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## The use of $\delta^{13}\text{C}$ in CO to determine removal of $\text{CH}_4$ by Cl radicals in the atmosphere

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This paper is dedicated to Carl A.M. Brenninkmeijer

### Abstract

The reaction of  $\text{CH}_4$  with chlorine (Cl) radicals in the atmosphere is associated with an extraordinarily strong isotopic fractionation, where  $^{12}\text{CH}_4$  reacts about 70 ‰ faster with Cl than  $^{13}\text{CH}_4$ . Therefore, although the Cl-based sink of  $\text{CH}_4$  constitutes only a small contribution to its total removal rate, the uncertainty in this small sink has been identified as one of the two largest uncertainties of isotope-based  $\text{CH}_4$  source apportionment at the global scale. The uncertainty arises from the fact that Cl levels in the atmosphere are so low that they cannot be detected directly. One very sensitive indirect method to identify and quantify the  $\text{CH}_4 + \text{Cl}$  reaction in the atmosphere is the detection of the extremely  $^{13}\text{C}$ -depleted reaction product carbon monoxide (CO) from this reaction. This article reviews the concept of this approach, its successful application in the atmosphere, its challenges and opportunities for identifying and quantifying Cl-based removal of  $\text{CH}_4$  at the regional and global scale and its potential to detect and evaluate possible attempts to enhance  $\text{CH}_4$  removal from the atmosphere.

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## Introduction

Methane (CH<sub>4</sub>) is the second most important anthropogenic greenhouse gas, and its enhanced emissions are responsible for about half a degree of warming since pre-industrial times (IPCC AR6, 2022). Due to its relatively short lifetime in the atmosphere of about 10 years, CH<sub>4</sub> is considered an attractive emission mitigation target and reduction in CH<sub>4</sub> levels could slow down global warming on a relative short term (Ocko et al., 2021, Cael and Goodwin, 2023). Therefore, more than 150 nations have joined the Global Methane Pledge to reduce anthropogenic CH<sub>4</sub> emissions by 30 % by the year 2030, compared to 2020 levels. This is an ambitious plan given the wide range of sources from anthropogenic activities, which include exploration, transport, storage and use of fossil fuels, waste management, ruminant and rice agriculture and industrial combustion and non-combustion processes (Saunio et al., 2020). Numerous activities in the past decades have addressed quantifying and reducing CH<sub>4</sub> emissions across all these sectors, e.g. (Brandt et al., 2014, Alvarez et al., 2018, Smith et al., 2021, Stavropoulou et al., 2023, Wang et al., 2023, Shindell et al., 2021). Nevertheless, CH<sub>4</sub> levels in the atmosphere are still increasing, and the growth rate has been particularly high in the post-2020 years (Lan et al., 2023).

The causes of the multi-year variations in CH<sub>4</sub> over the last decades are still being debated, and different studies have attributed them to either increasing emissions from fossil fuel related sources (Zhang et al., 2021, Chandra et al., 2021) biogenic sources (Schaefer et al., 2016, Nisbet et al., 2016, Basu et al., 2022, Lan et al., 2021, Oh et al., 2022), both categories (Worden et al., 2017, Thanwerdas et al., 2023) or changes in the removal by the main sink, reaction with OH (Rigby et al., 2017, Turner et al., 2017, Stevenson et al., 2022). Key information comes from the temporal evolution of the carbon isotopic composition of CH<sub>4</sub>. The reversal of the temporal  $\delta^{13}\text{C}$  trend (Schaefer et al., 2016, Nisbet et al., 2016, Lan et al., 2021) suggests that the recent rise of CH<sub>4</sub> is different from the rise before the year 2000, and that fossil sources may no longer be responsible for the increase. However, in this case, the ongoing rise of CH<sub>4</sub> likely originates from biogenic sources, including the possibility that we already see a feedback of the global climate system to ongoing global warming, which is likely more difficult to mitigate than anthropogenic sources (Nisbet et al., 2023). Note, however, that Thanwerdas et al. (2023) suggest that the  $\delta^{13}\text{C}$  trend reversal could be explained by a shift in the source signatures without a large reduction in the relative share of the fossil sources. Notwithstanding, Kleinen et al. (2021) showed that increased emissions from natural sources may cause future CH<sub>4</sub> concentrations to rise higher than expected in current global projections. In this case, emission reductions from anthropogenic sources may not be adequate to reduce CH<sub>4</sub> sufficiently.

