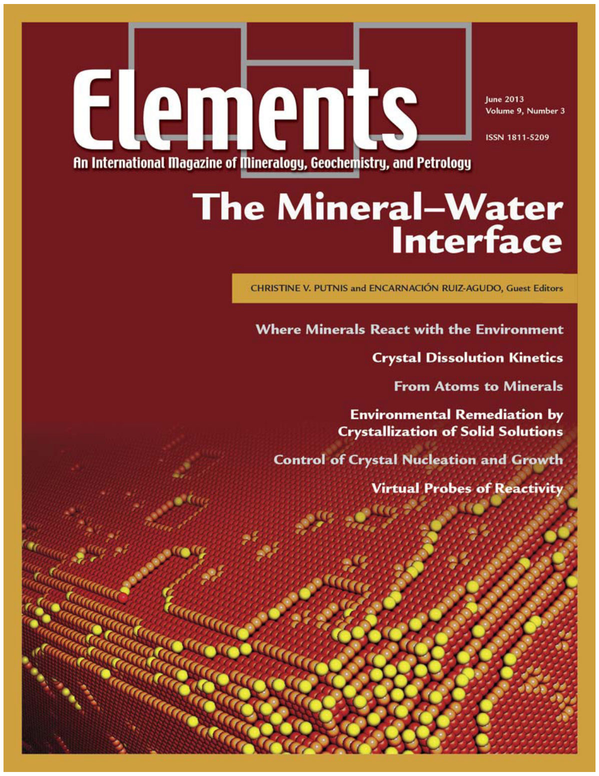

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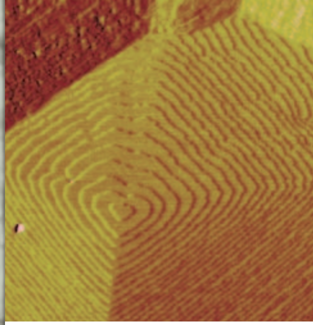
The Mineral–Water Interface

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

The Mineral–Water Interface: Where Minerals React with the Environment



AFM image of a calcite growth spiral influenced by the presence of selenium in the growth solution

Christine V. Putnis[1] and Encarnación Ruiz-Agudo[2]

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The reactions that occur at the mineral–water interface are central to all geochemical processes. They affect a wide range of important Earth processes, all of which involve geochemical element cycling. Examples include weathering and soil formation, nutrient availability, biomineralization, acid mine drainage, the fate of contaminants, nuclear waste disposal, and minor element incorporation and partitioning during mineral growth. Each of these processes, and its reaction rates, is ultimately controlled by reactions that occur at mineral surfaces. Through the development of advanced analytical methods, direct observations of mineral reactions at the nanoscale have enabled exciting new possibilities for clarifying the mechanisms governing mineral–fluid reactions.

Keywords: mineral surface, mineral–water interface, dissolution–precipitation, weathering, element cycling, nanoscale observations, atomic force microscopy

INTRODUCTION

Recent studies have characterized the molecular structure of mineral surfaces and the aqueous fluids in the near environment of these surfaces. As well, dynamic processes such as dissolution, growth, and mineral replacement have been investigated using state-of-the-art spectroscopic and microscopic techniques, complemented by molecular simulations to confirm or predict experimental results. These have led to new and significant insights into the kinetics and mechanisms of reactions occurring at mineral surfaces in key mineral–fluid systems. Furthermore, they have provided critical tests of the validity of predictions made in the light of theoretical studies of mineral–water reactivity. The results of this research have dramatically increased our ability to decipher and predict both the mechanisms and kinetics of surface-mediated reactions.

In a practical sense, nanoscale information obtained from in situ experiments is used to solve environmental problems. Such information can lead to the deciphering of a mechanism, which can then be controlled in order to diminish or avoid detrimental environmental effects. One case study involves the use of phosphates in fertilizers. Phosphorus is an essential element for life, and adding it to soils over the past 100 years has vastly improved crop yields and quality worldwide. However, not enough phosphorus or too much of it in runoff water, rivers, and estuaries can be harmful. A study by Wang et al. (2012) has shed light on the fate of dissolved phosphate species in diverse soil systems. Other studies are concentrating on crystal-growth-control strategies to alleviate problems such as damage to building stone, especially in relation to cultural-heritage sites and objects. The articles in this issue illustrate how studies of the mineral–water interface can be applied to the mediation of environmental issues.

DIRECT OBSERVATIONS AT THE NANOSCALE

When minerals come in contact with aqueous fluids with which they are out of equilibrium, reactions begin as the system seeks to establish a new equilibrium (lower energy state). If the aqueous fluid is undersaturated with respect to a mineral, the mineral will dissolve until the fluid becomes saturated with the mineral phase. However, if the fluid becomes supersaturated with any new mineral phase, the latter may precipitate by nucleation and subsequently grow.

Over the past 20 years, in situ techniques such as atomic force microscopy (AFM) and various interferometry methods (including vertical scanning interferometry, VSI) have given insights into the mechanisms of dissolution and growth (e.g. Dove and Hochella 1993; Pina et al. 1998; Teng et al. 2000; De Yoreo et al. 2009; Luttge and Arvidson 2010; Ruiz-Agudo and Putnis 2012).

