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Variability of Fe isotope compositions of hydrothermal sulfides and oxidation products at mid-ocean ridges

Xiaohu Li [a,*], Jianqiang Wang [a], Fengyou Chu [a], Hao Wang [a], Zhenggang Li [a], Xing Yu [a], Dongwei Bi [a], Yongsheng He [b]

[a] *SOA Key Laboratory of Submarine Geosciences, Second Institute of Oceanography, State Oceanic Administration, Hangzhou 310012, China*
[b] *State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Beijing 100083, China*

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ABSTRACT

Significant Fe isotopic fractionation occurs during the precipitation and oxidative weathering of modern seafloor hydrothermal sulfides, which has an important impact on the cycling of Fe isotopes in the ocean. This study reports the Fe-isotope compositions of whole-rock sulfides and single-mineral pyrite collected from hydrothermal fields at the South Mid-Atlantic Ridge (SMAR) and the East Pacific Rise (EPR) and discusses the impacts of precipitation and late-stage oxidative weathering of sulfide minerals on Fe isotopic fractionation. The results show large variation in the Fe-isotope compositions of the sulfides from the different hydrothermal fields on the mid-oceanic ridges, indicating that relatively significant isotope fractionation occurs during the sulfide precipitation and oxidative weathering processes. The Fe-isotope compositions of the sulfides from the study area at the SMAR vary across a relatively small range, with an average value of 0.01‰. This Fe-isotope composition is similar to the Fe-isotope composition of mid-oceanic ridge basalt, which suggests that Fe was mainly leached from basalt. In contrast, the Fe-isotope composition of the sulfides from the study area at the EPR are significantly enriched in light Fe isotopes (average value −1.63‰), mainly due to the kinetic fractionation during the rapid precipitation process of hydrothermal sulfide. In addition, the pyrite from different hydrothermal fields is enriched in light Fe isotopes, which is consistent with the phenomenon in which light Fe isotopes are preferentially enriched during the precipitation of pyrite. The red oxides have the heaviest Fe-isotope compositions (up to 0.80‰), indicating that heavy Fe isotopes are preferentially enriched in the oxidation product during the late-stage oxidation process. The data obtained from this study and previous studies show a significant difference between the Fe-isotope compositions of the sulfides from the SMAR and EPR. The relatively heavy Fe isotopes compositions of the sulfides from the SMAR may suggest the equilibrium fractionation process under high temperature conditions. The red Fe oxides are enriched in heavy Fe isotopes, indicating that the oxidative weathering processes result in the occurrence of significant Fe-isotope fractionation and the preferential enrichment of heavy Fe isotopes in the oxidation product.

1. Introduction

With the rapid development of the multicollector-inductively coupled plasma mass spectrometry (MC-ICPMS) analysis technique in recent years, the accuracy of Fe-isotope measurements has been dramatically improved. The accuracy of using MC-ICPMS to analyze Fe isotopes is generally <0.1‰ (2sd) (Kehm et al., 2003; Malinovsky et al., 2003; Weyer and Schwieters, 2003; Schoenberg and von Blanckenburg, 2005). Consequently, Fe isotopes have been widely used for investigating various geological processes in earth systems (Anbar et al., 2000; Zhu et al., 2000; Rouxel et al., 2004, 2005, 2008; Teng et al., 2008, 2011; Planavsky et al., 2009; Planavsky et al., 2012; Conway and John, 2014, 2015). Previously, the variations in the Fe-isotope compositions of hydrothermal vent fluids and hydrothermal sulfides in the modern seafloor mid-ocean ridge have been studied (Sharma et al., 2001; Beard et al., 2003; Rouxel et al., 2004, 2008; Bennett et al., 2009). The variations of the Fe-isotope compositions of hydrothermal fluids range from −1.79‰ to +0.14‰ (average δ^{56}Fe = −0.59 ± 0.39‰; n = 87). Compared with hydrothermal fluids, hydrothermal sulfides are enriched in lighter Fe isotopes. The variations of the Fe-isotope compositions of hydrothermal sulfides range from −2.14‰ to +0.35‰ (average δ^{56}Fe = −0.84 ± 0.61‰; n = 92). The differences in the Fe-isotope compositions of the hydrothermal fluids are mainly related to the vent temperature (Rouxel et al., 2004), physical and chemical properties of the fluid (pH, Eh, etc., Severmann et al., 2004) and chemical composition of the fluid (Sharma et al., 2001). In comparison, the Fe-isotope compositions of hydrothermal sulfides are mainly related to mineral

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* Corresponding author.
E-mail address: xhli@sio.org.cn (X. Li).

