

Barite growth rates as a function of crystallographic orientation, temperature, and solution saturation state

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Cryst. Growth Des., **Just Accepted Manuscript** • DOI: 10.1021/acs.cgd.9b01506 • Publication Date (Web): 23 Apr 2020

Downloaded from pubs.acs.org on April 29, 2020

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Abstract

Barite growth kinetics was investigated as a function of crystallographic orientation for temperatures between 10 and 70 °C, and initial saturation indices (SI) of 1.1 and 2.1. The growth rates were estimated for (001), (210), and (101) faces using vertical scanning interferometry. Overall, face-specific barite growth rates ($r^{(hkl)}$) can be successfully described by the following rate law:

$$r^{(hkl)} = A^{(hkl)} \cdot \exp(-E_a^{(hkl)}/RT) \cdot (10^{SI} - 1)$$

where $A^{(hkl)}$ and $E_a^{(hkl)}$ represent the face-specific Arrhenius pre-exponential factor and activation energy, respectively, R is the gas constant, and T refers to the absolute temperature. In addition, because of the modest growth anisotropy of the various investigated faces, the following isotropic rate law can be used to satisfactorily account for the measured rate data:

$$r^{(hkl)} = A \cdot \exp(-E_a/RT) \cdot (10^{SI} - 1)$$

with average values of $A = \exp(13.59) \text{ nm} \cdot \text{h}^{-1}$ and $E_a = 35.0 \pm 2.5 \text{ kJ} \cdot \text{mol}^{-1}$. Over the range of conditions investigated in the present study, our results suggest that barite growth kinetics is surface-controlled, while possibly verifying the principle of detailed balancing and micro-reversibility. These results imply that previous modeling exercises of steady-state barite growth based on isotropic rate laws may remain valid, at least over the range of conditions investigated in the present study.

Keywords: barite; anisotropic growth; geothermal reservoir; scaling; growth rate law

1. Introduction

Several industrial, environmental, and geological concerns require a detailed understanding of barite (BaSO_4) growth kinetics. From an industrial standpoint, barite scale formation spontaneously occurs within geothermal wells¹ and inside fractures within geothermal reservoirs² (Fig. 1), which disturb both the continuous running of geothermal power plants and the efficiency of fluid circulation due to the reduction in reservoir permeability². The development of new reagents that could efficiently prevent or delay the barite scale formation crucially relies on our understanding of the mechanisms of barite precipitation^{3,4}.



Figure 1. Photograph of a section of 78 mm-diameter, cylindrical sandstone core (from the Buntsandstein unit) taken from the Soultz-sous-Forêts (France) EPS-1 exploration borehole, a borehole fully cored from a depth of 930 m to a depth of 2227 m in 1990-1991 (see ⁵⁻⁷ for information on the Soultz-sous-Forêts drilling project). The sandstone core, red/green in color, was taken from a depth of 1374 m and contains a 1-2 cm-wide fracture (in the center of the core). The fracture is partially filled with barite crystals (white in color) that have precipitated from the circulating geothermal fluids.

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3 53 From an environmental standpoint, the formation of barite is known to be frequently associated
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5 54 with the accumulation of elevated concentrations of radionuclides such as ^{226}Ra , which has stimulated
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8 55 several studies dedicated to quantify the uptake of radionuclides during barite precipitation (e.g., ⁸⁻¹¹).
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10 56 Finally, from a geological standpoint, barite formation provides insight into past seawater chemistry
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12 57 (e.g. ^{12, 13}), indirectly raising the question of the mechanisms of barite precipitation from environments
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15 58 that contained only trace amounts of sulfate. This issue has puzzled the geochemical community for
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17 59 decades¹⁴, and further emphasizes the need for a more accurate picture of the mechanisms of barite
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19 60 nucleation and growth⁴.

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22 61 In spite of the indisputable interest associated with barite formation, our knowledge regarding
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24 62 barite growth kinetics remains incomplete. With the noticeable exception of a few recent studies
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26 63 focused on barite growth on the specific (001) face over a wide range of temperatures (from 30 °C to
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28 64 108 °C)¹⁵⁻¹⁷, most existing studies were limited to the low temperature domain^{12, 18} and were derived
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31 65 from experiments conducted on powders. While the resulting isotropic growth rate laws derived from
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33 66 powder experiments have proved useful for modeling exercises (e.g., ²), it is noteworthy that they
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35 67 remain essentially empirical, which may cast doubt on their predictive ability. In particular, a recent
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38 68 study by Godinho and Stack¹⁹ has shown that barite growth is an anisotropic process. Importantly,
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40 69 isotropic kinetic rate laws were demonstrated to be unreliable and of low relevance to model
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42 70 anisotropic processes such as mineral dissolution/precipitation (e.g., ¹⁹⁻²²), unless the same rate-
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45 71 limiting step controls the dissolution/growth kinetics of all faces. Among the main consequences of
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47 72 this anisotropic reactivity are (i) the non-uniqueness of the relation between dissolution/growth rate
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49 73 and the saturation state of the solution²², (ii) the existence of a transient regime where the crystal habit
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51 74 continuously evolves, resulting in an equal gradual evolution of the apparent dissolution/growth rate
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54 75 “constant”^{19, 21-24}, and (iii) the existence of distinct equilibrium morphologies for a given crystal, which
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56 76 depend on the face-specific dissolution/growth rates of the considered crystal and therefore on reaction
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58 77 conditions such as temperature, fluid saturation state, and the potential catalytic / poisoning effects of
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3 78 specific (bio)molecules²⁵⁻²⁷. Therefore, in addition to the expected improvement of reactive transport
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5 79 simulations, knowledge of the variables that influence the face-specific growth rates of minerals can
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8 80 also help decipher the factors that shape crystals, which might be useful to provide insights into the
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10 81 putative biological origin of minerals recovered from environments on Earth and on other planets (²⁶
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12 82 and references therein).

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14
15 83 To sum up, the study by Godinho and Stack¹⁹ paved the way for a radically new description of
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17 84 barite growth kinetics, and provided the very first data in that respect. However, their study was limited
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19 85 to ambient temperature, whereas barite formation may occur over a wide range of environmental
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22 86 conditions, ranging from slightly above the freezing point in oceans to several tens to hundreds of
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24 87 degrees in geothermal reservoirs. To this end, the present study was principally aimed at extending
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26 88 this dataset to a wider range of temperatures and to eventually derive an activation energy for face-
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28 89 specific barite growth rate. We also provide rate data for an additional face that was not investigated
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31 90 in the study by Godinho and Stack¹⁹, at two different fluid saturation states. Taken together, we show
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33 91 that the activation energy is the same for all faces (within uncertainties), which is compatible with the
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35 92 assumption that all faces may have the same unique rate-limiting step. In addition, this activation
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38 93 energy is close to that determined by Zhen-Wu et al.¹² for barite dissolution, which is compatible with
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40 94 their hypothesis of micro-reversibility of barite dissolution/precipitation process.
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2. Materials and methods

2.1 Starting materials and preparation

Single crystals of barite (~50-100 mm in length / diameter) were collected in Puy de Chateix (France). The chemical composition of the crystals was analyzed following the protocol described by Bracco et al.¹⁶, revealing K, Sr and Al as the main impurities (0.14%, 0.10%, and 0.05% mol/mol Ba, respectively). The crystals were cleaved along (210) and (001) and cut along the (101) plane. The crystallographic orientations were first verified using Electron Backscatter Diffraction (EBSD) on a Tescan Vega 2 scanning electron microscope (SEM) and polished through a multi-step abrasive sequence with a final polishing step in a colloidal silica suspension. The oriented samples were divided into small pieces with a surface area (SA) between $\sim 0.25 \text{ cm}^2$ and 0.50 cm^2 . The faces not under study were protected with room-temperature vulcanizing (RTV) glue. For the faces under investigation, only a portion of their surface was protected with $\sim 1 \text{ mm}$ -diameter RTV glue spots to provide a reference surface (see similar protocol in ^{19, 28}). The initial roughness of each surface was measured at different scales with a ZYGO® NewView 7300 vertical scanning interferometer (VSI). For each sample, the initial average arithmetic roughness (Ra), defined as the arithmetic average of the absolute values of the roughness measured by the VSI, ranged between 10 and 20 nm. These initial roughness parameters were measured on $270 \times 360 \mu\text{m}^2$ VSI images.

