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An overview of crystallization in gels

Manuel Prieto

Department of Geology, University of Oviedo, Spain. E-mail: mprieto@geol.uniovi.es

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Considerable experimental and theoretical work concerning crystallisation in gels can be found in the scientific literature. After the pioneer book by Henish [1], crystal growth in gels has shown to be a simple and suitable method for making single crystals of sparingly soluble salts, small-molecule compounds, and macromolecules, e.g.: [2,3]. The gel medium suppresses convection and advection only allowing diffusion of the aqueous species, which eventually can react to form solids. From experimental data it is abundantly clear that gels reduce the nucleation chance and, in that sense, offer certain research opportunities that crystallization from ”free” aqueous solutions cannot provide. So, in the context of purposeful crystal growth, the suppression of nucleation is the principal function of the gel because a lower nucleation density favours the development of larger crystals. However, a more fundamental interest of gels arises from their possibilities to explore crystallisation behaviour in a variety of environments, including microgravity, and to simulate a diversity of unusual crystallization phenomena, e.g.: [4-10]. Here, we present a brief review of previous work carried out with this kind of systems, which includes a miscellany of topics, such as 1) nucleation behaviour of stoichiometric compounds and solid solutions in porous media, 2) reaction paths and generation of patterns during the growth process, 3) metastable crystallization and subsequent solvent-mediated phase transformations, 4) simulation of biomineralization processes and generation of biomimetic crystalline aggregates, 5) sorption of pollutants by surface precipitation of pollutant-bearing phases on minerals embedded in gel media, and 6) simulation of mineral replacement and other mineral-fluid interaction phenomena.

[1] Henish, H.K. *Crystal Growth in Gels*, 1973, Pensylvania Univ. Press.
[2] Lefaucheux, F.; Robert, M.C. In: *Handbook of Crystal Growth,* 1994, 1273.
[3] García-Ruiz, J.M.; Gavira, J.A.; Otalora, F.; Guasch, A.; Coll, M. *Mat. Res. Bull.,* 1998, 33, 1593.
[4] García-Ruiz, J.M.; Novella, M.L.; Otalora, F. *J. Cryst. Growth,* 1999, 703.
[5] Prieto, M.; Putnis, A., Fernández, L.; López.-Andrés, S. *J. Cryst. Growth*, 1994, 142, 225.
[6] Prieto, M.; Fernández, A.; Putnis, A.; Fernádez, L. *Geochim. Cosmochim. Acta*, 1997, 61, 3383.
[7] García-Ruiz, J.M. *Geology*, 1998, 26, 843.
[8] Oaki, Y.; Imai, H. *Crystal Growth & Design*, 2003, 3, 711.
[9] Prieto, M.; Cubillas, P.; Fernández, A. *Geochim. Cosmochim. Acta*, 2003, 67, 3859.
[10] Carotenuto, L.; Piccolo, C.; Castagnolo, D.; Lappa, M.; Tortora, A.; García-Ruiz, J.M. *Act. Cryst. D*, 2002, 58, 1628.

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Why space crystallisation? Answers based on experimental results

K. Tsukamoto, P. Dold, E. Ono, M. Koizumi

Graduate School of Science, Tohoku University, Sendai, 980-8578, Japan and G. Sazaki: Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, 980-8577 Japan

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Space environment has been regarded as one of the most ”comfortable” environments for crystal growth. This is because 20% of space-grown crystals have shown better perfection than earth-grown crystals, though no convincing answer has been given to explain ”why?”.
We have investigated how defects are formed in protein (lysozyme) crystals by in-situ observation, employing phase-shift interferometry, confocal differential interferometry and some other phase-sensitive microscopy [1,2]. Since these optics are capable of resolving mono-molecular growth and dissolution steps, direct observation of step movement followed by the slight dissolution has been made at molecular resolution. In order to reveal the defects, short-time dissolution has been applied to the mono-molecular growth steps to reveal the character of the defects generated during the movement of these steps. We found by dissolution, at least two types: dislocation pits and shallow pits which related to micro-defects which, we suppose, are the origin of the mosaicity of protein crystals. It was found that more numbers of micro-defects are generated in a single step formed by 2D nucleation than in the steps generated by spiral growth from a dislocation. The spiral steps were found to move faster with less impurity effects in the spiral step shape.
In conclusions, more impurities (dimmers) are incorporated to lysozyme crystals with the help of convection or flow under gravity, which would give rise to the formation of micro-defects in the crystal. The number of defects generated in crystals is closely related to the time for the step to be exposed in the solution.
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[1] G. Sazaki, *K. Tsukamoto*, S. Yai, M. Okada, K. Nakajima, In situ observation of dislocations in protein crystals during growth by advanced optical microscopy, Crystal Growth & Design 5 No.5 (2005) 1729-1735.
[2] G. Sazaki, T. Matsui, *K. Tsukamoto*, N. Usami, T. Ujihara, K. Fujiwara, K. Nakajima, In-situ observation of elementary growth steps on the surface of protein crystals by laser on confocal microscopy, J. Crystal Growth 262 (2004) 536-542.