Cu isotope systematics of conduit-type Cu–PGE mineralization in the Eastern Gabbro, Coldwell Complex, Canada

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Abstract
Chalcopyrite from the Cu–PGE sulfide deposits in the Eastern Gabbro, Coldwell Complex, Canada, exhibit a > 2‰ variation in \( \delta^{65}\text{Cu} \). In the Marathon deposit, the \( \delta^{65}\text{Cu} \) of chalcopyrite increases from the lower Footwall Zone (~1.49 to ~0.75‰), to the Main Zone (~1.04 to 0.08‰), to the upper W Horizon (~0.35 to 1.07‰). In the northern deposits, chalcopyrite at Four Dams and Sally have \( \delta^{65}\text{Cu} \) that range from ~0.08 to 0.47‰ and ~0.59 to ~0.05‰, respectively. Notably, samples from the Marathon deposit with lower chalcopyrite \( \delta^{65}\text{Cu} \) values tend to have higher S/Se and Cu/Pd ratios. Integrated geological and geochemical evidence suggests that secondary hydrothermal alteration and redox processes are unlikely to have been the primary causes of the observed Cu isotope variation. Numerical modeling of \( \delta^{65}\text{Cu} \)-Cu/Pd–S/Se of mineralization in the Eastern Gabbro illustrates three key aspects of Cu isotope behavior in magmatic Ni–Cu–PGE systems. First, \( R \) factors less than ~10,000 can exhibit significant control on the \( \delta^{65}\text{Cu} \) of sulfides. Second, sulfide liquid–silicate melt fractionation factors for Cu (\( \Delta^{65}\text{Cu}_{\text{sil-ss}} \)) greater than ~0.5‰ are applicable to Ni–Cu–PGE systems. Third, sulfide segregation exhibits no measurable control on the \( \delta^{65}\text{Cu} \) of sulfides at degrees of fractionation typical of Ni–Cu–PGE systems (~0.3%). In the Marathon deposit, the range of \( \delta^{65}\text{Cu} \)-S/Se–Cu/Pd is attributed to the addition of Archean sedimentary Cu to a pool of sulfide liquid located at depth, followed by progressive dilution of the contaminated \( \delta^{65}\text{Cu} \)-S/Se signature and decrease in Cu/Pd ratio by influxes of uncontaminated pulses of magma (i.e., increasing \( R \) factor), some of which had Cu isotope compositions heavier than the mantle. Variably contaminated and enriched, with respect to Pd, sulfides from this pool were entrained by magma pulses and emplaced to form the Marathon deposit. This contribution demonstrates that Cu isotopes can fractionate at high temperatures and, when combined with other geochemical proxies, can be valuable in characterizing magmatic–post-magmatic processes in Ni–Cu–PGE sulfide deposits and for identifying PGE-rich sulfide deposits.

Keywords Cu isotopes · Ni–Cu–PGE · Marathon deposit · Coldwell Complex

Introduction
Platinum-group elements (PGE) are a group of heavy transition metals that have chalcophile and siderophile geochemical behaviors (Eckstrand et al. 1996). The concentration of the PGE in the bulk silicate Earth is extremely low (~150 times lower than chondritic abundances) as they were concentrated into the metallic core during differentiation of the Earth (Robb 2004). The most economically important sources of PGE occur in magmatic base–metal sulfide deposits that are hosted by mafic–ultramafic igneous plutons (Holwell and McDonald 2010). These deposits account for over 96% of the world’s PGE production (Mudd and Jowitt 2014). Generation of high-grade PGE deposits requires a complex interplay of several geologic processes: generation of a mafic–ultramafic magma by partial melting of the mantle, ascent of the magma through the mantle and into the crust, segregation of an immiscible...
sulfide liquid from the magma, scavenging of PGE by interaction of the sulfide liquid with large volumes of silicate melt (R factor, Campbell and Naldrett 1979), and finally, concentration of the sulfide liquid in a small volume of magma (Naldrett 2010).

The origin of PGE mineralization in mafic–ultramafic systems remains controversial because the host environments are complex systems involving the interaction between fluids, rocks, and magmas (Maier 2005). Much of the research aimed at characterizing the processes that generated and modified the mineralization and host rocks in these systems has focused on whole-rock and mineral trace-element chemistry. For example, due to the discrepancy in partition coefficients between a sulfide liquid and silicate melt ($D_{\text{Cu}}$ for Cu ($D_{\text{Cu}} = \text{up to 2000}$) and Pd ($D_{\text{Pd}} = \text{up to 500,000}$) (Barnes and Ripley 2016), bulk-rock Cu/Pd ratios in PGE deposits have been used to understand the silicate melt/sulfide liquid mass ratio (R factor) and/or segregation/retention of sulfides at depth (Barnes et al. 1993). Copper has two naturally occurring stable isotopes ($^{63}\text{Cu}$ and $^{65}\text{Cu}$) and recent advances in multicollector inductively coupled plasma mass spectrometry (MC–ICP–MS) permit routine measurement of $^{65/63}\text{Cu}$ ratios with a precision of better than ± 0.1‰ in $^{65}\text{Cu}$ (Albarède 2004; Beard and Johnson 2004; Albarède and Beard 2004), making it possible to characterize PGE mineralization using the isotopic variability of Cu.

Copper isotopes have commonly been applied to study hydrothermal mineralizing systems (Fig. 1), including porphyry deposits (Larson et al. 2003; Graham et al. 2004; Mathur et al. 2005, 2009), volcanogenic massive sulfide deposits (Mason et al. 2005), modern black smokers (Rouxel et al. 2004), sediment-hosted Cu deposits (Asael et al. 2007), and vein-type Cu–Ag deposits (Markl et al. 2006; Haest et al. 2009). Applications of Cu isotopes to characterize the genesis of high-temperature magmatic Ni–Cu–PGE sulfide systems, however, are relatively scarce (Malitch et al. 2014; Ripley et al. 2015; Zhao et al. 2017, 2019). Existing studies have revealed a variation in $^{65}\text{Cu}$ of up to 5‰ in magmatic Ni–Cu–PGE systems (Fig. 1). The causes of these high-temperature Cu isotope variations, however, remain ambiguous and have been ascribed either to contamination with sedimentary rocks (Ripley et al. 2015), isotopically distinct magma sources (Malitch et al. 2014), or redox-related processes (Zhao et al. 2017, 2019). The genesis of PGE deposits requires extensive interaction between sulfide droplets and silicate melts (i.e., high R factors), yet no studies have discussed the effects that R factor may have on the Cu isotope composition of sulfides. Although the effects of sulfide segregation/retention on Cu isotopes has been considered

![Fig. 1 Box-whisker diagram illustrating the range of sulfide and whole-rock $^{65}\text{Cu}$ from a variety of magmatic–hydrothermal sulfide deposits and mantle-derived rocks. $^{65}\text{Cu}$ values are from Zhu et al. (2000), Larson et al. (2003), Graham et al. (2004), Rouxel et al. (2004), Mathur et al. (2005), Asael et al. (2007), Maher and Larsen (2007), Haest et al. (2009), Li et al. (2010), Malitch et al. (2014), Ripley et al. (2015), Asp (2016), and Zhao et al. (2017). The Cu isotope composition of the mantle (light gray field) is from Liu et al. (2015). $n$ = the number of data points](image)
(Ripley et al. 2015), the importance of this mechanism in fractionating Cu isotopes has not been demonstrated. These two processes, however, are critical in controlling the grade of mineralization. Accordingly, if these processes also fractionate Cu isotopes, then this isotope system may be a valuable tool for identifying zones of high-grade Ni-Cu–PGE mineralization. Such novel geochemical exploration tools are becoming increasingly important as mineral deposit exploration shifts to identifying deep-seated mineralization.

