Electrochemistry at Deep-Sea Hydrothermal Vents: Utilization of the Thermodynamic Driving Force towards the Autotrophic Origin of Life

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Abstract: Temperature gradients are an under-utilized source of energy with which to drive chemical reactions. Here, we review our past efforts to understand how deep-sea hydrothermal vents may harness thermal energy to promote difficult chemical reactions such as CO_2 reduction. Strategies to amplify the driving force using temperature will be covered first, followed by a discussion on how spatially separated thermodynamic gradients can be used to regulate reaction selectivity. Although desirable material properties of hydrothermal vent walls have been inferred previously from the bioenergetic membranes of modern cells, strategies based on fundamental laws of physical chemistry allow naturally-occurring chimney minerals to circumvent the lack of structural and catalytic optimization. The principles which underlie both the establishment and the utilization of the thermodynamic driving force at hydrothermal vents can be employed in abiotic systems such as the modern chemical industry, yielding insights into carbon fixation reactions important today and possibly at the autotrophic origin of life.

1. Introduction

Efficient utilization of energy is an important aspect of any applied chemical process.[1,2] In industrial chemical synthesis or in energy conversion, energy efficiency is one of the most influential parameters of economical and industrial feasibility.[1,2] From a biological standpoint, energy efficiency can dictate what species can fill an environmental niche,[3] which in turn affects evolution.[4] From a number of perspectives then, it is important to understand the factors which control how thermodynamic driving forces (energy availability) can be utilized to drive chemical reactions more efficiently, especially those from diffuse and fluctuating sources.

Deep-sea hydrothermal vents and the ecosystems which surround them, provide valuable insight into this question.[5-15] These environments lack sunlight, which constitutes the primary energy source of terrestrial ecosystems.[16] This has resulted in the emergence of unique and sophisticated strategies to utilize other energy sources, such as chemical[10] and thermal energy.[5,12,14,15, 17,] The 3-dimensional columnar structure of the chimney wall establishes spatial thermodynamic gradients, [5,12] and the catalytic nature of its exterior[10] is thought to allow CO_2 to be reduced electrochemically to CO, HCOOH, and CH_4.[10,18,19] Previously, these reactions were considered to be driven primarily based on the enormous reductive energy discharged from the hydrothermal vents, such as from H_2 and H_2S. [8,20] However, at least in terms of standard electrochemical potentials, the thermodynamic driving force derived from these reducing agents alone is insufficient,[22,23] and the lack of driving force must be somehow supplemented by other energy sources. Additionally, even if the thermodynamic driving force were sufficiently large, directing the selectivity of CO_2 reduction to desired products requires regulation and suppression of a multitude of side reactions.[24] This is an especially difficult challenge in a “messy” environment containing various chemical species, because directing the selectivity of electrochemical CO_2 reduction is difficult even with state-of-the-art catalysts in a pure environment.[22-26] Understanding how this may become possible based on the laws of physical chemistry would yield critical insight into how life had originated from inorganic molecules (i.e., autotrophic innovation), which is one of the vital questions of natural science.[27-36]

Here, we will provide a brief summary of our past attempts to understand the energy conversion strategy which takes place at deep sea hydrothermal vents. In section 2.1, we will highlight how the electrically conductive yet thermally insulative nature of the chimney wall can sufficiently decrease the electrochemical potential negatively such that CO_2 reduction, which would otherwise be thermodynamically unfavourable, may proceed. This manipulation of the electrochemical driving force is based purely on the Nernst equation[37] and the chemical disequilibria which exists across a conducting barrier, and thus requires no complex, molecular-scale machinery such as ion pumps[38] seen in contemporary biology. This will be followed by section 2.2, where we will highlight how these strategies are actually implemented on metal sulphide minerals[10,18] similar to those obtained from deep sea hydrothermal vents. Finally in section 2.3, we will discuss the possibilities of how the interconversion between chemical potentials (pH) and electrochemical potentials (E) can be utilized to regulate the selectivity of CO_2 reduction products.[39] This selectivity is a result of electrochemical reactions exhibiting different pH and potential dependences, based on the nature of their particular reaction intermediates.[40,41]

