

Supporting Material for Characterization of hydrated magnesium carbonate materials with synchrotron radiation-based scanning transmission X-ray spectromicroscopy

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Region of interests of brucite

Related to XANES spectra presented in Fig. 1 of the main article, Fig. S1 (a) and (b) presents average images of STXM recordings between 532-558 eV (O K-edge) and 1306-

1342 eV (Mg K-edge), respectively, with ROIs and I_0 area marked with red dashed lines. The choice of ROIs was done based on the O K-edge recording, the limiting factor is the much higher absorbance of brucite around O K-edge than at Mg K-edge. Using density of 2.37 g/cm³¹ and web-based interface to calculate the attenuation lengths^{2,3}, the attenuation length of X-rays has been estimated to drop to 0.3 μm at O K-edge and to 1.2 μm at Mg K-edge. In practice, at O K-edge, only the thin parts of the crystal agglomerate had enough transmission that extraction of non-saturated spectra was possible. The agglomerates of crystals in Fig. S1 (a) have a periodic curly shape. We associated this waviness to the instabilities of the scanning stage in early commissioning beamtime, and as the much stable recording at Mg K-edge in Fig. S1 (b), it is not related to the sample itself.

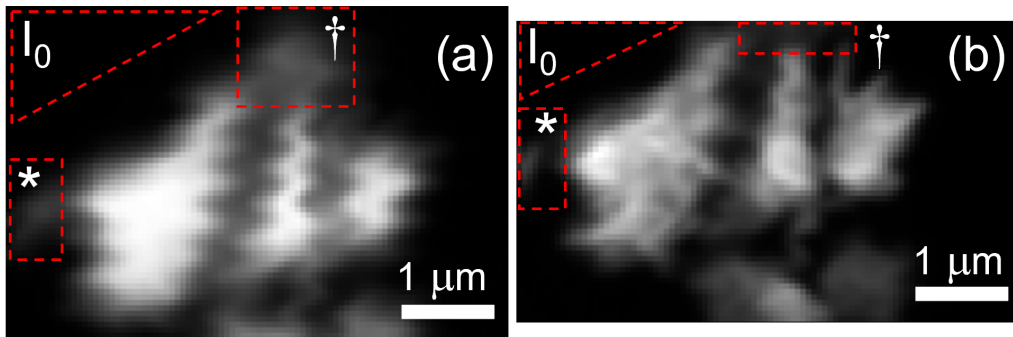


Figure S1: ROIs from which the spectra presented in Figure 1 of main article have been extracted. (a) O K-edge measurement (image is an average of measurements between 531.6 and 557.6 eV). (b) Mg K-edge measurement (1306-1342 eV). ROI marked with * indicates region producing a spectrum with parallel orientation between polarization vector of light \mathbf{E} and crystal axis c and \dagger indicates correspondingly perpendicular orientation. Region marked with I_0 shows an approximate area for extracting the reference photon flux through the empty part of the silicon nitride membrane.

SEM image of HMC precipitates formed after 1-day reaction time in water

Figure S2 shows a SEM image recorded from the precipitates formed after 1 day of reaction in water. The crystals in this image clearly indicate the platelet morphology (front view) which is in the form of HMC phase dypingite as also mentioned in the main paper. The

platelets or flake-like structure are very thin when viewed from the side (marked with red arrow). We were able to record these flakes of dypingite using STXM, as presented in Fig. 2 of main paper. Electron microscopy was performed with 5 kV electron acceleration using Zeiss Ultra plus Field Emission SEM (Carl Zeiss GmbH, Oberkochen, Germany) at Centre for Material Analysis at University of Oulu, Finland.

