Clouds and Aerosols from the Atmospheric Chemistry Experiment (ACE) and SAGE-III-ISS: Overview and latest results

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and

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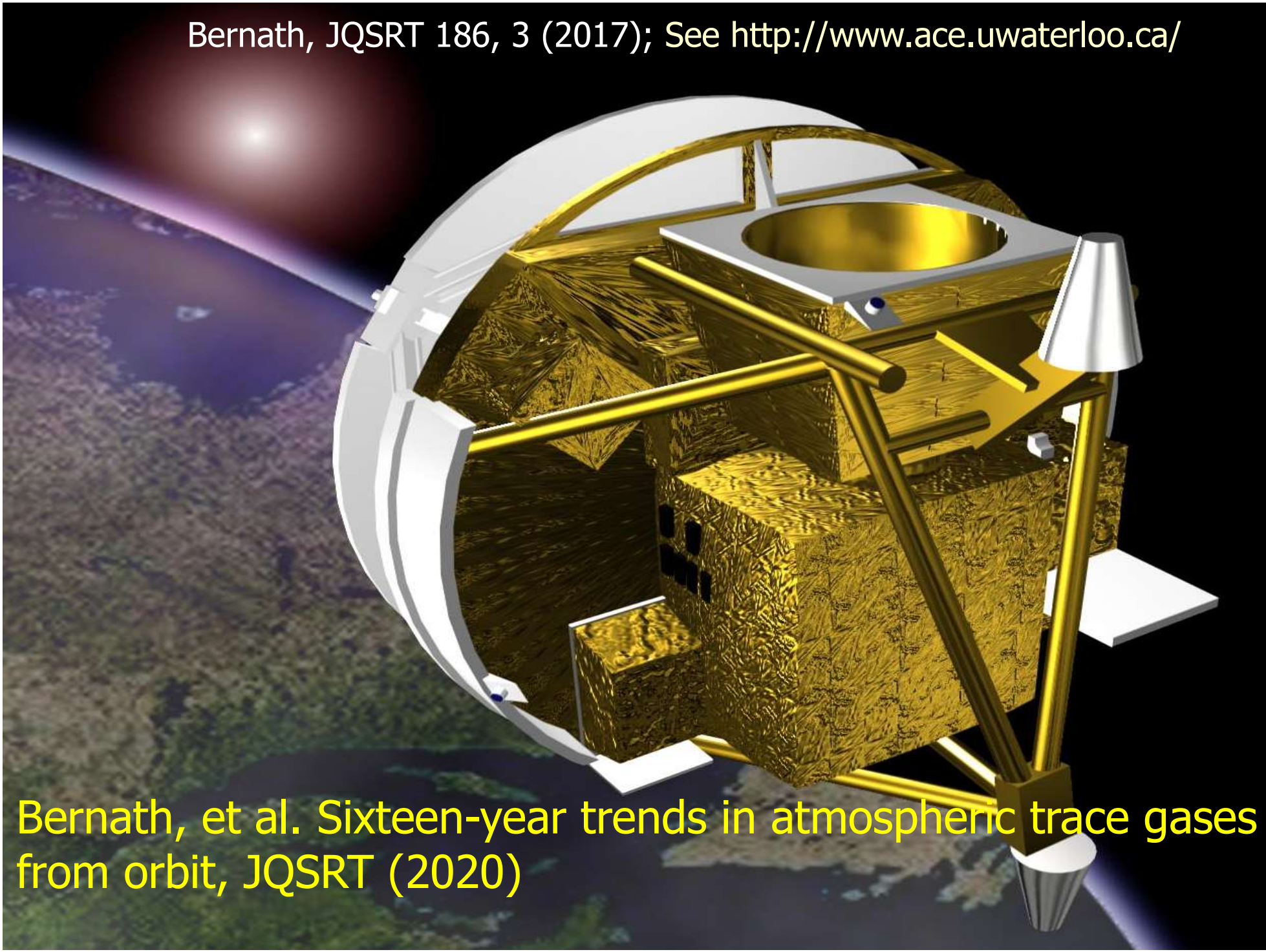
1998 Original Proposed Primary ACE Goal

To investigate the chemical and dynamical processes that control the distribution of ozone in the stratosphere and upper troposphere with a particular focus on the Arctic winter stratosphere.

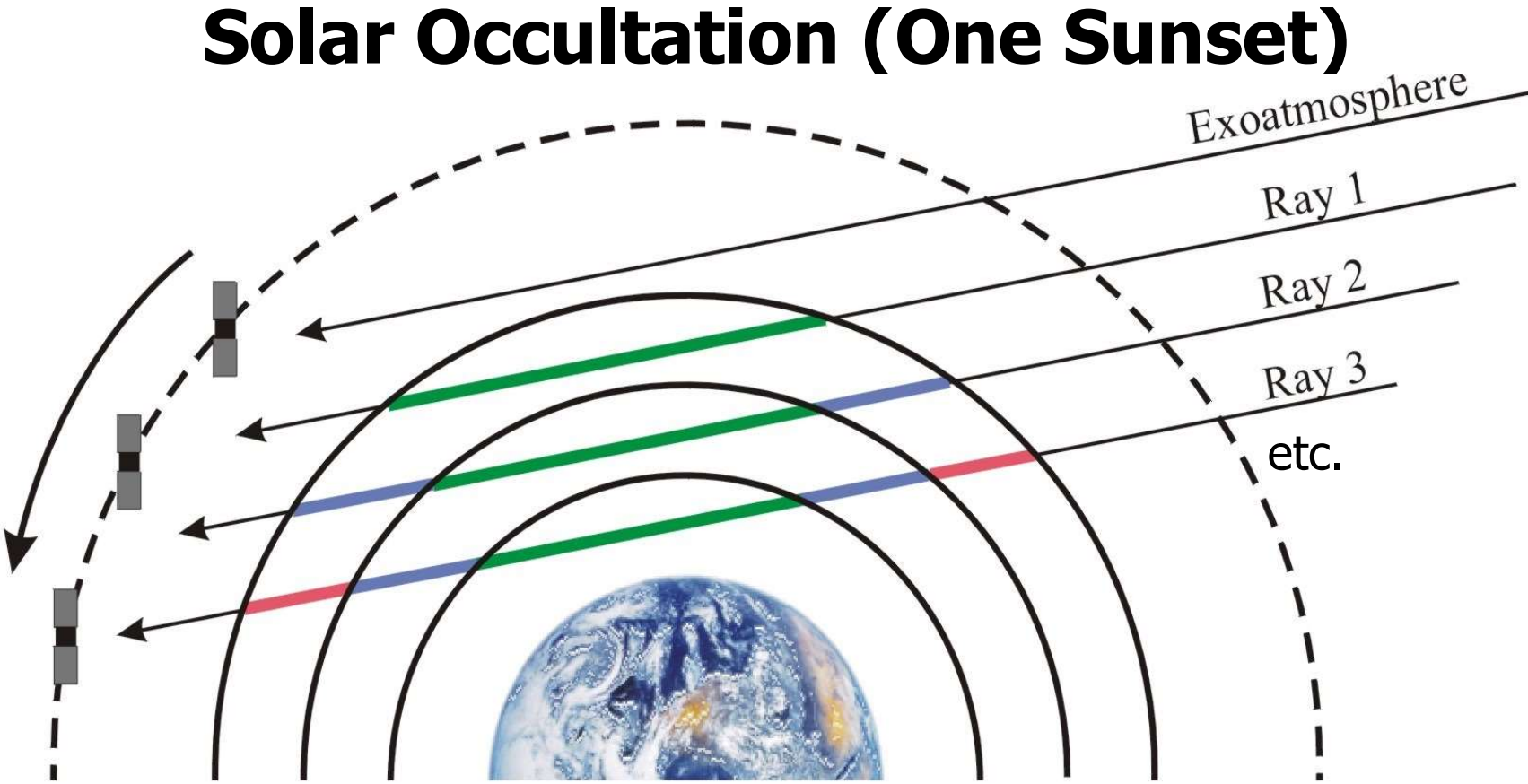
- Temperature and pressure measured.
- Aerosols measured and quantified.

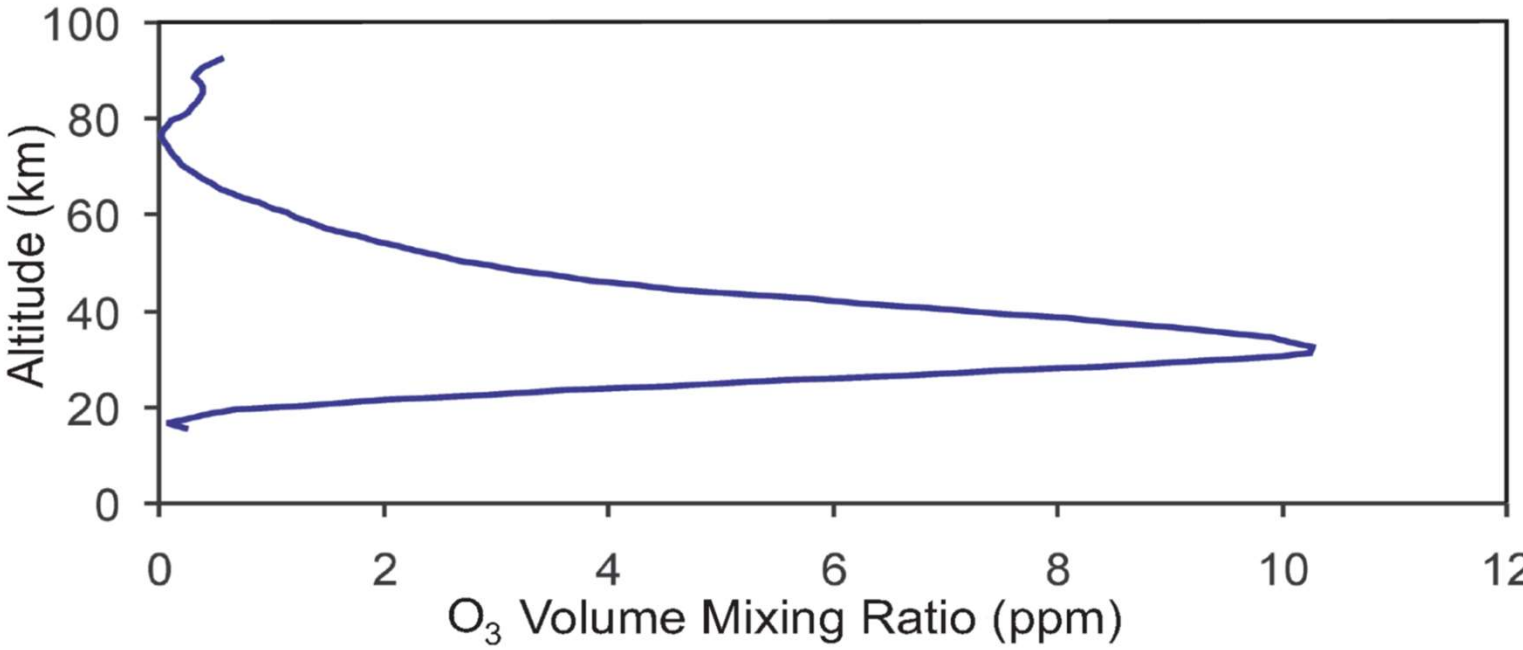
2022 **Main focus** on climate change, e.g., trends in atmospheric composition; return to aerosols and ozone.

ACE Satellite



Solar Occultation (One Sunset)





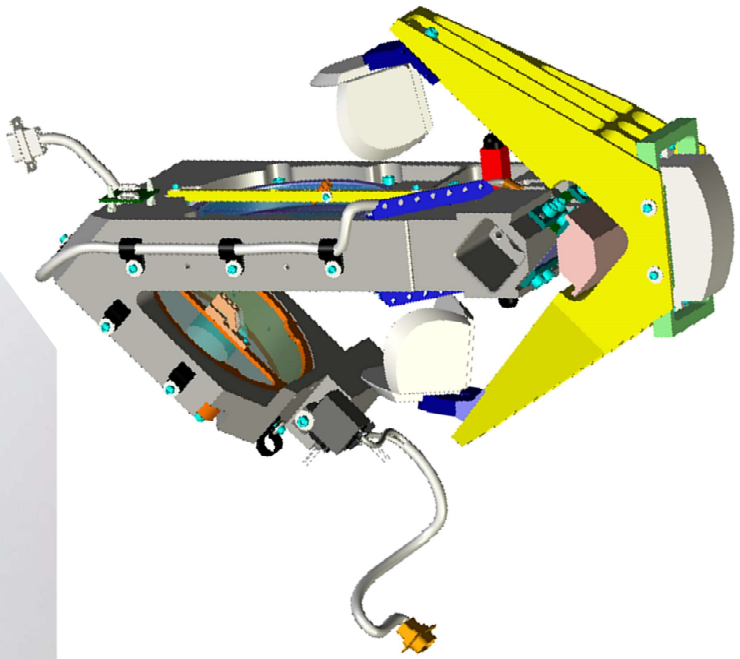
ACE makes 30-40 measurements per occultation to give one altitude profile.

