

**Cu and Re-Os isotopic systematics of Ni-Cu-PGE sulfide mineralization in the Duluth Complex, the Tamarack deposit and the Eagle deposit, Midcontinent Rift System, Minnesota and Michigan**

**Final Technical Report**

**USGS Grant G14AP00051**

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Department of Geological Sciences

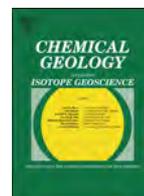
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The final technical report for USGS Grant G14AP00051 is divided into two parts. Part I is a peer-reviewed publication in *Chemical Geology* that describes the rationale for the study, the Cu isotope results, and a discussion of the potential meaning of the isotopic results. We are working on additional analyses on low-Cu rocks in the Midcontinent Rift System which will be used in an upcoming proposal to the National Science Foundation. During the course of analytical work with rocks of low-Cu concentration it was clear that Cu isotope ratios abruptly changed when Cu concentrations dropped below ~ 1 wt. %. Part II of this report deals with the development of an analytical protocol for the analysis of mafic and ultramafic rocks with low Cu contents. The results of this phase of the research are being prepared for publication in *Chemical Geology*.

This proposal was submitted as a two-year project which was to include Re-Os isotope analyses. Funding was approved for year 1 only, and as proposed by the Review Panel only the Cu isotope portion of the planned research was undertaken. A one year, no-cost extension allowed the development of the analytical protocol for analyses of mafic and ultramafic rocks with low Cu concentrations.

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# Cu isotope variations between conduit and sheet-style Ni–Cu–PGE sulfide mineralization in the Midcontinent Rift System, North America

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## ABSTRACT

Disseminated Ni–Cu–PGE sulfide mineralization in sheet-like intrusions of the Duluth Complex are characterized by elevated bulk rock Cu/Ni ratios, typically in the range of 3 to 8. In order to evaluate whether the addition of crustal Cu to parental magmas may have contributed to the high Cu/Ni ratios, Cu isotope ratios were measured from sulfide minerals in the disseminated mineralization found within the sheet-style Partridge River and South Kawishiwi Intrusions of the Duluth Complex, as well as sulfide mineralization in geometrically distinct conduit-style deposits in the Eagle Intrusion and Tamarack Igneous Complex. These intrusions were emplaced during early stages of rift evolution (~1110–1105 Ma) from picritic parental magmas, with associated mineralization characterized by lower Cu/Ni ratios. In addition, Cu isotope ratios were determined from sulfidic and carbonaceous sedimentary country rocks to the intrusions.  $\delta^{65}\text{Cu}$  values of disseminated sulfide mineralization in intrusions of the Duluth Complex range from  $-0.85$  to  $0.45\%$  whereas values from the Eagle Intrusion and the Tamarack Igneous Complex range from  $0.69$  to  $1.84\%$ .  $\delta^{65}\text{Cu}$  values of the sedimentary rocks range from  $-0.33$  to  $1.18$ , with two samples showing higher values of  $2.65$  and  $3.12\%$ . The  $\delta^{65}\text{Cu}$  values of the Duluth Complex mineralization is consistent with the assimilation of significant amounts of sedimentary Cu only if the  $\delta^{65}\text{Cu}$  value of the parental mantle-derived magma was lower than  $-0.25\%$ , a value less than that proposed for the mantle based on analyses of terrestrial mafic igneous rocks. The distinct difference in  $\delta^{65}\text{Cu}$  values between the sheet-style and conduit-style mineralization suggests that either mantle sources of the parental magmas in the rift differed, or that Cu isotope fractionation accompanied magmatic processes (i.e., variable degrees of melting and sulfide retention, sulfide liquid fractionation) that were responsible for the relative enrichment of Cu in the sheet-style intrusions of the Duluth Complex.

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## 1. Introduction

Magmatic Ni–Cu–PGE mineralization in the ~1.1 Ga Midcontinent Rift System (Fig. 1) in North America can be broadly divided into three types (see a recent review by Ripley, 2014). Disseminated sulfide mineralization occurs within multiple, sheet-like intrusions that comprise a large portion of the Duluth Complex. Exploration continues in the Partridge River and South Kawishiwi intrusions (Fig. 2), with initial mining operations possibly beginning in 2016. Disseminated, net-textured and massive sulfide mineralization is found in smaller, olivine-rich dike-like bodies or irregular intrusions (chonoliths). The Eagle Intrusion in Michigan (Fig. 2) typifies this type of occurrence; ore production began at Eagle in 2014. A third type of low-sulfide deposit is PGE-enriched layers (reefs) in small tholeiitic bodies, such as the Sonju Lake Intrusion (Fig. 2). In terms of composition, the sheet-style occurrences differ from the conduit-type deposits in their Cu/Ni ratios, both in overall grade and sulfide tenor. Cu/Ni ratios of the mineralization in the Partridge River

Intrusion are commonly cited as 3.3/1, but locally reach values as elevated as 8:1 (Taib, 2001). In contrast, Cu/Ni ratios at Eagle are near 1, not unlike those of the much larger Ni–Cu–PGE deposits at Sudbury, Noril'sk and Jinchuan which are in the range of 0.5 to 1 (Keays and Lightfoot, 2004; Arndt, 2011; Tonnelier, 2010). The first order explanation of this difference is that sulfide saturation was attained earlier in the crystallization of the picritic parental magma at Eagle relative to that of the high-Al olivine tholeiite (HAOT) parental magma of the sheet-style intrusions of the Duluth Complex. In this case Ni, as well as Cu, is strongly partitioned into early forming sulfide liquid and where sulfide saturation was attained later, Ni was sequestered by early crystallizing olivine. Because of Cu's incompatibility in silicate phases, fractional crystallization and the attainment of later sulfide saturation gives rise to sulfide mineralization with elevated Cu/Ni ratios. A second potential reason has to do with the generation of picritic versus HAOT parental magmas. Picrites are generally considered to be melts derived from relatively high-degrees of mantle melting, whereas the origin of HAOT remains unclear. They may represent lower degree mantle melts or derivative magmas produced via fractional crystallization of a picritic parental magma. In either case the Ni content of the high-Al olivine tholeiite would be less than that

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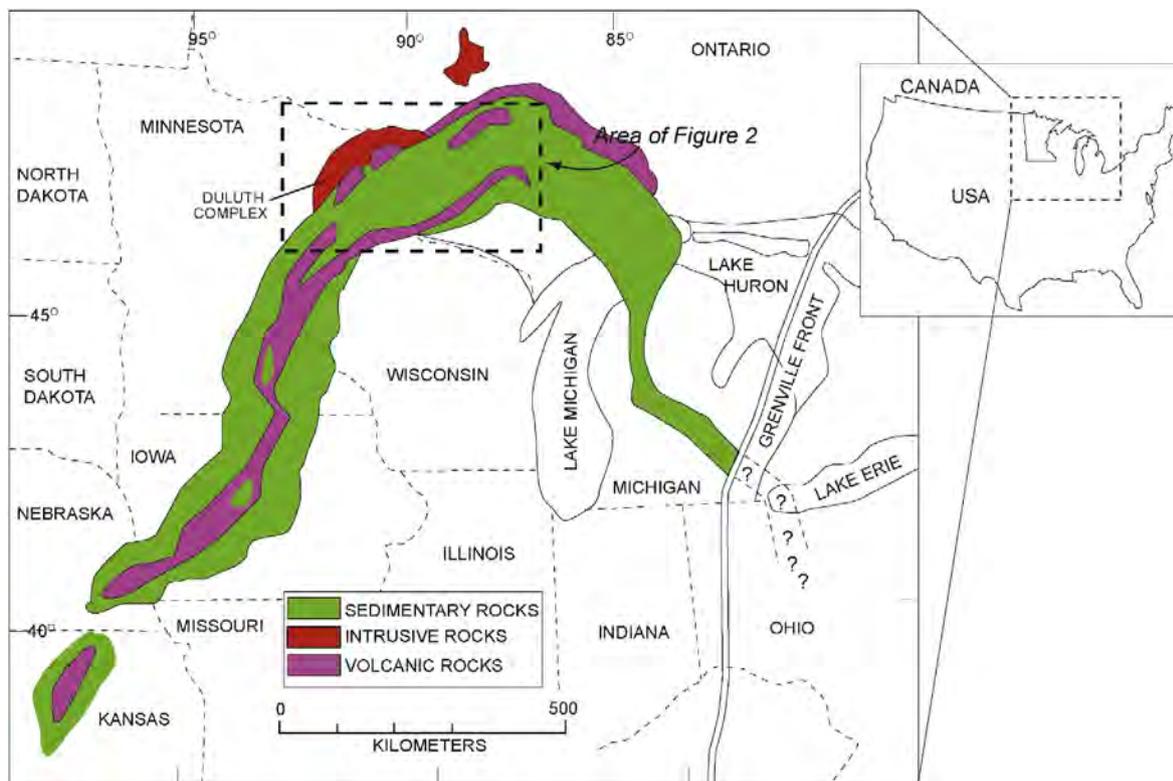


Fig. 1. Location of the Midcontinent Rift System in North America (modified from Hauck et al., 1997).

