Analyses of FeS-precipitates by TEM and SEM in a polymersome based prebiotic protocell model

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Keywords: Iron-Sulfur-World, FeS-precipitates, polymersome, TEM/Cryo-TEM, SEM/EDX

The SynthCells project analyses vesicles as biochemical reactors in order to form a protocell model that is based on the Iron-Sulfur-World [1]. The Iron-Sulfur-World is defined by an autocatalytic and energy reproducing redox system ($FeS + H_2S \rightarrow FeS_2 + H_2$) [1, 2]. The energy release out of the iron sulfide/pyrite redox reaction ($\Delta G° = -38$ kJ / mol, pH 0) can be used for the synthesis of organic molecules, such as amphiphilic oligomers and polymers [3].

We developed a model for this process by encapsulation of an iron complex solution of pyrazine dicarboxylic acid [$Fe(pdc)_2^{2-}$] into polymer based vesicles (polymersomes) composed of 1,2 Polybutadiene-Polyethylenoxide (PB-PEO, M = 2988 g/mol) using the film-hydration-extrusion-method. The separation of $Fe(pdc)_2^{2-}$ loaded polymersomes from non-entrapped, external $Fe(pdc)_2^{2-}$ solution was achieved by dialysis. The intra-vesicular precipitation of FeS was induced by incubation of the polymersomes with hydrogen sulphide (H_2S).

The FeS-precipitates were analyzed by TEM/Cryo-TEM and SEM/EDX. We examined air- dried vesicles on carbon foil in the TEM and found indications that FeS-precipitates were enclosed in vesicular structures. We found structures with an electron dense region within a spherical envelope (Figure 1A). Chemical analyses of the polymersome solution also provided evidence for precipitated FeS within the samples.

In order to analyse the aqueous state of the polymersomes we used the Cryo-TEM technique. By Cryo-TEM it is possible to make a native snapshot of structures in a liquid system like polymersomes in buffer. The data reveal circular or elongated vesicular structures (Figure 1B) with dimensions mainly between 200 and 300 nm formed of the polymer (PB-PEO). The polymer membranes of the vesicles had a thickness of 6-7 or 11-12 nm whereas the 12 nm membranes often showed a bilayer-like structure.

In SEM/EDX investigations additional indication for an intra vesicular precipitation was obtained. Air-dried polymersomes were examined on a clean glass surface by backscatter electron imaging. Bright appearing electron dense bodies were found enclosed in envelopes (Figure 2A). EDX spectra taken at these bodies revealed an iron peak at 6.4 keV and a sulfur peak at 2.3 keV (Figure 2B). In control samples of polymerosme solution without $Fe(pdc)_2^{2-}$ (Figure 2B) no electron dense bodies and no iron and sulfur peaks could be found.

W. Grogger, F. Hofer, P. Pölt (Eds.): MC2009, Vol. 3: Materials Science,
DOI: 10.3217/978-3-85125-062-6-417 , © Verlag der TU Graz 2009

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4. This research was supported by the Sixth Framework Programme FP6 of the European Union

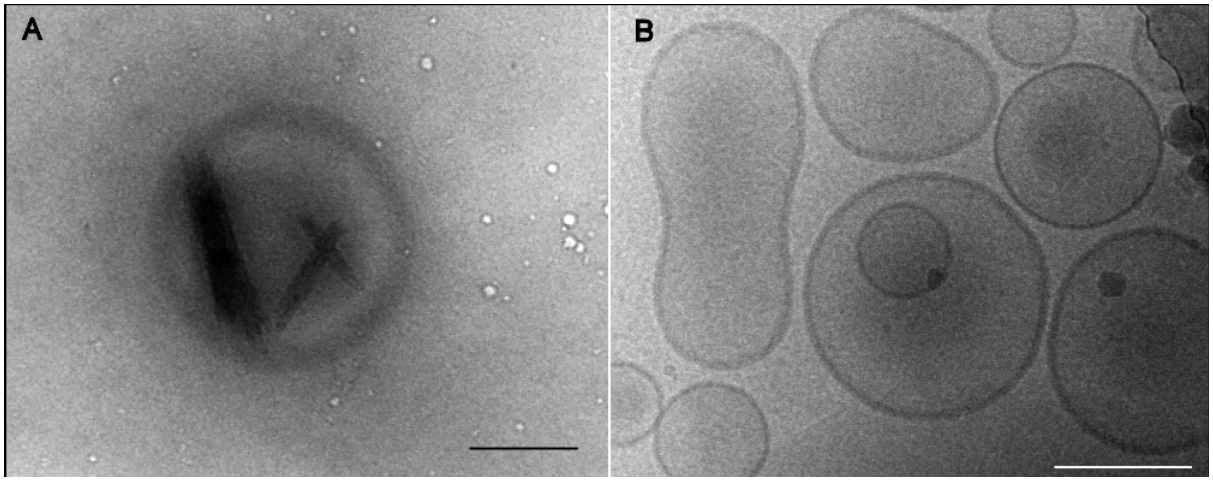

Figure 1. TEM image of iron sulfide containing polymersomes showing an electron dense structure within a spherical envelope (A). Cryo-TEM image of polymersomes without Fe-complex solution (B) shows circular and elongated vesicular structures with a membrane thickness of 6-7 or 11-12 nm. Bars: 200 nm.

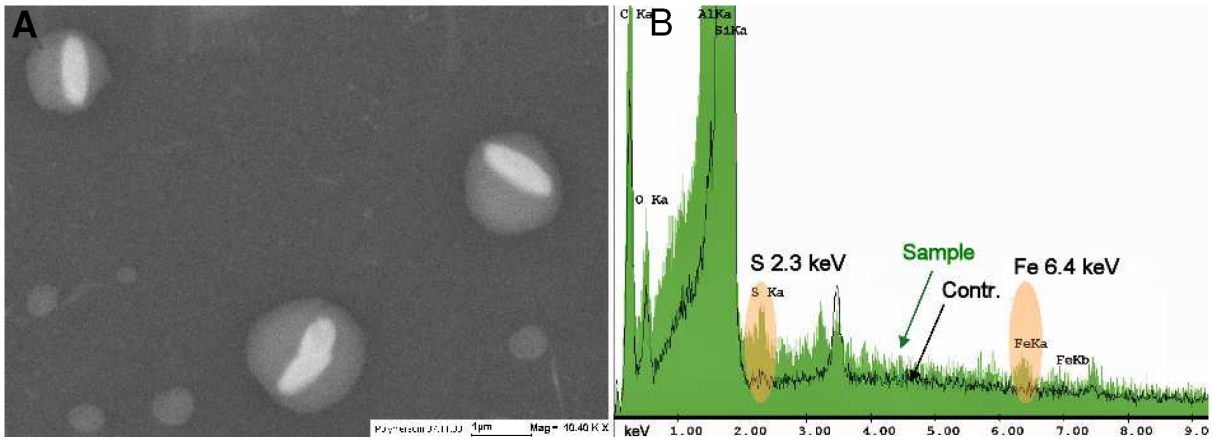

Figure 2. SEM image (BSE) of iron sulfide containing polymersomes on a glass substrate surface (A). Overlay of two EDX spectra (B); black: negative control of non-incubated polymersomes without Fe and S peaks; green: iron sulfide containing polymersome sample with Fe peak at 6.4 keV and S peak at 2.3 keV. The green spectrum was taken at the electron dense bright appearing structures.

DOI: 10.3217/978-3-85125-062-6-417 ,