Observational Constraints on Mixing State Parameterization

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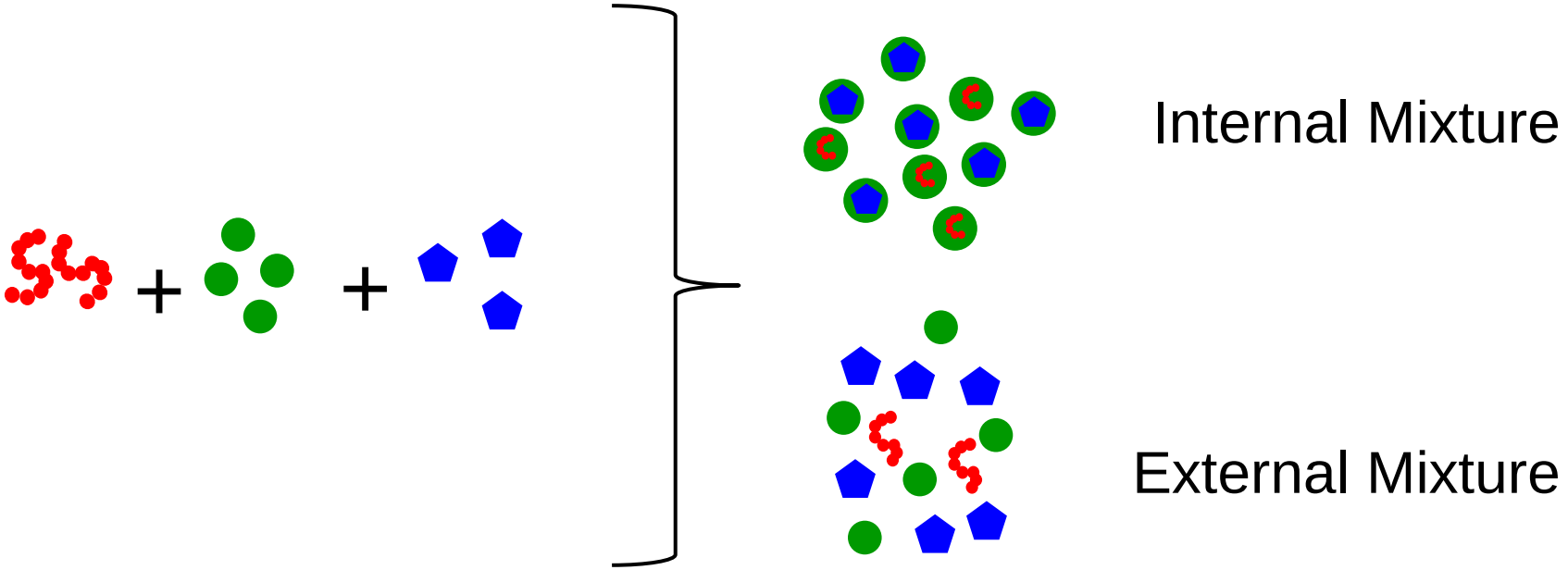
ASR Atmospheric System Research

Aerosol Mixing State

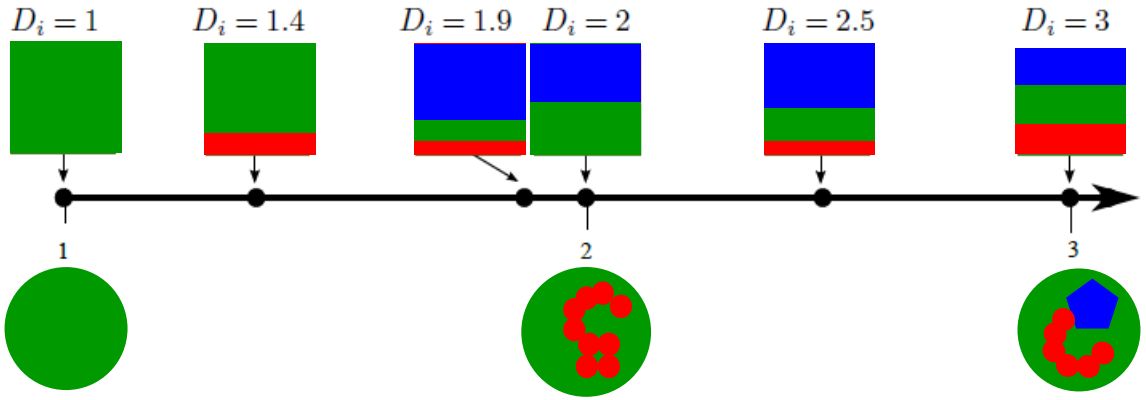


Mixing State Impacts:
Optical Properties, hygroscopicity, lifetime

Aerosol mixing state evolves with aging

Mixing State Parameterization

Particle Diversities → Effective number of species within a particle



- **Dα** = average per particle diversity
- **Dγ** = bulk population diversity
- χ = mixing state index

$$\chi = \frac{D\alpha - 1}{D\gamma - 1}$$

χ = 30% → 30% internally mixed, 70% externally mixed

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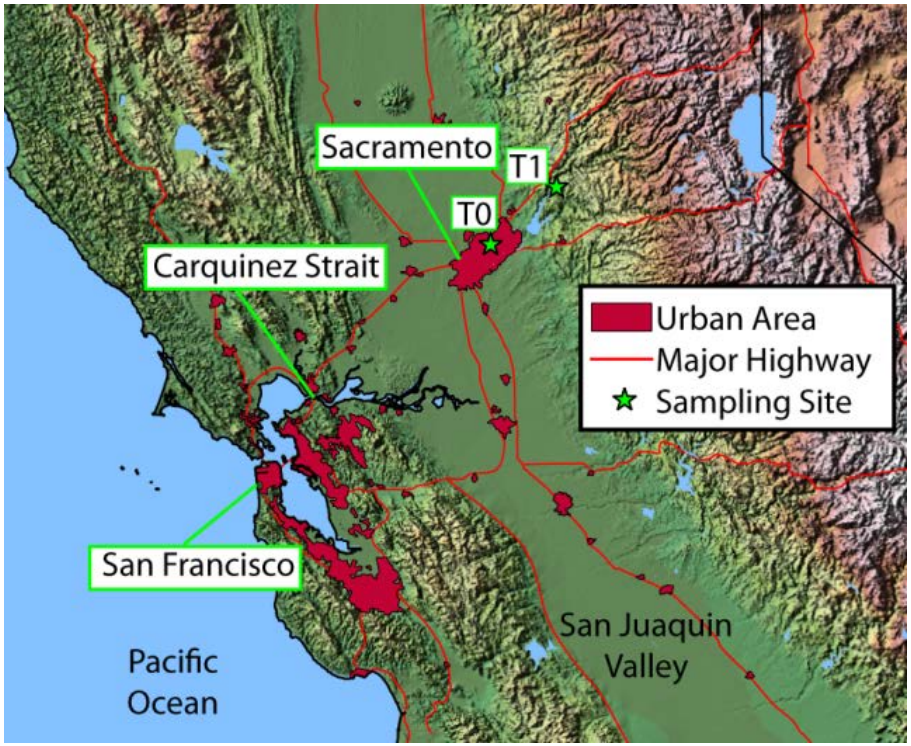
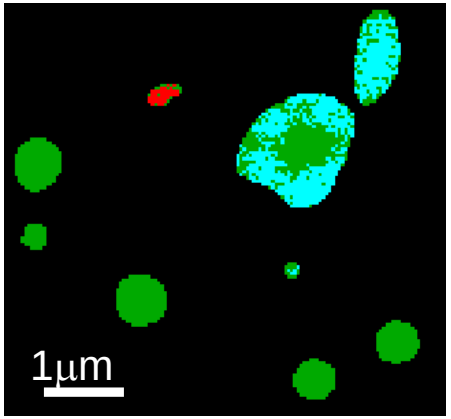
Cares 2010

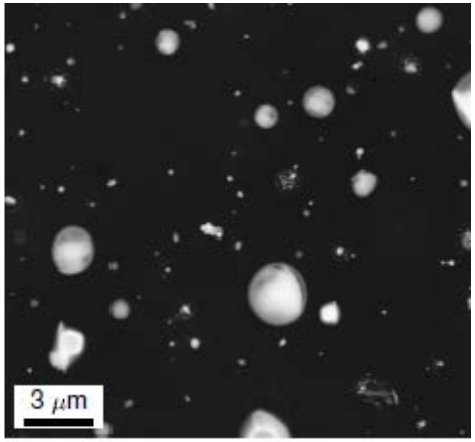
15 min samples
June 27th and 28th



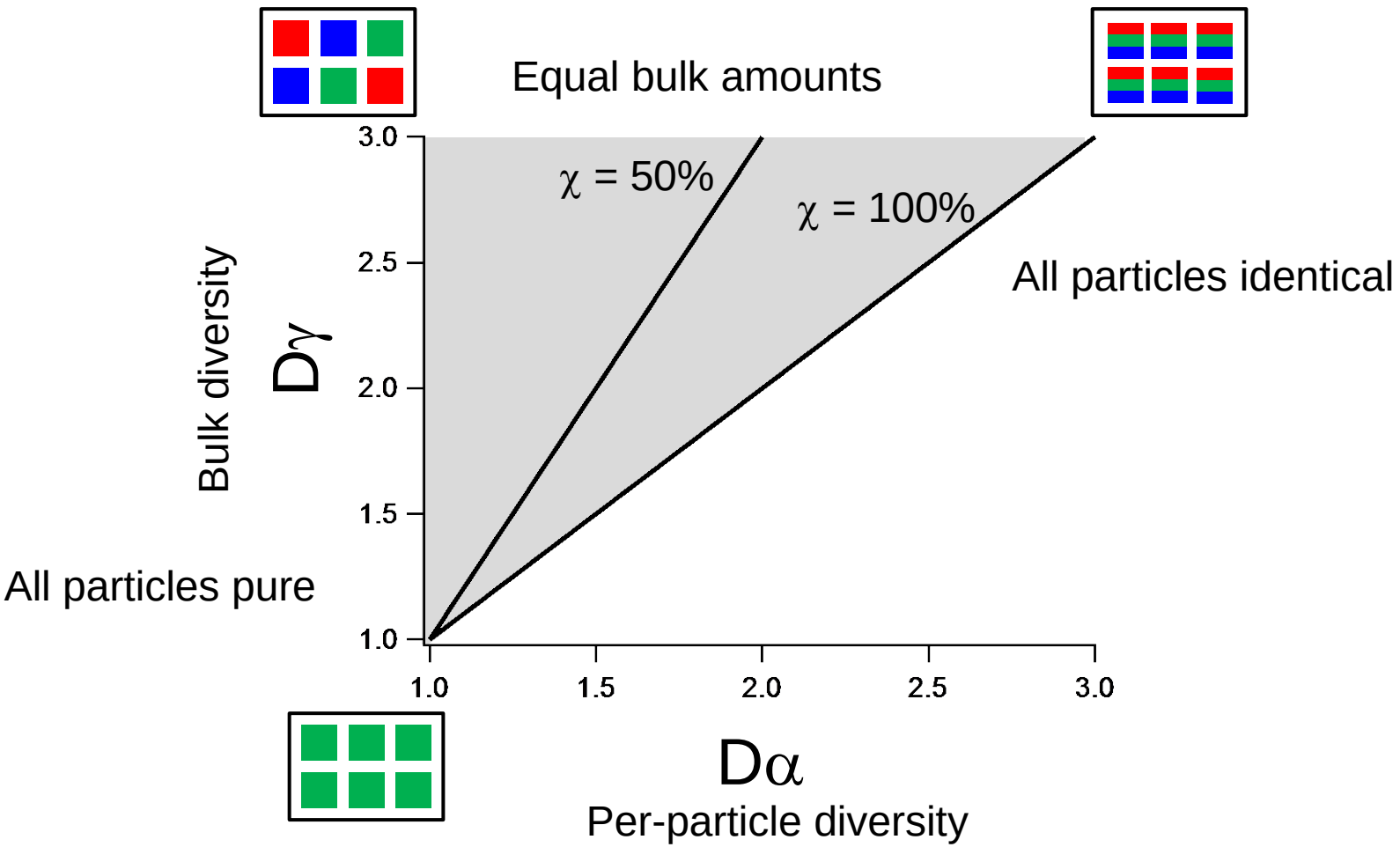
Scanning Transmission X-ray Microscopy (STXM)



Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDX)