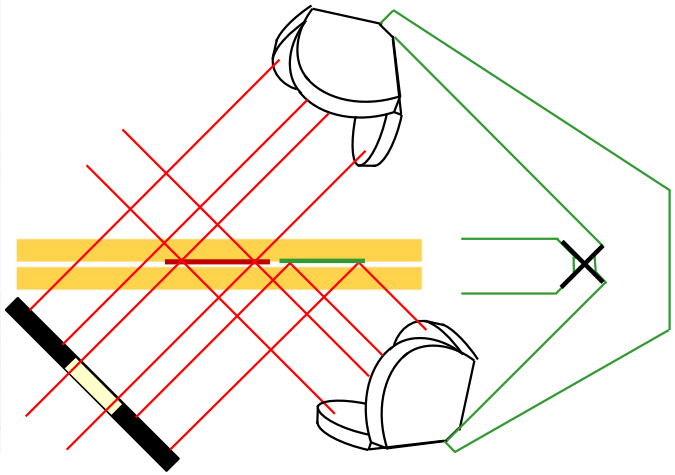
FTS design (ABB-Bomem)

Spectral resolution: 0.02 cm^{-1}
Spectral coverage: 750-4400 cm^{-1}
Vertical resolution: about 3 km
Also has 2 solar imagers at 1 & 0.5 µm

- Interferometer side

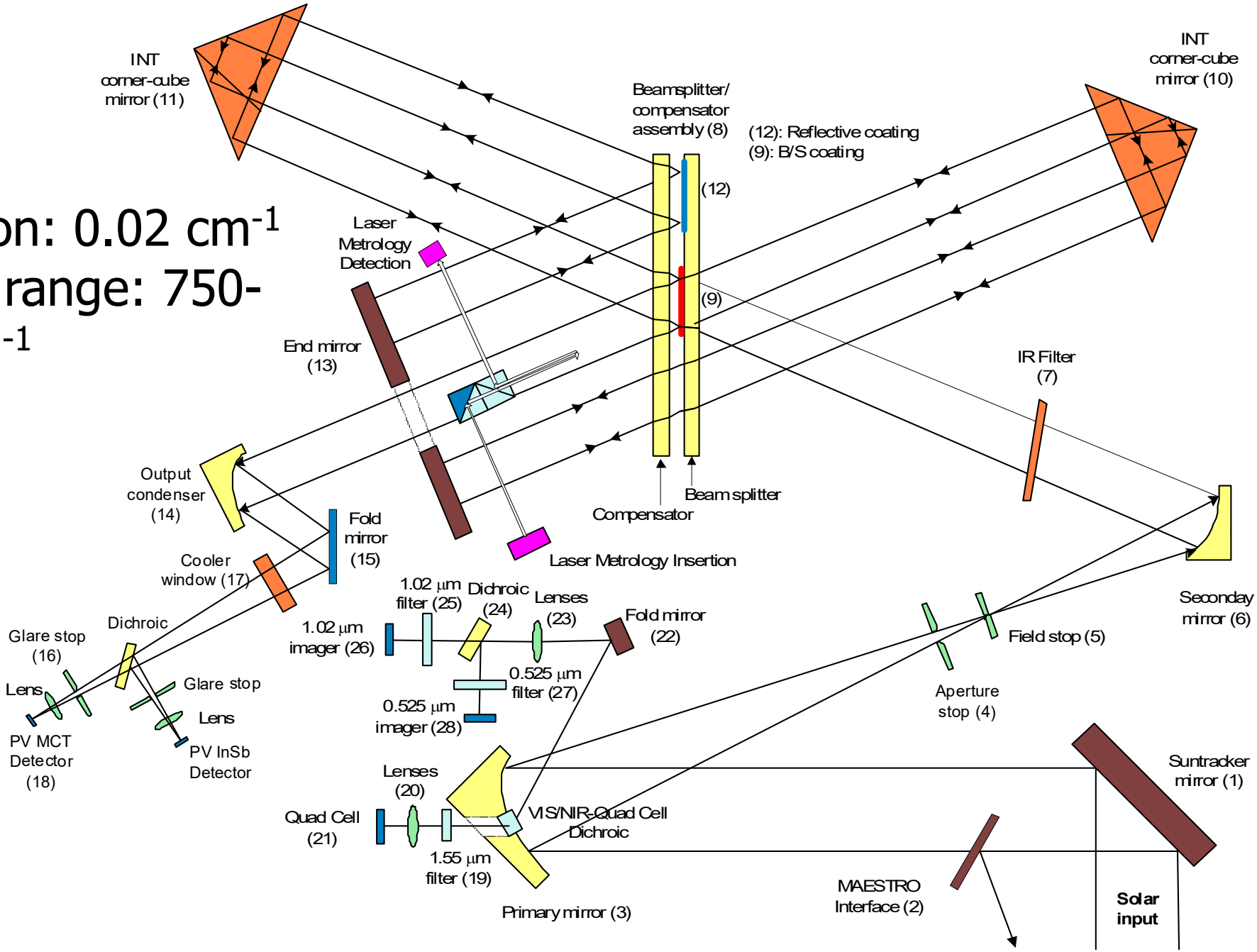
- Input side





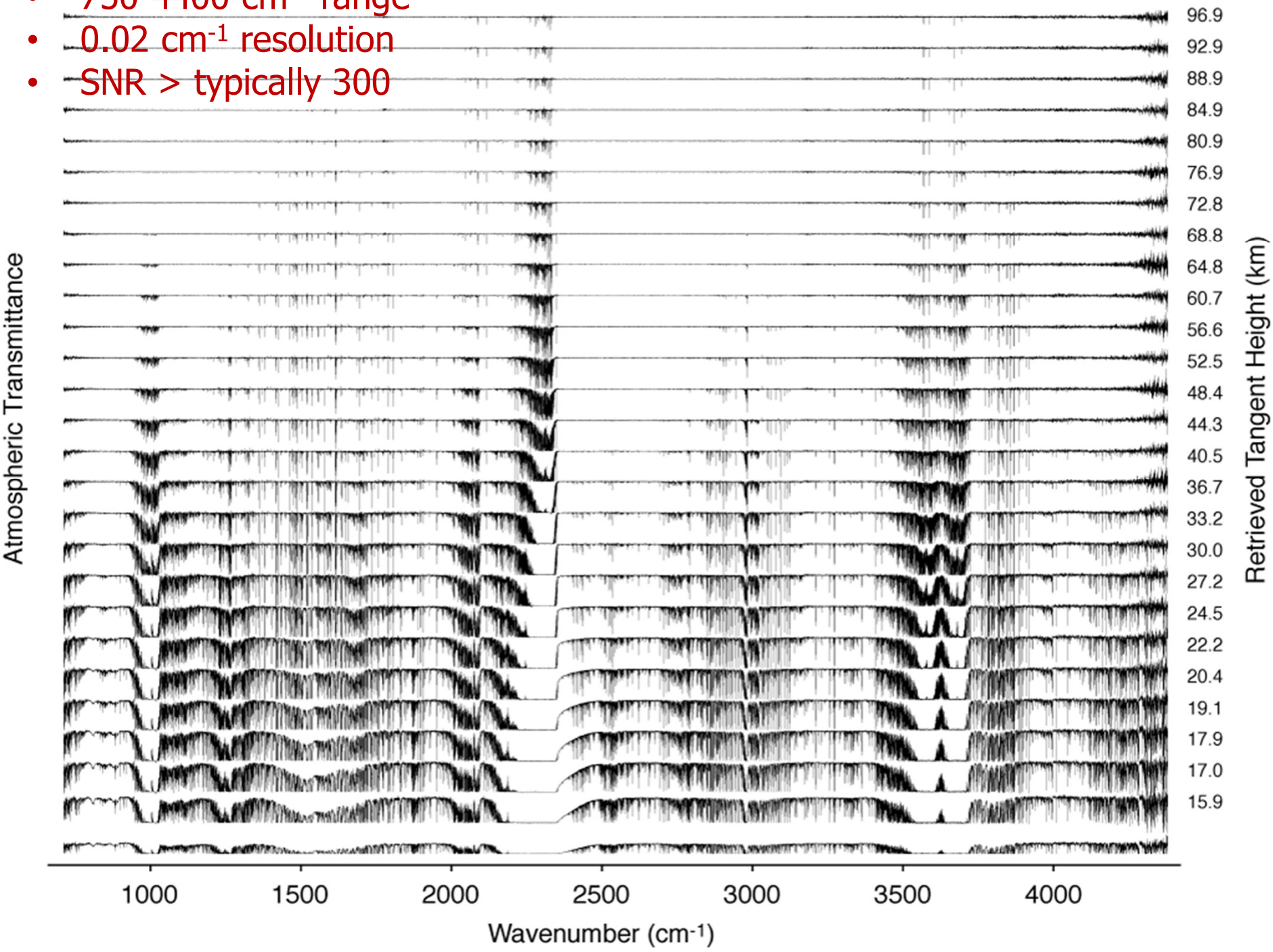
FTS Optical Layout (ABB-Bomem)

Resolution: 0.02 cm^{-1}
Spectral range: 750-4400 cm^{-1}



Occultation Sequence

- 750-4400 cm^{-1} range
- 0.02 cm^{-1} resolution
- SNR > typically 300



ACE-FTS Version 4.1/4.2 & 5.0 Species

Tracers: H_2O, O_3, N_2O, NO, NO_2, HNO_3, N_2O_5, H_2O_2, HO_2NO_2, O_2, N_2, SO_2

Halogen-containing gases: HCl, HF, ClO, $ClONO_2$, CFC-11, CFC-12, CFC-113, COF_2, $COCl_2$, COFCl, CF_4, SF_6, CH_3Cl, CCl_4, HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, HFC-23, HOCl, HFC-32

HOCl is a key new ACE molecule for stratospheric ozone depletion.

Carbon-containing gases: CO, CH_4, CH_3OH, H_2CO, HCOOH, C_2H_2, C_2H_6, OCS, HCN, $CH_3C(O)CH_3$, CH_3CN, PAN, high and low altitude CO_2 as well as pressure and temperature from CO_2 lines

Isotopologues: $H_2{}^{18}O$, $H_2{}^{17}O$, HDO, $O^{13}CO$, $OC^{18}O$, $OC^{17}O$, $O^{13}C^{18}O$, $^{18}OO_2$, $O^{18}OO$, $O^{17}OO$, $OO^{17}O$, $N^{15}NO$, ^{15}NNO, $N_2{}^{18}O$, $N_2{}^{17}O$, ^{13}CO, $C^{18}O$, $C^{17}O$, $^{13}CH_4$, CH_3D, $OC^{34}S$, $O^{13}CS$, $^{15}NO_2$, $H^{15}NO_3$

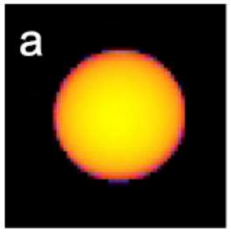
New routine species in v.5.0 are in red.

ACE is now in its 19th year on orbit. This longevity makes trend analysis feasible (with care). The change in atmospheric composition is the primary driver of climate change.

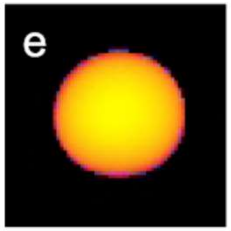
ACE retrieves 46 molecules plus 24 isotopologues.

ACE Imagers (1.02 & 0.525 µm)

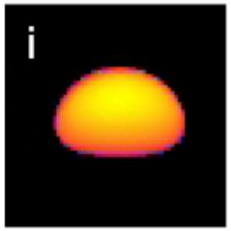
New v. 5.0 of ACE Imager processing provides extinction profiles at 1.02 µm that agree with SAGE-III-ISS values.



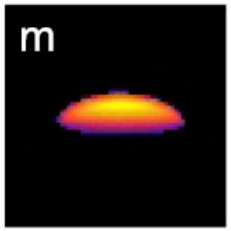
58.7 km



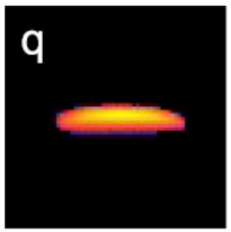
40.1 km



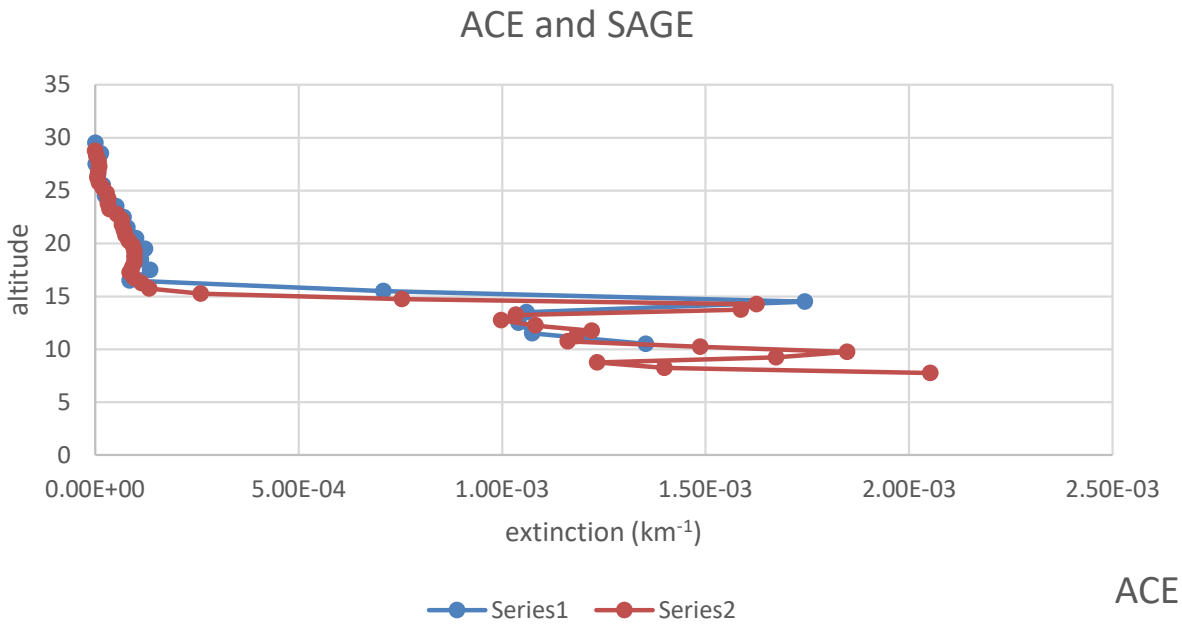
24.9 km



15.4 km

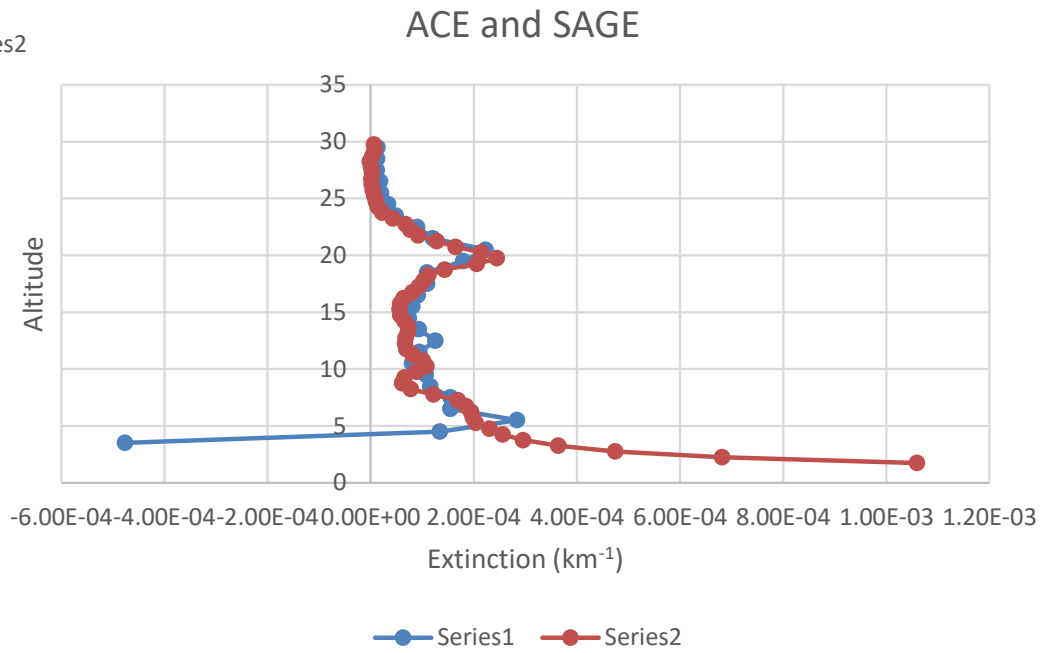


9. 9 km



ACE (blue)

