

THE ATMOSPHERIC DEPOSITION OF DICARBOXYLIC ACIDS AEROSOLS TO THE FORMATION OF THE DAMAGE LAYERS

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Abstract: Study of the morphology of calcium carbonate with the presence of Dicarboxylic Acids (DCA's) aerosol has been carried out. The experiments show that oxalic acid readily converts calcium carbonate to calcium oxalate and malonate. However, the higher molecular weight of DCA's tend not to lead to calcium dicarboxylate quite so readily. Calcium succinate and calcium adipate were observed, but more significantly succinic, adipic and glutaric acids seem to block some of calcium carbonate sites in the lattice and inhibit crystal formation. These higher molecular weight DCA's appear to encourage the transformation among the three polymorphs of calcium carbonate: calcite, aragonite and vaterite. Vaterite was especially evident in the case of adipic and glutaric acids. The presence of vaterite may be a clue to the activities of the higher DCA's. The conversion of calcium carbonate to calcium dicarboxylate by the presence of DCA's can be considered as the morphology transformation of the carbonatic stone from the crystallisation-dissolution in the porous matrix of the DCA's, that lead to mechanical stresses and chemical alterations that can damage monuments and historical buildings.

KEYWORDS: Dicarboxylic Acids, Calcium Carbonate, calcite, aragonite, vaterite, building materials

Introduction

Calcium carbonate (CaCO_3) is a common substance found as a limestone, dolomite etc in many parts of the world (Darweesh, 2001; Liu *et al.*, 2007). The alkaline aerosols derived from calcareous regions are known to react with acids in the atmosphere. It is reasonable to consider whether aerosol DCA's are likely to form under ambient conditions. This study showed that DCA's can influence the calcium dicarboxylate formation by blocking some of the calcium carbonate sites in the lattice and modifying crystal growth. The conversion of calcium carbonate to calcium dicarboxylate by the presence of DCA's can be considered as the morphology transformation of the carbonatic stone from the crystallisation-dissolution in the porous matrix of the DCA's, that lead to mechanical stresses and chemical alterations that can damage monuments and historical buildings.

It has been proven that DCA's can also influence one or several crystallisation steps (nucleation, crystal growth, aggregation) and, as a

consequence, can control the formation of various crystal phases, which are not easily formed under natural environments (Liu *et al.*, 2007). In addition, DCA's complexation have been used as micro-reactors for preparation of specific morphologies, sizes or new crystal structures of inorganic or organic materials (Okochi and Brimblecombe, 2002a).

Some water-soluble organic compounds are well stabilised in industries, which are sometimes used together with the CaCO_3 . The complex interaction between DCA's and CaCO_3 may play an important role in controlling crystallisation of inorganic materials, which can be exploited as confined crystallisation environment (Wei *et al.*, 2003). The different morphology of the crystal is attributed to the shield effect of the compounds on the adsorption of DCA's on the crystal surface.

An important rationale behind this was an observation by a large number of workers who stated that DCA's have an influence on calcium carbonate formation by blocking some of the carbonate sites in the lattice and crystal

growth (Mann *et al.*, 1990). In the presence of dicarboxylates, three polymorphs of calcium carbonate: calcite, aragonite and vaterite, could be formed, depending on the reaction condition. The three crystalline phases of calcium carbonate can often be easily recognised from their distinctive shape as shown in Figure 1.

The aim of this chapter is to investigate the crystallisation of calcium dicarboxylate in the presence of DCA's to shed light on how different each one of the low molecular weight (LMW) of DCA's can influence the crystallisation behaviour of calcium carbonate under vigorous super-saturated and stirring condition.

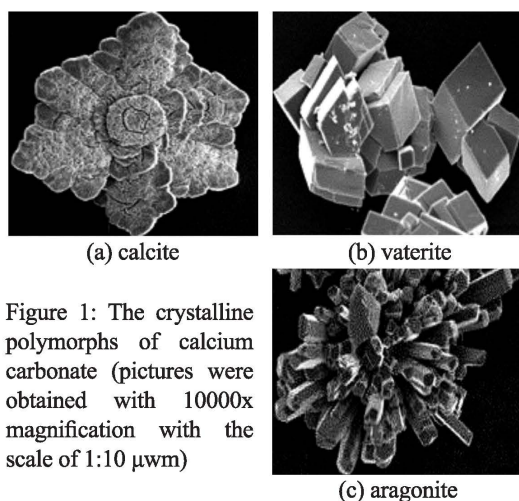


Figure 1: The crystalline polymorphs of calcium carbonate (pictures were obtained with 10000x magnification with the scale of 1:10 μm)

