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

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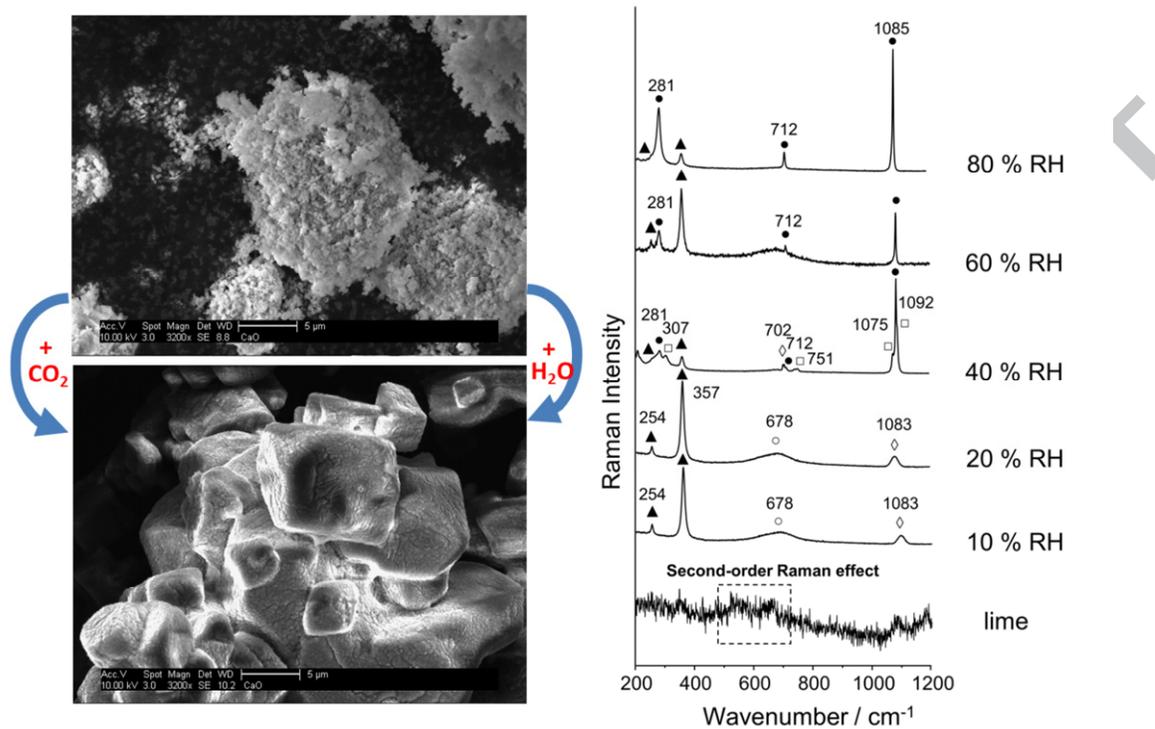
10 **Abstract**

11 Micro-Raman spectroscopy has been used to follow the reaction of free lime (CaO) exposed
12 for 24 hours to moist air at 80 °C under conditions of different relative humidities (10 – 80 %
13 RH). X-ray diffraction and SEM imaging were applied as complementary techniques. The
14 conversion of lime to calcium hydroxide and its subsequent carbonation to various calcium
15 carbonate polymorphs was found to strongly depend on the relative humidity. At low RH (10
16 – 20 %), only Raman spectroscopy revealed the formation of early amorphous CaCO₃ which
17 in the XRD patterns was detected only at ≥ 40 % RH. However, XRD analysis could identify
18 the crystalline polymorphs formed at higher relative humidities. Thus, between 20 and
19 60 % RH, all three CaCO₃ polymorphs (calcite, aragonite and vaterite) were observed via
20 XRD whereas at high relative humidity (80 %), calcite was the predominant reaction product.
21 The results demonstrate the usefulness of Raman spectroscopy in the study of minor cement
22 constituents and their reaction products on air, especially of amorphous character.