SAGE (red)



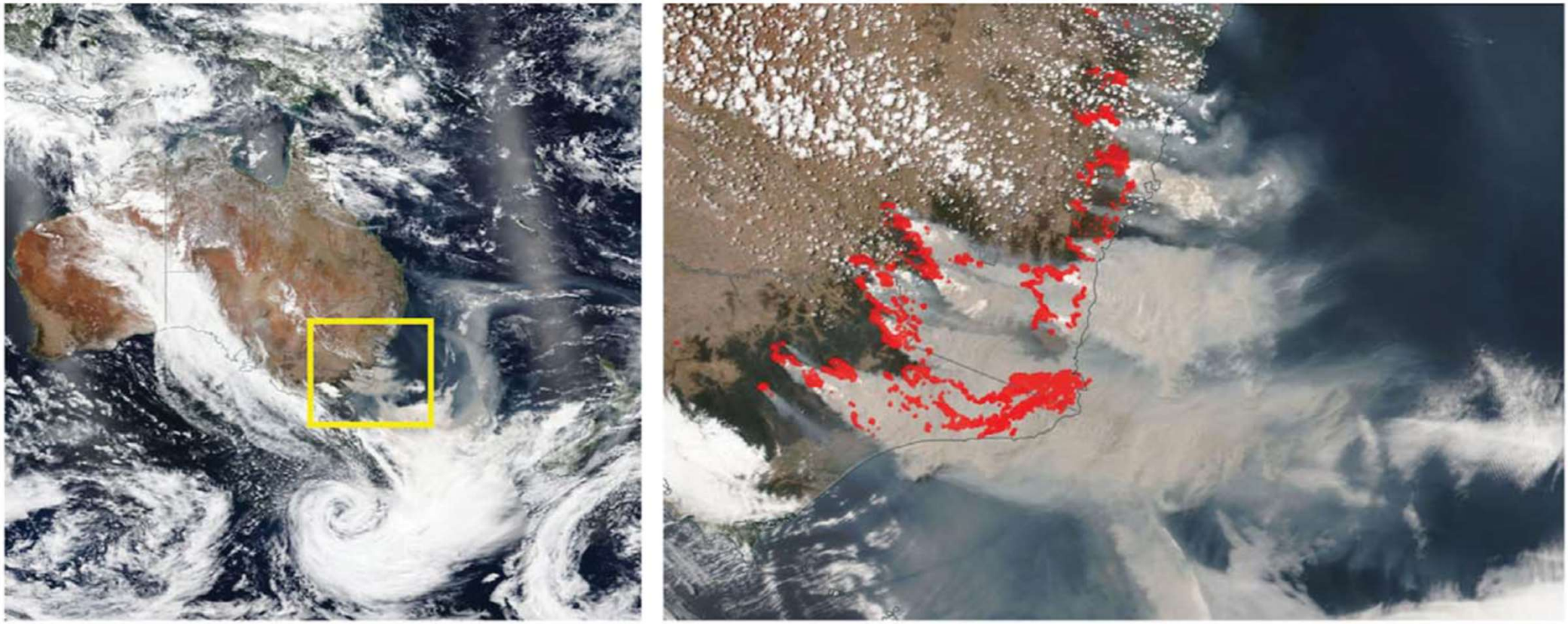
Pyrocumulonimbus Clouds, PyroCb

Clouds (except for PSCs and PMCs) are usually confined to the troposphere.

"The 'pyroCb' is a fire-started or fire-augmented thunderstorm that in its most extreme manifestation injects huge abundances of smoke and other biomass-burning emissions into the lower stratosphere." Fromm et al. BAMS (2010)

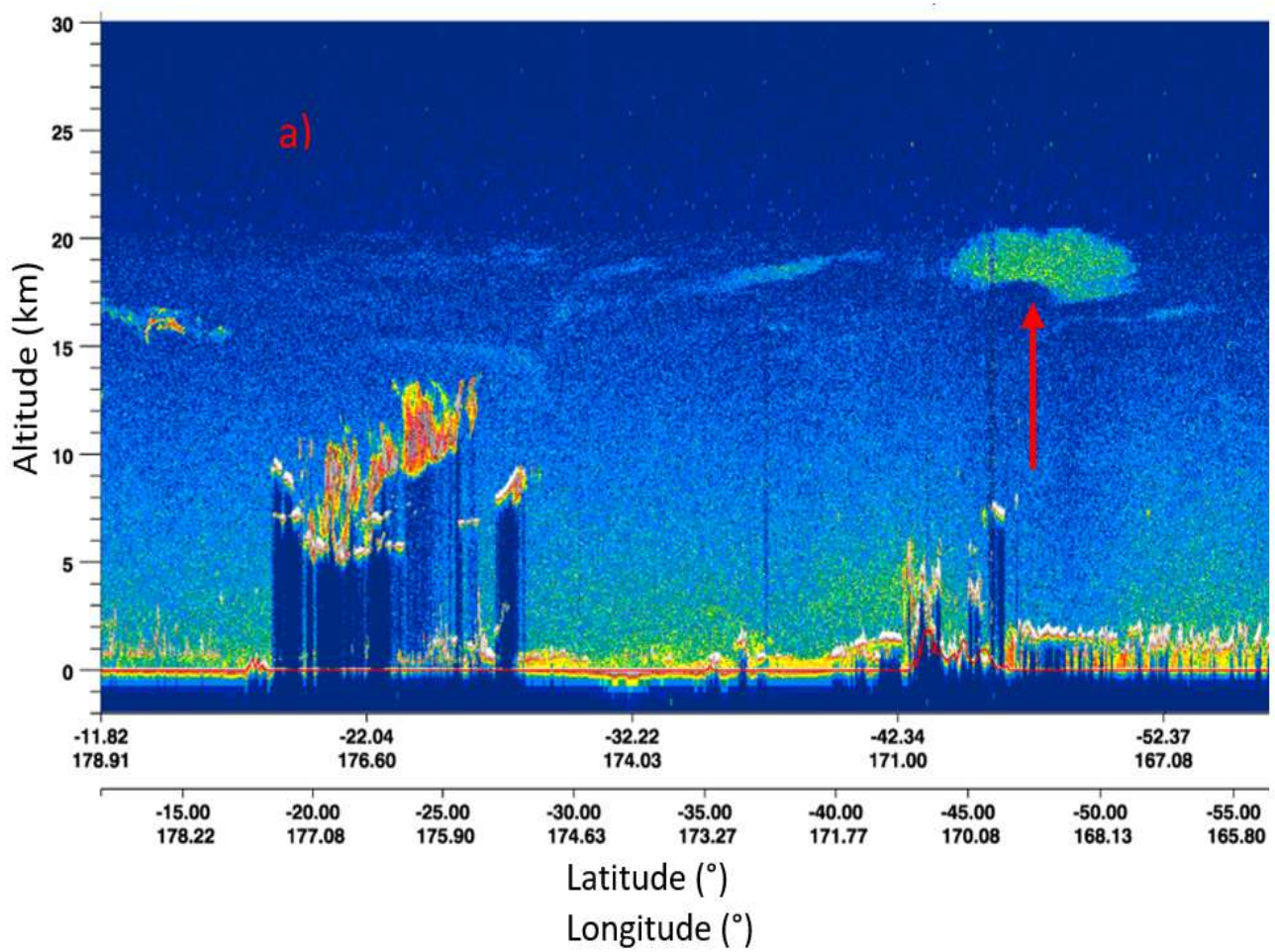
Australian Fires, 4 Jan 2020

Visible Infrared Imaging Radiometer Suite (VIIRS) images over Australia. Red dots mark the locations of fires.



Hirsch and Koren, *Science* **371**, 1269 (2021)

Aerosols from Fires (Pyrocumulonimbus)



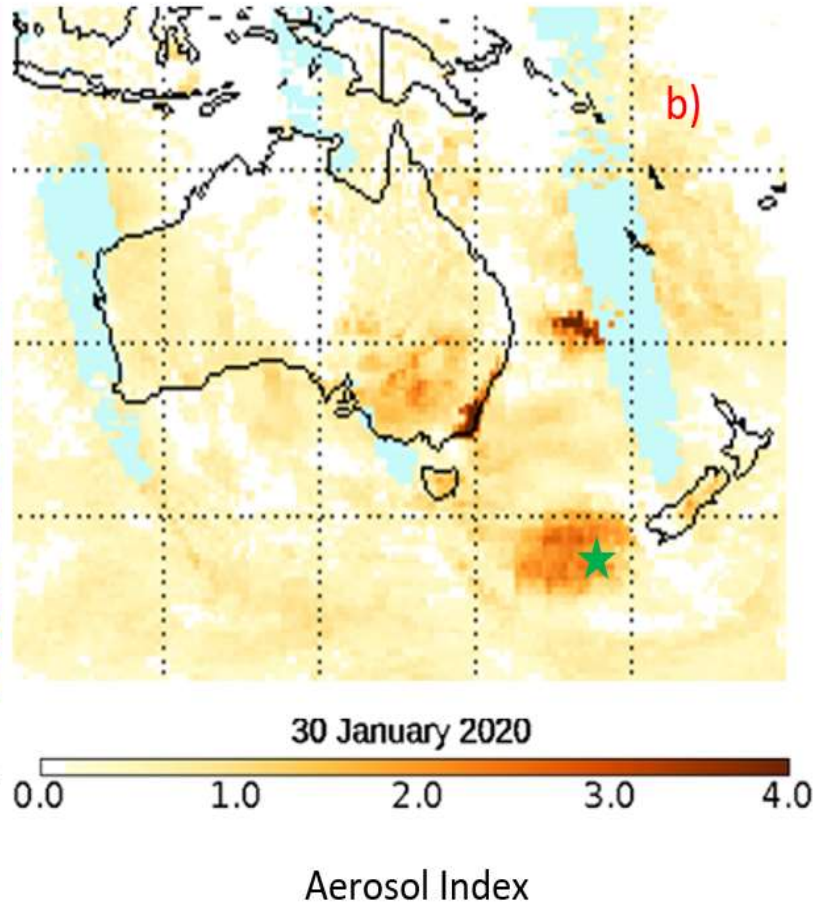


Fig. 1: a) CALIPSO measurement from January 30th, 2020, 14:00 UTC. The red arrow indicates the latitude of the ACE-FTS ss88712 measurement. The CALIPSO curtain probed the plume about 6° east in longitude from the ACE-FTS measurement. b) The OMPS aerosol index map from January 30th, 2020, recorded approximately five hours prior to the ACE-FTS ss88712 measurement. The green star indicates the location of the ACE-FTS measurement.

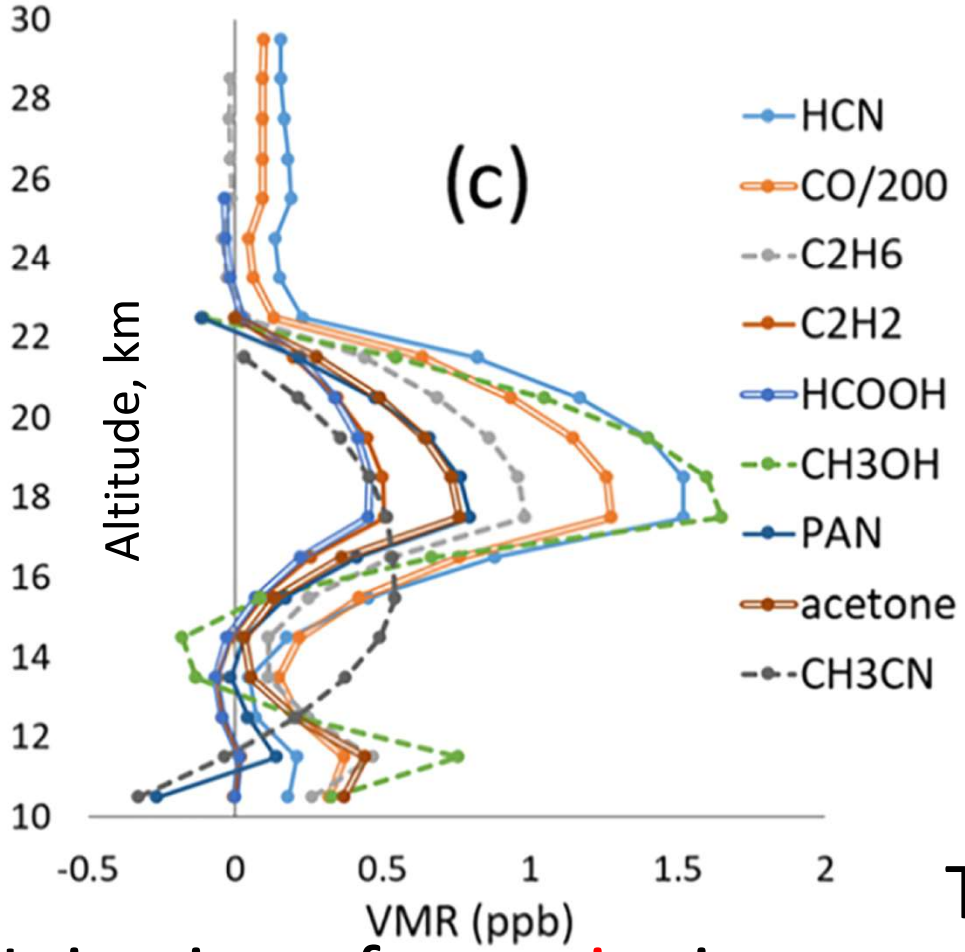
Pyrocumulonimbus Stratospheric Plume Injections Measured by the ACE-FTS