of a picritic parental magma. However, it can be shown that if typical mantle values of Ni and Cu of 2500 and 30 ppm (e.g., [Palme and O'Neill, 2014](#)) are used, the depletion in Ni caused by fractionation of olivine or lower degrees of mantle melting are insufficient to explain the low Cu/Ni ratio of the sulfide liquid, now represented by the bulk sulfide mineral assemblages. The Voisey's Bay deposit in Labrador is a case in point, where Cu/Ni ratios are near 0.6 (e.g., [Lightfoot et al., 2012](#)) and the parental magma was a HAOT (e.g., [Scoates and Mitchell, 2000](#)). For

these reasons it has also been suggested that Cu from country rocks may have been added to the magmas that produced the mineralization in the Duluth Complex. This is not unreasonable as the sulfidic and organic-rich metasedimentary country rocks of the intrusions have been shown to have contributed sulfur and Os to the magmas (e.g., [Ripley et al., 1999, 2001a,b, 2007](#)). Cu contents of the organic-rich rock types may exceed 200 ppm ([Ripley, 1986](#); also see results below), held primarily in sulfide but also within organic material. A fourth possible

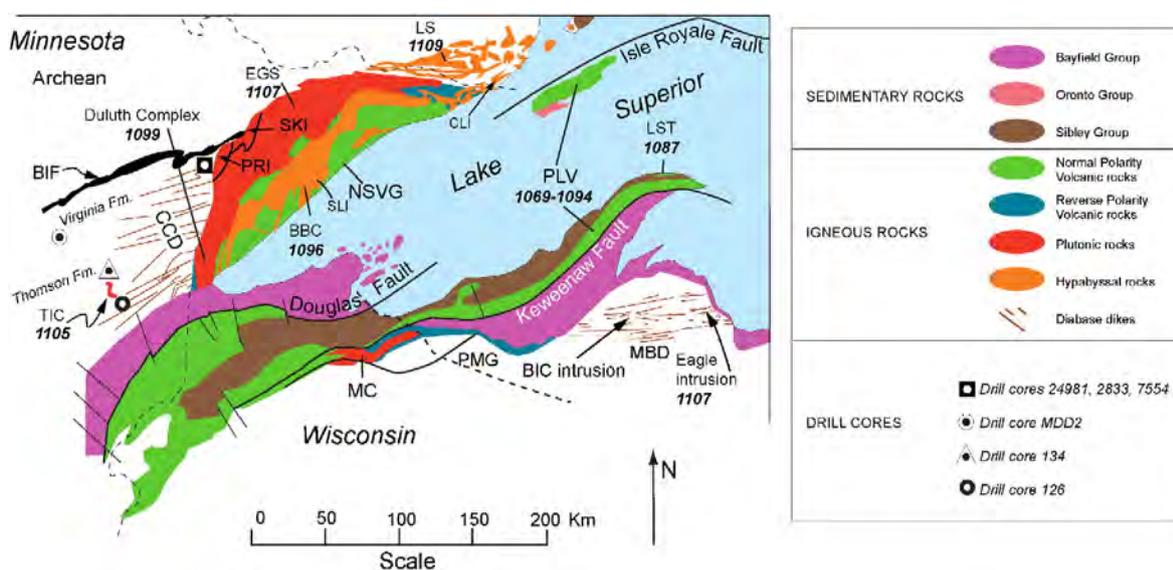


Fig. 2. Geologic map of the Lake Superior area showing location of the Partridge River (PRI) and South Kawishiwi (SKI) Intrusions of the Duluth Complex, the Tamarack Intrusive Complex (TIC), and the Eagle Intrusion (modified from [Paces and Miller, 1993](#)). Other igneous units are: EGS, Early Gabbro Series; BBC, Beaver Bay Complex; NSVG, North Shore Volcanic Group; CCD, Carlton County dikes; LS, Logan Sills; MBD, Marquette–Baraga dikes; PLV, Portage Lake Volcanics; LST, Lake Shore traps; PMG, Powder Mill Group; MC, Mellen Intrusive Complex; SLI, Sonju Lake Intrusion; CLI, Crystal Lake Intrusion. Published high precision U–Pb dates are given in bold italics (in Ma). Note the location of the Eagle intrusion within the Marquette–Baraga dike swarm and the Tamarack Intrusive Complex within the area of the Carlton County dikes. Sampled drill cores containing sulfidic and carbonaceous country rocks are also shown.

explanation for the elevated Cu/Ni ratios in the Duluth Complex is that the disseminated sulfide mineralization represents the incorporation of strongly fractionated and Cu-enriched sulfide liquid in the HAOT parental silicate liquid. This scenario would at first seem to be a very unlikely one for the reason that sulfide liquid fractional crystallization (with monosulfide solid solution then remaining at depth) takes place at temperatures where more evolved silicate liquid relative to the HAOT would be expected. In addition, this model requires a uniform retention of early crystallized sulfide in the staging chambers for both the Partridge River and South Kawishiwi intrusions.

In order to better understand the Cu systematics of the different types of sulfide occurrences in the Midcontinent region, with an emphasis on evaluating the potential for external Cu addition, we initiated a study of Cu isotopes in sulfide minerals in sheet-like intrusions (represented by the Partridge River and South Kawishiwi intrusions) and conduit-style intrusions (Eagle and Tamarack), as well as Cu within metasedimentary country rocks for both intrusive types. We compare our results to those reported for the Noril'sk deposits by Malitch et al. (2014) and to the relatively few other analyses from magmatic sulfide occurrences. The clear Cu isotope distinction that we find between the sheet-style and conduit mineralization has important ramifications for possible melt-country rock interaction, as well as for potential Cu isotope heterogeneity in the mantle or isotope fractionation related to crystallization of sulfide liquid.

## 2. Geologic setting and sampling

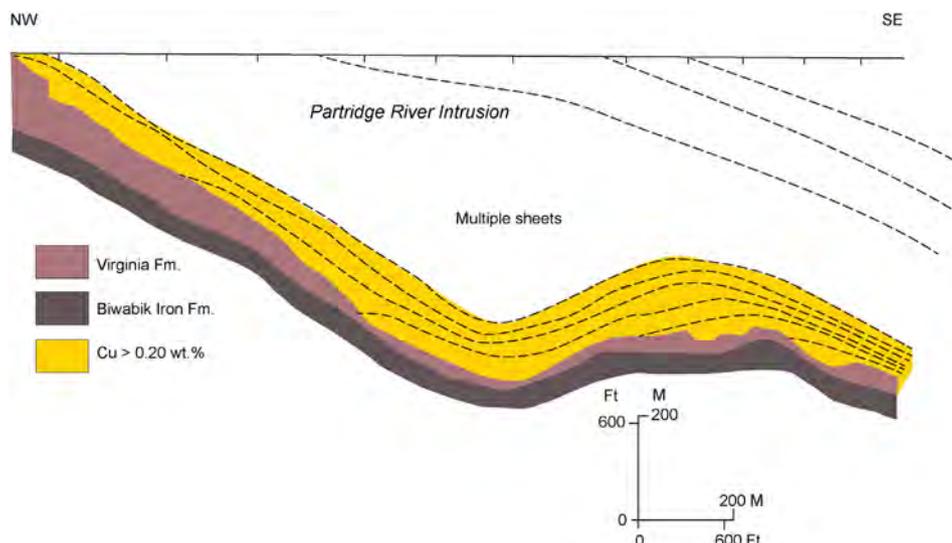
Sulfide mineralization in the Duluth Complex (Fig. 2) is primarily disseminated in form (Fig. 3), with host rocks including troctolite, gabbro, and locally gabbro-norite or norite. The sulfide-bearing rocks occur as sheet-like bodies that occur between underlying Proterozoic or Archean country rocks and overlying intrusive sheets that contain minor or no sulfide mineralization (Fig. 4). Only two of the intrusions that comprise the Duluth Complex are known to contain potentially

economic sulfide mineralization. Sulfide-bearing zones occur in the lower portions of both the Partridge River and South Kawishiwi intrusions (Fig. 2). Sulfide-bearing zones are heterogeneous in terms of rock types, mineral compositions and degree of sulfide mineralization. Principal sulfide minerals are pyrrhotite, chalcopyrite, cubanite and pentlandite. Minor minerals include bornite, talnakhite, chalcocite, digenite, violarite, mackinawite, native Cu, and a variety of Pt-group minerals. Drill core samples were collected from mineralized horizons in both the Partridge River and South Kawishiwi intrusions. Although most samples represent disseminated sulfide mineralization, one sample was taken from a rare, massive sulfide zone within the Partridge River intrusion. The Eagle Ni–Cu deposit is hosted by the Eagle mafic-ultramafic intrusion, associated with the Marquette–Baraga dikes (Fig. 2). Of particular significance is that the form and composition of the intrusion are distinctly different from those that host disseminated mineralization in the Duluth Complex. The intrusion is a sub-vertical dike-like body that intrudes Proterozoic metasedimentary deposits (Fig. 5). Rock types are olivine-rich and include feldspathic peridotite, melatroctolite and melagabbro. Massive, net-textured (Fig. 3), and disseminated sulfides are present, composed of variable amounts of pyrrhotite, chalcopyrite, cubanite, pentlandite and magnetite. Drill core samples for this study were primarily net-textured, but both disseminated and massive samples were also analyzed.