To address the gap in our understanding of Cu isotopes, this study focuses on the Cu–PGE mineralization in the Eastern Gabbro of the Coldwell Complex, Ontario, Canada. The geology and geochemistry of this mineralized system has been well-characterized in recent literature (Good et al. 2015, 2017; Ames et al. 2016, 2017; Cao et al. 2018, 2019; Shahabi Far et al. 2018, 2019; Good and Lightfoot 2019; Brzozowski et al. 2020a, b, c). By combining the large database of mineralogical–geochemical data available with new Cu isotope data of chalcopyrite, we aim to expand the current knowledgebase of Cu isotope systematics in conduit-type magmatic Ni–Cu–PGE systems, address questions that have remained ambiguous in the Eastern Gabbro, and ascertain whether Cu isotopes can be utilized to identify zones of Ni–Cu–PGE mineralization. On a broader scale, the results of this study are also applicable to mantle geochemistry as they bear on the effects that sulfide liquation has on the Cu isotope composition of residual silicate melts. Accordingly, the following specific questions are addressed: (i) How is the Cu isotope composition of chalcopyrite affected by variable R factors and sulfide segregation at depth? (ii) Are potential differences in the contaminant in the various mineralized zones in the Eastern Gabbro recorded in the Cu isotope composition of their sulfides? (iii) Is there a correlation between high-grade Cu–PGE mineralization and Cu isotopes? To accomplish this, the Cu isotope composition of chalcopyrite from a suite of well-characterized samples that encompass the range of mineralization styles in the Eastern Gabbro is investigated. The mineralogy and chemistry of chalcopyrite and other sulfides has previously been documented in detail (Brzozowski et al. 2020a), providing critical background for interpretation of their isotope compositions.

Geology and mineralization

Eastern Gabbro of the Coldwell Complex

The alkaline Coldwell Complex, Ontario, Canada (Fig. 2a), is an unmetamorphosed and undeformed composite pluton that intruded Archean rocks of the Schreiber–Hemlo greenstone belt as part of the North American Midcontinent rifting event circa 1.1 Ga (Fig. 2b). Several Ni–Cu–PGE sulfide deposits were emplaced along the periphery of the rift during this event, including the Duluth Complex (the Partridge River and South Kawishiwi intrusions), the Tamarack intrusion, and the Eagle intrusion (Ripley et al. 2015), as well as the mineralized zones in the Eastern Gabbro, which are the focus of this study.

Based on crosscutting relationships, petrographic characteristics, and whole-rock and mineral chemistry, the Eastern Gabbro, which wraps around the eastern and northern margins of the Coldwell Complex (Fig. 2c), is subdivided into two genetically distinct rock series, the Layered Series and the Marathon Series, which experienced different magmatic histories prior to emplacement into a metabasalt package (Good et al. 2015; Shahabi Far et al. 2019; Brzozowski et al. 2020c). The barren metabasalt occurs throughout the Eastern Gabbro and consist of basalt flows and sills that have been metamorphosed to hornfels grade by later injection of the Layered and Marathon series magmas (Good and Lightfoot 2019). The Layered Series makes up the majority of the Eastern Gabbro and occurs above the metabasalt package at the Marathon Cu–PGE deposit (Fig. 2d) (Good et al. 2015). It comprises olivine gabbro that exhibits modal layering characterized by variations in the proportions of plagioclase and pyroxene, as well as subunits of oxide augite melatroctolite (Good et al. 2015). The Layered Series is devoid of PGE mineralization, but secondary chalcopyrite and pyrrhotite occur locally in association with actinolite and albite alteration (Good et al. 2015).

The Cu–PGE mineralized Marathon Series represents the youngest and most complex of the mafic intrusive events. It comprises several coegenetic mafic–ultramafic rocks that crystallized from variably evolved melts (Good et al. 2015; Shahabi Far et al. 2019; Brzozowski et al. 2020c). Rocks of the Marathon Series are generally unaltered with no evidence of hydrothermal overprinting (Good et al. 2015). At the Marathon deposit, the Marathon Series is dominated by the Two Duck Lake Gabbro, a coarse-grained to pegmatitic subophitic gabbro. The Two Duck Lake Gabbro intruded the metabasalt package just above the contact with Archean country rocks, which, in the vicinity of the Marathon deposit, comprise intermediate pyroclastic metavolcanic rocks (Fig. 2d) (Walker et al. 1993; Good and Lightfoot 2019). Other units in the Marathon Series include sill- to pod-like bodies of oxide melatroctolite, apatite (olivine) clinopyroxenite, and a layered troctolite sill, the latter of which is a marker horizon that overlies the mineralized Main Zone (Fig. 2d) (Good et al. 2015). Syenite dykes crosscut all of the mafic–ultramafic rocks and represent the final stage of magmatism in the Eastern Gabbro;
Fig. 2  a Simplified map of Canada illustrating the location of the North American Midcontinent Rift in Ontario. Simplified geological map illustrating b the location of the Coldwell Complex and other Ni–Cu–PGE deposits in the North American Midcontinent Rift (modified from Good et al. 2015) and c the location of the Eastern Gabbro and the various zones of Cu–PGE mineralization in the Coldwell Complex (modified from Good et al. 2015). d A cross-section of the Marathon deposit illustrating the relationships between the metabasalt, Layered Series, and Marathon Series rocks, as well as the three mineralized zones (modified from Shahabi Far et al. 2018)

no mineralogical–textural evidence exists to suggest that these dykes affected the Cu–PGE mineralization.

Mineralization

Mineralized zones in the Eastern Gabbro are divided into two groups based on their location (ESM 2 Table B1). The first group comprises the Marathon deposit, a 116-Mt sulfide deposit with 0.25% Cu, 0.73 ppm Pd, 0.23 ppm Pt, and 0.08 ppm Au (Bradfield et al., 2020), which lies on the eastern margin of the complex (Fig. 2c). Mineralized zones in the second group are located on the northern margin of the complex, northwest of the Marathon deposit (Fig. 2c); hereafter, they will be referred to as the northern deposits. These zones of mineralization comprise the Four Dams occurrence, the Sally deposit (formerly known as Area 41), and the
Redstone occurrence (Fig. 2c). It is important to note that both the Marathon deposit and the northern deposits are hosted by cogenetic rocks of the Marathon Series (McBride 2015). Details regarding the texture of the ore, the sulfide mineralogy, and the metal grades from each of the mineralized zones (from representative intervals of drill core) are described in ESM 2 Table B1.

