ELECTROCHEMISTRY OF INORGANIC MEMBRANES AT ALKALINE HYDROTHERMAL VENTS - ENERGY SOURCES FOR EMERGING LIFE ON WET ROCKY PLANETS.

L. M. Barge[1], I. J. Doloboff[1], I. Kanik[1], M. J. Russell[1] ([1]Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena CA 91109.)

Introduction: Electrochemical cells made with two contrasting solutions interfacing at a semi-permeable membrane can generate voltages and facilitate oxidation/reduction reactions. It has been suggested that similar processes in hydrothermal vent systems on the early Earth may have given rise to metabolism ([1], Figure 1). The prebiotic ocean (on Earth but also any terraqueous world with a CO_2 atmosphere) would have been anoxic though still mildly oxidizing, containing abundant electron acceptors as well as dissolved CO_2 (acidifying the ocean to about pH ~5.5); e.g., NO, NO_3^- and Fe^{III}. This ocean would also have held mM concentrations of dissolved Fe^{2+} and µM amounts of phosphate in solution. Serpentinization reactions in the crust would have generated alkaline hydrothermal fluid (pH ~ 11) containing dissolved H_2, HS^-, methane, formate and possibly methanol, as well as silicate, and trace amounts of Mo/W [2,3]. At off-axis hydrothermal vents this reducing, alkaline hydrothermal effluent would have titrated into the oxidizing, acidic ocean. The chemical disequilibrium resulting from gradients of pH, Eh, temeprature and composition would have led to precipitation, forming an inorganic gel of iron/silicate/phosphate/sulfide which would continue to grow into a self-assembling chemical garden type structure similar to those observed at present-day alkaline hydrothermal vents [4]. It is thought that this semi-permeable inorganic membrane containing catalytic iron sulfides, maintaining the tension between acidic/oxidizing and alkaline/reducing aqueous solutions, could have maintained enough electrochemical energy to reduce CO_2 from the ocean into formate and formaldehyde (with hydrothermal H_2 as the electron donor), and hence initiated a "proto-metabolism" analogous to the reductive acetyl co-A pathway [5], a suggestion yet to be demonstrated experimentally.

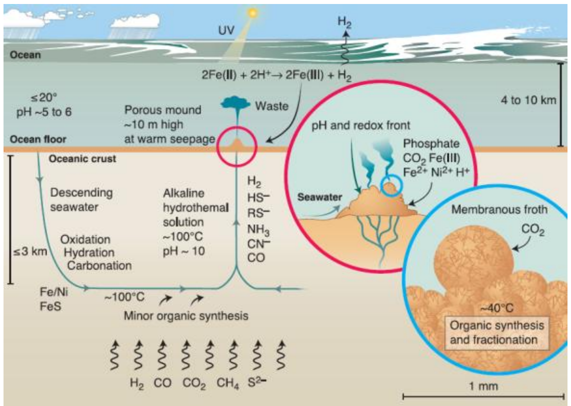

Figure 1. Alkaline hydrothermal model for the emergence of metabolism on wet rocky planets. A carbonic ocean interfaces with alkaline hydrothermal fluid (altered by serpentinization) to form precipitates of iron sulfide (+ silicates, phosphates). These precipitates can be thought of as inorganic "membranes" separating acidic, oxidizing and alkaline, reducing solutions, similar to both an electrochemical fuel cell and modern cell membranes.

Previous work in this area has shown that self-assembling iron sulfide membranes can form in simulated alkaline hydrothermal systems [3], and these membranes should generate electrical potentials [6] that might be useful for driving further reactions in the system. However the magnitude of the membrane potential generated in similar experiments with iron-silicate-phosphate was shown to vary greatly with experimental conditions [7], and little is known about the electrochemical properties of similar structures of iron sulfide. We have studied iron sulfide membranes under hydrothermal conditions relevant to the early Earth by growing Fe_xS_y films on a synthetic membrane template placed between contrasting solutions, and utilizing voltage measurements and Electrical Impedance Spectroscopy to characterize the electrochemical properties of the membrane under different experimental conditions.

Methods: An acidic, $FeCl_2$-bearing solution was separated from an alkaline, Na_2S-containing solution by a synthetic semi-permeable membrane of dialysis tubing that allows ions to diffuse through but dissallows solution mixing. Iron and sulfide concentrations were varied from 10-100 mM and all solutions contained 0.6 M NaCl to approximate ocean salinity, and the temperature was varied between 25-85°C. Platinum wires were inserted into solution on either side of the membrane to measure voltage and impedance, and the apparatus was temperature controlled in a hot bath and kept anoxic under N_2. After precipitation, the iron sulfide membranes were placed between conducting salt solutions to measure capacitance. Voltage curves were recorded with an Agilent 34972A Data Acquisition Switch Unit and BenchLink data logger software. Impedance was measured with Potentiostatic Electrochemical Impedance Spectroscopy (PEIS) and equivalent circuits were modeled using ZSimpWin EIS modeling software (Princeton Applied Research).

