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Micro-Raman spectroscopy applied to depth profiles of carbonates formed in lime mortar

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Abstract

Carbonation takes place in building materials when atmospheric CO_2 reacts with Ca^{2+} present in the pore solution. Of the three crystallized forms of calcium carbonate, calcite is the most thermodynamically stable. Raman spectroscopy is a very useful technique for distinguishing between calcite, aragonite and vaterite. In the present study, micro-Raman techniques are used for the first time to establish the existence of various forms of calcium carbonate at different depths in fully carbonated lime mortar, in trials conducted at a temperature of 20 °C and 75% relative humidity in a chamber with atmospheric CO_2. A new model is introduced for samples containing two or three polymorphs. The size of the calcite crystals formed, also determined with this technique, was estimated to be between 25 and 30 μm.

Keywords: Spectroscopy; Carbonation; $CaCO_3$

1. Introduction

Carbonation is a factor of major importance in building materials such as cement, lime pozzolan mortars or concrete, as a number of significant properties (porosity, mechanical strength, etc.) are closely related to this process, which takes place when atmospheric CO_2 molecules react with Ca^{2+} ions present in the pore solution. Calcite is usually the primary polymorph formed during carbonation, although vaterite and aragonite may also appear as secondary products.

Depending on experimental conditions, calcium carbonate crystallizes as calcite, aragonite or vaterite. Calcite is the most thermodynamically stable of the three, followed by aragonite and vaterite in that order.

Behens et al. [1] and Anderson [2] reported that vibrational spectroscopic techniques such as Raman spectroscopy are highly effective in distinguishing among calcite, vaterite and aragonite. In calcite three vibration modes are Raman-active: ν_1, ν_3, ν_4 (1085, 1450 and 712 cm^{-1}, respectively). In the Raman spectrum for aragonite signals are detected for vibration modes ν_1 (1085 cm^{-1}), ν_3 (very weak) and ν_4 (doubly-degenerate—700 and 704 cm^{-1}). The ν_2 vibration is also observed at 852–854 cm^{-1} although the intensity is very weak [3]. Six Raman-active vibration modes appear in vaterite spectra. Vibration mode ν_1, which is expected to be nondegenerate, actually splits into a doublet at 1074 cm^{-1} and 1090 cm^{-1}. The ν_4 vibration mode also splits into a doublet at 740 and 750 cm^{-1}. Here also, modes ν_2 and ν_3 are very weak, and as such undetectable.

The most intense Raman bands in the lattice vibration region appear at 280, 205 and 300 cm^{-1} for calcite, aragonite and vaterite, respectively.

Unfortunately, the strongest signals in all three calcium carbonate phases, at 1090 cm^{-1} for vaterite and 1085 cm^{-1} for calcite and aragonite, overlap and cannot be used for analytical purposes.

Gabrielli et al. [4] used SEM and TEM to investigate the structure and morphology of small nuclei of the three varieties of calcium carbonate. They found that calcite and

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aragonite crystals were always of excellent quality, with well-defined habits and with very few flaws in the crystals. By contrast, three different types of vaterite nuclei were identified on the grounds of morphology, which the authors described as ‘hemispherical spherulite’, ‘volcano shape’ and ‘apricot kernel’.

In lime mortars, generally a rather thick material, carbonation on the outer surface may well differ from the process inside the mortar, since the CO_2 diffusion coefficient and steric hindrance may impact crystal growth.

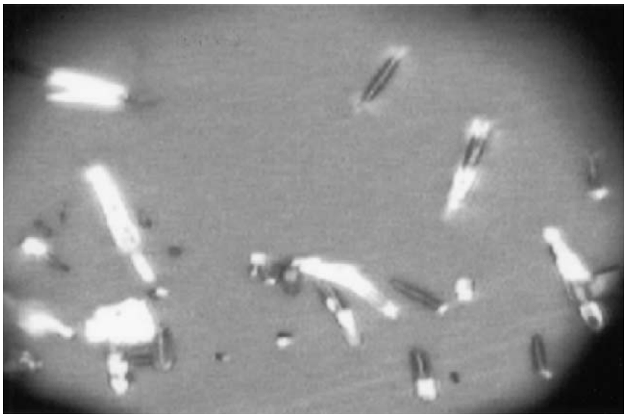
This paper report on the first study conducted with micro-Raman spectroscopy of the calcium carbonate polymorphs formed at different depths in lime mortar as a result of CO_2 diffusion. Calcite, aragonite and vaterite as well as binary and ternary mixtures were synthesised to establish the marker bands with which to identify the different forms of calcium carbonate. A new model was formulated for samples containing two or three polymorphs. The size of the calcite crystals formed could also be determined with this spectroscopic technique.

