

Exploring the Geological Relevance of Iron-Silica Self-assembled Membranes

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INTRODUCTION

Silica gardens are membranous self-assembled forms of hollow filaments or film-like structures that precipitate spontaneously upon reaction of silica with Me-salts based on a combination of osmosis, buoyancy and chemical reaction, at a pH range of 11.4-12.5. Me-silica membranes and particularly Fe-silica membranes exhibit a series of astonishing properties; they provoke space compartmentalization separating two distinct chemical environments across the membrane for which chemical and diffusion potential generate up to 550mV, they provide shielding against UV radiation to the inner environment of the membrane and can selective catalyze the synthesis of biogenic relevant organic compounds in the presence of formamide (NH₂CHO) (Glaab et al., 2016; 2017; Saladino et al., 2016).

Up to now, Me-silica membranes have been prepared with model solutions of sodium (tri)silicate and it was recently shown that they can also precipitate from natural, alkaline and silica-rich spring water (Ney area, California) (Garcia-Ruiz et al., 2017). The Ney spring water has more than 4000 ppm of silica and a pH of 11.89 and therefore fulfills the chemical requirements needed for the precipitation of the self-assembled membranes.

In this work we: i) compare the formation of the Fe-silica membranes prepared with the model solution to those prepared with the Ney water, ii) investigate the precipitation of the Fe-silica membranes by varying the pH, silica concentration, temperature, and atmospheric composition, and iii) perform new experiments by replacing the Fe-salt pellets of FeCl₂•4H₂O and

Fe₂(SO₄)₃•9H₂O with micro-drops of saturated Fe-salt solutions and focus on the characterization of the membranes at sub-micron scale.

MATERIALS AND METHODS

Three mL of sodium (tri)silicate solution were poured into four mL glass vials, while, Me-salt pellets of FeCl₂•4H₂O and Fe₂(SO₄)₃•9H₂O, were placed, separately (pellets were prepared using an agate mortar, until reaching the powder fraction, and a press up to 10 tons). The same experiment was performed by using the Ney water, instead of the model solution. In another set of experiments we replaced the Fe-salt pellets with saturated solutions of FeCl₂ and FeCl₃ by varying the silica concentration from 0.9 M to 7.6 M. The experiments were conducted in ambient conditions and inside the glove box (N₂ atmosphere) by varying the pH from 10.5 to 14 and the size of the micro-drops from 0.2 µL to 2 µL.

Following the formation of the Fe-silica filamentous membranes and the termination of the phenomenon, the membranes were studied ex-situ. To identify the mineral crystalline phases of the membranes we used high resolution powder X-ray diffraction (HRXRD) with a D8 Advance Bruker AXS diffractometer, (Cu-K_α X-ray generator) operating at 40 kV acceleration voltage and 40 mA current. Phase identification was carried out with the Diffrac.Eva v. 4.1 Software and the American Mineralogist Crystal Structure Database. For the textural and chemical characterization of the sub-micron mineral phases we used a ZEISS SUPRA 40 VP, FESEM-EDS equipped with an Oxford energy-dispersive X-ray spectrometer (EDS), operating at 5keV-20KeV. The high resolution images were obtained at 5kV and at 2mm working

distance, both in SE and BS mode, while for the elemental analyses operating conditions were set at 15 kV accelerating voltage and 7.5 mm working distance and the AZtec 30 SP1 EDS software was used. Also, micro-Raman spectroscopy was used to acquire information about the Fe-phases of the membrane that were previously detected with the FESEM-EDS. Spectra were recorded using a HORIBA Jobin Yvon LabRAM HR UV-VIS spectrometer equipped with an Olympus BX41 optical microscope with binocular and Koehler illumination and a CCD detector, at excitation wavelengths of 532 nm.

In the case of the gas production upon reaction of the Fe(III)-salts with the Ney water, GC-MS was used to identify the gas phase using an Agilent VARIAN (now Bruker) 450 GC 240-MS Ion Trap Mass Spectrometer (40mL manual injection, gas type syringe). For the measurement standard air samples as well as blank samples of the Ney solution were used.

