

Zinc stable isotopes in seafloor hydrothermal vent fluids and chimneys

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Received 17 July 2007; received in revised form 6 December 2007; accepted 10 December 2007

Available online 23 December 2007

Editor: M.L. Delaney

Abstract

Many of the heaviest and lightest natural zinc (Zn) isotope ratios have been discovered in hydrothermal ore deposits. However, the processes responsible for fractionating Zn isotopes in hydrothermal systems are poorly understood. In order to better assess the total range of Zn isotopes in hydrothermal systems and to understand the factors which are responsible for this isotopic fractionation, we have measured Zn isotopes in seafloor hydrothermal fluids from numerous vents at 9–10°N and 21°N on the East Pacific Rise (EPR), the TAG hydrothermal field on the Mid-Atlantic Ridge, and in the Guaymas Basin. Fluid $\delta^{66}\text{Zn}$ values measured at these sites range from +0.00‰ to +1.04‰. Of the many physical and chemical parameters examined, only temperature was found to correlate with fluid $\delta^{66}\text{Zn}$ values. Lower temperature fluids (<250 °C) had both heavier and more variable $\delta^{66}\text{Zn}$ values compared to higher temperature fluids from the same hydrothermal fields. We suggest that subsurface cooling of hydrothermal fluids leads to precipitation of isotopically light sphalerite (Zn sulfide), and that this process is a primary cause of Zn isotope variation in hydrothermal fluids. Thermodynamic calculations carried out to determine saturation state of sphalerite in the vent fluids support this hypothesis with isotopically heaviest Zn found in fluids that were calculated to be saturated with respect to sphalerite. We have also measured Zn isotopes in chimney sulfides recovered from a high-temperature (383 °C) and a low-temperature (203 °C) vent at 9–10°N on the EPR and, in both cases, found that the $\delta^{66}\text{Zn}$ of chimney minerals was lighter or similar to the fluid $\delta^{66}\text{Zn}$. The first measurements of Zn isotopes in hydrothermal fluids have revealed large variations in hydrothermal fluid $\delta^{66}\text{Zn}$, and suggest that subsurface Zn sulfide precipitation is a primary factor in causing variations in fluid $\delta^{66}\text{Zn}$. By understanding how chemical processes that occur beneath the seafloor affect hydrothermal fluid $\delta^{66}\text{Zn}$, Zn isotopes may be used as a tracer for studying hydrothermal processes.

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Keywords: hydrothermal; trace metals; isotopic fractionation; Zn isotopes; sulfide

1. Introduction

With the advent of multi-collector inductively coupled plasma mass spectrometry (ICPMS), stable isotope variability of transition metals has been seen in many natural samples (Johnson et al., 2004; Anbar and Rouxel, 2007). Zinc (Zn)

isotopes have been studied in rocks (Maréchal et al., 2000; Chapman et al., 2006), marine sediments (Pichat et al., 2003), biological materials (Maréchal et al., 2000; Weiss et al., 2005), seawater (Bermin et al., 2006), and ore deposits (Mason et al., 2005; Wilkinson et al., 2005). Several metal and metalloid isotopes have been studied in active hydrothermal systems include iron (Fe) isotopes (Sharma et al., 2001; Rouxel et al., 2004b; Severmann et al., 2004), copper (Cu) isotopes (Zhu et al., 2000; Rouxel et al., 2004a), molybdenum (Mo) isotopes (McManus et al., 2002), selenium (Se) isotopes (Rouxel et al., 2004b), and antimony (Sb) isotopes (Rouxel et al., 2003). By

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studying the distribution of Zn isotopes in hydrothermal systems it is hoped that they can be also used as tracers of seafloor hydrothermal processes, helping us to better understand the plumbing and chemistry of hydrothermal vents.

Zn isotope measurements in ancient hydrothermal deposits have uncovered large variations in $\delta^{66}\text{Zn}$ values of sulfide minerals, including both the heaviest and lightest Zn isotope samples reported to date ($\delta^{66}\text{Zn} = -0.43\text{‰}$ and $\delta^{66}\text{Zn} = +1.33\text{‰}$) (Mason et al., 2005; Wilkinson et al., 2005). Thorough studies of Zn isotopes carried out in the Alexandrinka volcanic-hosted massive sulfide ore deposit in Urals, Russia (Mason et al., 2005) and the Irish Midlands ore field (Wilkinson et al., 2005) have related Zn isotopes to hydrothermal processes. The Alexandrinka ore deposit was formed as a seafloor hydrothermal system similar to modern systems studied here. Samples from the Alexandrinka deposit were analyzed from the hydrothermal-metasomatic stockwork believed to be the feeder zone to the hydrothermal deposit, a seafloor chimney, and some clastic sediments. $\delta^{66}\text{Zn}$ values from the deposit ranged from -0.43‰ to $+0.23\text{‰}$. A systematic increase in $\delta^{66}\text{Zn}$ values from the chimney core to the chimney rim was attributed to either a temperature dependence in the fractionation factor for precipitation or Rayleigh distillation as fluids diffuse through the chimney wall. Zn isotopes in the Irish Midlands ore field show a general trend of lighter Zn isotopes precipitated in the deep feeder veins and heavier Zn isotopes near the top of the hydrothermal system. Based on these data, Wilkinson et al. (2005) were the first to suggest that the precipitation of isotopically light Zn into Zn sulfides could influence the $\delta^{66}\text{Zn}$ of hydrothermal samples. Other studies have investigated Zn isotopes in sulfides from various ore deposits (Maréchal et al., 1999; Albarède, 2004) and in sulfides recovered from Archean shales (Archer and Vance, 2002).