2. Experimental

Lime mortar specimens measuring 5 × 3 × 0.5 cm, whose composition and preparation have been described previously [5], were cured in a chamber with atmospheric CO_2 at a temperature of 20 °C and 50% relative humidity until the initial $Ca(OH)_2$ was totally carbonated. X-Ray diffraction and FTIR spectroscopy techniques were used to determine total carbonation.

Only analytical grade chemical reagents were used in this experiment.

Aragonite was precipitated by adding 20 ml of a thermostatted solution (70 °C) of 1.0 M $Ca(NO_3)_2$ to a stirred and thermostatted solution (70 °C) of 200 ml 0.1 M Na_2CO_3. The resulting solution was stirred for 5 min, filtered immediately, washed with water at 70 °C, and finally allowed to air-dry (method described by Mikkelsen et al. [6] as modified by Wray and Daniels [7]). The Raman spectra of the sample showed that the aragonite synthesised contained calcite impurities.



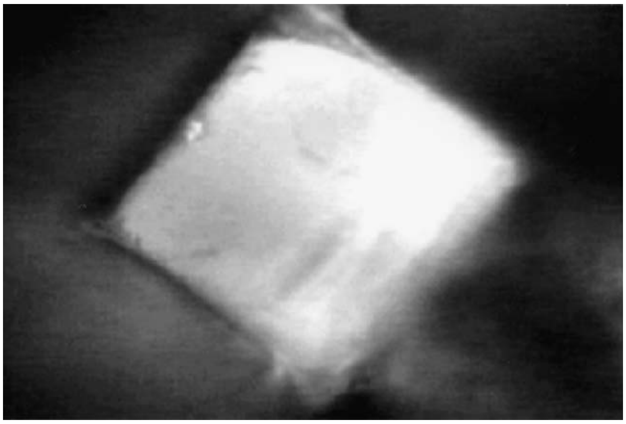
Micrograph 2. Aragonite needlelike crystal shape observed at × 500 magnifications.

A similar procedure was to precipitate vaterite, but at a lower temperature, namely 33 °C (Ref. [6] as modified in Ref. [7]). As in the case of aragonite, the Raman spectra showed that the sample contained calcite impurities.

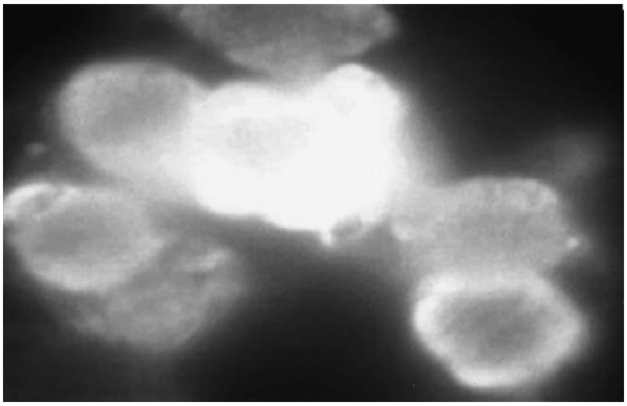
Aragonite (with calcite impurities) and vaterite (likewise with calcite impurities) were mixed to obtain a sample with all three calcium carbonate polymorphs.

Two different micro-Raman spectra were obtained for the sample containing two forms of calcium carbonate. The first was collected at a low magnification (× 100) to provide an overview of the sample with the spectra of both polymorphs. The second was obtained at a higher magnification (× 500) to show the results for only one of the polymorphs at a time.

A cross section in depth of the lime mortar specimens was micro-Raman analysed to assess the calcium carbonate polymorphs formed during carbonation. Raman spectroscopy was performed from the surface of the sample to collect spectra at the following depths: 0, 0.1, 0.5, 1.2, 2.1, 3.7, 4.5, 4.8, and 5.0 mm.



Micrograph 1. Calcite rhomb crystal observed at × 500 magnifications.



Micrograph 3. Vaterite spherulites crystal shape observed at × 500 magnifications.

