Raman Spectroscopy

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# Reactions of Alkaline Minerals in the Atmosphere**

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The excessive exploitation of watercourses for human activities affects the water balance of many lakes around the world. A well-known dramatic example is the desiccation of the Aral Sea,[1] which currently has almost disappeared. One of the consequences of the desiccation of saline water bodies as the Aral Sea is the phenomenon known as "salt storms", which transport huge amounts of salt over long distances. Some "soda lakes" (alkaline lakes), for example, the Owens Lake (USA), are also affected by desiccation processes, resulting in the wind transport of the alkaline dust.[2]

In spite of the remarkable scientific efforts to study heterogeneous reactions taking place in the atmosphere, the reactions between solid species under the influence of humid air have not received the necessary attention. To our knowledge, the chemical reaction between $CaCO_3$ and $(NH_4)_2SO_4$ in the presence of humid air[4] is the only report of reactions taking place between solid salts in the presence of humid air. However, there are other salts which should also be considered; $Na_2CO_3{\cdot}H_2O$ (thermonatrite) and $Na_3(HCO_3)(CO_3){\cdot}2\,H_2O$ (trona) were identified in the alkaline dust transported from the Owens (dry) Lake by wind.[2] Trona and $Na_6(CO_3)(SO_4)_2$ (burkeite) were identified in the salt efflorescences of playas of the Mojave Desert (USA), which are periodically removed (and transported) by wind.[3]

Depending on the size of the emitted particles, they can sediment or remain suspended for many days. The suspended material (fine particles) undergoes different atmospheric processes, one of them is coagulation (two particles combining to form one). Coagulation processes can produce internally mixed particles. This means that different solid substances are in contact in single particles (each particle is a mixture). If there is a chemical reaction between two solid compounds present in a single micrometer particle, this reaction takes also place on a macroscale, that is, in a bulk powder mixture. Kinetic differences between experiments on micro- and macroscales can be expected, fundamentally because of the surface area and gas diffusion. Since the reaction rate in a bulk solid mixture may be lower than that in a single particle, it is more likely to detect intermediate products. This is the reason why we use bulk powder mixtures in this work.

We report here, for the first time, solid-state reactions of the alkaline salts thermonatrite, trona, and burkeite with $(NH_4)_2SO_4$ in the presence of humid air (about 70 % relative humidity) at ordinary temperatures (21–23 °C). These solid-state reactions can be attributed to the interaction of ions in a liquid film formed on the solids. The observation of changes in the relative amount of reactants over time, as well as the identification of the reaction products were achieved using Raman spectroscopy. We also demonstrate that the reactivity between solid salts is not restricted to alkaline salts.

Considering both the experiments reported by Mori et al.[4] and our own results, the chemical reactivity of the solid powder mixtures seems to be strongly linked to the humidity of the air. When the solid mixtures are exposed to ordinary conditions, that is, temperatures ranging between 21 and 23 °C and a relative humidity (RH) of air below 50 %, the chemical reaction rate is very slow; the Raman spectra of mixtures exposed to ambient conditions during 24 h show no or only weak bands of the reaction products (see Figure S1 in the Supporting Information). Remarkable reactivity was observed consistently on exposing the solid powder mixtures to higher RH values. An unequivocal sign that reactions were taking place in the mixtures was the release of $NH_3$, which is a product of acid–base reactions involving $CO_3^{2-}$ and/or $HCO_3^-$, and $NH_4^+$ ions. The formation of $CO_2$ can be deduced from these reactions.

Figure 1 a shows the Raman spectra recorded at different times from an equimolar mixture of $(NH_4)_2SO_4$ and $Na_2CO_3{\cdot}H_2O$ (thermonatrite) exposed to humid air (70 % RH). After 5 minutes two new bands at 1079 and 996 $cm^{-1}$ are observed, which belong to anhydrous $Na_2CO_3$ and $Na_2SO_4$ in phase III, respectively. $Na_2SO_4$ in phase III (a high-temperature phase) was observed in earlier crystallization experiments of single droplets[5,6] and it is known to transform slowly to phase V (room-temperature phase). After 30 minutes a small band emerges at 1045 $cm^{-1}$ (which can be assigned to $NaHCO_3$ and/or $NH_4HCO_3$), while the band of anhydrous $Na_2CO_3$ decreases, obviously as a consequence of the water-vapor absorption to regenerate $Na_2CO_3{\cdot}H_2O$. After 3 h the bands belonging to anhydrous $Na_2CO_3$ and $Na_2CO_3{\cdot}H_2O$ (1069 $cm^{-1}$) disappear, instead a band at 984 $cm^{-1}$ (lecontite, $NH_4NaSO_4{\cdot}2\,H_2O$) appears. A band emerges and grows gradually at 993 $cm^{-1}$ ($Na_2SO_4$ in phase V), while the band of $Na_2SO_4$ in phase III decreases and finally disappears. There is evidence of a phase transition $Na_2SO_4(III) \rightarrow Na_2SO_4(V)$, probably because of the contact with humid air, since the stability of phase III has been associated to dry conditions.[7]

