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CONCENTRATION OF METALS ASSOCIATED WITH THE NATIVE COPPER DEPOSITS OF NORTHERN MICHIGAN

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ABSTRACT

The Keweenaw Peninsula of northern Michigan is home to the largest accumulation of native copper in the world. Native copper deposits are hosted in the 1.1 billion-year old midcontinent rift which extends from Kansas, up through Lake Superior, around into lower Michigan, but is only exposed in the Keweenaw region. Native copper is found in the vesicular and brecciated flow tops of the volcanism associated with this rift, within the interflow conglomerate that developed in-between individual flows, and also minor native copper deposits are found with the copper sulfide deposits in the Nonesuch Shale. The purpose of this study was to examine the concentrations of zinc, lead, and silver associated with native copper in each of these depositional environments in hopes of gaining an understanding of the geochemistry of the native copper in this area. Eleven copper samples were examined using X-Ray fluorescence spectroscopy. Three geologic areas of copper deposition studied were: the brecciated and amygdaloidal flow tops of the Portage Lake Volcanics (PLV), conglomerate layers in between PLV basalt flows, and fracture fillings of the Nonesuch Shale, as seen in the White Pine Copper Mine. The volcanic flow tops exhibited decreased Zn, Pb, and Ag with increasing Cu. Within the interflow conglomerates, chemical relationships showed an increase in Zn but a decrease in Pb and Ag with increasing Cu. In both of these sets, chemical ratios of Pb/Zn decreased with increasing Cu/Ag in a decay-like curve. The native copper as fracture filling in shale had a different chemical signature in which the Ag increased with Cu. Chemical data from this study may help in our understanding of fluid composition associated with hydrothermal copper mineralization.

KEY WORDS: Keweenaw Peninsula, Midcontinent Rift, Nonesuch Shale, Portage Lake Volcanics, White Pine Copper mine, Precambrian Supereon, Mesoproterozoic, Superior Craton, Great Lakes Tectonic Zone, Marquette Supergroup, Penokeon Orogeny, Bovine Igneous Complex, Duluth Complex

INTRODUCTION

Our study focused on the concentrations of trace metals associated with native copper deposition in Michigan's Keweenaw Peninsula. The Keweenaw Peninsula is unique geologically for several reasons. The peninsula represents the largest deposit of native copper in the world, and was economically important to the development of Michigan and the United States for over a century. Most copper is found in association with sulfide minerals, consequently extensive native copper deposits are rare. The Keweenaw Peninsula is centered in the 1.1-billion-year old Midcontinent Rift, which represents a stage in a fascinating history of Precambrian tectonism. The volcanism associated with this failed rift system provided the source of the copper, which is hosted in the stratigraphy of the rift basin. This paper will summarize the geologic setting, tectonic history, and copper mineralization of this distinctive area, as well as provide the data and results of our X-ray fluorescence analysis of several native copper samples studied to gain a better understanding of the trace metals associated with the native copper during deposition.

GEOLOGIC SETTING

To present a full picture of the native copper mineralization in the Upper Peninsula of Michigan, the bedrock geology of the region must be considered. The somewhat complex bedrock geology extends over a significant block of time during the Precambrian Supereon, and the Keweenaw Peninsula of northern Michigan centers around the late Mesoproterozoic

midcontinent rift. The Midcontinent Rift extends over 3,219 km (2,000 mi) from Kansas, up through Minnesota, Wisconsin and Michigan's Upper Peninsula, and down into the Lower Peninsula of Michigan (Hinze, 1997). The rifting event cut through preexisting Paleoproterozoic and Archean rocks (Morey and Van Schmus, 1988). Consequently, it is pertinent to this study to have a basic understanding of the preexisting crust prior to rifting, as well as a full understanding of the volcanics and sedimentary units associated with the rifting event.

Archean gneisses in the Superior Craton represent the oldest rocks found within the region of interest (fig. 1). In addition to these gneisses, there are areas of granite and greenstone also of Archean age (Morey and Van Schmus, 1988; Bornhorst and Brandt, 2009). Together, the Archean gneisses, greenstone, and granitic plutons provide evidence of active, convergent margin tectonics to form the Great Lakes Tectonic Zone (Sims *et al.*, 1980; Bornhorst and Brandt, 2009). Younger metasedimentary units of the Marquette Supergroup were deposited during the Paleoproterozoic. Though these units have been folded and metamorphosed, the original sedimentary units of sandstone, dolomite, tillite, turbidite, and ironstones provide some insight to the depositional environments during this time (Morey and Van Schmus, 1988; Bornhorst and Brandt, 2009). Though several Paleoproterozoic, sedimentary rock units are recognized within the Great Lakes region, the Marquette Supergroup is the closest within the area of interest. Metamorphism of the

Marquette Supergroup, as well as numerous other units within the Lake Superior region, has been attributed to the Penokee Orogeny (Schultz and Cannon, 2007). Active subduction, from 1880 to 1830 Ma., not only provided volcanic activity, but ultimately led

to the formation of foliated rocks, indicative of continental collision, followed by plutonic igneous activity, evident in granitic plutons in the area (Schultz and Cannon, 2007).

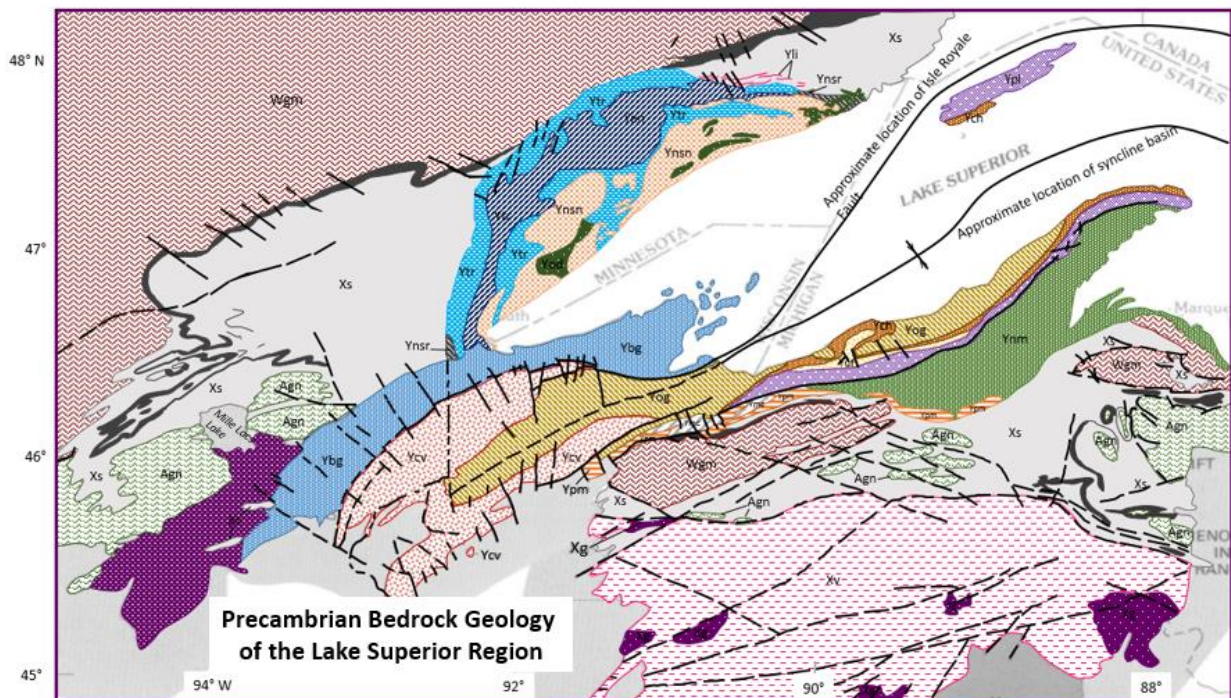





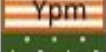


Figure 1. Map of the Precambrian bedrock in the Lake Superior region highlighting the generalized geology and major structural features. (After Morey and Van Schmus, 1987)

A significant erosional unconformity separates Archean and Paleoproterozoic crust with overlying units associated with the Midcontinent Rift. Beginning stages of the large-scale rifting appear to be recorded in plutonic mafic rocks such as the Duluth Complex (Hauck *et al.*, 1997) and the smaller Bovine Igneous Complex (Foley, 2011). Mafic igneous activity intruded the existing bedrock of Archean, Paleoproterozoic, or in some cases, the early



volcanic sequence of the rifting event (Hauck *et al.*, 1997). In any case, there is a wide variety of lithologies that made up the continental crust at the time of igneous activity. Igneous rocks associated with the rift system have been dated between 1109 to 1094 Ma (Morey and Van Schmus, 1988; Davis and Paces, 1990; Hinez *et al.*, 1997). According to Morey and Van Schmus (1988), the rift sequence near the Keweenaw Peninsula included the Bessemer

