Individual aerosol particles in hazes of North China

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Brown hazes have far-reaching effects at both regional and global scales, influencing both climate change and human health. In recent decades, brown hazes have caused the atmospheric air quality to deteriorate all over eastern China, where regional haze layers over both large cities and rural areas exhibit surprisingly high loadings of atmospheric pollutants. To evaluate regional brown hazes in northern China, transmission electron microscopy was employed to study individual haze particles produced by different kinds of haze episodes. We classified brown hazes into three types: smoke-urban-haze, industrial-urban haze, and coal-burning haze.

Keywords: Aerosol particles; Elemental composition; Mixing properties of aerosols; Single particle analysis; Electron microscopy; Aircraft

1. Smoke-urban haze

Emissions from agricultural biomass burning (ABB) in northern China have a significant impact on the regional and global climate. In northern China in June 2007, the monthly average aerosol optical depth (AOD) at 550 nm reached a maximum of 0.7. The AOD measurements are consistent with the occurrence of regional brown hazes and observations of severe aerosol pollution at that time. Aerosol particles were collected in urban Beijing from 12 to 30 June 2007 during a period of high haze and studied by transmission electron microscopy (TEM) and energy-dispersive X-ray spectrometry. The dominant particle types collected in the fine fraction (diameter < 1 μm) were ammonium sulfate, soot, K_2SO_4, KNO_3, and organic matter, although the K salts were minor between 21 and 30 June (Figure 1). The K-rich particles, which can be used as tracers of biomass burning, together with wildfire maps show that intense regional ABB in northern China contributed significantly to the regional haze observed between 12 and 20 June. We therefore classified the haze into two episodes: a type 1 (smoke-urban) haze between 12 and 20 June and a type 2 (industrial-urban) haze between 21 and 30 June. During the first haze episode, soot particles were mixed with the other particle types. Abundant organic matter and soluble salts emitted by ABB increased the particle sizes during transport and resulted in more hygroscopic aerosol particles in downwind areas, where they became cloud condensation nuclei. The high AOD (average 2.2) in Beijing during 12 to 20 June can be partly explained by the hygroscopic growth of fine aerosol particles and by the strong absorption of internally mixed soot particles, both coming from regional ABB emissions. These findings show that it is important to consider the origins of a haze, because different origins lead to different types of particles [1].

2. Industrial-urban haze

To evaluate a wintertime regional brown haze in northern China (Figure 2), trace gases and aerosols were measured at an urban site between 9 and 20 November 2009. Ion chromatography and TEM were used to investigate soluble ions in $PM_{2.5}$ and the mixing state of individual particles. The contrasts between clear and hazy days were examined in detail. Concentrations of the primary gases, including NO (55.62 ppbv), NO_2 (54.86 ppbv), SO_2 (83.03 ppbv), and CO (2.07 ppmv), on hazy days were two to six times their levels on clear days. In contrast, concentrations of O_3 remained low (5.71 ppbv) on hazy days. Mass concentrations of $PM_{2.5}$ (135.90 μg m^{-3}) and black carbon (7.85 μg m^{-3}) were three times higher on hazy days than on clear days. By TEM analysis, it was estimated that fractions of both ammoniated

sulfate (AS)-soot (20%) and AS-soot/organic matter/fly ash (20%) were larger on hazy days than on clear days (13% and 12%), implying that coagulation is an important mixing process in polluted air.

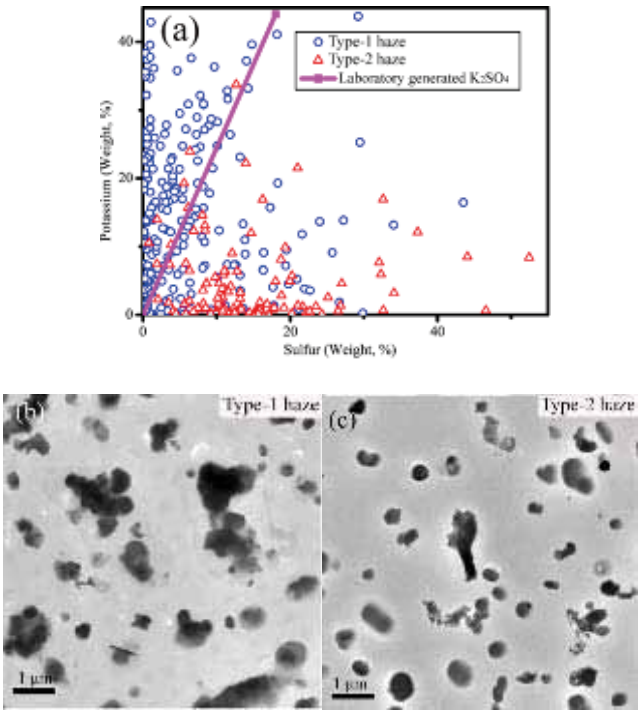

Figure 1 Potassium and sulfur contents of individual particles of type 1 and type 2 hazes.

