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**PRESSURE, TEMPERATURE, COMPOSITION AND STATE
OF THE FLUID
DURING SILVER ARSENIDE VEIN FORMATION,
COBALT, ONTARIO**

by

Daniel D. Marshall, B.Sc

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of
Master of Science

Ottawa-Carleton Geoscience Centre

and

Department of Earth Sciences

Carleton University

Ottawa, Ontario

June 30, 1990

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The undersigned hereby recommend to
The Faculty of Graduate Studies and Research
acceptance of the thesis,

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for the degree of Master of Science

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June 30, 1993

ABSTRACT

Silver in the Cobalt mining camp occurs in calcite-quartz-arsenide veins that cross-cut Proterozoic metasediments, Archean metavolcanics and diabase sills. Pre-, syn- and post-ore fluid inclusions are found in hydrothermal axinite, calcite and quartz. Pre- and post-ore inclusions contain liquid + vapour + halite at room temperature and occur in assemblages of uniform phase ratios. These inclusions homogenize on the halite liquidus at 230-250°C, at pressures well above the liquid + vapour field. SIMS analysis yields Ca:Na:K ratios of approximately 5:2:1, in agreement with microthermometry and qualitative SEM-EDS measurements. Although the fluid was originally in equilibrium with calcite, CO₂ in the fluid inclusions is below Raman microprobe detection levels. The inclusions, with a constant bulk composition of approximately 10 mol% CaCl₂, 4 mol% NaCl, 2 mol% KCl and 84 mol% H₂O, were trapped from a homogeneous (one phase) vein fluid.

Syn-ore fluid inclusions consist of liquid + vapour at room temperature. Ice melts between -8 and -26°C, and the inclusions homogenize into the liquid over a range of temperatures up to 320 °C. The intersection of fluid inclusion isochores with the stability bounds for the vein mineral assemblages indicates vein- and ore-formation between 280-365 °C and 480-1500 bars.

Previous fluid inclusion studies of the Ag-transporting fluids identified boiling as a major control on ore precipitation. This study presents fluid inclusion evidence from the Siscoe, Beaver-Temiskaming and Silverfields Mines that contradicts the interpretation of boiling. These data suggest that ore precipitation occurred when the highly saline, Ag-bearing, pre-ore fluid mixed with a second, genetically unrelated, weakly saline fluid. Variable dilution upon mixing formed the syn-ore fluid, decreasing the solubility of the Ag-chloride complexes, resulting in precipitation of native silver.

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CHAPTER I: INTRODUCTION

Saline fluids in minerals from Cobalt were first described by Taylor (1970). Subsequent to the work of Taylor, little has been done to characterize the saline components, or to establish whether volatiles such as CO₂, CH₄, N₂ or H₂S were present in the system and perhaps responsible for the transport and deposition of the silver.

The aim of this study is to determine the pressure, temperature and composition of the ore-bearing fluids responsible for the native silver deposits in the Cobalt Silver Camp. The pressures and temperatures are derived from stable mineral assemblages within the vein and wall rock (Jambor, 1971) in equilibrium with a fluid, having the composition of the primary fluid inclusions within the minerals of the stable assemblages.

The identification of the complexing ligand of Ag will enable the modelling of silver vein formation in the Cobalt deposits. The transporting ligand may have been one (or more) of many possibilities, but at present solubility data are available for silver chloride complexes (Seward, 1976, Gupta, 1978), silver carbonate complexes (Kozlov, 1985), sulphide complexes AgHS, Ag(HS)⁻² and HAg(HS)₂ (Gammons and Barnes, 1989, Smith and Martell, 1976, Wood *et al.*, 1987 respectively), as well as Ag⁺ (Zotov *et al.*, 1986) and Ag⁰ (Zotov *et al.*, 1985).

Sulphide ligands may facilitate the transport of silver, as proposed by early authors and supported by the spatial association of the Archean sulphide units and

the silver veins (Nicols, 1988). On the other hand chloride ligands may be responsible for silver transport. An objective of this study is to use fluid inclusion data to assess each of these ligands as possible agents for transport of silver at Cobalt. Chloride and sulphide (in addition to the previously mentioned) ligands may also represent only a part of the complex geochemical system responsible for the silver deposits at Cobalt.

The samples used in this study were collected, during underground work, from the Beaver-Temiskaming, and Silverside mines. Additional samples from the Siscoe mine were supplied by the National Museum of Canada. The silver veins occurring within these three mines are hosted within the three major lithologies of the Cobalt camp (*ie* metavolcanic, metasedimentary rocks and diabase) and thus are considered representative of the area.

CHAPTER II: REGIONAL GEOLOGY

Introduction

The Cobalt area comprises the northeastern extremes of the Southern Geological Province (Wilson, 1986). The oldest rocks, the Archean rocks, are unconformably overlain by the rocks of the Huronian Supergroup. The 300 metre thick Nipissing Diabase has intruded both of the above rock types but generally follows the Archean-Huronian unconformity. The Archean and Proterozoic rocks are unconformably overlain by Silurian and Ordovician limestones and Pleistocene and Recent sediments. Figure 1 depicts the geologic relationships between the

Figure 1. Idealized geological cross section of the Precambrian rocks of the Cobalt area. The three rock types unlabelled are the Temiskaming sediments shown in the folded smaller conglomerate pattern, the Haileyburian dykes shown in the lined pattern and the Matachewan dykes shown in the closely spaced black dotted pattern. Silver veins are shown in black, schematically representing some of the observed associations of the veins to the different rock types.

major rock types of the Archeozoic and Proterozoic, and the minor units within these two eons.

Archean Metavolcanic and Metasedimentary Rocks

The volcanic rocks and associated interflow sediments are the oldest rocks in the Cobalt camp (Jambor, 1971). This unit is dominantly intermediate to mafic flows with some pyroclastic units and felsic volcanic rocks, minor interflow sediments with chert and sulphide minerals, iron formation and schists (Smyk, 1987). The Timiskaming-type lithic and feldspathic arenites, wackes and conglomerates unconformably overlie the volcanic rocks (Jambor, 1971). These rocks have been intruded by dykes and sills of lamprophyre, mafic and ultramafic rocks. The Archean rocks were metamorphosed to greenschist facies and folded isoclinally during the Kenoran Orogeny. Contemporaneous with the orogeny was the emplacement of the Algoman granites.

Proterozoic Sedimentary Rocks

The Coleman Member of the Gowganda Formation unconformably overlies the Archean rocks in the Cobalt area. The Coleman Member is predominantly conglomerate with sandstone and laminated siltstone (Scammel, 1984; Mustard, 1985; Rainbird, 1985) with a maximum thickness of 180 metres. The Coleman is conformably overlain by the Firstbrook Member of the Gowganda. The Firstbrook is a laminated siltstone with a maximum thickness of 610 metres (Jambor 1971).

The Lorrain Formation conformably overlies the Gowganda Formation. The maximum observed thickness of 320 metres (Jambor, 1971) is cut by an erosional surface; this thickness includes only the lower arkose unit and not the overlying quartz arenite that the lower unit grades into. The quoted thickness of 320 metres does not represent the true thickness of this unit.

Nipissing Diabase

The Nipissing Diabase has the bulk composition of an olivine tholeiite (Jambor 1971). It is mainly well differentiated sills (Hriskevich, 1968; Jambor, 1971) but dykes are documented (Andrews, 1986). The sills generally have shallow dips that define broad basin and dome structures (Petruk, 1971), although locally the diabase has been shown to follow preexisting faults (Thompson, 1967).

Textural and mineralogical zoning occur within the diabase (Hriskevich, 1968; Jambor, 1971). The lowest zone consists of a greenish chilled margin of 5 to 10 mm. This grades into the lower quartz diabase that is generally 15 to 30 metres thick. The quartz diabase grades into hypersthene diabase that may occupy up to two thirds of the thickness of the sill. The hypersthene diabase grades upwards into a variably textured diabase; this unit has variable grain size, and may be locally aplitic, granophyric or pegmatitic. The varied texture diabase is gradational into an upper quartz diabase that is generally not as thick as the lower unit. An upper chilled margin, with widths of up to 10 mm marks the contact with the intruded country rocks.

Fault Patterns

There are three major fault patterns in the Cobalt area. A major southeast trend is represented by faults such as the Montreal River, Cross Lake and Quinze Dam faults (Wilson, 1986). These faults can be traced up to hundreds of kilometres. Precambrian movement along these faults is difficult to prove but the intrusion of a post-Nipissing diabase dyke parallel to the Cross Lake fault might indicate lines of weakness in Precambrian times (Thompson, 1967). Post-Silurian movement of up to 300 metres has been reported by Lovell and Caine (1970) along the Lake Temiskaming fault.

A second set of faults trends northeast. The largest of these, the Cobalt Lake fault, has been shown to offset the Nipissing Diabase prior to silver deposition (Thompson, 1967). Jambor (1971) has stated that these faults and the southeast trending set "do not control the distribution of the silver veins and nearly all large faults are barren".

The third set of faults trend East-Southeast. These faults are generally normal, vertical faults with displacements of up to 7.5 metres (Wilson, 1986). These faults are smaller than the northeast and southeast trending faults and some host silver veins (Wilson, 1986).

Veins

Two types of veins exist in the Cobalt area, the so called vertical "ore veins" and "flat veins" (Andrews *et al.*, 1986). These two vein types may be sheared or dilatant (Andrews *et al.*, 1986). Geological relationships indicate that the flat veins

are coeval with or later than the ore veins (Andrews *et al.*, 1986). The ore veins are dominated by carbonate minerals with silver and sulpharsenides of cobalt, nickel and iron. The flat veins have dominantly silicate minerals, including quartz, potassic feldspar, epidote, axinite and carbonate. The intersections of flat and ore veins can sometimes be preferred sites for high-grade ore (Andrews *et al.*, 1986). The ore veins vary in width from a few millimetres to over 30 centimetres with an average width of less than 5 centimetres (Jambor, 1971). The silver-arsenide veins may be over 300 m long and 100 m deep but may not be ore grade over the entire length and depth. The flat veins range in width up to 15 cm.

Geochronology

A K-Ar age of 2525 ± 72 Ma (Jambor, 1971) for a quartz monzonite pluton intruding the Archean metavolcanic rocks to the southeast of Cobalt provides an upper age constraint on the volcanic rocks. The Gowganda Formation has yielded a Rb-Sr isochron age of 2288 ± 87 Ma (Fairbairn *et al.*, 1969). The Nipissing diabase has recently been dated by U-Pb at 2219 ± 3.6 Ma (Andrews *et al.*, 1986). The silver veins cut the diabase and are therefore younger than 2219 ± 3.6 Ma. U-Pb analyses of primary baddeleyite, from the Nipissing diabase and vein-related secondary rutile yield ages of 2217.5 ± 1.6 and 2217.0 ± 6 Ma respectively (Andrews *et al.*, 1986). Although these data indicate no difference in age between diabase intrusion and vein formation, an age difference of 8.1 Ma is possible within the limits of uncertainty.

