DIVERSITY OF PRECIOUS-METAL MINERALIZATION IN FOOTWALL Cu-Ni-PGE DEPOSITS, SUDBURY, ONTARIO: IMPLICATIONS FOR HYDROTHERMAL MODELS OF FORMATION

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Abstract

The magmatic origin of contact orebodies of the Sudbury structure, in Ontario, is widely accepted. The remobilization of some of the metals from the magmatic environment to the footwall by hydrothermal processes is not as widely accepted as a possible mode of formation of Cu–Ni–PGE orebodies in the footwall. However, precious-metal minerals (PMM) occur most commonly in chalcopyrite near, or at, the contact with alteration minerals such as actinolite, quartz and epidote in footwall Cu–Ni–PGE mineralization of the Sudbury Structure. Study locations include the Barnet Property, Deep Copper and Copper zones of the Strathcona mine, McCreedy West mine (Cu stringers), and the Fraser mine (Epidote Zone). The most common PMM are Pt-, Pd- and Ag-rich tellurides and bismuthides. Each deposit has a characteristic assemblage of PMM, with distinct compositions of these minerals. Among Cu–Ni–PGE mineralized zones, distinct Pt, Pd, Bi and Sb variations are most common in sobolevskite, michenerite, merenskyite, moncheite and melonite. Comparison of whole-rock concentrations of Cu, Ni, Ir, Rh, Pt, Pd and Au for the Barnet Property with that of other Cu-rich footwall deposits further illustrates the individuality of each deposit. The close spatial association of PMM with hydrous, locally Cl-bearing alteration and other rare minerals (including halides) is compatible with the influence of a H–O–Cl–S–Fe–Cu–Ni–Te–Se–Bi–As-bearing fluid in deposition of the PMM. The assemblages of the PMM and geochemical distinctions of each Cu-rich footwall deposit are a function of the interaction of contact magmatic sulfide assemblages with fluids whose compositions were buffered by rock compositions in the footwall. The metals scavenged from these primary base-metal sulfides were transported into the footwall and subsequently deposited in hydrothermal cells.

Keywords: Sudbury, footwall deposits, platinum-group elements, precious-metal minerals, hydrothermal mineralization, Ontario.

SOMMAIRE

L'origine magmatique des zones minéralisées le long du contact inférieur de la structure de Sudbury, en Ontario, ne fait plus l'objet de discussions. En revanche, la remobilisation possible de certains des métaux par lessivage des assemblages ignés et le transfert de ces métaux vers les roches sous-jacentes de la paroi inférieure ne sont pas aussi généralement acceptés comme mode de formation des gisements à Cu, Ni et éléments du groupe du platine (EGP) dans ce milieu. Toutefois, les minéraux porteurs des métaux précieux s'y trouvent le plus couramment dans la chalcopyrite près du contact ou au contact avec les minéraux associés à l'altération hydrothermale, par exemple, actinolite, quartz et épidote. Nous avons étudié l'indice Barnet et les zones Deep Copper et Copper de la mine Strathcona, la mine McCreedy West (filonnets à Cu), et la mine Fraser (zone Epidote). Les minéraux porteurs de métaux précieux sont des tellurures et des bismuthides riches en Pt, Pd et Ag. Chacun de ces gisements contient un assemblage caractéristique de ces minéraux, avec des compositions distinctes des minéraux. Parmi les zones minéralisées en Cu, Ni et EGP, des variations en Pt, Pd, Bi et Sb sont courantes dans la sobolevskite, michenerite, merenskyite, monchéite et mélonite. Une comparaison des teneurs en Cu, Ni, Ir, Rh, Pt, Pd et Au des roches globales à l'indice de Barnet avec celles des autres gisements cuprifères de la paroi inférieure illustre l'individualité de chacun. L'association étroite des minéraux porteurs de métaux précieux avec des zones hydrothermalement altérées, enrichies en Cl et minéraux rares, y compris des halogénures, est compatible avec l'hypothèse voulant qu'une phase fluide à H-O-Cl-S-Fe-Cu-Ni-Te-Se-Bi-As a été impliquée dans leur déposition. Les assemblages de ces minéraux et les distinctions géochimiques de chaque gisement cuprifère reflètent l'interaction des assemblages magmatiques près du contact avec une phase fluide dont la composition était tamponnée par la composition des roches de la paroi inférieure. Les métaux lessivés à partir des sulfures primaires ont été transportés dans la paroi inférieure et ensuite déposés au cours de la circulation hydrothermale.

(Traduit par la Rédaction)

Mots-clés: Sudbury, gisements de la paroi inférieure, éléments du groupe du platine, minéraux porteurs de métaux précieux, minéralisation hydrothermale, Ontario.

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INTRODUCTION

The dominantly magmatic origin for the Sublayer-hosted contact deposits of Ni, Cu, and platinum-group elements (PGE) of the Sudbury Structure is well established (Hawley 1962, Naldrett & Kullerud 1967, Keays & Crocket 1970, Chyi & Crocket 1976, Naldrett 1979, 1984, Hoffman et al. 1979, Naldrett et al. 1982, 1986). In addition, the genesis of Cu-rich footwall ores has also been ascribed to the magmatic fractionation of crystals of Ni-bearing Fe monosulfide solid-solution to form the contact ores, and to the segregation and subsequent migration of a Cu-rich residuum to crystallize as dikes in the footwall (Hoffman et al. 1979, Naldrett et al. 1982, Li et al. 1992, 1993, Ebel & Naldrett 1996). These Cu-rich veins commonly have selvages showing hydrothermal alteration, and saline fluid inclusions occur in both silicate and sulfide minerals (Farrow et al. 1994). However, the nature of the footwall rocks to the Sudbury Structure and their possible influence on Cu, Ni and PGE deposition have been the subject of speculation for some time. Specific questions concern what the possible control of the Sudbury Breccia in the development of footwall Cu-rich veins (Bleeker 1992, Farrow 1994, Fedorowich 1996), the influence of ultramafic units on sulfide mineralization in the Footwall Breccia (Coats & Snajdr 1984, Farrow 1994, Farrow & Watkinson 1996), and the composition of the footwall rocks (Farrow 1994). Many of the footwall deposits along the North Range of the Sudbury Structure (i.e., Barnet, Strathcona mine Copper, Deep Copper and newly discovered Cu-rich vein zones, and the veins of the McCreedy West and East deposits) are Cu-rich and PGE-bearing. Other documented examples of deposits that have formed as a result of hydrothermal concentration or modification of previously existing magmatic deposits also involve Cu and PGE-rich assemblages, and include those in Lac-des-Iles (Watkinson & Dunning 1979, Macdonald 1988), the Coldwell Complex (Good & Crocket 1989, Ohnenstetter et al. 1992), Rathbun Lake, northeastern Ontario (Rowell & Edgar 1986), Lac Sheen, Quebec (Cook & Wood 1994), Alaska (Watkinson & Melling 1992), New Rambler, Wyoming (McCallum et al. 1976, Nyman et al. 1990), the Duluth Complex. Minnesota (Mogessie et al. 1991), and Egypt (Helmy et al. 1995). In Sudbury, only the Epidote Zone orebody of the Fraser mine is unusual in that it is a hydrothermally modified deposit composed of a Ni-rich, Cu-poor sulfide assemblage, dominated by pentlandite, pyrrhotite and pyrite (Farrow & Watkinson 1992, 1996, Farrow 1994), Several fluid-inclusion studies of both silicate and sulfide host minerals have focused on the hydrothermal aspects of deposits in the Sudbury footwall (Farrow & Watkinson 1992, Li & Naldrett 1993a, Farrow 1994, Farrow et al. 1994, Watkinson et al. 1993, Watkinson 1994).

In this paper, we present the first detailed study of the platinum-group-element mineralogy of several footwall Cu–Ni–PGE occurrences in the North Range at Sudbury, including the Barnet property and the Epidote Zone, Fraser mine; we summarize these and other PGM occurrences elsewhere in the Sudbury structure. These results, in addition to a synthesis of precious-metal geochemistry of ore from selected deposits along the North Range, are used to support a model of development of footwall Cu–Ni–PGE mineralization that emphasizes the importance of aqueous fluids in the Sudbury footwall as an alternative to more traditional models based on magmatic fractionation.

GEOLOGICAL CONTEXT

Cu-Ni-PGE deposits evaluated in this study (Fig. 1) are located in footwall units at the base of the Sudbury Igneous Complex (SIC). These units consist of Archean mafic to felsic gneisses and migmatites of the Levack Gneiss Complex in the North Range, and sedimentary and volcanic rocks of the Huronian Supergroup that have been intruded by granitic plutons in the South Range. Pseudotachylitic Sudbury Breccia is developed as irregularly oriented veins and masses throughout the footwall to the SIC. The Sublayer and Footwall Breccia comprise lenses and sheets between the basal norites of the SIC and footwall units (Cowan 1968, Greenman 1970, Pattison 1979, Coats & Snajdr 1984, Sweeny et al. 1990). These breccias host the volumetrically most important contact Ni-Cu-PGE deposits of the North Range of the Sudbury structure. Detailed descriptions of some Cu-Ni-PGE deposits and associated host-rocks in the Onaping-Levack area are provided by Coats & Snajdr (1984) and Farrow (1994).

