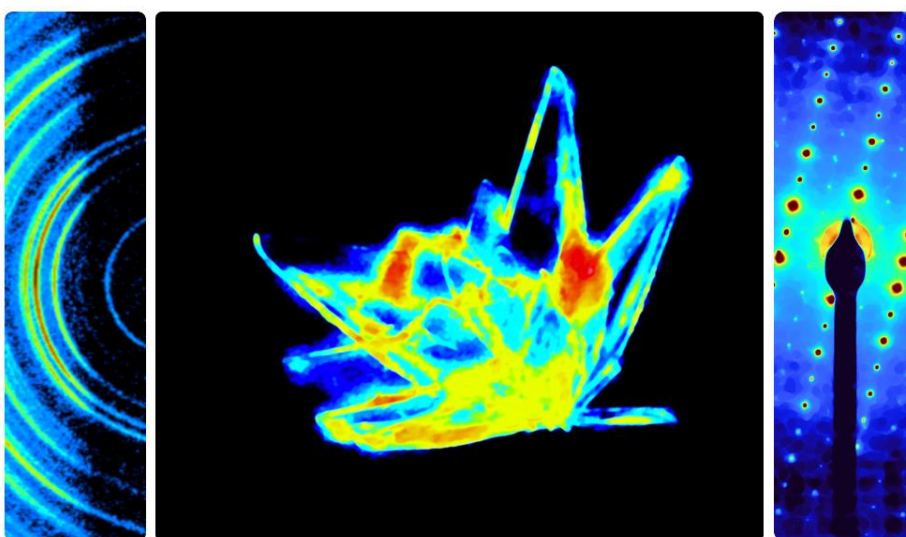


Doctoral Thesis

Phase Formation and Transformations in the $\text{CaSO}_4\text{-H}_2\text{O}$ System: Implications for the Conservation of Plasterworks



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*“Y si fuera mi vida una escalera
me la he pasao’ entera
buscando el siguiente escalón”*

...

“La vereda de la puerta de atrás” – Extremoduro, 2002

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Si comenzar una Tesis Doctoral no es una tarea trivial, terminarla lo es aún menos. El camino de la Ciencia es, cuanto menos, arduo dada la cantidad y variedad de problemas que a diario se nos plantean, y a los cuales debemos darle una solución basada siempre en la evidencia y en el conocimiento previo. Como dijo un buen amigo hace tiempo, *“la Ciencia es una amante exigente”*. Qué razón tenías, Alberto. Allá donde quiera que estés, de buena te has librado.

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RESUMEN

El yeso, junto con la cal, ha sido empleado desde el Neolítico (12000 - 2000 a.C.) y a lo largo de las civilizaciones posteriores como un aglutinante hidráulico clave. El uso tradicional de este material involucra el procesado térmico del yeso ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), necesario para la obtención de bassanita (hemihidrato) y/o anhidrita ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ y CaSO_4 , respectivamente). Este material, globalmente conocido como “yeso de París”, se mezcla con agua para promover la formación de yeso, su fraguado y endurecimiento (Kingery *et al.*, 1988). En analogía al conocido “ciclo de la cal”, a este conjunto de reacciones de deshidratación y rehidratación podría atribuírsele el nombre de “ciclo del yeso” (Elert *et al.*, 2002; Elsen 2006; Gartner, 2009; Rodríguez-Navarro *et al.*, 2013).

En la actualidad, el yeso (refiriéndose de forma genérica a las tres fases cristalinas principales descritas para el sulfato de calcio) sigue siendo uno de los minerales más demandados en el mundo, especialmente por su aplicación en el ámbito de la construcción (U.S. Geological Survey, Mineral Commodity Summaries, 2023). Aunque el yeso ha tenido una relevancia histórica y un uso generalizado, presenta diversas limitaciones, como una resistencia mecánica reducida en estado húmedo o una solubilidad relativamente alta. Esto hace que los materiales elaborados a partir de este mineral sean especialmente susceptibles al deterioro en ambientes húmedos o bajo condiciones climáticas severas (*e.g.*, Charola and Koestler, 2006; Brimblecombe and Grossi, 2009; Palha *et al.*, 2012; Jroundi *et al.*, 2014; Molina *et al.*, 2017; Jiang *et al.*, 2021; Xu *et al.*, 2022). Estos procesos de deterioro se hacen patentes en numerosos elementos arquitectónicos y yeserías ornamentales en monumentos (y otras construcciones recientes) de reconocida importancia cultural, como es el caso de La Alhambra de Granada. Para abordar este problema, recientemente se han desarrollado y aplicado diversos procedimientos de conservación, habiéndose logrado grandes avances tecnológicos en la fabricación de réplicas y la sustitución de materiales, como es el caso del Mortero Alhambra® (Rubio-Domene, 2010). Sin embargo la aplicación de los llamados “consolidantes” es necesaria para mejorar la cohesión mecánica de sustratos ya desgastados y

preservar las obras de arte originales (e.g., Bradley, 1984; Hansen *et al.*, 2003; Sanjurjo-Sánchez *et al.*, 2010; Scherer and Wheeler, 2009; Elert *et al.*, 2022). Sin embargo, hasta ahora no se ha profundizado lo suficiente en la elaboración de consolidantes adecuados para las yeserías.

Estos precedentes sientan las bases principales del proyecto abordado. De esta forma, y conforme al título de esta tesis doctoral, el objetivo principal de este trabajo puede resumirse en “conocer y controlar los procesos de formación y transformación de las distintas fases del sistema $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ con el fin de diseñar productos para la conservación de yeserías”.

Para tal fin, profundizar en aspectos cristalográficos y físico-químicos fundamentales resulta indispensable. De esta manera, en este estudio se han analizado, desde un punto de vista estructural, los cambios de fase que ocurren durante la deshidratación y rehidratación del yeso, así como los procesos de cristalización (homogénea y heterogénea) que conducen a la precipitación y el crecimiento del yeso y los distintos factores que influyen sobre ellos (Rodríguez-Navarro *et al.*, 2009; Ruiz-Agudo and Rodríguez-Navarro, 2010).

Como se discute más adelante, los resultados obtenidos demuestran: (I) los procesos de formación y transformación en el sistema químico estudiado responden a mecanismos multietapa controlados principalmente por procesos acoplados de disolución-precipitación y/o de agregación orientada de nanopartículas (Cölfen and Antonietti, 2008; Van Driessche *et al.*, 2012; Stawski *et al.*, 2016). La descripción de estos mecanismos se encuentra muy alejada del paradigma clásico de la cristalización, y (II) la incorporación de aditivos (desde un punto de vista bio-inspirado o bio-mimético) resulta ser una estrategia eficaz para la modificación de las propiedades físico-químicas del yeso a raíz de la alteración controlada de los mecanismos de nucleación y crecimiento cristalino (e.g., Hamdona and Al Hadad, 2008; Rabizadeh *et al.*, 2014; Harouaka and Kubicki, 2017; Ossorio *et al.*, 2017; Nicoleau *et al.*, 2019; Madeja *et al.*, 2023).

Empleando el conocimiento adquirido acerca de los factores que afectan a la cristalización de las distintas fases de sulfato de calcio se han diseñado diferentes

productos minerales nanoestructurados, destinados a ser utilizados como consolidantes para la conservación del patrimonio histórico construido deteriorado. Así, se ha desarrollado un protocolo versátil de síntesis solvo-termal para producir y modificar nanopartículas de bassanita para la consolidación efectiva de materiales elaborados a partir de yeso, de uso muy extendido tanto en construcción como en el patrimonio histórico (Burgos-Ruiz *et al.*, 2021). Tras su síntesis, estas nanopartículas son re-dispersadas en alcoholes alifáticos de cadena corta, como pueden ser el etanol o el propanol, de manera que puedan conservarse durante mucho tiempo sin sufrir fenómenos secundarios de recrecimiento, y para facilitar enormemente su posterior aplicación. En contacto con el vapor de agua, presente en la atmósfera como uno de sus componentes mayoritarios, estas nanopartículas de bassanita se hidratan para, finalmente, formar un cemento de yeso en el interior de sustrato tratado. Además, desde el punto de vista de la conservación, se trataría del tratamiento más compatible con los materiales elaborados a partir de yeso, ya que ambos, sustrato y consolidante, comparten composición química y estructura.

Por otro lado, se ha investigado cómo la calceína (un quelante orgánico fluorescente) afecta tanto a la cristalización del yeso (modificando los mecanismos de nucleación y crecimiento cristalino), como a la hidratación del consolidante de nano-bassanita obtenido mediante esta nueva ruta de síntesis. Se ha observado, además, que el yeso resultante de la hidratación del consolidante químicamente modificado muestra una mayor resistencia a la disolución cuando la calceína queda ocluida en el interior de los cristales de yeso neo-formados. La fluorescencia, además, aporta una solución complementaria para la conservación de las yeserías. Dado que la calceína queda ocluida en los cristales de sulfato de calcio y que, en dosis mínimas, no altera las propiedades organolépticas de los materiales tratados, la identificación de las zonas tratadas y de la profundidad alcanzada por el consolidante resulta viable. De otra forma sería prácticamente imposible conocer la localización espacial de estos tratamientos, puesto que tanto consolidante como sustrato se componen esencialmente de sulfato de calcio. Además, estos tratamientos han resultado ser efectivos, al haberse demostrado que producen un aumento significativo de la resistencia mecánica de los sustratos tratados.

Por último, dado su alto rendimiento y versatilidad, ha sido posible adaptar esta ruta solvo-termal de síntesis de nano-bassanita para la obtención de otros materiales minerales nanoestructurados. En concreto, mediante esta estrategia se prepararon suspensiones alcohólicas de nanopartículas de hidróxido de calcio (Ca(OH)_2 ; conocidas como “nanocales” en el campo de la conservación), que fueron funcionalizadas con recubrimientos de gel de sílice (Burgos-Ruiz *et al.*, 2023). Esta modificación química permite modificar por completo el comportamiento coloidal de estas partículas en función del medio en el que se dispersan. Mientras que en suspensión alcohólica permanecen estables durante largos periodos de tiempo, en presencia de agua tienden a desestabilizarse, agregarse y sedimentarse muy rápidamente, evitando así los fenómenos de retroceso (migración de nanopartículas hacia la superficie tratada) que normalmente impiden aprovechar en su totalidad el potencial efecto cementante de los consolidantes. De este modo, el campo de aplicación de las “nanocales” puede ampliarse a otros tipos de materiales porosos, como la arenisca, donde los recubrimientos de sílice actuarían como agentes de acoplamiento entre el sustrato y el consolidante.

SUMMARY

Gypsum, along with lime, has been used since the Neolithic period (12,000 - 2,000 B.C.) and throughout subsequent civilizations as a key hydraulic binder. The traditional utilization of this material as a binder involves the thermal processing of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), necessary for the production of bassanite and/or anhydrite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ and CaSO_4 , respectively). This material, globally known as "*plaster of Paris*", is mixed with water to induce gypsum formation, setting, and hardening (Kingery *et al.*, 1988). In analogy to the well-known "lime cycle," this set of dehydration and rehydration reactions could be called the "gypsum cycle" (Elsen 2006; Gartner, 2009; Elert *et al.*, 2002; Rodriguez-Navarro *et al.*, 2013).

Currently, gypsum (*i.e.*, in general the three main crystalline phases in the CaSO_4 - H_2O system) remains one of the most demanded minerals in the world, especially for its application in the construction industry (U.S. Geological Survey, Mineral Commodity Summaries, 2023). Although gypsum has had historical relevance and widespread use, it presents various limitations, such as reduced mechanical strength in wet conditions or relatively high solubility. This makes materials based on this mineral particularly susceptible to deterioration in humid environments or under severe climatic conditions (*e.g.*, Charola and Koestler, 2006; Brimblecombe and Grossi, 2009; Palha *et al.*, 2012; Jroundi *et al.*, 2014; Molina *et al.*, 2017; Jiang *et al.*, 2021; Xu *et al.*, 2022). These deterioration processes are evident in numerous architectural elements and ornamental plasterwork in monuments (and other recent constructions) of recognized cultural importance, such as the Alhambra in Granada. To address this issue, various conservation procedures have been recently developed and implemented, leading to significant technological advancements in replica manufacturing and material substitution, such as the Mortero Alhambra® (Rubio-Domene, 2010). However, the application of so-called "consolidants" is necessary to improve the mechanical cohesion of already worn substrates and preserve original artworks (*e.g.*, Bradley, 1984; Hansen *et al.*, 2003; Sanjurjo-Sánchez *et al.*, 2010; Scherer and Wheeler, 2009; Elert *et al.*, 2022). Nevertheless, until now, little attention has been given to the development of suitable consolidants for gypsum plasterwork .

These precedents lay the main foundations of the present project. Thus, in accordance with the title of this doctoral thesis, the main objective of this work can be summarized as "understanding and controlling the processes of formation and transformation of the different phases of the $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ system in order to design products for the conservation of plasterwork".

To achieve this goal, delving into fundamental crystallographic and physico-chemical aspects is indispensable. Therefore, throughout this study, the phase transitions occurring during gypsum dehydration and rehydration, as well as the crystallization processes (homogeneous and heterogeneous) leading to gypsum precipitation and growth are analyzed from a structural perspective (Rodríguez-Navarro *et al.*, 2009; Ruiz-Agudo and Rodríguez-Navarro, 2010).

As discussed later on, the results obtained demonstrate: (I) the formation and transformation processes in the studied chemical system respond to multi-stage mechanisms –diverging from the classical paradigm of crystallization– primarily controlled by coupled dissolution-precipitation processes and/or oriented aggregation of nanoparticles (Cölfen and Antonietti, 2008; Van Driessche *et al.*, 2012; Stawski *et al.*, 2016), and (II) the incorporation of additives (from a bio-inspired or bio-mimetic perspective) proves to be an effective strategy for modifying the physical-chemical properties of gypsum by impacting nucleation and crystal growth mechanisms (*e.g.*, Hamdona and Al Hadad, 2008; Rabizadeh *et al.*, 2014; Harouaka and Kubicki, 2017; Ossorio *et al.*, 2017; Nicoleau *et al.*, 2019; Madeja *et al.*, 2023).

These results have been employed to design nanostructured mineral products for their intended use as consolidants for the conservation of deteriorated built heritage. Thus, a versatile solvo-thermal synthesis protocol has been developed for the preparation and modification of bassanite nanoparticles for the effective consolidation of gypsum-based materials (Burgos-Ruiz *et al.*, 2021), widely used in construction and heritage conservation. After synthesis, these nanoparticles are redispersed in short-chain aliphatic alcohols, such as ethanol or propanol, so that they can be preserved for a long time without undergoing secondary regrowth phenomena and to greatly facilitate their subsequent application. In contact with water vapor, which is one of the main components of the atmosphere, these bassanite nanoparticles

hydrate to form a gypsum cement inside the treated substrate. Moreover, from a conservation point of view, it would be the most compatible treatment for gypsum-based materials, since both the substrate and the consolidant have the same chemical composition and crystal structure.

Furthermore, research has been conducted on how calcein (a fluorescent organic chelating agent) affects both the formation of gypsum from solution and the hydration of the produced nano-bassanite consolidant. One major result is that gypsum formed upon the hydration of the chemically-modified bassanite shows greater resistance to dissolution when calcein is occluded between gypsum crystal domains. Additionally, fluorescence provides a complementary solution for plasterwork conservation. Since calcein becomes occluded in the calcium sulfate crystals and, in minimal doses, does not alter the organoleptic properties of the treated materials, the identification of treated areas and the depth reached by the consolidant becomes viable. Otherwise, it would be practically impossible to detect the spatial location of these treatments, since both consolidant and substrate essentially consist of calcium sulfate. Furthermore, these treatments have proven to be effective, as they have demonstrated a significant increase in the mechanical strength of the treated substrates.

Finally, given its high yield and versatility, we adapted this solvo-thermal route of nano-bassanite synthesis to obtain other nanostructured mineral materials. Specifically, this strategy was necessary to prepare alcoholic suspensions of calcium hydroxide nanoparticles ($\text{Ca}(\text{OH})_2$; known as "nanolimes" in the field of conservation) which were functionalized with silica gel coatings (Burgos-Ruiz *et al.*, 2023). This chemical modification allows to modify the colloidal behavior of these particles depending on the medium in which they are dispersed. While they remain stable for long periods of time in alcoholic suspension, in the presence of water they tend to destabilize, aggregate and sediment very quickly, thus avoiding back-migration phenomena that normally hinder the potential cementing effect of the consolidants. In this way, the range of application of "nanolimes" can be extended to other types of porous materials, such as sandstone, where silica coatings would perform as coupling agents between the substrate and the consolidant.

CHAPTER 1. INTRODUCTION

1. *Calcium Sulfate in Nature*
2. *Calcium Sulfate Mineral Phases*
 - 2.1 *Gypsum*
 - 2.2 *Bassanite*
 - 2.3 *Anhydrite*
3. *Phase Transformations in the $\text{CaSO}_4\text{-H}_2\text{O}$ System*
 - 3.1 *Dehydration Processes*
 - 3.2 *Hydration Processes*
4. *The Solubility Diagram in the $\text{CaSO}_4\text{-H}_2\text{O}$ System*
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 - 5.1 *Classical Nucleation*
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6. *Crystal Growth Phenomena*
7. *Applications of Calcium Sulfate*
 - 7.1 *Gypsum throughout History*
8. *Decay and Conservation of Plasterworks*
9. *Hypotheses and Objectives*

1. CALCIUM SULFATE IN NATURE

In nature, calcium sulfate ($\text{CaSO}_4 \cdot n\text{H}_2\text{O}$) occurs in a variety of crystalline phases, depending primarily on its degree of hydration (Christensen *et al.*, 2008; Voigt *et al.*, 2020; Ritterbach, 2021; Shi *et al.*, 2022). The most relevant phases are gypsum (dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), bassanite (hemihydrate, $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), and anhydrite (anhydrous, CaSO_4). These minerals are the most prevalent sulfates on the Earth's surface and are found in a wide variety of geologic environments.

Gypsum is a very common mineral that can be found in several varieties, such as selenite, fibrous selenite or "satin spar," alabaster, and desert rose (Watson, 1985; Al-Kofahi *et al.*, 1993; Gustavson *et al.*, 1994). Anhydrite is also a common mineral in Nature and is usually found in its pure form, despite its extremely slow formation kinetics under Earth surface pressure and temperature conditions (Ossorio *et al.*, 2014). Both minerals are mainly found in areas with a history of marine transgression and regression cycles, where the evaporation of saline water masses allows the precipitation of calcium sulfate. A prominent example of such sedimentary cycles occurred between 5.96 – 5.33 million years ago, during the "Messinian Salinity Crisis", when the Mediterranean Sea experienced near-total evaporation as a result of its separation from the Atlantic Ocean (closure of the precursor of the Gibraltar Strait) (Ryan, 2008). This process led to the formation of massive salt deposits and it is thought to have contributed to the upwelling of other minerals, including gypsum and anhydrite (e.g., Gargani and Rigollet, 2007; Govers, 2009; García-Castellanos and Villaseñor, 2011; Roveri *et al.*, 2014; Christeleit *et al.*, 2015; Scribano *et al.*, 2017; Hovland *et al.*, 2018; Madof *et al.*, 2019). In fact, it is easy to find traces of these geological events in local areas near Granada, such as Escúzar, Las Gabias or La Malahá, as well as in the Guadix-Baza basin and near the Gorafe desert (e.g., Rodríguez-Fernández and Sanz de Galdeano, 2006; Escavy *et al.*, 2012; García-Veigas *et al.*, 2013). Anhydrite and gypsum are minerals that can also form in geologic environments with hydrothermal conditions, including areas of volcanic activity, submarine hydrothermal systems (e.g., Bischoff and Seyfried, 1978; Styrk *et al.*, 1981; Humphris *et al.*, 1995; Lowell

and Yao, 2002), and regions with active tectonics (Heard and Rubey, 1966). A notable example is the “*Cave of the Crystals*” in Naica (Chihuahua, Mexico), where extreme relative humidity and temperature conditions (*i.e.*, 90-99% RH, 55-58 °C) have led to the formation of giant selenite and anhydrite crystals with lengths of up to twelve meters and thicknesses of more than one meter (García-Ruiz *et al.*, 2007; Van Driessche *et al.*, 2011). These extraordinary crystals have attracted the interest of scientists around the world who have been studying the complexities of crystal growth in other extreme hydrothermal environments during the last two decades (*e.g.*, Galdenzi and Maruoka, 2003; Bonny and Jones, 2003; De Waele *et al.*, 2016; Otálora *et al.*, 2018). Another clear example of this type of formations is the Pulpí geode in Almería (García-Guinea *et al.*, 2002), which was formed through karstic-hydrothermal processes involving the dissolution of dolomite and the subsequent crystallization of gypsum, thanks to the injection of geothermal water from remnants of volcanic activity. In contrast, bassanite is a metastable phase under standard pressure and temperature conditions, which makes it a relatively rare mineral because of its rapid hydration or dehydration kinetics to form gypsum or anhydrite, respectively. Bassanite crystals do not typically exceed one centimeter in size and are found in Nature as pseudomorphs of gypsum in very arid environments, such as the Death Valley, California (Hunt *et al.*, 1975), southern Egypt (Mees and De Dapper, 2005), western Australia (Arakel, 1980; Benison and Bowen, 2013), or Kuwait (Gunatilaka *et al.*, 1985). They have also been found in cavities of leucite-tephrite blocks ejected from active volcanoes, as occurs in the vicinity of Mount Vesuvius in Naples, Italy (Zambonini, 1910; Pelloux, 1927).



Figure 1.1. Different calcium sulfate varieties commonly found in nature. From left to right: Optical quality idiomorphic gypsum crystals, “spearhead” gypsum, desert rose and anhydrite. Specimens from the mineral collection of the Department of Mineralogy and Petrology, Faculty of Sciences, UGR.

Many gypsum deposits of considerable size have also been discovered on the surface of Mars and have been studied remotely for years. These discoveries have involved ground-based telescopes, orbiters, landers, and rovers. For example, data from the OMEGA orbiter's mineralogical spectrometer have demonstrated the presence of significant amounts of gypsum in the northern polar region of Mars (Langevin *et al.*, 2005). Since then, calcium sulfate phases have been detected at several other sites, including *Meridiani Planum*, *Noctis Labyrinthus*, *Mawrth Vallis* or the Gale Crater using portable X-ray diffraction systems installed in exploration rovers (e.g., Mars Science Laboratory - Curiosity rover; Grotzinger *et al.*, 2005; Wray *et al.*, 2010; Weitz *et al.*, 2013; Nachon *et al.*, 2014; Vaniman *et al.*, 2014). These minerals are thought to have primarily formed by chemical precipitation from shallow, saline, acidic surface waters and from post-depositional subsurface fluids (e.g., Langevin *et al.*, 2005; Grotzinger *et al.*, 2005; Bibring *et al.*, 2006; Catling *et al.*, 2006; Andrews-Hanna *et al.*, 2010; Grotzinger *et al.*, 2014; Nachon *et al.*, 2014; Kah *et al.*, 2018). In addition, a number of alternative mechanisms have been proposed, including deposition of ejected Martian surface fragments from meteorite impacts (Knauth *et al.*, 2005), alteration and deposition of sulfur-rich basalts, ash, and volcanic aerosols (McCollom and Hynek, 2005; Catling *et al.*, 2006; Fishbaugh *et al.*, 2007; Dehouck *et al.*, 2012), or acid weathering in frozen water deposits (Niles and Michalski, 2009). The analysis of these data aims to provide more information about the geologic events that led to the formation of these minerals, thereby contributing to a better understanding of different geochemical processes on Mars (and, by extension, on other moons and/or planets), the climate and habitability conditions on its surface.

In addition to their presence in the terrestrial and extraterrestrial geology, these minerals have also been found to play an important role in certain marine organisms, in particular in some cnidarians of the *Cubozoa* and *Sciphozoa* classes (Tiemann *et al.*, 2002; Becker *et al.*, 2005; Boßelmann *et al.*, 2007). These animals use small gypsum and/or bassanite crystals as statoliths, which allow them to detect the direction of gravity and accordingly adjust their position, thus ensuring their survival. It is extremely peculiar that these species show the ability to crystallize bassanite with such high selectivity under such unfavorable conditions

(i.e., in the presence of liquid water and at low temperature). Most notably, and despite the fact that calcium sulfate is not a common biomineral, gypsum has also been found to be part of the complex structure of the impact surface in the raptorial appendages of some species of stomatopod crustaceans of the *Odontodactylus scyllarus* type (better known as "*mantis shrimp*"), which they use as powerful hammers propelled at extreme speeds of about 23 m s^{-1} to break mollusk shells (Amini *et al.*, 2014).

2. CALCIUM SULFATE MINERAL PHASES

As stated above, calcium sulfate exhibits several main phases, including gypsum, bassanite, and anhydrite. The physicochemical properties and crystallographic characteristics of each mineral are detailed below:

2.1. Gypsum

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is the dihydrate phase of calcium sulfate. It is stable under standard conditions of pressure and temperature and crystallizes in the monoclinic system, and several space groups have been used for convenience to describe its structure (i.e., $A2/a$, Heijnen and Hartman, 1991; $C2/c$, e.g., Comodi *et al.*, 2008; $I2/a$, e.g., Schofield *et al.*, 1996; and $I2/c$, e.g., Henry *et al.*, 2009). Gypsum commonly adopts the shape of flattened prismatic crystals, frequently twinned into shapes resembling "arrowheads or spearheads", or "swallowtails" (Van Driessche *et al.*, 2019). Although gypsum crystals are usually colorless or white, the wide range of shades that this mineral can present depends on the variety in which it is found and the type of inclusions it contains, encompassing colors such as red, yellow or even black.

The characteristic crystal structure of gypsum is composed of regular $[\text{S-O}_4]^{2-}$ tetrahedra and irregular $[\text{Ca-O}_8]^{14-}$ polyhedra connected by their edges (Fukami *et*

al., 2015; Reiss *et al.*, 2021; Wehman *et al.*, 2023). These groups are arranged forming chains parallel to the *c*-axis of the crystal (as described assuming the morphological space group, $A2/a$; chains are arranged parallel to $[101]$ in the *I*-centered space groups) and exposing two water molecules that lay in the (*a* – *b*) plane. These chains are arranged in parallel sheets that are interconnected by relatively weak hydrogen bonds, where the $O_{w1}H \cdots O_{w2}$ distances are between 2.806 – 2.883 Å at room temperature. The arrangement of $[S-O_4]^{2-}$ tetrahedra and $[Ca-O_8]^{14-}$ polyhedra, as well as the arrangement of water molecules in double layers in the gypsum structure explains its physical and chemical properties, such as its relatively high solubility in water (2.23 g L⁻¹ at 20 °C), its low density (2.3 g cm⁻³) and hardness (1.5 – 2.0 on the Mohs scale) and its perfect exfoliation on {010}.

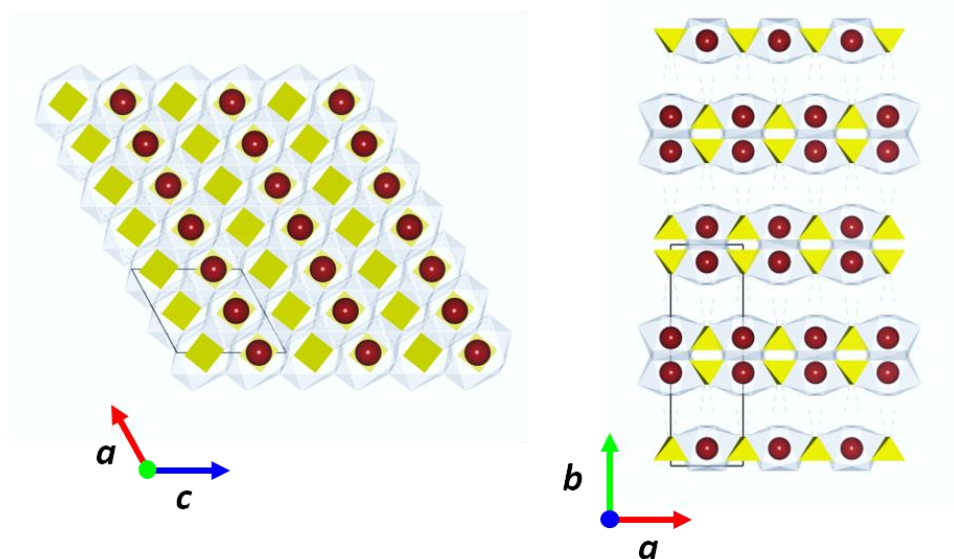


Figure 1.2. Projection of the gypsum structure from the $[010]$ and $[001]$ directions (space group $I2/c$).

2.2. Bassanite

Bassanite ($CaSO_4 \cdot 0.5H_2O$) is the hemihydrate phase of calcium sulfate. It is a metastable phase under standard conditions of pressure and temperature, which means that bassanite readily transforms into gypsum or anhydrite. Although

this aspect is still controversial, it is generally assumed that bassanite shows polymorphism, with two distinct structures described in the literature (e.g., Follner *et al.*, 2002; Singh and Middendorf, 2008; Weiss and Bräu, 2009; Christensen *et al.*, 2010): α - and β -bassanite. Also, different sub-hydrates containing varying amounts of structural water ($\text{CaSO}_4 \cdot n\text{H}_2\text{O}$; where $0.6 < n < 0.8$) have been reported (Schmidt *et al.*, 2011; Bezou *et al.*, 1995). However, this is controversial. Based on structural considerations, Lager *et al.* (1984) argue that it is highly unlikely that these sub-hydrate phases can exist. Moreover, it has been recently argued that these intermediate phases are just hemihydrate containing different amounts of non-structural and non-stoichiometric adsorbed water molecules (Weiss and Bräu, 2009).

On the one hand, α -bassanite crystallizes in the trigonal system (space group $P3_221$; Schmidt *et al.*, 2011) and is obtained by heating gypsum up to 130 °C under high relative humidity conditions, by homogeneous precipitation synthesis procedures under conditions of elevated temperature and ionic strength (e.g., in the presence of NaCl at a concentration above 4.5 M and above 80 °C), and/or from hydroalcoholic solutions (Tritschler *et al.*, 2015; Burgos-Ruiz *et al.*, 2021). α -Bassanite crystals usually exhibit a very regular prismatic morphology, with a low aspect ratio and a higher density than gypsum (2.76 g cm^{-3}) due to its more compact structure.

On the other hand, β -bassanite crystallizes in the monoclinic system (space group $I2$; Ballirano *et al.*, 2001) and is obtained by heating gypsum up to temperatures between 120 – 130 °C under low relative humidity conditions (Freyer and Voigt, 2003; Singh and Middendorf, 2007). This polymorph is better known as "*plaster of Paris*", and it is widely used as a hydraulic binder in cements and building materials. β -bassanite crystals exhibit much more irregular prismatic morphologies and a slightly lower density (2.64 g cm^{-3}), as compared to α -bassanite. In essence, there are no real differences between both crystal structures. They exhibit channels along the c -axis, which accommodate water molecules that are weakly bound to the $[\text{Ca-O}_8]^{14-}$ polyhedra. The theoretical diameter of these channels is 6.930 Å, 7.18 Å and 6.71 Å, as measured for the $\text{S} \cdots \text{S}$, $\text{Ca}_1 \cdots \text{Ca}_1$ and $\text{Ca}_2 \cdots \text{Ca}_2$ distances, respectively

(Bezou *et al.*, 1995). This would explain the relatively high instability of bassanite, since these structural channels have the ability to release or capture water molecules extremely easily.

Additionally, it should be noted that the rehydration products of the two different bassanite polymorphs show divergent mechanical properties (Singh and Middendorf, 2007). While gypsum plasters obtained from β -bassanite exhibits compressive strengths of less than 10 MPa (Chen *et al.*, 2021), hydration of α -bassanite has been shown to result in a considerably stronger material, with compressive strengths that can reach more than 50 MPa (Xie *et al.*, 2023). This is why the latter is used in dentistry, and is commonly known as "dental gypsum".

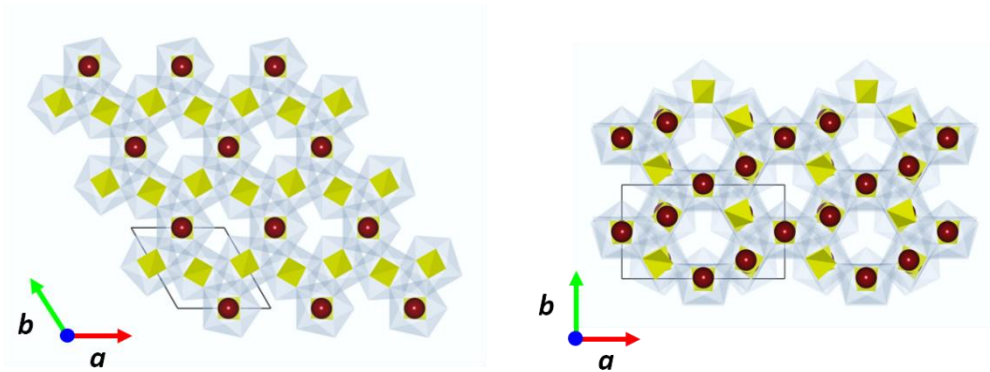


Figure 1.3. Projections of the α - and β -bassanite structures from the $[001]$ direction (space groups $P3_221$ and $I2$, respectively).

2.3. Anhydrite

Anhydrite (CaSO_4) is the anhydrous phase of calcium sulfate. It is stable under standard pressure and temperature conditions and also exhibits polymorphism, showing three different structures: γ -, β - and α -anhydrite.

The γ -anhydrite ("soluble" or type III anhydrite) (Ritterbach, 2021) crystallizes in the hexagonal system (space group $P6_222$). This structure can be understood as a dehydrated bassanite (Seufert *et al.*, 2009), in which the channels along the c -axis, exhibiting a radius of 6.696 Å, are preserved after the removal of water molecules

(Hawthorne and Ferguson, 1975). It is obtained by heating bassanite up to ca. 165 – 172 °C, or by bottom-up synthesis methodologies involving the formation and subsequent solvolysis of precursor species at moderate temperature, where extremely high supersaturation levels and minimal water activities are achieved (Tritschler *et al.*, 2015a; Tritschler *et al.*, 2015b). γ -anhydrite transforms into β -anhydrite ("insoluble" or type II), which crystallizes in the orthorhombic system (*Amma* space group; Hawthorne and Ferguson, 1975) upon heating up to ca. 280 – 462 °C (Christensen *et al.*, 2008). This phase is characterized by its slow dissolution and rehydration kinetics, explained by the absence of zeolitic channels allowing the incorporation of water molecules in its structure. Nonetheless, insoluble anhydrite shares the same basic structural motif of soluble anhydrite: Ca-SO_4 chains along the *c*-axis, which might imply that the transformation of soluble to insoluble anhydrite can take place with minimal structural modifications (Sella and Sella, 1962). The latter points to a topotactic transformation, which nonetheless has not been yet fully demonstrated.

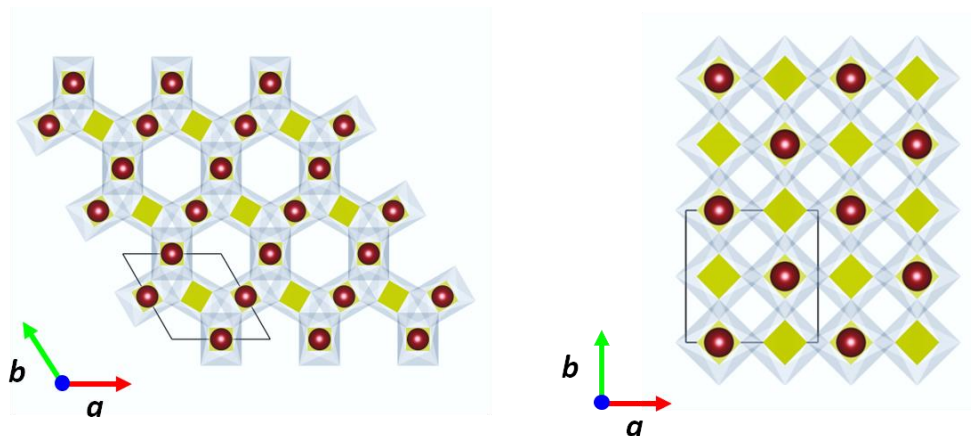


Figure 1.4. Projections of the γ - and β -anhydrite structures from the [001] direction (*i.e.*, "soluble" and "insoluble" anhydrite; space groups $P6_222$ and *Amma*, respectively).

In addition, it has been demonstrated that the rehydration kinetics of insoluble anhydrite are affected by the temperature reached during the calcination of gypsum. This is partially due to sintering phenomena whereby the specific surface area of the product resulting from the calcination process is greatly reduced (Elert

et al., 2023). Finally, α -anhydrite (type I) is only stable at temperatures above 1180 °C (Charola *et al.*, 2008; Ritterbach, 2021).

Anhydrite crystals are commonly found as translucent white prisms, although there are varieties with bluish-gray coloration such as angelite. All known anhydrite phases have a more compact structure than gypsum and bassanite, resulting in a higher density (2.5 – 3.0 g cm⁻³) and hardness (3.0 on the Mohs scale).

3. PHASE TRANSFORMATIONS IN THE $\text{CaSO}_4\text{-H}_2\text{O}$ SYSTEM

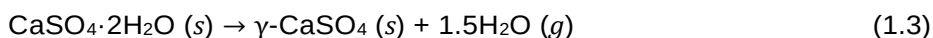
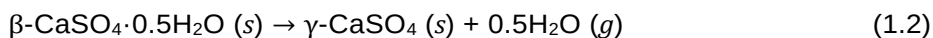
As previously illustrated, in the $\text{CaSO}_4\text{-H}_2\text{O}$ system a whole thermodynamical complex of intertwined hydration and dehydration reactions describe the so-called "gypsum cycle" (Rodriguez-Navarro *et al.*, 2013), which is an analogy to the well-known "lime cycle" (Elert *et al.*, 2002). These reactions comprise the reversible processes of dehydration (*i.e.*, calcination) and hydration (*i.e.*, setting), and constitute the fundamentals for understanding the use of calcium sulfate as a hydraulic binder. Controlling the gypsum cycle and the properties of the products obtained through each reaction is crucial for evaluating the performance of set gypsum materials, since each stage of the cycle determines the physical-chemical properties of the resulting phase in the next stage.

3.1. Dehydration Processes

The use of calcium sulfate as a hydraulic binder typically entails the thermal treatment of gypsum, a process referred to as calcination (Elert *et al.*, 2023), to obtain the dehydrated/sub-hydrated calcium sulfate phases. Despite extensive study, the complete decomposition pathway from gypsum up to the formation of bassanite and/or anhydrite remains unclear and continues to be a subject of intensive study and controversy (*e.g.*, Freyer and Voigt, 2003; Chio *et al.*, 2004;

Ballirano *et al.*, 2009; Charola *et al.*, 2008; Van Driessche *et al.*, 2017; Schmid *et al.*, 2020).

It has been demonstrated that the mechanism of complete thermal dehydration is directly influenced by the conditions of temperature and water vapor partial pressure (*i.e.*, $p_{\text{H}_2\text{O}}$ or relative humidity) (*e.g.*, Weiser *et al.*, 1936; McAdie, 1964; Ball and Norwood, 1969; McConell *et al.*, 1987; Abriel and Reisdorf, 1990; Putnis *et al.*, 1990; Strydom *et al.*, 1995; Badens *et al.*, 1997). Under high $p_{\text{H}_2\text{O}}$ conditions, this process consists of two consecutive steps involving the formation of bassanite as an intermediate phase and its subsequent decomposition at higher temperatures to generate soluble anhydrite. Alternatively, gypsum can dehydrate directly into soluble anhydrite in a single step under extremely low relative humidity conditions. This interdependence with water vapor pressure significantly hinders the thermodynamic (and kinetic) analysis of gypsum dehydration. Thus, the most relevant reactions during gypsum calcination are described as follows:



To elucidate this phenomenon, several mechanisms based on kinetic studies have been proposed. For instance, Ball and Norwood (1969) determined that the complete dehydration of gypsum in the temperature range of 80 – 110 °C, under controlled humidity conditions, can be described by a two-step bassanite nucleation-growth mechanism, or by a single-step phase boundary-controlled transition. However, they argue that at temperatures above 110 °C, this process is controlled by water vapor diffusion mechanisms.

Subsequently, Putnis *et al.* (1990) employed thermogravimetric analyses combined with *in situ* infrared spectroscopy, concluding that there was a continuous loss of water throughout the process, leading to the formation of bassanite and, finally, γ -anhydrite. This process follows a two-step nucleation-growth mechanism for both phase transitions. Carbone *et al.* (2008) investigated the dehydration kinetics of gypsum under low relative humidity conditions using energy dispersive X-ray

diffraction (EDXRD) and argued that this mechanism fits a one-step Avrami-Erofe'ev type nucleation-growth model.

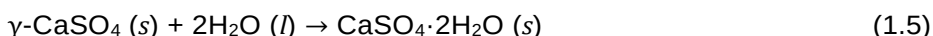
Lou *et al.* (2011) conducted thermogravimetric and calorimetric (TG-DSC) tests, demonstrating that the transition from gypsum to γ -anhydrite occurs in a single step following a phase boundary-controlled mechanism at low $p_{\text{H}_2\text{O}}$ under non-isothermal conditions, and below 100 °C under isothermal conditions. In contrast, complete dehydration occurs in two steps through the nucleation and growth of bassanite under autogenous $p_{\text{H}_2\text{O}}$ (*i.e.*, water vapor pressure generated during the dehydration of gypsum) under non-isothermal conditions, and above 100 °C under isothermal conditions.

More recently, Tang *et al.* (2019) employed theoretical thermodynamic analyses using Monte Carlo simulations and concluded that gypsum dehydrates in two steps at high $p_{\text{H}_2\text{O}}$ and in a single step at low $p_{\text{H}_2\text{O}}$. These analyses allowed the calculation of an approximated Gibbs free energy value for the formation of the different phases involved in the gypsum dehydration process, delimiting the stability zones of these $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ phases as a function of temperature and water vapor partial pressure.

Furthermore, gypsum dehydration upon calcination occurs through solid-state reactions with the release of gaseous water. From a structural point of view, this reaction has typically been described as a topotactic process (Abriel *et al.*, 1990), meaning that the atoms or ions in the initial crystal lattice retain their spatial arrangement and relative position as it transforms into a new crystalline phase with a lower degree of hydration. Topotacticity is an intriguing phenomenon in solid-state chemistry, enabling the control and prediction of the resulting physical-chemical properties of a phase based on the parent crystal structure. Also, gypsum dehydration is a pseudomorphic process (Sipple *et al.*, 2001), meaning that, at the macroscopic level, the thermal decomposition products can preserve the overall morphology of the parent gypsum crystal. This topic will be explored in depth in Chapter 2.

3.2. Hydration Processes

The final stage of the gypsum cycle involves the hydration and setting of the dehydrated/sub-hydrated calcium sulfate phases. Given the historical importance of gypsum-based binders and construction materials, these processes have been studied for more than two centuries (e.g., Lavoisier, 1765; DeMarignac, 1873; Lavoisier, 1765; Le Châtelier, 1887; Cavazzi, 1913; Budnikoff, 1928; Traube, 1919; Hansen, 1930; Ridge and Surkevicius, 1962; Schiller, 1962). However, as indicated for the case of the dehydration processes, the mechanisms of hydration of γ -anhydrite and bassanite remain a subject of major scientific debate. These processes include the following reactions:



The formation of gypsum from both soluble anhydrite and bassanite has been classified as a coupled dissolution-precipitation process, as first proposed by Le Châtelier (1887). Since both bassanite and γ -anhydrite are more soluble than gypsum under standard conditions, in contact with liquid water they readily dissolve generating a supersaturated solution, where the precipitation is marked by the less soluble solid phase (*i.e.*, gypsum). Numerous kinetic studies have tried to describe this mechanism, which can be considered as an autocatalytic process, since the precipitation of gypsum causes a decrease in the activity of Ca^{2+} and SO_4^{2-} ions in solution, promoting successive cycles of dissolution of bassanite and/or anhydrite and the precipitation of the dihydrate.

Despite all the accumulated evidence, this mechanism has remained relatively unclear until recently. Saha *et al.* (2012) carried out transmission electron microscopy analyses under cryogenic conditions (cryo-TEM) in order to elucidate the earliest stages of rehydration of bassanite in solution. They used supersaturated solutions with respect to bassanite (not a dispersion of such crystals), observing that gypsum formation did not follow a classic crystallization route. Instead, they observed the formation of an amorphous calcium sulfate

nanophase (ACS), followed by its aggregation and subsequent transformation into crystalline gypsum. Yet in these experiments they did not disclose the role of bassanite crystals on the subsequent formation of gypsum, which should be the relevant scenario for the hydration setting of *plaster of Paris*, neither disclosed the actual mechanism for the amorphous-to-crystalline phase transition. On the other hand, Gurgul *et al.* (2019) studied the hydration of a *plaster of Paris* paste *via in situ* monitoring the high-resolution X-ray diffraction patterns obtained with synchrotron radiation (synchrotron HR-XRD) and succeeded in fitting the kinetics of such a process to an Avrami-Erofe'ev type model, in agreement with a nucleation and growth mechanism. More recently, La Bella *et al.* (2023) studied the hydration of bassanite aggregates using *in situ* synchrotron diffraction and imaging at high resolution. The authors observed the dissolution of bassanite crystals and the subsequent growth of gypsum crystals with no structural (epitaxial) relationship between parent and product phases. This contrasts with a recent *in situ* fluid-cell TEM study by Jia *et al.* (2022) showing that bassanite offers a low energy interface for the epitaxial growth of gypsum.

