Sulfidic Anion Concentration on Early Earth for Surficial Origins-of-Life Chemistry

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A key challenge in origin-of-life studies is determining the environmental conditions on early Earth under which abiogenesis occurred. While some constraints do exist (e.g. zircon evidence for surface liquid water), relatively few constraints exist on the abundances of trace chemical species, which are relevant to assessing the plausibility and guiding the development of postulated prebiotic chemical pathways which depend on these species. In this work, we combine literature photochemistry models with simple equilibrium chemistry calculations to place constraints on the plausible range of concentrations of sulfidic anions (HS^-, HSO_3^-, SO_3^{2-}) available in surficial aquatic reservoirs on early Earth due to outgassing of SO_2 and H_2S and their dissolution into small shallow surface water reservoirs like lakes. We find that this mechanism could have supplied prebiotically relevant levels of SO_2-derived anions, but not H_2S-derived anions. Radiative transfer modelling suggests UV light would have remained abundant on the planet surface for all but the largest volcanic explosions. We apply our results to the case study of the proposed prebiotic reaction network of Patel et al. (2015), and discuss the implications for improving its prebiotic plausibility. In general, epochs of moderately high volcanism could have been especially conducive to cyanosulfidic prebiotic chemistry. Our work can be similarly applied to assess and improve the prebiotic plausibility of other postulated surficial prebiotic chemistries that are sensitive to sulfidic anions, and our methods adapted to study other atmospherically-derived trace species.

[1] Patel et al. (2015), *Nat. Chem.* 7, 301.

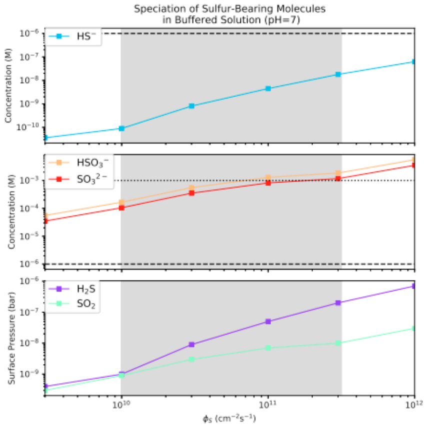

Figure 1: Speciation of sulfur-bearing molecules in an aqueous reservoir buffered to pH=7 as a function of total sulfur emission flux Φ_s. Horizontal dashed and dotted lines demarcate micromolar and millimolar concentrations,