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## **LIME BASED MATERIALS IN CONSTRUCTION**

### **Experimental investigations for the development and validation of atomistic models**

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#### **ABSTRACT**

Recent advances in computing power make atomistic modelling a viable approach for the study of complex chemical processes in a variety of applications. Atomistic modelling has, thus, the potential to explain some of the mechanisms of the most complex reactions occurring in construction materials such as carbonation of hydrates and the decomposition of carbonates. The research described in this paper seeks to highlight the potential of atomistic modelling applied to the materials used in the construction industry by investigating the decomposition process of dolomite. The paper, in particular, describes the results of experimental investigations that will be used to design and validate computational models. Studies undertaken using thermal gravimetric analysis, X-ray diffraction and Raman spectroscopy suggest that dolomite decomposes through the formation of Mg-rich calcite phases that, in turn, decompose forming lime and periclase. Results suggest that the view held by some researchers which describe the decomposition of dolomite through the formation of both, Ca and Mg carbonates as intermediate compounds may not be completely accurate and consequently, this process can be disregarded in developing the computational models.

**KEYWORDS:** Lime, Dolomitic lime, Dolomite, TGA, XRD, Raman spectroscopy, Mg-calcite

#### **1 INTRODUCTION**

A growing demand for low-carbon/energy materials and a move away from a reliance on cement-based binders in construction is a key future challenge. The research described in this paper seeks to address this through the development of advanced lime-based materials. This is particularly relevant as the Department of Energy and Climate Change, United Kingdom reports that the country is now committed to reducing its anthropogenic carbon dioxide gas emissions by at least 80% by 2050 relative to 1990 levels.

Lime is of traditional importance for construction, especially in new-build and conservation sectors and is enjoying renewed interest as an essential component in many emerging low carbon building technologies (Hansen et al., 2003) as it has the natural ability to sequester carbon dioxide (CO<sub>2</sub>) through carbonation.

Use of lime in the modern construction industry, however, is somewhat limited by the relatively slow carbonation time especially when used as thick layers of mortar and render. This partly explains why it was largely replaced by faster setting cement based materials.

Despite this limitation, lime has many advantages over cement, such as a higher permeability to water vapour (hence reduced damp problems), the ability to absorb a high degree of deformation before breakage, self-healing characteristics (autogeneous healing) and mild antiseptic properties against fungal growth.

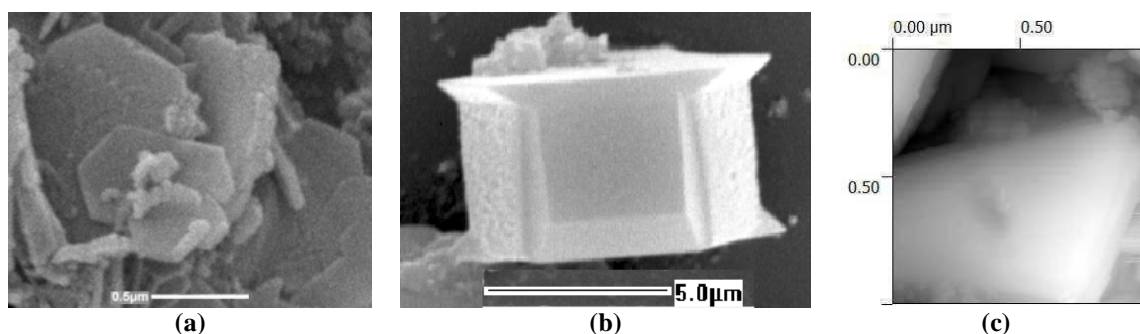
These characteristics can be easily observed in both, practical evidence (e.g. historic buildings) and scientific literature. A practical example of the ability of lime based mortars to

absorb a high degree of deformation before breakage is illustrated by the omission of thermal expansion joints in lime built structures, such as St. Pancras station where the facade is over 100m in length.

