Hydrothermal atomic force microscopy observations of barite step growth rates as a function of the aqueous barium-to-sulfate ratio

Bracco, Jacquelyn N.^{a,1}; Gooijer, Yiscka^{a,b}; Higgins, Steven R.^{a*}

a. Chemistry Department, Wright State University, 3640 Col. Glenn Hwy., Dayton, Ohio 45435

b. Hogeschool Utrecht, Institute for Life Sciences and Chemistry, Utrecht, the Netherlands

1. Current address: Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439

Abstract

The rate of growth of ionic minerals from solutions with varying aqueous cation:anion ratios may result in significant errors in mineralization rates predicted by commonly-used affinity-based rate equations. To assess the potential influence of solute stoichiometry on barite growth, step velocities on the barite (001) surface have been measured at 108°C using hydrothermal atomic force microscopy (HAFM) at moderate supersaturation and as a function of the aqueous barium:sulfate ratio (r). Barite growth hillocks at $r \sim 1$ were bounded by $\langle 120 \rangle$ steps, however at $r < 1$, kink site densities increased, steps followed a direction vicinal to $\langle 120 \rangle$, and the [010] steps developed. At $r > 1$, steps roughened and rounded as the kink site density increased. Step velocities peaked at $r = 1$ and decreased roughly symmetrically as a function of r , indicating the attachment rates of barium and sulfate ions are similar under these conditions. We hypothesize that the differences in our observations at high and low r arise from differences in the attachment rate constants for the obtuse and acute $\langle 120 \rangle$ steps. Based on results at low r , the data suggests the attachment rate constant for barium ions is similar for obtuse and acute steps. Based on results at high r , the data suggests the attachment rate constant for sulfate is greater for obtuse steps than acute steps. Utilizing a step growth model developed by Stack and Grantham (2010)

the experimental step velocities as a function of r were readily fit while attempts to fit the data using a model developed by Zhang and Nancollas (1998) were less successful.

1. Introduction

Sparingly-soluble minerals play a significant role in a variety of subsurface geochemical systems such as those utilized for contaminant remediation (Curti et al., 2010), CO₂ sequestration (Oelkers and Cole, 2008), and long-term storage of nuclear waste (e.g., the Waste Isolation Pilot Plant). Chemical and physical processes spanning a broad range of time and length scales in these systems can be influenced by mineral growth and dissolution through changes in permeability and porosity, incorporation of impurities in mineral lattices, and through surface complexation. Mineral growth in many geochemical systems is predicted using reactive transport models, which assume growth will be constant at a given saturation state (e.g., IAP/K_{sp} , IAP is ionic activity product, K_{sp} is the solubility product) regardless of the proportion of solute cations (A) and anions (B) in aqueous solution. However, subsurface geochemical conditions are highly variable, leading to regions where aqueous concentrations of one constituent ion (A or B in a mineral of formula AB) may be significantly greater than concentrations of the other ion, such as during the injection of fluids into reservoir rocks. This injection process may lead to a change in the aqueous A:B ratio (r), a factor that is not expressed in functions describing the degree of supersaturation of a fluid, nor is this factor included in most geochemical kinetics models for mineral growth and dissolution from aqueous solution.

Barite, an AB-type mineral with an orthorhombic crystal lattice, is found in ocean sediments (Paytan et al., 2007) and also precipitates when sulfate-rich seawater is injected into barium-rich geologic formations. Barite growth can be described using modern crystal growth

theory, which is derived from the terrace-step-kink (TSK) model (Stranski, 1928) and the Burton, Cabrera, and Frank (1951) crystal growth theory in which the energy required for growth units to attach to or detach from the surface is determined by the coordination environment. As such, the kink sites, sites with only half of their bonds remaining to the bulk crystal, will be more reactive than sites in a terrace or step edge and reactions at the kinks will be the most important to consider for crystal growth. Frank (1974) further derived a kinematic model for growth along a step in which growth is dependent on the rate of nucleation events, which create kinks, and the subsequent rate of propagation of these kinks. Propagation of kinks will end when left-hand and right-hand kinks meet (annihilation) or when a kink reaches the end of the step. In this model, there are two distinct growth regions. The first is a region in which the step velocity is dependent on the length of the step:

$$v = aLR_{kn} \quad (1)$$

where a is the atomic size (0.70 nm, half the distance between two barium atoms with the same z dimension along a $\langle 120 \rangle$ step), L is the step length, and R_{kn} is the rate of kink site nucleation per unit length ($\text{nm}^{-1}\text{s}^{-1}$). Equation (1) is valid as long as the number of kinks along a step is small ($n_k < 1$) (Frank, 1974; Higgins et al., 2000). This condition is met when L is small and completion of a row of growth units occurs before the next nucleation event. The second is a step length independent growth region in which the step velocity depends on R_{kn} and R_{kp} (where the latter is the propagation velocity of kink sites in nm/s):

$$v = a\sqrt{2R_{kn}R_{kp}} \quad (2)$$

Barite step velocities are independent of step length after the steps have grown short distances (Higgins and Hu, 2006), implying the need to consider both kink propagation and kink nucleation. The kink density along steps on the barite (001) surface (at 90-125 °C) was suggested

to be controlled by non-equilibrium processes rather than equilibrium thermal excitation/exchange (Higgins et al., 2000). Thus, the kink density can be described using Frank's (1974) kinetic step growth model at moderate supersaturations and $r = 1$ (Higgins et al., 2000). Further evidence for the impact of kink kinetics on barite growth comes from Kowacz and coworkers (2007) who found that 2-dimensional island spreading rates (at room temperature) were maximized near $r = 10$. Experimentally-derived attachment rate constants for calcite (Perdikouri et al., 2009; Stack and Grantham, 2010; Larsen et al., 2010; Bracco et al., 2012; Bracco et al., 2013;), celestite (Bracco et al., 2016), and magnesite (Bracco et al., 2014) are, in some instances, slightly greater for anions than cations, resulting from experimental observations of peak step velocities occurring at values of r slightly larger than unity.

