

Investigating Calcite Growth Rates Using a Quartz Crystal Microbalance with Dissipation (QCM-D)

Bo Cao¹, Andrew G. Stack², Carl I. Steefel³, Donald J. DePaolo³, Laura N. Lammers⁴, and Yandi Hu^{1*}

¹Department of Civil & Environmental Engineering,

University of Houston, Houston, TX 77004

²Chemical Sciences Division,

Oak Ridge National Laboratory, Oak Ridge, TN 37831

³Earth Sciences Division,

Lawrence Berkeley National Laboratory, Berkeley, CA 94720

⁴Department of Environmental Science, Policy, and Management,

University of California-Berkeley, Berkeley, CA 94720

***To Whom Correspondence Should Be Addressed**

E-mail: yhu11@uh.edu

Phone: (713)743-4285

Fax: (713)743-4260

<http://www.cive.uh.edu/faculty/hu>

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1 **Abstract**

2 Calcite precipitation plays a significant role in processes such as geological carbon sequestration
3 and toxic metal sequestration and, yet, the rates and mechanisms of calcite growth under close to
4 equilibrium conditions are far from well understood. In this study, a quartz crystal microbalance
5 with dissipation (QCM-D) was used for the first time to measure macroscopic calcite growth
6 rates. Calcite seed crystals were first nucleated and grown on sensors, then growth rates of
7 calcite seed crystals were measured in real-time under close to equilibrium conditions (saturation
8 index, $SI = \log (\{Ca^{2+}\}/\{CO_3^{2-}\}/K_{sp}) = 0.01-0.7$, where $\{i\}$ represent ion activities and $K_{sp} = 10^{-8.48}$
9 is the calcite thermodynamic solubility constant). At the end of the experiments, total masses
10 of calcite crystals on sensors measured by QCM-D and inductively coupled plasma mass
11 spectrometry (ICP-MS) were consistent, validating the QCM-D measurements. Calcite growth
12 rates measured by QCM-D were compared with reported macroscopic growth rates measured
13 with auto-titration, ICP-MS, and microbalance. Calcite growth rates measured by QCM-D were
14 also compared with microscopic growth rates measured by atomic force microscopy (AFM) and
15 with rates predicted by two process-based crystal growth models. The discrepancies in growth
16 rates among AFM measurements and model predictions appear to mainly arise from differences
17 in step densities, and the step velocities were consistent among the AFM measurements as well
18 as with both model predictions. Using the predicted steady-state step velocity and the measured
19 step densities, both models predict well the growth rates measured using QCM-D and AFM. This
20 study provides valuable insights into the effects of reactive site densities on calcite growth rate,
21 which may help design future growth models to predict transient-state step densities.

22

23 1. Introduction

24 Calcite, as a major mineral in sedimentary rocks, can precipitate in many natural and
25 anthropogenic systems (Tucker and Wright, 1990; Morse and Arvidson, 2002; Morse et al.,
26 2007). Quantitatively understanding the extent, location and rate of calcite precipitation provides
27 important information on paleo-environments as well as on the geochemical processes taking
28 place during geological carbon sequestration and toxic metal sequestration (Marshall and
29 McCulloch, 2002; Fantle and DePaolo, 2005; Lagneau et al., 2005; Eisenhauer et al., 2009;
30 Bracco et al., 2012; Stack, 2014).

31 The kinetics of calcite growth as a function of solution chemistry has been studied
32 extensively for decades by both macroscale and microscale experimental techniques.
33 Macroscopic calcite growth rates have been determined by either monitoring solution
34 composition changes or measuring the mass change of calcite seed crystals (Nancollas and
35 Reddy, 1971; Reddy and Gaillard, 1981; Christoffersen and Christoffersen, 1990; Zhong and
36 Mucci, 1993; Zuddas and Mucci, 1994, 1998; Nehrke et al., 2007; Lopez et al., 2009;
37 Gebrehiwet et al., 2012). However, some of these methods may not be able to provide real-time
38 measurements of slow growth rates under close to equilibrium conditions. For example, Nehrke
39 et al. (2007) used a microbalance with a resolution of 0.1 μg to measure the growth rates of a
40 calcite seed crystal in solution at a saturation index ($\text{SI} = \log (\{ \text{Ca}^{2+} \} / \{ \text{CO}_3^{2-} \} / K_{sp})$, where $\{i\}$
41 represent ion activities and $K_{sp} = 10^{-8.48}$ is the calcite thermodynamic solubility constant) of 0.70.
42 After 266 hrs, the total mass increase of the calcite seed crystal was only 33 μg . In recent
43 decades, calcite growth has been studied under different solution conditions using *in situ* atomic
44 force microscopy (AFM) (Gratz et al., 1993; Teng et al., 2000; Larsen et al., 2010; Stack and
45 Grantham, 2010; Ruiz-Agudo et al., 2011a; Bracco et al., 2012; Bracco et al., 2013). Based on

46 the observed steady-state step densities and step velocities, macroscopic growth rates can
47 theoretically be inferred from these sub-microscale images. However, the growth rates calculated
48 based on these AFM observations were limited to growth that occurred on single spirals and did
49 not include other growth mechanisms, such as single-sourced multi-spiral growth and 2-D
50 nucleation (Teng et al., 2000). Moreover, calcite growth and dissolution may occur
51 simultaneously at different locations on the crystal surface (Stack and Grantham, 2010).
52 Therefore, localized microscopic calcite growth rates measured by AFM may not necessarily
53 represent macroscopic growth rates, which are required to predict large-scale calcite growth in
54 geologic settings using reactive transport modeling (Steeffel et al., 2005). Little has been reported
55 on the macroscopic growth rates of calcite under close to equilibrium conditions ($SI < 0.10$),
56 despite the fact that this is a common condition in natural geologic systems (Plummer, 1975;
57 Zhong and Mucci, 1993). Zuddas and Mucci (1994) reported macroscopic calcite growth rates
58 under atmospheric pressure condition but at relatively high solution supersaturations ($SI > 0.15$).
59 Data on macroscopic calcite growth rates under close to equilibrium conditions at atmospheric
60 pressure conditions are still extremely limited.