More recently, research carried out by Ball et al. (2009) clearly illustrates an enhanced ability of lime to accommodate movement in cement, hybrid and lime samples with aggregate of identical particle size distribution. According to these results, for movement to occur, bonds within the binding phase or at the binding phase/aggregate interface must be broken. On an atomistic scale this can be described as a dissolution and precipitation process on the crystal surfaces and cracking within the crystal.

Within this case, atomistic modelling can help in distinguishing between the underlying dissolution and precipitation mechanisms of calcite and how these two processes may be modified by doping the initial carbonates. The atomistic models that can be developed based on these experimental findings can facilitate the engineering of new lime materials with modified cation compositions and, consequently, with improved movement properties.

From a more general point of view, an understanding of carbonation and de-carbonation at an atomistic scale will deepen the current theoretical understanding of the production processes of lime based materials and will help identify methods of improving the carbonation rate of lime in building construction and associated applications. Recent studies, for instance, have already highlighted the importance of crystal morphology on the chemical behaviour of calcium hydroxide during carbonation (Van Balen et al., 1994; Van Balen et al., 2005). Preliminary atomistic modelling on theoretically perfect structures yields carbonation energies of 240 (i.e. endothermic) and -11 kJ/mol for the {100} side face and (001) top face of portlandite. These results are in agreement with experimental observations from real building materials: figure 1a shows portlandite plates in a lime/cement/sand mortar preferentially carbonating on their {100} side faces. Etching on the {100} faces of a portlandite crystal that highlight their reactivity is shown in figure 1b, while preliminary studies with atomic force microscopy (AFM; figure 1c) show carbonate formation on the (001) surface of a nanolime crystal following sensitisation by scratching.

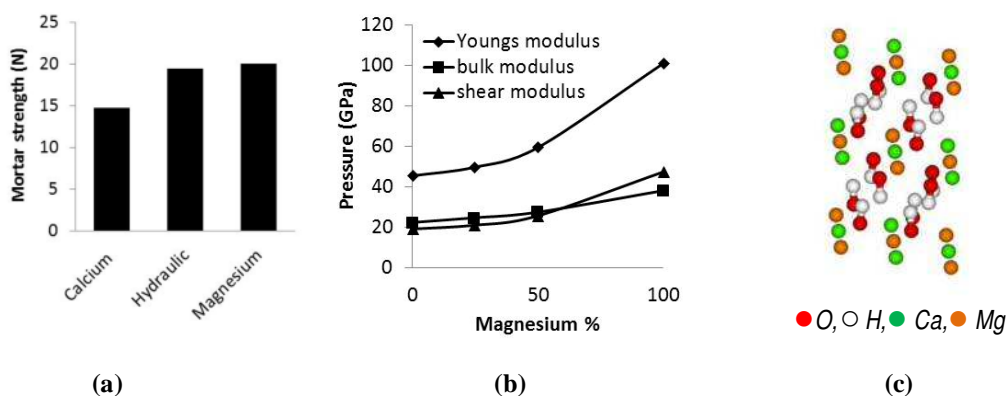


**Figure 1 - (a) Portlandite crystals in a lime/cement mortar showing preferential reaction on the {100} faces (image courtesy of Stella Kioy, Department of Architecture and Civil Engineering, University of Bath, UK), (b) Laboratory grown Portlandite crystal showing preferential etching on the {100} faces (image courtesy of Graham Griffiths, Interface Analysis Centre, University of Bristol, Bristol, UK), (c) AFM image showing carbonate formation on (001) faces following sensitisation by scratching**

Results presented in this paper, investigate the decomposition process of naturally occurring dolomite (containing equal amounts of calcium and magnesium) for the production of lime. The study of lime containing group II metals is particularly timely considering the renewed interest of the building industry in dolomitic lime. The enhanced performance of this binder compared to pure

calcic lime has already been documented previously (Allen et al., 2008; Beruto et al., 2003a; Beruto et al. 2003b). The medieval mosaics in St Mark's Basilica in Venice, for instance, are bonded with dolomitic lime mortars containing magnesium. Under mechanical testing these show superior strength development and performance compared to a non-dolomitic equivalent (Figure 2a).