The above results show that certain details of this mechanism are still unknown and are indeed a matter of current discussion. For instance, it has not been fully clarified whether the transition from bassanite to gypsum actually involves the formation and destabilization of an amorphous intermediate phase, which could theoretically be stabilized in solution under various supersaturation conditions. The precise nature of the hydration process, specifically whether the conversion of γ -anhydrite to gypsum takes place in a single step or, similar to the dehydration process, follows a two-step mechanism involving the formation of bassanite, has not been well-defined either. Additionally, the factors that govern such a mechanism remain unclear.

As observed in the case of bassanite, hydration reactions have traditionally been characterized as pseudomorphic processes under high relative humidity atmospheres (Triollier and Guilhot, 1976; Melikhov *et al.*, 1991). Nevertheless, more recent studies propose that under these conditions, the condensation of water vapor by deliquescence on the crystalline surfaces of bassanite initiates

dissolution-precipitation processes until gypsum is formed (Putnis, 2009; Putnis and Ruiz-Agudo, 2013). The nature of these phenomena remains a subject of debate. Historically, it has been widely accepted that the hydration of bassanite is a topotactic process (Sipple *et al.*, 2001). However, Jia *et al.* (2022) recently demonstrated that the formation of gypsum occurs through the dissolution of bassanite and the subsequent epitaxial regrowth of gypsum along the *c*-axis of the pre-existent bassanite crystals, which provide a low-energy interface that facilitates the heterogeneous nucleation phenomenon. Conversely, both La Bella *et al.* (2023) and Ilett *et al.* (2022) conclude that no such structural (epitaxial) relationship between parent and product phases exists during bassanite hydration.

Since the hydration processes in the $\text{CaSO}_4\text{-H}_2\text{O}$ system are predominantly controlled by nucleation phenomena in solution, this topic will be covered in Chapter 3.

4. THE SOLUBILITY DIAGRAM IN THE $\text{CaSO}_4\text{-H}_2\text{O}$ SYSTEM

Although it is not the main focus of this doctoral thesis, understanding the solubility diagram in the $\text{CaSO}_4\text{-H}_2\text{O}$ system is extremely important, since it is the thermodynamic basis that determines the relative stability limits of each phase as a function of the temperature of the system. Specifically, these diagrams are designed to describe the phenomenology of dissolution and precipitation in aqueous solutions and, together with a series of kinetic factors, allow predicting the outcome of any type of crystallization process. This is of great technological and industrial relevance, as it greatly facilitates the design of new ways to selectively obtain any crystalline phase of interest, and also allows to determine the geological processes and environments that have led to the formation of minerals in Nature and the climatic conditions that triggered them.

This is why the solubility of the various mineral phases of $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ has been extensively investigated since the late-19th century, in various scenarios such as

multicomponent systems involving salts and other organic and inorganic additives, or even under different total pressure conditions. However, despite the development of advanced and efficient computational software for simulating thermochemical systems, a significant degree of uncertainty persists regarding the stability limits for the gypsum $\rightarrow$ anhydrite, and bassanite $\rightarrow$ anhydrite transitions in solution.

The study of solubility equilibria in the $\text{CaSO}_4\text{-H}_2\text{O}$ system has primarily focused on the gypsum $\rightarrow$ anhydrite transition due to its relevance in terrestrial evaporite geology. Initially, Van't Hoff *et al.* (1903) attempted to delimit the temperature range for this phase transformation through thermodynamic calculations, yielding values between 60 – 66 °C. Subsequently, numerous experimental and theoretical analyses were conducted during the mid-20th century (*e.g.*, Hill, 1937; Posnjak, 1938; Kelley *et al.*, 1941; Zen, 1965), and they consistently reported that this phase transition occurred around 42 °C. However, these findings were later contradicted by Hardie (1967), who extrapolated data obtained under isothermal conditions and established a gypsum $\rightarrow$ anhydrite transition temperature in water of approximately 58 °C.

At the beginning of this century, Freyer and Voigt (2003) reviewed the wide numerical variability in published gypsum $\rightarrow$ anhydrite transformation temperatures. They determined that the significant variation in data could be attributed to extremely slow kinetics of the anhydrite dissolution-precipitation process at temperatures below 80 °C. This sluggish kinetics arise because anhydrite is metastable in solutions at low temperatures, either undersaturated or supersaturated, preventing equilibrium conditions from being reached within reasonable timeframes. Consequently, the kinetically favorable formation of gypsum contributes to the disparity in reported transformation temperatures.

Van Driessche *et al.* (2017) reiterated this widespread uncertainty and suggested a potential solution by measuring the solubility kinetics of anhydrite at temperatures above 80 °C and extrapolating the results through thermodynamic calculations to lower temperatures. While this approach aligns with the values obtained previously, such as those by Shen *et al.* (2019) at around 42 °C, it should be noted that this

method may not accurately reflect reality since the solubility of gypsum still needs to be unambiguously determined.

The gypsum $\rightarrow$ bassanite transition has received considerably less attention as compared to the reverse transformation, as bassanite is a metastable phase under the conditions of pressure and temperature at the Earth's surface, eventually transforming into anhydrite or gypsum. In water, the transition from gypsum to form bassanite theoretically occurs between 80 – 110 °C. As previously discussed, the ability to obtain bassanite under these conditions instead of anhydrite is attributed to the extremely slow nucleation and growth kinetics of the latter crystalline phase.

Despite the limited number of studies on this transformation, there is consensus regarding the temperature at which this phenomenon is expected to occur. Van't Hoff *et al.* (1903) provided the initial result of 106 °C, obtained through dilatometric and tensiometric experiments, while Posnjak (1938) obtained a value of 97 ± 1 °C based on solubility data of bassanite and gypsum, consistent with results obtained previously by Partridge and White (1929). More recently Azimi *et al.* (2007) and Shen *et al.* (2019) calculated the solubility of the different $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ phases *via*

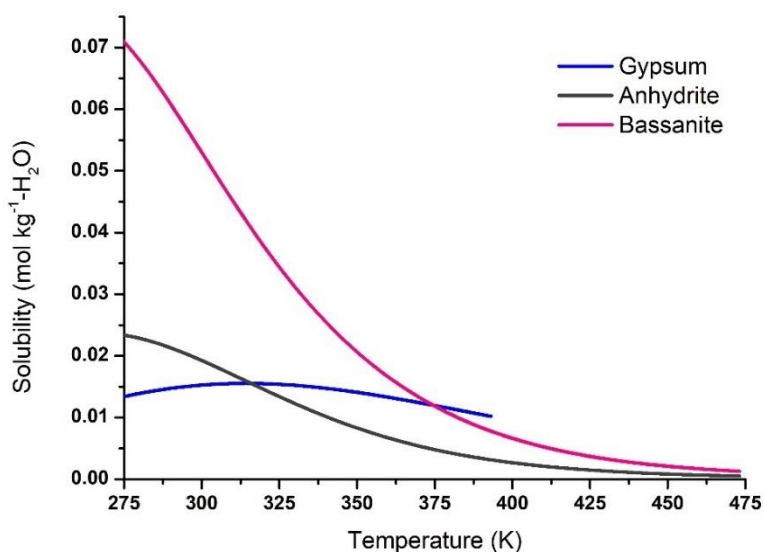


Figure 1.5. Solubility curves of gypsum, bassanite and anhydrite in pure water as calculated by L. Shen *et al.* (J. Chem. Eng. Data 2019, 64, 6, 2697-2709) for different temperatures using data published in previous literature.

thermodynamic simulations and reported values for the gypsum $\rightarrow$ bassanite transition of 99 ± 2 °C and 101.4 °C, respectively.

Bassanite is metastable (more soluble than anhydrite) in pure water in the temperature range from 50 – 120 °C. This is the reason that explains why the temperature of the bassanite $\rightarrow$ anhydrite transition cannot be accurately determined. Although there are no records on this aspect, Ossorio *et al.* (2014) observed that bassanite can transform very slowly into anhydrite in contact with 0.8 M NaCl solutions at temperatures above 99 °C, but in this case the ionic strength and water activity conditions are quite far from a standard system composed only of calcium sulfate and water. Alternatively, Stawski *et al.* (2023) investigated the impact of temperature and ionic strength on the stability fields of bassanite and gypsum. They analyzed 0.2 M calcium sulfate solutions using *in situ* Raman micro-spectroscopy and isotropic X-ray diffraction/scattering. Their findings led to the conclusion that gypsum destabilizes at around 35 °C, resulting in the formation of bassanite under extremely saline conditions (*i.e.*, $[\text{NaCl}] > 4.0$ M).

5. FORMATION OF $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ PHASES FROM SOLUTION

Every single precipitation process of any existing solid phase can be described by two sequential phenomena: nucleation and growth. From a broad perspective, nucleation represents one of the two fundamental mechanisms governing first-order phase separations, with the second mechanism known as spinodal decomposition.

While, by definition, these two types of phase separation occur in distinct thermodynamic contexts, the formation of a stable solid phase can involve both processes through intricate multi-stage mechanisms marked by the sequential succession of local energetic maxima and minima. Moreover, these mechanisms are susceptible to modification through changes in the chemical composition of the system, such as the introduction of additives or preformed physical surfaces.

Generally, the problem of crystallization has been approached from the Classical and Non-Classical nucleation perspectives.

5.1. Classical Nucleation of $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$

Historically, the study of crystallization phenomena has been approached within the framework of the "Classical Nucleation Theory" (CNT), stemming from the late-19th century works published by Gibbs and Smith in 1874. The theory was subsequently refined by notable contributors such as those of Stransky, Volmer, Weber, Becker, Döring, and Zeldovich during the 20th century (Becker and Döring, 1935; Volmer, 1939; Zeldovich, 1943; Gutzow *et al.*, 1997). In classical terms, nucleation from a solution involves the successive addition of monomeric species, such as ions, molecular complexes, or colloids, to a growing particle referred to as "nuclei" (De Yoreo and Vekilov, 2003; Kashchiev and Van Rosmalen, 2003). These nuclei serve as the starting point for crystal growth, and can originate homogeneously, when they are formed spontaneously from solution, or heterogeneously, when they are initiated on solid surfaces or impurities already present in solution.

According to the CNT, only a fraction of these proto-particles will become stable nuclei of the final solid phase, as there is an interfacial tension between the new solid phase and the mother solution. The formation of a physical surface involves an energetic cost, which depends on the interfacial free energy and the surface area of the newly formed particle. On the other hand, the free energy of the system decreases in relation to the chemical potential associated with the movement of the species in solution to form the new solid phase, which is proportional to the volume of the nuclei. Thus, the relationship between the area-dependent and the volume-dependent terms varies with particle size. When the nucleus is small, the area-dependent term predominates, but this situation is reversed when this particle reaches a sufficiently large volume. This thermodynamic competition as a function of particle size defines a single energy barrier (according to CNT) whose maximum coincides with a "critical nucleus radius", establishing that nuclei with a size smaller than the critical radius will dissolve, while those with a larger size will spontaneously

grow to macroscopic dimensions through the continuous addition of monomeric species in solution (Gibbs and Smith 1874; Kashchiev and Van Rosmalen, 2003) following an Ostwald ripening mechanism.

Numerous studies in the mid-20th century began to classify the crystallization of gypsum from this classical perspective, assuming that nucleation occurred in a single step and that these particles would evolve and grow to macroscopic dimensions (e.g., Schierholtz, 1958; Smith and Sweett, 1971; Liu and Nancollas, 1973; Packter, 1974). More recently, induction times corresponding to the initial nucleation phenomenon were calculated as a function of temperature and supersaturation during gypsum precipitation (e.g., Klepetsanis and Koutsoukos, 1991; He *et al.*, 1994; Klepetsanis *et al.*, 1999; Lancia *et al.*, 1999; Prisciandaro *et al.*, 2001; Fan *et al.*, 2010). These results were then fitted to equations determining the nucleation rate, J (Kashchiev, 2000), described according to the CNT model as follows:

$$J = A \cdot e^{(-E_a/kT)} \cdot e^{(-\Delta G_c/kT)} \quad (1.6)$$

$$\Delta G_c = B \cdot (\gamma^3/\sigma^2) \quad (1.7)$$

Where A is the pre-exponential factor, E_a is the activation energy of the processes associated with structural rearrangements during phase separation leading to nucleation, ΔG_c is the free energy barrier associated with the nucleation phenomenon, k is the Boltzmann constant, and T is the temperature of the system. In turn, B is a parameter representing the density and shape factor of the growing nuclei, while the energy barrier is inversely proportional to the square of the supersaturation of the system, σ , and directly proportional to the cube of the interfacial free energy, γ , between the solution and the growing nucleus (De Yoreo and Vekilov, 2003). For the specific case of homogeneous nucleation of calcium sulfate, an interfacial free energy of about 40 J m⁻² has been determined.

The application of the Classical Nucleation Theory (CNT) has proven useful in understanding the nucleation kinetics of calcium sulfate. However, the interfacial free energy is merely a value that indicates the "ease" or "difficulty" (with respect to

other phases studied according to the CNT) with which the nucleation phenomenon occurs. It does not provide any additional information about the species that precede the formation of these nuclei. This is actually one of the main shortcomings of the Classical Nucleation Theory.

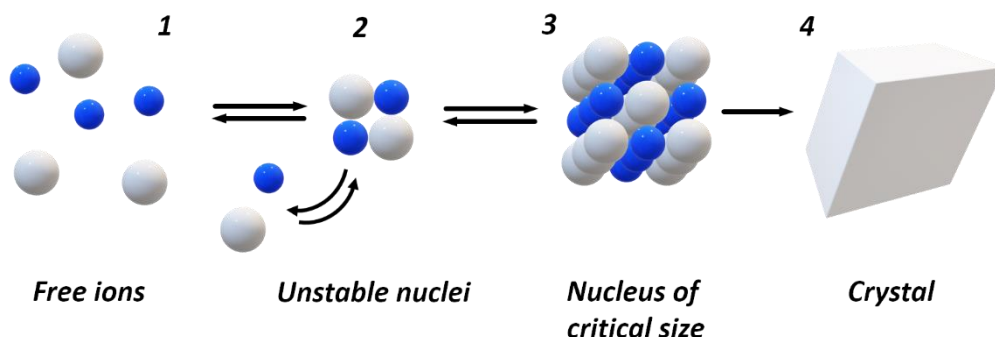


Figure 1.6. Summarized schematic representation of the formation of a crystal from solution according to the Classical Nucleation Theory.

5.2. Non-Classical Nucleation of $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$

The CNT is not able to explain the complex mechanisms by which other relevant minerals are formed in nature, such as calcium carbonate or calcium phosphates. In fact, a multitude of recent studies on the crystallization of calcium carbonate have demonstrated that nucleation is not such a simple process and that it involves the interaction of precursor species (stable or metastable) that coexist in equilibrium with free ions in solution prior to the nucleation events (Gebauer *et al.*, 2008; Pouget *et al.*, 2009; Habraken *et al.*, 2013; Burgos-Cara *et al.*, 2017; Rodriguez-Navarro *et al.*, 2020). These pre-critical species are generally referred to as "pre-nucleation clusters" (*i.e.*, PNC) and their existence has become evident in multiple investigations on the crystallization of CaCO_3 (among many other crystalline phases), by the observation of: (a) a distinct ion complexation effect during potentiometric titrations, consistent with a multi-ionic binding model (Kellermeier *et al.*, 2016; Gebauer *et al.*, 2018); (b) the identification of sedimentation peaks, determined through the analytical ultracentrifuge technique (AUC), corresponding to species exhibiting higher sedimentation coefficients,

indicative of larger size and mass compared to free ions themselves (Jiang *et al.*, 2017; Gebauer *et al.*, 2022; Sowoidnich *et al.*, 2023); and (c) molecular dynamics simulations in simplified thermodynamic systems predicting the formation of ion-pair aggregates with diverse polymeric structures (Demichelis *et al.*, 2011; Raiteri *et al.*, 2012).

Another important deficiency of the CNT lies in the fact that it does not contemplate the existence of amorphous phases that precede the formation of, for example, the three different calcium carbonate polymorphs, where the phase selectivity is driven by the conditions of the precipitation environment (*i.e.*, ionic strength, temperature, presence of additives and supersaturation, among other factors). The existence of these amorphous phases is challenging to explain within the CNT framework since, according to the theory, nuclei must possess identical crystallographic and physical-chemical properties to the resulting macroscopic crystal. It is worth mentioning that the existence of other amorphous precursors is common in many mineral systems, such as amorphous calcium phosphate (*i.e.*, ACP; Lotsari *et al.*, 2018) and amorphous calcium hydroxide (*i.e.*, ACH; Rodriguez-Navarro *et al.*, 2020).

The existence of PNCs in equilibrium with the initial monomers in solution also implies that the nucleation phenomenon does not necessarily occurs with a single energy barrier, as suggested by the CNT. Instead, PNCs coalesce and evolve into a solid by much more complex multistage aggregation mechanisms. In this context, spinodal decomposition mechanisms can also be considered. Spinodal decomposition is a first-order phase separation process, which is alternative to nucleation, and occurs without free energy barriers (Bray, 2002; Scheifele *et al.*, 2013). However, for phase separation *via* spinodal decomposition to occur, the system must attain supersaturation values where the free energy associated with the phase transition is comparable to the kT product (Scheifele *et al.*, 2013). In a spinodal regime, the theoretical PNCs can grow through coalescence, inducing bi-continuous liquid-liquid separations between very dilute and highly concentrated regions.

For the specific case of a moderately concentrated CaCO_3 solution, molecular dynamics simulations performed by Raiteri and Gale (2010) suggested that aggregates of ion pairs grow without an energetic cost to originate compact clusters that exhibit an ionic diffusivity very similar to that of a liquid. Subsequently, Wallace *et al.* (2013) simulated the aggregation of these clusters and their dehydration by randomly removing water molecules in the system up to a Ca/CO_3 ratio comparable to that of amorphous calcium carbonate (ACC). These results led to the conclusion that the formation of ACC could involve a complex mechanism featuring an initial liquid-liquid separation into a very dilute liquid phase and a highly concentrated one, where nucleation becomes considerably more favorable. Nonetheless, there is ongoing debate regarding whether this process occurs through spinodal demixing. In this scenario, for the formation of the initial solid phases an additional liquid-solid separation is still required.

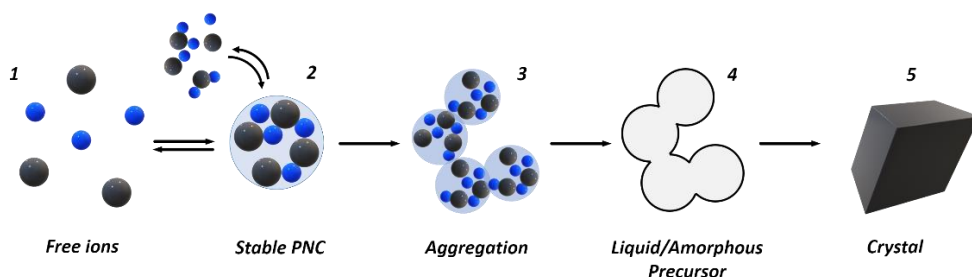


Figure 1.7. Schematic representation of one of the possible pathways leading to the formation of a crystal from solution in the framework of the Non-Classical Nucleation perspective.

In light of an increasing body of evidence indicating that crystallization processes (especially in key systems such as calcium phosphate or calcium carbonate) (Figure 1.7) deviate significantly from the paradigm of the CNT, there has been a reassessment of the calcium sulfate precipitation case over the past decade. These new findings suggest that this process may occur *via* a "non-classical" multi-stage mechanism, mirroring the observed patterns in the cases of calcium carbonate and calcium phosphate. In a study conducted by Wang *et al.* (2012), the formation of gypsum was investigated through the mixing of equimolar aqueous solutions of CaCl_2 and Na_2SO_4 . A transient amorphous phase became evident shortly after the

mixing of both solutions, reaching CaSO_4 concentrations of 25 and 50 mM, representing low-to-moderate supersaturation conditions with respect to gypsum. Transmission electron microscopy (TEM) combined with selected area electron diffraction (SAED) revealed patterns with diffuse halos characteristic of amorphous phases, allowing the detection of this transient phase. Moreover, extended exposure to the electron beam was found to induce the crystallization of gypsum. On the other hand, it was shown that bassanite could form under conditions far outside its stability region, where gypsum would be the only phase to be expected. These results indicated that both the amorphous precursor phase and bassanite became less stable with increasing supersaturation. This led to the hypothesis that, under high supersaturation conditions, gypsum could potentially originate from an amorphous precursor (*i.e.*, amorphous calcium sulfate, ACS), which would later transform into bassanite, in turn being the direct structural precursor of gypsum.

Simultaneously, Van Driessche *et al.* (2012) explored early pre-nucleation phenomena in solutions exhibiting diverse levels of supersaturation with respect to gypsum. The investigation employed *in situ* turbidity measurements, complemented by *ex situ* analyses by means of high-resolution transmission electron microscopy (HR-TEM) and electron diffraction. Cryo-quenching and/or anti-solvent quenching of aliquots from various solutions obtained at different points of interest were used to prepare samples. Although no amorphous precursor was observed in this case, they proposed a mechanism delineating the formation of gypsum from supersaturated solutions in three distinct phases. Initially, bassanite nanoparticles, approximately 5 nm in size, were formed (remarkably, under conditions of apparent undersaturation), subsequently growing to lengths of about 100 nm. Following this, these bassanite nanoparticles aggregated into larger structures oriented along the *c*-axis direction, culminating in the eventual convergence into a single gypsum crystal.

Additional support for the idea of a multi-stage precipitation pathway for gypsum was provided by Saha *et al.* (2012). In this study, cryogenic transmission electron microscopy (cryo-TEM) was employed to examine the early stages of nucleation in a solution that was supersaturated with respect to gypsum, achieved by dissolving

bassanite. The analysis revealed the transformation of small nanoclusters, ranging from 2 to 4 nm in size, into particles exhibiting an apparently amorphous nature with a diameter of approximately 100 nm. Subsequently, these particles aggregated to give rise to gypsum crystals. It is worth mentioning that this whole process occurs extraordinarily quickly, with gypsum crystals being observed in a scale of tens of seconds.

Jones (2012) monitored the crystallization of calcium sulfate during the evaporation of a solution of this salt using *in situ* attenuated total reflection (ATR) Fourier transform infrared spectroscopy (FTIR). In this instance, the intensity of the infrared absorption bands corresponding to the structural water present in the various $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ phases increased as the crystallization process advanced. This observation suggests that, initially, water molecules occupy random positions and subsequently rearrange adopting more defined structural configurations. Based on these findings, it was inferred that the crystallization process involves the formation of an amorphous phase that progresses into crystalline gypsum, potentially through an intermediate bassanite phase.

Subsequently, Stawski *et al.* (2016) conducted homogeneous calcium sulfate precipitation tests at temperatures ranging from 12 to 40 °C. The experimental approach involved mixing equimolar solutions of CaCl_2 and Na_2SO_4 , and the analysis of small- and wide-angle X-ray scattering (SAXS/WAXS) patterns utilizing synchrotron radiation. The results revealed a mechanism for gypsum precipitation comprising several stages: (I) the formation of elongated "anhydrous" primary CaSO_4 species, of less than 3 nm in length and approximately 0.5 nm in thickness; (II) the initial aggregation of these primary species through density fluctuations into dispersed domains, where the interparticle distance exceeds twice the radius of gyration of each primary particle; (III) the condensation of these domains into denser aggregates made up of the same primary units; (IV) oriented growth and aggregation of the primary units, culminating in the formation of gypsum, with an increase in crystallinity over the analysis period. This investigation, however, did not confirm the existence of bassanite as a crystal preceding the formation of gypsum. Additionally, it could not conclusively establish whether the primary Ca-

SO₄ units could be regarded as pre-nucleation species or even an amorphous precursor.

More recently, the formation mechanism of gypsum underwent re-examination through *in situ* Raman micro-spectroscopy (μ -Raman) assays conducted by Zhang and Xue (2020). These researchers opted to prepare solutions with varying levels of supersaturation with respect to gypsum, using CaCl₂ and Na₂SO₄ solutions. The crystallization process was monitored at 24 °C and 30% relative humidity. Their findings revealed that gypsum is formed directly from an amorphous precursor. However, it is noteworthy that no other intermediate phase, such as bassanite, was detected in the process.

Despite substantial efforts to elucidate the mechanism of calcium sulfate crystallization, significant disagreement persists regarding the existence (or not) of an amorphous precursor and whether bassanite serves as a necessary intermediate for gypsum precipitation. Conversely, there is a consensus that these processes deviate from the classical pathway, and the plausibility of sequential multi-stage mechanisms is acknowledged to explain the mineralization of the different CaSO₄·*n*H₂O phases. Aspects regarding the non-classical crystallization of gypsum are further explored in Chapters 3 and 4.

5.3. Influence of Organic Additives

Following numerous studies on biomineralization, it is generally accepted that a variety of organic compounds significantly influence the crystallization of certain minerals, primarily calcium carbonate and calcium phosphate. The effect of additives on the mineralization of calcium sulfate has been significantly less explored, and mainly limited to determining the retarding effect of certain polymers (*i.e.*, "anti-scalants" such as poly(acrylic acid), PAA, or poly(aspartic acid), PASP) on the precipitation of this salt, primarily in industrial processes. In these cases, the formation of large gypsum and/or anhydrite scale in pipes or heat exchangers can lead to substantial economic losses associated with efficiency reductions in these elements, as seen in water desalination plants (*e.g.*, Brusilovsky *et al.*, 1992;

Linnikov, 2000; Ahmed *et al.*, 2004; Mi and Elimelech, 2010; Al-Khaldi *et al.*, 2011; Olajire, 2015; Rosenberg *et al.*, 2012). However, these studies do not delve into other effects that organic compounds can induce during nucleation and crystal growth phenomena. This is investigated in other publications (e.g., Hamdona and Al Hadad, 2008; Rabizadeh *et al.*, 2014; Harouaka and Kubicki, 2017; Ossorio *et al.*, 2017; Nicoleau *et al.*, 2019; Madeja *et al.*, 2023), whose results show that certain organic compounds, such as amino acids, proteins, and polyphenols, can influence the crystallization process of calcium sulfate, inhibiting or accelerating it. Additionally, it has been found that certain biomolecules, such as α -amylase (Cody and Cody, 1989), humic acids (Cao *et al.*, 2022), or certain (co)polymers, such as PVP-co-PAA, can induce morphological and crystalline habit changes, and can even lead to the formation of twinned gypsum crystals or crystals with unconventional block or pseudohexagonal plate morphologies in a reproducible manner (Madeja *et al.*, 2023; Wang *et al.*, 2023). It is noteworthy, moreover, that the reference experiments without organic matter did not produce the typical crystalline morphologies observed in natural environments, indicating the enormous impact of organic chemistry on the control of gypsum crystallization, whether in natural or artificial environments.

The alteration in crystal habit induced by the presence of organic molecules is usually reflected by changes in the aspect ratio (*i.e.*, length/thickness ratio). These changes are attributed to variations in the growth rates of the faces that conform the morphology of a crystal. The growth rate of specific faces may experience variations due to the adsorption of additives (e.g., carboxylates) on the surface of gypsum faces, where Ca^{2+} ions are exposed (Barcelona and Atwood, 1978; Cody and Cody, 1991; Harouaka and Kubicki, 2017). However, it is still not entirely clear under what circumstances these compounds modify nucleation phenomena or control the formation of twins (Ossorio *et al.*, 2017). Most organic additives have been found to be nucleation inhibitors, and act by prolonging the precipitation induction period (e.g., Prisciandaro *et al.*, 2003; Rabizadeh *et al.*, 2014; Ossorio *et al.*, 2017; Nicoleau *et al.*, 2019). There are two possibilities to explain this inhibitory effect. First, organic additives may function as ion-chelating agents (e.g., Ca^{2+}), leading to a decrease in effective supersaturation as free ions are removed from

dissolution. Then, these compounds can stabilize the formation of PNCs and adsorb onto their interfaces, preventing aggregation phenomena and, consequently, the transformation of these PNCs into stable solid phases. In fact, calcium sulfate precipitation can be significantly affected by these additives, even at very low concentrations. Currently, it is thought that the chelating effect is not as critical as that of PNC stabilization. In this regard, Ossorio *et al.* (2017), through *in situ* SAXS analyses, showed that the presence of citric acid largely prevents the formation of primary particles, while Nicoleau *et al.* (2019) concluded that the nucleation kinetics and the formation of crystalline phases are slowed down due to a drastic decrease in the number of collisions between pre-nucleation species in the presence of polymers.

Alternatively, organic compounds can directly influence the phase selectivity during $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ precipitation. Recently, it has been observed that alkyl carboxylate-type compounds (*e.g.*, betaine or propionate) or surfactants of the alkyl carboxylate family (*e.g.*, polyoxyethylene-8-octyl ether carboxylate) can be good candidates for the selective production of bassanite from aqueous solutions, even at mild temperatures around 40 – 50 °C (Reigl *et al.*, 2023). Scientific progress in this direction is extremely relevant, as it seems to be a suitable way to produce this widely used mineral without the need for energetically intensive methods (*i.e.*, high-temperature calcination) or solvents other than water.

As mentioned above, the mechanism causing this phase selectivity is thought to involve the interaction of these additives with the theoretical precursor PNCs and/or with the surfaces of the growing crystals. It is further believed that in these cases, water activity may be locally modified, leading to the formation of metastable bassanite, or even γ -anhydrite, while inhibiting gypsum formation. This occurs similarly in extreme salinity environments or in hydroalcoholic solutions with low water content, which has even led to low-temperature anhydrite (Tritschler *et al.*, 2015).

The possibility of using organic additives to provide gypsum crystals with new functionalities (*e.g.*, fluorescence) *via* the modification of the nucleation and crystallization mechanisms is explored in Chapter 3.

6. CRYSTAL GROWTH PHENOMENA

As in the case of nucleation phenomena, the processes associated with crystal growth can be described by two main theoretical approaches. The first is the Classical Growth Theory (CGT), originally proposed by Kossel and Stranski (1928) and refined by Burton, Cabrera and Frank (1958). The CGT postulates that the increase of crystal size occurs primarily through monomer-by-monomer addition onto the surface of a previously formed post-critical nucleus. In this case, the driving force by which crystal growth occurs is defined as the difference in the chemical potential of a non-dissociated species, $\Delta\mu$, as a function of the ratio between the activity of this species in solution, a , and the activity of this species when it is forming a precipitated solid, a_{eq} , as follows:

$$\Delta\mu/RT = \ln (a/a_{eq}) \quad (1.8)$$

In the case of minerals, where each formula unit is composed of a number ν of ions, being the sum of the number of cations, ν_+ , and anions, ν_- , the previous equation becomes:

$$\Delta\mu/RT = \nu \cdot \ln (a_{\pm}/a_{\pm,eq}) \quad (1.9)$$

Where $a_{\pm}$ is the average activity of ions in solution, defined as the product of the free ion concentration in solution, c , by the average ionic activity coefficient, $\gamma_{\pm}$. For crystals composed of two divalent ions, as is the case of CaSO_4 , and considering the supersaturation ratio as $S_a = a_{\pm}/a_{\pm,eq}$, the equation becomes as follows:

$$S_a = \sqrt{\frac{c_{\text{Ca}^{2+}} \cdot c_{\text{SO}_4^{2-}} \cdot \gamma_{\pm}^2}{K_{sp, \text{CaSO}_4}}} \quad (1.10)$$

This classical view of crystal growth has been useful for understanding, to some extent, the main parameters influencing morphology and physical properties in

simple crystal models, but it only allows predicting the growth of crystal faces predefined by the unit cell structure.

In contrast, non-classical crystallization (*i.e.*, NCC) mechanisms provide a rational explanation for the formation of much more complex three-dimensional structures, such as those observed in nacre, bone tissues, or branched nanocrystals. This would be quite complicated to explain solely through the monomer-to-monomer addition model proposed by the CGT. The NCC is a general concept that encompasses all crystallization processes in which no atoms, ions, or monomeric molecular building units are involved, as in classical crystallization (Cölfen and Antonietti, 2008). An alternative notation is crystallization by particle aggregation (*i.e.*, CPA; De Yoreo *et al.*, 2015). In this case, the building units can also be liquid species, complexes, clusters, or oligomers, which are not monomeric species *per se*. NCC processes hold an enormous potential, not only for understanding complex crystallization scenarios occurring in nature, such as biomineralization or bio-mimetic/bio-inspired mineralization (Wolf *et al.*, 2016; Rodriguez-Navarro *et al.*, 2016; Gebauer *et al.*, 2019; Jehannin *et al.*, 2019), but also for the design of highly sophisticated solid-state materials with advanced properties. For example, it has been shown that the formation of biomineral structures, such as sea urchin spines, tooth enamel, or the exoskeleton of a multitude of invertebrates (among many other structures), occurs through the aggregation of amorphous nanoparticles (*e.g.*, ACC or ACP), stabilized by biological macromolecules, which are subsequently transformed into crystalline phases such as calcite or apatite (*e.g.*, Weiss *et al.*, 2002; Killian *et al.*, 2009; Gong *et al.*, 2012).

Another process that can be described according to the NCC is the formation of mesocrystals, 3D superstructures that were first defined by Helmut Cölfen (2005). Their formation is explained by oriented aggregation mechanisms (*i.e.*, oriented attachment, OA; Figure 1.8), where the mesocrystal-forming blocks are crystallographically aligned but spatially separated from each other. These mesocrystals can either remain kinetically stable due to the presence of adsorbed species on the surface of the particles (Cölfen and Antonietti, 2008; Fang *et al.*, 2011) or form a single crystal through the fusion of their structural units (Schwan *et*

al., 2007). In this latter situation, additives would remain either occluded between the crystalline domains or expelled and adsorbed on the surface of the final crystal due to recrystallization processes.

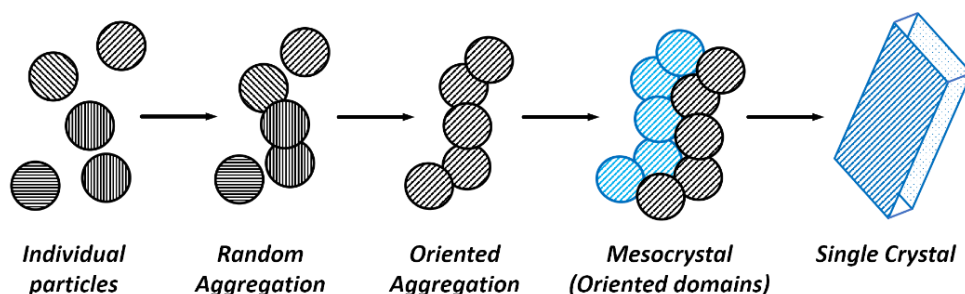


Figure 1.8. Schematic representation of the growth mechanism by oriented attachment of particles.

In fact, the transformation of bassanite into gypsum in solution could possibly follow a complex oriented attachment mechanism, where bassanite nanoparticles arrange along the [001] direction (of the hemihydrate) to form mesocrystals. Further dissolution of bassanite and re-precipitation of gypsum would originate a larger gypsum single crystal (Van Driessche *et al.*, 2012; Stawski *et al.*, 2019).

From this point on, gypsum crystals can develop by the addition of ions as described in the CGT, or by the incorporation of pre-nucleation species that subsequently stabilize on the crystal interfaces, following non-classical pathways. In general, and under moderate temperature conditions, the addition of structural units can occur anywhere on a crystal face (*i.e.*, kinks, steps and terraces), leading to the formation of steps. These steps can be generated from dislocations, giving rise to growth spirals, or through the heterogeneous nucleation of 2D and/or 3D islands. Thus, the habit, dimensions, and mechanical properties of a crystal are directly influenced by the growth mechanism and kinetics. In the case of gypsum, both growth mechanisms are prevalent on (010) faces, although it is not known to what extent supersaturation affects the crystallogensis mechanism of this mineral.

7. APPLICATIONS OF CALCIUM SULFATE

Calcium sulfate is one of the most demanded inorganic salts worldwide (Weiss and Bräu, 2009), with an estimated average annual production of more than 150 million metric tons (U.S. Geological Survey, Mineral Commodity Summaries, 2023) solely through mining activities. Interestingly, Spain is one of the major producers of gypsum (understood as the three main $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ phases) in the world (~7% of the total production) and the major producer of this mineral in Europe. Calcium sulfate is also obtained as a by-product of other industrial processes, such as flue gas desulfurization (FGD), hydrogen fluoride production, phosphoric acid, or zinc refining.

This compound plays a crucial role in a wide variety of industrial sectors, thanks to its versatility and essential properties in multiple manufacturing and production processes (Sharpe and Cork, 2006). In agriculture, calcium sulfate is used as a fertilizer and soil conditioner. In the food and pharmaceutical industry, it is used as a thickening agent, stabilizer and binder in the formulation of a wide range of products, from food to drugs and supplements (Fu *et al.*, 2003). Likewise, in the textile industry and paper manufacturing (Foti *et al.*, 2019), calcium sulfate is used as a bulking and filling agent, increasing the strength and durability of these materials and contributing significantly to color fixation during textile dyeing and printing processes.

Calcium sulfate also finds application in specialized fields, including its biomedical use for treating bone fractures, bone and dental implantology (Nandi *et al.*, 2010), and localized and controlled drug release systems (Hesaraki *et al.*, 2009). However, the construction industry stands out as the sector with the highest demand for this compound, playing an indispensable role in producing gypsum panels, coatings, and moldings extensively used in interior construction for their fireproofing and insulating properties.

Moreover, gypsum is gaining relevance over other species, such as lime, as a candidate material for the formulation of more sustainable construction materials

for two reasons. In the one hand, the calcination of gypsum shows lower energetic requirements as compared to the decomposition of limestone (*i.e.*, 120 – 460 °C for the dehydration of gypsum vs > 800 °C for the calcination of limestone). Typically, industrial heating is achieved by the combustion of fossil fuels, releasing huge amounts of CO₂ (and other gases) to the atmosphere.

In the other hand, the dehydration of gypsum occurs with the release of water vapor, while the decomposition of limestone comes with the release of CO₂ (44.01 grams of CO₂ per mole of processed CaCO₃). Note that the construction industry is registered as one of the most CO₂-emitting activities in the world (8% of the total industrial CO₂ emissions come from the production of cement; UN Reports, 2023), which is probably the main reason why so many efforts are being done in order to find more sustainable alternatives to the use of lime or cement as a binder. Gypsum is, therefore, a valid candidate for this task.

7.1. Gypsum throughout History

Throughout the history of humanity, materials derived from gypsum have played a pivotal role in the evolution of architecture, emerging as a versatile and indispensable component of human civilization.

In particular, numerous archaeological findings from Neolithic settlements (12,000 – 2,000 B.C.) in Europe and the Middle East underscore the early utilization of gypsum, alongside lime, as one of the initial hydraulic binders processed through pyrotechnology (Kingery *et al.*, 1988; Elsen, 2006; Gartner, 2009). During this age, gypsum found application in crafting figurines and artifacts primarily for decorative purposes, concurrently marking its inception as a coating material for basic building structures.

In the subsequent course of history, gypsum retained its significance as a foundational material in the artistic and architectural expressions of succeeding civilizations. Whether in Mesopotamia and Ancient Egypt (3,100 - 30 B.C.; Ragai 1988; Regourd *et al.*, 1988), Ancient Greece (800 - 146 B.C.; Gárate Rojas, 1999;

Elsen, 2006), or other ancient societies, bassanite, soluble anhydrite and insoluble anhydrite played a pivotal role in the construction of monuments and temples. The extended setting time of insoluble anhydrite made it useful as a lubricating material in these structures. Additionally, these phases were employed to craft reliefs, ornaments, and statues. The notable presence of gypsum is observed in iconic structures like the Great Pyramid of Giza and the temples of Karnak and Luxor (Rubio-Domene, 2010). Gypsum held substantial importance in Ancient Rome as well (753 B.C. - 476 A.D.). Pliny the Elder, in his *Naturalis Historia*, described the use of large sheets of translucent selenite, referred to as “*Lapis Specularis*”, which were extensively used for the manufacture of windows, particularly in the provinces of Hispania (Gómez and di Monti, 2004).

Throughout the Middle Ages in Europe, as well as in the Near and Middle East, gypsum remained a crucial material for constructing cathedrals, castles, and various monuments due to its fire-resistant properties and malleability. A striking illustration of plaster craftsmanship is evident in Islamic architecture, particularly from the Islamic Golden Age (7th - 13th century A.D.). During this period, intricate plasterwork featuring complex geometric patterns, arabesques, and calligraphic inscriptions, with muqarnas as noteworthy elements, was crafted. The Alhambra in Granada stands as the (local) apex of this architectural style, encapsulating centuries of intercultural evolution with immeasurable historical and economic significance (Arredondo, 1991; Luxán *et al.*, 1995; Rubio-Domene, 2010; Bel-Anzue *et al.*, 2017).

Gypsum, renowned for its easy moldability and the achievement of exceptionally smooth finishes, gained prominence during the Renaissance (14th - 17th century A.D.). Its high total porosity and suitable setting time facilitated optimal pigment fixation. This contributed to its widespread use in the creation of frescoes and mural paintings, exemplified by works such as those found in the Chapel of the Catholic Monarchs in the Cathedral of Granada or the Monastery of San Lorenzo del Escorial in Madrid, among numerous other masterpieces across all Europe.

In present times, gypsum stands as a cornerstone in the construction industry, recognized for its versatility, durability, and functional attributes. Over time, the

techniques and applications of this material have undergone significant advancements, becoming a staple in constructing suspended ceilings, partitions, walls, and interior cladding. Furthermore, innovative products like Pladur®, comprising high-density gypsum sheets interspersed with cellulose sheets, have been introduced. These advancements endow the material with properties such as exceptional lightweight quality, heightened mechanical strength, commendable thermal and acoustic insulation, and a substantial reduction in construction times linked to gypsum setting.

8. DECAY AND CONSERVATION OF PLASTERWORKS

Despite their widespread use and importance in a variety of cultural and architectural contexts, gypsum materials have limited mechanical properties and relatively high solubility, making them prone to deteriorate relatively easily when exposed to a variety of environmental and anthropological usage factors (e.g., Charola and Koestler, 2006; Brimblecombe and Grossi, 2009; Palha *et al.*, 2012; Jroundi *et al.*, 2014; Molina *et al.*, 2017; Jiang *et al.*, 2021; Xu *et al.*, 2022).

In the field of conservation science, prolonged exposure to high levels of relative humidity and extreme temperature fluctuations, as occurs every year in the area of Granada (*i.e.*, fluctuations of ~32.9 °C / ~34 % RH between summer and winter; as recorded from the Granada-Albayzín Meteorological Station; Prof. Nicolás Velilla, UGR), has been identified as a major source of damage to plasterworks (Molina *et al.*, 2017). Gypsum is a mineral that becomes unstable at temperatures above 42 °C, and it is known that under these conditions it can dehydrate to form bassanite or anhydrite, a transition that is accompanied by a significant reduction in molar volume (Schofield *et al.*, 1996; Ballirano *et al.*, 2001; Christensen *et al.*, 2008; Schmidt *et al.*, 2011; Ritterbach, 2021) which triggers mechanical stresses in the material, manifesting in the form of cracks, spalling and, in more serious cases,

partial or total disintegration of the original structure (Figure 1.9a and b) (Price and Doehne, 2011).

Moreover, gypsum is a soluble and deliquescent salt, which implies that its interaction with liquid or condensed water in environments of high relative humidity can result in the partial dissolution of the material, originating loss of relief and chromatic alterations (Rubio-Domene, 2010; Molina *et al.*, 2017; Cardell and Guerra, 2022). In some cases, the recrystallization of the dissolved gypsum can induce salt erosion in nearby objects, as can be observed in the marble columns of the Court of the Lions of the Alhambra in Granada (Figure 1.9c), located just below muqarnas and other ornamental plasterworks. The phenomenon of salt crystallization is typically the primary cause of deterioration in porous stone materials (Schiro *et al.*, 2012; Ruiz-Agudo *et al.*, 2017). In environments with high relative humidity, water condensation leads to the dissolution of salts like chlorides, nitrates, and sulfates present in these materials (Ruiz-Agudo, 2007). These solutions travel through capillarity along the porous structure of the material, where the salts precipitate due to abrupt shifts in temperature and/or relative humidity as well as solvent evaporation. The precipitation of these new crystalline phases in confined spaces generates a crystallization pressure, often reaching values several orders of magnitude higher than the fracture modulus of gypsum plaster and even other more resilient materials (Scherer, 2004; Steiger, 2005). As these salts are considerably soluble, they undergo cycles of dissolution and precipitation with continuous changes in humidity and temperature, usually generating significant destructive effects in concrete, mortars and other structural elements.

