

# Microwave-Induced Self-Organization of Liophilic Colloids During Enhanced Hydrolytic Polymerization



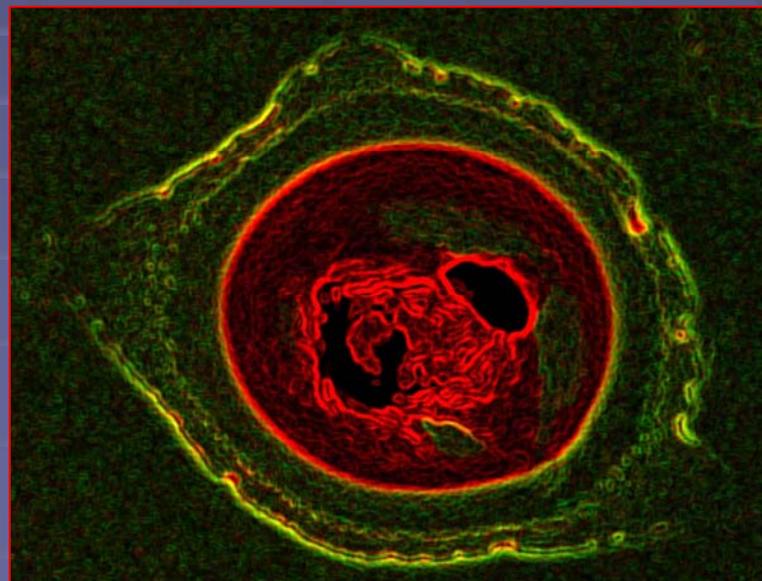
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# Introduction

- ***Wet chemical synthesis using conventional hydrolysis approaches, including sol-gel methods, is a common technique for preparing functional inorganic materials, particularly, metal oxide nanoparticles***
- ***Microwave-assisted synthesis is a convenient, green and efficient method to obtain functional nanoparticles for catalytic, sensing and biomedical applications***
- ***Microwave treatment provides heating and direct energy supply to the whole system, facilitates chemical reactions and accelerates reaction-diffusion processes***

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# Introduction

- *In recent years, most of the studies on microwave-assisted chemical synthesis of iron-containing inorganic materials were focused on the particle size distribution, crystalline structure, as well as chemical and phase composition of the resulting products.*
- *However, little attention has been paid to the microscopic structure of the system at the initial stages of the hydrolytic process preceding a complete desolvation, especially to the self-organization of the colloidal system under microwave treatment. Most of the studies have not addressed morphology of the dissipative structures emerging in the course of sol-gel transition in the colloidal precursor.*
- *In this report we briefly discuss the multifactor nature of self-organization processes and self-assembly of dissipative microstructures in liophilic inorganic colloids at the initial steps of microwave-enhanced hydrolytic polymerization of ferric oxides / oxohydroxides.*



Fig. 1. FeCl<sub>3</sub>, 200 W, 2.45 GHz, 1 min.

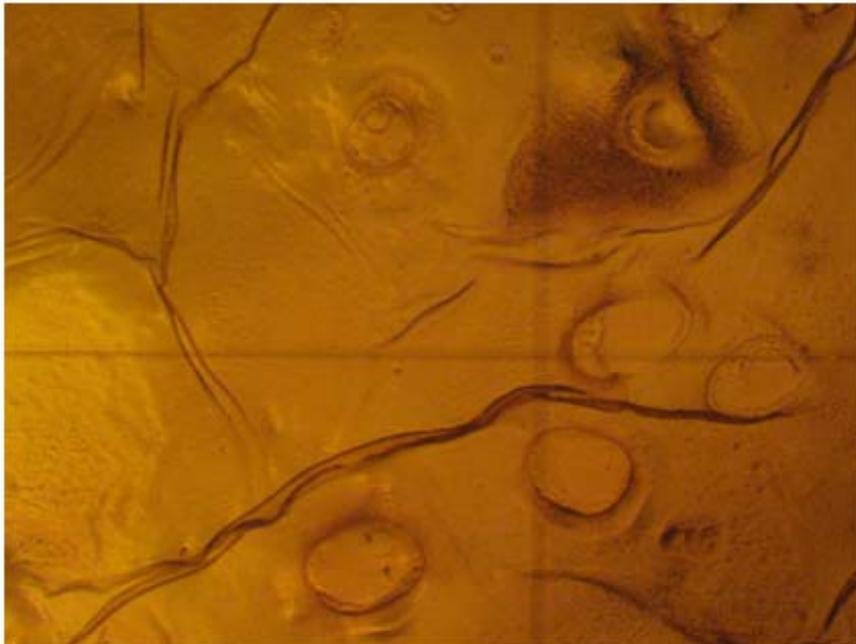


Fig. 2. FeCl<sub>3</sub>, 200 W, 2.45 GHz, 1 min.



Fig. 3. FeCl<sub>3</sub>, 200 W, 2.45 GHz, 1 min.

*Saturated ferric chloride solutions were irradiated in a thin layer (1-3 mm) on a glass Petri dish using a standard 2.45 GHz magnetron microwave source with the power varying from 200 to 800 W. Morphological characterization of the resulting structures has been performed at magnification of 100-200x using an optical microscope POLAM-111 combined with a photcamera Canon A590 IS with processor DIGIC III (based on iSAPS technology) for 9-point or 1-point focusing regimes.*