The Tamarack Intrusive Complex (TIC) is located approximately 75 km west of Duluth (Fig. 2), and near the western margin of the dominantly NE–SW trending Carlton County dike swarm (Green et al., 1987). The sulfide mineralization associated with intrusions of the TIC is also different than that found in the Partridge River and South Kawishiwi intrusions, and is considered to be conduit-type (Taranovic et al., 2015). The trend of the magnetic anomaly associated with the Complex is generally north–northwest, and no genetic association with rocks of the dike swarm has as yet been shown. However, the occurrence of the Eagle Intrusion near the margin of the Marquette–Baraga dike swarm provides a potential similarity. The TIC is considered to be a satellite



**Fig. 3.** A) Disseminated sulfide mineralization in troctolitic (plagioclase + olivine) rocks from the Partridge River Intrusion, Duluth Complex. B) Net-textured sulfide mineralization from the Eagle Intrusion: cp = chalcopyrite, po = pyrrhotite. Dark grains are olivine and pyroxene. C) Massive sulfide mineralization from the Eagle deposit with stringers of chalcopyrite (cp) within pyrrhotite (po).



**Fig. 4.** Cross section through the Partridge River Intrusion illustrating the multiple sheets from which the intrusion has been built, and the presence of sulfide mineralization in the lowest (early emplaced) sheets.

intrusion to the Duluth Complex (Nicholson et al., 1992), but is enriched in olivine compared to the sulfide-mineralized troctolitic intrusions in the Duluth Complex, and in this regard is similar to Eagle. Goldner (2011) obtained a U-Pb baddeleyite date of  $1105.6 \pm 1.2$  Ma, which indicates that the intrusion crystallized during the early stages of rift development (Miller and Nicholson, 2013), again similar to the Eagle intrusion. The overall shape in the northern portion of the TIC is an irregular funnel, or chonolith. The wide top portion is composed of mostly fine grained peridotite, feldspathic peridotite, feldspathic pyroxenite, and melagabbro. This intrusive sequence hosts mostly disseminated and patchy net textured sulfide mineralization. The narrow, dike like, bottom portion is composed of coarse-grained peridotite, feldspathic peridotite, melatroctolite and melagabbro. This intrusive sequence hosts sulfide mineralization only locally. Both disseminated and net-textured sulfide mineralization from drill cores were sampled for this study.

Country rocks into which magmas of the Duluth Complex were emplaced include both Archean and Paleoproterozoic rocks (Fig. 2). Archean rocks are of sedimentary, volcanic, and intrusive origin. The Paleoproterozoic rocks are members of what is known as the Animikie Group and include the Biwabik Iron Formation, and the Virginia and Thomson Formations (Fig. 2). Of particular significance for the genesis of sulfide mineralization in the Duluth Complex is the fact that argillites, siltstones, and graywackes of the Virginia Formation contain variable quantities of pyrite (e.g., Ripley and Al-Jassar, 1987; Poulton et al., 2010; Pufahl et al., 2010; see Fig. 6). Near the contact with the Partridge River intrusion, pyritic and carbonaceous units of the Virginia Formation have been converted to pyrrhotite and graphite-rich, cordierite-bearing hornfels (e.g. Andrews and Ripley, 1989).

The TIC is hosted in Paleoproterozoic slates and graywackes of the Upper Thomson Formation of the Animikie Group. Rocks of the Thomson Formation are correlative with the Virginia and Rove Formations located to the north (Fig. 1; Hemming et al., 1995). In the immediate vicinity of the TIC the Thomson Formation consists of graphitic slates (Lower Thomson) and metagraywackes (Upper Thomson). The slates may contain layers of disseminated and massive pyrite, locally converted to pyrrhotite. Along contacts with the igneous rocks of the TIC country rocks are partially melted and recrystallized to a fine-grained mixture of muscovite, chlorite and quartz containing andalusite and cordierite porphyroblasts and are generally sulfide-poor.

Country rocks for the Eagle intrusion are also Archean and Paleoproterozoic in age. Archean rocks include gneiss, granitoids, and lower grade metasedimentary and metavolcanic rocks. Paleoproterozoic

rocks include metasedimentary and metavolcanic rocks of the Marquette Range Supergroup. Quartzites, carbonates, iron formations, volcanic rocks and turbidities are found in what is called the Baraga Group (e.g. Rossell, 2008). Sedimentary rocks of the Baraga Group are comprised of two fining upward sequences. Each of the two assemblages is capped by up to 300 m of carbonaceous slate with 1 to 10% pyrite and/or pyrrhotite. The uppermost slate unit at the top of the Marquette Range Supergroup is known as the Michigamme Formation. The Animikie Basin correlates with the Baraga Basin in upper Michigan and northern Wisconsin; the Thomson, Virginia and Rove Formations are thought to be correlative with the Michigamme Formation in the Baraga Basin.

Country rocks sampled as part of this study included relatively Cu-rich, sulfidic carbonaceous slates from the Virginia, Thomson and Michigamme formations (Fig. 6). Locations of sampled drill cores are shown in Fig. 2.

### 3. Analytical methods

Polished slabs of igneous rocks containing disseminated and net-textured sulfide minerals, as well as samples of massive sulfides, were prepared to permit microdrilling of individual sulfide minerals. A 0.5 mm carbide tipped drill was used. Three milliliters of 10 mol/L HCl, 0.8 ml of 15 mol/L HNO<sub>3</sub>, and 0.5 ml of 24.5 mol/L HF were added to each 5 to 10 mg sample, and the vessels were placed on a hot plate at 130 °C for 24 h. Samples were allowed to dry and taken up in 7 M HCl for column chemistry or 0.32 M HNO<sub>3</sub> for metal analysis. All extractions were conducted in a clean laboratory with acid-cleaned teflon PFA vessels. All nitric and hydrochloric acids used in this study were purified by sub-boiling distillation in PFA stills (Savillex®, USA). TraceMetal™ Grade hydrofluoric acid was used for sample digestion (Fisher Chemical, USA). Acids and experimental solutions were prepared with 18.2 MΩ/cm grade deionized water (Millipore®, USA).

For sedimentary rock samples approximately 70 mg of whole rock powder was weighed into a crucible and placed in a 1000 °C furnace for four hours. After this ashing process (designed to oxidize organic matter prior to acid dissolution), the remaining sample was weighed in a PFA vial (Savillex®, USA), and 1 ml of 10 mol/L HCl, 2 ml of 15 mol/L HNO<sub>3</sub>, and 1 ml of 24.5 mol/L HF were added. The PFA vials were placed on a hot plate at 130 °C for 24 h. After the samples were fully digested, the dried sample was re-dissolved once in 0.5 ml 15 mol/L HNO<sub>3</sub> and once in 0.5 ml 10 mol/L HCl, to remove possible HF remaining in the digested samples. Samples were finally taken up