CHAPTER III: PETROGRAPHY

Introduction

This section will be devoted to the petrographic relationships between the early silicate assemblages, vein calc-silicate assemblages, ore assemblages and the two generations of fluid that can be placed in a paragenetic sequence for the Cobalt veins. For a general description of vein and wall rock petrography the reader is referred to the work of earlier authors (Jambor, 1971; Petruk, 1971; Goodz, 1985; Smyk, 1987).

Unfortunately thermodynamic data are unavailable for the majority of minerals found in the Cobalt camp. Some data are, however, available for the minerals, and reactions that occur in the veins, involving quartz, dolomite, calcite, tremolite, diopside and a water-carbon dioxide fluid. The petrographic relationships among these phases will be discussed further on in the text.

Fluids Related To Mineral Paragenesis

Axinite is a mineral occasionally found in the flat and vertical (ore) veins within the camp. The axinites are generally idiomorphic, range in size from .1 mm to 4 cm, and display growth zones petrographically (Plate 1-A). The primary fluid inclusions trapped within axinite growth zones from the Beaver-Temiskaming mine, have consistent phase ratios and contain a salt cube, vapour bubble and salt saturated brine at room temperature. Pseudosecondary fluid inclusions have also been identified within the axinites. These are equated to the primary inclusions

Plate 1

- 1A Sample BT-28: Overgrowth in an axinite crystal, from the Beaver-Temiskaming mine. Scale bar (top right hand corner) is 110 micrometres. Photograph taken in plane polarized light.
- 1B Sample BT-69: Primary (pre-silver) three-phase fluid inclusions in quartz from the Beaver-Temiskaming Mine. This inclusion contains a halite cube (H), a vapour bubble (V) and a halite saturated liquid (L). Photograph taken in plane polarized light. The longest edge of the salt cube is eight micrometres.
- 1C Sample BT-69: Veinlets of arsenide (As) and silver (Ag) crosscutting quartz (Qtz) and axinite (Ax), from the Beaver-Temiskaming mine. Photograph taken in reflected light. the scale bar is 140 micrometres long.
- 1D SEM photograph of an octahedral halite cube (NaCl) adhering to the walls of an opened fluid inclusion. The host mineral is quartz. The white scale bar shown in the bottom right hand corner is 10 micrometres long.

on the basis of similar phase ratios and microthermometric behaviour similar to that of the primary three-phase fluid inclusions. Three-phase fluid inclusions contained within the quartz (Plate 1-B), coexisting with the axinites (Plate 1-C), display heating and freezing behaviour similar to the primary and pseudosecondary fluid inclusions within the axinites. Veinlets of silver and arsenides crosscut, and therefore postdate both the axinite and quartz (Plate 1-C). It follows from this observation that the primary and pseudo-secondary inclusions with the axinites predate ore deposition, and represent a fluid that was associated with the veins prior to and possibly up to the time of silver deposition.

Fluid inclusions in quartz from the Siscoe mine have similar phase ratios and microthermometric behaviour to the primary and pseudosecondary fluid inclusions in the axinites and quartz from the Beaver-Temiskaming and Silverside mines; fluid inclusions from the Siscoe mine also contain accidental inclusions of native silver (frontispiece). These accidental inclusions of native silver cannot have precipitated from the small amount of fluid within the fluid inclusion after entrapment; this indicates that the fluids within the inclusions are either post- or syn-silver mineralization. The similar microthermometric behaviour of these later three-phase fluid inclusions, to the fluid inclusions contained within the axinites and quartz suggests that this saline brine existed prior to, after and possibly during silver deposition.

Rare trails of native silver inclusions (Plate 2-A) along healed fractures in quartz also contain two-phase fluid inclusions. The fluid inclusions occur both

Plate 2

- 2A** Sample COB-002: Photograph showing trails of solid silver (Ag) inclusions in a quartz (Qtz) host with arsenides (As), from the Siscoe mine. Photograph taken in reflected light. The scale bar is 30 micrometres long.
- 2B** Sample COB-002: Higher magnification and focused just below the surface photographed in 2A, showing two-phase liquid (L) + vapour (V) fluid inclusions, intimately associated with the solid silver inclusions. Photograph taken in plane polarized light. The longest dimension of the labelled fluid inclusion is 25 micrometres.
- 2C** Sample BT-28: The stable assemblage Tremolite (Tr) + Calcite (Cc) is being replaced by Arsenide (As) and Silver (Ag). Photograph taken in simultaneous transmitted and reflected light. The scale bar is 75 micrometres in length.
- 2D** Sample COB-002: The assemblage Tremolite (Tr) + Quartz (Qtz) + Calcite (Cc) crosscut by veinlets of arsenides (As) and silver (Ag). Photograph taken in simultaneous transmitted and reflected light. The scale bar is 100 micrometres long.

separately and wrapping around the inclusions of native silver. These fluid inclusions are never saturated with salt at room temperature and they rarely exhibit the consistent phase ratios, which are often present in the three-phase fluid inclusion trails. One trail of fluid inclusions (Plate 2-B) displays consistent phase ratios, and is associated with a plane of solid silver inclusions, suggesting that the ore precipitated from a fluid similar to that contained within the fluid inclusions along this trail.

A third type of fluid inclusion is also found in the Cobalt samples. These two-phase vapour dominant fluid inclusions can be found along fractures, therefore eliminating necking down as a possible genesis for the inclusions. The inclusions do display consistent phase ratios, but unfortunately these inclusions are rare and no petrographic evidence was found to relate them to any part of the paragenetic sequence.

In summary, there appear to be three types of fluid inclusions. One type represented by three-phase (Liquid + Vapour + Halite) fluid inclusions at room temperature can be shown to pre- and post-date silver precipitation. Another type represented by two-phase (Liquid + Vapour) fluid inclusions can be shown to be intimately associated with the silver. The third type (vapour-dominant two-phase) cannot be petrographically related to the mineral paragenesis.

Calc-Silicate Mineral Paragenesis

Previous studies of paragenetic sequences (Goodz, 1985) indicate that the silicates and carbonates are the earliest of the vein minerals. Therefore the

pressures and temperatures experienced by these early minerals should be indicated by the calc-silicate assemblage.

The assemblage Tremolite + Calcite (Plate 2-C) is limited by the reaction

Tremolite and calcite predate the deposition of silver as the calc-silicate assemblage is sometimes replaced by silver and arsenides. Tremolite and calcite, with or without quartz (Plate 2-D), are therefore assumed to be stable in the brine defined by the three-phase fluid inclusions since both minerals and fluid are indicated by petrography as being present prior to ore deposition.

CHAPTER IV: FLUID INCLUSIONS

Previous Work

The preceding section has emphasized the importance of the three fluid-inclusion populations that represent samples of the hydrothermal fluids present within these rocks during the history of the Cobalt camp. However, earlier workers (Scott and O'Connor, 1971; Kerrich *et al.*, 1986) have documented the existence of 5 types of fluid inclusions contained within quartz and calcite from the Cobalt and surrounding Lundy Township areas. The five types are I (Liquid), II (Liquid + Halite), III (Liquid + Vapour), IV (Liquid + Vapour + Halite), V (Vapour). Of these five inclusion types, only two (types III and IV) fit the pressure and temperature constraints for the Cobalt area. The other three types of inclusions represent failure of earlier authors to recognize necking down, metastability or misidentification of very small amounts of a phase that experimental evidence (Bodnar and Sterner, 1987) indicates must be there.

The liquid only and liquid + halite fluid inclusions require isochores, in the system NaCl-H₂O (Fig. 17), that are extremely steep at lower temperatures; therefore it would require that a near vertical isochore intersect the three-phase (L+V+H) curve below room temperature. This requires that the inclusion be trapped at temperatures less than room temperature but in excess of 1 bar pressure. Mineral assemblages indicate that the veins formed at temperatures higher than 25 °C. A similar argument can be developed for the vapour only fluid inclusions; in this case the isochores must have a very shallow slope, and the

inclusions would have to be trapped at high temperatures and low pressures.

Again, the mineral assemblages preclude this possibility.

A further subdivision of one of the remaining types (type III) is desirable. The type III inclusions (Liquid + Vapour) occur in Vapour-dominant and Liquid-dominant varieties. The distinction is that these inclusions, upon heating, will homogenise to a vapour or a liquid respectively. The three-phase (liquid + vapour + halite) inclusions are the most abundant, followed by the two-phase (liquid + vapour) liquid-dominant inclusions. The vapour-dominant inclusions are rare but are easily found upon close inspection.

In an effort to distinguish valid fluid inclusion assemblages, either primary or secondary, from assemblages that may have formed from necking down, only data from inclusions that appear along healed fractures or in clusters displaying consistent phase ratios have been used. This assumes that any necking down of the fluid inclusions took place in a different "phase field" of pressure-temperature than the original trapping took place. Necking down of the fluid inclusions within a different "phase field" of pressure-temperature space than the original trapping yields inconsistent phase ratios and homogenisation temperatures. This criterion has been used to identify fluid inclusions, existing along trails and showing consistent phase ratios, that can be placed into the paragenetic sequence for the deposits. Inconsistent-phase-ratio fluid inclusions that are interpreted to be the products of necking down of original inclusions subsequent to the deposition of the ore minerals have been excluded from the present study.

Salinities

Scott and O'Connor (1971) reported salinities greater than 30 wt. % NaCl. Kerrich *et al.* (1986) observed NaCl-CaCl₂ brines of up to 54 wt. % NaCl equivalent, in a liquid + halite fluid inclusion.

Pressures and Temperatures

Recent H, O, C and Sr isotope work (Kerrich *et al.*, 1986), petrography and wall rock chemistry (Andrews *et al.*, 1986), S isotope geochemistry (Goodz *et al.*, 1986) indicate that the Cobalt-Gowganda deposits formed from highly saline brines at depths in the order of 2 kilometres (600 bars hydrostatic pressure), in the temperature range 150-250 °C (Andrews, 1986).

Fluid Inclusion Homogenisation Temperatures

An early study on smythites and fluid inclusions in quartz from the Silverfields Mine (Taylor, 1970) reported vapour-homogenisation temperatures of 40 to 120 °C. The fluid inclusion vapour-homogenisation temperatures of Scott and O'Connor (1971) range from 125 to 275 °C. The fluid inclusion studies of Kerrich *et al.* (1986) obtained homogenisation temperatures that range from 100 to 560 °C.

Scott and O'Connor (1971) realized that liquid and liquid + halite inclusions represented a metastable fluid or a necked down inclusion. However Kerrich *et al.* (1986) reported heating and freezing data from their type II (liquid + halite) inclusions.

Homogenisation temperatures for liquid to vapour and vapour to liquid transitions reported by Kerrich *et al.* (1986) of coexisting inclusions fail to agree with the experimental evidence for simultaneously trapped inclusions from a two-phase fluid. Typically the temperature for liquid to vapour homogenisation is 10 to 20 °C less than the temperature for the vapour to liquid homogenisation, due to the so called "wetting" of the inclusion walls (Bodnar, 1985). Kerrich *et al.* report homogenisation data for only four two-phase inclusions but have never the less suggested boiling as an explanation for the liquid-dominant and vapour-dominant inclusions.

