The transformation of solid atmospheric particles into liquid droplets through heterogeneous chemistry: Laboratory insights into the processing of calcium containing mineral dust aerosol in the troposphere

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[1] Individual calcium carbonate particles reacted with gas-phase nitric acid at 293 K have been followed using Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) analysis as a function of time and relative humidity (RH). The rate of calcium carbonate to calcium nitrate conversion is significantly enhanced in the presence of water vapor. The SEM images clearly show that solid CaCO3 particles are converted to spherical droplets as the reaction proceeds. The process occurs through a two-step mechanism involving the conversion of calcium carbonate into calcium nitrate followed by the deliquescence of the calcium nitrate product. The change in phase of the particles and the significant reactivity of nitric acid and CaCO3 at low RH are a direct result of the deliquescence of the product at low RH. This is the first laboratory study to show the phase transformation of solid particles into liquid droplets through heterogeneous chemistry. INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0325 Atmospheric Composition and Structure: Evolution of the atmosphere; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry. Citation: Krueger, B. J., V. H. Grassian, A. Laskin, and J. P. Cowin, The transformation of solid atmospheric particles into liquid droplets through heterogeneous chemistry: Laboratory insights into the processing of calcium containing mineral dust aerosol in the troposphere, Geophys. Res. Lett., 30(3), 1148, doi:10.1029/2002GL016563, 2003.

1. Introduction

[2] It has been reported that approximately 1000–3000 Tg of mineral aerosol are injected into the atmosphere as wind-blown soils annually [Jonas et al., 1995]. In the coming years, this value is predicted to increase because of the global expansion of arid regions [Sheehy, 1992]. Fine mineral dust can be transported long distances in the atmosphere [McKendry et al., 2001; Perry et al., 1997; Tratt et al., 2001] and thus have the potential to undergo a variety of heterogeneous reactions with atmospheric gases. In principle, it is possible that heterogeneous chemistry of atmospheric aerosol can change both the gas-phase chemical balance of the atmosphere and the physicochemical properties of individual particles. Changes in the properties of individual particles, such as size, shape, composition and hygroscopicity, will alter aerosol optical properties and thus may have an impact on the Earth’s climate. The ways in which mineral dust aerosol impact atmospheric processes such as climate forcing [Sokolik and Toon, 1999; Myhre and Stordal, 2001], heterogeneous atmospheric chemistry [Den- tene et al., 1996; Jacob, 2000; Schurath, 1999] and phase transitions of ammonium salts containing dust inclusions [Martin et al., 2002; Han et al., 2002] are just beginning to be understood.

[3] Calcium carbonate is a common component of mineral dust and may be a very reactive component of the aerosol present in the Earth’s atmosphere [Song and Char- michael, 2001]. In the study described here, the heterogeneous chemistry of individual calcium carbonate particles with nitric acid, a pervasive gas-phase species, to form calcium nitrate according to reaction (R1),

\[
\text{CaCO}_3 + 2\text{HNO}_3 \rightarrow \text{Ca(NO}_3)_2 + \text{H}_2\text{CO}_3 \rightarrow \text{Ca(NO}_3)_2 \text{H}_2\text{O}.
\]

(R1)

is examined. The data show that the reactivity of nitric acid is significantly enhanced in the presence of water vapor. The data also show that solid particles of calcium carbonate are transformed into aqueous calcium nitrate droplets as the particles react. This process occurs in a two-step mechanism. The first step is shown in reaction (R1) and the second step, which involves the deliquescence of the calcium nitrate product, is shown in reaction (R2),

\[
\text{Ca(NO}_3)_2(s) \rightarrow \text{Ca(NO}_3)_2(aq)
\]

(R2)

The conversion of solid particles into liquid droplets through heterogeneous chemistry has important atmospheric implications in terms of the continued reactivity of the aerosol and the impact of the reacted aerosol on climate. As shown here, single particle analysis can be used to determine changes in particle morphology, relative reaction...
rates and the extent of reaction of individual particles as a function of particle size.