A schematic section through the Strathcona area (Fig. 2) shows the location of the Barnet Main Cu Zone, Longvack open-pit mine, Strathcona Deep Copper and Copper zones, and the Fraser mine Epidote Zone, and their geological settings projected onto one plane.

Cu-Ni-PGE deposits of the North Range footwall

Cu-Ni-PGE deposits of the North Range footwall commonly consist of complex networks of chalcopyriterich veins in zones of Sudbury Breccia and, less commonly, in weakly brecciated gneiss and migmatite of the Levack Gneiss Complex. On a broad scale, the development of Sudbury Breccia is localized along lithological boundaries. On a smaller scale, the distal extensions of systems of Cu-rich veins show that individual veins and stringers are localized along clast-matrix boundaries within Sudbury Breccia.

The Main Cu Zone of the Barnet property is 1500 m northeast of the Strathcona and Coleman mine headframes, and less than 500 m from the mined-out Longvack Ni–Cu open pits. The complex system of Cu-rich veins is located at the contact between a zone of Sudbury Breccia and footwall tonalitic diatexite (Farrow 1994).

The Strathcona mine is located at a zone of thickened Sublayer referred to as the Strathcona Embayment (Coats & Snajdr 1984). The Copper and Deep Copper zones are composed of Cu-rich veins in footwall units approximately 300 and 600 m, respectively, from the contact. The Copper Zone occurs in weakly brecciated footwall gneiss and





FIG. 2. Schematic cross-section through the Strathcona mine area, looking east. The section has been simplified to show only Cu–Ni–PGE mineralization examined in this investigation, and not contact orebodies. Modified from Farrow & Watkinson (1996).

migmatite, whereas the Deep Copper Zone is located in Sudbury Breccia.

The McCreedy West (formerly Levack West) deposit is located at the western end of the Onaping-Levack Ni-Cu-PGE mineralized belt. The main ore-zone at McCreedy West consists of mineralized Footwall Breccia that occupies a footwall embayment (Hoffman *et al.* 1979, Coats & Snajdr 1984). This zones continues into a Footwall Ore Zone composed of Cu- and locally Ni-rich veins that extend into footwall units and associated Sudbury Breccia (Coats & Snajdr 1984, Morrison *et al.* 1994).

Ni-Cu-PGE mineralization in the Footwall Breccia

The Longvack open-pit mine, located approximately 1000 m northeast of the Strathcona mine headframes, was operated from 1956 to 1961 (Coats & Snajdr 1984). It consisted predominantly of pyrrhotite-rich Footwall Breccia ore that extended down-dip along the basal contact of the SIC. Small chalcopyrite-rich stringers and veinlets occur in the footwall gneisses and migmatites, Sudbury Breccia, and locally in the Footwall Breccia, in the vicinity of the Longvack mine.

The Epidote Zone of the Fraser mine consists of lenticular masses of altered rock largely developed in Footwall Breccia. They are dominantly composed of epidote and amphibole, with less abundant magnetite, pyrite and pentlandite (Farrow & Watkinson 1992, 1996, Farrow 1994). They range in thickness from approximately 1 to 150 m and are typically oriented subparallel to the SIC contact.

Lindsley 4b deposit of the South Range footwall

The Lindsley 4b Ni–Cu–PGE orebody occurs as irregular to vein-like footwall ore-zones of massive sulfide in granitic rocks of the Murray pluton, near the margin of the Contact Sublayer of the SIC (Binney *et al.* 1992, 1994, Watkinson 1994). Most of the samples analyzed for this investigation are from the contact of the 4b zone with the Murray pluton.

ALTERATION-RELATED ASSEMBLAGES

Abel et al. (1979) and Abel (1981) recognized dark alteration-induced selvages adjacent to most of the Cu-Ni-PGE veins in the footwall rocks of the Strathcona mine. Li et al. (1992) and Li & Naldrett (1993a) described "hydrothermal ore" as Cu-rich mineralization characterized by abundant epidote, quartz and calcite at terminations of sulfide veins that make up "magmatic ore". Two different styles of alteration are associated with Cu-Ni-PGE deposition in the North Range of the Sudbury structure (Farrow & Watkinson 1992, Farrow 1994). They consist of alteration assemblages of amphibole (actinolite and rare hastingsite) + epidote + chlorite + quartz \pm albite \pm K-feldspar ± calcite that occur adjacent to Cu-rich veins, and amphibole (actinolite to ferro-actinolite) + epidote + titanite \pm magnetite \pm pyrrhotite \pm pentlandite \pm pyrite \pm quartz in the concentrically zoned Epidote Zone of the Fraser mine. On the basis of field relationships, Farrow (1994) suggested that both types of alteration developed after emplacement of the contact orebody and of the SIC.

Sulfides in Cu-rich veins replace alteration minerals at the boundary of the sulfide and silicate grains. They overgrow epidote, quartz, amphibole and albite, and commonly invade amphibole along cleavage traces and grain boundaries. Locally, alteration minerals (especially quartz and epidote) and sulfides seem to have coprecipitated. Where sulfides have formed with alteration minerals such as epidote, the silicate contains numerous irregularly shaped inclusions of sulfide. Calcite tends to occur as a late replacement of previously precipitated alteration-related silicates; it is seldom found with precious-metal minerals. The only exception is an association with native Ag in bornite. The individual alteration-related masses of the Epidote Zone are most intensely altered in their central part. They have been subdivided into facies identified by epidote, amphibole and magnetite "index" minerals that correspond to increasing degrees of alteration and associated changes in fluid composition (Farrow & Watkinson 1992, 1996, Farrow 1994). The final mineralogical change occurs in the magnetite-rich facies, where calcite partially replaces magnetite.

SULFIDE MINERALOGY

The Cu-rich sulfides of the Copper and Deep Copper zones, McCreedy West Cu stringers and Barnet Main Cu Zone occur as massive veins (up to 3 m wide), veinlets and disseminations. The dominant sulfide is chalcopyrite, with variable amounts of cubanite, pentlandite, pyrrhotite and minor pyrite. Millerite and bornite are most common in the thin (<20 cm wide) extensions of the large systems of veins. Magnetite and, less commonly, ilmenite, are most strongly developed near vein margins, and are commonly replaced by chalcopyrite and cubanite along grain edges. Disseminated sulfides, especially very fine-grained chalcopyrite, are ubiquitous in most strongly developed alteration-induced selvages and extend into the host rock even around thin chalcopyrite-rich veinlets. Trace minerals in footwall vein sulfides are sphalerite (ZnS), galena (PbS), Se-bearing galena (Pb[S,Se]), altaite (PbTe) and parkerite (Ni₃[Bi,Pd]₂S₂). Ferrotantalite (FeTa₂O₆) was identified in quartz inclusions in chalcopyrite in one sample. Bismuthinite (Bi2S3) and a variety of bismuth tellurides also have been identified in Cu-rich stringers.

The presence of minor chalcopyrite, the development of epidote-, actinolite- and magnetite-rich alteration, and a Ni-rich, pyrite-, pentlandite- and pyrrhotite-dominated sulfide mineral assemblage are characteristic of the Epidote Zone. Later-formed, subhedral pyrite typically overgrows other sulfide minerals. In the magnetite-rich Epidote Zone, chalcopyrite, although rare, occurs more commonly than in the actinolite- and epidote-dominated facies (Farrow 1994, Farrow & Watkinson 1996).

PRECIOUS-METAL MINERALS

A wide variety of accessory minerals and precious-metal minerals, dominantly Pt- and Pd-rich bismuthides and tellurides, have previously been identified in the Deep Copper (Strathcona) and McCreedy West orebodies (Hawley & Berry 1958, Cabri & Laflamme 1976, Springer 1989, Watkinson 1990, Li & Naldrett 1992, 1993b). As part of this investigation, PGM-bearing samples from the Barnet property, Copper Zone of the Strathcona mine and the Epidote Zone of the Fraser mine, as well as from other Sudbury deposits, were studied for comparative purposes. The precious metals most commonly occur as discrete minerals in base-metal sulfides, oxides or silicates, not only in the Deep Copper Zone (Springer 1989, Li & Naldrett 1993b), but in other deposits as well (Cabri & Laflamme 1976, Naldrett 1984, Jago *et al.* 1994).

Samples from the Barnet property were taken from



FIG. 3. a. Back-scattered electron image of a composite grain of sobolevskite (s), froodite (f) and hessite (h), located at contact between chalcopyrite and amphibole. Sample 27A0C0–K1B from the Copper Zone, Strathcona mine. b. Back-scattered electron image of a large composite grain of froodite (f), michenerite (m), parkerite (p) and hessite (h), located at contact between blebby chalcopyrite and epidote. Sample 27A0C0–K1B from the Copper Zone, Strathcona mine. c. Back-scattered electron image of a large composite grain of froodite (f), michenerite (mo), parkerite (p) and hessite (h), located at contact between blebby chalcopyrite and epidote. Sample 27A0C0–K1B from the Copper Zone, Strathcona mine. c. Back-scattered electron image of a large composite grain of hessite (h) and moncheite (mo), located at contact of chalcopyrite (cp), chlorite and epidote. Epidote and titanite grains are almost enveloped by the composite precious-metal minerals. Sample MW–600–1 from McCreedy West. The grains are hosted by chlorite and epidote at the margin of a chalcopyrite vein. Sample MW–600–1.

the Main Cu Zone, both from chalcopyrite-rich veins >20 cm across and from disseminated chalcopyrite in Sudbury Breccia. All the precious-metal minerals from the Barnet property are small (commonly <5 μ m in diameter), individual grains of telluride and selenide. Hessite (Ag₂Te), merenskyite ([Pd,Pt]][Te,Bi]₂), naumannite (Ag₂Se) and Pd-bearing melonite ([Ni,Pd]Te₂) were identified. Chalcopyrite is the most common host mineral, with others being epidote, pyrite, quartz and amphibole. In one sample, numerous grains of naumannite coexist with abundant inclusions of chalcopyrite in pyrite, suggesting that Ag and Se may have existed as trace constituents within the chalcopyrite before it was replaced by subhedral pyrite.

