

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

C. E. HARMAN^{1,2*}, A. A. PAVLOV³, D. BABIKOV⁴, J. F. KASTING⁵

¹NASA Goddard Institute for Space Studies, New York, New York 10025, USA; chester.e.harman@nasa.gov

²Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York 10025, USA

³Planetary Environments Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA; alexander.pavlov@nasa.gov

⁴Department of Chemistry, Marquette University, Milwaukee, WI 53021, USA; dmitri.babikov@marquette.edu

⁵Geosciences Department, Penn State University, University Park, PA 16802, USA; jfk4@psu.edu

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. We investigate here a recently proposed source of fractionation during gas-phase formation of elemental sulfur, which would form S₄ and S₈ with negative Δ³³S and positive Δ³⁶S values. Back-reactions during chain formation pass sulfur having the opposite fractionation to atomic S, and thence to other sulfur species, causing H₂S, SO₂, sulfate, and short-chain elemental sulfur to have positive Δ³³S and negative Δ³⁶S. The simulated fractionations are large, but could be modulated by life. Last year’s model has been updated to include condensation of short-chain sulfur species. This reduces the magnitude of the predicted fractionation but leaves the sign unchanged.

Figure 1: Reactions leading to sulfur chain formation from volcanic SO₂ and H₂S. The number associated with each step shows the percentage of the source material reacting via the listed chemical pathway for our base case. The steps that introduce fractionation are marked with red arrows.

