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Zn and Cu isotopic variability in the Alexandrinka volcanic-hosted massive sulphide (VHMS) ore deposit, Urals, Russia

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Abstract

Copper and Zn isotope ratios of well-characterized samples from three ore facies in the Devonian Alexandrinka volcanic-hosted massive sulphide (VHMS) deposit, southern Urals, were measured using multi collector ICP-MS (MC-ICP-MS) and show variations linked to depositional environment and mineralogy. The samples analysed derived from: a) hydrothermal–metasomatic vein stockwork, b) a hydrothermal vent chimney, and c) reworked clastic sulphides. As the deposit has not been significantly deformed or metamorphosed after its formation, it represents a pristine example of ancient seafloor mineralization. Variations in δ^{65}Cu (where $\delta^{65}Cu=[(^{65}Cu/^{63}Cu)_{sample}/(^{65}Cu/^{63}Cu)_{standard}-1]*1000$) and δ^{66}Zn (where $\delta^{66}Zn=[(^{66}Zn/^{64}Zn)_{sample}/(^{66}Zn/^{64}Zn)_{standard}-1]*1000$) of 0.63 and 0.66‰, respectively, are significantly greater than analytical uncertainty for both isotope ratios (± 0.07‰, 2σ). Very limited isotopic fractionation is observed in primary Cu minerals from the stockwork and chimney, whereas the Zn isotopic composition of the stockwork varies significantly with the mineralogy. Chalcopyrite-bearing samples from the stockwork have lighter δ^{66}Zn by ~0.4‰ relative to sphalerite dominated samples, which may be due to equilibrium partitioning of isotopically light Zn into chalcopyrite during its precipitation. δ^{66}Zn also showed significant variation in the chimney, with an enrichment in heavy isotopes toward the chimney rim of ~0.26‰, which may be caused by changing temperature (hence fractionation factor), or Raleigh distillation. Post-depositional seafloor oxidative dissolution and re-precipitation in the clastic sediments, possibly coupled with leaching, led to systematic negative shifts in Cu and Zn isotope compositions relative to the primary sulphides. Copper shows the most pronounced fractionation, consistent with the reduction of Cu(II) to Cu(I) during supergene mineralization. However, the restricted range in δ^{65}Cu is unlike modern sulphides at mid oceanic ridges where a large range of Cu isotope, of up to 3‰ has been observed [Rouxel, O., Fouquet, Y., Ludden, J.N., 2004. Copper isotope systematics of the Lucky Strike, Rainbow, and Logatchev sea-floor hydrothermal fields on

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1. Introduction

Since the advent of multiple collector inductively-coupled plasma mass spectrometry (MC-ICP-MS) it has become possible to study the isotope geochemistry of transition metals in natural systems. Precisions for Cu and Zn ratios are typically ±0.1‰ (2σ) or better for both Zn/Cu doping and sample standard bracketing techniques (Mason et al., 2004a,b). This has led to the discovery of significant isotope fractionation of these elements caused by various geochemical and biogeochemical processes (Johnson et al., 2004; Larson et al., 2003; Rouxel et al., 2004; Weiss et al., 2005; Zhu et al., 2002, 2000).

Owing to elevated metal contents and well-constrained formation conditions, ore deposits are particularly suitable for studies of isotope fractionation. Consequently, a number of preliminary investigations of hydrothermal and magmatic ore forming environments (marine and terrestrial alike) have been conducted and possible controlling mechanisms have been proposed. Most of this work has concentrated on Cu (Blix et al., 1957; Gale et al., 1999; Graham et al., 2004; Jiang et al., 2002; Larson et al., 2003; Maréchal et al., 1999; Rouxel et al., 2004; Shields et al., 1965; Zhu et al., 2000), which is expected to show more significant isotope variations due to the importance of redox-reactions, with very little information on the behaviour of Zn (Wilkinson et al., in press).

Published δ^{65}Cu data for primary Cu-rich minerals from terrestrial and marine hydrothermal deposits display a relatively narrow range from −1.06 to 1.41‰ with a mean value of 0.03‰ (relative to NIST-SRM 976 Cu) (Gale et al., 1999; Graham et al., 2004; Larson et al., 2003; Maréchal et al., 1999; Shields et al., 1965; Walker et al., 1958; Zhu et al., 2000). By contrast, supergene Cu minerals that formed during oxidation and weathering of primary sulphide ores yield a wide range of δ^{65}Cu values (from −8.4 to 9.1‰, including early TIMS data), with a general shift towards isotopically heavy compositions compared with inferred precursor minerals. For example, native Cu from the Michigan District (USA) defines a relatively narrow range of Cu isotopic compositions of c. 0.1‰ compared to secondary Cu-sulphides and arsenides from the same deposits that yield a range of c. 2‰ (Larson et al., 2003). Large isotopic variations for Cu have also been reported in a sediment-hosted hydrothermal vein-type deposit from Jinman, China (Jiang et al., 2002), with a range in δ^{65}Cu of −3.70 to 0.30‰. The most negative δ^{65}Cu values were from chalcopyrite precipitated at lower temperatures (c. 150 °C), while the most positive value represented a chalcopyrite from a high-temperature feeder vein (c. 286 °C), linking δ^{65}Cu to formation temperature. Graham et al. (2004) conducted the only study on igneous intrusions to date, using three intrusions that make up the Grasberg Igneous Complex. δ^{65}Cu showed a limited range from 0.02 to 1.34‰ and two dominant processes were put forward to explain the observed variation: (i) isotope fractionation during distillation from the underlying source and establishment of hydrothermal cells associated with each intrusion and (ii) isotope fractionation as the ore bearing fluid moved outward from a central core (Graham et al., 2004).

Copper isotope data from modern submarine hydrothermal vent systems support the link between shifts in δ^{65}Cu and secondary, low-temperature processes (Rouxel et al., 2004; Zhu et al., 2000). Chalcopyrite separates from active hydrothermal chimneys from the East Pacific Rise, Galapagos Ridge, and Broken Spur hydrothermal fields, yielded positive δ^{65}Cu values from 0.31 to 1.16‰, while inactive chimneys from the same sites were systematically lighter, with δ^{65}Cu values between −0.48 and −0.19‰ (Zhu et al., 2000). These variations possibly reflect selective leaching of ^{65}Cu from the source