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# PGE geochemistry of the Eagle Ni–Cu–(PGE) deposit, Upper Michigan: constraints on ore genesis in a dynamic magma conduit

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Abstract The Eagle Ni-Cu-(PGE) deposit is hosted in mafic-ultramafic intrusive rocks associated with the Marquette-Baraga dike swarm in northern Michigan. Sulfide mineralization formed in association with picritic magmatism in a dynamic magma conduit during the early stages in the development of the ~1.1 Ga Midcontinent Rift System. Four main types of sulfide mineralization have been recognized within the Eagle deposit: (1) disseminated sulfides in olivinerich rocks; (2) rocks with semi-massive sulfides located both above and below the massive sulfide zone; (3) massive sulfides; and (4) sulfide veins in sedimentary country rocks. The disseminated, massive and lower semi-massive sulfide zones are typically composed of pyrrhotite, pentlandite and chalcopyrite, whereas the upper semi-massive sulfide ore zone also contains pyrrhotite, pentlandite, and chalcopyrite, but has higher cubanite content. Three distinct types of sulfide mineralization are present in the massive sulfide zone: IPGE-rich, PPGE-rich, and PGE-unfractioned. The lower and upper semi-massive sulfide zones have different PGE compositions. Samples from the lower semi-massive sulfide zone are characterized by unfractionated PGE patterns, whereas those from the upper semi-massive sulfide zone show moderate depletion in IPGE and moderate enrichment in PPGE. The mantle-normalized PGE patterns of unfractionated massive and lower semi-massive sulfides are subparallel to

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those of the disseminated sulfides. The results of numerical modeling using PGE concentrations recalculated to 100% sulfide (i.e., PGE tenors) and partition coefficients of PGE between sulfide liquid and magma indicate that the disseminated and unfractionated massive sulfide mineralization formed by the accumulation of primary sulfide liquids with similar R factors between 200 and 300. In contrast, the modeled R factor for the lower semi-massive sulfide zone is <100. The fractionated sulfide zones such as those of the IPGE-rich and PPGE-rich massive sulfides and the upper semi-massive sulfide zone can be explained by fractional crystallization of monosulfide solid solution from sulfide liquids. The results of numerical modeling indicate that the sulfide minerals in the upper semi-massive sulfide zone are the products of crystallization of fractionated sulfide liquids derived from a primary sulfide liquid with an R factor similar to that for the disseminated sulfide mineralization. Interestingly, the modeled parental sulfide liquid for the IPGE-rich and PPGE-rich massive sulfide zones has a higher R factor (~400) than that for the unfractionated massive sulfide mineralization. Except one sample which has unusually high IPGE and PPGE contents, all other samples from the Cu-rich sulfide veins in the footwall of the intrusion are highly depleted in IPGE and enriched in PPGE. These signatures are generally consistent with highly fractionated sulfide liquids expelled from crystallizing sulfide liquid. Collectively, our data suggest that at least four primary sulfide liquids with different R factors (<100, 200-300, ~400) were involved in the formation of the Eagle magmatic sulfide deposit. We envision that the immiscible sulfide liquids were transported from depth by multiple pulses of magma passing through the Eagle conduit system. The sulfide liquids were deposited in the widened part of the conduit system due to the decreasing velocity of magma flow. The presence of abundant olivine in some of the sulfide ore zones indicates that the ascending magma also carried olivine crystals. Sulfide saturation was attained in the parental magma due in large part to the assimilation of country rock sulfur at depth.

**Keywords** Eagle Ni–Cu deposit · Michigan · PGE systematics · Midcontinent Rift System

## Introduction

The Eagle Ni–Cu–(platinum-group element, PGE) deposit in northern Michigan is associated with mafic-ultramafic intrusions that formed during the early stages of picritic magmatism in the ~1.1 Ga Midcontinent Rift System (a, bin Fig. 1). Ding et al. (2010, 2011) have described the general setting of the deposit, age, characteristics of the parental magmas, and their petrochemical evolution. The Eagle intrusion occurs within the Marquette–Baraga dike swarm (*c* in Fig. 1), and the magmatic sulfide deposition (Fig. 2) that is associated with the intrusion typifies what is known as "conduit-related" mineralization (e.g., Lightfoot et al. 2011; this volume). According to a company report the geologic resource of the Eagle sulfide deposit is estimated at 4.05 million tons with an average grade of 3.57% Ni, 2.9% Cu, 0.10% Co, 0.28 ppm Au, 0.73 ppm Pt, and 0.47 ppm Pd (Rossell and Coombes 2005). More than 90% of the sulfide ores of the Eagle deposit occur in the irregularly shaped massive sulfide zone above the keel of the intrusion. Prior to the Eagle discovery, sulfide mineralization in the Midcontinent Rift System (MRS) was



Fig. 1 *a* Extent of the Midcontinent Rift System as defined by gravity anomalies and outcrop (after Van Schmus et al. 1987). *b* Geologic map of the Lake Superior region showing the southern limit of the