An additional possible way to reduce atmospheric CH<sub>4</sub> levels is the acceleration of its removal. Most of the CH<sub>4</sub> is removed by reaction with the hydroxyl radical (OH), with small contributions from soil uptake and removal by atomic oxygen and chlorine (Cl) radicals. The Cl-based sink in the troposphere is very difficult to quantify because Cl levels are so low that they cannot be measured directly. Thus they have to be quantified by indirect measurements of Cl precursors, either in combination with models of atmospheric photochemistry (Hossaini et al., 2016) or by measurable effects that reactions with Cl imprint on more stable species. This paper discusses the potential, challenges and opportunities of using the carbon isotopic composition of CO, the product of atmospheric oxidation reactions of CH<sub>4</sub>, as a tool to quantify the contribution of Cl to the removal of CH<sub>4</sub> and to identify regions and processes where CH<sub>4</sub> is removed by Cl in the atmosphere.

## Isotope-based detection and quantification of Cl

The basis of this method is the extraordinarily strong  $^{13}\text{C}/^{12}\text{C}$  kinetic isotope effect in the reaction CH<sub>4</sub> + Cl. Saueressig et al. (1995) discovered that in the range of tropospheric

temperatures Cl reacts about 70 ‰ faster with  $^{12}\text{CH}_4$  than with  $^{13}\text{CH}_4$ , an astonishingly strong kinetic stable carbon isotope effect. Thus, wherever this reaction is significant, it leads to a  $^{13}\text{C}$  enrichment in the remaining  $\text{CH}_4$ , and a depletion in the CO produced.

The carbon isotopic composition of CO is quantified in the common delta ( $\delta$ ) notation as

$$\delta^{13}\text{C}_{\text{CO}} = \frac{{}^{13}\text{R}_{\text{CO}}}{{}^{13}\text{R}_{\text{VPDB}}} - 1 \quad (1)$$

where  ${}^{13}\text{R}$  is the  $^{13}\text{C}/^{12}\text{C}$  ratio and VPDB is the international reference material Vienna PeeDeeBelemnite with  ${}^{13}\text{R}_{\text{VPDB}} = 0.011180(28)$  (Zhang et al., 1990). For  $\text{CH}_4$ ,  $\delta^{13}\text{C}_{\text{CH}_4}$  is defined analogously. The kinetic fractionation factor  $\alpha$  of a certain reaction is the ratio between the rate coefficients of the reactions of the different isotopologues.  $\alpha$  also is equal to the isotope ratio of the instantaneously produced reaction product (here CO, assuming complete conversion to CO) relative to the one of the substrates (here  $\text{CH}_4$ ), thus

$$\alpha_{\text{Cl}+\text{CH}_4} = \frac{{}^{13}k_{\text{Cl}+\text{CH}_4}}{{}^{12}k_{\text{Cl}+\text{CH}_4}} = \frac{{}^{13}\text{R}_{\text{CO}}}{{}^{13}\text{R}_{\text{CH}_4}} = \frac{\delta^{13}\text{C}_{\text{COCl}+\text{CH}_4} + 1}{\delta^{13}\text{C}_{\text{CH}_4} + 1}. \quad (2)$$

For the reaction under consideration, when  $\text{CH}_4$  ( $\delta^{13}\text{C}_{\text{CH}_4} = -48$  ‰) is removed via the  $\text{Cl}+\text{CH}_4$  reaction ( $\alpha_{\text{Cl}+\text{CH}_4} = 0.935$ )  $\delta^{13}\text{C}$  of the produced CO is

$$\delta^{13}\text{C}_{\text{COCl}+\text{CH}_4} = \alpha_{\text{Cl}+\text{CH}_4} (\delta^{13}\text{C}_{\text{CH}_4} + 1) - 1 = 0.935 * 0.952 - 1 = -110 \text{ ‰}. \quad (3)$$

Thus, if only 1 ppb of CO with this depleted signature is added to an ambient reservoir of 100 ppb of CO with  $\delta^{13}\text{C}_{\text{CO}_{\text{amb}}} = -25$  ‰, the mixture will have a significantly different isotopic composition

$$\delta^{13}\text{C}_{\text{CO}_{\text{mix}}} = \frac{100 * \delta^{13}\text{C}_{\text{CO}_{\text{amb}}} + 1 * \delta^{13}\text{C}_{\text{COCl}+\text{CH}_4}}{101} - 1 = -25.8 \text{ ‰}. \quad (4)$$

