



Selenium incorporation into calcite and its effect on crystal growth: An atomic force microscopy study

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ABSTRACT

The atomic processes leading to calcite growth are still debated. The presence of foreign impurities in solution is known to change the rate of step propagation during growth as well as the growth mechanism. Among trace elements, selenium, in the form of oxyanions, can incorporate into the calcite structure by replacing the carbonate group. In the present study, we record the effect of organic and inorganic selenium on calcite growth at room temperature by using in-situ time-lapse atomic force microscopy (AFM) and we confirm the observations by performing batch reactor experiments. Our results show that the incorporation of Se(IV) during calcite growth could be observed in-situ and the presence of this element modifies the morphology of growth features formed on a cleaved calcite surface, transforming typical pyramidal spiral growth hillocks into more complex heart-shape and tear-shape patterns. This effect is reversible as changing the solution back to a selenium-free composition recovers the original hillock pattern. Conversely, Se(VI) does not incorporate, but catalyzes the step propagation rate without changing the growth pattern. We have also observed that the presence of organic selenium (Se(−II)), in the form of seleno-L-cystine, has an effect on the nucleation of calcite crystals and their aggregation in clusters, but has no measurable effect on the morphology of growing steps at the calcite surface. These results indicate that calcite could represent a reservoir of selenite, whereas selenate would remain preferentially in solution, as observed in the composition of sea waters worldwide.

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1. Introduction

Carbonate minerals are widespread at the surface of the Earth. They control the global carbon cycle by storing this element in various sedimentary formations. They also play a crucial role in the development of life by their presence in many living systems, from the shells of sea planktons to the bones of vertebrates. Among carbonates, calcite is the most common, shaping the surface of the Earth in many sedimentary basins and mountain ranges in the form of limestones and marbles. Understanding how calcite can nucleate and precipitate represents crucial challenges targeted since the 1970s' (Bischof, 1968; Nancollas and Reddy, 1971), including processes of biomineralization (Teng et al., 1998). However, a complete understanding of calcite growth processes, including trace element partitioning, at the atomic scale is still a challenging subject.

The study of calcite growth by direct in-situ observations provides valuable information on the detailed mechanisms of ion incorporation and how the complex structure of the calcite surface, with the

presence of a large number of reactive sites (i.e. cleavage steps and kink sites), may control precipitation (Ruiz-Agudo and Putnis, 2012 and references therein). Such measurements also allow visualizing the effect of trace ions on the propagation of the calcite steps during growth and can help decipher whether trace elements either incorporate directly into calcite, or produce co-precipitates that would poison the calcite surface. For example, using a scanning force microscope, Dove and Hochella (1993) observed that phosphate modifies the geometry of the steps at the calcite surface, transforming relatively straight steps into jagged steps. The effects of ion activity ratio (Larsen et al., 2010) and the nature of the background ions in solution (Ruiz-Agudo et al., 2011) could be monitored at the atomic scale, providing useful insights necessary to link microscopic processes to macroscopic measurements of calcite growth. Under hydrothermal conditions (80–105 °C), it was possible to observe in situ, using an atomic force microscope (AFM), the growth of another carbonate, magnesite (Saldi et al., 2009) and measure the effect of fluid supersaturation on the growth rate of steps by a mechanism of hillock development similar to that of calcite.

The incorporation of impurities during calcite growth has been studied extensively (Staudt et al., 1994; Paquette and Reeder, 1995; Temman et al., 2000; Fujita et al., 2004; Lee and Reeder, 2006; Stipp

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et al., 2006; Heberling et al., 2008; Ruiz-Agudo et al., 2011), as the presence of trace ions in the calcite structure could be used to infer past fluid circulations, fluid composition and degree of water-rock interaction. The incorporation of trace ions can lead to intersectoral zoning of the calcite crystals during growth, allowing probing the different surface sites and the controlling parameters of ion incorporation at the steps of the calcite surface (Staudt et al., 1994; Paquette and Reeder, 1995). The surface control is exerted by the presence of steps and kink sites at the calcite surface. For example, the incorporation of divalent ions with radii smaller than Ca^{2+} is favored at steps that have smaller kink sites, whereas ions with larger radii are preferentially incorporated at less-constrained and larger kink sites. As a result, even if the composition of the fluid is homogeneous, the composition of the growing calcite can be heterogeneous when considering the incorporation of trace elements.

Among trace elements that may incorporate into calcite and change its growth rate, we focus here on how selenium oxyanions may incorporate or not into calcite during growth. Concerning selenate, different effects have been described (Reeder et al., 1994; Cheng et al., 1997; Montes-Hernandez et al., 2009). On the one hand, Reeder et al. (1994) proposed that Se(VI) could be incorporated into calcite, based on X-ray adsorption fine-structure XAFS spectroscopic studies and calculations of the distance between selenium atoms and their nearest atom neighbors. On the other hand, Montes-Hernandez et al. (2009) did not observe Se(VI) incorporation or adsorption, based on the solution analysis before and after calcite precipitation in batch reactors. Conversely, the incorporation of selenite Se(IV) could be observed under hydrothermal conditions, based on solution chemistry analysis and synchrotron extended X-ray adsorption fine-structure (EXAFS) spectroscopy (Montes-Hernandez et al., 2011).

