USING COPPER ISOTOPE RATIOS FOR MINERAL EXPLORATION AT THE PEBBLE PORPHYRY CU-AU-MO DEPOSIT, ALASKA

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ABSTRACT

We measured copper isotope ratios from natural waters such as ponds, seeps, and groundwater to gain an understanding of weathering of subsurface Cu-bearing minerals that encompass the Pebble porphyry Cu-Au-Mo deposit property in Alaska. We hypothesize that copper isotope ratios can be used to determine active weathering of sulfide minerals because oxidative dissolution of Cu-rich sulfides results in solutions that have enriched δ^{65}Cu signatures. Therefore, enriched copper isotope ratios in surface and subsurface waters signify weathering of Cu-rich minerals at depth. Our data support this notion because it is evident on the Pebble deposit property that levels of the heavier δ^{65}Cu isotopes are higher in surface waters (δ^{65}Cu = 0.67‰ to 1.4‰) than in surface waters proximal to deposit (δ^{65}Cu = -0.52‰ to -0.01‰). Measurement of copper isotope ratios in natural waters aids in the exploration of new deposits and the monitoring of heavy metal dispersal during chemical weathering.

INTRODUCTION

The Pebble Porphyry Cu-Au-Mo deposit is located 200 miles southwest of Anchorage, Alaska. It is estimated that the deposit contains 5.94 billion tons of ore valued at more than $300 billion dollars (Rebagliati, 2008). It is the largest known deposit of its kind in the world (Duttweiler). The deposit has two main sites: Pebble East and Pebble West, and is part of a horst and graben system (Figure 1). The mineral ores in Pebble East Zone (PEZ), which are in the graben, are buried deeper and overlain by more glacial gravel than in Pebble West Zone (PWZ), which is located in the horst (Eppinger, in print). In the PEZ, sills lead into a granodiorite pluton. Intrusion of these igneous bodies caused recrystallization and mineralization of the ore bodies (Rebagliati, 2008). A series of diorite sills, granodiorite cupolas and associated breccias are found in the fault system of the PWZ (Rebagliati, 2008).

Figure 1. Map of the Pebble Deposit.

Bedrock in the Pebble deposit contains copper-bearing sulfides, which naturally weather and release copper ions into ponds, seeps and groundwater. During low runoff periods, ponds are recharged with groundwater, which passes through the subsurface and comes in contact with the copper ions. Seeps also pass through the subsurface and trap ions. In areas with copper bearing minerals such as chalcocite, chalcopyrite, bornite, covellite, and tetrahedrite, the water will likely trap more Cu-ions than an area with little to no Cu-bearing minerals.

In this study we analyzed water samples from ponds, seeps, and groundwater located at the Pebble deposit to determine their dissolved copper ion content. When subject to weathering processes, Cu isotopes fractionate from Cu-bearing sulfides. Water (from ponds, seeps and groundwater) oxidizes sulfides on the deposit and has enriched δ^{65}Cu signatures which are distinctly greater than δ^{65}Cu values from waters distal to the deposit not weathering sulfides. Copper isotope fractionation may be useful as tool for copper exploration and potentially monitor the migration of metals from the deposit.

METHODS

There were a total of 104 samples collected from the Pebble deposit location. The samples were hand-collected from ponds, seeps, and groundwater located near the porphyry. All of the samples were filtered after they were collected. Concentrations of base and trace metals were conducted at the University of Alaska at Anchorage by using the Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The concentrations of Cu in most samples were less than 10 ppb.

Once the samples were received at Juniata College, 35mL of each water sample were measured out and dried on a hotplate at around 45°C. 35mL were used to ensure that any traces of copper would be detected when the ICP-MS would be utilized later in the process. 2mL of 6N HCl were added to each dried sample in order to prepare them for column chemistry.

We used column chromatography as the chemistry method to remove isotopes other than copper from the water samples. The resin (approximately 10mL) inside the columns was cleaned first with Millipore water, HNO_3, and HCl. 5mL of 6N HCl were added to the 2mL water sample solutions. After these solutions completely dripped through the columns, 27mL of 6N HCl were added to the columns and collected.

At University of Arizona, the samples' Cu-isotope intensities were measured using the ICP-MS. The NIST 976 copper standard was used with standard-sample-standard bracketing to prevent constraint on any instrumentation mass bias amongst the samples.

