Chemistry of aerosol particles in the upper troposphere and lower stratosphere

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Outline

Introduction

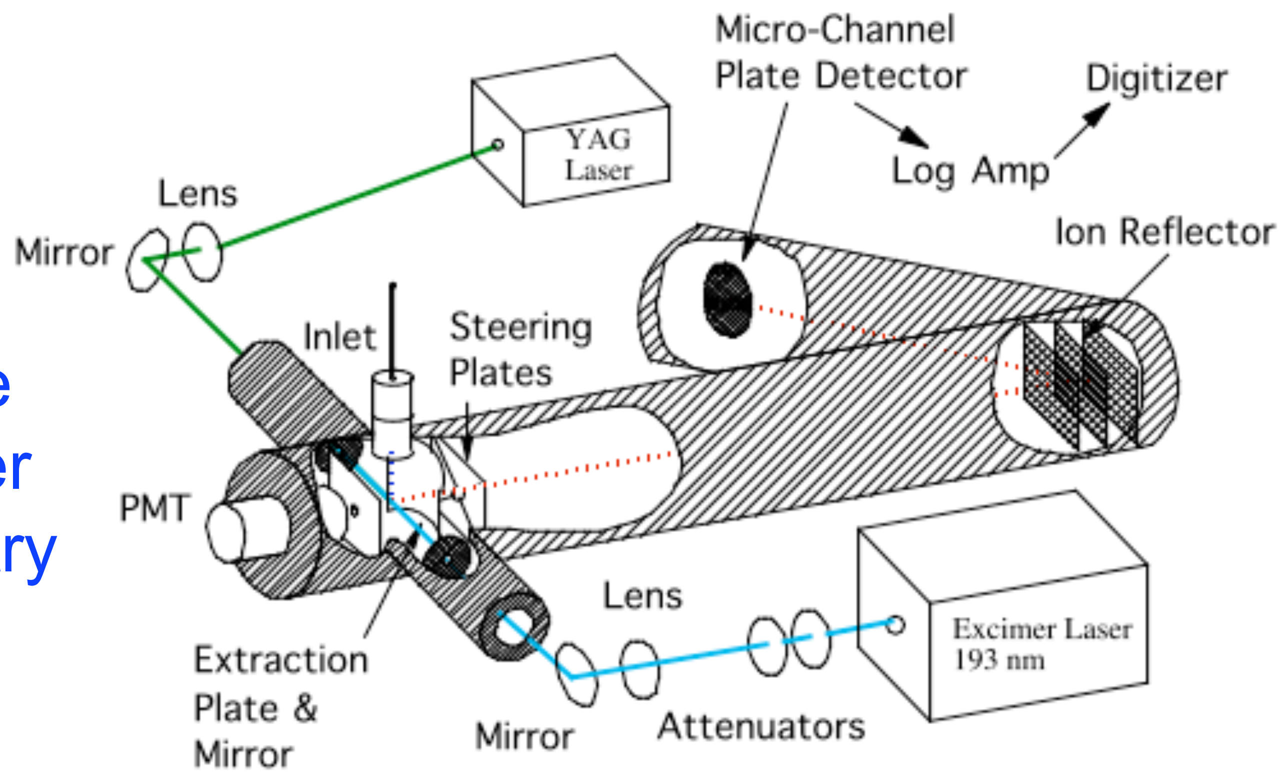
Stratospheric particles

- *where particles form*
- *lessons for understanding the lower atmosphere*

Tropical upper troposphere *(Karl Froyd)*

- *organic content*
- *methanesulfonate (from oceanic DMS)*
- *acidity*
- *implications for ice formation*

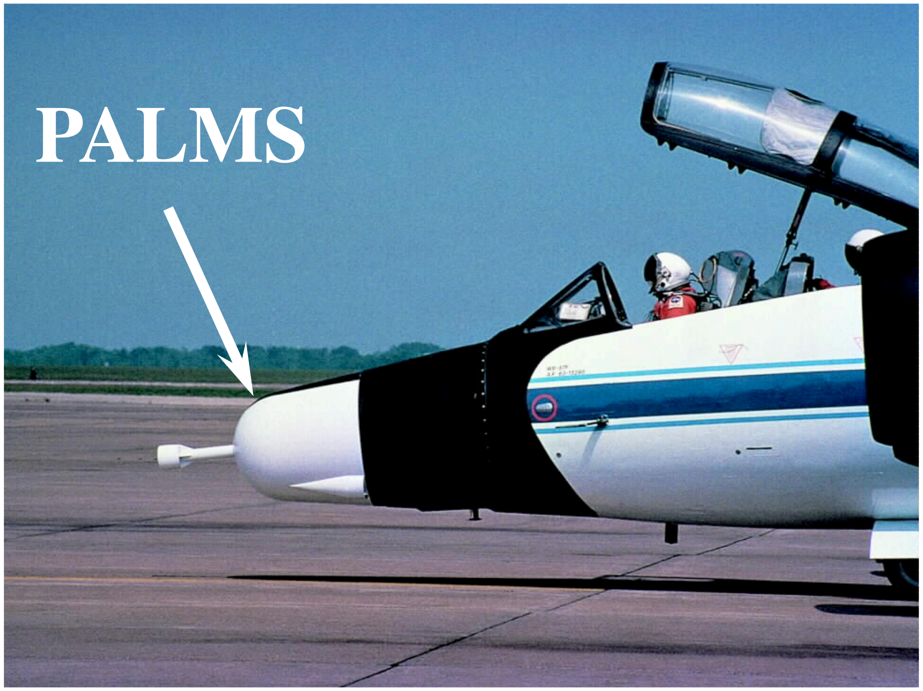
PALMS: Particle Analysis by Laser Mass Spectrometry

