

# Report for the Joint Use/Research of the Institute for Planetary Materials, Okayama University

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**Category:** General Joint Research

**Name of the research project:** Composition of “Extraterrestrial” Polyester Gel Microdroplets

**Principal applicant:** Tony Z. Jia

**Affiliated institution and department:** Earth-Life Science Institute, Tokyo Institute of Technology

## **Collaborator**

**Name:** (1) Chen Chen, Ruiqin Yi, Rehana Afrin; (2) Tak Kunihiro, Eizo Nakamura, Katsura Kobayashi, Christian Potiszil

**Affiliated institution and department:** (1) Earth-Life Science Institute, Tokyo Institute of Technology; (2) IPM

## **Research report:**

We first subjected a series of alpha hydroxyacids to dehydration synthesis to form polyesters, which were then subsequently screened for microdroplet assembly (forming protocells). These included pure phenyllactic acid (PA), and mixtures of PA with 4-amino-2-hydroxybutyric acid (4a2h) or malic acid (Malic). We then devised a novel ICP-MS analytical approach and applied it to polyester microdroplets, to determine the cation distribution within them following incubation with four different chloride salts (NaCl, KCl, MgCl<sub>2</sub> and CaCl<sub>2</sub>). We thus quantified the salt ion concentration inside and outside of the droplets after incubation with the different salts as a measure of salt uptake. ICP-MS was able to detect each of the four cations of the chloride salts (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>), but was not able to detect chloride anions. We observed that in all cases, cations were detected within the droplets, suggesting that protocells uptake all salt cations. For all cases, the concentrations of salt cations detected within the droplets as compared to the supernatant were all different, suggesting that the salt uptake process is likely selective and differential.

K<sup>+</sup> was generally uptaken by the droplets to the greatest degree compared to the other cations, with Mg<sup>2+</sup> uptaken the least. The relative amount of cations in solution uptaken was greater at lower overall salt concentrations; at low concentrations (1 mM), K<sup>+</sup> could be concentrated within the droplets. Finally, we observed that poly(PA) microdroplets tend to uptake salt ions with differential affinity and in order of decreasing affinity of (K<sup>+</sup> > Ca<sup>2+</sup> > Na<sup>+</sup> > Mg<sup>2+</sup>). The exact mechanism of this difference is not clear, and may be due to a number of factors such as differences in salt cation

structure, size and/or affinity with poly(PA). However, the order of decreasing affinity of cation uptake matches roughly with the order of decreasing ionic radius ( $K^+ > Ca^{2+} = Na^+ > Mg^{2+}$ ). If we consider just the divalent ions,  $Mg^{2+}$  is more strongly hydrated and with a larger hydration shell than  $Ca^{2+}$ , resulting in the formation of a larger hydration sphere around  $Mg^{2+}$  compared to  $Ca^{2+}$ . The larger hydration sphere could potentially result in a weakening of the interaction between  $Mg^{2+}$  with the apolar polyester droplet (compared to  $Ca^{2+}$ ) due to inhibition of interaction of the cation interior with the negatively charged polyester microdroplet surface, resulting in lower  $Mg^{2+}$  uptake compared to  $Ca^{2+}$ . When comparing just the monovalent ions,  $Na^+$  and  $K^+$  also follow a similar relative trend as  $Mg^{2+}$  and  $Ca^{2+}$ , respectively (i.e., the hydration shell of  $Na^+$  is larger than that of  $K^+$ ), which could modulate the relative propensity of  $Na^+$  and  $K^+$  to be uptaken.

If there are indeed some prebiotic evolutionary advantages to selective incorporation of  $K^+$  over the other salts tested, such as for generation or maintenance of protocell boundary chemical potential, then polyester microdroplets could have been able to utilize its ability to selectively uptake  $K^+$  to support some type of primitive type of evolution. We make this conjecture considering that intracellular  $K^+$  concentration is much higher than that of  $Na^+$ ,  $Mg^{2+}$  and  $Ca^{2+}$  in plant and animal cells, likely due to the action of potassium channels or the potassium-sodium pump, respectively. For instance, plants maintain a relatively high  $K^+$  (100–200 mM) and low  $Na^+$  concentration (1–10 mM) in their cytosol; animals also maintain a high  $K^+$  (~150 mM) and low  $Na^+$  concentration (~15 mM). Additionally, the modern ocean contains far more  $Na^+$  than  $K^+$ , while the ancient ocean also likely contained much more  $Na^+$  than  $K^+$ . Polyester microdroplets in ancient oceans which could selectively incorporate low-abundance  $K^+$ , while simultaneously excluding highly abundant  $Na^+$ , could have been one mechanism to achieve a local microenvironment containing a  $K^+/Na^+$  ratio more on par with modern biology.

These studies form the basis of a manuscript currently in preparation, to be submitted within this fiscal year, with all of the listed collaborators (and another IPM staff member, Chie Sakaguchi, who was instrumental in developing the ICP-MS technique) as co-authors; after publication, we will inform you of the article details. We plan to continue this work in the second term of FY2023, likely through another general joint research proposal.

