

SULFATE AND NITRATE COATINGS ON MINERAL DUSTS: CRYSTALLINE OR AQUEOUS?

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Observational evidence shows that mineral dusts in Asian outflows become coated by sulfates and nitrates. Layer thickness can range to hundreds of nanometers. At high relative humidity, the layers uptake water and are in aqueous form. For example, the deliquescence relative humidity of ammonium sulfate is 80% at 298 K while that of ammonium nitrate is 60%. The water content has several important effects. The particle volume increases with concurrent increases in the mass extinction coefficient, the single scatter albedo (in the infrared), and the asymmetry parameter. The aqueous coatings also provide milieu for aqueous chemical reactions, such as sulfate oxidation or N_2O_5 hydrolysis. At lower relative humidity, the aqueous coating crystallizes. There is a concomitant release of the water content to the vapor phase and associated decrease in particle volume. The mass extinction coefficient, single scatter albedo, and asymmetry parameter decrease. Important chemical transformation pathways are shut off.

At what critical relative humidity does the phase change from an aqueous to a crystalline coating occur?

The answer to this question shows that dependent factors are the size and the chemistry of the mineral dust core. Through detailed laboratory experiments, the governing polynomial are found to be:

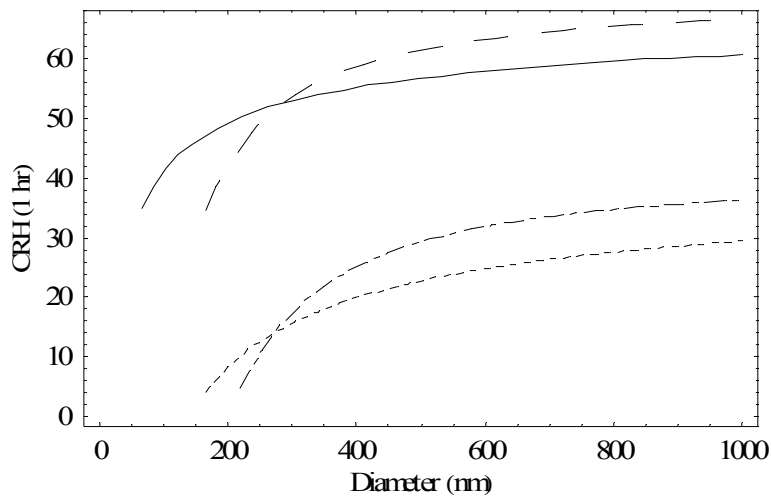
$$\begin{aligned} CRH_{AS} &= 71.6 - 235 (0.36)^{\log_{10} D_c}, D_c \geq 65 \text{ nm} \\ CRH_{AS} &= 70 - 25000 (0.052)^{\log_{10} D_h}, D_h \geq 65 \text{ nm} \\ CRH_{AN} &= 42.3 - 823 (0.25)^{\log_{10} D_c}, D_c \geq 165 \text{ nm} \\ CRH_{AN} &= 40.5 - 71000 (0.039)^{\log_{10} D_h}, D_h \geq 220 \text{ nm} \end{aligned}$$

for one hour observation times. The symbols are CRH = crystallization relative humidity; D = diameter (nm) of mineral core particle; AS = ammonium sulfate; AN = ammonium nitrate; c = corundum; and h = hematite.

The implication of the above equations is that there is a synergistic interaction between hygroscopic components of the aerosol such as sulfates and nitrates and insoluble components such as mineral dusts on the chemical and radiative properties of atmospheric aerosols.

The CRH equations are derived from laboratory experiments with submicron aqueous ammonium sulfate particles containing hematite ($\alpha\text{-Fe}_2\text{O}_3$) and corundum ($\alpha\text{-Al}_2\text{O}_3$) inclusions in an aerosol flow tube at 298 K. Ammonium sulfate coatings of different layer thicknesses are deposited on

metal oxide particles generated by spray pyrolysis methods. The heterogeneous nuclei (i.e., the mineral dust cores) regulate the RH of the phase transition from 35% up to 60% RH in the case of ammonium sulfate and 0 to 10% in the case of ammonium nitrate as the inclusion size varies from 50 to 500 nm. The strong size dependence is inconsistent with the application of classical nucleation theory on defect free surfaces. However, an active site model successfully interprets the data. Model optimization yields 10^{10} sites cm^{-2} and $m < 0$ for $\alpha\text{-Al}_2\text{O}_3$ and 10^9 sites cm^{-2} and $m \approx 0$ for $\alpha\text{-Fe}_2\text{O}_3$ particles.



solid = ammonium sulfate on corundum
 large dashed = ammonium sulfate on hematite
 small dashed = ammonium nitrate on corundum
 large-small dashed = ammonium nitrate on hematite

Figure 1. Plot of crystallization relative humidities of aqueous ammonium sulfate and ammonium nitrate outer layers on hematite and corundum cores.

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