Bio-inspired CO₂ conversion by iron sulfide catalysts under sustainable conditions†

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The mineral greigite presents similar surface structures to the active sites found in many modern-day enzymes. We show that particles of greigite can reduce CO₂ under ambient conditions into chemicals such as methanol, formic, acetic and pyruvic acid. Our results also lend support to the Origin of Life theory on alkaline hydrothermal vents.

Hydrothermal vents consist of porous chimney structures composed of colloidal barriers of continually forming iron sulfides in three-dimensional cavities.1 The chimneys comprise mostly iron, nickel and cobalt sulfides as well as silica gel, ferrous hydroxide and oxyhydroxides.2 It has been proposed that at the interface between hydrothermal fluids and the primordial ocean, H₂ and CO₂ would have reacted together to form small organic molecules, catalyzed by the FeS membranes formed in the plumes of the vents.1d Hydrothermal vents located on the ocean floor can be divided into two main types, those with acidic and alkaline effluents. Acidic hydrothermal vents, termed ‘black smokers’ are located directly above magma chambers,3 with a hot (up to 405 °C) acidic (pH 2–3) effluent.5 In contrast, alkaline hydrothermal vents have cooler (40–91 °C), more basic effluent (pH 9–11).6 Furthermore, the cavities in the chimneys restrict the diffusion of the vent springs leading to a natural chemiosmotic potential owing to the contrast in pH,7 which could provide the driving force required to overcome the initial thermodynamically unfavorable CO₂ reduction step.7

An attractive suggestion is the hypothesis that iron-sulfide minerals, such as greigite (Fe₃S₄), found in the chimney cavities of hydrothermal vents,8 catalyzed CO₂ reduction, forming a primitive acetyl-CoA pathway similar to that in contemporary enzymes.8 In fact, greigite is structurally similar to the Fe₄S₄ clusters found in ferredoxins,9 Fig. 1A, which have been shown to act as electron-transfer sites and to be catalytically active centers for molecule transformations.10 Such enzymes are highly product-specific and efficient, shown for example in formate dehydrogenases, which are able to reduce CO₂ to formate under moderate conditions, i.e. at low temperatures and pressures and at neutral pH.11 A recent study has highlighted the catalytic nature of greigite, showing that CO₂ could be converted to CH₄ and CO, but no solution-based products were detected in that study – an essential requirement for prebiotic chemistry.12 In addition, FeS has been shown to catalyze CO₂ reduction13 and into a range of thiols in the presence of H₂S.14

In this study, we show that CO₂ can be reduced to a range of small organic solution-based molecules that are required for the commencement of pre-biotic chemistry. The use of a greigite surface allows such transformations at a low overpotential, atmospheric pressure and room temperature. Furthermore, we have elucidated the mechanism of formation of formic acid and methanol, which explains the requirement of an alkaline environment.

Highly faceted greigite nanoparticles have been synthesized through the decomposition of iron(III) dithiocarbamate. Metal dithiocarbamates have been shown to be excellent precursors to metal sulfide materials.15 The particle morphology is a rectangular plate with faces terminating at (001) and edges at (111) surfaces (see ESI†). Computer modelling of both bulk materials and the surfaces predicts bond lengths that closely resemble those found in the synthesized particles, with differences of only 0.06 ± 0.02 Å and 0.13 ± 0.02 Å for the short and long bonds.†
These are also very similar to the Fe–S distances found in the CO
dehydrogenase enzyme, $\Delta d(\text{Fe–S}) = 0.01 \pm 0.02 \text{ Å}$ and $0.08 \pm
0.02 \text{ Å}$. The slightly longer Fe–S distances found in synthetic
and modeled greigite, compared with the enzymatic cubane
cluster, are due to periodic packing of the Fe and S atoms in a
crystal lattice, which is not applicable in the enzyme.

A series of electrochemical reduction experiments were performed
at room temperature and pressure, using a greigite-modified
electrode in CO$_2$-saturated aqueous solutions at pH 4.5,
6.5 and 10.5. The nano-carbon dispersed greigite particles were
drop-coated onto a carbon rod electrode and the electrode potential
was cycled continuously between 0.2 and $-0.8 \text{ V vs. NHE}$ at
1 mV s$^{-1}$. Dissolved reduction products were detected
ex situ at periodic intervals using quantitative $^1$H-NMR analysis. The major
reaction product under all three pH-conditions was formic acid and
the quantity detected with time is shown in Fig. 2A. Substantially
more formic acid is generated at pH 6.5 than at pH 10.5; only a
small quantity is produced at pH 4.5. Constant potential electrolysis
experiments at pH 6.5 showed the onset of formic acid production
at 0.4 V vs. NHE (see ESI†).

