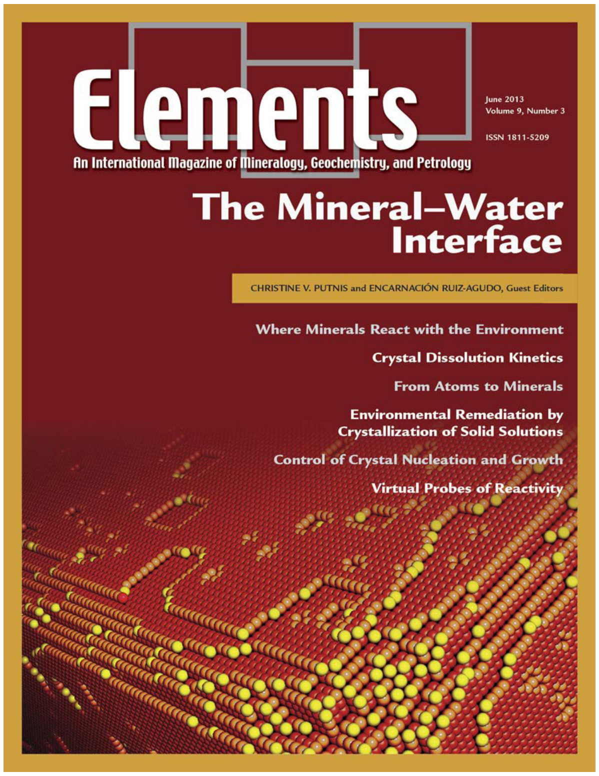
Elements
An International Magazine of Mineralogy, Geochemistry, and Petrology



Elements
An International Magazine of Mineralogy, Geochemistry, and Petrology

June 2013
Volume 9, Number 3

ISSN 1811-5209

The Mineral–Water Interface

CHRISTINE V. PUTNIS and ENCARNACIÓN RUIZ-AGUDO, Guest Editors

Where Minerals React with the Environment
Crystal Dissolution Kinetics
From Atoms to Minerals
Environmental Remediation by Crystallization of Solid Solutions
Control of Crystal Nucleation and Growth
Virtual Probes of Reactivity

Control of Crystal Nucleation and Growth by Additives

Salt damage
affecting the
Baños de Comares
at the Alhambra,
Granada (Spain).
PHOTO: E. SEBASTIAN PARDO

Carlos Rodriguez-Navarro[1] and Liane G. Benning[2]

1811-5209/13/0009-203$2.50 DOI: 10.2113/gselements.9.3.203

The survival of important pieces of our architectural and sculptural heritage is challenged by irreparable damage due to crystallization of soluble salts. Mineral precipitation is also a problem in many industrial processes, leading to costly scale formation. Most of the mechanisms that control these crystallization reactions can be modified or slowed down by using specific additives. Recent advances in elucidating the mechanisms of mineral nucleation and growth and molecular-level mineral–additive interactions have led to the development of novel treatments for the prevention of mineral scale and salt damage.

KEYWORDS: crystallization modifiers, additives, mineral scale, salt damage, heritage conservation, nucleation, crystal growth

INTRODUCTION

The pressure exerted by the crystallization of soluble salts within porous materials leads to massive damage to our architectural (FIG. 1) and sculptural heritage (Rodriguez-Navarro and Doehne 1999) as well as to modern construction. Moreover, the precipitation of sparingly soluble phases during industrial processes causes the formation of mineral scales. Such scales often plug pipes in oil and gas extraction systems and encrust/foul domestic and industrial fluid-transport devices (e.g. Zhang et al. 2001). Scaling resulting from the precipitation of alkali-earth metal sulfates, carbonates, and phosphates costs billions of US dollars annually in remediation and prevention. Mineral encrustations are also a problem in medical implants, triggering failure and increasing the risk of infection (Hildebrandt et al. 2001); they are also of concern in the food, pharmaceutical, and building industries. Both mineral-scaling and salt-damage reactions take place at the mineral–solution interface. In recent years, important advances in our understanding of the fundamental chemical and physical parameters controlling such interface interactions have led to the development of treatments based on the use of crystallization additives.

The most widely used industrial approach to reduce scaling is by adding specific inorganic or organic compounds into the processing loop (e.g. Tomson et al. 2002). To avoid or mitigate salt damage, existing buildings are treated with additives (e.g. Ruiz-Agudo et al. 2013). However, the effects and roles of crystallization additives are not well understood and are poorly quantified, especially at the molecular level. This is unfortunate because understanding molecular-level reactions would allow additive compositions and quantities to be optimized, reducing costs. Such information would also lead to the development of new approaches, thus improving efficiency and productivity.

Inorganic and, more often, organic additives have been tested and used in industry. Additives can prevent or delay mineral crystallization when dosed at substoichiometric concentrations (typically ≤10 mg/L; e.g. Gebauer et al. 2009). They are generally known as crystallization inhibitors. In some cases, however, the same compounds may also act as crystallization accelerators or promoters (i.e. the template effect; see Ruiz-Agudo et al. 2006), or they may change the crystallization pathways (Rodriguez-Blanco et al. 2012). Inhibitors/promoters typically interact with a particular mineral phase via adsorption at the mineral–water interface. Many recent studies have dealt with additive–mineral interactions; yet, many important aspects related to these interactions require further research. This is particularly true for additive–mineral interactions at the molecular level and for nonclassical nucleation and growth.

Here we will discuss reactions leading to macro- to atomic-level mineral-scale and salt-crystallization damage taking place at the mineral–additive interface in an aqueous solution. Specifically, we will focus on existing knowledge, but we will also highlight the gaps in quantifying the role and effects of additive molecules (inhibitors or promoters) in solution–mineral interaction processes. We will first introduce concepts and define the terminology; then, by using specific examples, we will discuss crystal-growth inhibition and mineral-scale control, and we will contrast this with the control of salt damage in building materials. Ultimately, an increased understanding of molecular-level processes will lead to more cost-effective and efficient industrial processes and better conservation strategies for our cultural legacy.

