# Phase transitions in calcium nitrate thin films†

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**Calcium carbonate is a ubiquitous mineral and its reactivity with indoor and outdoor air pollutants will contribute to the deterioration of these materials through the formation of salts that deliquesce at low relative humidity (RH). As shown here for calcium nitrate thin films, deliquescence occurs at even lower relative humidity than expected from bulk thermodynamics and lower than the recommended humidity for the preservation of artifacts and antiques.**

The deliquescence, *i.e.* the phase transition from solid to liquid as a function of relative humidity, of salts can impact several processes ranging from global climate change to heterogeneous atmospheric chemistry[1] to the deterioration of statues, museum showpieces and wall paintings[2] to cuticular penetration.[3] Here we report on the room temperature hygroscopic response of calcium nitrate thin films supported on calcium carbonate single crystal and particle surfaces. Calcium nitrate, $Ca(NO_3)_2$, thin films were formed from reaction of nitric acid vapor, a prevalent pollutant gas found mostly in outdoor but sometimes in indoor environments,[4] with calcite $(CaCO_3)$. The deliquescence relative humidity (DRH) of calcium nitrate thin films supported on calcium carbonate is found to be much lower than what is predicted from the thermodynamics of bulk phases.

From thermodynamic considerations, it is expected that $Ca(NO_3)_2$ will be converted to $Ca(NO_3)_2 \cdot 4H_2O$ at 11.8% RH.[5] From solution phase thermodynamics, the DRH should occur at the RH of a saturated solution, *i.e.* to say the DRH is equal to the water activity, $P/P_0$, times 100, where $P_0$ is the vapor pressure above pure water and $P$ is the water vapor pressure above the solution. In agreement with earlier measurements,[2] we have measured the vapor pressure above a saturated water solution of calcium nitrate to be 57 ± 5% RH at room temperature. Thus, the crystalline tetrahydrate phase is expected to deliquesce at 57% RH. Instead, a DRH near 10% is measured for calcium nitrate thin films supported on calcium carbonate. The reason for the discrepancy between the measured DRH and that predicted from thermodynamics is due to the fact that calcium nitrate forms a metastable amorphous layer that undergoes deliquescence instead of crystallization to the stable tetrahydrate phase at low relative humidity.

Since calcium carbonate is a ubiquitous mineral and is a component of shells, skeletons, statues and other artworks as well as indoor and outdoor building materials, its reactivity with indoor and outdoor air pollutants will contribute to the deterioration of these materials as these reactions often lead to the formation of salts that deliquesce at low RH. As shown here, the DRH can be considerably lower than the recommended relative humidity for the preservation of artifacts and antiques (typically above 30% RH).[6]

Thin films of $Ca(NO_3)_2$ were prepared by reaction of calcite polished single crystals (104 and 110 surface planes) or calcite particles (on the order of 0.5 µm in diameter) with nitric acid vapor (~200 mTorr). The reaction was done at room temperature ($T$ = 22 °C) and at low relative humidity (23% RH). After reaction of calcite with nitric acid vapor, the hygroscopic

response of the surface increased significantly. This can be readily seen in Fig. 1 which shows the hygroscopic response, measured by the number of water layers taken up by the surface, as a function of relative humidity for $CaCO_3(104)$ and (110) surfaces, before and after reaction with nitric acid vapor. The number of water layers taken up by the surface is determined from FT-IR spectroscopy by using the integrated absorbance of the water absorption band near 3400 cm$^{-1}$. The surface density of adsorbed water, $S(H_2O)$ in molecules per cm$^2$, is related to the integrated absorbance of the O—H band according to,[7,8]

$$S(H_2O) = \frac{2.303\tilde{A}(OH)\cos\phi}{N\bar{\sigma}} \quad (1)$$

where $\tilde{A}(OH)$ is the integrated absorbance of the O—H band (cm$^{-1}$), $N$ is the number of adsorption surface faces (6 in these experiments), $\bar{\sigma}$ is the integrated cross section of O—H band of liquid water and has a value of $1.07 \times 10^{-16}$ cm molecule$^{-1}$,[9] and $\phi$ is the angle of incidence, 45°. The number of adsorbed



