

3D microstructure controls on mineral carbonation

Anna Herring^{a,*}, Penelope L. King^b, Mohammad Saadatfar^a, Fatin Mahdini^c,
Afiz Muzhafar Kemis Yahyah^c, Edward Andò^d

^a Research School of Physics, The Australian National University, Canberra, Australia

^b Research School of Earth Sciences, The Australian National University, Canberra, Australia

^c College of Engineering and Computer Science, The Australian National University, Canberra, Australia

^d Univ. Grenoble Alpes, CNRS, Grenoble INP, 3SR, F-38000, Grenoble, France

ARTICLE INFO

Keywords:

Infrared analysis

Carbonation rates

X-ray computed tomography

Microstructure

Magnesium cement

ABSTRACT

Magnesium-based mineral carbonation experiments in model porous columns are presented. The temporal evolution and interplay of 3D microstructure and mineralogy was quantified using a novel combination of X-ray computerized tomography (CT), and mineralogical analyses, conducted at five timepoints over 108 days. We constrain bulk reaction progress (X-ray diffraction, XRD), surface 2D reaction rates (non-destructive diffuse reflectance Fourier transform infrared spectroscopy, DRIFTS) as well as 3D reaction progress (X-ray CT). A new method of normalizing X-ray CT attenuation intensity values was used to provide a proxy measurement for the evolving density of the cement phase to quantify reaction progress on a 3D, microscopic level. The results demonstrate how 3D structural characteristics impact reaction progress; e.g., regions within samples with reduced access to connected void volume exhibit slower reaction, while enhanced access to connected void promotes carbonate formation. Our study shows that 3D characterization is essential for understanding the fundamental processes in mineral carbonation, whereas non-destructive 2D characterization defines reaction rates at the surface–CO₂ interface.

1. Introduction

Mineral carbonation (a.k.a. “carbon mineralization”) describes a suite of geochemical reactions wherein various metal oxides (typically calcium or magnesium-based) react with gaseous carbon dioxide (CO₂) to produce carbonate minerals. Mineral carbonation processes are receiving increasing interest as a potential option to reduce CO₂ buildup in the atmosphere, from both “disposal” and “utilization” perspectives [1–3]. Carbonation reactions occur passively, for instance during mineral and mine tailings weathering [4–6]; and they can also be leveraged in engineered systems to produce enhanced CO₂ uptake, such as reaction with coal combustion fly-ash [7], or to create building materials with favorable structural characteristics [8–11]. Magnesium carbonate shows great potential as a building material and waste magnesium from brine desalination can be reacted with CO₂ to create these new materials [12], and magnesium-based cement has been proposed as an alternative to Portland Cement to prevent CO₂ leakage from well casing for geologic CO₂ sequestration schemes [13]. For scenarios where carbon emissions

are capped or taxed, mineral carbonation provides an avenue to turn waste products into financial assets [5,6].

In order for mineral carbonation to serve as a permanent and effective sink for CO₂ (and further, to be used as a process to create useful materials for construction or industrial applications), the carbonation reactions and products need to be accurately characterized in terms of: (1) reaction kinetics in 2D and 3D, (2) the type of reaction products and their stability, and (3) how 3D structure influences both kinetics and products. This study is aimed at establishing a protocol to evaluate all three factors for mineral carbonation experiments, using a novel combination of 3D X-ray computed tomographic (X-ray CT) microscopy, diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS), and X-ray diffraction (XRD). We demonstrate this protocol for ambient temperature-pressure mineral carbonation of magnesium oxide (MgO) in idealized porous column samples, and we present a brief overview of previous results relevant to these conditions.

Hydration of MgO occurs via reaction 1 to form brucite:



* Corresponding author at: Department of Applied Mathematics, Research School of Physics, Oliphant Building 60, Mills Road, The Australian National University, Canberra, ACT, 2601, Australia.

E-mail address: anna.herring@anu.edu.au (A. Herring).

<https://doi.org/10.1016/j.jcou.2021.101494>

Received 28 December 2020; Received in revised form 21 February 2021; Accepted 22 February 2021

Available online 10 March 2021

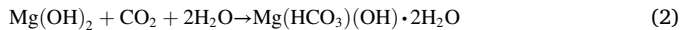
2212-9820/© 2021 The Authors.

Published by Elsevier Ltd.

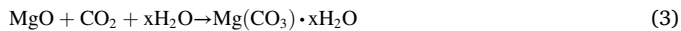
This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

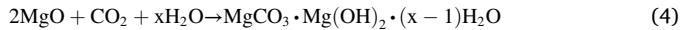
Subsequently, brucite can undergo carbonation to form a range of hydrated $\pm$ hydroxylated magnesium carbonates (HMCs; Table 1), e.g. hydromagnesite, dypingite, artinite, lansfordite; all carbonates of the form $x(\text{MgCO}_3) \cdot y(\text{Mg}(\text{OH})_2) \cdot z(\text{H}_2\text{O})$ [14,15]. The most commonly formed mineral reported in the literature for ambient pressure-temperature conditions is nesquehonite ($\text{Mg}(\text{HCO}_3)(\text{OH}) \cdot 2(\text{H}_2\text{O})$) which is strictly not an HMC, but will be included as one here [15,16]:



In addition, MgO carbonation may occur directly:



or



In engineered mineral carbonation processes (such as magnesium-based cement production), it is crucial that reactions proceed beyond reaction (1) and that brucite undergoes additional hydration and carbonation to form nesquehonite or other HMCs. This is necessary for the goal of CO₂ uptake, but also advantageous for the formation of useful end products with desirable material properties. For example, pastes of hydrated MgO (brucite) exhibit greatly reduced compressive strength compared to HMC pastes [17], with the latter demonstrating compressive strength values relevant to construction applications (e.g., almost 90 MPa uniaxial compressive strength for MgO-cement pastes with high levels of HMC product [16]). Experimental studies of MgO-based concrete cores/blocks show higher compressive strength for samples cured in elevated CO₂ atmospheres relative to those cured under ambient CO₂ conditions, due to formation of HMCs [11,18,19].

A significant hurdle in creating Mg-based cements, pastes or concretes is ensuring hydration-carbonation reactions proceed to full extent. Many studies report high levels of reactant MgO and brucite in the final product even after several days or weeks of curing [11,16]. Some studies have attempted to address this by incorporation of ‘hydration agents’ (e.g., acids and salts) in the cement mixes to enhance reactivity [11,18,19] or to stabilize reaction products [20]. The addition of these agents does improve carbonation extent; however, in the study of Dung and Unluer [11], even the sample with the most effective hydration agent still contained 18 wt% of unreacted MgO and 29 % brucite after 14 days of curing in elevated CO₂ conditions. Carbonation extent has been linked to structural characteristics as well: Pu et al. [21] showed that carbonation in cement cores is inversely related to distance from the sample surface (which provides direct access to CO₂), with internal regions showing significantly less carbonation even over 14 days of curing; and Harrison et al. [22] highlighted the importance of mineral-water-gas interfacial areas to mineral reaction extent in porous column experiments of brucite carbonation.

Table 1
Expected reactant and product components in magnesium-based mineral carbonation experiments.

Component name(s)	Chemical formula	Density, ρ (g/cm ³)
Nonreactive components		
Quartz, Silica	SiO ₂	2.65
Reactive Components		
Periclase, Magnesia	MgO	3.58 [15]
Magnesite, Magnesium Calcite	MgCO ₃	3.01 [15]
Brucite	Mg(OH) ₂	2.38 [15]
Nesquehonite	Mg(HCO ₃)(OH)•2(H ₂ O)	1.85 [15]
Lansfordite	MgCO ₃ •5H ₂ O	1.7
Hydromagnesite	4MgCO ₃ •Mg(OH) ₂ •4H ₂ O	2.16–2.2
Dypingite	4MgCO ₃ •Mg(OH) ₂ •5H ₂ O	2.15
Artinite	MgCO ₃ •Mg(OH) ₂ •3H ₂ O	2–2.03
Water	H ₂ O	Approx. 1

Complicating the evaluation of the extent of hydration-carbonation reactions in mineral carbonation studies is the formation of amorphous materials, phases with compositions that cannot be identified by mineral characterization methods. In their study of hydration of MgO-hydromagnesite pastes, Kuenzel et al. [17] reported the presence of an amorphous phase “of composition between that of brucite, hydromagnesite and water” indicated by Raman spectroscopy. In another paste-based magnesium carbonation study, Wang et al. [16] showed that the amount of amorphous phase increased with both gaseous CO₂ concentration and with time (reaching a maximum of approx. 30 wt%), indicating that a significant portion of HMC product is in amorphous form. In brucite carbonation column experiments, one of two main precipitants observed by Harrison et al. [22] was an X-ray amorphous phase with “stoichiometry and solubility similar to artinite” (i.e. MgCO₃Mg(OH)₂ • 3H₂O). Experiments on adsorption of CO₂ and H₂O on hydrotalcites showed bidentate carbonate species and bicarbonate species may be important intermediate species in formation of HMCs [23].

The stability of both amorphous and crystalline products must be considered for long-term storage and construction applications. Nesquehonite, the primary HMC product found in many MgO cement studies, is reported to be thermodynamically metastable or even unstable relative to hydromagnesite under environmentally-relevant conditions [24,25]; and may transform to dypingite in 57 days at 25 °C, and in 20 days at 35 °C [26]. Similarly dypingite (Mg₅(CO₃)₄(OH)₂•5H₂O) transforms to hydromagnesite [27]. Both of these transformations result in volume changes that affect the stability and usability of MgO-based concrete materials [15,27–29]. Phase transformations are observed between nesquehonite, hydromagnesite, dypingite, and amorphous phases under wetting/drying and freezing/thawing cycles [30]. Thus, the stability of amorphous HMCs (as well as the correct composition of these materials) is a significant concern for Mg-cement strength and longevity and for enhancing CO₂ uptake in Mg-rich materials.