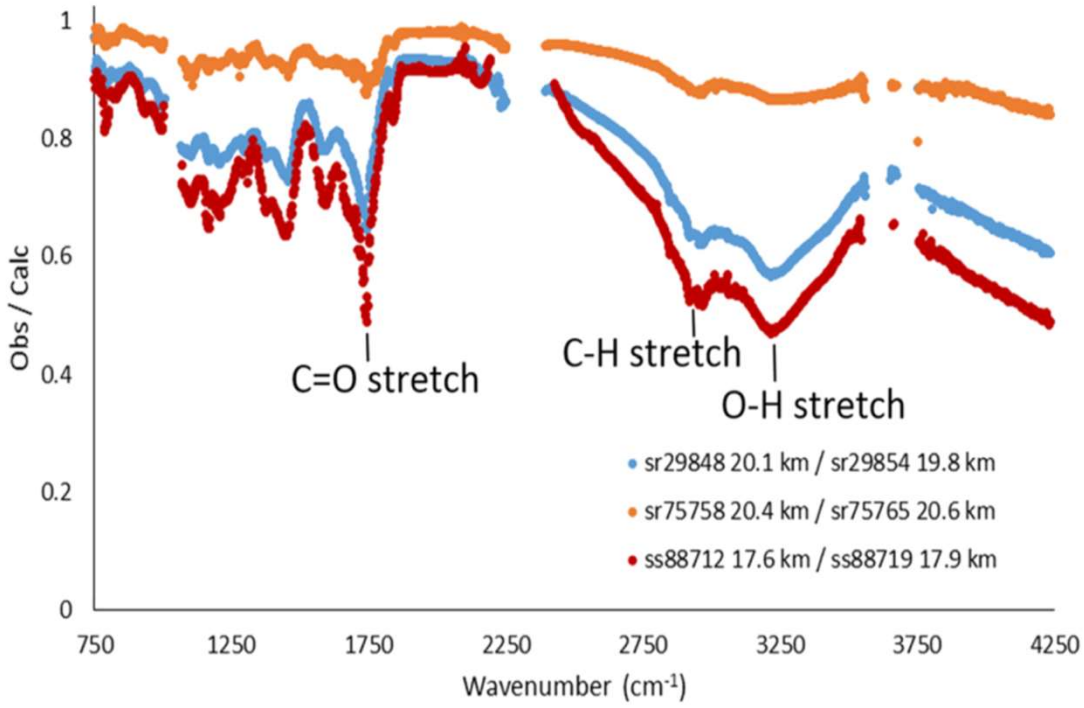
PyroCbs

C. D. Boone[1], P. F. Bernath[1,2], and M. D. Fromm[3]

GRL **47** (2020)

[1]Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada, [2]Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA, USA, [3]Naval Research Laboratory, Washington, DC, USA





Injection of organics into stratosphere

Typical Australian fire spectrum in red at 17.5 km: oxygenated soot; no obvious H_2SO_4; strong C=O str.

Effects of Smoke in the Stratosphere

Wildfire smoke destroys stratospheric ozone

Peter Bernath[1,2,3]*, Chris Boone[2], Jeff Crouse[2]

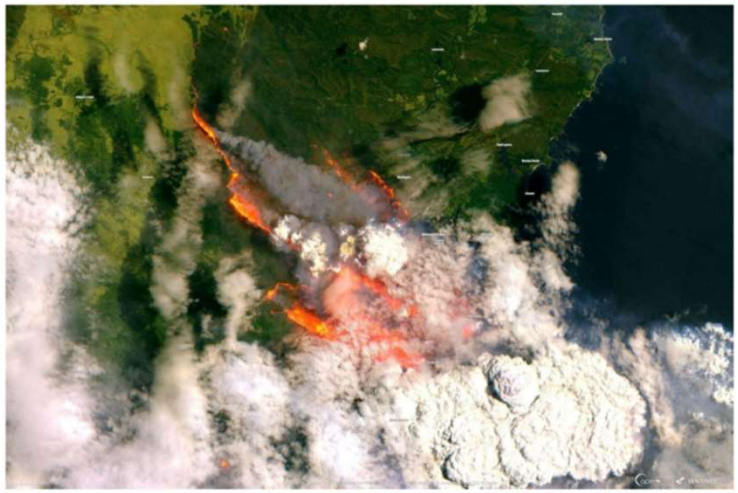
Large wildfires inject smoke and biomass-burning products into the mid-latitude stratosphere, where they destroy ozone, which protects us from ultraviolet radiation. The infrared spectrometer on the Atmospheric Chemistry Experiment satellite measured the spectra of smoke particles from the "Black Summer" fires in Australia in late 2019 and early 2020, revealing that they contain oxygenated organic functional groups and water adsorption on the surfaces. These injected smoke particles have produced unexpected and extreme perturbations in stratospheric gases beyond any seen in the previous 15 years of measurements, including increases in formaldehyde, chlorine nitrate, chlorine monoxide, and hypochlorous acid and decreases in ozone, nitrogen dioxide, and hydrochloric acid. These perturbations in stratospheric composition have the potential to affect ozone chemistry in unexpected ways.

Bernath *et al.*, *Science* **375**, 1292–1295 (2022) 18 March 2022

Wall Street Journal, Friday 18 March, 2022

Extreme Wildfires' Smoke Poses New Threat to Ozone Layer, Research Finds

Data from 2020 Australian blazes show smoke funneled into the atmosphere triggered a drop in levels of radiation-blocking ozone



An outbreak of vast wildfires in Australia two years ago lasted months and blasted moist smoke particles into the stratosphere.

PHOTO: EUROPEAN UNION/REUTERS

By Nidhi Subbaraman

March 17, 2022 2:00 pm ET

The deadly wildfires that scorched southeastern Australia in 2019 and 2020 triggered atmospheric changes miles high and thinned the ozone layer over large parts of the Southern Hemisphere for months, new research shows.

The research, published Thursday in the journal Science, suggests that wildfires pose a new threat to the ozone layer globally and that their affects on human health might be greater than previously recognized.

Ozone blankets the Earth in an invisible layer 9 to 18 miles above the ground, absorbing dangerous ultraviolet radiation from the sun. Radiation damages living

Stories in Australia and Belgium

Black Summer bushfire smoke altered ozone-depleting chemicals in atmosphere, study finds

ABC Science / By Genelle Weule

Posted Thu 17 Mar 2022 at 2:30pm, updated Thu 17 Mar 2022 at 5:32pm

Australia's Black Summer bushfires pumped enormous amounts of smoke into the atmosphere. *(Getty Images: Andrew Mercy)*

As they circled the globe, massive plumes of smoke from the devastating Black Summer fires kickstarted changes in the atmosphere that may have caused a drop in ozone levels, a new study suggests.

A team of researchers, led by Peter Bernath of the University of Waterloo, found smoke from the 2019-2020 fires caused extreme changes in a number of ozone-depleting gases at mid-latitude locations.

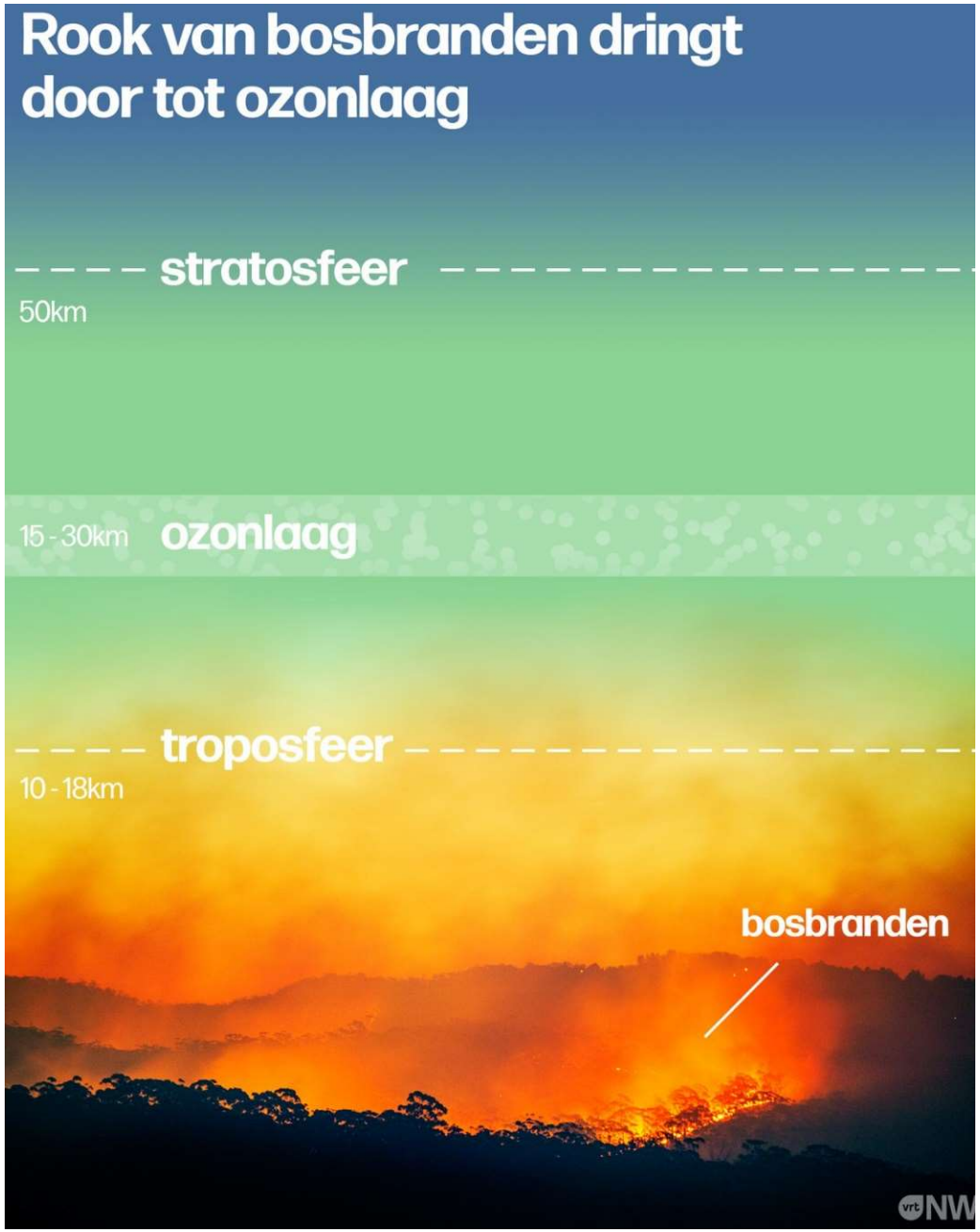
The changes were beyond anything that had been measured in the previous 15 years, they report today in the journal Science.

"We've seen smoke before, but we've never seen this type of effect on the stratosphere," Professor Bernath said.

The Black Summer fires produced huge weather systems known as pyrocumulonimbus clouds,

Key points:

- Analysis of satellite data shows changes in ozone-depleting gases in the atmosphere following the Black Summer fires
- The finding suggests that smoke may act as a catalyst for ozone depletion in mid-latitude locations
- The authors speculate that increasing frequency of wildfires with climate change may delay recovery of ozone



Stratospheric Australian Smoke Spectrum

Surface is likely acidic (carboxylic acid features) and hydrated.

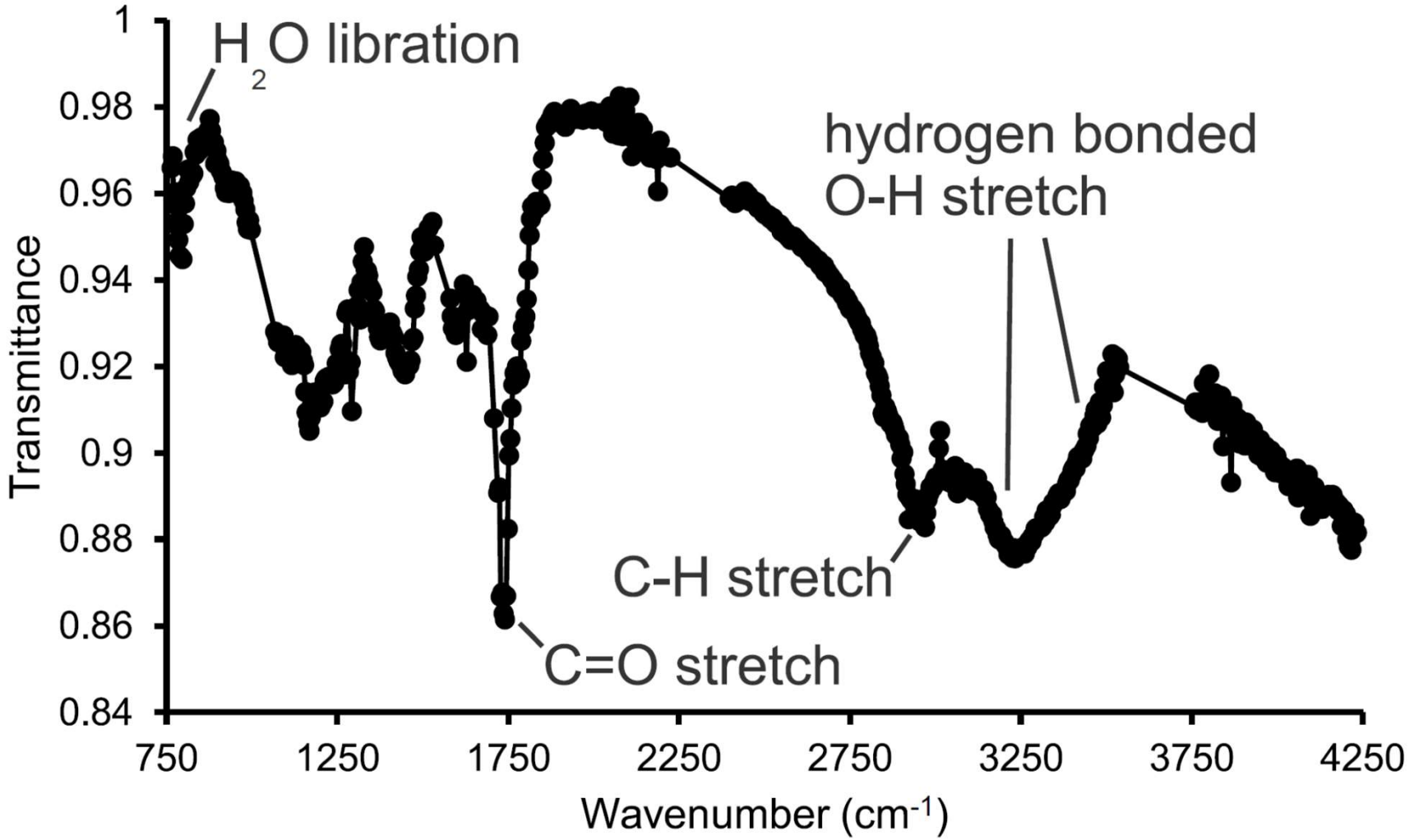


Fig. 1. The aerosol spectrum for tangent height 16.6 km from occultation ss88361 (where ss stands for sunset and 88361 is the number of orbits since launch, a unique identifier for the measurement), measured January 6, 2020 at latitude 58.8°S. Spectral features associated with selected functional groups are indicated.

