Volume changes upon heating of aerosol particles from biomass burning using transmission electron microscopy

Kouji Adachi\textsuperscript{a}, Arthur J. Sedlacek III\textsuperscript{b}, Lawrence Kleinman\textsuperscript{b}, Duli Chand\textsuperscript{c}, John M. Hubbe\textsuperscript{c}, and Peter R. Buseck\textsuperscript{d}

\textsuperscript{a}Atmospheric Environment and Applied Meteorology Research Department, Meteorological Research Institute, Tsukuba, Japan; \textsuperscript{b}Environmental and Climate Sciences, Brookhaven National Laboratory, Upton, NY, U.S.A; \textsuperscript{c}Atmospheric Sciences and Global Change Division, Pacific Northwest National Laboratory, Richland, WA, USA; \textsuperscript{d}School of Earth and Space Exploration & School of Molecular Sciences; Arizona State University, Tempe, AZ, U.S.A.

ABSTRACT
The responses of aerosol particles to heating are important for measurements of their chemical, physical, and optical properties, classification, and determination of origin. However, the thermal behavior of organic aerosol particles is largely unknown. We provide a method to analyze such thermal behavior through heating from room temperature to $>600$°C by using a heating holder within a transmission electron microscope (TEM). Here we describe in-situ shape and size changes and variations in the compositions of individual particles before and after heating. We use ambient samples from wildland and agricultural biomass in North America collected during the 2013 Biomass Burning Observation Project (BBOP). The results indicate that individual tar balls (TB; spherical organic material) from biomass burning retained, on average, up to 30% of their volume when heated to 600°C. Chemical analysis reveals that K and Na remain in the residues, whereas S and O were lost. In contrast to bulk sample measurements of carbonaceous particles using thermal/optical carbon analyzers, our single-particle results imply that many individual organic particles consist of multiple types of organic matter having different thermal stabilities. Beyond TBs, our results suggest that because of their thermal stability some organic particles may not be detectable by using aerosol mass spectrometry or thermal/optical carbon analyzers. This result can lead to an underestimate of the abundance of TBs and other organic particles, and therefore biomass burning may have more influence than currently recognized in regional and global climate models.

1. Introduction

Atmospheric aerosol particles influence the global climate directly through absorbing and scattering solar radiation and indirectly by becoming cloud-condensation nuclei. To analyze and catalog their properties, thermal evaporation or sublimation of aerosol particles is commonly used to 1) separate volatile materials from aerosol particles through a thermodenuder (e.g., Cappa et al. 2012; Nakayama et al. 2014), 2) classify carbonaceous materials (Chow et al. 1993), and 3) measure their chemical composition such as employed by using an aerosol mass spectrometer (AMS; Jimenez et al. 2003). In this study, we use controlled heating within a transmission electron microscope (TEM) to observe changes in volume and composition of individual particles through evaporation or sublimation before and after heating.

Several methods are used to analyze the effects of heating on aerosol particles. For example, thermodenuders are used to remove high volatility materials when the aerosol particles are passed through a heated tube ($\sim$200 to 400°C), allowing aerosol properties to be measured and compared with and without heating (Nakayama et al. 2014; Ueda et al. 2016; Zhou et al. 2017). For example, nanosphere soot (ns-soot) particles, which are carbonaceous materials consisting of graphitic nanosphere aggregates (Buseck et al. 2014), absorb sunlight and have an important influence on global climate (Bond et al. 2013). When mixed with sulfate or organic material, their light-absorption cross sections are enhanced by focusing incident light on them (Fuller et al. 1999; Adachi et al. 2010; Cross et al. 2010; Shiraiwa et al. 2010). By removing the high volatile components through heating, the effects of coating-enhancement on ns-soot light absorption can be probed. This approach identified light-absorption enhancement as 6% in California (Cappa et al. 2012), 22% in the Noto Peninsula (Ueda et al. 2016), and up to 70% in biomass-burning plumes (Lack et al. 2012), assuming that all coatings...
were removed within the denuder. However, the enhancement estimates have uncertainty if some coatings remain after the heating (Jacobson 2013; Ueda et al. 2016). Poulain et al. (2014) showed that nearly half of non-volatile aerosol particles heated to 300°C consist of low-volatility oxygenated organic aerosol particles. Thus, knowledge of aerosol-particle thermal behavior is important for evaluating the conclusions drawn when employing thermodenuders and is also expected to improve the interpretation of results from thermal/optical carbon analyzers and AMSs.

