Self-construction of complex forms: mimicking biological growth as a new technology for complex nano-structures.

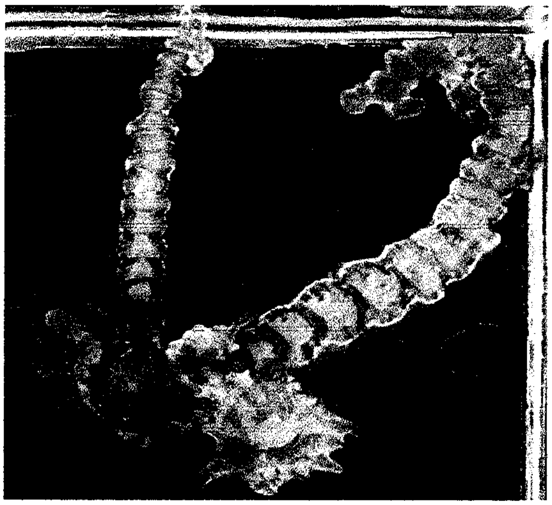
Brody Bessire

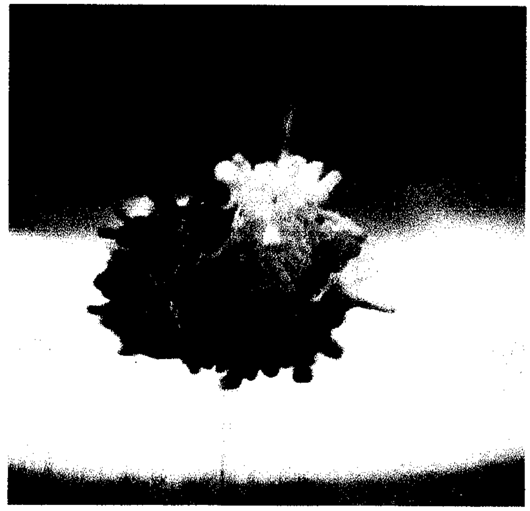
University of Alaska Anchorage

Undergraduate Research Grant

Abstract

Nature has supplied unique geological mineralization patterns that lead to structures such as chimneys that are found at hydrothermal vents in the ocean. It is supposed that these structures are created by the effects of thermal and chemical gradients that result in a radial symmetry that leads to the overall chimney structure.[1)] Another example of natural structures formed by precipitation are speleothem systems that produce the well known stalactites and stalagmites found in limestone or dolostone caves. Biological systems have also given us some insight into inorganic structures in the form of the silicate shells of diatoms and intricate seashell formations. The biological processes are extremely complex therefore hard to study, but fortunately there are systems that may allow us some insight into self-construction of these structure. (some systems are provided below). Very little is known about the mechanism and classification of these processes.[7)] It is the aim of our lab to use such inspiration from biological and geological systems to study the mechanism of self-construction of these patterns, along with their morphology and compositions that occur from varying concentrations of silicate solution with uniform aluminum pellets.





SCORPION **MONSTER I**

These are examples of some structures that have grown previously in Dr. Maselkos labs. Very little is known about the mechanism of growth of these structures.

Introduction

Crystal structures can be studied on many levels, from the basic unit crystal cell to the macroscopic wonders such as hydrothermal vents, speleothem structures and the terraces such as those found at Mammoth Hot Springs in Yellow Stone National Park. On an intermediate scale between the two extremes lie many different precipitation patterns, some of which include Liesegang rings, in which concentric rings form many layers, or snow flake formations. Snowflake fractal patterns have been studied and are the result of the curvature effect with the release of heat and diffusion as described by the Mullins-Serkerka instabilities.[2)] Liesegang rings have also been studied and have been shown to have a strong relationship with Turing instabilities.[3)] Through laboratory investigation, ice stalactites, formed from descending saline plumes under sea ice, have also been studied and have been found to fallow a simple diffuse growth law by means of double diffusion as well as solidification.[4-5)] Other models of precipitation growth have been studied recently such as the facilitated effects of a hydrothermal jet. These studies resulted in the discovery of repeatable experiments that exhibited a simple scale form within which the lengths of the precipitated tubes formed linearly with the mean jet velocity.[6)]

Studies have also been done similar to our proposition in which many of the elements where introduced into a silicate solution.[7)] The general mechanism by which chemical gardens grow starts with the dissolving of the cation salt which creates a gel around a pellet that has been introduced into the silicate solution, next water is driven past the semipermeable membrane by osmotic pressure, the salt remaining underneath the membrane is driven out which ultimately reacts with the anionic solution on the outside. Ultimately this reaction creates the tube like structures in chemical gardens. The mechanisms of these tubes are still somewhat unknown but Professor Pantaleone has been able to model this tube growth mathematically. Dr. Maselko has also studied similar systems.[9)] The resulting structures of the paper mentioned above where inspected by x-ray crystallography and scanning electron microscopes in order to understand the resulting structures composition and morphologies.

