PREBIOTIC CHEMISTRY IN CHEMICAL GARDEN STRUCTURES AT HYDROTHERMAL VENTS: THE IMPORTANCE OF GELS AND GRADIENTS.

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Introduction: Chemical garden structures, forming spontaneously at the interface of two contrasting fluids, exhibit certain charactics reminiscent of biological systems including formation of membranes transected by pH and chemical gradients [1]. Hydrothermal chimneys, a form of geological chemical garden, have many interesting properties relating to origin of life, e.g. mediating proton / electron / ion gradients across the inorganic membrane, and they adsorb and concentrate relevant components (e.g. P and organic species) in pores and on mineral surfaces. Chimneys can be simulated in the laboratory in a straightforward manner through injection chemical garden garden experiments [2] and offer a versatile system in which to test various prebiotic chemistry hypotheses. We describe several compelling features of chimneys and chemical gardens that make them an ideal environment in which to test reactions of interest to origin-of-life researchers.

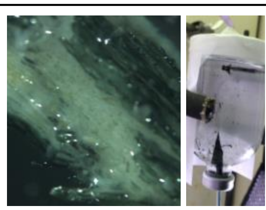

Figure 1: L – gelatinous interior of a chemical garden in an iron / silicate system; R – Formation of a simulated chimney in an injection chemical garden experiment.

1) Nonequilibrium Gradient Systems. The precipitate membrane of chemical garden has various interesting properties arising from its formation at the interface between two contrasting solutions: the inorganic membranes exhibit compositional gradients, they maintain the pH / chemical gradients between the interior and exterior yet are still somewhat porous to ions (i.e. they are semi-permeable), and the charge difference that is maintained across the membrane can be measured and harnessed as an electrical potential [3] which can drive reactions such as carbon reduction [4]. The thickness of a chemical garden wall can increase indefinitely as interior fluid flow continues; thus in a long-lived vent system the chimney membrane becomes a "flow-through reactor" across which gradients are maintained. Simultaneous gradients of pH, chemicals, redox, mineral composition, and temperature across the cross-section of the wall create a wide variety of chemical conditions for reactions within, all which are physically connected and able to exchange reactants and product. "Cycling" i.e. changing of conditions at a point in the membrane can occur through naturally changing composition of the interior solution [2], or even simply changing the flow path through the pores. The *non-equilibrium* nature of these experiments is crucial since it is the fact that the precipitate forms in a gradient that gives it these properties.

2) Gels Provide Dehydration and Concentration. Even though chemical gardens form in aqueous systems (including chimneys at a vent), the interior of the membrane between two solutions is actually a very low-water activity environment. This is due to the precipitation of inorganic gels such as silica gel [5], as well as minerals with active surfaces and interlayers such as iron sulfides and/or hydroxides. Gels not only promote dehydration / condensation reactions due to their low water activity, but they readily absorb and concentrate ionic components of interest, preventing their loss into the bulk ocean. Silica gel formation as a function of pH and salinity (also of interest to the oil industry regarding matrix acidization) is relevant to prebiotic chemistry in vents: silica gels form more quickly under acidic conditions meaning that they would be likely to precipitate on the ocean side of the chimney (as well as throughout); and increasing salinity favors silica gelation (with different oceanic salts e.g. NaCl, $MgCl_2$, having particular effects [6]). The existence of gels along with catalytic minerals in chimneys provide a reactive flow-through, system in which reactions are protected from external convection, dilution, and hydration.

Implications: Chemical garden experiments representing hydrothermal chimneys have been explored in the context of electrochemical processes, carbon fixation and organic-mineral feedbacks; and nucleotide polymerization has recently been demonstrated [7]. This environment may also provide a favorable experimental condition for reactions of amino acids, peptides, RNA, and other prebiotic components.

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