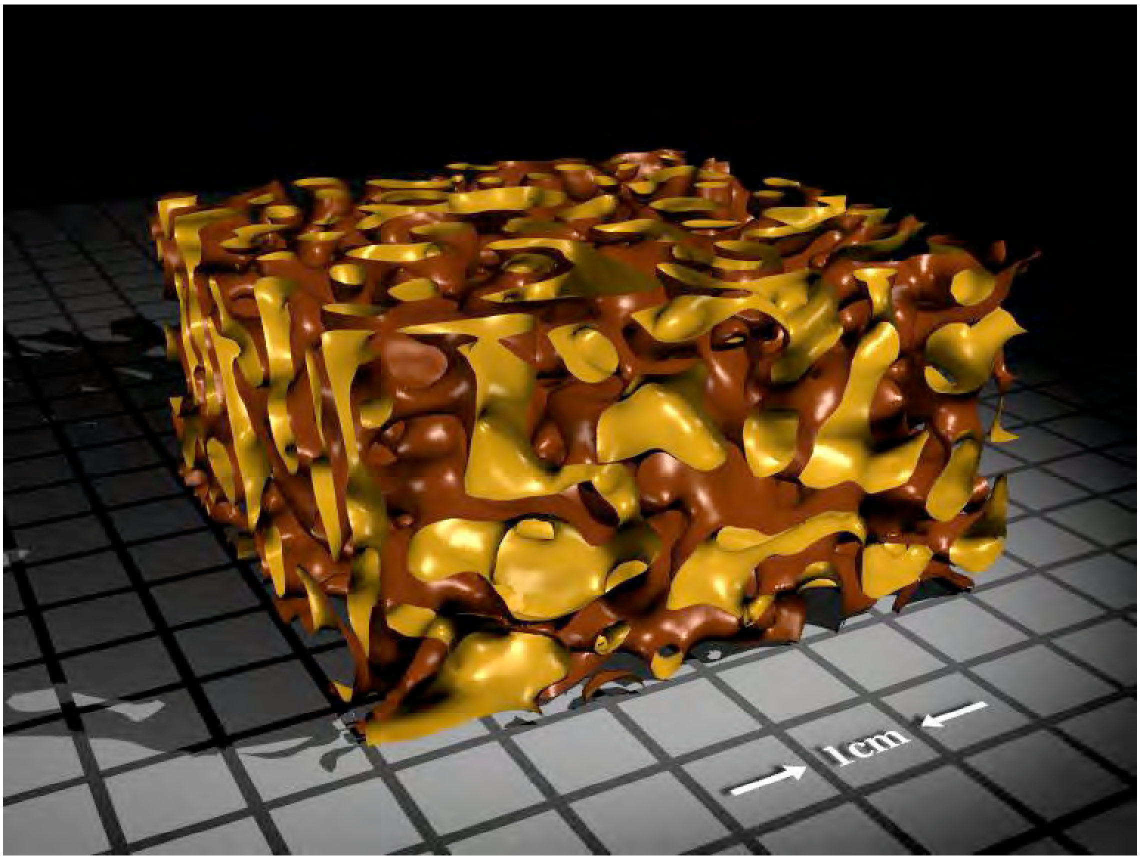
Artificial biomineralisation and metallic soaps



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A thesis submitted for the degree of Doctor of Philosophy of the
Australian National University

Applied Mathematics Department
March 1998

Cover image: X-ray tomograph of a hyperbolic interface within a termite nest
(produced with assistance from Tim Senden and Stuart Ramsden)

The bulk of the work reported in this thesis was carried out by myself.

Contributions were made by:

Stephen Hyde who co-authored the paper reproduced in Appendix 4.1;

David Hockless who co-authored the paper reproduced in Appendix 3.3. David was responsible for determining the positions of the atoms reported for this structure;

Barry Ninham who co-authored the paper reproduced in Appendix 8.4;

Rena Chao who performed all of the microanalysis of soaps and derivatives reported herein;

Peta Simmons who performed the nuclear magnetic resonance measurements upon lanthanide soaps;

Viveka Alfredsson who imaged many of the template products described in Appendix 8.2 using TEM.

Marilyn Karaman who synthesised many of the surfactants used in experiments described in Chapter 8;

David Llewellyn who I worked cooperatively with to obtain the TEM image in Figure 8.18;

John Martin who performed the measurements reported in Appendix 3.4;

Tanya Huang who performed all surface area analyses reported here;

Richard Bramley who measured the EPR spectra reported in Section 2.3.9.

Robert Corkery

March 1998

Acknowledgments

Stephen Hyde has endured the long haul of my learning process and spent many hours and much energy directing and suggesting ways ahead when none looked possible. Vittorio Luzzati' suggested that I work on the metallic soaps in the first place, so I thankyou Vittorio. Barry Ninham, who runs a vibrant and cross-disciplined department, has encouraged me to follow many paths that were not initially fruitful but turned out to be so. Many other people have contributed to this thesis indirectly. Sally Stowe and David Llewellyn from the Electron Microscope Unit helped me to learn the art of electron microscopy, and put up with many silly questions over several years. Tim Munson from the Geology Department museum has supplied many minerals for experimentation. Thanks also must go out to the fellow Applied Maths inhabitants, particularly Fiona Meldrum, Tim Senden, Mark Knackstedt, Stjepan Marcelja and Nick Wellham from EME who edited final drafts of this thesis at short notice. The technical task of making this thesis a document was made far easier by Tony Puclin's assistance. Tony you were a top office mate, and a great help with keeping my computer alive.