Mineralization in the Marathon deposit occurs in lens-shaped zones (Fig. 2d) that are texturally, mineralogically, and geochemically distinct from one another, although the character of the host gabbrro for the various zones is similar (Good et al. 2015). The Footwall Zone has the highest Cu/Pd (~ 6000–35,000) and lowest Cu/Ni (~ 11.7) of all of the mineralized zones in the Marathon deposit and occurs at the base of the Two Duck Lake Gabbro, at the contact with the Archean country rocks (Fig. 2d). The Main Zone is the thickest and most continuous zone of mineralization, has Cu/Pd of ~ 1000–20,000, and occurs above the Footwall Zone. The W Horizon occurs above the Main Zone, closer to the upper margin of the Two Duck Lake Gabbro. With the lowest Cu/Pd (~ 100–1000) and the highest Cu/Ni (~ 20) of all of the zones in the Marathon deposit, the W Horizon is of great economic interest as it hosts Pd and Pt concentrations (e.g., 67 ppm Pd and 39 ppm Pt over 2 m) that rank it as one of the highest-grade Ni–Cu–PGE deposits in the world (Armes et al. 2017).

Sulfides in the Footwall Zone comprise net-textured to disseminated pyrrhotite with lesser chalcopyrite (Fig. 3a) (Watkinson and Ohnenstetter 1992; Samson et al. 2008). In the Main Zone, sulfides are dominated by disseminated chalcopyrite and pyrrhotite, with minor cubanite and bornite (Fig. 3b). Although sulfides in the W Horizon are also disseminated, the W Horizon is distinguished from the Main Zone by a lower modal abundance of sulfides, a different suite of

**Fig. 3** Reflected light photomicrographs illustrating: **a** an equilibrium (magmatic) assemblage of chalcopyrite, pyrrhotite, and pentlandite (flames); **b** an equilibrium (magmatic) assemblage of chalcopyrite, pyrrhotite, and cubanite (laths); **c** an equilibrium (magmatic) assemblage of chalcopyrite, bornite, and platinum-group minerals (PGM); **d** disequilibrium (hydrothermal) chalcopyrite that has replaced magmatic pyrrhotite; and **e** disequilibrium (hydrothermal) chalcopyrite that is intergrown with hydrous silicates. **f** Polished block with disseminated chalcopyrite and pyrrhotite interstitial to silicates. The dots denote microdrill locations. The numbers are the δ̂⁰⁰Cu (± 2σ) of chalcopyrite from each of the sampled locations. Cub = cubanite, Ccp = chalcopyrite, Bn = bornite, Po = pyrrhotite, Pn = pentlandite, PGM = platinum-group mineral.
platinum-group minerals (PGM), a lower proportion of pyrrhotite, a distinctly higher proportion of bornite (Fig. 3c), and distinctly higher Pd contents (Good 2010; Ruthart 2013; Ames et al. 2016, 2017; Good et al. 2017; Shahabi Far et al. 2018; Brzozowski et al. 2020a).

The northern deposits contain disseminated chalcopryite with lesser pyrrhotite and cubanite, and rare bornite (McBride 2015; Brzozowski et al. 2020a). Mineralization at Four Dams and Sally was described by Brzozowski et al. (2020a), Cao et al. (2018), Good et al. (2017), and Ames et al. (2016). Mineralization at the Four Dams occurrence (0.012 ppm Pt and 0.011 ppm Pd) is characterized by Cu/Pd and Cu/Ni values that are consistently higher than those observed in the Marathon deposit. Mineralization in the Sally deposit has variable Cu/Pd (881–341,700) and Cu/Ni (12.8–21.2) values.

In all of these mineralized zones, the majority of sulfides exhibit smooth, curved equilibrium boundaries with each other and occur interstitial to primary silicates, oxides, and apatite with which they also share equilibrium boundaries (Fig. 3a–c); these sulfides are primary and crystallized from a sulfide liquid. Some chalcopryite, however, is secondary and occurs as a replacement of pyrrhotite (Fig. 3d) and as intergrowths with hydrous silicates (Fig. 3e), both of which can contain pseudomorphs comprising magnetite and carbonate (Samson et al. 2008; Shahabi Far et al. 2018; Brzozowski et al. 2020a).

Methods

The Cu isotope composition of chalcopryite was characterized for 32 sample blocks of Two Duck Lake Gabbro,apatite (olivine) clinopyroxenite, and a single sample of feldspathic clinopyroxenite from mineralized intervals in the Marathon deposit (Footwall Zone, Main Zone, W Horizon), the Four Dams occurrence, and the Sally deposit. Sampling focused on chalcopryite as it is the most common Cu sulfide in the Eastern Gabbro and is present in all of the mineralized zones.

Micromilling, sample digestion, and chromatography

Chalcopryite powders were obtained from semi-polished blocks using an ESI/New Wave precision micro-mill equipped with a tungsten carbide drill bit at the State Key Laboratory for Mineral Deposits Research in Nanjing University. Care was taken to choose relatively large chalcopryite grains (> 1 mm) that are isolated from other sulfides (e.g., pyrrhotite, cubanite, bornite) or where they occur in aggregates where these other sulfides could easily be avoided. Microsampling followed the method described in Li et al. (2010). The surface of the samples and the drill bit were cleaned with ethanol before and after each milling. Prior to milling, ≤ 10 μL of deionized water (> 18.2 MΩ) was pipetted onto the sampling surface to lubricate the drill bit and to create a slurry of the chalcopryite powder that could then be pipetted into Teflon beakers. To enhance recovery, the deionized water from the beakers was pipetted into the pit and transferred back to the tube several times. Powders from 1 to 4 chalcopryite grains were obtained from each of the sample blocks. Each sample powder comprises 1–4 millings located proximal to each other to ensure the availability of sufficient material for Cu isotope measurements.

After microsampling, the water–chalcopryite slurry was evaporated to dryness at ~ 98 °C. The resulting chalcopryite powder was digested in 2 mL of concentrated HNO₃ for 12–24 h. Upon evaporating the HNO₃ to dryness at ~ 98 °C, the residue was brought up in 1 mL of 7 M HCl and evaporated; this was repeated two times. The residue was then brought up a third time in 1 mL of 7 M HCl in preparation for anion exchange chromatography.

Copper was separated from matrix elements in chalcopryite by anion exchange chromatography using 0.2 mL of precleaned Bio-Rad AG MP-1 resin (100–200 mesh) in a microcolumn made of heat-shrink Teflon tubing. The purification method used in this study is similar to that of Maréchal et al. (1999) and Li et al. (2009), except that less acid was used as a consequence of the smaller resin volume; the process is summarized below. Prior to sample loading, the columns were washed with 1 mL of 2% HNO₃ followed by 1 mL of deionized water, and then conditioned with 2 mL of 7 M HCl. The samples, dissolved in 1 mL of 7 M HCl, were then loaded onto the column in one step and allowed sufficient time for the matrix elements to elute, leaving Cu, Fe, and Zn retained on the column. Copper was collected in the next 10 mL of 7 M HCl. Iron was then collected in the next 5 mL of 2 M HCl. Copper recovery using this method is 99.8 ± 1.2% (2σ, n = 68; measured by ICP-OES) based on analyses of elemental concentrations in the Cu-bearing elution fraction and the matrix element fraction for each of the samples and geologic reference materials. In addition to processing of samples, an in-house Cu standard (MCu) was processed through the columns during each chromatography session to monitor isotope fractionation.

