MORPHOLOGY AND OPTICAL PROPERTIES OF AEROSOL PARTICLES

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by

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Abstract

Major factors that affect climate change depend on gas and particulate phase components in the atmosphere. Gas phase species have been studied in great detail and are well understood, causing a warming effect on the atmosphere. The less understood major contributing factor in the atmosphere are aerosol particles, which range in size from nanometers up to microns. Aerosol particles can directly scatter and absorb light and also have secondary effects such as acting as a surface for gas phase reactions to occur or seed particles for cloud formation. Aerosol particles can cause health problems ranging from serious cardiovascular to respiratory effects. All climate and health effects of aerosol particles are dependent on particle composition, morphology, concentration, and size.

Since a large variety of particulate types exist in the atmosphere, we have focused on understanding the effect of mineral dust composition and morphology. Mineral dust is important because it is the second largest emission by mass. In order to study the optical properties of aerosol particles, we built a cavity ring-down spectrometer and developed methods to interpret the extinction cross section results for particles with a varied shape. We have studied the major components of mineral dust that include calcium carbonate, hematite, quartz, aluminosilicate clay minerals, and feldspars, along with a heterogeneous dust sample. We have found that non-absorbing species that have surface roughness and an aspect ratio close to one (such as calcite, quartz and feldspar) can be treated as spheres. Aerosol particles that are absorbing (hematite) that have an aspect ratio near one with a roughened surface need to be treated with more complex models; otherwise the extinction cross section will be underrepresented. For aerosol particles that are non-
absorbing but have a high aspect ratio (aluminosilicate clay minerals), additional modeling parameters are also needed that will account for shape and orientation. We have used Arizona Test Dust to determine if the models we have developed can be used to model the optical properties of a heterogeneous mixture. We have shown that the extinction cross section of the Arizona Test Dust can be modeled as long as individual components are treated independently and significant error would be introduced if all species were treated as spheres.

Organic aerosol particles are chemically complex species that originate from primary or secondary emissions. We have described mixed organic/ammonium sulfate particles in the submicron regime using TEM to understand phase separation. When the organic component has a high aqueous solubility, all particles exhibit a homogeneous morphology while at low aqueous solubility all particles exhibit a phase separated structure. Intermediate solubility organics show a size dependent morphology. For pimelic and succinic acid, small particles (under approximately 200 nm) have a homogeneous structure while the larger particles exhibit phase separated structures.

We have studied samples collected in Ulaanbaatar, Mongolia to better understand the types of particles and the effect of aging on these particles in an urban environment. The majority of the particles are soot, small spheres, or mineral dust. When we compared the monthly particle composition, we saw that there was an increased aging of the particles during the winter months due to pollution and a lower boundary layer leading to reduced atmospheric mixing. By understanding the particle composition present in areas and modeling the optical properties of individual particle types, better models can be created to give insight into aerosol particles affect on the atmosphere.
# Table of Contents

**List of Figures** .............................................................................................................. xi
**List of Tables** .................................................................................................................. xix
**Acknowledgements** ...................................................................................................... xx

**Chapter 1**

1. Introduction ......................................................................................................................... 1
   1.1 Properties of Aerosol Particles ........................................................................................ 1
   1.2 Mineral Dust ...................................................................................................................... 2
   1.3 Organic Aerosol ............................................................................................................... 4
   1.4 Ulaanbaatar, Mongolia Particulate Matter ....................................................................... 6
   1.5 Overview of Thesis ......................................................................................................... 7
   1.6 References ...................................................................................................................... 10

**Chapter 2**

2. Instrumentation ..................................................................................................................... 17
   2.1 Cavity Ring-Down Spectroscopy Experimental Setup ................................................... 17
   2.2 Particle Generation ........................................................................................................ 18
      2.2.1 Wet Generation ....................................................................................................... 18
      2.2.2 Dry Generation ....................................................................................................... 19
   2.3 Size Selection of Aerosol Particles ................................................................................. 21
   2.4 Cavity Ring Down Aerosol Extinction Spectroscopy ....................................................... 23
   2.5 Condensation Particle Counter (CPC) ............................................................................ 27
   2.6 Scanning Mobility Particle Sizing .................................................................................. 28
   2.7 Impaction of particles .................................................................................................... 29
   2.8 Particle Modeling Methods ............................................................................................ 29
      2.8.1 Mie Scattering Theory ............................................................................................ 30
      2.8.2 Discrete Dipole Approximation Method ................................................................. 30
   2.9 References ...................................................................................................................... 31

**Chapter 3**

3. Optical Properties of Calcium Carbonate Aerosol .............................................................. 33
   3.1 Introduction ...................................................................................................................... 35
   3.2 Experimental Methods ................................................................................................... 38
      3.2.1 Generation of Aerosol Particles ............................................................................. 39
      3.2.2 Size Selection of Aerosol Particles ....................................................................... 39
      3.2.3 Cavity Ring-Down Spectrometer .......................................................................... 41
      3.2.4 Transmission Electron Microscopy (TEM) .............................................................. 42
Chapter 4

4.1 Theoretical Approach: 

4.1.1 Basic Concepts of Dispersion Theory: ...................................... 89
4.1.2 Optical Properties of Particles: .................................................. 91
4.1.3 Discrete Dipole Approximation (DDA): ...................................... 92
4.1.4 Other Optical Properties: ............................................................ 93

4.2 Experimental Methods: ............................................................... 95

4.2.1 Sample Preparation: ................................................................. 96
4.2.2 Measurement Techniques: ......................................................... 97

4.3 Results and Discussion: ............................................................... 99

4.3.1 Particle Size Analysis: .............................................................. 100
4.3.2 Optical Properties: ................................................................. 101
4.3.3 Comparison with Literature: ..................................................... 102

4.4 Conclusions: .............................................................................. 104

4.5 Supporting Information: ............................................................ 106

4.5.1 Retrieval of Nigrosin Optical Properties: .................................. 106
4.5.2 Models used for DDA Calculations: ......................................... 107
4.5.3 Shape Parameters from TEM Analysis of Hematite: .................. 108
4.5.4 Comparison of roughened particles generated from spheres: .... 110
4.5.5 Comparison of spectral and optical constant averaging methods: 111
4.5.6 Phase Functions of Hematite: ................................................... 112

Chapter 5

5.1 Introduction: .............................................................................. 114

5.2 Experimental Methods: ............................................................ 116

5.2.1 Sample Preparation: ............................................................... 117
5.2.2 Measurement Techniques: ....................................................... 119

5.3 Results and Discussion: ............................................................. 121

5.3.1 Particle Size Analysis: ............................................................. 122
5.3.2 Optical Properties: ................................................................. 123
5.3.3 Comparison with Literature: ................................................... 124

5.4 Conclusions: ............................................................................. 126

5.5 Supporting Information: .......................................................... 128

5.5.1 Summary: ............................................................................ 129

Chapter 6

6.1 Introduction: ............................................................................ 144

6.2 Experimental Methods: ........................................................... 146

6.2.1 Generation of Aerosol Particles: ............................................. 146
6.2.2 Size Selection of Aerosol Particles: ....................................... 147
6.2.3 Optical Properties of Aerosol Particles: .................................. 148
6.2.4 Scanning Electron Microscopy (SEM): .................................... 148
6.2.5 Modeling Optical Properties of Aerosol Particles: .................. 149
6.2.6 Mie Scattering Calculations of Extinction Cross Section: ....... 150
6.2.7 Discrete Dipole Approximation calculations of extinction cross section: ................................. 151

6.3 Results and Discussion: .......................................................... 152

6.3.1 Size Distributions of Quartz: ................................................ 153
6.3.2 Size Distributions of Aluminosilicate Clay Minerals: ............ 154
6.3.3 Particle Shape and Size Selection: ....................................... 155
6.3.4 Optical Properties of Quartz Aerosol: ................................... 156
6.3.5 Optical Properties of Aluminosilicate Clay Mineral Dust Aerosol: .................................................. 157
6.3.6 Atmospheric Implications: ..................................................... 160
Chapter 9 Morphology of Submicron Mixed Organic/Inorganic Aerosol Particles by Cryo-TEM

9.1 Introduction ........................................................................................................... 221
9.2 Experimental Methods ......................................................................................... 223
9.3 Results and Discussion ....................................................................................... 227
9.4 Supporting Information for ................................................................................. 237
  9.4.1 Substrate Effects on Phase Separation and Morphology ............................... 239
  9.4.2 Effect of Temperature on Phase Separation and Morphology .................... 241
  9.4.3 Electron Beam Damage to Distinguish Different Particle Components .......... 241
9.5 References .......................................................................................................... 243

Chapter 10 Size Dependent Morphology of Mixed Organic/Inorganic Aerosol Particles

10.1 Introduction ......................................................................................................... 247
10.2 Results and Discussion ....................................................................................... 249
10.3 Supporting Information for ................................................................................. 256
  10.3.1 Experimental Methods: Cryogenic-Transmission Electron Microscopy ........ 256
  10.3.2 Experimental Methods: Optical Microscopy ................................................. 257
  10.3.3 Resolution of Phase Separation below 200 nm ........................................... 258
  10.3.4 Homogeneous Particles are Internally Mixed ........................................... 259
  10.3.5 References: .................................................................................................. 264
10.4 References .......................................................................................................... 265

Chapter 11 Aerosol Measurements in One of the Most Polluted Cities in the World:
Ulaanbaatar, Mongolia

11.1 Introduction ......................................................................................................... 269
11.2 Materials and Methods ...................................................................................... 273
  11.2.1 TEM/EDS Studies ....................................................................................... 273
  11.2.2 Ice Nucleation Studies .............................................................................. 273
11.3 Results and Discussion ....................................................................................... 274
  11.3.1 Characterization of Particle Types .............................................................. 274
  11.3.2 Seasonal Particle Concentration and Heterogeneous Chemistry ............... 276
  11.3.3 Ice Nucleation ............................................................................................ 279
11.4 Summary ............................................................................................................. 281
11.5 Supporting Information ...................................................................................... 281
  11.5.1 Description of Sampling Site ....................................................................... 281
  11.5.2 Additional Details of Transmission Electron Microscopy Experiments ....... 283
11.5.3 Transmission Electron Microscopy Images of Irregularly Shaped Particles .... 284
11.5.4 Particle Composition ................................................................. 286
11.5.5 Heterogeneous Chemistry .......................................................... 289
11.5.6 Additional Ice Nucleation Results .............................................. 291
11.5.7 References: .................................................................................. 294
11.6 References: .................................................................................... 295

Chapter 12 Conclusion and Future Directions ............................................ 297

12.1 Optical Properties of Mineral Dust Aerosol Particles ............................ 297
  12.1.1 Conclusion and Implications ...................................................... 297
  12.1.2 Future Directions: Size selection by mass ................................... 299

12.2 Organic Aerosol Particles ................................................................. 301
  12.2.1 Conclusion and Future Directions .............................................. 301

12.3 Mongolia ......................................................................................... 303
  12.3.1 Summary and Future Directions ................................................ 303

12.4 References ..................................................................................... 304
# List of Figures

**Figure 1-1:** Possible structures of organic/inorganic aerosol particles ........................................... 5

**Figure 1-2:** Comparison of the PM$_{10}$ concentrations for major population centers across the globe. Ahwaz, Iran is the most polluted city followed by Ulaanbaatar, Mongolia. Delhi, India is not within the top 10 for PM$_{10}$. ................................................................. 7

**Figure 2-1:** Schematic of the cavity ring-down spectrometer .......................................................... 18

**Figure 2-2-2:** Dry aerosol particle generation setup ................................................................. 21

**Figure 2-3:** Simplified cross section view of a differential mobility analyzer with dotted lines showing the path of particles through the DMA with blue particles being too small, red particles too large, and black particles being size selected ........................................ 23

**Figure 2-4:** Diagram of cavity ring-down spectrometer .......................................................... 24

**Figure 2-5:** Cavity Ring-Down Signal with and without sample .................................................. 25

**Figure 2-6:** Extinction coefficient vs. concentration for various sizes of polystyrene latex spheres. ................................................................................................................................. 27

**Figure 2-7:** Simplified Diagram of a condensation particle counter ........................................... 28

**Figure 3-1:** Schematic of our instrumental set up for cavity ring-down spectroscopy and for preparing samples for transmission electron microscopy. Particles can be generated from aqueous solution or from a dry powder. The particles are size-selected by a differential mobility analyzer. The extinction coefficient is measured at 643 nm in the optical cavity. The concentration of particles can be measured in the condensation particle counter, or particles can be impacted on TEM grids. For the ammonium sulfate particles, the impactor is placed after the differential mobility analyzer rather than after the optical cavity ................................................................. 38

**Figure 3-2:** Transmission electron microscopy images of ammonium sulfate size selected at mobility diameters of a) 400 nm and b) 600 nm. Two different TEM substrates are used for these samples: copper grids coated with a) a lacey carbon film and b) a continuous carbon film. The area of the particles is measured and converted into an area equivalent diameter by assuming that the particles are spherical. The number distributions of the area equivalent diameters are shown for mobility diameters of c) 400 nm and d) 600 nm. The triangle indicates the theoretical range of diameters expected ................................................................. 47

**Figure 3-3:** The extinction cross section vs. diameter for ammonium sulfate. The cavity ring-down data (circles) show the experimentally determined extinction cross sections. The dashed line is calculated using Mie scattering theory for spherical particles assuming that the particles are monodisperse. The triangles show the prediction for polydisperse spheres using the size distribution of area equivalent diameters determined from the TEM images. The error bars are from the standard deviation of several measurements ................................................................. 50
Figure 3-4: The same as Figure 3-2, but for calcium carbonate particles. Both TEM images were taken using copper grids coated with a continuous carbon film. ........................................ 51

Figure 3-5: The same as Figure 3, but for calcium carbonate particles. ........................................ 54

Figure 3-6: The size distribution for a) ammonium sulfate aerosol particles generated from aqueous solution and b) calcium carbonate aerosol particles generated from a dry powder. .................................................................................................................. 64

Figure 3-7: The extinction coefficients of four sizes of polystyrene latex spheres as a function of their concentration. Vertical error bars indicate the error between repeated measurements and horizontal error bars indicate the polydispersity of the polystyrene latex spheres. ........................................................................................................ 65

Figure 4-1: Schematic of the flow system for cavity ring-down aerosol extinction spectroscopy and particle collection for transmission electron microscopy analysis. See the text for additional details. .......................................................... 75

Figure 4-2: Particle shapes used for DDA calculations. ................................................................. 86

Figure 4-3: Transmission electron microscopy images of nigrosin size selected at (a) 300 nm and (c) 800 nm. The distributions of the area equivalent diameters are shown for mobility diameters of (b) 300 nm with a mean TEM size of 356 nm and (d) 800 nm ........................................................................................................................................ 88

Figure 4-4: Extinction cross sections vs. diameter for nigrosin. The blue circles indicate the experimentally determined extinction cross sections. The line was determined using Mie scattering theory for monodisperse spheres. The red diamonds are the Mie .... 90

Figure 4-5: Transmission electron microscopy images of hematite size selected at mobility diameters of (a) 250 nm with a mean TEM size of 260 nm and (c) 850 nm with a mean TEM size of 691 nm. The polydispersity at each mobility diameter is shown as a function of the transfer function. ........................................................................................................................ 91

Figure 4-6: Experimental extinction cross sections vs. diameter for hematite compared to (a) Mie scattering theory, (b) DDA calculations of spheroids, (c) DDA calculations of roughened spheres, and (d) DDA calculations of roughened spheroids. ...................... 94

Figure 4-7: Percent differences between the model results for polydisperse particles (Mie scattering theory and DDA) and the experimental extinction cross sections. The gray line denotes perfect agreement. ........................................................................................................ 95

Figure 4-8: Comparison of calculations for monodisperse particles using Mie scattering theory for spheres (black), the DDA for spheroids (red), the DDA for roughened spheres (blue), and the DDA for roughened spheroids (green). The light blue shading around the DDA calculations corresponds to the minimum and maximum values calculated. .................................................................................................................................................. 96

Figure 4-9: Reduced cumulative fractional difference (CFDR) plot for nigrosin. Darker shading corresponds to a lower CFDR value. In this case n=1.88 and k=0.26i with the minimum CFDR = 0.0148, whereas the average values over all measurements taken are n= .................................................................................................................. 99
Figure 4-10: TEM image of NaCl crystals on the surface of a nigrosin particle. A batch of nigrosin that did not produce particles with NaCl crystals was used for the refractive index retrieval in the manuscript. ................................................................. 99

Figure 4-11: View of six different angles of the (a-e) five roughened spheres and (f-g) roughened spheroids. ................................................................. 100

Figure 4-12: Comparison of the geometric parameters obtained from the TEM results (points) with the spheroids, roughened spheres, and roughened spheroids. For reference, spheres have a value of unity for all shape factors. ........................................... 102

Figure 4-13: Comparison of extinction cross-sections calculated using the DDA for monodisperse, roughened spheres. ...................................................... 104

Figure 4-14: Comparison of the optical constant averaging method (OCA) and spectral averaging method (SA) for spheres calculated using Mie scattering theory and roughened spheres calculated using the DDA. ................................................................. 105

Figure 4-15: Phase functions calculated for spheres (black line), spheroids with an aspect ratio of 1.8 (red dashed line), the average of the roughened spheres (blue dotted line), and the roughened spheroids (green dashed line). The light blue region corresponds to the minimum and maximum values from DDA calculations. ........................................... 106

Figure 5-1: a) A representative SEM image of the calcite particles in the top-down orientation. b) A representative SEM image of the calcite particles in the side-on orientation, imaged at an angle of 5° from normal. c) The distribution of calcite aspect ratios 122

Figure 5-2: SEM images of KGa-1b (kaolinite) in the a) top-down and b) side-on orientations. c) The distribution of aspect ratios determined for KGa-1b in the two orientations. d) SEM images of KGa-2 (kaolinite) in the top-down and e) side-on orientations .... 123

Figure 5-3: SEM images of NX-illite in the a) top-down and b) side-on orientations. c) The distribution of aspect ratios determined for NX-illite from the SEM images. d) SEM images of STx-1b (montmorillonite) in the top-down and e) side-on orientations. 124

Figure 5-4: Comparison of the aspect ratios for each species studied. For each type of mineral, the aspect ratios observed for the top-down and side-on orientations are shown. In a box and whiskers plot, the center line is the average of the data, the bottom....... 125

Figure 5-5: The aspect ratio as a function of the length of the longer of the two measured axes in the top-down and side-on orientations for a) calcite and b) quartz................. 133

Figure 5-6: The aspect ratio of kaolinite as a function of the length of the longer of the two measured axes in the top-down and side-on orientations for a) KGa-1b and b) KGa-2. .................................................................................................................. 134

Figure 5-7: The aspect ratio as a function of the length of the longer of the two measured axes in the top-down and side-on orientations for a) NX-illite, b) STx-1b montmorillonite, and c) SWy-2 montmorillonite. ......................................................................................... 135

Figure 6-1: Quartz size selected at a) 350 nm and c) 750 nm, b) comparison of bulk sample by SEM (bars) and SMPS (line), and SEM image of quartz at d) 350 nm and e)750 nm ................................................................. 154
Figure 6-2: Kaolinite (KGa-2) size selected at a) 350 nm and c) 750 nm, b) comparison of bulk sample by SEM (bars) and SMPS (line), and SEM image ......................................................... 155

Figure 6-3: NX-Illite size selected at a) 350 nm and c) 750 nm, b) comparison of bulk sample by SEM (bars) and SMPS (line), and SEM image ......................................................... 156

Figure 6-4: Montmorillonite (STx-1b) size selected at a) 300 nm and c) 700 nm, b) comparison of bulk sample by SEM (bars) and SMPS (line), and SEM image ........................................ 158

Figure 6-5: Comparison of mean volume equivalent diameter by SEM to the mobility diameter selected by the DMA. The line is a 1:1 fit where the average size would match the size selected. ......................................................... 160

Figure 6-6: Extinction cross section vs mobility diameter for quartz. Monodisperse Mie theory (solid line) and monodisperse spheroid line (dashed line) are compared to the extinction from CRD-AES (diamonds) and theoretical Mie calculations that include polydispersity from volume equivalent SEM measurements. ........................................ 163

Figure 6-7: Extinction cross section vs mobility diameter is shown for experimentally derived extinction for NX-illite, montmorillonite, and kaolinite compared to monodisperse Mie theory and DDA calculations. ......................................................... 165

Figure 6-8: Extinction cross section vs mobility diameter for KGa-2. The CRD-AES data (blue circles) shows the experimentally determined cross section at each mobility diameter. The solid lines represent the monodisperse fits for Mie theory, randomly oriented spheroids, and oriented spheroids. Polydispersity is taken into account to account for theory at 250 and 750 nm and is shown for both the particles treated as area equivalent spheres and volume equivalent spheres........................................ 167

Figure 6-9: Schematic of the mineral dust aerosol flow system for cavity ring-down aerosol extinction spectroscopy and particle collection for transmission electron microscopy analysis. ................................................................. 172

Figure 6-10: Quartz phase function for a) 250 nm b) 550 nm and c) 850 nm ..................... 173

Figure 6-11: NX-Illite phase function for a) 250 nm b) 550 nm and c) 850 nm ..................... 174

Figure 6-12: KGa-2 phase function for a) 250 nm b) 550 nm and c) 850 nm ..................... 175

Figure 6-13: STx-1b phase function for a) 250 nm b) 550 nm and c) 850 nm ..................... 176

Figure 7-1: SEM images of ATD from the a) top-down and b) side-on orientations with c) the distribution of aspect ratios determined for both orientations. ......................................................... 197

Figure 7-2: Experimental extinction cross section retrieved using CRD-AES (circles) compared to Mie calculations including ATD polydispersity (squares) and individual component polydispersity (diamonds)......................................................... 199

Figure 7-3: Experimental extinction cross section retrieved using CRD-AES (circles) compared to DDA spheroid calculations with an aspect ratio of 1.84. The solid line is the monodisperse theory with the ATD polydispersity (squares) and individual component polydispersity (diamonds)......................................................... 200
Figure 7-4: Experimental extinction cross section retrieved using CRD-AES (circles) compared to individual models for each component depending upon shape. The solid line is the monodisperse theory with the ATD polydispersity (squares) and individual component polydispersity (diamonds). ................................................................. 201

Figure 7-5: Percent difference between modeling results for polydisperse particles and the experimental extinction cross section from CRD-AES ................................................................. 202

Figure 7-6: a) A representative SEM image of labradorite particles in the top-down orientation. b) A representative SEM image of labradorite particles in the side-on orientation. c) The distribution of labradorite aspect ratios obtained from SEM images. The fraction of particles is plotted vs. aspect ratio. D) The top-down SEM image of orthoclase. E) Side-on orientation of orthoclase particles. F) The distribution of orthoclase aspect ratios obtained from SEM images. ................................................................. 205

Figure 7-7: Comparison of calculations for monodisperse particle for each model type with all particles treated as Mie spheres (black line), all particles treated as DDA spheroids with an aspect ratio of 1.84 (blue line), or particles treated as individual components (red line). ................................................................. 206

Figure 7-8: Modeled particle extinction vs. diameter for different particle orientations. a) Comparison of all particles modeled as spheroids with an aspect ratio of 1.84 where there is a large difference between the extremes of scattering compared to non-oriented particles. b) Difference between orientations for individual models is less due to some articles being treated as Mie Spheres and not having any orientation effects................................................................. 207

Figure 8-1: Possible core-shell reaction product of calcium carbonate particles with nitric acid vapor ........................................................................................................................................... 212

Figure 8-2: Diagram of movable injector setup where the particle and relative humidity flow is introduced through four inlets at the top of the reaction chamber. Nitric acid vapor is introduced through the movable injector that can move, changing the reaction volume inside the chamber. The resultant mixture is passed through an activated carbon drier to remove the nitric acid and a diffusion drier to remove water........ 214

Figure 8-3: Size selected calcium nitrate extinction cross section measurements compared to Mie scattering theory for calcium nitrate and hydrated calcium nitrate......................... 215

Figure 8-4: Comparison of size selected calcite particles with calcite exposed to nitric acid at varying relative humidity using CRDS. At low relative humidity, the calcite particles have a similar cross section to the non-reacted calcite particles, but at high relative humidity, they exhibit a much larger extinction cross section................................. 217

Figure 8-5: TEM images of 700 nm size selected a) calcium carbonate and b) calcium carbonate reacted with nitric acid at approximately 60% RH........................................................................ 218

Figure 9-1: Cryo-transmission electron microscopy images of highly soluble organic compounds, malonic acid, citric acid, and glutaric acid internally mixed with ammonium sulfate. The morphologies are homogeneous in structure...................................................... 229
**Figure 9-2:** Cryo-transmission electron microscopy images of particles composed of ammonium sulfate internally mixed with organic compounds with intermediate aqueous solubility, succinic and pimelic acid. The morphology of the particles is dependent on par ................................................................. 232

**Figure 9-3:** Cryo-transmission electron microscopy images of phase-separated particles composed of ammonium sulfate internally mixed with organic compounds of low aqueous solubility, adipic, suberic, and azelaic acid. ........................................... 235

**Figure 9-4:** SEM image of dry particles composed of pimelic acid and ammonium sulfate prepared on a TEM grid as described in the text and imaged under ambient conditions................................................................. 240

**Figure 9-5:** Pimelic acid/ammonium sulfate imaged with a TEM at room temperature ........ 241

**Figure 9-6:** TEM images of electron beam damage to a) ammonium sulfate, b) succinic acid, and c) pimelic acid/ammonium sulfate particles. The images on the left are the initial particles. The amount of damages increases from left to right. Images in (a) an .. 242

**Figure 10-1:** The three major types of observed particle morphologies for model aqueous aerosol particles composed of salt and soluble or insoluble organic compounds at a fixed relative humidity................................................................. 248

**Figure 10-2:** Optical microscopy images of the time evolution of particles drying for internal mixtures of ammonium sulfate with pimelic acid (top) and succinic acid (bottom). For pimelic acid, we show the a) initial particle, b) liquid-liquid phase separation, and c) crystallization. For succinic acid, we show d) the initial particle, e) crystallization, and f) complete crystallization. ................................................................. 250

**Figure 10-3:** Particle morphology observed using cryo-TEM for internally mixed particles composed of ammonium sulfate and a & b) pimelic acid or c & d) succinic acid. a & c) Larger particles are phase separated, where the organic component may contain some ammonium sulfate (see text). B & d) Smaller particles are homogeneous. .. 252

**Figure 10-4:** Morphology of internally mixed particles composed of ammonium sulfate with a) pimelic acid and b) succinic acid vs. area equivalent diameter. ......................... 254

**Figure 10-5:** Cryo-TEM images of a) a particle composed of azelaic acid and ammonium sulfate and b) a particle composed of adipic acid and ammonium sulfate showing phase separation in particles with diameters less than 200 nm. 259

**Figure 10-6:** Damaging behavior of homogeneous particles composed of succinic acid and ammonium sulfate in the cryo-TEM. a) The undamaged particle and b) damaged particle after exposure to the electron beam. The electron beam causes voids to form throughout the particle. ................................................................. 260

**Figure 10-7:** Extinction cross sections for a & c) ammonium sulfate, pimelic acid, and internally mixed ammonium sulfate/pimelic acid, and b & d) ammonium sulfate, succinic acid, internally mixed ammonium sulfate/succinic acid as a function of particle mobility diameter. A& b) Theoretical calculations using the experimental concentrations, as described in the text. The error is from the uncertainty in the concentration of the
particles. C & d) Experimentally measured extinction cross sections. The error shown is from the uncertainties in the concentration of the particles and the extinction coefficients.

Figure 11-1: The relationship of annual average PM10 concentration in selected cities reported in 2011 relative to the number of peer-reviewed scientific papers that have been published about air pollution in that city prior to and including 2011. Shown are some of the most well-studied cities (in blue), as well as the ten most PM10 polluted cities from the 2011 WHO report of over 1000 places worldwide (in red). The vertical, dashed gray line shows the sum of all of papers published on air pollution in those ten most PM-polluted cities. The WHO guideline for PM10 annual average concentration (20 μg m$^{-3}$) is the horizontal, dashed gray line.

Figure 11-2: Representative particles collected in Ulaanbaatar, Mongolia. Particles are classified first according to their shape (spherical, fractal, irregular) and then according to their elemental composition.

Figure 11-3: Size distributions for spherical, fractal, and irregularly shaped particles averaged over all the particles collected in this study as analyzed by TEM. The area of the particles in the TEM images was measured and converted to an area equivalent diameter by assuming that the particles are spheres and therefore are circular in the TEM images. The bins are the same size for spherical and fractal particles and larger for irregular particles. The normalized number of fractal particles in the smallest bin is 0.24.

Figure 11-4: The number of particles collected per TEM image per hour collection time for a) all particles, b) spherical particles, c) fractal particles, and d) irregularly shaped particles. The months November – March are shaded blue. Note that all of the panels have different y-axis scales. For June - Sept (labeled “summer”) and Nov – March (labeled “winter”), the percentage of the particles by number that contain sulfur is indicated in red, and the percentage by number without sulfur is indicated in black.

Figure 11-5: The supersaturation with respect to ice, $S_{\text{ice}}$, at the onset of heterogeneous ice nucleation for samples collected in this study. Error bars are determined from repeated experiments. The months November – March are shaded in blue.

Figure 11-6: Map of Ulaanbaatar Mongolia with relevant sites for this study marked. Ulaanbaatar is located at 1310 m in a valley between two mountainous areas. The main sources of particulate matter pollution are from the ger district, which blankets the Northern half of the city, as well as three coal-fired power plants in the outer areas of the western portion of the city. Note that Power Plant #1 is no longer functioning. The measurement site from this study is shown, as well. To note: Wind typically blows from a northwesterly direction over the city, with low winter wind speeds due to the Siberian High that sits over the region throughout the winter and highest windspeeds in the spring time.\textsuperscript{1,2}

Figure 11-7: TEM images of representative irregularly shaped particles of different compositions illustrating the wide range of particle shapes and compositions observed.
**Figure 11-8:** a) The number fraction of each particle type over the ten-month collection period. b) The area fraction of each particle type over the collection period. The area is calculated from the projected area of the particle seen in the TEM images. The legends for a and b are the same. The error bars shown in the figures are an upper estimate of the error caused by having a finite sample size, as described in the Materials and Methods Section. The fractions of the different particle types for each month sum to 1.0.

**Figure 11-9:** a) The elemental composition of the irregular particles. The particles are primarily composed of Ca, Al, and Si with smaller contributions from carbon and salts, which suggests the presence of Ca salts such as calcite and gypsum, aluminosilicates with and without calcium, silicates, fully collapsed soot, and salt. b) The fraction of irregular particles associated with sulfur. As seen in the main text, the fraction of particles with sulfur is higher in November – March. c) The fraction of irregular particles associated with iron and other trace metals (Fe, Cr, Ti) or F.

**Figure 11-10:** The composition of a) spherical, b) fractal, and c) irregularly shaped particles determined from EDS. For (a) and (b), if particles contain metal, they are grouped as “metal”, if the particles have no metal, but contain sulfur, then they are grouped as “carbon/sulfur”. All other particles contain carbon. For (c), the majority of particles contain metal, and as a result, they are grouped as containing sulfur or not containing sulfur. For each month, the fractions sum to 1.0. The months November – March are shaded in blue.

**Figure 11-11:** An ice crystal and the heterogeneous ice nucleus on which it formed. An ice crystal with a particle inside (marked with an arrow) is shown on the left. The ice is sublimed to reveal the particle shown on the right. This sample is from an experiment at 225 K on a November 2012 sample.

**Figure 11-12:** Number of ice nucleation active surface sites per m2 for monthly samples this study. As shown, the monthly ns values are all within error of each other. Thus, the ice nucleation onsets found in Fig. 11-5 are directly comparable, suggesting that a chemical mechanism is dictating the changes in S_{ice} values.

**Figure 11-13:** The diameter of particles that heterogeneously nucleated ice.

**Figure 12-1:** Simplified diagram of an Aerosol Particle Mass Analyzer where the system rotates along an axis allowing for size selection based on the momentum of the particles.
List of Tables

Table 4-1: Equations used to calculate particle shape factors................................................................. 80
Table 4-2: Shape factor results for TEM analysis of hematite particles compared to modeled structures used for DDA simulations.................................................................................................................. 93
Table 4-3: Geometric parameters of particles analyzed by TEM and particles generated for DDA calculations.......................................................................................................................... 103
Table 5-1: Average aspect ratios and standard deviations for the minerals used in this study for both the top-down and side-on orientations.................................................................................. 125
Table 5-2: Comparison of measured average aspect ratios to literature values for the clay minerals. The NX-illite is compared to measurements of illite. ....................................................... 127
Table 5-3: Specific surface area (SSA) measurements using SEM, BET, and AFM. The SSA calculations from the SEM calculations are performed assuming the particles are hexagonal prisms, rectangular prisms, and spheroids. NX-illite is compared to BET measurements. .................................................................................................................. 131
Table 6-1: Literature refractive index and effective Mie refractive index calculations for quartz, NX-illite, kaolinite, and montmorillonite. .......................................................... 169
Table 6-2: Literature refractive index and effect Mie refractive index calculations over various size ranges for quartz, NX-illite, KGa-2, and STx-1b............................................................... 178
Table 7-1: Description of parameters used for each model type................................................................. 195
Table 9-1: Organic acid molecular formulas, molecular structures, O:C ratio, and aqueous solubility. The mole fraction and volume fraction of the organic acid in the organic acid/ammonium sulfate mixtures is also listed. Ammonium sulfate properties are listed. ........................................................................................................... 225
Table 12-1: Effective refractive index from modeling DDA scattering results using Mie Scattering theory for mineral dust species.......................................................... 298
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Chapter 1  Introduction

1.1 Properties of Aerosol Particles

Aerosol particles pose the greatest uncertainty when quantifying the radiative forcing on the atmosphere.\(^1\) Aerosol particles can come from either natural or anthropogenic sources. The uncertainty of the modeled radiative forcing stems from an uncertainty in the size distribution, composition, concentration, position in the atmosphere, and shape of aerosol particles.\(^2\)\(^,\)\(^3\)\(^,\)\(^4\) Depending on these factors, aerosol particles can cause either a net warming or cooling effect. Aerosol particles can directly interact with light through either scattering or absorbing the light, known as the direct effect. The aerosol indirect effects are a myriad of interactions that include particles acting as cloud nuclei thus increasing cloud lifetime and cloud albedo. The total direct effect of aerosol particles has been calculated to be \(-0.5 \pm 0.4 \text{ W m}^{-2}\), while the indirect effect has been calculated to be \(-0.7 (-1.8 \text{ to } -0.3) \text{ W m}^{-2}\).\(^1\) The majority of particles that affect climate are in the accumulation mode (under approximately 2 µm) and can be transported long distances from the source region.\(^5\)\(^,\)\(^6\)\(^,\)\(^7\) Particles larger than approximately 2 µm will settle out quickly due to gravitational effects.\(^8\)

Atmospheric models mostly use externally mixed particles, but a dependence on the internal structure of particle to their radiative properties is has also been observed.\(^9\)\(^,\)\(^10\)\(^,\)\(^11\)\(^,\)\(^12\) Aerosol particles are mainly modeled using spheres, but have started to incorporate spheroids using a range of aspect ratios since particle shape is important for remote sensing retrieval algorithms.\(^13\)\(^-\)\(^16\) For aerosol retrieval methods, back scattered radiation is used to determine the type, concentration, and size of particles in the atmosphere. While most lidar measurements use Mie scattering theory to determine the
aerosol concentration, the phase functions of rough particles is different than smooth spherical particles.\textsuperscript{17, 18} More complex models have been used that use a distribution of spheroids instead of spheres to gain a better understanding of the optical scattering of mineral dust in the atmosphere.\textsuperscript{13-16}

1.2 Mineral Dust

Mineral dust is the second largest emission by mass of any aerosol particle type, with between 1000-3000 Tg emitted annually.\textsuperscript{1, 19, 20, 21} Large amounts of dust are transported globally, and it is estimated that about 52,000 metric tons of Asian dust under 2.5 μm were transported across the United States in April of 2001.\textsuperscript{22} The direct forcing of these particles is estimated to be -0.1 ± 0.2 W m\textsuperscript{-2} of the total -0.5 ± 0.4 W m\textsuperscript{-2} for all aerosol particle types.\textsuperscript{1} Mineral dust is one of the best ice nuclei, with feldspar minerals being the most active.\textsuperscript{23, 24, 25, 26} The primary source of mineral dust aerosol particles is the dust belt located in the mid-latitudes stretching from the Saharan region through central Asia.\textsuperscript{27} High latitude areas, such as Iceland, produce a substantial amount of mineral dust during the spring months.\textsuperscript{28} Of all the mineral dust emitted, it has been estimated that up to 50% is due to anthropogenic sources.\textsuperscript{1, 21} The composition of mineral dust can change dramatically while it is transported due to heterogeneous chemistry occurring on the particle surfaces. One of the most reactive mineral species present is calcite, which will react readily with nitric and sulfuric acid in the atmosphere and act as a sink for these species.\textsuperscript{19} During transport, it is estimated that up to 30% of calcium carbonate in mineral dust aerosol can be converted to CaSO\textsubscript{4} or Ca(NO\textsubscript{3})\textsubscript{2}.\textsuperscript{29}

Mineral dust aerosol is a complex mixture of many different mineral types. The composition of mineral dust aerosol particles is dependent on the source region. The
The major components of mineral dust are: quartz, calcite, and various aluminosilicate clay minerals. Quartz is the largest component of China Loess at more than 50% and calcium carbonate can be up to 12% by weight in Asian dust. Aluminosilicate clay minerals are one of the most common types of mineral dust, accounting for 50-64 wt.% of Saharan dust and up to 85% of Asian dust measured by electron microscopy analysis. The main ways to characterize the irregularity of mineral dust is through the roughness and elongation of the particles. Quartz and calcite both have aspect ratios near 1, but have surface roughness. Aluminosilicate clay minerals have a much more complex structure with alternating layers of tetrahedrally coordinated silicon and octahedrally coordinated aluminum. The ratio of these layers defines the clay type. Due to having many large flat sheets, aluminosilicate clay minerals adopt a disk-shaped structure with high aspect ratios that range from 4 to 500 for particles from approximately 100 nm to microns in size. The increased surface area to volume for high aspect ratio particles affects the optical properties and surface characteristics.

Hematite is the major absorbing species in mineral dust, with up to 1% in Saharan dust and up to 2.6% in Icelandic dust by mass. Hematite has a high real and imaginary refractive index ($m \approx 3 + 0.1i$), which leads to the species having large effects on mineral dust mixtures in small amounts. Additionally, iron acts as a nutrient in plant growth, and deposition of hematite in the oceans can act as an important source of soluble iron for living organisms. Modeling studies of hematite observe that small changes to the surface roughness of hematite will likely change the optical properties. Previous experimental research of bulk hematite aerosol scattering properties has not
been sensitive enough to show a difference between treating hematite as a sphere or including surface roughness.\textsuperscript{41, 42}

Arizona Test Dust (ATD) is a heterogeneous mixture of the major components of most mineral dust species and has been widely used to study ice nucleation, heterogeneous chemistry, and optical properties of mineral dust.\textsuperscript{23, 43-47} ATD consists of 17.1\% quartz, 33.2\% feldspar, 5.6\% carbonate, 7.5\% illite, 2\% kaolinite, 10.2\% smectites, and 24.4\% other aluminosilicate clays.\textsuperscript{23} Previous experiments to understand light scattering of a heterogeneous mineral dust source have been unsuccessful, with only empirical models of single components being able to fit the scattering.\textsuperscript{44, 47}

Mineral dust aerosol particles have a roughened shape, which leads to a difference in the optical properties from Mie scattering theory depending on particle type. Previous modeling research demonstrates that increasing the irregularity of the particles can cause a large difference in the scattering properties.\textsuperscript{17} Absorbing species with a high refractive index have the largest difference when irregularity is introduced.\textsuperscript{18, 48} Although when large degrees of irregularity are included, then non-absorbing species show much different properties from spherical as well.\textsuperscript{49} Previous research has look at bulk samples of mineral dust, but in our studies we have used cavity ring-down spectroscopy to determine the optical properties of size selected mineral dust species.

### 1.3 Organic Aerosol

Organic aerosol particles are composed of many compounds that are either primary or secondary emissions from anthropogenic or biogenic sources that partition into the particulate phase.\textsuperscript{50, 51} Organic aerosol particles are of great interest because of
the complex structures formed depending on the organic components involved. The reactivity, optical properties, and cloud nucleation activity are determined by the composition and internal morphology of organic aerosol particles. As organic/salt particles lose liquid water, they can undergo liquid-liquid phase separation between organic and inorganic components. This process of liquid-liquid phase separation occurs either through the process of nucleation and growth or spinodal decomposition.

The structure of the organic aerosol particles can be complex with the three major structures of homogeneous, partially engulfed, and core shell described in figure 1-1. The simplest morphology is a homogeneous mixture of salt and organic. More complex phase separated morphologies such as partially engulfed and core shell are also possible.

The morphology of micron size particles has previously been studied, but particle morphology under 1 µm has not been studied. The transition range between homogeneous and a phase separated structures occurs when organic compounds have O:C ratios of approximately 0.7. The properties of aerosol particles are dependent on size with particles under 30 nm in size exhibiting confinement effects for the deliquescence and efflorescence of particles. The morphology of mixed organic/salt particles in the atmosphere is of interest due to the homogenous or phase separated structures affecting optical properties and reactivity.

