

CHARACTERIZATION OF ELECTROCHEMICAL AND MORPHOLOGICAL PROPERTIES OF IRON-PHOSPHATE-SILICATE CHEMICAL GARDEN STRUCTURES. I. J. Doloboff¹, L. M. Barge¹, M. J. Russell¹, and I. Kanik¹. ¹Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA. 91109. (Ivria.Doloboff@jpl.nasa.gov).

Introduction: The hollow structures which form when a hydrated metal salt is introduced into a solution containing another reactive ion are called chemical gardens. A variety of morphologies, such as tubes and bulbous growths, are produced based on experimental conditions. In the following series of experiments, the metal salt $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ is introduced into solutions of sodium silicate and potassium phosphate, generating a membrane of gel precipitate around the surface of the metal salt grain. Chemical garden type precipitates exist in a variety of natural settings, and these semi-permeable membrane structures in hydrothermal systems have been proposed as a possible environment for the emergence of life [1,2]. Off-axis hydrothermal vents on the early Earth (or other wet rocky planets) containing, along with other deposits, ferrous iron sulfides precipitated from the mixing of warm, alkaline, HS^- -bearing hydrothermal fluid with the anoxic, acidic, Fe^{2+} -bearing ocean [3,1], are significant to the emergence of life because they could maintain steep pH and chemical gradients at the interface between mildly acidic ocean and alkaline hydrothermal effluent, as demonstrated in laboratory simulations [3,4,5]. The proton gradient across an inorganic membrane separating solutions of high and low pH and composition may be capable of providing a natural proton-motive force sufficient to drive prebiotic chemical reactions such as the formation of pyrophosphate and peptides in a synergistic feedback cycle [6].

Chemical garden structures grown in the laboratory may also maintain commensurate chemical and pH gradients between the inner and outer solutions. However, the self-assembling structures that form under the control of fluid dynamics and reactant concentrations may affect the gradients present in these systems. In these experiments we have examined the growth of chemical garden structures formed with Fe^{2+} , silicate, and phosphate – three important components of an early Earth prebiotic hydrothermal system – to better understand the properties of similar structures that may have formed at Hadean alkaline hydrothermal vents. [7].

Methods: Two hundred milligrams of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ crystals were introduced into 15 ml aliquots of solutions containing diluted sodium silicate and/or potassium phosphate. The alkaline silicate/phosphate solutions are composed of K_2HPO_4 salt, water, and a concentrated sodium silicate solution. When the

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ crystals settled upon the bottom of the test tube a precipitate membrane immediately formed around the crystal surface. The concentrations of both silicate and phosphate were varied in these experiments.

Additional experiments were performed in which an aqueous solution of FeCl_2 was fed slowly into the silicate/phosphate solution via a syringe. This setup allowed characterization of the effect of flow rate on morphology, and the measurement of voltage across the membranes. Membrane potentials were measured via a wire connected to a voltmeter around which the precipitate structure grew, and a second wire placed into the bulk silicate/phosphate solution. The voltage across the membrane was measured until the seed FeCl_2 was exhausted.

High resolution imaging and chemical analysis were performed on the various precipitate morphologies using an environmental scanning electron microscope (ESEM) with attached energy dispersive x-ray tube (EDX).

Results: When the $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ seed crystals were introduced into a solution containing silicate and phosphate, a layer of precipitate immediately formed around the crystal and began to expand upward.

Precipitate Morphology. Based on observations, the concentrations of silicate and phosphate strongly influence the varying precipitate morphologies. The resulting precipitates consistently fell into four general types: i) hairs (thin, fragile hair-like structures extending vertically from the crystal

(Fig. 1B)), ii) bulbs (smooth rounded bulbous structures, several mm across, that grew both vertically and in random directions (Fig. 1A)), iii) plumes (larger

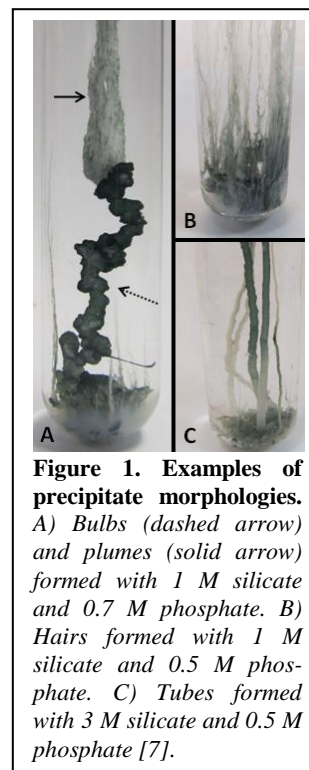


Figure 1. Examples of precipitate morphologies. A) Bulbs (dashed arrow) and plumes (solid arrow) formed with 1 M silicate and 0.7 M phosphate. B) Hairs formed with 1 M silicate and 0.5 M phosphate. C) Tubes formed with 3 M silicate and 0.5 M phosphate [7].

structures several mm across that always grew vertically (Fig. 1A)), and iv) tubes (mm-size hollow tubular structures, generally exhibiting bubble-led growth (Fig. 1C)). Examples of these are shown in Figure 1. Additionally, color changes varied with morphology. Plume precipitates were white and formation, but gradually turned dark green over several hours while bulbs rapidly transitioned from light green to dark green (possibly indicating rehydration of Fe^{+2}).

