Goldschmidt 2024 Abstract
https://doi.org/10.46427/gold2024.23186

Modeling the in-situ sulfur isotope fractionation with various sulfate profiles on the continental slope

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Current dataset of sulfur isotope fractionation factors in marine sediments is collected from mixed sources: (1) The ranges observed in pure culture under different environmental conditions, (2) the observed differences between the sulfate and sulfide (solutes or pyrite), and (3) the fractionation factor by Rayleigh model under the assumption of closed system instead of the reactive transport modeling (RTM), which do not always work in natural settings because of the low metabolic rates in the seabed compared to the pure culture and the effect of the physical processes. Only scarce in-situ studies used RTM to predict the fractionation and got values close to the thermodynamic equilibrium in the seabed similar to the laboratory work. However, they are mainly at the organoclastic sulfate reduction (OSR)-dominated sites with steady-state geochemical profiles. For the anaerobic methane oxidation (AOM) in natural environments, the fractionation factor is considered lower than OSR simply based on laboratory results and lacks in-situ model verification. Here, we emphasize the difference of term net fractionation factor in the natural environments compared to other datasets and discuss this parameter in the natural settings with various sulfate reduction processes, especially AOM-dominated. We determined the fractionation factor using reactive transport modeling at four sites with different shapes of porewater sulfate and its sulfur isotope profiles along the northern continental slope of the South China Sea. These sites are in the methane-diffusion areas, which are widespread along continental margins. Except for H71 in the Xisha Trough, the sulfate reduction at all sites is AOM-dominated. A steady-state model modeled geochemical profiles at CL44 (Qiongdongnan Basin) and H71. The other two sites, CL11 (Dongsha Area) and W19-15 (Shenhu Area) were modeled by a transient model. The results show that the fractionations are always close to the theoretical equilibrium isotope fractionations ($^{34}\varepsilon \approx 70‰$). This study further verifies the equilibrium value is widely shared across environments, also indicates an overall low metabolic rate in natural environments no matter for the microbes involved in OSR or sulfate-driven AOM, and contributes to a more accurate interpretation of the sulfur isotopic rock records.