61 The quartz crystal microbalance with dissipation (QCM-D) technique can detect
62 variations in mass as low as 0.5 ng/cm^2 on a quartz sensor, by monitoring changes in resonant
63 frequency and dissipation of an oscillating quartz sensor. The resonant frequency shift (Δf) is
64 related to the mass change on the sensor (Richter and Brisson, 2004; Dixon, 2008), and the
65 dissipation shift (ΔD) is related to the rigidity of the surface layer on the sensor (Richter and
66 Brisson, 2004; Dixon, 2008). QCM-D has been widely utilized to investigate interactions at
67 solid-liquid interfaces, including the adsorption of molecules (Maroni et al., 2015; Zhu et al.,
68 2016) and ions (Dai and Hu, 2014; Dai et al., 2016a; Dai et al., 2016b) as well as the deposition

69 of nanoparticles and biomolecules onto organic/inorganic coatings (Richter and Brisson, 2004;
70 Höök et al., 2008; Knoll et al., 2008; Chen et al., 2016). Here, QCM-D was used for the first
71 time to quantify macroscopic calcite crystal growth rates under close-to-equilibrium conditions.

72 **2. Materials and Methods**

73 *2.1 Setup of Calcite Growth Experiments*

74 Calcite growth on QCM-D sensors was conducted with a Q-Sense E4 system (Biolin
75 Scientific) at 25.0 ± 0.1 °C using the experimental setup shown in **Figure 1**. The prepared CaCl_2
76 and NaHCO_3 solutions were placed in a water bath to keep the temperature at 25.0 ± 0.1 °C.
77 Each solution was pumped by a peristaltic pump (IPC-N 4, Ismatec) at a flow rate of 0.125
78 mL/min. The CaCl_2 and NaHCO_3 solutions were mixed in a small mixing cell (volume: ~ 70 μl)
79 with magnetic stirring immediately before injection into the QCM-D chamber (temperature
80 maintained at 25.0 ± 0.1 °C, volume: ~ 40 μl).

81 *2.2 Solution Preparation*

82 ACS reagent grade chemicals ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, NaHCO_3) were used to prepare stock
83 solutions of CaCl_2 (0.00239 M) and NaHCO_3 (0.155 M). Ultrapure water (18.2 $\text{M}\Omega\text{-cm}$) was
84 sparged with air for 24 h to ensure complete equilibration with atmospheric CO_2 . Immediately
85 before each experiment, CaCl_2 and NaHCO_3 stock solutions were weighed with a Mettler Toledo
86 balance (0.1 mg precision) and diluted with the sparged ultrapure water to prepare separate
87 CaCl_2 and NaHCO_3 solutions with the desired concentrations. Using PHREEQC (version
88 3.3.3.10424) and the thermodynamic data from the Lawrence Livermore National Library
89 database (llnl.dat), the mixed solution compositions, pH, ion activities, and saturation indices
90 with respect to calcite were calculated, as given in **Table 1**. For all experiments, the pH values
91 (8.18-8.22) and activity ratios (0.97-1.07) of $\{\text{Ca}^{2+}\}/\{\text{CO}_3^{2-}\}$ in the mixed solutions were similar.

92 Two K_{sp} values for calcite at 25 °C, $10^{-8.54}$ (Teng et al., 1998) and $10^{-8.48}$ (Plummer and
93 Busenberg, 1982), have been used in previous studies (Plummer and Busenberg, 1982; Teng et
94 al., 1998; Teng et al., 1999; Teng et al., 2000; Larsen et al., 2010; Teng et al., 2011; Gebrehiwet
95 et al., 2012; Bracco et al., 2013). In this study, QCM-D experiments were conducted using a
96 solution with 8.46×10^{-5} M Ca^{2+} and 8.18×10^{-5} M CO_3^{2-} (**Sample #1, Table 1**). This solution is
97 supersaturated with respect to calcite if a $K_{sp} = 10^{-8.54}$ is used, and undersaturated if a $K_{sp} = 10^{-8.48}$
98 is used. The QCM-D measurements reported here (**Figure A1**) indicated that calcite dissolution
99 rather than growth took place in this solution. Thus $K_{sp} = 10^{-8.48}$ was used in this study to
100 calculate calcite supersaturations (**Table 1**, -0.01 – 0.70).

101 ***2.3 Real-time Calcite Growth Experiments in QCM-D Chamber***

102 QCM-D measurements were conducted in two steps (**Figure 2**): first, calcite seed crystals
103 were generated on sensors coated with OH-terminated self-assembled monolayers (SAMs)
104 (Aizenberg et al., 1999a; Aizenberg et al., 1999b; Wang et al., 2010) at a relatively high SI =
105 0.70 (Step I, details in Appendix A), and **second**, the growth rates of calcite seed crystals were
106 quantified under close to equilibrium conditions (Step II, SI = 0.01 – 0.50, **Table 1**).
107 Immediately after switching feed solutions, **the** flow rate was increased to 1.20 mL/min for five
108 mins to allow the new feed solutions (SI < 0.70) to fully replace the initial solution (SI = 0.70) in
109 the system. Thereafter, the pump was adjusted back to a flow rate of 0.125 mL/min.

110 ***2.4 QCM-D Data Analysis***

111 The real-time changes in resonant frequency (Δf) and dissipation (ΔD) of the sensors
112 (Figure 3) caused by calcite nucleation and growth were fitted to a Kelvin-Voigt viscoelastic
113 model (Voinova et al., 1999) (fitted curves are shown as black lines in Figure 3) using QTools

114 software (Version 3.0, Biolin Scientific AB). By obtaining the best fits of the QCM-D measured
115 frequency (Δf) and dissipation (ΔD) changes at different overtones (e.g., 15MHz, 25MHz,
116 35MHz and 45MHz), film viscosity, mass changes on sensors were calculated. More details of
117 model fitting can be found in Appendix A.

118 *2.5 Ex-situ Characterization of Calcite Coverage on Sensor Using Optical Microscopy*

119 At the end of each QCM-D experiment, the sensor was removed from the QCM-D
120 chamber, rinsed with ethanol to remove the residual solution, and dried with N₂ gas. To quantify
121 the surface coverage of calcite crystals on the sensor, the sensor surface was imaged by optical
122 microscopy (Optem, Qioptiq). Using a magnification of 500, a total of 50 pictures were taken to
123 cover the entire sensor surface. A typical image collected by the optical microscopy at 500 ×
124 magnification is shown in **Figure A3**. Using Image J software, the original optical image was
125 processed to a black-and-white version (**Figure A3**) and surface coverage of the sensor by dark
126 spots corresponding to calcite crystals was calculated. By analyzing all 50 images, the coverage
127 of calcite crystals on the entire sensor surface was calculated, as shown in **Table A1**.