In the current study, we aim to address some aspects of these questions by investigating mineral carbonation within a variety of idealized porous columns. The samples are comprised of 12 mm diameter, 36 mm long columns packed with a porous mixture of silica sand grains (three different grain size compositions were studied), crushed calcined MgO, and water. Expected (non-amorphous) reactants and products are listed in Table 1. Samples were placed in a closed chamber with elevated CO₂ concentration under ambient pressure and temperature for a total period of 108 days. Non-destructive 2D DRIFTS and 3D X-ray CT scans were acquired at five time points throughout the carbonation reactions (i.e., just after mixing on day 0, day 3, day 10, day 28 and day 108), and finally destructive XRD was used to characterize the endpoint mineralogy of the samples. The combination of non-destructive 2D characterization and 3D structural analyses provides new insights into 3D structural limits on mineral carbonation reactions, with an emphasis on the impacts of microscopic structural features. The relatively long timeframe of the experiments allows for investigation of component stability (under experimental conditions of high-CO₂ concentration). This study demonstrates the utility of combined X-ray CT, DRIFTS, and XRD as a potential avenue for further characterization and optimization of mineral carbonation reactions.

2. Materials and methods

2.1. Sample preparation and carbonation conditions

Three types of porous columns were created, using different sizes of sand aggregate: (A) monodisperse mesh 35 silica sand (grain diameter approx. 500 μm), (B) monodisperse mesh 70 silica sand (grain diameter approx. 210 μm), and (C) a 50:50 polydisperse mixture of mesh 35 and mesh 70 silica sand. The sand packings were mixed in a ratio (by mass) of sand : MgO : water = 2 : 1 : 0.8. The MgO was granular (minimum specification of 96.0 % MgO on a post-ignition basis, with limited

amounts of oxides of calcium, iron, aluminum, and silica present; Causmag® Granomag® AL7; Causemag International; Young, NSW Australia 2594) and crushed manually via mortar and pestle prior to mixing, such that the original 3 mm diameter granules achieved a distribution where the largest grains were approximately the size of the mesh 35 sand (500 µm), with most grains smaller than the mesh 70 sand (210 µm); this can be observed in Figs. S1, S3, S4, S5 in the Supplemental Materials. The MgO was calcined by the manufacturer to maximize reactivity, achieving a neutralizing values of 220 % (i.e. the amount acid the MgO can neutralize relative to the equivalent amount of pure calcium carbonate is 220 %). The dry components (silica sand and MgO) were mixed together prior to the addition of water. The resulting pastes were packed into cylindrical molds (diameter 12 mm, length 36 mm), using a tamping rod and vibration to reduce void space.

When not undergoing DRIFTS or X-ray CT scanning, samples were placed in an airtight container and gaseous CO₂ was injected into the container periodically (every several days for the duration of the 108 day experiment) at slightly above ambient pressure. We monitored CO₂ levels to ensure that they remained above 3,000 ppm (equivalent to a partial pressure of 0.003 atm, an order of magnitude larger than ambient air) for the duration of the experiment using a Perfect Prime C02000 Data Logger. A beaker of water was also placed in the container, which maintained monitored relative humidity (RH) at levels approaching 100 % and always greater than 85 % RH. Temperature was ambient (approx. 20 °C) over the duration of the experiments. To serve as a “control”, a fourth core with aggregate composition B was also prepared and placed in a constant humidity chamber, but with only ambient CO₂ levels (“NCB”, i.e. non-carbonated B).

For DRIFTS and X-ray CT scanning, samples were removed from the carbonation chamber, stacked in a cylindrical mount, and scanned in series; DRIFTS analysis was conducted either directly before or directly after X-ray CT acquisition. Thus, for each scan timepoint, the samples were in an ambient CO₂, ambient humidity environment for approx. 24 h. The timeframes indicated throughout this report indicate carbonated periods only (i.e. “day 3” indicates the samples have undergone three days of carbonation chamber environment and does not include the time of the day 0 X-ray CT or DRIFTS data acquisition).

2.2. 3D X-ray computed tomographic microscopy

2.2.1. Tomogram acquisition

CT scans were acquired at the CTLab at the Australian National University via a space-filling helical scanning trajectory [31], under the parameters detailed in Table 2.

3D X-ray CT has been used to characterize structural and material distribution for a wide range of geoscience and materials science applications [32–34]. For this study, transmission-based X-ray tomography is utilized, which characterizes the relative attenuation of different materials according to the Lambert-Beer law:

$$I = I_0 e^{-\mu x} \quad (5)$$

Where I_0 is the original intensity and I is the resulting attenuated intensity of X-ray photons after passing through an object of thickness x and linear attenuation coefficient μ (a function of electron density and material bulk density, ρ_{bulk}). In multi-component systems, the

attenuation coefficients of each component sum linearly in proportion to their fractional X-ray path distance. A 3D reconstruction of a sample can thus be achieved by acquiring a large number of X-ray projections (radiographs) through the sample over a sufficiently large range of angles in order that the attenuation at every point within the sample can be back-calculated. Reconstruction requires perfect alignment of all projections, and algorithms must accommodate discrepancies due to hardware inaccuracies and thermal drift. We implemented reconstruction algorithms at the ANU CTLab to account for these issues using a multi-resolution consistency check between reprojections (acquired at the end of the scan) and the original projections [35,36].

In practice, the Lambert-Beer law (Eq. 5) cannot be directly applied for lab-based X-ray CT systems; modifications must be made to account for the fact that laboratory scale X-ray sources emit a polychromatic spectrum of wavelengths rather than a single monochromatic X-ray energy. Although the linear attenuation coefficient μ is primarily a function of ρ_{bulk} and atomic electron density, it also varies with incident energy; and the incident X-ray spectrum cannot be assumed to be constant between scans, or even over the course of a single scan. These effects are accounted for via clearfield measurements that correct for beam spectrum distribution and aging during scan acquisition, so these effects are corrected within any given tomogram. However, the attenuation values calculated in a reconstructed tomogram cannot necessarily be compared directly to those in any other, particularly for samples with different material compositions, and additional processing is required to provide quantitative comparisons. Our approach for image processing is detailed in Section 2.2.3.

2.2.2. 3D volume processing and quantification of phase densities

Image processing was accomplished in a series of steps using Mango, a software developed by Applied Mathematics at ANU. First, data volumes taken at later time points (days 3, 10, 28, 108) were registered to the day 0 sample volume, masked to exclude core holder and external void space, and cropped so that all data volumes represented the same physical volume.

All the attenuation gray values in the final registered, masked, and cropped tomogram were quantified (Fig. 1). The histograms in Fig. 1a exhibit three peaks corresponding to three density groupings: very low attenuation values are associated with void space; intermediate values are associated with water, hydrated Mg compounds, and HMCs, collectively referred to in this study as “cement”; and high attenuation values indicate high density components (Table 1).

From this histogram, several important features were measured (Fig. 1b) representing the values associated with each phase (void, cement, and high density components) which were used subsequently to segment the tomogram into three phases (Fig. 2) and finally to rescale the cement attenuation values. Details of the segmentation are included in the Supplemental Materials.

To utilize the information contained in the attenuation values of the cement phase, a re-scaling protocol was implemented. As described in Section 2.2.2 above, attenuation values cannot be directly compared between different tomograms due to X-ray beam variability over time, and because as samples undergo reactions, they change in density and water content and thus attenuate the beam to different extent. To enable comparison of the different tomograms acquired over 108 days, we rescaled all cement-labeled attenuation values to consistent, unchanging, features in each sample (Fig. 2b). For every voxel which was labeled “cement” during the segmentation step, the attenuation value of the same voxel in the original tomogram was re-scaled on a range from 2 to 102, where the value 1 is equivalent to the attenuation value of the void peak (max_1) and the value 103 is equivalent to the high-density component peak (max_3). The high-density components in each sample are largely comprised of stable unreacted MgO and silica sand grains; the measured volume fraction for high-density components in carbonated samples varies by a maximum of 1% after day 0 (see phase volume quantification in Supplemental Materials). The rescaling step allows for

Table 2

Sample and X-ray CT acquisition parameters.

	Sample A	Sample B	Sample C	Sample NCB
Voxel size of day 0 scan (µm)	6.76	6.75	7.18	6.76
Scan time points (days)	0, 3, 10, 28, 108			
Field of view [X-Y-Z] (mm)	approx. 17-17-36			
Scan time (hours)	approx. 6–7			
X-ray Current (µ A)	50			
X-ray Voltage (kV)	100			

