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Carbonation of Hydrus Materials at the Molecular Level: a ToF-SIMS, Raman and DFT study

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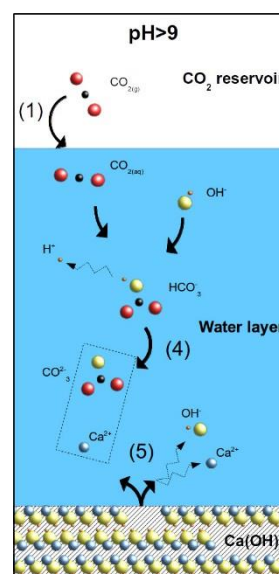
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Carbonation of hydrous minerals such as calcium hydroxide ($\text{Ca}(\text{OH})_2$), is an important process in environmental and industrial applications for the construction industry, geological disposal repositories for nuclear waste, and green technologies for carbon capture. Although the role of ions during the carbonation mechanism of $\text{Ca}(\text{OH})_2$ is still unclear, we identified the exchange of ions during the dissolution-and-precipitation process, by determining the change in isotopic composition of carbonation products using Time-of-Flight Secondary Ion Mass Spectrometry. Our samples of pure $\text{Ca}({}^{18}\text{OH})_2$ carbonated in air were characterized using Scanning Electron Microscopy and Raman spectroscopy, aided by Density Functional Theory calculations. Our results show that the carbonation process at high pH is a two-stage mechanism. The first stage occurs in a short time after $\text{Ca}({}^{18}\text{OH})_2$ is exposed to air and involved the dissolution of surface Ca ions and hydroxyl ${}^{18}\text{OH}$ groups, which reacts directly with dissolved CO_2 , leading to 1/3 of ${}^{18}\text{O}$ in the oxygen content of carbonate phases. The second stage occurs within 24h of exposure allowing a rebalance of the oxygen isotopic composition of the carbonate phases with higher content of ${}^{16}\text{O}$.



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Abstract

Carbonation of hydrous minerals such as calcium hydroxide ($\text{Ca}(\text{OH})_2$), is an important process in environmental and industrial applications for the construction industry, geological disposal repositories for nuclear waste and green technologies for carbon capture. Although the role of ions during the carbonation mechanism of $\text{Ca}(\text{OH})_2$ is still unclear, we identified the exchange of ions during the dissolution-and-precipitation process, by determining the change in isotopic composition of carbonation products using Time-of-Flight Secondary Ion Mass Spectrometry. Our samples of pure $\text{Ca}({}^{18}\text{OH})_2$ carbonated in air were characterized using Scanning Electron Microscopy and Raman spectroscopy, aided by Density Functional Theory calculations.

Our results show that the carbonation process at high pH is a two-stage mechanism. The first stage occurs in a short time after $\text{Ca}({}^{18}\text{OH})_2$ is exposed to air and involved the dissolution of surface Ca ions and hydroxyl ${}^{18}\text{OH}$ groups, which reacts directly with dissolved CO_2 , leading to 1/3 of ${}^{18}\text{O}$ in the oxygen content of carbonate phases. The second stage occurs within 24h of exposure allowing a rebalance of the oxygen isotopic composition of the carbonate phases with higher content of ${}^{16}\text{O}$.

Introduction

The carbonation process of hydrous materials and minerals such as calcium and magnesium hydroxides ($\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$, respectively) is important for a number of environmental and technological applications. These include carbon capture and storage (CCS)^{1,2}, scrubbing procedures of solid waste incinerators³, emerging low carbon building technologies for construction⁴⁻⁶, and geological disposal repositories for nuclear waste^{7,8} where portlandite content in cements becomes a critical factor. Despite its importance,^{2,4,9-14} the carbonation mechanism in high pH environments is debated and not yet fully understood. Hence, to devise successful and efficient strategies for carbon dioxide (CO_2) sequestration, soil stabilization in

geoengineering and building mortars with enhanced properties, a clear understanding of the details of carbonation mechanisms is required.

Two carbonation mechanisms have been proposed for portlandite at standard conditions, 25°C and 1atm, based on solid state and a dissolution-carbonation¹⁵⁻¹⁹ processes (the former is highly unlikely whereas the latter has been documented in a number of cases). Moorehead²⁰ suggested that carbonation of Ca(OH)₂ at room temperature in CO₂-rich environments is a solid-state reaction, which entails substitution of hydroxyl groups (OH⁻) with carbonate groups (CO₃²⁻) in a topotactic transition, leading to a change of the portlandite $d_{\{001\}}$ spacing.^{11,20-22} Other authors suggested that the reaction occurs via a dissolution-and-precipitation mechanism catalyzed by water molecules adsorbed on the mineral surfaces^{11,23-27} Overall, these two mechanisms would be expected to lead to different reaction rates, and result in the formation of passivating carbonate layers²⁸ effectively quenching the exploitation of Ca(OH)₂ surface properties.¹¹

Recent work by Rodriguez-Navarro and colleagues has involved detailed analysis of calcium carbonate formation from saturated solution and through the carbonation of calcium hydroxide nano-particles.²⁵⁻²⁷ These show that the formation of thermodynamically stable calcite can proceed through a cascade of hydrated and dehydrated amorphous calcium carbonate phases and include (or not) intermediate crystalline phases of vaterite and/or aragonite. In addition to the requirement for CO₂ for carbonation the presence of water, adsorbed from a high RH atmosphere was demonstrated. In the first instance the aim of the present work is to show that artificial doping of isotopes can be used to trace the history of the species involved in the formation of carbonate ions, and thus shed light on the mechanisms of portlandite carbonation. The natural variation of stable isotopes, such as carbon-13 (¹³C) or oxygen-18 (¹⁸O), can be exploited in the study of carbonation of surfaces, and thus provide complementary results to other techniques.²⁹⁻³² An isotope can be traced during chemical reactions and, as different

reaction mechanisms lead to different products with distinctive isotopic compositions²⁹⁻³⁴, it provides insights on the stages occurring during the reaction. Our research investigated the role of OH⁻ ions in the carbonation mechanism of Ca(OH)₂ by using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) on an artificial Ca(¹⁸O)OH₂ sample carbonated in air (rich in ¹⁶O) for 3 minutes (at 27% RH), 1, 8 and 137 days (50% RH). Samples were characterized using Scanning Electron Microscopy (SEM) and Raman spectroscopy. Density functional theory calculations were also employed to corroborate the Raman shifts associated with different degrees of isotopic substitution in Ca(OH)₂ and CaCO₃. We finally discuss critical factors in the carbonation process, which provides new insights of the carbonation mechanism of Ca(OH)₂.

