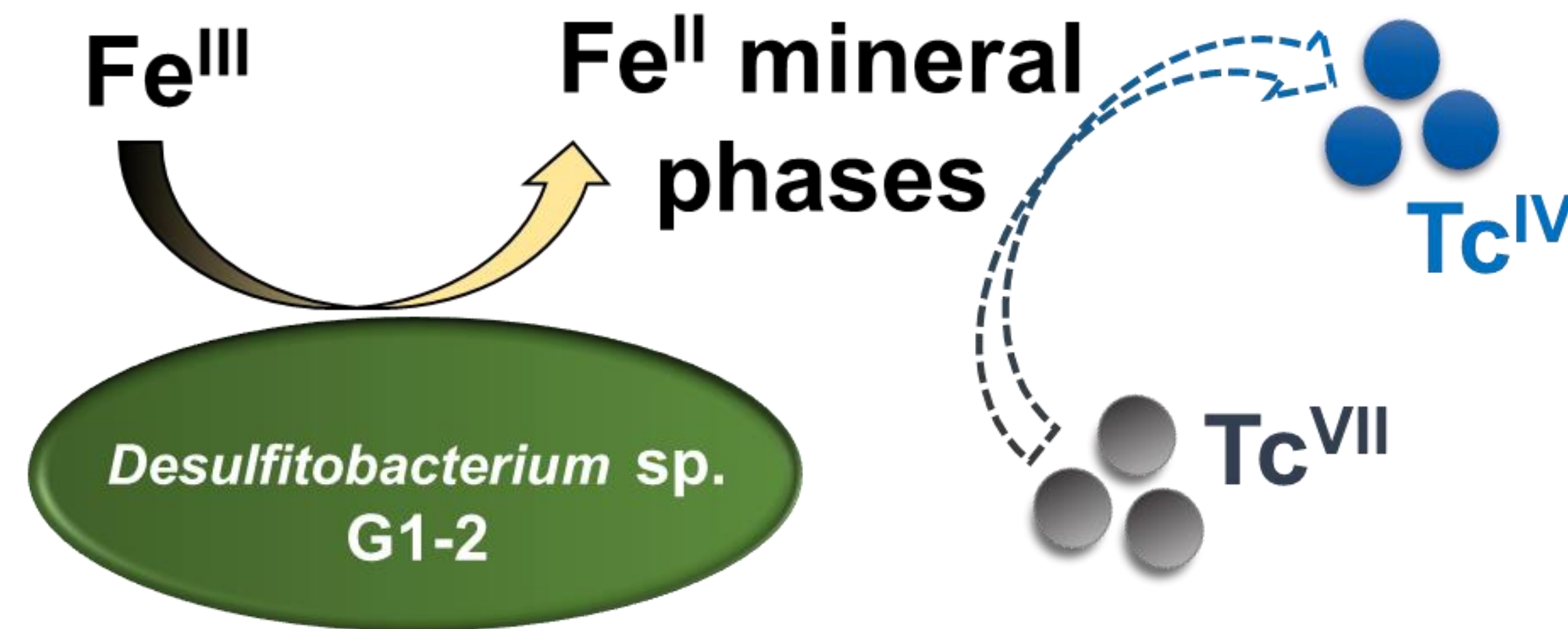# Biogenic minerals formation by an Fe^{III}-reducing *Desulfitobacterium* sp. isolate

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Dissimilatory Fe^{III} reduction for Tc^{VII} immobilization

- ^{99}Tc is a fission product present in spent nuclear fuel ($\tau_{1/2}$: 2.13·10^5 a)

- Under oxidizing conditions it is present as water-soluble $Tc^{VII}O_4^-$ with high mobility[1]

- Deep geological repositories (DGRs) for long-term radioactive waste disposal consist of a metal canister including the spent nuclear fuel, a buffering sealing material (e.g., bentonite) and the natural host rock[2]


- The Fe^{III} reducer *Desulfitobacterium* sp. G1-2 was isolated from bentonite[3]

- The genus *Desulfitobacterium* can perform anaerobic respiration using Fe^{III} as electron acceptor[4]

- Resulting Fe^{II} biogenic mineral phases may reduce $Tc^{VII}O_4^-$ to less mobile $Tc^{IV}O_2$, thus promoting ^{99}Tc immobilization[5]

