| ESRF | **Experiment title: Nanoscale characterization of mineral self-organized membranes in anoxic conditions: implications for the origin of life and life detection** | **Experiment number**: **es1042** |
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| **Beamline**: **ID15A** | **Date of experiment**: from: 5/2/2022 to: 7/2/2022 | **Date of report**: 25.09.2022 |
| **Shifts: 6** | **Local contact(s)**: Stefano Checchia | *Received at ESRF:* |

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# Experimental Report

## Objective of experiment

Inorganic, self-organized, **iron-silica(te) filamentous membranes** (known as chemical gardens) might have **served as redox catalysts** in the **early Earth** hydrothermal systems that are proposed as **niches** for the emergence of **metabolism**. At the same time, these **two-layer** membranes are implicated **in life detection studies** because they show similar morphologies and composition to biologic iron filaments found in silica-rich precipitates/rocks, including those considered the oldest microfossils on Earth. Yet, **available information** on the growth and mineralogy of these **nanocomposite membranes** comes from experiments-analyses performed **in presence of oxygen**. Thus, the objective of the experiment was to investigate the formation and composition of iron-silica(te) membranes in anoxic conditions, such as those prevailing in early Earth. To **characterize their composition and layered structure** at the **nanoscale** we used **nanofocused high-energy X-ray scattering**, combined with **PDF** analysis, while **maintaining** the samples in **inert** atmosphere ($N_2$ stream).

## Beamtime allocation & strategy

**Samples: I**. 2 vesicular membrane precipitates produced by reaction of water glass 2mM solution with $FeCl_2$ 0.5M solution **II.** 2 tubular membranes made by reaction of $FeCl_2 \cdot 4H_2O_{(solid)}$ + Sod. Silicate 2mM (one sample was grind to powder). **III.** 2 tubular membranes made by reaction of $FeCl_2 \cdot 4H_2O_{(solid)}$ + Sod. Silicate 6.25 M, 1:4 dilution (one sample was grind to powder). **IV.** Reference samples: powder of $FeCl_2 \cdot 4H_2O_{(solid)}$ , Sod. Silicate solution **V.** Blank capillary-background measurement

**Measurements:** High-energy X-ray scattering (E ~ 55 keV) and a large angle 2D detector (CdTe Pilatus), covering a large Q-range (1-30 Å-1), were used. Prior to the measurements ultra-fast acquisitions we measured for blank kapton capillaries and performed a test to check the effect of the beam on the samples by repeating five succecutive fast measurements in a fixed location and comparing the results (no effect was observed). Note that samples were streamed with $N_2$ during all measurements (Fig.1).

**Line scans of ~100 μm were acquired in sections of the vesicular and tubular membranes using a nanofocused beam size of 300 x 600 nm, crossing both layers of the membrane (outer and inner), while rotating the sample (45 º).** This allowed us to study the **compositon of the two different layers of the membrane** as well as to note possible **chemical heterogenities** across the membrane wall. In one of the vesicular samples we observed sample deformation and oxidation (change in color from green to orange) after the completion of the line scan acquisitions (4 h). So to look for possible changes in the mineralogy of the membranes owing to the beam we performed fast acquisition in point avarage/spinning mode in duplicate samples. The collected time-resolved scattering patterns were used (after proper background subtraction) for the

two membrane layers for pair distribution function analysis and allowed us to probe the structural changes between the outer and inner side of the membrane.

**Preliminary results**

All membrane measurements led to meaninglful data. Particularly the line scan acquisitions allowed us to detect differences in the outer silica layer (that was amorphous to convenional XRD analysis) from the inner iron-rich part of the membrane (see Fig. 1b, c). Preliminary analysis of the diffraction peaks of the internal side of the membrane match the pattern of a hydrous Fe(II)-silicate phase. This is different from what we knew up to now about the internal part of membranes grown in presence of oxygen that are composed of ferrous iron oxyhydroxides.

