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"Influence of Water Vapour and Carbon Dioxide on Free Lime during Storage at 80 °C, Studied by Raman Spectroscopy"

Dubina E.[1], Korat L.[2], Black L.[3], Strupi-Šuput J.[2], Plank J.[1]*

[1]Technische Universität München, Lehrstuhl für Bauchemie, Lichtenbergstr. 4, 85747
Garching bei München, Germany
[2]Slovenian National Building and Civil Engineering Institute, Dimičeva 12, 1000 Ljubljana,
Slovenia
[3]Institute for Resilient Infrastructure, School of Civil Engineering, University of Leeds, Leeds,
LS2 9JT, UK

Abstract

Micro-Raman spectroscopy has been used to follow the reaction of free lime (CaO) exposed for 24 hours to moist air at 80 °C under conditions of different relative humidities (10 – 80 % RH). X-ray diffraction and SEM imaging were applied as complementary techniques. The conversion of lime to calcium hydroxide and its subsequent carbonation to various calcium carbonate polymorphs was found to strongly depend on the relative humidity. At low RH (10 – 20 %), only Raman spectroscopy revealed the formation of early amorphous $CaCO_3$ which in the XRD patterns was detected only at $\geq$ 40 % RH. However, XRD analysis could identify the crystalline polymorphs formed at higher relative humidities. Thus, between 20 and 60 % RH, all three $CaCO_3$ polymorphs (calcite, aragonite and vaterite) were observed via XRD whereas at high relative humidity (80 %), calcite was the predominant reaction product. The results demonstrate the usefulness of Raman spectroscopy in the study of minor cement constituents and their reaction products on air, especially of amorphous character.

Keywords: micro-Raman; calcium oxide; moisture; carbonation; calcium carbonate polymorphs; SEM/EDX

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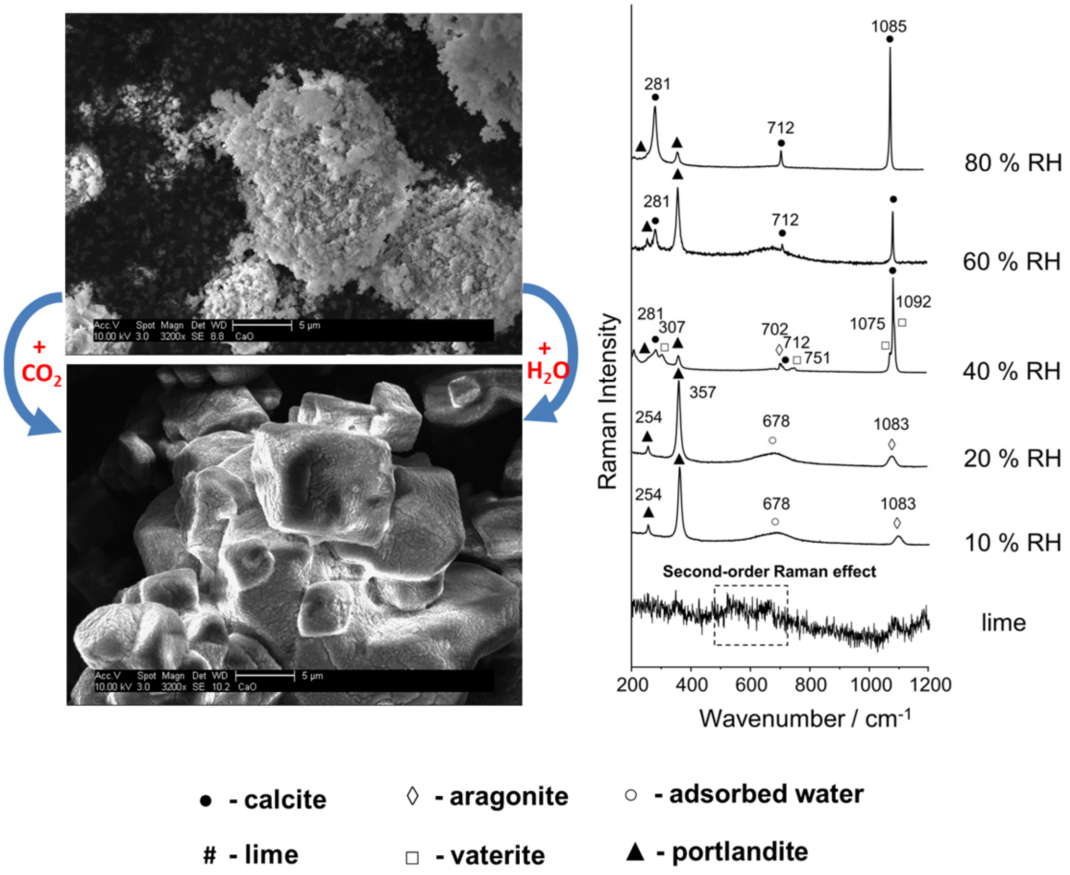
* Corresponding author: Email sekretariat@bauchemie.ch.tum.de (Johann Plank) Tel + 49 – 089 – 289 – 13151, Fax + 49 – 089 – 289 – 13152

