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

3
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18 **Abstract**

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

$$23 \quad r^{(hkl)} = A^{(hkl)} \cdot \exp\left(-E_a^{(hkl)} / RT\right) \cdot (10^{SI} - 1)$$

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

$$28 \quad r^{(hkl)} = A \cdot \exp(-E_a / RT) \cdot (10^{SI} - 1)$$

29 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
30 investigated in the present study, our results suggest that barite growth kinetics is surface-controlled,
31 while possibly verifying the principle of detailed balancing and micro-reversibility. These results
32 imply that previous modeling exercises of steady-state barite growth based on isotropic rate laws may
33 remain valid, at least over the range of conditions investigated in the present study.

34

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

36

37 **1. Introduction**

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

45



46

47 Figure 1. Photograph of a section of 78 mm-diameter, cylindrical sandstone core (from the Buntsandstein unit) taken
48 from the Soultz-sous-Forêts (France) EPS-1 exploration borehole, a borehole fully cored from a depth of 930 m to a
49 depth of 2227 m in 1990-1991 (see ⁵⁻⁷ for information on the Soultz-sous-Forêts drilling project). The sandstone core,
50 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
51 fracture is partially filled with barite crystals (white in color) that have precipitated from the circulating geothermal
52 fluids.

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

61 In spite of the indisputable interest associated with barite formation, our knowledge regarding
62 barite growth kinetics remains incomplete. With the noticeable exception of a few recent studies
63 focused on barite growth on the specific (001) face over a wide range of temperatures (from 30 °C to
64 108 °C)¹⁵⁻¹⁷, most existing studies were limited to the low temperature domain^{12, 18} and were derived
65 from experiments conducted on powders. While the resulting isotropic growth rate laws derived from
66 powder experiments have proved useful for modeling exercises (e.g., ²), it is noteworthy that they
67 remain essentially empirical, which may cast doubt on their predictive ability. In particular, a recent
68 study by Godinho and Stack¹⁹ has shown that barite growth is an anisotropic process. Importantly,
69 isotropic kinetic rate laws were demonstrated to be unreliable and of low relevance to model
70 anisotropic processes such as mineral dissolution/precipitation (e.g., ¹⁹⁻²²), unless the same rate-
71 limiting step controls the dissolution/growth kinetics of all faces. Among the main consequences of
72 this anisotropic reactivity are (i) the non-uniqueness of the relation between dissolution/growth rate
73 and the saturation state of the solution²², (ii) the existence of a transient regime where the crystal habit
74 continuously evolves, resulting in an equal gradual evolution of the apparent dissolution/growth rate
75 “constant”^{19, 21-24}, and (iii) the existence of distinct equilibrium morphologies for a given crystal, which
76 depend on the face-specific dissolution/growth rates of the considered crystal and therefore on reaction
77 conditions such as temperature, fluid saturation state, and the potential catalytic / poisoning effects of

78 specific (bio)molecules²⁵⁻²⁷. Therefore, in addition to the expected improvement of reactive transport
79 simulations, knowledge of the variables that influence the face-specific growth rates of minerals can
80 also help decipher the factors that shape crystals, which might be useful to provide insights into the
81 putative biological origin of minerals recovered from environments on Earth and on other planets (²⁶
82 and references therein).

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

95 **2. Materials and methods**

96 **2.1 Starting materials and preparation**

97 Single crystals of barite (~50-100 mm in length / diameter) were collected in Puy de Chateix
98 (France). The chemical composition of the crystals was analyzed following the protocol described by
99 Bracco et al.¹⁶, revealing K, Sr and Al as the main impurities (0.14%, 0.10%, and 0.05% mol/mol Ba,
100 respectively). The crystals were cleaved along (210) and (001) and cut along the (101) plane. The
101 crystallographic orientations were first verified using Electron Backscatter Diffraction (EBSD) on a
102 Tescan Vega 2 scanning electron microscope (SEM) and polished through a multi-step abrasive
103 sequence with a final polishing step in a colloidal silica suspension. The oriented samples were divided
104 into small pieces with a surface area (*SA*) between ~ 0.25 cm² and 0.50 cm². The faces not under study
105 were protected with room-temperature vulcanizing (RTV) glue. For the faces under investigation, only
106 a portion of their surface was protected with ~1 mm-diameter RTV glue spots to provide a reference
107 surface (see similar protocol in ^{19,28}). The initial roughness of each surface was measured at different
108 scales with a ZYGO® NewView 7300 vertical scanning interferometer (VSI). For each sample, the
109 initial average arithmetic roughness (*Ra*), defined as the arithmetic average of the absolute values of
110 the roughness measured by the VSI, ranged between 10 and 20 nm. These initial roughness parameters
111 were measured on 270 × 360 μm² VSI images.

