Supplementary Information:

Cement-on-a-chip: a microreactor for *operando* studies of the carbonation curing of cementitious materials

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Supplementary Files:

- **Chip_design.stl** - 3D CAD file of the cement microreactor
- **Holder_design.stl** - 3D CAD file of the microreactor mount for the X-ray diffractometer
- **Holder_design_45deg.stl** - 3D CAD file of the 45° microreactor mount for the X-ray diffractometer
- **2D_diffusion_model.mph** - COMSOL simulation file for 2D gas diffusion in the microreactor
- **Carbonation_data_fitting.py** - Python script for fitting experimental data
- **Raw_data.zip folder** - DAT files of XRD data from all microreactor carbonation experiments

Table S1: Elemental and by component composition of the ordinary Portland cement (OPC) powder (CEM I 52.5 N CE CP2 NF) used in this study (from manufacturer, CCB Gaurain).

Elemental Composition (%)		Composition by Component (%)	
CaO	63.2	Portland cement clinker	92.35
SiO2	20.6	Limestone (81.8% CaCO3)	3.85
Al2O3	4.5	Gypsum	3.3
SO3	3.3	Milling agent (CLOTER 5903)	0.33
Fe2O3	2.3	Reducing agent (FeSO4·H2O)	0.18
MgO	2.1		
K2O	0.73		
P2O5	0.3		
TiO2	0.3		
NaO2	0.16		
MnO	0.1		
Cl-	0.05		
S-	0.02		
Loss on ignition	2.1		

Table S2: Comparison of manufacturer's data and Quantitative Rietveld Phase Analysis of the CCB Gaurain OPC powder (CEM I 52.5 N CE CP2 NF). The uncertainty of the Rietveld analysis is ~3-5 wt%.

Phase	Composition from manufacturer (%)	Rietveld Composition (wt%)
C3S	65.41	66.4
C2S	9.62	21
C3A	8.66	2
C4AF	6.73	3
Calcite	3.15	4.6
Gypsum	3.3	2.2
Bassanite	–	0.7
Anhydrite	0	0
CaO (quicklime)	–	0
MgO (periclase)	2.2	0