The computer simulations, using accurate ab initio techniques
based on the Density Functional Theory (see ESI† for details),
suggest that the disparity in formic acid production over the pH
range can be attributed to the type and concentrations of aqueous
species present in the CO$_2$-saturated solutions. In agreement with
the equilibrium constants: at low pH, dissolved CO$_2$ mainly exists
as a neutral molecule; at neutral pH, the dominant solution species
is HCO$_3^-$ (bicarbonate) and at high pH, CO$_3^{2-}$ (carbonate) is the
majority species. These species interact with either the (001) or the
(111) surfaces of the greigite particles. The calculations reveal that
on the (001) surface the CO$_2$ molecule experiences electrostatic
repulsion between anionic surface sulfur atoms and the lone pairs
of the molecule’s oxygen atoms and it therefore does not bind to
this surface (Fig. 2B). In contrast, the metallic centers on the (111)
surface bind CO$_2$ through an Fe–O bond with a binding energy ($E_B$
$\approx -0.62 \text{ eV}$). However, the molecule remains linear and not
activated. Thus, at pH 4.5 the major solution species, i.e. neutral
CO$_2$, either does not bind to the surface or if it binds, it is not
activated for further reaction, although the over-potential and
elevated pressure existing at the hydrothermal vents may well
enhance the interaction of gases on a substrate beyond that shown
in our calculations. At pH 6.5, the major species present in solution
is HCO$_3^-$, which binds to both the (001) and (111) surfaces through
two O–Fe bonds perpendicular to the surface, thereby releasing
energies of 0.36 eV and 1.63 eV, respectively. In basic solution
(pH 10.5) the major species in solution is CO$_3^{2-}$, which does not
favorably adsorb onto the (001) surface ($E_B = +1.24 \text{ eV}$) but binds to
the (111) surface with $E_B = -0.46 \text{ eV}$. Based on these values, the
adsorption of HCO$_3^-$ to the (111) and (001) surfaces and CO$_2$ and
CO$_3^{2-}$ to the (111) surface should be considered as steps in possible
routes to products.

Clearly, water will compete with these species for binding at the
metallic centers. The H$_2$O molecule binds with $E_B = -0.42 \text{ eV}$ on the
(001) surface and considering that water is present in vast excess,
competitive adsorption of HCO$_3^-$ ($E_B = -0.36 \text{ eV}$) on the same
surface is therefore unlikely, leaving only H$_2$O bound to the (001)
surface at all pH values considered. On the (111) surface, water
binds with $E_B$ of $-0.56 \text{ eV}$, this time out-competing the CO$_3^{2-}$
species ($E_B = -0.46 \text{ eV}$). As such, only HCO$_3^-$ is able to adsorb
on the (111) surface, owing to a much higher binding energy, by
$\Delta E_B = -1.07 \text{ eV}$, compared to H$_2$O, implying that the (111) is the
most probable surface for CO$_2$ reduction and adsorbed HCO$_3^-$ is the
most likely reactive species. Consistent with the computed binding energies, the fastest experimentally observed rate of CO$_2$
conversion to formic acid is observed at pH 6.5. Although other
solution species dominate at pH 4.5 and 10.5, some HCO$_3^-$ will still
be present, allowing the conversion to formic acid to proceed under these
conditions albeit at reduced rates. A further plausible explanation
for the disparity of product concentrations, shown in Fig. 2A,
are the competitive processes occurring at the different pHs. The simulations suggest that active sites deactivate at high pH due to
surface OH accumulation, which adsorbs strongly on the Fe centres.
This can be seen experimentally in the reduction in formic acid
production over time at pH 10.5. At pH 6.5, the cycling potential bias
of up to 0.2 V vs. NHE is enough to remove the hydroxyl groups.
In addition, H$_2$ generation from the reduction of adsorbed H at low
pH (pH 4.5) competes with HCO$_3^-$ reduction, thereby decreasing the reduction efficiency.

