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The oxygen isotope anomaly in CO_2: photochemical kinetics experiments and stratospheric observations

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Ozone formed in both the atmosphere and laboratory has been found to have atypically large and non-mass-dependent enrichments in ^{17}O and ^{18}O relative to ^{16}O, with an anomaly of $^{17}\Delta \approx 40‰$ (where $^{17}\Delta = \ln^{17}\mathrm{O} - 0.52 \times \ln^{18}\mathrm{O}$). The $^{17}\Delta$ anomaly in ozone has been determined to originate in the three-body ozone formation reaction and cannot be explained by statistical reaction rate theories. Current theories focus on an unusual quantum symmetry effect that comes into play due to the short lifetime of the excited ozone complex during which energy cannot be statistically distributed among all degrees of freedom before the O_3 complex dissociates. A number of observations of stratospheric CO_2 have shown that it is also non-mass-dependently enriched in ^{17}O and ^{18}O, with an anomaly of up to $^{17}\Delta = 12‰$, which is thought to originate from O(^{1}D)-mediated isotope exchange between ozone and carbon dioxide. Because photochemical models of both atmospheric and laboratory measurements of CO_2 have often had difficulty reproducing measurements, however, some have postulated that an anomalous isotope effect may also exist in the O(^{1}D)+CO_2 isotope exchange reaction. An anomalous isotope effect similar to ozone's is not expected, though, since dynamics experiments have shown that the CO_3 collision complex is long-lived enough for energy to be randomly distributed before the complex dissociates. To investigate whether additional anomalous isotope effects beyond those in the ozone formation reaction are needed to explain the $^{17}\Delta$ anomaly in CO_2, we have conducted photochemical experiments with mixtures of O_2 and CO_2 and compared these and previous results with those from a photochemical kinetics model using known and hypothetical anomalous and mass-dependent isotope effects. At pressures of 100 Torr and an atmospheric O_2/CO_2 mixing ratio, we find that the $^{17}\Delta$ anomaly in CO_2 measured in our experiments can be explained solely by the anomalous kinetic isotope effects in ozone formation. We have also used the model to show how the observed $\ln^{17}\mathrm{O}/\ln^{18}\mathrm{O}$ slope of CO_2 in the laboratory and experiments is sensitive to any mass-dependent isotope effects that change the isotopic composition of either O(^{1}D) or CO_2, but the value of $^{17}\Delta$ is not. In addition, we present 88 new measurements of stratospheric CO_2 collected by aircraft- and balloon-borne whole air samplers. While the $\ln^{17}\mathrm{O}/\ln^{18}\mathrm{O}$ slope on the three-isotope plot for some of the aircraft data match the previously reported value of 1.7, the rest of the aircraft and balloon data show a statistically different and larger slope than what has been typically observed. This difference in slopes could potentially be explained by the relative importance of reactions involving either O(^{1}D) or CO_2 in different regions of the stratosphere. We show qualitatively using two-end member mixing scenarios how mixing and transport between these different regions of the stratosphere could account for the difference between these new observations and those reported previously.