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Great Lakes Tectonic zone (Sims et al. 1980). c Plan view of the Eagle and East Eagle intrusions and mafic dike distribution based on magnetic anomalies

Fig. 2 a Plan view of the Eagle intrusion at a depth of 100 m. b, c Cross-sections of the Eagle intrusion showing rocks types, sulfide types, and locations of drill cores



believed to occur mainly in the basal zones of large layered mafic intrusions such as the Duluth and Mellen complexes (Klewin 1990; Seifert et al. 1992; Miller and Ripley 1996; Ripley et al. 2007). However, Naldrett and Lightfoot (1993) highlighted the potential for the discovery of Noril'sk style mineralization within rocks of the MRS. The sulfide deposits in the large sheet-like mafic intrusions generally have low grades of Ni (<0.2 wt.%) and Cu (<0.6 wt.%) and were not considered to be economical until recent advancements in electrochemical methods of metal extraction.

Our previous studies (Ding et al. 2010) have shown that Ni-Cu-(PGE) sulfide mineralization at the Eagle deposit

occurs as disseminated and semi-massive occurrences in olivine-rich rocks, as massive sulfide, and as veins within sedimentary country rocks. Parental magmas were picritic or ferro-picritic (e.g., Nicholson and Schulz 2009), and the introduction of country rock-derived sulfur appears to have been a critical process for ore formation. The combination of relatively high degrees of mantle melting in the production of the picritic magma and early sulfide saturation led to Ni sequestration and the accumulation of Ni-rich sulfide ores. The accumulation of suspended olivine crystals and sulfide droplets from ascending magmas as they passed through wide parts of the conduits is interpreted to have played a critical role in the genesis of the olivine-rich rocks and sulfide ores in the Eagle intrusion. However, the distribution of PGEs in the Eagle deposit is variable and indicates that more complex processes operated from the early stages of sulfide accumulation through the later stages of sulfide fractionation during cooling. The purpose of this paper was to present the results of detailed studies of the sulfide mineralogy of the Eagle deposit and the distribution of PGEs in the deposit. We utilize these results to investigate the roles of multiple sulfide liquids with different R factors (ratio of magma to sulfide liquid) and subsequent fractional crystallization of the sulfide liquids in controlling PGE distribution in the deposit. In addition, we compare the PGE characteristics of the Eagle deposit to those of mineralization in the sheet-like intrusions of the Duluth Complex to better understand the role of magma composition in PGE mineralization.

#### **Geological setting**

The Eagle Ni–Cu–(PGE) sulfide deposit occurs in the Baraga Basin of northern Michigan, located south of the axis of the Midcontinent Rift System (a, b in Fig. 1). The Eagle intrusion has a length of ~480 m and a width of ~100–200 m (Fig. 2a). The vertical downward extension of the intrusion exceeds 300 m (Fig. 2a, b).

Three major rock types have been recognized in the Eagle intrusion: feldspathic peridotite, melatroctolite, and olivine melagabbro (Fig. 2a, b). In addition, minor

feldspathic pyroxenite is present locally as small pods within the intrusion. Feldspathic peridotite, the most olivine-rich unit in the intrusion, occurs as a sheet at the top of the sequence. The other two major rock units form a sandwich structure characterized by an olivine melagabbro core wrapped by melatroctolite. Feldspathic peridotite contains 30-60% olivine, 5-15% clinopyroxene, 15-40% orthopyroxene, and 15-25% plagioclase. Melatroctolite contains 30-45% olivine, 5-10% clinopyroxene, 20-25% orthopyroxene, and 25-35% plagioclase. Olivine melagabbro contains 10-35% olivine, 5-15% clinopyroxene, 20-45% orthopyroxene, and 25-40% plagioclase. Plagioclase is more common as an interstitial mineral in the feldspathic peridotite, with lesser amounts of interstitial plagioclase found in the melatroctolite and olivine melagabbro. Feldspathic pyroxenite is free of olivine and contains 30-45% orthopyroxene, 25-30% clinopyroxene, and 15-25% plagioclase. Hornblende, biotite, titaniferous magnetite, and sulfide (up to 5%) occur as interstitial minerals in all units. Variations in mineral compositions and incompatible trace element ratios reported by Ding et al. (2010) indicate that the rock types were produced by at least four compositionally distinct pulses of magma that were involved in the formation of the Eagle intrusion.