Graphical abstract



Introduction

By volume, ordinary Portland cement (OPC) presents the most abundant industrially manufactured material and it also constitutes one of the world's most commonly used building materials [1]. Unfortunately, cement powder is highly hygroscopic and eagerly sorbs water vapour in a process generally known as surface prehydration of cement [2, 3]. This phenomenon may occur already during the manufacturing process, e. g. in the clinker mill, or later during storage in cement silos where the temperature often is 80 °C and high relative humidities occur as a consequence of gypsum dehydration [4, 5]. The interaction of cement with water vapour has detrimental effects on its engineering properties. Those include decreased compressive strength and workability, increased setting time and higher water demand [6-8]. The extent to which these phenomena occur depends on the temperature and relative humidity [9].

Recently we have investigated the physicochemical effects of water vapour sorption by pure cement clinker phases and free lime. There, the relative humidity values ("thresholds") above which prehydration starts to occur were determined [10]. Among all cement components, free lime (CaO) showed the lowest threshold value of 14 % relative humidity (RH) only. Also, CaO can sorb large quantities of water which are chemically bound. This pronounced ability of CaO to bind atmospheric moisture quickly and irreversibly possibly reduces or even prevents the prehydration of other clinker constituents when cement is exposed to moisture. In current cements, typically about 0.5 – 1.5 wt. % of free lime are present [11]. Therefore, information on the reaction of CaO, or its subsequently formed hydrate, $Ca(OH)_2$ with moist air can provide insight into the behaviour of industrial cement and for example its storage history.

The potential of Raman spectroscopy for the characterisation of cementitious materials was first demonstrated in 1976 [12]. Also, more recently a review on this subject has been published [13]. New instruments are available now which offer the potential for micro-Raman spectroscopy. These enable capture of spectra from the surfaces of samples just a few microns thick and with minimal interference from environmental moisture [14]. Moreover, whilst for example x-ray diffraction requires crystalline analytes, Raman spectroscopy allows the detection of amorphous phases and provides information on the local chemical environment. Raman spectra can be obtained from almost all components present in anhydrous cement and from cement hydrate phases. One exception is calcium oxide which is Raman inactive. However, it is possible to observe second order effects which give rise to sharp bands at 530 and 660 cm^{-1}, as well as a broad signal at about 1000 cm^{-1} [15].

The aim of this study was to simulate storage conditions for CaO (80 °C and relative humidities between 10 and 80 %) which can occur in the cement silo and to investigate the impact of those conditions on the reaction of CaO with atmospheric water and CO_2. Special attention was given to the amount and type of $CaCO_3$ polymorphs formed during exposure to moist air.

Experimental

Preparation of CaO

CaO was prepared by calcination of $CaCO_3$ (Merck, 98.5 % purity) for 3 h at 1000 °C and subsequent grinding to particles possessing an average size of 4.7 µm (d_{50} value) and a specific surface area of 2.4 m^2/g (N_2, BET). Precautions were taken to prevent reaction with atmospheric CO_2 and water vapour by storing samples in sealed 20 mL glass vials under nitrogen.

Ageing of CaO

To establish the cause of the ageing phenomenon under those storage conditions, in a climate chamber heated to 80 °C CaO powder was spread out as a thin layer (1 mm) on a plastic tray and exposed for 24 hours to non-treated atmospheric air exhibiting different relative humidities (10, 20, 40, 60 and 80 %).