Figure 2: Membrane precipitate.

Results: When both solutions were added, a precipitate membrane of iron sulfides formed on the surface of the dialysis tubing (Fig. 2). Immediately upon precipitation the membrane generated electric potentials between 0.5-0.8 V depending on reactant concentration and temperature. In some cases the voltage generated was maintained for up to 1h; in some cases the voltage dropped off gradually with time. The impedance of a membrane made with solutions of 10 mM iron and sulfide at 25°C was measured as the membrane precipitated over 90 min, and while the complex impedance varied noticeably in the first 20 minutes, no further changes were observed after 40 minutes (possibly indicating reactant depletion). When membranes were rinsed with ddH_2O and placed between identical conducting solutions, voltage was generated that dropped off exponentially, demonstrating the electrical capacitance of the membrane.

Discussion: The electrical potential generated as iron sulfide membranes precipitate between contrasting solutions is likely due to the gradient in redox potential between the inner and outer membrane layers (and concurrently we expect that the membranes themselves exhibit compositional/mineralogical gradients between precipitate layers). This redox gradient is further illustrated by the fact that when the membrane was placed in identical conducting solutions, it generated an electrical potential between the solutions that fell off exponentially in the manner of a discharging capacitor. In some respects this semi-permeable inorganic membrane separating acidic/oxidizing and alkaline/reducing solutions is like an ion-exchange membrane fuel cell (Fig. 3), where an ion-selective membrane is sandwiched between two catalyst-coated electrodes (analogous to our different catalytic membrane surfaces), and the surface potentials combined with electrochemical gradients drive redox reactions in the two cells. Previous researchers have used membrane-electrolyte-based electrochemical cells to reduce CO_2 to formate by applying voltage to the catalytic electrodes [8,9]. This experimental system and the fuel cell in Fig. 3 are also broadly analogous to the alkaline hydrothermal vent system where similar membranes would have formed between acidic/oxidizing and alkaline/reducing solutions, and would have also generated electrical potential between the acidic Hadean ocean and alkaline hydrothermal fluid. In the hydrothermal system the membrane potential would be self-generated by the precipitation of iron sulfides/hydroxides between solutions of different Eh/pH, and the differing mineralogy of the inner and outer layers are analogous to catalytic electrodes with characteristic redox potentials. Our preliminary data on self-generated membrane potentials shows that enough energy may be present to drive prebiotic chemistry in these systems, and future work will seek to quantify surface potentials on the inner and outer membrane, to determine whether they are sufficient to drive CO_2 reduction and/or H_2 oxidation. The capacitance of the iron sulfide membranes at alkaline hydrothermal vents is significant as well, since iron sulfide functional groups in ferredoxin enzymes act as capacitors for biochemistry, storing and releasing electrons to metabolic reactions. Perhaps the iron sulfide-containing membranes in alkaline hydrothermal systems could have facilitated a primitive electron transport chain, possibly assisted by inter-membrane peptides, in addition to the ambient proton motive force (with protons from the carbonic acid ocean transferring down pH gradient to the alkaline interiors). The details of how electron transport proceeds in membranes produced in our simulation experiments are quite complex, and it is essential to better understand these mechanisms in order to make predictions about possible chemistry in related natural systems. Future work will aim to provide a detailed characterization of the electrical properties of iron sulfide membranes precipitated in simulated hydrothermal systems, to enable better understanding of the emergence of prebiotic chemistry within iron-sulfide precipitates.

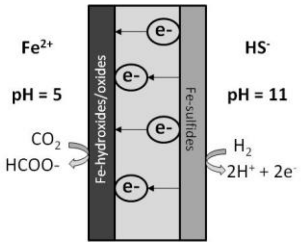

Figure 3: The experimental membrane system analogous to an ion-exchange membrane fuel cell.

References: [1] Russell M. J. and Hall A. J. (1997) *J. Geol. Soc. London*, 154, 377-402. [2] Mielke R. E. et al. (2010) *Astrobiology* 10, 799-810. [3] Mielke R. E. et al. (2011) *Astrobiology*, in review. [4] Martin W. et al. (2008) *Nature Reviews, Microbiology*, 6, 805-814. [5] Russell, M. J. and Martin, W. (2004) *Trends Biochem. Sci*. 29, 358–363. [6] Russell and Hall 2006 Russell M. J. and Hall A. J. (2006) in *GSA Memoir* 198, pp. 1–32. [7] Barge L. M. et al. (2011) *Langmuir*, in press. [8] Vladirov M. G. et al. (2004) *Orig. Life Evol. Biosph.* 34, 347–360. [9] Narayan S. R. et al. (2011) *J. Electrochem. Soc.* 158, A167.