---

[1] Department of Mineralogy and Petrology, University of Granada
Fuentenueva s/n, 18002 Granada, Spain
E-mail: carlosrn@ugr.es

[2] School of Earth and Environment, University of Leeds
Leeds, LS2 9JT, United Kingdom
E-mail: L.G.Benning@leeds.ac.uk

Figure 1 The Monastery at Petra, Jordan, capital city of the Nabataean kingdom (ca. 300 BC). This heritage site, carved out of a sandstone cliff, shows extensive damage due to salt weathering. Note the salt efflorescence (mainly halite) on the bottom part of the structure, shown by extensive white areas, and the loss of relief of carved elements such as the columns. Saline solutions rising from the ground evaporate at the surface and subsurface of the porous stone, thus resulting in salt efflorescence and deleterious sub-efflorescence. Daily and seasonal temperature and humidity changes also result in damage due to cyclic salt dissolution–crystallization events. Treatment of the sandstone with crystallization additives such as ferrocyanide could help prevent salt damage. Photo: M. Gómez Heras

CRYSTALLIZATION INHIBITORS AND PROMOTERS

Small quantities of specific additives can profoundly affect the macroscopic properties and behavior of minerals. For instance, lime- and gypsum-based building materials have been tailored since prehistoric times by adding common organics, such as blood, urine, milk, cheese (casein), egg white, and plant juices. Extensive and highly empirical research up to the early 20th century showed that crystal growth is macroscopically affected by the presence of inorganic and organic ions and molecules in solution (Buckley 1951) in that they can delay or alter the crystallization paths. For instance, Romé de L´Isle (1783) observed that halite (NaCl) crystals grown in the presence of urea developed {111} octahedra instead of the common {100} cube, disclosing one of the main features of additive–mineral interaction: the effect of additives as crystal-habit modifiers. However, the actual additive–mineral interaction mechanisms were, and still are, not fully understood.

Inorganic additives such as magnesium, sulfate, and phosphate/polyphosphate have a significant effect on mineral nucleation and growth (Buckley 1951; Rodriguez-Blanco et al. 2012; Bots et al. 2012). Today, however, the most often applied and industrially tested inhibitor/promoter additives are organics such as phosphate esters, (poly)phosphonates, polyacrylates, aspartates, polyaspartates, and various other phosphonate, sulfonate, and carboxylate polymers and copolymers (e.g. Tomson et al. 2002; Ruiz-Agudo et al. 2006). These compounds most commonly have carboxy and hydroxy functional groups, while their derivatives can incorporate other components such as amino moieties (e.g. aminocarboxylates and aminophosphonates), which enhance their effectiveness over a wide range of pH. Finally, the most recent developments focus on the search for "green," low-toxicity, and biodegradable crystallization inhibitors (Hasson et al. 2011).

Understanding the interactions between additives and mineral surfaces in an aqueous solution starts with kinetic studies and atomic-scale molecular models (Fig. 2). Additives can affect surface reactions in many different ways (see the classification of additive effects in Gebauer et al. 2009). Additives can adsorb to primary particles or clusters, thereby preventing the formation of new critical nuclei (Sommerdijk and De With 2008) and thus inhibiting nucleation (Fig. 2a). Note that various elemental reactions with manifold consequences may occur during the early stages of the nucleation of any phase. This is particularly true with respect to interactions between ions and molecules in systems with the propensity to form either stable prenucleation clusters (e.g. Gebauer et al. 2008) or poorly ordered or nanocrystalline intermediates (Gower 2008; Bots et al. 2012; Van Driessche et al. 2012). Certain inhibitor molecules can also act as crystallization promoters once adsorbed onto a substrate (Fig. 2b, c), fostering and controlling 2-D or 3-D heterogeneous nucleation (Sommerdijk and De With 2008; Pouget et al. 2009).