Four distinct types of sulfide mineralization occur at the Eagle deposit. They are described as disseminated (0.2–6 wt.% sulfur; Fig. 3a), semi-massive (11–30 wt.% sulfur; Fig. 3b), massive sulfide (30–35 wt.% sulfur; Fig. 3c), and sulfide veins in the Proterozoic sedimentary country rocks



Fig. 3 Photos of hand samples from the Eagle deposit. **a** Disseminated sulfide, **b** Semimassive sulfide, **c** Massive sulfide, **d** Cu-rich vein (Fig. 3d). Disseminated blebs of sulfide are found in feldspathic peridotite, feldspathic pyroxenite, melatroctolite, and olivine melagabbro. The semi-massive sulfide zones are bounded above and below by low-sulfide intrusive rocks. The transition between the disseminated mineralization and semi-massive sulfide mineralization is typically abrupt and occurs within a few centimeters. Semimassive sulfides occur in two separate zones that are separated by a zone of massive sulfides (Fig. 2). The boundaries between semi-massive and massive sulfide ores are also sharp; the transition occurs within less than a 1-cm interface. Massive sulfide mineralization forms a relatively large, coherent body that crosscuts the semi-massive mineralization (Fig. 2). In a number of locations, massive sulfides are separated from semi-massive sulfides by olivine melagabbro and sedimentary country rocks. Locally, massive sulfides also extend 10-20 m out into the sedimentary country rocks. Completely serpentinized olivines have been noted in some massive sulfide ore samples and are evidence of late hydrothermal fluid-rock interaction. Sulfide veins occur within the Proterozoic sedimentary country rocks located 5-10 m northwest of the semi-massive and massive mineralization. The boundaries between sulfide veins and sedimentary rocks are exceptionally sharp; the transition occurs within less than a 1-mm interface.

#### Sampling and analytical methods

Samples for the present study were collected from the Eagle intrusion from drill cores. Most of the samples used for establishing the principal features of the Ni–Cu–(PGE) mineralization of the deposit were collected from two drill cores (03EA034 and 04EA047; Fig. 2). Drill core 03EA034 intercepted the disseminated, semi-massive, and massive ores; samples from drill core 04EA047, which intersected the semi-massive and massive ores, illustrate the vertical variation of sulfide mineralization. Samples from drill cores 04EA081, 07EA172, 07EA174, 07EA176, and 07EA178 are sulfide veins that occur in sedimentary country rocks northwest of the semi-massive and massive and massive mineralization. Polished thin sections were examined using standard transmitted and reflected light microscopy.

Sulfide mineral compositions were determined by wavelength-dispersive X-ray analysis at 15 kV using a CAMECA SX50 electron microprobe at Indiana University. The analyses were performed using a 1- $\mu$ m beam, a beam current of 20 nA, and a counting time of 20 s. Platinum-group minerals in the sulfides were detected using backscattered electron images and their compositions were determined by wavelength-dispersive X-ray analysis.

Forty-five samples were analyzed for Cu, S, Pt, Pd, Ir, Rh, Ru, and Os at the University of Quebec Chicoutimi. Nickel was determined by X-ray fluorescence at McGill University, Montreal. Cu was determined by atomic absorption spectrophotometry and S by a combustion iodometric procedure using a Laboratory Equipment Company (LECO) titrator. The PGEs and Au were measured by instrumental neutron activation analysis using the method of Bedard and Barnes (1990), with the modification that corrections for Ta, Ba, and Lu interferences were made for Pt and Ru. The blank contained 0.3 ppb Au; blanks for all other elements fell below the detection limits (Os<0.4 ppb, Ir<0.2 ppb, Ru<2 ppb, Rh<0.3 ppb, Pt<2 ppb, Pd<2 ppb).

#### Results

Mineralogy and sulfide textures

The main sulfide minerals observed in the disseminated and massive sulfide mineralization are pyrrhotite, pentlandite, and chalcopyrite. In contrast, semi-massive sulfide ores are composed of pyrrhotite, pentlandite, and chalcopyrite with higher cubanite content than the disseminated and massive sulfide ores.

Disseminated sulfides (Fig. 4a) are irregular-shaped, polymineralic blebs that occur interstitially to silicate minerals. Some sulfide globules are also present within olivines (Fig. 4b). Interstitial sulfide assemblages comprised pyrrhotite, pentlandite, and chalcopyrite generally in a proportion of 6:2:2. Pyrrhotite occurs as anhedral or subhedral grains. Pentlandite occurs as either granular crystals or as exsolution flames in pyrrhotite (Fig. 4c). Minor primary magnetite occurs as granular grains disseminated within the sulfide assemblages. Secondary magnetite occurs in thin fractures cutting through pentlandite crystals. Minor violarite replaces pentlandite along fractures. Chalcopyrite may occur as a rim on pyrrhotite crystals or enclosed by pyrrhotite grains (Fig. 4d). Rare pyrite occurs as irregular inclusions in pyrrhotite or along the boundaries of other sulfides (Fig. 4e).

