New data on size dependent composition in the lower stratosphere.

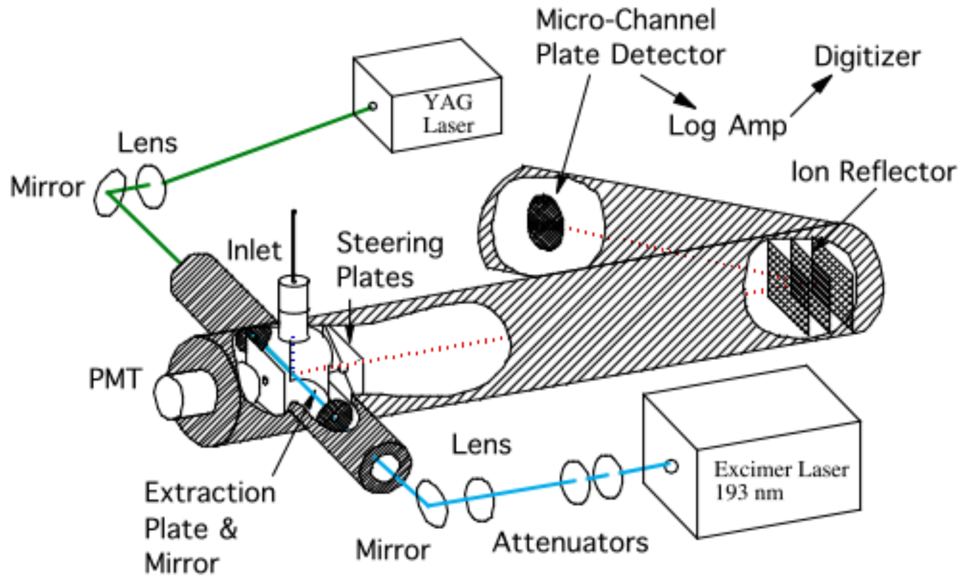
Daniel Murphy

NOAA ESRL / Chemical Sciences Division

Karl Froyd, Chuck Brock, many others

PALMS instrument

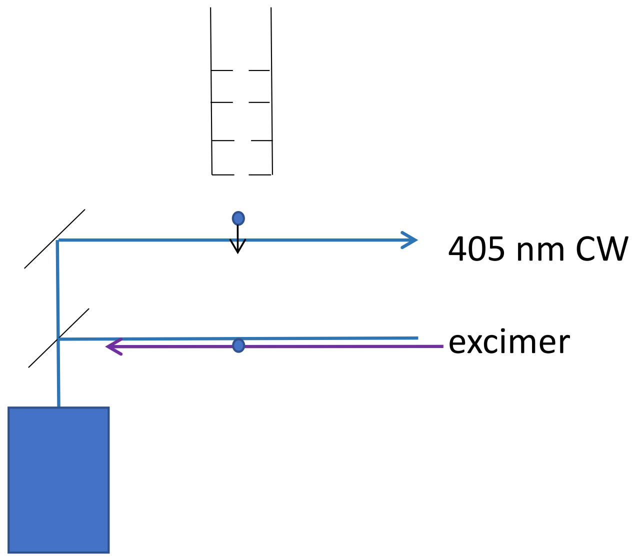
PALMS: Particle Analysis by Laser Mass Spectrometry



1) Particle enters vacuum. Trigger from light scattered from continuous laser.
2) Excimer laser beam hits particle.
3) Positive or negative ions analyzed with TOF mass spectrometer.
   - Size range about 0.25 (0.15 with low efficiency) to over 3 μm diameter

Much of the mass and light scattering
Minority by number

PALMS instrument detail

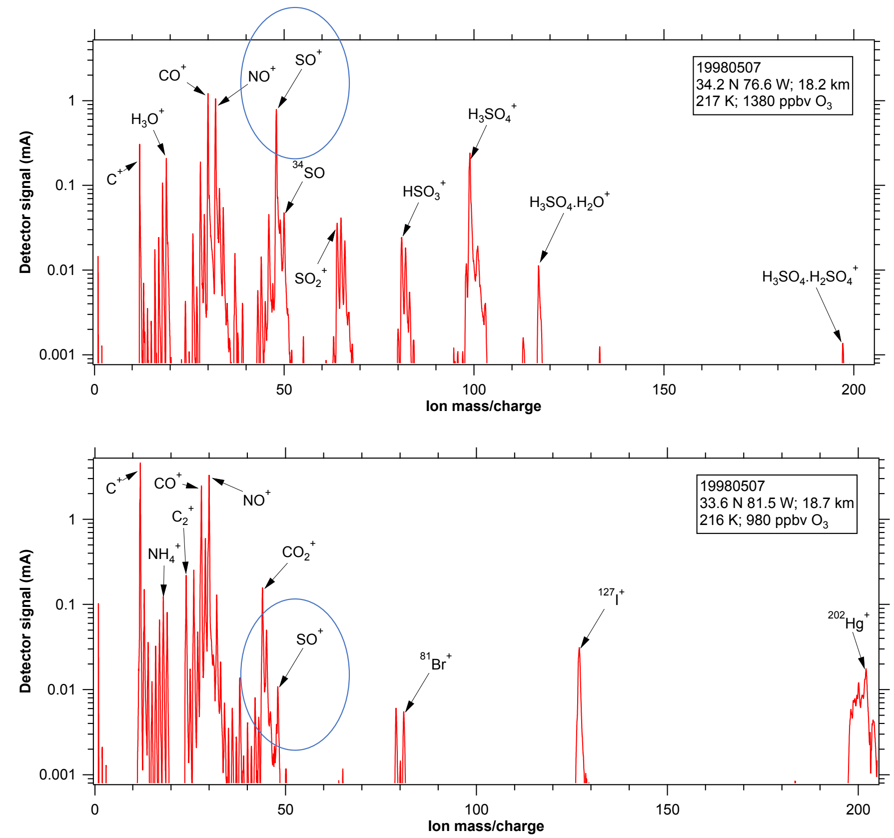


- Double trigger beam gives particle velocity
  => precise aerodynamic diameter
- Flow regime -> aerodynamic diameter is d*ρ rather than d*sqrt(ρ)