## Methods

For the new samples presented below, ambient air samples were collected in 1 L glass flasks at five fixed sampling stations (Izaña Atmospheric Observatory and Oceanographical Institute (both Tenerife), Cape Verde Atmospheric Observatory, Ragged Point (Barbados), Atto tower (Brazil), and on board of ships (Visby and Cap San Augustine) operated by Maersk, crossing the North Atlantic region affected by mineral dust. High precision measurements of the isotopic composition of atmospheric CO are performed using isotope ratio mass spectrometry (IRMS). CO is converted to  $\text{CO}_2$  using *Schütze reagent* (Smiley, 1965), an oxidant that only adds one O atom to the original CO atom. The earlier applications of the technique, e.g. (Brenninkmeijer, 1993, Stevens and Krout, 1972) required large air samples (hundreds of liters), because purified gases had to be inserted into the IRMS using dual inlet systems. The advantage of this was that many samples could also be analyzed for  $^{14}\text{C}$  using accelerator mass spectrometry (Brenninkmeijer, 1993). After the development of continuous-flow IRMS (Merritt et al., 1994), stable isotope measurements of CO became much less labor intensive since the analysis using such systems only requires about 100 mL of air (Mak and Yang, 1998, Pathirana et al., 2015, Vimont et al., 2019, Kirago et al., 2023). The CO isotope system at Utrecht University has been described in Pathirana et al. (2015), and the isotope scale is linked to the calibration scale established in earlier studies, e.g. (Brenninkmeijer and Röckmann, 1997, Brenninkmeijer, 1993) via a high concentration CO isotope calibration gas stored in a high pressure cylinder.

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2  
3 modelled  $^{13}\text{CO}$  at Barbados, resulting from Cl production from mix mineral dust / sea  
4 spray aerosols using global modeling, and that in the current paper we compare the results  
5 from an April 1997 model run with new  $^{13}\text{CO}$  measurements taken in April 2023 across  
6 the north Atlantic. We also present previously unpublished data from this model run for  
7 the southern hemisphere to evaluate the impact of the Cl from MDSA on  $^{13}\text{CO}$  in Baring  
8 Head and Scott Base.  
9

10  
11 Van Herpen et al. (2023) simulated the release of Cl from Mineral Dust - Sea spray Aerosol  
12 (MDSA), and its subsequent reaction with  $\text{CH}_4$ , on  $\delta^{13}\text{C}_{\text{CO}}$ . They implemented a simplified  
13 MDSA parameterization in the global 3-D Community Atmosphere Model with Chemistry  
14 (CAM-Chem) (Lamarque et al., 2012, Tilmes et al., 2016, van Herpen et al., 2023, Li et  
15 al., 2023, Saiz-Lopez et al., 2023). The MDSA mechanism (Wittmer and Zetzsch, 2016,  
16 van Herpen et al., 2023) involves photocatalytic cycling of iron ions (Fe(III) - Fe(II)) and  
17 chlorine in mixed mineral dust - sea spray aerosols. The parameters in the model were  
18 chosen to match observed aerosol composition measurements in the North Atlantic.  
19 Details are provided in (van Herpen et al., 2023). The reaction of the released Cl with  $\text{CH}_4$   
20 is calculated online in the model, and the effect on  $\delta^{13}\text{C}_{\text{CO}}$  is then calculated knowing the  
21 isotopic composition of the ambient and the formed CO (eq. 3 & 4). We present previously  
22 unpublished data from these simulations for the southern hemisphere to evaluate the  
23 impact of the Cl from MDSA on  $\delta^{13}\text{CO}$  in Baring Head, New Zealand.  
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### 25 $\delta^{13}\text{C}_{\text{CO}}$ - based detection of Cl in the stratosphere

26  
27 In the stratosphere, the reaction of  $\text{CH}_4$  with Cl that is produced from photolysis of CFCs  
28 in the ozone layer contributes strongly to  $\text{CH}_4$  removal, which affects the radiative effects  
29 of stratospheric  $\text{CH}_4$  and water vapor (Saiz-Lopez et al., 2023). This leads to a well-  
30 documented and large  $^{13}\text{C}$  enrichment with altitude and latitude (Sugawara et al., 1997,  
31 Röckmann et al., 2011, Rice et al., 2003, Brenninkmeijer et al., 1995, Wahlen et al.,  
32 1987). These observations can be reproduced in atmospheric models when the laboratory-  
33 based kinetic isotope effect in the Cl +  $\text{CH}_4$  reaction is included (McCarthy et al., 2003,  
34 Eichinger et al., 2015, Thanwerdas et al., 2022, Chandra et al., 2024), demonstrating that  
35 the effect is well understood.  
36