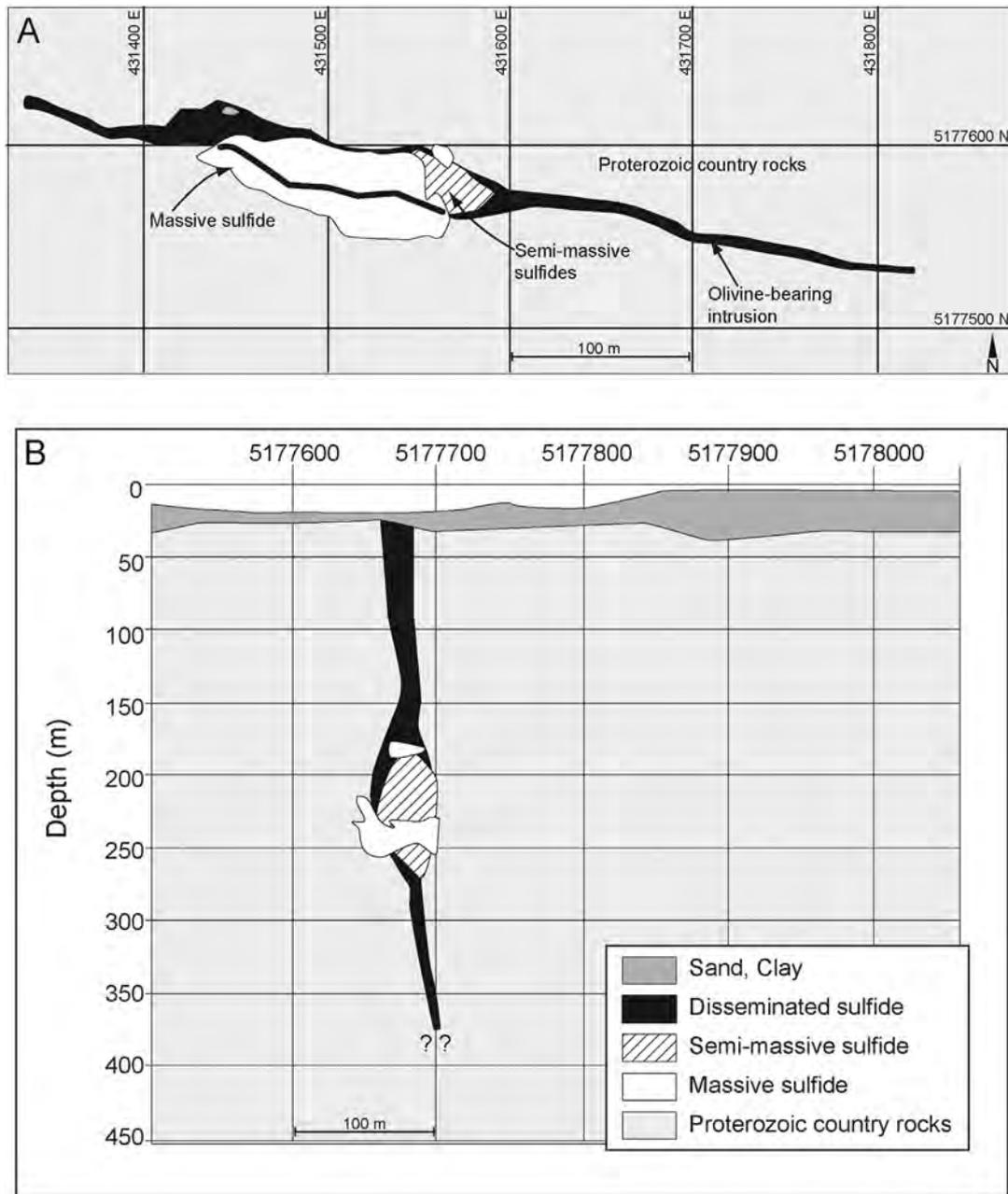


Fig. 5. A) Plan map of the Eagle Intrusion at the 200 m level. B) Cross section illustrating the dike-like geometry of the intrusion with associated mineralization.

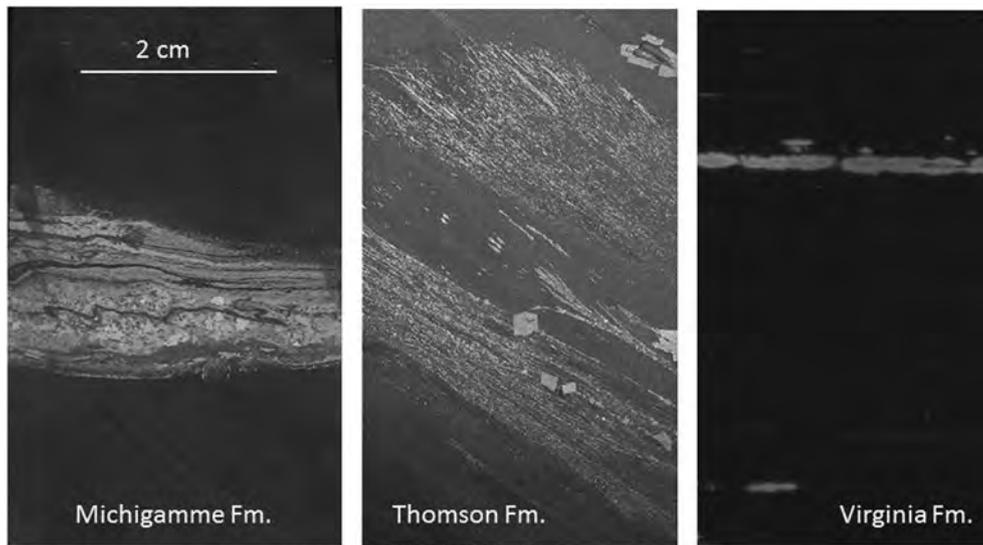
in 10 ml 7 mol/L HCl and stored for concentration analysis and Cu isotope ratio measurement.

For concentration analyses 9.95 ml of 0.3 mol/L  $\text{HNO}_3$  were added to 0.05 ml of the stock solution. Concentrations were measured using an Agilent 7700 ICP-MS (Agilent Technologies, CA, USA). The analytical precision is estimated from repeated analysis on different days of a mixture of single element solutions for quality control and is approximately 4% ( $n = 4$ , 2SD). The analytical accuracy and the digestion efficiency were tested by three repeated digestions and analyses of sulfide reference material Su-1. The measurement of the digested Su-1 was mixed in different analytical sessions, and result shown the Cu content of Su-1 was  $0.83 \pm 0.03\%$  ( $n = 3$ , 1SD), which is comparable with the certified value of  $0.87 \pm 0.01\%$  (Faye and Sutarno, 1976).

For isotope ratio measurements the digested samples were passed through an ion chromatography column to remove matrices that could interfere with the accuracy and precision of the Cu isotope ratio measurement. The chromatography column procedure was modified

from Chapman et al. (2006). Pre-acid cleaned Bio-Rad® AG MP-1 resin (100–200 mesh; Bio-Rad Laboratories, USA) and Bio-Rad® polypropylene columns (2 ml of resin support and 10 ml reservoir) were used for the separation. After the Cu fraction of each sample was collected with 30 ml 7 mol/L HCl, eluents were dried and refluxed with 15 mol/L  $\text{HNO}_3$  and dried again to break down and evaporate any organic matter from the resin. The samples were finally re-dissolved in 0.3 mol/L  $\text{HNO}_3$  for isotope analysis. The total blank for digestion, sample preparation and Cu separation was below 3 ng for ore samples and 10 ng for sedimentary rocks (presumably related to the ashing procedure for the sedimentary rocks). The recovery of Cu from each column was tested with ICP-MS. The sample was used for Cu isotope analysis when the recovery was  $100 \pm 4\%$ .

The Cu isotope ratios were determined using a Nu Plasma II (Nu Instruments Limited, UK) multiple-collector inductively coupled plasma mass spectrometer (MC-ICP-MS). The samples were introduced with an Aridus II Desolvating Nebulizer System (Teledyne Cetac, NE, USA)



**Fig. 6.** Drill core samples of pyritic and carbonaceous shales that are part of the Paleoproterozoic country rocks to the Eagle intrusion, the Tamarack Igneous Complex and the Duluth Complex: A) the Michigamme Formation, B) the Thomson Formation and C) the Virginia Formation.

and PTFE nebulizer. Data were collected as 1 block of 30 measurements (5 s integration time for each measurement) with samples run either three or four times. Numbers in Table 1 represent the average of these internal replicates. The wash out time between samples was 110 s using 0.3 mol/L HNO<sub>3</sub>. Instrumental mass bias effects were monitored and corrected for using standard sample bracketing with external normalization for Cu isotope measurements (Peel et al., 2008). A Zn solution was doped into each standard and sample that was measured. Samples were run using ~100 to 150 ppb of both Cu and Zn. The analyses consumed approximately 1 ml of solution, so 100 to 150 ng each of Cu and Zn were used per analysis. The isobaric interference from <sup>64</sup>Ni on <sup>64</sup>Zn was monitored using the intensity measurements of <sup>62</sup>Ni and was negligible (typically less than 15 ppm).

The NIST SRM 976 elemental Cu isotopic reference material (with the exact value of 0‰ defining the  $\delta^{65}\text{Cu}_{(\text{NIST } 976)}$  scale; Brand et al., 2014) was used as the standard in this study. The Cu isotope ratios are reported as  $\delta^{65}\text{Cu}_{(\text{NIST}976)}$  using  $\delta$ -notation (Coplen, 2011):

$$\delta^{65}\text{Cu}_{(\text{NIST } 976)} = \left( \frac{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{sample}}}{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{standard}}} \right) - 1$$

Values are reported in per mil (‰) deviation from the standard by multiplying the delta value by 1000. Replicate analyses of the Su-1 standard gave a value of  $-0.09 \pm 0.09\%$ ; the value recorded by Chapman et al. (2006) is  $-0.018 \pm 0.08\%$ . Duplicate or triplicate analyses of samples for this study indicate an uncertainty of  $\pm 0.15\%$ .

#### 4. Results

Results of copper isotope measurements of sulfide minerals in the igneous rocks and bulk sedimentary rocks are given in Table 1. Electron microprobe analyses (Cameca SX-50 at Indiana University) of pyrrhotite and pentlandite indicate that these minerals contain concentrations of Cu below detection limit (400 ppm); hence the Cu amounts are those contributed by chalcopyrite.  $\delta^{65}\text{Cu}_{(\text{NIST } 976)}$  values range from 0.45 to  $-0.85\%$  for samples from the South Kawishiwi and Partridge River intrusions (Fig. 7). In sharp contrast,  $\delta^{65}\text{Cu}_{(\text{NIST } 976)}$  values of samples from the Eagle intrusion range from 0.69 to 1.32‰ and samples from the TIC range from 0.99 to 1.84‰ (Fig. 7). Most samples of the Virginia and Thomson Formations range from  $-0.33$  to 1.18‰; two samples from the Virginia Formation have considerably higher values of 2.65 and 3.12‰. Most of the  $\delta^{65}\text{Cu}$  values of the sedimentary rocks overlap those of the sulfide minerals from the Eagle and Tamarack deposits.