The semi-massive sulfides form a net-textured matrix enclosing olivine, pyroxene, and rare plagioclase (Fig. 4f). The lower semi-massive sulfide zone, which occurs below the massive sulfide zone (Fig. 2b), is composed of pyrrhotite, pentlandite, and chalcopyrite in decreasing abundance. Pyrrhotite comprises from 70% to 80% of the sulfide assemblage. Pentlandite is closely associated with pyrrhotite and commonly forms subhedral and euhedral crystals enclosed by pyrrhotite (Fig. 4g). Pentlandite also commonly occurs as exsolution flames in pyrrhotite grains. Some pentlandite grains are partially replaced by violarite along cleavages and microfractures. Pentlandite abundance varies from 15% to 25% in the sulfide assemblage. Chalcopyrite occurs predominantly as anhedral grains along the margins of pyrrhotite crystals or as irregular grains Fig. 4 Photomicrographs showing typical textures of sufides from the Eagle intrusions. Po pyrrhotite, Pn penlandite, Cp chalcopyrite, Cb cubanite, Py pyrite, Mt magnetite, Ol olivine, Cpx clinopyroxene. a Irregularshaped, poly-mineralic disseminated sulfides. b Sulfide inclusions in olivine and clinopyroxene crystals. c Pent-

landite exsolution flame in pyrrhotite. d Chalcopyrite enclosed in pyrrhotite. e Pyrite enclosed in pyrrhotite and along the boundary of pyrrhotite. f Nettextured semi-massive sulfides enclosing olivine. g Chalcopyrite as irregular grains enclosed by pentlandite. h Discrete grains of cubanite associated with pyrrhotite and chalcopyrite. i Massive sulfide composed of pyrrhotite with stringers or wisps of pentlandite and chalcopyrite. j Chalcopyrite and pentlandite enclosed by pyrrhotite



enclosed by pyrrhotite and pentlandite. Chalcopyrite abundance in the disseminated sulfide ores varies from 3% to 10%. The upper semi-massive sulfide zone, which occurs above the massive sulfide zone (Fig. 2b), shows considerable variation in pyrrhotite (30-80%) and chalcopyrite (5-45%) contents. Pyrrhotite content generally decreases downward through 100 m, but then increases in the lower 120 m. The chalcopyrite content shows the opposite trend to that of pyrrhotite, and the pentlandite content (15-25%) is relatively constant. Pentlandite occurs in the upper semi-massive sulfide zone in much the same manner as in the lower semi-massive sulfide zone. Chalcopyrite in the upper semimassive sulfide zone occurs as intergrowths with pyrrhotite; in the chalcopyrite-poor portion, disseminated crystals are enclosed by pyrrhotite and pentlandite. Cubanite is much more abundant in the upper semi-massive sulfide zone than in the other sulfide-bearing zones. Cubanite occurs as discrete grains and as lamellae within chalcopyrite (Fig. 4h). Rare pyrite is present in both the lower and upper semi-massive sulfide zones. It occurs as disseminated grains in the grain boundaries of other base metal sulfides or irregular inclusions within pyrrhotite crystals.

Massive sulfide ore is mainly composed of pyrrhotite (65-85%) with lesser amounts of pentlandite (10-25%) and chalcopyrite (5-15%, Fig. 4i). Pyrrhotite occurs as anhedral grains enclosing small pentlandite and chalcopyrite grains. Minor amounts of pyrrhotite may also occur as intergrowths with pentlandite and chalcopyrite. Chalcopyrite and pentlandite primarily occur along pyrrhotite grain boundaries or form a chalcopyrite-penlandite schlieren (Fig. 3c). Outside the schlieren, chalcopyrite and pentlandite occur as disseminated in pyrrhotite (Fig. 4j). Primary magnetite occurs as discrete grains commonly bordering pyrrhotite crystals. Secondary magnetite occurs as small veins cutting through base metal sulfide minerals. Pyrite occurs as inclusions and along the boundaries of the other sulfide minerals. A trace amount (up to 3%) of galena (Fig. 5a) is found in some massive ore samples. The grain size of galena varies from 0.2 to 40 µm in diameter. Euhedral tsumoite (BiTe), varying in size from 0.5 to 100 µm in diameter, is associated with some galena crystals (Fig. 5a).

Sulfide veins in the country rocks have variable mineralogy. The Cu-rich veins contain variable amounts of chalcopyrite (25–100%), pyrrhotite (1–50%), and pentlandite (1–30%). Most chalcopyrite in sulfide veins occurs as discrete grains associated with pentlandite and/or pyrrhotite grains. In addition, a small amount of chalcopyrite is disseminated in the country rocks. Pentlandite usually occurs as anhedral grains along the margins of chalcopyrite and pyrrhotite. Euhedral quartz appears as inclusions in the chalcopyrite, pentlandite, and pyrrhotite crystals in sulfide veins. Chalcopyrite veins contain ~90% chalcopyrite with a minor amount of pyrrhotite (10%) and trace amount of

pentlandite (<1%). Pyrrhotite occurs disseminated in chalcopyrite. Rare galena and tsumoite are present in all types of sulfide veins.