Sample Characterisation

All fresh and prehydrated samples were analysed by x-ray diffraction, XRD, (D8 Advance, Bruker axs, Karlsruhe, Germany) using a Cu K_α X-ray source. Diffractograms were taken from 7 – 40 ° 2 θ at 21 °C, with a step size of 0.008 ° and a dwell time of 54 s. The mineralogical phases were identified by comparison with Diffract Plus EVA Application V.8.0 and JCPDS PDF-2 database [16].

Micro-Raman measurements were performed at room temperature using a Horiba Jobin Yvon HR 800 LabRAM instrument (Villeneuve d'Ascq, France) equipped with an Olympus BX40 microscope (focus graduation 1 µm), a laser working at $\lambda = 785$ nm and a multi channel air-cooled CCD detector. Each spectrum was acquired over the spectral range of 200 – 1200 cm^{-1} using a 10x objective. Prior to each experiment, the Raman shift was calibrated against the 520 cm^{-1} peak of silicon. Data handling was performed using LabSpec 5 software.

Scanning electron microscopic (SEM) images were obtained on uncoated samples using a FEI XL 30 FEG instrument (FEI, Eindhoven, Netherlands) under low vacuum conditions (1 mbar H_2O pressure) and an accelerating voltage of 10 kV. Dispersive x-ray spectroscopy was performed using a SUTW-Sapphire detector (EDAX, Mahwah, U.S.A.) under the same conditions as SEM imaging, however accelerating voltage was 15 kV.

Results and Discussion

The x-ray diffraction patterns of fresh lime and of samples exposed to air at 80 °C are displayed in **Figure 1**. There, reflections for unreacted CaO were visible only for the freshly calcined sample which was not yet exposed to air. After storage at low relative humidity (10 % RH), complete hydration of CaO to portlandite ($Ca(OH)_2$) was observed. No carbonation of this phase was detected at or below 20 % RH. However, after storage at 40 %, intensity of the reflections from portlandite decreased and partial carbonation became evident as signified by the appearance of new reflections attributable to $CaCO_3$ polymorphs. Namely, well defined and intense reflections for calcite and aragonite, and traces of vaterite were detected. In samples exposed to higher relative humidities (60 – 80 %), only portlandite and calcite were found. There, as RH increased, the reflections from calcite became more intense and sharp.

The micro-Raman spectra of the CaO samples exposed to different relative humidities are presented in **Figure 2**. They exhibited several distinct differences as compared to the XRD patterns. Apparently, Raman spectroscopy was able to capture also amorphous reaction products.

Analysis of the freshly calcined CaO showed very weak bands at ~ 530 and 660 cm^{-1} due to a second order Raman effect of lime. Following exposure of CaO to lower humidities (10 – 20 %), new bands at 254 and 357 cm^{-1} became visible which are characteristic for portlandite. Additionally, a broad band attributed to water adsorbed on the surfaces of portlandite appeared at 678 cm^{-1}. It has been reported earlier that surface adsorption of water occurs when CaO has quantitatively reacted to $Ca(OH)_2$ which then via van der Waals forces can physically bind additional water molecules on its surface as mono or multilayers [10]. Furthermore, a broad signal centred at 1083 cm^{-1} which was attributed to symmetric stretching of carbonate groups present in amorphous calcium carbonate became visible [17]. Thus, it became clear that already at 10 % RH partial carbonation of CaO had occurred which was not evident from the XRD patterns. There, the first carbonation products were found only at 40 % RH and higher. This signifies that compared to XRD, Raman spectroscopy constitutes a more sensitive technique to monitor early carbonation reactions.

In a similar study, rapid carbonation of portlandite present in hydrated calcium silicates has been investigated by Black *et al.*, also using micro-Raman spectroscopy. Like in our study, amorphous calcium carbonate was identified there as the first carbonation product [18].