The presence of moisture promotes the development and proliferation of microorganisms, including algae, lichens, fungi, and bacteria, on the surface of these materials. This microbial activity generates a biofilm that can accelerate corrosion, chemical degradation, and aesthetic damage, such as discolorations and blackening (e.g., Price and Doehne, 2011; La Russa and Ruffolo, 2021; Elchischeva *et al.*, 2021; Maundrill *et al.*, 2023). Addressing these issues often requires potentially destructive cleaning processes, as the biofilm can be highly resistant and challenging to remove. While numerous conservation methods and

materials have been developed to address similar pathologies in various building materials such as lime mortars, concrete, and stones like sandstone or calcarenites, the field of conservation science has not yet fully developed to adequately tackle the deterioration of gypsum materials. In practical terms, highly deteriorated plasterwork is often replaced with newly produced replicas (Rubio-Domene, 2010).

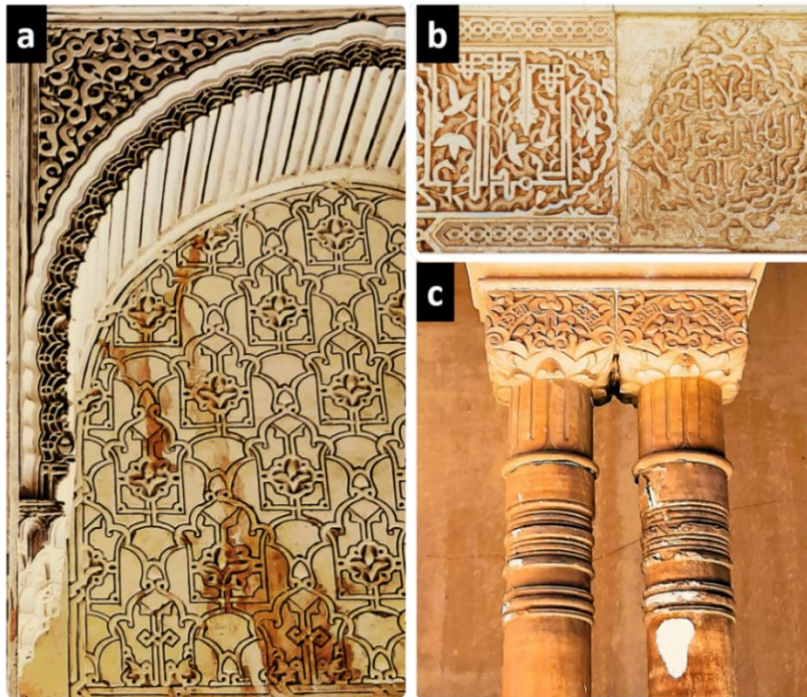


Figure 1.9. Different deterioration pathologies on historic ornamental plasterworks (a, water percolation damage; b, loss of material and erosion) found in the Alhambra (Granada, Andalucia). Associated salt crystallization on marble columns adjacent to gypsum plasterworks, probably as a consequence of the dissolution of calcium sulfate and the reprecipitation of (Ca, Na) sulfates.

Furthermore, in many restoration and conservation interventions involving authentic historic works, the use of consolidants becomes necessary. These consolidants contribute to strengthening the structural integrity and preventing further deterioration of these objects without significantly altering their original appearance (e.g., Bradley, 1984; Hansen *et al.*, 2003; Sanjurjo-Sánchez *et al.*,

2010; Scherer and Wheeler, 2009; Elert *et al.*, 2022). Typically, consolidants are applied as liquid suspensions on the material to be treated, penetrating its porous system and forming chemical or physical bonds that reinforce the cohesion between individual particles, preventing disintegration and material loss. In addition to strengthening the substrate, consolidants can offer protection against moisture, atmospheric agents, and environmental pollution.

However, the consolidation products currently used in conservation interventions on plasterwork are the same as those applied to lime mortars or stone materials. Consequently, there is still no consolidant that is entirely compatible with the physicochemical characteristics of gypsum plasters. These consolidation treatments encompass the use of acrylic and vinyl resins, alkoxysilanes, and other inorganic products like the so-called "nanolimes" (*i.e.*, alcoholic dispersions of portlandite, $\text{Ca}(\text{OH})_2$, nanoparticles) (*e.g.*, Ambrosi *et al.*, 2001; Giorgi *et al.*, 2010; Chelazzi *et al.*, 2013; Otero *et al.*, 2017; Rodriguez-Navarro and Ruiz-Agudo, 2018; Burgos-Cara *et al.*, 2018; Burgos-Ruiz *et al.*, 2023), or treatments involving barium hydroxide (*i.e.*, $\text{Ba}(\text{OH})_2$) (Price and Doehne, 2011). Despite the numerous attempts to consolidate this delicate material, several challenges have arisen. For instance, organic resins and alkoxysilanes prove compositionally incompatible, as they fail to establish sufficiently strong bonds with the substrate, posing a serious threat to the structural integrity of the plasterwork.

On the contrary, inorganic consolidants emerge as a potentially more effective and compatible alternative. This technology revolves around introducing substances that undergo *in situ* transformation into insoluble and robust cements within the porous system of the treated material (*e.g.*, Rodriguez-Navarro and Ruiz-Agudo, 2018; Burgos-Ruiz *et al.*, 2023). Consequently, nanolimes transform into calcium carbonate by capturing CO_2 from the air under moderate relative humidity conditions, while barium hydroxide can evolve into barium sulfate by capturing SO_2/SO_3 or by reacting with the gypsum substrate. These cementitious agents exhibit significantly lower solubility than gypsum, thus being theoretically less susceptible to deterioration in humid environments. Nonetheless, drawbacks such as surface crusting, cracking, and undesirable color and textural alterations have

been reported in original gypsum pieces post-treatment with these consolidants (Otero *et al.*, 2017).

Additionally, bio-consolidation treatments have been proposed using colonies of carbonatogenic bacteria of the strains *M. xanthus* and *B. diminuta* (Jroundi *et al.*, 2014, 2017; Mazzoli *et al.*, 2018; Palla *et al.*, 2020), which are capable of biomineralizing compact calcium carbonate structures as a defense mechanism in environments with excess calcium. Although this strategy has been applied in walls at the Alhambra and seems to give good results by improving in the mechanical resistance of the treated substrates (Elert *et al.*, 2022), it requires activation and careful treatment of the bacterial colonies, and does not produce a mineral phase fully compatible with calcium sulfate.

In Chapters 4 and 5, the aspects related to the use and synthesis of novel functionalized inorganic consolidants for gypsum plasters, as well as other porous substrates (*e.g.*, sandstone, used as a model porous material) are further discussed.

9. HYPOTHESES AND OBJECTIVES

This interdisciplinary thesis project aims to delve into the formation of different phases within the $\text{CaSO}_4\text{-H}_2\text{O}$ system, to understand their mechanisms and control the transitions governing the gypsum cycle. The primary objective is to design compatible and effective treatments for the conservation of gypsum plasterwork, stuccoes, and historical mortars. The research is guided by the following set of hypotheses and their corresponding objectives:

Dehydration and Re-hydration of $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$:

Hypothesis: Understanding the mechanisms of gypsum dehydration and bassanite/anhydrite re-hydration is critical to understand the physical-chemical properties and thermal behavior of set gypsum plaster.

Objective: Gaining further insight on the gypsum cycle to control and modify the physicochemical properties of gypsum materials resulting from the hydration of bassanite.

Non-Classical Crystallization of Calcium Sulfate:

Hypothesis: The precipitation of $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ phases from solution occurs through a non-classical multi-stage crystallization process.

Objective: Obtaining clearer evidence on the nucleation mechanisms of calcium sulfate in both low (homogeneous precipitation) and high (gypsum setting) solid/liquid ratio systems to design gypsum materials with enhanced chemical properties.

Phase Diagram and Phase Selectivity Control:

Hypothesis: Controlling the phase diagram of the $\text{CaSO}_4\text{-H}_2\text{O}$ system and the different factors that influence phase selectivity is crucial.

Objective: Optimizing solvothermal synthesis routes, with controlled water percentage, to selectively produce α -bassanite nanoparticles, contributing to the design of multifunctional materials with high added value.

Bio-Inspired Strategies to Produce Conservation Materials:

Hypothesis: Bio-inspired strategies can be used to produce advanced functional materials with tailored properties.

Objective: Implementing the use of organic and/or inorganic additives to produce a range of nanostructured consolidants. These consolidants, with different functionalities, aim to provide precise conservation treatments compatible with deteriorated plasterwork and other building materials. For this, two sub-objectives were proposed:

- Producing α -bassanite nanoparticles with added functionalities *via* the use of organic additives.
- Exploiting the previously mentioned phase-selective solvothermal synthesis protocol to produce other functionalized nanomaterials, such as calcium hydroxide to demonstrate its versatility.

In summary, this research project seeks to contribute to the understanding of CaSO_4 -related processes and develop innovative approaches for the enhancement of the physical-chemical properties of gypsum-based materials and the conservation of plaster and other closely related building materials.

“For the sake of readability, each of the ongoing chapters has been organized in four sections: Introduction, Experimental Section, Results and Discussion and Conclusion.”

CHAPTER 2. STRUCTURAL INSIGHTS INTO THE DEHYDRATION AND RE-HYDRATION OF GYPSUM

1. *Introduction*
2. *Experimental Section*
 - 2.1. *Calcination and Re-Hydration of Gypsum*
 - 2.2. *Mineralogical and Textural Analyses of Samples*
3. *Results and Discussion*
 - 3.1. *Dehydration of Gypsum*
 - 3.2. *Re-Hydration of Bassanite*
4. *Conclusion*

The work presented in this Chapter corresponds to the results of a journal publication being prepared for submission in Crystal Growth and Design (Burgos-Ruiz, M., Elert, K., Ruiz-Agudo, E., & Rodriguez-Navarro, C. (2024). Structural Insights into the Dehydration and re-Hydration of Gypsum, Crystal Growth and Design, Being prepared).

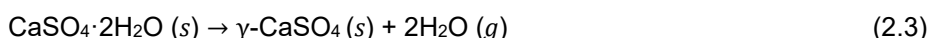
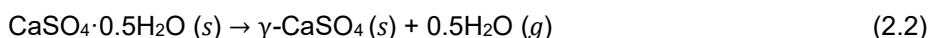
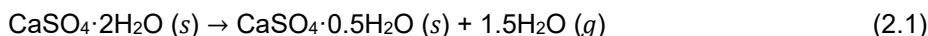
1. INTRODUCTION

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is the most abundant sulfate salt in the Earth's surface and is considered one of the most important industrial minerals in the world. Hence, the formation of gypsum and the phase transitions that occur in the CaSO_4 - H_2O system have been extensively investigated for more than 100 years. The thermal processing (calcination) of gypsum resulting in its dehydration, enables obtaining hemihydrate, the mineral bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), and/or soluble anhydrite (γ - CaSO_4), which are the main components of *plaster of Paris*, a hydraulic binder that has been widely used since prehistoric times to elaborate building materials, whether structural or decorative, including stuccoes, fire-resistant wall coatings and ceilings.

Calcium sulfate phases are not only relevant for the construction industry, but are also interesting for other specific applications such as bone and dental grafting, soil amendment and water retention in horticulture or as filler materials in the paper and pharmaceutical industries, among others (e.g., Foti *et al.*, 2019; Hesarakı *et al.*, 2009; Ahmed and Ugai, 2011). Due to the importance of these materials, the dehydration and (re)hydration reactions that conform the so-called “*gypsum cycle*”, analogous to the “*lime cycle*” (Rodríguez-Navarro, 2012), have been extensively studied, as they constitute the fundamentals not only to understand the use of *plaster of Paris* as a binder, but also the geologic events (*i.e.*, terrestrial or extra-terrestrial) that led to the formation of calcium sulfate minerals and their phase transitions. In this respect, gypsum dehydration has been long studied as a model for seismogenic and metamorphic dehydration processes that occur in Nature (e.g., during subduction), where the release of water flux has significant sedimentary and tectonic implications (Heard and Rubey, 1966; Otálora and García-Ruiz, 2014; Schrank *et al.*, 2020).

There is ample evidence showing the tight interdependence between temperature and water vapor partial pressure ($p\text{H}_2\text{O}$) conditions and the products obtained after gypsum calcination. While at low $p\text{H}_2\text{O}$ γ - CaSO_4 is obtained in a single step, the

dehydration of gypsum follows a two-step mechanism under moderate-to-high $p\text{H}_2\text{O}$ involving the formation of bassanite as an intermediate phase (e.g., Weiser *et al.*, 1936; McAdie, 1964; Ball and Norwood, 1969; McConell *et al.*, 1987; Abriel and Reisdorf, 1990; Putnis *et al.*, 1990; Strydom *et al.*, 1995; Badens *et al.*, 1997). The dehydration of gypsum can thus be described in terms of the following set of reactions:



Furthermore, γ -anhydrite transforms into β -anhydrite (“insoluble anhydrite”) at higher temperatures. This phase is extremely stable and less soluble than gypsum and bassanite at temperatures higher than $\sim 42^\circ\text{C}$ (Van Driessche *et al.*, 2017). Insoluble anhydrite can also be obtained directly from gypsum under extremely low $p\text{H}_2\text{O}$ conditions (e.g., high vacuum) or in high salinity hydrothermal environments (García-Ruiz *et al.*, 2007; Van Driessche *et al.*, 2011).

Additionally, the thermal dehydration of gypsum has been reported to involve the formation of sub-hydrates with formula $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ ($0 < n < 0.8$). Although the existence of such sub-hydrates has been challenged (Weiss and Brau, 2009), there is still controversy regarding this aspect and even new phases, such as “hydro- γ -anhydrite”, have been theorized to form during the full gypsum dehydration pathway (López-Buendía *et al.*, 2020).

Despite the difference in structural water content among the $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ phases (i.e., $0 < n < 2$), phase transitions in the $\text{CaSO}_4\text{-H}_2\text{O}$ system below 280°C (i.e., the point where the γ - to β -, or insoluble, anhydrite transition occurs) take place with little structural alterations, being commonly considered topotactic (Abriel *et al.*, 1990; Sipple *et al.*, 2001; Jordan and Astilleros, 2006).

Gypsum crystallizes in the monoclinic system: Note, however, that different unit cell choices and space groups (e.g., $A2/a$; $C2/c$, $I2/a$, and $I2/c$) have been reported (Wooster 1936; Cole and Lancucki, 1974; Pedersen and Semmingsen, 1982;

Schofield *et al.*, 1996; Comodi *et al.*, 2008; Henry *et al.*, 2009). Here we adopted the space group $I2/a$ (Schofield *et al.*, 1996), also used by Beaugnon *et al.*, 2022) in a recent study on the structural features of the thermal dehydration of gypsum single crystals.

Bassanite shows two polymorphs, α and β , whose structures have been respectively described as monoclinic (space group $I2$) and trigonal (space group $P3_221$) (Abriel and Nesper, 1998), although a more recent crystal structure refinement shows a monoclinic structure for the β -polymorph (space group $I2$) (Ballirano *et al.*, 2001) with twinning accounting for the apparently trigonal structure (Weiss and Brau, 2009). In essence, these two structures are identical, and they exhibit channels along the c -axis direction (diameter of 6.93 Å, 7.18 Å and 6.71 Å, as measured for the $S \cdots S$, $Ca_1 \cdots Ca_1$ and $Ca_2 \cdots Ca_2$ distances, respectively) which allows to easily accommodate or release weakly bound water molecules.

Soluble anhydrite crystallizes in the hexagonal system (space group $P6_222$) in which the channels along the c -axis direction (diameter of 6.70 Å) are preserved after the removal of water from bassanite (Christensen *et al.*, 2008). In fact, the structure of soluble anhydrite is typically understood as a dehydrated and slightly more compact version of the hemihydrate phases. Finally, orthorhombic insoluble β -anhydrite (space group $Amma$; Hawthorne and Fergusson, 1975) shows a more compact structure than the other phases but preserves the same strong $Ca-SO_4$ chains along $[001]$ forming the zeolitic channels of soluble anhydrite.

The structural similarities between these calcium sulfate phases are the reason why the dehydration of gypsum, whether in one or two steps, as well as the transformation of soluble into insoluble anhydrite, has been described as a topotactic and pseudomorphic process, as the relative atomic arrangement and crystal morphology are assumed to be preserved after the release of structural water molecules (Sipple *et al.*, 2001). However, X-ray diffraction analyses have failed to prove a clear structural relationship between parent and product phases during the thermal decomposition of gypsum which has casted doubts regarding whether such a phase transformation is topotactic (Abriel *et al.*, 1990; Sipple *et al.* 2001). In contrast, TEM-SAED analyses suggest that the transformation is indeed

topotactic (Sipple *et al.*, 2001), which might help explain the observed preferred orientation of fractures and dehydration products (Sipple *et al.*, 2001; Beaunon *et al.*, 2022).

Analogously, considering the structural similarities between gypsum and hemihydrate, as well as soluble anhydrite phases, it could be argued that the hydration of the former could also be topotactic. However, most evidence reported so far concludes that the hydration of hemihydrate (or soluble anhydrite, which rapidly hydrates in air to form bassanite) is a dissolution-reprecipitation process (Goto and Ridge, 1965; Ilett *et al.*, 2022). Nonetheless, no detailed crystallographic study has been performed so far to disclose whether the hydration step is structurally controlled. These phase transitions, and whether they are structurally controlled or not are crucial to predict and control the properties of the resulting product phase(s) as a function of the structural features of the parent crystalline phase. In this particular case, a topotactic decomposition of gypsum would facilitate the control over the physicochemical properties of the resulting product phase(s) (Glasser *et al.*, 1962). However, the textural and crystallographic relationships between the $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ phase(s) involved in the calcination of gypsum and the hydration of bassanite (and soluble anhydrite) are still not clear.

Here we explored the micro- and nanostructural changes that occur during the calcination of gypsum single crystals under low $p\text{H}_2\text{O}$ conditions and the subsequent vapor phase hydration of bassanite by means of two-dimensional X-ray diffraction (2D-XRD), field emission scanning electron microscopy (FESEM), *in situ* and *ex situ* transmission electron microscopy (TEM), and selected area electron diffraction (SAED) analyses. Our study shows that the solid-state decomposition of gypsum strongly depends on the crystal size. The macroscopic *ex situ* analysis results showed that these reversible processes result in crystals with no apparent shared structural or crystallographic relationships to the parent single gypsum crystal (during dehydration) or the final dehydrated pseudomorph (during rehydration). However, the nano- and microscopic results revealed the opposite, as they show a clear structural relationship between parent and product

phases during dehydration and rehydration. Further insights into these discrepancies are discussed in this chapter.

2. EXPERIMENTAL SECTION

2.1. Calcination and Re-Hydration of Gypsum

For the analysis of the thermal decomposition of gypsum, optical quality gypsum crystals (from Naica, Mexico) were cleaved along (010) using a blade to obtain millimeter-sized (approx. 2×2×1 mm) single crystals. Three different sets of gypsum crystals were separately heated in an air-ventilated furnace, from 25 °C to 100, 130 and 150 °C at a heating rate of 5 °C min⁻¹. Subsequently, samples were kept at the target temperature for 30 min. Finally, the resulting partially or fully dehydrated gypsum pseudomorphs were collected and stored in closed glass vials under dry N₂ atmosphere until further analysis.

Dehydrated gypsum pseudomorphs were subjected to re-hydration. These specimens were placed in a closed container for at least 12 months under the conditions of 25 °C and 100% relative humidity.

2.2. Mineralogical and Textural Analysis of Samples

Optical microscopy photomicrographs of {010} cleavage surfaces of dehydrated gypsum pseudomorphs were acquired using a Leica DVM2000 digital microscope.

Textural analyses of {010} cleavage surfaces of carbon-coated gypsum single crystals and calcined pseudomorphs (before and after rehydration) were carried out by means of FESEM, using a Carl Zeiss Auriga (10⁻⁶ Pa vacuum, 3 kV acceleration voltage, secondary electron imaging mode).

The 2D-XRD analysis of gypsum single crystals, their low temperature pseudomorphs and the re-hydration products was performed using a Bruker D8 Venture X-ray single-crystal diffractometer equipped with a PHOTON area detector. Patterns were collected using a 0.2 mm collimated beam, 120 s of exposure time and Mo-K α radiation (0.7107 Å). Samples were measured in reflection mode ($2\theta = 20^\circ$ and $\omega = 10^\circ$), and a sequence of 2D diffraction patterns were collected during a Phi scan with 5° steps (72 frames in total). The XRD2Dscan v.8.0 (PANalytical, The Netherlands) software package was used to analyze the collected 2D-XRD patterns and to prepare pole figures showing the crystallographic/structural relationship between parent and product phases.

To evaluate the effect of crystal size on the thermal dehydration of gypsum, and rehydration of bassanite, crystallographic features of gypsum and bassanite (obtained by thermal treatment of powder gypsum, see below) microcrystals and partially hydrated bassanite particles were determined by means of TEM, using a Thermo Fisher Scientific TALOS F200X microscope (operated at 200 kV acceleration voltage). Gypsum powder samples were prepared by grinding optical quality gypsum crystals (from Naica, Mexico) using an agate mortar. A fraction of the obtained powdered gypsum was then subjected to thermal dehydration (1 hour at 130°C) to obtain microcrystalline bassanite samples. The resulting powder samples were then sieved below $35\ \mu\text{m}$, dispersed in absolute ethanol and sonicated for 20 s before being deposited on carbon-coated Cu grids. The prepared samples were then plasma cleaned. TEM micrographs were obtained using a $40\ \mu\text{m}$ objective aperture.

In situ TEM was employed to accurately describe the electron beam induced dehydration of gypsum and bassanite at the nanoscale. For this, sequential high-resolution micrographs were obtained at high magnification and different e-beam irradiation periods, while detailed crystallographic information was obtained by measuring selected area electron diffraction (SAED) pattern collected using a $10\ \mu\text{m}$ objective aperture and fast Fourier transform (FFT) patterns of areas imaged at high resolution (HRTEM).

3. RESULTS AND DISCUSSION

3.1. Dehydration of Gypsum

Optical microscopy observation show that the individual gypsum single crystals acquire a milky appearance with increasing calcination T (Figure 2.1a-d). This is due to extensive fracturing along specific crystallographic direction on the (010) face, with the development of multiple, thermal dehydration nucleation sites with an hourglass shape, typically aligned along surface defects/discontinuities (e.g., cleavage planes and macrosteps, as well as subgrain boundaries) as shown by higher magnification optical microscopy imaging (Figure 2.1d). Such hourglass structures display marked striation along the bisector of the acute angle formed by two crosscutting fractures. Details of such hourglass structures, which are standard features of the thermal dehydration of gypsum single crystals (Fowler *et al.*, 1968; Beaunon *et al.*, 2022; Mukherjee and Misra, 2024), were observed at higher magnification using FESEM, as described below.

The most significant dehydration-induced microtextural change observed by FESEM was the formation of cracks ($\sim 0.5 - 21 \mu\text{m}$ wide) parallel to the gypsum main cleavage plane (*i.e.*, {010}). This is a standard feature of dehydration of gypsum single crystals, as shown by numerous studies (Fowler *et al.*, 1968; Takahashi and Setoyama, 1989; Sipple *et al.*, 2001; Brantut *et al.*, 2012; Beaunon *et al.*, 2022), and is consistent with the loss of structural water forming layers parallel to (010). Water molecules are coordinated to the Ca-SO_4 chains running parallel to [101] in the (010) planes of gypsum, so their loss causes shrinkage not only along [010] but also along $[10\bar{1}]$, resulting in cracks parallel to the $(10\bar{1})$ planes. The escape of water molecules (in the form of water vapor) along the cracks parallel to (010) is the main (*i.e.*, the fastest) way to dehydrate gypsum, since H_2O diffusion along [010] is hindered (Okhotnikov *et al.*, 1987). However, cracks also form along [101], as well as along [100] and [001] (Figure 2.1f), which would facilitate H_2O escape. Consequently, in addition to the cracks parallel to the (010) plane, hourglass-shaped cracks appeared on the (010) surface of the heat-treated

gypsum crystals as indicated above. As an additional feature of this type of cracks, non-striated and bent-up triangular areas were also observed, which probably formed by the combined effect of shear stress release along $[101]$ and compression along $[001]$. These standard textural features of dehydrated gypsum (Beaugnon *et al.*, 2022) occurs after random nucleation of dehydration thermal pits on $\{010\}$ surfaces (Jordan and Astilleros, 2006). The hourglass structures are apparently formed by coalescence of shrinkage cracks and formation of parallel hemihydrate/soluble anhydrite crystals arranged in opposing triangular substructures. In this case the cracks follow the $(10\bar{1})$ planes. Importantly, no shrinkage occurs along $[101]$, which explains why the hemihydrate fibers align in this direction on the (010) plane of dehydrated gypsum (Beaugnon *et al.*, 2022). In agreement with the cracking rules stipulated by Sipple *et al.* (2001), and according to the Periodic Bond Chain (PBC) theory developed by Hartman and Perdok (1955), the long and continuous cracks along $[101]$ on (010) are parallel to the strongly bonded Ca-SO_4 chains (primary PBC in gypsum; space groups $I2/a$ and $I2/c$), which should remain invariable throughout the atomic rearrangements that occur during the dehydration of gypsum. Considering this, cracks should also form parallel to the other two stable PBCs in gypsum.

Although the direction of PBCs depends on the selected space group, two of these strong PBCs follow the $[001]$ and $[100]$ directions, while a third one follows $[101]$, as indicated above. Here, we selected the $I2/a$ space group to describe the observed phenomenology. In fact, three types of cracks with different sizes (from bigger to smaller size, Type I, II and III) are visible on $(010)_{\text{gypsum}}$. As observed in Figure 2.1g, Type II and III cracks systematically intersect at an angle of $\sim 118^\circ$, which is approximately equal to the β parameter of the monoclinic unit cell of gypsum, while Type I and III, and Type I and II cracks intersect at an angle of $\sim 70^\circ$ and $\sim 60^\circ$, respectively, which are equal to the angles formed by the a - and c - axes with the diagonal $[101]$ direction in the gypsum unit cell (independently of the space group). Therefore, it seems reasonable to assume that the observed hourglass-shaped cracks develop on weakly bonded planes parallel to strong PBCs.

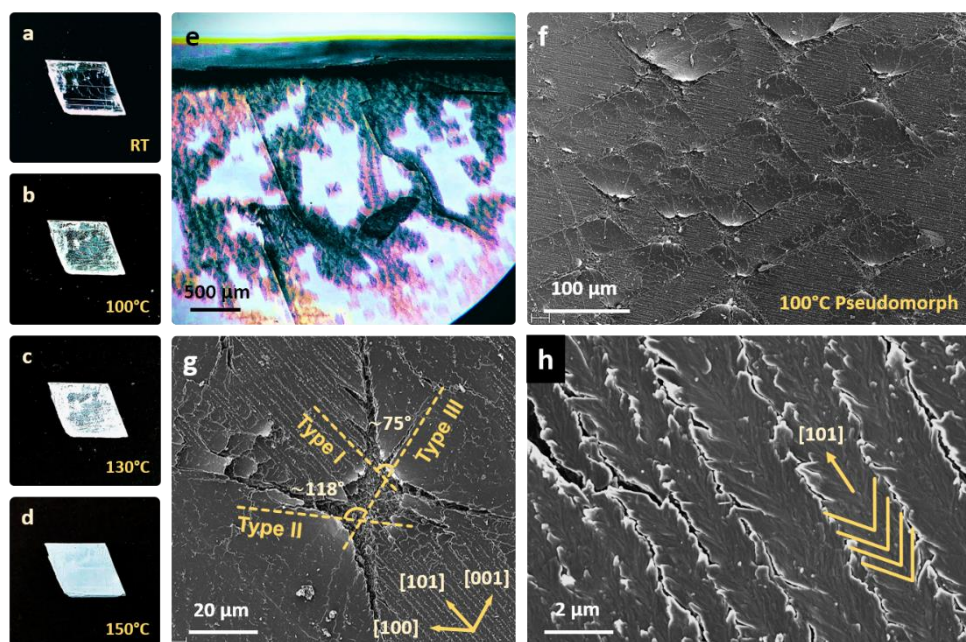


Figure 2.1. Textural and micro-textural variations observed after pseudomorphic thermal dehydration of gypsum single crystals (a-d) observed from $[0\bar{1}0]$. Optical micrographs (e) show the nucleation of thermal pits in random positions of the outermost $\{010\}$ gypsum surfaces. FESEM observations of thermal pits (f-g) showing the characteristic hourglass pattern described by microfractures oriented along $[101]$, $[100]$ and $[001]$ (i.e., Type I, II and III respectively) formed upon dehydration of gypsum, as defined for the $I2/a$ space group. Detail SEM micrograph of Type I microfractures (h) showing the formation of bassanite/anhydrite microneedles distributed adopting a characteristic “feather” or “fishbone” pattern.

To clarify these crack rules, we compared the polyhedral arrangement in the gypsum structure as observed along $[010]$ for the $C2/c$, $I2/a$ and $I2/c$ space groups. Figure 2.3 shows that equivalent PBCs – here denoted PBC-1, PBC-2 and PBC-3 – follow different directions because of the different spatial descriptors of the gypsum crystal structure and choice of unit cell. To verify the spatial relationships between these three settings, the $C2/c \rightarrow I2/c$ and $C2/c \rightarrow I2/a$ transformation matrices are presented below, so that unit cell vectors of the I -centered space groups can be described in terms of the vectors of the initial C -centered configuration, as follows:

$$C2/c \rightarrow I2/c; \begin{bmatrix} h_2 \\ k_2 \\ l_2 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ -1 & 0 & 1 \end{bmatrix} \begin{bmatrix} h_1 \\ k_1 \\ l_1 \end{bmatrix} = \begin{bmatrix} -h_1 \\ -k_1 \\ -h_1 + l_1 \end{bmatrix}$$

$$C2/c \rightarrow I2/a; \begin{bmatrix} h_2 \\ k_2 \\ l_2 \end{bmatrix} = \begin{bmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & -1 \end{bmatrix} \begin{bmatrix} h_1 \\ k_1 \\ l_1 \end{bmatrix} = \begin{bmatrix} -l_1 \\ k_1 \\ h_1 - l_1 \end{bmatrix}$$

Consequently, the $I2/a \rightarrow I2/c$ transformation matrix can be also calculated:

$$I2/a \rightarrow I2/c; \begin{bmatrix} h_2 \\ k_2 \\ l_2 \end{bmatrix} = \begin{bmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{bmatrix} \begin{bmatrix} h_1 \\ k_1 \\ l_1 \end{bmatrix} = \begin{bmatrix} -l_1 \\ -k_1 \\ -h_1 \end{bmatrix}$$

Thus, the direction of PBCs and, consequently, crack formation can be defined for the different space groups, as summarized in Table 2.1 and Figure 2.2.

Table 2.1. Summary of the orientation of the main PBCs in the structure of gypsum according to the relationships between the $C2/c$, $I2/a$ and $I2/c$ space groups.

*Main axial directions corresponding to the I -centered unit cells are given as transformed from the $C2/c$ group.

Space Group	<i>a</i> -axis	<i>b</i> -axis	<i>c</i> -axis	PBC-1	PBC-2	PBC-3
$C2/c$	[100]	[010]	[001]	[100]	[001]	[101]
$I2/a$	$[\bar{1}00]^*$	[010]*	$[\bar{1}01]^*$	[101]	[100]	[001]
$I2/c$	$[00\bar{1}]^*$	$[0\bar{1}0]^*$	$[10\bar{1}]^*$	[101]	[001]	[100]

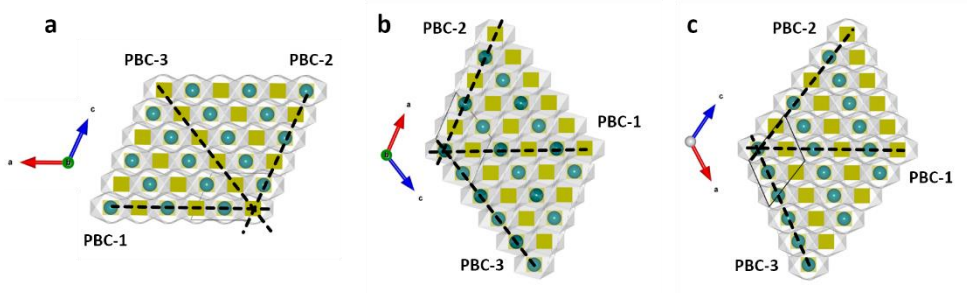


Figure 2.2. Summary of the orientation of the main PBCs in the structure of gypsum according to the $C2/c$ (a), $I2/a$ (b), and $I2/c$ (c) space groups.

For this reason, and to avoid confusion, in the case of gypsum not only crack formation, but also every other anisotropic property or crystallization process (e.g., epitaxial growth), should always be described according to a specific space group.

Takahashi and Setoyama (1989) and Beaunon *et al.*, (2022) showed that dehydration of gypsum resulted in the formation of cracks intercalated with acicular anhydrite domains in which micro-needles were arranged in a regular fishbone or chevron pattern. We observe the same fishbone pattern of rod-shaped β -bassanite and/or γ -anhydrite microcrystals on $\{010\}$ gypsum faces, with their long axis oriented at an angle of $\sim 35\text{--}45^\circ$ with respect to the $[101]$ direction. According to Beaunon *et al.* (2022), cracks along $[101]$ results from shrinkage along $[10\bar{1}]$, whereas the fish-bone structure results from shear stresses associated with the unit cell expansion along $[101]$ following the transition from gypsum into hemihydrate. Such stress energy is released *via* shear strain, likely along cleavage planes, so that the overall $[101]$ orientation of the fibers is not lost. Yet this implies multiple bond-breaking along the Ca-SO_4 chains, which seems not highly favorable. Alternatively, it could be argued that these “fishbone” structures are the result of multiple mechanical twinning along the $(10\bar{1})$ twin law. Interestingly, these microtextural features observed on the surface of the pseudomorphs were independent of the calcination temperature, as the general aspect of cracks and hemihydrate fishbone/chevron patterns was similar in all the studied cases.

Altogether, these textural features (*i.e.*, crystallographically oriented cracks and product bassanite nanocrystals) point to a topotactic solid-state mechanism for gypsum thermal dehydration. Note, however, that different textural features could have developed in the inner parts of the gypsum crystals (where water release is hindered) as a result of extensive cracking and deformation associated with the molar volume differences between parent and product phases, and/or secondary nucleation and growth processes (Krause *et al.* 2020; Pritzel *et al.* 2022). The latter seems to be the case as shown by areas on the (010) surface of dehydrated gypsum where craters formed, unveiling that the (nano)crystals underneath the surface were randomly oriented (Figure 2.3a-b). To disclose whether a preferred orientation between parent and product phases existed, 2D-XRD analyses of the

gypsum pseudomorphs were performed using Mo-K α radiation, which is ~ 10 times more penetrative than standard Cu-K α . Note that in the case of inorganic solids Cu-K α radiation typically has an effective penetration depth of only a few μm (Cullity, 1956). Figure 2.3c-e shows the 2D-XRD patterns and the calculated pole figures corresponding to the pseudomorphs dehydrated at increasing T as compared to those of the uncalcined gypsum control. The loss of diffraction spots corresponding to the parent gypsum single crystal, and the observation of clear Debye rings in the 2D-XRD patterns (which appeared independently of T) corresponding to the newly formed bassanite, suggest that the dehydration of gypsum and the formation of hemihydrate occur without any clear structural control. These results were further confirmed by the unexpected lack of intensity maxima (*i.e.*, complete absence of preferred orientations) in pole figures regardless of the selected Bragg reflection and calcination T .

Indeed, it is difficult to explain the extensive degree of disorientation of the product bassanite observed by 2D-XRD, while at the same time our FESEM observations showed a clear orientation of the product crystals and cracks. It could be argued that the clear orientation of the cracks along specific gypsum crystal planes/directions, and the observed orientation of the hemihydrate crystals are only present at the surface of the pseudomorphs, whereas there is a lack of product phase orientation in their interior. Note that significant distortion can take place in the pseudomorph core due to pervasive shrinkage and cracking associated with the molar volume differences between gypsum and hemihydrate, creating significant porosity. It is therefore very likely that the strain associated with the phase transition caused a general lack of clear orientation between the parent and product phases. Note also that it has been recently reported that in the interior of gypsum single crystals subjected to thermal dehydration, nucleation and growth of randomly oriented α -hemihydrate crystals occurs (Pritzel *et al.*, 2022), whereas a similar nucleation and growth process has been observed in polycrystalline gypsum rock undergoing thermal dehydration (Krause *et al.*, 2020). Because the released H_2O cannot easily escape, high- $p\text{H}_2\text{O}$ "microenvironments", similar to microhydrothermal chambers, can take place. Within such microenvironments α -hemihydrate can form by nucleation and growth rather than by a solid-state

process. Note that hydrothermal conditions are required for α -hemihydrate formation (Singh and Middendorf, 2007). The building-up of $p\text{H}_2\text{O}$ within gypsum crystals is also consistent with experimental results showing periodic fluctuations in dehydration rates measured during thermal decomposition of gypsum, which are associated with trapping and sudden release (after fracturing) of water vapor (Heide *et al.*, 1980).

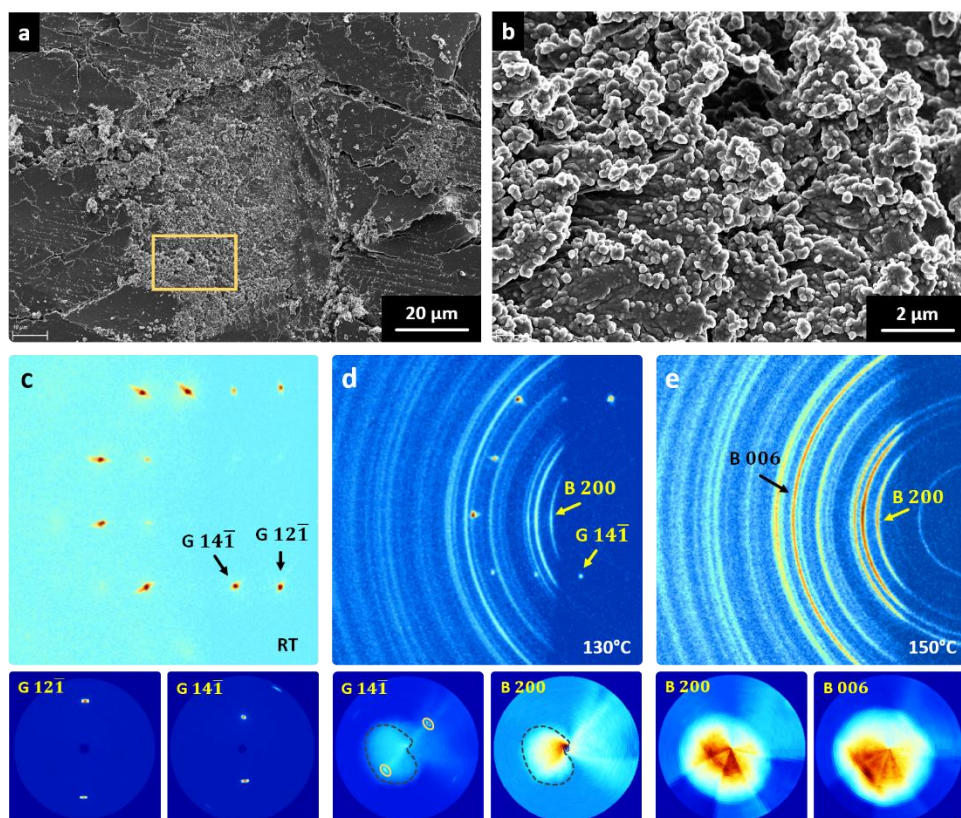


Figure 2.3. FESEM micrographs showing a micrometric thermal pit (a,b) formed upon dehydration of gypsum single crystals. The globular texture of the nanoparticles originated are indicative of secondary precipitation of bassanite by dissolution and nucleation processes due to the building-up of high $p\text{H}_2\text{O}$ in layers beneath the outermost $\{010\}$ surfaces of gypsum. Sequential 2D-XRD patterns and pole figures of an unaltered gypsum single crystal (c) and its pseudomorphs (130 °C, d; 150 °C, e), showing that bassanite was formed without clear preferred orientations. The calculated pole figures correspond to the Bragg reflections indicated by arrows.

In contrast, a topotactic solid-state reaction can occur in surface areas where the H₂O release is facilitated, preventing the building up of $p\text{H}_2\text{O}$ and favoring β -hemihydrate formation with preferred crystallographic orientations. To disclose the role of crystal size on the studied thermal dehydration process, decomposition of gypsum and bassanite microcrystals *in situ* and *in vacuo* was observed following exposure to the electron beam during TEM analyses. Figures 2.4 and 2.5 respectively show the effects of electron beam damage on both minerals. The gypsum crystal in Figure 2.4a (oriented along the [010] zone axis of gypsum, $I2/a$ space group; Figure 2.4b) transformed into an oriented aggregate of insoluble anhydrite nanoparticles (Figure 2.4c; space group $Amma$; Hawthorne and Ferguson, 1975), as revealed by the *post-mortem* SAED pattern (Figure 2.4d; [010] zone axis of insoluble anhydrite), where diffraction spots with a marked angular spread ($\sim 7\text{--}11^\circ$) were observed. Note that the dehydration of gypsum induced by the e^- beam is extremely fast under ultra-high vacuum conditions. Therefore, it would be possible to observe a characteristic streaking along the c -direction, as well as additional reflections from dehydrated CaSO_4 phases along with those of untransformed dihydrate domains. Van Driessche *et al.* (2016) and Stawski *et al.* (2019) performed HR-TEM analyses on gypsum and anhydrite microcrystals obtained from Naica, and attributed the observed streaking and angular broadening to a strong mosaicity imprinted from the initial stages of gypsum crystallization, involving the oriented aggregation of nanometric bassanite sub-domains. However, it would be reasonable to argue that the streaking along [001] and the angular spread observed as standard features during gypsum TEM measurements is a direct consequence of the strain increase due to the *in situ* gypsum $\rightarrow$ bassanite/anhydrite transformation by electron beam damage.

The anisotropic gypsum $\rightarrow$ anhydrite transformation occurs with an increase of the micro-strain, which could give an explanation to the slight orientation mismatch of the newly-formed aggregates of anhydrite nanoparticles. From the SAED analysis, the following reactant/product orientation relationships could be established: $[010]_G//[010]_A$ and $[101]_G//[001]_A$, which underlines the fact that the orientation of the Ca-SO_4 of parent and product phases is preserved. Overall, these results indicate that the gypsum $\rightarrow$ anhydrite transition is actually a topotactic process,

where particle orientation is preserved from the parent mineral phase – at least at the nano-scale. Further exposure to the electron beam resulted in the radiolytic decomposition of anhydrite and the formation of non-oriented aggregates of calcium oxide nanoparticles, as shown by the polycrystalline rings (*i.e.*, 111, 200 and 220 reflections) in the SAED pattern of the resulting pseudomorph (Figure 2.4d) and the high-resolution TEM micrographs (Figure 2.5).

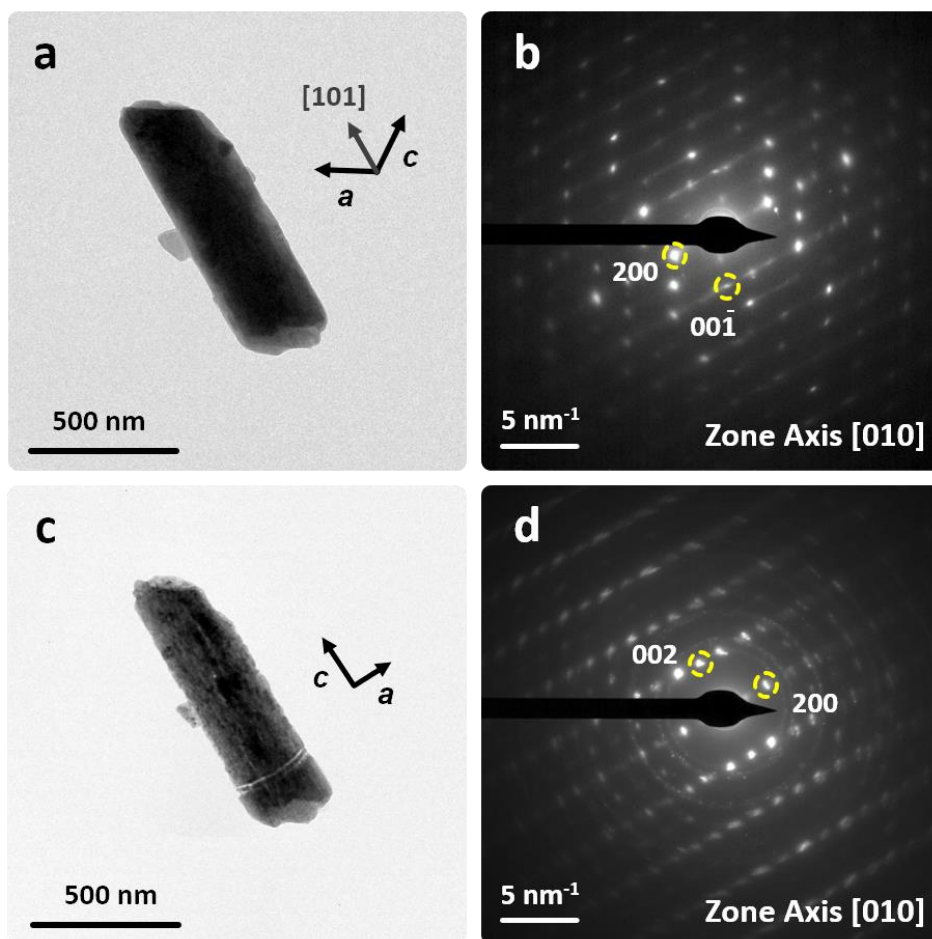


Figure 2.4. TEM images of a gypsum microcrystal undergoing *in situ* dehydration. (a,b) Micrograph and SAED pattern of the gypsum crystal in its initial state. (c,d) Micrograph and SAED pattern of the same crystal after dehydration induced by the electron beam. Note the clear $[101]_G/[001]_A$ orientation relationship, as visualized by comparing the SAED patterns for parent and pseudomorph crystals, indicating that the transformation is topotactic. Additionally, further exposition to the e-beam induced the decomposition of CaSO_4 into non oriented CaO nanoparticles, as observed by the polycrystalline Debye rings in the SAED corresponding to the pseudomorph (d).

