# Template based analysis of amorphous and nanocrystalline materials by TEM (part I)

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## Introduction

Calcium carbonate is one of the most abundant substances in nature (around 4% of the Earth crust) and one of the compounds most widely produced by humankind (Kudlacz, 2013). The popularity of calcium carbonate is directly related to the variety of its usage and application, just to mention food production, pharmaceutical industry, paper production, filler in ink, building and construction,. and many more. Nowadays we can observe growing demand for a product with very fine grain (sub-micrometer size) and well defined morphology, placing research on calcium carbonate in the field of nanotechnology. One of the most popular and effective way of the calcium carbonate production on an industrial scale involves its precipitation from lime water, i.e., saturated solution of calcium hydroxide reacting with carbon dioxide bubbled through the solution. This reaction is often referred to as solution-mediated carbonation process and is described by the overall equation: $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$. In such a system the formation of crystalline calcium carbonate (i.e., calcite) is proceed by the formation of amorphous calcium carbonate (ACC). From the scientific point of view it is very interesting to understand the transition between the amorphous and crystalline phase. This papers deals with the problem of the formation of ACC and its subsequent transformation into crystalline phase. In particular, special attention is paid to the characteristics of the short range order observed in ACC and its influence the selection of the crystalline phase in context of the so-called non classical nucleation. General characteristics of the short range order are made with the aid of TEM.

## Carbonation process

Here carbonation involved the precipitation of calcium carbonate at the solution/air interface in a crystallization dish filled with solution saturated with respect to calcium hydroxide. Precipitation of calcium carbonate followed 2 min. solution exposure to air at room $T$. Additionally, in a set of experiments, the pure solution was air bubbled for about 10 min in order to accelerate carbonation. Later precipitates were analyzed with the aid of a Philips CM20 transmission electron microscopy (TEM), operated at a 200 kV acceleration voltage. Prior to TEM observations samples were dispersed in ethanol, sonicated 2 min, and deposited on carbon-coated copper grids.
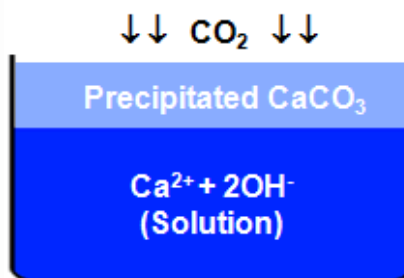
**Figure 1**. Schematic representation of experimental setup.

**Results and Discussion**

TEM and selected area electron diffraction (SAED) analyses of the precipitates formed after 2 min air exposure revealed interesting features of ACC and its further transformation into calcite. Figure 2a shows the initial formation of ACC as micrometer sized spheres. Instead of typical diffuse diffraction image, corresponding to a fully amorphous phase, rings indicating the formation of a short range order were observed (inset in Figure 2a). Furthermore, after 10 min of forced air bubbling, these spheres, with similar diameter as in the previous case were found (Figure 2a), yet with the internal structure of calcite, what is depicted in Figure 2b. Their SAED pattern indicates the following crystallographic orientation: $<100>_{calcite}$ normal to the image plane. A closer examination of such a pseudomorph shows that it developed an internal texture made of perfectly oriented nanocrystalline calcite grains (Figure 2c).
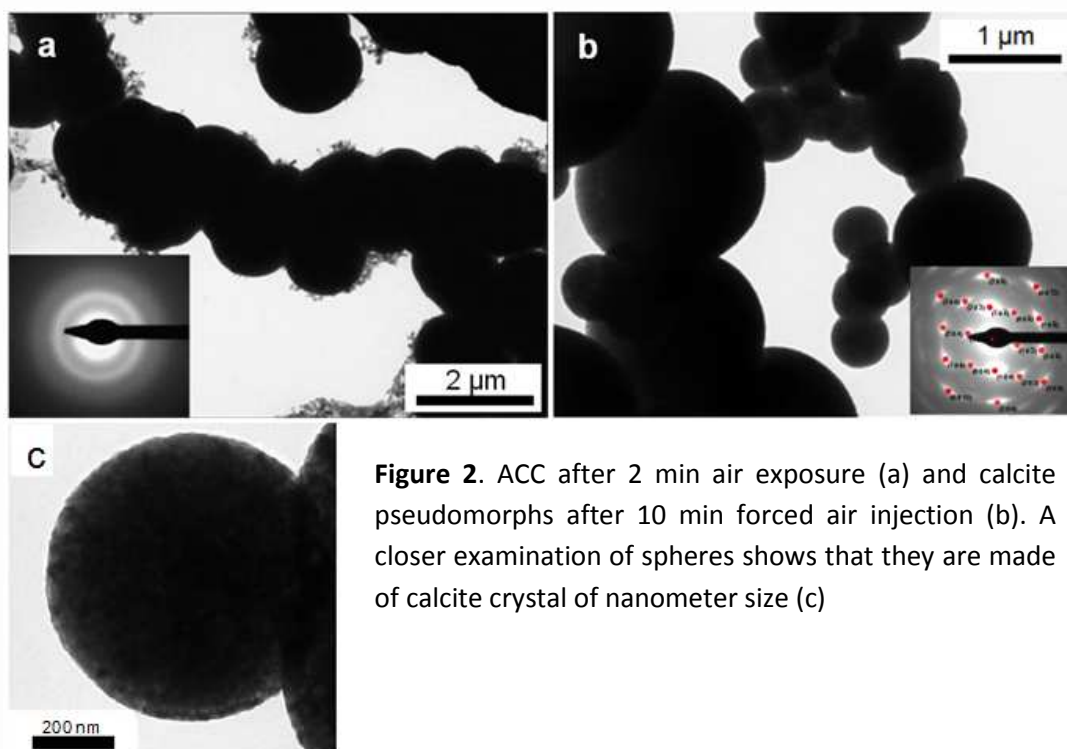