3 types describe >95% of stratospheric particles

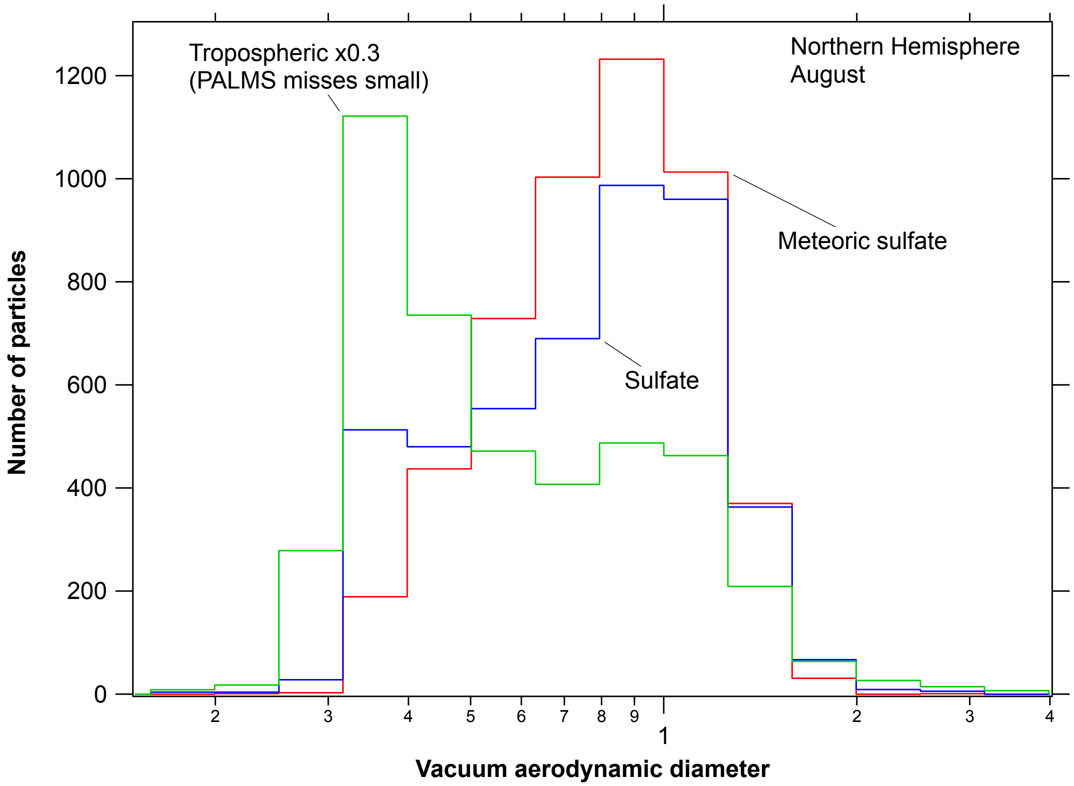
Type 1: Sulfuric acid with metals
Type 2: Sulfuric acid without metals

Type 3: Organic-sulfate mixtures
from the troposphere



Murphy et al., 2014

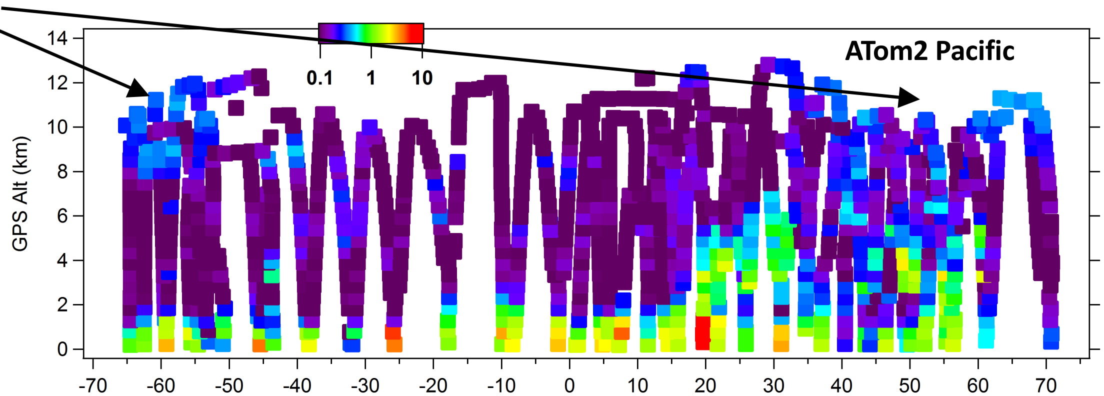
Tropospheric and stratospheric particles

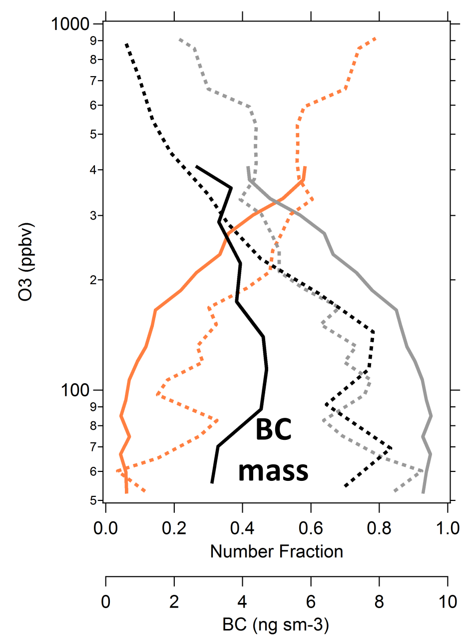


- Stratospheric particles well separated in vacuum aerodynamic diameter = d*ρ
- More overlap in optical diameter because of different densities
- PALMS cuts off lower portion of tropospheric size distribution

Polar Lower stratosphere and tropopause region

Aerosol Vol
Inversion:
LS > UT





- Gradual change in aerosol properties
  O_3=100 to 1000 ppbv

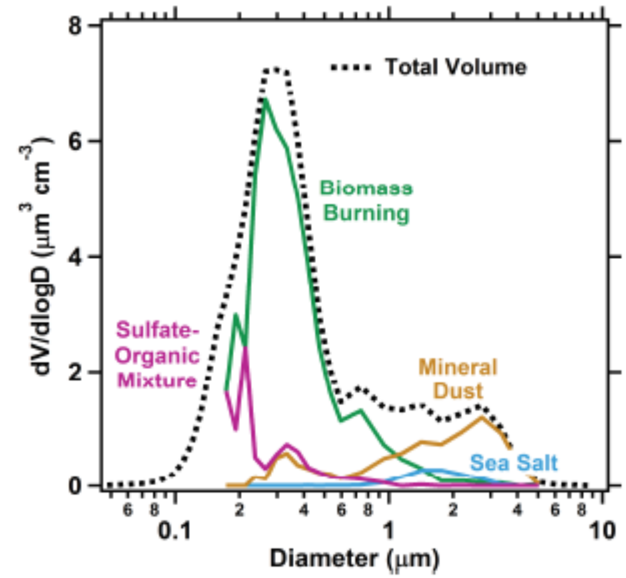
Composition-resolved size distributions

- Strong biases getting particles of different sizes into the PALMS laser beam
- How to overcome this?

