

TEMPLATE-INDUCED CRYSTAL GROWTH

John W. White, A. Brown, K. Edler, S. Holt, J. Watson, P. Reynolds, J. Ruggles
Research School of Chemistry
The Australian National University
Canberra ACT 0200, Australia

and

L. Iton
Materials Science Division
Argonne National Laboratory
Argonne, USA

KEYWORDS: Biomineralisation, Silicate, Film

ABSTRACT

The process of "mineralisation" in biology leads to a diversity of inorganic structures based on silica or calcium carbonate. Some of these are composite and, at the same time, highly crystalline. In all cases a molecular or self assembled "template" species has been identified as the promoter for the crystallisation of the new structure. In biology these "templates" are the end step in the conveyance of genetic information to the inorganic synthesis and an understanding of how they work is the key to mimicking biomineralisation in the laboratory. The lecture will describe how modern scattering methods, using x-rays and neutrons, have revealed the very first steps in the process from the first association of the inorganic with the "template" in zeolite and mesoporous silicate syntheses in the bulk and at interfaces. We now have some control of the phase diagram at surfactant interfaces and novel nanoscale structures have been produced and quantitative thermodynamic information on the kinetics of growth between 20Å and 1000Å will be discussed. It now seems to be possible also to reproducibly create structure at the micron scale and the lecture will describe some of these developments.

INTRODUCTION

Part of the future of chemical physics is to understand and control the ways in which intermolecular forces give rise to the diversity of structure and dynamics in biological systems. Mimicking phenomena like biomineralisation, in particular the role of molecular templates as a basis for growing inorganic structures, and using modern synchrotron x-ray and neutron scattering shows the way to make a variety of new materials. The structures produced in this way appear on the nanometer scale, the tens of nanometer scale and the micron scale. As the objective of our work is to understand formation mechanisms and to control growth, the combined use of equilibrium thermodynamic properties and kinetic paths to metastable states is of interest.

MOLECULAR TEMPLATES

In nature, molecular or macromolecular templates such as poly l serine have been invoked as the structure directing agents in the organisation of silica to form the beautiful structures observed in diatoms^{1,2} and proteins made by molluscs appear to give rise to the colourful composite "nacre" of shells³. The calcium carbonate here is of almost single crystal quality interspersed with organic matter⁴. An example for the laboratory is the formation of the zeolite, Silicalite or ZSM-5 directed by the tetra n-propyl ammonium ion as template. We have found that the influence of this ion is great, even at the earliest stages of hydrothermal synthesis at room temperature both in the gel phase⁵ and from clear preparations^{6,7}. Homogeneous nucleation around the template ion can thus be followed from the scale of about two nanometres to microns⁷. Figure 1 shows the *in situ* x-ray small angle scattering from a clear solution synthesis mixture as a function of time of heating at 100C.

LIQUID CRYSTAL TEMPLATES - THE TENS OF NANOMETER SCALE

The production⁸ of mesoporous materials with internal structures in the tens of nanometer scale using surfactant liquid crystal mesophases as templates for silicate growth was a major step upward in the scale of structures that could be induced by templates. That the chemistry and structure^{9,10,11} may be optimised by improvements to the synthetic conditions^{12,13} continues to suggest new means of control the structure directing process by modifying the surfactancy, the direction of surfactant phase transitions and by imposing external constraints.

By constraining growth to a surface - the air liquid interface, highly crystalline one and two dimensional structures may be studied^{14,15}. The structural problem is greatly simplified and mesoporous films with considerable potential practical application are produced. The kinetics of this form of growth are admirably studied by the new methods of x-ray and neutron reflectivity.

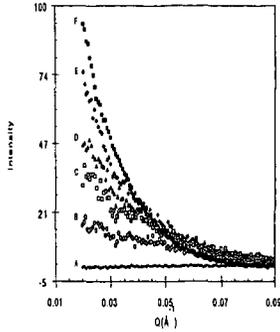


Figure 1. Small angle x-ray scattering patterns of the silicite solution after heating times of A) 0 min, B) 30 min, C) 60 min, D) 120 min, E) 360 min and F) 840 min.

