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Calcium sulfate precipitation pathways in natural and engineering environments

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Abstract

The solution-mediated formation of calcium sulfate minerals, i.e. gypsum, anhydrite and bassanite, is a common process in both natural and engineering settings. It plays a key role in the global sulfur cycle and serves as an indicator of past environmental conditions on Earth and Mars. Products relying on the crystallization of these minerals have been employed since antiquity, and today they are an essential part of a wide array of industrial applications. Accordingly, the fundamental aspects

of calcium sulfate mineralization have been the focus of intensive research during the past century. However, a recent flurry of studies addressing alternative, i.e. non-classical, nucleation and growth mechanisms has spurred a revisit of the precipitation pathway of the most common phase, gypsum. The newly obtained data sketch a far more complex picture of the mineralization process than previously assumed. This has important consequences for the interpretation of calcium sulfate deposits, both from a geochemical and industrial point of view. In order to shed light on this issue, we discuss in this review both recent and long-standing observations of abiotic formation routes of calcium sulfate minerals as a function of the physicochemical solution properties. By integrating both the classical and non-classical perspectives on crystallization we put forward a unified model for calcium sulfate crystallization. Using this model, we (re)-evaluate the phase stability and transformations taking place in the $\text{CaSO}_4\text{-H}_2\text{O}$ system. Next, we look into the formation of calcium sulfate minerals occurring in close association with the biosphere. Employing the abiotic case scenario as a benchmarking tool, the possible influence and/or control exerted by biological activity (and its byproducts) on the precipitation pathway is critically reviewed. Finally, we point out the central issues that need to be resolved if we wish to fully understand and control the formation of calcium sulfate solids in natural and engineering environments.

1. Introduction

1.1. The $\text{CaSO}_4\text{-H}_2\text{O}$ system

Calcium sulfate comprises a group of minerals commonly found in natural and engineering environments. When CaSO_4 is precipitated from aqueous solutions three crystalline phases can be obtained (Fig. 1): gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$), bassanite

($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) and anhydrite (CaSO_4). The intersection of the solubility curves of the different hydrates defines the thermodynamic stability field when precipitated from aqueous solution. The $\text{CaSO}_4\text{-H}_2\text{O}$ diagram shown in Fig. 1 tells us that at low temperatures (<40-60 °C) monoclinic gypsum is the most stable phase, while at higher temperatures, up to 1200 °C, orthorhombic anhydrite phase dominates. Bassanite (also called hemihydrate) is the more soluble calcium sulfate phase, and is thus metastable in aqueous solutions (and high humidity environments). Precise knowledge of the transition temperatures is paramount to understand for example under which environmental conditions evaporites formed in past time, or for optimizing the production/application of calcium sulfate-based materials in industrial processes e.g. for construction. Despite the ubiquity of calcium sulfates and many years of research devoted to these materials, a considerable spread of the solubility data still exists for all three phases (Fig. 1). This results in a marked uncertainty in the transition temperatures of the different calcium sulfate phases. This will be discussed in more detailed in section 2.3.

Besides the above-mentioned three main CaSO_4 phases, other polymorphs of anhydrite and bassanite are reported. In engineering environments hemihydrate, is often sub-divided into α -hemihydrate and β -hemihydrate. The latter is commonly known as Plaster of Paris (see section 1.3). Apart from differences in crystal habit, average size, and the preparation method, the existence of truly structurally distinct bassanite polymorphs is still a matter of debate (e.g. Follner et al. 2002; Singh and Middendorf, 2008; Weiss and Bräu, 2009; Christensen et al., 2010). The formation of α -hemihydrate occurs by dehydrating gypsum in the presence of electrolytes in acidic solutions/slurries, in water or in steam at the atmospheric pressure, or alternatively through direct precipitation by mixing Ca and SO_4 containing solutions at high

temperatures ($>80\text{ }^{\circ}\text{C}$, see section 2.3). On the other hand β -hemihydrate is obtained when gypsum is heated with little or no water vapor present. If this dehydration is slowly continued until all water is removed, γ -anhydrite will be obtained, also known as soluble anhydrite. β -anhydrite is the one formed from (hydrothermal) solutions, and the most common one in natural and engineering environments. At very high temperature, i.e. $>1200\text{ }^{\circ}\text{C}$, cubic α -anhydrite is the stable polymorph.

Figure 1. Structural motifs of the three calcium sulfate phases formed from aqueous solution: gypsum, bassanite and anhydrite (images were drawn with VESTA, Momma and Izumi, 2011). The green balls represent the Ca cations, red tetrahedra correspond to SO_4^{2-} anions, and the water molecules are drawn explicitly in blue), and solubility data for gypsum, bassanite and anhydrite in pure water as a function of temperature. These include both experimental values extracted from the literature (individual dots, Van Driessche et al., 2017, and references therein) and solubility curves calculated using the PHREEQC (dotted lines) and LLNL (stripe-dotted lines) databases (in the

PHREEQC code (Parkhurst and Appelo, 1999) the analytical expression for the temperature dependence of $\log K$ for a reaction is defined as: $\log K = A_1 + A_2T + A_3/T + A_4\log T + A_5/T^2 + A_6T^2$ (where T is in kelvin). The values of the coefficients, A_1 to A_6 , used to calculate the solubility curves are listed in the PHREEQC and LLNL databases). The green and blue shaded areas are a visual aid to highlight the thermodynamic stability region for gypsum and anhydrite, respectively. The white area represents the uncertainty in the transition temperature between both.

Depending on the formation conditions calcium sulfate minerals can adopt a wide variety of crystal habits / morphologies, and textures (Fig. 2). Gypsum usually appears as well-formed (highly) transparent single and twinned crystals (i.e. selenite, Fig. 2a), and as polycrystalline semi-opaque aggregates with randomly (alabaster) or parallel (satin spar) oriented crystals (Fig. 2b). Other, more peculiar types of gypsum are for example desert rose (Fig. 2c), usually formed through evaporation in sandy desert regions (Al-Kofahi et al., 1993; Watson, 1983), and ram's horn typical of cave environments (Fig. 2d). Anhydrite formed in hydrothermal environments may appear as well-formed translucent crystals (Fig. 2e), but most often will present a massive, granular or fibrous texture. "Chicken-wire" anhydrite, or nodular anhydrite, occurs as replacement of gypsum and it is typically found in a variety of sedimentary depositional environments. The few occurrences of bassanite (α -hemihydrate) in natural settings are usually as pseudomorphs after gypsum or as fiber/needle-like crystals (aggregates) (Fig. 2f).

Fig. 2. Characteristic appearances of calcium sulfate minerals: (a) idiomorphic gypsum crystal, i.e. selenite, from the Naica mine (Mexico), (b) gypsum satin spar from Benson, Arizona (USA), (c) gypsum desert rose (Southern Tunisia, D. Descouens, CC BY-SA 4.0), (d) gypsum ram's horn from Guangdong Province, China (R.M. Lavinsky, CC-BY-SA-3.0) (e) hydrothermal anhydrite fans from the Naica mine (Mexico, R.M. Lavinsky, CC-BY-SA-3.0) and (f) White needle shaped bassanite crystallites with some gypsum crystals from Eyre Peninsula in South Australia (John Sobolewski, CC BY 3.0).

1.2. Calcium sulfate minerals in natural environments

1.2.1. Earth surface

Calcium sulfate is the dominant terrestrial sulfate and can be found in a wide range of environments. Large (marine) sulfate evaporitic deposits have been forming since the great oxidation event in the Paleoproterozoic (e.g. Babel and Schreiber, 2014; reports of gypsum precipitation during the Archean, e.g. Buick and Dunlop (1990), are still debated (e.g. Warren, 2006)). In those settings, gypsum is almost exclusively the primary mineral phase, which after diagenesis tends to transform into anhydrite (if enough pressure/temperature is reached). One of the most studied evaporitic calcium sulfate formations is that found in the rock record of the Mediterranean basin (Fig. 3a). During the Messinian salinity crisis, some ~6 Ma ago, approximately $4 \cdot 10^{18}$ kg of salts (mainly NaCl and CaSO_4) were deposited (Ryan, 2008). This amount exceeds by a factor of 50 the expected amount of salt contained in

the Mediterranean Sea, and the precise origin/genesis of this, and other, salt giant(s), is still a matter of intense research and debate (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). Present day examples of gypsum precipitation in evaporitic environments are found in sabkhas of the Mediterranean coast of Egypt, salt lakes in South Australia (Warren, 1982) and India (Sinha and Raymahashay, 2004), salars of the Atacama desert (Fig. 3c, e.g. Rasuk et al., 2014; Farías et al., 2014) and high Andes (e.g. Benison and Karmanocky III, 2014), to name just a few. However, it should be mentioned that these present-day evaporitic environments sites are dwarfs compared to the salt giants formed during past geological times (Warren, 2010).

Although gypsum is usually considered a typical evaporitic mineral, non-evaporitic gypsum formation can also take place in (deep) marine sediments due to a variety of mechanisms such as, mixing of seawaters coupled to the dissolution of foraminiferal ooze (Briskin and Schreiber, 1978), salt diapirism (Haffert et al., 2013; Haffert and Haeckel, 2019), oxidation of sedimentary sulphide minerals in carbonate rich sediments (Pirlet et al., 2010), gas hydrate formation (Wang et al., 2004), brines seeping (Huguen et al. 2003), alteration of volcanogenic material or basaltic basement (Hoareau et al., 2011), or the serpentinization of ultramafic rocks (Scribano et al., 2017). In addition, gypsum crystals can also be formed as a result of oxidation of sulfides by calcium-rich, oxidizing ground water infiltration in a variety of sediment types (Bain, 1990). The precipitation of authigenic gypsum during the formation of sea ice was also reported (Geilfus et al, 2013; Wollenburg et al., 2018). Noteworthy, cryogenic and hydrothermal calcium sulfates on Earth are volumetrically less significant than salts derived through solar evaporation (Warren, 2010). Although it

has been proposed that large salt accumulations could be a consequence of hydrothermal processes associated with Wilson cycles (Hovland et al., 2018).

Although less frequent, and usually linked to rather unique geological conditions, gypsum can appear in non-marine and non-lacustrine environments as well. For example, gypsum formation was located in both actively forming and inactive sulfidic caves as old as 10 million years (e.g., Hill, 2000; Galdenzi and Maruoka, 2003; De Waele et al., 2016), terrestrial hydrothermal springs ($< \sim 100$ °C) in New Zealand (e.g. Bonny and Jones 2003;), and in the poly-extreme hydrothermal system of Dallol in Ethiopia (Talbot, 2007; Kotopoulou et al., 2019). Another example related to hydrothermal activity are the spectacular giant gypsum crystals discovered inside of the Naica Mine (Mexico, Fig. 3c). In this silver and lead mine, several natural cavities contain huge, faceted single and twinned gypsum crystal beams up to 11 m long (García-Ruiz et al., 2007; Van Driessche et al., 2011; Van Driessche et al., 2016). They formed from slowly cooling hydrothermal solutions that were saturated with respect to gypsum through the dissolution of anhydrite present in the bedrock (below $< \sim 55$ °C anhydrite is more soluble than gypsum). A similar mechanism might be responsible for the giant gypsum crystals, ranging up to 7 m in length, found inside El Teniente mine in Chile (Cannell et al., 2005). Other locations of meter-sized gypsum crystals are those hosted in a geode in Almeria (Spain, García-Guinea et al., 2002, Fig. 3d), the very transparent specimens mined by the Romans in Segóbriga (Spain, Bernárdez-Gómez et al., 2007), and those occurring in the Badian gypsum deposits in the northern margin of the Carpathian Foredeep (e.g. Babel, 2001), among others.

Under terrestrial evaporitic conditions, gypsum is the dominant primary mineral because the formation of anhydrite is both kinetically and thermodynamically

hindered (Ossorio et al, 2014). Only in very arid and hot supratidal environments (sabkha) has anhydrite been reported to form at (near) surface conditions directly from concentrated brines or replacing gypsum (e.g. Kinsman, 1966; Butler, 1969; Butler et al., 1982; Shearman, 1985; Gunatilaka, 1990; Aref and Taj, 2018). More commonly anhydrite appears in evaporitic settings through gypsum dehydration caused by burial to depths below the reaction isotherm (e.g. Murray, 1964; Yamamoto and Kennedy, 1969), although the transformation can be accelerated in the presence of highly saline brines (e.g. Kasprzyk, 1995). When these anhydrite-dominated deposits are uplifted above the reaction isotherm, and given that enough water is available, they will rapidly convert back to gypsum (e.g. Conley and Bundy, 1958; Murray, 1964; Yamamoto and Kennedy, 1969). On the other hand, anhydrite is an important primary mineral in hydrothermal systems located at mid-ocean ridges (e.g. (Bischoff and Seyfried, 1978; Styr et al., 1981; Humphris et al., 1995; Lowell and Yao, 2002), oceanic back-arc basin hydrothermal systems (e.g. James et al., 2014), continental hosted hydrothermal ore deposits (e.g. Rimstidt, 1997; Blundy et al., 2013), and possibly also due to serpentinization of ultramafic rocks and posterior hydrothermalism (Scribano et al., 2017). Noteworthy, due to the retrograde solubility of anhydrite below 150 °C (Fig. 1) much of the oceanic anhydrite is re-dissolved when it moves away from the heat source (e.g. Sleep, 1991; Alt, 1995). Hence, very little anhydrite is preserved in older oceanic crust. Likewise, in continental deposits anhydrite can be absent to depths of several hundred meters beneath the current surface due to supergene dissolution (e.g. Sillitoe, 2010).

Compared to gypsum and anhydrite, bassanite deposits are very scarce, because when this mineral is in contact with water, or humid environment, it will, depending on the temperature, readily transform into either gypsum or anhydrite.

Consequently, bassanite is usually only observed in arid and hot environments (e.g. Mees and Tursina, 2010), and typically forms in dry(ing) marine evaporitic settings, and dry(ing) lake beds or soils as dehydration product of gypsum. Examples can be found in southern Egypt (Mees and De Dapper 2005), Western Australia (Arakel 1980; Benison and Bowen, 2013), Death Valley (Hunt et al. 1966), and Kuwait (Gunatilaka et al. 1985). But, usually the stability of bassanite in these sediments is seasonal, and it will rehydrate to gypsum once wetter conditions return (e.g., Hunt et al. 1966; Apokodje, 1984; Gunatilaka et al. 1985). Remarkably, two classes of medusae (Scyphozoa and Cubozoa) use bassanite for gravitational sensing (Tiemann et al., 2002; Becker et al., 2005; Boßelmann et al., 2007). This is one of the few examples of calcium sulfate biomineralization by a eukaryotic organism, and will be discussed in more detail in section 3.3. of this review.

1.2.2. Mars surface

Earth-based telescopes and Mars-based orbiters, landers, and rovers have been involved in the detection of calcium sulfate minerals on the surface of Mars (e.g. Bell, 2008). Telescopic evidence for the presence of sulfate was already reported several decades ago, but identification of specific mineral phases remained challenging. Using data obtained with the orbital instrument OMEGA, gypsum was reported to be present in significant quantities in the northern polar region of Mars (Langevin et al., 2005) and lower latitudes (Gendrin et al., 2005). Since then, gypsum has been observed in many more locations on the Mars Surface, e.g.: Meridiani Planum (Grotzinger et al. 2005), Noctis Labyrinthus (Weitz et al., 2013) and the Gale Crater (Vaniman et al. 2018). The presence of bassanite was first reported at Mawrth Vallis (Wray et al., 2010). More recently, numerous calcium sulfate-containing veins were

detected *in situ* at Gale crater using the ChemCam instrument onboard the Curiosity rover (Nachon et al., 2014; Vaniman et al., 2014; Rapin et al., 2016). These veins contain mainly bassanite, but also anhydrite and gypsum have been observed (Vaniman et al., 2014; Rapin et al., 2016). Data collected with the CheMin X-ray diffraction instrument on Mars Science Laboratory confirmed that gypsum, bassanite, and anhydrite are common minerals at Gale crater (Vaniman et al., 2018).