1. Measure the size of each PALMS particle
   then apportion by size:
   for example in one portion of one flight:
   70% of 2 µm particles were dust
   90% of 0.5 µm particles were smoke

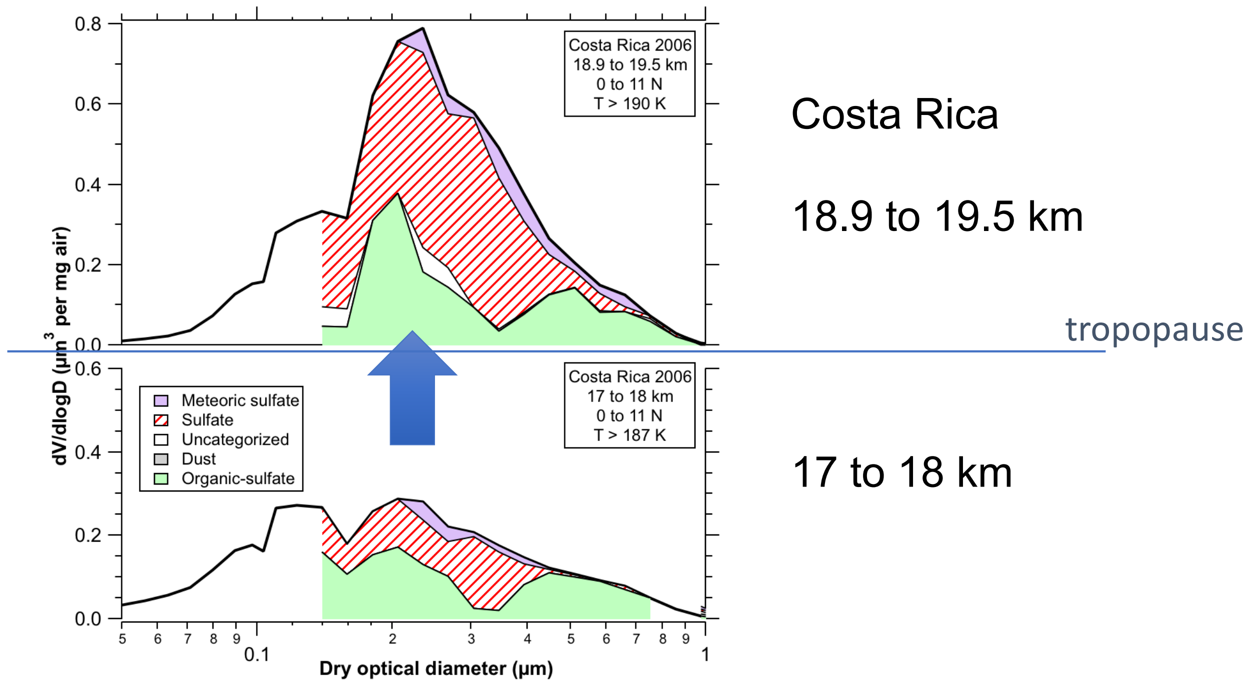
2. **Combine with a particle size distribution:**
   => *quantitative numbers by type of particle*

3. Simple in concept, many details, mostly from combining optical and aerodynamic diameters



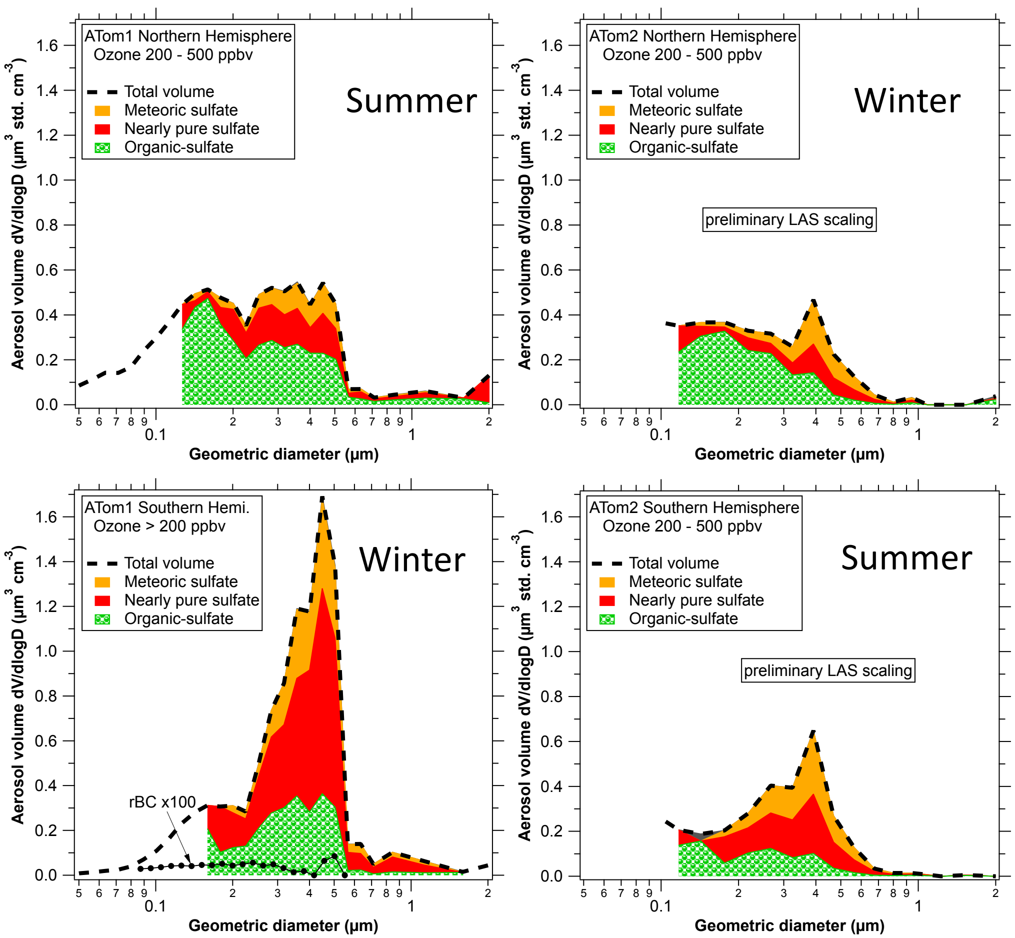
Dilute biomass burning plume over Alaska

