

Stabilization of aragonite on thiol-modified gold surfaces: effect of temperature

Jörg Küther and Wolfgang Tremel*

Institut für anorganische und analytische Chemie, Johannes Gutenberg-Universität Mainz, J. J. Becherweg 24, D-55099 Mainz, Germany

While the slow crystallization of calcium carbonate at 22 °C on self-assembled ω -substituted alkylthiol surfaces yields in most cases, depending on the surface, the vaterite and calcite modifications, elevating the temperature to 45 °C allows the stabilization of the aragonite modification as well.

The number of minerals known to be formed in biological systems has increased considerably during the past few years. The majority of these minerals contain Ca, and the precision by which these minerals are replicated in terms of structure, morphology and distribution indicates that the mechanisms of nucleation, growth and organization are specific for any biological system. Interest in the controlled crystallization of calcium carbonate is twofold. First, there is the geological and biological ubiquity of the various mineral modifications of CaCO_3 , viz., calcite, vaterite and aragonite. Secondly these are interesting model systems for heterogeneous nucleation at organic–inorganic boundaries, such as those involved in natural biomineralization processes.¹ Extensive studies on CaCO_3 crystals grown under Langmuir films and in the presence of additives have been reported.^{2,3} The crystallization of the calcite modification on self-assembled monolayers (SAMs) of substituted alkyl silanes on Si(001) has also been described.⁴ We have been interested in the factors that determine why one modification is preferred over another, as well as crystal habit and how it can be controlled. To this end, we have studied the slow crystallization of CaCO_3 on well characterized SAMs of ω -substituted alkylthiols of different chain lengths, which build up highly ordered surfaces.⁵ Depending on the ω -substituent, we are able to obtain calcite and vaterite phases at 22 °C either in pure form or as mixtures, with the actual proportions being determined by the Rietveld refinement of the powder X-ray profiles. In one case, to be described later, aragonite is also obtained. The focus of this work is our finding that by elevating the temperature at which the crystallization is carried out to 45 °C, we observe the stabilization of the aragonite modification as well. On certain surfaces, notably $\text{HS}(\text{CH}_2)_3\text{SO}_3\text{Na}$ -modified Au, aragonite is the principal phase. This is of some importance since previous reports of aragonite crystallization under mild conditions have been carried out only in the presence of extraneous molecules or cations such as Mg^{2+} or Li^+ ,^{6,7} with the exception of a recent report on the template-directed synthesis of aragonite under Langmuir films of 5-hexadecyloxyisophthalic acid.⁸ Here, we discuss the growth of CaCO_3 on a few surfaces, comparing the results of crystallization carried out at 45 °C with the results obtained on the same surfaces when the crystallization is carried out at 22 °C. We thus attempt to find factors that favour the formation of aragonite under these relatively mild conditions.

The glass/Cr/Au substrates used for crystallization were prepared by vacuum evaporation with film thickness being monitored using a quartz crystal oscillator. The SAMs were grown from ethanol solutions. Surface plasmon spectroscopy, contact angle measurements and reflectance FTIR spectroscopy were used to characterize the SAMs. Calcium carbonate crystallization was performed in a closed desiccator using solid $(\text{NH}_4)_2\text{CO}_3$ to raise, by diffusion,⁹ the CO_3^{2-} concentration of CaCl_2 solution.[†] The substrates were held downwards in

solution to prevent gravitational precipitation. The whole apparatus was placed in an oven to control the temperature. Crystallization times were typically 48 h. The formation of crystals was followed by SEM (Zeiss DSM 962) and by PXRD (Siemens D5000) in transmission geometry with the crystals transferred from the substrates to ScotchTM tape. Fig. 1(a) shows an SEM micrograph of CaCO_3 crystals on the $\text{HS}(\text{CH}_2)_{15}\text{CO}_2\text{H}$ -modified Au surface on which they have been grown. The three different crystal modifications are clearly seen, being small platelets of vaterite in the middle left, small well formed rhombs of calcite, and preponderantly, running diagonally across are clusters of aragonite needles.