Calcium sulfate minerals on Mars seem to have originated to a large extent through chemical precipitation from (acidic) saline shallow surface waters (e.g. playa evaporites) and from underground post-depositional fluid flow (e.g. Squyres et al., 2005, 2012; Langevin et al., 2005; Grotzinger et al. 2005; McLennan et al., 2005; Tosca 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). However, other plausible formation mechanisms have been proposed as well: these include deposition from the surge ejecta of meteorite impact (Knauth et al., 2005); alteration of volcanic ashes by vapours emitted from fumaroles (McCollom and Hynek, 2005); dry deposition of volcanic sulfate aerosols (Catling et al., 2006), or water/ice (Mangold et al., 2010); alteration of sand dune grains bearing high-calcium, Fe-rich pyroxene and sulfide (Fishbaugh et al., 2007); acid weathering inside massive ice deposits (Niles and Michalski, 2009); cation exchange reactions between smectites and hydrated Mg sulfate minerals (Wilson and Bish, 2011); or weathering of sulfide-enriched basalts (Dehouck et al. 2012). On going data analysis of the present, and future, Mars rovers will provide new insight on the precise mechanism of sulfate mineral formation. This in turn will help to better model the important sulfur cycle on Mars (King and McLennan, 2010), and elucidate past climate conditions that have been prevailing on the Mars surface.

Fig. 3. Calcium sulfate deposits in natural environments. (a) Large palmate gypsum formed during the Messinian salinity Crisis of the Mediterranean Sea, San Miguel Formation, Alicante (Spain, e.g. Corbí et al., 2016). (b) Gypsum stromatolitic-like domes growing in the Salar de Llamara (Atacama Desert, Chile). (c) Giant gypsum crystals inside of the cave of crystals in the Naica mine (Chihuahua, Mexico). Note human for scale. (d) Inside of the gypsum geode of Pulpí (Almería, Spain). The walls of this $\sim 11 \text{ m}^3$ ovoid cavity are covered with meter-sized highly transparent idiomorphic gypsum crystals (i.e. selenite). Note human for scale. (e) Calcium sulfate containing vein ($\sim 18 \text{ cm}$ long) located at the western rim of Endeavour Crater by the Opportunity rover (Image Credit: NASA/JPL-Caltech/Cornell/ASU).

1.3. Calcium sulfate phases in engineering environments

Since ancient times gypsum has been a much-used inexpensive material for construction purposes. For example, gypsum plaster, and its processing, had become a well-established technology for many applications in the Pre-Pottery Neolithic, ca. 7200-6000 B.C. (Kingery et al., 1988). Later on, Egyptians used gypsum-based mortars in many of their buildings, including pyramids (e.g. Regourd et al., 1988; Lucas and Harris, 2012; Harell, 2017). The Greeks and the Romans further developed the application of calcium sulfate binders and plasters (e.g. Stark and Wicht, 1999). In more recent history calcium sulfate was mainly used for decoration purposes or to protect buildings, i.e. starting from the 17th century in Paris the walls of wooden houses were covered with plaster as a protection against fire (Myers, 2007; Le Dantec, 2016). In order to produce the large amounts of plaster demanded, gypsum was extracted from the nearby quarries in Montmartre (Paris). This is the origin of the contemporarily often-used term “plaster of Paris”. One well-known example of gypsum stucco (i.e. plaster) decoration can be found at the Alhambra Palace located in Granada, Spain (Fig. 4a, e.g. Cardell-Fernández and Navarrete-Aguilera, 2006).

In post industrial times calcium sulfate is one of the most commonly used inorganic materials (in volume), and its demand is continuously increasing. In 2018, approximately 160 million tons of gypsum was obtained through mining activities

worldwide (US Geological Survey, Mineral Commodity Summaries, February 2019). Besides mined gypsum, important quantities of waste material (i.e. re-usable gypsum) and flue-gas desulfurization gypsum are also employed (depending on the region, the former or the latter gypsum source is more abundant). A large portion of the raw gypsum product is converted to bassanite (i.e. plaster of Paris) by heating up to ~ 160 °C. When mixed with water, bassanite will rapidly dissolve and recrystallize as gypsum needles, forming a moderately hard material. This is the main component of stucco and wallboard. During the production of wallboard, bassanite is mixed with additives (such as perlite, starch, fiberglass, or vermiculite), water, soap foam and accelerators forming a slurry that is deposited between continuous layers of paper (Fig. 4c). As the board moves down a conveyor line, the bassanite will convert to gypsum state and become bonded to the paper. The board is then cut to length and conveyed through dryers to remove any free moisture. The whole process takes approximately 4 min, and requires a very precise control over the crystallization process.

Unprocessed gypsum and anhydrite are also important components of cements and paints. In cement-based mixes they play an important role in controlling the setting rate and the strength of the final material (e.g. Lea, 1998; G. Tzouvalas et al., 2004). In paint, gypsum powder is used as a filler to adhere to the pigments and improve the paint's texture. Other common applications of gypsum are found in agricultural as soil conditioner/fertilizer (e.g. Shainberg et al., 1989; Iho and Laukkanen, 2012) and in the food industry as a flocculant (e.g. Sharpe and Cork, 2006). Although in much smaller absolute quantities, high purity calcium sulfate is often-used in a variety of clinical applications, such as regenerative material for bone

defects, dental plaster, or as a delivery vehicle for pharmaceutical agents (e.g. Thomas and Puleo, 2009).

Fig. 4. (a) View of a gypsum quarry in Montmartre, France. (b) Decorative stucco from the Alhambra Palace, Granada, Spain. (c) Schematic representation of the different steps in gypsum wallboard production, where different crystallization additives are used; A = accelerator and R = retarder (adapted from GIPS-Datenbuch).

Unfortunately, calcium sulfate solid phases also cause a lot of nuances in engineering environments (Fig. 5). Most importantly, unwanted precipitation of gypsum and anhydrite on the surface of water pipes (Fig. 5a) and heat exchanger leads to incrustations, i.e. scalants, which cause efficiency loss, and/or costly downtimes for cleaning, in desalination plants (Fig. 5a), oil recovery and mining activities (e.g. Brusilovsky et al., 1992; Linnikov O.D., 2000; Ahmed et al., 2004; Mi and Elimelech, 2010; Al-khaldi et al., 2011; Olajire, 2015; Lu et al., 2012; Rosenberg et al., 2012). Anhydrite is the predominant scale-forming phase at higher temperatures $>100\text{ }^{\circ}\text{C}$, while gypsum scaling prevails at lower temperatures. Associated with this problem is the frequently overlooked environmental impact of the large quantities of

additives used to prevent/retard/clean scale formation. Usually scale inhibitors persist for many years after their disposal and can for example lead to eutrophication in the case of polyphosphate-based polymers (Lattemann and Höpner, 2008).

Another downside of calcium sulfate precipitation is related to the role gypsum formation plays in the deterioration of construction materials (e.g. concrete, mortar, marble, etc.) during sulfate and acid attack (e.g. Charola et al., 2007; Neville, 2004; Kloppmann et al., 2011). The latter is of increasing importance due to the continuing acidification of rainwater. The formation of gypsum inside of concrete can lead to expansion causing irreversible damage in the building material, or in the case of CaCO_3 based materials (e.g. limestone or sandstone with carbonate cement) produce black crusts mainly composed of gypsum which accelerate the deterioration of the material (Fig. 5b, e.g. Camuffo et al., 1983; Ross et al., 1989; Torok A., 2005; Siegesmund et al., 2007; Graue et al., 2011).

Geotechnical problems related to calcium sulfate crystallization can occur during tunnel (or road) constructions that cross formations containing important amounts of (clay)-sulfate rocks (rich in anhydrite). These can be subject to heavy swelling when water from outside accesses the sulfate-rich formation and triggers the dissolution of anhydrite and re-precipitation of gypsum, which is accompanied by an important volume increase of up to 62.6% in an open system (e.g. Zanbak and Arthur, 1986). This can lead to significant tunnel floor heave (Fig. 5c) or development of swelling pressure (Kovári *et al.* 1988, Anagnostou et al, 2010; Butscher et al., 2011). Although not related to precipitation, the rapid dissolution of calcium sulfate deposits can lead to the formation of sinkholes, causing severe damage to buildings and roads in urban areas (Fig. 5d). This problem is of course specific to areas with a subground rich in gypsum/anhydrite, such as the aforementioned Montmatre neighbourhood in

Paris, the Permian gypsums of northern England (see Fig. 5d), gypsum terrains in NE Spain or in the NE of Italy (Benito et al., 1995; Cooper, 2002; Gutierrez et al., 2008; Calligaris et al., 2019).

Fig. 5. Unwanted calcium sulfate processes in engineering environments. (a) Scale formation (black arrows) inside of tubes of a desalination unit (Rosenberg et al., 2012), (b) gypsum crystallization on the surface of building material accelerates its deterioration (reproduced from Winkler (1975) by permission of Springer Nature, Photos by Dr. Schmidt-Thomsen), (c) swelling behaviour in sulfate rich rocks can induce severe floor heave (Pimentel, 2015), and (d) sinkhole formation in sulfate rich rocks causing severe damage to buildings (photo credit BGS NERC).

1.4 Why study the formation of calcium sulfate minerals?

Taking into account the above reviewed presence of calcium sulfate in a wide variety of natural and engineering environments, it should not come as a surprise that there are a number of reasons why it is important to have a holistic view of the formation process of these minerals. First of all, the precipitation and dissolution (weathering) of CaSO_4 deposits plays a key role in the global sulfur cycle (e.g. Brimblecombe, 2003), and sulfate evaporate minerals constitute an important archive

of the oxygen and sulfur cycles (e.g. Bao, 2015; Crockford et al., 2019). The removal of sulfur from the oceans is mainly controlled by microbial sulfate reduction (followed by pyrite burial) and precipitation of CaSO_4 (gypsum/anhydrite). The burial rates of sulfates are unsteady and linked to changes in the area of marine environments suitable for a stable evaporite formation (Halevy et al., 2012). The rock record shows that an episodic large-scale formation of such deposits over relatively short geologic time-scales can have a vast impact on the marine sulfate concentration, altering the rate of several biogeochemical processes, which finally leads to climate changes (e.g. Wortmann and Chernyavsky, 2007; Halevy et al., 2012; Wortmann and Paytan, 2012; Mills et al., 2017). Moreover, the burial dynamics of evaporite sequences also affects the distribution of co-precipitating elements (such as strontium) that exerts a major control on the skeletal chemistry of calcifying organisms, which possibly could have controlled the transition from calcite to aragonite seas in past times (e.g. Bots et al., 2011). To better understand and predict the dynamic nature of sulfur cycling and evaluate its role in regulating the chemistry of the ocean-atmosphere system, a solid constrain of global sulfate precipitation rates through time are paramount (e.g. Hurtgen, 2012). Consequently, to properly estimate those rates we need precise knowledge of the mechanism and kinetics of calcium sulfate formation as a function of the physicochemical conditions (e.g. T, salinity, pH, Eh, etc.). Moreover, we also need to take into account the possible role of (micro)organisms and the breakdown products on the precipitation dynamics, since this has been largely overlooked in the case of calcium sulfate deposits.

Secondly, on Mars, calcium sulfates can serve, among other mineral phases, as proxies for past environmental conditions (e.g. Parnell et al. 2004; Squyres et al. 2005; Borg and Drake 2005; Bibring et al. 2007; Murchie et al. 2009). Gypsum

indicates the existence of water-rock interactions on Mars that might reveal a wet geochemical environment in its geological history (Borg and Drake 2005). However, to be able to employ the presence of calcium sulfate phases as reliable indicators of past arid/humid environments, we need to precisely understand how they were formed, and as highlighted previously (section 1.2.2), many issues remain unanswered concerning the possible formation route(s) of calcium sulfate phases on the surface of Mars.

Thirdly, given the wide scope of applications of calcium sulfate based compounds (cf. section 1.3), there is always an industrial demand for the design of more efficient (and environmentally friendly) protocols providing control over the phase composition, size, morphology and mechanical properties of (hybrid) calcium sulfate functional materials (e.g. Yu, 2012; Nissinen et al., 2014; Asadi-Eydivand et al., 2016; Natarajan et al., 2018). This high level of control can only be achieved via solution synthesis if the underlying fundamental mechanisms are properly understood. Gypsum is also one of the very few construction materials, for which closed-loop recycling is possible, i.e. the waste is used to make the same product again. Nonetheless, during the production process of plaster, the raw product (be it gypsum from a quarry, waste construct material or flue-gas desulfurization gypsum) needs to heat up to ca. 160 °C to lose 1.5 molecules of H₂O and convert into bassanite. Approximately 95 % of the production cost goes into the heating process. Lowering, even by a few degrees, the temperature to achieve this conversion would supposedly result in substantially reduced energy consumption. Alternatively, the development of a more efficient solution-based synthesis route of bassanite could also lead to improved energy usage (and reduced environmental impact).

Fourthly, the scarcity of fresh water coupled to the declining quality of water resources, is an ever-increasing problem, especially in arid regions. Desalination of seawater, and other saline/brackish waters, constitutes an important alternative source for fresh water supply in coastal areas (e.g. Lattemand and Hopner, 2008). But, scale formation severely hampers the operation of both thermal and membrane desalination units and causes important operational, economical and environmental penalties. To satisfy our increasing need of drinking water in a sustainable way, new, effective and environmentally friendly antiscaling strategies for CaSO_4 have to be developed. This can only be achieved if we have a complete understanding of how these scalants are formed, and most importantly, how additives interact with the formation pathway of these solid phases.

In a nutshell, understanding the abiotic, and biotic, formation pathway of calcium sulfate minerals will help us to better understand the surface evolution of Earth and Mars, increase our ability to control the synthesis and properties of CaSO_4 -based functional materials, and help reduce its occurrence as a scalant in industrial operations. Accordingly, the goal of this review is to provide a critical summary of the thermodynamic and kinetic principles controlling the abiotic CaSO_4 mineralization process, and based on these insights to discuss the possible interaction of the biosphere with formation of CaSO_4 deposits in both natural and engineering environments.

2. Abiotic formation of calcium sulfate minerals

Any mineral precipitation process from solution can be divided into two consecutive steps: (1) nucleation and (3) growth of the mineral phase(s) (with the latter potentially involving aggregation phenomena). In general, nucleation starts by

random clustering of ions/species in solution, which form a cluster that may (or may not) evolve into a crystal with time. Due to competing contributions of bulk (favorable) and surface (unfavorable) interactions, the overall free energy of a nucleating system first increases, thus posing a barrier (Fig. 6) that differentiates precipitation (as a phase separation process) from other chemical reactions. Therefore, many of the initially formed clusters will quickly re-dissolve and only those that by fluctuation reach a certain critical size (where they become an actual nucleus), at which the gain in volume free energy equals the costs of surface free energy (maximum in ΔG) and any further addition of ions leads to a decrease in overall free energy, will grow to a mature crystal. According to the classical nucleation theory (CNT; e.g. Kashchiev, 2000), the formation of nuclei is a one-step process that will produce nanosized particles with the same characteristics (e.g. order, density, composition, etc.) as the fully-grown macroscopic crystals. This results in a single energy barrier for the transition from dissolved ions/species to crystalline entities (Fig. 6).

