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Acta Cryst. (2011) A67, C538**Time-dependent effects in counter-diffusion nucleation**

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Known kinetic models are relatively successful in predicting steady state nucleation. Transient nucleation has been also modeled in restricted situations (constant concentration and temperature) showing the origin of some time-dependent effects. Nevertheless, current setups for crystallization from solution, especially those based in counter-diffusion methods, display a higher level of time-dependent behavior: concentration of two or more reactants do change continuously along the crystallization volume and over time and, in some setups, it is also possible to have continuous, long term changes in other parameters affecting nucleation like pH or temperature.

This transient behavior can modify the output of the experiment in terms of the supersaturation at which nucleation happen, the nucleation flux, and can even have an active role in the selection of polymorph at nucleation time.

Experimental evidence of these effects has been collected in our laboratory, mainly from protein crystal growth in counter-diffusion experiments. In these experiments, nucleation at variable supersaturation and crystallization of different polymorphs is often observed but have never been explained in terms of transient nucleation, that is the objective of this work.

Equations describing the transient development of the precritical clusters population, coupled with the mass transport processes characteristic of counter-diffusion methods have been prepared and implemented in the form of a numerical simulation of counter-diffusion, with an special emphasis on nucleation.

The output of these simulations shows the relative role of the time required to setup an steady precritical distribution and the characteristic rate of macroscopic mass transport, that result in a definite rate of change of the critical size during the experiment. The supersaturation at which nucleation happen is mainly controlled by this rate of change in the critical size, that is dependent on the position at the experimental volume. Obviously, this transient, automatic selection of the nucleation conditions lead to situations out equilibrium following a path in the phase space that is time- and position-dependent. Under these circumstances, kinetic selection of different polymorphs is possible.

Keywords: nucleation, time-dependent, counter-diffusion

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Acta Cryst. (2011) A67, C538**Crystal Growth in Carbon Sequestration**

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Nano-scale approaches for a carbon sequestration have been started to understand how efficiently and economically to solidify carbon dioxide in air in the form of calcium carbonate crystals under the ground. In that field, varieties of crystal growth knowledge and technologies would be needed.

We have two different approaches, one is in laboratory to study the crystal growth mechanism of calcium carbonates, calcite, aragonite and vaterite by in-situ observation method, and another is the continuous monitoring or in-situ observation of natural crystal growth rate of

calcite under the ground. Some new approaches and new results will be shown in the presentation.

Keywords: crystallization, carbon sequestration, calcite.

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Acta Cryst. (2011) A67, C538**How slow do giant gypsum crystals grow?**

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Mineralogical processes taking place close to equilibrium, or with very slow kinetics, are difficult to quantify precisely. The determination of ultra slow precipitation rates should reveal characteristic timing associated to processes that are important at geological scale. We designed an advanced high-resolution white beam phase-shift interferometry microscope to measure growth rates of crystals at very low supersaturation values.

To test this technique, we selected the giant crystals of gypsum of Naica ore mines (Mexico), a challenging subject in mineral formation. They are formed by a self-feeding mechanism driven by solution-mediated anhydrite-gypsum phase transition, and are the result of an extremely slow crystallization process close to equilibrium [1]. To calculate the formation time of these crystals we measured the growth rates of the {010} face of gypsum growing from current waters from Naica at different temperatures. The slowest measurable growth rate was found at 55 °C, being $1.4 \pm 0.2 \times 10^{-5}$ nm/s, the slowest value measured for a crystal growth process. At higher temperatures growth rates increase exponentially due to decreasing gypsum solubility and higher kinetic coefficient [2]. At 50 °C neither growth nor dissolution was observed indicating that growth of giant crystals of gypsum occurred at Naica between 58 °C and current temperature of Naica waters, confirming formation temperatures determined from fluid inclusion studies.

Our results demonstrate the usefulness of applying advanced optical techniques in laboratory experiments to gain a better understanding of crystal growth processes occurring at a geological time scale.



[1] J.M. García-Ruiz, *Geology* **2007**, 35, 327-330. [2] A.E.S. Van Driessche, J.M. Delgado-Lopéz, G. Sasaki, *Crystal Growth and Design* **2010**, 10, 3909-3916.

Keywords: giant crystals, growth rates, phase-shifting interferometry