Most platinum-group minerals (PGM) we have found occur in the sulfide veins (85%, Fig. 5d–i), with only 15% of the PGM present in the semi-massive and massive sulfide types of mineralization (Fig. 5b, c). The PGM are sperrylite (PtAs<sub>2</sub>), kotulskite (PdTe), michenerite (PdBiTe), hexatestibiopanickelite ((Pd, Ni)(Te, Sb)), and testibiopalladite (PdTeSb). The grain sizes of the PGM vary from 0.15 to 8  $\mu$ m in diameter. In the semi-massive and massive sulfide ores, only sperrylite has been found, in association with pentlandite (Fig. 5b, c).

#### Sulfide mineral compositions

The results of sulfide mineral analyses are given in Electronic supplementary materials (ESM) Table 1. The concentration of Ni in pyrrhotite does not exceed 0.82 wt.% and averages 0.52 wt.%. The Fe/S atomic ratios of pyrrhotite are higher in the semi-massive sulfide ores than in the other sulfide ore types (Fig. 6a). Pentlandite has Ni/ Fe atomic ratios that vary slightly from 1.1 to 1.3 and Co contents that vary from 0.74 to 1.23 wt.% (Fig. 6b). Pentlandite from the upper semi-massive sulfide zone tends to have higher Co contents than that from other ore zones in the intrusion (Fig. 6b).

#### Metal tenors of sulfide ores

The contents of Ni, Cu, Au, and PGE in whole rocks from the Eagle intrusion (ESM Table 2) have been recalculated to 100% sulfide (i.e., metal tenors) using the average compositions of pyrrhotite, pentlandite, and chalcopyrite based on the assumption that the sulfide minerals in the samples are present exclusively as these three phases. The error introduced by minor amounts of cubanite or pyrite in the samples is negligible. Before the 100% sulfide recalculation was done, the amount of Ni from silicates in the samples was adjusted using the average content of Ni in sulfide-poor samples. The metal tenors of sulfide ores of the Eagle deposit are listed in ESM Table 2. The sulfide ores of the Eagle deposit have higher Ni/Cu ratios than those of the Duluth Complex (Fig. 7). Most of the Duluth sulfide samples plot within the field of flood basalt-related deposits, whereas most of the samples from the Eagle deposit plot within the field of high-MgO basalt-related deposits (Fig. 7). Primitive mantle-normalized patterns for the samples are shown in Fig. 8a-f. All of the samples from the lower semi-massive sulfide zone have metal patterns similar to those of the rocks that contain disseminated sulfide mineralization (Fig. 8a). Three samples from the overlying massive sulfide zone also show metal patterns



Fig. 5 Backscattered images of platinum-group minerals in sulfide zones of the Eagle deposit: **a** Galena (PbS) and Te–Bi compounds in massive sulfide. **b** Sperrylite in massive sulfide. **c** Sperrylite in semi-massive sulfide. **d** Michenerite in Cu-rich vein. **e** Sperrylite in Cu-rich

vein. **f** Kotulskite in Cu-rich vein. **g** Sperrylite in Cu-rich vein. **h** Hexatestibiopanickelite in Cu-rich vein. **i** Testibipalladite in Cu-rich vein

similar to those of rocks with disseminated sulfide mineralization (Fig. 8a). These three massive sulfide samples are referred to as unfractionated massive sulfide ores because they do not show enrichment in either IPGE (Os, Ir, Ru, and Rh) or PPGE (Pt and Pd), which are present in the other massive sulfide samples (Fig. 8b). Compared with the disseminated sulfide-bearing rocks, the samples from the upper semi-massive sulfide zone are depleted in IPGE, enriched in PPGE (Fig. 8c), and are higher in Cu (Fig. 9). Different types of sulfide veins in the country rocks have different metal patterns (Fig. 8d). Cu-rich veins, which are most common in the footwall, are significantly depleted in IPGE and strongly enriched in PPGE. Among the five Cu-rich vein samples, three of them have Ni tenors within the range of the upper semi-massive sulfide zone in the intrusion; the other two samples have much higher Cu



Fig. 6 Compositional variations of pyrrhotite (a) and pentlandite (b) from different sulfide zones in the Eagle deposit

tenors (Fig. 9). One sample contains in excess of 7 ppm Pt, 5 ppm Pd, and 8 ppm Au. A chalcopyrite vein with a composition close to pure chalcopyrite (Fig. 9) also exhibits a rather unusual metal pattern (Fig. 8d). IPGE in this sample are not as depleted as the Cu-rich veins, although their PPGE tenors are rather similar. In comparison with sulfides in the Duluth Complex, the metal patterns for the Eagle sulfide ores are relatively flat (Fig. 8e), i.e., less fractionation between IPGE and PPGE. Figure 8f illustrates the metal pattern of the Virginia Formation that forms the Proterozoic country rocks to the Duluth Complex. Also shown are normalized Os contents in Archean igneous rocks and Proterozoic sedimentary rocks in the region. In this plot, whole-rock contents are used instead of recalculated 100% sulfide concentrations because PGE in these rocks are not controlled only by sulfide abundance (concentrations with organic matter are also elevated; e.g., Ripley et al. 2002). The Virginia Formation is characterized by a positive Ir anomaly, which is not present in the sulfide ores of the Duluth Complex or the Eagle intrusion. The concentrations of Os in the Archean igneous rocks are lower than those of the Virginia Formation and the Proterozoic sedimentary rocks of the Eagle area.

