

SULFIDIC ANION CONCENTRATIONS ON EARLY EARTH RELEVANT TO SURFICIAL PREBIOTIC CHEMISTRY. Sukrit Ranjan^{1,*}, Zoe R. Todd², John D. Sutherland³, and Dimitar D. Sasselov², ¹MIT, 77 Massachusetts Avenue, Cambridge, MA 02139; sukrit@mit.edu, ²Harvard University, 60 Garden Street, Cambridge, MA 02138, ³MRC Laboratory of Molecular Biology, Francis Crick Avenue, Cambridge CB2 0QH, UK, *SCOL Postdoctoral Fellow.

Introduction: A key challenge in origin-of-life studies is determining the environmental conditions on early Earth under which abiogenesis occurred [1]. 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 molecules.

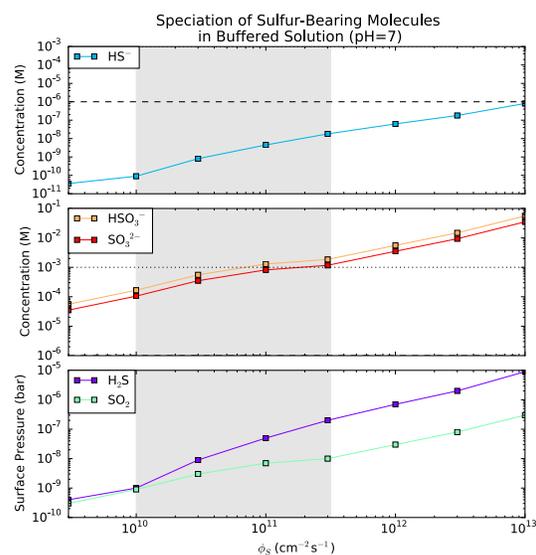
Sulfidic anions (S-anions; HS⁻, HSO₃⁻, SO₃²⁻) are a key family of molecules which are invoked in diverse prebiotic chemistries, from the synthesis of ribonucleotides, to the accumulation of carbohydrates, to the emergence of protometabolism [2,3,4]. However, the general availability of S-anions in terrestrial settings on prebiotic Earth has not been constrained.

Here, we use simple kinetic and equilibrium chemistry calculations to constrain the plausible range of concentrations of S-anions in terrestrial reservoirs on prebiotic Earth. We explore the implications for postulated prebiotic chemistries, and consider the consequences for laboratory studies of abiogenesis.

Methods: We consider the atmosphere as a source of S-anions, via volcanic outgassing of SO₂ and H₂S and their dissolution into shallow aqueous bodies in accordance with Henry's Law. We use literature photochemical modelling to estimate the atmospheric concentrations of SO₂ and H₂S under both steady-state conditions and during epochs of enhanced volcanism like the emplacement of basaltic plains [5]. We conduct equilibrium and kinetic steady-state calculations to constrain the accumulation of these molecules in shallow lakes and ponds and their subsequent speciation as S-anions. Atmospheric sulfur is a potential UV shield; we use two-stream radiative transfer models to estimate the coterminous UV irradiation [6]. Our codes are available for validation and extension at <https://github.com/sukritranjan/>.

Results: We find that the atmosphere supplied prebiotically-relevant levels ($\geq 1 \mu\text{M}$) of SO₂-derived anions (HSO₃⁻, SO₃²⁻; sulfites) to shallow aqueous reservoirs on early Earth, but not H₂S-derived anions (HS⁻; sulfide) [6]. This is because of the lower solubility and unfavorable first dissociation of H₂S compared to SO₂. Prebiotic chemistries which require HS⁻ must invoke a local concentration mechanism. On the other

hand, HSO₃⁻ and SO₃²⁻ would have been robustly available on early Earth in shallow bodies of water exposed to the atmosphere. The concentrations of these molecules would have been especially high after large volcanic explosions.



Concentrations of H₂S, SO₂, and their derived S-anions in shallow surface reservoirs assumed buffered to neutral pH as a function of sulfur flux to the atmosphere from volcanism. We also considered unbuffered solutions; the conclusions were the same. The range of enhanced S-fluxes possible during intense volcanic events is shaded in grey. Micromolar concentrations are demarcated by a dashed line, and millimolar by a dotted line. From [6].

We explored the implications of our findings by applying them to the case study of the cyanosulfidic chemistry proposed for the prebiotic synthesis of the ribonucleotides and other biomolecules by [2]. Experimental studies find that sulfite not only substitutes for sulfide in this chemistry, but that the efficiency increases by an order of magnitude and the requirement for geologically-rare copper is eliminated in favor of geologically-common iron [7]. The UV light required to power this chemistry remains abundant for all but the very largest volcanic explosions. Overall, improving the prebiotic plausibility of the cyanosulfidic chemistry by substituting sulfite for sulfide improves the plausibility of the chemistry along two other axes as well.

Conclusions: Our work indicates that sulfite should have been common in shallow aqueous reservoirs on early Earth, but sulfide would have required a local source or concentration mechanism. Epochs of high volcanism would have been especially clement for S-anion dependent prebiotic chemistries. Applying these insights to the case study of [7] indicates that substituting the more plausible sulfite for sulfide improves the plausibility of the chemistry along two other axes as well, demonstrating the positive interplay between theory and experiment. Our work can be applied to assess and improve the prebiotic plausibility of other postulated S-anion-dependent surficial prebiotic, and our methods adapted to study other atmospherically-derived trace species.

References: [1] Ruiz-Mirazo K., Briones C., and de la Escosura A. (2014) *Chem. Rev.*, 114, 285–366. [2] Patel B. H. et al. (2015) *Nat. Chem.*, 7, 301-307. [3] Kawai J. et al. (2019) *Astrobiology.*, 19, 1-11. [4] Bonfio C. et al. (2017) *Nat. Chem.*, 9, 1229-1234. [5] Hu R., Seager S., and Bains W. (2013) *ApJ.* 769, 1-14. [6] Ranjan S. et al. (2018) *Astrobiolog.* 18, 1-18. [7] Xu J. et al. (2018), *Chem. Comm.*, 45, 5566-5569.