Mixing State Diagram



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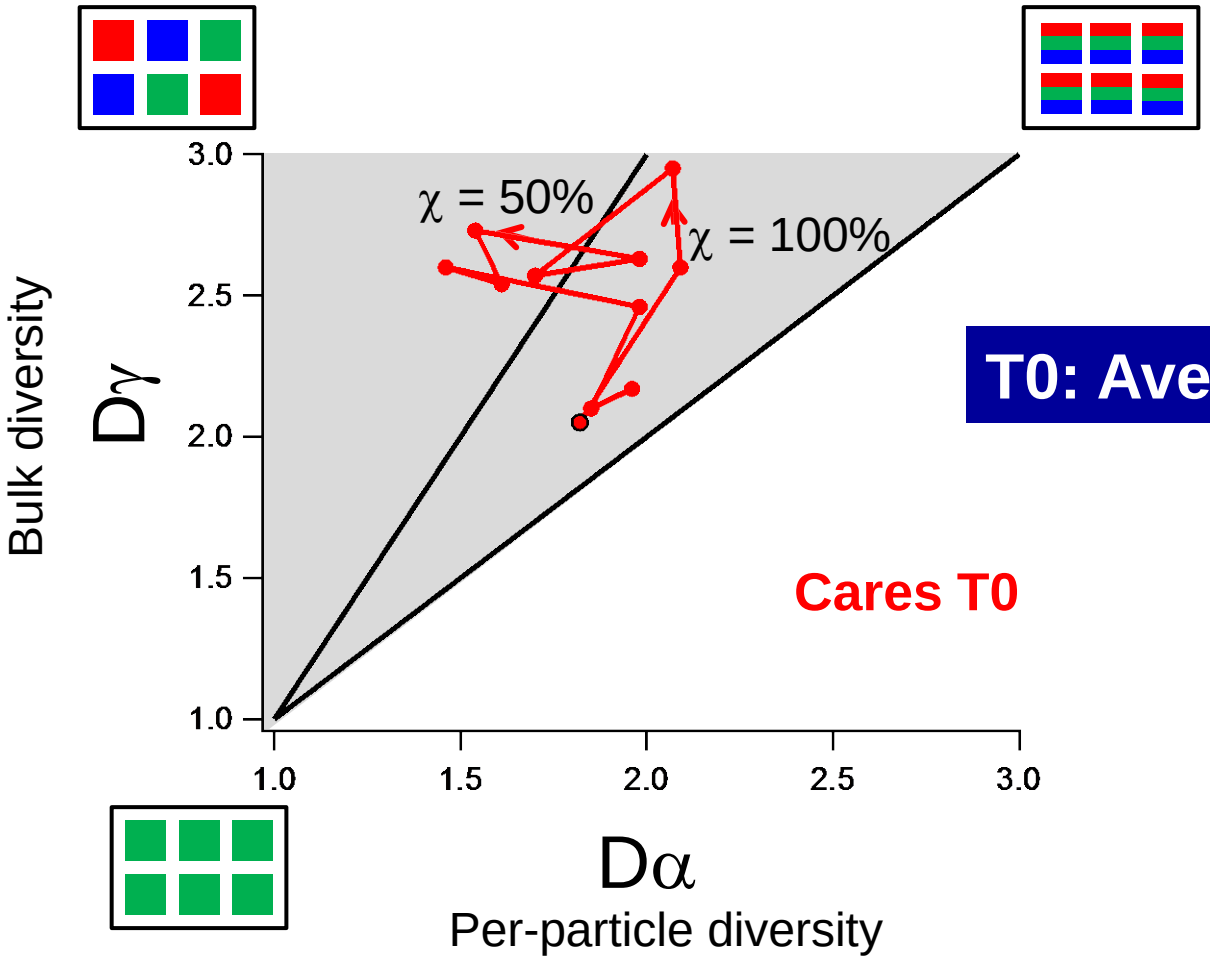
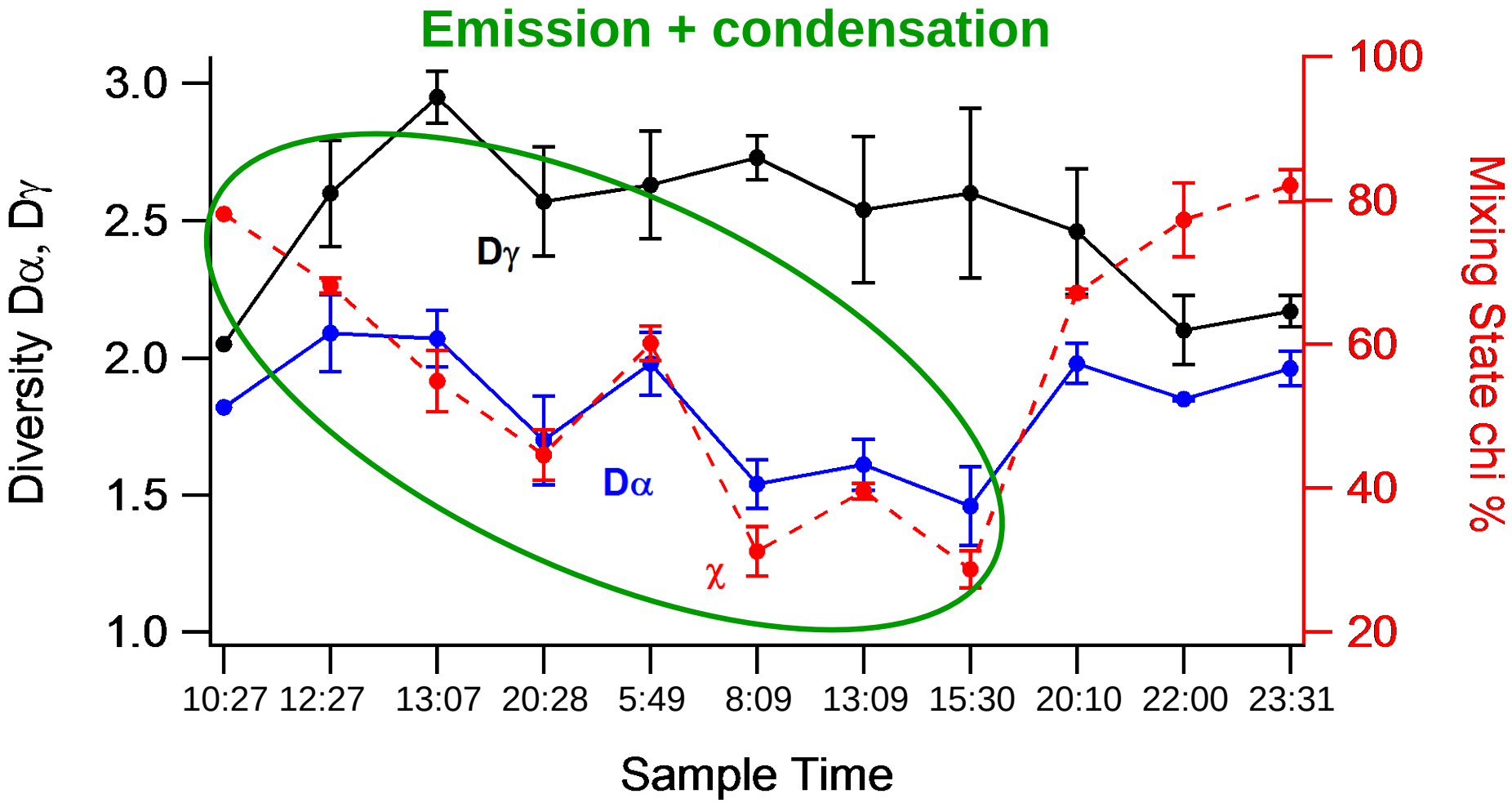
STXM Mixing State