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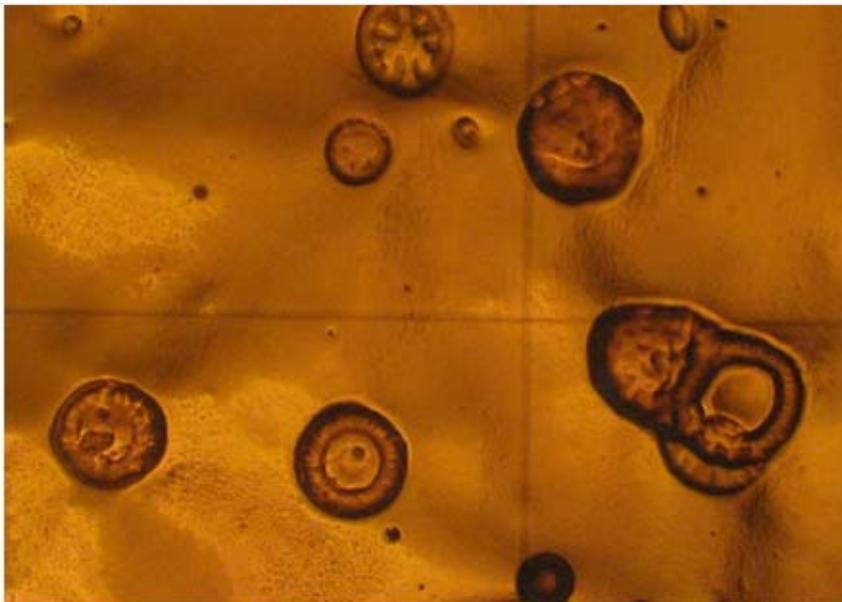


Fig. 4. FeCl<sub>3</sub>, 200 W, 2.45 GHz, 1 min.