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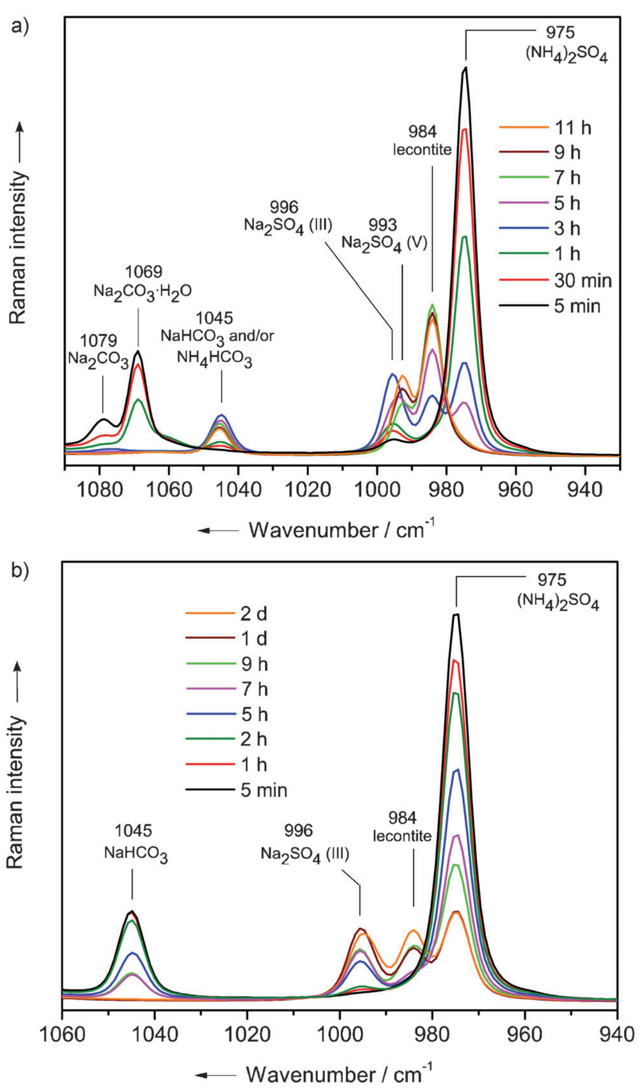

***Figure 1.*** Raman spectra recorded at different times from equimolar mixtures exposed to humid air (70% RH): a) $(NH_4)_2SO_4$ and $Na_2CO_3{\cdot}H_2O$ ($T$=21–22 °C) and b) $(NH_4)_2SO_4$ and $NaHCO_3$ ($T$=22–23 °C).

The characteristic band of lecontite increases until 7 h and afterwards a slight decrease is observed, which can be interpreted as a lecontite decomposition reaction.

The Raman spectra acquired at different times from an equimolar mixture of $(NH_4)_2SO_4$ and $NaHCO_3$ exposed to humid air (Figure 1 b) show the formation of both $Na_2SO_4$ in phase III and lecontite, and again the characteristic band of lecontite decreases towards the end of the experiment. When a new experiment for the $(NH_4)_2SO_4$–$NaHCO_3$ system is performed using a molar ratio of 1:3, only the band of $Na_2SO_4$ in phase V persists at the end of the experiment (Figure S2), confirming that a lecontite decomposition reaction is taking place. The proposed reactions (1)–(5) for the thermonatrite-$(NH_4)_2SO_4$ system are:

$$Na_2CO_3 \cdot H_2O + (NH_4)_2SO_4 \rightarrow Na_2CO_3 + (NH_4)_2SO_4 + H_2O \tag{1}$$

$$Na_2CO_3 \cdot H_2O + (NH_4)_2SO_4 + H_2O \rightarrow (NH_4)NaSO_4 \cdot 2\,H_2O + NaHCO_3 + NH_3 \tag{2}$$

$$Na_2CO_3 \cdot H_2O + (NH_4)_2SO_4 \rightarrow NH_4HCO_3 + Na_2SO_4 + NH_3 + H_2O \tag{3}$$

$$NaHCO_3 + (NH_4)_2SO_4 + H_2O \rightarrow (NH_4)NaSO_4 \cdot 2\,H_2O + NH_3 + CO_2 \tag{4}$$

$$(NH_4)NaSO_4 \cdot 2\,H_2O + NaHCO_3 \rightarrow Na_2SO_4 + NH_3 + 3\,H_2O + CO_2 \tag{5}$$