Films may be grown^{14,16,17} by slowly hydrolysing tetra ethoxy silane in the presence of an aqueous surfactant solution at about ten times the critical micellar concentration. The kinetics show a prolonged induction phase where there is no visible film growth for five to ten hours and then a fairly rapid growth of film to thicknesses of about a few microns. Changing the conditions allows thicker or thinner films to be made. X-ray and neutron reflectivity methods allow these processes to be followed in real time and the subsurface structures to be worked out at each stage. In these methods¹⁸ the intensity of specularly reflected x-rays or neutrons is analysed for reflection angles above the critical angle for external reflection.

Figure 2 shows the x-ray specular reflectivity from the air-water interface at which a templated silica film is growing. In the "induction phase" (a,b) the reflectivity is clearly modified from that of water or a surfactant solution of the same strength as that of the cetyl trimethyl ammonium bromide used for the preparation. The bump in the reflectivity shows that there is a surface excess and treatment of the data indicates that this "embryo film" is about 27Å thick. Its growth up to the point where a film can be seen has been followed^{14,15}. The data contain a strongly falling (Q_z^{-4}) Fresnel component which may be removed by multiplying by Q^4 to show the Kiessig fringe - the form factor - of this surface layer. At longer times of reaction (b,c) a clear Bragg peak emerges showing that a highly ordered film structure has been created at the interface.

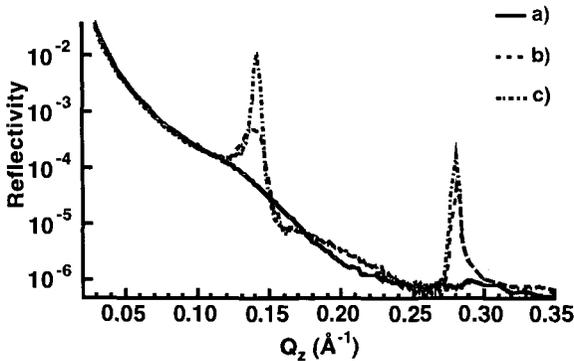


Figure 2. X-ray reflectivity from the air-water interface during the induction period showing the development of the reflectivity profile over time into diffraction peaks. a) 530 minutes, b) 608 minutes, and c) 687 minutes. The quality of the fits is shown.

Using neutron reflectivity and choosing deuterated and non deuterated surfactant against heavy water and air contrast matched water the contrast between the surfactant part and the silicate part of the film layer structure can be systematically varied¹⁵. In combination with the x-ray reflectivity results a complete picture of the development in one dimension, emerges. Figure 3 shows the Fresnel corrected reflectivity functions for several contrasts (left hand side) and the appropriately transformed real space densities at and below the growing surface at various times.