Nanoscale observations have shown, for example, that dissolution in pure water proceeds by the nucleation of etch pits on flat, cleaved mineral surfaces or by the removal of atomic layers at step edges, which may have spread from original etch pits. The latter can be seen in Figure 1, an AFM atomic-scale-resolution image of a calcite ($CaCO_3$) surface during dissolution in water. In the case of calcite, the etch pits are rhombohedral in form (Fig. 2a), as their morphology is controlled by the crystallography of the mineral structure. Similarly, growth of calcite occurs by nucleating rhombohedral islands or spirals (Figs. 2b, c), which then spread and merge until the surface of the calcite becomes covered by a new $CaCO_3$ layer.

APPLICATION OF NANOSCALE OBSERVATIONS TO EARTH SYSTEMS

In the Earth, aqueous fluids are never pure water. Nanoscale observations of mineral reactivity in contact with solutions of varying composition can shed light on the influence of the major and minor elements in natural systems, such as pore, river, and ocean waters. Direct observations can be made to test the effects of the composition of these fluids

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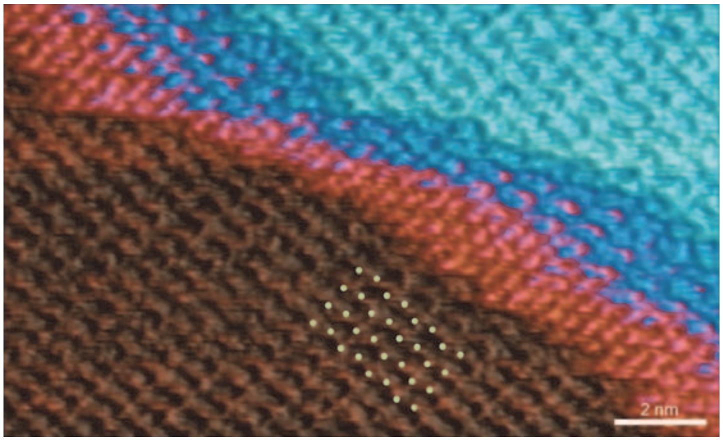

FIGURE 1 Atomic force microscopy image showing oxygen atoms on a calcite ($CaCO_3$) $(10\bar{1}4)$ surface undergoing dissolution in water. In the image, two crystal planes (brown and blue) are separated by the dissolving crystal front (pink). The atomic model of the oxygen atoms in the calcite has been overlaid on the lower plane (small white dots); the model reveals the zig-zag structure of the oxygen atoms. As well, individual defects in the crystal near the dissolution plane and a secondary facet brought out on the etch front are seen. The dissolution process has been imaged in situ, and progressive loss of crystal units to solution are seen with the retreat and roughening of step edges. IMAGE BY PERMISSION FROM BRUKER INSTRUMENT: DIMENSION FASTSCAN, BRUKER NANO SURFACES; OPERATING MODE: PEAK FORCE TAPPING

on mineral growth and dissolution, enabling the development of experiments that mimic natural conditions. The degree of supersaturation of the growth solution controls the dominant growth mechanism. However, if the growth solution contains other background ions (that is, ions other than those in the crystal-building units), changes in the growth pattern may be directly observed at the nanoscale (Ruiz-Agudo et al. 2012).

For example, selenium is an element essential for plant and animal growth. It is the element with the narrowest margin of concentration between beneficial and toxic effects (ingesting less than 40 micrograms per day produces a deficiency, whereas if more than 400 micrograms per day are consumed, it becomes highly toxic to humans). When selenium (IV) is present in a calcite growth solution, the normal growth pattern of rhombohedral islands and spirals is modified into more complex heart-shaped morphologies, as shown in FIGURE 2D (Renard et al. 2013). On the other hand, Se (VI) does not modify the normal growth pattern of calcite, which suggests that it does not significantly incorporate into calcite. These results give an explanation for the fact that selenate (SeO_4^{2-}) remains preferentially in solution, as indicated by the composition of seawater worldwide, and suggest that calcite could represent a reservoir of selenite (SeO_3^{2-}). In this case, the growth mechanism can be directly observed by AFM. The z-resolution (i.e. height) in AFM is always at the nanoscale, as the topography is imaged by tracking the interatomic surface forces between a sharp tip and the sample surface. Nano-imaging can also be achieved with VSI. Different topographical and textural information can be imaged. Microfeatures of dissolution of a calcite surface imaged using VSI are illustrated in FIGURE 3, where height in the z direction is higher than can normally be achieved with AFM.

