Diagenetic transformation of barite to pyrite: clues from in situ S isotopes in Devonian Marcellus Shale

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Devonian Marcellus Shale drill core from Beaver Meadows, NY, shows ellipsoid-shaped grains containing both barite and pyrite. Interestingly, the fraction of barite to pyrite within individual grains varies from 100% to <10% over a depth of a mm to cm in the core. Mineralogical characterization correlated with *in-situ* S isotope analysis (Secondary Ion Mass Spectrometry, or SIMS) was performed to better understand the diagenetic conditions under which these grains formed. The grain size and mineralogy of the barite-pyrite grains suggest a diagenetic origin (rather than biogenic), and that pyrite replaces barite. The median $\delta^{34}S$ of barite and pyrite in grains containing both minerals is 63.82 ±0.45‰ and 1.69 ±0.34‰, respectively. The median $\Delta_{sulfate-sulfide}$= 62.13‰ is greater than the 2-46‰ fractionation that is commonly associated with bacterial sulfate reduction in marine sediments. Mass balance calculations suggest that barite could not have been the sole source of reduced S in the replaced grains with 77% percent of the S in pyrite derived from an additional source with $\delta^{34}S$ = −16.4‰. Based on our results, we suggest the following model for the formation of the observed barite-pyrite grains: 1) dissolution of biogenic barite below the sulfate-methane transition zone (SMTZ) due to the depletion of pore water sulfate, 2) Ba^{2+} transport and reprecipitation of barite (authigenic) at the SMTZ, 3) burial of authigenic barite and partial dissolution below the SMTZ, 4) movement of the SMTZ (possibly due to variable methane flux) below the depth of the partially dissolved barite, and 5) precipitation of pyrite in the pore volume created by barite dissolution.

The proposed model suggests that these grains represent 'relict' diagenetic barite fronts that form at the SMTZ in sediments implying an oxic or suboxic water column during early diagenesis. We posit that similar barite-pyrite mineral assemblages can be used to reconstruct paleoredox conditions in similar sedimentary facies, and thus complement trace element enrichment studies. Future efforts will focus on using trace element chemistry and barite-pyrite assemblages to reconstruct redox conditions within the Marcellus Shale depositional basin.