Equation (2) is utilized in two common growth models (among others) for AB-type crystals. First is the Zhang and Nancollas (1998) model (ZN model), which was derived from a sodium chloride-type crystal lattice and defines the rate of kink site nucleation to be a 1-dimensional nucleation rate based on a cluster (Zhang and Nancollas, 1990) that is larger than a critical size (*i.e.*, the size for a cluster to grow irreversibly). The ZN model describes the step velocity according to:

$$v = 2av(S - 1)S^{1/2} \exp\left(-\frac{\epsilon}{kT}\right) q_g(r_i, S) \quad (3)$$

where $S = \left(\frac{[A]^\alpha[B]^\beta}{K_s}\right)^{\frac{1}{\alpha+\beta}}$ is the saturation state, $r_i = \frac{k_A[A]}{k_B[B]}$ is the kinetic ionic ratio, $\nu = K_{sp}^{1/2}(k_A k_B)^{1/2}$ is the detachment frequency,

$$q_g(r_i, S) = \left[\frac{S+1}{2} \left(\frac{1}{S+r_i^{1/2}} + \frac{1}{S+r_i^{-1/2}} \right) \frac{S+1}{\left[1 + \frac{S(r_i^{1/2} + r_i^{-1/2})}{2}\right]} \right]^{1/2}$$

is the correction function for non-stoichiometric solutions, ϵ is the kink formation energy, k_A and k_B are attachment rate constants,

α and β are the mineral formula stoichiometric coefficients, and K_{sp} is the solubility product. This model predicts that step velocity, the rate of kink site nucleation, and the rate of kink site propagation will decrease at high and low r_i . In this model the rates of kink site nucleation and propagation have units of s^{-1} , which differs from the units of Frank (1974). The difference arises from Frank's analytical (i.e., continuum model) approach to describing the density and motion of kink sites whereas the ZN model treats the step edge as being comprised of discrete growth units.

The ZN model is expected to apply to growth of sparingly soluble AB-type minerals and has been expanded upon by Nielsen and coworkers (2012) to account for isotopic partitioning and Wolthers and coworkers (2012) to account for surface complexation. However, there have been some difficulties applying the model to different step orientations (Larsen et al., 2010) and multiple saturation indices simultaneously on calcite (Bracco et al., 2012) and magnesite (Bracco et al., 2014). These difficulties may arise because the ZN model ties the forward reaction (attachment) to the reverse reaction (detachment) through the solubility product, which assumes the reaction is reversible. If the forward and reverse reactions have different mechanisms, or different rate limiting steps, the model may be unable to accurately reproduce experimentally derived step velocities. Using metadynamics simulations, Stack and coworkers (2012) determined that the rate limiting reactions for barium attachment and detachment to barite step edges were different, suggesting that models which assume reversible attachment may not be applicable to barite.

Hellevang et al. (2014) determined that the main limitation of the ZN model is due to the constraints imposed by the saturation state which defines the shape of the growth rate curve as a function of r_i , leading to model peak shapes that are broader than experimentally observed (e.g.,

Bracco et al. (2012)). The authors were instead able to use a symmetric, empirical function to reproduce experimental data:

$$g(t) = 2^\gamma \left(\frac{1}{t\delta} + t\delta \right)^{-\gamma} \quad (4)$$

where $t = \frac{n[A]}{m[B]}$ and γ and δ are empirical fit parameters and n and m are the number of anions and cations per formula unit, respectively. Here γ affects the broadness of the peak and δ affects the t value at which step velocities are maximized. However γ and δ in this equation are solution saturation state and ionic strength dependent, which prevents the use of this equation to predict step velocities and growth rates under conditions that have not been examined experimentally.

The second model to consider is the kink site nucleation and propagation model from Stack and Grantham (2010) (SG model). This model uses the same length independent step velocity (equation 2) and R_{kn} has a similar functional form to R_{kp} (units for rates of nucleation and propagation are s^{-1} , consistent with Zhang and Nancollas (1998), but different from that of Frank (1974)):

$$R_{kn} = \frac{k_A[A]k_B[B]V_m}{k_A[A] + k_B[B]} - k_{kn}V_m \quad (5)$$

$$R_{kp} = \frac{k_A[A]k_B[B]V_m - k_{kpA}k_{kpB}V_m}{k_A[A] + k_B[B] + k_{kpA} + k_{kpB}} \quad (6)$$

In Equations (5) and (6) k_{kpA} and k_{kpB} are detachment rate constants from a kink site, and k_{kn} is the detachment term for the reverse of nucleation. This model predicts that step velocity, the rate of kink site propagation, and the rate of kink site nucleation will decrease at low and high r . The SG model successfully fits experimental step velocities on calcite (Bracco et al., 2012; Bracco et al., 2013; Stack and Grantham, 2010), celestite (Bracco et al., 2016), and magnesite (Bracco et al., 2014), and combined with step densities, can fit growth rates, which are similar to many macroscopic calcite growth rates measured under similar conditions (Bracco et al., 2013).

Past AFM investigations of barite growth (Kowacz et al., 2007) documented 2D island spreading rates at room temperature with a maximum in rate near $r \sim 10$, however temperatures in geologic formations are usually much higher and it is unclear how temperature would affect step behavior. Therefore, there is a need for further research into the effect of r on barite growth at elevated temperatures. In this study we investigate the aqueous barium:sulfate ratio dependence of barite growth via a spiral growth mechanism using *in situ* hydrothermal atomic force microscopy (HAFM) by measuring the bilayer $\langle 120 \rangle$ step velocities on the (001) barite surface. We also test the suitability of the ZN and SG models in describing the morphological results and step velocity measurements.

2. Methods

2.1. Materials and Solution Preparation

Optically clear and colorless, freshly cleaved barite samples from Sichuan, China containing minor impurities were used for HAFM experiments (Table 1). Due to the slow dissolution of barite in acid (including concentrated hydrochloric acid, nitric acid, and aqua regia) barite samples were analyzed for metal impurities by dissolving a 100 mg sample in 100 mL of a 50 mM ethylenediaminetetraacetate (EDTA) solution at pH = 13 (adjusted using aqueous NaOH) at 80 °C for 72 hours. All reagents used during analysis were of at least 99.99% purity. This method was modified from that reported by Averyt et al. (2003). At least 95% of the sample could be dissolved in this manner based on gravimetric and inductively-coupled plasma optical emission spectroscopy (ICP-OES) analysis, though the 72-hour yield decreased at lower EDTA concentrations. Further details of the barite chemical analysis are available in the Electronic Annex.

