Growth kinetics of step edges on celestite (001) surfaces as a function of temperature, saturation state, ionic strength, and aqueous strontium:sulfate ratio: An in-situ atomic force microscopy study

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Abstract

Step velocities on the celestite (001) surface have been measured as a function of temperature (23-45°C), saturation state ($S = 1.1 - 2.2$), ionic strength ($I = 0.01, 0.06$, and 0.1 M), and aqueous strontium:sulfate ratio ($r = 0.01 - 100$) using atomic force microscopy (AFM). Celestite growth hillocks were flanked by [010]-aligned step edges, which are polar, and step edges vicinal to $\langle 120 \rangle$, which are non-polar. [010] step velocities increased with temperature and saturation state, however step velocities did not vary significantly with ionic strength. Step velocities were non-linear with saturation state, suggesting a change in mechanism at high S as compared with low S . At constant S , the step velocities were maximized at $r = 1$ and decreased significantly at extreme r , demonstrating the governing role of solute stoichiometry. We successfully fit the step velocity data as a function of r using the Stack and Grantham (2010) nucleation and propagation model. Based on the results as a function of ionic strength and r , the mechanism at low S is likely ion-by-ion attachment to the step with an activation energy of $75 (\pm 10) \text{ kJ mol}^{-1}$. At high S the mechanism is a combination of the one at low S and possibly attachment of a neutral species such as an ion pair with an activation energy of $43 (\pm 9) \text{ kJ mol}^{-1}$.

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1. Introduction

Mineral growth and dissolution plays a significant role in the environmental cycling of elements and ions, such as sulfate, which is the second most prevalent anion in ocean water. Removal of sulfate from ocean waters can occur via precipitation of sulfate minerals, including the isostructural minerals barite (BaSO_4), celestite (SrSO_4), and the intermediate members ($\text{Ba}_x\text{Sr}_{1-x}\text{SO}_4$), as many oceanic and pore waters are supersaturated with respect to barite and celestite (Bernstein et al., 1992; Monnin, 1999; Hoareau et al., 2010). Although a complete solid solution exists between barite and celestite, most minerals found in this series are either barium-rich or strontium-rich, likely due to the large difference in solubility products for the two minerals (Hanor, 2000). Due to these differences in solubility, celestite primarily forms where strontium concentrations are much greater than barium concentrations or when there is a process discriminating against barium co-precipitation (Hanor, 2000). Under these conditions, growth and dissolution of celestite will play a role in controlling both the sulfate and strontium compositions in the environment.

Predicting mineral growth and dissolution rates in a wide variety of geologic settings is an important objective in the modeling of geochemical reactions in the subsurface. However, the expressions used as “rate laws” in geochemical reaction modeling codes often are based on reaction affinity as the primary driver for dissolution or growth (Bethke, 1996). While affinity is an important quantity which forms a thermodynamic foundation for determining whether a reaction will proceed as written, affinity alone does not account for the observed change in rate of mineralization with solute stoichiometry (e.g., the calcium:carbonate ratio has been shown to affect calcite growth rates (Bracco et al., 2013)) and mechanisms for these processes may change as the solution composition varies (i.e., changes in pH, reaction affinity, ionic strength, foreign

ion composition). Celestite, belonging to the barite-group minerals, is a sparingly-soluble, ionically-bonded mineral with the potential to serve as a model mineral for this group, but surprisingly little has been reported on its growth mechanism.

Despite the reactivity of celestite at room temperature, the number of studies on celestite growth and dissolution have been quite limited. Experiments on the bulk dissolution kinetics of isostructural orthorhombic sulfates (barite, celestite, and anglesite) indicate, under similar conditions, that celestite dissolution rates are greater than anglesite dissolution rates, which in turn are greater than barite dissolution rates (Dove and Czank, 1995). This suggests dissolution rates are limited by the relative solvation affinity of the divalent metal ion, something which has been observed for sparingly-soluble AB-type carbonate minerals (Duckworth and Martin, 2004). Dissolution of the celestite (001) surface, a perfect cleavage face, has also been found to occur via the same mechanism as other sparingly soluble minerals, such as barite, with etch pit nucleation and mono- and bilayer step retreat occurring simultaneously under far from equilibrium solution conditions (Seo and Shindo, 1994; Shindo et al., 1999; Bose et al., 2008). Etch pit nucleation took place exclusively at high undersaturation so at near-equilibrium conditions, dissolution only occurred by mono- and bilayer step retreat (Bose et al., 2008). However, dissolution rates followed a non-linear function of solution saturation state which Bose et al. (2008) attributed in part to the presence of impurities, but which also suggests that basic crystal growth and dissolution models may not be sufficient for explaining celestite dissolution, particularly in light of the change in mechanism near-equilibrium. It is unknown if similar non-linear behavior occurs during celestite growth and if so, how these non-linearities can be modeled. Risthaus et al. (2001) found celestite grows via a spiral mechanism at room temperature and low supersaturations, similar to barite, though the growth hillocks for the two

minerals were shaped differently, a fact that was attributed to differences in interfacial tension of the respective mineral-water interfaces.

In contrast to the literature on celestite, there have been many studies on barite which demonstrate, among other features, that barite growth is affected by a variety of factors, including temperature (Higgins et al., 2000), saturation state (Bosbach et al., 1998; Pina et al., 1998a; Pina et al., 1998b; Higgins et al., 2000), ionic strength (Risthaus et al., 2001; Becker et al., 2002; Kowacz and Putnis, 2008; Godinho and Stack, 2015), and aqueous cation-to-anion ratio, r ($\{Ba^{2+}\}:\{SO_4^{2-}\}$) (Kowacz et al., 2007), where $\{i\}$ is the activity of the i^{th} species. Based on these results on barite, there are a number of important gaps in our understanding of celestite growth such as the effect of temperature, saturation state, ionic strength (I), and r . Recent studies on the effects of r on barite, magnesite, and calcite growth demonstrate that step velocities are maximized at r close to 1, or between 1-10, even for minerals with very large differences in cation hydration structure such as calcite and magnesite (Kowacz et al., 2007; Perdikouri et al., 2009; Larsen et al., 2010; Bracco et al., 2012; Gebrehiwet et al., 2012; Bracco et al., 2014). As before, it is unknown if r affects celestite growth in a manner different than growth of barite due to differences in cation hydration structure. The effect of I on celestite growth rates is also of interest, as barite island spreading rates (Kowacz and Putnis, 2008), step velocities (Risthaus et al., 2001; Becker et al., 2002), and crystal growth rates, as well of growth rates of the (001) face, increase with ionic strength (Godinho and Stack, 2015). To address some of the fundamental deficiencies in our understanding of celestite growth, in this study we investigate the influence of saturation state, I , temperature, and aqueous r on celestite growth via a spiral growth mechanism using *in situ* atomic force microscopy (AFM) by measuring bilayer [010] step velocities on the (001) celestite surface.

2. Methods

2.1. Materials and Solution Preparation

Optically clear, grayish-blue, freshly cleaved celestite samples, containing minor and trace impurities, were used (electronic annex Table 1). Celestite samples were analyzed for trace metal impurities by dissolving a 100 mg sample in 100 mL of a 50 mM EDTA solution at pH=13 with the subsequent solution analyzed by inductively-coupled plasma optical emission spectroscopy (ICP-OES). The complete details of this procedure can be found in the electronic annex and are adapted from Averyt et al. (2003). The most abundant cation impurity was calcium at 0.11 mol%. Aqueous supersaturated solutions for AFM experiments were prepared using stock solutions prepared from high-purity, trace metal grade reagents (of at least 99.99% purity). Stock solutions included $\text{Sr}(\text{NO}_3)_2$ and Na_2SO_4 , with the molarities for each experiment specified in Table 1 and either nominally 0.01 M or 0.1 M NaNO_3 , and deionized water (resistivity = $18.2 \text{ M}\Omega \cdot \text{cm}$; Table 1). The molarity of the strontium nitrate and sodium sulfate stock solutions was determined using ICP-OES (Table 1). PHREEQC was used to calculate solution speciation using the minteq.v4 database (Parkhurst and Appelo, 1999) which included a K_{sp} for celestite of $10^{-6.62}$ at 23°C , $10^{-6.61}$ at 35°C , and $10^{-6.60}$ at 45°C . The other databases available in PHREEQC utilize similar K_{sp} values, however the LLNL database used a K_{sp} of $10^{-5.6771}$ and predicts celestite should dissolve even at conditions where considerable growth on the (001) surface was observed. Solution compositions (calculated at 23, 26, 35, and 45°C) are given in Table 1 ($[i]$ and $\{i\}$ denote molar concentration and activity, respectively, of i^{th} species). Temperature variations based on the precision of the temperature controller were a few hundredths of a degree, though we consider $\pm 0.5^\circ\text{C}$ to be the uncertainty in temperature due to the possibility of inaccuracies in the thermocouple calibration. This temperature uncertainty had

127 a negligible effect on solution speciation calculations. Atmospheric CO₂ was not removed from
 128 solutions as it was not predicted to significantly affect saturation states or lead to appreciable
 129 concentrations of carbonate or bicarbonate in solution. The saturation states ($S = \sqrt{\frac{\{\text{Sr}^{2+}\}\{\text{SO}_4^{2-}\}}{K_{sp}}}$)
 130 studied at constant ionic strength ($I = 0.01\text{-}0.02$ M) and $r = 0.7\text{-}0.8$, ranged from 0.1 to 0.6 at 23-
 131 26 °C, 0.1 to 0.5 at 35 °C, and 0.1 to 0.4 at 45 °C. For experiments to determine the effect of r on
 132 growth rates, r was varied from approximately 0.01 to 100 at constant S ($S = 1.6, 1.9$, and 2.2)
 133 and constant I ($I = 0.06$ M). We were unable to carry out experiments at r greater than 120 or less
 134 than 0.0089 without introducing significant changes in ionic strength. For the ionic strength
 135 dependence experiments, NaNO₃ was used to maintain an ionic strength at values of 0.01 M,
 136 0.06 M, and 0.1 M at 26 °C and $r = 0.6\text{-}0.8$.