Middle Proterozoic

-  Ybg Bayfield Group, and Hinckley Sandstone and Fond du Lac Formation
-  Yog Oronto Group, undivided
-  Yuf Unnamed formation of White (1972)
-  Ych Copper Harbor Conglomerate
-  Ycv Chengwatana Volcanic Group and related rocks
-  Ypl Portage Lake Volcanics
-  Ymc Mellen Intrusive Complex
-  Ynm Jacobsville Sandstone
-  Ynsn North Shore Volcanic Group – normal polarity
-  Ynsr North Shore Volcanic Group – reversed polarity


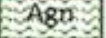
-  Ytr Troctolitic and Gabbroic series with related mafic and felsic rocks
-  Yaf Anorthosite series and related ultramafic to felsic rocks
-  Ypm Powder Mill Group and Bessemer Quartzite
-  Yod Olivine Diabase Intrusions
-  Yy Intrusions in Northern MN

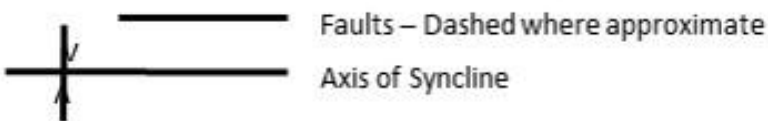
Early Proterozoic

-  Xg Granitoid rocks of tonalitic to granitic composition (1770-1890 Ma)
-  Xv Volcanic and granitoid rocks of the WI magmatic terrane

-  Xs Stratified rocks of the Animikie basin including iron formations

Archean

-  Wgm Archean rocks of the greenstone-granite terrane
-  Agn Archean rocks of the gneiss terrane



Quartzite, Powder Mill Group, Portage Lake Volcanics, Copper Harbor Conglomerate, Nonesuch Shale, and the Freda Sandstone in ascending order.

The oldest unit in the Keweenaw Supergroup is the Powder Mill Group, a series of subaerial basalt to basaltic-andesite flows associated with the earliest stages of the Midcontinent Rift extension (Hinze *et al.*, 1997). The Powder Mill Group is poorly exposed, and thus geophysical methods are used to infer stratigraphy. The Powder Mill Volcanics can be recognized apart from later volcanic flows due to a reversed magnetic polar orientation (Morey and Van Schmus, 1988; and Hinze *et al.*, 1997). These flows are relatively uniform in thickness, and are about 1-1.5 km in depth (Cannon and Nicholson, 2001).

Following the reversed polarity Powder Mill Group is the magnetic-normal unit of the Portage Lake Volcanics and the timing of the change in polarity is dated at 1097 Ma (Davis and Paces, 1990). The Portage Lake Volcanic Group is comprised of over 200 aluminum-rich subaerial tholeiitic flood basalt flows, ranging from 3-5 km (1.9-3.1 mi) thick in this region, (Bornhorst, 1997; Cannon and Richardson; Davis and Paces, 1990). Though predominantly basalt, there are interbedded siliciclastic rocks and some felsic volcanic units as well (Davis and Paces, 1990; Hinze *et al.*, 1997). The Portage Lake Volcanic section is of particular interest to this study because it serves as the host rock for much of the native copper mineralization (Bornhorst and Barron, 2011). Textures and structures of this volcanic section include vesicles and amygdules, as well as fissures

and fractures that later influenced fluid flow and mineralization. About one quarter of vesicular flow tops are also brecciated (Bornhorst, 1997). In addition to textural differences, chemical differences have been noted, with changes in the Ni content reflective of volcanic cycles (Hinze *et al.*, 1997). In the upper section, a characteristic greenstone flow is used as a marker bed to show position within the section and has been dated at 1094 Ma (Davis and Paces, 1990). The Portage Lake Volcanics represents the bulk of the volcanic activity with the rifting (Bornhorst and Lankton, 2009) and is followed by siliciclastic deposition with a few minor volcanic units during the remainder of the rifting.

Directly above the Portage Lake Volcanics lies the Oronto Group, consisting of the Copper Harbor Conglomerate, Nonesuch Shale, and the Freda Sandstone (Morey and Van Schmus, 1988). This group of rift-filling, sedimentary deposits formed after the majority of the volcanic activity in the region had ended. These sedimentary units are classified as “rift-filling” because during the period of deposition, they were deposited from multiple alluvial fans into the rift valley or graben (Daniels, 1982). Copper mineralization occurs within the Copper Harbor Conglomerate as native copper and in the Nonesuch Shale as copper sulfides (Bornhorst and Barron, 2011).

The Copper Harbor Conglomerate is a clastic zone of sedimentary conglomerate that generally fines upward towards sandstone (Daniels, 1982). The formation is confined to the interpreted rift valley and appears to have been deposited as alluvial fans, which fed into the basin (Elmore,

1984). According to Daniels (1982), clasts within the conglomerate are primarily volcanic ranging from mafic to intermediate to felsic compositions. Daniels (1982) also reported that the supporting sand matrix was similar in composition and dominated by lithic fragments of volcanic origin. However, this formation is not solely composed of sedimentary layers, as there are a few intermittent volcanic flows, including the Lake Shore Traps. This volcanic unit is been dated at 1087.2 Ma (Davis and Paces, 1990), which supports the rift valley fill interpretation. The alluvial fans exhibit some primitive form of grading, as the larger sediments have largely been sorted out by gravity at the boundary layer between the conglomerate and the shale. The movement of morphogenic hydrothermal fluids through the conglomerate/sandstone formation is facilitated by the 'oxidized red cement' that holds the conglomerate. The larger sediments in this series are also oxidized red (Brown, 2006) and the informal stratigraphic term "red bed conglomerate" has been applied to this formation.

Above the Copper Harbor Conglomerate lies the Nonesuch Shale (Morey and Van Schmus, 1988). The Nonesuch Shale is much harder to find, with exposures in only three major locations across the Keweenaw Peninsula (Morey and Van Schmus, 1988). Unlike the oxidized Copper Harbor Conglomerate below and the oxidized Freda Sandstone above, the Nonesuch shale is an unoxidized sequence of dark gray to black siltstone, shale and mudstone (Morey and Van Schmus, 1988). At the Bonanza Falls exposure, near the White Pine Mine, The Nonesuch Shale is

well laminated and exhibits both symmetrical and asymmetrical ripple marks, as well as trough-cross bedding (Bornhorst and Barron, 2011). Paleocurrent indicators of the Nonesuch Shale suggest deposition toward the center of the rift valley (Daniels, 1982). Composition of Nonesuch Shale, along with the sedimentary structures and thickness, suggest an anoxic, lacustrine depositional setting. The anoxic nature of this unit appears to distinctly influence the copper mineralization (Robertson, 1975).

Stratigraphically above the Nonesuch Shale lies the Freda Sandstone. The Freda Sandstone is a reddish brown, fine to coarse grained micaceous, lithic sandstone with occasional pebbly layers (Bornhorst and Barron, 2011). The Freda Formation is volumetrically the dominant rift filling sedimentary unit with an exposed thickness of over 4000 m along the margin of the rift and possibly even thicker under Lake Superior (Bornhorst and Barron 2011). The Freda Sandstone is more mature, as noted by the quantity of quartz compared to the Copper Harbor Conglomerate and Nonesuch Shale (Daniels, 1982).

TECTONIC HISTORY

Great Lakes Tectonic Zone. The Great Lakes Tectonic Zone (GLTZ) is an ancient zone of convergence between two Archean crustal blocks with ages of 2,700 - 3,500 Ma. Archean gneisses to the south of the GLTZ represent the older crustal terrane with ages up to 3,500 Ma (Sims et al., 1980). However, ages in this area cluster around 2,700 Ma (Morey and Van Schmus, 1988). The Great Lakes Tectonic Zone

shows multiple deformation characteristics, and include brecciated zones along faults, as well as metamorphic foliation overprinting in the Archean gneiss to the south. The GLTZ extends from western Minnesota eastward to Ontario (Sims *et al.*, 1980). In general, the GLTZ trends east-northeastward but, is obscured by Midcontinent Rift rocks on either side of Lake Superior and terminates within the Grenville Province (Sims *et al.*, 1980). Most of the exposed rocks associated with the GLTZ in the Lake Superior Region are overprinted by the Penokean Orogeny.

