

A ROUTE TO INORGANIC CARBON FIXATION IN ALKALINE HYDROTHERMAL VENTS.

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Introduction: Alkaline hydrothermal vents are natural, far-from-equilibrium electrochemical flow reactors that could be hatcheries for the origin of life [1]. Hadean oceans rich in dissolved CO₂ were acidic (pH 5-6) and ferruginous, while alkaline vents introduced warm (70-90°C), alkaline (pH 9-11) fluids with ~50 mM H₂ [2]. Early vents were likely microporous, with thin, inorganic barriers containing catalytic semiconducting Fe(Ni)S minerals, intersecting large pH, redox and temperature gradients [1]. Natural proton gradients across thin inorganic barriers are analogous to the proton-motive force powers all autotrophic cells today [3]. The reduction potential of H₂ at pH 10 should theoretically drive CO₂ reduction to formaldehyde at pH 6, driving abiotic carbon and energy metabolism via the reactive intermediates methyl thioacetate and acetyl phosphate [4]. In experimental investigations of this theory we have precipitated dynamic catalytic Fe(Ni)S chimney structures under anoxic conditions (examined using SEM and TEM) which show crystalline structures with unit cell dimensions comparable to mackinawite. We have also shown the reduction of CO₂ is possible under simulated vent conditions by detection of low amounts of formate and formaldehyde over 4 hours, detected by GC-MS analysis [5].

Further investigation of this process shows the CO₂ reduction takes place on the precipitate but also that the reduction products, particularly formaldehyde, remain preferentially attached to the precipitate surface rather than released into the bulk fluids (Figure 1). The reduction mechanism was confirmed using ¹³C labelled bicarbonate as a source of CO₂ in our experiments. We have observed the formation of a range of sugars via the formose reaction in the presence of Ca²⁺ including both ribose and deoxyribose from formaldehyde alone. We show the route to production of acetyl phosphate, an activated phosphorus species which can undertake the phosphorylation of ribose and, nucleosides. We demonstrate experimentally the capacity of alkaline hydrothermal systems to fix organic carbon from CO₂ and H₂ in the presence of natural proton gradients and catalytic Fe(Ni)S precipitates providing a plausible route into chemical evolution and life.

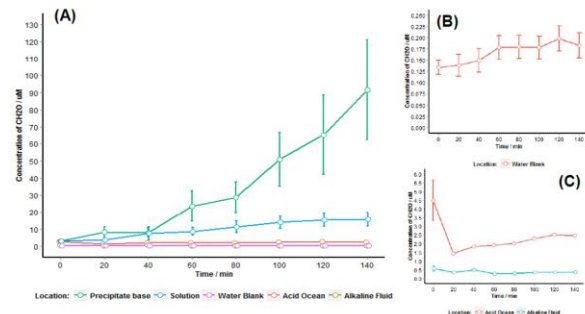


Figure 1. (A) Average concentration of derivatised CH₂O (PFBOA formaldoxime) sampled over 9 reactor runs. FeS precipitate and acid solution reactor samples were diluted one hundred-, ten- and two-fold in 3, 4 and 2 reactor runs, respectively. (B) Average concentrations of CH₂O in water blanks. (C) Undiluted acid ocean and alkaline hydrothermal fluid controls collected from a single reactor run. Error bars represent mean ± standard error of the mean (SEM).

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