137 Table 1: Solution compositions for the AFM experiments.

$[\text{Sr}^{2+}]_{\text{stock}}$ (M)	$[\text{SO}_4^{2-}]_{\text{stock}}$ (M)	T (°C)	mL $\text{Sr}(\text{NO}_3)_2$	mL Na_2SO_4	mL NaNO_3	mL H_2O	S	$[\text{Sr}^{2+}]$ (M)	$[\text{SO}_4^{2-}]$ (M)	$\{\text{Sr}^{2+}\}$ (M)	$\{\text{SO}_4^{2-}\}$ (M)	r	I (M)	v (nm s ⁻¹)
$1.02 (\pm 0.02) \times 10^{-2}$	$1.18 (\pm 0.08) \times 10^{-2}$	23	15.0	18.6	66.4	0.0	2.0	$1.32 (\pm 0.02) \times 10^{-3}$	$1.94 (\pm 0.13) \times 10^{-3}$	$7.90 (\pm 0.12) \times 10^{-4}$	$1.16 (\pm 0.08) \times 10^{-3}$	$6.80 (\pm 0.48) \times 10^{-1}$	0.017	0.470 (± 0.090)
$1.02 (\pm 0.02) \times 10^{-2}$	$1.18 (\pm 0.08) \times 10^{-2}$	23	14.0	17.4	68.6	0.0	1.9	$1.24 (\pm 0.02) \times 10^{-3}$	$1.83 (\pm 0.13) \times 10^{-3}$	$7.46 (\pm 0.11) \times 10^{-4}$	$1.10 (\pm 0.08) \times 10^{-3}$	$6.80 (\pm 0.48) \times 10^{-1}$	0.017	0.295 (± 0.046)
$1.02 (\pm 0.02) \times 10^{-2}$	$1.18 (\pm 0.08) \times 10^{-2}$	23	13.0	16.1	70.9	0.0	1.7	$1.16 (\pm 0.02) \times 10^{-3}$	$1.70 (\pm 0.12) \times 10^{-3}$	$7.01 (\pm 0.11) \times 10^{-4}$	$1.03 (\pm 0.07) \times 10^{-3}$	$6.83 (\pm 0.48) \times 10^{-1}$	0.016	0.189 (± 0.055)
$1.02 (\pm 0.02) \times 10^{-2}$	$1.18 (\pm 0.08) \times 10^{-2}$	23	12.0	14.9	73.1	0.0	1.6	$1.08 (\pm 0.02) \times 10^{-3}$	$1.58 (\pm 0.11) \times 10^{-3}$	$6.53 (\pm 0.10) \times 10^{-4}$	$9.57 (\pm 0.66) \times 10^{-4}$	$6.83 (\pm 0.48) \times 10^{-1}$	0.016	0.133 (± 0.058)
$1.02 (\pm 0.02) \times 10^{-2}$	$1.18 (\pm 0.08) \times 10^{-2}$	23	11.0	13.6	75.4	0.0	1.5	$9.94 (\pm 0.15) \times 10^{-4}$	$1.45 (\pm 0.10) \times 10^{-3}$	$6.08 (\pm 0.09) \times 10^{-4}$	$8.85 (\pm 0.61) \times 10^{-4}$	$6.87 (\pm 0.48) \times 10^{-1}$	0.015	0.0498 (± 0.024)
$1.02 (\pm 0.02) \times 10^{-2}$	$1.18 (\pm 0.08) \times 10^{-2}$	23	10.0	12.4	77.6	0.0	1.4	$9.10 (\pm 0.14) \times 10^{-4}$	$1.33 (\pm 0.09) \times 10^{-3}$	$5.60 (\pm 0.08) \times 10^{-4}$	$8.16 (\pm 0.56) \times 10^{-4}$	$6.87 (\pm 0.48) \times 10^{-1}$	0.015	0.0252 (± 0.0087)
$1.02 (\pm 0.02) \times 10^{-2}$	$1.18 (\pm 0.08) \times 10^{-2}$	23	9.00	11.2	79.8	0.0	1.3	$8.25 (\pm 0.12) \times 10^{-4}$	$1.20 (\pm 0.08) \times 10^{-3}$	$5.11 (\pm 0.08) \times 10^{-4}$	$7.45 (\pm 0.51) \times 10^{-4}$	$6.85 (\pm 0.48) \times 10^{-1}$	0.014	0.00609 (± 0.011)
$1.02 (\pm 0.02) \times 10^{-2}$	$1.18 (\pm 0.08) \times 10^{-2}$	23	8.00	9.90	82.1	0.0	1.1	$7.39 (\pm 0.11) \times 10^{-4}$	$1.07 (\pm 0.07) \times 10^{-3}$	$4.61 (\pm 0.07) \times 10^{-4}$	$6.66 (\pm 0.46) \times 10^{-4}$	$6.91 (\pm 0.48) \times 10^{-1}$	0.014	-0.00614 (± 0.0077)
$1.02 (\pm 0.02) \times 10^{-2}$	$1.18 (\pm 0.08) \times 10^{-2}$	35	14.0	17.4	68.6	0.0	1.8	$1.23 (\pm 0.02) \times 10^{-3}$	$1.81 (\pm 0.11) \times 10^{-3}$	$7.32 (\pm 0.11) \times 10^{-4}$	$1.08 (\pm 0.07) \times 10^{-3}$	$6.79 (\pm 0.48) \times 10^{-1}$	0.016	0.446 (± 0.081)
$1.02 (\pm 0.02) \times 10^{-2}$	$1.18 (\pm 0.08) \times 10^{-2}$	35	13.0	16.1	70.9	0.0	1.7	$1.15 (\pm 0.02) \times 10^{-3}$	$1.68 (\pm 0.12) \times 10^{-3}$	$6.89 (\pm 0.10) \times 10^{-4}$	$1.01 (\pm 0.07) \times 10^{-3}$	$6.38 (\pm 0.48) \times 10^{-1}$	0.016	0.250 (± 0.047)
$1.02 (\pm 0.02) \times 10^{-2}$	$1.18 (\pm 0.08) \times 10^{-2}$	35	12.0	14.9	73.1	0.0	1.6	$1.07 (\pm 0.02) \times 10^{-3}$	$1.57 (\pm 0.11) \times 10^{-3}$	$6.44 (\pm 0.10) \times 10^{-4}$	$9.43 (\pm 0.07) \times 10^{-4}$	$6.83 (\pm 0.48) \times 10^{-1}$	0.016	0.106 (± 0.026)
$1.02 (\pm 0.02) \times 10^{-2}$	$1.18 (\pm 0.08) \times 10^{-2}$	35	11.0	13.6	75.4	0.0	1.5	$9.88 (\pm 0.15) \times 10^{-4}$	$1.44 (\pm 0.10) \times 10^{-3}$	$5.98 (\pm 0.09) \times 10^{-4}$	$8.70 (\pm 0.06) \times 10^{-4}$	$6.88 (\pm 0.48) \times 10^{-1}$	0.015	0.0636 (± 0.024)
$1.02 (\pm 0.02) \times 10^{-2}$	$1.18 (\pm 0.08) \times 10^{-2}$	35	10.0	12.4	77.6	0.0	1.3	$9.05 (\pm 0.14) \times 10^{-4}$	$1.32 (\pm 0.09) \times 10^{-3}$	$5.51 (\pm 0.08) \times 10^{-4}$	$8.02 (\pm 0.06) \times 10^{-4}$	$6.87 (\pm 0.48) \times 10^{-1}$	0.015	0.0465 (± 0.035)
$1.02 (\pm 0.02) \times 10^{-2}$	$1.02 (\pm 0.01) \times 10^{-2}$	35	9.00	11.2	79.8	0.0	1.1	$8.29 (\pm 0.12) \times 10^{-4}$	$1.03 (\pm 0.01) \times 10^{-3}$	$5.12 (\pm 0.08) \times 10^{-4}$	$6.38 (\pm 0.07) \times 10^{-4}$	$8.04 (\pm 0.15) \times 10^{-1}$	0.014	0.0117 (± 0.036)
$1.02 (\pm 0.02) \times 10^{-2}$	$1.02 (\pm 0.01) \times 10^{-2}$	45	9.00	11.2	79.8	0.0	1.1	$8.26 (\pm 0.12) \times 10^{-4}$	$1.03 (\pm 0.01) \times 10^{-3}$	$5.06 (\pm 0.08) \times 10^{-4}$	$6.29 (\pm 0.07) \times 10^{-4}$	$8.05 (\pm 0.15) \times 10^{-1}$	0.014	0.891 (± 0.079)
$1.02 (\pm 0.02) \times 10^{-2}$	$1.02 (\pm 0.01) \times 10^{-2}$	45	10.0	12.4	77.6	0.0	1.2	$9.12 (\pm 0.14) \times 10^{-4}$	$1.13 (\pm 0.13) \times 10^{-3}$	$5.55 (\pm 0.08) \times 10^{-4}$	$6.88 (\pm 0.08) \times 10^{-4}$	$8.07 (\pm 0.15) \times 10^{-1}$	0.014	0.633 (± 0.15)
$1.02 (\pm 0.02) \times 10^{-2}$	$1.02 (\pm 0.01) \times 10^{-2}$	45	11.0	13.6	75.4	0.0	1.3	$9.96 (\pm 0.15) \times 10^{-4}$	$1.23 (\pm 0.12) \times 10^{-3}$	$6.03 (\pm 0.09) \times 10^{-4}$	$7.46 (\pm 0.09) \times 10^{-4}$	$8.08 (\pm 0.15) \times 10^{-1}$	0.015	0.233 (± 0.027)
$1.02 (\pm 0.02) \times 10^{-2}$	$1.02 (\pm 0.01) \times 10^{-2}$	45	12.0	14.9	73.1	0.0	1.4	$1.08 (\pm 0.02) \times 10^{-3}$	$1.34 (\pm 0.15) \times 10^{-3}$	$6.49 (\pm 0.20) \times 10^{-4}$	$8.08 (\pm 0.10) \times 10^{-4}$	$8.03 (\pm 0.15) \times 10^{-1}$	0.015	0.0465 (± 0.075)
$1.02 (\pm 0.02) \times 10^{-2}$	$1.02 (\pm 0.01) \times 10^{-2}$	45	13.0	16.1	70.9	0.0	1.5	$1.16 (\pm 0.02) \times 10^{-3}$	$1.44 (\pm 0.02) \times 10^{-3}$	$6.95 (\pm 0.10) \times 10^{-4}$	$8.64 (\pm 0.10) \times 10^{-4}$	$8.04 (\pm 0.15) \times 10^{-1}$	0.015	0.0162 (± 0.054)
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	2.60	3.70	93.7	0.0	1.9	$2.27 (\pm 0.05) \times 10^{-3}$	$3.01 (\pm 0.08) \times 10^{-3}$	$8.20 (\pm 0.18) \times 10^{-4}$	$1.09 (\pm 0.03) \times 10^{-3}$	$7.54 (\pm 0.26) \times 10^{-1}$	0.11	0.544 (± 0.13)
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	2.30	3.30	94.4	0.0	1.7	$2.02 (\pm 0.04) \times 10^{-3}$	$2.70 (\pm 0.73) \times 10^{-3}$	$7.32 (\pm 0.16) \times 10^{-4}$	$9.77 (\pm 0.26) \times 10^{-4}$	$7.48 (\pm 0.26) \times 10^{-1}$	0.11	0.314 (± 0.11)
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	2.10	3.00	94.9	0.0	1.6	$1.85 (\pm 0.04) \times 10^{-3}$	$2.46 (\pm 0.66) \times 10^{-3}$	$6.72 (\pm 0.15) \times 10^{-4}$	$8.93 (\pm 0.24) \times 10^{-4}$	$7.53 (\pm 0.26) \times 10^{-1}$	0.11	0.240