Experimental

Reagents

All the chemicals, including calcium chloride (CaCl_2 , >99%), sodium carbonate (Na_2CO_3 , 99.95%), oxalic acid (>99%), malonic acid (>99%), succinic acid (>99%), glutaric acid (>99%) and adipic acid (>99%) were of analytical grade and used without further purification. Doubly-deionised water was used to prepare aqueous solutions of CaCl_2 and Na_2CO_3 just before crystallisation experiment. In all the reaction systems, saturated dicarboxylic acids (DCA's) solutions were only added into Na_2CO_3 solution before mixing with CaCl_2 solution.

Crystallisation procedure and subsequent treatment of CaCO_3 crystals

CaCO_3 crystals were precipitated by the method of rapidly pouring aqueous solution of CaCl_2 (0.1 M, 100 ml) into a 300 ml beaker containing aqueous solution of Na_2CO_3 (0.1 M, 100 ml), which was stirred at a constant rate of 200 rpm by a teflon-coated magnetic stirring bar. The mixing solution was then continuously stirred at the same frequency to minimise the heterogeneous nucleation at the glass wall, and this process lasted 24 hours to allow further crystal growth by Ostwald ripening. In the process of precipitation, the reaction systems were all kept at $25^\circ\text{C} \pm 0.2^\circ\text{C}$ in a thermostatic bath and at a constant pH value of ca. 7.0. All samples were kept about a month for incubation and every additional acid was divided into two concentrations: saturated (2 M) solutions and unsaturated (0.01M) solutions. After the crystallisation experiment, the obtained CaCO_3 crystals were filtered through cellulose nitrated/acetate membrane filters (0.2 μm), and subsequently rinsed three times with doubly-deionised water, then dried in vacuum desiccators at room temperature for 24 hours.

Characterisation of CaCO_3 - dicarboxylate crystals

All samples were Au-coated prior to be examined by an Hitachi S-4300 scanning electron microscope (SEM), fitted with a field emission source and operated at an accelerating voltage of 15 kV. Selected area electron diffraction (SAED) of the synthesised CaCO_3 crystals was operated at the accelerating voltage of 200 kV on a JEOL 2010 transmission electron microscope. The X-ray diffraction (XRD) measurements were conducted using a Rigaku D/max-2400 powder X-ray diffractometer with $\text{Cu K}\alpha$ radiation (40 kV, 120 mA), and 0.02° step and 2 theta range of 20° – 60° were selected to analyse the crystal structure and crystal orientation. The absolute component of the crystal will show up as d-spacings/Å in accordance with the hkl on the table from the International Tables for X-Ray Crystallography database which was also occupied in the XRD. The DCA's content in the preparation of the CaCO_3 - dicarboxylate crystals was tested by thermo-gravimetric analysis (TGA)

using a Netzsch Sta409 TGA analyser, purged with nitrogen gas.

Results and Discussion

Characterisation of CaCO₃ with the presence of oxalic acid

The SEM investigation reveals that the structure of calcium oxalate monohydrate as shown at Figure 2 was elongated with bi-pyramid crystal shape. The calcium oxalate monohydrated crystals were normally a bi-pyramid shape due to the predominant development of $\{101\}$ crystal faces. This is supported by the research of Brecevic and Skrtic (1986). It is also very similar with the structure of the *weddellite* or calcium hydrate which crystallises in the tetragonal system with the classic crystal shape with bi-pyramid face and also the well known characterisation of the multi-cube shape (Sabbioni and Zappia, 1992).

In saturated condition, there was an outgrowth of the calcium oxalate monohydrate crystals along the different texture direction, resulting in elongated crystals and the development of the new crystal face. A separation surface between the oxalates and carbonate was not observed, but rather a layer where both salts are present, showing the characteristic structure of a metasomatic substitution.

The XRD diffractogram pattern from Figure 3 exhibits the characteristic reflection for calcium oxalate monohydrate (d -spacing/Å : 5.89, 3.65, 2.95, 2.49, 2.25, 2.06, 1.94, 1.81; corresponding to hkl : 110, 108, 100, 60, 40, 20, 60, 65) from the International Tables for X-Ray Crystallography database. In fast-reaction crystallisation experiments, the nuclei of amorphous CaCO₃, which is the most unstable solid-state phase, are initially obtained, and then transform to calcium oxalate. The nucleation mechanism depends on the supersaturation of the solution (Belcher and Gordon, 1964). Söhnle and Mullin suggested that in CaCO₃ crystallisation experiments, at low super saturations, nucleation is predominantly heterogeneous, whereas at high super saturations, homogeneous nucleation became predominant (Söhnle and Mullin, 1988).