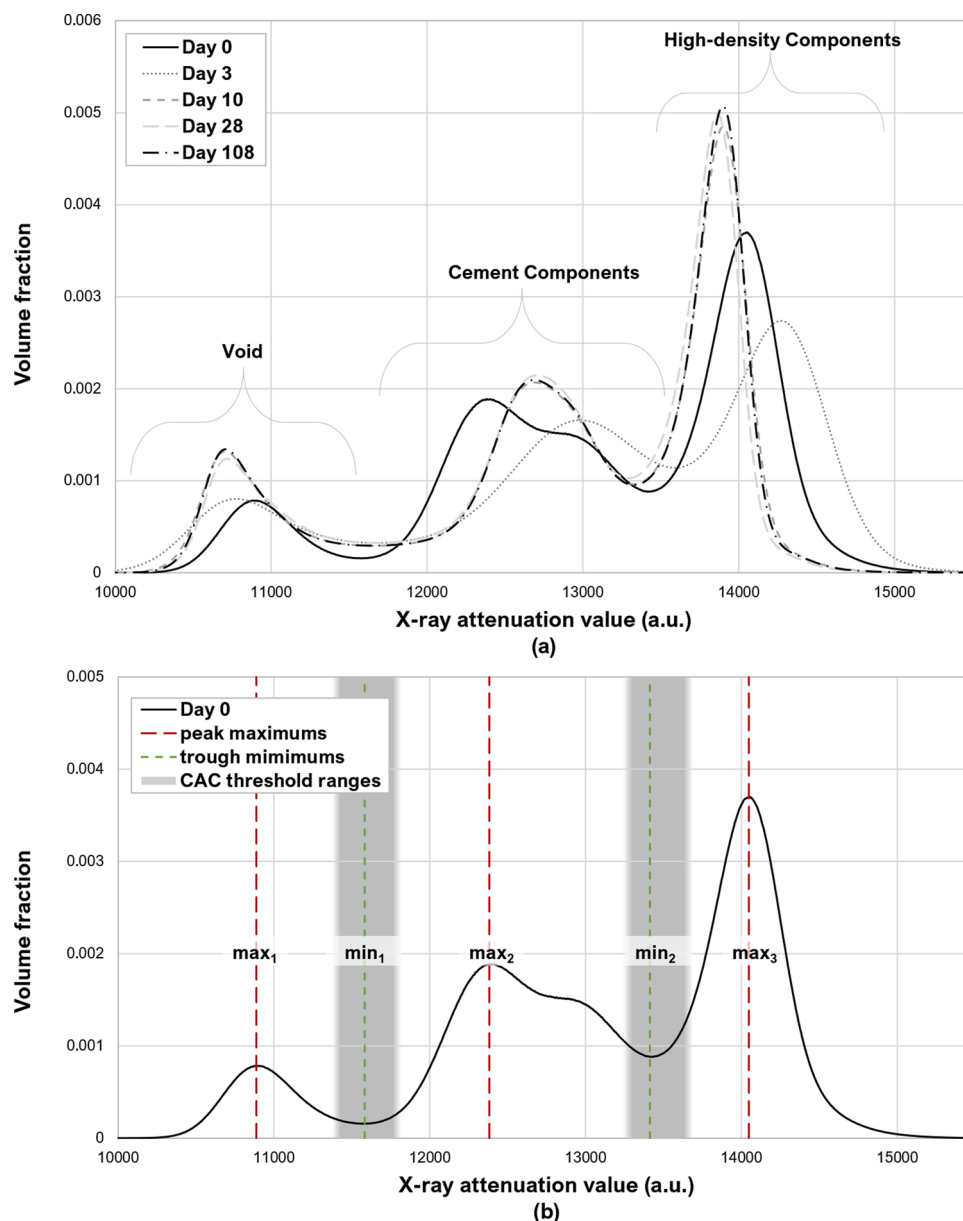


Fig. 1. Histograms of X-ray attenuation in X-ray CT volumes. (a) Shift in histograms over time for sample A (monodisperse 35 mesh silica sand), with regions corresponding to the different materials in the sample noted. (b) Histogram for day 0 with values measured for segmentation thresholds identified (see Supplemental Materials for additional information on segmentation parameters).

quantitative comparison of changes in attenuation in the cement phase by accounting for the shifts in attenuation of the sample overall. A similar approach has been previously used to quantify otherwise indeterminate microporosity in carbonate materials [37].

2.3. Mineralogical Analysis: DRIFTS spectroscopy and XRD

Diffuse-reflectance (DRIFTS) measurements were acquired over the top surface of each sample using an Aligent handheld 4100 ExoScan at time points corresponding to the CT scans. Spectra were measured in the IR range of 4000 cm^{-1} to 650 cm^{-1} at a resolution of 4 cm^{-1} , with 100 scans for each spectrum. Background spectra were collected on a rough Al surface prepared for this purpose. Fig. 3 shows spectral measurements from sample C for days 0, 3, and 108; demonstrating the typical progression of the DRIFTS spectra. The growth of the bands corresponding to carbonate stretching vibrations in HMCs are apparent; the sharp band

related to the OH stretching vibration corresponding to brucite is less obvious and requires baseline-normalized quantification to discern trends.

The DRIFTS measurements are non-destructive and spectral characteristics were measured at the top surface of the core only, detecting (bi)carbonate species in the HMC, and OH in the brucite on the surface directly exposed to CO₂. The region 1528–1555 cm^{-1} relates to asymmetric stretching vibrations of unidentate carbonate and 1435–1480 cm^{-1} corresponds to symmetric bicarbonate stretching modes in HMCs, including nesquehonite [23,38,39]. The band at 866 cm^{-1} is found in lansfordite and is related to carbonate stretching vibrations [40]. The 3689–3695 cm^{-1} band region corresponds to OH stretching vibrations in brucite [40]. The band intensities of the resulting spectra were quantified using spectra that was smoothed with an 11-point window and baselines defined using a window that encompassed the region immediately adjacent to the bands.

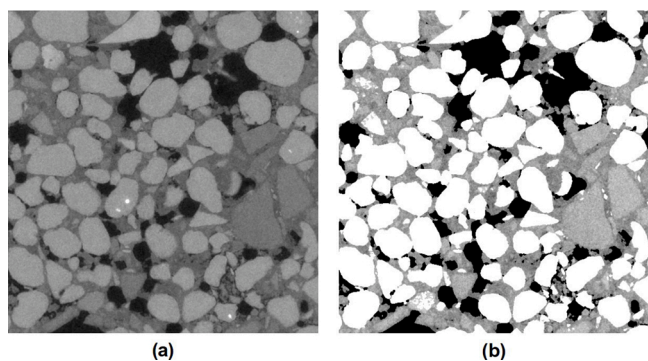


Fig. 2. Image processing workflow for a zoomed-in 2D cross-section of sample A. (a) Raw tomographic data. (b) Data segmented into three phases: void (black), and high-density grains (white), and cement (range of gray values). The cement attenuation values are re-mapped on a universal normalized scale (indicated by the brightness of the gray values in (b)) where the void phase and high-density component attenuation values are used as reference endpoints.

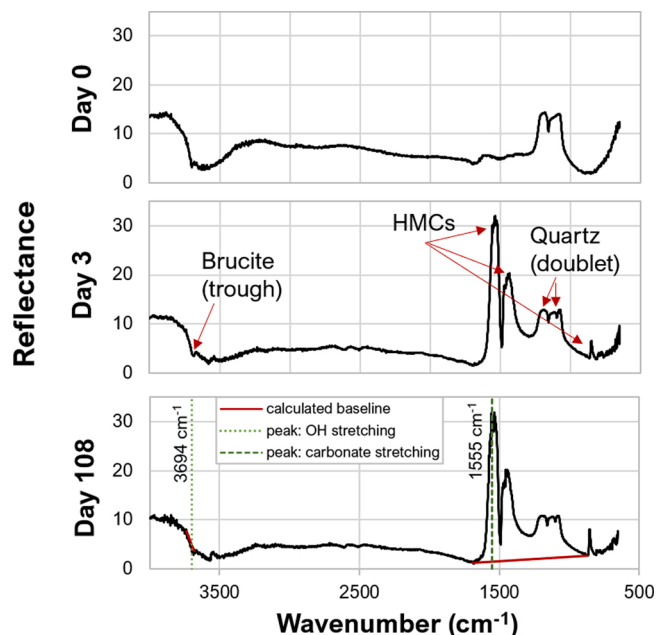


Fig. 3. DRIFTS spectra and measurement for sample C; days 0, 3, and 108. Peaks corresponding to OH stretching vibrations in brucite, (bi)carbonate stretching vibrations in HMCs, and O-Si-O stretching in quartz indicated. Quantification of bands was accomplished by measuring reflectance intensity relative to the baseline.

At the end of the curing process, subvolumes (approximately 50 % of original sample volume) of carbonated samples were ground, mixed with a corundum spike (Baikalox alumina polishing powder 1 μm), and the resulting powder was mounted on a silicon low-background sample holder and analyzed by X-ray diffraction using a Malvern Panalytical Empyrean X-ray diffractometer. Analyses were undertaken in Bragg-Brentano geometry from 5 to 85° 2 θ at a spacing of 0.01313° using a 3 kW X-ray generator and Cu K α radiation, and a PIXcel 3D detector. Mineral identification was through the SIEMENS software package Diffracplus Eva 10 [41] and ICDD PDF-2 database, and phase quantification using Rietveld refinement [42] with the program HighScore Plus V4.8. The amorphous (poorly crystalline or extremely fine-grained) component was identified by an elevated background ‘hump’, and quantified relative to the spike in the internal standard [43].

3. Results

Results of the experiments are presented in three sections: first, we examine the mineralogy of the reaction products using DRIFTS and endpoint XRD results to help constrain the CT values. Second, we validate the cement CT value rescaling procedure by comparison of temporally-resolved CT and concurrent DRIFTS data for carbonated and non-carbonated samples. We then present the structural and grayscale analysis derived from CT for carbonated samples.

Throughout the results and the following discussion, we refer to air-filled regions of the samples as “void” rather than porosity. Porosity is commonly understood to refer to non-solid regions of a porous material, which may be filled with gas or fluid. In these samples, the cement paste (comprised of MgO and water) was initially a fluid, and over time it solidified. Changes in void volume may thus be due to structural development of the samples, or due to consumption of water.

3.1. Phase characterization

At the end of curing (>108 days), the mineralogical composition of the bulk sample was determined by XRD for all carbonated samples (Table 3). The non-carbonated sample NCB was pulverized during compressive strength testing (results not reported here) and a representative (uncontaminated) sample was not able to be preserved for XRD analysis, so results reported here apply only to carbonated samples (carbonated samples also underwent compressive strength testing, but significant portions approximating 50 % of total sample volume were preserved intact and thus carbonated samples were able to be retained for further characterization). As expected, quartz (i.e., silica sand) is the predominant mineral present in all samples. All samples contain approximately the same level of periclase (i.e., unreacted MgO). Brucite makes up 8–10 wt% for all samples; while XRD-identified nesquehonite is higher in samples B and C, but lower in sample A. All samples contain a significant fraction of amorphous material (including HMCs), which further introduces challenges in determining quantitative mineralogy and reaction pathways using the endpoint bulk XRD data.

DRIFTS spectral intensities relate to the (bi)carbonate bonds in HMCs and OH bonds in brucite on the 2D surface of all the cores (both carbonated and uncarbonated) throughout the entire timeseries. The (bi)carbonate bands (1528–1555 cm^{-1} and 1435–1480 cm^{-1}) are not in the same position as bands reported in the literature for the specific minerals listed in Table 1, likely because multiple phases are present, including amorphous material. Nonetheless, the band positions observed allow us to rule out the presence of some proposed reaction products (Table 1). For instance, magnesite and hydromagnesite do not have the bands in the 1515–1560 cm^{-1} region that we observed and they both have a strong band at 888 cm^{-1} [44] that was not observed in our spectra. Artinite, lansfordite and dypingite do not have bands in the 1528–1555 cm^{-1} region [38,44,45] and of those materials, only lansfordite has a strong band at $\sim 866 \text{ cm}^{-1}$ also observed in our samples. In sum, the bands observed in the DRIFTS spectra are most consistent with (bi)carbonate-hydroxyl-water-bearing materials such as nesquehonite + amorphous HMCs $\pm$ lansfordite. This data suggests that reactions 1–4 may all have occurred in our experiments.

Table 3
XRD results at the endpoint of curing.