Thermal/optical carbon analyzers classify carbonaceous materials, including organic carbon (OC) and elemental carbon (EC), into several categories based on their thermal properties (Chow et al. 1993, 2015; Schauer et al. 2003; Gu et al. 2010; Khan et al. 2012; Kuchiki et al. 2015). The instruments are used to heat bulk samples collected on quartz filters, with and without oxygen, and measure the amount of carbon in the evaporated gases together with measurements of the reflectance and transmittance of laser light at specific temperatures. Thus, information on the thermal properties of each type of organic aerosol particle would be of great value in interpreting the data.

The AMS is widely used for measuring the composition of aerosol particles. Particles injected into an AMS hit a tungsten vaporizer heated to 600°C, and the vaporized materials (labeled as non-refractory) are detected as different types of aerosol (Jimenez et al. 2003). Refractory materials such as ns-soot, metal, and sea salt cannot be analyzed using a conventional AMS because the vaporization temperature for these materials is above the temperature of the tungsten filament. Thus, information on whether a material is refractory or non-refractory is critical for interpreting the results of AMS analyses and reported mass loadings.

Morphology and composition changes on small particles upon changing relative humidity or temperature can be analyzed using a TEM outfitted with an environmental cell (Wise et al. 2005; Freney et al. 2010; Adachi et al. 2011) or holders that can vary temperature or pressure. In the materials sciences, the thermal properties of various materials have been analyzed using a TEM with a heating holder, which can heat samples on a TEM grid within a furnace mounted on the holder (e.g., Reich et al. 2006; Petkov 2013) or a heating stage with a disposable, micro-electrochemical system (Asoro et al. 2013; Wu and Buseck 2013). The holder can be used to heat the samples to >1000°C while observing their morphological changes. Since the pressure within the TEM chamber is low (e.g., <10⁻⁵ Pa), evaporation or sublimation during heating can occur without oxidation. Recently, Wang et al. (2016) used heating in a TEM to analyze organic aerosol particles emitted from soil. In the current study, aerosol particles collected from biomass-burning smoke were heated within the TEM with the object of probing the thermal properties of organic particles produced in Boreal forest fires.

Aerosol particles from biomass burning are important to the global and regional climate as they can scatter and absorb incoming short-wave radiation as well as potentially become cloud-condensation nuclei (Lack et al. 2012; Bond et al. 2013). Biomass burning emits much organic matter, including tar ball (TB) s, which are amorphous, spherical, organic matter (Li et al. 2003; Póstai et al. 2004; Hand et al. 2005; Chakrabarty et al. 2010; Adachi et al. 2011; China et al. 2013). However, the detailed chemical and physical properties of TBs are largely unknown (Alexander et al. 2008; Chakrabarty et al. 2010; Tóth et al. 2014; Hoffer et al. 2016). For this study we collected samples during the Biomass Burning Observation Campaign (BBOP) 2013 in the United States (Presser et al. 2017; Zhou et al. 2017). In Sedlacek et al. (in preparation), we describe the formation, mass contribution to the particulate emission plume, and optical properties of TBs as well as a preliminary measurement of TB thermal properties. Here we describe a TEM-heating method for aerosol particles and measure the thermal properties upon heating of TBs and other viscous organic particles.

2. Materials and methods

2.1. Sampling

The TEM samples were collected from wildfires in North America during the BBOP campaign from July to October 2013. This campaign used a Gulfstream-1 (G-1) aircraft and measured the near-field evolution of particulate emissions from biomass burning. Aerosol particles from wildfires were collected in the Pacific Northwest (Idaho, Oregon, and Washington) and from agricultural burns in the Mississippi Embayment (Arkansas).

