

## Reactions on atmospheric mineral aerosol

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### Introduction

Airborne particulate matter plays a crucial role in determining the climate and weather of the Earth<sup>1</sup>. Particulate matter affects climate directly, by scattering and absorbing solar radiation, and indirectly, owing to its ability to act as cloud condensation nuclei, thus leading to an increase in cloud formation and changes to precipitation. Both the direct and indirect effects are influenced by the chemical composition of the aerosol.

The total source strength of mineral aerosol to the atmosphere is 2150 Tg year<sup>-1</sup><sup>1</sup>. Carbonate rocks provide a considerable fractional (30%) of mineral aerosol<sup>3</sup>.

The initial aim of the work was to optically trap and levitate mineral particles and study the phase changes accompanying atmospheric reactions by Raman spectroscopy and optical microscopy, as previously achieved for sea-water droplets<sup>2</sup>. Phase changes and changes in hygroscopicity of atmospheric particles are critical to cloud formation and cloud albedo. However, all the aerosol generation mechanisms attempted in this work on mineral aerosol resulted in charged particles which could not be held in the optical trap as the columbic forces are many orders of the magnitude greater than the photon force defining the trap. Thus in this report we present preliminary findings obtained using the Raman microscope, in anticipation of trapping mineral aerosol by other means at RAL in future work<sup>4</sup>.

### Experimental

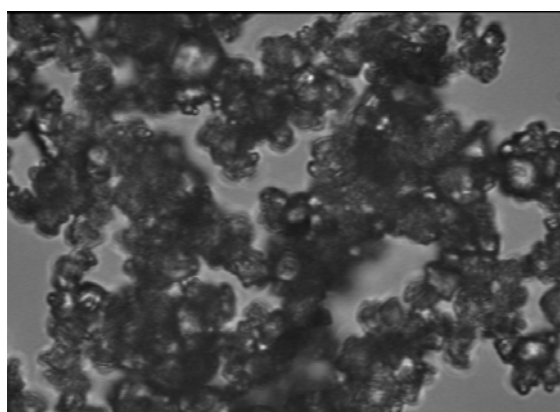
The simple reactions between carbonate species and atmospheric acids (HNO<sub>3</sub>, acetic and formic acids) were studied by using the Raman microscope. The Raman microscope was used to monitor the loss of carbonate and growth of the product (calcium nitrate, acetate and formate). The climatic impact of this aerosol reaction depends on the physical state the products are in and whether the products uptake atmospheric water. Samples of pure CaCO<sub>3</sub> were placed in an aluminum cell on a quartz window. Gas-phase samples of HNO<sub>3</sub> and the organic acids HCOOH and CH<sub>3</sub>COOH were introduced into the cell in the presence and absence of water vapour. The reactants and products were observed with Raman microscopy and the phase changes (or water uptake) were observed with optical microscopy.

### Results and Discussion

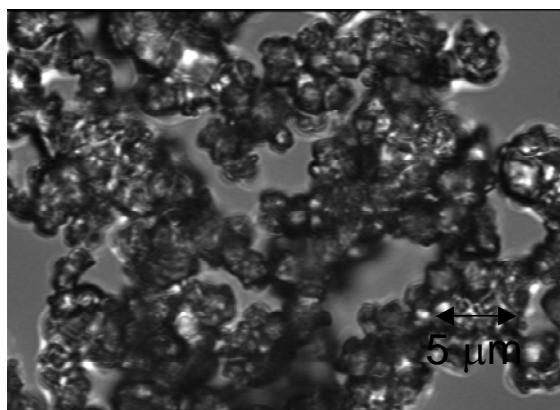
Calcium carbonate and nitric acid vapour:

