacts, may be explained by fractional crystallization of sulfide magma (Ebel and Naldrett, 1996). However, there are also Cu–PGE–Au-enriched deposits in the footwall rocks (for example Strathcona Deep Copper Zone, McCreedy West Cu–Ni veins along the North Range and Lindsley 4b deposit along the South Range) that have hydrothermal wall-rock alteration selvages, and saline fluid inclusions occur in both silicate and sulfide minerals (Farrow, 1994; Watkinson, 1994; Molnár, 1997).

In addition to the massive Sublayer ores, the Little Stobie Mine along the South Range of the Sudbury Structure (Fig. 1) contains vein-type ores with hydrothermal alteration of enclosing footwall rocks and enhanced PGE content. The purpose of this study is to outline the temperature–pressure–composition characteristics of fluids trapped in inclusions in quartz from these veins at and near the contact of the Little Stobie orebodies with granitic and metavolcanic rocks, and in barren veins in the adjacent granitic rocks. These data are used to evaluate the possible role of fluids in enrichment of PGE in vein-type ores hosted by the footwall units of the Sudbury Igneous Complex.

2. Geology, mineralogy and sampling

The Sudbury Igneous Complex is located in a meteorite impact-related elliptical structure along the boundary of the Archean gneissic rocks of the Superior Province and Proterozoic metasedimentary–metavolcanic and granitic basement rocks of the Southern Province of the Canadian Shield. The layered sequence of the SIC is composed of norite, gabbro and granophyre from bottom to top, and is emplaced in impact-related breccia (Onaping Formation) and subsequently deposited sedimentary rocks (Onwatin and Chelmsford Formations). Radiometric data indicate a 1.85-Ga age of the emplacement of the igneous rocks (Krogh et al., 1984). Disseminated or massive Fe–Ni–Cu sulfide ores of the SIC occur in a discontinuous ‘sublayer’ around the basal contact of the norite with the basement rocks. Most magmatic deposits occur in breccias (Contact Sublayer, Footwall Breccia, Offset Sublayer) characterized by igneous matrices with mafic–ultramafic and felsic clasts. Footwall-type deposits are located in the basement units along both the North and South Ranges (Morrison et al., 1994). These are vein-like to massive bodies in brecciated zones of the footwall rocks with Cu and precious metal enrichment compared to ores at the basal contact of the SIC.

The North Range of the Sudbury Structure is essentially unmetamorphosed; however, the South Range shows evidences of faulting, folding as well as metamorphism locally up to the amphibolite facies (Bennett et al., 1992; Cowan and Schwerdtner, 1994). Metamorphism and deformation of the South Range may be related to the Penokean Orogeny (1.7–1.9 Ga; Card et al., 1984) or a slightly younger contractional orogeny (1.44–1.45 Ga; Fueten and Redmont, 1997).

The local geology and setting of the Little Stobie Mine, Sudbury Structure (Fig. 1), are described by Davis (1984). Geochemical data from Little Stobie Mine were presented by Hoffman et al. (1979). Two orebodies in differing settings (Fig. 1) comprise the mine: Orebody 1 is a typical Contact Sublayer de-
Fig. 1. Generalized underground plan and sections of orebodies at the Little Stobie Mine (after Davis, 1984). Samples from the mine are from the contact zone of the No. 1 Orebody at the 2000-ft level and No. 2 Orebody at the 980-ft level ramp and the 1600-ft level stope.
pos at the contact of SIC norite with Murray Granite (2.4 Ga) and metavolcanic rocks (greenstone) of the Elsie Mountain Formation (about 2.5 Ga; Krogh et al., 1984). Orebody 2, perpendicular to the attitude of the Sublayer, is entirely in the footwall rocks, enclosed by breccia at the greenstone–Murray Granite contact. The latter orebody is enriched in precious metals by a factor of at least two (Hoffman et al., 1979). Davis (1984) pointed out that distal stringers to each orebody are characteristically enriched in chalcopryte and precious metals with respect to the orebody in general.

Sulfide-bearing vein samples near the footwall contact with the Murray granite were collected in areas of Cu-enrichment of Sublayer ore from orebody No. 1 (LS92-1 and LS92-2 from the 2000-ft level; Fig. 1). The textural evidence of Cu-enrichment is manifested by the replacement of pyrrhotite by chalcopyrite in the Sublayer ore. Veins (1–10 cm thick) hosted by the granite are characterized by xenomorphic quartz grains intergrown with sulfides, predominantly chalcopyrite. Along the contacts of quartz and sulfide grains, chlorite–epidote–amphibole alteration assemblages are present. Granite shows silicification and K-feldspar metasomatic alteration along the veinlets.

The sulfide bearing veins (thickness up to 20 cm) cut metavolcanic rocks of the Elsie Mountain Formation along the contact of Orebody 2. These veins were sampled at the 980-ft level ramp (LS-2 and LS-6) and the 1600-ft level stope (LS-1, LS-3 and LS-4). Xenomorphic quartz grains as large as several centimeters are enclosed in or intergrown with sulfides. Quartz is often associated with ankerite, Fe-rich and Cl-bearing (up to 2.45 wt.% Cl) amphibole, and chlorite. In LS-6, zoned tourmaline is also abundant. The enclosing metavolcanic rocks have chlorite–actinolite alteration along the veinlets.

In addition to chalcopryte, pyrrhotite and pentlandite, the veins also contain sphalerite, galena, michenerite, merenskite, kotulskite and bismuth–telurides. The quartz–sulfide textural relationships suggest that quartz was precipitated earlier than and synchronously with sulfides.

Barren veins were sampled from outcrops of granitic dikes (1.85 Ga, Krogh et al., 1984) cutting quartz-rich norite, (LS-S, 1 km north of the mine) and quartz gabbro (LS-R, from a roadcut 2.5 km northeast of the mine). These 2–5 cm thick veins have interlocking grains of xenomorphic quartz with K-feldspar, chlorite, sericite and calcite. No sulfide minerals were found in this paragenesis. The precipitation of barren veins post-dates the intrusion of the Sudbury Igneous Complex; however, the sulfide-rich veins occur exclusively below the norite (the lowermost unit of the SIC) and they do not cut the granophyre, quartz gabbro or norite.

3. Analytical methods

The fluid-inclusion study was carried out using a U.S.G.S. apparatus at Carleton University and on a Chaixmeca microthermochamber (Eötvös Loránd U.), both calibrated using phase changes in pure chemicals and synthetic fluid inclusions. Reproducibility of these measurements was 0.1°C at and below 0°C, and 2°C at 374°C. Analyses were carried out on 50–150 µm-thick, doubly polished sections of transparent minerals. Due to the complicated freezing behavior of inclusions, temperature cycling was used during the low temperature measurements. To study the chemical composition of daughter minerals in fluid inclusions, quartz grains were broken and immediately carbon-coated, then placed in the Jeol SEM, and analyzed using the Link eXL L24 instrument (Carleton U.). The details of analytical conditions were described by Farrow et al. (1994).