Figure 1-1: Possible structures of organic/inorganic aerosol particles
1.4 Ulaanbaatar, Mongolia Particulate Matter

Air pollution is the most lethal environmental hazard in the world, estimated to cause one in every eight deaths.\textsuperscript{64} The highest concentration of air pollution is within urban centers that contain most of the world’s population. In developing countries, it has been estimated that up to 25\% of deaths that occur annually in Mongolia are caused by particulate matter.\textsuperscript{65} Sources of pollution include dust from arid soils and soot mixed with sulfur oxides from coal for heat, factory and power plant emissions. Ulaanbaatar’s location in a valley and the arid climate exacerbate the effects of emissions due to poor circulation of pollutants out of the city. Up to 60\% of Ulaanbaatar’s population lives in areas where the major source of heat is from coal burning stoves.\textsuperscript{66} These stoves cause large emissions of soot in these residential areas.\textsuperscript{67, 68} These pollutants are most prevalent in developing countries where an increased economic development leads to increased energy needs. A quickly developing country will use fuels that produce higher amounts of airborne-pollutants. There have been advances in trying to curb the emissions in these areas by providing more efficient stoves, but no long term measurements of the pollutants within the city have been recorded. Long term measurements of particulate matter within Ulaanbaatar, Mongolia will lead to a better understanding of the particulate matter present and what steps can be made to curb emissions.

Ulaanbaatar, the capital of Mongolia, has a population of approximately 1.3 million and is the 2\textsuperscript{nd} most particulate matter polluted city in the world. The average concentration of particulate matter under 10 µm (PM\textsubscript{10}) is 279 µg/m\textsuperscript{3}.\textsuperscript{64} Particulate matter under 10 µm is monitored by the EPA because it poses dangers for both health and visibility, with the yearly average quality standard concentration being 50 µg/m\textsuperscript{3}. Figure
1-2 shows the annual PM$_{10}$ concentrations for major population centers and also a rural area, State College, PA. The average PM$_{10}$ concentrations in Ulaanbaatar (279 $\mu$g/m$^3$) are more than double that seen in Beijing, China (121 $\mu$g/m$^3$) and over an order of magnitude higher than in State College, PA (16 $\mu$g/m$^3$). Particulate matter under 2.5 micrometers (PM$_{2.5}$) is considered to have the highest degree of risk because it can penetrate deep into the lungs during inhalation, causing respiratory and cardiovascular ailments. The safe daily limit for PM$_{2.5}$ is 35$\mu$g/m$^3$, whereas the annual average in Ulaanbaatar is 63 $\mu$g/m$^3$ with areas reaching 350 $\mu$g/m$^3$.

![Comparison of PM$_{10}$ concentrations for major population centers across the globe.](image)

**Figure 1-2:** Comparison of the PM$_{10}$ concentrations for major population centers across the globe. Ahwaz, Iran is the most polluted city followed by Ulaanbaatar, Mongolia. Delhi, India is not within the top 10 for PM10.

### 1.5 Overview of Thesis

In this thesis, the primary focus is to understand how aerosol composition affects the shape of the particles. By understanding the optical extinction of aerosol particles, the radiative forcing of the atmosphere can be better understood. The scope of these types of
aerosol particles ranges from organic matter to mineral dust. In order to examine the morphology and composition of submicron aerosol particles, we use electron microscopy and energy dispersive x-ray spectroscopy. For the optical properties of aerosol particles, cavity ring down spectroscopy was used to determine how to model each particle type. Chapter 2 will focus on the types of instrumentation used to understand the physical and optical properties of aerosol particles. By understanding the composition and shape of mineral dust, the effect of the atmosphere can be well understood.

In chapters 3 through 6, the size selected optical properties of mineral dust species are investigated using cavity ring down spectroscopy. Chapter 3 focuses on calcium carbonate and it is observed that an independent technique is needed to verify the size selection of slightly rough particles. After accounting for the size distribution, the optical extinction of calcite can be treated using Mie scattering theory. Chapter 4 focuses on hematite which has a similar morphology to calcium carbonate, but absorbs light in the visible region. When the size selection is taken into account, additional modeling parameters beyond Mie scattering theory are needed to account for the optical extinction. Chapter 5 identifies a novel way to find the aspect ratio of high aspect ratio aluminosilicate clay mineral species. In chapter 6, the optical properties of aluminosilicate clay minerals are studied and due to the high aspect ratio of these particles, additional modeling parameters are again needed.

Chapters 7 and 8 focus on using the understanding obtained from individual mineral dust components to better understanding mineral dust interactions in the atmosphere. In chapter 7, Arizona Test Dust (a heterogeneous mixture of mineral dust types) is used to understand the applicability of single components on a mixture of
mineral dust species. Using different models for individual species did not match the experimental extinction cross sections well, but incorporating individual component polydispersity was the best fit. Chapter 8 focuses on the reaction of calcium carbonate with nitric acid vapor in a flow reactor. The morphology and optical properties of reacted mineral dust are changed when calcium carbonate is reacted at high relative humidity.

The morphology of submicron organic/inorganic particles is discussed in chapters 9 and 10. Chapter 9 describes the effect of the organic solubility on the morphology of dry submicron organic/ammonium sulfate particles. Particles containing organic compounds with a high aqueous solubility exhibit a homogeneous structure, while organics with low solubility exhibit phase separated structures. In chapter 10, the structure of intermediate aqueous solubility comonents is discussed. The structure of intermediate solubility organic/ammonium sulfate particles is dependent on the size of the particles, with smaller particles exhibiting a homogenous structure while larger particles have a phase separated structure. The internal structure of organic/inorganic aerosol particles affects the optical properties, heterogeneous chemistry, and ice nucleation properties.

Chapter 11 focuses on examining the types of particles present in Ulaanbaatar, Mongolia. Samples were collected bimonthly and the particle shape and composition was analyzed using transmission electron microscopy and energy dispersive x-ray spectroscopy. Additionally, the ice nucleation properties of these particles was also observed. An increase in the particle concentration was observed during the winter months as well as a composition change due to aging of the particles in a highly polluted environment.
1.6 References


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Chapter 2  Instrumentation

2.1  Cavity Ring-Down Spectroscopy Experimental Setup

Cavity ring-down spectroscopy is a useful technique to study aerosol particles due to the high sensitivity of a multipass system. Because of the high sensitivity of the cavity ring-down setup, aerosol particle optical properties of size selected particles can be analyzed. Additionally the high sensitivity allows for low particle concentrations that minimizes the effect of secondary light scattering. A schematic of the cavity ring-down spectroscopy setup is illustrated in figure 2-1, and each component is further discussed in following sections of this chapter. Briefly, the aerosol particles are generated either by agitating a powder and then directing a stream of nitrogen over it to suspend the particles (dry generation), or by atomizing an aqueous solution and drying the particles (wet generation). The generated aerosol particles are then size-selected using a differential mobility analyzer. Size selected aerosol particles are then passed through an optical cavity to determine the extinction coefficient. Particles are then either counted using a condensation particle counter or impacting for electron microscopy analysis.
2.2 Particle Generation

2.2.1 Wet Generation

For the wet generation technique, the species being analyzed is first dissolved in water to make a solution between 0.04 up to 0.6 wt. % analyte. The weight percent chosen is dependent on the species and the size of particle selected, with a higher weight percent needed to obtain a higher concentration of larger particles. A syringe pump is used to continuously pump the solution into an atomizer (TSI 3076). The aqueous solution of analyte is then atomized by combining the aqueous flow with a stream of nitrogen at 1.5 lpm dispersing small droplets into the nitrogen flow. After aqueous particle generation, the particles are passed through a drier to remove the water by bringing the relative humidity below 2%. To ensure the system has come to equilibrium, the size distribution is monitored for one hour using scanning mobility particle sizing,
described below. After equilibrium has been established, the concentration and size
distribution of the particles is constant on the order of hours.

Two different drier setups have been used for these experiments. The first drier
setup used was a 3 foot, quarter inch stainless steel tubing that contained Nafion tubing
(Permapure, Toms River, NJ).\(^1\) The aerosol is passed through the inside of the tubing.
The relative humidity in the flow is reduced through adsorption of the water by the nafion
membrane. With a decrease in the humidity of the flow, the aqueous aerosol particles lose
water, creating dry particles. The Nafion tubing was dried from the outside by enclosing
it in stainless steel tubing and flowing dry nitrogen over it at 2.5 lpm, causing a gradient
in the Nafion membrane that removed water from our system. Often two driers were
needed in series to obtain a relative humidity below 2%. The second method of drying the
particles was using a diffusion drier.\(^2\) For the drier, a 3 inch diameter acrylic tube, three
feet long, was filled with molecular sieves (13x, Sigma Aldrich). To direct the aerosol
particles through the drier, a channel was created using stainless steel mesh, creating a
gas permeable tube through the center of the molecular sieves. The wet aerosol flow was
passed through the channel and the relative humidity was lowered by the molecular
sieves absorbing water. With a lower relative humidity the water associated with the drop
evaporates, leaving dry aerosol particles. When the system was not being used, the
molecular sieves were dried by passing dry nitrogen through the setup.

2.2.2 Dry Generation

For the dry generation of aerosol particles, the species was first milled using a
SWECO agitation mill (GM005, Florence, KY). The particles were milled for 24 hours
while mixed with 40 mL of toluene and 100 g of mixed size zirconia beads (Tosoh,
Tokyo, Japan). The toluene was evaporated and the milled mineral dust was then dried in an oven overnight at 120 °C. The milling created particles that was more uniform and had a lower peak in the size distribution than the received mineral dust.

The particles were dry generated using a homemade setup described in Figure 2-2. The main chamber of the dry generation setup is a 6 inches long and 2 inches diameter stainless steel tube capped on one end. The stirring mechanism consists of a triangular stir bar that fits inside of the stainless steel tube and has posts on both ends to remove dust that has accumulated on the sides of the chamber. The stir bar is attached to a drive shaft that is driven by an electric motor. To seal the drive shaft, an aluminum sheath was machined to be slightly larger than the drive shaft and coated with high vacuum grease to maintain an airtight seal. Dry nitrogen was introduced perpendicular to the cylinder at the level of the sample. The combination of the mixing using the stir bar and a nitrogen flow over the powder leads to entrainment of the dust. The aerosolized dust particles were then directed into a 250 mL Erlenmeyer flask, where mixing takes place to obtain a steady concentration of aerosol particles. Before being directed to the differential mobility analyzer (DMA) for size selection, the concentration was controlled by pumping out excess aerosol particles and diluting the flow with additional nitrogen to bring the flow back up to 1.5 lpm.
2.3 Size Selection of Aerosol Particles

After aerosol particles are generated either by the dry or wet generation methods, they are size selected using a differential mobility analyzer. For our system, we use a TSI 3080 electrostatic classifier. The DMA size selects particles based on the electrostatic mobility through a flow chamber with an applied voltage. Before the particles reach the DMA they are first exposed to a sealed $^{85}$Kr source. This source neutralizes the charge of most particles, but a known charge distribution of $\pm 1$, $\pm 2$, $\pm 3$, etc. can be calculated. Only $\pm 1$ and $\pm 2$ charged particles need to be accounted for at low particle concentrations.
The population of each of these types of particles with a given charge, \( N \), was calculated according to

\[
f(N) = 10^{\sum_{i=0}^{N} a_i(N)(\log_{10}\frac{D_p}{nm})}
\]

where \( \varepsilon_0 \) is the dielectric constant, \( D_p \) the particle diameter, \( k \) as Boltzmann’s constant, and \( a_i(N) \) tabulated from Kim et al 2005. Higher order charges can also be calculated using the unsimplified equation found in Weidensohler 1988.

After the particles pass through the neutralizer, they are directed through the differential mobility analyzer (DMA). For our setup we use a TSI 3081 long DMA. A simplified diagram of the DMA is illustrated in Figure 2-3. The main component is an outer cylinder with a concentric inner rod with a maintained potential between the two cylinders. The aerosol particles are introduced into the system and mixed with the sheath flow. If the particles are charged, then they will be attracted to the inner or outer wall of the DMA. Depending on the potential applied, larger particles will not have sufficient time to move to the size selected inlet and pass through the flow system, while smaller particles will be impacted on the inner collection rod and also not be size selected. The size selection of the particles is based on the size of the particles, sheath flow rate, aerosol flow rate and potential applied. The shape of the particles also has an effect on the electrostatic mobility.\(^4\) The size of particle selected, \( D_p \), for spherical particles is based on the following

\[
\frac{D_p}{C} = \frac{2neVL}{3\mu q_{sh} L_{\ln} \frac{r_2}{r_1}}
\]

where \( C \) is the Cunningham slip correction, \( n \) is number of elementary charges on particle, \( e \) is the elementary charge, \( V \) is the average voltage on inner collector rod, \( L \) is
the length between exit slit and polydisperse aerosol inlet, $\mu$ is the gas viscosity, $q_{sh}$ is the sheath air flow rate, while $r_2$ is the outer radius of annular space, and $r_1$ is the inner radius of annular space.

![Diagram](image)

**Figure 2-3:** Simplified cross section view of a differential mobility analyzer with dotted lines showing the path of particles through the DMA with blue particles being too small, red particles too large, and black particles being size selected.

### 2.4 Cavity Ring Down Aerosol Extinction Spectroscopy

Cavity ring-down spectroscopy (CRDS) is a technique that is sensitive due to the long effective path length derived from the multipass system and independence from light intensity variation. Other methods that have been used to study the optical properties of aerosol particles include nephelometers and mid-IR spectrometers, but due to the
inherently high detection limit, only large concentrations and bulk size distributions of aerosol particles can be used.\textsuperscript{6-8} The setup of the cavity ring-down spectrometer is illustrated in figure 2-4. A diode laser with a wavelength of 643 nm is used due to a higher wavelength being more sensitive to larger sized particles. The laser is modulated at 500 Hz and is passively coupled to the cavity. The light from the laser is passed through a polarizer and quarter waveplate to remove backscattered light directed back into the laser. The two turning mirrors outside of the cavity allow the laser to be directed through the center of the cavity for maximum passes in the system. The cavity is 91 cm long and is capped by mirrors that are highly reflective (>99.9985\% at 640 nm). In front of each mirror, a purge flow of nitrogen at 30 ccm is used to keep the mirrors free of particulate matter and adsorbed gases. A photomultiplier tube is connected to the back mirror using fiber optic cable to detect transmitted light after each pass.

**Figure 2-4:** Diagram of cavity ring-down spectrometer.

Cavity ring-down spectroscopy uses highly reflective mirrors to obtain a high number of reflections inside the cavity. During each pass, light intensity is lost from transmission through the front and rear mirrors and absorption or scattering aerosol particles within the cavity. The light intensity lost through the back mirror is collected using a photomultiplier tube, and the intensity can be plotted for each laser pulse (Figure
2-5). There is an initial buildup time of the laser intensity inside the cavity that depends on the length of the pulse. After the initial buildup, a short plateau corresponds to the maximum intensity within the cavity. After the end of the pulse, the signal decays exponentially over time. The ring-down time ($\tau$) of the instrument is defined to be the time to reach $1/e$ of the initial intensity. For our instrument, the ring-down time is approximately 165 $\mu$s, corresponding to an effective path length greater than 48 km.

![Cavity Ring-Down Signal with and without sample](image)

**Figure 2-5:** Cavity Ring-Down Signal with and without sample

The extinction coefficient, $b_{\text{ext}}$, can be measured from the ring down time of the cavity

$$b_{\text{ext}} = \frac{R_L}{c} \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right)$$

where $\tau_0$ is the characteristic ring-down time (first order decay constant) for the system without sample, $\tau$ is the ring-down time with the sample in the cavity, $R_L$ is the ratio of the total cavity length to the length of the cavity occupied by the sample, and $c$ is the speed of light. The extinction cross section (which has units of $\mu m^2$) is given by
\[ \sigma_{\text{ext}} = \frac{b_{\text{ext}}}{N} \]

where \( N \) is the number of particles per cm\(^3\). The extinction efficiency, \( Q_{\text{ext}} \), is related to the extinction cross section according to

\[ Q_{\text{ext}} = \frac{\sigma_{\text{ext}}}{\pi r^2} \]

which is dependent on the particle radius, \( r \). Because the ring-down time is independent of the intensity of the laser, any variation in the intensity of individual pulses leads to no difference in the measured ring down time.

The cavity ring-down spectrometer was tested using polystyrene latex spheres (Polysciences, Warrington, PA) to determine if accurate extinction cross sections could be found and no multiple scattering was occurring within the cavity. Four different diameters of polystyrene latex spheres were used (119, 220, 356, and 456 nm) at different concentrations to check the theoretical extinction of our instrument as seen in figure 2-6. For each size of aerosol particles, the concentration was varied and the experimental extinction vs. concentration was compared to theoretical values, assuming the polystyrene latex spheres had a refractive index of 1.59. The theoretical extinction coefficients matched at all sizes, and since the plots were linear, the extinction coefficient measured at these concentrations was in the single scattering regime.
Figure 2-6: Extinction coefficient vs. concentration for various sizes of polystyrene latex spheres.

### 2.5 Condensation Particle Counter (CPC)

After size selection through the DMA, and extinction coefficient measurement through the CRDS, the particles are counted using a condensation particle counter (CPC; TSI 3775). Figure 2-7 is a diagram of a simplified CPC setup. The aerosol particles pass through the flow system where they are introduced to a saturated butanol atmosphere. The saturated flow is subsequently passed through a cooled condensation chamber, where the butanol becomes supersaturated, allowing for heterogeneous condensation of the butanol on the particles. The particle growth is controlled by the Kelvin equation where the pressure, $p$, to saturated pressure, $p_s$, is related according to
\[ \frac{p}{p_s} = \exp \left( \frac{4\sigma M}{\rho RTd} \right) \]

where \( \sigma \) is the surface tension, \( \rho \) is the density of the liquid, \( d \) is the Kelvin diameter, \( R \) the gas constant, \( M \) is the molar volume of the liquid, and \( T \) the temperature.\(^{10}\)

The particles can now be detected through optical counting methods since they have grown in size. By using this method, small particles down to 15 nm can be counted.\(^{19}\) The error associated with the CPC can range up to 10% depending on the concentration.\(^{11}\)

2.6 Scanning Mobility Particle Sizing

The size distribution of particles can be found by coupling the DMA to the CPC in series. By slowly adjusting the applied potential across the DMA, the selected mobility diameter of the particle changes and the particles can be counted at each mobility diameter using a CPC. This method is known as scanning mobility particle sizing.

\[ \frac{p}{p_s} = \exp \left( \frac{4\sigma M}{\rho RTd} \right) \]
(SMPS). In our system, we use software provided by TSI to control the DMA and CPC to gain an understanding of the mobility size distribution of the system being studied.

### 2.7 Impaction of particles

After size selection using the DMA, the aerosol flow can be directed into a cascade impactor (PIXE International Corp., Tallahassee, FL) for off line analysis using electron microscopy or other methods. The size of the particles collected is dependent on the velocity of the aerosol particles through the system. Aerosol particle velocity is controlled by a constant amount of air pumped out of the system and different sized orifices used to collect particles at different sizes. Nozzles create a vacuum between levels, with decreasing nozzle sizes to increase the speed of the air (and aerosol particles) moving through the system. The cutoff point diameter, $D_{50}$, is related according to

$$D_{50} = \frac{9\pi Stk\mu W^3}{4\rho_p C Q}$$

where $Stk$ is the stokes number, $\rho_p$ the particle density, $Q$ the volumetric flow rate, $C$ the Cunningham Slip Correction, $\lambda$ the gas mean free path, $\mu$ gas viscosity, and $W$ the nozzle diameter.$^{12}$

### 2.8 Particle Modeling Methods

Optical properties of aerosol particles obtained using CRDS, are modeled using two different models that depend on the complexity of the system. The methods used are Mie scattering theory calculations, which are exact solutions for spherical particles, and the discreet dipole approximation, which can describe any shape, but is more computationally intensive.
2.8.1 Mie Scattering Theory

Mie scattering theory is the solution to Maxwell’s equations that describes the scattering of light by spherical particles that are on the order of the wavelength of light. The solution used for Mie scattering theory is a series of Bessel functions for these spherical particles. Mie scattering theory is contrasted to Rayleigh scattering for particles that are much smaller than the wavelength of light. Rayleigh scattering is highly dependent on the wavelength of light with a $\lambda^{-4}$ relationship. For Mie scattering theory the extinction efficiency limit approaches 2 at large size parameters theory, which is double what is expected for geometric scattering. In bulk scattering no curved surfaces are taken into account using a spherical model. This effect should be taken into account when larger particles are being analyzed with diameters much larger than the wavelength of light.\(^{13}\) Reflected light scattering is important for remote sensing methods because they rely on how particle scatter light and change the polarizations of reflected light. Particle morphology will affect these properties as well.

2.8.2 Discreet Dipole Approximation Method

The discreet dipole approximation (DDA) was first introduced by DeVoe in 1964 to study aggregated particles, and has been adapted to be used by Drain 1994 for FORTRAN using fast Fourier transform methods.\(^{14-16}\) The DDA uses a finite number of dipoles to create a target geometry that is an exact solution for an object. For our systems, we use DDA to produce high aspect ratio spheroids and roughened spheres and spheroids to approximate mineral dust aerosol particles.

For accurate calculations of the absorption cross section ($C_{abs}$) and scattering cross section ($C_{sca}$) using the DDA, the volume equivalent radius ($a_{eff}$) is constrained by
where $\lambda$ is the wavelength, $m$ is the refractive index, and $N_d$ the number of dipoles in the system. Due to the small dipole spacing needed for large calculations, DDA calculations are only computationally viable for particles up to a few microns. In our calculations, we use spherical particles with 40 dipoles spanning the radius where we can accurately calculate extinction cross sections up to 4 $\mu$m in diameter according to equation ___. For accurate calculations of the phase functions, the effective volume equivalent diameter is can be calculated up to 2 $\mu$m.

2.9 References


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Chapter 3  Optical Properties of Calcium Carbonate Aerosol

This chapter has been adapted from: Daniel P. Veghte and Miriam A. Freedman, “The Necessity of Microscopy to Characterize the Optical Properties of Size-selected, nonspherical aerosol particles”, *Anal. Chem.*, **2012**, 84, 21, 9101-9108.

Abstract

It is currently unknown whether mineral dust causes a net warming or cooling effect on the climate system. This uncertainty stems from the varied and evolving shape and composition of mineral dust, which leads to diverse interactions of dust with solar and terrestrial radiation. To investigate these interactions, we have used a cavity ring-down spectrometer to study the optical properties of size-selected calcium carbonate particles, a reactive component of mineral dust. The size selection of nonspherical particles like mineral dust can differ from spherical particles in the polydispersity of the population selected. To calculate the expected extinction cross sections, we use Mie scattering theory for monodisperse spherical particles and for spherical particles with the polydispersity observed in transmission electron microscopy images. Our results for calcium carbonate are compared to the well-studied system of ammonium sulfate. While ammonium sulfate extinction cross sections agree with Mie scattering theory for monodisperse spherical particles, the results for calcium carbonate deviate at large and small particle sizes. We find good agreement for both systems, however, between the calculations performed using the particle images and the cavity ring-down data, indicating that both ammonium sulfate and calcium carbonate can be treated as polydisperse spherical particles. Our results indicate that having an independent measure of polydispersity is essential for understanding the optical properties of nonspherical particles measured with cavity ring-down spectroscopy. Our combined spectroscopy and
microscopy techniques demonstrate a novel method by which cavity ring-down spectroscopy can be extended for the study of more complex aerosol particles.
3.1 Introduction

Mineral dust is the second largest emission by mass into the atmosphere, but it remains unknown whether this class of particles has a net warming or cooling effect on the environment.\textsuperscript{1} The interaction of aerosol particles with solar and terrestrial radiation, termed the aerosol direct effect, is one of the largest uncertainties in our understanding of the climate system.\textsuperscript{1} The sign and magnitude of the direct effect of aerosol particles on climate depends on the optical properties of aerosol particles. These optical properties, specifically the wavelength-dependent scattering and absorption, are functions of the particle size, shape, composition, and internal structure. These properties can change as particles undergo atmospheric processing during transport. The difficulty in understanding the optical properties of mineral dust aerosol stem in part from its varied shape and composition both in source regions and as particles are aged during atmospheric transport. With laboratory studies, we can 1) perform highly controlled experiments that can aid our understanding of field and ground-based observations and 2) provide data that can be used to develop more accurate models of aerosol particles for climate models and satellite retrieval algorithms.

New analytical techniques and protocols are needed to characterize the optical properties of mineral dust aerosol. These methods should be developed to explore mineral dust aerosol from source regions as well as aged particles. The aging that occurs in the environment includes chemical reactions on the surface of particles, cloud processing, condensation of gaseous molecules, and aggregation with other particles. Each of these aging processes results in particles with a more complex internal composition that may depend on the size of the particles. As a result, to study aging on
mineral dust particles, we need a technique that is sensitive enough to allow us to study
the optical properties of size-selected aerosol particles.

The main laboratory techniques that have been used previously to measure the
optical properties of unprocessed mineral particles are polar nephelometry and mid-
infrared extinction spectroscopy. Polar nephelometers measure the scattering of particles
at visible wavelengths as a function of scattering angle.\textsuperscript{2, 3} Mid-infrared spectroscopy is
used to determine the extinction of mineral particles in this wavelength range.\textsuperscript{4, 5} These
techniques give a wealth of optical information about mineral particles, but require the
use of bulk samples. As a result, the measurements are dependent on the composition
and shape of the aerosol particles as well as their size distribution. To eliminate the
dependence on the size distribution, we can use techniques that are sensitive enough to
investigate size-selected particles.

The optical properties of size-selected aerosol particles can be measured with the
highly sensitive technique of cavity ring-down spectroscopy. This technique measures
the extinction cross section of particles, which is the sum of the scattering and absorption
cross sections. In laboratory studies, cavity ring-down spectroscopy has been used for
two major types of experiments: quantifying the extinction cross sections of particles and
measuring changes in extinction cross sections due to exposure of aerosol particles to
water vapor or coatings. Quantifying extinction cross sections for different particle types
has focused on simple spherical and nearly spherical aerosol systems with either
homogeneous or core-shell morphologies.\textsuperscript{6-8} The only complex aerosol shape that has
been studied is cubic sodium chloride particles.\textsuperscript{8, 9} In contrast, using cavity ring-down
spectroscopy to determine changes to optical properties upon exposure of particles to
water vapor and coatings has been performed on nearly spherical as well as nonspherical particles including mixed organic and inorganic spherical particles,\textsuperscript{10, 11} clay mineral dust aerosol,\textsuperscript{12, 13} and soot aerosol.\textsuperscript{14, 15} In determining changes to the optical properties of a system upon water uptake or coating, the extinction cross sections for the changed compared to the unchanged system are measured and, most commonly, the ratios of these values are reported.\textsuperscript{10-13, 15}

While it is clearly important to report ratios of extinction cross sections that are indicative of the aging processes of aerosol particles in the atmosphere, it is also crucial to show that we can accurately quantify the extinction cross sections themselves. The extinction cross sections of size-selected particles can be used to verify that the measured values match those expected from the literature before changes are made to the aerosol system. As described below, the size-selection process depends on the electrostatic mobility of charged particles, which is a function of the particle shape. To determine the effect of shape on the size selection, we can collect images of size-selected particles and use them to inform our calculations. For example, the utility of transmission electron microscopy for characterizing particle shape and internal structure has been widely demonstrated.\textsuperscript{16} We may find that particles with the same mobility diameter but different shapes have different polydispersities. These differences in the size-selection process could have an effect on the measured optical properties. Characterizing the extinction cross sections of mineral dust particles and comparing to literature values will aid us in determining the effects of atmospheric processing in future studies.

In this paper, we explore the use of cavity ring-down spectroscopy to characterize the optical properties of size-selected calcium carbonate particles. Calcium carbonate is
chosen because it comprises a significant fraction (11%) of Asian dust and is known to participate in heterogeneous chemistry during atmospheric transport.\(^{17}\) The results for nonspherical calcium carbonate aerosol particles are compared to nearly spherical ammonium sulfate particles.

### 3.2 Experimental Methods

A schematic of the experimental flow system for measuring aerosol optical properties and impacting aerosol particles on substrates is shown in Figure 3-1. Particles are generated from aqueous solution or powder, size selected, brought through the cavity ring-down spectrometer, and then either counted to obtain their number concentration or collected onto transmission electron microscopy (TEM) grids.

![Diagram of experimental flow system](image)

**Figure 3-1:** Schematic of our instrumental set up for cavity ring-down spectroscopy and for preparing samples for transmission electron microscopy. Particles can be generated from aqueous solution or from a
3.2.1 Generation of Aerosol Particles

Ammonium sulfate aerosol particles were generated from aqueous solution and calcium carbonate particles were generated from a dry powder. The preparation details are included in the supporting information for this paper. Aerosol particles pose an inhalation danger. As a result, care is taken to contain the particles within the enclosed flow system.

3.2.2 Size Selection of Aerosol Particles

Particles are size-selected using an electrostatic classifier (TSI 3080, Shoreview, MN) with a 0.71 μm impactor and differential mobility analyzer (TSI 3081, Shoreview, MN). This technique allows us to obtain size-selected populations of aerosol particles of diameters from approximately 10 nm to 1 μm. The focus of our study is smaller particles (less than 1 μm) because they are more likely to undergo long-range transport.\textsuperscript{18} In field studies of mineral dust aerosol, the peak in the number distribution occurs at diameters less than 1 μm.\textsuperscript{19} Within the electrostatic classifier, the particles are exposed to a sealed \textsuperscript{85}Kr source, which neutralizes most of the particles, but charges a small fraction to produce ±1, ±2, and higher order charges. The distribution of charges is well characterized.\textsuperscript{20} The charged particles are then size-selected based on their electrostatic mobility. This mobility, the measure of how easily the particle moves through an electric field, is inversely proportional to the diameter of the particle.\textsuperscript{21} In addition to the selected
size, a range of different sizes of particles will also be selected, leading to a degree of polydispersity in the selected size. This polydispersity depends on the selected sheath flow and aerosol flow within the differential mobility analyzer. The transfer function describes the probability that electrostatic mobilities around the selected mobility are transmitted through the differential mobility analyzer. In the supporting information, we discuss the conversion of the transfer function to units of mobility diameter. We use this calculation to determine the theoretical polydispersity of particle mobility diameters transmitted through the differential mobility analyzer.

To produce the smallest polydispersity of selected diameters, it is recommended to use an aerosol to sheath flow of 1:10. We have used aerosol to sheath flow ratios that are higher than this ratio for both ammonium sulfate and calcium carbonate. For the calcium carbonate particles, aerosol to sheath flows of 1:10 were used initially, but the low aerosol flows required resulted in the transmission of many small particles. As a result, we used an aerosol flow of 1.5 L/min with sheath flow rates of 2.7 L/min to 8.8 L/min. These flow rates allowed us to better size select the calcium carbonate particles. In order to obtain a large enough concentration of ammonium sulfate at large diameters and to use similar flow parameters to calcium carbonate, an aerosol flow of 1.5 L/min is used for ammonium sulfate. The sheath flow ranges from 8.8 L/min for the smallest sizes (300 nm) to 2.7 L/min for the largest size particles (900 nm). The size distribution of the ammonium sulfate and calcium carbonate particles as a function of the mobility diameter is discussed in the supporting information and shown in Figure 3-6.
3.2.3 Cavity Ring-Down Spectrometer

We have built a new cavity ring-down spectrometer for the study of mineral dust aerosol. Measurements of the extinction coefficient performed using the cavity ring-down technique are most sensitive for smaller diameters where the extinction coefficient increases linearly with the size parameter $\chi = \pi D/\lambda$ where $D$ is the diameter and $\lambda$ is the wavelength of light. Dust particles that are generated from a dry powder tend to have a peak in their size distribution at larger values of the mobility diameter than salts generated from aqueous solution. As a result, we chose a wavelength of 643 nm for our measurements in order to be more sensitive to the larger mineral dust particles. Our spectrometer is otherwise based on the design of Fuchs et al.\textsuperscript{22} Briefly, we passively couple a 643 nm diode laser with a 91 cm optical cavity. The diode laser is modulated at a frequency of 500 Hz. The cavity is capped with highly reflective mirrors (greater than 99.998 % reflective at 640 nm). A purge flow prevents aerosol particles from contaminating the mirror surface. Using a photomultiplier tube, we detect and fit the rate of decay of the intensity of light that is transmitted through the cavity (also known as the ring-down time). The characteristic ring-down time of our cavity with no particles is 140 μs to 160 μs, which corresponds to an effective path length of approximately 42 km to 48 km. When particles are present in the cavity, the ring-down time decreases due to the extinction of the particles. The extinction coefficient of the particles, $b_{\text{ext}} \ (cm^{-1})$, is calculated from the difference between the characteristic ring-down time, $\tau_0$, and the ring-down time when particles are present, $\tau$, according to the equation

$$ b_{\text{ext}} = \frac{R_L}{c} \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right) $$

(1)
where $R_L$ is the ratio of the cavity length to the sample length (1.18 for our system) and $c$ is the speed of light. The optical data in this paper are presented in terms of the related quantity, extinction cross section, $\sigma_{ext}$.

$$\sigma_{ext} = \frac{b_{ext}}{N}$$

(2)

where $N$ is the concentration of particles measured with a condensation particle counter (TSI 3775, Shoreview, MN). We plot the extinction cross section as a function of the mobility diameter of the particles. A thorough error analysis of the use of cavity ring-down spectroscopy for the measurement of aerosol extinction coefficients is given in Miles et al.\textsuperscript{23} To verify that our cavity ring-down spectrometer is working properly, we have taken measurements of polystyrene latex spheres (see description and Figure 3-7 in the supporting information). For each aerosol sample, five measurements are taken at every mobility diameter and the standard deviation is calculated over these repeated measurements. Each of these measurements is the average of 100 to 200 data points, where every data point is averaged over 400 laser shots. More information about the error in our experiment is discussed in the supporting information.

3.2.4 Transmission Electron Microscopy (TEM)

TEM images provide an independent measure of the size selection of salt and mineral dust particles. Grids made of 200 mesh copper coated with lacey or continuous carbon (SPI, West Chester, PA and Electron Microscopy Science, Hatfield, PA) were used as substrates. Two different TEM instruments were used: a Philips EM420T operated at an accelerating voltage of 120 kV and a JEOL JEM 1200 EXII operated at an accelerating voltage of 80 kV. An impactor (PIXE International Corp., Tallahassee, FL)
was used to expose the TEM grids to the flow of aerosol particles. A pump was used after the impactor to pull the aerosol flow through at approximately 1 L/min. For the ammonium sulfate particles, the impactor was placed in the aerosol flow after the differential mobility analyzer. For the calcium carbonate particles, the impactor was placed after the cavity ring-down instrument to better monitor for changes in concentration when long collection times were required. TEM images are collected as a function of mobility diameter. For each mobility diameter selected, the TEM images include both the singly and multiply-charged particles with equivalent mobility diameters.

TEM images show a projection of a particle onto a two-dimensional plane. To analyze the TEM images, we use image analysis software (ImageJ, National Institutes of Health, Bethesda, MD) to calculate the area of each particle. We generally determine the area of approximately 100 to 250 particles. If we assume that the particles are spherical, then the calculated area from the TEM image can be converted into an area equivalent diameter for a circle of equal area. Note that the area or volume equivalent diameter usually refers to the diameter of a spherical particle needed to give the same behavior in a given experimental procedure as the irregular particle of interest.\textsuperscript{21} In contrast, throughout this paper, we refer to area equivalent diameter only in terms of the geometry of the particles. For each mobility diameter, the concentration of particles at each area equivalent diameter can be plotted to obtain a distribution of particle sizes.

3.2.5 Mie Scattering Calculations

We compared our data from the cavity ring-down spectrometer to theory using Mie scattering calculations. To perform these calculations we use a version of BHCOAT
that has been adapted for MATLAB.\textsuperscript{24, 25} This code has been used previously to analyze results from cavity ring-down experiments.\textsuperscript{7, 9} Using the refractive index of a compound and the size parameter, the extinction efficiency can be calculated. Neither ammonium sulfate nor calcium carbonate absorbs substantially at visible wavelengths. Based on literature values, the refractive index for ammonium sulfate is 1.53 at 589 nm.\textsuperscript{26} Calcium carbonate is birefringent with refractive indices of 1.658 for the ordinary refractive index and 1.486 for the extraordinary refractive index at 589 nm.\textsuperscript{27} We assume that there is no preferred orientation of the calcium carbonate particles in the gas flow through the cavity ring-down spectrometer because they have an aspect ratio close to unity. We therefore use the average refractive index of 1.57 for calcium carbonate. For solid particles, the refractive index varies slowly as a function of wavelength away from absorption bands. As a result, the refractive index at 643 nm should be similar to the literature value at 589 nm. With these assumptions, we can calculate the extinction efficiency and extinction cross section as a function of the diameter of the particles.

We perform two different calculations using Mie theory to compare to our cavity ring-down spectroscopy data: a calculation for monodisperse spheres and a calculation for polydisperse spheres. To use Mie theory, we need to convert the mobility diameter of interest to a geometric diameter (such as the volume equivalent diameter) because the extinction cross section of a particle depends on the geometry of the particle rather than its behavior in an electrostatic field. Because we are assuming that the particles are spherical, the mobility diameter, $d_m$, the volume equivalent diameter, $d_{ve}$, and the area equivalent diameter, $d_{ae}$, are equal to each other. For the calculation for monodisperse spheres, we take each $d_{ae}$ and convert it to the size parameter $x_{ae} = \frac{d_{ae}}{\lambda}$. Using Mie
scattering theory, we use $x_{ae}$ and the refractive index $m$ to calculate the extinction efficiency $Q_{ext}$. We convert the extinction efficiency to the extinction cross section, $\sigma_{ext}$, using $\sigma_{ext} = Q_{ext} (d_{ae}/2)^2$. This value corresponds to the extinction cross section at the mobility diameter we selected. Note that we do not include a contribution from multiply charged particles in this calculation.

To use Mie theory to calculate extinction cross sections for polydisperse spheres, we use the data obtained in the TEM image analysis. For each mobility diameter, $d_m$, our image analysis gives a finite number, $n_{tot}$, of area-equivalent diameters, $d_{ae,i}$. We convert each $d_{ae,i}$ to $x_{ae,i}$. Using Mie scattering theory, we use each $x_{ae,i}$ and the refractive index $m$ to obtain $Q_{ext,i}$. Using the same calculation as above, we use $Q_{ext,i}$ to determine the extinction cross section $\sigma_{ext,i}$. We then determine a weighted average of the extinction cross sections using

$$\sigma_{ext} = \frac{1}{n_{tot}} \sum_{i=1}^{n_{tot}} \sigma_{ext,i}$$

(3)

This value, $\sigma_{ext}$, corresponds to the extinction cross section for the selected mobility diameter. Note that this calculation includes contributions from multiply charged particles as well as the polydispersity from the size selection process.

To estimate the error in the Mie scattering calculation based on the TEM images, we divide the TEM images into three groups. For each group, we determine the distribution of area equivalent diameters. From these area equivalent diameters, we calculate the extinction cross section for polydisperse spheres as described above. We determine the standard deviation in the three calculated extinction cross sections. This
standard deviation is an overestimate of the error that originates from counting a finite number of particles in the TEM images.

We note that using area equivalent diameters to represent all types of mineral dust particles can introduce uncertainties in modeling particle optical properties. Calcium carbonate particles have an aspect ratio near unity (in other words, the particles are roughly cubic in structure). As a result, for calcium carbonate, the area equivalent diameter is a good representation of the particles. For rod-shaped particles, only two axes have similar lengths. In these cases, TEM imaging can be used, but two axes are needed to model the optical properties. For disk-shaped particles, all three axes have different lengths. In this case, it is necessary to use a microscopy technique, such as atomic force microscopy, in which all three axes can be measured.

3.3 Results and Discussion

We have imaged the particle distribution and measured the optical properties of size-selected ammonium sulfate and calcium carbonate particles. Aqueous ammonium sulfate is nearly spherical, and is commonly used to verify the accuracy of cavity ring-down instruments. ammonium sulfate was therefore used to illustrate a well-studied aerosol system and to provide a contrast to the results for nonspherical calcium carbonate particles. We find that the polydispersity of the size selection of nonspherical particles is very sensitive to particle shape, indicating that an independent measure of the size selection is essential for the study of the optical properties of complex particle shapes. Comparison of our cavity ring-down spectroscopy and transmission electron microscopy (TEM) results indicate that calcium carbonate is well represented by spherical particles with the polydispersity observed in the transmission electron
microscopy images. Our method illustrates a technique to extend cavity ring-down spectroscopy to the study of nonspherical particles.

3.3.1 Ammonium Sulfate

We have characterized ammonium sulfate particles that were selected at mobility diameters from 200 nm to 900 nm using TEM (Figure 3-2). In order to have a sufficient concentration of particles, TEM samples were collected for 1-5 hours. The longest times were needed for the largest particles in order to collect a sufficient concentration of particles to image. Figures 3-2a and 3-2b show images of particles with mobility diameters of 400 nm and 600 nm. All of the TEM images of ammonium sulfate show that the particles are nearly spherical in shape and have a uniform size.

Figure 3-2: Transmission electron microscopy images of ammonium sulfate size selected at mobility diameters of a) 400 nm and b) 600 nm. Two different TEM substrates are used for these samples: copper grids coated with a) a lacey carbon film and b) a continuous carbon film. The area of the particles is
measured and converted into an area equivalent diameter by assuming that the particles are spherical. The number distributions of the area equivalent diameters are shown for mobility diameters of c) 400 nm and d) 600 nm. The triangle indicates the theoretical range of diameters expected.