112 **2.2 Growth experiments and analytical procedures**

113 Barite samples were placed over polytetrafluoroethylene (PTFE) tripods and introduced into 120
114 mL perfluoroalkoxy alkanes (PFA) Savillex® reactors. The reactors were filled with a volume (*V*) of
115 100 mL of solution and continuously stirred with magnetic bars throughout the experiments, incubated
116 at 10, 25, 40, and 70 °C for durations ranging from 10 minutes to 15 hours. Three selected
117 crystallographic planes were studied: (210), (001), and (101).

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

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

124 where a_{Ba} and a_{SO_4} refer to the activities of barium and sulfate ions in solution, respectively, and K_{sp}
125 refers to the solubility product of barite. The CHESS software calculates the solubility product at the
126 run temperature based on the interpolation between the K_{sp} values listed in Chess.tdb database, i.e., 10⁻
127 ^{10.49}, 10^{-9.97}, 10^{-9.61} and 10^{-9.51} at 0 °C, 25 °C, 60 °C and 100 °C, respectively.

128 The following input solutions containing 1:1 ratio of SO₄²⁻ and Ba²⁺ activities were studied: (1)
129 $SI = 1.1$ and (2) $SI = 2.1$. Those saturation indices were chosen in order to compare the results of this
130 study with the growth rates obtained by Godinho and Stack¹⁹ at room temperature.

131 Experiment durations ranged between 10 minutes and 15 hours, depending on the experimental
132 conditions (*SI* and temperature). In order to calculate the evolution of the saturation index, solution
133 sampling was carried out two to four times in each experiment. The aqueous samples were diluted 10
134 times and filtered using a 0.45-μm filter before analysis. Inductively coupled plasma atomic emission
135 spectroscopy (ICP-AES - Thermo ICAP 6000) was used for the analyses of Ba²⁺ and Na⁺, and ion
136 chromatography (ICS-5000 Thermofisher Dionex) was used for the analyses of SO₄²⁻ and Cl⁻. Because
137 foreign cations such as Sr can impact barite growth rates¹⁷, all input solutions were analyzed for major
138 (Na, K, Ca, Mg, Fe, Si, Al) and minor (Sr, Ni, Mn, Ti, Co, Cr, Zn, Cu) cations prior to the immersion
139 of the barite samples. The concentration of all of these elements was systematically below the detection
140 limit (≤ 5 ppb), except for Cu, for which concentrations up to 20 ppb (8×10⁻⁸ M) were occasionally

141 detected. The pH was also checked at the beginning and at the end of each experiment. The pH of all
142 solutions was 5.3 ± 0.1 and remained constant throughout the experiments.

