

Supplement to: Abundances, emissions and loss processes of the long-lived and potent greenhouse gas octafluorooxolane (octafluorotetrahydrofuran, $c\text{-C}_4\text{F}_8\text{O}$) in the atmosphere

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S-1 Introduction

The supplement of this article consists of this text file and the following separate tables, saved as ascii files:

Table S1. Infrared absorption spectra.

Table S2. O(¹D) reaction rates.

Table S3. Measurement results for archived air samples and in situ observations.

Table S4. Inversion results for archived air samples and in situ observations.

S-2 Analytical details

S-2.1 Infrared absorption spectra

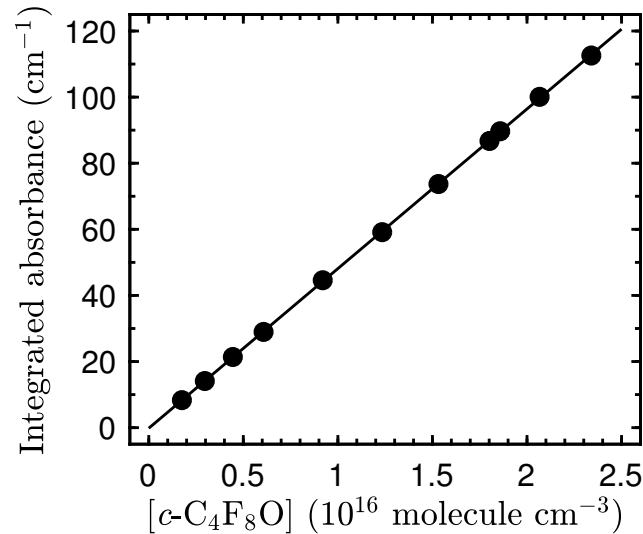


Figure S1. Beer’s law plot for the 296 K infrared spectra of octafluorooxolane (*c*-C₄F₈O) over the wavenumber region 900–1500 cm^{−1}. The line is a linear least-square fit to the data set, forced through the origin. The absorption length was 15 cm.

S-2.2 O(¹D) reaction

Table S5. Summary of the relative rate measurements for the reaction O(¹D) + *c*-C₄F₈O at 296 K.

Experiment	Pressure range (Torr)	k/k_{CHF_3} ^a	k (10 ^{−12} cm ³ molecule ^{−1} s ^{−1}) ^b
1	312–669	0.293±0.015	0.71
2	100–495	0.175±0.007	0.42
3	101–630	0.167±0.011	0.40

a) 2σ fit precision uncertainty

b) $k_{\text{CHF}_3}(\text{O}(\text{}^1\text{D}) + \text{CHF}_3) = 2.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

S-2.3 Medusa GCMS mass spectra

Mass spectra were measured on two instruments and results are given in Table S6. One *c*-C₄F₈O mass spectrum was measured on the Empa laboratory Medusa GCMS (Medusa-20), fitted with a Porabond Q column, using a diluted aliquot of the pure substance (SynQuest Laboratories, Inc., Alachua, Florida, USA, Lot #Q14B-29). The mass spectrum was measured in the range 49–225 mass/charge (m/z). Another mass spectrum was measured on Medusa-9, which is the instrument used for the archived air sample analysis. For this purpose, an aliquot of a diluted mixture of HCP-Carba-04 was combined with a selection of other pure compounds to produce a high-concentration multi-component mixture in synthetic air. Here the measured m/z scan range was chosen as 18–250. The percentages listed in Table S6 are relative to the most abundant fragment, which was chosen as 100 %. These mass spectra were somewhat surprising. Oxygen-containing fragments were only weakly present, C₂OF₃⁺ being the most abundant of them (3 %), followed by C₃OF₃⁺ (m/z 109) and C₃OF₄⁺ (m/z 128) at <1 % compared to the most abundant fragment. Also, the abundant m/z 69, which we interpret as CF₃⁺, is suggested to be the result of a rearrangement of atoms during ionization, because a simple break-up of the cyclic structure, which has two fluorines attached to each carbon, could not produce such a fragment. The same argumentation is true for m/z 169 (C₃F₇⁺) and m/z 119 (C₂F₅⁺), which are also relatively abundant. We have not found published mass spectra for *c*-C₄F₈O in the literature, with which we could compare our results. Such rearrangements are known for fully fluorinated cyclic fluorocarbons as is shown by Mohler et al. (1952) or on the internet by the National Institute of Standards and Technology (NIST, 2018). For example, for *c*-C₄F₈ (CAS 115-25-3), *c*-C₅F₁₀ (CAS 376-77-2), and *c*-C₆F₁₂ (CAS 355-68-0) the fragments with m/z 69 (high abundance) and 119 are both present in their mass spectra. Our own work also shows that for *c*-C₃F₆ (CAS 931-91-9), the CF₃⁺ fragment (m/z 69), is the second-most abundant fragment.

