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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 biopolymers are corroded by water[1]. The synthesis and concentration of water-alternative solvents with favorable properties for the formation of a variety of prebiotic polymers on the early Earth may have been one means of minimizing water's detrimental effects on these molecules. Formamide (HCONH₂), 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[2]. It has the advantageous properties of promoting dehydration condensation reactions and solubilizing phosphate minerals. It has also been shown to serve as a feedstock for several biologically relevant compounds including nucleobases, amino acids and carboxylic acids when placed in contact with a variety of mineral catalysts at elevated temperatures[3]. However, it is unclear whether formamide (or other high boiling temperature amides or nitriles) may be produced in sufficient quantities, or in environments that can reach sufficiently high temperatures, to carry out reactions of prebiotic significance. 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. 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 N₂ and CH₄ or radiolysis of ambient hydrogen cyanide, a radioactive placer deposit[4] can produce about 0.3-4.5 moles of formamide km⁻² year⁻¹. A natural uranium fission zone 10 m in diameter with 10kW total power output, comparable to the Oklo reactors in Gabon[5], 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. 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)PO₄), rutile (TiO₂), pyrite (FeS₂) and apatite (Ca₁₀(PO₄)₆(OH)₂)[6]. 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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