



From Chemical Gardens to Fuel Cells: Generation of Electrical Potential and Current Across Self-Assembling Iron Mineral Membranes**

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Abstract: We examine the electrochemical gradients that form across chemical garden membranes and investigate how self-assembling, out-of-equilibrium inorganic precipitates—mimicking in some ways those generated in far-from-equilibrium natural systems—can generate electrochemical energy. Measurements of electrical potential and current were made across membranes precipitated both by injection and solution interface methods in iron-sulfide and iron-hydroxide reaction systems. The battery-like nature of chemical gardens was demonstrated by linking multiple experiments in series which produced sufficient electrical energy to light an external light-emitting diode (LED). This work paves the way for determining relevant properties of geological precipitates that may have played a role in hydrothermal redox chemistry at the origin of life, and materials applications that utilize the electrochemical properties of self-organizing chemical systems.

Chemical garden structures are formed when a metal salt crystal dissolves in a solution containing a reactive anion (e.g. aqueous silicate or OH^-) that precipitates with a cation (e.g. Co^{2+} , $\text{Fe}^{2+/3+}$, Cu^{2+}), producing inorganic membranes that separate two contrasting solutions and maintain steep trans-

membrane ion/pH/potential gradients.^[1] Chemical gardens can also be produced by injecting a solution containing the reactive cation into the solution containing the reactive anion(s) (or vice versa)—a process which has been used to simulate geological chemical gardens such as hydrothermal vent chimneys that are thought to be significant for prebiotic chemistry.^[2] On the early Earth, interaction between the (anoxic, mildly acidic, CO_2 and Fe^{2+} -rich) early oceans and (Fe/Mg-silicate and pyrrhotite-bearing) ocean crust would have generated an alkaline, reducing, H_2 and sulfide-containing hydrothermal fluid, leading to the precipitation of a chimney containing catalytic metal sulfides/oxyhydroxides and transecting ambient geochemical E_h/pH gradients (E_h = redox potential).^[3] Previous investigations have measured the potentials generated by silicate chemical gardens^[4] and sulfide-containing membranes,^[5] and in modern black smoker vent systems, metal sulfide hydrothermal chimneys generate electrical energy.^[6] However, there have been few laboratory studies addressing the generation of electrical potential and current in chemical garden systems involving reactants that might be relevant to geological or prebiotic systems.

We conducted experiments to simulate the growth of hydrothermal chimneys comprising iron sulfides and iron oxyhydroxides to investigate whether these reaction systems can generate membrane potential and/or current in chemical garden and membrane precipitation experiments. The potentials generated by chemical gardens can be measured by placing electrodes close to either side of the membrane: one electrode inside the chemical garden that will contact the injection solution, and another in the external reservoir solution. (The distinction between cathode and anode depends on the arrangement of the two solutions; if the injection solution contains the electron donors then the internal electrode would be the anode.) Another technique useful for studying inorganic membranes involves separating the two solutions with a porous/permeable template such as parchment paper, so that the precipitate membrane forms on and is structurally supported by the template for analysis and electrochemical study.^[7]

We employed both injection experiments (giving chemical garden structures) and membrane precipitation experiments (using dialysis tubing as a porous separator in a two-chamber glass fuel cell apparatus) to produce iron-sulfide- and iron-hydroxide-containing inorganic membranes (Figure 1). Precipitates were formed by the interfacing of two solutions: 1) an acidic, iron-containing solution (broadly analogous to

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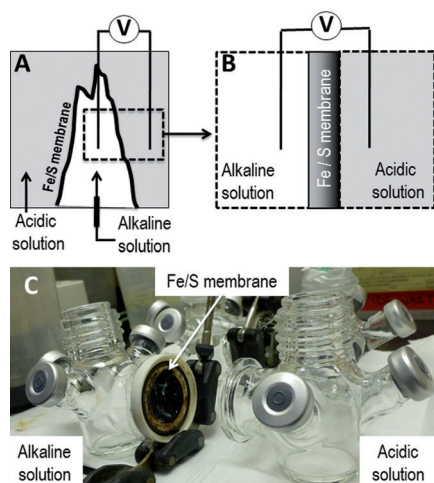


