

Chlorine isotope fractionation in the stratosphere

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Article

The isotopic composition of only a few stratospheric gases has been investigated to date (1, 2). One known effect is the relative enrichment of heavier isotopologues (= isotopically distinct species of a compound) for gases that are destroyed in the stratosphere (2). Such isotope effects are often characteristic for specific reactions and can help improve our understanding of the transport and reaction pathways of gases in this climate-sensitive atmospheric region (3-6). For example, position-dependent nitrogen isotope fractionation in nitrous oxide is different for photolysis and photo-oxidation of N₂O by O(¹D) (4). Similarly, the strong isotope effect in the reaction of chlorine radicals with methane leaves a "fingerprint" of stratospheric chemistry in the reaction product carbon monoxide (7).

Here, we present chlorine isotope ratio measurements of CF₂Cl₂ in air samples collected in 2005 and 2008 on board balloons flying in the tropical stratosphere. CF₂Cl₂ is the most abundant chlorofluorocarbon in the atmosphere and commonly known as CFC-12. It is a key anthropogenic greenhouse gas with an atmospheric lifetime of about 100 years (8) and plays a major role in stratospheric ozone depletion (9). A recent reanalysis of the retrieved trace gas data (10, 11) revealed that the isotopic composition of chlorine in CF₂Cl₂ changes with altitude. Chlorine has two stable isotopes, ³⁷Cl and ³⁵Cl, which occur in a ratio of about 24.24:75.76 (12, 13). Here, the isotopic composition is given as the relative ³⁷Cl/³⁵Cl isotope ratio difference, $\delta^{37}\text{Cl}$, between the sample and tropospheric air. We observed $\delta^{37}\text{Cl}$ values up to (27 ± 4) ‰ in the stratospheric air samples (Figure 1), almost double the total previously reported range of 16 ‰ for $\delta^{37}\text{Cl}$ in naturally occurring samples of any form (13-17). Furthermore, our data show that stratospheric $\delta^{37}\text{Cl}$ values increase with altitude, which is most probably due to the faster decomposition of

$\text{CF}_2^{35}\text{Cl}_2$ relative to $\text{CF}_2^{37}\text{Cl}^{35}\text{Cl}$ and $\text{CF}_2^{37}\text{Cl}_2$ by photolysis and by reaction with $\text{O}(^1D)$.

If such irreversible sinks with a constant isotopic fractionation were the causing process, the $\delta(^{37}\text{Cl})$ values should follow a Rayleigh-type fractionation with a linear correlation of the form $\ln[1 + \delta(^{37}\text{Cl})] \approx \varepsilon_{\text{app}} \ln(y_{\text{sample}}/y_{\text{entry}})$ (4), where $y_{\text{sample}}/y_{\text{entry}}$ is the ratio of stratospheric to tropospheric mixing ratios and ε_{app} is the apparent isotopic fractionation in the stratosphere. We observed a tight correlation with $\varepsilon_{\text{app}} = (-12.1 \pm 1.7) \text{‰}$. The apparent isotope fractionation observed in the stratosphere is expected to be lower than that caused by the fractionating reaction due to slow stratospheric transport and mixing (4). Based on the case of N_2O , which shares the same sinks as CF_2Cl_2 and has a similar lifetime of 120 years, the magnitude of the intrinsic photochemical fractionation could be twice as large as ε_{app} , i.e. $\leq -24 \text{‰}$. Predictions from simple zero-point energy theory calculations for photolytic isotope fractionation give only about -6 to -8‰ (18). More advanced theories are needed to quantitatively explain the observed effects but have only been developed for molecules with three atoms or less by now (19-21).