Increasing the exposure RH to 40 % led to a sharper carbonate υ_1 (symmetrical stretching) band in the range of 1000–1100 cm^{-1}, thus indicating formation of crystalline calcium carbonates. Deconvolution of the signal revealed a number of overlapping bands at 1075, 1085 and 1091 cm^{-1} (Figure 3). Also, a number of weaker υ_4 carbonate bands at around 700 cm^{-1} were detected. The precise positions of these various bands are influenced by the symmetry of the carbonate anion, thus enabling polymorph identification when the entire spectrum and not just individual bands are looked at. The doublet at 1075 and 1091 cm^{-1} can be attributed to vaterite which normally exhibits a characteristic triplet at 1075, 1081 and 1092 cm^{-1} [19]. Here, the band at 1081 cm^{-1} is overlapped by the more intense υ_1 carbonate band at 1085 cm^{-1} assigned to the aragonite and calcite polymorphs. Also, at 701 – 706 cm-1 υ4 carbonate bands corresponding to aragonite were observed. A second carbonate peak appeared at 711 cm-1 for calcite. In the range between 730 and 760 cm-1, three bands were observed at 739, 743 and 750 cm-1 which correspond to vibrations of vaterite.

The most intense Raman bands below 310 cm-1 which are characteristic for lattice vibrations appear at 152 and 281cm-1 for calcite, at 205 cm-1 for aragonite as well as at 269 and 301cm-1 for vaterite.

In the Raman spectra of the samples exposed to 60 and 80 % RH, bands at 1085 cm^{-1}, 712 cm^{-1} 357 cm^{-1} and 281 cm^{-1} were recorded. The band at 357 cm^{-1} is characteristic for portlandite, whilst the others are attributable to calcite [20]. Intensity of the calcite bands increased with increasing RH. Similar observations were made for lime based materials by El-Turki et al. [21].

The exposure of CaO to air possessing different RHs not only led to changes in the mineralogical composition, but also altered the crystal sizes of the samples. **Figure 4** exhibits

SEM images of the fresh and aged CaO samples. Exposure to water vapour led to the appearance of deposits over the entire substrate. Storage at 80 % RH produced larger crystals, compared with exposure to lower RHs. Furthermore, energy dispersive x-ray spectroscopy showed higher carbon and oxygen contents in samples stored at higher RH levels, thus indicating the presence of larger amounts of calcium carbonate in these samples. In CaO exposed to 40 % RH, a slightly higher oxygen content than in other samples was detected, indicating the simultaneous presence of $Ca(OH)_2$ as well as of $CaCO_3$ on the hydrated surface.

Conclusion

In the present work, the influence of relative humidity and atmospheric carbon dioxide on CaO (free lime), a minor constituent of Portland cement, was investigated. The combination of micro-Raman spectroscopy, x-ray diffraction analysis and SEM imaging allowed tracking of the changes occurring on the surface of CaO exposed to moist air at 80 °C. After exposure to low RH, total conversion of CaO to $Ca(OH)_2$ was observed. Subsequently, initially formed $Ca(OH)_2$ underwent partial carbonation into amorphous calcium carbonate. At low humidities (10 – 20 % RH), this reaction was observed only by Raman spectroscopy and not by x-ray diffraction. Exposure to higher relative humidities (≥ 40 %) led to the formation of crystalline calcium carbonates which were x-ray detectable. At moderate RH (40 %), the three different calcium carbonate polymorphs (calcite, aragonite and vaterite) co-exist while at increasing RH, calcite becomes increasingly prevalent. Exposure to different RH levels also impacts the crystal sizes of the reaction products, with larger crystals produced at higher RHs. The results confirm the potential of Raman spectroscopy in the study of the hydration behaviour of minor cement constituents, particularly when amorphous products are involved in the reaction processes.