Aerosol samples for TEM analyses were collected on lacy-carbon substrates on TEM copper grids using a two-stage aerosol impactor sampler (AS-16W, Arios Inc., Tokyo, Japan). On lacy-carbon substrates, parts of surfaces of solid particles attach themselves to the substrate, although most of their surfaces are free from the substrate, resulting in minimal substrate influences on the particles. We collected samples on up to 16 TEM grids per flight. Sampling times varied from 1 to 30 min depending on particle concentrations in the air and meeting the goal of collecting samples at different ages through a Lagrangian sampling strategy. The sampler has two stages, and the analysis was conducted on samples collected on the second stage, which has a lower and
upper 50% cutoff aerodynamic diameter of approximately 100 nm and 700 nm, respectively. During the BBOP campaign, approximately 400 TEM samples were collected during 33 research flights. This paper is based on nine samples from three flights (Table 1). They include samples from two wildfires and one agriculture burn. These samples were directly collected within smoke together with samples from background air.

### 2.2. TEM analyses

We used a 120 kV TEM (JEM-1400, JEOL) equipped with an energy-dispersive X-ray spectrometer (EDS; Oxford instruments) (Adachi et al., 2014, 2016) and a heating holder (628 single-tilt holder, Gatan). Following heating, sample composition and morphology of the non-volatile residues were measured using scanning transmission electron microscopy (STEM) with EDS at an acceleration voltage of 120 kV. The compositions of an average of 120 particles per sample were analyzed before and after heating. We chose different areas on the TEM grids for the STEM-EDS analyses to minimize electron-beam damage. For the EDS analysis, we measured the peak area for each element in a spectrum and then normalized the areas for the selected elements.

The heating experiments were conducted by increasing the temperature of the TEM grids. Heating within the vacuum of the TEM column is by radiation from the furnace around the grid. The furnace temperature was increased in 150 °C increments, i.e., room temperature (~25), 150, 300, 450, and 600 °C. We observed changes in particle shapes by obtaining TEM images at each thermal step from five or more areas on each TEM grid. During the heating experiments, we used a relatively weak acceleration voltage (80 kV) to minimize beam damage. Typical analysis time for a given 150 °C temperature step was one to two minutes and, in total, took about 10 min to go from room temperature to 600 °C, including the time to obtain images.

Volume changes in TBs and viscous organic particles upon heating were measured from TEM images using ImageJ software (National Institutes of Health, Bethesda, MD). Particles were distinguished from the substrates by choosing an appropriate threshold value of image intensity to yield binary images. Particles that impact a TEM grid are deformed to various extents according to their viscosity in the atmosphere (Bateman et al., 2017). Here, TBs are defined as solid, spherical organic particles that do not deform on the substrate and keep their spherical shapes (Adachi and Buseck, 2011). Ammonium sulfate or other sulfates are commonly coated by or embedded within organic matter in the BBOP samples, and thus, except for non-biomass burning samples, we did not have pure ammonium sulfate particles.

Electron-beam irradiation at high temperature can cause sample artifacts when using Cu TEM grids through the development of Cu nanoparticles by surface diffusion of metal atoms on carbon substrates at >600 °C (Zhang and Su, 2009). In our samples, such Cu diffusion occurred even below 600 °C. To evaluate the magnitude of this

### Table 1. TEM sample collection time, place, temperature, relative humidity (RH), types of plumes and burnt biomass, and flight information.

