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Doctor Thesis

Sulfur cycling in Ediacaran and early Cambrian periods reconstructed from quadruple sulfur isotope analysis and culture experiment of sulfate reducing bacteria

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Abstract

Sulfur isotopic compositions of the sulfates and the sulfides in marine sediments are a proxy of the oxidation state of the earth's surface. The sulfur isotope fractionation between seawater sulfate and sedimentary sulfides exceeds 50‰ in Phanerozoic marine sediments. However, in laboratory, the culture experiments of sulfate reducing bacteria generally yield smaller fractionation. The discrepancy between the experiments and natural systems may be explained by the onset of oxidative sulfur cycling through sulfur disproportionation at around Ediacaran-Cambrian boundary, though several studies on multiple sulfur isotopes suggested oxidative sulfur cycling have already started in Mesoproterozoic. In order to clarify the reason why the sulfur isotope fractionation increased at the terminal Proterozoic, it is also important to study the factors controlling the sulfur isotope fractionation by sulfate reducers.

To solve the problem, culturing experiment of sulfate reducing bacteria were conducted, particularly focusing on the relation between cell's growth phase and the sulfur isotope fractionation. The experimental results show that the fractionation during the cell's maintenance phase is larger than that of the exponential phase. In particular, the calculated fractionation by *Desulfovibrio desulfuricans*, one of the most typical sulfate reducer, exceeded 50‰ during maintenance growth phase, when glucose was used as an electron donor without iron source for the growth. These results imply that the maintenance metabolism may play a major role for controlling the overall sulfur isotopic ratio of sulfide in nature.

On the other hand, detailed quadruple sulfur isotope analysis was conducted using drill core samples of an Ediacaran-Cambrian boundary section in South China ranging from 635 Ma to ca. 510 Ma. A newly-developed extraction method was applied to extract carbonate associated sulfate and sulfides for constructing multiple sulfur isotope chemostratigraphy. The results indicate that the sulfide $\delta^{34}S$ values mainly reflect the degree of isotope fractionation between sulfate and sulfide. We identified the two negative $\delta^{34}S_{sulfide}$ excursion when the fractionation increase, and found that the $\delta^{34}S_{sulfide}$ profile is clearly correlated with carbon and strontium isotope profile. Based on the correlation, we conclude that the observed $\delta^{34}S_{sulfide}$ fluctuation reflects increase of oceanic sulfate reservoir due to enhancement of oxidative weathering of continental materials, particularly at the time of global $\delta^{13}C_{carbonate}$ excursion known as Shur あ m excursion event.

Table of contents

3. Sulfur isotopic fractionation in maintenance metabolism of sulfate reducing bacteria when glucose is used as electron donor

4. Ediacaran sulfur cycling reconstructed from an isotopic analysis of pyrite and carbonate associated sulfate

1. Overview

1-1. Sulfur isotope fractionation and Earth’s surface redox

Sulfur isotopic compositions of sedimentary sulfide and sulfate show us the evolution of the earth surface condition throughout the earth history. The large sulfur isotope fractionation between marine barite and sulfide included in the barite shows us sulfate reducing microbes existed 3.47-Gyr ago (Shen et al., 2001). The oxidation of earth surface is important for the evolution of organisms especially for the evolution of multicellular organisms. Sulfate is the second largest anion constitute of the present oceanic water next to the chloride ions. Since the sulfate containing oxygen, the evolution of the oceanic sulfate concentration shows us the oxygenation history of the earth surface. The maximum sulfur isotope fractionation between seawater sulfate and contemporaneous sedimentary sulfides denotes sulfur isotope fractionation from biological sulfur cycle. Through the Phanerozoic, the maximum sulfur isotope fractionation between seawater sulfate and contemporaneous sedimentary sulfides are about 55‰ and the Phanerozoic pattern of sulfur isotopic composition of sedimentary sulfide persists into 0.64 Ga (Canfield and Teske, 1996; Fig. 1-1). Canfield and Teske (1996) suggested the increase of atmospheric oxygen level over 10% PAL caused oxidative sulfur cycle, and the large sulfur isotope fractionation indicate the increase of the atmospheric oxygen. However, some recent studies show the oxidative sulfur cycle is not necessary to increase the sulfur isotope fractionation (Sim et al., 2011; Leavitt et al., 2013). In addition to the increase of the sulfur isotope fractionation during microbial process, the periodic average sulfur isotopic composition change drastically near 0.64 Ga. The average isotopic composition of sulfide increase through 700 to 636 Ma, and start decreasing after the increase in the Cryogenian age (Fig. 1-1). The decrease of the average isotopic composition of sulfide suggests the increase of the precipitation of sedimentary sulfate, and that indicates the increase of the oceanic sulfate concentration. Revealing the sulfur cycle including the oceanic sulfate concentration around the 0.64 Ga is important because the period coincident with the age of animal evolution. Some studies suggest the elevated sulfate concentration at the period from the data of fluid inclusions in halite deposits (Brennan et al., 2004). On the other hand, some studies suggest sustained low sulfate concentration from the d$^{34}S_{CAS}$ values with high stratigraphic variability (Loyd et al., 2012). To reveal the sulfur cycle through Ediacaran to early Cambrian we carried out two kinds of experiments.

