

Chain Formation as a Mechanism for Mass-Independent Fractionation of Sulfur Isotopes in the Archean Atmosphere

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The anomalous abundances of sulfur isotopes in ancient sediments provide the strongest evidence for an anoxic atmosphere prior to ~2.45 Ga, but the mechanism for producing this ‘mass-independent’ fractionation pattern remains in question. The prevailing hypothesis has been that it is created by differences in the UV photolysis rates of different SO₂ isotopologues. We argue instead that the dominant process involves combinatorial factors in sulfur chain formation. Because two minor S isotopes rarely occur in the same chain, the longer S₄ and S₈ chains should be strongly, and roughly equally, depleted in all minor isotopes. This gives rise to *negative* $\Delta^{33}\text{S}$ values and *positive* $\Delta^{36}\text{S}$ values in elemental sulfur. Positive $\Delta^{33}\text{S}$ values in elemental sulfur produced in laboratory SO₂ photolysis experiments are probably caused by a combination of self-shielding by the major isotopologue, combined with condensation of short-chain sulfur species on the walls of the reaction chamber. The fractionations produced by this mechanism can explain many of the patterns observed in sedimentary rocks laid down during the Archean.