The processes by which elements are incorporated into minerals during growth or released during dissolution are important questions when considering environmental issues. Examples of such applications include the use of minor element partitioning into biominerals to reconstruct past ocean conditions and hence to predict climate change, and the tracing of elements released and mobilized during dissolution to predict where they may be transported. In the case of element partitioning, Mg/Ca ratios can be utilized to infer past ocean temperature, and the incor-

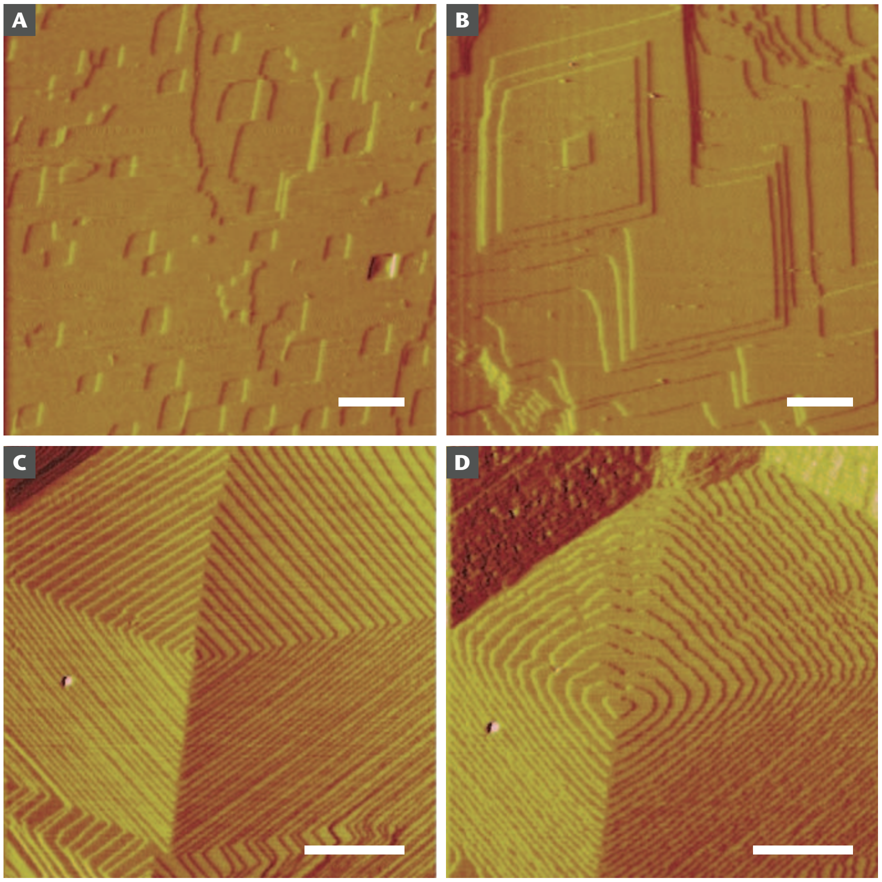

FIGURE 2 Atomic force microscopy images of a calcite surface dissolving in water. (**A**) Formation of characteristic rhombohedral etch pits, one unit cell deep (≈3.5 Å). (**B**) Growth islands forming on the surface exposed to a supersaturated growth solution. (**C**) Growth spiral or hillock forming on a calcite surface (spiral growth is more prevalent with less supersaturated solutions). (**D**) An observed change in the spiral growth pattern from a rhombohedral spiral to a heart-shaped form in the presence of Se (IV) ions, indicating adsorption or incorporation of these ions during calcite growth. Scale bar for all images is 1 μm.

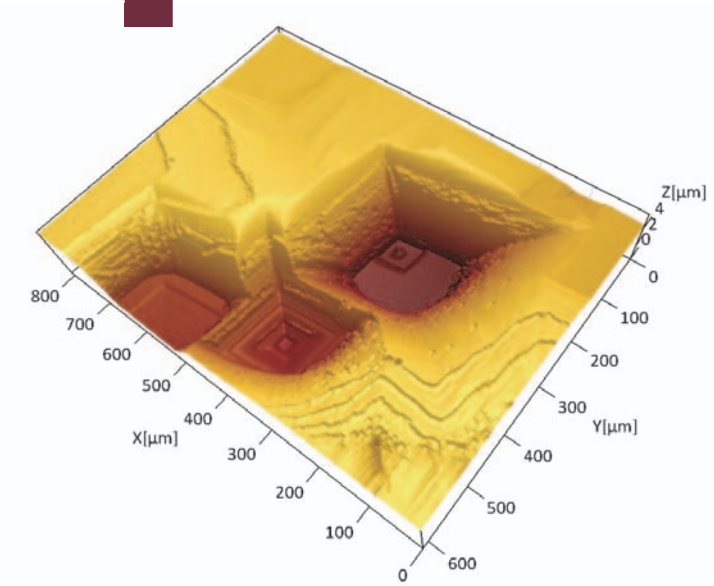

FIGURE 3 Vertical scanning interferometry image of a dissolving calcite surface showing typical etch pits (dark colour indicates depth). The maximum etch pit depth shown is 4 µm. IMAGE COURTESY OF ROLF ARVIDSON (BREMEN UNIVERSITY)

poration of B during $CaCO_3$ shell growth (for example, in foraminifera, which constitute a major source of carbonate for sedimentary rocks) can be used to estimate ocean pH and hence provide a measure of CO_2 dissolved in the ocean. Element release during mineral dissolution has implications for environmental contamination, such as acid mine drainage, and for element cycling in the Earth, leading for example to the formation of ore bodies. Element incorporation during the growth of solid solutions may also be a way to remove and immobilize contaminants from the environment. This process occurs, for example, in the removal of heavy metals by apatite (also the constituent of vertebrate bones), a mineral with the capacity to incorporate a wide variety of metal cations in its structure (Oelkers and Valsami-Jones 2008).