Moreover, the instruments used here (18) are not typical for carrying out isotope ratio studies. Their successful application overcomes the insufficient sensitivity of conventional isotope ratio mass spectrometers for very low (parts per trillion = 10^{-12}) abundances of trace gases and the difficulty to obtain large stratospheric samples. Many important greenhouse and ozone-depleting gases contain chlorine and should show similar enrichment. This could enable the quantification of the relative magnitudes of their stratospheric sinks. For CF_2Cl_2 , laboratory experiments suggest, that between 93 and 97 % is destroyed by photolysis, the remainder by $\text{O}(^1D)$ (22). As the altitude profile of the $\text{O}(^1D)$ loss is different from that of the photolysis sink, further measurements may be used to confirm and constrain the relative contribution of the $\text{O}(^1D)$ to the total loss of CF_2Cl_2 and other important ozone depleting substances. A subsequent reduction in the uncertainties of their atmospheric lifetimes (ranging from 79 to 113 years for CF_2Cl_2 (9)) would then lead to improvements in ozone recovery predictions. In addition, the explored measurement capabilities to detect chlorine isotope effects might help identifying and quantifying remaining sources of CFCs via their individual signatures. Finally, chlorine isotope

measurements could help unravel the human contribution to compounds that have both natural and anthropogenic sources, such as methyl chloride.

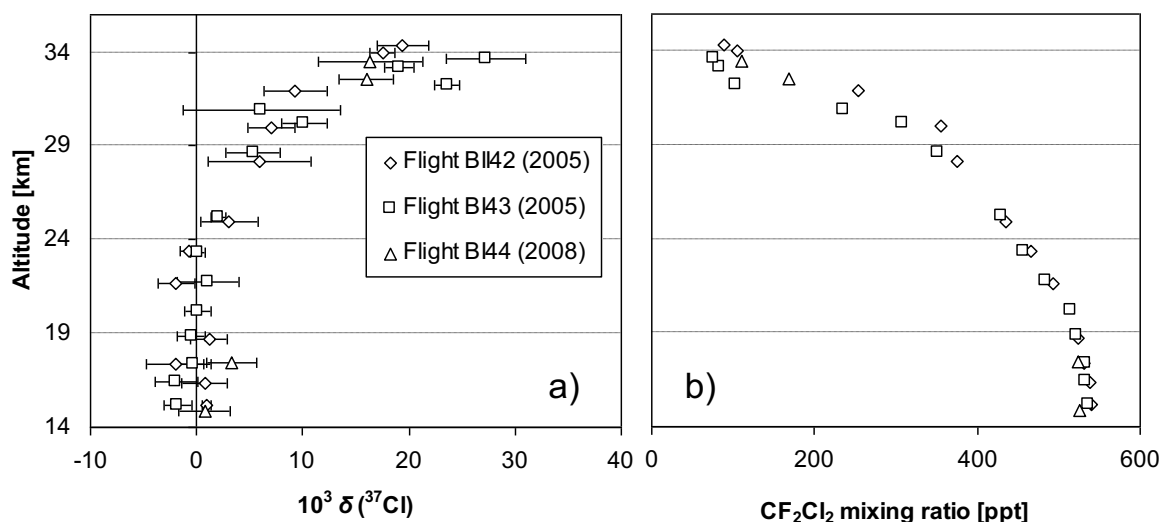


Figure 1. a) $\delta(^{37}\text{Cl})$, the relative $^{37}\text{Cl}/^{35}\text{Cl}$ ratio difference between CF_2Cl_2 in the stratosphere and the troposphere (average 1σ standard deviation of samples: $\pm 2.3\text{ ‰}$) and b) the corresponding mixing ratios of CF_2Cl_2 (all 1σ standard deviations less than size of the symbols).

References and Notes

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Supporting online material

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Materials and methods

The data presented here originate from two balloon-borne cryogenic whole-air-samplers (1), which were launched by the French Space Agency CNES (Centre National d'Etudes Spatiales) on three occasions in June 2005 and 2008 near Teresina, Brazil (5°04'S, 42°52'W). The 2005 samples were analysed using gas chromatography (GC) with an Agilent 5975 quadrupole mass spectrometric detector (MS, (2)).

We measured CF₂Cl₂ as ions with mass-to-charge ratio (m/z) of 85 (CF₂³⁵Cl⁺) and 87 (CF₂³⁷Cl⁺). No chromatographic interferences were found for these ions at the given retention time. The measured 87/85 ion current ratio of the tropospheric reference gas was 0.3247±0.0005, which is higher than the value of 0.3200±0.0008 that can be derived from the ³⁷Cl/³⁵Cl ratio of the international reference material NIST SRM 975 (3) and the δ values of (1.09±0.15) ‰ reported for industrial CF₂Cl₂ versus seawater chloride (4) and -0.34 ‰ reported for mean seawater chloride versus NIST SRM 975 (5). This difference would correspond to an instrumental fractionation factor of about 1.015, which is comparable to values for isotope ratio mass spectrometers (6).