RESULTS AND DISCUSSION

Following the classical protocol, we immersed soluble pellets of Fe(II)- and Fe(III)-, salts in the model solution and in the Ney water. In the case of Fe(II)-salt and the Ney solution we obtain the typical hollow, tubes, with twisted morphologies, similar to those produced with the model solution. Apart from the morphological resemblance with the Fe-silica membranes produced with the model solution, the Ney Fe-silica tubules show both the characteristic textural and compositional gradients across the membrane. The outer surface of the membrane, facing towards the Ney water, is smooth, rather homogeneous and silica-rich, whereas, the inner surface has complex texture of micro-rosettes and hexagonal plates of Fe-(oxy)hydroxides (Fig. 1). We should note

palabras clave: Fe-Silice, Membrana, Autoensamblado, Fuente de Ney, Microgotas

key words: Fe-Silica, Membrane, Self-assembly, Ney Spring, Micro-Drops

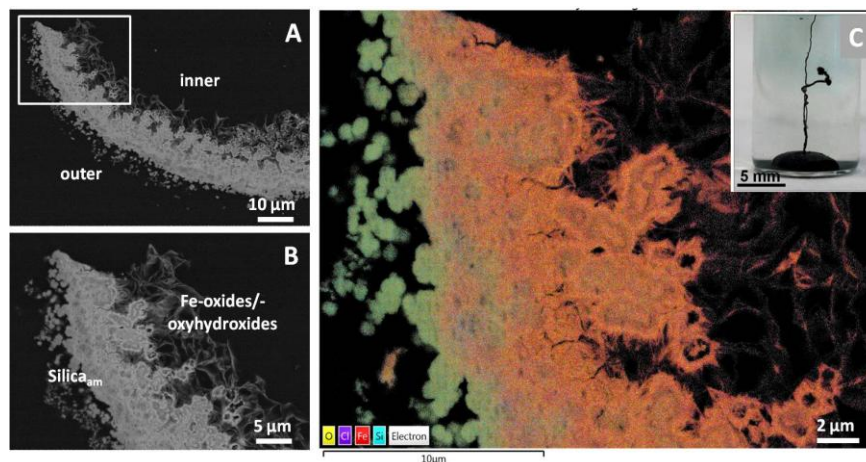


fig 1. FESEM-EDS/STEM study of the Fe(II)-silica filamentous membrane prepared with the Ney water and the Fe(II)-salt pellet. A-B. Section of the Fe(II)-silica tubular structure where we can see the distinct textural difference of the outer, compact, part and the inner, complex, part of the membrane. C. Elemental map of the tube that shows the silica globules of the outer part and the Fe-(oxy)hydroxides of the inner part.

that the formation of the tubules in the Ney water is relatively slow (range of hours) compared to the tubules made with the model solution (range of seconds). As shown with the FESEM and the micro-Raman investigation the outer part of the membrane consists of silica, while, the inner part of Fe-oxides, such as, hematite and Fe-oxyhydroxides, such as, goethite, lepidocrocite and akaganeite.

On the other hand with the immersion of the Fe(III)-salt in the Ney water a large amount of CO₂ bubbles is released (gas phase identified by GC-MS) leading to the premature bursting of the membrane almost simultaneously to its formation. This behavior that is not observed in the case of the model solution increases the availability of the surface area of both sides of the membrane and quickly releases the newly forming molecules. Both properties are particularly interesting for enhancing the role of membranous structures as catalysts in geochemical scenarios (see Saladino et al. 2016).

Concerning the experiments with the micro-drops, we mixed the drops of the Fe(II)-/(III)-salt solutions either by injecting them inside the sodium silicate solution or by pouring them on the surface of the silicate solution. In the first case we observed the instant formation of the membrane, while, in the second case the formation was gradual and exhibited two different morphologies: i) a vessel type, occurring at low silica concentration/low pH, and

ii) a branching type by disruption of the membrane, at high silica concentration/high pH. In all cases, the structures exhibited lower crystallinity compared to the ones made with the solid pellets, as was shown from the X-ray diffraction study. The aim of this experiment was to demonstrate the feasibility of the Fe-silica membrane formation upon mixing of Fe-rich, acidic fluids with silica-rich, alkaline fluids, that could occur in a submarine hydrothermal system or during acid rain deposition on alkaline waters.

CONCLUSIONS

In this communication we perform a detailed investigation on the Fe-silica membrane formation with the use of natural, alkaline, silica-rich, water from the Ney, California and demonstrate that Fe-silica membranes can occur upon fluid mixing, using micro-drops, a geologically relevant method to produce self-assembled, biomimetic membranes of iron and silica.

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