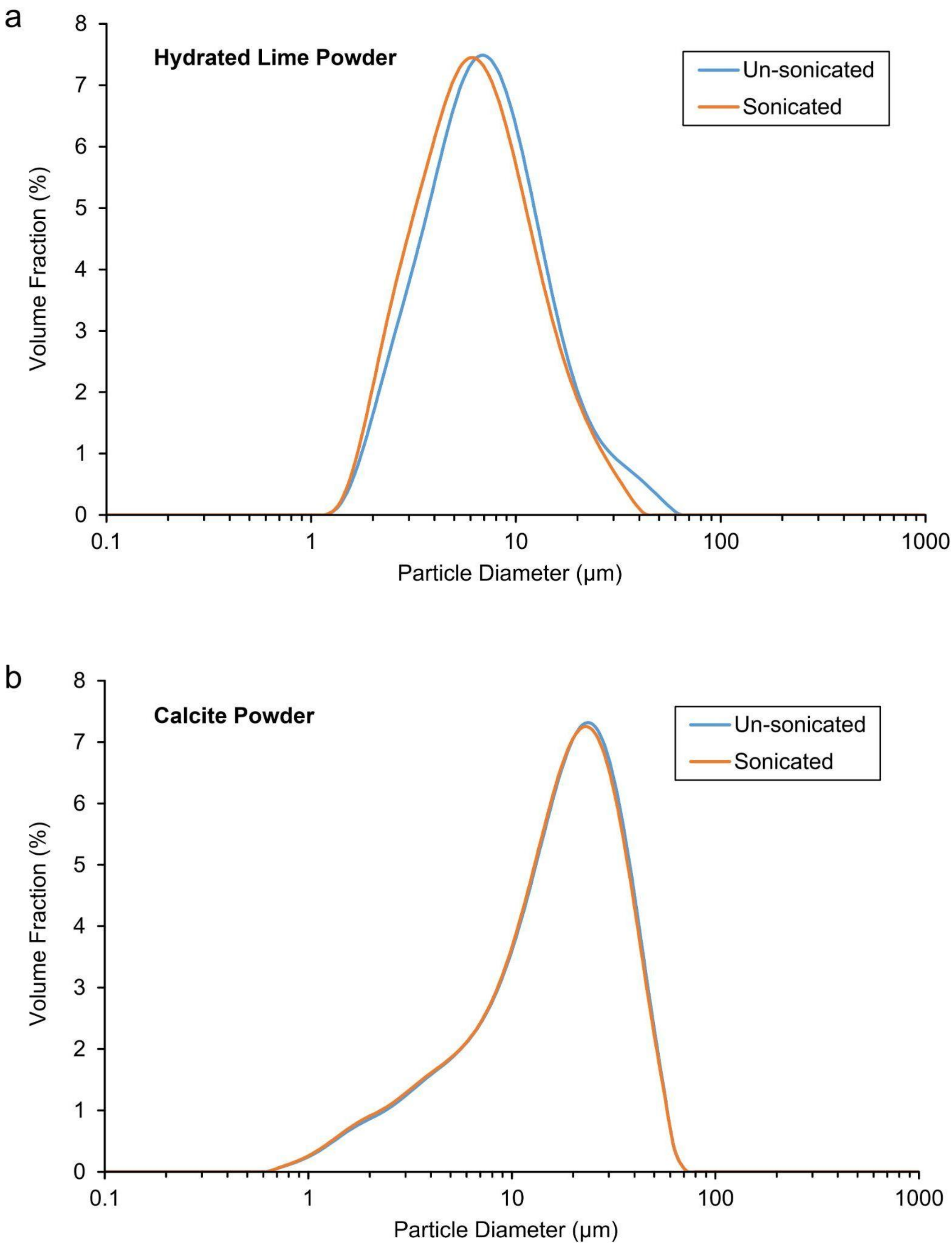

Figure S1: Particle size distribution (PSD) of (a) hydrated lime and (b) calcite powders obtained by laser diffraction measurements. PSDs are shown before and after agitation in an ultrasonic bath to check for the presence of aggregates. The hydrated lime is from ESV Aquarium Products and the calcite is from Sigma Aldrich.