Composition-resolved size distributions: tropical tropopause



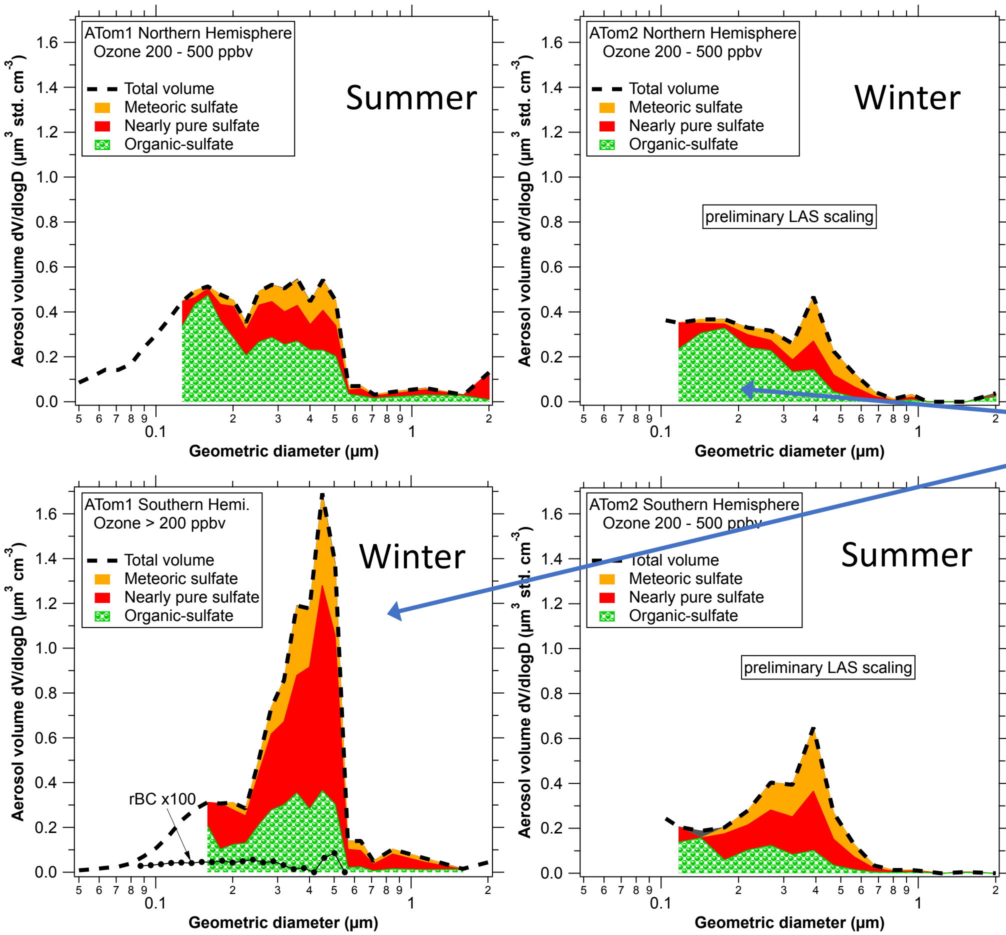
- Chuck Wilson optical counter size distributions apportioned by PALMS
- Additional sulfate just above tropical tropopause is mostly an external mixture
- Not much organic-sulfate lost through the tropopause

Size dependent composition in the lower stratosphere.

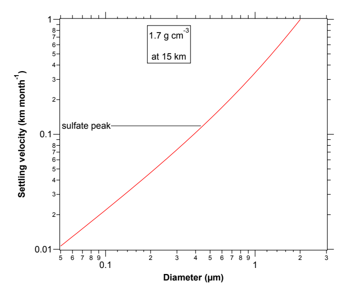


- DC8 – to just over 12 km, but folds reached into the stratosphere (ozone >> 200 ppbv)
- LEFT: Size NMASS+UHSAS+LAS
  RIGHT: LAS only
- Multiple seasons and hemispheres
- August 2016 and February 2017:
  non-volcanic
  August 2016 Southern some Calbuco?
- Stratospheric sulfate particles consistently bigger
- Spring and fall coming 2017-2018

Size dependent composition in the lower stratosphere.



- Sulfate particles have relatively narrow size distributions compared to organic-sulfates
- Sulfate with/without metals similar in size
- Relatively sharp upper limit may be partly optical counter binning. 0.6 µm diameter sulfuric acid sediments ~0.2 km/month



Lognormal fits to particle types

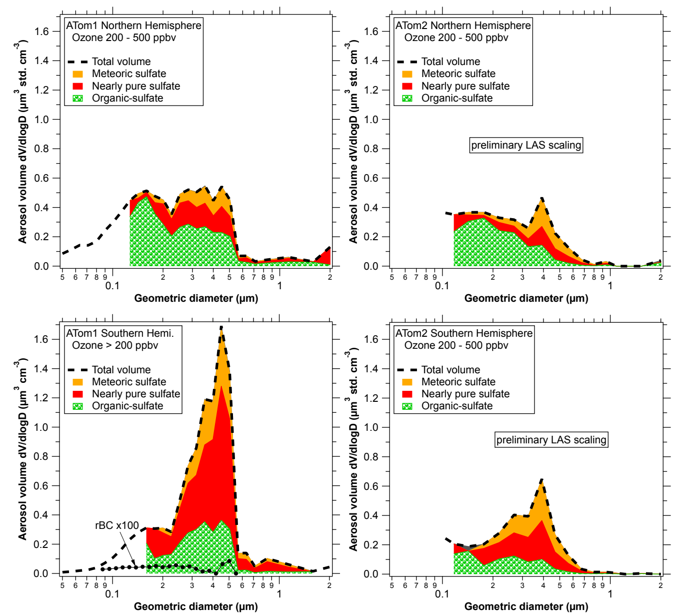
Sulfate

	MMD	Sigma (of volume fit)
NH August	0.38	1.6
NH February	0.40	1.4
SH August	0.42	1.5
SH February	0.35	1.6