Although a reaction environment with high pressure and temperature may seem to offer little towards realizing clean and sustainable chemical processes, many crucial industrial chemical processes today, such as ammonia synthesis[42] or olefin synthesis,[43] take place under such extreme conditions. Indeed, such is the importance of chemistry and catalysis under extreme conditions that an entire session at the Solvay conference on chemistry in 2016 was dedicated to this topic.[44] Therefore, previously overlooked strategies for the modern chemical industry may be obtained by interpreting the deep-sea hydrothermal vent as a natural analogue.

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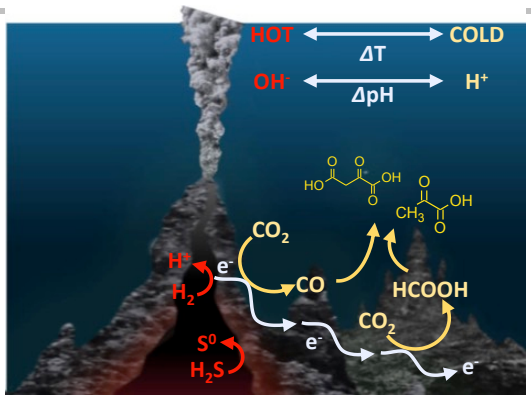

Figure 1. Schematic image of the redox chemistry at the vicinity of the hydrothermal vent triggered by geoelectricity.

2. Electrocatalysis at Deep-Sea Hydrothermal Vents

2.1. Theoretical model towards optimal harvesting of thermal and chemical driving forces

Hydrothermal vents are capable of establishing steep redox gradients between interior fluids and the surrounding ocean.[9,45] These gradients are sustained by continuous geothermal activity, and the fluids excreted from the vents can contain a variety of reducing chemical such as H_2, CH_4, reduced metals (Fe^{2+}, Ni^{2+}), and sulphides. The difference in the redox potential of the hydrothermal fluid and oxygen-containing seawater allows the hydrothermal vent to function similarly as an electrochemical fuel cell.[9-15] In line with this hypothesis, in 2010, we identified an electrical current passing through the chimney wall.[9]

However, another important discrepancy between the hydrothermal fluid and the seawater is the temperature. Thermal energy is an under-utilized source of driving force in industrial (artificial) electrochemical systems. Even systems which operate at elevated temperatures such as solid oxide fuel cells,[46] polymer electrolyte membrane electrolysers,[47] or thermocatalytic chemical reactors,[43] utilize temperature primarily as a means to boost reaction kinetics; either through increased charge carrier densities, increased mean free paths, or decreased activation barriers. On the other hand, temperature can be used to manipulate electrochemical potentials, and therefore the thermodynamic driving force, based on the Nernst equation (Eq. 1).[37]

$$E = E_0 + RT / nF \ln [Ox] / [Red] \quad \text{(Eq. 1)}$$

Here, E is the electrochemical potential, E_0 is the potential under standard conditions, R is the gas constant, T is the temperature, n is the number of electrons transferred, F is the Faraday constant, and [Ox] and [Red] are the concentrations of the oxidized and reduced species, respectively.

For example, at room temperature (300 K), changing the activity of a redox species by an order of magnitude modulates the electrochemical potential by 59 mV. On the other hand, at an elevated temperature of 500 K, such as that observed in the Iheya North hydrothermal field of the Okinawa Trough, Japan[11] this value increases to 100 mV. Considering the redox potential of hydrogen, a common reductant near hydrothermal vents, sufficient electrochemical potential to reduce CO_2 can be achieved by increasing the temperature to 500 K at pH 10 (a reasonable value for alkaline hydrothermal vents)[20, 48]. These conditions would boost the redox potential of H_2 oxidation from -0.41 V at room temperature and pH 7 — insufficient for CO_2 reduction — to -1.0 V. This value is on par with the photoexcited state of the photosynthetic enzyme, Photosystem I (PS I) (Figure 2), which is one of the most reducing enzymes in biology and responsible for making most of the biomass on Earth from CO_2.[49]

