Concentrations of Pb, Zn, and Ag Associated with Native Copper Deposition, Keweenaw MI

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ABSTRACT

The Keeweenawan Peninsula is home to the world's largest native copper deposits. Samples of native copper were analyzed from three distinct zones within the copper deposits including the interflow conglomerates, the brecciated/amygdaloidal flow tops of the Portage Lake Volcanics, and the fracture filling of the Nonesuch Shale. Data collected in this study, focused on Pb, Zn, and Ag concentrations associated with the native copper as analyzed using X-Ray fluorescence. Within the interflow conglomerates, chemical relationships showed an increase in Zn but a decrease in Pb and Ag with increasing Cu. The volcanic flow tops exhibited decreased Zn, 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. Finally, 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 shed some light on the fluid composition associated with hydrothermal copper mineralization. In each case discussed here, native copper was deposited in stratigraphic horizons where permeability was high facilitating fluid flow. Based on previous studies, this cupriferous fluid migration was influenced by both structural limitations and impermeable geologic units associated with the long geologic history of the region. Stratigraphic and structural controls of copper mineralization have been linked to the 1.1 Ga Midcontinent Rifting event that dominates the geology of the Keeweenawan Peninsula and subsequent compressional stresses attributed to the Grenville Orogeny.

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 with (1) copper sulfide minerals from the same area, and (2) native copper samples from other large porphyry deposits. 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.

Eight samples of native copper (5 normal and 4 still in the matrix), 6 samples of chalcocite, five samples of bornite, and 5 chalcopyrite from various locations were chosen and analyzed from the Calvin College collections. For each sample, 10 and 20 measurements were taken for 40 seconds to obtain an appropriately precise measurement to determine elemental concentration. Using this method, we also analyzed samples from the Dice Mineralogical Museum, which consisted of 9 native copper specimens, 7 from the Keweenaw, and 2 were specifically out of the White Pine Mine. Samples out of the White Pine Mine contained fragments of the host Nonesuch shale, which we analyzed separately to observe its composition.

In addition to the Calvin College samples, a suite of native copper samples from the Portage Lake Volcanic sequence was analyzed from the A.E. Seaman Mineral Museum at Michigan Technological University. These samples included native copper mineralization in the flow-top breccias as well as those found in the interbedded conglomerate layers. 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. Processed data patterns and concentrations were exported to an Excel Worksheet where they were plotted

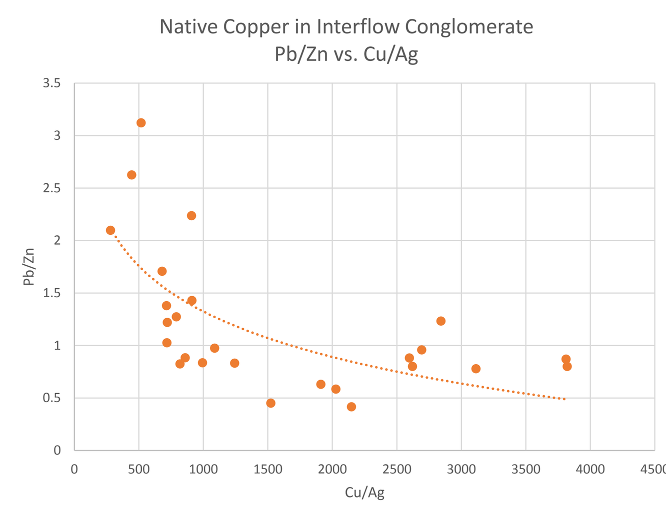


Figure 3a. Metal relationships in the interbedded conglomerate layers of the PLV.

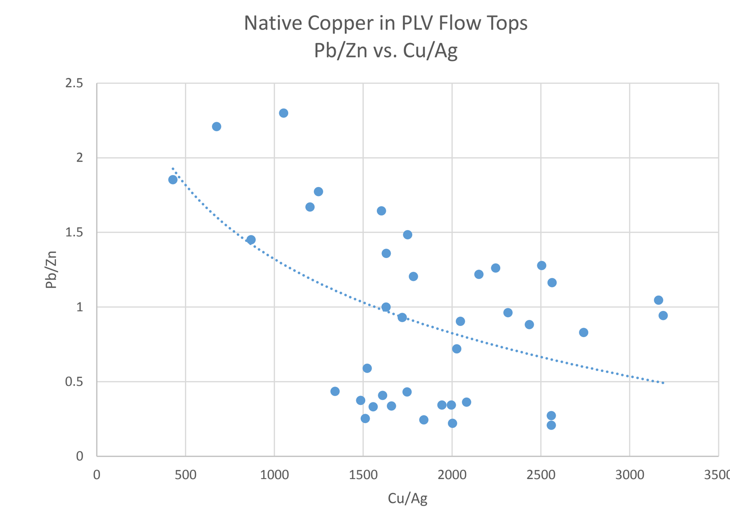
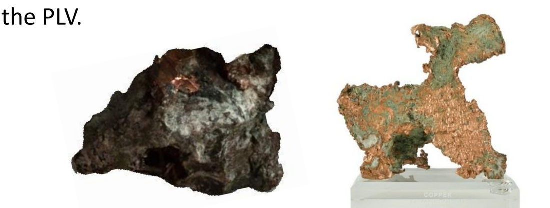