37 Brenninkmeijer et al. (1996) were the first to show that the  $^{13}\text{C}$  enrichment in  $\text{CH}_4$  is  
38 accompanied by a very strong depletion of  $^{13}\text{C}$  in stratospheric CO. Figure 1 shows  
39 extremely low  $\delta^{13}\text{C}_{\text{CO}}$  values in stratospheric air when the CO mole fraction decreases below  
40 35 ppb. The symbols are color-coded by the concentration of  $^{14}\text{CO}$ , an ultra-trace molecule  
41 that is formed in the upper troposphere and lower stratosphere from  $^{14}\text{C}$  that produced by  
42 cosmic radiation (Mak et al., 1994). Higher  $^{14}\text{CO}$  levels indicate a higher stratospheric  
43 character of the air mass, and it is evident that  $\delta^{13}\text{C}_{\text{CO}}$  drops very strongly as the  
44 stratospheric character of the air mass increases.  
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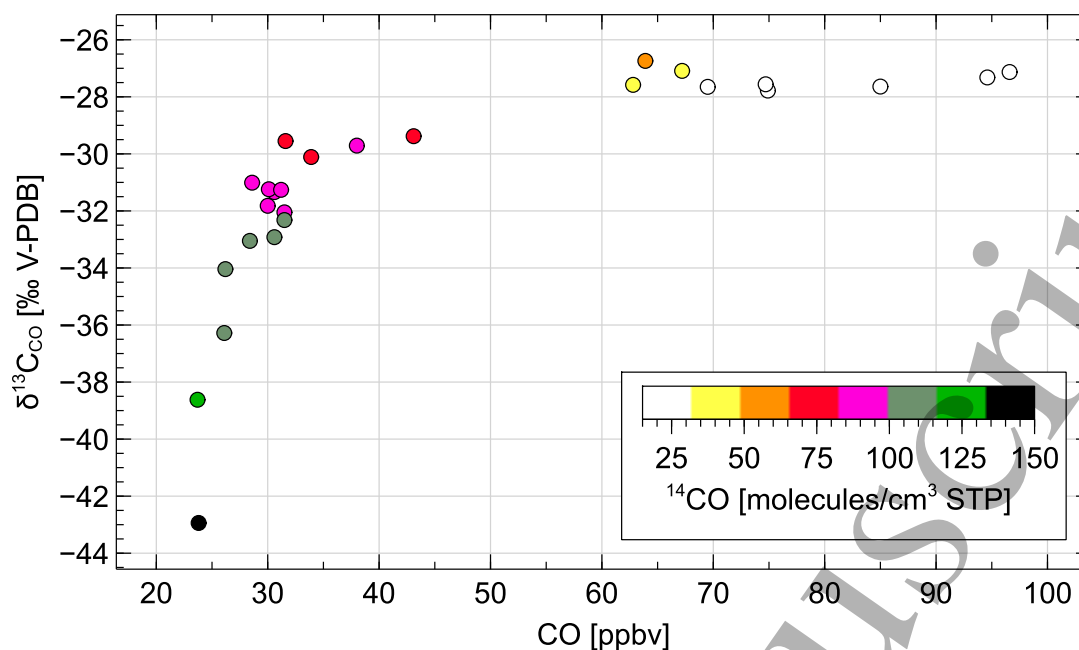


Fig. 1:  $\delta^{13}C_{CO}$  versus CO mole fraction, with a colour code of  $^{14}CO$  (in molecules  $cm^{-3}$  at standard temperature and pressure (STP)) for air samples collected on a C130 aircraft platform during flights in the southern polar lower stratosphere between New Zealand and Antarctica in October 1993 (modified from Brenninkmeijer et al., 1996).

#### $\delta^{13}C_{CO}$ – based detection of Cl in the troposphere: Ozone depletion events

Tropospheric Cl is much more difficult to detect and quantify than stratospheric Cl, because tropospheric Cl concentrations are extremely low, between  $10^2$  and  $10^5$   $cm^{-3}$ . Nevertheless, the  $\delta^{13}C_{CO}$  method has been successfully used to detect and quantify elevated Cl levels associated with ozone depletion events in the Arctic (Röckmann et al., 1999). Figure 2 shows an example of an ozone depletion event (ODE), when  $O_3$  levels drop from ambient values of  $\sim 40$  ppb to values near zero within hours. The black symbols show  $\delta^{13}C_{CO}$  during normal  $O_3$ , and the long-term trend reflects part of the seasonal cycle of  $\delta^{13}C_{CO}$ . During ODE episodes,  $\delta^{13}C_{CO}$  drops by about 1 ‰ relative to background levels (red circles in Fig 1). Note that the  $O_3$  destruction during ODEs is largely caused by Bromine-catalyzed  $O_3$  destruction (Herrmann et al., 2022) with additional contributions from Iodine (Benavent et al., 2022). However, the depletion in  $\delta^{13}C_{CO}$  (and hydrocarbon ratios (Ariya et al., 1998, Jobson et al., 1994) confirms that also Cl is produced in these events at levels that facilitate oxidation of roughly 1 ppb of  $CH_4$  upwind of the measurement location.