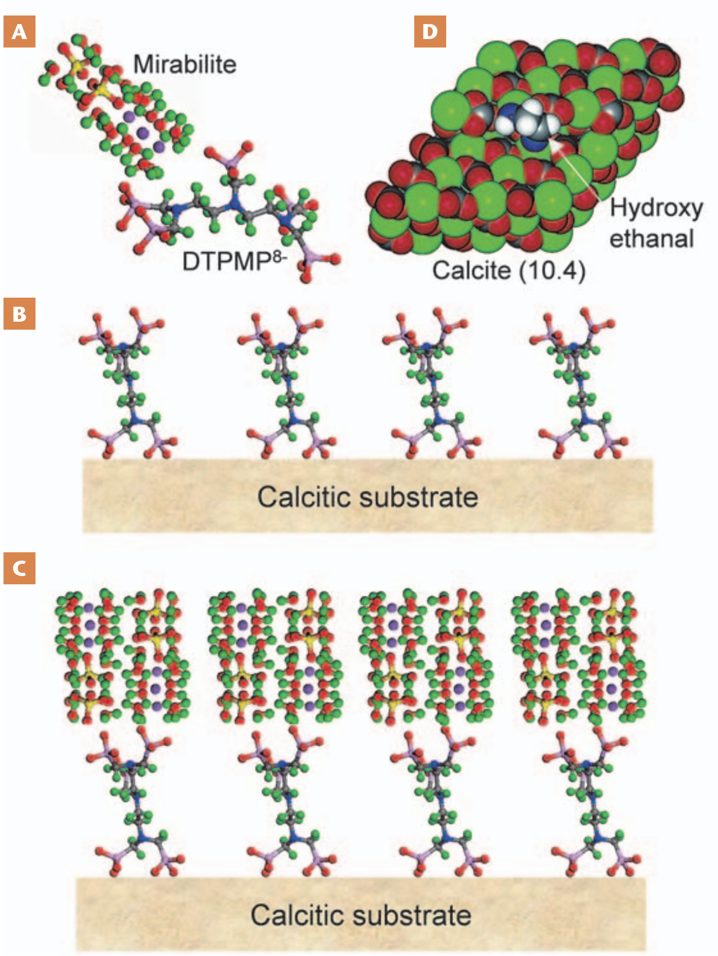


Figure 2 Schematic representations of the different modes of mineral–additive interactions. (**A**) Nucleation inhibition illustrated by mirabilite (half unit cell is shown) binding with a phosphonate, DTPMP^{8-}. (**B**) Formation of a soft template shown by DTPMP molecules adsorbed on a calcite substrate. (**C**) Crystallization promotion on a template shown by the heterogeneous crystallization of mirabilite on a DTPMP template. (**D**) Growth inhibition illustrated by a hydroxy ethanal molecule adsorbed to the calcite (10$\bar{1}$4) acute step. (A–C) From Ruiz-Agudo et al. (2013), with permission from the American Chemical Society; (D) From De Leeuw and Cooper (2004), with permission from the American Chemical Society

Such template-directed crystallization is of paramount importance in biomimetic reactions and in biomineralization (Gower 2008; Sommerdijk and De With 2008).

Once the nucleation stage is over, stable nuclei with sizes bigger than the critical size will grow during the second stage of crystallization. During this growth stage, adsorption of additive ions and molecules most often occurs at active growth sites, such as kinks and steps on specific faces of mineral particles (Fig. 2d). Depending on the additive–mineral system, such complex interactions can explain two principal additive effects: growth inhibition/promotion and habit modification. Observations using atomic force microscopy (AFM) demonstrate that step pinning and inhibition of 2-D island nucleation are common during crystal–inhibitor interaction (e.g. Pina et al. 2004) and that additive–step and additive–kink interactions are selective and likely involve some kind of molecular recognition (e.g. L- and D-aspartic acid promote chiral growth hillocks on calcite $(10\bar{1}4)$ cleavage planes; Orme et al. 2001).

Minor effects that additives can have on aqueous mineral systems include complexing and chelation (i.e. ion binding), which can reduce the saturation index with respect to a given mineral phase or lead to mineral dissolution.

Estimating the inhibition efficiency of a particular additive–mineral system is often initially done by monitoring changes in turbidity, conductivity, or refractive index in solution. This enables one to evaluate supersaturation at the onset of crystallization (i.e. critical supersaturation) and gauge the induction time (i.e. time before crystallization onset) and particle-size evolution (Tantayakom et al. 2005; Ruiz-Agudo et al. 2006; Bots et al. 2012). The roles and effects of additives on habit, polymorph selection, crystallographic orientation, and growth features are often studied using microscopic techniques (e.g. optical and scanning/transmission electron microscopy, AFM), infrared spectroscopy, thermal analysis, and X-ray diffraction (see, for instance, Pina et al. 2004; Rodriguez-Blanco et al. 2011, 2012; Bots et al. 2012). Details of the structure and orientational order of organics adsorbed on various substrates have been characterized with X-ray and transmission electron microscopy and X-ray absorption spectroscopy (e.g. Sommerdijk and De With 2008).

Atomic-level interactions are in many cases still too complex to follow experimentally. Thus, molecular simulation may contribute to a better understanding of additive–mineral interaction (e.g. De Leeuw and Cooper 2004). Minimization of structural mismatching between a particular additive molecule on specific (*hkl*) planes of a mineral, along with force field–based energy minimization of additive, mineral–solution, and mineral–additive structure and interactions can help to explain the efficiency and specificity of some additive–mineral interactions. Molecular simulation has also guided the design and selection of the most efficient inhibitor for a particular system (Bosbach et al. 2002). Recently such simulations also have tackled the effects of organic additives on the pre- and postnucleation stages of mineral phases (Raiteri et al. 2012).

Overall, such approaches complement one another and help clarify the crystallographic specificity of some additive–mineral interactions and explain the various phenomena related to the capacity of organic molecules to inhibit or promote scale formation or salt damage.

SCALE FORMATION AND INHIBITION

Among the many sparingly soluble salts that create mineral scales, barite (e.g. Bosbach et al. 2002), gypsum (e.g. Van Driessche et al. 2012), and calcite (e.g. Tomson et al. 2002; Chen et al. 2005) are the most studied. Here we will focus on calcite ($CaCO_3$) scaling because it is a very common industrial problem that often impacts our daily lives. For example, many of us are familiar with lime scale partially or totally plugging our shower nozzle or encrusting the pipes (Fig. 3a) in our washing machine.

Many antiscaling treatments are based on the use of inorganic or organic additives as adsorption and growth inhibitors. These have been tested and applied, but most studies aim only to find the best additive that changes the crystallization mechanisms or alternatively matches or stereochemically recognizes a specific crystal face. In industrial tests, scale-inhibition efficiency is usually determined by bulk jar experiments, turbidity probes, pH measurements, or bulk chemical analysis (e.g. Tomson et al. 2002). Such tests provide data about the role of inhibitors during bulk precipitation. However, they are poorly suited to quantifying inhibitor interaction with mineral or pipe surfaces in static or hydrodynamic flow conditions. They also do not provide quantitative information about the interaction mechanisms.

In the case of carbonate crystallization, these studies have yielded important results about the bulk effects of specific molecules. Nevertheless, questions about the role of additives as habit modifiers and about whether and how additives affect polymorph selection and kinetic stabilization are still unresolved. This is primarily because studying scale formation in solution or on pipe surfaces is not trivial. Why one or another carbonate polymorph nucleates and grows under specific conditions has been investigated through comparisons with the natural world of biomineralization. Gower (2008) showed that polymorph selection is highly dependent on minute changes in both chemical (e.g. pH, additive concentration and type) and physical (e.g. temperature, pressure, stirring, flow rate) parameters.