2. Experimental Methods

[4] Changes in morphology and chemical composition of individual calcium carbonate particles exposed to nitric acid vapor were monitored using SEM and EDX analysis. A detailed description of the experimental setup will be published elsewhere (Krueger et al., to be published in Anal. Chem.) and thus will be described only briefly here. Calcium carbonate particles (calcite) purchased from Alfa Aesar (99.95% purity) were lightly ground between two glass slides before being deposited onto grid-supported carbon films (Carbon Type-B on Au 200 grid, Ted Pella, Inc.). The particle density on the carbon films was estimated to be 18,000 particles mm⁻². The mean diameter of the particles was on the order of 1 μm. Prior to exposure to nitric acid, calcium carbonate particles were imaged using SEM and the chemical composition was determined by EDX analysis. After imaging, the grids containing the particles were then transferred in air to a glass reactor flow system where they were exposed to nitric acid vapor at different RH. Nitrogen was used as the carrier gas for a total pressure between 50 to 100 Torr. After exposure to nitric acid vapor at pressures relevant to those measured in the atmosphere, the particles were then transferred in air (~30% RH in the laboratory) to the microscope and analyzed again by SEM and EDX under vacuum. This process was repeated several times to increase the exposure time of the particles to nitric acid.

[5] A FEI XL30 Digital Field Emission Gun Environmental Scanning Electron Microscope was used in this study. EDX spectra were collected with an EDAX 136–10 spectrometer (EDAX, Inc.) with a lithium-drifted silicon detector of an active area of 30 mm² and super Atmosphere Thin Window (ATW2) that allows X-ray detection for elements higher than Beryllium (Z > 4). The microscope is equipped with “Genesis Particle/Phase Analysis” hardware and software (EDAX, Inc.) for computer controlled particle analysis. A detailed discussion on the application of SEM for automated analysis of individual particles can be found in earlier publications [Fletcher et al., 2001; Laskin et al., 2002].

3. Results

[6] Figure 1a shows a SEM image of calcium carbonate particles prior to exposure to nitric acid. The images shown in the next five panels (b–f) are for the same calcium carbonate particles after they have been exposed to 20 μtorr of HNO₃ (6.5 × 10¹¹ molecules/cm³ or 26 ppb relative to atmospheric pressures) for different total exposure times of 5, 10, 15, 20 and 26 hours. In this experiment, the relative humidity was kept at 17 ± 1% in the reaction flow chamber during nitric acid exposures. The samples were transferred in air to and from the reaction flow chamber and the electron microscope during the course of the experiment. After 5 hours of exposure, it can be seen that the smallest particles begin to change shape and become nearly spherical. In some case, when there are two separate particles in close proximity (e.g., the two particles in the upper left hand corner of

![Figure 1. SEM images of calcium carbonate particles exposed to 20 μtorr (6.5 × 10¹¹ molecules/cm³, equivalent to 26 ppb relative to atmospheric pressures) of HNO₃ at 17 ± 1% RH: (a) before exposure, and after exposure for (b) 5 hours, (b) 10 hours, (c) 15 hours, (e) 20 hours, and (f) 26 hours.](image-url)
The change in morphology of the particles imaged in both sets of experiments is consistent with the conversion of solid calcium carbonate to aqueous calcium nitrate via the two-step mechanism (reactions (R1) and (R2)) discussed in the Introduction. The increase in particle size is consistent with the uptake of water by the particle to form an aqueous phase droplet. Our results agree well with levitation experiments done by Tang and Fung [1997] who have shown that calcium nitrate amorphous particles deliquesce at relative humidities near 13%, well below that reported for bulk samples, and that under vacuum the particles retain their droplet-like shape. Here the images show that as calcium carbonate reacts with nitric acid, the calcium nitrate product deliquesces in the presence of water vapor forming an aqueous droplet of calcium nitrate. Deliquescence of the product most likely prevents the reaction from surface saturating, i.e., it prevents the calcium carbonate surface from saturating with a capping layer of calcium nitrate. The liquid layer provided by the deliquescence of the product allows the reaction to continue on and to proceed into the bulk of the particle. Earlier TEM images presented in Goodman et al. [2000] showed that reacted calcium carbonate particles were irregularly shaped. The different shape observed in that study may be due to the higher pressures of nitric acid used and the fact that the particles were stored in a desiccator for several weeks prior to imaging.

It is important to note that experiments done under very dry conditions (<0.5% RH) and with nitric acid exposures 100–1000 times greater than those used in the experiments described above did not show a change in particle morphology.