128 The sensor was only partially covered with calcite crystals (Figure A3), with a large
129 percentage of the sensor covered by SAM coatings. Therefore, it is possible that the mass
130 changes recorded by the sensor during seed crystal growth (Step II) may be partially generated
131 by ion adsorption and/or the nucleation of additional calcite on the SAMs. To investigate such
132 effects, control experiments were conducted using the same flow system (**Figure 1**), but by
133 directly flowing a solution with SI = 0.30 or 0.50 over a SAM-coated sensor without calcite seed
134 crystals. Minor changes in frequency and dissipation were observed over 4 hours for both
135 conditions (**Figure A4**), and the calculated mass change attributed to ion adsorption and calcite
136 nucleation on SAM coatings was less than 5 % of the mass increase observed during the growth

137 of seed crystals under the same solution conditions (Step II, **Figure 2**). Thus, we concluded that
138 the measured mass increases during Step II (**Figure 2**) were mainly caused by the growth of
139 preexisting calcite seed crystals.

140 *2.6 Ex situ Characterization of Calcite Amount on Sensors Using ICP-MS*

141 After quantifying the surface coverage of seed crystals on the sensor, the sensor was
142 soaked in a 5.00 mL 1.0 % HCl solution in a test tube. The test tube was then placed on a shaker
143 (Innova 2000, Expotech) at a speed of 100 rpm for 24 hours to dissolve all calcite seed crystals.
144 The dissolved Ca concentration was measured by inductively coupled plasma mass spectrometry
145 (ICP-MS, PerkinElmer) with an analytical error of ~10% and a detection limit of ~10 µg/L. The
146 total mass of calcite crystals on the sensor was calculated from the Ca concentration.

147 *2.7 Calcite Step Density Measurement Using Vertical Scanning Interferometer (VSI)*

148 Step densities on the calcite surface, which can affect its growth rate significantly, have
149 been measured using AFM in previous studies with calcite crystals (Teng et al., 1998; Teng et al.,
150 2000; Stack and Grantham, 2010; Bracco et al., 2012; Bracco et al., 2013). In this study, the seed
151 crystals generated on the Au sensors were very small (~ 1-5 µm), making it difficult to perform
152 AFM measurements. Vertical scanning interferometry (VSI, NewView™ 7300, Zygo) has been
153 utilized to quantify the changes in surface roughness during glass dissolution (Icenhower and
154 Steefel, 2015), and was used here to measure the step densities after growth experiments (Step
155 II). A similar two-step procedure was followed: First, a gold wafer coated with -OH terminated
156 SAMs was immersed in a mixed CaCl₂ and NaHCO₃ solution (SI = 1.50) for 12 hrs for seed
157 crystal generation. The mixed solution with a higher SI (1.50 instead of 0.70) was able to
158 generate bigger seed crystals (~ 20 - 30 µm, **Figure A5**) for high-quality VSI measurements.
159 **Second**, the gold wafer was immersed with solutions having SI = 0.02, 0.06, 0.10, 0.20, 0.30,

160 0.40, 0.50, or 1.00 for 1 h (Step II). Finally, the step densities of calcite crystals after the growth
161 in lower SI solutions (Step II) were measured by VSI (**Figures A5**). The detailed experimental
162 procedure for VSI measurements can be found in **Appendix A**. The measured VSI step densities
163 shown in **Figure A6** were fitted to an empirical expression:

$$\rho_{step} = y_0 + A \exp(-SI/\tau) \quad (1)$$

164 where y_0 , A and τ are fitting parameters, and each data point was weighted by its standard
165 deviation. The fit obtained was excellent, as shown in **Figure A6**, but it should be noted that the
166 solution used to generate the larger seed crystals required for VSI measurement had a higher
167 supersaturation ($SI = 1.50$) than the solution used to generate seed crystals ($SI = 0.70$) for QCM-
168 D experiments. Therefore, the step densities measured via VSI may not exactly correspond to the
169 step densities of calcite seed crystals on QCM-D sensors.

170 **3. Results**

171 *3.1 Validation of QCM-D Measurements: Comparison of Total Calcite Mass Measured by* 172 *QCM-D and ICP*

173 The full data sets of real-time QCM-D results under our experimental conditions (with
174 seed crystal generation under $SI = 0.70$ and later crystal growth under $SI = 0.01, 0.02, 0.03, 0.04,$
175 $0.05, 0.10, 0.30, 0.50$) are shown in **Figure 2**. During both the seed crystal generation ($SI = 0.70$,
176 Step I) and the later crystal growth ($SI = 0.01, 0.02, 0.03, 0.04, 0.05, 0.10, 0.30, 0.50$, Step II),
177 decreases in frequency (blue markers in **Figure 2**) and increases in dissipation (red markers in
178 **Figure 2**) are observed, indicating mass increases on sensors caused by calcite nucleation and
179 growth.

180 The real-time evolution of total calcite mass per unit surface area on the sensor was
181 calculated by the *Kelvin-Voigt* viscoelastic model (Voinova et al., 1999) (**Table A1**). By
182 multiplying the surface area of the sensor in contact with the solution ($7.70 \times 10^{-5} \text{ m}^2$), the total
183 mass of calcite crystals on the sensor surface at the end of each experiment was calculated, as
184 plotted on the Y-axis of **Figure 3**. The total mass of calcite on the sensor at the end of each
185 experiment calculated from the ICP-MS measurements is plotted on the X-axis of **Figure 3**. All
186 the data points fall along a 1:1 line (**Figure 3**), indicating that the total calcite mass on the sensor
187 measured by QCM-D was consistent with the mass calculated from ICP-MS analysis. This good
188 agreement demonstrates the validity of using the *Kelvin-Voigt* viscoelastic model to quantify
189 crystal growth on sensors. It should be noted that, whereas it was possible to measure the total
190 masses of calcite crystals after growth experiments using ICP-MS, this technique is not suitable
191 to determine the real-time change of dissolved Ca concentrations and the corresponding real-time
192 calcite growth rates under close to equilibrium conditions ($SI < 0.10$).