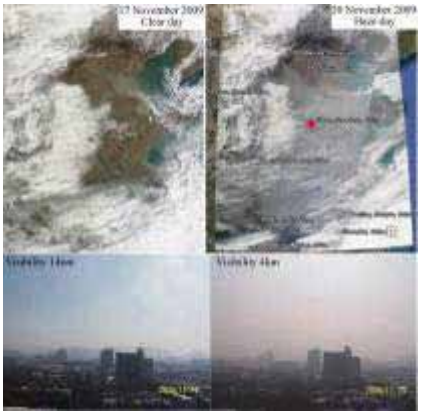

Figure 2 Reduction of visibility caused by a regional winter haze in northern China.

Emissions from coal combustion for power generation, industrial activities, and household heating led to the high SO_2 concentrations. Also, significantly high concentrations of secondary sulfates formed in the haze. Therefore, high concentrations of acidic gases contributed to the increased mass and number concentrations of secondary aerosols. Our study results indicate that metal-catalyzed oxidation in the aqueous phase is a major pathway of sulfate formation. The mixtures of aerosol particles, together with MODIS images, suggested that this haze covered not only the industrial cities but also extended into the neighboring rural regions [2].

3. Coal-burning haze

Heavy haze occurs frequently in winter over the Taiyuan Basin, northwestern China, a coal-burning region. During a research flight on 17–18 December 2010, aerosol particles were collected and the SO_2 concentration was monitored in a haze that occupied the atmosphere from the ground (780 m a.s.l) up to 4110 m altitude. Meteorological records revealed that the haze was stable and that it could be subdivided into three layers by chemical shifts at altitudes of about 1500 and 3000 m. From the surface to 1500 m (layer 1), the SO_2 concentration was 16–116 ppb (average, 58 ppb); from 1500 to 3000 m (layer 2), it was 2–45 ppb (average, 9 ppb); and above 3000 m (layer 3), it was 2–10 ppb (average, 4 ppb). The accumulation of SO_2 in layer 1 was attributable to the stable meteorological conditions and strong anthropogenic emissions as well as to the basin topography. Analyses of the collected particles by TEM revealed that organic particles and fly ash dominated in layers 1 and 2 and sulfate particles in layer 3. The organic aerosols frequently contained Si and Cl. Fly ash particles consisted of O and Si with minor Fe, Mn, Zn, Ti, Pb, As, Co, and Cr. These two types of aerosol particles are typically emitted during coal burning. Therefore, this haze is characterized primarily by aerosols produced as primary coal-burning emissions, in contrast to the hazes produced over the North China Plain, where secondary sulfate particles are dominant.

4. Conclusion

Although regional hazes occur frequently in China, the aerosol sources differ depending on the region and on the season, and various anthropogenic sources have resulted from economic development and the implementation of reforms throughout China. These regional hazes not only cause diverse health problems in continental China but also influence the regional and global climate. Compared with other areas in the world, many different atmospheric chemical mechanisms contribute to haze formation in this heavily polluted region because of the extremely high fine-particle loading in the atmosphere. Because how these haze aerosols influence cloud formation and precipitation is still unknown, haze aerosol particles from the upper atmosphere should be examined in future studies.

1 Li, W. J., L. Y. Shao, P. R. Buseck, 2010: Haze types in Beijing and the influence of agricultural biomass burning. *Atmos. Chem. Phys.*, **10**, (17), 8,119-8,130.

2 Li, W. J., S. Z. Zhou, X. F. Wang, Z. Xu, C. Yuan, Y. C. Yu, Q. Z. Zhang and W. X. Wang, 2011: Integrated evaluation of aerosols from regional brown hazes over northern China in winter: Concentrations, sources, transformation, and mixing states. *J. Geophys. Res.*, **116,** (D9), doi: 10.1029/2010JD015099.