<table>
<thead>
<tr>
<th>#</th>
<th>Sampling date</th>
<th>Start time</th>
<th>End time</th>
<th>Lat</th>
<th>Long</th>
<th>Altitude (m)</th>
<th>Ambient temperature (°C)</th>
<th>RH (%)</th>
<th>Plume</th>
<th>Type of burnt biomass</th>
<th>Flight information</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2013/08/14</td>
<td>18:01</td>
<td>18:15</td>
<td>43.74</td>
<td>−115.24</td>
<td>3994</td>
<td>4.7</td>
<td>40</td>
<td>Wildland smoke</td>
<td>Grass, sage with intermixed timber</td>
<td>Flight to Pony Express Fire complex north of Mountain Home in Idaho.</td>
</tr>
<tr>
<td>2</td>
<td>2013/08/14</td>
<td>19:24</td>
<td>19:27</td>
<td>43.65</td>
<td>−115.50</td>
<td>3848</td>
<td>6.2</td>
<td>39</td>
<td>Wildland smoke</td>
<td>Mixed conifer and hardwood forest of various ages, and brush</td>
<td>Flight to Mount Bachelor observatory and Douglas complex in Oregon.</td>
</tr>
<tr>
<td>3</td>
<td>2013/08/14</td>
<td>19:51</td>
<td>19:53</td>
<td>43.61</td>
<td>−115.48</td>
<td>3853</td>
<td>6.5</td>
<td>30</td>
<td>Wildland smoke</td>
<td>Mixed conifer and hardwood forest of various ages, and brush</td>
<td>Flight to Mount Bachelor observatory and Douglas complex in Oregon.</td>
</tr>
<tr>
<td>4</td>
<td>2013/08/14</td>
<td>19:18</td>
<td>19:22</td>
<td>43.30</td>
<td>−122.51</td>
<td>2352</td>
<td>12.1</td>
<td>75</td>
<td>Mixed conifer and hardwood forest of various ages, and brush</td>
<td>Mixed conifer and hardwood forest of various ages, and brush</td>
<td>Flight to Mount Bachelor observatory and Douglas complex in Oregon.</td>
</tr>
<tr>
<td>5</td>
<td>2013/08/14</td>
<td>19:42</td>
<td>19:46</td>
<td>42.86</td>
<td>−123.03</td>
<td>2354</td>
<td>10.9</td>
<td>76</td>
<td>Wildland smoke</td>
<td>Mixed conifer and hardwood forest of various ages, and brush</td>
<td>Mixed conifer and hardwood forest of various ages, and brush</td>
</tr>
<tr>
<td>6</td>
<td>2013/08/16</td>
<td>20:00</td>
<td>20:08</td>
<td>43.40</td>
<td>−122.19</td>
<td>2355</td>
<td>13.1</td>
<td>68</td>
<td>Wildland smoke</td>
<td>Mixed conifer and hardwood forest of various ages, and brush</td>
<td>Mixed conifer and hardwood forest of various ages, and brush</td>
</tr>
<tr>
<td>7</td>
<td>2013/10/21</td>
<td>20:38</td>
<td>20:48</td>
<td>34.84</td>
<td>−91.40</td>
<td>429</td>
<td>17.9</td>
<td>52</td>
<td>Agricultural smoke</td>
<td>Agricultural crop residues</td>
<td>Agricultural crop residues</td>
</tr>
<tr>
<td>8</td>
<td>2013/10/21</td>
<td>20:48</td>
<td>20:54</td>
<td>34.89</td>
<td>−91.90</td>
<td>433</td>
<td>17.9</td>
<td>55</td>
<td>Agricultural smoke</td>
<td>Agricultural crop residues</td>
<td>Agricultural crop residues</td>
</tr>
<tr>
<td>9</td>
<td>2013/10/21</td>
<td>20:54</td>
<td>21:09</td>
<td>35.05</td>
<td>−91.24</td>
<td>431</td>
<td>17.8</td>
<td>51</td>
<td>Agricultural smoke</td>
<td>Agricultural crop residues</td>
<td>Agricultural crop residues</td>
</tr>
</tbody>
</table>

a YYYY/MM/DD
b UTC.
c https://inciweb.nwcg.gov/incident/3614/
d https://inciweb.nwcg.gov/incident/3559/
artifact on the thermal behavior of aerosol samples, we used Mo TEM grids, which have higher thermal stability than Cu grids, for a test sample collected in Tsukuba, Japan. The Mo TEM grids did not form nanoparticles at 800°C, and the aerosol particles showed similar thermal behavior as those on Cu grids. The result suggests that the thermal behavior of aerosol samples collected on both Cu and Mo grids are the same, and the formation of Cu nanoparticles has negligible effects on our results.