Although native Ag was not recognized as a discrete phase as part of this study, an accidental inclusion of native Ag was previously identified with chlorargyrite (AgCl₂) in a fluid inclusion with chalcopyrite from the Barnet property (Farrow 1994, Farrow *et al.* 1994).

Platinum-group minerals (PGM) were identified in samples from all three levels (3700, 3900 and 4200) of the Deep Copper Zone. They were found in a chalcopyrite-rich vein, the quartz-rich altered margin to a chalcopyrite-rich vein, and the bornite-rich termination of a Cu vein. Precious-metal minerals identified from the Deep Copper Zone include sobolevskite (PdBi), moncheite ([Pt,Pd][Te,Bi]₂), froodite (PdBi₂), hessite (Ag₂Te),



FIG. 4. Concentrations of Pt versus Pd in samples (filled squares) from the Epidote Zone (whole-rock geochemical data from Farrow & Watkinson 1996). Circles represent samples that contain PGE-bearing minerals.

Pt-bearing melonite ([Ni,Pt]Te₂), and native Ag. This partial assemblage, richer in Bi than the assemblage at Barnet, is similar to that identified in recent studies of PGM in the Deep Copper Zone (Li & Naldrett 1992, 1993a, Springer 1989). Except for two grains of sobolevskite in chalcopyrite, all other precious-metal minerals were found in quartz and epidote, most commonly at grain boundaries. In their study, Li & Naldrett (1992, 1993a) determined that most of the PGM occur at the margins of sulfides. Chlorinebearing PGM also were reported by Li & Naldrett (1993a), and include an unnamed Pd–Bi chloride and an unnamed Cl-bearing Pd–Bi sulfide. In addition, a grain of native Ag 1 mm in diameter, enveloped by chlorargyrite (AgCl₂), has been identified in calcite and bornite in a sample from the Deep Copper Zone (Farrow 1994).

Samples from the Copper Zone were taken from the altered margins of chalcopyrite-rich veins on two levels in the mine. Froodite (PdBi₂) is the most common PGM in the Copper Zone of the Strathcona mine, and is found as part of large composite grains also composed of michenerite ([Pd,Pt]BiTe), sobolevskite (PdBi), hessite (Ag₂Te) and parkerite (Ni₃[Bi,Pb]₂S₂; Figs. 3a, b). Other precious-metal minerals from the Copper Zone are Au–Ag alloy, niggliite (PtSn), sperrylite (PtAs₂), native Ag, and unnamed (Pt,Pd)(Bi,Te)₂ that chemically resembles the (Pt,Pd)(Bi,Te,Sn)₂ reported by Li & Naldrett (1992, 1993b) from the Deep Copper Zone. Most of the precious-metal minerals occur at the contact between chalcopyrite and epidote or amphibole.

Samples from the McCreedy West orebody were taken along the altered margins of chalcopyrite-rich veins from the 500, 600 and 950 levels. Precious-metal minerals from Cu-rich stringers commonly occur as large composite grains that include michenerite (PdBiTe), platinian michenerite ([Pd,Pt]BiTe), hessite (Ag₂Te), tellurohauchecornite (Ni₉BiTeS₈), moncheite ([Pt,Pd][Te,Bi]₂) and unnamed bismuth tellurides (Figs. 3c, d). Composite moncheitehessite grains are the most common. The close relationship between moncheite and hessite also was found by Cabri & Laflamme (1976) in their study of PGM in the McCreedy West and Creighton orebodies. The most common host-mineral is chalcopyrite, with some grains in amphibole, and some at silicate-sulfide grain margins.

Merenskyite ([Pd,Pt][Te,Bi]₂), hessite (Ag₂Te) and a variety of Pb-bearing bismuth tellurides were identified in chalcopyrite, pyrite and epidote from the Longvack property. Samples that contain precious-metal minerals, which are disseminated chalcopyrite and pyrrhotite sulfides in Footwall Breccia, come from the remains of the walls of the Longvack open pit.

The discovery of PGM in the Epidote Zone was unexpected because of the low (<1000 ppb) levels of Pt and Pd in specimens from the various alteration-induced facies (Fig. 4). Investigated samples were taken from four exploration diamond-drill cores that intersected the Epidote Zone and surrounding rock-types in the Fraser mine. These samples are from a set that provided the basis for a detailed geochemical study of the Epidote Zone



FIG. 5. Back-scattered electron images taken of samples from the Epidote Zone, Fraser mine. a. Composite moncheite (mo) – hessite (h) grain in host pyrite at a contact with magnetite and pentlandite. Sample 147–11. b. Subhedral grain of moncheite (mo) in actinolite, with several smaller inclusions. Compositional domains in the actinolite are barely visible. Pentandite and pyrite are the nearby sulfides. Sample 287–6. c. Elongate grain of merenskyite (me) along actinolite (a) cleavages. The surrounding sulfide is pyrite. Host is altered ultramafic rock. Sample 150–13. d. Concentration of moncheite (mo) grains within irregularly shaped magnetite (ma) and serpentine (s). Host is altered ultramafic rock. Sample 150–13.

(Farrow & Watkinson 1996). All the precious-metal minerals identified are tellurides or bismuth tellurides, dominated by moncheite ([Pt,Pd][Te,Bi]2), and they are typically found in magnetite-bearing facies of the Epidote Zone (Fig. 5a). Other phases include hessite, merenskyite, Pd-bearing melonite and Pt-bearing melonite. The most common host-minerals are pyrite, pentlandite and amphibole (Figs. 5b, c). Typical characteristics of PGM-bearing samples are the existence of magnetite adjacent to the precious-metal host, and small (<10 µm in diameter) inclusions of Se-bearing galena in pyrite. Traces of seleniferous galena have also been identified in the copper-rich Victor Deep and McCreedy East orebodies (Jago et al. 1994). Moncheite and merenskyite were also encountered in samples of altered ultramafic rocks from the footwall and sublayer adjacent to a zone of well-developed Epidote Zone (Fig. 5d).

Farrow & Watkinson (1996) showed that Ir and Os contents increase, whereas Pt and Pd contents remain relatively constant, with increasing alteration in the Epidote Zone. However, no Ir- or Os-bearing PGM were identified in the Epidote Zone.

CHEMICAL COMPOSITION OF PRECIOUS-METAL MINERALS

Analytical techniques

Most of the chemical data and images were collected with Carleton University's JEOL 6400 digital scanning electron microscope, interfaced with a LINK eXL energy-dispersion X-ray analyzer. The operating conditions for analysis were: accelerating voltage 20 kV, beam current 0.5 nA, counting time 120 seconds. Pure metals and synthetic alloys were used as standards. The data were processed

TABLE 1. CHEMICAL COMPOSITION OF FROODITE AND SOBOLEVSKITE

			Ele	ments wt.	%		Atomic Proportions			
Sample	Mineral	Pd	Pt	Te	Bi	Total	Pd	Pt	Те	Bi
27A0C0-H1	Froodite	19.29	-	-	81.01	100.29	1.00	-	-	1.89
27A0C0-H1	Froodite	19.31	-	-	79.29	98.60	1.00	-	-	1.96
898-5A	Froodite	21.58	-	-	78.55	100.13	1.00	-	-	1.85
R-11	Froodite	19.45	0.96	-	79.25	99.66	0.97	0.03	-	2.02
R-11	Froodite	19.07	0.42	-	80,10	99.59	0. 99	0.01	-	2.11
R-9	Froodite	20,94	0.31	-	78.77	100.02	0.99	0.01	-	1.90
S37-1	Sobolevskite	33.03	-	8.70	56.62	98.35	1.00	-	0.22	0.87
S37-1	Sobolevskite	34.51	-	9.18	55,22	98.91	1.00	-	0.22	0.81

Sample 27A0C0-H1 is from the Strathcona mine, Copper Zone (at chalcopyrite-amphibole contact. Froodite coexists with nigglifte, electrum and insizwaite). Sample S37-1 is from the Strathcona mine, Deep Copper Zone (in chalcopyrite). All other samples are from the Lindsley mine, 4B Zone. - denotes below detection limits.