X-ray fluorescence data from individual particles were obtained in order to quantify changes in reaction rate from the time course measurements shown in Figures 1 and 2 as a function of relative humidity. There are several difficulties in obtaining quantitative information with the EDX analysis. Here we use EDX analysis to provide semi-quantitative insights into the chemical composition of these particles. We are interested in estimating the relative rates of reaction at different relative humidity and for particles of different sizes. EDX spectra were collected for about twenty particles but not for the particles shown in Figures 1 and 2 so as to avoid possible particle damage by the electron beam prior to EDX analysis. Selected EDX spectra for particles of different sizes (~0.5 and 5 µm), are shown in Figure 3. Two spectra are overlayed and shown for each particle. One spectrum is collected prior to exposure to nitric acid (gray circles) and the other is taken after exposure to nitric acid (black circles). The spectra shown in Figure 3 are for particles reacted with nitric acid at 17 ± 1 and 41 ± 1% RH. As the reaction proceeds, the C peak goes down and the O and N peaks grow in. Because the nitrogen peak is so weak, even in the spectra of Ca(NO$_3$)$_2$ standard (not shown), the peaks in the low energy region of the spectra have been curve fit to more clearly show the nitrogen peak at 0.392 keV.

**Figure 2.** SEM images of calcium carbonate particles exposed to 20 µtorr (6.5 × 10$^{11}$ molecules/cm$^2$, equivalent to 26 ppb relative to atmospheric pressures) of HNO$_3$ at 41 ± 1% RH: (a) before exposure, and after exposure for (b) 1 hour (b) 2 hours and (c) 4 hours.

**Figure 3.** EDX spectra are overlayed for calcium carbonate particles before (gray circles) and after (black circles) exposure to 20 µtorr of nitric acid at 17 ± 1 and 41 ± 1% RH. Spectra are shown for (a) 5.0 µm particles and (b) 0.5 µm particles exposed to 20 µtorr of HNO$_3$ at 41 ± 1% RH for 20 hours, (c) 5.0 µm and (d) 0.5 µm particles exposed to 20 µtorr of HNO$_3$ at 17 ± 1% RH for 2 hours. All spectra are normalized to the calcium peak area. The low energy peaks have been curve fit to show more clearly the peaks due to carbon, nitrogen and oxygen. The error bars shown in (c) and (d) are for the N and O peak heights for approximately 20 particles of a Ca(NO$_3$)$_2$ standard in the 0.5 µm and 5 µm size range.
The EDX spectra for calcium carbonate particles reacted at 41 ± 1% RH show that both the 0.5 (Figure 3b) and 5 μm (Figure 3a) particles have extensively reacted with nitric acid after 2 hours of exposure at 41 ± 1% RH. The EDX spectra recorded after 20 hours of exposure at 17 ± 1% RH show that the 0.5 μm particles have undergone extensive, almost complete reaction with nitric acid, as is evidenced by the large decrease of the carbon peak in the spectrum. For the 5 μm particle, there is very little evidence for the reaction with nitric acid from the EDX spectra after 20 hours of exposure to nitric acid at 17 ± 1% RH. The error bars shown in 17 ± 1% RH experiment (Figure 3c and d) are the scatter in the data for N and O peak heights for Ca(NO3)2 standard spectra. Using the O peak as a marker for the extent of reaction (assuming linearity), it is estimated that the 0.5 μm particles have reacted nearly completely at 17 and 41 ± 1% RH after 20 and 2 hours, respectively. The percent reaction for the 5 μm particles depends on RH and is approximately 2 and 40% at 17 and 41 ± 1% RH, respectively.

The data shown in Figure 3 indicate that the reactivity of nitric acid is increased greater than ten-fold at the higher relative humidity and that small particles convert more quickly than larger particles.

4. Atmospheric Implications

Song and Carmichael [2001] estimate that >30% of the total atmospheric nitrate is in the particulate phase and that nitrate and calcium are correlated. In the atmosphere, typical conditions of relative humidity range from 20–90%. This laboratory study suggests that atmospheric aerosol containing calcium carbonate, and perhaps even other calcium containing particles such as CaCl2 and CaO, will be a sink for nitric acid in the troposphere and that these reactions are surface reactions which change from a gas/solid interfacial mechanism to a gas/liquid/solid interfacial mechanism as the reaction proceeds. It is expected that the uptake coefficient will increase as the reaction mechanism changes given that reactions on liquid phase droplets have larger uptake coefficients than on solid particles by a factor of 10 to 100. It has been specifically shown that nitric acid reacts nearly ten times faster for deliquescent sodium carbonate than on solid particles by a factor of 2.5 to 3 greater than dry particles. In polluted areas this can be expected to reflect light more than unreacted mineral. In addition, these reacted particles will be more effective cloud condensation nuclei in the atmosphere.

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