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Protocell Self Assembly As Predicted by Mineral Surface Chemistry

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Introduction: The enclosure of functional biomolecules in a lipid bilayer membrane was an important process for the emergence of life on Earth. Single chain amphiphiles (SCAs) are considered for model protocell membranes because of their prebiotic availability and ability to self assemble. The effect of minerals in enhancing the rate of formation of SCA vesicles was reported in a seminal work [1]. However, no relationship with chemical properties of the minerals was identified and the reason for catalysis without direct contact remained unexplained. The aims of the present study were to re-examine the potential effects of minerals on the initial self-assembly of vesicles as model protocell membranes and their survival after formation, and to identify mineral-specific trends.

Methods: Decanoic acid (DA, pH 7, HEPES) and decanoic acid/decanol (DA/DOH = 2:1, pH 8.1, bicine) were used for this study. Komatiite and tonalite rocks, representing early oceanic and continental crusts; secondary minerals (oxides, oxyhydroxides, carbonates, sulfides, aluminosilicate) formed from weathering komatiite and tonalite were also used. Vesicle formation was monitored by fluorescence and absorbance spectroscopies and dynamic light scattering. Mineral-vesicle interactions were visualized by optical microscopy and cryo-TEM.

Results and Discussion: The critical vesicle concentration (CVC), apparently increased only in the presence of positively-charged minerals at $\geq 1 \text{ mg.mL}^{-1}$ loadings because of lipid adsorption and settling of the lipid-mineral aggregates [2]. Above the CVC, initial vesicle formation rates were promoted in the presence of all minerals and were shown, for the first time, to depend on the isoelectric point (IEP) of the minerals, which itself depends quantitatively on mineral chemistry, structure and interfacial hydration [3]. Initial rates were faster on more positively-charged minerals [2]. Membrane permeability remained unaffected by minerals once vesicles were formed. The initial rate-accelerating effect was ascribed to rapid lipid adsorption on mineral surfaces [2]. These adsorbed lipid islands serve as a matrix [4] for further lipid attachment and its rapid transformation to vesicles compared to a control system without minerals. Modified Deraguin-Landau-Verwey-Overbeek (DLVO) theory indicates that the electrostatic effect of the mineral's surface charge was effective even up to $\sim 15 \text{ nm}$ distance from the surface through 2-3 stacked lipid bilayers [5]. Our work confirms the original findings [1] and goes further in establishing the relationship of vesicle self-assembly to mineral IEP, and providing a theoretical basis for the catalytic effect without direct contact with the mineral surface [2, 5]. Both the thermodynamics and the kinetics of membrane self-assembly showed dependence on fundamental properties of minerals. The structure-activity relationships identified here between membrane self-assembly processes and the physical-chemical properties of minerals may help predict the plausible survival of protocell membranes in proximity of other minerals, which may have been present on early Earth and other rocky planets such as Mars.

References:

- [1] Hanczyc MM, Mansy SS and Szostak JW (2007) *Origins of Life and Evolution of Biosphere* 37:67–82 (2007). [2] Sahai N, Kaddour H, Dalai P, Wang Z, Bass G and Gao M (2017) *Scientific Reports*. 7:1–13. [3] Sverjsnky DA and Sahai N (1996) *Geochimica et Cosmochimica Acta* 60:377–3797. [4] Blöchliger E, Blocher M, Walde P and Luisi PL (1998) *Journal of Physical Chemistry B* 102:10383–10390. [5] Oleson TA and Sahai N (2010) *Journal of Colloid and Interface Science* 352:316–326.