Desulfitobacterium sp. G1-2: Fe^{II}-mineral phase formation and characterization
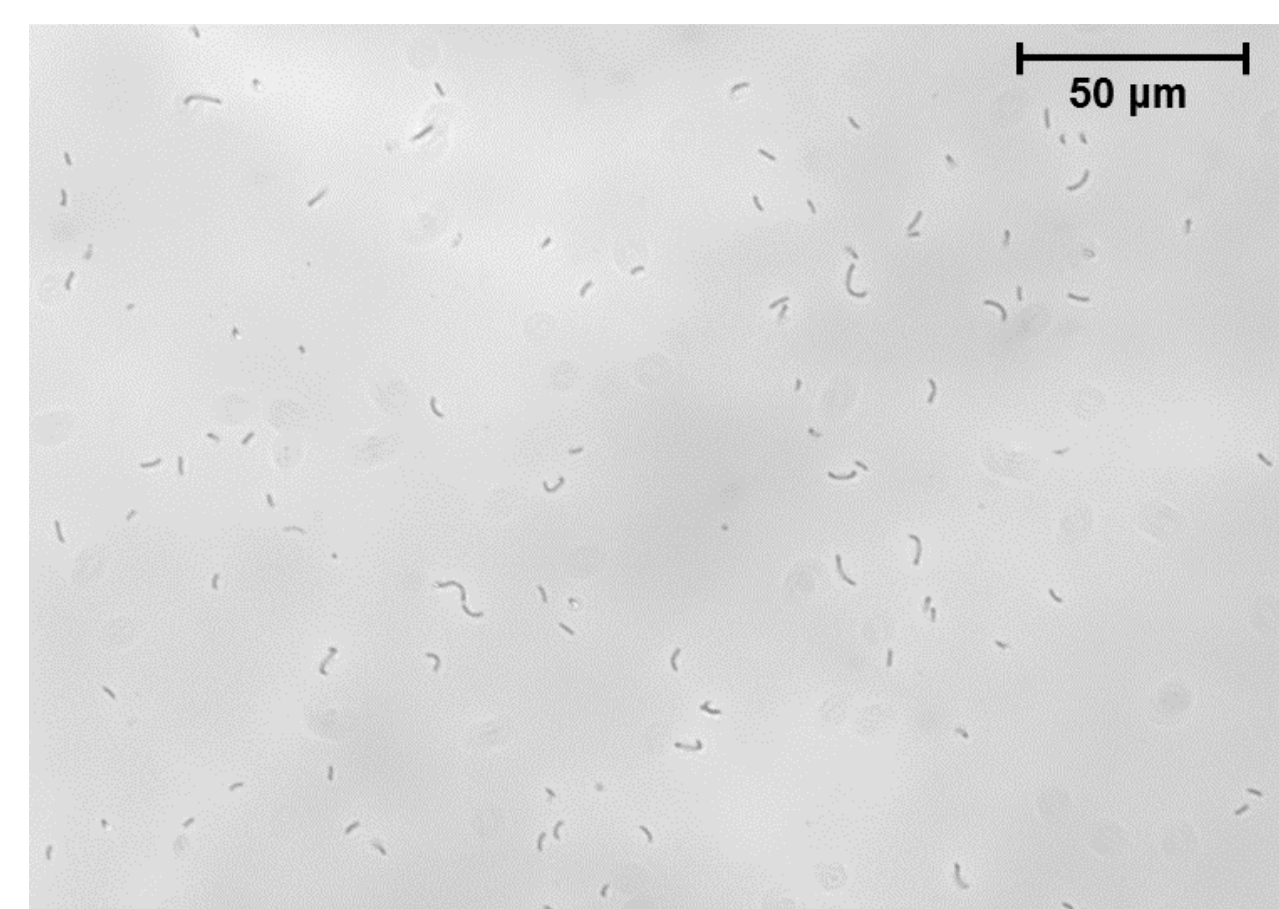
- Cultivation of *Desulfitobacterium* sp. G1-2 in medium DSMZ 579[8] (pH = 6.8) with Fe^{III} citrate as e^- acceptor in anaerobic serum flasks in triplicates