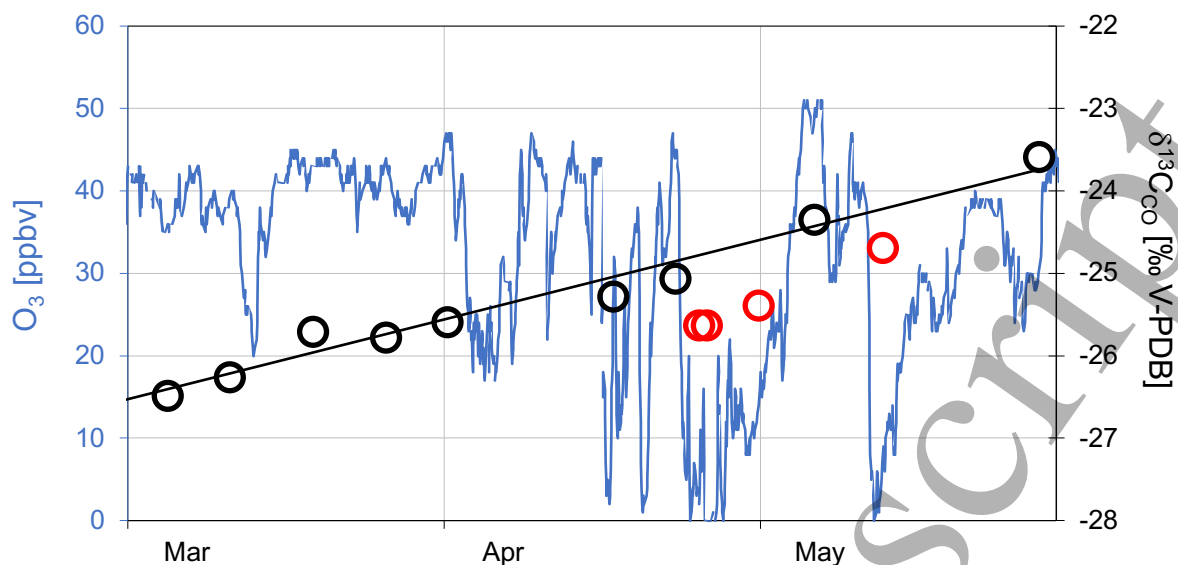


Fig. 2:  $O_3$  levels (blue line, left axis) drop from normal ambient values around 40 ppb to values near zero within hours during ODEs. Right axis:  $\delta^{13}C_{CO}$  of CO during background conditions (black circles, interpolated by black solid line) and ODEs (red circles) in spring 1997; modified from Röckmann et al. (1999).

### $\delta^{13}C_{CO}$ – based detection of Cl in the tropical troposphere

Are such negative  $\delta^{13}C_{CO}$  deviations also observable at other locations where Cl levels increase temporarily? The number of CO isotope observations made in the past is rather limited, but more than 20 years ago, Mak et al. (2003) reported unexpected  $\delta^{13}C_{CO}$  variability, including very depleted values, at Barbados. At other stations, much smoother seasonal evolutions and higher values of  $\delta^{13}C_{CO}$  are generally observed (Brennkmeijer, 1993, Röckmann et al., 1998, 2002, Mak and Kra, 1999, Kato et al., 2000, Mak et al., 2000, Gros et al., 2001). Mak et al. (2003) already suggested that the low  $\delta^{13}C_{CO}$  values could originate from the reaction  $Cl + CH_4$ , but at that time no source was known which could produce the relevant amounts of Cl in this region.

Van Herpen et al. (2023) recently suggested that Cl could be liberated photocatalytically when iron-containing mineral dust mixes with sea spray aerosol (SSA) above the Atlantic. When a corresponding Mineral Dust Sea spray Aerosol (MDSA) mechanism was implemented in a global atmospheric model, sufficient Cl was produced in the model to oxidize ppb-level quantities of  $CH_4$  during the passage of the air parcel over the Atlantic. Fig. 3 shows the expected deviation in  $\delta^{13}C_{CO}$  originating from this  $^{13}C$ -depleted CO source (Eq. 3) compared to a model without the MDSA mechanism for April 1997 from van Herpen et al. (2023). In the model, the strength and location of these isotope signals varies with season.



