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Copper and sulfur isotope ratios in Paleozoic-hosted Mississippi Valley-type mineralization in Wisconsin, USA

John Luczaj[a,*], Hui Huang[b]

[a] Department of Natural & Applied Sciences, University of Wisconsin-Green Bay, Green Bay, WI 54311, USA
[b] Department of Geological Sciences, Indiana University – Bloomington, Bloomington, IN 47405, USA

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ABSTRACT

We provide the first Cu-isotope data for chalcopyrite in Paleozoic carbonate-hosted Mississippi Valley-type (MVT) mineralization, along with corresponding sulfur isotopes, for eastern Wisconsin, USA. Chalcopyrite in this region occurs mainly as disseminated crystals and is associated with regionally extensive dolomite-hosted subeconomic MVT mineralization on the western edge of the ancestral Michigan Basin. A narrow range in δ^{65}Cu values (0 ± 0.5‰) for chalcopyrite is observed along a large region (125 km) of the western margin of the basin that is consistent with a homogeneous Cu-source in the crust with a δ^{65}Cu composition near 0‰, along with limited redox modification during regional flow or hydrothermal precipitation processes. Cu and S-isotope values, in conjunction with existing lead, strontium, and sulfur isotope data from other sulfide minerals in the region, are consistent with a Precambrian source similar to parts of the Midcontinent Rift System, but distinct from some other Precambrian deposits in the region.

1. Introduction

Copper isotopes have been applied to a wide range of geologic processes including magmatic and hydrothermal ore-forming environments (Zhu et al., 2000; Larson et al., 2003; Markl et al., 2006; Asadi et al., 2014; Berkenbosch et al., 2015), stratiform sedimentary copper ore deposits (Asael et al., 2007), Ni-Cu-PGE sulfide mineralization (Ripley et al., 2015), near-surface chemical settings (e.g., Kimball et al., 2009), and others. Available δ^{65}Cu data show natural variations of up to 9‰ (Larson et al., 2003), although samples from many settings fall in a more restricted range from about -1 to +1‰ (Hoefs, 2009). Mechanisms including redox reactions and equilibrium thermodynamic fractionations are thought to cause fractionation of copper isotopes (Larson et al., 2003).

Published literature contains examples of Cu- and Zn-isotopic data for many ore-forming environments (e.g., Zhu et al., 2000; Larson et al., 2003; Markl et al., 2006; Asadi et al., 2014; Berkenbosch et al., 2015; Wilkinson et al., 2005; John et al., 2008; Pašava et al., 2014), including Cu-isotope studies in the Lake Superior Region of North America (Larson et al., 2003; Ripley et al., 2015). The source of metals found in Mississippi Valley-type (MVT) deposits remains an important knowledge gap (Paradis et al., 2007, p. 198). Unlike Zn-isotopes, which have been applied to carbonate-hosted MVT ore deposits (e.g., Wilkinson et al., 2005; Pašava et al., 2014; Gao et al., 2017), Cu-isotope data are lacking in published literature for MVT mineralization. Along with sulfur isotope data, we provide the first Cu-isotope data for carbonate-hosted chalcopyrite in subeconomic MVT mineralization using a case example along the western edge of the ancestral Michigan Basin. Our results allow for constraints to be placed on the metals scavenging and MVT mineral precipitation processes in the study area.

2. Geologic setting

The states of Wisconsin, Michigan, and Minnesota (United States) lie in the western Great Lakes region of North America. The bedrock geology of eastern Wisconsin consists of eroded Precambrian crystalline rocks, overlain by a sequence of Lower and Middle Paleozoic quartz sandstone, dolomite, and shale up to 800 m thick (Fig. 1). Lower and Middle Paleozoic strata presently cover the southern half of the state and thicken to the east toward the Michigan Basin where they are overlain by younger Paleozoic and Mesozoic sedimentary rocks (Luczaj et al., 2016).

