A consistent simulation of oxygen isotope mass-independent fractionation (MIF) in CO and O₃ using AC-GCM EMAC Sergey Gromov¹, Patrick Jöckel^{1,2} and Carl A. M. Brenninkmeijer¹

¹ Max Planck Institute for Chemistry, Atmospheric Chemistry Department, Mainz, Germany ² Deutsches Zentrum für Juff- und Raumfahrt (DLR). Institut für Physik der Atmosphäre. Obernfaffenhofen, Weßling, Germany

Abstract

We present the most consistent estimate of the atmospheric distribution of oxygen mass-independent fractionation (MIF) of carbon monoxide (CO) inferred using the ECHAM/MESSy Atmospheric Chemistry (EMAC) model. 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. We further discuss the ozone isotope composition simulated by EMAC and application of CO MIF to gauging the global and local scale processes altering CO, such as emissions and sink in reaction with OH.

in CO

Oxygen isotopes and MIF in CO

Abundant Rare 160 17O, 18O Isotopic ratios: R = rare/abundant C¹⁸O/C¹⁶O C¹⁷O/C¹⁶O ${}^{17}R(CO) = {}^{17}O/{}^{16}O$ ~0.2% < 0.04% ${}^{18}R(CO) = {}^{18}O/{}^{16}O$ Conventional definitions: Delta notation: δ δ¹⁸CO(CO) = (relates to a reference R) Fractionation constant: ε ${}^{18O}\varepsilon(CO)_{sink} = \left(\frac{18R(CO)_{sin}}{18R(CO)}\right)$ (relates compartments, quantifies kinetic effects. enrichment/depletion)



For most processes isotope fractionation is proportional to the mass difference (called mass-dependent fractionation, MDF): $180_{E} \approx 2.170_{E}$



 $\Rightarrow \Delta^{17}O(CO)$ is an independent, photochemical signal in CO?

References



^[1] Jöckel, P., et al., Geosci. Model Dev., 3, 717-752, 2010. ^[2] Gromov, S., et al., Geosci. Model Dev., 3, 337-364, 2010. ^[3] Sander, R., et al., Atmos. Chem. Phys., 5, 445-450, 2005. ^[4] Lyons, J. R., Geophys. Res. Lett., 28, 3231-3234, 2001. ^[5] http://www.ecmwf.int/products/data/archive/descriptions/od [6] http://www.mnp.nl/edgar/model/v32ft2000edgar 7 Röckmann, T., et al., Atmos. Chem. Phys., 2, 147-159, 2002. S. Gromov acknowledges his stipend provided by the CARIBIC

project and the Max Planck Institute for Chemistry (Mainz).

$\Delta^{17}O(CO)$ as a proxy for $^{13C}\varepsilon$ and $^{18O}\varepsilon$

Being mostly OH-driven. MIF in CO is a powerful tool for inferring the "photochemical age" (i.e. exposure to OH) of CO in the air mass: The effective ¹³C. ¹⁸O and MIF fractionations correlate well in CO Nearly linear correlation in the BL, different slopes in the NH/SH



+(0.25=0.45)% accuracy for ^{13C}r. +(0.96=0.51)% accuracy for ^{18O}r in NH-SH

SPITSBERGEN



.

Trace gas emissions

EMAC model & isotope extension

background stations.[8]

 $\Delta^{17}O(CO)$ in the atmosphere (O_3) ?

photochemical age of CO?

· Can we use this tracer to quantify the

· What other applications would be?

What about the OH of the past?

In this study we employ the ECHAM5/MESSy Atmospheric Chemistry general circulation model (EMAC^[1]). To handle the isotope chemistry, the isotope tagging technique^[2] for the kinetic chemistry sub-model MECCA^[3] is applied. The isotope-enable EMAC setup includes:

· HO_, NO_, ozone- and NMHC hydrocarbons (up to C_) chemistry; simulating 98 species in 251 reactions. The isotope tagging of the mechanism involves additional tracing of 60 carbonaceous and 69 oxygen-bearing species in 140 and 237 reactions, respectively

· The oxygen stable isotope chemistry is extended with the isotope exchange reactions mechanism^[4,2], a set of kinetic isotope effects (KIE) is assigned to the relevant reactions of CO, CH,, NMHCs and O, (see Fig. 2).

The chemical and physical isotope effects are simulated explicitly for each species. We apply the diagnostic of the various source types (fossil fuel/biomass burning, methane carbon, VOCs "tags", etc.), which accounts for the chemical interchanges and allows the calculation of the CO yield from methane and VOCs. This study represents the simulations for the period 1997-2000. The model meteorology has been nudged with the ECMWF operational model analysis data^[5].



