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Mineral-catalyzed sugar synthesis under hydrothermal conditions

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Introduction: Sugars are important molecules with high biological interest. Found in cometary-like analogs (Meinert et al., 2016), carbonaceous meteorites (Cooper et al., 2001; Furukawa et al., 2019), and likely on early Earth, sugars may have contributed as a source of molecules for the emergence of prebiotic systems on Earth. Hence, it is of prime importance to investigate their formation in conditions relevant to these environments, and particularly in the presence of minerals. For example, sugar formation is achieved through the formose reaction: the dimerization of formaldehyde, forming glycolaldehyde, which then by aldol reactions with another formaldehyde, will form successively higher sugar homologues. A catalyst is usually required for the first step, the formation of glycolaldehyde (typically calcium hydroxide). However, there is a lack of studies exploring the potential of minerals on the classical formose reaction (Gabel and Ponnampuruma, 1967; Haas et al., 2020) and in conditions representative of prebiotic environments. Here, we focus on the formation of sugars from formaldehyde *via* the formose reaction in aqueous solution using minerals, simulating conditions in which planetary surfaces could have evolved at the beginning of the Solar System.

Experiments and methods: Experiments took place in aqueous systems under anoxic atmosphere at 80 °C. We choose olivine as a model silicate, which is omnipresent in the solar system, and designed a series of experiments differing formaldehyde (F), glycolaldehyde (G), calcium hydroxide Ca(OH)₂ (a) and olivine (O) compositions. We tested different combinations, O, F, FO, FG, FGO, Fa, FGa, for different durations 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 also at a weight ratio of 10/1. The mixtures were loaded in closed cells under argon atmosphere in a glove box before being heated in an oven at 80 °C. We used Gas Chromatography-Mass Spectrometry (GC-MS) and GC×GC-TOFMS for the identification and quantification of sugars formed in the individual samples.

Results: Identification of sugars in the different samples was performed comparing retention times and relative mass spectra with those of reference standards (oses, polyols, sugar acids and deoxy sugars acids).

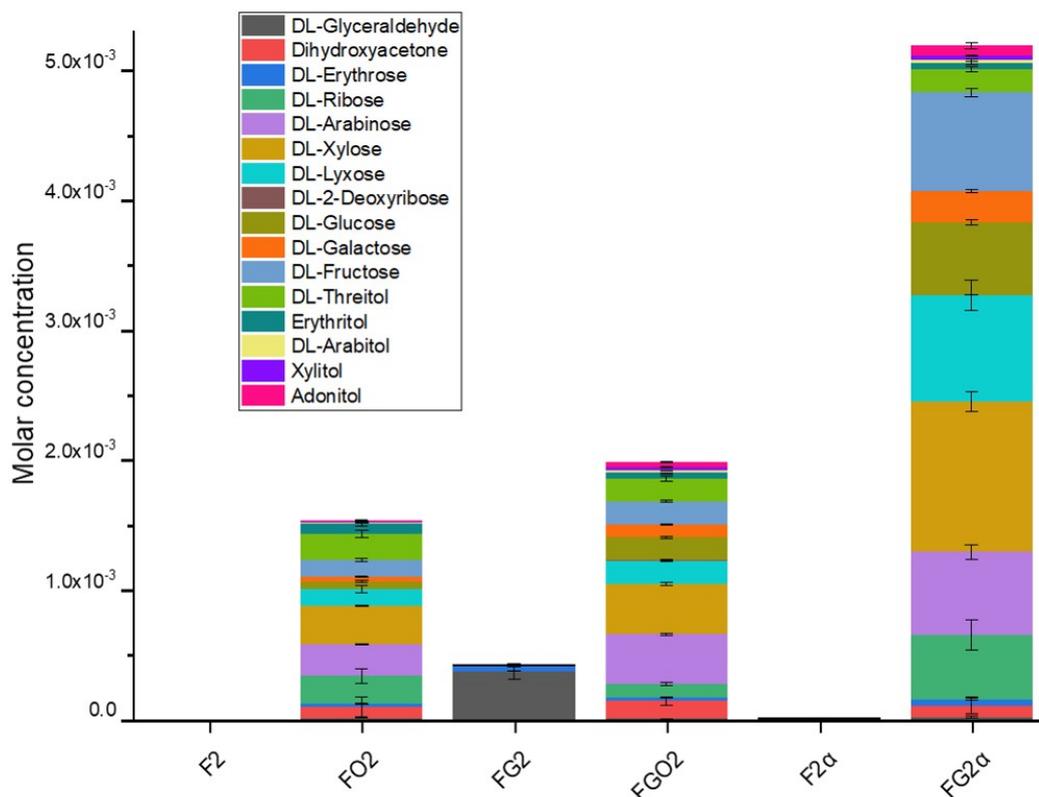


Figure 1: Molar concentration of sugars found in samples after 2 days of aqueous alteration at 80 °C initially composed of formaldehyde (F), glycolaldehyde (G), Olivine (O) or calcium hydroxyde (α).

Abundance of sugars found in samples after 2 days of reaction are shown in figure 1. No sugars have been identified in samples F₂, except minor contaminants from the derivatization protocol. In contrary, in the presence of olivine (sample FO₂), 16 sugars have been identified and quantified based on reference standards, and many more peaks seen in the chromatograms are suspected polyols based on their mass spectra. We observed the same sugars in the FGO samples, while only a few of them are observed in the FG samples. Most importantly, olivine allowed the detection of C₆ sugars after only 2 days of reaction, not observed in samples without olivine even after 45 days of hydrothermal reaction. When compared to experiments with the classical Ca(OH)₂ catalyst, identical sugars are identified with olivine with highest abundances found for Ca(OH)₂. For all samples, the diversity and quantity of sugars (mainly oses) decreased after 2 days of reactions, and mainly polyols remained in samples with olivine after 45 days.

Discussion: These experiments demonstrate that minerals may have played a crucial role in the chemical reactivity during evolution of chemical systems in aqueous environments. Here, sugars have been formed through a mineral-assisted formose reaction leading to a high molecular diversity and sugar abundance after short reaction times, without any other classical catalyst. 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 with olivine on longer times. 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 similar to prebiotic conditions on Earth (Vinogradoff et al., 2020).

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