It is important to underline that the orientation relationships observed between gypsum and insoluble anhydrite would be similar for the case of hemihydrate and soluble anhydrite, as their structures are very similar, all these product phases including Ca-SO₄ chains along the direction of the *c*-axis. It is very likely that the reason why we do not see the formation of either bassanite or soluble anhydrite during *in situ* TEM dehydration is due to the high energy supplied by the electron beam and the ultra-high vacuum conditions, which enabled the direct transition of gypsum to insoluble anhydrite and the decomposition of the latter forming non-oriented CaO nanoparticles.

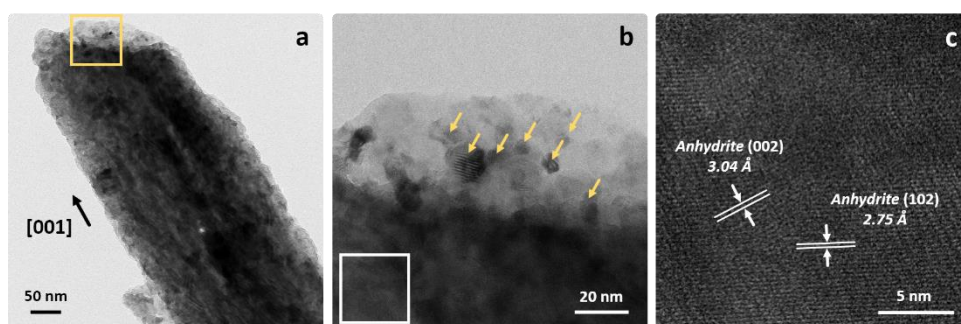


Figure 2.5. High resolution TEM micrographs of the dehydrated gypsum pseudomorph showing the formation of oriented insoluble anhydrite aggregates, alongside non oriented CaO nanoparticles (indicated by arrows).

Considering these results, it is plausible that crystal size plays an important role on the dehydration of gypsum. Therefore, it is reasonable to assume that, at the nanoscale, water should be easily released, thus avoiding the secondary dissolution of gypsum (favored by the building up of local high $p\text{H}_2\text{O}$) and the subsequent random nucleation of hemihydrate within the pseudomorph, while in larger-sized crystals the former process would only occur in the outermost layers of gypsum or areas near the edges of the crystal, where the liberation of water is not physically impeded, thereby enabling a (localized) topotactic replacement.

Comparable results were observed in the case of bassanite formed after *ex situ* thermal dehydration of gypsum powder. First, we observed that the bassanite pseudomorphs diffracted as single crystals, which demonstrated that the gypsum → bassanite transformation was structurally controlled and therefore was topotactic (Figure 2.6a and b).

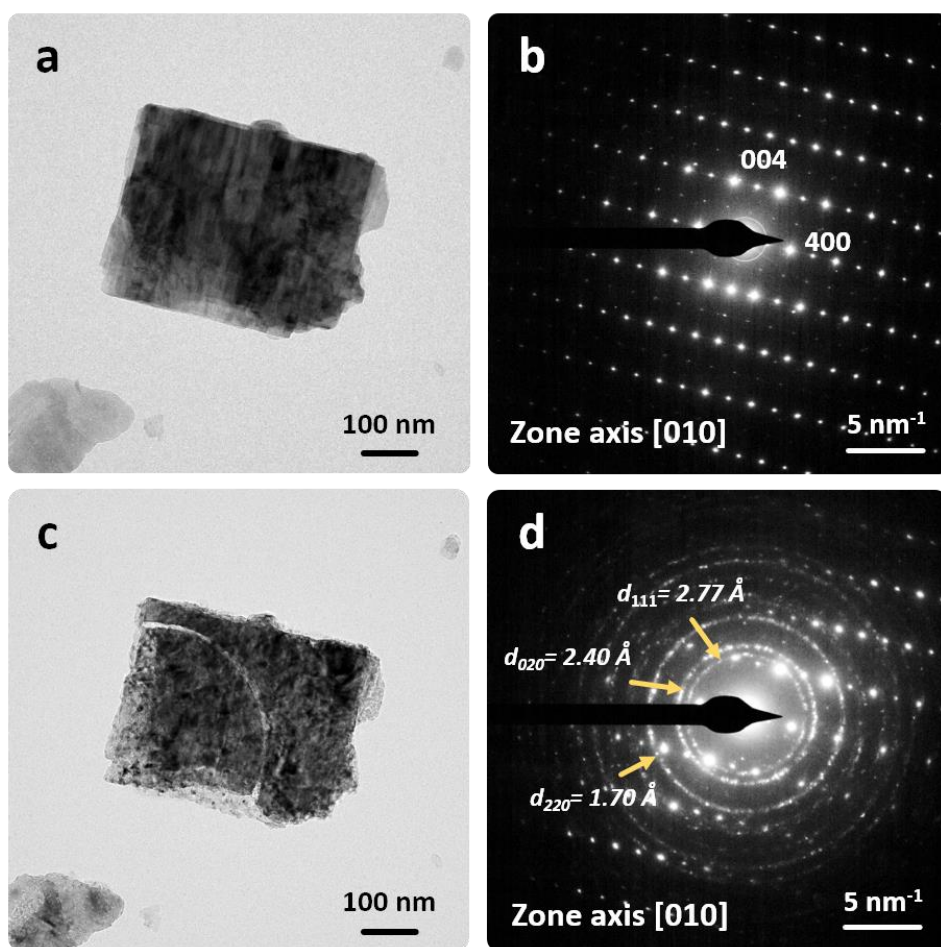


Figure 2.6. TEM images of a bassanite microcrystal (obtained by *ex situ* thermal dehydration of gypsum) undergoing *in situ* dehydration. (a,b) Micrograph and SAED pattern of the bassanite crystal in its initial state. (c,d) Micrograph and SAED pattern of the same crystal after transformation into insoluble anhydrite induced by the electron beam. Note that low intensity $h0l$ (where $l = \text{odd}$) diffraction spots were visible in the SAED pattern of the bassanite crystal, but not in the SAED pattern of the e-beam damaged crystal. This also evidences a clear $[010]_B/[010]_A$ and $[001]_B/[001]_A$ relationships indicating that this transformation is also topotactic. Polycrystalline rings correspond to CaO nanoparticles formed following the radiolytic decomposition reaction $\text{CaSO}_4 = \text{CaO} + \text{SO}_3$. The d_{hkl} spacings indicated in panel (d) correspond to CaO.

Further electron beam damage of bassanite pseudomorphs (oriented along the $[010]$ zone axis) resulted in the formation of a pseudomorph made up of insoluble anhydrite oriented along the same $[010]$ zone axis (Figure 2.6c and d). As indicated

above, bassanite and anhydrite are practically isostructural and the d -spacing corresponding to the $h00$, $0k0$ and $00l$ reflections remain almost constant during the bassanite $\rightarrow$ anhydrite (whether soluble or insoluble) phase transition. However, the low intensity $h0l$ (where $l = \text{odd}$) diffraction spots corresponding to consecutive $(00l)$ planes in the structure of bassanite and/or soluble anhydrite were not visible in the SAED patterns of the beam damaged pseudomorphs, thus indicating that the newly-formed solid phase was composed of insoluble anhydrite. These results confirm that the dehydration reaction, whether from gypsum or from bassanite, is a perfectly topotactic process. Again, randomly oriented aggregates of calcium oxide nanoparticles were formed after prolonged exposure to the electron beam, as observed in the *post-mortem* SAED and FFT patterns showing no preferential orientation for the 111 and 200 reflections corresponding to calcium oxide, and the lattice fringes of non-oriented CaO nanoparticles in the pseudomorph observed in high-resolution micrographs (Figure 2.7).

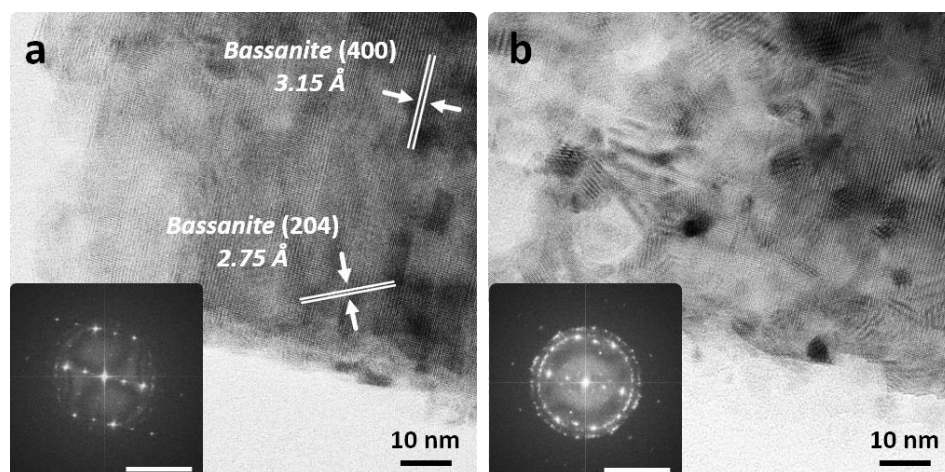


Figure 2.7. High resolution TEM micrographs and FFT patterns showing the dehydration of a bassanite single crystal (a) into oriented insoluble anhydrite aggregates (b) induced by the electron beam. Note that the same low intensity $h0l$ (with $l = \text{odd}$) bassanite reflections (inset in a) are not visible in the FFT of the transformed crystal (inset in b). Non oriented CaO nanoparticles, which are responsible for the ring pattern in the FFT, can be observed. Scalebars in FFT correspond to 5 nm^{-1} .

3.2. Rehydration of Bassanite

Pseudomorphs subjected to rehydration under high $p\text{H}_2\text{O}$ conditions showed similar textural and morphological features as compared to the dehydrated state. In general, fishbone patterns and cracks observed on the surface of the pseudomorphs are preserved during hydration. However, detailed high magnification FESEM images revealed that particles exhibited a nanogranular texture, most likely due to the regrowth of gypsum on the surface of bassanite micro-needles present on the surface of the pseudomorphs (Figure 2.8 a-c). This textural feature suggests that a highly supersaturated solution formed on the surface of bassanite particles upon their dissolution. Under these conditions high nucleation rates are favored, subsequently leading to the heterogeneous crystallization of non-oriented gypsum nano-granules, congruent with the overall disorientation observed in the 2D-XRD patterns and pole figures (Figure 2.8d). Furthermore, during the phase transition, particles showed a spherical/globular aspect rather than an acicular morphology. This swelling and expansion effect is likely due to the increase in molar volume associated with the hydration process (*i.e.*, $V_{m-B} = 53.16 \text{ cm}^3 \text{ mol}^{-1}$; $V_{m-G} = 74.53 \text{ cm}^3 \text{ mol}^{-1}$).

In any case, the overall appearance of the surface of the hydrated pseudomorphs pointed to a preferred orientation of the newly formed gypsum. However, only in the case of the partially dehydrated pseudomorphs obtained by calcination at 100°C , the recorded 2D-XRD patterns showed diffuse arcs with maxima instead of full Debye rings (Figure 2.8d), indicating that the newly formed gypsum grew using the orientation of the non-dehydrated gypsum domains still present in the core of the low- T pseudomorph. The fact that the preferred orientation was not due to toptaxy but to the existence of an untransformed gypsum core was confirmed by the 2D-XRD patterns of the pseudomorphs obtained at higher temperatures (*i.e.*, 130 and 150°C) where the gypsum-bassanite conversion was complete. They showed continuous Debye rings for the newly formed gypsum, and no preferred orientation was observed in the pole figures. This further demonstrates that the re-hydration of bassanite occurred by a dissolution-precipitation mechanism, by which the initial crystallographic features of the gypsum crystal can be hardly retained. It follows

that the preferred orientation of the newly formed phase in the low- T pseudomorph is due to a template effect (*i.e.*, self-epitaxy). The existence of self-epitaxy during bassanite hydration in the presence of an unreacted gypsum core should facilitate the progress of this reaction, explaining why addition of gypsum seeds to *plaster of Paris* strongly accelerates its hydraulic setting (Morgado et al., 2017).

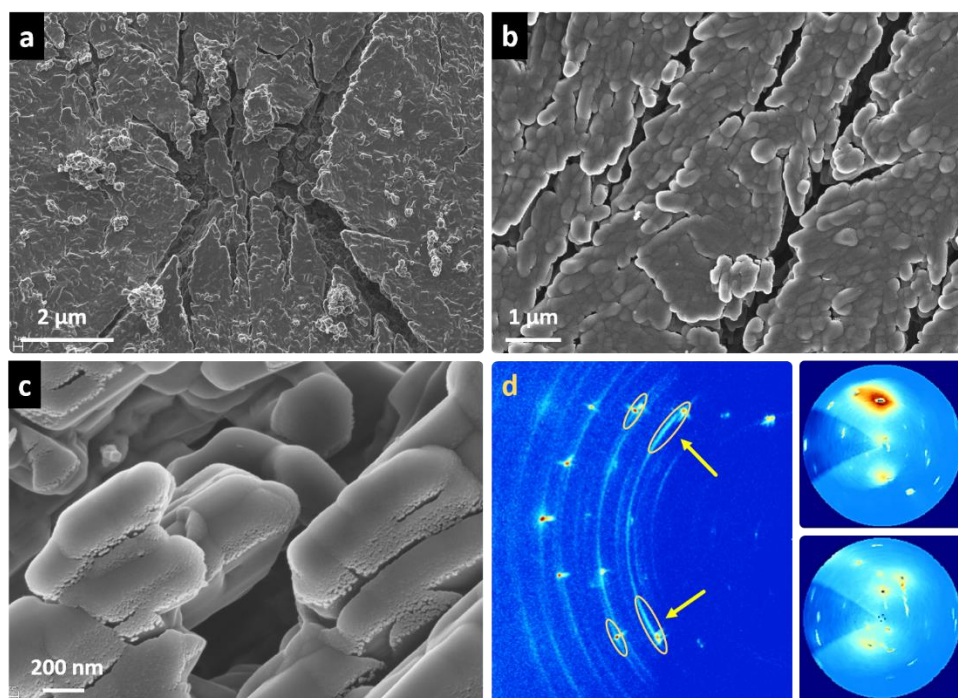


Figure 2.8. FESEM micrographs showing the textural aspect of re-hydrated gypsum crystals under 100% RH for 12 months. The globular (a,b) and nanogranular (c) textures of the hydrated particles indicate dissolution of bassanite/anhydrite and re-precipitation of gypsum on the surface of pre-existent bassanite particles. These textural features contribute to the non-oriented fraction of the newly formed gypsum, as observed in the 2D-XRD patterns and pole figures of the re-hydrated pseudomorphs. However, 2D-XRD patterns and pole figures corresponding to the re-hydrated low- T pseudomorph (100 °C; d) show discontinuous Debye rings with angularly-spread intensity maxima that can be interpreted as a template-effect induced by non-dehydrated gypsum domains still present in the core of the pseudomorph.

Overall, these results are fully consistent with the original model proposed by Le Chatelier (1887), and corroborated by more recent experimental results showing that the hydration of bassanite to form gypsum is a dissolution/precipitation process (La Bella *et al.*, 2023). Moreover, they point to a tight interface-coupled

dissolution/precipitation process as proposed by Putnis (2009). According to Putnis' model, a high supersaturation with respect to a product phase is reached within the fluid in contact with the dissolving parent phase. In this interfacial fluid the geochemical conditions (supersaturation) can be very different from those of the bulk solution, enabling far-from-equilibrium reactions (fast kinetics) favoring the pseudomorphic transformation of the parent phase into the product phase. However, it is not fully clear whether the formation of gypsum after bassanite involves the epitaxial growth of the former on specific crystal faces of the latter, as suggested by Jia *et al.* (2022). The lack of any preferred orientation between these two phases, determined here by the 2D-XRD analysis, prevents to disclose whether or not such possible epitaxy exists. Note, however, that the detailed synchrotron study by La Bella *et al.* (2023) shows that there is no epitaxy during such a hydration reaction.

Although it remains to be still demonstrated, these results could give a reasonable explanation to the existence of giant and pure selenite and anhydrite crystals, such as those found in Naica (Chihuahua, Mexico) or Pulpí (Almería, Spain). These locations are predominantly hydrothermal environments, where the cyclical injection of hot salt-water could favor interface-coupled dissolution-precipitation processes. This implies an overall re-crystallization of calcium sulfate, leading to the formation of crystals with progressively less structural defects. Mild T conditions and high salinity should also favor the formation of bassanite and/or anhydrite, and their accelerated transformation into gypsum after several low salinity water injection cycles. In our case, a single re-hydration cycle (at 100% RH) was not enough to achieve a perfectly oriented gypsum crystal. However, we demonstrate that the epitaxial re-growth of gypsum at a relatively fast rate after bassanite dissolution on oriented domains by a template effect is possible in mild T pseudomorphs.

4. CONCLUSION

Overall, our results show that the dehydration of gypsum to form bassanite and/or anhydrite, whether soluble or insoluble, is crystallographically controlled. However, the micro-textural variations resulting from this phase transformation depend on three different variables: temperature, $p\text{H}_2\text{O}$ and crystal size.

In the case of the thermal dehydration of millimetric gypsum single crystals, different textural features were observed. On the surface, the intersection of three different sets of micro-fractures resulted in the formation of hourglass-shaped cracks. These cracks, here called Type I, II and III, aligned parallel to the direction of the three main periodic bond chains (PBCs; [101], [100] and [001] respectively, according to the $I2/a$ space group), as observed along [010]. Most notably, bassanite/anhydrite microneedles were observed arranging in “chevron” or “fishbone” patterns, with their long axis oriented at an angle of $\sim 35\text{--}45^\circ$ with respect to the [101] direction. This regular spatial distribution of the newly formed hemihydrate/anhydrite fibers should display a certain degree of co-orientation. However, 2D-XRD analyses demonstrated that no orientation relationship existed between the parent gypsum and the pseudomorph phase(s), regardless the calcination temperature. Further micro-textural analysis showed random nucleation of hemihydrate nanoparticles several layers beneath the outermost (010) surface. Our hypothesis is that water vapor release is hindered in zones near the core of the crystals, thus a $p\text{H}_2\text{O}$ building-up is favored, allowing for the secondary nucleation of non-oriented bassanite nano-granular crystals. The two different pathways leading to the formation of hemihydrate/anhydrite contribute to the overall disorientation observed by 2D-XRD.

However, gypsum dehydration re-analysis by the *in situ* TEM decomposition of micrometric crystals showed that this transformation is perfectly topotactic, as demonstrated by the sequential SAED patterns obtained following phase transformation. Both parent gypsum and the resulting insoluble anhydrite pseudomorph diffracted as single crystals, and the $[010]_G/[010]_A$ and $[101]_G/[001]_A$

reactant/product orientation relationships were established. Analogously, the dehydration of bassanite to form insoluble anhydrite is also a topotactic process, evidenced by the $[010]_B//[010]_A$ and $[001]_B//[001]_A$ orientation relationships.

The re-hydration of millimetric gypsum pseudomorphs is affected by the presence (or absence) of untransformed gypsum. When calcination is incomplete, untransformed gypsum domains could serve as a template allowing the epitaxial growth of gypsum after the dissolution of bassanite/anhydrite, partially preserving the orientation of the original parent gypsum. However, when calcination is complete, the re-hydration by dissolution-precipitation results in a gypsum crystal where new gypsum domains form after random non-epitaxial nucleation.

CHAPTER 3. NON-CLASSICAL CRYSTALLIZATION OF GYPSUM (PART I): THE EFFECT OF CALCEIN ON THE NUCLEATION AND GROWTH OF GYPSUM

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 - 2.2. *General Characterization of Solids*
 - 2.3. *High Resolution Synchrotron X-Ray Diffraction Analyses*
 - 2.4. *Titration Experiments*
 - 2.5 *In situ Atomic Force Microscopy Analyses*
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 - 3.1. *Growth of Fluorescent Gypsum*
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 - 3.3. *Modulating Phase Selectivity in the $\text{CaSO}_4\text{-H}_2\text{O}$ System*
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The work presented in this Chapter corresponds to the results of a journal paper pending publication in Small (Burgos-Ruiz, M., Ilett, M., Roncal-Herrero, T., Elert, K., Rubio-Domene, R., Ruiz-Agudo, E., & Rodriguez-Navarro, C. (2024). Bio-Inspired Fluorescent Calcium Sulfate for the Conservation of Gypsum Plasterwork. Small, Accepted).

1. INTRODUCTION

Being an important branch of materials science and solid-state chemistry, crystal engineering stands out as a versatile discipline that offers innovative solutions for multitude of modern-day problems through the design and manipulation of crystal structures to produce materials with tailored advanced functionalities, ranging, for example, from biomedical and drug-delivery applications to the development of highly efficient semi-conductors, as well as nano-electronic and optical devices (Shin *et al.*, 2003; Fratzl, 2007; Yang *et al.*, 2018; Parker and Townley, 2007). In this context, biomimicry has drawn the attention of the scientific community over the last two decades as a powerful tool for replicating the functionalities of materials produced by living organisms and/or designing complex advanced materials (Deng *et al.*, 2022; Wegst *et al.*, 2017).

While the synthesis of biomaterials presents significant challenges, researchers have made remarkable progress by employing biomimetic and bio-inspired strategies, including the use of organic monomeric and/or polymeric species to artificially reproduce the effect of proteins and polysaccharides involved in natural biomineralization processes (*e.g.*, Ruiz-Agudo *et al.*, 2017; Addadi *et al.*, 1990; Weiner and Dove, 2003; Pokroy *et al.*, 2006; Weber and Pokroy, 2015). An illustrative example of such progress is the work of Cölfen *et al.*, who extensively investigated the impact of organic templates and additives on the crystallization of calcium carbonate (CaCO_3), among other phases (Nassif *et al.*, 2005; Gehrke *et al.*, 2005; Sedláč *et al.*, 1998; Yu *et al.*, 2002). They successfully developed mesoscale methodologies for the fabrication of complex biomimetic 3D superstructures, such as synthetic nacre and vaterite mesocrystals showing enhanced stability (Mao *et al.*, 2016; Xu *et al.*, 2006). However, these strategies have not been investigated in the case of calcium sulfates ($\text{CaSO}_4 \cdot n\text{H}_2\text{O}$). Although they are not the most prevalent biominerals in nature, bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) has been described as the main mineral phase in the statoliths of diverse Cubozoan and Sciphozoan medusae, serving as gravity and inertia sensors (Tiemann *et al.*, 2006; Becker *et al.*, 2005; Boßelmann *et al.*, 2007). Most notably, gypsum

($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) has been also found to be part of the impact surface in the raptorial appendages of some species of stomatopod crustaceans of the *Odontodactylus scyllarus* type (better known as "mantis shrimps"), which they use as powerful hammers propelled at extreme speeds of about 23 m s^{-1} to break mollusk shells (Amini *et al.*, 2014).

Furthermore, there is ample evidence proving that biomimetic approaches have been employed since ancient times for lime-based materials, whether fortuitously or intentionally, to elaborate durable cements, plasters and mortars by implementing natural organic additives, such as oils, animal glue or plant extracts, providing improved properties (e.g., hydro-repellency or greater mechanical strength) (Rodríguez-Navarro *et al.*, 2017 and 2023; Artioli *et al.*, 2019). In this context, gypsum-derived materials have also played a pivotal role in the evolution of architecture. Being processed through pyrotechnology since the Neolithic (12,000 – 2,000 B.C.), and alongside lime, gypsum has been employed as one of the most important hydraulic binders by subsequent civilizations, such as the Ancient Egypt (3,100 – 30 B.C.), Greece (800 – 146 B.C.), and Rome (753 B.C. – 476 A.D.) (Ragai, 1988; Regourd *et al.*, 1988; Bel-Anzué and Elert, 2021; Elsen, 2006). However, the most notable artistic expression in the use of gypsum was reached during the Islamic Golden Age (7th – 13th century A.D.). Since then, the Alhambra of Granada has remained the apex of this architectural style (Figure 1.9) (Stewart and Moore, 1982; Luxán *et al.*, 1995; Rubio-Domene, 2010; Bel-Anzué *et al.*, 2017).

Despite its widespread use and historic importance, gypsum has limited wet-mechanical strength and relatively high solubility, making it prone to deterioration when exposed to humid environments and/or to severe climate changes (e.g., Charola *et al.*, 2006; Grossi *et al.*, 2007; Palha *et al.*, 2012; Jroundi *et al.*, 2014; Molina *et al.*, 2017; Jiang *et al.*, 2021; Xu *et al.*, 2022). Due to these handicaps, numerous original architectural elements and ornamental plasterworks from monumental sites suffer from decay (Figure 1.1). For this reason, several conservation procedures have been recently developed and implemented. A relevant example is the product designed and patented by Rubio-Domene (*i.e.*,

Mortero Alhambra®; Rubio-Domene, 2008 and 2010), where a fluorescent copolymer is mixed with bassanite, quicklime or calcium carbonate powder in order to obtain luminescent conservation gypsum plasters or lime mortars and stuccoes, allowing to identify and locate recent conservation interventions under UV light. Despite the advances in the technology for the elaboration of replicas and material replacement, the use of consolidants is necessary in many conservation interventions in order to improve the mechanical cohesion of the weathered substrate and preserve original artwork. However, in the specific case of gypsum plasterwork, research regarding suitable consolidants is very limited (Jroundi *et al.*, 2014).

In this work we exploit the versatility of bio-inspired processes for the development of fluorescent gypsum crystals (Kahr and Shtukenberg, 2016; Magnabosco *et al.*, 2018). We investigated the effect of the occlusion of organic (macro)molecules during the crystallization of gypsum. In particular, we selected calcein (*i.e.*, a xanthene fluorescent chelating agent with specific affinity for divalent cations) to study its effect on the morphology, chemical and optical properties of gypsum crystals from both fundamental and applied perspectives. To this end, we first determined the role of this organic additive during the homogeneous (pre)nucleation of calcium sulfate from solution and the subsequent crystal growth processes. These results allowed us to describe the interaction mechanism between calcein and the structural growing units involved in the formation of gypsum, which led to important changes in the final crystal habit and physicochemical properties.

These fundamental results provide the basis for the development of novel approaches applied to gypsum-based materials to modify the physicochemical properties of calcium sulfate crystals, as will be further discussed in Chapter 4.

2. EXPERIMENTAL SECTION

2.1. Screening of Calcein Concentration for Morphology Control

Fluorescent gypsum crystals were obtained by mixing equimolar aqueous solutions of CaCl_2 and $(\text{NH}_4)_2\text{SO}_4$ up to a final Ca^{2+} and SO_4^{2-} concentration of 0.1 M, in the presence of increasing concentrations of calcein (*i.e.*, 0, 50, 150 and 250 μM) on sterile polystyrene crystallization microplates (6×4 wells, 3300 μL per well). Precipitates were set to crystallize for a total of six days under lab conditions (Figure 3.1a). Note that concentrations greater than 150 μM resulted in scarce gypsum precipitation after extremely long induction times (weeks). This is why here we consistently report the results for calcein concentrations up to 150 μM . Finally, precipitates were collected, dispersed in 96° ethanol and sonicated for 2 min in order to eliminate any interference of residual calcein adsorbed onto crystal surfaces.

2.2. General Characterization of Solids

Optical microscopy photomicrographs of gypsum crystals (*i.e.*, obtained in the presence of 0, 50 and 150 μM calcein) were acquired using a Leica DVM2000 digital microscope for size and morphology determination (Figure 3.1b). Samples were also irradiated with UV light ($\lambda = 365 \text{ nm}$) during optical microscopy observations.

The obtained solids were characterized by means of standard X-ray diffraction (XRD) and Fourier Transform Infrared spectroscopy (FTIR), respectively using a Panalytical X'Pert PRO diffractometer (Cu-K α radiation, $\lambda = 1.5405 \text{ \AA}$, voltage 45 kV, current 40 mA, and scanning angle ($^\circ 2\theta$) 3-70°, steps of 0.001 $^\circ 2\theta$ and goniometer speed of 0.01 $^\circ 2\theta \text{ s}^{-1}$) and a JASCO FT/IR 6600 in ATR mode (4000-400 cm^{-1} , resolution of 2 cm^{-1}) (Figure 3.1c).

In order to determine the content of intracrystalline calcein, 20 mg of dried fluorescent gypsum samples were dissolved in hydrochloric acid (2 mL, 3 M). The resulting solutions were then analyzed using a Thermo Scientific GENESYS 50 UV-Vis spectrophotometer. Calibration curves ($R^2 = 0.9999$) were obtained by measuring calcein solutions with known concentrations ranging from 1 to 25 μM using the previously mentioned hydrochloric acid buffer. The amount of intracrystalline calcein (*i.e.*, μmol calcein per mg of sample) was then calculated by the Beer-Lambert law using the maxima of absorbance at 445 nm (Figure A.1 and Table A.1).

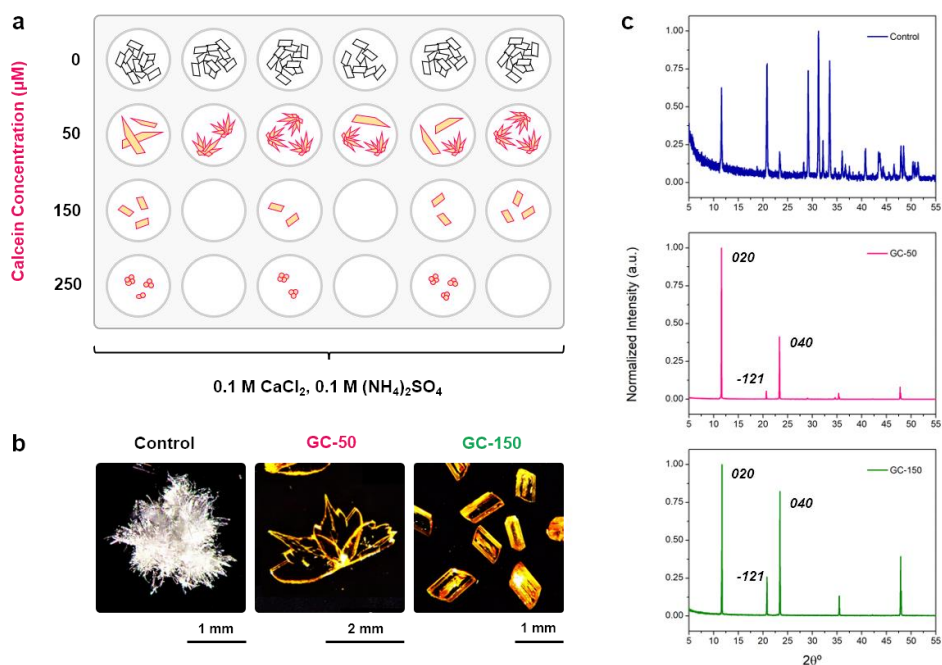


Figure 3.1. Simplified screening schematic of calcein concentration for morphology control.

2.3. High Resolution Synchrotron X-Ray Diffraction Analyses

HR-XRD analyses of fluorescent gypsum crystal samples were performed at the CRISTAL beamline of the SOLEIL Synchrotron (Paris, France), using a 2-circle diffractometer. For these measurements the selected wavelength was $\lambda = 0.67157 \text{ \AA}$ (18 keV). The beam line is equipped with a double-crystal 21-Si (111) monochromator, along with nine position-sensitive Dectris Mythen II detectors, positioned on a cylinder with a radius of 720 mm, providing a 55° 2θ coverage with small gaps of 0.5° 2θ . Borosilicate glass capillaries of 0.7 mm in diameter were loaded with powder samples and rotated during data collection to improve diffracting particle statistics. The data acquisition time was 3 min per pattern, with two iteration per measurement to obtain a good signal-to-noise ratio over the 0° to 55° 2θ angular range. To calibrate the equipment and reduce possible shifts during experimental analysis, LaB_6 standard (NIST-SRM660, cubic, space group $Pm\bar{3}m$) was used to acquire an instrumental resolution file. Under these data acquisition conditions, the angular resolution ranged from 0.02° to 0.04° (*i.e.*, full width at half maximum, β) for the whole 2θ range. The Rietveld refinement method was used to extract lattice parameters of gypsum, matching the experimental diffraction peaks with those calculated by Henry *et al.* (2009, space group $I2/c$), using FullProf Suite (v.5.10) and the EdPCR (v.2.0) software packages. Optical quality geologic gypsum (Naica, Chihuahua, Mexico) was used as standard to compare the XRD data from the synthesized fluorescent gypsum crystals.

To investigate the microstructural variations due to organic (macro)molecule incorporation in the structure of gypsum, the Thompson-Cox-Hastings pseudo-Voigt function with axial divergence asymmetry correction was used to fit the profile of the experimental diffraction patterns. In order to reduce the statistical discrepancy between experimental and fitting values, the profiles were refined until the minimum possible values of R_{wp} and χ^2 were reached. For our experiments, the obtained R_{wp} was < 8.5 , and the minimum achieved χ^2 values ranged from ~ 100 to ~ 130 . Note that, when refining datasets of both high resolution and number of counts, it is common to obtain large χ^2 values, even though the model obtained from that data is of high quality (Toby, 2006).

Microstrain fluctuations (η) and crystallite size (D_{hkl}) were calculated using the Williamson-Hall method, using six-order $h00$, $0k0$ and $00l$ Bragg reflections obtained from the Rietveld refinement profiles, by plotting $\beta \cos\theta$ vs $4 \sin\theta$ and adjusting the results to a linear fit as indicated below (Equation 3.1):

$$\beta \cos\theta = \frac{k\lambda}{D} + 4\eta \sin\theta \quad (3.1)$$

Where β is the experimental full width at half maximum peak, k is the shape factor (0.94), and λ is the synchrotron beam wavelength (0.067157 nm). For strain and crystallite size calculations, angular units were transformed into radian.

2.4. Titration Experiments

The effect of calcein on the nucleation and homogeneous precipitation mechanism of $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ was studied by means of potentiometric titration using a Methrom Titrando 905, equipped with an 856 Conductivity module and an 867 pH module. Homogeneous precipitation experiments were performed at 25 °C by the continuous addition of a 0.3 M $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ solution (0.24 mL min⁻¹ addition rate) into 100 mL of a 0.1 M $(\text{NH}_4)_2\text{SO}_4$ solution in the presence of increasing concentrations of calcein (*i.e.*, 0, 50, 150 and 250 μM). Values of Ca^{2+} potential and transmittance were continuously recorded using a Methrom Ca^{2+} selective polymer membrane electrode and a Methrom Optrode optical sensor ($\lambda = 610$ nm), respectively.

In order to obtain calibration curves for Ca^{2+} activity coefficients, blank experiments (*i.e.*, in the absence of SO_4^{2-} and calcein) were performed by adding a 0.3 M $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ solution (0.24 mL min⁻¹ addition rate) into 100 mL Milli-Q grade water. Ionic strength was previously adjusted by adding NaCl (*i.e.*, 0.25 M, calculated using PHREEQC as the equivalent ionic strength of a 0.1 M solution of $(\text{NH}_4)_2\text{SO}_4$).

2.5. *In Situ Atomic Force Microscopy (AFM) Analyses*

Growth experiments were carried out using a fluid cell coupled to a Bruker MultiMode 8-HR AFM powered by a Bruker NanoScope 6 AFM controller, working in contact mode at room temperature. Deflection images of the {010} surfaces of freshly cleaved gypsum crystals (from Naica, Chihuahua, Mexico) were collected using Si₃N₄ tips (SNL-10, Bruker) with nominal spring constants of 0.24 and 0.35 N m⁻¹. For these studies, growth solutions supersaturated with respect to gypsum were prepared by mixing equimolar CaCl₂ and (NH₄)₂SO₄ solutions up to a final Ca²⁺ and SO₄²⁻ concentration of 50 mM (saturation index, *SI* = 0.50 with respect to gypsum, calculated using the PHREEQC software) and injected using a syringe at a flow rate of ~0.13 mL min⁻¹. Growth solutions included different concentrations of calcein (*i.e.*, 0, 2.5 and 25 µM). 2D and 3D images and videos were produced using the Bruker NanoScope Analysis v1.40r1 software.

3. RESULTS AND DISCUSSION

3.1. Growth of Fluorescent Gypsum

Significant variations in size and morphology of gypsum crystals were detected with increasing additive concentrations when directly precipitated in aqueous solution in the presence of calcein, which rendered them fluorescence, as shown by optical microscopy observations with UV light illumination (Figure 3.2a-c). In the absence of calcein, numerous micrometer-sized gypsum crystals formed in less than 30 min after mixing the solutions. These crystals showed spherulitic fibro-radiated habits and multiple misalignments along the *c*-axis direction (Figure 3.2a). Conversely, in the presence of 50 μM calcein (GC-50), flower-like, thin gypsum twinned micro-crystals with "spearhead" or "swallowtail" shapes (*i.e.*, twin law $\bar{1}01$), Cotellucci *et al.*, 2023), measuring ~ 1.5 - 2.2 μm in size were observed. These crystals, however, were obtained ~ 8 h after the solutions were mixed and exhibited well-developed (010) faces (Figure 3.2b). In contrast, 150 μM calcein (GC-150) led to idiomorphic gypsum crystals with sizes of ~ 0.8 - 1.1 μm and no apparent twinning (Figure 3.2c). These crystals were obtained ~ 72 h after the mixing process. These results evidence that calcein, even when dosed in very small amounts, has a marked effect as a crystallization inhibitor, significantly delaying crystal precipitation. In addition, calcein strongly modified the morphology and texture of gypsum precipitates, which suggest that it also acted as a crystal growth modifier. Importantly, the strong and homogeneous fluorescence of gypsum crystals formed in the presence of calcein (Figures 3.2a-b) points to occlusion of this additive in the gypsum crystal structure.

Standard powder X-ray diffraction (XRD) analysis provided supporting evidence for these macroscopic observations (Figure 3.1c). Crystals precipitated without calcein exhibited intense $\bar{1}21$, 121 , $\bar{1}41$, and 022 Bragg peaks, corresponding to well-developed ($0kl$) and (hkl) faces. In contrast, GC-50 crystals exhibited intense 020 and 040 peaks, corresponding to well-formed ($0k0$) faces, and low intensity $\bar{1}21$, 200 , and 062 reflections that suggested poorly developed (hkl) faces. GC-150

crystals displayed intense $0k0$ reflections and moderately intense $\bar{1}21$, 200 , and 062 Bragg peaks, confirming the tendency of gypsum crystals to adopt the equilibrium morphology under these experimental conditions (Massaro *et al.*, 2010). Inoue and Hirasawa (2013) demonstrated the variability of gypsum morphology following precipitation in the absence and presence of several additives, including poly-(acrylic acid) and sodium carboxymethylcellulose, by analyzing the relative intensities of the main diffraction peaks of such crystals. They concluded that crystal growth was suppressed along the $[001]$ direction by organic additives having carboxyl groups, thus leading to a substantial change in morphology and a decrease in the aspect ratio from needle-like, to plate-like and granular gypsum microcrystals, in accordance with the increase in the relative intensity of the 021 , 041 and $\bar{2}21$ Bragg peaks.

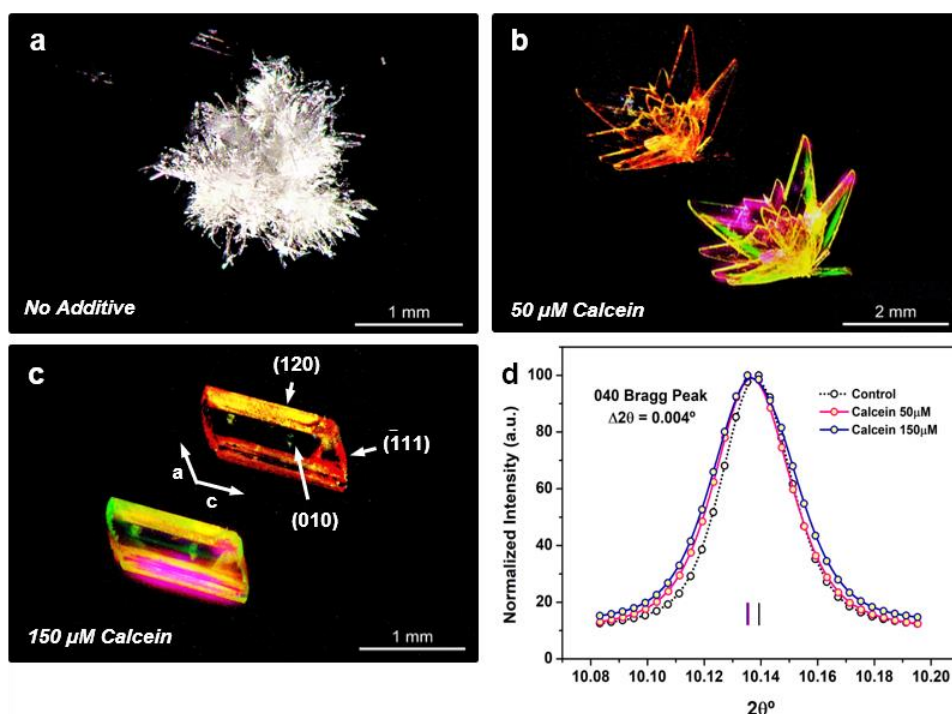


Figure 3.2. Optical microscopy images under UV light (a, b and c) and HR-XRD patterns (d) of gypsum microcrystals grown in the presence of different calcein concentrations. Vertical color bars in panel d) indicate the position of the point of maximum intensity corresponding to the 040 Bragg peak of each sample (black line, geologic control; red line, GC-50; blue line, GC-150).

Synchrotron high-resolution powder XRD analysis (HR-XRD) revealed a left shift in the position of the $0k0$ Bragg peaks of gypsum samples containing calcein (*i.e.*, increase in d_{0k0} -spacing), as compared to a calcein-free reference geologic gypsum (GG) (Figure 3.2d). The calculated lattice strain fluctuations ($\Delta b/b$) were 3.841×10^{-4} and 4.078×10^{-4} for GC-50 and GC-150 gypsum samples, respectively. This indicates that intracrystalline occlusion of calcein, which was evidenced by fluorescent light microscopy, resulted in a slight structural distortion that only affected the dimension of the b lattice parameter (no peak shift was observed in the case of $h00$, $h0l$, or $00l$ reflections, evidencing no lattice strain associated with the a and c lattice parameters). It has been widely reported that incorporation of macromolecules (*e.g.*, proteins) in biominerals (*e.g.*, calcite and aragonite in mollusk shells) and their biomimetics typically results in anisotropic lattice distortion disclosed by Bragg peak shifts in HR-XRD patterns (*e.g.*, Deng *et al.*, 2022; Pokroy *et al.*, 2006; Weber and Pokroy, 2015; Rodriguez-Navarro *et al.*, 2023; Kim *et al.*, 2016, 2019; Lang *et al.*, 2020). It has been reported that incorporation of large macromolecules, micelles and/or nanoparticles might not result in lattice strain (Magnabosco *et al.*, 2018; Lang *et al.*, 2020). In the case of calcein, possibly due to its large molecular size and/or steric constraints, occlusion does not result in large lattice distortion manifested by marked peak shifts, as also observed in the case of calcein incorporation within calcite and aragonite (Magnabosco *et al.*, 2018). For lattice modification to occur, the guest molecules have to replace specific ions (*i.e.*, as a "solute") in a homogeneous and systematic way as to achieve long range order (Pokroy *et al.*, 2010). In this case, considering that calcein interacts with Ca^{2+} through strong electrostatic bonds, the slight distortion of the b lattice parameter is most likely due to the adsorption and incorporation of calcein on the $\{010\}$ planes (Rae Cho *et al.*, 2016), and/or by non-homogeneous replacement of water molecules and/or sulfate groups by calcein during crystallization.