Identification and analysis of atmospheric aerosol particles (& climate implications)

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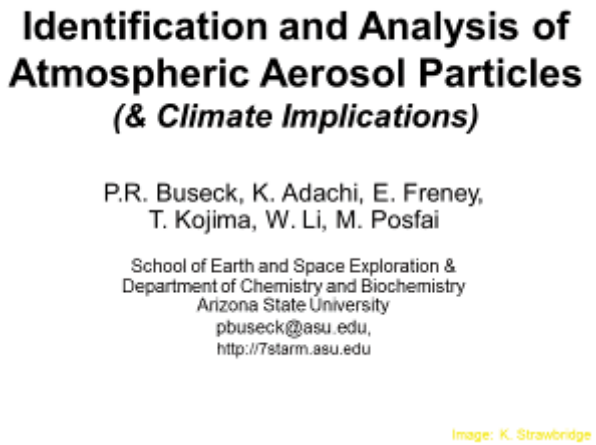
Aerosol particles are ubiquitous in the atmosphere and exert major influences on visibility, human health, and climate. The latter has received great attention in recent years and provides the primary justification for the research described in this talk. When solid, many aerosol particles are extremely small and yet have irregular shapes and, in many cases, form in complex mixtures. These variables control their interaction with solar radiation and thus determine whether they produce net heating or cooling effects.

Knowledge of their identities and physical characteristics is important for understanding reaction dynamics, source attribution and remediation, atmospheric modeling, and determining optical properties, important for climate effects. Desired parameters include size, composition, crystallographic structure, aspect ratio, and mixing state (single- or polyphase, coated or aggregated).

Many methods are available for determining sizes of individual particles, fewer for determining composition, but transmission electron microscopy (TEM) is unique for determination of structure (e.g., polymorphs or allotropes) and mixing states. Indeed, TEM is the only way to determine all of the above parameters, and it covers sizes from <1 nanometer to 10 or more micrometers. They represent a far richer and more complex world than is commonly assumed, and they contain more information than is commonly being recovered. Examples will be provided of imaging and analysis of particles from a range of environments, including discussions of their climate implications.

1



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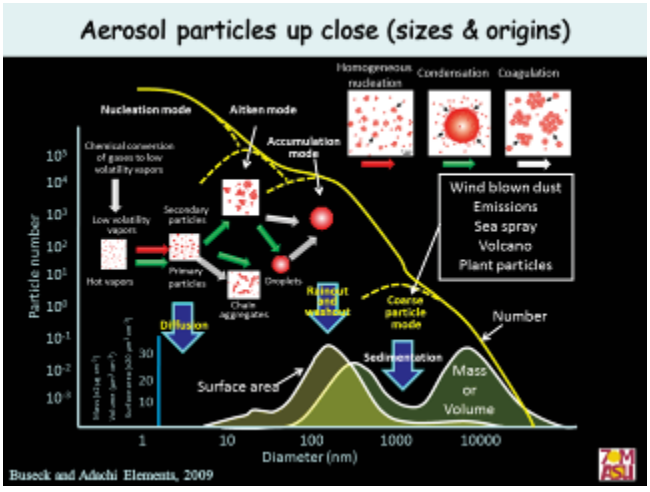