1-2. Sulfur isotope fractionation by sulfate reducing bacteria during maintenance metabolism

One approach we applied is culturing experiments of sulfate reducing bacteria and studied the mechanism of increasing sulfur isotope fractionation during microbial sulfate reduction. We studied the sulfur isotope fractionation during microbial sulfate reduction when cells are in their maintenance metabolism to reproduce the metabolism of the cells in natural environments.

A lot of culturing experiments of sulfate reducing bacteria to study sulfur isotope fractionation during microbial sulfate reduction have carried out since 1950s (Harrison and Thode, 1958; Kemp and Thode,1968; Chambers et al., 1975; Bottcher et al., 1999; Canfield, 2001; Habicht et al., 2002; Habicht et al., 2005; Canfield et al., 2006; Hoek et al., 2006; Johnston et al., 2007a; Sim et al., 2011a; Sim et al., 2011b; Leavitt et al., 2013). Recently maximum 65.6‰ of sulfur isotope fractionations by pure culture experiment are reported (Sim et al., 2011). Hence, large sulfur isotope fractionation between seawater sulfate and sedimentary sulfide exceeding 47‰ cannot simply be attributed to the oxidative sulfur cycle. Although sulfur isotope fractionation during microbial sulfate reduction came out to exceed 47‰, the mechanism to increase the sulfur isotope fractionation is still ambiguous. The only two things that clearly affect the fractionation are sulfate concentration and cell specific sulfate reduction rate. The fractionation becomes less than 6‰ when sulfate concentration is less than 200 μM, and sulfur isotope fractionation during microbial sulfate reduction is known to have negative correlation with cell specific sulfate reduction rate (Harrison and Thode, 1958; Sim et al., 2011b; Leavitt et al., 2013). Previous culture experiments of sulfate reducing bacteria focused on the sulfur isotope fractionation during the exponential phase of cell growth to study the relation between the fractionation and cell specific sulfate reduction rate. The cell specific sulfate reduction rates of the previous culture experiments are

7×10^{-1} to 5×10^{2} fmol/cell/day (Hoek et al., 2006; Sim et al., 2011b). However, cell specific sulfate reduction rates in natural environment are estimated as 4×10^{-7} to 9×10^{-3} fmol/cell/day in deep sea sediments, and 8×10^{-3} to 8×10^{-2} fmol/cell/day in coastal sediments (D'Hondt et al., 2002; Sahm et al., 1999). The quantity and quality of organic carbon delivery to the zone of sulfate reduction most often dictates sulfate reduction rates where sulfate is abundant (Leavitt et al., 2013), and cells in natural environment probably not grow exponentially because of the limitation of organic carbon delivery. Hence, culturing experiments of sulfate reducing bacteria were carried out in section 2 to reconstruct sulfur isotope fractionation in natural environment by studying sulfur isotope fractionation in maintenance metabolism. *Desulfovibrio desulfuricans* (DSM642) for culture strain and lactate as electron donor were selected to compare previous culturing experiments (Harrison and Thode, 1958; Canfield et al., 2006). *D. desulfuricans* is a type species of *Desulfovibrio* genus, and complete genome sequences of the *D. desulfuricans* are available (Field et al., 2008).

In addition we carried out batch culture experiments of *D desulfuricans* (DSM642) using glucose as electron donor in section 3. Sim et al. (2011a) reported cell specific sulfate reduction rate in exponential phase became 0.7 fmol/cell/day when glucose was used as electron donor in batch culture experiment of DMSS-1. The cell specific sulfate reduction rate is much slower than the cell specific sulfate reduction rate when lactate is used as electron donor. Sulfur isotope fractionation during sulfate reduction of DMSS-1 is larger in early exponential phase than later exponential phase, and the data of sulfur isotope fractionation in maintenance phase are lacking (Sim et al., 2011a,b). The aim of section 3 is to study sulfur isotope fractionation during microbial sulfate reduction of *D desulfuricans* using glucose as electron donor and sulfur isotope fractionation during maintenance metabolism.

1-3. Sulfur cycle from Ediacaran to early Cambrian

The second approach is the analysis of the sulfur isotopic composition of sedimentary sulfate and sulfide from the Ediacaran to early Cambrian. The interval from the Ediacaran to Cambrian is one of the most important times for the evolution of life, because the most ancient metabolically active biota appeared in the Ediacaran period and all documented animal phyla appeared in the Cambrian period. If the oxidation of Earth’s surface led to the evolution of complex and metabolically active life, than atmospheric oxygen levels must have increased over this interval of time. Ediacaran to Cambrian strata are widespread in South China. These strata contain many fossils of Ediacaran to Cambrian age. Analyzing the sulfur isotopic composition of sulfate and sulfide in these strata enables the study of the relationship between the oxidation of the surface Earth and the evolution of life.