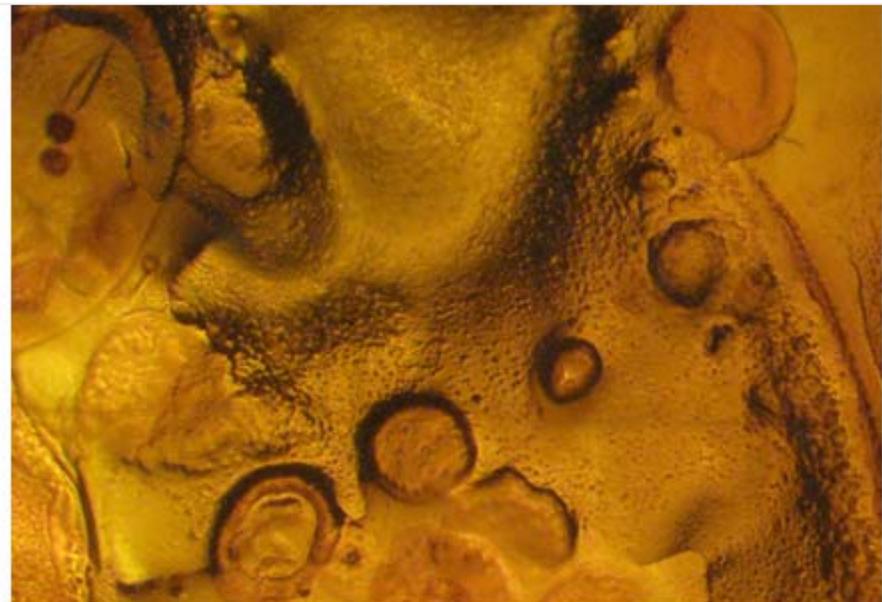


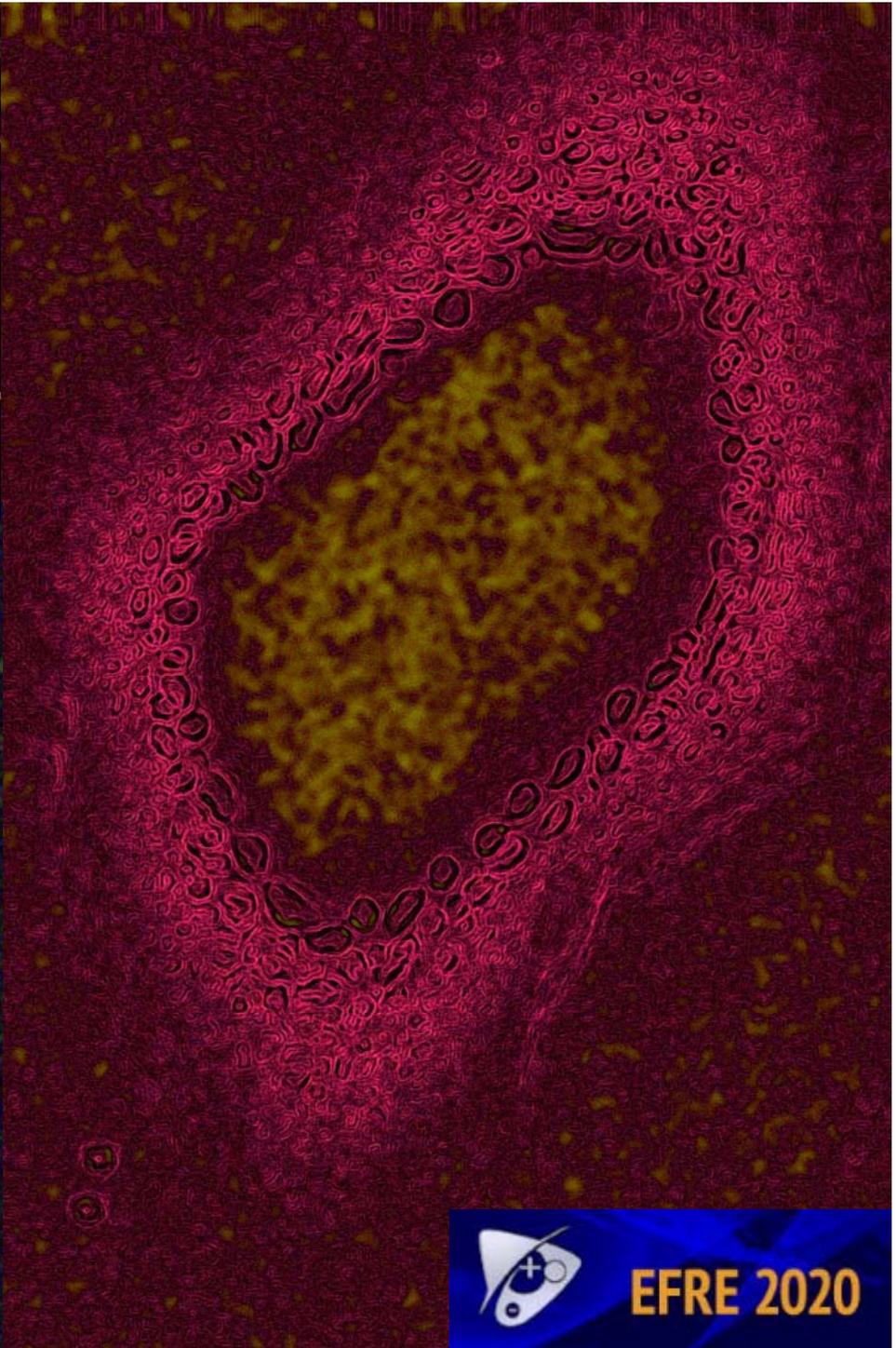
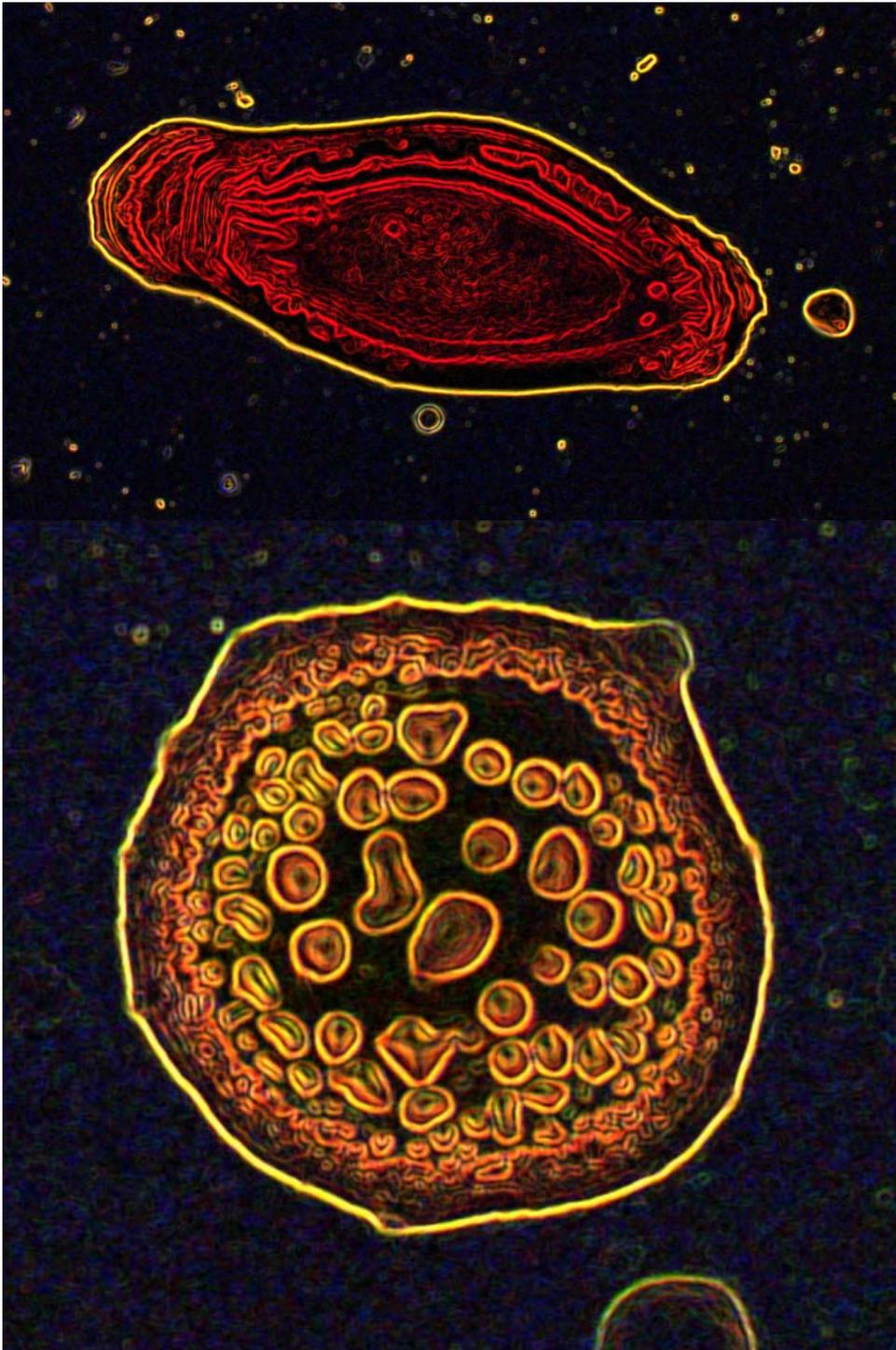
Fig. 6. FeCl<sub>3</sub>, 450 W, 2.45 GHz, 30 sec.