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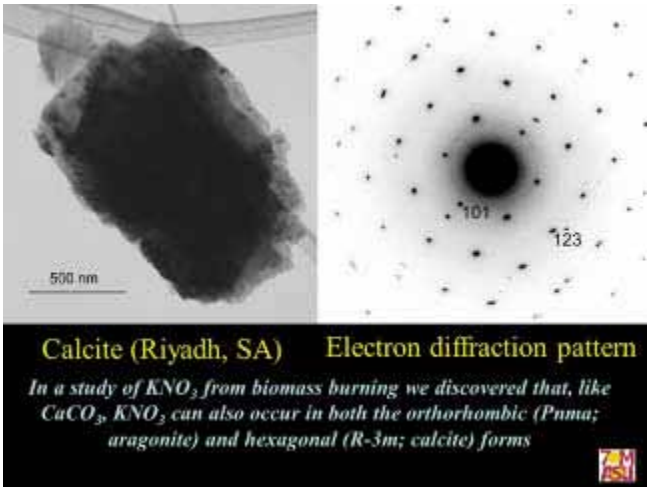
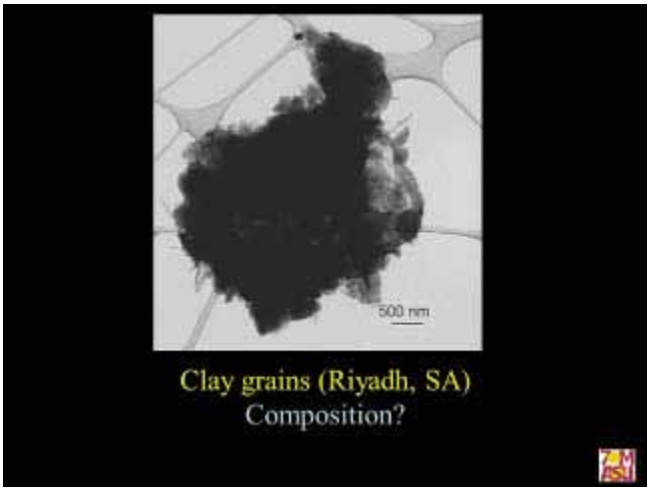
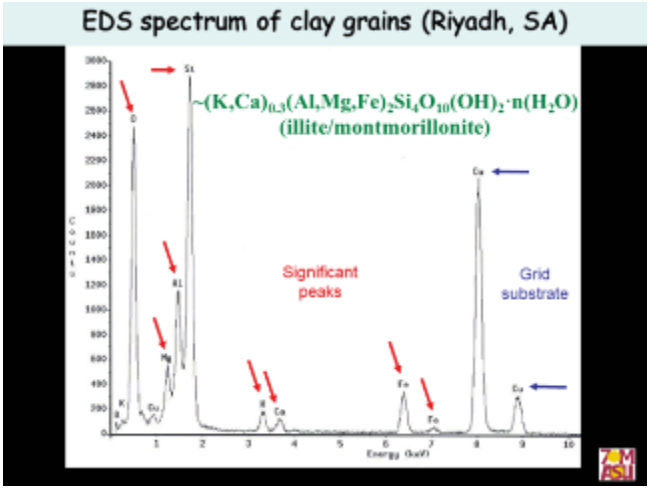

500 nm
101
123
Calcite (Riyadh, SA)
Electron diffraction pattern
In a study of KNO_3 from biomass burning we discovered that, like $CaCO_3$, KNO_3 can also occur in both the orthorhombic (Pnma; aragonite) and hexagonal (R-3m; calcite) forms

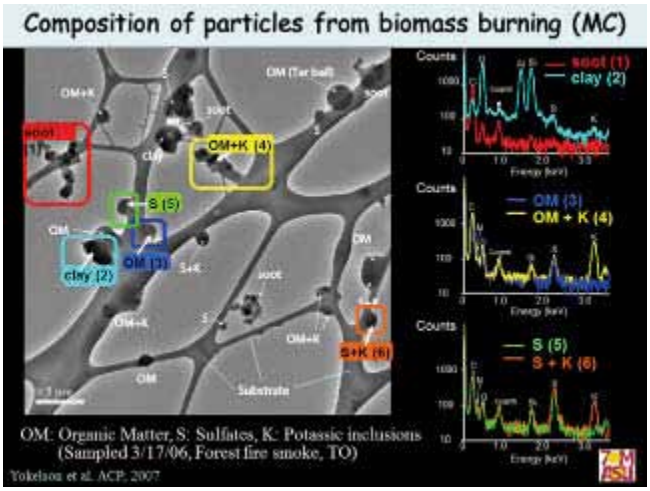
4


500 nm
Clay grains (Riyadh, SA)
Composition?

5


EDS spectrum of clay grains (Riyadh, SA)
~(K,Ca)0.3(Al,Mg,Fe)2Si4O10(OH)2·n(H2O)
(illite/montmorillonite)
Significant peaks
Grid substrate

6


Composition of particles from biomass burning (MC)
soot (1)
clay (2)
OM (3)
OM + K (4)
S (5)
S + K (6)
OM: Organic Matter, S: Sulfates, K: Potassic inclusions
(Sampled 3/17/06, Forest fire smoke, TO)
Yokelson et al. ACP, 2007