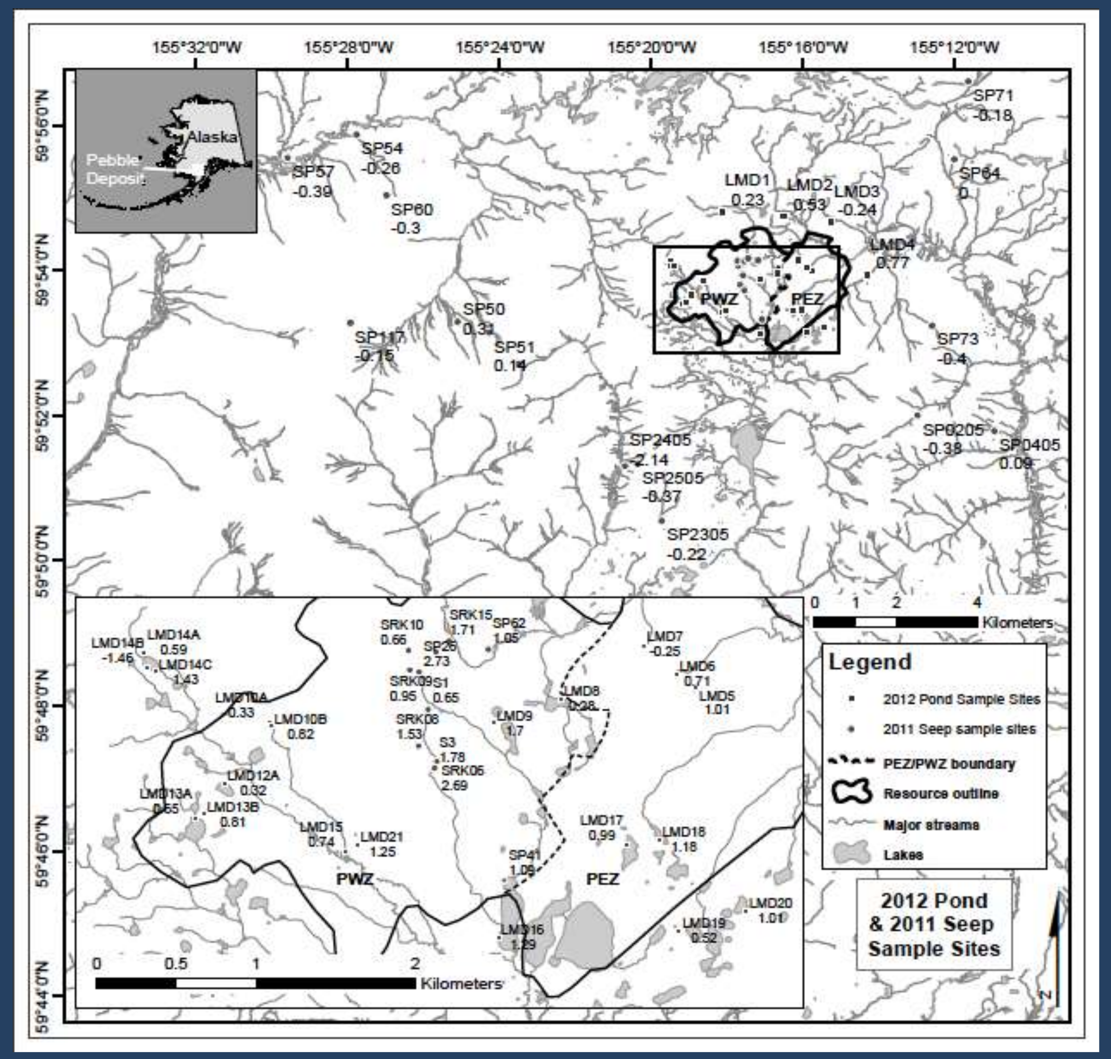


Figure 2. Map of surface waters and values

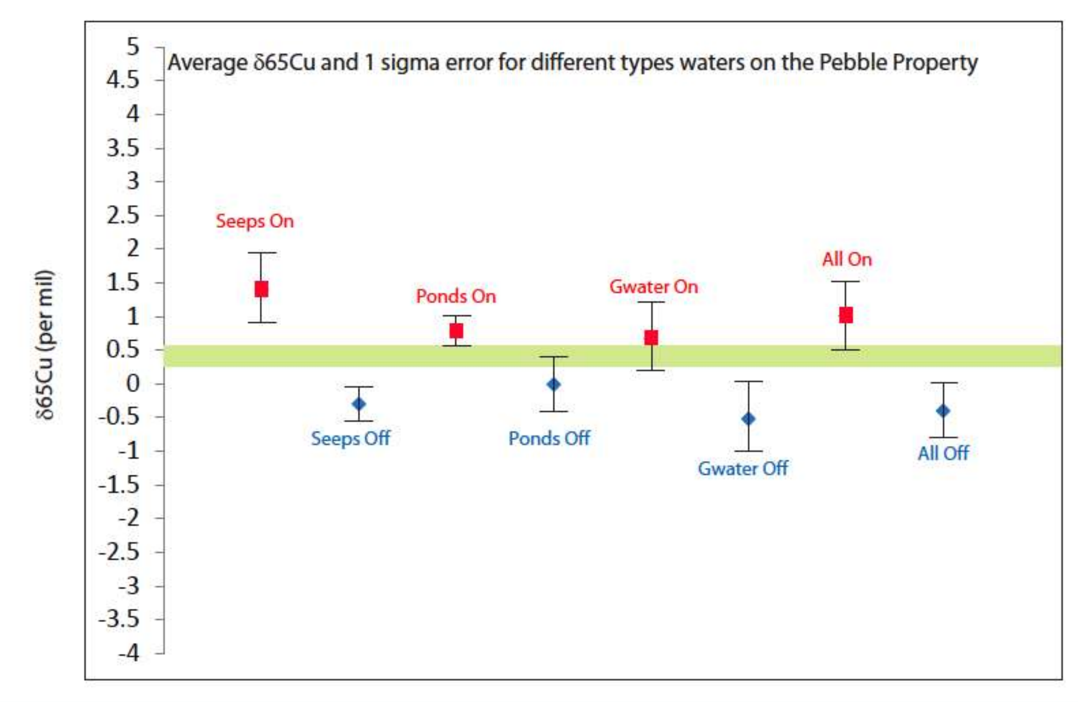


Figure 6: Averaged δ^{65}Cu enrichment signatures from all water types

RESULTS AND DISCUSSION

- A total of 104 water samples were collected on and near the Pebble deposit from ponds, seeps and groundwater over a four year period. Collection and analysis of samples has been ongoing for three years (2009-2012). The ICP-MS multicollector at the University of Arizona was used to measure the δ^{65}Cu signatures in the water samples. Figure 2 is a map of the location of all samples collected.

- Figures 3, 4 & 5 depict the number of water samples of each type collected versus the δ^{65}Cu signatures. On-deposit samples were