While studies of extinct hydrothermal systems have suggested several processes that may fractionate Zn isotopes, it can be difficult to distinguish which of these effects are most important. It is hoped that the study of Zn isotopes at active vents will elucidate the processes that most influence hydrothermal $\delta^{66}\text{Zn}$ by allowing $\delta^{66}\text{Zn}$ to be directly related to the physical (i.e. temperature) and chemical properties that document subsurface hydrothermal processes. We have chosen samples from a wide range of hydrothermal vent sites in order to establish the range in hydrothermal fluid $\delta^{66}\text{Zn}$ values and to constrain the hydrothermal conditions under which Zn isotopes are fractionated. At two sites, we have investigated the Zn-isotope composition of hydrothermal fluids and Zn sulfide minerals from the same vent, providing further constraints on how sulfide precipitation may fractionate Zn isotopes in hydrothermal systems.

2. Geologic settings and sample description

Samples analyzed in this study were selected from several distinct geographic regions along basalt-hosted mid-ocean ridges, including from the fast-spreading, un-sedimented East-Pacific Rise (9–10°N and 21°N EPR), from the sedimented Gulf of California (Guaymas basin) and from the slow spreading Mid-Atlantic ridge (TAG Active Mound). The 9–10°N EPR site is

located in a well-studied segment of the EPR between the Cliperton and Siqueiros Fracture Zones (Haymon et al., 1991; Haymon et al., 1993; Fornari et al., 1998; Shank et al., 1998; Von Damm, 2000; Von Damm and Lilley, 2004; Von Damm, 2004). The vent fluid chemistry in the area has been well documented and previous studies have reported temporal evolution of the vent systems since 1991 in relation to magmatic events (Von Damm et al., 1997; Von Damm, 2004). Hence, hydrothermal vents at EPR 9–10°N provide a unique opportunity to study Zn-isotope systematics in one of the youngest hydrothermal systems. Bio9'' vent is located at 9°50' N within an area where dramatic changes in the hydrothermal systems have taken place. In 1991, Bio9 was the only high-temperature vent sampled in the Bio9 area. By 1994, Bio9' vent was another distinct black smoker. By 1999, the number of smokers around Bio9 had further increased, replacing some of the areas that had previously been characterized by diffuse flow. Bio9'' is the third distinct smoker in the Bio9 area and was initially sampled in 2002. K-vent at 9°30' N is the most southerly active vent, before encountering a zone of extinct vents (Von Damm, 2000). Fluids from K-vent discharge at a distinctly lower temperature than other vents in this area. Present temperatures are even lower than the temperature reported in 1991 (263 °C) (Von Damm, 2000). At K-vent, the entire active chimney was removed and the fluids were subsequently sampled from the remaining base of the chimney. The 21°N EPR site was among the first ridge-crest hydrothermal systems to be studied (Von Damm et al., 1985a). Three of the vent sites (Ocean Bottom Seismometer (OBS), South West (SW), and Hanging Gardens (HG)) were typical high-temperature black smokers and their chemical composition remained quite stable over the three years between 1979 and 1981 (Campbell et al., 1988). The fourth (National Geographic Society (NGS)) was a black smoker when originally sampled in 1979 but had become sealed off when revisited in 1981 and it emitted low-temperature white smoker fluids when broken open. The Guaymas basin in the Gulf of California is also located along the EPR, but in contrast to 9–10°N and 21°N EPR sites, it is covered by a thick layer of sediment through which hydrothermal fluids pass before venting on the seafloor. The TAG hydrothermal field lies on the more slowly spreading Mid-Atlantic Ridge. This site is distinguished by the large extent of subsurface remobilization of previously deposited Zn sulfide, which is evidenced by Zn-rich compositions of white smoker fluids and chimney sulfides compared to high-temperature black smokers (Tivey et al., 1995).

In addition to hydrothermal fluid samples, two hydrothermal deposits were studied at EPR 9–10°N and include: (1) Cu-rich chimneys (black smokers) from Bio9'', and (2) Zn- and Fe-rich chimneys and diffusers from K-vent. Reflected light microscopy was used for mineral identification and textural interpretations, description of each hydrothermal deposit types are presented in more detailed in a companion paper (Rouxel et al., in press).

Deposits characterized by abundant Cu-rich sulfide (i.e. chalcopyrite) and are typical of black smokers such as Bio9'' that formed at temperatures higher than 300 °C. The hydrothermal chimney recovered at Bio9'' has a wide trunk (~40 cm wide) that bifurcates into two orifices, one that was venting vigorously, and a second inactive one. Sample ALV-4057-M1 represents the

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