In order to avoid introducing a bias for the low-concentration stratospheric samples, the 87/85 ion current ratio has to be independent of the pre-concentrated amount. To check for such a dependency we measured a static dilution series that consisted of six flasks with CF₂Cl₂ mixing ratios of (543.2 ± 2.7) ppt, (463.2 ± 2.3) ppt, (374.9 ± 1.9) ppt, (269.9 ± 1.4) ppt, (136.8 ± 0.7) ppt and (0.0 ± 0.1) ppt (7) together with the

samples. Ion current ratios showed a relative standard deviation of 3.2 ‰ and a random distribution around the average. This proves that injecting different amounts of CF₂Cl₂ does not have a significant effect on the measured ion current ratios.

The 2008 samples were analysed using an Agilent 6890 GC (GS-GasPro column, length 30 m, ID 0.32 mm) coupled to a sector-field mass spectrometer (VG/Waters EBE tri-sector). The latter was operated at a mass resolution of 1000 whilst measuring the CF₂Cl₂ fragment ions CF³⁵Cl₂⁺ (*m/z* 100.94), CF³⁵Cl³⁷Cl⁺ (*m/z* 102.93), and CF³⁷Cl₂⁺ (*m/z* 104.93). Due to the higher mass resolution, a possible interference from an unknown co-eluent is very unlikely and was not observed. To check for instrumental artefacts, different amounts of the same air sample (≈ 50, 100, 200 and 300 ml) were measured. We found a 1σ standard deviation of 2.7 ‰ for the ratio of 102.93/100.94 and 5.6 ‰ for 104.93/100.94 both showing a random distribution around the average. Comparable results (see Figures 1 and S1) were obtained for both mass spectrometers. Thus, we can rule out that the fragmentation of the molecule inside the mass spectrometers influenced the obtained chlorine isotopic composition. In addition, we measured CFC-115 (C₂F₅Cl) on the ions CF₂³⁵Cl⁺ (*m/z* 84.966) and CF₂³⁷Cl⁺ (*m/z* 86.963). CFC-115 is very long-lived and thus shows only a minor decrease with altitude in the observed stratospheric region (2). The reference gas was found to show a 37/35 ion current ratio of 0.31927±0.0013, whereas the stratospheric samples were scattered around this value with a standard deviation of 2.2 ‰. This is a strong indication that the fractionation observed for CF₂Cl₂ was not influenced by sampling artefacts.

The sink reactions of CF₂Cl₂ are photolysis (93-97 %) and reaction with O(¹D) (8). The kinetic isotopic fractionation due to CF₂Cl₂ photolysis can be calculated from absorption cross sections computed using quantum-chemical calculations. Yung and Miller (9, 10) pioneered this theoretical approach, which invoked zero-point energy (ZPE) differences between different N₂O isotopologues to explain isotope effects in stratospheric N₂O photolysis. But it soon became clear that the theory was only qualitatively correct and predicted too small isotope effects.

CF₂Cl₂ and N₂O have similar absorption spectra in the stratospheric ultraviolet window region between 190 and 230 nm (11). We use spectroscopic data (12-14) to calculate the zero point energy differences according to $\Delta E_0 = \frac{1}{2}hc\Delta\tilde{\nu}_0$. The result is

then used to derive the $\text{CF}_2^{35}\text{Cl}^{37}\text{Cl}$ by a corresponding wavelength-shift of the CF_2Cl_2 spectrum. We have calculated the wavelength-dependent ε values in the wavelength-region from 195 to 225 nm, in which 95 % of the stratospheric photolysis occur (altitude: 20 km, zenith angle: 30°). The expected stratospheric isotope fractionation ε_S was derived from the relative overlap of actinic flux, absorption cross-section $\sigma(\lambda)$ and $\varepsilon(\lambda)$ using data from (11) (Eq. S1).

