

Experimental study of S-MIF by SO₂ photolysis under CO atmosphere

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Sulfur mass independent fractionation (S-MIF) of Archean sediment is regarded as a proxy of the atmosphere at that time. S-MIF is produced by photolysis of SO₂ in oxygen-free environment. However, the elementary reaction and the mechanisms of fractionation in the atmosphere are not fully understood. We present here a newly developed experimental setup to reveal the atmospheric photochemistry observed in the geological record. The photochemical system consists of a D₂ light-source, two gas chambers attached to a monochromator and a UV detector designed to operate with no interference of atmospheric air. Here we present the first round of experiments of SO₂ photolysis conducted under SO₂ at low partial pressure (<5 Pa) and high amount of CO. The purpose of this experiment is to test a different experimental conditions from previously reported results where the environment of high pressure SO₂ is oxidative and optically thick, which may be significantly different from Archean atmosphere. Thus, our experiment condition hinders these problems. Additionally, this setting allow us to test the hypothesis that reducing atmosphere with a large amount of CO produces an stable amount of OCS [1]. In order to cut-off the large emission band of the deuterium lamp at 168 nm the chamber previous to the photochemical chamber was filled with CO₂. Analysis of reactions products confirms the production of OCS under CO atmosphere. The product OCS shows clear MIF signature. We calculated fractionation factors of SO₂ photolysis (185-220 nm) and also the chemistry associated with SO₂ photoexcitation (250-320 nm) as an additional source of MIF. We discuss a source of MIF involving not only SO₂ photodissociation but also the chemistry associated to the photoexcited SO₂* species in relation to the MIF signal measured on the geological record.

[1] Ueno *et al.* (2009) *PNAS* **106**, 14784-14789.

Barite precipitation in submarine hydrothermal vents: Insights from Sr-isotope ratios

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At submarine hydrothermal vents, barite precipitates within vent chimney walls as hot hydrothermal fluid comes into contact and mixes with cold seawater. The formation of barite is dependent upon temperature and the availability of Ba²⁺ and SO₄²⁻, from the hydrothermal fluid and local seawater, respectively. Fluid temperatures and ion availability are both intimately linked to the source fluids with respect to their amounts and degree of mixing. Thus, barite precipitation records the physical and chemical conditions of fluid mixing within the porous chimney walls. Here, we use ⁸⁷Sr/⁸⁶Sr values recorded in barite from hydrothermal vents along the intermediate-rate spreading Endeavour Segment of the Juan de Fuca Ridge, along with detailed petrography and electron microprobe analysis, in order to investigate the conditions of barite precipitation and fluid interactions within chimney walls.

The ⁸⁷Sr/⁸⁶Sr ratio in seawater differs from the ⁸⁷Sr/⁸⁶Sr ratio in hydrothermal fluid, making it possible to use the ⁸⁷Sr/⁸⁶Sr ratio in barite as a measure of the relative amount of local mixing between seawater and the hydrothermal fluids. The ⁸⁷Sr/⁸⁶Sr isotope ratios in a suite of 16 hydrothermal barite samples from the Endeavour Segment have been measured. The results demonstrate a broad scale of mixing, with the percent hydrothermal fluid component ranging from 25% to 90%. This variation in relative mixing suggests that barite can form under a variety of conditions. Petrographic examination of barite crystals show that barite in chimney walls can precipitate as a variety of different crystal habits, from dendritic to acicular and blocky. Variations in the relative amount of mixing are linked to barite crystal morphologies, providing further insights into the controls of ion availability on barite precipitation.

Electron microprobe analysis of barite crystals from the Endeavour vents reveals well-defined zones, characterized by varying Sr-concentrations within individual crystals. Two possible mechanisms for the formation of these zones are: 1) The relative contributions of seawater and hydrothermal fluid changes during the formation of the barite crystals; 2) The concentration of strontium in the seawater-fluid mixture changes as the crystals form. LA-MC-ICP-MS is used to determine the ⁸⁷Sr/⁸⁶Sr ratios of individual zones within the crystals, in order to evaluate the relative importance of these two processes.

The relationships between fluid mixing, barite crystal morphology, Sr content and ⁸⁷Sr/⁸⁶Sr ratios provide insights into the degree of conductive cooling relative to fluid mixing and into temporal variations in fluid chemistry as a control on mineral precipitation within vent chimney walls at Endeavour.