Other anthropogenic problems, such as the blocking of industrial pipes by scale [chalk ($CaCO_3$) or barite ($BaSO_4$)] formation, or damage caused to cultural heritage buildings and objects as a result of crystal growth, can be better understood at the molecular level, allowing the testing of possible remediation procedures (Rodriguez-Navarro et al. 2012).

DECIPHERING COUPLED DISSOLUTION–PRECIPITATION REACTIONS

The dissolution of a mineral is commonly followed by the precipitation of a new phase. Reactions involved in dissolution and precipitation are often tightly coupled at the mineral surface and are dependent on solution composition. In cases where the fluid becomes supersaturated with respect to another phase, the relevant fluid composition may be confined to the mineral–fluid interface (Putnis et al. 2005). This has often been described as a "thin film" of fluid whose composition may be very different from that of the bulk fluid. In situ AFM experiments frequently show the precipitation of a new phase even though the solution flowing over the mineral surface is undersaturated with respect to any possible precipitating phase (Ruiz-Agudo et al. 2012; Urosevic et al. 2012); this observation is direct evidence for the existence of a mineral–fluid interfacial layer (or boundary layer) that differs in composition from the bulk fluid.

Interface-coupled dissolution–precipitation has been suggested as the controlling mechanism in many large-scale Earth processes (Putnis and Putnis 2007; Putnis 2009; Putnis and John 2010) that operate in the presence of aqueous fluids, for example, metamorphism, metasomatism (Putnis and Austrheim 2010), and weathering, including the cycling of elements, such as carbon. Molecular-scale investigations, such as weathering experiments and studies of CO_2 incorporation during mineral growth, provide critical insights into mineral–fluid interactions occurring at several stages in the carbon cycle (FIG. 4).

Interest in elucidating coupled dissolution–precipitation processes extends from the global to the industrial scale. Examples are aluminosilicate mineral dissolution (weathering) and carbonate mineral growth, which have regulated the CO_2 distribution in Earth systems throughout geological time. The manufacture of cement from calcined limestone, which releases large amounts of CO_2 to the atmosphere, and the degradation of cement/portlandite [$Ca(OH)_2$] through the reformation of $CaCO_3$ are another example of coupled processes, although in this case dissolution and precipitation are spatially and temporally unconnected.

Direct in situ observations at the nanoscale have provided evidence of coupled processes occurring at the contact between minerals and aqueous fluids. As an example, the reaction of brucite [$Mg(OH)_2$] with carbonated water involves coupled dissolution and precipitation at the interface. Using AFM, Hövelmann et al. (2012) observed the coupled reaction that occurs when carbonated water (undersaturated with respect to any possible phase) is passed over the brucite mineral surface and a new carbonate phase precipitates (FIG. 5). This situation is relevant to the sequestration of CO_2 (Oelkers et al. 2008), which is currently being tested using various rock reservoirs (Gislason et al. 2010).

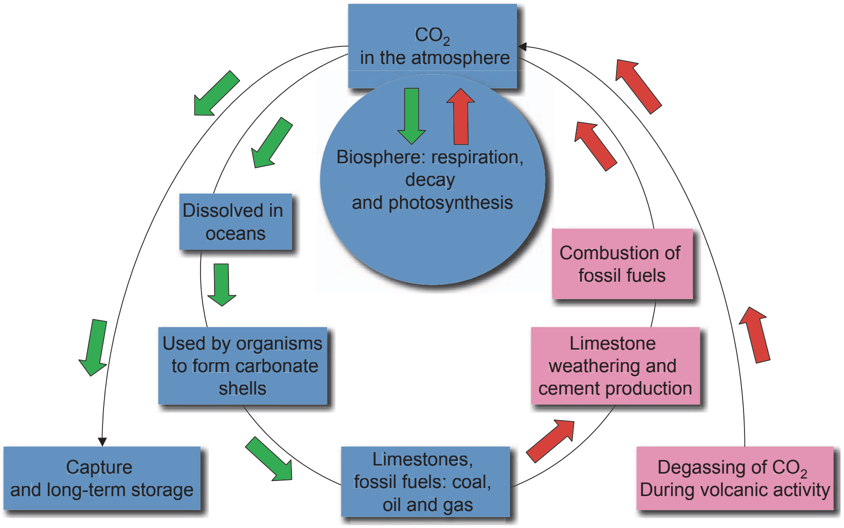

FIGURE 4 The carbon cycle indicates the role of the solid Earth when carbon, C, cycles from atmospheric CO_2 through various stages of incorporation in mineral structures and storage and then is released back to the atmosphere. At several stages in the C cycle, reactions at the mineral–water interface control the potential processes and reaction rates involved in the longer-term storage of CO_2. Green arrows show the incorporation of C within mineral structures, leading to storage, and red arrows indicate the release of C as CO_2 back to the atmosphere.