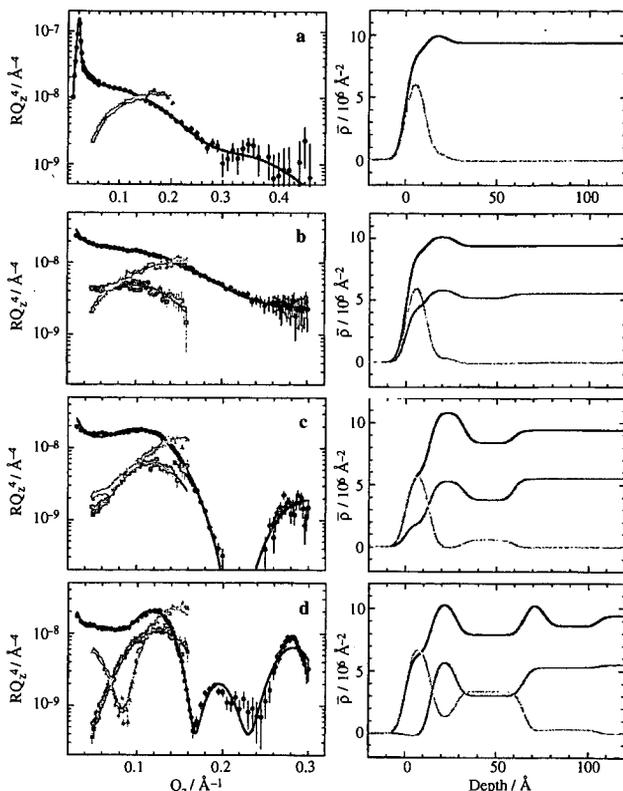


Figure 3. Fresnel corrected reflectivity profiles for both x-rays (black), deuterated surfactant on air contrast matched water (orange), and protonated surfactant on D_2O (blue) with the corresponding real space profiles for a growing silicate film at the air - water interface.

The real space model emerging from these data is of silicated, hexagonally arranged micelles lying parallel to the air-water interface as shown in Figure 4. Another aspect for the future comes from our recent work using x-ray and neutron reflectometry to study the induction phase for film growth and the origin of the hexagonally packed tubular micelle at apparently much lower concentrations of surfactant than would be expected for this phase in the pure surfactant. It now looks as though an anion induced phase transition from a glassy or cubic phase to the hexagonal occurs and that this may be controlled by chemical means¹⁹. A similar phenomenon has been observed by Aksay et al for calcium carbonate films templated by a porphyrin based surfactant²⁰.

MICRON SCALE STRUCTURES AND THE FUTURE

In experiments to improve our understanding of the chemistry behind the growth of three dimensional MCM-41 structures from cetyl trimethyl ammonium templated gels some remarkable structures on the micron scale were observed by transmission electron microscopy²¹ on the underside of the growing films. One of these is shown in Figure 5. Rod like, disc like and worm like structures were also recorded, some resembling the tactoids observed by Bernal and Fankuchen²² in tobacco mosaic virus solutions at concentrations above ca 1.5wt%. We and others^{17, 23} have recorded them frequently in film preparations such as those described above.

We suppose that such structures (particularly the worm-like structures) might be common in surfactant systems but are observable to us because that are "fossilised" by the silicate component and so are durable enough to see in the electron microscope. Clearly there is another length scale operating to form these structures. For example, inside the tactoids one can clearly see the ca 40Å diameter threads of the templated, silicated cylindrical micelles whose scale is determined by the surfactant size and silica coating. The balance of the surface and bulk energy created by such adhesion of tubules to form a tactoid bundle may provide the length scale determining the bundle size. That such structures might also be designed poses one of the fascinating future possibilities for the work described in this lecture.

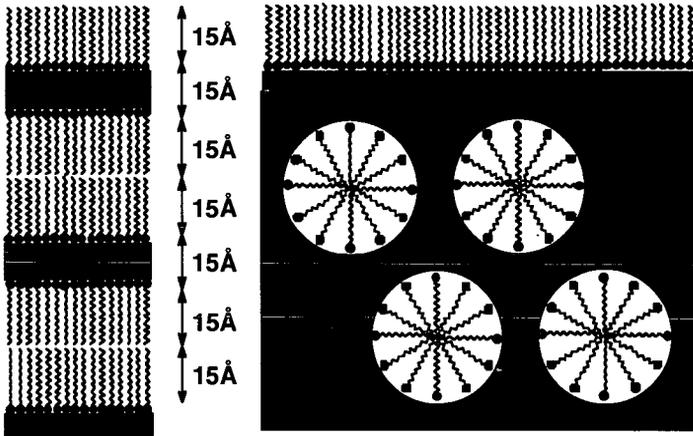


Figure 4. Model of the one dimensional structure at the air-water interface of a growing silicate film templated at 25°C by a cetyltrimethyl ammonium template.



Figure 5. Micron scale structure observed on the growing side of a silicate film templated by cetyl trimethyl ammonium bromide.