4. Fluid inclusion petrography

Quartz is characterized by abundant and relatively large fluid inclusions, whereas carbonates contain only a few populations of very small inclusions unsuitable for detailed microscopic and microthermometric investigations. Quartz contains four main, and several sub-types of fluid inclusions classified according to their phase proportions observed at room temperature (Fig. 2).

Type I: monophase aqueous inclusions. The absence of vapor at room temperature is related to either metastability (they occur with Type IIA aqueous inclusions and developed vapor during cooling) or to necking down of other inclusions (these latter inclusions may sometimes be characterized by an elongate tail and very irregular, angular shape).
Fig. 2. Types, abundance and mode of occurrence of fluid inclusions. Laq: aqueous liquid, V: vapor, LCO₂: CO₂ liquid, VCO₂: CO₂ vapor, SH: unknown daughter mineral, DF: degree of filling for aqueous inclusions (vol. liquid/vol. inclusion), DFC: degree of filling for carbonic inclusions (vol. CO₂ phases/vol. inclusion), N.O.: not observed, P: primary (single), S: secondary (hosted by fractures).

Type II: two-phase inclusions containing an aqueous phase and vapor. Based on the volume of the vapor bubble two subclasses were distinguished:

Type IIA: inclusions with 5–10 vol.% vapor (Fig. 3a), and Type IIB inclusions with 20–30 vol.% vapor.

Type III: polyphase inclusions containing aqueous + vapor + halite phases with or without additional...
Fig. 3. Photomicrographs of the most common type of inclusions. A—Type IIA, secondary inclusion, sample LS-3; B—Type IIIB, secondary inclusion with small sylvinite in addition to halite daughter mineral, sample LS-92-2; C—Type IIIC, single inclusion, sample LS-1. Note the difference in refractive index of daughter minerals; D—Type IIIE, secondary inclusion, sample LS-6. Note that halite is round in the presence of Fe–Mn chloride daughter mineral. E—Type IVA, secondary CO₂ inclusion without visible aqueous phase, sample LS-3; F—Type IVC secondary inclusion with halite in the aqueous phase, sample LS-3. The length of scale bar is 10 μm on each photomicrograph.
solid phases. Vapor usually occupies about 10–20 vol.% of the inclusion. Most solid phases dissolved during heating and are daughter minerals.

The chemical composition of solid phases was determined by SEM-EDS analyses carried out on opened fluid inclusions. Some phases which displayed anomalously low Cl-content in comparison to the sum of their cations may have experienced Cl-loss during analysis (Farrow, 1994) or partial oxidation after opening. The analytical results are semi-quantitative because (a) analyses were made on uneven surfaces of very small minerals in holes, (b) solid phases may be covered by a thin film of material quenched from liquid.

It is not possible to determine whether the SEM-EDS analyses were performed on isolated or fracture-related inclusions due to the lack of three-dimensional information. The analyzed phases are shown on Fig. 4. Na, K, Fe, Mn, Pb, Ba and C were the major metallic elements found in the solids. In some minerals, Ca and Mg were also detected. The anion is Cl in most cases, but S is more abundant than Cl in three minerals from LS-6 (phases 15, 19 and 20 on Fig. 4D and E). The sulfur-rich minerals also contain Fe and Cu and are probably chalcopyrite. Opaque minerals in polyphase inclusions were not observed under the polarizing microscope and their unusual presence found during SEM studies suggests that they are accidental and not daughter minerals.

In Cl-rich minerals, where Fe is the most abundant element, Mn is also present or vice versa. Pb and Ba occur together with Pb predominant. Na and K chlorides are usually poor in other elements. Ca is ubiquitously present as a minor constituent at concentrations below 2 wt.%; higher concentrations occurred only in Fe-chlorides of LS-6 (Fig. 4C and D). Some Ca-rich chlorides are round grains on the inclusion wall (Fig. 4C, grain 14) possibly due to deposition during opening of the inclusion. Mg occurs sporadically, mostly in Ca-bearing chlorides.

NaCl usually has a perfect cubic habit (Fig. 3B–C, Fig. 4F) in most Type III inclusions. Sylvite is always anhedral. Pb-rich chloride often forms bipyramidal or apparently rhombohedral weakly anisotropic crystals (Fig. 3D, Fig. 4H). PbCl₂ has orthorhombic–pseudohexagonal symmetry and BaCl₂ has the same crystal structure (Donnay and Ondik, 1973). The Fe–Mn rich chlorides in Type III inclusions have variable morphology and weak anisotropy. However, Fig. 3D, Fig. 4A and I clearly show their common acicular, hexagonal–prismatic appearance. Pure FeCl₃ (lawrencite) and MnCl₂ have trigonal symmetry (Donnay and Ondik, 1973), and their common occurrence in the same daughter mineral is compatible with this structural similarity. The presence of other cations in these phases may be related to deposition of chlorides on the surfaces of daughter minerals due to the evaporation of liquid during the opening of inclusions. In addition to the daughter minerals listed above an unknown solid phase composed of a fibrous, or granular mass of slightly anisotropic crystallites with intermediate refractive index (SH phase) was also observed in some inclusions with Fe–Mn and Pb–Ba chlorides.

In inclusions with acicular Fe–Mn-chloride daughter minerals, and rarely in inclusions with bipyramidal Pb–Ba chloride phases, a round isotropic phase with refractive index similar to halite cubes of other Type III inclusions was found (Fig. 3D). Round halite was observed during the SEM study (Fig. 4G, grain 25), and in petrographic study of unopened inclusions, confirming that this habit did not exclusively result from pressure-release on fracturing of quartz. Moreover, the crystal habit of halite may also be a function of the composition of the parent solution (e.g., in the presence of PbCl₂, octahedral faces appear on halite cubes); thus the modification of crystal morphology is expected in strongly saline heavy-metal-rich solutions. It was also observed that upon cooling after dissolution of daughter minerals, the previously round halite re-precipitated as cubes.

From the polarizing microscope and SEM study, five subclasses of Type III inclusions were determined according to their daughter mineral associations (see also Figs. 2 and 3B–D):