collected within the "Resource Outline" shown in Figure 2. The Resource Outline is defined as an area that has >0.5‰ soluble Cu which encompasses PEZ and PWZ. Off-deposit samples were collected outside of the Resource Outline, ranging from 0.1km to 10km from PEZ and PWZ.

- A general trend is seen in Figures 3, 4 & 5. Samples collected on-deposit average higher δ^{65}Cu signature levels than samples collected off-deposit. On-deposit δ^{65}Cu signature levels range from 0.67‰ to 1.4‰. Off-deposit signatures range from -0.52‰ to -0.01‰.

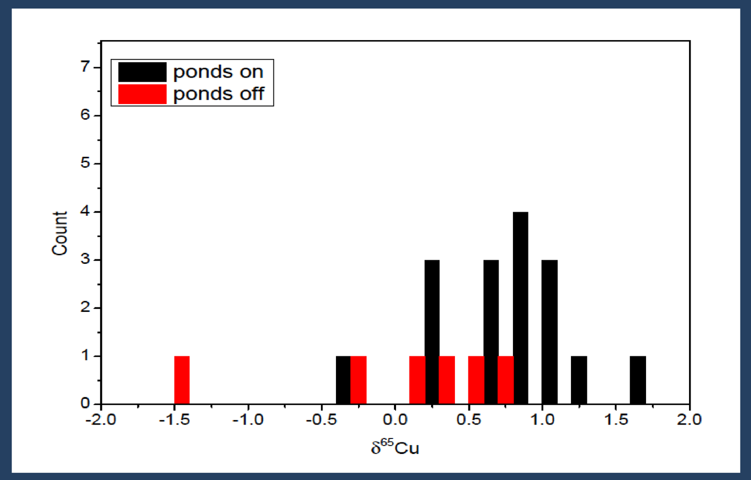
- Elevated δ^{65}Cu signatures are found near active mineralization locations, whereas lower δ^{65}Cu signatures do not indicate mineralization or weathering of sulfides.