193 **3.2 Calcite Growth Rates Determined by QCM-D**

194 The real-time QCM-D data of calcite seed crystal generation (Step I) and later growth
195 (Step II) are shown in **Figure 2**. For Step I ($SI = 0.70$), the initial slow changes in frequency and
196 dissipation (**Figure 2**) indicated the slow nucleation of calcite seed crystals on the sensor. With
197 the generation of a larger number of calcite seed crystals, a more rapid mass increase on the
198 sensor was observed, indicating that calcite growth became the dominant mechanism of mass
199 increase. For Step II, when the feed solutions were switched from $SI = 0.70$ to lower SI (**Figure**
200 **2**), the parabolic curves of frequency and dissipation changes indicated that the calcite growth
201 rates started to decrease after switching to the growth solution with lower SI . For both Steps I

202 and II (**Figure 2**), after the initial parabolic curves of frequency and dissipation changes with
203 time, linear curves (indicated by the shaded areas in **Figure 2**) were established. The calcite mass
204 increase (Δm , $\mu\text{g}/\text{m}^2$) over time (t , seconds) under both $\text{SI} = 0.70$ and $\text{SI} = 0.01, 0.02, 0.03, 0.04,$
205 $0.05, 0.10, 0.30, 0.50$ were calculated based on the fittings of data in shaded areas, as shown in
206 **Table A1**.

207 In the *Kelvin-Voigt* viscoelastic model, the calculated mass increase (Δm , $\mu\text{g}/\text{m}^2$) over
208 time (t) was normalized to the entire sensor surface area, but calcite crystals only partially
209 covered the sensors (**Figure A2**). In addition, the seed crystals grown on sensors were
210 rhombohedral, and therefore had five $\{10\bar{1}4\}$ surfaces exposed to the solution. Two
211 simplifications were made here to calculate the calcite surface area for growth rate
212 normalization: (1) all five $\{10\bar{1}4\}$ surfaces had the same surface area; (2) change in crystal
213 surface area during the slow growth period (shaded areas of Step II, **Figure 2**) was insignificant,
214 as the mass increase (Δm , $\mu\text{g}/\text{m}^2$) during this growth period t (s) from solutions with lower SI
215 values (0.01 – 0.50) was less than 5 % of the total calcite mass for each set of experiments
216 (**Table A1**). Therefore, the surface coverage (η , **Table A1**) of calcite crystals on the sensor
217 measured at the end of each set of experiment was used for growth rate (R , $\mu\text{mol}/\text{m}^2/\text{s}$)
218 calculations, according to eqn. (2):

$$R = \Delta m / (5M\eta t) \times 10^{-6} \quad (2)$$

219 where M is the molecular weight of calcite (100 g/mol)). As shown in **Table 1**, the QCM-D
220 measured calcite growth rates increased with the increase of SI. For solutions with $\text{SI} = -0.01 -$
221 0.05 (**Table 1**), the differences in Ca^{2+} concentrations were within 5%, and such small
222 differences could not be distinguished by ICP-MS. The observed calcite dissolution with $\text{SI} = -$

223 0.01 (**Figure A1**) and faster calcite growth at higher SI (**Figure 2a-2e**) indicated the consistency
224 of our solution preparation and QCM-D measurements.

225 **4. Discussion**

226 *4.1 Comparison of Growth Rates Measured by QCM-D and Other Macroscopic Measurements*

227 A number of experiments have been performed to investigate the macroscopic growth
228 rates of calcite using different measurement techniques, such as microbalance, auto-titration, and
229 ICP-MS (Nancollas and Reddy, 1971; Reddy et al., 1981; Reddy and Gaillard, 1981; Zuddas and
230 Mucci, 1994; Shiraki and Brantley, 1995; Zuddas and Mucci, 1998; Lin and Singer, 2005;
231 Nehrke et al., 2007; Tang et al., 2008a; Lopez et al., 2009; Gebrehiwet et al., 2012; Noiriél et al.,
232 2012; Tang et al., 2012). Calcite reactive site densities and solution conditions (e.g., aqueous
233 $\{Ca^{2+}\}/\{CO_3^{2-}\}$, temperature, background electrolytes, ionic strength, and solution pH) are
234 widely known to affect calcite growth rates (Nehrke et al., 2007; Larsen et al., 2010; Stack and
235 Grantham, 2010; Gebrehiwet et al., 2012; Wolthers et al., 2012; Bracco et al., 2013; Stack, 2014).
236 In some previous studies, the surface areas of calcite seed crystals or aqueous $\{Ca^{2+}\}/\{CO_3^{2-}\}$
237 were not clearly reported (Nancollas and Reddy, 1971; Reddy et al., 1981; Reddy and Gaillard,
238 1981; Lopez et al., 2009), or the reaction temperature was quite different from this study (Shiraki
239 and Brantley, 1995). Thus, their reported growth rates cannot be compared with those measured
240 in this study.

241 In the studies of Gebrehiwet et al. (2012), Nehrke et al., (2007), Lin and Singer (2005),
242 Zuddas and Mucci (1998), and Noiriél et al. (2012), the $\{Ca^{2+}\}/\{CO_3^{2-}\}$ were reported (**Table 2**),
243 and their experiments were conducted at similar temperatures (**Table 2**) to the present study.
244 Their experimental pH conditions were also similar to this study (pH 8.16 - 9.01; **Table 2**),
245 except for those of Nehrke et al. (2007) for which the pH was 10.2. The aqueous $\{Ca^{2+}\}/\{CO_3^{2-}\}$

246 was close to 1 in the study of Lin and Singer (2005) and varied in the other four studies (Zuddas
247 and Mucci, 1998; Nehrke et al., 2007; Gebrehiwet et al., 2012; Noiriél et al., 2012). Using the
248 relationship between aqueous $\{Ca^{2+}\}/\{CO_3^{2-}\}$ and calcite growth rate established by Nielsen et al.
249 (2012) in the ion-by-ion model, the reported calcite growth rates from solutions with the same
250 saturation index but with varied $\{Ca^{2+}\}/\{CO_3^{2-}\}$ were used to calculate the growth rates at
251 $\{Ca^{2+}\}/\{CO_3^{2-}\} = 1$. The detailed calculations can be found in **Appendix A**. These recalculated
252 rates at $\{Ca^{2+}\}/\{CO_3^{2-}\} = 1$ (Zuddas and Mucci, 1998; Nehrke et al., 2007; Gebrehiwet et al.,
253 2012; Noiriél et al., 2012), as well as the rate measured by Lin and Singer. (2005), are plotted in
254 **Figure 4**.

