Multi-step crystallization pathways in natural and engineered cements

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1. Introduction

A cement is a material with binding properties that hold together the different components of structures such as bridges, buildings and monuments. Engineered cements have been produced for centuries now, mostly from the calcination and melting of limestone and aluminosilicates. Ordinary Portland cement (OPC), is actually the most produced material in the world, with more than 4,000 million metric tons per year. Cement hydration involves a combination of dissolution and re-precipitation processes through which a variety of hydrated phases are formed. Calcium silicate hydrates (C-S-H, using the cement notation), are the most abundant family of binders. They have a complex, non-uniform stoichiometry (varying Ca/Si ratios and water content) and nanocrystalline character. C-S-H is the main phase in OPC, responsible for its strength and durability. Other engineered cements include for instance basanite ($CaSO_4 \cdot 0.5H_2O$, plaster of Paris), portlandite ($Ca(OH)_2$)) and geopolymers. The latter are a kind of supplementary cementitious materials (SCM_s) that are used in combination with OPC to decrease the CO_2 footprint from OPC production. OPC production accounts for 5–7% of the global human-made CO_2 emissions, posing a technological challenge in the search for 'green' OPC replacements.

In spite of the extensive use of engineered cements and the development of new families of SCMs to improve workability, setting rate and to lower the cement CO2 footprint, many aspects of the initial steps of the cement hydration process remain unknown, including the mechanisms of C-S-H nucleation *(Garrault-Gauffinet & Nonat, 1999)*. Moreover, the physico-chemical conditions under which cement hydrates form are extreme, such as the high alkalinity (cement pore water pH values of 13) and their crystallization in restricted, confined spaces. These are important points that hamper our ability to direct cement nucleation, for instance, for the restoration of cultural heritage or for healing of fractures and pores in engineered structures.

An analogy to cement materials can be made with the 'natural binders' that compose multiple structures such as our teeth, marine shells and bones, forming natural (nano) composites. These 'natural cements' are widespread, fundamental components of living organisms that offer them physical and chemical protection and articulate them *(Rieger et al., 2014)*. These include, to name a few examples, the apatite formed in the nanopores between collagen fibers of our teeth, the aragonite tablets in the nacre shells or the calcite that forms the spicules of the sea urchin *(Addadi et al., 2003)*. Biominerals are a clear example of directed mineral precipitation allowing functional development. Crystallization of biominerals is dictated by a complex interplay of organic and inorganic additives and external 'biological substrates' that direct the nucleation through multiple steps, allowing the controlled precipitation of a mineral phase at specific location, typically in a confined space, and at a given time. They offer a perfect benchmark from which to improve the development of our cement technology.
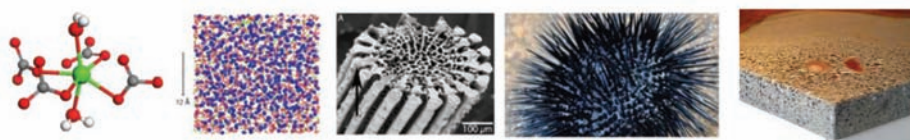
2. Multi-step crystallization pathways