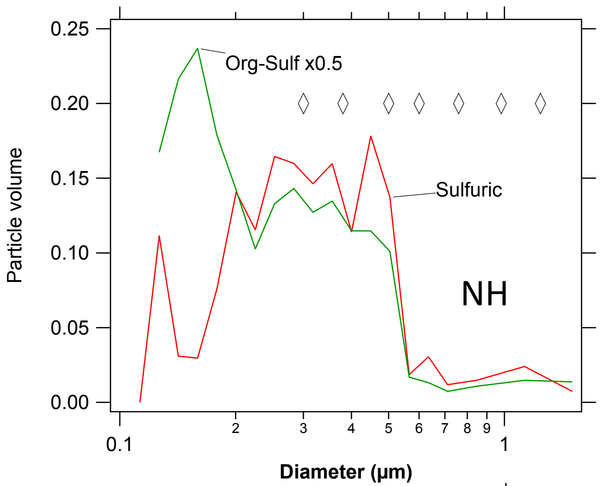
Inferred number mode radius ~0.1 to 0.15 µm

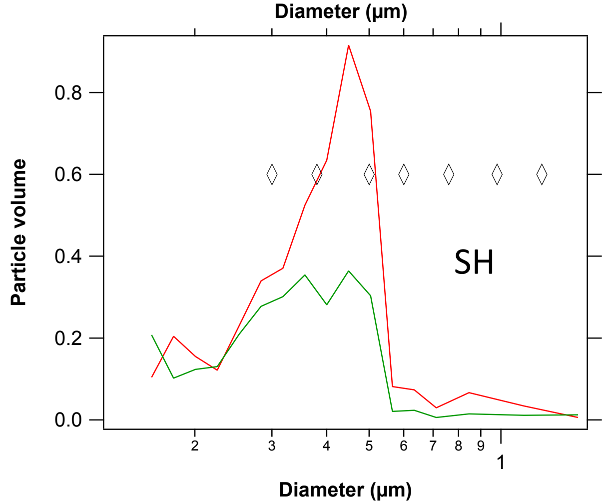
Organic-sulfate

	MMD	Sigma
NH August	0.13	2.2
NH February	0.17	1.9
SH August	(poor fit)	
SH February	0.13	2.3

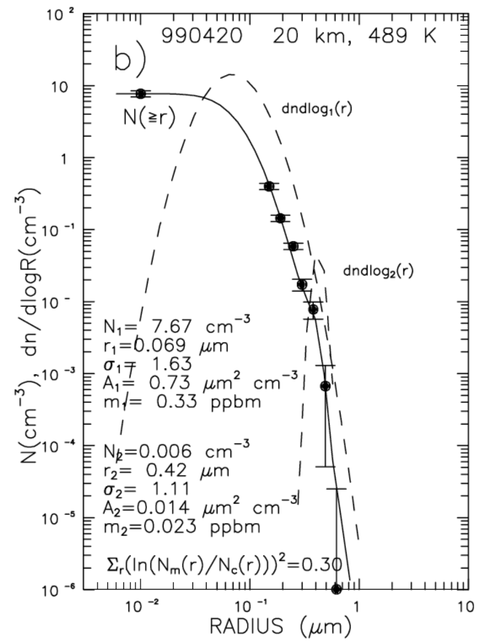


How do these relate to Wyoming bimodal fits?

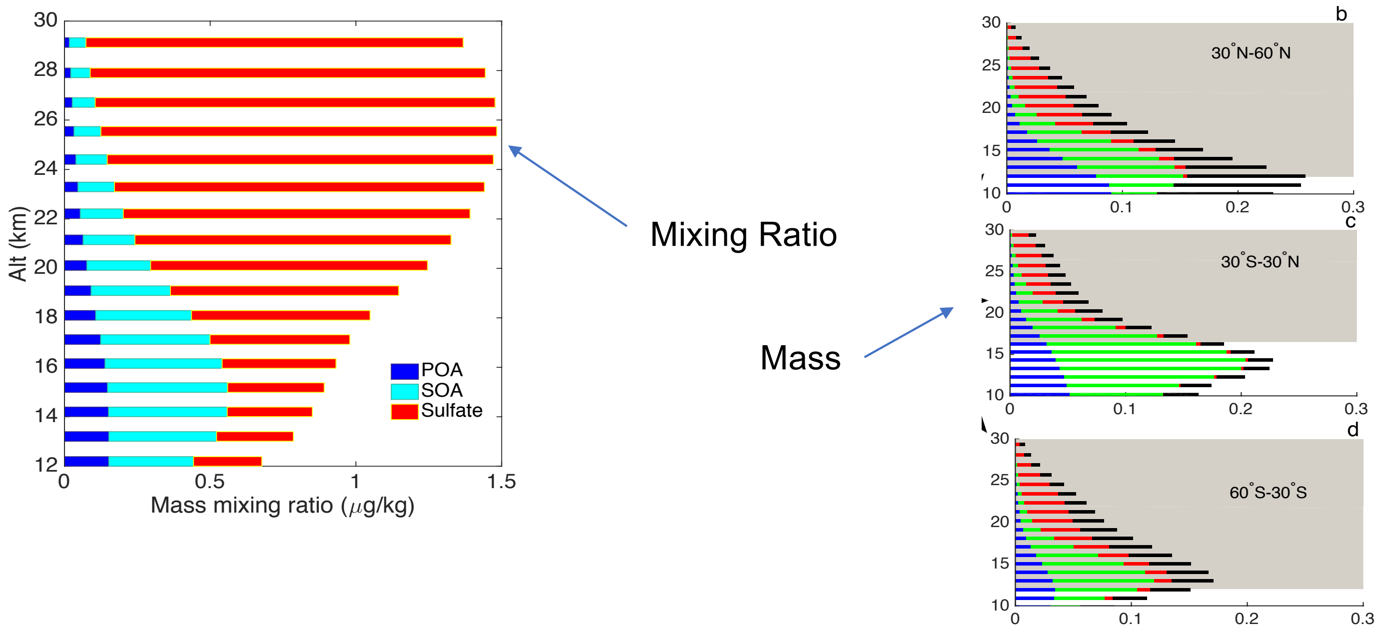




- In many cases, tropospheric and stratospheric aerosol modes likely to look like one broader mode
- Wyoming size bins could resolve narrow sulfate mode volume in some cases
- Bimodal fits are tricky, no clear relationship to these composition modes