Penokean Orogeny. The Penokean Orogeny is a tectonic event in which several microcontinents and island arcs converged onto the continental margin formed during the GLTZ. The accreted terrane was classified as an island arc and produced a change in subduction to the south and back arc extension in both the Superior craton and the island arc itself (Schulz and Cannon, 2007). The volcanic ranges remained active until about 1,850 Ma when another landmass, the Marshfield Craton, forced the rest of the Pembine-Wausau Range up over the Superior Craton, towards the north. Subsidence and sedimentation developed into a foreland basin within two very distinct time zones. In the north, the foreland basin began forming about 1853 Ma, and in the south the basin formation began about 1850 Ma. Along the southern fold and thrust belt, tectonic thickening resulted in high-grade metamorphism of the sediments by 1830 Ma (Schulz and Cannon, 2007). Following the metamorphism, multiple igneous plutons intruded the sedimentary and accreted arc

terrane marking the end of the Penokean Orogeny.

Midcontinent Rifting. A synclinal structure located under Lake Superior (fig. 1) is indicative of the failed Midcontinent Rift system that started approximately 1.1 billion years ago (fig. 2). Geophysical studies have confirmed the complex nature of sedimentary rocks overlying a thick section of mafic volcanic rocks (Hinze *et al.*, 1997) as indicated in Figure 3. This also helped to confirm the distance of the rift, which is almost 200 km (124 mi) long. There are two large faults that defined rift zone: The Keweenaw fault and the Isle Royale fault (Cannon, 1994). The Keweenaw fault travels the spine of the Keweenaw Peninsula and separates the Portage Lake Volcanic series from the Jacobsville Sandstone to the south, and the Isle Royale fault runs just north of Isle Royale (Bornhorst and Barron, 2011). Both of these faults are noted as reverse faults in the literature, with the Keweenaw fault dipping towards the northwest at an angle of 20 to 78 degrees (Daniel, 1982) though it was originally a normal fault produced by tensional forces of the rift zone. As a result, the Keweenaw fault must have experienced significant vertical displacement from where it was located during the normal faulting (Bornhorst, 1997) to become the reverse fault observed today.

Grenville Orogeny. The reactivation of the faults into reverse faults was brought about by the compressional forces of the Grenvillian Orogen. The Grenvillian compressional event marks the end of severe tectonic stress and activity in the region

brought upon by the Midcontinent Rift System. This period of tectonic stress is marked by reverse thrust faulting along both the Keweenaw and Isle Royale fault in the Lake Superior region along with uplift of previously deposited igneous and sedimentary layers. Tectonism within the Grenville province has been known to take place between 1,300 and 1,000 Ma leading scientists to the theory that the Keweenaw rift system opened up during a period of lessened compressional activity from the Grenville front, but was then sealed due to renewed compression from the Grenville province to the east (Cannon, 1994). The

temporal relationship between these events is shown in Figure 2. There is also a rapid change from extensional to compressional forces recorded in the Keweenaw region at 1,080 Ma with the reactivation of compression and high-angle reverse thrusting for about 30-40 million years (Cannon, 1994). At least two major pulses of convergence have been identified as the Elzevirian and Ottawan events, recorded within deformational features bordering the edge of the Grenville front. The Elzevirian pulse dates from 1,240 to 1,160 Ma and the Ottawan pulse is dated from 1,090 to 1,025 Ma (Cannon, 1994).

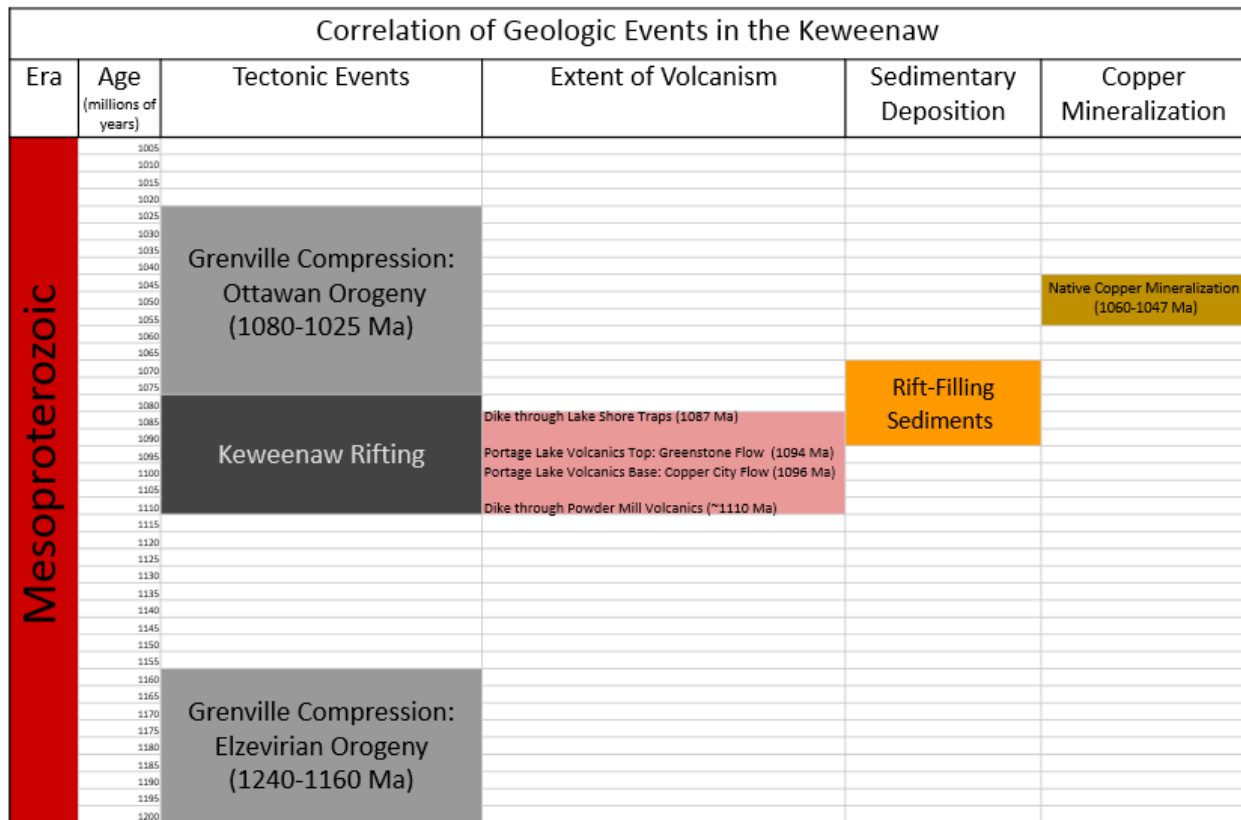


Figure 2. Correlation of events in the Keweenaw area. Tectonic date from Cannon (1994). Geologic events from Davis and Paces (1992) and Cannon (1994). Copper mineralization dates from Bornhorst (1988). Simplified stratigraphic column from Bornhorst (2011).

COPPER MINERALIZATION

Copper deposits in the Keweenaw Peninsula are separated into two distinct mining districts: The Porcupine Mountain Sediment Hosted Copper District, and the Keweenaw Peninsula Native Copper District (Bornhorst and Barron, 2011). Much of the information in the Porcupine Mountain Sediment Hosted Copper district has come from the White Pine Mine, which exhibits both sulfide and native copper

mineralization (Mauk *et al.*, 1992; Bornhorst and Barron, 2011). The Keweenaw Peninsula Native Copper Mining District has produced 14.4 billion pounds of high grade native copper, with an estimated potential to produce about 5 billion more (Bornhorst and Lankton; Bornhorst and Barron, 2011). Though copper is the primary metal being mined, significant quantities of native silver are also associated with both districts (Bornhorst and Barron, 2011).

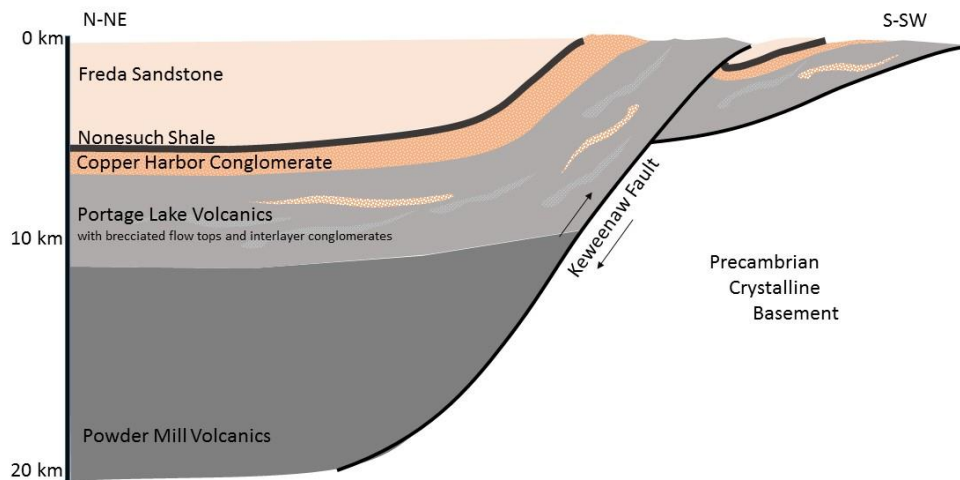


Figure 3. Simplified cross section and stratigraphy of the Keweenawan Supergroup based on Hinze *et al.*, 1997.