Preliminary atomic simulations of elastic moduli in lime containing both, calcium and magnesium, showed a correlation with data, figure 2b, provided the magnesium and calcium ions are adjacent. However the mixed cation lime structure employed in this instance is a checkerboard arrangement, figure 2c, and likely to be an over simplification which could be improved by reference to physical measurements derived from a more detailed approach.



**Figure 2 - (a) Enhanced performance of magnesium lime (right) compared to calcium lime (left) (b) Physical properties of limes containing different Ca to Mg cation ratios calculated using atomistic modelling, (c) Mixed cation lime structure**

It is therefore of particular importance to know the atomic ordering in dolomitic limes, for instance, whether calcium and magnesium ions are mixed or phase separated. This knowledge will facilitate the reproduction these arrangements in atomistic models which, in turn, will allow study of the role of defects such as substitute group II metal ions.

Once the model will be available, in fact, atomistic computational studies based upon classical potential modelling can give insight into the surface energies of different phases allowing particle morphologies to be generated and compared with experiment. Once validated, the models can then be used to estimate dissolution energies to determine likely pathways for dissolution. These can then be examined in more detail using more costly quantum techniques which allow the study of reactions. Additionally coarse grained techniques can be applied to particles of lime to determine the material properties of aggregates. By modelling the interactions between whole particles, far bigger systems and timescales can be accessed.

Ultimately new lime materials will be developed with enhanced reactive properties whilst retaining their beneficial material properties. The combination of experimental techniques and computational methods should prove valuable in both understanding results, determining experimental direction as well as giving insight into the design of new materials.

This paper marks the first stage in providing key data that will allow a step change in building practise by facilitating the development of atomistic models. The paper reports the initial results from a detailed study of the thermal decomposition of a naturally occurring dolomitic limestone which has been used for centuries by the construction industry. As already mentioned, these results will help support the development of atomistic models describing the formation mechanisms of calcium and magnesium oxides, lime and periclase phase that form during the thermal decomposition of dolomitic lime.

## 2 EXPERIMENTAL METHOD

The decomposition process of dolomite was investigated using a natural dolomite sourced from a quarry near the city of Genoa (Italy, southern Europe). This stone has been used for production of lime since the Middle Ages and the burnt materials formed have been used successfully over past centuries for the production of mortars and plasters (Beruto et al., 2003a; Beruto et al., 2003b). Material characterization was carried out by X-ray diffraction (XRD), Raman spectroscopy and thermo gravimetric/differential thermal analysis (TG-DTA).

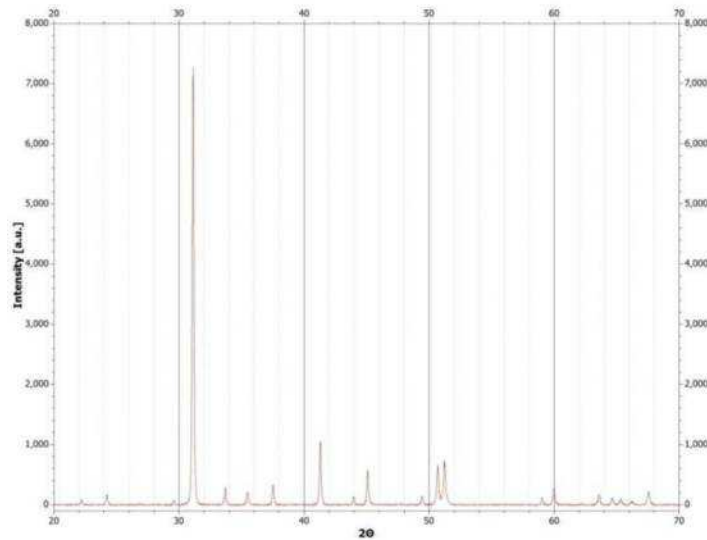


Figure 3 – XRD pattern of the natural dolomite used in the tests

Samples for XRD and Raman tests were prepared in a thermo-balance SETARAM for TG/DTA analysis model TGA 92\_1750 with a 1600°C module. Tests were carried out on samples of  $26.1 \pm 0.1$  mg using a dynamic regime, with a heating rate of 5°C/min and a cooling rate of 20°C/min. All tests ended at a temperature of about 80°C in order to minimize water condensation on the sample particles and, thus, prevent carbonation while the samples were moved to a different laboratory for the subsequent analyses. During the decompositions, air gas was fluxed inside the furnace (internal pressure 150KPa) in order to optimize the heat distribution and to promote the CO<sub>2</sub> removal from the crucible reproducing in this manner conditions similar to those existing inside traditional lime kilns.