The SEM images shown in Figure 2 indicated the obviously different morphology for different concentrations. For the unsaturated oxalic acid

(0.01 M) (see Figure 2a and 2b), it is very clear there is no obvious change in morphology except for the narrower size distribution. An interesting phenomenon is that more a smooth crystal face is obtained at the higher concentration than at low concentration.

Compared with the crystals prepared for the saturated system (concentration of oxalic acid = 2 M), both the crystal shape and the crystal size changed greatly with the variation of oxalic acid concentrations. When oxalic acid concentration is 2 M, mixture-shaped particles with average size of 3–4 μm are obtained (Figure 2c), which contain regularly rhombohedral crystal and irregular spheres with rough surface. Higher magnification image (Figure 2c, inserted as (e)) reveals that the irregular spheres are composed of many little rhombus slabs with length of 100–300 nm. Surprising results are obtained for system (Figure 2d). The rhombohedral crystals disappeared and mono-dispersed hollow-spherical particles with average size of 3–4 μm are obtained. Magnified picture shows that the hollow sphere with an opening hole is composed of very small crystallites (Figure 2d, inserted as (f)). It should be pointed out that higher oxalic acid concentration led to the formation of smaller crystal. There was no detection of CaCO₃ polymorph in the sample.

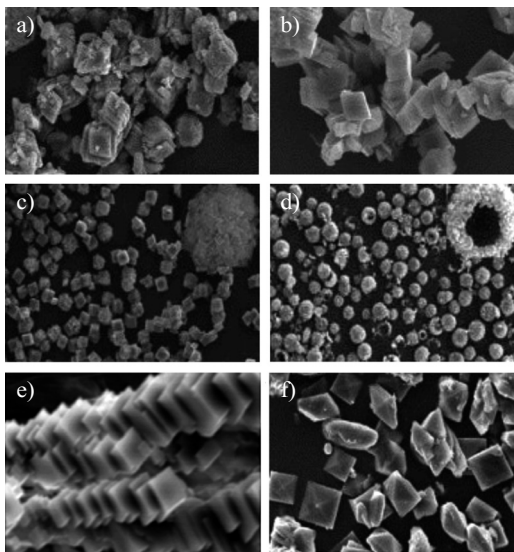


Figure 2: SEM imaging of the precipitated calcium oxalate monohydrate crystal; (a) – (d) at 2000x magnification with the scale of 1: 100 μm. (e) and (f) at 10000x magnification with the scale of 1: 10 μm.

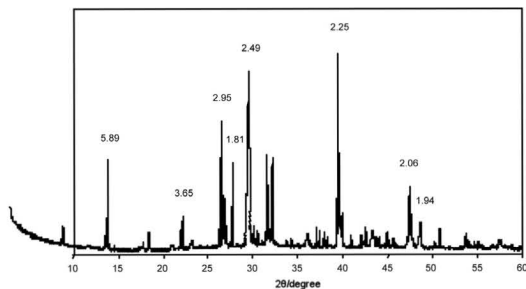


Figure 3: The XRD pattern of CaCO_3 particles precipitated in the presence of oxalic acid.

Indeed, the morphology of the samples on Figure 2 has similar structure with the calcium hydrate or *weddellite*. *Weddellite* can be formed easily in natural systems and must not be considered as a rare mineral, because it is widely distributed in nature (Sabbioni, 1995). It has been found to form a superficial layer on marbles and lime stones constituting monuments, historical buildings and artifacts from different sites and historical ages. Moreover, they also have been observed on marbles and limestone of natural outcrops.

Calcium carbonate is significantly more soluble than calcium oxalate at pH 7. The solubility of the carbonate increases until pH 5, beyond which irreversible dissolution occurs (Matteini, 1996). In the absence of pollution, rain has a pH of 5 and dilute sulphuric acid can be expected to have a pH of 3 or less. Thus the oxalate is far more acid resistant and not as susceptible to the degradation caused by acid gases.

Oxalic acid can react with calcium carbonate to form a thin calcium oxalate membrane on the stone surface. Lichens are one source of oxalic acid but not all varieties of lichens produce the oxalic acid, while fungi and bacteria can also be sources of the acid. Polysaccharides and lipids, the possible result of a purposeful application, can combine to form oxalates as well.