	A wt. %	B wt. %	C wt. %	NCB wt. %
Quartz	45.1	39.7	39.2	
Periclase	10.6	9.3	9.8	
Brucite	9.7	9.9	8.4	NA
Nesquehonite	5.3	9.4	8.0	
Amorphous fraction – including HMCs	27.5	30.1	33.5	
All others	<2.0	<2.0	<2.0	

3.2. Time-resolved X-ray CT attenuation and DRIFTS characterization

The rescaled cement X-ray intensity values increase over the first three days for all carbonated samples in both the whole core and the top 0.5 mm of the core; in contrast, rescaled cement X-ray intensity values decrease for the non-carbonated sample NCB (Fig. 4). From day 28 onwards, the X-ray intensity remains constant (sample A) or slightly increases (samples B and C) in carbonated samples. The non-carbonated sample shows larger variation in rescaled intensity, but values remain significantly lower than for carbonated samples.

DRIFTS results indicate a significant increase in the production of HMC over the first three days through an increase in the 1528–1555 cm^{-1} and 866 cm^{-1} bands and brucite by an increase in the 3689–3695 cm^{-1} band. At Day 10, there is a decrease in the HMCs for samples A and C, whereas it has stabilized for Sample B and reached a maximum value for Sample NCB. However, we note that a subsequent DRIFTS study on these materials determined that reflectance values could vary by approximately $\pm 5\%$ depending on the location of the DRIFTS measurement, due to surface heterogeneity (see Supplemental Materials). After Day 10, the DRIFTS results do not show a significant change in the concentration of most of the phases within expected measurement variability.

Combining both the XCT and the DRIFTS: the rescaled average attenuation values of the cement roughly approximate the DRIFTS time-series for carbonate growth over the first 3 days. Brucite formation does not significantly impact the rescaled X-ray intensity values (e.g., see sample NCB). After day 10, the rescaled attenuation values are relatively more stable than the mineral spectra results; this indicates that while solid and adsorbed phases may be undergoing reactions which change the measurable spectral vibrations (e.g., brucite converting to HMCs, or mineral phase to amorphous phase and/or surface adsorbed species), the density of the cement phase in carbonated samples is approximately constant. In other words, after day 10 both the XCT and DRIFTS data indicate that the cement phase is not taking up or releasing substantial CO₂ or water.

The comparison of cement rescaled intensity values with DRIFTS results demonstrates that the rescaled X-ray intensity is a proxy for cement phase carbonation, in addition to density. Correspondingly, the amorphous HMCs produced in carbonated samples have significantly higher density (and thus, higher rescaled X-ray intensity) than the hydrated non-carbonated “cement” phase produced in the non-carbonated

sample NCB.

3.3. Time-resolved 3D structural and attenuation characterization

Hereafter, analysis is focused on how structure influence carbonation, and only carbonated samples are considered. Fig. 5 shows 2D cross sections of raw and processed 3D X-ray CT data for carbonated samples at day 0 and day 108. Differences in pore structure due to the different silica sand compositions are readily apparent between the large grained (500 μm , sample A), small grained (210 μm , sample B), and mixed grained (50:50 500:210 μm , sample C) conditions. From a qualitative standpoint, the time-separated samples appear very similar, although increases in void space are apparent on close inspection. The homogeneity/heterogeneity of sample structures is also visible: while samples A and B are relatively well-mixed, there exists an obvious layer in sample C (near the vertical midpoint of the sample) where void space is suppressed.

Core-scale (i.e. averaged over the entire core sample) characteristics for each sample were calculated from the segmented data sets (Table 4). Despite the relatively large void spaces visible in Fig. 5, sample A contains the low total void, with the lowest connected void fraction and the lowest specific interfacial area between cement and connected void space; indicating that many void spaces in this sample are disconnected and would not facilitate gas transport. Sample B has both the largest void value (of which 65 % is connected) and the largest interfacial area between the cement phase and the connected void, factors that indicate favorable CO₂ transport throughout the core and into the cement phase. Sample C has an overall lower total void and interfacial area relative to sample B, but also exhibits the largest connected void fraction. These macroscopic parameters may be linked to reaction products, as discussed in Section 4.0.

In addition to core-scale measurements, these samples were analyzed on a microscale basis. In Fig. 6, values are averaged on the slice-by-slice basis throughout the vertical extent of each core. The rescaled intensity value of the cement phase (indicating the density and carbonation level of the cement) of the samples at each timepoint are plotted adjacent to the connected and total void values; with visualizations of slices at relatively high and low connected void for each sample for illustration. Several important features are observed:

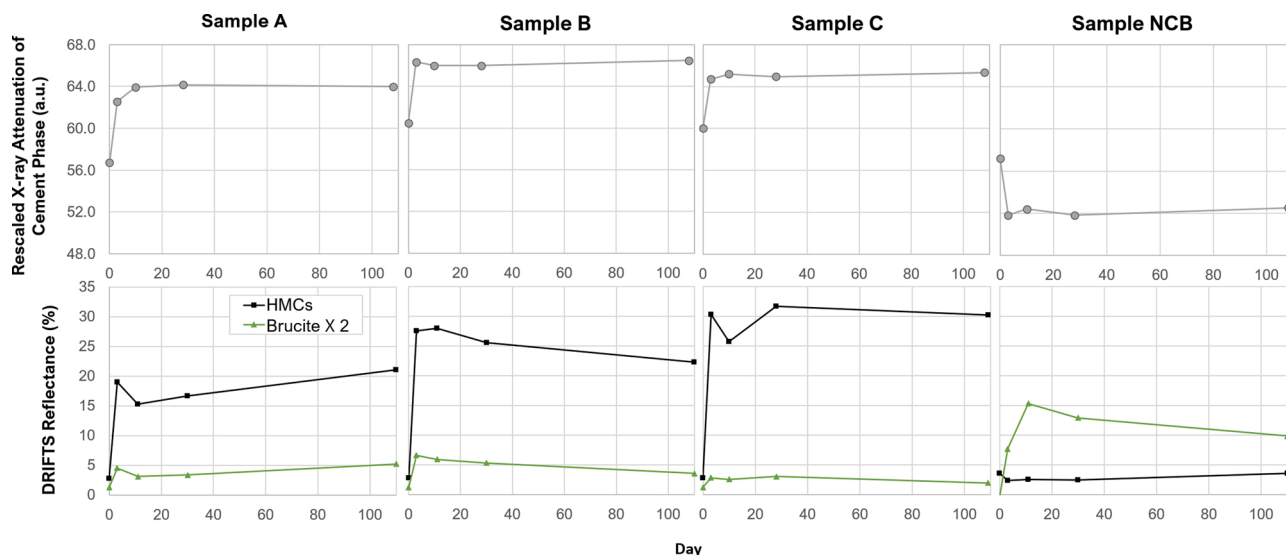


Fig. 4. Rescaled X-ray attenuation values for the cement phase for the four samples (whole core average) and baseline-corrected DRIFTS reflectance % values for HMC and brucite as measured on the top face of the samples. Note that reflectance values corresponding to brucite are shown multiplied by a factor of two for visibility.

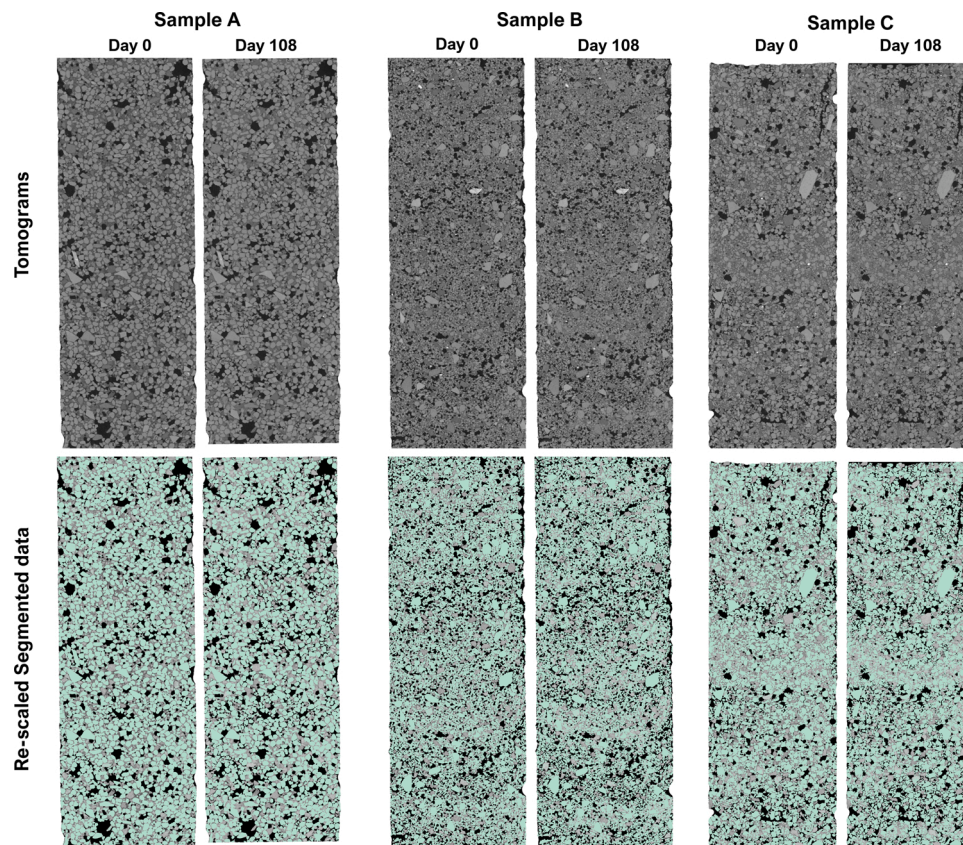


Fig. 5. CT data for the three samples at day 0 and day 108. 2D slices of 3D volumetric data are shown, including the raw tomographic data and processed segmented data with cement phase re-scaled.

Table 4

Structural characteristics of the samples calculated from segmented CT datasets.

Sample	Volumetric Void Fraction at Day 0 (-)	Connected Void at Day 0 (vol/vol)	Interfacial Area Connected Void - Cement at Day 0 (mm ² /mm ³)
A	0.15	0.52	0.43
B	0.19	0.65	1.16
C	0.14	0.76	0.93

- As shown in Fig. 4, rescaled intensity value increases over time, but at different rates. Sample A exhibits intermediate values at day 3 and stabilizes after day 10; while samples B and C show that intensity values at day 3 largely approximate the end-state intensity profile, with minor fluctuations thereafter.
- Regions with very low connected void values (e.g. depth of 18.1 mm in sample A, 16.0 mm in sample B, 10.0 mm and 17.0 mm in sample C) also have lower rescaled gray values relative to their respective endpoint values, indicating that progress towards a more carbonated cement endpoint is lagging compared to other regions of the core.