The scatter (greater than 475 °C) of homogenisation temperatures within the data (Kerrich *et al.*, 1986) for all inclusion types cited earlier is evidence for necking down of inclusions in the Cobalt veins. The observation of coincident vapour-liquid and liquid-vapour homogenisation temperatures is not necessarily indicative of a boiling fluid, and may be the result of necking down and/or mixing (Ramboz *et al.*, 1982). In addition to this Kerrich *et al.* (1986) failed to measure (or report) the salinities of these four inclusions (Kerrich *et al.*, 1986, numbers AJA-226-3, AJA-226-4, AJA-239-4, AJA-239-5) that suggest a "boiling system". The salinities should have been compared with the experimental results of Sourirajan and Kennedy (1962) to see if the inclusions represent conjugate pairs on the solvus of a boiling system or are indicative of necking down.

Microthermometric Behaviour

All microthermometric measurements were obtained using a modified U.S.G.S. gas flow heating and freezing stage (Roedder, 1984). The stage was modified by removing 4 of the 7 glass plates. This enhanced the optics of the apparatus allowing the observation of smaller fluid inclusions than would normally be possible. Repetitive measurements on samples with known homogenisation and ice melting temperatures indicated that all measurements made were within 1 and 0.1 °C respectively over the entire diameter of the heating-freezing stage sample holder. This combined with the 2 and 0.1 °C errors determined for the unmodified stage (Vanko *et al.*, 1988) yield a maximum error of 3 and 0.2 °C for the heating and freezing measurements respectively.

Three-phase Fluid Inclusions

The three-phase fluid inclusions consist of a halite cube, vapour bubble and liquid at room temperature. The halite cube and vapour bubble each occupy approximately five volume percent of the fluid inclusion. Upon cooling to -195 °C, there is often no observable change within the fluid inclusion. Occasionally there is the characteristic bubble jerk near -98 °C, due to a volume increase from the freezing of supercooled water.

Upon heating to approximately -60 °C the fluid inclusion appears to turn a brownish colour. This phenomenon may be the onset of melting just below the NaCl-CaCl₂-H₂O eutectic, or due to the refraction of light from cracks in the ice, antarcticite (CaCl₂·6H₂O), hydrohalite (NaCl·2H₂O) and metastable halite within

the fluid inclusion. Such cracks might be expected to develop from the different thermal expansivities of the host mineral and the variety of salt minerals that develop upon reheating of the fluid inclusion.

Halite exhibits a brighter yellowish colour and is easily distinguished from antarcticite and hydrohalite, both of which are clear and difficult to differentiate. Further heating results in the appearance of a liquid phase, in all cases, before -40°C . Antarcticite melts at approximately -32°C , leaving the 3 phase assemblage that is observed at room temperature (*ie.* halite, liquid and vapour).

Metastability in the $\text{NaCl-CaCl}_2\text{-H}_2\text{O}$ system is common (Vanko *et al.*, 1988; Roedder, 1984) and makes interpretation of microthermometric data difficult. The three-phase fluid inclusions of the Cobalt samples occasionally exhibit a phase that exists metastably until approximately $+15^{\circ}\text{C}$. At this temperature the metastable solid phase melts rapidly, and the halite cube grows, at an equally rapid rate.

Continued heating results in the homogenisation of the vapour into the liquid near 201°C . Finally the halite cube melts on average at 235°C . Generally the homogenisation of the vapour to liquid precedes the melting of halite, but not always as reported by some earlier authors (Scott and O'Connor, 1971). The melting of the halite prior to the homogenisation of the vapour into liquid was observed in one sample of this study and 50% of the samples from Kerrich *et al.* (1986). This behaviour may result from post-trapping volume changes or leakage from the fluid inclusions; these problems are difficult to recognize from

phase ratios at room temperature. The observation that the vapour bubble disappears prior to the melting of the salt cube in most of the samples from this study, all samples from Scott and O'Connor (1971), and 50% of the samples from Kerrich *et al.* (1986), provides useful information about the state of the fluid during inclusion trapping and will be discussed below.

In an effort to distinguish whether the phase observed melting at approximately -32 °C was hydrohalite or antarcticite, synthetic fluid inclusions with known compositions were produced, using the method of Sterner and Bodnar (1984), in the hydrothermal lab at Carleton University. Hydrohalite was observed in one of the synthetic standards. This standard, grown in a 24.2 wt.% NaCl and 75.8 wt.% H₂O solution with no calcium, reproduces the experimental conditions of synthesis upon heating and displays the correct ice-hydrohalite-liquid-vapour eutectic at -20.8 °C, indicating that the inclusions synthesised represent the 24.2 wt% NaCl starting fluid composition. At room temperature the synthetic fluid inclusions contained a vapour bubble, a halite cube and a halite saturated liquid. Upon freezing to -60 °C the inclusion contents formed ice + metastable-halite + vapour + hydrohalite. The edges of the halite grain were irregular, at lower temperatures, where the halite persisted metastably. Upon heating to -20 °C the halite was quickly consumed forming hydrohalite. Further heating resulted in the hydrohalite persisting metastably to a few degrees above zero on most occasions.

From the observations made on the synthetic fluid inclusions it appears that the phase observed melting at approximately -32 °C in the natural three-phase

(L+V+H) fluid inclusions does not behave in the manner expected of hydrohalite and is a different mineral. The evidence used to suggest this is from the observed microthermometric behaviour of the hydrohalite and halite within the synthetic fluid inclusions in the temperature range from -20 to 5 °C. The hydrohalite in the synthetic standard can be partially melted, in the presence of liquid and vapour, until only a small grain of the original crystal remains. Quickly cooling the sample results in the regrowth of the hydrohalite crystal, with no subsequent reappearance of the halite cube. This indicates that halite is metastable in the presence of hydrohalite, below 0° C.

This heating and freezing technique, described as "cycling" by Roedder (1984), was performed on the natural three-phase (L+V+H) fluid inclusions from the Silversides and Beaver-Temiskaming mines. The phase with a melting temperature of approximately -32 °C was cycled, over a 10° temperature range, in the presence of halite, liquid and vapour. Upon cooling the regrowth of the phase occurred, with no dissolution of the halite. If the phase in question was hydrohalite, microthermometric behaviour similar to that observed in the synthetic standard should be seen in the natural sample, as both the hydrohalite and halite have already nucleated, metastability should not prevent the growth of the stable phase. As the observed microthermometric behaviour is not the same as that of the synthetic standard, the phase that melts at -32 °C is not hydrohalite and is assumed to be antarcticite on the basis of the bulk composition constraints discussed later in this section.

Liquid-dominant Two-phase Fluid Inclusions

At room temperature the liquid-dominant inclusions consist of a liquid phase and a vapour phase. The liquid phase generally occupies greater than half the volume of the fluid inclusion, although significant variation in the liquid to vapour ratio occurs. Upon cooling to -195°C the fluid inclusion may exhibit a bubble jerk at around -95°C . When heated, the liquid-dominant fluid inclusions are brownish at approximately -60°C ; this phenomenon is similar to that described above for the three-phase fluid inclusions. Further heating causes the disappearance (melting) of ice from -27 to -4°C . Large differences in the liquid to vapour ratio of the liquid-dominant fluid inclusions, are reflected in the extremely variable homogenisation temperatures, ranging from 85°C (Kerrick *et al.*, 1986) to 325°C (this study). Temperatures higher than 325°C have been reported from other sources (Kerrick *et al.*, 1986), but it is surmised that necking down or the stretching of quartz at these higher temperatures, as observed in this study, may have lead to erroneous measurements by earlier authors.

Vapour-dominant Two-phase Fluid Inclusions

The vapour-dominant two-phase fluid inclusions generally have greater than 80 volume percent vapour with the liquid phase existing as a small outer ring "wetting" the inclusion walls. The small amount of liquid present in some of these fluid inclusions could lead to the misidentification of a "fifth type", or vapour only fluid inclusion from Cobalt (Kerrick *et al.*, 1986).

Upon cooling to -195°C there is virtually no change in the two-phases, or the proportions thereof. The small amount of liquid present in the inclusion makes precise observation difficult. Upon reheating to a few degrees below 0°C , the vapour bubble may be seen to move slightly, probably due to the final melting of ice, but as mentioned earlier, observation is extremely difficult due to small inclusion size and the limited amounts of liquid present. Upon heating to higher temperature ($>350^{\circ}\text{C}$), stretching of the inclusions has occurred yielding higher homogenisation temperatures than the mineral phase relations permit. Stretching is confirmed by higher homogenisation temperatures on previously measured fluid inclusions within the same sample.

Heating-Freezing Data

Reconnaissance petrography on over two hundred doubly polished plates revealed that the minerals from the silver veins contained abundant small fluid inclusions of varying phase composition. Microthermometric measurements were carried out on carefully selected fluid inclusions that could be related petrographically to the deposition of ore minerals. These inclusions can be divided into two groups; the three-phase fluid inclusions that appear to both predate and postdate the silver deposition (see above petrography section), and the two-phase liquid-dominant fluid inclusions that are contemporaneous with the ore.

Vapour homogenisation ($\text{L}+\text{V}+\text{H}=\text{L}+\text{H}$) and halite melting ($\text{L}+\text{H}=\text{L}$) temperatures were measured on twenty-six three-phase fluid

inclusions (Appendix 1 and Fig. 2). In all cases except one, the halite melting occurred at a higher temperature than the vapour homogenisation. The average vapour homogenisation temperature is 201 °C with a standard deviation of 19 °C. Halite melting temperatures occur at 235 °C on average with a standard deviation of 21 °C. Replicate halite melting and vapour homogenisation measurements indicate that the stretching of quartz does not occur at these temperatures. The freezing point depressions were measured in ten of these samples. The average is 32.7 °C with a standard deviation of 1.8 °C.

The freezing point depression, measured relative to the melting of ice (0 °C) in the pure water system, refers to the final melting temperature of the antarcticite in the presence of liquid, vapour and halite (Fig. 9). The liquid at this point is supersaturated with hydrohalite that fails to nucleate. Hydrohalite supersaturation has been previously documented by Roedder (1984) and he cites this "sluggishness" as a reason for not using hydrohalite as a calibration standard for heating/freezing apparatus.

Occasionally the hydrohalite will nucleate. However, when this occurs antarcticite fails to nucleate. Apparently the presence of hydrohalite inhibits the nucleation of antarcticite. Hydrohalite can be identified (Vanko *et al.*, 1988) on the basis of its bladed crystal habit and metastable behaviour; it persists to temperatures above 0 °C in some cases. Nucleation of hydrohalite is predicted at the temperatures slightly above the $\text{CaCl}_2\text{-NaCl-H}_2\text{O}$ eutectic (-52 °C), that involves hydrohalite rather than halite (Fig. 9). This phenomenon has been

Figure 2. Histogram of the vapour homogenization temperature (T_h) and the halite melting temperatures (T_m), for the three phase (liquid + vapour + halite) fluid inclusions. X = average and Stan Dev. = Standard deviation (1σ).

observed in the natural samples from Cobalt, but the occurrence is rare and unpredictable.