As described in the experimental methods section, the TEM images were analyzed to determine the area equivalent diameter of the particles collected at each mobility diameter. Histograms of the number of particles at each area equivalent diameter are shown for mobility diameters of 400 nm and 600 nm in Figures 3-2c and 3-2d. We have analyzed the mean area equivalent diameter, the presence of secondary peaks due to doubly charged particles, and the distribution of area equivalent diameters observed. The percent differences between the mean area equivalent diameters and the mobility diameters are 4.2% for a mobility diameter of 400 nm and 3.2% for a mobility diameter of 600 nm. The only sample for which the mean area equivalent diameter was not close to the mobility diameter was for a mobility diameter of 900 nm. These samples were collected for the longest time due to their low concentration, and as a result, it is not unlikely that we would observe a large degree of variation in this sample. For mobility diameters of 200 nm and 300 nm particles, two peaks in the size distribution were observed. The peak at the larger mobility diameter is likely to be due to doubly charged particles that have the same electrostatic mobility as the singly charged particles. For the 300 nm mobility diameter, the peaks are at area equivalent diameters of approximately 277 nm and 450 nm. These doubly charged particles should theoretically be at a mobility diameter of 462 nm if the particles were perfectly spherical. The ratio of the number of doubly charged particles to the singly charged particles is 0.0887. According to charging theory, we would expect a ratio of 0.486. The deviation between the theoretical and
Experimental results may be due to the small number of doubly charged particles collected for TEM analysis.

The theoretical polydispersity in the mobility diameter is calculated using the experimental sheath flow and aerosol flow as described in the supporting information. Assuming the particles are spherical, the mobility diameter and the area equivalent diameter are equivalent. With this assumption, we can plot the theoretical polydispersity as a function of area equivalent diameter. In Figure 3-2c and 3-2d, the theoretical distribution of sizes is shown by the triangle centered at the peak of the distribution. The calculated polydispersity shown is larger than would be expected if the aerosol flow to sheath flow was set to a 1:10 ratio. In addition, the expected polydispersity increases as the mobility size increases. For all particle sizes, the TEM-derived area equivalent diameters fall almost entirely within the expected polydispersity.

In Figure 3-3, we show the extinction cross section of size-selected ammonium sulfate particles using the cavity ring-down spectrometer (circles) and compared our results to Mie scattering calculations for 1) monodisperse particles (dashed line) and 2) polydisperse spherical particles with the size distribution observed in the TEM images (Figure 3-3). The error bars on the cavity ring-down data represent the standard deviation of repeated measurements. Only one point, for the TEM-based calculation at a mobility diameter of 900 nm, deviates from the spherical calculation. We expect that the deviation in the 900 nm data is due to the low number of particles collected for analysis by TEM, as discussed above. In contrast to the TEM measurements, the extinction cross sections found by cavity ring-down spectroscopy are averaged over orders of magnitude more particles. Overall, both the cavity ring-down results and the calculation based on
the TEM images match closely with the extinction cross sections calculated for monodisperse spherical particles using Mie scattering theory.

![Graph showing extinction cross section vs. diameter for ammonium sulfate.](image)

**Figure 3-3:** The extinction cross section vs. diameter for ammonium sulfate. The cavity ring-down data (circles) show the experimentally determined extinction cross sections. The dashed line is calculated using Mie scattering theory for spherical particles assuming that the particles are monodisperse. The triangles show the prediction for polydisperse spheres using the size distribution of area equivalent diameters determined from the TEM images. The error bars are from the standard deviation of several measurements.

The TEM analysis gives us insight into why the ammonium sulfate data agrees with Mie scattering theory for spherical monodisperse particles. That the cavity ring-down data matches the calculation for spherical particles is not surprising; many researchers have shown that they obtain the correct refractive index for ammonium sulfate particles generated from aqueous solution. But no one has taken this independent measurement to verify the mean diameter and polydispersity of particles that are actually being measured in the cavity ring-down spectrometer. From the TEM images and analysis, we see that the mean size is approximately 20 nm too small and there is a degree of polydispersity that increases with particle size. By using the TEM analysis to determine an approximation for the optical properties, we can include the actual mean
size and the polydispersity in the calculation. That the calculation based on the TEM images matches the cavity ring-down data is more convincing proof that the optical properties of ammonium sulfate were accurately determined.

3.3.2 Calcium Carbonate

The TEM images of dry-generated calcium carbonate are more irregularly shaped than ammonium sulfate. Figures 3-4a and 3-4b show particles with mobility diameters of 400 nm and 600 nm, respectively. The particles are clearly nonspherical and the sizing is more polydisperse.

![TEM images of calcium carbonate](image)

**Figure 3-4**: The same as Figure 3-2, but for calcium carbonate particles. Both TEM images were taken using copper grids coated with a continuous carbon film.
The calcium carbonate samples are analyzed to determine the area equivalent diameters of the particles and plotted in a histogram (Figures 3-4c and 3-4d). For all mobility diameters used, the particle sizes observed are a subset of the overall population of calcium carbonate particles shown in Figure 3-6b, which indicates that we are able to size select the particles based on their electrostatic mobility. However, the data show significantly different trends than observed for ammonium sulfate. The mean area equivalent diameter is larger than the mobility diameter for the smaller mobility diameters and smaller than the mobility diameter for the larger mobility diameters. The percent differences between the mean area equivalent diameters and the mobility diameters are 5.2% for a mobility diameter of 400 nm and 7.5% for a mobility diameter of 600 nm. In addition to the larger percent difference between the mobility diameters and the area equivalent diameters compared to ammonium sulfate, the polydispersity in area equivalent diameters is larger than the theoretical prediction based on the transfer function shown in Figure 3-4. In performing the calculation of the transfer function, we have again assumed that the particles are spherical to convert from the mobility diameter to the area equivalent diameter plotted in Figure 3-4. We note that the transfer function shown in Figure 3-4c does not match the peak of the distribution observed from the TEM data. We observe this deviation for a small subset of our ammonium sulfate and calcium carbonate data. We plot the transfer function to indicate the theoretical polydispersity expected. Similarly to the ammonium sulfate data, the polydispersity increases with increasing mobility diameter. We note that the presence of multiply charged particles could explain some of the polydispersity observed, especially for smaller mobility diameters. We would expect the presence of multiply charged particles to lead to a
broadening in the distribution at area equivalent diameters larger than the mean area equivalent diameter. The only diameters that have a greater deviation in mean size and polydispersity than the rest of the data are for the smallest (300 nm) and largest (900 nm) mobility diameters. The 300 nm particles have a larger mean area equivalent diameter and many larger sized particles and the 900 nm particles have a smaller mean area equivalent diameter and lots of small particles. These results indicate that we can size select the calcium carbonate with our experimental procedure, but the polydispersity is larger than predicted by calculations.

In Figure 3-5, the optical properties of calcium carbonate obtained with the cavity ring-down spectrometer (circles) are compared to Mie scattering calculations for 1) monodisperse spherical particles (dashed line) and 2) polydisperse spherical particles with the size distribution of area equivalent diameters determined from the TEM images (triangles). The error bars on the cavity ring-down measurements are calculated based on the standard deviation of five measurements. The cavity ring-down data differs from the calculation of monodisperse spherical particles. The calcium carbonate particles have larger extinction cross sections than the theory for monodisperse spherical particles at small mobility diameters and smaller extinction cross sections than the theory for monodisperse spherical particles at large mobility diameters. The TEM-derived calculation for calcium carbonate, however, matches the experimental extinction cross sections closely for all values except mobility diameters of 300 nm and 900 nm. Specifically, when the measured extinction cross section is higher than the theory for monodisperse spherical particles, then the prediction from the TEM data is higher than this theory. When the measured extinction cross sections are lower than the theory for
monodisperse spherical particles, then the prediction from the TEM data is lower than this theory as well.

**Figure 3-5:** The same as Figure 3, but for calcium carbonate particles.

In addition to the low numbers of particles collected at the largest diameters for both ammonium sulfate and calcium carbonate, the long time-scales required for the collection of a sufficient concentration of particles to analyze with TEM affected the results for calcium carbonate at a mobility diameter of 900 nm. The difference between the experimental procedure that is used to collect particles for TEM differs from cavity ring-down only in its time scale. To obtain a sufficient concentration of particles to analyze, we collect TEM samples for a much longer period of time (hours) compared with each cavity ring-down measurement (minutes). Because the particle concentration changes over time, it is necessary to adjust the flow rates. Sometimes, when the flow rate is adjusted, the particle concentration spikes momentarily, which we can observe if the
cavity ring-down spectrometer is used to monitor the extinction of the size-selected particles prior to the impactor. The concentration for ammonium sulfate was more constant, and as a result, the flow rate was not adjusted for any of these TEM samples. For calcium carbonate samples with concentration spikes, the polydispersity of the collected sample is too high and the TEM results deviate from the cavity ring-down results. This increase in polydispersity could occur due to a change in the aerosol flow to sheath flow ratio. We have managed to collect TEM samples without concentration spikes for all but the longest collection times, which correspond to the largest particles. This difference in collection times and the low numbers of particles collected explains the deviations observed for the 900 nm mobility diameter TEM-derived optical properties for calcium carbonate.

At the smallest sizes, the TEM-derived extinction cross section overestimates the cavity ring-down result. For the particles with a mobility diameter of 300 nm, we would expect doubly charged particles to be transmitted during the size selection. The inclusion of doubly charged particles would increase the observed polydispersity, leading to a larger value of mean diameter, as observed. Yet, the doubly charged particles should also affect the cavity ring-down measurement, and the TEM and cavity ring-down results do not match. A possible explanation is that the sticking coefficient for the small particles may be less than for the large particles, leading to a too large TEM-derived extinction cross section for the smallest sizes. For ammonium sulfate, the ratio of the observed ratio of the concentrations of doubly charged particles to singly charged particles was lower than expected by theory, but few doubly charged particles were collected in the TEM analysis. As a result, the data for ammonium sulfate do not support the idea that the
sticking coefficient caused the deviation observed at a mobility diameter of 300 nm in the
calcium carbonate data. Additional studies are therefore needed to determine why the
calculation based on the TEM images deviates from the extinction cross section measured
with cavity ring-down spectroscopy at a mobility diameter of 300 nm.

Overall, the calculation based on the TEM images has good agreement with the
cavity ring-down results for calcium carbonate. The calculation based on the TEM
images incorporates the polydispersity of the particles transmitted through the differential
mobility analyzer. In addition, the calculation is based on the assumption that the
particles are spherical. As a result, the agreement between the TEM-derived calculation
and the cavity ring-down data shows that calcium carbonate can be well modeled by a
polydisperse distribution of spherical particles around the wavelength (643 nm) at which
the cavity ring-down experiment was performed.

Based on the cavity ring-down results alone, we would not have predicted that the
calcium carbonate particles could be treated as spherical particles. We may have instead
concluded that the deviations observed from the theory for monodisperse spherical
particles at large mobility diameters were due to the nonspherical nature of the particles,
which is supported by the fact that shape effects are more likely to be observed for larger
particles sizes. For our experiment, the independent measurement of particle shape and
polydispersity was necessary to accurately determine the theoretical extinction cross
sections. As a consequence, microscopy was needed to understand the optical properties
of these nonspherical particles. Our procedure of combining cavity ring-down data with
microscopy images thereby demonstrates a method for extending cavity ring-down
studies to determine the optical properties of nonspherical particles.
3.4 Atmospheric Implications

Our paper illustrates a new method to extend cavity ring-down spectroscopy for the study of nonspherical particles. For nearly spherical particles, such as ammonium sulfate, we have demonstrated through the use of microscopy and calculations why Mie scattering codes for homogeneous, monodisperse spherical particles should be sufficient to measure the optical properties of these particles. For more complex particles, microscopy can be used to assess the polydispersity of the size selection. In this way, we can determine whether deviations from Mie scattering theory can be attributed to polydispersity or shape. For example, the optical properties of calcium carbonate are well modeled by polydisperse spheres; shape effects are not needed to describe the extinction cross sections of these particles. We expect, therefore, that shape effects will not be needed to understand the optical properties of particles with a similar shape as calcium carbonate. For more irregular particles, such as rod and disk-shaped particles, we expect that both polydispersity and shape will contribute to the observed aerosol extinction cross sections. We plan to extend this study to investigate more irregularly shaped particles to examine how our method can be applied to these cases.

Our results indicate that calcium carbonate particles are well modeled by polydisperse spheres around a wavelength of 643 nm. This result is in agreement with the literature for the optical properties of calcite. At visible wavelengths, the extinction cross sections of calcite particles are well modeled by Mie scattering theory for spherical particles between 100 nm and 2.5 µm with a lognormal size distribution.\textsuperscript{30} Shape effects for calcite need to be considered near absorption features at infrared wavelengths.\textsuperscript{5, 31, 32}
3.5 Conclusions

Through the combined use of cavity ring-down spectroscopy and microscopy, we have demonstrated a novel method that allows us to obtain accurate extinction cross sections of nearly spherical ammonium sulfate particles and nonspherical calcium carbonate particles. Both systems are well modeled by spheres in the wavelength and size regime explored. The ability to study these more complex particles increases the range of aerosol particle types that can be studied with cavity ring-down spectroscopy. This extension of the technique will allow us to study size-dependent changes to particles due to aging in the atmosphere. Studies of the evolution of aerosol optical properties will lead to more accurate models for the optical properties of mineral dust aerosol particles, which have the potential to lead to the improvement of the treatment of aerosol particles in climate models and satellite retrieval algorithms. Accurate treatment of aerosol particles will ultimately lead to a decrease in the uncertainty in the radiative effects of aerosol particles on climate.

3.6 References


3.7 Supporting Information

The supporting information includes additional information on our experimental procedures, as referenced in the text. Specifically, we discuss the procedure for generating aerosol particles from an aqueous solution and from a dried powder, the size
distribution of particles generated using these methods, cavity ring-down spectroscopy measurements of the extinction coefficient of polystyrene latex spheres, and a discussion of error in the measurement of extinction cross section. We have also included a discussion of the functional form of the transfer function in terms of mobility diameter. We have included figures of the size distribution of the ammonium sulfate and calcium carbonate particles and the extinction coefficients for measurements of polystyrene latex spheres as a function of concentration.
3.7.1 Generation of Aerosol Particles

Ammonium sulfate aerosol particles were generated from aqueous solution. Ammonium sulfate (> 99.0 %, EMD) was used without further treatment. Solutions of ammonium sulfate (0.05 wt% to 0.2 wt%) were made using ultrapure water (High-performance liquid chromatography grade). Aerosol particles were produced using a constant output atomizer (TSI 3076, Shoreview, MN) and nitrogen flow rates of approximately 1.5 L/min. Particles were dried using nafion tubing (Permapure, Toms River, NJ) to less than 10 % relative humidity. This procedure produces particles with a size distribution and concentration that is stable for several hours.

Calcium carbonate (> 99.95 %, Macron Chemicals) was used as a proxy for calcite. We milled the calcium carbonate in order to create a uniform distribution of particles at a smaller mean size. Approximately 30 g of calcium carbonate was mixed with approximately 40 mL of toluene and 100 g of yttria-stabilized zirconia beads of mixed sizes (Tosoh, Tokyo, Japan). A mill (SWECO GM005, Florence, KY) was used to grind the samples for 24 hours. Milling or grinding mineral samples prior to aerosolization is a common procedure that has been used in other studies of mineral optical properties.\(^1,2\) The toluene was evaporated by drying the samples at 120 °C. No further chemical or physical processing was used to treat the calcium carbonate. To preserve the hygroscopicity of the particles, calcium carbonate aerosols were dry generated based on a procedure in Sullivan et al.\(^3\) To produce particles, calcium carbonate was agitated while exposed to nitrogen gas. The agitation of the powder causes particles to become entrained in the nitrogen gas flow. The gas with suspended particles flows through a small Erlynmeyer flask in order to create a more constant
concentration of aerosol particles. To decrease the concentration of particles, most of the particles are pumped away and the flow is diluted with nitrogen gas. The size distribution of particles obtained is stable over hours and the number concentration of the particles is stable over minutes.

3.7.2 Size Distribution of Aerosol Particles

The size distribution of the particles as a function of the mobility diameter can be obtained by connecting the electrostatic classifier and differential mobility analyzer to a condensation particle counter (TSI 3775, Shoreview, MN). In Figure 3-6, the size distributions of aqueous generated ammonium sulfate particles and dry generated calcium carbonate particles are shown. The ammonium sulfate size distribution peaks at approximately 30 nm and the concentration decreases rapidly at larger concentrations. The calcium carbonate distribution is bimodal, with one peak at approximately 50 nm and the second at approximately 175 nm. The concentration decreases at larger diameters, though not as rapidly as for ammonium sulfate. A similar bimodal distribution has been observed in the literature for mineral dust aerosol generated from an atomized suspension of dust in water.⁴
3.7.3 Cavity Ring-Down Spectroscopy of Polystyrene Latex Spheres

To verify that the cavity ring-down spectrometer is working properly, we have taken measurements of polystyrene latex spheres (Polysciences, Warrington, PA). Figure 3-7 is a plot of the extinction coefficients of four sizes of polystyrene latex spheres measured in the cavity ring-down spectrometer as a function of their concentration. The inset shows the extinction coefficient vs. concentration for 119 nm particles. Polystyrene latex spheres have a refractive index of 1.59 at 589 nm. For solid particles, the refractive index does not vary significantly as a function of wavelength for wavelengths away from absorption bands. As a result, we assume that the refractive indices defined at 589 nm should be close to the refractive index at 643 nm. Using the refractive index of 1.59, the extinction coefficients match the prediction from Mie scattering theory. The
fact that the extinction coefficient increases linearly with concentration indicates that we are working in the single scattering regime.

![Figure 3-7](image)

Figure 3-7: The extinction coefficients of four sizes of polystyrene latex spheres as a function of their concentration. Vertical error bars indicate the error between repeated measurements and horizontal error bars indicate the polydispersity of the polystyrene latex spheres.

3.7.4 Measurement of Error in the Measured Extinction Cross Sections

In Figures 3-3 and 3-5 in the text, the error we show in the data points is the standard deviation of multiple measurements. An alternate way to estimate the error in our measurements is to use the standard deviation of the extinction coefficient, $b_{ext}$, and the standard deviation of the concentration, $N$, to calculate the error in the extinction cross section, $\sigma_{ext}$. The extinction cross section is given by $\sigma_{ext} = b_{ext}/N$, where $b_{ext}$ is the extinction coefficient and $N$ is the concentration. The error in the extinction cross section is given by

$$
\Delta \sigma_{ext} = \sigma_{ext} \left[ \left( \frac{\Delta b_{ext}}{b_{ext}} \right)^2 + \left( \frac{\Delta N}{N} \right)^2 \right]^{1/2}
$$

(S-1)

We find that the error calculated by Eqn. S-1 is a factor of 3 to 7 larger than the standard deviation obtained from multiple measurements. In the text, we use the standard
deviation taken over multiple measurements rather than the estimate of error determined from Eqn. S-1 because it is a more accurate representation of the precision of our measurements.

3.7.5 Aerosol Size Selection and the Transfer Function

Particles are size selected based on their electrostatic mobility, $Z_p$. The mobility of the particles is related to their mobility diameter, $d_m$, as shown by

$$\frac{d_m}{C(d_m)} = \frac{ne}{3\pi \mu Z_p}$$  \hspace{1cm} (S-2)

where $C(d_m)$ is the Cunningham slip correction, $n$ is the number of charges on the particle, $e$ is the elementary charge, and $\mu$ is the gas viscosity.\(^6\) Literature values were used for the gas viscosity.\(^7\) The Cunningham slip correction is a function of the mobility diameter, as given by

$$C(d_m) = 1 + \left( \frac{2\lambda}{d_m} \right) \left[ \alpha + \beta \exp \left( -\frac{\gamma d_m}{2\lambda} \right) \right]$$  \hspace{1cm} (S-3)

where $\lambda$ is the gas mean free path, and $\alpha$, $\beta$, and $\gamma$ are constants.\(^6\) Literature values were used for the gas mean free path and the empirical parameters, $\alpha$, $\beta$, and $\gamma$, in the Cunningham slip parameter.\(^7,8\) In the aerosol size selection process, the voltage, $V$, of the inner rod in the differential mobility analyzer (DMA), the clean sheath air inlet flow rate, $q_c$, and the main excess air outlet flow rate, $q_m$, determine the centroid electrical mobility, $Z_p^*$, according to

$$Z_p^* = \frac{(q_c + q_m) \ln \frac{r_2}{r_1}}{4\pi VL}$$  \hspace{1cm} (S-4)
where \( r_1 \) is the outer diameter of the inner rod in the DMA, \( r_2 \) is the inner diameter of the annular space within the DMA, and \( L \) is the length between the aerosol inlet and exit in the DMA.\(^9\)

Using Eqns. S-1 and S-4, we find the mobility diameter, \( d_{m}^* \), that corresponds to \( Z_p^* \), as shown by

\[
\frac{d_{m}^*}{C(d_{m}^*)} = \frac{4neVL}{3\mu(q_c + q_m)\ln\frac{r_2}{r_1}}
\]

We assume \( q_c = q_m \) for our set up. Starting with an initial guess for \( d_{m}^* \), we can iteratively solve for \( d_{m}^* \) until our calculated \( d_{m}^*/C(d_{m}^*) \) matches the value obtained from Eqn. S-5.

To determine the polydispersity of the size selection, we first calculate the half width of the mobility distribution, \( \Delta Z_p \), according to

\[
\Delta Z_p = \frac{q_a + q_s}{q_c + q_m} Z_p^*
\]

(\( S-6 \))

where \( q_a \) is the aerosol inlet flow rate and \( q_s \) is the aerosol sampling outlet flow rate.\(^9\) For our set up, we assume that \( q_a = q_s \). Combining Eqns. S-2, S-4, and S-6, we can calculate the distribution of mobility diameters according to

\[
\frac{d_{m} \pm \Delta d_{m}}{C(d_{m} \pm \Delta d_{m})} = \frac{ne}{3\pi\mu(Z_p^* m \Delta Z_p)}
\]

As in the case of Eqn. S-5, we can solve for \( d_{m}^* \pm \Delta d_{m} \) numerically.

The functional form that dictates the relative concentration of each size within the size-selected distribution is called the transfer function. In terms of the mobility, \( Z_p \), the transfer function, \( \Omega \), is given by\(^10,11\)

\[
\Omega = \frac{1}{2\beta(1 - \delta)} \left| \frac{Z_p}{Z_p^*} - (1 + \beta) \right| + \frac{Z_p}{Z_p^*} - (1 - \beta) - \frac{Z_p}{Z_p^*} - (1 + \beta\delta) - \frac{Z_p}{Z_p^*} - (1 - \beta\delta) \right|
\]

(\( S-8 \))

where
\[ \beta = \frac{q_a + q_s}{q_c + q_m} \]  
(S-9)

and

\[ \delta = \frac{q_s - q_a}{q_a + q_s} \]  
(S-10)

As stated above, we assume that \( q_a = q_s \) and \( q_c = q_m \). We do not consider diffusion effects, which can be important for aerosol particles with diameters under 50 nm. We can simplify Eqn. S-8 to

\[
\Omega = \frac{q_c}{2q_a} \left[ \frac{Z_p}{Z_p} \left( 1 + \frac{q_a}{q_c} \right) + \frac{Z_p}{Z_p} \left( 1 - \frac{q_a}{q_c} \right) - 2 \frac{Z_p}{Z_p} - 1 \right] 
\]  
(S-11)

Combining Eqns. S-2 and S-11, we obtain an expression for the transfer function in terms of the mobility diameter

\[
\Omega = \frac{q_c}{2q_a} \left[ \frac{C(d_m)}{C(d_m')} d_m' \left( 1 + \frac{q_a}{q_c} \right) + \frac{C(d_m)}{C(d_m')} d_m' \left( 1 - \frac{q_a}{q_c} \right) - 2 \frac{C(d_m)}{C(d_m')} d_m' - 1 \right] 
\]  
(S-12)

While Eqn. S-11 results in an isosceles triangle, the transfer function expressed in Eqn. S-12 as a function of the mobility diameter is a triangle that no longer has two sides of equal length. For spherical particles, the mobility diameter is equivalent to the volume and area equivalent diameters. We used Eqn. S-12 to plot the transfer function as a function of area equivalent diameter in Figures 3-2 and 3-4 in the manuscript.

REFERENCES:


Chapter 4  Influence of Shape on the Optical Properties of Hematite Aerosol

Abstract

Mineral dust aerosol particles are the second largest atmospheric emission by mass and contribute to the uncertainty in radiative forcing. Due to the changes in particle size, composition, and shape that are caused by physical processes and reactive chemistry, optical properties vary during atmospheric transport. Hematite is the major absorbing species in mineral dust aerosol. In this study, we have analyzed the extinction cross sections of nigrosin and hematite particles using cavity ring-down aerosol extinction spectroscopy and have measured particle shape and size distributions using transmission electron microscopy. The size-selected spherical nigrosin particles have a narrow size distribution, with extinction cross sections that are described well by Mie scattering theory. In contrast, the size distribution of size-selected hematite particles is more polydisperse. The extinction cross sections were modeled using Mie scattering theory and the discrete dipole approximation (DDA). The DDA was used to model more complex shapes that accounted for the surface roughness and geometry of the particles. Using additional parameters that account for particle shape is necessary to model the optical properties of hematite aerosol particles. This characterization will lead to better aerosol extinction cross section parameters for modeling aerosol optical properties.
4.1 Introduction

The largest uncertainties in quantifying the radiative balance of the Earth stem from the effects of aerosol particles.\textsuperscript{1} These particles originate from natural and anthropogenic sources. Of different particle types, mineral dust is the second largest emission by mass and anthropogenic sources compose up to 50\% of the emissions.\textsuperscript{2} The primary source of mineral dust is the dust belt, which is located in the mid-latitudes from the Saharan region through central Asia.\textsuperscript{3} High latitude sites, such as Iceland, produce substantial amounts of dust during the spring months as well.\textsuperscript{4} Emitted mineral dust can be transported long distances and can affect regions remote from the source.\textsuperscript{5, 6} While a large distribution of particle sizes are emitted at the source, only particles less than 1.8 \( \mu \text{m} \) tend to be transported long distances.\textsuperscript{5} Particles over approximately 1.8 \( \mu \text{m} \) readily settle out of the atmosphere due to gravitational effects.\textsuperscript{7} Large amounts of dust are transported globally, and it is estimated that about 52,000 metric tons of Asian dust under 2.5 \( \mu \text{m} \) were transported across the United States in April of 2001.\textsuperscript{8} Transported dust causes local solar radiation fluxes and health concerns.\textsuperscript{8, 9}

Iron is an important component of mineral dust aerosol in many regions of the world. For example, hematite (\( \text{Fe}_2\text{O}_3 \)) comprises up to 1 \% of Saharan dust and up to 2.6 \% of Icelandic dust by mass.\textsuperscript{4, 10} Because hematite has a high real part of the refractive index and is strongly absorbing (\( n \approx 3 + 0.1i \)) a small amount in a mineral dust aerosol particle may be significant for the optical properties of the whole particle. In addition, the deposition of iron from hematite aerosol particles in the oceans is important for biogeochemistry as a nutrient for plant growth.\textsuperscript{11, 12}
Radiative properties of aerosol particles are poorly understood due to the complexity of aerosol shape, composition, morphology, and size distribution. For example, the direct radiative forcing of aerosol particles has been calculated to be $-0.5 \pm 0.4$ W m$^{-2}$ with mineral dust aerosol particles contributing $-0.1 \pm 0.2$ W m$^{-2}$.\footnote{1} While composition and size are often accounted for in models and algorithms for remote sensing retrievals, shape and morphology are not commonly considered, and these may have a large impact on the radiative properties of particles. For example, modeling studies show that the backscattering cross section is changed by a factor of 2-3 when a small degree of surface roughness is included in calculations.\footnote{13} While most lidar measurements use Mie scattering to determine the aerosol concentration, the phase functions of rough particles are different than those for spheres.\footnote{13} In particular, for absorbing species, the lidar ratio is lower when surface roughness is added.\footnote{14} Liddqvist et al. (2014) has shown the optical properties of aerosol particles are modeled better when particle shape and composition derived from scanning electron microscopy (SEM) measurements are incorporated.\footnote{15} Porous particles have also been shown to have a lower extinction cross section than volume equivalent homogeneous particles.\footnote{16} Although most satellite retrieval algorithms use externally mixed particles, radiative properties may exhibit a large dependence on the morphology of internally mixed particles.\footnote{17, 18, 19, 20} Incorporation in satellite retrieval algorithms of the shape and morphology of particles as well as composition and size will lead to better predictions of aerosol loading.

Laboratory and computational studies on irregularly shaped particles have examined the effect of having a high real (scattering) component and an imaginary (absorbing) component of the refractive index on particle optical properties. For
laboratory studies modeling bulk polydisperse samples with a high real part of the refractive index (hematite, goethite, and rutile), polydisperse spheroids provided little improvement to calculated optical phase functions compared with Mie scattering theory.\textsuperscript{21} Even though it has been suggested that the optical properties of particles with high refractive indices should be sensitive to particle shape, experimental results for hematite have been modeled using Mie scattering theory.\textsuperscript{21, 22} Unlike for hematite, when the optical properties of elongated particles such as rod-like goethite aerosol particles are investigated, additional parameters are required to model the scattering properties.\textsuperscript{22}

In contrast to the laboratory studies discussed above, modeling studies have shown that the scattering phase function of hematite is affected by the shape of the particles.\textsuperscript{13, 23} In addition, Kahnert et al. (2012) showed that small scale roughness on spherical particles results in a larger extinction efficiency for both absorbing and non-absorbing particles, but the deviation is more pronounced for absorbing species.\textsuperscript{24} Similarly, Gasteiger et al. 2011 found that the extinction efficiency is shape dependent even for weakly absorbing particles (k=0.0172i).\textsuperscript{14} In addition, increases in elongation of the particles lead to decreases in the extinction efficiency at size parameters smaller than 5.\textsuperscript{14} These modeling studies have shown that small changes in particle shape affect the optical properties of absorbing species.

We have previously used cavity ring-down aerosol extinction spectroscopy (CRD-AES) to study the optical properties of size selected calcium carbonate particles.\textsuperscript{25} CRD-AES is a sensitive technique due to the long path length of the optical cavity and the fact that the measurements of extinction coefficients are independent of the intensity of the laser output.\textsuperscript{26, 27, 28} The optical properties of mineral dust aerosol particles have
previously been performed using nephelometers and mid-IR extinction spectrometers, but due to the inherently high detection limit, only large concentrations and bulk size distributions of aerosol particles have been used. In contrast, CRD-AES can be used to study the optical properties of size-selected aerosol particles.

In this paper, we have measured the extinction cross sections of spherical particles made from nigrosin, an absorbing dye, and hematite, a component of mineral dust that absorbs light and is similar in shape and aspect ratio to calcium carbonate. We have characterized the size selection of hematite particles using a differential mobility analyzer and electron microscopy. Transmission electron microscopy (TEM) was used for a measurement of the polydispersity of the particles as well as determining the shape factors required for modeling parameters. We use Mie scattering theory and the discrete dipole approximation (DDA) for spheroids and roughened particles to compare to the measured extinction cross sections.

4.2 Experimental Methods

4.2.1 Setup of Experiment

Figure 1 shows the setup used for the measurement of aerosol optical properties and for preparation of transmission electron microscopy (TEM) samples. This experimental system has been previously described in Veghte and Freedman (2012). Briefly, nigrosin particles are generated from aqueous solution, atomized, and dried through diffusion driers filled with molecular sieves. Mineral samples are dry generated by flowing nitrogen over an agitated powder and size selected by the differential mobility analyzer. Their extinction coefficient is measured using the cavity ring-down spectrometer (labeled “optical cavity” in Figure 4-1) at 643 nm. Finally, the
concentration of the particles is measured using a condensation particle counter (TSI 3075), or the particles are impacted on TEM grids for microscopy analysis.

4.2.2 Particle Generation

Nigrosin (Acros, water soluble, high purity biological stain) was used as a standard for spherical, absorbing particles for the CRD-AES analysis. Nigrosin particles were aerosolized from an aqueous solution (0.05-0.6 wt.% in high-performance liquid chromatography grade water). The solution was aerosolized at a nitrogen flow rate of approximately 1.5 lpm using a constant output atomizer (TSI 3076, Shoreview, MN). The atomized solution was then dried using a Nafion dryer (Permapure, Toms River, NJ) to make polydisperse dry aerosol. The peak mobility diameter in the scanning mobility particle sizer (SMPS) spectrum of nigrosin is approximately 70 nm with a rapidly decreasing concentration of particles at larger sizes. A steady concentration is obtained.
after 30 minutes, and the size distribution and concentration are then constant on the order of hours.

Hematite (Strem Chemicals >99.8%) aerosol particles were dry generated. The hematite powder was first processed by mixing together approximately 30 g with 100 g of mixed sized zirconia beads (Tosoh, Tokyo, Japan) and 40 mL of toluene. This slurry was milled for approximately 24 hours on an agitation mill (SWECO GM005, Florence, KY)) before being dried in an oven at 120°C overnight to remove residual solvent. The dried powder was aerosolized by stirring the powder constantly while introducing a stream of nitrogen in which to entrain the dust. The aerosolized hematite was then passed through an Erlenmeyer flask to maintain a constant concentration of particles and remove the largest particles. The concentration of the particles was adjusted by pumping away excess aerosol particles and diluting with nitrogen to the aerosol flow rate desired. The size distribution of the hematite particles in the SMPS spectrum was broader than that of nigrosin, with a peak at approximately 140 nm. The particle size distribution stayed constant throughout the experiment on the order of hours, and the concentrations were steady on the order of minutes.

### 4.2.3 Aerosol Particle Size Selection

After aerosol generation, the particles were size selected using an electrostatic classifier (TSI 3080, Shoreview MN) and a differential mobility analyzer (DMA; TSI 3081, Shoreview MN). Using this system, aerosol particles can be size selected from approximately 10 nm to 1.0 μm. For our systems, we size selected particles every 50 nm from 200 nm to 900 nm. To size select the particles, the aerosol particles are exposed to
an \(^{85}\text{Kr}\) neutralizer, which gives the particles a known distribution of charges (e.g. 0, ±1, ±2, etc.).\(^{35}\) These particles are then passed through the DMA and separated based on their electrostatic mobility in the applied field. The size of particle selected and the polydispersity of the size selection depend upon the aerosol and sheath flow rate, applied potential, and particle size. While it is recommended that the ratio of the aerosol flow to sheath flow should be approximately 1:10, we have shown previously that we obtain better size selection for irregularly shaped particles using a higher aerosol to sheath flow ratio. For the hematite particles, we used a flow rate of approximately 1.5 lpm and sheath flows from 2.7 to 8.8 lpm, depending upon the size of particles being analyzed. To compare our results for nigrosin to the literature, we used an aerosol flow rate of 0.3 lpm through the DMA and a sheath flow of 2.7 to 5.0 lpm. No difference was seen in the optical properties of nigrosin at either 0.3 or 1.5 lpm aerosol flow rate. After these aerosol particles are size selected in the DMA, they are directed into the CRD-AES to determine the optical properties. When an aerosol flow rate of 0.3 lpm was used, the subsequent flow out of the DMA was diluted to 1.5 lpm to provide adequate mixing with the purge flow in the cavity ring-down. After passing through the CRD-AES, the particles are either counted using a condensation particle counter (CPC) or impacted on TEM grids for offline analysis. While TEM analysis was used to obtain the size distributions shown in the figures in this paper, as described below, estimates of the size distribution of the generated aerosol particles were performed using an SMPS (TSI, Shoreview, MN).
4.2.4 Cavity Ring-Down Aerosol Extinction Spectroscopy (CRD-AES)

The extinction cross sections of the generated aerosol particles were measured using CRD-AES. We use a wavelength of 643 nm to be more sensitive to the larger sizes of mineral dust. The 643 nm diode laser is modulated at 500 Hz and is passively coupled to a cavity that is 91 cm in length. The cavity has mirrors that are highly reflective (>99.9985% at 640 nm). Light transmitted through the back mirror is detected using a photomultiplier tube. The decay of the light intensity is called the ring-down time, which for our instrument is 165 μs, corresponding to an effective path length greater than 48 km. The extinction coefficient can be measured from the ring down time, \( \tau \), of the cavity

\[
b_{\text{ext}} = \frac{R_L}{c} \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right)
\]

where \( \tau_0 \) is the ring-down time (first order decay constant) in the absence of any absorbing or scattering material, \( \tau \) is the ring-down time with the sample in the cavity, \( R_L \) is the ratio of the total cavity length to the length of the cavity occupied by the sample, and \( c \) is the speed of light. The extinction cross section (\( \mu m^2 \)) is given by

\[
\sigma_{\text{ext}} = \frac{b_{\text{ext}}}{N}
\]

where \( N \) is the number of particles per cm\(^3\). The extinction efficiency, \( Q_{\text{ext}} \), is related to the extinction cross section according to

\[
Q_{\text{ext}} = \frac{\sigma_{\text{ext}}}{\pi r^2}
\]

which is dependent on the particle radius, \( r \).

4.2.5 Transmission Electron Microscopy

TEM was used to determine the shapes and polydispersity of the particles size selected by the DMA. In our study of calcium carbonate optical properties, we found that TEM measurements were essential to obtain because size-selected irregularly shaped
particles have a much broader size distribution than predicted based on the transfer function of the DMA.\textsuperscript{25} Particles were collected using an aerosol flow of 1.5 lpm, which is directed into a cascade impactor (PIXE International Corp. Tallahassee FL). The impactor was backed with a pump at 1 lpm, allowing excess air to escape through a filter. The particles were collected on a variety of TEM grids (Continuous carbon coated grids, Dura SiN Film 200 nm; and homemade Formvar grids on 200 mesh Cu grids, EMS, Hatfield PA). Grids were coated with low molecular weight polymer (3M double-sided sticky tape) dissolved in HPLC grade chloroform to increase the collection efficiency. Particles were collected for 8 min up to an hour depending on their concentration. We monitored the concentration of particles collected for TEM imaging by having the aerosol flow through the CRD-AES before the impactor. Each sample was imaged using a JEOL JEM 1200 EXII TEM operated at an accelerating voltage of 80 kV.

The size distribution of nigrosin and hematite particles is determined as a function of their projected areas. ImageJ software (National Institutes of Health, Bethesda MD) was used to calculate the area of 200 - 400 particles per sample. The areas were converted to area equivalent diameters, assuming the particles are spherical and their projected area is circular. We used a variety of shape parameters to describe the imaged hematite particles.\textsuperscript{36} The parameters that relate to the roughness of the particles are the form factor, solidity, and convexity. The parameters that relate to the elongation of the particles are roundness, compactness and aspect ratio. The equations for each of these parameters are given in Table 4-1. Convex perimeter refers to the perimeter of the particle excluding concave inclusion and the convex area is the area contained within the
convex perimeter. A subset of TEM images of hematite particles that spanned the size distribution of the particles was used to determine the experimental shape factors.

Table 4-1: Equations used to calculate particle shape factors.

<table>
<thead>
<tr>
<th>Roughness Form Factors</th>
<th>Roundness Form Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Form Factor ( \frac{4\pi \cdot \text{Area}}{\text{Perimeter}^2} )</td>
<td>Aspect Ratio ( \frac{\text{Max Dimension}}{\text{Min Dimension}} )</td>
</tr>
<tr>
<td>Solidity ( \frac{\text{Area}}{\text{Convex Area}} )</td>
<td>Roundness ( \frac{4 \cdot \text{Area}}{\pi \cdot (\text{Max Diameter})^2} )</td>
</tr>
<tr>
<td>Convexity ( \frac{\text{Convex Perimeter}}{\text{Perimeter}} )</td>
<td>Compactness ( \frac{\sqrt{(4/\pi) \cdot \text{Area}}}{\text{Max Diameter}} )</td>
</tr>
</tbody>
</table>

4.2.6 Optical Properties

Hematite is birefringent and has an ordinary refractive index of \( n=3.08+0.055i \) and an extraordinary refractive index of \( n=2.78+0.104i \) at 643 nm.\(^{37}\) To model this system, two general approaches are taken. Previous research has taken an average of the ordinary and extraordinary rays, where both rays are weighted equally in the calculation, to give the optical constants.\(^{21, 22}\) We used a weighted average of the ordinary and extraordinary refractive indices because they are dissimilar for hematite. Because the system is uniaxial, an average is calculated by weighing the ordinary ray by a factor of \( 2/3 \) and the extraordinary ray by a factor of \( 1/3 \).\(^{38}\) This type of analysis is called optical constant averaging. In contrast, the most accurate way to model the optical properties of a uniaxial crystal is to take a weighted average of the extinction cross sections calculated for each refractive index. Mogili et al. (2007) showed that this spectral averaging method is more accurate than optical constant averaging for a variety of mineral types.\(^{30}\) It has been suggested that the spectral averaging method provides accurate results, but it is computationally more expensive than optical constant averaging and is generally not
necessary to model experimental results.\textsuperscript{13, 39} In our reported calculations below, we used the spectral averaging method. For comparison, we have also performed calculations by taking a weighted average of the optical constants. For hematite, only small differences are observed between the two types of averaging. Figures and further description of the optical constant averaging methods can be found in the supplemental information.

