

Borate Minerals Stabilize Ribose

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Evidence for an “RNA world,” an episode of life on Earth during which RNA was the only genetically encoded component of biological catalysts, is found in the ribosome (1), catalytic RNA molecules (2), and contemporary metabolism (3). That RNA could form spontaneously and persist under prebiotic conditions has been doubted, however (4, 5). Ribose and its sister pentoses (arabinose, xylose, and lyxose) are made under alkaline conditions from simple organic precursors (formaldehyde and glycolaldehyde) (6) known in interstellar space and presumably available on early Earth (7). Pentoses do not accumulate under these conditions, however; they rapidly decompose in a “browning” reaction to generate largely undecipherable polymeric mixtures.

Because borate forms complexes with organic molecules (such as pentoses) that carry 1,2-dihydroxyl groups, pentoses might accumulate if borate were present. Borate should not prevent the addition of the enolate of glycolaldehyde 1 (reacting as a nucleophile) with formaldehyde 2 (reacting as an electrophile) to form glyceraldehyde 3 (Fig. 1). As the first compound in the sequence to have a 1,2-diol, however, 3 should complex with borate. Because the complex is anionic, enolization of 3 should be suppressed, preventing 3 from

acting as a nucleophile. Compound 3 should still serve as an electrophile, however, reacting with the enediolate of 1 to give pentoses (4 to 7), including ribose 4.

Once formed, the cyclic forms of the pentoses should form stable, less reactive complexes with borate (8 to 11), because the cyclic complexes lack C=O groups (fig. S1). Our experiments supported this. Whereas ribose decomposed in minutes under alkaline conditions, it remained stable for days at room temperature in the presence of borate (figs. S2 and S3).

Next, we asked whether the presence of borate is compatible with ribose synthesis. With Ca(OH)₂ (0.5 M suspension; pH ~12; 25° and 45°C), a solution of 1 and 2 (each 0.5 mM) turned brown (1 hour and 10 min, respectively). Small but detectable amounts of pentoses were found after 20 min at 45°C. These were detected after derivatization with N,O-bis(trimethylsilyl)-trifluoroacetamide by gas chromatography–mass spectrometry (GC-MS) (fig. S4). Pentoses were nearly gone after a 1 hour incubation.

When the same incubation was done with borate minerals ulexite (NaCaB₅O₉·8H₂O), kernite (Na₂B₄O₇), or colemanite (Ca₂B₆O₁₁·5H₂O)

in synthetic form, the solution did not turn brown, even after incubation for 2 months (Fig. 1). To demonstrate the synthesis of pentoses under these conditions, the mixture was acidified (pH 5), filtered, and freeze-dried. Borate was removed as its trimethyl ester by evaporation two times with methanol and evacuation, and the sugars were derivatized. The presence of arabinose, lyxose, xylose, and ribose in similar amounts was confirmed by coinjection of authentic standards (fig. S5). Pentoses constituted the large majority of total carbon. Formation of ribose/ribulose was confirmed by treating the mixture with sodium borohydride to generate ribitol, followed by enzymatic analysis using D-ribitol dehydrogenase, which is specific for this sugar alcohol. Direct high-performance liquid chromatography (HPLC) analysis of the mixture detected the dipentose borate complex (mass 307) as the principal product (figs. S6 and S7).

Borate is incompatible with many silicate minerals, is concentrated in residual melts during rock formation, and frequently appears in igneous rocks as tourmalines. Weathering gives soluble borate salts, which often appear as alkaline evaporites. They are known in Death Valley, and they appear as crusts on outcrops in Antarctic dry valleys (8).

These experiments suggest that the formation of pentoses appears to be the natural outcome of the chemical transformation of organic molecules present in the nebula that form stars and planets in the presence of borate minerals. Because neither borate minerals nor interstellar organics are excluded from the early Earth, we also cannot exclude the availability of ribose formed prebiotically at the time when life emerged on Earth.

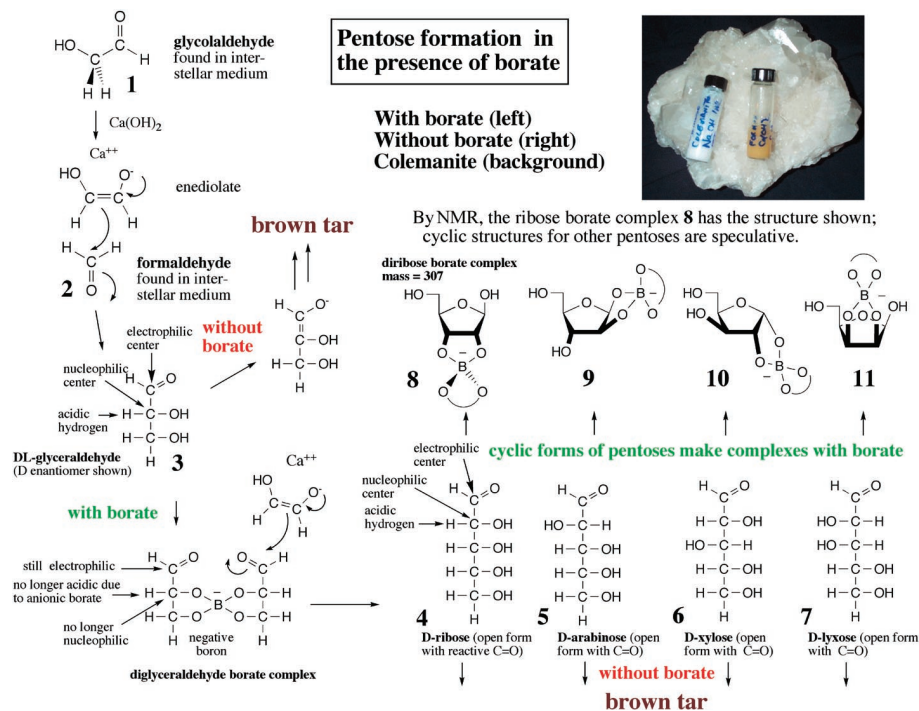


Fig. 1. Pentose formation in the presence of borate.

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Figs. S1 to S7

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