



Chlorine isotope fractionation in CFC-12 reflects the latitude dependence of stratospheric chemistry and transport rates

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In 2010, we reported the first measurements of chlorine isotope fractionation in stratospheric difluorochloromethane (CFC-12) (Laube et al., *Science* 329:1167, 2010). We found an increase in the relative isotopic enrichment, $\delta(^{37}\text{Cl})$, with altitude and a tight correlation between $\ln[1 + \delta(^{37}\text{Cl})]$ and $\ln(\text{mixing ratio})$. The derived apparent isotope fractionation at the tropical sampling location (5°S) was $\epsilon_{\text{app}} = (-12 \pm 2) \text{‰}$. We speculated that, similar to stratospheric N_2O and CH_4 , the intrinsic photochemical isotope effect could be up to twice this value, due to the attenuating effects of mixing and diffusion.

Since then, we have measured the isotope effect during CFC-12 photolysis under realistic temperature and light conditions, using a UV broadband lamp. Surprisingly, the derived photolysis isotope fractionation of $\epsilon_{\text{P}} = (-10.8 \pm 0.5) \text{‰}$ at 233 K (a temperature that is representative of the altitude of maximum CFC-12 photolysis in the tropics) was less negative than ϵ_{app} . The contribution of the reaction of CFC-12 with $\text{O}(^1\text{D})$ to the overall stratospheric sink is small (3–7 %) and in any case, the associated isotope fractionation likely to be even smaller. The reaction with $\text{O}(^1\text{D})$ is therefore unlikely to explain the discrepancy between stratospheric and laboratory measurements.

However, we also found a strong temperature dependence of the photolytic isotope fractionation: At 288 K, ϵ_{P} was $(-7.3 \pm 0.8) \text{‰}$, while at 203 K, it was $(-14.5 \pm 1.4) \text{‰}$. The cumulative contribution of photolysis at altitudes with colder temperatures, below the maximum loss rate at 30 km, therefore goes some way to explain the unexpectedly high magnitude of ϵ_{app} .

Moreover, these findings indicate that the attenuating effects of mixing and diffusion on ϵ_{app} in the tropics cannot be very strong, or in other words, the photochemical lifetime at the tropical sampling location is much longer than the transport lifetime. ϵ_{app} is expected to reflect the latitude-dependence of atmospheric chemistry and transport. To test this hypothesis, we analysed stratospheric aircraft samples from mid-latitudes (48 to 54°N) and high-latitudes (66 to 77°N). The mid-latitude samples showed a similar apparent isotope fractionation to the tropical ones of $(-12 \pm 1) \text{‰}$, whereas the high-latitude samples showed only $(-7 \pm 1) \text{‰}$.

These observations are roughly in agreement with isotope measurements in stratospheric N_2O (Kaiser et al., *Atmos. Chem. Phys.* 6:3535, 2006), which has an atmospheric lifetime similar to that of CFC-12 (≈ 100 years). We suggest that the latitude-dependence of the observed stratospheric isotope fractionation in long-lived stratospheric gases such as CFC-12 and N_2O reflects the relative chemical loss and transport rates. A full interpretation of these results is probably best done in the framework of two- or three-dimensional chemistry-transport model.