4.2.7 Mie Scattering Theory

To determine the effective refractive index of nigrosin, we compare results from Mie scattering theory to our experimental extinction cross sections. Experimental data from six particle diameters were used, ranging from 250 nm to 500 nm in 50 nm increments. The extinction cross sections were averaged over five runs. Larger diameters up to 900 nm were used to confirm the retrieved refractive index. The experimental data are corrected for the doubly charged particles that are transmitted through the DMA, as described in Hasenkopf et al. (2010) and Freedman et al. (2009).\textsuperscript{19, 40} Calculations were performed using a version of BHCOAT that has been adapted for MATLAB.\textsuperscript{20, 41} The refractive index that is the best fit to the observed extinction cross sections is determined by calculating the cumulative fractional difference (CFD\textsubscript{R}).\textsuperscript{19, 40} CFD\textsubscript{R} is calculated using the equation

\[
CFD_{R} = \frac{1}{P} \sum_{\text{All Sizes}} \frac{|b_{\text{ext-measured}} - b_{\text{ext-Mie}}|}{b_{\text{ext-measured}}}
\]

where \(P\) is the number of particle sizes selected. The minimum CFD\textsubscript{R} value corresponds to the best fit for the refractive index. Refractive index retrievals have also been performed in the literature using \(\chi^2\) to determine best fit, which result in the same
minimum (optimized) value as our methodology. An example plot of CFD\textsubscript{R} values for nigrosin is shown in the supplementary material (Fig. 4-9).

We also examine the effects of the polydispersity of the size selection process on the experimental extinction cross sections using Mie scattering calculations. In one set of calculations, the size selected particles are assumed to be monodisperse spheres; in the second, the particles are assumed to be polydisperse spheres with the polydispersity of the size selection for each mobility diameter determined from the TEM images, as described in Veghte and Freedman (2012). For spherical particles, the mobility diameter, \( d_m \), the volume equivalent diameter, \( d_v \), and the area equivalent diameter, \( d_{ae} \), are all equal. For each mobility diameter, we have a finite number of particles \( (n_{tot}) \) each with its own \( d_{ae} \) from the TEM analysis. Area equivalent diameters from the TEM images are binned into 20 nm increments. The extinction efficiency, \( Q_{ext} \), at each size is calculated using the retrieved (nigrosin) or known (hematite) refractive index, \( m \), and the size parameter \( x_{ae} = \pi d_{ae} / \lambda \) using the median diameter in each size bin, and is then converted to the extinction cross section, \( \sigma_{ext} \). The weighted average of the extinction cross sections is then calculated according to

\[
\sigma_{ext} = \frac{1}{n_{tot}} \sum_{i=1}^{n_{tot}} \sigma_{ext,i}
\]

for each binned diameter. Because the multiply charged particles are included in the TEM images, this calculation includes all particles measured. Error in the polydisperse calculations was estimated by randomly dividing the TEM images into three groups. From each of these groups, the polydisperse extinction cross section was found. The standard deviation from these three measurements is used as an overestimate of the uncertainty that stems from having a finite number of particles.
4.2.8 Discrete Dipole Approximation (DDA) Method

To include the effects of nonspherical shapes in the optical property calculations, we use the discrete dipole approximation (DDA). The DDA defines particles as a finite number of dipoles in an array. The DDA calculations were performed using DDSCAT 7.2.\textsuperscript{42, 43} For this analysis, it is assumed that the area equivalent diameter ($d_{ae}$), and volume equivalent diameter ($d_v$) are the same as the mobility diameter ($d_m$) from CRD-AES measurements as described above.

For accurate calculations of the absorption cross section ($C_{abs}$) and scattering cross section ($C_{sca}$) using DDA, the volume equivalent radius ($a_{eff}$) is constrained by

$$a_{eff} < 9.88 \frac{\lambda}{|m|} \left( \frac{N_d}{10^6} \right)^{1/3}$$  \hspace{1cm} 6

where $\lambda$ is the wavelength, $m$ is the refractive index, and $N_d$ the number of dipoles in the system. Dipole spacing was chosen so that there were 40 dipoles spanning the radius, which, according to Eqn. 6, leads to accurate scattering and absorption cross sections for spherical particles up to a 4 μm diameter. The extinction efficiency of spherical particles between 100 nm and 1 μm calculated with the DDA have an average percent difference from the extinction efficiency calculated for spheres with Mie scattering theory of 2.8% with a maximum percent difference of approximately 7%.

Previous studies have shown that calculations on irregular particles require 196 different particle orientations to obtain convergence of the calculated optical properties.\textsuperscript{44} Similarly, we observed that the optical properties of the roughened particles converge when 196 orientation angles are used, and more angles increase the computation time.
without significantly changing the extinction cross section or phase function of the particles. For example, increasing the number of orientations of the particles from 196 to 224 only changed the extinction cross section by an average of 0.07\% and a maximum of 0.30\%.

To account for heterogeneity in the particle shape, five different roughened particles were constructed from spherical particles. Because the hematite particles have an aspect ratio near unity, we constructed roughened particles from spheres. To facilitate the generation of the DDA input files for roughened spheres we developed a program to automate this [J. E. Moore, https://github.com/jensengrouppsu/ddscat-inputgen]. Using this program, roughened spheres were generated starting from a sphere on a cubic grid having 40 dipoles spanning the radius. From this initial sphere, we randomly removed 15-20 smaller spheres with 5-20 dipoles spanning the radius under the condition that these smaller spheres must intersect both the dipoles remaining in the initial sphere and the space around them. This condition guarantees the removal of only surface dipoles.

Out of the roughened particles that were generated from spheres, a subset of five particles was selected for the DDA calculations (Figure 4-2). This subset included three particles that were similar in structure and had a projected area that closely resembled the shape factors associated with the irregularly shaped hematite particles (Table 4-2). The other two particles are smoother and rougher than the three other particles and were used to estimate the upper and lower bounds for our calculations (Figure 4-2). The optical properties obtained from the calculations on these five structures were averaged to obtain the mean extinction cross section and the range of values associated with having an irregular shape.
In addition to performing calculations on spherical and roughened particles based on spheres, prolate and oblate spheroids with an aspect ratio of 1.8 and roughened particles based on these spheroids were also used. Spheroids of with an aspect ratio of 1.8 have been shown to model the optical properties of mineral dust well.\cite{14,45} Roughened spheroidal particles were constructed in the same manner as the roughened particles based upon spheres, with the optical properties measured from the average of the prolate and oblate roughened particles. Because spheroidal particles have multiple symmetry parameters compared to no symmetry in the roughened particles, fewer scattering angles were needed. For the spherical and spheroidal particles, only 24 particle orientations were used, which corresponded to the same number of orientations as the roughened particles when symmetry is accounted for. Views of all of the particles constructed for DDA calculations are shown in Fig. 4-2 in one orientation and from many angles in the supporting information (Fig. 4-11). To determine the shape factors for each particle, the two-dimensional projected images of six orientations of each particle were obtained and analyzed using ImageJ.
4.3 Results and Discussion

We have measured the optical properties of size-selected nigrosin and hematite using CRD-AES and subsequently determined the effect of the polydispersity of the size-selected particles on the optical properties. Because hematite is nonspherical, we have additionally examined the sensitivity of its optical properties to particle shape. To investigate these effects, Mie scattering theory and DDA were used.
4.3.1 Nigrosin

TEM was used to analyze the polydispersity of nigrosin particles that are size-selected by the DMA. As seen from the TEM images, the particles are spherical at mobility diameters of both 300 nm and 800 nm (Figs. 4-3a and 4-3c). The distribution of particle sizes transmitted through the DMA at a given mobility diameter and the theoretical transfer function are plotted in Figs. 4-3b and 4-3d. The area equivalent diameter that corresponds to the peak of the size distribution is close to the selected mobility diameter. An aerosol to sheath flow of 0.3:2.7 to 0.3:8.8 was used in these experiments. The transfer function narrows as the optimal aerosol to sheath flow of 1:10 is reached. The higher ratio of aerosol to sheath flow in this experiment was needed in order to size select particles with diameters of 500-900 nm. At all diameters, the measured polydispersity matched the theoretical transfer function well.
Figure 4-3: Transmission electron microscopy images of nigrosin size selected at (a) 300 nm and (c) 800 nm. The distributions of the area equivalent diameters are shown for mobility diameters of (b) 300 nm with a mean TEM size of 356 nm and (d) 800 nm.

4.3.2 Optical Properties of Nigrosin

The experimental extinction cross sections of nigrosin are plotted as a function of mobility diameter in Fig. 4-4 in comparison to theory. The line shows theoretical extinction cross sections calculated from Mie scattering theory for monodisperse sizes of particles. These extinction cross sections are obtained using our retrieved refractive index of $n=1.868 \pm 0.024$ and $k=(0.276 \pm 0.015)i$. Previous studies have reported an effective refractive index for nigrosin at 532 nm with a real part of $n=1.65$ to 1.75 and an imaginary part of $k=(0.24$ to $0.338)i$. Also plotted are Mie scattering calculations for polydisperse spheres that use the size distributions of area equivalent diameters found for each mobility diameter from Fig. 4-3. The CRD-AES data agrees well with Mie scattering theory for both monodisperse and polydisperse spheres. In the
inset, the extinction efficiencies versus mobility diameter are plotted for the CRD-AES data, the retrieved refractive index, and the literature results. The retrieved real part of the refractive index obtained at 643 nm could be higher than the literature values at 532 nm due to the fact that refractive indices can change rapidly around absorbance bands.\textsuperscript{48} Nigrosin has a maximum absorbance at 568 nm, which is between the wavelength used in the literature and this study. Another reason for the discrepancy could be the variable composition of nigrosin. The molecular formula of our sample was approximately \( \text{C}_{49}\text{H}_{22}\text{N}_{7}\text{S}_{3.5}\text{O}_{27} \) (analysis performed by Columbia Analytical), while one of the samples used in the literature had a molecular formula of \( \text{C}_{49}\text{H}_{20}\text{N}_{7}\text{S}_{3}\text{O}_{18} \).\textsuperscript{40} We also note that depending upon the manufacturer and batch of nigrosin, there are salt impurities that affect the shape of the particles (Fig. 4-10). Care was taken to use nigrosin without visible salt impurities.
Figure 4-4: Extinction cross sections vs. diameter for nigrosin. The blue circles indicate the experimentally determined extinction cross sections. The line was determined using Mie scattering theory for monodisperse spheres. The red diamonds are the Mie

4.3.3 Hematite

Hematite particles have an aspect ratio close to unity and a degree of surface roughness that is visually similar to calcite (Figure 4-5a and 4-5c). From our previous research we have seen that calcite particles can be modeled as polydisperse spheres using the size distribution obtained from the TEM images. A similar methodology was initially used for the hematite particles. For each mobility diameter of interest, the particles were collected for TEM imaging, and their extinction cross section was measured. Area equivalent diameters were calculated from the TEM images and plotted as shown in Figs. 4-5b and 4-5d. The transfer function is also shown. The peak in the size distribution is close to the selected mobility diameter. The hematite particles have a larger polydispersity than for spherical particles. The 250 nm mobility diameter distribution is slightly wider than the transfer function. The majority of the particles at a
mobility diameter of 850 nm are within the bounds given by the transfer function, but there is a distribution of particles with smaller diameters as well. These small particles are present in the size distribution for mobility diameters of 450 nm and larger. As the mobility diameter increases, the concentration of particles with small diameters that are transmitted through the DMA also increases.

Figure 4-5: Transmission electron microscopy images of hematite size selected at mobility diameters of (a) 250 nm with a mean TEM size of 260 nm and (c) 850 nm with a mean TEM size of 691 nm. The polydispersity at each mobility diameter is shown as a function of the transfer function.

4.3.4 Shape factor analysis of hematite and modeled particles

Irregularities in particle shape can be divided into irregularities due to elongation of the particles and irregularities due to roughness of the particles. To determine the effects of elongation, we used a combination of oblate and prolate spheroids to model the optical extinction as has been performed in previous studies.\textsuperscript{14, 21, 22, 45} The roughness of
the particles was modeled using roughened particles based on spheres and roughened particles based on spheroids that had a surface that was generated as described above. These modeled particles are compared to actual hematite particles from TEM analysis using parameters that describe the surface roughness (convexivity, form factor, and solidity) and elongation (aspect ratio, roundness, and compactness; Table 4-2). When the different roughness factors were analyzed, convexivity and form factor had size dependence in the TEM analysis (Figure 4-12), and as a result, the value at the median in the size range studied, 550 nm, was used. For all other shape factors, the averages across all particle sizes in the TEM analysis were used. In terms of roughness factors, the modeled DDA structures were similar to the experimental TEM values for the roughened particles based on spheres and roughened particles based on spheroids for the shape factors of form factor, convexivity, and solidity. The spheres and spheroids did not account for these factors and were not similar. When comparing the elongation factors, the mean aspect ratio of spheroids with an aspect ratio of 1.8, accounting for the 3 dimensions, is 1.53, which is slightly higher than the aspect ratio determined by TEM (1.38), but similar to other studies. The other elongation factors of roundness and compactness were close to the TEM results for the spheroids. In addition to matching the roughness factors, the roughened spheroid was also consistent with the elongation factors. Each particle is described in detail in the supporting information to give a full understanding of the range of particle shapes used (Table 4-3).
Table 4-2: Shape factor results for TEM analysis of hematite particles compared to modeled structures used for DDA simulations.

<table>
<thead>
<tr>
<th>Particle</th>
<th>Form Factor</th>
<th>Convexity</th>
<th>Solidity</th>
<th>Aspect Ratio</th>
<th>Roundness</th>
<th>Compactness</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEM</td>
<td>0.63 (550nm)</td>
<td>0.86 (550nm)</td>
<td>0.93 (avg.)</td>
<td>1.38 (avg.)</td>
<td>0.74 (avg.)</td>
<td>0.85 (avg.)</td>
</tr>
<tr>
<td>Sphere</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.71</td>
<td>0.83</td>
</tr>
<tr>
<td>Spheroids</td>
<td>0.83</td>
<td>0.95</td>
<td>1</td>
<td>1.53</td>
<td>0.71</td>
<td>0.83</td>
</tr>
<tr>
<td>Roughened Spheres</td>
<td>0.62</td>
<td>0.84</td>
<td>0.92</td>
<td>1.08</td>
<td>0.93</td>
<td>0.96</td>
</tr>
<tr>
<td>Roughened Spheroids</td>
<td>0.66</td>
<td>0.88</td>
<td>0.93</td>
<td>1.38</td>
<td>0.75</td>
<td>0.86</td>
</tr>
</tbody>
</table>

4.3.5 Optical properties of Hematite

We have measured the extinction cross sections of size-selected hematite aerosol particles using CRD-AES and compared our measurements to several models. In Fig. 4-6a, the experimental extinction cross sections are compared to the prediction from Mie scattering theory for monodisperse spherical particles. In addition, the extinction cross sections calculated from Mie scattering theory using the polydispersity of particle sizes observed in the TEM images are shown. Because of the large difference between the Mie scattering theory calculations and the experimental results, we conclude that spherical models are not suitable for modeling the optical properties of hematite. Particle shape and roughness need to be considered to better model the optical properties of hematite.

To understand the degree to which shape impacts the optical properties of hematite, the DDA was used to calculate the optical properties of spheroids, roughened spheres, and roughened spheroids (Figs. 4-6b-6d). The DDA calculations were run for the irregular particles that we constructed and compared to the experimentally obtained CRD-AES results. In each case, results for monodisperse and polydisperse distributions of particles are shown. To model hematite particles as spheroids, we used particles with an effective aspect ratio of 1.53, averaged over all dimensions, because it has been shown to model mineral dust mixtures well in the literature (Fig. 4-6b). The extinction cross sections of monodisperse spheroids match the experimental data better than the
calculations for monodisperse spheres. Similarly, the calculations for polydisperse spheroids match the results better than Mie scattering theory for polydisperse spheres.

Figure 4-6c shows the comparison of the measured extinction cross sections to calculations for roughened spheres. The calculation for monodisperse particles agrees well with the experimental values, but a polydisperse distribution of particles provides a better match. The roughened spheroids (Fig. 4-6d) had a slightly better match to the CRD-AES results than when just the roughened spheres were used with the average error dropping from 12.8% to 11.2%. By increasing the complexity of the model, a better agreement is seen for the hematite particles, but computational time is also greatly increased.

![Figure 4-6: Experimental extinction cross sections vs. diameter for hematite compared to (a) Mie scattering theory, (b) DDA calculations of spheroids, (c) DDA calculations of roughened spheres, and (d) DDA calculations of roughened spheroids.](image-url)
Figure 4-7 provides a comparison between the CRD-AES data and the theoretical calculations from Mie scattering theory and DDA. Roughened spheres and spheroids provide a better match to the experimental data than Mie scattering theory. In addition, a large improvement to Mie theory is observed by either using roughened spheres that closely model the roughness parameters of the aerosol particles (form factor, convexity, solidity) or by using the spheroids to capture the elongation (aspect ratio, roundness, compactness).

**Figure 4-7:** Percent differences between the model results for polydisperse particles (Mie scattering theory and DDA) and the experimental extinction cross sections. The gray line denotes perfect agreement.

4.3.6 Atmospheric Implications

We have shown that it is important to use models that incorporate the shape of particles for irregularly shaped, absorbing hematite aerosol. Figure 4-8 is a comparison of the four calculations performed for a monodisperse size distribution for spheres, spheroids, and roughened spheres and spheroids. The blue shading is the range of extinction cross sections for the different roughened spheres. As the particle complexity
is increased from spheres to roughened spheroids, the extinction cross sections of the particles increase. The higher extinction cross sections seen from the models for either the spheroids and/or roughened particles suggests that some type of irregularity must be introduced in order to sufficiently model atmospheric particles. By including these better, but more computationally intensive, models that incorporate elongation or roughness, improvements can be made in modeling absorbing mineral dust species. When the irregularity is included, there is an increase in the extinction cross section at most diameters over using Mie scattering theory.

![Graph showing comparison of calculations for monodisperse particles using Mie scattering theory for spheres (black), the DDA for spheroids (red), the DDA for roughened spheres (blue), and the DDA for roughened spheroids (green). The light blue shading around the DDA calculations corresponds to the minimum and maximum values calculated.](image)

**Figure 4-8:** Comparison of calculations for monodisperse particles using Mie scattering theory for spheres (black), the DDA for spheroids (red), the DDA for roughened spheres (blue), and the DDA for roughened spheroids (green). The light blue shading around the DDA calculations corresponds to the minimum and maximum values calculated.

In addition to the differences in extinction cross sections, the phase functions are different for each model. Phase functions are often used in remote sensing measurements
to calculate the type, size distribution, and composition of particles present in the atmosphere. We have additionally calculated the phase functions for all modeled particles (Fig. 4-15). The phase functions of the spheres generally have the lowest forward scattering, followed by the spheroids. The roughened spheroids have similar phase functions to spheroids at small diameters and are similar to roughened spheres at large diameters. For the irregularly shaped particles of both types, the Mie oscillations decrease in amplitude compared with the phase functions of spheres and spheroids, which is consistent with the literature. Example plots and further discussion of the phase functions are contained in the supporting information.

4.4 Conclusion

We have used CRD-AES to determine the optical properties of size-selected hematite particles and TEM to analyze the size selection of the particles. All of the DDA calculations that incorporate the elongation and/or roughness of the particles improve upon Mie scattering theory. The particle shapes that account for roughness are a better match than the spheroids with the best agreement obtained for roughened spheroids. Our results show that Mie scattering theory is not sufficient to model the optical properties of hematite particles and that the shape of the particles is important in determining particle optical properties. These results may be important for accurate remote sensing retrievals of absorbing mineral dust optical properties.
4.5 Supplemental Information

Overview

This supporting information contains additional details about our experimental methodology and additional results for the optical properties of nigrosin and hematite. We discuss the method used to obtain the refractive index of nigrosin and show transmission electron microscopy (TEM) images of impurities that were seen in some of the nigrosin samples. We also expand on our description of the roughened spheres and spheroids that were used for the discrete dipole approximation (DDA) calculations. Optical properties of hematite are also discussed, including the extinction cross section of individual irregularly shaped particles, a comparison of optical constant averaging methods, and phase functions.

4.5.1 Retrieval of Nigrosin Optical Properties

Nigrosin optical properties were retrieved using the cumulative fractional difference (CFD_R) as described in the manuscript. An example retrieval is plotted in Figure 4-9. For some sources of nigrosin, transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) show that the particles contain NaCl impurities that are clearly visible as small crystals surrounding the central particle (Figure 4-10). The batch of nigrosin used to retrieve refractive indices in the manuscript did not have these NaCl impurities.
4.5.2 Models used for DDA Calculations

Six different views of each roughened sphere and spheroid are shown in Figure 4-11. Each of these images is along the x, y, or z axis defined by the coordinate system for the discrete dipole approximation (DDA) calculations. Roughened sphere 2 is the particle with the least roughness while roughened sphere 5 has the greatest degree of roughness, as assessed from their form factor, convexity, and solidity. The oblate and prolate
roughened spheroids both have a roughness and elongation consistent with the analysis of hematite particles from TEM analysis.

![Image of roughened spheres and spheroids](image)

**Figure 4-11**: View of six different angles of the (a-e) five roughened spheres and (f-g) roughened spheroids.

### 4.5.3 Shape Parameters from TEM Analysis of Hematite

Six geometric parameters were calculated from the TEM images of hematite and the particles used for the DDA calculations. To describe surface roughness, the form factor, convexity, and solidity were calculated; and to describe elongation, aspect ratio,
roundness, and compactness were determined. The reported shape factors of the roughened particles constructed for the DDA calculations were calculated by taking an average over six different angles. The shape factors for the spheroids and roughened spheroids are also averaged over the results for oblate and prolate conformations. In the analysis of the TEM images of the hematite particles, the convexity and the form factor had a weak correlation with the size of the particles. None of the other factors had a dependence on particle size. To compare the geometric descriptors that had a dependence on particle size, a line was fit to the TEM results, and the value of the obtained fit at a particle diameter of 550 nm was reported. As seen in Figures 4-12a-c, and Table 4-3, the TEM analysis for form factor, convexity, and solidity match closely with our roughened particles but have lower values than the spheroids as would be expected. For comparison, the aspect ratio, roundness, and compactness agree well with the shape parameters for spheroids with an aspect ratio of 1.8. Roughened sphere 2 had the highest form factor and convexity, indicating it was the least rough, while roughened sphere 5 had the lowest form factor and convexity, indicating it had the most roughness. The solidity of all of the roughened spheres is approximately constant. Roughened spheres 2 and 5 were included to define the extremes of particle shape while the other three particles selected had values that corresponded closely to the shape factors seen in the TEM analysis of the actual particles.
Figure 4-12: Comparison of the geometric parameters obtained from the TEM results (points) with the spheroids, roughened spheres, and roughened spheroids. For reference, spheres have a value of unity for all shape factors.
Table 4-3: Geometric parameters of particles analyzed by TEM and particles generated for the DDA calculations.

<table>
<thead>
<tr>
<th>Particle</th>
<th>Form Factor</th>
<th>Convexivity</th>
<th>Solidity</th>
<th>Aspect Ratio</th>
<th>Roundness</th>
<th>Compactness</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEM</td>
<td>0.63 @550nm</td>
<td>0.86 @550nm</td>
<td>0.93 (avg.)</td>
<td>1.38 (avg.)</td>
<td>0.74 (avg.)</td>
<td>0.85 (avg.)</td>
</tr>
<tr>
<td>Sphere</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Spheroid</td>
<td>0.83</td>
<td>0.95</td>
<td>1</td>
<td>1.53</td>
<td>0.71</td>
<td>0.83</td>
</tr>
<tr>
<td>Roughened Sphere 1</td>
<td>0.64</td>
<td>0.85</td>
<td>0.92</td>
<td>1.13</td>
<td>0.88</td>
<td>0.94</td>
</tr>
<tr>
<td>Roughened Sphere 2</td>
<td>0.67</td>
<td>0.88</td>
<td>0.92</td>
<td>1.06</td>
<td>0.95</td>
<td>0.97</td>
</tr>
<tr>
<td>Roughened Sphere 3</td>
<td>0.61</td>
<td>0.84</td>
<td>0.91</td>
<td>1.07</td>
<td>0.94</td>
<td>0.97</td>
</tr>
<tr>
<td>Roughened Sphere 4</td>
<td>0.61</td>
<td>0.83</td>
<td>0.93</td>
<td>1.06</td>
<td>0.94</td>
<td>0.97</td>
</tr>
<tr>
<td>Roughened Sphere 5</td>
<td>0.55</td>
<td>0.79</td>
<td>0.91</td>
<td>1.07</td>
<td>0.94</td>
<td>0.97</td>
</tr>
<tr>
<td>Roughened Sphere Avg.</td>
<td>0.62</td>
<td>0.84</td>
<td>0.92</td>
<td>1.08</td>
<td>0.93</td>
<td>0.96</td>
</tr>
<tr>
<td>Roughened Spheroids</td>
<td>0.66</td>
<td>0.88</td>
<td>0.93</td>
<td>1.38</td>
<td>0.75</td>
<td>0.86</td>
</tr>
</tbody>
</table>

4.5.4 Comparison of roughened particles generated from spheres

Extinction cross sections for the five roughened spheres are compared in Figure 4-13. For this calculation, the particles are assumed to be monodisperse. Average values are shown in the manuscript. Roughened sphere 5, which has the highest degree of roughness, has the overall highest extinction cross section values across the size range. Although roughened sphere 2 has the smallest degree of roughness, it has similar extinction cross sections as the other roughened spheres.
Figure 4-13: Comparison of extinction cross-sections calculated using the DDA for monodisperse, roughened spheres.

4.5.5 Comparison of spectral and optical constant averaging methods

We have compared the optical constant averaging method (OCA) and spectral averaging method (SA). For the OCA method, the refractive indices are averaged before the model is run, whereas in the SA method, the model is run using both refractive indices and then the results are averaged. Figure 4-14 shows a comparison between spherical particles modeled using Mie scattering theory and roughened spheres modeled with the DDA. In each case, the two averaging methods agree well.
Figure 4-14: Comparison of the optical constant averaging method (OCA) and spectral averaging method (SA) for spheres calculated using Mie scattering theory and roughened spheres calculated using the DDA.

4.5.6 Phase Functions of Hematite

For the DDA, the effective radius \((a_{\text{eff}})\) is defined according to

\[
|m|2\pi d/\lambda < 0.5 \quad \text{S1}
\]

where \(m\) is the refractive index, \(d\) is the lattice spacing of the dipoles in the system, and \(\lambda\) is the wavelength. Since the target volume \((V)\) is related to the number of dipoles \((N_d)\) by

\[
V = N_d d^3 \quad \text{S2}
\]

and

\[
a_{\text{eff}} = (3V/4\pi)^{3/2} \quad \text{S3}
\]

then we have

\[
a_{\text{eff}} < 4.94 \frac{\lambda}{|m|} \left( \frac{N}{10^6} \right)^{1/3} \quad \text{S4}
\]
Calculations of the phase function are accurate when $a_{\text{eff}} < 2 \, \mu m$. For the phase function calculations, the 4x4 Mueller scattering matrix ($S_{ij}$) was calculated for all particle sizes. The phase function ($S_{11}$) is normalized to the total scattering by the function:

$$P(\theta, \alpha, m) = \frac{F(\theta, \alpha, m)}{\int_0^\pi F(\theta, \alpha, m) \sin(\theta) d\theta}$$

where $\alpha$ is the size parameter and $\theta$ is the angle of scattered light.$^{50}$ Figure 4-15 shows example phase function plots to compare the different models. The results are discussed in the manuscript.

*Figure 4-15:* Phase functions calculated for spheres (black line), spheroids with an aspect ratio of 1.8 (red dashed line), the average of the roughened spheres (blue dotted line), and the roughened spheroids (green dashed line). The light blue region corresponds to the minimum and maximum values from DDA calculations.
4.6 References


(20) Bohren, C. F. and D. R. Huffman (2004), *Absorption and Scattering of Light by Small Particles*; Wiley-VCH; Weinheim, Germany.


des/body_mie_type_codes.html (accessed May 2008).


Chapter 5  SEM of Clays Paper


**Abstract**

Mineral dust is the second largest atmospheric emission by mass and one of the least understood sources. The composition of mineral dust particles determines the shape of the particles, which has implications for particle optical properties and reactive surface area. Mineral dust particles are often approximated as spheroids to model their optical properties. In this study, scanning electron microscopy (SEM) is used to measure the aspect ratios of calcite, quartz, NX-illite, kaolinite (KGa-1b and KGa-2), and montmorillonite (STx-1b and SWy-2). In addition to traditional SEM images of the top of the particles, the SEM grids can be oriented approximately normal to the electron beam in order to image the side of the particles. In this manner, aspect ratios for the top and side orientation of the particles can be readily determined. Calcite particles have an aspect ratio of approximately 1.3 in both orientations, while quartz particles have an aspect ratio of 1.38 in the top orientation and 1.64 in the side orientation. The clay minerals studied all exhibited plate-like structures with aspect ratios of 1.35 to 1.44 for the top orientation and 4.80 to 9.14 for the side orientation. These values are used to estimate the specific surface areas of the clay minerals, which are compared to Brunauer-Emmett-Teller (BET) surface area measurements. Through this study, we present a
simple method for determining the aspect ratios of real aerosolized samples, rather than relying on literature values of model systems. As a result, this technique should provide a better method for determining the optical properties of mineral dust particles.
5.1 Introduction

Aerosol particles affect the radiative balance of the Earth through their interactions with light and clouds as well as their influence on atmospheric composition.\(^1\) How particles scatter and absorb light is determined by their shape, composition, and size. Mineral dust aerosol particles also act as nuclei for liquid water and ice clouds.\(^2\,3\,4\) In addition, heterogeneous chemistry on mineral dust aerosol particles can alter atmospheric composition.\(^5\,6\)

Mineral dust aerosol particles are the second largest emission by mass into the atmosphere, amounting to 1000 to 3000 Tg per year.\(^7\,8\,1\,9\) A major source of mineral dust comes from dust storms in arid regions that entrain large amounts of particulates in the atmosphere, which can subsequently be transported long distances from the source region.\(^10\,11\,12\) Up to 50\% of mineral dust emissions originate from anthropogenic sources such as agriculture.\(^1\,9\)

Aluminosilicate clay minerals are one of the most common types of mineral dust, accounting for 50-64 wt.\% of Saharan dust and up to 85\% of Asian dust.\(^5\,13\) Mineral dust is one of the most common ice nuclei, and aluminosilicate clay minerals are one of the most ice-active types of mineral dust.\(^2\,3\) Ice nuclei from field samples have been studied in great detail using scanning electron microscopy (SEM) and scanning transmission X-ray microscopy (STXM).\(^14\,15\) Among mineral dust components, clay minerals have the largest aspect ratios, with disk-like shapes and measured aspect ratios of approximately 4 to 500.\(^16\,17\) These shapes cause aluminosilicate clay minerals to have different optical properties than particles that have aspect ratios closer to unity. In addition, these particles have a large surface area to mass ratio because of their large aspect ratio. Because they
have a larger surface area to volume ratio than other types of particles, they are more active towards ice nucleation and heterogeneous chemistry per unit volume.

Clay minerals are composed of negatively charged aluminosilicate layers composed of alternating layers of tetrahedrally coordinated silicon and octahedrally coordinated aluminum, resulting in alternating tetrahedral and octahedral layers. Al\(^{3+}\) can be substituted into the tetrahedral layers and divalent cations (e.g. Mg\(^{2+}\)) can be substituted into the octahedral layers, which results in the net negative charge. Monovalent cations (e.g. Na\(^{+}\) and K\(^{+}\)) and calcium tend to sit in the interlayer sites, which holds the aluminosilicate layers together through electrostatic interactions.\(^{18}\) The number of tetrahedral to octahedral layers, e.g. 1:1 or 2:1, defines the particle type.\(^{19}\) For example, kaolinite is a 1:1 clay, while montmorillonite and illite are 2:1 clays that vary in the number and composition of interlayer ions.\(^{20}\)

Two other major components of mineral dust are quartz and calcite. Quartz is the largest component of China Loess, at greater than 50 wt.%.\(^{13}\) Calcium carbonate is a highly reactive component of mineral dust and a major fraction of Asian dust, contributing up to 12 wt.%.\(^{5, 13}\) A study of Asian dust collected over the Eastern North Pacific estimated that 5-30% of calcium carbonate was converted to CaSO\(_4\) or Ca(NO\(_3\))\(_2\) during transport.\(^5\)

Current uncertainties in the radiative impacts of mineral dust aerosol include size distributions, particle shape, and composition-resolved emission concentrations.\(^{21, 22, 23}\) Both satellite and ground based lidar measurements use algorithms that include particle shape to accurately derive aerosol mass loadings. Traditionally, shapes of particles in models are estimated by spheroids, where the axes of the spheroid are determined by the
particle aspect ratios (ratio of the width to the length or height of the particle). By using a distribution of particle aspect ratios, the radiative properties of particles have been more effectively modeled in aerosol retrieval algorithms. Many studies have found that incorporating the shape distribution with a large range of aspect ratios has improved models, but lack a physical reason for their choice of aspect ratios. Hudson et al. (2007) found that incorporating the shape of clay mineral particles (e.g. disc/needle) improves the agreement between models and laboratory results. Recently, Lindqvist et al. (2014) used SEM to characterize the shape and composition of supermicron mineral dust aerosol particles. They found a large difference between the scattering properties of spheres, spheriods, and particles with the measured shapes and compositions.

For the minerals of interest in this study, two aspect ratios are defined in reference to the substrate on which they are placed for this measurement. One aspect ratio is the ratio of the length to the width of the top of the particle (top-down orientation), and one is measured as the ratio of the length to the height of the side of the particle (side-on orientation). The axes are chosen such that the aspect ratio is greater than unity. For the larger of the two aspect ratios, it has been shown that calcite has an aspect ratio near 1, quartz has a slightly higher aspect ratio near 1.7-1.9, and clay minerals have aspect ratios from 3 to approximately 500. Previous studies have determined the high aspect ratios of clay minerals using transmission electron microscopy (TEM) and atomic force microscopy (AFM). To measure the aspect ratio using TEM, particles are coated (generally with Pt) at a known angle, approximately 10 degrees from normal. Due to the angle of the coating process, the height of the particle shields part of the substrate from being coated. The height of the particles can be calculated based on the width of the
uncoated region. Using the two dimensional projection of the particles visible in the TEM image and the height of the particle, the aspect ratios of the particle in the top-down and side-on orientations can be determined. This method assumes that the particle has no surface irregularities that may affect the observed height of the particle and that the particles do not move during the coating process. This technique has been used extensively to determine the volume of mineral dust particles. Aspect ratios for clay minerals have been as high as 1.68 for montmorillonite, 1.31 for kaolinite, and 5.33 for illite for the top-down orientation and as high as 448, 18, and 120, respectively, for the side-on orientation. Atomic force microscopy (AFM) has also been used to measure the dimensions of clay minerals without the use of a coating. In addition to microscopy methods used to study the dimensions of the particles, surface area measurements through gas adsorption studies (described below) can be used with microscopy methods to find the dimensions of the particles. Because of the need for a coating for the TEM measurement of the side aspect ratio and the nature of the AFM technique, these methods are slow. As a result, they are not used routinely to study field and laboratory samples. Instead, in studies where aspect ratios are needed for analysis, literature values are used, which may not be representative of the exact sample of interest. The development of techniques to easily measure aspect ratios for samples would help our analysis of field and laboratory samples because each sample of interest could be measured rather than depending on literature values for representative compounds. Where additional information is needed for complex particles, more time-consuming techniques such as electron tomography and focused ion beam SEM imaging can be used to obtain three-dimensional shape and composition information of particles.
Particle shape is also important for the measurement of specific surface area, which impacts aerosol reactivity and ice nucleation activity. There have been multiple strategies used to obtain a particle surface area, including scanning probe microscopy and gas adsorption. Atomic force microscopy has been used to study minerals, but it is time consuming to analyze a sufficient number of particles with this technique and it can miss some of the interior detail. The major method used for minerals is the measurement of Brunauer-Emmett-Teller (BET) surface area, where the adsorption of a non-reactive gas to the surface of the particles is used to determine the surface area. BET measurements can show variability for particles depending on the gas used with up to a 37% difference shown between N2 and Kr adsorption. For standard materials, differences from the same sample are observed from 0.19% to -12.77% for a high specific surface area material. New methods for the measurement of geometric surface area may provide a lower bound for the surface area of minerals.

In our study, we demonstrate a method for calculating the dimensions of mineral dust particles in the submicron regime using scanning electron microscopy (SEM). Previously, SEM has generally been used to describe particles larger than a micron and for elemental identification with energy dispersive x-ray spectroscopy. As described above, previous studies using TEM have required lengthy sample preparation techniques and additional assumptions to ascertain the height of particles. While AFM studies have been shown to give accurate detail of the particles, these methods are time consuming for the collection of information on hundreds of single particles. In contrast, high resolution SEM requires no sample preparation and large numbers of particles can
be analyzed quickly. We demonstrate our method on a variety of commercially available minerals.

5.2 Experimental Methods

Four types of clay minerals used were from the Source Clays Repository of the Clay Mineral Society: kaolinite, Washington County Georgia, USA (KGa-1b); kaolinite, Warren County Georgia, USA (KGa-2); montmorillonite, Gonzales County TX, USA (STx-1b); and Na-rich montmorillonite, Crook County WY, USA (SWy-2). The remaining minerals were: NX-illite (Arginotec, NX Nanopowder, B+M Notenkämper, Munich, Germany), calcium carbonate (>99.95%, Macron Chemicals), and silicon dioxide (quartz; >99%, Sigma Aldrich). Because the calcium carbonate and silicon dioxide were obtained from chemical companies, their physical and chemical properties may differ from geological sources. NX-illite is a mixture of minerals that has been suggested to have a similar composition as mineral dust that undergoes long-range atmospheric transport.2 In this study, we have investigated aerosolized samples, which may have a different composition than the bulk samples.

Aerosol particles were generated by directing a stream of nitrogen at 1.5 lpm toward the mineral dust while agitating it. The entrained dust particles were directed into a cascade impactor (PIXE International Corp., Tallahassee FL) backed with a pump at 1.0 lpm. Particles were impacted near the edge of the silicon wafer chips (Virginia Semiconductor Inc., Fredericksburg VA) for SEM analysis. For quartz particles, the silicon substrate was coated with a thin layer of Formvar 15/95 (Electron Microscopy Science, Hatfield PA) to prevent damage to the substrate from the particle impaction.
A FEI NanoSEM 630 FESEM operated at 3 keV was used to image the particles. Under these conditions, a resolution of < 2 nm can be obtained. Particles were imaged in top-down and side-on configurations. Top-down refers to the standard SEM configuration. To image side-on, the substrates were placed in a perpendicular orientation at an angle of 5° with respect to normal, and a tilt correction was used to remove distortion. The particles were imaged at an orientation that allowed for the greatest emission of secondary electrons towards the detector, which results in the best resolution. Top-down and side-on images were analyzed to measure the aspect ratios using ImageJ (National Institutes of Health, Bethesda MD). In the top-down orientation, the aspect ratio is the calculated from the ratio of the length to the width of the particle. The length is defined as the longest distance across the center of the particle; the width is measured across the longest distance in the orthogonal direction. In the side-on orientation, the aspect ratio is calculated as the ratio of the width to the height of the particle. In this study, we have investigated minerals that can be described by these two aspect ratios. We note, however, that some types of minerals have shapes that are best described by three aspect ratios (e.g. rectangular prisms). For these types of particles, the aspect ratio in the top-down orientation will not be close to unity. In this case, two aspect ratios will be averaged together in the side-on orientation. Using the top-down orientation, however, the length and width of the particles is measured, and the height is measured in the side-on orientation. By combining the top-down length and width measurements and side-on measurement of height, the three aspect ratios can be determined. Only particles with a dimension less than 1 μm were analyzed due to large quartz impurities present in some of the clay mineral samples. Using the top view of
the particles, 198 to 511 particles were analyzed for each sample. Due to the low depth of field with the SEM for the side view, 90 to 167 particles were analyzed for each sample.

The geometric specific surface area of the particles is defined as area per unit mass. To calculate the particle surface area, we have assumed three geometries for the particles: hexagonal prisms, rectangular prisms, and spheroids. Using the top-down SEM image, the length and width of each particle is measured. The aspect ratio for the side-on orientation is used to obtain the height of the particle. Using the geometry of interest, the ratio of the surface area to volume is calculated for each particle. The volumes are then normalized by the density of the particles to give units of m²/g. The densities used for the calculations were: 2.71 for calcite, 2.65 for quartz, 2.8 for illite, 2.65 for kaolinite, and 2.5 for montmorillonite. The specific surface areas for each particle are summed and divided by the number of particles to give an average specific surface area.

5.3 Results and Discussion

To demonstrate the use of scanning electron microscopy (SEM) for the measurement of the aspect ratios of mineral particles, we use commercially available samples of calcite, quartz, illite, kaolinite and montmorillonite, as described above. We report the values derived for these commonly used samples, but this technique can be extended to any sample of interest. In Figures 5-1 to 5-3, we show histograms of the aspect ratios for each type of mineral in the top-down and side-on orientations with representative SEM images. Figure 5-4 shows a box-and-whisker plot of the aspect ratios of all particle types measured for both orientations. The central value shown is the mean, the box indicates the 25th and 75th percentile, and the whiskers mark the 5th and 95th percentiles. Table 5-1 summarizes the mean aspect ratios obtained with standard
deviations. All of the particles have aspect ratios of approximately unity when only the top-down orientation is measured. The major difference between particle dimensions arises from the side-on view of the particles. There is no dependence of the aspect ratio on the size of the particles for the submicron diameters reported in this study. In the supermicron regime, a size dependence is present for some samples, such as the montmorillonite SWy-2, due to mineral contaminants. Plots of the aspect ratio as a function of particle size for submicron and supermicron particles are provided in the Supporting Information. While both kaolinite samples are > 96% pure, the STx-1b contains 67% montmorillonite and up to 3% quartz. The SWy-2 bulk sample contains 75% montmorillonite, 8% quartz, and 16% feldspar while the <2 micron fraction contains 95% montmorillonite and 4% quartz. We note that the described SEM technique can be extended without alteration to study supermicron particles.