$0.02) \times 10^{-1}$	$0.01) \times 10^{-1}$							$\times 10^{-3}$	$\times 10^{-3}$	$\times 10^{-4}$	$\times 10^{-4}$	$\times 10^{-1}$		(± 0.067)
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	1.90	2.70	95.4	0.0	1.4	$1.68 (\pm 0.04) \times 10^{-3}$	$2.22 (\pm 0.06) \times 10^{-3}$	$6.13 (\pm 0.13) \times 10^{-4}$	$8.08 (\pm 0.22) \times 10^{-4}$	$7.58 (\pm 0.26) \times 10^{-1}$	0.11	$0.150 (\pm 0.031)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	1.70	2.40	95.9	0.0	1.3	$1.51 (\pm 0.03) \times 10^{-3}$	$1.98 (\pm 0.05) \times 10^{-3}$	$5.52 (\pm 0.12) \times 10^{-4}$	$7.22 (\pm 0.20) \times 10^{-4}$	$7.64 (\pm 0.26) \times 10^{-1}$	0.11	$0.0557 (\pm 0.041)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	1.50	2.10	96.4	0.0	1.1	$1.34 (\pm 0.03) \times 10^{-3}$	$1.74 (\pm 0.05) \times 10^{-3}$	$4.90 (\pm 0.11) \times 10^{-4}$	$6.36 (\pm 0.17) \times 10^{-4}$	$7.72 (\pm 0.27) \times 10^{-1}$	0.11	$0.0421 (\pm 0.034)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	2.00	3.00	45.0	50.0	1.9	$1.82 (\pm 0.04) \times 10^{-3}$	$2.58 (\pm 0.07) \times 10^{-3}$	$7.90 (\pm 0.17) \times 10^{-4}$	$1.12 (\pm 0.03) \times 10^{-3}$	$7.06 (\pm 0.27) \times 10^{-1}$	0.060	$0.511 (\pm 0.11)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	1.70	2.70	47.0	48.6	1.7	$1.56 (\pm 0.03) \times 10^{-3}$	$2.34 (\pm 0.06) \times 10^{-3}$	$6.74 (\pm 0.15) \times 10^{-4}$	$1.01 (\pm 0.03) \times 10^{-3}$	$6.67 (\pm 0.25) \times 10^{-1}$	0.060	$0.266 (\pm 0.050)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	1.55	2.55	49.0	46.9	1.5	$1.42 (\pm 0.03) \times 10^{-3}$	$2.21 (\pm 0.06) \times 10^{-3}$	$6.13 (\pm 0.13) \times 10^{-4}$	$9.51 (\pm 0.26) \times 10^{-4}$	$6.44 (\pm 0.23) \times 10^{-1}$	0.060	$0.121 (\pm 0.067)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	1.40	2.40	49.0	47.2	1.4	$1.29 (\pm 0.03) \times 10^{-3}$	$2.09 (\pm 0.06) \times 10^{-3}$	$5.58 (\pm 0.12) \times 10^{-4}$	$9.02 (\pm 0.24) \times 10^{-4}$	$6.18 (\pm 0.22) \times 10^{-1}$	0.060	$0.0975 (\pm 0.021)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	1.20	2.20	51.0	45.6	1.3	$1.11 (\pm 0.02) \times 10^{-3}$	$1.92 (\pm 0.05) \times 10^{-3}$	$4.78 (\pm 0.11) \times 10^{-4}$	$8.26 (\pm 0.22) \times 10^{-4}$	$5.78 (\pm 0.20) \times 10^{-1}$	0.061	$0.0219 (\pm 0.031)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	1.10	2.00	53.0	43.9	1.2	$1.02 (\pm 0.02) \times 10^{-3}$	$1.75 (\pm 0.05) \times 10^{-3}$	$4.37 (\pm 0.10) \times 10^{-4}$	$7.48 (\pm 0.20) \times 10^{-4}$	$5.85 (\pm 0.20) \times 10^{-1}$	0.062	$-0.000768 (\pm 0.009)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	0.26	20.0	0.0	79.7	1.6	$1.66 (\pm 0.04) \times 10^{-4}$	$1.86 (\pm 0.05) \times 10^{-2}$	$7.26 (\pm 0.16) \times 10^{-5}$	$8.14 (\pm 0.22) \times 10^{-3}$	$8.92 (\pm 0.31) \times 10^{-3}$	0.058	$0.0547 (\pm 0.032)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	0.40	11.4	27.0	61.2	1.6	$3.03 (\pm 0.07) \times 10^{-4}$	$1.04 (\pm 0.03) \times 10^{-2}$	$1.31 (\pm 0.03) \times 10^{-4}$	$4.48 (\pm 0.12) \times 10^{-3}$	$2.92 (\pm 0.10) \times 10^{-2}$	0.061	$0.125 (\pm 0.038)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	0.70	6.00	42.0	51.3	1.6	$5.93 (\pm 0.13) \times 10^{-4}$	$5.35 (\pm 0.14) \times 10^{-3}$	$2.56 (\pm 0.06) \times 10^{-4}$	$2.31 (\pm 0.06) \times 10^{-3}$	$1.11 (\pm 0.039) \times 10^{-1}$	0.061	$0.177 (\pm 0.034)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	2.00	2.00	50.0	46.0	1.6	$1.86 (\pm 0.04) \times 10^{-3}$	$1.71 (\pm 0.05) \times 10^{-3}$	$8.00 (\pm 0.18) \times 10^{-4}$	$7.38 (\pm 0.20) \times 10^{-4}$	$1.08 (\pm 0.038) \times 10^0$	0.062	$0.323 (\pm 0.14)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	6.00	0.70	42.0	51.3	1.6	$5.78 (\pm 0.13) \times 10^{-3}$	$5.46 (\pm 0.15) \times 10^{-4}$	$2.48 (\pm 0.06) \times 10^{-3}$	$2.35 (\pm 0.06) \times 10^{-4}$	$1.06 (\pm 0.037) \times 10^1$	0.062	$0.254 (\pm 0.064)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	11.5	0.40	25.0	63.1	1.6	$1.13 (\pm 0.03) \times 10^{-2}$	$2.78 (\pm 0.08) \times 10^{-4}$	$4.87 (\pm 0.19) \times 10^{-3}$	$1.20 (\pm 0.32) \times 10^{-4}$	$4.06 (\pm 0.14) \times 10^1$	0.061	$0.0950 (\pm 0.040)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	20.0	0.27	0.0	79.7	1.6	$2.00 (\pm 0.04) \times 10^{-2}$	$1.60 (\pm 0.04) \times 10^{-4}$	$8.57 (\pm 0.19) \times 10^{-3}$	$6.88 (\pm 0.19) \times 10^{-5}$	$1.25 (\pm 0.043) \times 10^2$	0.062	$0.0546 (\pm 0.082)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	2.90	2.90	45.0	49.2	2.2	$2.65 (\pm 0.06) \times 10^{-3}$	$2.44 (\pm 0.07) \times 10^{-3}$	$1.14 (\pm 0.03) \times 10^{-3}$	$1.05 (\pm 0.03) \times 10^{-3}$	$1.09 (\pm 0.038) \times 10^0$	0.062	$1.02 (\pm 0.19)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	6.00	1.45	40.0	52.6	2.2	$5.71 (\pm 0.13) \times 10^{-3}$	$1.13 (\pm 0.03) \times 10^{-3}$	$2.45 (\pm 0.05) \times 10^{-3}$	$4.84 (\pm 0.13) \times 10^{-4}$	$5.05 (\pm 0.18) \times 10^0$	0.062	$0.858 (\pm 0.12)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	9.10	1.00	32.0	57.9	2.2	$8.80 (\pm 0.19) \times 10^{-3}$	$7.28 (\pm 0.20) \times 10^{-4}$	$3.76 (\pm 0.08) \times 10^{-3}$	$3.11 (\pm 0.08) \times 10^{-4}$	$1.21 (\pm 0.042) \times 10^1$	0.062	$0.723 (\pm 0.056)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	18.0	0.60	6.00	75.4	2.2	$1.78 (\pm 0.04) \times 10^{-2}$	$3.66 (\pm 0.10) \times 10^{-4}$	$7.61 (\pm 0.17) \times 10^{-3}$	$1.56 (\pm 0.04) \times 10^{-4}$	$4.87 (\pm 0.17) \times 10^1$	0.062	$0.117 (\pm 0.030)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	1.45	6.00	42.0	50.6	2.2	$1.23 (\pm 0.03) \times 10^{-3}$	$5.25 (\pm 0.14) \times 10^{-3}$	$5.25 (\pm 0.12) \times 10^{-4}$	$2.24 (\pm 0.06) \times 10^{-3}$	$2.35 (\pm 0.082) \times 10^{-1}$	0.063	$0.771 (\pm 0.18)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	1.00	9.10	34.0	55.9	2.2	$7.94 (\pm 0.17) \times 10^{-4}$	$8.10 (\pm 0.22) \times 10^{-3}$	$3.39 (\pm 0.08) \times 10^{-4}$	$3.46 (\pm 0.09) \times 10^{-3}$	$9.80 (\pm 0.34) \times 10^{-2}$	0.062	$0.449 (\pm 0.13)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	18.0	0.60	10.0	71.4	2.2	$4.00 (\pm 0.09) \times 10^{-4}$	$1.65 (\pm 0.04) \times 10^{-2}$	$1.71 (\pm 0.04) \times 10^{-4}$	$7.01 (\pm 0.19) \times 10^{-3}$	$2.43 (\pm 0.085) \times 10^{-2}$	0.063	$0.298 (\pm 0.06)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	2.40	2.40	49.0	46.2	1.8	$2.22 (\pm 0.05) \times 10^{-3}$	$2.04 (\pm 0.06) \times 10^{-3}$	$9.44 (\pm 0.21) \times 10^{-4}$	$8.68 (\pm 0.23) \times 10^{-4}$	$1.09 (\pm 0.038) \times 10^{-1}$	0.063	0.668