Although the matter is still debated, recent advances in our understanding of nonclassical crystallization mechanisms in the calcium carbonate system suggest that stable prenucleation clusters precede the formation of the first solid phase, which is an amorphous calcium carbonate, ACC (Gebauer et al. 2008). Nucleation inhibitors do not necessarily interact with an anhydrous crystalline polymorph with sizes below (or equal to) the critical size because these interactions require a high degree of structural selectivity. Nevertheless, inhibition/retardation at the prenucleation stage or when ACC starts to form can take place via nonspecific interactions, and additives (e.g. Mg) delay the dehydration and transformation of the hydrated clusters into ACC (Politi et al. 2010). The hydrated nature of the amorphous precursor ACC also affects its crystallization to vaterite ($CaCO_3$, a polymorph of calcium carbonate) and calcite (Fig. 3d–f; Rodriguez-Blanco et al. 2011 and references therein). Once ACC is formed in the presence of inorganic additives such as magnesium and sulfate, both the transformation mechanism and the rates of crystallization are affected (Fig. 3b, c; Rodriguez-Blanco et al. 2012; Bots et al. 2012). In contrast, organic additives often change the habits of the resulting crystals (Fig. 3g; Gower 2008; Sand et al. 2012). In situ studies have shown that ACC transforms to vaterite in the presence of low concentrations of magnesium or sulfate via spherulitic growth (Fig. 3c; Bots et al. 2012 and references therein). This vaterite in turn transforms to calcite via dissolution and reprecipitation (Rodriguez-Blanco et al. 2011, 2012). Interestingly, organics change the pathway, timing, and mechanism of transformation and may lead to aragonite or stable vaterite spherulites instead of calcite (e.g. Sand et al. 2012).

