

Carbonates

Linda Pastero ^{1,2} 

¹ Department of Earth Sciences, University of Turin, Via Valperga Caluso 35, 10125 Torino, Italy; linda.pastero@unito.it

² NIS—Nanostructured Interfaces and Surfaces, University of Turin, Via Quarello 15/A, 10135 Torino, Italy

Received: 3 November 2018; Accepted: 7 November 2018; Published: 8 November 2018



Keywords: carbonates; crystal growth; epitaxy; self-organized materials; bio-mineralogy; bio-inspired materials; bio-mimetic materials; environmental mineralogy

Although the minerals belonging to the carbonate group are a widely discussed subject, their relevance remains unchanged due to their many applications in a wide range of disciplines, from mineralogy, geochemistry and geology, to biology, medicine, industry and waste remediation. Besides, studying the interactions between carbonates and other organic or inorganic phases may disclose new opportunities for the understanding of the mechanisms involved in mineralization processes.

An open, multidisciplinary approach is mandatory when dealing with the phenomena behind the crystal nucleation and growth of carbonates, applied in so many contexts.

This Special Issue gathers a multidisciplinary collection of papers on carbonates covering many fields of interest, ranging from geological applications to their industrial and environmental exploitation, biomineralization, while not disregarding the fundamental aspects of crystal growth.

In this context, for example, the paper by Kosanović [1] addresses the precipitation of calcium carbonate in the presence of polysaccharides (alginate and xanthan). Biocompatible polysaccharides are considered to be suitable models for the study of the basic concepts of crystal growth applied to calcium carbonate crystal phases. Beginning with this assumption, control over the crystal size, polymorph selection and surface quality is an important achievement in the application of calcium carbonate to drug delivery models or hard tissue (bone) regeneration raw materials.

Sánchez and coworkers [2] started from the same assumption regarding the role exerted by biological functional molecules during the crystallization of carbonates. They introduced the effect of inorganic precursor species (IPS), namely amorphous phases and pre-nucleation clusters (PNCs) in order to understand the interactions between organic and inorganic phases, and discussed the effect of plain carbon nanotubes (CNTs) and alginate-functionalized CNTs on the nucleation and growth of carbonates using electrochemical (EC) and gas diffusion (GD) techniques.

The same crystal growth techniques were applied by Butto and coworkers [3] to obtain calcium carbonate crystals in the presence of phosphorylated chitin (Chi-P). Their study demonstrated that phosphate moieties of Chi-P act as inhibiting agents on the *in vitro* mineralization of CaCO₃, and as an efficient modifier of CaCO₃ crystallization, using both EC and GD methods. Moreover, EC techniques turned out to be a reliable method to control the polymorphism of CaCO₃, offering an opportunity for a deepened understanding of the crucial role of functionalized biomacromolecules on the stabilization of metastable forms of crystals in the biomineralization field.

Pastero [4] took a totally different technical approach: in fact, the paper presented dealt with the growth of calcium carbonate polymorphs in the presence of sericin, a silk protein, and CO₂ as the gas phase. In these conditions, the authors obtained an organic–inorganic composite that mimics the structure of nacre both in the polymorph selection and the rough structure. In this case, the organic component ordered as a bi-dimensional layer acted as a substrate for the nucleation and growth of aragonite (otherwise unstable) and then calcite.

A more environmental approach to the theme of biogenic carbonates was chosen by Hsu and colleagues [5]. In their paper, the authors evaluated the effects of bacteria monoculture (*S. pasteurii*) and biculture (*S. pasteurii* and *B. subtilis*) on the biogenic precipitation of calcium carbonate as a sand bioconsolidant, extending our knowledge of microbiologically precipitated carbonates.

Some practical applications of carbonates are proposed in two papers about cement and CO₂ capture. In the first paper, Atla and colleagues [6] proposed a new way to obtain highly hydrophobic cement surfaces for industrial applications via carbonation in the presence of stearic acid. The carbonation led to an increase in the micro-hardness of the cement, in turn depending on the morphology of the calcite crystals formed. The carboxylic group of the stearic acid chelates calcium while alkyl chains render the carbonate hydrophobic. The effect can be tailored by using different additives.

