	Experiment title: Mesopore structure in amorphous transition metal phosphate materials	**Experiment number**: A26-2-928
Beamline: BM26	**Date of experiment**: from: 19.11.2021 to: 23.11.2021	**Date of report**: *23/02/2022*
Shifts: 12	**Local contact(s)**: Daniel Hermida Merino	

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Report:

Phosphorous, ammonia and transition metals are common contaminants in waste waters and are highly harmful for the environment even in minor amounts. Consequently, these chemical species have to be extracted. One recovery method relies on the precipitation of transition metal phosphates. These recovered transitional metal phosphates, could act as storage materials for transition metals that may be potentially up-cycled for industrial applications as raw materials for transition metal phosphate (electro)catalysts and supercapacitors. In this regard, transition metal phosphate materials such as metal struvites $NH_4MPO_4 \cdot 6H_2O$ evolve mesoporous structures during heating in the course of degassing of volatile compounds. By using a LINKAM capillary heating heater in combined with in-situ SAXS/WAXS, we followed the temporal evolution of mesoporosity during an isothermal treatment at T = 90°C in Mg-, Ni- and Co-phosphates.

Based on the SAXS signal, the pore size distribution of Mg-struvite differs from that of Ni-struvite significantly (Figs. 1 and 2). Ni-struvite exhibits pore sizes with average radius of ~8.0 nm nm, while in Mg-struvite the pores evolve to ~3 nm in radius. Based on the WAXS signal both systems evolve pure amorphous phases during thermal treatment (Figs. 1 and 2), the occurrence of which is associated with the formation of pores. The Co-phosphate shows no real indicators for mesoporosity by the end of the decomposition processes (Fig. 3). This points out again to a sharp crystalline-crystalline phase transition between Co-struvite and Co-dittmarite, without any amorphous phase present.

