

# TRACE ELEMENTAL ANALYSIS OF COPPER INCLUSIONS IN THE PORTAGE LAKE VOLCANICS SERIES OF THE KEWEENAW PENINSULA, MI USING PARTICLE-INDUCED X-RAY EMISSION SPECTROSCOPY (PIXE)

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## Abstract

The Portage Lake Volcanics is a mid-Proterozoic series made up of over 200 individual subaerial thoeiilitic basaltic flows, which contain extensive amygdaloidal and brecciated flow tops in addition to interflow conglomerates, hosting the secondary copper deposits that make the Keweenaw Peninsula region of Michigan famous. The intent of this study is to explore variations in the trace elemental composition of copper deposits in the area and explore possible geological implications of such variations. Thick sections of conglomerates and basalts containing copper inclusions from the Centennial, Calumet & Hecla, Phoenix, and Allouez mines, among others, were analyzed using particle-induced x-ray emission spectroscopy. PIXE was performed in the Hope College Ion Beam Analysis Laboratory using a 1.7MV Pelletron tandem particle accelerator. The ion beam was focused on copper inclusions and spectra were collected and analyzed using gupix software. Ratios of trace nickel, silver, and arsenic to copper were calculated and compared across different inclusions in a single sample and across samples from different geographic locations, formations, and mine depths. Results show some variation in elemental ratios within samples, and greater variation across samples from different mines, formations, and depths. Elemental compositions are likely subject to a variety of factors influencing local conditions in copper mineralization.

## Geologic Context

The Portage Lake Volcanics (PLV) are made up mostly of basalt in at least 200 distinct lava flows ranging from 1 to 450 m thick. Less than 5 % of the sequence is made up of sedimentary units. These are predominantly pebble and boulder conglomerates with felsic clasts and a sand matrix. The PLV formed in the 1.15-1.0 Ga (Bornhorst & Barron, 2011) mid continental rift zone which is exposed in Michigan's Keweenaw Peninsula. Hydrothermal solutions circulated through the most permeable units including brecciated and vesicular flow tops, conglomerates, fault zones and fractures. At about 1.06 Ga (Bornhorst & Barron, 2011) these fluids precipitated native copper along with over 100 other hydrothermal minerals. This formed the basis of a major copper mining district with ores containing up to 2.9% Cu (Bornhorst & Barron, 2011).

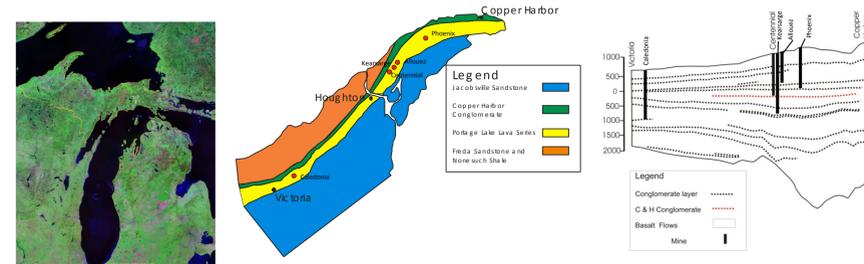


Figure 1: The left image shows a satellite photograph of the state of Michigan. The center map is of the Keweenaw Peninsula, located in the upper left of the left map. Locations of mines are plotted on the center map. On the right, a cross section from Victoria, MI to Copper Harbor, MI shows the locations and stratigraphic depths of various mines.

## Methods

Native copper from these deposits tends to contain trace amounts of other elements, such as nickel, silver, and arsenic (those examined in this study) among others (Bornhorst & Rose, 1994). The main goal of the study was to determine the feasibility of this trace elemental analysis using PIXE (particle induced x-ray emission). Development of an analytical method using PIXE on copper minerals would provide a nondestructive, quantitative measure of trace elements in a solid sample with low detection limits (in the ppm range) and high spatial resolution. Such analysis could be used to explore variations in the trace elemental composition of copper deposits and explore possible geological implications of such variations.



Figure 2 (left): The six sample slide maps, front and back, with sample sites of interest marked. Figure 3 (right): The HIBAL accelerator lab. The foreground shows the source oven and chamber. Subset image is the RBS chamber at the end of the line where samples are loaded.

Thick sections of rock samples from the Allouez (AL 12), Caledonia (CAL 855), Centennial (C 32, CM 310), Kearsarge (WAS 751), and Phoenix (PH 1) mines attached to glass slides were scanned in high resolution on both sides using a common flatbed scanner. Transparencies of both sides were overlain to determine sites on the slides where copper inclusions passed completely through the sample. These sites were marked using a coordinate system overlain on the slides in order to place the ion beam directly onto the sites of interest (Fig. 2).

PIXE was performed at the Hope College Ion Beam Analysis Laboratory (HIBAL) using a 1.7MV Pelletron tandem particle accelerator (Fig. 3). Protons were accelerated at 3.4 MeV and focused into a ~0.1 mm diameter beam on the sample targets. Beam intensity was kept to ~1 nA on target and the run length was adjusted to give approximately 1.5 μC of beam on target. As the charged particles collide with the atoms on the surface of the sample, atomic electrons are either ionized or became excited and move to outer shells. As electrons relax to fill the vacancies, they emit x-rays with specific energies characteristic of the target element (Fig. 4).