Figure 10a-f illustrates the stratigraphic variations of the sulfide modes, PGE compositions, and isotopic values in an

oblique drill core 03EA034 that penetrates the disseminated, lower semi-massive, and massive sulfide zones of the Eagle deposit (see Fig. 2). The Ir and Pt tenors of the disseminated sulfide ores are higher than those of the semi-massive sulfide ores. Pt/Ir ratios are <3 in the lower portion of the massive sulfide zone, increase to >16 in the middle and upper portions of the massive sulfide zone, and decrease to 4–7 at the top (Fig. 10d) where the three relatively PGE unfractionated samples occur (see Fig. 8a). The overlying semimassive sulfide zone has Pt/Ir ratios between 4 and 13, while the disseminated sulfide zone has slightly higher Pt/Ir ratios between 8 and 17.  $\Delta^{33}$ S values are negative and strongly anomalous in the semi-massive sulfide zone relative to values near 0‰ expected for uncontaminated mantle-derived sulfide (Fig. 10g; Ding et al. 2011).

Variations in the sulfide modes, PGE compositions, and isotopic values with depth in vertical drill core 04EA047 that penetrates the upper semi-massive sulfide zone and the massive sulfide zone in the Eagle intrusion (see Fig. 2) are illustrated in Fig. 11a–f. The Ir tenor in the upper semimassive zone varies positively with pyrrhotite abundance and negatively with chalcopyrite abundance and is lowest in the middle portion of this zone. The Pt tenor, Pt/Ir, and Os/Ir ratios are highest in the chalcopyrite-rich portions.  $\Delta^{33}$ S values are again variable and strongly anomalous in the semi-massive ore zone (Fig. 12).

#### Modeling and discussion

Variable R factors during sulfide segregation

Because of the low degree of fractionation shown by the disseminated, lower semi-massive, and unfractionated massive sulfides (Fig. 8a), their sulfide-normalized compo-



Fig. 7 Plot of Pd/Ir versus Ni/Cu. Data for the sulfides in the Duluth Complex are from Theriault and Barnes (1998) and Ripley et al. (2001). The fields of magmatic affinity are from Barnes et al. (1988)





Fig. 8 Primitive mantle-normalized patterns. a Disseminated sulfide, unfractionated massive sulfide, and lower semi-massive sulfide. b IPGE- and PPGE-rich massive sulfides. c Upper semi-massive sulfides. d Pd-rich vein, chalcopyrite vein, and Cu-rich vein. e Comparison of rocks containing disseminated sulfide in the Eagle deposit with sulfide-bearing rocks in the Duluth Complex. f Virginia Formation and Os concentrations in Archean igneous rock and

sitions are thought to be representative of initial sulfide liquids. Their metal concentrations are consistent with those from primary sulfide liquids that segregated from magma with variable R factors (Campbell and Naldrett 1979; Fig. 13). The inferred R factors for the disseminated and unfractionated massive sulfide ores are between 200 and 300. The inferred R factors for the lower semi-massive sulfide zone are close to 90. In our calculations, we used the sulfide/magma partition coefficients of 20,000 for Pt

Proterozoic sedimentary rock in the Eagle area. Data shown in the figures from **a** to **e** are concentrations normalized to 100% sulfide. Data shown in **f** are whole-rock concentrations from Ding et al. (2011). The primitive mantle values are from Barnes and Maier (1999) and McDonough and Sun (1995). The compositions of sulfides in the Duluth Complex are from Theriault and Barnes (1998) and Ripley et al. (2001)

and Ir. These values are within the ranges of experimental values by Fleet and Pan (1994) and Peach et al. (1990, 1994). The concentrations of Pt and Ir in the parental magma were estimated to be  $\sim$ 4 and  $\sim$ 0.5 ppb, respectively, based on the best fit to the data shown in Fig. 13. These values are within the ranges of data from undepleted picritic basalts (Keays and Lightfoot 2007; Lightfoot and Keays 2005). The compositions of primary sulfide liquids for other sulfide zones estimated from forward modeling of



Fig. 9 Plot of Ni tenor versus Cu tenor for different types of sulfide ores in the Eagle deposit

monosulfide solid solution (MSS)/liquid fractionation and mixing of solids and liquid are given in Figs. 14 and 15 below. The estimated primary sulfide liquid composition for the upper semi-massive sulfide zone is similar to the average sulfide liquid composition of disseminated sulfides in the intrusion. The concentrations of PGEs in the primary sulfide liquid estimated for the IPGE-rich and PPGE-rich massive sulfide ores are higher and require a higher *R* factor of ~400. This suggests that the massive sulfides and the overlying semi-massive sulfides originated from separate primary sulfide liquids. Independent support for such an interpretation includes the contrasting pyrrhotite Fe/S atomic ratios between these two ore zones (Fig. 6a) and their different  $\Delta^{33}$ S signatures (Fig. 12). Sulfide liquid fractionation