Experimental and Theoretical Methods

Material preparation

¹⁸O-calcium hydroxide was produced by reacting calcium metal of 99% purity with isotopic labelled water containing >99% ¹⁸O (Taiyo Nippon Sanso Corporation), on a platinum (Pt) foil 99.9% pure. To prevent oxygen contamination and carbonation of the Ca(OH)₂ sample, the reaction was performed in an inert atmosphere inside a glove bag filled with nitrogen, where CO₂ and RH were monitored using a K-30 10,000ppm sensor for CO₂, and a DHT22 sensor for temperature and humidity. Both sensors were controlled via an Arduino Uno microcontroller, which was also used for real time monitoring of the conditions.

Experiments were conducted as follows. 1) The equipment and materials were placed into a glove bag that was then filled with nitrogen. 2) The residual air in the bag was flushed using dry nitrogen until the sensor readings were 0 ppm CO₂ and <5% RH. 3) 20mg of Ca metal was weighed on a precision balance and deposited on a Pt foil, positioned inside an open crucible. 4) 800μl of ¹⁸O-water was reacted with the Ca metal using a glass Hamilton syringe equipped with a metal needle. The reaction was carried out in an excess of ¹⁸O-water to promote the

complete reaction of Ca. 5). To ensure the complete evaporation of excess of ^{18}O -water, the bag was flushed several times with dry nitrogen. 6) When the majority of the water had evaporated, portions of the sample were removed from the Pt foil. Portions were sealed inside a glass cell with a quartz window for the Raman analysis; the N_2 -rich atmosphere prevented carbonation before completion of the analysis. The same procedure was followed for samples for SEM analysis except samples were placed in a small vial and stored under low vacuum. Material for SIMS analysis remained on the Pt foil and stored in a glass vial under low vacuum.

ToF-SIMS analysis

In order to study the isotopic composition of carbonates at the very beginning of the reaction, the first ToF-SIMS analysis was carried out after approximately 3 minutes exposure to air at $23 \pm 2^\circ\text{C}$ and $27 \pm 10\%$ RH. Low RH levels were maintained to minimize the carbonation rate.²⁶ After initial analysis, the samples were removed from the instrument and allowed to stand in a dust-free controlled environment at $23 \pm 2^\circ\text{C}$ and $50 \pm 10\%$ RH for 1, 8 and 138 days before further analysis. Care was taken to analyze fresh areas of the samples that had not previously been exposed to the ion and electron beams. An Analar CaCO_3 powder was analyzed under similar conditions as a reference.

Static ToF-SIMS analyses were carried out using an ION-TOF ‘TOF-SIMS IV – 200’ instrument (ION-TOF GmbH, Münster, Germany) of single-stage reflectron design.³⁵ Positive and negative ion spectra of the samples were obtained using a Bi_3^{++} focused liquid metal ion gun at 20keV energy, incident at 45° to the surface normal and operated in ‘bunched’ mode for high mass resolution. This mode used 7ns duration ion pulses at 10kHz repetition rate. Charge compensation was effected by low-energy (ca. 20eV) electrons provided by a flood gun. The total ion dose density was less than 5×10^{16} ions m^{-2} in all cases. The topography of the sample surface and the ion gun mode of operation limited the mass resolution in this work to *ca. $m/\Delta m = 4000$* .

Positive and negative ion static SIMS spectra of the samples were recorded in triplicate at room temperature with a 128×128 pixel raster and a field of view of $50\mu\text{m} \times 50\mu\text{m}$. Sample preparation and data analysis was carried out according to the procedure detailed in the SI.

Raman analysis

Raman analysis was performed using a Renishaw inVia Raman Microscope equipped with a laser operating at a wavelength of 785 nm. The analysis was undertaken by focusing the laser with a 50x long distance objective. Laser power at the sample surface was set to 66mW at the sample surface and the acquisition time was set between 3 and 10s for each of the 10 accumulations acquired. Each spectrum was taken over the wavenumber range $77\text{--}1290\text{cm}^{-1}$. Three spectra per sample were acquired to evaluate variations between different locations. Prior to the analysis, the spectrometer was calibrated using a monocrystalline silicon standard specimen. Renishaw WiRe 4.0 software was applied for peak fitting and deconvolution of Raman spectra. The sample was initially kept in a N_2 -rich atmosphere inside the glass cell with quartz window to prevent contamination by atmospheric CO_2 . To investigate the initial stage of carbonation, the quartz window was removed and spectral acquisition of the carbonate phases formed at 23°C and $30\% \pm 10\% \text{RH}$ was started. These conditions reduced the carbonation rate and, therefore provided better evidence of the phase transformations related to carbonation. Spectra were taken at intervals up to 55 minutes from initial exposure of the sample to air.

SEM analysis

SEM images were obtained using a JEOL field emission scanning electron microscope (FESEM) model JSM6301F. Working distance for scanning and acquiring the images was 7mm, accelerating voltage was of 5kV and the spot size 7nm. Prior to analysis the sample powder was fixed to a metal holder using a double-sided carbon tape and then dried for 24 hours in a vacuum chamber before application of a 10nm thick layer of chromium using a

Quantum Q 150T Turbo-Pumped Sputter Coater to prevent surface charging. Once removed from the sputter coater, the sample was immediately inserted into the SEM and analyzed.