2.2 Growth experiments and analytical procedures

Barite samples were placed over polytetrafluoroethylene (PTFE) tripods and introduced into 120 mL perfluoroalkoxy alkanes (PFA) Savillex® reactors. The reactors were filled with a volume (V) of 100 mL of solution and continuously stirred with magnetic bars throughout the experiments, incubated at 10, 25, 40, and 70 °C for durations ranging from 10 minutes to 15 hours. Three selected crystallographic planes were studied: (210), (001), and (101).

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3 118 All solutions were prepared immediately prior to each experiment by diluting 0.01 M BaCl₂ and
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6 119 Na₂SO₄ stock solutions prepared from sodium sulfate and barium chloride powders (Acros Brand,
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8 120 purity ≥ 99%) to the desired concentrations. The in situ pH and ion speciation and activity were
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10 121 calculated using the CHESS software²⁹ implemented with the Debye–Hückel equation and Chess.tdb
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12 122 database (Lawrence Livermore National Laboratories EQ3/6 database, 8th version), and the saturation
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15 123 index (*SI*) with respect to barite was calculated from Eq. (1):

$$SI = \log \frac{a_{Ba}a_{SO_4}}{K_{sp}} \quad (1)$$

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21 124 where a_{Ba} and a_{SO_4} refer to the activities of barium and sulfate ions in solution, respectively, and K_{sp}
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23 125 refers to the solubility product of barite. The CHESS software calculates the solubility product at the
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26 126 run temperature based on the interpolation between the K_{sp} values listed in Chess.tdb database, i.e., 10⁻
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28 127 10.49, 10^{-9.97}, 10^{-9.61} and 10^{-9.51} at 0 °C, 25 °C, 60 °C and 100 °C, respectively.
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30 128 The following input solutions containing 1:1 ratio of SO₄²⁻ and Ba²⁺ activities were studied: (1)
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32 129 $SI = 1.1$ and (2) $SI = 2.1$. Those saturation indices were chosen in order to compare the results of this
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35 130 study with the growth rates obtained by Godinho and Stack¹⁹ at room temperature.
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37 131 Experiment durations ranged between 10 minutes and 15 hours, depending on the experimental
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39 132 conditions (*SI* and temperature). In order to calculate the evolution of the saturation index, solution
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42 133 sampling was carried out two to four times in each experiment. The aqueous samples were diluted 10
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44 134 times and filtered using a 0.45-μm filter before analysis. Inductively coupled plasma atomic emission
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46 135 spectroscopy (ICP-AES - Thermo ICAP 6000) was used for the analyses of Ba²⁺ and Na⁺, and ion
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49 136 chromatography (ICS-5000 Thermofisher Dionex) was used for the analyses of SO₄²⁻ and Cl⁻. Because
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51 137 foreign cations such as Sr can impact barite growth rates¹⁷, all input solutions were analyzed for major
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53 138 (Na, K, Ca, Mg, Fe, Si, Al) and minor (Sr, Ni, Mn, Ti, Co, Cr, Zn, Cu) cations prior to the immersion
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55 139 of the barite samples. The concentration of all of these elements was systematically below the detection
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58 140 limit (≤ 5 ppb), except for Cu, for which concentrations up to 20 ppb (8×10⁻⁸ M) were occasionally
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6 142 solutions was 5.3 ± 0.1 and remained constant throughout the experiments.

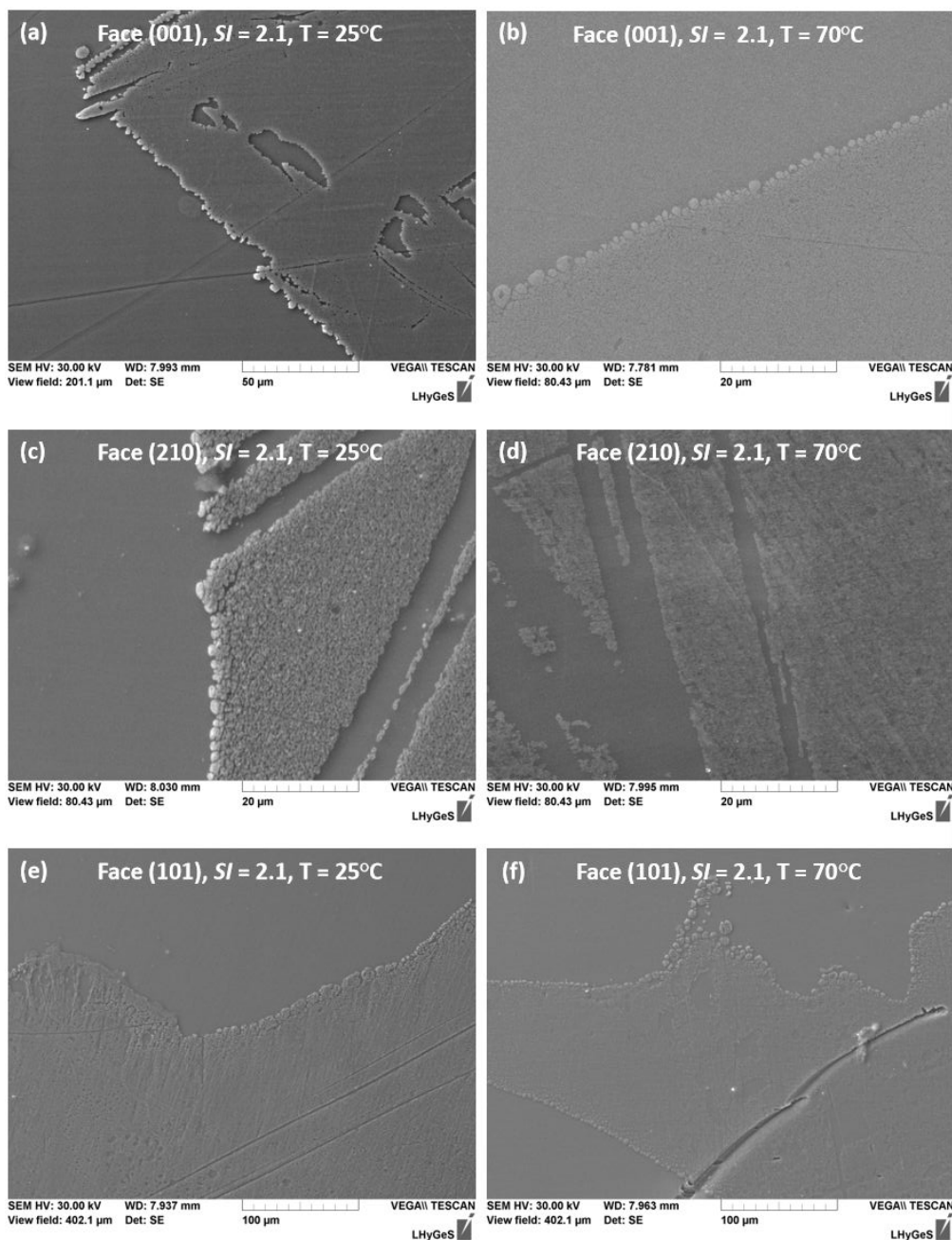
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8 143 At the end of each experiment, the sample was removed from the solution, rinsed with ultrapure
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10 144 water and sonicated for 10 min in ethanol to remove any possible secondary barite crystals nucleated
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12 145 from the solution and deposited on the surface, as classically done in literature to remove fine particles
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15 146 adhering on the surface of minerals³⁰. The RTV mask was then carefully removed and the sample
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17 147 topography was measured with VSI in stitching mode (magnification: $\times 5$) to evaluate average changes
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19 148 in height between the unreacted reference surface and the reacted mineral surface. For each surface,
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22 149 10 profiles across the interface were used to calculate the average thickness of the grown layer, which
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24 150 was used to calculate the face-specific growth rate. The uncertainties associated with these average
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26 151 values were estimated from the standard deviations calculated from the various profiles. For each
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29 152 oriented sample, growth rates were calculated according to Eq. (2):

