Prebiotic Chemistry and Habitability in Serpentinizing Hydrothermal Systems on Early Earth and Other Worlds

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Serpentinization environments generate free energy driven by redox, pH, chemical, and thermal gradients; these gradients are known to sustain life in hydrothermal systems and may be significant for the emergence of life on Earth. Serpentinization has likely occurred on Mars and similar hydrothermal systems may also be present on ocean worlds such as Europa and Enceladus, and therefore are of great interest to astrobiologists in the search for life. Hydrothermal sediments and chimney precipitates in hydrothermal systems on the early Earth could have contained reactive minerals such as iron (-nickel) sulfides and iron oxyhydroxides. Behaving like flow-through chemical reactors, these mineral precipitates may have promoted various reactions towards the emergence of life including amino acid synthesis, concentration and retention of organic products, phosphorus redox and polymerization, and rudimentary energetic processes by electrochemistry. In vents today, and perhaps on the early Earth and / or other worlds, the precipitation of electrically active or reactive minerals can create geological fuel cell systems that may support life via electron transfer processes. We have utilized various experimental systems for simulating physicochemical gradients and geochemical redox reactions in serpentinizing systems, including the formation and characterization of simulated hydrothermal chimneys, synthesis of reactive hydrothermal sediments over a range of pH / redox states, and use of fuel cells as planetary habitability test-beds to simulate redox geochemistry of vents. I will discuss these experimental approaches for simulating astrobiologically relevant chemistry in hydrothermal vents, as well as how understanding serpentinization is significant for the search for life on other worlds.
A seawater throttle on hydrothermal Fe oxidation in the ancient oceanic lithosphere

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Fe oxidation and coupled hydrogen (H₂) generation during seafloor serpentinization are thought to have provided a principle feedstock for earth’s earliest lifeforms and a pivotal counterbalance to photosynthetic oxygen (O₂) production following its metabolic evolution. However, the effect of differing ancient seawater chemistry on these fluxes and their seafloor expression remain unexplored, due to historically limited constraints on ancient seawater chemistry and the common assumption that seafloor hydrothermal systems are lithologically dominated rather than hydrogeochemically mediated. In recent years, however, quantitative estimates of the makeup of paleoseawater have increasingly come into focus¹⁻³ as field and experimental measurements have demonstrated important kinetic limitations on serpentinization reactions at temperatures representative of modern off-axis hydrothermal systems⁴. Here, we integrate recently published constraints on ancient seawater chemistry together with kinetic, thermodynamic and crystallographic constraints on water-rock interaction and redox evolution into a reactive transport model of early earth serpentinization. The results indicate that the chemical characteristics of ancient seawater would have limited the extent of Fe oxidation during serpentinization. This “seawater throttle” on Fe oxidation during serpentinization would have diminished the fluxes of H₂ from the oceanic lithosphere, with various implications for the coupled evolution of the planet’s early biosphere and atmosphere. Although the rock record available for comparison is limited, these calculations qualitatively agree with observations from this time.

Natural Hydrogen systems in continental environment: Redox conditions and carbon interaction

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The occurrence of hydrogen has been known in oceanic environments (mid-oceanic ridges and slices of oceanic crust preserved in mountain chains), and more recently in the middle of continents in larger and easily producible amounts. Drilling success of four natural hydrogen exploration wells in Mali in 2017 around the initial discovery has drawn attention to future world industrial potential. The H\(_2\) accumulations found originally looking for water in 1987 and was at shallow depths (100m) that means low drilling costs. The H\(_2\) is now burn to produce electricity. It seems that the most promising geological areas in continents are neo-Proterozoic rocks, with very low organic carbon content and reducing sedimentation conditions. It could be demonstrated that the presence of organic carbon reduces the time life of H\(_2\), as it is almost immediately reacting with carbon to generate hydrocarbon compounds, mainly methane.