$0.02) \times 10^{-1}$	$0.01) \times 10^{-1}$							$\times 10^{-3}$	$\times 10^{-3}$	$\times 10^{-4}$	$\times 10^{-4}$	$\times 10^0$		(± 0.11)
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	1.20	5.00	44.0	49.8	1.9	$1.04 (\pm 0.23) \times 10^{-3}$	$4.39 (\pm 0.12) \times 10^{-3}$	$4.46 (\pm 0.10) \times 10^{-4}$	$1.88 (\pm 0.05) \times 10^{-3}$	$2.37 (\pm 0.083) \times 10^{-1}$	0.061	$0.555 (\pm 0.10)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	0.80	7.50	40.0	51.7	1.8	$6.55 (\pm 0.14) \times 10^{-4}$	$6.77 (\pm 0.18) \times 10^{-3}$	$2.79 (\pm 0.06) \times 10^{-4}$	$2.89 (\pm 0.08) \times 10^{-3}$	$9.68 (\pm 0.34) \times 10^{-2}$	0.063	$0.373 (\pm 0.037)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	0.50	14.0	24.0	61.5	1.9	$3.58 (\pm 0.08) \times 10^{-4}$	$1.27 (\pm 0.03) \times 10^{-2}$	$1.54 (\pm 0.34) \times 10^{-4}$	$5.47 (\pm 0.15) \times 10^{-3}$	$2.81 (\pm 0.098) \times 10^{-2}$	0.061	$0.276 (\pm 0.067)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	14.0	0.50	24.0	61.5	1.8	$1.38 (\pm 0.03) \times 10^{-2}$	$3.30 (\pm 0.09) \times 10^{-4}$	$5.84 (\pm 0.13) \times 10^{-3}$	$1.40 (\pm 0.04) \times 10^{-4}$	$4.17 (\pm 0.15) \times 10^1$	0.063	$0.257 (\pm 0.049)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	7.80	0.80	36.0	55.4	1.9	$7.56 (\pm 0.17) \times 10^{-3}$	$5.98 (\pm 0.16) \times 10^{-4}$	$3.24 (\pm 0.07) \times 10^{-3}$	$2.56 (\pm 0.07) \times 10^{-4}$	$1.26 (\pm 0.044) \times 10^1$	0.062	$0.454 (\pm 0.062)$
$1.07 (\pm 0.02) \times 10^{-1}$	$1.01 (\pm 0.01) \times 10^{-1}$	26	5.00	1.20	44.0	49.8	1.9	$4.77 (\pm 0.11) \times 10^{-3}$	$9.56 (\pm 0.26) \times 10^{-4}$	$2.04 (\pm 0.05) \times 10^{-3}$	$4.08 (\pm 0.11) \times 10^{-4}$	$4.99 (\pm 0.17) \times 10^0$	0.062	$0.516 (\pm 0.068)$

2.2. AFM Experiments

Samples of celestite were cleaved using a razor blade with gentle tapping, exposing the (001) surface, which then was subjected to a stream of nitrogen gas to remove larger dust particles generated during the cleaving process. The sample was then fixed in a hydrothermal atomic force microscope (HAFM) with a titanium or gold wire (Higgins et al., 1998) and briefly exposed to deionized water to clean the surface. Experiments were performed *in situ* at room temperature (23-26°C; temperature for individual experiments noted in Table 1), 35, and 45 °C and 1.7 atm (N₂) in contact mode using platinum iridium double coated cantilevers with a nominal force constant in the range of 0.02 - 0.77 N/m (Nanoworld – CONTPt) in a constant flow-through condition. Cantilever loads were kept as small as was practicable and tests for tip influences on localized step growth did not indicate any significant effects due to the scanning tip. A solution flow rate of 10 mL/hr (~1 mL internal volume of the fluid cell) was utilized, as celestite growth rates were found to be independent of flow rate at each of the temperatures we utilized (electronic annex Figure 1). Changes in r and S did not significantly affect the flow rate at which growth became independent of flow.

Step velocities were determined after a steady-state step velocity had been reached following introduction of a new solution, which usually took place after approximately thirty minutes. Data for step velocity determinations were collected by disabling the slow scan axis at the apex of a spiral growth hillock and collecting four to ten position vs. time “images”. This enabled us to measure the angle that the trace of the step made with respect to the position axis over time, which can be related to the step velocity using the following equation: $v_s = \frac{R_s A}{L \tan \theta}$ where R_s is the scan rate (lines/second), A is the scan size (nm), L is the number of lines comprising the position vs. time image (lines/image), and θ is the angle with respect to the

horizontal (position) axis of the “image” (Teng et al., 2000). Scan rates varied from 0.2 – 6.0 Hz depending on the step velocity. Step velocities were averaged on both sides of the growth hillock (by symmetry, opposing [010] bilayer steps have the same structure and will have the same step velocity) to cancel any effects of drift. Averages and standard deviations are derived from ~8-10 measurements at the given conditions. Step lengths were sufficiently long to ensure growth rates were in a length independent step velocity regime (Higgins and Hu, 2006).

3. Results

3.1. Growth Hillock Morphology

The dominant growth mechanism for the solution conditions studied was spiral growth (Figure 1). At the highest S ($S=2.2$ and $T=26^{\circ}\text{C}$) used for step velocity analysis, two-dimensional nucleation was not observed, though it was observed at $T=50^{\circ}\text{C}$. At 26°C , two-dimensional nucleation was observed at $S > 2.3$, similar to results reported by Risthaus et al. (2001). The steps on the growth hillocks were primarily bilayer steps, though monolayer steps were observed very close to the center of the spiral. The growth hillocks were a mixture of different types including single-sourced single spirals, single-sourced multi spirals, Frank-Reed sourced spirals, and multi-sourced spirals, though single-sourced single spirals were rare, particularly at high S . Since the step density within a growth hillock depends on the details of the defect outcropping, the wide array of these outcroppings that was observed prevented us from measuring step densities and surface growth rates as a function of solution composition exclusively at single-sourced single spirals. However, regardless of the spiral source, all the hillocks were comprised of steps aligned along the [010] direction and steps vicinal to the $\langle 120 \rangle$ directions (referred to throughout as $\langle 120 \rangle_v$), though the [010] steps were much longer than the

183 $\langle 120 \rangle_v$ steps under all conditions, indicating $\langle 120 \rangle_v$ steps were migrating faster than the $[010]$
 184 step.

185

186

187

188 Figure 1: Monolayer $\langle 120 \rangle_v$ and bilayer $[010]$ and $\langle 120 \rangle_v$ steps on a celestite growth hillock with
 189 the step directions marked. Conditions for this experiment were $S=1.7$, $T=35^\circ\text{C}$, $r=0.7$, and
 190 $I=0.02\text{ M}$. The AFM image size is 700 nm by 700 nm.

191 Figure 1 shows the center of a growth spiral with the $[010]$ and $\langle 120 \rangle_v$ bilayer and
 192 monolayer step directions labeled. The morphology of the hillock shown in Figure 1 is consistent
 193 with that reported previously (Risthaus et al., 2001). Furthermore, unlike barite at low ionic
 194 strength, growth hillocks on celestite at low ionic strength are bounded by both the $\langle 120 \rangle_v$ and
 195 the $[010]$ steps, similar to the appearance of barite growth hillocks at high ionic strength ($I = 0.75$
 196 m) (Risthaus et al., 2001). To confirm the step orientations of the $\langle 120 \rangle_v$ steps, the angle (θ)
 197 between $[\bar{1}20]$ and $[120]$ steps (Figure 2c) was measured. Based on crystallography, the angle

198 between $[110]$ and $[\bar{1}10]$ steps should be $\theta = 115.042^\circ$ and the angle between $[120]$ and $[\bar{1}20]$
 199 steps should be $\theta = 76.298^\circ$. At $S = 2.0$ and $T = 23^\circ\text{C}$, $\theta = 37^\circ$, confirming that these steps are in
 200 fact vicinal to the $\langle 120 \rangle$ step direction and somewhere between the $\langle 140 \rangle$ step direction (the
 201 angle between $[140]$ and $[\bar{1}40]$ steps should be $\theta = 42.884^\circ$) and $\langle 150 \rangle$ step direction (the angle
 202 between $[150]$ and $[\bar{1}50]$ steps should be $\theta = 34.884^\circ$). Cross sections of bilayer $\langle 120 \rangle$ and
 203 $[010]$ step directions can be found in Figure 2a and 2b, respectively.

205

206 Figure 2: Cross-sectional view of orientations of acute and obtuse step terminations on a) the
 207 $\langle 120 \rangle$ steps on the celestite (001) surface (viewed along $[120]$), and b) the $[010]$ steps on the
 208 celestite (001) surface (viewed along $[010]$). c) is a (002) elementary half layer on the celestite
 209 surface with the $\langle 120 \rangle$, $[010]$, and $\langle 120 \rangle_v$ directions marked. Sr ions are represented as green
 210 spheres, sulfate ions are yellow tetrahedra.

211

212 3.2. Step velocity measurements

213 In this study, velocities of $[010]$ bilayer steps were measured. Due to the complexity of
 214 the defect outcroppings observed in this study, which generated hillocks of varying step source
 215 complexity, only step velocities, rather than step velocities and densities are reported. Steps on
 216 opposing sides of the hillock (Figure 1) are structurally equivalent and advance at the same rate.
 217 Similar to $\langle 120 \rangle$ steps on barite and celestite and the $[\bar{4}41]$ and $[48\bar{1}]$ steps on calcite and
 218 magnesite, the $[010]$ steps can either have an acute or an obtuse termination due to the
 219 orthorhombic unit cell. We speculate that the bilayer steps have an acute step termination as
 220 sulfate and strontium ions could approach the more open obtuse step configuration from a wider
 221 range of angles from solution than the acute step orientation, leading to ion attachment to the
 222 acute step orientation being the rate-limiting step for bilayer step advance.

