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Spatially resolved capture of hydrogen sulfide from the water column and sedimentary pore waters for abundance and stable isotopic analysis

D.A. Fike[a,*], J.L. Houghton[a,*], S.E. Moore[a], W.P. Gilhooly III[b], K.S. Dawson[c], G.K. Druschel[b], J.P. Amend[d], V.J. Orphan[c]

[a] Dept. of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130, USA
[b] Dept. of Earth Sciences, Indiana University-Purdue University Indianapolis, Indianapolis, IN 46202, USA
[c] Div. of Geological & Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA
[d] Depts. of Earth Sciences and Biological Sciences, University of Southern California, Los Angeles, CA 90089, USA

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ABSTRACT

Sulfur cycling is ubiquitous in sedimentary environments, where it plays a major role in mediating carbon remineralization and impacts both local and global redox budgets. Microbial sulfur cycling is dominated by metabolic activity that either produces (e.g., sulfate reduction, disproportionation) or consumes (sulfide oxidation) hydrogen sulfide (H_2S). As such, improved constraints on the production, distribution, and consumption of H_2S in the natural environment will increase our understanding of microbial sulfur cycling. These different microbial sulfur metabolisms are additionally associated with particular stable isotopic fractionations. Coupling measurements of the isotopic composition of the sulfide with its distribution can provide additional information about environmental conditions and microbial ecology. Here we investigate the kinetics of sulfide capture on photographic films as a way to document the spatial distribution of sulfide in complex natural environments as well as for in situ capture of H_2S for subsequent stable isotopic analysis. Laboratory experiments and timed field deployments demonstrate the ability to infer ambient sulfide abundances from the yield of sulfide on the films. This captured sulfide preserves the isotopic composition of the ambient sulfide, offset to slightly lower $\delta^{34}S$ values by $\sim 1.2 \pm 0.5$‰ associated with the diffusion of sulfide into the film and subsequent reaction with silver to form Ag_2S precipitates. The resulting data enable the exploration of cm-scale lateral heterogeneity that complement most geochemical profiles using traditional techniques in natural environments. Because these films can easily be deployed over a large spatial area, they are also ideal for real-time assessment of the spatial and temporal dynamics of a site during initial reconnaissance and for integration over long timescales to capture ephemeral processes.

1. Introduction

The biogeochemical sulfur cycle encompasses the aggregate metabolic activity of various microbial pathways (e.g., sulfate reduction, disproportionation, and sulfide oxidation) together with a suite of abiotic reactions (Fike et al., 2015). The sulfur cycle is intimately connected to the global carbon cycle, and thereby climate, through the remineralization of organic carbon. Sulfate reduction in marine sediments is thought to be responsible for the majority of organic matter respiration in many marine sediments (Jørgensen, 1982). The vast majority (> 90%) of the resulting sulfide formed from sulfate reduction in modern marine sediments is typically reoxidized back to sulfate (Jørgensen, 1977) – or intermediate valence sulfur species after interaction, e.g., with iron oxides (Flynn et al., 2014; Hansel et al., 2015). This network of biotic and abiotic reactions can result in spatially heterogeneous sulfur cycling characterized by strong gradients within microbial sediments over spatial scales as small as a few μm (Fike et al., 2008). Recent work has investigated this micro-scale variability by trapping ambient hydrogen sulfide within microbial mats and aggregates on metallic silver disks (Fike et al., 2008, 2009) or wires (Wilbanks et al., 2014), followed by high-resolution analysis using secondary ion mass spectrometry (SIMS). While this approach has provided new insights into small-scale biogeochemical gradients and ecological organization in these environments, it is fundamentally limited by the small size of samples that can be analyzed by SIMS and is difficult to correlate with geochemical and sedimentary data that are often collected over much larger (cm to m-scale) intervals.