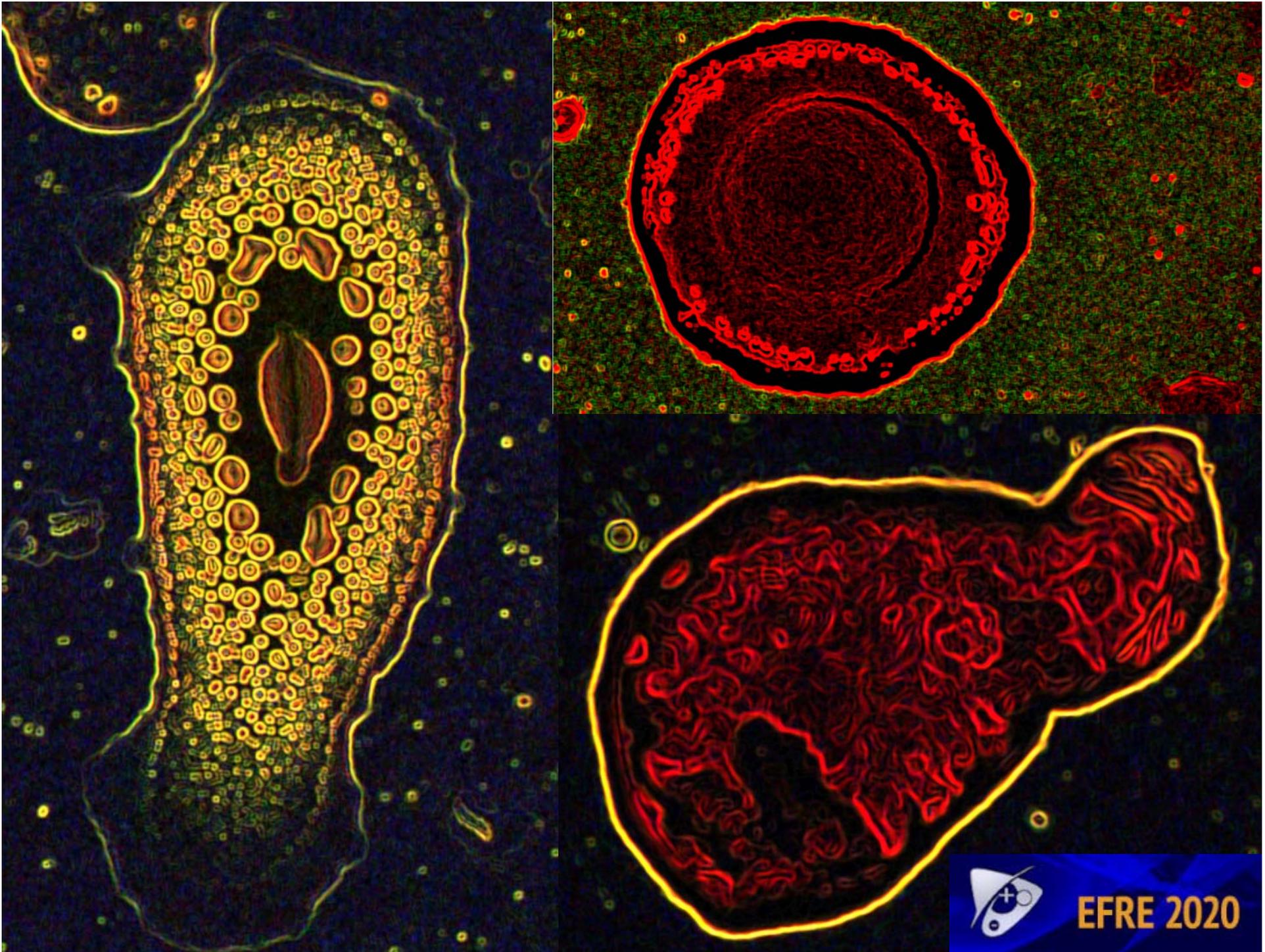


Fig. 5. FeCl<sub>3</sub>, 450 W, 2.45 GHz, 30 sec.



Fig. 7. FeCl<sub>3</sub>, 450 W, 2.45 GHz, 30 sec.





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# A possible mechanism of microwave-induced structure formation in colloidal precursors

- During microwave irradiation of the precursor, scattering occurs due to the loss of the beam energy through ionic conductivity and dipole rotation, leading to the energy dissipation. The larger the scattering coefficient of the precursor, the lower the microwave penetration. The latter are associated with the movement of ions and depend on the ion size, charge and electrical conductivity, as well as on the interaction of the ions with the solvent molecules.
- Ionic conductivity depends on the concentration of ions, their mobility and temperature of the solution, while an increase in the ion concentration leads to an increased scattering coefficient. Since ionic conductivity is due to the electrophoretic migration of ions in solution when an electromagnetic field is applied, they move within the irradiated precursor in the direction determined by the field parameters.
- Contributions of the electric and magnetic fields will be different depending on the magnetic susceptibility of the precursor, which suggests the contribution of magnetophoresis to the effects observed.

## A possible mechanism of microwave-induced structure formation in colloidal precursors

- Since the movement of ions represents currents leading to the energy losses equal to the amount of heat released due to the resistance to the ion flow, a local heating of the medium arises, depending on the ion composition of the flow emerging in the local region.
- Contribution of the certain ions is determined by their mobility, so there are prerequisites for heterogeneous medium composition at the local scale, determined by the difference in the chemical composition and the ion mobility. As a result of this, the ion concentrations in the local areas change, due to which a spatial disproportionation of the flows in these directions occurs, and the local increase in the ion concentration leads to an increase in the scattering coefficient and the media heating.
- Heating efficiency depends on the scattering coefficient (the ratio of the dielectric loss to the dielectric constant). So, microwave-activated processes in the layers of different thickness will proceed in different ways, due to the differences in the energy supplied, because the heat and mass transfer occurs not only in the horizontal direction, and the half-attenuation layer thickness is approximately inversely proportional to the square root of the microwave frequency.

## A possible mechanism of microwave-induced structure formation in colloidal precursors

- As the temperature increases, the dielectric losses occurring due to the contribution of the dipole rotation decrease (coherence increases), and the dielectric loss is determined by the ionic conductivity. Therefore, during irradiation there is a transition from orientational ordering in the medium to the structure formation due to the ionic conductivity in the irradiated precursor, accompanied by the heat and mass transfer as a result of heating.
- Since the heating efficiency in the framework of the rotational mechanism depends on the characteristic relaxation time of the dielectric, which depends on its viscosity, a transition from the orientational ordering to a heterophase system is directly related to the induced phase transitions, resulting in self-organization of a complex of the coupled processes of ionic conductivity or ion transfer, operating within a microheterogeneous colloidal system with dynamic membranes and morphologically-different colloidal phases.