In the second paper, Chen [7] proposed a CO₂ capture system the efficiency of which was experimentally determined. The carbon dioxide was converted into ammonia bicarbonate using aqueous ammonia. The method was successfully tested (the absorption rates and overall mass-transfer coefficient obtained were comparable with other solvents) on a bubble-column scrubber; the removal efficiency was adjusted by tuning the pH and the inlet gas temperature.

From the fundamental point of view, the evaluation of the surface energy of a crystal form is mandatory to describe its equilibrium shape and the growth morphology. In this context, the paper by Costa [8] described an unusual and straightforward method for the measurement of the contact angle by collecting zenithal pictures of droplets of a solution settled on the surface of a calcite crystal. The proposed method ensured high statistical reliability and took into account the effect of a real surface, presenting terraces and steps influencing the interfacial energy.

Finally, the geological background cannot be disregarded. The paper by Xu and colleagues [9] presents a geological work, included in this collection due to the careful consideration of the mechanisms of dissolution and recrystallization occurring at the mineral surfaces/interfaces associated with the porosity, linking the nano- and microscale studies with macroscale (geological) studies.

In summary, it is worth emphasizing that this Special Issue aimed to collect papers from authors with different scientific backgrounds and attitudes towards the timeless topic of the crystallization of carbonates, to make clear the unchanged relevance and undeniable multidisciplinary of this topic.

Funding: This work was supported by University of Turin.

Acknowledgments: The Guest Editor would like to thank all the authors that made this Special Issue possible and the *Crystals* publishing staff for their invaluable support.

References

1. Kosanović, C.; Fermani, S.; Falini, G.; Kralj, D. Crystallization of Calcium Carbonate in Alginate and Xanthan Hydrogels. *Crystals* **2017**, *7*, 355. [[CrossRef](#)]
2. Sánchez, M.; Vásquez-Quitral, P.; Butto, N.; Díaz-Soler, F.; Yazdani-Pedram, M.; Silva, J.; Neira-Carrillo, A. Effect of Alginate from Chilean *Lessonia nigrescens* and MWCNTs on CaCO₃ Crystallization by Classical and Non-Classical Methods. *Crystals* **2018**, *8*, 69. [[CrossRef](#)]
3. Butto, N.; Cabrera-Barjas, G.; Neira-Carrillo, A. Electrocrystallization of CaCO₃ Crystals Obtained through Phosphorylated Chitin. *Crystals* **2018**, *8*, 82. [[CrossRef](#)]
4. Pastero, L.; Aquilano, D. Calcium Carbonate Polymorphs Growing in the Presence of Sericin: A New Composite Mimicking the Hierarchic Structure of Nacre. *Crystals* **2018**, *8*, 263. [[CrossRef](#)]
5. Hsu, C.-M.; Huang, Y.-H.; Nimje, V.; Lee, W.-C.; Chen, H.-J.; Kuo, Y.-H.; Huang, C.-H.; Chen, C.-C.; Chen, C.-Y. Comparative Study on the Sand Bioconsolidation through Calcium Carbonate Precipitation by *Sporosarcina pasteurii* and *Bacillus subtilis*. *Crystals* **2018**, *8*, 189. [[CrossRef](#)]
6. Atla, S.; Huang, Y.-H.; Yang, J.; Chen, H.-J.; Kuo, Y.-H.; Hsu, C.-M.; Lee, W.-C.; Chen, C.-C.; Hsu, D.-W.; Chen, C.-Y. Hydrophobic Calcium Carbonate for Cement Surface. *Crystals* **2017**, *7*, 371. [[CrossRef](#)]
7. Chen, P.; Yu, S. CO₂ Capture and Crystallization of Ammonia Bicarbonate in a Lab-Scale Scrubber. *Crystals* **2018**, *8*, 39. [[CrossRef](#)]

8. Costa, E.; Aquilano, D. Experimental Value of the Specific Surface Energy of the Cleavage {10.4} Calcite Rhombohedron in the Presence of Its Saturated Aqueous Solution. *Crystals* **2018**, *8*, 238. [[CrossRef](#)]
9. Xu, W.; Wen, H.; Zheng, R.; Li, F.; Huo, F.; Hou, M.; Zhou, G. The Carbonate Platform Model and Reservoirs' Origins of the Callovian-Oxfordian Stage in the Amu Darya Basin, Turkmenistan. *Crystals* **2018**, *8*, 84. [[CrossRef](#)]



© 2018 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).