Precambrian rocks in the region exhibit considerable variation in lithology and tectonic origin. Assembly of this portion of North America occurred during the Penokean and Yavapai orogenies at 1.85 and 1.76 Ga, respectively (Schulz and Cannon, 2007). Later anorogenic granitic magmatism related to the Wolf River Batholith (1.5 Ga) and associated rocks occurred in northeastern Wisconsin (Dewane and Van Schmus,

* Corresponding author.
E-mail addresses: luczajj@uwgb.edu (J. Luczaj), hh26@indiana.edu (H. Huang).

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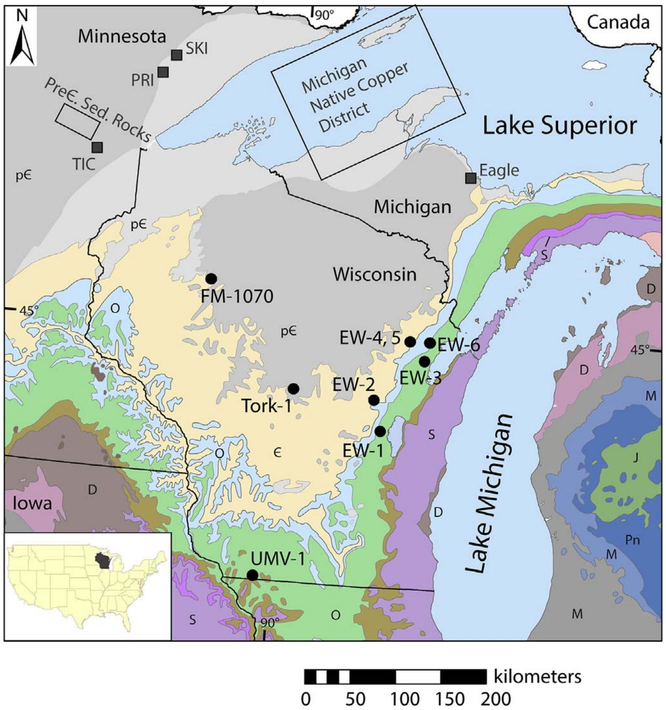

Fig. 1. Geologic map of the western Great Lakes region of the United States showing localities of samples analyzed in this study (black circles). Samples in eastern Wisconsin (EW-1 through EW-6) are Paleozoic-hosted chalcopyrite. Precambrian rocks in the region, for which Cu-isotopic data exist (Larson et al., 2003; Ripley et al., 2015), are represented by gray squares as follows: PRI = Partridge River Intrusion, SKI = South Kawishiwi Intrusion, TIC = Tamarack Intrusive Complex, and Eagle = Eagle Deposit. Larger areas with Cu-isotope data for Precambrian sedimentary rocks and the Michigan Native Copper district are shown as open rectangles. Precambrian areas are shown in gray, with light gray for the exposed Proterozoic Midcontinent Rift System. Other colors represent Paleozoic and Mesozoic bedrock with letters for Paleozoic and Mesozoic Periods. Inset map shows Wisconsin in the lower 48 contiguous United States. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

2007). Subsequent continental rifting occurred along the Midcontinent Rift System (MCRS) at 1.1 Ga, which led to the development of a 2000 km long series of rift basins that surround the study area on three sides (Ojakangas et al., 2001). Both the Penokean orogen and MCRS have extensive economic mineral deposits with abundant copper mineralization that have been mined historically (Bornhorst, 1997; LaBerge, 1996).

The upper Mississippi Valley region of southwestern Wisconsin, eastern Iowa, and northwestern Illinois, USA (Fig. 1) contains a historic MVT ore district (e.g., Heyl et al., 1959; Sverjensky, 1986). The main ore body types in the district were gash-vein deposits and pitch-and-flat deposits hosted by Ordovician carbonates, with lesser placer and residual deposits (Heyl et al., 1959).

Similar MVT mineralization (subeconomic) is also present throughout eastern Wisconsin, which was initially thought to represent outlying deposits of the main ore district (e.g., Bagrowski, 1940; Garvin et al., 1987), but is now recognized as a broad region containing MVT mineralization that originated from brines expelled from the Michigan Basin (Luczaj, 2006a; Luczaj et al., 2016). There has been no significant production from MVT mineralization in northeastern Wisconsin. Limited exploration for MVT ore deposits took place during the early 1980s through a subsurface coring program in eight southeastern Wisconsin counties by Mobil Mineral Resources, Inc. (Luczaj et al., 2016). Extensive Pleistocene glacial overburden, combined with an underdeveloped knowledge of the distribution and character of geologic structures, has hampered efforts to fully characterize the region's subsurface geology.