## A possible mechanism of microwave-induced structure formation in colloidal precursors

- Since microwave energy is absorbed during scattering by a dispersed precursor according to the scattering coefficient at each point of the medium, different dissipative processes can be observed at different points of the precursor, depending on the local nature of the material and leading to self-assembly of various structures.
- In the case of formation of the dynamic membranes and boundaries compartmentalizing the medium, the excess ion concentration on one side of the self-organizing membrane leads to the directed movement of ions under the microwave beam.
- Similar effect results from the formation of soft matter phases with a viscosity different from the initial solution, since the sample viscosity affects the ability of a substance to absorb microwave energy and limits its mobility (high viscosity limits the rotation of molecules). In the presence of both conductive and dielectric phases, the gradient will be sufficiently high, since it is known that microwave penetration is considered infinite for materials transparent to microwave radiation and equal to zero for reflecting ones (such as metals).

## A possible mechanism of microwave-induced structure formation in colloidal precursors

- A simple interpretation of the phenomena observed as a purely thermal effect of heating is unacceptable because of the selective mechanisms operating here, depending on the chemical composition of the medium, which dynamically changes during microwave irradiation, and the phases that are different in composition become separated in space. Therefore, the response of different structures at each new time period of their formation and metamorphism is different.
- For the small molecules / ions, the dielectric loss due to the contribution of the dipole rotation decreases with increasing temperature in accordance with the known laws of microwave electrochemistry, and for the large molecules / ions this is ambiguous. Therefore, at the points with a different number of ions, self-organization can proceed differently.

# A possible mechanism of microwave-induced structure formation in colloidal precursors

- Thus, dissipation and self-organization are directly related to the processes that occur during microwave scattering.
- As a result, the processes of microwave-induced structure formation in a colloidal media can be divided into conservative self-organization (microwave-assisted self-assembly similar to crystallization) and non-conservative or dissipative self-organization associated with the scattering gradients and mass transfer determined by the structures different both in chemical composition and microwave susceptibility (similarly to the way it occurs in phase reaction-diffusion processes with the participation of an activator and an inhibitor).

# A possible mechanism of microwave-induced structure formation in colloidal precursors

- From the chemical point of view, microwave-assisted hydrolysis of ferric chloride solutions is known to produce polymeric iron(III) oxyhydroxides / oxides. At lower temperatures (100-125°C) iron oxyhydroxide chloride is predominantly synthesized, while at higher temperatures (> 150 °C) iron(III) oxide is produced.
- This process begins from the partial dehydration of the hydrolysis products in saturated ferric salt solutions leading to the formation of sol by means of polycondensation of Fe(III) hydroxo complexes producing oligomer / polymer oxohydroxides (olation). Further cross-linking of the above precursors by oxo-bridges results in the gelation of the colloidal system (oxolation).
- Some of the structures obtained were shown to contain such mineral phases as acageneite ( $\beta$ -FeOOH), ferrihydrite, goethite ( $\alpha$ -FeOOH), hematite, lepidocrocite ( $\gamma$ -FeOOH), maghemite, etc.