The relationship between rescaled intensity and distance to connected and disconnected void is further interrogated in Fig. 7. The Euclidean distance between every cement voxel and the nearest connected (left column) and disconnected (right column) void region was calculated, and the average rescaled cement intensity was computed as a function of distance. The cumulative distribution of cement voxels (as a function of distance to void) up to 99.9 % of cement volume is also indicated in Fig. 7.

Voxels within approx. 0.2 mm of connected void regions (i.e. void spaces facilitating transport of high CO₂ concentration) exhibit a significant “peak” in rescaled intensity values for all samples; this peak is

not evident in voxels near disconnected void regions (Fig. 7). This indicates carbonation (and relatively higher-density mineral formation) is more likely to occur in regions within 0.2 mm of connected void. Average rescaled intensity values decrease as distance from connected void increases above 1–1.5 mm for samples A and C after day 0 (in sample B, 99.9 % of cement voxels are within 1.3 mm of connected void). Further, the day 3 data for samples A and C demonstrate a larger gradient in rescaled intensity values as a function of distance to connected void; this provides additional quantification of the reaction front in these samples.

Notably, the distance distributions for the three samples vary significantly. In sample B, 99.9 % of the cement volume is within 1.3 mm of connected void; samples A and C have a large fraction of cement volume further from connected void, both containing 99.9 % of cement volume within 3.0 mm of connected void. The distance distributions again point to sample B as having the pore structure most favorable to CO₂ transport.

We further investigate sample C using a local digital volume correlation (DVC) technique [46] to compare the evolution of X-ray attenuation intensity in this sample (Fig. 8). Using a local non-rigid image registration scheme correlating $420 \times 420 \times 420$ μm cubes spread on a regular grid, tomograms of scans from days 3–108 are correlated to that of day 0 (reference image). This allows us to compute the local strain field while at the same time measure changes in the rescaled attenuation values due to the formation of new pores or minerals by computing a grayscale *residual field* by applying the measured displacement field to the deformed configuration. Following Stavropoulou et al. [47], as gray levels are moved, they are also scaled by the local volumetric strain so that the transformation is thermodynamically sound (“gray level mass” is conserved). Fig. 8 presents the gray level residual using a color map to highlight differences in intensity for the time-series of data relative to day 0: blue indicates decreased intensity, red indicates increased

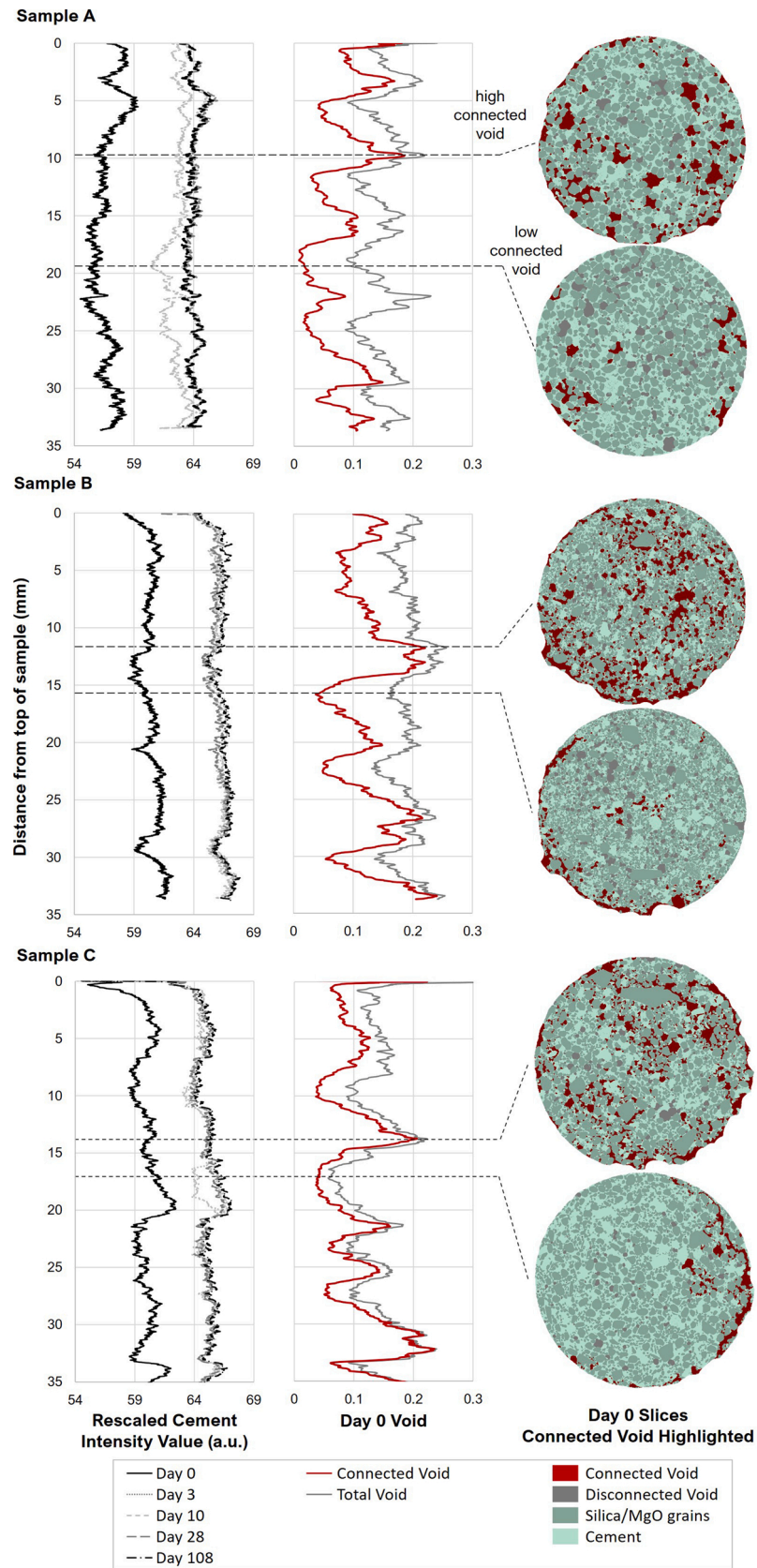


Fig. 6. Vertical profiles (on a slice-by-slice basis) of the three samples. Left: average rescaled cement intensity values over time. Center: total void and connected void at day 0. Right: Segmented slices illustrating high and low connected void regions, with connected void highlighted in red.

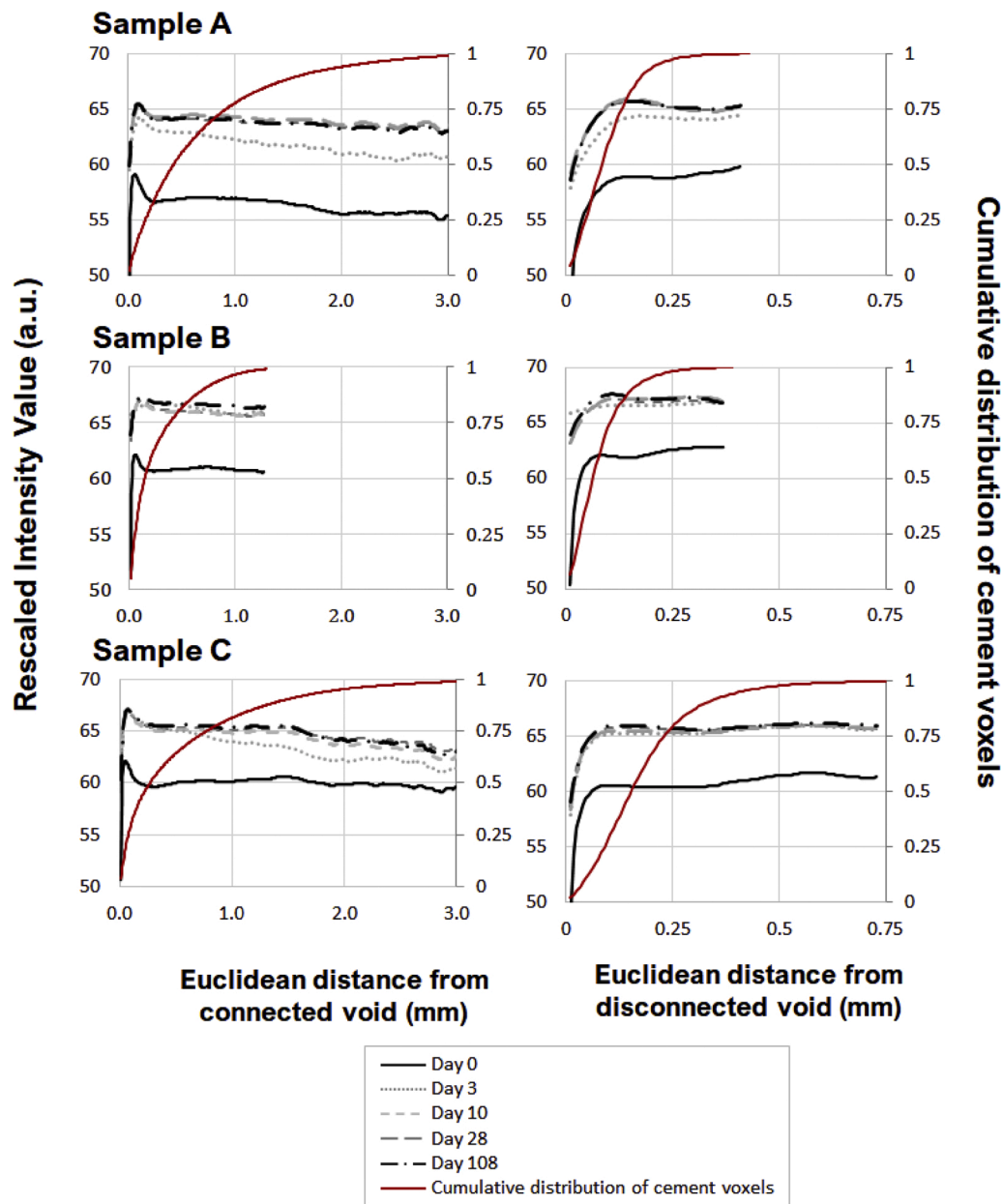


Fig. 7. Average rescaled attenuation value of cement as a function of Euclidean distance to connected (left column) and disconnected (right column) void.

intensity. Decreased intensity occurs in intra-granular regions indicating the consumption of water and the retreat of aqueous interfaces, resulting in the creation of additional void space. Increased intensity occurs in discrete high-intensity 'hot spots' that indicate high-density granular mineral formation, as well as more moderately within the intra-granular cement phase. The zoomed-in region in Fig. 8 includes the region near the vertical center of the sample that exhibits suppressed void volume (i.e. as previously highlighted in Fig. 6); it is evident that the intensity continues to evolve (both positively and negatively) in this region beyond day 3, whereas other regions of the sample are relatively stable from days 3–108. We further quantify the expansion/shrinkage of the local volumes by plotting the joint histogram of the volumetric strain and the porosity as measured in DVC subvolumes (many overlapping $420 \times 420 \times 420 \mu\text{m}$ subvolumes) and the results are shown in the right most column of Fig. 8. We observe that already at day 3, most of the local volumes experience shrinkage at low porosities ($<40\%$) while subvolumes with higher porosities ($>40\%$) exhibit expansion of volumes, as shown by red crosses in the figures. This trend is further enhanced by

day 108.