223 Velocities of $[010]$ steps were measured at $r = 0.7$ - 0.8 and $I = 0.01$ - 0.02 M at three
 224 different temperatures (23, 35, and 45°C) with varying S . Step velocities increased with
 225 saturation state and temperature (Figure 3), however step velocities were non-linear as a function
 226 of $\{\text{Sr}^{2+}\}$ suggesting there may be a change in mechanism at intermediate values of $\{\text{Sr}^{2+}\}$.
 227 Based on hillock morphology, the $[010]$ steps advance slower than the $\langle 120 \rangle_v$ steps under all
 228 solution conditions and changes in morphology as a function of saturation state were also

229 observed (Figure 4). The angle between monolayer steps did not change as a function of the
230 saturation state, though the angle between bilayer steps decreased at low saturation states.
231 Hillocks elongated parallel to the [010] step direction as saturation state decreases (Figure 4),
232 showing that the ratio of step velocities, $v_s(120)/v_s(010)$, increases as the solution composition
233 approaches equilibrium.

234

235

236 Figure 3: Celestite step velocities as a function of $\{Sr^{2+}\}$ for the a) full dataset and b) same data
 237 as in (a) but focusing on near equilibrium data. Step velocities increased with temperature and
 238 saturation state. All three datasets exhibit significant non-linearity, suggesting a change in
 239 mechanism at intermediate saturation states.

240

241 Figure 4: Celestite hillock morphology as a function of S at $T=23^\circ\text{C}$, $r=0.7$, and $I=0.02$ M. As S
 242 decreases, growth hillocks elongate parallel to the $[010]$ direction due to the relative changes,
 243 resulting from changes to S , in the $\langle 120 \rangle_v$ step velocity as compared with the $[010]$ step velocity.
 244 These images are deflection images, giving the appearance of an illumination source from the
 245 right-hand side.

246

247 Step velocities were also measured as a function of $\{\text{Sr}^{2+}\}/\{\text{SO}_4^{2-}\}$ ratio (r) at three
 248 different supersaturations ($S = 1.6, 1.9, 2.2$) at 26°C and $I = 0.06$ M. Under these conditions the
 249 concentration of the $\text{SrSO}_4(\text{aq})$ ion pair is not predicted to change with r based on PHREEQC
 250 calculations. For all three saturation states, step velocities were at a maximum at $r \sim 1$ while at

251 extreme r where sulfate or strontium ions dominate, step velocities decreased significantly for all
 252 saturation states (Figure 5).

253
 254 Figure 5: [010] step velocities as a function of r at three different saturation states and constant T
 255 and I . Step velocities are maximized at $r=1$ and decrease symmetrically at extreme r for all three
 256 datasets. The data were modeled (solid lines) using the equations from Stack and Grantham
 257 (2010).

258
 259 Whereas step velocities decreased roughly symmetrically at high and low r (Figure 5),
 260 there was not a significant change in hillock morphology as a function of r , though steps
 261 appeared to roughen at extremes in r (Figure 6). It is not clear what the mechanism for this
 262 roughening is as the [010] steps are likely terminated by one type of ion. The [010] steps are
 263 highly kinked even when they appear straight, and it is therefore unlikely that the roughening
 264 corresponds to an increase in kink density. We also observed some localized pinning and
 265 bunching of steps at extremes in r (Figure 6), which may be attributable to the presence of

defects or impurities, though more likely defects, based on our estimates of impurities in solution and in the samples (see section 3.4 and Table 1 in the electronic annex)

Figure 6: Hillock morphology at a) low, b) near unity, and c) high $\{\text{Sr}^{2+}\}/\{\text{SO}_4^{2-}\}$. Deflection images shown here give the appearance of an illumination source on the left-hand side.

Finally, we also measured [010] step velocities at $I = 0.1, 0.06$, and 0.01 M at varying S and $r = 0.7$ - 0.8 and $T = 23$ - 26°C . For the data at all three ionic strengths, step velocities increased with saturation state, though as with the data from section 3.2 (Figure 3), the changes in velocity were non-linear (Figure 7). Step velocities did not consistently change with ionic strength and morphological changes as a function of ionic strength were not observed. This is in contrast to previous results from Risthaus et al. (2001) who observed a four-fold increase in the island spreading rates perpendicular to the [010] direction on barite from an ionic strength of 0.0003 to 0.1011 M. These differences may arise either from differences in the measurements (island spreading velocity vs. step velocity) or differences in celestite and barite growth mechanisms.

Figure 7: Step velocities as a function of S at three different ionic strengths, 0.01, 0.06, and 0.1 M. Step velocities are similar at a given saturation state regardless of the ionic strength.

4. Discussion

4.1 Acute and obtuse step terminations

Celestite is isostructural with barite and anglesite and can be described using the *Pnma* space group ($a = 8.360 \text{ \AA}$, $b = 5.352 \text{ \AA}$, $c = 6.858 \text{ \AA}$ (Hawthorne and Ferguson, 1975); molar volume, $V_m = 46.25 \text{ cm}^3/\text{mol}$ (Swanson and Fuyat, 1953). Minerals in this space group have a 2_1 screw axis parallel to the c axis, so each successive monolayer will be related to the underlying monolayer by a 2-fold rotation. $\langle 120 \rangle$, $\langle 110 \rangle$, and $[010]$ (among others) monolayer steps will have two types of terminations (Figure 2): an acute and an obtuse termination (Pina and Jordan, 2010; De Antonio et al., 2013), where the “acute” and “obtuse” terminology is similar to $[\bar{4}41]$ and $[48\bar{1}]$ acute (or negative) and obtuse (or positive) designations used on the rhombohedral carbonate minerals (Jordan et al., 2001). These step terminations arise from a shift in the positions of the strontium and sulfate ions in a surface monolayer as compared to the underlying monolayer. On calcite and magnesite, the obtuse step orientation advances faster than the acute step orientation under most solution conditions presumably due to the more open obtuse configuration (Teng et al., 1999; Saldi et al., 2009). De Antonio et al. (2013) speculates a similar situation with the orthorhombic sulfates, due to the more open configuration of the obtuse step orientation, attachment of ions to obtuse steps is kinetically more facile than to acute steps, leading to the obtuse steps migrating faster than the corresponding acute steps. The orthorhombic sulfate minerals have a screw axis which leads to the faster obtuse steps “catching up” to slower acute steps migrating in the same direction in an adjacent layer, thereby creating the bilayer $\langle 120 \rangle$ or $\langle 120 \rangle_v$ and $[010]$ steps observed on the growth hillock. In this case, the rate-limiting

step for advancement of these bilayer steps would be attachment of strontium and sulfate ions to the acute $\langle 120 \rangle$ or $\langle 120 \rangle_v$ and $[010]$ step directions.

There is a significant difference in the appearance of growth hillocks on celestite and barite at low ionic strengths as hillocks on barite do not exhibit the $[010]$ steps readily observed on celestite (Risthaus et al., 2001). Risthaus et al. (2001) suggests the differences in barite and celestite growth hillock morphology may be due to a decrease in the interfacial tension for barite at high ionic strengths, leading to an interfacial tension closer to that of celestite at low ionic strengths (Risthaus et al., 2001; Becker et al., 2002). He et al. (1995a) determined that the interfacial tension for barite decreases from 93 mJ/m^2 at low ionic strength (0.003 m NaCl) to 79 mJ/m^2 (1 m NaCl), but for celestite the interfacial tension/energy decreases from 76 mJ/m^2 at low ionic strength ($< 0.13 \text{ m NaCl}$) to 67 mJ/m^2 (1 m NaCl) (He et al., 1995b). However, there are significant differences in other values reported for interfacial tension in the literature, even at similar ionic strengths, with values ranging from 38 to 150 mJ/m^2 for barite at $I < 0.03 \text{ m}$ (Nielsen, 1958; Lamer and Dinegar, 1951; Enustun and Turkevich, 1960; Mealor and Townshen, A, 1966; Carosso and Pelizzetti, 1984; Wojciechowski and Kibalczyk, 1986; Symeopoulos and Koutsoukos, 1992; He et al., 1995a;) and 43 to 103 mJ/m^2 for celestite at $I < 0.15 \text{ m}$ (Enustun and Turkevich, 1960; Mealor and Townshen, 1966; Furedimilhofer et al., 1977; He et al., 1995b). These ranges demonstrate the interfacial tension for both of the minerals is not particularly well constrained, thus barite and celestite may have similar interfacial tensions and attributing surface morphology changes to differences in the interfacial tension remains speculative.

The $[010]$ step direction corresponds to a polar step orientation where the step can be envisioned to be either terminated by strontium ions, sulfate ions, or “zig-zagging” strontium and

sulfate ions. Explaining the appearance of [010] steps on barite at high ionic strength (e.g., NaCl), Risthaus et al. (2001) suggest that sodium and chloride ions may be adsorbing to the steps, creating chains of $\text{Na}^+ - \text{SO}_4^{2-} - \text{Na}^+$ or $\text{Sr}^{2+} - \text{Cl}^- - \text{Sr}^{2+}$ (or Ba^{2+})-Cl which are suggested to be more stable than a step terminated by either sulfate or strontium/barium ions. These hypotheses were supported by subsequent *ab initio* theoretical calculations by Becker et al. (2002) where the [010] step edge energy on barite (in vacuum) was lowered by replacement of the divalent metal with Na^+ ions. However, celestite surfaces during growth develop the [010] step directions even in low ionic strength solutions where adsorption of background electrolyte species is less likely to contribute to the step stability. Even in the absence of these species, Becker et al. (2002) calculated a significant reduction in [010] step energy by terminating the step with every other site vacant, effectively creating mini-domains oriented parallel to $\langle 120 \rangle$ directions and a “zig-zag” step edge with no dipole on average.

