

## Structural stability of a colloidal solution of $\text{Ca}(\text{OH})_2$ nanocrystals exposed to high relative humidity conditions

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### ABSTRACT

The effect of high relative humidity (90% and 75% RH) on phase transformation and stability of  $\text{CaCO}_3$  polymorphs has been studied based on the structural and morphological changes from a colloidal solution based on  $\text{Ca}(\text{OH})_2$  nanocrystals. Carbonation process has been confirmed indicating differences in nucleation and stability of  $\text{CaCO}_3$  polymorphs as a function of RH. Local fluctuations in the water/alcohol ratio significantly affect the precipitation/dissolution of anhydrous and hydrated polymorphs that are reflected in the particle size. Changes in lattice parameters and particle size are related to surface tension fluctuations, release of residual water and time of exposure. These results highly contribute to evaluate the stability of the  $\text{Ca}(\text{OH})_2$  nanoparticles in high humidity conditions.

*Keywords:*  $\text{CaCO}_3$ , nanocrystals, relative humidity, portlandite, cell parameters, carbonation

### 1. Introduction

Nanoscience deals with a large diversity of research fields and applications considering that most of the properties of the nanomaterials are modified or improved by effect of the reduction in size. One of the main aspects in conservation of cultural heritage properties is to minimize or repair the decay of materials as a result of their exposure to different destructive agents [1], [2], [3] and the course of time. Nanostructured materials based on hydroxides such as  $\text{Ca}(\text{OH})_2$  (portlandite),  $\text{Mg}(\text{OH})_2$  or  $\text{Sr}(\text{OH})_2$  have been lately applied as consolidating products for restoring the loss of cohesion of carbonate stones [4], plasters [5], wall paintings or cellulose based products [6] belonging to the cultural heritage.

Among the synthesis methods for obtaining nanostructured materials, the colloidal synthesis has been converted in a successful method for obtaining nanosized materials by the “bottom up” process [7]. However, the structural stability of these nanomaterials for specific applications is still in evaluation. Carbonation is based on the spontaneous reaction produced when portlandite is exposed to open environments with  $\text{CO}_2$  and  $\text{H}_2\text{O}$  giving rise to  $\text{CaCO}_3$ . The produced polymorphs are in the form of anhydrous (calcite, aragonite, vaterite), hydrated (monohydrocalcite (MHC), ikaite), or in amorphous form (ACC). Phase transformation mechanisms from portlandite to  $\text{CaCO}_3$  have been widely studied in aqueous solutions at micrometric and macroscopic scales. However, important differences could happen when particles have nanoscale dimensions and when factors such as relative humidity (RH) or exposure time affect in different grade the stability of phases. Only few works consider the influence of the type of solvent and concentration [8], RH, aging [4, 9, 10], or additives [11]. Today commercial companies offer alcoholic colloidal nanoparticles of calcium hydroxide at different concentrations ranging between 5 and 50g / l [12]. Recently, research has been focused on the determination of the optimal concentration to achieve a total carbonation [10]. The effectiveness assessment has been proven on stone materials [9] or paintings (canvas or wall paintings [6]) that among other factors depends on the porous structure. Alcoholic solutions have low surface tension values that favour the penetration through the surface [6], however, both the concentration of the solution and the ambient temperature affect the surface tension [13].

The aim of this paper is not to advise what the best concentration of the solution is but to determine the stability of the  $\text{Ca}(\text{OH})_2$  nanocrystals under factors such as relative humidity and time, taking into account the influence of the surface tension.

The carbonation process has been evaluated using an alcoholic colloidal solution of  $\text{Ca}(\text{OH})_2$  nanocrystals exposed to high relative humidity during different exposure times, at room temperature, in a controlled atmosphere with no extra  $\text{CO}_2$  flux, no air in circulation and without additives. The structural analysis includes phase transformations, cell parameters variation, and morphological changes associated to the carbonation process produced by spontaneous growth.