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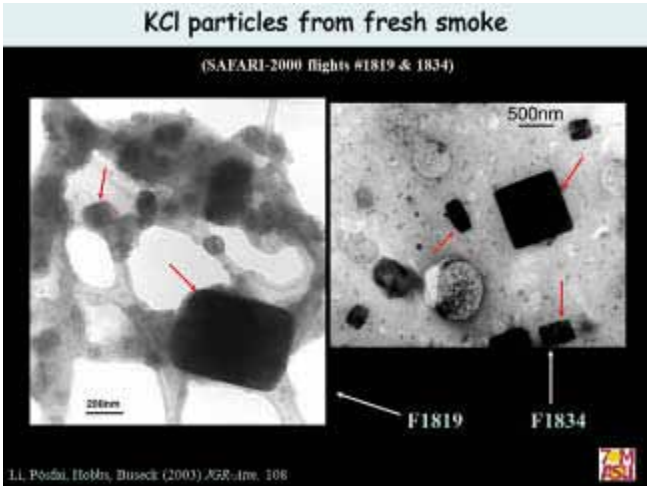
KCl particles from fresh smoke
(SAFARI-2000 flights #1819 & 1834)
500nm
F1819
F1834
Li, Posfai, Hobbs, Buseck (2003) ACP, 108

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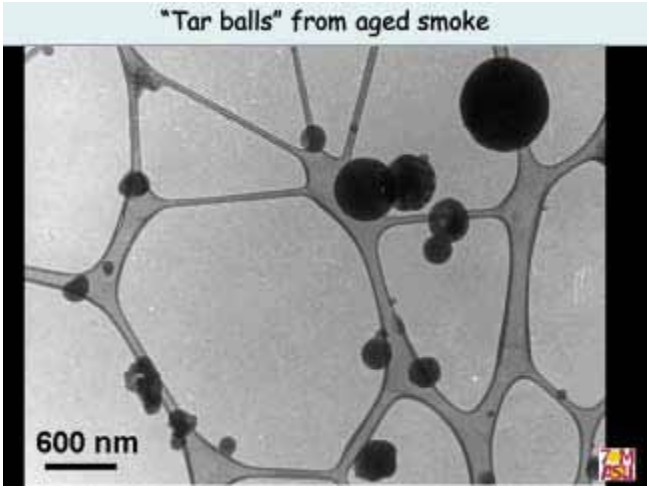
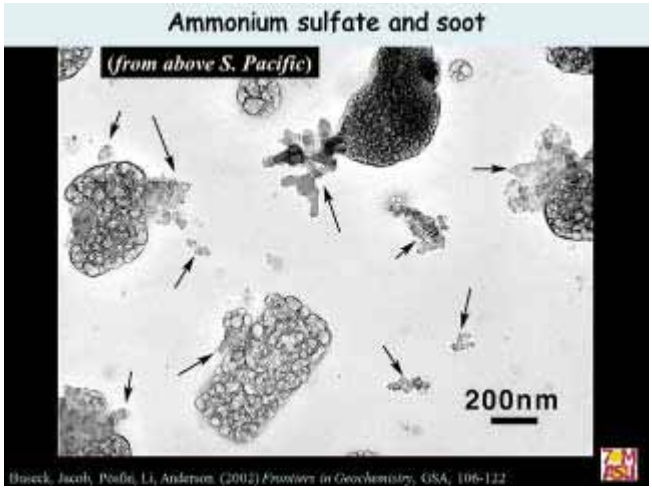

"Tar balls" from aged smoke
600 nm

9

10



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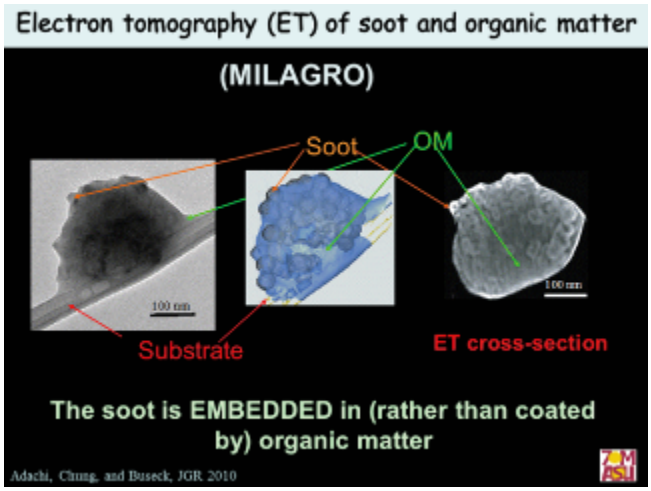