4.2. Step velocities as a function of S and T at constant r and I

According to the classical crystal growth model of Burton, Cabrera, and Frank (1951), step velocities of an isotropic material will follow:

$$v_s = \beta V_m ([A] - [A]_e) \quad (1a)$$

where v_s is the step velocity, β is the step kinetic coefficient, V_m is the molar volume of the material, $[A]$ is the concentration of solute in solution, and $[A]_e$ is the equilibrium concentration of the solute in solution. For most solutions, the concentrations in Eqn. 1a are appropriately replaced by activities, and thus for celestite, Eqn. 1a can be written:

$$v_s = \beta V_m (\{A\} - \{A\}_e) \quad (1b)$$

Chernov et al. (2005) extended this equation to ionic AB -type crystals by incorporating different attachment and detachment rate constants for A and B ions:

$$v_s = \frac{2ab}{\lambda_0} \frac{(k_A\{A\}k_B\{B\} - k_{-kpA}k_{-kpB})}{(k_A\{A\} + k_B\{B\} + k_{-kpA} + k_{-kpB})} \quad (2)$$

where a is the kink depth, b is the lattice spacing along the step, λ_0 is the kink density, $\{A\}$ and $\{B\}$ are the activities of A and B, k_A and k_B are the attachment rate constants to kinks for species A and B, and k_{-kpA} and k_{-kpB} are the detachment rate constants from kinks for A and B. Through rearrangement of terms, Eq. 2 becomes:

$$v_s = \frac{2abk_B}{\lambda_0} \frac{\left(\{A\}\{B\} - \frac{k_{-kpA}k_{-kpB}}{k_Ak_B}\right)}{\left(\{A\} + \frac{k_B\{B\}}{k_A} + \frac{k_{-kpA} + k_{-kpB}}{k_A}\right)} \quad (3)$$

Chernov et al. (2005) used the relation $K_{sp} = \frac{k_{-kpA}k_{-kpB}}{k_Ak_B}$, which assumes attachment and detachment reactions are reversible. Chernov et al. (2005) also defines $C_k = \frac{1}{2} \frac{k_{-kpA} + k_{-kpB}}{k_A}$, which simplifies Eq. 3 to:

$$v_s = \frac{2abk_B}{\lambda_0} \frac{(\{A\}\{B\} - K_{sp})}{\left(\{A\} + \frac{k_B\{B\}}{k_A} + 2C_k\right)} \quad (4)$$

If $\{A\} = \{B\}$, $k_A = k_B$, and $k_{-kpA} = k_{-kpB}$, then Eq. 4 simplifies to:

$$v_s = \frac{2abk_A}{\lambda_0} \frac{\left(\{A\}^2 - \frac{k_{-kpA}^2}{k_A^2}\right)}{\left(2\{A\} + \frac{2k_{-kpA}}{k_A}\right)} = \frac{abk_A}{\lambda_0} \left(\{A\} - \frac{k_{-kpA}}{k_A}\right) = \frac{abk_A}{\lambda_0} (\{A\} - \sqrt{K_{sp}}) = \beta V_m (\{A\} - \{A\}_e) \quad (5)$$

For our experiments, and replacing concentrations in the Chernov et al. (2005) equations with activities, $\{Sr^{2+}\} \cong \{SO_4^{2-}\}$, and if we assume $k_A = k_B$. (to be justified later), the data in Fig. 3 cannot be fit to Eqn. 4 even if $k_{-kpA} \neq k_{-kpB}$. This inequality results in non-linearity predicted from the model, however the degree of non-linearity is small over the range of supersaturation in our experiments and thus the model failed to fit the data trend.

According to the step growth model of Zhang and Nancollas (1990, 1998), which is functionally similar to that of Chernov et al. (2005), step velocities should be linear with $S^{1/2}(S-1)$. However the experimental step velocities followed a non-linear trend when plotted against $S^{1/2}(S-1)$ (electronic annex, Figure 2). Step velocities were also non-linear when plotted versus S^2-1 and Saturation Index ($SI = \log \frac{\{Sr^{2+}\}\{SO_4^{2-}\}}{K_{sp}}$) (electronic annex, Figure 2), though they were linear when plotted versus $(S^2-1)^2$ (Figure 8). Data at all temperatures followed $v_s = k(S^2-1)^2$ with $k = 0.042 (\pm 0.008)$ nm/s at 23°C, $k = 0.066 (\pm 0.004)$ nm/s at 35°C, and $k = 0.43 (\pm 0.03)$ nm/s at 45°C. However, since to our knowledge there is not a step growth model based on $(S^2-1)^2$ as the driving force, these coefficients are not directly comparable to step kinetic coefficients from previous studies (e.g., Teng et al., 1999; Higgins et al., 2000).

Figure 8: Step velocities plotted as a function of $(S^2-1)^2$.

Similar non-linear behavior in step velocity as a function of activity or $S^{1/2}(S-1)$ has also been observed on calcite during both growth (Teng et al., 1999) and dissolution (Xu et al., 2010),

during celestite dissolution (Bose et al., 2008), and for [010] steps on barite (Bunney et al., 2014). This behavior during growth is often attributed to impurities sorbing to the surface and becoming incorporated into the crystal during step migration, thereby yielding a superlinear dependence of step velocity on supersaturation, particularly at near-equilibrium conditions (Teng et al., 1999; Bose et al., 2008). Impurities also may cause a sublinear dependence (e.g. calcite acute steps (Teng et al., 1999)) when they interact with steps without incorporation and block attachment of ions rather than the observed superlinear behavior (Potapenko, 1993; Voronkov and Rashkovich, 1992). In addition to impurity-based explanations for the non-linear data trend, kinetic roughening, or changes in the distance between kinks, has also been suggested to lead to non-linearities (Teng et al., 1999). This roughening would result in a decrease in the kink-kink distance with increasing S . However considering the [010] steps to be fully-kinked, then it is unlikely that the kink-kink distance changes with S . Another consideration is the effect of the back reaction (detachment) on step advancement. Based on the crystal growth kinetic models of Zhang and Nancollas (1998), Chernov et al. (2005) and Stack and Grantham (2010), detachment reactions are a zeroth order reaction that do not depend on the concentrations of ions in solution. At high supersaturation, the detachment frequencies from kinks are not significant enough to exert an appreciable influence on step kinetics (Zhang and Nancollas, 1990; Zhang and Nancollas, 1998), though near equilibrium, these detachment rates may become more significant. However, if we consider that detachment frequencies may increase as equilibrium is approached, we would expect step velocities to approach zero with a rapid drop-off in velocities, demonstrating sublinear behavior, rather than the observed superlinear behavior, making it unlikely our observations arise from the back reaction.

In the context of existing crystal growth models and due to the observed non-linearities in our data, the lack of fit to Eq. 1 to the full range of $\{\text{Sr}^{2+}\}$ in Figure 3, suggests that there could also be different mechanisms at low and high saturation states, in which case different functions would need to be applied to the two parts of the dataset. If there are two mechanisms affecting growth above some critical activity ($\{\text{Sr}^{2+}\}_e^*$), the step velocity can be written as:

$$v_s = \beta_1 V_m(\{\text{Sr}^{2+}\} - \{\text{Sr}^{2+}\}_e) + \beta_2 V_m(\{\text{Sr}^{2+}\} - \{\text{Sr}^{2+}\}_e^*) \quad (6)$$

where β_1 and β_2 are the step kinetic coefficient for the first and second mechanisms respectively, and $\{\text{Sr}^{2+}\}_e^*$ is the strontium activity where the second mechanism becomes favorable (Figure 3a).

Near equilibrium, we fit the data in Figure 3b using Eq. 1 to obtain β_1 and $\{\text{Sr}^{2+}\}_e$ (Table 2; Figure 3b). Due to the rapid growth of barite at 45°C, it was unclear if the dataset near equilibrium should include the first two or three datapoints. Here we've chosen to include three datapoints, but clearly the third datapoint skewed the fit in Figure 3b, which leads to a larger slope for the 45°C near equilibrium dataset than if only the first two datapoints were used. Far from equilibrium a second mechanism appears to play a role in growth, so here the data has been fit to Eq. 6 using β_1 and $\{\text{Sr}^{2+}\}_e$ from the near equilibrium fit for the corresponding dataset to determine β_2 and $\{\text{Sr}^{2+}\}_e^*$. One data point was chosen as the point where the two linear functions intersect, and this point was included in both the low S and high S fits.

Table 2: Fit parameters for temperature and saturation state dependence fits.

	T=23°C	T=35°C	T=45°C
β_1 (cm/s)	$5.3 (\pm 2) \times 10^{-4}$	$1.5 (\pm 0.6) \times 10^{-3}$	$4.3 (\pm 1) \times 10^{-3}$
β_2 (cm/s)	$3.5 (\pm 0.7) \times 10^{-3}$	$6.5 (\pm 2) \times 10^{-3}$	$1.1 (\pm 0.2) \times 10^{-2}$
$\{\text{Sr}^{2+}\}_e$ (M)	$4.6 (\pm 0.2) \times 10^{-4}$	$4.9 (\pm 0.2) \times 10^{-4}$	$5.1 (\pm 0.1) \times 10^{-4}$

$\{\text{Sr}^{2+}\}_e^*$ (M)	$6.0 (\pm 0.1) \times 10^{-4}$	$6.5 (\pm 0.1) \times 10^{-4}$	$5.9 (\pm 0.1) \times 10^{-4}$
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For the near equilibrium data, $\{\text{Sr}^{2+}\}_e$, the strontium activity at which the first mechanism becomes favorable, varies with temperature and is in the range of $4.6\text{--}5.1 \times 10^{-4}$ M. The predicted K_{sp} based on $\{\text{Sr}^{2+}\}_e$ varies from $10^{-6.5}$ to $10^{-6.4}$, greater than the bulk K_{sp} ($10^{-6.62}$ at 23°C , $10^{-6.61}$ at 35°C , and $10^{-6.60}$ at 45°C), which may arise from step edges displaying an apparent solubility that is greater than the bulk thermodynamic solubility due to the step edge energy (Fan et al., 2006). β_1 values were in the range $5.3\text{--}43 \times 10^{-4}$ cm/s (Table 2; Figure 3b). β_1 is significantly less than β reported for both calcite (0.54 cm/s for obtuse steps and 0.30 cm/s for acute steps) (Teng et al., 1999) and barite (0.4 cm/s at room temperature, extrapolated from $90\text{--}125^\circ\text{C}$) (Higgins et al., 2000). At high S , $\{\text{Sr}^{2+}\}_e^*$ varies slightly with temperature, though the behavior is erratic as $\{\text{Sr}^{2+}\}_e^* (45^\circ\text{C}) < \{\text{Sr}^{2+}\}_e^* (23^\circ\text{C}) < \{\text{Sr}^{2+}\}_e^* (35^\circ\text{C})$. Both β_1 and β_2 increase with increasing temperature and can be described with the Arrhenius equation (Figure 9):

$$\beta = A e^{\frac{-E_a}{kT}} \quad (7)$$

where for β_1 , $A_1 = 8.1 (\pm 40) \times 10^9$ cm s $^{-1}$ and $E_a = 1.2 (\pm 0.2) \times 10^{-19}$ J, which corresponds to 75 (+/- 10) kJ/mol, and for β_2 , $A = 1.2 (\pm 4) \times 10^5$ cm s $^{-1}$ and $E_a = 7.1 (\pm 1.6) \times 10^{-20}$ J, which corresponds to 43 (+/- 9) kJ/mol. Based on the fits at high S , β_2 values were in the range $3.4\text{--}14 \times 10^{-3}$ cm/s, greater than those reported for the low S fits, though still much less than the coefficients for calcite (Teng et al., 1999) and barite (Higgins et al., 2000).

