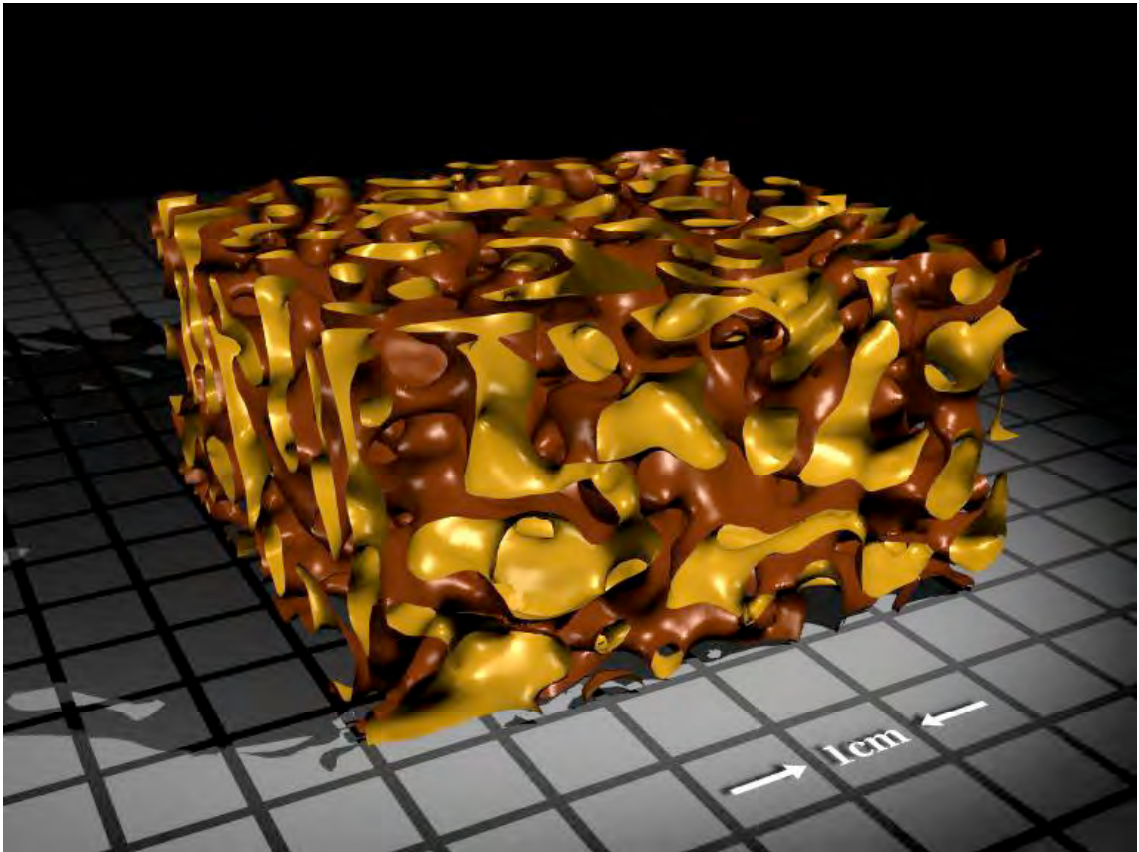


Artificial biomineralisation and metallic soaps



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*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;

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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 H₂S 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 $Im\bar{3}m$ are discussed.