Seventeen freezing point depression measurements (Appendix 1, Fig. 3) and 4 homogenisation measurements (Appendix 1) obtained from the liquid-dominant two-phase fluid inclusions contemporaneous with the ore yield an average freezing point depression of 15.0 °C with a standard deviation of 8.4 °C and an average homogenisation temperature of 332 °C, ranging from 309 to 344 °C.

The three-phase microthermometric data from this study agree well with the data of Scott and O'Connor (1971). In all cases except one, the homogenisation of the vapour occurs prior to the melting of the salt cube. The data of Kerrich *et al.* (1986) show some agreement with the microthermometric observations within this study and the work of Scott and O'Connor (1971), as illustrated on figure 4. Above line $T_h = T_m$ on figure 4 the vapour homogenises prior to the melting of the salt cube. The area below this line represents the field in which the vapour homogenises after the halite cube melts. Fluid inclusions trapped within the two-phase field (liquid + vapour) would also plot on or below the line $T_h = T_m$ in figure 4.

Figure 3. Freezing point depressions (T_m) histogram of the two phase (liquid + vapour) fluid inclusions petrographically related to silver deposition. Note the extreme variability in salinities and the depression relative to the NaCl-H₂O eutectic (-20.8 °C), indicating that some other chloride (possibly CaCl₂) is present.

Figure 4. Halite melting (Halite $\Rightarrow$ Liquid) versus vapour homogenization (Vapour $\Rightarrow$ Liquid + Halite) plot, for the three phase fluid inclusions. The triangles are the observations from this study. The crosses and squares are the fluid inclusion data of Kerrich *et al.* (1986), for inclusions hosted by calcite and quartz respectively. The data of Scott and O'Conner (1971) are shown in a stippled pattern, because only the vapour homogenization temperatures were determined, with the observation that in all cases the vapour homogenized prior to the melting of the salt cube. The line $T_h = T_m$ separates the fields of "boiling" (liquid + vapour) and "non boiling" (liquid + halite and liquid only). T_h is the temperature of vapour homogenization and T_m is the temperature of final melting of the salt cube.

Fluid Inclusion Aqueous Species

Secondary Ion Mass Spectrometry (SIMS)

SIMS analysis involves bombarding the surface of a target sample in a vacuum chamber with a 5 to 20 keV beam of ions, usually either O^- , O^+ , Ar^+ or Ca^+ . The impact of these energetic incident, or primary ions causes particles of the sample surface to be emitted into the surrounding vacuum via a process known as sputtering. The emitted particles include a variety of charged and neutral mono- and poly-atomic species, those with positive and negative charges being termed secondary ions. The intensity of sputtered particles of a given element is proportional to the concentration of that element in the sample surface. SIMS instruments are designed to collect a fraction of the emitted secondary ions and analyze them in a mass spectrometer, with a sensitivity of between 10^{-5} (one part per hundred thousand) and 10^{-9} (one part per billion). Thus, in principle, all elements and their isotopes may be analyzed by SIMS with the spatial resolution and sensitivity required for micrometre-sized fluid inclusions.

In the past, SIMS analysis of fluid inclusions (Nambu *et al.*, 1977; Nambu and Sato, 1981; Sato *et al.*, 1984) has yielded semi-quantitative analyses of fluid inclusion contents. Recently, SIMS calibration curves for Ca, Na and K ratios have been determined for aqueous chloride species in fluid inclusions (Diamond *et al.*, 1990). Spectral data (Fig. 5) collected using a Cameca 4f Secondary Ion Mass Spectrometer with a negative oxygen ion primary beam, have been integrated using the computer software for the SIMS or by hand if the computer file

Figure 5. Secondary Ion Mass Spectrometry (SIMS) spectra, showing secondary ion counts versus time (seconds). The numbers on the right indicate the masses of the detected ions. 56; Sodium; 23; Silicon doublet and 39; Potassium.

containing the spectrum was lost! Table 1 contains the integration limits, unadjusted SIMS Ca/Na and K/Na and adjusted Ca/Na and K/Na (Diamond *et al.*, 1990), to take account of the calibration procedures using synthetically prepared standards.

The integration limits record the time at which the fluid inclusion was breached by the ion beam, and the upper time at which the spectrometer returned to background.

Table 1. SIMS Data

Sample Number	Lower Integration limit (Sec.)	Upper Integration limit (Sec.)	SIMS data Ca/Na	SIMS data K/Na
BT-69-6A	1404	1573	3.38	0.31
BT-69-7A	325	1190	1.33	0.46
BT-69-7B	1000	1600	1.19	0.42
Average			1.66* (2.89)	0.38* (0.65)
Maximum			6.12* (10.67)	0.77* (1.30)
Minimum			0.44* (0.76)	0.14* (0.24)

*Diamond *et al.* (1990) have used synthetic fluid inclusions, with known chloride ratios, to produce calibration curves, expressing the cation ratios as a function of the SIMS peak areas. Weight ratios are given in brackets for the Average, Maximum and Minimum values. These values are the F factors used below in equations 4 and 5.

Concentration of Major Salt Components

The work of Zhang and Frantz (1987) is the only high temperature experimental data within the quaternary $\text{H}_2\text{O}-\text{CaCl}_2-\text{NaCl}-\text{KCl}$. Unfortunately these data are restricted to the two-phase (liquid + vapour) field and dilute salt solutions. Therefore the molar ratios Ca/Na and K/Na obtained from SIMS and the average halite melting temperature, from microthermometry, have been used to calculate the various chloride concentrations, enabling the interpretation of the microthermometric data using experimentally derived phase diagrams within the ternary $\text{H}_2\text{O}-\text{CaCl}_2-\text{NaCl}$. The method used is described below, and is similar to the treatment given by Weisbrod and Poty (1975) and Diamond (1986). Weisbrod and Poty (1975) and Diamond (1986) have used the melting temperature of ice to determine their NaCl equivalent values. In this study the melting temperature of halite in the presence of liquid is used to determine NaCl equivalent values. A second difference is that Weisbrod and Poty (1975) and Diamond (1986), used bulk leachate analyses to determine their chloride ratios. This study has determined the chloride ratios using SIMS, and has eliminated the effects of contamination from secondary inclusions that may occur in bulk techniques (Diamond *et al.*, 1990).

Analyses of salt residues by SEM-EDS (Scanning Electron Microscopy - Energy Dispersive Spectrometry) suggest that the major cations present are Ca, Na and K. Also SEM-EDS indicates that the ligand responsible for complexing and transport of Ca, Na and K is Cl (Appendix 2). For the purpose of the

concentration calculations it will be assumed that Cl is the only ligand in the system capable of complexing with Ca, Na and K. No Mg was detected during SEM-EDS salt residue analyses, although minor Mg must be present in the fluid because the fluid inclusions analyzed are in contact with chlorite and/or dolomite. The absence of Mg in the SEM-EDS spectra coupled with the limited SIMS time constraints (Diamond *et al.*, 1990) dictated that the samples would not be analyzed for Mg on the SIMS.

An assumption inherent in these calculations is that the microthermometric effects of the chlorides are exactly the same in the quaternary, $\text{CaCl}_2\text{-NaCl-KCl-H}_2\text{O}$, as in the two ternaries, $\text{NaCl-CaCl}_2\text{-H}_2\text{O}$ and $\text{NaCl-KCl-H}_2\text{O}$. The term NaCl(equiv) is used in fluid inclusion studies (Roedder, 1984) to describe the microthermometric behaviour observed within a fluid inclusion in terms of an experimentally determined system ($\text{H}_2\text{O-NaCl}$). For the purposes of these calculations it has been assumed that the only chlorides present in the system are NaCl, CaCl_2 and KCl. The general equation of a plane in the quaternary $\text{CaCl}_2\text{-NaCl-KCl-H}_2\text{O}$ is given by

$$\text{Wt\%NaCl(equiv)} = \text{Wt\%NaCl} + a \text{ Wt\%KCl} + b \text{ Wt\%CaCl}_2 \quad (2)$$

where a and b are values that determine the slope of the plane.

In order to model the quaternary system $\text{CaCl}_2\text{-H}_2\text{O-NaCl-KCl}$, the 235 °C isotherms on the halite liquidus in the two ternaries, $\text{CaCl}_2\text{-H}_2\text{O-NaCl}$ and $\text{H}_2\text{O-NaCl-KCl}$ are approximated by straight lines (Figs. 9 and 11). These straight lines represent approximations, based on the observation that the liquidus are

virtually straight lines over the experimentally measured range of compositions at the temperatures of interest.

The linear extrapolation of the 235 °C isotherm on the halite liquidus, using the data of Vanko *et al.* (1988) in the ternary $\text{CaCl}_2\text{-H}_2\text{O-NaCl}$ intersects the $\text{CaCl}_2\text{-H}_2\text{O}$ binary at 54 wt% CaCl_2 (Fig. 11). This liquidus is shown as line A-B in the ternary $\text{CaCl}_2\text{-H}_2\text{O-NaCl}$ (Fig. 10).

The graphical extrapolation of the 235 °C halite liquidus using the $\text{NaCl-H}_2\text{O-KCl}$ ternary data of Linke (1965) intersects the $\text{KCl-H}_2\text{O}$ binary at 64.1 wt% KCl (Fig. 11). The extrapolation of the 235 °C halite liquidus into the ternary ($\text{KCl-H}_2\text{O-NaCl}$) is represented by the line A-C on figure 10. The slopes of these two lines (AB and AC) are given by the expressions

$$34.0 \text{ wt\% NaCl} / 64.1 \text{ wt\% KCl} = 0.5304 \quad \text{and}$$

$$34.0 \text{ wt\% NaCl} / 54.0 \text{ wt\% CaCl}_2 = 0.6296$$

To ensure that the plane ABC (Fig. 10) reproduces the linear extrapolations of the 235 °C isotherms on the halite liquidus of the two ternaries $\text{CaCl}_2\text{-NaCl-H}_2\text{O}$ and $\text{KCl-NaCl-H}_2\text{O}$, these ratios now become the two (a and b) coefficients for equation 2

$$\text{wt\% NaCl(equiv)} = \text{wt\% NaCl} + 0.5304 \text{ wt\% KCl} + 0.6296 \text{ wt\% CaCl}_2 \quad (3)$$

Equation 3 is the equation of the plane containing the points 64.1 wt.% KCl , 54 wt.% CaCl_2 and 34 wt.% NaCl , in the respective binaries with H_2O (Fig. 10).

Using the weight ratios obtained from the SIMS, wt% CaCl_2 and wt% KCl are expressed as functions of wt% NaCl

$$\text{wt\% CaCl}_2 = \text{wt\% NaCl} * F_{(\text{Ca/Na})\text{SIMSWEIGHT}} \quad (4)$$

$$\text{wt\% KCl} = \text{wt\% NaCl} * F_{(\text{K/Na})\text{SIMSWEIGHT}} \quad (5)$$

Equations 4 and 5 each define the equation of a plane within the quaternary $\text{CaCl}_2\text{-NaCl-KCl-H}_2\text{O}$ (Fig. 10). Equations 3, 4 and 5 allow us to solve for the three unknowns. Using the maximum, minimum and average weight fractions obtained by SIMS (Table 1.) yields the weight fractions of NaCl, KCl, CaCl_2 and H_2O (Table 2).