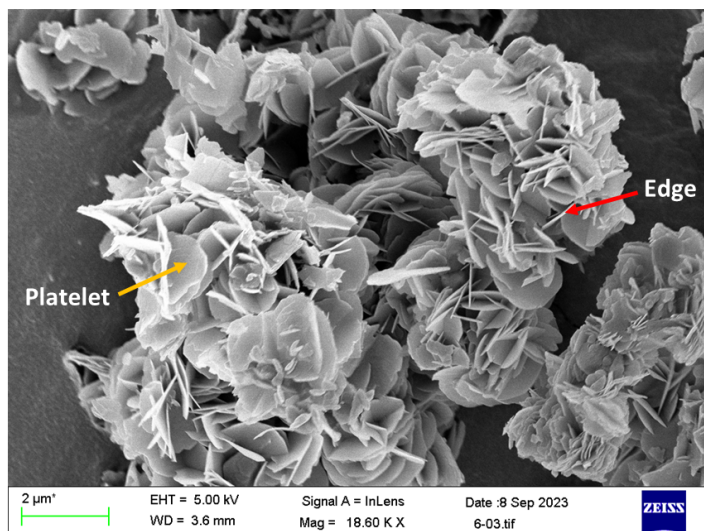


Figure S2: SEM image of HMC precipitates collected after 1-day reaction time in water. The yellow arrow indicates the usual platelet shape dypingite whereas the red arrow indicating the edge of this platelet.

HMC formed after 1-day reaction time with Mg-acetate

Figure S3 (a) presents an HMC precipitate formed in presence of Mg-acetate after 1-day reaction time. The XANES spectra in Fig. S3 (b) recorded at Mg K-edge has been extracted from different region of precipitates in S3 (a). The red grains as observed on the edge of long crystal are unreacted brucite, recognized from its familiar triplet structure in the XANES spectrum in Fig. S3 (b). The light blue spectrum is extracted from a upper small area of nesquehonite crystal in Fig. S3 (a) and shows completely different trend than of brucite XANES. As also observed in the XANES spectrum of nesquehonite in the main paper, the

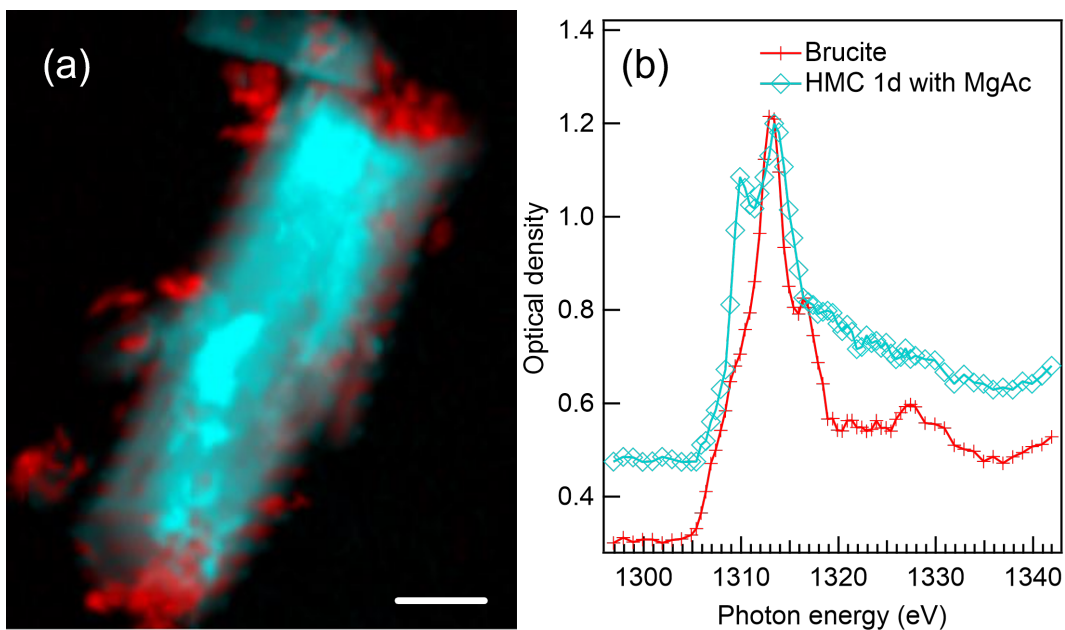


Figure S3: a) Color composite map of STXM recording at Mg K-edge of precipitates formed after 1 d reaction time in presence of Mg-acetate. HMC crystals are shown in light blue whereas residual brucite in red. b) Corresponding XANES spectra of brucite (red line with crosses) and HMC crystal (blue line with diamonds). Scale bar 2 μm .