Figure 3b. Metal relationships in the mineralized flow tops of the PLV.



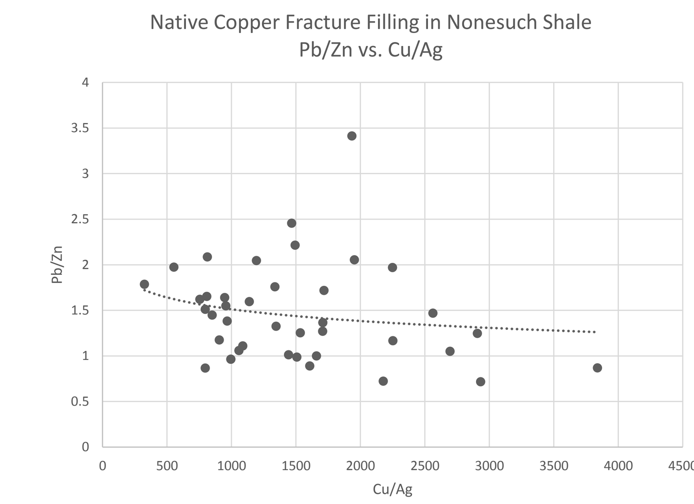
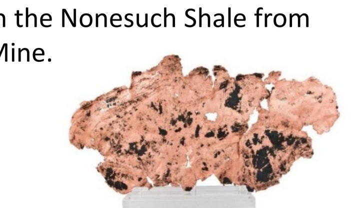


Figure 3c. Metal relationships native copper fracture fillings in the Nonesuch Shale from the White Pine Mine.



Results:

Data from 11 samples were processed and plotted in Figure 3a.-c. This data set included samples from both the A.E Seaman museum and the Dice Mineralogical Museum. 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.

Native copper from the interflow conglomerate layers shows 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 as shown in Figure 3a.

Data of native copper from the brecciated/amygdaloidal flow tops of the Portage Lake Volcanics were more variable. Notable outliers are in the data, especially at lower Cu concentrations, however, there is 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 as seen in Figure 3b.

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 exhibited in Figure 3c.