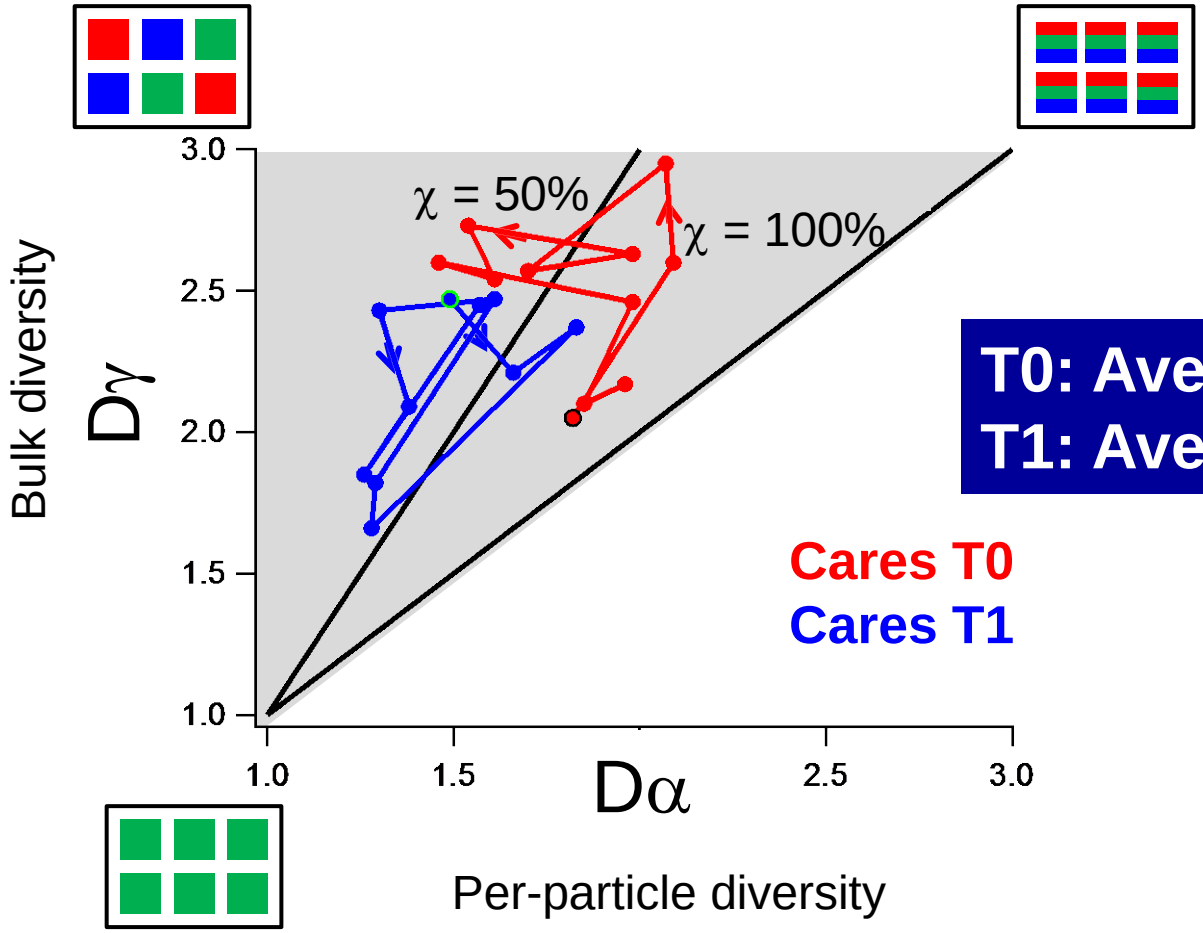
T0: Average χ = 60%

Time Series and Correlations

See decrease in the middle → χ is anti correlated with OC from EC/OC



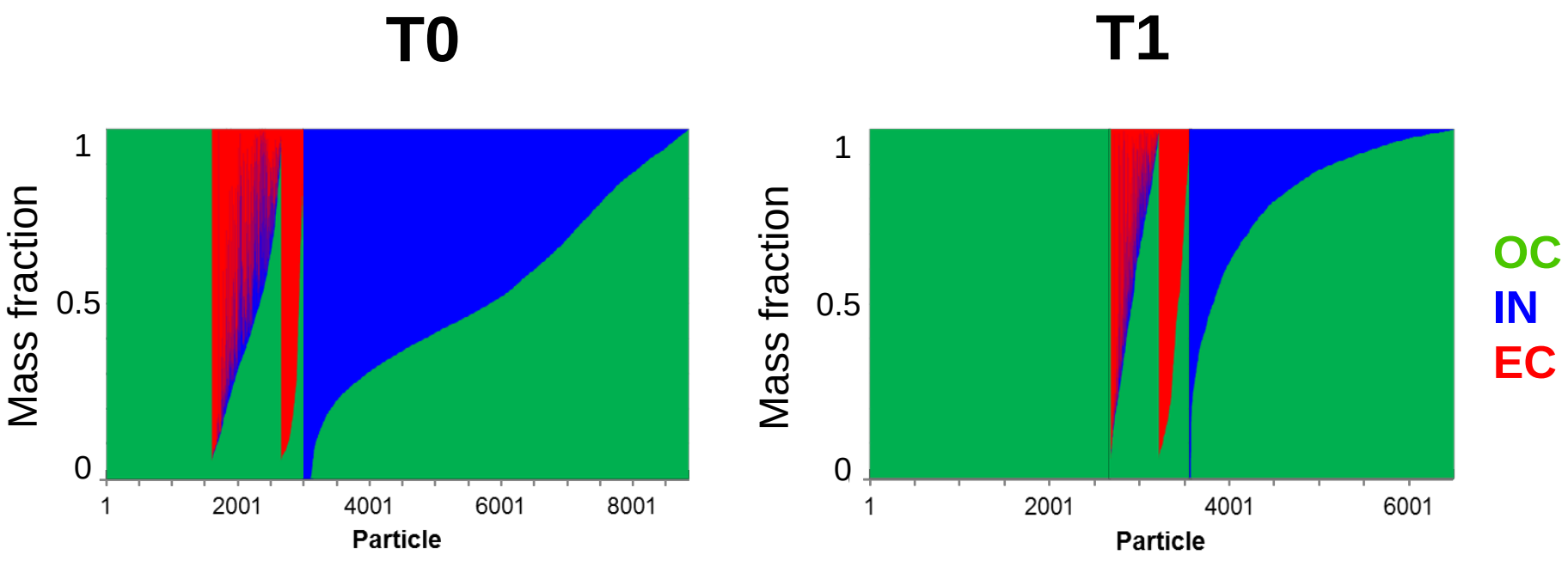
STXM Mixing State T0 vs. T1



T0: Average χ = 60%
T1: Average χ = 40%

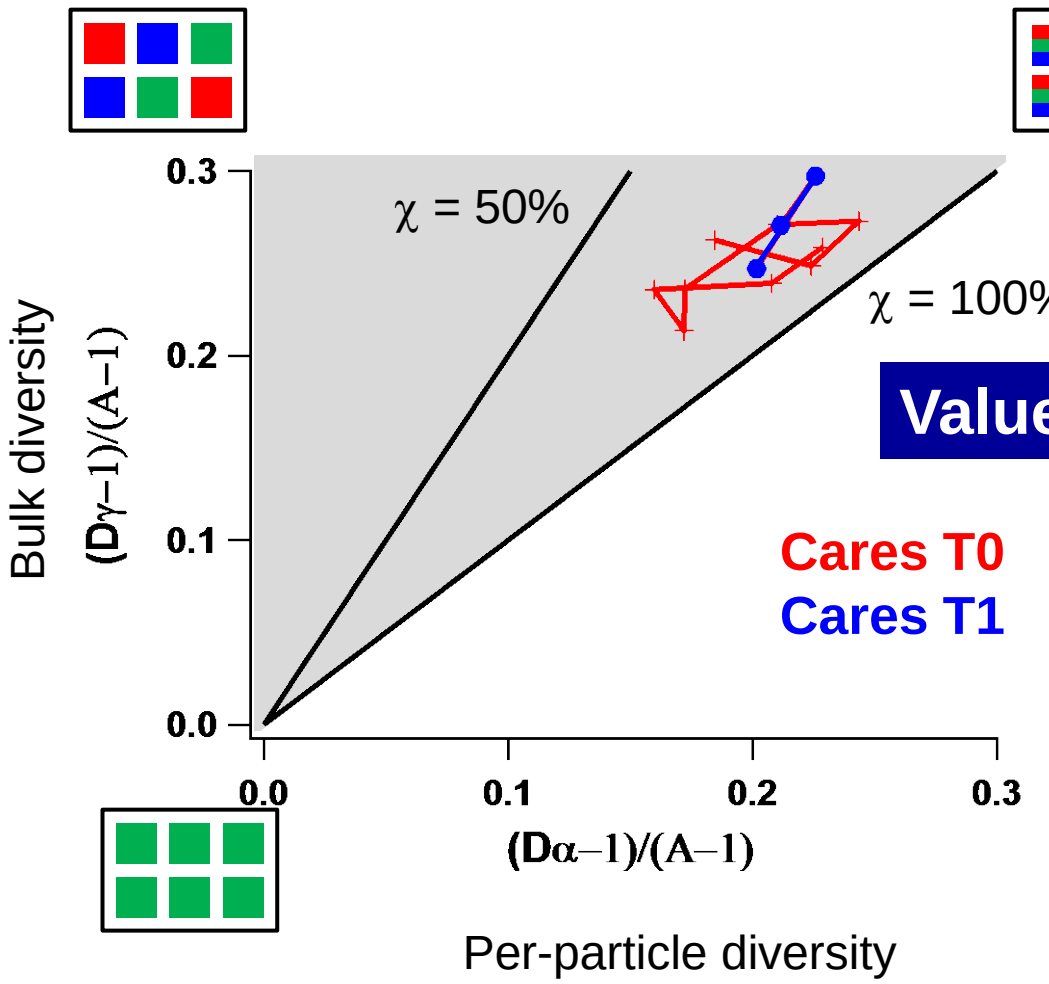
Composition T0 vs. T1

Pictorial Dα → Mass fraction per particle



More organic particles + more OC in mixed particles

SEM/EDX



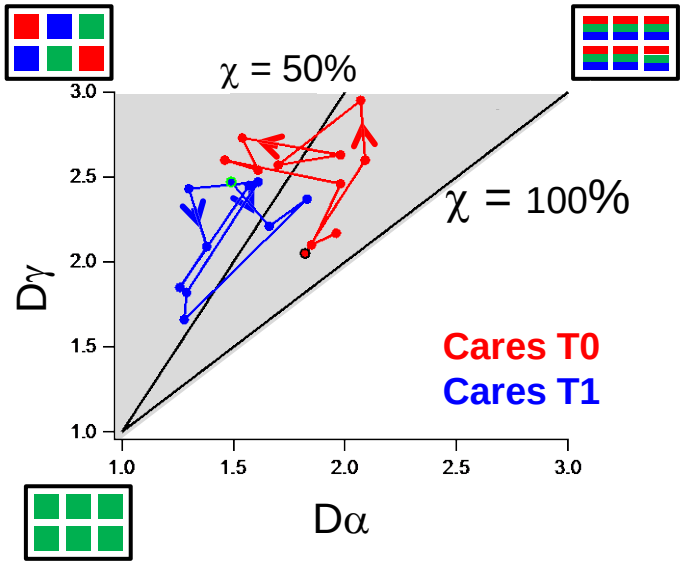
Values around χ = 80%

Cares T0

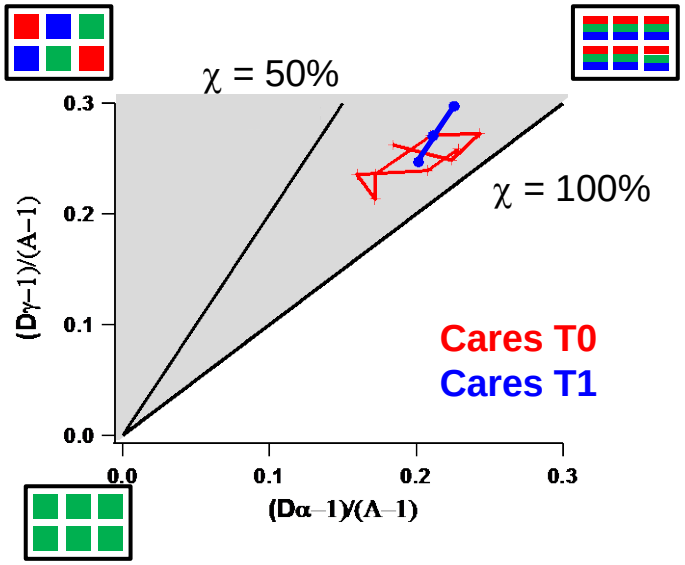
Cares T1

What is *Pure*?

Values around χ = 40-60%



Values around χ = 80%



Organic dominated particle in STXM is NOT pure in SEM
→ SEM looks more mixed.

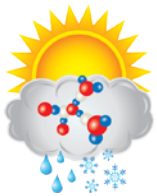
Conclusions

- Mixing state (χ%) is ~40-60% for STXM and ~80% for SEM
  - Comparing across different techniques is non-trivial
- Trends at T0 consistent with an OC buildup
- Cares T1 has lower Dα, Dγ, and χ values → primarily driven by higher Organic
- **Future Work**
- Looking at the Mixing state as a function of size
- Looking at correlations with concurrent optical, hygroscopic, etc. measurements

Acknowledgments

- LBNL and University of the Pacific
  - Mary Gilles & Ryan Moffet's groups
  - Tolek Tyliszczak, David Kilcoyne
- PNNL (SEM data)
  - Alexander Laskin, Bingbing Wang
- University of Illinois at Urbana-Champaign
  - Nicole Riemer and Matthew West
- Funding:
  - DOE, LBNL, PNNL

Lawrence Berkeley National Laboratory

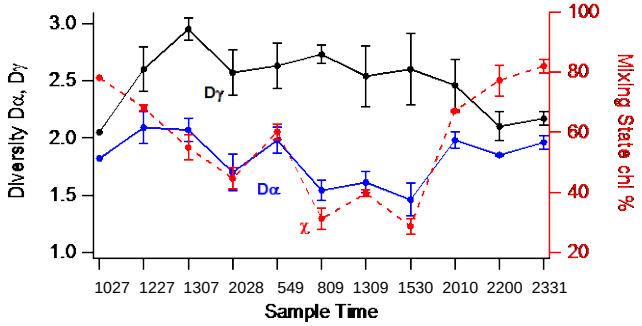


ASR
Atmospheric System Research

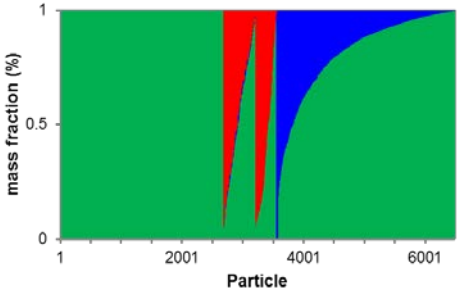
Conclusions

- Mixing state (χ%) is ~40-60% for STXM and ~80% for SEM
  - Comparing across different techniques is non-trivial

- Trends at T0 consistent with an OC buildup



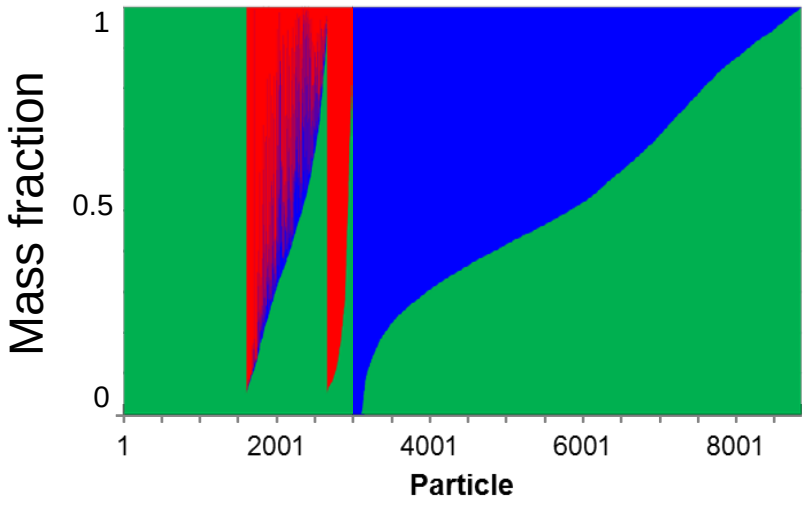
- Cares T1 has lower Dα, Dγ, and χ values → primarily driven by higher **Organic**