Elevated Aerosol Extinction (1 µm Imager)

Stratospheric smoke during 2020,
45-60°S latitude monthly averages

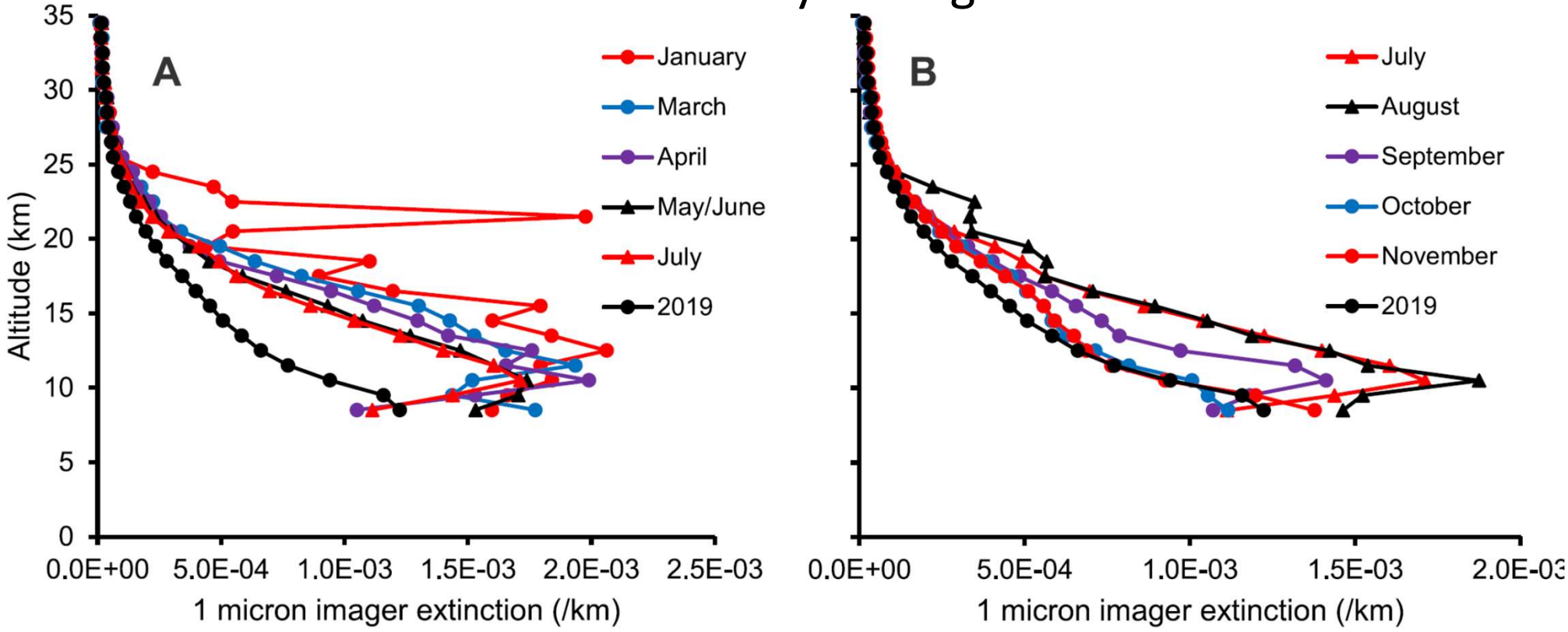


Fig. S1.

Evolution of atmospheric extinction profiles in 2020 for the latitude range 45 to 60°S as measured by the 1 µm imager on the ACE satellite. The yearly average profile for 2019 is used to estimate background aerosol conditions. (**A**) January through July. Peaks in the profile for January indicate the presence of coherent plumes injected by pyroCB eruptions. (**B**) July through November. As of November 2020, aerosol levels are approaching background levels but remain slightly elevated in this latitude region.

Ozone Time Series

O_3 enhanced Jan-Mar 2020 from organic injection; O_3 declines for rest of 2020 and into 2021

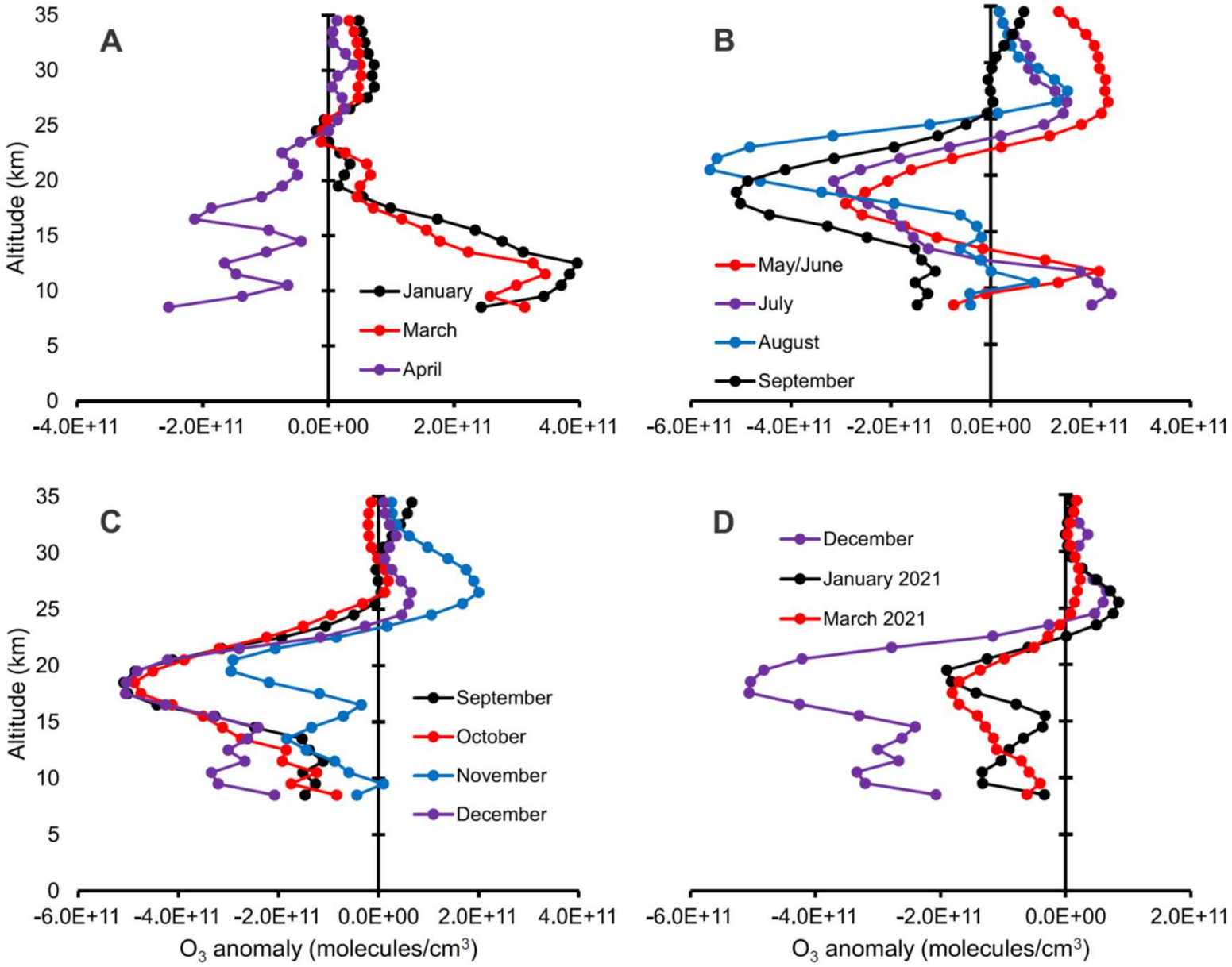


Fig. S2.

Ozone anomalies, the difference between the average profile from 2020 (unless otherwise indicated) and the average profile from all previous years (2005-2019) for the latitude range 45 to 60°S. (**A**) January, March, and April 2020. (**B**) Late May / early June, July, August, and September 2020. (**C**) September, October, November, and December 2020. (**D**) December 2020, January 2021, and March 2021.

HCl, $ClONO_2$, HOCl, ClO (May-June 2020)

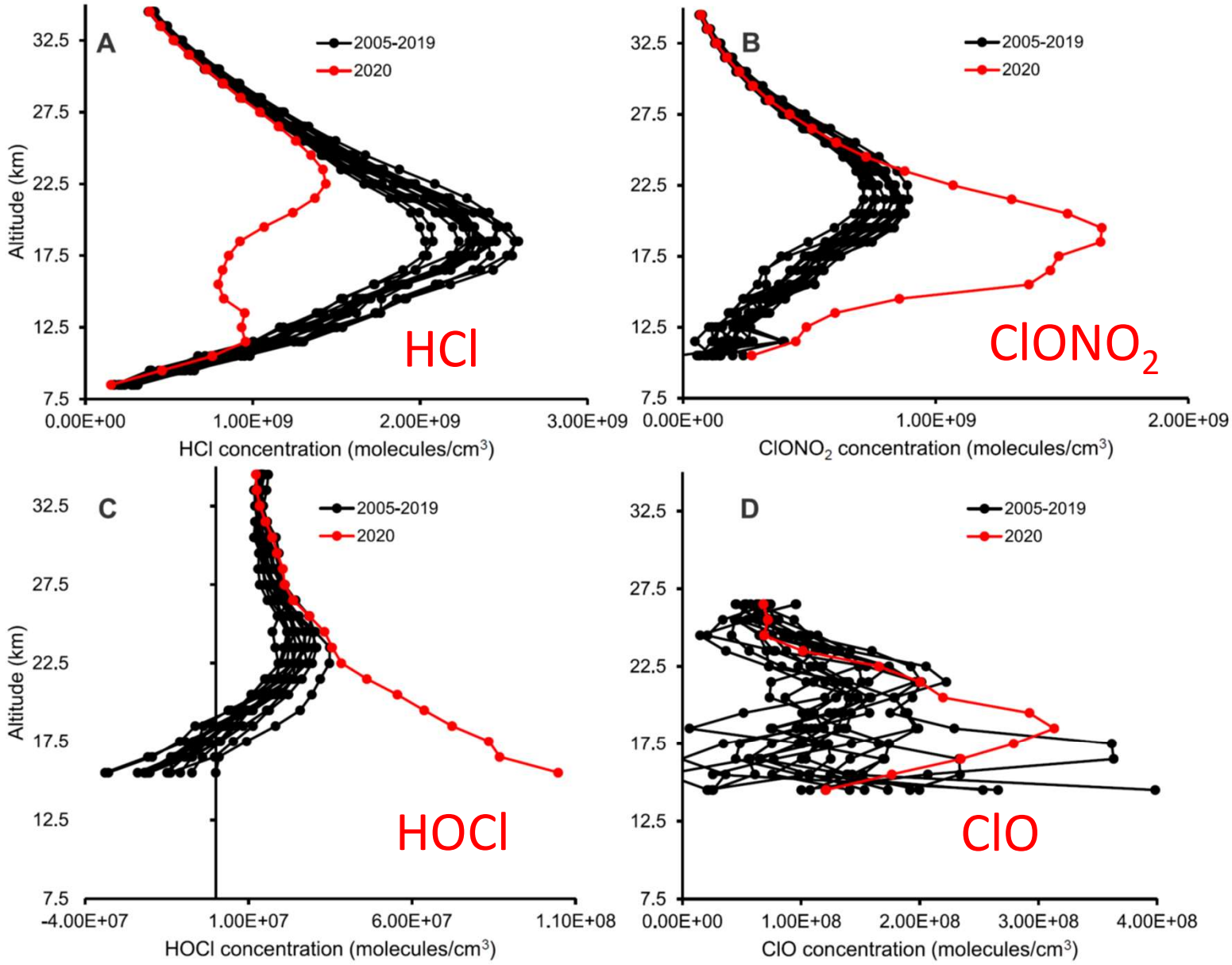


Fig. 3. Concentrations of chlorine-containing molecules for the latitude range 45 to 60°S for ACE-FTS occultations in late May / early June. Profiles for all years prior to 2020 measured by the ACE-FTS are shown in black, while the average profile for 2020 is in red. (**A**) HCl. (**B**) $ClONO_2$. (**C**) HOCl. (**D**) ClO.

Possible Smoke Chemistry

Smoke surfaces catalyze the reaction:

$HOCl + HCl \rightarrow Cl_2 + H_2O$

HCl decreases and Cl_2 photolyzes to 2Cl

ClO_x cycle then destroys O_3

$Cl + O_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow Cl + O_2$

Also HOCl photolyzes to OH and Cl

Therefore, ClO increases as observed.

At night N_2O_5 is hydrolyzed on hydrated smoke:

$N_2O_5 + H_2O \rightarrow 2HNO_3$

N_2O_5 is made from NO_2, which thus decreases.

Implications

Extreme wildfires are becoming more frequent because of climate change (2021 IPCC report). These pyroCbs perturb the HOx cycle, reactive nitrogen and halogen chemistry in the stratosphere, destroying ozone. Wildfire smoke has the potential to delay the recovery of stratospheric ozone.