Samples were prepared by firstly crushing the stone with a hammer and, then, the fragments obtained were finely powdered with a ceramic mortar and pestle. The resulting powder was sieved and particles between 60 and 125 μm were used for the analyses.

In order to study the decomposition process of dolomite, samples were decomposed at 778 and 850°C in order to investigate the mineralogical characteristics of the partly decomposed and the fully decomposed dolomite (respectively point 2 and 3 in figure 4).

XRD analyses were carried out using a Bruker D8-Advance X-ray diffractometer with CuK<sub>α</sub> radiation, 2θ with a step of 0.016° and step time of 269s between 10° and 70°.

Raman spectra were acquired using a Renishaw inVia Raman Microscope. The system was equipped with lasers operating at wavelengths of 582 and 785 nm. The analyses were performed by focusing the laser with objective magnification 50x. Laser power was reduced to 50% whereas the acquisition time was set at 3s for each of the 3 accumulations acquired. Each spectrum was taken over the wavenumber range 100–3200 cm<sup>-1</sup>. Prior to the analysis, the spectrometer was calibrated

using a monocrystalline silicon standard specimen. Peak fitting and deconvolution of Raman spectra was performed using Reinshaw WiRe 4.0 software.

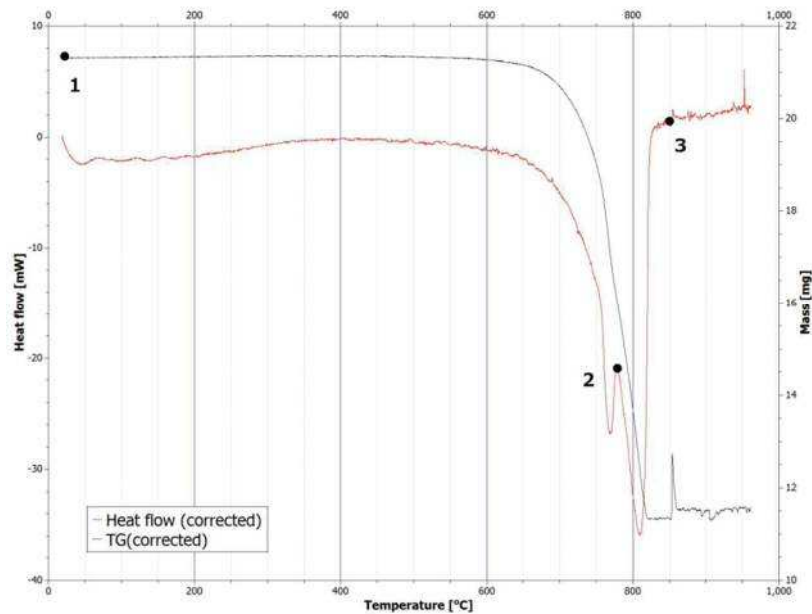


Figure 4 – Thermo-gravimetric analysis and differential thermal analysis of the natural dolomite used during the tests. Point 1, 2 and 3 represent the decomposition temperatures of the analyzed samples