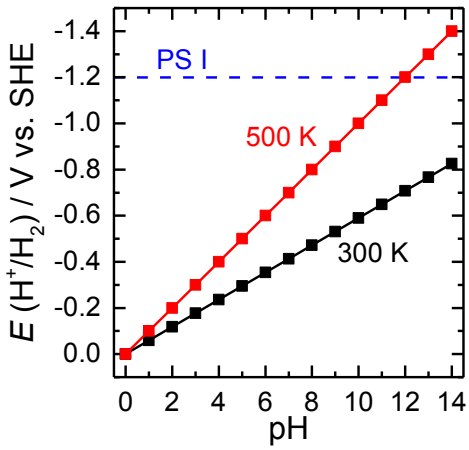

Figure 2. Modulation of the electrochemical potential according to the Nernst equation at different temperatures. The redox potential of PS I is shown as a dotted blue line for reference.

We emphasize that the boost in the thermodynamic driving force is possible only because there are two distinct environments separated by a mineral wall. If we imagine a scenario where CO_2 is reduced by mixing directly with the reductive hydrothermal fluid, there is no difference in the temperature or pH between the vent fluid and the CO_2, because they coexist in the same environment.[20, 50] In other words, several hundred mVs worth of reductive energy is lost, purely because the single chamber system fails to harvest the thermodynamic disequilibria between the vent fluid and the sea water. Furthermore, a single chamber system has inherent difficulties in maintaining the reductive potential required to reduce CO_2, due to the depletion of reductive chemicals in the vent fluid. One way to counteract this problem may be to surround the chamber with semi-porous walls which allow the transport of specific chemical species (Figure 3A). Such structures surrounded by “leaky” membranes would allow sustained CO_2 fixation, stimulating hypotheses as possible origins of life.[51-54] Even in such a system, it is possible to supplement the thermodynamic driving force by pumping ions across the membrane, much like a modern cell.[38] However, the molecular machinery required to couple ion transport with chemical reactions is an additional degree of complexity[55] which is unnecessary in a two chamber system. Therefore, while we realize that many of the theories concerning the origin of life have focused on single chamber systems due to similarities with the modern cell,[51-54] we feel a system with multiple chambers (Figure 3B) is inherently more favourable and thus a more plausible candidate for primitive cells.[56]

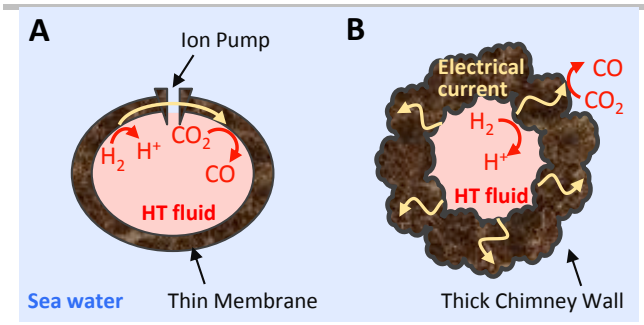

Figure 3. Schematic cross sectional image of a semi permeable one chamber system adopted from ref. 53 (A), and a two chamber system adopted from ref. 10 (B). By spatially separating the reduction reaction with the oxidation reaction via an electronically conductive but thermally insulative material, thermal and pH gradients can both be harnessed for redox reactions such as CO_2 reduction.

Furthermore, it is noteworthy that at least some hydrothermal vents are composed of materials with low thermal conductivity. This would help maintain the thermal discrepancy between the inside and outside of the hydrothermal vent, which is beneficial only in the case of a two chamber system. One example is the chalcopyrite minerals ($Cu_{1+x}Fe_{1-x}S_2$) obtained from the Snow Chimney black smoker vent of the Mariner field in the southern Lau Basin.[5] Due to their surface microstructure, these minerals exhibited a combination of low thermal conductivity and high electric conductivity, leading to thermoelectric properties. Although the thermoelectric efficiency (ZT value) was two orders of magnitude lower than the most efficient artificial materials known today,[58] it is nonetheless remarkable that a naturally occurring mineral can decouple the two conductivities to convert a temperature gradient into an electrical one while simultaneously maintaining the temperature gradient.