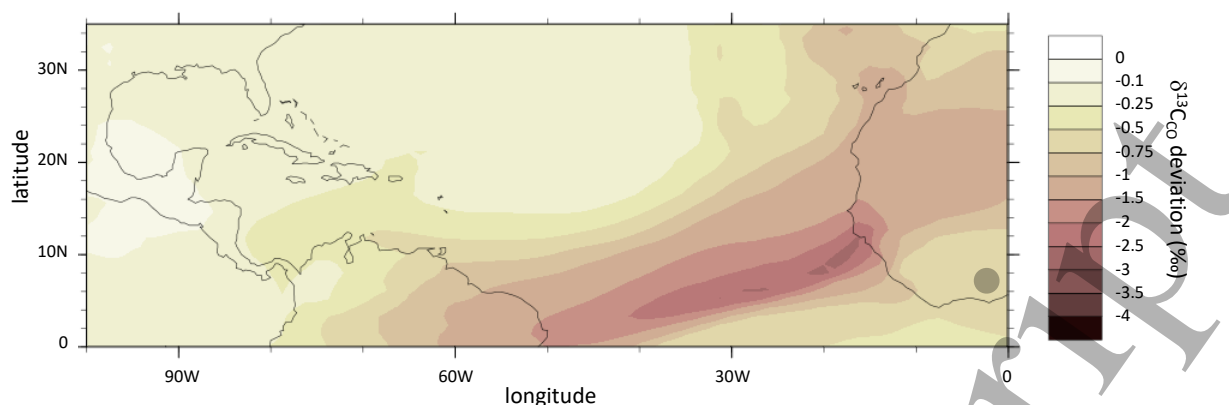


Figure 3: The spatial extent of the decrease in  $\delta^{13}\text{C}_{\text{CO}}$  resulting from  $\text{CH}_4$  oxidation by  $\text{Cl}$  that is produced in a model with MDSA mechanism in the CESM model for April 1997 (monthly average) compared to the default model without this mechanism. This figure uses model simulations from van Herpen et al. (2023).

To further confirm the MDSA hypothesis, air sampling programs have been recently initiated on several Atlantic islands, and on commercial ships. According to the modeling of MDSA performed in van Herpen et al. (2023), the  $\delta^{13}\text{C}_{\text{CO}}$  depletion should be strongest at around  $30^\circ\text{W}$  longitude, with negative shifts in  $\delta^{13}\text{C}_{\text{CO}}$  of up to 4 ‰ (Fig 3). The dust chemistry should lead to slightly lower  $\delta^{13}\text{C}_{\text{CO}}$  depletions at the permanent stations compared to the ship track, based on the location of the aerosol dust plume during this period.

Figure 4 shows  $\text{CO}$  and  $\delta^{13}\text{C}_{\text{CO}}$  data from air samples collected during two ship tracks that transected a large Sahara dust plume on 6-7 April 2023 (around  $30^\circ\text{W}$ ,  $7\text{--}11^\circ\text{N}$ , Maersk Visby, back triangles) and 12-13 April 2023 ( $22\text{--}25^\circ\text{W}$ ,  $7\text{--}11^\circ\text{N}$ , Cap San Augustine, grey circles). We also include data from our fixed stations at Tenerife, Cape Verde and Barbados that were taken during the same period, and samples from the Southern Hemispheric station Baring Head. The air samples collected on the Visby between April 5 and 10 as well as all samples from the San Augustine were collected in a period associated with high levels of Saharan dust. Fig. 4 shows that during these days the  $\delta^{13}\text{C}_{\text{CO}}$  of samples collected on the ship was much lower than the reference data from Barbados, Tenerife and Cape Verde. The Visby samples had relatively higher  $\text{CO}$  concentrations (Fig. 4b), likely due to an extra source from combustion, either technological or forest burning. This is evident from the high  $\delta^{18}\text{O}$  values that are indicative of combustion  $\text{CO}$  (Brenninkmeijer and Röckmann, 1997). However, combustion derived  $\text{CO}$  cannot explain the  $^{13}\text{C}$  depletion in these samples, as  $\text{CO}$  from combustion sources has a similar or higher  $^{13}\text{C}$  content than the ambient  $\text{CO}$  (Brenninkmeijer et al., 1999).  $\text{CO}$  in the dust-associated ship samples between April 5 – 10 is depleted in  $^{13}\text{C}$  by more than 2 ‰ (average value of  $-31.6$  compared to the reference average of  $-29.4$ ). Such low values are found in the Southern Hemisphere (see data from Baring Head in Fig. 4), but the  $\text{CO}$  mole fraction and  $\delta^{18}\text{O}$  values are too high at the Atlantic stations to reflect Southern Hemispheric air. The addition of a very small amount of strongly  $^{13}\text{C}$ -depleted  $\text{CO}$  from the  $\text{Cl} + \text{CH}_4$  reaction in the middle of the Atlantic can explain the negative  $\delta^{13}\text{C}$  excursions in the ship samples. The  $\text{Cl} + \text{CH}_4$  signal is weaker at the island stations that are further outside the dust plume, in line with the model prediction by van Herpen et al. (2023).