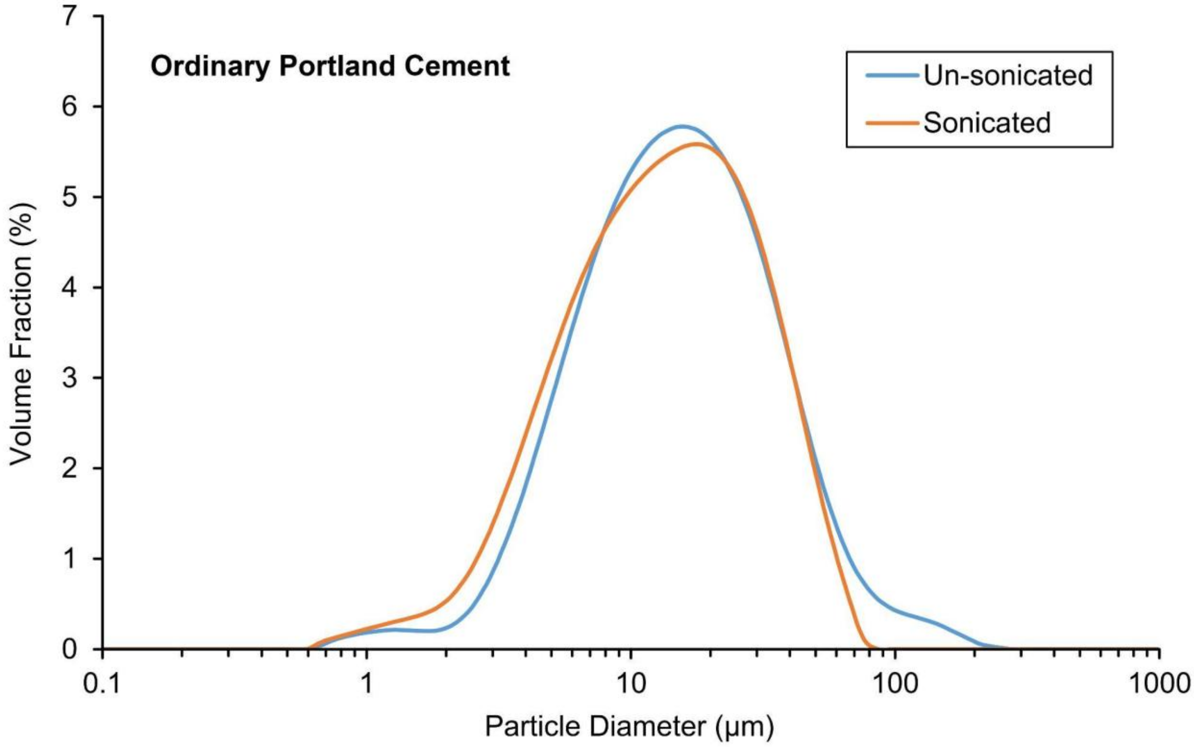

Figure S2: Particle size distribution (PSD) of the ordinary Portland cement (OPC) used in this study. PSDs are shown before and after agitation in an ultrasonic bath to check for the presence of aggregates. The OPC is from CCB Gaurain.

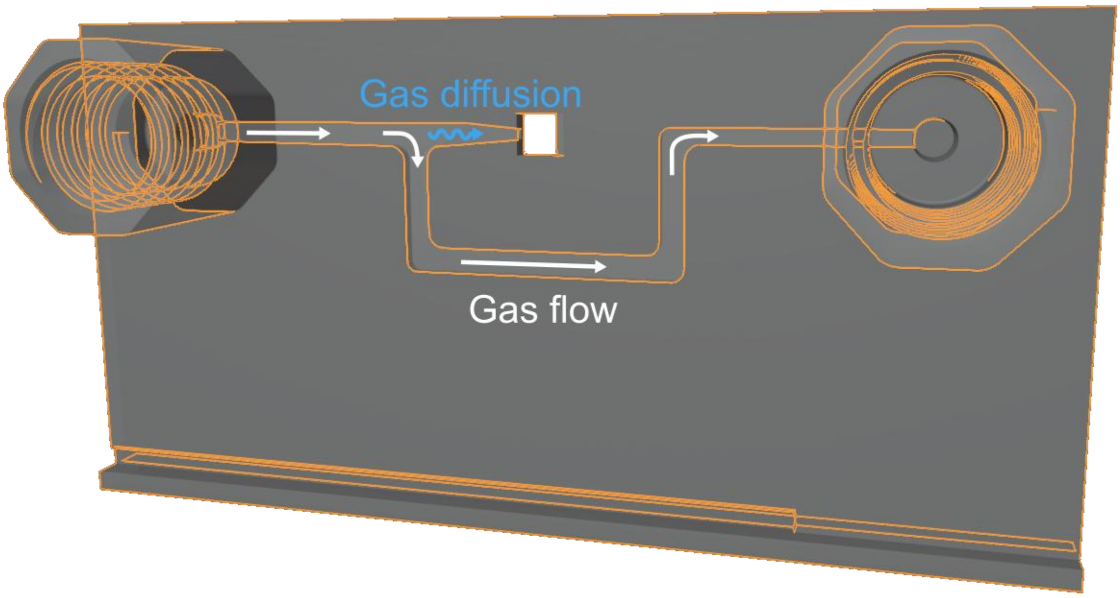

Figure S3: Illustration of the transport of gas inside of the cement microreactor. CO_2 diffuses to the sample across the 5 mm long conduit in *ca*. 1 s (blue), while depleted CO_2 is replenished by the main gas flow around the sample (white).