Detailed analysis of space-resolved X-ray scattering patterns using pair distrubtion function analysis is currently taking place. **Preliminary results of this experiment were presented in the international workshop on 'Self-Organization in Geological Systems' of the COST action 'Chemobrionics' (abstract at the end).** Moreover, these data, together with ex situ (S)TEM/HAADF/EELS data performed in FIB-milled sections of the same samples **will be presented into a upcoming publication.**

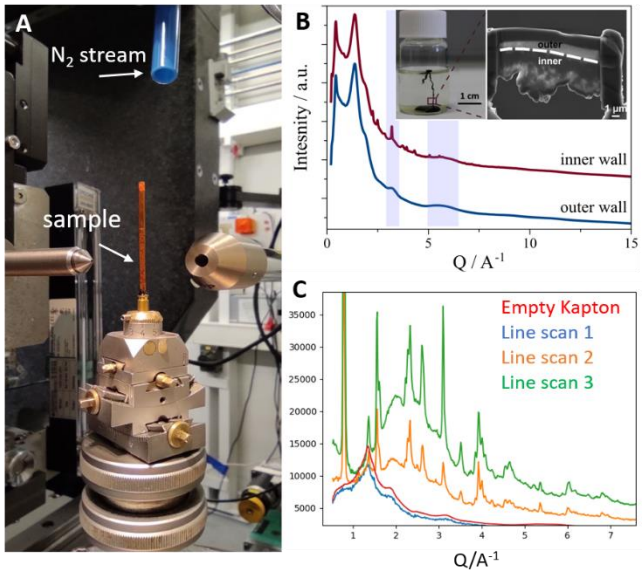


*Figure 1A. Experimental set up. B. The scattering patterns of the outer and inner parts of the membrane. C. Scattering patterns crossing the sample, starting from the Kapton capillary (red color), to the outer wall of the membrane (scan 1, blue) and the inner wall (scans 2 & 3, orange and green accordingly).*

**Outlook and general comments:**

To the best of our knowledge, the performed exepriments allowed for the first time the study of iron-silica membranes structure and compostion at the nanoscale, in anoxic conditions. As such we aspire that these results will greately advance our knowledge on early Earth mineralogy, provide insights on the possible catalytic role of such mineral membranes in prebiotic chemistry and help us distinguish inorganic from biologic traces in the rock record of Earth and beyond.

**Finally we would like to remark the excellent operation of the beamline and the great assistance received from the local contact.**

**Submitted abstract to COST action 'Chemobrionics' workshop, Edinburgh, 6-10 June, 2022**

**'Abiotic yet biomorphic; iron-silica self-organization reactions in early Earth and their significance for Life detection studies'**

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Life detection on Earth and other planets or moons requires the unequivocal recognition of remnants of Life/biosignatures in the rocky record. However, the origin of biomorphic structures preserved in rocks is much debated. Recent studies have shown that abiotic, iron-silica self-organization reactions can give rise to biomorphic features displaying morphological, structural and chemical resemblance to iron-rich microfossils hosted in cherts. So far, iron-silica self-organization experiments were either completely or partially exposed to the modern, oxidizing atmospheric conditions. Moreover, the majority of these experiments was performed using unrealistically high concentration of reactants. Consequently, the morphology and mineralogy of abiotic, biomorphic features grown from solutions containing geochemically relevant iron-silica concentrations under anoxic conditions remains unknown.To shed light on this we grew iron-silica biomorphic filaments and vesicles inside a $N_2$(+$CO_2$-$H_2$-$CH_4$) glovebox chamber from solutions that simulated ferrous iron/silica concentrations in early Earth oceans. The chemical and mineralogic composition of the resulting structures was characterized using state-of-the-art nanoscopic Synchrotron-based X-ray scattering coupled to paid distribution function (PDF) and X-ray fluorescence, while maintaining the samples in oxygen-free conditions. Here we will discuss the results of this ongoing study that will allow us to evaluate the true relevance of iron-silica self-organization reactions for Life detection in the rock record.