A Si(Li) x-ray detector mounted at 135° degrees from the beam collects x-ray counts across a range of energies. A 381 μm aluminum filter was placed in front of the ion beam to greatly attenuate the counts for Cu, allowing a greater proportion of counts from other elements to be recorded for greater trace concentration precision. Data were collected for each sample for 10 minutes at multiple sites.

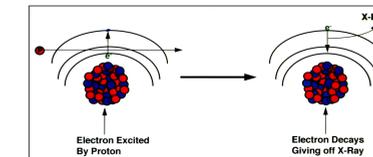


Figure 4: A schematic illustration of PIXE principles.

A commercial peak fitting program, GUPIXWin (Campbell et al., 2010), was used to fit the x-ray spectrum for each sample analyzed (Fig. 5). The energies of the peaks were calibrated to known target standards and the absolute concentrations of the elements were fit to a NIST glass standard reference material (#1412)(NBS, 1985). The GUPIXWin software calculates the absolute concentrations of each of the elements in question, with associated statistical errors.

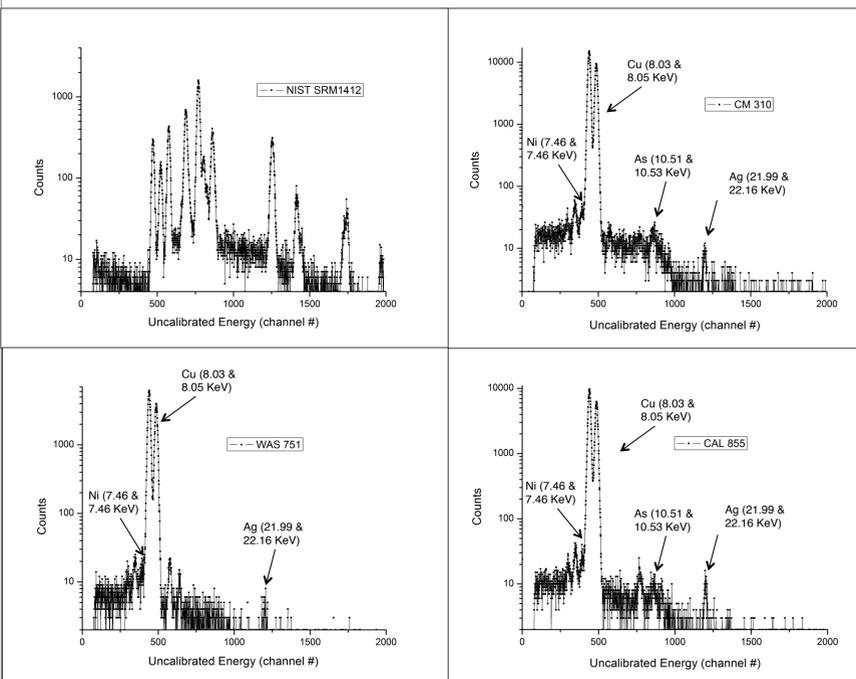


Figure 5: Spectra output from GUPIXWIN for the standard reference material as well as three samples.

## Results

Average concentration values were calculated for trace elements in each sample from 3 different sampling sites within the sample slide, and these values are plotted in Figure 6 with their respective errors. Trace element concentrations tended to vary at different sites within a sample, which contributed the error on the average, but concentrations varied more across different samples. Note that for all samples but CM 310 and WAS 751, the concentration of Arsenic was below the limit of detection (LOD), expressed by large errors below concentrations of ~100ppm As. Samples are statistically distinct in terms of Ni, and Ag levels are rather consistent.

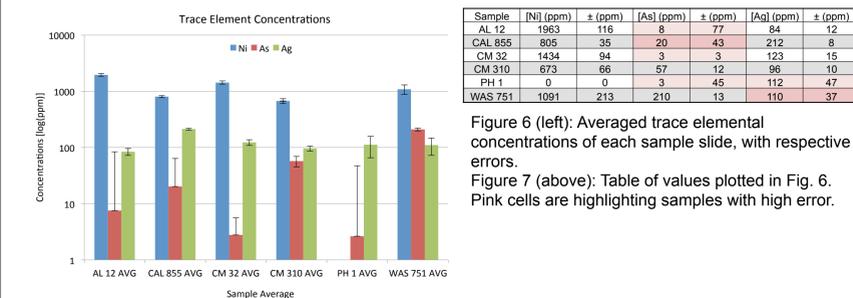


Figure 6 (left): Averaged trace elemental concentrations of each sample slide, with respective errors. Figure 7 (above): Table of values plotted in Fig. 6. Pink cells are highlighting samples with high error.

## Conclusion and Future Interests

It is apparent through the study of these six samples that this method of analysis may be helpful in the future for the analysis of trace elements in Cu minerals. There is not enough data yet to make statements about the implications of variations in elemental concentrations. These methods could be used to produce more data from which conclusions about lithology and location may be drawn. It may be possible to increase the precision of the measurement by increasing run times or tuning the ion beam to a more concentrated area on sample. More work could be done on optimizing Cu peak attenuation to increase resolution of trace element peaks. Ion beam analysis could prove as a helpful technique for studying mechanisms that led to the mineralization of native copper in the Keweenaw Peninsula.

## References

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