A consistent simulation of oxygen isotope mass-independent fractionation (MIF) in CO and O_3 using AC-GCM EMAC

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We present the most consistent estimate of the atmospheric distribution of oxygen mass-independent fractionation (MIF) of carbon monoxide ($\Delta^{17}O(CO) = (\delta^{17}O(CO)+1)/(\delta^{18}O(CO)+1)^{\beta}-1$, $\beta = 0.528$, V-SMOW scale) inferred using the **E**CHAM/**ME**SSy **A**tmospheric **C**hemistry (EMAC) model (Jöckel *et al.*, 2010). Although MIF of CO is largely determined by its removal reaction with OH, implementing a comprehensive chemistry scheme and detailed surface emissions in EMAC allows to single out the lesser inputs of MIF due to oxygen from ozone and other atmospheric oxygen reservoirs. The model shows that less than 2% of CO molecules inherit their oxygen atoms from O_3 (mostly via ozonolysis reactions) which translates into an additional +0.60‰ in the average tropospheric $\Delta^{17}O(CO)$ value. The remaining non-MIF oxygen (from water and atmospheric O_2) outbalances this input by -0.24‰ respectively. The chemical kinetics of alkene ozonolysis (*viz.* yield of CO per reacted O_3 and O atoms transfer to CO) simulated in EMAC is in good agreement with the laboratory studies of Röckmann *et al.* (1998a). This also pertains to the inferred (OH) sink-induced effective tropospheric MIF of +(4.3±0.2)‰ in comparison to +(4.1±0.3)‰ reckoned by Röckmann *et al.* (1998b).

The explicitly simulated tropospheric $\Delta^{17}O(O_3)$ value in EMAC averages at +30.4‰ and has small variation, which is consistent with that expected from the laboratory data. Instead, the most recent observations of ozone tropospheric MIF (Vicars and Savarino, 2014) suggest a value of +25‰ being the most representative, which renders the simulated MIF input from O_3 in CO potentially overestimated by $\sim$20%. The EMAC-simulated $\delta^{18}O(O_3)$, however, agrees well with observational data, whilst sensitivity studies confirm non-negligible increase in atmospheric $\delta^{18}O(CO)$ due to input of O_3 oxygen to CO. A pronounced CO enrichment in heavy oxygen is expected in the stratosphere via the reactions of methane and $O(^1D)$, provided that the latter inherits the isotope composition of O_3. Despite slightly underestimated variation, the simulated $\Delta^{17}O(CO)$ surface seasonal cycles are in very good agreement with the observations in the NH. For the SH, where observations of CO MIF are not available to date, the model predicts a substantially higher average and smaller variation of $\Delta^{17}O(CO)$. Finally, EMAC ascertains that boundary layer ^{13}C and ^{18}O sink effective enrichments of CO tightly correlate with the $\Delta^{17}O(CO)$ signal, indicating that the latter can be used as a measure of CO chemical age, *i.e.* exposure to OH. Moreover, the MIF of CO constitutes a tool for inferring the actual (*i.e.* not modified by sink fractionation) isotope composition of its sources.

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