

Triple sulfur isotope relationship during sulfate reduction via anaerobic oxidation of methane

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Sulfate-driven anaerobic oxidation of methane (SD-AOM) plays a critical role in regulating global methane budget. Diagnostic isotope fractionation factor $^{34}\alpha$ and triple isotope exponent $^{33}\theta$ ($=\ln^{33}\alpha/\ln^{34}\alpha$) for SD-AOM can help to identify and quantify SD-AOM activities and the rates of microbial sulfate reduction in nature. Past Earth surface redox history can also be examined through the measurement of multiple sulfur isotope compositions in sedimentary records. Due to difficulties in culturing anaerobic methanotrophs or sampling of pore-water sulfate in methane-excess environments, however, the $^{34}\alpha$ and $^{33}\theta$ values for the process of SD-AOM have not been constrained. We propose that a set of modern cold-seep associated barite samples with a consistently low $\Delta\delta^{18}\text{O}/\Delta\delta^{34}\text{S}$ value have recorded residual pore-water sulfate during SD-AOM, and the multiple sulfur isotope composition of these barites can be used to deduce the $^{33}\theta$ values. We applied a 1-D diagenetic reaction-transport model to fit a set of $\Delta^{33}\text{S}$ and $\delta^{34}\text{S}$ values of modern cold seep barite collected from multiple sites from Gulf of Mexico. Based on the obtained negative correlation ($R^2=0.75$) between $\Delta^{33}\text{S}$ and $\delta^{34}\text{S}$ values, we calculated a $^{33}\theta$ value ranging from 0.5100 to 0.5112 (± 0.0005) given a $^{34}\alpha$ value of 0.97 to 0.99, an expected range for SD-AOM processes according to independent studies. This $^{33}\theta$ value is lower than that of the typical organoclastic sulfate reduction processes in marine environments where the isotope fractionation is usually larger than that of the SD-AOM processes. In addition, only seep barite data display a negative $\Delta^{33}\text{S}-\delta^{34}\text{S}$ correlation whereas pore-water sulfates from all non-methane settings show positive correlations. The negative $\Delta^{33}\text{S}-\delta^{34}\text{S}$ trend of instantaneous H_2S in methane-excess environment can be archived in pyrite as a diagnostic isotope signature for AOM, if the iron is rich enough comparing to the generated H_2S . These diagnostic parameters and correlation will allow us to identify the occurrence of SD-AOM in methane-excess environment in geological records.