Eight Aerosol and Cloud Spectra

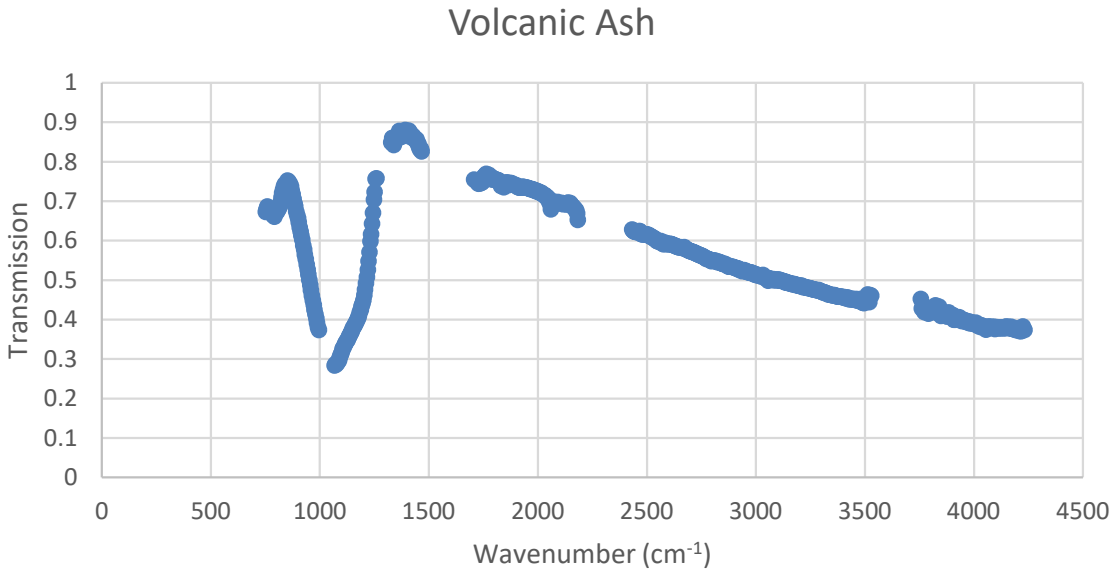
ACE-FTS records characteristic IR absorption spectra of particles

1. Polar Mesospheric Clouds (PMCs)
2. Smoke from fires

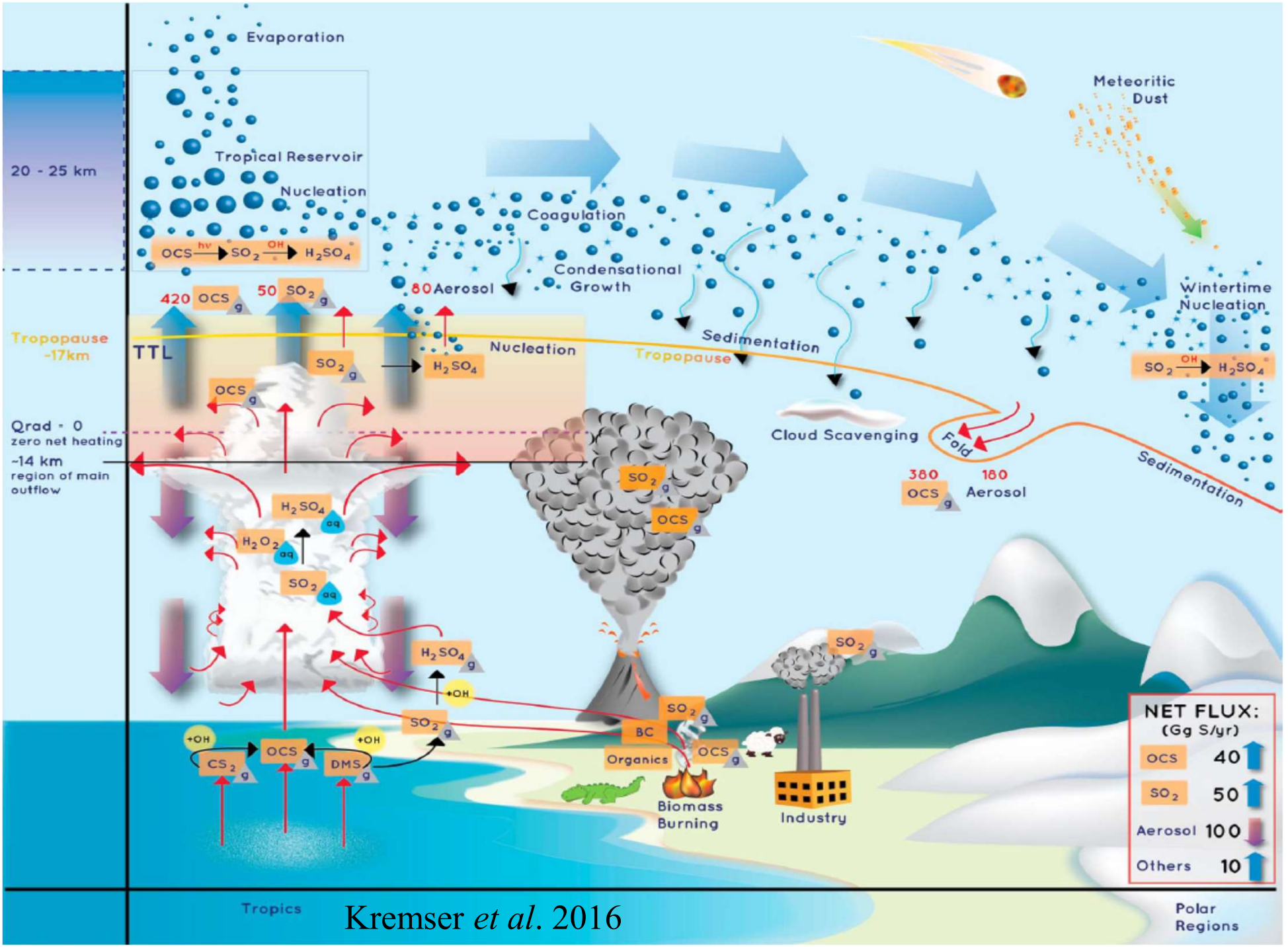
Polar Stratospheric Clouds (PSCs)

3. Nitric acid trihydrate (NAT)
4. Sulfuric/nitric acid and water (STS)
5. Ice

6. Cirrus clouds (ice)
7. Volcanic ash --->
8. Sulfate aerosols



Lifecycle of Sulfate Aerosols



Kremser *et al*. 2016

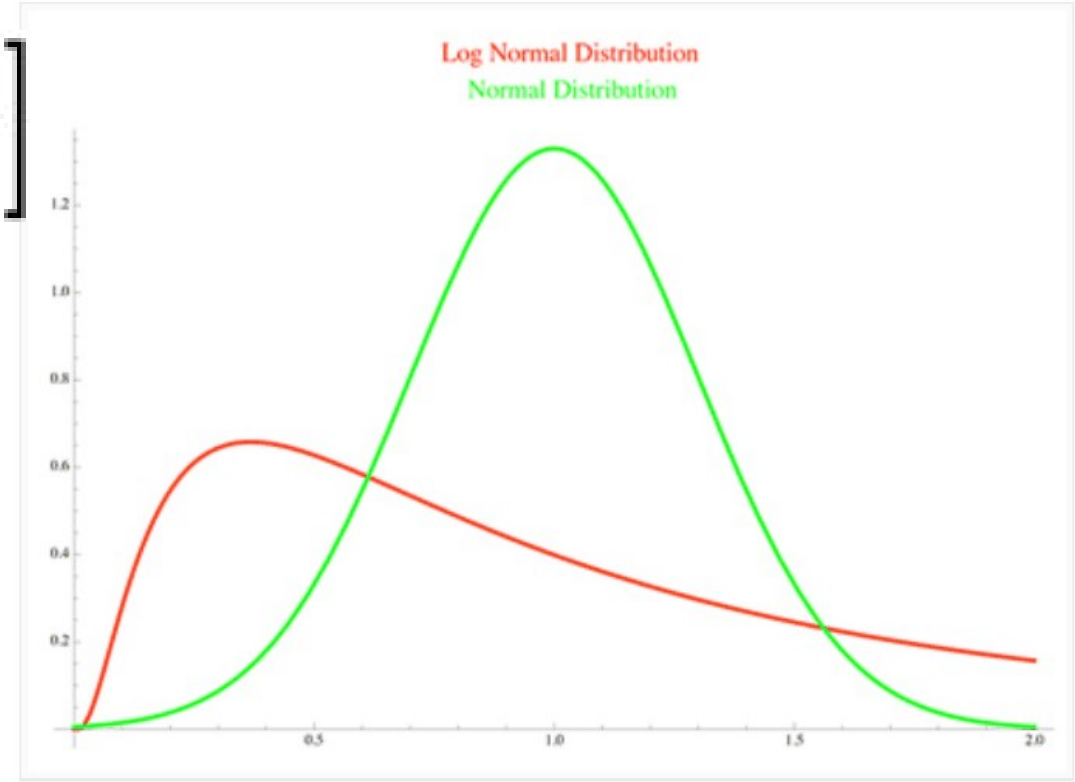
Aerosol Parameters (4)

1. Particle column density (particle density, N_0, particles/cm^3 x Pathlength, cm; N_0L)
2. Composition: wt% sulfuric acid

Size distribution: assume lognormal

3. r_m: median radius
4. S : spread of distribution (SD in lnr space)

$$n(r) = \frac{N_0}{\sqrt{2\pi}\ln(S)}\frac{1}{r}\exp\left[-\frac{(\ln r - \ln r_m)^2}{2\ln^2(S)}\right]$$



Raikoke Volcanic Eruption

Raikoke

Smithsonian Institution
National Museum of Natural History
Global Volcanism Program

Country	Russia
Volcanic Region	Kuril Islands
Primary Volcano Type	Stratovolcano
Last Known Eruption	2019 CE

Latitude	48.292°N
Longitude	153.25°E
Summit Elevation	551 m 1808 ft
Volcano Number	290250

19 June-25 June 2019

Cite this Report

A powerful eruption at Raikoke that began on 22 June (after 95 years of dormancy) was identified based on satellite observations, prompting KVERT and SVERT to raise the Aviation Color Code to Red. A series of at least nine explosions (six within the first 25 minutes) beginning at 0505 and continuing to about 1900 produced ash plumes, with a significant sulfur dioxide component, that rose 10-13 km (32,800-42,700 ft) a.s.l. and drifted E and NE. Lightning was detected in the eruption plumes. Strong explosions at 1640 on 22 June generated ash plumes that rose to 10-11 km (32,800-36,100 ft) a.s.l. The ash and gas was entrained by jet streams and by a cyclone around the Komandorskiye Islands, causing parts of the material to spiral counterclockwise as it drifted farther NE. By 23 June the leading edge of the plume had drifted 2,000 km ENE. According to a news article, at least 40 flights in that region were diverted.

On 23 June ash plumes continued to be visible, rising to 4.5 km and drifting NE. The Aviation Color Code was lowered to Orange. Gas-and-steam plumes possibly with some ash rose to 4.5 km (14,800 ft) a.s.l. and drifted 60 km NW. That same day observers on a passing ship approached the island from the W side; they photographed the island and sent out a drone. An expedition member noted that the entire island was mantled with light-colored ash deposits up to several dozen centimeters thick. In some of the drainages and at the base of some drainages deposits were several meters thick. In some areas along the shoreline waves interacted with the deposits, causing steam explosions and dark brown steam emissions. Gas-and-ash plumes rose 1.5 km above the summit crater rim and drifted W. Minor ashfall was reported in Severo-Kurilsk (340 km NE) during 1830-1920. On 25 June ash plumes continued to be produced, rising as high as 2 km (6,600 ft) a.s.l. and drifting NW.

Sources: Kamchatkan Volcanic Eruption Response Team (KVERT); Sakhalin Volcanic Eruption Response Team (SVERT); NHK (Japan Broadcasting Corporation)

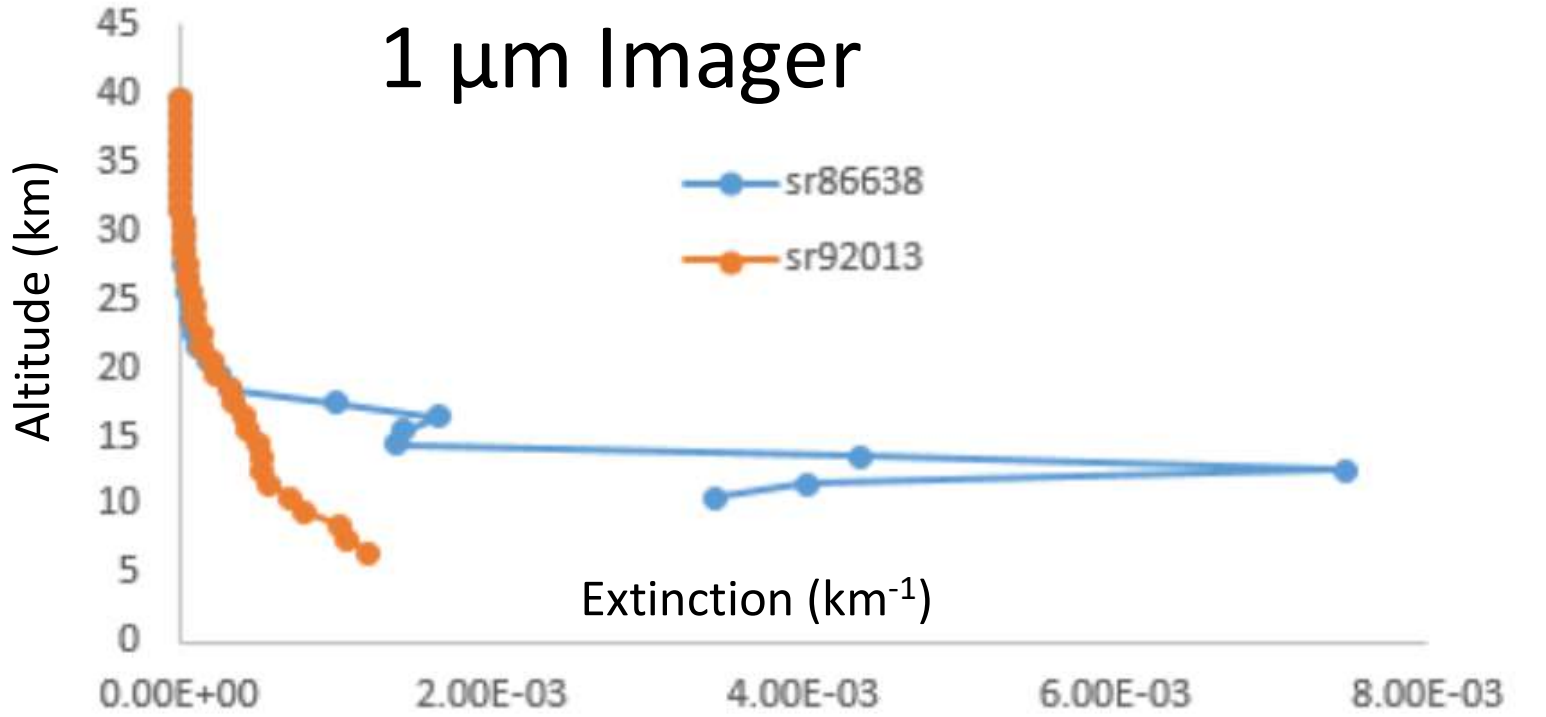
manuscript submitted to Journal of Geophysical Research: Atmospheres