Oxalic acid can also be produced through the transformation of hydrocarbons from industrial and urban areas (Ford *et al.*, 1994). However, Bonazza *et al.* stated that the amount of oxalic acid produced and accumulated over time was really small and insoluble. They suggested that biological activity is the main source of oxalic acid accumulation on the natural outcrops.

Characterisation of CaCO_3 with the presence of succinic acid

The crystal structures of calcium carbonate (CaCO_3) with the presence of succinic acid have been determined by SEM and single crystal x-ray diffraction. The same experimental approaches have been applied from the calcium oxalate procedure. The general structure is highly polymeric and nearly identical to those structures of CaCO_3 with the presence of glutaric acid. Structural studies of calcium-dicarboxylates were undertaken to provide a general knowledge for calcium-dicarboxylate formation from the succinic acid and also the partitioning ability of the organic compound into the formation of calcium complex in ambient atmospheric temperature.

Figure 4 shows the SEM images of CaCO_3 particles obtained in the presence of succinic acid. Hexagonal flower-like particles with monolayer petals were precipitated when the succinic acid concentration was as low as 0.01 M, as shown in Figure 4(a). With an increase of the succinic acid concentration, the petals changed from monolayer to multilayer, see Figure 4(b) and (c), where [succinic acid] was 0.01 M and 2 M, respectively. From the enlarged SEM pictures of Figure 4(d), it can be clearly observed that the petals of flower are composed of nano-crystals with size less than 100 nm.

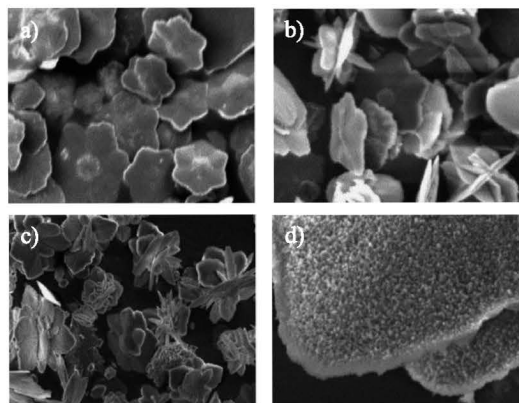


Figure 4: SEM images of CaCO_3 in the presence of succinic acid; (a)-(c) obtained with 10000x magnification and scale of 10 μm . (d) is the enlarged picture of (c) obtained with 100000x magnification and scale of 1: 1 μm .

The XRD spectrum (Figure 5) also shows the diffraction peaks characteristic of vaterite. However, the appearance of the characteristic diffraction peak of calcite at $2\theta = 18.4^\circ$, and of aragonite at 26.23° , indicated a small amount of calcite and aragonite exist. Because there is no chemical interaction among samples present or overlap of the XRD peaks used for the analysis, the polymorphic ratio of vaterite, calcite, and aragonite can be calculated by using equations described in a recent publication (Huang *et al.*, 2007):

$$f_A = \frac{3.57I_A^{221}}{I_C^{104} + 3.157I_A^{221} + 7.691I_V^{110}} \quad 1$$

$$f_C = \frac{I_C^{104} f_A}{3.157I_A^{221}} \quad 2$$

$$f_V = 1.0 - f_A - f_C \quad 3$$

The subscripts A, C and V indicate aragonite, calcite and vaterite, respectively. The content of vaterite increased from 88.3% to 93.5% when the concentration of succinic acid was increased from 0.01 M to 2 M. The contents of calcite and aragonite changed from 7.4% and 4.3% to 1.6% and 4.9%, respectively.

Compared with the conclusion made in a recent report (Jeong *et al.*, 2005) that succinic acid did not affect the morphology and polymorph of CaCO_3 precipitated by rapidly mixing CaCl_2 with Na_2CO_3 solution at ambient temperature under continuously stirring of 24 hour, this result suggests that the control ability of succinic acid may depend on the reaction method. For the fast-reaction of the crystallisation experiment, the precipitate is dominated by vaterite in the early stage, which then transforms to calcite as the incubation time increases. The study however did not carry out the details about the specific transformation time, but concentration of succinic acid deposited with Ca^{2+} ion may play an important role in the formation of flower-like particles by dynamically adsorbing and desorbing on the particle surfaces. Without the shearing effect and high supersaturation performed in this experiment, the adsorption of succinic acid may retard the transformation of vaterite to calcite and regulate the morphology.