In order to classify the gray level change, this information (gray level change corrected for volumetric strain) is combined with the identified phases in the first scan. Using the same subvolumes used for the DVC analysis, each subvolume is classified as being mostly pore, cement, or high-density aggregate components, and the mean gray level change is computed for each subvolume. Fig. 9 presents a histogram of gray level change for each phase and each increment (day 0 to day 3, day 0 to day 10, etc.). This reveals that already between the first two scans subvolumes containing mostly voids have a marked tendency to increase in gray value, related to mineral formation and density/carbonation increases in the cement phase adjacent to high-porosity regions (i.e. similar to the results presented in Fig. 7). The subvolumes containing mostly high-density unreacted MgO/silica sand aggregates essentially have a mean gray value change close to zero, again affirming the stability of these components throughout the duration of experiments. A small decrease of gray values can be seen in subvolumes containing mostly cement, corresponding to water consumption and water interface

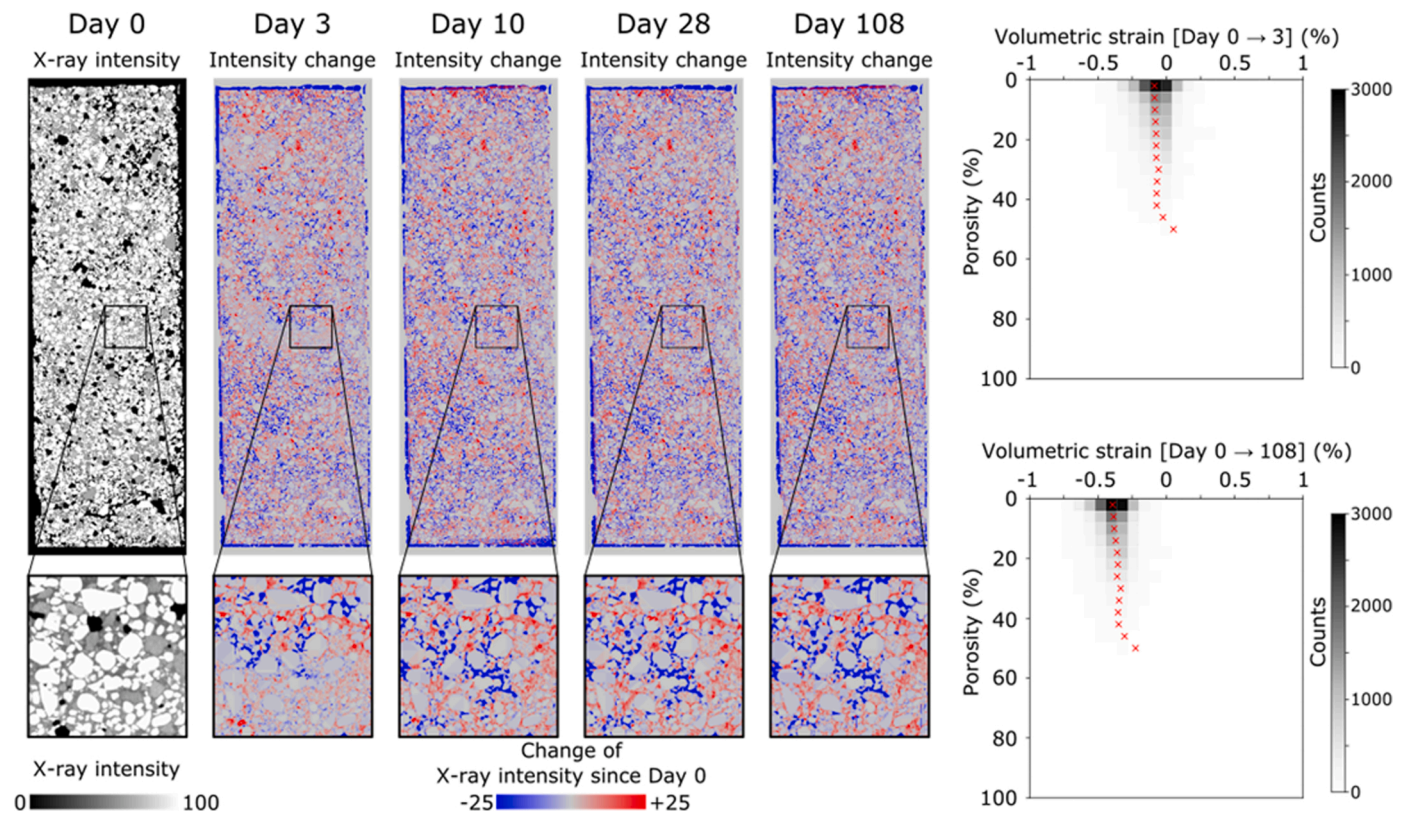


Fig. 8. DVC analysis of sample C showing X-ray intensity differences relative to the sample at day 0. Blue colors represent intensity decreases (due to consumption of water and retreat of aqueous interfaces in void spaces); red colors indicate intensity increases (due to mineral formation and cement phase density/carbonation increasing). The zoomed-in subset includes the region of suppressed void volume near the vertical center of sample C. The column on the right shows change of volumetric strain as a function of porosity between days 0, 3 & 108 measured in DVC subvolumes. A large amount of positive and negative volumetric strain is observed especially in low porosity subvolumes. Red crosses connect the centre of mas of the mean volumetric strain showing a slight upward trend (local volume expansion) as the porosity increases.

retraction (which creates additional low gray level void space).

4. Discussion

4.1. Linked structural and mineralogical analyses

Mineralogical (XRD) and spectral (DRIFTS) analyses were used to constrain the X-ray CT image processing; this enabled the isolation of stable phases (void, high-density components) from the phase undergoing carbonation and hydration reactions (“cement”). The stability of the high-density components (comprised primarily of silica sand and MgO grains) was verified via quantification of phase volumes and was supported by subvolume-level analysis showing that subvolumes dominated by these high-density components showed essentially no change in gray level over time (Fig. 9). Based on these stable, unchanging features in each sample, the X-ray CT attenuation of the reactive cement phase was re-scaled to a normalized universal scale that enabled comparison of cement phase attenuation and density over time. Comparison of the re-scaled attenuation values with DRIFTS measurements (Fig. 4) confirmed that the re-scaled attenuation values can also be used as a proxy for level of carbonation.

Reaction process (as measured by rescaled CT values and DRIFTS measurements) is not uniform across different samples (Fig. 4), nor is it uniform throughout individual cores (Figs. 6–8). Reaction process appears to be linked to connected void; i.e. regions with low connected void within samples show lagging reaction progress compared to other regions within the core on the same day (Fig. 6). The link between reaction progress and proximity to connected void space is further illustrated by distance to connected void-rescaled attenuation curves (Fig. 7)

and the histograms of gray value change as a function of dominant subvolume phase (Fig. 9).

The XRD results support the supposition that sample B, i.e. the sample with the most favorable structural characteristics for CO₂ transport (high connected void, high cement-connected void interfacial area, 99.9 % of cement voxels within a distance of 1.3 mm to connected void), produced the highest carbonation levels, with the highest amount of classifiable HMC (nesquehonite). Sample C had slightly less favorable structural characteristics and produced slightly lower nesquehonite and slightly higher amorphous content. The relatively high level of brucite in sample A may be linked to the low connected void in that sample (i.e. there was limited direct access to CO₂ in that sample). These observations support the results of previous studies demonstrating that carbonation becomes limited further from the CO₂-exposed surface [21].

Rescaled intensity values of cement phase are stable or slightly increasing after day 10 for all samples (Figs. 4,6,7), although DRIFTS results show some variability over time (Fig. 4). These trends indicate that the cement phase carbonated content and density is stable, suggesting that after the initial reactive phase from day 0–10, the samples do not lose CO₂ or water over the 108 day time-frame of the experiments. We note that these insights into phase stability are only relevant to the conditions of the experiments, i.e. ambient temperature and pressure, with stable relative humidity and high gaseous CO₂ concentrations.