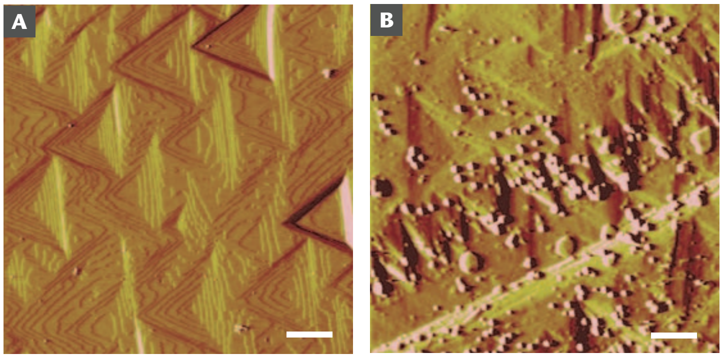

FIGURE 5 Atomic force microscopy image of brucite [$Mg(OH)_2$] surfaces dissolving in carbonated water. (**A**) Triangular etch pits show initial brucite dissolution. (**B**) With increasing time of exposure to carbonated water, particles of a hydrated Mg carbonate phase nucleate and grow on the surface. Scale bar = 1 μm. IMAGES COURTESY OF J. HÖVELMANN

"LEACHED" LAYERS ON MINERAL SURFACES

The dissolution of many multicomponent minerals is known from flow-through experiments to occur nonstoichiometrically, that is, the ratio of elements in the mineral is different from the ratio released to solution. This has been traditionally presented as the result of preferential "leaching" of elements from a mineral surface, resulting in the formation of an altered surface layer or "leached" layer (Casey et al. 1993). However, direct nanoscale observations have shown that many of these minerals actually dissolve stoichiometrically, but the subsequent precipitation of a new phase results in the nonstoichiometric signature observed in the fluid. In pioneering work, Hellmann et al. (2003, 2012) presented high-resolution transmission electron microscopy (HRTEM) evidence for the coupling of dissolution and precipitation during the weathering of silicate minerals and the formation of surface silica layers. This conclusion was supported by Daval et al. (2011) and King et al. (2011), who used Raman spectroscopy to track ^{18}O isotope incorporation from an enriched solution into a newly precipitated silica phase during the replacement of olivine by amorphous silica.

Direct evidence of silicate dissolution coupled with amorphous silica precipitation has also been seen where wollastonite ($CaSiO_3$) has come into contact with acidic solutions (Ruiz-Agudo et al. 2012). This system was studied because wollastonite is considered a model silicate mineral on account of its simple structure and chemistry. Although nanoscale observations support dissolution and precipitation, this process remains a topic of debate and leaching continues to be presented as a mechanism for mineral dissolution (Schott et al. 2012). Similarly, the formation of altered layers has been observed during the dissolution of other multicomponent minerals, such as carbonates. Urosevic et al. (2012) reported on the dissolution of dolomite [$CaMg(CO_3)_2$], which initially releases much more Ca than Mg to solution because the dissolution (seen in the continuous spreading of etch pits) is immediately followed by the precipitation of a hydrated $MgCO_3$ phase.

MINERAL–FLUID REACTIONS IN ROCKS AND THE DEVELOPMENT OF POROSITY

When an aqueous fluid moves through a rock, reactions at the mineral–fluid interface induce changes in the mineral composition and texture while releasing elements to solution that were previously bound within mineral structures. Therefore, careful examination and analysis of minerals provide clues for unraveling the rock's history. The minerals in rocks are effectively the evidence we have for deciphering the history of our planet. For example, large ore deposits are commonly accompanied by albitization of the country rocks (Oliver et al. 2004; Engvik et al. 2008), that is, the original feldspar (a calcium-rich, aluminosilicate, rock-forming mineral) has been replaced by a sodium-rich feldspar, albite ($NaAlSi_3O_8$). As Na-bearing fluids are ubiquitous near the surface of the Earth, albitization is a common reaction process. An example of albitization is seen in FIGURE 6A, which shows an outcrop of metasediments from the Curnamona Province, South Australia (a very large area of mineralization that includes the vast Broken Hill Zn–Pb–Ag deposits). Here the albite-rich zone is associated with fractures and fluid infiltration (Clark et al. 2005). The scanning electron microscopy (SEM) image (FIG. 6B) shows the natural albite porosity that has allowed aqueous fluids to penetrate the rock. This reaction has been reproduced experimentally by Hövelmann et al. (2010). In these albitization experiments, the reaction interface showing the chemical and textural changes accompanying the albitization reaction can be seen directly, as shown in FIGURE 6C–D.