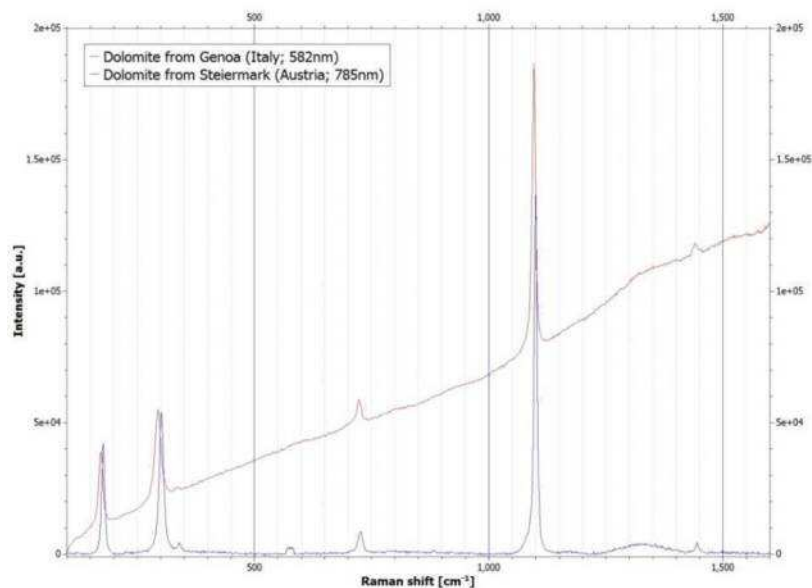
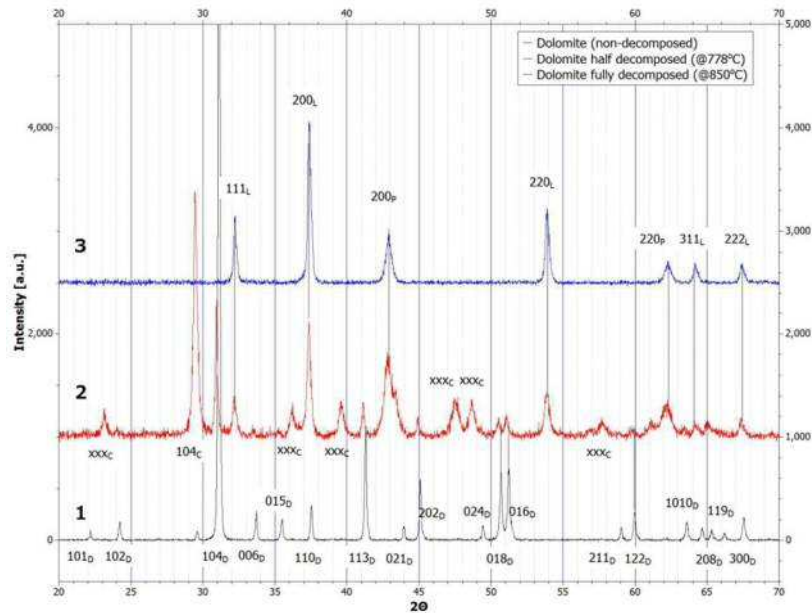


Figure 5 – Comparison of a typical Raman spectrum of natural dolomite from Genoa (Italy) with that of a natural Dolomite from Bruck an der Mur (Austria).

### 3 RESULTS



**Figure 6 – XRD analyses of as-received (spectrum 1), partly-decomposed (spectrum 2, decomposition temperature 778°C) and fully-decomposed dolomite (spectrum 3, decomposition temperature 850°C). The Miller indices corresponding to the diffracting planes (*hkl*) are indicated for the main peaks. Dolomite peaks are denoted by the letter “D”, calcite peaks with the letter “C”, lime peaks with the letter “L” and periclase peaks with the letter “P”.**

Figure 3 shows the XRD pattern of the analysed samples. The spectrum shows that the crystalline phases within the stone consist mainly of dolomite and a very small amount of calcite represented by the peak around 29.5° 2θ.

Figure 4 shows the TG and the DTA analyses of dolomite decomposed in air (both lines have been plotted after removal of buoyancy effect.). TG results shows that this reaction starts at about 600°C and follows a two-stage decomposition route, although at the heating rate and environmental conditions used the end of the first stage and the beginning of the second one is detectable only by a very small shoulder at about 770°C. The beginning of the decomposition is quite slow but at about 750°C it reaches a higher speed that is maintained until the end of the process that suddenly stop at about 820°C. It is interesting to note that existence of two-stage has been associated to a specific threshold in the  $p_{CO_2}$  [21], which in turn is related to the sample mass and to the atmosphere conditions (e.g. static or dynamic). Weight loss calculated for the sample is about 41.26% not far from the theoretical value of 47.73%.