Furthermore, local strain fields around the occluded molecules can cause peak broadening and asymmetry (Kim *et al.*, 2011). Here, we observed these effects (Figure 3.2d) leading to a reduction in crystallite size and an increase in microstrain fluctuations (*i.e.*, D_{020} , D_{002} , D_{200} and η , respectively, as calculated using the Williamson-Hall method; Figure A.2), which provides further evidence of the

intracrystalline occlusion of calcein. The calculated lattice strain, as well as the crystallite size and average microstrain fluctuation values for GC-50 and GC-150 as compared to GG are presented in Table 3.1.

Table 3.1. Summary of calculated lattice parameter b , lattice distortion, crystallite size and microstrain fluctuations for GC-50 and GC-150 as compared to geologic gypsum (GG).

	b	$\Delta b/b$	D_{020} (nm)	D_{002} (nm)	D_{200} (nm)	η
GG	15.20441 ± 0.00013	-	166.17 ± 0.04	110.24 ± 1.71	99.28 ± 0.78	0.00120 ± 0.00010
GC-50	15.21025 ± 0.00011	3.841×10^{-4}	151.29 ± 0.54	97.86 ± 0.24	87.57 ± 0.57	0.00125 ± 0.00004
GC-150	15.21061 ± 0.00012	4.078×10^{-4}	146.41 ± 0.39	88.11 ± 0.43	78.11 ± 0.68	0.00148 ± 0.00005

UV-Vis spectrophotometry analyses of bleached (to eliminate any adsorbed additive) and then dissolved fluorescent crystals enabled the determination of the intracrystalline calcein content in the different gypsum samples (see Experimental Section; Figure A.1 and Table A.1). For GC-50 and GC-150, the intracrystalline additive net content was $5.148 \cdot 10^{-4} \mu\text{mol mg}^{-1}$ and $8.997 \cdot 10^{-4} \mu\text{mol mg}^{-1}$, respectively. Additionally, powders precipitated with $250 \mu\text{M}$ calcein exhibited an additive net content of $1.527 \cdot 10^{-3} \mu\text{mol mg}^{-1}$. These results demonstrate significant and dose-dependent occlusion of calcein within gypsum crystals, thus explaining their UV fluorescence and the observed structural effects (Figure 3.2). They are also relevant for potential biomedical applications, including controlled drug-delivery, as they demonstrate that occlusion of organic molecules of small-to-medium sizes is feasible in a biocompatible mineral phase like gypsum (Ning *et al.*, 2019; Izquierdo-Barba *et al.*, 2009).

3.2. Non-Classical Crystallization of Calcein-Loaded Gypsum

From a fundamental *non-classical* crystallization perspective, it is widely acknowledged that additives (whether organic or inorganic) can significantly impact the different pre- and post-nucleation events that take place during the precipitation of pure mineral phases (*e.g.*, Rodriguez-Navarro *et al.*, 2017, 2020; Gebauer *et al.*, 2008; Pouget *et al.*, 2009; Habraken *et al.*, 2013). This is a promising strategy for

the design of materials with tailored morphologies, physical-chemical properties and, therefore, technical applications. In line with this, and because we aimed to develop and test a novel bio-inspired functional (*i.e.*, fluorescent) and fully compatible consolidant for the conservation of deteriorated historical gypsum plasterwork, we first assessed the effect of calcein during the early stages of gypsum crystallization (*i.e.*, pre- and post-nucleation stages).

Potentiometric titration was employed to study the evolution of $[\text{Ca}^{2+}]_{\text{free}}$ during the pre-nucleation, nucleation and post-nucleation stages of calcium sulfate in both the absence and presence of the fluorescent additive (Figure 3.3). In order to provide a precise depiction of the interaction mechanism between calcein and Ca^{2+} , the titration curves were segmented into three sections: (I) pre-nucleation stage, (II) nucleation stage, and (III) post-nucleation stage (*i.e.*, particle growth).

During the pre-nucleation stage, the measured $[\text{Ca}^{2+}]_{\text{free}}$ consistently remained lower than the total dosed Ca^{2+} . According to Gebauer *et al.* (2009, 2022), this phenomenon indicates the stabilization of pre-nucleation clusters (PNCs), which are described as polynuclear associates that typically precede the formation of more complex condensed phases, such as liquid precursors and/or amorphous solids. The concentration-dependent stabilization of PNCs by calcein was demonstrated by the increase in $[\text{Ca}^{2+}]_{\text{bound}}$, as shown by a flattening of the slope of the $[\text{Ca}^{2+}]_{\text{free}}$ vs time curves during the pre-nucleation stage as compared with the control curve. This effect of PNC stabilization has been extensively documented in other systems (*e.g.*, $\text{CaCO}_3\text{-H}_2\text{O}$) for other carboxylate-rich organic additives, such as poly(acrylic acid) (PAA), poly(aspartic acid) (PASP), citric acid and several polysaccharides (Bewernitz *et al.*, 2012; Picker *et al.*, 2012; Rao *et al.*, 2014; Wolf *et al.*, 2011), but its implications in the $\text{CaSO}_4\text{-H}_2\text{O}$ system are relatively unexplored. As we moved along the reaction coordinate, $[\text{Ca}^{2+}]_{\text{free}}$ exhibited a linear increase as Ca^{2+} was dosed until a point where the slope decreased, followed by a sudden drop in $[\text{Ca}^{2+}]_{\text{free}}$, indicating the nucleation of the first solid particles. Calcein, as observed in the initial bulk crystallization experiments, inhibited crystallization, even at exceedingly low additive concentrations. This inhibitory effect was evidenced in the titration experiments by a significant delay in the nucleation of the first $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$

particles. In the presence of 50 μM calcein, the induction time for nucleation increased 2.7 times as compared to the control. The impact of calcein became more apparent as the additive concentration increased to 150 μM , where complete inhibition of nucleation was observed. Even after more than 10 h, no visible precipitates were observed. As previously reported by Nicoleau *et al.* (2019), organic additives (e.g., PAA) inhibit the nucleation of gypsum by hindering collisions between PNCs, which in turn decreases their attachment probability and increases their kinetic persistence in solution.

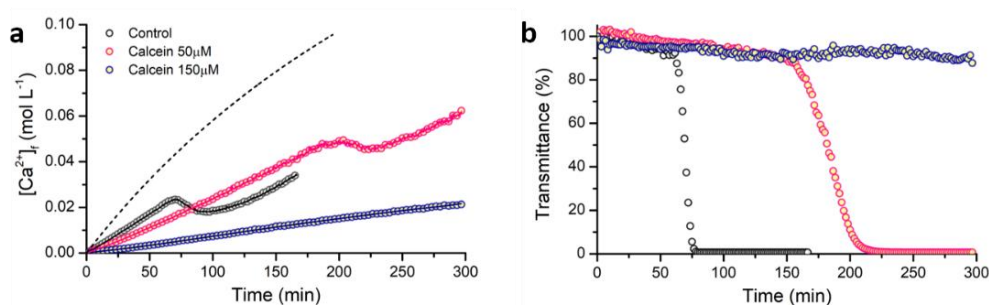


Figure 3.3. Time development of the free Ca^{2+} concentration (a) and transmittance (b) during gypsum precipitation experiments in the absence (black dots, control) and presence of calcein (red dots, 50 μM ; blue dots, 150 μM), in comparison with the total dosed Ca^{2+} concentration (dashed line).

Considering the chemical structure of calcein, which exhibits a strong affinity for divalent cations and behaves as a bidentate chelating agent similar to EDTA (with four carboxylic groups deprotonated at $\text{pH} < 6$; $\text{pK}_{\text{a}1} = 2.1$, $\text{pK}_{\text{a}2} = 2.9$, $\text{pK}_{\text{a}3} = 4.4$, $\text{pK}_{\text{a}4} = 5.5$; and two tertiary amine groups), it is reasonable to infer that the complexation of Ca^{2+} may potentially play a role in the nucleation and growth mechanisms. The complexation of Ca^{2+} by calcein is demonstrated by the delay in the initial increase of measured $[\text{Ca}^{2+}]_{\text{free}}$ at the beginning of the titration experiments (Figure A.3). Specifically, $[\text{Ca}^{2+}]_{\text{free}}$ starts increasing only once the complexation capacity of the additive is reached. In titrations using 50 μM calcein, the complexation delay with respect to the control curve (*i.e.*, elapsed time from probe stabilization to $[\text{Ca}^{2+}]_{\text{free}}$ initial increase) was ~ 0.8 min, while in the presence of 150 μM calcein, this delay was extended to ~ 2.2 min, indicating a concentration-

dependent effect on the initial complexation process. Nevertheless, the observed inhibitory effect cannot be solely attributed to Ca-calcein complexation. This is so because the total molar concentration of the additive is orders of magnitude lower than the total added Ca^{2+} during the titration experiments. Moreover, it is expected that most of the calcein would be coordinated to Ca^{2+} at the very beginning of the experiment (Duchstein *et al.*, 2022). Ultimately, the possible inhibitory effect of Ca^{2+} complexation can be disregarded at such low additive concentrations.

We also analyzed the events that occur near the nucleation onset by comparing the evolution of $[\text{Ca}^{2+}]_{\text{free}}$ with the corresponding transmittance measurements. In control runs, the transmittance suffers a sudden drop, which however, precedes (by *ca.* 15 min) the sudden decrease in measured $[\text{Ca}^{2+}]_{\text{free}}$, marking the nucleation and subsequent growth of the initial calcium sulfate particles. This decoupling between the drop in transmittance and the $[\text{Ca}^{2+}]_{\text{free}}$ decrease was more evident in calcein-including runs. In the presence of 50 μM calcein, the measured transmittance decreases gradually before reaching the nucleation onset marked by the drop in measured $[\text{Ca}^{2+}]_{\text{free}}$. This suggests that both in the control run and, specially, in the presence of calcein (and other polymeric species, such as PAA), the initial stage of nucleation occurs following a liquid-liquid phase separation, where a dense liquid phase (most likely made up of highly hydrated PNCs) separates from a less concentrated solution, as observed in other systems (Avaro *et al.*, 2020). However, this possibility must be carefully evaluated using more advanced techniques, such as SAXS and/or analytical ultracentrifugation. Finally, as discussed above, higher concentrations of calcein lead to complete nucleation inhibition, resulting in no discernible change in transmittance throughout the time course of these experiments.

In situ fluid-cell AFM observations conducted on gypsum {010} cleavage surfaces, both in the absence and presence of calcein, revealed a pronounced modification of anisotropic step propagation kinetics by this additive. Specifically, the introduction of calcein led to a discernible alteration in growth dynamics at the nanoscale. During control experiments conducted without the additive (Figure 3.4a), the rapid emergence of multiple steps aligned with the [101] and [001]

directions was observed, followed by their advancement and a swift step-bunching after approximately 16 s. This implies that growth by ion adsorption along the a - and c -axis directions was not impeded. Note that gypsum grows extremely fast, even at low saturation index values (*i.e.*, $SI = \log(IAP/K_{sp})$, being IAP the ion activity product and K_{sp} the solubility product of the relevant phase; see Experimental Section). Although we decided to increase scan rate by compromising image quality, in the absence of calcein growth rates could not be accurately measured. In the presence of 2.5 μM calcein, the growth rate (*i.e.*, velocity of step advancement) along the c -axis direction sharply decreased, and was almost completely inhibited along the a -axis direction (Figure 3.4b). This also resulted in a reduction of the step-bunching effect. Increasing the concentration of calcein by an order of magnitude (*i.e.*, 25 μM) resulted in much slower growth kinetics than in the previous cases (Figure 3.4c).

Considering the morphological evolution of gypsum crystals obtained at different calcein concentrations (*i.e.*, spherulitic $\rightarrow$ arrowhead $\rightarrow$ idiomorphic), our hypothesis is that the adsorption of calcein onto each dominant face of the gypsum structure (*i.e.*, $\{010\}$, $\{120\}$, and $\{\bar{1}11\}$; Figure 3.2) results in the inhibition of crystal growth, regardless of their relative stability (*i.e.*, interfacial free energy). Note that, for example, if poisoning by the organic additive occurs on the $\{010\}$ surfaces, growth by ion addition in the b -axis direction would be impeded, but it is still viable along the a - and c -axis directions, resulting in large area (010) faces. Increasing calcein concentration leads to a more exaggerated situation of the same inhibitory effect, so that gypsum crystals showing equilibrium morphologies can be obtained even under high supersaturation conditions.

These observations regarding macroscopic morphology correlate well with AFM measurements, and are in accordance with the recorded conventional XRD patterns of gypsum crystals grown both in the absence and presence of calcein dosed at different concentrations. They are also congruent with the HR-XRD results. The observed slight lattice distortion along the b -axis direction due to intracrystalline calcein is consistent with surface adsorption of calcein molecules on $\{010\}$ faces followed by their occlusion by advancing growth steps (Rae Cho *et*

al., 2016). Indeed, adsorption followed by occlusion seems to be the predominant interaction mechanism between calcein and the growing gypsum, ultimately leading to morphology variations.

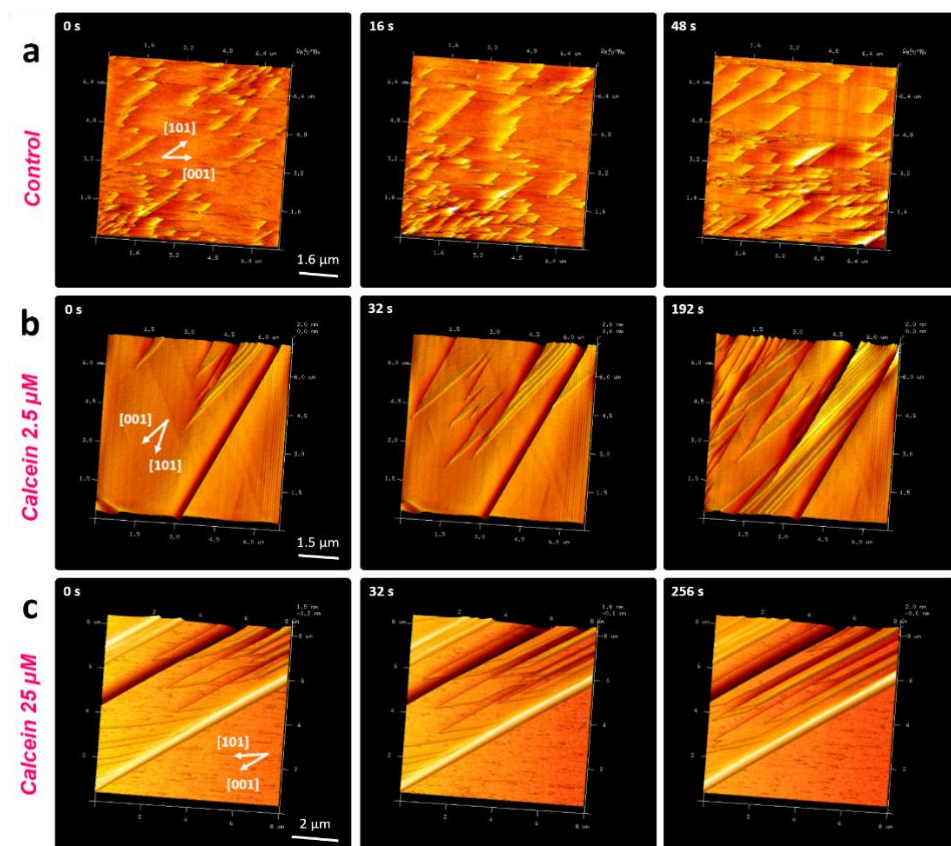


Figure 3.4. Time sequence of AFM deflection images of {010} cleavage surfaces of gypsum crystals obtained following growth in the absence (a) and presence of 2.5 and 25 μM calcein (b and c). Growth directions [001] and [101] are indicated by arrows.

Understanding how calcein modifies the crystallization pathway of gypsum from solution and its physicochemical properties was crucial for the design of novel $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ nano-consolidants. It is important to mention that bassanite is the direct precursor of gypsum plasters, which are widely used as construction and ornamental materials. For this reason and because we also aimed to produce novel consolidants for the conservation of plasterworks, we synthesized fluorescent

bassanite nanoparticles (NB-C; see Chapter 4) and evaluated the behavior of calcein during their transformation into gypsum cement.

3.3. Modulating Phase Selectivity in the $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ System

With the goal of achieving phase-pure bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) production, we investigated the anti-solvent effect of ethanol on the homogeneous precipitation of $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ phases. It is worth noting that diverse strategies to induce bassanite formation have been described, involving precipitation under conditions of high ionic strength, temperature and/or the presence of organic additives (Reigl *et al.*, 2023). While these methodologies generally share a common principle (*i.e.*, reducing water activity and inducing supersaturation by modifying the solvation sphere enveloping ions to lower the interfacial energy barrier required for the liquid-solid phase transition) our selection of the anti-solvent approach was motivated by its ability to circumvent the interference of excessive secondary electrolytes or the need for using additives other than calcein.

To accomplish this, we conducted a series of homogeneous precipitation experiments, involving the dropwise addition of a 0.3 M $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ hydroalcoholic solution, preloaded with 50 μM calcein, into a 0.1 M $(\text{NH}_4)_2\text{SO}_4$ hydroalcoholic solution (Figure 3.5a-b). Various ethanol-to-water ratios were employed (*i.e.*, 50%, 80%, and 90% vol./vol. EtOH/ H_2O). Note that in 0.1 M hydroalcoholic solutions, and under standard conditions, the solubility limit for $(\text{NH}_4)_2\text{SO}_4$ is approached at ~90% vol./vol. ethanol-to-water ratio. It is important to highlight that, despite the miscibility of water and ethanol as solvents, calcein remains insoluble in ethanol. This aspect is relevant for the design of fluorescent nano-bassanite consolidants, particularly with regard to their intended dispersion in absolute ethanol for practical conservation applications. Note also that ethanol enables the formation of stable nano-bassanite dispersions, and once applied to a substrate this solvent rapidly evaporates without leaving any residue. Ethanol also prevents the early hydration of (nano)bassanite, as could occur in an aqueous dispersion, thereby preventing pore-clogging during conservation applications (see Chapter 5).

Under the described experimental conditions, we observed that, independently of the ethanol-to-water ratio, a fluorescent solid phase precipitated instantaneously after the addition of each drop of the calcein-loaded CaCl_2 hydroalcoholic solution. Examination of the obtained solids *via* XRD and FTIR analysis (Figure 3.5c-d) unveiled that this hydroalcoholic precipitation route led to the co-precipitation of bassanite alongside gypsum. While gypsum dominated as the primary product at a 50% ethanol content, the proportion of precipitated bassanite increased with ethanol content exceeding 80%. This was shown by the increased intensity of the 110 and 114 Bragg reflections corresponding to bassanite, concomitant with a diminishing intensity of the 020 Bragg peaks corresponding to gypsum.

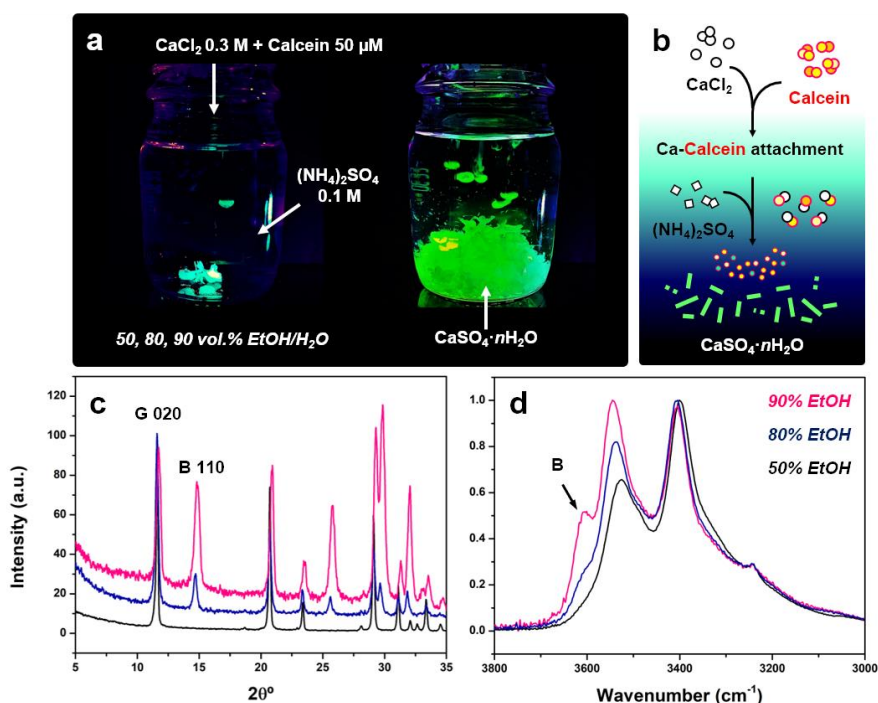


Figure 3.5. Phase selectivity in the $\text{CaSO}_4\text{-H}_2\text{O}$ system as a function of water activity in hydroalcoholic solutions (*i.e.*, from 50 to 90% EtOH/ H_2O).

Additionally, significant variations were evident in the FTIR spectra, specifically in the O-H stretching (ν_1 , H_2O) and bending (δ_1 , H_2O) vibration modes associated with structural water. A notable increase in intensity of the shoulder detected at 3604

cm^{-1} in the stretching region, corresponding to bassanite, was identified for solids obtained employing an ethanol content higher than 80%, congruent with the X-ray diffractograms.

These results served as the fundamentals to understand how phase selectivity can be controlled in the $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ system as a function of water availability. Furthermore, understanding how calcein modifies the crystallization pathway of gypsum from solution and its physicochemical properties was crucial for the design of novel $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ nano-consolidants. Note that bassanite is the direct precursor of gypsum plasters, which are widely used as construction and ornamental materials. For this reason and to fulfill one of the main objectives described for this thesis, we used this knowledge to design an alternative solvothermal synthesis procedure to produce phase-pure fluorescent bassanite nanoparticles for their later use as fully compatible consolidants for the specific case of gypsum plasterwork. Despite the fact that we could obtain nano-bassanite nanoparticles with strong fluorescence using this alcoholic route, the observation that gypsum co-precipitated along with nanobassanite even at high alcohol/water ratios prompted us to search for an alternative route for the precipitation of phase-pure nanobassanite that could be used as an effective consolidant for ancient gypsum plasterwork.

The synthesis protocol, the physicochemical properties and the application of the resulting nano-structured consolidants (including nanolimes and nano-bassanite) with and without different functionalities (*e.g.*, fluorescence) are further detailed in Chapters 4 and 5.

4. CONCLUSION

Our detailed study on the bio-inspired precipitation of calcium sulfate in the presence of calcein shows that this additive is incorporated (whether by adsorption and/or intracrystalline occlusion) into the structure of gypsum, as demonstrated by the HR-XRD, UV-Vis microscopy analyses. Crystal growth experiments showed that calcein had an important effect over the morphological and physical-chemical characteristics of gypsum.

Through coupled potentiometric and transmittance analyses during titration experiments, a non-classical multi-step crystallization mechanism was proposed for the case of gypsum (formed in the absence and presence of calcein). First, the stabilization of highly hydrated PNCs occurs in the presence of calcein (and probably other organic additives such as PAA and PASP). Then, as will be discussed later in Chapter 4, further interaction between pre-nucleation species leads to the formation of dense liquid precursors upon a liquid-liquid phase separation. Solidification of the more concentrated liquid fraction likely leads to the formation of amorphous solids (ACS), which in turn transform into crystalline gypsum.

Analogously, crystal growth was hindered by the adsorption of calcein, on all dominant faces of gypsum as observed by means of *in situ* AFM measurements. The variations of the growth rates are concomitant with the observed calcein concentration-dependent morphology changes.

Finally, focusing on the production of phase-pure bassanite, phase-selective procedures involving the direct precipitation of calcium sulfate from hydroalcoholic solutions at room T were investigated. However, gypsum was still the main precipitate.

These results were fundamental for the design of a solvo-thermal synthesis method for the production of phase-pure bassanite and fluorescent bassanite nanoparticles, intended for their application as consolidants for deteriorated gypsum plasters, as detailed in the next chapter.

CHAPTER 4. NON-CLASSICAL CRYSTALLIZATION OF GYPSUM (PART II): SYNTHESIS AND APPLICATION OF NANO-BASSANITE CONSOLIDANTS

1. *Abstract*
2. *Experimental Section*
 - 2.1. *Synthesis of Nano-Bassanite and Fluorescent Nano-Bassanite*
 - 2.2. *Preparation of Plaster of Paris (β -Hemihydrate) Control*
 - 2.3. *Characterization of Precursor and Product Phases*
 - 2.4. *TEM Analyses*
 - 2.5. *Measurement of the Hydration Kinetics of Nano-Bassanite*
 - 2.6. *Dissolution Resistance Tests*
 - 2.7. *Nanoindentation*
 - 2.8. *Consolidation Tests*
3. *Results and Discussion*
 - 3.1. *Characterization of Nano-Bassanite*
 - 3.2. *Hydration Kinetics of Nano-Bassanite*
 - 3.3. *Characterization of Fluorescent Nano-Bassanite*
 - 3.4. *The Hydration of Fluorescent Nano-Bassanite*
 - 3.5. *Weathering Resistance*
 - 3.6. *Mechanical Properties*
 - 3.7. *Consolidation of Gypsum Plaster using Fluorescent Nano-Bassanite*
4. *Conclusion*

The work presented in this Chapter correspond to a combination of results published in Chemical Communications (Burgos-Ruiz, M., Pelayo-Punzano, G., Ruiz-Agudo, E., Elert, K., & Rodriguez-Navarro, C. (2021). Synthesis of high surface area $\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$ nanorods using calcium ethoxide as precursor. Chemical Communications, 57(59), 7304-7307) and pending publication in Small (Burgos-Ruiz, M., Ilett, M., Roncal-Herrero, T., Elert, K., Rubio-Domene, R., Ruiz-Agudo, E., & Rodriguez-Navarro, C. (2024). Bio-Inspired Fluorescent Calcium Sulfate for the Conservation of Gypsum Plasterwork. Small, Accepted).

1. ABSTRACT

The effect of calcein on the crystallization of gypsum was studied in the previous chapter. In this regard, it is equally important to study the effect of this additive on the formation and hydration of bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$). The hydration of bassanite is the key reaction in the "gypsum cycle" that allows the setting and hardening of gypsum plaster; however, limited research has been done on the effect of organic additives during this process.

For this purpose, and using phase-selective strategies to modify the water activity, bassanite nanoparticles (NB) and fluorescent bassanite nanoparticles (NB-C) were synthesized by a solvo-thermal method for their direct application as consolidants for the conservation of gypsum plasters. The hydration kinetics of NB were studied and compared with those of a standard hemihydrate prepared by thermal decomposition of gypsum. In addition, detailed analyses of the hydration of these potential consolidants were performed in order to describe the mechanisms governing the transition from bassanite to gypsum. Using advanced microscopy techniques such as cryo-TEM, a transient amorphous calcium sulfate phase formed during the hydration of NB-C was identified. Further evidence for the non-classical dissolution-precipitation driven epitaxial growth of gypsum along the [001] direction of bassanite, and the oriented attachment of NB-C particles during hydration was collected.

The solubility of hydrated NB and NB-C was compared with that of a geologic gypsum control. While hydrated NB dissolved at the same rate as the control, hydrated NB-C showed a slower dissolution rate. Furthermore, the incorporation of calcein affected the overall mechanical properties of gypsum crystals, which became more plastic and tough. Thus, improved chemical and physical weathering resistance is possible through bio-inspired strategies (*i.e.* incorporation of organic additives). Finally, consolidation tests of gypsum plaster mock-ups were carried out with the obtained fluorescent NB-C, which showed a good penetrability and a noticeable mechanical reinforcing effect. These enhanced physical-chemical

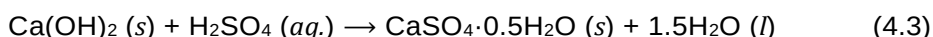
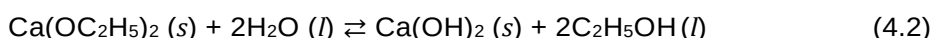
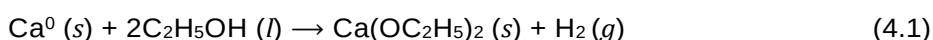
properties of the resulting gypsum cement are features that are pertinent for the effective consolidation of decayed historical gypsum plasterworks.

Additionally, the incorporation of calcein into bassanite nano-consolidants provides a complementary solution for the conservation of plasterwork. In extremely low doses, calcein does not affect the appearance in the visible spectrum neither before nor after the hydration of fluorescent nano-bassanite, a critical issue in heritage conservation. Moreover, when excited with UV radiation, the fluorescent consolidant exhibits an intense green luminescence, allowing conservators to precisely identify areas where the new material is deposited, as well as its penetration depth. This breakthrough enables targeted and accurate conservation applications, preventing under- or over-consolidation and ensuring the preservation of the historical artwork. We also demonstrate that calcein modifies crystal growth upon nano-bassanite hydration and the resulting gypsum structure, which also displayed fluorescence, thus enabling to spot areas where the consolidant was applied (simply by illumination with an UV lamp).

2. EXPERIMENTAL SECTION

2.1. Synthesis of Nano-Bassanite and Fluorescent Nano-Bassanite

Bassanite nanorods (NB) were obtained by a solvothermal route involving the formation of amorphous calcium ethoxide and its subsequent reaction with sulfuric acid, as described by the following reactions:



The entire synthesis consists of three sequential steps performed in a single reactor (*i.e.*, one-pot synthesis). These steps are described below for a typical synthesis run:

First, the irreversible redox reaction between 2 g of metallic calcium (99%, granular, Scharlau) and 200 mL of absolute ethanol (Scharlau) takes place for 24 h at 78 °C under reflux condensation, under anhydrous conditions and constant magnetic stirring in a 500 mL glass (or Teflon®) reactor (Equation 4.1). This step results in a whitish ethanolic suspension of calcium ethoxide, which serves as the initial precursor of bassanite nanoparticles.

Subsequently, 80 mL of toluene (99.9%, Scharlau) and 10 mL of a 5 M sulfuric acid solution (prepared from H₂SO₄, 95-98%, Sigma-Aldrich) preheated to 78 °C are added (dropwise) to the previously obtained suspension. The reaction is carried out at 78 °C under continuous magnetic stirring for different periods of time: 35, 45, 55 and 60 min. This promotes the following simultaneous processes: On the one hand, sulfuric acid can react directly with the calcium alkoxide particles in the suspension, while the presence of water allows the hydrolysis of these precursor particles, producing Ca(OH)₂ (Equation 4.2), an intermediate species that is later neutralized

by sulfuric acid (Equation 4.3). Both pathways converge in the precipitation of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ as the final product.

In addition, this approach results in a substantial increase in the saturation index (SI), which exceeds the equilibrium SI for the three different $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ phases (*i.e.*, anhydrite, bassanite, and gypsum). This sudden increase in SI effectively promotes increased nucleation rates and reduced particle sizes, ensuring the formation of phase-pure bassanite nanoparticles, which is advantageous for their penetration into porous substrates (*e.g.*, during the consolidation of gypsum plasterwork).

Finally, NB particles are separated from the solvent mixture by rotary evaporation at 80 °C and ~7 mbar. The resulting solids are then oven dried at 80 °C for 30 min and stored under an N_2 atmosphere. The yield of a typical synthesis run was $\geq 99\%$, resulting in the production of ~7 g phase-pure $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ per batch (starting from 2 g Ca^0).

In the case of fluorescent nano-bassanite (NB-C), 4 mL of a 2.5 mM aqueous calcein solution is added during the second step of the synthesis protocol, resulting in a final calcein concentration of ~50 μM . To ensure Ca-calcein complexation, the mixture is stirred for approximately 5 minutes. The concentrated H_2SO_4 solution is then added and the reaction continues as described above. As an additional step to process the fluorescent nanobassanite, the resulting powder is dispersed in 96% ethanol, sonicated for 2 minutes, and centrifuged at 6000 rpm for 15 minutes to remove any excess adsorbed calcein from the nanoparticle surface.

2.2. Preparation of β -Hemihydrate (Plaster of Paris) Control

The bassanite control was prepared by oven heating (under air atmosphere) of commercially available gypsum (Sigma-Aldrich) at a temperature of 105 °C for 24 h. The obtained hemihydrate showed a SSA of 3.72 $\text{m}^2 \text{g}^{-1}$, an average particle size of 1-2 μm (as determined by TEM), and a crystallite size (calculated using the Scherrer equation, using the most intense 200 Bragg

reflection) of 49 ± 2 nm. Note that the SSA given above for the obtained β -hemihydrate is standard for *plaster of Paris* (Park *et al.*, 2011).

2.3. Characterization of Precursor and Product Phases

Powders of the precursor (calcium ethoxide), the product phases of the different runs carried out and the control (*plaster of Paris*, see below) were characterized using different analytical techniques. Phase composition was determined by X-ray diffraction (XRD) using a PANalytical X'Pert Pro equipped with a Ni filter (measurement parameters: Cu-K α radiation $\lambda = 1.5405$ Å, 45 kV, 40 mA, 3 to 70 $^{\circ}2\theta$ exploration range, steps of 0.001 $^{\circ}2\theta$, and goniometer speed of 0.01 $^{\circ}2\theta$ s $^{-1}$). Powder samples were placed in zero background Si sample holders for analysis. Mineral phases were identified by comparison with JCPDS (Joint Committee on Powder Diffraction Standards) powder spectra and quantified by the reference intensity ratio (RIR) method using X Powder software (Martín-Ramos, 2004). This software was also used to determine the Scherrer crystallite size of the crystalline product phases.

Thermogravimetry coupled with differential scanning calorimetry (TG-DSC; Mettler-Toledo TGA/DSC1) was used to determine the amount of adsorbed and structural water in the product phase(s), as well as to identify the presence of residual (unreacted) precursor Ca(OH) $_2$ and possible carbonates (formed upon exposure to atmospheric CO $_2$ during sample handling). DSC was used to identify α - and β -hemihydrate (Powell, 1958). For each run, the temperature was raised from 25 $^{\circ}$ C to 950 $^{\circ}$ C at a heating rate of 20 K min $^{-1}$ under either flowing air or N $_2$. No significant differences in the TG/DSC traces were observed between analyses performed in oxidizing and inert atmospheres, except for the 35 min run. In the latter case, a small exothermic band at 380-400 $^{\circ}$ C was observed, corresponding to thermal oxidation of residual calcium ethoxide, which was absent in the N $_2$ atmosphere.

Solids were also analyzed by Fourier transform infrared spectroscopy using an attenuated total reflectance sample holder (ATR-FTIR, JASCO FT/IR 6600) in the spectral range of 4000 - 400 cm $^{-1}$ with a step size of 0.48 cm $^{-1}$.

The particle size distribution (PSD) of the NB powders obtained at different reaction times was studied by dynamic light scattering (DLS). Solids were dispersed in ethanol, sonicated for 60 s and measurements were performed at a scattering angle of 180° using a Microtrac NANO-flex particle size analyzer equipped with a diode laser ($\lambda = 780$ nm, 5 mW) and a 1 m long flexible probe (8 mm diameter) with a sapphire window as sample interface. Scattering analysis was performed with an acquisition time of 30 s during at least 10 consecutive measurements. PSDs were calculated using the Microtrac FLEX application software package (v.11.1.0.2).

N₂ sorption isotherms of the different NB products obtained at different reaction times, as well as the control sample (*plaster of Paris*), were obtained at 77 K on a Micromeritics TriStar 3000. Prior to measurement, powder samples (~250 mg sample mass) were heated at 80 °C for 4 h and outgassed to 10⁻³ Torr using a Micromeritics Flowprep. BET analysis (Pierotti and Rouquerol, 1985) was used to determine the total specific surface area (SSA).

To determine the content of intracrystalline calcein in NB-C, 20 mg of dried sample was dissolved in hydrochloric acid (2 mL, 3 M). The resulting solutions were then analyzed using a Thermo Scientific GENESYS 50 UV-Vis spectrophotometer. Calibration curves ($R^2 = 0.9999$) were obtained by measuring calcein solutions of known concentrations ranging from 1 to 25 μ M using the aforementioned hydrochloric acid buffer. The amount of intracrystalline calcein (*i.e.*, μ mol calcein per mg sample) was then calculated from the Beer-Lambert law using the absorbance maxima at 448 nm.

2.4. TEM Analyses

Micro- and nanostructural features of the synthesized NB and NB-C particles, as well as their hydration product (*i.e.*, gypsum), were determined by means of transmission electron microscopy (TEM) using a FEI Titan S/TEM microscope (operated at 300 kV acceleration voltage). Powder samples were dispersed in absolute ethanol and sonicated for 20 s before being deposited on carbon coated Cu grids. Prepared samples were then plasma-cleaned. TEM

photomicrographs were obtained using a 40 μm objective aperture. Detailed crystallographic information was obtained by measuring selected area electron diffraction (SAED) patterns, collected using a 10 μm objective aperture. A high-angle annular dark field (HAADF) detector operated in scanning TEM (STEM) mode was used to obtain Z-contrast images and compositional energy dispersive X-ray (EDX) spectra and maps.

Additional TEM analyses were performed on an FEI Titan3 Themis 300 X-FEG operating at 300 kV equipped with an FEI Super-X energy dispersive X-ray (EDX) system and a Gatan OneView CCD. For this, supersaturated CaSO_4 solutions (*i.e.*, extracted at the onset of nucleation) were prepared at 25 $^\circ\text{C}$ by the continuous addition of a 0.3 M CaCl_2 solution over a 0.1 M $(\text{NH}_4)_2\text{SO}_4$ solution, in the absence and presence of 2 ppm of poly(acrylic acid) (PAA). Samples were prepared by cryo-quenching as follows: a 3 μL droplet of the nucleating solution was transferred onto a plasma-treated continuous TEM grid after set times. Sample loaded grids were then rapidly plunged into liquid ethane using an FEI Vitrobot[®], allowing the sample to remain in its native state with any water rapidly transforming into amorphous ice.

Alternatively, in order to determine if the objects observed by full Cryo-TEM analyses were artifacts or not, grids were then transferred into a vacuum desiccator to allow the sublimation of the vitreous ice, and re-analyzed under normal TEM conditions.

2.5. Measurement of the Hydration Kinetics of Nano-Bassanite

As indicated in the main text, two different experiments were conducted to study the rate of hydration of the synthesized nano-bassanite in comparison to the control (*plaster of Paris*). The first experiment, designated as liquid-phase (LP) hydration, employed dissolution-reprecipitation to investigate the dissolution and precipitation of bassanite in a liquid phase. The second experiment, vapor-phase (VP) hydration, utilized diffusion and condensation to examine the vaporization and condensation of bassanite in a gaseous phase.

For the liquid-phase (LP) experiments, approximately 0.7/1 (wt/wt) water/bassanite mixtures of the nano-bassanite (product obtained after 45 minutes of reaction time) and the control (standard β -hemihydrate, *i.e.*, *plaster of Paris*) were prepared and immediately placed on zero-background silicon sample holders for X-ray diffraction (XRD) analysis. X-ray diffraction (XRD) patterns were collected continuously over an exploration range of 10–30 °2 θ . The collection of each diffractogram required approximately seven minutes. Sequential XRD patterns were collected until the complete conversion of bassanite to gypsum was achieved. To quantify the fractional conversion (α), quantitative XRD analyses were performed using the RIR method. The fractional conversion was calculated using the following equation (Equation 4.4):

$$\alpha = \frac{X_{\text{gypsum}}}{X_{\text{bassanite}}} \quad (4.4)$$

Where X_{gypsum} and $X_{\text{bassanite}}$ represent the mass fractions of gypsum and bassanite, respectively, at each measurement time.

For the VP experiments, powdered NB (obtained after 35, 45 and 60 min of reaction) and a control sample (standard β -hemihydrate) were evenly spread on Petri dishes and placed inside a climatic chamber at a constant temperature of 22 °C and relative humidity of 90%. In this case, the fractional conversion of bassanite into gypsum was monitored over the course of one week and quantified by means of XRD.

2.6. Dissolution Resistance Tests

The effect of calcein on the weathering resistance of hydrated nano-bassanite particles (*i.e.*, both calcein-modified and non-functionalized nano-bassanite products) was investigated through potentiometric titration using a Methrom Titrando 905, equipped with an 856 Conductivity module and an 867 pH module. Dissolution resistance tests were conducted by dispersing 40 mg of hydrated fluorescent nano-bassanite (NB-C), hydrated non-fluorescent nano-

bassanite (NB), and geologic gypsum (GG) into 100 mL of milli-Q grade deionized water (pH ~6.25, $T = 25^{\circ}\text{C}$). For this purpose, the samples were first sieved to a particle size range between 50 and 100 μm . The values of Ca^{2+} potential and transmittance were continuously recorded using a Methrom Ca^{2+} selective polymer membrane electrode and a Methrom Optrode optical sensor ($\lambda = 610 \text{ nm}$), respectively.

In order to obtain calibration curves for Ca^{2+} activity coefficients, blank experiments were conducted in the absence of SO_4^{2-} and calcein. A 0.3 M $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ solution (0.24 mL min^{-1} addition rate) was added to 100 mL Milli-Q grade water. The ionic strength was previously adjusted by the addition of NaCl (0.25 M, calculated using PHREEQC as the equivalent ionic strength of a 0.1 M solution of $(\text{NH}_4)_2\text{SO}_4$).

2.7. Nanoindentation

Nanoindentation of micrometric calcein-loaded gypsum crystals (GC-50 and GC-150) as well as of millimetric geologic gypsum crystals was performed using a Bruker Hysitron TI Premier nanoindenter, equipped with a diamond Berkovich tip (with trigonal pyramidal shape, semiangle = 65.3°) and scanning probe microscopy.

Measurements were performed on $\{010\}$ planes of both fluorescent and non-fluorescent gypsum crystals under controlled conditions of T and relative humidity (20 $^{\circ}\text{C}$, 40% RH). We performed a minimum of 16 measurements per tested sample using grids of 4×4 indentations (spaced at 9 μm both in the lateral and vertical directions) per sampled area. Load control indentation mode was selected, using a maximum load of 2500 and 5000 μN to ensure that the indentation depth was larger than any surface feature (roughness). No marked variations in the calculated reduced elastic modulus (E_r) and hardness (H) were observed when comparing load control runs at both 2500 and 5000 μN . Indentation measurements were performed at a loading/unloading rate of 200 $\mu\text{N s}^{-1}$ with a holding time of 10 s. The Oliver and Pharr (1992) model was used to determine E_r and H from the Load-Displacement curves (L-D; where P and h represent the load and displacement,

respectively). The reduced elastic modulus was calculated using the following equation (Equation 4.5):

$$E_r = \frac{\sqrt{\pi}}{2\beta} \frac{S}{\sqrt{A}} \quad (4.5)$$

Where S is the contact stiffness (calculated as the slope of the unloading curves, $S = dP/dh$), A is the projected contact area of the indenter tip, which depends on its geometry and the reached indentation depth (*i.e.*, h), and β is a factor that depends on the geometry of the indenter tip (*i.e.*, 1.034 for a Berkovich tip).

Hardness values were calculated using the following equation (Equation 4.6):

$$H = \frac{P_{max}}{A} \quad (4.6)$$

Where P_{max} is the maximum load reached.

Calibration of the indenter tip was performed using fused quartz standard before sample analysis.

2.8. Consolidation Tests

The consolidation effectiveness of ethanolic suspensions containing calcein-loaded nano-bassanite (5 g L⁻¹) was evaluated using gypsum plaster as a substrate. The specimens were formulated to emulate the historic Islamic gypsum plaster-making process at the Alhambra (Figure A.4). The plaster mock-ups were prepared by mixing *plaster of Paris* and water in a 1:1.2 ratio, in order to obtain a substantially porous substrate with a total open porosity of approximately 52.5%. The plaster paste was poured into molds and allowed to set and cure for a minimum of two weeks. Subsequently, cubic specimens (2×2×2 cm³) were obtained and subjected to a further curing period of at least two months under controlled conditions (25 °C and 90% relative humidity).

Prior to consolidation treatments, cubic gypsum plaster samples were laterally covered with parafilm. Subsequently, the calcein-loaded nano-bassanite suspension was uniformly sprayed onto one horizontal surface (the upper surface) until complete imbibition was achieved. This procedure was repeated up to ten times to ensure an adequate consolidation effect. Subsequently, the samples were allowed to cure for one month under the specified temperature and relative humidity conditions. It should be noted that at low doses, calcein does not result in significant chromatic variations on the original (visible) color of the nano-bassanite consolidant product, while it is capable of emitting intense green luminescence under UV radiation.

The penetrability of the fluorescent nano-bassanite consolidant was evaluated by irradiating vertically fractured treated gypsum plaster specimens with UV light ($\lambda = 365$ nm), while the consolidation effect was determined by means of mercury intrusion porosimetry (MIP) and drilling resistance tests (DRMS) on treated and untreated cured gypsum plaster samples.

The changes in total porosity and pore size distribution were determined using a Micromeritics Autopore III mercury intrusion porosimeter. For the MIP experiments, samples of approximately 0.5 g were extracted from the top part of treated and untreated cubic plaster mock-ups. These specimens were dried in an oven at approximately 60 °C for 8 h. The mechanical resistance of the untreated and treated samples was analyzed using a SINT Technology drilling resistance measurement system. Drilling resistance tests were conducted along a depth profile normal to the treated surface using the following parameters: a 5 mm diameter drill bit with a flat diamond head, 10 mm drilling depth, 20 mm min⁻¹ penetration rate, and 200 rpm rotation speed. For both MIP and drilling resistance analyses, at least four replicates per sample were performed.