Here we investigate the use of photographic film as an alternative

* Corresponding author at: 1 Brookings Dr., CB1169, Washington University, St. Louis, MO 63130, USA.
E-mail addresses: dfike@levee.wustl.edu (D.A. Fike), jhoughton@levee.wustl.edu (J.L. Houghton).

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sulfide capture approach that will integrate micro- and mesoscale observations. In taking this approach, we follow the work of others who have sought to use a variety of silver-based approaches to capture environmental sulfide. For example, Pal et al. (1986) used glass tubes filled with a gelatin-silver nitrate mixture to capture gaseous H_2S, as insoluble Ag_2S. Horwell et al. (2004) noted that photographic film, essentially a resin impregnated with silver halide (bromide, iodide or chloride) crystals on an organic backing (e.g., cellulose acetate), should work in a similar manner. Following this, photographic films were used to successfully capture atmospheric (gaseous) H_2S at and around volcanic sites (Horwell et al., 2004, 2005). Like H_2S sensors recently developed (Yin et al., 2017), large-format (e.g., dm-sized) photographic films can be used to visually document in the field the presence of hydrogen sulfide and the spatial variability in its abundance (Gilhooly et al., 2014). In addition to the large format, this film-based approach is beneficial because it is inexpensive and easy to deploy, which allows for the capture of multiple, independent snapshots of dynamic systems, and can accumulate signal over long timescales (up to 24 h) to capture ephemeral processes. These characteristics are particularly important when investigating complex environmental systems with no a priori knowledge of the scales of their spatial and temporal variability.

The captured sulfide can be analyzed to determine its abundance and isotopic composition. In the case of atmospheric capture, it is possible to quantify the resulting sulfide abundance photometrically (Horwell et al., 2004, 2005). In aqueous settings, however, it is not possible to reliably use photometric approaches to assess sulfide abundance because of secondary reactions of silver with halides in solution and/or sunlight, both of which can discolor the films. Instead, abundance must be quantified in the laboratory, for example, by extraction of the captured sulfide as acid-volatile sulfide (AVS) (Kaplan and Hulston, 1966). After deployment and retrieval, the films can be sectioned in the laboratory into mm- or cm-scale strips and subsequent chemical extraction can quantify sulfide concentrations. Moreover, the resulting sulfide can be purified as Ag_2S for isotopic analysis using traditional isotope ratio mass spectrometry (IRMS) (Fike et al., 2006). Here, we document the kinetics of sulfide uptake onto photographic films and demonstrate the reliability of these films for estimating ambient sulfide concentrations and preserving the sulfur isotopic signature of aqueous sulfide in laboratory experiments. The utility of this approach is then highlighted in a variety of natural settings.

2. Methods

2.1. Experimental design

Black and white film sheets (Ilford Delta 100 Professional) were used in this study. ISO 100 films have the finest grained silver particles and therefore should have the highest rates for chemical sulfide capture and also react the most slowly to ambient sunlight during field deployments. For laboratory experiments, film pieces of 1 cm × 9 cm were cut in the dark and then soaked in MQ water until all water-soluble dye was removed (~10 min for first soak, ~2 min for second soak), rinsed, and dried overnight. Experiments were conducted under anoxic conditions in replicate glass Balch tubes (~26 mL) sealed with butyl rubber stoppers and sacrificed sequentially at each time step. Balch tubes were covered in foil to prevent reaction with light. Each tube contained a strip of film of known mass and 3 borosilicate beads (6 mm diameter) to ensure well-mixed solutions during experiments. Each Balch tube was then filled most of the way with anoxic water (either de-ionized or an artificial seawater solution) with a small headspace to allow the stopper to be put in place. Any remaining headspace and bubbles were removed through a vent needle prior to adding sulfide by displacement with anoxic water stock solution via a small syringe. The de-ionized water or seawater used in each experiment was made anoxic just prior to setting up the tubes by the addition of 2 mL/L of reductant (1 M ascorbic acid in 2 M sodium hydroxide). This concentration of reductant (2 mM) was sufficient to reduce the dissolved oxygen in the water and any oxygen from air in the headspace of the Balch tube during assembly. Synthetic seawater was prepared with 25 g/L NaCl, 1.2 g/L $MgCl_2{\cdot}6H_2O$, 0.2 g/L NH_4Cl, 0.4 g/L $CaCl_2{\cdot}2H_2O$, 0.2 g/L $NaHCO_3$ in DI water. For experiments at pH < 11, the reduced water was also acidified with HCl so that subsequent addition of the sulfide stock solution (pH 11) resulted in the desired pH.

