A novel analytical method for measuring high-resolution vertical profile of stratospheric trace gas mole fractions using a GC-ECD

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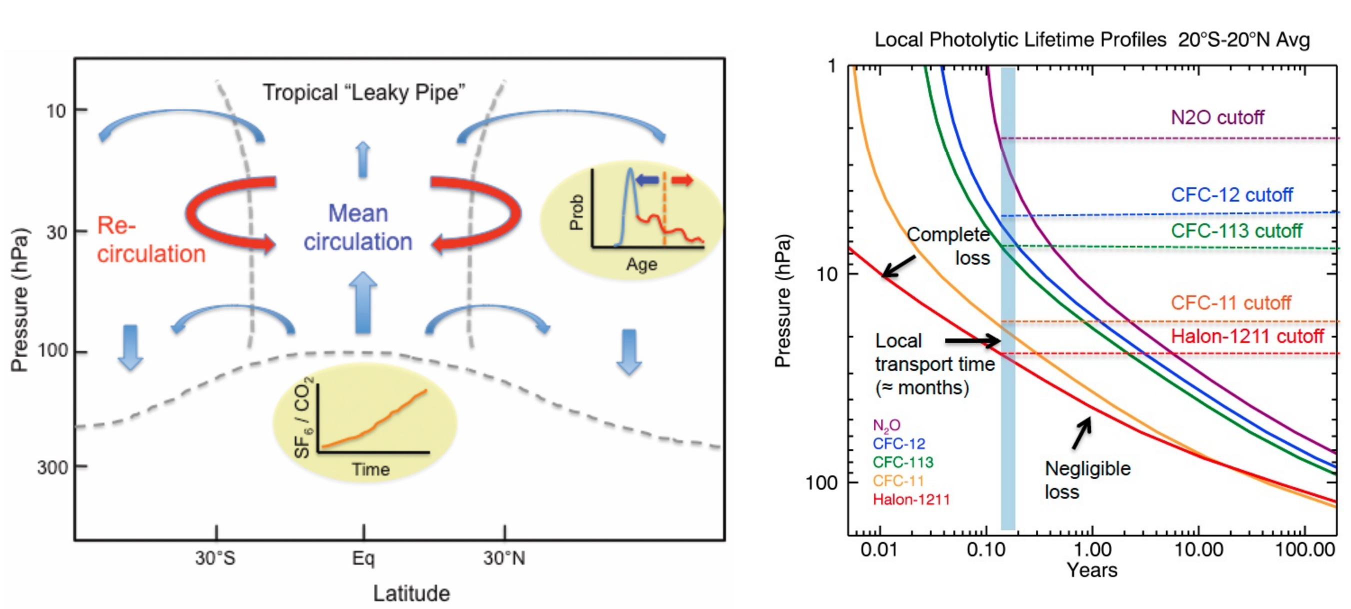
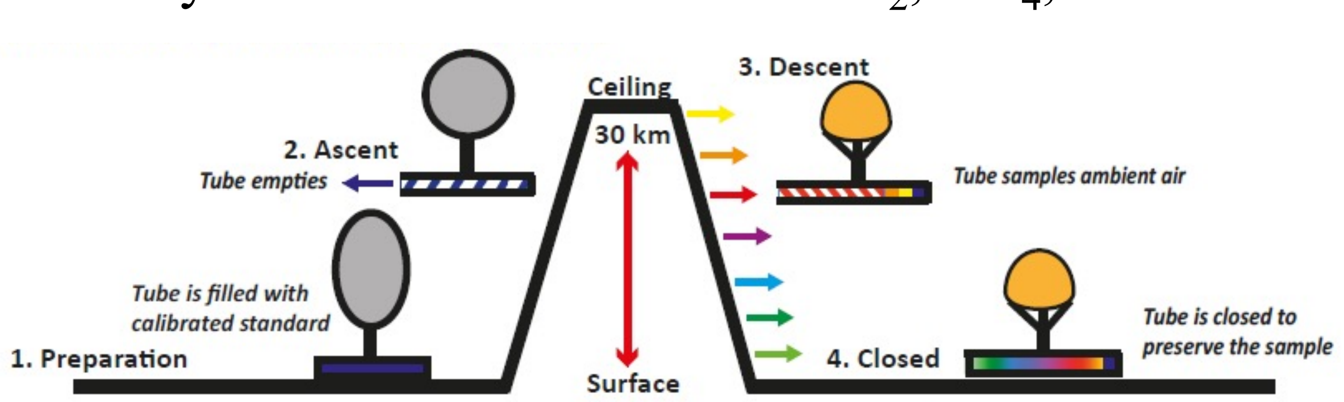
Introduction