TABLE 2.	CHEMICAL	COMPOSITION O	F MICHENERITE

		1	Elements wt.	%		Atomic Proportions					
Sample	Pd	Pt	Te	Bi	Total	Pd	Pt	Te	Bi		
L-25	21.86	0.85	29.2	47.74	99.65	0.98	0.02	1.09	1.09		
R-16	17.4	8.67	28.17	45.39	99.63	0,79	0,21	1.05	1.04		
MW-950-LC	14.22	13.06	25.22	46.92	99.42	0.65	0.35	1.00	1.1		
MW-950-LC	14.43	12.73	25.78	46.03	98.97	0.67	0.33	0.92	1.01		
MW-950-LC	15.01	12.68	26.05	46.53	100.27	0,70	0.31	0.95	1.05		
MW-950-LC	14.09	13.57	26.26	46.23	100.15	0.65	0.35	1.00	1.05		
MW-950-LC	14.5	11.8	25.89	45,83	98.02	0.69	0.31	0.91	1.00		

Sample L-25 is from the Lindsley mine, 4B Zone. High-Pt nichenerite sample R-16 is from the Lindsley mine, 4B Zone. Sample MW-950-LC is from the McCreedy West Cu-rich stringers (hosted by chalcopyrite and amphibole).

with LINK ZAF4-fls deconvolution matrix software. Analyses of material from the Lindsley suite were made at the BRGM–CNRS, Orléans, France, with conditions of analysis as described by Ohnenstetter *et al.* (1992).

Froodite, PdBi₂

Froodite was encountered only in samples from the Copper Zone. It ranges from pure PdBi₂ to compositions with minor substitution of Pt for Pd (Table 1). The froodite is similar in composition to that reported from the nearby Deep Copper Zone (Li & Naldrett 1992, 1993a) and Coleman (Cabri & Laflamme 1976) deposits, and several South Range mines (Cabri & Laflamme 1976).

Sobolevskite, PdBi

Sobolevskite was found in both the Deep Copper and Copper zones. The only previously reported occurrences of sobolevskite in the Sudbury area are from the Deep Copper Zone, where it was found to be intergrown with froodite, native bismuth and bismoclite (BiOCl; Li & Naldrett 1992, 1993a), and from the Victor Deep and McCreedy East orebodies (Jago *et al.* 1994). The compositions that they reported showed no substitution for either Pd or Bi. However, our data show up to 22 at.% replacement of Bi by Te (Table 1). One analysis of material from the Deep Copper Zone yielded considerable Sb (1.3 wt.%) and Pb (3.6 wt.%).

Michenerite, (Pd, Pt)BiTe

Michenerite from the Copper Zone contains no Pt (Table 2). However, all but one analysis from McCreedy West show significant Pt substitution for Pd (range 4.5 to 13.6 wt.%). The range of Pt incorporation recorded from this study is much higher than that reported by Li & Naldrett (1992, 1993a) from the Deep Copper Zone, but is similar to that from McCreedy West (Cabri & Laflamme 1976). Cabri & Laflamme (1976) reported the presence of Pt, less commonly with smaller quantities of Sb, as characteristic of michenerite along the North Range, in comparison to michenerite from South Range deposits. However, michenerite from the Lindsley mine in the South Range shows ubiquitous substitution of Pt for Pd, ranging from 0.62 to 7.78 wt.%. Conversely, ubiquitous substitution of Sb for Bi in the michenerite from Lindsley (range 0.21 to 3.16 wt.%) supports the statement made by Cabri & Laflamme (1976) that South Range michenerite is more Sb-rich than that from North Range deposits. On a Bi - (Te + Se) - (Pd + Pt + Ni) projection (Fig. 6), the fields for michenerite from the Copper Zone and McCreedy



FIG. 6. Bi – (Pd + Pt + Ni) – (Te + Se) plot (atomic proportions) showing the compositional characterisitics of michenerite (both Pt-rich and Pt-poor) from the Copper Zone of the Strathcona mine and McCreedy West Cu stringers (data from this study), compared to data reported by Cabri & Laflamme (1976) for several locations, and by Li & Naldrett (1992) and Li et al. (1993) for the Deep Copper Zone. Also shown are compositions of merenskyite from the Epidote Zone of the Fraser mine, Barnet, Longvack and Lindsley orebodies.

West documented here overlap with compositions reported for the Deep Copper Zone (Li & Naldrett 1992, 1993a). However, the data on michenerite reported by Cabri & Laflamme (1976) and those from the Lindsley 4B orebody are more depleted in Bi and enriched in Te than those from this study. Hoffman & MacLean (1976) determined that michenerite forms an extensive solid-solution by substitution involving Bi and Te, from Pd_{0.99}Bi_{0.79}Te_{1.22} to Pd_{0.95}Bi_{1.11}Te_{0.94} below 489°C, the start of melting of Bi-rich michenerite.

Merenskyite, (Pd,Pt)(Te,Bi)₂ and moncheite, (Pt,Pd)(Te,Bi)₂

Merenskyite has been identified in samples from the Barnet and Longvack properties, whereas moncheite occurs in the Epidote and Deep Copper zones, and in the McCreedy West Cu-rich stringers (Table 3). All grains of merenskyite analyzed in this study contain Pt (up to 8.5 wt.%). Similarly, Bi contents vary widely among analyzed samples, with the highest encountered in samples from the Epidote Zone (Fig. 7). The Ni content in merenskyite from the Epidote Zone also is higher (between 1.7 and 2.2 wt.%) than in that from other locations, likely a reflection of the more Ni-rich nature of this deposit.

Bismuth contents of moncheite, like merenskyite, vary widely within and among deposits (Fig. 8). Moncheite from the Epidote Zone contains up to 2.0 wt.% Ni, whereas moncheite from the McCreedy West Cu-rich stringers and Deep Copper Zone contain very little to no Ni (up to 0.53 wt.%). The moncheite from McCreedy West analyzed in this study is compositionally similar to that analyzed by Cabri & Laflamme (1976).

Insizwaite, (Pt,Pd)(Bi,Te)₂

One grain of $(Pt,Pd)(Bi,Te)_2$ was found adjacent to froodite in the Copper Zone, near grains of hessite, sperrylite, niggliite and Au–Ag alloy. The small grain-size has limited the determination of its optical characteristics. It is similar to the $(Pt,Pd)(Bi,Te,Sn)_2$ phase identified by Li & Naldrett (1992) in the Deep Copper Zone, although it does not contain Sn. According to these authors, this unnamed phase also is associated with froodite and hessite. The grain analyzed in this study also is similar to insizwaite $[Pt(Bi,Sb)_2]$, although it does not contain Sb.A $Pt(Bi,Te,Sn)_2$ phase also was mentioned by Springer (1989) from the Deep Copper Zone, but it was identified as niggliite. However, the "moncheite" identified by Springer (1989) in the Deep Copper Zone bears considerable resemblance to the phase analyzed here.

Niggliite, PtSn

Niggliite was identified as part of a composite grain with Au-Ag alloy and froodite in the Copper Zone. It displays

				Elemen	ts wt.%						Atomic	Ргорог	tions		
Sample	Pd	Pt	Ag	Ni	Bi	Те	Sb	Total	Pd	Pt	Ag	Ni	Bi	Te	Sb
CFA-91-2	25.01		2.33		5.25	64.37	-	96.96	0.90	-	0.10	-	0.07	1.23	
L-04	26.55	0.62	0.17	-	16.05	55.81	0.58	99.78	0.98	0.01	0.01	-	0.3	1.71	0.02
L-12B	24.59	2.22	-	0.49	15.34	56.33	0.53	99.5	0.92	0.05	-	0.03	0.29	1.76	0.02
L-12B	24.7	2.49	-	0.51	15.77	56.19	0.38	99.56	0.92	0.04	-	0.03	0.3	1.75	0.01
L-13A	24.28	2.49	0.3	0.32	21.15	51.11	0.33	99.98	0.92	0.05	0.01	0.02	0.4	1.6	0.01
L-13A	24.14	2.54	0.06	0.38	21.42	50.71	0.36	99.61	0.92	0.05	0.002	0.03	0.41	1.59	0.01
L-13B	24.3	2,77	0.22	0.29	21.56	50.65	0.45	100.24	0.91	0.06	0.01	0.02	0.41	1.58	0.01
L-13B	24.5	2.41	0.28	0.19	21.71	50.81	0.39	100.29	0.93	0.05	0.01	0.01	0.41	1.59	0.01
L-17	23.53	5.43	0.08	0.03	22.18	49.09	0.36	100.70	0.88	0.11	0.003	0.002	0.42	1.52	0.01
S 37-1	2,35	35.05		-	23.4	37.25	-	98.06	0.11	0.89	-		0.55	1.45	-
MW600-1	3.58	32.66		0.38	21.46	40.68	-	98.76	0.16	0.81	-	0.03	0.47	1.46	
MW600-1	3.5	33.83	-	-	20.92	41.57	-	99.82	0.16	0.84	-	-	0.49	1.58	
MW500-1	2.11	36.03	•	-	22.36	38.96	-	99.46	0.1	0.9	-	-	0.52	1.49	-
147-11	1.87	33.07		1.98	10.06	52.33	-	99.31	0.08	0.77	-	0.15	0.22	1.86	-
150-13	7.34	29.76	-	-	14.62	50.12	-	101.84	0.31	0.69	-	-	0.28	1.58	-
287-6	1.98	36.43	-	1.38	2 63	58 24		100.66	0.10	0.90		-	0.05	1 85	-

TABLE 3. CHEMICAL COMPOSITION OF MERENSKYITE AND MONCHEITE

Mercesskyits-bearing sample CFA-91-2 is from the Barnet Property (chalcopyrite host). Samples L-04, L-12B, L-13A, L-13B, and L-17 are from the Lindsby mine, 4B Zone. Monohetic-bearing sample S37-1 is from the Strathcona Deep Copper Zone (pridote and quartz box). Samples MW600-1 (chalcopyrite bast, commonly as part of composite garais with hessite and michaenerite) and MW7-00-1 (hosted by chalcopyrite and epidote) are from the McCreedy West Cu-rich stringers. Samples 147-11 (MAGZ attention facies, at contact between pyrite and magneticits, part of composite garai with hessite). S10-13 (n atterout humanifor rook occurring with magnetite and serpentino), and 287-6 (ACTZmag alteration facies, hosted by amphibole) are from the Fraser mine, Epidote Zone. - denotes below detection limits.

a similar incorporation of Pd (0.80 to 0.94 wt.%) as niggliite reported from the Deep Copper Zone (Li & Naldrett 1992, 1993a). Sb contents in the same grain range from 0 to 2.3 wt.%, consistent with those in material from the nearby Deep Copper Zone (Li & Naldrett 1992, 1993a) and Coleman mine (Cabri & Laflamme 1976).