255 As shown in **Figure 4**, the macroscopic growth rates measured by QCM-D (this study),
256 Lin and Singer (2005), and Gebrehiwet et al. (2012) were similar, and were approximately 1.5
257 orders of magnitude higher than those measured by Nehrke et al. (2007), and were approximately
258 two orders of magnitude higher than those measured by Noiriél et al. (2012) and Zuddas and
259 Mucci (1998). The discrepancies could partly result from the differences in the electrolyte
260 compositions, pH, temperature, and ionic strength of solutions (**Table 2**) (Ruiz-Agudo et al.,
261 2011a; Ruiz-Agudo et al., 2011b;). Moreover, these discrepancies might also result from the
262 surface area normalization (Hodson. 2006). In Nehrke et al. (2007) and this study, the geometric
263 surface area used for growth rate normalization was measured by optical microscopy; **whereas**
264 Zuddas and Mucci (1998), Lin and Singer (2005), Gebrehiwet et al. (2012) and Noiriél et al.
265 (2012) used specific surface areas measured by BET. Irrespective, the surface areas measured by
266 either BET or microscope does not represent the real reactive site densities on mineral surfaces
267 (Fisher et al., 2013). A systematic investigation of how to quantify surface reactive site densities
268 is an important future direction but is not the focus of this paper.

269 4.2 Comparison of Calcite Growth Rates Measured by QCM-D and AFM

270 Many calcite growth experiments have been conducted using *in situ* AFM (Teng et al.,
271 2000; Perdikouri et al., 2009; Larsen et al., 2010a, b; Stack and Grantham, 2010; Ruiz-Agudo et
272 al., 2011; Bracco et al., 2012; Bracco et al., 2013). Most of these studies used measured step
273 velocities to determine spiral growth rates on the $\{10\bar{1}4\}$ surface (Teng et al., 2000; Ruiz-Agudo
274 et al., 2011a; Bracco et al., 2013). To make these rates comparable with QCM-D data, the step
275 velocity (v_s , m/s) and step density (ρ_{step} , μm^{-1}) measured by AFM on single spirals (Teng et al.,
276 2000; Bracco et al., 2013) are needed to calculate the macroscopic calcite growth rate (R ,
277 $\mu\text{mol}/\text{m}^2/\text{s}$, **Figure 5**) using eqn. (3):

$$R = \rho_{step} v_s h / V_m \times 10^9 \quad (3)$$

278 where V_m is the molar volume of calcite ($36.93 \text{ cm}^3/\text{mol}$), h is the step height of an individual
279 molecular layer (0.31 nm). Neither Larsen et al. (2010a) nor Perdikouri et al. (2009) reported
280 step densities. Thus, those step velocities could not be converted to macroscopic growth rates. In
281 the studies of Bracco et al. (2013), Teng et al. (2000), and Ruiz-Agudo et al. (2011a), step
282 velocities with aqueous $\{\text{Ca}^{2+}\}/\{\text{CO}_3^{2-}\} \approx 1$ were measured using AFM. Step densities (ρ_{step} ,
283 μm^{-1}) were also measured and reported in Bracco et al. (2013) and Teng et al. (2000), whereas
284 Ruiz-Agudo et al. (2011a) used an average value of 0.026 ± 0.015 to represent the slope (slope =
285 $\rho_{step} \times h$) of the calcite surface, which **can** be used to calculate the step densities (ρ_{step}).
286 Therefore, using the step velocity and step density values reported in these three studies,
287 macroscopic calcite growth rates (R , $\mu\text{mol}/\text{m}^2/\text{s}$) were calculated using eqn. (4) and were
288 compared with our QCM-D measurements (**Figure 5**). In Bracco et al. (2013) and Ruiz-Agudo et
289 al. (2011a), a K_{sp} value of $10^{-8.48}$ was used, the same as in this study. The SI values reported in

290 Teng et al. (2000) were originally calculated with $K_{sp} = 10^{-8.54}$, but were recalculated here using
291 $K_{sp} = 10^{-8.48}$.

292 The macroscopic growth rates inferred from these *in situ* AFM studies (**Figure 5**) were,
293 in general, consistent with the rates measured by QCM-D (**Figure 5**), validating that both QCM-
294 D and *in situ* AFM can be used to accurately capture the macroscopic growth rate of calcite at
295 low SI. This finding suggests that AFM can likely capture the representative growth mechanisms
296 at low SI. As shown in **Figure 5**, the growth rates measured by QCM-D in this study were in
297 good agreement with those measured by Ruiz-Agudo et al. (2011a) and Teng et al. (2012) at $SI >$
298 0.10, and were approximately 2 - 5 times higher than those measured by Teng et al. (2000) at
299 close to equilibrium conditions ($SI < 0.1$). Finally, our QCM-D derived rates and those of Teng
300 et al. (2012) and Ruiz-Agudo et al. (2011a) were about **one** order of magnitude higher than those
301 measured by Bracco et al. (2013).

302 As the growth rates (**Figure 5**) were calculated using eqn. (4), the discrepancies in those
303 growth rates could derive either from errors in step velocity or step density. Accordingly, the
304 step velocities measured by AFM under similar SI conditions (**Table 3**) were compared. The
305 obtuse step velocities reported by Bracco et al. (2013) and Teng et al. (2000) at $SI \approx 0.4$ were
306 quite similar, 7.89 and 8.10 nm/s (**Table 3**), respectively. The sum of obtuse and acute step
307 velocities (V_{sum} , **Table 3**) measured by Bracco et al. (2013) and Ruiz-Agudo et al. (2011a) at SI
308 ≈ 0.8 were also similar, 14.47 ± 3.3 and 10.14 ± 1.34 nm/s, respectively. The small
309 discrepancies (within 40%) in measured step velocities of these calcite crystals growing from
310 solutions under similar SI conditions might be attributed to the differences in solution pH and the
311 composition and concentration of solution electrolytes (Detailed discussion in **Appendix A**).

312 Considering the minor differences in measured step velocities (**Table 3**, within 40%), the
313 much larger discrepancies in macroscopic growth rates among these previous AFM studies must
314 mainly originate from differences in step densities of the calcite seed crystals. As shown in
315 **Table 3**, the step density measured by Teng et al. (2000) at $SI \approx 0.40$ was $9.09 \mu\text{m}^{-1}$, 6.4 times
316 larger than that measured by Bracco et al. (2013) at $1.41 \mu\text{m}^{-1}$, whereas that reported by Ruiz-
317 Agudo et al. (2011a) at $SI \approx 0.80$ was $100 \mu\text{m}^{-1}$, 36 times larger than that measured by Bracco et
318 al. (2013) at $2.86 \mu\text{m}^{-1}$.