• Do changes in global OH have similar effect on global $\Delta^{17}O(CO)$? - Adjusting East Asian emissions (ZE) vs. Adjusting tropospheric CH4 source (ZM)

Equal increase in tropospheric CO source, rather unequal response • Global/local averages of $\Delta^{17}O(CO)$ cannot be described in the

simplified "box-like" framework Mixing, transport and non-linearity of the CH₄-CO-HO₂-OH system render the

atmospheric system too complex





Fig. 3. Zonal averages of the simulated $\Delta^{17}O(CO)$ in EMAC. The color code denotes the MIE "noise" signal from Associated sources the anomalously enriched O3 contributing to CO via NMHCs ozonolysis and other pathway 0.528 biogenic (plant VOCs,



locations. Abbreviations refer to: K95 – Krankowsky et al. [1995]. JT97 – Johnston and Thiemens [1997], V13 – Vicars [2013], C1 – CARIBIC-1 / Gromov&Brenninkmeijer [2015]. Subscripts refer to the observational locations: L – La Jolla, P – Pasadena, W – White Sand, G – Grenoble, PS – R/V Polarstern (expedition No. 88), DC – Dome C. The hatched area spans the range of $\Delta^{17}O$ in the terminal oxygen atoms of O_3 inferred by V13 (excluding DC). The unpublished observational data on $\delta^{18}O(O_3)$ and $\Delta^{17}O(O_3)$ measured at G/PS/DC are kindly provided by W. Vicars, LGGE - CNRS / Université Joseph Fourier, Grenoble, France.

MAX-PLANCK-INSTITUT FÜR CHEMIE

• • • • • • •

0.00000

.

MAX-PLANCK-GESELLSCHAFT

4⁵0(co) [3

CO MR [pob] CO MR [pob]





-REF - AE - Z - ZE - observatio

Fig. 5. Observed and simulated CO mixing ratios and MIF at various surface locations. Box and whisker plots present the distribution of the compositions simulated in the control simulation. The thick dotted/dashed lines present the values simulated in sensitivity simulations contrasting the inpu of ozone MIF to $\Delta^{17}O(CO)$. Analogously, the thin solid/dotted lines present the simulated sink effective Δ17O enrichment in CO contrasting the input of the MDF sources to Δ17O(CO). Step-lines denote the observations, with shaded areas equating the interquartile range (IRO) of the data



Fig. 6. Estimated O3 input to CO MIF (upper panel) and 818O(CO) (lower



Fig. 7. Ozone MIF as simulated by isotope-enabled EMAC

Fig. 4. Observed and simulated ozone mixing and bulk isotope ratios at various surface

is suitable for gauging the large changes in past CO burden ⇒ atmosphere's oxidative capacity

Simulated $\Delta^{17}O(CO)$ and $\Delta^{17}O(O_2)$

contributing sources, viz. alkene ozonolysis. Results:

oxidation by OH (~+6‰) and surface sources contribution

CO sink (+4 7%)

tropospheric CO

∆¹⁷O(CO), [‰]

EMAC simulates the MIF of the O3 and its transfer to CO

through the various intermediates, together with directly

Δ¹⁷O(CO) is dominantly controlled by the seasonality of the CO

 $(\Delta^{17}O(CO)\sim0\%)$ diluting this effect, particularly in winter ^(Figs. 3, 4) · We single out the small tropospheric inputs of the MIF from ozone

• Simulated tropospheric $\Lambda^{17}O(O_2)$ values are comparable to those

Kinetic tagging indicates that <2% of all O₃ oxygen ends up in

(+0.6%), waters and air O₂ (-0.2%) compared to the MIF due to the

customarily assumed from the lab data (\sim 30 3%) with a small variability

within 4.5‰ due to the pressure/temperature seasonal variations, and overestimated compared to the likely tropospheric value (~26‰) (Figs. 4. 7)

 At δ¹⁸O(O₂)~75‰, the ozone input to δ¹⁸O(CO) may be as large as 2‰ \Rightarrow affects the estimates of $\delta^{18}O$ from CH₄/NMHCs sources (Fig. 6)

• Simulated $\Delta^{17}O(CO)$ seasonality at the high latitude NH locations is well

reproduced, however the summer maxima are underestimated by 1-2‰

• Characteristic sensitivities of $\Delta^{17}O(CO)$ to changes in global CO and

OH are low. Further studies are required to ascertain that CO MIF





formulation with 8 ± 0.52 BC alculated accuming biogenic sources with 8¹⁰0 ± 0% ¹¹C alculated accuming 0, derived CH, and R. Outerland NRM

The inventory we use resembles that of EVAL2 setup of EMAC, including the industrial/anthropogenic (EDGAR FT2000 v2.3), biogenic (GEIA/OLSEN) and biomass burning (GFED v2.1) categories. Being all MDF, the oxygen-bearing sources however reflect the slight variations in Δ^{17} O, relating to the two distinct terrestrial O reservoirs: waters and atmospheric O₂. Table 1 elucidates how we allocate the respective $\Delta^{17}O$ signatures to the given sources.