- Cell counting using a Neubauer chamber for five days

- Observation of different phases in the cultures over time

- Collection of the phases and transfer into a Raman cell in a N_2-glovebox (O_2 < 0.1 ppm)
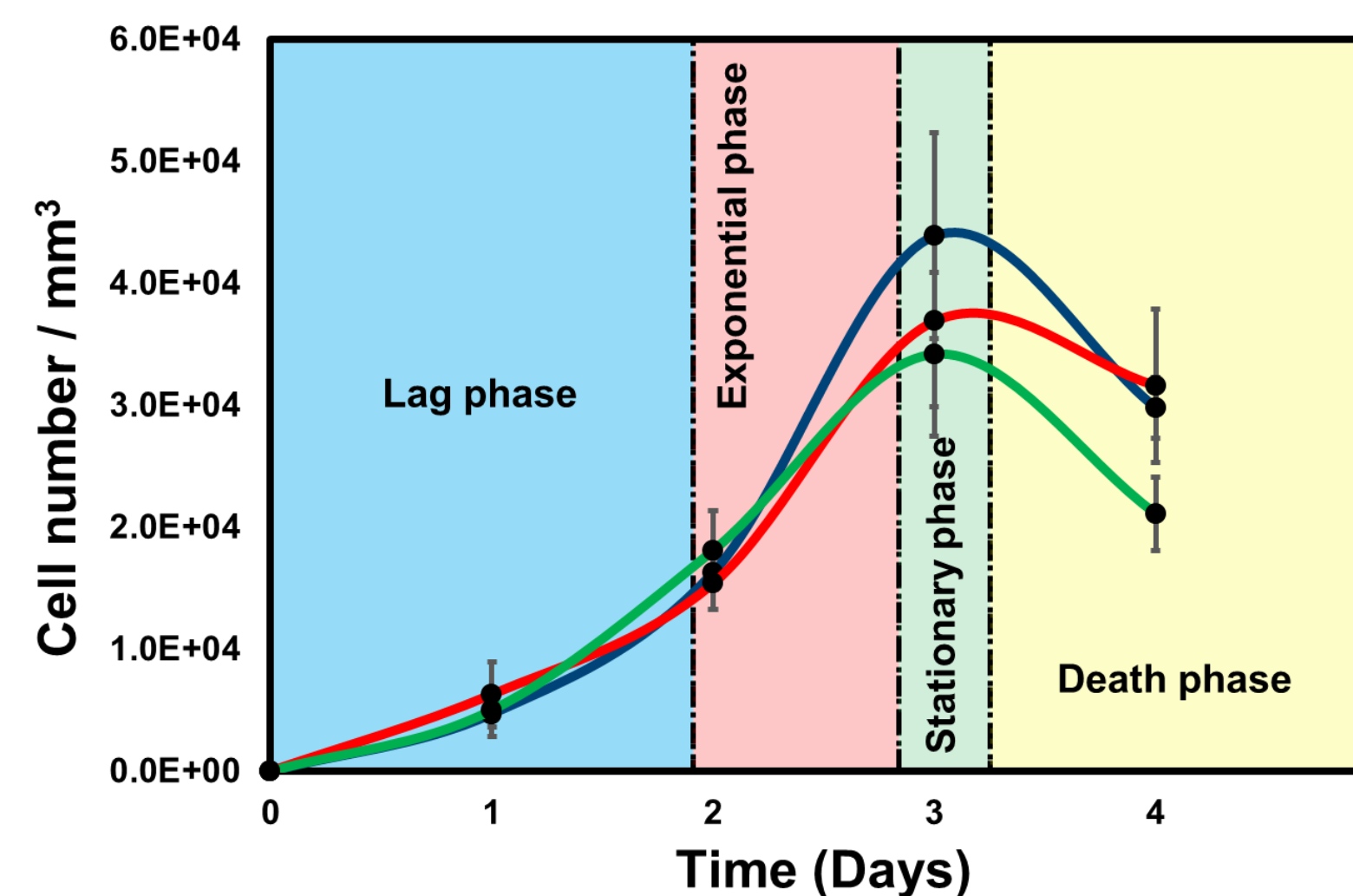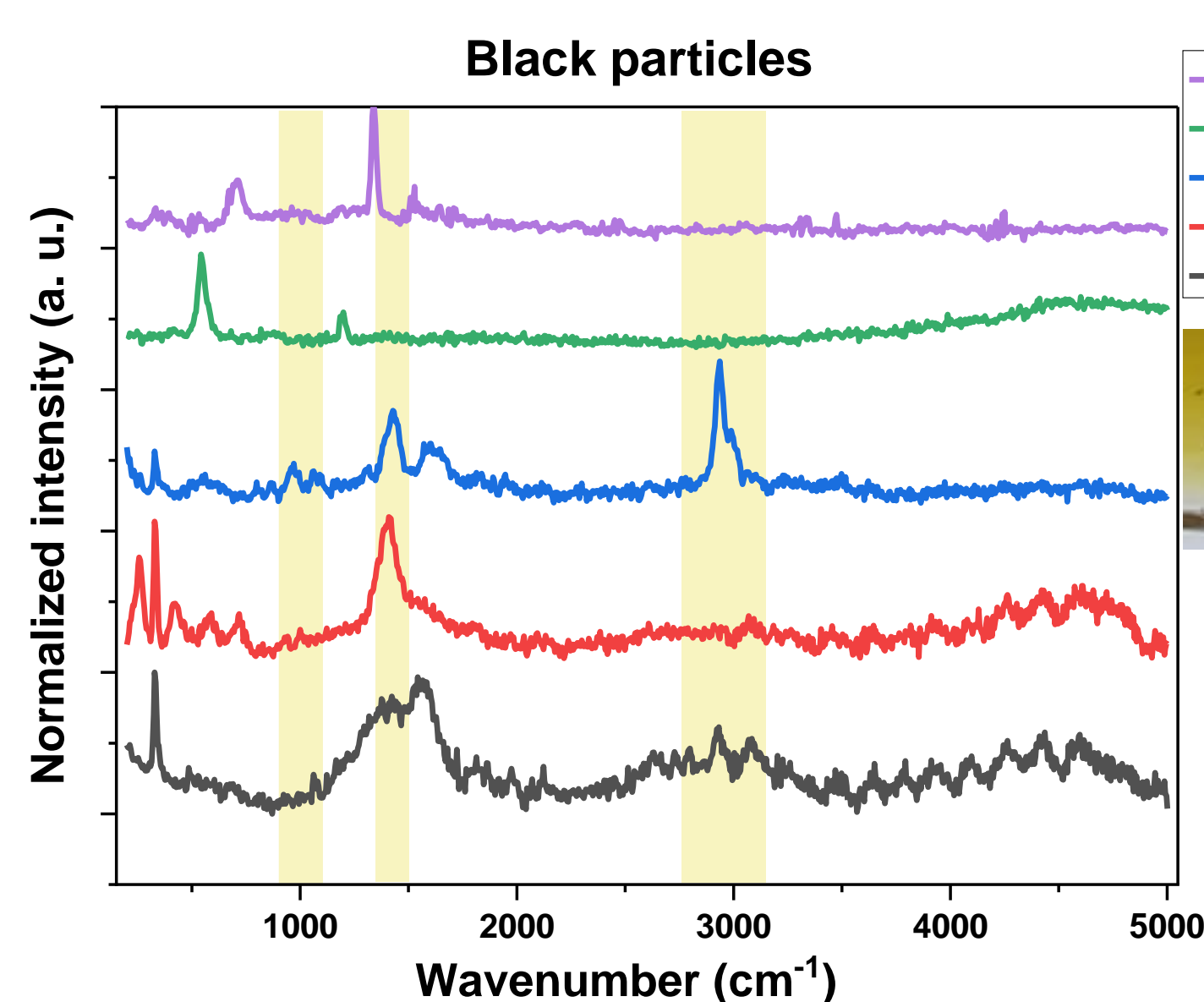