## 2. Experimental Section

A precursor solution of 20g/l of CaLoSiL® dissolved in isopropanol and diluted down to 1.5g/l (surface tension: 23.75 dy/cm at 22.9°C) was used for the electron microscopy characterization. The solution was exposed to 75% and 90% RH, during 7, 14, 21 and 28 days without  $\text{CO}_2$  flow and no air in circulation.

X-ray diffraction (XRD) (X'Pert Pro MPD Panalytical X'Celerator diffractometer) was used for the phase identification using the JCPDS database. Rietveld refinements [14] were carried out for unit cell parameters calculation and phases quantification. Environmental scanning electron microscopy (ESEM) (Fei Quanta-EDAX- dx4) and Transmission electron microscopy-selected area electron diffraction (TEM-*saed*) (Jeol JEM- EDS Link at 200 KV) were performed for morphological, structural and chemical analyses.

## 3. Results and Discussion

The starting solution before being placed in the climatic chambers shows six-sided crystals of portlandite (38 to 148.5nm) (TEM image, Fig. 1a). The *saed* (as inset) reveals a polycrystalline material indexed according to portlandite ( $\text{Ca}(\text{OH})_2$ , jcps=72-0156). At 90% RH, after 14 days (TEM image, Fig. 1b), the solution exhibits acicular and clay like habit crystals of  $\text{CaCO}_3$ . *Saed* patterns confirm the aragonite and calcite phases (as inset). The aragonite *saed* along the [-864] zone axis shows streaking due to lattice defects. Also the textured ring pattern of the calcite indicates high defect content. At 75% RH, after 14 days, (TEM image, Fig. 1c) the particles show a better crystallization with vaterite, calcite and aragonite crystals associated to clay like habit crystals of  $\text{CaCO}_3$ . *Saed* patterns (as inset) confirm the calcite rings and the aragonite along the [6-33] zone axis. ESEM images show differences in the crystallization shape at 90% RH (Fig 2a) and at 75% RH after 21 days (Fig 2b). Table 1 summarizes the shape, particle size and percentage of each phase at 90% and 75% RH.

Experimental XRD patterns confirm the carbonation process with the identification of  $\text{CaCO}_3$  polymorphs and the evolution of cell parameters at 90% RH (Fig. 2c) and 75% RH (Fig. 2d). Fig. 3a shows the refinement results when the solution is exposed to 90% RH during 28 days. The good agreement between the observed and calculated intensities obtained for the calcite phase confirms that no other polymorph except calcite is present after 28 days. Unit cell parameters calculated for each anhydrous polymorph show a variation depending on RH conditions. In the anhydrous polymorphs, calcite (Fig. 3b), vaterite (Fig. 3c) and aragonite (Fig. 3d), the "c" unit cell parameter suffers a progressive decrease with the increase in the exposure time, with higher values at 90% RH. The same behaviour takes place with the other constant distances (*a* and *c*) of the crystal lattice.

Based on XRD, ESEM and TEM results, in very wet conditions (90%RH), calcite nucleation occurs at very fast rate. However, the high humidity affects calcite stability generating hydrated and anhydrous  $\text{CaCO}_3$ . The fast precipitation of calcite after 7 days, and the still very humid conditions after 14 and 21 days, contribute to the formation of other unstable anhydrous (vaterite and aragonite) and hydrated  $\text{CaCO}_3$  phases (MHC). However, only calcite phase is present after 28 days. The high humidity conditions under which carbonates have been formed, favour high