Computational procedure

Simulations were used to determine the vibrational shifts and Raman spectra for ^{16}O and ^{18}O -calcium hydroxide ($\text{Ca}(^{16}\text{OH})_2$, $\text{Ca}(^{18}\text{OH})_2$ respectively), as well as calcite containing different amounts of ^{18}O ($\text{CaC}^{18}\text{O}_x^{16}\text{O}_{(3-x)}$ with $x=0,1,2,3$). Calculations were performed at the DFT level using the VASP³⁶⁻³⁹ code with the PBE^{40,41} exchange-correlation functionals including the van der Waals correction optB86b-vdW^{42,43}, which improves the description of layered materials. The Brillouin zone was sampled using $4 \times 4 \times 4$ Monkhorst-Pack k-point mesh for portlandite and $4 \times 4 \times 1$ for calcite with a plane wave cut-off of 500 eV. Convergence criteria were 10^{-8} eV for the electronic relaxation and 10^{-4} eV \AA^{-1} for ionic forces, allowing both the atoms and lattice to relax.

The calculated structure of portlandite contains 1 $\text{Ca}(\text{OH})_2$ unit and had lattice parameters of $a = b = 3.573\text{\AA}$, $c = 4.794\text{\AA}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$, which compared well with the experimental values of Desgranges *et al.*⁴⁴. The calculated structure of calcite contained 6 CaCO_3 units and had lattice parameters of $a = b = 5.03\text{\AA}$, $c = 16.80\text{\AA}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$, and agreed with the experimental values of Effenberger *et al.*⁴⁵

From the minimized structures, the vibrational frequencies were obtained using finite displacements⁴⁶ and the Raman activity^{47,48} was then estimated by calculating the polarizability of the vibrational modes. As noted, the minimized structure for portlandite compares well with the experimental values (Table S1) and this model has recently been shown to perform well for the calcium oxide and carbonate.⁴⁹ Additional calculations were undertaken to predict the shift in Raman frequencies due to isotopic substitution and compared to the DFT predicted Raman active peaks. Each vibrational mode is composed of specific motions of the atomic species associated with it. The interaction between the species involved can be related to a bond and

this can be illustrated by considering a diatomic molecule. From the initial calculation we obtain a force constant k from which the frequency, f , can be calculated according to Equation 1, where μ is the reduced mass of the components of the mode given by Equation 2, and, m_1 and m_2 are the masses vibrating.

$$f = \sqrt{\frac{k}{\mu}} \quad (1)$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (2)$$

When accounting for the difference in mass between ^{16}O and ^{18}O the reduced mass changes according to the O isotope. In practice, we evaluate and diagonalise the complete mass-weighted force constant matrix.⁵⁰⁻⁵²

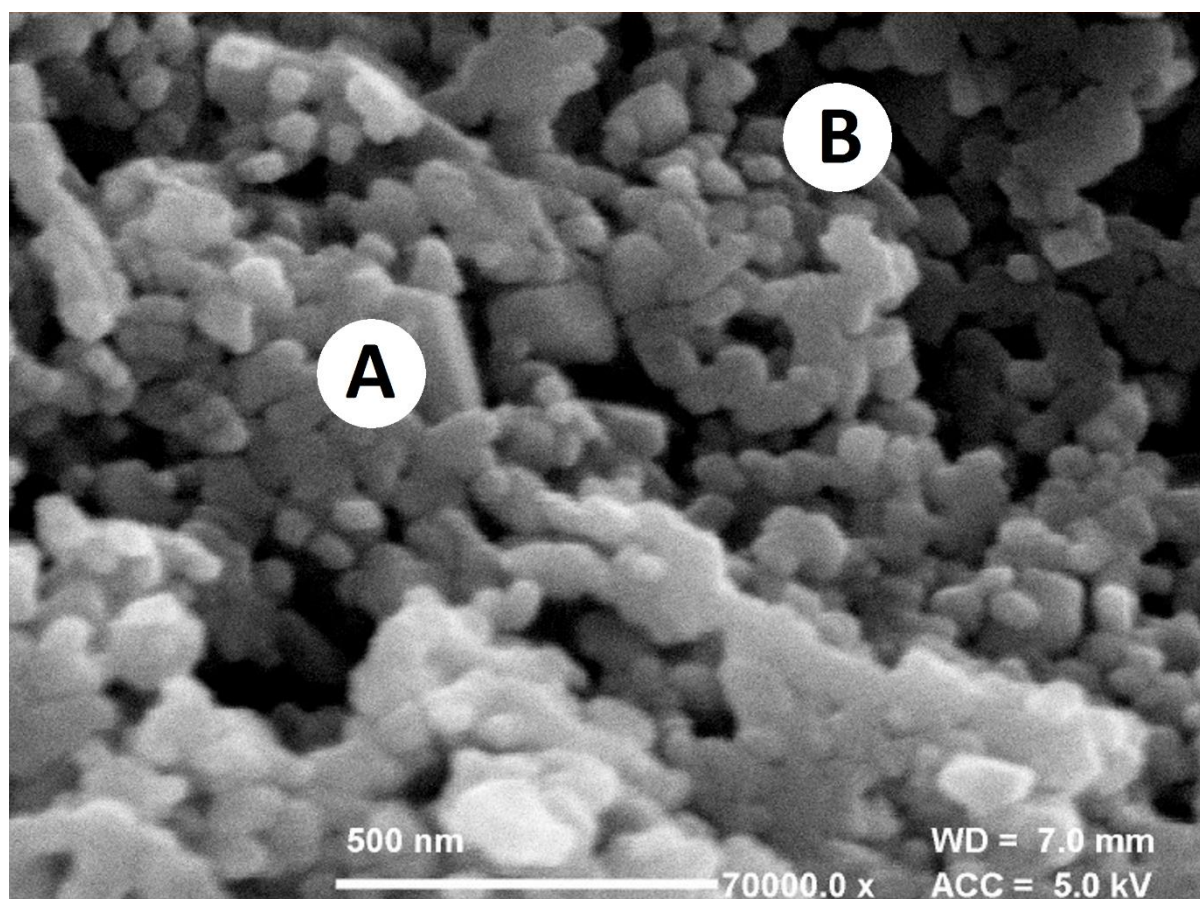


Figure 1 - FESEM image of the $\text{Ca}(^{18}\text{OH})_2$ produced by reacting calcium with H_2^{18}O . Some hexagonal plate-shaped nano-particles typical of $\text{Ca}(\text{OH})_2$ are visible (A) but the material is mostly in smaller irregular shaped crystalline particles (B).