Table S6. Mass spectra for *c*-C₄F₈O based on gas-chromatography Electron-Impact (EI) ionization mass spectrometry (Agilent 5975 MS) for two Medusa-GCMS instruments. The range chosen for Medusa-20 was m/z 49–225, and that for Medusa-9 was 18–250.

Medusa-20			Medusa-9		
abundance in %	measured m/z	assumed fragment	abundance in %	measured m/z	assumed fragment
100	100	C ₂ F ₄ ⁺	100	100	C ₂ F ₄ ⁺
38	69	CF ₃ ⁺	46	69	CF ₃ ⁺
37	150	C ₃ F ₆ ⁺	29	150	C ₃ F ₆ ⁺
25	169	C ₃ F ₇ ⁺	16	169	C ₃ F ₇ ⁺
7	131	C ₃ F ₅ ⁺	5	50	CF ₂ ⁺
5	119	C ₂ F ₅ ⁺	5	131	C ₃ F ₅ ⁺
5	50	CF ₂ ⁺	4	119	C ₂ F ₅ ⁺
3	97	C ₂ OF ₃ ⁺	3	97	C ₂ OF ₃ ⁺

S-2.4 Medusa-GCMS Nonlinearity Experiments

Two different types of nonlinearity tests were performed as part of the archived air analysis. In a first test (volume-non-linearity), variable volumes of the standard E-146S were measured, alternating with measurements of 3 L volume samples of this standard. Within measurement uncertainties, and when volume-corrected, this showed a constant response relative to the standards' injections. However because of the relatively high mole fraction of *c*-C₄F₈O in E-146S (~500 ppq) and limitations to the instrumental technique, this method did not allow for the complete coverage of the full range measured in our archived air samples (only to ~50 ppq). In a second experiment, a molar non-linearity was determined by a pressure-based dilution of an aliquot of the standard E-146S, which was measured (two measurements per dilution) against the undiluted E-146S each time before it was further diluted in the same canister (4.5 L internally electropolished stainless steel tank, Essex Industries, USA).

10 The canister was immersed in a water bath to thermally stabilize and pressure was allowed to equilibrate after each dilution step. Pressure was accurately measured (pressure gauge CRYSTAL XP2i, Crystal Engineering Corporation, San Luis Obispo, CA, USA). For the dilution, purified synthetic air was used, which was prepared similar to that described by Vollmer et al. (2015) and shown to be free of *c*-C₄F₈O. The measured mole fractions in the diluted sample measurements were compared to the calculated mole fraction and also to the mole fraction of compounds with large peak sizes (CCl₂F₂ and CCl₃F). This

15 test showed linearity within the measurement uncertainties for a tested range covering 500 ppq (upper limit) to the detection limits (~5 ppq). These tests further showed the absence of blanks, memory effects, nafion drier interferences, or other potential systematic biases as the fitted curve of the mole fraction vs. the dilution ratio intersected the origin, and the slope of the fit equaled (within measurement uncertainties) the mole fraction of the E-146S standard. These results are presented in Figure S2, and zoomed into the more relevant range for this analysis, in Figure S3.

