Surface directed protocell formation

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Abstract

Origin of life research takes various forms but in general tries to understand how organic organization can bootstrap from inorganic structures or constraints, or how more sophisticated protocellular structures can bootstrap from more primitive forms. The demonstration of these transitions can be difficult to implement in the real world. Here we focus on how inorganic structures, formed in the presence of simple organics, can lead to novel hybrid inorganic-organic 3D architectures that support simple membrane formation. We analyzed both the mineral and hybrid structures, and vesicle formation in the presence of these geochemical surfaces using different physio-chemical techniques. This study shows a potential route that the first cellular structures could have taken through their interaction with hybrid organic-inorganic abiotic structures in their environment. Such model systems can also be insightful for artificial life studies regarding the importance of self-assembly promoted between two different systems: inorganic and organic.

Introduction

The creation of artificial cells is one of the pillars of synthetic biology Malinova et al. (2012). Different categories of model structures exist and are implemented by the Artificial Life community and beyond, to examine the fundamental properties of living systems. As a first category, droplets of nonpolar oil, and also some amphiphiles (e.g. decanol Hanczyc (2014); Čejková et al. (2017); Holler et al. (2018); Holler and Hanczyc (2020); Löffler et al. (2023) in an aqueous environment autonomously phase separate, minimizing their energy, and creating protocellular like structures with self-motion and collective properties Hanczyc (2014). A second category are coacervate-based compartments Wu and Qiao (2022), condensed liquid-like droplets, usually formed by oppositely charged polymeric molecules Yewdall et al. (2021). The third, most complex, and more similar to the real cell category, are vesicles Chen and Walde (2010). Vesicles are generated by amphiphiles, molecules with an hydrophobic and hydrophilic portion, that have the inherent ability to autonomously organize into spherical membrane compartments, when suspended without any constraint within an aqueous environment Evans (1988).

Early studies have demonstrated the possibility of amphiphile synthesis under prebiotic conditions Hargreaves et al. (1977). The abiotic synthesis of lipid species and their inherent capacity for spontaneous self-assembly into organized membranous structures present two supporting arguments for the plausibility of liposomal compartments as components of primitive cells.

The abiogenesis hypothesis posits that on the early Earth, conditions such as a reducing atmosphere Urey (1952), volcanic activity Damer and Deamer (2020), and strong water-rock interactions Macleod et al. (1994) driven by geothermal gradients such as those found at underwater hydrothermal vents provided the necessary ingredients, chemical gradients and energy for the formation of complex organic molecules like amino acids, nucleotides, and lipids Miller and Urey (1959); Joyce (1989); Sutherland (2016). Mineral particles have been in the past implicated in early chemistry and polymerization reactions Bernal (1949); Ferris et al. (1996); Sowerby et al. (2001); Monnard (2005), and only in recent years it was endeavored to analyze the hypothesis whether mineral surfaces and released mineral particles could have favored protocell formation Hanczyc et al. (2007); Holler et al. (2023). For example, on the ocean floor, in the presence of hydrothermal vents (HV), hot, mineral-rich water was released into the cold, oxygen-poor ocean, creating a unique environment where chemical reactions could take place and serpentinization occurred Russell and Hall (1997); Martin et al. (2008); Sander and Koschinsky (2011); Sojo et al. (2016); Cartwright and Russell (2019). Under these conditions molecules such as alcohols could have formed Shock and Schulte (1998). Decanol is an amphiphilic alcohol with a 10-carbon chain that exhibits characteristics of a weak surfactant and demonstrates low solubility in water Barton (1984). Decanol presents an intriguing candidate for investigation as a potential component in prebiotic membranes Apel et al. (2002). These properties highlight the significance of exploring the role of short chain alcohols, such as decanol, in ancient alkaline vent environments Holler et al. (2023).

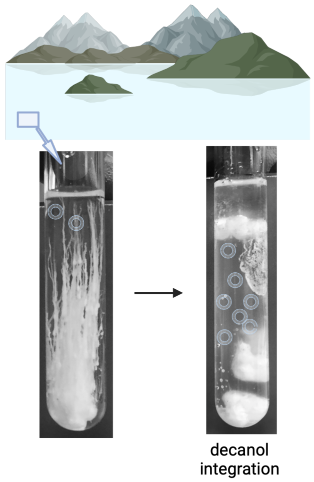

Figure 1: Hydrothermal vent proxies and protocell formation.

Surface directed membrane assembly

How protocells could have organized in presence of inorganic surfaces was first analyzed by Hanczyc et al. (2007). For the first time, Hanczyc et al., studied membrane formation and RNA encapsulation in relationship to the presence of inorganic mineral surfaces. They devised simple tests to search for mineral-directed vesicle formation by monitoring the phase transition from myristoleate (C14:1), palmitoleate (C16:1) and oleate (C18:1) micelles to lamellar vesicles. A broad range of surfaces were tested including natural clays (e.g. Montmorillonite), different types of silicates, and glasses. Most surfaces and particulates accelerated vesicle formation. Under more controlled and uniform conditions, they observed that silica spheres of varying concentration and diameter, directly associated with higher vesicle formation rates. Here we evolve this concept further. We report for the first time the integration of organic molecules within inorganic crystals. The resulting hybrid structures were tested for enhanced vesicle formation Holler et al. (2023) (see Figure 1). In addition, vesicles stability over a broad pH range was further tested.

The inorganic crystal garden precipitates were created from sodium silicate and calcium chloride. These structures were obtained both with and without the presence of an organic molecule, decanol. The structures were formed in both a vertical tube system and in a horizontal flat dish system. Immediately, it was noticed that the structures formed in presence of decanol were visibly different from the structures formed without the addition of the organics. More detailed analysis of the structures were performed by Scanning Electron Microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDXS), and X-ray Photoelectron Spectroscopy (XPS). It was determined that also the microstructures were different between the samples, and in the system containing decanol, carbon enrichment from the decanol was detected in the solid structures. After seeing and characterizing the differences between the two systems, it was tested whether the purely inorganic or the hybrid inorganic-organic structures could influence fatty acid vesicle production. Three model fatty acids with varying and increasing chain length were tested: decanoic, myristoleic, and oleic acid. These are representative of simple surfactants with different acyl chains and degrees of unsaturation to explore the effects of these differences in chemical composition on the system. The formation of vesicles, at concentrations far lower than critical vesicle concentration (cvc), was observed in the presence of 3D mineral structures with decanol integrated. Decanoic acid also showed an increased range of pH that supported vesicle formation. Decanoic acid normally forms vesicles at neutral pH, and in this case of incubation with hybrid structures, vesicles formed also at pH higher than 8.

In conclusion, the integration of a fatty alcohol, decanol, in hydrothermal vent proxies, caused the structure variation of the crystals and the discovery of an innovative feature of these structures: triggering vesicle formation at concentration far lower than cvc. This study establishes the groundwork for incorporating organic compounds into silicate chemical gardens, specifically focusing on compounds like fatty acids and fatty alcohols, which could have played a role in or facilitated the formation of vesicles. Future investigations could delve into the interaction between additional organic molecules (such as DNA or amino acids) with hydrothermal vent-like structures. Understanding how these molecules compartmentalize into vesicles could pave the way for developing novel experimental models that explore the interplay between inorganic and organic systems in understanding how the origin of life arose.

Materila and Methods

Material and methods are reported in Hanczyc et al. (2007) and Holler et al. (2023).

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