In recent years, complex multi-stage nucleation pathways have been reported for iron oxides, carbonate, phosphate and sulfate minerals. These so-called non-classical pathways include the formation of stable or kinetically trapped aqueous species that act as precursors of the final crystalline polymorphs *(Benzerara et al., 2014; Gebauer et al., 2008; Wallace et al., 2013)* (see *Fig. 1*). Pre-nucleation clusters (PNCs) *(Gebauer et al., 2008)*, polymer-induced liquid precursors (PILP) *(Gower & Odom, 2000)*, or dynamically ordered liquid like oxyanion polymers (DOLLOP) *(Demichelis et al., 2011)*, are examples of aqueous precursor species reported for the CaCO3 system. These precursor species have been shown to aggregate in solution, forming amorphous calcium carbonate (ACC), an amorphous material that subsequently crystallizes as a $CaCO_3$ polymorph. Amorphous precipitates have been also reported for the phosphate system, forming as well from aqueous clusters. These aqueous species and amorphous precursors offer 'shortcuts' throughout the free energy landscape for the formation of crystalline polymorphs, supposedly decreasing the interfacial free energies and consequently lowering the barrier(s) to nucleation *(Navrotsky, 2004)*. This contrasts with the 'classical view' of a crystal growth process via ion-by-ion addition. A prototypical example in the field of biomineralization is that of the sea-urchin *(Politi et al., 2008)*. At the early stages of development, sea urchin spicules are made out of ACC that crystallizes into calcite at later stages. The moldable hydrated structure of ACC procures that the sea urchin, among other organisms, can create the intricated shapes of their shells and/or skeletons, acting as a very effective cement, with pore-filling character *(Yang et al., 2011)*.
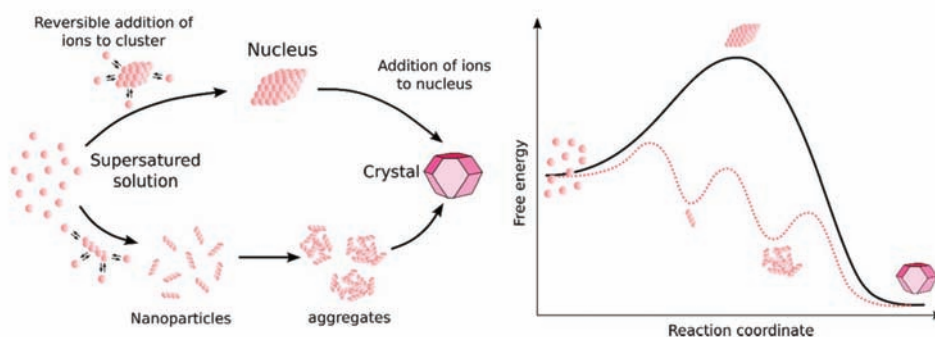

Fig. 1. Classical (top arrow) and so-called 'non-classical' (bottom arrow) nucleation pathways through the formation of nanoparticles, aggregates (amorphous intermediates), and a schematic energetic landscape. Adapted from (Sleutel & Van Driessche, 2014).

Biomimicry: enabling new cement technologies

The discovery of the PILP intermediate by L. Gower in the early 2000s *(Gower, 2008; Gower & Odom, 2000)* started a slow-developing revolution in the way mineral precipitation processes were and are used for engineered applications. Specifically, the so-called PILP process, i.e., the occurrence of a liquid-liquid separation in $CaCO_3$, was reported also for apatite, opening the way for the development of dental remineralization strategies based on the same principle: the kinetic stabilization of a liquid polymer-like mineral (apatite) precursor that is able to diffuse within the pores of the (collagen) matrix, directing crystallization into the internal pores *(Burwell et al., 2012)*. This technology is a paradigmatic example of biomimicry, with high potential for many other applications in the cement industry.

In spite of all these advances, there are still fundamental question that remain open about (i) the structure of the aqueous clusters leading to the formation of the amorphous / liquid-like precursors, and (ii) the specific factors that control the stability of these precursors,

their dehydration, and their further crystallization into crystalline polymorphs. In addition, the physico-chemical parameters controlling polymorph selections mechanism remain unknown. Some authors have proposed that water plays an important role as stabilizer of the amorphous structure *(Raiteri & Gale, 2010)* in the $CaCO_3$ system. At the same time, it is known that non-collagenous proteins and inorganic ions are present naturally occurring crystallization intermediates, but their roles in the stability and crystallization processes are still unknown *(Addadi et al., 2003; Ihli et al., 2013)*. More research in these fields will enable the next generation of 'cement' products inspired by nature.