Sperrylite, PtAs₂

One grain of sperrylite was found in amphibole, along with chalcopyrite, froodite, niggliite, Au–Ag alloy, hessite and possible insizwaite from the Deep Copper Zone. The extent of Sb-for-As substitution (1.7 to 2.5 wt.%) is higher in this grain than in sperrylite from the Deep Copper Zone (Li & Naldrett 1992), from a variety of South Range deposits and the Coleman mine (Cabri & Laflamme 1976), and from the Lindsley mine.

Melonite, (Ni,Pd)(Te,Bi)₂ and (Ni,Pt)(Te,Bi)₂

Palladium-bearing melonite has previously been reported from the Sudbury area (Cabri & Laflamme 1976, Chen 1993). Compositions of samples analyzed from the Epidote Zone and the Barnet property are similar to those reported by Cabri & Laflamme (1976), but have considerably lower Bi contents (less than 4.1 wt.%). Although there is no Pt in Pd-bearing melonite from the Epidote Zone, Pt contents range from 3.9 to 5.1% at Barnet (Table 4). This is higher than in any other reported example of Pd-bearing melonite at Sudbury. Platinum-bearing melonite has been identified in samples from the Epidote and Deep Copper zones.

Rucklidge (1969) and Cabri & Laflamme (1976) have reported that a solid solution exists between melonite and merenskyite. Similar observations have been reported from Italy (Garuti & Rinaldi 1986) and Egypt (Helmy *et al.* 1995). Data compiled in this investigation indicate that a solid solution exists between Pd- and Pt-bearing melonite and moncheite. Compositions of moncheite and Pd-bearing melonite from a variety of locations are shown on a Pd-Ni-Pt plot (Fig. 9). Nickel-bearing moncheite from the Epidote Zone has been included. Despite the extent of Pd incorporation in these samples, a trend can be identified from the Pt apex to Pd-bearing melonite with a Ni:Pd ratio of approximately 3:1.

Ag-Au Alloy

Considerable interference by the host sulfides affected the analysis of grains of Ag–Au alloy from the Copper Zone because of their small size. However, compositions range from Ag₆₀ to Ag₇₄ (Table 5). This Au content is lower than that reported by Money (1992) for Ag–Au alloy from the nearby Deep Copper Zone (Ag₅₃₋₆₈) and by Jago *et al.* (1994) for McCreedy East (~Ag₅₀). Au–Ag alloy from McCreedy West is much richer in Au (Au₅₉₋₆₃). Native Ag was identified in bornite, and in epidote and amphibole, from the Deep Copper and Copper zones.

Hessite, Ag₂Te

Hessite is the most common precious-metal mineral identified in this investigation. It occurs alone or with PGM, and is typically very close to its ideal composition (Table 6). However, Se contents in hessite from the Deep Copper Zone range from 0 to 0.84 wt.%. Although data are limited, Se substitution for Te in hessite from Longvack ranges from 0.71 to 0.88 wt.%.



FIG. 7. Pd – (Te + Bi) – Pt plot (atomic proportions) of merenskyite and moncheite compositions (data from this study) compared to those from other Sudbury locations. Additional data on "moncheite" from the Deep Copper Zone, Strathcona mine are from Springer (1989). Data on material from the Creighton mine and McCreedy West mine are from Cabri & Laflamme (1976).

Naumannite, Ag₂Se

Naumannite was identified only at Barnet, both in polished thin section and as an accidental phase in fluid inclusions in chalcopyrite. It displays very limited substitution of Se by Te and As (Table 7).

Tellurohauchecornite, Ni₉BiTeS₈

Although hauchecornite has been previously identified in the Deep Copper Zone (Snajdr 1985, Springer 1985, Springer & Collins 1982), the hauchecornite-group mineral analyzed from McCreedy West contains no Sb, but subequal proportions of Bi and Te. There is minor substitution of Co for Ni (0.88 to 1.1 wt.%) and of Pb for Bi (0 to 2.6 wt.%). The presence of tellurohauchecornite has also been reported in the Victor Deep and McCreedy East deposits, although no analyses were made (Jago *et al.* 1994).

THE GEOCHEMISTRY OF METALLIC ELEMENTS IN THE CU-RICH VEINS

Eight samples from the Barnet Property were analyzed for Cu, Ni, S, Ir, Rh, Pt, Pd and Au (Table 8). These data have been combined with a geochemical database of more than 400 samples collected from drill-core sampling, channel sampling and grab sampling, provided by Falconbridge Limited (Exploration). The distribution of metallic elements at the Barnet Property is compared to that of other Cu-rich footwall deposits, including the Deep Copper (Li *et al.* 1992, Money 1992, 1993) and Copper (Li *et al.* 1992) zones at the Strathcona mine, and the McCreedy West Cu-rich stringers (Hoffman *et al.* 1979).

A comparison of Pt/(Pt + Pd) frequency plots from Barnet, Copper Zone, Deep Copper Zone and McCreedy West Cu-rich stringers shows that samples from the Barnet property have a higher Pt/(Pt + Pd) value, averaging 0.55, than from any of the other locations (Fig. 10). Samples with Pt and Pd contents below detection limits are not included on these diagrams. Samples from the Deep Copper Zone have much lower Pt/(Pt + Pd) values (~0.4), but the distribution is skewed to higher values. The Pt/(Pt + Pd) values at Barnet are most similar to those from the Copper Zone. Further comparison of PGE ratios with other Cu-rich vein deposits also illustrates the geochemical variation among the various Cu-rich zones in the footwall. The Barnet main zone has a considerably lower value of $(Pt + Pd)/Ir (3 \times 10^3)$ than do both Deep Copper Zone (9×10^4) , Copper Zone (11×10^4) and McCreedy West Cu-rich stringers owing



FIG. 8. Bi – (Pd + Pt + Ni) – (Te + Se) plot (atomic proportions) showing moncheite compositions from the Epidote Zone, Cu-rich stringers from the McCreedy West mine, and Deep Copper Zone of the Strathcona mine, compared to those from McCreedy West and Creighton mines reported by Cabri & Laflamme (1976).

			TAB	le 4. Che	MICAL CO	OMPOSITIC	DN OF ME	LONTTE			
			Eleme	nts wt.%		Atomic Proportions					
Sample	Pd	Pt	Ni	Te	Bi	Total	Pd	Pt	Ni	Te	Bi
5C1	7.14	5.05	11.21	73,56	1.36	98,32	0.24	0.09	0.67	1.8	0.02
287-7	3.04	20.07	6.16	62.51	5.25	97.04	0.13	0.43	0.44	1.86	0.1
287-7	3,79	20.18	5,8	63.01	5.52	98,29	0.15	0.43	0.41	1.85	0.1

Pd-rich melonite-bearing sample 5C1 is from the Barnet Property, Pt-rich melonite-bearing sample 287-7 is from the Fraser mine, Epidote Zone (ACTZ alteration facies, hosted by pyrite).

to its lower Pt and Pd abundances. Ni/Cu values in the Barnet suite average 0.03, similar to those from Copper Zone (0.01), but less than those from Deep Copper zone and McCreedy West Cu-rich stringers. This finding is compatible with the abundance of pentlandite and millerite, respectively, in the chalcopyrite-rich veins of these orebodies. Pd/Ir values in the Barnet suite (1900) are similar to those from McCreedy West, but are slightly lower than those reported for either of Strathcona's Cu-rich orebodies. A chondrite-normalized diagram of the Barnet data and those from Deep Copper and Copper zones, and both disseminated and massive sulfide vein ore in Sudbury Breccia from McCreedy West, is shown in Figure 11. The profiles are all steep, yet slightly variable. However, profiles for the Copper and Deep Copper zone show relative enrichment in Ni, Pt and Pd. Although total PGE contents are lower for Copper Zone than those for Deep Copper Zone, they are not nearly as low as those for Barnet. Disseminated Cu-rich sulfides from McCreedy West display a similar profile, but lower values.



FIG. 9. Pd – Ni – Pt plot (atomic proportions) showing moncheite and Pd-bearing melonite compositions from the Epidote Zone of the Fraser mine, Barnet, and the Deep Copper Zone of the Strathcona mine. Data for Falconbridge, Crean Hill and additional samples from the Strathcona mine are from Cabri & Laflamme (1976).