$$\varepsilon_S = \frac{\int_{195 \text{ nm}}^{225 \text{ nm}} I(\lambda)\sigma(\text{CF}_2^{37}\text{Cl}^{35}\text{Cl})d\lambda}{\int_{195 \text{ nm}}^{225 \text{ nm}} I(\lambda)\sigma(\text{CF}_2^{35}\text{Cl}_2)d\lambda} - 1 = \frac{\int_{195 \text{ nm}}^{225 \text{ nm}} I(\lambda)\sigma(\lambda)\varepsilon(\lambda)d\lambda}{\int_{195 \text{ nm}}^{225 \text{ nm}} I(\lambda)\sigma(\lambda)d\lambda} \quad (\text{S1})$$

The integrated values for ε_S are between -6 and -8 ‰ for altitudes between 20 and 40 km and temperatures between 210 K and 273 K. The isotope effect is in the same direction as the measured value of (-12.1 ± 1.7) ‰, but smaller in magnitude.

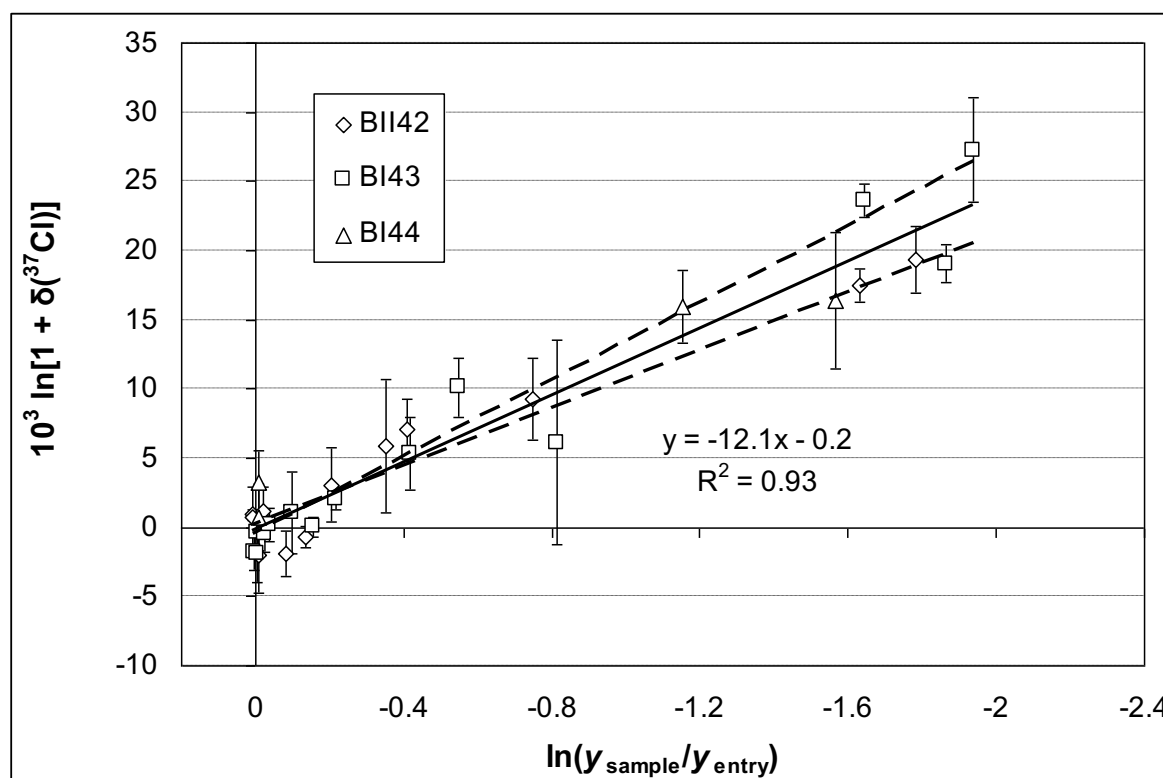


Figure S1. The stratospheric CF_2Cl_2 data set shown in a Rayleigh fractionation plot (y : mixing ratio).

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