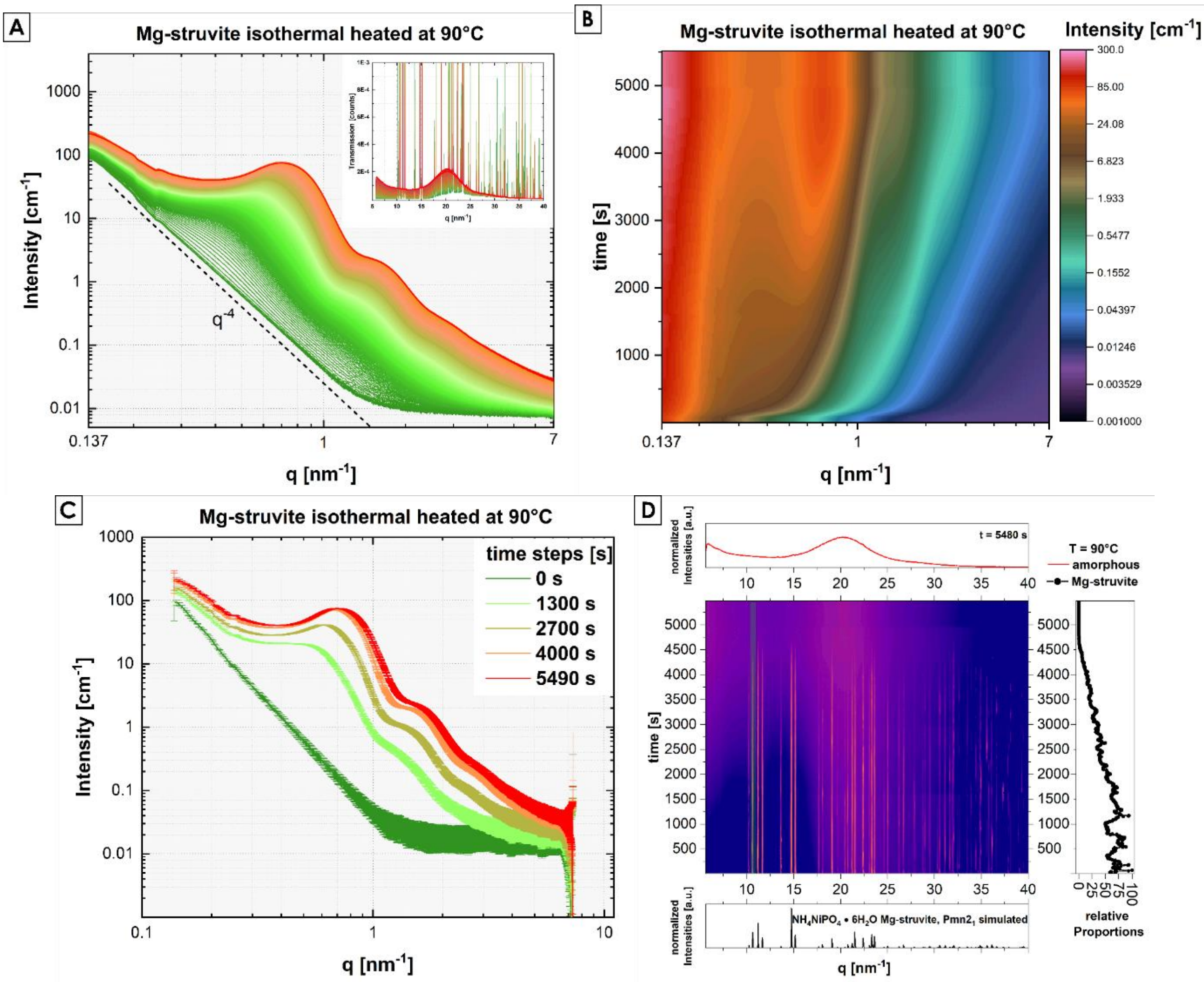

Figure 1: *in-situ SAXS measurements from heating of Mg-struvite at 90°C from 0-5480 s (A) in-situ SAXS patterns from t = 0 - 5490 s with colour gradient of the patterns indicates 10 s time steps between each pattern (5 frames of t = 2 s were averaged black dashed line: q^{-4} dependence; inset: in-situ WAXS diffractograms (5 frames of t = 2 s were averaged); note the amorphization and the decrease of intensity in struvite reflexes with progressive heating; (B) heatmap of in-situ SAXS patterns with q[nm^{-1}] vs. time [s] of isothermal hated Mg-struvite at T = 90°C from t = 0 - 5490 s with the respective intensities [cm^{-1}] marked by colour bar showing development of pores through time; note the evolution of mesopores as is indicated by the maxima at 0.2 - 1 nm^{-1} and 1 -2 nm^{-1};(C) in-situ SAXS graphs of Mg-struvite isothermal heated at T = 90°c with y-error bars of selected time steps for clarity; at very low and high q error bars increase rapidly (D) in-situ WAXS heatmap q [nm^{-1}] vs. time [s] of isothermal heated Mg-struvite at T = 90°C with the respective transmission [counts] marked by colour bar from 5.62 < q < 40 nm^{-1} and t = 0 - 5490 s; lower part: simulated XRD pattern of Mg-struvite reference COD 9007674; right side: normalized Intensity of (101) reflex of Mg-struvite over time marked with transparent rectangular in heatmap; upper part: diffractogram of time step t = 5480 s showing a complete amorphous phase after end of experiment*

