

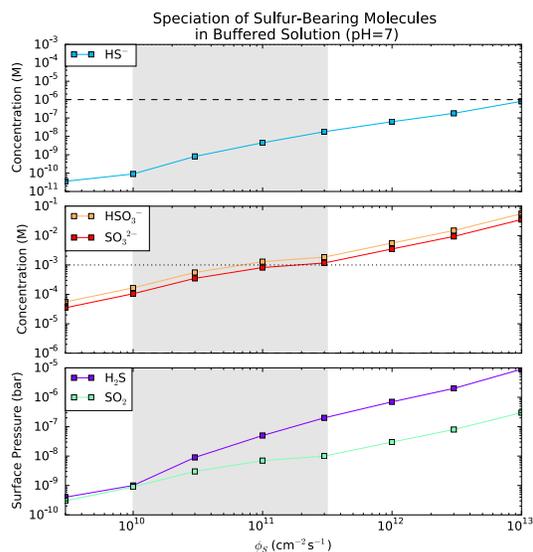
Planetary Sources for Reducing Sulfur Compounds for Cyanosulfidic Origins of Life Chemistry. S. Ranjan^{1,5}, Z. Todd², J. Sutherland³, and D. D. Sasselov⁴. ¹Harvard-Smithsonian CfA, 60 Garden Street, Cambridge, MA 02138; sranjan@cfa.harvard.edu, ²Harvard-Smithsonian CfA, 60 Garden Street, Cambridge, MA 02138; zoe.todd@cfa.harvard.edu, ³MRC Laboratory of Molecular Biology, Francis Crick Avenue, Cambridge Biomedical Campus, Cambridge CB2 0QH, UK.; johns@mrc-lmb.cam.ac.uk, ⁴Harvard-Smithsonian CfA, 60 Garden Street, Cambridge, MA 02138; dsasselov@cfa.harvard.edu, ⁵MIT EAPS, 77 Massachusetts Ave., Cambridge, MA 02139

Introduction: A key challenge in origin-of-life studies is understanding the chemistry that lead to the origin of the key biomolecules of life, such as the components of nucleic acids, lipids, and proteins. Prebiotic reaction networks based upon reductive homologation of nitriles (e.g., [1,2], and sources therein), are building a tantalizing picture of sustained abiotic synthesis of activated ribonucleotides, amino acids, sugars, and lipid precursors under environmental conditions thought to have been available on early Earth. Sulfidic anions in aqueous solution (e.g., HS^- , HSO_3^-) under near-UV irradiation play important roles in these chemical pathways. However, the sources and availability of these anions on early Earth have not yet been quantitatively constrained. Here, we evaluate the potential for the atmosphere to serve as a source of sulfidic anions, via dissolution of volcanically-outgassed SO_2 and H_2S into water reservoirs.

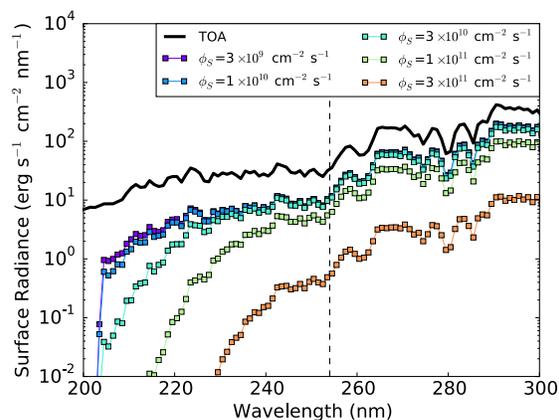
Methods: We combine photochemical modeling from the literature [3] with equilibrium chemistry calculations to place constraints on the partial pressures of SO_2 and H_2S required to reach the elevated concentrations of sulfidic anions ($\geq 1 \mu\text{M}$) thought to be necessary for prebiotic chemistry.

Results: We find that micromolar levels of SO_2 -derived anions (HSO_3^- , SO_3^{2-}) are possible through simple exposure of aqueous reservoirs like shallow lakes to the atmosphere, assuming total sulfur emission flux comparable to today. Millimolar levels of these compounds are available during the epochs of elevated volcanism, due to elevated sulfur emission flux. Radiative transfer modeling suggests the atmospheric sulfur will not block the near-UV radiation also required for the cyanosulfidic chemistry. However, H_2S -derived anions (e.g., HS^-) reach only sub-micromolar levels from atmospheric sources, meaning that prebiotic chemistry invoking such molecules must invoke specialized, local sources. Prebiotic chemistry invoking SO_2 -derived anions may be considered more robust than chemistry invoking H_2S -derived anions. In general, epochs of moderately high volcanism may have been especially conducive to cyanosulfidic prebiotic chemistry

References: [1] Patel B. H., et al. (2015) *Nat Chem*, 7, 301. [2] Xu J. et al. (2017) *Nat Chem*, 9, 303. [3] Hu R., et al. (2013) *ApJ*, 769, 6.



Speciation of sulfur-bearing molecules in an aqueous reservoir buffered to $\text{pH}=7$ as a function of total sulfur emission flux ϕ_S . The range of ϕ_S for emplacement of basaltic plains on Earth is shaded in grey. The horizontal dashed and dotted lines demarcate micromolar and millimolar concentrations, respectively.



UV surface radiance for the early Earth as a function of ϕ_S , using the models of [3]. The black solid line indicates the irradiation incident at the top of the atmosphere from the young Sun. The vertical dashed line demarcates 254 nm, the emission wavelength of the low-pressure mercury lamps commonly used in prebiotic chemistry studies.