Engineered cements

Calcium silicate hydrate (C-S-H) is the most important binding phase in ordinary Portland cement. It forms as a result of a dissolution-reprecipitation process involving highly reactive clinker materials. C-S-H is by nature poorly crystalline, with an atomic structure similar to that of a disordered tobermorite, including turbostratic disorder and the presence of $Ca(OH)_2$ sheets at high Ca/Si values. The formation process of C-S-H is therefore dominated by nucleation, with only limited growth. Whereas many studies have focused on the mesoscale structural evolution of the process of cement hydration only a few studies have addressed the formation mechanisms of C-S-H in detail *(Bligh et al., 2016; Garrault-Gauffinet & Nonat, 1999)*. *Garrault-Gauffinet & Nonat (1999)* used changes in electrical conductivity to follow C-S-H formation, and interpreted their results using classical nucleation theory (CNT). Whereas their results are self-consistent within the framework of CNT, the lack of physical and chemical characterization of the initial precipitates renders their claim of CNT little credibility. Indeed, the recent advances in the understanding of carbonate formation processes have taught us about the need for in situ characterization of the early stages. A recent study on C-S-H nucleation has brought into light the existence of a Si-rich amorphous precursor to C-S-H. However, its structural and dynamical characteristics, as well as its chemical composition

and its transformation to C-S-H remain elusive as of today *(Krautwurst et al., 2017)*. Work remains to be done in order to put in perspective the importance of this amorphous precursor to C-S-H.

3. Crystallization under confinement

Nucleation phenomena in engineered and natural cements take place often in micro- or nanoscopic pores. Understanding the factors that control nucleation and growth of solid phases in porous media, and how they differ from the bulk, is still an ongoing task. The reason is related to the different levels of complexity related to the problem. These include: (i) the lack of a unified picture of water structure, dynamics and energetics in confined spaces; (ii) a poor understanding of ion speciation in confinement and under reduced water activity; and (iii) a lack of knowledge about the interplay of the different factors controlling nucleation (pore controlled solubility vs. interfacial chemistry). Points (i) and (ii) are not treated here. A wide array of literature exists regarding these issues. Moreover, the development of advanced scattering, spectroscopic and imaging techniques, as well as computer simulation, is advancing these questions at significant pace. The point (iii), related to the nucleation process under confinement itself, has been addressed by different authors over the last three decades. Some of the main ideas are discussed here.

Pore-size controlled solubility effects

A pore-size control on the solubility of crystals growing in confined pores has been widely reported *(Flatt, 2002; Scherer, 1999)*. This phenomenon, called the 'Pore-size Controlled Solubility' effect (PCS), comes from the fact that an extra energetic term is present for highly curved (small) crystals growing in confinement. It is explained by classical thermodynamics. According to the Young–Laplace equation, the pressure difference, Δp, across a solid?liquid interface is proportional to the curvature of the interface, with the interfacial tension being the proportionality constant. A complete thermodynamic treatment of this effect is described in Scherer (2002). This excess pressure shifts

the solubility of the crystal from the bulk solubility S_0 to an effective solubility S_d. For a crystal forming in a cylindrical pore this can be expressed as:

$$\frac{S_d}{S_0} = \exp\left(\frac{-\Delta pv}{nRT}\right) = exp\left(\frac{-v}{nRT}\frac{2\gamma\cos\theta}{d}\right)$$

[equation 1]

where v is the molar volume of the crystallizing solute, T is the absolute temperature, R is the ideal-gas constant, n is the number of moles crystallizing, d is the pore diameter and is the contact angle between the growing crystal and the pore surface. PCS effects have been also incorporated recently to reactive transport models that account for the observed cementation of large pores during fluid transport through a heterogeneous rock matrix *(Emmanuel et al., 2007; Emmanuel & Ague, 2009)*. Plots of S_d/S_0 values are shown in *Fig. 2*, as a function of pore size, d, and of the interfacial free energy of the growing cluster/water interface, *(Emmanuel & Ague, 2009)*.
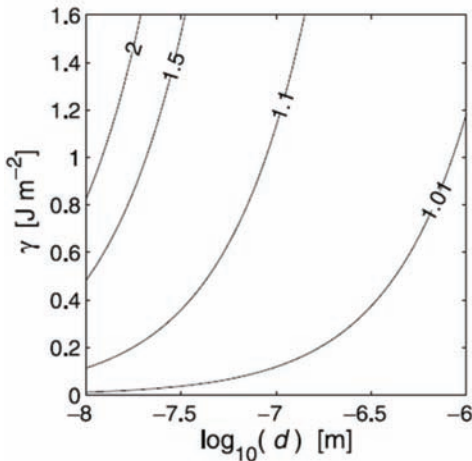

