Molecular organization of Maillard-type reaction products as a protocell analogue

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It has been thought that a protocell played an important role in the chemical evolution to origins of life. Experimental studies on the formation of organic microspherules have been historically reported. However, how the microspherules gained biofunction is unknown. We investigated the sizes, shapes, and distributions of organic microspherules formed by Maillard-type reaction of formaldehyde and ammonia which were thought to be present ubiquitously on the early Earth, in order to understand their formation and dynamics.

Paraformaldehyde (120 mg), glycolaldehyde (120 mg), NH_3(aq) (54 μl), $Ca(OH)_2$ (30 mg) in 2 ml of water in a glass tube was heated at 90°C for 3-100 days. After heating, the precipitation was rinsed with HCl and dried. The purified organic solids were observed by a SEM and optical microscope, and analyzed by ATR-IR, synchrotron-based micro-FTIR (BL43IR, SPring-8) and STXM (BL4U, UVSOR).

Sizes of the organic microspherules were 3-5 μm after heating for 5 days, and increased to 10-20 μm after 50 days, but afterward smaller ones of 10 μm increased. The microspherules had diversity in shape, such as round-, donut-, dumbbell-, and irregular-shapes. From the ATR-IR spectra of the organic solids, hydroxyl group, alkyl groups, aromatic carbons, imine, amide, and nitrogen heterocyclics were identified, while the functional group compositions were constant over heating time. Micro-FTIR and STXM measurements show that microspherules and host organics have similar functional group compositions. On the other hand, chemical heterogeneities between the individual microspherules were locally observed. These results suggest that the diversity in size and shapes of microspherules is not related to the chemical compositions but self-assembly behaviors of amphiphilic molecules with different polarities. Local chemical heterogeneities may be explained by budding and/or birthing division of microspherules with the progress of heating. These cell-like phenomina could have been occurred not only in the early Earth but also in other planets.