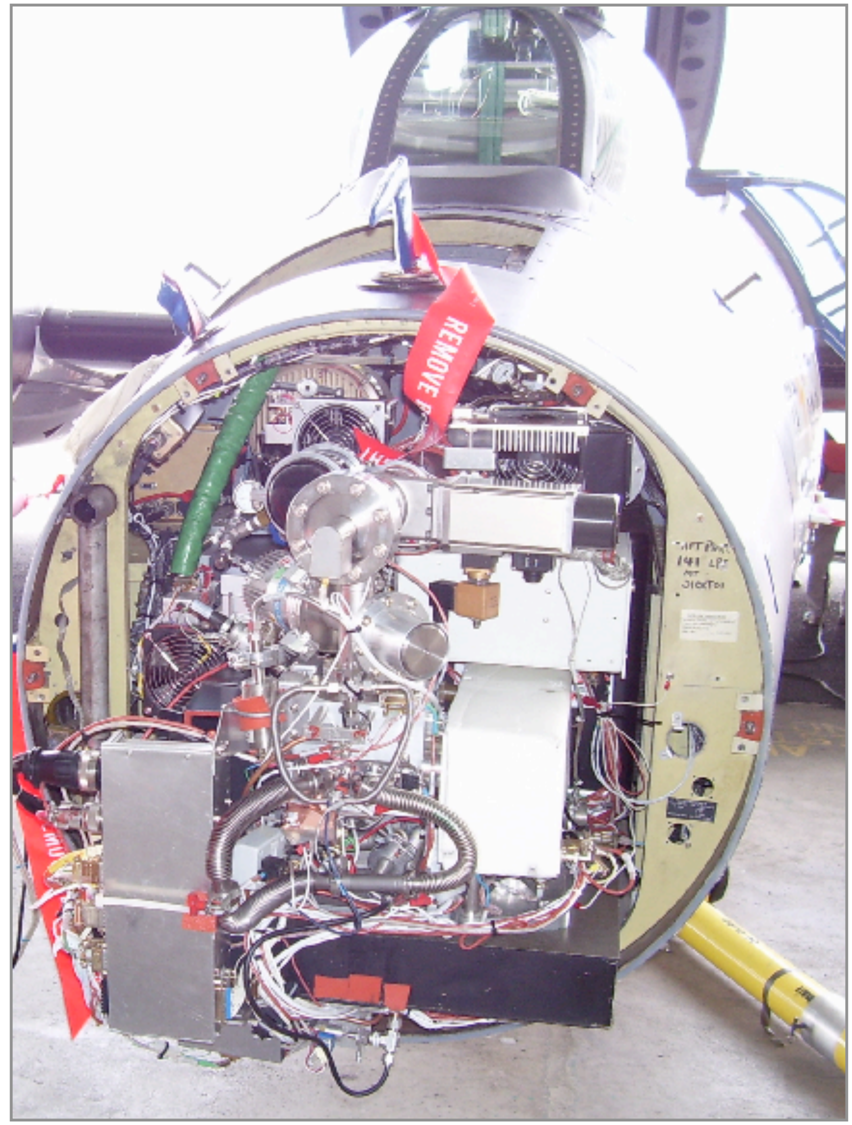


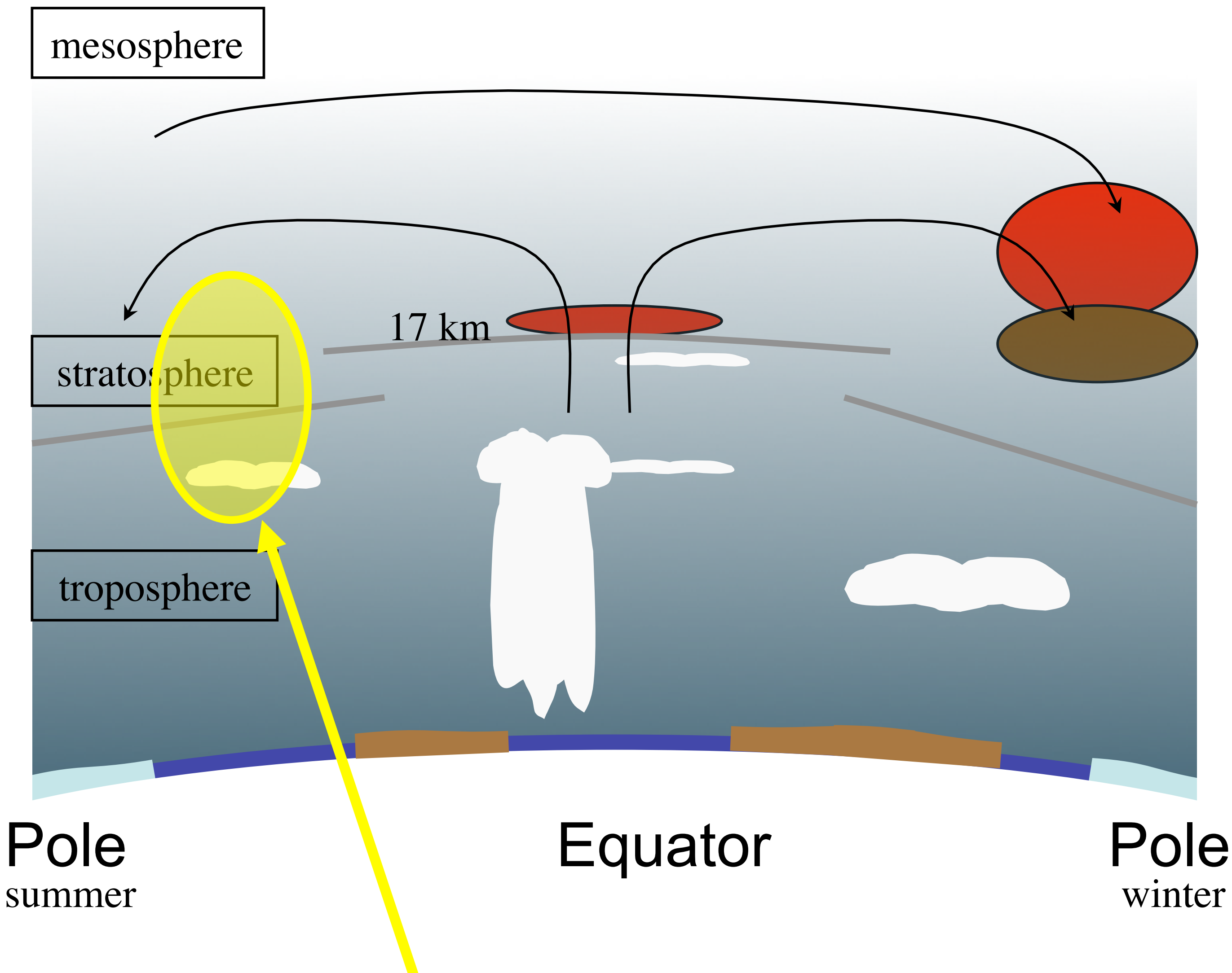
1) Particle enters vacuum. Trigger from light scattered from continuous laser.
2) Excimer laser beam hits particle.
3) Positive or negative ions analyzed with TOF mass spectrometer.
   - Size range about 0.25 to over 3 μm diameter

Much of the mass and light scattering
Minority by number

NASA WB-57F







Stratosphere

Long residence time: months to years

Very oxidizing

Almost no high molecular weight organics in gas phase

New particle formation

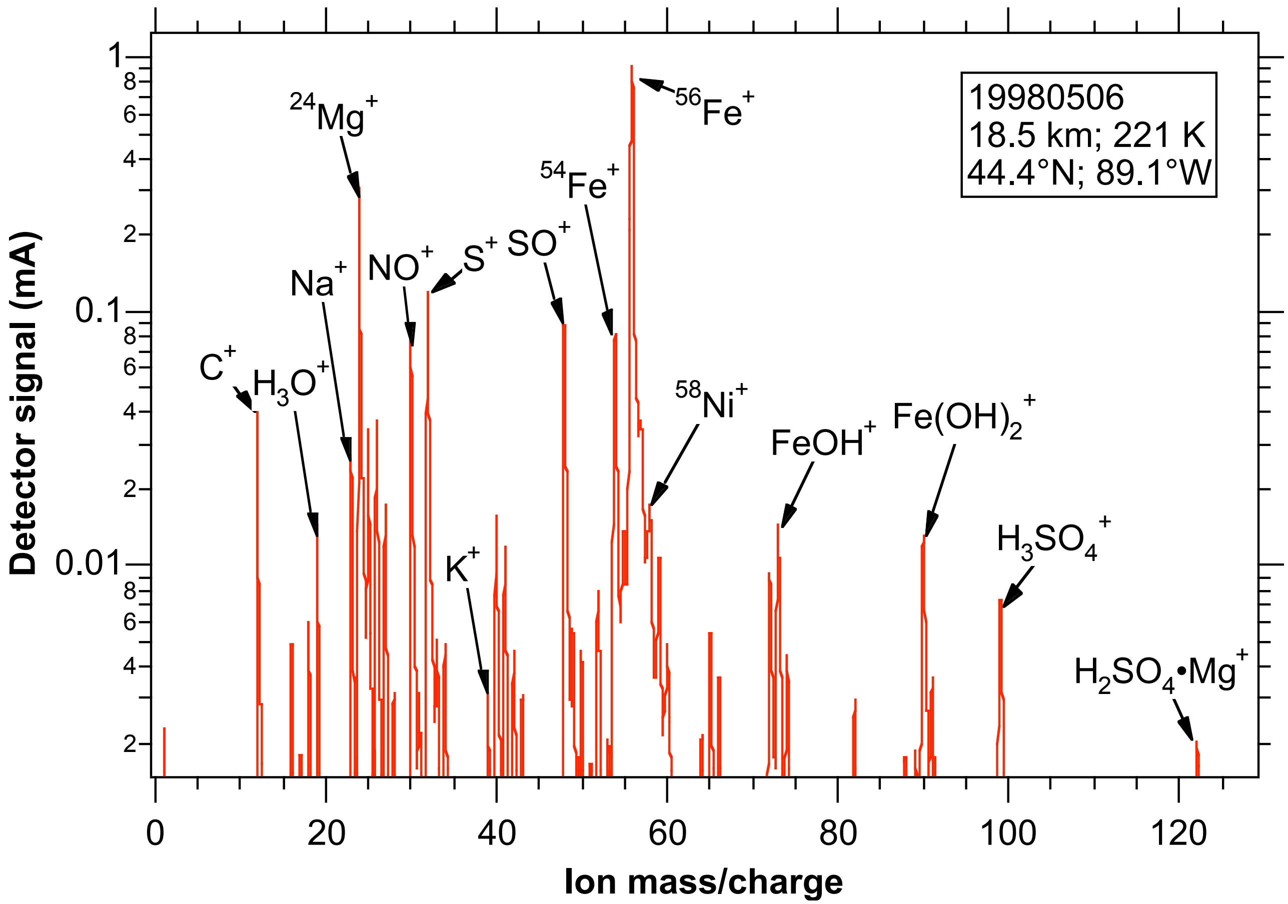
Brock, Rosen, Wilson et al.

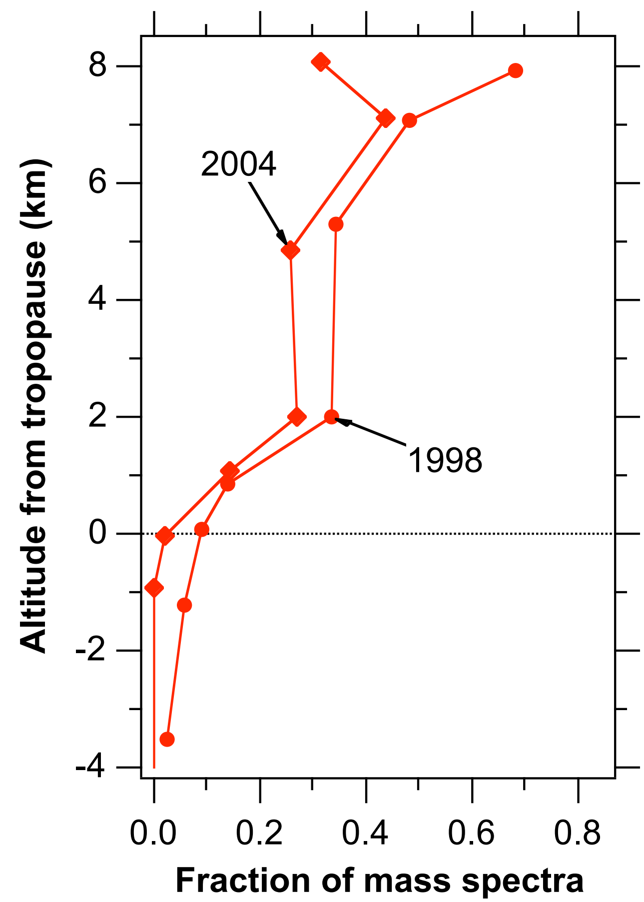
Nonvolatile CN

Curtius et al.