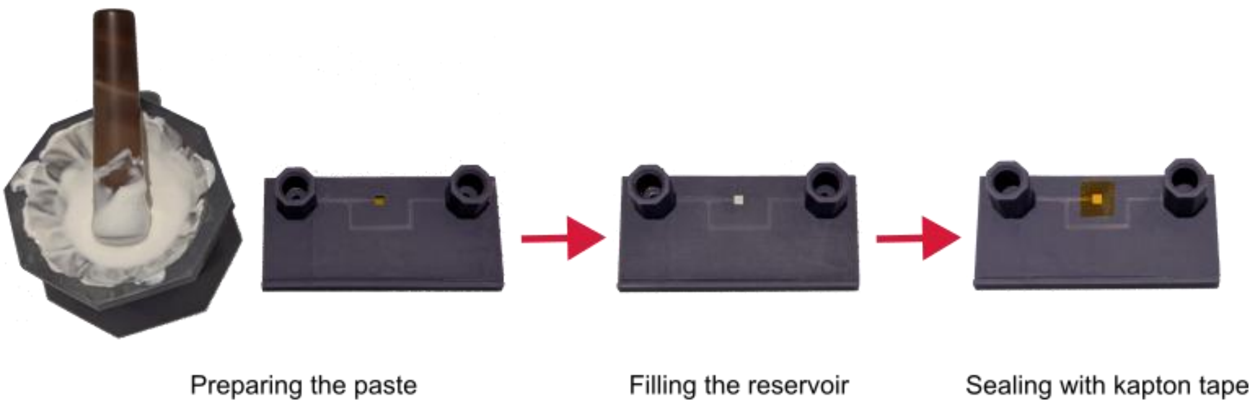

Figure S4: Photo montage of the loading of the paste in the microreactor and sealing of the device with Kapton tape.

