THE CHEMICAL DETAILS OF HOW LIFE COULD HAVE, WOULD HAVE, AND SHOULD HAVE STARTED ON MARS. S. A. Benner. Foundation for Applied Molecular Evolution, 13709 Progress Blvd., Alachua, FL 32615 USA

Introduction. Recent advances in our understanding of the prebiotic chemistry of RNA have come by a focus on paradoxes that make RNA a "prebiotic chemists nightmare". These include the easy ability of precursors of ribose (as well as ribose) to decompose to give tars, the challenge of making phosphate esters in water, the difficulty of making glycosidic bonds to join ribose to the nucleobases, and the difficulty of making nucleobases in the redox neutral atmosphere believed to have dominated early Earth and Earth-like planets such as Mars and Venus. This focus helps prevent our going down “rabbit holes” that become decreasingly relevant to the origins problem as we descend.

Seeking chemistry that could not possibly not have happened. Key to solving these paradoxes is a focus on “bespoke” chemistry unavoidable on a prebiotic Earth. For example, HCHO and, at ~ ppm, glycolaldehyde, must have been formed in Hadean atmospheres. It seems likewise indisputable that volcanism delivered SO_2 at nearly the same rate. Thus, it is impossible to avoid production of stable bisulfite addition products of these in aerosols [1]. Also unavoidable were aldol reactions to give higher carbohydrates that rained onto a surface containing oxidized minerals, including borate, that stabilized them.

Also unavoidable were phosphate anhydrides in semi-arid subaerial environments. The atmosphere, but not the mantle, would also have been unavoidably reduced, once or a few times prior to ~ 4.3 Ga, by metallic Fe and Ni delivered with late veneer elements via 10^{22}-10^{23} kg impactors. These unavoidably must have given precursors for nucleobases. Bespoke chemistry combines trimetaphosphate, ribose, and ammonia to give cyclic ribose phosphate, which (with Ni^{2+}) gives ribonucleosides, converted to ribonucleoside phosphates by Mg borophosphate minerals. Various silicates assemble and stabilize these to give oligomeric RNA. The combined models [1][2] have all of this likely complete before 4.25 Ga. The model lacks only provision for homochirality.

Mars shows some advantages. The unavoidable on Earth was also unavoidable on Mars. The Martian regolith contains key minerals (including borates, see the Nellessen *et al*.) whose presence has been doubted on earlier Earth. Mars volcanism also produced SO_2, and Mars likely suffered impacts that reduced its atmosphere, all with similar implications for the prebiotic formation of RNA on Mars.

The availability of dry land on the Hadean Earth is the largest source of uncertainty in this model. But Mars likely had more semi-arid subaerial surface than Earth, providing more opportunity for the necessary chemistry without dilution into a global ocean. Thus, if life emerged under an "RNA First" model, it was more likely to emerge on Mars via this bespoke chemistry. While the nucleobases and other details might well have been different, the Schrodinger and polyelectrolyte requirements would have been the same. This constrains the molecular biology of any Martian life that may have survived to the present.

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References: [1] Benner et al. (2019) When did life likely emerge on Earth with RNA first? ChemSysChem in press, arXiv2816362. [2] Mojzsis et al. (2019) Astrophys. J., 881, 44-56