23
24 **Keywords:** micro-Raman; calcium oxide; moisture; carbonation; calcium carbonate
25 polymorphs; SEM/EDX

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26 Graphical abstract



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37 Introduction

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

49 Recently we have investigated the physicochemical effects of water vapour sorption by pure
50 cement clinker phases and free lime. There, the relative humidity values (“thresholds”) above
51 which prehydration starts to occur were determined ^[10]. Among all cement components, free
52 lime (CaO) showed the lowest threshold value of 14 % relative humidity (RH) only. Also,
53 CaO can sorb large quantities of water which are chemically bound. This pronounced ability
54 of CaO to bind atmospheric moisture quickly and irreversibly possibly reduces or even
55 prevents the prehydration of other clinker constituents when cement is exposed to moisture. In
56 current cements, typically about 0.5 – 1.5 wt. % of free lime are present ^[11]. Therefore,
57 information on the reaction of CaO, or its subsequently formed hydrate, Ca(OH)₂ with moist
58 air can provide insight into the behaviour of industrial cement and for example its storage
59 history.

60 The potential of Raman spectroscopy for the characterisation of cementitious materials was
61 first demonstrated in 1976 ^[12]. Also, more recently a review on this subject has been
62 published ^[13]. New instruments are available now which offer the potential for micro-Raman

63 spectroscopy. These enable capture of spectra from the surfaces of samples just a few microns
64 thick and with minimal interference from environmental moisture ^[14]. Moreover, whilst for
65 example x-ray diffraction requires crystalline analytes, Raman spectroscopy allows the
66 detection of amorphous phases and provides information on the local chemical environment.
67 Raman spectra can be obtained from almost all components present in anhydrous cement and
68 from cement hydrate phases. One exception is calcium oxide which is Raman inactive.
69 However, it is possible to observe second order effects which give rise to sharp bands at 530
70 and 660 cm^{-1} , as well as a broad signal at about 1000 cm^{-1} ^[15].
71 The aim of this study was to simulate storage conditions for CaO (80 °C and relative
72 humidities between 10 and 80 %) which can occur in the cement silo and to investigate the
73 impact of those conditions on the reaction of CaO with atmospheric water and CO₂. Special
74 attention was given to the amount and type of CaCO₃ polymorphs formed during exposure to
75 moist air.

76

77 **Experimental**

78 *Preparation of CaO*

79 CaO was prepared by calcination of CaCO₃ (Merck, 98.5 % purity) for 3 h at 1000 °C and
80 subsequent grinding to particles possessing an average size of 4.7 μm (d₅₀ value) and a
81 specific surface area of 2.4 m^2/g (N₂, BET). Precautions were taken to prevent reaction with
82 atmospheric CO₂ and water vapour by storing samples in sealed 20 mL glass vials under
83 nitrogen.

84

85 *Ageing of CaO*

86 To establish the cause of the ageing phenomenon under those storage conditions, in a climate
87 chamber heated to 80 °C CaO powder was spread out as a thin layer (1 mm) on a plastic tray

88 and exposed for 24 hours to non-treated atmospheric air exhibiting different relative
89 humidities (10, 20, 40, 60 and 80 %).

90

91 *Sample Characterisation*

92 All fresh and prehydrated samples were analysed by x-ray diffraction, XRD, (D8 Advance,
93 Bruker axs, Karlsruhe, Germany) using a Cu K_{α} X-ray source. Diffractograms were taken
94 from $7 - 40^{\circ} 2\theta$ at 21°C , with a step size of 0.008° and a dwell time of 54 s. The
95 mineralogical phases were identified by comparison with Diffract Plus EVA Application
96 V.8.0 and JCPDS PDF-2 database ^[16].

97 Micro-Raman measurements were performed at room temperature using a Horiba Jobin Yvon
98 HR 800 LabRAM instrument (Villeneuve d'Ascq, France) equipped with an Olympus BX40
99 microscope (focus graduation $1\ \mu\text{m}$), a laser working at $\lambda = 785\ \text{nm}$ and a multi channel air-
100 cooled CCD detector. Each spectrum was acquired over the spectral range of $200 - 1200\ \text{cm}^{-1}$
101 using a 10x objective. Prior to each experiment, the Raman shift was calibrated against the
102 $520\ \text{cm}^{-1}$ peak of silicon. Data handling was performed using LabSpec 5 software.