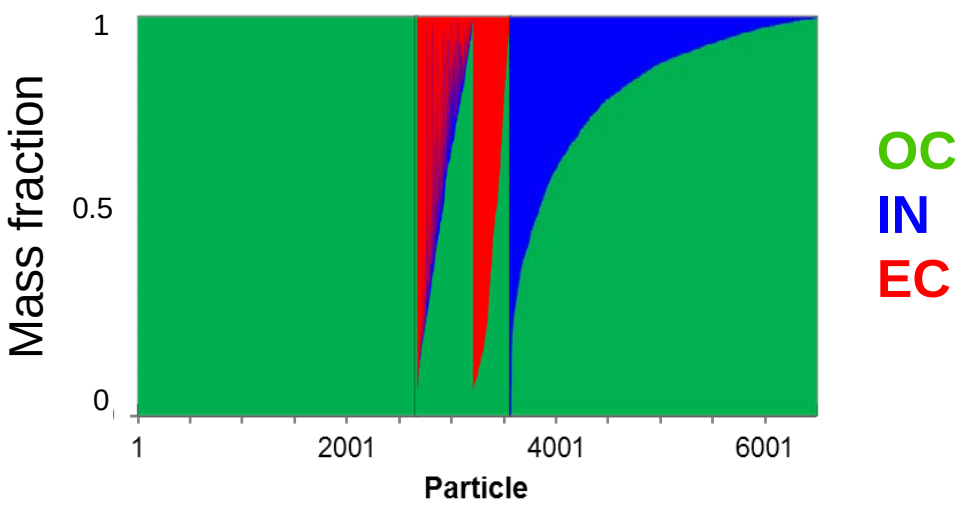
Composition T0 vs. T1

Pictorial Dα → Mass fraction per particle

T0



T1

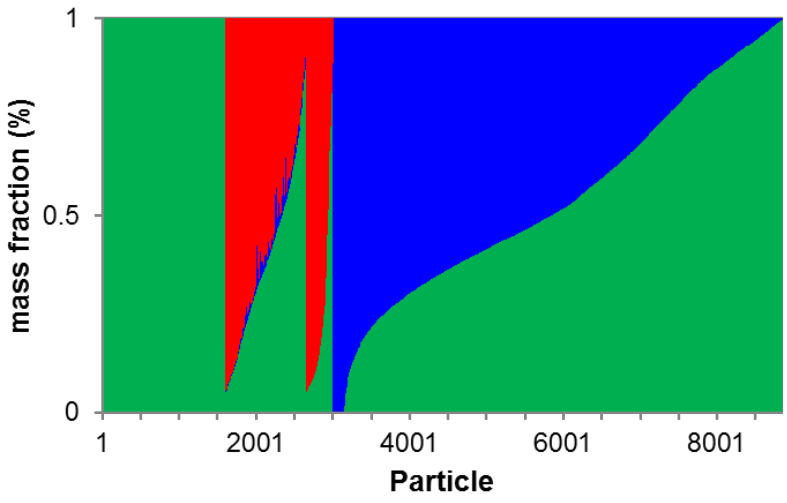


More organic particles + more OC in mixed particles

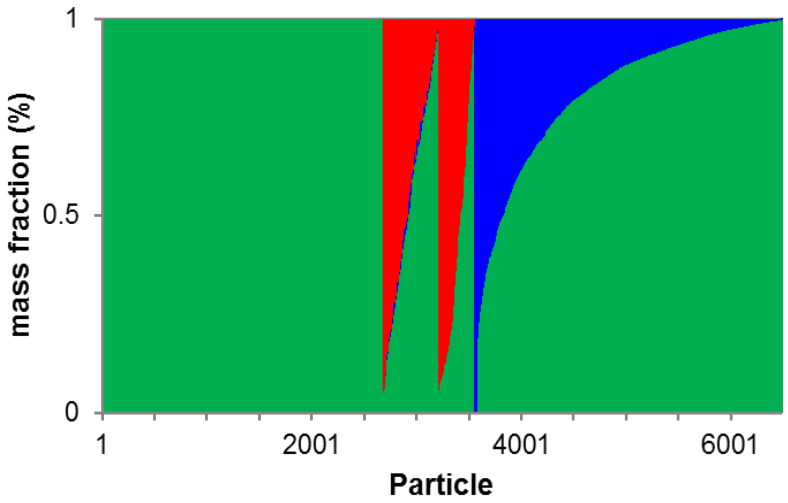
Composition T0 vs. T1

Pictorial Dα → Mass fraction per particle

T0



T1

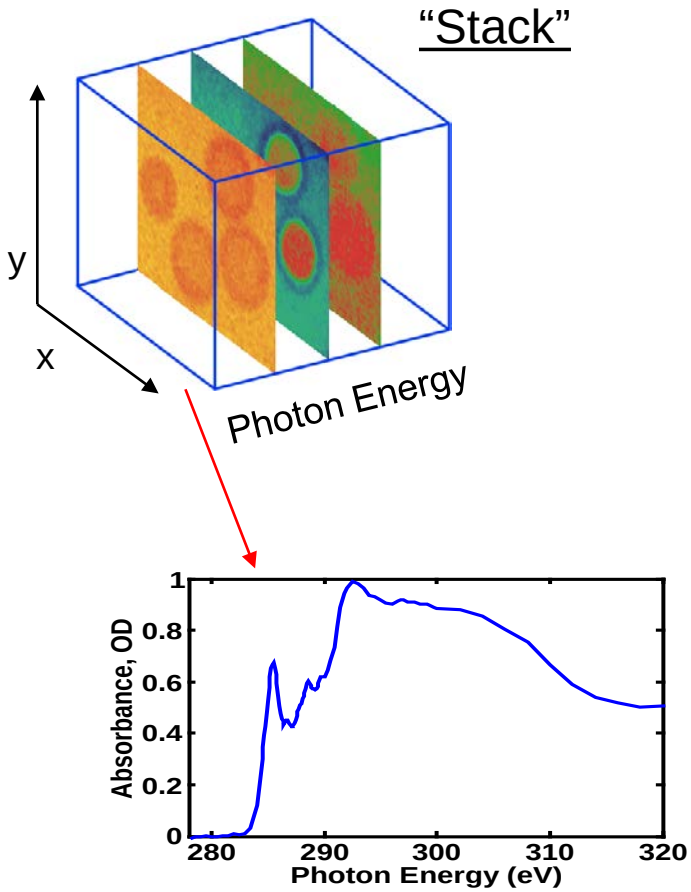


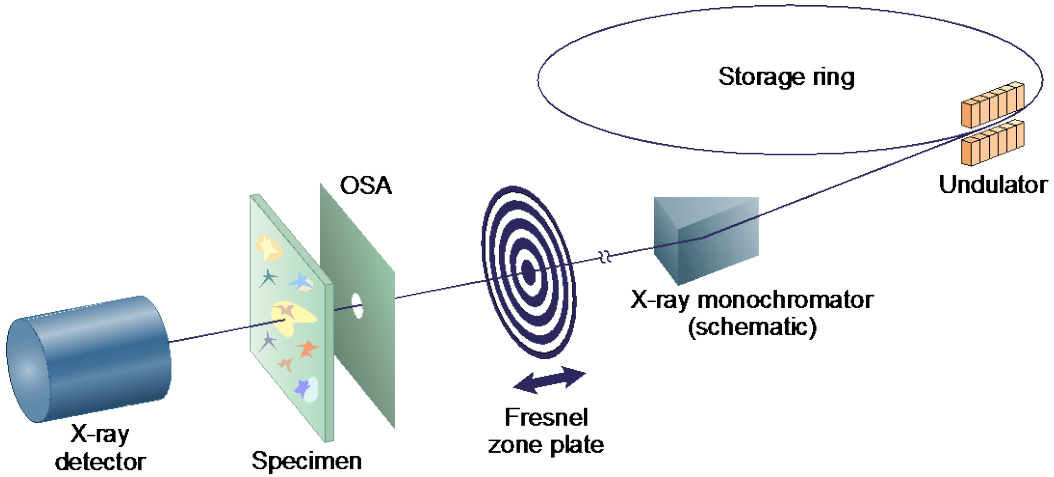
OC
IN
EC

More organic particles + more OC in mixed particles

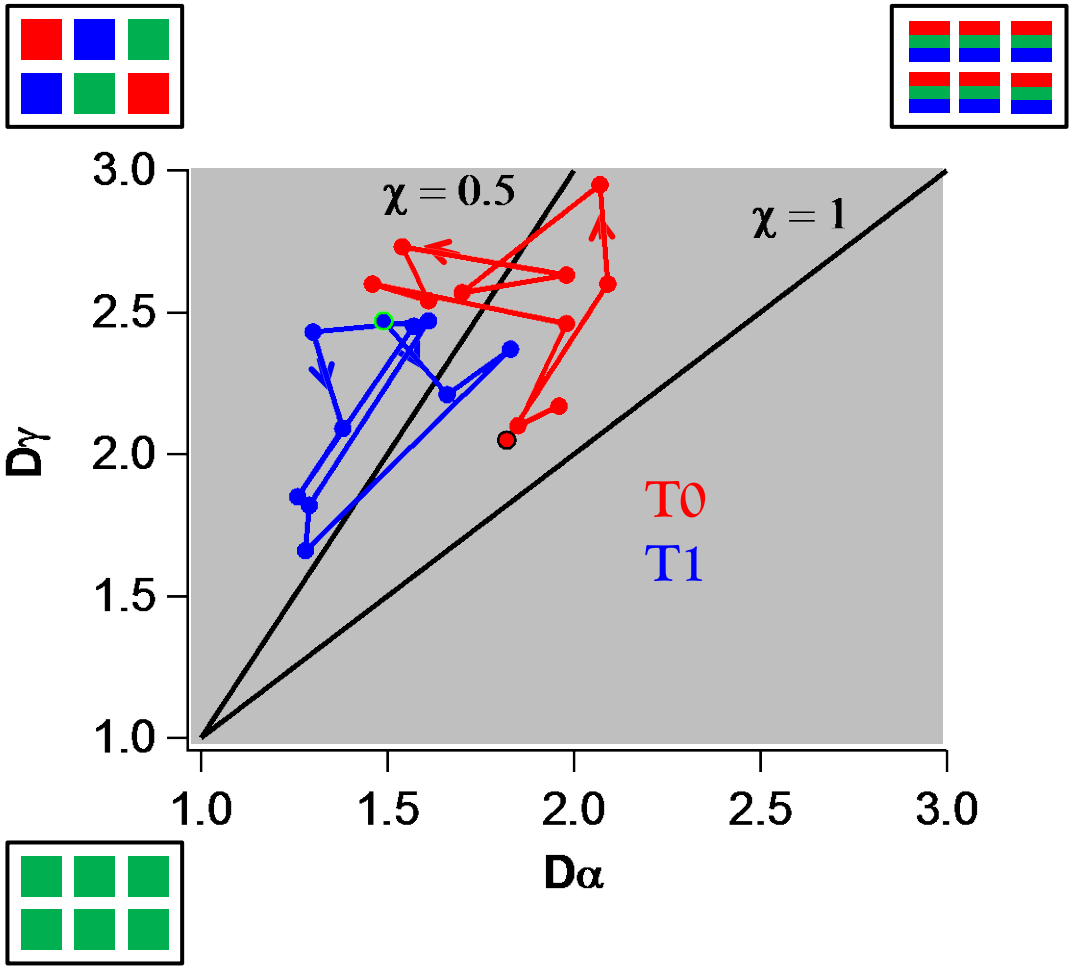
STXM/NEXAFS

- Scanning Transmission X-ray Microscopy (STXM):
  - ~25-40 nm resolution from zone plate
  - Sample raster scanned in fixed beam

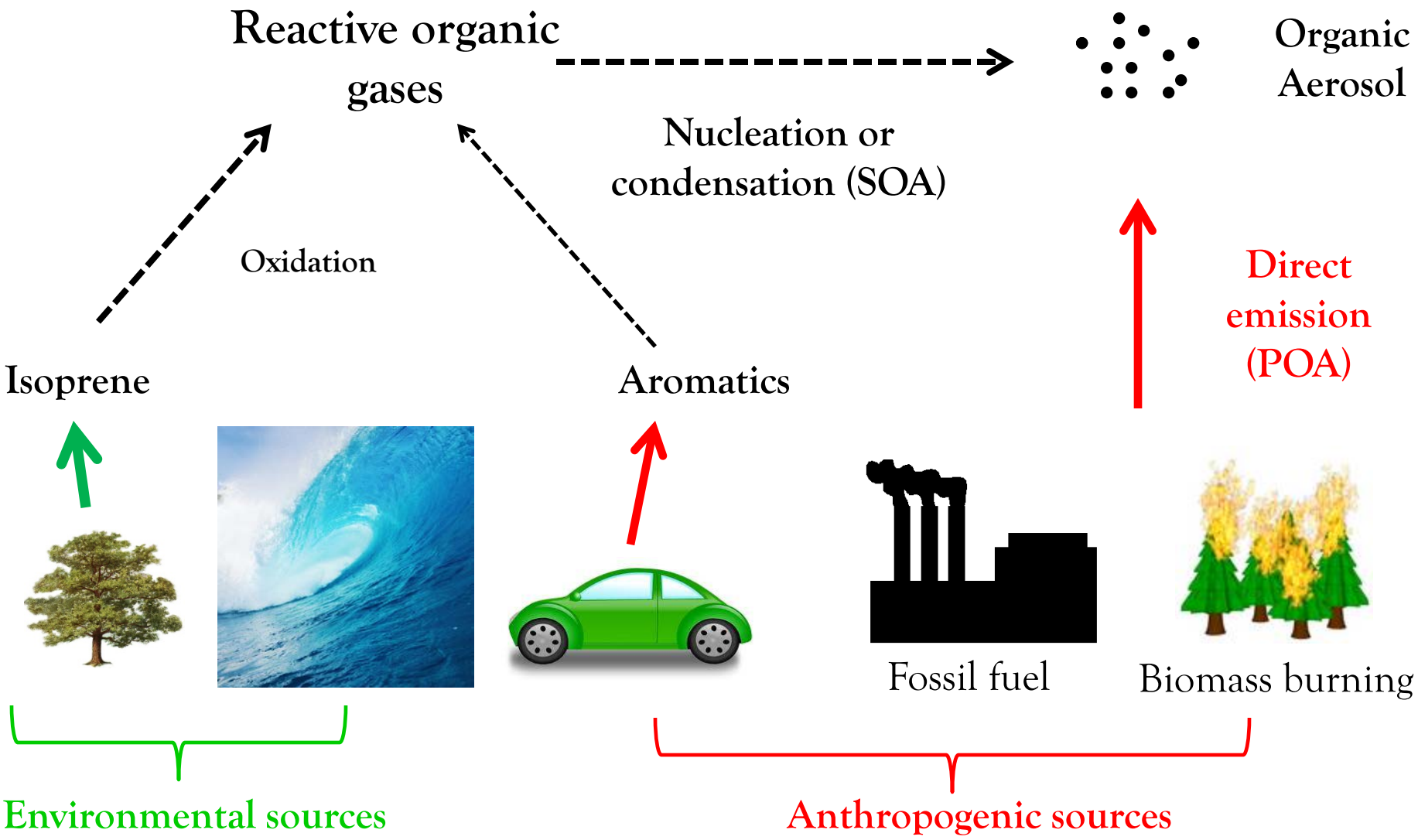




Mixing



Primary and Secondary Aerosols

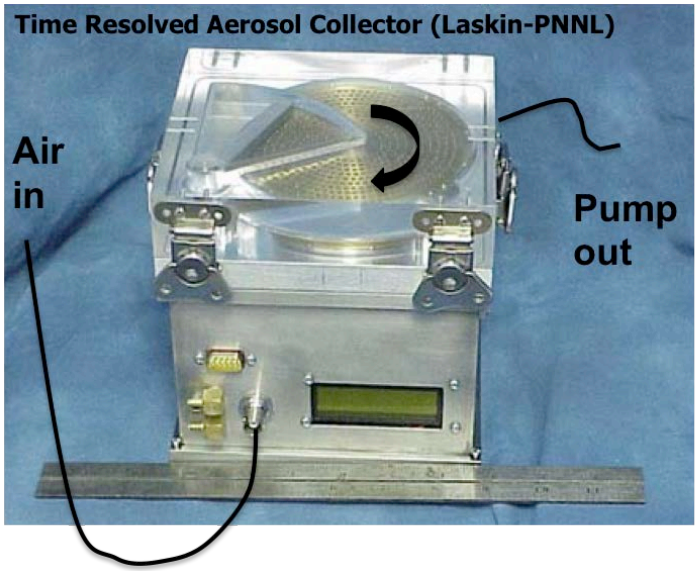


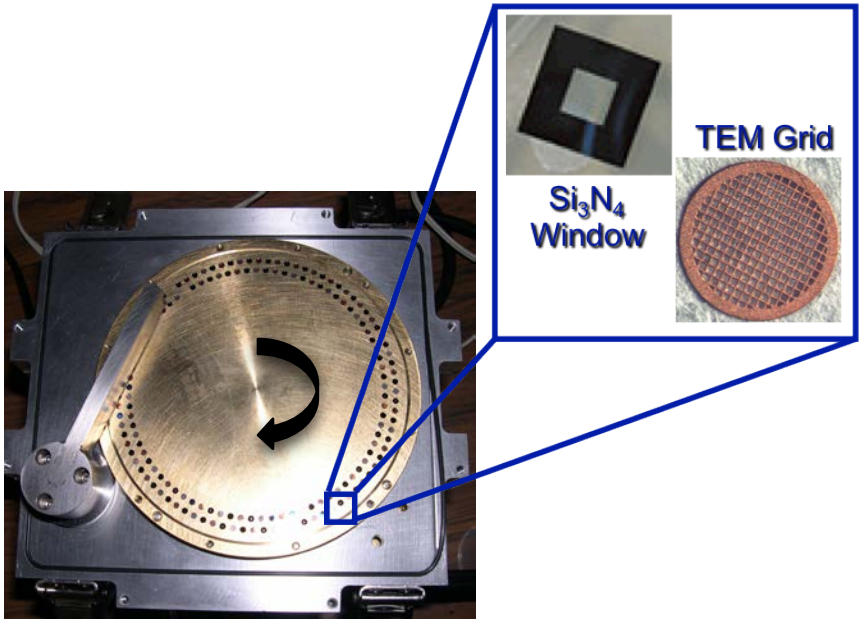
Population Diversities

Masses Estimated from Microscopy Techniques:

STXM→ Two dimensional Area and Optical Density

SEM → Two dimensional Area and assume Hemisphere


Time Resolved Aerosol Collector (Laskin-PNNL)
Air in
Pump out


TEM Grid
Si_3N_4 Window

Time Series and Correlations

See decrease in the middle → χ is anti correlated with OC from EC/OC

Other correlations- to be determined…
Photochemical age, hygroscopicity, scattering

What are aerosols?