Fig. 2. Plot of the effective saturation (S_d/S_0) as a function of pore size, d, and interfacial energy, γ, for a crystal growing in a cylindrical pore. Calculated from eq. 1 using values in Table 1 with T = 373 K. From (Emmanuel & Ague, 2009).

It is interesting to see that the pore-size effect can be considered as negligible in cases where the interfacial free energy is relatively low. For instance, solid/water interfacial free energies for the most common crystallographic faces of gypsum and calcite (two widely used minerals in cement applications) are in the order of $\gamma CaSO_4 = 0.01$ J/m^2 and $\gamma CaCO_3 = 0.1$ J/m^2. This makes that, in the whole range of pore sizes, from the micron to the nanoscale, the enhancement of the supersaturation is not expected to exceed a 10%, i.e., $S_d/S_0 < 1.1$.

Kinetic effects

A seminal paper in this field was published by *(Prieto et al., 1990)*. These authors observed that the supersaturation attained by salts nucleating in gel pores was proportional to the increase rate of the supersaturation itself. They introduced the concept of 'threshold supersaturation' *(Prieto et al., 1990; Putnis et al., 1995)* meaning the supersaturation that has to be attained to spark crystallization at a given supersaturation rate. Note that this is a kinetic concept, defined after non-equilibrium experiments with solution supersaturation values evolving in time. The experiments were performed using a porous medium consisting of a column with a silica aerogel, with pores in the range 2 – 200 nm. The system is fed with an anionic and a cationic solution, one arriving from each side. This geometry yields a non-uniform distribution of solution supersaturation values along the column that evolves with time. An empirical law relating supersaturation rate (q) and threshold supersaturation (σt) was proposed (see *Fig. 3*):