These samples exhibit relatively high levels of nesquehonite (and HMCs) and relatively low levels of reactant MgO and brucite compared to studies in the literature; for example, only considering the non-quartz component of the XRD analysis (i.e. values in Table 3 re-calculated with quartz neglected), sample B contains 16 wt% unreacted MgO, 17 wt%

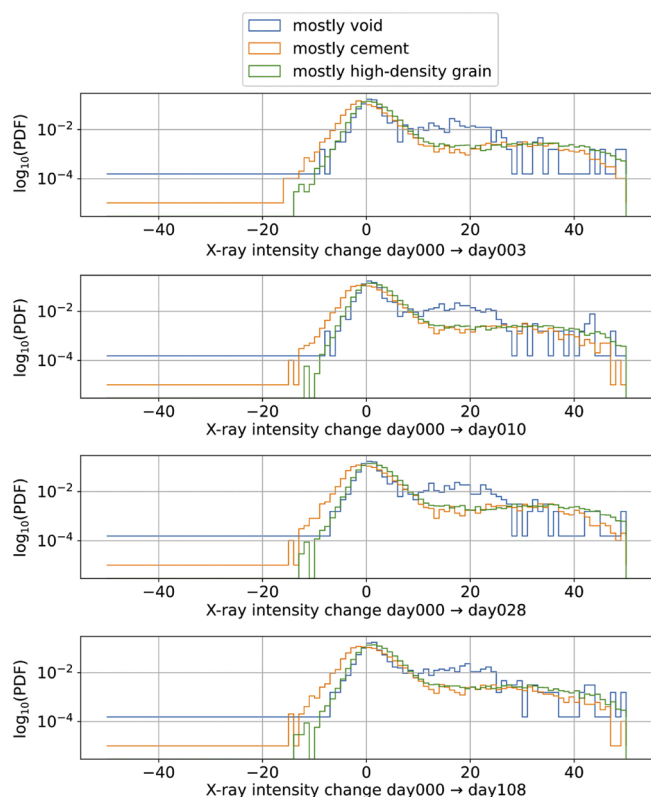


Fig. 9. Histograms of greylevel change classified by most present phase in analysis subvolume, presented separately for each day.

brucite, and 16 wt% nesquehonite. These values are favorable compared to those of Dung and Unluer [11] who performed similar experiments but with the addition of hydration agents, and in the best case observed 18 wt% of unreacted MgO and 29 % brucite in cement paste. Based on the analysis presented in this study, we hypothesize that the relatively high level of carbonation observed in these microcores is largely due to their high connected void properties. We note, however, that high connected porosity is undesirable for many applications where water infiltration might lead to material degradation, e.g. construction applications.

4.2. Methodological improvements

A primary assumption in this analysis is that the CT values can be rescaled by assuming two unreactive, constant features exist within the samples: void space (filled with air during scanning) and the high-density silica sand and unreacted MgO grains. The CT value for the void/air phase is trivial to identify in X-ray tomographic histograms (Fig. 1); however, the histogram peak for silica sand may become distorted if a significant volume of phases formed in the cement achieve a density approaching that of the high-density components. While we have demonstrated that the high-density components (mostly silica sand and unreacted MgO grains) in this study are indeed identifiable and separate from the cement throughout all stages of this experiment, an alternative option would be to embed a secondary (and possibly, and intermediate tertiary) standard within the samples for attenuation normalization. Standards would need to be selected to provide density comparisons relevant to the expected mineral products, but not so high as to create image artifacts in the CT data. Incorporation of additional standards would allow for more robust comparison across samples and could potentially be used as a reference for the DRIFTS measurements also. We also suggest that future studies could include replicates of samples to allow destructive XRD analysis at all time points, rather just

at the final stage, to help constrain the image processing and interpretation.

5. Conclusions

We have demonstrated a novel methodology that combines X-ray CT, DRIFTS, and XRD analyses; with this approach we analyzed magnesium-based mineral carbonation experiments conducted in idealized porous columns over 108 days. The mineralogical (XRD) and spectral (DRIFTS) analyses constrain the phases present in samples and allowed for separation of stable (void, high-density grains) and reactive (carbonate cement) phases in X-ray CT scans, enabling 3D quantitative image analysis of reaction progress. We applied a new method of re-scaling X-ray CT attenuation values to provide a proxy for the evolving density and carbonation level of the cement phase. This combination of analyses facilitated quantification of the temporal evolution and interplay of 3D structure and mineralogy over length scales ranging from the scale of individual voxels (Fig. 8) up to the entire core (Fig. 4). We provide some suggestions for potential methodological improvements for future mineral carbonation studies in Section 4.2.

Low connected void slows carbonation reactions in regions within samples, while access to connected void promoted classifiable HMC formation at the core-scale (Tables 3 and 4), as well as higher density and carbonation at the microscale (Figs. 6,7,9). In these microcore experiments, carbonation occurred rapidly during the first three days, and no significant further reaction occurred after 10 days (e.g. Fig. 4). The largest increases in cement density/carbonation level occur in regions with short straight-line distances (i.e. < 0.2 mm) to the connected void (Fig. 7).

We observe higher levels of mineral HMC (nesquehonite) and lower levels of reactant (MgO) and non-carbonated mineral products (brucite), compared to studies of core-scale mineral carbonation in the literature. We attribute this high level of carbonation to the very high connected void content of our samples, while also acknowledging that high connected void is not necessarily an attractive feature for some potential industrial applications (e.g. building materials). To investigate reaction rates and the role of the 2D and 3D networks, future work could examine shorter timeframes (less than 3 days). This study demonstrates a need to develop sample mixing/curing protocols that facilitate both mineral carbonation and application-specific material characteristics.

CRedit authorship contribution statement

Anna Herring: Conceptualization, Methodology, Formal analysis, Project administration, Writing - original draft. **Penelope L. King:** Methodology, Formal analysis, Writing - review & editing. **Mohammad Saadatfar:** Formal analysis, Writing - review & editing. **Fatin Mahdini:** Investigation. **Afiq Muzhafar Kemis Yahyah:** Investigation. **Edward Andò:** Formal analysis.

Declaration of Competing Interest

The authors report no declarations of interest.

Acknowledgements

U Troitzsch undertook the XRD analysis. A.H. acknowledges financial support via Australian Research Council (ARC)DE180100082 and the ANU/UNSW Digicore Research Consortium; and A.H. and M.S. both acknowledge financial support from ARC IC180100008. The PANalytical Empyrean X-ray diffractometer and Agilent DRIFTS spectrometer were obtained by PL King through ANU funds (Major Equipment funds and start-up). The DRIFTS work was partially supported by ARC grant DP200100406 to PL King.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jcou.2021.101494>.

