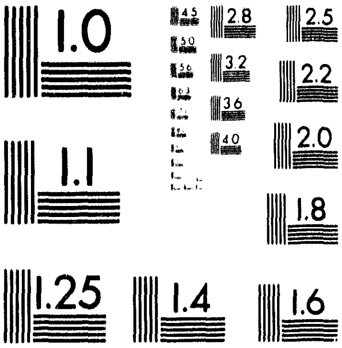
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Isotopically Labeled CO_2 from Stratosphere: A tracer of carbon biogeochemistry

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Objective: It has been recently discovered that the stratosphere is a source of isotopically enriched CO_2: $CO^{18}O$ and $CO^{17}O$. The cause of this isotopic enrichment is exchange between heavy O_3 and CO_2 via the excited radical $O(^1D)$. The research effort consists of a coordinated laboratory and model studies of isotopomers of CO_2. The laboratory study yields data on the chemical kinetics of oxygen exchange between CO_2 and O_3. The modeling study uses the laboratory results as well as atmospheric measurements to model the source and sinks of CO_2 isotopomers in the stratosphere and troposphere. It is expected that this combined study will bring new insights on the exchange of CO_2 between the atmosphere and the biosphere.

The goals may be further described in detail as follows:

1. To study the kinetic pathways for isotopic exchange between O_2 and CO_2. The currently proposed scheme for isotopic exchange is via O_3:

$$\begin{array}{rcl} OQ + h\nu & \rightarrow & O + Q \\ Q + O_2 + M & \rightarrow & OOQ + M \\ OOQ + h\nu & \rightarrow & Q(^1D) + O_2 \\ Q(^1D) + CO_2 & \rightarrow & O + COQ \\ O + O + M & \rightarrow & O_2 + M \\ \hline \end{array}$$

$$\text{Net:} \quad OQ + CO_2 + h\nu \rightarrow O_2 + COQ.$$

where Q = ^{17}O or ^{18}O. We can write a similar scheme for the reverse process:

$$O_2 + COQ + h\nu \rightarrow OQ + CO_2.$$

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The purpose of the laboratory experiments is to simulate atmospheric conditions and verify that this scheme is correct.

2. To study the exchange rate of isotopically labelled CO_2 between the stratosphere and the troposphere. Using the Caltech-JPL two-dimensional model we can simulate the spatial and temporal variation COQ in the tropospheres. This should serve to establish our baseline tropospheric model, and quantify the sinks of COQ. The knowledge gained from the successful modeling of the COQ cycle can be used to refine that of CO_2 since the biogeochemistry of COQ and CO_2 is nearly identical.

Product: The laboratory investigation will lead to a fundamental understanding of isotopic exchange for oxygen between O_2 and CO_2. The modeling results can set constraints on the rates of exchange between atmospheric CO_2 and the biosphere and the oceans.

Approach: The experimental set up consists of a light source (Hg lamp, laser or sunlight), samples of O_2 and CO_2 of known isotopic composition, and a mass spectrometer. Of particular interest is that the experiment always measures ^{16}O, ^{17}O and ^{18}O simultaneously. This three-isotope study will allow distinction between mass-dependent and mass-independent fractionation. The modeling work is based on the Caltech/JPL two dimensional model of the terrestrial atmosphere. The model has been tested by simulating the distribution of atmospheric tracers. They dynamics has been computed self-consistently. Once the stratospheric source of COQ is specified, the model predicts the rate that this COQ is transported into the troposphere, and ultimately to the planetary surface.

Results: During the past funded year a series of experiments were performed to quantitatively determine the oxygen isotopic systematics associated with the exchange of $O(^1D)$ and CO_2. The results have been submitted as a publication to the Journal of Geophysical Research (Wen and Thiemens, 1992). The results show that the exchange of oxygen atoms with CO_2 clearly requires that the atom be electronically excited $O(^1D)$. It was shown that $O(^3P)$, prepared by photolysis of O_3 is incapable of undergoing isotopic exchange with CO_2. The oxygen atoms were created via ozone photolysis at several energies to determine the role of energy upon the isotopic exchange process (185, 254, 532 nm and also sunlight photolysis). The rate at which isotopic steady-state was determined from time-evolutionary laboratory studies. These results are particularly important for modeling the increasing data set and apparently complex CO_2 isotopic data from the stratosphere. Electronically excited atomic oxygen, was shown to be the species which exchanges with CO_2. The exchange, at steady state, produces a mass independent isotopic fractionation, with equal ^{17}O, ^{18}O depletion in the atomic oxygen. The value of the quasi-reduced partition function at steady state is -40°/∞ for both $\delta^{17}O$ and $\delta^{18}O$. This represents the first determination of the position of isotopic exchange equilibrium between electronically excited and ground state species. The studies have further demonstrated the role of the CO_3* activated complex in the electronic quenching process.

In a series of experiments utilizing ozone (and consequently $O(^1D)$ atoms resulting from its photolysis) of variable isotopic composition it was demonstrated that the position of isotopic equilibrium attained at steady state is independent of the composition of the $O(^1D)$. This is particularly important for future interpretations of stratospheric CO_2 and O_3 oxygen isotopic measurements. In order to fully understand the extent of interaction between stratospheric CO_2 and O_3 it is imperative that this dependency be precisely resolved. If, as may be the case, the dependence upon energy, rate and isotopic composition be known. During the past year the Thiemens group has analyzed a number of stratospheric CO_2 samples for $\delta^{17}O$ and $\delta^{18}O$ which have further demonstrated the link between O_3 and CO_2. There are many puzzling variations observed and future laboratory experiments and sample analysis will address these observations. Of particular interest is the question as to whether steady-state is actually attained and what the source of the isotopic variations (temporal and altitudinal) are.

An attempt was made by Yung and DeMore to explain the ^{18}O enrichment in O_3. A careful examination of the laboratory experiments to date suggests that the only well-documented mechanism for heavy O_3 enrichment is the O_2-O bond-forming step. However, the Chapman reaction is the only known reaction for producing atmospheric O_3. After considerable search, we propose that there may be a hitherto unknown exchange reaction between O_2^* and O_3, which can result in the formation of a new O_3 bond, and hence the possibility of heavy O_3 enrichment. This idea is being tested in a quantitative model of the stratosphere.

Publications

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