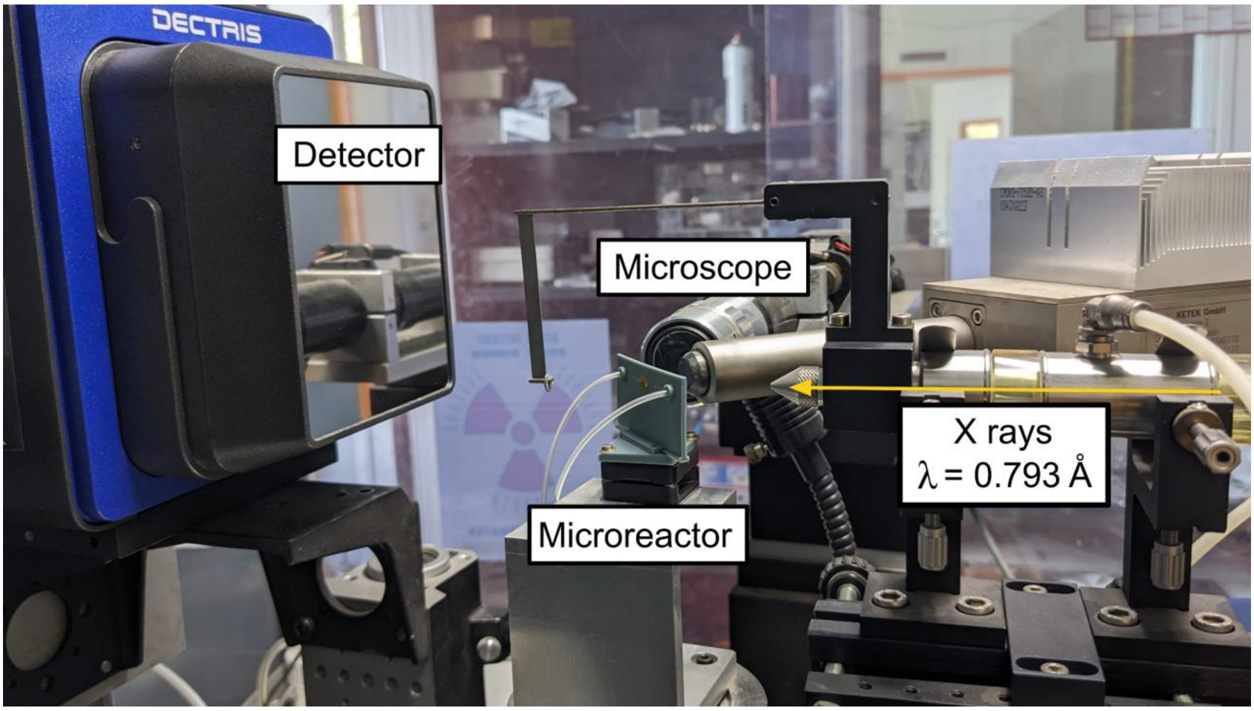

Figure S5: Annotated photograph of the cement microreactor mounted in the X-ray diffractometer in the configuration used for hydrated lime experiments.