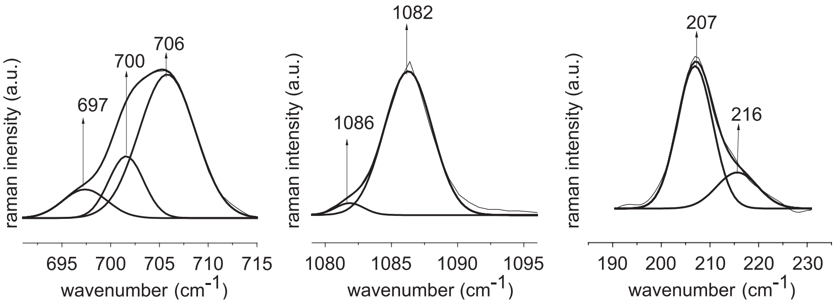


Fig. 1. Micro-Raman spectra of spherouloids observed in the aragonite sample at high magnifications (× 500). Characteristic Raman bands from aragonite are observed.

2.1. Raman instruments

FT-Raman spectra were obtained with using an RFS 100/S Brucker spectrophotometer. Excitation of the 1064-nm excitation line was provided by an Nd:YAG laser. Resolution was set at 4 cm^{-1} and 180° geometry was employed. The laser output power at the sample was 50 mW.

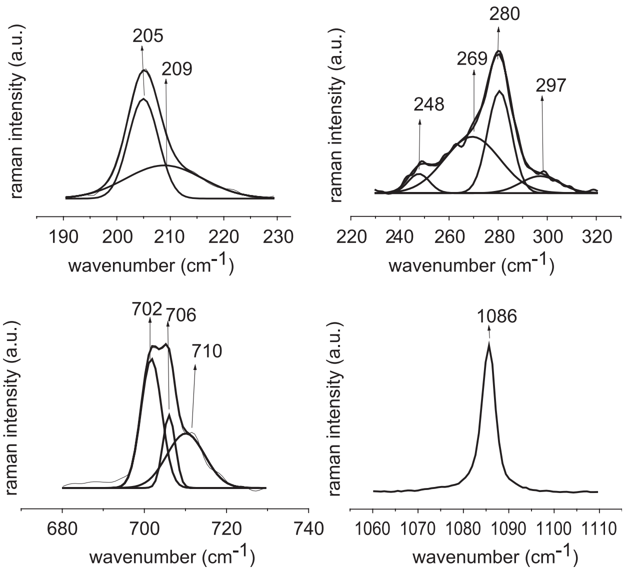


Fig. 2. Micro-Raman spectra of aragonite sample at low magnifications (× 100). Characteristic Raman bands from both calcite and aragonite are observed.

Micro-Raman and confocal micro-Raman measurements were taken with an RM1000 Renishaw Raman Microscope System equipped with a diode laser at 782 nm, a Leica microscope and an electrically refrigerated CCD camera. The spectra shown here were obtained with the following magnification objective lenses: 5 × , 20 × , 50 × and 100 × . The laser output was 25 mW. The software employed for data acquisition and analysis was WIRE for Windows and Galactic Industries' GRAMS/32TM.

The spectra were fitted using a computer program (Origin Version 6.0) for better peak resolution.

3. Results and discussion

The Raman spectra of the three polymorphs prepared concurred well with previously reported results [8–10]. The optical micrograms found for calcite (Micrograph 1), aragonite (Micrograph 2) and vaterite (Micrograph 3) confirmed the rhombus, needlelike and spherulite crystal shapes, respectively, of the crystals of these compounds. FT-Raman techniques were used to characterize the calcite, aragonite, vaterite and mortar specimen surfaces. Micro-Raman spectroscopy has been shown to be a useful tool in the study of microscopic samples. This technique combines the properties of traditional vibrational spectroscopy, fur-

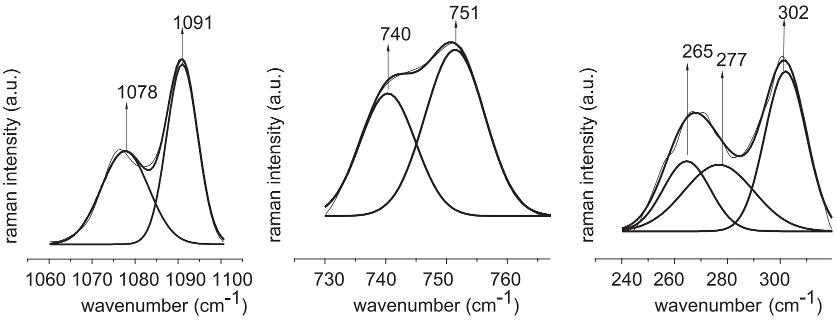


Fig. 3. Micro-Raman spectra of some needles observed in the vaterite sample at high magnifications (× 500). Characteristic Raman bands from vaterite are observed.

nishing compositional and chemical bonding information simultaneously, with the additional advantages afforded by a much smaller analysis spot than in conventional Raman techniques. Moreover, micro-Raman spectroscopy provides for the simultaneous observation and analysis of different crystal or phase morphologies.