Table 1: Minor and trace impurities in barite

Element	Percentage element in barite
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	(mol/mol Ba%)
Ca	$2.9 \pm (0.2) \times 10^{-2}$
Cu	bdl (2.2×10^{-4})
Fe	$3.9 (\pm 0.2) \times 10^{-3}$
Mg	$1.20 (\pm 0.03) \times 10^{-2}$
Mn	bdl (1.2×10^{-5})
Pb	bdl (2.2×10^{-5})
Sr	$1.40 (\pm 0.01) \times 10^{-2}$

bdl: below detection limit

Supersaturated aqueous solutions for HAFM experiments were prepared using stock solutions prepared from high-purity reagents (of at least 99.99% purity). Stock solutions included 1.05 (± 0.02) mM Ba(NO₃)₂, 0.624 (± 0.02) mM Na₂SO₄, nominally 1 mM NaNO₃, and deionized water (resistivity = 18.2 MΩ·cm; Table 2). The molarity of the barium nitrate and sodium sulfate stock solutions were determined using ICP-OES (analysis of Na⁺ was used for determining SO₄²⁻ concentrations). PHREEQC was used to calculate solution speciation using the LLNL database (Parkhurst and Appelo, 1999) which included a K_{sp} for barite of 10^{-9.48} at 108 °C. Solution compositions (calculated at 108 °C) can be found in Table 2 ([i] denotes concentration of *i*th species). Atmospheric CO₂ was not removed from solutions as it does not significantly affect saturation states, and predicted concentrations of CO₂ were significantly lower than those required to inhibit growth (Sanchez-Pastor et al., 2013). The saturation indices (

$$SI = \log \left[\frac{(Ba^{2+})(SO_4^{2-})}{K_{sp}(barite)} \right], (i) \text{ denotes activity of species } i) \text{ studied were } SI = 0.12, 0.33, \text{ and } 0.52$$

and the pH was not intentionally fixed, though the pH calculated using PHREEQC was 6.2 for all solutions.

Table 2: Solution compositions for the HAFM growth experiments.

SI	r ([Ba ²⁺]/[SO ₄ ²⁻])	mL Ba(NO ₃) ₂	mL Na ₂ SO ₄	mL NaNO ₃	[Ba ²⁺] (M)	[SO ₄ ²⁻] (M)	I (M)	<120> step velocity (nm/s)
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0.14(±0.03)	$1.78(\pm 0.07) \times 10^{-2}$	0.33	32.0	67.7	$3.45(\pm 0.07) \times 10^{-6}$	$1.94(\pm 0.1) \times 10^{-4}$	$1.27(\pm 0.04) \times 10^{-3}$	0.25 (±0.02)
0.12(±0.04)	$7.77(\pm 0.31) \times 10^{-2}$	0.67	14.9	84.4	$3.45(\pm 0.20) \times 10^{-6}$	$1.94(\pm 0.06) \times 10^{-5}$	$1.14(\pm 0.02) \times 10^{-3}$	0.54 (±0.03)
0.12(±0.04)	$2.95(\pm 0.12) \times 10^{-1}$	1.30	7.60	91.1	$1.36(\pm 0.030) \times 10^{-5}$	$4.60(\pm 0.30) \times 10^{-5}$	$1.09(\pm 0.01) \times 10^{-3}$	0.78 (±0.04)
0.12 (±0.04)	$1.67(\pm 0.07) \times 10^0$	3.10	3.20	93.7	$3.24(\pm 0.07) \times 10^{-5}$	$1.94(\pm 0.10) \times 10^{-5}$	$1.09(\pm 0.01) \times 10^{-3}$	1.26 (±0.05)
0.12 (±0.03)	$2.71(\pm 0.11) \times 10^1$	12.6	0.80	86.6	$1.32(\pm 0.03) \times 10^{-4}$	$4.85(\pm 0.30) \times 10^{-6}$	$1.28(\pm 0.01) \times 10^{-3}$	0.71 (±0.04)
0.12 (±0.03)	$2.71(\pm 0.11) \times 10^1$	12.6	0.80	86.6	$1.32(\pm 0.03) \times 10^{-4}$	$4.85(\pm 0.30) \times 10^{-6}$	$1.28(\pm 0.01) \times 10^{-3}$	0.81 (±0.02)
0.10 (±0.04)	$1.72(\pm 0.07) \times 10^2$	32.0	0.32	67.7	$3.34(\pm 0.07) \times 10^{-4}$	$1.94(\pm 0.10) \times 10^{-6}$	$1.69(\pm 0.02) \times 10^{-3}$	0.36 (±0.04)
0.36 (±0.03)	$1.57(\pm 0.06) \times 10^{-2}$	0.40	44.0	55.6	$4.19(\pm 0.09) \times 10^{-6}$	$2.66(\pm 0.02) \times 10^{-4}$	$1.370(\pm 0.05) \times 10^{-3}$	0.78 (±0.10)
0.35 (±0.03)	$6.58(\pm 0.26) \times 10^{-2}$	0.80	21.0	78.2	$8.37(\pm 0.20) \times 10^{-6}$	$1.27(\pm 0.08) \times 10^{-4}$	$1.19(\pm 0.02) \times 10^{-3}$	0.36 (±0.01)
0.33 (±0.03)	$2.76(\pm 0.11) \times 10^{-1}$	1.6	10.0	88.4	$1.67(\pm 0.04) \times 10^{-5}$	$6.05(\pm 0.40) \times 10^{-5}$	$1.12(\pm 0.01) \times 10^{-3}$	1.24 (±0.07)
0.33 (±0.03)	$1.73(\pm 0.07) \times 10^0$	4.00	4.00	92.0	$4.18(\pm 0.09) \times 10^{-5}$	$2.42(\pm 0.20) \times 10^{-5}$	$1.12(\pm 0.01) \times 10^{-3}$	1.86 (±0.07)
0.32 (±0.04)	$1.08(\pm 0.04) \times 10^1$	10.0	1.60	88.4	$1.04(\pm 0.02) \times 10^{-4}$	$9.69(\pm 0.06) \times 10^{-6}$	$1.23(\pm 0.01) \times 10^{-3}$	1.13 (±0.03)
0.33 (±0.03)	$4.52(\pm 0.19) \times 10^1$	21.0	0.80	78.2	$2.19(\pm 0.05) \times 10^{-4}$	$4.85(\pm 0.30) \times 10^{-6}$	$1.46(\pm 0.02) \times 10^{-3}$	0.59 (±0.01)
0.53(±0.04)	$1.89(\pm 0.08) \times 10^2$	44.0	0.40	55.6	$4.58(\pm 0.10) \times 10^{-4}$	$2.43(\pm 0.20) \times 10^{-6}$	$1.94(\pm 0.03) \times 10^{-3}$	0.54 (±0.02)
0.54 (±0.03)	$2.31(\pm 0.09) \times 10^{-2}$	0.60	45.0	54.4	$6.29(\pm 0.10) \times 10^{-6}$	$2.72(\pm 0.20) \times 10^{-4}$	$1.386(\pm 0.05) \times 10^{-3}$	0.45 (±0.04)
0.54 (±0.03)	$1.12(\pm 0.05) \times 10^{-1}$	1.30	20.0	78.7	$1.36(\pm 0.03) \times 10^{-5}$	$1.21(\pm 0.08) \times 10^{-4}$	$1.19(\pm 0.03) \times 10^{-3}$	0.94 (±0.05)
0.52 (±0.04)	$4.32(\pm 0.18) \times 10^{-1}$	2.50	10.0	87.5	$2.61(\pm 0.06) \times 10^{-5}$	$6.05(\pm 0.40) \times 10^{-5}$	$1.14(\pm 0.01) \times 10^{-3}$	1.66 (±0.03)
0.52 (±0.04)	$1.73(\pm 0.07) \times 10^0$	5.00	5.00	90.0	$5.22(\pm 0.10) \times 10^{-5}$	$3.03(\pm 0.20) \times 10^{-5}$	$1.15(\pm 0.01) \times 10^{-3}$	2.63 (±0.03)
0.52 (±0.03)	$6.90(\pm 0.28) \times 10^0$	10.0	2.50	87.5	$1.04(\pm 0.02) \times 10^{-4}$	$1.51(\pm 0.10) \times 10^{-5}$	$1.24(\pm 0.01) \times 10^{-3}$	2.04 (±0.10)
0.52 (±0.04)	$2.65(\pm 0.11) \times 10^1$	20.0	1.30	78.7	$2.09(\pm 0.04) \times 10^{-4}$	$7.88(\pm 0.50) \times 10^{-6}$	$1.44(\pm 0.02) \times 10^{-3}$	1.18 (±0.02)