However, experimental results gathered in the last decades have challenged this *classical* picture by showing that the pathway from a supersaturated solution to a solid crystalline material can involve multiple stages, in which distinct precursors and intermediate phases occur and interconvert across different length and time scales (Fig. 6, e.g. De Yoreo et al., 2015; Van Driessche et al., 2017). Importantly, such a multi-stage (or so-called “non-classical”) pathway also implies a different energetic landscape for nucleation and early growth. For example, it is possible that some of the formed intermediates correspond to local free energy minima separated by individual barriers (dotted profile in Fig. 6), which for transformation need to be overcome (note that each transformation step can involve a new nucleation event, either in the

condensed phase (structural reorganization) or in solution after re-dissolution). Nonetheless, free energy minima are not a prerequisite for multi-stage crystallization pathways to occur, since precursor species can also emerge due to the competition between thermodynamics and kinetics during cluster formation on a continuous uphill energy profile (Durán-Olivencia et al., 2018; Lutsko, 2019). In the case of gypsum, recent studies have indeed also shown that more complex crystallization mechanisms ought to be considered for a wide range of conditions (e.g. Van Driessche et al., 2017, and references therein). In this section, these newly gathered insights into the formation of gypsum from solution will be discussed in detail, leading to a unified picture for calcium sulfate crystallization integrating both the “classical” and “non-classical” perspectives on the nucleation process.

Fig. 6. Schematic representation of one- and multi-step pathways for the formation of crystals from supersaturated solutions (left) and their tentative associated energy landscapes (right).

2.1. Nucleation

2.1.1. Experimental observation of abiotic CaSO_4 nucleation pathways

The first systematic studies on the precipitation of CaSO_4 from aqueous solutions were performed during the late 19th and early 20th centuries, and were mostly based on solubility measurements. Such an approach provided an easy

(macroscopic) access to the thermodynamic properties of the considered phases (i.e. the difference between the aforementioned initial and the final stage of a crystallization, dissolution or transformation process). Later on, driven by both the geological and industrial interests, research became more and more focused on the kinetics – and, with it, the mechanisms – of gypsum precipitation from supersaturated solutions. Those early studies (e.g. Schierholtz 1958; Smith and Sweet, 1971; Liu and Nancollas, 1973; Packter, 1974) assumed that a first crystalline nucleus is formed within a single step in solution and then it continues to grow into a macroscopic gypsum crystal - which, in essence, represents the classical view of crystallization (Fig. 6, e.g. Kashchiev, 2000). More recent work determined the induction time (i.e. the period required to form crystal nuclei, or detectable particles) of gypsum precipitation as a function of supersaturation and temperature (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). The collected experimental data showed clear dependencies on temperature and solution speciation, and were fitted using the CNT equation for the nucleation rate (e.g. Kashchiev, 2000):

$$J = A \cdot \exp(-B \cdot \gamma_{\text{eff}}^3 / \sigma^2) \quad (\text{eq. 1})$$

where A is a pre-exponential factor, σ is the supersaturation and the coefficient B contains factors, such as the volume of a lattice molecule and the absolute temperature. γ_{eff} is the effective interfacial free energy between the growing phase and the solution and represents the energy penalty that has to be “paid” to create this new interface. For homogeneous gypsum nucleation from aqueous solution, γ_{eff} was estimated to be $\sim 40 \text{ mJ/m}^2$ (see Table 1 for details). Since for given solutions conditions (i.e. a given bulk term) the interfacial energy determines the height of the barrier to nucleation, it provides us with an estimation of how “difficult” (or “easy”) it

is to form gypsum under these conditions (note, for instance, that free energies determined for the $\text{CaCO}_3/\text{H}_2\text{O}$ interface are significantly higher, e.g. 98 mJ/m^2 as reported by Söhnel and Mullin (1982), and hence calcite should be rather difficult to crystallize homogeneously compared to gypsum). However, the γ_{eff} value *per se* does not reveal anything about the precise nature (e.g. structure) of a specific phase formed upon nucleation. Thus, despite the large amount of experimental data collected on gypsum precipitation over the years, the nature of the species occurring during the early stages of the reaction, and their spatiotemporal evolution, remained largely unknown.

A number of recent works have made an attempt to fill this void by exploring in detail the nucleation pathway of gypsum using a variety of characterization techniques and crystallization procedures (Wang et al. 2012, Van Driessche et al. 2012; Saha et al. 2012; Jones, 2012; Stawski et al., 2016; Ossorio et al., 2017; He et al., 2018). The general consensus of these studies is that gypsum formation can in fact involve one, or more, precursor and/or intermediate phases. However, the particular pathways revealed by these studies also show certain discrepancies (e.g. related to the question whether an amorphous phase and/or bassanite occur(s) as an intermediate at ambient conditions or not). These ambiguities may imply that there is not one universal pathway to gypsum formation, but different possible channels, of which the kinetically most accessible will be selected according to the respective physicochemical conditions. Different experimental observations could however also arise from a lack of spatial and/or temporal resolution of the implemented *in situ* and *ex situ* methods, with the latter bearing the additional risk of isolation artefacts biasing the results (for a detailed discussion see Van Driessche et al., 2017). These limitations can be overcome, up to a certain degree, by using for example synchrotron-based

small- and wide-angle X-ray scattering (SAXS/WAXS). This approach allows us to study *in situ* the formation of mineral phases from solution at high enough spatial and temporal resolution (e.g. Stawski and Benning, 2013). Truthfully, also this methodology has its limitations, especially those related to the detection of the nanoparticles forming during the early stages of the reaction, when their volume fraction and/or scattering contrast with respect to the bulk medium are still rather low. It appears that in the case of calcium sulfate it is possible to conduct experiments at sufficiently low levels of supersaturation so that the kinetics of the process are not too fast but the nucleation density and/or concentration of relevant precursors in (pseudo-)equilibrium prior to macroscopic phase separation is still high enough to result in detectable volume fractions (even during the early stages of the reaction). Using this approach, the mechanisms of gypsum formation from supersaturated solutions (50 to 150 mM CaSO_4) were studied in detail (Stawski et al., 2016; Besselink et al. 2016, Ossorio et al. 2017). The obtained *in situ* data confirmed previous reports about gypsum forming via a multi-step process, and showed that once a solution at or above a critical supersaturation is created, crystals of gypsum emerge as a result of four consecutive steps (Fig. 7a): (1) rapid formation of primary nanosized Ca-SO_4 -species (<3 nm) and presumably “anhydrous” character in their core, which (2) assemble into loose domains, where the interparticle distance remains still fairly large (at least twice the radius of gyration of the individual primary particles). These domains subsequently (3) undergo densification, forming disordered aggregates in which the primary units can still be recognized. Finally, these aggregates (4) transform into gypsum through growth, reorganization and ordering of the primary species within the initially disordered assembly.

Fig. 7. (a) Schematic representation of the four stages of gypsum formation based on the results of *in situ* SAXS experiments. Stage 1, formation of sub-3 nm primary species; Stage 2, assembly of the primary species into loose domains (the inset shows that individual scatterers are separated by a distance that on average is larger than two times the radius of gyration). Stage 3, densification into large surface-fractal structures. Stage 4, growth, coalescence and ordering of the primary species within the aggregates, finally transformation to crystalline gypsum. The inset between stages 3 and 4 shows the successive evolution at the nano- and mesoscale, where the primary units first grow – either by ion attachment or aggregation/coalescence – in length and subsequently in all dimensions, yielding structural domains of increasing size and crystallinity. (b) Structural model for the rod-shaped primary species as derived from PDF analysis of *in situ* HEXD experiments (left) and their dynamic properties as probed by unbiased MD simulation using polarizable force fields (AMOEBA) (right). In both cases, longitudinal (LV) and cross-sectional views (CV) are shown (adapted from Stawski et al., 2019 with the permission of the American Chemical Society).

A central aspect in this new picture of CaSO_4 nucleation from solution is the formation of nanoscopic primary units with rather well-defined size and composition. Very recently, the structure and dynamic properties of these primary units have been revealed on the basis of high-energy X-ray diffraction (HEXD) data collected from supersaturated CaSO_4 solutions (Stawski et al., 2019). A nanostructural model was derived by pair distribution function (PDF) analysis of the data as well as unbiased molecular dynamics (MD) simulations with polarizable force fields. This combined study suggests (Fig. 7b) that the central units of the primary species consists of a well-defined and quite rigid square structure (cf. cross-sectional views in Fig. 7b) with a $\text{Ca}^{2+}:\text{SO}_4^{2-}$ stoichiometry of 1:1 and no nominal structural water. In turn, the terminal

units/edges of the primary species are rather flexible (as they only maintain half of the electrostatic interactions).

The mechanistic pathway outlined above is in many aspects consistent with the results of other recent studies obtained for solutions with similar CaSO_4 concentrations (≥ 15 mM CaSO_4). For instance, the aggregation of the primary units into disordered domains (Stages (2) and (3) in Fig. 7a) may correspond to the amorphous phase reported by several other authors (Wang et al., 2012; Saha et al., 2012; Jones, 2012). However, there are also evident disagreements, especially regarding the question whether nanoparticulate bassanite occurs as an intermediate phase on the way to gypsum at ambient conditions (i.e. room temperature) and low salinity, as suggested by some studies (Wang et al., 2012; Van Driessche et al., 2012, Tritschler et al., 2015a; He et al., 2018) but not observed in others (Saha et al. 2012; Jones, 2012; Stawski et al., 2016). A possible clue to this conundrum was provided in the work of Tritschler et al. (2015a), who studied the precipitation behavior of calcium sulfate from mixtures of water and organic (co)solvents at different ratios. They showed that below a critical water content (40-50 wt%) bassanite nanorods form as the main crystalline phase. Thus, the occurrence of bassanite particles in the aforementioned studies may actually be induced by the use of ethanol (and other solvents) to quench the reaction, which simultaneously reduced the amount of available water, and thus promoted transformation of the precursor phase to the bassanite instead of gypsum. In any case, the bassanite particles traced by Tritschler et al. at some point aggregated in an oriented fashion parallel to their long axis and eventually transformed collectively into gypsum (Tritschler et al., 2015a). This confirmed the previous reported observation of this oriented attachment mechanism (Van Driessche et al., 2012). In any case, this particular gypsum formation

mechanism seems to be relevant for low water activity environments, perhaps such as those present on the surface of Mars in past times, which would explain the substantial quantities of bassanite detected on Mars (e.g. Wray et al, 2010; Vaniman et al., 2018).

Contrary to gypsum, no microscopic details are known so far about the nucleation mechanisms of the two other crystalline CaSO_4 phases, i.e. bassanite and anhydrite, from aqueous solutions. The only available information on the nucleation kinetics of these phases was generated by induction time measurements in direct precipitation experiments (i.e. simple mixing of Ca^{2+} - and SO_4^{2-} -containing solutions) carried out as a function of supersaturation and temperature, with the aim of extracting the interfacial free energy of the calcium sulfate crystals in electrolyte solutions (quite akin to the early works on gypsum described above). For example, Guan and co-workers (2010) studied the nucleation kinetics of bassanite in concentrated CaCl_2 solutions at 90 °C and found an interfacial energy of 9 mJ/m^2 (Table 1). The kinetics of anhydrite precipitation in aqueous media were studied by Fan et al. at temperatures between 100 and 200 °C (i.e. hydrothermal conditions) and at a constant salt content of 1 M NaCl (Fan et al., 2010). No precipitation was observed at 118 and 148 °C, and induction times could only be measured at 178 °C. Based on these results, the authors estimated the effective interfacial energy of anhydrite to be 92.9 mJ/m^2 (Table 1), in line with the general consensus that it is very difficult to produce anhydrite by precipitation from aqueous solutions. Interestingly, this issue can be resolved by conducting the precipitation process in media of very low water content, e.g. organic solvents with trace amounts of water, which below some critical threshold (ca. 0.2%) will yield phase-pure anhydrite at a room temperature (Tritschler et al., 2015b).

In light of the results discussed above, it is worth to note that even though the particular mechanisms underlying nucleation may delineate a pathway that is fundamentally different from the classical picture drawn in textbooks, CNT can still provide an acceptable interpretation, and quantification of the kinetics of the process. This is not surprising if we take into account that CNT was originally developed to describe the condensation of water from supersaturated vapors (see e.g. Volmer and Weber, 1926; Farkas, 1927; Becker and Döring, 1935), and as such, the theory should intrinsically be more readily applicable to liquid/amorphous species than to crystalline nuclei. This also highlights that CNT does *per se* not assume any specific mechanism for nucleation, but nevertheless it proves to be a robust framework for capturing the overall kinetics of any type of nucleation process – be it single- or multi-step.

Table 1. Effective interfacial energy (γ), activation barrier (E_A) and kinetic factor (β) (where available) for nucleation and growth of gypsum, anhydrite and bassanite (errors are quoted for studies in which they were reported).

Phase	γ mJ/m ²	E_A kJ/mol	β cm/s	Method	ref
Gyp	41.1			Induction times of precipitation between 25-90 °C	He et al., 1994
	37.0			Induction times of precipitation between 25-90 °C	Lancia et al., 1999
		62.8		Growth of seed crystals between 30-90 °C	Smith and Sweet, 1971
		66.9±6.3		Growth of seed crystals between 25-55 °C (Rapid growing faces only)	Lui and Nancollas, 1973
		58.6		Growth of seed crystals between 60-105 °C.	Nancollas et al., 1973
		75±6.3		Growth of seed crystals between 10-30 °C	Mile et al., 1982
		60.0		Growth of seed crystals between 25-60 °C	Witkamp et al., 1990
		61		Growth of seed crystals between 10-40 °C	He et al., 1994
		64.0		Growth of seed crystals between 10-40 °C	Kontrec et al., 2002
			T / °C		
			20.0	Step kinetics measured on the (010) surface as a function of supersaturation	Van Driessche et al. 2009
			38.9		
			57.3		
			75.7		
	25.0-35.0±0.7			<i>In situ</i> WAXS of early stages of crystal growth	Ossorio et al. 2017

Anh	92.9		Induction times of precipitation at 178 °C	Fan et al., 2010
		T / °C		
		~65	$2.0 \cdot 10^{-3}$	
		~78	$3.8 \cdot 10^{-2}$	
	73 ± 5	~88	$2.1 \cdot 10^{-1}$	Step kinetics measured on the (100) surface as a function of supersaturation
		~98	$4.7 \cdot 10^{-1}$	
		~110	$2.4 \cdot 10^0$	
Bas	9		Precipitation at 90 °C in a 3.74 M CaCl ₂ solution	Guan et al., 2010
	40		Growth of seed crystals in CaCl ₂ /MgCl ₂ /KCl solution between 80-100 °C	Yang et al., 2009

2.1.2. Towards a unified model for the nucleation of CaSO₄ phases from solution

Based on a detailed analysis of the findings reviewed above, a general, and unified, model for calcium sulfate precipitation from solution can be formulated, which is schematically illustrated in Fig. 8. In undersaturated solutions, calcium and sulfate occur both as individual ions and associated ion pairs (Garrels and Christ, 1965). Whether they also form larger equilibrium species, akin to the pre-nucleation clusters suggested for other salt systems (e.g. Gebauer et al., 2014), still needs to be clarified. The evidence available so far indicates that when supersaturation is established, nanosized particles are formed through the assembly of multiple Ca²⁺ and SO₄²⁻ ions into elongated, rather flexible, nanoclusters (Fig. 7b). These primary units can be considered as a proto-structure of crystalline CaSO₄. Once a critical concentration of primary units is reached, they will assemble into disordered aggregates that contain an appreciable amount of solvent. In order to transform into ordered arrays of CaSO₄ with more (gypsum), less (bassanite) or no (anhydrite) interspersed water layers, the disordered aggregates have to reorganize through the alignment and coalescence of the primary particles to form larger coherent units. Consequently, during this rearrangement step, the local availability of water and the particular degree of hydration of the precursor units should play a key role in

controlling the crystalline phase that will be favored under the given conditions. As both of these factors are inherently time-dependent, kinetics are likely to have a strong impact on the final outcome. Once structural rearrangement has afforded an ordered lattice (i.e. the crystalline state has nucleated), growth takes over and rapidly yields larger particles due to the high concentration of (still disordered) CaSO_4 units in the local microenvironment.