The sulfide ores with fractionated mantle-normalized metal patterns in the Eagle deposit can be modeled by fractional crystallization of MSS from sulfide liquids. Our modeling results for these samples are presented in Figs. 14 and 15 using the graphical presentation that was first introduced by Li and Naldrett (1994, 1994). In our calculations, the MSS/ liquid partition coefficients of 0.2 for Cu, 3.5 for Ir, 0.1 for Pt, and 0.1 for Pd were used. These values are within the ranges of experimental values by Fleet et al. (1993), Li et al. (1996), and Barnes et al. (1997). Most of the sulfide ore samples plot between MSS and coexisting sulfide liquid, suggesting that they represent mixtures of these two coexisting phases during fractional crystallization. The chalcopyrite vein in the footwall has unusual PGE compositions that are inconsistent with the evolution of magmatic sulfide liquids represented by the sulfide ores in the intrusion (Fig. 15a-d). Significant PPGE enrichment in this sample is not coupled with IPGE depletion. This feature is inconsistent with either a hydrothermal origin or a highly fractionated sulfide liquid. Some Cu-rich veins plot outside of the MSS/liquid mixing fields (Fig. 15a-d). This is not surprising because PGE fractionation by other phases such as pentlandite, intermediate solid solution, and PGM at the late stages of sulfide liquid evolution is not included in our calculations. However, modeling of the fractional crystallization of various proportions of MSS from a sulfide liquid reproduces most of the trends relative to primitive mantle observed for the Cu-rich veins (Fig. 8). In addition, interaction between the sulfide veins and circulating fluids in the country rocks may have also affected the observed PGE patterns.



Fig. 10 Stratigraphic variations of sulfur content (a), Ir tenor (b), Pt tenor (c), Pt/Ir ratio (d), Os/Ir ratio (e),  $\delta^{34}$ Svalue (f), and  $\Delta^{33}$ S value in drill cores 03EA034 (g)



Fig. 11 Stratigraphic variations of sulfur content (a), Ir tenor (b), Pt tenor (c), Pt/Ir ratio (d), Os/Ir ratio (e),  $\delta^{34}$ S value (f), and  $\Delta^{33}$ S value in drill cores 04EA047 (g)

Sulfide saturation, transportation, and concentration

The presence of rounded sulfide inclusions in olivine crystals in the Eagle intrusion (Fig. 4b) suggests that sulfide saturation took place before or during olivine crystallization. We have used the parental magma composition estimated by Ding et al. (2010), the MELTS program of Ghiorso and Sack (1995) for simulation of crystallization, and the equation of Li and Ripley (2009) for estimation of the content of sulfur at sulfide saturation to



Fig. 12 a Os/Ir versus  $\delta^{34}$ S value. b Ru/Ir versus  $\delta^{34}$ S value. c Os/Ir versus  $\Delta^{33}$ S value. d Ru/Ir versus  $\Delta^{33}$ S value for the Eagle deposit



**Fig. 13** *R* factor modeling for unfractionated massive sulfides, rocks containing disseminated sulfide, and samples from the lower semimassive sulfide zone of the Eagle deposit (values normalized to 100% sulfide). These samples are thought to be representative of initial sulfide liquids. The compositions of (1) and (2) are based on forward modeling of MSS/liquid fractionation (see Figs. 14 and 15)

evaluate the origin of sulfide saturation in the Eagle system. Fractional crystallization was simulated at 1 kb and an oxidation state equivalent to the QFM-2 buffer. The results are illustrated in Fig. 16. As pointed out by Ding et al. (2010), the estimated parental magma for the Eagle intrusion contains 13.64 wt.% MgO and is in equilibrium with olivine Fo<sub>86</sub>. The inferred olivine Fo content is significantly lower than that of mantle olivine which is ~90 mol%. The difference suggests that the parental magma of the Eagle intrusion was not a primary mantle-derived magma but was a derivative magma produced as a result of olivine crystallization and crustal contamination at depth. As olivine is the