3 types describe >95% of stratospheric particles

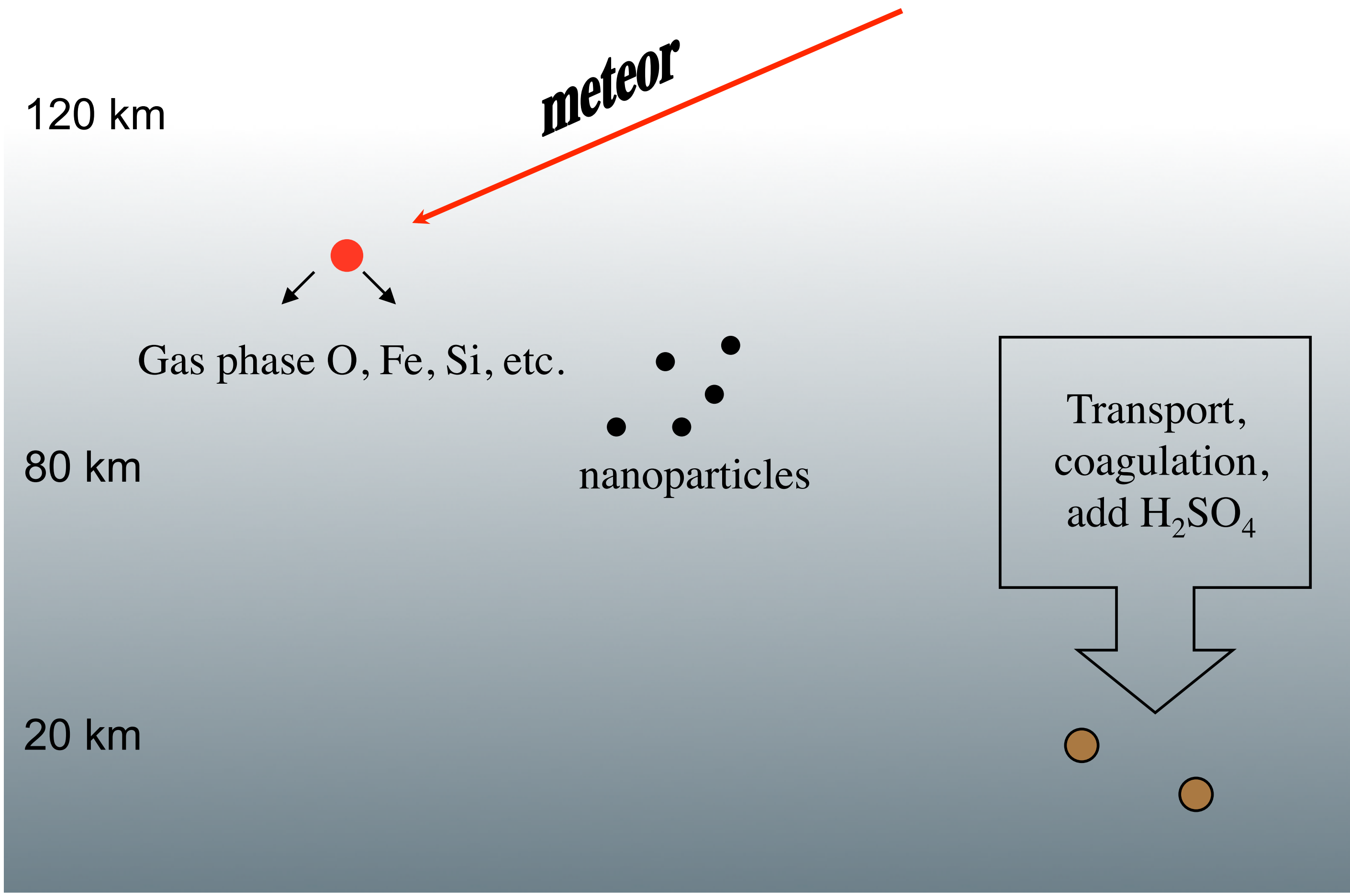
Type 1: Sulfuric acid with metals





Murphy et al., JGR, 2007

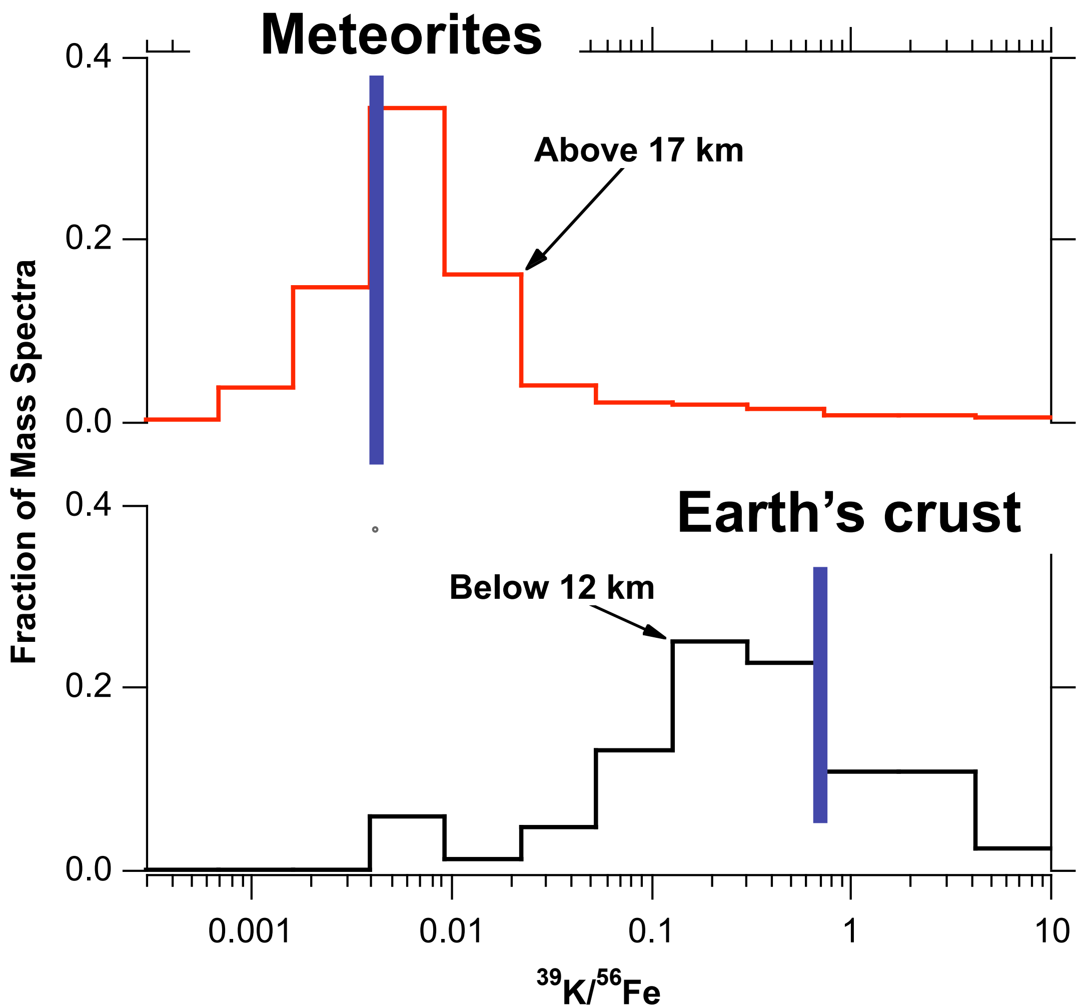
Mechanism



Sidelight: Calibrations for Fe::S constrain the flux of meteors.