REFERENCES

1. R.E. Hecky *et al.*, *Marine Biology*, **19**, 326-330, (1973).
2. Chia-Wei Li and B.E. Volcani, *Protoplasma*, **124**, 10-29, (1985).
3. B.L. Smith, *Chemistry and Industry*, 17 August, 649-653 (1998).
4. X. Shen, A.M. Belcher, P.K. Hansma, G.D. Stucky and D.E. Morse, *J. Biol., Chem.*, **272**, 32472-32481, (1997).
5. T.O. Brun, J.E. Epperson, S.J. Henderson, L.E. Iton, F. Trow and J.W. White *Langmuir*, **8**, 1045-1048, (1992).
6. J.N. Watson and J.W. White, *Chemical Communications*, 2767-2768, (1996).
7. J.N. Watson, L.E. Iton, R.I. Keir, J.C. Thomas, T.L. Dowling and J.W. White *Journal of Physical Chemistry B*, **101**(48), 10094-10104, (1997).
8. Beck, J. S., Vartuli, J. C., Roth, W. J., Leonowicz, M. E., Kresge, C. T., Schmitt, K. D., Chu, C. T.-W., Olson, D. H., Sheppard, E. W., McCullen, S. B.; Higgins, J. B. and Schlenker, J. L., *J. Am. Chem. Soc.*, **114**, 10834, (1992).
9. G.D. Stucky, A. Monnier, F. Schüth, Q. Huo, D. Margolese, D. Kumar, M. Krishnamurthy, P. Petroff, A. Firouzi, M. Janicke and B.F. Chmelka, *Mol. Cryst. Liq. Cryst.*, **240**, 187, (1994).
10. K.J. Edler and J.W. White, *J. Chem. Soc., Chem. Commun.*, 155-156 (1995).
11. D. Cookson, K.J. Edler, P.A. Reynolds and J.W. White, *Journal of the Chemical Society, Faraday Transactions*, **93**, 199-202 (1997).
12. R. Ryoo, and J.M. Kim, *J. Chem. Soc., Chem. Commun.*, **711** (1995).
13. K.J. Edler, P.A. Reynolds, D. Cookson and J.W. White, *Chemistry of Materials*, **9**, 1226-1233, (1997).
14. A.S. Brown, S.A. Holt, Thien Dam, M. Trau and J.W. White, *Langmuir*, **13**(24), 6363-6365, (1997).
15. A.S. Brown, S.A. Holt, P.A. Reynolds, J. Penfold and J.W. White, *Langmuir*, **14** (19), 5532-5538, (1998).
16. I.A. Aksay, M. Trau, S. Manne, I. Honma, N. Yao, L. Zhou, P. Fenter, P.M. Eisenberger, S.M. Gruner, *Science*, **273**, 892 (1996).
17. H. Yang, N. Coombs, G.A. Ozin, *Journal of Materials Chemistry*, **8**, 1205 (1998).
18. J. Penfold, R.M. Richardson, A. Zarbakhsh, J.R.P. Webster, D.G. Bucknall, A.R. Rennie, R.A.L. Jones, T. Cosgrove, R.K. Thomas, J.S. Higgins, P.D.I. Fletcher, E. Dickinson, S.J. Roser, I.A. McLure, A.R. Hillman, R.W. Richards, E.J. Staples, A.N. Burgess, E.A. Simister and J.W. White, *J. Chem. Soc., Faraday Trans.*, **93**(22), 3899-3917, (1997).
19. J.L. Ruggles*, S.A. Holt, P.A. Reynolds and J.W. White. Submitted to *Langmuir*, (1999).
20. G. Xu, N. Yao, I.A. Aksay and J.T. Groves, *J. Amer. Chem. Soc.*, **120**, 11977-11985, (1998).
21. K.J. Edler, J. Dougherty, R. Durand, L. Iton, G. Kirton, G. Lockhart, Z. Wang, R. Withers and J.W. White, *Colloids and Surfaces*, **102**, 213-230 (1995).
22. J.D. Bernal and I. Fankuchen, *J. Gen., Physiol.*, **25**, 111, (1941).
23. M. Trau, Private Communication (1998).