References

- [1] K.S. Lackner, C.H. Wendt, D.P. Butt, E.L. Joyce, D.H. Sharp, Carbon dioxide disposal in carbonate minerals, *Energy* 20 (1995) 1153–1170, [https://doi.org/10.1016/0360-5442\(95\)00071-N](https://doi.org/10.1016/0360-5442(95)00071-N).
- [2] A.A. Olajire, A review of mineral carbonation technology in sequestration of CO₂, *J. Pet. Sci. Eng.* 109 (2013) 364–392, <https://doi.org/10.1016/j.petrol.2013.03.013>.
- [3] A. Sanna, M. Uibu, G. Caramanna, R. Kuusk, M.M. Maroto-Valer, A review of mineral carbonation technologies to sequester CO₂, *Chem. Soc. Rev.* 43 (2014) 8049–8080, <https://doi.org/10.1039/c4cs00035h>.
- [4] S.A. Wilson, A.L. Harrison, G.M. Dipple, I.M. Power, S.L.L. Barker, K.U. Mayer, S. J. Fallon, M. Raudsepp, G. Southam, Offsetting of CO₂ emissions by air capture in mine tailings at the Mount Keith Nickel Mine, Western Australia: rates, controls and prospects for carbon neutral mining, *Int. J. Greenh. Gas Control.* 25 (2014) 121–140, <https://doi.org/10.1016/j.ijggc.2014.04.002>.
- [5] M. Hitch, G.M. Dipple, Economic feasibility and sensitivity analysis of integrating industrial-scale mineral carbonation into mining operations, *Miner. Eng.* 39 (2012) 268–275, <https://doi.org/10.1016/j.mineng.2012.07.007>.
- [6] M. Hitch, S.M. Ballantyne, S.R. Hindle, Revaluing mine waste rock for carbon capture and storage, *Int. J. Mining, Reclam. Environ.* 24 (2010) 64–79, <https://doi.org/10.1080/17480930902843102>.
- [7] G. Montes-Hernandez, R. Pérez-López, F. Renard, J.M. Nieto, L. Charlet, Mineral sequestration of CO₂ by aqueous carbonation of coal combustion fly-ash, *J. Hazard. Mater.* 161 (2009) 1347–1354, <https://doi.org/10.1016/j.jhazmat.2008.04.104>.
- [8] W. Ashraf, Carbonation of cement-based materials: challenges and opportunities, *Constr. Build. Mater.* 120 (2016) 558–570, <https://doi.org/10.1016/j.conbuildmat.2016.05.080>.
- [9] L. Mo, D.K. Panesar, Effects of accelerated carbonation on the microstructure of Portland cement pastes containing reactive MgO, *Cem. Concr. Res.* 42 (2012) 769–777, <https://doi.org/10.1016/j.cemconres.2012.02.017>.
- [10] S. Ruan, C. Unluer, Influence of mix design on the carbonation, mechanical properties and microstructure of reactive MgO cement-based concrete, *Cem. Concr. Compos.* 80 (2017) 104–114, <https://doi.org/10.1016/j.cemconcomp.2017.03.004>.
- [11] N.T. Dung, C. Unluer, Sequestration of CO₂ in reactive MgO cement-based mixes with enhanced hydration mechanisms, *Constr. Build. Mater.* 143 (2017) 71–82, <https://doi.org/10.1016/j.conbuildmat.2017.03.038>.
- [12] J. Morrison, G. Jauffret, J.L. Galvez-Martos, F.P. Glasser, Magnesium-based cements for CO₂ capture and utilisation, *Cem. Concr. Res.* 85 (2016) 183–191, <https://doi.org/10.1016/j.cemconres.2015.12.016>.
- [13] G. Dávila, J. Cama, S. Galí, L. Luquot, J.M. Soler, Efficiency of magnesium hydroxide as engineering seal in the geological sequestration of CO₂, *Int. J. Greenh. Gas Control.* 48 (2016) 171–185, <https://doi.org/10.1016/j.ijggc.2016.01.031>.
- [14] D. Langmuir, Stability of Carbonates in the System MgO-CO₂-H₂O, *J. Geol.* 73 (1965) 730–754, <https://doi.org/10.1086/627113>.
- [15] S.A. Walling, J.L. Provis, Magnesia-Based Cements: A Journey of 150 Years, and Cements for the Future? *Chem. Rev.* 116 (2016) 4170–4204, <https://doi.org/10.1021/acs.chemrev.5b00463>.
- [16] L. Wang, L. Chen, J.L. Provis, D.C.W. Tsang, C.S. Poon, Accelerated carbonation of reactive MgO and Portland cement blends under flowing CO₂ gas, *Cem. Concr. Compos.* 106 (2020) 103489, <https://doi.org/10.1016/j.cemconcomp.2019.103489>.
- [17] C. Kuenzel, F. Zhang, V. Ferrándiz-Mas, C.R. Cheeseman, E.M. Gartner, The mechanism of hydration of MgO-hydromagnesite blends, *Cem. Concr. Res.* 103 (2018) 123–129, <https://doi.org/10.1016/j.cemconres.2017.10.003>.
- [18] C. Unluer, A. Al-Tabbaa, Enhancing the carbonation of MgO cement porous blocks through improved curing conditions, *Cem. Concr. Res.* 59 (2014) 55–65, <https://doi.org/10.1016/j.cemconres.2014.02.005>.
- [19] C. Unluer, A. Al-Tabbaa, Impact of hydrated magnesium carbonate additives on the carbonation of reactive MgO cements, *Cem. Concr. Res.* 54 (2013) 87–97, <https://doi.org/10.1016/j.cemconres.2013.08.009>.
- [20] P. Kristova, L.J. Hopkinson, K.J. Rutt, H.M.A. Hunter, G. Cressey, Carbonate mineral paragenesis and reaction kinetics in the system MgO-CaO-CO₂-H₂O in presence of chloride or nitrate ions at near surface ambient temperatures, *Appl. Geochem.* 50 (2014) 16–24, <https://doi.org/10.1016/j.apgeochem.2014.08.005>.
- [21] L. Pu, C. Unluer, Investigation of carbonation depth and its influence on the performance and microstructure of MgO cement and PC mixes, *Constr. Build. Mater.* 120 (2016) 349–363, <https://doi.org/10.1016/j.conbuildmat.2016.05.067>.
- [22] A.L. Harrison, G.M. Dipple, I.M. Power, K.U. Mayer, The Impact of Evolving Mineral-Water-Gas Interfacial Areas on Mineral-Fluid Reaction Rates in Unsaturated Porous Media, 2015, <https://doi.org/10.1016/j.chemgeo.2015.12.005>.
- [23] K. Coenen, F. Gallucci, B. Mezari, E. Hensen, M. van Sint Annaland, An in-situ IR study on the adsorption of CO₂ and H₂O on hydrotalcites, *J. CO₂ Util.* 24 (2018) 228–239, <https://doi.org/10.1016/j.jcou.2018.01.008>.
- [24] A.M. Chaka, A.R. Felmy, Ab initio thermodynamic model for magnesium carbonates and Hydrates, *J. Phys. Chem. A* 118 (2014) 7469–7488, <https://doi.org/10.1021/jp500271n>.
- [25] E. Königsberger, L.C. Königsberger, H. Gamsjäger, Low-temperature thermodynamic model for the system Na₂CO₃-MgCO₃-CaCO₃-H₂O, *Geochim. Cosmochim. Acta* 63 (1999) 3105–3119, [https://doi.org/10.1016/S0016-7037\(99\)00238-0](https://doi.org/10.1016/S0016-7037(99)00238-0).
- [26] A.L. Harrison, V. Mavromatis, E.H. Oelkers, P. Bénéth, Solubility of the hydrated Mg-carbonates nesquehonite and dypingite from 5 to 35 °C: implications for CO₂ storage and the relative stability of Mg-carbonates, *Chem. Geol.* 504 (2019) 123–135, <https://doi.org/10.1016/j.chemgeo.2018.11.003>.
- [27] P. Ballirano, C. De Vito, S. Mignardi, V. Ferrini, Phase transitions in the MgCO₂H₂O system and the thermal decomposition of dypingite, Mg₅(CO₃)₄(OH) 25H₂O: implications for geosequestration of carbon dioxide, *Chem. Geol.* 340 (2013) 59–67, <https://doi.org/10.1016/j.chemgeo.2012.12.005>.
- [28] S.A. Walling, J.L. Provis, A discussion of the papers “Impact of hydrated magnesium carbonate additives on the carbonation of reactive MgO cements” and “Enhancing the carbonation of MgO cement porous blocks through improved curing conditions”, by C. Unluer & A. Al-Tabbaa, *Cem. Concr. Res.* 79 (2016) 424–426, <https://doi.org/10.1016/j.cemconres.2015.09.010>.
- [29] C. Unluer, A. Al-Tabbaa, Reply to the discussion of the papers “Impact of hydrated magnesium carbonate additives on the carbonation of reactive MgO cements” and “Enhancing the carbonation of MgO cement porous blocks through improved curing conditions”, by S.A. Walling and J.L. Pr, *Cem. Concr. Res.* 79 (2016) 427–430, <https://doi.org/10.1016/j.cemconres.2015.09.009>.
- [30] A. Entezari Zandani, F. Larachi, G. Beaudoin, B. Plante, M. Sciortino, Nesquehonite as a carbon sink in ambient mineral carbonation of ultramafic mining wastes, *Chem. Eng. J.* 314 (2017) 160–168, <https://doi.org/10.1016/j.cej.2017.01.003>.
- [31] A.M. Kingston, G.R. Myers, S.J. Latham, B. Recur, H. Li, A.P. Sheppard, Space-filling X-Ray source trajectories for efficient scanning in large-angle cone-beam computed tomography, *IEEE Trans. Comput. Imaging* 4 (2018) 447–458, <https://doi.org/10.1109/tci.2018.2841202>.
- [32] D. Wildenschild, A.P. Sheppard, X-ray imaging and analysis techniques for quantifying pore-scale structure and processes in subsurface porous medium systems, *Adv. Water Resour.* 51 (2013) 217–246, <https://doi.org/10.1016/j.advwatres.2012.07.018>.
- [33] M. Saadatfar, F. Brink, S. Latham, P. King, J. Middleton, U. Troitzsch, M. Turner, R. W. Henley, High resolution 3D mapping of grain kinematics during high temperature sequestration of so₂ from flue gas by carbonate aggregates, *Sci. Rep.* (2020), <https://doi.org/10.1038/s41598-020-58216-y>.
- [34] K.N. Dalby, J.A. Berger, H.E.A. Brand, J.M. Cairney, K. Eder, S.M. Eggs, A. Herring, R.L. Hervig, P.B. Krieder, T.P. Mernagh, A.B. Palm, C.J. Renggli, U. Troitzsch, L. Yue, P.L. King, Analytical techniques for probing small-scale layers that preserve information on Gas–Solid interactions. *Rev. Mineral. Geochemistry, Mineralogical Society of America*, 2018.
- [35] S.J. Latham, A.M. Kingston, B. Recur, G.R. Myers, O. Delgado-Friedrichs, A. P. Sheppard, Reprojection alignment for trajectory perturbation estimation in Microtomography, *IEEE Trans. Comput. Imaging* 4 (2018) 271–283, <https://doi.org/10.1109/tci.2018.2811945>.
- [36] J. Dengler, A multi-resolution approach to the 3D reconstruction from an electron microscope tilt series solving the alignment problem without gold particles, *Ultramicroscopy* 30 (1989) 337–348, [https://doi.org/10.1016/0304-3991\(89\)90063-6](https://doi.org/10.1016/0304-3991(89)90063-6).
- [37] R.M. Sok, M.A. Knackstedt, T. Varslot, A. Ghous, S. Latham, A.P. Sheppard, Pore scale characterization of carbonates at multiple scales: integration of micro-CT, BSEM, and FIBSEM - OnePetro. Soc. Petrophysicists Well-Log Anal, 2010 (accessed May 10, 2020), <https://www.onepetro.org/journal-paper/SPWLA-2010-v51n6a1>.
- [38] E.E. Coleyshaw, G. Crump, W.P. Griffith, Vibrational spectra of the hydrated carbonate minerals ikaite, monohydrocalcite, lansfordite and nesquehonite, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 59 (2003) 2231–2239, [https://doi.org/10.1016/S1386-1425\(03\)00067-2](https://doi.org/10.1016/S1386-1425(03)00067-2).
- [39] R.L. Frost, S.J. Palmer, Infrared and infrared emission spectroscopy of nesquehonite Mg(OH)(HCO₃)·2H₂O-implications for the formula of nesquehonite, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* 78 (2011) 1255–1260, <https://doi.org/10.1016/j.saa.2010.12.059>.
- [40] R.L. Frost, J.T. Klopogge, Infrared emission spectroscopic study of brucite, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* 55 (1999) 2195–2205, [https://doi.org/10.1016/S1386-1425\(99\)00016-5](https://doi.org/10.1016/S1386-1425(99)00016-5).
- [41] Bruker, DIFFRACplus BASIC Evaluation Package EVA 10.0, User's Manual, Karlsruhe, Germany, 2004.
- [42] H.M. Rietveld, A profile refinement method for nuclear and magnetic structures, *J. Appl. Crystallogr.* 2 (1969) 65–71, <https://doi.org/10.1107/s0021889869006558>.
- [43] I.C. Madsen, N.V.Y. Scarlett, A. Kern, Description and survey of methodologies for the determination of amorphous content via X-ray powder diffraction, *Zeitschrift Fur Krist.* 226 (2011) 944–955, <https://doi.org/10.1524/zkri.2011.1437>.
- [44] W.B. White, *The carbohydrate minerals*, Ch. 12. *Infrared Spectra Miner.*, Mineralogical Society, London, 1974.

- [45] L. Hopkinson, K. Rutt, G. Cressey, The transformation of nesquehonite to hydromagnesite in the system $\text{CaO-MgO-H}_2\text{O-CO}_2$: an experimental spectroscopic study, *J. Geol.* 116 (2008) 387–400, <https://doi.org/10.1086/588834>.
- [46] O. Stamati, E. Andò, E. Roubin, R. Cailletaud, M. Wiebicke, G. Pinzon, C. Couture, R. Hurley, R. Caulk, D. Caillerie, T. Matsushima, P. Bésuelle, F. Bertoni, T. Arnaud, A. Laborin, R. Rorato, Y. Sun, A. Tengattini, O. Okubadejo, J.-B. Colliat, M. Saadatfar, F. Garcia, C. Papazoglou, I. Vego, S. Brisard, J. Dijkstra, G. Birmpilis, Spam: software for practical analysis of materials, *J. Open Source Softw.* 5 (2020) 2286, <https://doi.org/10.21105/joss.02286>.
- [47] E. Stavropoulou, E. Andò, E. Roubin, N. Lenoir, A. Tengattini, M. Briffaut, P. Bésuelle, Dynamics of water absorption in callovo-oxfordian claystone revealed with multimodal X-Ray and neutron tomography, *Front. Earth Sci.* 8 (2020) 6, <https://doi.org/10.3389/feart.2020.00006>.