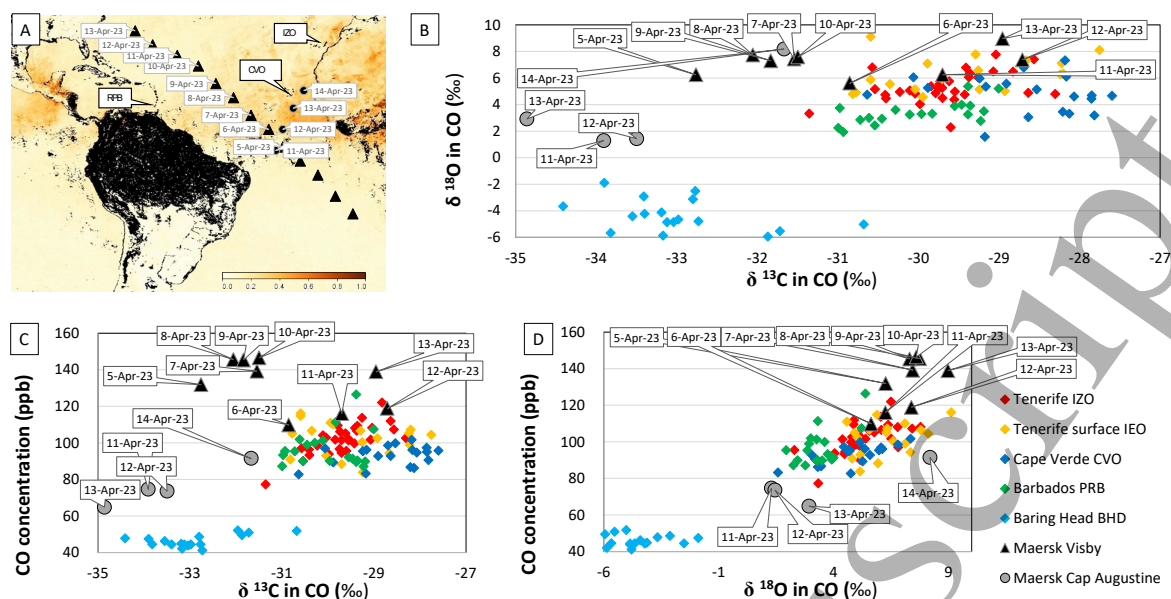


Fig. 4: (A) ship trajectories overlaid on a satellite image showing the April 2023 average aerosol optical depth (imagery produced by NASA based on data provided by the MODIS Atmosphere Science Team, NASA Goddard Space Flight Center). (B) ship data compared with fixed stations shows  $^{13}\text{C}$  depletions for dust-associated locations. (C)  $\delta^{13}\text{C}(\text{CO})$  vs. CO. (D)  $\delta^{18}\text{O}(\text{CO})$  vs. CO. We only analyze northern hemisphere ship flasks, because the isotopic composition of CO in the Southern Hemisphere is very different (see data from Baring Head, New Zealand).

### Global scale considerations

Allan and co-workers (Allan et al., 2001, 2005, 2007) used the seasonal co-variation of  $\text{CH}_4$  and  $\delta^{13}\text{C}_{\text{CH}_4}$  (referred to as *phase ellipses*) at high southern latitudes to quantify the possible role of Cl. They showed that the slopes of the phase ellipses are much larger than the one expected from the kinetic isotope effect in the removal of  $\text{CH}_4$  by OH (i.e., 3.9 ‰ according to Saueressig et al. (1995) and 5.4 ‰ according to Cantrell et al. (1990)). They concluded that this can only be caused by a significant contribution of tropospheric Cl to the sink, with a seasonal amplitude of  $6 \times 10^3 \text{ cm}^{-3}$ . From a similar analysis, Platt et al. (2004) estimated that the contribution of Cl to the tropospheric  $\text{CH}_4$  sink could be as high as 3.3 %, or 19 Tg  $\text{CH}_4/\text{yr}$ . A weakness of their argument is that the slope of the phase ellipse also exhibits strong interannual variation. In particular over the first years of the record, it varied from 17 ‰ in 1997 to 6 ‰ in 1999. This would correspond to a change in the Cl contribution of several percent, and if this was caused by Cl, it should also have affected the overall  $\delta^{13}\text{C}$  of atmospheric  $\text{CH}_4$  to a degree that is incompatible with atmospheric observations.

Gromov et al. (2018) illustrated this issue from the perspective of the reaction product CO. They argue that large interannual variations in Cl-based oxidation of  $\text{CH}_4$  in the extra tropical southern hemisphere (ETSH) would necessarily result in strong corresponding variations of  $\delta^{13}\text{C}_{\text{CO}}$  as the CO produced in this reaction is strongly depleted in  $^{13}\text{C}$  (Eq. 1). However, corresponding variations in  $\delta^{13}\text{C}_{\text{CO}}$  in the ETSH have not been observed. Interpreting the available atmospheric model results, they put an upper limit of  $n_{\text{Cl}} = 0.9 \times 10^3 \text{ cm}^{-3}$  on the variation of mean Cl levels in the ETSH, far less than the levels proposed by Allan and co-workers. Moreover, they argue that a large Cl source in the ETSH would lead to even lower background  $\delta^{13}\text{C}_{\text{CO}}$  values, which are already hard to reconcile with the understanding of the global CO cycle.