**Figure 5-1:** a) A representative SEM image of the calcite particles in the top-down orientation. b) A representative SEM image of the calcite particles in the side-on orientation, imaged at an angle of 5° from normal. c) The distribution of calcite aspect ratios
**Figure 5-2:** SEM images of KGa-1b (kaolinite) in the a) top-down and b) side-on orientations. c) The distribution of aspect ratios determined for KGa-1b in the two orientations. d) SEM images of KGa-2 (kaolinite) in the top-down and e) side-on orientations
Figure 5-3: SEM images of NX-illite in the a) top-down and b) side-on orientations. c) The distribution of aspect ratios determined for NX-illite from the SEM images. d) SEM images of STx-1b (montmorillonite) in the top-down and e) side-on orientations.
Figure 5-4: Comparison of the aspect ratios for each species studied. For each type of mineral, the aspect ratios observed for the top-down and side-on orientations are shown. In a box and whiskers plot, the center line is the average of the data, the bottom

Table 5-1: Average aspect ratios and standard deviations for the minerals used in this study for both the top-down and side-on orientations.

<table>
<thead>
<tr>
<th>Species</th>
<th>Aspect Ratio Top</th>
<th>Aspect Ratio Side</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>1.29 ± 0.20</td>
<td>1.27 ± 0.20</td>
</tr>
<tr>
<td>Quartz</td>
<td>1.38 ± 0.28</td>
<td>1.64 ± 0.49</td>
</tr>
<tr>
<td>NX-Illite</td>
<td>1.44 ± 0.32</td>
<td>4.80 ± 2.23</td>
</tr>
<tr>
<td>Kaolinite KGa-1b</td>
<td>1.35 ± 0.22</td>
<td>7.98 ± 3.94</td>
</tr>
<tr>
<td>Kaolinite KGa-2</td>
<td>1.39 ± 0.27</td>
<td>8.89 ± 3.72</td>
</tr>
<tr>
<td>Montmorillonite STx-1b</td>
<td>1.38 ± 0.25</td>
<td>7.49 ± 4.20</td>
</tr>
<tr>
<td>Montmorillonite SWy-2</td>
<td>1.44 ± 0.29</td>
<td>9.14 ± 4.67</td>
</tr>
</tbody>
</table>
The top-down and side-on orientations of calcite have similar aspect ratios of 1.29 ± 0.20 and 1.27 ± 0.20, respectively. The range of aspect ratios observed is shown in Figure 5-1a, where the peaks that represent the measured aspect ratios for top-down and side-on orientations match closely. Figures 5-1b and 5-1c show SEM images that illustrate that the particles have a near unity aspect ratio in both orientations. Note that surface roughness affects the aspect ratios of these particles, which accounts for the aspect ratios being slightly greater than one.

Quartz has a higher aspect ratio than calcite in the top-down orientation of 1.38 ± 0.28, and deviates more from calcite with its side-on aspect ratio of 1.64 ± 0.49. These aspect ratios indicate that quartz is slightly elongated, while calcite is approximately spherical, in agreement with the literature. Figure 5-1d-f shows that the distribution of the aspect ratios for quartz in the side-on orientation peaks at a higher value than for calcite. From the top-down and side-on SEM images of quartz, the surface of these particles is smooth in contrast to the roughness of the calcite particles (Figures 5-1d and 1e).

The aspect ratios of the clay minerals in the top-down orientation range from 1.35 to 1.44, in agreement with literature values of approximately 1.4 (Table 5-2). These values are larger than the aspect ratio of calcite in the top-down orientation at 1.29 ± 0.20, but are similar to that of quartz at 1.38 ± 0.28. This result indicates that when looking at the particles in the top-down orientation in SEM or TEM, the particles look approximately spherical or cubic. The range of aspect ratio values for the top-down
orientation is similar for all clay minerals used in this study (Figures 5-2c, 2f, 3c, 3f, and 3i).

Table 5-2: Comparison of measured average aspect ratios to literature values for the clay minerals. The NX-illite is compared to measurements of illite.

<table>
<thead>
<tr>
<th>Species</th>
<th>Top</th>
<th>Side</th>
<th>Lit. Top</th>
<th>Ref.</th>
<th>Lit. Side</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NX-Illite</td>
<td>1.44</td>
<td>4.80</td>
<td>min = 2.10</td>
<td>17</td>
<td>min = 11.3</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>max = 5.33</td>
<td>16</td>
<td>max = 120</td>
<td>16</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>1.35-</td>
<td>7.98-</td>
<td>min = 1.29</td>
<td>31</td>
<td>min = 2.8</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>1.39</td>
<td>8.89</td>
<td>max = 1.14</td>
<td>31</td>
<td>max = 17.67</td>
<td>16</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>1.39-</td>
<td>7.49-</td>
<td>1.68</td>
<td>16</td>
<td>min = 3.10</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>1.44</td>
<td>9.14</td>
<td>max = 448</td>
<td>16</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The aspect ratios measured for the side-on orientation of the clay mineral dust are significantly different than the other minerals. The two kaolinite samples studied (KGa-1b and KGa-2) have similar aspect ratios in both top-down and side-on orientations and similar particle morphologies (Figure 5-2). The distribution of aspect ratios is wide, but similar for the two types of kaolinite (Figure 5-2c and 2f). The particles have regular polygonal structures with sharp defined edges and flat surfaces (Figures 5-2b, 2c, 2d, and 2e). Literature values for the aspect ratio of kaolinite measured with TEM report median values of approximately 10 with a minimum of 2.8 and a maximum of 17.67 (5-2).31,32,33,34 The kaolinite aspect ratios obtained in this study have values near the median of the literature results.

Of the clay minerals, the lowest aspect ratio is measured for the NX-illite sample at 4.80 ± 2.23. The distribution of aspect ratios of the NX-illite particles is wide when compared to calcite or quartz, but smaller than the spread for the aspect ratios of kaolinite.
and montmorillonite (Figure 5-3a-c). NX-illite samples vary in composition, but are greater than 60% illite with additional contributions from illite-smectite mixed layers, feldspar, kaolinite, quartz, and carbonates. As a result, the SEM images show different types of particles, rather than just illite. The measured aspect ratio is an average over this diverse composition, which could result in a lower aspect ratio compared to the other clay minerals. TEM studies have reported aspect ratios for illite from 2.10 to 120 (Table 5-2). From the SEM images, the particles are irregular and feathery in morphology (Figures 5-3a and 3b).

The montmorillonite particles (STx-1b and SWy-2) have the largest range of aspect ratios among the clay minerals (Figures 5-3d-i) even though they have similar average aspect ratios to kaolinite (Table 5-1). They also have the largest variation in particle morphology. STx-1b particles have a feathery appearance with rough edges (Figures 5-3d and 3e). SWy-2 has structures with flat regular features, but there are also particles similar in morphology to STx-1b and NX-illite. The SWy-2 structures were closer in morphology to the kaolinite samples than the STx-1b, but did not have the regular hexagonal structure of kaolinite (Figures 5-3g and 5-3h). In our experimental measurements, the kaolinite and montmorillonite particles have similar mean aspect ratios in both the top-down and side-on orientations, but the montmorillonite particles have a much greater range of measured values (Figure 5-4). This range of measurements is reflected in the larger standard deviation of the montmorillonite aspect ratios in comparison to kaolinite (Table 5-1). Previous studies of montmorillonite have had a much larger range of aspect ratios than kaolinite from 3.10 to 448 (Table 5-2).
Specific surface area (SSA) was calculated from the SEM images of our aerosolized samples to compare with previously published BET and AFM measurements of bulk samples. As stated previously, the composition of the aerosolized, submicron samples may differ from the bulk composition. The SSA of calcite and quartz were calculated and are expected to be close to BET measurements because of their smooth surface. Because the particles studied have a variety of shapes, we have calculated the specific surface area for each type of particle studied assuming that the particles are hexagonal prisms, rectangular prisms, and spheroids. Because BET measurements use a bulk sample for analysis, the polydispersity of the samples have to be calculated using top-down SEM images. The areas of individual particles from the top-down view were analyzed and the volume equivalent diameters were calculated using the average aspect ratios previously obtained. This distribution was then used to calculate the bulk geometric specific surface area of the submicron fraction. When our measurements are compared to the BET measurements for the same species, there is good agreement for the kaolinite species between the SEM data, BET measurements, and AFM measurements (Table 5-3). We would expect good agreement in this case because of the smooth shape of the particles. The specific surface area of the SWy-2 montmorillonite sample was overestimated, which can be accounted for by the large difference between bulk composition of SWy-2 and the <2 μm fraction. While the bulk sample contains up to 8% quartz and 16% feldspar, the <2 μm fraction contains up to 4% quartz. Quartz has a smaller specific surface area than montmorillonite, which will especially effect the calculation of specific surface area in the supermicron regime. As a result, the bulk specific surface area reported in the literature will be smaller than our experimental
estimate of the submicron fraction. The specific surface area of NX-illite is underestimated compared with measurements for illite because NX-illite is a mixture of minerals rather than pure illite. The specific surface area of STx-1b is also significantly underestimated because these species are not regular polygons. Instead, they have a wispy/flakey structure that results in additional surface area that is accounted for in the BET measurement, but not in the SEM measurement. While BET measurements with N2 do not penetrate the interlayer spacing of montmorillonite\textsuperscript{20}, they measure surface heterogeneities and pores, and therefore may result in larger values than the SEM measurements. Water in interstitial spacings is removed by heating prior to BET measurements and depleted by the vacuum conditions in the SEM. As a result, both BET and SEM measurements are unlikely to be affected by the amount of interstitial water. In summary, our calculations based on the SEM images show that there is good agreement between the specific surface area measurements found with SEM and BET when the particles are smooth in shape, and that we obtain an underestimate for more complex particle morphologies.
Table 5-3: Specific surface area (SSA) measurements using SEM, BET, and AFM. The SSA calculations from the SEM calculations are performed assuming the particles are hexagonal prisms, rectangular prisms, and spheroids. NX-illite is compared to BET measurements.

<table>
<thead>
<tr>
<th>Specie</th>
<th>SSA hex. (m²/g)</th>
<th>SSA rect. (m²/g)</th>
<th>SSA spheriod (m²/g)</th>
<th>BET (m²/g)</th>
<th>Ref.</th>
<th>AFM (m²/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>8.8</td>
<td>12.0</td>
<td>12.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>9.1</td>
<td>11.9</td>
<td>12.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>NX-illite</td>
<td>33.5</td>
<td>38.3</td>
<td>45.6</td>
<td>min = 94</td>
<td>53</td>
<td>53</td>
<td></td>
</tr>
<tr>
<td>KGa-1b</td>
<td>19.6</td>
<td>21.5</td>
<td>27.4</td>
<td>min = 10.7</td>
<td>40</td>
<td>10.1</td>
<td>38</td>
</tr>
<tr>
<td>KGa-2</td>
<td>28.7</td>
<td>31.1</td>
<td>40.4</td>
<td>min = 22.4</td>
<td>52</td>
<td>24.1</td>
<td>38</td>
</tr>
<tr>
<td>STx-1b</td>
<td>45.1</td>
<td>49.6</td>
<td>62.9</td>
<td>min = 82.9</td>
<td>54</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>SWy-2</td>
<td>54.5</td>
<td>58.9</td>
<td>77.1</td>
<td>min = 31.82</td>
<td>50</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>max = 83.8</td>
<td>50</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>max = 34.0</td>
<td>54</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.4 Conclusions

SEM provides a method of characterizing the aspect ratios of particles in the top-down and side-on orientations with little sample preparation. To demonstrate this technique, we have used common, commercially available components of mineral dust, including calcite, quartz, NX-illite, kaolinite (KGa-1b, KGa-2), and montmorillonite (STx-1b, SWy-2). In the top-down orientation (i.e., the usual SEM orientation), all mineral dust components studied have an aspect ratio of approximately unity. In the side-on orientation, the aspect ratio of calcite is approximately unity, and the aspect ratio of quartz is slightly greater than for the top-down orientation. The clay minerals that we investigated have significantly larger aspect ratios in the side-on orientation than calcite and quartz. NX-illite has the smallest aspect ratio of the clay minerals and montmorillonite has the largest range of observed values. These aspect ratio measurements were coupled with the size distribution to estimate the geometric specific surface area of the particles. The results are similar to BET measurements for smooth kaolinite particles, while they underestimate the surface area determined with BET for non-smooth illite and STx-1b montmorillonite. The SEM method introduced in this paper will allow a fast, easy measurement of the aspect ratios of mineral dust samples of interest. As a result, it has the potential to improve the calculation of the optical properties of nonspherical mineral dust particles for climate modeling and remote sensing.
5.5 Supporting Information

5.5.1 Summary

This supporting information shows additional figures of the dependence of the measured aspect ratios on particle size. Only submicron particles were used to determine the aspect ratios reported in the manuscript.

Figure 5-5: The aspect ratio as a function of the length of the longer of the two measured axes in the top-down and side-on orientations for a) calcite and b) quartz.
Figure 5-6: The aspect ratio of kaolinite as a function of the length of the longer of the two measured axes in the top-down and side-on orientations for a) KGa-1b and b) KGa-2.
Figure 5-7: The aspect ratio as a function of the length of the longer of the two measured axes in the top-down and side-on orientations for a) NX-illite, b) STx-1b montmorillonite, and c) SWy-2 montmorillonite.
5.6 References


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Chapter 6  Size Selection and Optical Extinction of Quartz and Aluminosilicate Clay Mineral Aerosol

Abstract

Mineral dust aerosols contribute to the second largest emission by mass to particulate matter in the atmosphere. Aerosol particles affect the radiative forcing budget through directly scattering and absorb light, acting as cloud condensation nuclei, and surfaces for heterogeneous chemistry. Through these effects it is uncertain whether aerosol particles cause a net warming or cooling effect. Factors that affect how the particles scatter and absorb light include composition, shape, size, and concentration. In our previous studies we have looked at the basic components of mineral dust including calcite and hematite which have an aspect ratio near one. We have currently studied the scattering properties of non-absorbing particles with higher aspect ratios than calcite. Quartz was studied and was shown to have an aspect ratio slightly greater than one, but through modeling the DDA spheroids, there was no significant improvement over the Mie theory for spheres. For the clay minerals that have a high aspect ratio, the scattering was dependent greatly upon the shape of the particle along with orientation of the particles within the flow. Size selection of these disk shaped particles using the Differential Mobility Analyzer was very small and contributed to minimal size selection of the particles due to the irregular disk shape in the flow system. A comparison of the actual size distribution from SEM measurements to the Scanning Mobility Particle Sizer shows that the SMPS system has a much larger size distribution than the actual size distribution of irregularly shaped particles. From the models we have developed for those
simple species from Mie calculations for spheres or more complex shapes through the Discrete Dipole Approximation (DDA).
6.1 Introduction:

Mineral dust is the second largest emission of particulate matter by mass into the atmosphere with 1000-3000 Tg emitted annually.\textsuperscript{1-4} The major source of this dust is the dust belt that stretches from the Sahara through central Asia\textsuperscript{5}. Up to 50% of the total dust may originate from anthropogenic sources.\textsuperscript{3, 4} The majority of this dust will gravitationally settle near the source region, but particles under 1.8 μm can undergo long range transport.\textsuperscript{6} The fine particulate matter emitted into the atmosphere can cause cardiovascular and respiratory problems.\textsuperscript{7, 8} Aluminosilicate clay minerals are one of the most abundant types of mineral dust, composing 50-60 wt. % of Saharan dust and up to 85% of Asian dust.\textsuperscript{9, 10} The other major type of mineral dust is quartz, which composes up to 50% of atmospheric dust.\textsuperscript{9}

Particle interactions with solar and terrestrial radiation are termed the aerosol direct effect. The direct radiative effect from aerosol particles has been calculated to be \(-0.5 \pm 0.4 \text{ W m}^{-2}\) with mineral dust aerosol particles contributing \(-0.1 \pm 0.2 \text{ W m}^{-2}\).\textsuperscript{3} The unknowns of composition, emission amounts, size distribution, and shape of mineral dust contribute to uncertainties in radiative balance.\textsuperscript{11-13} Models tend to use externally mixed particles, but particle radiative properties depend on the internal structure of particle as well.\textsuperscript{14-16} While particles are often modeled using spheres, researchers have started to incorporate spheroids with a large range of aspect ratios that more accurately model the scattering properties of mineral dust.\textsuperscript{17-20}

Particle shape has been shown to be important for modeling the optical properties of mineral dust aerosol particles.\textsuperscript{21, 22} Particles such as aluminosilicate clay minerals consist of alternating layers of tetrahedrally coordinated silicon and octahedrally
coordinated aluminum and have large aspect ratios.\(^{23}\) The reported aspect ratios of aluminosilicate clay minerals range from 3:1 to 500:1.\(^{24-26}\) In contrast, quartz (\(\text{SiO}_2\)) has an aspect ratio near unity at 1.7-1.9.\(^{27}\) Not only is the size important for the optical properties of particles, but can have an effect on the nucleation ability of the particles. Previous nucleation studies have shown a difference between the ice nucleation ability of size selected particles using a differential mobility analyzer, with larger mobility diameters acting as better ice nuclei.\(^{28-30}\)

The scattering and extinction cross sections of high aspect ratio mineral dust aerosol have been investigated previously using polar nephelometers and long pass infrared instruments. For aluminosilicate clay minerals, Mie scattering theory does not model the phase functions well and either simulated phase function from experimental data or models that account for the high aspect ratios of these particles are needed.\(^{31-33}\) For these studies, spheroids showed a great improvement in the modeling of the experimental phase function compared to the spheres modeled with Mie scattering theory.\(^{32-35}\) Even though better agreement with theory is observed for these models, they underestimate the scattering of the particles. Quartz has also been modeled as spheres and spheroids, and elongated shapes were found to provide a better model for the optical properties of the particles.\(^{31, 33, 36}\)

Cavity ring-down aerosol extinction spectroscopy (CRD-AES) has been previously used to study mixed organic/salt particles, mineral dust species.\(^{15, 37-42}\) CRD-AES has a high sensitivity due to having a long effective path length and independence from laser output intensity.\(^{39, 43}\) Because of the high sensitivity of CRD-AES, it can be used for size selected samples at a low concentration. This high sensitivity has been
recently been demonstrated by the use of CRD-AES for single particle extinction cross section measurements.\textsuperscript{44} Other techniques to measure the scattering properties of aerosol particles include nephelometers and mid-IR extinction spectrometers but these are limited due to their high detection limit and need to use bulk samples.\textsuperscript{45-47}

We have characterized the extinction cross sections and size selection of aluminosilicate clay minerals (kaolinite, montmorillonite, and NX-illite) and quartz using CRD-AES and electron microscopy. Electron microscopy has been used to obtain the shape of the particles, which we incorporated into models to provide aspect ratios for spheroid calculations, but the shape has not been used.\textsuperscript{48} From our previous experiments, the aspect ratios of each species are known and used in this paper to model the particles using the Discreet dipole approximation (DDA).\textsuperscript{26} The extinction using DDA is compared to Mie scattering theory to understand the effect of shape on the particle optical properties. As we have shown previously, electron microscopy is essential for understanding the polydispersity of the size selection of the particles.

6.2 Experimental Methods:

6.2.1 Generation of Aerosol Particles:

Particles were aerosolized using the dry generation method previously described in earlier publications.\textsuperscript{41, 42} Mineral dust analogs studied included: NX-illite (Arginotec, NX Nanopowder, B+M Notenkämpfer, Munich, Germany), silicon dioxide (quartz; >99\%, Sigma Aldrich), kaolinite, Warren County Georgia, USA (KGa-2); and montmorillonite, Gonzales County TX, USA (STx-1b). Each species was aerosolized by directing a flow of nitrogen at 1.5 lpm over the powder while constantly stirring. These
aerosolized particles were then directed through an Erlenmeyer flask to maintain a steady concentration of particles. Excess particles were pumped away and the flow was diluted to 1.5 lpm. A diagram of the setup is included in the supplemental information.

6.2.2 Size Selection of Aerosol Particles:

Aerosolized particles were size selected using an electrostatic classifier (TSI 3080, Shoreview MN) and a differential mobility analyzer (DMA; TSI 3081, Shoreview MN) for sizes ranging from 250 nm up to 900 nm. The particles were first introduced to a sealed $^{85}$Kr source to give them a known charge distribution of 0, ±1, ±2, etc. Particles then passed through a DMA where a potential is applied across concentric cylinders, where only particles with the correct electrostatic mobility will be size selected. Generally the ratio of the sheath flow to aerosol flow is 1:10, but previously we have shown better size selection for larger, irregularly shaped particles with a lower ratio. Each particle type was passed through the DMA at 1.5 lpm, adjusting the sheath flow rate from 2.7 to 8.8 lpm depending on the size selected. These size selected particles are then passed through the CRD-AES to determine optical extinction before being counted by a condensation particle counter (CPS; TSI 3775, Shoreview MN). Size distributions of the particles were determined using the scanning mobility particle sizer (SMPS) (TSI, Shoreview, MN).
6.2.3 Optical Properties of Aerosol Particles:

A cavity ring-down aerosol extinction spectrometer was then used to determine the optical extinction of the size selected particles as described in previous publications. A laser with a wavelength of 643 nm was modulated at 500 Hz and passively coupled to a 91 cm long cavity. At each end of the cavity there are highly reflective mirrors (>99.9985 at 640 nm). The transmitted light from each pass is then collected using a fiber optic cable and the signal amplified using a photomultiplier tube. The signal is then analyzed using LabView software (National Instruments, Austin, TX). The characteristic ring-down time for our instrument is 165 μs, corresponding to an effective path length longer than 48 km. The extinction coefficient can be calculated from the ring-down time of each pulse using

$$b_{ext} = \frac{R_L}{c} \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right)$$

where \(\tau_0\) is the decay constant of the ring down time without aerosol particles and \(\tau\) is the ring-down time with aerosol particles in the cavity. The constants in Eqn. 1 are \(R_L\), the ratio of the total cavity length to that occupied by aerosol particles, and \(c\), the speed of light. The extinction cross section can be calculated according to

$$\sigma_{ext} = \frac{b_{ext}}{N}$$

where \(b_{ext}\) is the extinction from the cavity, and \(N\) is the number of particles per cm\(^3\).

6.2.4 Scanning Electron Microscopy (SEM):

SEM was used to constrain the size selection of the aerosol particles from the DMA. We have shown previously the utility of electron microscopy to observe the size
selection of irregular particles to model aerosol optical properties.\textsuperscript{41, 42} SEM was used because it can be used to obtain information about both the top-down and side-on aspect ratios of the particles.\textsuperscript{26} After size selection with the DMA, the aerosol flow was directed into a cascade impactor (PIXE International Corp. Tallahassee FL) that was backed with a pump at 1.0 lpm. Particles were collected on silicon wafer chips (Virginia Semiconductor Inc., Fredericksburg VA) for SEM analysis. For quartz particles, the silicon substrate was coated with a thin layer of Formvar 15/95 (Electron Microscopy Science, Hatfield PA) to prevent damage to the substrate from the particle impaction. For all species, the silicon was coated with low molecular weight polymer (3M double-sided sticky tape) dissolved in HPLC grade chloroform to increase the collection efficiency. Concentrations of the particles being collected were monitored by CRD-AES to obtain enough particles for analysis. A FEI NanoSEM 630 FESEM operated at 3 keV was used to image the particles at each size selected, and 419 to 643 particles were analyzed per sample.

From the SEM images, the area equivalent diameter of each particle could be calculated using ImageJ software (National Institutes of Health, Bethesda, MD). The side-on aspect ratios, which account for the height of the particles, were used from our previous study and the volume equivalent diameters were calculated assuming that the particles were spheroids.\textsuperscript{26} Values used for the top-down/side-on aspect ratios were: quartz (1.38/1.64), NX-illite (1.44/4.80), KGa-2 (1.39/8.89), and STx-1b (1.38/7.49).\textsuperscript{26}

6.2.5 Modeling Optical Properties of Aerosol Particles:

Quartz is a birefringent material with an ordinary and extraordinary refractive index of approximately 1.55. All the clay minerals are biaxial, causing a trirefringence in
the particles. Because of the complex behavior of the refractive indices of the clay minerals, the literature refractive indices are reported as an average over a bulk sample with no orientation effects.\textsuperscript{51} For illite, the range of refractive indices reported was 1.54-1.60 with an average value of 1.57. Kaolinite had a refractive index range of 1.55-1.57, which averages to 1.56. Montmorillonite had the lowest refractive index of these clay minerals with a range of 1.49-1.55, which averages to 1.52.\textsuperscript{51, 52} None of the minerals absorb significantly at 643 nm.

6.2.6 Mie Scattering Calculations of Extinction Cross Section:

Optical properties were determined for spherical and non-spherical particles. For modeling spherical particles, Mie scattering theory was performed using a MATLAB version of BHCOAT.\textsuperscript{15, 16, 39, 53} To calculate the extinction efficiency, $Q_{\text{ext}}$, at each size, the refractive index, $m$, is known and the size parameter $x_{ae} = \pi d_{ae}/\lambda$ can be calculated from the diameter. The extinction cross section of each volume equivalent diameter was calculated based on the literature values of the refractive indices, as described above. The extinction cross section, $\sigma_{\text{ext}}$, can then be calculated using $\sigma_{\text{ext}} = \pi Q_{\text{ext}} (d_{ae}/2)^2$. A weighted average of the extinction cross sections was then used to calculate the extinction cross section for polydisperse spheres at each mobility diameter according to

$$\sigma_{\text{ext}} = \frac{1}{n_{\text{tot}}} \sum_{i=1}^{n_{\text{tot}}} \sigma_{\text{ext},i}$$

for mobility diameters from 250 to 900 nm. We did not assume the particles were spherical from the SEM, and as described above, the volume equivalent diameter can be calculated using the aspect ratios and normal SEM imaging. Error was estimated by
dividing each of the SEM images into three subgroups. For each of these three subgroups, the polydisperse extinction cross section was found and the standard deviation between these three measurements is used as an overestimation of the error.

6.2.7 Discreet Dipole Approximation calculations of extinction cross section:

To model the disk-like shape of high aspect ratio particles, the discreet dipole approximation (DDA) was used to calculate the scattering properties of irregular spheroid particles. In the DDA, a particle is defined as a finite number of dipoles in an array. DDA calculations were performed using DDSCAT 7.2 developed for FORTRAN-90.\textsuperscript{54, 55} The volume equivalent diameters calculated from SEM were used to obtain the polydispersity at each mobility diameter. The accuracy of the scattering cross section of particles using DDA is acceptable up to a certain size ($a_{\text{eff}}$), which depends on the number of dipoles used in the dipole array according to

$$a_{\text{eff}} < 9.88 \frac{\lambda}{|m|} \left(\frac{N_d}{10^6}\right)^{1/3}$$

where $\lambda$ is the wavelength, $m$ is the refractive index, and $N_d$ is the number of dipoles in the array.

For calculations of the scattering properties of roughened particles, an average of 196 scattering angles is required to get convergence of each extinction cross section.\textsuperscript{42, 56} Because spheroidal particles have multiple symmetry axes compared to roughened particles, less scattering angles are needed. As a result, only 24 scattering angles were used for the spherical particles due to the symmetry of the particles. This number
corresponds to the same number of particle orientations as the roughened particles from our previous study.\textsuperscript{42}

Mie scattering theory calculations were used to fit the extinction cross section obtained from the DDA calculations of each spheroid. The effective refractive index calculations were performed using the results from the DDA calculations at various size ranges and fitting a Mie scattering curve using the cumulative fractional difference (CFD\textsubscript{R}).\textsuperscript{16, 42, 57} The minimum CFD\textsubscript{R} value corresponds to the best fit for the refractive index \( n \) for

\[
\text{CFD}_R = \frac{1}{P} \sum_{\text{All Sizes}} \frac{|b_{\text{ext, DDA}} - b_{\text{ext, Mie}}|}{b_{\text{ext, DDA}}}
\]

where \( P \) is the number of particle sizes selected. For each mineral type, best fit parameters were determined for the diameter ranges: 30-1010 nm, 30-490 nm, 510-1010 nm, 30-210 nm, 230-410 nm, 430-610 nm, 630-810 nm, and 830-1010 nm. Using multiple size ranges allows us to account for a best fit effective refractive index dependent upon size.

6.3 Results and Discussion:

The optical properties of mineral dust components with an aspect ratio greater than unity have been studied using CRD-AES and computational methods. To characterize the size selection of the mineral dust particles, SEM was used to analyze the volume equivalent diameters at various mobility diameters selected using the DMA, as described above. Additionally, a comparison of the size selection of particles by DMA was compared to SEM measurements. The obtained size distributions from the SEM
measurements were used to calculate the theoretical optical extinction cross sections at each mobility diameter.

6.3.1 Size Distributions of Quartz

Figures 6-1a and 6-1c show a comparison of size distributions plotted as a function of volume equivalent diameter for particles size selected at mobility diameters of 350 nm and 750 nm. For a mobility diameter of 350 nm, the mean particle size is 269 nm. For a mobility diameter of 750 nm, a distribution of smaller particles that is similar to the size distribution for the bulk sample is observed in the SEM measurements. The large amount of small particles can be accounted for by the large particles that are size selected are aggregates that break apart when impacted on the substrate. When the size selected size distributions were compared to calcite both had a maximum near the mobility diameter selected, but with a higher polydispersity than was seen for spherical ammonium sulfate particles. SEM images of the collected particles for mobility diameters less than 550 nm show single particles. In contrast, in SEM images of particles impacted at mobility diameters of ≥ 650 nm, were aggregates that broke apart when impacted on the SEM substrates (Figure 6-1e). As a result, the size distributions obtained with SEM for particles at a mobility diameter larger than 550 nm have peaks at volume equivalent diameters that were similar to that of the bulk sample. Additionally, the size distribution from SMPS, which is plotted as a function of mobility diameter, was compared to the size distribution obtained by SEM images, which is plotted as a function of volume equivalent diameter. The peak in the SMPS spectrum occurs at a mobility diameter of 217 nm, whereas the peak in the size distributions of the bulk powder
obtained from SEM occurs at a volume equivalent diameter of 160 nm. This difference can be accounted for by the elongated shape of the quartz particles. Additionally, we have seen for size selected particles above 500 nm, there are many aggregates formed. When the aggregates are impacted for SEM analysis, some break apart to form particles that are between 100 and 200 nm in size. The breakup of these aggregates would contribute to making the SEM size distribution of the bulk sample skewed towards smaller particle sizes.

Figure 6-1: Quartz size selected at a) 350 nm and c) 750 nm, b) comparison of bulk sample by SEM (bars) and SMPS (line), and SEM image of quartz at d) 350 nm and e)750 nm

6.3.2 Size Distributions of Aluminosilicate Clay Minerals

SEM analysis of bulk samples of KGa-2 yield the largest average particle size of the clay mineral species studied with a maximum at a volume equivalent diameter of approximately 80 nm (Fig. 6-2b). In comparison, the size distribution from the SMPS system has a peak at a mobility diameter of 136 nm and a broader distribution. When
these particles were size selected, little difference was observed in the size distributions of volume equivalent diameters at mobility diameters of with the peak of the distribution centered at volume equivalent diameters of approximately 80 nm (Figure 6-2a and 2c). The major difference in the size selection of the particles is that for a mobility diameter of 750 nm, particles above a volume equivalent diameter of 300 nm are allowed to pass through. At a selected mobility diameter of 750 nm, the average volume equivalent diameter is 105 nm while size selected particles at 250 nm have an average volume equivalent diameter of 87 nm. This difference in the SEM volume equivalent size and SMPS size shows that the size selection of the particles by the DMA is not good and will let many small particles through at every mobility diameter as seen for size selected particles at 250 nm and 750 nm. A representative SEM micrograph of KGa-2 particles is shown in Figure 6-2d.

**Figure 6-2:** Kaolinite (KGa-2) size selected at a) 350 nm and c) 750 nm, b) comparison of bulk sample by SEM (bars) and SMPS (line), and SEM image
For NX-Illite, the size selection of the particles was similar to KGa-2 in that the range of volume equivalent diameters transmitted through the DMA increased with mobility diameter. The peak in the distribution of volume equivalent diameters for both the 250 nm and 750 nm size selected particles was 30 nm, but as is seen in Figures 6-3a and 3c, the number of particles transmitted that are larger than 100 nm is greater for a mobility diameter of 750 nm. The peak in the distribution of volume equivalent diameters for the bulk NX-illite sample was also 30 nm, with a similar shape of the distribution compared with the to the size selected samples. In contrast, the SMPS size distribution (Figure 6-3b) has a peak at a mobility diameter of 188 nm includes particles with mobility diameters greater than 500 nm. This large difference in the peak of the SMPS and SEM size distributions, suggests that particle shape affects the size selection. A representative SEM image of the NX-illite particles is shown in Figure 6-3d.

![Figure 6-3: NX-Illite size selected at a) 350 nm and c) 750 nm, b) comparison of bulk sample by SEM (bars) and SMPS (line), and SEM image](image)
The distributions of volume equivalent diameters for bulk and size-selected STx-1b are similar to the NX-illite species in that the peak volume equivalent diameter for all samples occurs at 30 nm (Figure 6-4a, 4b and 4c). Particles size selected at a mobility diameter of 700 nm have more particles with a volume equivalent diameter larger than 100 nm than for a mobility diameter of 300 nm. This result is similar to KGa-1b and NX-illite samples in that larger mobility diameters result in a larger range of volume equivalent diameters. The peak in the distribution of volume equivalent diameters for bulk NX-illite is 30 nm, compared to 269 nm for the peak in the size distribution of mobility diameters obtained with SMPS. The distribution of mobility diameters obtained from SMPS of the STx-1b species has the largest range of sizes of any of the aluminosilicate clay minerals studied here, which could indicate that their flakey shape (Figure 6-4d) has a large effect on the electrostatic mobility of the particles in the DMA. To summarize, for all three aluminosilicate clay minerals, little difference in the size distribution of volume equivalent diameters as a function of mobility diameter was observed. The size selected particles furthermore have a similar distribution of volume equivalent diameters as the bulk samples. The major difference between mineral types is that KGa-2 has a larger peak volume equivalent diameter.
Figure 6-4: Montmorillonite (STx-1b) size selected at a) 300 nm and c) 700 nm, b) comparison of bulk sample by SEM (bars) and SMPS (line), and SEM image

6.3.3 Particle Shape and Size Selection:

The mobility diameter selected is compared to the mean volume equivalent diameter obtained from electron microscopy (Figure 6-5). The line corresponds to the case when the mobility diameter is the same as the mean volume equivalent diameter. Nearly spherical ammonium sulfate particles fall on this line. We have previously observed that nearly spherical particles are transmitted through the DMA with a narrow distribution of volume equivalent diameters that can be modeled well by the transfer function. The quartz particles are smooth but have aspect ratios of 1.38 and 1.64. The mobility diameter of particles size selected at a mobility diameter of 500 nm agrees well with the mean volume equivalent diameter, but have a much higher polydispersity than
spherical particles due to their elongated shape. Above a mobility diameter of 500 nm, the particles aggregate broke apart when impacted on the SEM substrates, leading to a large difference between mobility diameter and mean volume equivalent diameter. For the aluminosilicate clay minerals, the mean volume equivalent diameter is smaller than the mobility diameter selected. The mean volume equivalent diameter increases slightly with mobility diameter indicating that there is some size selection occurring. We have shown that when the irregularity of particles is increased from spherical particles to slightly irregular particles to high aspect ratio particles, the size selection through the DMA decreases. With added irregularity the size distributions at each mobility diameter approaches the bulk polydispersity. The size selection of these different types of particles has implications whenever particles are size selected to analyze.
Figure 6-5: Comparison of mean volume equivalent diameter by SEM to the mobility diameter selected by the DMA. The line is a 1:1 fit where the average size would match the size selected.

Particle size selection through a DMA is contingent on factors that include aerosol flow rate, sheath flow rate, applied potential, particle size, and particle shape. Previously we have shown that when roughened particles with an aspect ratio close to unity are transmitted through a DMA, a more polydisperse size distribution of particles is transmitted than would be calculated based on the transfer function for spherical particles.\textsuperscript{41,42} In our studies of calcite and hematite, we assumed that they would not have a preferred orientation in the flow because their aspect ratio was close to unity. Particles with a high aspect ratios, such as those used in this study, it are expected to adopt a preferred orientation parallel to the flow direction.\textsuperscript{58-62} To account for orientation, the dynamic shape factor ($\chi$) would have to be used,
with \( F_D^p \) being drag force of the actual non-spherical particle and \( F_D^{pe} \) being the drag force of a volume equivalent sphere. Values of the dynamic shape factor are generally >1 for rough spheres, but for spheroids it is generally <1 due to their orientation in the flow.\(^{63}\) Previous studies have shown that when there are aggregates of spheres, they will orient in the flow.\(^{64, 65}\)

### 6.3.4 Optical Properties of Quartz Aerosol:

Quartz minerals have a slightly elongated shape with aspect ratios of 1.38 and 1.64.\(^{26}\) Because the shape is elongated, the optical properties of these particles are different than for spherical particles. Previous experiments have shown that the scattering phase functions of these particles are better modeled by spheroids than spheres.\(^{31, 34, 36}\) Total extinction in the IR region is better modeled through incorporation of a spheroid model.\(^{33}\)

Figure 6-6 shows the results from CRD-AES measurements for quartz. As we previously observed, the polydispersity of volume equivalent diameters at each mobility diameter is large and needs to be incorporate to accurately model the extinction cross sections of these particles.\(^{41}\) For mobility diameters smaller than 450 nm, the extinction cross sections from CRD-AES (red diamonds) are higher than predicted by Mie scattering theory for monodisperse spheres (black line) and lower for mobility diameters greater than 450 nm. When the polydispersity in volume equivalent diameters for each
mobility diameter was incorporated into the calculation of theoretical extinction cross section, Mie scattering theory modeled the experimental results well for mobility diameters up to 550 nm. At larger sizes, the calculated extinction cross sections were lower than the experimental results because larger aggregated particles break apart when impacted on the SEM substrates, resulting in a larger number of smaller particles. As a result, the calculated extinction cross sections are lower than the experimental results.

The quartz particles were also analyzed using the DDA for spheroids with aspect ratios of 1.64. The DDA calculations did not greatly differ from Mie scattering theory. The major difference between the two sets of calculations was that the oscillations present in the Mie scattering theory calculations were dampened in the DDA calculations (Figure 6-6). Even when the polydispersity of the size distribution is included in the calculations, no improvement was observed between modeling quartz particles as spheroids or spheres. The major difference between Mie scattering theory and the DDA calculations is in the scattering phase functions of the particles (Figure 6-9).
Figure 6-6: Extinction cross section vs mobility diameter for quartz. Monodisperse Mie theory (solid line) and monodisperse spheroid line (dashed line) are compared to the extinction from CRD-AES (diamonds) and theoretical Mie calculations that include polydispersity from volume equivalent SEM measurements.

6.3.5 Optical Properties of Aluminosilicate Clay Mineral Dust Aerosol:

The extinction cross sections of the aluminosilicate clay mineral particles were measured using CRD-AES. Previous research has shown that Mie scattering theory does not model the optical properties of these compounds well, and that accounting for shape allows the models to better agree with the measured scattering properties. Our measured extinction cross sections were much lower than predicted from calculations. Mie scattering theory calculations for monodisperse particles are compared to the experimental results in Figure 6-7. Each type of aluminosilicate clay mineral has lower values for the extinction cross sections than predicted from calculations except at small diameters. When the polydispersity of volume equivalent diameters observed at each mobility diameter was incorporated into the Mie scattering theory calculations, both NX-
illite and STx-1b calculations were lower than the measured extinction cross sections because the maximum in the size distribution occurred at a volume equivalent diameter of 30 nm. While KGa-2 had a maximum in the size distribution at a volume equivalent diameter of approximately 80 nm, these particles exhibited the lowest experimental extinction cross sections. As a result, we analyzed KGa-2 to determine what shape parameters are needed to model the extinction cross sections of these particles. We note that the kaolinite particles have a smoother surface morphology than NX-illite or montmorillonite. The rough features of NX-illite and montmorillonite increase the overall surface area of the particles, allowing for more light scattering.