TABLE 5. CHEMICAL COMPOSITION OF Au-Ag ALLOY

		I	Elements wt.9		Atomic Proportions				
Sample	Pd	Ag	Au	Se	Total	Pd	Ag	Au	Se
MW600-1	-	24.74	75.71		100.45	-	0.37	0.63	-
MW600-1	-	23.36	77.85	-	101.22	-	0.35	0.65	-
MW600-1	-	23.96	77.86	-	101.82	-	0.36	0.64	-
27A0C0-H1	-	73.81	23.12	0.85	100.77	-	0.82	0.17	0.01

Sample MW600-1 from the McCreedy West Cu-rich stringers (hosted by chalcopyrite in contact with chlorite). Sample 27A0C0-H1 is from the Strathcona mine, Copper Zone (at contact between chalcopyrite and amphibole. Nearby precious-metal minerals include spertylite, froodite, hessite, niggliite and insizwaite). - denotes below detection limits.

			E	lements w	t.%			Atomic Proportions					
Sample	Pd	Ag	Pt	Te	Bi	Se	Total	Pd	Ag	Pt	Te	Bi	Se
CFA-2	1.4	56.85	-	36.9	-	-	96.51	0.04	1.96	-	1.09	-	-
S37-1	-	62.64	-	36,68	-	0.76	100.08	-	2.00	-	0.99	-	0.03
S37-1	-	64.12	-	37.02	-	-	102.42	-	2.00	-	0.98	-	-
27-H 1	-	60.78	-	36.36	÷	-	97.70	-	2.00	-	1.02	-	-
27-K1B	-	63.8	-	37,73	-	-	101.53	-	2.00		1.00	-	-
600-1	-	62.32	-	36.81		-	99.13	-	2.00	-	1.00	-	-
500-I	-	64.25	-	37.19	-	-	101.44	-	2.00		0.98	-	-
500-1	-	63.62	-	36.71	-	-	100.33	-	2.00	-	0.97	-	-
147-11	-	63.66	-	38.42	-	-	102.08	-	2.00		1.01	-	-
CEL .48	1.69	47 10	3.07	40.27	4 52	0.71	07 44	0.07	1 86	0.07	1 26	90.0	0.04

TABLE 6. CHEMICAL COMPOSITION OF HESSITE

Sample CFA-2 from the Barnet property (chalcopyrite host). Sample S37-1 from the Strathcona mine, Deep Copper Zone (at epidote-quartz contact). Samples 27-H1 (in chalcopyrite with amphibole; occurs with sperryline, froodite, nigglitte, electrum and insixweito) and 27-K11 g(at contact between beleby chalcopyrite and amphibole) are from the Strathcona mine, Copper Zone. Samples 600-1 (chalcopyrite host) and 500-1 (chalcopyrite host) and 500-1 (chalcopyrite host) are from the McCreedy West Cu-rich stringers. Sample 147-11 (MAGZ atternite facts, at contact between pyrite and magnetic, part of composite grain with hesiste) is from the Fraser mine, Epidote Zone. Sample CFL-48 (chalcopyrite host) is from the Longvack property. - denotes below detection limits.

TABLE 7. CHEMICAL COMPOSITION OF NAUMANNITE

	Ele	ments wt	Atomic Proportions					
Ag	Se	Те	As	Total	Ag	Se	Te	As
74.11	22.74	-	-	96.86	2.00	0.84	-	
72.54	23.26	1.5	-	97.30	2.00	0.85	0.03	-
72.82	25.58	-	-	98.66	2.00	0.96	-	-

All analytical results pertain to sample CFA-016B from the Barnet Property (chalcopyrite host). - denotes below detection limits.

DISCUSSION

Lithological control

Geological mapping at Barnet (Tirschmann 1989, Farrow 1994) and Deep Copper Zone (Bleeker 1992, Fedorowich 1996) has shown the Sudbury Breccia to have been completely lithified during development of Cu–Ni–PGE veins in the footwall. Regardless of its origin, the Sudbury breccia was critical to the permeability of the rocks after the Sudbury event owing to contrasts in competency of its clasts and matrix compared to the host Archean gneisses and migmatites; thus, the breccia may have functioned as a structural trap for Ni-, Cu- and PGE-rich sulfide mineralization. Alteration is more common in Sudbury Breccia zones than in their host Archean rocks (Sweeny & Farrow 1990), also suggesting that these zones were more permeable to overall penetration by fluid.

Alteration

Alteration associated with Cu–Ni–PGE footwall mineralization has traditionally been ignored or considered insignificant. However, the spatial relationships of ore deposition, alteration and lithological variation exist on two scales, and provide convincing evidence for fluid activity in metal deposition. Large-scale, broad alteration and geochemically significant zones are related to areas of Sudbury Breccia and Cu-rich mineralization (Tirschmann 1989, Farrow & Watkinson 1992, Farrow 1994, Morrison *et al.* 1994). On a smaller scale, Cu-rich veins, stringers and disseminations are commonly rimmed by alteration selvages that may include epidote, amphibole, chlorite, quartz, albite and calcite (Farrow & Watkinson 1992, Li & Naldrett 1993b, Farrow 1994, Jago *et al.* 1994). In thin section, the sulfides locally appear to overgrow the alteration-related silicates (Farrow & Watkinson 1992, Farrow 1994). This finding suggests that hydrothermal fluids existed in the system and formed an assemblage of alteration of a hydrothermal fluid during the final stage of evolution of a sulfide liquid, as suggested by Li & Naldrett (1993a).

Several investigators have also presented micromineralogical and microtextural evidence that Cl-rich aqueous fluid was present during the development of Cu-rich, PGE-bearing footwall ores, leading to the occurrence of chloride minerals and halide-bearing fluid inclusions with platinum-group minerals (Springer 1989, Li & Naldrett 1993a, b, Jago et al. 1994). However, these investigators suggested that the halogen-rich fluids were exsolved from a highly fractionated sulfide melt as it approached its solidus (Li & Naldrett 1992, 1993a, b, Jago et al. 1994). The progressive macroscopic transition from the massive sulfide veins to the alteration assemblages along the margins and quartz-rich terminations indicates that they formed from the same event. Although timing relationships deduced from petrographic observations show that the PGM-bearing sulfides postdate the alteration minerals, both contain similar populations of fluid inclusions, interpreted to have formed from the same, or similar, fluid-dominated systems (Farrow 1994, Farrow et al. 1994). This evidence is contrary to a process invoking the formation of alteration minerals and PGM by hydrothermal fluids separated by the progressive cooling and crystallization of the sulfide liquid. It also renders unlikely the process suggested by Li et al. (1992), by which hydrothermal alteration was superimposed on areas that had already been enriched in PGE by a highly fractionated sulfide liquid.

	TYPE	O. DARNET	TROPERT 1 P	vi, Cu, Co, S,	<u>д, ка, г., г</u>		OCHEMIC/	T DVIV	······
Sample #	Ni (wt.%)	Cu (wt.%)	Co (wt.%)	\$ (wt.%)	Ir (ppb)	Rh (ppb)	Pt (ppb)	Pd (ppb)	Au (ppb)
CFAS-5	0.09	15.0	0.006	15.3	1.48	59.41	142	76	205.4
CFAS-7	0.13	30.0	0.007	31.5	0.13	48.69	45	107	22.25
CFAS-8	0.07	27.4	0.005	27.6	0.47	98.79	149	242	67.6 8
CFAS-10	0.06	7.9	0.052	12.1	0.22	2.93	144	31	50.44
CFA-92-1	0.05	0.61	0.014	2.8	0.14	1.62	164	34	27.86
CFA-92-3	0.04	23.3	0.016	25.2	0.06	123.8	76	397	82.05
CFA-92-4	0.10	0.92	0.011	1.18	0.16	1.90	689	876	96.67
CFA-92-6	0.11	14.3	0.015	15.9	0.22	88.86	173	254	60.94

TABLE 8. BARNET PROPERTY Ni, Cu, Co, S, Ir, Rh, Pt, Pd AND Au GEOCHEMICAL DATA

Samples were analyzed for Cu, Ni and S using Falconbridge Limited's standard procedures at the Metallurgical Technology Centre in Falconbridge, Ontario. Copper and Ni analyses involved digestion of a fraction of the sample in heated aqua regia, dissolution in perchloric acid, dilution with water and analysis by inductively coupled plasma – mass spectrometer (ICP-MS). Analyses for the platinum-group elements were earied out at the Geological Survey of Canada, Ottawa, Ontario, using a standard Ni sulfide preconcentration method and a SCIEX ELAN 5000 ICP-MS instrument. The instrument operation, ion counting and data reduction were controlled with an IBM microcomputer and software provided by SCIEX. Detection limits (in ppb) are as follows: Ru 0.35, Rh 0.14, Pd 0.33, Ir 0.08, Pt 0.30, Au 1.69.



FIG. 10. Comparison of Pt/(Pt + Pd) frequency plots from a) Barnet, b) Deep Copper Zone, Strathcona mine, c) Copper Zone, Strathcona mine, and d) Cu-rich stringers, McCreedy West mine. Samples from Barnet have higher Pt/(Pt + Pd) values than those from the other locations. Numbers in a) indicate contributions from geochemical analyses conducted during the course of this investigation: other data from Falconbridge Ltd. (Exploration). Data for the Deep Copper Zone from Money (1992) and Li & Naldrett (1992, 1993b). Data for Copper Zone from Li & Naldrett (1992, 1993b). Data for McCreedy West from Hoffman et al. (1979).