concentration of structural defects as shown by *saed*. The high disorder degree contributes to the fast phase transformation from metastable vaterite and aragonite to stable  $\text{CaCO}_3$ . When the solution is exposed to 75% RH, the carbonation process is slower than to 90% RH. The beginning of carbonation is clear with the formation of MHC after 7 days, which coexists with anhydrous  $\text{CaCO}_3$  polymorphs (vaterite and aragonite) after 14 days. However, calcite only precipitates after 21 days, together with MHC. After 28 days, not all the  $\text{CaCO}_3$  has been transformed into calcite, remaining some vaterite and aragonite phases (Fig 2d). In other nanomaterials [15], the lattice contraction has been associated to changes in surface tension affecting the phase transformations. At 90% RH higher amount of water is present as vapour phase, modifying the concentration of the precursor solution by increasing the water content. This water excess in the solution increases the surface tension. The water/alcohol ratio at 90% RH is slightly higher than at 75% RH as it can be shown by the stability and crystallinity of  $\text{CaCO}_3$  polymorphs. Local changes in the water/alcohol ratio significantly affect the precipitation/dissolution of anhydrous and hydrated polymorphs that are reflected in the particle size. Table 1 shows the differences on the particle size growth of  $\text{CaCO}_3$  polymorphs. In the early stages of carbonation (7 and 14 days) the particle size reached by the product when this is exposed to 75% RH is larger compared to its exposure at 90%RH in both calcite and aragonite. Aragonite has reached larger sizes compared to calcite, which shows a better crystallization but smaller crystals. Vaterite grows slowly compared to the other polymorphs. The behaviour is different after 21 days of exposure; calcite is the predominant polymorph at 90%RH, and its size at this RH is larger than at 75%RH. However, after 28 days, its size decreases becoming smaller in both RH, though is still larger than at 75% RH. During the time of exposure both aragonite and vaterite behave as unstable polymorphs. These differences may be related to modifications in the equilibrium with the surrounding solvent. At higher RH, the ratio water/alcohol is changing by the presence of  $\text{H}^+/\text{OH}^-$  ions and it would determine the rate of chemical reactions. The strong difference in the particle size could be explained applying the Oswald ripening phenomenon [16]. The solubility of the smaller particles of vaterite is higher than the larger particles of aragonite. Consequently, there would be a net diffusion of the  $\text{CaCO}_3$ , from the proximity of the smaller particles to the proximity of the larger ones. To maintain the equilibrium, the  $\text{CaCO}_3$  will be deposited onto the surface of the larger particles (aragonite). The smaller particles (vaterite) have to continue dissolving in order to compensate the amount of  $\text{CaCO}_3$  that is being diffused; while the larger particles of aragonite get larger. Changes in lattice parameters and particle size with aging are explained by a variation in the energy produced by chemical reaction, releasing of residual water, surface tension fluctuations and improvement in the crystallinity.

Although alcoholic colloidal solutions of calcium hydroxide nanocrystals can be used in several applications, including its use in preservation of cultural heritage, it should be taken into account the different factors that affect their effectiveness. The effect of relative humidity, time of exposure and potential fluctuations in the surface tension, of both the initial concentration of the precursor solution and that produced by the effect of the environmental exposure to high relative humidity, determine their structural stability. It is therefore necessary to combine these factors to achieve the most effective treatment for materials to improve the degree of consolidation.

#### 4. Conclusions

Structural and morphological differences have been observed in the alcoholic colloidal solution of  $\text{Ca}(\text{OH})_2$  nanocrystals when exposed to 75% or 90% RH. The carbonation process and growth rate of  $\text{CaCO}_3$  polymorphs is slightly different. The local variations in the alcohol/water ratio directly affect the surface tension leading to differences in the nucleation and stability of each polymorph. A better crystallization has been observed in the solution exposed to 75% than to 90% RH along time. Calcite precipitates in both systems. Vaterite and aragonite behave as unstable phases and MHC is very common during all the process. Local fluctuations in the water/alcohol ratio significantly affect the

precipitation/dissolution of anhydrous and hydrated polymorphs that are reflected in the particle size. Changes in lattice parameters and particle size with time are explained by releasing of residual water, surface tension fluctuations and improvement in the crystallinity of the particles during carbonation.