319 The larger discrepancies in step densities were also the main cause of the growth rates
320 differences between QCM-D and AFM measurements. Using the step densities measured by VSI
321 (**Figure A6**), the step velocities were calculated from QCM-D growth rates based on eqn. (4).
322 These calculated step velocities (**Table 3**, 1.99 nm/s at $SI = 0.10$, 3.10 nm/s at $SI = 0.30$ and
323 11.20 nm/s at $SI = 0.50$) are within a factor of $\sim 1.1 - 1.6$ of the values (**Table 3**, 1.18 nm/s at SI
324 $= 0.09$, 5.18 nm/s at $SI = 0.30$, and 13.10 nm/s at $SI = 0.56$) reported in Teng et al. (2000),
325 whereas larger difference existed in step densities. The measured step densities determined by
326 VSI (**Table 3**, $5.11 \mu\text{m}^{-1}$ at $SI = 0.10$, $11.66 \mu\text{m}^{-1}$ at $SI = 0.30$ and $12.36 \mu\text{m}^{-1}$ at $SI = 0.50$) were
327 $\sim 1.1 - 2.3$ times the values (**Table 3**, $2.27 \mu\text{m}^{-1}$ at $SI = 0.09$, $7.14 \mu\text{m}^{-1}$ at $SI = 0.30$ and 11.11
328 μm^{-1} at $SI = 0.56$) reported in Teng et al. (2000) at similar SI conditions.

329 The significant differences in step densities of calcite crystals may be due to the
330 application of different processes in the generation and pretreatment of calcite seed crystals
331 among the various studies. In these previous AFM studies, Iceland spar calcite crystals were
332 used, whereas, in the current QCM-D study, calcite seed crystals were generated on SAM
333 coatings. Furthermore, different crystal pretreatments were used. Teng et al. (2000) pretreated
334 their calcite crystals with a slightly supersaturated and near equilibrium solution for 1 h before

335 the *in situ* AFM measurements. Bracco et al. (2013) pretreated their calcite crystals with an SI =
336 1.0 solution for 1 h, whereas Ruiz-Agudo et al. (2011a) did not pretreat their freshly-cleaved
337 calcite crystals. In the current study, the seed crystal surfaces were pretreated with an SI = 0.7
338 solution. In the classical spiral growth model, the step spacing, the reciprocal of the step density,
339 is determined by the critical step length at the top of the hillock, a function of the solution
340 supersaturation with respect to calcite (Teng et al., 1998; Teng et al., 2000). To completely reset
341 the step spacing of a given growth hillock, growth must proceed at a fixed SI for a sufficiently
342 long time for the first step, nucleated under that condition, to propagate across the entire width of
343 the growth hillock. The total time required to reset the step spacing will depend on the step
344 velocity and the spacing (and thus size) of the growth hillocks. For example, Bracco et al. (2013)
345 observed that after switching growth solutions of varied SIs, the step velocity of calcite could
346 quickly (within 20 min) reach steady-state under different SI, while it took a much longer time (>
347 40 min) for the step density to reach steady-state under some solution conditions, especially
348 those with low calcium-to-carbonate ratios. In other words, the surface step density may not only
349 be affected by the instantaneous solution saturation state but may also inherit step spacing from
350 the previous solution, i.e., a memory artifact (Bracco et al., 2013; Stack. 2014). The use of
351 different generation and pretreatment processes for calcite seed crystals used in these studies
352 may have affected the step densities on the calcite crystals and therefore resulted in the
353 discrepancies in the calculated macroscopic calcite growth rates. The comparison made here
354 points out the importance of quantifying step densities for interpreting overall growth rates and
355 sheds some light on the effects of pretreatment on step density.

356 ***4.3 Comparison of Calcite Growth Rates Measured by QCM-D and AFM with Model*** 357 ***Predictions***

358 Both macroscopic and microscopic models have been developed to describe calcite
359 growth and dissolution processes (Burton et al., 1951; Zhang and Nancollas, 1990; Zuddas and
360 Mucci, 1994; Zhang and Nancollas, 1998; Zuddas and Mucci, 1998; De Yoreo, 2003; De Yoreo
361 et al., 2009; Anderssson et al., 2016). Burton et al. (1951) developed the terrace-ledge-kink
362 (TLK) theory, which was applied by Teng et al. (1998; 1999; 2000) and Larsen et al. (2010a) to
363 model calcite growth from aqueous solutions. However, DeYoreo et al. (2009) pointed out that
364 the application of TLK theory is not valid for calcite, as the kink formation rate limits calcite
365 growth. Instead, a model of kink creation, propagation and collision (CPC), developed by Zhang
366 and Nancollas (1990; 1998), is believed to capture the kink density-dependent growth rate of
367 calcite accurately. More recently, Nielsen et al. (2012) developed an ion-by-ion model based on
368 the CPC approach to predict calcite growth rates as a function of solution composition. Another
369 process-based crystal growth model was also developed in previous studies, i.e., the Stack-
370 Bracco-Grantham-Higgins (SBGH) model (Stack and Grantham, 2010; Bracco et al., 2012;
371 Bracco et al., 2013; Bracco et al., 2016a; Bracco et al., 2016b). A third microkinetic model was
372 developed by Anderson et al. (2016) to predict step velocity of calcite growth under varied
373 aqueous conditions, but this model does not predict the step density and, thus, cannot estimate
374 the macroscopic calcite growth rates as do the ion-by-ion and SBGH models. Therefore, only the
375 ion-by-ion and SBGH model predictions were compared with the rates measured by QCM-D,
376 and detailed descriptions of the two models are in Appendix A.