The proposed *idealized* general pathway presented in Fig. 8 implies that the outcome of the precipitation process of CaSO_4 phases is controlled by the amount of water available during the reaction. This notion has been experimentally explored and verified by using defined mixtures of water and organic solvents (Tritschler et al. 2015a; 2015b). Apart from the use of organic solvents, the hydration of the precursor species can also be influenced through electron irradiation of the solution inducing bubble formation, which locally increasing ion concentration (He et al., 2018), or simply by changing the bulk salinity and/or temperature of the solution (e.g. Ossorio et al., 2014). Increasing any of the two latter parameters is expected to decrease the degree of hydration, as higher temperatures should favor the return of hydration water into the bulk (for entropic reasons) (Paula et al., 1995; Damasceno et al., 2012), while microscopic osmotic forces should also remove water from the precursors at high salt content (Di Tommaso et al., 2014). This hypothesis is supported by the well-established trend that bassanite replaces gypsum as the primary phase formed at increased temperatures and/or salinities (Cruft and Chao, 1970; Ossorio et al, 2014). Moreover, it may explain the kinetic inhibition of anhydrite crystallization observed under various conditions (see also section 2.3): regardless of any thermodynamic stability fields, it is very difficult to remove enough water from the precursors in an aqueous environment for anhydrite to be able to compete with the formation kinetics

of bassanite and gypsum. Drastically decreasing the availability of water, for example by working in organic solvents that contain only trace amounts of H₂O (Tritschler et al., 2015b) or by increasing salinity to extreme values (Cruft and Chao, 1970), can change the situation and induce direct anhydrite formation, although the particular precipitation procedure seems to play an important role here as well (Dixon et al., 2015).

Fig. 8. General nucleation pathway proposed for the formation of the three different crystalline CaSO₄ phases from solution, with the involved species shown in (top) close-up and (bottom) bird's view. The selection of the crystalline phase to be formed essentially depends on the availability of water in the medium (respective water contents are quoted) and the temperature and salinity of the solution (tentative conditions are indicated). For a certain range of conditions (intermediate water content, high salinity and moderate temperature), bassanite will appear as first crystalline phase and, over time, transform into either gypsum or anhydrite, again depending on the three parameters mentioned above.

Additional experimental evidence supporting the nucleation pathway outlined in Fig. 8 has recently been provided by detailed electron microscopy studies on the internal structure of natural and laboratory-synthesized crystals of gypsum, bassanite and anhydrite. Careful low-dose dark-field (DF) transmission electron microscopy (TEM) and electron diffraction (ED) analyses showed that the presumed single crystals of all three phases are actually composed of nanoscopic crystalline domains

(about 10-20 nm in diameter), which appear to be slightly misaligned with respect to one another and separated by disordered regions of several nanometers in width (Fig. 9). This “brick-in-the-wall” pattern is also reflected in SAXS data obtained from faceted microscopic single crystals (Besselink, et al 2016), which at low scattering angles are characteristic for large and internally homogeneous structures (i.e. integer crystals) while at high scattering angles the data contain scattering features originating from nanosized subunits (Stawski, et al., 2016; Besselink, et al 2016). This characteristic internal structure is likely to result from the reorganization of the disordered aggregates to a more ordered structure (see Fig. 7 and 8), during which the primary CaSO_4 species (originally <3 nm in length) grow in size forming larger nanoparticulate subunits within the growing crystals. To achieve this structural change, the nanoparticles must move inside the aggregates, which arguably is much slower than e.g. ion (or cluster) transport in bulk solution (Stawski et al. 2019). Therefore, re-structuring and coalescence within the emerging solid phase proceed very slowly and hence it takes quite long until an internally homogeneous single crystal is obtained. As a consequence, the particle-based mechanism of CaSO_4 nucleation and early growth is “fossilized” (i.e. kinetically trapped) within the texture of the crystals (Stawski et al. 2019). The fact that this “brick-in-the-wall” structure is observed for all three crystalline phases, and both for lab-grown and natural crystals, strongly supports the general model for calcium sulfate nucleation described in Figs. 7 and 8. Although the early stages of CaSO_4 crystallization appear to be controlled by nanoparticle aggregation and collective transformation, the subsequent stage of further growth is found to be occur mainly through ion-by-ion addition, as will be discussed in detail in the next section.

Fig. 9. TEM analysis of the internal structure of calcium sulfate crystals. (a) Bright-field transmission electron microscopy (BF-TEM) image of a representative gypsum crystal formed by precipitation from a 50 mM CaSO_4 solution and subsequent equilibration for 2 days in contact with the mother solution at room temperature; the different exposed faces are indicated by red lines and indexed with their respective Miller indices. (b) Dark-field (DF) image corresponding to (a); the contrast has been enhanced using a local histogram equalization technique and the intensity was remapped according to an "inferno" fake-color scale. The inset shows a zoom-in of the selected region indicated by the white rectangle. (c) BF-TEM image of a representative bassanite crystal synthesized by precipitation from a 50 mM CaSO_4 with subsequent ageing for 2 days in 4.3 M NaCl solution at 80 °C for 8 hours. (d) DF-TEM image corresponding to (c). (e) DF-TEM analysis of a focused ion beam (FIB) cut foil taken from a natural anhydrite single crystal. (f) Fourier transform (FT) filtered representation of a high-resolution (HR) TEM image acquired from a small section of the anhydrite FIB-cut foil. For detailed explanations see the main text. (Figure adapted from Stawski et al., 2019 with permission from the American Chemical Society).

2.2. Crystal growth in the CaSO_4 system

Once a nucleus has been formed in a supersaturated solution, the system enters into a deterministic regime and the nucleus will start to grow driven by the remaining excess amount of ions (or larger species). Usually, the term “crystal growth” refers to the moment when crystal faces have been established and growth can proceed through ion-by-ion addition (Fig. 6). The incorporation of the growth units takes place at so-called kink sites, which are present at steps on both flat and stepped surfaces, and occur virtually everywhere on rough surfaces (e.g. Chernov, 1980). In the case of flat surfaces, most common for crystal growth from solution at mild temperatures ($< 100^\circ\text{C}$), two mechanisms for step generation are frequently observed: (i) outcrops of dislocations, creating spiral hillocks, and (ii) nucleation of 2D islands. The predominant mechanism will determine how the resulting net growth rate responds to changes in supersaturation, and as such the rate at which crystals are forming. Understanding the growth mechanisms of specific crystallographic faces is equally important, because it determines the morphology, size, and the mechanical properties of the crystalline materials obtained under the respective conditions. Consequently, crystal growth is best studied using two complementary approaches: (i) bulk measurements focusing on the dynamic behaviour at the macroscale, and (ii) local in situ observations of the growth mode of specific crystal faces at the mesoscopic and/or nanoscopic level.

2.2.1. Gypsum

A significant amount of research effort has been dedicated to the bulk growth of gypsum (i.e. the sum of all crystallographic faces) from aqueous solutions. Either seeded (i.e. adding a constant mass, or volume, of gypsum crystals to a supersaturated

solution) or spontaneous crystallization experiments were used. In both cases, the rate of precipitation was determined by measuring the conductivity (e.g. Smith and Sweett 1971; Van Rosmalen *et al.* 1981; Christoffersen *et al.* 1982) or the calcium concentration of the solution (e.g. Liu and Nancollas 1970; 1973, 1975; Nancollas *et al.* 1973; Packter 1974; Brandse *et al.* 1977; Barcelona and Atwood 1978; Christoffersen *et al.* 1979; Mile *et al.*, 1982; He *et al.*, 1994), or by observing growth *in situ* using microscopic techniques (e.g. Liu and Nancollas 1973; Tadros and Mayes 1979). The obtained growth rates were related to supersaturation using the so-called general rate law for crystal growth (see e.g. Nielsen, 1984 or Nielsen *et al.*, 1984):

$$R=k(S-1)^n, \quad (\text{eq. 2})$$

where S is the supersaturation, R the rate of crystal growth, k the rate constant, and n the order of the growth process, which is dictated by the respective rate-determining step (i.e. $n = 1$ for diffusion control, $n = 2$ for surface control with dominance of spiral growth, and $n = 3$ for surface control with dominance of 2D nucleation).

Gypsum crystal growth occurring from seeded or unseeded solutions at relatively low saturation and ionic strength is best described by a reaction of second order, i.e. $n = 2$ (see, among others, Liu and Nancollas, 1970; 1973; Smith and Sweett 1971; Liu and Nancollas, 1973; Brandse *et al.* 1977; Christoffersen *et al.*, 1982; Mile *et al.*, 1982; Witkamp *et al.*, 1990; He *et al.*, 1994; De Meer *et al.*, 2000; Reznik *et al.*, 2009). Only Barcelona and Atwood (1978), who performed growth experiments using natural seawater, found a third-order rate dependence on supersaturation, whereas Packter (1974) reported growth to be a fourth-order process. In a few other cases, n was found to increase towards 3 or 4 when growth was carried out at high supersaturation (Liu and Nancollas 1973; Brandse *et al.* 1977; Christoffersen *et al.* 1982; De Meer *et al.*, 2000) or high ionic strength (Witkamp *et al.*, 1990), although

the type of used electrolytes matters here as well (i.e. specific ion effects are at play) (He et al., 1994). As already mentioned above, second-order kinetics for crystal growth indicate a surface-controlled process (Nielsen, 1984), usually interpreted as spiral growth (e.g. Burton et al., 1951). Deviations from this behavior at higher levels of supersaturation were interpreted as a change in the growth mode towards two-dimensional surface nucleation (Lui and Nancollas, 1973). In the case of a fractional reaction order, growth will be controlled by more than one mechanism. Also, different growth mechanisms can occur on different faces (e.g. Parsieglä and Katz, 1999, and references therein).

Hence, elucidating the dominant growth mechanism for a given condition based on bulk rate measurements alone is not a trivial task. But, with the advent of atomic force microscopy (AFM), it became possible to image *in situ* the surface topography of growing crystal faces. Natural gypsum crystals can readily be cleaved along the (010) plane (due to the double layer of water in the crystal structure), providing an ideal surface to image crystal growth. Pioneering *in situ* AFM studies on such surfaces found that layer-by-layer growth is the dominant mechanism for this face (Bosbach and Rammensee, 1994; Hall and Cullen, 1996; Bosbach et al, 1996), which at least partially confirms the results of most previous bulk studies. However, these first AFM experiments did not allow for step generation to be directly observed, i.e. it was not possible to distinguish between active spiral dislocations and nucleation of 2D islands as potential sources of new steps. One study reported the formation of 2 islands (about 0.7 nm thick, corresponding to half a unit cell of gypsum along the b-axis) on the (010) face of a dried gypsum sample that had previously been exposed to a supersaturated solution (Bosbach et al, 1996), but obviously this could have been the result of drying. In a more recent work, the combination of AFM and laser

confocal differential interference microscopy (LCM-DIM) revealed nucleation of highly anisotropic islands on the (010) face (Fig. 10a) for a broad range of supersaturations (Van Driessche et al, 2010). 2D nucleation appeared to be the main step generation mechanism (Fig. 10b), even at low supersaturation, and only indirect evidence of spiral hillocks was found. Quite surprisingly, an important fraction of the nucleated acicular islands were in fact multi-layered (i.e. 3D) entities (Fig. 10c), containing up to ~40 monolayers of CaSO_4 (Fig. 10d; Van Driessche et al, 2010). A possible explanation for this non-classical growth behavior could be the role of nanoparticles, which may have pre-formed in the bulk solution and at some point settle on the surface to initiate 3D islands, which act as a source of monolayer steps that then grow laterally by incorporation of further ions, much like what has been observed for the growth of organic crystals in a recent work (Jiang et al., 2017). This notion is to some extent supported by the results of another AFM study, which reported the frequent occurrence of growth hillocks with a nucleation point in the center on the (010) face of gypsum (Mbogoro et al., 2017). However, the AFM images shown in this work were collected in air (i.e. *ex situ*) after growth had been abandoned; therefore, it is difficult to argue about whether these peculiar surface features are the result of a screw dislocation or localized 2D nucleation. In any case, it is interesting to note that nanoparticle units seem to be actively involved in gypsum crystallization at various stages of the process – from nucleation (Fig. 7) over early (Fig. 9) to mature growth (Fig. 10). In summary, it can be concluded that both spiral and 2D/3D nucleation growth may occur on the (010) face, although at present it remains unclear if supersaturation plays a pivotal role in deciding which of the possible mechanisms will be dominant under certain conditions.

Fig. 10. *In situ* AFM imaging of growth on a (010) face of gypsum in contact with a slightly supersaturated solution (18 mM CaSO₄ at 23°C). (a) Acicular islands observed on the surface with corresponding height profiles (b,c) as indicated by numbers. The three islands shown on top of the inset in (a) have a height of ~0.76 nm (monolayer, i.e. 2D islands) while the one on the bottom of the image is about 2.4 nm in height (multilayer, i.e. 3D island). (d) Histogram showing the relative abundance of islands with different thickness, as given by the respective number of CaSO₄·2H₂O layers constituting the island. The black line represents a third-order exponential fit of the data. (e) Sequence of AFM images showing nanoparticles on the (010) surface that lead to the formation of growth steps. White arrow indicates a particle that has just landed on the surface. In the following two images new growth steps are continuously created (black triangles indicate the step fronts) while the particle is being consumed. White full circles indicate a second particle on the surface that also continuously spurred the formation of new growth steps on the surface. (a-d is reproduced from Van Driessche et al. (2010) with permission from the American Chemical Society).