Cu isotope ratio measurement

Copper isotope ratios were measured using a Thermo Fisher Scientific Neptune Plus MC–ICP–MS at the State Key Laboratory for Mineral Deposits Research, Nanjing University. The instrument was operated at low resolution,
with $^{66}\text{Zn}$, $^{65}\text{Cu}$, and $^{64}\text{Ni}$ in the H1, H2, and H1 cups, respectively, $^{63}\text{Cu}$ in the axial cup, and $^{65}\text{Ni}$, $^{64}\text{Ni}$, and $^{66}\text{Ni}$ in the L1, L2, and L3 cups, respectively. Samples were introduced using a self-aspirating nebulizer and a glass spray chamber at an uptake rate of $\sim$ 100 $\mu$L/min. Prior to introduction, the standards and purified samples were diluted to $\sim$ 500 ppb in 2% HNO$_3$ and doped with 1 ppm Ni (NIST SRM 986). The signal intensities for 500 ppb Cu ranged from 14.2 to 19.2 V for $^{65}\text{Cu}$ and 6.7 to 9 V for $^{65}\text{Cu}$ throughout the analytical sessions. The sample-standard bracketing method was employed for Cu isotope ratio measurements; Ni dopant was used as a monitor for mass bias (Li et al. 2009). Each analysis consisted of 50 blocks of 4.2 s integrations. Typical internal precision (2 standard error) for the $^{65}\text{Cu}$ ratio measurement was better than $\pm$ 0.03‰. Two replicate analyses were conducted for each chalcopyrite grain; the $^{65}\text{Cu}$ values reported are the average of these two measured values.

Copper isotope data are reported in standard δ–notation as per mil (‰) deviation from NIST SRM 976 ($^{65}\text{Cu} = 0$‰):

$$δ^{65}\text{Cu}_{\text{NIST976}} = \left(\frac{^{65}\text{Cu}_{\text{sample}}}{^{65}\text{Cu}_{\text{NIST976}}} - 1\right) \times 1000$$

(1)

The Cu isotope composition of three standards were measured during each analytical session: ERM-AE633, ERM-AE647, and an in-house Cu standard (MCu). The average $δ^{65}\text{Cu}_{\text{NIST976}}$ values of ERM-AE633, ERM-AE647, and MCu are 0.00 ± 0.04‰ (n = 10), 0.20 ± 0.00‰ (n = 10), and 0.22 ± 0.04‰ (n = 10), respectively. These average values are in excellent agreement with the calibrated values (Moeller et al. 2012). The in-house Cu standard (MCu) exhibits no evidence of Cu isotope fractionation after column chemistry. The long-term reproducibility (2σ) of $^{65}\text{Cu}$ measurements based on analyses of multiple standards is estimated to be ± 0.06‰.

**Trace-element analysis**

The majority of chalcopyrite Se contents are from Brzozowski et al. (2020a). The Se contents of an additional 22 chalcopyrite grains from 12 thin sections were obtained at Hefei University of Technology using an Agilent 7900 mass spectrometer coupled with a Photon Machines Aaylhe HE 193 nm ArF excimer laser. The laser was operated using an energy of 2 mJ, a repetition rate of 7 Hz, and a spot size of 40 μm. Analyses represent spots that included 20 s of gas background and 40 s of ablation and signal acquisition. The masses analyzed were $^{29}\text{Si}$, $^{33}\text{S}$, $^{34}\text{S}$, $^{43}\text{Ti}$, $^{51}\text{V}$, $^{57}\text{Fe}$, $^{59}\text{Co}$, $^{60}\text{Ni}$, $^{65}\text{Cu}$, $^{66}\text{Zn}$, $^{68}\text{Zn}$, $^{75}\text{As}$, $^{77}\text{Se}$, $^{78}\text{Se}$, $^{82}\text{Se}$, $^{107}\text{Ag}$, $^{111}\text{Cd}$, $^{118}\text{Sn}$, $^{120}\text{Sn}$, $^{123}\text{Sn}$, and $^{206}\text{Bi}$. Silicon and Ti were used to monitor for silicate and Fe–Ti oxide inclusions, respectively. MASS-1 was used as the external standard (Wilson et al. 2002). The stoichiometric concentration of Fe in chalcopyrite was used as the internal standard as the Fe content of chalcopyrite does not vary significantly (Brzozowski et al. 2020a). Data reduction was carried out using ICPMS DataCal (Lin et al. 2016). The regions of the laser ablation spectra were integrated following the method of Brzozowski et al. (2020a).

**Results**

At the sample scale, the Cu isotope composition of chalcopyrite grains is homogeneous (Fig. 3f), which supports the representativeness of isotope data from individual chalcopyrite grains in different samples. Chalcopyrite samples from mineralized zones in the Eastern Gabbro exhibit $δ^{65}\text{Cu}$ values that range from $-1.49$ to $1.07$‰, a variation of over 2.5‰. In general, the $δ^{65}\text{Cu}$ values of chalcopyrite increase in the order of Footwall Zone, Main Zone, and W Horizon in the Marathon deposit; the $δ^{65}\text{Cu}$ values of chalcopyrite from Sally and Four Dams are generally close to 0‰ (Fig. 4).

Variations in $δ^{65}\text{Cu}$ are compared to Cu/Pd and S/Se (Fig. 5) because (i) their behaviors during various magmatic–hydrothermal processes are well understood (Queffurus and Barnes 2015) and (ii) each of the mineralized zones in the Eastern Gabbro has distinct Cu/Pd ratios (Good et al. 2015). Chalcopyrite in the Footwall Zone and Footwall–Main zone transition has low $δ^{65}\text{Cu}$ ($-1.49$ to $-0.75$‰, n = 12), but high S/Se (6300–14,500) values compared with mantle rocks, whereas the bulk Cu/Pd (5400–8300) lies within the upper limits of the mantle range (Fig. 5, ESM 2 Table B2). Chalcopyrite in the Main Zone has low $δ^{65}\text{Cu}$ ($-1.04$ to $0.08$‰, n = 18) and mantle-like Cu/Pd values (1700–10,200), but has S/Se values (1900–5300) that extend from the mantle range to values slightly lower than the mantle range (Fig. 5, ESM 2 Table B2). Chalcopyrite in the W Horizon samples is compositionally unique to chalcopyrite from the other two mineralized zones in the Marathon deposit. They have $δ^{65}\text{Cu}$ ($0.35$ to $1.07$‰, n = 11) that range from values lower than mantle rocks to values that are notably higher than mantle rocks, Cu/Pd (100–170) values that are consistently lower than mantle rocks, and S/Se values (700–4400) that range from values similar to mantle rocks to values lower than mantle rocks (Fig. 5, ESM 2 Table B2).