This paper will also discuss the production mechanisms that are likely involved in the process of hydrogen generation. The feasibility of hydrogen generation in geological settings involves two major sources of natural H\(_2\): water reduction with ferrous iron as the reducing agent, and ammonium ions decomposition in metapelites, generating H\(_2\) and N\(_2\) in reducing environments. The proportion of N\(_2\) (between 1 to 100\%), correlated with high helium concentrations (up to 3\%) would indicate the relative importance of ammonium decomposition as well as the Redox conditions in the kitchen of generation.
The role of ammonium in native H$_2$ production in continental lithosphere

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Following the discovery of hydrogen seepages within the continental lithosphere, discovered earlier at mid-oceanic ridges, questions have arisen concerning (i) the origin of this gas, (ii) the mechanisms for such production, and (iii) the conditions of preservation during its migration, since H$_2$ is known for its rapid diffusion and high reactivity.

In these intracratonic environments, the prevalent H$_2$ generation hypotheses are the radiolysis of water or/and its reduction by ferrous iron from ultrabasic rocks in the deep basement, over geologic time scale. Nevertheless, the covariation of nitrogen with hydrogen seems to emphasize a common origin for both gases. H$_2$/N$_2$ natural seepages are commonly associated in continental contexts with the occurrences of ultrabasics rocks, related to the presence of an ophiolitic belt or an aborted rift, and sediments. Within the continental lithosphere, nitrogen is predominantly present under the form of ammonium (within clay minerals, or micas in granitic rocks) or in the form of N-rich organic mater. However, organic mater is uncommon in basement rocks and ammonium could therefore play an important role in both H$_2$ and N$_2$ formation in intracontinental context.

In order to understand the interactions between NH$_4^+$ present in sediments and ferrous iron in ultrabasic rocks, as well as their implications for natural H$_2$/N$_2$ generation, analogic water-rock interactions experiments were carried out. Multiple runs mixing various ratios of FeO and NH$_4$Cl were conducted in gold tubes placed within a batch reactor for 3 weeks, at 150°C or 300°C, and 200 bars. Analyses of the gas, water and powder composition were performed after the reaction through GC, IDP-OES, SEM and XRD.

The results of these experiments bring back into question the role of NH$_4^+$ as the source for direct H$_2$ production. This study highlights the implication of NH$_4$Cl as a possible catalyst in the reduction of H$_2$O and the FeO oxidation.
Production of H$_2$ on Mars Through Radiolysis and Implications for Habitability

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Protected from harmful radiation, subfreezing temperatures, and low pressures, subsurface rock-hosted habitats likely provide a sustainable refugia for microbial ecosystems inside small rocky planets, such as ancient Mars. On Earth, subsurface microbial ecosystems are widespread in both marine and terrestrial sediment and crust. Subsurface life requires energy to sustain metabolic activity. For many chemolithotrophic communities on Earth, water-rock alteration reactions have been shown to produce the key electron donors and acceptors necessary to sustain microbial life on geologic timescales. In this study we quantitatively demonstrate that radiolysis likely generated sufficient concentrations of dissolved H$_2$ to sustain microbial communities in the subsurface during Mars’ early history prior to 3.5 Gyr. When considering an environment with H$_2$O groundwater, dissolved H$_2$ concentrations range from 0-253.9 µM in a cold early Mars climate scenario and 0-205.2 µM in a warm early Mars climate scenario, while when considering an environment with eutectic NaCl brine groundwater, dissolved H$_2$ concentrations range from 0-349.9 µM in a cold early Mars climate scenario and 0-282.9 µM in a warm early Mars climate scenario, with higher dissolved concentrations near the surface in both cases. Radiolytic H$_2$ likely produced $[1.28-4.79] \times 10^{10}$ moles H$_2$ per year globally during the Noachian depending on the assumed surface porosity and groundwater composition. We demonstrate that the region immediately beneath a cryosphere likely contained dissolved H$_2$ concentrations and temperatures suitable for life regardless of the background climate scenario, making it the most consistently habitable environment on ancient Mars in terms of reductant availability. Modern access to this zone in the ejecta and uplifts of relative recent impacts makes it an intriguing astrobiological target for testing the subsurface biosphere hypothesis.
A pyroclastic protolith for the most widespread carbonate- and serpentine-bearing ultramafic rock on the martian surface