So far, only the growth behavior of the (010) face has been studied in such level of detail with microscopy techniques, since experimentally this face is most readily accessible and also because growth on (010) is slowest for most relevant conditions (which is why (010) is usually the dominant exposed face in the final habit of gypsum crystals). Nonetheless, most of the bulk volume of gypsum crystals is actually created by the growth of its other faces: (120), (111) and (011). Notwithstanding, these faces have received far less attention. Indeed, Liu and Nancollas (1973) measured *R* for the fastest growing faces ((011) and/or (111)) and

found that for a wide range of supersaturation, the growth kinetics obeyed a second order law (again interpreted as spiral growth). In an attempt to further elucidate microstructural details of growth on the less common faces of gypsum, we recently succeeded in preparing oriented samples of natural gypsum in a way that they are accessible for in situ AFM growth studies, as will be reported in detail in a forthcoming publication (Browne et al., 2019). Briefly summarized, growth on (111) was found to be governed by spiral hillocks and isotropic 2D islands, while on (011) growth is rough. These findings comply with, and explain, the macroscopic appearance of gypsum crystals in their characteristic needle-like morphology, which results from fast growth along the c-axis i.e. through the (111) and (011) faces. Moreover, the latter is usually the first face to disappear from the typical crystal morphology because it exhibits the highest growth rate – well in line with the generally accepted notion that rough faces exhibit the highest growth rates (e.g. Chernov, 1980). The remaining (120) face is found to be quite unique with respect to growth behavior: actually it does not grow by itself but rather by small terraces of the neighboring (010) face, which are separated by macrosteps. This combination of terraces and macrosteps eventually establishes the characteristic angle between the (120) and (010) faces in the typical habit. However, the angle between these two faces can also change depending on the growth conditions, creating (1k0) faces instead of the predicted (120). Based on the proposed terrace/macrostep growth mechanism, the occurrence of (1k0) faces in natural crystals, such as those found within the Naica caves (e.g. García-Ruiz et al., 2007), can be rationalized.

Finally, it is worth mentioning that rate constants for growth measured as described above can also be leveraged to determine the activation energy (E_A) for gypsum growth. This is achieved by an Arrhenius plot of temperature-dependent k

values obtained from growth experiments at different levels of supersaturation, giving a face-averaged activation energy of $\sim 60 \text{ kJ mol}^{-1}$ in good agreement across different studies (see Table 1). In one particular case, the step velocity was directly measured on the (010) face as a function of supersaturation at different temperatures (Van Driessche et al., 2010). From the resulting step rate coefficient, the face-specific activation energy could be estimated to $\sim 70.7 \text{ kJ mol}^{-1}$. This – compared to the face average – slightly, but significantly higher value confirms that (010) is the most stable, and thus the slowest growing face, which should dominate the overall habit of the crystals – as observed for most relevant conditions.

2.2.2. *Anhydrite*

Compared to gypsum, much less research has been devoted to understanding the growth mechanisms and kinetics of anhydrite. Indeed, no bulk growth rate data are available for this phase, but growth on anhydrite cleavage faces (namely (100), (010) and (001)), was imaged with AFM at room temperature (which in fact is outside the stability field of anhydrite, see Fig. 1). This study (Pina, 2009) revealed that in contact with a supersaturated solution growth on the (010) and (100) faces takes place at steps with a height of $\sim 0.35 \text{ nm}$, which corresponds to one layer of CaSO_4 (due to the high roughness of the (001) face no steps could be imaged there). The formation of these monolayers occurred exclusively at pre-existing cleavage steps, whereas no spiral hillocks or 2D nucleation islands were observed. The rate of step propagation increased rapidly with increasing supersaturation on both imaged faces and showed strong anisotropy along different directions. This indicates that growth is controlled by the orientation, structure, and stability of the periodic bond chains (PBCs) that define the step edges of anhydrite monolayers (Pina, 2009, and references therein).

More recently, the window of in situ growth observations on the (100) face of anhydrite was successfully extended to conditions within the stability field of this mineral (60-120 °C) by AFM experiments in a supersaturated hydrothermal environment (Morales et al., 2012a,b). It was found that monomolecular growth steps originate mainly at screw dislocations (Fig. 11, upper panel), whereas nucleation of 2D islands (again monolayers) only occurs at high levels of supersaturation with very low nucleation densities (ca. 1 nucleus/ μm^2). Hence, the authors concluded that 2D nucleation is not an effective growth mechanism for the (100) face of anhydrite at temperatures of up to 120 °C.

Fig. 11. Results of in situ studies on the growth behavior of anhydrite (100) faces under hydrothermal conditions. (Upper panel) Sequence of AFM deflection images showing spiral growth on (100) at 90 °C. It is evident that the rate of step advancement rate changes with the relative current orientation of the step, which can lead to the formation of bilayers (indicated by dashed white lines) when a fast-moving step catches up with one that is moving much slower (as seen in images b, c and h). Moreover, spiral growth can be reactivated upon interaction with fast-moving steps originated from cleavage steps or other screw dislocations (c, d). (Lower panel) Schematic drawing of a projection along the [010] direction, illustrating the opposite orientation of sulfate groups in successive monolayers. The different geometry of parallel [010] steps that advance along [001] and [00-1] within the same monolayer is

evidenced. For further explanations see text. (Figure adapted from Morales et al. (2012) with permission from the American Chemical Society)

Thus, screw dislocations seem to be the dominant source of new steps on (100) faces of anhydrite. It should be noted, however, that the development of spiral growth on this face is strongly related to the fact that (100) face is perpendicular to a 2_1 screw axis in the crystal structure (e.g. Shindo et al., 2010) and contains highly anisotropic directions (Pina, 2009). As a result of this anisotropy, advancing steps move at a varying rate as they turn around a dislocation outcrop (Fig. 11, upper panel). Moreover, the fast-moving direction in one monolayer is equivalent to the slow-moving direction in the monolayer underneath as per the 2_1 axis (Fig. 11, lower panel) and thus, as fast-moving steps spread they catch up with slow-moving steps below, leading to the frequent occurrence of bilayer steps on the surface. When two steps from adjacent layers collide in such a way, growth of the (100) face of anhydrite virtually stops (Morales et al., 2012a). This phenomenon had already been described previously for barite and was referred to as a structure-induced growth self-inhibition process (Pina et al., 1998). Importantly, growth at a bilayer step will resume when a fast-moving monolayer reaches the slow-moving “lower” monolayer of the bilayer and thereby creates a surface for the upper “faster” monolayer to spread on. Consequently, for spiral growth to be efficient on the anhydrite (100) surface, a high density of active screw dislocations is required to provide sufficient interactions between monolayer and bilayer steps.

Hydrothermal AFM experiments also provided data on the growth kinetics of anhydrite. By measuring rates of step propagation on the (100) face as a function of supersaturation, the corresponding rate constant could be determined for different temperatures (Morales et al., 2012b). As in the case of gypsum, k increases with temperature, but the absolute values are up to two orders of magnitude lower (see

Table 1). Using an Arrhenius plot, the activation energy for step advancement was estimated to 73 ± 5 kJ/mol, which is comparable to the value reported for the (010) face of gypsum (70.7 ± 5 kJ/mol), and only slightly higher than face-averaged activation energies extracted from gypsum bulk growth experiments (cf. Table 1). This suggests that dehydration of ions (or other growth units/precursors) – and not ion incorporation – is the limiting factor for crystal growth of anhydrite from solution, which would rationalize why anhydrite is not prone to grown at mild temperatures (i.e. < 100 °C), as discussed in more detail in Section 2.3. This notion is corroborated by the observation (see Section 2.1) that anhydrite can readily be obtained at room temperature from liquid media that contain very low amounts of water (Tritschler et al. 2015b), which obviously should facilitate the dehydration step.

2.2.3. *Bassanite*

Studies dealing with the growth behavior of bassanite (calcium sulfate hemihydrate) crystals in aqueous solutions are scarce, mainly because this mineral phase is metastable throughout the entire phase diagram of the $\text{CaSO}_4\text{-H}_2\text{O}$ system (cf. Fig. 1). The work performed so far was mainly motivated by the role of bassanite in industrial processes such as the production of phosphoric acid or the conversion of (waste) gypsum into hemihydrate for e.g. construction applications; therefore, the experimental conditions chosen for bassanite growth studies were meant to mimic the actual process. For example, El Moussaoui et al. (1997) investigated homogeneous precipitation of hemihydrate in phosphoric acid media and showed that bulk growth rates vary as a function of the squared relative supersaturation, indicating a reaction of second order. Similar results were reported for the growth rate of bassanite in aqueous solutions of KCl, CaCl_2 and MgCl_2 at elevated temperatures (Yang et al., 2009). This second order dependency suggests that screw dislocations govern growth of bassanite,

although no spiral patterns could be observed on the growing hemihydrate. However, this conclusion was based on *ex situ* scanning electron microscopy images only, whereas no *in situ* analyses with high enough resolution (such as AFM) were performed. The same authors also reported that the growth rate of hemihydrate increases with temperature (from 80 to 100 °C), giving a comparatively low activation energy of ~40 kJ/mol for bassanite growth (cf. Table 1). In essence, it is evident that much more work needs to be done to foster our understanding of bassanite crystal growth.

2.3. Stability fields and phase transitions

To fully understand and predict mineral formation in natural and engineering environments it is of utmost importance to have precise knowledge about the phase(s) that will first appear under a given set of conditions, and if these phase(s) remain stable over time, i.e. if a certain phase transforms or not, and which factors drive this transformation. Generally, thermodynamic phase diagrams based on the solubility of the involved phases in the system are very useful tools that accurately indicate which phase(s) to expect. However, in the case of the $\text{CaSO}_4\text{-H}_2\text{O}$ system, despite many years of research, there is still considerable ambiguity with respect to the gypsum-to-anhydrite transition temperature (an overview on reported values is given in Table 2). Solubility measurements and thermodynamic calculations indicate that anhydrite should be the stable phase above 40-60 °C at ambient pressure (cf. Fig. 1 and Table 2), but due to very slow nucleation/dissolution/growth kinetics of anhydrite at temperatures lower than ~80 °C a more precise determination of the transition temperature remains challenging. Analysis of monophasic fluid inclusions found in the giant gypsum beams of Naica (Fig. 3c) show that these crystals were growing at a

temperature of 54.5 ± 2.0 °C (Krüger et al., 2013). Moreover, based on isotope studies, we know that they formed through the dissolution of hydrothermal (Garcia-Ruiz et al., 2007) and sedimentary anhydrite (Van Driessche et al., 2016), which tells us that the temperature for gypsum to transform into anhydrite at equilibrium must be above this value for low-salinity waters (Van Driessche et al., 2011).

Considerably less attention has been paid to the gypsum/bassanite transition temperature, due to the fact that at the Earth's surface bassanite is metastable – i.e. at the conditions where gypsum transforms to bassanite, anhydrite will be the thermodynamically stable phase (see Fig. 1). While the exact value of the gypsum/bassanite transition temperature seems to be of little importance to natural phenomena, it is indeed highly relevant for the production of plaster of Paris and other industrial hemihydrate-based materials. According to solubility data reported in the literature (cf. Table 2), the temperature for gypsum to transform into bassanite in a metastable equilibrium is located somewhere between ~80 and 110 °C (cf. Fig. 2A).

Table 2. Reported values for the temperature of gypsum-to-anhydrite and gypsum-to-bassanite transformation in aqueous environments.

Minerals	T / °C	Method	Authors
Gypsum to anhydrite	60-66	Determination of dissociation pressure curves and thermodynamic calculations	Van't Hoff et al. (1903)
	38-39	Solubility measurements of anhydrite at high temperature and extrapolation	Partridge and White's (1929)
	42 ± 1	Solubility measurements of anhydrite at lower temperatures and interpolation	Hill (1937)
	42 ± 2	Solubility measurements of gypsum, anhydrite and bassanite	Posnjak (1938)
	40	Measurements of thermochemical properties of solid gypsum and anhydrite	Kelley et al. (1941)
	42	Solubility measurements of anhydrite and gypsum	Bock (1961)
	42	Solubility measurements of CaSO_4 and its hydrates	Marshall et al. (1964)
	46 ± 25	Calculations based on revised thermodynamic data of Kelley et al. (1941)	Zen (1965)
	41 ± 1	Solubility measurements of gypsum and anhydrite	Power et al. (1964)
	58 ± 2	Water activity measurements	Hardie (1967)
	56 ± 3	Solubility measurements of anhydrite at high temperature ($> 70^\circ\text{C}$) and extrapolation	Blount and Dickson (1973)
	55.5 ± 1.5	Equilibration experiments in solutions containing both gypsum and anhydrite	Knacke and Gans (1977)

	49.5 ± 2.5	Solubility measurements of gypsum and anhydrite	Innorta et al. (1980)
	42.6 ± 0.4	Thermodynamic calculations	Corti and Fernandez-Prini (1983)
	46	Solubility measurements at high pressure and extrapolations to 1 atm	Hamad (1985)
	59.9	Thermodynamic calculations	Raju and Atkinson (1990)
	40	Solubility measurements and phase transition experiments	Kontrec et al. (2002)
	40 ± 2	Modelling of CaSO ₄ solubility	Azimi et al. (2007)
	>54.5 ± 2.0	Growth temperature of gypsum crystals in the Naica cave	see text
Gypsum to bassanite	106	Experiments and thermodynamic calculations	van't Hoff et al. (1903)
	98-100	Solubility measurements of gypsum and bassanite	Partridge and White (1923)
	97 ± 1 °C	Solubility measurements of gypsum, anhydrite and bassanite	Posnjak (1938)
	99 ± 2 °C	Modelling of CaSO ₄ solubility	Azimi et al. (2007)

Besides the uncertainties in the transition temperatures (and thus stability fields) of the different crystalline forms of calcium sulfate, the interpretation of the CaSO₄-H₂O phase diagram is further complicated by the fact that up to 90°C gypsum is the main crystalline phase obtained from direct precipitation experiments (i.e. mixing Ca²⁺- and SO₄²⁻-containing solutions), while at higher temperatures bassanite appears as the dominant solid phase (Cruft and Chao, 1970; Ossorio et al, 2014). So far, primary anhydrite formation in direct precipitation experiments from aqueous solutions has only been observed under hydrothermal conditions at 174 °C (Fan et al., 2010), although recently Dixon et al. (2015) reported the occurrence of anhydrite during the dissolution of jarosite (KFe₃(OH)₆(SO₄)₂) in saturated CaCl₂ brines at room temperature. When conducted in a batch reactor (i.e. a closed system), these experiments gave a mixture of gypsum and bassanite, whereas anhydrite was the main phase obtained in a flow-through setup. This represents the first experimental evidence corroborating the previously predicted stability region of anhydrite in high-

salinity brines at ambient conditions (Bock, 1961; Hardie, 1967). On the other hand, in direct precipitation experiments the onset of primary bassanite formation can be shifted to lower temperatures by increasing salinity. For example bassanite is the main phase obtained at 80 °C in the presence of 4.3 M NaCl (Ossorio et al., 2014), while a temperature of around 50 °C is sufficient to produce pure hemihydrate from solutions containing >6 M CaCl₂ and small amounts of Na₂SO₄ (which, in addition to sheer salinity effects, may or may not be related to the extreme stoichiometry, i.e. calcium/sulfate ratio chosen in these studies) (Cruft and Chao, 1970). A summary of the crystalline phase(s) to expect upon direct precipitation at different temperatures (up to 120°C) and salinities (up to 4.3 M NaCl) is given in Fig. 12. Bassanite formed in high-salinity media at elevated temperatures remains stable for long periods of time (e.g. up to 2 months in the presence of 4.3 M NaCl, cf. Fig. 12), before transforming into anhydrite (the thermodynamically stable phase at these temperatures). Also, bassanite can form spontaneously when droplets of CaSO₄ solutions are rapidly evaporated (i.e. when the level available hydration water is rapidly decreased) at ambient conditions (Qian et al., 2012; Shahidzadeh et al., 2015).