Chalcopyrite in the northern deposits has different Cu isotope compositions and S/Se ratios compared to those in the Marathon deposit. Four Dams is characterized by Cu/Pd ratios (10,100–1,530,000) that are notably higher than the mantle range, with chalcopyrite having $δ^{65}\text{Cu}$ ($-0.08$ to $0.47$‰, n = 6) that range from mantle values to values greater than the mantle range and S/Se (1600–2000) that are consistently lower than the mantle range (Fig. 5, ESM 2 Table B2).
Fig. 4 Box-whisker diagrams illustrating the variation in δ⁶⁵Cu of chalcopyrite and Δ³⁴S of various sulfides in the different mineralized zones in the Eastern Gabbro. The light gray field represents the mantle range of δ⁶⁵Cu (0.06 ± 0.2‰; Liu et al. 2015). Sulfur isotope data is from Shahabi Far et al. (2018). Copper/Ni and Cu/Pd values represent averages of 5 samples (~20 kg of rock) from 10 m of representative drill core.

A deposit is characterized by Cu/Pd ratios (300–501,000) that range from notably higher to notably lower than the mantle range, with chalcopyrite having δ⁶⁵Cu (~0.59 to ~0.05‰, n = 4) and S/Se (1300–2800) that are lower than the mantle range (Fig. 5, ESM 2 Table B2).

Discussion

Hydrothermal alteration

Hydrothermal activity can induce Cu isotope fractionation (Mathur et al. 2010). Evidence for hydrothermal activity in the Eastern Gabbro include the presence of (i) secondary chalcopyrite that represents the complete remobilization of primary chalcopyrite at a scale no larger than within a given mineralized zone (Fig. 3d, e) (Brzozowski et al. 2020a), (ii) late-stage veins (< mm in width) of Fe–Mg phyllosilicates that crosscut rocks of the Eastern Gabbro (Brzozowski et al. 2018), and (iii) minor local alteration. It is, therefore, important to assess whether hydrothermal fluids played a role in fractionating Cu isotopes in the Marathon Series. Multiple lines of evidence indicate that the Cu isotope composition of chalcopyrite was not affected by hydrothermal fluids to any significant degree. The evidence includes the following:

(i). The degree of hydrous alteration of the Marathon Series rocks is low and limited to local replacement of olivine and pyroxene by chlorite–amphibole–serpentinite assemblages (Good et al. 2015; Brzozowski et al. 2018, 2020a). This is distinct from magmatic–hydrothermal systems (e.g., porphyry, skarn) that exhibit intense system-wide alteration (Graham et al.
similar S isotope composition of primary and remobilized chalcopyrite (Shahabi Far 2016).

(iii). The Footwall and Main zones exhibit similar degrees of hydrous alteration in sample and thin section (Shahabi Far 2016), yet they exhibit distinctly different $\delta^{65}$Cu (Fig. 5).

Therefore, we conclude that the variation in $\delta^{65}$Cu exhibited by chalcopyrite in the various mineralized zones in the Eastern Gabbro cannot be attributed to hydrothermal processes.

**Redox processes**

Changes in the redox state of Cu are known to induce significant Cu isotope fractionation at low temperatures (Zhu et al. 2002; Markl et al. 2006); this has recently been proposed by Zhao et al. (2017, 2019) as a mechanism that can potentially fractionate Cu isotopes in high-temperature magmatic Ni–Cu–PGE systems. In their model, the enrichment of Fe$^{3+}$ during melt evolution (caused by preferential removal of Fe$^{3+}$ by pyroxene and olivine crystallization) generates more Cu$^{2+}$ in the silicate melt via the reaction Cu$^{+}$ + Fe$^{3+}$ ⇌ Fe$^{2+}$ + Cu$^{2+}$, allowing the redox transformation Cu$^{2+}$ molten to Cu$^{2+}$ cop and, hence, redox-induced isotope fractionation to occur. Accordingly, because mafic rocks have lower Fe$^{2+}$/Fe$^{3+}$ ratios than ultramafic rocks, Fe and Cu could theoretically occur as 3+ and 1+ cations, respectively, in chalcopyrite in mafic rocks, and as 2+ cations in chalcopyrite in ultramafic rocks. Since lighter isotopes are concentrated in phases that contain the element in its lower oxidation state (Schauble 2004), then chalcopyrite in mafic rocks should be characterized by isotopically lighter Cu than chalcopyrite in ultramafic rocks. Although this trend is, in general, observed among the mafic and ultramafic rocks in the Marathon Series, there is considerable overlap, with many gabbro-hosted chalcopyrite having similar or heavier $\delta^{65}$Cu than clinopyroxene-hosted chalcopyrite (Fig. 6, ESM 2 Table B2). Accordingly, we do not find definitive evidence to support redox-induced Cu isotope fractionation in the Eastern Gabbro, which is in line with the evidence that Cu in chalcopyrite exists as Cu$^{1+}$ rather than Cu$^{2+}$, precluding the possibility of isotope variability caused by differences in Cu valence (Goh et al. 2006).

**Intermineral fractionation**

The W Horizon and the northern deposits are mineralogically distinct from the Footwall and Main zones because significant amounts of bornite occur in the former and cubanite in the latter. About 0.4‰ difference in $\delta^{65}$Cu between chalcopyrite and
bornite has been reported in early studies on porphyry Cu deposits (Larson et al. 2003; Maher and Larson 2007); however, a later study failed to define definitive evidence for intermineral Cu isotope fractionation between these two Cu sulfides (Li et al. 2010). There have been no studies on Cu isotope fractionation between bornite and chalcopyrite. In this study, due to restrictions of the sampling technique, we did not measure the Cu isotope compositions of bornite and bornite as they typically occur as complex intergrowths with chalcopyrite that are too small to sample (Fig. 3b, c). Therefore, we could not directly evaluate the effects of intermineral Cu isotope fractionation on the Cu isotope signatures we observed. Nonetheless, a lack of correlation between δ⁶⁵Cu and bulk-rock Cu/S ratio in Fig. 7 indicates that δ⁶⁵Cu of chalcopyrite is not correlated with the relative proportion of chalcopyrite to bornite or bornite, implying that intermineral isotope fractionation between these sulfides is unlikely to have been responsible for the Cu isotope variability observed in the Eastern Gabbro.

**Sulfide segregation at depth**

Early sulfide segregation at depth is a common process that can affect Ni–Cu–PGE sulfide deposits. Because the mantle has Cu/Pd ratios between 1000 and 10,000 (Barnes et al. 1993, 2015), and Pd has a stronger chalcopyhile behavior than Cu, Cu/Pd ratios > 10,000 in Cu–PGE ores suggest prior sulfide segregation, which preferentially removed Pd from the magma (Barnes and Ripley 2016). The northern deposits display a wide range of Cu/Pd ratios from > 10⁵ at Four Dams to ~ 200 at Sally. The fact that the majority of the studied samples from the northern deposits have higher than mantle Cu/Pd values indicates that sulfides segregated at depth during an earlier sulfide ligation event. Therefore, the northern deposits provide an excellent opportunity to evaluate the effects of sulfide segregation on the Cu isotope composition of a silicate melt and, hence, the sulfide that liquates from it.