We also calculated the extinction cross sections using DDA of volume equivalent spheroids for monodisperse and polydisperse systems. The calculated extinction cross sections of the spheroidal particles is smaller than the calculated extinction cross sections from Mie scattering theory, and the oscillations present for Mie scattering theory are dampened. The CRD-AES measurements were lower than the calculations due to the size selection of the minerals and orientation of the particles in the optical cavity as discussed above. For the phase functions, the forward scattering is enhanced for the spheroids (Figures 6-10).
Because the CRD-AES extinction cross sections of the aluminosilicate clay minerals deviated from the calculations for spheres and spheroids, additional parameters were used to investigate the role of particle orientation on the extinction cross sections. In Figure 6-8, the experimental extinction cross sections for kaolinite are compared to the calculations for spheres, spheroids, and spheroids oriented parallel to the flow. The spheroidal DDA calculations differed greatly from the Mie calculations depending on the orientation of the spheroids. The oriented averaged particles had a lower extinction cross section than Mie, while particles oriented parallel to the flow, there is a lower extinction cross section below approximately 600 nm and a higher extinction cross section at diameters greater than 600 nm. Neither of these two models addressed the difference in scatter as would be expected because we have shown above that there is little size selection of these particles at any diameter. When the polydispersity of the particles was
included to see the difference, if only the area equivalent diameter was used (not using
the height obtained using SEM) then there is a match at 250 nm, but as the size selection
gets higher the extinction cross section that includes polydispersity drops slightly. When
a volume equivalent diameter is used that includes the height of the particles from SEM
analysis it is seen that the match is actually worse than any of the monodisperse fits.
Additionally it can be seen that incorporation of the polydispersity utilizing the volume
equivalent diameters that there is an increase in the extinction of the particles which
would be expected from the CRD-AES measurements. Even though a good match of the
CRD-AES data was not obtained for these measurements utilizing the monodisperse or
polydisperse match, the correct direction of scattering can be found as long as the shape
of the particles is taken into account when correcting for the polydispersity in the
samples. The low extinction cross sections obtained from the modeling could be due to
an increase in the concentration of kaolinite in the center of the cavity due to the lift
forces. Since the laser is centered in the CRD-AES instrument cavity, an increase in
particle concentration in the center of the cavity would increase the values of the
extinction coefficients observed, but not affect the particle concentration measured with
the CPC. Additionally, spheroids have a smaller surface area for scattering than the
actual kaolinite particles; which could reduce the calculated extinction cross sections.
Figure 6-8: Extinction cross section vs mobility diameter for KGa-2. The CRD-AES data (blue circles) shows the experimentally determined cross section at each mobility diameter. The solid lines represent the monodisperse fits for Mie theory, randomly oriented spheroids, and oriented spheroids. Polydispersity is taken into account to account for theory at 250 and 750 nm and is shown for both the particles treated as area equivalent spheres and volume equivalent spheres.

Additional considerations include the introduction of irregular particles that orient in the flow of the cavity, such as disk like aluminosilicate clay minerals. These minerals have a preferred orientation in the flow and orient the long axis in the direction of the flow.\textsuperscript{58-61} This orientation of the particles is dependent on flow rates and sizes of the particles. Previously the alignment has been described by systems that have a Reynolds number greater than 0.1 will have some alignment to the flow.\textsuperscript{59} For our system, inside the cavity itself the Reynolds number is much higher than 0.1 at approximately 182, which would lead to orientation of disk type particles. Since the particles are oriented parallel to the flow there will be additional interactions that can be of consequence for this particle type. For flow systems there is created a lift force away from the walls created by a pressure and flow differential pushing the particles away from the walls towards the center of the cavity.\textsuperscript{66} This force will affect disk shaped particles oriented in
the flow greater than spherical particles and cause a particle gradient within the cylinder. The combination of orientation of the particles and a possible concentration increase in the center of the cavity of the particles will lead to a change in the optical extinction compared to randomly distributed particles in the atmosphere.

6.3.6 Atmospheric Implications:

Mie scattering theory was used to fit each refractive index at different size ranges for quartz, NX-illite, KGa-2, and STx-1b from scattering from spheroids modeled using the DDA. The fits were done over different size ranges to determine what effective refractive index can be used for Mie scattering theory instead of more complex spheroids. Table 6-1 shows the literature refractive index used for the calculations of spheroids and the retrieved effective refractive index obtained from Mie scattering theory. Because the quartz particles have a low aspect ratio (1.64), the retrieved refractive index was the same as the literature value at 1.55. For the aluminosilicate clay minerals, the retrieved refractive indices were 0.05 to 0.09 lower than the literature refractive indices (Table 6-1). In the supporting information, we retrieve refractive indices for different size ranges to obtain more accurate approximations of the calculations for spheroids. From these spheroid calculations fitted to Mie scattering theory at different size ranges, Mie scattering theory can be used to accurately determine the extinction of high aspect ratio particles in different size regimes.
Table 6-1: Literature refractive index and effective Mie refractive index calculations for quartz, NX-illite, kaolinite, and montmorillonite.

<table>
<thead>
<tr>
<th>Species</th>
<th>Lit Refractive Index</th>
<th>Equivalent Refractive index for Mie from DDA (fit-value) (30-1010 nm fit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>1.55</td>
<td>1.55 (0.032)</td>
</tr>
<tr>
<td>NX-Illite</td>
<td>1.572</td>
<td>1.52 (0.096)</td>
</tr>
<tr>
<td>KGa-2</td>
<td>1.564</td>
<td>1.47 (0.114)</td>
</tr>
<tr>
<td>STx-1b</td>
<td>1.522</td>
<td>1.45 (0.108)</td>
</tr>
</tbody>
</table>

Quartz and aluminosilicate clay minerals have been studied to investigate the impact that shape has on the size-selection and the extinction cross sections of the aerosol particles. When particles are elongated or rough in shape, the polydispersity of the size selection increases. When particles have high aspect ratios, as in the case of aluminosilicate clay minerals, the samples are effectively not size selected by the DMA. We have additionally shown that the extinction cross sections non-absorbing mineral dust with low aspect ratios can be modeled as polydisperse spheres, but shape needs to be incorporated to model the optical properties of non-absorbing particles with high aspect ratios. The experimental extinction cross section for the clay minerals is smaller at most diameters than any of the models used. For aluminosilicate clay minerals, the shape, orientation, and concentration at different parts of the flow need to be accounted for in reference to the radiation source.

6.4 Conclusion:

We have used cavity ring-down aerosol extinction spectroscopy to measure the extinction cross sections of quartz and clay minerals. SEM was used to determine the size distribution of bulk and size selected particles for comparison with SMPS results.
For the quartz particles which have an aspect ratio near one, the size selection corresponded closely to that of the mobility size selected. For the disk shaped clay minerals, there was shown to be very little size selection of the particles through the DMA, with the bulk size distribution found at each mobility diameter with only a slight size cutoff of larger particles at smaller mobility diameter selected. Comparison of the SMPS size distributions and clay minerals by SEM, the actual size distribution by SEM was considerably smaller than the SMPS size distribution. In order to model the optical properties of the mineral species, two approaches were taken. First using the spherical Mie theory, then using spheroids from DDA calculation. For quartz, there was no discernable difference between spherical models and models that had spheroids with an aspect ratio of 1.64. For the clay minerals, the spheroids with high aspect ratios use (4.8-8.89) showed considerable improvement over spherical models, but due to very little size-selection and orientation effects in the flow system, considerations of shape and flow orientation are needed to better model the optical properties of these disk shape particles.

We have shown that shape is important and needs to be accounted for in models and aerosol retrieval methods for clay minerals with high aspect ratios.

6.5 Supplemental Material

Summary

The supporting information contains additional details about our experimental methodology and additional results for the optical properties of quartz and clay minerals. We discuss the methods used to generate, size-select, and analyze the mineral dust
species. Additional discussion and figures for phase function comparison of Mie and DDA calculations are described for all species studied. Mie fits for the different size ranges calculated from the DDA calculations are discussed.

6.5.1 Experimental Setup

Figure 6-9 is a diagram of the experimental setup for generation, size selection, optical extinction, counting, and collection of aerosolized mineral dust particles. The mineral dust is first aerosolized by flowing nitrogen over a powder that is constantly agitated. The aerosolized mineral dust is then flowed through an Erlenmeyer flask to maintain a constant concentration. Concentration of the particles is maintained by pumping out the flow and diluting it to 1.5 lpm. The flow is directed through the differential mobility analyzer to size select the particles. The size-selected aerosol particles are then passed through the cavity ring-down spectrometer to measure the optical extinction. The particles are then counted by the condensation particle counter or collected for TEM analysis.41, 42
6.5.2 Comparison of Phase Function Models

Phase functions show the directions and intensity of light scattered off of a given target. Calculations of the phase function for our DDA measurements are accurate when $a_{\text{eff}} < 2 \, \mu\text{m}$.\textsuperscript{42} For the phase function calculations the 4x4 Mueller scattering matrix ($S_{ij}$) was calculated for all particle sizes. The phase function ($S_{11}$) is normalized to the full scattering by the function:

$$
P(\theta, \alpha, m) = \frac{F(\theta, \alpha, m)}{\int_{0}^{\infty} F(\theta, \alpha, m) \sin(\theta) d\theta}
$$

where $\alpha$ is the size parameter and $\theta$ is the scattering angle.\textsuperscript{68} Figure 6-10 to 6-13 show example phase function plots to compare the different models for each of the species studied. Even though we have shown that quartz matches closely with either Mie theory for spheres, or spheroids with an aspect ratio of 1.64, there is a difference in the phase
functions between models (Figure 6-10). Clay minerals DDA models with high aspect ratios tend to have higher forward scattering at all sizes than Mie spheres (Figures 6-11 to 6-13).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6-10.png}
\caption{Quartz phase function for a) 250 nm b) 550 nm and c) 850 nm}
\end{figure}
Figure 6-11: NX-Illite phase function for a) 250 nm b) 550 nm and c) 850 nm
Figure 6-12: KGa-2 phase function for a) 250 nm b) 550 nm and c) 850 nm
Figure 6-13: STx-1b phase function for a) 250 nm b) 550 nm and c) 850 nm
6.5.3 Effective Mie Refractive Indices from DDA Disk Calculation

Different ranges were used to model the DDA particles to determine effective refractive index as Mie scattering theory (Table 6-2). Over the span of the particle sizes calculated (30-1010 nm) quartz Mie models matched the refractive index used in the DDA calculations, showing that there is no major difference between the Mie scattering and scattering of particles with a small aspect ratio (1.64). The clay minerals were fit for size smaller size ranges to see how the retrieved refractive index would change if they were spherical particles. When the whole range of 30-1010 nm was used, the retrieved Mie refractive index was lower for all of the species. When smaller ranges were taken of the particles, the fit in the range of 20-210 nm was slightly higher than the actual refractive index for the NX-Illite. For the KGA-2 and the STx-1b, the retrieved refractive indices were close to the bulk refractive indices. When larger sizes were analyzed the retrieved refractive index went down for all the clay species. When a larger range of sizes was used the retrieved Mie refractive indices were again lower for all size ranges.
Table 6-2: Literature refractive index and effect Mie refractive index calculations over various size ranges for quartz, NX-Illite, KGa-2, and STx-1b.

<table>
<thead>
<tr>
<th>Literature Refractive Index</th>
<th>Quartz</th>
<th>NX-Illite</th>
<th>KGa-2</th>
<th>STx-1b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equivalent Refractive index for Mie from DDA (fit-value) (30-1010 nm fit)</td>
<td>1.55 (0.032)</td>
<td>1.52 (0.096)</td>
<td>1.47 (0.114)</td>
<td>1.45 (0.108)</td>
</tr>
<tr>
<td>30-490 (fit)</td>
<td>-</td>
<td>1.54 (0.107)</td>
<td>1.48 (0.145)</td>
<td>1.46 (0.122)</td>
</tr>
<tr>
<td>510-1010 (fit)</td>
<td>-</td>
<td>1.49 (0.042)</td>
<td>1.45 (0.045)</td>
<td>1.43 (0.046)</td>
</tr>
<tr>
<td>30-210 (fit)</td>
<td>-</td>
<td>1.59 (0.085)</td>
<td>1.55 (0.161)</td>
<td>1.52 (0.108)</td>
</tr>
<tr>
<td>230-410 (fit)</td>
<td>-</td>
<td>1.52 (0.046)</td>
<td>1.46 (0.031)</td>
<td>1.44 (0.027)</td>
</tr>
<tr>
<td>430-610 (fit)</td>
<td>-</td>
<td>1.50 (0.031)</td>
<td>1.46 (0.026)</td>
<td>1.44 (0.024)</td>
</tr>
<tr>
<td>630-810 (fit)</td>
<td>-</td>
<td>1.48 (0.031)</td>
<td>1.45 (0.027)</td>
<td>1.43 (0.023)</td>
</tr>
<tr>
<td>830-1010 (fit)</td>
<td>-</td>
<td>1.42 (0.027)</td>
<td>1.40 (0.039)</td>
<td>1.39 (0.041)</td>
</tr>
</tbody>
</table>
6.6 References:


(60) Baron, P. A., Sorensen, C. M., and Brockmann, J.E. Nonspherical Particle Measurements: Shape Factors, Fractals, and Fibers. In Aerosol


Chapter 7  Optical Properties of Heterogeneous Mineral Dust

Abstract

Aerosol particles contribute to highest degree of uncertainty when calculating the radiative forcing from the atmosphere. It is unknown if mineral dust particles cause a net warming or cooling effect. This uncertainty stems from how particles are modeled in the atmospheres including how they directly scatter and absorb light. How particles scatter and absorb light is dependent upon particle composition, shape, size, and concentration. In previous studies we have looked at independent components of mineral dust and seen how single components need to be modeled. In this study, we look at the extinction of Arizona test dust, a heterogeneous mineral dust mixture consisting of quartz, feldspar, carbonates, and clay minerals using cavity ring-down aerosol extinction spectroscopy. From electron microscopy we see that there is a range of particle aspect ratios that would indicate multiple types of particles in the system. In order to model this mixture, three approaches were taken that included treating the particles as Mie spheres, spheroids with an aspect ratio with the median particle aspect ratio, and treating each component individually from previous studies. Polydispersity calculations were included using either the Arizona test dust or individual component polydispersity. From these calculations we have shown that individual components better model the system and that clay minerals are underrepresented in simple spheroid models.
7.1 Introduction

The largest uncertainty in calculating radiative forcing is due to the effects of aerosol particles. The shape, composition, concentration, and size distribution of aerosol particles determines whether they cause a warming or cooling effect on the atmosphere.\textsuperscript{1} \textsuperscript{2} \textsuperscript{3} \textsuperscript{4} Particles affect radiative forcing through direct scattering and absorption of light or by acting as seeds for cloud particle formation. The direct effect of aerosol particles is \(-0.5 \pm 0.4\) W m\(^{-2}\), of which mineral dust aerosol contributes approximately \(-0.1 \pm 0.2\) W m\(^{-2}\).\textsuperscript{2} The size distribution of mineral dust particles is broad. Particles under 1.8 \(\mu\)m in diameter have the longest atmospheric lifetime, while larger particles gravitationally settle near the source region.\textsuperscript{5} When particles are transported long distances, they affect not only the regional climate and heath, but also locations distant from the source. For example, approximately 52,000 metric tons of Asian dust with a size under 2.5 microns was transported to the United States in the course of a single month.\textsuperscript{6}

Mineral dust is the second largest particulate emission by mass into the atmosphere. Mineral dust emissions have numerous natural and anthropogenic sources, with anthropogenic effects responsible for up to 50\% of the dust emitted annually.\textsuperscript{7} The primary source of mineral dust emissions comes from the dust belt that is located in the mid-latitudes, stretching from the Saharan region through central Asia.\textsuperscript{8} Mineral dust is a heterogeneous mixture of different mineral types, and its composition depends on its source. The major components of mineral dust consist of quartz, carbonates and aluminosilicate clay minerals. Quartz composes up to 50 wt. \% of mineral dust, clay...
minerals compose approximately 60% of Saharan dust and 85% of Asian dust, and carbonates compose up to 11% of Asian dust.\textsuperscript{9,10}

Arizona Test Dust (ATD) has been used as a heterogeneous mineral dust model for experimental studies of ice nucleation, heterogeneous chemistry, and optical properties.\textsuperscript{11-16} The composition of ATD consists of quartz (17.1 wt. %), feldspar (33.2 wt. %), carbonate (5.6wt. %), illite (7.5 wt. %), kaolinite (2 wt. %), smectites (10.2wt. %) and other aluminosilicate clays (24.4 wt. %).\textsuperscript{15} These components have a range of refractive indices from 1.522 to 1.601.\textsuperscript{17,18} In addition, each particle type has a different shape, with quartz, carbonates, and having aspect ratios close to unity while the aluminosilicate clay mineral components (kaolinite, illite, and smectites) have large aspect ratios.\textsuperscript{19,20,21}

The optical properties of individual components of mineral dust have been studied using techniques to measure extinction cross sections and scattering phase functions. Previous research has shown that calcite and quartz particles that have an aspect ratio close to one can be modeled well as spheres in the visible region.\textsuperscript{22-27} Aluminosilicate clay mineral dust particles have not been modeled well as spheres, and instead require models that incorporate their high aspect ratios.\textsuperscript{19,25,28,29} For a heterogeneous mixture of mineral dust types, Mie scattering theory has not been able to model the phase functions of Arizona Test Dust; only empirical models have been able to accurately describe the scattering properties.\textsuperscript{16,28} Current retrievals generally use spheres to calculate particle concentration and type, but some have started to incorporate spheroids to model the difference between particle types.\textsuperscript{30-33}
Cavity ring-down aerosol extinction spectroscopy (CRD-AES) is an ideal technique to use for measurements of particle extinction cross section due to the long effective path length and independence of the signal on the laser output intensity.\textsuperscript{34, 35, 36} CRD-AES has been used previously to study different types of aerosol particle systems ranging from organic and salts\textsuperscript{36, 37, 38, 39} to mineral dust species.\textsuperscript{22, 23, 40} Recently CRD-AES has also been used to study single particle systems.\textsuperscript{41} Other optical techniques are used to look at the scattering of mineral dust systems, but are limited by a high detection limit requiring the use of bulk polydisperse samples.\textsuperscript{42}

In this study, we have investigated the optical properties of Arizona Test Dust using CRD-AES to determine how best to model the extinction cross sections of a heterogeneous mineral dust mixture and if individual modeling parameters from previous studies can be used. We have previously shown that particles that do not absorb light in the wavelength range of interest and with an aspect ratio close to unity can be modeled as polydisperse spheres using Mie scattering theory, while non-absorbing particles with large aspect ratios, such as aluminosilicate clay minerals, need to be modeled using more complex methods.\textsuperscript{22-24} In this paper, we have modeled the extinction cross sections of ATD as spheres using Mie scattering theory, as spheroids with one aspect ratio using the discreet dipole approximation (DDA), and as a mixture of spheres and spheroids with a range of aspect ratios.
7.2 Experimental Methods

7.2.1 Generation of Aerosol Particles

Arizona test dust (0-3μm fraction, Powder Technology Inc., Burnsville MN) was dry generated using the methods previously described. Briefly, the mineral dust was aerosolized by directing a flow of nitrogen at 1.5 lpm over the sample while it was constantly agitated by stirring. The particles suspended in the nitrogen are then directed into a flask to stabilize the concentration of the particles. The desired concentration is obtained by pumping out some of the aerosol flow and then diluting the aerosol flow to 1.5 lpm.

7.2.2 Size selection

Aerolized particles were size selected using an electrostatic classifier (TSI 3080, Shoreview MN) and a differential mobility analyzer (DMA; TSI 3081, Shorview MN) to produce particles with mobility diameters of 250 nm to 900 nm. In the size selection process, particles obtain a known charge distribution after exposure to a sealed $^{85}$Kr source. After obtaining a known charge distribution, the particles are directed through the DMA under an applied potential. Only particles with the correct mobility diameter are transmitted through the DMA. We size selected particles using an aerosol flow of 1.5 lpm and a sheath flow of 2.7 to 8.8, depending upon the mobility diameter selected. Generally, the most monodisperse distribution of spherical particles is obtained when using an aerosol to sheath flow ratio of 1:10, but we have shown that we get a slightly better size selection for rough particles with a higher aerosol flow rate. After the size
selection, the particles are passed through the cavity ring-down aerosol extinction spectrometer (CRD-AES) and then counted using a condensation particle counter (CPC) or impacted for analysis with scanning electron microscopy (SEM). The size distribution as a function of the mobility diameter can be determined using the DMA and CPC in series, known as a scanning mobility particle sizer (SMPS).

7.2.3 Optical Extinction

After the size selection of the particles, the optical extinction cross sections of the particles were measured using CRD-AES. A 643 nm diode laser is passively coupled to a cavity that is approximately 91 cm in length and modulated at 500 Hz. The cavity is capped on both ends with highly reflective mirrors (>99.9985% at 640 nm) and the light transmitted through the back mirror is detected using a photomultiplier tube. The decay of the transmitted light through the back mirror is termed the ring-down time ($\tau$). For our system, the ring-down time is approximately 165 $\mu$s, which corresponds to an effective path length of greater than 48 km. The extinction coefficient ($b_{ext}$) for particles in the system can be measured from the difference between the ring-down times of the instrument without particles ($\tau_0$) and with particles ($\tau$) according to

$$b_{ext} = \frac{R_L}{c} \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right)$$

where $R_L$ is the ratio of the total length of the cavity to the length occupied by the aerosol particles and $c$ is the speed of light. The extinction cross section ($\sigma_{ext}$) can be calculated according to

$$\sigma_{ext} = \frac{b_{ext}}{N}$$

where $N$ is the number concentration of particles measured with the CPC. The extinction efficiency ($Q_{ext}$) can be related to the extinction cross section by
which depends upon the radius of the particle, $r$.

7.2.4 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to determine the polydispersity of the ATD particles that are size selected by the DMA. We have additionally used SEM to determine the aspect ratios of the ATD particles as well as feldspar samples. Two feldspars were used to determine the aspect ratios of these species. Labradorite (Sonora, Mexico, Ward’s Scientific) and orthoclase (Lago, Maggiore, Baveno, Italy, Ward’s Scientific) were ground using a mortar and pestle. Samples for SEM were prepared by directing the particle laden aerosol flow into a cascade impactor (PIXE International Corp. Tallahassee FL) backed by a rotary pump. Particles were collected on silicon wafers. The concentration of the ATD particles collected for size distribution measurements were monitored using the CRD-AES to collect enough particles to analyze. A FEI NanoSEM 630 FESEM operated at 3keV was used to image all particles.

Images obtained from the SEM were analyzed using ImageJ software (National Institutes of Health, Bethesda, MD). Aspect ratios of the ATD and feldspar species were measured using top-down and side-on view, as we have described previously. A top-down perspective was achieved using normal SEM imaging. To obtain a side-on aspect ratio, the SEM stage was tilted to an angle of 85 degrees with respect to normal SEM imaging using a tilt correction factor. ATD particles up to 2 μm in diameter and feldspar particles up to 4 μm in diameter were analyzed. Volume equivalent diameters for ATD were calculated assuming that the particles were spheroids with the two aspect ratios obtained from SEM analysis.
7.2.5 Modeling Optical Properties

ATD is a mixture of the major components of mineral dust and can be used as proxy for mineral dust species. ATD is composed of quartz (17.1%), feldspar (33.2%), carbonate (5.6%), illite (17.7%), kaolinite (2%), and other smectites (24.4%). For each of these components the average refractive index has been calculated by weighing the ordinary refractive index by 2/3 and the extraordinary refractive index by 1/3. The spectral averaging method of combining the extinction cross sections is the most accurate way to model birefringent components due to modeling each refractive index separately. Although taking a spectral average of the refractive indices is more accurate, generally only small differences are found between optical constant averaging and spectra averaging for mineral dust systems. Using optical constant averaging, the refractive indices used are 1.548 for quartz, 1.565 for feldspar, 1.601 for carbonate, 1.52 for illite, 1.564 for kaolinite, and 1.553 for the other aluminosilicate clay minerals. Taking into account the composition in ATD, the overall weighted average refractive index is 1.562. The calcite and quartz species are treated as spheres in all models since they have an aspect ratio close to one and are non-absorbing. Feldspar is non-absorbing at 643 nm and we demonstrate below that the aspect ratio of feldspar is similar to calcite and quartz. As a result, feldspars are treated as a spheres for modeling purposes. The clay mineral aspect ratios that we have used in this study are 4.80 for illite, 8.89 for kaolinite, and 7.49 for montmorillonite.

7.2.6 Mie Scattering Theory

The obtained CRD-AES results have been modeled using Mie scattering theory calculations. These calculations were performed for each species using a version of
BHCOAT that has been optimized for MATLAB.\textsuperscript{36, 38, 45} Two different types of calculations were performed for each species. In the first type of calculation, the samples were assumed to be monodisperse. In the second type of calculation, the clay mineral particles were assumed to be spheroids with the aspect ratio obtained from SEM. Using the experimental aspect ratios, the volume equivalent diameters of the particles were calculated. In the second type of calculation, the polydispersity was included from either individual components in the ATD mixture, as determined from previous research\textsuperscript{22, 24}, or from the polydispersity of ATD measured using SEM. In either case, this polydispersity was determined for each mobility diameter of interest using analysis of electron microscopy images. The extinction cross section at the volume equivalent diameter of each component is calculated using the refractive index, as described above. A weighted average is taken of the extinction cross sections at each volume equivalent diameters to find the average extinction cross section at each mobility diameter according to

\[ \sigma_{\text{ext}} = \frac{1}{n_{\text{tot}}} \sum_{i=1}^{n_{\text{tot}}} \sigma_{\text{ext},i} \]

for each mobility diameter between 250 nm and 900 nm. The error is calculated by dividing the SEM particles into three subgroups. The extinction cross section is found for each subgroup, and the standard deviation between groups is used to overestimate the error in the results. For the ATD polydispersity, the modeled extinction spectra used was a combination of single mineral component spectra combined in the relative ratios described above. The ATD polydispersity could then be applied to this combined spectral averaged to get the polydisperse fit. For the individual component polydispersity, the polydispersity of the individual mineral component was used with the Mie spectra for that component to get an extinction at a given mobility diameter. The polydisperse
calculation was done for each of the species (calcite, quartz, feldspar, illite, kaolinite, and montmorillonite) at each mobility diameter. These polydisperse calculations at each mobility diameter could then be combined using a weighted average from the components of ATD listed above.

7.2.7 Discreet Dipole Approximation Method

Spheroids were used to model the median aspect ratio for ATD as well as individual clay minerals with high aspect ratios using the DDA. For the DDA calculations, the particle shape is defined by a finite number of dipoles in an array that make up the shape. The DDA calculations were performed using DDSCAT 7.2.\textsuperscript{46, 47} To model the particles accurately using DDA, the maximum size ($a_{\text{eff}}$) is dependent upon the number of dipoles in the system ($N_d$) according to

$$a_{\text{eff}} < 9.88 \frac{\lambda}{|m|} \left(\frac{N_d}{10^6}\right)^{1/3}$$

where $m$ is the refractive index and $\lambda$ is the wavelength of light. We have previously noted that spheroids can be modeled using only 24 different orientations due to their high degree of symmetry.\textsuperscript{23, 24}

The DDA calculations were used for two different types of calculations. The first used a spheroid with an aspect ratio of 1.84. The aspect ratio of 1.84 was used because it is the median resultant aspect ratio from SEM analysis. The second method modeled each component separately depending upon whether a sphere or spheroid has been shown to best model the extinction cross section. For calcite and quartz, Mie theory calculations have been shown previously to model the optical properties well.\textsuperscript{22, 24} Based upon feldspar being a non-absorbing mineral at 643 nm and having a small aspect ratio similar to calcite and quartz, Mie theory was used to calculate the optical extinction. For the clay
mineral species of illite, kaolinite, and montmorillonite, spheroids with an aspect ratio that is the same as the actual aspect ratios of the species were used.24

7.3 Results and Discussion

The extinction cross section of ATD, a heterogeneous mixture of mineral dust components, has been measured using CRD-AES. The results have been compared to theory to understand the complexity in the description of particle shape needed to model the extinction cross sections of dust mixtures. We compare our results to models that include Mie scattering theory, spheroids, and using a combination of spheres and spheroids depending upon particle composition as described in Table 7-1. Polydispersity is included in two different ways. First the bulk polydispersity of ATD is found at each mobility diameter and secondly the polydispersity of individual components was used.22.

Table 7-1: Description of parameters used for each model type

<table>
<thead>
<tr>
<th>Species</th>
<th>Calcite</th>
<th>Quartz</th>
<th>Feldspar</th>
<th>Kaolinite</th>
<th>Montmorillonite</th>
<th>Illite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.6%</td>
<td>17.1%</td>
<td>33.2%</td>
<td>2%</td>
<td>24.4%</td>
<td>17.7%</td>
<td></td>
</tr>
<tr>
<td>Refractive Index</td>
<td>1.601</td>
<td>1.548</td>
<td>1.565</td>
<td>1.564</td>
<td>1.552</td>
<td>1.572</td>
</tr>
<tr>
<td>Mie Model</td>
<td>Mie</td>
<td>Mie</td>
<td>Mie</td>
<td>Mie</td>
<td>Mie</td>
<td>Mie</td>
</tr>
<tr>
<td>Spheroid Model (Aspect Ratio)</td>
<td>Spheroid (1.84)</td>
<td>Spheroid (1.84)</td>
<td>Spheroid (1.84)</td>
<td>Spheroid (1.84)</td>
<td>Spheroid (1.84)</td>
<td>Spheroid (1.84)</td>
</tr>
<tr>
<td>Individual Components Model (Aspect Ratio)</td>
<td>Mie</td>
<td>Mie</td>
<td>Mie</td>
<td>Spheroid (8.89)</td>
<td>Spheroid (7.49)</td>
<td>Spheroid (4.80)</td>
</tr>
</tbody>
</table>

7.3.1 ATD Particle Morphology

To characterize the ATD particles, SEM was used to analyze the shape of the particles. Figure 7-1a shows irregularly shaped particles, of similar roughness to particle
types that we have studied previously. From the side-on orientation (Fig. 7-1b), different particle aspect ratios are observed, ranging from near unity to having aspect ratios up to 7. Figure 7-1c shows the range of aspect ratios for the top-down and side-on orientations. From a top-down orientation, the particles have a fairly uniform aspect ratio with a median aspect ratio of 1.41. From a side-on view, two different modes are observed: a mode with an aspect ratio near unity at 1.2-1.6 and a mode with a relative maximum at 4.4. Particles with high aspect ratios are indicative of clay minerals that have been shown to have aspect ratios from 4.80 to 8.89. The mean aspect ratio from a side-on view is 2.09, but for modeling purposes the median AR of 1.84 is used that represents the majority of the particle better. Additional discussion and figure of the aspect ratios of ATD are in the supplemental information.
Figure 7-1: SEM images of ATD from the a) top-down and b) side-on orientations with c) the distribution of aspect ratios determined for both orientations.

Additional information was needed to model the feldspar species. As in our previous work, we used SEM to measure the aspect ratios of two different feldspars. Both feldspars had aspect ratios near unity. Labradorite had a top-down aspect ratio of 1.62 and side-on aspect ratio of 1.65 while orthoclase had a top-down aspect ratio of 1.58 and a side-on aspect ratio of 1.53. Species with similar aspect ratios that do not absorb
light at 643 nm such as calcite and quartz have been modeled well using Mie scattering theory.\textsuperscript{22, 24} We have therefore used Mie scattering theory to model feldspars.

7.3.2 Optical Properties of ATD

Since ATD is a mixture of different components, three methods were used to model the experimental CRD-AES results. When the CRD-AES results were compared to any of the models that did not include polydispersity at each mobility diameter, there was no agreement. The first method used was treating each component in ATD as a collection of monodisperse or polydisperse spheres and using Mie scattering theory to calculate the extinction cross sections. In this analysis, the extinction cross section for each of the mineral components was calculated separately at each mobility diameter and the weighted average extinction cross section of ATD at each mobility diameter was calculated based upon the composition of ATD (Fig. 7-2). Using the polydispersity from either bulk ATD or individual components were a better match to the experimental CRD-AES results than when the polydispersity is not included. When the ATD size distribution is used for the calculations, the extinction cross section is underestimated at all diameters except 450 nm. The average percent difference from the CRD-AES results is 38.7%. When the size distributions of the individual components are used, much better agreement between the experimental results and theory is seen. The theoretical results have a higher extinction cross section than the data at 300 nm, but are lower than the experimental data for the other mobility diameters. When the size distributions of the individual species are used, the average percent difference with the experimental results is 27.8%.
We next modeled the optical properties using the discrete dipole approximation to calculate the extinction cross sections of spheroids with an aspect ratio of 1.84, which is the median side-on aspect ratio of the ATD particles. In the literature, several models have shown that spheroids with an aspect ratio of 1.8 model the optical properties of mineral dust better than spheres.\textsuperscript{33, 48} As for the Mie scattering theory calculations, three different ways of accounting for the size distributions of the particles were used: 1) particles were assumed to be monodisperse spheroids, 2) particles were assumed to be polydisperse spheroids where the size distribution of each species was assumed to be the same as the size distribution of ATD, and 3) particles were assumed to be polydisperse spheroids where the individual size distributions of each species were used (Fig. 7-3). Incorporation of polydispersity into the model provides better agreement to the experimental data. Similar to the Mie scattering calculations, the extinction cross sections
of spheroids that use the ATD size distribution gave lower values than the CRD-AES results except at a mobility diameter of 450 nm. The average percent difference between the experimental results and spheroid calculations using the ATD size distributions was 35%. When the individual size distributions were used in the calculations, the average percent difference was 26.8%.

Figure 7-3: Experimental extinction cross section retrieved using CRD-AES (circles) compared to DDA spheroid calculations with an aspect ratio of 1.84. The solid line is the monodisperse theory with the ATD polydispersity (squares) and individual component polydispersity (diamonds).

In the final approach to modeling the optical properties of ATD, each component was treated individually, meaning that some species were treated as spheres and others as spheroids with different aspect ratios. The quartz, feldspar, and carbonate components were treated as spheres and modeled using Mie scattering theory. Each of the aluminosilicate clay minerals were treated as spheroids. The aspect ratios of kaolinite, montmorillonite, and illite were modeled as 8.89, 7.49, and 4.80, respectively. As for
the calculations for spheres and spheroids, the same two methods were used to account for the particle size distributions. When the ATD size distribution is used, then the average percent difference from the experimental results is 37.8%, which is similar to the percent differences reported above. Incorporation of individual size distributions yields an average percent difference compared to the experimental results of 27.8%, which, again, is similar to the percent differences reported above. As a result, we find that treating each component individually as spheres or spheroids depending upon the particle type yields no significant improvement over treating all the particles as spheres or spheroids.

![Graph](image)

**Figure 7-4**: Experimental extinction cross section retrieved using CRD-AES (circles) compared to individual models for each component depending upon shape. The solid line is the monodisperse theory with the ATD polydispersity (squares) and individual component polydispersity (diamonds).

A comparison of the percent differences for the different calculations is shown in Figure 7-5. When the size distributions of the individual components are included instead of the size distribution of ATD, the CRD-AES data are modeled better. The average
percent difference between using individual vs. ATD size distributions was 10%. The only model that showed significant difference from the others was spheroids with the ATD polydispersity, with an average percent difference of 3% better than either Mie theory or using individual components.

![Figure 7-5: Percent difference between modeling results for polydisperse particles and the experimental extinction cross section from CRD-AES. Other papers have shown that Mie scattering theory cannot account for the scattering properties of ATD, and instead use empirical models.\textsuperscript{16, 28} For all three model types, the extinction cross section was underrepresented. Our previous results have shown that just using spheroids to model the extinction cross sections of high aspect ratio aluminosilicate clay minerals is not suitable. This model can be improved by using an empirical correction factor that can be calculated from our previous work.\textsuperscript{24} The factors by which the model results need to be increased to agree with the CRD-AES data are 67 for a mobility diameter of 750 nm and 207 for a mobility diameter of 250 nm. Using]
these correction factors for the aluminosilicate clay minerals in the ATD sample, the average percent difference can be reduced from 27.8 to 23.6% using a factor of 67 or 22.8% using 207. Based on these results, we expect that much of the error in modeling the extinction cross sections of ATD stems from error in modeling the optical properties of aluminosilicate clay minerals. Additional factors that would affect the modeling of the ATD mineral dust mixture include a possibility that the aerosolized portion of dust is different from the bulk as well as having different compositions at different sizes selected.

7.4 Conclusion:

Though incorporating polydispersity into the different model types, we show that there is not a large difference in modeling the particles by either spheres or spheroids, but individual polydispersity at each size is important. The polydispersity of the sample is important, but each component needs to be treated separately in order to have a good match between theory and experimental results. By using models that just used either spheres or spheroids as their scattering properties, there was an underestimation of the scattering at all sizes larger than 300 nm. This is most likely due to the clay fraction being underrepresented in the scattering calculations and having a much higher impact on the overall extinction of the mineral dust mixture.

7.5 Supporting Information

Summary

The supporting information contains additional information about the models used for calculating the theoretical extinction spectra from Mie and discreet dipole
approximation calculations. The aspect ratios of two different feldspar species are discussed to show that each has an aspect ratio of approximately one. A comparison of monodisperse theory is made between the three different modeling types used as well as the difference when particles are oriented in different directions rather than randomly.
7.5.1 Aspect ratios of feldspars

The top-down and side-on aspect ratios of both feldspar minerals are similar to each other with aspect ratios near 1 (Figure 7-8-e, f). The labradorite has a top-down aspect ratio of 1.62 and a side-on aspect ratio of 1.65, while the orthoclase has a top-down aspect ratio of 1.58 and a side-on aspect ratio of 1.53. The distributions of aspect ratios are similar between the top-down and side-on views. These aspect ratios are similar to what was seen for both calcite particles and quartz particles which can be treated using polydisperse Mie theory.\textsuperscript{19}

Figure 7-6: a) A representative SEM image of labradorite particles in the top-down orientation. b) A representative SEM image of labradorite particles in the side-on orientation. c) The distribution of labradorite aspect ratios obtained from SEM images. The fraction of particles is plotted vs. aspect ratio. D) The top-down SEM image of orthoclase. E) Side-on orientation of orthoclase particles. F) The distribution of orthoclase aspect ratios obtained from SEM images.
7.5.2 Comparison of modeling types

A comparison of the three different monodisperse models used in this paper is shown in Figure 7-10. The model that uses spheroids with an aspect ratio of 1.84 is very similar to that of the monodisperse Mie model, but with dampening of the oscillations. The individual components model is lower than the other two due to the introduction of the spheroids for the clay components, but as was noted in the paper that these models were lower than the experimental extinction and could be corrected by using an empirical correction factor for the clay mineral species that increases the scattering of the clay components by a factor of 67 to 207.

![Figure 7-7: Comparison of calculations for monodisperse particle for each model type with all particles treated as Mie spheres (black line), all particles treated as DDA spheroids with an aspect ratio of 1.84 (blue line), or particles treated as individual components (red line).](image)

7.5.3 Orientation dependent scattering

When spheroids are used for calculations, there is a dependence of the scattering of the particles upon angle of the particles. Hew we demonstrate the effect of orientation upon the different model types. For the single spheroid model with an aspect ratio of 1.84 (Figure 7-11), there is a large difference between two orientations. This effect is much
smaller when the particles are treated as individual components with the feldspar, quartz, and carbonates components being treated as spheres and the clays as spheroids (figure 7-11).

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**Figure 7-8**: Modeled particle extinction vs. diameter for different particle orientations. a) Comparison of all particles modeled as spheroids with an aspect ratio of 1.84 where there is a large difference between the extremes of scattering compared to non-oriented particles. b) Difference between orientations for individual models is less due to some articles being treated as Mie Spheres and not having any orientation effects.
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Chapter 8  Optical Properties of Reacted Calcite

8.1  Mineral Dust Aging

Calcium carbonate comprises a significant fraction (11%) of Asian dust and is known to participate in heterogeneous chemistry during atmospheric transport. We were interested in studying the reaction of calcite with nitric acid since we have previously described the optical properties of calcite using CRDS. One of the major pathways of heterogeneous reactions on calcite is with nitric and sulfuric acid species. In the reaction of calcite with acid species, the minerals act as a sink for nitric and sulfuric acid and release CO$_2$ as a byproduct under certain relative humidity conditions. We expect that we can create morphologies of reacted calcium carbonate starting with a small reacted shell (Fig. 8-1) and reacting to the calcium nitrate product. The calcium nitrate product increases the size of the particles due to uptake of water and additional mass from the nitrate species and changes morphology after reaction of calcite with nitric acid. $^2,^3$

Figure 8-1: Possible core-shell reaction product of calcium carbonate particles with nitric acid vapor

8.2  Experimental setup

To mimic how particles are reacting in the atmosphere, a movable injector setup was built to react the suspended aerosol particles in the gas phase for different reaction times. Using this setup, the residence time of the particles can be adjusted as well as the nitric acid concentration and relative humidity. Before the reaction chamber, particles
are size selected using the DMA before being exposed to the reactant gas. After the passing through the reaction chamber, the particles are directed through the CRDS to determine the extinction cross section then either counted using the CPC or impacted for electron microscopy analysis. The setup for the movable injector setup is described in Figure 8-2. The reactor design is based on reaction setup in Wagner et al. 2007. There have been numerous other studies that have used long flow chambers for reactions. The chamber itself is approximately 3 feet long with a 2 inch inner diameter and is constructed of glass coated on the inside with halocarbon wax (Series 1500, Halocarbon Products Corp., River Edge, NJ) to prevent buildup or reaction of the nitric acid on the glass surface. The aerosol particles and relative humidity were mixed before the chamber and introduced through four inlets at the top. The nitric acid vapor is produced by mixing sulfuric acid and nitric acid to produce a known concentration of nitric acid in the vapor phase. The nitric acid was then brought in at a low flow rate using Teflon tubing to prevent adhesion and reactions on the tubing. The injection rod introducing nitric acid can move to change the residence time of the aerosol particles with the nitric acid from a few seconds up to 2 minutes. The reacted particles are then passed through a nitric acid removal chamber built similarly to the diffusion driers described previously. The nitric acid removers were filled with activated carbon to diffusively remove nitric acid vapor. Other methods that were used to remove the nitric acid included a chemical denuder design based on Sioutas et al. (1996) coated with either MgO or Na₂CO₃. The chemical denuder was not a viable method to remove nitric acid because the denuder aerosolized particles in small quantities that interfered the extinction cross section of the
aerosol particles being studied through measuring the extinction of the particles in the optical cavity and particle counting by the CPC.