The native copper of the Keweenaw Peninsula Native Copper district area is largely found in the porous, vesicular and brecciated flow tops of the Portage Lake Volcanics, and in the interflow conglomerate layers which accumulated on top of lava flows during pauses in volcanism (fig. 3). Within the over 200 individual flows of the Portage Lake Volcanic unit, there are twenty-two of these siliciclastic

interflow conglomerates (Merk and Jirsa, 1982; Bornhorst *et al.*, 1988). The interflow layers are polymictic clastic conglomerates, and are derived from the surrounding basalt flows, uplifted extrusive and intrusive rocks of Keweenawan age, and pre-Keweenaw bedrock (Merk and Jirsa, 1982). While these conglomerates contribute less than 5% of the total volume of the Portage Lake Volcanic group, they produce 40% of the total native

copper in the Keweenaw (Bornhorst 1997; Merk and Jirsa, 1982). The high porosity and permeability of the flow tops and interflow beds acted as conduits, directing the flow of cupriferous hydrothermal fluids. The richest lode extracted from the Native Copper District was from the Calumet and Hecla Conglomerate, an interflow layer that yielded 4.2 billion pounds of copper (Bornhorst & Barron, 2011; from Weege and Pollack, 1971). Copper occurs in the Portage Lake basalts in concentrations of around 70 ppm (Jolly, 1974), which was more than enough to produce the copper deposits seen in this area considering the massive scale of these volcanics. There are over 100 other hydrothermal minerals associated with the native copper, again found as vesicle fillings (amygdules), in the fragmental volcanic flow tops, or in the spaces around clasts in the conglomerate interflow layers (Bornhorst 2011). Some of the more common metamorphic minerals include, calcite, epidote, chlorite, albite, prehnite, pumpellyite, and quartz (Bornhorst and Lankton 2004).

METHODS

An INAM Expert-Mobile X-Ray Fluorescence Portable Express Analyzer (XRF) was used to examine chemical variations in the native copper from the Keweenaw Peninsula to compare different host rocks for the native copper. This XRF instrument is capable of detecting elements from Mg to U, down to 1 ppm concentrations. Sample fluorescent spectra

were analyzed as alloys specifically looking for the mass fraction of the elements Ti, Cu, Zn, Ag, Sn, and Pb, at 45.00 kV.

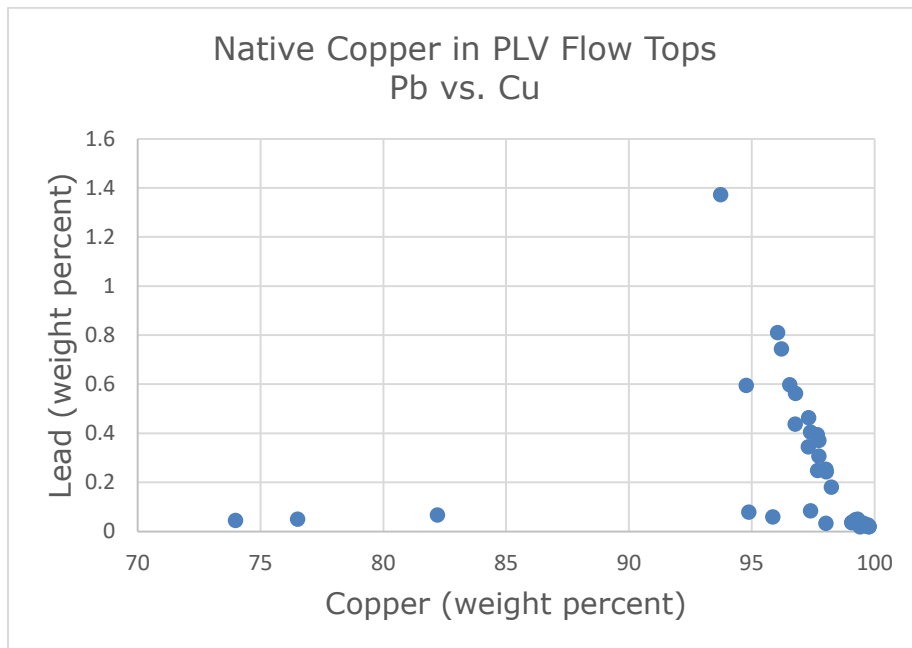
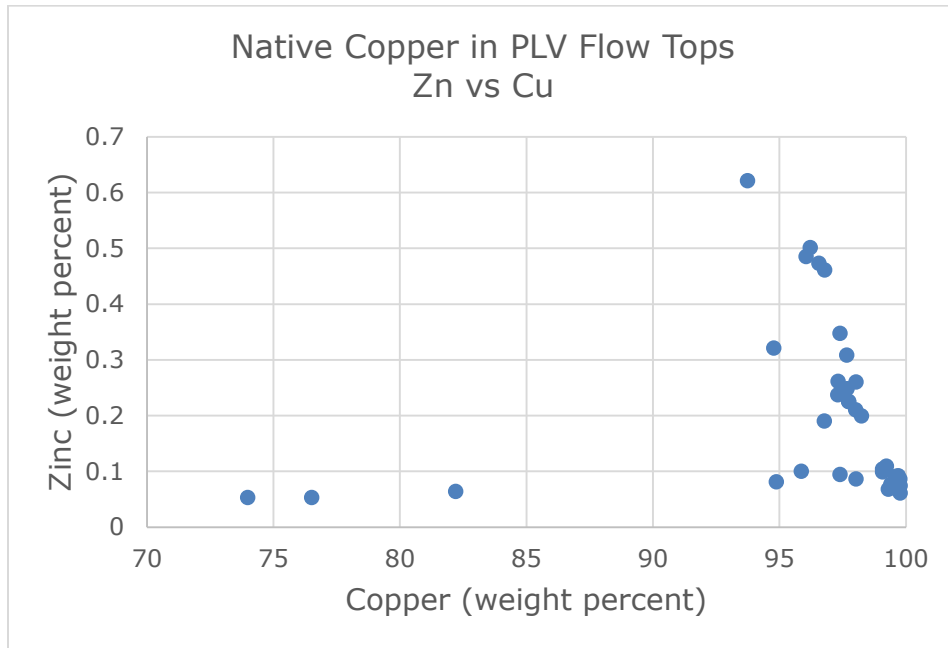
For each sample, 10 to 20 measurements were taken for 40 seconds to obtain an appropriately precise measurement to determine elemental composition by weight. Using this method, we analyzed 4 native copper specimens from the Dice Mineralogical Museum at Calvin College. A sample of native copper from the Quincy mine from the Calvin College collection was also analyzed (Appendix A).