- *Desulfitobacterium* sp. G1-2 in DSMZ 579[8], close-up of precipitate structure units observed after 10 days with possible exposure to air, magnification: 100X
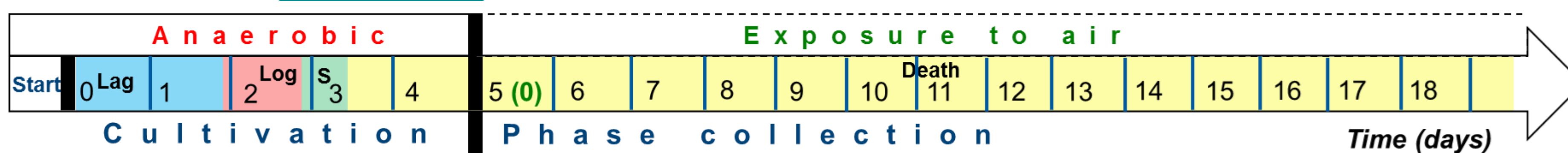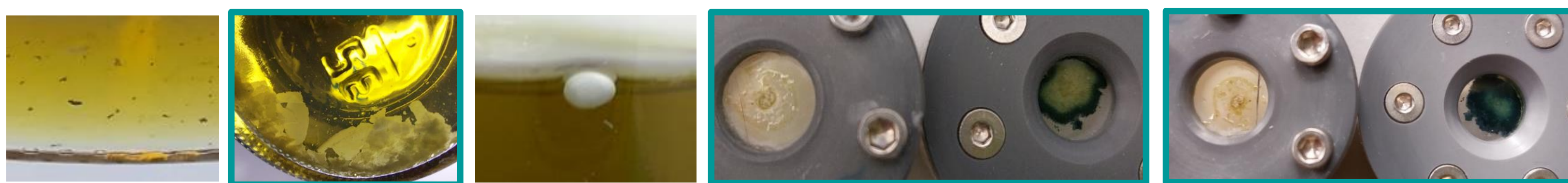
What is the phase composition?