8.3 Results

8.3.1 Calcium Nitrate Optical Properties

We first constrained the reaction product using aqueous generated calcium nitrate particles. Figure 8-3 shows the results for calcium nitrate extinction cross section over the size range of 200 to 900 nm. The calcium nitrate CRDS results match Mie scattering theory for spherical particles. The calcium nitrate particles could either be pure calcium nitrate, or more likely would be calcium nitrate tetrahydrate. The difference in the refractive index is minimal, with the calcium nitrate being refractive index of 1.48 and the hydrated species refractive index of 1.47. The best fit using Mie scattering theory of the CRDS data is a refractive index of 1.48±0.01 matching the calcium nitrate the best, not significantly different from the calcium nitrate hydrate species.
8.3.2 Calcium Carbonate Reaction with Nitric Acid - Optical Properties

Reaction of nitric acid with calcite was performed using a low concentration of nitric acid and variable amount of relative humidity. The approximate concentration of nitric acid was 980 ppm as calculated from Taleb et al. 1996. This concentration is higher than polluted atmospheric conditions at 35 ppb seen in Mexico city, but higher concentrations are needed since shorter exposure times are used. The relative humidity was varied from a low relative humidity (12%) to a high relative humidity (56%) to determine how the optical properties of calcite would change with reaction of nitric acid. Previous papers observe the reaction can occur at relative humidity higher than approximately 21%. Figure 8-4 shows the CRD results compared to Mie scattering theory of the reacted calcium carbonate at 300 nm, 500 nm, and 700 nm at low and high relative humidity. At the lower relative humidity (~12%) no difference in the CRD results is seen between the particles passing through the reaction chamber and nonreacted calcium carbonate particles, indicating that no bulk change in the particles took place.
When the relative humidity was increased to approximately 56%, there was an increase in the extinction cross section of the particles at all sizes selected, indicating a change in the particle. To model this increase, two different approaches were taken: either to use anhydrous calcium nitrate (increases the volume by approximately 1.2 times), or use the hydrated species that would increase the volume of the particles by approximately 1.5 due to the addition of the water. Using Mie scattering theory for monodisperse spheres, neither calcium nitrate nor hydrated calcium nitrate matched the experimental CRDS results. We would expect that the experimental CRDS results would cross over the Mie scattering theory for monodisperse spheres line at approximately 550 nm since the polydispersity is the same as calcite. The increased polydispersity from using calcite would make the lower diameter extinction cross sections higher and larger diameter extinction cross sections lower. The Mie scattering theory calculations for anhydrous calcium nitrate particles is lower at every diameter than the experimental CRDS results, while the experimental results cross over the hydrate species between 300 and 500 nm. This would indicate that the hydrated species is more likely, but further analysis of the final polydispersity would be needed. Additional experiments studying the composition would need to be performed to understand the exact species produced in the flow chamber such as using IR spectroscopy to determine the composition of collected particles.
8.3.3 Reaction of Calcium Carbonate with Nitric Acid - Morphology

TEM analysis of the reaction products was performed to observe how the morphology changes when the calcium carbonate particles were reacted with nitric acid. Figure 8-5 shows TEM images of the original 700 nm size-selected calcite particles with no reaction and after reaction with nitric acid at 60% relative humidity. No phase contrast between the core and the rest of the particle is observed, thus are assumed to be homogeneous, as would be expected at high relative humidity and nitric acid concentration. Additionally, the particles change shape from particles with a roughened perimeter to spherical morphology indicating that they have undergone a change in composition. Determining the change in projected area of the particles is difficult due to the low deliquescence point of calcium nitrate and adsorbed water that allows the particles to wet the grids and appear larger.
Figure 8-5: TEM images of 700 nm size selected a) calcium carbonate and b) calcium carbonate reacted with nitric acid at approximately 60% RH

Only preliminary results for the reaction of calcite with nitric acid could be obtained, since the nitric acid removal system only worked sporadically. Additional experiments allowed nitric acid vapor into the CPC causing damage to the system. The nitric acid removal system was not reliable due to a change in activated carbon from the original source, therefore only a few sample days of data were obtained. If a consistent system for acid removal could be devised, the reaction products could then be analyzed using CRDS. No additional experiments were performed after those described in this section.

8.4 References


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Chapter 9 Morphology of Submicron Mixed Organic/Inorganic Aerosol Particles by Cryo-TEM


Abstract

The effects of aerosol particles on heterogeneous atmospheric chemistry and climate are determined in part by the internal arrangement of compounds within the particles. To characterize the morphology of internally mixed aerosol particles in the accumulation mode size regime, we have used cryo-transmission electron microscopy to investigate the phase separation behavior of dry, submicron particles composed of ammonium sulfate mixed with carboxylic acids (adipic, azelaic, citric, glutaric, malonic, pimelic, suberic, and succinic acid). Determining the morphology of dry particles is important for understanding laboratory studies of aerosol optical properties, reactivity, and cloud condensation nucleus activity, results from field instruments where aerosol particles are dried prior to analysis, and atmospheric processes like deposition mode heterogeneous ice nucleation that occur on dried particles. We observe homogeneous morphologies for highly soluble organic compounds. For organic compounds with limited aqueous solubility, partially engulfed structures are observed. At intermediate aqueous solubilities, small particles are homogeneous and larger particles are partially
engulfed. Results are compared to previous studies of liquid-liquid phase separation in supermicron particles and the impact of these dry particle morphologies on aerosol-climate interactions are discussed.

9.1 Introduction

Aerosol particles influence the climate by scattering and absorbing electromagnetic radiation, altering atmospheric composition through heterogeneous chemistry, and influencing the formation, optical properties, and lifetime of clouds.\(^1\) These aerosol-climate interactions are determined by aerosol composition, size, shape, and the internal arrangement of the components of the particle.\(^2\)-\(^5\) Particle composition is of particular interest for organic aerosol, which is composed of myriad compounds from primary and secondary emissions that partition to the particulate phase.\(^6\),\(^7\) The arrangement of inorganic and organic species within an organic aerosol particle depends on the degree of phase separation between the components of the particle and determines the particle reactivity, optical properties, water accommodation, and ice nucleation activity.\(^2\),\(^8\)-\(^19\)

Liquid-liquid phase separation in the bulk and in micrometer-diameter aqueous organic aerosol have been investigated using theory and experiment.\(^20\)-\(^32\) Accounting for the fact that the components within an aerosol particle can partition between an aqueous electrolyte phase and a less hydrophilic organic phase allows for a more accurate determination of total particulate mass in atmospheric models.\(^25\)-\(^27\) In an aqueous particle, the initial phase separation takes place as the liquid water content of the aerosol is reduced. Phase separation in aerosol containing organic acids and ammonium sulfate occurs through two mechanisms: nucleation and growth, which involves an activation
barrier to form a nucleus of the new phase, and spinodal decomposition, which does not have an energy barrier.\textsuperscript{28} For particles consisting of ammonium sulfate mixed with an organic compound composed of C, H, and O atoms, experiments have found that liquid-liquid phase separation occurs when the ratio of O to C is less than approximately 0.7,\textsuperscript{29} though molecular structure and the ratio of the mass of the organic component to sulfate also impact the O:C ratio at which phase separation occurs.\textsuperscript{29,30} Experiments on suspended particles several micrometers in diameter composed of organic compounds and aqueous sodium chloride and complementary computational studies have found that most liquid-liquid phase separated particles with O:C < 0.4 form partially engulfed structures.\textsuperscript{31} Another recent study has shown that dicarboxylic acid/ammonium sulfate particles tend to form partially engulfed structures, sometimes at the liquid-liquid phase separation relative humidity and sometimes as the particles are dried to lower relative humidities.\textsuperscript{32} Through these studies, the phase separation behavior and morphology of model systems of micrometer-diameter particles can be predicted.

In this paper, we have extended the study of the structure of organic aerosol to the accumulation mode regime (100 nm to 2.5 μm), which corresponds to the aerosol particles with the longest atmospheric lifetime.\textsuperscript{4} Methods for studying the morphology of aerosol particles in the accumulation mode size regime need to be developed to investigate whether the structures observed in the supermicron regime are consistent with the morphology of atmospherically relevant sizes of particles. Aerosol properties, such as efflorescence, deliquescence, growth factor, cloud condensation nucleus formation, and ice nucleation, have been found to depend on particle size.\textsuperscript{5,27,33-40} In terms of liquid-liquid phase separation, Ciobanu et al. observed a decrease in the number of
ammonium sulfate satellite inclusions in the poly(ethylene glycol)-rich phase as the particle size was reduced from 67 μm to 12 μm. To investigate phase separation and morphology at submicron diameters, we have used cryo-transmission electron microscopy (cryo-TEM) to study particles that are generated and dried in the gas phase. We have used aerosol particles composed of equal masses of ammonium sulfate, a standard anthropogenic salt, and either dicarboxylic acids, a common component of water-soluble organic matter, or citric acid, a commonly-used oxidized organic compound. Prior research has focused on liquid-liquid phase separation rather than the structure of dried particles in part because organic aerosol particles are thought to exist primarily in an aqueous state in the environment. Dry particles, however, are used in many laboratory studies of aerosol optical properties, reactivity, and cloud condensation nucleus activity, and aerosol particles are often dried prior to analysis with field instruments. In addition, some atmospheric processes, such as some modes of heterogeneous ice nucleation, likely occur on dry particles. As a result, it is important for correlating laboratory and field studies to atmospheric processes and for understanding heterogeneous ice nucleation to study the structure of dried particles. Application of cryo-TEM for the study of the morphology of internally mixed, organic-containing aerosol particles introduces a complementary technique that can allow us to determine the extent to which results obtained in the supermicron regime can be extended to submicron particles.

9.2 Experimental Methods

Aerosol particles composed of carboxylic acids and ammonium sulfate were generated in the laboratory from aqueous solution. Ammonium sulfate (>99.0 %, EMD), adipic acid (>99%, Acros), azelaic acid (>98%, Alfa Aesar), citric acid (>99%, Alfa Aesar), glutaric acid (>99%, Alfa Aesar), malonic acid (>99%, Alfa Aesar), pimelic acid
(>98%, Acros), suberic acid (>99%, Alfa Aesar), and succinic acid (>99%, Sigma Aldrich) were used without further purification. Properties of these compounds are compiled in Table 9-1. Solutions containing 0.025 wt.% ammonium sulfate and 0.025 wt.% organic acid were made using ultrapure water (High-performance liquid chromatography grade). Aerosol particles were generated from these solutions using a constant output atomizer (TSI 3076, Shoreview, MN) with a nitrogen flow rate of approximately 1.5 L/min. Particles were dried rapidly (estimated rate = 99.7 %RH s⁻¹) to below 2% relative humidity using a diffusion dryer containing molecular sieves (13X mesh size, Sigma Aldrich).

Samples were prepared for imaging using a cascade impactor (PIXE International Corp., Tallahassee, FL) to collect the particles onto 200 mesh continuous carbon coated transmission electron microscopy (TEM) grids (Electron Microscopy Science, Hatfield, PA). After the aerosol particles were generated, the stream of particles was directed into the impactor at a flow rate of 1.0 L/min. A small mechanical pump backed the impactor. Aerosol particles pose an inhalation danger. As a result, care is taken to contain the particles within the enclosed flow system. Previous studies have shown that impacting particles for imaging studies can affect their morphology in cases where the particle and substrate have attractive interactions. We have used SEM to image the particles edge-on to show that there is little interaction between the particles imaged in this study and the TEM substrates, as described in the Supporting Information (Fig. 9-11). Samples were analyzed using a Philips EM420T TEM operated at an accelerating voltage of 120 kV. Samples were cooled to approximately 104 K using a liquid nitrogen cooled cryo-TEM holder before exposure to electron radiation to reduce damage to the particles. In
the Supporting Information, we show that we also observe the phase separation under room temperature TEM imaging (Fig. 9-12). Even under cryogenic conditions, the samples are too fragile to perform energy dispersive X-ray spectroscopy (EDS) to obtain elemental composition. As a result, we use the electron beam damaging behavior of the particles to verify that the particles are internal mixtures of organic acids and ammonium sulfate, as shown in the Supporting Information (Fig. 9-13). In a previous publication, we additionally used cavity ring-down spectroscopy to measure the extinction cross sections of succinic acid/ammonium sulfate and pimelic acid/ammonium sulfate particles to verify that the particles are internal mixtures down to diameters of 100 nm. Aerosol mass spectrometry has also been used to show that the composition of succinic acid/ammonium sulfate particles > 200 nm in diameter generated with an atomizer is the same as the aqueous solution from which they are produced.

Table 9-1: Organic acid molecular formulas, molecular structures, O:C ratio, and aqueous solubility. The mole fraction and volume fraction of the organic acid in the organic acid/ammonium sulfate mixtures is also listed. Ammonium sulfate properties are listed.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Molecular Structure</th>
<th>O:C ratio</th>
<th>Mole Fraction</th>
<th>Volume Fraction</th>
<th>Solubility (g/100mL) at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium Sulfate</td>
<td>(NH₄)₂SO₄</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>76.4a</td>
</tr>
<tr>
<td>Malonic Acid</td>
<td>$\text{C}_3\text{H}_4\text{O}_4$</td>
<td><img src="image" alt="Malonic Acid structure" /></td>
<td>1.33</td>
<td>0.4050</td>
<td>0.5219</td>
<td>161&lt;sup&gt;b, c&lt;/sup&gt;</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>$\text{C}_6\text{H}_8\text{O}_7$</td>
<td><img src="image" alt="Citric Acid structure" /></td>
<td>1.17</td>
<td>0.5925</td>
<td>0.5102</td>
<td>162&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Succinic Acid</td>
<td>$\text{C}_4\text{H}_6\text{O}_4$</td>
<td><img src="image" alt="Succinic Acid structure" /></td>
<td>1.00</td>
<td>0.4719</td>
<td>0.5397</td>
<td>8.8&lt;sup&gt;b, c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Glutaric Acid</td>
<td>$\text{C}_5\text{H}_8\text{O}_4$</td>
<td><img src="image" alt="Glutaric Acid structure" /></td>
<td>0.800</td>
<td>0.5000</td>
<td>0.5783</td>
<td>116&lt;sup&gt;b, c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Adipic Acid</td>
<td>$\text{C}<em>6\text{H}</em>{10}\text{O}_4$</td>
<td><img src="image" alt="Adipic Acid structure" /></td>
<td>0.667</td>
<td>0.5285</td>
<td>0.5987</td>
<td>2.5&lt;sup&gt;b, d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Pimelic Acid</td>
<td>$\text{C}<em>7\text{H}</em>{12}\text{O}_4$</td>
<td><img src="image" alt="Pimelic Acid structure" /></td>
<td>0.571</td>
<td>0.5478</td>
<td>0.6223</td>
<td>6.73&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Suberic Acid</td>
<td>$\text{C}<em>8\text{H}</em>{14}\text{O}_4$</td>
<td><img src="image" alt="Suberic Acid structure" /></td>
<td>0.500</td>
<td>0.5686</td>
<td>0.6253</td>
<td>0.242&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Azelaic Acid</td>
<td>$\text{C}<em>9\text{H}</em>{16}\text{O}_4$</td>
<td><img src="image" alt="Azelaic Acid structure" /></td>
<td>0.444</td>
<td>0.6048</td>
<td>0.6965</td>
<td>0.5&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
</tbody>
</table>


9.3 Results and Discussion

We observe that the morphology of the particles depends on the aqueous solubility of the organic component. The highest solubility organic compounds (>100 g/100 mL), malonic acid, citric acid, and glutaric acid, form homogeneous mixtures with ammonium sulfate (Figure 9-1). These particles are predominantly spherical in shape with some deviation toward rod-shaped particles for malonic acid. The rod-shaped structures likely form due to aggregation of the particles, which we also observe for other systems used in this study when higher concentrations of particles are impacted on the TEM grids. We dilute the particle flow with N₂ prior to drying to limit the amount of aggregation. The uniform contrast that we observe in the TEM images shows that electron transmission is uniform across the particle, which indicates that the particle is homogeneous in composition within our resolution. We note that Raman microscopy of dry particles tens of micrometers in diameter shows malonic and glutaric acid have a higher concentration near the particle edge while ammonium sulfate is depleted at the interface, and other studies have demonstrated that these organic compounds are surface active.⁴⁵,⁴⁶ Surface activity, however, does not imply that a new phase has formed, but rather that a compound has an enhanced concentration at the particle surface. Based on their O:C ratios, we would expect that these compounds do not undergo liquid-liquid phase separation,²⁴, ²⁹, ³⁰ and as a result, our data are in agreement with optical microscopy studies.
Our results additionally indicate that particles containing these highly soluble organic compounds do not undergo phase separation as they dry. Studies have shown that particles composed of a 1:1 molar ratio of glutaric acid to ammonium sulfate effloresce at higher relative humidities than ammonium sulfate,\textsuperscript{47} while particles composed of a 1:1 molar ratio of malonic acid or citric acid mixed with ammonium sulfate do not effloresce or lack full efflorescence.\textsuperscript{47, 48} For all of these organic compounds, water can be retained in the organic component below the efflorescence relative humidity of ammonium sulfate.\textsuperscript{47} We also note that the homogenous structures we observe are not likely to be due to the particles undergoing a glass transition. Some organic compounds, such as sucrose, form glassy particles at room temperature at low relative humidity,\textsuperscript{49} which results in slow uptake and release of water.\textsuperscript{50} Micrometer particles composed of citric acid and ammonium sulfate at a 1:1 ratio by mass are not glasses at room temperature for any relative humidity.\textsuperscript{49} Because glutaric acid and malonic acid have lower molecular weights than citric acid and are also internally mixed with ammonium sulfate, we expect that their glass transition temperatures are less than room temperature for all relative humidities.\textsuperscript{51, 52} It is possible, however, that these compounds become highly viscous at low relative humidity, as has been observed for secondary organic aerosol,\textsuperscript{51, 53, 54} and that this viscous state could influence the particle morphology.
Figure 9-1: Cryo-transmission electron microscopy images of highly soluble organic compounds, malonic acid, citric acid, and glutaric acid internally mixed with ammonium sulfate. The morphologies are homogeneous in structure.
At intermediate solubilities (6-9 g/100mL), for succinic and pimelic acid, the morphology exhibits a dependence on particle size (Figure 9-2). Small particles have a homogeneous morphology, whereas larger particles phase separate into a partially engulfed morphology. We differentiate the organic component from the ammonium sulfate through image contrast and electron beam damaging behavior (see Supporting Information). For succinic acid, the largest homogeneous particle that we observe is 196 nm and the smallest phase separated particle is 170 nm. For pimelic acid, the largest homogeneous particle is 276 nm and the smallest phase separated particle is 270 nm. These cutoffs resulted from the analysis of 519 pimelic acid/ammonium sulfate particles, of which 440 were homogeneous, and 324 succinic acid/ammonium sulfate particles, of which 234 were homogeneous. The analyzed particles ranged in size from 20 nm to 900 nm in diameter. We have explored this size dependence in detail in a separate manuscript. We note that phase separation could be due to liquid-liquid phase separation, crystallization of the organic component, or crystallization of the inorganic component. From our cryo-TEM images, we cannot differentiate which of these processes occurs. From predictions based on O:C ratios in the previous literature, we expect that liquid-liquid phase separation takes place for the large pimelic acid particles, but not for the succinic acid system. Bertram et al. provides a parameterization for the relative humidities at which efflorescence, deliquescence, and liquid-liquid phase separation occur as a function of O:C ratio and the mass fraction of organic to sulfate using polynomial fits of data in their study and in the literature. Based on the parameterizations in Bertram et al., the relative humidity at which liquid-liquid phase separation takes place (separation relative humidity; SRH) for pimelic acid/ammonium
sulfate is 76% RH, compared with the efflorescence relative humidity of 34 %RH. As a result, we hypothesize that the phase separation that we observe is a result of liquid-liquid phase separation rather than crystallization of one of the phases. We note that when liquid-liquid phase separation occurs, the phases may contain ammonium sulfate, organic matter, and water in varying ratios, rather than pure components. In contrast, we expect that succinic acid and ammonium sulfate phase separate upon crystallization. Based on the fact that the efflorescence relative humidity of succinic acid/ammonium sulfate at a 1:1 mole fraction is 48.3 %, which is higher than the efflorescence of ammonium sulfate, Choi and Chan have hypothesized that the organic component crystallizes first, forming a seed for crystallization of ammonium sulfate. This result indicates that the phase separation we observe in the succinic acid/ammonium sulfate system is due to crystallization of the organic component.
Figure 9-2: Cryo-transmission electron microscopy images of particles composed of ammonium sulfate internally mixed with organic compounds with intermediate aqueous solubility, succinic and pimelic acid. The morphology of the particles is dependent on par

The lowest solubility organic compounds (< 1 g/100mL) form phase-separated structures for all observed diameters (Figure 9-3). Particles containing suberic acid form partially engulfed morphologies, while the images of particles containing adipic or azelaic show core-shell and partially engulfed particles. We note that particles impact on the TEM grid in all orientations, and that the projection of a randomly oriented partially engulfed structure onto two dimensions will sometimes appear partially engulfed and sometimes core-shell. In contrast, a core-shell particle in any orientation will appear core-shell when projected onto two dimensions. As a result, we conclude that adipic,
azaelaic, and suberic acids form partially engulfed structures when mixed with ammonium sulfate. From the literature, we expect that these compounds undergo liquid-liquid phase separation based on their O:C ratio. Based on the parameterization given in Bertram et al., we have calculated SRH and efflorescence relative humidity (ERH) for adipic, azaelaic, and suberic acid. The values for SRH are 52 %RH, 93 %RH, and 87 %RH, respectively, and the value for ERH is 34 %RH for all the compounds of interest. We therefore expect that the phase separation in the dry systems observed with TEM is due to liquid-liquid phase separation rather than crystallization of the organic or inorganic compounds. Because liquid-liquid phase separation is caused by the salting out of the organic component, we expect the particles remain phase separated as the particle continues to dry and the aqueous salt component becomes more concentrated. As we have commented above, the spatial distribution of the two phases may not match the distribution of organic acid and ammonium sulfate throughout the particle because phases can contain both organic acid and ammonium sulfate. Mapping of adipic acid and ammonium sulfate within a particle for larger particle sizes has been reported by Zelenay et al. At the resolution at which our images were obtained, we confirmed that all particles were phase separated down to particle sizes below 100 nm. Our results are consistent with Reid et al. who showed that particles composed of an aqueous salt and organic component with limited aqueous solubility will preferentially form partially engulfed structures. Another recent study has shown that dicarboxylic acid/ammonium sulfate particles tend to form partially engulfed structures, but that these structures sometimes form during the drying of particles with core-shell morphologies. Whether the partially engulfed structures we observe form upon liquid-liquid phase separation or
upon further drying cannot be determined from our data, and will be a topic of future studies.
**Figure 9-3:** Cryo-transmission electron microscopy images of phase-separated particles composed of ammonium sulfate internally mixed with organic compounds of low aqueous solubility, adipic, suberic, and azelaic acid.
We note that our results suggest that dry particle morphology depends on the aqueous solubility of the organic compound, rather than the O:C ratio. Insoluble compounds undergo liquid-liquid phase separation. Compounds of intermediate solubility that do not undergo liquid-liquid phase separation phase separate during efflorescence. In contrast, the soluble organic compounds used in this study have been shown to either retain significant water in the organic component and/or inhibit efflorescence of ammonium sulfate. As a result, these particles remain homogeneous. Based on our study, we can predict whether a dry particle, containing one organic dicarboxylic acid and ammonium sulfate, will be phase separated or not based on the aqueous solubility of the organic component, with highly soluble organic compounds (>100 g/100mL) forming homogeneous structures, intermediate solubility compounds (approximately 5-10 g/100mL) forming size dependent structures, and low solubility compounds (<1 g/100mL) forming phase separated structures. Determining the solubility at which transitions between these solubility regimes occur will be a focus of future experiments. In addition, the phase separation behavior of mixtures of organic compounds with ammonium sulfate is of interest for understanding the much more complex system of ambient aerosol.

Aerosol particles with partially engulfed and homogeneous structures rather than core-shell structures will have different reactive chemistry, radiative properties, and interactions with clouds. Reactive chemistry with the aqueous core of an aerosol particle is reduced or suppressed by the presence of a coating, though this has a dependence on the molecular and mesoscopic structure of the coating layer. Similarly, water uptake can be slowed by the presence of an organic coating, leading to a higher
supersaturation or a larger critical nucleus needed to form a cloud condensation nucleus.\textsuperscript{19} Deposition mode ice nucleation takes place at higher supersaturations on organic particles,\textsuperscript{56} suggesting that a coating will result in a higher supersaturation for the onset of nucleation. Radiative properties are also a strong function of particle morphology.\textsuperscript{2} The absence of a complete coating through formation of a partially engulfed or homogeneous structure will increase reaction rates with the aqueous core, change radiative properties, and lower the supersaturation needed to form cloud condensation and ice nuclei.

In summary, through the use of cryo-TEM, we have characterized the morphology of accumulation mode particles (100 nm to 2.5 mm) generated and dried in the gas phase. We observe homogeneous morphologies for the most soluble organic compounds and partially engulfed morphologies for the least soluble organic compounds. The morphology of particles at intermediate solubilities exhibits a dependence on particle size. The O:C ratios of the organic compound for which we observe phase separation in submicron particles are consistent with observations for supermicron particles except when organic compounds of intermediate solubility are used.\textsuperscript{24, 29, 30} These observations demonstrate the use of a cryo-TEM for investigating morphology of model internally mixed aerosol in the accumulation mode size regime. By characterizing the morphology of these particles, we will ultimately be better able to predict their reactivity, optical properties, and ability to participate in cloud formation. These constraints on aerosol properties will lead to a better understanding of the role of aerosol particles in heterogeneous atmospheric chemistry and the Earth’s climate system.
9.4 Supporting Information for

Cryo-transmission electron microscopy imaging of the morphology of submicron aerosol containing organic acids and ammonium sulfate

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Abstract

This supporting information contains additional details of our experimental methods for the cryo-transmission electron microscopy (cryo-TEM) experiments. Specifically, we discuss the effect of temperature and microscopy substrates on our results. Information is also provided regarding differentiating different components of the particles based on their damage in the electron beam.
9.4.1 Substrate Effects on Phase Separation and Morphology

We have evaluated the extent to which the substrates used in our experiments affect the presence/absence of phase separation and the observed phase separated structure. In studies of phase separation performed with optical microscopy, researchers have noted that the substrate can affect the phase separation behavior of the particles.\textsuperscript{1, 2} In contrast to these studies, our particles are dried in the gas phase and are subsequently impacted on TEM grids. Any phase separation that occurs as the particles are drying therefore takes place in the absence of a substrate. As a result, the presence or absence of phase separation is not influenced by the substrate.

Previous studies have shown that the morphology of submicron organic aerosol particles can be affected by the substrate on which they are impacted due to the wetting of the organic component on the substrate.\textsuperscript{3} To determine the extent to which the organic component wets the carbon coated TEM grid, we have taken scanning electron microscopy (SEM) images of the particles at ambient temperature. Samples for this analysis were prepared on TEM grids using the same procedure as for cryo-TEM analysis. The TEM grids were affixed to silicon wafers using carbon tape for support. A FEI NanoSEM 630 FESEM operated at 3kV was used to image the particles. The substrates were placed in a perpendicular orientation at an angle of 5° with respect to normal in order to image the particles edge-on. Due to the perpendicular orientation, only a small line of particles is in focus in each image. The focal point can be changed to capture images of many particles on each sample. Cryogenic conditions were not available, so the particles were imaged under ambient temperatures. As a result, the particles damaged quickly and only images containing partially damaged structures were
attainable. We observe that the particles do not wet the carbon coating of the TEM grids and remain roughly spherical (Figure 9-11).

We note that the impaction process is likely to result in initial deformation of the particles as they collide with the surface before they reform their equilibrium shape on the substrate. Energy is imparted to the particles during the collision, which could cause components of the particle to move with respect to one another. We observe some organic acid/ammonium sulfate systems that form only core-shell structures (not discussed in this manuscript) and some that only form partially engulfed structures (Figure 9-3b). As a result, we know that core-shell structures are not all converted to partially engulfed structures during the impaction process and vice versa. That core-shell and partially engulfed structures are maintained during impaction also suggests that the impaction energy cannot transform particles between phase-separated and homogeneous morphologies.

**Figure 9-4:** SEM image of dry particles composed of pimelic acid and ammonium sulfate prepared on a TEM grid as described in the text and imaged under ambient conditions.
9.4.2 Effect of Temperature on Phase Separation and Morphology

In order to show that the temperature at which we obtain the images does not affect the phase separation or morphology of the particles, we have also taken TEM images of particles at ambient temperature (Figure 9-12). Under these conditions, the particles are extremely fragile in the electron beam and begin to damage almost immediately. The morphology we observe in Figure 9-12 is consistent with the cryo-TEM results shown in Figure 9-2 in that the pimelic acid/ammonium sulfate particles are phase separated in a partially engulfed morphology. As a result, we conclude that the low temperatures we use in the cryo-TEM imaging do not affect our results.

Figure 9-5: Pimelic acid/ammonium sulfate imaged with a TEM at room temperature.

9.4.3 Electron Beam Damage to Distinguish Different Particle Components

Particles composed of ammonium sulfate, dicarboxylic acids, and mixtures of these compounds are highly fragile in the electron beam in a TEM instrument. Imaging at approximately 100 K leads to added stability of the particles, but longer exposures still damage the particles. Figure 9-13 shows the damaging behavior of pure ammonium
sulfate, pure succinic acid, and an internally mixed pimelic acid/ammonium sulfate particle. Ammonium sulfate forms voids in the interior of the particle when it is damaged, while organic acids damage through disappearance of the compound from the edges of the particle. In mixed particles, the ammonium sulfate and organic acid damage in the same way as in pure salt and organic particles. Based on the differences between the damaging of ammonium sulfate and organic acids, we can distinguish between the organic and inorganic components in internally mixed particles.

Figure 9-6: TEM images of electron beam damage to a) ammonium sulfate, b) succinic acid, and c) pimelic acid/ammonium sulfate particles. The images on the left are the initial particles. The amount of damages increases from left to right. Images in (a) an
9.5 References


(20) Zuend, A.; Marcolli, C.; Luo, B. P.; Peter, T., Atmos. Chem. Phys. 2008, 8, 4559-4593.


Chapter 10 Size Dependent Morphology of Mixed Organic/Inorganic Aerosol Particles


**Abstract**

The effects of aerosol particles on heterogeneous atmospheric chemistry and climate are determined in part by the internal arrangement of compounds within the particles. We have used cryo-transmission electron microscopy to investigate the phase separation behavior of model organic aerosol composed of ammonium sulfate internally mixed with succinic or pimelic acid. We have found that no particle with a diameter less than 170 nm for succinic acid and 270 nm for pimelic acid is phase separated. Larger particles adopt a phase separated, partially engulfed structure. We therefore demonstrate that phase separation of aerosol particles is dependent on particle size, and discuss implications for aerosol-climate interactions.

**10.1 Introduction**

The greatest uncertainties in our understanding of the climate system are aerosol interactions with light and clouds.¹ In particular, organic aerosol particles have been the focus of much current scientific interest due to their chemical complexity and importance in the troposphere.² Organic aerosol reactivity, optical properties, and ability to participate in cloud formation are determined in part by the internal arrangement of
compounds within the particle. This morphology is governed by the degree of phase separation between the particle components.

Theory of bulk solutions and experiments on particles micrometers in diameter have shown that aqueous solutions of atmospherically relevant compounds can undergo liquid-liquid phase separation to form coexisting liquid phases when these compounds are present in sufficiently high concentration.\textsuperscript{3-11} Specifically, solutions of ammonium sulfate and organic molecules composed of C, H, and O that have a ratio of O atoms to C atoms of less than approximately 0.7 undergo liquid-liquid phase separation,\textsuperscript{4} though molecular structure also impacts which compounds phase separate.\textsuperscript{10} As a particle is dried, phase separation may occur through nucleation and growth or spinodal decomposition mechanisms.\textsuperscript{3} Possible morphologies that have been observed for laboratory proxies for aqueous organic aerosol include homogeneous, partially-engulfed, and core-shell structures (Figure 10-1).\textsuperscript{3-7}

![Figure 10-1: The three major types of observed particle morphologies for model aqueous aerosol particles composed of salt and soluble or insoluble organic compounds at a fixed relative humidity.](image)

Current technologies are limited in their ability to characterize particle morphology in the accumulation mode size regime (100 nm to 2.5 mm), which corresponds to the particles with the longest atmospheric residence time.\textsuperscript{12} We note that liquid-liquid phase separation has also been studied extensively by the biochemistry
community. The advent of new bioimaging analysis techniques and laser methods has led to the rise of super resolution techniques, which allow for imaging at length scales below 100 nm, but generally require the use of fluorescent dyes. In contrast to these technologies, we would ideally like to obtain information on unaltered aerosol particles at length scales smaller than the diffraction limit. Cryo-transmission electron microscopy (cryo-TEM) provides a method to characterize the structure of organic aerosol in the accumulation mode size regime that are dried in the gas phase.

In this paper, we report on the size dependence of aerosol morphology observed in the accumulation mode size regime. We use particles generated from aqueous solutions composed of equal weight percents of ammonium sulfate and succinic or pimelic acid that are dried in the gas phase and collected on transmission electron microscopy grids. Samples were analyzed at approximately 104 K to minimize electron damage of these fragile samples. We use image contrast and particle electron beam damage to characterize the phase separation. We have shown that substrate effects and the low imaging temperature have little effect on our results.

### 10.2 Results and Discussion

In order to compare the structures we observe in our TEM images to the optical microscopy data provided in the literature, we have used optical microscopy to investigate phase separation and drying of particles approximately 100 mm in diameter that are composed of ammonium sulfate and pimelic or succinic acid (Figure 10-2). For particles composed of pimelic acid and ammonium sulfate, we observe phase separation of the liquid components prior to crystallization. In contrast, in particles composed of
succinic acid and ammonium sulfate, crystallization occurs prior to any observation of phase separation. These results are consistent with the literature.\textsuperscript{5,6}

**Figure 10-2:** Optical microscopy images of the time evolution of particles drying for internal mixtures of ammonium sulfate with pimelic acid (top) and succinic acid (bottom). For pimelic acid, we show the a) initial particle, b) liquid-liquid phase separation, and c) crystallization. For succinic acid, we show d) the initial particle, e) crystallization, and f) complete crystallization.

In the cryo-TEM images, we observe that large particles have partially engulfed, phase separated structures and small particles are homogeneous (Figure 10-3). We analyzed four samples of each composition, which consisted of 519 pimelic acid/ammonium sulfate particles (440 homogeneous and 79 phase separated) and 324 succinic acid/ammonium sulfate particles (234 homogeneous and 90 phase separated). For particles composed of succinic acid and ammonium sulfate, the smallest phase separated particles are 170 nm in diameter and the largest homogeneous particles are 196 nm in diameter. For particles composed of pimelic acid and ammonium sulfate, the smallest phase separated particles are 270 nm in diameter and the largest homogeneous
particles are 276 nm in diameter (Figure 10-4). Particles larger than these size regimes are partially engulfed, and smaller particles are homogeneous. The region in Figure 10-4 where both morphologies are observed may result from plotting area equivalent diameters for non-spherical, phase-separated particles. We note that cryo-TEM can resolve phase separated particles less than 200 nm in diameter as shown for internally mixed particles composed of ammonium sulfate and adipic or azelaic acid (Fig. 10-11). Because the O:C ratio of pimelic acid is in between that of adipic and azelaic acids, our results do not suggest a shift in the O:C ratio at which liquid-liquid phase separation occurs. Based on the optical properties of the particles that we have measured using cavity ring-down spectroscopy and the electron beam damaging behavior of the particles, we conclude that the homogeneous particles are internally mixed (see supporting information).
Figure 10-3: Particle morphology observed using cryo-TEM for internally mixed particles composed of ammonium sulfate and a & b) pimelic acid or c & d) succinic acid. a & c) Larger particles are phase separated, where the organic component may contain some ammonium sulfate (see text). B & d) Smaller particles are homogeneous.

Based on our optical microscopy results, we hypothesize that larger pimelic acid and ammonium sulfate particles undergo liquid-liquid phase separation, which then results in phase separation in the dry particle. In contrast, larger succinic acid and ammonium sulfate particles phase separate as the succinic acid crystallizes, resulting in the observed phase separation in the dry particle. According to phase diagrams for liquid-liquid coexistence, the primarily organic phase may also contain ammonium sulfate. Our findings also indicate that small particles composed of these organic acids do not undergo phase separation as they dry. While the salt/organic acid systems that we have worked with are unlikely to exhibit glassy dynamics at room temperature, they could be high viscosity liquids. In a high viscosity liquid, molecules could be hindered
from initiating phase separation. Pimelic acid/ammonium sulfate is likely to undergo liquid-liquid phase separation at above 60% relative humidity (RH) based on its O:C ratio and succinic acid/ammonium sulfate undergoes efflorescence at approximately 48% RH. Based on studies of secondary organic material, these relative humidities correspond to diffusion coefficients that are indicative of semi-solid behavior. Combined with the rapid drying rates used in our particle generation setup (estimated to be 99.7 % RH/s), phase separation may be inhibited in these systems. The viscosity of the particles, however, cannot solely explain the observed size dependence. Viscosity of secondary organic aerosol decreases with size for particles with diameters less than 30 nm. Because our particles are significantly larger, we do not expect that particles 100 nm in diameter have a different average viscosity than particles at larger sizes. We therefore hypothesize that another mechanism contributes to the observed size dependence. Slowing the drying process could illuminate the mechanism by which phase separation exhibits dependence on particle size, and will be pursued in future studies.
Figure 10-4: Morphology of internally mixed particles composed of ammonium sulfate with a) pimelic acid and b) succinic acid vs. area equivalent diameter.

We can roughly compare the surface activity of homogeneous, partially engulfed, and core-shell structures using geometric arguments. Consider the ammonium sulfate to contain the active sites for reactive or non-reactive (e.g., water or ice) uptake. In core-shell structures, the organic coating covers all the active sites leading to suppression of reactions,\textsuperscript{21} and requiring higher supersaturations for cloud condensation nucleus and ice nucleus onset.\textsuperscript{22, 23} We note that molecular and mesoscale structure of the coating can limit the degree of this inhibition.\textsuperscript{24-26} For a partially engulfed structure, only some of the active sites are coated with the organic compound. Take $I/f$ to be the fraction of the
surface area $4\pi r_{pe}^2$ of a partially engulfed particle of radius $r_{pe}$ that is not coated. A homogeneous particle of radius $r_h$ has active sites over its whole surface area $4\pi r_h^2$. The particles have the same activity when $r_h = f^{1/2} r_{pe}$, meaning that a smaller homogeneous particle can have the same activity as a larger partially engulfed particle. In addition, the interaction of aerosol particles with electromagnetic radiation is determined by aerosol optical properties, which are a sensitive function of aerosol structure in the accumulation mode size regime. As a result, forming partially engulfed and homogeneous structures rather than core-shell structures will impact the calculated aerosol optical depth due to organic aerosol.

In summary, through the use of cryo-TEM, we observe that the morphology of model organic aerosol particles is dependent on their size. Homogeneous morphologies are observed for aerosol particles with diameters smaller than 196 nm for particles composed of succinic acid and ammonium sulfate and approximately 276 nm for particles composed of pimelic acid and ammonium sulfate. At diameters larger than 170 nm for particles composed of succinic acid and ammonium sulfate and 270 nm for particles composed of pimelic acid and ammonium sulfate, partially engulfed structures are seen. These results demonstrate that for some systems liquid-liquid phase separation ceases at or below the diffraction limit. In contrast to core-shell particles, the partially engulfed and homogeneous structures we observe should increase reaction rates with the aqueous core and enhance cloud condensation and ice nucleus formation activity. In addition, homogeneous particles will have higher reaction rates and cloud/ice nucleus activity compared with partially engulfed particles. As a result, these morphology differences have consequences for heterogeneous atmospheric chemistry as well as
aerosol interactions with electromagnetic radiation and clouds, which are the largest uncertainties in our understanding of the climate system. In addition to the systems studied here of relevance to atmospheric chemists, the breakdown of liquid-liquid phase separation at the nanoscale likely affects systems of interest to the wider chemistry community.

10.3 Supporting Information for

Summary

This supporting information contains detailed experimental methods for the cryo-transmission electron microscopy (cryo-TEM) experiments and optical microscopy. We also include information regarding the resolution of the cryo-TEM technique and evidence that the small, homogeneous particles are internally mixed.

10.3.1 Experimental Methods: Cryogenic-Transmission Electron Microscopy

Aerosol particles composed of dicarboxylic acids and ammonium sulfate were generated in the laboratory from aqueous solution. We use particles composed of dicarboxylic acids, one of the most common components of water-soluble organic matter in the atmosphere, and ammonium sulfate, a common salt found in tropospheric particles. Ammonium sulfate (> 99.0 %, EMD), pimelic acid (>98%, Acros), and succinic acid (>99%, Sigma Aldrich) were used without further purification. Solutions
containing 0.025 wt.% ammonium sulfate and 0.025 wt.% organic acid were made using ultrapure water (High-performance liquid chromatography grade). Aerosol particles were generated from these aqueous solutions using a constant output atomizer (TSI 3076, Shoreview, MN) with a nitrogen flow rate of approximately 1.5 L/min. Particles were dried below 2% relative humidity (RH) using a diffusion dryer containing molecular sieves (13X mesh size, Sigma Aldrich). Based on the length of the diffusion dryer, we estimate that particles are dried at a rate of 99.7% RH/s.