Solid and liquid particles suspended in air

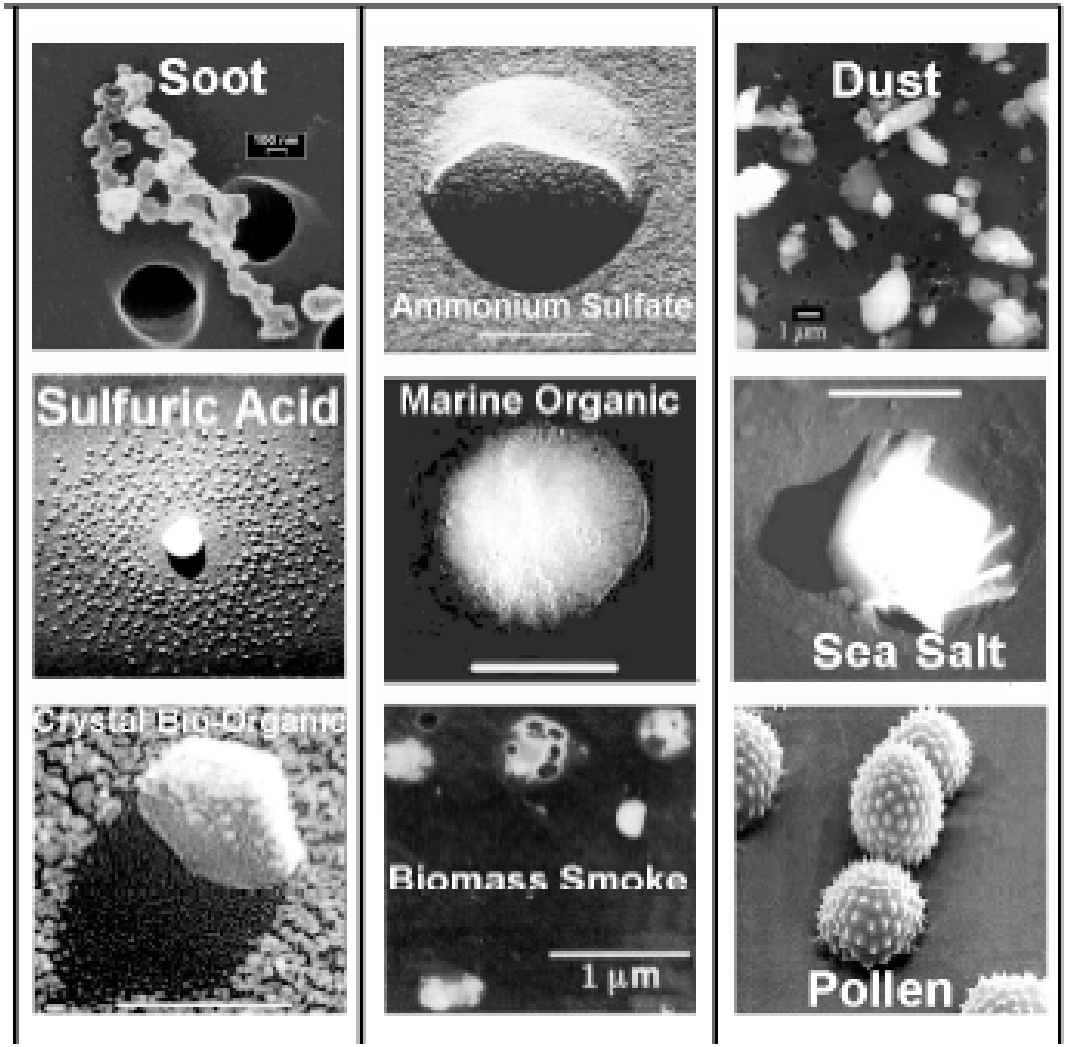
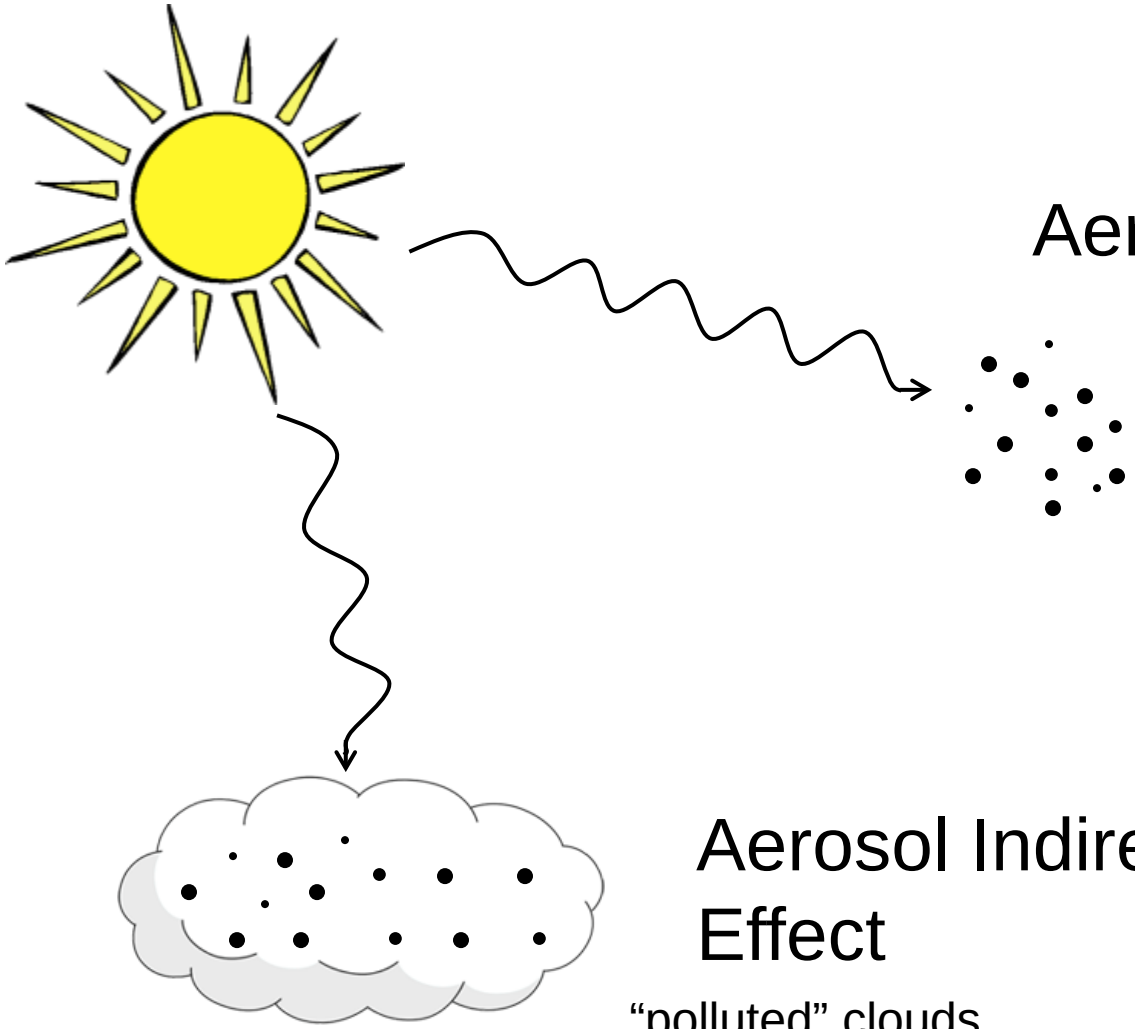


Image from C. Leck

Climate Effects of Aerosols



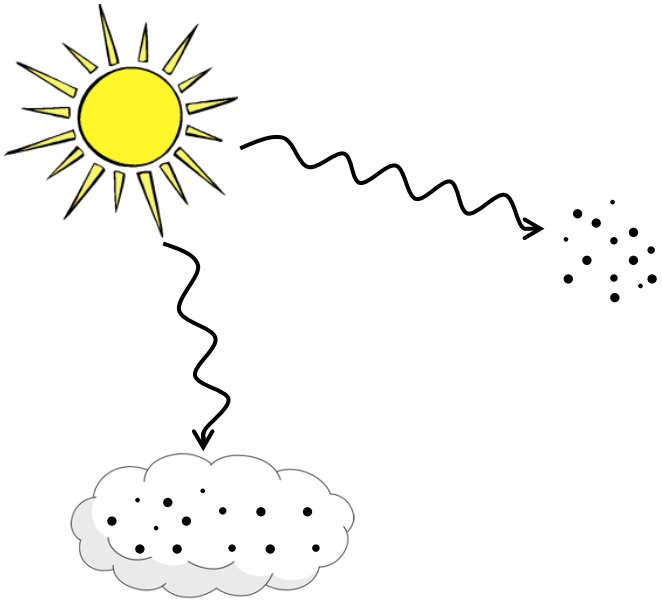
Aerosol Direct Effect

Absorbing (warm) and Scattering (cool) radiation

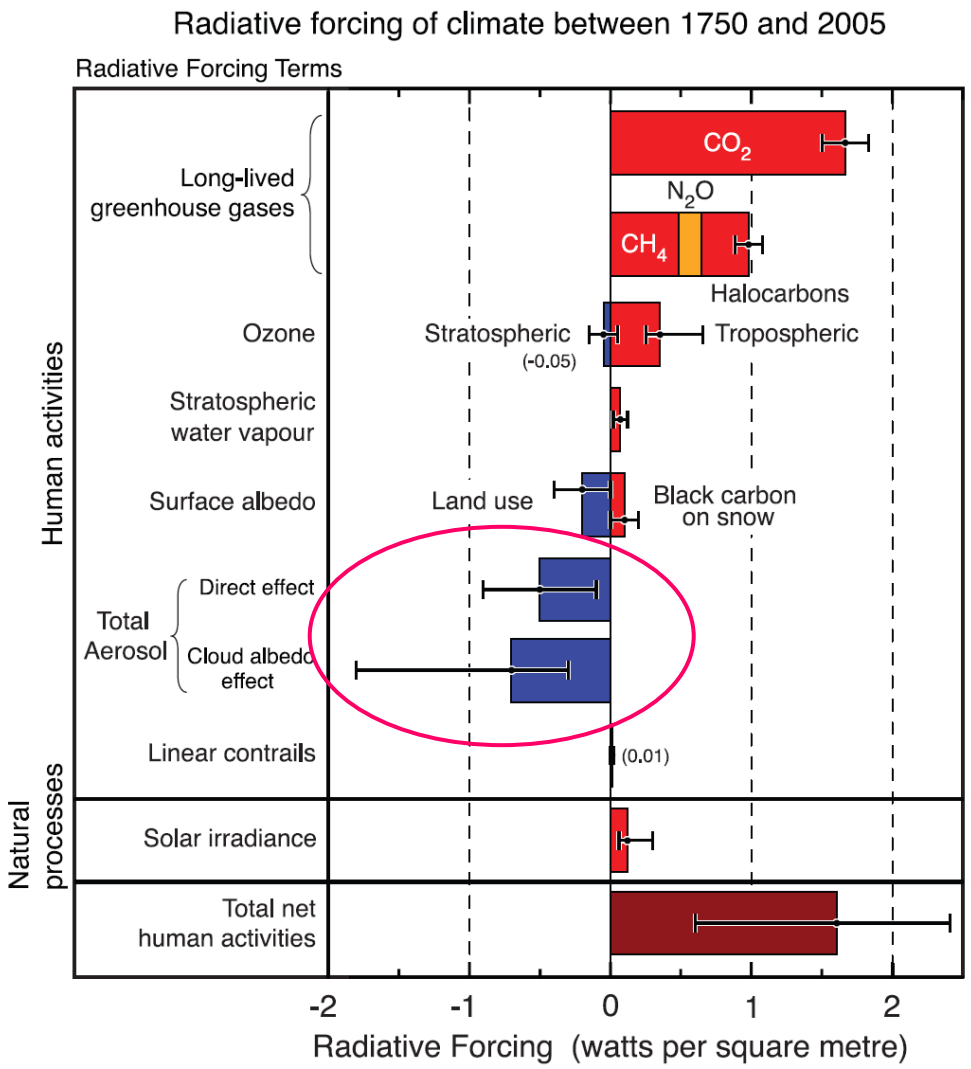
Aerosol Indirect Effect

"polluted" clouds
Higher albedo
Less rainfall (longer lifetime)