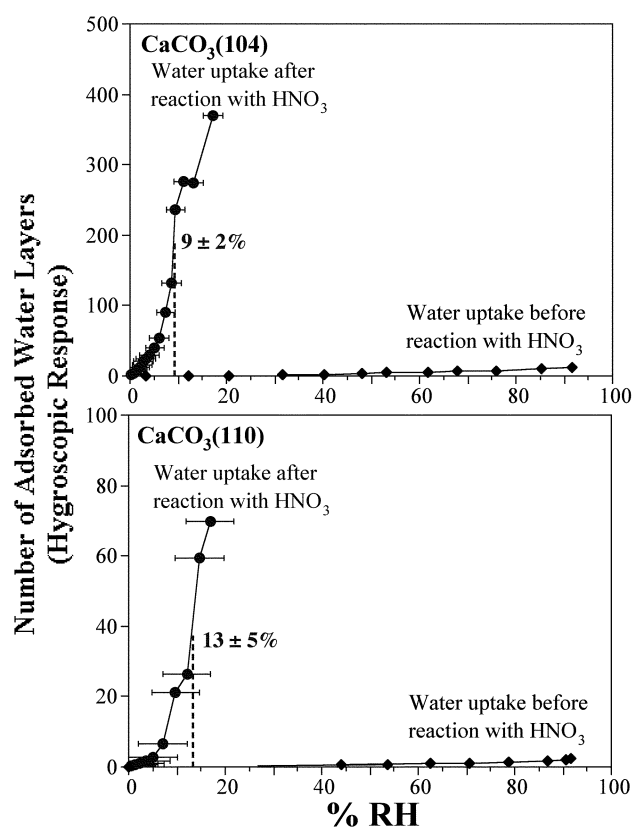**Fig. 1** The number of adsorbed water layers on single crystal calcite surfaces, $CaCO_3(104)$ and $CaCO_3(110)$, before and after reaction with nitric acid vapor at 23% RH is plotted as a function of relative humidity. There is clearly an increase in the hygroscopic response of these surfaces after reaction with nitric acid which is attributed to the deliquescence of the $Ca(NO_3)_2$ product at 9 ± 2% and 13 ± 5% RH for $CaCO_3(104)$ and $CaCO_3(110)$, respectively.

† Electronic supplementary information (ESI) available: Colour Fig. 1–3. See http://www.rsc.org/suppdata/cc/b3/b308632a/

water layers can be calculated by normalizing $S(H_2O)$ values to the surface density of the hydroxylated calcite surface which is for an unreconstructed surface estimated to be $1 \times 10^{15}$ water molecules cm$^{-2}$.[10] Although errors associated with these assumptions may change the absolute values of the $y$-axes shown in Fig. 1 by as much as a factor of two, they do not affect the main conclusions of this report or the value of the DRH for $Ca(NO_3)_2$ thin films determined in this study (vide infra).

The reaction of nitric acid with $CaCO_3$ around 20% RH has been previously shown to form thin films of calcium nitrate,[11] according to the reaction $CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + CO_2 + H_2O$. The mechanism for the reaction of $CaCO_3$ and nitric acid vapor is depicted in Fig. 2. Based on the FT-IR spectra of nitric acid reacted $CaCO_3$ particles, these films appear to be an amorphous form of $Ca(NO_3)_2$ with some strongly bound water associated with the salt that is not removed even when the sample is held under vacuum overnight at a pressure of $1 \times 10^{-6}$ Torr. These amorphous films are then exposed to water vapor as a function of increasing relative humidity. It is observed that there is a large increase in the hygroscopic response of the film at a RH greater than 5% RH. For nitric acid reacted surfaces, the absorbance spectra in the 3400 cm$^{-1}$ region saturate above 20% RH and become nonlinear. Such a large increase in hygroscopic response is due to the deliquescence of the thin $Ca(NO_3)_2$ films. Similar results are seen for nitric acid reacted $CaCO_3$ particles. The deliquescence relative humidity is taken as the midpoint of the increase in the hygroscopic response above 5% and when complete saturation of the spectrum is observed. This midpoint occurs at $9 \pm 2$ and $13 \pm 5\%$ RH for amorphous calcium nitrate films grown on $CaCO_3$ (104) and (110), respectively. The total amount of water uptake is a function of the film thickness and, of course, the solubility of $Ca(NO_3)_2$ in water. These films are estimated to be on the order of 100 and 20 nm thick, for the 104 and 110 surfaces, respectively.

