

A NEW LESSON FROM TITAN: NITROGEN ISOTOPES AS A POSSIBLE RECORDER OF PREBIOTIC CHEMISTRY ON THE EARLY EARTH.

C. R. Glein¹, M. E. Colley², D. C. Catling³, and J. D. Toner³,
¹Southwest Research Institute (cglein@swri.edu), ²Department of Chemistry, University of Texas at San Antonio,
³Department of Earth and Space Sciences and Astrobiology Program, University of Washington.

Introduction: Hydrogen cyanide (HCN) is often recognized as a fundamental building block in the field of prebiotic chemistry. Miller [1] showed that HCN can be synthesized in methane-bearing atmospheres, and it was found that HCN combines with aldehydes to produce amino acids via the Strecker synthesis. HCN is also commonly implicated in the formation of heterocyclic nitrogen compounds, most notably the nucleobases in ribonucleic acid (RNA). Oró [2] showed that adenine can be synthesized in aqueous solutions of relatively concentrated HCN. These pioneering studies set the course of research for decades. Recent work by Saladino et al. [3] has emphasized the possible role of formamide (the hydration product of HCN) in the genesis of an RNA world [4]. Sutherland et al. [5] have focused on the essential role of cyanide in a systems chemistry framework for the origin of life.

While Titan is presently a very cold world, this may be beneficial in preserving its atmosphere in a chemically primitive state, which could bear some resemblance to the atmosphere of the prebiotic Earth. A common refrain is that Titan can serve as a natural laboratory for prebiotic chemistry on Earth [6]. While we hold an agnostic view with regards to this assertion, the possibility is of great enough interest to motivate the development of testable hypotheses linking novel aspects of Titan's atmospheric chemistry to the prebiotic Earth. Here, we introduce the idea, inspired by new data from Titan, that the first sign of the classic RNA world might be finding an anomalous enrichment of heavy organic nitrogen in old rocks/minerals.

Atmospheric synthesis of HCN: HCN is the most abundant nitrogen-bearing product of photochemistry in Titan's N₂-CH₄ atmosphere [7]. Making HCN requires N₂ to be dissociated. On Titan, there are two general ways to initiate the dissociation of N₂. The first is via the absorption of extreme ultraviolet (XUV) solar photons. Cosmic rays and magnetospheric electrons impact the atmosphere and can also cause N₂ to be dissociated. Atomic N derived from both of these processes can subsequently react with CH₃ or CH₂ from the photolysis of CH₄ to produce HCN. The HCN subsequently undergoes additional photochemistry in the atmosphere, or is delivered to the surface.

Such chemistry could have occurred in the prebiotic atmosphere of the Earth [8,9]. However, a key uncertainty is whether there would have been sufficient abiotic methane in the atmosphere to enable HCN production. One can envision a substantial geochemical

source of methane from more vigorous and ubiquitous submarine outgassing of ultramafic crust in the Hadean. If generated in sufficient quantities, HCN would have rained out, and participated in prebiotic chemistry possibly leading to the origin of an RNA world.

Nitrogen isotopic fractionation: One surprising discovery in Titan's atmosphere is that HCN is isotopically fractionated from N₂ [10,11]. This fractionation is extreme, and contrasts with the lack of carbon isotopic fractionation between HCN and CH₄ (Fig. 1). The current paradigm to explain the large fractionation in nitrogen isotopes is that a self-shielding effect leads to the preferential photodissociation of ¹⁴N¹⁵N at greater optical depths, which enhances the relative production rate of ¹⁵N and correspondingly HC¹⁵N [12].

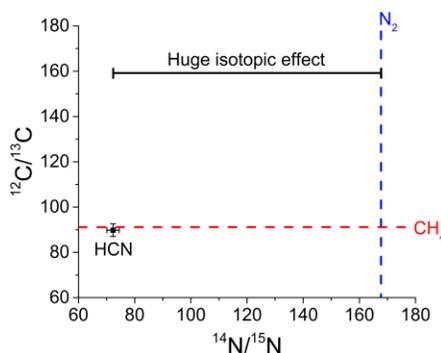


Fig. 1. Isotopic fractionation of HCN in Titan's atmosphere. Observational data from [10,11].

The ¹⁴N/¹⁵N value for HCN can be explained as a mixture of heavy N from photodissociation, and unfractionated N from charged-particle dissociation [12,13]. This can be represented as follows

$$\left(\frac{^{15}\text{N}}{^{14}\text{N}} \right)_{\text{HCN}} = f_h \times \left(\frac{^{15}\text{N}}{^{14}\text{N}} \right)_h + (1 - f_h) \times \left(\frac{^{15}\text{N}}{^{14}\text{N}} \right)_n,$$

where subscripts *h* and *n* stand for heavy and normal isotopic sources of HCN. The isotopic fractionation factor (α) between HCN and N₂ was estimated quantum mechanically to be ~8 [12]. Alternatively, an α value of ~6 can be derived using the above mixing model with the most recent isotopic data [10,11] and $f_h = 28\%$ [13]. We therefore consider α between 6 and 8 to be representative of Titan's atmosphere.