Acknowledgements

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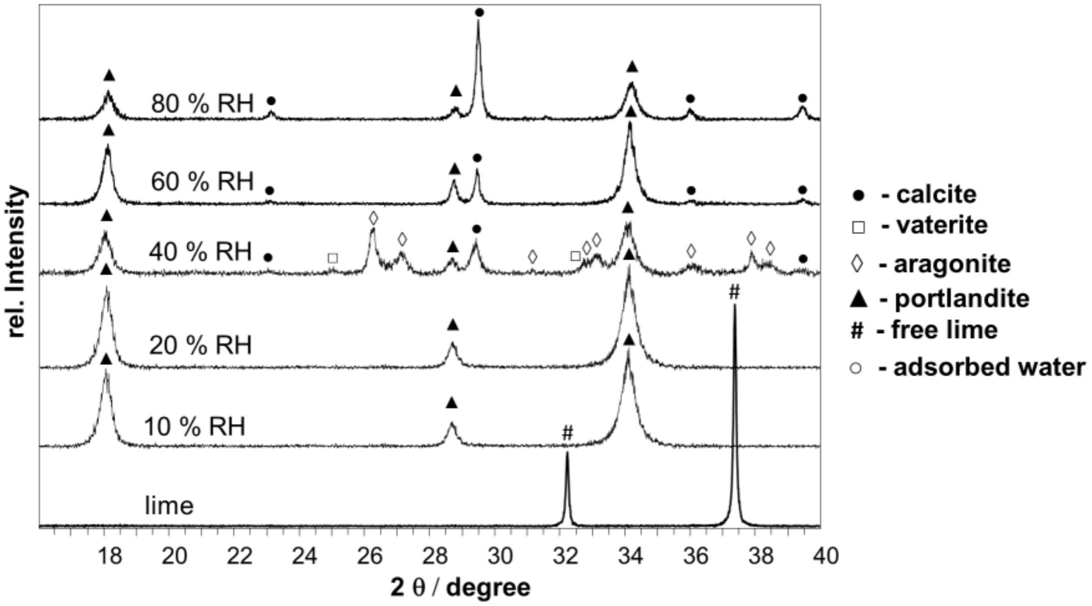
Figure 1. X-ray diffraction patterns of fresh and exposed CaO to moist air showing the formation of different hydration and carbonation products

Figure 2. Micro-Raman spectra of fresh and exposed CaO to moist air showing the formation of different hydration and carbonation products

Figure 3. Micro – Raman spectra for CaO prehydrated for 24 h at 40 % rel. humidity and 80 °C deconvoluted for the individual components portlandite, calcite, aragonite and vaterite present in the sample, shown in four different ranges.

Figure 4. SEM micrographs and EDX spectra of CaO samples, fresh **(a)** and stored at 20 % RH **(b)**, 40 % RH **(c)** and 80 % RH **(d);** storage conditions: 80°C, 24 hours; magnification: 12800 x

Figures:



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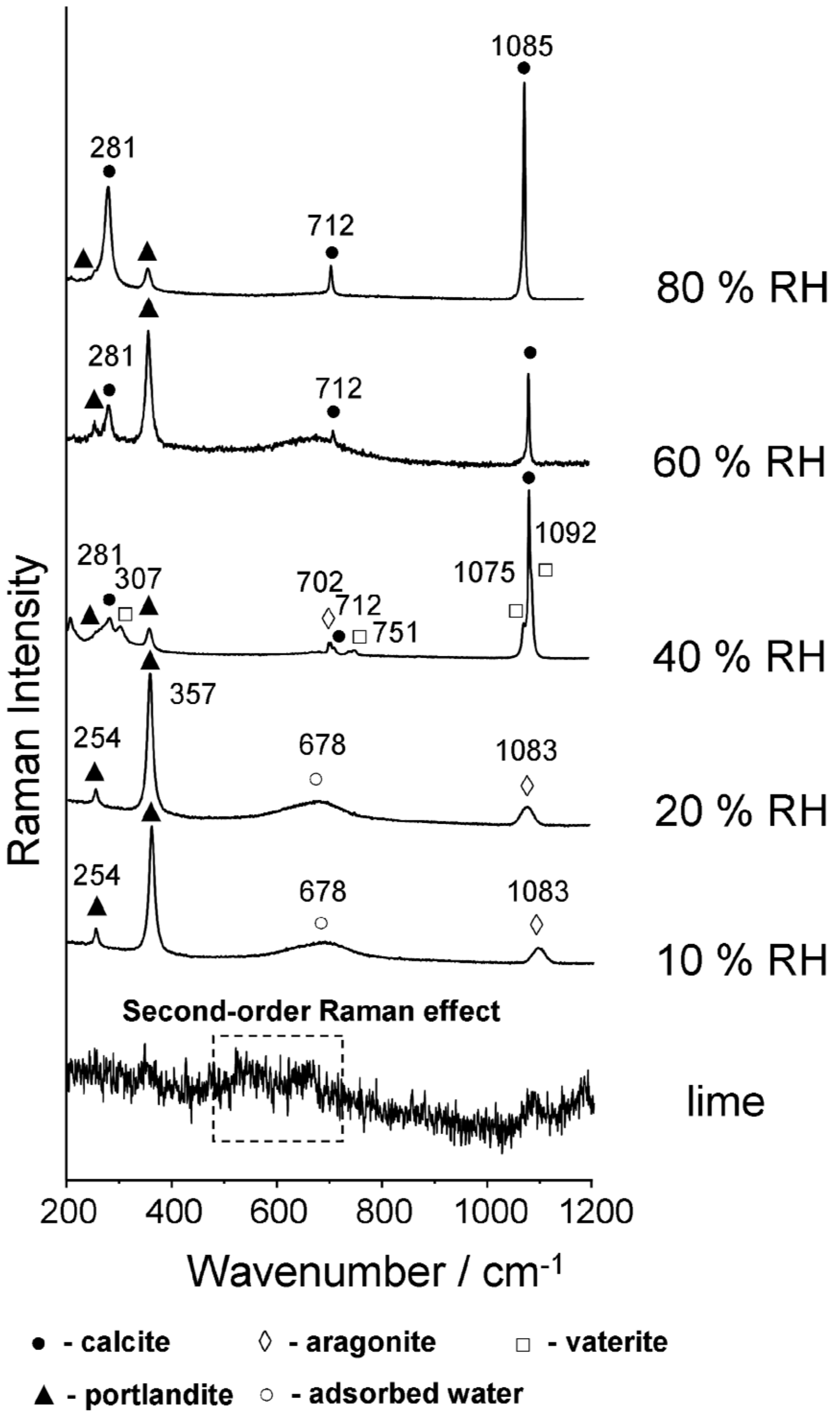