Cziczo et al., Science, 2001

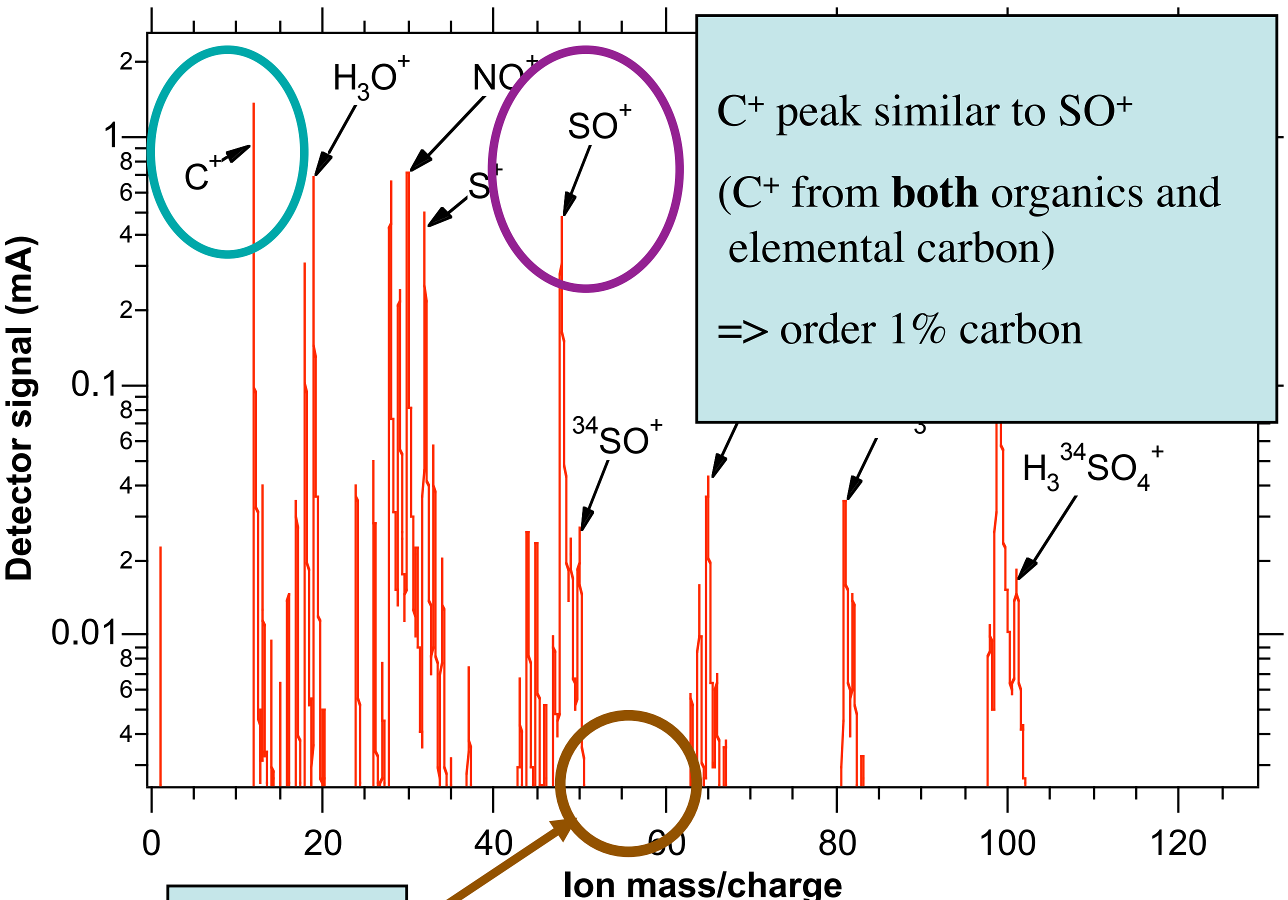
Source of stratospheric metals



Na, Mg, Ca, Mn, Ni also match meteoric ratios

2500 kg yr^{-1} global flux of meteoric K

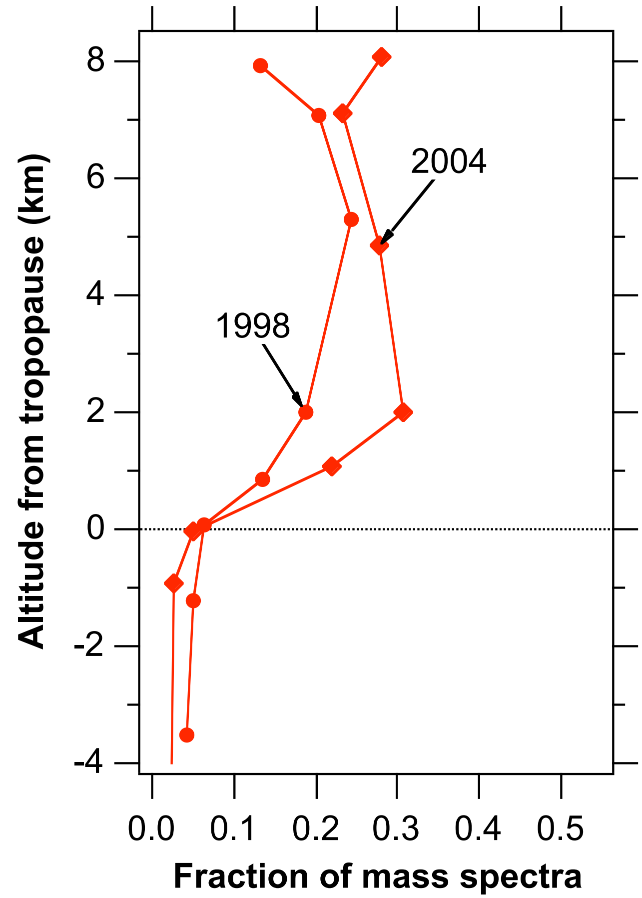
Type 2: Sulfuric acid without metals



C^+ peak similar to SO^+

(C^+ from **both** organics and elemental carbon)

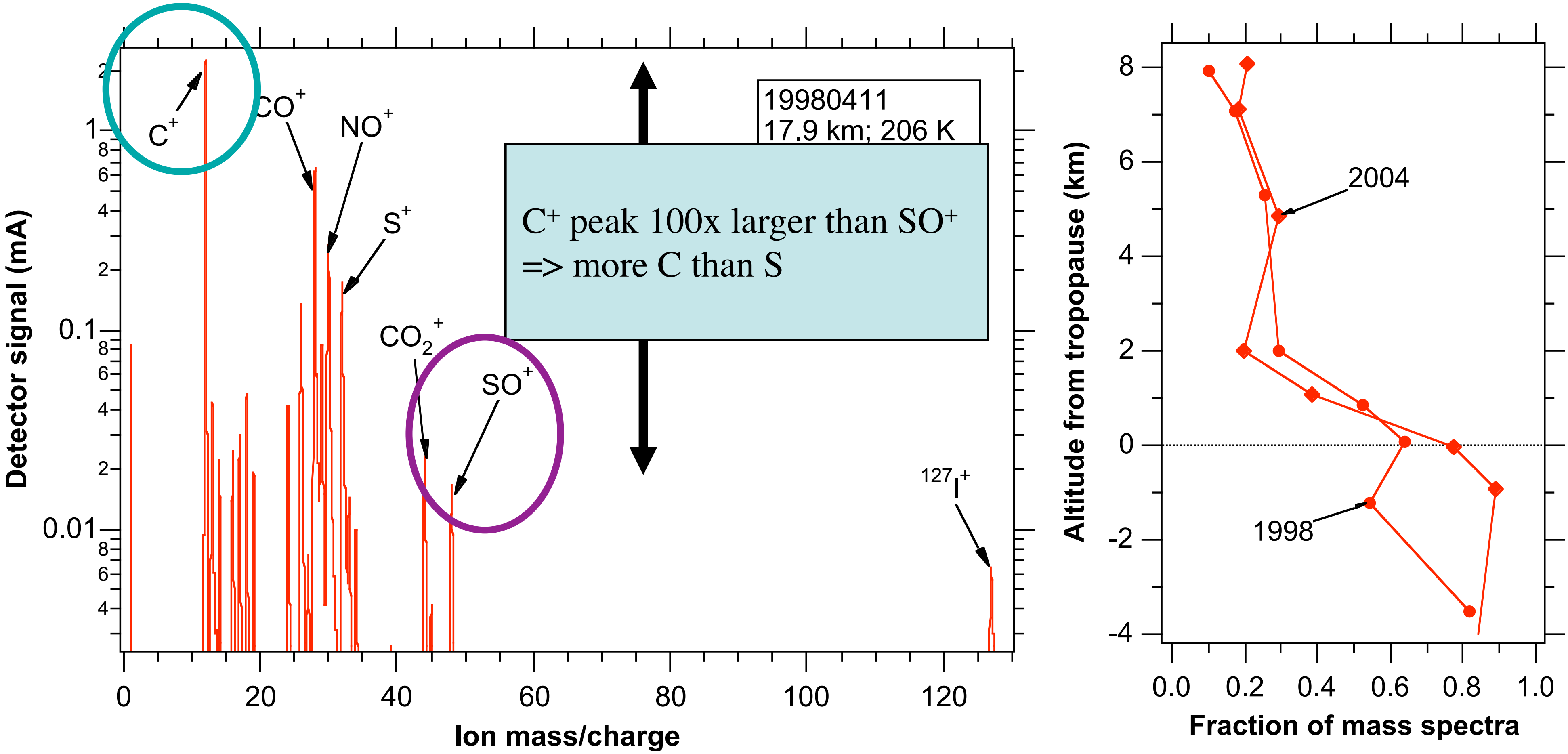
=> order 1% carbon



No Fe!