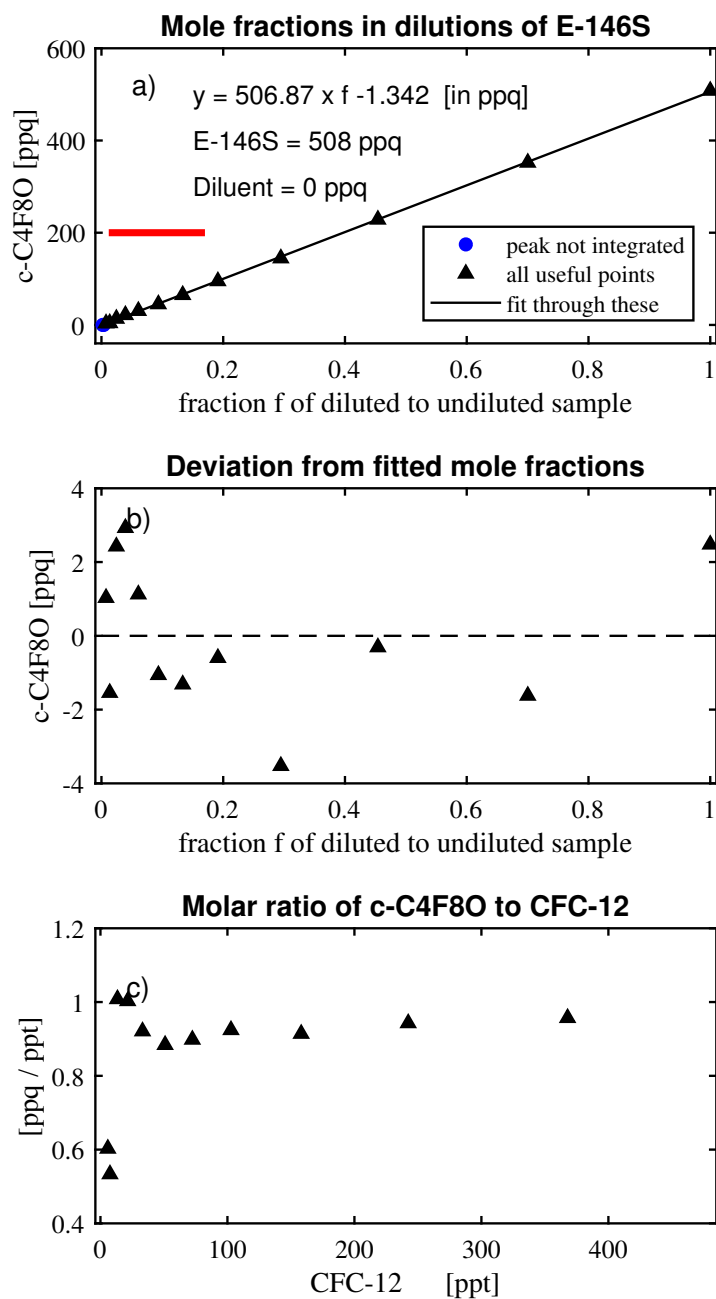


Figure S2. Results of experiments to test for non-linearity of response in measurements of $c\text{-C}_4\text{F}_8\text{O}$ using pressure-based dilutions of an aliquot of the standard E-146S. a) Measured mole fractions as a function of the dilution ratio to E-146S — dilutions were made from an aliquot of E-146S (at $f=1.0$, from right to left). The slope of the fit agrees well with the mole fraction in the undiluted sample and the $f=0$ crossing is close to zero. The red bar denotes the mole fraction range of the measured air samples. b) Deviation from fit in a). c) Molar ratio to CFC-12. These results suggest a linear system response within the range of the measured sample mole fractions.