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precipitation and late-stage metasomatism and recrystallization processes (Polyakov et al., 2007; Polyakov and Mineev, 2000; Polyakov and Soultanov, 2011).

Hydrothermal sulfide precipitation is generally the main factor that leads to Fe-isotope fractionation during the hydrothermal fluid cycling. However, experimental studies have shown that the late-stage oxidative weathering processes of sulfide minerals also result in significant Fe-isotope fractionation (Fernandez and Borrok, 2009; Rouxel et al., 2003). Under oxidative conditions, Fe(II) can be easily oxidized to Fe(III) at pH 5, forming Fe-hydroxides and Fe-oxides through precipitation. The newly formed minerals are preferentially enriched in heavy Fe isotopes (Fernandez and Borrok, 2009). A study of Fe isotopes in the Gaosong polymetallic sulfide ore in Gejiu, Yunan province (Chen et al., 2014), shows that primary sulfides with a relatively low oxidation level were enriched in light Fe isotopes and that the heavy Fe-isotope composition increased as the oxidation level increased. Currently, few studies of the Fe-isotope compositions of seafloor hydrothermal sulfides have been conducted. The only existing reports regarding the Fe-isotope compositions of seafloor hydrothermal sulfides are for the hydrothermal field at the East Pacific Rise (EPR) 9–10°N and for some individual hydrothermal fields at the North Mid-Atlantic Ridge (NMAR). Even less knowledge is available regarding the variations of the Fe-isotope compositions of sulfides during the late-stage oxidative weathering process. This study reports the Fe-isotope compositions of different types of sulfides from the hydrothermal fields at the South Mid-Atlantic Ridge (SMAR) and EPR to determine whether a significant difference in the Fe-isotope compositions of hydrothermal sulfides from the different hydrothermal fields at the mid-ocean ridge exists and the influences of the late-stage oxidative weathering process of hydrothermal sulfides on the Fe-isotope composition.

2. Samples and analysis methods

2.1. Sample descriptions

Majority of samples were collected from the EPR during the Chinese DY115–20 cruise in 2008 and the SMAR during the Chinese DY125–26 cruise in 2012. Sample location and description are shown in Fig. 1 and Table 1. The three massive sulfide samples (samples EPR1 to EPR3) obtained from the hydrothermal field at the EPR were mainly rich in Zn, with Zn contents of up to 17.8 wt%. The five massive sulfide samples (samples SMAR1 to SMAR5) obtained from the hydrothermal field at the SMAR were divided into three different types: Cu-rich type (with a Cu content of 3.5 wt%), Zn-rich type (with a Zn content of 18.2 wt%), and Fe-rich type. Four pyrite mineral grain samples were separated from the sulfides which were collected from the EPR (sample EPR-S4-TVG1), Central Indian Ridge (sample CIR-S19-TVG9) and Southwest Indian Ridge (samples SWIR-S23-TVG14 and SWIR-S33-TVG15) during the Chinese DY115–20 cruise in 2008. The micro-observation shows that the massive sulfide samples are dominated by pyrite with little chalcopyrite and sphalerite. In addition, one red muddy oxidative sample (sample NMAR-1) obtained from the hydrothermal field at the 26°N at the NMAR were subjected to Fe-isotope composition analysis.

2.2. Analysis methods

The samples were crushed and finely ground in an agate mortar. Copper, Zn contents of the sulfide samples were determined by complete digestion of powder by ICP-MS analysis, and S isotopic composition measured using a MAT 253 Stable Isotope Ratio Mass Spectrometer coupled to a Costech ECS 4010 Elemental Analyzer at the ALS Minerals in Guangzhou.$\delta^{34}S$ values were calculated by normalizing the $^{34}S/^{32}S$ ratios in the sample to that in the Vienna Canyon Diablo Troilite (VCDT) international standard, values are reported using the delta (δ) notation in units of permil (‰) and are reproducible to 0.2‰.