Type IIIA: liquid + vapor + halite (cubic).
Type IIIB: liquid + vapor + halite (cubic) + sylvite (anhedral).
Type IIIC: liquid + vapor + halite (cubic or round) + Pb-Ba chloride (anhexdral to bipyramidal or apparently rhombohedral morphology, slightly anisotropic, high refractive index).
Type IIID: liquid + vapor + halite (cubic or round) + Pb-Ba chloride + sylvite. SH phase with
Fig. 4. SEM photographs of opened fluid inclusions. A—sample LS-6, 1: Fe–Mn–(Na–Ca)–Cl, 2: calcite, 3: quartz; B—sample LS-6, 4: Na–(Pb–Mn–Ca–K)–Cl, 5: Mn–Fe–K–(Na–Ca)–Cl, 6: Pb–Ba–K–(Ca)–Cl, 7: Mn–(K–Fe–Ca–Na)–Cl, 8: Pb–Ba–K–(Na,Ca)–Cl, 9: Mn–(K–Fe–Ca–Na)–Cl; C—sample LS-6, 10: Fe–Mn–(Na–Ca)–Cl, 11: Fe–Ca–(Mn–Na–Mg–K)–Cl, 12: Fe–Ca–(Mn–Na–Mg–K), 13: Fe–Ca–(Mn–Mg–K–Na)–Cl, 14: Fe–Ca–(Na–Mn–Mg–K)–Cl, D—sample LS-6, 15: Fe–Cu–(Ca)–S–(Cl), 16: Fe–Ca–(Mn–Na–K)–Cl, 17: Fe–Na–Ca–(Mn–Pb–K)–Cl, 18: quartz; E—sample LS-6, 19: Cu–Fe–S–(Cl), 20: Cu–Fe–(Pb–Cu–Mg)–S–Cl; F—sample LS-1, 21: Na–Cl–(S), G—sample LS-1, 22: Pb–Ba–K–(Na)–Cl–(S), 23: Na–(Pb–Ba–K)–Cl, 24: K–(Na–Pb)–Cl, 25: Na–K–(Pb)–Cl, H—sample LS-4, 26: Pb–K–Cl, I—sample LS-4, 27: Fe–(Mn–Cu–Na–Ca)–Cl, 28: Fe–(Mn–Na–Ca)–Cl, 29: Fe–Na–Mn–(Ba–Pb–Ca)–Cl, 30: Na–(Fe–Pb–Ba–Mn–Ca)–Cl. The background mineral in all cases is quartz. The order of elements displays their relative abundance after substraction of Si and Al from the host mineral. Concentrations of elements in brackets are less than 2 wt.%. Numbers on scale bars are in micrometers.
unknown composition is also present in some
inclusions.

Type IIIE: liquid + vapor + halite (round) + Fe–
Mn chloride (acicular, slightly anisotropic, inter-
mediate refractive index) Pb–Ba chloride +
sylvite + SH.

A very few fracture-hosted inclusions of Type
IIIA, IIIB and IIIC from orebody No. 1 also contain
a red-brown flake (probably hematite).

Type IV: carbon dioxide-rich inclusions. Accord-
ing to the volume of the CO$_2$-phase and the presence
of other phases, the following subtypes were distin-
guished (Fig. 2):

Type IVA: CO$_2$-inclusions without visible aque-
ous phase (Fig. 3E).

Type IVB: inclusions with aqueous liquid and
liquid CO$_2$. The phase ratios are very variable
even along the same fracture.

Type IVC: inclusions with aqueous liquid + liquid
CO$_2$ + halite (Fig. 3F). In a few inclusions other
daughter minerals also occur. Phase ratios are also
variable.

Some Type IV inclusions may contain gas within
liquid CO$_2$ at room temperature depending on its
density.

The shapes of the inclusion types are highly
variable. Type IIA and Type IV inclusions most
commonly have round, negative crystal shapes. Their
greatest diameter is most typically less than 20 $\mu$m;
single Type IV inclusions may be larger. Type III
inclusions are usually large, attaining 50–80 $\mu$m,
and they are most commonly angular to round, some-
times with almost negative crystal shapes.

Almost all types of inclusions occur in all samples
(Fig. 2). Type I and IIA inclusions are ubiquitous in
all samples and they occur in fractures cutting quartz
grain boundaries. Type IIB inclusions are also sec-
ondary, but they were observed only from barren
veins (LS-S and LS-R), and from orebody No. 2
(LS-3 and LS-6). In barren veins, they occur in
fractures cutting the trails of Type IIA inclusions.
The shape of Type IIB inclusions is usually more
irregular than Type IIA inclusions.

Type IIIA inclusions occur in all samples, most
commonly along fractures cutting quartz grain
boundaries. In some Type IIA inclusion trails, these
inclusions also occur sporadically. Thus some Type
IIA inclusions probably have metastable phase com-
positions due to the lack of halite nucleation. This
interpretation is also supported by the precipitation
of halite in a few IIA inclusions during freezing.
Isolated Type IIIA inclusions were also observed and
they may be primary (Roedder, 1984). The mode of
occurrence of Type IIIB and IIIC is identical to Type
IIIA inclusions, but their abundance is less in most
samples. These inclusions with differing phase com-
positions may occur along the same fractures, and
the absence of solid phases other than halite may be
related to their metastable phase composition at room
temperature.

Type IIID and IIIE inclusions occur most com-
monly in isolation, and Type IIIE inclusions are
essentially restricted to orebody No. 2, although a
few were found in LS92-1 from orebody No. 1.
However, they also occur in fractures, but some of
these trails terminate in quartz grains. Crosscutting
relationships of trails of Type IIA and Type III
inclusions suggest that the two-phase inclusions were
trapped later.

Type IV (CO$_2$-rich) inclusions are less abundant
(Fig. 2), especially in orebody No. 1. In most sam-
ple they are isolated as well as fracture-hosted
inclusions. However, in LS-6 and LS-S, Type IVC
occurs only as isolated inclusions. Type IVA inclu-
sions were found only from orebody No. 2.

CO$_2$-rich inclusions with high variability in the
volume of the CO$_2$ phase occur together with Type
II or Type III inclusions in fractures. This suggests
that the observed volume ratios are the result of
inhomogeneous trapping and an unmixed CO$_2$ rich
phase existed at the time of entrapment (Diamond,
1994). Alternatively, the variation in the phase com-
position may also result from necking down; how-
ever, petrographic observations do not support this.
The presence of halite in some CO$_2$-rich inclusions
may also reflect the heterogeneity; miscibility of
CO$_2$ with highly saline solutions is very restricted
even at high T and P (Bowers and Helgeson, 1983;
Trommsdorff and Skippen, 1986).

The petrographic observations support the follow-
ing chronology of inclusion entrapment:
1. Isolated Type III and isolated Type IVA, B, and
   C inclusions.
2. Type III and Type IVA, B and C inclusions in the
   same fractures.
3. Type IIA, Type I (metastable or necked down)
and some Type IVA and IVB inclusions along fractures.
4. Type IIB inclusions in fractures.

5. Microthermometry

5.1. Heating runs

Fig. 5A shows the frequency distribution of homogenization temperatures measured in Type II inclusions; statistical evaluation of these data is in Table 1. In agreement with the observations on the degree of filling, Type IIB inclusions usually have higher homogenization temperatures (190–300°C) than Type IIA inclusions (60–210°C).

The vapor phase of Type III inclusions homogenized at a lower temperature than the dissolution of the last solid phase in most runs. During homogenization of polyphase inclusions the heating rate in the temperature range of daughter mineral dissolution was about 2–3°C/min. The dissolution of daughter minerals was reproducible with ±5°C confidence in verification measurements. The re-precipitation of daughter minerals was usually observed after cooling down to room temperature or several hours after their homogenization; halite was always the first phase to nucleate. The total homogenization of the relatively large fluid inclusions was not achieved in many runs due to leaking or decrepitation after homogenization of the vapor phase.

In Type IIIB, D and E inclusions, sylvite most commonly dissolved between 50 and 100°C during heating (Fig. 6). Homogenization of Pb–Ba-chloride took place in two temperature ranges: at about 100° and above 200°C. The unnamed SH phase in Type IIID inclusions dissolved at various temperatures. Acicular Fe–Mn chloride phases homogenized between 150 and 200°C in Type IIIE inclusions with a slight increase of dissolution temperature towards low total homogenization (Th halite) temperatures. The observed variation in the dissolution temperature of various daughter minerals probably reflects the effect of bulk composition on the solubility of the chloride phases or the occurrence of double salt formation (Linke, 1965; Roedder, 1984). The last homogenizing phase was halite in the vast majority of inclusions.