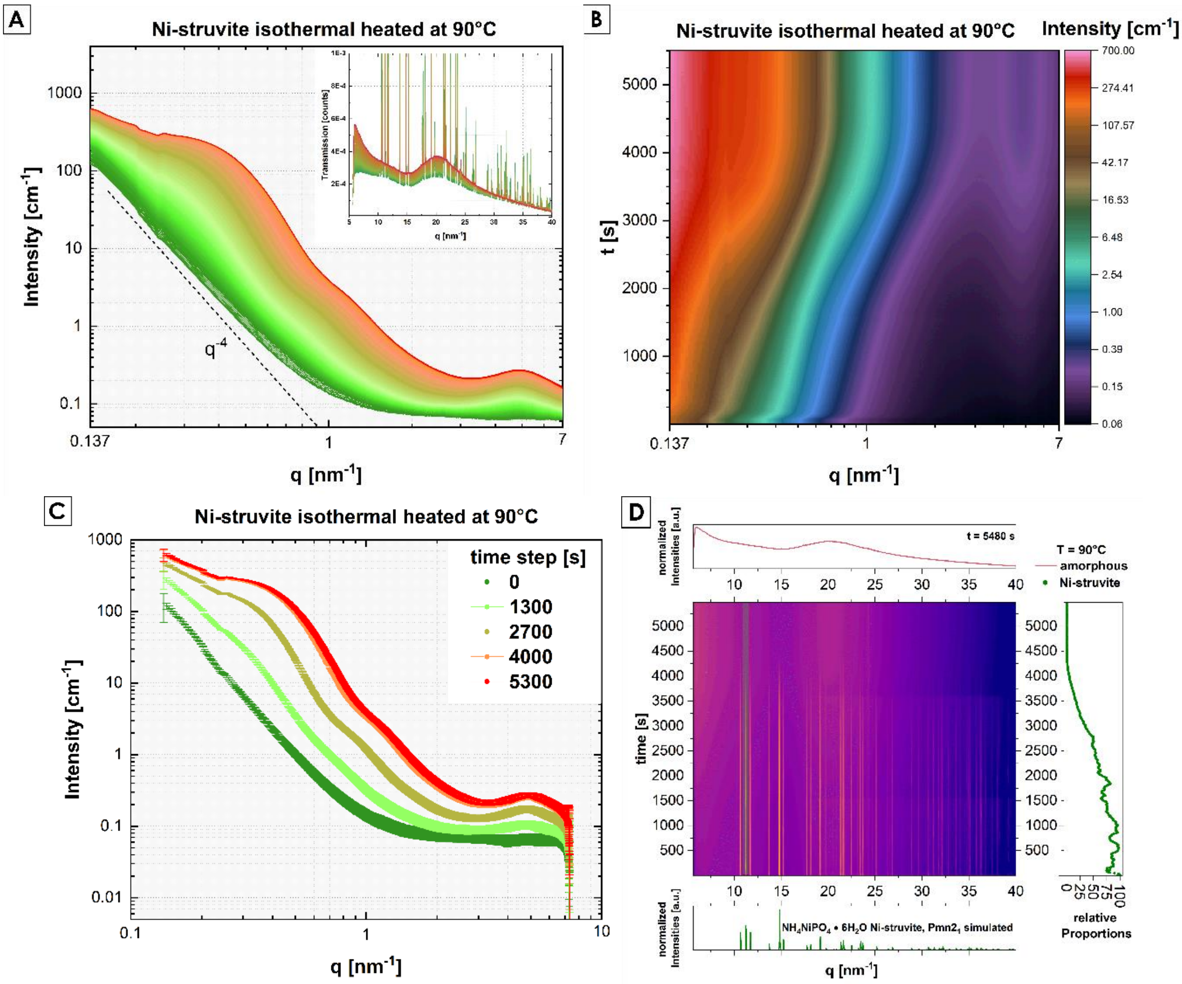

Figure 2: *in-situ SAXS/WAXS measurements of heating Ni-struvite at 90°C from t = 0-5480 s; (A) in-situ SAXS patterns with colour gradient of the patterns indicates 10 s time steps between each pattern (5 frames of t = 2 s were averaged for clarity); inset: in-situ WAXS diffractograms; (B) heatmap of in-situ SAXS patterns with q[nm^{-1}] vs. time [s] of isothermal heated Ni-struvite at T = 90°C with the respective intensities [cm^{-1}] marked by colour bar showing development of pores through time; note the evolution of mesopores around 0.2 - 1 nm^{-1} and 1 -2 nm^{-1};(C) in-situ SAXS graphs of Ni-struvite isothermal heated at T = 90°C with y-error bars of selected time steps for clarity; at very low and high q error bars increase rapidly; (D) in-situ WAXS heatmap q [nm^{-1}] vs. time [s] of isothermal heated Ni-struvite at T = 90°C with the respective transmission intensities [counts] marked by colour bar; lower part: simulated XRD pattern of Ni-struvite reference ICSD 403058; right side: normalized Intensity of (002) reflex of Ni-struvite over time marked with transparent rectangular in heatmap; upper part: diffractogram of time step t = 5480 s showing a complete amorphous phase after end of experiment*