Samples were prepared for imaging using a cascade impactor (PIXE International Corp., Tallahassee, FL) to collect the aerosol particles onto 200 mesh carbon coated transmission electron microscopy (TEM) grids (Electron Microscopy Science, Hatfield, PA). After the aerosol particles were generated, the stream of particles was directed into the impactor at a flow rate of 1.0 L/min. A small mechanical pump backed the impactor. Samples were analyzed using a Philips EM420T TEM operated at an accelerating voltage of 120 kV. Samples were cooled in the TEM to approximately 104 K using a liquid nitrogen cooled cryo-TEM holder before exposure to electron radiation to reduce damage to the particles.

10.3.2 Experimental Methods: Optical Microscopy

The drying of droplets approximately 100 μm in diameter composed of ammonium sulfate internally mixed with pimelic or succinic acid was explored using optical microscopy. Solutions containing inorganic and organic components with a 1:1 ratio by mass were made at higher concentrations than the solutions for the TEM samples. Specifically, one solution contained 1.25 wt.% pimelic acid and 1.25 wt.%
ammonium sulfate, and the other solution contained 2.55 wt.% succinic acid and 2.55 wt.% ammonium sulfate. The droplets were produced through generation of fine spray using an aqueous solution in a Pasteur pipette. This spray was collected onto a glass slide treated with a commercial silanizing agent to make a hydrophobic substrate. High vacuum grease was used between the slide and cover slip to make an environmental chamber for the droplet. The incomplete sealing provided by the grease allowed the relative humidity around the droplet to be reduced from its saturation relative humidity to ambient relative humidity over a time scale of tens of minutes. This time scale allowed us to capture the phase separation and crystallization of components of the particle using a CCD camera coupled to a 40x objective.

10.3.3 Resolution of Phase Separation below 200 nm

In the cases of particles of ammonium sulfate mixed with pimelic acid or succinic acid, all particles with diameters smaller than 170 nm are homogeneous in morphology. This observation is not due to the resolution of the cryo-TEM technique. For samples of azelaic and adipic acid mixed with ammonium sulfate, for example, we observe phase separation at diameters less than 200 nm (Figure 10-11). Azelaic and adipic acids are simple dicarboxylic acids with O:C ratios of 0.444 and 0.667, respectively, and as a result, we expect them to undergo liquid-liquid phase separation.² We also expect that they should remain phase separated in the dry particle. Unlike pimelic acid/ammonium sulfate and succinic acid/ammonium sulfate particles, we do not observe a size dependence of the phase separation of azelaic acid/ammonium sulfate and adipic acid/ammonium sulfate in the accumulation mode size regime.
10.3.4 Homogeneous Particles are Internally Mixed

Evidence that the homogeneous particles are internally mixed comes from the preparation method, the damaging behavior of the particles in the electron beam, and the extinction cross sections of the particles measured with cavity ring-down spectroscopy. Based on the preparation method, we expect particles to be internal mixtures composed of equal masses of ammonium sulfate and organic acid. Specifically, internally mixed particles are produced by atomizing an aqueous solution of the compounds of interest. Because the solution contains the salt and organic components, we assume the liquid droplets contain both species, which would produce dry particles that contain both compounds. In terms of the damaging behavior, we have shown that we can differentiate ammonium sulfate and the organic acids based on their behavior in the electron beam.
Specifically, ammonium sulfate damages through the formation of voids in the interior of the particle, while organic acids damage by the disappearance of material from the borders of the particle. In internally mixed, phase separated particles, each component damages similarly to particles composed of pure salt. In Figure 10-12, we show that the small, homogeneous particles damage through the formation of voids homogeneously distributed throughout the particle. This damaging behavior indicates that ammonium sulfate is evenly distributed throughout the particle.

![Figure 10-6: Damaging behavior of homogeneous particles composed of succinic acid and ammonium sulfate in the cryo-TEM. a) The undamaged particle and b) damaged particle after exposure to the electron beam. The electron beam causes voids to form throughout the particle.](image)

We have described using cavity ring-down spectroscopy (CRDS) to study size-selected aerosol particles made from aqueous solution in a previous publication. We have shown using a combination of TEM and CRDS that spherical particles are size selected well in our flow system down to small diameters. Using our CRDS flow system, we have measured the extinction coefficients, $b_{ext}$, and concentrations, $N$, of size selected, internally mixed aqueous aerosol particles at small diameters. The extinction cross section, $\sigma_{ext}$, of the particles is given by $b_{ext}/N$. The error in the extinction cross
section is determined from the uncertainty in the measurement of extinction coefficient and concentration. In the size selection process, particles are flowed through an $^{85}$Kr sealed-source neutralizer, which gives the particles a known distribution of charges.\textsuperscript{5} Positively charged particles are selected based on their electrostatic mobility, which is inversely proportional to the particle diameter.\textsuperscript{6} Based on the theoretical distribution of charges and the size distribution of the particles, as measured with a scanning mobility particle sizer (TSI 3938L75, Shoreview, MN), the number of particles with a +1 charge is much larger for the data set discussed (particles with diameter $\geq$ 100 nm) than the number of particles with higher charges. The ratio of the concentration of multiply charged particles to the concentration of singly charged particles is greatest for the smallest particle sizes.

In addition to our measured extinction cross sections, shown in Figure 10-13, we have calculated theoretical extinction cross sections that are corrected for +2 and +3 charged particles. Using Mie scattering theory, we calculate the extinction efficiency, $Q_{\text{ext, +1}}$, of ammonium sulfate for particle sizes from 100 nm to 250 nm using a refractive index of 1.53.\textsuperscript{7} We use a refractive index of 1.45 for succinic acid,\textsuperscript{8} and we assume a refractive index of 1.45 for pimelic acid because it is an unsaturated hydrocarbon that is similar in structure to succinic acid. We also calculate the extinction efficiencies of the +2 diameters, $Q_{\text{ext, +2}}$, and +3 diameters, $Q_{\text{ext, +3}}$. Generally, optical properties are corrected for +2 particles; we have chosen to also correct for +3 particles because higher order charges may be important for the small particle diameters examined in this experiment. We convert each of these extinction efficiencies to extinction coefficients using the equation $b_{\text{ext}}=NQ_{\text{ext}}\pi r^2$, where $r$ is the particle radius and $N$ is the particle
concentration in units of cm$^{-3}$. Based on the experimental concentration and the known distribution of charges, we can calculate the concentrations of +1, +2, and +3 particles. We label the extinction coefficients and concentrations according to the particle charge they are calculated for, e.g. $b_{\text{ext},+1}$, $b_{\text{ext},+2}$, $b_{\text{ext},+3}$, $N_{+1}$, $N_{+2}$, $N_{+3}$. For example, $b_{\text{ext},+1}=N_{+1}Q_{\text{ext},+1}\pi r_{+1}^2$. We then calculate the total theoretical extinction cross section according to

$$
\sigma_{\text{ext}} = \frac{1}{N} \left( b_{\text{ext},+1} + b_{\text{ext},+2} + b_{\text{ext},+3} \right)
$$

For the internally mixed particles, we need to make an assumption about the effective refractive index and the shape of the particles. To get an approximate extinction cross section from Mie scattering theory, we assume that the particle is homogeneous with a volume weighted average refractive index. We note that core-shell particles and homogeneous particles have relatively similar extinction cross sections,$^9$ and partially-engulfed particles may have a similar magnitude of deviation from the extinction cross sections of homogeneous particles as core-shell particles. As a result, this approximation may be reasonable for small concentrations of multiply charged particles. The uncertainty in the theoretical calculation stems from the standard deviation of the concentration measurement.

The theoretical extinction cross sections show that the internally mixed pimelic acid/ammonium sulfate particles should have a refractive index between that of ammonium sulfate and the organic acid, but closer to the value of the organic acid. The experimentally obtained extinction cross sections for pimelic acid/ammonium sulfate show that the extinction cross sections of the internally mixed system are always less than ammonium sulfate, and higher than or the same as the pimelic acid within the
experimental uncertainty. Because we know that ammonium sulfate is contained in these particles due to the damaging behavior, but the extinction cross section is close to that of the organic acid, we conclude that the internally mixed particle contains both ammonium sulfate and pimelic acid.

For the succinic acid/ammonium sulfate particles, the relative magnitudes of the extinction cross sections match the theoretical prediction for all diameters except 250 nm. For this diameter, the ammonium sulfate and succinic acid extinction cross sections differ from the theory, but the internally mixed particles have the highest magnitude, as predicted. We note that the theoretical extinction cross sections are higher for the succinic acid and internally mixed particles than ammonium sulfate, even though the refractive index of ammonium sulfate is higher than the refractive index of succinic acid. The theoretical extinction cross sections are sensitive to the concentration of multiply charged particles especially at these small diameters, where the fraction of multiply charged particles is higher than at larger diameters. The difference in the concentration of multiply charged particles of ammonium sulfate, succinic acid, and internally mixed particles causes the extinction cross sections of succinic acid and internally mixed particles to be larger than the extinction cross section of ammonium sulfate at each diameter. Because succinic acid/ammonium sulfate particles match the relative magnitudes of extinction cross sections predicted, we assume that these particles are internally mixed. The optical properties and electron damaging behavior therefore show that the homogeneous succinic acid/ammonium sulfate particles and the pimelic acid/ammonium sulfate particles are internally mixed.
Figure 10-7: Extinction cross sections for a & c) ammonium sulfate, pimelic acid, and internally mixed ammonium sulfate/pimelic acid, and b & d) ammonium sulfate, succinic acid, internally mixed ammonium sulfate/succinic acid as a function of particle mobility diameter. A& b) Theoretical calculations using the experimental concentrations, as described in the text. The error is from the uncertainty in the concentration of the particles. C & d) Experimentally measured extinction cross sections. The error shown is from the uncertainties in the concentration of the particles and the extinction coefficients.

10.3.5 References:


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10.4 References


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Chapter 11 Aerosol Measurements in One of the Most Polluted Cities in the World: Ulaanbaatar, Mongolia

This chapter has been adapted from: Christa A. Hasenkopf, Daniel P. Veghte, Gregory P. Schill, Sereeter Lodoysamba, Miriam Arak Freedman, and Margaret A. Tolbert. “Aerosol Measurements in One of the Most Polluted Cities in the World: Ulaanbaatar, Mongolia” Environmental Science and Technology Letters, Submitted.

Abstract

Air pollution is attributable to 7 million deaths per year, or one out of every eight deaths globally. In particular, high concentrations of particulate matter (PM), a major air pollutant, have significant impacts on health and regional climate in urban centers. Many of the most polluted places, largely in developing countries, go severely understudied. In this letter, we characterize the physical and chemical properties of PM in one of the most PM-polluted cities in the world: Ulaanbaatar, Mongolia. Bimonthly aerosol samples were collected over 10 months from a central location and analyzed for composition and ice nucleation activity. Almost all particles collected were inhalable, consisting primarily of mineral dust, soot, and sulfate-organic. In winter, all classes of PM concentrations increase, with increased sulfur concentrations, and the particles are less active towards heterogeneous ice nucleation. These measurements provide the longest and most comprehensive seasonal set of PM data from Ulaanbaatar.
11.1 Introduction

Driven by urbanization, overall increasing populations, and improved economic development, developing countries must often meet higher energy demands with fuels that produce airborne-pollutants as byproducts. In addition to affecting climate, these pollutants compromise the health of billions, especially those in developing countries, which account for more than 80% of the world’s population.\textsuperscript{1} The World Health Organization (WHO) deems air pollution the most lethal environmental hazard on the planet, responsible for one of every eight deaths.\textsuperscript{2}

Despite the threats air pollution poses, the most polluted places are vastly understudied. Fig. 11-1 compares the annual average concentration of PM10 (particulate matter, PM, 10μm or less in diameter) in cities around the world with the number of scientific papers that have been published about air pollution in a given city through 2011.\textsuperscript{3} As well as showing well-researched cities, Fig. 11-1 shows the ten most PM10-polluted cities from the 2011 WHO Outdoor PM10 Survey of over 1000 cities.\textsuperscript{3}
Fig. 11-1 shows Ulaanbaatar, Mongolia as the city with the second highest annual average PM10 levels. Additionally, a 2011 World Bank study reports monthly Ulaanbaatar average PM2.5 (particles with diameters less than 2.5 μm) concentrations in December 2008 and January 2009 exceeding 1000 μg m⁻³ – more than 40 times WHO guidelines. A study by Allen et al. conservatively estimates that up to 25% of deaths annually in Ulaanbaatar are caused by PM.

The majority of Ulaanbaatar’s 1.3 million people live in the ger district, comprised of traditional Mongolian homes (gers) and wooden buildings, typically heated by coal-burning stoves that emit incompletely combusted fuel as soot from chimneys 3-4m high. Coal-fired heat-only boilers (HOBs) are also prevalent in the ger district for heating in larger buildings. With
60% of the city’s residents living in the ger district, it is unsurprising that the PM emissions from stoves and HOBs have been found to be main sources of PM-pollution.\textsuperscript{7,8} Ulaanbaatar’s sub-arctic, semiarid climate influenced by the Siberian High and its geography exacerbate the effects of pollution from the ger district. Ulaanbaatar is situated at an altitude of 1,350m in a valley, and also experiences typical impediments to mixing that are common in cities located in higher altitude valleys.

Recently, donor organizations such as the U.S.’s Millennium Challenge Corporation (MCC) and World Bank have, along with the Mongolian Government, taken several PM-pollution mitigation measures. These measures included a 41 million USD effort by MCC to sell nearly 100,000 efficient stoves and Mongolian government-subsidized alternative fuels.\textsuperscript{9} Despite these efforts, there is not currently a robust, long-term method of monitoring the outcomes of these actions, in terms of outdoor air pollution concentrations, health impacts, or comparing either metric to previous baseline studies.

To understand the sources, chemistry, and consequences of PM for air quality and regional climate, long-term data sets are needed in which particle composition and physical properties such as ice nucleation onset are investigated. We have collected bimonthly samples from a residential location in Ulaanbaatar, as described in the supporting information, over ten months (June 2012 to March 2013; Fig. 11-11). Samples were analyzed for type and elemental composition by transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) as well as for ice nucleation onset.
11.2 Materials and Methods

11.2.1 TEM/EDS Studies

Transmission Electron Microscopy (TEM) samples were prepared by impacting particles on TEM grids (200 mesh copper coated with continuous carbon, Electron Microscopy Science, Hatfield, PA). Particles were imaged using a Philips EM420T operated at an accelerating voltage of 120kV. Particles were classified based on shape (spherical, fractal, irregular). The area of each particle was determined using ImageJ software (National Institutes of Health, Bethesda, MD). A size distribution for each shape was calculated by converting the area calculated for each particle to an area-equivalent diameter, assuming the particles are spheres and consequently, the projected area of the particles on the TEM images are circles. The error caused by having a finite number of particles is estimated by dividing the images into three subsets and calculating a standard deviation for the number of each particle type as in Veghte and Freedman. To obtain the elemental composition of the particles, the EDS detector on the Philips EM420T was used. Error is not calculated for the EDS data.

11.2.2 Ice Nucleation Studies

The experimental setup used for ice nucleation experiments has been described previously. Briefly, a Nicolet Almega XR Raman microscope, equipped with an Olympus BX-51 microscope, has been coupled to a Linkam THMS600 environmental cell. The temperature inside the cell is controlled by a Linkam TMS94 temperature controller (accuracy of ±0.1 K). Water vapor inside the environmental cell is controlled by mixing dry and humidified flows of N₂; the partial pressure of water is measured by a Buck Research CR-1A chilled mirror hygrometer in line with the cell, (accuracy of ±0.15 K). As in Schill et al., the relative humidity over the sample was controlled by keeping the water partial pressure constant, and slowly
lowering the temperature at a rate of 0.1 K min$^{-1}$. Ice particles were detected visually, confirmed spectrally, and video of the ice sublimation process revealed the IN.

11.3 Results and Discussion

11.3.1 Characterization of Particle Types

Fig. 11-2 shows TEM images of the types of particles we observed. The type of particle is determined first by its characteristic shape (spherical, fractal, irregular) and then by its elemental composition. Based on composition, spherical particles were assigned to be organic and sulfate-organic particles with a small amount of fly ash and possibly also tar balls. Fractal particles are composed of soot and fly ash, where the soot can be partially collapsed due to additional material. Irregularly shaped particles are assumed to be mineral dust because they primarily contain Al, Si, and Ca, with a small fraction of anthropogenic particles and fully collapsed soot (Figs. 11-2, 11-12). Spherical particles consistently have the highest number concentration, followed by fractal particles, and finally irregularly shaped particles (Fig. 11-13).
The effect of particulates on human health depends in part on their size, where particles less than 10 μm are inhalable, and particles less than 2.5 μm have the strongest correlation with mortality rates. To determine the fraction of respirable particles, size distributions of the spherical, fractal, and irregular particles were determined from the two-dimensional projections of the particles observed in the TEM images. As shown in Fig. 11-3, all particles observed with TEM are in the inhalable range, with almost all particles less than 2.5 μm. Particles were also collected for ice nucleation experiments. The substrates for the ice nucleation experiments are larger than the TEM grids and therefore collect more particles over the same time period. The size distribution of these particles was analyzed using optical microscopy, which is sensitive to larger particle sizes (> 500nm). As a result, particles observed with optical microscopy were most likely irregularly shaped particles. Chemical compositions of the particles collected for the ice
nucleation experiments were not obtained because all of the particles fluoresced, which is consistent with mineral dust and soot samples. The average particle size detected with optical microscopy was $1.9 \pm 1.5 \mu m$. Less than 1% of the particles observed each month were greater than 10 $\mu m$ in diameter. From the TEM and optical microscopy analysis, it can be seen that almost all particles collected fall within the size regime that is important to consider for human health.

![Figure 11-3: Size distributions for spherical, fractal, and irregularly shaped particles averaged over all the particles collected in this study as analyzed by TEM. The area of the particles in the TEM images was measured and converted to an area equivalent diameter by assuming that the particles are spheres and therefore are circular in the TEM images. The bins are the same size for spherical and fractal particles and larger for irregular particles. The normalized number of fractal particles in the smallest bin is 0.24.](image)

11.3.2 Seasonal Particle Concentration and Heterogeneous Chemistry

To assess the impact of particles on human health as a function of season, we estimate the particle number concentration in each month. The relative particle concentrations are estimated in a given month by plotting the number of particles per
TEM image per hour of collection time (Fig. 11-4). Relating this calculation to the absolute particle concentrations assumes that the collection efficiency is the same in every collection and that the levels of particulate matter on the collection days are representative of that month. Even with the variability shown in Fig. 11-4, however, the particulate concentrations are consistently higher during the colder months (Nov-March) than in the warmer months (June-Oct). Increasing concentrations of particulates during the winter months is consistent with previous literature.4,5,13

To estimate the degree of aging in the Ulaanbaatar particles, we have investigated how the amount of sulfur in the particles varies during the year for spherical, fractal, and irregular particles (Figs. 11-4, 11-14, 11-15). For all particle types, sulfur is found in a larger number of particles in November – March compared with June – October. Our results are consistent with a study of total suspended particulates and PM10 in Xian, China during September 1996 - August 1997, in which sulfate content was found to be highest in winter due to residential heating, lowest in summer, and at intermediate concentrations during the spring and autumn.15 The increase in sulfur observed in winter in Ulaanbaatar is consistent with increased domestic stove, HOBs, and coal-fired power plant use in winter, given the elemental profiles of these energy sources from Davy et al., and that these three sources are associated with 95% of sulfur dioxide emissions in Ulaanbaatar.8,16
Figure 11-4: The number of particles collected per TEM image per hour collection time for a) all particles, b) spherical particles, c) fractal particles, and d) irregularly shaped particles. The months November – March are shaded blue. Note that all of the panels have different y-axis scales. For June - Sept (labeled “summer”) and Nov – March (labeled “winter”), the percentage of the particles by number that contain sulfur is indicated in red, and the percentage by number without sulfur is indicated in black.
11.3.3 Ice Nucleation

In addition to classifying the ambient particles by size, shape, and composition, the critical ice saturation ratios ($S_{\text{ice}}$) required for the onset of heterogeneous ice nucleation were determined (Fig. 11-5). $S_{\text{ice}}$ is calculated as the ratio of the partial pressure of water vapor to the saturation vapor pressure over ice at a given temperature. For each month, $S_{\text{ice}}$ values are averaged over three temperatures, 230, 235, and 240 K. A minimum of nine experiments was performed for each month. Water uptake prior to ice nucleation was not observed within the limits of our instrument, suggesting that deliquescent salts and hygroscopic organics do not contribute a large mass fraction to heterogeneous ice nuclei. Resolution of the optical microscope did not allow for visual identification of the types of particles (spherical, fractal, irregular) that nucleated ice. Particle number, diameter, and surface area loadings from month-to-month are comparable, however, suggesting that differences in particle type and chemistry are dictating differences in ice nucleation ability (Figs. 11-16 to 11-18). The onset $S_{\text{ice}}$ values show clear seasonal variation; particles are generally more efficient ice nuclei (require lower supersaturations with respect to ice for the onset of nucleation) from June - September than December - March.
Figure 11-5: The supersaturation with respect to ice, $S_{\text{Ice}}$, at the onset of heterogeneous ice nucleation for samples collected in this study. Error bars are determined from repeated experiments. The months November – March are shaded in blue.

Ice nucleation activity is lowest when the fraction of particles containing sulfur is highest. Deactivation of kaolinite, montmorillonite, illite, quartz, and Arizona test dust due to exposure to sulfuric and nitric acid has been observed in heterogeneous ice nucleation experiments in which particles are exposed to subsaturated water vapor.\textsuperscript{17–23} Based on these experiments, we hypothesize that the observed deactivation in the winter months is due to changes in the degree of processing as indicated by the fraction of particles that contain sulfur. This result is consistent with field studies that have found reduced sulfate content in cirrus residuals.\textsuperscript{24–26} As a result of processing, mineral dust
particles in the region may be more likely to form liquid or mixed phase clouds rather than ice clouds in the winter months, which could in turn affect regional climate.

11.4 Summary

We have characterized bimonthly samples of aerosol particles from Ulaanbaatar, Mongolia over a 10-month period from June 2012 to March 2013. These samples primarily consist of spherical particles (organic and sulfate/organic), fractal soot particles, and irregularly shaped mineral dust particles. Almost all particles collected were less than 10 μm in diameter, and are therefore, inhalable. In the winter months, the concentration of particulate matter increases, the sulfur content of the particles increases, and the heterogeneous ice nucleation activity of the particles decreases. We hypothesize that the decrease in ice nucleation activity is due to reaction with sulfur-containing compounds. This decrease could affect the types of clouds that are formed in the winter months. These measurements are the first long-term seasonal study of particulate matter in one of the most PM10-polluted cities in the world.

11.5 Supporting Information

Summary: The supporting information contains additional information about the sampling site and transmission electron microscopy experiments. In addition, additional text and figures from the chemical characterization and ice nucleation experiments are included. Specifically, we address:
1) Description of the sampling site

2) Additional Details of Transmission Electron Microscopy Experiments

3) Transmission Electron Microscopy Images of Irregularly Shaped Particles

4) Particle Composition

5) Heterogeneous Chemistry

6) Additional Ice Nucleation Results
11.5.1 Description of Sampling Site

The sampling site (Fig. 11-6) was located east and slightly north of the city center, approximately 10 km from the city’s coal-fired power plants and 600 meters away from the southern edge of the ger district. The sampling site was on a balcony, approximately 15 m above the ground, facing south. No filter was used to prevent the collection of larger particles.

![Figure 11-6: Map of Ulaanbaatar Mongolia with relevant sites for this study marked. Ulaanbaatar is located at 1310 m in a valley between two mountainous areas. The main sources of particulate matter pollution are from the ger district, which blankets the Northern half of the city, as well as three coal-fired power plants in the outer areas of the western portion of the city. Note that Power Plant #1 is no longer functioning. The measurement site from this study is shown, as well. To note: Wind typically blows from a northwesterly direction over the city, with low winter wind speeds due to the Siberian High that sits over the region throughout the winter and highest windspeeds in the spring time.1,2](image)

11.5.2 Additional Details of Transmission Electron Microscopy Experiments
For the transmission electron microscopy (TEM) analysis, 20-30 images per TEM grid were taken to average over 1000 particles per sample for a total of 23049 particles investigated. A total of 19124 spherical particles, 3685 fractal particles, and 240 irregular particles were counted. For each bimonthly TEM sample, an average of 956 spherical particles (minimum = 148, maximum = 2443), 184 fractal particles (minimum = 12, maximum = 638), and 12 irregular particles (minimum = 3, maximum = 24) were analyzed.

To determine elemental composition with energy dispersive X-ray spectroscopy (EDS), 20 particles of each of the three types (spherical, fractal, or irregular) were analyzed. Because the particles are inhomogeneous and irregular in structure, no quantitative data could be obtained, but high intensity peaks correspond to the predominant species in each sample. Carbon and copper could not be observed due to the use of a carbon coated copper substrate. Oxygen was present in the background signal, and as a result, it was also not included in the analysis. Nitrogen is obscured by the carbon peak, and cannot be detected.

11.5.3 Transmission Electron Microscopy Images of Irregularly Shaped Particles

Additional images of irregularly shaped particles are shown in Fig. 11-7.
Figure 11-7: TEM images of representative irregularly shaped particles of different compositions illustrating the wide range of particle shapes and compositions observed.
11.5.4 Particle Composition

The fraction of each particle type (spherical, fractal, irregular) is plotted by number and area for each month in Figures 11-8a and 11-8b, respectively. The area is calculated from the projected area of the particles observed in the TEM images. While spherical particles dominate the number fraction, they are generally small in area. Irregular particles, which compose the smallest number fraction, are the largest fraction by area. The number fraction of particles is dominated by the spherical particles, except in October 2012 when a large number of fractal particles were collected. The area fraction is dominated by irregular particles, though fractal particles are within the experimental error in October 2012 – December 2012 and March 2013, and spherical particles are generally within error of the irregular particles in November 2012 – March 2013.
Figure 11-8: a) The number fraction of each particle type over the ten-month collection period. b) The area fraction of each particle type over the collection period. The area is calculated from the projected area of the particle seen in the TEM images. The legends for a and b are the same. The error bars shown in the figures are an upper estimate of the error caused by having a finite sample size, as described in the Materials and Methods Section. The fractions of the different particle types for each month sum to 1.0.

We have used EDS to obtain the elemental composition of the spherical, fractal, and irregularly shaped particles. For the spherical particles, 58% contain sulfur, of which 21% contain potassium and 5% contain phosphorous, 39% contain only carbon and oxygen, and 4% contain metals (Fe, Mg, Al, Ca, Ti, Mn). Some of the metal-containing particles also contain sulfur. For the fractal particles, 86% contain only carbon, 12% contain sulfur, and 3% contain metal (Fe, Ti, Al, Zn).

Because the irregular particles mostly contain mineral species, the divisions we chose included calcium with no other major species, aluminum and silicon with calcium, aluminum and silicon with no other major species, silicon with no other major species,
carbon only, salts (Na or K with Cl), and “other”, which includes particles that mainly contained other elements (Fe, Cr, Ti, F) as major species (Fig. 11-9). Because iron is a major absorbing species in mineral dust aerosol particles, we additionally investigated the iron composition in these samples. We observe that much of the dust (60%) is composed of aluminosilicates and aluminosilicates with calcium. Silicon is also a major contribution to the observed dust (15.8%), which is reasonable because dust also tends to contain silica in high concentrations. The label “other” refers to particles containing metals (Fe, Cr, Ti) or F. Iron and sulfur are also commonly found in the minerals. Elements associated with the sulfur included calcium and silicon. Some of the sulfur associated with calcium could be the mineral gypsum. For mineral dust particles, sulfur is a large component throughout the year (61% annual average), but is enhanced from November - March (71%). Monthly trends in iron concentration are also shown in Fig. 11-9.
Figure 11-9: a) The elemental composition of the irregular particles. The particles are primarily composed of Ca, Al, and Si with smaller contributions from carbon and salts, which suggests the presence of Ca salts such as calcite and gypsum, aluminosilicates with and without calcium, silicates, fully collapsed soot, and salt. b) The fraction of irregular particles associated with sulfur. As seen in the main text, the fraction of particles with sulfur is higher in November – March. c) The fraction of irregular particles associated with iron and other trace metals (Fe, Cr, Ti) or F.

11.5.5 Heterogeneous Chemistry

The number fraction of particles containing sulfur is shown as monthly averages in Fig. 11-9. From the EDS data, spherical and fractal particles were divided into three subcategories:
carbon, sulfur and carbon, and metal-containing (Fe, Cr, Si, Mg, Ca, Ti, Ni). When particles had the same composition as the grids with no other elements, we classified them as carbon-containing particles. Because the mineral dust particles often contain metals, they are only classified in Fig. 11-9 in terms of whether they contain sulfur.

![Figure 11-10](image)

**Figure 11-10**: The composition of a) spherical, b) fractal, and c) irregularly shaped particles determined from EDS. For (a) and (b), if particles contain metal, they are grouped as “metal”; if the particles have no metal but contain sulfur, then they are grouped as “carbon/sulfur”. All other particles contain carbon. For (c), the majority of particles contain metal, and as a result, they are grouped as containing sulfur or not containing sulfur. For each month, the fractions sum to 1.0. The months November – March are shaded in blue.
11.5.6 Additional Ice Nucleation Results

An example image of an ice crystal and its subsequent IN is shown in Fig. 11-11. By recording video of the sublimation process, the particle responsible for ice nucleation can easily be identified. As mentioned above, however, the optical resolution of the microscope prevents classification of IN by shape and fluorescence prevents classification by Raman spectroscopy. The average size of the IN, however, suggests that the majority of IN are irregular mineral dust particles. In all cases, great care was taken to ensure that the first ice event was detected. If multiple IN were detected in the same field of view, that point was discarded and another ice nucleation experiment was conducted.

![Figure 11-11: An ice crystal and the heterogeneous ice nucleus on which it formed. An ice crystal with a particle inside (marked with an arrow) is shown on the left. The ice is sublimed to reveal the particle shown on the right. This sample is from an experiment at 225 K on a November 2012 sample.](image)

For particle number, diameter, and surface area analysis, five 20x images were taken at random across the disc. To determine the total number of particles on the fused-silica disc, the number of particles from the five 20x images was extrapolated to the area of the entire disc. The area and spherical equivalent diameter of each particle were
determined using ImageJ software. The smallest detectable particle diameter under these conditions was ~0.74 µm.

Since heterogeneous ice nucleation is a surface-related process, it has been suggested that ice nucleation onsets are surface-area dependent. In order to confirm that the month-to-month $S_{\text{ice}}$ values are directly comparable, a surface-area parameterization was applied. This parameterization, the ice nucleation active surface site density ($n_s$), assumes that time dependence is of secondary importance\textsuperscript{3,4}. The number of ice nucleation active sites per surface area is defined as

$$n_s = \frac{FF \cdot T}{SA_{\text{aerosol}}}$$

where FF is the frozen fraction, T is temperature, and $SA_{\text{aerosol}}$ is the average surface per particle. Since care was taken to ensure that the first ice nucleation event was observed, only one $n_s$ value was determined per experiment. The $n_s$ values for each month can be found in Fig 11-12. The error bars are determined from the range of observed surface areas. As shown, the $n_s$ values of the monthly samples are the same, within error. Further, the $n_s$ values do not correlate with the trends in ice onsets found in Fig. 11-5. This indicates that the particle number, diameter, and surface area are similar from month to month. Thus, the $S_{\text{ice}}$ values found in Fig. 11-5 are directly comparable.
Figure 11-12: Number of ice nucleation active surface sites per m² for monthly samples this study. As shown, the monthly ns values are all within error of each other. Thus, the ice nucleation onsets found in Fig. 11-5 are directly comparable, suggesting that a chemical mechanism is dictating the changes in $S_{\text{ice}}$ values.

Of the three particle types characterized in the TEM images, the particles that nucleate ice are likely to be irregularly shaped particles, as discussed above. The irregularly shaped particles consist mainly of mineral dust with only a small contribution from condensed soot (4.2%). The average size of the condensed soot particles is 780 nm in diameter with a maximum size of 3 µm. In contrast, the sizes of the ice nucleating particles are generally greater than 3 µm (Fig. 11-12). We conclude that ice nucleation was most likely observed on mineral dust particles.
Figure 11-13: The diameter of particles that heterogeneously nucleated ice.

11.5.7 References:


(2) Air Quality Analysis of Ulaanbaatar: Improving Air Quality to Reduce Health Impacts; Washington DC, 2011.


11.6 References


(3) *Urban Outdoor Air Pollution Database*; Geneva, Switzerland, 2011.

(4) *Air Quality Analysis of Ulaanbaatar: Improving Air Quality to Reduce Health Impacts*; Washington DC, 2011.


(9) MCC Fact Sheet on Mongolia Project to Address Air Pollution http://iipdigital.usembassy.gov/st/english/texttrans/2013/04/20130424146351.html #ixzz3FaQ7rCAb (accessed Oct 8, 2014).


Chapter 12 Conclusion and Future Directions

12.1 Optical Properties of Mineral Dust Aerosol Particles

12.1.1 Conclusion and Implications

The extinction cross sections of individual components of mineral dust were studied using cavity ring down spectroscopy. For mineral dust species that are non-absorbing and have an aspect ratio near one, Mie scattering theory is sufficient to model the extinction cross section. Species well modeled using Mie scattering theory accounting for polydispersity include: calcium carbonate, quartz, and feldspars. When additional complexity is added to the particles by either increasing the irregularity or using an absorbing species, additional modeling parameters are needed. For hematite (an absorbing species with surface roughness and an aspect ratio near one), the DDA was used to better model the optical properties through roughened spheres, spheroids, or a combination of roughened spheroids. For aluminosilicate clay minerals that are nonabsorbing, but high aspect ratios, better fits were found when the shape of the particle was included. Arizona test dust was used to model a heterogeneous mixture of mineral dust types. Using individual models that incorporate the best match between model and optical extinction from CRDS, there was not a good match between experimental CRDS results and the model. When individual polydispersity from each component were included, a better match between the ATD and theory was found. Understanding individual components polydispersity and modeling parameters leads to a better model to predict the optical properties of heterogeneous mineral dust samples.
The models that best matched the experimental extinction cross sections from CRDS were fitted using Mie scattering theory to retrieve an effective refractive index. By using an effective refractive index, computation time for modeling the optical properties can be shortened. Mie scattering theory was used over the size range from 30 nm to 1010 nm and subgroups to determine the best refractive index to be used different components and sizes of mineral dust aerosol particles (Table 12-1). Quartz is a particle that has an aspect ratio near one (1.64), and spheroids with an aspect ratio of 1.64 match closely to Mie scattering theory. For the more complex systems of hematite and clay minerals, an effective refractive index using Mie scattering theory is calculated from the DDA models. The DDA extinction cross section calculations are fitted using Mie scattering theory to simplify the complex model. The real part of the refractive index is smaller for all species than the bulk refractive index. When the particles are modeled using smaller size ranges, smaller particles tend to have a higher effective refractive index, while larger particles have a lower effective refractive index due to models being more sensitive to shape for larger particle sizes. Utilizing Mie scattering theory, effective refractive index can be used to reduce the computation time needed to model individual components.

Table 12-1: Effective refractive index from modeling DDA scattering results using Mie Scattering theory for mineral dust species.

<table>
<thead>
<tr>
<th>Species</th>
<th>Literature</th>
<th>30-1010</th>
<th>30-510</th>
<th>530-1010</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>1.55</td>
<td>1.55</td>
<td>1.55</td>
<td>1.55</td>
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<tr>
<td>Hematite</td>
<td>2.98+0.07i</td>
<td>2.89+0.14i</td>
<td>2.9+0.14i</td>
<td>1.61+0.15i</td>
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<tr>
<td>NX-Illite</td>
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<td>1.52</td>
<td>1.54</td>
<td>1.49</td>
</tr>
<tr>
<td>KGa-2</td>
<td>1.564</td>
<td>1.47</td>
<td>1.48</td>
<td>1.45</td>
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<tr>
<td>STx-1b</td>
<td>1.522</td>
<td>1.45</td>
<td>1.46</td>
<td>1.43</td>
</tr>
</tbody>
</table>
12.1.2 Future Directions: Size selection by mass

In our experiments using CRDS to analyze the optical properties of irregularly shaped mineral dust aerosol particles, we have seen that rough or elongated particles have a larger size distribution than the transfer function of the DMA derived for spherical particles.\textsuperscript{1} With this broad distribution of particles, other techniques were needed to determine the polydispersity of the size selected aerosol samples from the DMA.\textsuperscript{1} A possible improvement to size selecting the irregular particles would be using an aerosol particle mass analyzer (APM) in addition to a DMA due to size selection based on the mass of the particle instead of the electrostatic mobility.
APM are often used in series with a DMA to first size select the particles based on mobility diameters (DMA), then separate out individual aerosol species that have different densities, but same size using the APM. A simplified diagram of an APM is shown in Figure 12-1. Before introduction into the APM, the particle flow is given a known charge distribution using a radioactive source similar to the DMA setup. The APM consists of two cylindrical electrodes where the aerosol particles are introduced into the annular space between them. A potential is applied between the two cylinders to...
attract the charged particles. The two cylindrical electrodes are rotated with an angular velocity in which the particles are selected based on mass where they have a stable path that balances the electrostatic and centrifugal forces. The relationship between the mass, \( m \), of the particle selected can be described below according to

\[
m\omega^2 r = \frac{qeV}{r \ln(r_2/r_1)}
\]

where \( \omega \) is the angular velocity, \( q \) is the number of elementary charges on the particle, \( e \) is the elementary charge, \( V \) is the voltage, \( r \) is the radius to the center of the space, \( r_1 \), is the inner electrode, and \( r_2 \) is the outer electrode. The shape will still affect the size selection of the APM since it is a flow system, but better size selection is possible since size selection is dependent on the momentum of the particles instead of just the electrostatic mobility. Experiments would show how an APM would size select versus a DMA and see if better size selection was present for roughened and elongated particles.

### 12.2 Organic Aerosol Particles

#### 12.2.1 Conclusion and Future Directions

The morphology of dry submicron organic/inorganic aerosol particles was studied using TEM. Mixtures of 1:1 organic and ammonium sulfate were aerosolized, dried, and collected to study the organic dependent structure of the aerosol particles. At high (116-162 g/100 mL water) and low (0.24-2.5 g/100 mL water) aqueous solubility of the organic component, the morphologies matched closely that of supermicron sized particles. For organic components with a high aqueous solubility, homogeneous morphologies were observed; while for low solubility organic components, phase separated structures were observed. When organic compounds with an intermediate
solubility (6.73-8.8 g/100 mL water) were used, a size dependent morphology was observed. For succinic acid, particles larger than 196 were phase separated, while particles under 170 nm were homogeneous. For pimelic acid, particles larger than 276 nm were phase separated, while particles under 270 nm were homogeneous. The morphology of these particles will affect light scattering, ice nucleation, and heterogeneous chemistry.

Additional organic species will need to be studied to better understand the relationship between the morphology of the particles and the solubility of the individual components. For similar species, a full analysis of the solubility versus structure will be obtained to determine if the morphology of the particles is dependent on the O:C ratio or more closely linked to the aqueous solubility of the organic component. Depending on the functional groups present, there could be a change in morphology and the range where a size dependent structure is observed. Additionally, in the intermediate solubility range, the size dependent morphology will need to be further understood. The morphology could be kinetically controlled by the drying rate of the particles, or confinement effects due to small particle size. The shape of these mixed organic/inorganic aerosol particles will affect the optical properties, so CRDS experiments could be performed to better understand how the optical properties need to be modeled in the atmosphere. By understanding the morphology and optical properties of these mixed organic/inorganic particles better, a significant aerosol population will be better constrained for atmospheric modeling.
12.3 Mongolia

12.3.1 Summary and Future Directions

Aerosol particles in Ulaanbaatar, Mongolia have been studied to identify the concentration and types of particles present in the air. The major morphologies of particle present include: small spherical particles, fractal particles, and large irregularly shaped particles. The largest number of particles are small spherical particles mainly consisting of sulfate/organic components. The large irregularly shaped particles have the lowest number concentration, but have the largest total surface area. The fractal particles have dimensions that can be large, but they have a much lower contribution to the total area than the irregular particles. The composition of the particle types is variable over different seasons. Each of the particle types exhibited an increased number containing sulfur in the winter months. Additional sulfur indicates the particles have aged, changing the morphology and composition and affecting the chemistry of the particles. When the fractal soot particles contain sulfur, their shape changes from a fractal structure to a compact structure. Ice nucleation experiments were performed for particles and when the particles had a higher amount of sulfur, the ice nucleation activity decreased.

Understanding the types of particles present has consequences for understanding the health and radiative effects. An understanding of the particulate matter types present in the second most PM$_{10}$ polluted city has now been studied for a ten month period. Additional monitoring of the particulate matter is needed to understand the changes between years of the particulate matter. With an increased push towards using more fuel efficient stoves, the particulate matter load and type should be dramatically decreased.
12.4 References


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