Fig 12. Experimental results showing the main CaSO₄ phase(s) obtained by direct precipitation as a function of time, salinity and temperature. Experiments at 60 °C were monitored over periods of up to two years of reaction, but the precipitate remained phase-pure gypsum (according to PXRD, with its detection limit of around 1%) in all studied cases (Ossorio et al., 2014). This suggests either that the gypsum/anhydrite transition temperature is above 60 °C, or that anhydrite formation

is under severe kinetic inhibition at the given conditions. Figure adapted from Ossorio et al. (2014) by permission of Elsevier.

The experimental evidence described above highlights that (i) within the time frame of laboratory experiments anhydrite does not readily precipitate as primary phase across large parts of its predicted stability field, and (ii) bassanite is an important primary (precursor) phase in high-salinity environments already at relatively mild temperatures (≥ 50 °C). Both observations stand in stark contrast with the large amounts of anhydrite that supposedly have formed on the Earth's surface in evaporitic environments (< 60 °C) (e.g. Warren, 2006), and the concurrent marginal terrestrial occurrence of bassanite and its significant abundance on Mars (in amounts at least high enough to be detected using remote sensing (Wray et al., 2010; Vaniman et al., 2014, 2018)).

These contradicting observations can be reconciled if we consider both the mechanisms and kinetics of nucleation and growth of calcium sulfate minerals. According to the new picture of CaSO_4 crystallization outlined in Section 2.1, all three crystalline phases follow a common precipitation pathway, and the rate of the final step along that pathway, i.e. the transformation of the initial disordered to the final ordered phase, should strongly depend on the interfacial free energy (γ) of the latter. According to CNT, the nucleation rate scales inversely with the third power of γ (cf. Eq. 1) (Kashchiev, 2000). Although we now know that CaSO_4 phases do not form via “classical” nucleation processes (see Section 2.1), the *effective* interfacial free energy (γ_{eff}) obtained from CNT fits of nucleation rates still provides a meaningful estimation of the relative energetic costs (i.e. the height of the nucleation barrier resulting from thermodynamic contributions) for a solid to form from solution (see Section 2.1). Hence, based on this reasoning we can assume that gypsum ($\gamma_{\text{eff}} \approx 40$ mJ/m²) and bassanite ($\gamma_{\text{eff}} \approx 9$ mJ/m²) should nucleate much more readily than

anhydrite ($\gamma_{\text{eff}} \approx 90 \text{ mJ/m}^2$) for similar levels of supersaturation. After nucleation, crystal growth will dominate – which in the case of anhydrite is again severely hampered due to the structure-induced self-inhibition phenomena discussed in Section 2.2.2. Only when spiral dislocations occur at high areal densities on the surface, growth of anhydrite will proceed uninterruptedly (Morales et al., 2012a). Moreover, direct comparisons between growth on the main faces of anhydrite and gypsum shows that step growth kinetics are considerably slower on anhydrite (see Table 1). For example, at 75°C and similar levels of supersaturation, the average step velocity on the (010) face of gypsum is >300 nm/s, while on the (100) face of anhydrite it does not exceed 5 nm/s (Van Driessche et al., 2010; Morales et al., 2012b). In fact, the growth rate of anhydrite becomes significant only at temperatures higher than ~100 °C (Morales et al., 2012b). Hence, even once a (post)critical nucleus of anhydrite has been formed (which itself is intrinsically difficult for thermodynamic and kinetic reasons), it will still take a considerable period of time until detectable amounts of this mineral are obtained (see Fig. 12). This notion of inherently slow growth is corroborated by the fact that metastable gypsum forms within the stability field of anhydrite even in the presence of anhydrite seeds (Nancollas et al., 1973). Thus, we can conclude that the formation of anhydrite as a primary phase is hindered both thermodynamically (high apparent interfacial free energy) and kinetically (dehydration of ions, limiting both nucleation and growth rates). This unifies laboratory observations with those made in natural environments: time is the crucial factor for anhydrite to occur in a system at low temperatures (< 100 °C) – which on geological scales is not an issue, but it clearly limits anhydrite occurrence in the lab.

The importance of (de)hydration effects during the crystallization process of calcium sulfate (as already discussed in Section 2.1) is highlighted by the fact that

high salinities promote the precipitation and (kinetic) stability of bassanite, as clearly shown by Fig. 12). In concentrated salt solutions (i.e. brines), the activity of water decreases significantly, which facilitates the dehydration of the primary species during the transition of the initial disordered state into an ordered crystalline phase, thus favoring the formation of bassanite over gypsum. Anhydrite crystallization is still inhibited under these conditions due to its higher surface free energy (and persisting barriers related to dehydration), and therefore will only occur spontaneously at very high salt contents (Dixon, 2015) or extremely low water contents like in the work of Tritschler et al. (2015b). In addition, hydrodynamics seem to play an important role in that context, as anhydrite formation at extreme levels of salinity was only observed during flow-through, and not batch experiments in the study of Dixon et al. (2015). Finally, we note that high salinity could also be a key aspect to explain the abundance of bassanite on Mars, as opposed to its rare occurrence on Earth. Calculations performed by Tosca et al. (2008) suggest that a number of Martian locations hosted fluids that were 10 to 100 times more saline than halite-saturated terrestrial waters – which when linked to the low water content in the atmosphere of Mars, could explain why initially precipitated bassanite did not transform into gypsum in these settings (in contrast to terrestrial environments, where bassanite deposits usually hydrate to gypsum over time, except in very arid areas).

In summary, the insights gained on the mechanisms and kinetics of calcium sulfate mineral formation from the studies reviewed in this chapter provide a solid basis to predict the outcome of abiotic precipitation from CaSO_4 solutions over a broad range of conditions in both natural and engineering environments.

3. Biotic formation pathway of CaSO_4 minerals

Fig. 13 shows a schematic overview of the mineralization “pipeline” in natural environments, indicating the possible biotic factors that may influence or control the outcome (phase selection, morphology, texture etc.) of calcium sulfate precipitation. Depending on the extent of biological involvement, usually three different types of mineralization processes are distinguished (e.g. Dupraz et al., 2009): (i) Biologically influenced mineralization, where mineral formation is an inadvertent side effect of a biological process. These accidentally formed byproducts are usually not beneficial for the organism. (ii) Biologically induced mineralization, where the organism alters the chemistry of the surrounding environment creating appropriate conditions for mineral precipitation to occur, yet without exerting a direct control over the particular pathways of nucleation and growth. The obtained minerals may or may not be beneficial for the organism(s) that influenced their formation. (iii) Biologically controlled mineralization, where the organism actively directs mineral formation through the use of highly specific (macro)molecules at the cellular level, and where the obtained biogenic minerals have a specific function for the organism.

The vast majority of biominerals are composed of carbonates (e.g. calcite/aragonite), phosphates (e.g. apatite), silicates (e.g. opal), or oxides (e.g. magnetite), whereas sulfates play a much smaller role in biomineralization (e.g. Boßelmann and Epple, 2008). The information available about biotic precipitation pathways of calcium sulfate is rather scarce and scattered throughout the literature. Moreover, most evidence for a direct link between biomolecules/organism and calcium sulfate minerals is based on macroscopic observations and the biological involvement still awaits confirmation at the microscopic and molecular levels. Importantly, it has been shown that calcium sulfate minerals can preserve co-deposited organic molecules (e.g., amino acids), and host endolithic organisms in

geobiological environments (e.g. Parnell et al., 2004; Aubrey et al. 2006; Benison and Karmanocky III, 2014; Panieri et al., 2010; Schopf et al., 2012) As such calcium sulfates are considered to be valuable targets in searching for evidence of ancient and present life, on both Earth and Mars. Moreover, certain small organic molecules are known to be efficient modifiers used to control the formation pathway of calcium sulfate, either to obtain an end product with tailored properties (e.g. by the wallboard industry) or to avoid/retard sulfate precipitation altogether (e.g. in water desalination).

Fig. 13. Schematic representation of the mineralization “pipeline” in natural environments, indicating various possible factors that can control and/or influence the precipitation process and its final outcome.

3.1 Mineralization in the presence of organic molecules

In natural environments, detectable quantities of quite complex organic molecules can form through strictly abiotic processes (e.g. McCollom and Seewald, 2007; Ménez et al., 2018) and may affect inorganic mineralization to a greater or lesser degree. However, actual biological activity (e.g. of microbes), and its breakdown products (e.g. metabolites), can have much more substantial effects on the overall yield and complexity of the formed mineral assemblies. Here we will first

consider the influence of small organic molecules on CaSO_4 precipitation in the absence of living organisms.

Organic compounds of biological origin have been shown to influence the precipitation of for example calcium carbonate in natural environments, a process occasionally referred to as organomineralization (Trichet and Défarge, 1995; Défarge and Trichet, 1995; Défarge, 2011). In the case of CaSO_4 , one of the first studies addressing this issue used organic molecules extracted from natural seawater, which were found to act as inhibitors of gypsum precipitation and influence the morphology of the obtained crystals (Barcelona et al., 1976; Barcelona and Atwood, 1978). Since then, a variety of organic molecules (plausible to occur in Nature in sufficiently high amounts) have been tested in laboratory experiments with respect to their influence on CaSO_4 , in particular gypsum crystallization. For example, certain amino acids, proteins or polyphenols, can significantly alter the crystallization kinetics of calcium sulfate in aqueous media (either impeding or accelerating) already at low concentrations (Barcelona and Atwood, 1978; Bosbach and Hochella, 1995; Prisciandaro et al., 2003; Hamdona and Hadad, 2008; Rabizadeh et al., 2014; Harouaka et al., 2017; Ossorio et al., 2017; Nicoleau et al., 2019), resulting in changes of crystal habit and/or the aggregation behavior (Fig 14; e.g. Cody, 1979, 1991; Cody and Cody, 1988a,b, 1989, 1991; Harouaka et al., 2017). Noteworthy, specific biomolecules promote the formation of twinned gypsum crystals (Fig. 14; Cody and Cody, 1989; Cody, 1991). For example, α -amylase – an enzyme commonly excreted by certain bacteria, algae, and plant roots – was found to produce peculiar gypsum twins (often called Montmartre twins, cf. Fig. 14a) very similar to those present in the Eocene deposits of the Paris Basin (Cody and Cody, 1989). Importantly, reference experiments conducted in the absence of organic matter did not yield the typical non-

prismatic crystal morphologies observed in natural settings. On the other hand, many common natural gypsum habits can be reproduced in the lab in the presence of analogous organic molecules – emphasizing the key role of organic chemistry in controlling crystallization of gypsum in natural environments.

Fig. 14. Control over gypsum crystal habits achieved by organic crystallization modifiers. (a) Morphologies of gypsum crystals and crystal aggregates formed at different pH and α -amylase concentrations (Cody and Cody, 1989, reprinted by permission of Elsevier). (b) Gypsum crystals grown in the presence of 0.01% humic acid soil extracts. (c) Gypsum crystals obtained from solutions containing 1% tannic acid (gallotannic acid). The aggregate consists of plate-like and lenticular individual crystal subunits, which are arranged in a regular manner to build a rose-like architecture (similar to the typical desert shown in Fig. 2c). Scale bar is 0.5 mm. (images (b) and (c) are reproduced from Cody (1991) by permission of the Society for Sedimentary Geology).

To the best of our knowledge, there are no systematic studies on the influence of organic molecules on the crystallization behavior of bassanite and anhydrite. Indeed, it was reported that certain organic (macro)molecules, such as polycarboxylates and phosphate esters, can promote the formation of anhydrite over gypsum at mild temperatures (~ 60 °C; Cody and Hull, 1980). Unfortunately, when repeating these experiments in our lab, no anhydrite was ever detected, even at 80 °C (Ramirez et al., 2019).

Modifications of the habit of gypsum crystals forming in the presence of organic molecules are usually manifested through changes in the aspect ratio

(length/width) (Fig. 14a). These changes result from modulations of the different relative growth rates of the faces constituting the crystal morphology. Growth rates of specific faces are modified, and usually slowed down, when molecules adsorb onto them. For instance, it was shown that organic molecules carrying anionic carboxylate groups can bind to Ca^{2+} ions at the surface of gypsum faces and thus alter their growth kinetics (e.g., Barcelona and Atwood, 1978; Cody and Cody, 1991; Harouaka et al., 2017). While the mechanisms underlying modulations of individual growth rates and habit modification are reasonably well understood at the molecular level (e.g. inhibition of the growth of specific faces in favor of other faces, option (7) in Fig. 15), the circumstances allowing organic molecules to alter the early stages of precipitation (i.e. nucleation and twinning) are still unclear (e.g. Ossorio et al, 2017). Most organic molecules were found to retard the onset of mineral formation (nucleation), i.e. they increase the characteristic induction time of precipitation (e.g. Prisciandaro et al., 2003; Rabizadeh et al., 2014; Ossorio et al., 2017; Nicoleau et al., 2019), which is generally assumed to rely on two mechanisms (e.g. Sangwal 2007; Amjad and Demadis, 2015): (1) organic molecules act as chelators, sequestering at least one of the lattice ions, and thus lowering the effective supersaturation of the solutions, and/or (2) organic molecules adsorb on the interface of (pre-)nucleation clusters and prevent their further growth and aggregation/coalescence into larger entities. Due to the relatively high solubility of gypsum ($> 0.015 \text{ mol.kgw}^{-1}$, see Fig. 1), the concentration of organic molecules necessary to significantly reduce the net supersaturation of the solution by complexation of lattice ions is unlikely to occur in most natural environments. Moreover, it has been observed that very low levels of organic molecules can be sufficient to alter the kinetics of nucleation. Thus, in natural environments binding of organic molecules to crystal nuclei formed during the early

stages of precipitation seems to be the most, if not the only, plausible mechanism for interaction. This is indirectly supported by the fact that many nucleation-inhibiting molecules also show distinct affinities to adsorb onto specific faces of the final crystals. However, the latter notion relies on the classical view of nucleation (see Fig. 6), where nuclei are assumed to have identical properties (i.e. the same structure, density etc.) as those of fully-grown macroscopic crystals. As discussed in Section 2.1, the nucleation of gypsum is more complex than that envisaged in the classical picture, involving a sequence of multiple stages from dissolved ions to stable crystals.

In light of this alternative pathway, a variety of plausible mechanisms, classified into overall eight types of interaction, for organic modulation of inorganic CaSO_4 mineralization is schematically depicted in Fig. 15. Some of the indicated mechanisms have already been supported by experimental evidence. For example, in situ SAXS experiments have shown that in the presence of citric acid the formation of primary particles is hindered (interaction type (1) in Fig. 15; Ossorio et al., 2017). Based on induction time measurements of gypsum nucleation in the presence of organic additives (mainly polymers) and complementary determination of gypsum/water interfacial energies, a very recent study (Nicoleau et al., 2019) concludes that mineral formation is delayed because polymer molecules impede the collision between primary species (i.e. clusters of ions) and further aggregation/growth by prevailing in the vicinity of their surface and thus effectively lowering their attachment frequency (interaction types (2) and (3) in Fig. 15). Although the results of these studies are already an important step forward, much more dedicated (preferably in situ) experimental and computational work is necessary to fully understand, at the molecular level, how organic molecules influence the different stages of calcium sulfate precipitation.