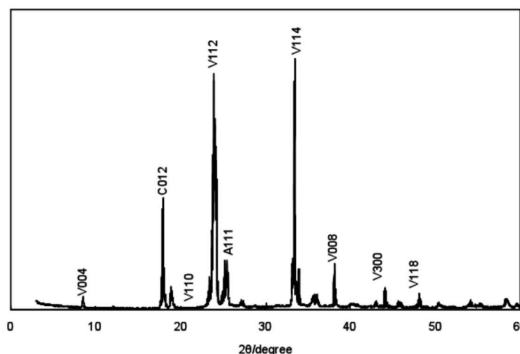


Figure 5: The XRD pattern of CaCO_3 particles precipitated in the presence of succinic acid.

1 **Characterisation of CaCO_3 with the presence of glutaric acid**

2 The crystal structures of calcium carbonate with the presence of glutaric acid have been determined by single crystal x-ray diffraction and SEM. The same experimental approaches have been applied from the calcium oxalate procedure but with an additional concentration of glutaric acid with 4 M and 6 M instead of 0.01 M and 2 M. From the XRD analysis, (d-spacing/ \AA :5.89, 9.65, 18.95, 19.20, 24.49, 26.25, 28.06, 32.89, 33.45, 38.51, 45.54 and 48.65; corresponding to *hkl*: 55, 40, 80, 100, 95, 65, 18, 25, 30, 35, 14 and 25 taken from the International Tables for X-Ray Crystallography database) the sample was detected as triethylene diammonium glutarate compound (see figure 6) and there is no detection of calcium glutarate.

However, the mixtures of calcite, aragonite and vaterite were found over the particle under observation (Figure 7a) with rhombic and sharp spherical particles with porous constituent crystals. Vaterite becomes the major product and was found to have a barrel-shaped morphology in Figure 7b. The sharp and strong peaks at Figure 6 also confirmed that the products were well-crystallised vaterite. The above results indicate that glutaric acid favours the formation of vaterite, which agrees with the results obtained in the fast-reaction crystallisation experiment carried out in the presence of succinic acid. The diameters of the ball-shaped polycrystalline aggregates ranged from 10 to 100 μm . The proportion of vaterite formed was generally higher than the other compounds.

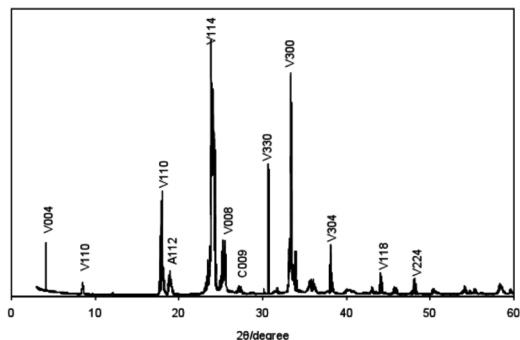


Figure 6: The XRD pattern of CaCO_3 particles precipitated in the presence of glutaric acid.

The rose-shaped particles without obvious hexagonal edges appeared at low concentration of glutaric acid, such as is shown in Figure 7(c) where the glutaric acid concentration was 0.01 M. High magnification picture inserted in Figure 7(c) indicated the particles also had coarse surfaces. When [glutaric acid] was 2 M, the dominant particles were rose-shaped particles with polished surfaces as shown in Figure 7(d). Further increase of glutaric acid concentration to 4 M resulted in the generation of hexagonal flower-like particles with larger central bulge than those shown in Figure 4(a). They were somewhat similar to those produced by Cölfen group in the presence of double hydrophilic substance (Rudloff and Cölfen, 2004) (Figure 7(e)). When [glutaric acid] reached to 6 M, bi-cone-like particles were precipitated, as shown in Figure 7(f). The size seemed to be broadly dispersed with a few particles about $10\ \mu\text{m}$ down to many small particles less than $5\ \mu\text{m}$. These results show that the morphologies of CaCO_3 particles are remarkably affected by the variation of [glutaric acid]. Usually vaterite is unable to expose (0 0 1) face that consists of a hexagonal lattice of CO_3^{2-} or Ca^{2+} ions. The attachment of positively-charged group to the negatively-charged (0 0 1) plane leads to surface stabilisation and inhibition of growth along the [0 0 1] direction (Xu *et al.*, 2006) and probably, for seeking a lower energy state, the vaterite particles show hexagonal morphology (see Figure 8).