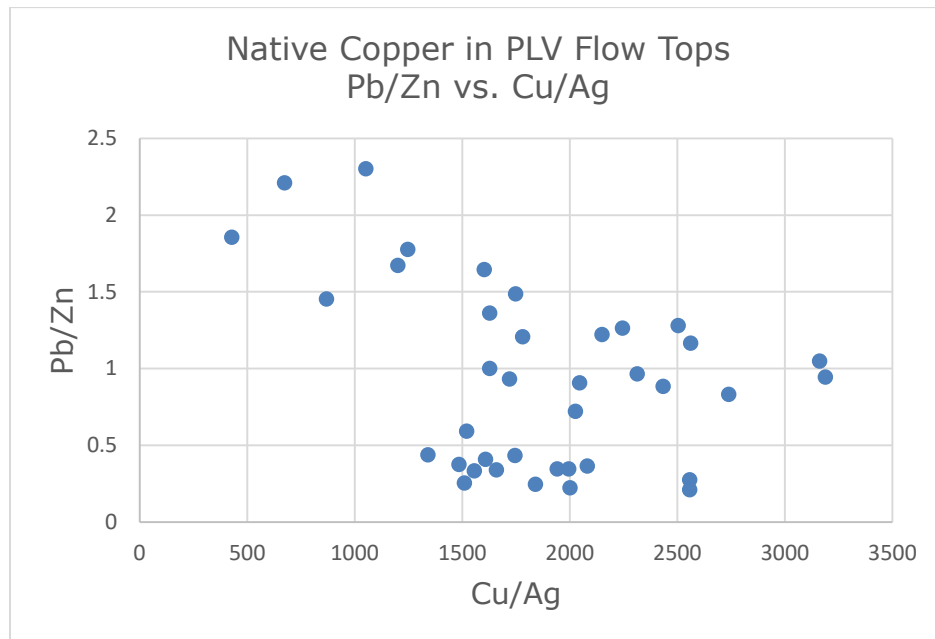
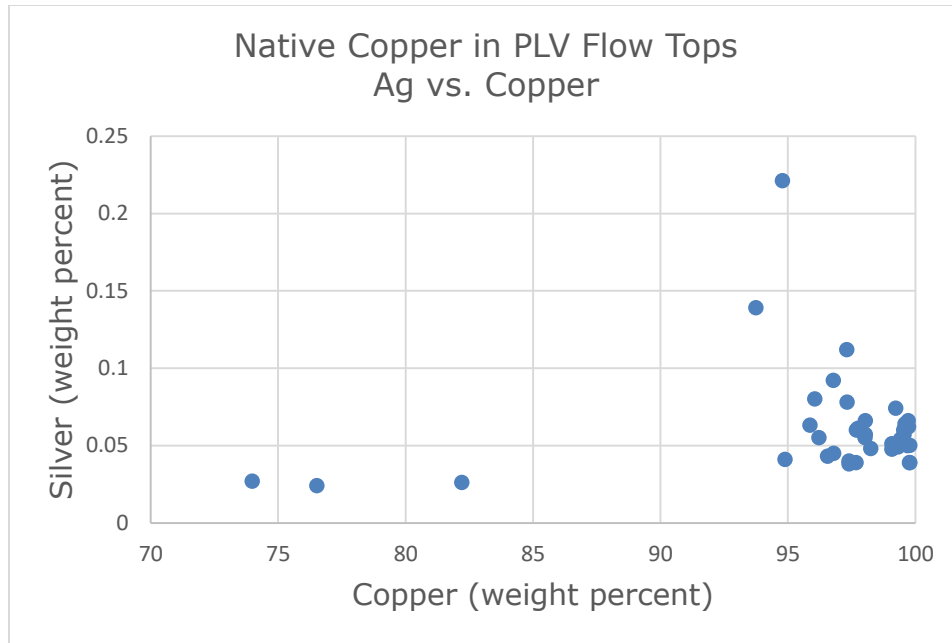
In addition to the Calvin College specimens, a selection of native copper samples from the Portage Lake Volcanic sequence, belonging to the A.E. Seaman Mineral Museum at Michigan Technological University, were analyzed. These samples included native copper mineralization in the flow-top breccias, as well as those found in the interbedded conglomerate layers, and 3 to 15 measurements were taken for each. For the interflow conglomerate labeled MT5, measurements were taken of the whole rock, including the rhyolite clasts. Only measurements that read over 50% copper were included with this study.

To gain an understanding of the bulk chemistry of the host rocks, rhyolite clasts from a sample from the Calumet Conglomerate were analyzed with the XRF spectrometer, as well as a powdered sample of a brecciated flow top collected from the Quincy mine.

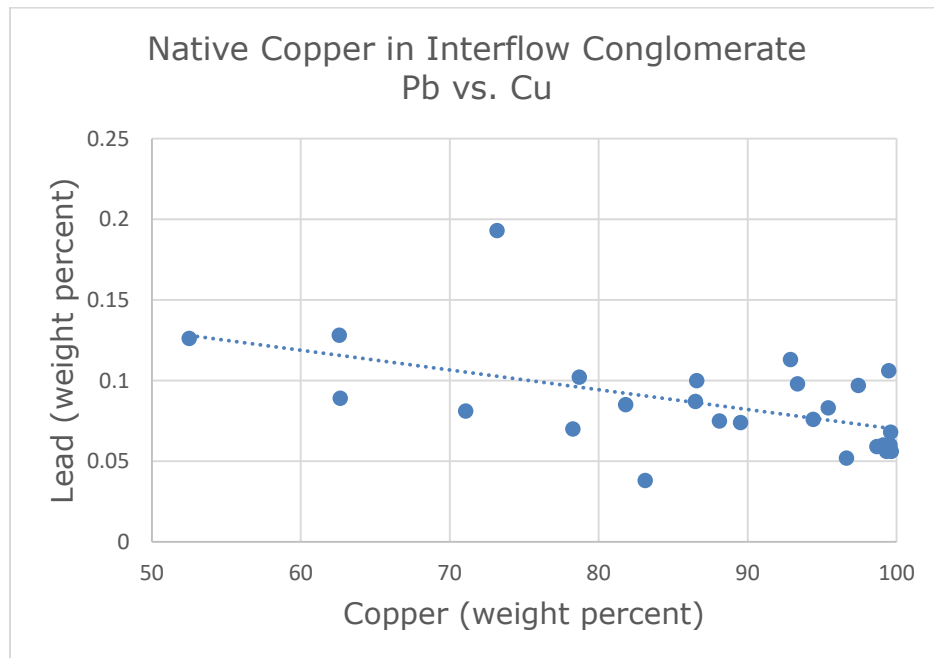
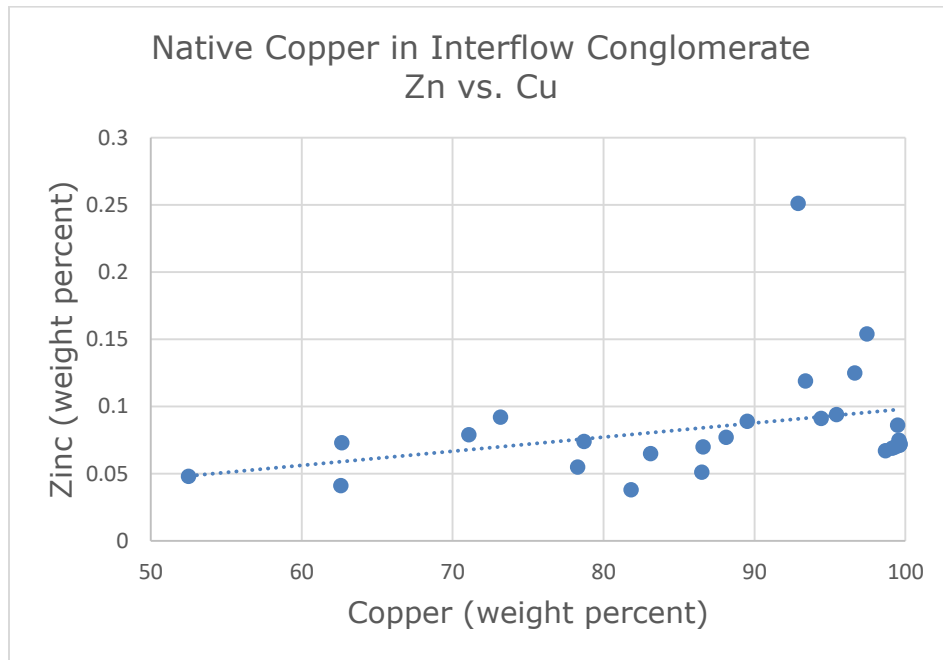
Processed data patterns and concentrations were exported to an Excel Worksheet where they were plotted (fig. 4-6).

