

ANALYSIS OF SILICATE-CATALYZED SUGAR SYNTHESIS UNDER HYDROTHERMAL CONDITIONS

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Introduction: Carbohydrates are essential building blocks for the origin and evolution of life on Earth, but their production on early Earth is still unclear. The formose reaction appears as a prebiotically-relevant framework to produce long-chain monosaccharides, as well as other sugar-related compounds potentially useful for metabolism, from the oligomerization of formaldehyde, known to be readily formed in prebiotic simulation experiments and abundant in interstellar environments [1]. The formose network comprehends a set of enolization, aldol addition, retro-aldol and Cannizzaro reactions that require certain pH and concentration conditions to occur [2]. As several sugars and sugar related compounds have been found in cometary-like analogs [3] and carbonaceous chondrites [4,5], it has been suggested that the dilute concentration of formaldehyde in primitive oceans can be overcome by meteoritic input, but there is a lack of studies on the mechanisms for their production in extraterrestrial settings. Here, we focus on the formation of sugars under conditions simulating alteration processes on asteroids using olivine, an abundant silicate in chondritic meteorites, as a mineral catalyst and compare these results with the typical formose catalyst, $\text{Ca}(\text{OH})_2$, to elicit the plausibility of a formose-like mechanism.

Experiments and methods: Experiments took place in aqueous systems under anoxic atmosphere at 80 °C. We designed a series of experiments differing formaldehyde (F), glycolaldehyde (G), calcium hydroxide $\text{Ca}(\text{OH})_2$ (α) and olivine (O) compositions and tested different combinations: O, F, FO, FG, FGO, F α , FG α , with time variations up to 45 days. Formaldehyde (under the form of polyoxymethylene) was introduced with glycolaldehyde or calcium hydroxide at a weight ratio of 10/1 and olivine/formaldehyde at a weight ratio of 10/1. We used GC \times GC-TOFMS for the identification and quantification of sugars formed in the individual samples employing reference standards and literature data.

Results and discussion: Abundances of C3 to C6 monosaccharides and polyols found for the different experimental settings are shown in Figure 1. The catalyzing effect of olivine is considerable when compared with the sugar variety and abundances of F and FG samples. When compared to experiments with the classical $\text{Ca}(\text{OH})_2$ catalyst, identical sugars are identified in the presence of olivine with higher abundances found for $\text{Ca}(\text{OH})_2$. For all samples, the diversity and quantity of sugars (mainly oses) decreased after 2 days of reaction, and mainly polyols remained in samples with olivine after 45 days. Typical formose Cannizzaro reaction products such as branched alcohols, sugar acids and hydroxycarboxylic acids were also identified in samples catalyzed by olivine. These experiments demonstrate

that minerals may have played a crucial role in the chemical reactivity under hydrothermal alterations in interstellar environments through a mineral-assisted formose reaction leading to high molecular diversity and sugar abundances after short reaction times. The silicate likely ensures the selection and stabilization of the C3-C4 sugars allowing rapid aldolisation to C6, unlike solutions without silicate. However, decomposition of sugars with time is inevitable; nonetheless, surprisingly polyol-sugars survive hydrothermal alteration in the presence of olivine on longer time scales. These experiments raise again the question of mineral impact on the organic evolution, even as simple as olivine, in conditions mimicking aqueous environments on planetary surfaces resembling prebiotic conditions on Earth [6].

References: [1] Cleaves H. J. (2008) *Precambrian Research* 164: 111–118. [2] Haas M. et al. 2020. *Communications Chemistry* 3. [3] Meinert C. et al. 2016. *Science* 352: 208–212. [4] Cooper G. et al. 2001. *Nature* 414: 879–883. [5] Furukawa Y. et al. 2019. *Proceedings of the National Academy of Sciences* 116: 24440–24445. [6] Vinogradoff V. et al. 2020. *Geochimica et Cosmochimica Acta* 269: 150–166.

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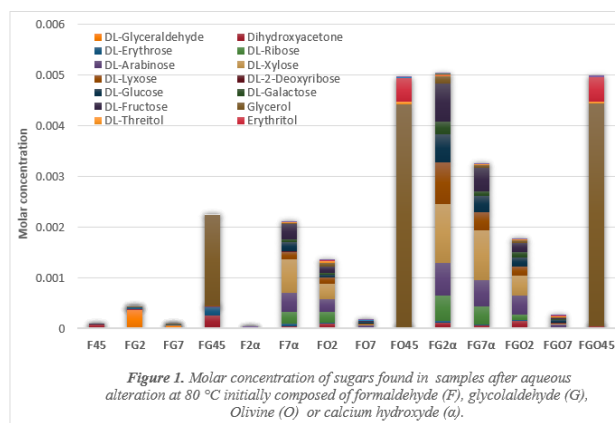


Figure 1. Molar concentration of sugars found in samples after aqueous alteration at 80 °C initially composed of formaldehyde (F), glycolaldehyde (G), Olivine (O) or calcium hydroxide (α).