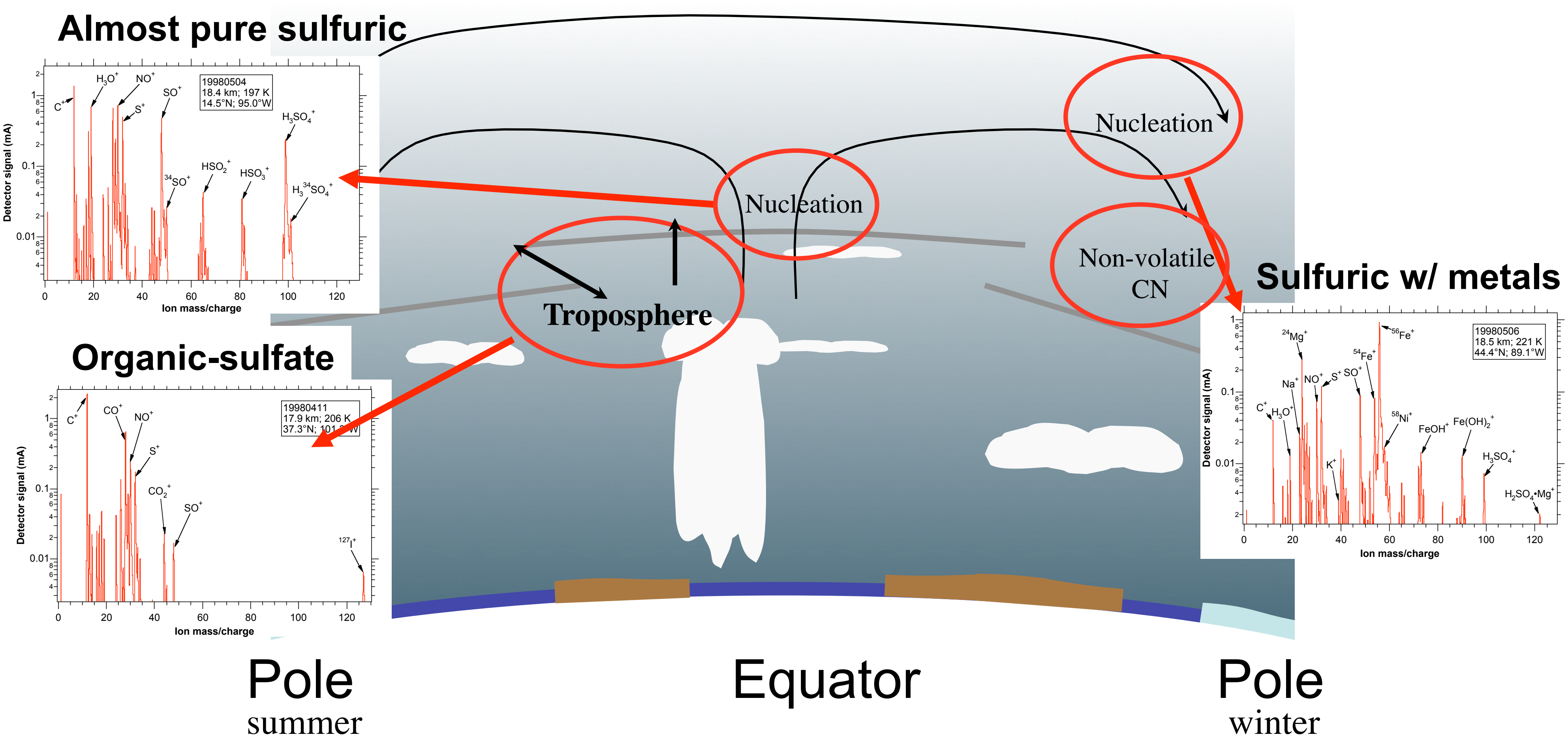
Also stratospheric in origin

Type 3: Organic-sulfate mixtures



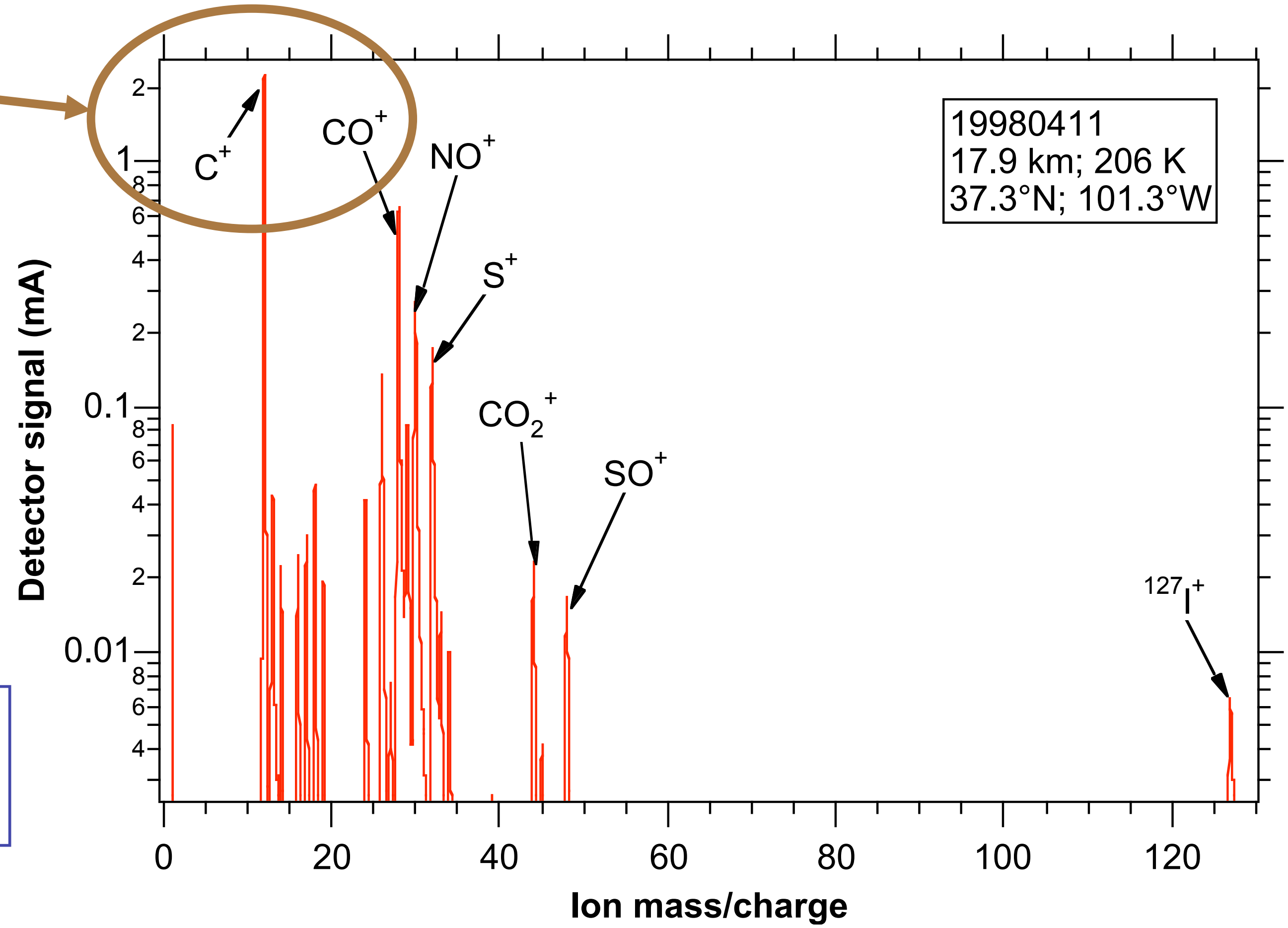
Upper tropospheric particles

Stratospheric particles



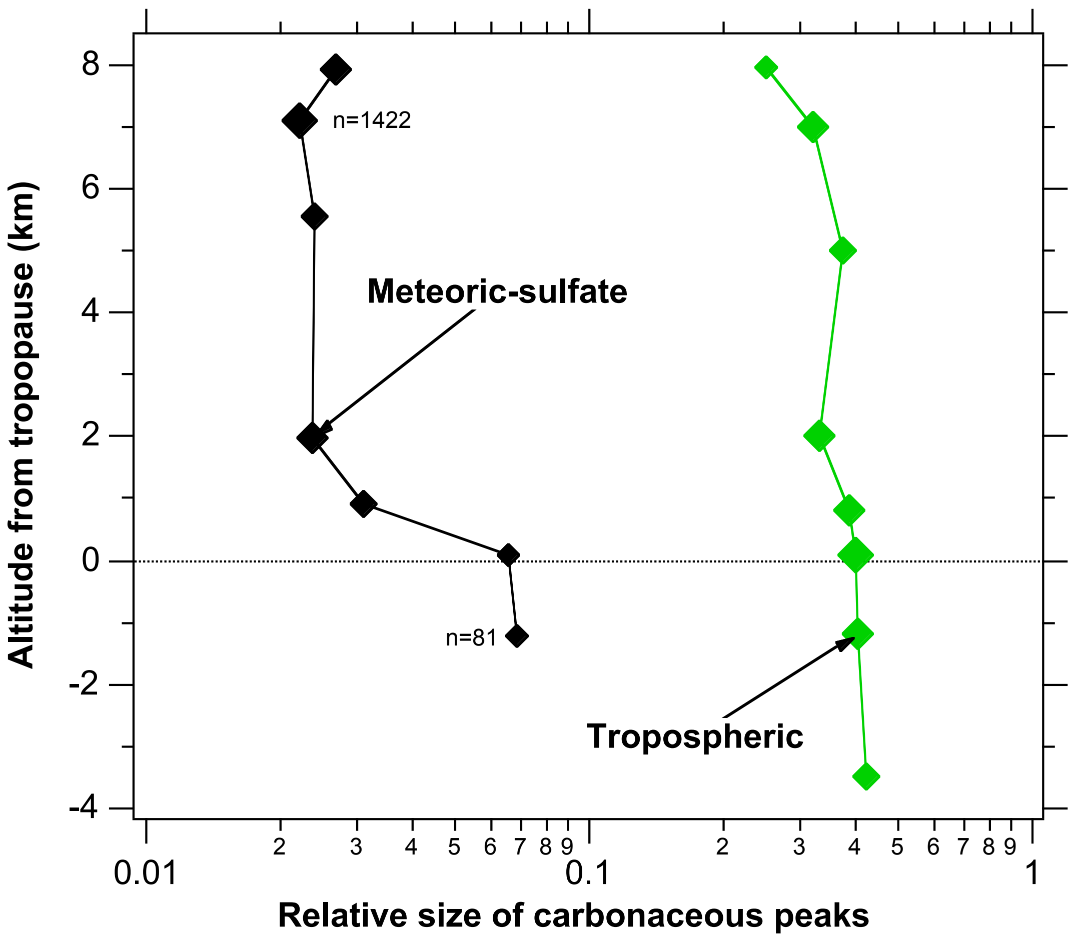
Learn about carbonaceous material

Look at the relative size of these peaks (*Mostly organic carbon)*



Sort by type of particle

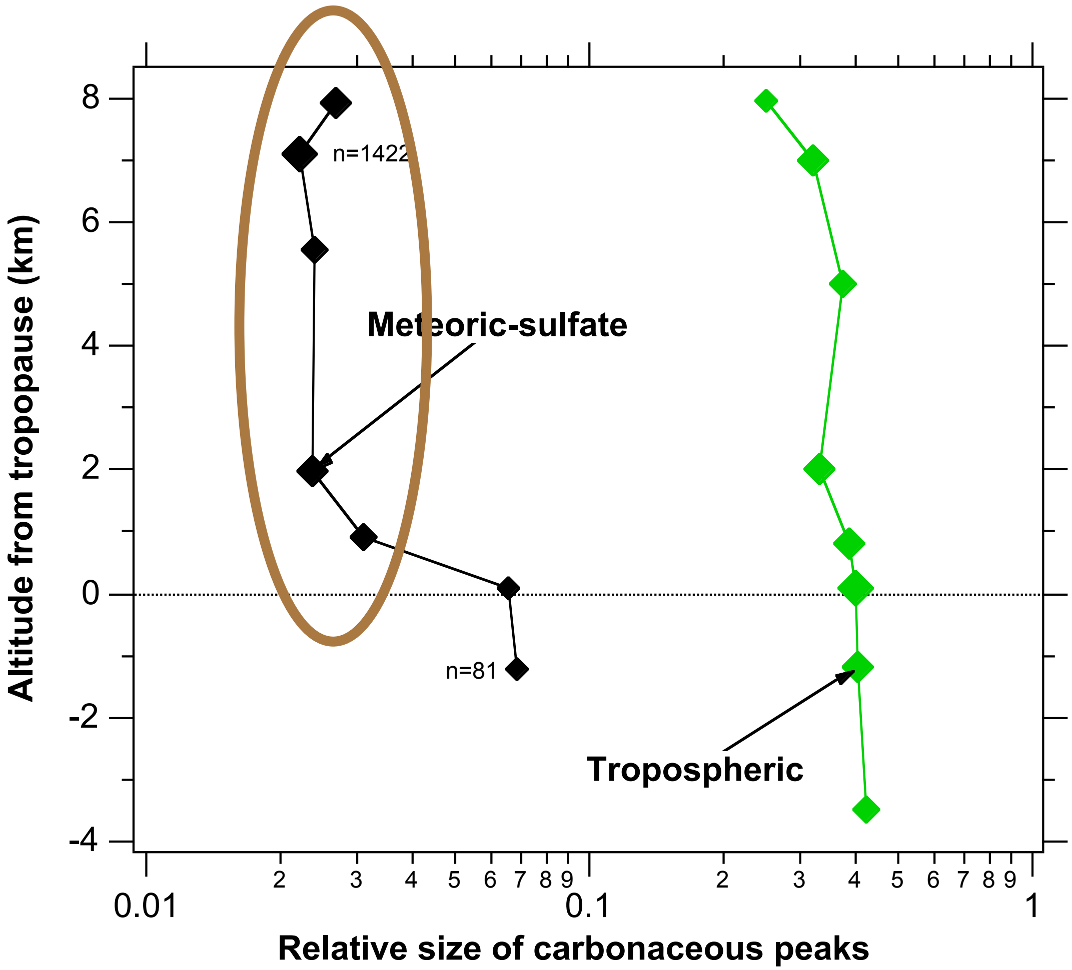
Learning from the stratosphere



Obvious:

Particles formed in the troposphere have more organic content.