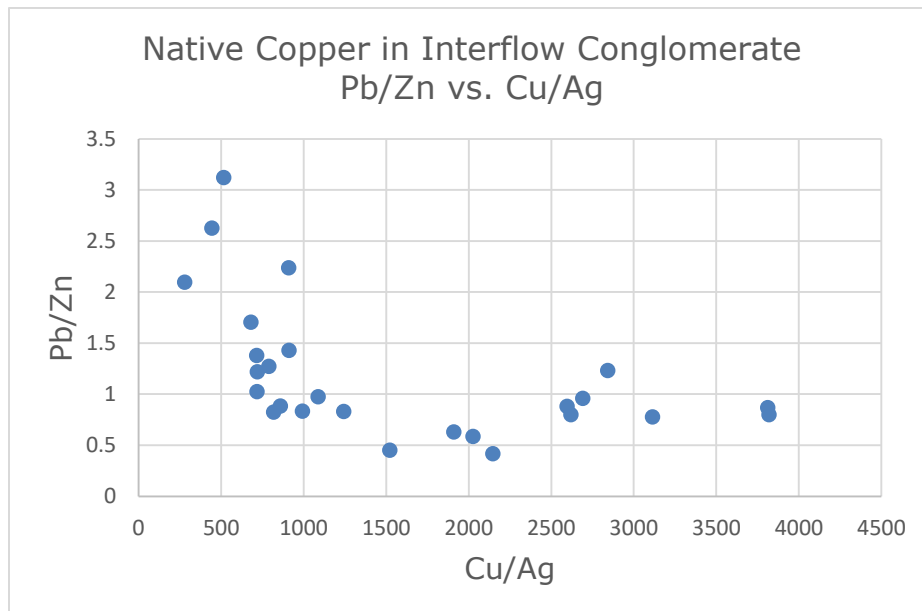
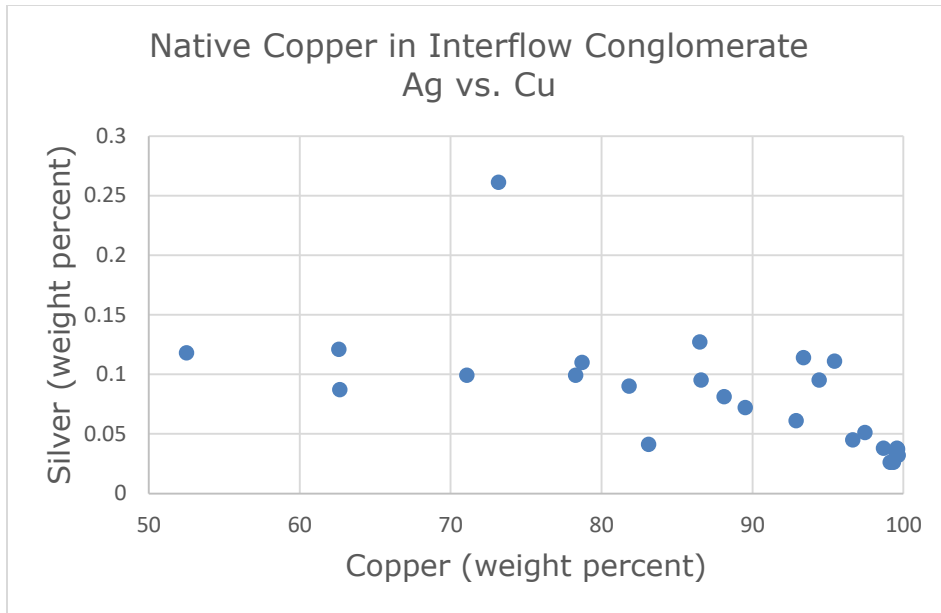
Figures 4a-d. Copper in basalt flow tops (supported by data in Appendix B).



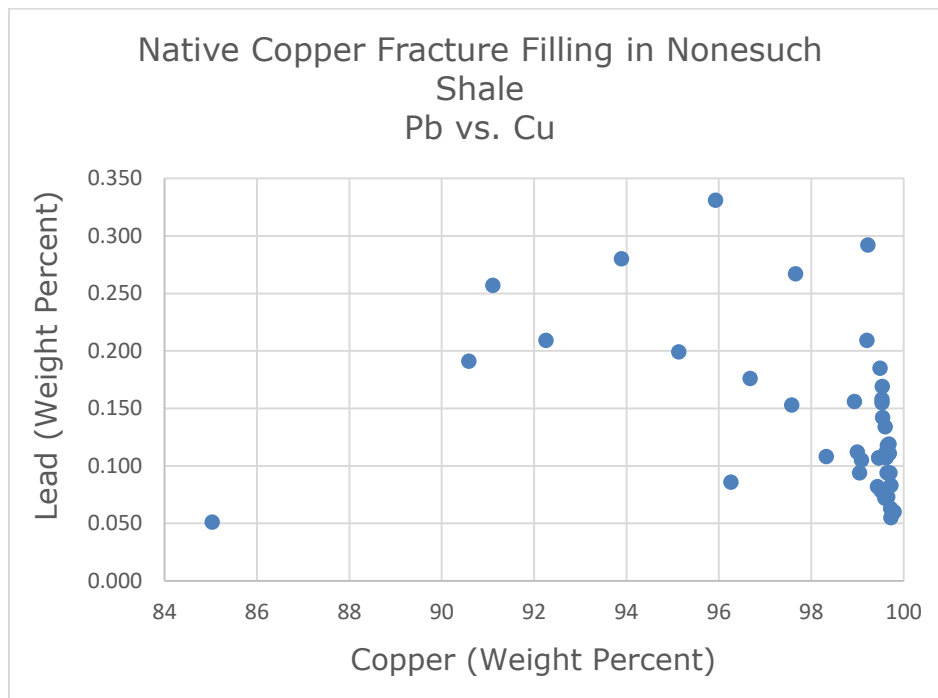
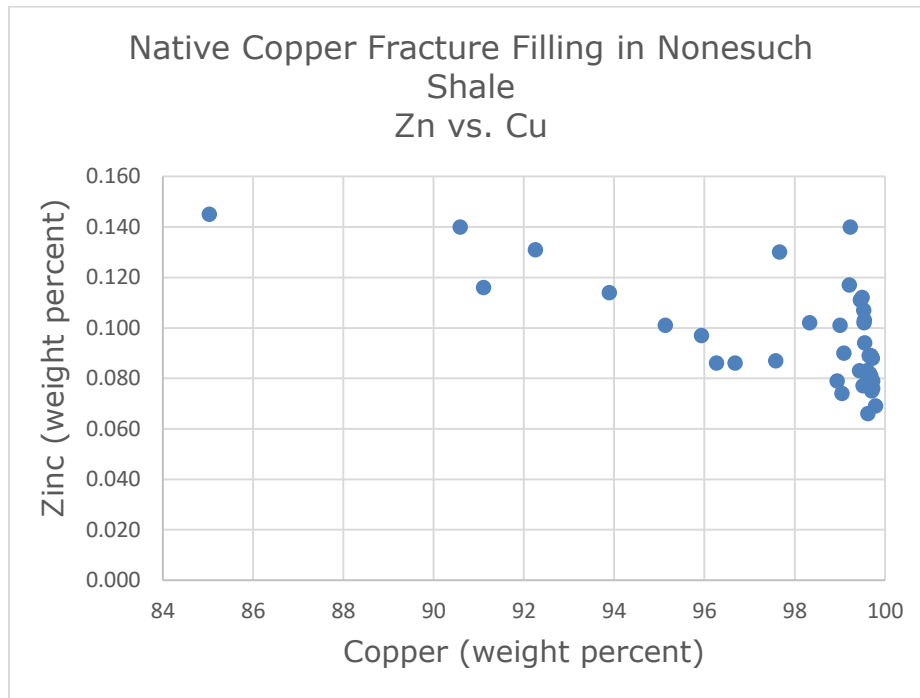


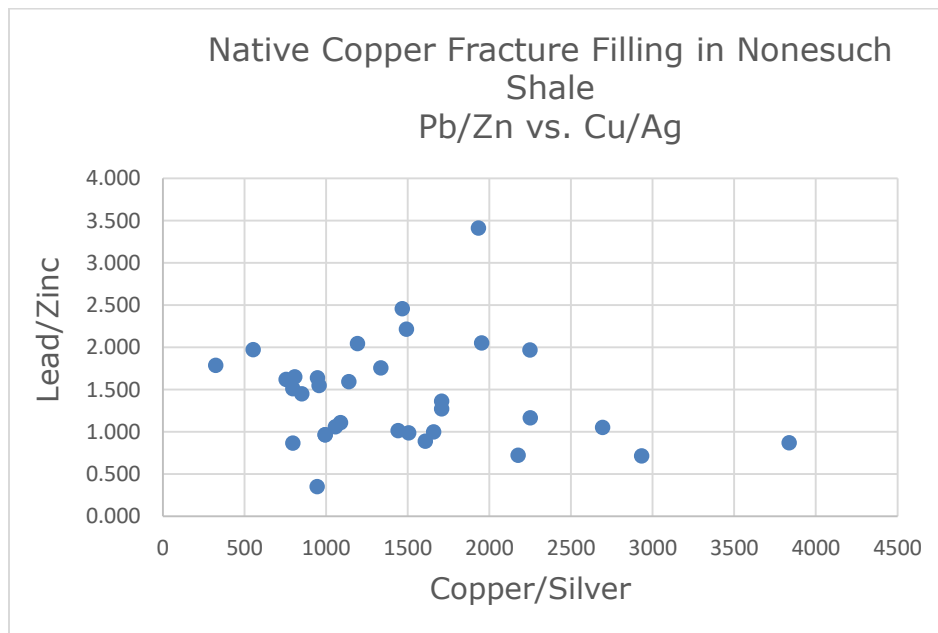
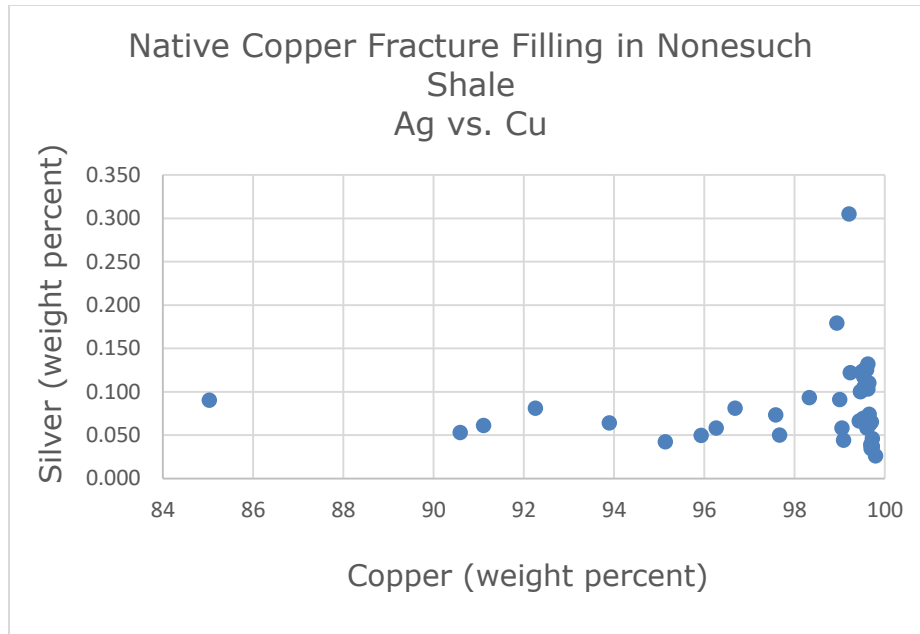
Figures 5 a-d: Copper in interflow conglomerates (supported by data in Appendix B).