# Conclusions

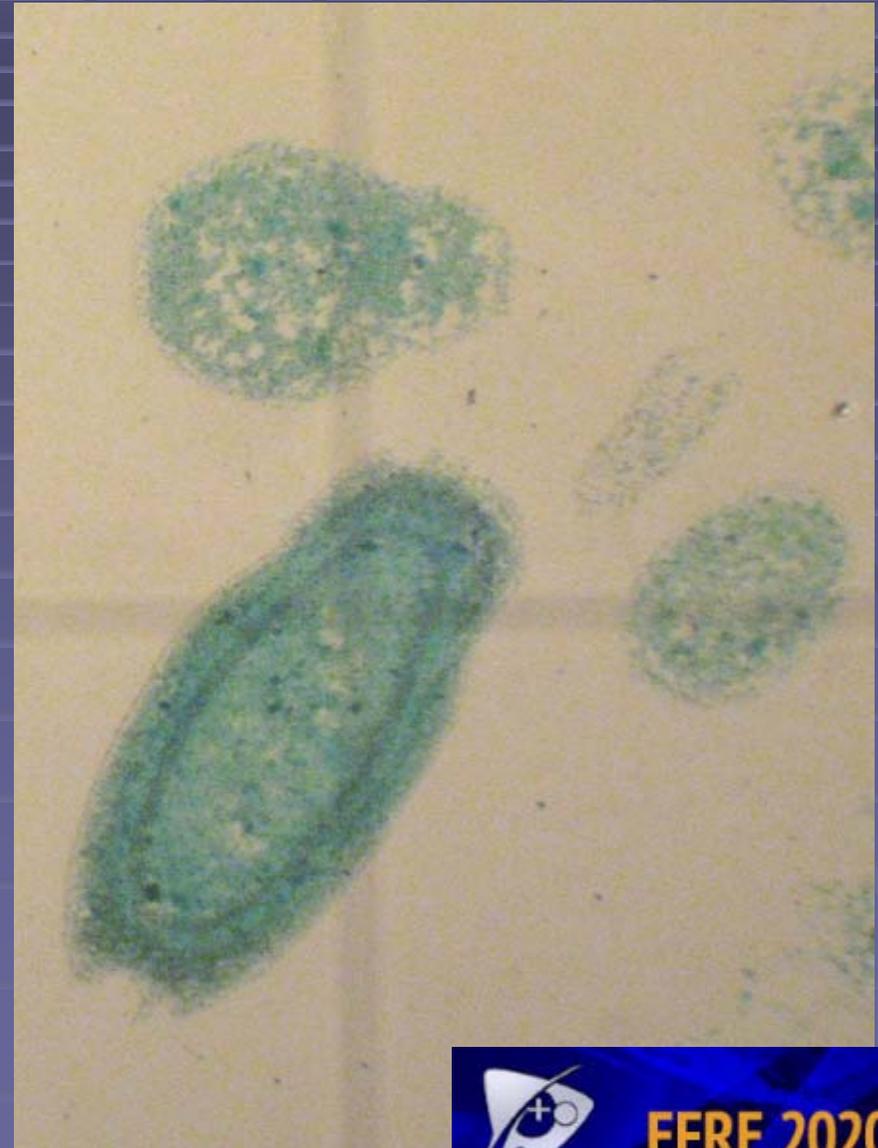
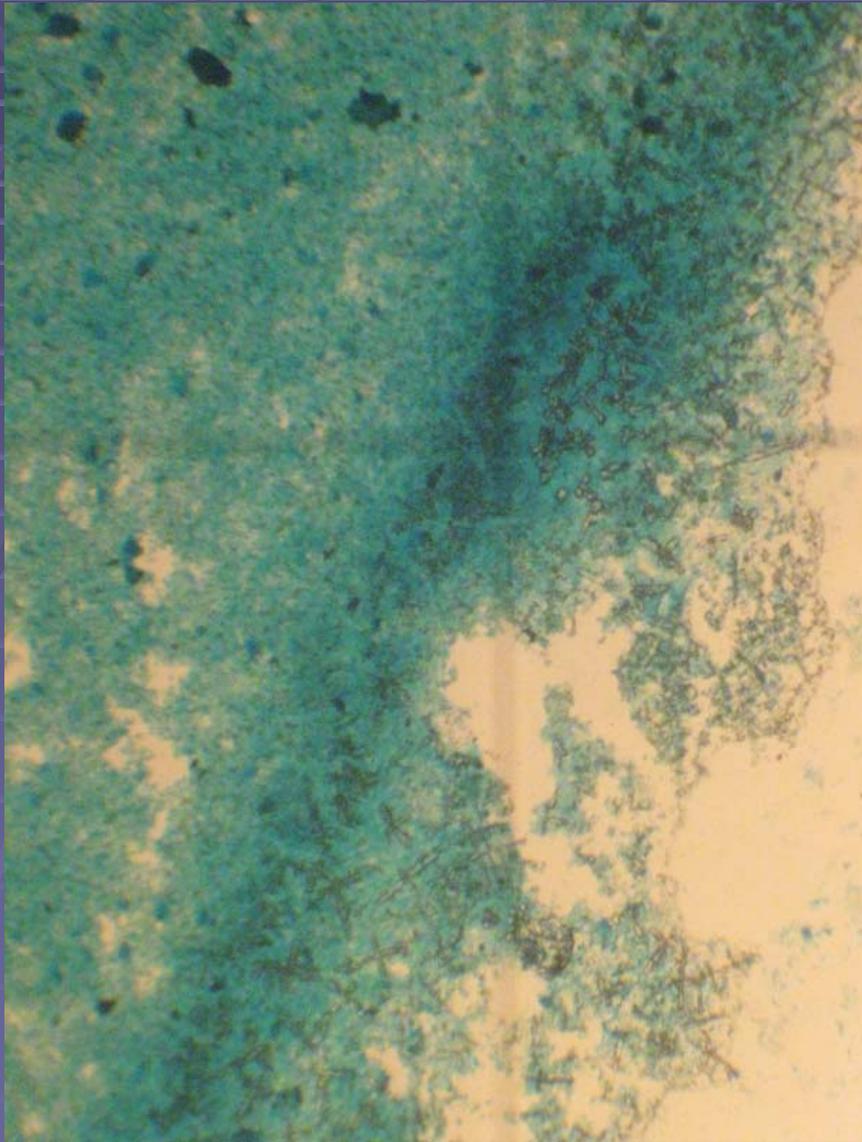
- Microwave-induced self-organization in liophilic colloids results in the dissipative microstructure formation at the initial stages of hydrolytic polycondensation process.
- Morphological diversity of the self-organization products is maximal at the nucleation stage, since the high viscosity and heterogeneity of the system favors reaction-diffusion processes to occur.
- Further irradiation leads to a complete dehydration of the gel, accompanied by the increase in crystallinity of the resulting products, decreasing their morphological diversity.
- Thus, the intermediate states during the transition between a colloidal soft matter through an amorphous precipitate towards the solid state nanocrystals are capable of self-organization into dissipative structures.

Thank you for your attention!