The reaction (1) shows the dehydration of thermonatrite because of the high hygroscopicity of $(NH_4)_2SO_4$. Apparently this strong affinity to $H_2O$ forces the extraction of the $H_2O$ molecule from the thermonatrite structure producing anhydrous $Na_2CO_3$. The $H_2O$ molecules, initially proceeding from thermonatrite and afterwards from the humid air, deposit on the solid $(NH_4)_2SO_4$. Since $(NH_4)_2SO_4$ and thermonatrite (and anhydrous $Na_2CO_3$) are intimately mixed, the prolonged exposure to humid air results in the formation of a "liquid $H_2O$ film" on the solids and the partial dissolution of these salts (Figure 2). When $CO_3^{2-}$, $HCO_3^-$, and $NH_4^+$ ions are in solution in this "film", acid–base reactions take place eliminating the gaseous products $NH_3$ and $CO_2$ and precipitating new salts. This can explain the formation of $NaHCO_3$, $(NH_4)NaSO_4{\cdot}2H_2O$, and $Na_2SO_4$ in the solid mixture at different times. $Na_2SO_4$ (phase III) is already observed at 5 minutes and it seems unlikely that the fast formation of $Na_2SO_4$ is explained only by the two consecutive reactions (2) and (5), therefore reaction (3) is also postulated.

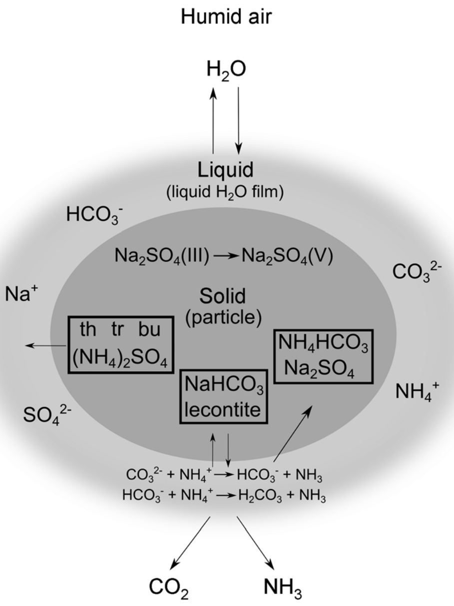

***Figure 2.*** Interaction scheme of a solid particle consisting of a mixture of thermonatrite (th), trona (tr), or burkeite (bu), and $(NH_4)_2SO_4$ suspended in humid air (the actual thickness of the liquid phase compared to the particle size is expected to be much smaller than that shown in the figure).