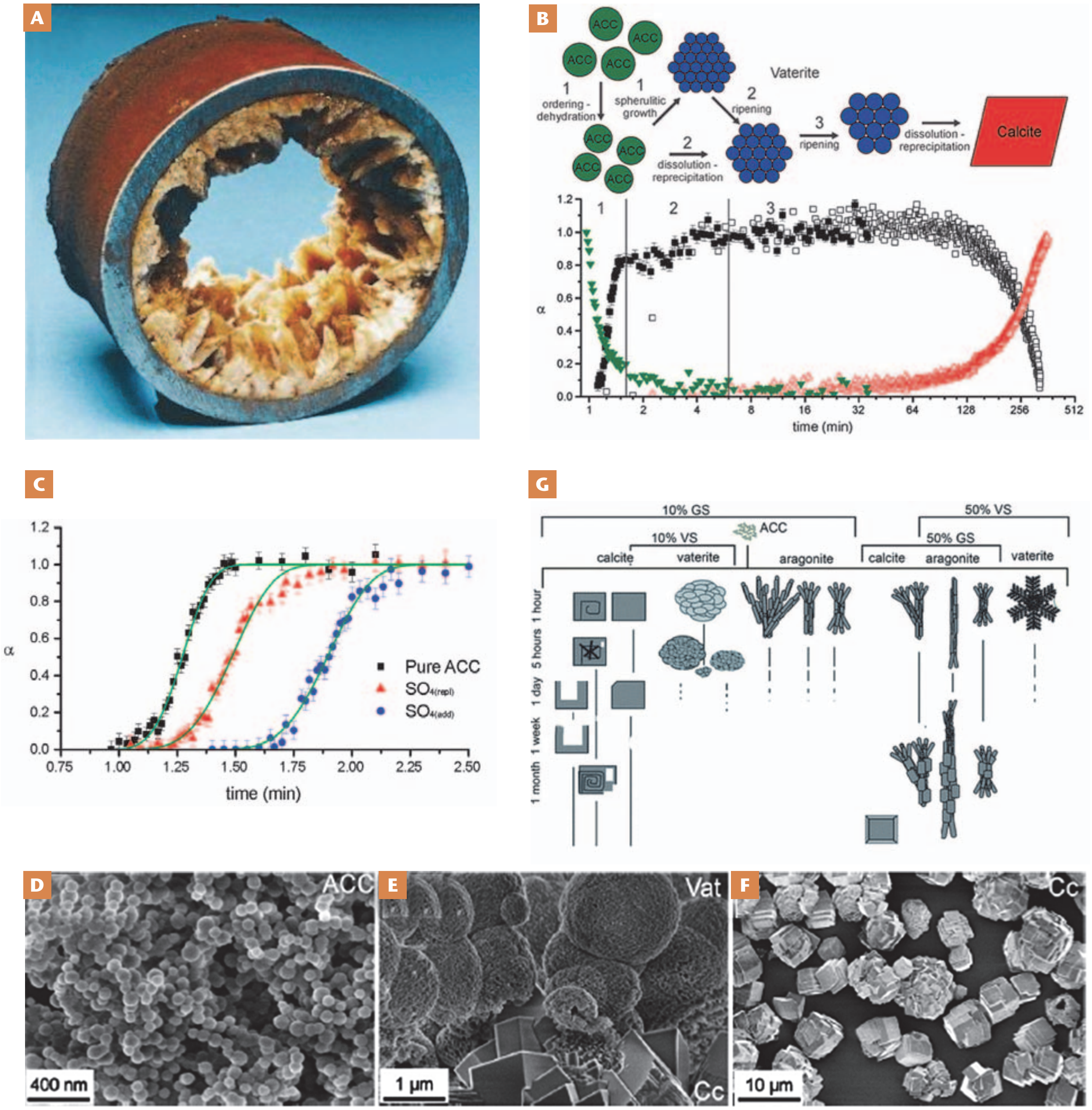


FIGURE 3 Mineral-scaling processes. (**A**) An encrusted pipe. (**B**) Multistage, in situ crystallization of amorphous calcium carbonate (ACC) to vaterite via dehydration, spherulitic growth, and Ostwald ripening (stages 1 and 2) and of vaterite to calcite via dissolution and reprecipitation (stage 3) at 21 °C in the absence of additives, shown as reaction progress, α, versus time. (**C**) The effect of sulfate (SO_4) on the reaction progress, α, of the ACC-to-vaterite transformation, showing an up to 20% increase in induction time. (**D–F**) Photomicrographs showing the changing sizes and morphologies of ACC, vaterite, and calcite in an experiment at 25 °C. (**G**) The crystallization of ACC to various calcium carbonate polymorphs as a function of gentle versus vigorous shaking (GS versus VS), time (vertical axis), and additive concentration (10% versus 50% ethanol). B and C from Bots et al. (2012), reprinted with permission from the American Chemical Society; E and F from Rodriguez-Blanco et al. (2012), reprinted with permission from Elsevier; G from Sand et al. (2012), reprinted with permission from the American Chemical Society

Attempts to quantify the effects of additives on calcite growing on, for example, pipe surfaces or under turbulent flow conditions are in their infancy. Early results suggest that nucleation, growth, and dissolution change dramatically with variations in physical environment (e.g. roughness of surfaces and variations in eddy viscosity during growth). Future studies need to include both additive–mineral surface interface reactions and the properties of the growth surfaces. These surfaces can be smooth or rough and can corrode or be passivated by additives. Invariably, scale minerals in the real world will be affected by flow eddies, changes in viscosity, and the 3-D shape of the interface (e.g. a cylindrical pipe or a flat surface). Another area for further research is the formation of mixed scales where no single inhibitor is effective and the use of inhibitor "cocktails" is required. Finally, the presence of bacteria or algae, which are often ubiquitous in scaling environments, has also to be taken into account because the surface properties of living organisms and the effect of their organic exudates highly complicate any purely inorganic model of scale-mineral formation. Little is known about these effects.

CRYSTALLIZATION MODIFIERS FOR PREVENTING SALT DAMAGE

Priceless antiquities, such as the Sphinx and the Great Pyramids in Egypt, Petra in Jordan (Fig. 1), the Maya pyramids in Tikal and Copan, Mohenjo Daro in Pakistan, and the Gothic cathedrals in Europe, all suffer the deleterious effects of salt weathering, which also affects modern construction (Rodriguez-Navarro and Doehne 1999). Salts cause damage to porous materials mainly by generating crystallization pressure, which is proportional to supersaturation (Schiro et al. 2012). When in-pore salt crystallization occurs at a supersaturation level high enough to result in a crystallization pressure that is higher than the tensile strength of a porous material, mechanical failure occurs (e.g. crack development, fracturing, and granular disintegration; Fig. 4a).

Past conservation treatments applied to porous stones affected by salt damage are only partially successful because in most cases they do not arrest salt weathering but only cover up its effects. Recent progress in understanding in-pore salt crystallization is leading to the development of novel, more efficient conservation treatments based on the use of crystallization additives, either inhibitors (Rodriguez-Navarro et al. 2002) or promoters (Schiro et al. 2012; Ruiz-Agudo et al. 2013).

Inhibitors delay the precipitation of salts within a porous system subjected to evaporative crystallization, the most common situation during salt damage (Rodriguez-Navarro and Doehne 1999). Such a delay fosters the eventual formation of a salt surface precipitate (i.e. efflorescence), which leads to little or no damage to the substrate and can be mechanically eliminated. Adding ferrocyanide ($[Fe(CN)_6]^{4-}$, commonly used to prevent caking of table salt) in millimolal concentrations results in a significant increase in the induction period and critical supersaturation (about a tenfold increase) for halite crystallization (Rodriguez-Navarro et al. 2002), enabling the salt solution to flow though the porous system of salt-laden stones without crystallizing. When the solution reaches the stone surface, evaporation causes massive precipitation of harmless efflorescence (Fig. 4b). Ferrocyanide ions in solution reversibly bind to halite nuclei with dimensions below or close to the critical size, leading to a strong nucleation inhibition, thereby explaining its effectiveness when used to enhance desalination of NaCl-contaminated stones.

Additives, however, are salt-specific, and ferrocyanide does not enhance efflorescence growth when applied to stones contaminated with other common and highly deleterious salts, such as sodium and magnesium sulfates. This has led to the search for other additives, including those most commonly used in scale control (Ruiz-Agudo et al. 2006).