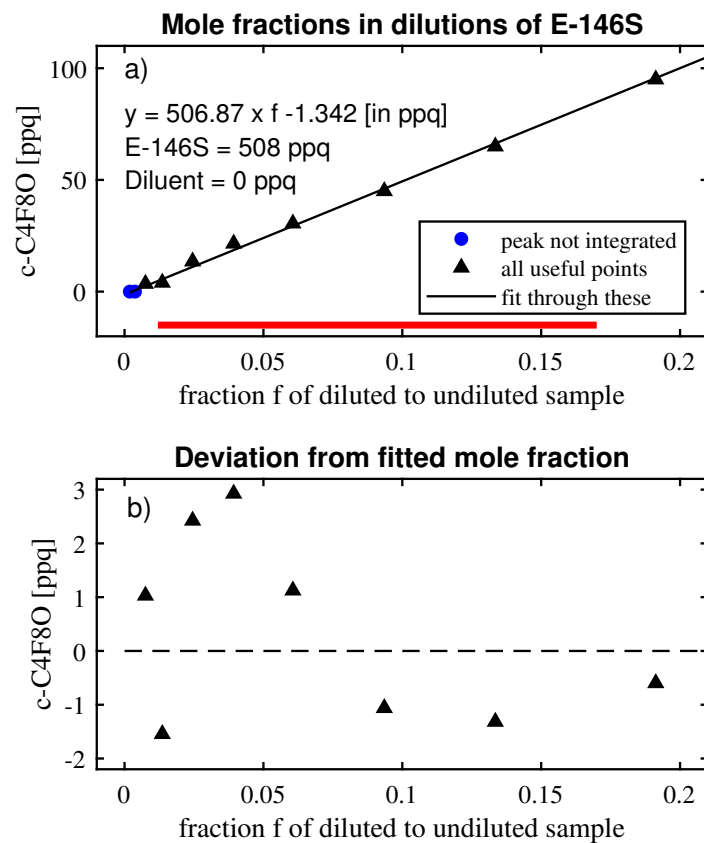


Figure S3. Results of experiments to test for non-linearity of response in measurements of *c*-C₄F₈O using pressure-based dilutions of an aliquot of the standard E-146S. Same as Figure S2 but for a narrower range of the dilution factor *f*.

S-2.5 Measurements of *c*-C₄F₈O on other instruments

Measurements of *c*-C₄F₈O using the “traditional” AGAGE Medusa-GCMS Porabond Q chromatography column (Miller et al., 2008) revealed some difficulties. We have routinely measured *c*-C₄F₈O in ambient air samples at Jungfraujoch and urban Dübendorf (Switzerland) since late 2012 using Porabond Q columns. However on the columns used in these two Medusa-GCMS (Medusa-12 and Medusa-20, respectively), *c*-C₄F₈O elutes shortly after *c*-C₄F₈ (PFC-318), normal and iso-C₄F₁₀, and occasionally and also after another unidentified compound, and is negatively influenced by common ion fragments. Integrations of the small *c*-C₄F₈O chromatographic peaks are difficult and error-prone. For this reason we refrain from reporting the >5 year long records at these two stations. However within the uncertainties of the measurements we can report the absence of pollution events over this period indicating the absence of significant *c*-C₄F₈O emissions within the footprints of the two sites.

Larger chromatographic peaks, such as those resulting from measurements of standards spiked with *c*-C₄F₈O were not negatively influenced by the above-mentioned interference and allowed to maintain and propagate an internally consistent set of calibration standards.

S-3 Inversion details

The inversion calculation estimates annual *c*-C₄F₈O emissions using the two Aurora Basin North (ABN) firm measurements and annual values from a smoothing spline fit (with 50 % attenuation at periods of 10 years) to CGAA and Aspendale in situ observations. We calculate the uncertainty in estimated emissions using a bootstrap resampling method, where the inversion is repeated using observations that have been perturbed according to their uncertainty, with the ensemble of firm model parameters to represent firm model uncertainty, a range in the background mole fraction (we use up to 1.0 ppq for *c*-C₄F₈O) and various plausible choices for the north-south distribution of emissions. The year-to-year uncertainty in annual values from the spline is small because interannual variability has been strongly suppressed by the spline smoothing; we therefore do not independently perturb the annual values from the spline according to their uncertainty, as this leads to unrealistically high variability in the estimated emissions. Instead we independently perturb only the firm measurements, and for the annual means we add values from a temporally-correlated function with periods of around 10 years or more. The function we use is

$$f = p_1 \times \cos(2\pi(t + p_2)) + p_3 \times \cos(2\pi(t + p_4)) + p_5 \times \cos(2\pi(t + p_6))$$

where t is $(\text{year} - 1978)/(2019 - 1978)$ and the parameters p_1 - p_6 are random numbers in the range [0,1]. The integral of this function over the period 1978 to 2018 is zero, and the magnitude is less than 1.0 most of the time. The function is scaled to achieve the level of systematic error required, for *c*-C₄F₈O we have chosen a magnitude of 1.0 ppq, representing 2σ . We also perturb all mole fraction data by a constant amount (2σ range of $\pm 15\%$) to incorporate the absolute uncertainty in the measurements, predominantly due to uncertainty in the calibration scale.