3. Results and discussion

3.1. Standard samples

The temperature of the heating holder is controlled by the current using a rheostat hot-stage controller. However, as the temperature is not uniform across the TEM grids, the measured values can differ from the actual particle temperatures (Kim et al. 2015). Our measurements were calibrated by using standard metal particles (Sn and Pb) and glucose (Figure 1). The TEM-measured values of these standard particles were between 0 and 42°C above the theoretical melting temperatures. Thus, although particle sizes, shapes, and the contact angle between a particle and a substrate can influence particle melting temperatures on TEM grids (Asoro et al. 2013), it is likely that our measured values have an uncertainty of ~10% from the actual temperatures of the heated particles.

The experimental setup was tested using a fresh aerosol sample collected from ambient air that was dominated by ammonium sulfate with ns-soot inclusions. The sample was heated within one hour after collection. The ammonium sulfate particles sublimated at ~180°C, whereas the ns-soot remained on the substrate without any apparent morphological changes up to 800°C (Figure 2). Our result is generally consistent with measurements of ambient aerosol using a thermodenuder, which showed loss of ammonium sulfate starting at 150°C (Huffman et al. 2008) or ~180°C (Pinnick et al. 1987) at atmospheric pressure. Pure ammonium sulfate particles decomposed to ammonium bisulfate and started to sublimate at ~150°C (Johnson et al. 2004). The lack of change in shape of the ns-soot reflects its thermal stability and lack of oxygen within the TEM chamber.

3.2. BBOP samples

3.2.1. Volume decreases upon heating

The sublimation, decomposition, or both of the organic particles was examined using the BBOP samples. In
contrast to ammonium sulfate, TBs and other viscous organic particles did not completely disappear from view but uniformly shrunk without major shape changes and gradually decreased in volume during heating (Figures 3 and 4). The decreases in particle volumes ($V_h/V_i$), where $V_h$ and $V_i$ are volumes of heated and initial particles, respectively, was $\sim 50\%$ by $300^\circ C$ ($\sim 0.2\%$ in volume loss per $1^\circ C$) and $\sim 30\%$ at $600^\circ C$ ($\sim 0.1\%$/°C from 300 to 600°C) for all measured samples (Figure 5). Although the number fraction of TB in the agricultural burning is small, TB thermal behaviors from different fuel sources were similar among the samples.

Our TEM results show roughly the same volume decreases among TBs and other viscous organic particles, indicating that the thermal behavior of TBs and other viscous organic particles in our samples are essentially the same (Figure 5). Novakov and Corrigan (1996) showed that about 20% of total organic material collected on filters from their biomass-burning smoke was nonvolatile when heated to $550^\circ C$, although our results were obtained from individual particles. Yu et al. (2004) showed that humic acid, levoglucosan, and oxalate did not completely volatilize when heated to $800^\circ C$ in helium gas. Zhou et al. (2017) found that biomass-burning organic aerosol with low volatility (BBOA-3) contributed 31% by mass of the organic aerosol in the biomass-burning plume collected at the Mt. Bachelor Observatory during the BBOP campaign and that $\sim 60\%$ of BBOA-3 remained at $200^\circ C$ using a thermodenuder. Our TEM samples 1–6 were collected in the same region during the campaign, although the result of Zhou et al. (2017) was obtained using on-line measurements, whereas our TEM result was from the samples collected on TEM grids. TEM results in Figure 5 show smaller changes in volume upon heating ($\sim 70$–$80\%$ for $V_h/V_i$) than their study at $200^\circ C$. Loss of volatile materials before the TEM analyses and substrate effects could influence the TEM results. Nevertheless, these results suggest that BBOA-3 may consist of TBs, although further study is needed to confirm the hypothesis.