Figure 1. Injection and fuel cell precipitation experiments. A) A chemical garden grows around an electrode at the injection point, allowing measurement of membrane potential. B,C) Isolating the 'wall' of the chemical garden for electrochemical study by forming the membrane on a flat template placed between the same two solutions.

early Earth oceans) and 2) an alkaline and sometimes sulfidic solution (representing the alkaline hydrothermal fluid produced by chemical interactions of primordial seawater with ocean crust.^[3]). In injection experiments, a chemical garden structure formed that continued to grow until the injection was terminated (Figure 2), whereas in fuel cell experiments the precipitate formed as a film in/on the dialysis tubing separating the two solution reservoirs. Chemical gardens grew in varying shapes and sizes depending on experimental conditions (Figure 2), and the membranes formed on the dialysis tubing were composed of multiple layers of material (Figure 3). In all experiments, a membrane potential was generated immediately upon precipitation. For chemical gardens, potentials maintained or increased slightly during the three-hour injection, and when terminated, the potential slowly declined as the system proceeded toward equilibrium. In fuel-cell experiments, membrane potentials reached their highest value as soon as the precipitate membrane formed

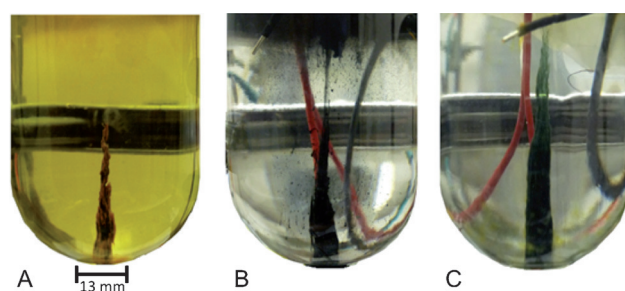


Figure 2. Chemical gardens formed via injection. A) Injection = 0.1 M NaOH + 20 mM CH₃OH; Reservoir = 25 mM FeCl₂·4H₂O + 75 mM FeCl₃·6H₂O + 20 mM NaNO₃, membrane potential = 1.2 V, current = 0.005 mA. B) Injection = 20 mM Na₂S·9H₂O; Reservoir = 20 mM FeCl₂·4H₂O, membrane potential = 1.4 V, current = 0.005 mA. C) Injection = 0.1 mM NaOH; Reservoir = 20 mM FeCl₂·4H₂O + 10 mM NaNO₃, membrane potential = 0.64 V, current = 0.002 mA.

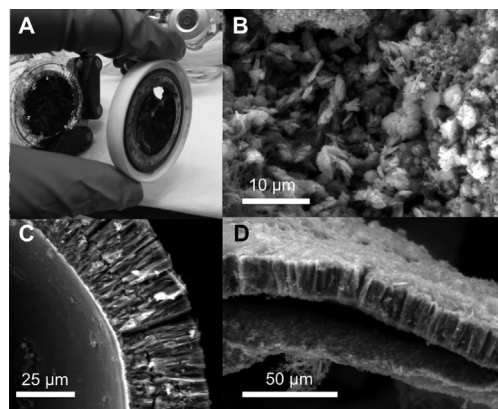


Figure 3. Inorganic membranes formed in systems of iron sulfide and/or hydroxide. A) Inorganic membrane formed between an acidic solution of 50 mM FeCl₂·4H₂O and an alkaline solution of 50 mM Na₂S·9H₂O. B) Membrane formed between acidic solution of 75 mM FeCl₂·4H₂O + 25 mM FeCl₃·6H₂O and alkaline solution of 0.1 M NaOH. C,D) Membrane formed between acidic solution of 50 mM FeCl₂·4H₂O and alkaline solution of 50 mM Na₂S·9H₂O.

