The history of the United States cent revealed through copper isotope fractionation

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ABSTRACT

Copper isotope fractionation in United States cents traces changes in the source of copper and identifies historical events. Application of copper isotopes as a geochemical tracer requires consistent isotopic signatures of the ores and refined metals. Overlapping isotopic signatures of crushed ores, chalcocite and refined metal extracted from Morenci, Arizona indicate modern mining processes that produce distinguishable single ore deposit geochemical signatures. The coincidence of copper isotope ratios in metals and ore deposits also exists within the United States cents analyzed here. Specifically, historical records confirm two different sources for copper in cents from 1800 through 1867. The copper isotope composition of the 1828, 1830, 1836, 1838 and 1843 cents coincides with the Cornwall ores of England, and cents post 1850 (1859, 1862) correspond with the Michigan ores of the United States. Three of the thirty-six post 1867 cents measured possess fractionated copper isotope ratios and indicate the change in source of copper for the United States cent.

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1. Introduction

Understanding where metals originated in ancient artifacts provides critical information regarding trading routes and indicates the interaction of cultures. To this point, geochemical techniques such as trace elements and Pb isotopes demonstrate promise in linking ore deposits and sources of metals in artifacts. Data from new transition metal stable isotope techniques show significant isotopic fractionation in ore deposits which provides potential application of transition metal isotopes systems to trace metals in artifacts (Zhu et al., 2000; Hull et al., 2008; Gale et al., 1999). Of all the reported transition metal isotope data, copper isotopes reveal the greatest degree of fractionation thereby this isotopic system provides the most promise as a geochemical tracer in metal artifacts (Zhu et al., 2000, 2002; Larson, 2004; Maher et al., 2007; Markl et al., 2006; Asael et al., 2007; Ehrlich et al., 2004; Marechal et al., 1999; Mason et al., 2005; Rouxel et al., 2004; Larson et al., 2003).

The obstacle for using copper isotopes to trace copper in artifacts resides in the fact that no data indicate distinct copper isotopic signatures for single ore deposits. Several studies report several permil variations within one ore deposit (Zhu et al., 2000; Markl et al., 2006). However, isotopic ranges exist within ore deposits when comparing the copper isotopic composition of the ore minerals formed in high ($>250\,^{\circ}$C, such as chalcopyrite, $CuFeS_2$) versus low ($<100\,^{\circ}$C, such as chalcocite, Cu_2S) temperature hydrothermal environments. Fig. 1 illustrates that low temperature processes fractionate copper isotopes whereas higher temperature mineralization processes do not cause significant fractionation. This observation correlates with several laboratory experiments (Zhu et al., 2002; Ehrlich et al., 2004; Mathur et al., 2005). With this in mind, identification of Cu isotopic differences in metal artifacts should reflect high versus low temperature ore sources.

To examine this predicted difference in copper isotope signatures of ores, we analyzed 40 United States cents coined between 1828 and 1972 (Table 1) and originating from Philadelphia, Denver and San Francisco Mints. Determination of the source of copper through copper isotope analysis in United States cents provides an ideal study in metallic artifacts for two main reasons. First, the annual report from the United States Mint, along with other historical documents, tracks the purchasing history of copper for cents. The historical documentation unequivocally identifies the source of copper. Secondly, both high and low temperature ores supplied copper for the cent. For instance, initially the United States Mint purchased copper from the Soho Mint which obtained copper from the high temperature ($>400\,^{\circ}$C) magmatic ores of Cornwall,

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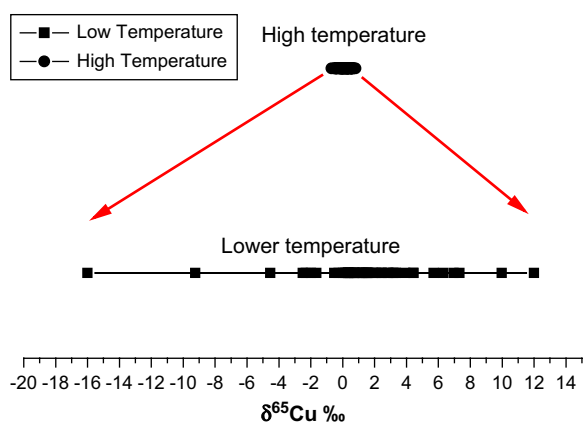   E-mail address: mathur@juniata.edu (R. Mathur).

Fig. 1. Variation of the copper isotope composition of copper minerals formed in high temperature and low temperature hydrothermal environments (Zhu et al., 2000; Hull et al., 2008; Larson, 2004; Maher et al., 2007; Markl et al., 2006; Asael et al., 2007; Ehrlich et al., 2004; Mason et al., 2005; Rouxel et al., 2004; Mathur et al., 2005; Graham et al., 2004; Jiang et al., 2002; Weiss et al., 2004).