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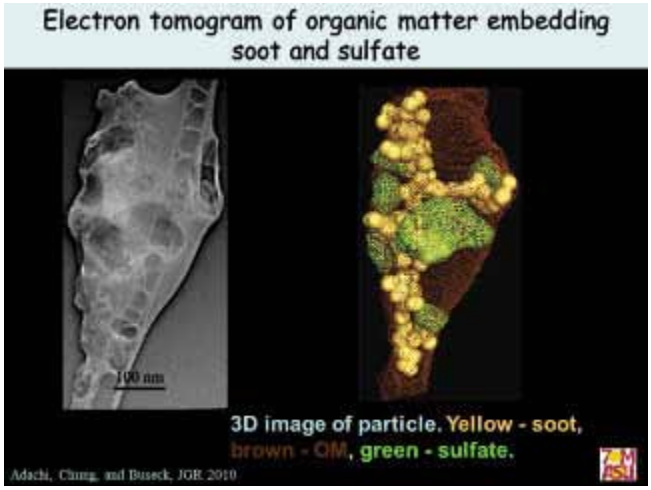

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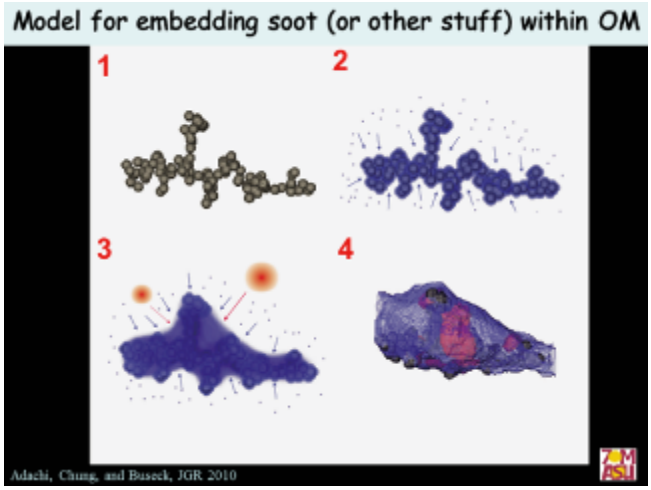

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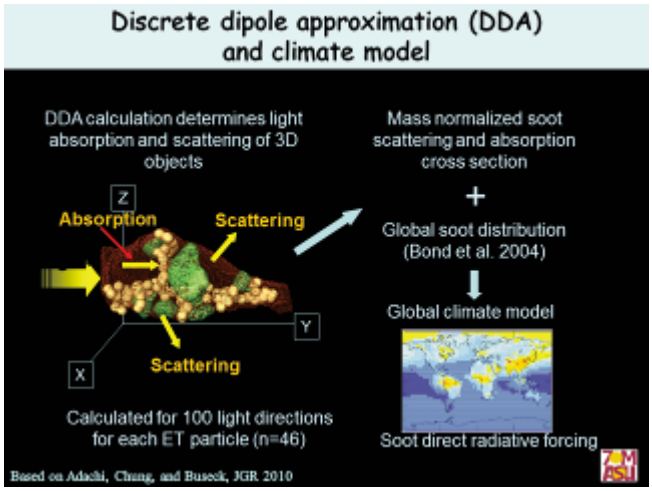

Thoughts & goals for the future

Use accurate and appropriate particle data in climate models

For example, produce models of "black carbon" that match the shapes and configurations that are actually observed

Reconcile measurements of individual particles with those from remote sources such as aircraft and satellites

The people and facilities at MRI seem to make this an ideal place for such research advances

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Thank you very much for inviting me to this very interesting and promising symposium!

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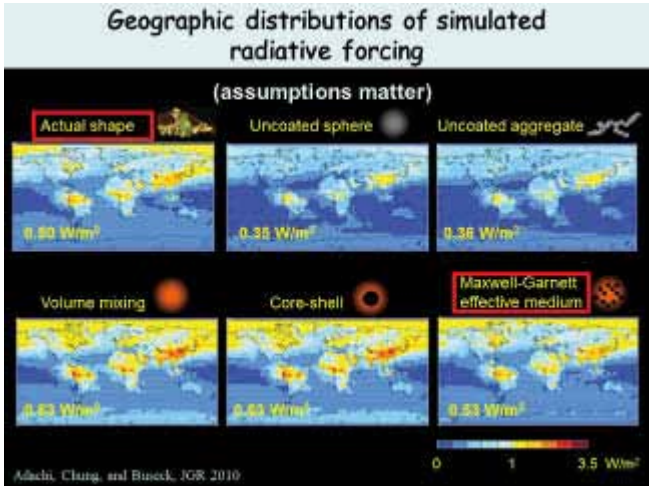

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