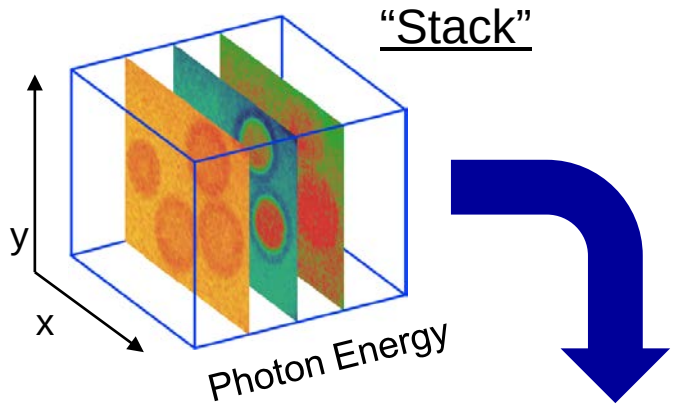
Radiative Forcing



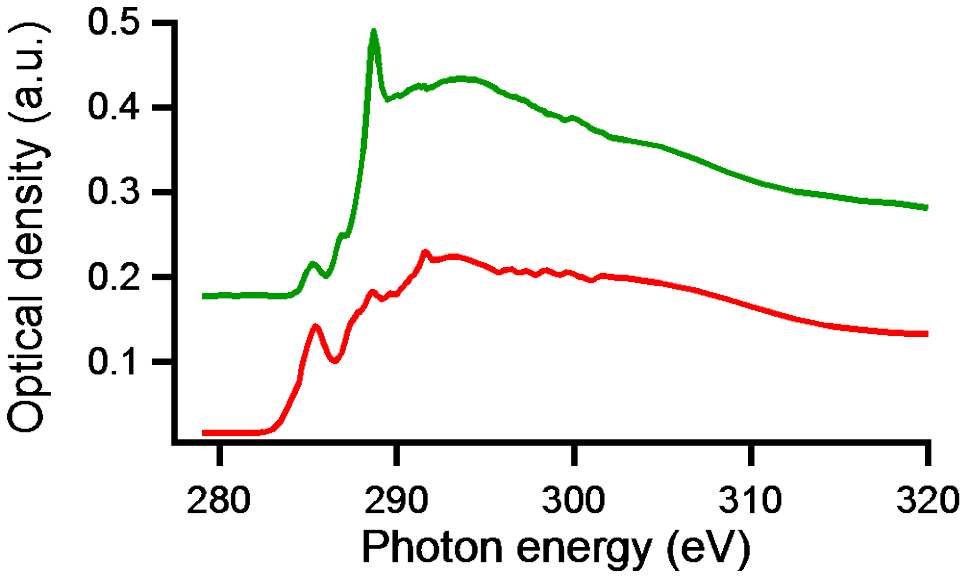
Largest uncertainties in radiative forcing → Aerosols!