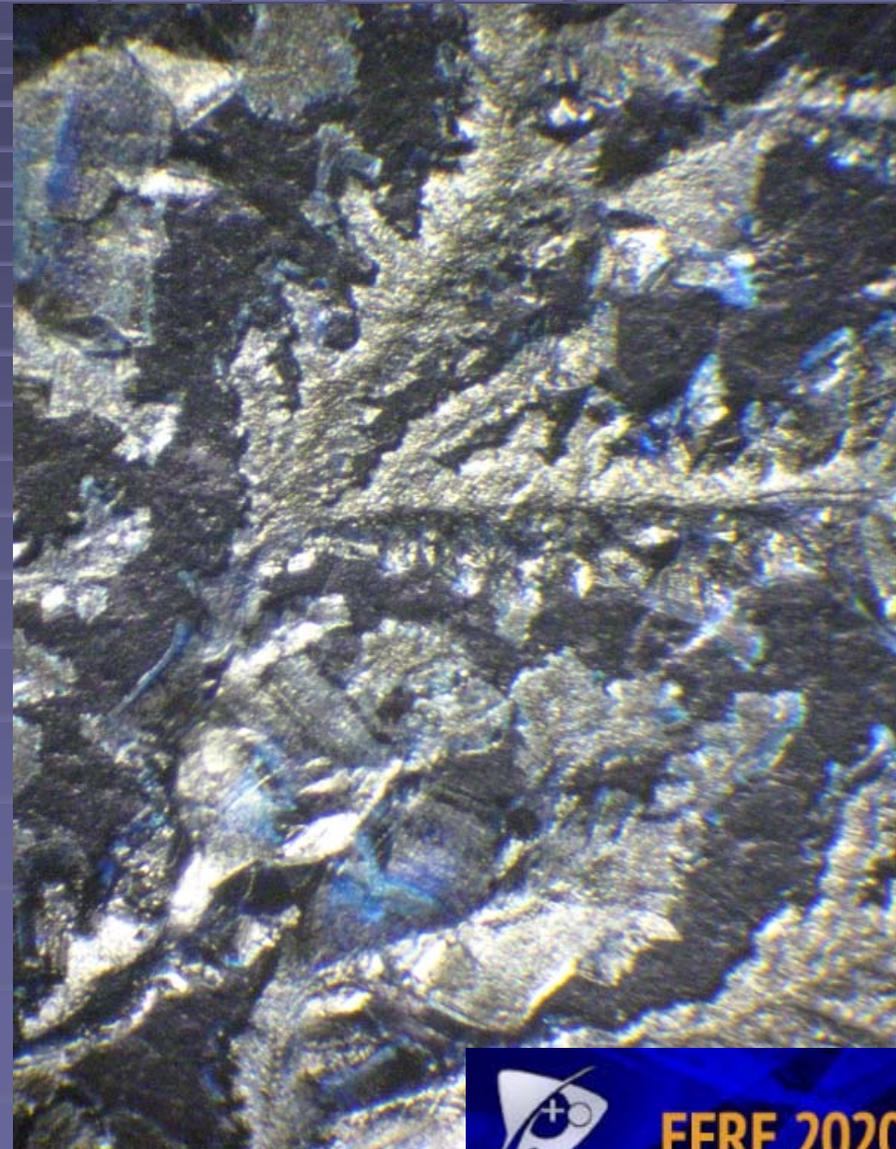
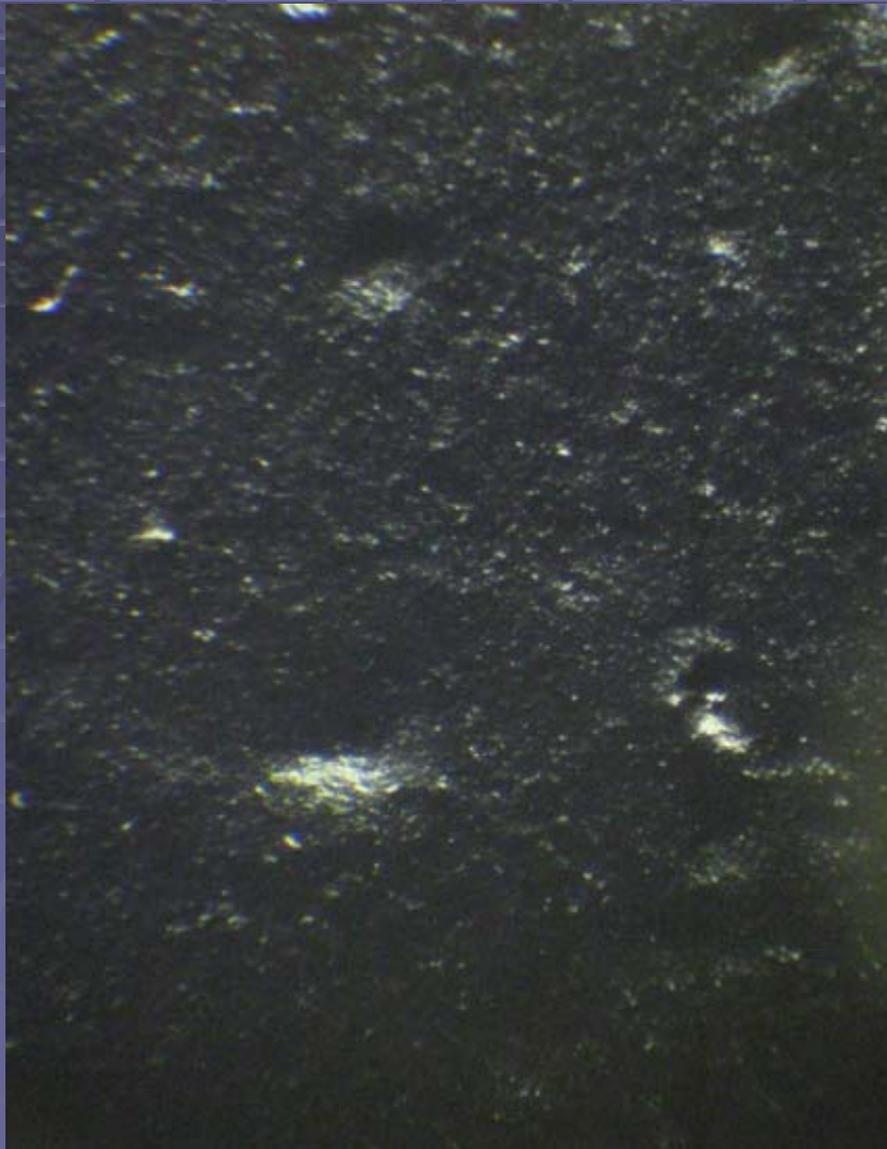
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# Supplementary information