Table of Contents

Chapter 1	
Introduction	1
1.1 Introduction to metallic soaps.....	3
Appendix 1.1 A history of metallic soaps	7
Chapter 2	
Syntheses of metallic soaps	25
2.1 Overview.....	25
2.1.1 Contemporary uses of metallic soaps	25
2.1.2 General synthesis	26
2.2 The double decomposition method.....	26
2.2.1 Metal solutions.....	26
2.2.2 Alkali soap "solutions"	27
2.2.3 Precipitation of metallic soaps.....	28
2.2.4 Washing, drying and recrystallisation	29
2.3 Characterisation	30
2.3.1 X-ray diffraction (XRD).....	30
2.3.2 High-T X-ray diffraction (HT-XRD).....	31
2.3.3 Transmission electron microscopy and electron diffraction (TEM & TED)	31
2.3.4 Infrared spectroscopy (IR).....	31
2.3.5 Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).....	31
2.3.6 Microanalysis.....	32
2.3.7 Small angle x-ray scattering (SAXS) and High-T SAXS (HT-SAXS).....	33
2.3.8 Optical microscopy and hot stage microscopy	33
2.3.9 Electron paramagnetic spin resonance (EPR).....	33
2.3.10 Ultra-violet/visible absorption spectroscopy (UV-VIS).....	33
2.3.11 Atomic force microscopy (AFM).....	34
2.3.12 Nuclear magnetic resonance spectroscopy (NMR)	34
2.3.13 Scanning electron microscopy (SEM), field emission SEM (FESEM).....	34
2.3.14 Surface area analysis (BET)	34
2.4 General checks of purity	35
2.5 Data tables	37
Appendix 2.1 Syntheses of alkaline earth soaps.....	45
Appendix 2.2 Syntheses of transition metal soaps	49
Appendix 2.3 Syntheses of soaps of the p-group elements	59
Appendix 2.4 Syntheses of lanthanide or rare-earth soaps.....	66
Appendix 2.5 Syntheses of soap complexes with pyridine	80
Chapter 3	
Structural aspects of metallic soaps - particularly the lanthanide soap series of lamellar compounds	85
3.1 Introduction.....	85
3.1.1 Basic structure of metallic soaps	85
3.1.2 Self-assembly of soaps	86
3.1.3 Polymorphism and the nomenclature of lamellar phases	87
3.2 Molecular structure.....	90
3.2.1 Carboxylate groups and metal centres.....	90
3.2.2 Hydrocarbon chains.....	93
3.3.1 Long spacings	97

Chapter 3

Structural aspects of metallic soaps - particularly the lanthanide soap series of lamellar compounds cont.

3.4 Soap short spacings and two main chain-packing modes - crystalline and smectic rotor phases.....	107
3.4.1 Crystalline chain-packing peaks.....	107
3.4.2 Rotor phases.....	108
3.4.3 Headgroup superstructures.....	108
3.5 Conclusions.....	110
Appendix 3.1 IR data.....	113
Appendix 3.2 Transition metal soap complexes with pyridine.....	118
Appendix 3.3 A water-bridged dinuclear complex of cobalt(II), pyridine and stearic acid.....	123
Appendix 3.4 Laser spectroscopy of samples of lanthanum laurate doped with europium laurate and pure europium laurate.....	127

Chapter 4

Applications of the properties and structure of soaps..... 133

4.1 The splayed-conformation in soaps, lipids and analogues.....	133
Appendix 4.1 On the swelling of amphiphiles in water.....	137
Appendix 4.2 Langmuir-Blodgett (L-B) multilayer films.....	139
Appendix 4.3 Aluminium soaps and their use in laboratory scale oil-spill cleanup experiments.....	143

Chapter 5

Liquid crystal aspects of precipitated metallic soaps - thermotropic mesomorphism..... 155

5.1 Thermotropic phases.....	155
5.2 Alkaline earths.....	168
5.2.1 Magnesium soaps.....	168
5.2.2 Calcium soaps.....	169
5.2.3 Strontium soaps.....	171
5.2.4 Barium myristate.....	177
5.3 Transition metal soaps.....	181
5.3.1 Iron soaps.....	181
5.3.2 Cobalt soaps.....	184
5.3.3 Nickel soaps.....	187
5.3.4 Copper soaps.....	188
5.3.5 Zirconium soap.....	191
5.3.6 Rhodium stearate.....	191
5.3.7 Silver myristate.....	192
5.3.8 Cadmium myristate.....	194
5.4 Soaps of p-group metals.....	196
5.4.1 Aluminium soaps.....	196
5.4.2 Indium myristate.....	200
5.4.3 Thallium stearate.....	201
5.4.4 Lead myristate.....	203
5.5 Lanthanides.....	207
5.5.1 Thermal history and the general phase sequence.....	211
5.5.2 Crystalline lamellar to disordered crystalline rotor phase.....	212
5.5.3 Disordered crystalline rotor phase to disordered (molten) rotor phase.....	212
5.5.4 Transition from disordered rotor phase to tilted, molten chain lamellar phase (SmB-SmC).....	216
5.5.5 Smectic C to Smectic C' transition.....	218
5.5.6 Liquid crystalline to melt phase transitions.....	221
5.5.7 Cooling behaviour.....	226
5.5.8 Decomposition of lanthanide soaps.....	229
5.6 Conclusions.....	232