Fig. 1(b) shows one such cluster of aragonite needles at higher magnification. The morphology is familiar from previous work, with the growth (needle) axis being in the c direction of the unit cell. Nucleation of the clusters take place along a line, as seen from panel (a) of this figure, and this

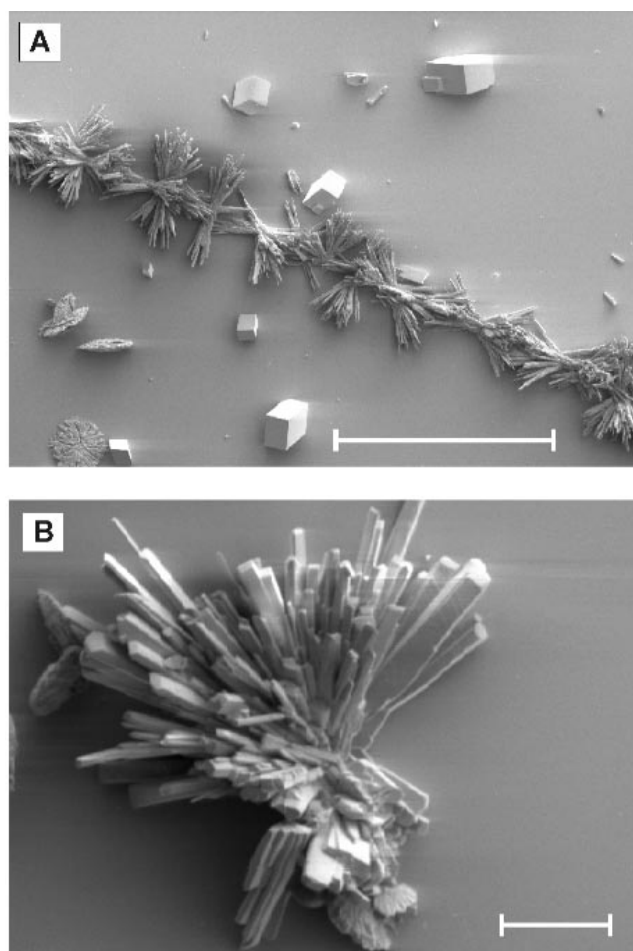


Fig. 1 Scanning electron micrographs of calcium carbonate crystals on a $\text{HS}(\text{CH}_2)_{15}\text{CO}_2\text{H}$ -modified Au surfaces. (a) Low magnification (bar = 200 μm), (b) high magnification (bar = 20 μm) of a cluster of aragonite needles.

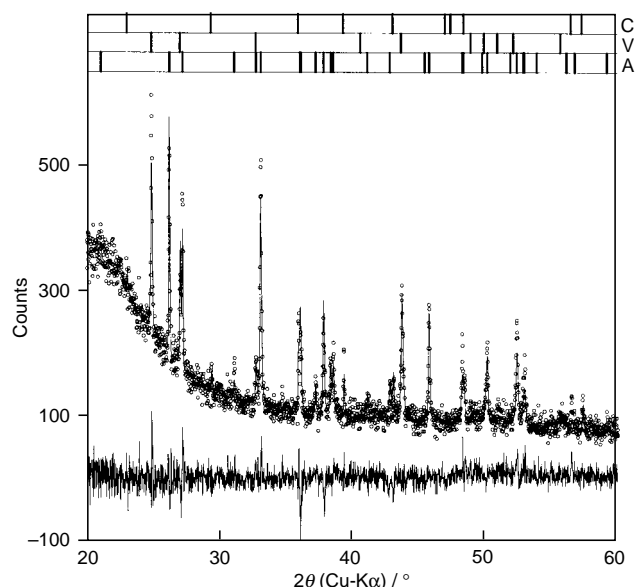


Fig. 2 Powder X-ray data (points), Rietveld profile fits (lines) and difference profiles of CaCO_3 crystals grown on a $\text{HS}(\text{CH}_2)_3\text{SO}_3\text{Na}$ -modified surface at 45 °C. The horizontal lines mark expected reflection positions for calcite (C), vaterite (V) and aragonite (A).