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

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

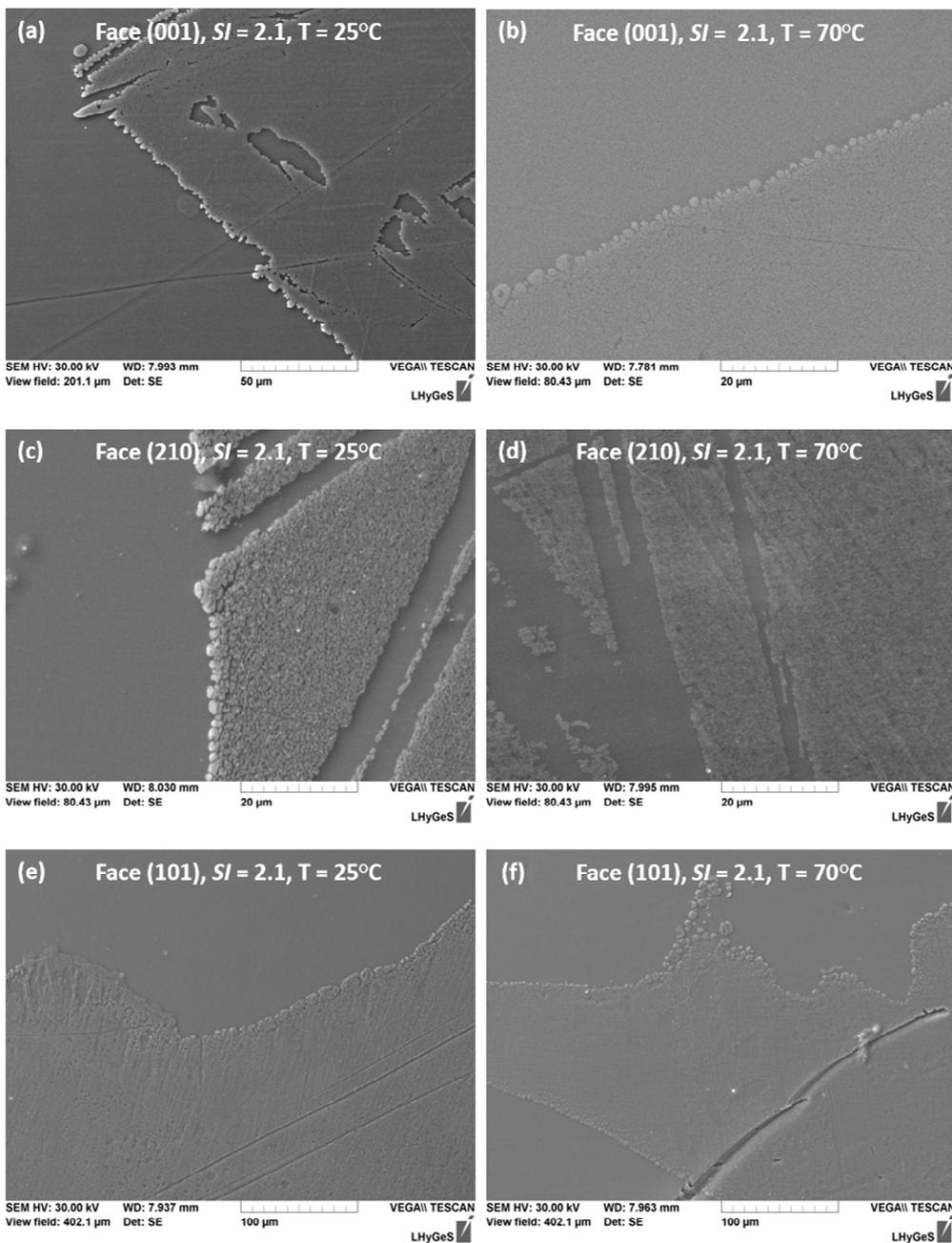
153 where $r^{(hkl)}$ ($\text{nm}\cdot\text{h}^{-1}$) is the growth rate of the (hkl) face, Δh is the average surface step resulting from
154 barite growth (nm), and Δt is the duration of the experiment (s).

155

156 **3. Results and discussion**

157 **3.1 Face-specific growth patterns**

158



159

160

161 Figure 2. Barite growth features observed using scanning electron microscopy a) Face (001), $SI = 2.1$, T
162 = 25 °C; b) Face (001), $SI = 2.1$, $T = 70$ °C; c) Face (210), $SI = 2.1$, $T = 25$ °C; d) Face (210), $SI = 2.1$, $T = 70$
163 °C; e) Face (101), $SI = 2.1$, $T = 25$ °C; f) Face (101), $SI = 2.1$, $T = 70$ °C.