The reaction between humid HNO<sub>3</sub> vapour and calcium carbonate particles was studied. Although the reaction is known to produce nitrogen species, there is debate in the literature as to whether or not the reaction ceases after surface passivation<sup>3</sup>. The photographs (Figures 1-3) and Raman spectra obtained in this work clearly demonstrate that the particles react, to form a surface coating of calcium nitrate, which then uptakes water and the reactions continues until all CaCO<sub>3</sub> is consumed. Figure 4 exemplifies the Raman signals followed. The reaction is very quick, as shown by the kinetic plot, Figure 5. Any water uptake by an atmospheric particle initially

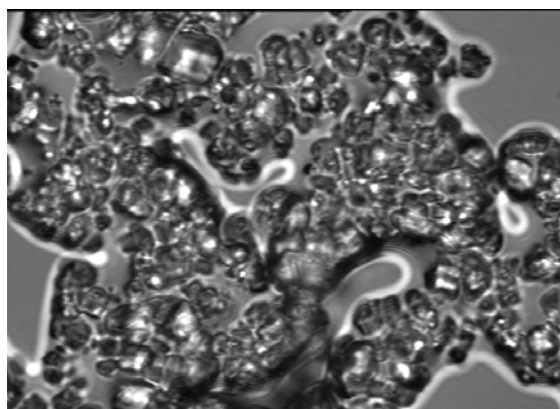
composed of calcium carbonate would imply aerosol growth and cloud droplet activation, with a change in the cloud water content (likely rain out) and optical properties (decreased albedo). Experiments were undertaken with 'dry' HNO<sub>3</sub> and no water uptake was observed. When CaO, instead of CaCO<sub>3</sub>, particles were used the reaction stopped after surface passivation.



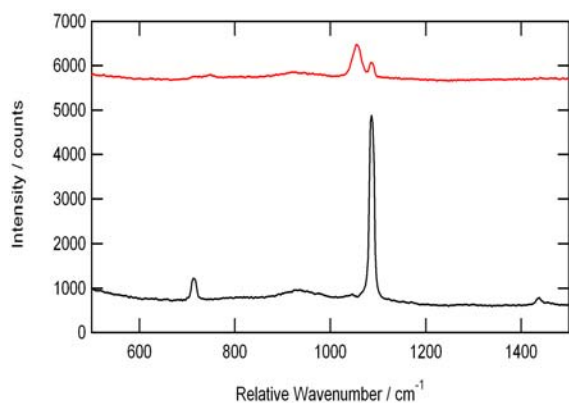
**Figure 1.** CaCO<sub>3</sub> particles initially.



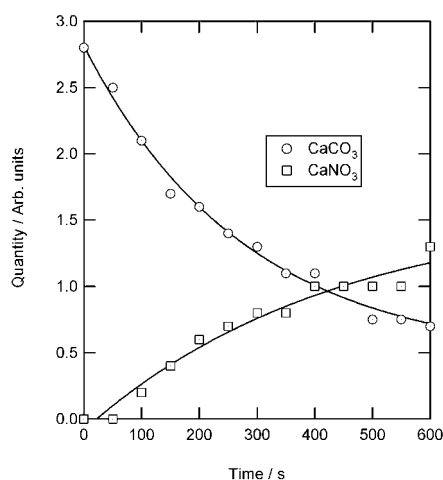
**Figure 2.** Surface reaction of HNO<sub>3</sub> and uptake of water.



**Figure 3.** Deliquescence and water uptake.



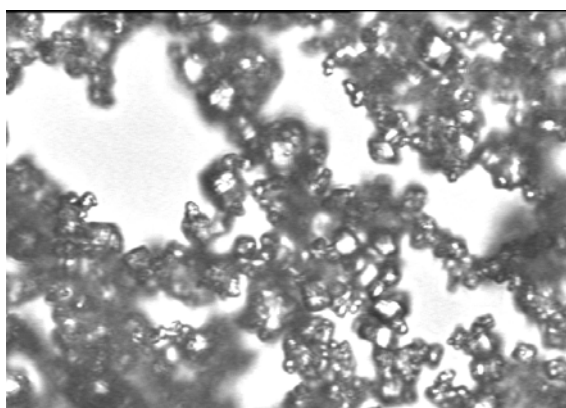
**Figure 4.** Raman spectrum of reactant,  $\text{CaCO}_3$  (black) and after reaction with  $\text{HNO}_3$ , (red, off-set on y-axis, assigned as  $\text{CaNO}_3$ ).



