Mercury and Sulphur Isotope Compositions of Cinnabar and Stibnite Constrain the Source Rocks of a World-Class Hot Spring Mine District (Mt. Amiata, Italy)

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Abstract. The cinnabar (±stibnite) deposits of the Mt. Amiata geothermal system (Italy) and the associated hot springs and gas vents form a world-class hot spring ore district. Here, we combine 22 $\delta^{34}S$ ratios of cinnabar, marcasite, and stibnite with their $\delta^{202}Hg$ and $\Delta^{199}Hg$ ratios, as well as a Bayesian mixing model, to constrain the source rocks in this geological environment. Cinnabar shows a relatively large range of $\delta^{202}Hg$ (from -3.64 to +0.17‰) and $\Delta^{199}Hg$ (from -0.43 to +1.06‰), although samples from individual deposits show a much narrower $\delta^{202}Hg$ range. Most cinnabar, stibnite, and marcasite samples yielded $\delta^{34}S$ ratios between -0.9 and +5 ‰. We interpret these data as the products of mixing of dominantly magmatic, metamorphic, and marine sedimentary sources of Hg (Sb) and S. Although Rayleigh fractionation likely played a role at Mt. Amiata, it was not explicitly modelled in our study. A comparison between the Hg isotopic signatures of the Mt. Amiata and those of world-class *submarine* geothermal systems (Almadén, Spain; Idrija, Slovenia, with typically: $\delta^{202}Hg<2‰$; $\Delta^{199}Hg<0.3‰$) show significant differences. This indicates that the range of fractionation processes occurring in submarine and continental geothermal systems are substantially different.

1 Introduction

Geothermal systems are unique geological environments because the hydrothermal fluids used for energy production also forms base- and precious-metal deposits (Barnes and Seward 1997).

Mercury is a geothermal metal that was intensely exploited in the past but that is currently ranked by the WHO as a priority pollutant. This metal is an indicator of ore deposits in active geothermal systems and was mainly documented in the form of Hg sulfides (cinnabar – HgS – or metacinnabar) and native mercury (Barnes and Seward 1997). Such enrichment in hot springs is part of a crustal cycle that involves initial mobilization from source rocks, transport by hydrothermal fluids, and later dispersal into the lithosphere, hydrosphere, and atmosphere.

A key method used to quantify Hg sources and sinks in the crust is the determination of its isotopic compositions (Blum et al. 2014). Mercury (200.6 g/mol) comprises seven natural stable isotopes (^{196}Hg, $^{198-202}Hg$, ^{204}Hg) that display both mass-dependent and mass-independent fractionations (Blum et al. 2014). The most typical mass-dependent fractionation (MDF) is measured by even-mass-number isotopes and is defined as the ‰ deviation of the $^{202}Hg/^{198}Hg$ ratio relative to the NIST SRM 3133 Hg standard ($\delta^{202}Hg$). The less typical mass-independent fractionation (MIF) is generated by nuclear volume or magnetic isotope effects and causes photo-chemical reactions of Hg species in the environment. It is determined by odd-mass-number isotopes and is expressed as $\Delta^{199}Hg$. These types of fractionations are used to define biotic vs. abiotic Hg processes and can be used to distinguish pristine earth reservoirs from biogeochemical processes that cause Hg isotopic variability of natural samples.

Here, we present a dataset consisting of Hg and S isotopic compositions on an important Hg mine district of Europe, i.e. the hot-spring Hg(±Sb) district associated with the geothermal system of Mt. Amiata, Italy (Fig. 1). This mine district is a Hg reservoir of global importance because it produced in total c. 117,000 t of Hg (Segreto 1991) during an exploitation history that lasted for c. one and half centuries (from 1846 to 1982).

2 The Mt. Amiata geothermal system

This is a continental geothermal system that formed within the thick, E-NE-verging stack of nappes of the Northern Apennine thrust-and-fold belt (Gianelli et al. 1988). After the Miocene continental collision, the nappe stack started collapsing due to extension (Jolivet et al. 1998), during which a set of horst and graben structures formed.