main absorption region, contain two peaks with less intense first peak and an intense second peak. No sign of broad peak in the post edge region of HMC XANES further support our claim about the polarisation effect on the spectra of oriented crystal. The long and wide tilted crystal of nesquehonite does not have any absorption maximum around 1324 eV in the post edge region, similarly to the tilted crystal of 1 day MgAc precipitates in the main paper and opposite to the observation of vertical crystal (Fig. 4a in the main paper).

HMC formed after 7-day reaction time in water

Two STXM recordings of precipitates formed after 7 days of reaction in water are shown in Fig. S4. Results shown in (a) and (b) indicate agglomerates of small dypingite platelets. The two main peaks at the HMC absorption edge have almost the same relative intensity. The XANES of brucite (in red color) indicate its regular triplet XANES structure. Measurement shown in Figs. S4 (c) and (d) have been carried out for the same sample, but after storing

it in a plastic bottle for 18 months. The agglomerate consists of unreacted brucite (red) and HMC (light blue) in the form of thin intertwined structures. The XANES of brucite has regular triplet structure and dypingite also follows the same trend as described in the main paper with the intense first peak and less intense second peak in the main absorption region.

HMC formed after 28-day reaction time in water

Figure S5 (a) shows a color composite map of STXM recording from precipitates formed after 28 days in water. Similarly to the Fig. 9 in the main article, the formation of dypingite (green color) and brucite (red) along with the second unknown phase (blue) is observed. The undefined phase of HMC is considered to be an amorphous content or a different type of dypingite with higher hydration degree. Additionally, We have also considered the possibility of the undefined phase to be a mixture of brucite and dypingite. While an overlap of these is difficult to avoid when selecting the region for SVD fits, the selection was guided by principal component and cluster analysis using MANTiS software⁴.

