Mercury isotopic composition of hydrothermal systems in the Yellowstone Plateau volcanic field and Guaymas Basin sea-floor rift

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ABSTRACT

To characterize mercury (Hg) isotopes and isotopic fractionation in hydrothermal systems we analyzed fluid and precipitate samples from hot springs in the Yellowstone Plateau volcanic field and vent chimney samples from the Guaymas Basin sea-floor rift. These samples provide an initial indication of the variability in Hg isotopic composition among marine and continental hydrothermal systems that are controlled predominantly by mantle-derived magmas. Fluid samples from Ojo Caliente hot spring in Yellowstone range in δ^{202}Hg from −1.02‰ to 0.58‰ (±0.11‰, 2SD) and solid precipitate samples from Guaymas Basin range in δ^{202}Hg from −0.37‰ to −0.01‰ (±0.14‰, 2SD). Fluid samples from Ojo Caliente display mass-dependent fractionation (MDF) of Hg from the vent (δ^{202}Hg=0.10‰±0.11‰, 2SD) to the end of the outflow channel (δ^{202}Hg=0.58‰±0.11‰, 2SD) in conjunction with a decrease in Hg concentration from 46.6 pg/g to 20.0 pg/g. Although a small amount of Hg is lost from the fluids due to co-precipitation with siliceous sinter, we infer that the majority of the observed MDF and Hg loss from waters in Ojo Caliente is due to volatilization of $Hg^0_{(aq)}$ to $Hg^0_{(g)}$ and the preferential loss of Hg with a lower δ^{202}Hg value to the atmosphere. A small amount of mass-independent fractionation (MIF) was observed in all samples from Ojo Caliente (Δ^{199}Hg=0.13‰± 10.06‰, 2SD) but no significant MIF was measured in the sea-floor rift samples from Guaymas Basin. This study demonstrates that several different hydrothermal processes fractionate Hg isotopes and that Hg isotopes may be used to better understand these processes.

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1. Introduction

Mercury (Hg) is a redox-active metal with gaseous, aqueous, and solid forms in the environment. Mercury isotope variations have the potential to inform studies of global metal cycling, paleo-redox conditions, ore deposit formation, and environmental contamination (Smith et al., 2005, 2008; Bergquist and Blum, 2007; Kritee et al., 2007; Biswas et al., 2008; Gehrke et al., 2009). As a neurotoxic element, Hg poses serious threats to human health largely through the consumption of fish that bioaccumulate monomethylmercury (MeHg) (Clarkson and Magos, 2006). Anthropogenic activities such as fossil fuel combustion and natural processes such as volcanic activity and Hg evasion from geothermally enriched regions contribute Hg to the environment (Mason et al., 1994; Mason and Sheu, 2002; Pyle and Mather, 2003; Nacht et al., 2004; Engle et al., 2006; Gustin et al., 2008). However, because the biogeochemical cycling of Hg through different Earth reservoirs is complex, it is often difficult to directly link Hg sources to human and wildlife Hg exposure (Morel et al., 1998; Mason and Sheu, 2002; Gustin et al., 2008).

Several recent studies demonstrate that potential sources of Hg emissions may be isotopically distinct (Hintelmann and Lu, 2003; Smith et al., 2005, 2008; Bergquist and Blum, 2007; Biswas et al., 2008; Jackson et al., 2008). As a result, it may be possible to use Hg isotopes to trace Hg from a variety of sources into environmental reservoirs. Measurements of the isotopic composition of anthropogenic Hg emissions from some ore deposits and fossil fuels are now available (Smith et al., 2005, 2008; Biswas et al., 2008), but the Hg isotopic composition of natural volcanic emissions have only been reported from one volcano in Italy (Vulcano, Aeolian Islands) (Zambardi et al., 2008). Additionally, although recent investigations have measured Hg isotopes in crustal rocks and sediments (Hintelmann et al., 2008; Smith et al., 2008; Gehrke et al., 2009), very little work has been done to describe the Hg isotopic composition of mantle-derived materials. It is of fundamental importance to characterize mantle-derived Hg because mantle materials represent an important source of Hg to other Earth reservoirs.

Mantle-derived Hg can enter the surface environment in many tectonic settings including hot spots and oceanic spreading centers. In these regions, meteoric water and seawater percolates through crustal rocks and is conductively heated (Barnes and Seward, 1997; German and Von Damm, 2004). The hot fluid then leaches, concentrates, and

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transports Hg and other metals from the volcanic rocks (Varekamp and Buseck, 1984; Krupp, 1988; Smith et al., 2005). As the fluids move upward, the changing temperature and pressure conditions cause the solubility of Hg to decrease and Hg can precipitate in Hg minerals (e.g. cinnabar, HgS), in solid solution with sulfides, or as impurities in other minerals (Varekamp and Buseck, 1984; Krupp, 1988; Smith et al., 2005). Additionally, $Hg^0_{(aq)}$ in fluids can be volatilized to $Hg^0_{(g)}$ and subsequently lost to the atmosphere (Spycher and Reed, 1989; Engle et al., 2006). These processes produce economically viable Hg deposits, may cause the export of Hg to marine environments, and can result in substantial gaseous Hg emissions from geothermally enriched continental regions (Varekamp and Buseck, 1984; Stoffers et al., 1999; Zehner and Gustin, 2002; Kraepiel et al., 2003; Lamborg et al., 2006; Engle et al., 2006).