$$r^{(hkl)} = \frac{\Delta h}{\Delta t} \quad (2)$$

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34 153 where $r^{(hkl)}$ ($\text{nm}\cdot\text{h}^{-1}$) is the growth rate of the (hkl) face, Δh is the average surface step resulting from
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37 154 barite growth (nm), and Δt is the duration of the experiment (s).

3. Results and discussion

3.1 Face-specific growth patterns



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4 = 25 °C; b) Face (001), $SI = 2.1$, $T = 70$ °C; c) Face (210), $SI = 2.1$, $T = 25$ °C; d) Face (210), $SI = 2.1$, $T = 70$
5 162 °C; e) Face (101), $SI = 2.1$, $T = 25$ °C; f) Face (101), $SI = 2.1$, $T = 70$ °C.
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11 165 Both SEM and VSI investigations confirmed that, over the course of the experiments, barite
12 growth did not result from homogeneous nucleation in the solution, as revealed by the absence
13 166 of euhedral secondary barite crystals on the surface of each investigated face, or the subsistence
14 167 of polishing scratches in the grown layer of barite. The results show that the temperature
15 168 variation seems to have no effect on the growth features of the faces under study. Pina et al.³¹
16 169 described growth patterns which exhibit features specific to each investigated face (001) and
17 170 (210), consistent with the anisotropy of the barite structure and the Periodic Bond Chain (PBC)
18 171 theory. In the present study, the (001) and the (101) faces exhibit a growth morphology that
19 172 resembles the circular sector shape described during the early stage of barite growth monitored
20 173 using atomic force microscopy (AFM) by Sanchez-Pastor et al.³². Conversely, the two-
21 174 dimensional islands formed in the experiments conducted at 25 and 70 °C and a saturation index
22 175 of 2.1 could not be easily related to the needle-shaped morphology described by Pina et al.³¹
23 176 and Sanchez-Pastor et al.³² for the face (210). Possible explanations include the difference of
24 177 resolution between AFM and SEM, as well as the difference in terms of reaction progress, since
25 178 the study by Sanchez-Pastor et al.³² focused on the early stage of barite growth, whereas the
26 179 present study reports on results obtained at a later stage of the reaction process. Therefore, part
27 180 of the original islands documented in e.g. Sanchez-Pastor et al.³² might have been overgrown,
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53 183 **3.2 Face-specific growth rate of barite as a function of solution saturation state**

54 184 3.2.1 Time-resolved fluid analyses

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3 185 The evolution of the fluid composition during all experiments is provided in Table 1.
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5 186 The Ba²⁺ to SO₄²⁻ mole ratios in the aqueous solutions are consistent with the stoichiometric
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7 187 precipitation of barite. From the Ba²⁺, Na⁺, SO₄²⁻, and Cl⁻ concentrations, the saturation index
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9 188 with respect to barite was determined at up to four different time steps in each experiment using
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11 189 the CHESS code.

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14 190 The extent to which the evolution of the fluid composition resulted from barite growth
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16 191 of the oriented barite surface sample can be estimated based on the thickness of the grown layer
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18 192 measured by VSI following:

$$\Delta[i] = \frac{\Delta h \cdot SA \cdot \rho_{BaSO_4}}{M_{BaSO_4} \cdot V} \quad (3)$$

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25 193 where $\Delta[i]$ is the variation of Ba²⁺ (or SO₄²⁻) concentration resulting from barite growth, ρ_{BaSO_4}
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27 194 and M_{BaSO_4} are respectively the density (4.48 g.cm⁻³) and molar mass (233 g.mol⁻¹) of barite.
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29 195 Knowing that the surface area of each investigated sample never exceeded 0.5 cm², and using
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31 196 150 nm as an upper bound for the thickness of the grown layer (consistent with our VSI
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33 197 measurements), the decrease in sulfate or barite concentration should never exceed 1.5×10⁻⁶ M.
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35 198 This value is about two orders of magnitude greater than the actual decrease measured in some
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37 199 of our experiments (see Table 1), suggesting that in addition to barite growth, homogeneous
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39 200 barite nucleation in the solution or heterogeneous nucleation on the walls of the reactor should
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41 201 have occurred as well. This result is consistent with the observations reported by Jindra et al.³³,
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43 202 who showed that solutions supersaturated in barite with $SI \geq 1$ were unstable with respect to
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45 203 barite nucleation. This limitation illustrates that classical kinetics experiments based on the sole
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47 204 evolution of the fluid composition would be poorly informative to deconvolve the nucleation
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49 205 from the growth steps under such conditions, and further justifies the use of surface sensitive-
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51 206 techniques to probe growth kinetics, such as AFM^{15-17, 33} or VSI¹⁹.

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53 207 The rapid nucleation of barite complicated the conduction of experiments at a fixed
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55 208 value of SI , and the duration of the experiment had consequently to be adjusted to (i) yield an