The geochemistry of the assemblages of alteration-related minerals has provided information on the nature of the fluids that were responsible for precipitation of the vein minerals, as well as the alteration minerals (Farrow & Watkinson 1992, Farrow 1994). Large bodies of alteration assemblages, such as in the Epidote Zone of the Fraser mine, may represent channelways for the movement of metal-bearing fluids out of the Footwall Breccia into hydrothermal cells in the footwall (Farrow 1994, Farrow & Watkinson 1996), or areas where hydrothermal fluids were focused into pre-existing sulfide mineralization (Chai & Eckstrand 1995). Precious-metal minerals in Cu-rich footwall vein deposits occur most commonly in chalcopyrite near, or at, the contact with alteration-related silicate minerals such as actinolite, quartz and epidote. These minerals are not compatible with those expected from the crystallization of a sulfide or silicate liquid (Watkinson 1994). In addition, the local decrease in Cu/Ni, reflected by an increase in the millerite content in the extremities of the Cu-rich vein deposits, is not consistent with models of magmatic fractionation (Li et al. 1992). However, the close spatial association of PGM with alteration-related silicate minerals, Cl-bearing PGM and other rare phases is compatible with the involvement of a fluid bearing H-O-Cl-S-Fe-Cu-Ni-Te-Se-Bi-As in deposition of the PGM.

Precious-metal minerals

In all deposits considered here, hessite is the most common precious-metal mineral. It is associated with both tellurides (merenskyite and moncheite) and bismuthides (froodite and tellurohauchecornite). Assemblages of precious metal minerals (PMM) investigated here are consistent with data from previously published studies. There are no PMM assemblages specific to either sulfide or silicate hosts. However, each location studied has its own dominant assemblage, regardless of sample location within each deposit. For example, the Barnet property assemblage is characterized by merenskyite, hessite and naumannite. At McCreedy West, moncheite, michenerite and hessite are the dominant phases. Although both the Deep Copper and Copper zones contain abundant froodite, there are other differences in their assemblages. Despite the limited data from the Longvack property, the assemblage is merenskyite and hessite, similar to that from Barnet. Thus, as with the geochemical data for whole rocks, the composition of each Cu-rich footwall deposit is a function of the contact magmatic mineralization, and of the fluids that scavenged metals from the primary base-metal sulfides, and subsequently deposited them as footwall Cu-Ni-PGE mineralization (Farrow & Watkinson 1996).



FIG. 11. Chondrite-normalized concentrations of Ni, Ir, Rh, Pt, Pd, Au and Cu. Samples from the Barnet Property are compared to those from the Deep Copper and Copper zones, Strathcona mine, and to disseminated and massive sulfide vein ores in Sudbury Breccia from McCreedy West. Data for the Deep Copper and Copper zones are from Li & Naldrett (1992, 1993b). Data for McCreedy West are from Hoffman *et al.* (1979). Chondrite values selected for normalization of the PGE and Au concentrations are taken from Naldrett & Duke (1980), and for normalization of Ni and Cu concentrations, from Naldrett (1981).

The assemblage of PMM in the Epidote Zone is moncheite-rich. Although whole-rock PGE totals are relatively low in comparison to other PGM bearing deposits mentioned in this study (Farrow & Watkinson 1996), Pt- and Pd-bearing PGM have been identified within the Epidote Zone. This finding suggests that most of the Pt and Pd is not in solid solution in base-metal sulfides, but rather in discrete PGM and Ni-rich tellurides. The PMM in the Epidote Zone tend to occur in magnetite-bearing alteration facies, with individual PGM near a contact with magnetite. Involvement of a fluid consistent with magnetite development appears to have resulted in the development of discrete PGM (Farrow & Watkinson 1996).

It is uncertain as to why a Pt-rich phase dominates the assemblage of PMM throughout the Epidote Zone, although whole-rock PGE geochemistry shows that abundances of Pt and Pd are subequal (Farrow 1994, Farrow & Watkinson 1996), and that they show a positive correlation (Fig. 4). The PGM-bearing samples exist in the upper 50% of total Pt and Pd for analyzed samples, although these totals are low compared to those of other PGM-bearing deposits. However, Pt-rich minerals also dominate the PGM assemblages investigated in Cu-rich mineralization at McCreedy East and Victor Deep deposits (Jago *et al.* 1994).

End-member compositions of the PGM are rare in any of the investigated locations. Compositional variation within a given platinum-group mineral from a given sample provides evidence that there were fluctuations in fluid composition, temperature, and pulses of hydrothermal activity during the evolution of the hydrothermal system, consistent with its continued reaction with footwall rocks (Farrow 1994). On the scale of this study, compositions of platinum-group minerals are deposit-specific, and in the case of the Epidote Zone, location-specific.

Influence and composition of the fluid

Field and experimental geochemical studies have traditionally suggested that Pd and, to a lesser extent, Pt, are the most mobile of the PGE in hydrothermal environments (Mountain & Wood 1988a, b). The Cu⁺ ion has the same affinity toward soft ligands as do Pt²⁺ and Pd²⁺, hence their common association in many hydrothermal deposits (Mountain & Wood 1988a, b, Wood

et al. 1989) and in the footwall veins of the North Range. The thermodynamically predicted order of PGE solubility as chlorides at 25°C is Pd > Pt > Os > Ir (Mountain & Wood 1988a). Extrapolated to higher temperatures (from 25 to 300°C), significant Pt and Pd solubility is attained only in highly acidic and oxidizing Cl-rich aqueous fluids (Wood 1987, Mountain & Wood 1988a, Wood et al. 1989, 1994, Gammons et al. 1992). Recently, numerous investigators cited earlier have shown the importance of Cl-rich aqueous fluids in the development of Sudbury footwall Cu-Ni-PGE mineralization. Chlorine- and S-rich fluids that existed during the development of Cu-rich veins and the Epidote Zone could transport Pt and Pd as aqueous PtS2 and PdS (Gammons et al. 1992, Gammons & Bloom 1993, Wood et al. 1994). However, the occurrence of precious-metal mineralization dominantly as tellurides and bismuthides in footwall deposits precludes further evaluation of this mode of transport until appropriate data on their solubilities become available.

The spatial and temporal association of precious-metal mineralization, alteration and evidence for the existence of a Cl-rich fluid are compatible with transportation of the precious metals by Cl-rich fluids in the footwall at Sudbury. Li et al. (1992) noted that PGE abundances in the alteration zone and quartz + sulfide vein terminations are similar in the Deep Copper Zone at Strathcona, Likewise, we have shown that assemblages of precious-metal minerals are similar within each deposit, regardless of host-rock mineral assemblage. Native silver and selenide minerals have been identified in saline fluid inclusions in chalcopyrite and bornite from the Deep Copper Zone and the Barnet property, and PbCl₂ associated with hessite and merenskyite has been found as inclusions in a chalcopyrite-rich sample from Barnet (Farrow 1994, Farrow et al. 1994). A Cl-bearing, Pd-Bi compound in association with magnetite, chalcopyrite, insizwaite, sperrylite, electrum, michenerite, hessite, and chlorite was identified in Deep Copper Zone ore (Li & Naldrett 1993b). Springer (1989) identified Fe-Mn chlorides, Cl-bearing pyrosmalite and phlogopite, an Fe-rich analogue of sepiolite, and a ferric-iron-rich amphibole in Deep Copper Zone veins. At Lindsley, where amphibole, biotite, stilpnomelane, greenalite and ferropyrosmalite are in contact with PGM or gold, they contain elevated Cl and Mn contents (Watkinson 1994).

Fluid compositions associated with the development of the Epidote Zone were estimated from the evolution of the dominant sulfide and oxide phases with increasing degree of alteration by Farrow & Watkinson (1996). Log $f(O_2)$ values as high as -27 and pH values as low as 3 were involved in the transport of Cu, Ag and Au out of the Epidote Zone. An increase in pH due to possible mixing of such acidic fluid with more alkaline fluid derived from the alteration of footwall meta-ultramafic units resulted in a decrease in solubility of these elements (Farrow & Watkinson 1996). Precious-metal mineralization was limited to highly altered, magnetite-bearing facies.

Assemblages of alteration-related silicates along the Cu-rich veins and in the Epidote Zone are similar (dominated by epidote, actinolite, etc.), but their levels of concentration of metallic elements is very different. The similarity of Fe-bearing silicates in these alteration assemblages suggests that the fugacity of oxygen of the fluid associated with Cu-bearing veining was close to that estimated for the development of the Epidote Zone. Sulfate accidental phases in fluid inclusions from both Cu-rich footwall veins and in the Epidote Zone suggest high $f(O_2)$ of the fluid (Farrow 1994, Farrow et al. 1994, Farrow & Watkinson 1996). In addition, similar changes in the evolution of the hydrothermal system that resulted in the instability of magnetite, and in the stability of calcite, are characteristic of both styles of deposit. As a result, differences in fluid composition may have been related either to variations in pH or $f(S_2)$. Although total S content of the fluid is difficult to assess, it is possible that differences in acidity could partially explain the distinctions in PMM between the Cu-rich and Ni-rich deposits.