Clearly, these mineral-replacement reactions result in changes in mineral and fluid composition and ultimately allow for element mobilization within the crust of the Earth. Mineral replacement is invariably accompanied by textural changes, most commonly the development of porosity in the product phases. Such porosity is often at the nanoscale, and the former exposure of a rock to fluid infiltration and reaction can be assessed by nano-imaging (Putnis et al. 2007). Porosity is developed in a mineral as a result of a reaction producing a volume decrease. However volume changes associated with dissolution and precipitation reactions during mineral replacement are controlled by the relative solubilities of parent and product minerals (within the aqueous fluid at the mineral–fluid interface) and not only by their molar volume differences (Pollok et al. 2011). Porosity development allows the fluid to penetrate further into the previously solid mineral grain and hence advance the mineral–fluid reaction interface within the grain. Whereas fractures and grain boundaries will allow for fast fluid movement through rocks, mineral–fluid reactions occurring at mineral–fluid interfaces result in porosity development within the new phase and ultimately promote the exchange and mobilization of elements, which can then be transported elsewhere.

IN THIS ISSUE

The recent advances in our understanding of molecular-scale processes at the mineral–water interface constitute the theme of this issue. Each of the articles highlights exciting new research fields that focus on the involvement of surfaces in mineral reactions. Our goal is to illustrate the importance of performing molecular-scale investigations for addressing key, large-scale geochemical processes. The articles draw attention to up-to-date research at the nanoscale on the topics listed below.

Mineral dissolution Chemical weathering is among the most widespread and important geochemical processes that occur on the Earth's surface. In the last decades, research in this field has focused on the kinetics and mechanisms of mineral-dissolution reactions. The development of techniques that allow direct, molecular-scale observation of mineral surfaces during dissolution has significantly contributed to a better understanding of the dynamics of mineral–fluid reactions (Lüttge et al. 2013 this issue).

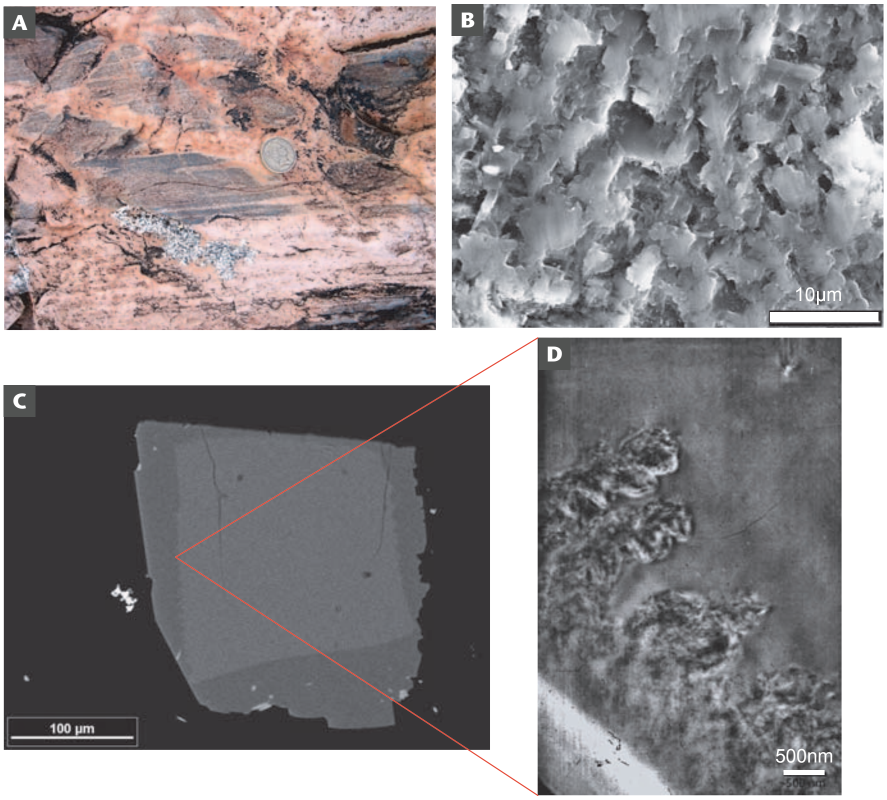

FIGURE 6 (**A**) Albitization, marked by a pink coloration (nanoscale hematite inclusions) in metamorphosed rocks in Curnamona Province, South Australia, involves replacement alteration during water–mineral interactions. Albitization starts along fractures and then affects the whole rock by a process of infiltration through porosity, which provides a pathway for mass transport. (**B**) Scanning electron microscope (SEM) image showing porosity in albite. (**C**) Backscattered SEM image of an experimental feldspar crystal ($An_{70}Ab_{30}$) after 14 days in a sodium silicate solution at 600 °C and 2 kbars. The darker rim is almost pure albite (Ab_{99}, $NaAlSi_3O_8$). (**D**) Transmission electron microscopy image of the reaction interface in (C) showing a sharp but highly irregular interface between altered and unaltered feldspar, as well as a complex diffraction contrast indicating a defective structure, consistent with nanoporosity in the replaced rim. IMAGES C AND D, COURTESY OF J. HÖVELMANN

Mineral growth Nanoscale studies dealing with interfacial processes occurring during mineral growth in simple model systems have enabled a significant advance in the understanding of the fundamental controls on the complex phenomenon of mineralization. Classical and nonclassical crystal-nucleation and crystal-growth theories can now be tested using state-of-the-art nano-imaging techniques. In recent studies of aqueous-solution systems, nanometer-size structural units already present in solution before nucleation—the so-called prenucleation clusters—have been imaged directly (Teng 2013 this issue).