Fig. 15. Schematic representation of the possible types of interactions between organic molecules (OMs) and the mineral species occurring in different stages along the nucleation pathway of gypsum: (1) OMs alter the association/dissociation constants of ion and ion pairs to form primary particles; (2) OMs bind to primary particles and modulates their interaction potential; (3) properties of the hydrated layers around primary particles (and thus again their mutual interactions) are changed due to the nearby presence of OMs; (4) OMs are incorporated inside of the emerging larger disordered aggregates and may affect their reorganization dynamics; (5) OMs adsorb on the interface of the larger aggregates and may influence the kinetic persistence (lifetime) of these species; (6) interaction types (4) and (5) occur simultaneously; (7) OMs bind (selectively) on the surface(s) of a formed crystalline gypsum seed and thereby may alter its growth behavior; (8) OMs become incorporated into the forming crystals and may influence their mechanical properties. Note that in general, OMs can interact with mineral species at one or multiple stages, either delaying or accelerating the transition from one stage to another. At the moment, experimental evidence exists for interaction types (1), (3)/(4) and (7) (see the text for detailed explanations).

Finally, it should be noted that there is large body of literature on the evaluation of different polymeric additives (such as poly(aspartic acid), poly(acrylic acid) and polyphosphonates) for the prevention of calcium sulfate precipitation in the context of scale inhibition. However, most of these studies focused on quantifying the antiscaling efficiency of an additive by measuring its ability to delay mineral precipitation, without providing actual insight into the interplay of these macromolecules with the different mineral species along the precipitation pathway outlined above. Therefore, we consider a detailed discussion of these works as being outside of the scope of this review and refer the interested reader to dedicated treatise on the topic of scale prevention (e.g. Amjad and Demadis, 2015).

3.2 Mineralization in the presence of prokaryotic microorganisms

It is almost impossible to find natural environments on the Earth's surface and subsurface where prokaryotic microorganisms do not occur and thrive. They have been found in the deepest oceans (Kato et al., 1998), the driest deserts (e.g. Wierzchos et al., 2011), as well as in the coldest climates (e.g. Cockell et al., 2010). Since the advent of life, microorganisms have played a pivotal role in the physical and chemical processes associated with mineral formation from solution (e.g. Dupraz and Visscher 2005). In evaporitic environments, microorganisms often occur as endoevaporitic mats (Rothschild et al. 1994), which can be responsible for the formation of microbialites, i.e. organosedimentary deposits that have accreted as a result of a benthic microbial community trapping and binding detrital sediment and/or forming the locus of mineral precipitation (Burne and Moore, 1987). Although carbonate- and siliciclastic-dominated microbialites are most common (e.g. Riding and Awramik, 2000), evidence of gypsum-dominated microbialites has been found throughout the geological record (e.g. Yousef, 1988; Aref, 1998; Rouchy and Monty 2000; Arp et al., 2008). For example, such organosedimentary(-like) structures are abundant in the calcium sulfate deposits formed in the Mediterranean and Paratethys Sea during the salinity crisis of the Messinian and Badenian, respectively (e.g. Vai and Ricci Lucchi, 1977, Rouchy and Monty 1981, 2000; Peryt, 1996, 2013; Babel 2011; Allwood et al., 2013). Most frequently, they appear as dome-shaped stromatolite structures (see Fig. 16 and Fig. 3b). When a clear internal layering is absent, these structures are best described as thrombolites (e.g. Riding, 2011). Rouchy and Monty (1981, 2000) proposed the term “gypsified microbial deposits” to be more appropriate in the case of gypsum deposits formed by the passive incorporation of microbe-derived matter during purely inorganic precipitation of gypsum. However, at present it remains

challenging to differentiate between both scenarios in the rock record (as discussed in more detail below).

Fig. 16. Evidence for the presence of microorganisms during calcium sulfate precipitation in past and present environments. (a1) Columnar and (a2) dome-shaped stromatolite structures in Miocene gypsum deposits at Yiou, Cyprus (Rouchy and Monty, 2000, reprinted by permission from Springer Nature), (c) Gypsum microbialite domes covered with crusts of selenite crystals (white arrows) displaying variable morphology and many orders of crenulations (Verenchanka quarry, Ukraine) (Babel et al., 2011, reprinted by permission from Springer Nature). (c) Present-day salina (SA) in the Sawda Nathil depression (Qatar), containing water-covered gypsum stromatolites, fringed by temporarily exposed gypsum stromatolites carrying a halite crust (white arrows). The inset shows a side view of a single, mushroom-like gypsum stromatolite, and a cross-section revealing gypsum-encapsulated green cyanobacteria (Strohmenger and Jameson, 2018, reprinted by permission from Springer Nature). (d) General view of modern gypsum-dominated thrombolites growing in Laguna Pirata, Los Roques (Venezuela). The inset shows a microbial mat coating a thrombolite composed of microcrystalline gypsum. The mat exhibits distinctive layering originating from a vertical array of bacterial communities (Petrash et al., 2012, reprinted by permission from Elsevier). (e) Present-day gypsum deposits exposed at the southern bank of a concentration pond next to Lake Quaron (Egypt). The insets show (top) a fine-grained gypsum microbialite sub-facies (scale bar: 1 cm), (bottom left) a large and well-developed gypsum dome, and (bottom right) a laminated, grass-like selenite sub-facies (Ali-Bik et al., 2011, 2013, reprinted by permission from Springer Nature and Dipòsit Digital de Documents de la UAB under license CC BY-SA 3.0). (f1-3) Series of transmission electron micrographs showing progressive gypsum precipitation on cell wall of *Synechococcus*. f1: Occurrence of numerous

nucleation sites on the cell surface (black arrows). f2: Gypsum crystals grow away from the cell surface and appear to be covered by a thin layer of bacterial slime. f3: *Synechococcus* cell divides and sheds some of the precipitated gypsum (adapted from Thompson and Ferris, 1990).

Present-day examples of subaqueous gypsum-dominated microbialites (Fig. 16a-e and Fig. 3b) are found in hypersaline environments around the globe, such as the Gotomeer on the island of Bonaire in the Netherlands Antilles (Kobluk and Crowford 1990), the Guerrero Negro sabkha and saltern system in Mexico (Vogel et al., 2009; 2010), the hypersaline lagoon of the Archipelago Los Roques in Venezuela (Petrash et al., 2012), several salt ponds in Egypt (Taher et al., 1995; Alik-Bik et al., 2011; 2013; Taher, 2014), the salinas of Sawda Nathil in Qatar (Strohmenger and Jameson, 2018), and the salars in the Atacama desert and High Andes (e.g. Farías et al., 2014, Rasuk et al., 2014; Ercilla Herrero, 2019). Although these microbialite/thrombolite/stromalite(-like) structures share several common features (e.g. Fig. 16a-e), no general model for their formation has been proposed yet. Nevertheless, certain agreement seems to exist about the notion that (cyclic) fluctuations in water salinity (due to seasonal and/or long-term variations in the ratio of water inflow and evaporation rate) coupled to changes in water depth, column stratification and circulation are largely responsible for the laminated and domal gypsum formations (e.g. Warren, 1982; 2006; Taher et al., 1995; Gerdes et al., 2000; Babel, 2004; 2011). However, also other signs for the involvement of microbial mats in the formation of these structures have been reported (e.g. Gerdes et al., 2000; Vogel et al., 2010; Petrash et al., 2012; Farías et al. 2014; Rasuk et al., 2014). For example, Allwood and coworkers (2013) propose a combination of abiotic and biotic mechanisms to explain different gypsum structures observed in the Messinian rock record from Crete and Sicily. These include columnar and domal stromatolites in fine-

grained gypsum, microbially laminated selenite and columnar selenitic stromatolites. In present-day environments, gas accumulation below microbial mats seem to be the origin of domal structures, which then are preserved through gypsification (e.g. Farías et al., 2014; Ercilla Herrero, 2019). In any case, it is obvious that the contribution of (endo)evaporitic microbes to the formation of gypsum domes needs further investigation.

A less common feature indicative of microbial activities in evaporitic environments becomes manifest in the gypsum ooid facies from the Miocene–Pliocene playa lakes in Turkey (Tekin et al., 2008). Evaporation-induced gypsum formation in the presence of cyanobacteria was also observed in stalactite-like structures, which grow on the roof of an undercut cliff facing the lagoon of the Aldabra Atoll in the Indian Ocean (Braithwaite & Whitton, 1987). Mineral precipitation under the influence of microorganisms has also been observed in environments with very low water content. For example, in a saline soil alluvial plain shaped by the Gela river in Sicily, a strong correlation between the presence of cyanobacteria and salt crust covers was observed. Lenticular gypsum crystals formed a first layer of inorganic material embedding cyanobacterial filaments, while halite subsequently mineralized over the gypsum layer. In some filaments, calcite was the first embedding mineral layer, on which gypsum then crystallized (Canfora et al., 2016). Gene sequencing showed that sulfur-oxidizing bacteria were colocalized with the mineralized cyanobacteria. The authors proposed that the formation of an envelope made of calcium and sulfur-based compounds (carbonates or/and sulfates) protects the microorganisms from immediate contact with the NaCl layer and thus reduces salt stress. To further illustrate the widespread habitat of microorganism in water-deprived environments, we note the occurrence of gypsum neogenesis in the

presence of bacteria (*Arthrobacter*) inside weathered and remobilized gypsum deposits from exposed mid-Ordovician marine evaporite beds in the polar desert of Devon Island in the Canadian High Arctic (Cockell et al., 2010). Electron microscopy images show gypsum crystals associated with the surface of bacterial cells and carbonaceous materials in natural and laboratory-grown samples, respectively. However, the largely unchanged sulfur isotopic composition of the gypsum crystals indicates that microorganisms do not seem to play a major role in the biogeochemical sulfur cycling of gypsum itself.

In several non-marine and low-salinity environments, examples of gypsum precipitation in the presence of microorganisms have also been reported. Most notably, epicellular biomineralization of gypsum, calcite, and magnesite was observed in the laboratory using filter-sterilized natural alkaline lake water, which was slightly supersaturated with respect to gypsum and inoculated with *Synechococcus*, isolated from Fayetteville Green Lake in New York (Thompson and Ferris, 1990). During the laboratory experiments, gypsum was first nucleated close to the bacterial cell walls (Fig. 16f1-f3). Later, calcite started to form due to the photosynthetic metabolism of *Synechococcus*, causing alkalization of the microenvironment. Further research, using both natural and simulated lake water, confirmed that gypsum nucleation was induced at the bacterial surface layer, i.e. the s-layer (Schultze-Lam et al., 1992). Unfortunately, no control experiments without bacterial cells were reported, so it is difficult to evaluate the true potential of this s-layer to control crystallization.

Gypsum deposits present in the Frasassi Caves (Italy) are another example of bacterially mediated mineralization in a non-marine environment. Gypsum is formed, at least partially, from sulfate supplied from microbial oxidation of H₂S in the cave atmosphere and calcium obtained through local dissolution of the limestone cave

walls (Galdenzi and Maruoka, 2003; Mansor et al., 2018). A similar model has been proposed for the Lower Kane Cave in Wyoming (Engel et al., 2004). Complementary gypsum precipitation experiments carried out in the lab by Harouaka et al. (2016) at low pH and in the presence of the sulfur-oxidizing bacterium *Acidithiobacillus thiooxidans* (extracted from the cave) showed a small, but significant, Ca isotopic fractionation effect compared with abiotic gypsum. Moreover, the biotic precipitates had irregular morphologies with smaller average aspect ratios compared to their abiotic counterparts. The observed isotope and morphology effects are explained by the combined action of both soluble organic molecules and insoluble organic matter (i.e. biofilms, comprising both living and dead cells) on the growth of the gypsum crystals. Additional experimental work showed that the Ca isotopic fractionation during gypsum precipitation is impacted by growth inhibition in the presence of amino acids (Harouaka et al., 2017). The authors argued that the mechanism by which organic molecules affect the morphology of a mineral can also account for changes in its isotopic composition. Another example of the interaction between microorganisms and gypsum precipitation in non-marine waters at low salinity is found at the modern Miette Hot Springs (Jasper National Park, Alberta, Canada), a complex hydrothermal system characterized by a diverse microbiota and atypical mineral precipitates (Bonny and Jones 2003). Here, gypsum precipitation is induced in the proximal vent environment where the oxidation of H_2S gas in the spring water produces sulfate, while calcium is derived from the spring water and/or from dissolution of limestones overhanging the spring vents. Rocks and microbial mats act as nucleation substrates for the growth of coarse gypsum rinds close to the spring vents, while small gypsum particles nucleated in suspension commonly adhere to the sticky sheaths of microbial filaments.

A few cases of gypsum formation in the presence of microorganisms have been reported for human-altered environments. For instance, dense biofilms have been discovered underneath gypsum efflorescence layers formed on the prehistoric decorated walls of the Sorcerer's cave (France). The biofilm matrix contains autotrophic sulfur-oxidizing bacteria and a relatively high abundance of *Actinobacteria*, which could be responsible for biologically induced and/or influenced gypsum mineralization (Lepinay et al., 2018). The potential of autotrophic sulfur-oxidizing bacteria to induce the formation of gypsum crusts on stone buildings in tropical environments had already been suggested in a previous work (Kumar and Kumar, 1999). More recent microscopic observations of the interactions between endolithic microorganisms and stone facades of historic buildings subject to urban pollution in a sub-tropical climate showed that cyanobacterial filaments were encrusted with gypsum minerals (Gaylarde et al., 2017). The microbial populations identified on the facades caused an increased degradation due to acid production, leading to solubilization of the host rock and reprecipitation of crystalline materials, such as gypsum, at the surface. As a result, a hard but brittle outer crust was formed on the surfaces of endolithic cells.

The above-described examples of close spatial association between microbial cells/biofilms and gypsum crystals in both past- and present-day geochemical environments seem to suggest that microbes and/or microbial activity can play both indirect and direct roles in the process of calcium sulfate precipitation. Their influence can be twofold: either the microorganisms change the solution speciation of the (micro)environment, or they directly influence the process of mineral nucleation and growth. Regarding the former aspect, it is well known that the metabolic activity of microorganisms can alter the physicochemical conditions of the local environment,

such as pH, Eh, ion concentration etc. (cf. Fig. 13). These changes can lead to an increasingly supersaturated solution with respect to a given mineral phase. This has been extensively documented for CaCO_3 , where bacterial photosynthesis and sulfate reduction are known to increase alkalinity and thus promote carbonate precipitation (e.g. Dupraz et al., 2009). In the case of CaSO_4 , sulfur-oxidizing bacteria can convert H_2S (or elemental S) into sulfate, and the accompanying decrease in pH can provide sufficient Ca^{2+} supply via carbonate dissolution. A few field and lab observations have shown that these coupled processes can result in a solution supersaturated with respect to gypsum promoting its formation (e.g. Bonny and Jones, 2003; Galdenzi and Maruoka, 2003; Engel et al., 2004; Petrash et al., 2012; Harouaka et al., 2016; Mansor et al., 2018). The cell wall of bacteria and the frequently associated exo-polymeric substances (EPS) are typically rich in anionic functional groups, such as carboxylates and phosphates. These tend to scavenge metal ions (e.g. Ca^{2+}) from the surrounding solution and may create a local environment with increased ion concentration (e.g. Beveridge et al., 1983, Gallagher et al., 2010 and references therein). The abundant amounts of gypsum associated with biofilms observed in past and modern environments (e.g. Rouchy and Monty, 2000; Fariás et al., 2014) could thus be a consequence of the retention of (originally dissolved) salts within biofilms, which ultimately crystallize during the later course of evaporation.