3. RESULTS AND DISCUSSION

3.1. Characterization of Nano-Bassanite

X-ray diffraction (XRD) patterns of powder samples obtained at different reaction times (35, 45, 55, and 60 minutes) demonstrated that in all cases, a monoclinic (space group $I2$; Bezou *et al.*, 1995) hemihydrate phase was obtained (Figure 4.1a). Nevertheless, at 35 minutes, characteristic Bragg peaks of portlandite were also detected, indicating that calcium hydroxide preceded the precipitation of hemihydrate. Portlandite was no longer observed after longer reaction times. The crystallite sizes of bassanite, as determined by the Scherrer equation, exhibited a gradual increase from 17 ± 2 nm at 35 min to 25 ± 2 nm at 60 min. In contrast, a commercial β -hemihydrate (control) obtained after calcination of gypsum exhibited a crystallite size of 49 ± 2 nm.

The FTIR analysis of the synthesis products collected at 45, 55, and 60 minutes revealed the presence of two moderate intensity bands at 3554 and 3610 cm^{-1} , which were attributed to the ν_1 symmetric stretch and the ν_3 antisymmetric stretch of water molecules, respectively. Additionally, the δ -OH bending band at 1618 cm^{-1} indicated the presence of a single type of crystalline water in bassanite (Figure 4.1b) (Bensted and Prakash, 1968). The $\nu_1(\text{SO}_4)$ symmetric stretch band at 1006 cm^{-1} and the $\nu_3(\text{SO}_4)$ antisymmetric stretch band at ~ 1100 cm^{-1} , which are typically split into three peaks (Bensted and Prakash, 1968), were also identified. The solid sample collected after 35 minutes exhibited an additional weak shoulder at 3650 cm^{-1} and a weak and broad doublet at 1412-1485 cm^{-1} (ν_3 asymmetric CO_3 stretch), indicative of the presence of trace amounts of $\text{Ca}(\text{OH})_2$ and amorphous calcium carbonate (likely formed upon the carbonation of $\text{Ca}(\text{OH})_2$ during sample handling and/or analysis). Additionally, very weak bands at 2975, 2937, and 2884 cm^{-1} , corresponding to $-\text{OCH}_2\text{CH}_3$ groups, were also detected in this latter sample. These findings indicate that a minor quantity of unreacted calcium alkoxide and calcium hydroxide precursors remained present after 35 minutes of reaction time.

Simultaneous TG-DSC analyses showed that the samples collected after 45, 55 and 60 min of reaction display a marked weight loss of ~8 wt% and an endothermic peak at 160 °C, corresponding to the removal of adsorbed water (1.9 wt%) and structural water of bassanite (6.1 wt%) (Figure 4.1c). In addition, the DSC trace shows a small exothermic peak at 200 °C, demonstrating the presence of α -hemihydrate (Bensted and Prakash, 1968). This phase transformed into γ -CaSO₄ upon dehydration, which in turn transforms into insoluble anhydrite (β -CaSO₄) at such T (Powell, 1958). However, we also observed an exothermic peak at 345 °C, reportedly corresponding to the transformation γ -CaSO₄ $\rightarrow$ β -CaSO₄, after dehydration of β -hemihydrate (Powell, 1958). This indicates that the product is a mixture of α - and β -hemihydrate. No other weight loss event was observed, which allowed us to estimate a reaction yield of at least 99%. TG-DSC analysis of samples obtained after 35 minutes revealed a weight loss of 1.1 wt% at temperatures below 100 °C due to adsorbed water, followed by a significant weight loss of 6.1 wt% attributed to bassanite dehydration. Additionally, a single exothermic band was observed at 190 °C, indicating the exclusive presence of α -hemihydrate (Figure 4.1c). Furthermore, a weight loss of 0.9 wt% at 400 °C and 1.9 wt% at 600 °C, attributed to the dehydroxylation of calcium hydroxide ($\text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$) and the thermal decomposition of calcium carbonate ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$), respectively, indicates the presence of 3.43 wt% portlandite and 3.97 wt% calcium carbonate due to an incomplete reaction.

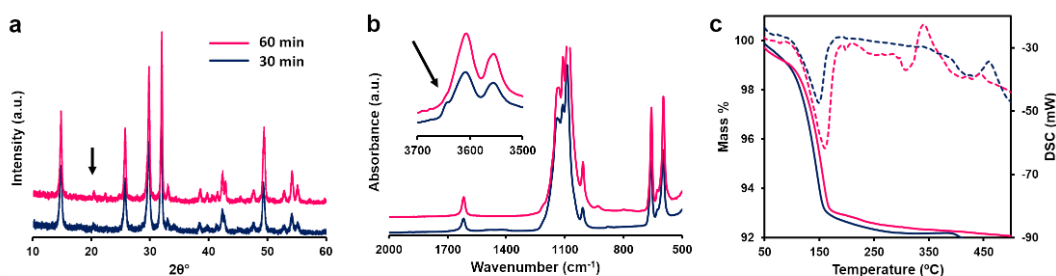


Figure 4.1. Characterization of NB particles obtained after 35 and 60 min of reaction. a) XRD patterns of the products. Note the presence, in addition of the intense bassanite peaks, of a small broad peak corresponding to 100 portlandite (arrow) in the sample collected after 35 min; b) FTIR spectra of products. The inset shows detail of the O-H stretching of crystal water in bassanite and the shoulder at 3650 cm⁻¹ of portlandite (after 35 min, arrow); d) TG/DSC analyses.

TEM was employed for a detailed microstructural analysis of the solid products. The sample collected after 35 min showed multiple non-oriented aggregates of rod-like hemihydrate nanocrystals 25-50 nm in length (measured along the *c*-axis) and 15-20 nm thick, along with larger shapeless or globular amorphous particles (*i.e.*, unreacted amorphous calcium ethoxide and calcium hydroxide) (Figure 4.2a and b). After 45 min these amorphous species were not detected, indicating the complete reaction of precursors. Figure 4.2c shows the SAED pattern of the rod-like nanoparticles with features of the reciprocal lattice and d-spacings corresponding to bassanite with space group *I*2 (Bezou *et al.*, 1995).

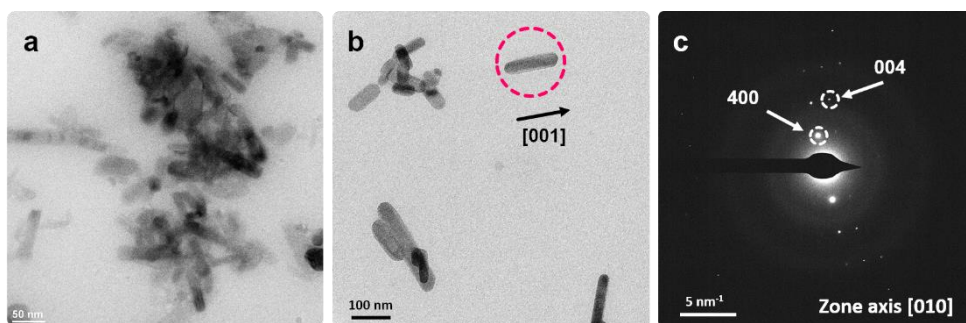


Figure 4.2. TEM-SAED analysis of nano-bassanite: a) Aggregates of bassanite nanorods (less than 200 nm in size) obtained after 35 min of reaction. b) Bassanite nanorods after 45 min of reaction. The indicated individual bassanite nanorod is oriented along the [001] direction, considering the SAED pattern in c).

Analysis of particle size distribution (PSD) using TEM images showed a narrow Log-normal distribution. As an example, Figure 4.3a shows the DLS-derived PSD for the 35, 45 and 60 min runs. These particles have a mean length of 120 nm, and a mean width of 22 nm. DLS analysis shows an average particle size of 330 nm after 35 min reaction time, consistent with the presence of larger aggregates of unreacted amorphous calcium ethoxide and calcium hydroxide observed using TEM. At longer reaction times (≥ 45 min) and complete transformation, bassanite nanorods were the only particles contributing to the PSD observed with DLS. The change in the average PSD of the products obtained after 45 and 60 min of reaction is consistent with a coarsening mechanism.

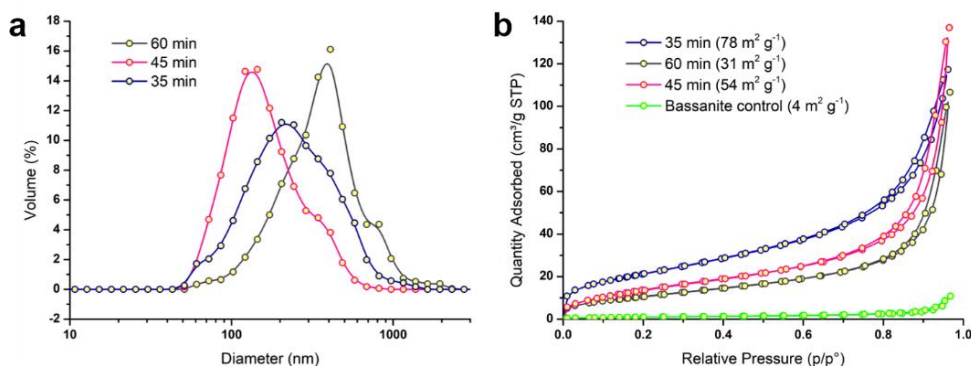


Figure 4.3. Particle size distributions (a), as calculated by means of dynamic light scattering (DLS), and N₂ sorption analyses of NB products obtained using the proposed solvo-thermal procedure after 35, 45 and 60 min of reaction (blue, red and black curves, respectively). Note that controlling the reaction time is crucial to optimize both particle size and specific surface area of the produced nanoparticles.

N₂ sorption analysis shows that the product obtained at 35 min had a SSA of 78 m² g⁻¹. However, the actual contribution of the hemihydrate versus the untransformed precursors to such a huge SSA is unclear. The SSA of the phase-pure hemihydrate sample collected after 45 min was 54.2 m² g⁻¹, and decreased to 44 and 31 m² g⁻¹ after 55 and 60 min, respectively, due to the observed overall increase in particle size. To our knowledge, 54.2 m² g⁻¹ is the highest SSA value for a hemihydrate product reported so far. NB displays a Type II isotherm with a H3 hysteresis loop (Figure 4.3b), corresponding to non-microporous solids with interparticle (slit-shaped) meso- and macro-pores (Pierotti and Roquerol, 1985). This is consistent with the features of hemihydrate nanorod aggregates observed by means of TEM (Figure 4.2a-b).

These results show that a careful control of the reaction time is critical to achieve maximum conversion of precursors, minimum increase in crystal size by coarsening effects, and a maximum specific surface area.

3.2. Hydration Kinetics of Nano-Bassanite

Considering that a main application of bassanite involves its conversion to gypsum *via* hydration, we evaluated the dissolution/hydration kinetics of NB, as compared with those of standard β -hemihydrate, showing a BET SSA of $3.72 \text{ m}^2 \text{ g}^{-1}$ and a particle size ranging between $1\text{-}2 \text{ }\mu\text{m}$ (Park *et al.*, 2011). Solids were subjected to: (i) vapor-phase (VP) hydration (relevant for alcohol dispersions of nano-bassanite, similar to nanolimes (Rodriguez-Navarro and Ruiz-Agudo, 2018), designed to be used as a potential consolidant for historic gypsum plaster) and (ii) through-solution liquid-phase (LP) hydration (relevant for the reactivity -dissolution and setting- of NB, with potential application in orthopedics and the pharmaceutical industry) (Rauschmann *et al.*, 2005; Sidqui *et al.*, 1995; Butta *et al.*, 2005).

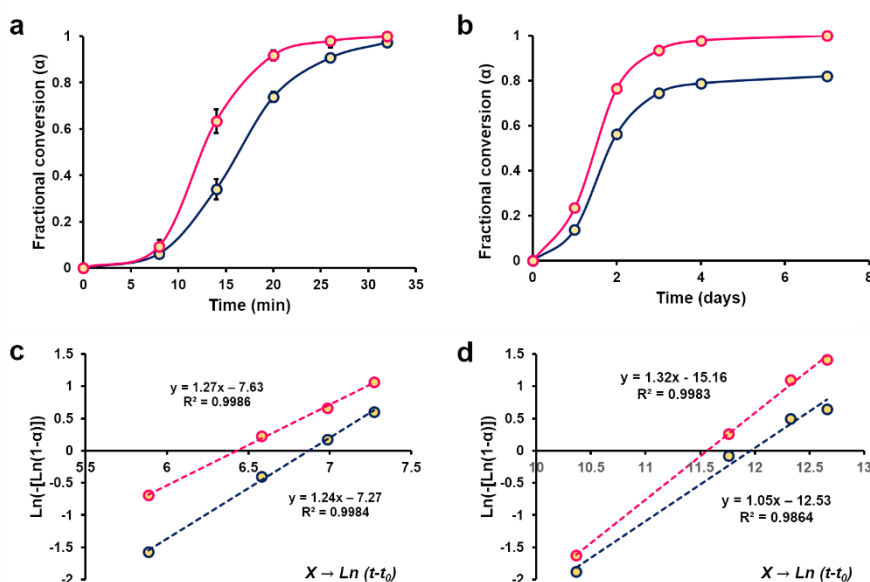


Figure 4.4. Hydration kinetics of NB. Time evolution of the fractional conversion (α) of NB (red circles/curves) and control (*plaster of Paris*, β -hemihydrate; blue circles/curves) into gypsum following through-solution (a; LP) and vapor phase (b; VP) hydration. Error bars show StDev. The black dashed lines show the tangent to the inflection point used to calculate the induction time, t_0 . Sharp-Hannock plots for the through-solution (c; LP) and vapor phase (d; VP) hydration of (nano)bassanite. The red and blue circles are experimental points for nano-bassanite and β -hemihydrate, respectively. The corresponding dashed lines are the best linear fits to such experimental points using the Avrami-Erofe'ev equation (fitting parameters and R^2 values are indicated).

Figures 4.4a and 4.4b show the evolution of the fractional conversion of (nano)bassanite into gypsum during VP and LP hydration, respectively. Considering that the α vs time curves showed a characteristic “S” or sigmoidal shape, and the fact that previous studies have indicated that the hydration kinetics of bassanite can be best described by an Avrami-type model (*i.e.*, corresponding to a nucleation-growth mechanism) (Gurgul *et al.*, 2019). Here we fitted our experimental data to the integral form ($g(\alpha)$) of the Avrami-Erofe'ev equation, which is widely used to describe solid state-transformations (Avrami, 1940):

$$\alpha = 1 - \exp[-k(t - t_0)^n] \quad (4.7)$$

Where α is the fractional conversion, n is a reaction exponent which provides information on the mechanisms of the reaction, k is the rate constant (conversion rate), t is the elapsed time, and t_0 is the induction time (extent of the induction period). Values of t_0 were determined by the intersection with the x-axis of the fitting line obtained by regression of the linear part of the α vs. t plot for each hydration experiment. Equation 4.7 is commonly considered to be valid for $0.15 < \alpha < 0.85$, but it has been used for higher (and lower) values of α (Hand, 1994). Here, it was used for $0.06 < \alpha < 0.99$.

A convenient way to rewrite Equation 4.7 is the following:

$$\ln[-\ln(1 - \alpha)] = n \ln k + n \ln(t - t_0) \quad (4.8)$$

Plotting $\ln[-\ln(1 - \alpha)]$ vs $\ln(t - t_0)$ (*i.e.*, the Sharp-Hancock plot) yields a linear graph if the Avrami-Erofe'ev model is valid for the system studied. A linear fit to such plotted experimental results will yield n as the slope of the regression line, and k as the y-axis intercept.

The Avrami-Erofe'ev equation showed an overall good fitting (Figure 4.4c-d, $R^2 \geq 0.97$) for all our experimental values. From this kinetics analysis apparent rate constants (k) were calculated: (LP) $k_{\text{Control}} = 1.72 \cdot 10^{-3} \text{ s}^{-1}$ ($n = 1.14$) and $k_{\text{Nanobass}} =$

$2.56 \cdot 10^{-3} \text{ s}^{-1}$ ($n = 1.27$) (Figure 4.4c). (VP) $k_{\text{Control}} = 6.21 \cdot 10^{-6} \text{ s}^{-1}$ ($n = 1.05$) and $k_{\text{Nanobass}} = 9.96 \cdot 10^{-6} \text{ s}^{-1}$ ($n = 1.32$) (Figure 4.4d).

The obtained n values were close to 1.0, which would mean that growth is one-dimensional (1D), as has been previously observed for the kinetics of hemihydrate hydration (Mróz and Mucha, 2017). However, it is difficult to unambiguously determine the mechanism of reaction just based on n values, as they could indicate multiple possibilities (Gurgul *et al.*, 2019). The k values for liquid-phase hydration obtained here ($1.72 \cdot 10^{-3}$ to $2.56 \cdot 10^{-3} \text{ s}^{-1}$) are within the range of those previously reported for this reaction (Gurgul *et al.*, 2019). As expected, those obtained for vapor-phase hydration were (three) orders of magnitude lower. These results also demonstrate that the hydration of the synthesized nano-bassanite proceeds at a significantly faster rate than the low-surface area control.

3.3. Characterization of Fluorescent Nano-Bassanite

Nano-bassanite was synthesized in the absence or presence of calcein following the solvothermal method described above. Details of this solvothermal synthesis are presented in the Experimental Section. Figure 4.5a schematically shows the different steps of such a synthesis route, whereas Figure 4.5b shows the final product synthesized in the presence of calcein, which is fluorescent under UV light.

XRD analysis (Figure 4.5c) revealed that the synthesis product (NB-C) was pure-phase monoclinic bassanite (space group *I*2, Bezou *et al.*, 1995). Furthermore, FTIR spectra (Figure 4.5d) showed moderate intensity bands at 3554 and 3610 cm^{-1} , corresponding to the ν_1 asymmetric and ν_3 antisymmetric O-H stretch vibrations, along with the moderate intensity δ OH bending band at 1618 cm^{-1} , corresponding to structural water in bassanite. In the fingerprint region we observed a quadruplet at 1010, 1086, 1108 and 1137 cm^{-1} , along with a doublet at 595 and 660 cm^{-1} , corresponding to the $\nu_1 - \nu_4$ stretching vibration modes of SO_4 groups. We also observed low-to-moderate intensity bands ranging from 694 to 941 cm^{-1} that were ascribed to the incorporated calcein. Note that the main IR absorption bands (*i.e.*,

corresponding to C-O, C-H and C=C bonds) of calcein overlap with the stretching modes of SO_4 groups and could not be properly identified. The UV-Vis analysis of dissolved NB-C (Figure A.1 and Table A.1) further confirmed the presence of the additive in the nano-bassanite crystals, and revealed a calcein net content of $4.81 \cdot 10^{-4} \mu\text{mol mg}^{-1}$.

TEM analysis showed that the synthesized product consisted of nano-crystalline rod-like bassanite aggregates, similarly to the particles observed in Figure 4.2. This observation is supported by their SAED pattern exhibiting diffraction spots corresponding to the 114, $\bar{3}14$, 334, and 240 reflections (Figure A.5a). The particle equivalent length, measured along the *c*-axis direction, ranged from 90 to 500 nm, with widths measured along the *a*- or *b*- directions ranging between 40 to 80 nm. More importantly, S/TEM EDX elemental mappings (Figure 4.5e-g) and spectra (Figure A.5b) were decisive to prove that calcein was evenly distributed inside the bassanite nanocrystals, as confirmed by areas of increased signal intensity in the elemental carbon map.

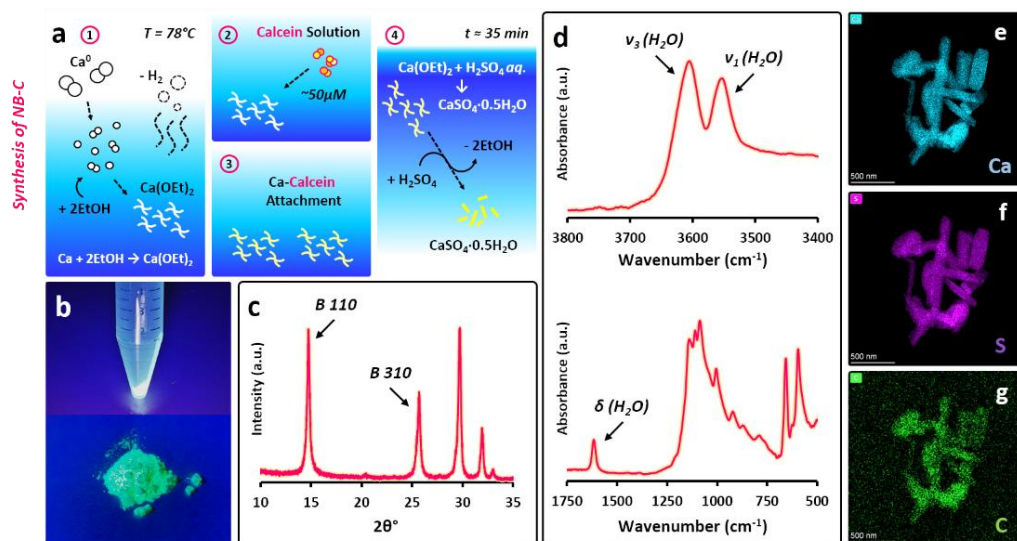


Figure 4.5. Synthesis (a and b) and characterization (c-g) of fluorescent nano-bassanite (NB-C). XRD pattern (c), FTIR spectrum (d) and EDX elemental mappings (e-g) show that the obtained product is phase-pure bassanite, which also contains calcein.

3.4. The Hydration of Fluorescent Nano-Bassanite

The synthesized NB-C particles were subjected to hydration at room T in a high relative humidity atmosphere ($RH > 90\%$) for at least two weeks to obtain partially hydrated bassanite (*i.e.*, a mixture of bassanite and gypsum).

TEM analyses showed that the newly formed gypsum grew by epitaxy along the c -axis direction of the pre-existing bassanite nanocrystals (Figure 4.6a). Jia *et al.* (2021) have previously shown that the low-energy interfaces of bassanite faces along the c -axis direction promotes the heterogeneous nucleation and growth of gypsum in solution. Note, however, that we did not use liquid water to promote the hydration of bassanite. Instead, deliquescence on the surface of the hemihydrate was the primary source of water in our experimental setup. Moreover, we observed that the diffuse diffraction spots corresponding to the SAED pattern of the tip of individual hydrated bassanite nanocrystals were elongated along the $[001]$ direction (*i.e.*, long axis and growth direction), indicating that Bragg reflections show a marked broadening (*i.e.*, reduced crystallite size), whereas those corresponding to newly formed gypsum also show broadening and significant arcing ($\sim 8\text{-}12^\circ$) indicative of limited crystallinity and misalignment among coherent domains (Figure 4.6a-c). As previously discussed, these effects are likely caused by the presence of structural defects, microstrain and reduced crystallite size, compatible with the incorporation of calcein in the structure of both nano-bassanite and the newly-grown gypsum.

Interestingly, during TEM analyses we also observed small amorphous structures resembling liquid-like fractals of nanodroplets (Figure 4.6d-f). EDX analyses and mappings revealed the presence of elemental Ca and S (Figure 4.6g-i), suggesting the formation of an amorphous calcium sulfate (*i.e.*, ACS) phase during the hydration of NB-C. These amorphous structures were extremely sensitive to the electron beam, which is indicative of a high degree of hydration. Recently, Ilett *et al.* (2022, 2024) have detected similar ACS structures in samples prepared by cryogenic quenching and vacuum sublimation of 50 mM CaSO_4 solutions (in the absence of additives) using high-resolution TEM.

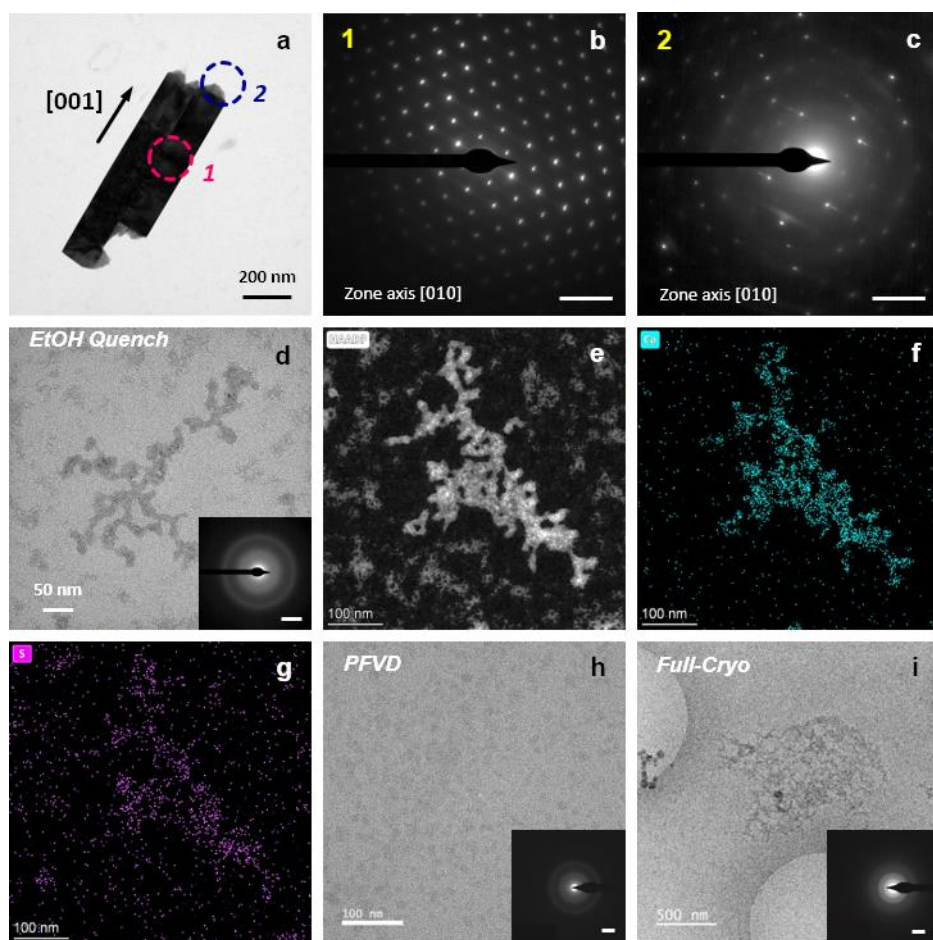


Figure 4.6. (a-c) TEM and SAED analyses of the epitaxial growth of fluorescent gypsum on a bassanite nanorod, driven by a coupled non-classical dissolution-precipitation mechanism. (d) TEM image of fractal-like structures made up of nanodroplets (transformed into ACS during EtOH quenching and drying) observed during the hydration of calcein-loaded nano-bassanite. (e-g) HAADF imaging and corresponding EDX elemental Ca and S mappings corroborate that the observed fractals are amorphous calcium sulfate structures; (h, i) TEM and Cryo-TEM images of dispersed nanodroplet (liquid precursor of ACS) formed by direct precipitation of calcium sulfate in the presence of PAA. Note the textural/structural similarity of the individual isolated droplets with those forming aggregates in (d). All scale bars in SAED images correspond to 5 nm^{-1} .

We further analyzed cryo-quenched aliquots of supersaturated CaSO_4 solutions where PAA was used as a proxy for calcein, under full Cryo-TEM and normal TEM analysis conditions after eliminating the formed frost by vacuum sublimation (*i.e.*,

plunge-freezing and vacuum sublimation, PFVD; see Experimental Section) (Figure 4.6h-i and Figure A.6). Note that, in essence, carboxylate-rich organic additives, whether monomeric or polymeric (e.g., calcein and PAA), function as nucleation inhibitors by sequestering Ca^{2+} and stabilizing PNCs and/or amorphous precursors (e.g., amorphous calcium carbonate, ACC) (Sun *et al.*, 2016; Xu *et al.*, 2018). In the presence of PAA, we observed individual globular amorphous structures with the same dimensions as the nanodroplets that conform the previously shown fractal structures.

Our hypothesis is that these ACS fractals are formed following a diffusion-limited colloidal aggregation mechanism (Lin *et al.*, 1989). This evidence supports the idea that the amorphous structures we have observed are not artifacts resulting from sample preparation. It also proves the existence of a highly hydrated transient ACS phase during the bassanite $\rightarrow$ gypsum transition, which must be the same, or at least very similar in nature, as the widely reported ACS species that precedes the direct formation of gypsum from solution (Wang and Meldrum, 2012; Saha *et al.*, 2012; Jones, 2012; Zhang and Xue, 2020).

Moreover, TEM micrographs showed micron-sized mesocrystals composed of multiple nano-sized bassanite particles which were co-oriented, but slightly misaligned, along their *c*-axis direction (Figure 4.7a and c). This was confirmed by the SAED patterns in Figure 4.7b and d, where diffraction spots with angular spread ($\sim 10 - 12^\circ$) corresponding to the 004 and 400 reflections of bassanite (space group *I*2; Bezou *et al.*, 1995) were observed. Furthermore, STEM/EDX elemental mappings (Figure 4.7e-h) demonstrated that the organic additive remained adsorbed and/or occluded within the bassanite particles during aggregation and coarsening. This implies that the bassanite $\rightarrow$ gypsum transition follows a rather complex mechanism in the presence of calcein (and by extension, of other organics). Recently, Tritschler *et al.* (2022) elaborated a polymer/gypsum hybrid material *via* the hydration of disordered bassanite nanoparticles in the presence of a PBOx-Chol-COOH polymer. In their work, it was shown that the hydration of bassanite and formation of micron-sized gypsum aggregates occurred following an oriented attachment mechanism (*i.e.*, by the oriented aggregation of bassanite

nanoparticles and a subsequent fusion of particles) that could be assisted by the adsorbed polymer. Subsequently, under high humidity conditions (*i.e.*, ~100% RH) bassanite oriented aggregates transform into gypsum micron-sized crystals, where the polymer would be partially occluded between oriented crystalline domains. Herein, we observed the same effect.

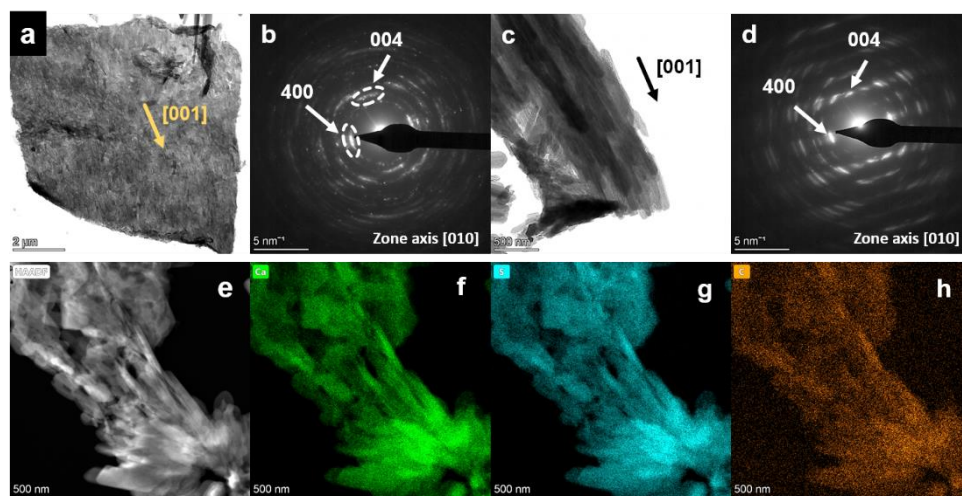


Figure 4.7. TEM photomicrographs of micrometric bassanite mesocrystals (a and c) formed *via* oriented attachment –facilitated by the adsorbed/occluded organic additive– during hydration under 100% RH conditions. SAED patterns showing preferred orientations confirm that one of the steps of the hydration of bassanite involves oriented attachment. STEM images and EDX elemental mappings (e-h) also demonstrate that the organic additive remains adsorbed/occluded within nanoparticles upon hydration.

These results show that the bassanite → gypsum phase transition occurs *via* a non-classical dissolution-precipitation mechanism, described as follows: (I) under high $p\text{H}_2\text{O}$ atmospheres, water is able to condensate on the surfaces of bassanite crystals, thus enabling partial dissolution (Putnis and Ruiz-Agudo, 2013); (II) the resulting solution is supersaturated with respect to gypsum and also contains calcein, which stabilizes PNCs and, subsequently, highly hydrated transient ACS nanodroplets; (III) the formation of fractal structures of ACS occurs through diffusion-limited colloidal aggregation; (IVa) mass transport and heterogeneous precipitation of ACS occurs on the tips of the pre-existent bassanite crystal, and after an amorphous-to-crystalline phase transition, the new calcein-loaded gypsum (*i.e.*, the most stable $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ phase under standard P and T and humid

conditions) grows epitaxially along the [001] direction of bassanite; (IVb) oriented attachment and fusion of bassanite nanoparticles mediated by organic additives to form micrometric bassanite mesocrystals. Further hydration would ultimately lead to the formation of gypsum microcrystals *via* the coupled dissolution-precipitation mechanism previously described.

Note that the hydration of bassanite to form gypsum is the main chemical process that leads to setting, cementation and hardening of gypsum-based building materials, and it is, in fact, the reason why we focused on producing organic-modified bassanite nanomaterials. Below the specific implications of fluorescent nano-bassanite hydration in the field of heritage conservation are further discussed.

3.5. Weathering Resistance

One major issue regarding gypsum-based building and decorative materials is the relatively high solubility of this material (*i.e.*, $\sim 2.5 \text{ g L}^{-1}$ at 25°C), especially in environments with marked and cyclical humidity variations. For this reason, we evaluated the effect of the intra-crystalline calcein in fully hydrated NB-C particles on their dissolution kinetics, as compared to both a geologic gypsum (GG) and a non-functionalized hydrated nano-bassanite (NB) control. Through bulk dissolution experiments in milli-Q grade deionized water ($\text{pH} \sim 6.25$, $T = 25^\circ\text{C}$) we analyzed the time variation of $[\text{Ca}^{2+}]_{\text{free}}$ (Figure 4.8). We observed that the dissolution rate of the hydrated NB-C, calculated as apparent dissolution rate constants, was lower ($k_{\text{NB-C}} = 1.315 \times 10^{-4}$) than those of the non-functionalized controls ($k_{\text{GG}} = 1.878 \times 10^{-4}$; $k_{\text{NB}} = 1.808 \times 10^{-4}$).

Moreover, in the case of the hydrated NB-C sample, the maximum (*i.e.*, asymptotic) $[\text{Ca}^{2+}]_{\text{free}}$ value reached was lower than that of the non-functionalized controls. In this case, complexation of Ca^{2+} by calcein might contribute to a lower measured $[\text{Ca}^{2+}]_{\text{free}}$. However, the molar amount of occluded calcein is extremely low (*ca.* 4.8×10^{-8} moles of calcein per 100 mg of fluorescent gypsum) as compared to the total amount of Ca in gypsum (*ca.* 5.8×10^{-4} moles of Ca per 100 mg of gypsum). For this reason, the decrease in the measured $[\text{Ca}^{2+}]_{\text{free}}$ and dissolution rate cannot be

solely attributed to complexation. It is thus likely that due to the short time-span of the dissolution experiment, the system did not reach equilibrium. Therefore, due to its slower dissolution kinetics, the maximum solubility of calcein-loaded gypsum was not reached.

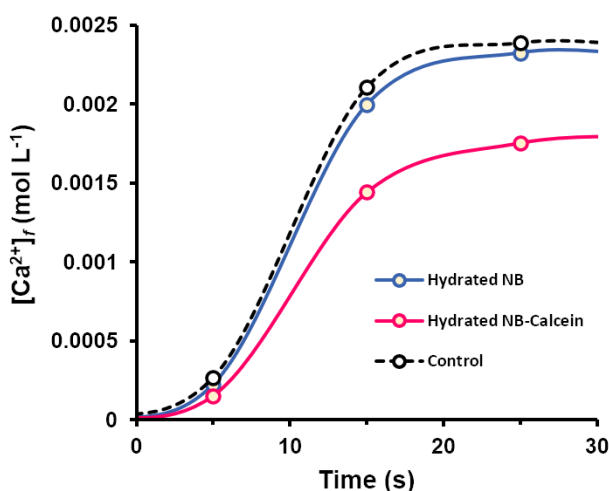


Figure 4.8. Time variation of the free Ca^{2+} concentration upon dissolution of gypsum formed after hydration of fluorescent nano-bassanite (red line, NB-C) as compared to gypsum formed after hydration of a non-functionalized nano-bassanite control (NB, blue line) and a geologic gypsum (GG, black line).

It is worth mentioning that occlusion of organics in calcium carbonate biominerals and their biomimetics has been reported to modify not only their physical-mechanical properties, but also their resistance to chemical weathering (*i.e.*, dissolution) (Rodriguez-Navarro *et al.*, 2023). A similar effect is apparently achieved here by the occlusion of calcein in gypsum crystals formed after calcein-containing nano-bassanite, explaining the observed reduction in dissolution rates. This effect has strong implications in heritage conservation as the use of calcein-inclusive nano-bassanite for the consolidation of historical gypsum plasterwork will not only enhance the mechanical resistance of treated substrates (see below), but also increase their weathering resistance.

3.6. Mechanical Properties of Calcein-Modified Gypsum

To investigate the effect of the occluded calcein on the mechanical properties, nanoindentation analyses were performed on {010} planes of both additive-including (GC-50 and GC-150) and non-modified (GG) gypsum crystals (see Experimental Section). Experimental L-D curves of calcein-containing gypsum microcrystals showed a clear concentration-dependent decrease of the reduced elastic modulus (E_r) and hardness (H) when compared to the values for the geologic gypsum control. The calculated E_r and H are shown in Table 4.1.

Table 4.1. Summary of the calculated reduced elastic modulus (E_r) and hardness (H) of additive-including (GC-50 and GC-150) and non-modified (GG) gypsum crystals. Nanoindentation measurements were performed on {010} planes. Error is represented as the standard deviation (σ) of 16 indentation measurements per sample type.

	E_r (GPa)	H (GPa)
GG	29.182 ± 0.993	1.770 ± 0.065
GC-50	7.728 ± 0.315	0.835 ± 0.029
GC-150	1.439 ± 0.110	0.201 ± 0.016

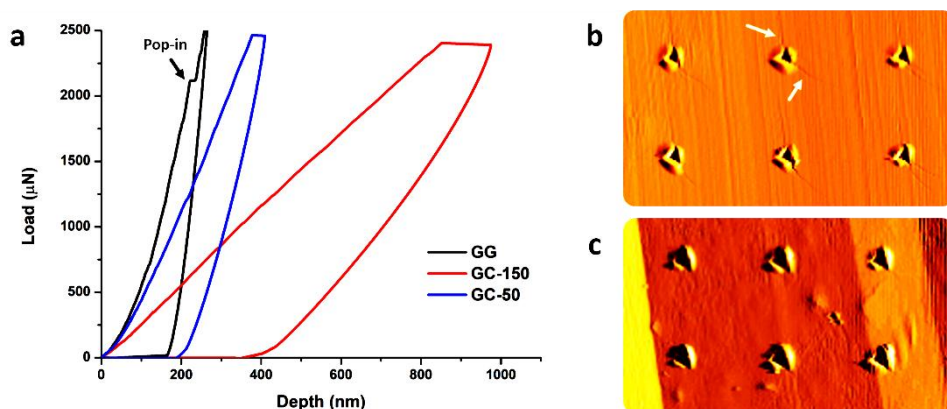


Figure 4.9. Representative Load-Displacement nanoindentation curves (a) obtained for additive-including (GC-50 and GC-150) and non-modified (GG) gypsum crystals and atomic force microscopy images of {010} surfaces of crystal samples after indentation (b,c). Note the variation of the slope of the loading and unloading curves, indicating that gypsum crystals become more plastic with the increase of calcein concentration. Note also that cracks (indicated by arrows) are observed in the AFM images of GG and GC-50 (b), but not in the case of GC-150 (c). This points to a concentration-dependent increase in the damage tolerance of crystals grown in the presence of calcein.

This implies that the additive modified crystals develop a more plastic behavior with increasing occluded calcein concentration and, therefore, they are more resistant to cracking. This latter effect was confirmed by atomic force microscopy imaging after indentation, revealing piling-up and micro-fractures in the case of GG and GC-50 crystals (*i.e.*, characteristic of brittle materials), but only piling-up without fractures was observed in the case of GG-150. Also, no pop-in was observed in the L-D curves corresponding to the organic-modified gypsum crystals, indicative of a greater toughness and a more progressive deformation behavior (*i.e.*, less brittleness). Overall, these effects induced by the presence of calcein should increase the damage tolerance of gypsum crystals towards structural stress and physical weathering phenomena (*e.g.* thermal expansion or pore-salt crystallization pressure).

3.7. Gypsum Plaster Consolidation Using Fluorescent Nano-Bassanite

Cubic plaster mock-ups (mimicking the historic Islamic gypsum plasters present at the Alhambra) were sprayed with ethanol dispersions of fluorescent nano-bassanite consolidants (with occluded calcein) on one horizontal face until saturation of the substrate was achieved (see details in the Experimental Section).

To verify the cementation and mechanical reinforcement effects of the produced fluorescent nano-structured bassanite particles once applied to the plaster substrate and converted into gypsum following hydration, we evaluated the penetration of the consolidant ethanolic dispersion by exposing treated, cured, and vertically fractured gypsum plaster specimens to UV light ($\lambda = 365$ nm). UV irradiation revealed the extent of penetration achieved by the fluorescent nano-bassanite particles, which reached a depth of approximately 4 mm within the porous gypsum plaster samples (Figure 4.10b).

TEM-EDX maps confirmed that calcein was homogeneously distributed inside the initial bassanite nanoparticles and the final gypsum crystals, which is the actual cementing phase obtained upon the hydration of bassanite. The insolubility of this dye in pure ethanol should prevent any desorption from the particle surface, if any

calcein were not only occluded but also adsorbed. These two factors play a pivotal role in ensuring that only the newly incorporated bassanite particles and their hydration product emit green luminescence, thus providing an effective strategy for easily monitoring the penetration capacity of the consolidant, which is a key factor in determining the efficacy of a consolidation treatment. Note also that the luminescence of calcein-containing gypsum would also enable to easily and non-destructively spot consolidated areas once the treatment is applied *in situ* by simply illuminating the surface with UV light (Price and Doehne, 2011).

Mercury intrusion porosimetry analyses were conducted on treated and cured (*i.e.*, following conversion of bassanite into gypsum) plaster samples (Figure 4.10c), revealing a 5% reduction in total porosity, as compared to the untreated control (*i.e.*, total porosity of treated and untreated samples being 47% and 53%, respectively). Furthermore, the median volume corresponding to pores with diameters of 7 μm experienced a sharp reduction, accompanied by an increase in the volume of pores with diameters of 2 and 4 μm , which is consistent with the partial filling-in effect of the treatment (*i.e.*, deposition of the newly-formed gypsum cement on the pore walls of larger pores, thereby reducing their diameter) (Burgos-Ruiz *et al.*, 2023). Additionally, these results demonstrate that there was no pore-clogging, thereby ensuring that the treated substrate is able to "breathe", that is, to maintain an appropriate water vapor permeability. This is critical to ensure physical compatibility of this consolidation treatment. Also, the chemical compatibility is fully ensured as both the consolidant and substrate are of similar composition and structure (*i.e.*, gypsum).

Drilling resistance measurements (Figure 4.10d) provided additional evidence for the effectiveness of the nano-bassanite consolidation treatments. The drilling resistance of treated and cured gypsum plaster increased over the first two millimeters of the drilling profile, reaching a maximum increment of $1.56 \pm 0.23 \text{ N}$ (*i.e.*, $279.31 \pm 26.44\%$) as compared with the untreated plasters. This increase in the mechanical strength is in good agreement with the reduction in total porosity and with the observed penetrability of the fluorescent consolidation treatment. It is also a proof that the transformation of nano-bassanite into gypsum during the

curing of the treated samples (a transformation that led to fluorescent gypsum as shown by the UV illumination), results in an effective consolidation.