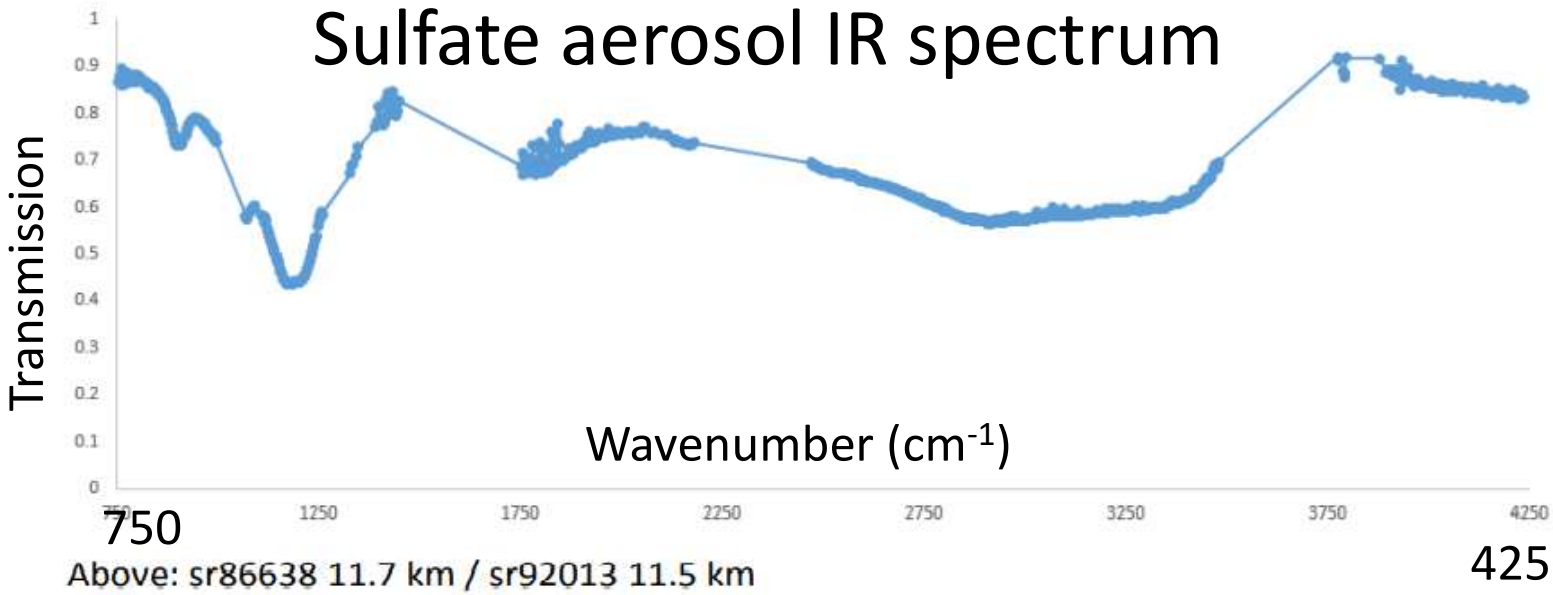
Stratospheric Aerosol Composition Observed by the Atmospheric Chemistry Experiment Following the 2019 Raikoke Eruption

Chris D. Boone[1], Peter F. Bernath[1,2,3], Keith Labelle[3], and Jeff Crouse[1]

Infrared aerosol spectra derived from Atmospheric Chemistry Experiment measurements following the 2019 Raikoke volcanic eruption are used to evaluate the composition of stratospheric aerosols in the Northern Hemisphere. A blanket of aerosols, spanning an altitude range from roughly 9 to 20 km, persisted in the stratosphere over northern latitudes for several months. The composition of aerosols within this blanket was almost exclusively sulfate. There was a significant altitude gradient in H_2SO_4 content for sulfate aerosols within the aerosol blanket, with lower H_2SO_4 levels at lower altitudes. In the sulfate aerosol droplets, H_2SO_4 dropped from > 70% in September 2019 to < 50% in March 2020. No indication of stratospheric smoke was observed in the Arctic region during the time period investigated (July 2019 through March 2020).

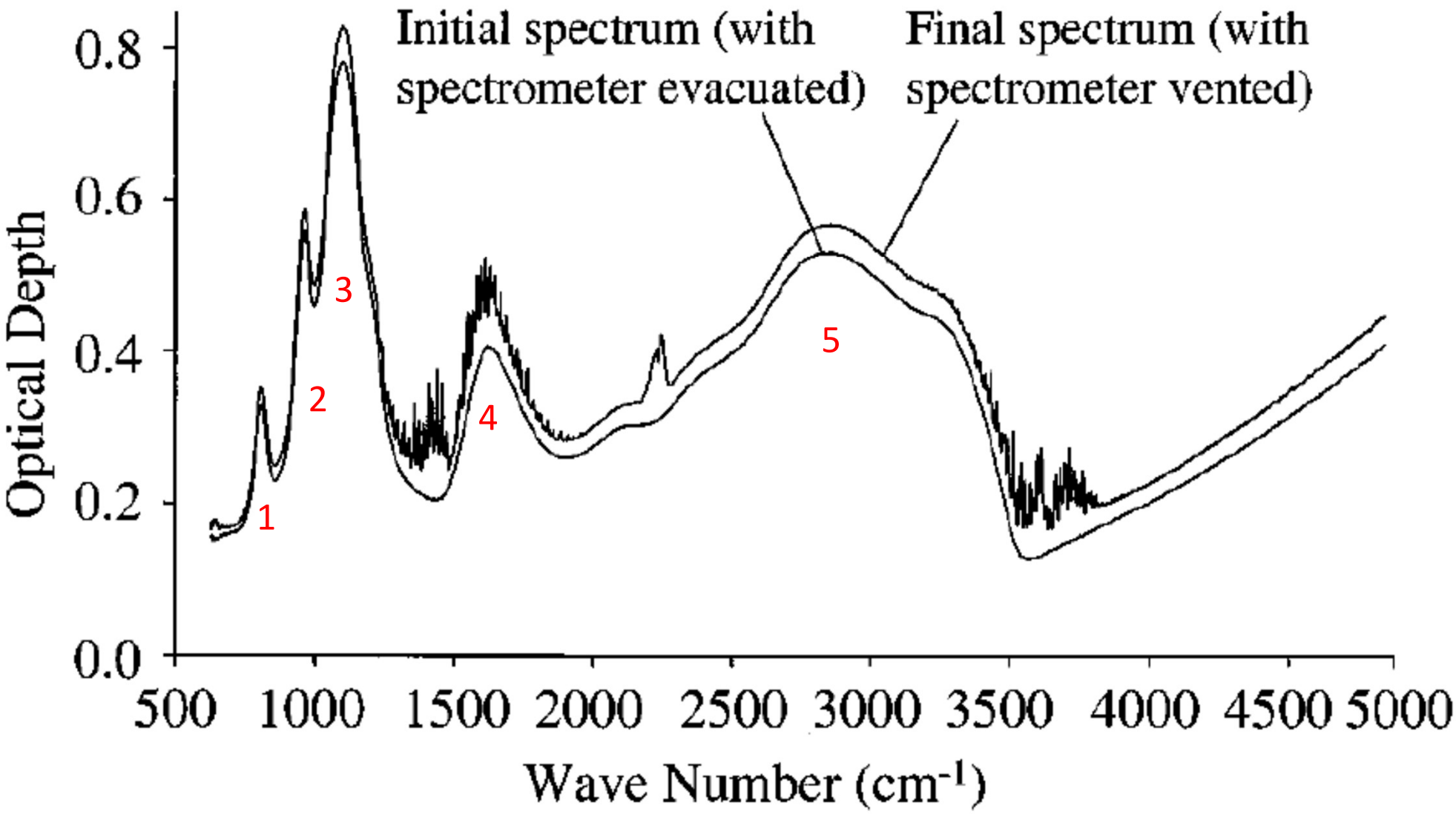
ACE-FTS “Residual” Spectra (Raikoke)





Above: sr86638 11.7 km / sr92013 11.5 km

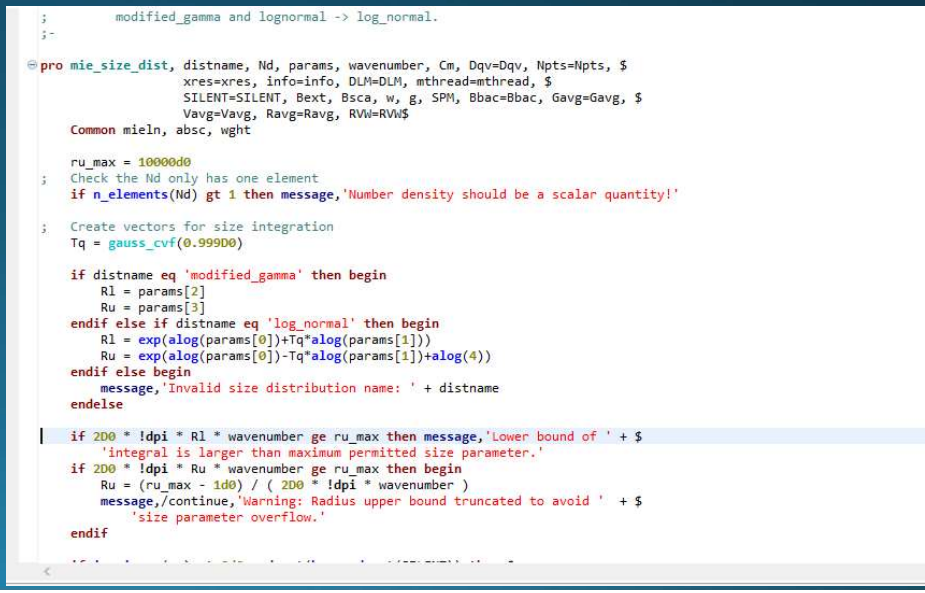
Lab Spectrum H_2SO_4 Aerosols



Room temperature, large particles; Heathfield *et al*. 1999

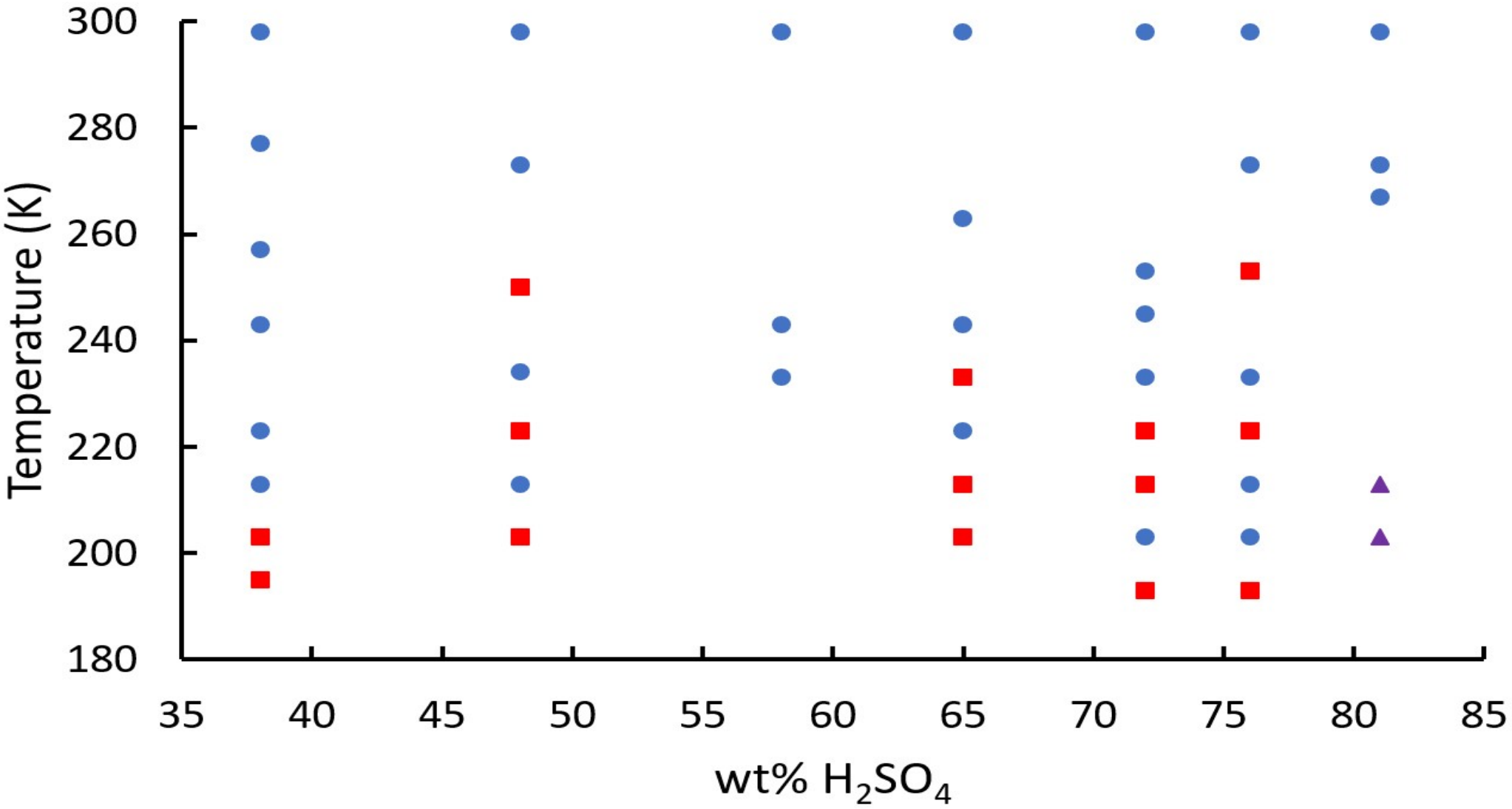
Modeling

- Working with Mie scattering IDL programs
  - Developed by Earth Observation Data Group at Oxford University
- Two main programs used:
  - Single Particle (mie_single.pro)
  - Distribution (mie_size_dist.pro)



```
;         modified_gamma and lognormal -> log_normal.
;-

pro mie_size_dist, distname, Nd, params, wavenumber, Cm, Dqv=Dqv, Npts=Npts, $
                   xres=xres, info=info, DLM=DLM, mthread=mthread, $
                   SILENT=SILENT, Bext, Bsca, w, g, SPM, Bbac=Bbac, Gavg=Gavg, $
                   Vavg=Vavg, Ravg=Ravg, RVW=RVW$
    Common mieln, absc, wght

    ru_max = 10000d0
;   Check the Nd only has one element
    if n_elements(Nd) gt 1 then message,'Number density should be a scalar quantity!'

;   Create vectors for size integration
    Tq = gauss_cvf(0.999D0)

    if distname eq 'modified_gamma' then begin
        Rl = params[2]
        Ru = params[3]
    endif else if distname eq 'log_normal' then begin
        Rl = exp(alog(params[0])+Tq*alog(params[1]))
        Ru = exp(alog(params[0])-Tq*alog(params[1])+alog(4))
    endif else begin
        message,'Invalid size distribution name: ' + distname
    endelse

    if 2D0 * !dpi * Rl * wavenumber ge ru_max then message,'Lower bound of ' + $
        'integral is larger than maximum permitted size parameter.'
    if 2D0 * !dpi * Ru * wavenumber ge ru_max then begin
        Ru = (ru_max - 1d0) / ( 2D0 * !dpi * wavenumber )
        message,/continue,'Warning: Radius upper bound truncated to avoid '  + $
            'size parameter overflow.'
    endif
```