Halite homogenization temperatures from fracture-hosted Type III inclusions (Fig. 5B) group into two main ranges (220–370°C and 100–210°C). The high-temperature range is characteristic of both orebodies and barren veins, but the lower halite dissolution temperatures occur mostly in samples from orebodies.

Data from isolated (primary) inclusions differ between the two orebodies (Fig. 5C); those from orebody No. 2 have much higher halite homogenization temperatures (280–350°C) than those from orebody No. 1 (180–270°C). Data from barren veins are in both temperature ranges.

The high Th liquid (180–280°C)—high Th halite (240–350°C) data population occurs uniquely in single and fracture-hosted inclusions of orebody No. 2 (population ‘3’ of Fig. 7B). The other data of orebody No. 2 are from fracture-hosted inclusions. Population ‘2’ (Fig. 7B) is mainly composed of Type IIIA inclusions. A similar population (‘2’ in Fig. 7A) may be recognized from orebody No. 1. However, most isolated and fracture-hosted inclusions of this orebody form population ‘1’ (Fig. 7A). This population with Th liquid data of 140–210°C and Th halite data 170–300°C differs from data of Type III inclusions in orebody No. 2 and in the barren veins (Fig. 7C), although some overlap occurs. Most inclusions from barren veins show similar Th liquid–Th halite data pairs to inclusion population ‘4’ detected in orebody No. 2.

Total homogenization of Type IVB and Type IVC inclusions was never achieved due to decrepitation above 200–250°C.

5.2. Freezing data and composition of inclusions

5.2.1. Type II inclusions

Freezing data for Type II inclusions are summarized in Table 1. Type IIA inclusions froze at about −80°C. At the temperature of freezing, inclusions became ‘hazy’ brown. Eutectic melting with clearly visible liquid occurred between −68 and −52°C. Above the eutectic temperature the remaining solids were still ‘hazy’ but further rapid melting and subsequent ‘clearing’ of color occurred between −50 and −40°C in many inclusions. This ‘clearing’ was reproducible with about ±2°C confidence. In one inclusion, temperature cycling in this range caused...
the growth of a small, birefringent phase which melted at $-45^\circ$C. In inclusions with very low ice-melting temperatures, the ‘clearing’ was not observed and these inclusions had large amounts of liquid with a few round ice grains after eutectic melting between $-55$ and $-65^\circ$C.

The melting of ice in Type IIA inclusions took place between $-50$ and $-10^\circ$C with average values between $-22.3$ and $-31.7^\circ$C in samples from orebody No. 1, between $-31.4$ and $-34.6^\circ$C in samples from orebody No. 2 and $-28.7^\circ$C in samples from barren veins (Table 1).
Table 1
Microthermometric data for Type II inclusions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Inclusion type</th>
<th>Th (°C) n Mean s.d.</th>
<th>Te (°C) n Mean s.d.</th>
<th>Tc (°C) n Mean s.d.</th>
<th>Tm ice (°C) n Mean s.d.</th>
<th>Salinity mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>LS-1</td>
<td>IIA</td>
<td>9 136.3 25.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LS-2</td>
<td>IIA</td>
<td>12 102.5 27.7</td>
<td>3 -56.0 3.6</td>
<td>3 -44.0 2.7</td>
<td>7 -22.3 10.8</td>
<td>21.7 (Ca)</td>
</tr>
<tr>
<td>LS-3</td>
<td>IIA</td>
<td>23 102.8 26.4</td>
<td>3 -52.5 2.5</td>
<td>-</td>
<td>-</td>
<td>4 -24.7 0.5</td>
</tr>
<tr>
<td>IIB</td>
<td></td>
<td>17 267.6 23.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6 -0.7 0.7</td>
</tr>
<tr>
<td>LS-4</td>
<td>IIA</td>
<td>15 162.1 52.6</td>
<td>8 -59.7 4.0</td>
<td>6 -48.9 2.1</td>
<td>13 -31.7 5.4</td>
<td>25.4 (Ca)</td>
</tr>
<tr>
<td>LS-6</td>
<td>IIA</td>
<td>11 125.1 43.5</td>
<td>7 -58.9 5.9</td>
<td>7 -44.4 2.9</td>
<td>7 -23.4 4.5</td>
<td>22.2 (Ca)</td>
</tr>
<tr>
<td>LS92-1</td>
<td>IIA</td>
<td>11 110.1 22.2</td>
<td>2 -62.5 -</td>
<td>1 -40.0 -</td>
<td>2 -31.4 -</td>
<td>25.3 (Ca)</td>
</tr>
<tr>
<td>LS92-2</td>
<td>IIA</td>
<td>7 125.6 28.5</td>
<td>4 -59.3 2.8</td>
<td>3 -48.7 2.3</td>
<td>3 -34.6 1.3</td>
<td>26.4 (Ca)</td>
</tr>
<tr>
<td>LS-S</td>
<td>IIA</td>
<td>4 119.1 26.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LS-R</td>
<td>IIA</td>
<td>5 144.1 39.5</td>
<td>4 -65.5 1.6</td>
<td>4 -43.9 1.9</td>
<td>4 -28.7 3.1</td>
<td>24.4 (Ca)</td>
</tr>
<tr>
<td>IIB</td>
<td></td>
<td>5 208.1 8.7</td>
<td>2 -63.2 -</td>
<td>2 -48.3 -</td>
<td>2 -28.9 -</td>
<td>24.4 (Ca)</td>
</tr>
</tbody>
</table>

Th—homogenization temperature of the vapor phase; Te—eutectic melting; Tc—coticect melting of hydrohalite; Tm ice—melting temperature of ice; n—number of measurements; s.d.—standard deviation; (Ca) salinity in CaCl₂ equiv. wt.%; (Na) salinity in NaCl equiv. wt.%.

The freezing behavior of Type IIA inclusions may be interpreted in the NaCl-CaCl₂-H₂O system (Crawford, 1981; Shepherd et al., 1985; Haynes, 1985; Vanko et al., 1988; Oakes et al., 1990; Schiffries, 1990). The eutectic temperature of the ternary system is −52°C where antarcticite (CaCl₂·6H₂O) melts in the presence of hydrohalite, ice, liquid and vapor; the observed lower temperatures

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**Type III inclusions**

Fig. 6. Dissolution temperatures of various solid phases (Th solid) as a function of halite melting temperatures (Th halite) in Type III inclusions.
Fig. 7. Distribution of halite dissolution temperatures ($T_h$) as a function of homogenization temperatures of the vapor phase ($T_h$). The differences among various populations may be related to the differences in chemical composition of inclusion liquids influencing halite dissolution temperatures.

may correspond to metastable melting or recrystallization of the CaCl$_2$·4H$_2$O phase (Davis et al., 1990). Above the eutectic temperature, hydrohalite, ice, liquid and vapor may coexist and if the last melting phase is ice, hydrohalite melting temperatures are related to the NaCl/(NaCl + CaCl$_2$) ratio of liquid. Melting of a birefringent phase at $-45^\circ$C in one inclusion and the reproducible ‘clearing’ with increase in volume of liquid between $-40$ and $-50^\circ$C may correspond to cotectic melting of hydrohalite. Thus the NaCl/(NaCl + CaCl$_2$) ratios for these inclusions are less than 0.1 and the total salin-
ity may be calculated as $\text{CaCl}_2$ equiv. wt.% (Oakes et al., 1990). The calculated average salinity values of Type IIA inclusions are 21–27 $\text{CaCl}_2$ equiv. wt.% (Table 1).