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3 209 appreciable thickness of the grown layer of barite while (ii) limiting the intrinsic evolution of
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5 210 the solution composition resulting from barite nucleation. Importantly, for the experiments
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8 211 conducted under the less reactive conditions (i.e., $T = 10\text{ }^{\circ}\text{C}$, $SI = 1.1$), in spite of several
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10 212 attempts, it has not been possible to run experiments for which the evolution of SI was modest
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12 213 while measuring an appreciable thickness of the grown layer at the same time. In other words,
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14 214 for these experiments, essentially barite nucleation occurred over short durations (with no
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16 215 observable grown layer), while over long durations (up to 15 hours), barite growth was
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18 216 observed, but with large variation of the fluid saturation index (between $\pm 18\%$ and $\pm 34\%$),
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20 217 complicating the definition of the SI at which growth actually occurred. Therefore, the results
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22 218 of experiments conducted at $SI = 1.1$ and $T = 10\text{ }^{\circ}\text{C}$ will have to be considered with caution (see
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24 219 Section 3.2.2 for a confirmation of this statement). In the end, the variation of SI was $\pm 6\%$ for
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26 220 the 12 experiments run at an initial saturation index of 2.1, and $\pm 5\%$ for the 9 experiments run
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28 221 at $SI = 1.1$ (excluding the 3 experiments run at $10\text{ }^{\circ}\text{C}$).
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37 223 Table 1. Evolution of fluid composition (concentration of Ba^{2+} , SO_4^{2-} , Cl^- , and Na^+ in mol/L) measured
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39 224 by ICP-AES and ion chromatography for the growth experiments realized on the (001), (101), and (210) surfaces
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41 225 at 10, 25, 40, and $70\text{ }^{\circ}\text{C}$. The fluid composition was measured at up to four time steps in each experiment. The
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43 226 saturation index of the experiments was determined from the fluid composition using the CHESS software.
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		SI=2.1											SI=1.1													
face		001				210				101			001				210				101					
t		0	60	120	180	0	40	80	120	0	40	80	120	0	900			0	900			0	900			
10°C	Ba ²⁺	8.41 *10 ⁻⁵	7.14 *10 ⁻⁵	6.69 *10 ⁻⁵	4.56 *10 ⁻⁵	9.35 *10 ⁻⁵	7.72 *10 ⁻⁵	6.61 *10 ⁻⁵	5.61 *10 ⁻⁵	5.01 *10 ⁻⁵	7.68 *10 ⁻⁵	6.42 *10 ⁻⁵	6.51 *10 ⁻⁵	5.78 *10 ⁻⁵	4.46 *10 ⁻⁵	2.44 *10 ⁻⁵			3.51 *10 ⁻⁵	2.31 *10 ⁻⁵			3.94 *10 ⁻⁵	2.56 *10 ⁻⁵		
	SO ₄ ²⁻	1.13 *10 ⁻⁴	1.04 *10 ⁻⁴	9.60 *10 ⁻⁵	9.35 *10 ⁻⁵	1.32 *10 ⁻⁴	1.14 *10 ⁻⁴	1.01 *10 ⁻⁴	9.57 *10 ⁻⁵	1.16 *10 ⁻⁴	9.12 *10 ⁻⁵	9.80 *10 ⁻⁵	8.63 *10 ⁻⁵	5.16 *10 ⁻⁵	3.43 *10 ⁻⁵				4.66 *10 ⁻⁵	3.20 *10 ⁻⁵			4.64 *10 ⁻⁵	3.35 *10 ⁻⁵		
	Na ⁺	1.69 *10 ⁻⁴	1.49 *10 ⁻⁴	1.56 *10 ⁻⁴	1.53 *10 ⁻⁴	1.71 *10 ⁻⁴	1.73 *10 ⁻⁴	1.72 *10 ⁻⁴	1.72 *10 ⁻⁴	1.54 *10 ⁻⁴	1.63 *10 ⁻⁴	1.49 *10 ⁻⁴	1.54 *10 ⁻⁴	6.95 *10 ⁻⁵	6.95 *10 ⁻⁵				6.12 *10 ⁻⁵	5.97 *10 ⁻⁵			6.60 *10 ⁻⁵	6.68 *10 ⁻⁵		
	Cl ⁻	1.99 *10 ⁻⁴	1.98 *10 ⁻⁴	2.00 *10 ⁻⁴	2.02 *10 ⁻⁴	2.17 *10 ⁻⁴	2.17 *10 ⁻⁴	2.12 *10 ⁻⁴	2.23 *10 ⁻⁴	1.97 *10 ⁻⁴	2.03 *10 ⁻⁴	1.95 *10 ⁻⁴	2.03 *10 ⁻⁴	1.14 *10 ⁻⁴	1.12 *10 ⁻⁴				9.57 *10 ⁻⁵	9.89 *10 ⁻⁵			1.08 *10 ⁻⁴	1.06 *10 ⁻⁴		
	SI	2.12	2.04	1.96	1.86	2.15	2.02	1.81	1.83	2.08	1.90	2.00	1.85	1.54	1.01				1.39	1.06			1.44	1.12		