Figure 9: Natural logarithm of the step kinetic coefficients β_1 and β_2 as a function of $1/T$.

Despite some uncertainty in the physicochemical origins of the non-linearity in the step velocity data in Figure 3a, the magnitudes of the kinetic coefficients remain unaffected and are significantly less than other commonly studied sparingly soluble minerals. The differences between the β values reported here and those reported on calcite and barite are intriguing as they suggest that while the mechanism for barite (001) and calcite (104) growth is likely similar (e.g., attachment to non-polar steps), the mechanism for celestite (001) growth may be different. This difference may arise in celestite due to slow growth of the polar [010] step orientations. The coefficients we calculate here are in the range of those for protein crystallization and hydroxyapatite growth (Onuma, 2006; Qiu and Orme, 2008; Oyane et al., 1999), the latter of which has been suggested to grow via formation and attachment of ion clusters rather than ion-by-ion attachment. We therefore hypothesize that the [010] steps on celestite may grow via attachment of ion pairs or larger ion clusters to a step edge in addition to ion-by-ion attachment.

A final consideration is the effect of step separation on step velocities. The [010] step density increased at saturation states closer to equilibrium as revealed in Figure 4, which was unexpected as hillock step density was expected to decrease as equilibrium was approached (Teng et al., 2000) due to an increase in the thermodynamic critical step length. The density of [010] steps near the hillock top in Figures 4c and 4d is large enough to preclude resolution of the individual steps by the AFM probe. This unexpectedly high step density near equilibrium is possible if there exists significant step-step interactions such that the proximity of steps influences their rate of advance. Based on the classical crystal growth theory of Burton, Cabrera, and Frank (1951), when the step separation is significantly less than the mean displacement of adsorbed species, the step velocity is approximately proportional to the step separation. If the step separation increases with saturation state, we would expect the effect of step separation to become less pronounced at higher saturation states, leading to a larger slope than near equilibrium, which is consistent with our observations. However, systematically varying the step separation at constant saturation state was not possible, thus preventing a determination of step velocity as a function of step density and therefore there is no basis for an estimate of the mean displacement of adsorbed species. This raises the possibility that the non-linear step velocity trend in Figure 3a may arise from step spacings that are less than the mean diffusion distance of adsorbed ions.

4.3. Growth as a function of r and S at constant I and T

To first test if an ion-by-ion attachment mechanism is involved in [010] step growth, we can examine the effect of r on step velocities as shown in Figure 5. Our observations of a decrease in step velocity at extreme r is consistent with an ion-by-ion attachment mechanism.

The peak at $r \sim 1$ suggests attachment rate coefficients to the [010] steps are similar for strontium and sulfate ions. This is consistent with previous results on the acute steps on calcite (Stack and Grantham, 2010; Bracco et al., 2012). Previous results on barite island spreading rates as a function of the cation:anion ratio suggest that barium attachment may be rate limiting for barite growth (Kowacz et al., 2007). However, it is difficult to make a direct comparison between our results and those of Kowacz et al. (2007) since the observations were different (island spreading rates in Kowacz et al. (2007) vs. single step velocities in this work). Thus, the Kowacz et al. (2007) measurements of island spreading rates represents the sum of the velocity of acute and obtuse monolayer steps on barite, whereas here we are exclusively measuring acute (or possibly, obtuse) bilayer step velocities. As a point of comparison, on calcite, the obtuse and acute step velocities peak at different ratios depending on the step termination (Stack and Grantham, 2010; Larsen et al., 2010; Bracco et al., 2012), with obtuse steps peaking at an order of magnitude greater r .

The data in Figure 5 add to a growing body of literature on kinetics of mineralization reactions that highlight the importance of solute stoichiometry (Lin and Singer, 2005; Stack and Grantham, 2010; Chernov et al., 2006; Kowacz et al., 2007; Nehrke et al., 2007; Tai et al., 2005; Larsen et al., 2010; Bracco et al., 2012; Gebrehewiet et al., 2012; Bracco et al., 2014) in governing the rates of step edge motion and growth rates. While this study demonstrates the relationship between step velocity and r , by considering that the expression for the rate of surface advance (i.e., the growth rate) is a simple product of the step velocity and the hillock slope:

$$R = pv_s \quad (8)$$

where p (hillock slope) is a function of the supersaturation (Teng et al., 2000) (and potentially a function of r), we conclude that geochemical rate laws, which are usually based on the overall driving force for the reaction (e.g., $R = f(\Delta G_{\text{rxn}})$ and independent of the specific ion composition, should include a term that captures the behavior documented here and in other recent studies as solute stoichiometry is varied. As part of the discussion on the Figure 5 data below, we consider one such step growth model that fits the observed behavior.

Step velocities were fit using the Stack and Grantham (2010) kink site nucleation and propagation model (Figure 5; Table 3; Eqs. 9-11). For data fitting, the step velocities for each saturation state were combined and fit to the following equations using a Newton-Raphson minimization:

$$v_s = a\sqrt{2R_{\text{kn}}R_{\text{kp}}} \quad (9)$$

where a is the atomic size ($a = 0.687$ nm), R_{kn} is the rate of kink site nucleation, and R_{kp} is the rate of kink site propagation. R_{kn} is expressed as:

$$R_{\text{kn}} = \frac{k_{\text{Sr}^{2+}}\{\text{Sr}^{2+}\}k_{\text{SO}_4^{2-}}\{\text{SO}_4^{2-}\}V_m}{k_{\text{Sr}^{2+}}\{\text{Sr}^{2+}\}+k_{\text{SO}_4^{2-}}\{\text{SO}_4^{2-}\}} - k_{-\text{kn}}V_m \quad (10)$$

where $k_{\text{Sr}^{2+}}$ and $k_{\text{SO}_4^{2-}}$ are attachment rate coefficients for strontium and sulfate, $k_{-\text{kn}}$ is an overall detachment term for nucleated double kink sites, V_m represents the molar volume, and

$$R_{\text{kp}} = \frac{(k_{\text{Sr}^{2+}}\{\text{Sr}^{2+}\}k_{\text{SO}_4^{2-}}\{\text{SO}_4^{2-}\}-k_{-\text{kp}}k_{-\text{kp}})V_m}{k_{\text{Sr}^{2+}}\{\text{Sr}^{2+}\}+k_{\text{SO}_4^{2-}}\{\text{SO}_4^{2-}\}+k_{-\text{kp}}+k_{-\text{kp}}} \quad (11)$$

where k_{-kp} ($k_{-kpA}=k_{-kpB}$) (fit values given in Table 3) is the detachment rate to propagate kink sites, a value which is assumed to be equal for Sr^{2+} and SO_4^{2-} . Without this assumption, there was significant covariance between fit parameters.

Table 3: Fit coefficients (Eqns. 9-11) for step velocities vs r data.

$k_{Sr^{2+}} (M^{-1} \cdot s^{-1})$	$3.3 (\pm 0.3) \times 10^3$	$k_{Sr^{2+}}/V_m (s^{-1})$	$7.1 (\pm 0.6) \times 10^4$
$k_{SO_4^{2-}} (M^{-1} \cdot s^{-1})$	$3.3 (\pm 0.2) \times 10^3$	$k_{SO_4^{2-}}/V_m (s^{-1})$	$7.1 (\pm 0.4) \times 10^4$
$k_{-kn} (s^{-1})$	$0.22 (\pm 0.04)$	$k_{-kn}/V_m (M \cdot s^{-1})$	$4.7 (\pm 0.9)$
$k_{-kp} (s^{-1})$	$2.3 (\pm 0.2)$	$k_{-kp}/V_m (M \cdot s^{-1})$	$4.9 (\pm 0.4) \times 10^1$

The model fits our data quite well at all three saturation states. However we were unable to obtain a satisfactory fit to a combination of r dependent data and saturation state dependent data (Figure 3) due to the observed non-linearity as a function of $\{Sr^{2+}\}$. We do not report our failed attempts to fit our data using the Zhang and Nancollas (1998) model because the model was explicitly developed for non-polar step orientations. Based on these results, we can conclude that an ion-by-ion attachment mechanism is operable for [010] steps on celestite, though these results do not preclude the possibility of appearance of a second mechanism as we will consider next.

4.4. Growth as a function of I and S at constant r and T

To ascertain if emergence of a second mechanism, such as a change from ion-by-ion attachment to ion pair attachment, is responsible for the non-linearity in the data as a function of $\{Sr^{2+}\}$, we can evaluate the effect of ionic strength on step velocities. Based on our observations, ionic strength does not have a significant effect on step velocities both close to and far from equilibrium. Due to the non-linearity of the data, we were unable to fit each ionic strength dataset to a single fit function. Following a similar procedure as was used in fitting the data in Figure 3, we have fit the ionic strength-dependent data to Eq. 6 for each of the ionic strength conditions.

As a function of I , β_2 did not change significantly while β_1 increased from $I=0.01$ M to $I=0.06$ M and was not statistically different at $I=0.06$ M and $I=0.1$ M (Table 4) allowing us to conclude that I has a marginal, if any, effect on the advancement of [010] steps.