Sulfide segregation can be modeled by Rayleigh fractional crystallization (after Rollinson 1993) (Fig. 8b):

\[
\delta^{65}_{\text{Cu}} = \delta^{65}_{\text{Cu}} \times F^{(\Delta_{\text{sal-sil}} - 1)}
\]

where \(\delta^{65}_{\text{Cu}}\) is the Cu isotope composition of the silicate melt after segregation of sulfides, \(\delta^{65}_{\text{Cu}}\) is the initial Cu isotope composition of the silicate melt, \(F\) is the fraction of silicate melt remaining, and \(\Delta_{\text{sal-sil}}\) is the sulfide liquid–silicate melt fractionation factor for Cu isotopes. A range of \(\delta^{65}_{\text{Cu}}\) were used that covered the range of mantle values suggested by Liu et al. (2015) (0.06 ± 0.20‰). A negative sulfide liquid–silicate melt fractionation factor \(\Delta_{\text{sal-sil}}\) of −0.2‰ was used as previous studies have shown that (i) sulfide segregation preferentially removes the lighter isotope (Savage et al. 2015; Huang et al. 2016; Ying et al. 2019); (ii) at temperatures pertinent to core formation, the \(\delta^{65}_{\text{Cu}}\) is likely to be −1‰ (Savage et al. 2015); and (iii) the \(\Delta_{\text{sal-sil}}\) becomes less negative with decreasing temperature (Savage et al. 2015; Ying et al. 2019). The same equation was used to model the variations in Cu/Pd using the concentration of Cu (100 ppm) and Pd (0.011 ppm) in unit 3 of the metabasalt as the initial silicate melt composition since these rocks are thought to be co-genetic with the Two Duck Lake Gabbro (Good and Lightfoot 2019). Maximum sulfide liquid/silicate melt partition coefficients for Cu \(K_{\text{Cu}}^{\text{Cu}} = 2130\) and Pd \(K_{\text{Cu}}^{\text{Pd}} = 536,000\) were used (Barnes and Ripley 2016).

Modeling results show that in order to modify the δ⁶⁵Cu of mantle-derived magmas to values outside of the mantle range requires roughly 10% sulfide segregation (ESM 1 Fig. A1). The Cu/Pd ratios observed in the northern deposits (up to 1,000,000), however, require segregation of less than 0.3% sulfides, depending on the partition coefficient values used for Cu and Pd (Barnes and Ripley 2016). Therefore, early sulfide segregation prior to emplacement of the northern deposits could not have caused the significant Cu isotope fractionation, and some other processes must have contributed to the variability in δ⁶⁵Cu in the northern deposits. Early sulfide segregation did not affect the Cu isotope composition of the Marathon deposit given their mantle-like and low Cu/Pd ratios.

**Contamination**

Mantle-derived melts are typically undersaturated in S because S solubility increases with decreasing pressure (Mavrogenes and O’Neill 1999). Accordingly, in order to generate an immiscible
sulfide liquid required for the formation of Ni–Cu–PGE deposits, S must become saturated in the silicate melt. Although several mechanisms can lead to S saturation in a melt, such as fractional crystallization, magma mixing, and addition of SiO₂, these mechanisms are generally considered to be of little importance in the formation of economic deposits (Robb 2004; Ripley and Li 2013). Many Ni–Cu–PGE deposits, however, exhibit evidence for the addition of externally derived S and Cu either from their immediate country rocks or at depth (Maier and Barnes 2010; Ihlenfeld and Keays 2011; Ripley et al. 2015; Smith et al. 2016; Samalens et al. 2017).

It is known that the melts from which the Marathon deposit crystallized were contaminated at depth by Archean sedimentary rocks based on the negative correlation between Δ⁸⁷Sr and Δ³⁴S (Shahabi Far et al. 2018). Although sedimentary rocks are typically characterized by S/Se ratios that are lower than the mantle range of 2632–4350 (Stanton 1972; Eckstrand and Hulbert 1987; Palme and O’Neil 2014; Queffurutus and Barnes 2015), only sparse data exists on the δ⁶⁵Cu of sedimentary rocks, which exhibit a range from 3.12 to −3.41‰, a large proportion of which are negative (Albarède 2004; Asael et al. 2007, 2009; Ripley et al. 2015; Chi Fru et al. 2016). Accordingly, the increase in both δ⁶⁵Cu and S/Se from values lower than the mantle in the Footwall Zone to values higher than the mantle in the W Horizon suggests that the Footwall Zone experienced the greatest degree of contamination, followed by the Main Zone, and then the W Horizon (Fig. 5a). This apparent decrease in the degree of contamination through the mineralized zones is similar to the interpretation made by Shahabi Far et al. (2018) based on a similar variation in S isotopes (Fig. 4).

The effects of the addition of variable amounts of S-rich sedimentary rock on the δ⁶⁵Cu and S/Se of chalcopyrite are illustrated in Fig. 8a using the isotopic mixing model of Lesher and Burnham (2001):

\[
R_{Cu}^f = \frac{R_{Cu,MB}^{0} \times \chi_{Cu,MB}^{0} F + R_{Cu,CON}^{0} \times \chi_{Cu,CON}^{0} (1-F)}{\chi_{Cu,MB}^{0} F + \chi_{Cu,CON}^{0} (1-F)}
\]

where \(R_{Cu}^f\) is the δ⁶⁵Cu of the sulfide liquid after mixing, \(R_{Cu,MB}^{0}\) and \(R_{Cu,CON}^{0}\) are the δ⁶⁵Cu values of the igneous and sedimentary endmembers, respectively, \(\chi_{Cu,MB}^{0}\) and \(\chi_{Cu,CON}^{0}\) are the concentrations of Cu in unit 3 of the metabasalt and contaminant, respectively, and \(F\) is the mass fractionation of a component. A Cu concentration of 100 ppm was used for the metabasalt (Good and Lightfoot 2019) and 300 ppm for the Archean sedimentary contaminant, which is in the range of other Archean sedimentary rocks (Queffurutus and Barnes 2015). Average mantle values of δ⁶⁵Cu (0.06 ± 0.2‰, Liu et al. 2015) were used as the initial isotope composition of the silicate melt. The Se content of unit 3 of the metabasalt was calculated based on the average S contents of this unit (~260 ppm) and the S/Se contents of typical mantle-derived melts (2632); the calculated Se value (0.099 ppm) is within
Fig. 8 Numerical model illustrating the variation between $\delta^{65}\text{Cu}$ and a S/Se and b Cu/Pd as a function of variable $R$ factor (solid colored lines), segregation of sulfides (dashed colored lines), and contamination (black solid lines). The color of the lines in the $R$ factor and sulfide segregation models represent different starting silicate melt compositions. The light gray fields represent the mantle ranges for S/Se (2632–4350; Eckstrand and Hulbert 1987; Palme and O’Neil 2014), Cu/Pd (1000–10,000; Barnes et al. 1993, 2015), and $\delta^{65}\text{Cu}$ (0.06 ± 0.2‰; Liu et al. 2015). A value of −0.2‰ was used for the sulfide liquid–silicate melt fractionation factor ($\Delta^{65}\text{Cu}_{\text{melt/silicate}}$) (Savage et al. 2015; Huang et al. 2016; Ying et al. 2019). The colored fields represent the range of $\delta^{65}\text{Cu}$ and S/Se of chalcopyrite in the various mineralized zones in the Eastern Gabbro and the Cu/Pd of their respective host rocks. FWZ = Footwall Zone, MZ = Main Zone, W = W Horizon, 4D = Four Dams, and SD = Sally deposit.