Nevertheless, the argument for high Cl based on the  $\delta^{13}\text{C}_{\text{CH}_4}$  phase ellipses has been supported by recent model analyses of the temporal and spatial trends in  $\delta^{13}\text{C}_{\text{CH}_4}$ , which

can only be reproduced in atmospheric models that use a strong isotope fractionation in the removal of CH<sub>4</sub> (Basu et al., 2022, Lan et al., 2021, Thanwerdas et al., 2022). This requires either a high fractionation in the OH sink or a large contribution of Cl to the total sink. Whitehill et al. (2017) reported 6.1 ‰ for the fractionation in the OH sink, higher than the previous reported values of 3.9 ‰ (Saueressig et al., 1995) or 5.4‰ (Cantrell et al., 1990). A stronger fractionation in the OH sink would require a small contribution from Cl, whereas a weaker fractionation in the OH sink would require a much larger contribution from Cl to explain the atmospheric observations.

Is it possible that a large source of Cl from MDSA near South America can provide enough Cl to explain the phase-ellipses observed by (Allan et al., 2001, 2005, 2007), but not affect  $\delta^{13}\text{C}_{\text{CO}}$  at the Baring Head and Scott Base sites in a corresponding way? We examined the CESM model output from van Herpen et al. (2023), which included an extrapolation to the global scale. The model output shows an additional strong Cl source near South America, and a modest source of Cl near Australia. Between July 1996 and June 1998, the modelled monthly average  $n_{\text{Cl}}$  in the southern hemisphere varied between 400 and 2200 atoms cm<sup>-3</sup>, resulting in  $\Delta n_{\text{Cl}}$  exceeding  $2 \times 10^3 \text{ cm}^{-3}$ , which is of the order of magnitude suggested by Allan et al. (2007). At Baring Head, the model output shows a  $\delta^{13}\text{C}_{\text{CO}}$  of less than 0.3 ‰, in line with the analysis made by Gromov et al. (2018). The inter-annual variation in the model output is even less pronounced. Note, however, that the model setup used in van Herpen et al. (2023) was not targeted at the global scale, in particular it does not include a polar halogen source module (Fernandez et al., 2019).

These results suggest that a large regional Cl source, far away from the remote observatories in the SH could at the same time provide a high average [Cl] exposure to explain the phase ellipses for CH<sub>4</sub>, without making a large effect on  $\delta^{13}\text{C}_{\text{CO}}$ . In addition, a large and previously unaccounted-for source of Cl in the NH could potentially alleviate difficulties in modeling the rather small interhemispheric gradient in  $\delta^{13}\text{C}_{\text{CO}}$ , which was previously attributed to a possibly unrealistically low yield of CO from CH<sub>4</sub> oxidation (Bergamaschi et al., 2000, Manning et al., 1997), one of the key parameters of the tropospheric CO budget that is yet rather uncertain (Gromov et al., 2018). Further modeling is needed to confirm the global scale relevance and implications of this potentially large Cl source.

## Implications

Measurements of the carbon isotopic composition of CH<sub>4</sub> have been widely used to quantify the relative contribution of emissions from different source sectors to the observed variations in the growth rate of CH<sub>4</sub> over the past decades (Lan et al., 2021, Basu et al., 2022, Thanwerdas et al., 2022, Nisbet et al., 2016, 2019, 2023, Schaefer et al., 2016, Worden et al., 2017). The kinetic isotope effect in the total removal of CH<sub>4</sub> is a key parameter influencing this partitioning. An error in the assumption of its value will invariably translate to an error in the partitioning between fossil fuel related and biogenic source categories. Basu et al. (2022) identified the uncertainty in the fractionation (both related to the uncertainty in the fractionation of the CO + OH reaction, and the contribution of Cl) as the single most important parameter precluding a more reliable separation between the different source sectors. Consequently, it is important to reduce this uncertainty using new measurement techniques, such as  $\delta^{13}\text{C}_{\text{CO}}$ . Finally, we note that measurements of  $\delta^{13}\text{C}_{\text{CO}}$  may be a valuable tool to quantify the efficiency of possible future CH<sub>4</sub> mitigation policies that may involve accelerating Cl-based destruction of CH<sub>4</sub>.

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### 13 **Data availability**

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15 The new CO isotope data used in this publication are included in the supplemental  
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17 [https://neo.gsfc.nasa.gov/view.php?datasetId=MYDAL2\\_M\\_AER\\_OD&date=2023-04-01](https://neo.gsfc.nasa.gov/view.php?datasetId=MYDAL2_M_AER_OD&date=2023-04-01)  
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### 19 **Competing interest**

20  
21 The authors declare no competing interest.  
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