**Figure 2**. ACC after 2 min air exposure (a) and calcite pseudomorphs after 10 min forced air injection (b). A closer examination of spheres shows that they are made of calcite crystal of nanometer size (c)

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In order to get insights into structural short range order characteristics of early carbonate precipitates formed in lime water, the intensity of pixels in corresponding SAED patterns were radially integrated using dedicated software written by the author. This operation allows to plot the diffraction intensity as a function of scattering vector length, $k$ (i.e., distance form (0,0,0) point in reciprocal lattice), and can be consider as an equivalent of electron powder diffraction pattern (EPDP) (Czigany and Hultman, 2010). Figure 3 shows the EPDP corresponding to precipitates formed in lime water. To these plots a series of three Pearson VII functions were fitted including a polynomial function representing the background baseline, in order to estimate the peak profiles (i.e., its center – $k$ and full width at half medium (FWHM)). The result of fitting are presented in Table 1.
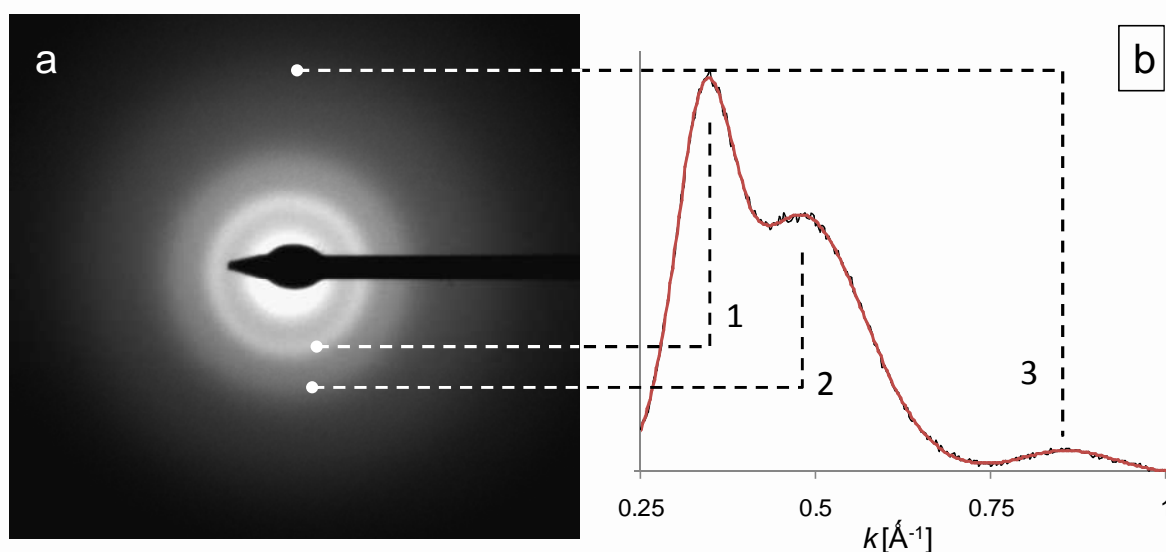


**Figure 3**. SAED pattern of $CaCO_3$ spheres formed in run A sample after 2 min (a) and corresponding EPDP (b). The black pattern represents the results of the integration while the red line corresponds to the fitted functions ($k$ is scattering vector length).