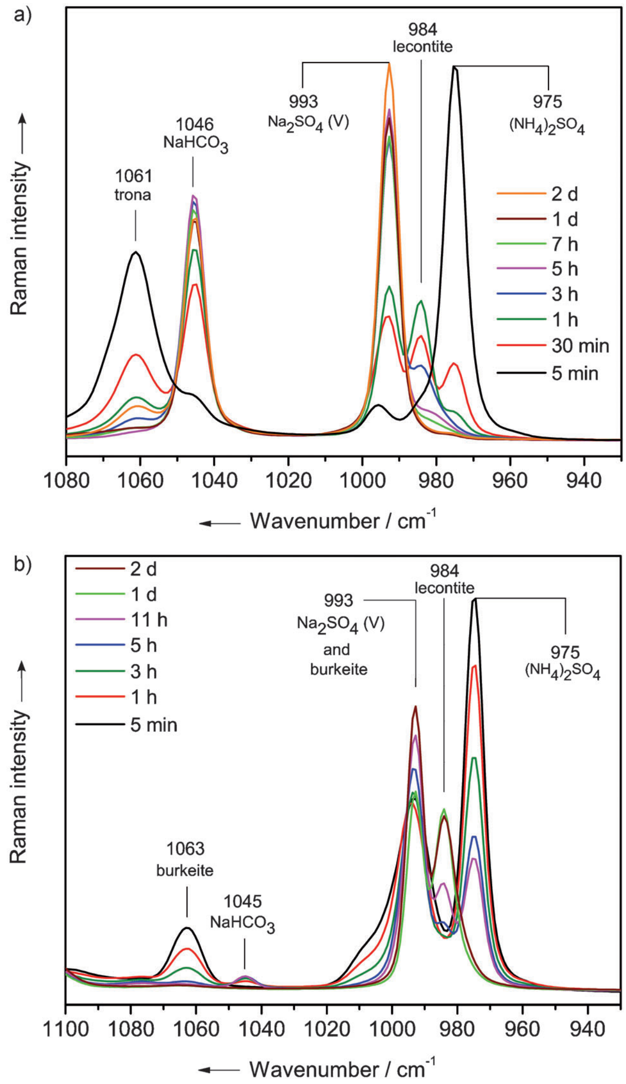

***Figure 3.*** Raman spectra recorded at different times from equimolar mixtures exposed to humid air (70% RH): a) $(NH_4)_2SO_4$ and $Na_3(HCO_3)(CO_3)\cdot 2H_2O$ ($T=21$–$22\,^\circ C$) and b) $(NH_4)_2SO_4$ and $Na_6(CO_3)(SO_4)_2$ ($T=21$–$22\,^\circ C$).

Figure 3a shows the Raman spectra recorded at different times from an equimolar mixture of $(NH_4)_2SO_4$ and $Na_3(HCO_3)(CO_3)\cdot 2H_2O$ (trona) exposed to humid air. After 5 minutes bands at 1046 and 996 $cm^{-1}$ can be observed, indicating that $NaHCO_3$ and $Na_2SO_4$ in phase III appear in the solid mixture at this short time. The fast growing of the band at 1046 $cm^{-1}$ suggests that not only $NaHCO_3$, but also $NH_4HCO_3$ is formed. After 30 minutes the band at 984 $cm^{-1}$ (lecontite) is clearly distinguishable and starts to decrease as soon as all $(NH_4)_2SO_4$ has reacted. The final products of the reactions are $Na_2SO_4$ in phase V, $NaHCO_3$, and $NH_4HCO_3$. The proposed reactions (6) and (7) for the trona–$(NH_4)_2SO_4$ system are:

$$\begin{aligned} &Na_3(HCO_3)(CO_3)\cdot 2\,H_2O + (NH_4)_2SO_4 \rightarrow \\ &2\,NaHCO_3 + (NH_4)NaSO_4\cdot 2\,H_2O + NH_3 \end{aligned} \tag{6}$$

$$\begin{aligned} &Na_3(HCO_3)(CO_3)\cdot 2\,H_2O + (NH_4)_2SO_4 \rightarrow \\ &NH_4HCO_3 + NaHCO_3 + Na_2SO_4 + NH_3 + 2\,H_2O \end{aligned} \tag{7}$$

The formation of $NaHCO_3$ and the evident decomposition of lecontite suggest that the reactions (4) and (5) are also taking place in this system. At the end of the experiment (after two days), a weak band at 1061 $cm^{-1}$ appears; this anomaly can be explained by a local heterogeneity of the mixture resulting in the presence of unreacted trona, or a possible interaction of the mixture with atmospheric $CO_2$ to recrystallize trona. The interaction of alkaline brines with atmospheric $CO_2$ to crystallize trona was proposed by Eugster[8] to explain natural deposits of this mineral.

Figure 3b shows the Raman spectra taken at different times from an equimolar mixture of $(NH_4)_2SO_4$ and $Na_6(CO_3)(SO_4)_2$ (burkeite) exposed to humid air. After 1 h a band at 1045 $cm^{-1}$ ($NaHCO_3$ and/or $NH_4HCO_3$) emerges. The $SO_4^{2-}$ symmetric stretching ($\nu_1$) of burkeite is characterized by a strong band at 993 $cm^{-1}$ with a shoulder at 1005 $cm^{-1}$ (see Figure S10), therefore the emergence of the characteristic bands of $Na_2SO_4$ in phases III and V (996 and 993 $cm^{-1}$, respectively) cannot be observed within the first minutes and hours of the experiment. Only at the end of the experiment (after two days) the large increase of the intensity of the band at 993 $cm^{-1}$ and the emergence of the weaker bands of $Na_2SO_4$ in phase V indicate the formation of $Na_2SO_4$ in this mixture. The band of lecontite (984 $cm^{-1}$) becomes prominent after 5 h, grows until one day and stabilizes. Taking into account these observations, the main reaction (8) taking place in the burkeite–$(NH_4)_2SO_4$ system is:

$$\begin{aligned} &Na_6(CO_3)(SO_4)_2 + (NH_4)_2SO_4 + 2\,H_2O \rightarrow \\ &2\,Na_2SO_4 + (NH_4)NaSO_4\cdot 2\,H_2O + NaHCO_3 + NH_3 \end{aligned} \tag{8}$$