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### References

- [1] P.N. Manoudis, I. Karapanagiotis, A. Tsakalof, I. Zuburtokudis, B. Kolinkeová, C. Panayiotou: *Appl.Phys. A* 97, 351-360 (2009)
- [2] S.A. Ruffolo, M.F. La Russa, M. Malagodi, C. Oliviero-Rossi, A.M. Palermo, G.M. Crisci: *Appl.Phys. A* 100: 829-834 (2010)
- [3] L.. Maldonado, L. Veleva, L. Díaz-Ballote: *Appl Phys A*, DOI 10.1007/s00339-010-6049-6
- [4] P. López-Arce, L.S.Gomez-Villalba, L. Pinho., M.E.Fernández-Valle, M.Álvarez de Buergo, R.Fort: *Mater. Charact* 61, 168-184 (2010)
- [5] E. Ciliberto, G.G. Condorelli, S. La delfa, E. Viscuso: *Appl.Phys. A* 92, 137-141 (2000)
- [6] P. Baglioni, R.Giorgi: *Soft. Matter* 293-303 (2006)
- [7] G. Cao. Nanostructures and nanomaterials, Synthesis, properties and applications, (Imperial College Press, London; Chapter 3 2004)
- [8] S.F.Chen, S.H.Yu, J.Jiang, F. Li., Y.Liu: *Chem. Mater* 18, 115-122 (2006)
- [9] P. López-Arce, L.S. Gomez-Villalba, S.Martinez-Ramirez, M. Alvarez de Buergo, R. Fort: *Powder Technol.*, 205, 263-269 (2011)
- [10] G. Daniele, V.Taglieri: *J. Cult. Herit.* 11, 102-106 (2010)
- [11] H. Matahwa, V. Ramia, R.D Sanderson: *J. Cryst. Growth* 310,4561-4569 (2008)
- [12] G. Ziegenbald: Proceedings of 11th International congress on deterioration and conservation of stone III: 1109, (2008).
- [13] G. Vazquez, E. Alvarez, J.M. Navaza: *J. Chem. Eng. Data*, 40, 3, 611–614 (1995)
- [14] J. Rodriguez-Carvajal: Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCR. Toulouse, France: 127 (1990)
- [15] Z. Huang, P.Thomson, Di S.: *J. Phys. Chem. Solids* 68, 530-535 (2007)
- [16] L. Ratke, P.W. Voorhees, , *Materials Processing*; (New York: Springer-Verlag Berlin Heidelberg 2002)