Results

SEM and Raman results

A microscopic FESEM image is shown in Figure 1 of a $\text{Ca}(^{18}\text{OH})_2$ sample comprising hexagonal plate-shaped crystals of 200-400nm and crystalline particles of 70-150 nm. The presence of many irregular shaped crystals is consistent with the exothermic reaction of calcium with water. The rapid evaporation of the excess H_2^{18}O is likely to have resulted in a high nucleation rate. This then subsequently led to numerous seed crystals competing for ions from which to grow and provided a limited opportunity for Ostwald ripening of typical hexagonal nanoparticles. The reaction and storage conditions ensured that no carbonation could take place and only $\text{Ca}(\text{OH})_2$ could form.

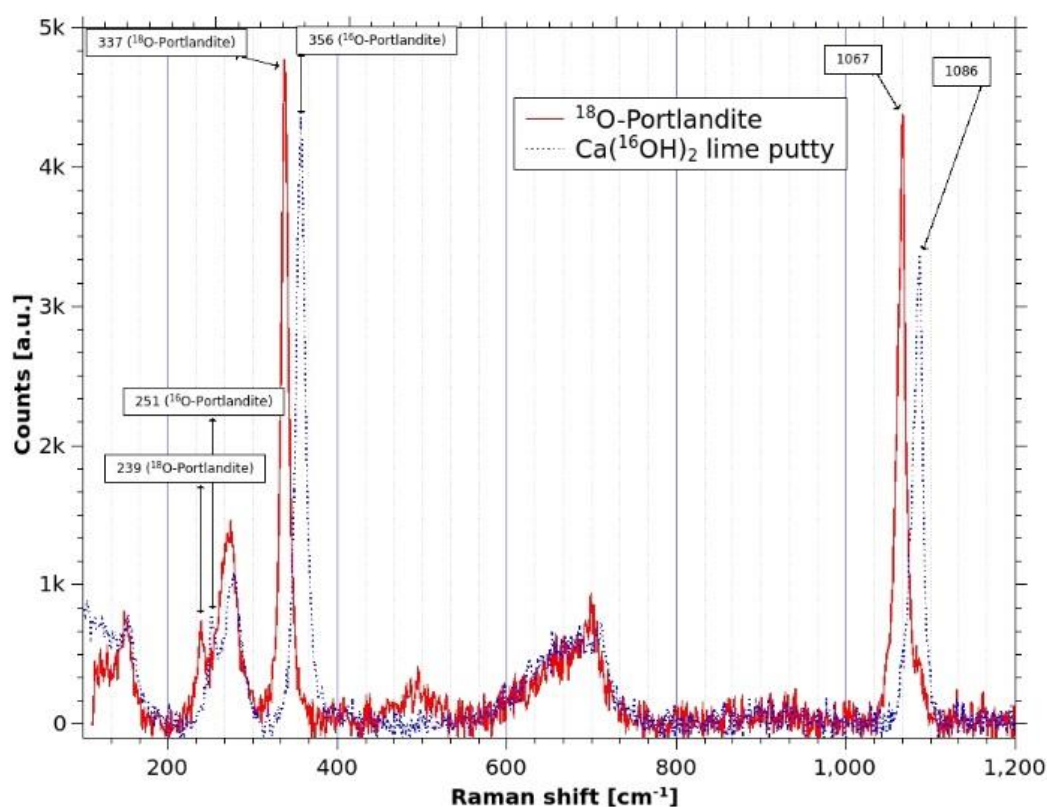


Figure 2 - Raman spectrum of the $\text{Ca}(^{18}\text{OH})_2$ produced during the experiments, compared with the Raman spectrum of a generic ^{16}O - $\text{Ca}(\text{OH})_2$ (lime putty).

Figure 2 shows the Raman spectrum from 100 to 1200 cm^{-1} of $\text{Ca}(^{18}\text{OH})_2$ after about 10 minutes from exposure to air, compared with the spectrum of a generic ^{16}O -lime putty partially

exposed to air. Both spectra contain portlandite and calcite peaks. Several peaks of $\text{Ca}(^{18}\text{OH})_2$ are shifted to lower wavenumbers compared to the $\text{Ca}(^{16}\text{OH})_2$. Of the peaks due to portlandite the peak at 356cm^{-1} is shifted $\sim 19\text{cm}^{-1}$ to 337cm^{-1} , the peak at 251cm^{-1} is shifted $\sim 12\text{cm}^{-1}$ to 239cm^{-1} . We also observe that the peak at 1086cm^{-1} resulting from some carbonation of the samples is shifted $\sim 19\text{cm}^{-1}$ to 1067cm^{-1} .