377 The growth rates predicted by the ion-by-ion (solid blue line in **Figure 6**) and SBGH
378 models (solid red line in **Figure 6**) as a function of SI with $\{Ca^{2+}\}/\{CO_3^{2-}\} = 1$ were compared
379 with the rates measured by QCM-D (black markers in **Figure 6**). Both the ion-by-ion and SBGH
380 models underpredicted the growth rates measured by QCM-D, especially at low SI. Based on the

381 discussion in **Section 4.2**, the discrepancies in calcite growth rates between measurements and
382 model predictions may also arise mainly from the differences in step densities instead of step
383 velocities. Therefore, steady-state step densities and step velocities predicted by both models
384 (details of the calculation are provided in **Appendix A**) were compared with the QCM-D and
385 VSI measurements (**Table 3**). Over the SI range of 0.02 – 0.50, differences in measured and
386 predicted step velocities varied from 0.8 to 600 % (**Table 3**); whereas the differences in
387 measured and predicted step densities were much higher, varying from 87 to 1865 % (**Table 3**).
388 Similarly, the model predicted step velocities and step densities were compared with the AFM
389 measurements (**Table 3**). Over the SI range of 0.05 – 0.56, differences in measured and model-
390 predicted step velocities varied from 2 to 90 % (**Table 3**), whereas the differences in measured
391 and predicted step densities were much higher, varying from 25 to 270 % (**Table 3**). This is
392 because the step densities predicted by both models did not account for “memory effects” as
393 discussed in **Section 4.2**. After crystal pretreatment, step velocities can quickly respond to
394 changes in solution composition and could be predicted by both the ion-by-ion and SBGH
395 models using the current solution compositions; whereas step densities require much longer time
396 to reach a steady-state and could be significantly affected by the pretreatment procedures. The
397 comparisons of model-predicted step densities and step velocities with AFM and QCM-D/VSI
398 measurements confirmed the ability of both models to predict step velocities using the current
399 solution conditions, meanwhile suggesting that better predictions could be achieved if transient-
400 state step densities could be taken into account.

401 As larger discrepancies in growth rates originated from differences in step densities, a
402 second set of model calculations was conducted. The step densities measured by VSI were fitted
403 as a function of SI (**Figure A6**), and these were combined with the model predicted step

404 velocities to calculate the growth rates using eqn. (4). Results of the calculation are plotted as
405 dashed lines in **Figure 6**. Compared with the original SBGH and ion-by-ion model predictions
406 (solid red and blue lines, respectively) using predicted step densities, the modified predictions
407 (dashed red and blue lines) using fitted step densities from VSI measurements agreed much
408 better with the measured growth rates (black markers) by QCM-D (**Figure 6**). The good
409 agreement between the predictions using spiral-growth models (dashed lines in **Figure 6**) and the
410 QCM-D measurements also indicated that single-spiral growth was the dominant mechanism in
411 our study for calcite growth under near-equilibrium conditions (i.e., low SI).

412 **5. Conclusions**

413 Quantitative determination of mineral precipitation rates is essential for successful
414 prediction of the fate of nutrients and contaminants, as well as for the safety and efficiency of
415 many surface and subsurface operations. For example, accurate prediction of calcium carbonate
416 precipitation rates is critical to determine the efficiency of sequestration of toxic metals such as
417 strontium and selenium (Putnis et al., 2013), but the dearth of accurate growth rates at close to
418 equilibrium conditions limits how well we can predict calcite precipitation at the reservoir scale
419 using reactive transport modeling. In this study, QCM-D was successfully applied for the first
420 time to quantify macroscopic calcite growth rates at atmospheric pressure under close to
421 equilibrium conditions, and the method developed was validated with traditional techniques.
422 This novel method can be adopted for many different applications and could greatly benefit both
423 the geochemistry and nanochemistry communities.

424 The calcite growth rates measured by QCM-D were compared with results of previous
425 studies using other macroscopic and microscopic techniques, as well as with ion-by-ion and
426 SBGH model predictions. Whereas discrepancies between experimental and model results will

427 not be resolved in a single study, the present study provides valuable insights on the importance
428 of reactive site density in the quantification of calcite growth rates and illustrates the importance
429 of coupling macroscopic and microscopic rate data to interpret these rates accurately.
430 Nevertheless, the agreement between growth rates measured by QCM-D, AFM and model
431 predictions using steady-state step velocities and the measured step densities highlight the ability
432 of these models to predict calcite growth rates. The discrepancy among the measured and the
433 predicted step densities likely result from a memory artifact, i.e., step density was not only
434 controlled by the reactive solution composition but also affected by the pretreatment solution
435 conditions. The memory artifact implies that a revised model, which considers not only the
436 steady-state step density but also the transient-state step density changes after solution condition
437 changes, could predict better calcite growth rates. A systematic investigation of the effects of
438 pretreatment solution conditions on step densities of calcite seed crystals, which could help
439 design such models, is an important future direction of research.

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444 National Laboratory. We thank Dr. Namhey Lee and Dr. Kevin Knauss for helping with VSI
445 measurements and Dr. Mariëtte Wolthers for sharing the recalculated growth data of Nehrke et
446 al. (2007).

447 ***Appendix A. Supplementary material***

448 Supplementary data associated with this article can be found in the online version.

449

450 **List of tables**

451 **Table 1.** Solution compositions for calcite growth experiments and the calculated growth rates.
452 Concentration of ions ($[Ca^{2+}]$, $[CO_3^{2-}]$), activities of ions ($\{Ca^{2+}\}$, $\{CO_3^{2-}\}$), calcium/carbonate
453 activity ratios ($\{Ca^{2+}\}/\{CO_3^{2-}\}$), saturation indices (SI) with respect to calcite, ionic strength
454 values (IS), pH, and calculated calcite growth rates are listed.

455 **Table 2.** Experimental conditions and recalculated calcite growth rates of previous macroscopic
456 measurements.

457 **Table 3.** Experimental conditions, and the measured/calculated step velocities (v_s) and step
458 densities (ρ_{step}) of calcite in previous AFM studies and the current QCM-D study.

