Understanding the isotopic composition of sedimentary sulfide

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Multiple sulfur isotope calibrations of microbial biosignatures enable the diagnosis of different sulfur-based metabolic processes, including sulfate reduction, sulfide oxidation and sulfur disproportionation. All carry distinct geochemical consequences for S cycling in modern systems, and are particularly powerful for paleoenvironmental reconstructions. To further develop a quantitative context for understanding early diagenetic sulfur isotope signals, we constructed a multiple S isotope reaction-transport model for the sediments of a geochemically well-characterized system (Aarhus Bay, Denmark). The model reconciles porewater and solid-phase concentration profiles of the major species associated with Fe/S/C cycling, and includes multiple S isotope systematics to predict the isotope profiles of the major S species (including porewater sulfate, sulfide and notably sedimentary pyrite). We note that large intrinsic fractionations associated with sulfate reduction (approx. 70‰) are required to reproduce the observed porewater profiles, despite smaller observed isotopic offsets between phases. That is, microbial sulfate reduction demonstrates large fractionations not expected for shallow, organic- rich continental margin systems. The observation of effects of this magnitude are commonly attributed to oxidative sulfur cycling processes. These predictions for near equilibrium behavior carry over to the minor sulfur isotopes, and further explain signatures observed in a range of different depositional environments (e.g., the California borderland basins). Little isotopic contribution from oxidative S cycling is required despite the juxtaposition of an oxygenated water column with highly reduced and sulfidic sediments. All told, these results challenge the paradigm that sedimentary sulfur isotope signatures from pyrite are a direct, unaltered record of microbial activity throughout Earth history.