In three freezing runs on LS-3, different melting paths were observed in Type IIA inclusions associated with Type IIIA inclusions along the same fracture. Eutectic melting took place in the same temperature range as in other Type IIA inclusions, but small birefringent phases remained after ice melting between $-21.8$ and $-23.8^\circ$C. Temperature cycling close to final melting of these phases resulted in single birefringent crystals with monoclinic habit indicative of hydrohalite. The reproducible melting of these phases was between $-6.9$ and $-13.9^\circ$C but it was not accompanied by precipitation of halite. This melting path may also be explained in the $\text{NaCl}–\text{CaCl}_2–\text{H}_2\text{O}$ system and it suggests that the composition of these inclusions is within the hydrohalite stability field, or that halite failed to nucleate during the melting of hydrohalite (Vanko et al., 1988). This latter statement is supported by the presence of halite in other inclusions associated with these peculiar ones along the same fracture. Thus these inclusions show metastable phase assemblages at room temperature and their salinity cannot be determined exactly.

Type IIB inclusions from LS-R had similar freezing behavior to Type IIA inclusions (Table 1). However in LS-3, Type IIB inclusions froze between $-40$ and $-50^\circ$C, initially melted above $-10^\circ$C with ice rapidly melting close to $0^\circ$C. This high-melting temperature indicates that these inclusions have very dilute fluids with about 1 NaCl equiv. wt.% salinity. Dilute KCl–H$_2$O, alkali–sulfate or alkali–bicarbonate–carbonate solutions may have this kind of freezing behavior (Shepherd et al., 1985).

5.2.2. Type III inclusions

Type III inclusions had very variable freezing behavior. In the vast majority, freezing was not achieved even by supercooling to $-180^\circ$C. This behavior is not uncommon in highly saline inclusions due to the sluggish nature of ice nucleation related to high viscosity of saturated liquids (Shepherd et al., 1985). Some fracture-hosted Type IIIA inclusions from LS92-2 developed small aggregates of acicular isotropic phases with low refractive index at the apices of halite during cooling. The freezing of these inclusions was also never achieved, and the newly formed phases melted in the same temperature range (at about 60°C) as did sylvite in Type IIIIB inclusions of this sample. This observation also suggests that the phase composition is metastable in some Type IIIA inclusions at room temperature.

When freezing was observed, it took place at about $-80$ to $-90^\circ$C in Type IIIA, IIIIB, IIIIC and some Type IIIID inclusions. The formation of ice was a relatively slow process starting from one point of the inclusion wall in some cases. After ice formation, the inclusion color became dark brown. The appearance of liquid was detected between $-54$ and $-78^\circ$C, with subsequent formation of hydrohalite in some cases. However, halite remained virtually intact in many inclusions, although some hydrohalite deposition was finally achieved by temperature cycling. Complete reaction of halite to hydrohalite was never achieved. Ice melting took place between $-20.8$ and $-45^\circ$C (Fig. 8), and metastable (non-reproducible) hydrohalite melting took place above 0.1°C. In inclusions with hydrohalite, rapid supercooling from a temperature close to hydrohalite melting resulted in the sudden appearance of ice at about the eutectic temperature.

Although SEM-EDS analyses proved that fluids of Type III inclusions are enriched in heavy-metals, freezing may also be explained by phase transitions known in the $\text{NaCl}–\text{CaCl}_2–\text{H}_2\text{O}$ system. The first melting temperatures are lower than the eutectic temperature of this system which may be related to metastable melting and/or recrystallization related to the presence of the metastable $\text{CaCl}_2·4\text{H}_2\text{O}$ phase.

Metastable behavior and the very complex composition of fluids did not permit the exact determination of salinity. Taking into account the halite melting temperatures, for inclusions in which hydrohalite was present at the melting of ice, salinity values (Vanko et al., 1988) are between 49.4 and 39.3 NaCl + CaCl$_2$ wt.% with NaCl/(NaCl + CaCl$_2$) ratios at about 0.5 for the lower values and between 0.65 and 1 for the higher values. However, these salinity data are only estimates due to the presence of other chloride species. Halite melting after homogenization of vapor also complicates the determination of exact salinity (Bodnar and Vityk, 1994).
Some Type IIID and IIIE inclusions froze between −30 and −60°C. Halite of these inclusions did not show observable resorption by, or transformation to, hydrohalite. After freezing, the inclusions remained clear, and the phase formed at freezing had yellowish–greenish anisotropy. During the formation and melting of the anisotropic phase, corrosion and redeposition of acicular Fe–Mn chloride was observed in some inclusions. A very small amount of liquid was formed between −20.5°C and −23.3°C in most runs, but between −30 and −35°C in two inclusions and at about −55°C in one inclusion. The anisotropic phase melted between +10 and +35°C (Fig. 8), and these melting temperatures were reproducible. Recooling before their final melting caused regrowth of phases without deposition of ice. During melting of this anisotropic phase, very small acicular crystallites appeared in five of these inclusions, and they dissolved between 66.5–68.2°C.

The melting behavior described above cannot be fully explained by the available data for chloride systems, but an attempt may be made considering low-temperature behavior in the Ca-rich part of the NaCl–CaCl₂–H₂O system. Schiffries (1990) described similar inclusions from the Bushveld Complex. His type-1 inclusions showed initial melting at about −35°C, with melting of antarcticite (CaCl₂ · 6H₂O) between +22 and +29°C. Melting between −20.5 and −23.3°C in the Little Stobie samples may correspond to the peritectic point at −22°C of the CaCl₂–NaCl–H₂O system, where antarcticite, halite, hydrohalite and liquid may coexist. Observed stable melting of the anisotropic phase well above 0°C may correspond to the melting of antarcticite. However, SEM-EDS analyses proved that Type IIIE inclusions are saturated with respect to Fe–Mn chlorides.

FeCl₃ and MnCl₂ have various hydrated phases. The eutectic temperature for FeCl₃–H₂O is −35°C (Linke, 1965). If the FeCl$_3$ content is more than 30.4 wt.%, FeCl$_3$ · 6H$_2$O may persist to +12.3°C. In a solution with very high salt content (above 38 wt.%) FeCl$_3$ · 4H$_2$O may be the stable phase to 76.5°C. In the MnCl₂–H₂O system the eutectic temperature is −5.6°C where ice, liquid and MnCl₂ · 6H₂O coexist (concentration = 30.4 wt.%). This hydrate is stable to −2°C, where it may convert to MnCl₂ · 4H₂O which is stable to 58°C in high salinity fluids. Both systems have other hydrated phases. These examples demonstrate that the observed phase transitions may also be explained by decomposition of these hydrates. However, the exact concentration of these
inclusions cannot be determined, due to the lack of data for the high-temperature solubility of halite in these very complex solutions.