Higher magnifications (× 500) of the aragonite sample (Fig. 1) revealed that parts of the precipitate consisted of spheruloids only (Micrograph 2). Micro-Raman spectra of the spheruloid sample had bands characteristic of aragonite [1085 cm^{-1} (ν_1), 700, 704 cm^{-1} (ν_4) and 205 cm^{-1} (lattice mode)]. At lower magnifications (× 100) both spheruloid and rhombus crystals were observed and tested; the peaks on the resulting Raman spectra were characteristic of calcite and aragonite (Fig. 2). The strongest Raman signal found for calcite and aragonite was at 1085 cm^{-1}. A secondary carbonate peak, namely an in-plane band, appeared at 712 cm^{-1} for calcite, and observed to split into two nondegenerate components in aragonite, at 700 and 704 cm^{-1}.

Needles (Micrograph 3) with Raman spectra typical of vaterite were observed in vaterite samples under high magnification [× 500) (1090 and 1076 cm^{-1} (ν_1); 740, 750 and 701 cm^{-1} (ν_4); and 267 and 302 cm^{-1} (lattice mode)] (Fig. 3). At the lower magnification (× 100) a mixture of needles and rhombus crystals (vaterite and calcite respectively) were observed. The respective micro-Raman spectra showed bands characteristic of calcite and vaterite (Fig. 4). In this case the highest calcite peak, at 1085 cm^{-1}, overlapped with the vaterite signal at 1090 cm^{-1}. Smaller peaks also appeared at 712, (ν_4 for calcite), 740 and 750 cm^{-1} (ν_4 for vaterite) and 210, 280 and 300 cm^{-1} in the lattice mode vibration region for both salts.

In the sample containing all three polymorphs (calcite, vaterite and aragonite), spectra were only collected at the lower magnification (× 100) (Fig. 5), since the individual spectra for the three salts, found at the higher magnification, had already been obtained. The strongest signal at 1084 cm^{-1}, corresponding to vibration mode $\nu_{3,}$ is produced by

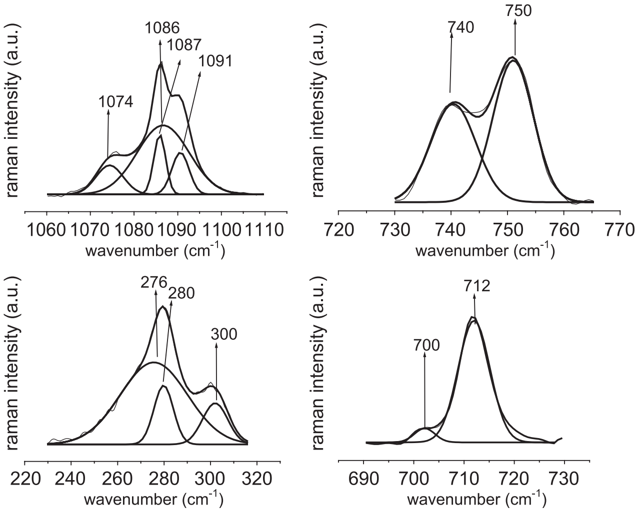


Fig. 4. Micro-Raman spectra of vaterite sample at low magnifications (× 100). Characteristic Raman bands from vaterite are observed.