164

165 Both SEM and VSI investigations confirmed that, over the course of the experiments, barite
166 growth did not result from homogeneous nucleation in the solution, as revealed by the absence
167 of euhedral secondary barite crystals on the surface of each investigated face, or the subsistence
168 of polishing scratches in the grown layer of barite. The results show that the temperature
169 variation seems to have no effect on the growth features of the faces under study. Pina et al.³¹
170 described growth patterns which exhibit features specific to each investigated face (001) and
171 (210), consistent with the anisotropy of the barite structure and the Periodic Bond Chain (PBC)
172 theory. In the present study, the (001) and the (101) faces exhibit a growth morphology that
173 resembles the circular sector shape described during the early stage of barite growth monitored
174 using atomic force microscopy (AFM) by Sanchez-Pastor et al.³². Conversely, the two-
175 dimensional islands formed in the experiments conducted at 25 and 70 °C and a saturation index
176 of 2.1 could not be easily related to the needle-shaped morphology described by Pina et al.³¹
177 and Sanchez-Pastor et al.³² for the face (210). Possible explanations include the difference of
178 resolution between AFM and SEM, as well as the difference in terms of reaction progress, since
179 the study by Sanchez-Pastor et al.³² focused on the early stage of barite growth, whereas the
180 present study reports on results obtained at a later stage of the reaction process. Therefore, part
181 of the original islands documented in e.g. Sanchez-Pastor et al.³² might have been overgrown,
182 and no longer identifiable by SEM at such late stages of observation.

183 **3.2 Face-specific growth rate of barite as a function of solution saturation state**

184 3.2.1 Time-resolved fluid analyses

185 The evolution of the fluid composition during all experiments is provided in Table 1.
186 The Ba^{2+} to SO_4^{2-} mole ratios in the aqueous solutions are consistent with the stoichiometric
187 precipitation of barite. From the Ba^{2+} , Na^+ , SO_4^{2-} , and Cl^- concentrations, the saturation index
188 with respect to barite was determined at up to four different time steps in each experiment using
189 the CHESS code.

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

$$\Delta[i] = \frac{\Delta h \cdot SA \cdot \rho_{\text{BaSO}_4}}{M_{\text{BaSO}_4} \cdot V} \quad (3)$$

193 where $\Delta[i]$ is the variation of Ba^{2+} (or SO_4^{2-}) concentration resulting from barite growth, ρ_{BaSO_4}
194 and M_{BaSO_4} are respectively the density ($4.48 \text{ g}\cdot\text{cm}^{-3}$) and molar mass ($233 \text{ g}\cdot\text{mol}^{-1}$) of barite.
195 Knowing that the surface area of each investigated sample never exceeded 0.5 cm^2 , and using
196 150 nm as an upper bound for the thickness of the grown layer (consistent with our VSI
197 measurements), the decrease in sulfate or barite concentration should never exceed $1.5 \times 10^{-6} \text{ M}$.
198 This value is about two orders of magnitude greater than the actual decrease measured in some
199 of our experiments (see Table 1), suggesting that in addition to barite growth, homogeneous
200 barite nucleation in the solution or heterogeneous nucleation on the walls of the reactor should
201 have occurred as well. This result is consistent with the observations reported by Jindra et al.³³,
202 who showed that solutions supersaturated in barite with $SI \geq 1$ were unstable with respect to
203 barite nucleation. This limitation illustrates that classical kinetics experiments based on the sole
204 evolution of the fluid composition would be poorly informative to deconvolve the nucleation
205 from the growth steps under such conditions, and further justifies the use of surface sensitive-
206 techniques to probe growth kinetics, such as AFM^{15-17, 33} or VSI¹⁹.

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

209 appreciable thickness of the grown layer of barite while (ii) limiting the intrinsic evolution of
210 the solution composition resulting from barite nucleation. Importantly, for the experiments
211 conducted under the less reactive conditions (i.e., $T = 10\text{ °C}$, $SI = 1.1$), in spite of several
212 attempts, it has not been possible to run experiments for which the evolution of SI was modest
213 while measuring an appreciable thickness of the grown layer at the same time. In other words,
214 for these experiments, essentially barite nucleation occurred over short durations (with no
215 observable grown layer), while over long durations (up to 15 hours), barite growth was
216 observed, but with large variation of the fluid saturation index (between $\pm 18\%$ and $\pm 34\%$),
217 complicating the definition of the SI at which growth actually occurred. Therefore, the results
218 of experiments conducted at $SI = 1.1$ and $T = 10\text{ °C}$ will have to be considered with caution (see
219 Section 3.2.2 for a confirmation of this statement). In the end, the variation of SI was $\pm 6\%$ for
220 the 12 experiments run at an initial saturation index of 2.1, and $\pm 5\%$ for the 9 experiments run
221 at $SI = 1.1$ (excluding the 3 experiments run at 10 °C).