Specific Aim

It is the aim of our experiment to further progress in understanding the chemical and physical principles behind chemical reactions of the chemical garden variety. We simply want to discover if the aluminum and silicate will provide unique phenomena and we would like to discover the mechanism behind the different structures that grow from these systems. Mathematical modeling of the growth of these structures will be aided by Dr. Pantaleone of the UAA Physics/Astronomy Department. Given either unique or similar results we will add to the scientific data bank as not many individuals have studied this specific system.

If all goes well it is also a desire to present findings in the form of a poster session at the American Chemical Society national meeting, if accepted in the early fall or a meeting of similar stature in order to showcase UAA Chemistry undergraduate research.

Experimental Design

Because there is little known about these structures we propose to study this system in detail in the following manner.

1. To study the phase diagrams of these reactions and to analyze the formation of these structures and their classification, with changing parameters like silicate concentrations and pH.
2. To study in detail, the properties of these structures such as height, length, and radius that can be measured as function of system parameters.
3. Understand mechanism that controls formation of different forms.
4. Develop mathematical models for observed phenomena with the help of prof. Jim Pantaleone

To begin the experiment several pellets will be made and dropped into a gradient of solutions. We will start with 6 molar silicate and move to lower concentrations (i.e. .01 molar) to observe the related phenomena. This will be done by making pellets and submersing them in cylinders filled with an appropriate concentration of silicate. As patterns emerge from the gradient described above we will focus in on the interesting phenomena such as tube growth rates, height, diameter and shape using optical methods as well as qualitative observations. We will measure relations between these observable properties and the systems parameters. The conditions of this experiment will be basic, in the range of 11-12pH and this may have an effect on the overall structure. The pH will be monitored throughout the experiment. Finally after these relationships have been established we will be able to provide a better understanding of the actual chemical identity of the structures through X-ray crystallography and the morphology through Scanning Electron Microscopes.

Anticipated Results

Preliminary runs with the aluminum and silicate solution indicate that we will observe a large amount of branching at intermediate concentrations of silicate (2-4 molar). From this we know we will have a system to study but the particular details lay further ahead. In anticipation of different structural growth it is likely that we will be adding to a growing data base of useful knowledge on creating spontaneous self-constructing permanent structures. These structures may provide an inexpensive means of constructing tubes with a desired morphology and composition.

Project Budget

Chemicals from Sigma Aldrich and VWR

- Chemical funding is provided by an existing NSF Grant.

Hardware

- Quick Press kit with 7mm die set. International Crystal Laboratories. Item# 0012-4586 $879.00

Funding necessary to travel to present poster at national conference or similar (if accepted).

- As of 11/30/2011 Priceline quote $681 to Denver (ACS National meeting)
- Hotel Accommodations downtown Denver. $300 4 nights (hotel quote from expedia)
- Total : $1,860

Budget Justification

Dr. Maselko has also reviewed this list and finds it to be accurate from his experience. The press is necessary in order to produce repeatable pellets. The final quote for airfare is understood to be conditional upon acceptance into the American Chemical National Conference or similar meeting. Of the chemicals present in the experiment cautionary measures will take place in order to dispose of the reagents properly.

Project References

- **Note on references. In some instances the title of the paper is unknown. Some of the references are pre-existing and the original title cannot be found. These references are from pre-existing, (read) articles that provide scientific evidence of claims made in this and other papers.**

1. Corliss, J.B.; Dymond, J.; Gordon, L.I.; Edmond, J.M.; van Hergen, R. P.; Ballard, R.D.; Green, K.; William, D.; Bainbridge, ; Crane, K.; VanAndel, T.H.; Science 1979, 203,1073-1083.
2. Mullins, W; Sekerki, K.; **Morphological Stability of a Particle Growing by Difusion or Heat Flow.** J. Appl. Phys. 1963, 34, 323.
3. Ross, J; Arkin, A.; **Experimental Evidence for Turing Structures.** J. Phys Chem. 1995, 99, 10417.
4. Martin, S. Ice Stalactites: **Comparison of a Laminar Flow Theory woth Experiment**. J Fluid Mech. 1974, 63, 51-79.
5. Perovich, D.K.; Richeter-Menge, J.A.; Morison, J.H.; **The Formation and Morphology of Ice Stalactites Observed in Deforming Lead**, J. Glaciol. 1995, 41, 305-312.
6. Stone, D.A.; Lewellyn, B.; Baygents, J.C.; Goldstien, R.E; Langmuir 2005, 21, 10916-101919.
7. Juylan H.E. Cartwright, Bruno Escribo, and C. Ignacio Sainz-Diaz, **Chemical-Garden Formation, Morphology, and Composition.** Langmuir, 2011, 27, 3286-3293.

8. J. Pantaleone, A. Toth. D. Horvath, L. RoseFifura, J. Maselko, **Pressure Oscillations in Chemical Garden**, Phys. Rev. E 79056221 2009.

9. A. Baker, A. Toth, D. Horvath, J. Walkbush, A. Ali, W. Morgan, A. Kukovecz, J. Pantaleone, J. Maselko. **Precipitation Pattern Formation in the Copper(II) Oxalate System with Gravity Flow and Axial Symmetry** J. Phys. Chem. A, 2009, 113(29), 99 8243-8248.