$$q = k\sigma_t^m \qquad \text{(equation 2)}$$

where k and m are a proportionality constant and an exponent respectively. This empirical law applies also in the case of supercooled solutions (supercooling: lowering the temperature of a liquid below its freezing point without it becoming a solid). Studies over the last few decades have shown that undercooling ΔT ($\Delta T = T_{freeze}-T_{cryst}$) is maximized in confinement and by increasing solution cooling rates *(Kashchiev et al., 2010)*. Whether the supersaturation is attained by cooling or by increasing the concentration of a salt in a solution this law is of general applicability. The exponent m and the proportionality constant depend then on the nature of the nucle-
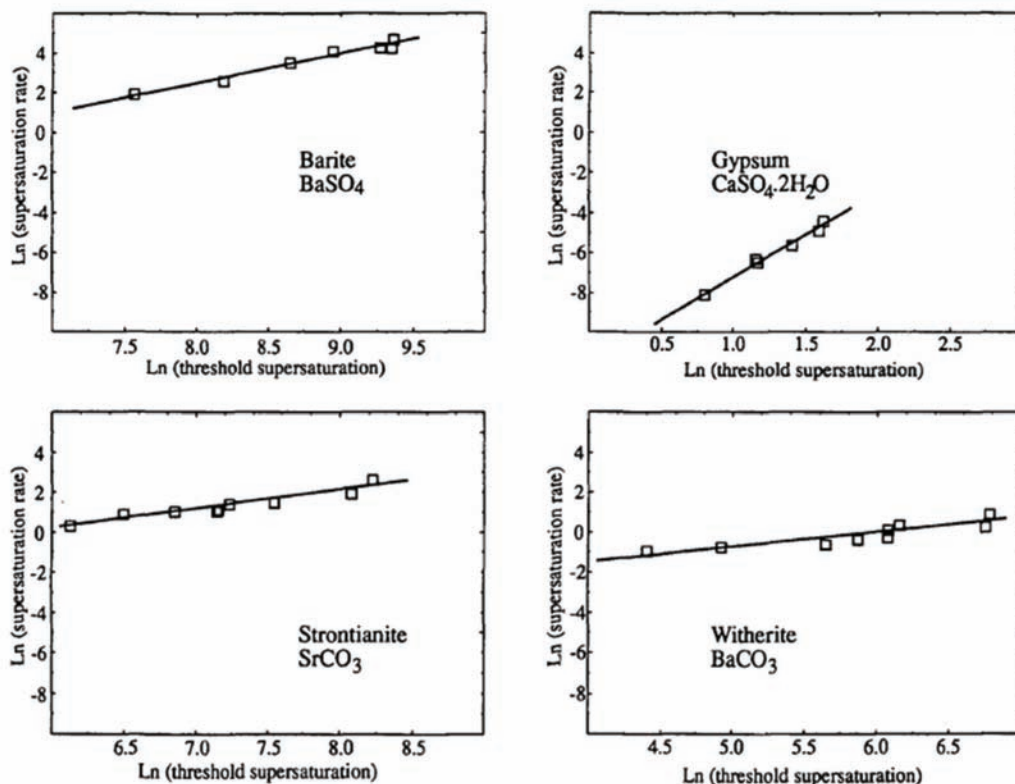
Fig. 3. Plots of the supersaturation rate as a function of the threshold supersaturation for barite, gypsum, strontianite and witherite. From (Putnis et al., 1995).

ated solid, on the volume (confinement) and on the thermal history of the solution.

The explanations to these phenomena were attributed to kinetic effects related with the limited supply of growth units to a growing nucleus in a nanopore. Restricted dynamics of aqueous solutions in confined media have been reported to occur in nanopores filled with $CaCl_2$ and LiCl *(Mamontov et al., 2008)*. Interestingly, the greatest suppression of water dynamics is found for $CaCl_2$ solutions, indicating that there may be a collaborative effect of cation charge, hydration environment and confinement geometry. More studies on this field are needed to understand what are the limiting mechanisms for solute transport, and the influence of pore surface chemistry.