2.2. Usage of 3-dimensional structures for driving CO_2 reduction

The benefits of the aforementioned strategies to boost the electrochemical driving force were observed directly in our previous studies using iron sulfides.[10] These materials are a major component of the modern black smoker type chimneys and perhaps existed in ancient hydrothermal vents.[56,57,59] They are also known to exhibit electrocatalytic activity to reduce CO_2 to CO and CH_4 (Figure 4A). However, these reactions possess standard redox potentials more negative than the redox couple of H^+/H_2, the most reducing species in a hydrothermal fluid.[8] In other words, the chimney wall is catalytically active for CO_2 reduction, but the driving force is insufficient under standard conditions.

However, based on the discussion of section 2.1, this lack of driving force can be overcome if there is a difference in the pH (proton concentration) and temperature across the chimney wall. For example, if the pH of the hydrothermal fluid at an alkaline hydrothermal vent is assumed to be 10 and that of the outer seawater to be pH 5.5, this difference of 4.5 pH units corresponds to a 265 mV increase in the driving force at room temperature. This would shift the H^+/H_2 redox potential from -330 mV (Figure 4B, black line) to -590 mV (Figure 4B, blue line). Although this potential is sufficient to initiate CO_2 reduction on NiFe sulphide (Figure 4A), only CO was observed at -600 mV, suggesting a larger driving force is necessary to transfer more than two electrons.[10] This driving force can be obtained if we also consider the elevated temperature of the hydrothermal fluid (~500 K), as the H^+/H_2 redox potential is shifted even more negatively to -780 mV (Figure 4B, red line). Therefore, at least in the case of our lab-synthesized FeNi sulfide, the driving force from the temperature and pH difference is clearly sufficient for CO_2 reduction,[10] giving insight into how the first organic molecules necessary for prebiotic life may have originated due to the catalytic activities of the inorganic hydrothermal vent.[10,18]

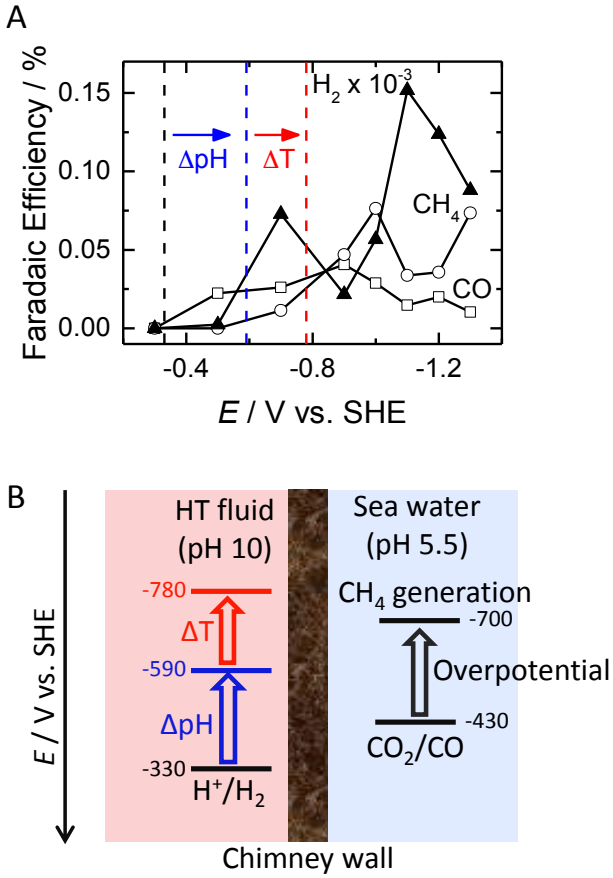

Figure 4. Panel A: Faradaic efficiencies of CO_2 reduction on FeNi sulfide. Data obtained from ref. 10. Panel B: Energy diagram of CO_2 reduction and the effect of ΔpH and ΔT. Numbers indicate equilibrium potentials at pH 5.5 in mV units. The potential of the hydrothermal (HT) fluid has also been indicated in Panel A as a dotted line in the corresponding color.