A similar mechanism could also apply for non-evaporitic environments, where a supersaturated state is created locally at the cell wall of (cyano)bacteria (Thompson and Ferris, 1990, Schultze-Lam et al., 1992; Cockell et al., 2010) or cyanobacterial filaments (Canfora et al., 2016, Gaylarde et al., 2017). Alternatively, the formation of gypsum on cell walls, filaments and/or EPS could also be interpreted as surface-induced (i.e. heterogeneous) nucleation (e.g. Kashchiev, 2000). The sheer presence of

a foreign surface can considerably lower the energy barrier associated with the nucleation process (as shown in Fig. 6), accelerating nucleation kinetics and thus favoring mineral formation at the interface (e.g. Liu, 2000). In addition to providing a (non-specific) surface to nucleate on, the organic matrix can further promote nucleation through specific interactions with the emerging inorganic phase, such as electrostatic, geometric or stereochemical matching, which will further reduce interfacial energies and the nucleation barrier (e.g. Mann et al., 1993). For stereochemical matching, experiments dealing with CaCO_3 crystallization have shown that stronger binders lead to higher heterogeneous nucleation rates because the net interfacial energy is lowered (Hamm et al., 2013). In the case of gypsum, it was reported that certain organic monolayers can accelerate gypsum nucleation kinetics (Douglas and Mann, 1994, Wang et al., 2016), to a degree that seems to correlate with the calcium binding capacities of those layers (Wang et al. 2016). Moreover, such monolayers can also induce specific crystallographic orientations of gypsum crystals growing on these templates (Douglas and Mann, 1994). Hence, stereochemical, electrostatic and/or geometric factors can play an important role in organic template-mediated nucleation of gypsum. Moreover, gypsum crystals with perfect alignment along the (010) face were found to form on polar organic monolayers. This suggests that molecular recognition of hydrated surfaces, such as the (010) face of gypsum, requires ordered layers of water molecules formed through directional hydrogen bonding at the organic/inorganic interface (Douglas and Mann, 1994). Despite these important pieces of experimental evidence, there is still only very few direct molecular-scale observations of surface-induced mineral formation, and as such the precise pathway and the nature of relevant nucleation sites remain elusive in the presence of organic surfaces. More specifically, in the case of heterogeneous

nucleation it needs to be resolved if a direct (i.e. single-step) or a multi-step pathway dominates, or both. An overview on the possible pathways and interactions is schematically represented in Fig. 17. It is evident that the way in which the (stereo-)chemistry of functional groups residing at organic templates affect mineral formation will crucially depend upon the particular mechanism(s) of nucleation.

Fig. 17. Heterogeneous nucleation of minerals according to the paradigms of the direct (top) and the multistep (bottom) pathway. In the latter case, a variety of scenarios is plausible (in analogy to recent observations for homogeneous nucleation): (1) Ions and ion pairs concentrate on the surface, leading to the formation of primary particles at the surface, which then undergo aggregation and final transformation into a crystalline phase; (2) Primary particles form in solution and subsequently adsorb on the surface, where they aggregate and transform into a crystalline phase; (3) primary particles form in solution, aggregate directly on the surface and transform into the final crystalline phase; (4) Disordered aggregates form in solution and adsorb on the surface, afterwards they transform into a crystalline phase; (5) The whole pathway takes place in solution and only the final crystalline seed deposits on the surface.

Based on evidence discussed above, it remains challenging to interpret the particular influence of microorganisms, be it active (e.g. sulfur oxidation) or passive (e.g. s-layer/EPS), on the formation mechanisms of CaSO_4 deposits. In most environments, it seems reasonable to assume that evaporation is the main driving force for calcium sulfate precipitation, and as such, this purely inorganic mechanism can probably explain many (though not all) of the observed textures. Nevertheless, some of the above-discussed observations seem to indicate that involvement of

microbes might be of significant relevance, at least under some conditions. For example, in the case of microbial mats and associated thrombolite/stromatolite(-like) structures, evaporation is still the main driving force, but the fact that bacteria and the associated EPS do bind Ca^{2+} would explain the formation of calcium sulfate in those mats at considerably higher rates than elsewhere in the system. Furthermore it could also explain the existence of typical dome/mushroom-shaped structures. Although microorganisms have been shown to mediate heterogeneous nucleation of other sulfate minerals (such as bloedite, epsomite and mirabilite) from undersaturated brines (Cabestrero et al., 2018), in the specific case of calcium sulfate dedicated experimental work is still needed to quantify the influence of microbial activity on precipitation kinetics. Without this additional input, it will remain unclear which of the proposed mechanisms, or a combination of them, is relevant for calcium sulfate precipitation in the presence of microorganisms. This information is also of utmost importance to correctly model the burial rate of sulfates when considering the sulfur cycle (see section 1.4).

3.3 Calcium sulfate biomineralization by eukaryotic organisms

Eukaryotic organisms have developed an extraordinary ability to control mineral formation. Cellular activity guides the precipitation process, to form for example an external or internal skeleton, such as those found in mollusks and mammals, respectively (e.g. Lowenstam and Weiner, 1989). The vast majority of eukaryotic organisms use carbonates or phosphates, and only a few species have opted for sulfate biominerals. The most compelling example of CaSO_4 biominerals is found in water-dwelling organisms: two classes of medusea, Scyphozoa and Cubozoa, use bassanite in their gravitational sense organ (Tiemann et al., 2002; Becker et al.,

2005; Boßelmann et al., 2007; Sötje et al., 2011). The *tour de force* achieved by these medusea is double: on the one hand they stabilize a highly hygroscopic material (i.e. bassanite immediately transforms to gypsum when in contact with moisture) and on the other hand they produce well-formed macroscopic bassanite crystals at an average temperature of surrounding sea water, something that in the lab can only be achieved starting from ~50-80 °C and extremely high salinities (e.g. Cruft and Chao, 1970; Ossorio et al., 2014; Fig. 12). At present no direct experimental data is available to explain the formation of these biominerals. But, taking into account the general nucleation mechanism proposed for calcium sulfate in section 2, we hypothesize that these organisms create a low water activity environment, making use of a high density matrix of organic molecules (such as proteins, peptides, or polysaccharides), and/or confinement promoting the formation of bassanite and avoid its further transformation to gypsum. Support for this hypothesis has been obtained from reported CaSO_4 mineralization experiments conducted in carboxy- and amino-functionalized reverse micelles (Tartaj et al., 2015). Strong binding between calcium and carboxylate groups lead to long-term (up to 5 months) stabilization of nano-bassanite.

Recently, calcium sulfate, in the form of gypsum, has also been detected in the impact region of stomatopod dactyl segments (Fig. 18b; Amini et al., 2013). Raman spectroscopy measurements show that calcium sulfate is co-localized with fluorapatite in the raptorial appendages. Ab initio computations suggest that fluorapatite/calcium sulfate interfaces provide binding stability and promote the disordered-to-ordered transition of fluorapatite (Fig. 18b). No information is available on how gypsum formation is induced/controlled by these organisms.

Fig. 18. Examples of biomineralization of calcium sulfate by different organisms; (a1) The medusa *Periphylla periphylla* contains statocysts (white arrows) which are composed of bassanite. (a2) Microtomography of a statocyst, composed of statoliths, which are single crystals of calcium sulfate hemihydrate. (a3) A SEM micrograph of an individual bassanite crystal statolith (Tiemann et al., 2002; Sötje et al. 2011 reprinted by permission from Springer Nature and Royal Society of Chemistry). (b1) View of a 'Smasher'-type stomatopod with extended dactyl clubs and optical micrograph showing the two subdomains (II and III) of the impact region (Scale bar, 500 mm). (b2) Raman spectra profiles from bulk to impact surface of the smashing dactyl segments. Broad band centred at $1,080\text{ cm}^{-1}$ is amorphous calcium carbonate (ACC), band centred at 955 cm^{-1} is amorphous calcium phosphate (ACP), sharp band shifted towards 965 cm^{-1} is crystalline fluorapatite (FAP) and the band at $1,007\text{ cm}^{-1}$ (only found in the impact region) is calcium sulphate (CAS, gypsum). (b3) FAP/CAS interfaces computed by ab initio simulations. Hydrogen bonding network is predicted to stabilize the interface along the $[100]$ directions of both crystals. The binding energy in FAP/CAS is 2 kCal.mol^{-1} stronger per hydrogen bond than in hydroxyapatite (HAP)/CAS. (Amini et al., 2014 reprinted by permission from Springer Nature) (c) SEM micrographs of a CaSO_4 crystal found in plants. (c1) crystal sand in a mesophyll, and (c2) a tabular crystal druse in a parenchyma cell of a phyllode of *Acacia roborum* (He et al., 2012, reprinted with permission Oxford University Press), (c3) cross section of a longleaf pine needles showing CaSO_4 formations with stalks connecting them to the juncture of guard cells at the stomatal aperture, and (c4) large angular CaSO_4 crystals embedded within a matrix of smaller fibrillar material (adapted from Pritchard et al. 2000).

Noteworthy, is the response of calcifying brown algae (*P. pavonica*) to ocean

acidification (OA) along a natural pCO₂ gradient off Panarea Island (Italy). It was found that during OA the calcified regions were reduced, and, quite surprisingly, the mineralogy shifted from aragonite to calcium sulfate (Goffredo et al., 2014; Iluz et al., 2017). A similar response was also observed for three genera (*Lithophyllum*, *Titanoderma* and *Phymatolithon*) of coralline algae growing on tiles placed in the proximity of shallow volcanic CO₂ vents occurring at Ischia island, Italy (Kamenos et al., 2016). At the lowest pH (~6.9), the size of the coralline algae was greatly reduced and the skeletal mineralogy was altered from calcite, or calcite and aragonite, to gypsum, compared to red algae grown at higher pH. But, the physiological condition of the coralline algae collected from the extreme low pH is unknown. Thus, these algae could be either all healthy but small in size, or already dead and decomposing. If the coralline algae had been dead, they may have not survived in the extreme low pH treatment despite the mineralogical changes. For both calcifying brown and red algae, the mechanism behind the pH-induced switch in mineralogy remains unknown. So far, we know that when pH decreases from ~8.1 (regular present-day seawater) to ~7.4 (close to a CO₂ vent), the solubility of calcite and aragonite will strongly increase, decreasing the supersaturation of seawater with respect to these mineral phases. Although for a pH value as low as 6.9, the seawater around Panarea remains supersaturated with respect to calcite and aragonite (e.g. Goffredo et al., 2014). For the observed pH range of the seawater in both studies, the solubilities of calcium sulfate phases are practically unaffected, and all these mineral phases remain undersaturated with respect to seawater. Hence, if the fact of the formation is not an artifact of sample preparation (a possibility, although remote, for a detailed discussion see Goffredo et al., 2014; Kamenos et al., 2016; Iluz et al., 2017), these algae manage to induce the precipitation and stabilization of calcium sulfate phases in seawater. Iluz

and coworkers (2017) hypothesize that this might occur through superficial, or excreted macromolecules by the brown algae, although the precise mechanism is not proposed. Hence, further research efforts are needed to clarify the switch in mineralogy for red and brown algae suffering OA.

Calcium minerals are also commonly observed in plants, where calcium oxalate is the most frequently occurring biomineral (e.g. Franceschi and Nakata, 2005). Although, biogenic formation of calcium sulfate crystals in plants has been reported in a few instances. For example, gypsum crystals have been observed in saltcedar (e.g. Storey and Thomson 1994), longleaf pine seedlings (Pritchard et al., 2000) and desert shrub of north-western Australia (He et al., 2012). Bassanite has been detected in the so-called “toothbrush” tree in Africa (Dogan et al., 2005). Although very little is known about the role of calcium sulfate crystals in plants, a variety of functions have been proposed including the removal of excess calcium and sulfur, protection against herbivores and detoxification of aluminium and heavy metals (Storey and Thomson 1994; Pritchard et al., 2000; He et al., 2012). Pritchard and coworkers (2000) and He and coworkers (2012) showed by using greenhouse experiments that the formation of crystals was biologically induced, but the exact factors, and mechanisms that induce the formation of calcium sulfate crystals remains unresolved (He et al., 2012). Notwithstanding, it is generally assumed that the morphologies and precise locations of crystals in plants is under strict genetic control (e.g. Franceschi and Nakata, 2005). But, as mentioned before, their functions are still not well understood and many questions remain answered regarding their ecological and physiological significance as well as their occurrence and prevalence in both time and space (Pritchard et al., 2000).

4. Future perspectives

Significant headway has been made in our understanding of the mechanistic, thermodynamic and kinetic principles governing the abiotic formation of calcium sulphate minerals. Nonetheless, before we attain a truly complete picture of how these minerals emerge from ions in an aqueous solution a few pieces of the puzzle are still missing. The main issues that still need to be sorted out are: (i) the ion association and complexation occurring in undersaturated solutions (do CaSO_4 pre-nucleation clusters exist?) and the link between these phenomena and the primary species forming in supersaturated solutions, (ii) the hydration degree of the precursor phases as a function of the solution conditions and the role this plays during phase selection; (iii) the importance of the kinetic (e.g. desolvation of ions) and the thermodynamic (e.g. interfacial energy) barrier in controlling the formation rate of calcium sulphate minerals; (iv) the solubility of the stable and precursor phases of calcium sulphate (e.g. precise determination of gypsum/anhydrite transition temperature); (v) the switch from “non-classical” particle-based nucleation and growth to “classical” ion-by-ion growth, and how this influence the final crystal morphology and/or texture; (vi) establish a (straightforward?) connection between crystal morphology and the deposition environment; (vii) confirm the proposed nucleation mechanism of anhydrite and bassanite through *in situ* observations. In a broader context, it would be also of interest to compare the formation pathway of calcium sulphate minerals with those of other sulfate minerals, such as BaSO_4 and SrSO_4 to identify general trends. Trends that could then be extended to other mineral systems to help construct a general framework for mineral formation.

While great progress has been made for abiotic calcium sulfate mineralization, much is still left to be unveiled about the biotic formation pathway. The overarching,

and fundamental, question that remains answered is whether biological activity can significantly influence, or control, the formation of calcium sulfate deposits by changing the rate of formation, crystal morphology, deposit texture/structure, mineral assembly or any combination of those factors (cf. Fig. 13). In other words, we still lack systematic criteria for assessing the biogenicity of CaSO_4 facies. To provide clues to help resolve this complex matter the following issues need to be addressed: (i) is nucleation in the presence of living organisms (e.g. bacteria) a biologically activated or rather a passive process; (ii) at which stage(s) of the formation pathway can biomolecules interact with the precursor species; (iii) can biomolecules act upon the initial process of phase selection and/or the kinetic stability of nucleated phases by modulating local hydration phenomena; (iv) what is, if any, the role of microorganisms in the formation of gypsum dominated microbialites; (vi) how do eukaryotic organism control calcium sulphate biomineralization, and why did they choose calcium sulphate; (vii) can specific mineral morphologies, textures and assemblies be related to specific biotic environmental conditions. Providing insight into these matters will not only help us to improve our geochemical interpretation of calcium sulfate deposits on Earth and Mars, but will also provide us with a toolbox to develop more effective anti-scaling strategies and create novel functional hybrid materials.

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