The BBOP samples were stored in a desiccator prior to TEM analysis. To check the effects of storage, we measured the thermal behavior of TB particles within three hours from sample collection (Figure 6). They showed similar thermal behavior to the BBOP samples. Huffman et al. (2009) and Cappa and Jimenez (2010) reported that biomass burning emits semi-volatile organic aerosol,

![Figure 2. Heating of fresh aerosol particles collected in Tsukuba, Japan. Ammonium sulfate particles appear dark in the left image (a). Typical particles are magnified in the lower plots for ease of comparison. Sulfate particles decompose and sublimate at $\sim 180^\circ C$. Ns-soot particles, which appear in aggregates or as black dots in images (b) and (c) show no changes. The sample was collected at 4:37–4:42 (UTC) on June 12, 2014. The heating experiment was done at 5:54 (UTC) on the same day.](image-url)
Figure 3. Changes in particle shapes and sizes upon heating using a BBOP sample collected from the Pony Express fire complex (sample # 3). TB particles in white squares are enlarged in the right bottom. These particles retained their spherical shapes but gradually shrank upon heating to 600°C. Color of the substrate became lighter as temperature increased, possibly because a carbon layer on the substrate was lost.
and Lee et al (2010) showed significant mass loss below 150°C. In our study, we did not observe such highly volatile organic particles because they were likely lost shortly after sampling or when placed in the vacuum of the TEM chamber. Such losses of volatile organic particles cause more changes in volume upon heating than those shown in Figure 5. This loss of volatile materials is important when comparing to the results from on-line instruments with a thermodenuder.

3.2.2. Particle compositions before and after heating
Normalized EDS intensities for each element were compared before and after the heating experiments (I_{af} and I_{be}). The I_{af}/I_{be} values for S and O were 0.51 (std, \sigma = 0.45) and 0.84 (\sigma = 0.13), respectively, showing that the particles lost mass, possibly through the sublimation of ammonium sulfate or other volatile sulfates within the particles. On the other hand, the I_{af}/I_{be} values for Na and K were 7.2 (\sigma = 6.3) and 3.4 (\sigma = 2.4), respectively. Since most Na and K occurred as sulfates, with respective melting temperatures of 884 and 1069°C, it is probable that they were relatively enriched in the particles during loss of ammonium sulfate and organic matter. We also detected C, N, Mg, Al, Si, Cl, Ca, Mn, and Fe, but found no significant differences before and after heating. Since the heating occurred within the vacuum of the TEM, and thus in the absence of oxygen, the products are presumably similar to char, which is carbonaceous matter obtained by heating organic matter and formed directly from pyrolysis with limited access to air (Han et al. 2010).

3.3. Implications for measurements using other instruments
Understanding the thermal behavior of individual organic aerosol particles is expected to be useful for correctly interpreting aerosol measurements that exploit this behavior such as thermal/optical carbon analyzers, thermodenuders, and AMS. Our results indicate that TBs do not completely sublimate or decompose when heated at 600°C. This thermal resistance agrees with thermodenuder measurements that show some organic particles remain through heating up to 300°C (Poulain et al. 2014; Ueda et al. 2016; Zhou et al. 2017).

Figure 4. Examples of particle-shape changes upon heating (BBOP samples). Top (a–b): sample #5 (wildfire BB smoke collected on August 16). Bottom (c–d): sample #8 (agricultural BB smoke collected on October 21). Arrows indicate examples of measured particles.
The semi-continuous carbonaceous aerosol analyzer (Sunset Laboratory Inc.) is a cornerstone instrument for measuring organic carbon (OC) and elemental carbon (EC), thereby facilitating the cataloging of carbonaceous aerosol emission inventories. Since this measurement technique exploits the thermal stability of carbonaceous aerosol particles, there are potential uncertainties in data interpretation brought about by the thermal stability of TBs and other viscous organic materials. As briefly described earlier, aerosol particles collected onto a quartz filter are purged with helium, followed by a stepped-temperature ramp to 850°C. Following this step, an oxidizing gas stream is injected into the chamber to oxidize EC. To account for potential interference from charring of OC that would be misinterpreted as EC, the instrument uses a 660-nm diode laser to probe for EC. In this way, optical

