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Modelling the abundance of $^{18}O^{18}O$ in the atmosphere and its sensitivity to temperature and ozone photochemistry

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Ozone photochemistry and atmospheric temperature play dominant roles in setting the abundance of $^{18}O^{18}O$ isotopologues (expressed as Δ_{36}) of atmospheric oxygen (Yeung et al., 2016). The ECHAM/ MESSy Atmospheric Chemistry (EMAC) model was used to simulate the abundance of $^{18}O^{18}O$ in the global atmosphere (Gromov et al., 2010; Jöckel et al., 2016). Atmospheric transport and kinetic chemistry of Δ_{36} are explicitly modelled, i.e. with the rate of $O+O_2$ isotope equilibration towards the value expected for thermodynamic equilibrium being dependent on simulated $O(^3P)$ and temperature distributions. Additionally, equilibration temperature and pressure are recorded and used to diagnose the influence of transport on the distribution of Δ_{36}. The average equilibration temperatures for different atmospheric compartments (troposphere, tropopause, lowermost stratosphere and stratosphere) agree with the temperatures inferred from the simulated Δ_{36} distributions and the theoretical temperature vs. Δ_{36}relation, confirming the consistency of the modelling framework. We find that in the present atmosphere, approximately 60% of tropospheric O_2 re-equilibrates in the upper troposphere, whereas 40% of the clumped isotope signature reflects equilibration conditions the lower stratosphere.

The temporal evolution of Δ_{36} and its sensitivity to temperature and ozone photochemistry in the stratosphere and troposphere were analysed for the period 1960 to 2010. Over this time period, the model predicts a decrease of $\sim$0.03 ‰ in the tropospheric Δ_{36} value, mainly caused by an increase in the tropospheric ozone burden of $\sim$15 %. The model also predicts perceptible short-term negative departures in Δ_{36}, strongest in the lowermost stratosphere and tropopause regions, associated with the large volcanic eruptions that occurred over the period of interest (Mount Agung in 1963, El Chichon in 1982, Pinatubo in 1991). These signals are attributable to local warming, which indicates that clumped isotope measurements can in principle be used to quantify the effect of volcanic eruptions on the upper troposphere and lowermost stratosphere temperatures. Integrated over the large atmospheric domains, however, the signals become smaller (maximum decrease in Δ_{36} was 0.03 ‰ observed in early 1993 in the tropopause region).

A temperature sensitivity analysis shows that an increase/decrease in the tropospheric temperature by 4 ^{o}C results in a decrease/increase in the Δ_{36} value by 0.09 ‰

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