H_2SO_4 Optical Constants

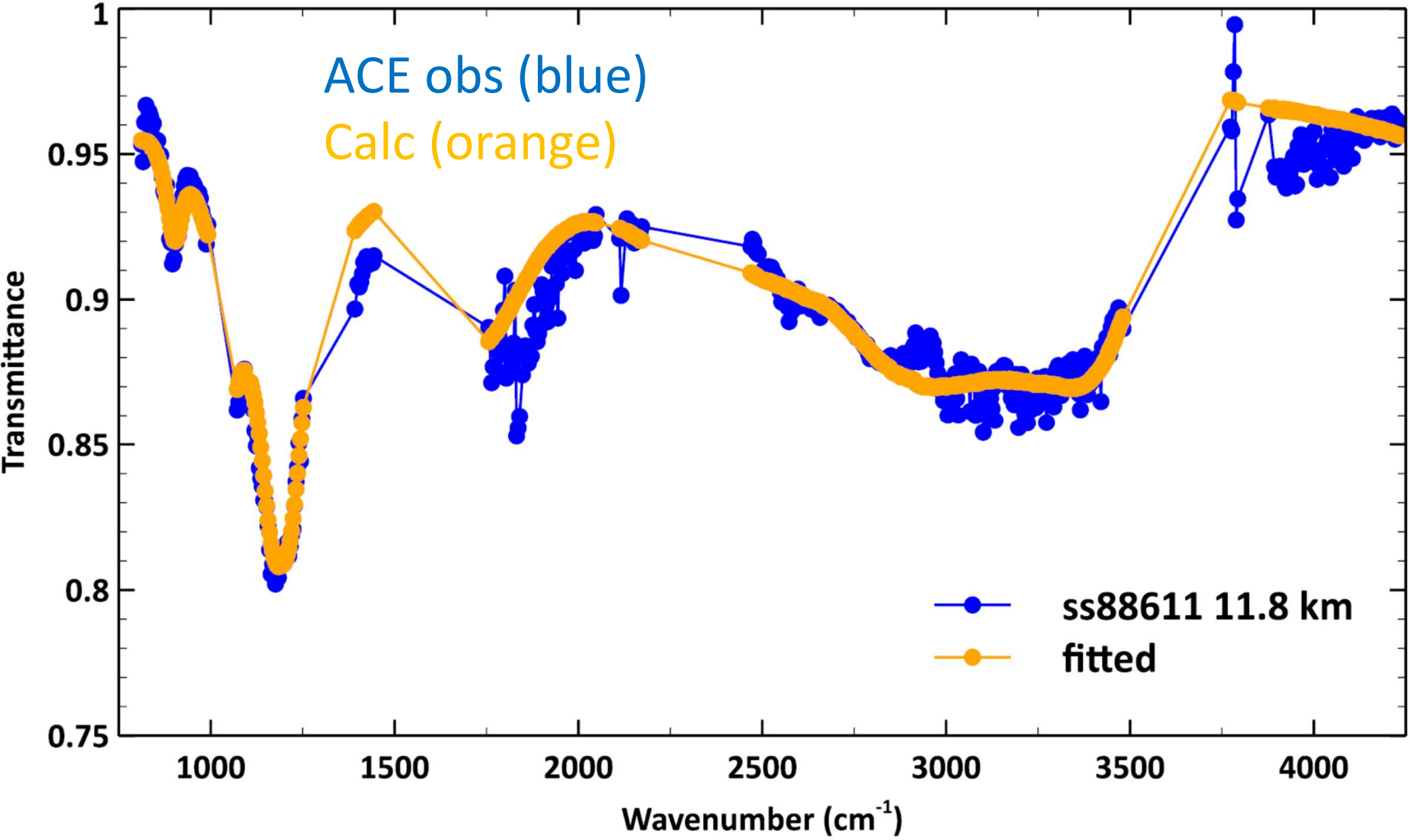


Blue circles indicate data calculated using the Lund Myhre et al. (2003) optical constants, red squares indicate data interpolated or extrapolated in temperature, and purple triangles indicate data extrapolated in wt% H_2SO_4.

Fitting the Spectra

- The Oxford IDL programs were used to calculate spectra for all 46 sets of optical constants for r_m = 0.1, 0.2, … 1.0 μm with S = 1.1 (fixed).
- Tests showed that ACE spectra were not sensitive to the distribution width, S.
- C. Boone fitted the observed ACE transmission spectra (τ) with equation, $\tau = Ae^{-\alpha L}$, adjusting the composition (wt%) and r_m, as well as A (baseline) and L (pathlength). Interpolation used to obtain calculated extinctions, α.

Sulfate Aerosol Fit



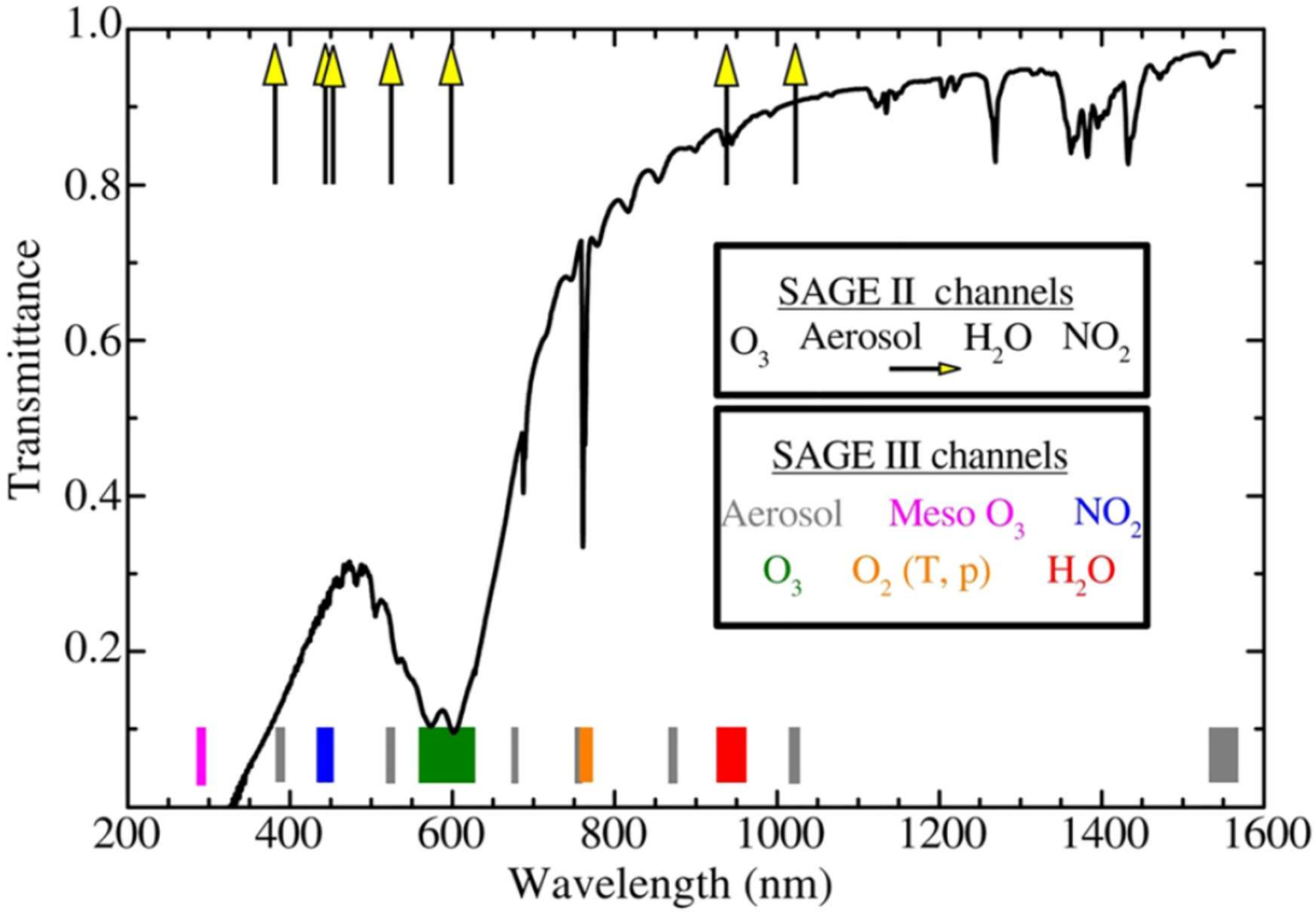
Parameters: 65.3±0.8%(wt), r_m = 0.28±0.06 µm, T = 227 K (fixed), S=1.1 (fixed) or 65.3±0.8%(wt), r_m = 0.22±0.05 µm, T = 227 K (fixed), S=1.3 (fixed); 3.4×10^8 particles/cm^2

ACE-FTS Sulfate Aerosol Retrievals

- ACE sulfate aerosol spectra are due mainly to absorption with some scattering at higher wavenumbers.
- ACE data alone: composition is well determined; r_m is determined; N_0L, particle column density is determined; distribution width, S, is not determined.
- SAGE-III-ISS aerosol extinctions are mainly scattering and will improve ACE retrievals of r_m and S.

SAGE-III-ISS Aerosol Channels

Chan-nel	λ (nm)
1	384.2
2	484.5
3	520.5
4	601.5
5	676.0
6	755.9
7	869.1
8	1021.2
9	1543.9

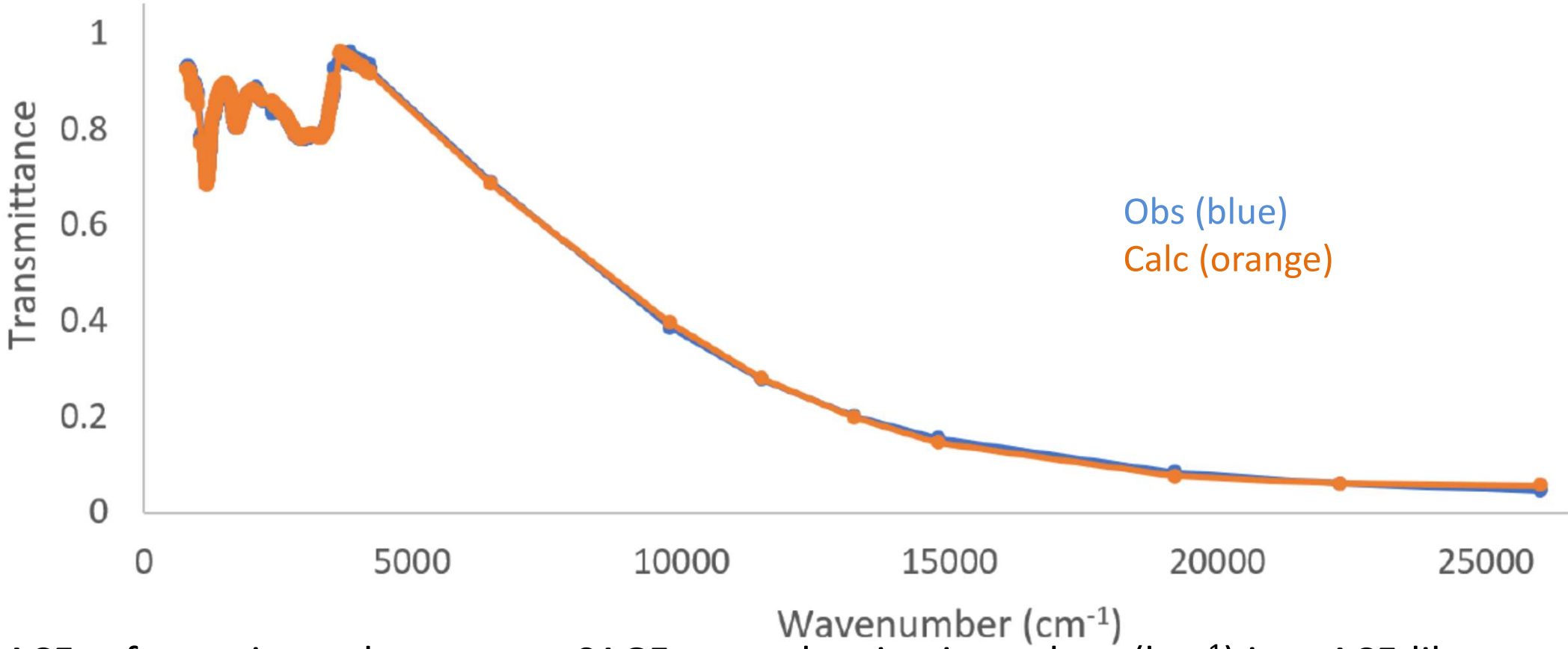


Sulfuric Acid Optical Constants for Near UV, Visible and Near IR

- Palmer and Williams (1975) data seem to be the standard but are at 300 K.
- Refractive index can be shifted in temperature using Lorentz-Lorenz equation. Densities ρ(T, wt%) are needed and values from Lund Myhre et al. (2003) were used.
- Optical constants for SAGE-III-ISS wavelengths calculated for atmospheric temperatures.

ACE-FTS and SAGE-III-ISS

Raikoke plume at 20 km; ACE and SAGE are 2 days apart



ACE software is used to convert SAGE aerosol extinction values (km^{-1}) into ACE-like limb transmission.

Results: r_m = 0.241 ± 0.004 µm, H_2SO_4 = 64.9 ± 0.5 %, S = 1.30 ± 0.01, N_0L = 4.8 ± 0.2 x10^8 particles/cm^2

ACE-FTS data alone: r_m = 0.27 µm, H_2SO_4 = 66.3 %, S= 1.1 (fixed).

Conclusions

- ACE-FTS residual spectra provide a unique dataset for characterization of clouds and aerosols.
- For sulfate aerosols, ACE-FTS data alone provides 3 of 4 parameters (r_m, wt%, N_0L).
- Adding co-incident SAGE-III-ISS data adds S, distribution width, for a complete set of sulfate aerosols parameters, assuming a lognormal distribution.
- ACE aerosol extinctions (version 5.0) derived from 1 micron imager agree with corresponding SAGE-III-ISS values.

Acknowledgements

Robin

Chris Boone
Jeff Crouse
Johnny Steffen
Dennis Cok
Mike Lecours

Ryan Johnson
Keith LaBelle
Randika Dodangodage
Doug Cameron
Jason Sorensen

It's All Spectroscopy

Textbook aimed at graduate students and senior undergrads. Particularly useful treatment of the confusing topic of line intensities needed for remote sensing. 4th edition (April 2020) includes atmospheric and astronomical spectroscopy.