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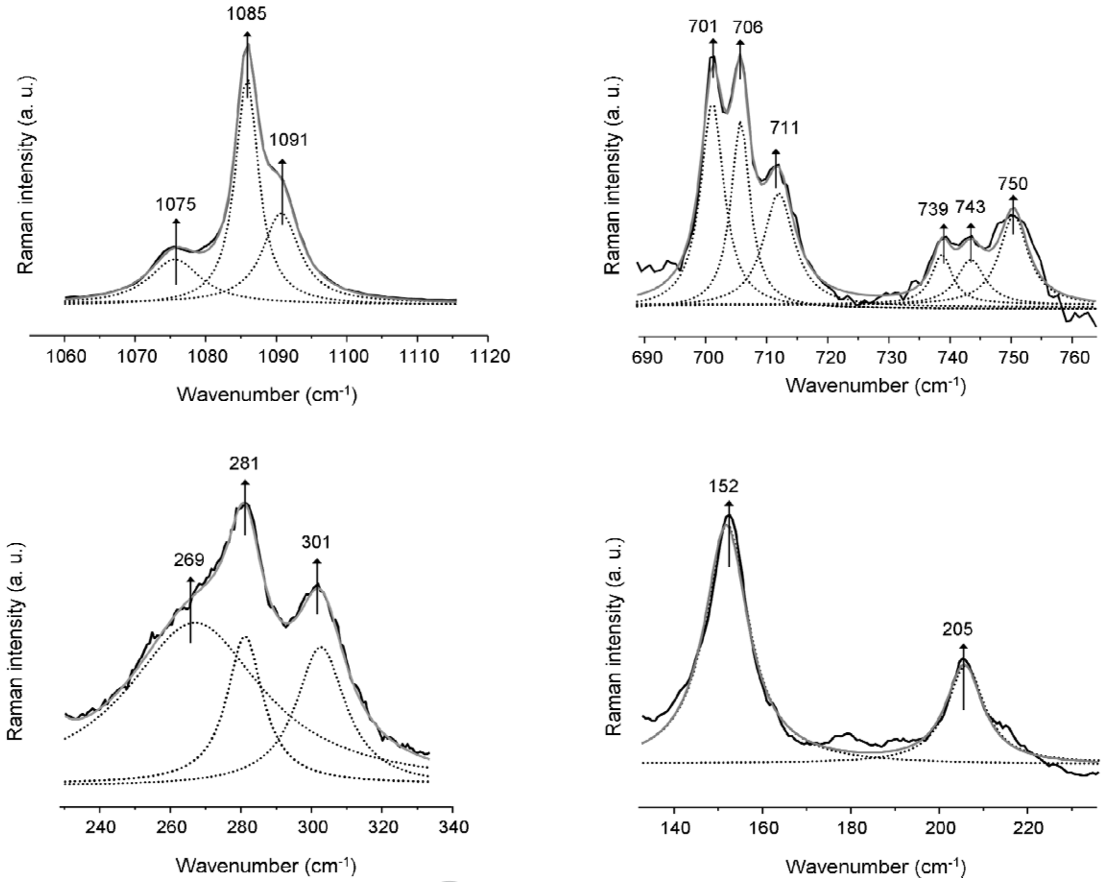