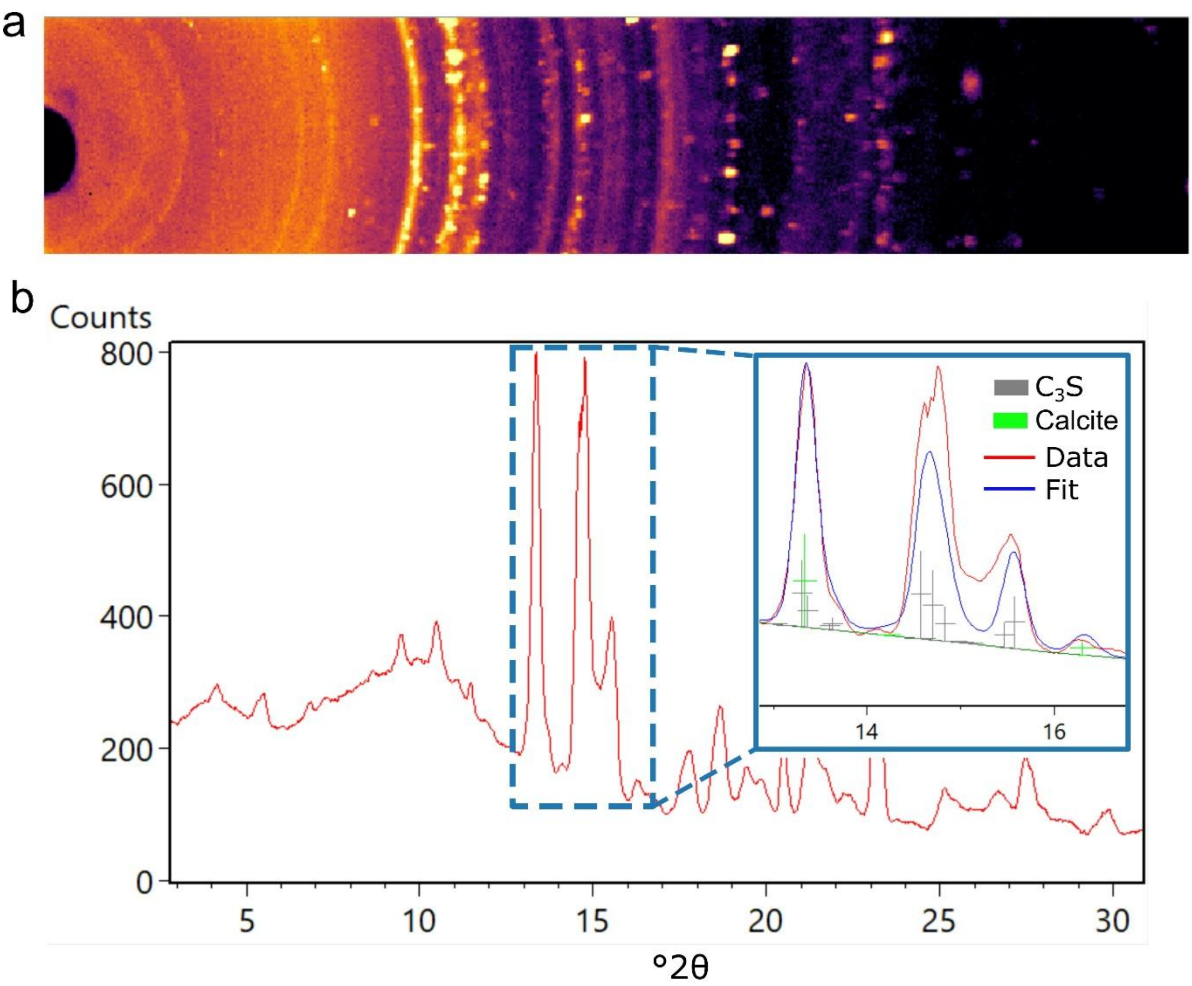

Figure S6: Example data from *operando* X-ray diffraction of the carbonation curing of ordinary Portland cement paste in the microreactor. (a) Raw 2D diffraction pattern (b) 1D azimuthally integrated pattern with Rietveld refinement for calcite and C_3S. Due to problems resulting from the quality of the patterns (e.g., noise, peak overlap, and powder coarseness), we were not confident in the whole pattern Rietveld fit, therefore we used only the higher accuracy fit of the calcite 104 peak as an estimate of the degree of carbonation. The inset shows a magnification of the region around the 104 peak after model fitting.

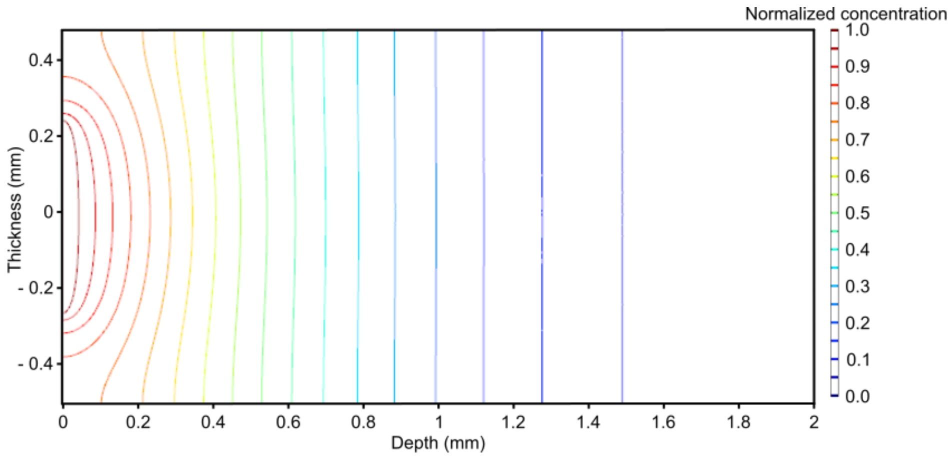

Figure S7: The concentration profile across the domain at the end of our time-dependent 2D finite element simulation of CO_2 gas diffusion in the microreactor reservoir. The simulation was performed in COMSOL Multiphysics using an automated "extra fine" mesh consisting of 49666 mesh elements and 26632 degrees of freedom (plus 905 internal degrees of freedom).