222

223 Table 1. Evolution of fluid composition (concentration of Ba^{2+} , SO_4^{2-} , Cl^- , and Na^+ in mol/L) measured
224 by ICP-AES and ion chromatography for the growth experiments realized on the (001), (101), and (210) surfaces
225 at 10, 25, 40, and 70 °C. The fluid composition was measured at up to four time steps in each experiment. The
226 saturation index of the experiments was determined from the fluid composition using the CHESS software.

227

		SI=2.1											SI=1.1												
10°C	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	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		
	25°C	t	0	40	80	120	0	20	40	60	0	30	60	90	0	140	280	420	0	60	180	300	0	140	280
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
40°C	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
	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
70°C	t	0	5	10		0	5	10		0	5	10		0	60	120		0	60	120	180	0	40	80	120
	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

229 3.2.2 Vertical Scanning Interferometry data:

230 Table 2. Face-specific growth rates (nm.h⁻¹) calculated from the thickness of the grown layer measured by VSI on the
 231 (001), (101), and (210) surfaces of crystals grown in two different solutions: (1) *SI* = 1.1 and (2) *SI* = 2.1. Experiments
 232 were performed at 10, 25, 40, and 70 °C. The numbers between parentheses indicate the uncertainties of the growth rates,
 233 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)

234

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

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

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

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

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

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

272

273 Table 3. Estimation of the reaction order (n) of barite growth kinetics for all investigated faces and temperatures
 274 following Eq. (5). Note that the values in italic were not considered for the calculation of the mean value of n for each
 275 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

276

277 **3.3 Face-specific growth rate of barite as a function of temperature**

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

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

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

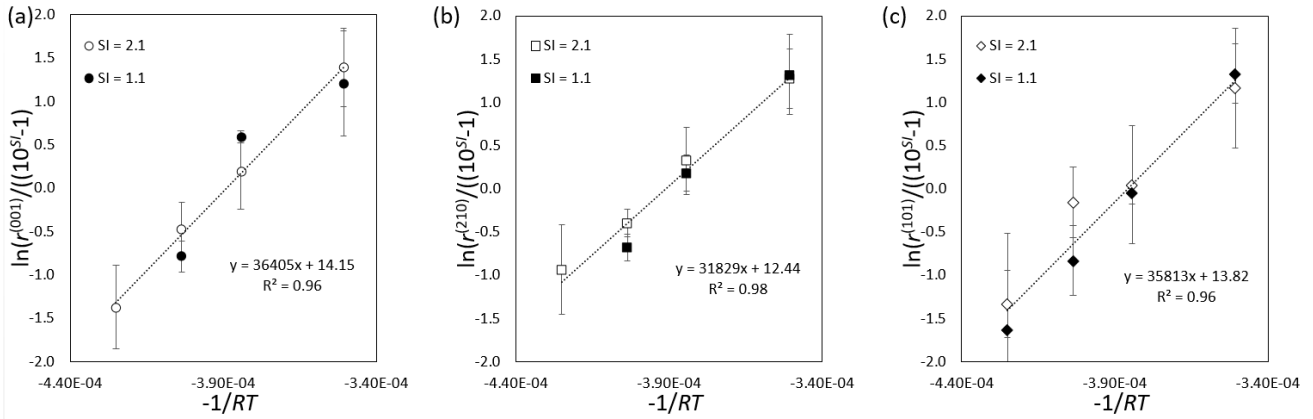
287 where A represents the Arrhenius pre-exponential factor, E_a denotes the activation energy, R is the gas
 288 constant, and T refers to the absolute temperature. By combining Eq. (6) with Eq. (4) and assuming
 289 that $n = 1$ (see above), we can determine the value of A and E_a experimentally following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

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

290 This equation was applied to the data generated in this study using the Arrhenius plots shown in Fig.
291 3. The errors reported on the data points account both for the uncertainties on the growth rates
292 (resulting from the variability of the thickness of the grown layer) and the variation of SI over the
293 course of the experiment (resulting from the precipitation of barite). Excluding the rate data obtained
294 at 10 °C and $SI = 1.1$ (see above), the activation energy was found to be virtually independent of the
295 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),
296 (210), and (101) faces, respectively. The uncertainties on the activation energies were determined
297 based on the errors associated with the data depicted in Fig. 3.