- Figure 6 is a comparison of all water samples collected from 2009 to 2012 and their average δ^{65}Cu signatures. As seen on the graph, the on-deposit samples have higher δ^{65}Cu signatures than the off-deposit samples, concluding that elevated δ^{65}Cu signatures mark locations of active oxidative weathering of copper sulfides.

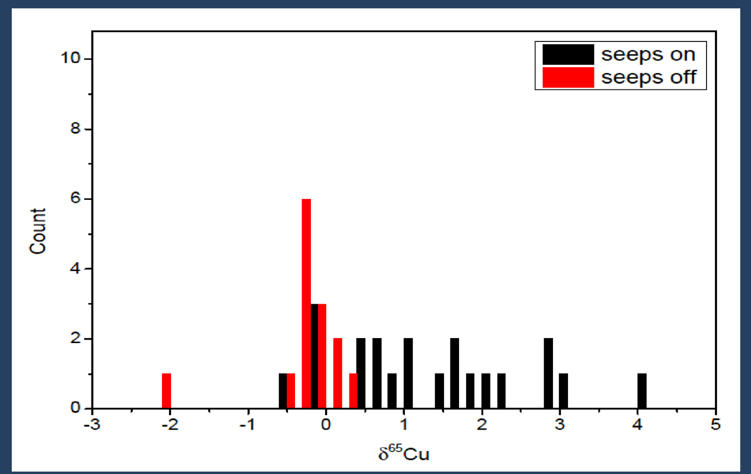
- The water samples analyzed in this study were collected from undeveloped land, so the spatial distribution of the δ^{65}Cu signatures is the basis map for deviation for pre-mining activities on the Pebble deposit. Oxidative signatures can be traced once mining begins, so if elevated δ^{65}Cu values migrate into areas that originally had lower δ^{65}Cu values, we know the copper signatures are coming from the mine. This allows mining activities to be monitored.

CONCLUSION

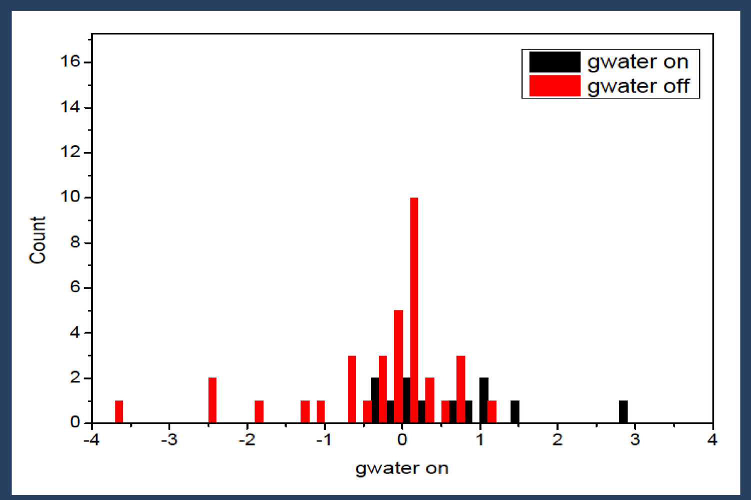
This study has established that measuring δ^{65}Cu signatures in a variety of fluids on and off the Pebble deposit is an economically viable method. δ^{65}Cu signatures reveal locations of active weathering sulfides of the ore deposit, and they can be used to monitor heavy metal discharge and dispersal from mining activities. From an environmental standpoint, the ability to be aware of heavy metasl dispersion helps the mining companies to know when their activities have begun to affect areas surrounding the deposit.



Pond Water (22 samples)
Figure 3: δ^{65}Cu enrichment data



Seep Water (35 samples)
Figure 4: δ^{65}Cu enrichment data



Groundwater (47 samples)
Figure 5: δ^{65}Cu enrichment data

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