Table 2. Weight Percent Chloride Concentrations from SIMS data

Highest Halite Melting Temperature Average+2σ=277 °C				Average Halite Melting Temperature 234 °C			Lowest Halite Melting Temperature Average-2σ=193°C		
	Max *	Avg *	Min *	Max *	Avg *	Min *	Max *	Avg *	Min *
H ₂ O	45.7 (.822)	50.1 (.830)	57.3 (.846)	47.9 (.835)	51.6 (.838)	58.0 (.849)	53.2 (.862)	55.2 (.857)	59.6 (.858)
CaCl ₂	44.7 (.131)	31.7 (.085)	16.3 (.039)	42.9 (.121)	30.8 (.081)	16.0 (.038)	38.5 (.101)	28.5 (.072)	15.4 (.036)
NaCl	4.2 (.023)	11.0 (.056)	21.3 (.097)	4.0 (.022)	10.7 (.054)	21.0 (.095)	3.6 (.018)	9.9 (.047)	20.2 (.090)
KCl	5.4 (.024)	7.2 (.029)	5.1 (.018)	5.2 (.022)	6.9 (.027)	5.0 (.018)	4.7 (.019)	6.4 (.024)	4.8 (.016)

*Max (Maximum), Avg (Average) and Min (Minimum) refer to the SIMS ratios for K/Na and Ca/Na used. Mole fractions are shown in brackets.

The mole fractions of the fluid represented by the three-phase (L+V+H) assemblage at room temperature are $X_{\text{H}_2\text{O}} = 0.822$ to 0.858 , $X_{\text{CaCl}_2} = 0.036$ to 0.131 , $X_{\text{NaCl}} = 0.018$ to 0.097 , and $X_{\text{KCl}} = 0.019$ to 0.029 .

The three major sources of error in these calculations are the error associated with the SIMS Ca/Na and K/Na ratios, the error associated with the

microthermometric measurements and the error from the linear extrapolation of the 235 °C isotherms on the halite liquid in the two ternaries.

The error associated with the SIMS measurements and the calibration curve of Diamond *et al.* (1990) have been taken into account. The maximum and minimum peak-area ratios obtained from the 3 SIMS analyses have been added to the error (1σ) associated with the calibration curve. These values are the adjusted values presented in Table 1.

The error associated with the halite melting measurements has been accounted for by adding or subtracting the 2σ value (95% confidence limit) from the average halite melting temperature value. These values have been used to perform the calculations tabulated in Table 2.

Possibly the greatest source of error associated with the calculations is the linear extrapolation of the 235 °C isotherms on the halite liquid in the two ternaries. It is impossible to determine the error associated with this approximation, because no experimental data exist in the ternary $\text{CaCl}_2\text{-H}_2\text{O-NaCl}$ for the bulk compositions and trapping temperatures, determined in this study for the three-phase (L+V+H) fluid inclusions. Therefore it should be emphasized that these calculations represent the best approximation to the bulk composition without performing a computer modelling "*tour de force*" as recently presented by Spencer *et al.* (1990) for ice, liquid, vapour and salt hydrate phase transitions below 25 °C.

Scanning Electron Microscopy and Energy Dispersive Analyses of Fluid

Inclusion Residues

Eadington (1974) proposed the use of SEM/EDS for qualitative and semi-quantitative analyses of salt residues. This method has been applied to natural deposits by many authors (Ypma and Fuzikawa, 1980; Chrysosoulis and Wilkinson, 1983; Haynes and Kessler, 1987). This technique has recently been tested using hydrothermally synthesized fluid inclusions (Sterner and Bodnar, 1984), using thermal decrepitation methods, on fluid inclusions of less than 23 wt% NaCl equivalent in the system $\text{CaCl}_2\text{-NaCl-KCl-H}_2\text{O}$ (Haynes *et al.*, 1988). Other authors (Kelly and Burgio, 1983; Roedder, 1984) have described similar techniques for the analyses of daughter crystals within fluid inclusions.

A modification of the Kelly and Burgio method has been employed for this study. A crystal of quartz is cut using a micro-saw until the crystal resembles a loaf of sliced bread with a small piece still connecting each piece of loaf together (Kelly and Burgio, 1983). This loaf is then placed in a bath of liquid nitrogen (-194°C) for sixty seconds to ensure that the contents of all the fluid inclusions have been frozen. The sample is then removed from the liquid nitrogen and allowed to sit at room temperature to remove some of the condensate that forms on the quartz. A small chisel is then used to pry the pieces of the loaf apart and to expose some of the frozen inclusions. These slices are then mounted on the SEM sample holder, carbon coated and placed in the sample chamber of the Scanning Electron Microscope. This technique could be further enhanced by

using a dry nitrogen gas atmosphere to perform all the heating, thawing and carbon coating operations; this would eliminate the frosting of the sample when exposed to the air, following sample immersion in liquid nitrogen.

Using a JEOL electron-microprobe with SEM/EDS capabilities the measured molecular proportions of 24 breached fluid inclusions are shown in Appendix 2. Shown graphically it can be seen that for both the K:Na (Fig. 6) and Ca:Na (Fig. 7), the ratios are less than one and in general close to zero. This is also evident from the analysis (Fig. 8) of a well preserved salt cube (Plate 1-D). This result seems contradictory to the previously reported SIMS data, but when the experimental technique is critically evaluated, it can be seen from figure 9 and the experimental work in the ternary system $\text{H}_2\text{O}-\text{CaCl}_2-\text{NaCl}$ (Vanko *et al.*, 1989), that decreasing temperature will result in NaCl reaching saturation first in a liquid equilibrated with vapour; NaCl is therefore preferentially retained in the opened inclusion.

Figure 6. Histogram of the K/Na from the SEM/EDS analysis of "opened" fluid inclusion residues.

Figure 7. Histogram of the Ca/Na from the SEM/EDS analysis of "opened" fluid inclusion residues.

By assuming that the SIMS analyses are correct and that it is possible to model the system ($\text{CaCl}_2\text{-NaCl-KCl-H}_2\text{O}$) by the system $\text{CaCl}_2\text{-NaCl-H}_2\text{O}$ by assuming KCl behaves as NaCl, it is possible to predict that the NaCl should be the first salt to precipitate. The line connecting point P to the NaCl apex (Fig. 9) suggests that any fluid in the inclusions from -22.4°C to room temperature will have virtually all of the CaCl_2 as a dissolved species and that the solid present will be NaCl. Therefore the technique used to prepare the samples should have utilized the dry nitrogen gas as this would have preserved all or most of the fluid inclusion contents. The method used in this work resulted in the fluid carrying all the CaCl_2 and KCl away as dissolved species leaving a cube (or residuum) of halite, in the breached inclusion.

Figure 8. EDS spectra of an octahedral halite cube (photo 1-D) adhering to the walls of an "opened" fluid inclusion. The units for the abscissa are counts per channel, increasing from the bottom to top.

Metastability in the System $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2$

The supersaturation and metastability of hydrohalite make interpretation of phase diagrams in the system $\text{H}_2\text{O}-\text{CaCl}_2-\text{NaCl}$ difficult, but some conclusions can be drawn. Although the optics are not ideal, it appears that antarcticite melts at approximately -32°C , well below the -22.4°C reported by Yanatieva (1946) for point P (Fig. 9). It can therefore be assumed that if hydrohalite nucleated, the heating trajectory would continue from the system eutectic, along the boundary between the L + Antarcticite (ANT) and L + Hydrohalite (HH) fields, towards point P. Further heating, assuming no metastability and the presence of hydrohalite, moves the liquid bulk composition from point P along the liquid + halite - liquid + hydrohalite boundary, until all the hydrohalite has melted. Therefore, the area above the line P-NaCl apex (Fig. 9) defines the possible fluid inclusion contents in the system $\text{H}_2\text{O}-\text{CaCl}_2-\text{NaCl}$.

The agreement between the calculated chloride concentrations and the observed phase relations in the ternary system, $(\text{CaCl}_2-\text{H}_2\text{O}-\text{NaCl})$ shown in figure 9 indicates that the use of the SIMS curves calibrated with fluid inclusions without chloride daughter phases may also be used for fluid inclusions containing halite daughter cubes. Also the ternary $(\text{CaCl}_2-\text{H}_2\text{O}-\text{NaCl})$ may be used to model the "Cobalt" fluids assuming that the KCl contained within the fluid inclusions behaves as NaCl (Fig. 9).

Figure 9. Polythermal-polybaric section of the system H₂O-CaCl₂-NaCl showing the three phase fluid inclusion composition as determined by SIMS (stippled area), in combination with the heating/freezing constraints. T_e is the system eutectic temperature (-52°C) and point P represents the cotectic temperature (-22.4°C) of coexisting hydrohalite (HH), antarcticite (ANT), liquid (L), vapour (V) and halite. Data from Yanatieva (1946), after Vanko *et al.* (1988).

Figure 10. The quaternary $\text{CaCl}_2\text{-NaCl-H}_2\text{O-KCl}$ showing the graphical extrapolation (plane ABC) of the 235 °C isotherm on the halite liquidus

Figure 11. Polythermal-polybaric section of the system $\text{H}_2\text{O-KCl-NaCl}$, showing the various phase fields in the heavy signature, the graphical extrapolation (dashed line AB) of the 235 °C isotherm on the halite liquidus, and liquidus for halite and sylvite, shown in the light signature. HH is Hydrohalite. Data from Linke (1965).

Gaseous Species in Fluid Inclusions

Laser Raman Microscopy

The Raman effect was first described by Raman and Krishnan (1928) and is a measure of the interaction (scatter) between light and the molecular vibrations within a substance. Raman spectroscopy has been applied to fluid inclusions by various authors (Wopenka and Pasteris, 1987; Naumov *et al.*, 1987; Pasteris *et al.*, 1988).

The laser Raman spectrometer used was a Spex Triplemate with a green (514.5 nm) incident Argon laser and Princeton Instrument diode array detector. All samples were unmounted doubly polished plates of quartz, axinite or calcite. The vapour phases from the liquid-dominant two-phase and the three-phase liquid + vapour + halite inclusions were analyzed for CO₂, CH₄, N₂ and H₂S. Sensitivity of the instrument was verified using interlaboratory standards.

The liquid-dominant two-phase inclusions intimately associated with silver (Plate 2-B) yield the spectra shown in figure 12. The arrow indicates the position of the appropriate gas peaks. It may also be noted that the nitrogen gas is content is below the detection, of the Raman spectrometer.