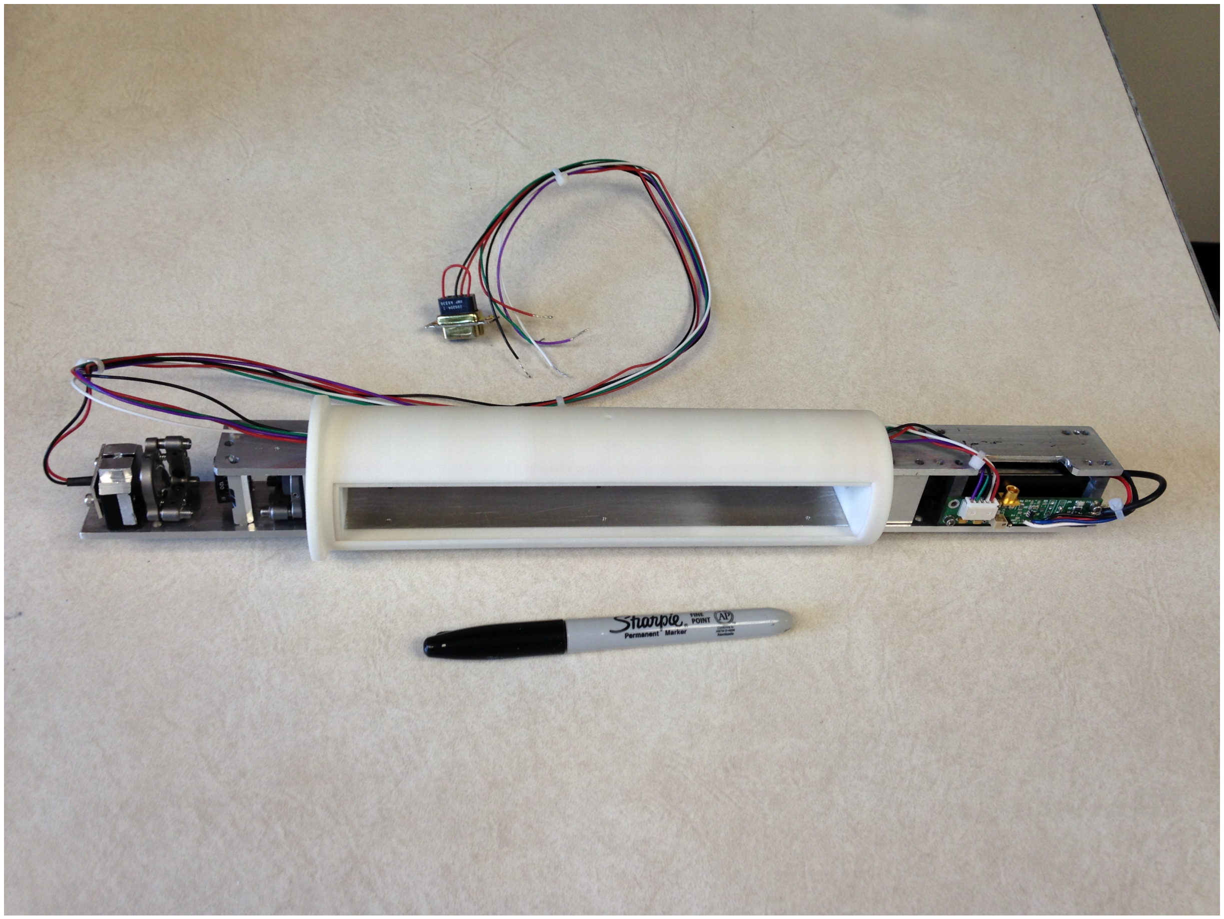
How important is lowermost stratosphere?



(black is sulfate not from OCS)

- CARMA model results
- Junge layer is there: almost all sulfate above 20 km, from OCS
- *But there is a lot of mass near ~15 km*

Side topic: Potential balloon instrument



Cavity ringdown extinction

Shown includes laser and detector, not computer

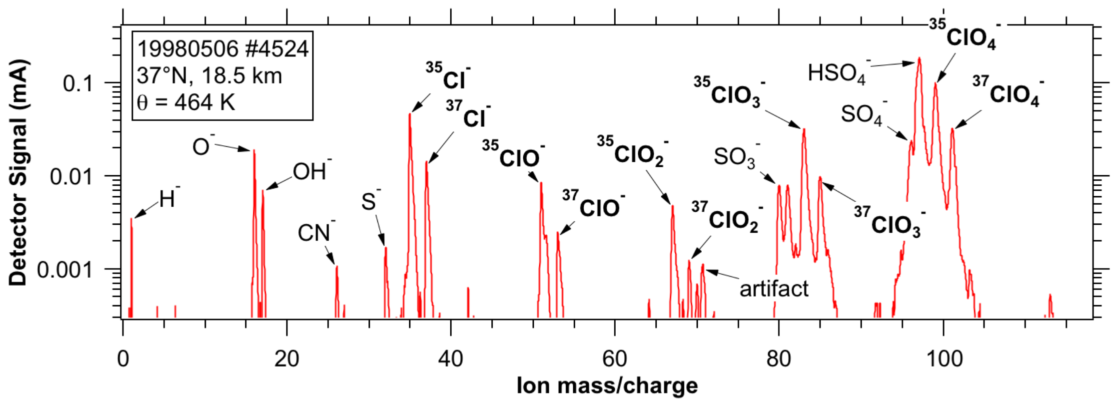
But… fly POPS and calculate extinction?