Figures 6 a-d: Copper as fracture filling in Nonesuch Shale (supported by data in Appendix B).





Appendix A. Descriptions and study labels of specimens analyzed with XRF.

Descriptions of Native Copper Samples Studied		
Sample Label	Description	From
<i>Native Copper in Amygdaloidal/Brecciated Flowtops of the Portage Lake Volcanics</i>		
Cu1	Quincy mine, Hancock MI, Keweenaw MI	Calvin College Collection
MT1	Champion no.3 mine, Painsdale MI, Houghton co.	A.E. Seamen Museum, Michigan Technological University
MT2	Copper in fault Breccia, #1 shaft, collected by W. Seaman	A.E. Seamen Museum, Michigan Technological University
O29*	Keweenaw Peninsula	The Dice Mineralogical Museum, Calvin College
<i>Native Copper in Interflow Conglomerates Between Volcanic Flows</i>		
MT3	Calumet and Hecla lode, "copper skull", (MTU label: RSF 124)	A.E. Seamen Museum, Michigan Technological University
MT4	Calumet and Hecla lode, "copper skull", (MTU label: RWD27 2A-B)	A.E. Seamen Museum, Michigan Technological University
MT5**	Copper in conglomerate, Kingston mine, Ahmeele, Mich	A.E. Seamen Museum, Michigan Technological University
MT6	Tamarack Mine, MI (This is the Calumet and Hecla conglom.)	A.E. Seamen Museum, Michigan Technological University
<i>Native Copper as Fracture Fillings in the Nonesuch Shale White Pine Mine</i>		
O34	Copper in Nonesuch shale, White Pine Mine- Keweenaw Peninsula	The Dice Mineralogical Museum, Calvin College
O21	White Pine Mine, Keweenaw	The Dice Mineralogical Museum, Calvin College
B33*	Copper District, Keweenaw Peninsula	The Dice Mineralogical Museum, Calvin College
<i>Bulk Rock Chemistry of Rhyolite and Basalt</i>		
BRC 1	Calumet Conglomerate, 3 slabs. Copper hosted in Rhyolitic Conglom.	Calvin College Collection
BRC 2	Altered basalt from the PLV at the Quincy Mine, Hancock MI	Collected by Calvin College Geology department, 2016
*The specific mines where these samples were found are not explicitly stated, and we infer the general depositional host rock based on minerals and rocks present on the specimens. B33 is a piece of sheet of copper with shale, and O29 has epidote and calcite associated with it, which is consistent with copper from the Portage Lake Volcanics.		
** MT5 contains data points from the total rock chemistry. Only readings above 50% copper are used in the graph.		

Appendix B. X-ray fluorescence data of Keweenaw Native Copper.

Native Copper from Brecciated/Amygdaloidal Flow Tops of the Portage Lake Volcanics					
	N	MIN	MAX	MEAN	STD. DEV
Cu	38	73.987	99.789	96.328	5.861
Zn	38	0.053	0.621	0.191	0.152
Pb	38	0.024	0.221	0.061	0.035
Ag	38	0.018	1.372	0.240	0.296
Ti	38	0.004	0.214	0.079	0.049
Sn	38	0.045	1.491	0.218	0.304
Cu/Ag	38	428.910	3188.542	1851.924	615.360
Pb/Zn	38	0.208	2.300	0.928	0.586

Native Copper from Interflow Conglomerates					
	N	MIN	MAX	MEAN	STD. DEV
Cu	26	52.515	99.660	86.945	13.40092
Zn	26	0.038	0.251	0.084	0.042463
Pb	26	0.038	0.193	0.086	0.031616
Ag	26	0.026	0.261	0.081	0.049779
Ti	26	0.003	2.807	0.745	0.801411
Sn	26	---	---	---	---
Cu/Ag	26	280.421	3821.192	1569.399	1065.896
Pb/Zn	26	0.416	3.122	1.187	0.66901

Appendix B. X-ray fluorescence data of Keweenaw Native Copper (cont.).

Native Copper as Fracture Fillings in the Nonesuch Shale, White Pine Mine					
	N	MIN	MAX	MEAN	STD. DEV
Cu	41	85.031	99.796	97.952	3.182
Zn	41	0.066	0.145	0.096	0.020
Pb	41	0.051	0.331	0.140	0.070
Ag	41	0.026	0.305	0.084	0.049
Ti	41	0.022	0.997	0.282	0.325
Sn	41	0.046	0.196	0.087	0.042
Cu/Ag	41	325.279	3838.308	1485.845	743.206
Pb/Zn	41	0.352	3.412	1.432	0.561

RESULTS

Data from eleven samples were processed and plotted in Figures 4-6. This data set included samples from both the A.E Seaman museum, the Dice Mineralogical Museum, and from the Calvin College collection. In total, four samples of brecciated/amygdaloidal flow tops, four samples of interflow conglomerate layers and three samples of native copper from the White Pine area were analyzed.

Data of native copper from the brecciated/amygdaloidal flow tops of the Portage Lake Volcanics were variable. Notable outliers are present in the data, especially at lower Cu concentrations. Sample MT2 in particular had a relatively low percentage of copper, between 70 – 85%. However, there seems to be a general decrease in Pb and Zn with increasing copper. A plot of the Pb/Zn ratio to Cu/Ag exhibits a similar decay curve to that of the interflow conglomerate copper (fig. 4d).

Native copper from the interflow conglomerate layers tends to show a positive relationship between Cu and Zn. However, with increasing percentage of Cu, the Pb and Ag concentrations decrease. The comparison of the ratios of Pb/Zn to Cu/Ag show a decay curve, rather than a linear relationship (fig. 5d).

Native copper fillings in the Nonesuch Shale had the most variable trends of the three categories studied. As the copper content increased, Zn decreased and the Pb content also seemed to decrease, but the spread of the data was greater. Unlike the native copper from the flow tops or interflow conglomerate layers, the associated Ag in the fracture fillings of the Nonesuch shale exhibited an increase with increasing Cu. When comparing the ratios of Pb/Zn vs. Cu/Ag, the data is scattered, and no obvious trend exists from the data (fig. 6c).

A rhyolite clast interflow conglomerate and brecciated basalt sample were analyzed to understand the bulk

chemistry of the copper host rocks. The rhyolite showed high silica, averaging around 74%, as well as high aluminum at around 10%. The basalt sample was low in silica, around 39%, and high in copper, around 8%. When recalculated to account for the particularly high copper concentration, the silica level was around 42%.