the range of unmineralized rock in other Ni–Cu–PGE deposits (Queffeurus and Barnes 2015). Values of 30,000 ppm, 40,000 ppm, and 50,000 ppm were used for the S content of the Archean sedimentary rocks, and a value of 3.1 ppm was used for Se (Queffeurus and Barnes 2015). In order to generate the range of $\delta^{65}\text{Cu}$ and S/Se observed in the Footwall Zone, which is interpreted to be the most contaminated zone (Shahabi Far et al. 2018), the Archean sedimentary endmember would need to have had a $\delta^{65}\text{Cu}$ of at least −1.6‰; this would have required the addition of ~25–90% sedimentary Cu (Fig. 8a). Such a high proportion of external Cu might not be unreasonable given the pyrrhotite-rich nature of the Footwall Zone sulfides (Cu and Cu/S as low as 0.517 wt% and 0.24, respectively, ESM 2 Table B1). Accordingly, assimilation of only a small amount of sedimentary sulfides would have had a considerable impact on the Cu isotope value of early formed sulfides in the Footwall Zone.
Sulfide liquid to silicate melt mass ratio

There is a broad negative correlation between δ⁶⁵Cu and Cu/Pd and S/Se in the Marathon deposit (Fig. 5), indicating that the processes causing variations in Cu/Pd and S/Se ratios may have also contributed to the variability in Cu isotopes. Copper/Pd ratios lower than mantle values are indicative of extreme Pd enrichment. Given the high sulfide liquid/silicate melt partition coefficients of the PGE (Barnes and Ripley 2016), attaining such low Cu/Pd values requires a sulfide liquid to interact with large volumes of silicate melt (high R factor) (Kerr and Leitch 2005). Variations in Cu/Pd and S/Se in an open Ni–Cu–PGE system can be modeled iteratively using the closed-system model of Ripley and Li (2003) and sequential steps of batch equilibration (Fig. 8):

\[ C'_{\text{sil,R}} = C'_{\text{sil}} + (R \times C'_{\text{sil}})/1 + \left(R/D'_{\text{sil/sil}}\right) \]  

(4)

where \( C'_{\text{sil}} \) is the initial concentration of element i in the silicate melt, \( C'_{\text{sil,R}} \) is the concentration of element i in the sulfide liquid after it interacted with silicate melt, \( D'_{\text{sil/sil}} \) is the sulfide liquid/silicate melt partition coefficient for element i, and R is the R factor. A value of 100 was used for the R factor of each sequential pulse of magma. The concentration of Cu (100 ppm) and Pd (0.011 ppm) in unit 3 of the metabasalt was used as the starting silicate melt composition (Good and Lightfoot 2019). A value of 0.099 ppm was used for the Se content of the metabasalt. The initial concentrations of Cu, Pd, and Se used for the sulfide liquid are 20 wt%, 30 ppm, and 5 ppm, respectively; the Cu and Pd values are within the range of metal tenors in the Marathon deposit (Ruthart 2013), and the Se contents are within the range of mineralized rock from other Ni–Cu–PGE deposits (Queffurut and Barnes 2015). Maximum \( D'_{\text{sil/sil}} \) values from Barnes and Ripley (2016) are used for the calculation (2130 for Cu, 536,000 for Pd, and 2339 for Se).

Variations in the δ⁶⁵Cu of chalcopyrite as a function of variable R factor were modeled following the open-system equation of Ripley and Li (2003) (Fig. 8):

\[ \delta^{65}\text{Cu}_{\text{aul,R}} = \delta^{65}\text{Cu}_{\text{aul}} + R^0 \times (\delta^{65}\text{Cu}_{\text{aul}} + \Delta^{65}\text{Cu}_{\text{aul-sil}})/(1 + R^0) \]  

(5)

where \( \delta^{65}\text{Cu}_{\text{aul,R}} \) is the Cu isotope composition of the sulfide after isotope exchange with the silicate melt, \( \delta^{65}\text{Cu}_{\text{aul}} \) and \( \delta^{65}\text{Cu}_{\text{sil}} \) are the initial Cu isotope compositions of the silicate and sulfide melts, respectively, \( \Delta^{65}\text{Cu}_{\text{aul-sil}} \) is the fractionation factor between sulfide liquid and silicate melt, and \( R^0 = C_{\text{sil}}/C_{\text{aul}} \times R \), where \( C_{\text{sil}} \) (100 ppm) and \( C_{\text{aul}} \) (20 wt%) are the concentrations of Cu in the silicate melt and sulfide liquid, respectively. The concentration of Cu in the sulfide liquid is within the range of metal tenors in the Marathon deposit (Ruthart 2013). A value of 100 was used for the R factor of each sequential batch of magma, equating to an \( R^0 \) of 0.05. A value of −1.6‰ was used for \( \delta^{65}\text{Cu}_{\text{aul}} \) as it permits generation of the lowest δ⁶⁵Cu observed in the Eastern Gabbro; this value is assumed to be produced as a result of contamination by low δ⁶⁵Cu Archean sedimentary rocks. A value of −0.2‰ was used as the Cu isotope fractionation factor between sulfide liquid and silicate melt (\( \Delta^{65}\text{Cu}_{\text{aul-sil}} \)). A range of δ⁶⁵Cuaul were used that cover the range of mantle values suggested by Liu et al. (2015) (0.06 ± 0.2‰).

The fact that this modeling can accurately reproduce the range of δ⁶⁵Cu–Cu/Pd–S/Se in the Marathon deposit is indicative of an important characteristic regarding the behavior of Cu isotopes with respect to R factor. That is, R factors lower than ~10,000 can potentially exhibit significant control on the δ⁶⁵Cu of a sulfide liquid (Fig. 8). These R factors are pertinent to Ni–Cu–PGE deposits that exhibit a range of mineralization styles from low to high grade. Copper isotopes may, therefore, be useful as exploration tools for high-grade PGE mineralization. Since the range of δ⁶⁵Cu observed in the Eastern Gabbro (apart from the heavy δ⁶⁵Cu of some W Horizon sulfides) can be generated using \( \Delta^{65}\text{Cu}_{\text{aul-sil}} \) of −0.2, this modeling may also place further constraints on the value of \( \Delta^{65}\text{Cu}_{\text{aul-sil}} \) that is applicable at high temperatures typical of Ni–Cu–PGE systems.

