

Experimental ultraviolet (UV) photooxidation of ferrous iron and carbonate bearing solutions as an analog for sunlit water bodies on early Mars

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Ultraviolet (UV) photooxidation has been proposed as a pathway to oxidize iron(II) and influence the chemical conditions in early Martian surface aqueous environments. UV photooxidation has been invoked as the process that created jarosite-hematite deposits in Meridiani Planum [1,2] as well as the redox stratification inferred from iron oxide deposits in Gale Crater [3]. An understudied component of previous Mars-focused UV photochemistry studies is the influence of the presence of dissolved inorganic carbon (DIC) in solution. In this study, we examine UV photooxidation of ferrous iron (1.79 mM) and carbonate (35.0 mM) solutions under anoxic conditions at varying initial pH conditions for three hours. The experiments were conducted in open and closed system setups to evaluate and minimize the effect of CO₂ degassing. The open system experiments were conducted within a 1 L reaction vessel in which the Hg lamp was placed within an interior container and solution was collected at different time intervals. Closed system experiments were conducted within a fused quartz vessel that was completely sealed during the experiment. In the open system experiments we observed two mineral pathways with different initial pH conditions. At pH ~5.0, the solution acidified and iron (III) oxyhydroxides precipitated. At pH >5.5, the pH rapidly increased to ~9.2-9.5 and mixed valence iron minerals precipitated. With the closed system experiments, the change was limited to 0.02-0.9 pH units and minerals have been observed at pH>6.5, the mineralogy of which is not yet resolved. Chemical changes in open systems were affected principally by CO₂ degassing rather than UV photooxidation. When minimizing CO₂ degassing, the carbonate in solution buffers pH changes from UV irradiation and minimal photooxidation occurs, suggesting that Fe-DIC complex formation in solution may have the effect of preventing Fe-photooxidation, providing a mechanism that stabilizes Fe(II) in solution. Further examination of UV photooxidation of aqueous iron(II) chemistry and its products will aid in defining inorganic chemical conditions in early Mars surface waters.

References: [1] Hurowitz, J.A. et al. (2010) *Nat. Geo.*, 3(5), 323-326. [2] Nie, N.X. et al. (2017) *EPSL*, 458, 179-191. [3] Hurowitz, J.A. et al. (2017) *Science*, 356(6341).