Learning from the stratosphere



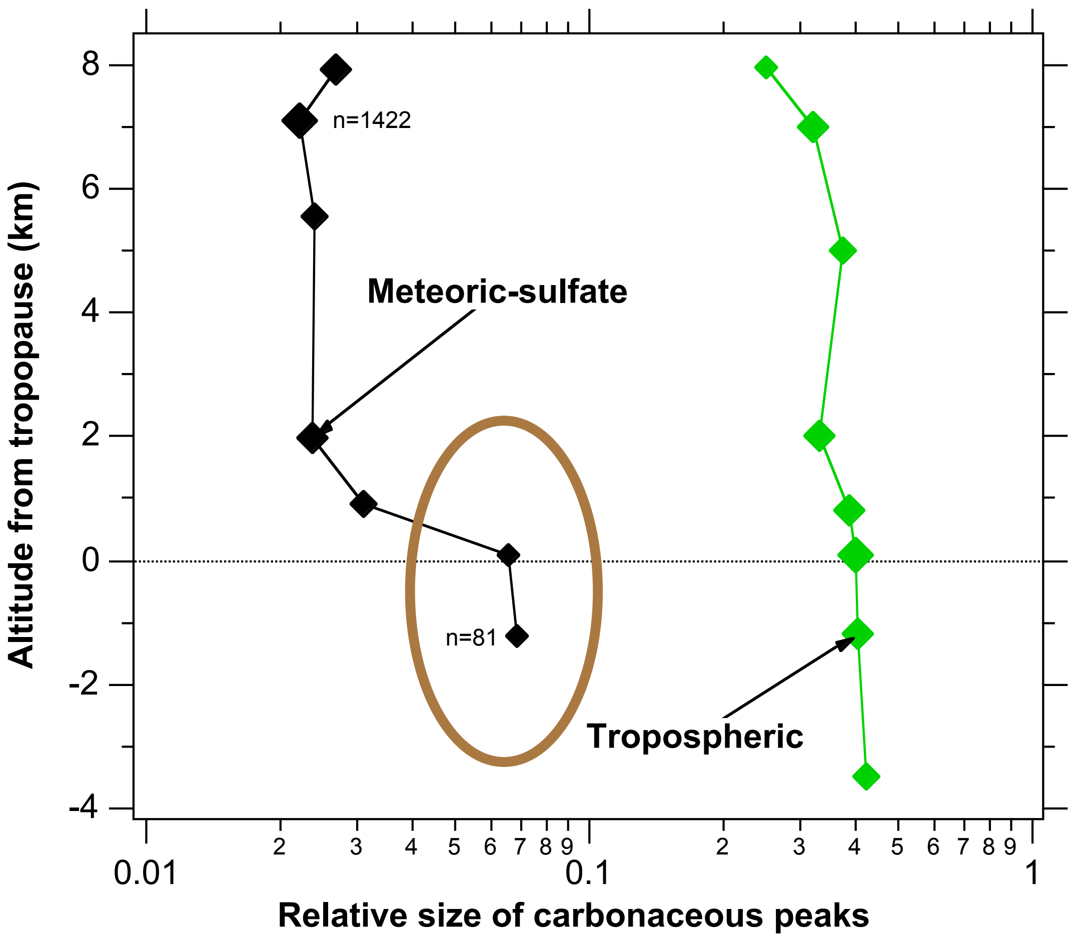
Lesson 1:

Particles that spend their lives in the stratosphere have very little organic content.

Limited acid-catalyzed polymerization with small organics like formaldehyde (e.g. Iraci and Tolbert, 1997)

Murphy et al., JGR, 2007

Learning from the stratosphere

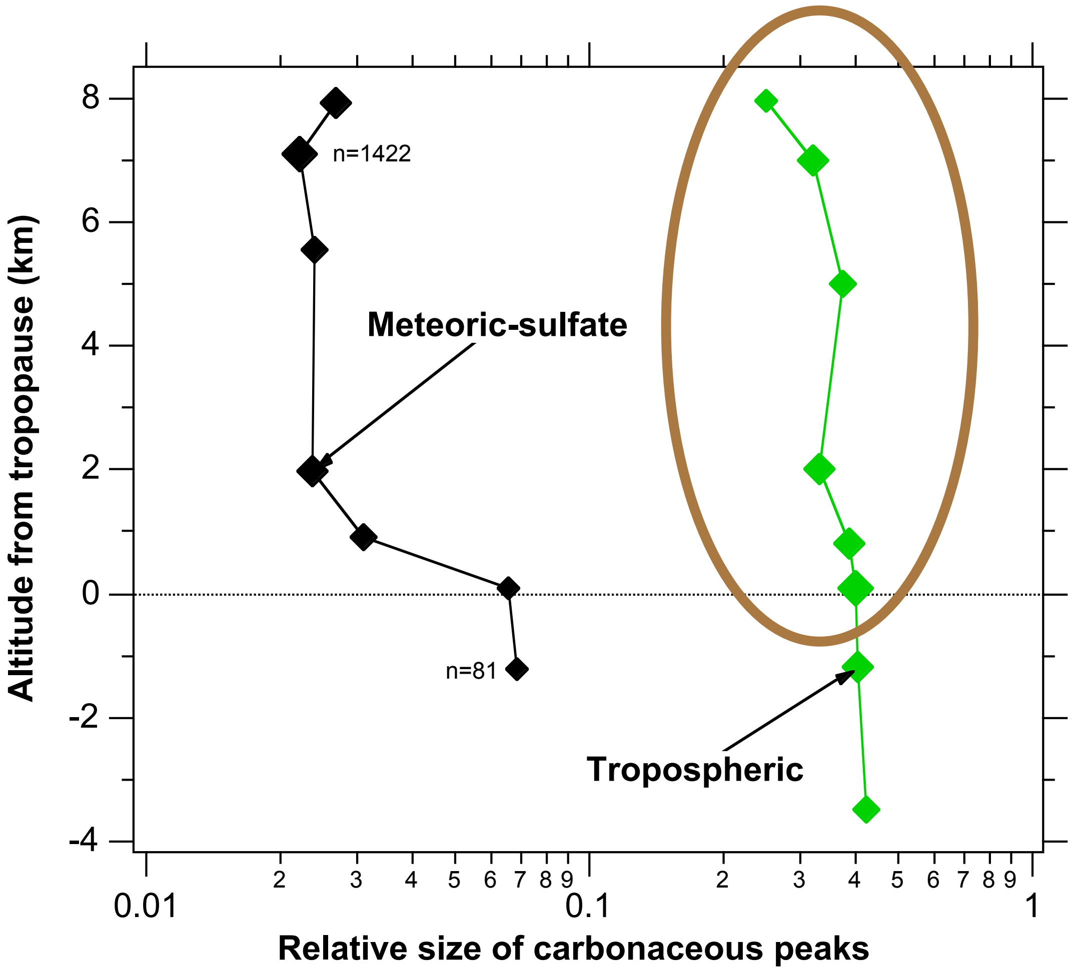


Lesson 2:

Particles acquire carbon when they first encounter tropospheric air.