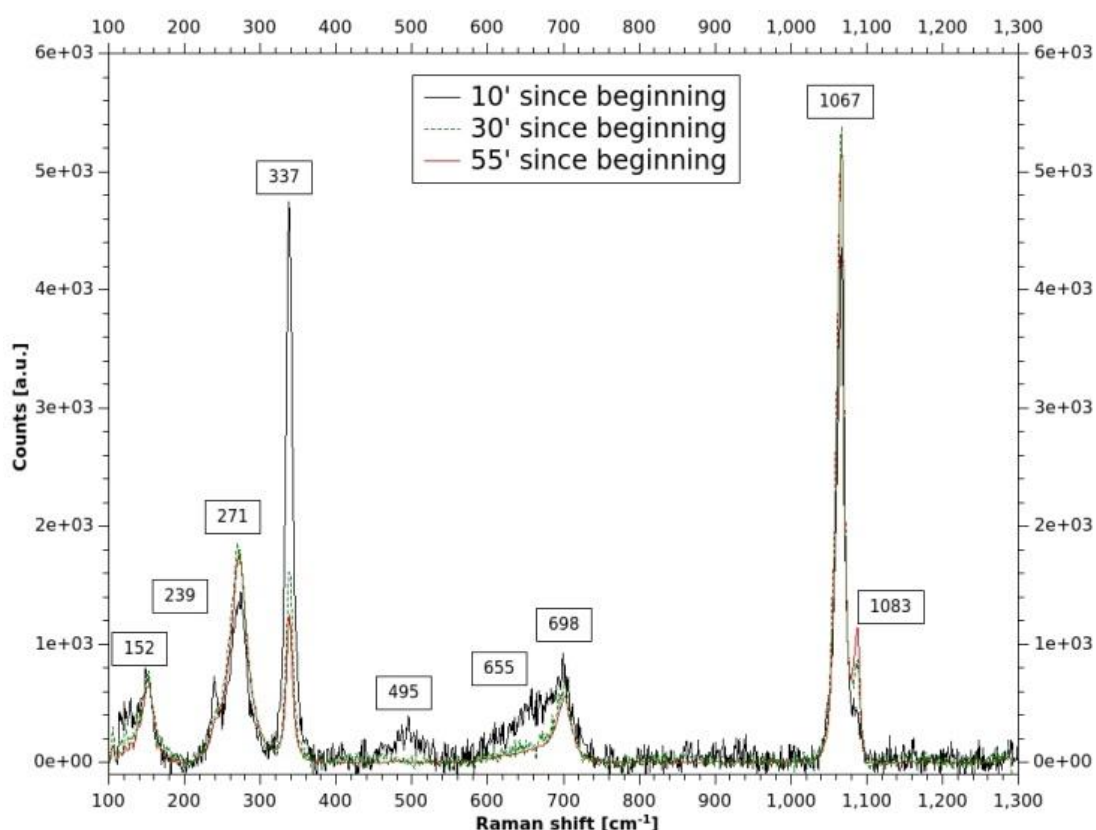


Figure 3 - Raman spectrum of the $\text{Ca}(^{18}\text{OH})_2$ produced partially carbonated. Spectra taken after 10', 30' 55' since the beginning of the tests, which exposes the sample to air.

Figure 3 shows the Raman spectra from 100 to 1300cm^{-1} of the $\text{Ca}(^{18}\text{OH})_2$ produced, after 10, 30 and 55 minutes from opening of the cell, which allowed contact of the sample with air. Peaks at 239 , 337 and 655cm^{-1} are related to $\text{Ca}(^{18}\text{OH})_2$ and become weaker over time. This provides evidence of $\text{Ca}(^{18}\text{OH})_2$ reacting with atmospheric CO_2 containing ^{16}O and forming CaCO_3 . According to our simulations, peaks at 152 , 271 , 698 and 1067cm^{-1} can be best

modelled as calcite with each carbonate containing a single ^{18}O (although it is possible that the peak at 1067cm^{-1} also includes a contribution of ^{18}O -enriched ACC; see discussion later in this paragraph). These peaks are shifted to lower wavenumbers compared to literature spectra of ^{16}O -calcite (Table S4). The intensity of the peak at 152 cm^{-1} remains unaltered over time, whereas the intensity of peaks at 271 , 698 and 1083 cm^{-1} increase, suggesting progression of the carbonation reaction with the formation of an increasing amounts of ^{16}O -calcite. The broad peaks at 450 cm^{-1} disappearing after 10 minutes reaction, suggests the presence of a metastable phase such as ACC (main peak included in the 1067cm^{-1} peak as previously mentioned).

Computation Results

Table 1 compares Raman active modes of a natural ($\text{Ca}(^{16}\text{OH})_2$) and an isotopically labelled ($\text{Ca}(^{18}\text{OH})_2$) portlandite calculated using DFT with experimental values. Although, the relative positions of the peaks are captured for both minerals, there is a systematic displacement of the predicted peaks relative to the experimental positions⁴⁸. This is a well-known effect of DFT calculations and relates to the estimation of bond strengths.

Table 1 - Comparison of experimental and simulated Raman active modes of portlandite. The Raman shift due to the different O isotopes, denoted Δ , is compared to the theoretically derived values (Equation 1).

Experiment [cm^{-1}]			Simulation [cm^{-1}]			Theory [cm^{-1}]
$\text{Ca}(^{16}\text{OH})_2$	$\text{Ca}(^{18}\text{OH})_2$	Δ	$\text{Ca}(^{16}\text{OH})_2$	$\text{Ca}(^{18}\text{OH})_2$	Δ	Δ
251	239	-12	256	242	-14	-14
356	337	-19	381	361	-20	-19
675	675	0	715	715	0	0

The two low frequency peaks of portlandite are associated with vibrations of the hydroxide ions relative to each other in plane and out of plane. In the case where two hydroxide ions are vibrating as whole units the individual masses in the pure case are $m_1=m_2=17$ while for full isotopic substitution with ^{18}O these increase to $m_1=m_2=19$. The reduced masses are $17/2$ and $19/2$ respectively, and thus the theoretical treatment as in Equation 1 predicts the isotopically doped system has a frequency to $(17/19)^{1/2}$ of the natural case corresponding to shifts of -14cm^{-1} (for peak 1 at 251cm^{-1}) and -19cm^{-1} (peak 2). In contrast, the high frequency portlandite peak at 675cm^{-1} is associated with the rocking mode of individual hydroxide ions. Since this is a rotational vibration, any shift is due not to the change in effective mass associated with isotopic substitution but with the moment of inertia. The resulting Raman shift due to isotopic composition is predicted to be $\sim 0.3\%$ (compared with $\sim 5\%$ in the previous cases) which is consistent with no observed shift in the experimental and simulated spectra. While Raman can be used to identify isotopic variation,⁵³ the comparison with calculation can help to identify the constitution of our samples and give insight into the processes during their formation.

