



Kinetic S-34/S-32 fractionation during degassing and hydroxylation of hydrogen sulfide, and protonation of hydrogen bisulfide

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Transport of hydrogen sulfide across the sediment-water interface and diffusion into the atmosphere may occur in modern coastal marine environments with enhanced microbial activity in surface sediments and accumulation of dissolved H_2S in near-surface pore waters. The process is also in discussion to have been involved during phases of mass extinctions during Earth's history (e.g, Permian-Triassic boundary). The transport process of H_2S will lead to a pH-dependent fractionation of the stable sulfur isotopes, which has so far only been investigated for selected acidic to neutral pH values, and no experiments have been conducted with seawater, sofar. S-34/S-32 fractionation during degassing of H_2S from aqueous solution was investigated experimentally at 21 ± 1 °C in the dominance field of dissolved hydrogen sulfide, bisulfide, and mixtures of both species, corresponding to pH values between 2.6 and 11. Overall isotope enrichment factors between -0.7 and +3.4‰, were observed, with dissolved sulfide enriched in ^{34}S and ^{32}S compared to the liberated H_2S at low and high pH values, respectively. pH-independent isotope effects with respect to individual dissolved sulfur species are -0.7 (H2Saq) and +3.4 (HS-). Experiments in seawater solution showed no influence of increased ionic strength on sulfur isotope effects. During the chemical absorption of gaseous hydrogen sulfide by an aqueous alkaline solution, S-32 is enriched in the dissolved bi-sulfide by about 7.5 per mil.