	t	0	40	80	120	0	20	40	60	0	30	60	90	0	140	280	420	0	60	180	300	0	140	280	420	
25°C	Ba ²⁺	8.74 *10 ⁻⁵	9.45 *10 ⁻⁵	9.21 *10 ⁻⁵	9.35 *10 ⁻⁵	1.16 *10 ⁻⁴	1.17 *10 ⁻⁴	1.08 *10 ⁻⁴	1.06 *10 ⁻⁴	9.50 *10 ⁻⁵	1.01 *10 ⁻⁴	7.62 *10 ⁻⁵	7.31 *10 ⁻⁵	3.42 *10 ⁻⁵	3.41 *10 ⁻⁵	3.19 *10 ⁻⁵	3.20 *10 ⁻⁵	3.28 *10 ⁻⁵	3.37 *10 ⁻⁵	3.30 *10 ⁻⁵	3.27 *10 ⁻⁵	4.53 *10 ⁻⁵	3.56 *10 ⁻⁵	4.32 *10 ⁻⁵	4.15 *10 ⁻⁵	
	SO ₄ ²⁻	1.25 *10 ⁻⁴	1.15 *10 ⁻⁴	1.05 *10 ⁻⁴	9.81 *10 ⁻⁵	1.65 *10 ⁻⁴	1.57 *10 ⁻⁴	1.52 *10 ⁻⁴	1.49 *10 ⁻⁴	1.79 *10 ⁻⁴	1.58 *10 ⁻⁴	1.37 *10 ⁻⁴	1.25 *10 ⁻⁴	4.92 *10 ⁻⁵	4.55 *10 ⁻⁵	4.50 *10 ⁻⁵	4.49 *10 ⁻⁵	3.54 *10 ⁻⁵	3.54 *10 ⁻⁵	3.63 *10 ⁻⁵	3.56 *10 ⁻⁵	5.72 *10 ⁻⁵	5.71 *10 ⁻⁵	5.70 *10 ⁻⁵	5.68 *10 ⁻⁵	
	Na ⁺	1.95 *10 ⁻⁴	1.79 *10 ⁻⁴	1.76 *10 ⁻⁴	1.90 *10 ⁻⁴	1.79 *10 ⁻⁴	1.91 *10 ⁻⁴	1.83 *10 ⁻⁴	1.89 *10 ⁻⁴	1.99 *10 ⁻⁴	1.99 *10 ⁻⁴	2.21 *10 ⁻⁴	1.89 *10 ⁻⁴	7.42 *10 ⁻⁵	7.52 *10 ⁻⁵	7.39 *10 ⁻⁵	7.39 *10 ⁻⁵	6.94 *10 ⁻⁵	7.11 *10 ⁻⁵	7.22 *10 ⁻⁵	7.09 *10 ⁻⁵	8.55 *10 ⁻⁵	8.61 *10 ⁻⁵	8.55 *10 ⁻⁵	8.43 *10 ⁻⁵	
	Cl ⁻	2.50 *10 ⁻⁴	2.52 *10 ⁻⁴	2.54 *10 ⁻⁴	2.54 *10 ⁻⁴	3.12 *10 ⁻⁴	2.94 *10 ⁻⁴	2.95 *10 ⁻⁴	3.01 *10 ⁻⁴	3.29 *10 ⁻⁴	3.09 *10 ⁻⁴	3.03 *10 ⁻⁴	3.01 *10 ⁻⁴	9.18 *10 ⁻⁵	9.22 *10 ⁻⁵	9.01 *10 ⁻⁵	8.95 *10 ⁻⁵	5.55 *10 ⁻⁵	5.86 *10 ⁻⁵	5.36 *10 ⁻⁵	5.33 *10 ⁻⁵	1.04 *10 ⁻⁴	1.03 *10 ⁻⁴	1.04 *10 ⁻⁴	1.04 *10 ⁻⁴	
	SI	1.90	1.9	1.88	1.83	2.13	2.11	2.06	2.05	2.07	2.05	1.89	1.82	1.13	1.1	1.06	1.06	0.98	0.99	0.99	0.98	1.32	1.22	1.3	1.22	
	t	0	30	60	90	0	20	40	60	0	15	30	60	0	130	260	500	0	80	160	200	0	80	160	200	
40°C	Ba ²⁺	1.25 *10 ⁻⁴	1.26 *10 ⁻⁴	9.70 *10 ⁻⁵	8.57 *10 ⁻⁵	1.32 *10 ⁻⁴	1.21 *10 ⁻⁴	9.08 *10 ⁻⁵	9.73 *10 ⁻⁵	1.67 *10 ⁻⁴	7.41 *10 ⁻⁵	8.13 *10 ⁻⁵		4.27 *10 ⁻⁵	4.24 *10 ⁻⁵	4.38 *10 ⁻⁵	4.35 *10 ⁻⁵	4.50 *10 ⁻⁵	4.48 *10 ⁻⁵	3.88 *10 ⁻⁵	4.44 *10 ⁻⁵	4.22 *10 ⁻⁵	3.93 *10 ⁻⁵	4.05 *10 ⁻⁵	4.12 *10 ⁻⁵	
	SO ₄ ²⁻	1.93 *10 ⁻⁴	1.76 *10 ⁻⁴	1.53 *10 ⁻⁴	1.31 *10 ⁻⁴	2.02 *10 ⁻⁴	1.86 *10 ⁻⁴	1.74 *10 ⁻⁴	1.61 *10 ⁻⁴	2.09 *10 ⁻⁴	1.21 *10 ⁻⁴	1.14 *10 ⁻⁴		5.63 *10 ⁻⁵	5.44 *10 ⁻⁵	5.33 *10 ⁻⁵	5.36 *10 ⁻⁵	4.74 *10 ⁻⁵	4.28 *10 ⁻⁵	4.40 *10 ⁻⁵	4.31 *10 ⁻⁵	4.58 *10 ⁻⁵	4.99 *10 ⁻⁵	4.89 *10 ⁻⁵	5.07 *10 ⁻⁵	
	Na ⁺	2.17 *10 ⁻⁴	2.14 *10 ⁻⁴	2.17 *10 ⁻⁴	2.07 *10 ⁻⁴	2.34 *10 ⁻⁴	2.11 *10 ⁻⁴	2.36 *10 ⁻⁴	2.23 *10 ⁻⁴	2.78 *10 ⁻⁴	2.76 *10 ⁻⁴	2.72 *10 ⁻⁴		8.52 *10 ⁻⁵	8.42 *10 ⁻⁵	8.38 *10 ⁻⁵	8.38 *10 ⁻⁵	1.09 *10 ⁻⁴	8.91 *10 ⁻⁵	9.10 *10 ⁻⁵	9.01 *10 ⁻⁵	8.64 *10 ⁻⁵	9.11 *10 ⁻⁵	9.52 *10 ⁻⁵	9.36 *10 ⁻⁵	
	Cl ⁻	3.61 *10 ⁻⁴	3.60 *10 ⁻⁴	3.63 *10 ⁻⁴	3.92 *10 ⁻⁴	3.55 *10 ⁻⁴	3.47 *10 ⁻⁴	3.56 *10 ⁻⁴	3.55 *10 ⁻⁴	4.37 *10 ⁻⁴	4.35 *10 ⁻⁴	4.34 *10 ⁻⁴		1.07 *10 ⁻⁴	1.05 *10 ⁻⁴	1.04 *10 ⁻⁴	1.04 *10 ⁻⁴	7.36 *10 ⁻⁵	7.43 *10 ⁻⁵	7.12 *10 ⁻⁵	7.49 *10 ⁻⁵	8.24 *10 ⁻⁵	8.96 *10 ⁻⁵	7.40 *10 ⁻⁵	7.31 *10 ⁻⁵	
	SI	2.02	1.99	1.87	1.7	2.06	1.99	1.84	1.84	2.17	1.6	1.62		1.08	1.07	1.07	1.07	1.04	1.00	0.95	0.99	1.00	1.00	1.01	1.03	
	t	0	5	10		0	5	10		0	5	10		0	60	120		0	60	120	180	0	40	80	120	
70°C	Ba ²⁺	1.91 *10 ⁻⁴	1.86 *10 ⁻⁴	1.38 *10 ⁻⁴		1.86 *10 ⁻⁴	1.63 *10 ⁻⁴	1.37 *10 ⁻⁴		1.95 *10 ⁻⁴	1.56 *10 ⁻⁴	1.25 *10 ⁻⁴		6.32 *10 ⁻⁵	4.88 *10 ⁻⁵	3.71 *10 ⁻⁵		6.04 *10 ⁻⁵	5.68 *10 ⁻⁵	5.09 *10 ⁻⁵	4.64 *10 ⁻⁵	6.32 *10 ⁻⁵	3.95 *10 ⁻⁵	5.74 *10 ⁻⁵	5.81 *10 ⁻⁵	
	SO ₄ ²⁻	2.00 *10 ⁻⁴	1.88 *10 ⁻⁴	1.47 *10 ⁻⁴		2.21 *10 ⁻⁴	1.95 *10 ⁻⁴	1.78 *10 ⁻⁴		2.73 *10 ⁻⁴	2.08 *10 ⁻⁴	1.64 *10 ⁻⁴		9.83 *10 ⁻⁵	8.00 *10 ⁻⁵	7.67 *10 ⁻⁵		9.26 *10 ⁻⁵	8.65 *10 ⁻⁵	8.24 *10 ⁻⁵	7.39 *10 ⁻⁵	6.74 *10 ⁻⁵	6.78 *10 ⁻⁵	6.74 *10 ⁻⁵	6.53 *10 ⁻⁵	
	Na ⁺	3.97 *10 ⁻⁴	4.00 *10 ⁻⁴	4.02 *10 ⁻⁴		4.07 *10 ⁻⁴	4.10 *10 ⁻⁴	5.1 *10 ⁻⁴		4.07 *10 ⁻⁴	3.73 *10 ⁻⁴	3.73 *10 ⁻⁴		1.84 *10 ⁻⁴	1.71 *10 ⁻⁴	1.83 *10 ⁻⁴		9.84 *10 ⁻⁵	1.07 *10 ⁻⁴	1.09 *10 ⁻⁴	9.90 *10 ⁻⁵	1.33 *10 ⁻⁴	1.38 *10 ⁻⁴	1.34 *10 ⁻⁴	1.34 *10 ⁻⁴	
	Cl ⁻	4.20 *10 ⁻⁴	4.06 *10 ⁻⁴	4.10 *10 ⁻⁴		3.96 *10 ⁻⁴	3.95 *10 ⁻⁴	4.95 *10 ⁻⁴		5.81 *10 ⁻⁴	5.80 *10 ⁻⁴	5.97 *10 ⁻⁴		1.88 *10 ⁻⁴	1.95 *10 ⁻⁴	1.98 *10 ⁻⁴		1.36 *10 ⁻⁴	1.37 *10 ⁻⁴	1.41 *10 ⁻⁴	1.34 *10 ⁻⁴	1.19 *10 ⁻⁴	1.16 *10 ⁻⁴	1.16 *10 ⁻⁴	1.17 *10 ⁻⁴	
	SI	2.00	1.97	1.74		2.03	1.93	1.81		2.1		1.7		1.25	1.14	0.92		1.21	1.16	1.1	1.0	1.11	0.91	1.07	1.06	