Table 4: Fit parameters for ionic strength and saturation state dependence fits.

	$I=0.01\text{M}$	$I=0.06\text{M}$	$I=0.1\text{M}$
β_1 (cm/s)	$5.3 (\pm 2) \times 10^{-4}$	$1.7 (\pm 0.4) \times 10^{-3}$	$1.9 (\pm 0.8) \times 10^{-3}$
β_2 (cm/s)	$3.5 (\pm 0.7) \times 10^{-3}$	$3.1 (\pm 2) \times 10^{-3}$	$2.3 (\pm 2) \times 10^{-3}$
$\{\text{Sr}^{2+}\}_e$ (M)	4.59×10^{-4}	4.59×10^{-4}	4.59×10^{-4}
$\{\text{Sr}^{2+}\}_e^*$ (M)	$6.03 (\pm 0.1) \times 10^{-4}$	$6.09 (\pm 0.4) \times 10^{-4}$	$6.32 (\pm 0.8) \times 10^{-4}$

In order to describe how the step kinetic coefficients might be independent of I , we consider the kinetic electrolyte effect (e.g. (Atkins, 1990)) which describes the change in a rate constant as a function of ionic strength of a reaction:

$$\log(k_{\text{TS}}) = \log(k_{\text{TS}}^\circ) + 2Z_A Z_B \sqrt{I} \quad (12)$$

where k_{TS}° is the rate constant when $I = 0$, and Z_A and Z_B are the charges of the two interacting species A and B, which are involved in forming the activated complex. Based on Eq. 12, if the species charges involved in a reaction have the same sign, increasing the ionic strength increases the rate constant. This arises due to the increased electrolyte screening at increased I which in turn permits closer approach of two like-charged species. When species involved in a reaction have opposing charges, increasing I decreases the rate constant since the favorable electrostatic forces between species are lessened by the screening electrolyte solution. If a neutral species is involved in a reaction, changing the ionic strength does not change the rate constant, as long as

specific effects of the electrolyte on the water structure and dynamics in the hydration shells of the aqueous ions do not cause significant changes in the rates of species attachment and detachment from the step edges (see Kowacz et al. (2008) for further discussion of electrolyte-specific effects on barite growth).

Based on the derived kinetic coefficients, neither β_1 nor β_2 changes significantly with I , in which case the mechanisms may involve an uncharged species, such as a neutral ion pair (e.g., $\text{SrSO}_4(\text{aq})$) or possibly an uncharged step edge. Our results at low saturation state, while consistent with an uncharged species involved in the mechanism, are partially refuted by the observations in Figure 5 where the data clearly show that the relative activities of the solute ions (at constant S) affect the step velocity. Thus, the data in Figure 5 strongly support a mechanism of ion-by-ion attachment as opposed to neutral ion pair attachment and the weak dependence of β_1 on I may require further experimentation to better constrain the step velocities and further consideration of electrolyte-specific effects, such as the influence of Na^+ and NO_3^- ions on the structure and dynamics of coordinating water molecules.

The insignificant changes to either β_1 or β_2 with I (within the uncertainties of our data) remain open to interpretation. What we cannot address directly with experimental observations is the possibility that the [010] step behaves as a neutral entity and thus leads to a weak, or non-existent kinetic salt effect. According to Becker et al. (2002), the [010] step orientation on barite (or by extension, on celestite) can achieve a non-polar configuration (normal to the step edge) by having every 2nd site on the [010] step populated by a cation (or anion) with the remaining sites left unpopulated. This “zig-zag” termination resulted in a decrease in step edge energy, relative to a termination with all cation edge sites populated, according to *ab initio* calculations in

vacuum. When electrolyte ions were considered (i.e., NaCl), Becker et al. (2002) reported a further reduction in step energy when all Ba^{2+} sites on the [010] step contained a Na^+ ion with the step remaining dipole-free. While the step, on average, would not possess a dipole, there still exist discrete charges along the step edges and associated electric fields whose electrostatic influence on approaching ions would remain. Thus, it is unclear if, and perhaps unlikely that [010] steps can be treated as charge-neutral entities at all. While the [010] monolayer steps are unlikely to be neutral entities, the bilayer steps may be terminated with sulfate ions in one layer and strontium ions in another layer, which could make these bilayer steps electrically neutral.

The general trend of non-linearity of the step velocity data with $\{\text{Sr}^{2+}\}$, as an alternative explanation, could be associated with impurities introduced through the reagents used in this work. Trace metal grade reagents with at least 99.99% purity and high purity celestite samples were used throughout, although this alone does not rule out impurities as a source of the non-linearity. We can approximate a maximum impurity concentration based on the most prevalent impurities in the sodium nitrate reagent. The most prevalent divalent cation impurity was barium at ≤ 1 ppm and the most prevalent anion impurities were sulfate and nitrite at ≤ 30 and ≤ 20 ppm, respectively (based on the certificate of analysis), which is two orders of magnitude less than the reported impurities in Teng et al. (1999). Phosphate, which is a known inhibitor of calcite growth, was only present at ≤ 2 ppm. Based on these results, the predicted maximum concentration of barium is 6×10^{-8} M, the additional sulfate from NaNO_3 is 3×10^{-6} M (compare with Table 1 experimental sulfate concentrations), and the predicted maximum concentration of phosphate is 2×10^{-7} M, which are 3-4 orders of magnitude less than the minimum concentrations of strontium and sulfate in our solutions. For impurities to be an important factor in the observed non-linearity we would expect step velocities to be increasingly inhibited with

increasing ionic strength and a widening “dead zone” (e.g., De Yoreo et al. (2009)) should have appeared as the ionic strength was increased (Figure 7). Our experimental observations, in light of these impurity concentrations, suggest it is unlikely that impurities play a significant role.

At high saturation state, there are likely two mechanisms responsible for step growth: (1) the mechanism responsible for growth at low S and (2) a new mechanism that is activated at high S . Based on the results from the celestite growth studies as a function of r , one of the two mechanisms must be ion-by-ion addition (consistent with the low S observations) as changes in step velocity with r were observed at constant S . Based on our results, β_2 (Table 4) is statistically indistinguishable at $I = 0.01$ M, 0.06 M, and 0.1 M, supporting the hypothesis that the mechanism at high saturation state involves a neutral species attaching to a site on the [010] step edge.

4.5. Implications for Geochemical Modeling

The geochemical implications of this work are significant when considering that most “rate laws” in geochemical modeling do not capture the relationship between growth rates and solute stoichiometry nor are they generally based on the behavior of elementary step edges. Most modern reactive transport codes, such as TOUGHREACT, PHREEQC, and CRUNCHFLOW, have successfully incorporated kinetic treatment of mineral growth and dissolution allowing for non-linear growth and dissolution rates (e.g., $R = A_m k_m \left[\left(\frac{IAP}{K_{sp}} \right)^n - 1 \right]^m$, where R is the growth rate, A_m is the reactive surface area, k_m is the rate constant, IAP is the ion activity product, n and m are experimentally or theoretically derived), and the term containing the $\left(\frac{IAP}{K_{sp}} \right)$ term is often referred to as the “affinity term” and predicts the dependence based on saturation state or Gibbs

energy (Steefel et al., 2015). While the non-linearity in our step velocity data could be described by such a model (e.g., $m = 2$), it is still unclear whether a physical model for rough step advancement would yield this second-order dependence on driving force. However, our fitting to two separate linear functions (Figures 3 and 7) precludes the use of standard geochemical models to describe step velocities, and by extension, face growth rates as r varies. Alternative geochemical models predict irreversible growth and dissolution rates, which may or may not depend on concentration rather than affinity, but these rate laws may only be valid in conditions far from equilibrium. Research on the effect of r on step densities on different minerals would also be beneficial for parameterizing reactive transport models, however here we did not report step densities or overall growth rates due to the complexity of the defects on the surfaces.

To the best of our knowledge, none of these reactive transport models are able to incorporate the effects of r , which has been shown to significantly affect not only step velocities demonstrated here and in other work (Stack and Grantham, 2010; Kowacz et al., 2007; Chernov et al., 2006; Larsen et al., 2010; Bracco et al., 2012; Bracco et al., 2014), but also mineral growth rates (Lin and Singer, 2005; Nehrke et al., 2007; Gebrehewiet et al., 2010; Tai et al., 2007) for sparingly-soluble AB-type minerals. Based on these studies and our results, under conditions where r_i ($r_i = \frac{k_A}{k_B} r$) is far from unity, reactive transport models may predict mineral precipitation (and presumably dissolution) rates much greater, possibly up to ten times greater, than what would be predicted by a model accounting for the effects of r .

5. Conclusions

In conclusion, between $S = 1.1$ -2.2 and 23-45°C, celestite grows *via* spiral hillock formation with lateral spreading occurring primarily through advance of bilayer [010] steps.

While it is unclear precisely how these polar steps are terminated, these are likely to be an acute step orientation rather than an obtuse orientation. Step velocities increased significantly with S and T at constant r , though non-linear behavior was observed as a function of S . Step kinetic coefficients were derived from the data based on the following equation: $v_s = \beta_1 V_m(\{Sr^{2+}\} - \{Sr^{2+}\}_e) + \beta_2 V_m(\{Sr^{2+}\} - \{Sr^{2+}\}_e^*)$ with the second term applying at $\{Sr^{2+}\} \geq \{Sr^{2+}\}_e^*$. Step velocities were also maximized at $r = 1$ and decreased roughly symmetrically at high and low r . The step velocities at varying r were fit using the Stack and Grantham (2010) nucleation and propagation model, suggesting an ion-by-ion attachment mechanism is involved in the growth process. While the ionic strength had minimal effect on kinetic coefficients, suggesting involvement of a neutral species in the mechanism, we could not envision the steps on celestite to behave as neutral species and thus suggest that we do not have sufficient information to explain the independence of v_s on I . The change in slope of v_s versus $\{Sr^{2+}\}$ suggests another mechanism may play a role at high S , such as ion pair addition to a step edge.

Supplementary Material

An electronic annex is available containing our methodology for analyzing impurities in celestite, a table of impurities in celestite, a figure of step velocities plotted as a function of solution flow rate, a figure of step velocities plotted as a function of SI , $S^{1/2}(S-1)$, (S^2-1) , and a note about how use of the disabled slow scan axis method differs in sulfate and carbonate minerals.

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