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General Information
Submission
Review
Production
Subscription
Comment on a Paper

Volumes and Issues Contents of Issue 2

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Investigations of the photochemical isotope equilibrium between O_2, CO_2 and O_3

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Abstract. Contrary to tropospheric CO_2 whose oxygen isotopic composition follows a standard mass dependent relationship, i.e. $\delta^{17}O \sim 0.5\delta^{18}O$, stratospheric CO_2 is preferentially enriched in ^{17}O, leading to a strikingly different relation: $\delta^{17}O \sim 1.7\delta^{18}O$. It has been shown repeatedly that the isotope anomaly is inherited from O_3 via photolytically produced $O(^1D)$ that undergoes isotope exchange with CO_2 and the anomaly may well serve as a tracer of stratospheric chemistry if details of the exchange mechanism are understood. We have studied the photochemical isotope equilibrium in UV-irradiated O_2-CO_2 and O_3-CO_2 mixtures to quantify the transfer of the anomaly from O_3 to CO_2 at room temperature. By following the time evolution of the oxygen isotopic compositions of CO_2 and O_2 under varying initial isotopic compositions of both, O_2/O_3 and CO_2, the isotope equilibria between the two reservoirs were determined. A very strong dependence of the isotope equilibrium on the O_2/CO_2-ratio was established. Equilibrium enrichments of ^{17}O and ^{18}O in CO_2 relative to O_2 diminish with increasing CO_2 content, and this reduction in the equilibrium enrichments does not follow a standard mass dependent relation. When molecular oxygen exceeds the amount of CO_2 by a factor of about 20, ^{17}O and ^{18}O in equilibrated CO_2 are enriched by (142±4) ‰ and (146±4) ‰, respectively, at room temperature and at a pressure of 225 hPa, independent of the initial isotopic compositions of CO_2 and O_2 or O_3. From these findings we derive a simple and general relation between the starting isotopic compositions and amounts of O_2 and CO_2 and the observed slope in a three oxygen isotope diagram. Predictions from this relation are compared with published laboratory and atmospheric data.

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