England (from 1800 to 1849). By 1850 the Mint purchased copper exclusively from lower temperature metamorphic ores (130–200 °C) of the Keweenaw Peninsula, Michigan, USA (Brown, 2006; Scofield, 1976). Finally post 1867, the influx of copper from

Table 1
Copper isotopic compositions of cents with $2\sigma - 0.08$‰. The source mint abbreviations are P = Philadelphia, Pennsylvania; D = Denver, Colorado; S = San Francisco, California. * Indicates samples measured at Washington State University and the University of Arizona.

Year	δ^{65}Cu (‰)	Mint
1911	0.54	D
1918	0.16	D
1920	0.53	D
1926	0.90	D
1946	0.18	D
1956	1.05	D
1968	0.34	D
1828	0.00	P*
1830	0.04	P*
1836	−0.06	P
1838	0.00	P
1843	−0.02	P
1856	0.32	P
1862	0.33	P
1880	−0.33	P
1881	0.59	P
1888	0.42	P
1891	2.02	P
1892	0.41	P
1893	0.38	P
1895	0.37	P
1896	0.25	P
1897	0.31	P
1898	1.40	P*
1899	0.04	P
1904	0.23	P
1907	0.13	P*
1911	0.18	P
1915	0.04	P
1918	0.06	P
1920	0.22	P
1939	−0.01	P*
1942	0.72	P
1946	0.37	P
1946	0.38	P
1947	−0.03	P
1956	−0.49	P
1972	−0.05	P
1945	0.38	S
1946	0.37	S
1947	0.28	S

mixed high and low temperature ores present in porphyry copper deposits dominated the source of copper in the cent.

The application of Cu isotopes for provenancing in the United States cent establishes the technique. In other words, the study builds a foundation for application in the field of Cu isotope fractionation for Cu, trade, and provenance studies in both recent and ancient artifacts (Tylecote et al., 1977; Rothenberg, 1990).

2. Sampling and methods

The sampling, preparation and isotopic analysis of crushed ore samples, chalcocite, refined metal and cents involved several steps. Three types of samples (crushed ore samples, chalcocite and refined metal) from the porphyry copper deposit in Morenci, Arizona were analyzed to assess the copper isotopic signature of the deposit. The crushed ore (preleach feed) contained pebble to sand grain-sized particles originating from the Garfield Pit in Morenci. The hand-picked chalcocite samples were collected from 2 drill cores and 6 different locations in the active mine area. The refined metal samples were collected in three different years from the onsite electroplating facility.

Shavings of cents, powders of ore and pure chalcocite and metal were weighed (between 0.02 g and 0.05 g) and dissolved in ultra pure nitric acid, dried and diluted in 2% nitric acid to 100 ppb Cu. The dilute solutions were injected into a Multicollector Inductively Coupled Plasma mass spectrometer (MC-ICPMS, the Micromass Isoprobe at the University of Arizona and Neptune at Washington State University) in low-resolution mode using a microconcentric nebulizer. Measurements of several samples on both instruments yielded the same result within the reported error and the average value is reported in Tables 1 and 2. The intensity of the ^{63}Cu beams the standard and samples remained between 1 and 2 V. No potential isobars (Mg and Na) were detected for ore samples and preleach samples. Both on and off-peak blank corrections were applied to the data and yielded the same result.

Copper isotope ratios are reported according to the following expression:

$$\delta^{65}CU‰ = \left\{ \left(\frac{(^{65}CU/^{63}CU)sample}{(^{65}CU/^{63}CU)standard} \right) - 1 \right\} 1000$$

Table 2
Copper isotopic compositions of metals, ores and minerals with $2\sigma - 0.14$‰. * Indicates samples measured on the multicollector ICPMS at the University of Arizona and Washington State University.

Source	Phase	δ^{65}Cu (‰)
Morenci, AZ*	preleach ore	2.24
Morenci, AZ*	preleach ore	2.21
Morenci, AZ*	preleach ore	2.42
Morenci, AZ*	chalcocite	2.61
Morenci, AZ*	chalcocite	2.54
Morenci, AZ	chalcocite	1.92
Morenci, AZ	chalcocite	0.89
Morenci, AZ	chalcocite	1.65
Morenci, AZ	chalcocite	2.62
Morenci, AZ	chalcocite	3.63
Morenci, AZ	chalcocite	2.55
Morenci, AZ	*Average cc*	*2.30*
Morenci, AZ	Cu nugget	2.45
Morenci, AZ	Cu nugget	2.51
Morenci, AZ	Cu nugget	2.22
Morenci, AZ	*Average Cu*	*2.39*
Morenci, AZ*	*chalcopyrite*	*0.55*
Morenci, AZ	*malachite*	*5.42*
Keweenaw, Michigan	Cu metal	0.45
Keweenaw, Michigan	Cu metal	0.54
Keweenaw, Michigan	Cu metal	0.38
Keweenaw, Michigan	*Average Cu metal*	*0.46*