The concentrated sodium sulfide stock solution was made fresh for each experiment in a 100 mL gas-tight glass syringe (Hamilton, USA) in anoxic de-ionized water. A large crystal of $Na_2S{*}9H_2O$ was rinsed in anoxic water to remove any oxidized surface coating, dried, and weighed to obtain the concentration of the stock needed for the planned experimental conditions. Using a syringe adapter, 0.9 mL of sulfide stock solution was transferred to a 1 mL gas-tight glass syringe (Hamilton, USA), which was then fitted with a needle. This volume of sulfide was injected quickly through the stopper into the Balch tube, allowing the displaced solution from the tube to exit through a vent needle with a syringe attached. The displaced solution was then discarded and the initial expected concentration in each tube calculated accounting for this dilution. Tubes were agitated with mixing beads to homogenize the solution during the experiments. Although this method creates slight differences between replicate tubes due to differences in volume displaced, we found it maintained the anoxic conditions required to achieve mass balance at each time step. The exposure time for the film in each tube is reported as the time between the injection of sulfide solution and the removal of the film. For each set of experiments, four control tubes, which contained the same initial sulfide concentration but no film, were also assembled. Two controls were sacrificed at the initial time and two at the final time to measure any pH change and assess potential degassing and/or oxidation reactions by comparing the measured sulfide concentration to the expected value.

The procedure for sacrificing each tube depended on the expected concentration of sulfide in solution. For solutions < 1 mM sulfide, a 1 mL aliquot was taken and immediately fixed in Cline reagent for sulfide concentration determination (see Method below). To facilitate this initial sampling in zero headspace gas-tight tubes, a 1 mL syringe was flushed and filled with He, which was then injected into the Balch tube, creating slight overpressure and making it easier to pull the sample. Immediately following the removal of this sample, the remaining solution in the Balch tube was fixed with 0.5 mL of 1 M zinc acetate solution buffered in 1 M acetic acid to prevent sulfide degassing and/or oxidation. The zinc acetate was allowed to completely react with sulfide for 5 min before removing the septum. Films were removed from the solution, any ZnS on its surfaces was rinsed off with de-ionized water into glass serum bottles, along with the remaining solution, and the films were allowed to dry overnight before being processed further.

For experiments conducted at sulfide concentrations higher than 1 mM, the solutions needed to be diluted prior to analysis by the Cline (1969) methylene blue method. In these experiments, the sampling procedure at each time was modified by fixing the entire volume in the Balch tube with 0.5 mL of 1 M zinc acetate, capturing the excess volume in a syringe attached to a vent needle. After 5 min, the entire volume, including the excess in the syringe, was then transferred to a serum bottle. Films were separated from the solution and then rinsed into the serum bottle as usual before drying them overnight. The fixed solutions were diluted into a range appropriate for sulfide concentration analysis (see below). In this modified procedure, the extra volume added during rinsing was included in the dilution factor applied to correct the Cline measurement.

2.2. Oxidized sulfur compounds

Experiments were conducted under oxic conditions to test film reactivity with alternate sulfur compounds in solution: sulfite ($NaHSO_3$, BDH), thiosulfate ($Na_2S_2O_3{\cdot}5H_2O$, Alfa Aesar), tetrathionate ($K_2S_4O_6$, Aldrich), elemental sulfur, and L-cysteine (97% pure, Aldrich).