As to how this driving force is used to reduce CO_2, it is worth noting that the thermodynamics become more favourable upon transferring more electrons (Table 1). For example, the 2 electron reduction from CO_2 to CO has an equilibrium potential of -0.52 V vs SHE (standard hydrogen electrode) at pH 7, whereas the 8 electron reduction from CO_2 to CH_4 may occur at a potential 280 mV more positive.[22,23] Therefore, if sufficient driving force is available to drive the initial steps of CO_2 reduction, i.e., activation of CO_2, it is possible to expect further reduced compounds to also be produced. This is reflected in microbial methanogenesis, where the exergonic formation of methane is coupled to the otherwise endergonic CO_2 reduction.[60-62] Non-biologically, this is partly evident in the fact

that CH_4 is a commonly observed product of both heterogeneous and homogeneous CO_2 reduction catalysts.[14, 26, 63-65]

At the same time however, carbon compounds with intermediate oxidation states such as CO, HCOOH, and to a lesser extent, C_2H_4, are also well known CO_2 reduction products.[23] Furthermore, virtually all biologically-relevant molecules, such as nucleic acids, sugars, and proteins, possess a moderate carbon oxidation state (i.e., formal oxidation states between that of CH_4 and CO_2).[66] At least under the assumption of standard conditions, the formation of these molecules is thermodynamically unfavourable, because either CO_2 would not be reduced at all, or CO_2 would be reduced to CH_4. Therefore, kinetic regulation of CO_2 reduction is a physicochemical requirement which must be satisfied prior to the abiotic synthesis of organic molecules necessary for the emergence of life. Needless to say, selective synthesis of biologically relevant chemicals is also desirable for the chemical and pharmaceutical industry.[67] Strategies to make this possible will be covered in the following section.

Table 1. Electrochemical potentials of CO_2 reduction under standard conditions[22,23]

# of electrons[a]	Product (Potential / V vs SHE at pH 7)		
2	CO (-0.52)	HCOOH (-0.61)	
4	HCHO (-0.48)		
6	C_2H_4 (-0.34)	MeOH (-0.38)	EtOH (-0.33)
8	CH_4 (-0.24)		

[a] per carbon atom

2.3. Usage of sequential proton-electron transfer (SPET) to regulate the selectivity of CO_2 reduction

In this section, we would like to briefly note that the selectivity of CO_2 reduction can be regulated by specifically tuning the thermodynamic driving force. Up to this date, there have been many studies in the field of electrocatalysis, where the catalyst has been shown to markedly influence the selectivity and activity (overpotentials) of this reaction.[18,23,24] The reactivity trends across different materials have been rationalized largely based on the d-band theory and the Sabatier principle.[68-79] The general conclusion derived from this model is "An ideal catalyst must bind each reaction intermediate at an optimum binding strength".[70-72] This is because tuning the stability of intermediates via their binding energy allows regulation of the driving force of each elementary step. However, there are also other physicochemical parameters, such as the pH, which offer alternative methods to optimize the thermodynamic landscape.[76] These additional parameters may be especially useful to enhance the selectivity between similar products, because scaling relationships between the binding energy of structurally similar intermediates increases the difficulty of tuning multiple thermodynamic landscapes independently.[68,69,77-79]