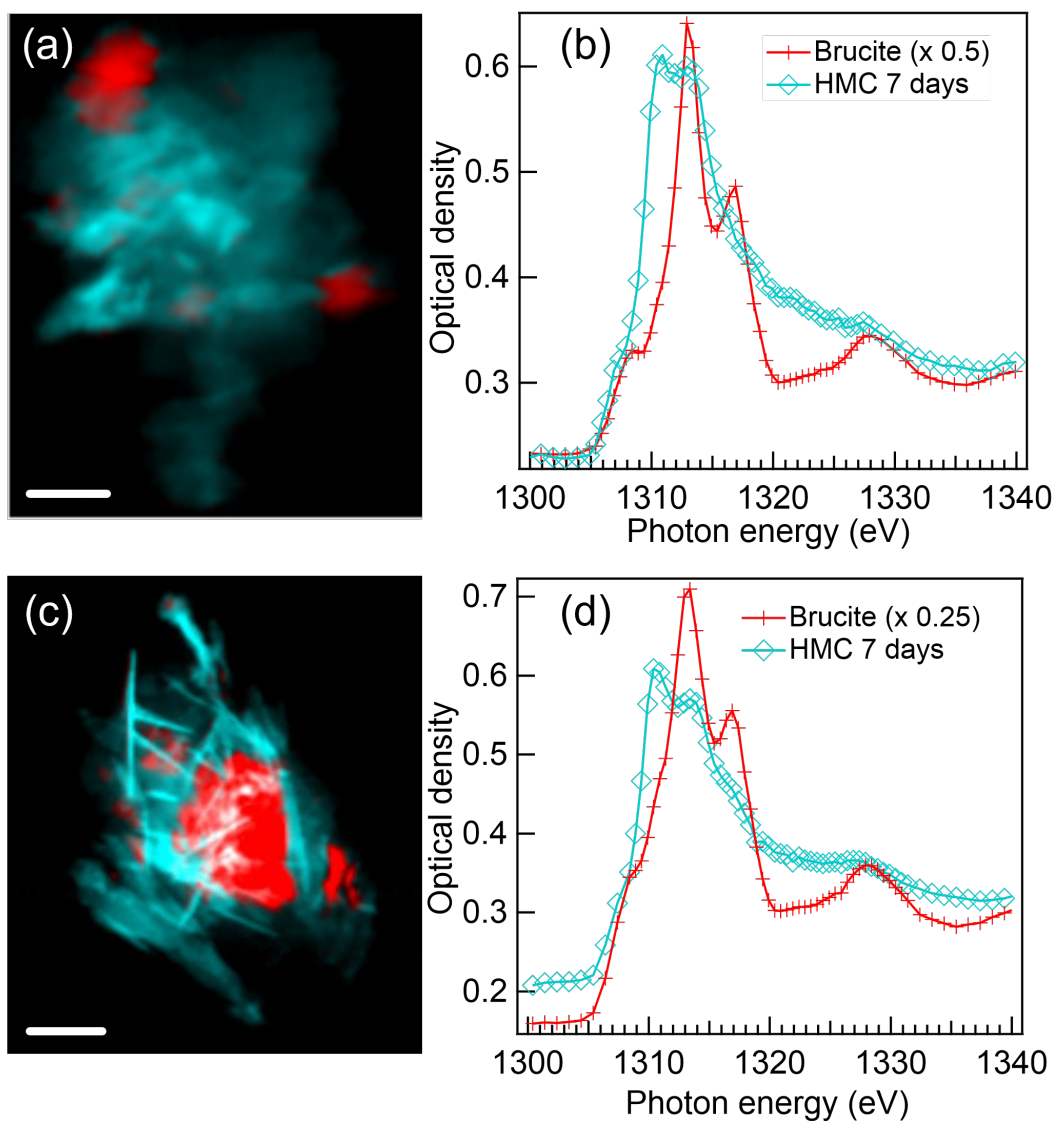


Figure S4: Color composite maps and XANES spectra of two different STXM recordings at Mg K-edge. These precipitates have been formed after 7 d reaction time in water. (a) HMC in light blue and brucite in red. Scale bar is $0.9 \mu\text{m}$. (b) XANES spectra used to fit (a), HMC indicated with light blue line with diamonds and brucite with red line with crosses. (c) HMC in light blue and brucite in red. Scale bar is $2 \mu\text{m}$. (d) XANES spectra used to fit (c), HMC indicated with light blue line with diamonds and brucite with red line with crosses.

