

Clay mineral assists borate to stabilize ribose. Y. Furukawa¹, A. Nitta¹, T. Kakegawa¹, S. A. Benner²,
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Introduction: Ribose is a key component of RNA connecting nucleobases to its sugar phosphate backbone. However, ribose is an unstable sugar and this makes difficult to accumulate ribose on the prebiotic Earth. The formose reaction is condensation of formaldehyde and a probable formation pathway for prebiotic ribose. Borate is known to stabilize ribose even under alkaline conditions that facilitate the formose reaction (Ricardo et al. 2004). Previous studies applied high borate concentrations (80–280 mM) to stabilize ribose in high pH Ca²⁺ solutions (Furukawa et al. 2013; Kim et al. 2011). However, it has been debated whether such high borate concentrations were reasonable and whether more abundant minerals such as clay interfere the stabilization by borate (Grew et al. 2011). We tested this using a clay mineral, kaolinite, which is known to catalyze the formose reaction (Gabel and Ponnampertuma 1967). Kaolinite has no exchangeable cation but has a positive surface charge over pH 4 and forms ion-pairs with borate under alkaline conditions with divalent cations like Ca²⁺ (Mattigod et al. 1985). Thus, this mineral has the potential to concentrate borate in sediments. Kaolinite is also seen in borate deposits at Death Valley National Park, although it is not abundant.

Experimental: Ribose (10 mM) was incubated in 10 mL aqueous solution of sodium tetraborate decahydrate (40 mM borate) and calcium hydroxide (30 mM) at 45°C with continuous stirring (pH 12). The solutes were completely dissolved in the solution. Then, different amounts of kaolinite powder (14.82 m²/g) were added to the system. Aliquots of the suspension solution were removed, acidified, diluted with acetonitrile, and analyzed with liquid chromatography MS (Waters 2695 and Quatromicro API) to measure the residual ribose concentration. The chromatography was conducted under HILIC mode using an amino column (3.6×150mm, 3µm; TOSO). Details were shown in our previous publication (Furukawa et al, 2013)

Results: In 40 mM borate solution without kaolinite, ribose decomposed exponentially with elapsed time. First-order rate constant of the decomposition was $k = 0.005$. With 50 mg kaolinite in 40 mM borate solution, the rate constant did not show much difference, with remaining $k \approx 0.005$. However, the rate was decreased significantly to $k = 0.0007$ and almost stabilized in 40 mM borate solution with 500 mg kaolinite. This

amount of kaolinite has a surface area of 7.4 m². Considering the crystal structure of kaolinite, the molar amounts of silanol on this kaolinite powder is comparable order to the molar amounts of borate and ribose.

Discussion: In the system with 500 mg kaolinite and 40 mM borate, ribose was significantly stabilized. Without kaolinite, this level of stabilization can be achieved only with higher borate concentration (80 mM borate solution) (Furukawa et al. 2013). Therefore, kaolinite does not interfere the stabilization of ribose by borate. Conversely, kaolinite helps borate stabilize ribose. The stability of ribose does not improve with 50 mg of kaolinite in borate-free solution. Further, dissolved silicate have smaller effect to improve the stability of ribose (Nitta et al. 2016). Thus, kaolinite might not work independently to stabilize ribose but assist borate to stabilize ribose. Many other clay minerals and even oxide minerals have negative surface charge under alkaline conditions. Further investigations on the effects by borate-mineral may construct more reasonable prebiotic conditions for the stabilization and accumulation of ribose on the early Earth.

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