5.2.3. Type IV inclusions

Type IVA as well as the CO$_2$ phase of IVB and IVC inclusions froze at about $-100^\circ$C. The melting of solid CO$_2$ occurred between $-61.3$ and $-56.6^\circ$C; average values are distributed between $-56.6$ and $-59.1^\circ$C (Table 2). The Tmelt CO$_2$ data for single IVA inclusions and for those which are associated with Type III inclusions along fractures are lower than data for CO$_2$ inclusions occurring together with Type IIA inclusions from orebody No. 2, and for IVB and IVC inclusions from barren veins.

Regarding the Th CO$_2$ L–V (L) values, Type IVA isolated inclusions also form a discrete group in comparison to Type IVA, IVB, and IVC inclusions occurring in fractures (Table 2). These latter inclusions have higher Th CO$_2$ L–V (L) values. Two Type IVA inclusions from LS-3 associated with Type IIA secondary inclusions revealed critical homogenization during the shrinkage of vapor phase at about $+29^\circ$C. Type IVB and IVC inclusions from barren veins are characterized by relatively high Th CO$_2$ L–V (L) data; these high values occur only in a very few inclusions from samples of orebody No. 2 (Table 2).

The slight depression of Tmelt CO$_2$ data from $-56.6^\circ$C indicates that these inclusions contain additional constituents (Burruss, 1981). Qualitative Raman studies (St. Kliment Ohridski U., Sofia, Microdil 28 equipment powered by a 30 mW Ar laser) on these inclusions revealed only methane, in addition to CO$_2$. Using the V–X diagrams of the CO$_2$–CH$_4$ system (Thiery et al., 1994), the freezing data for single Type IVA inclusions correspond to $X_{CH_4} = 0.05–0.11$ with molar volume of $46–50$ cm$^3$/mole; and for those which are associated with Type IIA inclusions, they are $X_{CH_4} = 0–0.19$ and $v = 49–55$ cm$^3$/mole in samples from orebody No. 2. Two inclusions in this latter group with critical homogenization lower than $31.1^\circ$C the critical temperature of CO had Tmelt CO$_2$ at $-56.6^\circ$C, thus the deviation from the critical temperature of CO$_2$ is probably related to the uncertainty of the observations during critical homogenization and not to the presence of other

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type of inclusion</th>
<th>Description</th>
<th>$n$</th>
<th>Tmelt CO$_2$ (°C) mean ± s.d.</th>
<th>$Tm_{CO_2,clath}$ (°C) mean ± s.d.</th>
<th>$Th_{CO_2}$ (°C) mean ± s.d.</th>
<th>$X_{CH_4}$ (min. – max.)</th>
<th>$v$ (cm$^3$/mole) (min. – max.)</th>
</tr>
</thead>
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<tr>
<td>Ore-body No. 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>LS-1 IVA</td>
<td>single (P)</td>
<td>2</td>
<td>$-59.0$</td>
<td>$-3.0$</td>
<td>0.08–0.1</td>
<td>48–49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IVA</td>
<td>in fractures with type III inclusions</td>
<td>20</td>
<td>$-58.2 ± 1.2$</td>
<td>$9.7 ± 7.2$</td>
<td>0.01–0.16</td>
<td>48–71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IVA</td>
<td>in fractures with type III inclusions</td>
<td>2</td>
<td>$-59.1$</td>
<td>$-8.5$</td>
<td>$8.3$</td>
<td>0.09</td>
<td>54–57</td>
<td></td>
</tr>
<tr>
<td>IVC</td>
<td>in fractures with type III inclusions</td>
<td>2</td>
<td>$-58.9$</td>
<td>$-9.2$</td>
<td>$12.8$</td>
<td>0.03–0.16</td>
<td>53–66</td>
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</tr>
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<td>LS-3 IVA</td>
<td>in fractures with type IIA inclusions</td>
<td>10</td>
<td>$-57.2 ± 1.4$</td>
<td>$6.8 ± 4.9$</td>
<td>0.0–0.19</td>
<td>49–55</td>
<td></td>
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<tr>
<td>IVA</td>
<td>in fractures with type IIA inclusions</td>
<td>2</td>
<td>$-56.6$</td>
<td>$28.9$ (C)</td>
<td>0.0</td>
<td>94</td>
<td></td>
<td></td>
</tr>
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<td>single (P)</td>
<td>8</td>
<td>$-59.0 ± 0.7$</td>
<td>$-8.4 ± 4.7$</td>
<td>0.05–0.11</td>
<td>46–50</td>
<td></td>
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<td>Barren veins</td>
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<td></td>
<td></td>
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<tr>
<td>LS-S IVC</td>
<td>single (P)</td>
<td>4</td>
<td>$-57.8 ± 0.2$</td>
<td>$12.5 ± 0.3$</td>
<td>$19.0 ± 9.6$</td>
<td>0.04–0.05</td>
<td>50–84</td>
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<tr>
<td>LS-R IVB</td>
<td>single (P)</td>
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<td>$-57.0$</td>
<td>$12.4$</td>
<td>$25.1$</td>
<td>0.02</td>
<td>64</td>
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</tr>
<tr>
<td>IVC</td>
<td>single (P)</td>
<td>1</td>
<td>$-56.8$</td>
<td>$11.1$</td>
<td>$26.4$</td>
<td>0.01</td>
<td>65</td>
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</tbody>
</table>

$n$—Number of measurements; Tmelt CO$_2$—melting temperature of CO$_2$; $Tm_{CO_2,clath}$—melting temperature of CO$_2$ clathrate; $Th_{CO_2}$—homogenization temperature of the CO$_2$ phase; $X_{CH_4}$—mole fraction of CH$_4$; $v$—molar volume of the carbonic phase; (C)—critical homogenization.
volatiles. These inclusions are considered to be pure CO2 fluids with critical molar volume (94 cm3/mole).

The CO2-rich phases of Type IVB and IVC inclusions associated with Type III inclusions from orebody No. 2 have compositions between those of single and fracture-hosted Type IVA inclusions. The CO2-rich phase of Type IVB and IVC inclusions from barren veins has very similar composition (with XCH4 = 0.01–0.05 and ν = 50–84 cm3/mole) to Type IVA inclusions associated with Type IIA inclusions from the ore veins.

The determination of an eutectic melting temperature of the aqueous phase in Type IVB and IVC inclusions was not possible due to melting and clathrate formation involving the CO2 phase. Average CO2-clathrate melting temperatures group between 8.5 and 12.7 °C (Table 2) corresponding to the very high salinity of the aqueous phase. The exact salinity cannot be calculated from these data due to the possibly heavy-metal rich composition of the aqueous phase and presence of methane in the carbonic phase. The CO2 clathrate at -10 °C corresponds to 24.3 NaCl equiv. wt.% concentration of the aqueous phase in the NaCl–CO2–H2O system or 22.6 CaCl2 equiv. wt.% in the CaCl2–CO2–H2O system (Darling, 1991; Bakker et al., 1996). The actual salinity of these inclusions may be higher due to the effect of methane content on clathrate melting temperatures.

