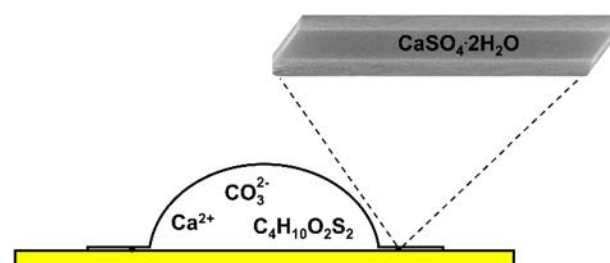# Nanoscale-Specific Reaction in a Precursor Film: Mixing Sodium Carbonate, Calcium Chloride, and an Organic Thiol to Produce Crystals of Calcium sulfate

Kathryn A. Melzak,* Fabrice Laye, and Stefan Heißler

ABSTRACT: The ultrathin precursor film surrounding droplets of liquid on a solid surface is used here as a confined reaction medium in order to drive a reaction that would not occur in bulk fluid. Sodium carbonate and calcium chloride mixed together in the presence of the organic thiol dithiothreitol (DTT) produced crystals of gypsum, or calcium sulfate, instead of the otherwise expected calcium carbonate. The possible sources of sulfate in the system are contaminants in the DTT or the oxidation product of the DTT sulfhydryl. The amount of gypsum produced implies that contaminants do not account for the total sulfate present in the system, suggesting that the DTT could be oxidized. The reaction quotient may be skewed in favor of this unexpected reaction by a combination of efficient removal of sulfate by precipitation and the concentration of DTT at the leading edge of the precursor film through the coffee ring effect during a brief drying step.

INTRODUCTION

The behavior of liquids in thin films differs greatly from their behavior in bulk. As films of liquid get thinner, the effective viscosity goes up, increasing by as much as a factor of 10^6 at nm scale distances from hydrophilic surfaces.[1] The behavior of solute molecules in such films can also vary: the diffusion of hydrated sodium in thin films may be up to 40 times slower than diffusion in bulk solution.[2] One application of these effects has been the use of picoliter droplets to slow down the crystallization of $CaCO_3$, permitting the observation of intermediate forms in the crystallization process.[3] In the work presented here, nanoscale reaction conditions result in a product that would not be obtained in the bulk solution. The small scale crystals of the reaction product are formed in patterns, a result that also has some potential relevance to biomineralization, in which well defined crystalline arrays are formed in confined surroundings.

Drops of liquid applied to solid substrates can take different forms: they can remain as cap shaped drops, they can spread outward to generate flat pancake shapes, or they can exist in an intermediate regime in which a droplet retains a spherical cap shape but is surrounded by a thin film of liquid that spreads outward to cover the surrounding surface.[4] The thickness of this precursor film is predicted to be on the order of a few angstroms,[4] sufficient to allow the passage of small solute molecules or ions. It is therefore possible to modify a surface far beyond the macroscopically visible boundaries of an applied drop of solution, as illustrated in Figure 1.
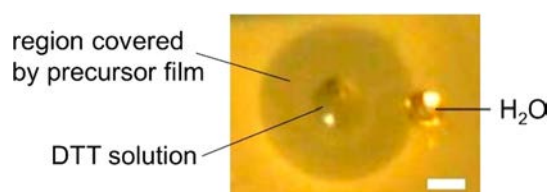

Figure 1. Breath pattern illustrating the extent of the spread of a precursor film around the base of a drop of 50 mM DTT. The drop on the left is 50 mM DTT; the drop on the right is water, applied to the surface of the gold at the same time. The scale bar is 1 mm. The brightness and contrast have been adjusted.

The original intent of the experiments described here was to use the precursor film surrounding drops of DTT on gold as a confined volume for the formation of calcium carbonate crystals, inspired by experiments described elsewhere in which the early stages of calcium carbonate crystal formation were observed in picoliter droplets on thiol layers on gold substrates.[3] The unexpected result, however, was that gypsum crystals were formed instead of calcium carbonate.