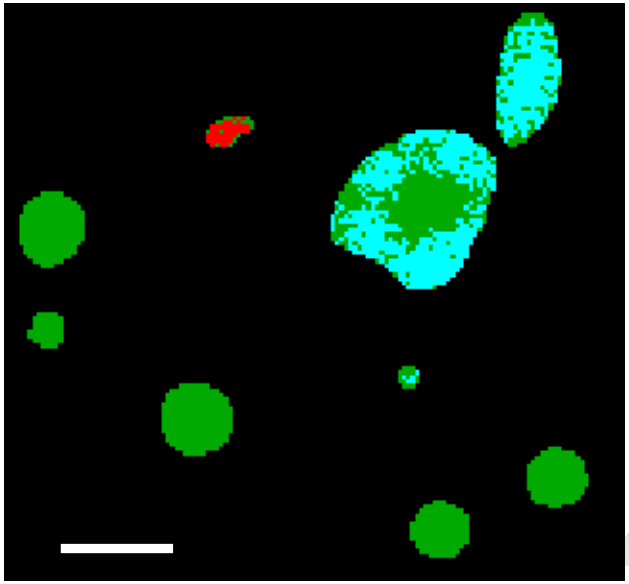


STXM Data



Chemical Map: composition and morphology

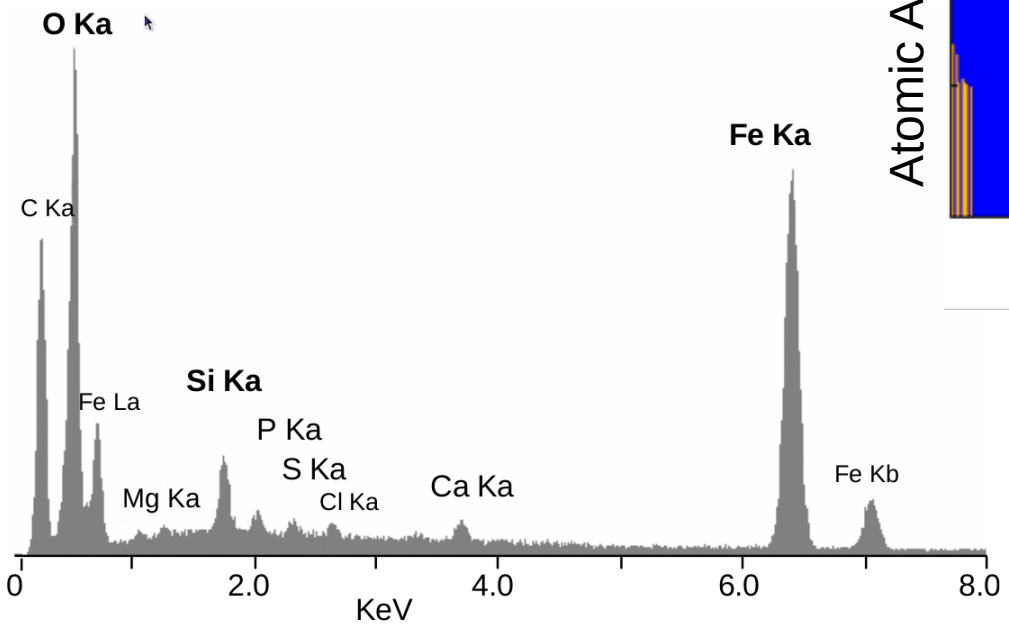


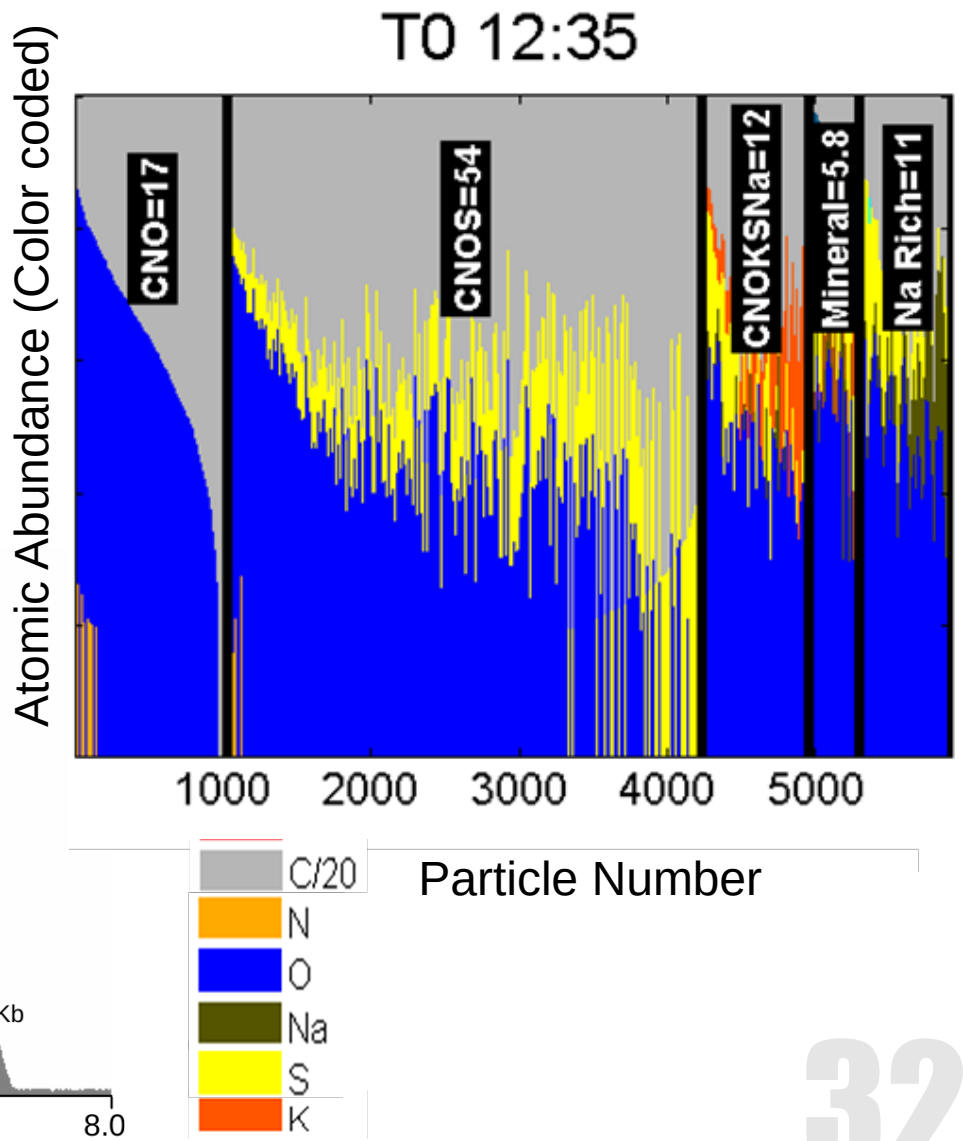


SEM/EDX Data

Measure Characteristic x-rays

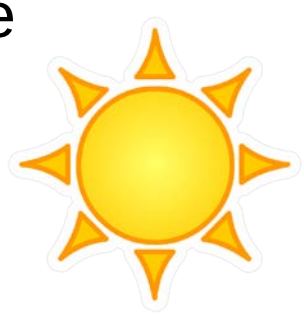
→ **Atomic % of Elements**





Sources + Aging

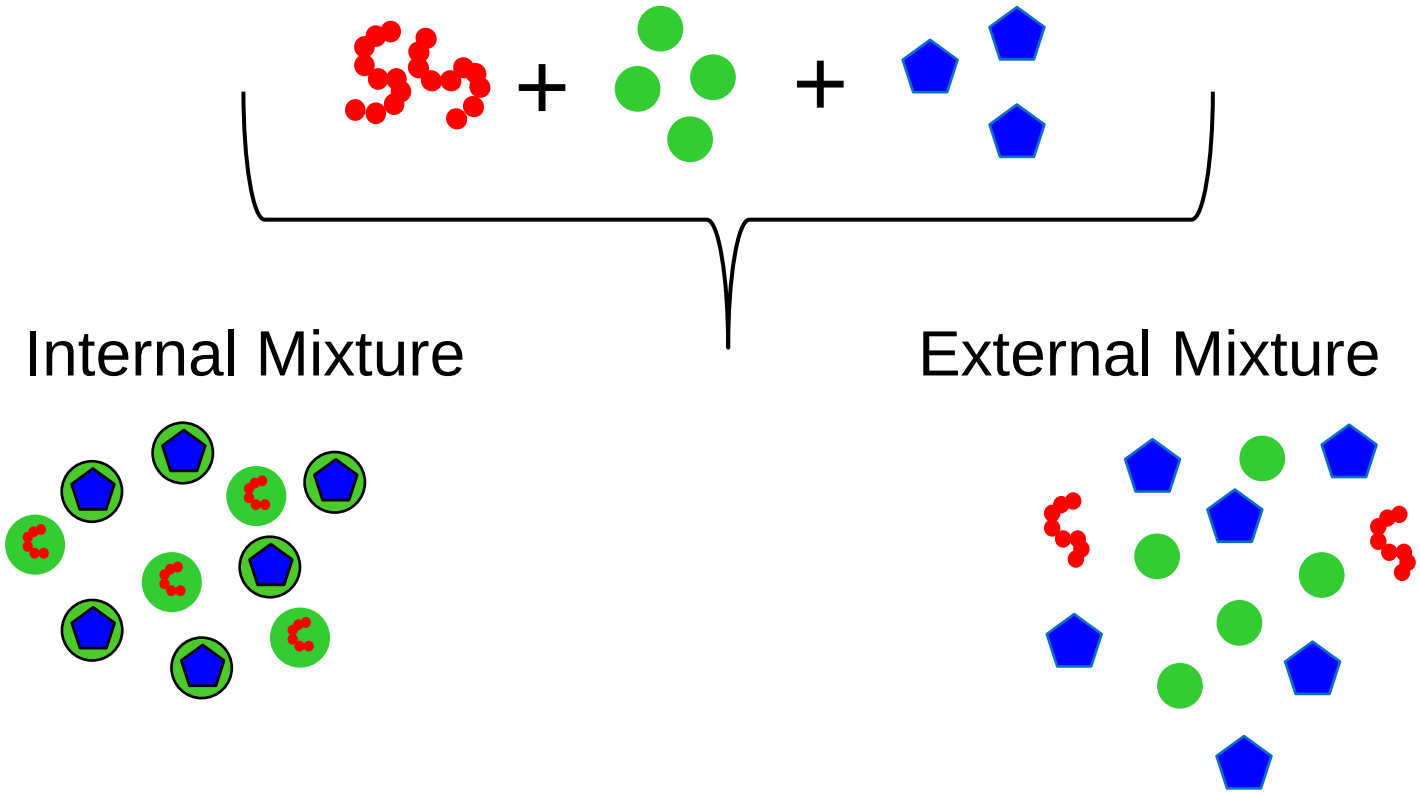
Aerosol lifetime
~1 week



Condensation
Coagulation

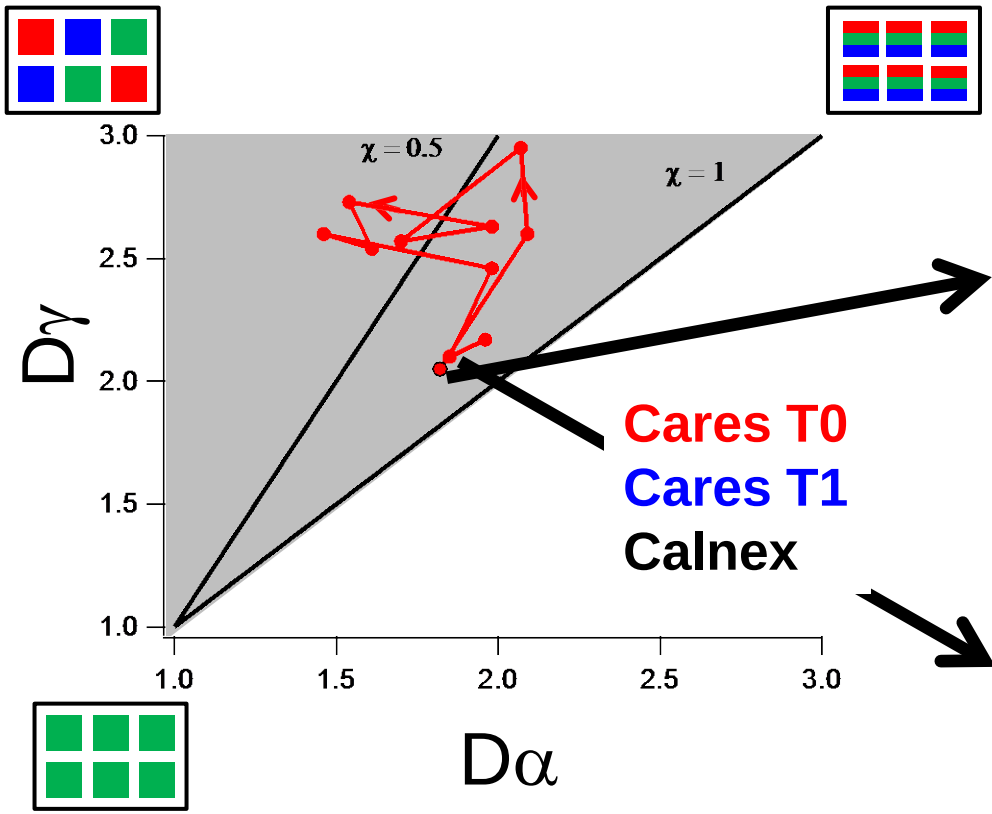
Climate Effects

Aerosol Mixing State

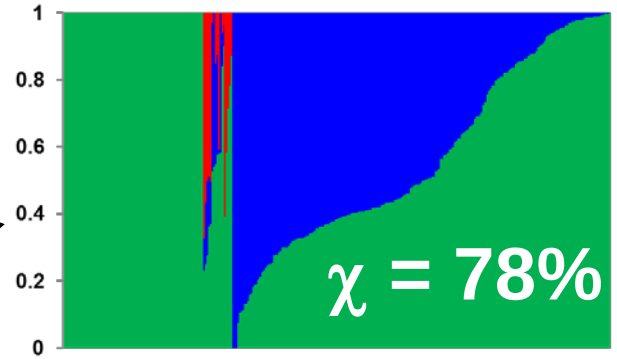


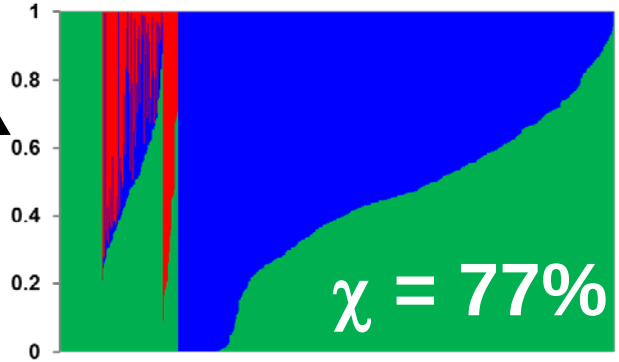
Mixing State Impacts:
Optical Properties, hygroscopicity, lifetime

χ vs. Chemical Composition



Cares T0
Cares T1
Calnex





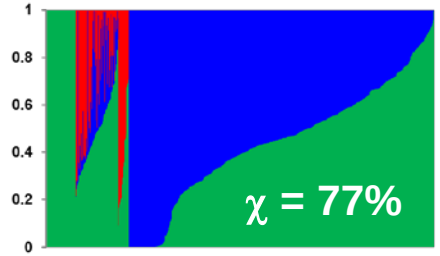
OC
IN
EC

Similar χ values ≠ similar populations

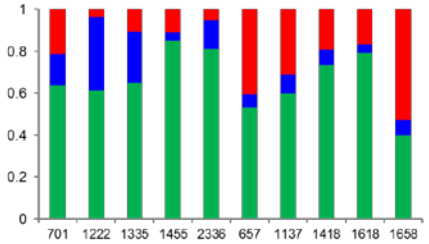
Conclusions

- Mixing state (χ%) is ~50% for STXM and ~80% for SEM
  - Comparing across different techniques is non-trivial

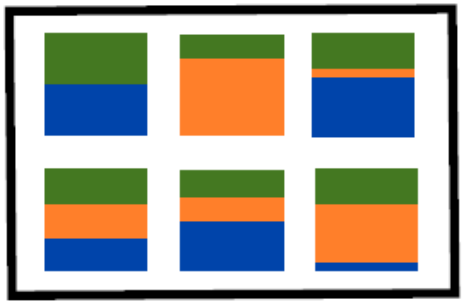
- Different particle populations can have very similar mixing state parameters.



- Cares T1 has lower Dα, Dγ, and χ values → primarily driven by higher **OC**, lower **IN**
  - Correlations are complex



Population Diversities



- $D\alpha$ = average per particle diversity
- $D\gamma$ = bulk population diversity
- χ = mixing state index

$$\chi = \frac{D\alpha - 1}{D\gamma - 1}$$

χ = 30% → 30% internally mixed, 70% externally mixed

Calculated using:

- **Mass fraction** of particle i in the population
- **Mass fraction** of species a in the population

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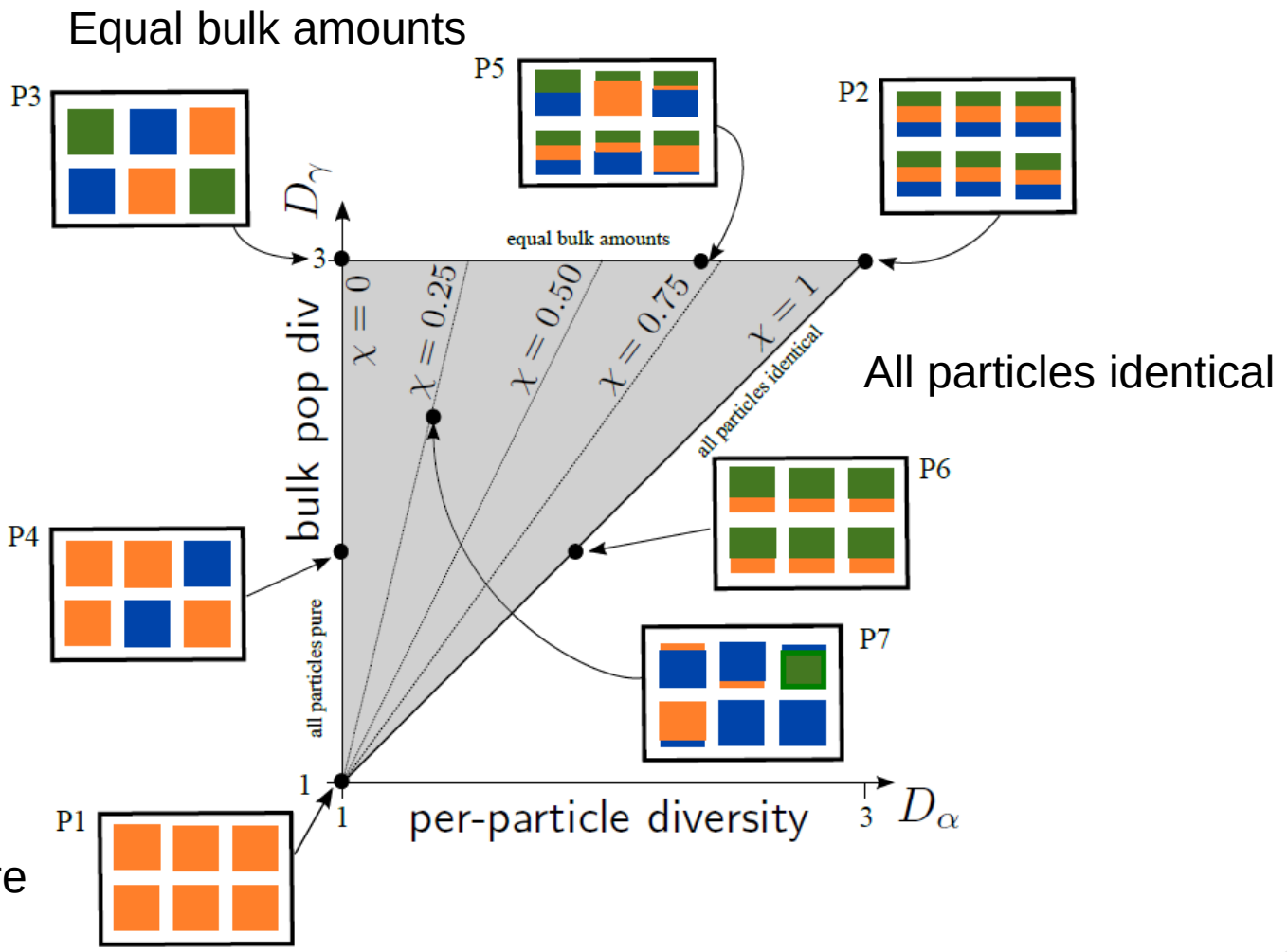
Mixing State Diagram