3.2.2 Vertical Scanning Interferometry data:

Table 2. Face-specific growth rates (nm.h⁻¹) calculated from the thickness of the grown layer measured by VSI on the (001), (101), and (210) surfaces of crystals grown in two different solutions: (1) *SI* = 1.1 and (2) *SI* = 2.1. Experiments were performed at 10, 25, 40, and 70 °C. The numbers between parentheses indicate the uncertainties of the growth rates, estimated from the variability of the thickness of the grown layer averaged on 10 measurements (see Section 2.2).

(1) <i>SI</i> = 1.1				
Face	(0 0 1)			
T (°C)	10	25	40	70
r (nm/h)	0.60 (0.07)	5.1 (0.5)	19.9 (1.3)	38.7 (4.2)
Face	(2 1 0)			
T (°C)	10	25	40	70
r (nm/h)	1.4 (0.7)	4.4 (0.7)	10.7 (1.3)	46.9 (1.2)
Face	(1 0 1)			
T (°C)	10	25	40	70
r (nm/h)	2.3 (0.3)	6.8 (2.8)	8.9 (0.8)	37.6 (4.9)
(2) <i>SI</i> = 2.1				
Face	(0 0 1)			
T (°C)	10	25	40	70
r (nm/h)	25.0 (6.3)	46.1 (14.9)	96.6 (8.9)	318 (38)
Face	(2 1 0)			
T (°C)	10	25	40	70
r (nm/h)	39.0 (4.4)	86.2 (4.7)	125 (18)	296 (27)
Face	(1 0 1)			
T (°C)	10	25	40	70
r (nm/h)	25.5 (4.2)	82.7 (9.1)	131 (15)	285 (71)

The growth rates perpendicular to the three studied surfaces were calculated from the measured thickness of the layer grown whilst in solution. The results highlight an effect of the saturation index on growth rate. For example, in the experiments with a starting saturation index of 2.1, the growth rates are about 5 to 40 times faster (depending on the face and temperature) than in the solution with *SI* = 1.1 (Table 1).

Surface-controlled precipitation rates are commonly fitted to the following rate law (e.g. ³⁴ and references therein):

$$r = k.(10^{SI} - 1)^n \quad (4)$$

where *k* is the growth rate constant and *n* is a fitting coefficient generally referred to as the reaction order. Although Eq. (4) essentially remains empirical, the value of the reaction order is usually attributed to the rate-controlling reaction mechanism (a reaction order of 1 is typically attributed to a

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245 simple surface adsorption mechanism and a reaction order of 2 to spiral growth; see ³⁵). For each face,
246 the value of the reaction order at each temperature (n_T) can therefore be estimated following:

$$n_T = \frac{\log r_2^T - \log r_1^T}{\log(10^{SI_2^T} - 1) - \log(10^{SI_1^T} - 1)} \quad (5)$$

247 where r_i^T refers to the growth rate measured at the corresponding saturation index SI_i^T (i.e., ~2.1 or
248 ~1.1), for a given temperature T . Eq. (5) was used to estimate the value of n for each face and all
249 investigated temperatures (Table 3), leading to average values of $n = 1.39 \pm 0.76$, 1.26 ± 0.42 , and 1.12
250 ± 0.19 for the (001), (210), and (101) faces, respectively. Of note, the large standard deviations
251 associated with the value of n for the (001) and (210) faces are essentially due to the value of n derived
252 for these faces at 10 °C ($n = 2.50$ and 1.88 , respectively). The large uncertainties associated with the
253 estimation of slow growth rates at low temperature and saturation index may partially contribute to
254 this observation, as emphasized above (Section 3.2.1). In particular, the large variation of SI over the
255 duration of these experiments, which result from the fact that barite precipitation occurred almost
256 exclusively through homogeneous nucleation, considerably complicated the definition of the value of
257 SI at which barite growth occurred. Therefore, the uncertainties associated with these experiments and
258 the switch in barite precipitation mechanism at low temperature justifies the need to remove the rate
259 data collected at 10 °C and $SI = 1.1$ for further processing of the dataset . If these rates are discarded
260 from the dataset, the average values then become $n = 1.02 \pm 0.19$; 1.05 ± 0.07 and 1.11 ± 0.13 for the
261 (001), (210) and (101) faces, respectively. Therefore, with the noticeable exception of rate data
262 obtained at 10 °C, our results show that a simple linear relation between r and $(10^{SI} - 1)$ can account
263 for our observations for all faces, irrespective of the temperature (see Supporting Information for a
264 plot displaying the general agreement over the whole dataset). Therefore, this study extends the similar
265 conclusion previously reached by Zhen-Wu et al. ¹² from powder experiments to a broader range of
266 temperatures and saturation indices, while suggesting that the reaction order (n) does not depend on
267 the investigated face, at least for temperatures ranging from 25 °C to 70 °C. This result is also

consistent with the second order reaction with respect to Ba concentration reported by Christy and Putnis¹⁸, since a first order reaction with respect to barite saturation state is equivalent to a second order reaction with respect to either aqueous barium or aqueous sulfate concentration, as recalled by Zhen-Wu et al.¹².

Table 3. Estimation of the reaction order (n) of barite growth kinetics for all investigated faces and temperatures following Eq. (5). Note that the values in italic were not considered for the calculation of the mean value of n for each face. See text for details.

	10 °C	25 °C	40 °C	70 °C
(0 0 1)	<i>2.50</i>	1.16	0.80	1.10
(2 1 0)	<i>1.88</i>	1.11	1.06	0.97
(1 0 1)	<i>1.14</i>	1.37	1.04	0.92

3.3 Face-specific growth rate of barite as a function of temperature

In experiments conducted with an input solution with $SI = 1.1$, growth rates range from 0.60 nm.h⁻¹ to approximately 47 nm.h⁻¹, with the slowest rates at 10°C and the fastest rates at 70 °C (Table 1). For each face, the growth rate increases with temperature but generally, the (001) and (101) faces are the slowest growing faces (Table 1), in accordance with the results obtained by Godinho and Stack¹⁹. For face (001) reacted in a solution with $SI = 1.1$, an increase in temperature by 60 °C increases the rate by almost a factor of 60 (Table 1). At a starting saturation index of 2.1, the growth rates are about one order of magnitude greater at 70 °C than at 10 °C for all faces.

The dependence of the mineral growth rate constant on temperature is usually described following the Arrhenius equation:

$$k = A.\exp \left(-E_a/RT \right) \quad (6)$$

where A represents the Arrhenius pre-exponential factor, E_a denotes the activation energy, R is the gas constant, and T refers to the absolute temperature. By combining Eq. (6) with Eq. (4) and assuming that $n = 1$ (see above), we can determine the value of A and E_a experimentally following the relation:

$$\ln (r/(10^{SI} - 1)) = \ln A - E_a/RT \quad (7)$$

This equation was applied to the data generated in this study using the Arrhenius plots shown in Fig. 3. The errors reported on the data points account both for the uncertainties on the growth rates (resulting from the variability of the thickness of the grown layer) and the variation of SI over the course of the experiment (resulting from the precipitation of barite). Excluding the rate data obtained at 10 °C and $SI = 1.1$ (see above), the activation energy was found to be virtually independent of the considered face, with values of 36.4 ± 4.0 , 31.8 ± 3.3 , and 35.8 ± 3.7 kJ.mol⁻¹ for the growth on (001), (210), and (101) faces, respectively. The uncertainties on the activation energies were determined based on the errors associated with the data depicted in Fig. 3.

The activation energy determined for the growth on the (001) face is in excellent agreement with that determined by Higgins et al.³⁶ (37.3 ± 4.6 kJ.mol⁻¹). More broadly, these values agree, within uncertainties, with those reported by Christy and Putnis¹⁸ (22.0 ± 14.3 kJ.mol⁻¹) for the growth of barite monitored on powder experiments over the temperature range 44-85 °C. This result further indicates that if a barite crystal form is developed based on the three faces investigated in the present study, the morphology of barite crystals will be negligibly affected by temperature variations, such that the morphology of barite crystals cannot be used as a criterion to determine the temperature at which they crystallized.