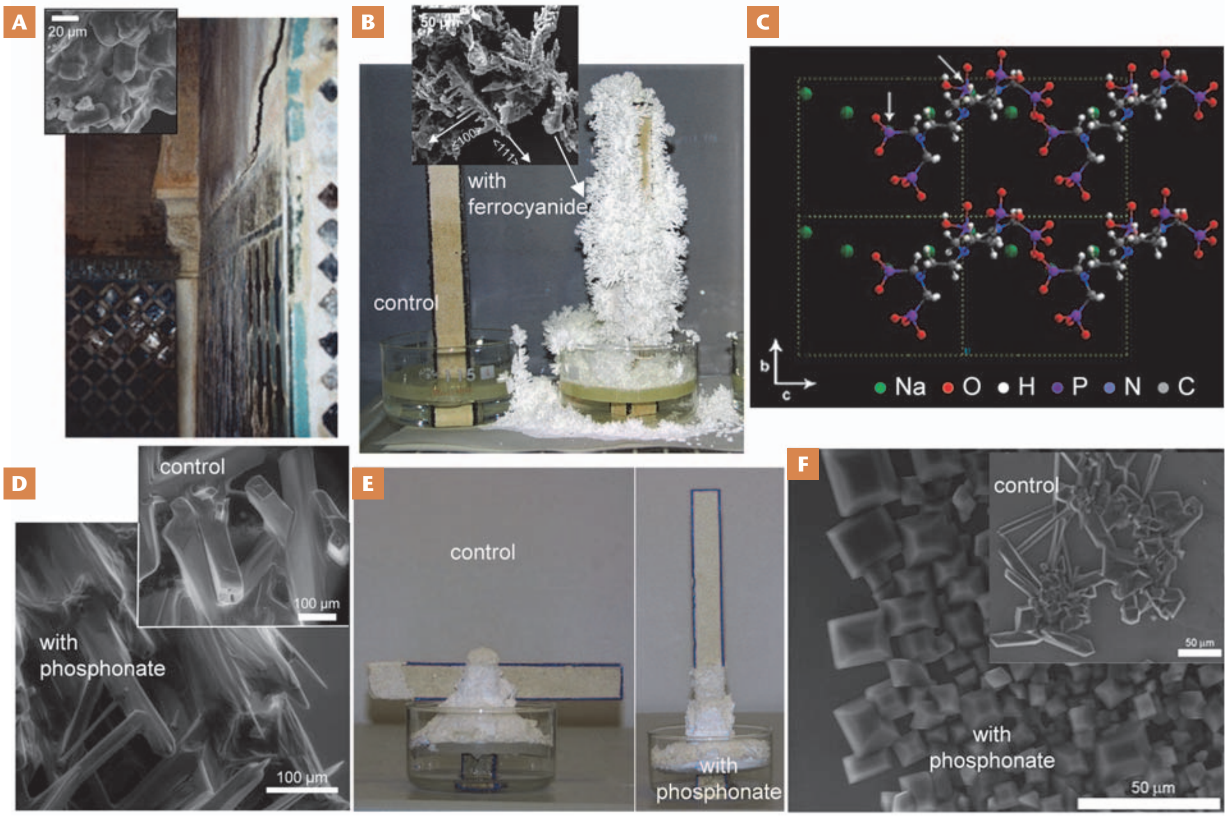


Figure 4 Crystallization additives and prevention of salt damage. (**A**) Example of salt damage at Los Baños de Comares, La Alhambra (Granada, Spain). The inset shows salt crystals (scale bar = 20 µm). (**B**) Macroscale salt-crystallization test using porous limestone blocks in contact with an evaporating, saturated NaCl solution (in glass beaker), with no additives (control) and with 0.1 mM ferrocyanide added; the additive results in enhanced efflorescence and desalination. The inset shows a SEM photomicrograph of efflorescent halite crystals (scale bar = 50 µm). From Rodriguez-Navarro et al. (2002), with permission from Elsevier. (**C**) Molecular simulation of additive–mineral interactions: the model shows possible docked positions of $DTPMP^{8-}$ on mirabilite (100) with arrows indicating bonding between the additive and Na (for clarity, only Na cations are shown). From Ruiz-Agudo et al. (2006), with permission from the American Chemical Society. (**D**) Effects of phosphonates (ATMP) on the crystal habit of epsomite ($MgSO_4 \cdot 7H_2O$) compared to the control (inset) (scale bars = 100 µm). (**E**) Macroscale effects after 14 days of evaporative crystallization of sodium sulfate within porous limestone; the addition of 0.01 M DTPMP phosphonate is compared with the control. (**F**) SEM image of oriented mirabilite crystals formed on a DTPMP template adsorbed on (10$\bar{1}$4) calcite. The inset shows the random orientation of sodium sulfate crystals formed in the absence of DTPMP (scale bars = 50 µm). From Ruiz-Agudo et al. (2013), with permission from the American Chemical Society

Various organophosphonates can act as effective inhibitors for sodium sulfate crystallization in solution and as habit modifiers. Molecular simulation shows a good structural match between $DTPMP^{8-}$ (the main species at pH 8.5, when the highest inhibition is achieved) and the (100) faces of mirabilite ($Na_2SO_4 \cdot 10H_2O$), resulting in binding to two Na^+ ions and a habit change (FIG. 4C). However, a nonspecific additive adsorption via H-bonding with structural H_2O molecules in mirabilite also explains the observed results. Similar effects are observed in the case of magnesium sulfate, where a maximum crystallization inhibition is observed with both phosphonates and polyacrylates. Interestingly, AFM and scanning electron microscopy (SEM) observations of habit modification (FIG. 4D) and molecular simulation show that attachment occurs on the (110) and (010) planes of epsomite ($MgSO_4 \cdot 7H_2O$), which have the highest density of structural water. This suggests that the additive–crystal interaction is not specific, taking place via H-bonding between the deprotonated functional groups of the additives and the structural water molecules in the salt crystal. It follows that in both salt systems, crystallization inhibition could be effective in promoting desalination, as shown for the case of halite and ferrocyanide (FIG. 4B). Unexpectedly, tests performed to gauge the effectiveness of these organic additives in preventing salt damage using real porous limestone and model porous media (glass frits) laden with these sulfate salts show no promotion of efflorescence growth. However, a significant damage reduction is observed (FIG. 4E).

Tests using calcite single crystals as a support show oriented mirabilite and epsomite crystallization in the presence of organophosphonate, which strongly adsorbs onto calcite surfaces via the formation of a template (FIG. 2). This leads to the oriented heterogeneous nucleation of sulfate salt crystals on the carbonate substrate (FIG. 4F) at a very low supersaturation. Ultimately, the adsorbed additive acts as a crystallization promoter, leading to the in-pore heterogeneous nucleation and growth of sulfate salt crystals, which produce a very low crystallization pressure and therefore less damage. These results show that the application of crystallization modifiers is an effective conservation method to promote desalination and prevent salt damage in building stone and other porous materials. In fact, on-site testing has shown that this type of conservation treatment is highly effective. Spraying a 0.01 M DTPMP solution on porous limestone walls at the Monasterio de San Jerónimo (Granada, Spain) affected by magnesium sulfate crystallization led to a 50% reduction in material loss.