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469 **Table 1.**

Sample No.	[Ca ²⁺] (10 ⁻⁵ M)	[CO ₃ ²⁻] (10 ⁻⁵ M)	{Ca ²⁺ } (10 ⁻⁵)	{CO ₃ ²⁻ } (10 ⁻⁵)	{Ca ²⁺ }/ {CO ₃ ²⁻ }	SI ^a	IS (mM)	pH	Calcite growth rate (10 ⁻² μmol/m ² /s)
# 1	8.46	8.18	5.83	5.55	1.05	-0.01	8.82	8.22	-3.1 ± 0.2
# 2	8.69	8.42	5.96	5.69	1.05	0.01	9.05	8.22	1.4 ± 0.1
# 3	8.81	8.54	6.03	5.76	1.05	0.02	9.18	8.22	3.2 ± 0.7
# 4	8.94	8.68	6.11	5.83	1.05	0.03	9.31	8.22	4.7 ± 0.6
# 5	9.06	8.81	6.18	5.91	1.05	0.04	9.44	8.22	6.4 ± 0.3
# 6	9.17	8.94	6.24	5.98	1.05	0.05	9.57	8.22	7.6 ± 0.8
# 7	9.58	9.54	6.45	6.32	1.05	0.10	10.16	8.22	13 ± 0.1
# 8	12.6	12.6	8.09	7.96	1.02	0.30	13.24	8.21	30 ± 6.4
# 9	17.1	16.4	10.5	9.93	1.07	0.50	17.12	8.20	138 ± 15
# 10	22.3	23.7	12.7	13.1	0.97	0.70	24.18	8.18	226 ± 22

470 **Table 2.**

References	pH	{Ca ²⁺ }/{CO ₃ ²⁻ }	SI	Ionic strength (M)	T (°C)	Electrolytes	Reported growth rates with varied {Ca ²⁺ }/{CO ₃ ²⁻ } (R, μmol/m ² /s)	Recalculated growth rate at {Ca ²⁺ }/{CO ₃ ²⁻ } = 1 (R, μmol/m ² /s)
Gebrehiwet et al. (2012)	8.5	0.032	0.95	0.1	25	CaCl ₂ NaHCO ₃ KCl	0.69	1.16
Nehrke et al. (2007)	10.2	0.018	1.15	0.1	20	CaCl ₂	1.12	2.22
	10.2	0.022	0.70			K ₂ CO ₃ NaCl	1.05	1.80
Noiriel et al. (2012)	8.16	94.9	0.15	0.006- 0.017	22	CaCl ₂	0.0013	0.0023
	8.41	74.7	0.57			NaHCO ₃	0.0055	0.0107
	8.25	70.9	0.42				0.0032	0.0060
	8.20	115	0.82				0.0123	0.0280
Lin and Singer (2005)	9.01	1.0	0.72	0.1	25	CaCl ₂ Na ₂ CO ₃ KCl	2.38	2.38
Zuddas and Mucci (1998)		3.3 × 10 ³	0.15	0.1	25		0.0004	0.0018
		2.8 × 10 ³	0.23				0.0005	0.0022
		2.6 × 10 ³	0.25			CaCl ₂	0.0006	0.0026
		2.2 × 10 ³	0.33			Na ₂ CO ₃	0.0006	0.0027
		1.5 × 10 ³	0.48			NaCl	0.0006	0.0025
		1.3 × 10 ³	0.54			NaHCO ₃	0.0007	0.0027
		1.2 × 10 ³	0.60				0.0007	0.0026
		1.1 × 10 ³	0.61				0.0007	0.0027
	0.9 × 10 ³	0.70		0.0008	0.0029			

471

472 **Table 3.**

Reference s	pH	{Ca ²⁺ } / {CO ₃ ²⁻ }	SI	Ionic strength (M)	T (°C)	Electrolytes	Measured v_s (10 ⁻⁹ m/s)	Calculated v_s by SBGH model (10 ⁻⁹ m/s)	Calculated v_s by ion- by-ion model (10 ⁻⁹ m/s)	Measured ρ_{step} (μm^{-1})	Calculated ρ_{step} by ion-by-ion model (μm^{-1})
Bracco et al. (2013)	9.07	1.27	0.77	0.005	N/A	CaCl ₂ NaHCO ₃	10.10 (v_{sum} : 14.47) ^a	9.82	23.78	2.86	10.00
	8.68	1.02	0.41	0.004			7.89	5.08	8.20	1.41	5.26
Teng et al. (2000)	8.50	1.04	0.05	0.10	25	CaCl ₂ NaHCO ₃ NaCl	0.52	1.28	0.65	2.33	0.65
			0.09				1.18	1.78	1.25	2.27	1.19
			0.14				1.63	2.32	2.00	2.44	1.82
			0.15				1.89	2.42	2.24	1.96	2.00
			0.16				2.44	2.52	2.44	1.89	2.13
			0.17				2.52	2.62	2.60	4.00	2.27
			0.23				3.59	3.23	3.75	5.56	3.03
			0.30				5.18	3.93	5.31	7.14	4.00
			0.39				8.10	4.87	7.67	9.09	5.26
			0.46				9.46	5.64	9.84	11.11	6.25
0.56	13.10	6.84	13.50	11.11	7.14						
Ruiz- Agudo et al. (2011)	8.50	1.00	0.81	0.10	25	CaCl ₂ NaHCO ₃ NaCl	10.14 (v_{sum}) ^a	10.47	26.56	100.00	11.11
QCM-D	8.22	1.05	0.02	0.009	25	CaCl ₂ NaHCO ₃	1.99 ^b	0.78	0.25	5.11	0.26
	8.22	1.05	0.10	0.010			2.62 ^b	1.89	1.40	6.74	1.32
	8.21	1.02	0.30	0.013			3.10 ^b	3.93	5.31	11.66	4.00
	8.20	1.07	0.50	0.017			11.20 ^b	6.11	11.30	12.36	6.61

473 Note: v_s is the obtuse step velocity. ^a v_{sum} is the sum of obtuse and acute step velocity. ^b: The step velocities were not directly measured
474 but calculated using eqn. (4), as the step densities and growth rates were measured via VSI and QCM-D, respectively.

475 **Figure Captions**

476 **Figure 1.** Schematic plot of the flow through set up for QCM-D experiments.

477 **Figure 2.** QCM-D measurements of calcite seed crystal generation (Step I, $SI = 0.70$) and growth
478 in solutions with lower SI values (Step II, $SI = 0.01, 0.02, 0.03, 0.04, 0.05, 0.10, 0.30,$ and $0.50,$
479 Figures a-h). The blue markers indicate frequency changes shown on the left Y axis. The red
480 markers indicate dissipation changes shown on the right Y axis. Data in shaded areas were fitted
481 to calculate calcite growth rates, and the solid black lines were model fittings.

482 **Figure 3.** Calcite masses on sensors calculated from QCM-D and ICP-MS measurements

483 **Figure 4.** Calcite growth rates measured by QCM-D and other macroscopic techniques.

484 **Figure 5.** Calcite growth rates measured by QCM-D and AFM and predicted by the ion-by-ion
485 and the SBGH models.

486 **Figure 6.** Calcite growth rates measured by QCM-D as well as predicted by the ion-by-ion and
487 SBGH models.

488

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