Calcite with different isotopic composition ($\text{CaC}^{16}\text{O}_{3-x}\text{O}_x$) shows Raman shifts to lower wave number with increasing x , the number of ^{18}O per carbonate ion (Table 2). The peak at about 152cm^{-1} in the experimental spectra is noisy and difficult to isolate in both the natural and ^{18}O -sample but the remaining Raman active peaks are relatively well defined and more easily characterized. Overall, the computational results are in good agreement with the measured spectra. The advantage of the calculation is that the vibrational motion associated with each active mode can be identified.⁵² For example, we can clearly identify the peak at 1086cm^{-1} as the symmetric stretch of the C-O bond in the carbonate ions, whereas the peak at 700cm^{-1} is an antisymmetric coupling between carbonate ions in different layers. The vibrations of the remaining peaks are complex motions of carbonate bending in different layers.

Table 2 - Comparison of experimental and simulated Raman active modes of calcite. In brackets the Raman shift due to the different O isotopes compared to $\text{CaC}^{16}\text{O}_3$. The two columns in the experimental results are related to carbonate phases with different ^{18}O content.

Peak	Experiment [cm^{-1}]		Simulation [cm^{-1}]			
	CaCO_3 $^{18}\text{O} >$ ^{16}O	CaCO_3 $^{18}\text{O} <$ ^{16}O	$\text{CaC}^{16}\text{O}_3$	$\text{CaC}^{18}\text{O}^{16}\text{O}_2$	$\text{CaC}^{18}\text{O}_2^{16}\text{O}$	$\text{CaC}^{18}\text{O}_3$
1	152	152	159-165	156-162 (-3)	154-160 (-5)	151-157 (-8)
2	277	282	293	288 (-5)	285 (-8)	282 (-11)
3	698	713	680	672-665 (-8/-15)	661-652 (-19/-28)	645 (-35)
4	1066	1086	1055	1036 (-19)	1015 (-40)	995 (-60)

ToF-SIMS Results

ToF-SIMS allows the determination of the elemental, isotopic, or molecular composition of surfaces to a maximum depth of 1-2 nm. It is a destructive technique that reveals, using a mass spectrometer, the mass:charge ratio of secondary ions ejected from the surface when a primary ion beam is fired against it. Therefore, during the analysis secondary ions may be positively and negatively charged depending on their composition and mass. Data analysis has therefore to take into account both polarities. Full details of mass:charge ratio of ejected secondary ions considered in this study are in Tables S2 and S3 where a detailed analysis of the results is also reported. To assess the accuracy of the ToF-SIMS measurement, we tested an Analar CaCO_3 reference sample, which gave an average $^{18}\text{O}:^{16}\text{O}$ ratio of 0.021 (Table 3) in agreement with the isotopic ratio between 0.019 and 0.021⁵⁶⁻⁵⁸ of naturally occurring samples. Data for the carbonated $\text{Ca}(^{18}\text{OH})_2$ samples, show a reduction in the relative intensities of species containing ^{18}O over time, and a simultaneous increase of the intensities of species containing ^{16}O (Figures S1-S3 in the SI). Simultaneously, species containing carbon such as $[\text{HC}^{18}\text{O}_3]^-$ and $[\text{C}^{18}\text{O}_3]^-$ (Figures S1-S3) show an increase. This is clear evidence of the carbonation of

portlandite surfaces as secondary ions ejected from the surface destruction have greater carbon content.

Table 3 reports the $^{18}\text{O}:^{16}\text{O}$ ratio calculated for all the secondary ions produced by the destruction of the surface over the duration of the experiment. Data shows an initial isotope ratio of 0.62 for positive ions and a ratio of 0.51 for negative ions. The weighted average value of 0.54 suggests that, at very early stages of the carbonation reaction, for every atom of ^{18}O in carbonate ions, there would be two ^{16}O (theoretical $^{18}\text{O}:^{16}\text{O}$ ratio 0.5). However, from day 0 to day 1 the data shows a dramatic decrease in the $^{18}\text{O}:^{16}\text{O}$ ratio to a value of 0.038 that shows little variation in the following days. This value shows little variation after 137 days of carbonation. The isotope ratio for positive and negative species converges towards the same value of 0.046, which is approximately double the value for natural samples.

Table 3 - $^{18}\text{O}:^{16}\text{O}$ ratio calculated from the intensity of the ToF-SIMS counts for the ionic species with positive and negative polarity

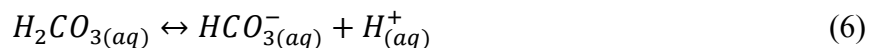
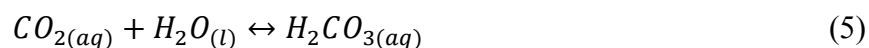
	Analar CaCO_3	Carbonated $\text{Ca}(^{18}\text{OH})_2$			
		Day 0	Day 1	Day 8	Day 137
$[^{18}\text{O}/^{16}\text{O}]^+$	0.035	0.616	0.057	0.044	0.046
$[^{18}\text{O}/^{16}\text{O}]^-$	0.007	0.509	0.032	0.029	0.046
Weighted Average	0.014	0.537	0.038	0.033	0.046

Discussion

The combination of complementary results from the vibrational fingerprint of the materials with different isotopic composition and the ToF-SIMS experiments show that we can elucidate the carbonation mechanism of hydrous materials. However, before discussing our data, the role

of the pH in the carbonate precipitation and on the behavior of different isotopes during the process should be highlighted.