Regarding the pre-exponential factor, Fig. 3 reveals that it only slightly varies with the considered orientation, from $\exp(12.4)$ nm.h⁻¹ for the (210) face to $\exp(14.1)$ nm.h⁻¹ for the (001) face. Following the reasonable assumption that the activation energy does not depend on the crystallographic orientation for the three investigated faces, this translates into a modest anisotropy of barite growth rate of a ~5-fold factor between the fastest and slowest growing faces, which is in reasonable agreement with our experimental data.

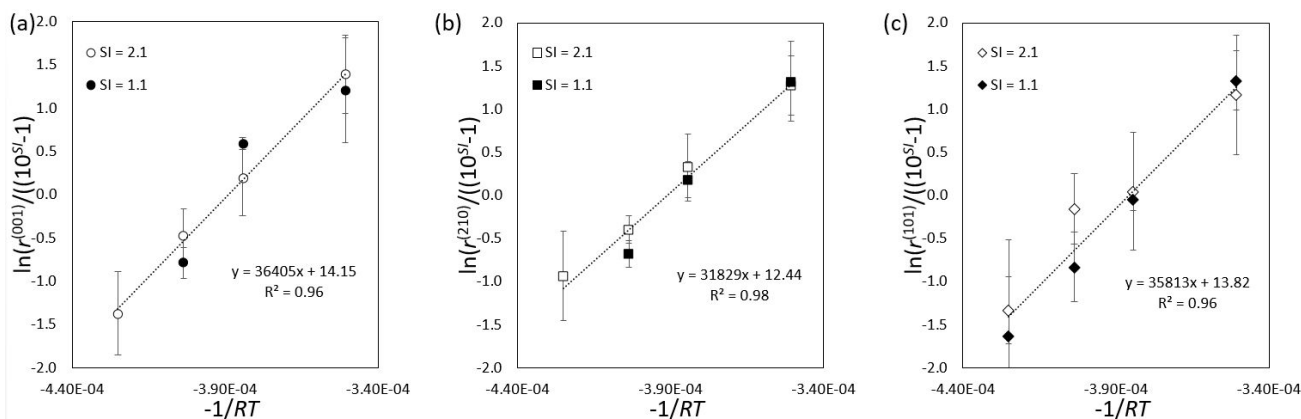


Figure 3. Determination of the face-specific activation energy ($E_a^{(hkl)}$) and pre-exponential factor ($A^{(hkl)}$) of barite growth rate over the temperature range 10-70 °C for the (a) (001), (b) (210), and (c) (101) faces. Of note, the rate data obtained at 10 °C and $SI = 1.1$ for the faces (001) and (210) were dismissed from the regressions (see section 3.3 for details).

The agreement between the multiple regressions described above and the experimental data can be assessed in Fig. 4, for growth rates varying over about two orders of magnitude. In Fig. 4a, the measured rates were compared with the corresponding values calculated following the overall face-specific growth rate law given by:

$$r^{(hkl)} = A^{(hkl)} \cdot \exp\left(-E_a^{(hkl)}/RT\right) \cdot (10^{SI} - 1) \quad (8a)$$

for which the values of $A^{(hkl)}$ and $E_a^{(hkl)}$ were derived from the plots depicted in Fig. 3. Of note, the agreement between calculated rates and measured rate data is negligibly affected if one considers an overall isotropic growth rate law for all faces following:

$$r^{(hkl)} = A \cdot \exp\left(-E_a/RT\right) \cdot (10^{SI} - 1) \quad (8b)$$

with average values of $A = \exp(13.59) \text{ nm}\cdot\text{h}^{-1}$ and $E_a = 35.0 \pm 2.5 \text{ kJ}\cdot\text{mol}^{-1}$ (Fig. 4b). In addition, both rate laws perfectly account for the rate data reported by Godinho and Stack¹⁹ at $T = 22.2 \text{ °C}$ and $SI = 2.1$ for the faces (001) and (210), while overestimating the rate values obtained at $SI = 1.1$. Possible explanations might reside in the difference in chemical composition of the crystals used to conduct the studies, since impurities such as strontium are known to decrease barite growth rates at low concentrations¹⁷.

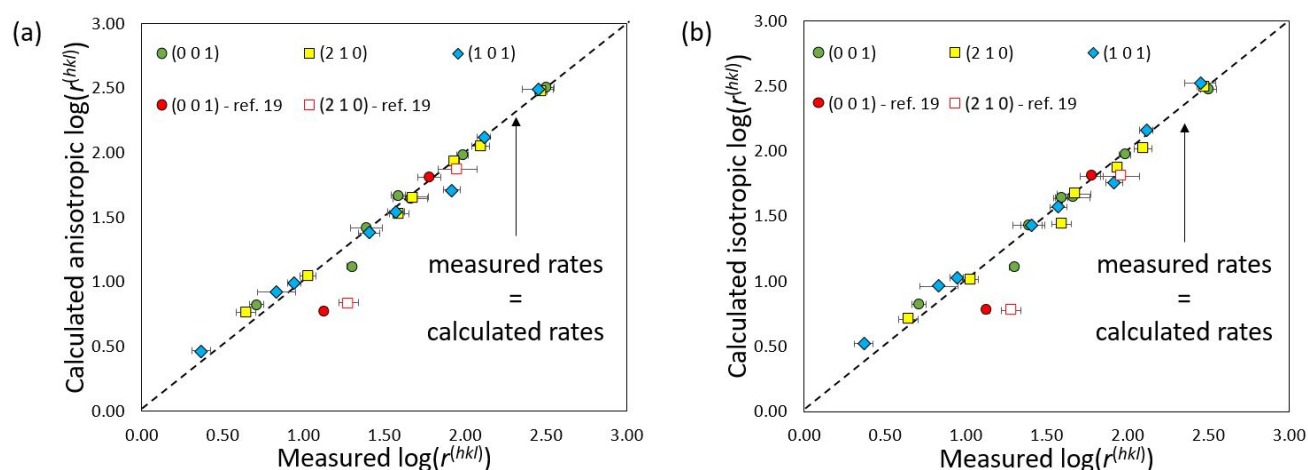


Figure 4. Comparison of barite growth rates calculated using (a) Eq. (8a) or (b) Eq. (8b) with those measured in the present study or reported in Godinho and Stack¹⁹.

3.4 Comparison with previously published data and mechanistic insights

Overall, this study largely confirms both the measurements of face-specific barite growth rates and the reaction mechanisms reported in previous studies.

Regarding the anisotropy of barite growth, Godinho and Stack¹⁹ reported that the reactivity of the (210) face was about 1.5 times greater than that of the (001) face at ambient temperature and for *SI* conditions ranging from 1.1 to 2.1. These values are in excellent agreement with our measurements under the same conditions, which show that the reactivity of the (210) face is approximately between 1.7 and 1.9 times greater than that of the (001) face. At *SI* = 2.1, the absolute values of the growth rates of the two studies overlap as well, within uncertainties.

