



Confirmed estimate of anomalous oxygen isotope enrichment in CO₂ produced from O+CO

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The occurrence of anomalous heavy isotope enrichment in ozone has been established by a series of measurements in stratosphere and laboratory. Besides ozone, this type of anomalous effect has also been observed in a wide range of atmospheric molecules like CO₂, N₂O, CO and aerosol sulfate demonstrating that the non mass dependent enrichment processes are not restricted to ozone formation. Early attempts to explain these anomalous isotope effects lead to the conclusion that symmetry controls the relevant fractionation process. To further constrain the role of symmetry, oxygen isotope fractionation associated with O+CO→CO₂ reaction was investigated in laboratory where the oxygen atom was derived from ozone or oxygen photolysis. The isotopic composition of the product CO₂ was analyzed by mass spectrometric methods. A commercially available model of chemical reaction simulation (Kintecus) was used to calculate the expected CO₂ composition using the available reaction rates and their modifications for isotopic variants of the participating molecules.

A comparison of the experimental data and model predictions shows that the product CO₂ is anomalously enriched in heavy oxygen isotopes. The enrichment varies from 70 to 136 ‰ for ¹⁸O and 41 to 83 ‰ for ¹⁷O. The level of enrichment seen in the CO₂ produced by O+CO reaction is in general similar to that observed in case of O₃ produced by O+O₂ reaction. Cross-plot of the two oxygen isotope ratios of the product CO₂ defines a line with a slope of ~1. It is also seen that the observed enrichment does not depend on the isotopic composition of the O atom used. A cross-plot of two enrichments (defined relative to the model predictions), Δ(¹⁷O) versus Δ(¹⁸O), shows linear correlation with the best fit line having a slope of ~0.8.

The anomalous enrichment in CO₂ can be explained by invoking the concept of differing randomization/stabilization time scales for the two types of intermediate transition

complex which form symmetric ($^{16}\text{O}^{12}\text{C}^{16}\text{O}$) molecules in one case and asymmetric ($^{16}\text{O}^{12}\text{C}^{18}\text{O}$ and $^{16}\text{O}^{12}\text{C}^{17}\text{O}$) molecules in the other.