Assemblages of daughter minerals in fluid inclusions in quartz of the Sudbury footwall (Farrow & Watkinson 1992) and in sulfides (Farrow et al. 1994) from various Cu-rich zones and the Epidote Zone are dominated by Na, Ca, Fe and Pb chlorides, which suggests that the fluids were compositionally similar. Farrow et al. (1994) attributed variations to the partial control of fluid composition by host-rock lithologies. As a result, fluid inclusions from the granite-hosted Lindsley 4A zone are particularly BaCl₂-rich, whereas those from Cu veins along the North Range, within plagioclase-rich gneiss and migmatite, are enriched in Ca. Our interpretation that the fluids interacted with and were buffered by their host rocks is also compatible with Rb-Sr and Sm-Nd isotope evidence from concentrates of alteration minerals, which show that there was a significant influence of footwall rocks during the evolution of fluids in the North Range (Farrow et al. 1992a, b).

Temperatures of formation of Cu-rich veins in the footwall along the North Range and of the Epidote Zone, deduced from fluid-inclusion and stable-isotope studies, were found to be between 200 and 350°C (Farrow & Watkinson 1992, Fouillac et al. 1993, Farrow 1994). Distance from the SIC was the major control on temperature, with the lowest temperatures associated with Cu-rich footwall vein deposits furthest from the SIC, and the highest in the Epidote Zone. Temperatures of formation are not as well constrained in the South Range, but may have been higher at Lindsley than in North Range deposits, resulting in some relatively broad variations in PGM composition. Assemblages and compositions of the PMM specific to deposit location and type are the result of different compositions of the fluid (i.e., metallic element contents) and conditions [*i.e.*, $f(O_2)$, $f(S_2)$, pH, and temperature] in the Cu-Ni-PGE mineralization of the North Range (Table 9). These variations would affect the solubility of elements being remobilized and the resulting compositions of the precious-metal minerals.

TABLE 9. SUMMARY INFORMATION CONCERNING DISTANCE FROM SUDBURY IGNEOUS COMPLEX (SIC), TEMPERATURE OF FORMATION, ASSEMBLAGE OF ORE MINERALS, TRACE AND PRECIOUS METAL MINERALS, AND Pt/(Pt + Pd) FOR DEPOSITS EXAMINED IN THIS STUDY

Deposit	Distance from SIC contact	Estimated T of Formation	Ore Minerals (dominant in bold)	Trace Minerals	Precious-metal Minerals	Pt/(Pt + Pd) value
Barnet	~300 m	190–320°C¹	chalcopyrite CuFeS ₂₅ pyrite FeS ₂₅ millerite NiS, bornite, magnetite Fe ₃ O ₄ , chalcocite Cu ₂ S covellite		native Ag^2 , hessite Ag_2Te , naumannite Ag_2Se merenskyite (Pd,Pt)(Te,Bi) ₂ melonite (Ni,Pd)(Te,Bi) ₂	0.49
Longvack	: <50 m	?	pyrrhotite Fe _{1-x} S chalcopyrite pyrite, pentlandite magnetite	tsumoite BiTe	hessite merenskyite	
Strathcon mine, Copper Zone	a ~300 m	similar to Barnet? ¹	chalcopyrite millerite cubanite magnetite pentlandite pyrite bornite		native Ag, hessite Au-Ag alloy (Au,Ag) froodite (Pd,Pt)(Bi,Te) ₂ michenerite PdBiTe sobolevskite (Pd,Pt)Bi niggliite (Pt,Pd)Sn sperrylite (Pt,Pd)As ₂	0.45 ³
Strathcor mine, Deep Copper Zone	na ~600 m	154-435°C¹	chalcopyrite, cubanite pentlandite, pyrrhotite millerite, bornite pyrite, covellite magnetite sphalerite ZnS	galena PbS parkerite Bi ₂ Ni ₃ S ₂ altaite PbTe	mative Ag native Ag hessite sobolevskite moncheite (Pt,Pd)(Te,Bi) ₂ melonite (Ni,Pt)(Te,Bi) ₂	0.4 8 ³
McCreed West mine Cu veins	ly ∼250 m	?	chalcopyrite millerite magnetite, bornite pyrite, pyrrhotite	galena bismuthinite Bi ₂ S ₃ tellurohauchecornite Ni ₉ (Bi, Te) ₂ S ₈	hessite Au-Ag alloy michenerite (Pd,Pt)BiTe moncheite	0.364
Fraser mine Epidote Zone	<100 m	206–509°C ¹	pyrite pentlandite pyrrhotite chalcopyrite	galena (Se-bearing) tsumoite	hessite merenskyite melonite moncheite	0.58 ⁵ 0.52 0.48
Lindsley 4B Zone	~100 m		chalcopyrite pyrrhotite pyrite	galena parkerite	froodite, insizwaite michenerite, merenskyite sperrylite, kotulskite	

¹ Estimated temperatures of formation from fluid-inclusion and stable-isotope data, from Farrow & Watkinson (1992), and Farrow (1994).

² Native Ag at Barnet identified as accidental phase in fluid inclusion (Farrow et al. 1994).

³ From Li et al. (1992). ⁴ Calculated from data in Hoffman et al. (1979). ⁵ Calculated from data in Farrow & Watkinson (1996); the three values of Pt/(Pt + Pd) pertain to three alteration facies: epidote, actinolite and magnetite, respectively.

Potential sources of Cl-rich fluids in the footwall at Sudbury are connate fluids from the country rocks enclosing the SIC or late-magmatic fluids. The compositions of fluids now trapped as primary inclusions in quartz and sulfide minerals (Farrow *et al.* 1994, Watkinson 1994) and the isotopic compositions of the alteration minerals precipitated from them (Farrow *et al.* 1992a, b, Fouillac *et al.* 1993) are compatible with fluids from present-day deep sources in the footwall of the SIC (Frape & Fritz 1982, Farrow *et al.* 1994). Late-magmatic fluids appear to have been much less important as a source of fluid. Farrow & Watkinson (1996) have suggested that these fluids were heated and formed individual hydrothermal cells in the footwall. The resulting Cu–Ni–PGE deposits developed individual geochemical (metallic element, isotopic, fluid inclusion) signatures and assemblages of precious-metal minerals. The geochemical distinction of each deposit was further influenced by the hydrothermal scavenging of metals from geochemically distinct contact-magmatic Ni–Cu–PGE deposits from the Footwall Breccia and the Sublayer (Farrow & Watkinson 1996). Variation among magmatic deposits is a function of several factors, including initial composition of sulfide liquid, *R*-factor (mass ratio of silicate to sulfide liquid), temperature, $f(O_2)$ and $f(S_2)$. In the footwall, the hydrothermal cells and fluids evolved, buffered by host-rock compositions.

CONCLUSIONS

The major ore-forming processes in the Sudbury area involved the emplacement of sulfide magmas. Compositional differences in magmatic ores could be the result of variations in *R*-factor or composition of the sulfide magma that separated under different conditions of temperature, $f(O_2)$ or $f(S_2)$. These magmatically derived compositional variations have been further modified by secondary processes in the footwall. In fact, significant hydrothermal interaction occurred at, and was responsible for, enrichments in Cu, the PGE and, locally, Ni in footwall environments. The textural, mineralogical and geochemical evidence presented here does not conclusively support the hypothesis that footwall ore-forming processes were dominated by hydrothermal fluids, but it provides convincing indications of the importance of aqueous hydrothermal fluids.

Although there is a similarity of PGM assemblages between some deposits (i.e., Deep Copper and Copper zones), there are distinct characteristics in mineral chemistry typical of individual deposits. At Barnet, the assemblage of precious-metal minerals is characterized by tellurides, including hessite, merenskyite and palladian melonite. However, naumannite is the only selenide to commonly occur in any of the deposits studied. The assemblages of precious-metal minerals in the Deep Copper and Copper zones are very similar, despite the fact that there is variation in the sulfide minerals within the networks themselves. They are characterized by much more complex variations in mineral chemistry than the other deposits; the minerals are tellurides (hessite, platinian melonite and moncheite), bismuthides (sobolevskite and froodite), Sn-bearing niggliite, and an arsenide (sperrylite). The assemblage of precious-metal minerals in the McCreedy West copper stringers is composed of tellurides and bismuth tellurides, as is the assemblage in the Epidote Zone, with both Ptand Pd-bearing PGM. Similarly, the composition of individual minerals tends to be distinct for each deposit. The greatest variation exists between North and South Range (Lindsley) deposits.

Whole-rock geochemical characteristics of sulfide mineralization are also location-specific. Individual Cu-rich vein-type deposits have distinct Pt/(Pt + Pd) values and chondrite-normalized PGE patterns. For example, Pt/(Pt + Pd) values for the Barnet property are most commonly between 0.6 and 0.7, whereas those from the Deep Copper Zone are approximately 0.4.

In this comparative geochemical study, each Cu-rich footwall vein deposit has its own geochemical signature (Figs. 10, 11), suggesting that each was part of individual hydrothermal cells developed in the footwall (Farrow & Watkinson 1996). Each deposit inherited characteristics from the magmatic sulfides that supplied the Cu, Ni, Te, Bi, Sb, As, PGE and some other elements to the fluid phase for later deposition in the footwall. The Deep Copper and Copper zones are most similar geochemically, and are spatially more closely related than other locations considered here. The magmatic Ni–Cu–PGE mineralization that provided the source of metals for the Copper and Deep Copper zones may have been the same.

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