Selectivity is an especially critical issue not only for CO_2 reduction at the chimney vicinity,[80] but also for industrial (artificial) CO_2 reduction[23-26,81-83] and other multi-step electrochemical processes in general,[39,84] because of the difficulty and importance of maintaining selectivity in an environment containing multiple reactants. For example, even in a "pure" electrolyte with only CO_2 as the reactant, CO_2 can theoretically be reduced for the synthesis of any carbon compounds, all of which may potentially act as substrates for further reduction reactions.[24, 85] In reality, seawater contains various species of organic carbon in the order of 1 mg C/L,[86] which corresponds to μM concentrations. Furthermore, protons derived from the solvent water molecule itself can also be reduced via the hydrogen evolution reaction,[87] which is almost always a leading cause for the diminished efficiency of CO_2 reduction.[23,24] Therefore, maintaining selectivity in such a "messy" system with a multitude of chemical components is a challenge inherent to all multi-step (electro)chemical reactions. It is also to be noted here that enhancing the reaction selectivity is a critical issue for theories concerning the autotrophic origin of life. This theory postulates that five universal intermediates (acetyl-CoA, pyruvate, oxaloacetate, succinate, and α-ketoglutarate) were produced non-enzymatically via an incomplete version of the reductive tricarboxylic acid (rTCA) cycle, where multiple undesirable side-reactions must be suppressed to maintain the on-cycle reactions.[88-92]

The answer in biology was to develop enzymes with highly substrate-specific binding sites,[93-95] but it is difficult to replicate such a degree of control in artificial systems,[67] much less in naturally-occurring chimney minerals. However, just as we have used thermodynamics to circumvent the inherent lack of driving force in single chamber systems (section 2.1), here we will discuss how laws of physical chemistry may allow us to circumvent the lack of chemoselectivity.

The reduction of CO_2 is a multi-step electrochemical process involving the transfer of multiple protons and electrons. For example, even the simple reaction of reducing CO_2 to CO is a 2 electron, 2 proton reaction ($CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$). If we consider reducing CO_2 to CH_2O, which shares the typical oxidation state found in proteins and amino acids,[66] this is a 4 electron 4 proton process. Considering that these numbers for electrons and protons are *per carbon atom*, the reaction pathway becomes considerably more complicated if we consider biologically relevant organic molecules with more carbon atoms. Therefore, regulating selectivity boils down to how efficiently the catalyst can transfer electrons and protons to specific atoms to generate desired chemical compounds.

The key to resolve this issue lies in the fact that each of these elementary reactions can be influenced differently by pH and electrochemical potentials.[40,41,96] Therefore, tuning these electrochemical reaction environments via the interconversion of thermal, electrical, or chemical energy may lead to selectivity enhancement. For example, we have demonstrated that the 6 electron, 6 proton reduction of HNO_2 to N_2 ($2HNO_2 + 6e^- + 6H^+ \rightarrow N_2 + 4H_2O$) can be catalysed selectively by optimizing the pH (proton component).[39, 84] The theoretical basis of how this can be done was originally proposed by Marc Koper in 2013.[40,41] Here, we will assume a 1 electron 1 proton reduction reaction for simplicity, but the overall idea of regulating the driving force independently to optimize reaction rates remains relevant even for more complex reactions.

When an electron and proton are transferred in a step-by-step manner, the driving force for the electron (ΔG_e) is dictated by the electrochemical potential, while that of the proton (ΔG_H) is dictated by the pH.[40,41] Namely,

$$\Delta G_e = F(E_{elec} - E_0)$$

$\Delta G_H = RT \ln 10 (pH - pK_a)$

Here, E_{elec} stands for the electrode potential, and ln 10 is the natural logarithm of 10 (~2.3025). Such a reaction pathway is often referred to as sequential (stepwise) proton-electron transfer (SPET), and is in contrast to a reaction pathway where the proton and electron are transferred concertedly during a single elementary step. Due to the independence of the proton transfer and electron transfer, the reaction rate for the entire reaction is dictated by whichever step is less favourable. In other words, it is not the total driving force ($\Delta G_{total} = \Delta G_e + \Delta G_H$) which dictates the reaction rate, but its individual components (ΔG_e and ΔG_H). For example, if the Gibbs free energy change for electron transfer is more positive than that of proton transfer ($\Delta G_e > \Delta G_H$), the overall reaction would be inhibited by electron transfer (Figure 5A, red pathway). In such a scenario where electron transfer is rate-limiting, the pH is expected to have no influence on the overall reaction rate, because the driving force for electron transfer (ΔG_e) is independent of pH. In essence, although the total driving force is the sum of proton and electron transfer ($\Delta G_{total} = \Delta G_e + \Delta G_H$), any driving force attributed to proton transfer (ΔG_H) is "wasted" because it does not promote the rate-limiting step and hence, does not influence the observed reaction rate. The exact opposite can be said when $\Delta G_e < \Delta G_H$ (Figure 5A, blue pathway). Therefore, the thermodynamically optimum condition is when $\Delta G_e = \Delta G_H = 1/2 \Delta G_{total}$ (Figure 5A, green pathway), which yields:

$$pH = pK_a + F(E_{elec}-E_0) / (RT \ln 10) \qquad \text{Eq. 1}$$

In other words, optimum reactivity can be realized at a specific potential E_{elec} and pH. These parameters are dictated by the equilibrium potential (E_0) of electron transfer and the equilibrium pH (pK_a) of proton transfer, which are unique to the reaction of interest.

Figure 5B shows how two reactions with different pK_as will behave, based on Eq. 1. The difference of optimum pH for each reaction results in a pH window which can enhance the selectivity for a desired reaction. Although the exact values of optimum pH and E_{elec} may deviate slightly from Eq. 1 due to reaction kinetics,[40,41] it still serves as a first approximation to understand and predict how the selectivity of complex reactions can be manipulated. There are many empirically-obtained, log-linear relationships between the thermodynamic driving force and reaction rates such as the Arrhenius equation[97] or the Hammett law,[98] and Eq. 1 is expected to provide reasonable estimates when these laws are maintained. Therefore, the selectivity of classical reactions in which quantum mechanics do not play a prevalent role can be optimized by changing the pH and electrode potential E_{elec}.

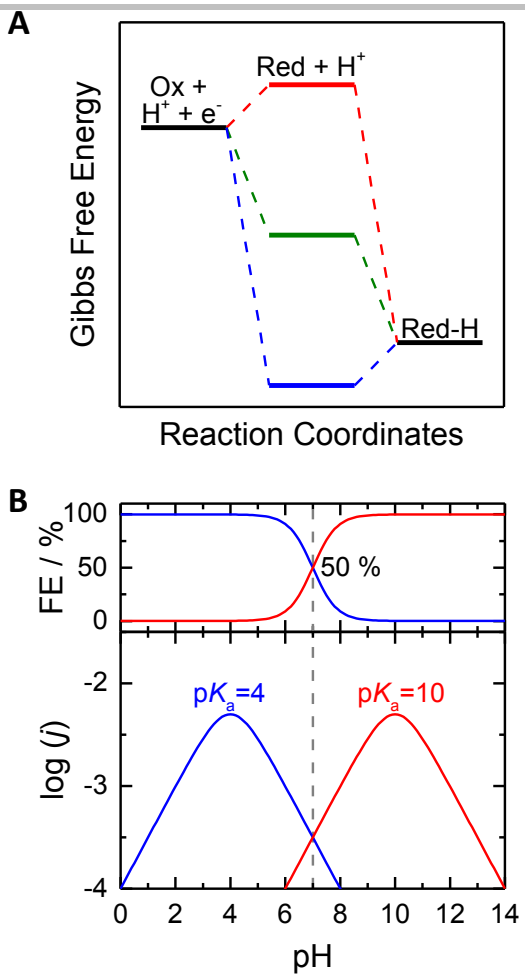

Figure 5. A Selectivity enhancement using SPET. Panel A: Energy diagram of a 1-electron 1-proton SPET reaction. Ox: oxidized state, Red: reduced state. Red, green, and blue pathways correspond to $\Delta G_e > \Delta G_H$, $\Delta G_e = \Delta G_H$, and $\Delta G_e < \Delta G_H$, respectively. Panel B: The bottom panel shows the rate of two SPET pathways with different pK_as (blue: $pK_a = 4$, red: $pK_a = 10$), calculated based on refs. 40 and 41. The upper panel shows their Faradaic efficiency (FE).