6. Estimation of trapping conditions for fluid inclusions

Trapping of different inclusion generations took place in the immiscibility field of CO2-rich and aqueous solutions, as CO2-bearing inclusions with variable carbonic liquid/aqueous liquid volume ratios are associated with synchronously trapped aqueous inclusions. Inclusions trapping end member immiscible fluids should homogenize by dissolution of either phase at the same temperature, and the pressure in inclusions at the homogenization temperature equals the trapping pressure. In P–T space, the intersection of isochors for coevally trapped end member fluids is located at this unique point, which in turn is the same as the intersection of their solvus curves (Diamond, 1994).

Primary magmatic ores of the South Range were formed at a minimum depth of about 8 km (Souch et al., 1969; Hoffman et al., 1979) and were uplifted to their present position by about 5–6 km. Thus the minimum paleodepth of fluid migration processes recorded by fluid inclusions was 2–8 km. This depth corresponds to 550–2200 bars lithostatic pressure using 2.74 gm/cm2 average density for the rocks of the SIC and the Sudbury Basin (density data are from Megrah and Broome, 1994).

The available data for the H2O–NaCl–CO2 system show that the solubility of CO2 in aqueous saline liquid or solubility of saline liquid in CO2 is very restricted even at relatively high temperature as salinity increases in this pressure range (Bowers and Helgeson, 1983). Interpolating these data for the extremely saline fluids of this study, the aqueous part of the immiscible system may contain so little CO2 or the CO2-rich phase may dissolve so little aqueous solution that these phases may be undetected (or overlooked due to the deposition of various chloride hydrate phases in inclusions of this study) in inclusions trapped at a temperature about 300 °C. This is more pronounced at lower temperatures. The observation of the total homogenization of the CO2-poor saline inclusions is not a problem (‘normal’ homogenization by the disappearance of vapor bubble or halite) in these inclusion pairs, but detection of homogenization of CO2-rich inclusions (i.e., disappearance of a very thin aqueous film along the wall of inclusion) is improbable.

Assuming that Type IVA inclusions trapped the carbonic endmember and Type IIA and Type III inclusions in association with them trapped the aqueous endmember of the immiscible fluid system, microthermometric data can be used for the estimation of the minimum trapping pressure. This minimum pressure is determined by that pressure which corresponds to the homogenization temperature data for Type IIA and Type III inclusions along the isochors of coevally trapped Type IVA inclusions.

Fig. 9 shows isochors for CO2-rich inclusions. Most typical halite homogenization temperatures for isolated Type III inclusions from orebody No. 2 correspond to 1800–2200 bars minimum pressure along the isochore of isolated Type IVA inclusions.
Data for the same type, but fracture-hosted inclusions are 1400–2000 and 700–1200 bars. The minimum trapping pressure corresponding to the homogenization temperatures of Type IIA inclusions (sample LS-3) is 200–900 bars.

The range of minimum trapping pressures estimated for single Type III and IVA inclusions includes the upper minimum pressure limit calculated from the paleodepth data. The pressure data for very late, Type IIA secondary inclusions cluster around the lower minimum pressure limit calculated from the paleodepth data (Fig. 9). Marshall et al. (1999) also showed that inclusions with similar microthermometric data to Type IIA inclusions of this study were trapped under low pressure conditions (at about 950 bars) in veins postdating the deposition of Cu–Ni–PGE ores.

7. Discussion

High-temperature fluids trapped as polyphase inclusions in quartz associated with sulfides (inclusion population ‘1’ and ‘3’ on Fig. 7) exhibit different microthermometric behavior in comparison with barren veins in the vicinity of the Little Stobie Mine. The differences seen on Fig. 7 may reflect the differ-
ent chemical composition of inclusions, because halite solubility is strongly influenced by the presence of other cations (Linke, 1965; Roedder, 1984). However, there are differences in these data not only between orebodies and barren veins, but between veins at contacts of the two orebodies. Since these veins are hosted by different rock types at the two orebodies, the observed differences may be the result of water–rock interaction. Late fluids trapped as secondary fluid inclusions are present in both orebody contact zones (population ‘2’ on Fig. 7), and in orebody veins and barren veins (population ‘4’ on Fig. 4 and Type II inclusions). Therefore, fluids that may be responsible for sulfide-vein formation were those trapped as high-temperature, polyphase inclusions in samples from the orebodies (populations ‘1’ and ‘3’ on Fig. 7). Minimum trapping temperatures reflected by the Th halite data for these inclusions are between 180 and 350°C. This range is in agreement with the stable isotope thermometric data (230–340°C) from amphibole and epidote in association with quartz of similar veins from the Sudbury Structure (Marshall et al., 1999). Later, low-temperature fluids trapped in secondary inclusions were present regionally, and they probably did not play a role in the deposition of PGE enriched ore in veins. Marshall et al. (1999) showed that similar low-temperature inclusions of late veins postdating the deposition of Ni–Cu–PGE ores are related to neotectonic (5–13 Ma) fluid mobilization.

Fluid-inclusion microthermometric data indicate that some minerals in vein-type, Cu- and PGE-rich deposits in the North Range footwall were deposited from intermediate-temperature (130–440°C), highly saline fluids (Farrow and Watkinson, 1992; Li and Naldrett, 1993; Farrow, 1994). Molnár et al. (1997) have shown that similar fluids at similar temperatures were involved in disseminations and veins of Cu–PGE–Au ore enrichment at the contact of the Lindsdale 4b Mine of the South Range. SEM-EDS analyses on opened inclusions from quartz and sulfides from these deposits also revealed substantial amounts of heavy-metal phases (Pb, Fe, Mn, Ba). North Range fluid inclusion data differ from those of Lindsdale and Little Stobie only in the absence of CO₂-rich inclusions. In contrast to the North Range, South Range rocks were more strongly affected by the Penokean Orogeny (1.7–1.9 Ga; Card et al., 1984) that was penecontemporaneous with the emplacement of the SIC (1.85 Ga; Krogh et al., 1984). Therefore the presence of carbonic fluids along the South Range may indicate the incorporation of metamorphic fluids into the hydrothermal system.

The results of this study and data for other vein type ore show that hydrothermal activity involving highly saline and heavy-metal rich fluids was not uncommon in the footwall of the SIC. Areas of footwall rocks affected by these highly saline hot fluids are characterized by consistent wall-rock alteration assemblages with Cl-bearing amphibole, epidote, chlorite, stilpnomelane, K-feldspar and similar vein-filling mineral parageneses with PGE minerals (Farrow, 1994; Watkinson, 1994). These similarities suggest that hydrothermal processes responsible for wall rock alteration and deposition of vein-type ore had a common origin.