The formation of $NaHCO_3$ and lecontite suggests that the reactions (4) and (5) can also take place in this system. The production of $NH_4HCO_3$ seems to be unlikely, since the band at 1045 $cm^{-1}$ disappears towards the end of the experiment. This indicates that the signal at 1045 $cm^{-1}$ belongs to $NaHCO_3$ and this salt is completely consumed by the reactions (4) and (5).

The reactions of solid mixtures are not restricted to alkaline materials; in a solid mixture of $CaSO_4\cdot 2H_2O$ (gypsum) and $(NH_4)_2SO_4$ we observed the following reaction (9), see Figure S3:

$$CaSO_4\cdot 2\,H_2O + (NH_4)_2SO_4 \rightarrow (NH_4)_2Ca(SO_4)_2\cdot H_2O + H_2O \tag{9}$$

Gypsum, $(NH_4)_2SO_4$ and $(NH_4)_2Ca(SO_4)_2\cdot H_2O$ (koktaite) were reported in atmospheric particulate matter.[9] It is clear that koktaite can be produced not only by precipitation from aerosol solutions,[6] but also by a reaction of solid material in the presence of humid air.

In summary, reactions taking place between alkaline minerals and $(NH_4)_2SO_4$ in the presence of humid air have been studied using Raman spectroscopy. Products such as $Na_2SO_4$ (phases III and V), $NaHCO_3$ and/or $NH_4HCO_3$, and lecontite have been identified. Moreover, reactions involving solid mixtures are not restricted to alkaline minerals; the formation of koktaite is reported as a product of the reaction between gypsum and $(NH_4)_2SO_4$ in the presence of humid air. This kind of reactions has to be considered in atmospheric studies (aerosol chambers and models), since aerosol coagulation and subsequent chemical reactions may have implications not only on the atmospheric chemistry, but also on the climate.

## Experimental Section

Details of the reactants, the synthetic methods of minerals, and the instruments used in this study can be found in the Supporting Information. The reactions of $Na_2CO_3 \cdot H_2O$ (thermonatrite), $Na_3(HCO_3)(CO_3) \cdot 2H_2O$ (trona), $Na_6(CO_3)(SO_4)_2$ (burkeite), and $CaSO_4 \cdot 2H_2O$ (gypsum) with $(NH_4)_2SO_4$ were studied using powder solid mixtures in an equimolar ratio. For normalization purposes, an amount of $TiO_2$ (anatase) equivalent to about 5% of the mass of $(NH_4)_2SO_4$ was included in the mixtures. To generate the mixtures, appropriate amounts of the salts were placed in a porcelain mortar and finely milled. The temperature and relative humidity (RH) of air during the manipulation of the reactants and the milling process were 21–23 °C and less than 50%, respectively (ambient conditions). The resulting powder was placed in a Petri dish (80 mm diameter), homogeneously distributed, and disposed in a glovebox with an inner RH of 70%. The formation and release of $NH_3(g)$ was verified by its characteristic odor and the color change of a wet piece of pH paper. A powder sample was taken at specific times of exposition to the humid air (starting at 5 minutes) and its Raman spectrum was recorded immediately. The sampling process was performed until no more significant changes were observed in the Raman spectra or the solid mixture deliquesces (the thermonatrite-$(NH_4)_2SO_4$ system). The samples were collected from the mixture including both the upper (in direct contact with air) and lower (in contact with the Petri dish glass) portion of the bulk mixture. In addition, the reactivity of solid mixtures containing $(NH_4)_2SO_4$ and $NaHCO_3$ in molar ratios 1:1 and 1:3 were evaluated using the same method. To evaluate the reactivity of the mixtures at low relative humidities, the Raman spectra were recorded from small portions of each mixture after 24 h of exposure to ambient conditions. The Raman spectra of all synthetic minerals and reactants used in this study were recorded (see Figures S4–S15).

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