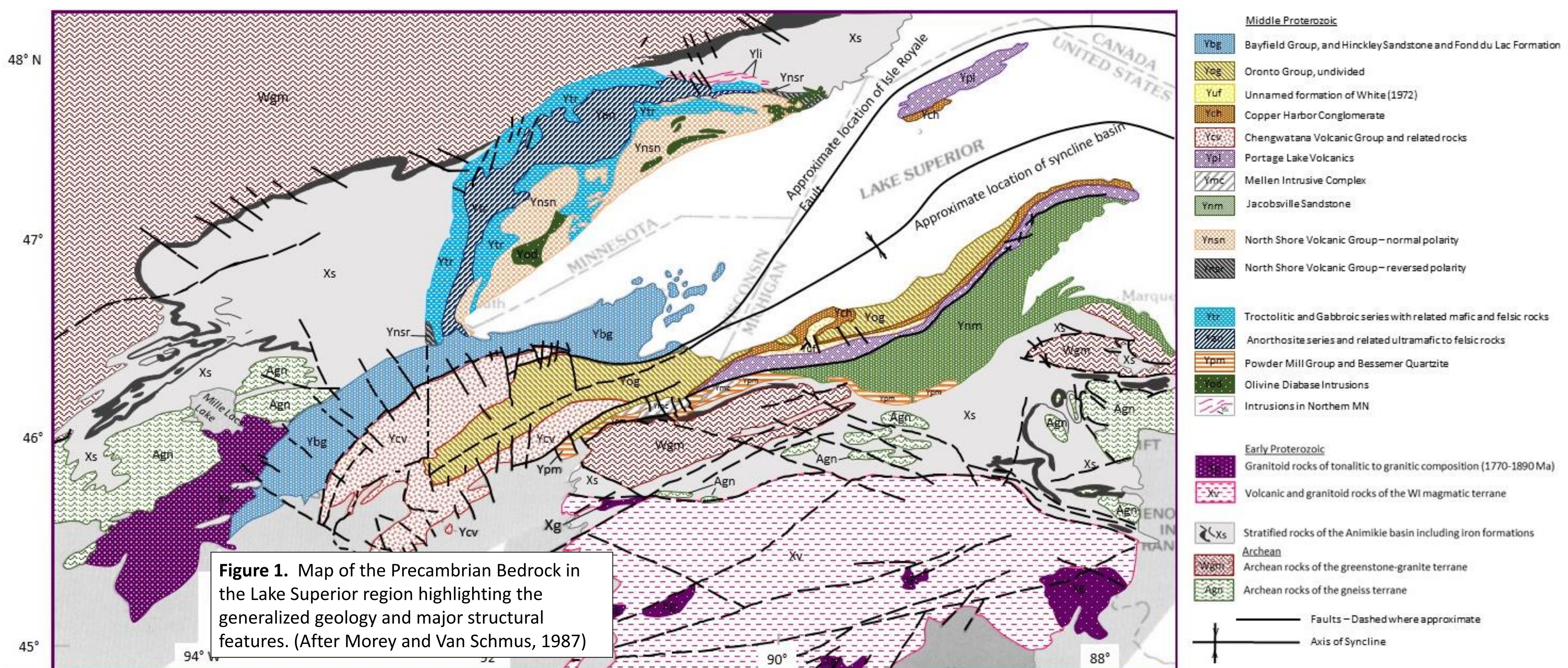
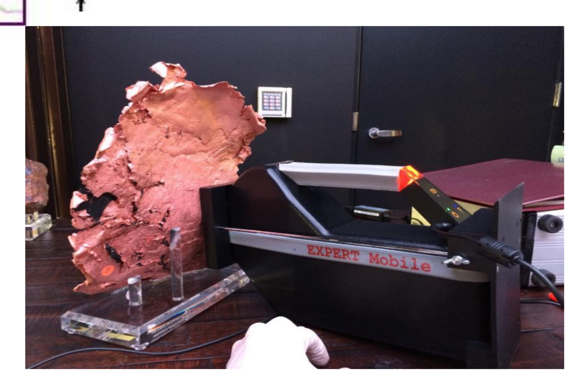


Figure 1. Map of the Precambrian Bedrock in the Lake Superior region highlighting the generalized geology and major structural features. (After Morey and Van Schmus, 1987)



GEOLOGIC SETTING

For a full picture of the copper mineralization in the upper peninsula of Michigan, it is necessary to consider the bedrock geology of the region. The bedrock geology is somewhat complex and extends over a significant block the Precambrian Eon. Bedrock geology in and around the Keweenaw Peninsula centers around the late Mesoproterozoic Midcontinent Rift, which extends over 2,000 miles from Kansas, up through Lake Superior through to the lower peninsula of Michigan (Hinze, 1997). This rifting event cut through preexisting Paleoproterozoic and Archean rocks (Morey and Van Schmus, 1988).

Archean gneisses in the Superior Craton, represent the oldest rocks found within the region of interest (Figure 1). There are areas of granite and greenstone that are 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). Overlying 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). Metamorphism of the Marquette Supergroup has been attributed to the Penokeon Orogeny (Schultz and Cannon, 2007). Active subduction dated at 1880-1830 Ma provided volcanic activity a led to the formation of high-grade, foliated metamorphic rocks, followed by plutonic igneous activity, as granitic plutons (Schultz and Cannon, 2007).

After an extended period of erosion exhibited by an unconformity, the next units are 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). 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 Quartzite, Powder Mill Group, Portage Lake Volcanics (PLV), Copper Harbor Conglomerate (CHC), Nonesuch Shale, and the Freda Sandstone in ascending order.

The oldest volcanic unit in this Keeweenawan Supergroup or sequence, is the Powder Mill Group, a series of subaerial basalt to basaltic-andesite flows (Hinze et al., 1997). 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, at about 1-1.5 km in depth (Cannon and Nicholson, 2001). Following the Powder Mill Group, the magnetic-normal unit of the Portage Lake Volcanics (PLV) has been dated at 1097 Ma (Davis and Paces, 1990). The PLV group is comprised numerous tholeiitic flood basalt flows, ranging from 3-5 km thick. (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, Merk). The PLV 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 as well, with changes in the Ni content reflective of volcanic cycles (Hinze et al., 1997). The PLV 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 PLV lies the Oronto Group which includes the Copper Harbor Conglomerate (CHC), Nonesuch Shale, and the Freda Sandstone (Morey and Van Schmus, 1988). The CHC 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 that 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. He also reported that the supporting sand matrix was similar in composition being 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 dated at 1087.2 Ma (Davis and Paces, 1990).

