PRODUCTION AND CONCENTRATION OF WATER-ALTERNATIVE SOLVENTS ON THE PREBIOTIC EARTH.

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Introduction: Water creates special problems for prebiotic chemistry, notably that complex polymers presumably require a living system to combat the constant effects of hydrolysis. The synthesis and concentration of water-alternative solvents with favorable properties for the formation of a variety of polymers of prebiotic molecules on the early Earth may have been one means of minimizing water's detrimental effects on these molecules. Formamide ($HCONH_2$), which is a liquid under normal terrestrial surface temperature and pressure conditions, has been advanced as an alternative to water that could enable chemical complexification [1-3]. It has the advantageous properties of promoting dehydration condensation reactions [4,5] and solubilizing phosphate minerals [6]. It has also been shown to serve as a feedstock for several biologically relevant compounds including nucleobases [7-9], amino acids and carboxylic acids when heated in contact with a variety of mineral catalysts at elevated temperatures [10,11]. However, little is known about the production of formamide and other high-boiling temperature amides or nitriles in terrestrial environments. The most common prebiotic source of formamide is via the hydration of hydrogen cyanide, but formamide hydrolyzes to ammonium formate on similar time scales. For this reason, other sources of formamide that bypass large bodies of water such as cometary or meteoritic impacts have been invoked in conjunction with 'desert-like', shallow lake or periodically dry settings as a means for concentrating formamide [12-14]. We report here the conversion of aqueous acetonitrile and hydrogen cyanide into formamide, acetamide, succinonitrile and a host of other compounds by γ-irradiation under conditions mimicking exposure to radioactive minerals [15]. The formamide may be concentrated upon evaporation of water in near-surface geochemical settings. The maximum observed yield of formamide from 100 mM aqueous acetonitrile was ~0.55%. We estimate that starting with production of acetonitrile from irradiation of atmospheric N_2 and CH_4 or radiolysis of ambient hydrogen cyanide, a radioactive placer deposit can produce about 0.3-4.5 moles of formamide km^{-2} $year^{-1}$. A natural uranium fission zone [16] 10 m in diameter with 10kW total power output, comparable to the Oklo reactors in Gabon [17], can produce up to 0.1-1.7 moles of formamide m^{-2} $year^{-1}$ from initial acetonitrile and hydrogen cyanide, which is 2-6 orders of magnitude greater than other proposed scenarios of formamide production for which reaching neat concentrations of formamide are problematic (e.g., cometary influx and steady-state hydrolysis of hydrogen cyanide). Radioactive mineral deposits capable of producing and trapping formamide would also place the solvent in contact with a variety of placer mineral types relevant to prebiotic chemistry, including monazite ((Sm, Gd, Ce, Th)PO_4), rutile (TiO_2), pyrite (FeS_2) and apatite ($Ca10(PO_4)6(OH)_2$). Radioactive mineral deposits may thus be favorable settings for prebiotic polymer formation through a combination of emergent geologic processes and formamide-mediated organic chemistry.

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