Recent work on the precipitation of carbonates in natural systems (i.e. at approximately neutral pH) shows that an isotopic equilibrium is reached between the solution and the precipitated solid, which only depends on temperature.^{34,58} On the other hand, precipitation of carbonates from saturated solutions of $\text{Ca}(\text{OH})_2$ take place under high pH (12.4 at 23°C)¹⁴ and therefore is in non-equilibrium conditions. As a consequence, the main phenomenon producing fractionation during precipitation is the reaction kinetics related to the solution high pH.²⁹⁻³³ At pH values above 9, various authors^{29,31-33} suggested that the direct reaction of CO_2 with the hydroxyl group (OH^-) produced by the dissociation of water is the primary pathway for carbonate ion formation (Equation 3).²⁹ This pathway is suggested to be faster than the one leading to the formation of CO_3^{2-} from the reaction of CO_2 in natural waters at neutral pH⁵⁷ (Equations 4-7) and, consequently, it prevents isotope equilibration of gaseous $\text{CO}_{2(g)}$ with the dissolved $\text{CO}_{2(aq)}$ (Equation 4). Since heavier isotopes react slower than lighter isotopes, in the carbonate precipitates at high pH we would expect a lower concentration of ^{18}O and ^{13}C compared to the carbonates precipitated under equilibrium conditions.²⁹ Examples of carbonate phases with a very different isotope signature are limestone of marine and continental origins, and carbonates produced during cement setting.³¹⁻³³



Equilibrium in Equation 3 implies that the carbonate ion contains a mixture of the isotopic composition of aqueous $\text{CO}_{2(\text{aq})}$ (similar to the isotopic composition of gaseous $\text{CO}_{2(\text{g})}$) and OH^- ions.^{29,31,33} The ^{18}O composition of these carbonates ($n^{18}\text{O}$) can be described by considering the abundance of ^{18}O in the different species, according to Equation 8.

$$n^{18}\text{O}_{\text{carbonate}} \leftrightarrow \frac{1}{3}n^{18}\text{O}_{\text{OH}} + \frac{2}{3}n^{18}\text{O}_{\text{CO}_2(\text{g})} \quad (8)$$

Letolle et al.²⁹ have calculated that one third of the oxygen in the carbonates formed under high pH conditions, is provided by the OH^- ions originated from the dissociation of H_2O molecules catalyzing the reaction between $\text{Ca}(\text{OH})_2$ and aqueous $\text{CO}_{2(\text{aq})}$. This implies that the ^{18}O content of OH^- groups is related to the isotopic composition of H_2O . Letolle et al.²⁹, however, did not provide any information on the role of OH^- ions produced by the dissolution of $\text{Ca}(\text{OH})_2$ on the isotopic composition of carbonate phases.

To demonstrate that hydroxyl groups from the surface have a fundamental role in the formation of carbonate phases, we have studied $\text{Ca}(^{18}\text{OH})_2$ samples containing ^{18}O . Therefore, during the carbonation of $\text{Ca}(^{18}\text{OH})_2$, the sample itself is by far the most significant source of ^{18}O (a very limited contribution can be due to the CO_2 and H_2O ^{59,60}) whereas the atmospheric water and CO_2 are the only source of ^{16}O . Any mixture of the isotope in the resulting carbonate phases provides the most likely source of oxygen in the formation of carbonate ions and therefore the carbonation mechanism.

The Raman spectrum of $\text{Ca}(^{18}\text{OH})_2$ confirms the purity of the sample but also the high surface reactivity, as demonstrated by the formation of carbonate phases after 10 minutes from exposure to atmospheric CO_2 . This is in agreement with the results of previous studies on the carbonation kinetics and on the role of water vapor on the $\text{Ca}(\text{OH})_2/\text{CO}_2$ solid-gas reaction.^{12,61} The shift observed for the Raman peaks of portlandite and calcite can be associated with variations in the isotopic composition of the minerals and are supported by ab initio

calculations. In the case of portlandite, the shifts in the Raman peaks arise from substitution of all the ^{16}O with ^{18}O (Figure 2), whereas the shift in the Raman peaks of carbonate phases formed after the reaction with atmospheric CO_2 arise from partial substitution of ^{16}O with ^{18}O (Figure 3). DFT data (Table 2) support that the experimental peaks at 152, 271, 698 and 1066 cm^{-1} are associated with calcite containing 1/3 of ^{18}O ($^{18}\text{O}:^{16}\text{O}$ ratio 0.5). The main vibrational fingerprint of this phase could be identified in the peak at 1066 cm^{-1} (Figure 3). The peak at 1083 cm^{-1} belongs to ^{16}O -calcite, which is a minor phase at the beginning of the reaction which then grows over the time.

SIMS results allow calculation of the $^{18}\text{O}:^{16}\text{O}$ ratio for the secondary ions ejected from surface destruction. At the early stage of carbonation (~3 minutes exposure to air), the ratio is of 0.51 (Table 3). This value is in good agreement with the results of our theoretical analysis of Raman shifts and with Letolle's proposition²⁹. This indicated that in carbonate precipitates at high pH, 2/3 of oxygen is supplied by CO_2 whereas 1/3 of the oxygen is provided by OH^- ions. However, unlike Letolle's proposition suggesting that the OH^- groups involved in the carbonation originate from the dissociation of H_2O molecules, our results clearly demonstrate that the $\text{Ca}(\text{OH})_2$ plays an important role in the formation of hydroxyl groups. ToF-SIMS data displays carbonate species that contain 1/3 of ^{18}O (the remaining 2/3 comes from C^{16}O_2), which in our case can only be produced by the dissolution of the surface and not by the dissociation of adsorbed water molecules, which comprise mainly ^{16}O . This is also supported by PHREEQC^{56,62} modelling (see model description and Table S5 in the SI) showing that the concentration of OH^- ions produced by the dissolution of $\text{Ca}(\text{OH})_2$ in pure water at 25°C, is several orders magnitude greater than the concentration of OH^- ions produced by the natural dissociation of pure water. Therefore, the OH^- ions from $\text{Ca}(\text{OH})_2$ are more likely to take part in the carbonation reaction compared to those from water. As a consequence, it is possible to infer that in highly alkaline conditions, the isotopic composition of precipitated carbonates,

which is generally described by Equation 8, can be rewritten by considering the abundance of ^{18}O in the CO_2 and in the $\text{Ca}(\text{OH})_2$ as reported in Equation 9. This new equation marks the very early stage of the carbonation reaction where the dissolution of the surface is the rate-limiting step. Although this equation is a simplification of the real process, since it omits contributions from the equilibration of $^{18}\text{OH}^-$ from the surface and from water, it can be used to describe the process in basic terms.