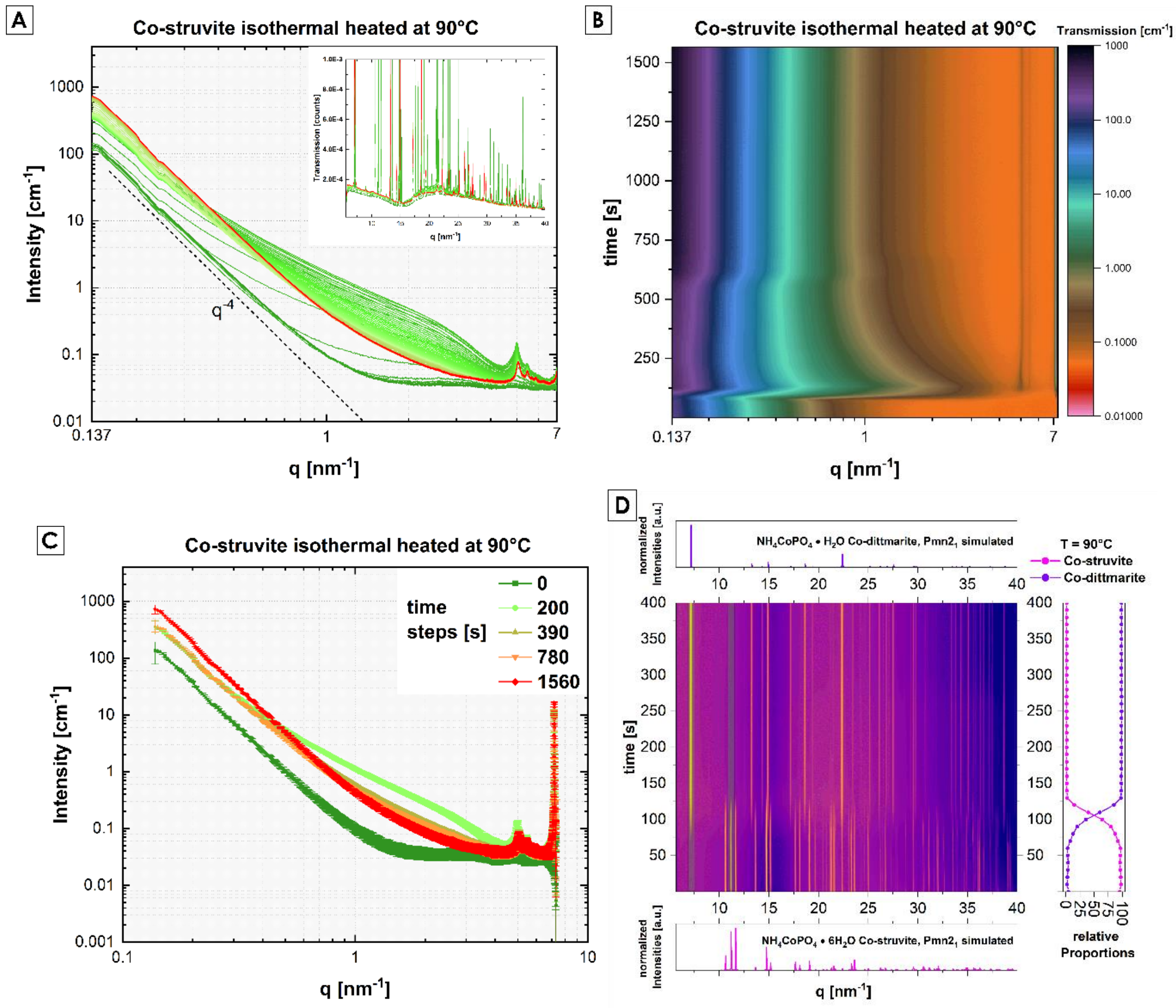

Figure 3 *: in-situ SAXS/WAXS measurements of heating Co-struvite at 90°C from t = 0-1560; (A) in-situ SAXS patternss with colour gradient of the patterns indicates 10 s time steps between each pattern (5 frames of t = 2 s were averaged for clarity); inset: in-situ WAXS diffractograms; Co-dittmarite recrystallizes when Co-struvite decomposes; (B) heatmap of in-situ SAXS patterns with q[nm^{-1}] vs. time [s] of isothermal heated Co-struvite at T = 90°C with the respective intensities [cm^{-1}] marked by colour bar showing development of pores through time; note the formation and later disappearance of mesopores around 0.4 - 3 nm^{-1} and the occurrence of micropores at around 5 nm^{-1};(C) in-situ SAXS graphs of Co-struvite isothermal heated at T = 90°C with y-error bars of selected time steps for clarity; at very low and high q, y-error bars increase rapidly (D) in-situ WAXS heatmap q [nm^{-1}] vs. time [s] of isothermal heated Co-struvite at T = 90°C with the respective transmission intensities marked by colour bar on a detailed time window of t = 0-400 s ; lower part: simulated XRD pattern of Co-struvite reference ICSD 170042; right side: normalized Intensity of (002) reflex of Co-struvite and (001) reflex of Co-dittmarite over time marked with transparent rectangles in heatmap; upper part: simulated XRD pattern of Co-dittmarite reference COD 2008122.*