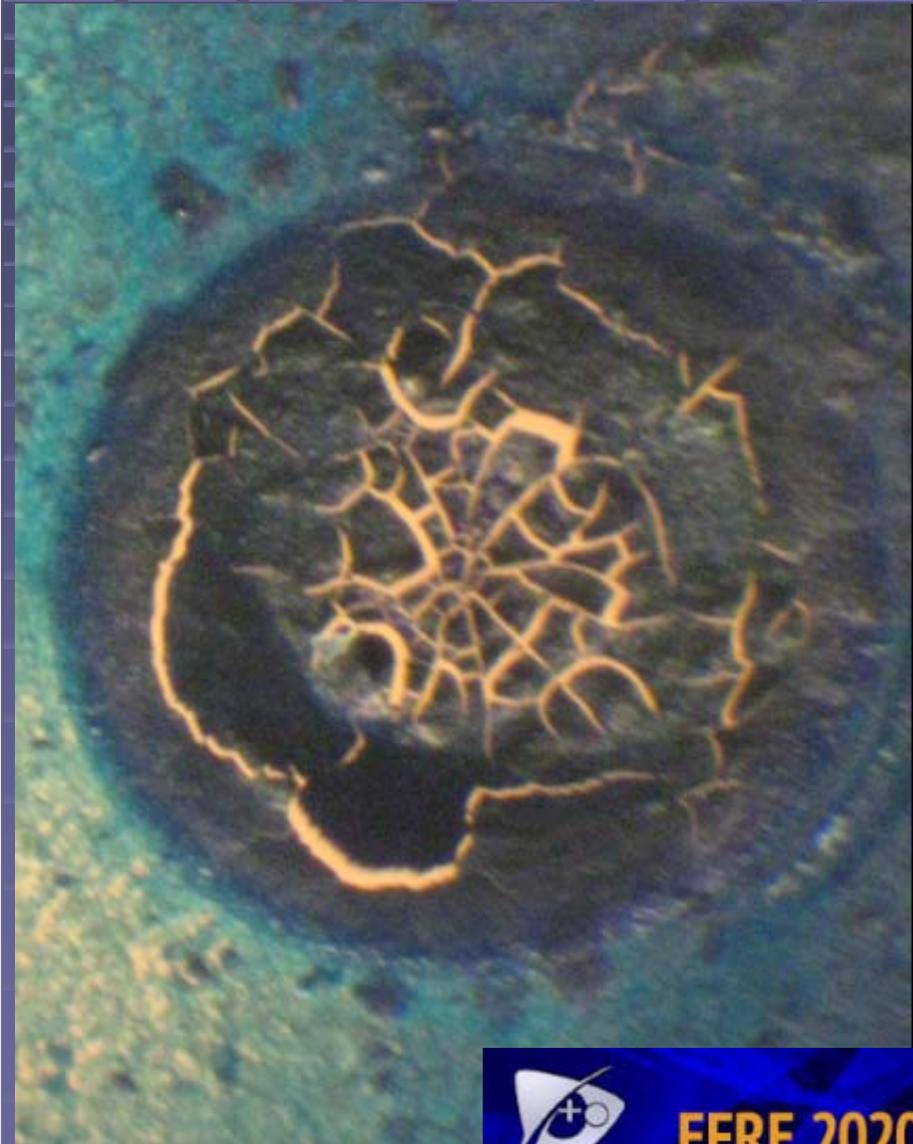
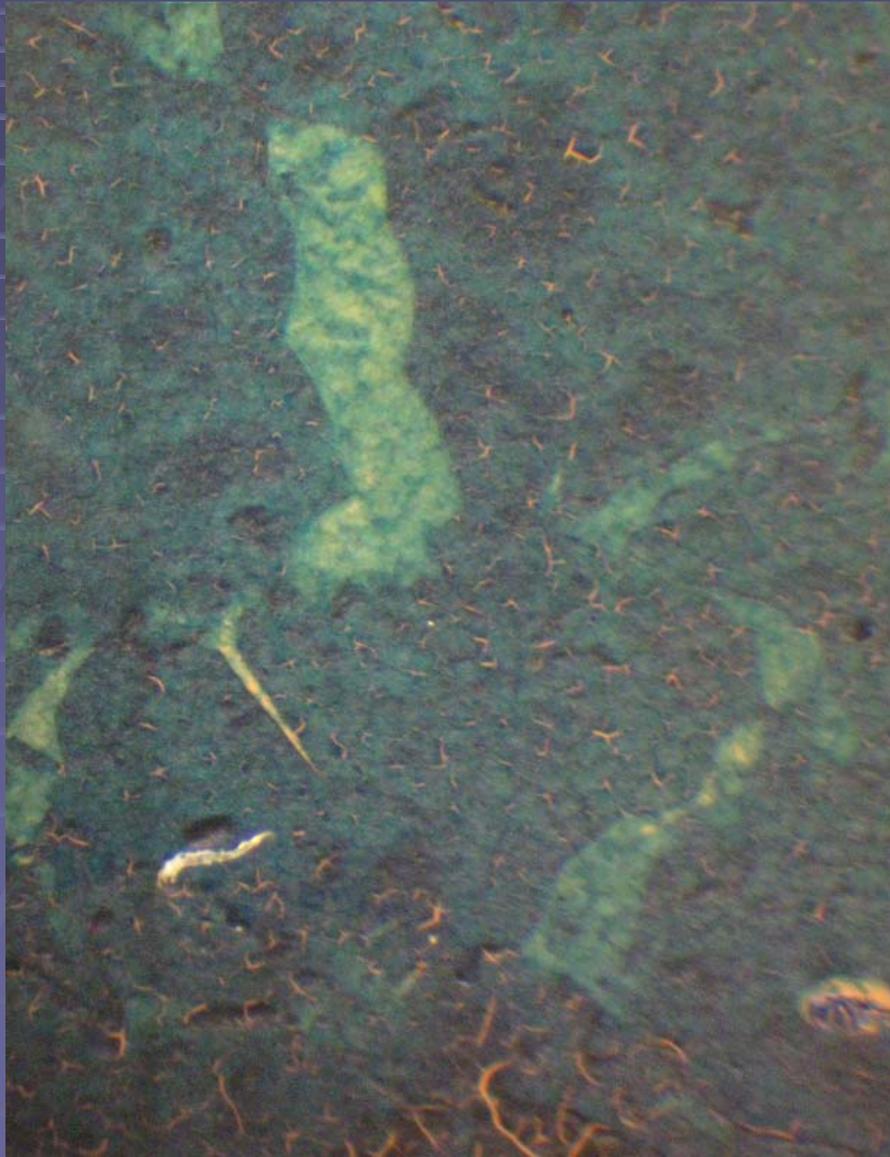
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# Supplementary information



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