Environmental remediation This may be achieved by the incorporation of elements during solid-solution mineral growth. The optimization of strategies for remediation of waters contaminated by toxic metals based on coprecipitation with mineral phases requires a sound knowledge of the underlying mechanisms of trace element partitioning, particularly regarding the nanoscale processes occurring at mineral surfaces during trace element incorporation (Prieto et al. 2013 this issue).

Controls on crystal growth By the selective implementation of growth inhibitors, crystal growth may be modified or controlled. Inhibitors are important for the remediation of anthropogenically induced problems, such as scaling in industrial pipes, in water treatment, and in geothermal systems. Strategies to prevent the damage caused by salt crystallization in cultural heritage objects such as building stone, statues, and frescoes, is also benefiting from improved knowledge of the controls on crystal growth (Rodriguez-Navarro and Benning 2013 this issue).

Introduction to modeling approaches Modeling is used in mechanistic studies aimed at gaining an understanding of surface reactivity. Modeling approaches complement direct, in situ, molecular-scale observations of processes occurring at mineral–water interfaces. The complexity of such reactions requires the development of molecular models that describe the surface forces, energy, structure, and dynamics of water near mineral surfaces. Recently proposed molecular dynamics models that include water properties near mineral surfaces have improved our understanding of experimental results concerning the kinetics and mechanisms of mineral–water interactions. Molecular simulations can also indicate the need for further experimental research—that is, simulations can either confirm interpretations made from experimental results or indicate the direction of an experimental approach (Stack et al. 2013 this issue).

Given the rapid development of research in this field and the fact that the field is interdisciplinary—including environmental science, geochemistry, hydrogeology, oceanography, biomineralization, and soil science—the topic of mineral–water interactions is continually evolving and maturing. The scene is now set for further exciting developments, with the ultimate aim of gaining a better understanding of important, dynamic Earth processes.

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REFERENCES

Casey WH, Westrich HR, Banfield JF, Ferruzzi G, Arnold GW (1993) Leaching and reconstruction at the surfaces of dissolving chain-silicate minerals. Nature 366: 253-256

Clark C, Schmidt Mumm A, Faure K (2005) Timing and nature of fluid flow and alteration during Mesoproterozoic shear zone formation, Olary Domain, South Australia. Journal of Metamorphic Geology 23: 147-164

Daval D, Sissmann O, Menguy N, Saldi GD, Guyot F, Martinez I, Corvisier J, Garcia B, Machouk I, Knauss KG, Hellmann R (2011) Influence of amorphous silica layer formation on the dissolution rate of olivine at 90 °C and elevated $p\mathrm{CO}_2$. Chemical Geology 284: 193-209

De Yoreo JJ, Zepeda-Ruiz LA, Friddle RW, Qiu SR, Wasylenki LE, Chernov AA, Gilmer GH, Dove PM (2009) Rethinking classical crystal growth models through molecular scale insights: consequences of kink-limited kinetics. Crystal Growth & Design 9: 5135-5144

Dove PM, Hochella MF Jr (1993) Calcite precipitation mechanisms and inhibition by orthophosphate: In situ observations by Scanning Force Microscopy. Geochimica et Cosmochimica Acta 57: 705-714

Engvik AK, Putnis A, Fitz Gerald JD, Austrheim H (2008) Albitization of granitic rocks: the mechanism of replacement of oligoclase by albite. Canadian Mineralogist 46: 1401-1415

Gislason SR and 11 coauthors (2010) Mineral sequestration of carbon dioxide in basalt: A pre-injection overview of the CarbFix project. International Journal of Greenhouse Gas Control 4: 537-545

Hellmann R, Penisson J-M, Hervig RL, Thomassin JH, Abrioux MF (2003) An EFTEM/HRTEM high-resolution study of the near surface of labradorite feldspar altered at acid pH: evidence for interfacial dissolution-reprecipitation. Physics and Chemistry of Minerals 30: 192-197

Hellmann R, Wirth R, Daval D, Barnes J-P, Penisson J-M, Tisserand D, Epicier T, Florin B, Hervig RL (2012) Unifying natural and laboratory chemical weathering with interfacial dissolution–reprecipitation: A study based on nanometer-scale chemistry of fluid–silicate interfaces. Chemical Geology 294-295: 203-216

Hövelmann J, Putnis A, Geisler T, Schmidt BC, Golla-Schindler U (2010) The replacement of plagioclase feldspars by albite: observations from hydrothermal experiments. Contributions to Mineralogy and Petrology 159: 43-59

