# Isotopic mixing of stratospheric CO$_2$

J.R. LYONS

Institute of Geophysics and Planetary Physics, UCLA, Los
Angeles, CA 90095-1567 (jrl@ess.ucla.edu)

Measurements of the oxygen isotopes of stratospheric CO$_2$ by Lammerzahl et al. (2002) demonstrate a surprisingly strong enrichment in ^{17}O, forming a line of slope ~ 1.7 from tropospheric CO$_2$ on a δ^{17}O-δ^{18}O plot (Fig. 1). The linear array of δ-values for stratospheric CO$_2$ is strongly suggestive of a 2-component mixing process, involving tropospheric CO$_2$ and a highly ^{17}O-enriched end member. Bulk ozone is not a suitable end member because it forms an array that is not sufficiently enriched in ^{17}O. Stratospheric CO$_2$ acquires its ^{17}O enrichment during exchange reactions between O(^{1}D) and CO$_2$ (Yung et al. 1991). In the stratosphere O(^{1}D) is produced by spin-allowed photolysis of O$_3$ in the Hartley band. The angular distribution of photoproducts, O(^{1}D) and O$_2$($^1\Delta$), suggests that the central atom is not ejected during photolysis. Thus, the preferential enrichment of asymmetric isotopomers during O$_3$ formation (Mauersberger et al. 1999) is passed to O(^{1}D) during photolysis. This results in an O(^{1}D) array that intersects the slope 1.7 mixing line for stratospheric CO$_2$ (Fig. 1). Figure 1 does not include mass-dependent fractionation, so the O(^{1}D) array may also shift along a slope 0.52 line. I will present model results for stratospheric CO$_2$ and O$_3$ isotopomers, and consider the recent suggestion of mass-independent fractionation during O$_3$ photolysis (Chakraborty and Bhattacharya 2003).
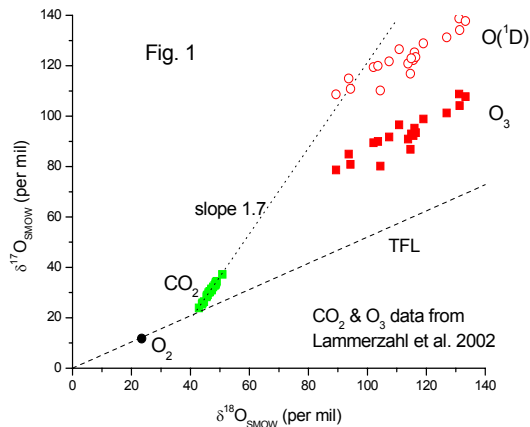
It seems unlikely that a sulfur analog to the above mechanism, i.e., formation of ^{33}S-enriched S(^{1}D) from S$_3$ photolysis, contributed to formation of Archean pyrites with δ^{33}S-δ^{34}S slopes ~ 1.5 (Ono et al. 2003).

Progress and challenges in using global climate models to interpret the Δ17O sulfate geological record

BECKY ALEXANDER

University of Washington, Department of Atmospheric
Sciences, Seattle, WA, USA (beckya@u.washington.edu)

The Δ^{17}O of sulfate and nitrate aerosols preserved in the geological record is currently the most promising proxy for elucidating past variations in the oxidation capacity of the atmosphere. This measurement also provides important information regarding the formation pathways of these aerosols, information that is crucial for calculating the magnitude of their radiative impact on climate, and how this may have varied in the past. The potential of Δ^{17}O measurements for providing quantitative information on the global scale will not be realized without the use of a global climate model (GCM). Our work incorporating the Δ^{17}O tracer in the GEOS-CHEM model, a global 3D chemical transport model (CTM) of the present-day atmosphere, has provided a first quantitative constraint on sulfate aerosol formation processes in the boundary layer and implications for the magnitude of their climate impacts.

Figure 1. Yearly average surface Δ^{17}O sulfate values in the GEOS-CHEM model.
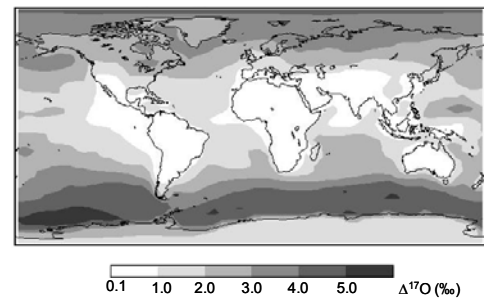
Our work with the GEOS-CHEM model has also revealed challenges and uncertainties to be addressed before we can quantitatively interpret the Δ^{17}O record on the global scale. I will show our progress in modeling the Δ^{17}O of sulfate in the present day atmosphere by comparing with available present day measurements, and discuss the potential of the Δ^{17}O proxy for providing information about global oxidant concentrations in the atmosphere. I will then focus on the challenges and opportunities for interpreting the Δ^{17}O record on the glacial-interglacial timescale, and progess towards coupling the GEOS-CHEM CTM with the NASA-GISS GCM to help reveal the full potential of this Δ^{17}O proxy over the geological record.