Figure S4 shows the sensitivity of calculated emissions to a number of model choices and inputs, including the regularization parameter α , that weights the sum of year-to-year emission changes relative to the model-data mismatch in the cost function (Trudinger et al., 2016), calibration uncertainty, diffusion coefficient of *c*-C₄F₈O in air relative to CO₂ in air, the prior emissions

estimate (used only as a starting point for the inversion and not included in the cost function) and the north-south distribution of emissions. The preferred values of these inputs are indicated in the legends with the asterisks. The preferred value of α is chosen to allow plausible variations in emissions, but not what seem like unrealistic variations. The range in emissions corresponding to $\pm 15\%$ uncertainty in absolute mole fraction is shown by the range in Figure S4c. The diffusion coefficient

5 alters the emissions estimate prior to 1978 when the CGAA begins — low values of the relative diffusion coefficient cause high emissions in the 1950s that are probably unrealistic. The results are fairly insensitive to the prior emissions estimate and north-south emissions distribution.

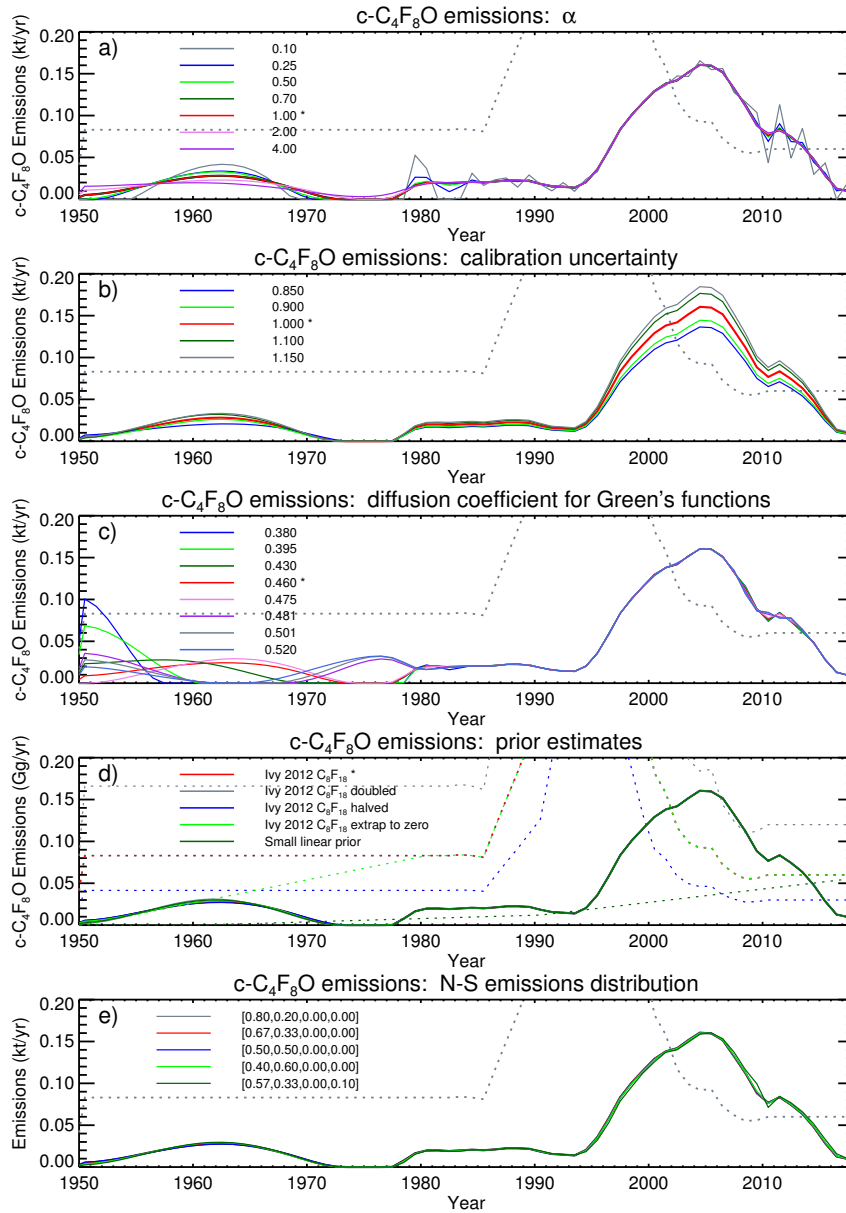


Figure S4. Sensitivities to various parameters in the inversion calculation. a) The parameter α weights the term in the cost function that involves the sum of year-to-year changes in emissions, relative to the model-data mismatch term, b) calibration uncertainty for $c\text{-C}_4\text{F}_8\text{O}$ measurements, that is included in the bootstrap uncertainty calculation, c) diffusion coefficient of $c\text{-C}_4\text{F}_8\text{O}$ relative to the diffusion coefficient of CO_2 that is used in the firm model to calculate the Green's functions, d) prior emissions used as a starting point for the inversion and e) the proportion of emissions emitted from each semi-hemispheric box in the model, assumed constant for each inversion calculation. In the legend of each panel, the asterisk indicates the choice used in our best case.