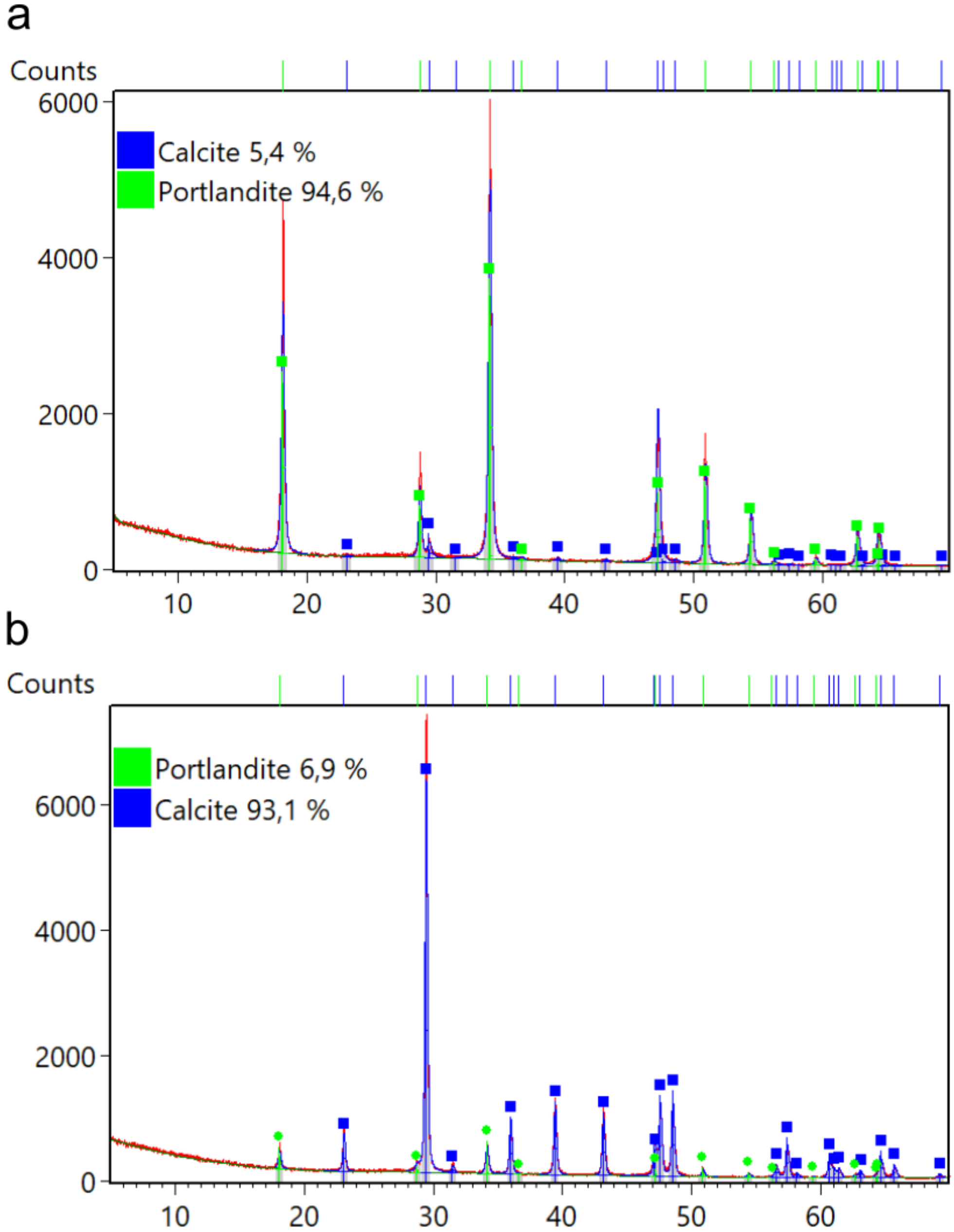

Figure S8: X-ray diffraction patterns of cm-scale samples from (a) low density and (b) high density regions of X-ray tomograms confirming their non-carbonated and carbonated nature, respectively.