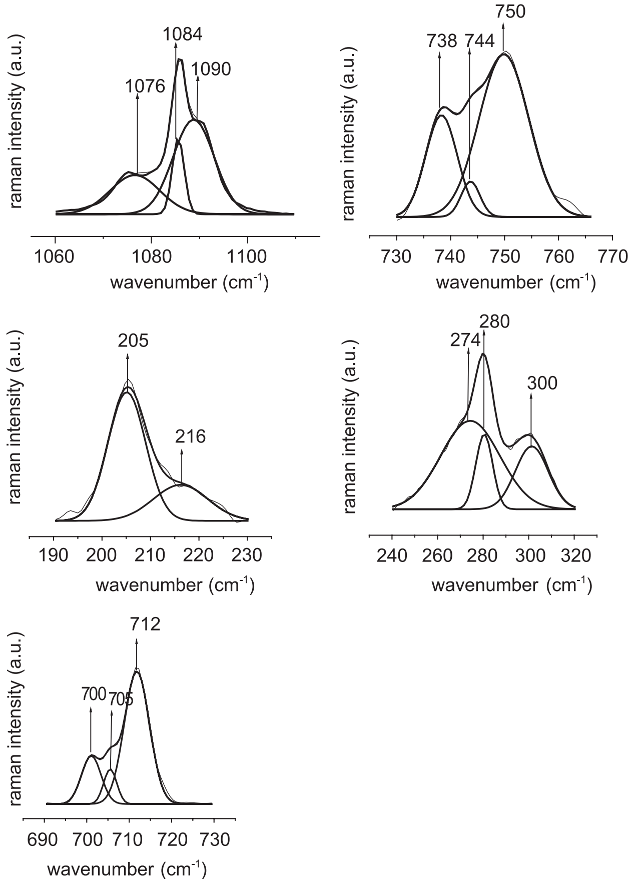


Fig. 5. Micro-Raman spectra of a mixture of calcite, aragonite and vaterite at × 100 magnifications.

Table 1
Main vibrations observed in the lime mortar at different deepness

Distance (mm)	ν_1	ν_4	Lattice mode
0	1084	707	274
	1087	712	280
		721	293
0.1	1084	712	280
	1087		
0.5	1086	710	277
	1088	712	280
1.2	1084	704	264
	1088	712	277
			280
2.1	1084	712	280
	1088		
3.7	1086	712	261
			280
4.5	1084	703	263
	1087	712	280
4.8	1084	700	280
	1087	712	
5.0	1084	701	277
	1088	712	280

Table 2
Polymorphic form of calcium carbonate at different deepness obtained from areas ratio

	A_{704}/A_{712}	A_{300}/A_{280}	A_{300}/A_{750}	A_{264}/A_{712}	Polymorphic form
Calcite				19.1	
Aragonite					
Vaterite			4.8		
Cal–Arag	0.4			3.4	
Cal–Vat		0.9	2.8	1.7	
Cal–Arag–Vat	1.1	1.4	7.5	3.0	
Mortar deepness (μm)					
0				4.4	calcite
0.1	0.5			8.4	cal, arag
0.5				4.9	cal
1.2	0.1			2.9	cal, arag
2.1				5.9	cal
3.7				4.7	cal
4.5				5.1	cal
4.8	0.09			6.6	cal, arag
5.0	0.1			2.9	cal, arag

Table 3
A_{280}/A_{712} ratio for calcite crystals with different sizes

Calcite size (μm)	A_{280}/A_{712}
10	18.8
15	11.5
20	15.4
25	10.2
30	3.4
agglomerate	3.6

both calcite and aragonite. The two small peaks at 1090 and 1074 cm^{-1} reflect the v_1 double degenerate signal in vaterite. In the v_3 range, i.e., 700–750 cm^{-1}, six bands were observed at 700, 704, 712, 738, 740 and 750 cm^{-1}. The first two correspond to aragonite, the third to calcite and the last three to vaterite vibrations. Bands reflecting lattice mode vibrations were found at 205, 216, 274, 280 and 300 cm^{-1}.

These results clearly show that the highest peak, produced by v_1 vibrations, is not suitable for identification in mixtures with two or three polymorphs.

Table 1 shows the v_1, v_4 and lattice mode values for lime mortar at different depths. As quartz, which peaks at 205 cm^{-1}, is present in all the samples, the 200–250 range is not shown since this band may overlap with the calcite signal.

In order to ascertain whether more than one polymorph was present at different depths of the mortar, the ratio of the areas (relative intensity) of different nonoverlapping peaks of the various forms was analysed. The bands at 280 and 712 cm^{-1} were selected for calcite and at 300 and 750 cm^{-1} for vaterite. Only the band at 704 cm^{-1} could be used for aragonite, since the peak at 205 cm^{-1} overlaps with the quartz band and the strongest signal, at 1084 cm^{-1}, overlaps with vibration mode ν_1 in calcite. The results are shown in Table 2.

The Raman spectra for lime mortar at different depths are shown in Fig. 6. The characteristic Raman bands for calcite in the internal mode ν_1 region (symmetric stretching) at 1084 cm^{-1}, in ν_4 (in plane bending) at 712 cm^{-1} and in the lattice mode vibration region at 280 cm^{-1} are readily distinguishable. In lime mortar, Raman bands characteristic of quartz, at 465, 360, 396, 205 and 130 cm^{-1}, are also observed. The main peaks obtained at different depths in the lime mortar specimens are presented in Table 1.