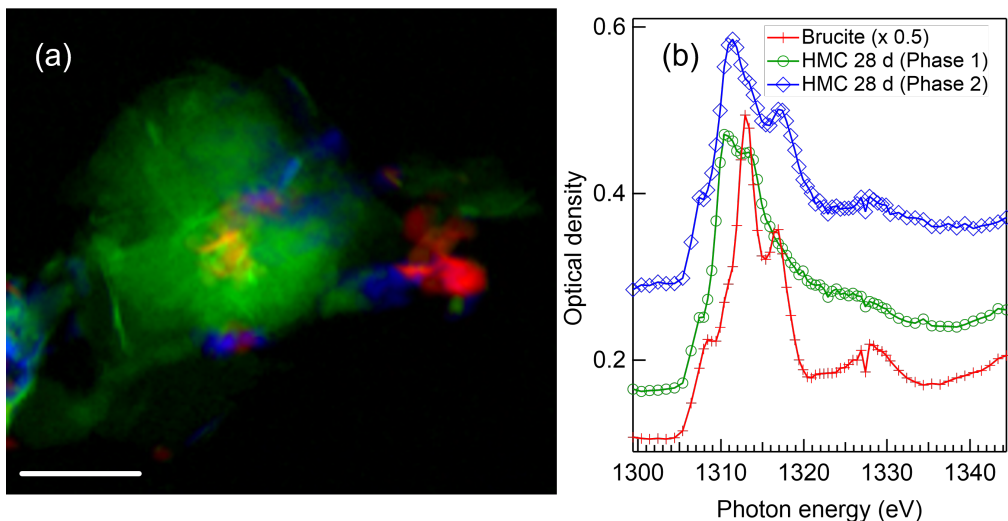


Figure S5: (a) Color composition map of precipitates formed after 28-days of reaction in water. Brucite areas are depicted in red, and two HMC phases in green and blue. b) Corresponding Mg K-edge XANES spectra extracted from the measured precipitate agglomerate showing brucite with a red line with crosses, a dypingite-like HMC phase with a green line with spheres and an undefined HMC phase with a blue line with diamonds. Scale bar is 2 μm .

HMC formed after 28-days reaction time with Mg-acetate

Figure S6 (a) shows a set of precipitates formed after 28 days with Mg-acetate. Only one type of spectrum was found in this STXM recording, and it is presented in Fig. S6 (b). No indication of unreacted brucite in the precipitates reflects higher reaction degree of brucite in presence of Mg-acetate. This measurement was seriously affected by the instability of scanning stages, and the thin needles had a curly shape in each image. The image presented in Fig. S6 (a) is an average of several energies (1308.4 - 1316.9 eV), which averages the shaking out, but presents the needles a bit thicker than they are. The HMC spectrum of this precipitate match with the XANES of small needle-shaped giorgiosite precipitates presented in Fig. 10 (b) of main paper.

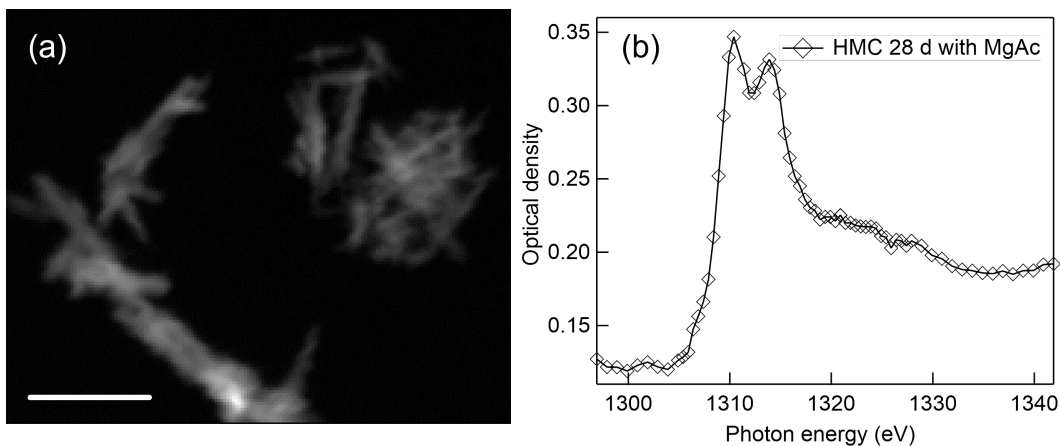


Figure S6: (a) Precipitates formed after 28 days of reaction with Mg-acetate. Since only one type of XANES spectrum was present in this sample, instead of a color composition map, the image is an average of energies across the main Mg $K\alpha$ absorption edge (1308.4 - 1316.9 eV). (b) XANES spectrum of thin needle-like precipitates indicating the HMC phase to be giorgiosite. Scale bar is 2 μm .

References

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