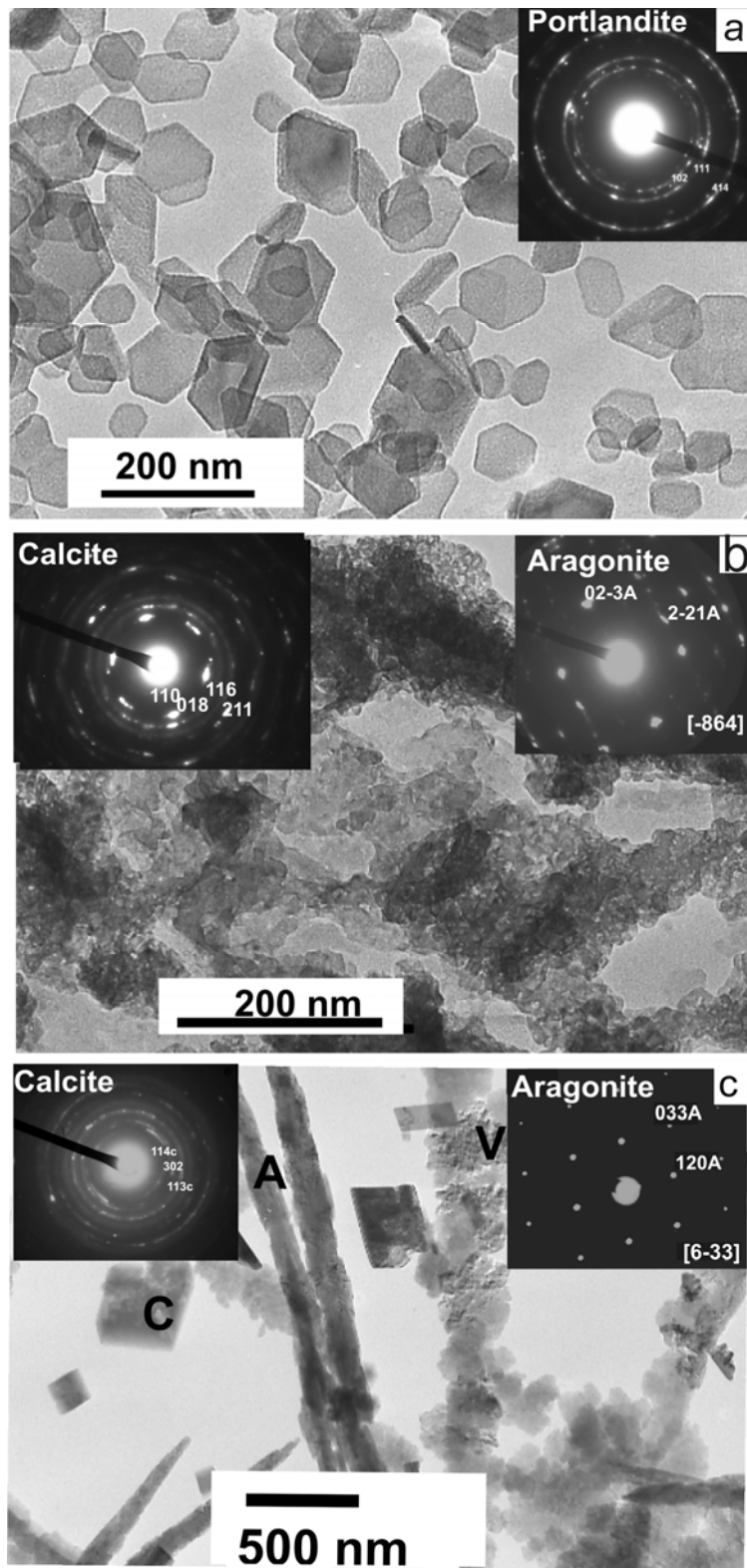


Fig. 1 TEM- *saed* images of the starting solution (a), after 14 days at 90% RH (b), at 75% RH (c) (A: Aragonite, V: Vaterite, C: Calcite).