Chapter 6

Derivatives of metallic soaps:

synthesis of metal sulphides and oxides.....	235
6.1 Templating with soaps - semiconductors	235
6.2 Introduction to soaps and their reaction with H ₂ S.....	237
6.2.1 Aspects of the molecular and crystal structures of soaps, and their characteristic XRD and IR signatures	237
6.2.2 Sulfides and L-B Films.....	238
6.2.3 Monolayer formation of sulfides in soaps and L-B films.....	238
6.2.4 Model for monolayer growth.....	238
6.3 Experimental.....	239
6.3.1 Reaction of the soaps with H ₂ S gas.....	239
6.4 Results.....	241
6.4.1 Iron soap - H ₂ S	244
6.4.2 Cobalt soap - H ₂ S	245
6.4.3 Cubic Nickel oleate - H ₂ S	249
6.4.4 Copper soap - H ₂ S	254
6.4.5 Zinc soap - H ₂ S	258
6.4.6 Silver Soap - H ₂ S.....	260
6.4.7 Cadmium soap - H ₂ S	261
6.4.8 Indium soap - H ₂ S	263
6.4.9 Tin soap - H ₂ S	264
6.4.10 Lead-soap - H ₂ S	272
6.4.11 Bismuth soap - H ₂ S	273
6.5 A diffusion model for growth of layered semi-conductors in soap.....	275
6.6 Conclusions.....	279
Appendix 6.1 X-ray and electron diffraction results	280

Chapter 7

Basic iron soaps:

their structure and conversion to ultra-small magnetic particles.....	285
7.1 Introduction.....	285
7.1.1 Iron soap structures - monomeric and dimeric species.....	286
7.1.2 Iron soap structures - trimeric species	286
7.1.3 Nano-structured metal oxide formation.....	289
7.2 Experimental.....	289
7.2.1 Syntheses of iron soaps.....	289
7.2.2 Syntheses of iron oxide nanoparticles	289
7.3 Results.....	290
7.3.1 Chemical analyses	290
7.3.2 XRD results	291
7.3.3 Thermal analyses	294
7.3.4 IR spectra.....	296
7.3.5 TEM and electron diffraction	298
7.4 Discussion of results.....	301
7.4.1 Soap syntheses and products - molecular structures.....	301
7.4.2 Impurities in Femy1-5	302
7.5 Simple models for the crystalline unit cell of trimeric iron soaps.....	303
7.5.1 The fully polymerised headgroup model.....	303
7.5.2 What was assumed in the building of the FPHG model?.....	305
7.5.3 Construction of alternative crystal structure models	306

Chapter 7

Basic iron soaps:

their structure and conversion to ultra-small magnetic particles cont.

7.6 Reproduction of observations by models.....	309
7.6.1 XRD long spacing	309
7.6.2 XRD short spacing, area per hydrocarbon chain, and the liquid crystalline rotor phase	309
7.6.3 Ash weights	310
7.6.4 Nature of the trimeric cores.....	310
7.6.5 Infrared spectra.....	311
7.6.6 Electron diffraction and the model structure.....	312
7.6.7 Disorder in the model of the room temperature soaps	313
7.6.8 Thermal behaviour below the decomposition temperature	313
7.7 Decomposition of soaps	314
7.7.1 General decomposition of iron soaps	314
7.7.2 Heat treatment and conversion to maghemite	315
7.8 Conclusions	318

