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Walter S. Borowski
Eastern Kentucky University, w.borowski@eku.edu

Namcy M. Rodriguez
Shell

Charles K. Paull
MBARI

William Ussler III
MBARI

Enrichments of heavy sulfur (^{34}S) in sulfide minerals: Gas hydrates, methane delivery, and anaerobic methane oxidation

Walter S. Borowski[1*], Nancy M. Rodriguez[2], Charles K. Paull[3], and William Ussler III[3]

[1]Eastern Kentucky University, Richmond, KY 40475-3102
(*Correspondence: w.borowski@eku.edu)

[2]Shell, Houston TX 77079

[3]MBARI, Moss Landing, CA 95039-0628

The sulfur isotopic composition of authigenic, sedimentary sulfide minerals is largely controlled by sulfate reduction and related processes within sedimentary environments. Histograms show that that $\delta^{34}S$ values of sulfide minerals forming in depositional and diagenetic environments are most often negative ($\delta^{34}S < 0‰$ CDT) reflecting the original isotopic composition of seawater sulfate (now ~21‰), microbially-mediated fractionations of ~-8 to -40‰ (α = 1.029-1.059) during sulfate reduction, and more extreme fractionations caused by sulfur disproportionation. Enrichments of heavy sulfur ($\delta^{34}S > 0‰$) in sulfide minerals represent about 18% of measured $\delta^{34}S$ values worldwide and reflect certain diagenetic conditions. Excluding seafloor seepage sites, most (59%) heavy sulfur enrichments are associated with anaerobic methane oxidation (AMO or AOM) occurring at the sulfate-methane interface (SMI or SMTZ).

Blake Ridge (offshore southeastern USA) sediments associated with methane gas hydrates experience higher rates of upward methane diffusion than sediments in similar depositional environments not coincident with hydrate occurrences. Methane delivery to the SMI fuels AMO and results in $\delta^{34}S$ values within sulfide minerals of up to +23.6‰. $\delta^{34}S$ values in the sulfate reduction zone are negative (-46.6 to –8.4‰) but become more positive approaching the SMI where maximum enrichments of heavy sulfur in interstitial sulfate and authigenic sulfide minerals generally occur. ^{34}S enrichments below the SMI most likely reflect positions of earlier SMIs. Heavy ^{34}S values seen in the sedimentary record with appropriate depositional and diagenetic settings may indicate the presence of ancient gas hydrate deposits, larger amounts of upward methane flux, and AMO as an important sulfate-depletion mechanism. Such ^{34}S enrichments are not diagnostic but should be distinguished by their depositional settings and differing diagenetic signals.

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