Based on the calculated binding energies, we propose a reaction
mechanism to transform adsorbed HCO$_3^-$ to formic acid on the
Fe$_3$S$_4$(111) surface with surface H atoms, generated through
dissociation of water. To identify the HCO$_3^-$ transformation reactions,
many intermediates and transition states were explored, leading to
the multiple pathways plotted in Fig. S23 (ESI†). Our calculated
energy barriers agree with the substantial kinetic barriers found in previous experiments on the formation of HCOO$^-$ and CO$_2$.18

![Fig. 2](image-url)

**Fig. 2** (A) Formic acid formation as a function of time under different pH conditions; (B) representation of reactants on both the (001) and (111) surfaces as a function of the solution pH, binding energies ($E_B$) provided as inset; (C) potential energy surface for the mechanism of HCO$_3^-$ reduction to HCOOH on the Fe$_3$S$_4$(111). Adsorbed intermediate species are denoted by * and their proposed structures are shown as insets in the figure.
However, the energy barriers are expected to decrease with applied negative electrode potential, and the model therefore represents the ‘worst case scenario’ for the energy barriers that need to be overcome in the conversion of HCO\textsubscript{3}\textsuperscript{−} to formic acid.

Fig. 2C shows the computed thermodynamic and kinetic energy profile for the reduction of HCO\textsubscript{3}\textsuperscript{−} on the (111) surface. As described above, adsorption of water onto the (111) surface releases 0.56 eV per molecule, although the energy barrier to dissociate the molecule to generate the surface H atoms and OH is calculated to be 0.94 eV. HCO\textsubscript{3}\textsuperscript{−} binds favorably with the surface with $E_b = \text{−1.63 eV}$ to give HCO\textsubscript{2}*, which further reacts with a co-adsorbed H atoms to release $\text{H}_2\text{O}$, requiring 1.31 eV to overcome the energy barrier. Although this is a substantial barrier, we postulate that if the system is not immediately equilibrated this barrier can be overcome by the energy released in the preceding adsorption step. An additional energy input of 0.36 eV is then required to activate CO\textsubscript{2}* to a bent geometry (OCO\textsuperscript{*}), where both O and C interact with Fe and S surface atoms, respectively. This structure is stabilized by neighboring adsorbed H atoms, as shown in Fig. 2C inset. Hydrogenation of OCO\textsuperscript{*} on the carbon atom results in intermediate a1 (HCOO\textsuperscript{*}) and addition of a further H atom finally leads to formation of formic acid. Formic acid is bound to the surface ($E_b = \text{−1.10 eV}$) and some energy is required to release the formic acid into solution.

The computed reaction profile shows that from the zero energy starting point the transformation of HCO\textsubscript{3}\textsuperscript{−} into formic acid is thermodynamically and kinetically favorable. The reaction is driven by the energy released by thermodynamically favorable steps such as adsorption of the HCO\textsubscript{3}\textsuperscript{−} and generation of the formate (a1) on the (111) surface. However, for the reaction to proceed, H ad-atoms are required on the surface, which requires an energy input of 0.94 eV from adsorbed molecular water. In our experiments, we have applied a modest over-potential of up to 1.1 eV, which is more than sufficient to generate the H ad-atoms required for this reaction. Thus, the calculations reveal a feasible mechanism for the production of formic acid under the moderate experimental conditions employed.

In addition to formic acid, other reaction products were experimentally detected under the three pH conditions investigated, as shown in Fig. 3A–C. At pH 4.5, low concentrations of acetic acid and methanol were detected, in accord with the low production of formic acid. On increasing the pH to 6.5, acetic acid, methanol and pyruvic acid were all detected in higher concentrations. At pH 10.5, the only additional product to formic acid is acetic acid, in intermediate concentrations. The concentrations of the products have been justified earlier, when we considered the concentration of HCO\textsubscript{3}\textsuperscript{−} in solution. The disparity in the reduced products at varying pH can be accounted for by considering viable routes to methanol production. The overall faradaic efficiency for the production of formic, acetic, and pyruvic acid and methanol is calculated to be ca. 8% at pH 6.5.