#### 5. Discussion

##### 5.1. Cu isotope variations in mafic rocks and related ore deposits

The  $\delta^{65}\text{Cu}_{(\text{NIST } 976)}$  value of the mantle remains poorly defined, although available analyses indicate that the value is close to 0‰ (e.g., Luck et al., 2003; Ben Othman et al., 2006). Luck et al. (2005) reported values of  $-0.5$  to 0.5‰ for iron meteorites and  $-1.5$  to 0.0‰ for carbonaceous chondrites. Based on these values Luck et al. (2005) suggested the presence of two isotopically distinct primordial reservoirs of Cu. Bishop et al. (2012) showed that iron meteorites may range from those with  $\delta^{65}\text{Cu}$  values that center on 0‰ to those with more negative values as low as  $\sim -1.5\%$ . Mantle peridotites analyzed by Ben Othman et al. (2006) yielded  $\delta^{65}\text{Cu}_{(\text{NIST } 976)}$  values of 0.0 to 0.18‰, whereas basalt values given by Luck et al. (2003) range from  $-0.10$  to  $-0.03\%$ . Herzog et al. (2009) reported one terrestrial basalt at 0 to  $-0.1\%$  and lunar basalts between 0.1 and 1.4‰. They suggest that the higher  $\delta^{65}\text{Cu}$  values of lunar basalts relative to terrestrial basalts are due to lunar igneous processes. Dekov et al. (2013) reported  $\delta^{65}\text{Cu}$  values of basalts and native Cu within them of 0.0 to 0.3‰. Zhu et al. (2000) reported five values of chalcopyrite from Sudbury, and Larson et al. (2003) reported an additional two, with all values between  $-0.25$  and 0.16‰. The values for Sudbury are most likely misleading in terms of a mantle indicator, as the impact event that generated the Sudbury structure produced a melt sheet that was composed of both crustal (sedimentary) and mantle derived (mafic intrusions) material (e.g., Keays and Lightfoot, 2004; Ames et al., 2008). Malitch et al. (2014) report a value of  $-0.1\%$  for chalcopyrite from the PGE-rich J-M Reef of the Stillwater Complex. The only systematic study of magmatic Ni–Cu–PGE deposits has been that of Malitch et al. (2014) of the Noril'sk–Talnakh region. The deposits of the Noril'sk area are much higher grade than those in the Duluth Complex, but bear similarities in terms of their localization in sill or sheet-like intrusions and in their S isotope compositions, which are strongly indicative of the involvement of crustal S in the ore-forming process (e.g., Malitch et al., 2014; Ripley, 2014). Malitch et al. (2014) document a progression in Cu isotope values from those of relatively low values at the Kharaelakh deposit ( $-2.3$  to  $-0.9\%$ ) and the Talnakh occurrences ( $-1.1$  to 0.0‰) to the higher values of the Noril'sk-1 intrusion ( $-0.1$  to 0.6‰). The  $\delta^{65}\text{Cu}$  values of the South Kawishiwi and Partridge River intrusions are in the range of the values from the Talnakh and Noril'sk-1 intrusions, whereas the values from the conduit style Eagle and Tamarack deposits are higher. Malitch et al. (2014) suggest that the differences between the deposits in the Noril'sk region may

**Table 1**

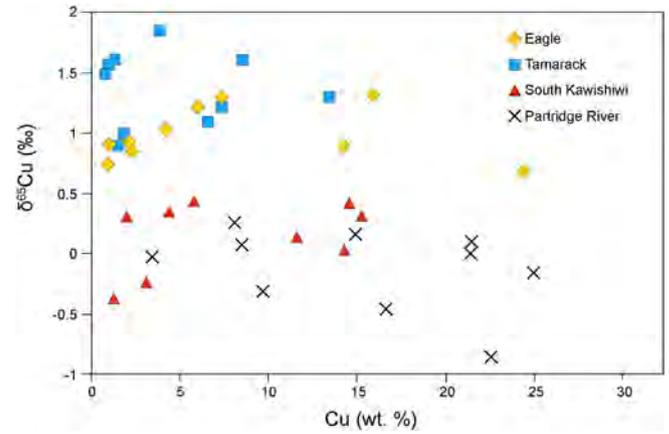
Cu isotope values of sulfide mineralization and sedimentary rocks from the Midcontinent Rift System.

Sample no.	Type	$\delta^{65}\text{Cu}$ (‰)	2SD	Cu (wt.%)
<i>Eagle Deposit</i>				
04EA047-352	net-textured	0.93	0.08	2.09
06EA122-286.74	net-textured	1.32	0.12	15.88
04EA044-730	disseminated	0.90	0.04	14.25
06EA122-315.83	massive	0.69	0.08	24.41
06EA122-293.96	disseminated	1.03	0.06	4.19
04EA065-86.27	net-textured	1.21	0.11	6.01
04EA065-89.27	net-textured	1.31	0.08	7.38
05EA092-194.57	net-textured	0.91	0.11	1.09
04EA076-197.92	net-textured	0.86	0.11	2.38
07EA176-279.28	net-textured	0.74	0.08	0.99
<i>Tamarack</i>				
120/483.25	disseminated	1.59	0.04	8.58
96/292.6	net-textured	1.29	0.12	13.64
14/163.1	disseminated	1.84	0.08	3.9
127/347.9	disseminated	1.10	0.05	6.60
49/447	disseminated	1.60	0.09	1.33
120/420.8	disseminated	1.55	0.10	1.03
07/195.05	disseminated	1.66	0.07	0.90
49/438.7	net-textured	1.21	0.16	7.37
67/505.6	disseminated	0.99	0.11	1.86
120/447.0	disseminated	1.49	0.08	0.94
<i>South Kawishiwi</i>				
34,870-A-563.57	disseminated	0.42	0.09	14.53
34,870-A-562.35	disseminated	-0.36	0.10	1.36
34,870-A-441.41	disseminated	-0.23	0.06	3.14
32,706-640	disseminated	0.45	0.10	5.77
32,715-600	disseminated	0.33	0.10	15.30
32,715-340	disseminated	0.03	0.07	14.19
32,706-580	disseminated	0.35	0.10	4.42
32,715-500	disseminated	0.15	0.07	11.59
34,870-A-560	disseminated	0.32	0.09	2.00
<i>Partridge River</i>				
B4W - drift	massive	-0.46	0.09	16.59
189-618.74	disseminated	0.16	0.05	14.90
189-610.51	disseminated	0.10	0.04	21.43
189-624.23	disseminated	-0.02	0.05	3.45
189-621.18	disseminated	0.01	0.07	21.42
189-613.56	disseminated	0.07	0.06	8.51
189-673.63	disseminated	-0.85	0.11	22.52
10,053-159	disseminated	-0.15	0.09	24.95
146-569.36	disseminated	0.26	0.09	8.06
136-529.74	disseminated	-0.30	0.08	9.69
<i>Sedimentary Rocks</i>				
24,981-156	Virginia Fm.	2.65	0.05	0.0697
24,981-210.7	Virginia Fm.	1.06	0.11	0.0255
24,981-213.5	Virginia Fm.	0.25	0.06	0.0265
24,981-212.5	Virginia Fm.	0.56	0.04	0.0152
MDD2-433.12	Virginia Fm.	0.91	0.04	0.0122
MDD2-434.03	Virginia Fm.	0.82	0.06	0.0096
2833-70.5	Virginia Fm.	-0.33	0.40	0.0085
2839-55.5	Virginia Fm.	0.61	0.08	0.0111
7554-69.5	Virginia Fm.	0.63	0.04	0.0135
7554-64.0	Virginia Fm.	1.11	0.08	0.0244
126-497.59	Thomson Fm.	3.12	0.12	0.0041
126-449.21	Thomson Fm.	1.18	0.04	0.0023
134-152.88	Thomson Fm.	0.38	0.10	0.0085
134-186.30	Thomson Fm.	0.61	0.05	0.0113
134-167.10	Thomson Fm.	0.78	0.04	0.0089

be due to magmatic fractionation of Cu isotopes, to differences in the Cu isotope ratio of primary parental magmas, or to assimilation of Cu from external sources.

## 5.2. Cu isotope variations in rocks from the Midcontinent Rift System

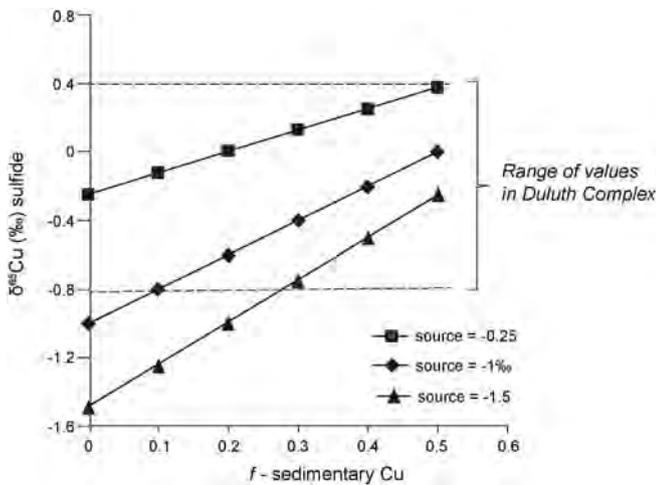
Data on the Cu isotope ratios of sedimentary rocks are limited. Albarede (2004) has noted that Cu associated with Mn nodules is characterized by  $\delta^{65}\text{Cu}$  values of  $0.31 \pm 0.23\%$ . Dekov et al. (2013) report



**Fig. 7.**  $\delta^{65}\text{Cu}$  values versus Cu concentration for sulfide mineralization from the Duluth Complex (Partridge River and South Kawishiwi Intrusions), the Eagle Intrusion and the Tamarack Igneous Complex.