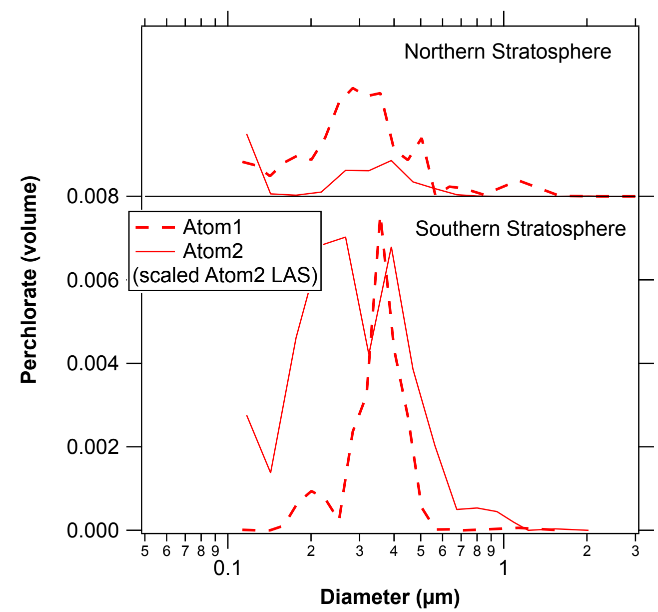
Conclusions

- Lowermost stratosphere has a mixture of tropospheric mixed particles and stratospheric sulfuric acid particles
- *What looks like a broad size distribution can be a sum of tropospheric and stratospheric modes.*
- Sulfuric acid particles are consistently larger with mass median diameter ~0.4 µm
- Sulfuric acid particles have fairly narrow size distributions, $\sigma \leq 1.6$
- Sulfuric acid and mixed particle similar refractive index *until* they encounter moderate RH and take up water.
- Tropospheric particles are almost neutralized => effloresce at stratospheric RH => slightly nonspherical?
- More work to see effect on Wyoming OPC, satellite retreivals

- These newer data are consistent with our Yu et al. paper showing a significant radiative effect from tropospheric aerosol entering the stratosphere.
  Anthropogenic changes in troposphere => radiative *forcing* of about -0.07 W m^{-2}

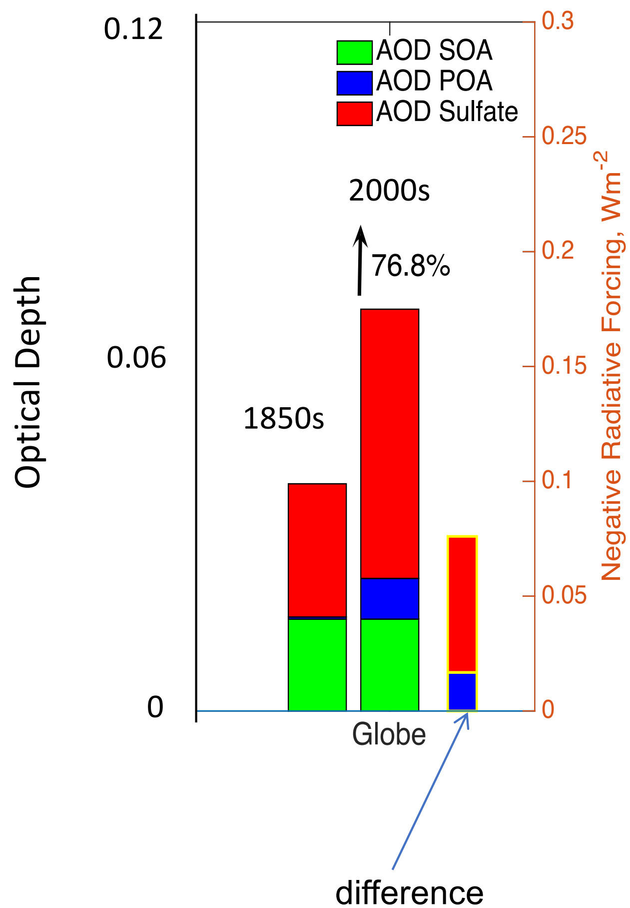
Side topic: Perchlorate





- ~3% of lower stratospheric particles are rich in perchlorate (much of aerosol Cl, small fraction of gas-phase Cl)
- Much more Southern Hemisphere February than any previous measurements (still small amount, not significant for mass or light scattering)
- Left over from ozone hole?

Model Radiative Forcing: nonvolcanic stratosphere

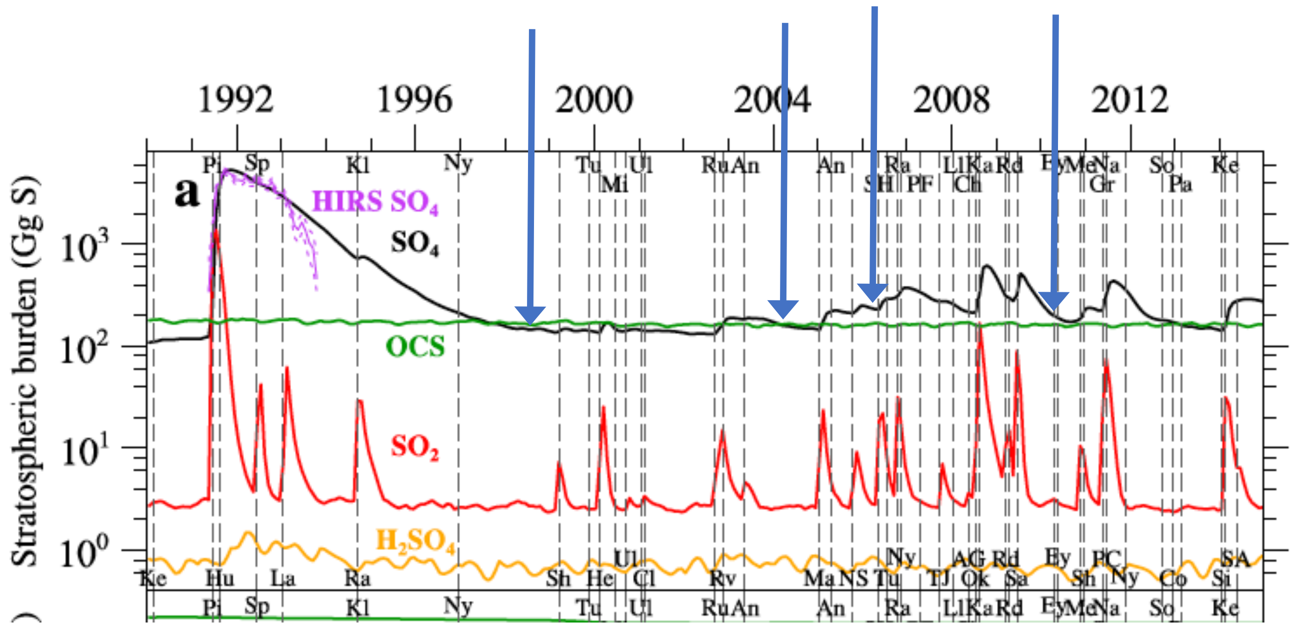


- Globally, 1.7x change in stratospheric optical depth from 1850s
- Forcing is mostly from sulfate - anthropogenic SO_2, some OCS
- Anthropogenic sulfate mostly <u>enters stratosphere as aerosol, not SO_2</u>
- Small but significant forcing from organics
- About -0.07 W m^{-2}