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178 NaNO_3 was used to maintain an ionic strength (I) in the range of 0.0011 - 0.0020 M for

179 consistency with prior HAFM studies of barite by Higgins et al. (2000) since background

electrolyte identity and ionic strength have been shown to have an effect on growth rates (Godinho et al., 2015) and step velocities (Kowacz et al., 2008).

2.2. HAFM Experiments

Samples of barite 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 with a gold wire (Higgins et al., 1998) and briefly exposed to deionized water at room temperature to clean the surface. Experiments were performed *in situ*, in constant flowing solution, at 108 °C and 4.1 atm (N₂) in contact mode using platinum iridium two-side coated cantilevers with a force constant in the range of 0.02 - 0.77 N/m (Nanoworld – CONTPt). A solution flow rate of 16.5 mL/hr (~1 mL internal volume of the fluid cell) was utilized; a rate at which growth was not limited by flow in this reactor configuration for barite (Figure 1). These flow rates were significantly higher than rates necessary for non-transport limited magnesite growth (Bracco et al., 2014), however flow rates were lower than those utilized during previous work on calcite (Bracco et al., 2012; Bracco et al., 2013; Stack and Grantham, 2010). Although required flow rates may differ due to differences in mineral reactivity, the HAFM fluid cell has more efficient mass transport near the cantilever (e.g., Bose et al., 2008) than in many commercial AFM fluid cells, thus enabling lower flow rates to be utilized in general.

Figure 1: Step velocities as a function of solution flow rate and nozzle velocity. Step velocities are independent of solution flow rate at flow rates > 12 mL/hr.

Step velocities were determined approximately 30 min after change of the solution composition, which ensured velocities had reached a steady value. For step velocity measurements, the data were collected by orienting the fast scan axis to be perpendicular to the steps of interest (in these experiments, the steps were oriented parallel to $\langle 120 \rangle$ directions) and disabling the slow scan axis at the apex of a spiral growth hillock and collecting four to ten position vs. time “images”. These “images” enabled us to measure the angle that the trace of the position of the step made over time with respect to the “image” horizontal axis, which can be related to the step velocity using the following equation:

$$v = \frac{R_s A}{L \tan \theta} \quad (7)$$

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 – 1.0 Hz depending on the step velocity. Step velocities were averaged on both sides of the growth hillock

(by symmetry, opposing $\langle 120 \rangle$ steps have the same structure and will have the same step velocity) to cancel possible effects of drift. Averages and standard deviations are derived from ~8-10 determinations at the given conditions. Step lengths were sufficiently long to ensure velocities were in a length independent step velocity regime (Higgins and Hu, 2006).

During scanning, small voids (as observed in Figure 2) were found on some of the surfaces. To investigate possible sources of contamination that could have produced the voids, stock solutions and outlet solutions from the fluid cell were collected and analyzed for total organic carbon and trace inorganic impurities, all of which were below a 1 ppm detection limit for the total organic carbon, below the 0.1 ppm detection limit for lead, and below the 0.01 ppm detection limit for strontium, calcium, iron, copper, manganese, and magnesium (based on ICP-OES). Formation of these voids was also not temperature dependent, suggesting they are not due to gas exsolution initiated on the barite surface during the experiment, a problem encountered at lower system pressures. It is possible that the dissolution of the crystal when initially exposed to deionized water leads to localized concentrations of impurities released from the crystal and readsorbed onto the surface which in turn lead to inhibition of growth in localized regions.

Figure 2: In-situ HAFM deflection images showing step morphologies on barite at a) and c) near unity r , b) low r and d) high r . Images display hillocks with the effect of an illumination source on the left. The crystallographic axes are the same in a) and b) and the same in c) and d). At $r \sim 1$ hillock morphologies follow the typical $\langle 120 \rangle$ step directions, however at low r the $[010]$ step is expressed and the other steps are vicinal to the $\langle 120 \rangle$ directions, suggesting an increase in the kink site density. At high r , roughening and rounding occur, leading to an increase in the kink site density.

3. Results

3.1. Morphological Observations

Growth hillocks comprised of bilayer steps were consistently observed on the barite (001) surface at all three saturation indices studied (SI=0.12, 0.33, and 0.52). At $r \sim 1$, the hillocks (Figure 2a and 2c) were comprised of steps oriented parallel to the [120] and $[\bar{1}20]$ directions. Similar to $[\bar{4}41]$ and $[48\bar{1}]$ steps observed on calcite $\{10\bar{1}4\}$ surfaces, the $\langle 120 \rangle$ steps on barite (001) can either be obtuse or acute steps (Figure 3a). Due to the 2_1 screw axis on barite (space group: *Pnma*), successive monolayers on the surface are related to each other by a two-fold rotation about the c axis (parallel to [001]). Each half-unit cell height monolayer (3.6 Å) is comprised of two straight step edges (parallel to $\langle 120 \rangle$), which are speculated to be the acute termination, and a curved, rough step, purportedly the obtuse termination (de Antonio Gomez et al., 2013). At room temperature and under moderate supersaturation with $r \sim 1$ (Pina et al., 1998a; Pina et al., 1998b), this rough step advances significantly faster than the straight $\langle 120 \rangle$ step edges. As a result, each successive curved step edge meets the slow growing $\langle 120 \rangle$ steps in the underlying monolayer, leading to a hillock comprised of [120] and $[\bar{1}20]$ bilayer steps of height 7.15 Å. The bilayer steps will be terminated in the lower half-layer by acute $\langle 120 \rangle$ steps, as long as the acute steps advance more slowly than the obtuse steps (de Antonio Gomez et al., 2013). Straight steps following two other directions, the [010] direction, and $\langle 110 \rangle$ directions were not observed on growth hillocks at $r \sim 1$ (Figure 2). Based on the crystallography of barite monolayers (Figure 1 in the Electronic Annex), unless the bilayer $\langle 120 \rangle$ steps bifurcate, the [010] steps will have the opposite termination (obtuse or acute) as the $\langle 120 \rangle$ steps to either side, which arises from the shift in the positions of the sulfates in the underlying layer. Additional directions are also possible (Hartman and Strom, 1989), but not relevant here.