Regarding the reaction mechanisms, several lines of evidence suggest that barite growth may observe the principle of detailed balancing and micro-reversibility. First, our rate data are consistent with an isotropic activation energy with an average value of $35.0 \pm 2.5 \text{ kJ}\cdot\text{mol}^{-1}$, suggesting that the reaction is surface-controlled. Moreover, if the rate-limiting step of barite growth were to change with surface orientation, then the activation energies of barite growth rate would be face-specific. Therefore,

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3 349 and even though the activation energies estimated in the present study remain essentially apparent, the
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6 350 unicity of the activation energy is compatible with the suggestion that the same elementary step is rate-
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8 351 limiting for all faces. In addition, this value is consistent with the isotropic value reported by Christy
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10 352 and Putnis¹⁸ ($22.0 \pm 14.3 \text{ kJ.mol}^{-1}$), itself very similar to the activation energy of barite dissolution
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12 353 reported by Zhen-Wu et al.¹² ($25 \pm 2 \text{ kJ.mol}^{-1}$). Second, the growth rate was found to be a linear
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15 354 function of the saturation state of the solution (i.e., $r \propto 10^{SI}$) for all faces at temperatures ranging
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17 355 between 25 and 70 °C (this statement remains questionable at lower temperatures). This result is
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20 356 consistent with previously published studies^{12, 18} and is typical of adsorption-controlled growth
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22 357 processes³⁵, for which the concept of micro-reversibility necessarily applies.
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27 359 **3.5 Implications for natural and anthropogenic systems**

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30 360 As highlighted above, a growing number of studies have emphasized the need to go beyond the
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32 361 classical development of isotropic rate laws to model the dissolution and/or the growth kinetics of
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35 362 minerals, partly because of their anisotropic reactivity. Notwithstanding, switching to more complex
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37 363 rate laws that are not implemented so far in classical reactive transport codes has to be justified through
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39 364 quantitative measurements of this anisotropy, as well as its dependence to fundamental rate-controlling
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42 365 parameters such as temperature or solution saturation state, in order to assess the extent to which
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44 366 isotropic models fail to reproduce quantitatively the actual mineral reactivity. In that respect, our
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46 367 results underline that (i) the anisotropic reactivity of barite growth remains modest, at least for the
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48 368 three studied faces and (ii) the growth activation energy is similar for all faces and possibly equivalent
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51 369 to the dissolution activation energy. These results have at least two practical implications for natural
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53 370 and anthropogenic systems:

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55 371 (i) Regarding the reaction mechanisms, our study suggests that the principle of detailed
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58 372 balancing may be respected over the range of T and SI investigated in the present study (see section
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60 373 3.4). Because the dissolution and precipitation rates of barite are relatively rapid, this result implies

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3 374 that at ambient temperature and close-to-equilibrium conditions, the isotope composition of barium
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6 375 may be quickly reset, consistent with the results of Curti et al.⁸. Because the isotopic and elemental
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8 376 compositions of barite are used as a proxy for past seawater chemistry (¹² and references therein), our
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10 377 study contributes to the general warning regarding the preservation of isotopic signatures in minerals
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12 378 over geological timescales to trace paleoenvironmental conditions³⁷⁻⁴⁰.

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15 379 (ii) Regarding geothermal systems, a viable geothermal resource requires a reservoir with a
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17 380 high permeability, often provided by fractures (e.g., ⁴¹), to provide the flow rates required for efficient
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19 381 energy production. The hydrothermal brines circulating through these reservoirs typically contain a
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22 382 rich assortment of dissolved elements (e.g., ⁴¹⁻⁴⁴) that can precipitate in surface installations and within
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24 383 permeability-enhancing fractures within the reservoir as a result of, for example, changes in
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26 384 temperature (e.g., ²). Barite scaling can play havoc at geothermal surface installations, requiring time-
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29 385 consuming and expensive mechanical removal (e.g., ¹⁸), and can dramatically reduce the permeability
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31 386 of fractures within the reservoir. For example, Griffiths et al.² highlighted that the Buntsandstein unit,
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33 387 a ~400 m-thick unit of sandstone that directly overlies the granitic reservoir at geothermal sites
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36 388 throughout the Upper Rhine Graben (e.g., ⁴⁵⁻⁴⁷), contains abundant barite-filled fractures (e.g., Fig. 1).
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38 389 Additionally, Griffiths et al.² estimated the time needed to seal a 2 mm-wide fracture with barite to be
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40 390 on the order of about a month. These calculations, however, were performed using data collected on
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42 391 powdered barite samples¹⁸. Our new face-specific data show that the activation energy is, within
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45 392 uncertainty, the same for all of the studied crystal faces. These new data provide additional confidence
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47 393 in the barite growth timescales provided in Griffiths et al.², which suggest that the permeability of the
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49 394 geothermal reservoir adjacent to the injection well could be, unless preventative measures are taken,
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52 395 greatly reduced over short timescales during production.

4. Summary and conclusions

Barite growth experiments combined with vertical scanning interferometry measurements of the surface topography have been conducted to study the effect of the saturation index (SI) and the temperature on the growth rates and surface features of the (001), (210), and (101) faces of barite. The results confirmed that barite growth is anisotropic with a rate that is promoted by elevated saturation indices and temperatures, while the growth morphologies observed by scanning electron microscopy did not significantly vary with temperature or SI . It was determined that barite growth rate observes a first order reaction with respect to barite saturation state for all faces at all temperatures, with the exception of rate data obtained at 10 °C. Therefore, our results show that a simple linear relation between r and $(10^{SI} - 1)$ can account for barite growth. From the dependence of the rate of barite growth with temperature, the activation energy could be defined for each face using the Arrhenius equation, yielding an average value of 35.0 ± 2.5 kJ.mol⁻¹, with no significant difference between the three faces. This result indicates that the morphology of barite crystals will be negligibly affected by temperature variations for a crystal composed of the faces under study. Therefore, the morphology of barite crystals cannot be used as a criterion to determine the temperature at which they crystallized. These data are also compatible with a reaction rate is surface-controlled, with the same rate-limiting step for all faces. The pre-exponential factor in the Arrhenius equation slightly varies with the considered orientation, from $\exp(12.4)$ nm.h⁻¹ for the (210) face to $\exp(14.1)$ nm.h⁻¹ for the (001) face, which represents a modest anisotropy of barite growth rate. Taken together, this study largely confirms both the measurements of face-specific barite growth rates and the reaction mechanisms reported in previous studies, and may contribute to improve modeling of barite growth rates in natural and anthropogenic systems.

Acknowledgements

This study was partly funded by LABEX grant ANR-11-LABX-0050_G-EAU-THERMIE-PROFONDE (this research therefore benefited from state funding managed by the Agence National de la Recherche (ANR) as part of the “Investissements d'avenir” program) and ANR grant CANTARE (ANR-15-CE06-0014-01). The authors are grateful to the National Scientific and Technical Research Council (CONICET) PIP2011-0392 which provided a post-doctoral grant. We also acknowledge the Mincyt-ECOS project for supporting international collaboration between the ICGyC/IIMyC in Argentina and the LHyGeS in France. Colin Fournet and René Boutin (LHyGeS) are warmly thanked for their help with IC and ICP-AES measurements. Finally, we are grateful for the careful reviews and detailed suggestions made by two anonymous reviewers, which significantly improved an earlier version of the present paper.

Supporting information

Additional data processing and graph illustrating the linear relation between barite growth rates and the saturation state of the solution.

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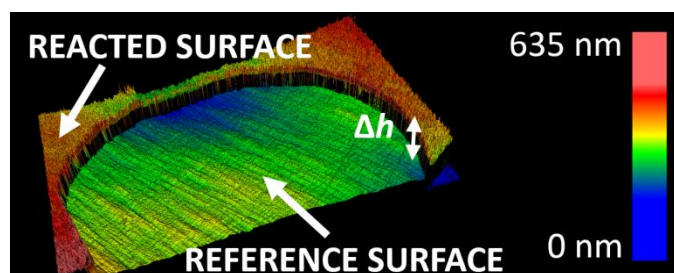
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28 578 **TOC Graphic**



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44 581 **Synopsis**

46 582 Barite growth rate was monitored as function of crystallographic orientation, temperature, and solution
47 583 saturation state by measuring the thickness of the grown layer using vertical scanning interferometry
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