Elucidation of the Origins of Stratospheric Sulfate Aerosols by Isotopic Methods

Thesis by

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Thesis Abstract

Stratospheric sulfate aerosols (SSA) play an important part in regulating the climate of the earth and in the maintenance of important stratospheric species, including stratospheric ozone. The sources of stratospheric sulfate aerosol sulfur remain an unresolved issue because of uncertainties in the global sulfur budget and model limitations. The origins of SSA particles should be reflected in their isotopic composition. In this thesis project, the sulfur isotopic fractionation factors of processes that produce stratospheric sulfate aerosols (SSA) were quantified using a variety of theoretical and experimental techniques. RRKM (unimolecular dissociation) theory was applied to compute the isotopic fractionation of the homogeneous oxidation of SO_2 via OH radicals. The overall isotopic enrichment associated with the total OCS loss pathways in the stratosphere was determined by analyzing high resolution FT-IR data from balloon flights. The isotopic fractionation of the photolytic decomposition of OCS was estimated by measuring the absorption spectra of OCS sulfur isotopologues. We also measured the isotopic composition of stratospheric aerosols sampled during the period 1973-1974, in the course of the Department of Energy's AIRSTREAM campaign. Combining our results with literature values of the sulfur isotopic composition of SSA precursors, we modeled the steady-state isotopic composition of sulfur compounds in the atmosphere using the JPL/Caltech 1-D chemical transport model. Our data supports the view that OCS and SO_2 are both important in the maintenance of the background stratospheric sulfate aerosol layer.

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