Figure 3: Cross-section view of acute and obtuse step terminations on barite (001). a) monolayer $\langle 120 \rangle$ steps, b) monolayer $[010]$ steps, c) bilayer $\langle 120 \rangle$ steps, and d) bilayer $[010]$ steps. Additional terminations are possible for the $[010]$ steps.

On growth hillocks at $r \sim 1$ (Figure 2a and 2c), there are two distinct types of corners where the $\langle 120 \rangle$ steps meet. The first is an acute angle (78.281° , based on crystallography) which is formed where $[120]$ and $[\bar{1}20]$ bilayer steps must bifurcate (Figure 4b) due to the barite symmetry, forming the angle ϕ as shown in Figure 2a. The second is an obtuse angle (101.719°), θ (Figure 2a), which is formed by the intersection of $[120]$ and $[\bar{1}20]$ bilayer steps. In comparison, ϕ between crystallographically equivalent $\langle 110 \rangle$ steps is much smaller, at 63.130° and θ between $\langle 110 \rangle$ steps is 116.870° . The experimentally measured angle, ϕ , between these steps at $r \sim 1$ was $78 \pm 0.2^\circ$, confirming that the straight steps in Figure 2a and 2c are bilayer $\langle 120 \rangle$ steps, most likely of the acute orientation.

Figure 4: Schematic of barite hillock morphology observed at a) low r , b) near unity r , and c) high r . Thick lines represent bilayer steps and thin lines represent monolayer steps.

The hillock morphology changed significantly at extreme r . At $r \ll 1$, two step directions were observed, straight steps vicinal to the $\langle 120 \rangle$ directions and straight steps parallel to the $[010]$ direction (Figure 2b; Figure 5). The angle, ϕ , at which two of the vicinal steps met was $69.1 \pm 0.4^\circ$, which suggests a step direction approximately halfway between the $\langle 120 \rangle$ and $\langle 110 \rangle$ directions. Based on the difference between ϕ at $r \ll 1$ and $r \sim 1$, the vicinal steps may have a

higher kink density compared to $\langle 120 \rangle$ steps at $r \sim 1$. This kink density, which should be regarded as a minimum based solely on unidirectional kinks, can be calculated by:

$\tan\left(\frac{\phi_{\langle 120 \rangle} - \phi_{\text{vicinal}}}{2}\right)/a$, where a is the kink depth (0.70 nm), $\phi_{\langle 120 \rangle}$ is the angle at which $\langle 120 \rangle$ steps meet at $r \sim 1$ (78.3°), and $\phi_{\text{vicinal}} = 69.1^\circ$, which gives a kink density of 0.12 (± 0.003) nm^{-1} . In Higgins et al. (2000), the kink density at 108°C was estimated at 0.025 nm^{-1} at $\text{SI} \sim 0.1$ and $r \sim 1$, which is almost an order of magnitude less than that observed here at $\text{SI} = 0.12$ and $r \ll 1$. At $r \gg 1$, the steps rounded and roughened parallel to the $[010]$ step direction (Figure 2d), though unlike at $r \ll 1$, straight $[010]$ steps were not observed. A movie of a hillock growing at $r \gg 1$ can be found in the Electronic Annex demonstrating that in both the height and deflection AFM images, the steps parallel to the $[010]$ direction were quite rough and this observation is unlikely to be due to the resolution of the images. Microdomains of steps parallel to $[010]$ may exist below the resolution of our images.

Figure 5. A (002) elementary half layer on the barite surface with the $\langle 120 \rangle$, $[010]$, and $[100]$ directions marked. The zigzagging red lines along the $[010]$ direction are periodic

bonded chains predicted by Hartman and Strom (1989). Heights for the barium ions and sulfur ions in the sulfate tetrahedral are indicated using black and dark blue for the high positions and gray and light blue for the low positions. Steps observed on barite growth hillocks follow the $\langle 120 \rangle$ step direction at $r \sim 1$, but change as a function of r as the kink site density changes.

3.2. Step Velocity Measurements

Whereas changes in r had a significant influence on the morphology of the spiral growth hillocks (Figure 2), these same changes also influenced the velocities of propagating step edges. For each of the saturation indices studied, step velocities were maximized at $r \sim 1$ (Figure 6), and decreased roughly symmetrically at high and low r . Similar to previous results on calcite (Larsen et al., 2010, Stack and Grantham, 2010; Bracco et al., 2012), magnesite (Bracco et al., 2014), and celestite (Bracco et al., 2016), the maximum step velocities occurred at r close to or slightly greater than 1, possibly due to differences in cation and anion dehydration frequencies in solution and at the mineral surface. At extreme r , similar velocities were measured for all three SIs. When compared with velocities near $r \sim 1$, this suggests the shape of the step velocity curve flattens at low SI, consistent with model predictions (Stack and Grantham, 2010; Zhang and Nancollas, 1998) and previous results on obtuse and acute steps on calcite (Bracco et al., 2012).

Figure 6: a) Barite step velocities as a function of r and b) the residuals from the model fit.

It is speculated that these steps are likely the acute step termination. Model fits are to the Zhang and Nancollas (1998) model using the formulation from Nielsen et al. (2012) where the detachment rate constants are assumed to be different for barium and sulfate ions. The kink formation energy is from Higgins et al. (2000) and is assumed to be the same for barium and sulfate ions.