- Characterizing stratospheric circulation is crucial for a better understanding in the climate;
- Direct observation of stratospheric circulation is difficult, but the dynamics can be inferred from the abundance of a suite of trace gases;
- A combination of "age tracer" gases (CO_2, SF_6) and photochemical reactive trace gases (N_2O, CFC-11, CFC-12, CFC-113, H-1211) is a great tool for investigating stratospheric circulation;



Left: sketch of stratospheric circulation. Right: photochemical lifetime of various trace gases. Both figures are from Moore et al. (2013).

- Direct stratospheric observations are rare due to the high cost of aircraft campaigns;
- **AirCore** (Tans 2009, Karion et al., 2010) provides a novel approach for stratospheric observation;
- NOAA/GML brought AirCore technique to operational level over 10+ years;
- AirCore samples are analyzed by continuous analyzer for mole fractions of CO_2, CH_4, and CO

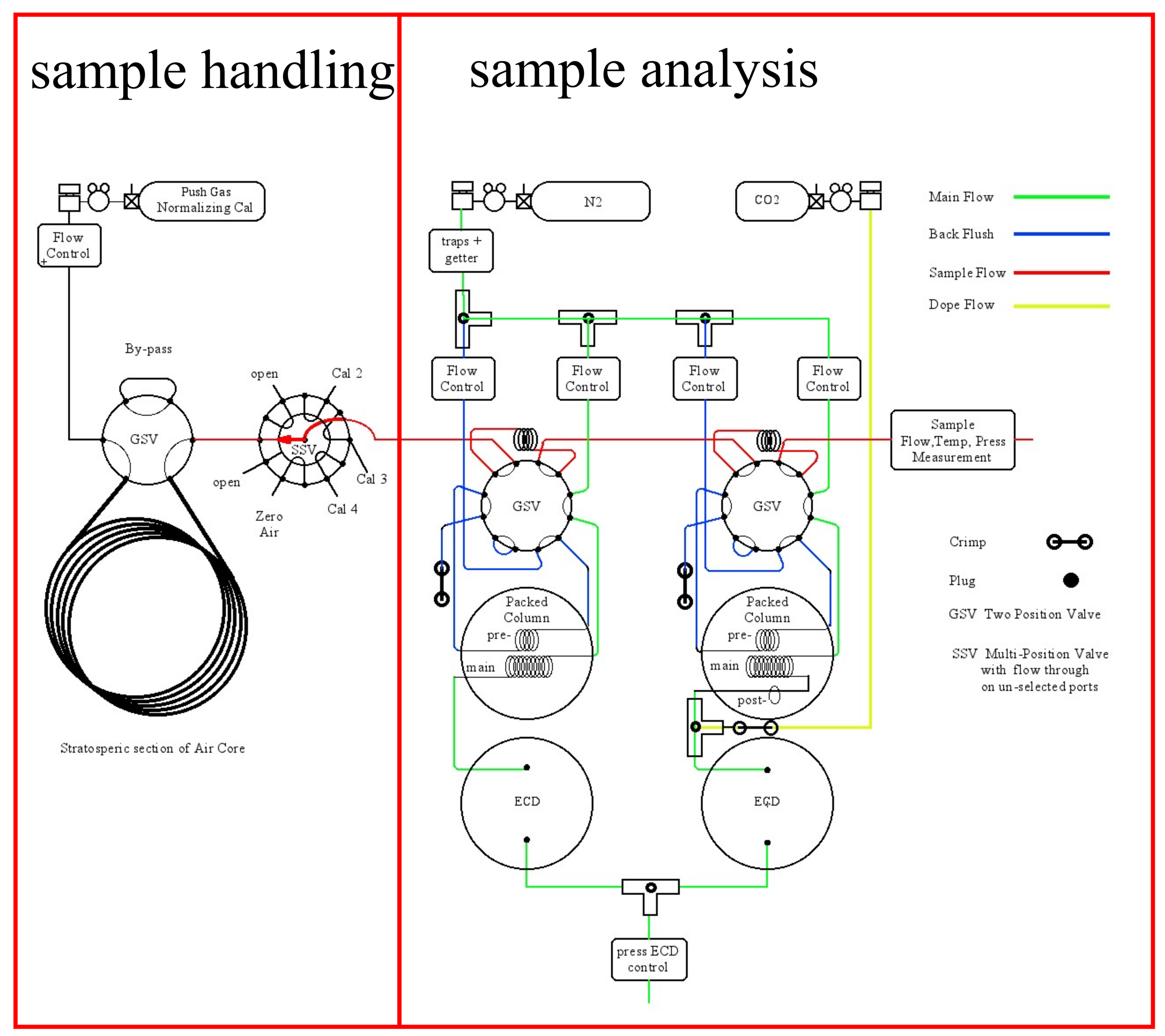


Schematic description of the five steps of the AirCore sampling method. From Membrive et al. (2017).

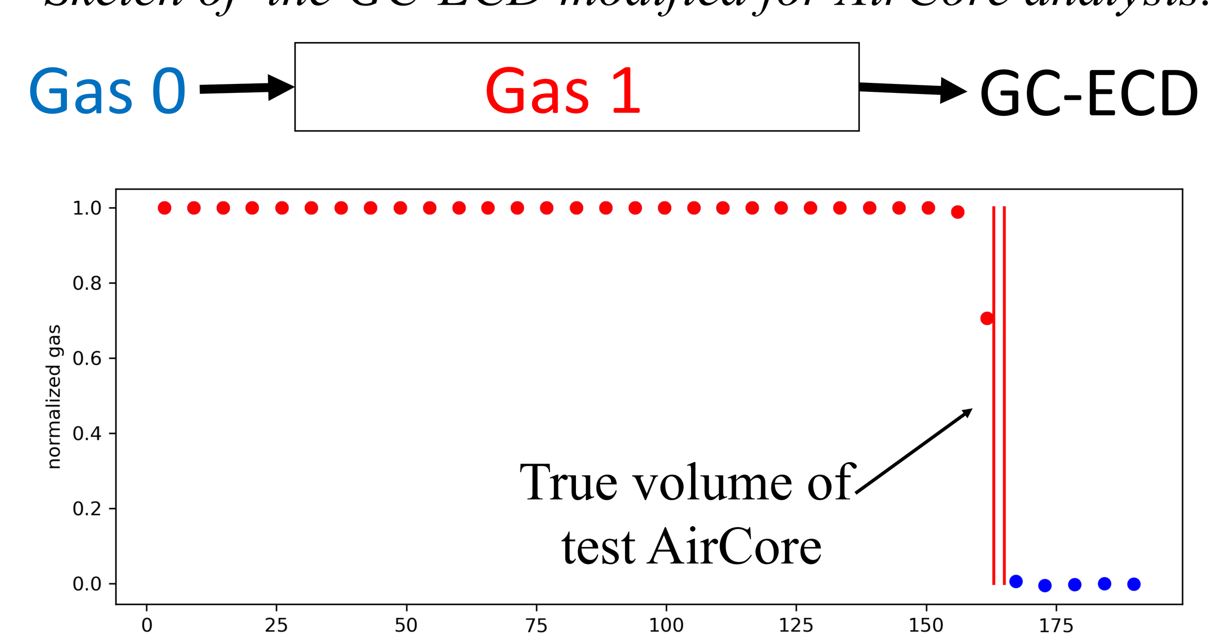
A new method for measuring more trace gas species (SF_6, N_2O, CFC-11, CFC-12, CFC-113, and H-1211) in AirCore is needed.

