

**PREDICTING MODEL PROTOCELL MEMBRANE SELF-ASSEMBLY AND SURVIVAL BASED ON MINERAL SURFACE CHEMISTRY.** Nita Sahai,<sup>1,\*</sup> Hussein Kaddour<sup>1</sup> and Punam Dalai<sup>1</sup>, <sup>1</sup>Department of Polymer Science, 170 Univeristy Ave., University of Akron, Akron, OH 44325-3909. \*sahai@uakron.edu

**Introduction:** The self-assembly of lipid bilayer membranes to enclose functional biomolecules, thus defining a “protocell,” was a seminal moment in the emergence of life on Earth at ~ 4.4 – 3.8 Ga. This event likely occurred at the mineral-water interface, which offers a reactant-concentrating environmental niche. Single chain amphiphiles (SCAs), mainly fatty acids and fatty alcohols, are used as model protocell membranes in origins of life studies because non-enzymatic, abiotic synthesis of modern membrane-forming molecules (phospholipids) is considered to be too difficult. Evidence for the prebiotic existence of SCAs lies in their occurrence in carbonaceous chondrites and synthesis under hydrothermal conditions.

The effect of 24 minerals in accelerating the rate of formation of SCA vesicles was shown 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. In contrast, phospholipid membrane formation at mineral surfaces depends systematically on the surface charge of minerals (isoelectric point, IEP). Hence, the goals of the present study were: (i) to re-examine the potential effects of minerals on the initial SCA vesicle self-assembly and survival after formation, and (ii) to identify mineral-specific trends, if any. We examined the influence of a range of minerals on the thermodynamic stability (critical vesicle concentration, CVC); formation rates; and membrane permeability (protocell “survival” up to 16 h) of SCA vesicles [2].

**Methods:** We used decanoic acid (DA, pH 7, HEPES buffer) and decanoic acid/decanol (DA/DOH = 2:1, pH 8.1, bicine buffer) at 25 °C [2]. Komatiite and tonalite, representing early oceanic and continental crustal rocks; secondary minerals (oxides, oxyhydroxides, carbonates, sulfides, aluminosilicate) formed from weathering komatite and tonalite; and some model minerals were chosen. All experiments were conducted in the presence and absence of minerals at 25 °C, pH 7 (DA, HEPES buffer) or pH 8.1 (DA/DOH = 2:1, bicine buffer). Mineral-vesicle interactions were visualized by cryo-TEM and optical microscopy [2].

**Results:** The CVC apparently increased in the presence of positively-charged minerals at high loadings ( $\geq 1 \text{ mg}\cdot\text{mL}^{-1}$ ) because of lipid adsorption and settling of the lipid-mineral aggregates. Thus, positively-charged mineral surfaces would have had a slightly deleterious thermodynamic effect near the CVC [2]. Above the CVC, initial vesicle formation rates were promoted in the presence of all minerals and correlated with the IEP of the minerals. Initial rates were faster on more posi-

tively-charged minerals [2]. The IEP depends on the crystal structure, chemical composition and surface hydration of the mineral [3]. Once formed, membrane permeability was unaffected by minerals. Thus, protocells could have survived on rock surfaces.

**Discussion:** The initial rate-enhancing effect may be interpreted as a result of rapid lipid adsorption on mineral surfaces as controlled by a combination of van der Waals, H-bonding and electrostatic forces [2]. The adsorbed lipid islands then serve as a template or “matrix” [3] for further lipid attachment from solution and its rapid transform to vesicles compared to the slower micelle-micelle interactions forming vesicles without minerals. Modified Deraguin-Landau-Verwey-Overbeek (DLVO) theory indicates that the electrostatic effect of the mineral’s surface charge is effective even up to ~ 15 nm distance from the surface through two or three stacked lipid bilayers [4]. Specifically, the presence of the lipid bilayers results in solvent and counter-ion exclusion from the proximity of the mineral surface, thus effectively extending the electric double layer away from the surface. Our work confirms the original results [1] and goes further in establishing (a) the relationship of vesicle self-assembly to mineral IEP, and (b) providing a theoretical basis (modified DLVO theory) for the catalytic effect occurring without direct contact with the mineral surface [2, 4].

**Conclusions:** Both the thermodynamics and the kinetics of membrane self-assembly showed rational 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 contact with a myriad other minerals not included here, which may have been present on early Earth and other rocky worlds such as Mars, moons of Earth, Jupiter and Saturn and exo-solar planets. Lipid-inorganic solid interactions are also relevant to diverse other processes such as drug delivery, improved medical implant biocompatibility, enhanced ore- and petroleum- recovery, and nanoparticle cytotoxicity.

**References:** [1] Hanczyc M. M., Mansy S. S. & Szostak J. W. (2007) *Orig. Life Evol. Biosph.* **37**, 67-82 (2007). [2] Sahai N., Kaddour H., Dalai P., Wang Z., Bass G. & Gao M. (2017) *Sci. Rep.* in press. [3] Blöchliger E., Blocher M., Walde P. & Luisi P. L. (1998) *J. Phys. Chem. B* **102**, 10383-10390. [4] Oleson T. A. and Sahai N. (2010) *J. Coll. Interf. Sci.* **352**, 316-326.