Calculated reaction profiles reveal energetically feasible routes for methanol production, shown in Fig. 3D. The initial energetic profile is synonymous with that for formic acid production from HCO\textsubscript{3}\textsuperscript{−} on the Fe\textsubscript{3}S\textsubscript{4}(111) surface (Fig. 2C), leading to the activated, bent OCO\textsuperscript{*} intermediate. At this point, hydrogenation of the carbon atom eventually leads to formic acid, but an alternative route is hydrogenation of an oxygen atom to give intermediate b1 (COOH\textsuperscript{*}). Although intermediate a1 is more stable thermodynamically than b1, by 1.1 eV, the difference between their transition states is only 0.1 eV, suggesting that both processes may take place competitively. Exothermic hydrogenation of the OH group of b1 leads to free $\text{H}_2\text{O}$ and CO\textsuperscript{*} bound to Fe (b2). This intermediate is reduced to b3 (HCO\textsuperscript{*}) after overcoming an energy barrier of 0.7 eV. At this stage, oxygen is preferentially hydrogenated, leading to b4 (HCOH\textsuperscript{*}). Further hydrogenation of carbon leads to CH\textsubscript{3}OH, under a thermodynamic driving force (0.8 eV); although the transition state is 1.1 eV above the previous intermediate. Finally, a 1.2 eV barrier must be overcome for the final hydrogenation step to produce methanol (CH\textsubscript{3}OH\textsuperscript{*}). Similar to the reaction pathway to form formic acid, the calculated reaction profiles suggest that methanol production is kinetically and thermodynamically favorable.

The formation of products such as acetic and pyruvic acid is explained by the slow process of releasing methanol into the solution, the activation barrier of b4 to b5 to methanol, as well as the endothermic nature of the final step. Consequently, b4 and b5 and methanol compounds accumulate on the surface where they can participate in coupling reactions to generate acetic or pyruvic acid. At low pH, however, a large amount of H is available on the surface, preventing significant coverage by b4 and b5, whereas at lower coverage of H ad-atoms (pH 10.5), the adsorbed CH\textsubscript{3}OH is more likely to undergo a dehydration reaction with formic acid to produce acetic acid. Formation of pyruvic acid at pH 6.5 is proposed to be the result from the dehydration of acetic acid and formic acid, which were present in higher concentrations at this pH. The relatively low concentrations of formic and acetic acid at pH 4.5 and 10.5 reduced the likelihood of pyruvic acid formation, which was hence not observed under these conditions.

This study has shown that the iron sulfide mineral greigite is able to promote the formation of small soluble organic molecules.
from CO₂ in aqueous solution on application of a relatively small potential and under mild conditions. We found that pH 6.5 is the optimum pH for the effective reduction of dissolved CO₂ at the greigite surface, with soluble organic molecules formed at an 8% faradaic efficiency. When we relate this pH to the acidic and alkaline hydrothermal vents on the ocean floor, only the alkaline hydrothermal vents provide the environment where this pH can be achieved, when considering their effluents at pH 10 mixing with the primordial ocean of pH 5.5.19 We note that a alkaline hydrothermal vent systems on the ocean floor, only the faradaic efficiency. When we relate this pH to the acidic and could contribute about one volt to the overall system,3 beside the tion between minerals surface and coupled redox processes that could contribute about one volt to the overall system, besides the pH and temperature gradients which contribute ~ 300 millivolts.8,20 Similarly, chemi-osmotic gradients are required for both modern acetogenesis and methanogenesis, suggesting that ancient processes may have used chemi-osmotic coupling mechanisms naturally existing at alkaline vents.21 Moreover, as shown by others, the products obtained in our study can be transformed into key interactions between mineral surfaces and coupled redox processes that could contribute about one volt to the overall system,3 beside the pH and temperature gradients which contribute ~ 300 millivolts.8,20 Similarly, chemi-osmotic gradients are required for both modern acetogenesis and methanogenesis, suggesting that ancient processes may have used chemi-osmotic coupling mechanisms naturally existing at alkaline vents.21 Moreover, as shown by others, the products obtained in our study can be transformed into key biomolecules through reaction with ammonia and phosphates, reactants which are reported to be present around such vent systems.21,22 Thus, our combined experimental and computational study provides evidence that the crucial first step in this pathway from CO₂ to biomolecules is feasible, and it therefore strongly supports the hypothesis that alkaline hydrothermal vent systems provided one possible environment for the pre-biotic chemistry preceding the onset of life.

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Note and references