We undertook drilling through the PC/C boundary in South China, where there is a complete sequence from the Neoproterozoic to Cambrian with abundant fossils allowing for detailed biostratigraphy. The drill-sampling allowed us to minimize the effects of secondary alteration and oxidation on the sample surfaces and to make a densely populated chemostratigraphic column at the millimeter scale. Indeed, measurements of $\delta^{13}C$, $\delta^{18}O$, $\delta^{15}N$, $^{87}Sr/^{86}Sr$, $^{88}Sr/^{86}Sr$, and molecular fossils have already been reported (Ishikawa et al., 2008; Sawaki et al., 2008; Sawaki et al., 2010; Ishikawa et al., 2013; Kikumoto et al., 2013; Tahata et al., 2013; Yamada et al., 2013; Ishikawa et al., 2014). The aim of this study is elucidate the relation between increasing sulfur isotope fractionations and the oxidation of the surface of the Earth by constructing the sulfur isotope record from the Ediacaran to early Cambrian. The ultimate goal of this study is to elucidate the relationship between the evolution of life and oxidation of the surface of the Earth.

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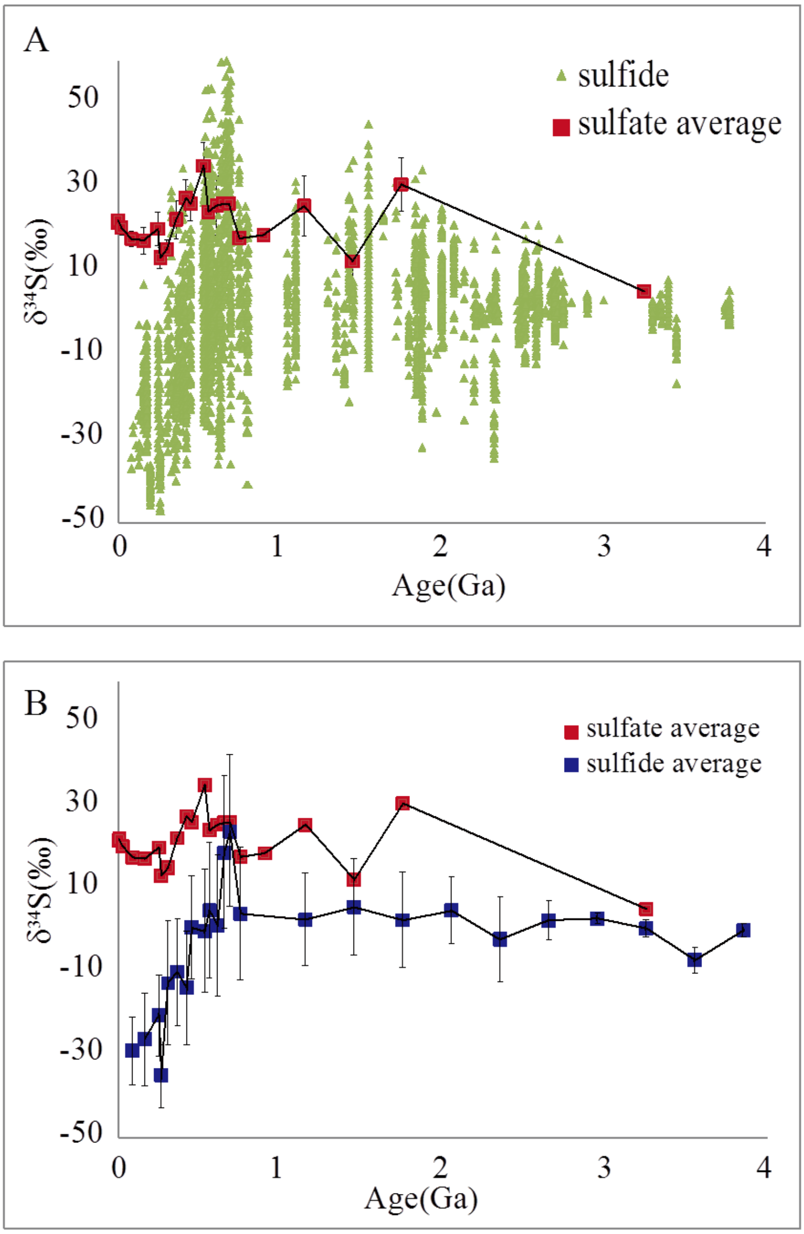

Fig. 1-1 A: Sulfur isotopic composition of sedimentary sulfide and the periodic average of seawater sulfate. Data and age classification are from Canfield and Farquhar (2009). Through the Phanerozoic, the data has been binned from individual Periods, and in the Precambrian, the data were binned in the time intervals: 542-580 Ma, 580-636 Ma, 636-660 Ma, 660-700 Ma, 750-805 Ma, 805-1000 Ma, and into 300 Ma bins hereafter. Only sulfides probable biological origin are included in this figure and isotopic

composition of sulfate are determined from evaporitic sulfate minerals. The line represents the 3 points moving average of the averaged values. B: Periodic average of sulfur isotopic composition of sedimentary sulfide and seawater sulfate.