



Oxygen three-isotope distributions in tropospheric and stratospheric CO₂ – potential inferences from high precision isotope measurements of carbonate decomposition

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It was demonstrated several years ago (Miller et al., *Proc. Natnl. Acad. Sci. USA* **99**, 10988–10993, 2002) that thermal decomposition of carbonates (including NBS18 and NBS19), under high vacuum conditions to minimize back-reaction, is accompanied – remarkably – by a small but distinctive ‘mass-independent’ isotopic fractionation, with the resulting CO₂ being anomalously enriched in ¹⁷O ($\Delta^{17}\text{O} \sim 0.15$ per mil). Re-examination of isotopic data from both CO₂ and solid oxide reaction products indicates that terrestrial carbonates appear to fit a fractionation line of slope 0.524 on the logarithmic form of the oxygen three-isotope plot. This is notably lower than the value of 0.528 which characterises natural waters. Furthermore, the few published high precision measurements of both $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ in tropospheric CO₂ suggest that its oxygen three-isotope composition is also in accord with that of carbonate minerals, rather than waters. This finding is of relevance to the ‘¹⁷O correction’ to $\delta^{13}\text{C}$ measurements of CO₂ at the highest levels of accuracy and precision.

In contrast, CO₂ from the lower and middle stratosphere is characterised by a slope of 1.7 on the oxygen three-isotope plot (Lämmerzahl et al., *Geophys. Res. Lett.*, **29**, 1582, 10.1029/2001GL014343, 2002). Whereas CO₂ + O(¹D) → CO₃* → CO₂ +

O(³P) is generally regarded as the mechanism by which the ¹⁷O and ¹⁸O enrichments in stratospheric ozone are transferred into coexisting CO₂, a satisfactory explanation for the slope of the fractionation line remains elusive. The possibility that formation and/or decomposition of the CO₃* might also be associated with a ‘mass independent’ isotopic fractionation was first suggested by Wen and Thiemens (*J. Geophys. Res.* **98** D7, 12801–12808, 1993). If thermal decomposition of the carbonate ion is analogous to the CO₃* → CO₂ + O(³P) reaction, isotopic behaviour during the former may be relevant to an explanation of the very unusual oxygen three-isotope distribution in stratospheric CO₂. However, whereas the carbonate ion has D_{3h} symmetry, it has long been known that the ground state CO₃* isomer has C_{2v} symmetry, although interconversion to the D_{3h} isomer should readily occur, as the energy state of the latter is only 0.42 kJ mol⁻¹ higher, with an isomerization barrier of 18.4 kJ mol⁻¹. The first experimental detection of the D_{3h} isomer of CO₃* occurred only recently (Jamieson et al., COSPAR 2006-A-03495), but this discovery strengthens the potential link with the carbonate decomposition reaction. As the lifetime of CO₃* is only ~10⁻¹²s, multiple cycles of the formation and decomposition of this entity from CO₂ + O(¹D) in the stratosphere might be a contributory mechanism to not only the range of ¹⁸O enrichments of stratospheric CO₂ relative to the tropospheric CO₂ reservoir, but also to the attendant slope of 1.7 on the oxygen three-isotope plot.