$$n^{18}\text{O}_{\text{carbonate}} \leftrightarrow \frac{1}{2}n^{18}\text{O}_{\text{Ca}(\text{OH})_2} + \frac{2}{2}n^{18}\text{O}_{\text{CO}_2(\text{g})} \quad (9)$$

Subsequent to the formation of ^{18}O rich carbonate phases in the first stage of the carbonation mechanisms, when the dissolution of portlandite surfaces must occur, our ToF-SIMS data show a dramatic reduction in $^{18}\text{O}:^{16}\text{O}$ ratio within the first day of carbonation (Table S6). This is also shown by the growth of the Raman peak at 1083 cm^{-1} of ^{16}O -calcite over time (Figure 3) and can be explained by the transformation of the initial metastable carbonates into more stable phases over time.⁶³⁻⁷⁶ Figure 3 shows the disappearance over time of a peak at 495 cm^{-1} that can be related to metastable hydrated phases^{54,55}. A possible explanation of this re-equilibration of $^{18}\text{O}:^{16}\text{O}$ ratio is the dissolution of metastable phases that give up some ^{18}O and the subsequent recrystallization of more stable phases that acquire ^{16}O during the precipitation process occurring under equilibrium conditions.

This marks the second stage of carbonation, which involves the transformation carbonate phases from lesser stable to more stable forms. A detailed explanation of this transformation has been recently provided by Rodriguez Navarro et al.²⁷

Earlier, Rodriguez-Blanco et al.⁶⁹ described the transformation mechanism of ACC to calcite as a two stage process: 1) ACC particles rapidly dehydrate and crystallize forming individual particles of vaterite; 2) the vaterite dissolves and re-precipitates as calcite (Ogino et al.⁷⁰ also confirmed the latter stage also for aragonite). Stage 1, mainly entails the release of water

molecules initially embedded in the structure of hydrated phases. Stage 2, involves the release of CO_3^{2-} ions that, according to equations 2-5, can lead to an exchange of oxygen atoms with the water molecules. We infer that our data is consistent with this proposition. The oxygen exchange and the formation of new carbonate phases richer in ^{16}O at the top of the carbonate phases initially formed (stage 1) explains the sudden variation of the $^{18}\text{O}:^{16}\text{O}$ ratio within the first 24h. Therefore, it is possible to infer that, whereas precipitation of meta-stable phases takes place under non-equilibrium conditions (i.e. at high pH, which does not allow isotope equilibration), the dissolution-and-precipitation mechanism leading to the formation of stable carbonate phases and the precipitation of new carbonate phases richer in ^{16}O , occurs at lower pH allowing an isotopic equilibrium of carbonates. It is worth noting that in our experiments this equilibration occurred within the initial 24 hours even at 50% RH (a relatively low RH value for carbonation) and this suggests that stage 2 of the carbonation is a fast kinetic pathway.

Conclusions

Our results show new insights in the carbonation mechanism of portlandite. They demonstrate that during the early stage of the carbonation reaction (first 3 minutes, in our experiments) the surface hydroxyl groups are the source of oxygen for the formation of carbonate ions and hence the growth of carbonate begins by the dissolution of hydroxyl and calcium ions followed by the formation of metastable calcium carbonate. The second stage of the reaction occurs within the 24h after the carbonation started. This involves the transformation of the metastable carbonate phases into stable calcite. During this transformation there is a release of water, which is the source of oxygen for the formation of new carbonate ions.

Our results show how artificial isotopic doping can be used to study processes such as carbonation and have brought new insights into the early carbonation process. This knowledge should further the understanding of many processes involving carbonation such as carbon

sequestration technologies, carbonation of construction materials, precipitated carbonate products and geological disposal facilities for nuclear waste.

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Supporting Information Description

(1) ToF-SIMS sample preparation; (2) ToF-SIMS data analysis; (3) PHREEQC calculations; (4) detailed plots of the SIMS results; (4) experimental and simulated lattice parameters for portlandite; (5) Plot of the $^{18}\text{O}:^{16}\text{O}$ ratio over the time; (6) Table of experimental and simulated lattice parameters for portlandite; (7) List of all ions considered in this research; (8) list of ions considered for calculating the $^{18}\text{O}:^{16}\text{O}$ ratio; (9) peak position of the Raman spectra for different CaCO_3 phases; (10) OH^- concentration in different aqueous solutions, calculated using PHREEQC. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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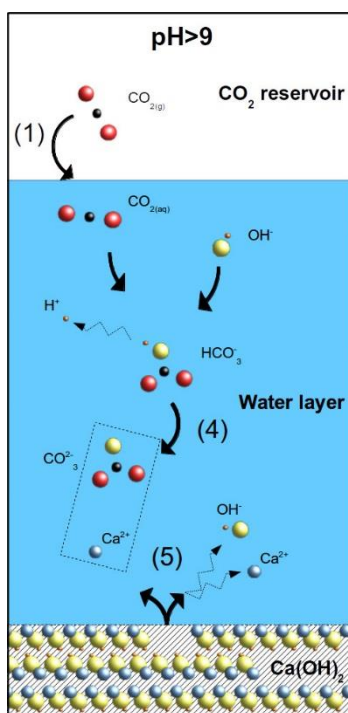
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For Table of Contents Use Only

Carbonation of Hydrous Materials at the Molecular Level: a ToF-SIMS, Raman and DFT study

Giovanni L. Pesce, Ian W. Fletcher, James Grant, Marco Molinari, Stephen C. Parker, Richard J. Ball



SYNOPSIS: At pH above 9, the direct reaction of CO_2 with the hydroxyl group produced by the dissolution of Ca(OH)_2 is the primary pathway for carbonate ion formation. This pathway is faster than the one leading to the formation of CO_3^{2-} from the dissolution of CO_2 in natural waters at neutral pH