This experimental result give ample evidence to allow assumption to be made that high molecular weight of DCA's i.e. succinic and

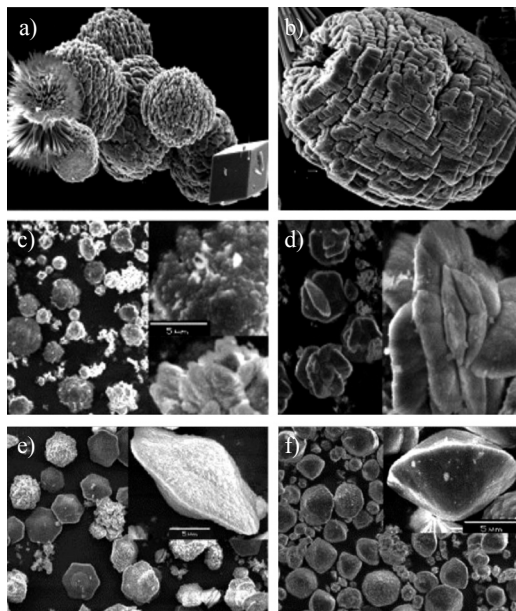


Figure 7: The typical SEM images of CaCO_3 particles with the presence of glutaric acid: (a)-(b) obtained with 100000x magnification and scale of $1:1\ \mu\text{m}$. (c)-(f) obtained with 1000x magnification and scale of $1:10\ \mu\text{m}$.

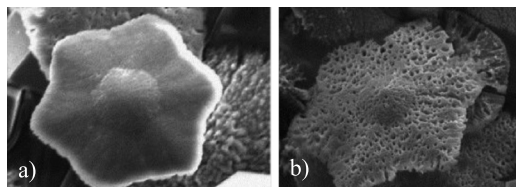


Figure 8: The typical SEM images of CaCO_3 particles with the presence of additional concentration of glutaric acid: both pictures were obtained with 100000x magnification and scale of $1:1\ \mu\text{m}$.

glutaric acid, are not suitable compounds to block or precipitate with calcium carbonate compound. It was only oxalic acid which had an influence on the formation of calcium dicarboxylate in this study. These higher molecular weight DCA's appear to encourage the transformation among the three polymorphs of calcium carbonate: calcite, aragonite and vaterite. Vaterite was especially evident in the case of succinic and glutaric acids. The presence of vaterite may be a clue to the activities of high molecular weight DCA's. Indeed, there is some support from Davis *et al.* observation of vaterite in aerosols in Shanghai and Beijing (Davis and Jixiang, 2000).

Calcium dicarboxylates on the building materials

Apart from the oxalates, the remaining DCA's have few salts of interest to mineralogists. The oxalates on stone surfaces accumulate over time and offer some protection to the degradation of carbonate stones, especially those used in buildings. The natural surfaces of calcareous rocks often exhibit the presence of calcium oxalates (*weddellite*) which have been detected in the first section of the present experiment. They were produced by pervasive transformation and also displacement of CO₂ from calcium carbonate. Both oxalate minerals are also found on monuments and artifacts, such as town walls, boundary walls and milestones, as well as on natural outcrops. However the concentrations of oxalic acid in the urban atmosphere are too low to account for the *weddellite* on buildings stones. The presence of vaterite may be a good indicator to the activities of the higher DCA's. There is evidence of the importance of small amounts of succinic and glutaric acid, encouraging the vaterite formation of crusts on building stone. Vaterite, like aragonite, is a metastable phase of calcium carbonate at ambient conditions at the surface of the building. It is found on building materials and it is typically associated with cement. Indeed, Signorelli *et al* (1996) have also determined the vaterite distribution in bonding mortars of marble inlays at Florence Cathedral (Signorelli *et al.*, 1996). Its presence in crust would be an interesting indicator of transformations due to DCA's or other organic materials.

Conclusion

The laboratory experiments showed that oxalic acid readily converts calcium carbonate to calcium oxalate. By contrast, the experiments suggested that higher molecular weight DCA's tend not to lead to calcium dicarboxylate quite so readily. These DCA's appear to take on a more complex behaviour. Calcium succinate was observed, but more significantly succinic and glutaric acids seem to have the tendency to block some of the calcium carbonate sites in the lattice and inhibit crystal formation. These higher molecular weight DCA's appear to encourage the transformation among the three polymorphs of calcium

carbonate: calcite, aragonite and vaterite. Vaterite was especially evident in the case of succinic and glutaric acids. The presence of vaterite may be a clue to the activities of the higher DCA's and there is some support to this from observation of vaterite in aerosols in Chinese cities (Davis and Jixiang, 2000).

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