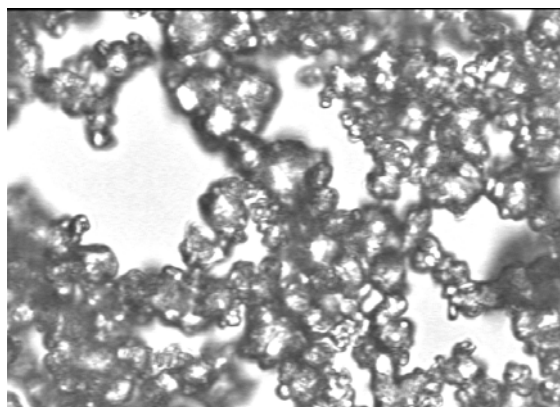
**Figure 5.** Kinetics of the reaction between  $\text{CaCO}_3$  and  $\text{HNO}_3$ .

Calcium carbonate and organic acids:

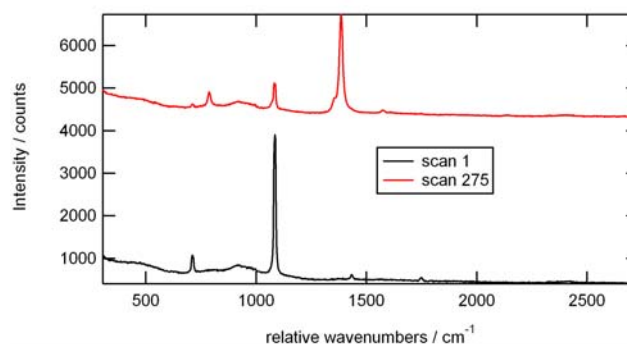
The reactions between acetic and formic acids with mineral  $\text{CaCO}_3$  particles were also studied. The reaction with formic acid produced a surface coating of formate and then the reaction appeared to stop after a surface passivation; Figures 6-8. The particles did not appear to uptake water. The reaction with acetic acid produced separate crystals and slowly continued to react over several hours. Neither reaction appeared to lead to deliquescence. These studies suggest that reaction of formic acid with  $\text{CaCO}_3$  may simply be a sink for formic acid in the atmosphere whilst the reaction of acetic acid with  $\text{CaCO}_3$  may be atmospherically and climatologically important, but requires further study.



**Figure 6.**  $\text{CaCO}_3$  before reaction with formic acid.



**Figure 7.**  $\text{CaCO}_3$  after reaction with formic acid. No uptake of water.



**Figure 8.** Raman spectrum before (black/lower trace) and after (red/upper trace off-set on y-axis) for reaction of  $\text{CaCO}_3$  with moist formic acid. The Raman spectrum of the product confirms that the surface reaction produces formate.

## Conclusions

- I. Raman spectroscopy and optical microscopy good for studying mineral reaction pertinent to atmosphere
- II. Reactions of nitric, acetic acid with carbonaceous aerosol could potentially be important in the climate balance of the Earth.

## Acknowledgements

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## References

1. Climate Change 2001: The Scientific Basis, Edited by Houghton, J T.; Ding, Y.; Griggs, D J.; Noguera, M; van der Linden, P J.; Dai, X; Maskell, K; Johnson, C A, Intergovernmental Panel on Climate Change, Cambridge University Press.
2. M D King, K C Thompson, and A D Ward, J. Am. Chem. Soc. 126 51 16711 (2004) [Please see accompanying New scientist Article 18th Dec 2004, 184,2478 p9]
3. C R Usher, A E Michel and V H Grassian, Chem Rev. 103, 4883 (2003)
4. R Omori, T Kobayashi, and A Suzuki, Optics letters, 22 11, (1997)