Fe-isotope analysis was performed using MC-ICPMS at the State Key Laboratory of Isotope Geochemistry at the China University of Geosciences (Beijing). Fe was purified in HCl media using AG1X-8 (an anion resin). The base elements (Cu, Pb, Zn, etc.) were removed using 16 mL of 6 mol/L HCl. Fe was eluted from the anion resin using 10 mL of 0.4 mol/L HCl and then collected. This process was repeated once to ensure that the base elements were completely removed. The final eluted Fe was acidified and stored in 200 μL of concentrated HNO_3. Next, the samples were dissolved in 3% HNO_3 and analyzed using MC-ICPMS. The detailed sample treatment processes and analyses methods have been discussed in the literature (He et al., 2014).

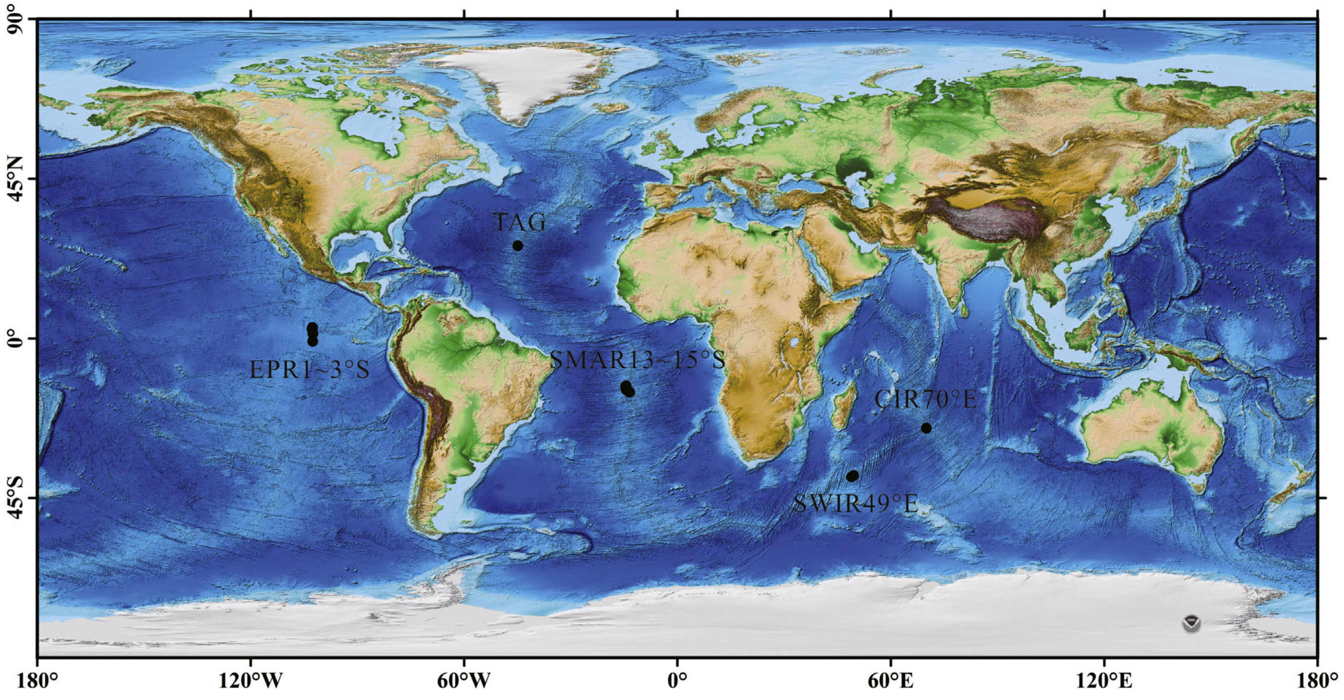

Fig. 1. Map showing sampling sites of the hydrothermal sulfides analyzed in this study.

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