It is known that sulfides in all of the mineralized zones in the Marathon deposit experienced variable R factors between 1000 and 1,000,000 (Good et al. 2017; Brzozowski et al. 2020a). Therefore, although the melt from which the sulfides liquated likely had negative δ⁶⁵Cu and lower than mantle S/Se due to sedimentary contamination, the δ⁶⁵Cu and S/Se of the contaminated sulfides could be increased by interaction and equilibration with multiple pulses of uncontaminated melt at high R factors in an open system (Fig. 8a) (Lesher and Burnham 2001); such high R factors would also have decreased the Cu/Pd ratio of the sulfides (Fig. 8b). This mechanism is similar to the model suggested by Shahabi Far et al. (2018) to explain the increase in Δ³³S in sulfides from the Footwall Zone to the Main Zone to the W Horizon (Fig. 4).

Because a positive sulfide liquid–silicate melt fractionation factor for Cu is unlikely based on previous experimental studies (Savage et al. 2015; Ying et al. 2019), then according to our model, the higher than mantle δ⁶⁵Cu values exhibited by some chalcopyrite in the W Horizon (Fig. 8) can be explained by interaction of the sulfide liquid with pulses of
silicate melt that were characterized by $\delta^{65}$Cu values higher than the mantle range (Fig. 8). Mineralogical, textural, and geochemical evidence suggests that the Two Duck Lake Gabbro crystallized from multiple pulses of melts, with the Footwall Zone, Main Zone, and W Horizon all crystallizing from compositionally distinct pulses (Shahabi Far et al. 2019; Brzozowski et al. 2020c). Based on the decoupled behavior of Ba, Sr, and K from light rare-earth elements (LREE), and LREE from high field strength elements, Good and Lightfoot (2019) suggested that the mantle source for the Eastern Gabbro was variably metasomatized. Metasomatized mantle has been demonstrated to have variable $\delta^{65}$Cu, with values as high as 1.82% (Liu et al. 2015). It is, therefore, possible that sulfides in the W Horizon interacted with pulses of melt that had variable $\delta^{65}$Cu ranging from mantle values to isotopically higher values. The reasons for this variability in $\delta^{65}$Cu could be due to either the variability in the degree of metasomatism or variability in the isotopic composition of the metasomatising agent(s); further work is required to discern between these two potential scenarios. This heterogeneity in source composition may be more evident in the W Horizon sulfides as they experienced higher $R$ factors than sulfides in the other mineralized zones, increasing the probability of sulfides interacting with a range of isotopically diverse silicate melt compositions. With that said, contamination by Archean sedimentary rocks with high $\delta^{65}$Cu cannot be completely ruled out; this scenario is difficult to assess, however, as contamination occurred at depth. Given the evidence supporting a heterogeneously metasomatized mantle source for the Eastern Gabbro and the current lack of evidence for the presence of sedimentary rocks with high $\delta^{65}$Cu in the area, a model involving mantle metasomatism is the preferred explanation for the higher than mantle $\delta^{65}$Cu of some sulfides in the W Horizon.

Implications for the formation of Cu–PGE mineralization in the Marathon deposit

Consider a conduit-type system with a pool of sulfide liquid located in a trap at depth and which formed by the addition of S and Cu from Archean sedimentary rocks ($\delta^{65}$Cu of $\approx$ 1.6%) (Fig. 9 I). As pulses of uncontaminated silicate melt with variable $\delta^{65}$Cu ranging from mantle (0.6 ± 0.2%) to greater than mantle values (up to 1.3%) flow through the system and interact with the pool of sulfide liquid, the $\delta^{65}$Cu–$\Delta^{34}$S and S/Se of the sulfides will progressively increase and decrease, respectively, toward mantle values. The sulfides that interact with and are mobilized by the first pulses of melt retain much of their contaminated $\delta^{65}$Cu–$\Delta^{34}$S–S/Se signature; emplacement of these sulfides generates the high-Cu/Pd Footwall Zone mineralization (Fig. 9 II). As subsequent pulses of melt interact with and mobilize sulfides from the sulfide pool (higher $R$ factor), the contaminant signature is progressively diluted toward mantle values; emplacement of these sulfides generates the Main Zone mineralization (Fig. 9 III). Interaction of the sulfide pool with significantly larger volumes of melt (highest $R$ factors) completely dilutes the contaminant signature and causes the $\delta^{65}$Cu and $\Delta^{34}$S of sulfides to approach or exceed mantle values depending on the isotopic composition of the melt pulses in which the sulfide liquids were entrained (Figs. 4 and 8), and S/Se of sulfides to decrease to values lower than the mantle range (Fig. 8a); emplacement of these sulfides generates the low Cu/Pd W Horizon mineralization (Fig. 9 IV).

This model is supported by several lines of evidence. First, it can collectively explain the variations in $\delta^{65}$Cu, S/Se, Cu/Pd (Figs. 5 and 8), and $\Delta^{34}$S (Fig. 4) (Shahabi Far et al. 2018). Second, it is consistent with the continuous range of $R$ factors experienced by sulfides in the various mineralized zones in the deposit (Footwall Zone < Main Zone < W Horizon) (Good et al. 2017; Brzozowski et al. 2020a). Third, it is consistent with the presence of massive sulfides below disseminated sulfides in other Ni–Cu–PGE systems, such as Noril’sk (Malitch et al. 2014).

Conclusions

The $\delta^{65}$Cu of chalcopyrite in the Marathon deposit ranges from −1.49 to 1.07%, whereas chalcopyrite in the Four Dams occurrence and the Sally deposit largely have mantle $\delta^{65}$Cu. The range of $\delta^{65}$Cu in the Marathon deposit, from lower than mantle to mantle values, is attributed to the addition of Archean sedimentary Cu to a pool of sulfide liquid located at depth, followed by progressive dilution of the contaminated $\delta^{65}$Cu signature by influxes of uncontaminated melt at increasing $R$ factors. The higher than mantle $\delta^{65}$Cu values in the W Horizon are likely due to sulfides having interacted with pulses of magma that had Cu isotope compositions heavier than the mantle (as high as 1.3%). These pulses of uncontaminated and isotopically distinct melts entrained sulfide liquid from this pool, forming the Footwall Zone (most contaminated), Main Zone, and W Horizon (least contaminated) upon emplacement. This model is consistent with the variations exhibited by $\delta^{65}$Cu, Cu/Pd, S/Se, and $\Delta^{34}$S. The largely mantle $\delta^{65}$Cu, but lower and higher than mantle S/Se and Cu/Pd observed at Four Dams and Sally, were likely the result of sulfide segregation at depth and contamination by igneous rocks that experienced S loss. The applicability of Cu isotopes to exploration for PGE-rich deposits is demonstrated given
that the high \( R \) factors required to generate these deposits are recorded by distinct variations in \( \delta^{56}\text{Cu} \).

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