$\delta^{65}\text{Cu}$  values of 0.41 to 0.95‰ for Cu in oceanic sedimentary layers. Cu in seawater itself shows positive values between 0.8 and 1.5‰ (Vance et al., 2008; Takano et al., 2013; Thompson et al., 2013). Experimental studies of  $\text{Cu}^{2+}$  adsorption onto iron oxyhydroxides detected an enrichment of  $^{65}\text{Cu}$  in the minerals (Balistrieri et al., 2008; Pokrovsky et al., 2008). It remains unclear if the  $^{65}\text{Cu}$  enrichment in the sedimentary material relative to most mafic rock types is due to adsorption processes or to redox related processes that may strongly fractionate Cu isotopes in low-to moderate temperature environments (e.g., Rouxel et al., 2004; Mathur et al., 2005; Mason et al., 2005; Sherman, 2013), or to both. Although the conditions under which the sulfidic and carbonaceous rocks of the Virginia and Thomson Formations were deposited were relatively reducing, it is probable that much of the Cu present in the rocks was derived via leaching of oceanic crustal material in a back arc environment (e.g., Ripley et al., 2001a,b). Re–Os isotopic data from the Virginia Formation (kerogen and sulfides) indicates that seawater must have interacted with mantle-derived rocks and a back-arc environment is consistent with the interpretation for the development of the Animikie Basin (Hemming et al., 1995). For this reason redox-controlled Cu isotope fractionation could have accompanied the leaching process and affected the Cu isotope composition of local seawater. Both S and Re–Os isotopic data from the mineralization in the Duluth Complex (see recent review by Ripley, 2014) strongly indicate that crustal S, Re and Os were added to most of the magmatic pulses that contributed to the development of the sulfide-mineralized horizons.

In assessing the Cu isotope variations between the sheet-style and conduit-style mineralization, we first address the potential for Cu assimilation from country rocks. The  $\delta^{65}\text{Cu}$  values of the S- and C-rich sedimentary rocks of the Virginia and Thomson Formations that would be the likely sources of Cu are in general similar to those of sulfides from the Eagle and Tamarack deposits. Our expectations were then that perhaps externally derived Cu could contribute to the high Cu/Ni ratios and the overall Cu-rich nature of the mineralization in the lower portions of the South Kawishiwi and Partridge River Intrusions. The Cu isotope values of the sedimentary rocks and those from the Duluth Complex may support such a process, but the choice of the mantle end-member is critical. Although the  $\delta^{65}\text{Cu}$  value of the mantle is still not well-defined, the values for igneous rocks and meteorites given above (including those from lunar basalts) suggest that values of mantle-derived magmas could reasonably range from about -1.5 to 1.4‰. Mixing of Cu from a mantle source with a  $\delta^{65}\text{Cu}$  value near -1 (similar to values reported by Luck et al., 2005, and many iron meteorites reported by Bishop et al., 2012) with Cu from sedimentary rocks having a  $\delta^{65}\text{Cu}$  value near 1‰ could generate the relatively low  $\delta^{65}\text{Cu}$  values found in the sulfide mineralization of the Duluth Complex (Fig. 8). In



**Fig. 8.** Mixing diagram showing the Cu isotope values of various mixtures of mantle-derived Cu with  $\delta^{65}\text{Cu}$  values of  $-0.25$ ,  $-1.0$  and  $-1.5$ ‰ and sedimentary Cu with a  $\delta^{65}\text{Cu}$  value of  $+1$ ‰. Most of the values in the Duluth Complex can be the result of the addition of up to  $\sim 50\%$  crustal Cu if the source mantle value was between  $-0.25$  and  $-1.5$ ‰.

this scenario as much as 50% of the Cu in the sulfide mineralization in the intrusions of the Duluth Complex could be of sedimentary origin. With a source mantle  $\delta^{65}\text{Cu}$  value of  $-0.25$ ‰ or greater (perhaps more reasonable given the values from Luck et al., 2003; Ben Othman et al., 2006) it is difficult to generate the 0 to negative  $\delta^{65}\text{Cu}$  values of the Cu in the sulfide mineralization via mixing involving Cu from the sedimentary rocks. The  $\delta^{65}\text{Cu}$  values of the mineralization in the South Kawishiwi and Partridge River intrusions can only be a result of mixing with country rock Cu if the source mantle  $\delta^{65}\text{Cu}$  value was  $-0.25$ ‰ or less. The Cu isotope values of the sulfide minerals at Eagle and Tamarack are very similar to those of Cu from the sedimentary rocks of the Virginia and Thomson Formations, and very different from a potential mantle source with a negative  $\delta^{65}\text{Cu}$  value. The S and Re–Os isotopic data from Eagle and Tamarack do not show the extreme signals of contamination that mark much of the mineralization in the Duluth Complex (e.g., Ripley, 2014). Ding et al. (2010) and Taranovic et al. (in press) have attributed the lack of strong isotopic signals for contamination to possible isotopic exchange in the conduit involving sulfide accumulations and new inputs of relatively pristine magma. The result of the interaction is the return of isotopic signals that corresponded to extensive contamination to values approaching those of uncontaminated mantle-derived magma. Although such a process is reasonable for S and Os, it is less reasonable for Cu. With the assumption that the primary mantle  $\delta^{65}\text{Cu}$  (NIST 976) value is not far removed from 0 (potentially negative), and that the rate of Cu isotope exchange is not significantly different from those of S and Os, the elevated values now observed in the sulfide mineralization at Eagle and Tamarack would point toward values in the contaminant material that would have been considerably higher than the  $\delta^{65}\text{Cu}$  values now observed. An end-member with such elevated  $\delta^{65}\text{Cu}$  values seems unlikely in the stratigraphic columns for either Eagle or Tamarack. For these reasons we reject the process of isotopic exchange in the conduit systems as a major control on the  $\delta^{65}\text{Cu}$  values.

In order to produce the distinct Cu isotope ranges observed in the Eagle and Tamarack occurrences relative to those of the mineralization in the Duluth Complex two alternatives may be considered. One is that the mantle sources from which the picrite and HAOT parental magmas were derived differed in Cu isotope values. Nicholson and Schulz (2009) proposed that picrites in the Midcontinent Rift System were derived from the central, hottest portions of the plume as it rose through the mantle. The HAOT magmas that were parental to voluminous volcanic rocks in the rift, as well as the troctolite-rich sequences in the Duluth Complex, were potentially produced from lower degree melting in

areas surrounding the plume head (e.g., Beccaluva et al., 2009). It is possible that the two source areas in the mantle are characterized by distinct isotopic compositions. A related scenario is that in the picritic melts Cu isotope values reflect those of the source as a result of complete sulfide dissolution during high-degree melting (with Cu held primarily as sulfide in the mantle). Partial retention of sulfide in the mantle in the case of lower degree melts may produce isotopic fractionation and a difference between sulfide in the picritic and HAOT melts.

The second alternative is that the HAOT are derived via fractional crystallization from a picritic parent. We have previously shown (e.g., Ripley and Li, 2013) using the MELTS algorithm (Ghiorso and Sack, 1995) that this process is feasible and can account for the differences in olivine compositions and lower overall Ni content of the HAOT liquids relative to the picrites. However, the process of fractional crystallization alone, without the involvement of S, should do little to affect Cu isotope ratios as Cu is an incompatible element whose concentration will increase with fractional crystallization. If sulfide saturation were reached either due to fractional crystallization alone or due to external sulfide addition during the fractional crystallization process, then perhaps Cu isotope fractionation could have occurred as sulfide liquid accumulated in much the same manner as proposed above for sulfide retention in the mantle. Studies by Williams and Archer (2011) suggest that Cu isotope fractionation in iron meteorites may accompany the diffusive transfer of Cu from metal into exsolving sulfide. Both a kinetic isotope effect and incomplete equilibrium between metal and sulfide were proposed. These mechanisms bear some similarity to those proposed here in that Cu isotope fractionation may be related to a kinetic effect accompanying the accumulation of Cu in a sulfide liquid.