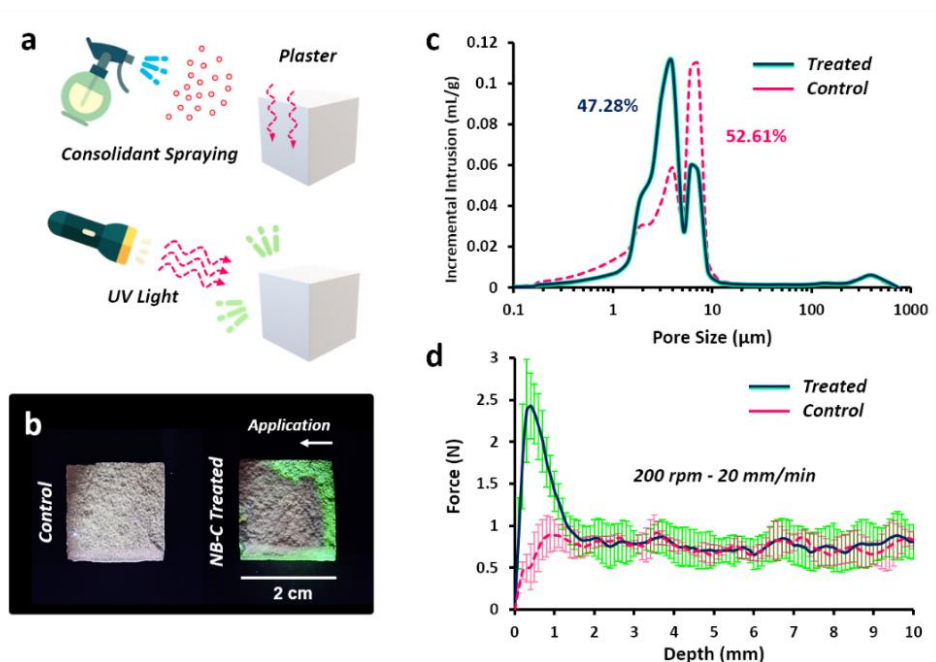


Figure 4.10. Consolidation treatment of gypsum plaster specimens using ethanolic suspensions of fluorescent nano-bassanite (a). Green luminescence under UV irradiation allowed to determine the degree of penetrability of the consolidant (samples were split in half to observe luminescence in their interior) (b), which ultimately produced a decrease of the total porosity of the treated plaster as show by MIP results (c) and an increase of the drilling resistance (d).

According to the nano-bassanite hydration results discussed above, cementation occurs through the sequential dissolution of bassanite and re-precipitation of gypsum. Because there is gypsum in the treated plasters, the heterogeneous regrowth of gypsum on such pre-existing gypsum crystals is also possible. In both cases, the bassanite $\rightarrow$ gypsum transition produces a lattice expansion accompanied by an increase in the molar volume, leading to a higher degree of structural compaction (La Bella *et al.*, 2023). Consolidation results and the functionalities imparted by calcein demonstrate the potential and efficacy of nano-bassanite as the first fully compatible (chemically and physically) consolidant for decayed gypsum plasterwork. Furthermore, luminescence tests carried out 10

months after application of the consolidant showed that the fluorescence of the calcein-modified nano-bassanite resisted chemical degradation after long periods of time (Figure A.7).

4. CONCLUSION

Herein we report a novel route for the synthesis of high specific surface area (SSA), rod-shaped bassanite nanoparticles following a one-pot, solvothermal route that involves the formation of amorphous Ca-ethoxide and its transformation into nano-bassanite after acid-base neutralization using concentrated sulfuric acid. The hydration kinetics study confirmed the exceptionally high reactivity of the synthesized nanomaterial as compared to a commercial control. The proposed solvo-thermal synthesis allowed for exhaustive control over the particle size and, to our knowledge, nano-bassanite produced this way shows the highest SSA ($54.2 \text{ m}^2 \text{ g}^{-1}$) described so far for this mineral phase. Similar features are obtained following the synthesis of nano-bassanite in the presence of a fluorescent calcein dye. Both nano-bassanite and, particularly, the novel functional fluorescent nano-bassanite are of special interest for applications in heritage conservation. In particular, by analogy to nanolimes having wide ranging applications in heritage conservation, the synthesized nano-bassanite can be dispersed in ethanol (e.g., $5\text{--}10 \text{ g L}^{-1}$) and applied (e.g., by brushing or spraying) as consolidant to decayed porous gypsum-based substrates.

The obtained results about the hydration and cementation of calcein-loaded nano-bassanite consolidants – produced through the above-described solvo-thermal synthesis method – furthers the gained insight on the crystallization mechanism of gypsum in the presence of calcein, previously presented in Chapter 3. In combination with these results, we propose that the bassanite $\rightarrow$ gypsum phase transition follows a non-classical dissolution-precipitation mechanism: In environments with high water vapor partial pressures, water condenses on bassanite crystal surfaces, facilitating partial dissolution. PNCs are stabilized by

calcein, which leads to the formation of highly hydrated transient ACS nanodroplets in a supersaturated regime. Mass transport and heterogeneous precipitation occur on the tips of existing bassanite crystals, with new calcein-loaded gypsum growing epitaxially along the [001] direction. At the same time, micron-sized bassanite mesocrystals are formed by the oriented attachment of calcein-loaded nanobassanite along [001]. Finally, the dissolution of bassanite would lead to the precipitation of gypsum, which is the most stable $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ phase under normal conditions of P and T .

We demonstrate that gypsum formed after hydration of calcein-containing nanobassanite particles showed increased dissolution resistance, whereas application of the fluorescent nano-bassanite consolidant to gypsum plaster mock-ups demonstrates excellent penetrability and good mechanical reinforcement. Furthermore, nanoindentation results demonstrated that calcein affected the mechanical properties of gypsum crystalized in the presence of this organic additive, resulting in a concentration-dependent decrease of both the reduced elastic modulus and hardness. Overall, calcein-containing gypsum crystals developed a more plastic behavior and higher tolerance to physical damage. Altogether, we show that this novel bio-inspired consolidation treatment is effective both from a physical-mechanical and chemical point of view, with (apparently) no detrimental drawbacks.

Ultimately, our work demonstrates the importance of investigating the intricacies of crystallization and phase transition mechanisms in the $\text{CaSO}_4\text{-H}_2\text{O}$ system, from nucleation to crystal growth, and how controlling these processes by including specific additives enables the design of advanced functional materials with tailored physical-chemical properties. In this particular case, we developed an effective and fully compatible consolidant for historic gypsum plasterwork, offering a facile and controlled strategy for enhancing gypsum plaster durability while enabling real-time monitoring of treatment efficacy.

CHAPTER 5. EXPLORING THE POTENTIAL OF SOLVO-THERMAL SYNTHESIS OF NANOPARTICLES FOR HERITAGE CONSERVATION

1. Introduction

2. Experimental Section

Detailed Synthesis of Nanolimes and TEOS-Nanolimes

Material Characterization

Carbonation of Nanolimes

pH, Colloidal Stability and ζ -Potential Measurements

Consolidation Tests

3. Results and Discussion

Characterization of Nanolimes

Colloidal Behavior of Nanolimes

Consolidation of Sandstone using Nanolimes

Mechanism of Carbonation and Consolidation

4. Conclusion

The work presented in this Chapter corresponds to the results published in Small (Burgos-Ruiz, M., Elert, K., Ruiz-Agudo, E., Cölfen, H., & Rodriguez-Navarro, C. (2023). Silica-Functionalized Nanolimes for the Conservation of Stone Heritage. Small, 19(33), 2300596).

1. INTRODUCTION

In the previous chapter, we showed that the newly developed solvothermal route for nanoparticle synthesis was highly effective for the preparation of nanobassanite, which proved to be an effective consolidant for gypsum plasters when applied as an alcoholic dispersion. As a follow up study, we further explored the possibility of using this route to synthesize other types of nanoparticles with the potential to be used in heritage conservation. In particular, our aim was to obtain effective nanoparticle-based consolidants that could be modified with specific functionalities. Considering that nanolimes have been developed as effective conservation materials for a range of substrates, our approach here was to prepare and evaluate calcium hydroxide nanoparticles that were functionalized during the synthesis route to overcome the shortcomings of standard nanolimes (*e.g.* back-migration). As a feasibility study, the newly synthesized and functionalized nanolimes were applied in a model porous substrate. Prior to application in gypsum plaster, we wanted to clearly visualize their penetration and consolidation capacity in a non-carbonate and non-sulfate substrate, where product development is difficult to evaluate due to compositional and textural similarities between consolidant products (*i.e.*, carbonates) and substrate. Therefore, in this preliminary study, the nanoconsolidant was applied to a porous silicate substrate (Prague sandstone). Ultimately, a full experimental plan will be designed to test the applicability of this novel nanoconsolidant for plasterwork.

The survival of our architectural and sculptural heritage greatly depends on the design of effective strategies to counteract the many menacing chemical, physical and biological alteration processes it faces, whether natural or anthropogenic in nature (*e.g.*, Rodriguez-Navarro and Sebastian, 1996; Rodriguez-Navarro and Ruiz-Agudo, 2018; Wrinkler, 1997; Warscheid and Braams, 2000; Jimenez-Gonzalez *et al.*, 2008; Price and Doehne, 2011; Schiro *et al.*, 2012; Vergès-Belmin, 2008). Over the last two decades, nanotechnology has contributed to the development of promising solutions for the protection and conservation of cultural heritage, among several other applications (Mosquera *et al.*, 2023). For this reason,

nanolimes (*i.e.*, calcium hydroxide nanoparticles) have been central for both scientists and conservators, as they provide an effective solution to the shortcomings of conventional consolidation treatments for porous substrates (*e.g.*, stone, mortars, ceramics, and wall paintings), specifically the usually poor compatibility, limited durability and effectiveness of synthetic polymers and alkoxysilanes (Lazzarini and Tabasso, 1998; Selwitz, 1992; Scherer and Wheeler, 2009; Baglioni *et al.*, 2021; Chelazzi *et al.*, 2018).

Nanolimes consolidate a porous substrate *via* reaction with atmospheric CO₂, forming CaCO₃ cement. This carbonation reaction also occurs during application of limewater (*i.e.*, a saturated Ca(OH)₂ aqueous solution), used as a traditional consolidant for centuries (Giorgi *et al.*, 2010; Favaro *et al.*, 2008). However, the low solubility of portlandite (Ca(OH)₂) limits its efficacy (Hansen *et al.*, 2003), as the use of large volumes of limewater is required to achieve a reasonable degree of consolidation. This is especially prohibitive in the case of water-sensitive substrates (Ashurst and Ashurst, 1988; Boynton, 1980). To overcome the limitations of limewater, alcoholic calcium hydroxide suspensions were introduced, containing larger amounts of consolidant and displaying good colloidal stability, low surface tension, and an acceptable penetration capacity in porous substrates (Rodriguez-Navarro *et al.*, 2013; Tomasin *et al.*, 2019). Their dispersion in aliphatic alcohols eliminates any possible water-related damage (*e.g.*, salt mobilization, or freeze damage). Aiming at producing nanosized, highly reactive Ca(OH)₂ crystals, Baglioni's group developed a homogeneous synthesis method to produce particles 50-500 nm in size (with a specific surface area, SSA, of up to ~35 m² g⁻¹), which are dispersed in ethanol or isopropanol and commercialized under the tradename Nanorestore® (Baglioni *et al.*, 1998, 2005 and 2005). However, this method involved tedious purification processes using water, which lead to particle coarsening (Rodriguez-Navarro *et al.*, 2016). This is an important drawback, because particles with larger sizes generally have lower SSA, reactivity and penetrability in a porous substrate. Ziegenbalg *et al.* (2005) patented a solvothermal procedure for the synthesis of nanolimes (though, conditions of synthesis were not specified) whereby highly reactive particles 30-300 nm in size (SSA of up to ~35-40 m² g⁻¹) are obtained and commercialized as alcoholic dispersions under the trademark

Calosil. While in the case of carbonate substrates (e.g., limestone, plaster, and marble) an adequate consolidation upon application of these nanolimes is often reported, some drawbacks have been encountered: (a) limited reactivity after particle coarsening during synthesis and purification; (b) poor penetration in porous substrates associated with back-migration of the nanoparticles during solvent evaporation; and (c) lack of proper bonding between the newly-formed CaCO_3 cement and silicate substrates (e.g., sandstone, tuff, granites or ceramics) (Rodríguez-Navarro and Ruiz-Agudo, 2018; Price and Doehne, 2011; Scherer and Wheeler, 2009; Rodríguez-Navarro *et al.*, 2013).

The potential use of $\text{Ca}(\text{OH})_2$ nanoparticles to capture gaseous pollutants (e.g., CO_2 or SO_2) has also prompted research into different methods to produce calcium and magnesium hydroxide nanoparticles. Kirchgessner *et al.* (1987, 1988 and 1995) patented a method for the synthesis of calcium hydroxide by slaking quicklime in the presence of calcium lignosulfonate. In this way, micrometric size portlandite aggregates with SSA of up to $40 \text{ m}^2 \text{ g}^{-1}$ were obtained for their use in SO_2 capture. More recently, the company Lhoist S.A. developed a high-yield industrial process for obtaining highly porous and reactive $\text{Ca}(\text{OH})_2$ particles by controlled hydration of calcium oxide using industrial hydrators and mill flash dryers (Lorgouilloux *et al.*, 2015 and 2016). The disadvantage of this method lies in the poor control over the particle size and the formation of large oriented aggregates, which cannot be re-dispersed in alcohol (Rodríguez-Navarro *et al.*, 2005). Also, the efficacy of this product is limited due to the formation of passivation layers that prevent complete reaction, making further purification steps necessary to reuse the unreacted material (Montes-Hernandez *et al.*, 2010).

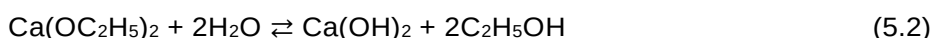
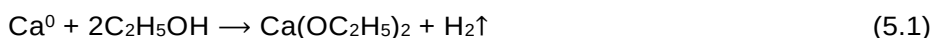
Here we report on a novel method to obtain silica-functionalized portlandite nanoparticles (Si-NL) showing well-developed (001) faces and plate-like morphology, minimal aggregation, and extremely high SSA, using a one-pot solvothermal synthesis procedure, originally developed by our group for the production of phase-pure bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) nanorods *via* hydrolysis of amorphous calcium ethoxide as the main intermediate species (Burgos-Ruiz *et al.*, 2021). This method solves several limitations of previous synthesis strategies, as it

has a high yield, does not require the removal of residual salts or additives, and allows for a circular production as all solvents can be distilled and recycled. In addition, it enables the simultaneous functionalization of the portlandite nanoparticles with silica-gel derivatives that are able to generate nano-cementitious CSH interfaces. These silica-functionalized nanolimes are very promising candidates not only for improved consolidation treatments in the field of heritage conservation, but also for other technical applications such as acid gas capture and storage, heterogeneous catalysis or the design of advanced building and biomedical materials (Bradley, 1989; Turova *et al.*, 1998; Mehrotra, 1988; Koper *et al.*, 1997). They could also have potential for the consolidation of damaged cement/concrete in modern construction, which is becoming the built heritage of the 19th and 20th centuries (Mosquera *et al.*, 2023).

2. EXPERIMENTAL SECTION

2.1. Detailed Synthesis of Si-NL and TEOS-NL

Portlandite Si-NL nanoparticles were obtained through a solvothermal route involving the formation of amorphous calcium ethoxide and its subsequent hydrolysis, as described by the following reactions (see Figure 5.1a below):



The overall synthesis consists of three consecutive stages performed in a single glass reactor (*i.e.*, one pot synthesis). Below we describe these stages for a typical synthesis run:

a) During the first stage (Equation 5.1), the irreversible redox reaction between 2 g of metallic calcium (99 %, granular, Scharlau) and 200 mL of absolute ethanol (Scharlau) takes place for 24 h at 78 °C under reflux condensation, anhydrous conditions, and constant magnetic stirring in a 500 mL glass reactor. This step results in a whitish ethanolic suspension of calcium ethoxide, which serves as initial precursor of the portlandite nanoparticles.

b) During the second stage, 80 mL of toluene (99.9 %, Scharlau) and 10 mL water are added (dropwise) into the previously obtained suspension. The hydrolysis reaction (Equation 5.2) progresses at 78 °C under continuous magnetic stirring for 55 minutes.

c) The final stage involves the separation of the portlandite nanoparticles from the mixture of solvents through rotary evaporation at 80 °C and ~7 mbar. The obtained solids are then oven-dried at 80 °C for at least 30 minutes and stored under N₂ atmosphere.

The yield of this typical synthesis run was $\geq 95\%$ as described below, with approximately 3.5 g of dry product obtained per experiment.

In an analogous way, TEOS-NL nanoparticles were prepared using the same methodology as previously described. However, in this case we performed the whole synthesis using Teflon® heat-resistant reactor and we additionally introduced 50 mg of pure TEOS during the first stage (99%, Sigma-Aldrich) per synthesis run.

The addition of TEOS seemed to hinder the total yield percentage of the synthesis by the inhibition of calcium ethoxide hydrolysis and/or by competition between different reactions involving the hydrolysis and condensation of TEOS units. For this reason, we incremented the reaction time during the second stage up to 70 min.

2.2. Material Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Panalytical X'Pert PRO diffractometer (Cu-K α radiation, $\lambda = 1.5405 \text{ \AA}$, voltage 45 kV, current 40 mA, and scanning angle ($^{\circ}2\theta$) 3-70°, steps of 0.001 $^{\circ}2\theta$ and goniometer speed of 0.01 $^{\circ}2\theta \text{ s}^{-1}$) to determine the mineralogical composition of the obtained products. The Scherrer equation was used to calculate the crystallite size of crystalline phases using the X PowderX software package.

Fourier transform infrared (FTIR) spectra of the dry powder were obtained using a JASCO FT/IR 6600 in ATR mode. The amount of unreacted calcium ethoxide, the purity of the material and the yield of the total reaction were calculated by means of thermogravimetry and differential scanning calorimetry (TG-DSC), using a Mettler-Toledo TGA/DSC 1 (temperature range 25 – 950 $^{\circ}\text{C}$, heating rate 10 K min^{-1} , in both air and N₂ at a flowing rate of 120 mL min^{-1}).

Micro- and nanostructural features were determined by means of high-resolution transmission electron microscopy (HR-TEM) using a FEI Titan S/TEM microscope (operated at 300 kV acceleration voltage). Powder samples were dispersed in

absolute ethanol and sonicated for 20 s before being deposited on carbon coated Cu grids. TEM photomicrographs were obtained using a 40 μm objective aperture. Detailed crystallographic information was obtained by measuring selected area electron diffraction (SAED) patterns collected using a 10 μm objective aperture. HAADF-STEM mode was used to obtain Z-contrast images and compositional EDX spectra and maps.

Solid-state ^1H and ^{29}Si nuclear magnetic resonance spectroscopy analyses, performed on a Bruker Advance III 400 solid-state NMR (gemma 400), allowed the structural assignment of the silica/CSH-enriched nanofilms for both non-carbonated and carbonated Si-NL nanoparticles.

Nitrogen adsorption-desorption isotherms were obtained at 77 K using a Micromeritics TriStar 3000, after degasification of samples at 90 $^{\circ}\text{C}$ and 0.2 atm for one day using a Micromeritics Flowprep. The Brunauer-Emmett-Teller (BET) model was used to calculate the specific surface area (SSA). Wavelength dispersive X-ray fluorescence (XRF) spectrometry analyses were performed on a Panalytical Zetium system in order to determine the average Si content (calculated as SiO_2 wt%) in the samples prepared using glassware.

2.3. Carbonation Process

The obtained Si-NL and Calosil dried powder samples were evenly distributed in plastic Petri dishes and stored under atmospheric $p\text{CO}_2$ and controlled T ($20 \pm 2^{\circ}\text{C}$) and relative humidity ($80 \pm 3\%$ RH) conditions. As the carbonation rate depends on $p\text{H}_2\text{O}$, a high RH was chosen to promote the carbonation process. In order to compare the carbonation rate of the two different samples, XRD measurements were performed periodically during one week. The portlandite-to-calcite ratio was calculated by the Reference Intensity Ratio (RIR) method.

2.4. pH, Colloidal Stability and ζ -Potential Measurements

Although pH measurements performed in non-aqueous environments are not reliable (*i.e.*, pH scale is only described for the autoprotolysis of water and its own equilibrium constant), we registered the apparent pH of both ethanolic and hydroalcoholic (*i.e.*, 50 % vol./vol.) dispersions of Si-NL using a calibrated Metrohm Ecotrode Plus 6.0262.100 coupled to a Metrohm 905 Titrando.

The relative colloidal stability of dispersions (either in pure ethanol or in 1:1 ethanol to water ratio) of Si-NL and Calosil was measured by continuously registering their optical density at 600 nm for a period of 1200 min, using a Varian CARY-5E UV-Visible spectrometer and standard plastic cuvettes with an optical path of 10 mm.

The ζ -Potential of Si-NL and Calosil was measured using a Particle Metrix ZETA-Check in order to get further insight into the colloidal behavior of the different samples. Particles were suspended in limewater (*i.e.*, saturated $\text{Ca}(\text{OH})_2$ solution) instead of pure water in order to minimize coarsening of particles mediated by dissolution and precipitation.

2.5. Consolidation Treatment with Nanolimes

The consolidation effectiveness of Si-NL was evaluated and compared to that of Calosil using Prague sandstone slabs (4×4×2 cm in size) as substrate. This quarzitic sandstone, profusely used in the sculptural and built heritage of Prague (Czech Republic), was chosen as it has a relatively large grain size (~200 μm), high total porosity (~29%), and lacks carbonates, so newly formed CaCO_3 mineral phases in the pore system can be recognized easily. Its relatively low strength also facilitates the detection of a consolidation-induced increase in mechanical strength. In addition, its silicate nature enables to gauge the effectiveness of nanolimes as a consolidant for non-carbonate substrates.

Nanolimes were applied to only one of the largest faces of the slabs in order to mimic *in situ* treatment conditions. Initially, 5 g L⁻¹ ethanolic dispersions of both products were prepared and applied ten times by brush until complete imbibition was achieved. Thereafter, more concentrated nanolimes (25 g L⁻¹) were applied four times. Upon completion, water was applied on the surface of treated sandstone slabs in order to induce coagulation of nanoparticles inside the treated material and hamper back-migration of the nanolime during solvent (ethanol) evaporation. Note that back-migration is a common and highly detrimental process during nanolime treatment application, which leads to the formation of thin surface layers that limits in-depth consolidation. Samples were cured in a plastic container (partially open to enable atmospheric CO₂ diffusion and nanolime carbonation) for two weeks at $\sim 20 \pm 2$ °C and $\sim 80 \pm 3\%$ RH. Each treatment was performed in duplicate for better representativity.

To track consolidant penetration, profile images of carbon-coated fracture surfaces (*i.e.*, fracture normal to the largest face of the prismatic samples) were obtained by means of scanning electron microscopy (SEM) using a FEI Quanta 650 FESEM microscope and a ThermoFisher Scientific Phenom XL G2 desktop microscope. To quantify the newly deposited calcium carbonate, thermogravimetric analyses of powder aliquots obtained from different depth levels of the treated and cured stones were performed.

A concentrated ethanolic phenolphthalein solution was sprayed on dried freshly fractured samples (two hours after the first treatment application) in order to evaluate back-migration of nanolimes and the influence of the water treatments on such a process.

Changes in total porosity and pore size distribution were determined by mercury intrusion porosimetry (MIP) using a Micromeritics Autopore III equipment. To examine the mechanical properties of untreated and treated samples, a SINT Technology drilling resistance measurement system (DRMS) was used, which enables obtaining DR values along a depth profile normal to the treated surface. The following parameters were used for drilling resistance measurements: 5 mm diameter drill-bit with a flat diamond head, 10 mm drilling depth, 20 mm min⁻¹

penetration rate, and 200 rpm rotation speed. At least four replicates per sample were performed.

Color changes were determined using a Minolta CM-700 spectrophotometer, equipped with a standard illuminant D65 and observer oriented at 10°, using the CIELAB color space. The total color difference, ΔE^* , originated by the consolidation treatment was calculated according to Equation 5.3:

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (5.3)$$

Where ΔL^* is the variation in luminosity (varying from black to white), and Δa^* and Δb^* are the changes in the color coordinates (red-green and blue-yellow respectively). Ten measurements were performed for each sample.

3. RESULTS AND DISCUSSION

3.1. Characterization of Si-NL

The X-ray diffraction (XRD) patterns of Si-NL show broad **00l** and **0kl** and narrow **h00** Bragg peaks of portlandite (***P*3̄m1**) indicating poorer crystallinity along the *c*-axis than along the *a*-axis (Figure 5.1b). This is consistent with Scherrer crystallite size measurements, yielding $D_{001} = 8$ nm and $D_{100} = 28$ nm. These results indicate that the Si-NL powder is composed of extremely thin hexagonal plates of about ten to fifteen unit-cells (measured along the **[001]** direction), which is in good agreement with the results obtained by transmission electron microscopy (TEM, see below).

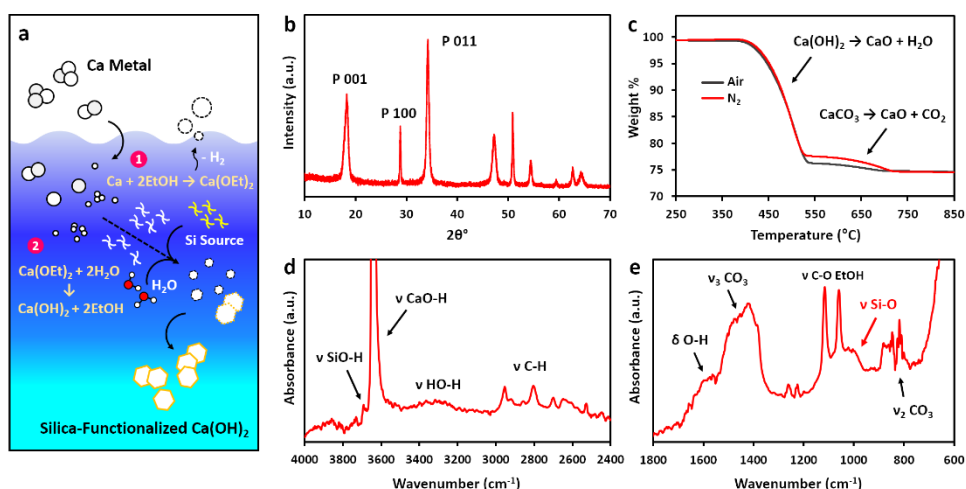


Figure 5.1. Synthesis schematic (a) and characterization of Si-NL. Broad 00l and 0kl Bragg peaks in the XRD patterns (b) confirm that Si-NL is composed of extremely thin portlandite plates. TGA (c) in both air (black) and N₂ (red) allowed to determine that the yield % of the complete synthesis was >95%. The FTIR spectra (d and e) revealed small amounts of unreacted calcium ethoxide (low-intensity sharp bands at 1114 and 1058 cm⁻¹) and silanol groups (broad Si-O stretching band at ~1000 cm⁻¹ and weak Si-O-H stretching peak at 3692 cm⁻¹), along with Ca(OH)₂ (sharp and intense O-H stretching band at 3642 cm⁻¹).

Fourier-transform infrared (FTIR) spectra of Si-NL (Figures 5.1d and e) showed an intense narrow band at 3642 cm⁻¹ associated with O-H bonds (ν O-H) in calcium

hydroxide, along with a band at 1650 cm^{-1} ascribed to the bending (δ O-H) of water, a broad band at 1440 cm^{-1} (ν_3 *asym.* CO_3) and a narrow band at 880 cm^{-1} (ν_2 *asym.* CO_3) corresponding to a small amount of amorphous calcium carbonate (ACC, formed during sample handling), consistent with the absence of calcite Bragg peaks in the Si-NL XRD pattern. Furthermore, traces of unreacted calcium ethoxide were identified as a band triplet of C-H bond stretch vibrations (ν C-H) at 2956, 2900 and 2800 cm^{-1} , along with a moderately intense C-O stretching doublet (ν C-O) in the fingerprint region at 1114 and 1058 cm^{-1} (Liu *et al.*, 2008). The presence of trace amounts of silica derivatives was confirmed by a low intensity broad band ranging from 960 to 1040 cm^{-1} and a low intensity peak at 3692 cm^{-1} , respectively, corresponding to Si-O (ν Si-O) and SiO-H (ν SiO-H) bonds in the silica coatings (Figures 5.1d and e) (Higl *et al.*, 2018).

Thermogravimetry (TGA) curves obtained both in air and N_2 permitted the calculation of the amount of unreacted calcium ethoxide in the final product (Figure 5.1c). Under inert N_2 atmosphere conditions, a weight loss of 24.00 wt% from 450°C to 600°C , associated with the endothermic dehydroxylation of calcium hydroxide ($\text{Ca}(\text{OH})_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$), and a small weight loss of 1.40 wt% from 600°C to 800°C , ascribed to the thermal decomposition of calcium carbonate ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$), could be observed. Under oxidizing conditions, in contrast, these endothermic processes resulted in mass losses of 22.80 wt% and 2.70 wt% respectively, indicating that the combustion of calcium ethoxide and the spontaneous carbonation of the originated calcium oxide ($\text{Ca}(\text{OCH}_2\text{CH}_3)_2 + 6\text{O}_2 \rightarrow \text{CaO} + 4\text{CO}_2 + 5\text{H}_2\text{O}$; $\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$) occurred simultaneously with the dehydroxylation of $\text{Ca}(\text{OH})_2$ (Rodriguez-Navarro *et al.*, 2016). The difference between the amount of decomposed CaCO_3 indicates that the synthesized nanolime was minimally carbonated (2.40 wt%) and contained a small amount of unreacted calcium ethoxide (4.70 wt%). The remaining wt% corresponded to pure portlandite (92.87 wt%) and adsorbed water (0.03 wt%). Considering that ACC originates from sample manipulation, a yield higher than 95% can be assumed.

TEM analysis (Figure 5.2a) revealed that Si-NL consisted of non-oriented aggregates (as shown by the angular spreading of the 110 reflections shown in the

SAED pattern (Figure 5.2a, inset) made up of crystalline and relatively monodisperse plate-like portlandite nanoparticles. The measured particle equivalent diameter (along the *a* or *b* directions) ranged from 20 to 120 nm and their widths (measured along the *c* direction) ranged from 5 to 25 nm, dimensions that are significantly smaller than those of commercial nanolimes. Scanning TEM (STEM) energy dispersive x-ray spectrometry (EDX) elemental maps and spectra were decisive to prove that silica accumulated on the surface of the produced $\text{Ca}(\text{OH})_2$ nanoparticles (Figures 5.2b and c). Further analyses performed on carbonated Si-NL (Figures 5.2d-f) showed that the silica coatings remained on the surface of newly formed calcite particles after carbonation, suggesting the formation of calcium silicate hydrate (CSH) interfaces.

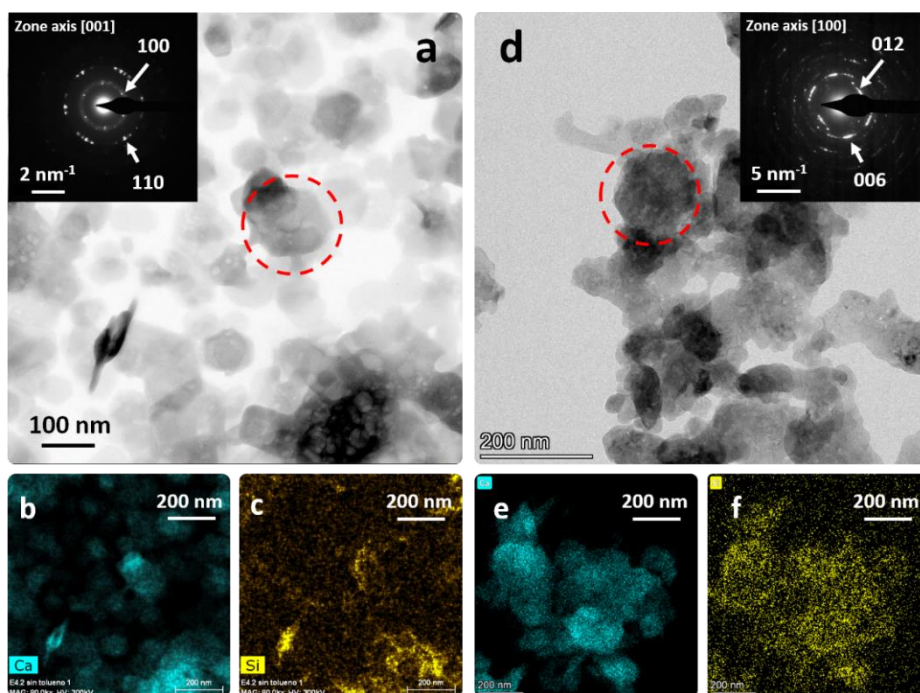


Figure 5.2. TEM and STEM photomicrographs and solid-state NMR spectra of non-carbonated and carbonated Si-NL. a) General overview and b) detail of non-oriented aggregates (as shown by the angular spread in the SAED (c)) of thin plate-like portlandite nanoparticles (20-120 nm in size) obtained through the solvothermal synthesis route. The STEM EDX elemental Si map (d) confirmed the presence of Si nanofilms covering the portlandite nanoparticles. Carbonation of Si-NL led to the formation of non-oriented calcite aggregates (e and f) that remained coated by the Si nanofilms even after CO_2 capture as shown by the Si and Ca/Si EDX maps (g and h).

Solid-state NMR results provided additional qualitative information about the chemical nature of the silica nanostructures. The ^{29}Si NMR spectra of both carbonated and non-carbonated Si-NL (Figures 5.3a and b) showed a broad band of moderate intensity at $\delta(^{29}\text{Si})$ ranging from -50 to -150 ppm, with a maximum at -108.1 ppm and a shoulder at -117.7 ppm corresponding to Q^3 and Q^4 -Si-O-Si- structures, respectively, typically ascribed to amorphous SiO_2 (*i.e.*, silica-gel). Additionally, a low intensity peak at -71.8 ppm alongside a shoulder at -82.5 ppm and a maximum at -92.6 ppm could be ascribed to Q^0 , Q^1 and Q^2 structural units, respectively, corresponding to CSH species (Walkley and Provis, 2019; Pustovgar *et al.*, 2016). Silanol and siloxane functional groups were also identified by the moderate intensity shoulder at -130.6 ppm and the low intensity peak at -146.2 ppm respectively.

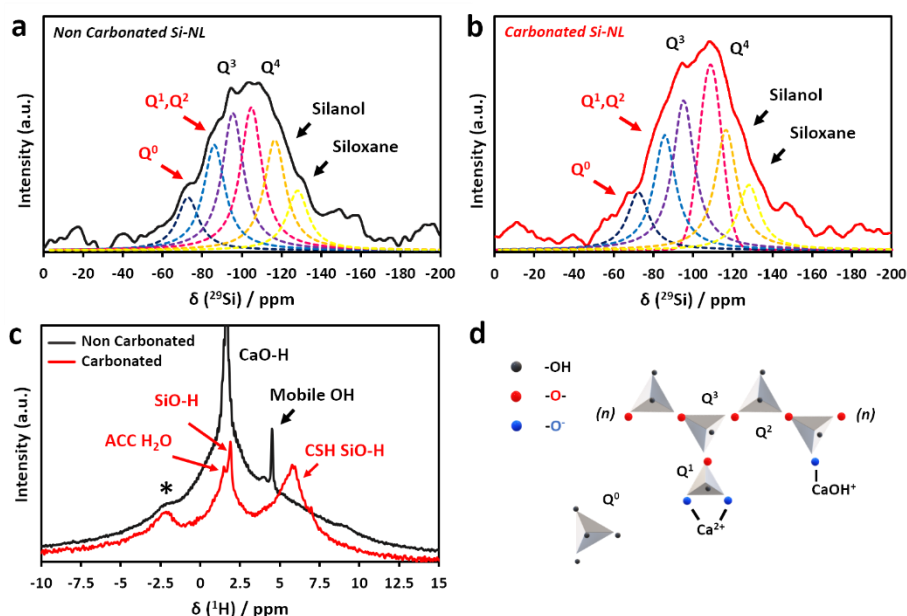


Figure 5.3. ^{29}Si solid state NMR spectra of non-carbonated (a) and carbonated (b) Si-NL demonstrating the presence of CSH (including Q^0 - Q^2 structural groups), and other silica derivative species (Q^3 - Q^4) originating $\delta(^{29}\text{Si})$ chemical shifts between -50 and -150 ppm. Deconvolution ($R^2\text{a} = 0.957$ and $R^2\text{b} = 0.945$) allowed to distinguish between Q^0 to Q^4 units, silanol and siloxane structural groups. Chemical shift $\delta(^1\text{H})$ signals in the NMR spectra (c) revealed that the composition of nanofilms evolved upon hydration and carbonation of Si-NL, leading to the formation of CSH phases (intense O-H band at +6.2 ppm). Negative NMR $\delta(^1\text{H})$ shifts (*) might correspond to spinning sidebands. The schematic in (d) represents the expected silica/CSH moieties present in the nanocoatings.

^1H NMR spectra (Figure 5.3c) for both samples suggest that nanofilms initially contained small amounts of CSH, as revealed by the peak at +6.2 ppm (CSH; Si-O-H bonds), which showed a significant increase in intensity after carbonation. This latter confirms that the concentration of CSH phases increases upon carbonation (see below).

XRF analyses of Si-NL and the calcium ethoxide precursor synthesized in a glass reactor (Table A.2) revealed that both contained Si in low concentrations of 0.01 and 0.02 wt% (measured as SiO_2 wt%), respectively. This means that SiO_2 lixiviation from glassware occurred not only during the hydrolysis of calcium ethoxide, but also during its formation. Silica lixiviation is due to the high pH reached during synthesis (note that silica solubility increases exponentially at $\text{pH} > 9$) (Crundwell, 2017). Because the $\text{Ca}(\text{OH})_2$ surfaces, and in particular the (001) faces (those with the highest development in the plate-like particles of Si-NL), are positively charged due to the presence of abundant $-\text{CaOH}_2^+$ surface species at alkaline pH, a strong interaction with negatively charged deprotonated silica derivatives takes place, resulting in the formation of silica-coatings on the portlandite nanoparticles (Zheng *et al.*, 2020; Rodriguez-Navarro *et al.*, 2017). This fortuitous silica functionalization of nanolimes is of special interest, as it opens up unexplored frontiers in the field of stone consolidation. For this reason, the synthesis was replicated using a Teflon reactor in the presence of pure tetraethyl orthosilicate (TEOS) to simulate the effect of the silica lixiviated from the glassware. The use of TEOS was preferred over other silicates (e.g., K_2SiO_3 or Na_2SiO_3) to avoid co-precipitation of non-portlandite solids during solvent evaporation, thus eliminating the need for further purification steps. In practice, 50 mg TEOS were added prior to the hydrolysis of calcium ethoxide, which resulted in a product (TEOS-NL) with similar characteristics as the one obtained *via* fortuitous silica functionalization, suggesting that controlled mass production of silica-functionalized nanolime is feasible (Figure A.8-11).

These observations suggest that the silica coating was key for the obtention of $\text{Ca}(\text{OH})_2$ plate-like nanoparticles with the smallest size and highest SSA of any existing nanolimes. Indeed, Kellermeier *et al.* (2010 and 2012) have shown that

trace amounts of silica (dosed as Na_2SiO_3) enabled the stabilization of prenucleation clusters (PNC, a few nm in size) and ACC nanoparticles *via* the formation of a surface coating that prevented further growth and transformation into crystalline CaCO_3 . It is, therefore, reasonable to assume that a similar effect was at work in our system during the formation of Ca(OH)_2 nanoparticles, limiting their growth and resulting in smaller size and extremely high SSA.

3.2. Colloidal Behavior of Si-NL

Optical density measurements showed high colloidal stability of all tested nanolimes when dispersed in ethanol. When water was added, Calosil nanoparticles started aggregating and settled within 450 min. Flocculation was much faster in the case of Si-NL, the particles only taking 60 min to form aggregates (Figures 5.4a and b). Two factors could have contributed to the sedimentation mechanism: On the one hand, the addition of water might have induced particle coarsening, leading to faster settling rates. However, this effect should be minor due to the relatively low solubility of Ca(OH)_2 . On the other hand, aggregation is strongly dependent on the electrical nature of the particle-fluid interface and changes in particle surface charge likely played an important role (Clogston *et al.*, 2010).

Electrokinetic analyses revealed that the ζ -potential of suspensions of nanolimes in limewater decreased from $+10.7 \pm 0.4$ mV to -2.1 ± 0.2 mV in the case of Calosil and Si-NL (Rodriguez-Navarro *et al.*, 2013), respectively, demonstrating that the silica nanocoating modified the surface charge and made the functionalized nanolimes more susceptible to aggregation in hydro-alcoholic solutions as compared to Calosil (Rodriguez-Navarro *et al.*, 2017). However, the colloidal stability of Si-NL in alcohol was not altered by the silica coating. Having the ability to induce on-demand sedimentation of nanoparticles inside a porous substrate by changing the dielectric constant (ϵ) of the carrier solvent right after applying the nanolime treatment, is an interesting result for practitioners working in the field of heritage conservation. In this way, the treatment efficacy can be maximized by preventing back-migration during solvent evaporation, which is one of the main

drawbacks of this type of consolidants, greatly contributing to the formation of poorly soluble CaCO_3 veils that cause dramatic color changes of the treated surface and limits in-depth consolidation (Lopez-Martinez and Otero, 2021; Normand *et al.*, 2020; Borsoi *et al.*, 2017).

Spraying a phenolphthalein solution on freshly fractured surfaces of consolidated sandstone slabs confirmed that the application of nanolimes resulted in a homogeneous distribution of the $\text{Ca}(\text{OH})_2$ nanoparticles inside the treated sandstone specimens immediately after application. However, the material underwent significant back-migration during solvent evaporation, being accumulated in a few mm-thick surface layer after only two hours (Figure 5.4 b-left image). This effect was substantially reduced, especially in the case of Si-NL, when water (*i.e.*, 5 mL cm⁻²) was applied on the stone surface minutes after the consolidation treatment (Figure 5.4b-right image). The beneficial effect of the water application was confirmed by TGA analyses of samples collected from the core of the treated specimens (*i.e.*, 1 cm depth), revealing that nanolimes were distributed throughout the porous sandstone specimens. Remarkably, the measured weight loss corresponding to CaCO_3 decomposition was approximately double in the case of samples treated with Si-NL than those treated with Calosil (Figure 5.4d), suggesting a more homogeneous distribution of Si-NL inside the porous system due to a more efficient aggregation after the application of water, while Calosil tended to form crusts on the treated surface.

3.3. Consolidation Tests

Mercury intrusion porosimetry (MIP) results showed a significant porosity reduction of 20.2% and 14.6% for Si-NL and Calosil treated sandstone, respectively, as compared to the untreated control (*i.e.*, total porosity of untreated control samples and specimens treated with Si-NL and Calosil being 28.7%, 22.9%, and 24.5%, respectively) (Figure 5.4e). Furthermore, the median pore size decreased from 40 μm (untreated control) to 30 and 20 μm upon treatments in the case of Calosil and Si-NL, respectively, as nanoparticles deposited and carbonated within the porous system. The volume corresponding to pores with diameters larger

than 100 μm also experienced a sharp reduction, consistent with the filling-in effect of the treatment.

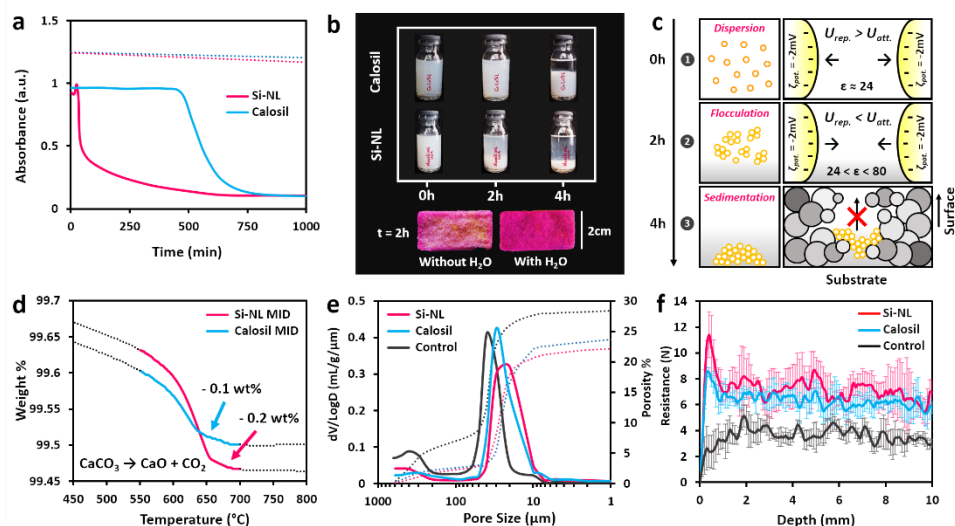


Figure 5.4. Colloidal behavior of Si-NL and Calosil hydro-alcoholic dispersions analyzed by optical density measurements (a and b). Dashed and solid lines in (a) correspond to dispersions in pure ethanol and ethanol-water, respectively. The phenolphthalein test (bottom images in (b)) demonstrated that the addition of water induced on-demand aggregation and inhibited back-migration, as detailed in the schematic (c). Consolidation effects of Si-NL treatments (red curves) on cured sandstone specimens as compared to Calosil treatments (blue curves) and an untreated control sample (black curve), measured by means of TGA (d), MIP (e) and drilling resistance (f), proving that silica-functionalized Si-NL distributed more homogeneously along the stone depth profile than Calosil (*i.e.*, double the amount of decomposed CaCO_3 (TGA results) in the core of sandstone samples treated with Si-NL), originating a sharper decrease in the total porosity and median pore size, and conferring a remarkable drilling resistance over the entire drilling profile (error bars indicate the St.Dev.).