4. Discussion

4.1. Morphological Implications

The appearance of the [010] steps at low r as shown in Figure 2b demonstrates that the [010] step velocity has decreased significantly compared to its velocity at higher r where the [010] step direction is absent (Figure 2a). While [010] steps are found on barite at high ionic strength ($I = 0.75$ M; (Risthaus et al., 2001)), the differences in ionic strength at $r \sim 1$ and $r \ll 1$ are well below that threshold at 0.0011 and 0.0013 M, respectively. These [010] steps also would be acute terminated steps (assuming the $\langle 120 \rangle$ steps are acute) based on the bifurcation of the bilayer $\langle 120 \rangle$ steps. Since the $\langle 120 \rangle$ steps have bifurcated, this also leads to both obtuse and acute $\langle 120 \rangle$ steps being expressed at low r (Figure 4a), implying that the obtuse and acute $\langle 120 \rangle$ steps are traveling at the same rate at $r \ll 1$, something which has been observed on calcite both at $r \ll 1$ ((Bracco et al., 2012; Stack and Grantham, 2010) and under near equilibrium conditions (Teng et al., 1999). The presence of the [010] step on barite at low r is intriguing, as it is unclear how the [010] step is terminated. Possibilities include termination by a single ion, likely sulfate at low r , or zigzagging chains of bariums and sulfates (Figure 5) based on periodic bond chain theory (Hartman and Strom, 1989; Pina et al., 1998b). This zig-zag step termination would be electrostatically neutral and comprised of micro-steps parallel to $\langle 120 \rangle$, which would represent a highly kinked configuration. Risthaus et al. (2001) and Becker (2001) suggest that since these steps are highly kinked they would be more sensitive to dissolution, but if sodium or chloride ions adsorb to the step, the steps would be electrostatically neutral and more stable than steps without the ions adsorbed. The sodium and chloride ions would then be desorbed and replaced with barium and sulfate ions as the step grows. For either type of termination, the [010] steps are likely rougher at the atomic scale than the $\langle 120 \rangle$ steps and probably represent a highly kinked configuration in which attachment of barium ions, present in the minority, at sulfate kinks is rate-

limiting. The barite hillock morphology is in contrast to growth hillocks observed on celestite (Risthaus et al., 2001), where growth hillocks were comprised of [010] steps and steps vicinal to the $\langle 120 \rangle$ direction. It is unclear why [010] steps are found on celestite but not barite at low ionic strength, but may be due to slower attachment kinetics to the [010] direction for celestite than barite as the [010] steps will only appear when step velocities are approximately equal to or less than velocities of the $\langle 120 \rangle$ steps.

The observations of simultaneous obtuse and acute terminations for $\langle 120 \rangle$ bilayer steps in Figure 2b has important implications for the ion attachment kinetics at step edges. At $r \ll 1$, equations 2, 5 and 6 simplify to $v = ak_{Ba}[Ba^{2+}]$ assuming the detachment reactions are insignificant. Based on the resultant hillock morphology observed here (i.e., bifurcation of $\langle 120 \rangle$ bilayer steps), this suggests that the attachment rate constants for barium ions to both obtuse and acute $\langle 120 \rangle$ steps are similar, which leads to similar step velocities for the two step orientations at low r . At $r > 1$ (Figure 2d), no bifurcation is observed for the bilayer $\langle 120 \rangle$ steps, which suggests that the obtuse steps travel faster than the acute steps even at $r > 1$, which has also been observed on calcite (Bracco et al., 2012; Stack and Grantham, 2010). At high r , equations 2, 5 and 6 simplify to $v = ak_{SO_4}[SO_4^{2-}]$ again assuming detachment reactions are not significant. For the obtuse orientation to travel faster than the acute orientation even at $r > 1$, there would need to be a significant difference in the attachment rate constants for sulfate ions to the obtuse and acute steps with $k_{SO_4(obtuse)} > k_{SO_4(acute)}$. In addition to the absence of straight [010] steps at $r > 1$, the $\langle 120 \rangle$ steps roughened and at the most extreme r , the bilayer steps rounded, taking on a curvilinear (Figure 4c), but roughened (Figure 2d), morphology. Morphological changes with respect to r have also been observed on barite at room temperature. At low r on barite at room temperature, growth occurred primarily through advancement of pre-existing steps, but as r

increased, growth occurred primarily through nucleation and spreading of two-dimensional islands (Kowacz et al., 2007). Morphological changes were also observed on calcite growth hillocks (Bracco et al., 2012; Larsen et al., 2010; Stack and Grantham, 2010), including roughening and rounding of steps at low r , suggesting an increase in the kink site density with changes to r , similar to the roughening and rounding observed here on barite at high r . We were unable to estimate a kink density on the vicinal steps at $r > 1$ due to the degree of rounding, but based on the mesoscale step morphology (Figure 2d), steps appeared significantly rougher than at $r \sim 1$ (Figure 2a and 2c). This is consistent with the Zhang and Nancollas (1998) model, which predicts kink densities will be maximized at extreme r_i and minimized at $r_i = 1$.

A previous study on the effect of r on barite at room temperature reported maximum island lateral spreading rates at $r \sim 10$ and nonsymmetrical decreases in rate with respect to r (Kowacz et al., 2007). These observations appear to be inconsistent with the results of the current study, however, there are a number of reasons why there may be differences between two sets of results. First, differences in growth mechanism may arise from the differences in temperature and saturation state. The experiments in Kowacz et al. (2007) were carried out at room temperature, much lower than what we report here, and at higher saturation indices (SI = 1.1 and 0.86) than those here (SI = 0.12, 0.33, and 0.53). The differences in supersaturation may be important to consider if peak velocities shift with supersaturation, however, the data in Figure 6 refute this possibility over the range of SI employed here. In our experiments, the dominant growth mechanism was spiral growth, while it was two-dimensional island nucleation and spreading in Kowacz et al. (2007). Another potential reason for the discrepancy in the two studies is that measurements of island spreading rates are a convolution of the step velocities of the obtuse and acute steps, whereas in the present work we measured the step velocity of the

396 slower advancing steps, likely of the acute orientation, exclusively. While we speculate that the
397 obtuse and acute steps on barite (001) may display peak velocities at different cation:anion
398 ratios, there is evidence for this in the case of calcite where the obtuse step peak velocity is at a
399 higher r than the peak for acute steps (Larsen et al., 2010; Stack and Grantham, 2010; Bracco et
400 al., 2012). As reported by Larsen et al. (2010) for calcite growth, a difference in the r at which
401 step velocities peak for two different step orientations implies that the step velocities are partially
402 controlled by the dehydration rates of ions on step edges or geometric constraints. The
403 differences in our observations from previous barite observations may also be attributable to
404 differences in fluid cell configurations. Kowacz et al. (2007) utilized an intermittent flow-
405 through system, which may lead to transport limited growth rates, whereas we used a
406 continuous-flow fluid delivery system and measured step velocities which were independent of
407 solution flow rates. The reported differences may also arise from changes in the hydration
408 structure for barium or sulfate at elevated temperatures. The metadynamics derived attachment
409 rate constants from Stack et al. (2012) were similar at 415 K and 385 K, indicating non-
410 Arrhenius behavior that is possibly attributable to changes in the interfacial water structure, such
411 as changes to the coordination number, which may in turn lead to a shift in the value of r at
412 which step velocities are maximized. Differences in pH (Ruiz-Agudo et al., 2015), ionic strength,
413 and background electrolyte (Kowacz and Putnis, 2008) are not expected to be significant enough
414 to account for the differences in peak position. Unlike step velocities on calcite, which are
415 strongly affected by the pH of the solution (Ruiz-Agudo et al., 2011), step velocities on barite at
416 constant r and SI are pH independent from pH $\sim$ 3 -10 (Ruiz-Agudo et al., 2015). This may be
417 due to differences in surface complexation on barite and calcite surfaces and suggests that while

pH affects the r value at which calcite step velocities peak (Hong and Teng, 2014), it is unlikely that pH significantly influences the r value at which barite step velocities peak.