Chapter 8

Synthesis of mesoporous silicates from kanemite:

aspects of curvature in folded sheet materials (FSM's).....	319
8.1 Introduction	319
8.1.1 Scope of this chapter	319
8.1.2 What are FSM's?	320
8.1.3 What is understood about the structure of kanemite?	321
8.2 Experimental	322
8.2.1 Materials and methods.....	322
8.2.2 General synthesis of kanemite.....	322
8.2.3 Kanemite synthesis for this study.....	323
8.2.4 Magadiite and single-chained quaternary ammonium surfactants.....	325
8.2.5 Result of templating magadiite.....	326
8.3 Templating kanemite - syntheses of FSM's.....	327
8.3.1 Syntheses of FSM and related materials here	327
8.4 Characterisation of reaction products.....	330
8.4.1 General characterisation	330
8.5 Results	330
8.6 Discussion	334
8.6.1 Making sense of the large number of results - lamellar and hexagonal phases.....	334
8.6.2 Double-chain quaternary ammonium surfactants yielding mainly lamellar structures	334
8.6.3 Single-chain surfactants yielding non-lamellar structures	336
8.6.4 Single-chain surfactants with large headgroups yielding non-lamellar structures	343
8.6.5 Single-chain surfactants yielding lamellar structures.....	343
8.6.6 Short-chain analogues of the longer chain surfactants - their intercalation into kanemite.....	347
8.6.7 Cobalt cage surfactants and their exchange with Na in kanemite	348
8.7 Post-synthesis experiments	350
8.7.1 Swelling.....	350
8.7.2 High temperature XRD	351
8.7.3 Hydrothermal or metamorphic optimisation of FSM synthesis	353
8.8 The intrinsic geometry of mesostructured FSM's - swelling laws	355

Chapter 8

Synthesis of mesoporous silicates from kanemite:

aspects of curvature in folded sheet materials (FSM's) cont.

8.9 Conclusions.....	358
Appendix 8.1 Differential geometry for theoretical plots of surface area and pore volume	359
Appendix 8.2 Swelling of talc and pyrophyllite with liquid crystalline metallic soaps.....	360
Appendix 8.3 -Templating various types of silica with metallic soaps	370
Appendix 8.4 Low temperature synthesis and characterisation of a stable colloidal TPA-silicalite-1 suspension.....	371

Chapter 9

Melanophlogite - a study of surface embeddings for clathrate networks379

9.1 Introduction.....	379
9.1.1 König's theorem for embedding networks in surfaces.....	379
9.2 Proof that Type-I & -II clathrate networks do not tessellate intersection free, triply periodic hyperbolic surfaces	379
9.2.1 Introduction.....	379
9.2.2 Background.....	380
9.2.3 Overview of the MEP structure	380
9.2.4 Combinatoric proof of self-intersection of the triply periodic hyperbolic surface tessellated by the MEP network (type-I clathrate structure)	381
9.2.5 Combinatoric proof of self-intersection of the triply periodic hyperbolic surface tessellated by the type-II clathrate structure	383
9.3 A self-intersecting, triply periodic hyperbolic surface into which the MEP net can be embedded	384
9.3.1 The WI-10 surface and the MEP network.....	384
9.4 Generation of a genus-25 triply periodic surface	387
9.4.1 Introduction.....	387
9.4.2 Asymmetric units, unique atoms, Bashkirov stereohedra and Flächenstück	387
9.4.3 The MEP asymmetric unit and unique Si atoms	388
9.4.4 Generating fundamental circuits within the $Pm\bar{3}n$ asymmetric unit	389
9.4.5 Compliance of the fundamental circuits to the $Pm\bar{3}n$ symmetries.....	390
9.4.6 Balanced circuits.....	390
9.4.7 The short list	390
9.4.8 Generating the Flächenstück from the fundamental circuit.....	390
9.4.9 Representation of the surface using the "Surface Evolver".....	391
9.4.10 Parametrisation and trigonometric approximations of the surface.....	393
9.5 Conclusions.....	394
9.5.1 Embedding the MEP network in the WI-10 surface.....	394
9.5.2 Generation of a genus-25 surface	394
Appendix 9.1 Fundamental circuit of the WI-10 surface	395

Chapter 10

Conclusions397

References401