TOWARDS A GENERAL MODEL FOR ADDITIVE–MINERAL INTERACTION AND OUTLOOK

It is clear that crystallization inhibition/promotion can be induced by the same additive molecules, most often depending on whether they act in the bulk solution or are adsorbed on a substrate. Crystallization inhibition and promotion thus appear to be mirror images of a fundamentally similar process. This is nicely shown by the effect of phosphonates on the crystallization of sodium and magnesium sulfate in the absence (inhibition) or presence (promotion) of a calcite substrate (Ruiz-Agudo et al. 2013).

Interestingly, highly hydrated, metastable precursor or intermediate phases often precede the crystallization of stable mineral phases. This and the fact that additive–mineral interaction commonly takes place via electrostatic interactions and H-bonding with structural water in the mineral phase suggest that in most studied systems additive–mineral interactions may not be highly specific. This means that stereochemical recognition is not a key factor in such interactions. In many systems in which scale minerals form and salt damage occurs, prenucleation clusters sometimes form prior to the precipitation of metastable amorphous or nanocrystalline precursor phases (e.g. Kellermeier et al. 2012). After variable and additive-dependent induction times, the stable end-product phase crystallizes. These observations challenge classical views on additive–mineral interactions. Additive–prenucleation cluster and additive–amorphous precursor interactions can explain nucleation inhibition (Gebauer et al. 2009). However, template-directed crystallization should not be significant if one considers the formation of an amorphous precursor, because no stereochemical or structural recognition between the template and the amorphous precursor structure would exist (Gower 2008). However, Pouget et al. (2009) have reconciled classic template-directed nucleation theories with the new view emerging from the observation of stable prenucleation clusters and amorphous precursors. Using cryomicroscopy, they showed that prenucleation clusters aggregate into ACC, which is stabilized at the solution–organic template interface. The transient ACC mediates the transfer of crystallographic information from the template to the final crystalline phase through the selective stabilization and development of a preferred crystallographic orientation (see review by Sommerdijk and De With 2008). Thus the early stages of additive interactions do not seem to require a structural or stereochemical match to inhibit or promote nucleation.

In the study of many salt-damage and mineral-scale systems, the focus should be on the possible existence of hydrated prenucleation clusters and/or amorphous precursors. Their existence and properties/stabilities may help explain why many different additives, with highly different compositions and structures, show such a high nucleation-inhibition efficiency (i.e. they can increase induction times from a few seconds or minutes to hours or days). This could be explained by the bonding (e.g. H-bonding) of the additive with water molecules in the precursor clusters whose size is below the critical size or by the stabilization of an amorphous precursor phase (Gebauer et al. 2009). This could be achieved in systems such as calcium carbonate, calcium sulfate, calcium phosphate, and calcium oxalate, as well as hydrated salts responsible for salt damage. Note however that a general, nonspecific additive–mineral interaction at the onset of any nucleation stage may not translate in relevance to the crystal-growth stage where a structural or stereochemical match is common (i.e. particularly in biomineralization and biomimetics).

Research should focus on understanding why some additives are more efficient than others in preventing nucleation, including stabilization or inhibition during prenucleation cluster formation (Raiteri et al. 2012), and why some additives affect only the postnucleation stage (Gebauer et al. 2009).

A challenge for the future is to develop novel ways to quantify whether such a general additive–mineral interaction mechanism is phase or additive specific, whether it obeys a stereochemical/structural recognition, and whether it occurs principally via H-bonding between water molecules in the structure or at the surface of a given mineral phase or its metastable, hydrated precursor.

Reactions occurring not just between the mineral phases and the additives but also between the additive–mineral composites and the surface, where scaling and salt damage occur, need to be evaluated and novel methods developed to follow such reactions, ideally in situ and in real time. Combining all these results with *ab initio* and molecular simulations will bring us closer to understanding the fundamental steps in the nucleation, growth, and crystallization reactions in systems where scaling and salt damage have major economic or cultural-heritage impacts.

We have shown that additives play a critical role in a range of processes involving nucleation and growth of sparingly soluble and soluble mineral phases, resulting in scale formation and salt damage to our sculptural and architectural heritage. It is also clear that a more complex and quantitative understanding, both spatial and temporal, of additive–mineral interactions and the development of complementary approaches are needed. Yet, we also have to be aware that such approaches need to be realistic, cost-efficient, and simple if we aim to ameliorate or prevent, if not fully solve, mineral-scale and salt-damage problems affecting our cultural heritage.

ACKNOWLEDGMENTS

LGB acknowledges the support of the EU-FP6 Mineral Nucleation and Growth Kinetics (MIN-GRO) Marie Curie Research and Training Network, Grant MRTNCT-2006-035488 and the EU-FP7 MINSC ITN (Initial Training Research network), Project number 290040. The work of CRN has been supported by EU-FP7, Marie Curie Actions, (DELTA-Min) grant PITN-GA-2008-215360, by the Spanish government (grants MAT2009-11332 and CGL2012-35992), and by the research group RNM-179 (Junta de Andalucía, Spain). We thank E. Ruiz-Agudo and C. V. Putnis for their contributions on research related to salt–additive interactions and S. Shaw, P. Bots, K. Sand, and J. D. Rodriguez-Blanco for their collaboration on carbonate nucleation and growth processes.