A regional hydrothermal system operated along the western margin of the Michigan Basin at temperatures between about 60 and 120 °C, with sulfide mineralization likely occurring between about 80 and 110 °C (Luczaj, 2000, 2006a). A suite of MVT minerals, including pyrite and marcasite (FeS_2), galena (PbS), sphalerite (ZnS), chalcopyrite ($CuFeS_2$), fluorite (CaF_2), celestine ($SrSO_4$), bravoite/vaesite (Ni-Co-Fe-sulfide), and others is well documented in Paleozoic rocks throughout the region (Luczaj et al., 2016). While abundant MVT minerals are present in Cambrian-Devonian strata, the Ordovician strata show more substantial concentrations of sulfide minerals. A particularly well-developed zone of sulfide mineralization occurs at the top of the Ordovician Ancell Group sandstones and is known as the "sulfide cement horizon" or SCH (e.g., Schreiber et al., 2000). The SCH occurs throughout eastern Wisconsin from the Illinois border in the south to the Michigan border in the north (Luczaj, 2006a; Luczaj et al., 2016). While copper is known to be present in the SCH at concentrations up to 1620 mg/kg (Luczaj et al., 2016), discrete crystals of chalcopyrite suitable for isotopic analysis were only observed in Ordovician carbonates.

Chalcopyrite in eastern Wisconsin is found typically as 1-3 mm disphenoid-shaped crystals associated with late dolomite and other minerals (Fig. 2). Vug-filling chalcopyrite and associated malachite are also observed rarely. Although chalcopyrite represents a small fraction of the mass of MVT sulfides in eastern Wisconsin, it occurs over a wide region as crystals large enough to sample for δ^{65}Cu analysis. Luczaj (2006a) and Luczaj et al. (2016) provide further details of the mineralogy and thermal characteristics of the dolomite-hosted MVT system.

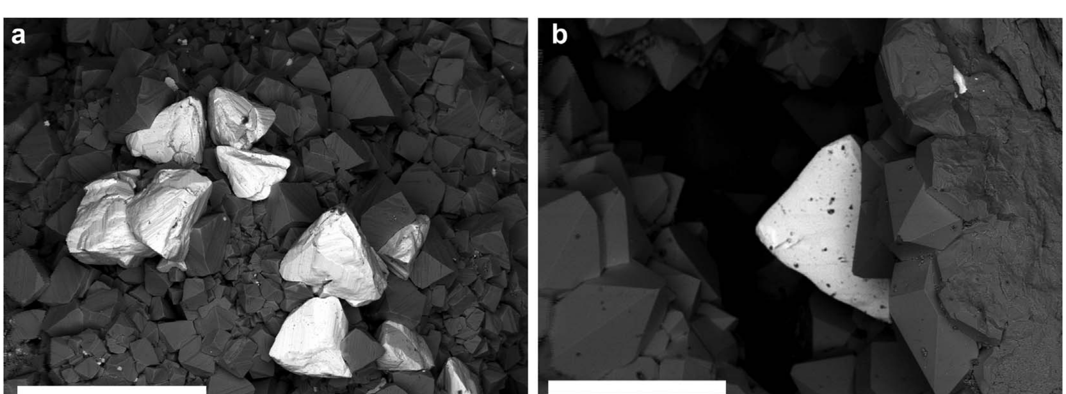

Fig. 2. SEM-BSE images showing typical morphology and associations for eastern Wisconsin chalcopyrite (bright phase). Scale bars are 1 mm. (a) Disphenoid-type crystals associated with euhedral dolomite and microscopic bravoite and pyrite in a crystal-lined vug from locality EW-3 (Luczaj et al., 2016, p. 14). (b) Chalcopyrite associated with quartz from near locality EW-2.