4.2. Model Fitting

We fit our step velocity data using Newton-Raphson minimizations to two different models: the Zhang and Nancollas (1998) model (equations 2-3), which is shown with the data in Figure 6 and the Stack and Grantham (2010) nucleation and propagation model (equations 2 and 5-6), which is shown with the same data in Figure 7. In the ZN model, the detachment frequencies (ν) and the kink formation energies (ϵ) for the two component ions are assumed to be the same since the same bond is assumed to be created and broken. Since the step velocities peak at $r = 1.7$, here $\frac{k_A}{k_B} = \frac{1}{1.7}$, so $r_i = r \frac{k_A}{k_B} = \frac{1}{1.7} r$. We were unable to satisfactorily fit the data using this model, despite evaluating it using a number of different assumptions including (1) values for ν and ϵ from Higgins et al., 2000 (Figure 2 in Electronic Annex): $\nu = 187 \text{ s}^{-1}$ and $\epsilon = 0.15 \text{ eV}$, (2) $\epsilon = 0.15 \text{ eV}$ with ν (k_A can be calculated from ν) allowed to vary ($\nu = 86.8 \text{ s}^{-1}$) (Figure 3 in Electronic Annex), and (3) ν , ϵ , and K_{sp} allowed to vary (Figure 4 in Electronic Annex): $K_{sp} = 1.72 \times 10^{-11}$, $\nu = 28.8 \text{ s}^{-1}$, and $\epsilon = 0.20 \text{ eV}$. Aside from a poor fit in this last case, the K_{sp} value is unrealistically small in comparison to the literature value. Finally, we used the Nielsen et al., (2012) formulation of the Zhang and Nancollas (1998) model (note that in this model the authors

define $S = \frac{\{A\}^\alpha \{B\}^\beta}{K_{sp}}$ rather than $S = \left(\frac{\{A\}^\alpha \{B\}^\beta}{K_{sp}} \right)^{1/(\alpha+\beta)}$):

$$v = h/2 \left\{ \exp\left(\frac{-2\epsilon_{Ba}}{kT}\right) \frac{\nu_{SO4}^{3/2} (S\nu_{Ba}r)^{1/2}}{\nu_{SO4} + (S\nu_{Ba}\nu_{SO4})^{1/2}} + \exp\left(\frac{-2\epsilon_{SO4}}{kT}\right) \frac{\nu_{Ba}^{3/2} (S\nu_{SO4}/r)^{1/2}}{\nu_{Ba} + \left(\frac{S\nu_{Ba}\nu_{SO4}}{r}\right)^{1/2}} \right\} \times$$

$$\left[\frac{\nu_{Ba} + \nu_{SO4} + (S\nu_{Ba}\nu_{SO4}/r)^{1/2} + (S\nu_{SO4}/r)^{1/2}}{\nu_{Ba} + \nu_{SO4}} \right]^{1/2} \times \left[\frac{2\nu_{Ba}\nu_{SO4}(S-1)}{\nu_{Ba} + \nu_{SO4} + (S\nu_{Ba}\nu_{SO4}/r)^{1/2} + (S\nu_{SO4}/r)^{1/2}} \right] \quad (8)$$

This version of the ZN model allows for different detachment rates and kink formation energies for the two component ions, a supposition for which there exists some supporting computational evidence. For example, in molecular dynamics simulations of barite {120} acute steps by Stack (2009), significantly larger energies were necessary to detach a barium ion from a straight step to form a double kink site than to detach a sulfate ion, which suggests that the detachment dynamics may also be different for the two ions. For the fit in Figure 6, we fixed the kink formation energy for barium and sulfate at 0.15 eV, the value from Higgins et al. (2000). When we did allow the kink formation energies to vary, the covariance among parameters was too high to yield a unique set of fit parameters. We also fixed the K_{sp} at $10^{-9.48}$, the value utilized in the PHREEQC calculations at 108 °C. Using Equation 8, we were still unable to obtain an appropriate fit to our data (Figure 6; Table 3). Table 3 includes rate constants that have been divided by the molar volume of barite ($52.24 \text{ cm}^3/\text{mol}$) to convert the rate constants to the appropriate units to compare with metadynamics results by Stack et al. (2012). The rate constant for the rate limiting step for attachment of a barium ion to an acute [120] barite step derived from metadynamics computations is $3.3 (+/- 1) \times 10^7 \text{ s}^{-1}$ (Stack et al., 2012) which agrees well with this model fit ($4.0 (+/- 0.1) \times 10^7 \text{ s}^{-1}$). However, the rate constant for detachment of a barium ion from a step using metadynamics was $7.3 (+/- 2) \times 10^5 \text{ s}^{-1}$, which is four orders of magnitude higher than the rate constant that is obtained by fitting our data to the Nielsen et al. (2012) adaptation of the ZN model ($29 (+/- 0.7) \text{ s}^{-1}$). This latter rate constant is significantly closer to the detachment frequency reported as $187 (+/- 17) \text{ s}^{-1}$ in Higgins et al. (2000). A plot of the residuals (step velocity - predicted step velocity) as a function of r can be found in Figure 6b. The residual plot clearly displays a peak, with deviations from the observed step velocity maximized at $r \sim 1$ and decreasing roughly symmetrically at high and low r . This residual

structure demonstrates that the model is missing a key component of the data, which is particularly important to include at the higher step velocities observed at $r \sim 1$.

Figure 7: a) Barite step velocities as a function of r and b) the residuals from the model fit. Model fits are to the kink site nucleation and propagation model from Stack and Grantham (2010).

Table 3: Fit Parameters to the Nielsen et al., 2012 crystal growth model derived from Zhang and Nancollas (1998) and the Stack and Grantham (2010) model.