Raman microscopy

- Multiple spectra in the white precipitate have been attributed to vivianite [(Fe$^{II}_3$(PO$_4$)$_2$·8H$_2$O]. The kinetics of the phase formation was monitored.

- The band shifting in successive spectra of the white precipitate may indicate vivianite oxidation and therefore, the change of the phase to green rust

- The filtration of air in the Raman cell may have caused oxidation which is most probably the reason of the change of the phase chemistry

- Black particles have also been observed in the cultures. Raman spectra reveal the possible formation of vivianite, pyrite, siderite, ferrihydrite, hematite and magnetite

Biogenic vivianite

Vivianite (reference)[9]; $Fe^{II}_3(PO_4)_2·8H_2O$
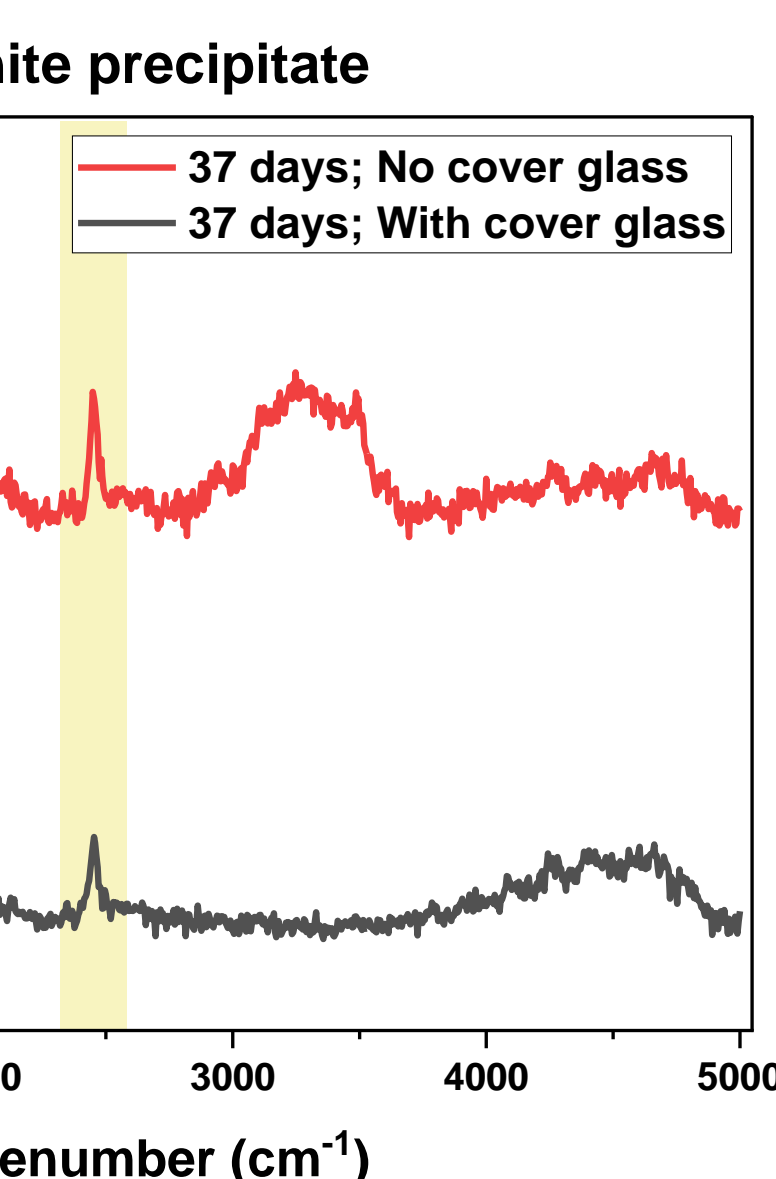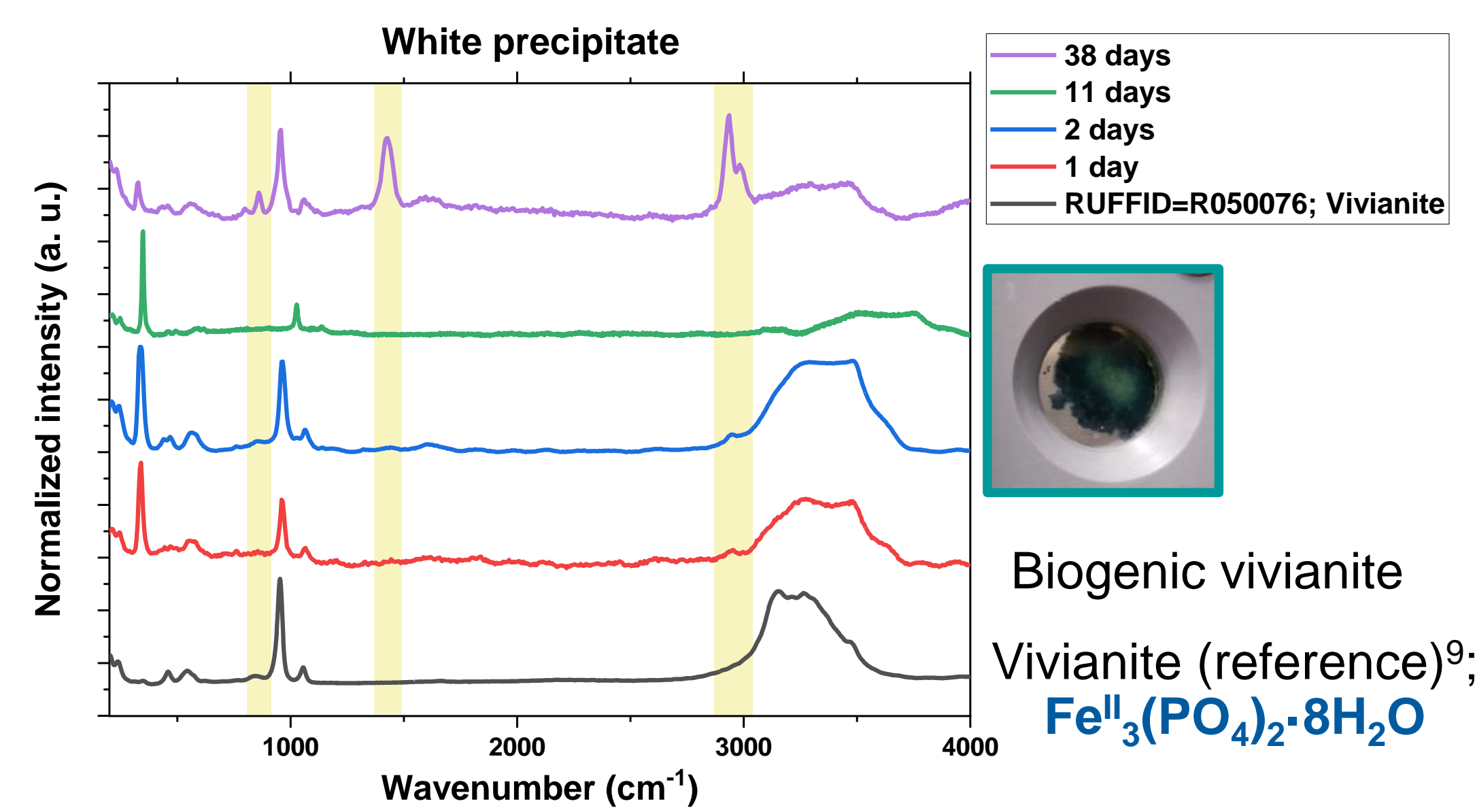
X-ray diffraction
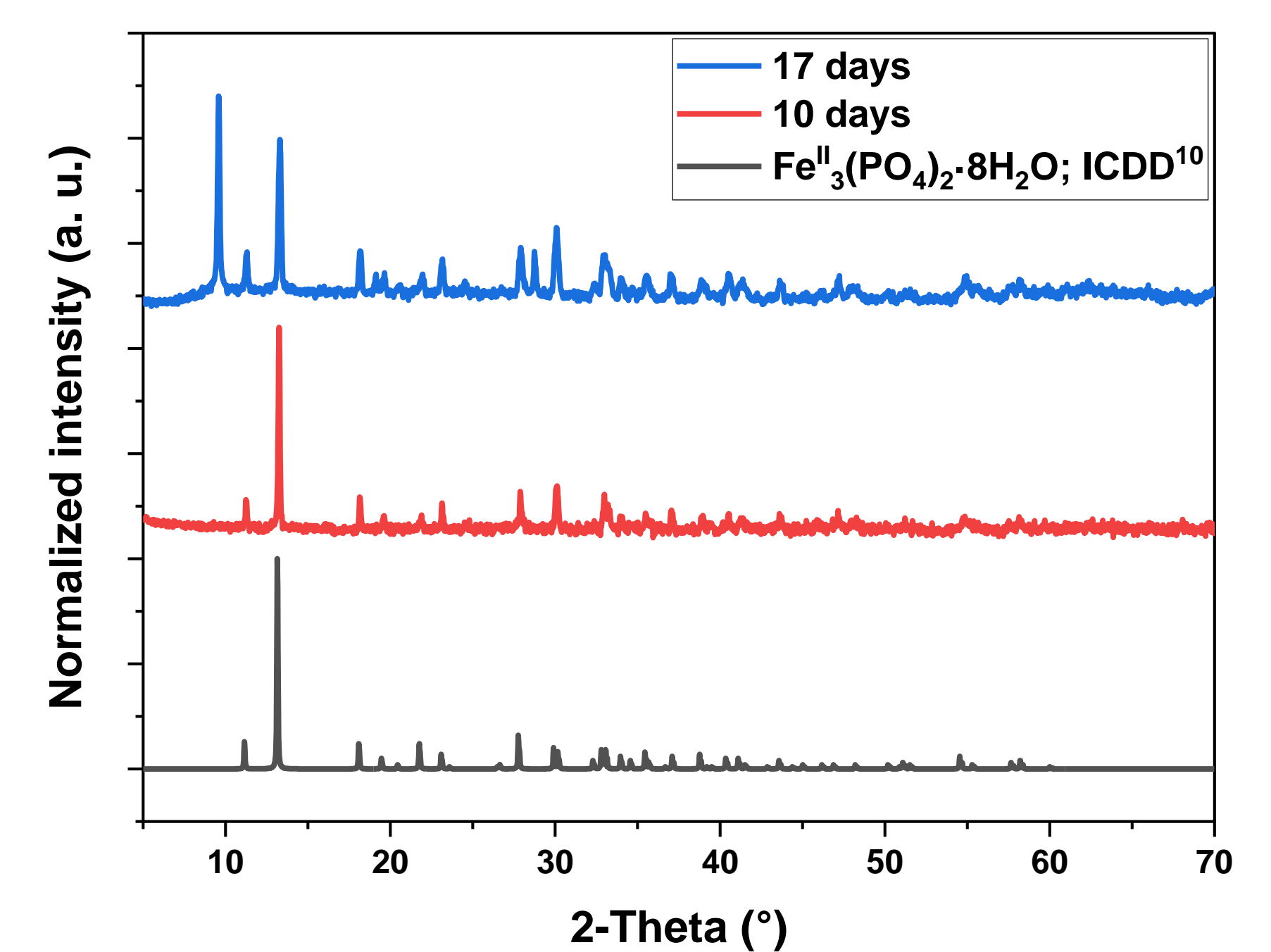
- Multiple measurements over time for the same sample of white precipitate, in order to examine the phase formation kinetics