A large geophysical dataset indicates that extension affected the Mt. Amiata area (e.g., Cassinis et al. 2005). This dataset was coupled with available petrological data of the magmatic rocks of the region and with drill hole data from geothermal exploration to build a comprehensive tectonic model of southern Tuscany and Mt. Amiata in particular (Marroni et al. 2015, and ref. therein). Based on this model, a volcanic-plutonic complex formed at Mt. Amiata, which affected the nappe stack and the Neogene sedimentary deposits. The pluton is probably located at a depth of 5-6 km, has a laccolithic shape, and was emplaced starting approximately in the Lower Pliocene. The volcano is made of trachydacitic to olivine-latitic lava flows and domes, which were emplaced between 305 and 231 ka. The basement rocks of Mt. Amiata (Palaeozoic to Middle Triassic Tuscan Metamorphic Complex) are a metasedimentary sequence of graphite-rich phyllite, greywacke, graphite-bearing marble, phyllite, and dolostone.

Figure 1. Schematic geological map of the Mt. Amiata geothermal system and distribution of its cinnabar-stibnite deposits, hot springs, and gas vents (mod. after: Calamai et al. 1970). The three largest deposits of the district are shown with larger letters. The inset shows the district location in south Tuscany.

The basement rocks do not outcrop in the study area (Fig. 1), but in the drilled locations they have a thickness exceeding 3000 m (Barelli et al. 2010). However, basement schist outcrop c. 40 km northwest of Mt. Amiata along the Farma river, where they occur as fine- to coarse grained greywacke containing graphite-rich phyllite (Farma Schists).

The caprocks of the geothermal system are the poorly permeable shale, marls, and siltstone deposited onto the Ligurian-Piemontese oceanic basin (Ligurian Units, Fig. 1), as well as the Neogene shallow marine and lacustrine deposits. Other rocks forming the geothermal system are the more permeable late Triassic-early Miocene sediments representing the cover of the Adria paleo-continental margin (Tuscan Units).

3 Materials and methods

Twenty-three cinnabar samples were selected for this work from museums and a private collection because the ore bodies are not accessible anymore for environmental and safety reasons. These samples were selected from the two largest mines of the district (Abbadia S. Salvatore and Solforate), a medium-sized mine (Morone), and five minor mines (Cortevecchia, Cerreto Piano, Monte Labbro, Bagnore, and Cornacchino). Samples from the mine called *Cerreto Piano* were also included in this study because of the historical relevance of this deposit although this was located outside the area of Fig. 1, c. 16 km southwest of the Catabbio mine. Two samples from a representative outcrop of the phyllites and quartzites of the Tuscan Metamorphic Complex (Farma Schists) were collected outside the study area, along the Farma river 40 km NW of Mt. Amiata.

All samples were individually screened with a binocular microscope, crushed manually in an agate mortar, and hand-picked to separate cinnabar, stibnite, and marcasite from the host rocks and gangue minerals. In most samples, two aliquots of these minerals were prepared to enable coupled measurements of Hg and S isotopes.

The Hg isotopes were measured at the University of Modena and Reggio Emilia using a multi-collector inductively coupled plasma-mass spectrometer equipped with a cold vapor generation and a desolvating apparatus as sample introduction system.

The Hg-MDF isotope ratios are expressed in ‰ by δ^{xxx}Hg:

$$\delta^{xxx}\mathrm{Hg}\ (‰) = [(^{xxx}\mathrm{Hg}/^{198}\mathrm{Hg}_{spl})/(^{xxx}\mathrm{Hg}/^{198}\mathrm{Hg}_{std}) - 1)] \times 1000$$

where ^{xxx} denotes the 199, 200, 201, or 202 isotopes (spl: sample; std: standard).

We use the conventional δ^{202}Hg to evaluate MDFs (Blum et al. 2014, and ref. therein). The Hg-MIF isotope ratios are reported with the Δ notation, which identifies the difference between the measured and predicted δ^{xxx}Hg, in ‰ units. The expression is:

$$\Delta^{xxx}\mathrm{Hg} = \delta^{xxx}\mathrm{Hg} - \delta^{202}\mathrm{Hg} \times \beta$$

where β is equal to 0.2520, 0.5024, and 0.7520 for Δ^{199}Hg, Δ^{200}Hg, and Δ^{201}Hg, respectively (Blum et al. 2014).

The S isotope ratios were determined at the Activation Laboratories Ltd. (Ontario, Canada) on 22 aliquots of cinnabar, stibnite, and marcasite samples. These aliquots were split from the same samples used for the Hg isotope measurements. Analyses were carried out with a Mat 253 Thermo Scientific isotope ratio mass spectrometer coupled with a Fisons Instruments element analyser.