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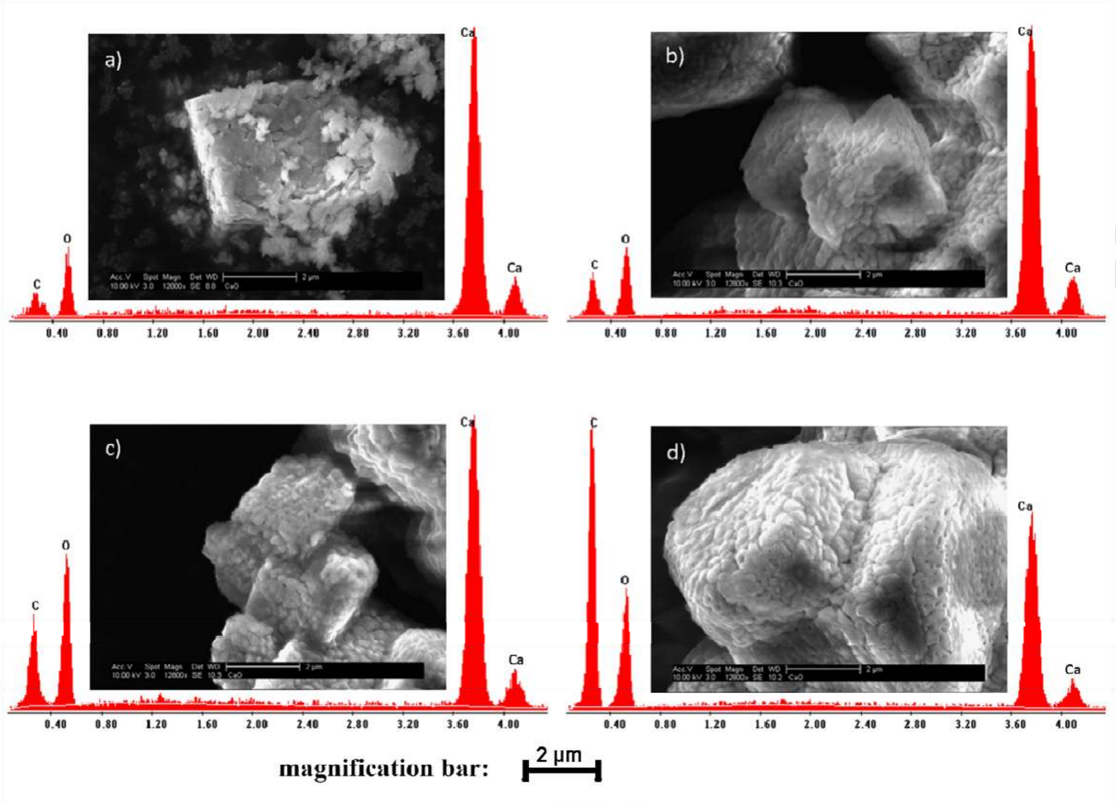

