PRECIPITATION PATTERNS OF IRON MINERALS IN A CHEMICAL GRADIENT: A LABORATORY ANALOG TO HYDROTHERMAL ENVIRONMENTS ON THE EARLY EARTH. L. M. Barge, M. J. Russell, I. Kanik. Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA. 91109, USA

Introduction: Iron sulfide precipitates formed in Hadean hydrothermal systems may have been crucial to the origin of life on Earth - providing enclosed "membranes" capable of harnessing the natural proton and redox gradients formed when alkaline, H_2-rich hydrothermal fluid interfaced with acidic CO_2–bearing ocean water [1, 2]. There are two examples of submarine alkaline springs generating mounds on the ocean floor today - Lost City and Eyjafjordur [3, 4] - and such systems may have been even more prevalent on the early Earth, before the formation of extensive continental crust. The alkaline hydrothermal origin of life scenario proposes that the ambient proton motive force acting through an inorganic membrane composed of silica and iron sulfides (and other metal catalysts such as Ni, Co, Mo and W) may have generated important prebiotic products [1, 5]. One such example is the condensation of pyrophosphate from orthophosphate, which is significant since pyrophosphates/ATP are used as the energy currency of cells [5]. This origin of life hypothesis is also applicable to other worlds in the solar system, such as Europa, that may host hydrothermal activity .

Laboratory simulations of hydrothermal systems under particular early Earth conditions have generated hollow iron sulfide bubbles and chimneys similar to 350-Ma fossilized hydrothermal deposits from Tynagh and Silvermines in Ireland [6]. The morphology and mineralogy of these laboratory precipitates are dependent on experimental variables such as pH, Fe/S concentrations, presence of organic or inorganic ions, and CO_2 and silica concentrations. These hollow tubular structures comprising iron sulfide have a second level of structure as well, with various minerals/morphologies layered in the chimney wall [6].

The pH, redox, and chemical gradients at the interface of the Hadean ocean and hydrothermal alkaline solutions would have resulted in formation of an inorganic precipitate, that would have likely exhibited complex internal structure as redox and pH environments varied within the hydrothermal mound. Here we present preliminary results of precipitation experiments in silica gels, which provide a simplified environment in which to investigate the details of precipitation along redox and pH gradients. Gels create a diffusion-controlled system where reactive ions are mobile but precipitated particles are not - preserving self-organized structures that form in the diffusion gradient, and allowing for maturation of the precipitate via competitive particle growth [7, 8]. Gel precipitation experiments therefore allow larger-scale examination of chemical processes that may be occurring within an inorganic membrane precipitated in a hydrothermal system. In particular we looked at iron phosphate and pyrophosphate precipitates, and the patterns that are formed when Fe(II) precipitates with both sulfide and phosphate/pyrophosphate. These experiments are a first step in a detailed study of iron-phosphate-sulfide mineralization in pH and redox gradients applicable to a putative origin of life in alkaline low-temperature hydrothermal environments.

Methods: We performed experiments where interdiffusing ions reacted in a silica gel column to simulate the chemical reactions that may occur within the walls of a hydrothermal chimney containing iron sulfides and silica. Silica gels were formed by mixing sodium silicate solution (pH ~ 11) with acidic solutions containing mM concentrations of ferrous chloride (pH ~ 5). The gels also contained up to 0.6 M NaCl to simulate the salinity of the Hadean ocean. Various silicate and NaCl concentrations were tested to determine the optimum gelling conditions. Mixing the alkaline silicate solution and the acidic Fe(II) solution caused a gel to form in ~30 min, and after the gel solidified, a solution containing sodium sulfide, sodium orthophosphate, and/or sodium pyrophosphate (outer solution pH ranging from 9-11) was added to the top of the gel. The tubes were then purged with N_2 and sealed, and allowed to react for 5 days.

Results: Silicate solutions at ~0.7 M silicate concentration formed gels when mixed with acidic solutions. However in the presence of 0.6 M NaCl, only about 60 mM silicate was required for a gel to form, due to charge shielding by the excess Na^+ ions [9]. The outer reactants (sulfide, phosphate, and/or pyrophosphate) diffused into the gel column, precipitating with Fe(II). When Fe(II) precipitated with orthophosphate or pyrophosphate (or 50/50 mixtures of the two), reproducible periodic bands of precipitates were formed. Fe-sulfide precipitates appeared more amorphous and did not show banded patterns in most cases. When both phosphate and sulfide anions were present, banded patterns of iron-phosphates and iron-sulfides formed. As precipitates oxidized, further patterns became apparent, as iron sulfides and iron oxides stratified along the gradient. Color changes were apparent as well; for example white iron phosphate precipitates turned green as oxidation occurred (Figure 1).