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

108

109 **Results and Discussion**

110 The x-ray diffraction patterns of fresh lime and of samples exposed to air at 80°C are
111 displayed in **Figure 1**. There, reflections for unreacted CaO were visible only for the freshly
112 calcined sample which was not yet exposed to air. After storage at low relative humidity
113 (10 % RH), complete hydration of CaO to portlandite ($\text{Ca}(\text{OH})_2$) was observed. No

114 carbonation of this phase was detected at or below 20 % RH. However, after storage at 40 %,
115 intensity of the reflections from portlandite decreased and partial carbonation became evident
116 as signified by the appearance of new reflections attributable to CaCO_3 polymorphs. Namely,
117 well defined and intense reflections for calcite and aragonite, and traces of vaterite were
118 detected. In samples exposed to higher relative humidities (60 – 80 %), only portlandite and
119 calcite were found. There, as RH increased, the reflections from calcite became more intense
120 and sharp.

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

125 Analysis of the freshly calcined CaO showed very weak bands at ~ 530 and 660 cm^{-1} due to a
126 second order Raman effect of lime. Following exposure of CaO to lower humidities (10 –
127 20 %), new bands at 254 and 357 cm^{-1} became visible which are characteristic for portlandite.
128 Additionally, a broad band attributed to water adsorbed on the surfaces of portlandite
129 appeared at 678 cm^{-1} . It has been reported earlier that surface adsorption of water occurs when
130 CaO has quantitatively reacted to Ca(OH)_2 which then via van der Waals forces can
131 physically bind additional water molecules on its surface as mono or multilayers ^[10].
132 Furthermore, a broad signal centred at 1083 cm^{-1} which was attributed to symmetric
133 stretching of carbonate groups present in amorphous calcium carbonate became visible ^[17].
134 Thus, it became clear that already at 10 % RH partial carbonation of CaO had occurred which
135 was not evident from the XRD patterns. There, the first carbonation products were found only
136 at 40 % RH and higher. This signifies that compared to XRD, Raman spectroscopy constitutes
137 a more sensitive technique to monitor early carbonation reactions.

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

141 Increasing the exposure RH to 40 % led to a sharper carbonate ν_1 (symmetrical stretching)
142 band in the range of 1000–1100 cm^{-1} , thus indicating formation of crystalline calcium
143 carbonates. Deconvolution of the signal revealed a number of overlapping bands at 1075,
144 1085 and 1091 cm^{-1} (Figure 3). Also, a number of weaker ν_4 carbonate bands at around
145 700 cm^{-1} were detected. The precise positions of these various bands are influenced by the
146 symmetry of the carbonate anion, thus enabling polymorph identification when the entire
147 spectrum and not just individual bands are looked at. The doublet at 1075 and 1091 cm^{-1} can
148 be attributed to vaterite which normally exhibits a characteristic triplet at 1075, 1081 and
149 1092 cm^{-1} ^[19]. Here, the band at 1081 cm^{-1} is overlapped by the more intense ν_1 carbonate
150 band at 1085 cm^{-1} assigned to the aragonite and calcite polymorphs. Also, at 701 – 706 cm^{-1}
151 ν_4 carbonate bands corresponding to aragonite were observed. A second carbonate peak
152 appeared at 711 cm^{-1} for calcite. In the range between 730 and 760 cm^{-1} , three bands were
153 observed at 739, 743 and 750 cm^{-1} which correspond to vibrations of vaterite.

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

157 In the Raman spectra of the samples exposed to 60 and 80 % RH, bands at 1085 cm^{-1} ,
158 712 cm^{-1} , 357 cm^{-1} and 281 cm^{-1} were recorded. The band at 357 cm^{-1} is characteristic for
159 portlandite, whilst the others are attributable to calcite ^[20]. Intensity of the calcite bands
160 increased with increasing RH. Similar observations were made for lime based materials by El-
161 Turki *et al.* [21].

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

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

171

172 **Conclusion**

173 In the present work, the influence of relative humidity and atmospheric carbon dioxide on
174 CaO (free lime), a minor constituent of Portland cement, was investigated. The combination
175 of micro-Raman spectroscopy, x-ray diffraction analysis and SEM imaging allowed tracking
176 of the changes occurring on the surface of CaO exposed to moist air at 80 °C. After exposure
177 to low RH, total conversion of CaO to $\text{Ca}(\text{OH})_2$ was observed. Subsequently, initially formed
178 $\text{Ca}(\text{OH})_2$ underwent partial carbonation into amorphous calcium carbonate. At low humidities
179 (10 – 20 % RH), this reaction was observed only by Raman spectroscopy and not by x-ray
180 diffraction. Exposure to higher relative humidities (≥ 40 %) led to the formation of crystalline
181 calcium carbonates which were x-ray detectable. At moderate RH (40 %), the three different
182 calcium carbonate polymorphs (calcite, aragonite and vaterite) co-exist while at increasing
183 RH, calcite becomes increasingly prevalent. Exposure to different RH levels also impacts the
184 crystal sizes of the reaction products, with larger crystals produced at higher RHs. The results
185 confirm the potential of Raman spectroscopy in the study of the hydration behaviour of minor
186 cement constituents, particularly when amorphous products are involved in the reaction
187 processes.