- Diffractograms corresponding to vivianite [(Fe$^{II}_3$(PO$_4$)$_2$·8H$_2$O] have been observed

- Successive diffractograms showed changes confirming the oxidation of vivianite and the formation of green rust

Scanning electron microscopy
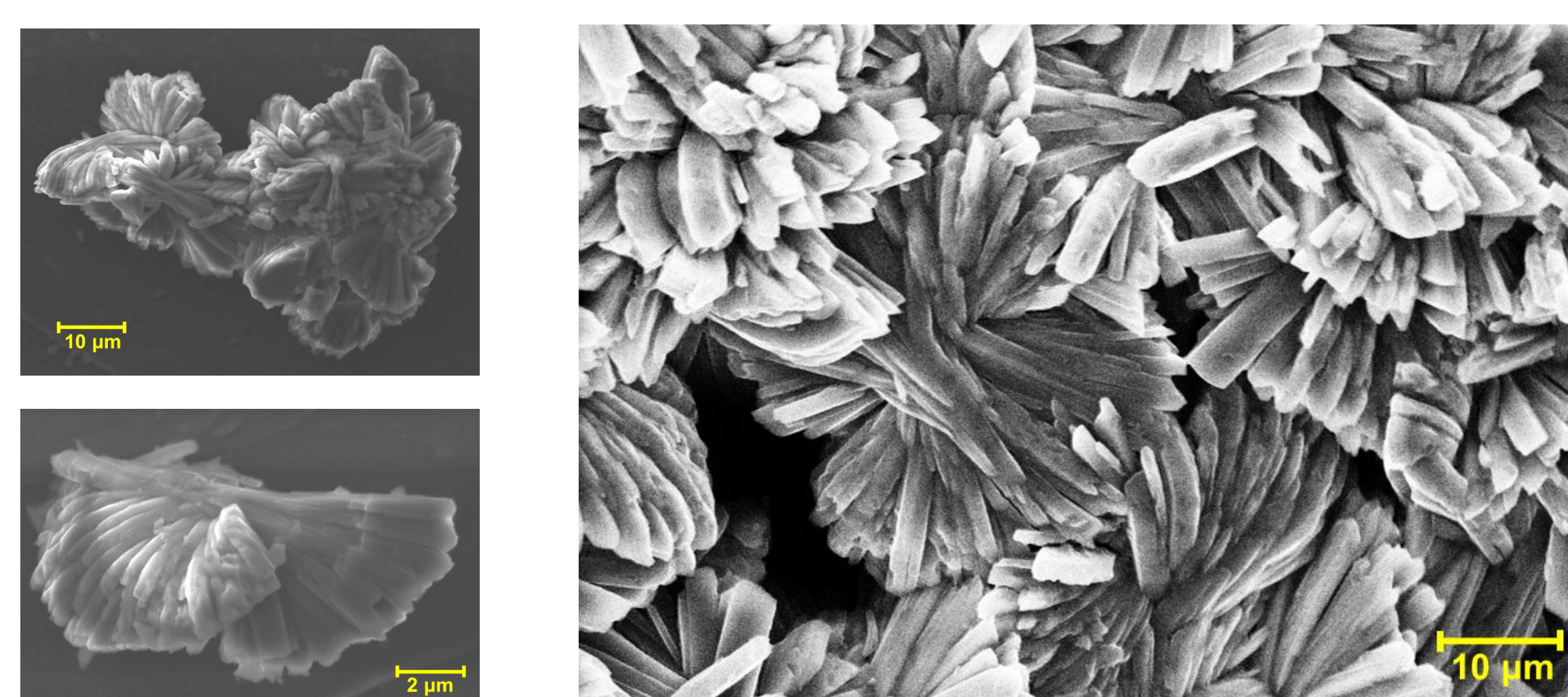
Conclusions and outlook

- Vivianite [Fe$^{II}_3$(PO$_4$)$_2$·8H$_2$O] has been identified as the biogenic mineral which is formed during the exponential growth of *Desulfitobacterium* sp. G1-2

- Secondary minerals (pyrite, siderite, ferrihydrite, hematite, green rust, magnetite) have been observed after air exposure

- The interaction of biogenic vivianite with Tc will be examined in order to achieve the reduction of Tc^{VII} to Tc^{IV}, as well as compared with that of synthetic vivianite

References

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[3] Drozdowski J., *et al.*, 2018, *HZDR Annual Report*, pp. 40, ISSN 2191-870
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[9] RRUFF™ Project, https://rruff.info/
[10] International Centre for Diffraction Data, https://www.icdd.com/