**Table 1.** Results of EPDP fitting from the precipitate formed in lime water after 2 min air exposure

| Nº | $k$ [Å$^{-1}$] | FWHM [Å$^{-1}$] | $k^{-1}$ [Å] | FWHM$^{-1}$ [Å] |
|----|----------------|-----------------|--------------|------------------|
| 1  | 0.337          | 0.096           | 2.967        | 10.406           |
| 2  | 0.488          | 0.200           | 2.050        | 5.003            |
| 3  | 0.860          | 0.163           | 1.163        | 6.143            |

At his point one could ask if there is a possibility to evaluate the extent of the short range order observe in Figure 2, or in such patterns in general, as well as its structural features. Czigany and Hultman (2010) proposed a model according to which amorphous material can be treated as an aggregate of ultra fine grains (clusters) of different size, shape and orientations. This approach gives

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the possibility of the characterization of the type of ordering in amorphous phase. On the other hand, Ciupina et al. (2007) described a method of evaluating the crystallite size based on the Scherrer equation applied to the electron diffraction images of magnesium oxide nanocrystals. The Scherrer equation, expressed in the following way:

$$< D > = \frac{k\lambda}{\beta\cos(\theta)} \quad \text{(Equation 1)}$$

where: <D> crystallite (cluster) size, k - shape factor, λ - wavelength, β - the full width at half maximum, and θ - Bragg angle (β and θ, both in radians, are parameters of the EPDP peaks) can be reduced to the (if θ is small):

$$< D > = \frac{k}{FWHM} \quad \text{(Equation 2)}$$

where FWHM is the full width at half maximum (in $Å^{-1}$). Therefore assuming that the cluster has a spherical shape (i.e., k = 1) it can be stated that the extend of short range order is equal to the reciprocal value of FWHM, which for the first peak in Figure 2b is ~10 Å.

In an attempt to evaluate the structural characteristics of the short range order of ACC the peak positions (estimated by fitting) could be compared with the theoretical positions of four calcium carbonate crystalline phases, i.e., aragonite, vaterite, calcite and monohydrocalcite, which serves as a matching template. It could be argued that these peaks may be the product of overlapping of other peaks. However, comparison of the position of the peaks, in particular the first one, with the theoretical peak positions of the four calcium carbonate polymorphs, shows that the first matches with calcite 104 Bragg peak (3.036 Å) and monohydrocalcite 102 Bragg peak (3.069 Å). It also should be mentioned that these peaks are well separated from other peaks (i.e., both in the case of calcite and monohydrocalcite). They also significantly exceed the other ones in terms of intensity, what is especially vivid in the case of calcite (e.g., 104 Bragg peak has the highest intensity). The comparison of the other peaks positions with theoretical positions of calcium carbonate crystalline phases is more complex due to possible overlapping, and cannot be easily estimated. Nevertheless, the observed short range order in the ACC precursor, which presents structural similarities to the calcite and monohydrocalcite structures, predetermines the formation (i.e., phase selection) of crystallites. The origin of the short range order could be associated with the formation of stable prenucleation clusters with proto-calcite or proto-monohydrocalcite structure (Gebauer et al. 2008, 2010). The formation of crystallites seen in Figure 2b and 2c (their size estimated according to the Equation 2 for the 104 Bragg peak is ~30 Å from EPDP obtained in the same way as this one seen in Figure 2) could be the result of the oriented aggregation of these clusters (Figure 4). Moreover, the preservation of the external shape of a sphere in the case of ACC formed calcium hydroxide solution, suggests that the ACC to calcite transformation involves either a solid state transformation, i.e., ACC dehydration (Radha et al. 2010) or a coupled dissolution/precipitation pseudomorphic replacement mechanism (Rieger et al. 2007).
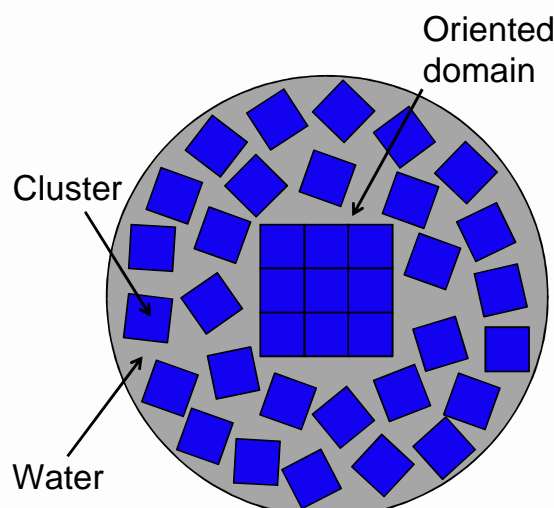
**Figure 3.** Schematic representation of ACC and its transformation into a crystalline phase via oriented aggregation of the stable pre-nucleation clusters.

## Conclusions

This papers presents insights into to the problem of the formation of amorphous calcium carbonate and its subsequent transformation into calcite studied by TEM. Presented results suggest that solution mediated carbonation of calcium hydroxide occurs via non classical route. Initial precipitation of amorphous calcium carbonate and its subsequent transformation into crystallite form (calcite) may be the result of the aggregation of the stable pre-nucleation clusters with structure similar to monohydrocalcite or calcite. This hypothesis could explain why no metastable aragonite nor vaterite is observed during the process. The paper also proposes a method of characterization of the short range order in amorphous materials based on the idea of clusters, which can be viewed as crystals with ultrafine grains (here ~1nm). In the next paper we will explore the possibility of modeling the clusters out of different calcium carbonate structures and compared theoretical electron diffraction patterns with the experimental ones.

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