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242 **List of captions for all figures**

243

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

246

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

249

250 **Figure 3.** Micro – Raman spectra for CaO prehydrated for 24 h at 40 % rel. humidity and 80
251 °C deconvoluted for the individual components portlandite, calcite, aragonite and
252 vaterite present in the sample, shown in four different ranges.

253

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

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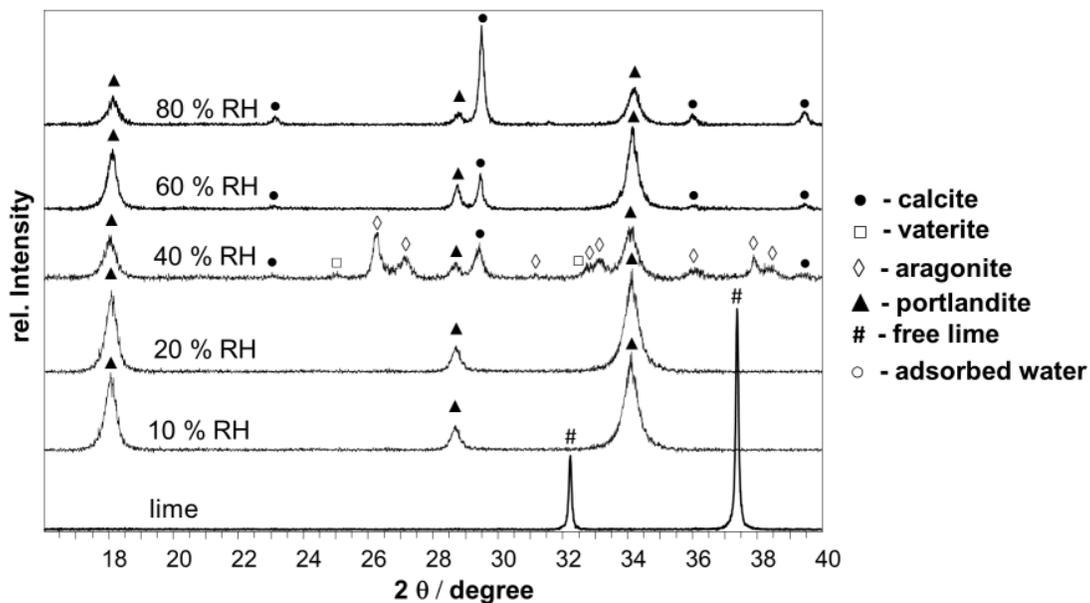
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276 **Figures:**

277

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 279 formation of different hydration and carbonation products