Hövelmann J, Putnis CV, Ruiz-Agudo E, Austrheim H (2012) Direct nanoscale observations of CO_2 sequestration during brucite [$\mathrm{Mg(OH)}_2$] dissolution. Environmental Science & Technology 46: 5253-5260

King HE, Plümper O, Geisler T, Putnis A (2011) Experimental investigations into the silicification of olivine: Implications for the reaction mechanism and acid neutralization. American Mineralogist 96: 1503-1511

Lüttge A, Arvidson RS (2010) Reactions at surfaces: A new approach integrating interferometry and kinetic simulations. Journal of the American Ceramic Society 93: 3519-3530

Lüttge A, Arvidson RS, Fischer C (2013) A stochastic treatment of crystal dissolution kinetics. Elements 9: 183-188

Oelkers EH, Valsami-Jones E (2008) Phosphate mineral reactivity and global sustainability. Elements 4: 83-87

Oelkers EH, Gislason SR, Matter J (2008) Mineral carbonation of CO_2. Elements 4: 333-337

Oliver NHS, Cleverley JS, Mark G, Pollard PJ, Fu B, Marshall LJ, Rubenach MJ, Williams PJ, Baker T (2004) Modeling the role of sodic alteration in the genesis of iron oxide–copper–gold deposits, Eastern Mount Isa Block, Australia. Economic Geology 99: 1145-1176

Pina CM, Becker U, Risthaus P, Bosbach D, Putnis A (1998) Molecular-scale mechanisms of crystal growth in barite. Nature 395: 483-486

Pollok K, Putnis CV, Putnis A (2011) Mineral replacement reactions in solid solution-aqueous solution systems: Volume changes, reaction paths and end points using the example of model salt systems. American Journal of Science 311: 211-236

Prieto M, Astilleros JM, Fernández-Díaz L (2013) Environmental remediation by crystallization of solid solutions. Elements 9: 195-201

Putnis A (2009) Mineral replacement reactions. Reviews in Mineralogy & Geochemistry 70: 87-124

Putnis A, Austrheim H (2010) Fluid-induced processes: metasomatism and metamorphism. Geofluids 10: 254-269

Putnis A, John T (2010) Replacement processes in the Earth's crust. Elements 6: 159-164

Putnis A, Putnis CV (2007) The mechanism of reequilibration of solids in the presence of a fluid phase. Journal of Solid State Chemistry 180: 1783-1786

Putnis A, Hinrichs R, Putnis CV, Golla-Schindler U, Collins L (2007) Hematite in porous red-clouded feldspars: evidence of large-scale crustal fluid–rock interaction. Lithos 95: 10-18

Putnis CV, Tsukamoto K, Nishimura Y (2005) Direct observations of pseudomorphism: compositional and textural evolution at a fluid-solid interface. American Mineralogist 90: 1909-1912

Renard F, Montes-Hernandez G, Ruiz-Agudo E, Putnis CV (2013) Selenium incorporation into calcite and its effect on crystal growth: An atomic force microscopy study. Chemical Geology 340: 151-161

Rodriguez-Navarro C, Benning LG (2013) Control of crystal nucleation and growth by additives. Elements 9: 203-209

Rodriguez-Navarro C, Jroundi F, Schiro M, Ruiz-Agudo E, González-Muñoz MJ (2012) Influence of substrate mineralogy on bacterial mineralization of calcium carbonate: Implications for stone conservation. Applied and Environmental Microbiology 78: 4017-4029

Ruiz-Agudo E, Putnis CV (2012) Direct observations of mineral-fluid reactions using atomic force microscopy: the specific example of calcite. Mineralogical Magazine 76: 227-253

Ruiz-Agudo E, Putnis CV, Rodriguez-Navarro C, Putnis A (2012) Mechanism of leached layer formation during chemical weathering of silicate minerals. Geology 40: 947-950

Schott J, Pokrovsky OS, Spalla O, Devreux F, Gloter A, Mielczarski JA (2012) Formation, growth and transformation of leached layers during silicate minerals dissolution: The example of wollastonite. Geochimica et Cosmochimica Acta 98: 259-281

Stack AG, Gale JD, Raiteri P (2013) Virtual probes of mineral–water interfaces: The more flops, the better. Elements 9: 211-216

Teng HH (2013) How ions and molecules organize to form crystals. Elements 9: 189-194

Teng HH, Dove PM, De Yoreo JJ (2000) Kinetics of calcite growth: surface processes and relationships to macroscopic rate laws. Geochimica et Cosmochimica Acta 64: 2255-2266

Urosevic M, Rodriguez-Navarro C, Putnis CV, Cardell C, Putnis A, Ruiz-Agudo E (2012) In situ nanoscale observations of the dissolution of $\{10\bar{1}4\}$ dolomite cleavage surfaces. Geochimica et Cosmochimica Acta 80: 1-13

Wang LJ, Ruiz-Agudo E, Putnis CV, Menneken M, Putnis A (2012) Kinetics of calcium phosphate nucleation and growth on calcite: Implications for predicting the fate of dissolved phosphate species in alkaline soils. Environmental Science & Technology 46: 834-842