A Bayesian mixing model was set up to estimate the proportions of Hg source rocks that have potentially generated the measured set of δ^{202}Hg and Δ^{199}Hg values in our samples. Bayesian mixing models are statistical determinations of quantitative apportionments of the likely sources that control a set of stable isotope data (Parnell et al. 2010). This model was implemented in the open-source R package called “Mixing models for Stable Isotope Analyses in R – MixSIAR” – Version 3.1.12 (Stock et al. 2018, and ref. therein) via the setup of a script. The five source rocks we considered for the model – and whose MDF and MIF were determined in previous studies – are *i*) the upper continental crust, *ii*) the primitive mantle, *iii*) the marine sediments, *iv*) the Mediterranean sapropel (Tian et al. 2023, and ref. therein), and *v*) a continental sediment composition that results from the combination of the Farma schists with the continental soils (Demers et al. 2013). These five model source rocks provide a range of geologically plausible Hg sources of Mt. Amiata, showing the largest possible variation of MDF and MIF. Notably, our Bayesian model takes explicitly into consideration photo-reduction processes, which are shown by the Δ^{199}Hg/Δ^{201}Hg ratio of the dataset and cause systematic changes in the pool of pristine δ^{202}Hg and Δ^{199}Hg source values.

4 Results

4.1 Hg and S isotopic compositions

The cinnabar samples show a δ^{202}Hg range between -3.64 and +0.17 ‰ and Δ^{199}Hg values between -0.43 and +1.06 ‰ (Fig. 2a), but samples from individual deposits show a much narrower δ^{202}Hg range. No systematic variations of δ^{202}Hg and Δ^{199}Hg are evident as a function of geographical location or depth within the ore bodies. Notably, 13 out of 23 samples belonging to Abbadia S. Salvatore, Solforate, Morone, Cerreto Piano, Cortevecchia, and Mt. Labbro have δ^{202}Hg ratios between -1.11 ‰ and +0.17 (Fig. 2a). These samples have Δ^{199}Hg values between -0.41 and +0.15‰. The 10 samples showing δ^{202}Hg values between -3.64 and -1.62 ‰ have Δ^{199}Hg between -0.35 and +1.06 ‰. The samples of the Palaeozoic Farma Schists (total Hg concentration: 229-327 μg/kg) have δ^{202}Hg ranging between -3.61 and -2.94 ‰ and Δ^{199}Hg between -0.45 and -0.03 ‰, respectively. Notably, all the studied cinnabar samples display a positive correlation between Δ^{199}Hg and Δ^{201}Hg in which the Δ^{199}Hg/Δ^{201}Hg is equal to c. 0.96.

Fourteen out of 22 cinnabar, stibnite, and marcasite samples (from Abbadia S. Salvatore, Morone, and Cortevecchia) have δ^{34}S ratios between -0.9 and +5 ‰ (Fig. 2b). The other samples show compositions that are either significantly enriched (Morone) or significantly depleted in ^{34}S (Cortevecchia, Cerreto Piano, Monte Labbro). The entire δ^{34}S interval varies between -12.8 and +11.6 ‰.

5 Discussion

5.1 Discriminating Hg and S sources

Mercury isotope compositions may discriminate source signatures combining Hg-MDF with the Hg-MIF. Closed-system, dynamic evaporation experiments conducted at atmospheric pressure and 0-22 °C showed that Rayleigh distillation causes a liquid-vapor $\alpha_{202/198}$ of 1.0067±0.0011 (Estrade et al. 2015). This fractionation would be sufficient to generate a condensed vapor phase with negative δ^{202}Hg ratios like those of Mt Amiata after only 30% of evaporation, while other processes like hydrothermal alteration would be less effective (Blum et al. 2014). However, there is evidence for MIF and heterogeneous Hg sources controlling the bulk isotopic compositions of cinnabar.