Secondary organics even in the upper troposphere

Learning from the stratosphere



Lesson 3:

Tropospheric particles that spend months in the stratosphere don't lose much organic content.

Little loss of semi-volatiles

Very slow loss of organic mass due to heterogeneous reactions with OH and O_3.

Molina et al. 2004: 6 days

For carbon loss via OH $\gamma << 0.1$

Stratosphere summary

We can determine the source of *individual particles*:

- Organic-sulfate mixtures: *troposphere*
- Sulfate with meteoric metals: *upper stratosphere, polar vortex*
- Sulfate without metals: *lower stratosphere*

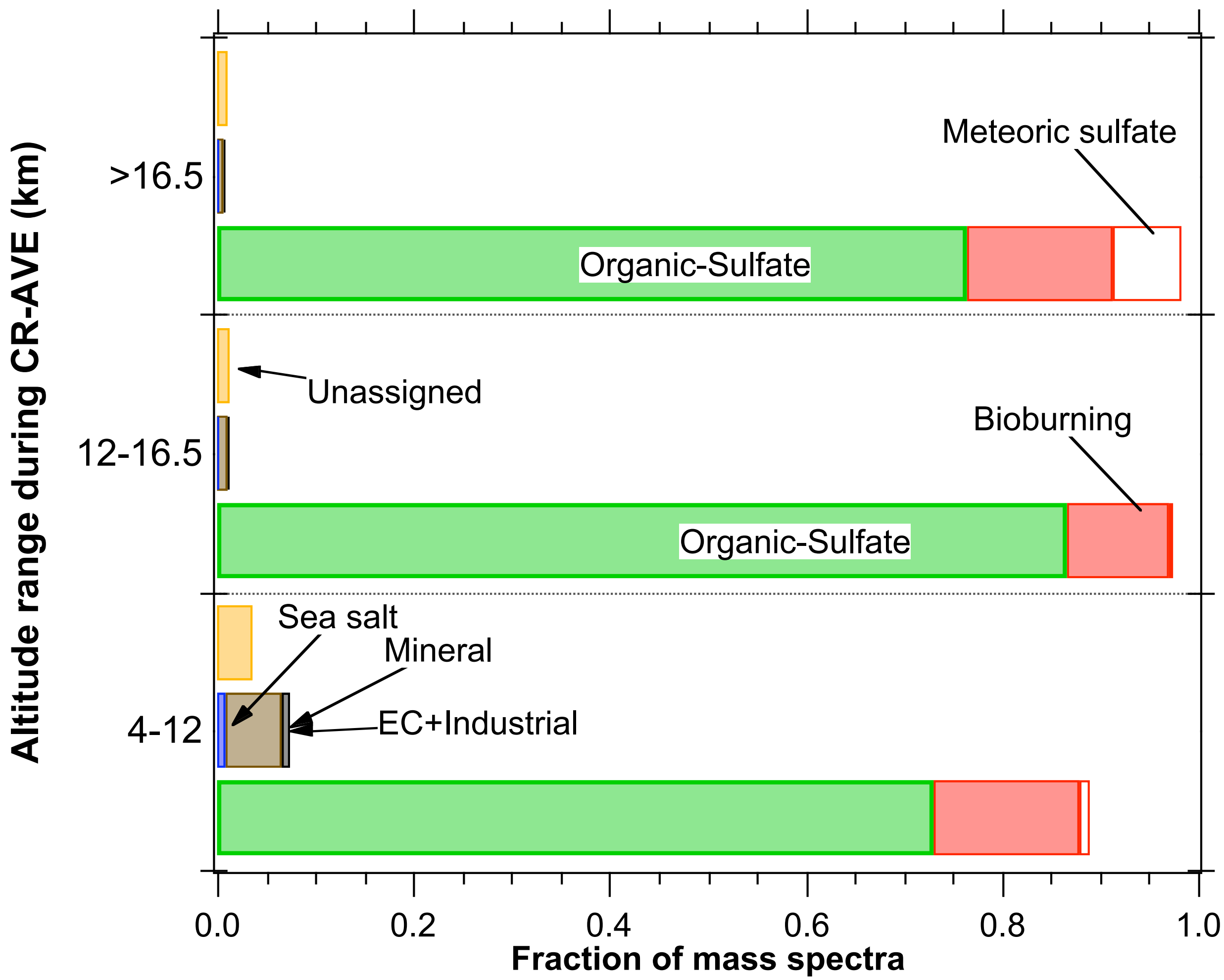
Organic content carries lessons:

Why stratosphere useful: minimal complications with gas-phase organics

- Organics added to particles at the tropopause
- Organics in atmospheric particles are much more resistant to carbon loss than organics used in lab studies
- Limited acid-catalyzed formaldehyde chemistry

Particle types during CR-AVE

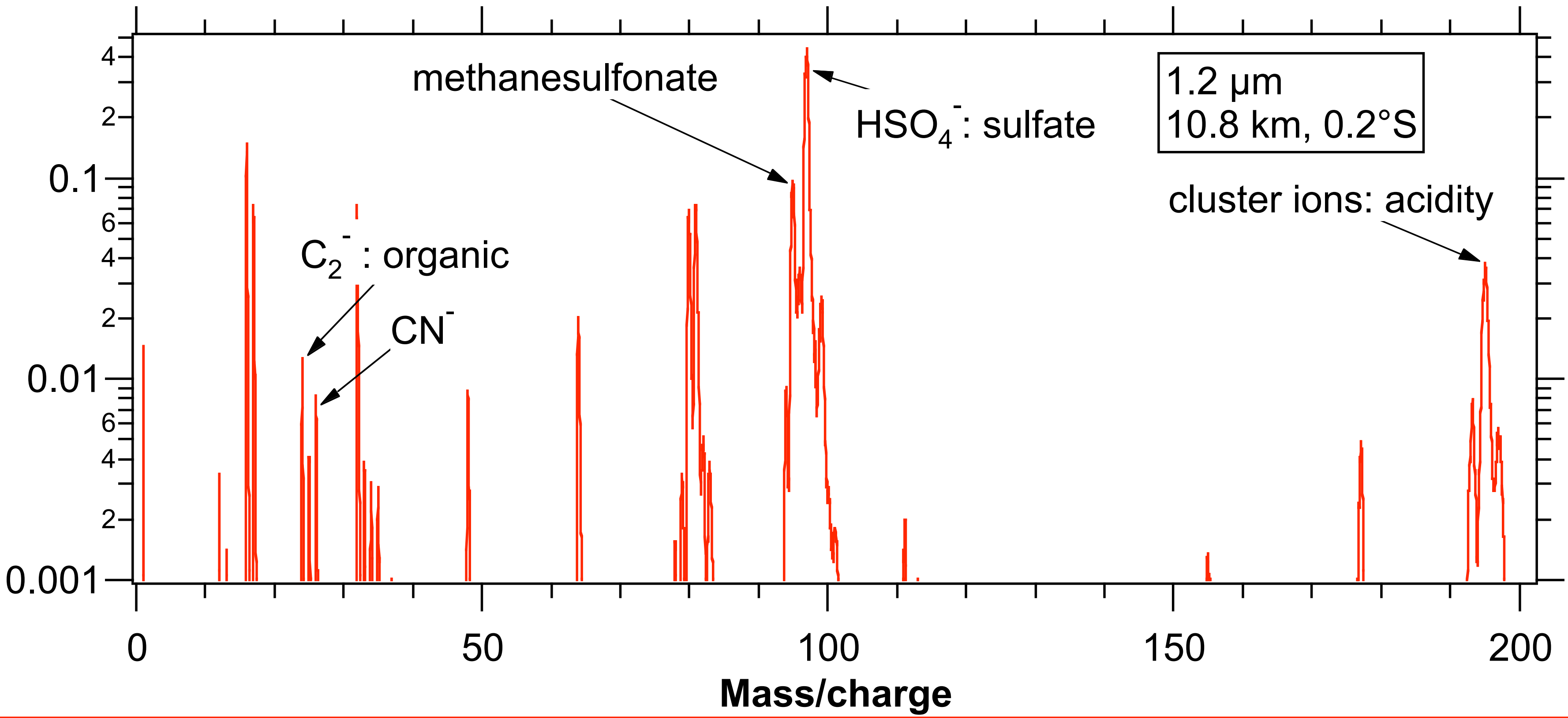
Near Costa Rica, February 2006



- Larger than ~ 250 nm

12-16 km: 100% particles contained carbon

Single tropospheric spectrum (-)



Convert relative peak areas to mass fractions using

- lab calibrations (MSA)
- correlations to AMS and PILS on low altitude flights (organics, acidity)