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The origins of olivine-rich ultramafic rocks on the martian surface and the geologic context of their aqueous alteration to serpentine, Mg-carbonate, and other minerals remain poorly constrained. Previous origin hypotheses for these serpentinized ultramafic protoliths include emplacement as basement intrusions [1], melt from large impact events [2], and flood lavas [3]. We evaluate the protolith origin of the ~70,000 km² Circum-Isidis olivine-rich unit, which is ~3.7 Ga in age [2] and locally altered to Mg-carbonate (~10%) and serpentine [4], by synthesizing 1:50,000-scale geologic mapping and quantitative geomorphology of >100 unit outcrops with previous physical and orbital spectroscopic modeling. Our observations and measurements of the unit’s stratigraphy, thickness, internal banding, and orientation indicate that the unit was likely an ash-fall deposit from Syrtis Major, consistent with previous modeling and spectroscopy.

The cold emplacement temperatures of martian distal tephra deposits rule out internally-sourced heat for serpentinization within the unit or the diverse alteration mineralogy observed in underlying rock units. The high permeability and porosity of clastic rocks, generally, and the high specific surface area of pyroclasts, specifically, suggests that lesser volumes of water may have been necessary to produce the serpentine and carbonate minerals detected spectroscopically from orbit. In conjunction with partially carbonated ultramafic pyroclasts observed in situ at Columbia Hills [5] and the absence of aqueous alteration minerals in massive olivine-rich ejecta of Argyre and Hellas, our work suggests that the protolith textures of clastic ultramafic rocks may be a primary control on the water-limited serpentinization and carbonation of the martian crust.

Abiogenic formation of short-chain organic compounds within a serpentinite mud volcano over the Marianna Trench (IODP Exp. 366)

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The only known active serpentinite-hosting mud volcanoes, located in the Marianna forearc subduction zone, were drilled during IODP Expedition 366. Recovered samples from Asüt Tesoru seamount provide new insights on the generation of organic matter from fluid-rock interactions in deep oceanic environments, through Fischer-Tropsch-Type (FTT) reactions. The reduction of water by ferrous iron produces hyperalkaline pore fluids (pH 12.5) rich in H₂ (up to 2 mM), prone to react with accompanying DIC (up to 4.5 mM). High amounts of sulfide/oxide minerals observed within the mud may have catalyzed the reaction. This situation is ideal to produce carbon species like volatile fatty acids (VFAs), short-chain alcohols, and light hydrocarbons.

We acquired the full set of stable carbon isotope information of those compounds. VFAs are mostly composed of formate and acetate (up to 100 and 40 µM), associated with methanol (up to 30 µM). These short-chain components have extreme carbon isotope compositions, with heavy δ¹³C values of up to +4.8‰ for formate, -8.0‰ for acetate and +2.3‰ for methanol, strongly suggesting an abiogenic origin and formation during CO₂ reduction with H₂. The gas phase of the serpentine mud is composed of a mix of H₂ and CH₄ (up to 95%). Associated molecular composition monitored via C¹/C²+ ratios barely varies down to 100 mbsf, implying low or even absent microbial activity. Corresponding δ¹³C values of methane as positive as -16 ‰ are in good agreement with reported abiogenic values. In addition, measured ³He concentration and extrapolated ³He/CO₂ ratios suggest a primarily mantle-derived inorganic carbon source. The fractionation between the δD values of CH₄, H₂ and H₂O was also measured, and can be used to discuss potential temperature formation conditions at isotopic equilibrium.