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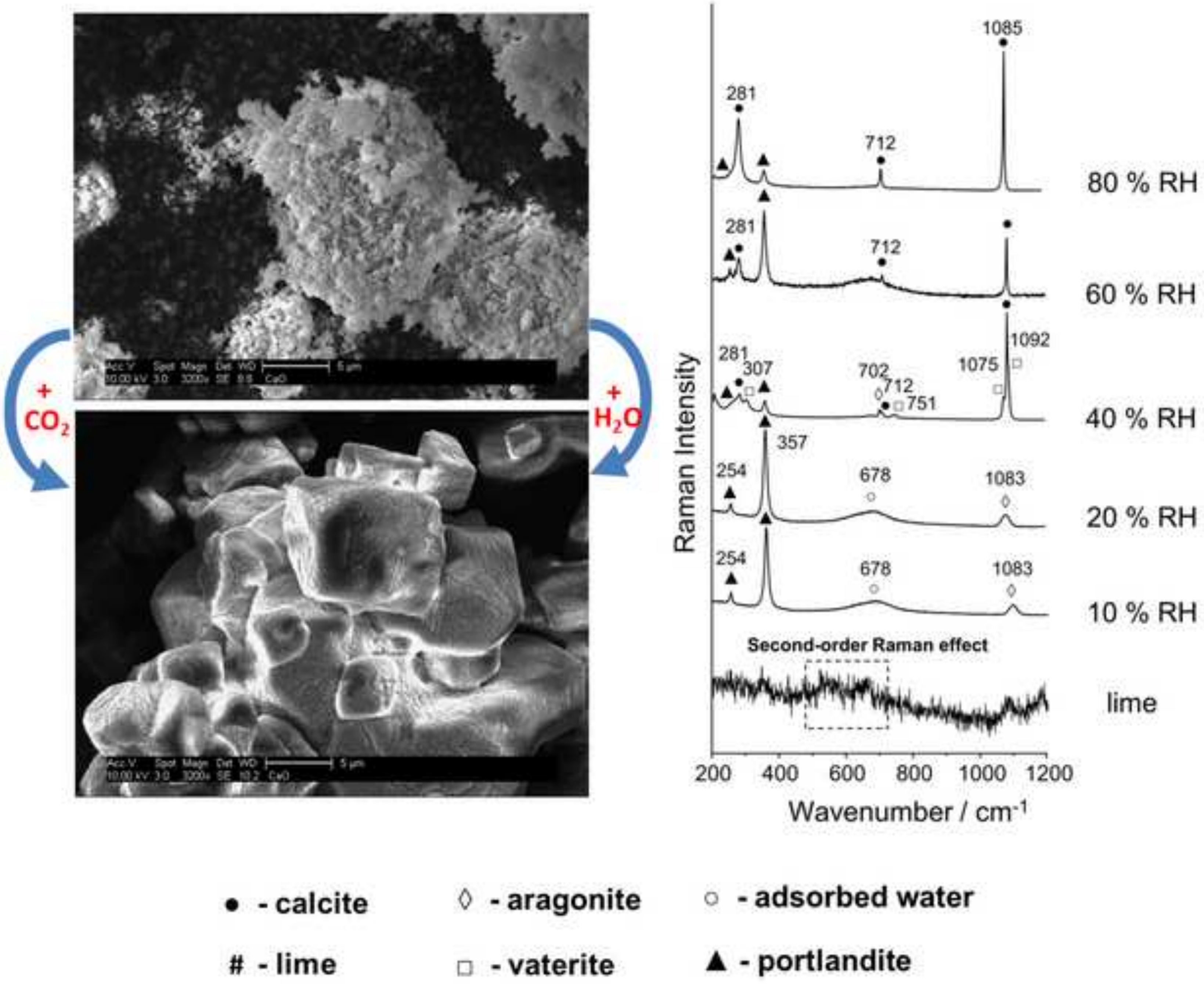
+ CO$_2$
+ H$_2$O
5 µm
CaO
Raman Intensity
Wavenumber / cm^{-1}
200
400
600
800
1000
1200
1085
281
712
80 % RH
281
712
60 % RH
281
307
702
712
751
1075
1092
40 % RH
357
254
678
1083
20 % RH
254
678
1083
10 % RH
Second-order Raman effect
lime
● - calcite
◊ - aragonite
○ - adsorbed water
- lime
□ - vaterite
▲ - portlandite

Highlights

(1) Micro-Raman spectroscopy was used to monitor the reaction of CaO with water vapour

(2) At low RH values, total conversion of CaO to $Ca(OH)_2$ was observed

(3) $Ca(OH)_2$ underwent partial carbonation into amorphous calcium carbonate

(4) At low RH, only Raman spectroscopy revealed the formation of amorphous $CaCO_3$

(5) Importance of Raman spectroscopy in the study of amorphous products is shown