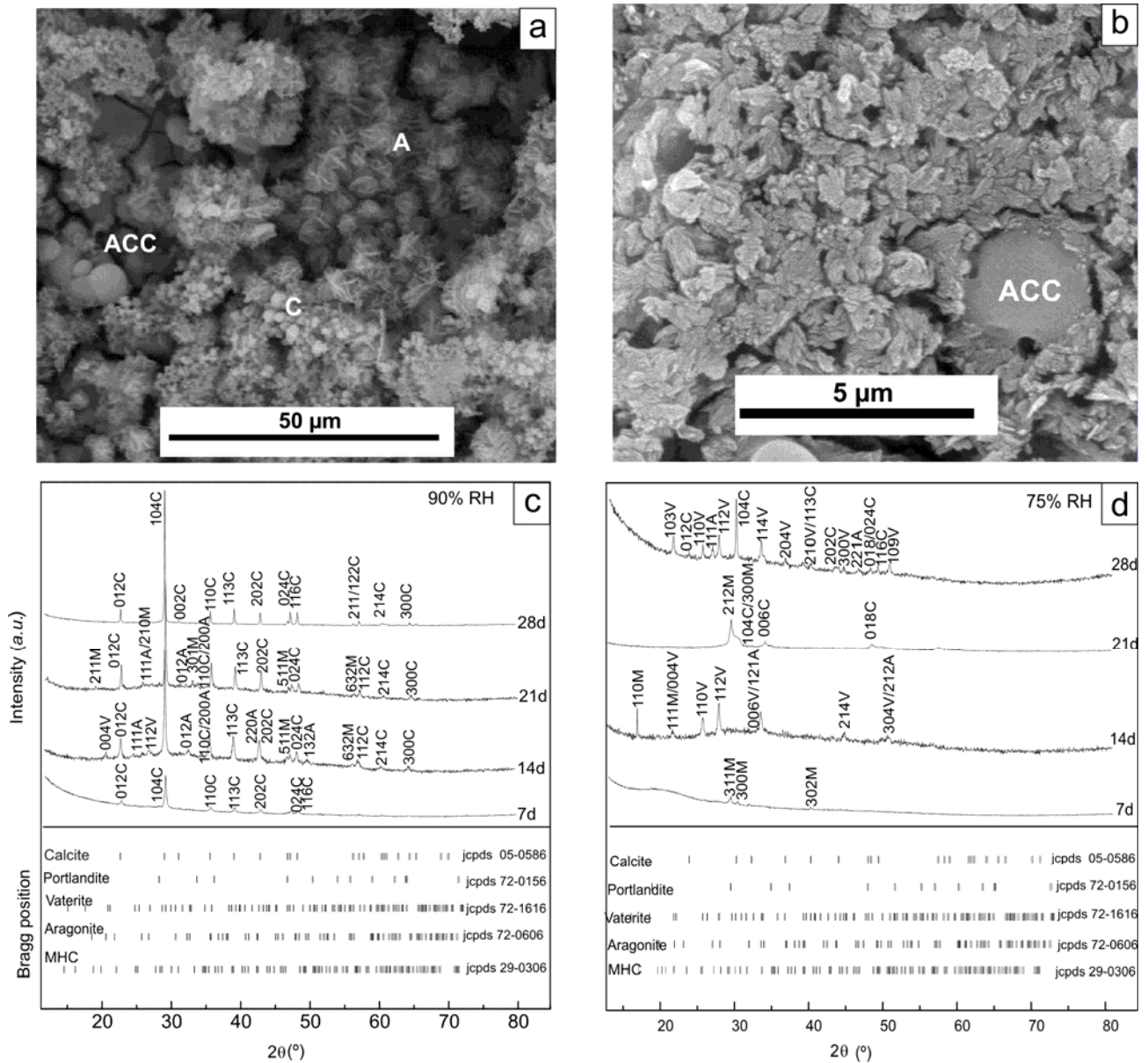


Fig 2 ESEM images of the solution after 21 days at 90% RH (a), at 75% RH (b). XRD patterns at 7, 14, 21 and 28 days at 90%RH (c) at 75%RH (d). (A:Aragonite, C:Calcite, M: Monohydrocalcite, ACC: Amorphous calcium carbonate)