between the two solution reservoirs, and then decreased over the succeeding days as the two solution reservoirs equilibrated. In one experiment where a Fe^{II,III}-hydroxide membrane was allowed to precipitate in a fuel cell for 70 h, the potential reached its highest value of 0.85 V as precipitation began, then decreased fairly consistently at about 4 mV per hour until the experiment was terminated (Figure 4). The membrane potentials generated by individual chemical gardens or inorganic membranes in Fe-sulfide and/or hydroxide systems in this work ranged from 0.15 to 1.11 V—substantially higher than the potentials previously measured for metal-silicate systems.^[4] For chemical gardens, the injection rate of the alkaline solution into the acidic solution (tested between 0.16–1.6 μL per second) had no significant effect on the voltage produced. The membrane potential generated in a given experiment was unaffected by the structure of the chemical garden itself; as long as the inorganic membrane

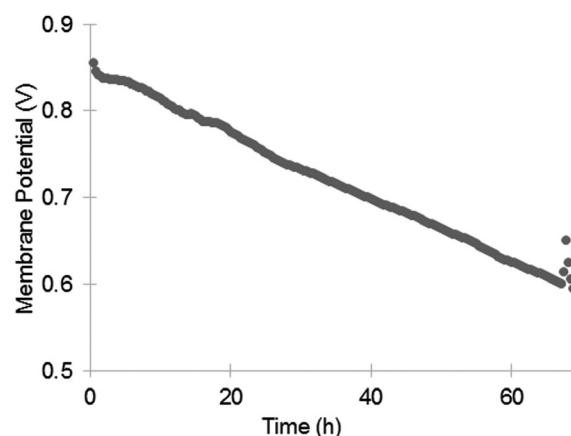


Figure 4. Membrane potential over 70 h in a fuel cell experiment containing 75 mM FeCl₂·4H₂O + 25 mM FeCl₃·6H₂O in the acidic solution and 0.1 M NaOH in the alkaline solution.

properly maintained physical separation of the two solutions. We also tested whether temperature (between 25 and 90 °C) affected the membrane potential of Fe-sulfide membranes (in fuel cell instead of injection experiments, since it was possible to submerge the whole fuel cell apparatus in a heated water bath), but could measure no reproducible effect.

The electrical potential and current generated by inorganic precipitate membranes and chemical gardens could, in some cases, be increased by including different electron acceptors or donors in the system. Generally speaking, the inclusion of sulfide in the alkaline solution substantially increased the membrane potential of chemical gardens, compared to precipitates that were grown with hydroxide as the sole precipitating anion (Figure 2B versus 2C). We also used a combination of Fe^{2+} and Fe^{3+} as precipitating cations (where Fe^{3+} was a potential electron acceptor), and tested the inclusion of soluble non-precipitating electron donors (methanol) or acceptors (nitrate/nitrite). The electrical current generated by our chemical garden or membrane experiments containing only Fe^{2+} was usually quite low (less than 0.01 mA). However, in systems which contained $\text{Fe}^{2+}/\text{Fe}^{3+}$ (and sometimes nitrite or nitrate) in the acidic solution and OH^-/HS^- (and sometimes methanol) in the alkaline solution, currents reached as high as 1.2–1.4 mA (see Table S1 in the Supporting Information). A similar effect has been observed in chemical garden systems at black smoker hydrothermal vents, where metal sulfide hydrothermal precipitates can conduct electrons as hydrothermal sulfide is oxidized to sulfur while O_2 dissolved in seawater is reduced,^[6] and early Earth laboratory simulations of hydrothermal chimney precipitation also produce electrons to reduce CO_2 .^[8] It is reasonable to expect that laboratory-grown chemical gardens or membranes could also function as a battery, if the appropriate electron donors/acceptors were to be present. To provide a demonstration of the battery-like properties of laboratory chemical garden/inorganic membrane systems, we were able to link two or more chemical garden experiments electrically in series, by connecting the “inner” electrode inside one chemical garden to the “outer” electrode in the reservoir of another chemical garden experiment in a separate vessel being fed by a separate syringe (Figure 5). The potential generated upon chemical garden or template-supported membrane precipitation increased accordingly when multiple experimental rigs were linked together in series. When four injection experiments—containing as precipitating ions $\text{Fe}^{2+}/\text{Fe}^{3+}$ (in the acidic reservoir) and OH^-/HS^- (in the alkaline reservoir), but also nitrate as an electron acceptor and methanol as an electron donor—were linked thus, the system generated a combined membrane potential of 3.5 V and current of 0.8 mA. A light emitting diode (LED) was then connected as the load between the “outer” electrode of the first chemical garden and the “inner” electrode of the fourth chemical garden, and the linked chemical garden experiments were able to illuminate the LED for several hours (Figure 5; compare Ref. [6b]). (Fuel cell experiments could be linked to one another in an analogous manner. When four fuel cells with this same solution chemistry were linked in series, the system generated 1.2 mA and 4.1 V, which was also sufficient to light the LED.)