Fig. 14 Modeling of MSS fractional crystallization from sulfide liquid using Pt versus Ir (a), Pd versus Ir (b), Au versus Ir (c), and Cu versus Ir (d). The IPGE- and PPGE-rich massive sulfides are consistent with the fractionated products of a common parental sulfide liquid. The contents of Pt, Au, Cu, and Ir in the Pd-rich vein are similar to the compositions of the primary sulfide liquid for the massive sulfides, but the Pd content in the Pd-rich vein is abnormally high by comparison

first phase to crystallize from this derivative magma on cooling at shallow depths, the composition of the primary magma may be estimated by incrementally adding olivine with Fo contents varying from 86 to 90 mol% to the parental magma until the bulk composition is in equilibrium with olivine of Fo<sub>90</sub> based on the (FeO/MgO)<sup>Ol</sup>/(FeO/MgO)<sup>Liq</sup> of 0.3 (Roeder and Emslie 1970). Our inverse calculation indicates that the MgO content of the primary magma was ~17.8 wt.%. The total amount of olivine added in the inverse calculation is ~12%. This suggests that parental magma of the Eagle intrusion may have experienced ~12% olivine crystallization at depth. According to the numerical modeling of Naldrett (2010), the degree of mantle partial melting required to produce a mantle melt containing 17.9 wt.% MgO is 18%. If the content of S in the source mantle was 250 ppm S, as suggested by Lesher and Burnham (1999), the maximum amount of S in a primary magma produced by 18% partial melting of the mantle would have been 1389 ppm if no sulfide was retained in the mantle. After 12% olivine crystallization without sulfide segregation, the content of S in the fractionated magma with a composition similar to that of the parental magma of the Eagle intrusion would increase to 1,578 ppm. As shown in Fig. 16, an additional 12% of olivine fractional crystallization would have been required to induce sulfide saturation in the magma. By this time, the Fo content of olivine would have been 81 mol%, which is 2 mol% lower than that of olivine which contains rounded sulfide inclusions. To induce sulfide saturation during the early stages of fractional crystallization corresponding to the formation of olivine

![](_page_12_Figure_6.jpeg)

Fig. 15 Modeling of MSS fractional crystallization from sulfide liquid using Pt versus Ir (a), Pd versus Ir (b), Au versus Ir (c), and Cu versus Ir (d). Samples from the upper semi-massive sulfide zone and some Cu-rich veins are consistent with the fractionated products of a common parental sulfide liquid. It is difficult to model several Cu-rich veins and the chalcopyrite vein by MSS/ liquid fractionation

![](_page_13_Figure_2.jpeg)

Fo<sub>83</sub> with sulfide inclusions, external S would have been required (Fig. 16). Trace elements and Os, Nd, and O isotopes of the host intrusive rocks are consistent with <5% of bulk contamination by Proterozoic and Archean country rocks (Ding et al. 2011). Sulfur isotope data indicate that the proportion of sulfide contributed by country rocks could have been as much as 50% (Ding et al. 2011). Thus, we suggest that sulfide saturation in the Eagle magma was primarily triggered by the addition of crustal S.

As shown in Fig. 16, the S content at sulfide saturation decreases during olivine crystallization. This means that as olivine crystallizes from a sulfide-saturated magma, immiscible sulfide liquid will continue to segregate from the magma. The mass ratio of olivine to sulfide liquid in the system is commonly referred to as a cotectic ratio. Our calculations indicate that the cotectic ratios for the Eagle magma were ~80 during olivine crystallization and ~300 when clinopyroxene and plagioclase were also crystallizing. The average silicate-to-sulfide ratio for the entire Eagle intrusion is one order of magnitude lower (~30). The best explanation for this is that most of the sulfide liquids were transported by magma from depth. The magma may have also carried some olivine crystals, but the ratio of olivine/ sulfide in the ascending magma was significantly lower than the cotectic ratio. We envision that the olivine crystals and immiscible sulfide droplets carried by the ascending magma were deposited at Eagle due to the sudden decrease in magma velocity in response to a dramatic increase in conduit size (see Fig. 2b). As the velocity of the ascending magma decreased, its ability to carry the denser materials was significantly reduced.

#### Conclusion

Sulfide mineralization at the Eagle deposit was formed by the deposition of immiscible sulfide droplets together with olivine crystals in the widened portion of a magma conduit. Multiple sulfide liquids and parental magmas were involved in the development of the Eagle deposit. PGE zonation in

![](_page_13_Figure_8.jpeg)

Fig. 16 Comparison of the SCSS with residual S enrichment during fractional crystallization of a parental magma for the Eagle intrusion. The composition of the parental magma for the Eagle intrusion is from Ding et al. (2010). We estimate the S content of the derivative mantle-derived melt as discussed in the text. Fractional crystallization is simulated assuming 0.5 wt.%  $H_2O$  in the initial liquid, QFM-2, and 1 kbar using the MELTS program of Ghiorso and Sack (1995). The SCSS is calculated using the equation of Li and Ripley (2009). As noted, sulfur addition is required to induce sulfide saturation before substantial amounts of olivine crystallization and associated sequestration of Ni

some areas of mineralization within the deposit developed as a result of fractional crystallization of MSS from sulfide liquids on cooling. Most small sulfide veins in the footwall represent highly fractionated sulfide liquid expelled from the overlying sulfide-rich mineralization associated with the Eagle intrusion.

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