The spectra shown in figure 13 are the analyses of the vapour phase of the three-phase (L+V+H) inclusions (Plate 1-B). No nitrogen or hydrogen sulphide gases were detected in these inclusions. The two-phase vapour-dominant fluid inclusions were also analyzed using the Raman spectrometer and as in the previous two cases no CO₂, CH₄, N₂ or H₂S were detected. It would appear that

Figure 12. Laser Raman spectra from the vapour phase of a two phase fluid inclusion associated with silver deposition. The abscissa units are counts/diode (total counts) and the ordinate units are diode number, which is proportional to wavenumber. The arrows indicate the calibrated peak positions of the gas species indicated.

Figure 13. Laser Raman spectra from the vapour phase of a three phase (liquid + vapour + halite) fluid inclusion, that predates silver deposition. The abscissa units are counts/diode (total counts) and the ordinate units are diode number, which is proportional to wavenumber. The arrows indicate the calibrated peak positions of the gas species indicated.

all the inclusions from the Cobalt samples contain concentrations of these volatiles that are below the detection limit of the Raman microprobe.

Petrographic evidence indicates that all the samples analyzed were in contact with carbonate, and therefore should contain some CO_2 . Maximum values will be placed on the CO_2 within the inclusions based on crushing analyses as described below.

Analyses from Crushing Experiments

Deicha (1950) showed that useful geological data can be obtained by crushing fluid inclusion samples between two plates of glass. The samples are mounted in mineral oil between two plates of glass and then crushed while being viewed under a microscope. This technique has been described by Shugurova (1968) and by Diamond and Marshall (1990).

The crushing stage tests the possibility that any volatiles in the fluid inclusions are at an internal pressure of greater than one bar. When the inclusion is breached, a vapour phase, at greater than one atmosphere pressure, will expand against the mineral oil (Fig. 14) which is at 1 atmosphere. If however the vapour phase of the fluid inclusion is made up of volatiles at less than one atmosphere pressure, then the bubble will collapse under the 1 atmosphere mineral oil pressure. Since pure H_2O vapour must be at less than one atmosphere pressure at room temperature, the observation of an expanding bubble requires the presence of additional components such as CO_2 and CH_4 in the vapour.

Figure 14. Pictorial representation of fluid inclusion crushing analyses. (from Diamond and Marshall, 1990).

In all three types of inclusions from the Cobalt samples the bubbles always collapsed. This indicates that the fluid inclusion internal pressure in all cases was less than 1 atmosphere. Crushing tests did occasionally produce bubbles in the mineral oil. In these few instances it was impossible to say if the bubbles were trapped air along grain walls or existing fractures in the sample. But in all cases when careful observation was possible, none of the inclusion types produced any evidence of CH_4 or CO_2 .

Maximum CO_2 Calculations

Although the theoretical detection limit for the crushing technique is one atmosphere, the limit by Raman spectroscopy has been estimated at 8 bars CO_2 by Naumov *et al.* (1987) and 1.3 bars by Wopenka & Pasteris (1987). A maximum CO_2 fugacity of 8 bars is therefore assumed in subsequent calculations.

The Raman is a non-destructive technique. This allows samples to be analyzed by petrographic and microthermometric techniques, to place a particular inclusion within the paragenetic sequence. Crushing is a destructive technique and viewing of a particular fluid inclusion is difficult if not impossible. The rarity of fluid inclusions from the Cobalt samples that define the paragenetic sequence dictates that the definitive samples not be destroyed by crushing. As the samples that have been related to the paragenetic sequence yielded microthermometric and Raman data and have **NOT** been crushed, the maximum constraint on CO_2 must come from the Raman literature.

To perform the calculations converting from bars to X_{CO_2} , it is necessary to make some assumptions

- 1) that the volume proportions of L:V:H are 89.7:4.5:5.8, as determined by photographing 6 fluid inclusions, cutting out the appropriate areas, weighing the individual phases, and averaging the results.
- 2) that any CO_2 in the inclusion behaves as an ideal gas at 25 °C.
- 3) that CO_2 dissolved in the liquid or solid phase of the fluid inclusion is insignificant.
- 4) that water in the inclusion is saturated with respect to NaCl (23.2 wt%) and therefore has a density of 1.176 g/cm^{-3} (Rogers and Pitzer, 1982).
- 5) that the amount of H_2O vapour within the vapour phase is negligible.

Then

At $P_{\text{CO}_2} = 8.0$ bars	$X_{\text{CO}_2} = 3.3 * 10^{-4}$
At $P_{\text{CO}_2} = 1.3$ bars	$X_{\text{CO}_2} = 5.3 * 10^{-5}$
At $P_{\text{CO}_2} = 1.0$ bars	$X_{\text{CO}_2} = 4.1 * 10^{-5}$

The fluid-inclusion CO_2 estimate by Kerrich *et al.*, (1986) from mass spectrometry indicates carbon dioxide partial pressures much higher than those obtained in this study. The $0.00277 X_{\text{CO}_2}$ (2770 ppm.) reported by Kerrich *et al.* (1986), using mass spectrometry after gas separation by gas chromatography on bulk quartz samples, fails to account for the presence of salt in the inclusions. If this is corrected for a 30 wt. % NaCl solution the corrected X_{CO_2} is 0.00245.

The order of magnitude discrepancy between the Raman study and the chromatography of quartz samples (Kerrick *et al.*, 1986) could arise from small inclusions of carbonate trapped within the quartz and not removed by the acid treatment. These tiny inclusions could be exposed as the quartz fractures due to the incremental heating techniques used by Kerrich *et al.*, (1986). The discrepancy could also result from the application of the detection limits of Naumov *et al.* (1987) and Wopenka and Pasteris (1987) to samples that are not optimal for Raman studies. Assumption 3 may not be valid because the liquid does have the ability to dissolve some CO₂.

Silver Detection by Secondary Ion Mass Spectrometry within the Primary

Three-phase Fluid Inclusions

The SIMS has the ability to detect any mass from 1 to 500 atomic mass units. This allows for detection of any element in the periodic table and to distinguish between their isotopes, barring mass interference problems. Natural fluid inclusions from Cobalt were selected to determine if the SIMS has the ability to detect silver in natural inclusions. The conclusions of this study have indicated that these samples, which were petrographically related to silver deposition at Cobalt, should contain silver.

The SIMS analysis (Fig. 15) displays the data for the four species monitored. Potassium was monitored so the breaching of the inclusion could be determined (Fig. 5, and Diamond *et al.*, 1990). Both isotopes of silver ¹⁰⁷Ag and

Figure 15. Secondary Ion Mass Spectrometry (SIMS) spectrum displaying secondary ion counts versus time (seconds), for a three phase (L+V+H) fluid inclusion. Si (mass number 15) matrix was monitored to assure beam stability throughout the experiment. Potassium (K, mass number 39) was monitored in order to recognize fluid inclusion breaching (peak at 500 seconds) and the two isotopes of silver (masses 107 and 109) were monitored to determine if the inclusions contained detectable silver.

^{109}Ag were monitored. In addition to these species, Si_3 (the silicon triplet) was also monitored to insure beam stability throughout the analysis.

Figure 15 indicates there are mass interference problems that prevent the measurement of either of the two isotopes of silver, because the background count rates are so high. Although mass interference is most likely the problem, the high background counts could be due to contamination during sample preparation, or perhaps the gold used for gold coating contains small amounts of silver.

Another possible source of difficulty in the experiment is that the fluid inclusion may not contain any measurable silver. This problem will be looked at later using synthetic fluid inclusions of gold and silver chloride, but for the moment these studies are beyond the scope of this thesis.

CHAPTER V: PRESSURE-TEMPERATURE CONDITIONS OF VEIN FORMATION

Calc-Silicate Assemblages within the Ore Veins

Reaction 1 (Plate 2C) provides a minimum constraint on the pressure-temperature conditions during vein formation at the Beaver Temiskaming mine. The product assemblage, tremolite + calcite, from this reaction (Fig. 16) is observed in the veins, indicating that pressure-temperature conditions were on the high temperature side of the reaction. Similarly for a sample from the Siscoe mine (Plate 2D) the stable assemblage tremolite + calcite + quartz corresponds to reaction 1 going to completion by exhausting the supply of dolomite.

Two other equilibria involving assemblages contained within the product mineral assemblage from curve 1 (Fig. 16) can be used to provide upper pressure-temperature constraints on the vein samples:

Reaction 6 provides an upper constraint on the Beaver Temiskaming veins (Fig. 16 and Plate 2C), as the tremolite and calcite have not reacted to form diopside. The Siscoe vein sample (Plate 2D) shows the reactant assemblage tremolite + calcite + quartz. As no diopside was found in either sample the pressure-temperature conditions for the Siscoe and Beaver-Temiskaming veins must lie on the low temperature side of reactions 6 and 7 (Fig. 16) respectively.

Figure 16. Pressure-Temperature diagram at fixed $X_{\text{CO}_2} = 0.003$ showing the calc-silicate mineral equilibria observed within the silver veins, from the Beaver-Temiskaming and Siscoe mines, near Cobalt, Ontario. Enthalpies, entropies and heat capacity coefficients, from Berman (1988); Fugacity coefficients for CO_2 and H_2O from programme MODRK (Connelly and Bodnar, 1983).

The positions of mineral equilibria 1, 6 and 7 have been calculated using the enthalpies, entropies and heat capacity coefficients of Berman (1988). The CO_2 fugacities have been generated by the programme MODRK (Connolly and Bodnar, 1983). At such low CO_2 fugacities there is a large uncertainty associated with the equilibria temperatures, as a small change in the CO_2 fugacity results in a large temperature shift (Skippen, 1974). The equilibria shown in figure 16 have been calculated using an X_{CO_2} of 0.003; this is the lowest X_{CO_2} that reproduces the mineral assemblages observed within the veins. The discrepancy in X_{CO_2} between the Raman and observed values, could result from inaccuracies in the thermodynamic data and fugacity models or overly optimistic Raman detection limits, as discussed above.

Fluid Inclusion Isochores

Although the SIMS, EDS-SEM, and microthermometric data suggest that chloride species other than NaCl exist within the fluid inclusions, the lack of high pressure-high temperature density (isochoric) measurements permits the modelling of the Cobalt fluids in the binary system H_2O -NaCl only. Figure 17 shows a 30 weight percent isopleth, which is the salinity corresponding to the average melting temperature (235 °C) of the salt cube in the Cobalt samples. The two-phase (L + V) field and isochores are from Bodnar (1985). The liquidus slope is extrapolated from Chou *et al.* (1987); the intersection of the three-phase curve and the liquidus is given by the data of Sourirajan and Kennedy (1962).

Figure 17. 30 wt.% isopleth showing the three phase (L+V+H) curve, liquidus (L+H $\rightarrow$ L), two phase liquid + vapour (L+V) and vapour + halite (V+H) fields. Three isochores of densities (ρ) of 1.090, 1.081 and 1.072 are shown. The dashed line indicates the cooling path for a fluid inclusion trapped along the 1.081 density isochore. Liquidus data from Keevil (1946), phase boundaries and isochores from Bodnar (1985).