I have enjoyed great friendship and support from Tim Munson, Chris Wilkinson, Deb Scott and Michael Wingate during this PhD. Thanks for the tennis, the talks of things astronomical, the pool games, and all the other good times that rescued me from academic saturation, and from even worse misadventures. Des Patterson has also been one to suggest and enjoy extracurricular alternatives to tapping on a computer or mixing up chemicals, like driving to Las Vegas in a convertible during mid-winter. Paul Ferguson, Jim Luders and Ben Nicolson have also made great contributions to out of hours experiences. Dave John Brown has been there for many a deep discussion of cosmology and Rachmaninov, often involving red wine, a VB or a homebrew.

Many other people have helped in small and big ways, and I am grateful to you.

Thanks too to Kevin and Kate, my parents who have been waiting a long time for this thesis.

Abstract

In this thesis, geometry is used as a basis for conducting experiments aimed at growing and arranging inorganic minerals on curved interfaces. Mineralisation is directed using crystalline and liquid-crystalline metallic soaps and surfactant/water systems as templates.

A review of the history, syntheses, structure and liquid crystallinity of metallic soaps and other amphiphiles is presented as a foundation to understanding the interfacial architectures in mesostructured template systems in general.

In this study, a range of metallic soaps of varying chain length and cation type are synthesised and characterised to find potentially useful templates for mineral growth. These include alkaline-earth, transition metal, heavy metal and lanthanide soaps. These are systematically characterised using a variety of analytical techniques, including chemical analyses, x-ray diffraction (XRD) infrared spectroscopy (IR) and differential scanning calorimetry (DSC). Their molecular and crystal structures are studied using transmission electron microscopy (TEM), cryo-TEM, electron diffraction (ED), electron paramagnetic spin resonance (EPR), absorption spectroscopy (UV-VIS), high resolution laser spectroscopy, atomic force microscopy (AFM), nuclear magnetic resonance spectroscopy, scanning electron microscopy (SEM), electron dispersive x-ray analysis (EDXA), thermal gravimetric analysis (TGA) and magnetic measurements. Models for the molecular and crystal structures of metallic soaps are proposed. The soaps are predominantly lamellar crystalline or liquid crystalline lamellar rotor phases with tilted and/or untilted molecular constituents. These display evidence of varying degrees of headgroup organisation, including superstructuring and polymerisation. A single crystal structure is presented for a complex of pyridine with cobalt soap. Simple models for their structure are discussed in terms of their swelling properties in water and oils. Experiments are also presented to demonstrate the sorbent properties of aluminium soaps on oil spills.

The thermotropic liquid crystallinity of alkaline earth, transition metal, heavy metal and lanthanide soaps is investigated in detail. This is done to assess their suitability as templates, and to document their novel thermotropic behaviour, particularly the relatively unknown lanthanide soaps. Liquid crystalline behaviours are studied using high-temperature XRD (HTXRD), hot-stage optical microscopy and DSC. Models for a liquid crystalline phase progression from crystals to anisotropic liquids are discussed in terms of theories of self-assembly and interfacial curvature. The terminology required for this is drawn from various nomenclature systems for amphiphilic crystals and liquid crystals. General agreement with previous studies is reported for known soaps, while liquid crystallinity is demonstrated in the lanthanide and some non-lanthanide soaps for the first time. A general phase progression of crystalline lamellar through liquid crystalline lamellar to non-lamellar liquid crystalline is discussed in terms of models concerned with the molecular and crystal structures of the soaps and their phase transitions via headgroup and chain re-arrangements.

Experiments aimed at guiding growth of metal sulfides using metallic soaps as templates are described, and a model for this growth is discussed. Metal sulfides have been successfully grown by reacting crystalline and liquid crystalline transition metal and heavy metal soaps with H_2S gas at room temperature and at elevated temperature. These have been characterised using XRD, TEM, ED and IR. Sulfide growth is demonstrated to be restricted and guided by the reacting soap template architecture. Zinc, cadmium, indium and lead soaps formed confined nanoparticles within the matrix of their reacting soap template. In contrast, curved and flat sheet-like structures, some resembling sponges were found in the products of sulfided iron, cobalt, nickel, copper, tin and bismuth soaps. A model to explain this behaviour is developed in terms of the crystal and liquid crystal structures of the soaps and the crystal structures of the metal sulfide particles.

Liquid crystalline iron soaps have been subjected to controlled thermal degradation yielding magnetic iron oxide nanoparticles. Some XRD and TEM evidence has been found for formation of magnetic mesostructures in heat-treated iron soaps. Models for the molecular and liquid crystalline structure of iron soaps, their thermotropic phase progression and eventual conversion to these magnetic products are discussed.

Systematic syntheses of mesoporous silicates from sheeted clays are discussed. The templates that have been used are cationic surfactants and small, organic molecular salts. Experiments are reported where a cooperative self-assembly of surfactant/water/kanemite plus or minus salt and oils yields 'folded sheet materials' (FSM'S). Templating of kanemite has also been achieved using cobalt cage surfactants. A theoretical prediction of the specific surface areas and specific volumes of homologous sets of FSM's gave excellent agreement with measured values. The geometry and topology of the mesostructures are discussed. A theoretical model is also discussed regarding the curvature found in the sheets of natural clays , and results of templating clays and silica using metallic soaps are presented. Experiments and a model for low temperature nucleation and growth of microporous silicalite-1 are described in terms of silica templating by water clathrates.

Finally, the problem of finding minimal surface descriptions of crystal networks is addressed. Combinatoric methods are used to disprove the existence of possible embeddings of type I and II clathrate networks in non-self intersecting periodic minimal surfaces. The crystal network of the clathrate silicate, melanophlogite is successfully embedded in the WI-10 self-intersecting surface. Details of a previously unreported, genus-25 periodic surface with symmetry $Im\underline{3}m$ are discussed.

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