EXPERIMENTAL SECTION

For these experiments, a small drop (0.2−0.5 μL) of a freshly prepared solution of 50 mM dithiothreitol (DTT; $CH_2SHCHOHCHOHCH_2SH$), 5 mM $CaCl_2$, and 1 mM Na_2CO_3 was applied to a sputter coated or else plasma cleaned gold surface within 2−5 min of the surface being exposed to air; the film was allowed to spread outward for 5−10 min at room temperature in a chamber saturated with water vapor; the chamber lid was then opened for 5−10 s to allow the precursor film to dry, after which the lid was replaced, allowing the outward spread of the precursor film to continue. The samples were allowed to sit overnight and then analyzed after being dried in air. Experiments were also carried out with no carbonate.

RESULTS AND DISCUSSION

Crystals were found to form in a ring outside the boundaries of the spot of the solution. The crystals were identified as gypsum on the basis of the crystal morphology (Figure 2) and
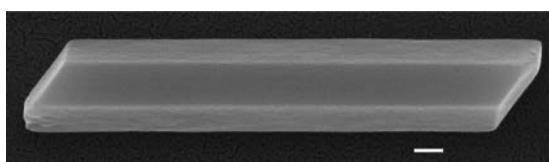

Figure 2. SEM image of a single crystal formed from a solution of 50 mM DTT, 5 mM $CaCl_2$, and 1 mM Na_2CO_3, on a sputter coated gold surface prepared with a Bal Tec sputter coater. The image was acquired after sputter coating the sample with a 5 nm layer of gold. Scale bar indicates 200 nm; the crystal is approximately 3.5×0.6 μm.

identification was confirmed by Raman spectroscopy (Figure 3). Raman bands sensitive to the orientation of polarized light also supported the identification of gypsum (see Supporting
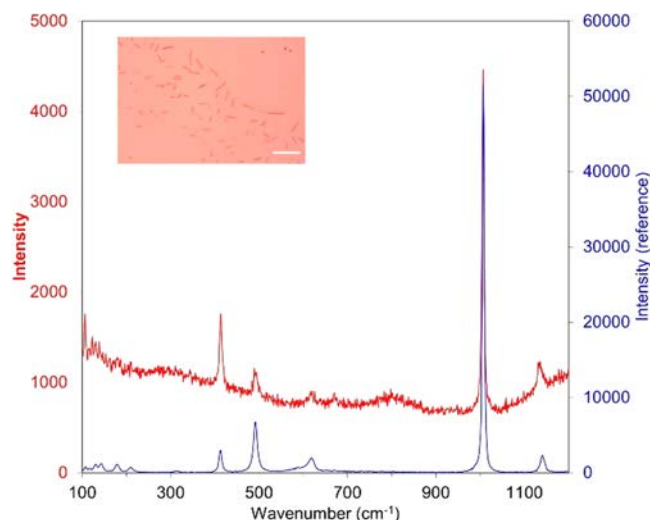

Figure 3. Raman spectra of crystal (red line, top, axis at left) compared to reference spectrum for gypsum (blue line, at bottom, axis at right);[5] crystals were prepared on a gold coated slide with solution conditions as for Figure 2, but with a 0.5 μL drop; the precursor film was allowed to spread outward for 10 min, followed by a 15 s drying step, after which the drop was left to dry overnight. Inset shows image of the measured sample, scale bar 20 μm. Images acquired after the measurement did not show evidence of sample destruction. The weak band at 670 cm^{-1} is a polarization dependent feature (see Figure S1) present in some gypsum reference spectra[6] but not in others.[5]

Information Figure S1). The crystals formed only when the precursor films were allowed to dry briefly, an observation supported by the production of multiple lines of crystals in association with multiple drying steps (Figure 4). Control experiments with no carbonate produced only small crystals, which were confirmed as gypsum by Raman bands at 1009.4 cm^{-1} (strong), 494.94 (w/med), and 416.04 (w/med).
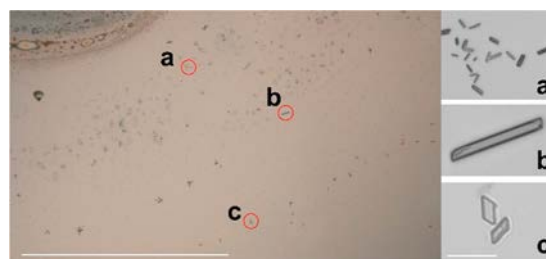

Figure 4. Three lines of crystals produced by three successive drying steps; scale bar on large image is 0.5 mm; scale bar on insets is 10 μm. The insets a−c show details of the corresponding circled regions on the large image. See also Supporting Information Figure S2 for comparison to an SEM image.