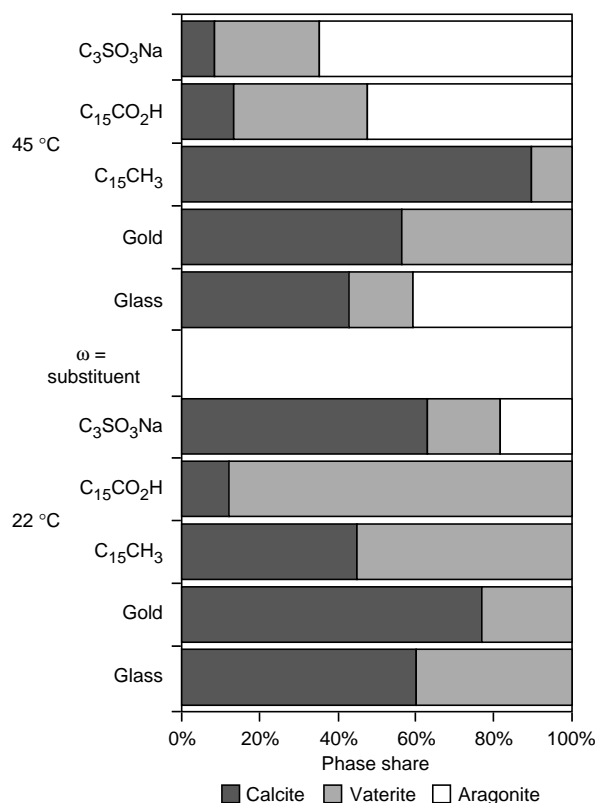


Fig. 3 Histogram of phase composition obtained from Rietveld refinements of powder X-ray profiles from crystals of CaCO_3 grown at 22 and 45 °C on different substrates (indicated). C_{15}CH_3 refers to $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$, ($\text{C}_{15}\text{CO}_2\text{H}$) to $\text{HS}(\text{CH}_2)_{15}\text{CO}_2\text{H}$ and $\text{C}_3\text{SO}_3\text{Na}$ to $\text{HS}(\text{CH}_2)_3\text{SO}_3\text{Na}$. We estimate the absolute errors to be <10%.

provides some clues to factors that favour aragonite formation as discussed presently.

To improve quantification, we have acquired powder X-ray profiles and analyzed them using the Rietveld method¹⁰ incorporated in the XND program.¹¹ Scale factors, lattice and profile parameters, including preferred orientations were refined. The structures were taken from the literature.^{12–14} Actual

mass fractions were estimated from the scale factors using the procedures discussed in ref. 15. Since estimating volumes of the crystallites is difficult in the present case, Brindley corrections were not applied.¹⁶ These and other factors such as disparate crystallite sizes and poor powder averaging (due to the sub-milligram quantities used) are expected to decrease the reliability of such estimates. Fig. 2 shows a typical Rietveld profile fit for CaCO_3 grown on a $\text{HS}(\text{CH}_2)_3\text{SO}_3\text{Na}$ -modified Au surface. Using this Rietveld procedure we illustrate in Fig. 3 histograms of the quantities of the different modifications of CaCO_3 grown on five different surfaces, clean glass, clean gold, and SAMs of $\text{HS}(\text{CH}_2)_{15}\text{CO}_2\text{H}$, $\text{HS}(\text{CH}_2)_3\text{SO}_3\text{Na}$ and $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$, at 22 and at 45 °C. It is interesting that a small temperature difference can result in such large changes in the preference of one modification over others.

We now attempt to identify the factors that might favour aragonite growth. We note that aragonite formation in solution is generally favoured at higher temperatures.¹⁷ Clearly, the fact that aragonite grows on clean glass disallows templating being invoked as the only responsible parameter in the present case. Since clean gold and the long chain alkyl terminated thiol do not show up any aragonite even at 45 °C, we believe that aragonite is not favoured on highly ordered surfaces. Polar, short-chain (and hence less ordered) SAMs on the other hand, seem to favour aragonite. Indeed of the ten or more surfaces examined, the SAM of $\text{HS}(\text{CH}_2)_3\text{SO}_3\text{Na}$ is the only one which is able to induce aragonite crystallization even at 22 °C. Going back to Fig. 1(a), we see that the nucleation in this case takes place along a line which is probably a step or a terrace boundary on the surface, where the local roughness might be high. The present observation of aragonite on certain surfaces and not on others at 45 °C thus is likely to be due to the combined effects of promotion on the one hand as well as inhibition on the surfaces where it is not observed.

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Footnotes and References

- * E-mail: tremel@indigotrem1.chemie.uni-mainz.de
- † Crystals of calcium carbonate were grown on gold-coated (50 nm thick) glass substrates in a 10 mm solution of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (Merck, Suprapur™) in pure water (Barnstead Easypure UV, $\rho > 18.3 \text{ M}\Omega \text{ cm}$); the pH was adjusted to 10 with 0.1 M NaOH. Temperatures for crystallization were 22 ± 3 and 45 ± 2 °C.
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