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

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



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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:

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

321

322

323

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:

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

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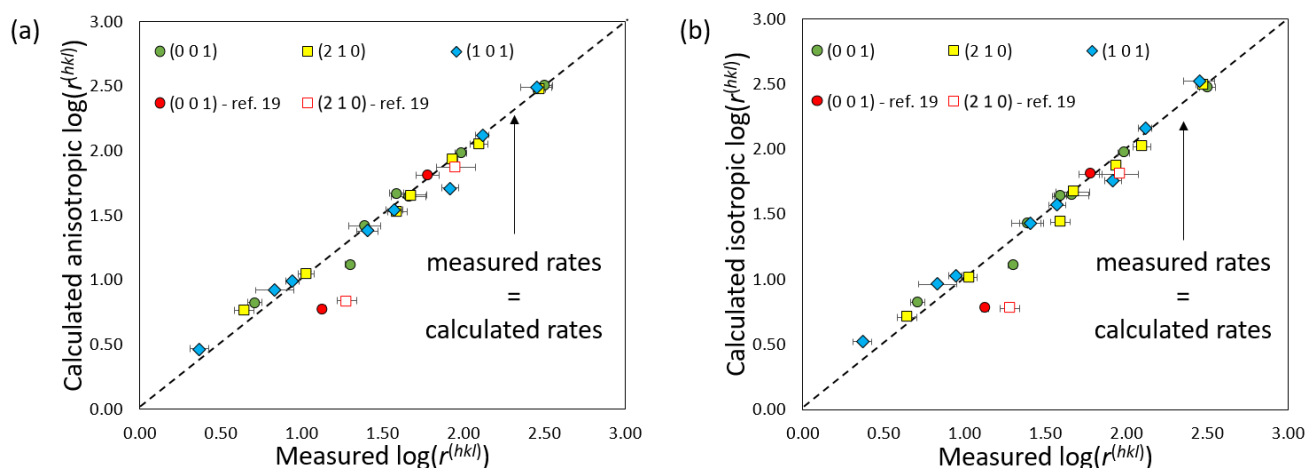
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with average values of $A = \exp(13.59) \text{ nm}\cdot\text{h}^{-1}$ and $E_a = 35.0 \pm 2.5 \text{ kJ}\cdot\text{mol}^{-1}$ (Fig. 4b). In addition, both rate laws perfectly account for the rate data reported by Godinho and Stack¹⁹ at $T = 22.2 \text{ °C}$ 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.

330



331

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

334

335 3.4 Comparison with previously published data and mechanistic insights

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

338 Regarding the anisotropy of barite growth, Godinho and Stack¹⁹ reported that the reactivity of
 339 the (210) face was about 1.5 times greater than that of the (001) face at ambient temperature and for
 340 *SI* conditions ranging from 1.1 to 2.1. These values are in excellent agreement with our measurements
 341 under the same conditions, which show that the reactivity of the (210) face is approximately between
 342 1.7 and 1.9 times greater than that of the (001) face. At *SI* = 2.1, the absolute values of the growth rates
 343 of the two studies overlap as well, within uncertainties.

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

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

358

359 **3.5 Implications for natural and anthropogenic systems**

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

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

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

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

396

397

398 **4. Summary and conclusions**

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

420

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432

433 **Supporting information**

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

436

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438

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569 **For Table of Contents Use Only**

570

571 **Manuscript Title**

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

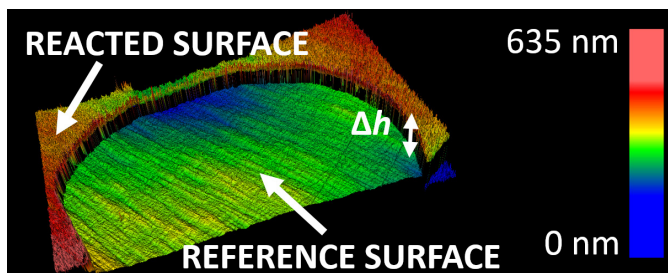
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578 **TOC Graphic**



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581 **Synopsis**

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

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