Above the CHC lies the Nonesuch shale (Morey and Van Schmus, 1988). This formation called the Nonesuch Shale is much harder to find, being exposed in only three major locations across the Keweenaw Peninsula (Morey and Van Schmus, 1988). Unlike the oxidized CHC 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). The Nonesuch formation is interpreted as rift-flanking lacustrine sediments, and is rich in pyrite and organic matter (Daniels, 1982). The anoxic nature of this unit appears to distinctly influence the copper mineralization in this unit (Robertson, 1975).

COPPER MINERALIZATION

According to previous studies, there were two distinct phases of copper mineralization in the Keweenaw. The first deposited copper sulfides into the Nonesuch formation and the second precipitated native copper into the Portage Lake Volcanics (PLV), about the time of the Grenvillian compression event (Mauk et al., 1992; Swenson et al. 2004). These copper deposits are separated into two distinct mining districts, the Porcupine Mountain Sediment Hosted Copper District and the Keweenaw Peninsula Native Copper District (Bornhorst & Barron, 2011). Much of the information in this district has come from the White Pine Mine which exhibits both sulfide and native copper mineralization (Mauk et al., 1992; 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).

Copper Sulfide Mineralization

Chalcocite is the most abundant copper sulfide mineral in the region (Robertson, 1975; Mauk et al., 1992). Chalcocite found in the White Pine Mine is hosted in the Nonesuch Formation (Bornhorst and Lankton, 2009) as well as the sandstone of the upper Copper Harbor Conglomerate (CHC) (Bornhorst & Barron, 2011). It occurs as disseminated grains, stratiform with the basal layers of the Nonesuch shale. Interpretation of the mainstage copper sulfide mineralization is one of compaction-driven, upward leakage of copper rich fluids through the CHC (Swenson et al., 2004). Deposition of the Freda Sandstone may have provided the pressure necessary to produce the upward movement of cupriferous brines to discharge from the aquifer upward into the overlying Nonesuch shale, and outward, focused into the formation margins (Swenson et al. 2004). The White Pine Mine, located near the Iron River Syncline (Bornhorst and Barron, 2011), was one of the most successful mines (Bornhorst and Lankton, 2004). Eighty percent of the copper ore mined is chalcocite, with the remaining 20% native copper (Mauk et. al 1992; Bornhorst and Lankton, 2004). The chalcocite ore in the Nonesuch Shale grades upward into pyritic shale which lacks copper (Brown 1971).

Native Copper Mineralization

Current interpretations suggest that the second stage native copper mineralization originated in the lower PLV section, and the cupriferous fluid leached upward into the volcanic section along structural fractures and faults during compressional (Bornhorst et al., 1988; Jolly, 1974), but other models have been proposed. Native copper of the Keweenaw Peninsula Native Copper district area is found in the vesicular and brecciated flow tops of PLV flows, and in interflow conglomerate layers. While these clastic layers contribute under 5% of the total volume of the PLV group, they produce 40% of the total native copper in the Keweenaw (Bornhorst 1997; Merk and Jirsa, 1982). 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 PLV basalt in concentrations of around 70 ppm (Jolly, 1974), and may have been the source of the copper brines. Other minerals associated with the native copper are found in 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 hydrothermal minerals include, calcite, epidote, chlorite, albite, prehnite, pumpellyite, and quartz (Bornhorst and Lankton 2004). 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 these associated amygdaloidal minerals.