Surface chemistry

Confinement also influences pore surface chemical properties, potentially impacting heterogeneous nucleation phenomena. *(Wang et al., 2003)* have shown that the acidity constants (pK_{a1} and pK_{a2}) of functional groups in mesoporous alumina are shifted with respect to those of a bulk alumina, the porous material having neutral charge over a narrower range of pH. This gives rise to a high surface charge density in mesoporous materials, which influences their ion adsorption edges enhancing ion adsorption. Similarly, convex curved surfaces have been reported to shift acidity constants of functional groups on the external surface of imogolite nanotubes with respect to those of gibbsite (its planar counterpart) *(Fernandez-Martinez, 2009)*.
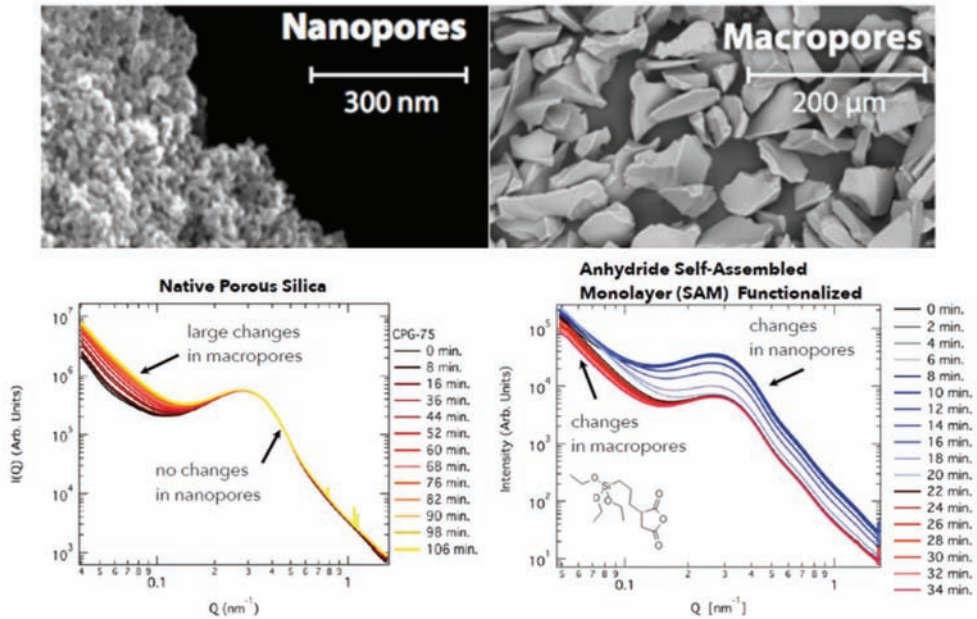
Fig. 4. Top: SEM image of the mesoporous silica material (CPG-75) used in the Small-Angle X-ray Scattering (SAXS) experiments, showing the nanopores and macropores. Bottom: SAXS patterns taken during the in-situ CaCO$_3$ precipitation experiment. The left graph shows an increase in the intensity at low angle with time, indicating precipitation in the raw SiO$_2$ macropores. The right graph shows changes in the intensity at the nanopore scale, as a result of CaCO$_3$ precipitation in the carboxyl-terminated silica material. Modified from Stack et al., (2014).

Whereas the inhibition of mineral nucleation in nanopores has been explained successfully by the PCS effect in many cases *(Emmanuel et al., 2007; Emmanuel & Ague, 2009; Putnis & Mauthe, 2001)*, recent observations suggest that the PCS effect is not dominant in cases where surface chemistry offers a preferential template for mineral nucleation (*Stack et al., 2014*). This hypothesis has been recently reinforced by statistical physics models of heterogeneous nucleation *(Hedges and Whitelam, 2013)*. Indeed, *Stack et al. (2014)* showed that CaCO$_3$ nucleated preferentially in nanopores functionalized with carboxyl-terminated organic moieties that offered a good template for precipitation *(Fig. 4)*. ACC was determined to be the nucleated form of CaCO$_3$. Interestingly, ACC has been shown to be stabilized under confinement *(Stephens et al., 2010)*. This fact points to confinement as a hypothetic important parameter controlling CaCO$_3$ nucleation in biominerals, and governing the crystallization kinetics of

PILP or amorphous intermediates. These results highlight the need for further investigations in order to develop consistent thermodynamic models of precipitation phenomena at the nanoscale.

4. Conclusions and perspectives

Studies addressing nucleation and growth of biominerals have significantly impacted our understanding of the fundamental mechanisms underlying these complex phenomena. The discovery of multi-step nucleation processes and of aqueous intermediates to nucleation, together with the phase separation occurring in the liquid state of highly supersaturated solutions, opens new perspectives for the development of biomimetic materials, especially in the field of engineered materials. However, significant gaps remain present in our knowledge of fundamental processes. These include the applicability of classical nucleation theory to these multi-step nucleation pathways, or the numerous physico-chemical factors affecting nucle-

ation in confined spaces.

A feedback between our studies on natural and engineered systems is necessary. Recent studies on C-S-H nucleation have brought into light the existence of an amorphous precursor to C-S-H. Determining the crystallization pathway is of special relevance for the development of effective cement retardants and for the chemical industry: the potential occurrence of aggregation-based processes of the initially formed amorphous 'droplets' (i.e., a physical process) would open new possibilities for the stabilization of these C-S-H precursors.

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