Since the peaks at wave-numbers below 400 cm^{-1} are related to the lattice mode, we propose a new model to determine the crystal size of calcium carbonate polymorphs, using the A_{280}/A_{712} ratio in calcite, A_{205}/A_{705} in vaterite and A_{300}/A_{750} in aragonite.

In the sample containing only calcite, the ratio of the areas (A_{280}/A_{712}) was nearly 19, which was taken as the reference value for calcite. The size of the rhombus crystals analysed was 10 μm. This ratio was lower than 19 at all depths in the lime mortar and in the sample containing more than one polymorph. Micro-Raman (× 500) investigations were performed on calcite crystals and the ratio of the areas A_{280}/A_{712} of the crystal determined to attempt to explain these results. The size of the calcite crystals used here refers to the length of the side of the rhombus. It may be readily deduced from these values, presented in Table 3, that as calcite size increases the ratio of the areas A_{280}/A_{712} decreases, with a sharp decline for sizes under 25 μm. As the size of the calcite crystal used for the A_{280}/A_{712} ratio

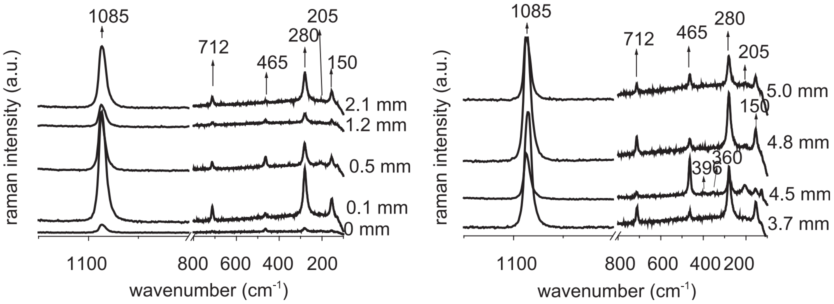


Fig. 6. Raman spectra of lime mortar at different depth.

Table 4
A_{205}/A_{704} ratio for aragonite needles with different size

Aragonite size (μm)	A_{205}/A_{704}
7	1.5
9	1.6
3	4.1

was 10 μm, it may be assumed that the calcite crystals formed in the lime mortar were larger than 10 μm.

Unfortunately, the same area ratio for vaterite could not be found, given that the rather amorphous shape of this compound makes it very difficult to determine the size of the particle shown in the micro-Raman spectrum.

For the needle-shaped aragonite crystals, the A_{205}/A_{705} ratio for the larger needles was nearly constant, with values around 1.5 (Table 4). This value corresponds to needle length. In smaller crystals (3 μm), the peak area ratio increases. As the band at 205 cm^{-1} overlaps with the quartz peak, the size of the aragonite needles present in the mortar could not be ascertained.

The amount of any polymorphic phase of calcium carbonate in lime mortar is closely related to band intensity. Since this is not the only factor that affects the intensity of the bands, the ratio of two bands was used to establish the relative amounts of calcite and aragonite present. No bands were observed at 300 cm^{-1} or 750 cm^{-1} at any depth, indicating that the sample contained no vaterite.

The A_{705}/A_{712} ratio found for the calcite–aragonite mixture was 0.4 (Table 2). In the mortar at a depth of 1 mm this ratio was 0.5, indicating that both calcite and aragonite were present in amounts similar to those contained in the standard sample. No conclusions could be drawn with respect to the relative amounts of the two polymorphs present at other depths.

The last column in Table 2 shows the $CaCO_3$ polymorphs present in the sample.

4. Conclusions

Micro-Raman spectroscopy can be used to quantify the calcium carbonate polymorphs formed at different depths in lime mortar without destroying the sample. Although calcite is apparently the only form of calcium carbonate in the mortar, analysis at different depths also revealed the existence of aragonite in the sample. Lime mortar contains no vaterite at any depth.

The size of the calcite crystals in lime mortar estimated with the new method presented here was between 25 and 30 μm. Unfortunately, it was not possible to determine the size of the aragonite formed since one of the bands overlaps with the signal produced by the aggregate used in lime mortar preparation.

The results of this study show no clear relationship between calcium carbonate polymorphs and lime mortar depth. Further research is required at different carbonation stages and this line should be pursued in the future.

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