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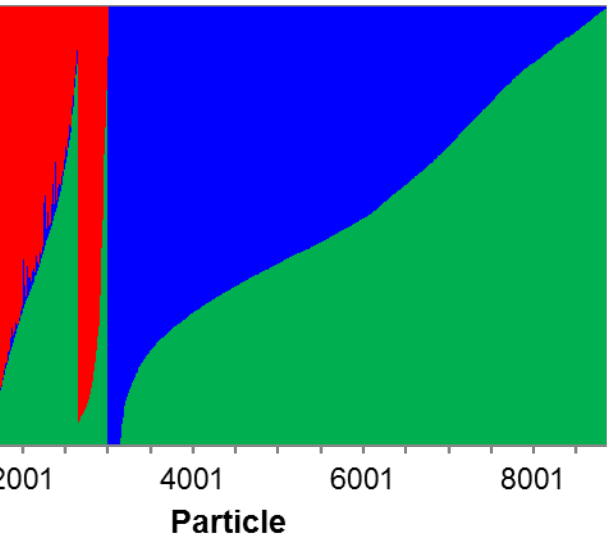
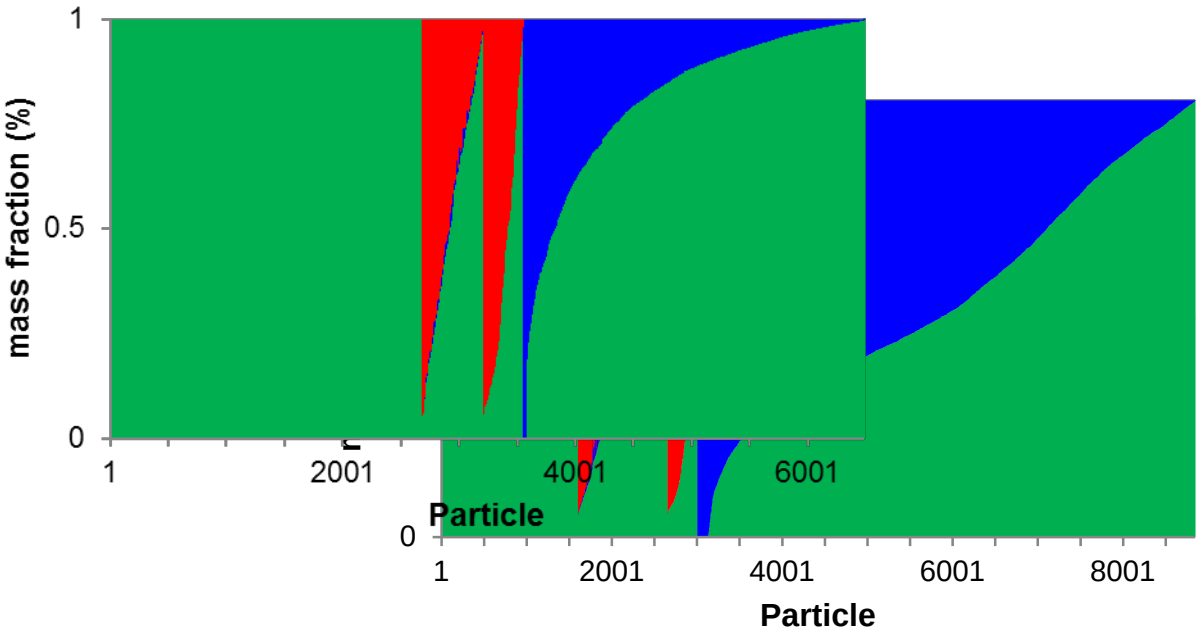
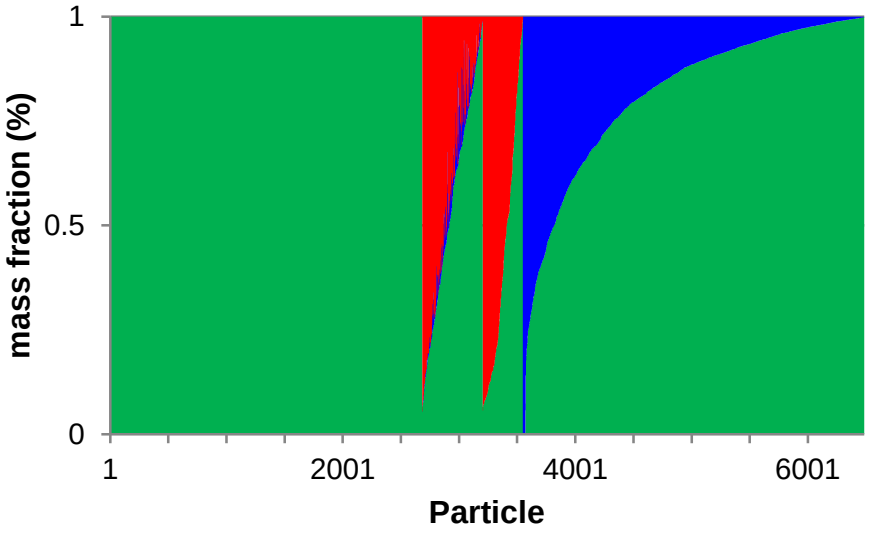
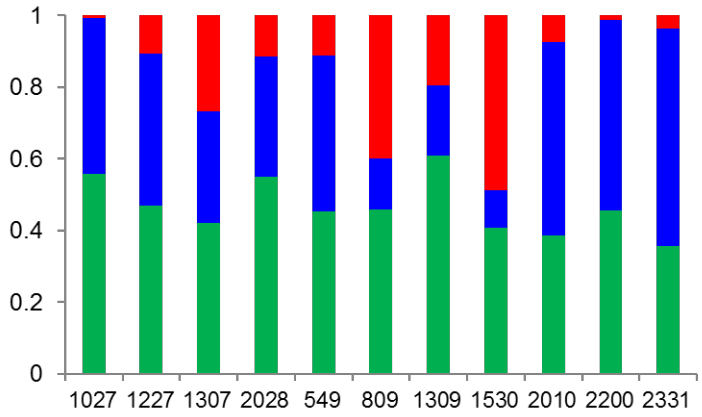

2001
4001
6001
8001
Particle

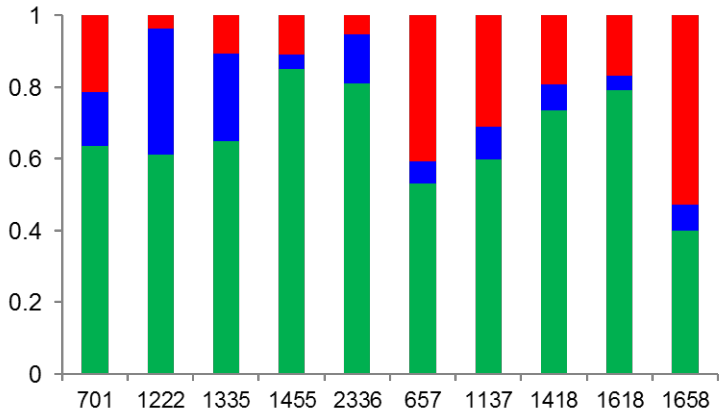

mass fraction (%)
1
0.5
0
1
2001
4001
6001
Particle
0
1
2001
4001
6001
8001
Particle

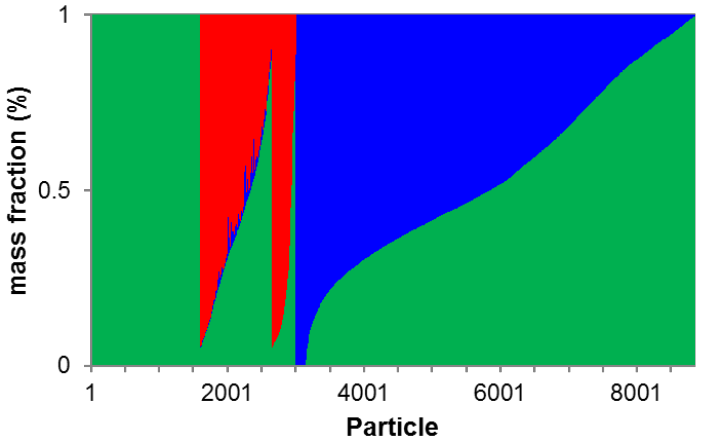

mass fraction (%)
1
0.5
0
1
2001
4001
6001
Particle

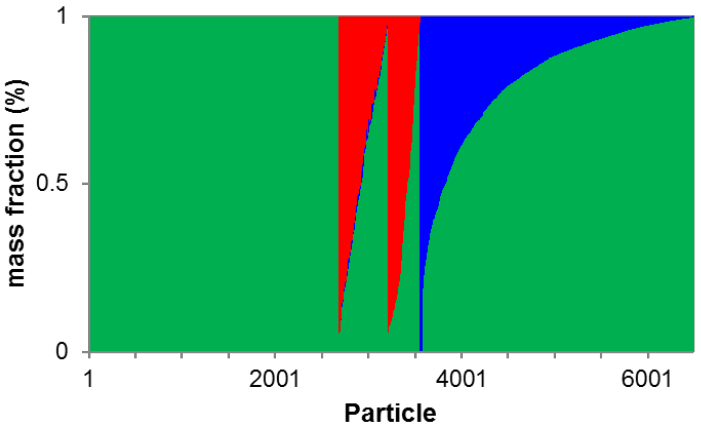
Composition T0 vs. T1

Pictorial Dγ → More OC and less IN at T1



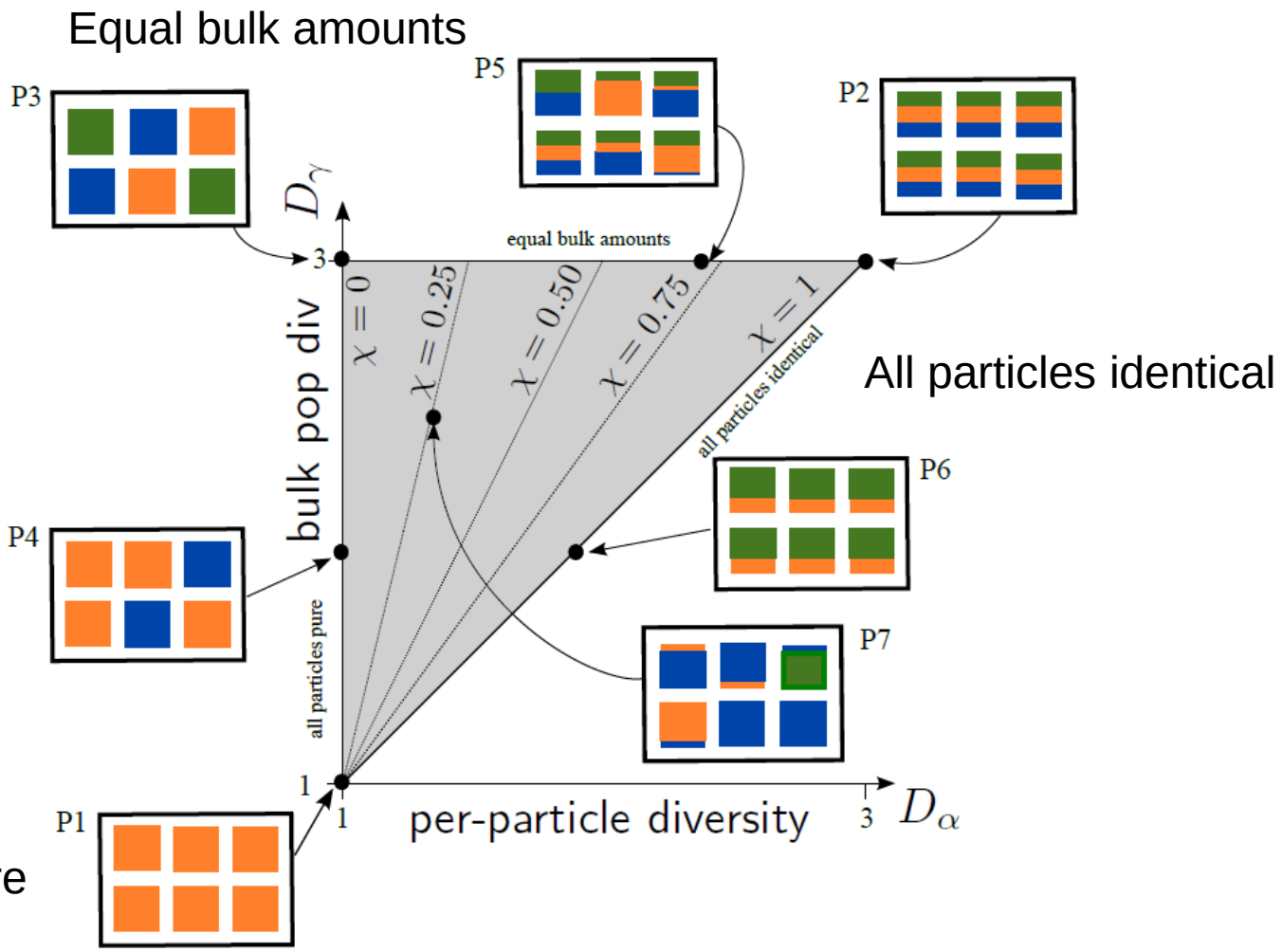






OC
IN
EC

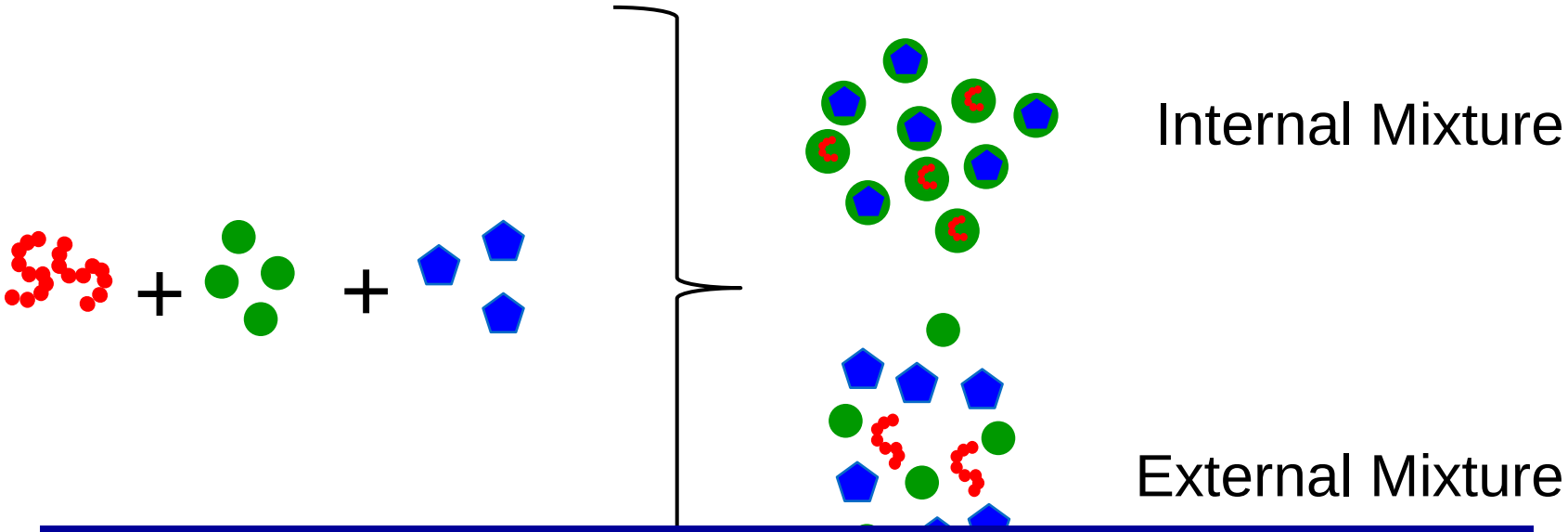
Mixing State Diagram



N. Riemer and M. West [2013], A*tmos. Chem. Phys.*, **13**, 11423-11439

Aerosol Mixing State

- Atmospheric impact of aerosols depends on the mixing state of individual particles
- Aerosol mixing state evolves with atmospheric aging



Mixing State Impacts:
Optical Properties, hygroscopicity, lifetime

Cares 2010

15 min samples over June 27th and 28th