Our dataset thus points to the abiogenic formation of low molecular weight organic compounds in the Marianna’s mud volcanoes. Furthermore, it brings new constraints on the reaction pathways leading to the formation of precursor molecules essential to life in serpentinizing environments.
Formation processes of methane in submarine mud-volcanoes from the Marianna trench (IODP Exp. 366)

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Active serpentine mud volcanoes located on the overlying plate in the Mariana subduction fore-arc are unique geological features. Hydrogen and methane (among other volatile species) are locally produced within the serpentinite, the latter being a potential byproduct of deep microbial activity. Alternatively, these species could have been produced abiotically, for instance during Fischer-Tropsch type (FTT) reactions.

IODP expedition 366 (dec. 2016-feb. 2017) on the Mariannas convergent margin recovered a suite of core drills and associated pore fluids from three serpentine mud volcanoes. In order to determine the contribution of biogenic and abiotic gases, we measured the abundances of doubly-substituted methane isotologues, $^{13}$CH$_3$D and $^{12}$CH$_2$D$_2$ in 10 gas samples from the Asút Tesoru seamount. The samples are from three different drill cores and have been collected at depth ranging between 1 and 100 meters below the sea-floor. Measurements were performed using the Panorama (Nu-Instruments) mass spectrometer at UCLA, using a mass resolving power of ~40,000.

The $\delta^{13}$C and $\delta^D$ values range between -5 and -23.6‰ ($\pm$0.1‰, vs. PDB) and between -95 and -112‰ ($\pm$2‰, vs. SMOW) respectively. The abundances of clumped isotopologues show small but significant variations: $\Delta^{13}$CH$_3$D values range between 2.3 and 4.3‰ ($\pm0.2‰$) and $\Delta^{12}$CH$_2$D$_2$ range between 9.7 and 11.7‰ ($\pm0.8‰$).

If formed under thermodynamic equilibrium, the temperatures derived from the abundance of $\Delta^{13}$CH$_3$D would range between +120 and 220°C. However, all samples display small but significant $\Delta^{12}$CH$_2$D$_2$ enrichments or depletions at a given $\Delta^{13}$CH$_3$D value, relative to values predicted for equilibrium. These disquilibriums range between -2 and +5‰, indicating that mixing or mass fractionation had occurred during or after the formation of methane in the Mariannas mud volcanoes. However, no simple combination of methane formed at high- (250-300°C) and low-temperature (< 90°C) can account for the observed gas compositions. As an alternative, preliminary interpretations involve isotope mass fractionation of methane within the serpentinite volcanoes.
Abiotic methane in HP ophicarbonates from Chinese southwestern Tianshan: Implications for immiscible hydrocarbon fluids in subduction zones

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Subduction zones play a significant role in the deep carbon cycle – they carry carbon at the surface into the deep mantle, as well as documenting the mechanisms of mobility and precipitation of carbonic fluids from subducted slabs. Previous researches are mainly focused on carbonates to shed light on the behaviours of COH fluids from subducted slabs while investigations of hydrocarbon fluids have long been overlooked. The abiotic methane, uncommonly formed at subduction zones, may control the redox state of the mantle and provide insight into the mechanisms of carbon mobility in the deep\textsuperscript{[1]}. Here, we have recognized numerous dolomite-hosted methane-bearing fluid inclusions in HP ophicarbonates from Chinese southwestern Tianshan. We propose that the massive production of abiotic methane at reduced conditions is responsible for the abnormally high carbon isotopes of dolomites ($\delta^{13}$C = +9.2‰ ~ +11.5‰) while the olivines from HP ophicarbonates (and surrounding UHP serpentinites\textsuperscript{[2]}) may provide potential H\textsubscript{2} for the reduction. We suggest that the abiotic methane was formed during retrogression, which is also evidenced by the transition of antigorite to lizardite in the hosting HP ophicarbonates. However, the recognition of the decarbonation reaction (Dol+H\textsubscript{2}O→Cal+Brc+CO\textsubscript{2}), also documented in HP ophicarbonates without abiotic methane from the same study area, may indicate the increasingly oxidized environments. The transition from reduction to oxidation during exhumation may be attributed to the limited olivines in the ultramafics.