Myhre et al. 2004: -0.05 W m^{-2} (no organics)

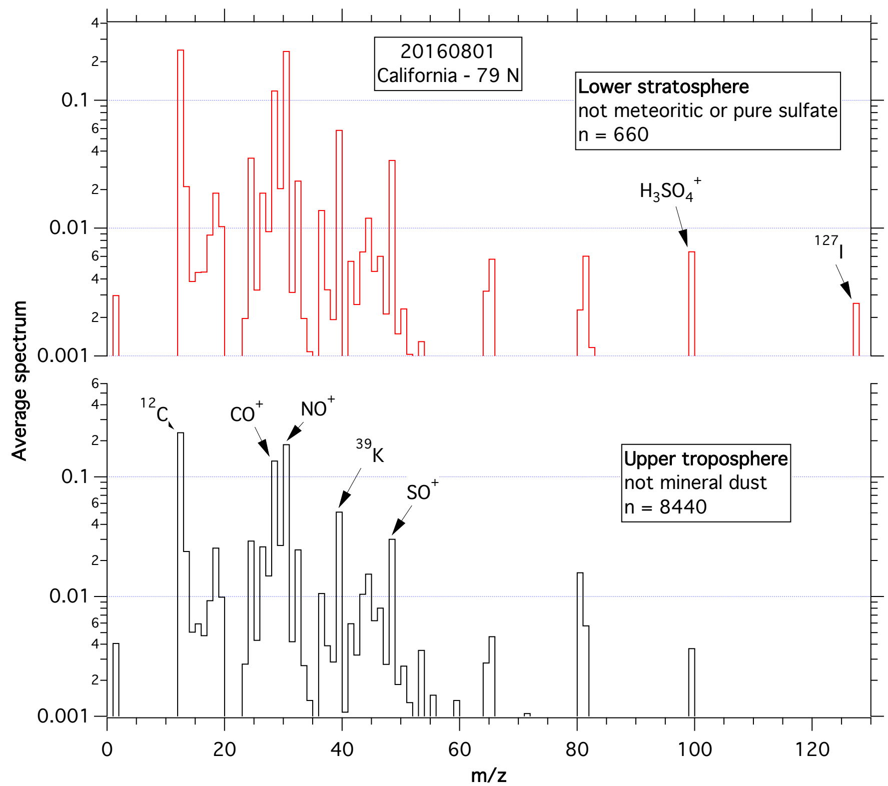
Volcanic and non-volcanic conditions

- PALMS data are in non-volcanic conditions



Mills et al., 2016

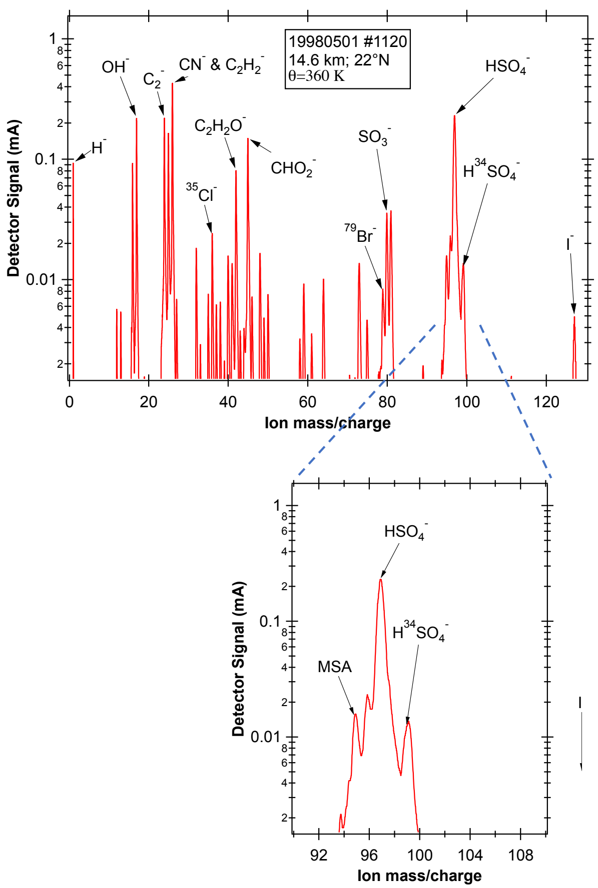
Compare mixed particles in troposphere and the stratosphere:

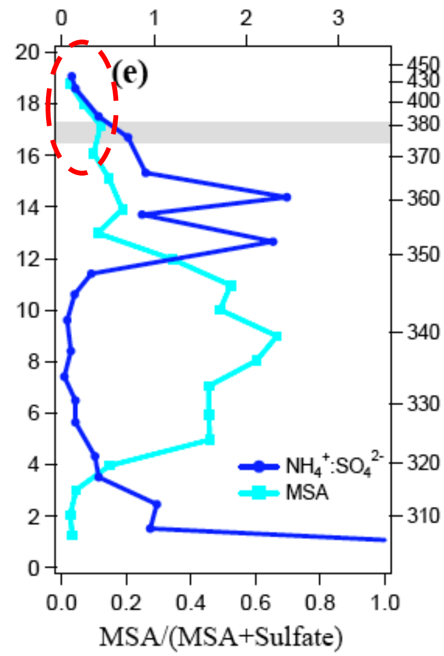


- Almost identical average mass spectra
- The mixed particles in the stratosphere came from the troposphere (Not necessarily from right underneath)

- PALMS organic fragments are not super informative, but they are very similar across large regions of the upper troposphere – lower stratosphere (**glop**)
- About 20 to 40% originated as smoke

Detail: Sulfur sources





- SO_2 and OCS both make mostly H_2SO_4
- DMS makes significant amounts of CH_3SO_3H (MSA)
- Stratospheric sulfate has little MSA
- Either DMS is a minor source or MSA decays
- Maritime convection rarely reaches the tropopause
- *Continental* convection is a major route to the tropopause

Sedimentation