Figure S5a shows the two ABN measurements of $c\text{-C}_4\text{F}_8\text{O}$ in firn, with the modeled depth profile for the inferred emissions. Fig. S5b shows the $c\text{-C}_4\text{F}_8\text{O}$ Green's functions from the firn model for the two ABN depths, with colors matching the measurements shown in Fig. S5a. The thick line shows the preferred Green's function, with this lines showing the ensemble of Green's functions, although they differ little from the preferred function. The shallow ABN sample (from 30.4 m) is shown in blue and contains air mainly from the 2000s up to the firn sampling date in 2013, with a small amount of air from the 1990s and possibly 1980s. The deep ABN sample (from 101.9 m) is shown in green and contains a mix of ages from before 1950 up to at least the 1980s. We know from the CGAA record that atmospheric $c\text{-C}_4\text{F}_8\text{O}$ was non-zero in the 1980s, so even if the background level was zero we would expect to see non-zero mole fraction in this sample. We can therefore not determine from the measurements used in this study whether $c\text{-C}_4\text{F}_8\text{O}$ is entirely anthropogenic with a zero background, or has a non-zero background level.

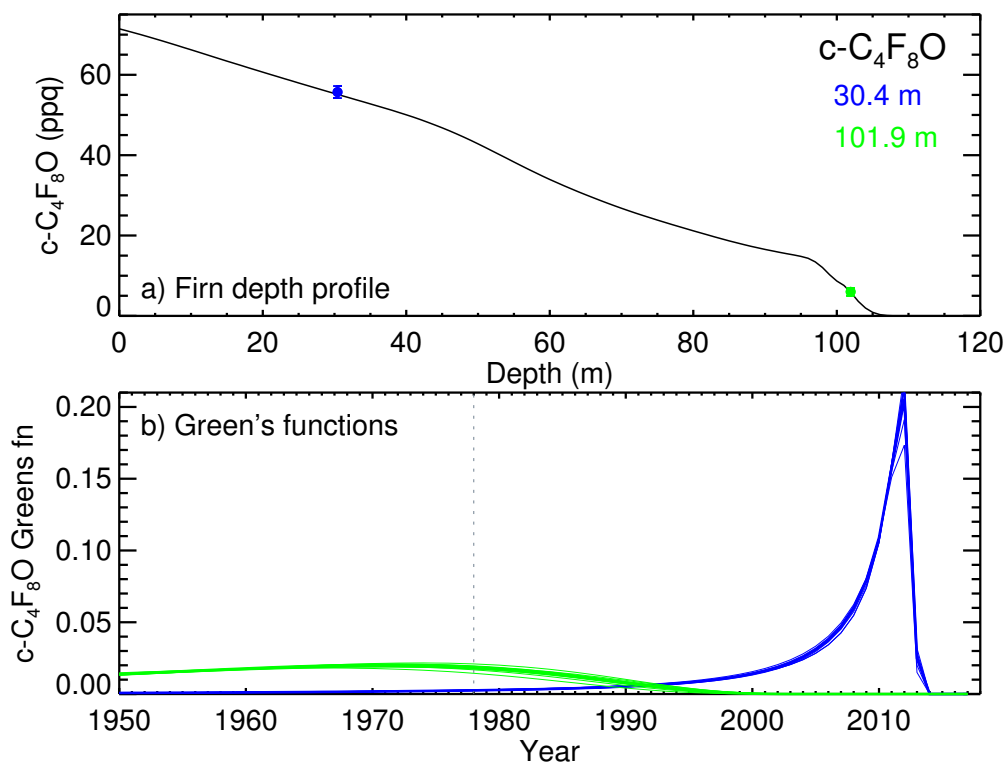


Figure S5. a) Modeled depth profile corresponding to the inferred emissions and b) Green's functions for the two Aurora Basin North (ABN) firn samples, with the sample from 30.4 m shown in blue, and from 101.9 m shown in green.

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