Tectonic Setting

Great Lakes Tectonic Zone

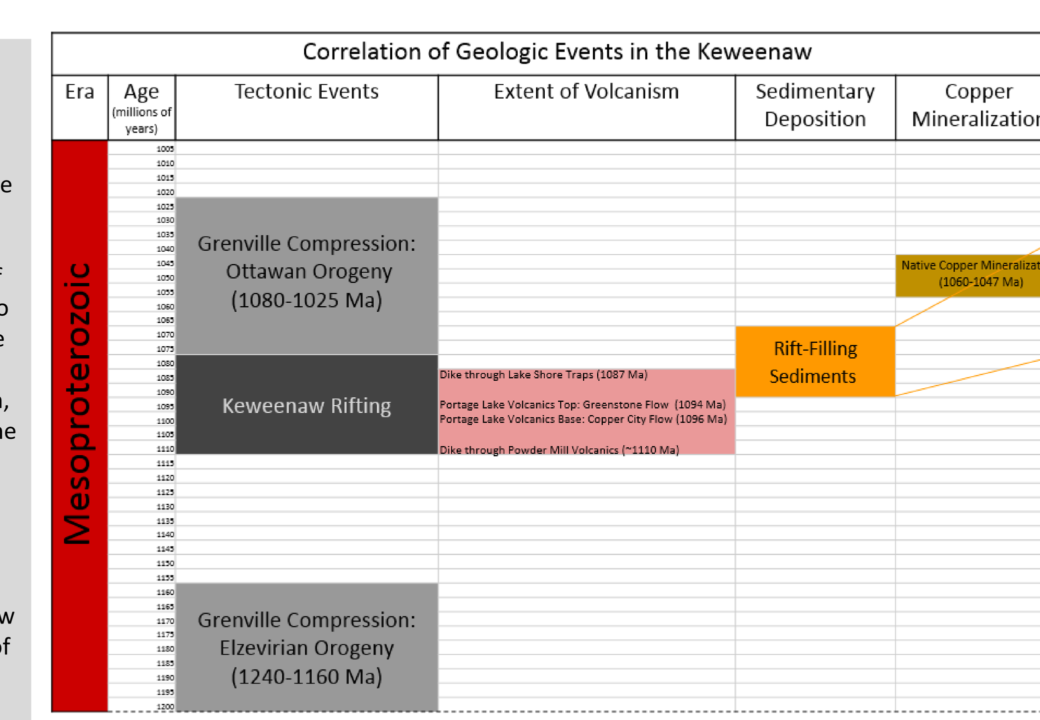
The Great Lakes Tectonic Zone (GLTZ) is an ancient zone of convergence between two Archean crustal blocks with ages ranging from 2,700 - 3,500 Ma. Archean gneisses to the south of the GLTZ represent the older crustal terrane with ages up to 3,500 Ma (Sims et al., 1980). However, ages in this area cluster around 2,700 Ma (Morey and Van Schmus, 1988). This major tectonic event, represented by the GLTZ, shows multiple deformation characteristics. These characteristics 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, it 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.

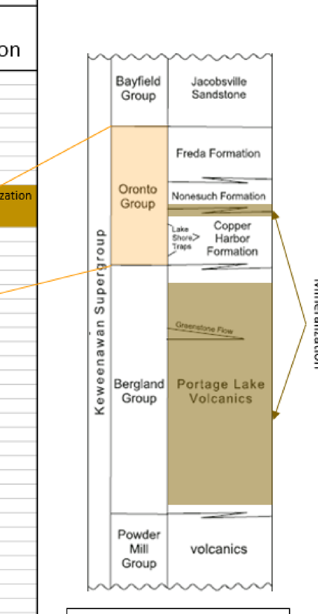
Penokean Orogeny

The Penokean Orogeny is a tectonic event in which several microcontinents and island arcs converged onto the continental margin formed during the GLTZ. This 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). These volcanic ranges remained active till about 1,850 when another landmass called the Marshfield craton forced the rest of the Pembine-Wausau range up over the Superior Craton, towards the north. This caused a foreland basin to form because of subsidence, and sedimentation was started in two very distinct time zones. In the north, it started at about 1853 Ma, and in the south it started at 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 terranes marking the end of the Penokean orogeny.

Midcontinent Rifting

A synclinal structure located under Lake Superior (Figure 1) is indicative of the failed Midcontinent Rift system that started approximately 1.1 billion years ago. Geophysical studies have confirmed the complex nature of sedimentary rocks overlying a thick section of mafic volcanic rocks (Hinze et al., 1997). This also helped to confirm the distance of the rift, which is almost 200 km long. In regards to the stress fractures crisscrossing the region, there are two massive 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.





Generalized Stratigraphic Section of Keweenawan Rocks (after Bornhorst and Barron 2011)

Figure 2. Correlation of Events in the Keweenaw Area. Tectonic data taken from Cannon, 1994. Geologic events taken from Davis and Paces 1992; Cannon 1994. Copper mineralization dates from Bornhorst 1988. Simplified stratigraphic column from Bornhorst 2011.

Grenville Orogeny

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). 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 Elzeverian and Ottawan events, recorded within deformational features bordering the edge of the Grenville front. The Elzeverian pulse dates from 1,240 to 1,160 Ma and the Ottawan pulse is dated from 1,090 to 1,025 Ma (Cannon, 1994) as shown in Figure 2.

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