Methods

- A Gas Chromatography – Electron Capture Detector (GC-ECD) is adapted for analyzing mole fractions of SF_6, N_2O, CFC-11, CFC-12, CFC-113, and H-1211 in the AirCore from tropopause to mid-stratosphere;
- The system separates one AirCore sample into ~3.5-5 mL (4 hPa per sample) of discrete aliquots without inducing extra mixing;
- Each aliquot is then accurately analyzed by the GC-ECD (precision for most gases <0.25%);



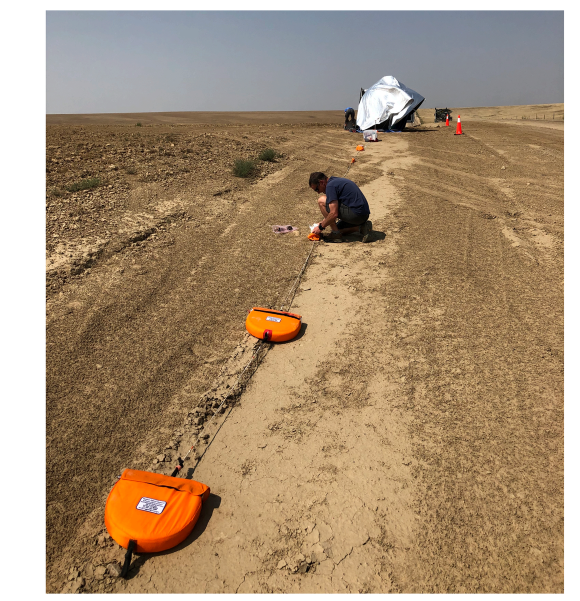
Sketch of the GC-ECD modified for AirCore analysis.