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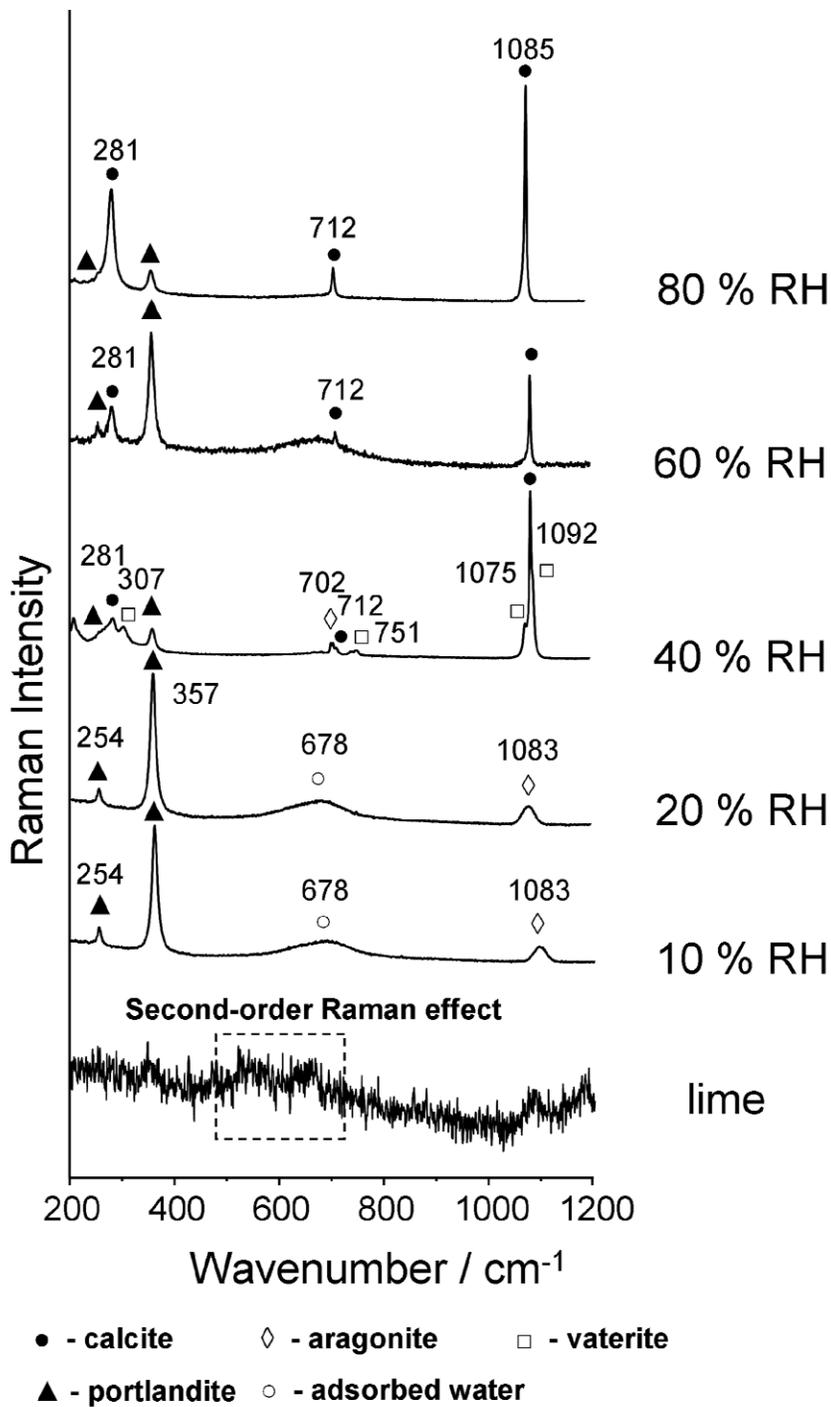
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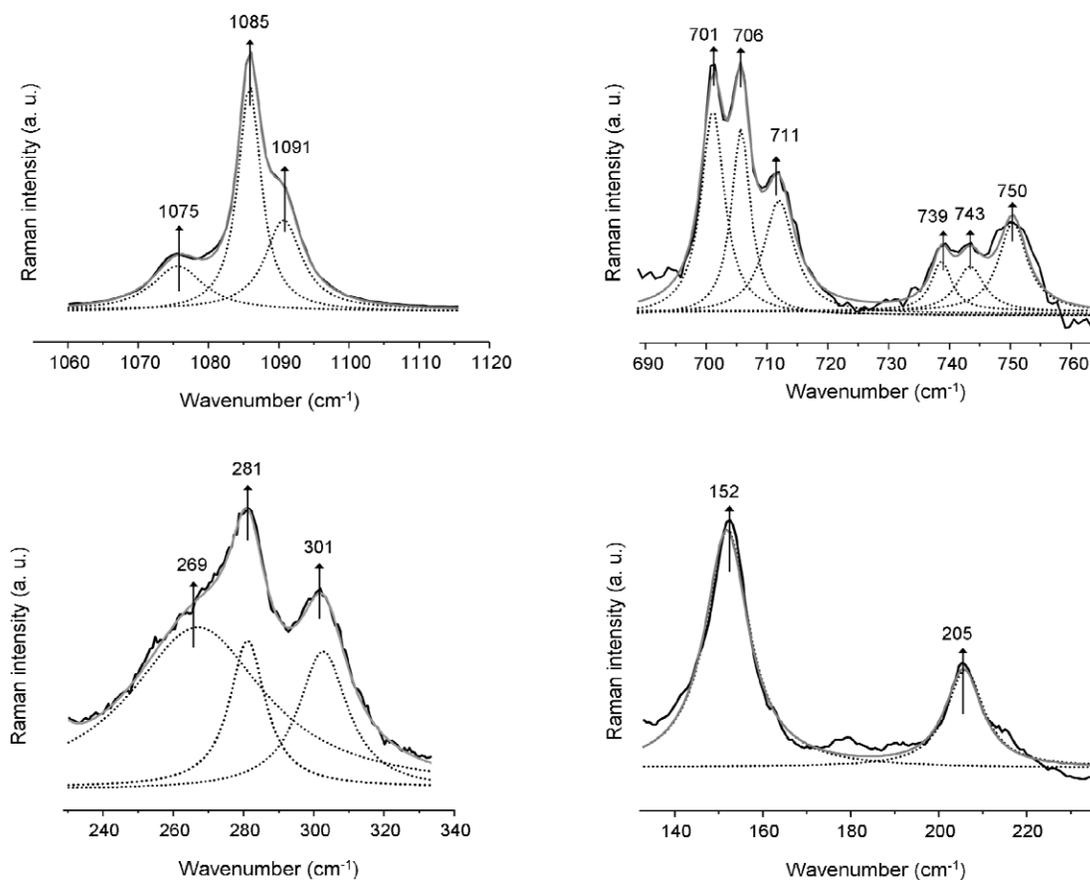
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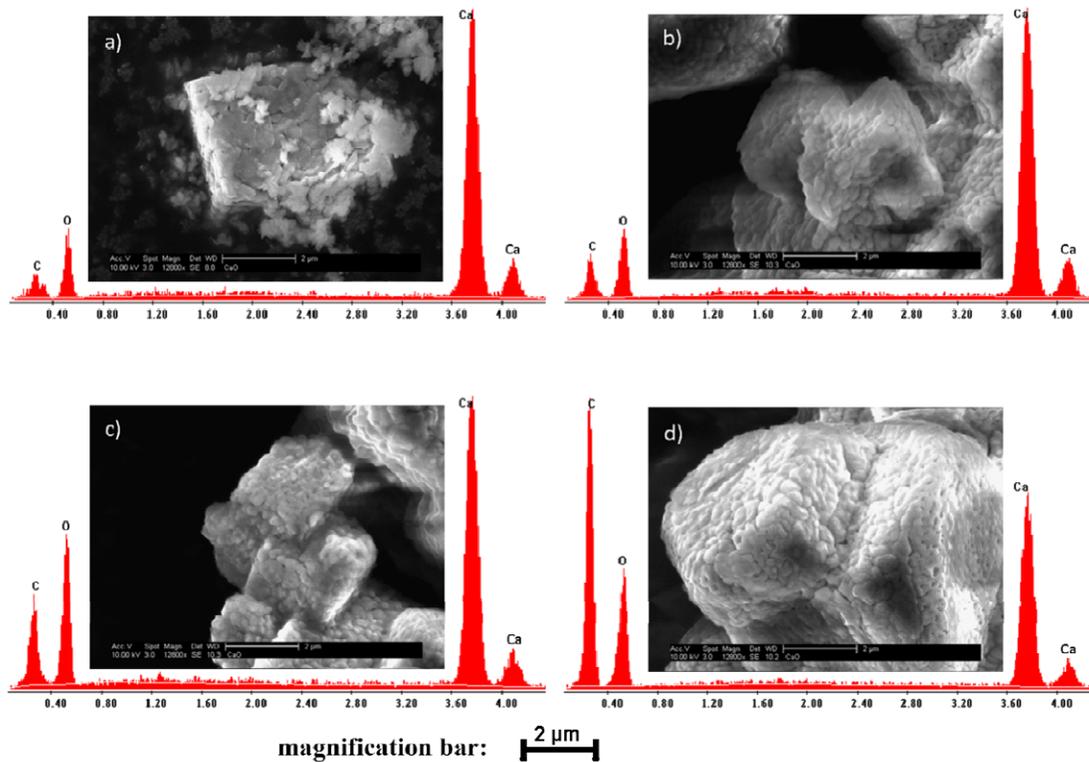
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317 **Figure 4.** SEM micrographs and EDX spectra of CaO samples, fresh (a) and stored at 20 %
 318 RH (b), 40 % RH (c) and 80 % RH (d); storage conditions: 80 °C, 24 hours;
 319 magnification: 12800 x

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 CaCO₃
- (5) Importance of Raman spectroscopy in the study of amorphous products is shown