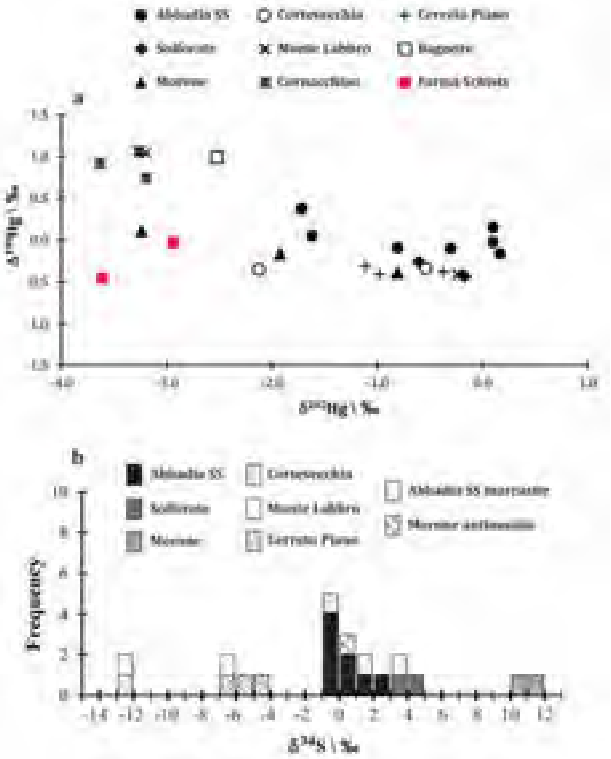

Figure 2. a. MIF (δ^{202}Hg) vs. MIF (Δ^{199}Hg) determined for the analysed samples of the Mt. Amiata geothermal system. **b.** Sulphur isotope ratios of cinnabar, marcasite and stibnite for the same aliquots of samples.

A heterogeneous source region is suggested by the δ^{202}Hg values of the Abbadia San Salvatore, Solforate, and Cerreto Piano samples and those of the Cornacchino and Bagnore samples (Fig. 2a). These data tend to cluster around specific values, which suggests the existence of inherently distinct Hg sources rather than by hydrothermal fractionation.

The Δ^{199}Hg values from Abbadia S. Salvatore, Morone, Solforate, Cortevecchia, and Cerreto Piano range between -0.43 and +0.37 ‰, while those from Cornacchino and Bagnore are between 0.75 and 1.06‰. As previous works have documented the MIF signature in sediments from marine and continental deposits (e.g., Meng et al. 2019), we suggest that the positive MIF signature preserved by the Cornacchino and Bagnore samples reflects inheritance from the marine sedimentary sequences of the Tuscan and Ligurian nappes. In contrast, the Δ^{199}Hg of -0.43 to -0.31‰ displayed by the cinnabar from Cortevecchia and Cerreto Piano indicates an inherited signature from marine or continental source rocks rich in organic matter that are abundant within the Tuscan Metamorphic Complex and of which the Farma Schists are a representative lithology. The Farma Schists show a negative MIF (Δ^{199}Hg between -0.45 and -0.03‰), a δ^{202}Hg as low as -3.61‰, and THg concentrations (229-327 mg/kg) that are at least one order of magnitude higher than those of the upper continental crust (Tian et al. 2023). This implies that the lithologies making the Tuscan Metamorphic Complex may represent significant source rocks of Hg of the geothermal system, and that several ore deposits inherited to some degree its signature. Finally, the Δ^{199}Hg of <0.30‰ for most samples from Abbadia S. Salvatore and Solforate and the corresponding δ^{202}Hg ranging between -1.62 and +0.17 ‰ are consistent with a provenance from the primitive mantle or from the upper continental crust (Tian et al. 2023).

The Bayesian mixing model shows that that the primitive mantle might have provided >50% of the Hg in the mine district, whereas marine sapropel and continental crust might have a cumulative contribution of c. 30%. Sensitivity analysis shows that these results are not affected by uncertainties of the fractionation factors. However, they should be considered with caution because they do not include the potentially large effect of Rayleigh fractionation.

Finally, a heterogeneous S source is indicated by the δ^{34}S range of cinnabar, stibnite, and marcasite from Mt. Amiata. A typical mantle or magmatic signature (Ohmoto and Goldhaber 1997) is indicated by the δ^{34}S ratios between -0.9 and +3.5 obtained on cinnabar, stibnite, and marcasite from Abbadia San Salvatore. In contrast, the negative δ^{34}S values for cinnabar from Cortevecchia (-12.8 ‰), Monte Labbro (-12.5 to -6.9 ‰), and Cerreto Piano (-6.8 to -4.65 ‰) suggest that a proportion of S derived from sediments rich in organic matter.

5.2 Metallogenic implications

Mt. Amiata is a world-class continental geothermal system in which heterogeneous source rocks (mantle and caprocks of continental and marine derivation), as well as Rayleigh hydrothermal fractionation, were functional to determining the ranges of Hg and S isotopic compositions of cinnabar and other sulphides. These signatures differ strikingly from those of the other world-class, submarine geothermal systems (Almadén and Idrija), which typically show δ^{202}Hg<2‰ and Δ^{199}Hg<0.3‰. This indicates that Hg cycling in geothermal systems occurs differently in continental and submarine environments.

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