HCN produced by photodissociation of N₂ on the early Earth should also be subject to self-shielding. To

illustrate the potential isotopic consequences, we calculated the $^{15}\text{N}/^{14}\text{N}$ ratio of HCN using the above mixing model. Because self-shielding leads to a large fractionation, it is not difficult to generate enrichments in $\delta^{15}\text{N}$ that would be considered geologically significant (Fig 2). For comparison, the figure includes the largest “extreme” ^{15}N enrichment found in Archean lake sediments [14]. It can be seen that even more extreme δ values can be obtained for f_h values as small as $\sim 1\%$.

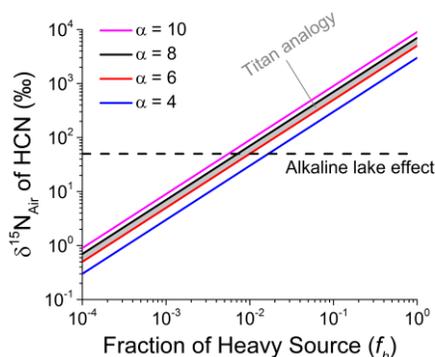


Fig. 2. N isotopic composition of HCN as a function of the fractionation factor for photodissociation, and the fraction of total HCN that is derived from photodissociation. The alkaline lake effect has been attributed to the degassing of isotopically light NH_3 [14].

If the isotope chemistry of HCN on Titan is indeed a suitable model for early Earth, then this analysis suggests that it may be unavoidable for HCN on the prebiotic Earth to acquire an anomalously large enrichment in ^{15}N . That enrichment would be propagated to organic compounds synthesized from HCN such as nucleobases [2], and perhaps even RNA molecules [5]. Therefore, a defining feature of this type of prebiotic chemistry would be a high ratio of $^{15}\text{N}/^{14}\text{N}$.

The rock record: Can we find geological evidence of prebiotic chemistry made possible by the photochemical production of HCN? An advantage of the proxy proposed here is that it relies upon an extreme isotopic effect. Fragile molecules, such as RNA, do not need to survive metamorphism intact; only their isotopic signatures need to survive. Also, the large magnitude of the effect should make it relatively “easy” to identify should it be found. Contrary to widespread perception, it may be premature to assume that geological activity has obliterated all traces of prebiotic chemistry on Earth.

Nitrogen associated with graphite in 3.8 Ga old rocks [15] do not reveal the hypothesized heavy isotopic signature. This may imply that a significant quantity of ^{15}N -rich HCN was not being produced at that time,

which would be consistent with the presence of an already established biosphere [16]. Evidently, older samples are needed to search for isotopic evidence of prebiotic chemistry. Hadean-age zircons might provide the best prospects, although measuring trace organic ^{15}N would be exceptionally challenging.

Potential problems: What could go wrong? We have identified three possibilities: (1) atmospheric or hydrothermal NH_3 , lightening or impact production of HCN, or extraterrestrial delivery of organics might have been key sources of fixed N on the prebiotic Earth, rather than photochemically derived HCN; (2) there may not be sufficient N in such old samples because thermal processing decreases the N/C ratio in carbonaceous matter [17]; or (3) any prebiotic signature could have been overprinted by the incorporation of nitrogen from younger metamorphic fluids. Nevertheless, the knowledge payoff would be worth the risk of searching.

Next Steps: In addition to analyzing old materials on Earth, it would be useful to look for isotopic evidence of prebiotic chemistry if impact ejecta from Earth were found on the Moon, where such evidence would be more likely to be preserved [18]. Here and now, we can make progress in testing the hypothesis of a ^{15}N -rich RNA world (or its precursor) by expanding models of prebiotic atmospheric chemistry to include N isotopes [8,9,12], and by performing pyrolysis experiments with RNA molecules to understand how metamorphism affects their bulk composition.

Acknowledgements: This work was supported by Simons Collaboration on the Origins of Life grant 511570.

References: [1] Miller (1955) *J. Am. Chem. Soc.* 77, 2351. [2] Oró (1960) *Biochem. Biophys. Res. Commun.* 2, 407. [3] Saladino et al. (2012) *Phys. Life Rev.* 9, 84. [4] Robertson & Joyce (2012) *Cold Spring Harb. Perspect. Biol.* 4, a003608. [5] Sutherland (2016) *Angew. Chem. Int. Ed.* 55, 104. [6] Sagan et al. (1992) *Acc. Chem. Res.* 25, 286. [7] Hörst (2017) *J. Geophys. Res. Planets* 122, doi:10.1002/2016JE005240. [8] Zahnle (1986) *J. Geophys. Res. Atmospheres* 91, 2819. [9] Tian et al. (2011) *Earth Planet. Sci. Lett.* 308, 417. [10] Molter et al. (2016) *Astron. J.* 152, doi:10.3847/0004-6256/152/2/42. [11] Niemann et al. (2010) *J. Geophys. Res. Planets* 115, E12006. [12] Liang et al. (2007) *Astrophys. J.* 664, L115. [13] Krasnopolsky (2016) *Planet. Space Sci.* 134, 61. [14] Stüeken et al. (2015) *Earth Planet. Sci. Lett.* 411, 1. [15] van Zuilen et al. (2005) *Geochim. Cosmochim. Acta* 69, 1241. [16] Bell et al. (2015) *Proc. Natl. Acad. Sci. USA* 112, 14518. [17] Boudou et al. (2008) *Geochim. Cosmochim. Acta* 72, 1199. [18] Armstrong et al. (2002) *Icarus* 160, 183.