The isochore with a density of 1.072 (Fig. 17) provides a minimum pressure, maximum temperature boundary. This is due to the observation that in most samples, the bubbles in the inclusions homogenise prior to the melting of the halite cubes. The upper isochore ($\rho=1.090$) provides an upper pressure, lower temperature constraint because the metastable extension of this isochore, across the liquidus intersects the three-phase curve at the average homogenisation temperature (201 °C) of the vapour bubbles within Cobalt fluid inclusions. The slope of the isochore depends upon the change in the molar volumes of the liquid and solid (halite) within the inclusion. As it is generally true that

$$\left(\frac{\partial P_{\text{Liquid}}}{\partial T}\right)_{v,x} \gg \left(\frac{\partial P_{\text{Solid}}}{\partial T}\right)_{v,x} \quad (8)$$

the slope of the fluid inclusion pressure-temperature path in the L+H region will tend to be less than the slope of the isochore at the point of intersection with the liquidus; this has been taken into account along the dashed isochore shown on figure 17.

Maximum Lithostat Calculation

A maximum lithostatic pressure can be calculated by estimating the maximum possible thickness of sedimentary rocks overlying the ore veins at the time of formation. Figure 18 shows a 4.7 kilometre maximum thickness of sediment (Roscoe, 1973 and pers. comm.). Jambor (1971) estimated a 300 metre

Figure 18. Idealized section of the maximum possible sediment thickness overlying the Cobalt silver veins at the time of formation (after Rainbird, 1986).

thickness of Nipissing diabase. Therefore the maximum possible thickness of overlying rock, during vein formation is 5 kilometres. This corresponds to a lithostatic pressure of 1500 bars, assuming a rock density of 3.0 gm/cm^3 .

CHAPTER VI: DISCUSSION AND CONCLUSIONS

The purpose of this study was to determine the pressure, temperature, fluid composition, and state of the ore transporting fluids responsible for the formation of the silver veins at Cobalt, Ontario. The data obtained during the course of this study also may also be used to place some constraints on the silver transporting ligand, the mechanisms responsible for silver deposition, and the source of the silver.

Pressures and Temperatures of Vein Formation

Three independent methods have been used to place constraints on the pressures and temperatures of vein formation. These are 1) Maximum lithostat calculations; 2) Stable calc-silicate vein assemblages petrographically related to ore deposition and 3) Isochores derived from the fluid inclusion data and experimental data in the system $\text{NaCl-H}_2\text{O}$. Each of these methods define an area of pressure-temperature space (figs. 16 through 18). The combination of these fields represents the area of pressure-temperature space that satisfies all three independent methods (fig. 19). These data indicate that the conditions of vein formation at Cobalt ranged from 48 to 150 Megapascals (480 to 1500 Bars). The temperature range from the same data constrains vein formation at 280 to 365 °C.

The mineral-equilibria-temperature dependence upon X_{CO_2} discussed above indicates that the mineral equilibria may not provide a suitable pressure and temperature constraint for the Cobalt veins. Therefore the lower pressure and temperature constraint may be provided by the fluid inclusion data. Using

Figure 19. Pressure-Temperature diagram showing all the possible pressure-temperature constraints for the Cobalt veins superimposed. The dashed lines represent the vein calc-silicate mineral equilibria. The heavy dark signature is the maximum lithostat. The sloping lines are the bounding isochores from the fluid inclusion data. The stippled area represents the area of pressure-temperature space that satisfies all the constraints.

the intersection of the liquidus with the three-phase (L+V+H) curve (Fig. 17) as the lower constraint indicates pressures of formation from 2.1 to 150 Megapascals and temperatures from 235 to 365 °C.

Fluid Compositions

The three-phase (L+V+H) fluid inclusion compositions have been determined, in the ternary system $\text{H}_2\text{O}-\text{CaCl}_2-\text{NaCl}-\text{KCl}$, by two independent methods. The first involves using the K/Na and Ca/Na ratios determined by SIMS analyses and the melting temperatures of halite, within the fluid inclusions. These data can be used to construct three planes in the ternary system $\text{H}_2\text{O}-\text{CaCl}_2-\text{NaCl}-\text{KCl}$. These three planes intersect at a unique composition. This calculation is performed iteratively using the range of SIMS ratios (Table 1.) and the two 95% confidence levels (2σ) for the melting of halite, obtained by microthermometric observations (Table 3).

The second method used to determine the composition of the three-phase (L+V+H) fluid inclusions utilizes the microthermometric freezing data. This method is hampered by the metastability of the phases Hydrohalite ($\text{NaCl}\cdot 2\text{H}_2\text{O}$) and Antarcticite ($\text{CaCl}_2\cdot 6\text{H}_2\text{O}$). This metastability inhibits the determination of the bulk composition. Therefore the microthermometric observations limit the bulk composition to the area bounded by Point P, the NaCl apex and the ice + liquid univariant line (Fig 9). Therefore the SIMS method provides a better estimate of the bulk composition and yields:

$$X_{\text{H}_2\text{O}} = 0.822 (45.7) \text{ to } 0.858 (59.6 \text{ wt.\%})$$

$$X_{\text{CaCl}_2} = 0.036 \text{ (15.4) to } 0.131 \text{ (44.7 wt.\%)}$$

$$X_{\text{NaCl}} = 0.018 \text{ (3.6) to } 0.097 \text{ (21.3 wt.\%)}$$

$$X_{\text{KCl}} = 0.019 \text{ (4.7) to } 0.029 \text{ (7.2 wt.\%)}$$

The compositions of the two-phase liquid- and vapour-dominant fluid inclusions have been analyzed by Raman spectroscopy and microthermometrically. The Raman data indicate that the concentrations of CO_2 , CH_4 , H_2S and N_2 are below detection limit. Eutectic temperatures below the H_2O - NaCl binary eutectic (-20.8°C) indicate some other component(s) within the fluid inclusions, possibly CaCl_2 or MgCl_2 (Crawford, 1981).

State of the Fluid

The three types of fluid inclusions considered in this study are represented at room temperature by 1. a three-phase (L+V+H) assemblage; 2. a liquid-dominant two-phase (L+V) assemblage and 3. a vapour-dominant two-phase (V+L) assemblage. All of the three fluid-inclusion types occur as populations and represent a fluid, present at some time during the history of these rocks. These populations indicate that these inclusions are not the result of a post-trapping phenomenon such as necking down.

The three-phase inclusions appear to pre- and post-date the two-phase liquid-dominant fluid inclusions associated with ore deposition. No timing relationships between the vapour-dominant fluid inclusions and the other two

types were observed. Therefore the timing of these inclusions cannot be related to ore deposition, as can the other two types.

The pressure and temperature estimates from calc-silicate vein assemblages and three-phase fluid inclusion isochore data indicate fluid inclusion trapping occurred within a one-phase (Liquid) field (fig. 19). Therefore the three-phase fluid inclusions cannot be the product of a boiling system.

The two-phase liquid-dominant fluid inclusions associated with the ore, could be the result of trapping in a one-phase (liquid) field or trapping of the liquid portion of a two-phase (liquid + vapour) field.

The two-phase liquid-dominant fluid inclusions may be the result of mixing of a less saline fluid with the fluid represented by the three-phase fluid inclusions.

The mixing of two such fluids accounts for the lower salinity observed in the two-phase liquid-dominant fluid inclusions, relative to the earlier fluid represented by the three-phase inclusions at room temperature.

The two-phase vapour-dominant fluid inclusions may also represent the conjugate solvus pair to the two-phase liquid-dominant fluid inclusions. The presence of these fluid inclusions as distinct populations indicates that these inclusions are not the product of necking down. Unfortunately the rarity of these populations makes the paragenetic significance difficult to establish. The stretching of the quartz, yielding higher homogenisation temperatures for these inclusions than the mineral assemblages would predict, has obliterated any microthermometric evidence that could be used to relate the vapour-dominant

two-phase fluid inclusions to the other two fluid inclusion types observed at Cobalt or clarify the ambiguity between mixing and boiling.

Transporting Ligand of Silver

Silver chloride complexes (Seward, 1976) are considered as the likely transporting species of silver due to the high salinities found within the fluid inclusions from this study area. The close spatial association of the silver to sulphide and carbonate vein minerals dictates that silver sulphide complexes (Barnes and Gammons, 1989) and silver carbonate (Kozlov, 1985) be considered as well.

The failure to detect any sulphur species within the fluid inclusions associated with ore, either petrographically or by laser Raman spectroscopy, suggests that the silver is not transported as a sulphide complex. The data of Kozlov (1985) indicates that silver carbonate species are not stable at higher temperatures. Furthermore no CO_2 was detected by Raman spectroscopy within the fluid inclusions associated with ore deposition. Therefore it is concluded that silver was likely transported as a chloride complex.

The SEM/EDS data (Appendix II: Table 4.) and fluid inclusion observations indicate that the dominant species present are chlorides. An average Cl^- molality of 16.3, calculated from the combined microthermometric and SIMS data, and extrapolation of the 197 and 277 °C AgCl solubility curves from Seward (1986) indicates silver chloride solubilities on the order of 4 molal (Fig. 20).

Figure 20. Polythermal polybaric silver chloride solubility versus chlorinity plot (from Seward, 1976).

Mechanisms of Silver Deposition

Three possible mechanisms of silver deposition are discussed. These mechanisms all assume that the silver is transported as a chloride complex. The three mechanisms are 1) boiling of a silver saturated saline solution; 2) cooling of this same fluid and 3) mixing of this fluid with a less saline fluid (possibly of meteoric or magmatic origin).

Earlier authors (Andrews, 1986; Kerrich *et al.*, 1986) have indicated, but shown little evidence, that boiling was the mechanism responsible for silver deposition. The evidence obtained in this study from fluid inclusions and stable vein assemblages has yielded a possible range of pressure-temperature conditions shown in the stippled pattern in figure 19. The range of possible pressure-temperature conditions, based on the mineral assemblages above displays a small amount of overlap with the two-phase (liquid + vapour) or "boiling" field; however the microthermometric data are incompatible with a boiling system.

The experimental data of Seward (1976) and Gupta (1978) indicate that silver solubility is proportional to chloride concentration (Fig. 20). Boiling of a saline fluid would increase the salinity of the residual fluid, increasing the silver solubility. Although this observation of course does little to tell us what the silver deposition mechanism was, it does suggest that the mechanism was probably not boiling.

The mechanism for silver deposition that appears to agree with the data presented in this study is mixing of a silver saturated brine solution with a less

saline fluid. The three-phase fluid inclusions that pre- and post-date silver deposition represent a fluid that must have been prevalent in the Cobalt rocks throughout the ore forming process. The two-phase inclusions that are syn-silver are less saline than the three-phase fluid inclusions. The two-phase inclusions could represent the mixture of the prevalent saline fluid, represented by three-phase fluid inclusions, with a less saline fluid.

The experimental data of Seward (1976) and Gupta (1978) suggest that fluid containing silver chloride complexes could possibly saturate with respect to silver chloride (Seward, 1976) if mixed with a less saline solution.