Varying Silicate Concentration. As silicate concentration increased, the precipitate morphology progressed from hairs (between 0 – 1 M silicate) to bulbs and plumes with occasional tubes (between 1 – 2 M silicate) to only tubes (3 M silicate).

Varying Phosphate Concentration. In subsequent experiments, silicate concentration was kept constant at 1 M while phosphate concentration was varied between 0.1 - 0.7 M. Below 0.3 M phosphate, only hairs were formed. Above ~0.4 M phosphate bulbs and plumes formed.

Fluid Flow Rate. To determine the influence of flow rate upon morphology, alternate experiments were performed using a FeCl_2 solution slowly fed via syringe pump into the silicate/phosphate solution. In FeCl_2 solution experiments where concentrations of 1 M silicate and 0.5 M phosphate were used, bulb growth occurred with a flow rate of 80 ml/hr while plume growth occurred when the flow rate was lowered to 50 ml/hr. However, when the silicate concentration was raised to 2 M, bulbs with attached plumes formed at both 80 and 50 ml/hr.

Visual and Compositional Analysis.

ESEM images of the hollow bulbs show that the interior of the membrane is particulate. The exterior appears smooth and amorphous. Semi-quantitative ratios

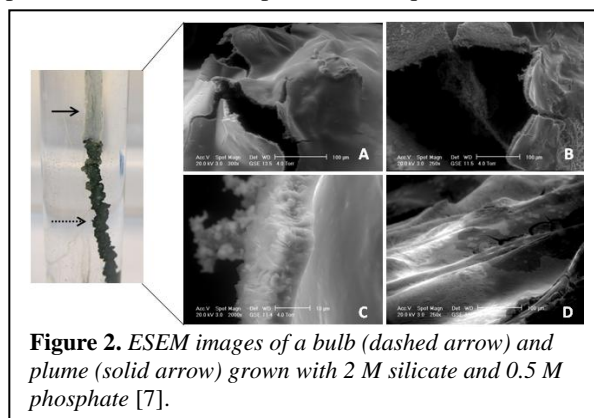


Figure 2. ESEM images of a bulb (dashed arrow) and plume (solid arrow) grown with 2 M silicate and 0.5 M phosphate [7].

were calculated from EDX spectra collected over the inner membrane of the bulb (Fig. 2C) and yielded a Fe:P:Si ratio of approximately 1:0.1:0.6. Ratios calculated for the smooth exterior layer of the bulb (Fig. 2A) yielded a Fe:P:Si ratio of approximately 1:2.9:3.6.

These ratios indicate a compositional gradient: the inner particles are relatively iron-rich and the outer membrane is silicate- and phosphate-rich.

Membrane potentials. As the precipitates grew, the attached voltmeters recorded a voltage increase in the outer solution and voltage decrease inside the membrane. The total potential across the membrane was measured with time (as the difference in exterior (VE) and interior (VI) voltage), for various silicate concentrations and injection rates of FeCl_2 of 50 or 80 ml/hr.

When exterior solutions contained 1 M silicate and 0.5 M phosphate, the voltage remained largely constant (between 150-200 mV) after the precipitates stopped growing (i.e., when growth met the liquid surface). For exterior solutions containing 2 M silicate and 0.5 M phosphate, the final potential was between 150-200 mV for a flow rate of 50 ml/hr but and only ~100 mV at a 80 ml/hr flow rate.

Conclusions: The compositional gradient of these precipitation structures revealed in ESEM and EDX analysis indicate a steep chemical gradient across the chemical garden membrane; bulbs produced the most significant chemical gradient. Electrochemical gradients were also demonstrated in experiments where voltage was measured across the chemical garden membrane. The semipermeable membrane of the chemical garden is a satisfying analog to the hydrothermal chimney membrane, whose inorganic compartments and electrochemical / pH gradients may have played a significant role in the emergence of life. Biological membranes have similar osmotic properties and similar pH and electrochemical gradients to those measured in the experiments presented here. The electrochemical gradients measured in these experiments, and the examination of varying morphologies, is significant in understanding the growth of large-scale, self-organizing membrane precipitates at off-axis alkaline hydrothermal vents and the rise of chemical complexity leading to the emergence of life.

References: [1] Russell, M. J.; Daniel, R. M.; Hall, A. J.; Sherringham, J. A. J. *Mol. Evol.* 1994, 39, 231-243. [2] Russell, M. J.; Hall, A. J. In *Geological Society of America Memoir*; Kesler, S.E.; Ohmoto, H., Eds.; 2006, 198, p. 1-32. [3] Russell, M. J.; Hall, A. J.; Turner, D. *Terra Nova* 1989, 1, p.238-241. [4] Mielke, R. E.; Russell, M. J.; Wilson, P. R.; McGlynn, S. E.; Coleman, M.; Kidd, R. D.; Kanik, I. *Astrobiology* 2010, 10, 799-810. [5] Mielke, R. E.; Robinson, K. J.; White, L. M.; McGlynn, S. E.; McEachern, K.; Bhartia, R.; Kanik, I.; Russell, M. J. *Astrobiology* 2011, in review. [6] Milner-White, E. J.; Russell, M. J. *J. Cosmol.* 2010, 10, 3217-3229. [7] Barge, L. M., Doloboff, I. J. et al. (2011) *Langmuir*, in press.