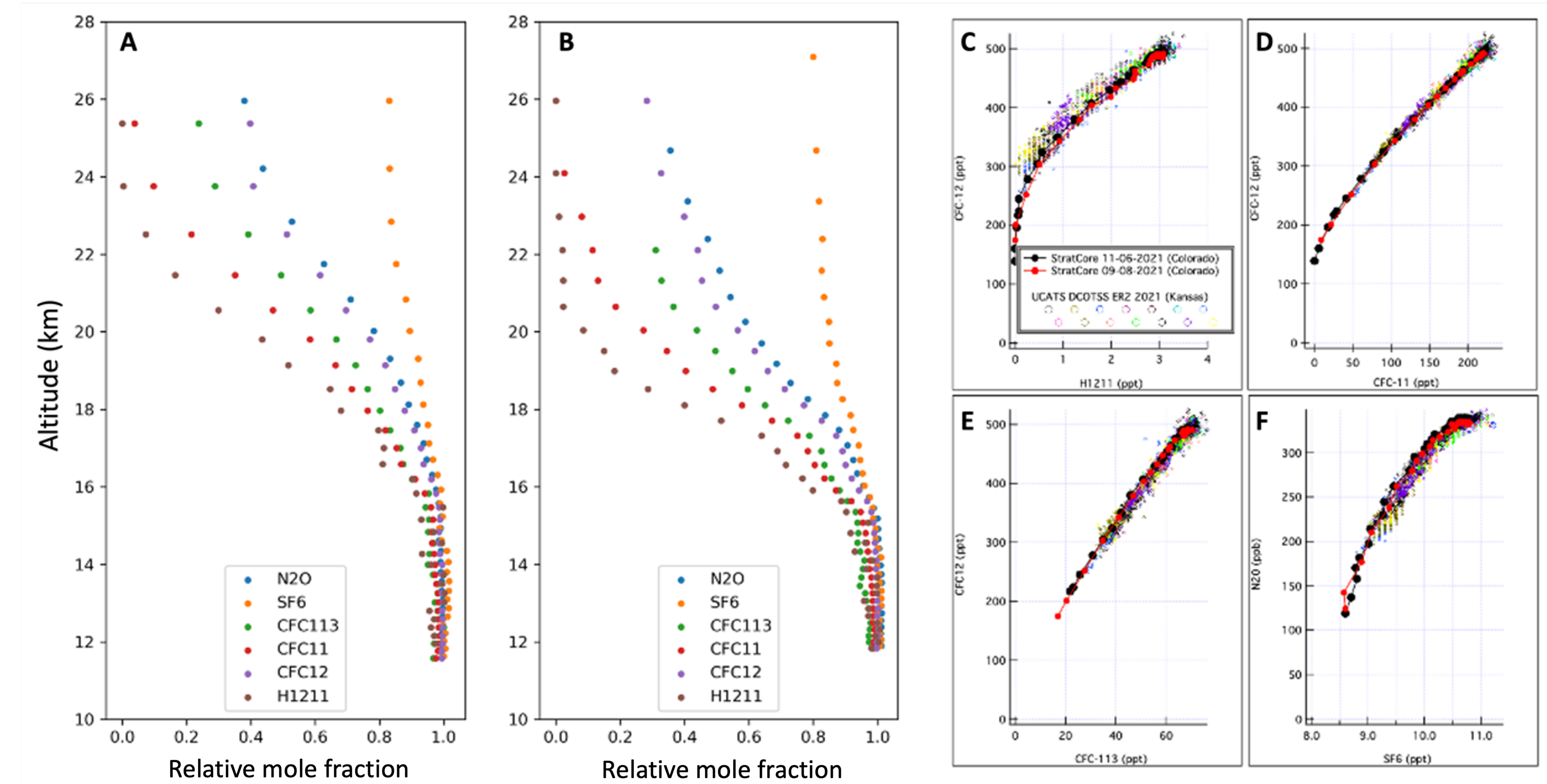
Results of GC-ECD analysis to test the degree of mixing during AirCore analysis.

- Test run showing minimum mixing during the sample injection process;
- Volume registration by the GC-ECD system is accurate.

Results



- Two AirCore flights (each with 2 AirCore samples per flight) were conducted in northeastern Colorado during fall/winter 2021;
- In each flight, one AirCore sample was used to analyze mole fractions of SF_6, N_2O, CFC-11, CFC-12, CFC-113, and H-1211 using GC-ECD;
- Another AirCore sample was used for CO_2, CH_4 and CO measurement;
- GC-ECD provided 35-45 stratospheric measurements per AirCore;
- The results showed expected dynamic ranges of trace gases from tropopause to ~26 km;
- Excellent agreement on tracer-tracer relationships with aircraft *in situ* measurements during the NASA Dynamics and Chemistry of the Summer Stratosphere (DCOTSS) campaign.



A, B: Relative mole fraction (compared with average tropospheric value) profiles of SF6, N2O, CFC-12, CFC-113, CFC-11, and H-1211 measured in two AirCores on Sept. 8 (A) and Nov. 16, 2021 (B). C-F: tracer-tracer relationships of trace gases measured in two AirCores.

Conclusion and outlook

- The novel method provides a promising, low-cost approach to directly observe the mole fractions of trace gases well into the mid-stratosphere beyond current technology;
- Adaptation of current 600 mL AirCore sampler is underway to improve the sampling efficiency in the stratosphere at ~31 km MSL;
- Routine deployment of this low-cost observation platform will advance our understanding of stratospheric dynamics.

References

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Acknowledgement

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