Photographic film-based capture of the spatial and temporal heterogeneity in aqueous $\delta^{34}S_{H2S}$

J. L. HOUGHTON*, S. MOORE, C. JONES, D.A. FIKE

Department of Earth & Planetary Sciences, Washington University, St. Louis, MO, 63130 USA;
*correspondence: jhoughton@wustl.edu;
s.moore@wustl.edu; clivejones@wustl.edu; dfike@wustl.edu

The ability to easily deploy, subsample and analyze photographic film makes it an ideal tool for capturing the spatial and temporal variability of hydrogen sulfide (H_2S) in complex natural environments. Using bulk extractions, we can resolve variability in sulfide $\delta^{34}S$ in exposed films in areas as small as 1.5 cm^2; using secondary ion mass spectrometry (SIMS), $\delta^{34}S_{H2S}$ can be analyzed over distances as small as 100 μm. The captured sulfide is depleted in ^{34}S relative to the sulfide in solution by 1.5‰, a fractionation that is independent of salinity, pH and sulfide concentration in solution.

Isotopic analysis using SIMS produces reproducible values ($2\sigma < 0.7$ ‰; n = 8) that match the bulk $\delta^{34}S$ for a wide range of sulfide abundance (8-55 μmol S/ g film) using a 35 μm raster (3nA Cs^+, FC detectors). The calibration of $\delta^{34}S$ using SIMS is not sensitive to variable Cl concentration, indicating minimal matrix effects from halides within the film during this analysis. However, due to the gradual diffusion/capture process within the film during exposure to sulfide, a correction must be applied to account for the variable S counts with depth. The minimum sulfide abundance that can be reliably analyzed with the FC method is ~8 μmol S/ g film. For abundances below this threshold, the analytical conditions need to be modified to a 50 μm raster (200pA Cs+, EM detector). Sulfide images can also be produced as large as 100 μm x 100 μm using the EM method for films that display either high $\delta^{34}S$ heterogeneity in the bulk analysis or a patchy/speckled appearance on the surface of the film related to shifts in flux and subsurface microbial activity, capturing evidence of diurnal shifts in the microbial sulfur cycle.