The experimental data (Seward, 1976 and Gupta, 1978) indicate that another possible mechanism is cooling of a silver-chloride saturated solution. If cooling was the mechanism at Cobalt, the fluid would quickly become saturated with NaCl as it cooled across the liquidus (Fig. 19) and solid inclusions of halite could be observed, as fluid inclusion trapping would occur in the Liquid + Halite stability field as observed by Skippen and Trommsdorff (1986).

Possible Sources of Silver

The spatial association of the Cobalt deposits with Archean rocks, Nipissing diabase, and Huronian sedimentary rocks suggests that any one or a combination of these rock types could have been the source of the silver. This spatial association allows the magmatic source for the diabase to be considered as the source of the silver for these deposits (Halls and Stumpfl, 1969). Lead (Thorpe *et al.*, 1986) and strontium (Kerrick *et al.*, 1986) isotopes are homogeneous, over a

wide area, and fail to identify any of the host rock types as a source for vein material (Kerrick *et al.*, 1986).

The Archean interflow sediments are the richest in As, Sb, Ag, Hg, Bi, Cu, Pb, Zn, Ni and Co (Boyle and Dass, 1971) and "many nickel-cobalt-arsenide-native silver deposits in other parts of the world cut rocks containing pre-existing sulphides".

Smyk (1987) estimated that the total amount of silver mined from the Cobalt camp, until 1987, was 500 million ounces. Jambor (1971) has shown that the Nipissing diabase could have contained sufficient quantities of silver to account for all the silver mined at Cobalt. He has calculated the amount of silver available from the Nipissing diabase, assuming an original silver content 0.5 ppm silver and 0.2 ppm silver after leaching. The lack of alteration in the diabase does suggests that large scale mass transfer of silver from the diabase has not occurred.

The Huronian sediments contain very low concentrations of metals but some thick black shale sequences within the Huronian sediments have elevated concentrations of Ag, Co, Ni and As (Kerrick *et al.*, 1986).

A parent magma source was suggested (Tyrrel, 1907 and Miller, 1913) but subsequent work has failed to produce any supporting evidence for this theory (Jambor, 1971).

The work presented in this study cannot identify any rock type as a source of silver for the veins. However, considering that the most viable mechanism of silver deposition is the mixing of a silver saturated saline brine with a less saline

fluid, there are some problems if the Huronian sediments are considered as a source of silver (Appleyard, 1980). Most of the deposits are found in small slivers of the Huronian trapped between the Archean rocks and the diabase. If the fluids responsible for the deposition of silver have come from the Huronian sediments above the diabase, it would require that the ore fluids penetrated downwards through a hot mass of diabase to deposit the silver. As the Huronian rocks do not contain high concentrations of silver, they seem a less likely source of silver.

Ideas for Further Research

Stable isotopes have been used to document mixing as the depositional mechanism for porphyry copper deposits (Sheppard and Taylor, 1974). If new mines are opened and accessible within the Cobalt camp, detailed mapping and combined fluid inclusion and stable isotope work may help to determine the mechanism(s) of silver deposition, as reconnaissance work has yielded inconclusive results (Kerrick *et al.*, 1986). Combined fluid inclusion and stable isotope work performed on deposits thought to have formed by mixing have yielded mixing lines in $\delta^{18}\text{O}$ -Wt% NaCl space (Taylor, 1987). As an appetizer to future students of Cobalt silver deposition, a plot in this space of the four samples from Kerrich *et al.* (1986) that have combined $\delta^{18}\text{O}$ and salinity determinations has been compiled (Fig 21.). Future work should include δD determinations on the fluid inclusions, to avoid reequilibration of the fluids with the oxygen bearing host minerals, at subsequent temperatures within the thermal history of the deposits, or

Figure 21. A plot of $\delta^{18}\text{O}$ in fluid inclusion waters vs. Wt% NaCl (equivalent). The four data points are from Kerrich *et al.* (1986).

$\delta^{18}\text{O}$ determinations on fluid inclusions contained within the non-oxygen bearing minerals within the deposit.

Preliminary work on fluid inclusions trapped within proustite and pyrargyrite from the cobalt deposits reveals abundant fluid inclusions. Unfortunately the extremely low salinities and the petrographic relations indicate that these minerals are alteration products of the silver and are not contemporaneous with vein formation at Cobalt.

Conclusions

Fluid inclusion studies reveal the presence of a pre- and post-ore saline fluid, represented by three-phase (L+V+H) fluid inclusions at room temperature. A fluid contemporaneous with ore deposition is represented by two-phase (L+V) liquid-dominant fluid inclusions at room temperature. A third fluid represented by two-phase (L+V) vapour-dominant fluid inclusions has been identified, but the relationship between this fluid and ore deposition has not been established.

Laser Raman spectroscopy has failed to detect CO_2 , CH_4 , N_2 and H_2S within these three fluid inclusion types.

Pressure-Temperature constraints were obtained from: 1) Petrography of calc-silicates within the veins from the Beaver-Temiskaming and Siscoe mines; 2) the three-phase fluid inclusion data; and, 3) a maximum lithostat calculation. These data yield constraints of 480 to 1500 bars and 280 to 365 °C.

SIMS analyses of the three-phase fluid inclusions, and extrapolation of existing experimental data in the $\text{CaCl}_2\text{-NaCl-H}_2\text{O}$ and $\text{NaCl-KCl-H}_2\text{O}$ ternaries into the quaternary $\text{CaCl}_2\text{-NaCl-KCl-H}_2\text{O}$ produce mole fractions of

$$X_{\text{H}_2\text{O}} = 0.822 \text{ to } 0.858, X_{\text{CaCl}_2} = 0.036 \text{ to } 0.131, X_{\text{NaCl}} = 0.018 \text{ to } 0.097, \text{ and } X_{\text{KCl}} = 0.019 \text{ to } 0.029.$$

From these observations boiling and cooling of a silver-bearing fluid seem unlikely mechanisms for silver deposition. Mixing of a silver-saturated saline brine with a less saline fluid agrees with the observation of less saline fluid inclusions associated with the ore deposition, and appears to be the most viable method of silver deposition in the veins at Cobalt, Ontario.

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APPENDIX I: Fluid Inclusion Heating/Freezing data

Table 3. Microthermometric data from three-phase (L+V+H) fluid inclusions.

Sample #	T _h (°C)	T _m _{Halite} (°C)	T _m _{ice} (°C)	T _e (°C)	Mine
BT28-R1	206.	241.		-48	BT
BT28-R2	208.	238.		-48	BT
BT28-R3	196.	236.			BT
BT28-R4	206.	239.			BT
BT28-R5	236.	243.			BT
BT28-R6	209.	247.			BT
BT28-R7	211.	230.			BT
BT28-R8	211.	227.			BT
BT28-R9	185.	243.			BT
BT28-R10	198.	237.		-42	BT
BT28-R11	218.	241.			BT
BT28-R12	215.	239.			BT
BT28-R13	206.	236.			BT
BT28-R14	217.	238.			BT
BT28-R15	199.	234.			BT
BT69-1	222.	276.			BT
BT69-4	212.	201.			BT
SS4f-FV-B3	229.	155.	-31.7		SS
SS4f-FV-B8	166.	241.	-33.1		SS
SS4f-FV-B16	193.	229.	-31.4		SS
SS4f-FV-B18	156.	230.			SS
SS4f-FV-B20	181.	245.			SS

Table 3. (Continued)

Sample #	T _h (°C)	T _m Halite (°C)	T _m ice (°C)	T _e (°C)	Mine
SS4f-FV-B24	180.	255.			SS
SS4f-FV-B25	202.	232.			SS
SS4f-FV-B1			-32.1		SS
SS4f-FV-B4			-31.7		SS
SS4f-FV-B6			-32.9		SS
SS4f-FV-B7			-32.2		SS
SS4f-FV-B11			-32.0		SS
SS4f-FV-B22			-32.4		SS
SS4f-FV-B23			-37.8		SS
E West G1	190.	215.			BT
E West G2	170.	256.			BT
Average	201.	235.	-32.7		
Standard Dev.	19.	21.	1.8		

Table 4. Microthermometric data from the two-phase (L+V) liquid-dominant fluid inclusion of the Siscoe Mine.

Sample Number	T_h	$T_{m_{ICE}}$	$T_{Eutectic}$
COB002-R1	344	-25.2	-42
COB002-R2	309	-25.3	
COB002-R3	343	-25.2	
COB002-R4	<350	-24.9	
COB002-R5	<350	-25.5	
		-11.1	
		-11.5	
		-3.5	
		-20.0	-42
		-20.0	
		-6.6	
		-20.0	
COB002-R18		-15.5	
COB002-R19		-12.5	
COB002-R7		-15.0	
COB002-R8a		-4.0	
COB002-R8b		-5.0	
Average	332	-15.0	
Stan Dev		8.4	

APPENDIX II: EDS Data from Fluid Inclusion Residues**Table 5. ATOMIC PERCENTAGES**

Sample #	Na	Cl	K	Ca	Ca:Na	K:Na	Cation/Cl
BT-69-SEM	1.73	4.38	0.23	0.75	0.43	0.13	0.79
	9.22	20.20	0.21	1.90	0.21	0.02	0.65
	7.69	20.91	0.00	1.80	0.23	0.00	0.54
	9.40	20.05	0.26	1.91	0.20	0.03	0.67
	3.16	7.49	0.16	0.69	0.22	0.05	0.63
	12.63	22.42	0.32	1.11	0.09	0.03	0.68
	5.01	9.37	0.14	0.64	0.13	0.03	0.69
	3.73	10.22	0.41	1.38	0.37	0.11	0.68
	22.15	25.03	0.24	1.35	0.06	0.01	1.00
	5.35	6.56	0.00	0.11	0.02	0.00	0.85
	2.15	3.19	0.00	0.36	0.17	0.00	0.90
	20.94	23.60	0.11	0.37	0.02	0.01	0.92
	36.73	33.80	0.05	0.39	0.01	0.00	1.11
	31.90	27.15	0.00	0.00	0.00	0.00	1.17
	37.95	33.73	0.06	0.90	0.02	0.00	1.18
	32.77	31.10	0.15	0.75	0.02	0.00	1.11
	41.11	43.20	0.10	0.35	0.01	0.00	0.97
	54.90	43.81	0.02	0.00	0.00	0.00	1.25
	0.00	12.81	0.76	6.95			1.14
	0.49	14.50	0.24	5.23	10.67	0.49	0.77
	0.94	8.28	0.59	3.79	4.03	0.63	1.10
	5.77	26.97	1.32	4.81	0.83	0.23	0.62
	4.67	12.91	0.45	3.51	0.75	0.10	0.94
	0.00	3.56	0.21	1.32			0.80
	0.38	2.22	0.03	0.65	1.71	0.08	0.77
	5.15	8.73	0.13	1.63	0.32	0.03	0.98
	0.00	1.16	0.01	0.48			0.84
Average	13.18	17.68	0.23	1.60	0.12	0.02	0.94
Stan Dev	15.37	12.20	0.28	1.73	0.11	0.02	
Pure NaCl	52.89	46.95	0.11	0.05	0.00	0.00	1.13

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