In Fig. 3, a tapping mode atomic force microscopy (AFM) image (height data) of a $CaCO_3$ (104) surface is compared to a $CaCO_3$ (104) surface that has been reacted with nitric acid vapor
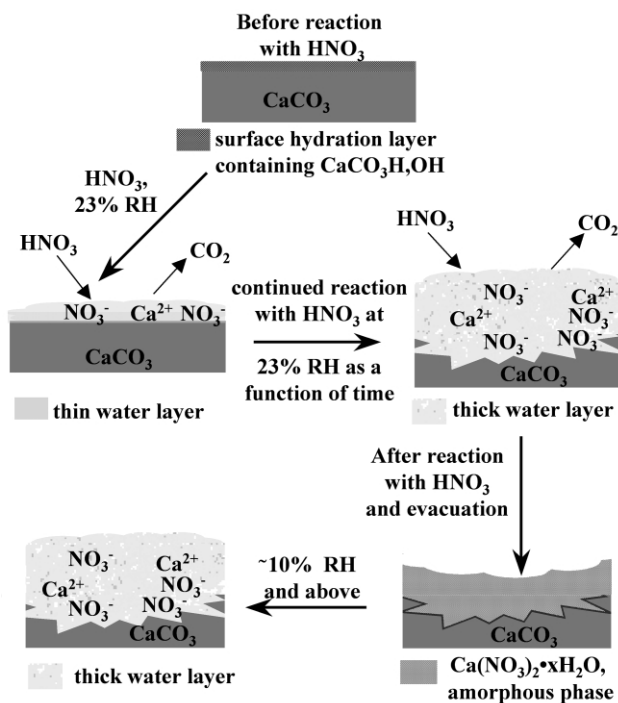


**AFM image of CaCO₃(104) at 20% RH**

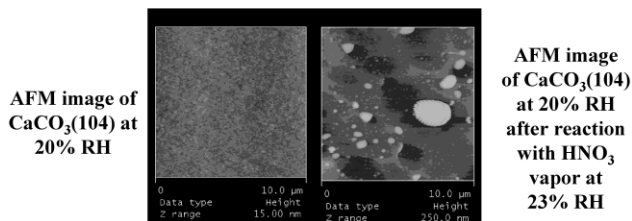**AFM image of CaCO₃(104) at 20% RH after reaction with HNO₃ vapor at 23% RH**

**Fig. 3** Tapping mode AFM images showing a $CaCO_3$ (104) surface (left) and a $CaCO_3$ (104) surface that was reacted with nitric acid vapor (right). The images were taken at 20% RH. The $z$-range contrast for the height image in the figure on the left extends from 0 to 15 nm whereas the one on the right extends from 0 to 250 nm. The bright spots in the image are due to liquid droplets on the nitric acid reacted surface.

at 23% RH. It is clear that the calcite surface changes and roughens considerably after reaction with nitric acid. The AFM images were taken at 20% RH, water droplets on the surface can be seen in the image shown for the nitric acid reacted surface (bright spots in the image shown on the right).

The resulting aqueous electrolyte layer that forms after deliquescence provides a medium for further reaction as well as biological activity that will contribute to the additional deterioration of calcium carbonate based structures. Furthermore, the results described below indicate that calcium carbonate containing mineral dust aerosol when reacted with nitric acid vapor will convert the aerosol from a solid to a liquid droplet. This change in phase will also result in a change in chemical reactivity and optical properties of the aerosol. The results reported herein are of importance because they impact many research areas including atmospheric science,[1] plant science[3] and art and museum showpiece conservation.[2] It is important to note that it does not appear that the calcium carbonate support plays an important role in the formation of the metastable amorphous state of calcium nitrate. In a series of very different experiments,[5] pure calcium nitrate levitated microcrystals were observed to also undergo deliquescence at low relative humidity (near 15% RH). Thus, the particles and thin films behave similarly.

A further understanding of metastable phases of salts is warranted if these non-equilibrium phases form at ambient conditions of temperature and relative humidity.[15,16] The effect of inorganic and organic impurities and any size dependence[17] on these metastable phases is equally worthy of further investigation.

## Notes and references

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**Before reaction with HNO₃**

**CaCO₃**

**surface hydration layer containing CaCO₃H,OH**

HNO₃, 23% RH

HNO₃    CO₂

NO₃⁻   Ca²⁺ NO₃⁻

**CaCO₃**

**thin water layer**

**continued reaction with HNO₃ at 23% RH as a function of time**

HNO₃    CO₂

NO₃⁻   Ca²⁺
Ca²⁺   NO₃⁻
NO₃⁻   NO₃⁻

**CaCO₃**

**thick water layer**

**After reaction with HNO₃ and evacuation**

~10% RH and above

NO₃⁻   Ca²⁺
Ca²⁺   NO₃⁻
NO₃⁻   NO₃⁻

**CaCO₃**

**thick water layer**

**CaCO₃**

**Ca(NO₃)₂·xH₂O, amorphous phase**

**Fig. 2** A mechanism for the reaction of nitric acid vapor with $CaCO_3$ is depicted. The surface of $CaCO_3$ initially contains a hydration layer of $HCO_3^-$ and $OH^-$ groups.[12–14] This layer then reacts with nitric acid at 23% RH to form a liquid layer of $Ca(NO_3)_2(aq)$. Under evacuation this liquid layer evaporates leaving behind an amorphous layer of solid $Ca(NO_3)_2$ which contains some absorbed water. This amorphous layer deliquesces at low relative humidity.