The relatively high temperatures (up to 350–400°C) in all hydrothermal environments examined in the Sudbury footwall units suggest that an appropriate heat source for the circulation of fluids existed. This source can not be of metamorphic origin related to the Penokean Orogeny that affected the South Range because North Range deposits also display similarly high temperatures. Moreover, Cl-bearing alteration minerals in contact with sulfides are not typical for metamorphosed magmatic–sulfide deposits of South Range (Watkinson, 1994), which also suggests that the hydrothermal activity was not exclusively generated by metamorphism. Therefore, it is reasonable to relate the circulation of hot fluids to the thermal effect of the large volume and complicated intrusive activity of the SIC.

The thermal effect of the SIC is expressed as a contact metamorphic aureole, 1–1.5 km wide, preserved along the North Range (Dressler, 1984). As well, near the Little Stobie Mine, a granite-dike swarm that cuts back into the SIC (Fig. 1) is interpreted to be the result of partial remelting of the Murray Granite by the SIC (Peredery and Morrison, 1984). Recent studies on the radiometric age of the hydrothermal alteration of the Onaping Formation that was invaded by the SIC also demonstrate that widespread hydrothermal activity took place in connection with SIC emplacement (Ames et al., 1998). These data imply that heat originating from the SIC penetratively affected the country rocks and could
have caused fluids to circulate. Convenient channels for fluid circulation were the brecciated zones along the contacts of the footwall units (e.g., the greenstone–granite contact at the Little Stobie Mine) or the fracture systems developed due to the emplacement of Sudbury Igneous Complex (1.85 Ga) and subsequent faulting and thrusting accompanying the pencontemporaneous Penokean Orogeny (1.9–1.7 Ga).

The source of these fluids is not clear. Fluid inclusion data from PGE-enriched sulfide pods or veins of the Bushveld Complex (Ballhaus and Stumpf, 1986) and from a shear-zone related PGE deposit at New Rambler, WY (Nyman et al., 1990) show that saline fluids similar to those found in the Little Stobie Mine were also present during the formation of these deposits. They are considered to be the result of fluid activity related to late stages of magmatic activity in the Bushveld (orthomagmatic–deuteric enrichment of PGE in pegmatoids) or fluid mobilization along shear zones at New Rambler. Farrow and Watkinson (1996) assumed that deposition of Cu-rich veins from the North Range of the Sudbury Structure was related to a magmatic–hydrothermal system, where saline fluids of possibly formational brine origin were circulated by the heat of the SIC.

Frape and Fritz (1982) suggested that modern, highly saline Ca-rich fluid in the Sudbury Structure was related to equilibration of formational fluid with Archean metamorphic rocks. The ubiquitous, secondary, Type IIA inclusions rich in divalent cations as reflected by their freezing behavior, and their possible trapping conditions, suggest a minimum 1–4 km depth with temperatures about 100 °C. If the geothermal gradient had averaged 3 °C/100 m in this area of the Canadian Shield during migration of these fluids it is reasonable to assume that they are the equivalents of the present-day, Ca-rich formational fluids. Low-density CO₂-rich fluid could be channeled into this system along deep faults related to thrusting and neotectonic activity. The late CO₂-rich fluids had different characteristics than do those of higher density which were associated with high-temperature, more saline solutions trapped as Type III inclusions. This association may indicate that the hydrothermal system had mixed magmatic and metamorphic components as is suggested by stable isotope data from the mineral assemblages of vein type ores (Marshall et al., 1999). However, the magmatic signature of these fluids may just reflect the isotopic composition of heated brines from the footwall having been significantly modified during interaction with magmatic sulfides and rocks. This interaction in the high-temperature regime of the SIC is reflected by the modification of primary ore textures (e.g., replacement of pyrrhotite by chalcopyrite) and resulted in enrichment in heavy-metal cations. Due to the increased amounts of these cations, fluids trapped in Type III high temperature inclusions have significantly different phase composition than do late secondary, low-temperature inclusions.

Saline fluids with high Cl-activity are convenient agents for mobilization not only of Fe, Cu, and Pb, but for precious metals, especially Pt and Pd (Wood and Mountain, 1992; Gammons et al., 1992). Thus, interaction of hot, highly saline fluids with primary magmatic ores could cause the remobilization and precipitation of metals in convenient structures such as stringers and veins penetrating the footwall leading to the deposition of vein type ore with high precious-metal grades.

8. Conclusions

Magmatic Fe–Ni–Cu–PGE sulfide deposition accompanied the emplacement of the Sudbury Sublayer, Footwall Breccia, and norite of the SIC. Some Cu–Ni–PGE–Au enrichment of typical Sudbury ore, and Cu-rich veins, in some cases with high contents of Pt, Pd, and Au, were subsequently generated in parts of the footwall. The characteristics of fluid inclusions in quartz-bearing rocks containing pyrrhotite and chalcopyrite as major minerals suggest that hydrothermal processes were involved in metal redistribution near the ore contact.

In orebodies of the Little Stobie Mine, high-temperature hydrothermal processes were outlined by fluid-inclusion studies. The temperature of early fluids was at least 280–350°C near the contact of orebody No. 2, and 180–270°C near orebody No. 1 on the basis of the total homogenization temperatures of isolated inclusions. These processes were followed by several lower-temperature fluid-migration stages, down to about 100°C. Compositional difference between early and late saline fluids is
reflected in the phase assemblages of fluid inclusions. High-temperature inclusions contain NaCl, KCl, Fe–Mn chloride, Pb–Ba chloride, as well as other daughter minerals, whereas late secondary inclusions are not saturated with heavy-metal chlorides. Exact salinities of early fluids cannot be determined due to the lack of the appropriate solubility data for chlorides in these multi-component systems. Late fluids were also saline (21–27 CaCl₂ equiv. wt.%). All inclusion generations were associated with unmixed CO₂-rich fluids; the latter contain minor methane. The density of these carbonic fluids decreased from early high-temperature stages to the late stages. The minimum pressure during the early stages was about 2 kbars, and in the late stages below 1 kbar. The origin of low-salinity (about 1 NaCl equiv. wt.%) and high-temperature (min. 200–300°C) fluids trapped in secondary fluid inclusions is not clear.

Although highly saline, high-temperature fluids were also found in the fluid inclusions from barren veins in the vicinity of the Little Stobie Mine, their microthermometric properties differ from those at the orebody contacts suggesting their different chemical composition.

The circulation of highly saline hot fluids was probably driven by intrusive activity of the SIC. The origin of CO₂ may be related to metamorphism and deformation accompanying the Penokean Orogeny. The North Range was less severely affected by this orogeny and was emplaced at shallower depth; hydrothermal quartz there does not have CO₂-rich inclusions detectable by microscopic methods.

The interaction of hot, saline fluids with primary magmatic ore could cause the mobilization of base and precious metals with subsequent deposition as sulfides in veins and stringers near the footwall contact. These processes occurred not only at the Little Stobie Mine, but at other places along the South and North Range. Areas where the activity of hydrothermal fluids is revealed by the presence of high-temperature, high-salinity fluids would be prospective targets in exploration for Cu + PGE-enriched vein-type ores.

The low-temperature, Ca-rich brines, as well as very dilute fluids trapped in late secondary inclusions did not play a role in the redistribution of base and precious metals.

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