Drilling resistance measurements provided additional proof for the effectiveness of the nanolime treatments. The drilling resistance of treated sandstone increased consistently over the whole drilling profile, by 3.51 ± 1.17 N ($101.5 \pm 33.8\%$) and 2.84 ± 0.80 N ($82.1 \pm 23.1\%$) in the case of Si-NL and Calosil, respectively (Figure 5.4f). The higher mechanical resistance shown by the sandstone specimens treated with Si-NL is in good agreement with the greater reduction in total porosity and the presence of silica/CSH interfaces acting as coupling agents between the newly formed CaCO_3 cement and the sandstone silicate substrate, also enhancing

the aggregation behavior of nanoparticles as previously mentioned (Zheng *et al.*, 2020).

Spectrophotometric results showed that the treatments affected the chromatic appearance of the stone surfaces due to the formation of a white veil, which led to an increase in luminosity (*i.e.*, ΔL^* values being 11.8 ± 1.9 and 12.4 ± 1.6 for Si-NL and Calosil treated surfaces, respectively), being the main cause of the overall chromatic changes (*i.e.*, ΔE^* values being 12.9 ± 1.1 and 13.3 ± 1.7 for Si-NL and Calosil, respectively). This is problematic, since conservation treatments should not produce visually detectable chromatic changes (*i.e.*, $\Delta E > 3.0$) (Schanda, 2007). Here, highly concentrated nanolime dispersions of up to 25 g L^{-1} were used to obtain a maximum strengthening effect. Therefore, to avoid the formation of white veils, the use of less concentrated dispersions and immediate elimination of excess surface deposits using a wet cloth is recommended, as it is routinely done by conservators applying nanolimes in the field (Otero *et al.*, 2022).

3.4. Mechanism of Carbonation and Consolidation

The comparison of the carbonation kinetics between Si-NL and the commercial Calosil nanolime revealed a much faster carbonation rate and a higher portlandite-to-calcite conversion efficacy of the former, being ~86% in the case of Si-NL and only ~40% in the case of Calosil after 72 h (Figure A.12). These are very promising results, as overcoming low conversion efficacy has been one of the most challenging issues in the development of commercial products for gas capture applications.

In the particular case of heritage conservation, fast carbonation is also a highly desirable feature for nanolimes, as it also ensures a rapid consolidation effect (Rodríguez-Navarro and Ruiz-Agudo, 2018). Remarkably, silica nanofilms did not reduce the reactivity of Ca(OH)_2 nanoparticles. In fact, these highly porous condensed polymeric silica species seemed to have contributed to a faster carbonation rate and better consolidation efficacy by a mechanism that implies enhanced water absorption and can be summarized as follows:

First, at high humidity conditions (80% RH), water condensates on the surface of Si-NL and is quickly absorbed by the highly porous silica nanocoating. This initial transport of liquid water allows the dissolution of the calcium hydroxide particles, leading to a pH increase and a partial dissolution of the silica coating. Subsequently, free Ca^{2+} interacts with the silica derivatives leached from the coating to form a CSH interface (Figure 5.5a) (Zheng *et al.*, 2020).

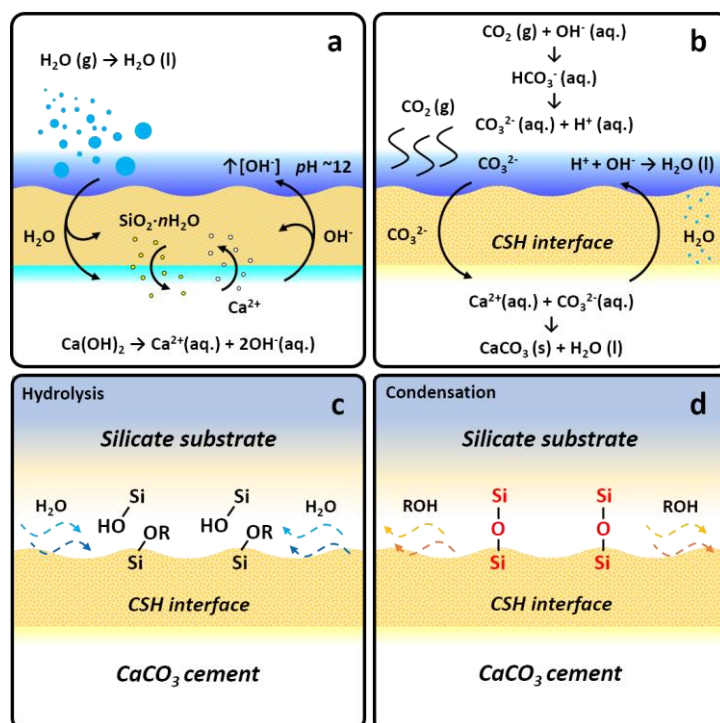


Figure 5.5. Schematic representation of the carbonation of Si-NL, and CSH formation. In a first stage (a) water condensates on the surface of Si-NL and penetrates through the porous silica nanofilm, facilitating the dissolution of calcium hydroxide. This phenomenon gives rise to an increase in pH and the free Ca^{2+} concentration, enabling the partial dissolution of the silica nanofilm and the precipitation of CSH phases. Afterwards, CO_2 is hydrated to HCO_3^{-} (b), which quickly dissociates to form CO_3^{2-} that interacts with free Ca^{2+} to precipitate CaCO_3 . Coupling of the Si-NL nanoparticles to the silicate substrate occurs *via* hydrolysis and condensation (c and d) of terminal silanol groups from both the substrate and the silica nanofilms covering the newly formed CaCO_3 cement.

In a second stage, atmospheric CO_2 capture is promoted by the high pH at the surface of Si-NL nanoparticles (pH ~ 12.4), proceeding *via* the formation of HCO_3^{-}

ions that readily dissociate to form H^+ that neutralize OH^- originated from the dissolution of calcium hydroxide, and CO_3^{2-} that interacts with the remaining free Ca^{2+} ions to form $CaCO_3$ (Figure 5.5b). It is not likely that the released product H_2O interferes with this process as water will diffuse out of the $Ca(OH)_2$ -solution interface through the porous Si-coating, allowing both the nanoparticles and the coatings to stay almost intact during carbonation. Indeed, product H_2O probably contributes to the progress of the carbonation reaction by enabling further dissolution of portlandite (*i.e.*, autocatalytic carbonation; Montes-Hernandez *et al.*, 2010).

Finally, in the case of silicate substrates (sandstone in this case), the silica nanofilm acts as a self-integrated coupling agent between the substrate and the $CaCO_3$ cement. New Si-O-Si covalent bonds are formed by the hydrolysis and condensation of terminal Si-OH groups from both the sandstone (*i.e.*, from mineral phases such as quartz and feldspar; Matison, 2012) and the silica/CSH covering the nanoparticles, conferring greater mechanical strength to the consolidated substrate (Figures 5.5c and d) as evidenced by the drilling resistance tests. This effect solves another important drawback of conventional nanolimes when used as consolidants, as $CaCO_3$ by itself would not establish covalent bonds with non-calcareous substrates such as sandstone, thus only acting as pore fillers (Wheeler, 2005). This effect also opens new possibilities for the consolidation and strengthening of other silicate-based building materials such as cement and concrete.

4. CONCLUSION

In this work we describe a novel and easily reproducible, high-yield solvothermal procedure for the synthesis of silica-functionalized nanolimes for their application as consolidants in the conservation and restoration of the built and archaeological heritage, involving the formation and hydrolysis of calcium ethoxide as the main intermediate species.

Based on FTIR, TEM, STEM/EDX and solid state ^{29}Si and ^1H NMR results we demonstrate that considerable amounts of different silica-derived species (*i.e.*, monomeric and/or polymeric), including CSH, silica-gel and siloxanes, accumulates on the surface of nanolimes in the form of a porous film that inhibited crystal growth upon adsorption on portlandite faces, thus limiting coarsening effects, irreversible oriented aggregation and allowing for a better control of the particle size. Altogether, these effects lead to the production of very small, plate-like portlandite nanoparticles, displaying surface area values nearly two times higher than those of commercial nanolimes.

Functionalization is a promising strategy to solve two of the most common handicaps of nanolimes when used as consolidants, including the control over back-migration and the lack of cohesion between the new CaCO_3 cement (*i.e.*, from $\text{Ca}(\text{OH})_2$ carbonation) and the treated substrate, typically diminishing the efficacy of the consolidation treatment.

Significant differences in the ζ -potential and kinetic stability between limewater suspensions of Si-NL and Calosil demonstrated that silica nanofilms affected the electrostatic nature of the surface of nanoparticles and their colloidal behavior. While pure calcium hydroxide particles (Calosil) showed high stability over time, Si-NL particles aggregated much faster when dispersed in a hydroalcoholic solution. However, they both showed a remarkable stability when dispersed in ethanol, which is a key feature for the proper application of nanoparticle-based consolidant treatments. Back-migration of Si-NL nanoparticles, one of the most important drawbacks of nanolimes, was drastically reduced by simply changing the dielectric

constant of the carrier solvent, inducing an effective on-demand aggregation of the particles, as shown by the phenolphthalein tests. TGA analyses of samples collected from the innermost part of the treated sandstone blocks confirmed that in the case of Si-NL, back-migration and the problematic accumulation of CaCO_3 near the surface was significantly reduced after the application of a small volume of water.

Furthermore, functionalization did not negatively interfere with the subsequent carbonation of the calcium hydroxide particles, but was even beneficial as the highly porous silica facilitated water absorption and the partial dissolution of $\text{Ca}(\text{OH})_2$, catalyzing the capture of CO_2 in the highly alkaline pore solution, fostering and the precipitation of CaCO_3 cement. Most importantly, it enabled the formation of silica/CSH interfaces, which acted as coupling agents between the consolidant and the treated silicate substrate by establishing strong covalent Si-O-Si bonds, as shown by the increase in the drilling resistance of the stone specimens treated with Si-NL.

Finally, the fortuitous silica functionalization set the fundamentals for the synthesis of TEOS-functionalized nanolimes in non-glass reactors, displaying similar features as those obtained using glassware. The latter demonstrates the enormous potential of this methodology for controlled and scalable industrial production of functionalized nanolimes with a huge added value. Although the effectiveness of this solvothermal route has been demonstrated for the synthesis of nano-bassanite and nanolime, it could be used for the synthesis of nanoparticles of any arbitrary chemistry. For instance, it would be worth to explore the potential for synthesizing other mineral nanoparticles (*e.g.*, calcium phosphate or magnesium carbonate), which might find effective application not only for heritage conservation, but also as a biomaterial in biomedicine, for example in bone grafting and regeneration/re-integration. Future research should be carried out to exploit different possibilities for the functionalization of these nanoparticles. For example, as demonstrated for the case of fluorescent nano-bassanite, calcein could be employed as well for the functionalization of nanolimes and/or other nano-structured materials with a particular scientific interest (*e.g.*, calcium phosphate).

CONCLUDING REMARKS

In this thesis, the different phase transitions and transformations in the $\text{CaSO}_4\text{-H}_2\text{O}$ system have been thoroughly explored. The main objective of the work performed was to relate the fundamental crystallography and physical chemistry characteristics of such a system with their direct applicability in the field of heritage conservation.

Here, a summary of the most relevant conclusions pertaining to the results discussed throughout this thesis is presented below, which are directly connected to the different hypotheses and objectives raised at the beginning of this project:

1. The dehydration of gypsum to form either bassanite and/or anhydrite is actually a topotactic process. However, this phase transition is greatly affected by particle (crystal) size. In the one hand, the thermal dehydration of millimetric gypsum single crystals results in the formation of bassanite/anhydrite aggregates with a low degree of orientation as a result of coupled dissolution-precipitation processes favored by the $p\text{H}_2\text{O}$ building-up in the interior of gypsum crystals. In the other hand, the *in situ* dehydration of micrometric crystals induced by the electron beam during TEM analysis showed that this transformation is perfectly topotactic, as demonstrated by the clear crystallographic control observed when comparing the SAED patterns of both parent gypsum and the resulting anhydrite pseudomorph, which diffract as single crystals. Analogously, the dehydration of bassanite to form insoluble anhydrite is also a topotactic process.
2. The re-hydration of millimetric gypsum pseudomorphs is affected by the presence (or absence) of untransformed gypsum. When calcination is incomplete, untransformed gypsum domains could serve as a template allowing the epitaxial growth of gypsum after the dissolution of bassanite/anhydrite, partially preserving the orientation of the original parent gypsum. However, when calcination is complete, the re-hydration

by dissolution-precipitation results in a gypsum crystal where new gypsum domains form after random non-epitaxial nucleation, thereby showing no preferred crystallographic orientation.

3. The crystallization of $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ is importantly affected by the presence of organic additives. In the specific case of the addition of calcein (or other additives, such as PAA) non-classical crystallization mechanisms govern the formation of calcium sulfate from solution. The stabilization of PNCs was demonstrated by means of the analysis of the time evolution of free Ca and transmittance measurements during titration experiments, and the formation of amorphous precursor phase (ACS) was later confirmed by means of cryo-TEM. This non-classic crystallization behavior is similar to that observed during the bio-mimetic production of other minerals, such as calcium carbonate or calcium phosphate.
4. The adsorption and intracrystalline occlusion of organic additives, such as calcein, greatly modify the morphology and physical-chemical properties of gypsum obtained using bio-inspired or bio-mimetic strategies. Additive-containing gypsum crystals developed resistance to both chemical (greater dissolution resistance) and physical weathering (greater physical damage tolerance).
5. Phase-selective methods can be effectively applied for the unambiguous production of calcium sulfate hemihydrate. The solvo-thermal synthesis protocol described in this work allowed to produce phase-pure nano α -bassanite with more than a 99% yield. Furthermore, this procedure was optimized for the chemical modification of nano-bassanite, thus allowing to produce fluorescent nano-bassanite by adding small amounts of calcein into the reaction medium. In this way, functional bassanite nanomaterials were obtained for their intended use as alcoholic suspensions for the consolidation of gypsum plasterworks.
6. The hydration of calcein-modified nano-bassanite occurs by a complex non-classical multi-stage mechanism involving: (a) the sequential

dissolution of bassanite and re-precipitation of gypsum; (b) the oriented aggregation of nano-bassanite units – facilitated by the adsorbed calcein – and their later fusion by dissolution of bassanite and precipitation of gypsum, to ultimately form gypsum single crystals.

7. Dissolution kinetics of hydrated fluorescent nano-bassanite is slower than that of non-modified hydrated nano-bassanite and geological gypsum. This is a major result that demonstrates that bio-inspired synthesis procedures are feasible to obtain calcium sulfate (and other minerals) materials with tailored properties, such as enhanced weathering resistance.
8. Alcoholic suspensions of nano-bassanite and calcein-modified nano-bassanite were demonstrated to be effective consolidants when applied in highly porous gypsum plasters. As a result, drilling tests showed that an overall strengthening effect ($279.31 \pm 26.44\%$; as compared with the untreated plasters) was achieved in the first two millimeters of the depth profile of plasters treated with the calcein-modified nano-bassanite. Additionally, MIP results demonstrated that there was no pore-clogging, thereby ensuring that the treated gypsum plaster is able to maintain an appropriate water vapor permeability.
9. The incorporation of calcein in the structure of bassanite and its hydration product might be an important tool for heritage conservation purposes. Since the fluorescent marker becomes occluded in the calcium sulfate crystals and does not significantly alter the organoleptic properties of the treated substrates, the identification of treated areas and the depth reached by the consolidant is enabled. Otherwise, it would be impossible to distinguish the spatial location of the newly-formed cementitious phase, since both consolidant and substrate consist of calcium sulfate.
10. The one-pot solvo-thermal synthesis protocol developed here for the production of nano-bassanite can be adapted for the production of other nanomaterials with a composition different to calcium sulfate. Here we used this method to obtain portlandite (calcium hydroxide, $\text{Ca}(\text{OH})_2$)

nanoparticles (*i.e.*, nanolimes), and demonstrated that further functionalization is possible. In particular, portlandite nanoparticles were functionalized with silica-gel/calcium silicate hydrate (CSH) nano-coatings in a single step.

11. Silica nano-coatings not only increase the carbonation rate of calcium hydroxide nanoparticles, but also allow to modify the colloidal behavior of such particles. When dispersed in solvents with a low dielectric constant (*e.g.*, ethanol), functionalized nanolimes are kinetically stable for long periods of time. Alternatively, when the dispersant has a greater dielectric constant (*e.g.*, water) functionalized nanolimes tend to quickly aggregate and sediment. In contrast, non-functionalized nanolimes have a lower kinetic stability in alcohols, and do not aggregate rapidly in contact with water. This functionalization enables on-demand aggregation (just by adding water) when nanolime dispersions are applied as consolidants on porous materials.
12. Colloidal stability modulation *via* functionalization is indeed critical to prevent back-migration phenomena, a problematic issue that typically hinders the potential of nanolime consolidation treatments for the conservation of building materials.
13. High-porosity CSH nano-coatings facilitate water absorption and the partial dissolution of $\text{Ca}(\text{OH})_2$, thus catalyzing the capture of CO_2 and fostering the precipitation of CaCO_3 cement and the formation of silica/CSH interfaces.
14. Alcoholic suspensions of silica-functionalized nanolimes were demonstrated to be effective consolidants when applied in highly porous materials, such as sandstone. Drilling tests showed that a good strengthening effect ($101.5 \pm 33.8\%$ increase, as compared with the untreated sandstone control) was achieved in the first two millimeters of the depth profile of the specimens treated with the silica-modified nanolimes.

CONCLUSIONES

En esta tesis se han explorado a fondo las diferentes transiciones y transformaciones de fase en el sistema $\text{CaSO}_4\text{-H}_2\text{O}$. El objetivo principal del trabajo realizado ha sido relacionar las características cristalográficas y fisicoquímicas fundamentales de dicho sistema químico con su aplicabilidad directa en el campo de la conservación del patrimonio.

A continuación se presentan las conclusiones más relevantes de los resultados discutidos a lo largo de esta tesis y que están directamente relacionadas con las diferentes hipótesis y objetivos planteados al inicio de este proyecto:

1. La deshidratación del yeso para formar bassanita y/o anhidrita es, de hecho, un proceso topotáctico. Sin embargo, esta transición de fases se ve muy afectada por el tamaño de partícula (cristal). Por un lado, la deshidratación térmica de monocristales milimétricos de yeso da lugar a la formación de agregados de bassanita/anhidrita con un bajo grado de orientación como resultado de procesos acoplados de disolución-precipitación favorecidos por el incremento de $p\text{H}_2\text{O}$ en el interior de los cristales de yeso debido a la liberación de agua estructural durante el proceso de deshidratación. Esto podría indicar que el proceso no es topotáctico. Sin embargo, la deshidratación in situ de cristales micrométricos inducida por el haz de electrones durante las medidas de TEM mostró que esta transformación es perfectamente topotáctica, como demuestra el claro control cristalográfico observado al comparar los patrones de SAED tanto del yeso como del pseudomorfo de anhidrita resultante, que difractan como cristales únicos. Análogamente, la deshidratación de la bassanita para formar anhidrita es también un proceso topotáctico.
2. La rehidratación de pseudomorfos milimétricos de yeso se ve afectada por la presencia (o ausencia) de yeso no transformado. Cuando la calcinación es incompleta, los dominios de yeso no transformado actúan como plantilla

permitiendo el crecimiento (auto)epitaxial del yeso tras la disolución de la bassanita/anhidrita, preservando parcialmente la orientación del yeso original. Sin embargo, una vez completada la calcinación, la rehidratación por disolución-precipitación del pseudomorfo da lugar a un cristal de yeso en el que se forman nuevos dominios de yeso tras una nucleación aleatoria no epitaxial.

3. La cristalización de $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ se ve muy afectada por la presencia de aditivos orgánicos. En el caso concreto de la adición de calceína (u otros aditivos, como el PAA), la formación de sulfato cálcico en solución está gobernada por mecanismos de cristalización no clásicos. La estabilización de PNCs se demostró mediante medidas de la evolución temporal del Ca libre y de la transmitancia durante los ensayos de valoración potenciométrica, y posteriormente se confirmó la existencia de una fase precursora amorfa (ACS) mediante cryo-TEM. Este comportamiento es similar al observado durante la síntesis biomimética de otros minerales, como el carbonato de calcio o el fosfato de calcio que siguen un proceso de cristalización no-clásico.
4. La adsorción y la oclusión intracristalina de aditivos orgánicos, como la calceína, modifican en gran medida la morfología y las propiedades físico-químicas del yeso obtenido mediante estrategias bio-inspiradas o biomiméticas. Los cristales de yeso obtenidos en presencia de calceína desarrollan una mayor resistencia al deterioro, tanto químico (mayor resistencia a la disolución) como mecánico (mayor tolerancia al daño físico).
5. Es posible obtener sulfato de calcio hemihidrato con un elevado rendimiento utilizando métodos de producción selectiva. El protocolo de síntesis solvo-termal descrito en este trabajo permite producir nano-bassanita (hemihidrato α) selectivamente con un rendimiento superior al 99%. Además, este procedimiento se optimizó para la modificación química de la nano-bassanita, permitiendo así producir nano-bassanita fluorescente mediante la adición de pequeñas cantidades de calceína en

un solo paso. De este modo, se han obtenido suspensiones alcohólicas de nano-bassanita para su uso como consolidantes para yeserías.

6. La hidratación de la nano-bassanita modificada con calceína se produce siguiendo un complejo mecanismo no clásico multi-etapa que implica: (a) la disolución secuencial de la bassanita y la re-precipitación del yeso; (b) la agregación orientada de unidades de nano-bassanita – facilitada por la calceína adsorbida – y su posterior fusión por disolución de la bassanita y precipitación del yeso, para formar finalmente monocristales de yeso.
7. La cinética de disolución de la nano-bassanita fluorescente hidratada es más lenta que la de la nano-bassanita sin modificar e hidratada, y que la del yeso geológico. Este resultado es importante, ya que demuestra que los procedimientos de síntesis bio-inspirados son factibles para obtener materiales de sulfato cálcico (y otros minerales) con propiedades a medida, como la mayor resistencia al deterioro.
8. Las suspensiones alcohólicas de nano-bassanita y nano-bassanita funcionalizada con calceína resultaron ser consolidantes eficaces cuando se aplicaron en yesos de elevada porosidad. Como resultado, las pruebas de resistencia a la perforación mostraron que se consiguió un efecto de consolidación adecuado (incremento de la resistencia a la perforación del $279.31 \pm 26.44\%$, en comparación con los yesos no tratados) en los dos primeros milímetros del perfil de profundidad de los yesos tratados con el consolidante de nano-bassanita fluorescente. Además, los resultados de MIP demostraron que no había obstrucción de poros, asegurando así que el yeso tratado mantuviese una permeabilidad al vapor de agua adecuada.
9. La incorporación de la calceína en la estructura de la bassanita y del yeso resultante de su hidratación podría ser una estrategia importante para la conservación del patrimonio. Dado que el marcador fluorescente queda ocluido en los cristales de sulfato cálcico y no altera significativamente las propiedades organolépticas de los sustratos tratados, se posibilita la identificación de las zonas tratadas y de la profundidad alcanzada por el

consolidante. De lo contrario, sería imposible distinguir la localización espacial de la fase cementante recién formada, ya que tanto el consolidante como el sustrato están formados por sulfato cálcico.

10. El protocolo de síntesis solvo-termal aquí desarrollado puede adaptarse para la producción de otros nanomateriales de composición diferente al sulfato de calcio. Así, se ha utilizado este método para obtener nanopartículas de portlandita (hidróxido de calcio, Ca(OH)_2) (*i.e.*, nanocales), demostrando que es posible su posterior funcionalización. En concreto, estas nanopartículas fueron funcionalizadas con recubrimientos nanométricos de gel de sílice/silicato de calcio hidratado (CSH) en un solo paso de síntesis.
11. Los recubrimientos de sílice no sólo permiten aumentar la velocidad de carbonatación de las nanopartículas de hidróxido de calcio (dada su elevada área superficial específica), sino que también permiten modificar el comportamiento coloidal de dichas partículas. Cuando se dispersan en disolventes con una constante dieléctrica baja (*e.g.*, etanol), las nanocales funcionalizadas son cinéticamente estables durante largos periodos de tiempo. En cambio, cuando el dispersante tiene una constante dieléctrica mayor (*e.g.*, agua), estas partículas tienden a una rápida agregación y sedimentación. Por el contrario, las nanocales no funcionalizadas tienen una menor estabilidad cinética en alcoholes, y no se agregan tan rápidamente en contacto con el agua. De esta forma es posible inducir la agregación de las partículas de nanocal bajo demanda, lo que tiene implicaciones muy importantes en la mejora de la efectividad de estas como consolidante.
12. La modulación de la estabilidad coloidal a través de la funcionalización es fundamental para evitar los fenómenos de retroceso (migración de nanopartículas hacia la superficie tratada durante la evaporación del disolvente -alcohol-), una problemática que suele obstaculizar el potencial de los tratamientos de consolidación con nanocales para la conservación de materiales de construcción.

13. Los recubrimientos de CSH de alta porosidad facilitan la absorción de agua y la disolución parcial de $\text{Ca}(\text{OH})_2$, catalizando, por un lado, la captura de CO_2 y fomentando la precipitación de CaCO_3 cementante y, por otro lado, la formación de interfases de sílice/CSH.
14. Las suspensiones alcohólicas de nanocales funcionalizadas con sílice resultaron ser consolidantes eficaces para su aplicación en materiales muy porosos, especialmente aquellos no carbonáticos (en los que es difícil establecer enlaces entre el sustrato y el consolidante de nanocal), como es el caso de la arenisca. Las pruebas de perforación han mostrado que se consigue un buen efecto consolidante (incremento de la resistencia al taladrado del $101.5 \pm 33.8\%$, en comparación con el control de arenisca no tratada) en los dos primeros milímetros del perfil de profundidad de las muestras tratadas con el consolidante funcionalizado.

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APPENDICES

FIGURES

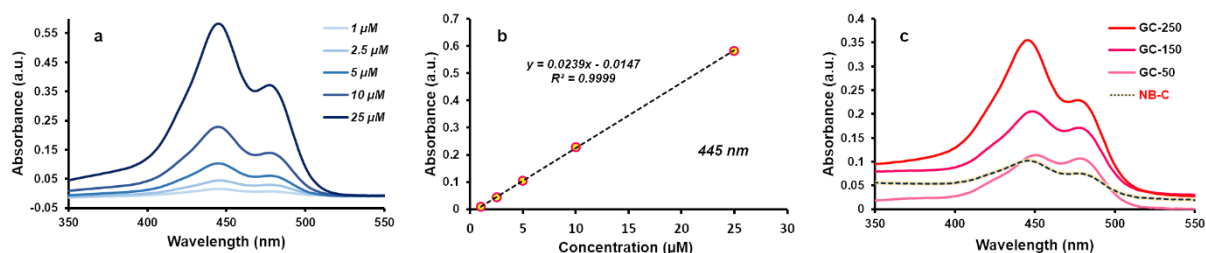


Figure A.1. UV-Vis analysis of bleached and dissolved fluorescent gypsum crystals and nano-bassanite. The calibration curve (a, b) was obtained by measuring the absorbance maxima at 445 nm of aqueous solutions with increasing concentrations of calcein (i.e., 1 to 25 μM calcein; HCl, 3 M buffer). The Beer-Lambert equation was used to calculate the concentration of calcein occluded in the obtained fluorescent calcium sulfate samples (i.e., fluorescent gypsum crystals, GC-50, GC-150, GC-250; and fluorescent nano-bassanite NB-C), using the same absorbance maxima as previously mentioned (c).

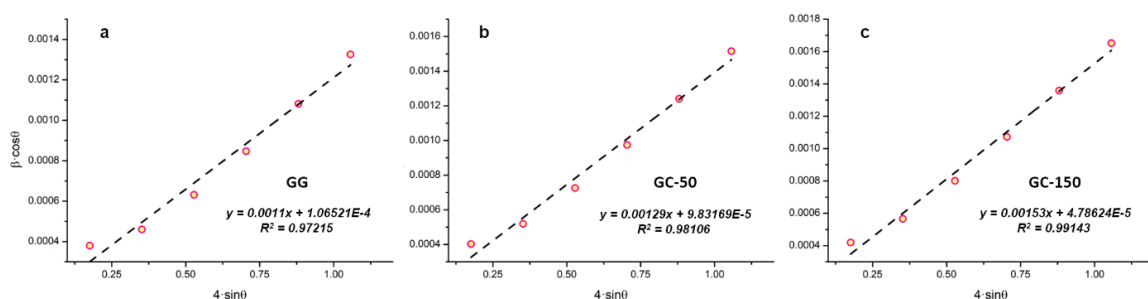


Figure A.2. Williamson-Hall plot of six-order $0k0$ Bragg reflections from synchrotron HR-XRD refined profiles of (a) geologic gypsum control (GG), (b) GC-50 and (c) GC-150 samples. Linear fitting was used to calculate the microstrain and crystallite size values reported in Table 3.1 (see Chapter 3).

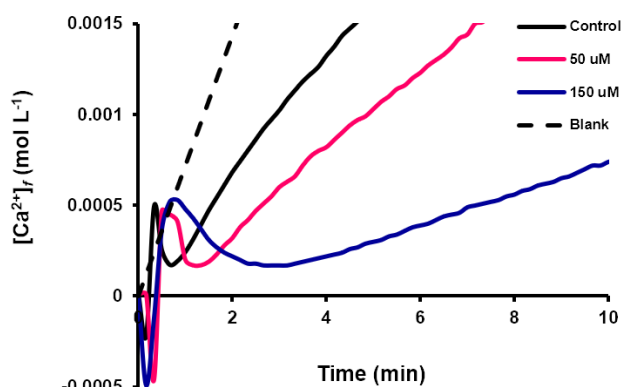


Figure A.3. Time development of the free Ca^{2+} concentration during the first minutes of gypsum precipitation experiments in the absence (black line, control) and presence of calcein (red line, 50 μM ; blue line, 150 μM), in comparison with the total dosed Ca^{2+} concentration (dashed line). Note that the increase of the measured free Ca^{2+} concentration is delayed up to ~ 0.8 and ~ 2.2 min when the initial calcein concentration was 50 and 150 μM , respectively. *Signal fluctuations in the first recorded data points are probably induced by the sudden addition of Ca^{2+} ions into the solutions.



Figure A.4. Preparation of the gypsum plaster mock-ups used for the assessment of the consolidation efficacy of the prepared fluorescent nano-bassanite consolidant ethanolic suspensions. These specimens were prepared and cured at the plasterwork workshop of the Council of the Alhambra and Generalife. a) Mixing of bassanite with water; b) Pouring of the fresh paste into the mold; c) Final plaster board.

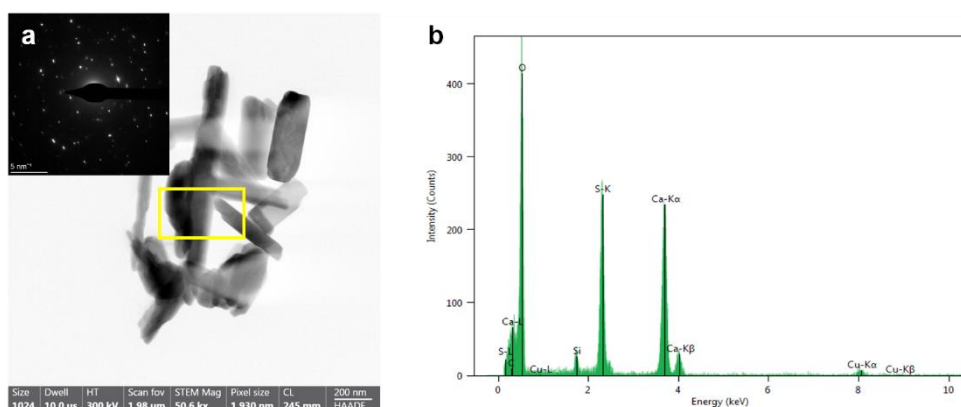


Figure A.5. Additional S/TEM (a) and EDX (b) analysis of fluorescent nano-bassanite. The obtained SAED (inset in a) indicates that the resulting product consists of pure-phase bassanite aggregates of nanosized particles. The EDX spectrum corresponds to the selected area indicated in (a).

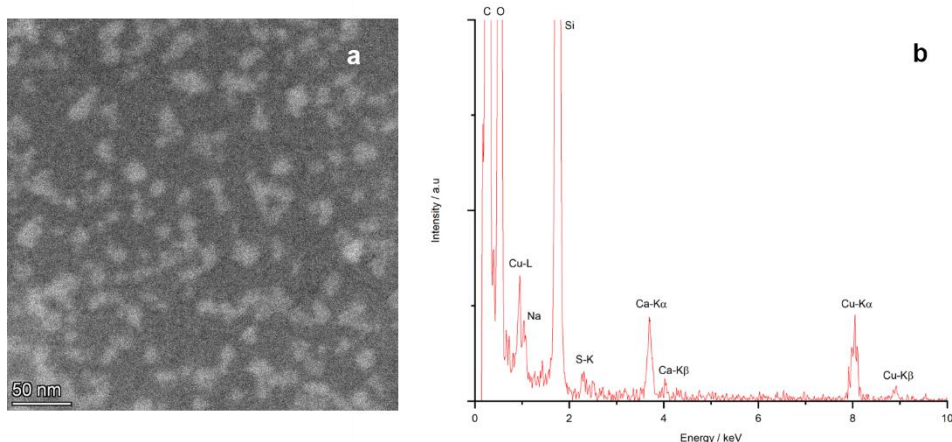


Figure A.6. S/TEM photomicrograph (a) and EDX spectrum (b) of amorphous calcium sulfate nanodroplets/fractals observed by plunge-freezing and vacuum-drying aliquots of supersaturated CaSO_4 aqueous solutions containing 5 ppm of poly(acrylic acid). Note that we used this additive as a proxy for calcein. Note that the Si and Cu peaks corresponds to the signal from the EDX detector and the Cu grid, respectively. The Na signal corresponds to the background electrolyte.

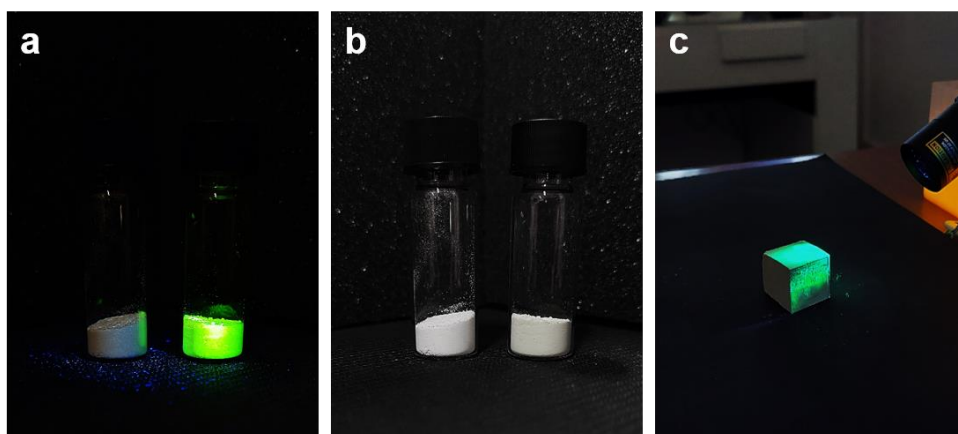


Figure A.7. Photographs of powdered fluorescent nano-bassanite consolidants as compared to a non-fluorescent gypsum powder (a, b). Note the intense green luminescence under UV radiation (a) and that color is not drastically affected by calcein, in low doses under standard white illumination (b). An example of treatment detection is indicated in (c).

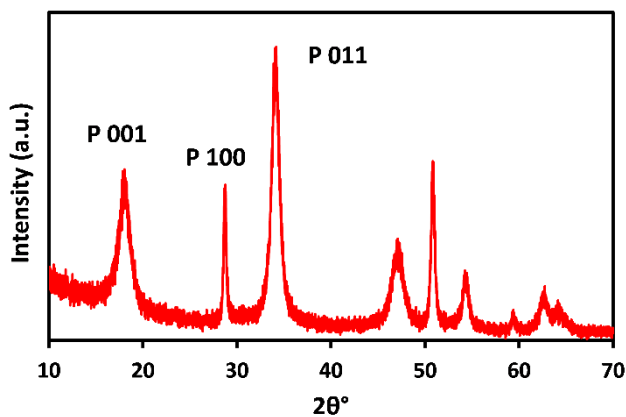


Figure A.8. Powder XRD pattern of TEOS-NL dried powder samples.

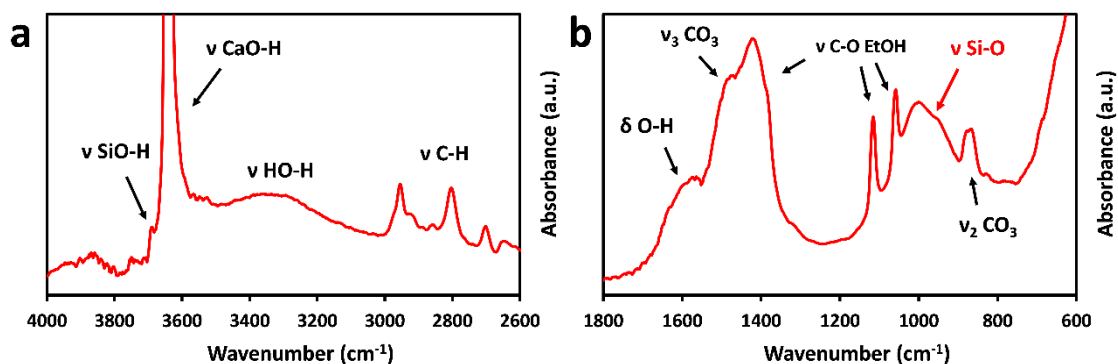


Figure A.9. Detailed FTIR spectra of TEOS-NL powder samples.

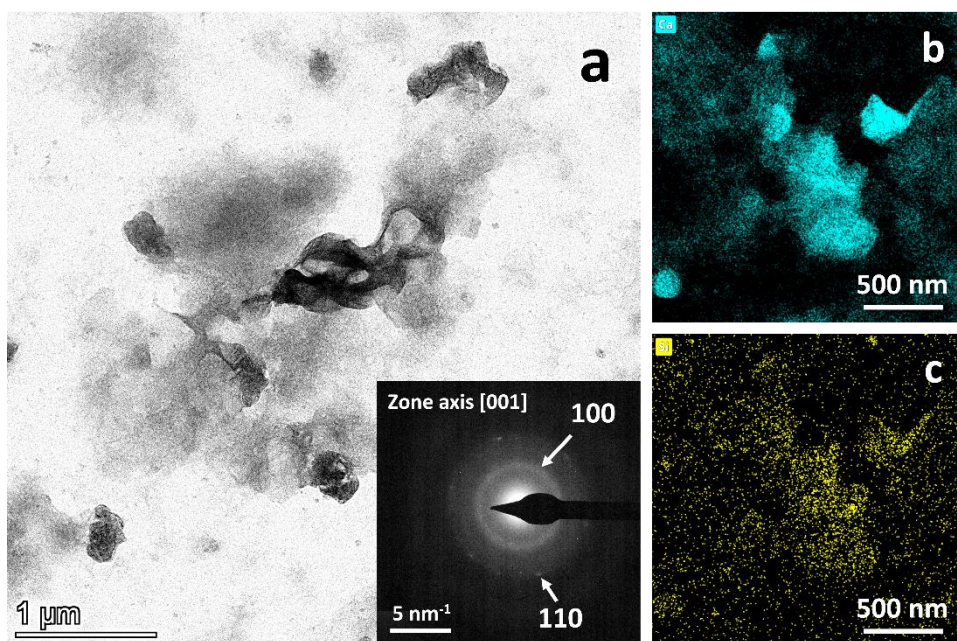


Figure A.10. TEM and STEM characterization (a-c) of TEOS-NL. Note that it is evidenced that Si-enriched compounds tend to concentrate at the particles edges (c). Elemental Ca map (b) included for reference

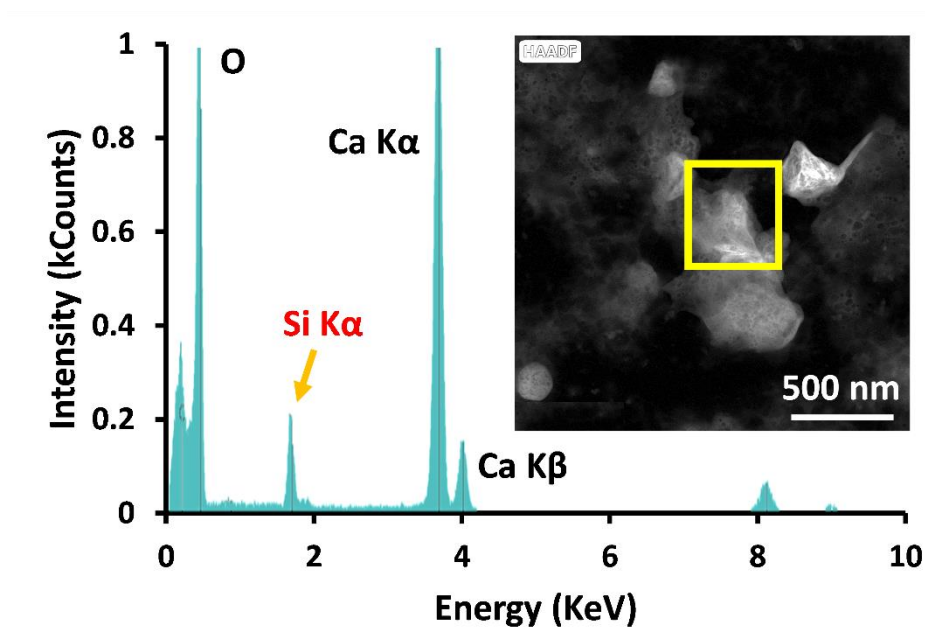


Figure A.11. EDX spectrum obtained for aggregate of TEOS-NL nanoparticles in the squared area of the HAADF image (inset), where a significant concentration of Si is detected by the moderate intensity Si-K α signal at 1.739 keV.

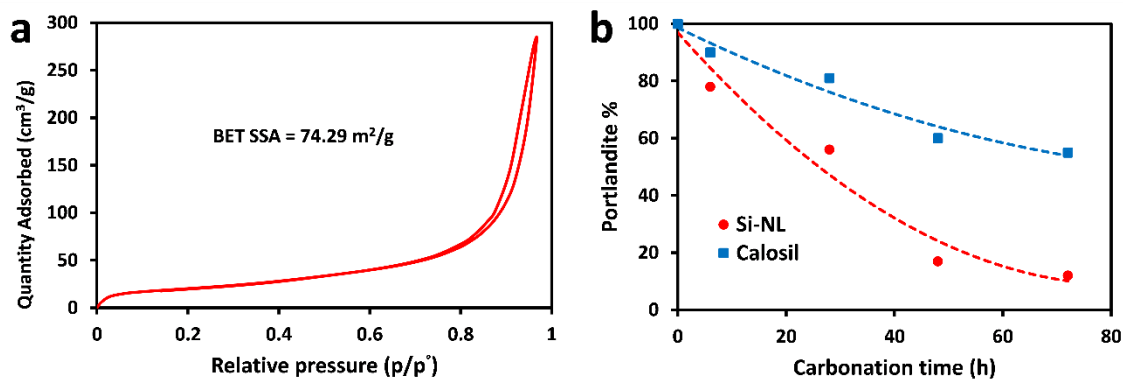


Figure A.12. N₂ sorption isotherm of Si-NL (a) and carbonation kinetics followed by periodical XRD measurements (b) of Si-NL as compared to Calosil. Note the almost complete carbonation of Si-NL (red curve) within 72 h. Dashed curves represent best exponential fits to the experimental values.

TABLES

Table A.1. Quantification of the occluded calcein content in fluorescent gypsum (GC) precipitated in the presence of different concentrations of calcein (50, 150, and 250 μM) and fluorescent nanobassanite (NB-C) samples as calculated using the Beer-Lambert equation. *Error is represented as the standard deviation for three replicates of the UV-Vis absorbance measurements.

	Abs. (a.u.)	Calcein Conc. (μM)	n (μmol)	Calcein Load ($\mu\text{mol}/\text{mg}$)	Calcein Load ($\mu\text{g}/\text{mg}$)
NB-C	0.101 ± 0.001	4.841 ± 0.042	0.009682 ± 0.000084	0.0004810 ± 0.0000042	0.299447 ± 0.002615
GC-50	0.108 ± 0.0006	5.148 ± 0.024	0.010296 ± 0.000048	0.0005148 ± 0.0000024	0.320489 ± 0.001494
GC-150	0.200 ± 0.003	8.997 ± 0.105	0.017994 ± 0.000210	0.0008997 ± 0.0000105	0.560108 ± 0.006537
GC-250	0.350 ± 0.003	15.273 ± 0.135	0.030546 ± 0.000270	0.0015273 ± 0.0000135	0.950821 ± 0.008404

Table A.2. XRF Analysis of Si-NL dried nanoparticles.

	SiO ₂ (wt.%)	CaO (wt.%)	SO ₃ (wt.%)	LOI (wt.%)	Sr (ppm)	Br (ppm)	Ni (ppm)	Cu (ppm)	Cl (ppm)
Si-NL	0.02	74.42	0.01	25.4	286	12	32	131	986