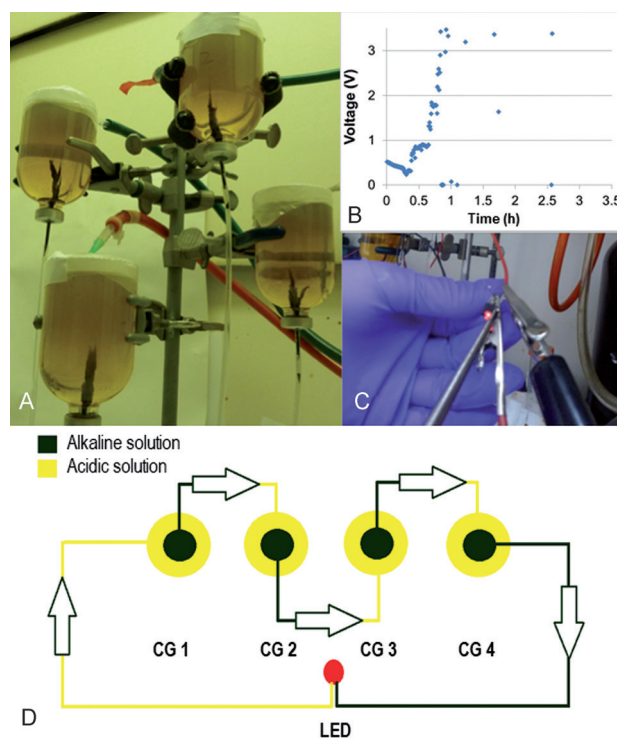


Figure 5. Electrical connection of four chemical gardens in series. The acidic solution was 75 mM $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ + 25 mM $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ + 20 mM NaNO_3 , and the alkaline solution was 50 mM $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ + 0.1 M NaOH + 20 mM CH_3OH . The chemical gardens (A) were electrically connected as shown in (D); combined they generated a membrane potential of about 3.5 V (B) and current of about 0.8 mA which was sufficient to light an LED (C).

In precipitation systems that combine Fe^{2+} and Na_2S aqueous solutions, the primary precipitate formed at ambient temperature is mackinawite (FeS),^[9] and chemical gardens or inorganic membranes formed with this reaction system may also contain greigite (Fe_3S_4) as well as $\text{Fe}^{\text{II,III}}$ -oxyhydroxides/oxides (e.g. green rusts and lepidocrite).^[2] The generation of potential and current in inorganic membrane systems results from an unequal distribution of charged species across the membrane (Gibbs-Donnan effect) but, depending on the components incorporated into the solutions and the precipitate, might also involve redox reactions. Chemical gardens, whether formed in the laboratory or in natural systems such as hydrothermal vents, could constitute fuel-cell-like systems if the membrane were to be composed of a sufficiently electrocatalytic material, and oxidants and reductants were present on either side of the membrane. Hydrothermal chimneys could possibly form fuel-cell-like systems in any planetary geological environment, assuming that the self-assembling precipitate remains capable of separating the contrasting seawater and vent fluids, and that fuels and oxidants continue to feed into the system. For example, on the early Earth, interaction of anoxic seawater (bearing oxidants Fe^{3+} , Mn^{4+} , NO_3^- and CO_2) with ocean crust would have generated a high-pH hydrothermal fluid rich in H_2 and CH_4 as fuels.^[3] The precipitated hydrothermal mound formed at the interface would have constituted a variety of minerals, including $\text{Fe}^{\text{II,III}}$ -oxyhydroxides (green rust) and Fe/Ni-sul-

