

Sulfur cycling in shallow-sea hydrothermal vents, Milos Greece

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Milos is a volcanic island positioned along the Southern Aegean Volcanic Arc. Shallow-sea (5 m) hydrothermal venting is extensive throughout our study area, Paleochori Bay. Pore fluids exhibit elevated temperatures (115°C), acidic conditions (pH 5), dissolved sulfide (3 mM), and either dilute or elevated chloride (1.5x Mediterranean seawater). The shallow hydrothermal vents offered an ideal opportunity to target microbial processes that presumably transition from sulfide delivered with volcanic gases to sulfide produced by dissimilatory sulfate reduction in background sediments. Seafloor vent features include large (> 1 m²) white biofilms containing elemental sulfur and orange/yellow patches of arsenic-sulfides. We investigated three patches of colored seafloor, a non-vent area as a control site, and a brine. Pore waters, push-cores, surface films, and water column samples were collected by SCUBA from seafloor patches and background sediments. One goal of the study was to measure $\delta^{34}\text{S}$ spatial variability along environmental gradients that included volcanic vents and 'normal' ocean bottom.

We observed strong geochemical spatial patterns across each patch of colored seafloor. Temperature profiles within the upper 20 cm of the sediments ranged 35 to 111°C. Pore water sulfate concentrations (ranging 8 to 25 mM) and $\delta^{34}\text{S}$ values (ranging +17.5‰ to +21.4‰), show a clear decrease toward the center of each hydrothermal feature that coincided with maximum measured temperatures. We interpret the inverse relationship between temperature and sulfate $\delta^{34}\text{S}$ as a mixing process between oxic seawater and anoxic magmatic inputs. To better constrain this relationship, we collected endmember samples of seawater and vent gas sulfide. The $\delta^{34}\text{S}$ values of pore water sulfate extracted from low temperature (< 60°C) sediments along the fringe of the patches were identical to seawater ($\delta^{34}\text{S} = +21\text{‰}$). In contrast, hydrogen sulfide in the free gas sampled from all study sites had uniform values, $\delta^{34}\text{S} = +2.5 \pm 0.28\text{‰}$ (n = 4) that were nearly identical to pore water sulfide, $\delta^{34}\text{S} = +2.7 \pm 0.36\text{‰}$ (n = 21). The relationship between the isotopic composition of dissolved sulfur species suggests the oxidation of dissolved sulfide by the entrainment of oxic seawater potentially mixed an isotopically light pool of secondary sulfate with the ambient pore water sulfate pool. An isotopic mass balance model demonstrates that the data plot along a conservative mixing array between seawater and a chloride rich, sulfidic fluid. Any biological sulfur cycling potentially operating within these hydrothermal systems is masked by abiotic chemical reactions.

INTERPRETING THE TRACE METAL RECORDS OF ANCIENT EPEIRIC SEAWAYS: LESSONS FROM THE TOARCIAN (JURASSIC) BLACK SHALES OF EUROPE

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There is an ongoing discussion concerning the global-versus-local origins of trace metal records expressed in sedimentary successions from ancient epicontinental (epeiric) seaways. Properly deciphering these records is of considerable importance because they factor prominently in our understanding of the redox history of the Earth surface environment. Particularly useful and contentious examples of this debate are the black shales deposited in the north European epicontinental seaway (NEES) during the Toarcian Stage of the Early Jurassic. Despite the fact that these marine shales are extremely rich in organic matter and sedimentary sulfides, some show little to no enrichment beyond crustal abundances of many redox-sensitive elements (e.g., Cu, Mo, Ni, V, Zn, U). As these organic-rich rocks have been linked to an interval of widespread marine anoxia/euxinia — the Toarcian Oceanic Anoxic Event (T-OAE) — the muted enrichments have consequently been purported to reflect diminished global seawater inventories of these elements. Conversely, some workers attribute the lack of trace metal enrichment to restriction of the seaway from the open ocean.

In this study, we present a variety of geochemical data from various locations in the northern Europe to explore the character of the Toarcian trace metal record. High-resolution stratigraphic iron and sulfur redox proxy data from within the seaway (Fe/Al, Fe_{HR}/Fe_{total}, Fe_{py}/Fe_{HR}, $\delta^{34}\text{S}_{\text{pyrite}}$) reveal variable redox conditions and also suggest hydrographic restriction of the seaway, both of which likely played roles in the trace metal depletions. Furthermore, the trace metals records show higher enrichments at locations more proximal to the open ocean, also pointing to restriction within the NEES. However, all the study localities record a temporal pattern of subdued metal enrichment and rates of metal accumulation, which together suggest a global marine depletion during the OAE. Perhaps not surprisingly, therefore, ancient trace metal records of organic-rich rocks contain both global and local features, which can be deciphered through careful integration of parallel geochemical and sedimentological data.