The obvious weakness for models involving Cu isotope fractionation related to mantle source area or to magmatic processes that may involve sulfide liquids is that the exact cause of such fractionation is unclear. Experimental studies at high temperatures are needed to evaluate potential Cu isotope fractionation mechanisms. Presumably such fractionation would be related to the incorporation of small amounts of Cu into early crystallizing monosulfide solid solution (MSS) during sulfide liquid differentiation relative to the retention of major amounts of Cu in the residual liquid. In the Duluth Complex if the anomalously high Cu/Ni ratios are related to the incorporation of highly evolved sulfide liquid, then perhaps Cu isotope fractionation related to a Rayleigh process has merit. In addition, large scale studies of picrites and basalts in flood basalt and other provinces are needed to determine if the Cu isotope differences between the picrite-related conduit deposits and the disseminated mineralization in the HAOT-related sheet-type intrusions are universal or specific to the Midcontinent Rift System.

## 6. Conclusions

Cu isotope values of sulfide mineralization in sheet-like intrusions and conduits in the Midcontinent Rift are distinctly different.  $\delta^{65}\text{Cu}_{\text{(NIST 976)}}$  values of samples from the Eagle intrusion range from 0.69 to 1.32‰ and samples from the TIC range from 0.99 to 1.84‰. The isotopic composition of Cu in sulfidic and carbonaceous sedimentary rocks are similar to those in the conduit-related deposits of Eagle and Tamarack; the values of the sulfide mineralization in the South Kawishiwi and Partridge River intrusions are much lower and range from  $-0.85$  to 0.45‰. Although S and Re–Os isotopic data indicate the involvement of crustally derived S and Os in the mineralization of the sheet-style mineralization, the addition of crustally derived Cu to the parental magmas is consistent with Cu isotope values only if the mantle source magma was characterized by negative  $\delta^{65}\text{Cu}$  values. The potential assimilation of country rock Cu by magmas that gave rise to mineralization in the Duluth Complex can only in part explain the differences in  $\delta^{65}\text{Cu}$  values observed for the Duluth Complex mineralization versus those for the Eagle intrusion and TIC. There appear to be two broad additional alternatives to explain the Cu isotope variations. One is that Cu isotope variations exist in the mantle and that the picritic and HAOT

parental magmas originated from different mantle sources in the rift. A corollary to this mechanism is that the source did not vary, but different degrees of mantle melting led to partial retention of Cu in the source and isotopic fractionation accompanied the process. The other is that magmatic processes that led to Cu enrichment in the sheet-style intrusions also produced Cu isotope fractionation. One such process may have been Rayleigh fractionation during the crystallization of a sulfide liquid. Experimental studies of potential Cu isotope fractionation at high temperatures and detailed studies of rock types from various mantle sources are needed to resolve the origin of Cu isotope variations that have now been documented in rift-related magmatic sulfide occurrences.

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*Part II. Cu isotope measurements of mafic and ultramafic rocks with low Cu concentrations*

During our analyses of Cu-bearing sulfide assemblages from igneous rocks in the Midcontinent Rift it became apparent that as Cu concentration dropped below approximately 1 weight percent, Cu isotope ratios markedly deviated from the plateau values at higher Cu concentrations. The figures below show results from synthetic mixtures of standard chalcopyrite and pyrrhotite (< 400 ppm Cu) or troctolite (Fig. 1), and natural samples from the Eagle deposit (Fig. 2).

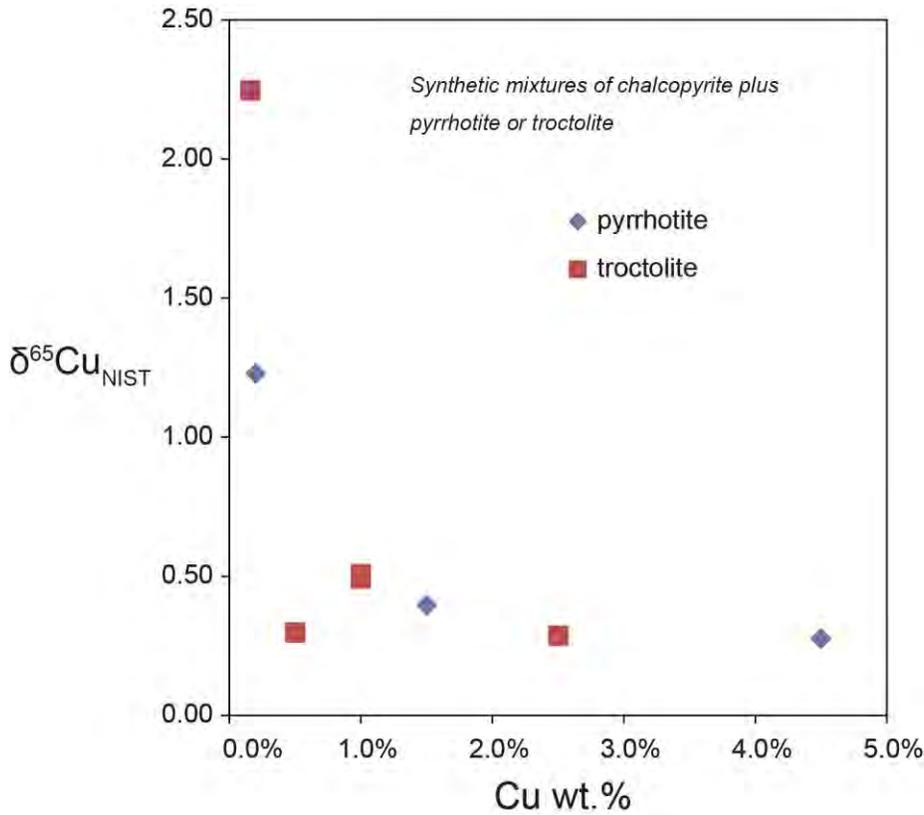


Figure 1. Laboratory mixtures of chalcopyrite and either pyrrhotite or troctolite. Note the strong change in Cu isotope ratios at concentrations < ~ 1 wt.%.

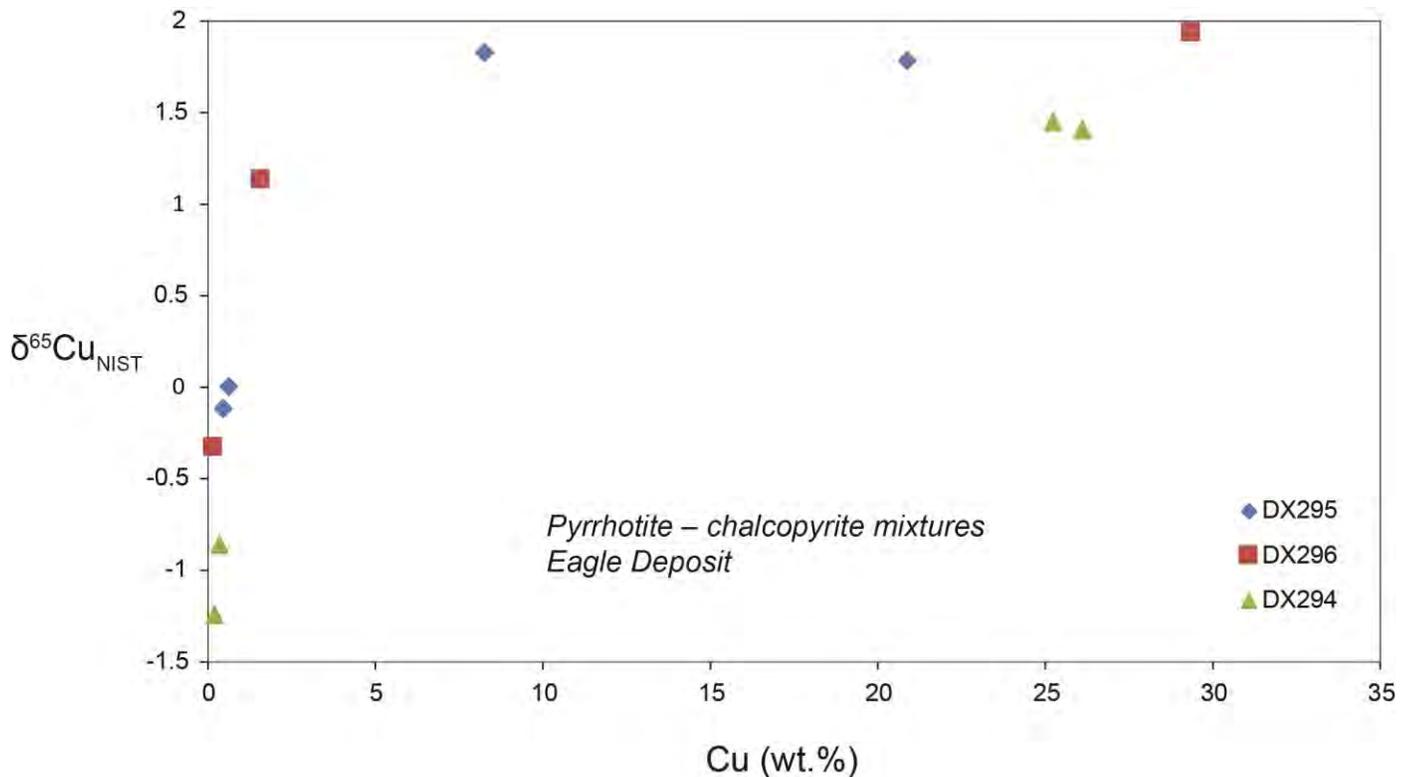


Figure 2. Natural pyrrhotite-chalcopyrite mixtures from the Eagle deposit. Again note the strong change in Cu isotope ratios at Cu concentrations  $< \sim 1$  wt.%.