fides broadly analogous to the precipitates formed in our experiments, that may have served as electron/proton conductors and redox catalysts to drive prebiotic reactions. Similar geochemical disequilibria may have existed on other worlds where water-rock interfaces are, or were, present, for example, early Mars or icy worlds such as Jupiter's moon Europa. Laboratory simulations as we have employed here could help establish the electronic and protonic gradients present in a particular hydrothermal system on any wet rocky world. In particular, chemical gardens containing both Fe^{2+} and Fe^{3+} as precipitating cations might lead to some systems with as yet, undiscovered and diverse properties. Precipitation of iron(II/III)-containing double layered hydroxides might lend catalytic properties to chemical gardens, as these minerals are capable of absorbing and concentrating phosphate and organic molecules, are redox-active catalysts, and may, as we have said, have played a role in prebiotic chemistry.^[10]

In summary, we generated self-assembling membranes in iron-sulfide and iron-hydroxide reaction systems using injection and solution interface methods. Future studies which incorporate other non-precipitating fuels and oxidants in chemical garden/membrane precipitation experiments can help determine the free energy transducing properties of geochemical precipitates that may have played a role in hydrothermal redox chemistry, and could also pave the way to materials applications that utilize the electrochemical properties of self-organizing chemical systems.

Experimental Section

Preparation of solutions: Acidic solutions contained dissolved $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and/or $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and sometimes also NaNO_3 or NaNO_2 . Alkaline solutions contained dissolved NaOH or $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, and sometimes CH_3OH . A headspace of N_2 was maintained in the reaction vessels to keep anoxic conditions.

Injection experiments: The alkaline solution was fed into the acidic solution by a syringe pump at a controlled rate ($0.556 \mu\text{L} \cdot \text{sec}^{-1}$). Potentials were measured by growing the chemical garden around an electrode (copper wire) and a second electrode was placed into the reservoir. To link experiments electrically in series, the "interior" wire in one chemical garden was connected to the "exterior" wire of a separate vessel (fed with a separate syringe), and so forth; the two end leads were connected to an electrochemical analyzer or an LED (Digi-Key, rated $1.8 \text{ V}/2 \text{ mA}$).

Fuel cell experiments: A synthetic ion-permeable template (dialysis tubing; Fisher, 3500 MCW) was clamped between two fluid reservoirs in a custom-made glass membrane fuel cell apparatus (Adams & Chittenden glassware). The acidic/alkaline solutions were added to the separate half-cells and allowed to interface across the dialysis template, upon which the precipitate formed. Titanium or copper electrodes were inserted in each half-cell to measure membrane potential and current. The fuel cell apparatus was submerged in a temperature-controlled water bath for precipitation experiments above room temperature. Both chambers were kept anoxic with N_2 during experiments.

Analysis: Potential was measured with an Agilent LXI Data Acquisition/Data Logger Switch Unit and current measured periodi-

cally with a Fluke 87 multimeter. High-resolution imaging was carried out with an environmental scanning electron microscope (ESEM) using a voltage of 20 kV and a working distance of 10 mm.

Keywords: chemical gardens · hydrothermal chimneys · inorganic membranes · iron sulfide · membrane potentials

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