![Figure 5](image1.png)

**Figure 5.** Changes in volume of representative particles upon heating. The temperature was increased in 150°C steps up to 600°C. Bold lines indicate the average values. Three samples from each of three flights were used. (a–c): results for TBs. (d–f): results for other organic particles. Volume was estimated from the two-dimensional areas of particles, assuming they were spherical. Volume decrease was determined from the volumes at heated temperature (\( V_h \)) divided by those at initial, room temperature (\( V_i \)). \( n = 42, 25, 4, 46, 65, \) and 26 for panels from (a) to (f), respectively.

![Figure 6](image2.png)

**Figure 6.** Heating of fresh aerosol samples collected at Tsukuba, Japan, March 4, 2015. The sample was collected on a Mo grid and used for the heating experiment~3 hour after sampling. This TB particle is attached to ns-soot. The TB remained but shrunk during heating, similar to those in the BBOP samples.
transmission through the filter can be compared before and after the first heating ramp. If the transmission decreases, simple subtraction is used to correct for this char product. An underlying assumption is that the only absorbing species at 660 nm is EC. Although this assumption is reasonable for semi-volatile OC, the legitimacy of this underlying assumption in the presence of TBs from wildland fires and other viscous organic material could result in misinterpretation. Further, our TEM observations also imply that the organic matter within the individual particles can be classified into several organic fractions using a thermal/optical carbon analyzer, with the relationship being that both methods determine mass loss of carbonaceous matter through heating.

In contrast to the thermal/optical carbon analyzers discussed above, the AMS uses a filament heated to ~600°C to flash vaporize non-refractory material (Jimenez et al. 2003; Drewnick et al. 2015). A difference in the current study is that our heat ramp normally takes ~10 minutes to go from room temperature to ~600°C. This distinction may result in differing impacts on organic particles. Nevertheless, some residues of organic particles measured in our TEM analysis may have low detection efficiencies with an AMS.

4. Conclusion

We demonstrate a method within a TEM to measure changes in aerosol particles upon heating. The results indicate that TB particles do not completely sublimate or decompose even at 600°C but retain ~30% of their volumes. These residues have more Na and K and less S and O than the original particles. Although this TEM heating experiment uses only particles collected on substrates and heated in vacuum, it illustrates that changes in particle shape, size, and composition can occur during heating. The results have implications for measurements from other instruments that rely on sample heating such as thermodenuders, thermal/optical carbon analyzers, and AMS. The presence of less-volatile organic particles implies a risk in underestimating the amount of atmospheric organic aerosol particles using thermal/optical carbon analyzers and related instruments. Since organic particles are important contributors to aerosol optical depth and global climate, this underestimation could contribute to the uncertainty in their quantifications and the numerical simulations.

Acknowledgments

We acknowledge the DOE Atmospheric Radiation Measurement (ARM) Climate Research program and facility, and the Atmospheric System Research (ASR) for the support to carry out the BBOP campaign and for use of the G-1 research aircraft. The authors also gratefully acknowledge the skill and safety exemplified by the ARM AAF (ARM Aerial Facility) pilots.

Funding

This research was performed under sponsorship of the U.S. DOE Office of Biological & Environmental Sciences (OBER) Atmospheric Radiation Program (ASR) under contracts DESC0012704 (BNL). DC and JMH acknowledge support from PNNL which is operated for DOE by Battelle Memorial Institute under Contract DE-AC06–76RLO1830. KA thanks the support of the Global Environment Research Fund of the Japanese Ministry of the Environment (2–1403, 5–1605, and 2–1703) and JSPS KAKENHI (grant numbers JP25740008, JP16K16188, JP16H05620, JP15H02811, and JP16H01772).

References