Selenium is the element with the narrowest margin of concentration between essential and toxic effects. For example, dietary deficiency for humans occurs for consumption of selenium below 40 micrograms per day, whereas for concentration above 400 micrograms per day, it becomes toxic (Levander and Burk, 2006). As an example, the recommended European population intake is 55 micrograms per day (European Council Scientific Committee on Food, 2003). Ecotoxicological effects of selenium have been recognized for a long time (Draize and Beath, 1935; Ellis et al., 1937), with negative impact on living systems. Since then, this element has been largely studied because several environmental and health issues emerged due to the too low or too high consumption level by plants and animals, including humans, and its bioaccumulation in the food chains – see for example the review by Hamilton (2004).

Selenium is found in its natural form in volcanic rocks (Floor and Román-Ross, 2012), geothermal areas (Rouxel et al., 2004), coal (Yudovich and Ketris, 2006; Li and Zhao, 2007) and therefore potentially concentrated in mine waste, soils, waters and the atmosphere, and is transported in the environment (Malisa, 2001; Fernandez-Martinez and Charlet, 2009). The anthropogenic production of selenium, released into the atmosphere, is in the form of aerosols and dust and is mainly due to the industrial and domestic burning of coal, oil refinery and the pyrometallurgical production of several metals such as copper, nickel or zinc (Conde and Sanz Alaejos, 1997). This selenium is then delivered into soils during rain and snow precipitation. Another factor of selenium concentration in living systems is the use of seleniferous waters for irrigation in crop production leading to selenium oxyanion contamination in drainage waters and its accumulation in reservoirs (Mayland et al., 1989). Finally, Se-79 is a long lived (650000 years) radioactive mobile fission element, present in nuclear fuels and wastes resulting from reprocessing this fuel, and thus has the potential to contaminate the far-field environment around storage locations.

In the present study, we characterize how the presence of selenium, either inorganic and in two different oxidation states (selenite: Se(IV) and selenate: Se(VI)) or in an organic molecule (seleno-L-cystine: Se-Cys), modifies the growth of calcite. The direct effect of selenium

on calcite growth was characterized using AFM imaging of calcite surfaces during precipitation and growth of pyramidal hillocks (spiral growth) studied at room temperature during flow-through experiments. The main result of this study is that inorganic selenite has a strong effect on calcite growth and is incorporated into the calcite crystal structure, presumably by replacing carbonate groups (CO_3^{2-}) by selenite groups (SeO_3^{2-}). This replacement has a strong effect on the morphology of precipitated calcite, transforming the pyramidal hillocks into heart-shaped forms. Conversely, selenate does not show any significant incorporation during calcite growth, but catalyzes the rate of step propagation. Finally, the organic selenium displays a complex effect. Only a small part of the selenite, produced by the chemical fragmentation of the Se-Cys, may be incorporated into the calcite. Moreover, the organic acid and amine groups may adsorb onto the calcite reactive surfaces and exert a control on the patterns of growing precipitates (Montes-Hernandez et al., 2011). All these AFM conclusions are confirmed by batch reactor experiments where calcite was synthesized at 30 °C in the presence of various concentrations of selenium. Direct observations have shown that Se(IV) can be incorporated into calcite, whereas Se(VI) is not, confirming the results presented by Montes-Hernandez et al. (2011). The new achievement in the present study is the direct observation, using AFM observations, of the effect of selenium on calcite growth at room temperature and the measurements of calcite precipitation rates at the atomic scale when varying the concentration of various selenium oxyanions in the fluid.

2. Materials and methods

2.1. Precipitation of calcite imaged using atomic force microscopy

For the AFM studies, solutions supersaturated with respect to calcite were prepared, to which selenium was added. CaCl_2 and NaHCO_3 1 M stock solutions were prepared at room temperature (23 °C) from reagent grade sodium bicarbonate and calcium chloride salts that were dissolved into double-deionized water. The calcite growth solution was produced by mixing relevant proportions of these two stock solutions into double-deionized water. The pH of the solutions was close to 8.2 and the $\text{Ca}^{2+}/\text{CO}_3^{2-}$ ratio was equal to 1. The supersaturation of the solution was calculated as $\Omega = \text{IAP}/K_{\text{sp}} = 6.46$ where IAP is the ion activity product and K_{sp} is the calcite solubility product, equal to $10^{-8.48}$ at 25 °C, based on the PHREEQC database (Parkhurst and Appelo, 1999). Growth solutions containing various concentrations of selenium (0.8, 4, 8, 40, 70, 200 and 400 ppm) were also prepared. The selenium was either inorganic (selenite $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ or selenate Na_2SeO_4) or incorporated into an organic molecule, the seleno-L-cystine ($\text{C}_6\text{H}_{12}\text{N}_2\text{O}_4\text{Se}_2$). All chemical agents were obtained from Sigma Aldrich. The proportions of the various solutions (stock solutions and selenium solutions) were calculated using the PHREEQC software (Parkhurst and Appelo, 1999) and the concentrations are given in Table 1. Potential errors in the given concentrations come mainly from the 1 μL precision when sampling volumes of solutions.

Fresh calcite surfaces were prepared by cleaving a natural calcite (Iceland spar, Chihuahua, Mexico) along the $\{10\bar{1}4\}$ crystallographic plane, which because of its lowest atomic density represents a natural plane of weakness of the crystal. Time-lapse in-situ AFM observations of these calcite surfaces were performed using a flow-through fluid cell coupled to a Digital Instrument Nanoscope III multimode AFM (Bruker) working in contact mode at room temperature. Over the time-scale of the experiments, we assume that there would be no significant exchange between the fluid cell and the outside air. AFM images in the deflection mode were collected using Si_3N_4 tips (Veeco Instruments, tip model NP-S20) with spring constants 0.12 and 0.58 N.m^{-1} . The images were analyzed using the NanoScope software (Version 5.31r1) and exported into TIFF files that were processed using the Matlab software.

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