We can clearly identify gypsum, which indicates that there is sufficient sulfate present in the system to form the observed crystals. A rough calculation of the amount of sulfate required to produce the observed volume of crystals was done with a preparation that produced a relatively well defined line (Figure S3); the calculations were based on the assumption that there was sufficient gypsum to form a continuous track two crystals wide and two crystals high with a diameter of 3 mm, for crystals 0.3 μm wide, which would correspond to sulfate being present as 0.25% of the initial DTT in the drop applied to the gold surface. This is a plausible level of impurities but it would only be sufficient to produce the observed crystals if all the sulfate left the bulk of the drop and traveled at the advancing front of the precursor film. This seems unlikely and is also not consistent with the observation that repeated drying steps can produce multiple rings of crystals. Additionally, Raman mapping of the dried remnants of the applied drop did not reveal any calcium sulfate peaks; although this would be consistent with the suggestion that all the hypothetically present sulfate leaves the drop and concentrates at the front of the precursor film, it would also, more plausibly, suggest that the amount of sulfate present as a contaminant is too low to explain our results.

The solubility product of calcium carbonate is $10^4 \times$ lower than that of calcium sulfate;[7] for reactions in which carbonate was added to the solution, the preferential formation of gypsum implies that the sulfate is present at much higher concentrations than the carbonate. One possibility is that the carbonate does not travel through the precursor film; if we follow the model in which the source of the sulfate is a contaminant of the DTT that appears, based on required amounts for the observed crystals, to travel at the front of the precursor film, we would then have to assume a very efficient separation of the two ions. Solubilities will vary with pH, and pH can be affected close to surfaces, but the formation of calcium carbonate crystals that has been observed in picoliter droplets on gold surfaces[3] implies that the calcium carbonate has not been made soluble for some reason when in close proximity to a modified gold surface.

The other possible source of the sulfate comes from the thiol groups of the DTT, which could potentially be oxidized; oxidation of organic thiols to sulfates has been noted previously in bacteria, occurring via complex pathways.[8] Thiols can interact with gold to form self assembled monolayers; it is this interaction that probably drives the spread of the precursor film through reactive wetting of the surface.[9] If we are to explain an unusual reaction of thiols near a gold surface, we would have to have unusual conditions. In the present case, this includes the thickness of the precursor film. As mentioned above, the behavior of highly confined liquids differs from that in bulk. The structural relaxation time for water in thin films between molecularly smooth surfaces also differs from the bulk value: a value of $t \approx 0.01$ s has been measured for 0.6 nm thick films between mica sheets, as measured with a surface force apparatus, in contrast to values on the order of ps measured in the bulk liquid.[10] In addition, reactions with ambient oxygen could be affected because there will not be a requirement for the oxygen to diffuse a substantial distance away or even possibly any distance away from the air—water interface. The crystallization of calcium carbonate may be slow in confined conditions,[3] but it seems unlikely that kinetic control can slow down the calcium carbonate formation to negligible levels while permitting the formation of calcium sulfate.

The gypsum crystals described here are formed only when there is a brief drying step. Drying could provide nucleation sites to initiate crystal growth, but lack of nucleation sites does not appear to be the factor limiting the crystal growth as indicated by multiple lines of precipitated material that form without associated formation of crystals and seen in Figure S4 of the Supporting Information. Drying also concentrates surface active solutes at the outer rim of the drying spot by the coffee ring effect;[11] this remains as a possible factor driving the formation of the gypsum crystals.

CONCLUSION

In summary, we see gypsum crystals produced under conditions where we would not expect to have much sulfate present. One possible source is a contaminant from the DTT, which would require the sulfate to travel at the front of the precursor film at very efficient separations from the carbonate ions; the other possible source is the oxidation product of DTT, which would require some unexpected oxidations in air. The procedures described here provide a way to form small scale crystals arranged in concentric lines, with reactions that would not occur in the bulk solution. The conditions required in these experiments to produce the precursor film, which is to say high concentrations of thiol on gold, would limit potential applications but precursor films have been described for other systems,[12] and so other systems could possibly be employed as well.

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Author Contributions

Author K.A.M. prepared samples, obtained Raman spectra (Renishaw), and wrote the paper; F.L. acquired SEM and optical microscopy images; S.H. acquired and interpreted Raman spectra. All authors have given approval to the final version of the manuscript.

ABBREVIATIONS

DTT dithiothreitol

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