We expect such a mechanism may have indeed contributed to selectivity at ancient deep sea hydrothermal vents, due to the difference in the pH of the alkaline vent fluid (~10) and the sea water in the Hadean eon. Although the pH of seawater is approximately ~8 today,[99] the higher partial pressure of CO_2 at that time has been proposed to lower the pH to 5 or 6.[100] Depending on fluid flow, and if the chimney is somewhat leaky, this pH difference would lead to the formation of a pH gradient along the exterior of the chimney wall where CO_2 reduction is expected to take place. This pH range spans the majority of pH ranges relevant for biological processes,[101] and the exposure of catalytic sites to different pH would have allowed deep sea hydrothermal vents to effectively "scan" or "search" the electrochemical conditions to promote a specific reaction abiotically (Figure 6). A different product distribution upon changing the pH is a relatively common observation in electrocatalysis.[102-105] These trends are not dependent on the exact reaction mechanism. For example, while the participation of a CO_2 radical anion has been proposed experimentally[102,103] explain the selectivity with respect to the competing hydrogen

evolution reaction, the theoretical conclusions derived here do not necessarily require this specific intermediate to form. Rather, what defines the pH dependence of a specific pathway is the ratio of protons and electrons transferred during the rate-limiting step.[106] Therefore, as long as this ratio is different between two competing pathways, the pH will serve to regulate the reaction selectivity.[104-106]

At a hydrothermal vent, the pH varies depending on the degree of mixing and diffusion, which would expose active sites along the chimney wall to different local pH (Figure 6). This variability could allow specific reactions to proceed and concentrate in a certain niche environment. Going further, this may possibly even lead to a multi-step chemical conversion system, either as cascade catalysis,[107-109] or as several chemical reactors connected in series. This is a critical difference from previous origin of life theories such as the soup model and pond model, where no pH or potential gradients were available to guide the selectivity of prebiotic reactions.

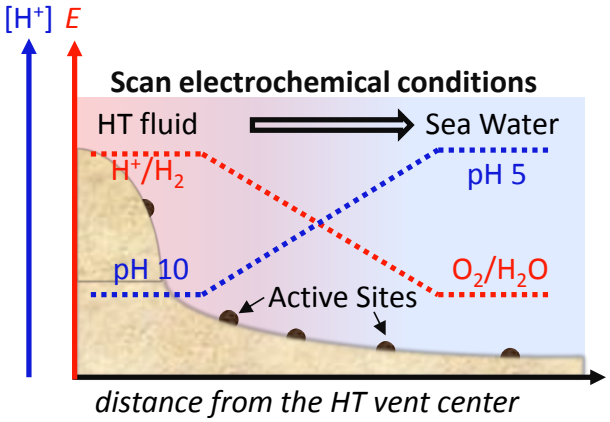

Figure 6. Schematic image of how the deep sea hydrothermal vent and its surrounding environment may "scan" electrochemical conditions for CO_2 reduction.

3. Summary and Outlook

The environment at deep-sea hydrothermal vents differs drastically from terrestrial environments, and there is still much to be learned from these unique ecosystems. In this review, we have highlighted how the deep-sea environment can harness thermal and chemical energy efficiently, and how this may be used to drive specific chemical reactions such as CO_2 reduction. This is possible due to the material properties of the chimney wall, namely their electrical conductivity and thermal insulation.[5] These features allow the thermal and chemical gradients to be maintained, leading to gradual change of reaction environments which would likely create a reaction environment which is suitable for the generation of a specific CO_2 reduction product. In this way, hydrothermal vents occupy a large chemical reaction space, and may "search" for the optimum spatial and physicochemical environments for CO_2 reduction. In light of the fact that many industrial process require high temperature,[42,45,46] the efficient utilization of heat at the deep sea hydrothermal vent may provide an important blue print.

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Keywords: Electrochemistry• Heterogeneous Catalysis • Origin of Life •Sequential Proton-Electron Transfer • Thermodynamics

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