In order to make precise measurements of low-Cu samples such as basalts, gabbros and troctolites, we have found that a wet plasma is necessary, as well as very efficient separation of both Ni and Ti to eliminate matrix effects. Figures 3 and 4 illustrate the effects of Ti and Ni on measurements of Cu isotope ratios. The technique of standard-sample bracketing works well for reducing effects of Ni, but not Ti. This is important because of the relatively high Ti contents of basalts, gabbros and troctolites in the Midcontinent Rift System. We have designed new elution columns for better separation of Cu, Ni and Ti. The columns are much longer with a special frit and initial tests indicate that efficient separation of Ni and Ti from Cu can be achieved (Figure 5). We are currently completing the elution tests and will begin to make Cu isotope measurements of low-Cu samples soon. Our pilot study of low-Cu picrites and basaltic rocks with a high-Al olivine tholeiite parentage will be used in an NSF proposal that we plan to submit for the next target date in Decemebr.

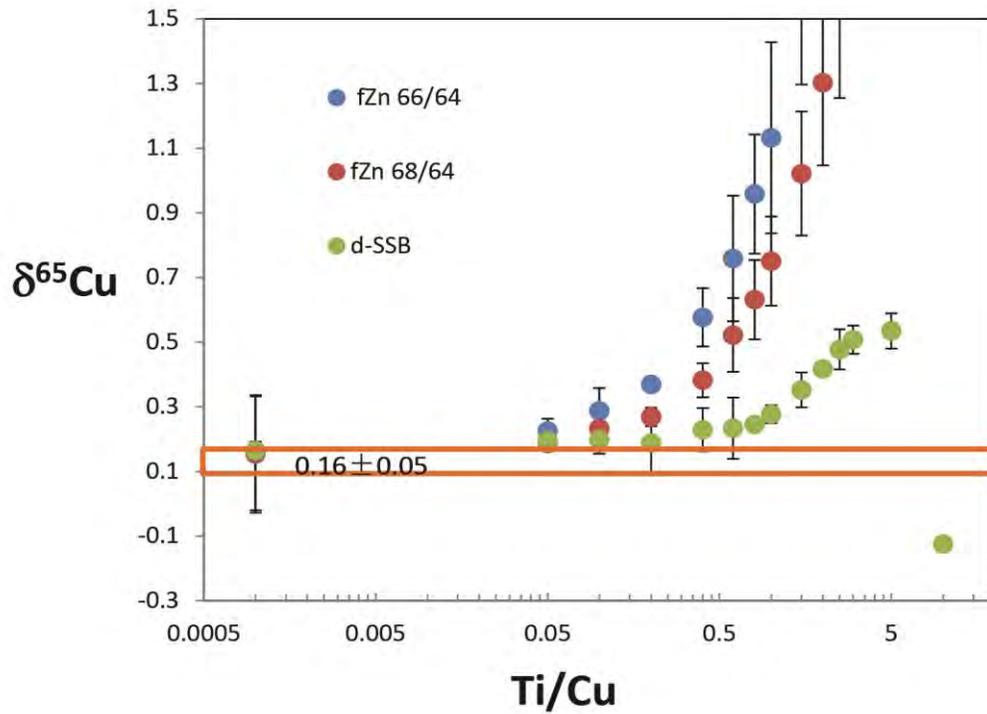


Figure 3. Copper isotope ratio versus Ti/Cu ratio. At Ti/Cu values in excess of  $\sim 0.05$  isotopic deviation from the acceptable value occurs, whether the calibration is based on Zn isotope ratios or via standard-sample bracketing.

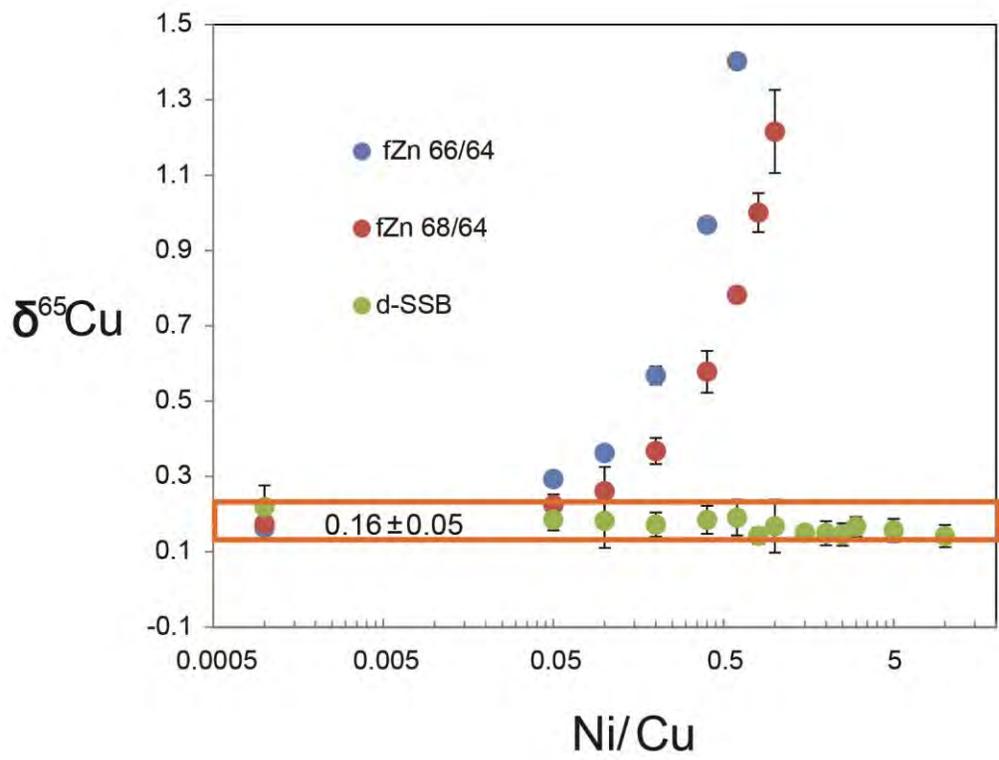


Figure 4. Copper isotope ratio versus Ni/Cu ratio. For Ni matrix effects the technique of standard-sample bracketing works well but is time intensive, and is not effective for effects related to Ti abundance.

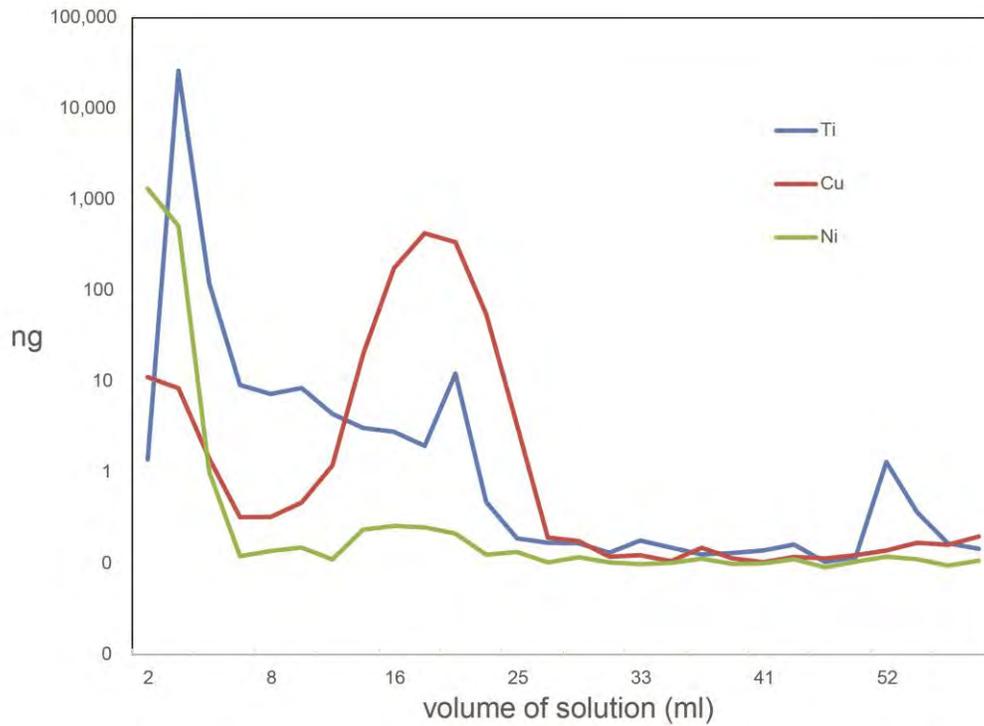


Figure 5. Separation of Ti and Ni from Cu using new, longer, elution columns. Cu collection from the 8<sup>th</sup> to the 33<sup>rd</sup> ml removes 99.93% Ti and 99.88% Ni, with collection of 99% Cu. We are investigating the Cu that is eluted in the first 6 ml. This may be related to Cu oxidation state.