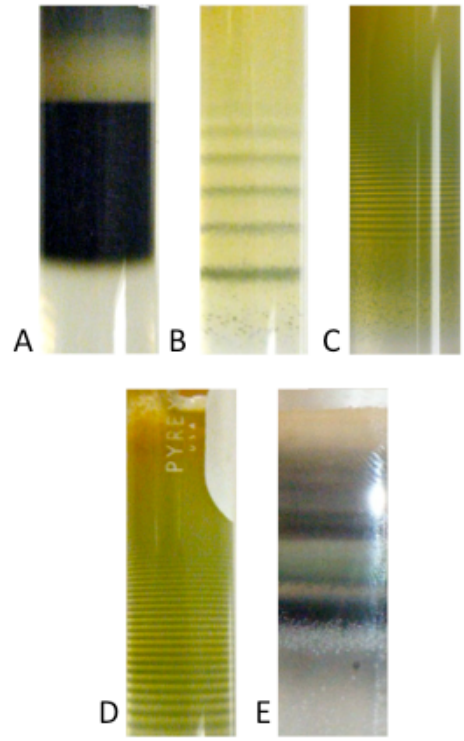

Figure 1: Iron precipitates in silica gels. A) Iron (II) sulfide, B) Iron (II) phosphate, C) Iron (II) pyrophosphate, D) Iron (II) phosphate/pyrophosphate, E) Iron(II) precipitating with sulfide and phosphate.

Conclusions: Precipitating iron sulfide and iron phosphate minerals in silica gels yields a variety of self-organized banded patterns, from Liesegang patterning of a single precipitate to stratification of various mineral types (Figure 1). The positions and thicknesses of bands are approximately reproducible, and after 5 days there appear to be alternating mineral compositions within the gel column. The simplified gel precipitation experiment reveals processes that may be affecting the morphology and composition of precipitates in a hydrothermal mound. Further experiments are needed to determine how addition of simple organic molecules and/or other entities relevant to the origin of life (e.g., Mg, Mo, W [10]) will affect the self-organized patterns produced.

Although the purpose of these silica gel experiments was to study the precipiation gradients within an inorganic membrane on a larger scale, the use of silica gel also has direct relevance to the possible origin of life in alkaline hydrothermal systems. Hydrothermal fluids on the early Earth would likely contain contain mM concentrations of dissolved silica [6] as would the Hadean ocean, and an effective titration of the former into the latter as well as a sharp drop in temperature when the ~100°C hydrothermal fluid interacts with cool ocean water would cause solutions to become supersaturated with silica [11]. Silica precipitation and polymerization would result, probably as a gel-like material that would later crystallize to chalcedony or agate. (Although our silica gels had very high concentrations of silicate compared to that expected in hydrothermal solution [6], it is conceivable that a silica precipitate could build up at the interface between hydrothermal fluid and ocean water, thus concentrating silica sufficient to form a more stable gel). Along with the catalytic effects of iron sulfide minerals and the natural proton gradient in the hydrothermal mound, the presence of silica gel, an insulating barrier to electron flow, may have played a part in driving prebiotic reactions in such systems. Moreover, polymerized silica could contribute to membrane durability since a gel could hold amorphous Fe-S precipitates or nanocrysts in place and undisturbed that might otherwise disaggregate in aqueous solution (cf. [12]). Precipitation occurring in a diffusion-controlled gel system often forms reproducible, periodic patterns [7, 13] and mineral precipitation morphologies in gels can be affected by the presence of organic molecules in predictable ways (e.g., [14]). Thus, a gel environment might have provided a stability and reproducible complexity to iron sulfide-bearing membranes interacting with organic molecules in hydrothermal systems. Silica gel also has proton conductive capabilities over a wide range of temperatures [15], and this may add to the chemiosmotic potential of the iron sulfide membrane.

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