It is the first time to report abiotic methanogenesis during exhumation in subduction zones, contributing to comprehend the redox state and mechanisms of carbon mobility during uplift of the subducted slabs.

Mantle metasomatism in subduction zones: insight from in-situ B isotopes

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The sources of fluid responsible for mantle metasomatism are difficult to identify, but likely can be inferred based on B isotopes and B content of serpentinites. Hence, serpentinites have been selected worldwide to better constrain the B isotopic signature of the different fluid sources affecting the mantle. The δ¹¹B of serpentinites coming from ophiolite (Cuba, Iran) range from +1 to +18‰, whereas samples from suture zones display contrasted values. Samples coming from the deep mantle wedge (Iran) have significantly negative to moderately positive δ¹¹B (-7 to +8‰), whereas samples from forearc (Nicaragua and Japan) have intermediate values (0 to +13‰). Sample coming from the mantle underneath the slab (Corsica and Alps) have significantly positive δ¹¹B, ranging from +14 to +34‰. By comparing these values obtained in-situ with published whole-rock values, both on subduction-related serpentinites and on current seafloor serpentinites, it appears that the ophiolitic serpentinites measured in this study are in agreement with values published on Oman, and the fluids responsible for metasomatism is a mixture of seawater and low-grade metamorphic fluids. For suture zones serpentinites, the negative values are only encountered in serpentinites from deep mantle wedge (Iran), and are in good agreement with metamorphic fluids released from metabasites sampled next to these serpentinites. Such negative values have already been observed in mantle wedge samples from Guatemala. Intermediate δ¹¹B observed in Japan and Nicaragua represent serpentinitization by low-grade metamorphic fluid occurring in the forearc (i.e. at shallow depths) during subduction. This hypothesis is also supported by the δ¹¹B of low-grade metabasites and metasediments in contact with these serpentinites, which are in agreement with the release of a fluid with a moderately positive δ¹¹B. Finally, serpentinites from the mantle underneath the slab (Corsica and Alps) display strongly positive δ¹¹B, in the same range of what is observed for current seafloor serpentinites, indicating that serpentinitization occurred during seafloor residency, and that the seawater-derived signature is preserved through subduction event.
Evaluation of physico-chemical characteristics of thermal spring water of Odisha, India

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The Indian state of Odisha has 8 thermal springs, namely, Attri, Tarabalo, Deulajhari, Taptapani, Bankhol, Badaberena, Magarmuhan and Boden. To observe the seasonal changes in physico-chemical characteristics, thermal spring water samples were collected during pre-monsoon, monsoon and post-monsoon seasons. The water discharging from these springs shows moderately acidic to moderately alkaline character (pH: 5.05–8.93) and the surface temperature ranges from 28 °C (Boden) to 58 °C (Tarabalo). Total dissolved solids (TDS) also shows a wide variation between 16.9 (Bankhol) and 595 mg/L (Deulajhari). The water mainly is distinguished into 3 types: Na-Cl, Na-HCO₃ and Ca-HCO₃ type. The thermal water from Attri, Tarabalo and Deuljhori belong to Na-Cl type. Higher Na and Cl concentration along with lower Mg, K and Li content indicate that the water is circulated through granite rocks. The higher F content (3.88 to 12.2 mg/L) in these thermal springs further conforms that water composition is evolved from the interaction with granitic rocks. Due to lower calcium concentrations, the water does not reach the solubility product of fluorite resulting in higher concentration [1]. In Bankhol and Magarmuhan, the discharging thermal water belongs to Ca–HCO₃ water type. The water from these thermal springs is poorly mineralized and has lower TDS values ranging between 16.9 and 20.9 mg/L. Shorter resident time in the subsurface coupled with heavy mixing with the shallow groundwater may cause the lowering of the TDS content [2]. The thermal spring water showing Na/Ca–HCO₃ type characteristics are a typical indicator of shallow groundwater. This suggests prominent mixing of shallow water which is believed to have been circulated within the alluvium or sedimentary formations with the ascending thermal water.

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