

ABIOTIC REDOX REACTIONS OF QUINONES DRIVEN BY OCEAN WORLD RELEVANT MINERALS.

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Introduction: Metabolism on Earth is a complex system that is dependent on various enzymes and cofactors to sustain life. Much like the origins of life on earth, how modern metabolism arose has many unanswered questions. Understanding these questions is critical for both understanding how life evolved on earth as well as where and how to search for life on other worlds. While enzymes play a large role in biological functions, they are considered too complex to have been present at the origins of life and previous studies have found many of the cofactors to be ancient and important during early prebiotic reactions [1]. One type of compound involved in many biological reactions as a cofactor are quinones. Quinone compounds are vital within many biological reduction/oxidation reactions. For example, Coenzyme Q10 or ubiquinone acts as an electron transporter in the Electron Transport Chain (ETC).

Minerals present in planetary environments are also found to play important roles in fundamental biological reactions. Elements such as Fe are known to play an important role in many proteins observed in a wide range of metabolic reactions, in addition to being abundant in a variety of planetary settings including the early Earth, Mars, and possibly ocean worlds [2–6]. It has also been noted that FeS minerals can be similar in structure to biological Fe-S clusters which are also redox-active cofactors in metabolic reactions [7,8].

Hydrothermal systems are thought to be present in Europa's subsurface ocean [9,10], creating an important environment for astrobiological study. Additionally, Early earth oceans likely contained FeS minerals at hydrothermal settings [11]. As hydrothermal vents are also thought to be present on Enceladus [12], the environment might be similar. With FeS minerals likely present on both early Earth and Europa [5,11], investigating the reactions incorporating Fe can be useful in astrobiological studies, as understanding these mineral's potential functions within prebiotic context can aid in biosignature detection and development [13].

In order to better constrain the origin of metabolism on Earth as well as apply that to the other worlds mentioned above, researchers have been exploring whether prebiotic reactions analogous to metabolism could be driven by reactive minerals or other geologically available components. In a previous study, it was demonstrated that another biological organic cofactor (NAD⁺) could be reduced by a simple FeS mineral, which is analogous to the biological system where NAD(H) is oxidized / reduced by electrons from Fe-S clusters and

other cofactors in the ETC [14]. Herein, we expand on these results by observing the ability of FeS minerals to reduce quinone structures as a prebiotic analog for the ETC cofactor Coenzyme Q10.

Methods: For our study, we utilized 1,4-benzoquinone at 100 mM as our ubiquinone analog along with various quantities of FeS mineral to generate hydroquinone in the resulting solutions. The FeS mineral was obtained from Sigma Aldrich and used without any additional purification. Control spectra of the benzoquinone (Figure 1) and hydroquinone (its reduced product) were taken prior to beginning reaction testing. Unless otherwise noted, all reactions were ran in a nitrogen filled Coy glovebox. Samples were taken at t = 0 h, 24 h, 1 week, 2 weeks, 3 weeks, and 4 weeks to observe reaction progression over time. These samples were frozen for analysis. Analysis of collected samples was then conducted with ¹³C and ¹H nuclear magnetic resonance (NMR) and UV-Vis. Post reaction, the mineral samples were collected and freeze dried for analysis.



Figure 1: Control sample of benzoquinone in DI water at t=0.

Results : ¹H NMR was used to observe the spectral difference between 1,4-benzoquinone and its reduced form hydroquinone. It was determined in control reactions that the benzoquinone was less stable than its reduced counterpart via NMR (Figure 2). Small values of hydroquinone within benzoquinone samples can be attributed to natural benzoquinone degradation. Nonetheless our control spectra still demonstrates the ability of our protocol to distinguish between both compounds in our samples.

Progress has been made in understanding the reactivity of benzoquinone with FeS mineral and these reactions have been analyzed by NMR as well. We hypothesize that reaction time will impact the yield of the resulting hydroquinone. Stirring and temperature will also be explored in this reaction, as the FeS mineral creates a heterogeneous reaction system.

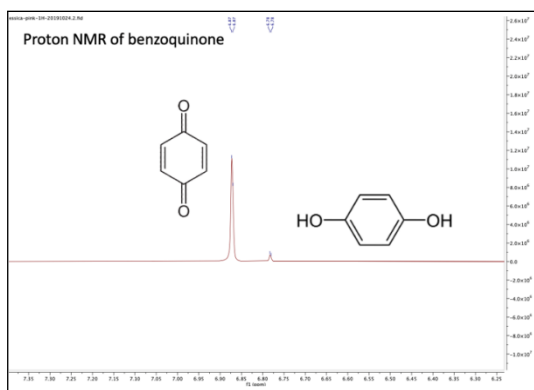


Figure 2: NMR spectra of control samples containing benzoquinone in DI water.

Conclusions: Our preliminary experiments have demonstrated that benzoquinone / hydroquinone – a prebiotic analog of the Coenzyme Q10 cofactor in biology – can undergo redox reactions with FeS minerals. In the biological electron transport chain, the transport of electrons from NADH to quinone is facilitated by a chain of enzymatic Fe-S clusters. Our work here and in previous studies [11] attempts to recapitulate a prebiotic version of this redox pathway using only geologically available components (FeS minerals and prebiotically available quinone structures). Understanding the potential for minerals to facilitate precursors to important biological reactions can provide vital information to understanding the origins of life on Earth as well as the possibility for prebiotic chemistry and the emergence of life on other worlds; understanding where and how prebiotic reactions can occur can help inform our target environments for astrobiological study as well as biosignature detection efforts [10]. Specifically on ocean worlds such as Enceladus and Europa where hydrothermal environments may be present and contain reactive metals / minerals, it is possible that prebiotic chemistry could have occurred in the past or perhaps even be ongoing today, yielding organics that might be detectable by future missions. Our future work will further investigate abiotic quinone (to benzoquinone) reduction reactions facilitated by FeS minerals in anoxic environments, and eventually, expand this to ocean world relevant conditions.

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