Oxygen Isotopic Composition in Atmospheric Carbon Dioxide

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Abstract
The mass-independent nature of the isotopic composition of ozone is caused by none-statistical partitioning in its intermediate state to the formation of ozone, resulting in $\delta^{18}O_{O_3} \approx \delta^{16}O_{O_2} \approx 100 \%$, relative to atmospheric $O_2$. This isotopic anomaly is large compared with other commonly known biogeochemical processes, and can transfer to other trace molecules such as CO$_2$ through the exchange reaction with O($^1D$), a photolytic product of O$_3$. Higher in the upper stratosphere and mesosphere, Lyman-$\alpha$ photolysis of O$_2$ provides a more important source of heavy O($^1D$) than O$_3$ photolysis. Here, we present a two-dimensional simulation for the isotopic composition of CO$_2$ from the surface to an altitude $\sim$130 km. The model can adequately reproduce the observed seasonal cycle of CO$_2$ in the upper troposphere and the age of air in the stratosphere. We find that the isotopic composition of CO$_2$ originally in the troposphere/biosphere can be affected by the downwelling air from the stratosphere through the stratosphere-troposphere exchange, and this effect is detectable by the current instrumentation. Our model suggests that the stratosphere-troposphere exchange not only modifies the level of heavy CO$_2$ in the lower troposphere, but also influences its seasonal cycle. Implications for the use of the isotopic composition of CO$_2$ to constrain the gross carbon flux between the atmosphere and terrestrial biosphere and the dynamics in the remote mesosphere are discussed.

Isotopic Exchange Reactions
1. Mechanism (see Liang et al. 2006a):

\[ ^{16}O(1D) + C^{16}O^{16}O \rightarrow C^{16}O^{16}O + ^16O \]

2. Isotopic fractionation of oxygen in CO$_2$:

\[ \delta^{18}O_{CO_2} = f[\delta^{18}O(1D) - \delta^{18}O(CO_2)] \]

where tropospheric $\delta^{18}O(CO_2)$ and $\delta^{18}O$ are 21 and 41 $\%$ relative to V-SMOW. The factor $f$ denotes dilution due to transport; the value is about 0.1 at 45 km, where the O($^1D$) peaks.

Implications
1. Two major sources of heavy O($^1D$): stratospheric O$_2$ photolysis and mesospheric O$_2$ Lyman-$\alpha$ photolysis
2. The former gives slope (in three-isotope plot of oxygen in CO$_2$) $\sim$1.5-1.6; the latter gives slope 0.3.
3. Observed slope in the mesosphere is 1.2; not reproduced in the current model, because of weak dynamical exchange between upper and lower mesosphere. So the observed slope coupled with dynamical simulations would refine our knowledge of mesospheric dynamics.
4. All known biological and geochemical processes have slopes $\sim$0.5.
5. Coupled with three-dimensional chemical transport model provides a new tool to the biogeochemical cycles involving CO$_2$.

Two-Dimensional Chemical Transport Model
1. Caltech/JPL two-dimensional chemical transport model is used.
2. The model is driven by vertical ($K_{zz}$) and horizontal ($K_{yy}$) eddy mixing processes and residual circulations ($\psi$) derived from three-dimensional dynamics.
3. The model can reproduce the age of air in the stratosphere [Morgan et al., 2004] and seasonality of CO$_2$ [Shia et al., 2006] in the upper troposphere.
4. The isotopologues and isotopomers of O$_2$ are taken from Liang and Yung (2006b).
5. Several $K_{yy}$, $K_{zz}$, and $\psi$ are used. See Table.

References

Two-Dimensional Chemical Transport Model
1. Modeled $\delta^{18}O(CO_2)$ for January, April, July and October, using Model B circulation. The mean tropospheric values ($\delta^{18}O(CO_2)$) have been subtracted.
2. Note that the seasonality is weak in and below the stratosphere. The $\delta \approx 0\%$ in the troposphere, due to fast $K_{yy}$ and $K_{zz}$ and fixed lower boundary conditions.
3. Strong seasonality in the upper mesosphere; the variation is as large as a factor of 2.

Carbon dioxide is an important greenhouse gas. The understanding of its sources and sinks is far from satisfactory. The major difficulty is caused by fast exchange processes between the atmosphere and planetary surface, resulting in large seasonality of surface CO$_2$ level. For example, as reported by IPCC [2001], the exchange flux of CO$_2$ between the atmosphere and the surface is $\sim$200 PgC/year, and the “net” uptake on surface is $\sim$3 PgC/year. So an accuracy better than 1% or CO$_2$ mixing ratios $<$3 ppmv is required to quantify the sources and sinks of CO$_2$. The discovery of mass-independent isotopic fractionation (MIF) of oxygen in middle atmospheric CO$_2$ [Thiemens et al., 1995; Lammerzahl et al., 2002; Boering et al., 2004] provides a window of opportunity to the sources and sinks of surface CO$_2$. [Hoag et al., 2005]. Because the known sources and sinks of surface CO$_2$ are mass-dependent, the MIF originating in the middle atmosphere could therefore trace the biogeochemical processes involving CO$_2$ in the biosphere. Higher in the upper stratosphere and mesosphere, the isotopic composition of CO$_2$ provides a unique tool for studying atmospheric transport and chemistry, because of its high abundance ($\sim$370 ppmv in the stratosphere, dropping to $\sim$100 ppmv at the homopause); the concentrations of other common tracers (e.g., CH$_4$, N$_2$O, SF$_6$, and the CFCs) are too low to be detected. The MIF of CO$_2$ is thought to be caused by isotopic exchange reactions with O($^1D$), produced by the photolysis of O$_3$. 

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