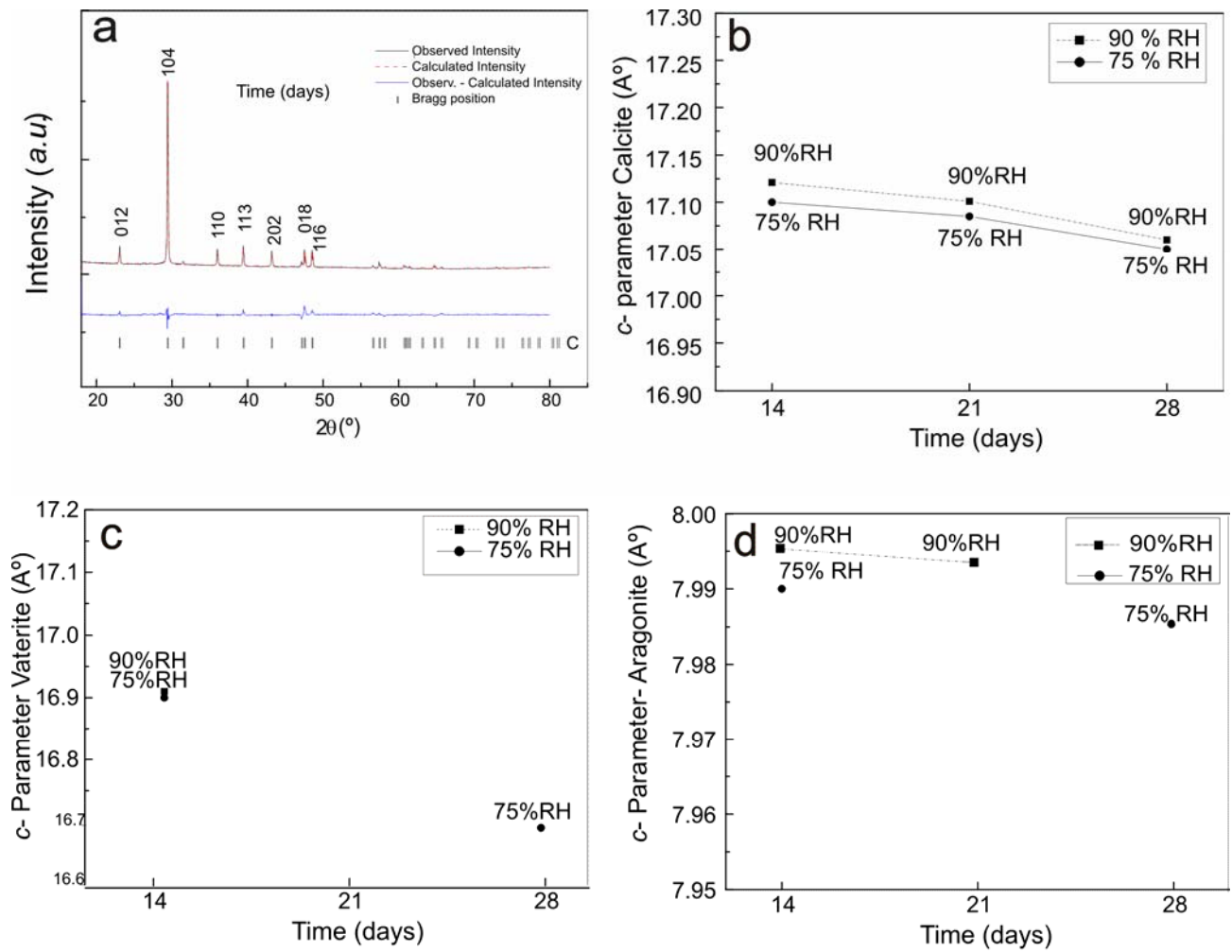


Fig 3 Rietveld refinement of the solution after 28 days at 90%RH, diffraction maxima indexed according to calcite (a), “c” unit cell parameters calculated for calcite (b), vaterite (c) aragonite (d) at 90% and 75% RH

**Table 1** Crystalline phases at 90% and 75% RH

Time (Days)	90% RH				75% RH			
	Phase	Shape	Particle size	%	Phase	Shape	Particle size	%
7	Calcite	Rhombohedral	40±20nm	100	MHC	Clay- like	350±100 nm	100
14	Calcite	Rhombohedral	91± 16nm	21	Calcite	Rhombohedral	463± 170nm	10
	Vaterite	Acicular	112±38 nm	17	Vaterite	Acicular	110± 49 nm	65
	Aragonite	Interleaved sheets	608±385 nm	48	Aragonite	Fiber like	1755±718nm	15
	MHC	Clay like	1300± 200nm	14	MHC	Clay like	750± 200 nm	10
21	Calcite	Rhombohedral	830±180 nm	72	Calcite	Rhombohedral	616± 180 nm	35
	Aragonite	Rosette like	1.9 ±0.8 µm	19	MHC	Clay-like	900±200 nm	65
	MHC	Clay-like	4.9±1.5 µm	9				
28	Calcite	Rhombohedral	563 ± 264 nm	100	Calcite	Rhombohedral	400±100nm	45
					Vaterite	Prismatic	179±31nm	50
					Aragonite	Columnar	2.2 ± 0.5µm	5