Methane flux fingerprint on the bulk and in-situ sulfur isotope systematics of pyrite

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Sulfate-driven anaerobic oxidation of methane (SD-AOM) is a ubiquitous process in marine sedimentary environments, significantly influencing the redox conditions of the oceans both in present settings and throughout Earth's geological history. Pyrite, a key byproduct of SD-AOM, has sulfur isotopic compositions ($\delta^{34}S_{py}$) that are widely utilized as tracers of the SD-AOM process. However, previous case studies were unable to systematically evaluate the impact of methane flux and sedimentary environment on $\delta^{34}S_{py}$. Here, we developed a 1D model of reaction and transport of sulfur, carbon and iron compounds during sediment diagenesis and explored the relationship between methane flux and $\delta^{34}S_{py}$. Simulation results show that under high methane flux environments, $\delta^{34}S_{py}$ do not exceed the $\delta^{34}S$ value of seawater sulfate ($\delta^{34}S_{SW}$ = +21.2‰), and under low methane flux, $\delta^{34}S_{py}$ will exceed $\delta^{34}S_{SW}$.

To verify the model conclusions, we utilized nanoscale secondary ion mass spectrometry (Nano-SIMS) to analyze the $\delta^{34}S$ values of authigenic pyrite from two sediment cores (ROV05, DS17) on the northern continental slope of the South China Sea. This analysis was supplemented by measurements of the $\delta^{34}S$ values and content of bulk pyrite, the morphology of handpicked pyrite aggregates, and the concentration and sulfur isotopic composition of porewater sulfate ($\delta^{34}S_{SO4}$) and sulfide ($\delta^{34}S_{H2S}$). Additionally, we quantified total carbon, total organic carbon, total nitrogen, and total sulfur contents. Our calculations of methane flux indicate that core ROV05 (1.26 mol/m2/yr) exhibits a higher methane flux compared to core DS17 (0.08 mol/m2/yr). In core ROV05, the bulk $\delta^{34}S_{py}$ values, Nano-SIMS $\delta^{34}S_{py}$ values, and $\delta^{34}S_{H2S}$ values are all lower than $\delta^{34}S_{SW}$. In contrast, core DS17 displays bulk $\delta^{34}S_{py}$ values ranging from -45.1‰ to +41.2‰, with $\delta^{34}S_{SW}$ value exceeded in the methane sulfate transition zone (SMTZ). Furthermore, Nano-SIMS analysis reveals that the $\delta^{34}S_{py}$ values can surpass $\delta^{34}S_{SW}$ value in both current- and paleo-SMTZs.

This study elucidates the compositional characteristics of $\delta^{34}S_{py}$ under varying methane flux conditions, emphasizes the role of sulfate diffusion in porewater on $\delta^{34}S_{py}$ during early diagenesis, and provides a foundation for tracing past methane fluxes.