REFERENCES

Bosbach D, Coveney PV, Griffin JLW, Putnis A, Risthaus P, Stackhouse S, Whiting A (2002) The rational design, synthesis and demonstration of the recognition and binding of a diaza-dioxa-12-crown-4 diphosphonate macrocycle to all crystal growth faces of barium sulfate. Journal of the Chemical Society, Perkin Transactions 2: 1238-1245

Bots P, Benning LG, Rodriguez-Blanco J-D, Roncal-Herrero T, Shaw S (2012) Mechanistic insights into the crystallization of amorphous calcium carbonate (ACC). Crystal Growth & Design 12: 3806-3814

Buckley HE (1951) Crystal Growth. John Wiley & Sons, New York, 571 pp

Chen T, Neville A, Yuan M (2005) Calcium carbonate scale formation—assessing the initial stages of precipitation and deposition. Journal of Petroleum Science and Engineering 46: 185-194

De Leeuw NH, Cooper TG (2004) A computer modeling study of the inhibiting effect of organic adsorbates on calcite crystal growth. Crystal Growth & Design 4: 123-133

Gebauer D, Völkel H, Cölfen H (2008) Stable prenucleation calcium carbonate clusters. Science 322: 1819-1822

Gebauer D, Cölfen H, Verch A, Antonietti M (2009) The multiple roles of additives in $CaCO_3$ crystallization: A quantitative case study. Advanced Materials 21: 435-439

Gower LB (2008) Biomimetic model systems for investigating the amorphous precursor pathway and its role in biomineralization. Chemical Reviews 108: 4551-4627

Hasson D, Shemer H, Sher A (2011) State of the art of friendly "green" scale control inhibitors: A review article. Industrial & Engineering Chemistry Research 50: 7601-7607

Hildebrandt P, Sayyad M, Rzany A, Schaldach M, Seiter H (2001) Prevention of surface encrustation of urological implants by coating with inhibitors. Biomaterials 22: 503-507

Kellermeier M, Rosenberg R, Moise A, Anders U, Przybylski M, Cölfen H (2012) Amino acids form prenucleation clusters: ESI-MS as a fast detection method in comparison to analytical ultracentrifugation. Faraday Discussions 159: 23-45

Orme CA, Noy A, Wierzbicki A, McBride MT, Grantham M, Teng HH, Dove PM, De Yoreo JJ (2001) Formation of chiral morphologies through selective binding of amino acids to calcite surface steps. Nature 411: 775-779

Pina CM, Putnis CV, Becker U, Biswas S, Carroll EC, Bosbach D, Putnis A (2004) An atomic force microscopy and molecular simulations study of the inhibition of barite growth by phosphonates. Surface Science 553: 61-74

Politi Y, Batchelor DR, Zaslansky P, Chmelka BF, Weaver JC, Sagi I, Weiner S, Addadi L (2010) Role of magnesium ion in the stabilization of biogenic amorphous calcium carbonate: A structure-function investigation. Chemistry of Materials 22: 161-166

Pouget EM, Bomans PHH, Goos JACM, Frederik PM, De With G, Sommerdijk NAJM (2009) The initial stages of template-controlled $CaCO_3$ formation revealed by cryo-TEM. Science 323: 1455-1458

Raiteri P, Demichelis R, Gale JD, Kellermeier M, Gebauer D, Quigley D, Wright LB, Walsh TR (2012) Exploring the influence of organic species on pre- and post-nucleation calcium carbonate. Faraday Discussions 159: 61-85

Rodriguez-Blanco JD, Shaw S, Benning LG (2011) The kinetics and mechanisms of amorphous calcium carbonate (ACC) crystallization to calcite, *via* vaterite. Nanoscale 3: 265-271

Rodriguez-Blanco JD, Shaw S, Bots P, Roncal-Herrero T, Benning LG (2012) The role of pH and Mg on the stability and crystallization of amorphous calcium carbonate. Journal of Alloys and Compounds 536/S1: S477-S479

Rodriguez-Navarro C, Doehne E (1999) Salt weathering: influence of evaporation rate, supersaturation and crystallization pattern. Earth Surface Processes and Landforms 24: 191-209

Rodriguez-Navarro C, Linares-Fernandez L, Doehne E, Sebastian E (2002) Effects of ferrocyanide ions on NaCl crystallization in porous stone. Journal of Crystal Growth 243: 503-516

Romé de L'Isle J-BL (1783) Crystallographie. L'Imprimerie de Monsieur, Paris

Ruiz-Agudo E, Rodriguez-Navarro C, Sebastián-Pardo E (2006) Sodium sulfate crystallization in the presence of phosphonates: Implications in ornamental stone conservation. Crystal Growth & Design 6: 1575-1583

Ruiz-Agudo E, Putnis CV, Pel L, Rodriguez-Navarro C (2013) Template-assisted crystallization of sulfates onto calcite: Implications for the prevention of salt damage. Crystal Growth & Design 13: 40-51

Sand KK, Rodriguez-Blanco JD, Makovicky E, Benning LG, Stipp SLS (2012) Crystallization of $CaCO_3$ in water-alcohol mixtures: Spherulitic growth, polymorph stabilization, and morphology change. Crystal Growth & Design 12: 842-853

Schiro M, Ruiz-Agudo E, Rodriguez-Navarro C (2012) Damage mechanisms of porous materials due to in-pore salt crystallization. Physical Review Letters 109: 265503

Sommerdijk NAJM, De With G (2008) Biomimetic $CaCO_3$ mineralization using designer molecules and interfaces. Chemical Reviews 108: 4499-4550

Tantayakom V, Fogler HS, Charoensirithavorn P, Chavadej S (2005) Kinetic study of scale inhibitor precipitation in squeeze treatment. Crystal Growth & Design 5: 329-335

Tomson MB, Fu G, Watson MA, Kan AT (2002) Mechanisms of mineral scale inhibition. Society of Petroleum Engineers paper 74656

Van Driessche AES, Benning LG, Rodriguez-Blanco JD, Ossorio M, Bots P, García-Ruiz JM (2012) The role and implications of bassanite as a stable precursor phase to gypsum precipitation. Science 336: 69-72

Zhang Y, Shaw S, Farquhar R, Dawe R (2001) The kinetics of carbonate scaling—application for the prediction of downhole carbonate scaling. Journal of Petroleum Science and Engineering 29: 85-95


Do You Think Ions
Like Queuing Up?
R&D 100
2011
SPECTRO Analytical Instruments
SPECTRO MS