The DTA analysis shows more clearly the two-stage process, with a first endothermic peak at about 768°C and a second endothermic peak at about 809°C.

Figure 5 shows a comparison of the Raman spectrum acquired for the dolomite sourced from Genoa with a sample of natural dolomite from Austria. Results highlight that the sample from Genoa mainly consists of pure dolomite.

Figure 6 shows a comparison of the XRD analyses carried out on the as-received (spectrum 1), partly-decomposed (spectrum 2) and fully decomposed dolomite (spectrum 3) within the 2θ range 20°-70°. Results highlight formation of periclase (peaks labelled with the letter “P” in figure

6) and lime (peaks labelled with the letter “L” in figure 6) at the end of the thermal treatment (850°C). Half-decomposed dolomite shows peaks of periclase, lime, but also dolomite (peaks labelled with the letter “D”) and calcite (peaks labelled with the letter “C”).

#### 4 DISCUSSION

According to the results already obtained by other researchers (Beruto et al., 2003a; Beruto et al., 2003b; Rodriguez-Navarro et al., 2012), thermal treatment of dolomite at 850°C leads to the production of two phases: lime and periclase although the main peaks of these two oxides were already visible at 778°C. This data is in agreement with the results obtained by Rodriguez-Navarro and colleagues (Rodriguez-Navarro et al., 2012) that found small and broad peaks of lime and periclase from 600°C in a powdered sample of natural dolomite.

As demonstrated by the XRD pattern of partly-decomposed dolomite (spectrum 2 in figure 6), the transition from dolomite to lime and periclase, is a complex process. At 778°C the intensity of the main dolomite peaks is reduced when compared to the initial conditions and some of the smallest peaks disappeared. Calcite is represented by the main peak at a  $2\theta$  value of approximately 29.5°. This peak was relatively broad when compared that of pure calcite and a number of the smaller peaks. Since all samples were prepared and treated in the same manner, it is unlikely that the calcite formed due to a carbonation reaction. Interestingly, Rodriguez-Navarro and colleagues attribute the main broad peak of calcite to a Mg-calcite phase that, according to these authors, becomes pure calcite at higher temperatures. This phase is located on the surface of the dolomite crystals and is believed to be produced by a re-carbonation process of impure CaO in the CO<sub>2</sub> rich environment of the crucible. While the reaction progresses, the interface between the Mg-calcite and dolomite moves from the surface toward the bulk of crystals until the complete disappearance of dolomite and, with rising temperature, until the complete decomposition of calcite. According to the same authors, in fact, the Mg-calcite phase is a transient phase that quickly transforms in pure calcite and periclase and, at higher temperature, calcite is decomposed in lime and gaseous CO<sub>2</sub>. It is important to note that, despite its reduced thickness (Rodriguez-Navarro and colleagues found a thickness of about 100nm), this layer is readily identified in our XRD spectrum due to the low-penetrative radiation used by the diffractometer (CuK<sub>α</sub>).

No evidence of magnesite was identified from the analyses. The experiments reported in this paper are in agreement with those of Rodriguez-Navarro et al., (2012) and support the formation of magnesium-calcite as the intermediate phase.

#### 5 CONCLUSIONS

The following conclusions can be drawn from the current study:-

- X-ray diffraction and Raman spectroscopy analysis demonstrated that the crystalline phases within the dolomite samples from Italy contained a very small amount of calcite.
- Thermal decomposition of the dolomite initiated around 600°C and followed a two-stage decomposition route detected by a small shoulder at 770°C. The two-stage process has been previously associated with a specific threshold in the  $p_{CO_2}$
- The results suggest that atomistic models of the thermal decomposition of dolomite should be based on the formation of an intermediate magnesium rich calcite phase as opposed to formation of calcite and magnesite.



## 6 ACKNOWLEDGEMENTS

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