DISCUSSION

In considering the trace metals that are associated with the native copper, a discussion on the interpretation of events that lead to its precipitation is pertinent. It is generally accepted that the ore fluid originated by metamorphic processes, but there has been some debate as to the mechanisms that govern precipitation of the native copper. Bornhorst (1998) summarizes three plausible models of native copper precipitation: By cooling of the ore fluid, by fluid-rock interactions, or by fluid mixing. Bornhorst states that cooling cannot be the sole mechanism of precipitation, as copper is most likely complexed as copper chloride but found as native copper, the difference here being in the oxidation state of the copper. He argues that fluid-rock interaction is unlikely, as the high water/rock ratios in ore zones would limit the effectiveness of accounting for the total mass of the copper ore bodies. He instead supports a fluid mixing mechanism for copper precipitation, where the metamorphic ore fluid would have contacted "resident reduced fluids". Brown (2006) suggests a model of native copper precipitation that included a meteoric water component, in order to account for the reddening of

sediments. Bornhorst believes that oxidized meteoric interaction is not likely as a model, because native copper requires reduction, not oxidization to precipitate (Bornhorst, 1998). Bornhorst et al. (1988) dates the age of native copper mineralization to be between 1060 and 1047 +/- 20 M.a, using Rb/Sr dating of associated amygdaloidal minerals. These dates are consistent with a metamorphic model of copper ore generation. Jolly (1974) suggested that the chemical change in metamorphic zones from epidote facies (dehydration) to prehnite-pumpellyite facies (hydrated) in the Portage Lake Volcanics is related to the mobilization of copper in the low grade metamorphic fluid. Copper originated in the epidote zone, now containing very little copper, and was leached and driven up into the prehnite-pumpellyite zone, where copper is often present. This chemistry supports a metamorphogenic model of copper deposition. A significant characteristic of the Portage Lake Volcanics is its lack of sulfur. This can be explained by rapid degassing of SO₂ from the cooling lava (Jolly 1974), which helps explain why copper forms in its native state here rather than sulfides as seen in the White Pine Mine, where the sulfur-rich Nonesuch was conducive to copper sulfide replacement.

While we cannot draw any definitive conclusions about whether there are significant differences with metal associations with copper, our data seems to indicate that there may be distinctive trends within the interflow conglomerates with the ratio between Pb/Zn and Cu/Ag, and possibly with the basalt flow tops as well. More data is needed to develop more

definitive relationships, which presents opportunity for future study.

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REFERENCES CITED

Bornhorst, T.J., 1997. Tectonic context of native copper deposits of the North American Midcontinent Rift System, *in* Ojakangas, R.W., Dikas, A.B., and Green, J.C., eds., *Middle Proterozoic to Cambrian rifting, central North America*, Geological Society of America Special Paper 312, p. 127-136.

Bornhorst, T.J., Paces, J.B., Grant, N.K., Obradovich, J.D., and Huber, N.K., 1988. Age of native copper mineralization, Keweenaw Peninsula, Michigan. *Economic Geology*, v. 83, p. 619–625.

Bornhorst, T. J., and Brandt, D.S., 2009. Michigan's Earliest Geology: The Precambrian, *in* Schaetzl, R.J., Darden, J.T., and Brandt, D.S., 2009, eds., *Michigan Geography and Geology*, NY Custom Publishing, p. 24-39.

Bornhorst, T.J., and Lankton, L.D., 2009. Copper Mining: A Billion Years of Geologic and Human History, *in* Schaetzl, R.J., Darden, J.T., and Brandt, D.S., 2009, eds.,

Michigan Geography and Geology, NY Custom Publishing, p. 150-159.

Bornhorst, T.J., and Barron, R.J., 2011. Copper deposits of the western Upper Peninsula of Michigan, *in* Miller, J.D., Hudak, G.J., Wittkop, C., and McLaughlin, P.I., eds., *Geological Society of America Field Guide 24*, p. 83-99.

Brown, A.C., 1974. The copper province of northern Michigan, U.S.A., *Annales de la Société géologique de Belgique*, Publications spéciales = special publications, Gisements stratiformes et provinces cuprifères - Centenaire de la Société Géologique de Belgique, p. 317-330.

Brown, A.C., 2006. Genesis of Native Copper Lodes in the Keweenaw District, Northern Michigan: A Hybrid Evolved Meteoric And Metamorphogenic Model. *Economic Geology*, v. 101, p. 1437–1444.

Cannon, W.F., and Nicholson, S.W., 2001. *Geologic Map of the Keweenaw Peninsula and Adjacent Area*, MI: U.S.G.S. map.

Cannon, W.F., 1994. Closing of the Midcontinent rift-A far—field effect of Grenvillian compression. *Geology*, v. 22, p. 155–158.

Cooke, D.R., Hollings, P., and Walshe, J.L., 2005. Giant porphyry depositions: Characteristics, distribution, and tectonic controls. *Bulletin of the Society of Economic Geologists*, v. 100, p. 801-818.

- Daniels, P.A., 1982. Upper Precambrian Sedimentary Rocks: Oronto Group, Michigan- Wisconsin, in Wold, R.J., and Hinze, W.J., eds., *Geology and Tectonics of the Lake Superior Basin*, GSA Memoir 156, p. 107–134.
- Davis, D., and Paces, J., 1990. Time resolution of geologic events on the Keweenaw Peninsula and implications for development of the Midcontinent Rift system. *Earth and Planetary Science Letters*, v. 97, p. 54–64.
- Elmore, R.D., 1984. The Copper Harbor Conglomerate: A late Precambrian fining-upward alluvial fan sequence in northern MI. *Geological Society of America Bulletin*, v. 95, p. 610–617.
- Foley, D.J., 2011. *Petrology and Cu-Ni-PGE mineralization of the Bovine Igneous Complex*. Baraga County, Northern Michigan State University Master's thesis.
- Green, J.C., 1982. Geology of Keweenaw an Extrusive Rocks, in Wold, R.J., and Hinze, W.J., eds., *Geology and Tectonics of the Lake Superior Basin*, Geological Society of America Memoir 156, p. 47–56.
- Hauck, S.A., Severson, M.J., Zanko, L.M., Barnes, S.J., Morton, P., Alminas, H.V., Foord, E.E., and Dahlberg, E.H., 1997. An overview of the geology and oxide, sulfide, and Pt-group element mineralization along the western and northern contacts of the Duluth Complex, in Ojakangas, R.W., Dikas, A.B., and Green, J.C., eds., *Middle Proterozoic to Cambrian rifting, central North America*, Geological Society of America Special Paper 312, p. 137–185.
- Hinze, W.J., Allen, D.J., Braile, L.W., and Mariano, J., 1997. The Midcontinent Rift System: A major Proterozoic continental rift, in Ojakangas, R.W., Dikas, A.B., and Green, J.C., eds., *Middle Proterozoic to Cambrian rifting, central North America*, Geological Society of America Special Paper 312, p. 7–35.
- Jolly, W.T., 1974. Behavior of Cu, Zn, and Ni During Prehnite-Pumpellyite Rank Metamorphism of the Keweenaw Basalts, Northern Michigan. *Economic Geology*, v. 69, p. 1118–1125.
- Mauk, J.L., Kelly, W.C., van der Pluijm, B.A., and Season, R.W., 1992. Relations between deformation and sediment-hosted copper mineralization: Evidence from the White Pine part of the Midcontinent rift system. *Geology*, v. 20, p. 427–430.
- Merk, G.P., and Jirsa, M.A., 1982. Provenance and Tectonic Significance of the Keweenaw an Interflow Sedimentary Rock, in Wold, R.J., and Hinze, W.J., eds., *Geology and Tectonics of the Lake Superior Basin*, Geological Society of America Memoir 156, p. 97–105.
- Morey, G.B., and Van Schmus, W.R., 1988. *Correlation of Precambrian rocks of the Lake Superior region, United States*. Washington, U.S. Geological Survey Professional Paper 1241-F, 35 p.

Robertson, J.M., 1975. Geology and Mineralogy of Some Copper Sulfide Deposits near Mount Bohemia, Keweenaw County, Michigan. *Economic Geology*, v. 70, p. 1202–1224.

Schmus, W.R.V., Green, J.C., and Halls, H.C., 1982. Geochronology of Keweenawan rocks of the Lake Superior Region, in Wold, R.J., and Hinze, W.J., eds., *Geology and Tectonics of the Lake Superior Basin*, Geological Society of America Memoir 156, p. 165–172.

Schulz, K.J., and Cannon, W.F., 2007. The Penokean orogeny in the Lake Superior region. *Precambrian Research*, v. 157, p. 4–25.

Sims, P.K., Card, K.D., Morey, G.B., and Peterman, Z.E., 1980. The Great Lakes tectonic zone — A major crustal structure in central N. America, *Geological Society of America Bulletin*, v. 91, p. 690-698.

Swenson, J.B., Person, M., Raffensperger, J.P., Cannon, W.F., Woodruff, L.G., and Berndt, M.E., 2004. A hydrogeologic model of stratiform copper mineralization in the Midcontinent Rift System, northern Michigan, USA. *Geofluids*, v. 4, p. 1–22.