It is likely that some of the hydrothermal processes that lead to the formation of Hg-enriched deposits and Hg emissions cause isotope fractionation (Smith et al., 2005, 2008; Zheng et al., 2007). Because Hg has seven stable isotopes (196, 198, 199, 200, 201, 202, and 204) and active redox chemistry, it is fractionated during a wide variety of reactions (Smith et al., 2005; Foucher and Hintelmann, 2006; Bergquist and Blum, 2007; Kritee et al., 2007; Jackson et al., 2008). For example, Hg isotope fractionation has been observed in fossil hydrothermal systems due to the preferential vapor phase transport of isotopically light Hg (Smith et al., 2005) and in laboratory experiments during volatilization of $Hg^0_{(aq)}$ to $Hg^0_{(g)}$ (Zheng et al., 2007). However, minimal Hg isotope fractionation occurs during the hydrothermal leaching of Hg from source-rocks (Smith et al., 2008) and, by analogy to other heavy metals (Beard and Johnson, 2004; Johnson and Beard, 2005), we expect that magmatic processes such as partial melting and magma cooling should fractionate Hg to a lesser degree than lower temperature processes. We hypothesize that the Hg isotopic composition of hydrothermal fluids and precipitates is determined by the original composition of the mantle-derived materials and processes occurring in the hydrothermal systems. To date, no studies have measured Hg isotope fractionation in active hydrothermal systems to characterize the processes that affect the Hg isotopic composition of fluids, precipitates, and gaseous emissions.

For this initial investigation of Hg isotopes in modern hydrothermal systems we studied a large continental magmatic–hydrothermal system (Yellowstone Plateau volcanic field, Wyoming, U.S.A.) and a sea-floor rift magmatic–hydrothermal system (Guaymas Basin, East Pacific Rise, Gulf of California). Both regions are associated with shallow magma bodies that provide heat and a source of Hg to extensive and active hydrothermal systems (Eaton et al., 1975;
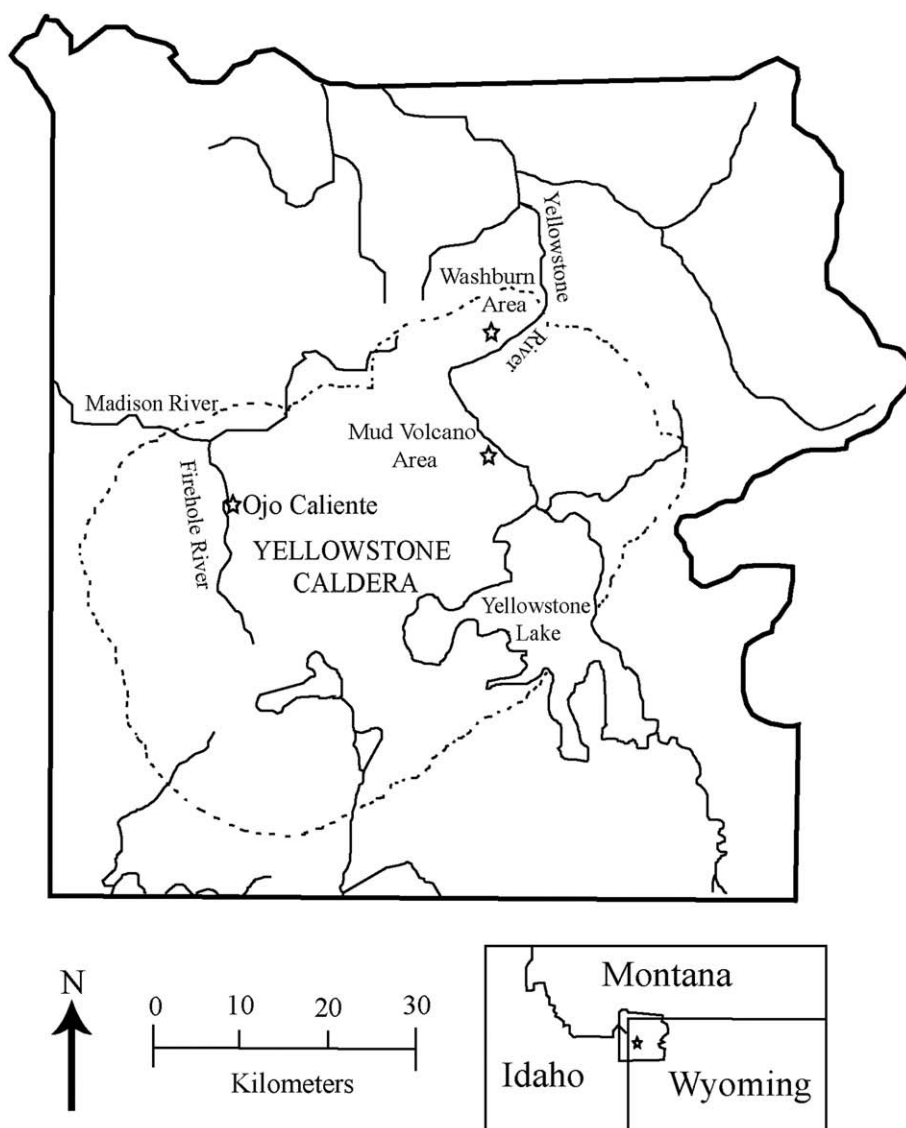

Fig. 1. Map of Yellowstone National Park boundary with the rim of the Yellowstone Caldera outlined and study areas indicated. Adapted from Ball et al. (1998), Xu et al. (1998), Christiansen (2001).