Assumption: high altitude particles ionize like those below 7 km

Two missions, both Costa Rica in NH winter

Pre-AVE 2004; CR-AVE 2006

Convective influence from L. Pfister

Bulk composition *of organic-sulfate particles*

Pre-AVE:
Amazon
convection

CR-AVE:
Maritime
convection

Sulfate chemistry in CR-AVE

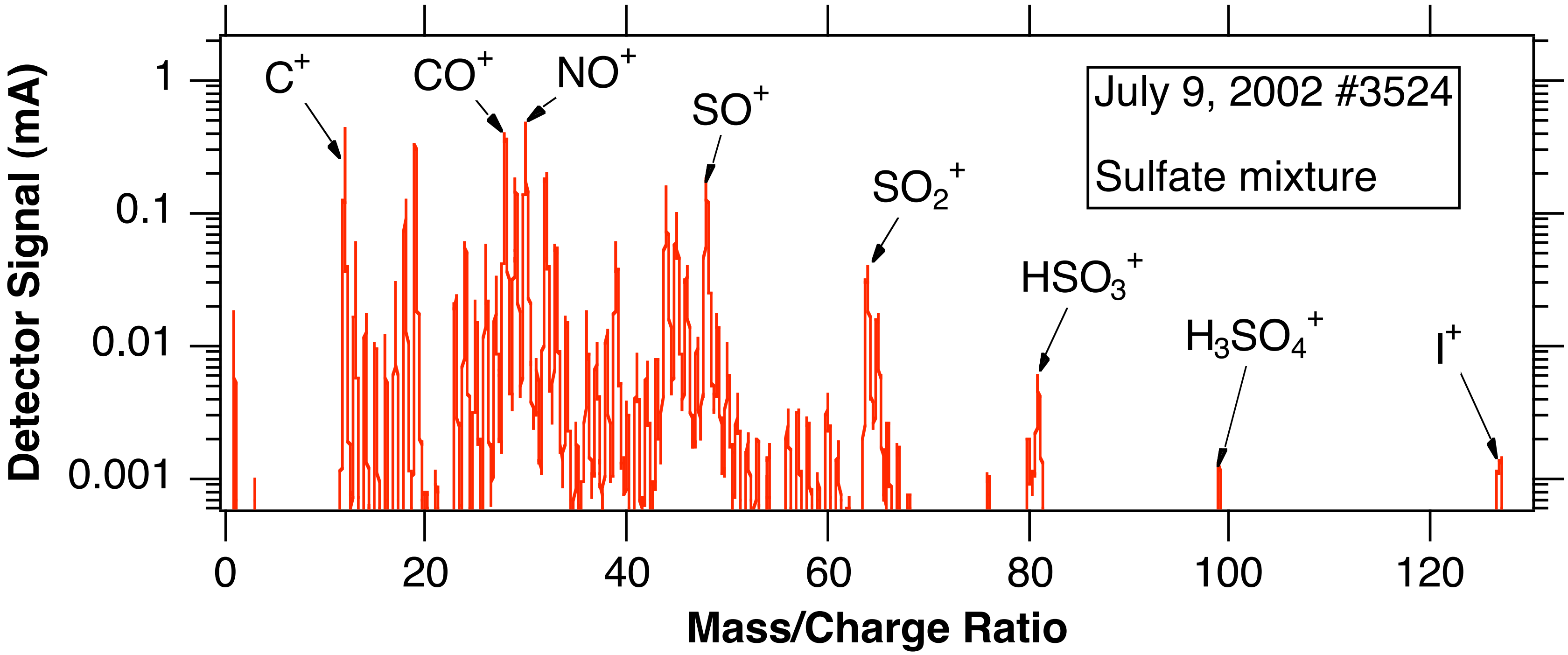
TTL less acidic than bisulfate

Acidic, high MSA
Maritime outflow tops out at ~12 km

Very high MSA fraction from reactions of lofted DMS

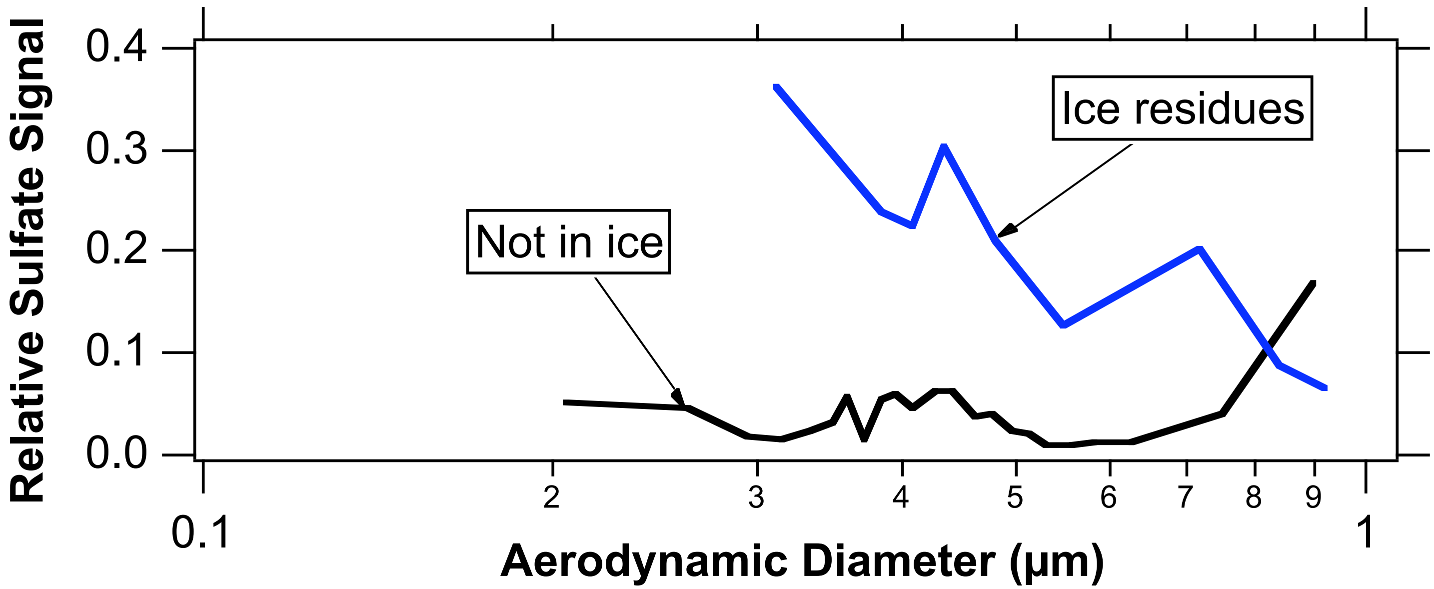
Some ice residues (CRYSTAL -FACE)

- Near Yucatan at 45,000’
- No nearby thunderstorms



Cziczo et al., JGR, 2004

Only organic-sulfate nuclei:



- At this altitude almost every particle is an organic/sulfate mixture
- But not all the same, and particles with more sulfate freeze better.
- Smaller particles seem more sensitive to chemical composition.
- *Water uptake and freezing probabilities (Kärcher and Koop, 2005)*

Cziczo et al., GRL, 2004

Upper troposphere summary

Entry condition to stratosphere:

• Organic-sulfate mixtures

TTL:

• Aerosol chemistry in TTL distinct from convective outflow at 10-12 km

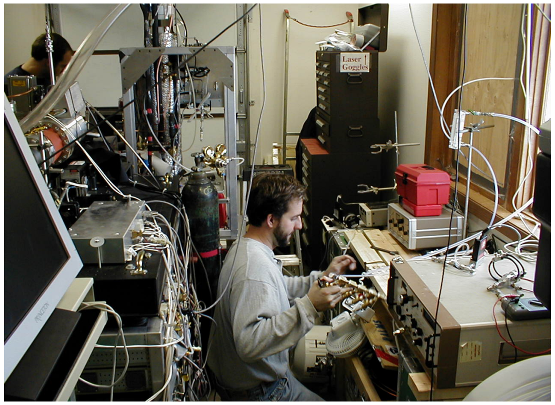
Ice formation:

• High organic content => glassy states possible

• Not very acidic => possible heterogeneous nucleation of ammonium sulfate

• High organic content in TTL
  - deeper continental convection carries up organics?
  - sustained by preferential removal of sulfate?

Thank you for your attention!



Dan Cziczo, Storm Peak

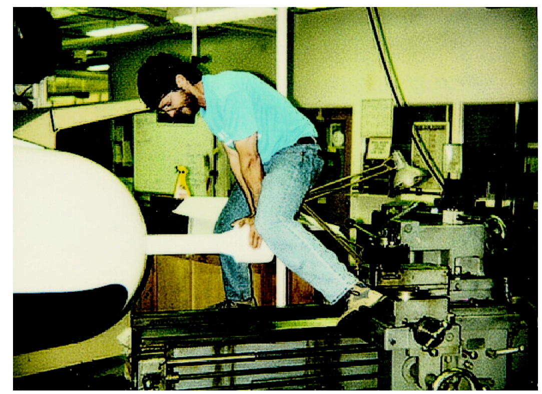
Karl Froyd, on DC-8

Troy Thornberry, Costa Rica

Dave Thomson, Costa Rica

Paula Hudson, Houston

Todd Sanford, Costa Rica



Mike Schein, Boulder

Stratosphere: Murphy et al., *J. Geophys. Res.*, *112*, D04203, 2007
Tropics: Froyd et al., *in preparation*.