Nielsen et al., 2012 rate coefficients		
	fit value	fit value/ V_m
$k_{Ba} (M^{-1} \cdot s^{-1})$	$2.1 (\pm 0.05) \times 10^6$	$4.0 (\pm 0.1) \times 10^7 (s^{-1})$
$k_{SO4} (M^{-1} \cdot s^{-1})$	$3.6 (\pm 0.09) \times 10^6$	$7.0 (\pm 0.1) \times 10^7 (s^{-1})$
$k_{kpBa} (s^{-1})$	$29 (\pm 0.7)$	
$k_{kpSO4} (s^{-1})$	$86 (\pm 2)$	
$\epsilon_{Ba} (eV)$	0.15	
$\epsilon_{SO4} (eV)$	0.15	
Stack and Grantham (2010) rate coefficients		
	fit value	fit value/ V_m
$k_{Ba} \cdot V_m (M^{-1} \cdot s^{-1})$	$8.9 (\pm 0.3) \times 10^4$	$1.7 (\pm 0.06) \times 10^6 (s^{-1})$
$k_{SO4} \cdot V_m (M^{-1} \cdot s^{-1})$	$1.6 (\pm 0.05) \times 10^5$	$3.0 (\pm 0.09) \times 10^6 (s^{-1})$
$k_{kn} \cdot V_m (s^{-1})$	$0.061 (\pm 0.03)$	$5.5 (\pm 0.09) \times 10^2 (s^{-1})$
$k_{kpBa} \cdot V_m (s^{-1})$	$0 (s^{-1})$	
$k_{kpSO4} \cdot V_m (s^{-1})$	$0 (s^{-1})$	

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470 Aside from the difficulty in fitting the current experimental data with the ZN model, this

471 model has also been found to be unable to fit step velocities observed on calcite and magnesite as

472 a function of r (Bracco et al., 2012; Bracco et al., 2014; Larsen et al., 2010). Further evidence for

473 difficulties using the model for predicting growth of sparingly soluble minerals comes from

474 Hellevang et al. (2014) in which the authors evaluated the suitability of the model for various

475 AB-type crystals. They found that the ZN model could not reproduce bulk growth rates of calcite

476 (Nehrke et al., 2007; van der Weijden and van der Weijden, 2014) and gypsum (Zhang and

477 Nancollas, 1992), nor could the model predict step velocities on barite (Kowacz et al., 2007) and

478 calcium oxalate (Chernov et al., 2006). We hypothesize that the model does not replicate these

479 step velocities because it is based on the assumption that kink site attachment is reversible,

480 thereby linking forward and reverse rate constants by the solubility product. For some minerals

481 this may be the case (i.e., reversible attachment/detachment), but if the attachment and

482 detachment reactions have different mechanisms, the model assumption does not hold. The ZN

model also may not apply to barite $\langle 120 \rangle$ steps because the model was designed for a sodium chloride-type cubic crystal lattice, while crystal lattices for minerals such as calcite and barite possess lower symmetry. Due to barite $\langle 120 \rangle$ steps taking on a vicinal step direction at extreme r , it is also likely the steps take on an orientation that is not in accordance with the assumptions inherent in the model, particularly those involving the kink annihilation term. In the Zhang and Nancollas (1990) paper, kinks are assumed to be uniformly distributed along a step edge, with the probability of left and right hand facing kinks each being equal to $\frac{1}{2}$. However, in the case of a vicinal step orientation, one type of kink will be in excess over the other, leading to an accumulation of either left or right facing kinks. Thus, annihilation of kinks opposing the step vicinality becomes more probable than kinks facing the same direction as those in excess. This formation of vicinal steps due to asymmetry in the kink propagation rates for opposing kinks has been demonstrated through Monte Carlo simulations of retreating steps by Jordan et al. (2001) and by Xu et al. (2011). For the Zhang and Nancollas model (1990, 1998), only non-vicinal step orientations possess the kink symmetry that is assumed, thus the Zhang and Nancollas (1990) annihilation rate does not apply to vicinal steps.

We also fit the step velocity data using the model from Stack and Grantham (2010) for kink site nucleation and propagation (Figure 7; equations 2, 5-6). The fit to the SG model was much improved over the ZN model. The residuals can be seen in Figure 7b and all are between -0.25 – 0.35, whereas half of the residuals for the ZN model fell outside this range. Unlike the ZN model, the residual plots for the SG fit displayed very little structure as residuals for similar step velocities were often both greater than or less than zero, indicating no relationship between the residuals and step velocities. This suggests the model contains all of the necessary parameters. The fit coefficients for the best fit to our data are listed in Table 3. The values for k_{Ba} and k_{SO4}

are approximately three orders of magnitude less than the attachment rate coefficient derived using metadynamics simulations by Stack et al. (2012) and detachment of kinks, k_{pA} and k_{pB} , is not significant. This leads to the fit for the nucleation and propagation model being equally good as a fit to the nucleation portion of the equation or the propagation portion of the equation as they have very similar functional forms.

4.3. Implications for Geochemical Modeling

Prediction of mineral precipitation and dissolution in subsurface environments is often achieved through the use of reactive transport modeling, which computes mineral growth and dissolution rates using an affinity based model (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). At extreme values of r these models predict that growth rates are the same as those at $r = 1$, whereas our research demonstrates that step velocities may be up to an order of magnitude different on barite. This has significant implications for geochemical applications involving barite, such as scale formation during oil recovery, but perhaps most importantly remediation of radium through incorporation into crystallizing barite (Curti et al., 2010). Recently we discovered inhibition of calcite growth by strontium is dependent on the aqueous calcium-to-carbonate ratio and that the inhibition of growth was correlated to the strontium-to-calcium ratio (Bracco et al., 2012). This suggests accurately predicting the effect of foreign ions on growth rates depends not only on the saturation state and concentration of foreign ions, but also on r . Based on our results on barite growth, the Stack and Grantham (2010) model

can successfully be used to describe quantitatively mineral growth rates and also has a functional form that is simplistic enough to replace common affinity based models in reactive transport code. Taken into consideration with previous results on calcite (Stack and Grantham, 2010; Bracco et al., 2012; Bracco et al., 2013) and magnesite (Bracco et al., 2014), the present work further highlights the solution cation-to-anion ratio as an important parameter that can affect mineral growth rates by an order of magnitude or more, suggesting that incorporation of process based models is an important step for further refining the accuracy of reactive transport modeling for applications such as contaminant remediation by co-crystallization.

4. Conclusions

In situ observations of barite growth as a function of r reveal changes in both kink densities and step velocities. Step velocities peaked at $r \sim 1$ which means attachment rate constants for barium and sulfate ions are similar under our solution conditions. While the peak step velocity differs from a previous study by Kowacz et al. (2007), this is likely due to differences in the temperatures of the studies and basic differences in the measured quantities but leaves remaining the possibility that the obtuse and acute $\langle 120 \rangle$ step velocities peak at different r . Step velocities decreased significantly at extreme r and the kink site densities increased either through roughening, at $r > 1$, or through steps adopting different directions at $r < 1$. While the Zhang and Nancollas (1998) model predicts an increase in kink densities which is consistent with our observations at extreme r , the model is unable to replicate our experimental step velocities. In comparison, the Stack and Grantham (2010) model provided a much improved fit to experimental step velocities as a function of r .

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