Effect of Lanthanum on the Crystal Growth of Barium Sulfate

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ABSTRACT: Dipositive cation substitution in sulfate minerals has been a topic of investigation both experimentally and computationally. Here the possibility of tripositive cation substitution with accompanying vacancy formation is considered, specifically lanthanum ion substitution in barium sulfate. Experimentally, the lanthanum ions impact “bulk” crystallization in a way that is best explained by considering the solution phase ion-pair interactions. However, morphological results suggest that lanthanum ions do more than impact the free sulfate levels. Atomic force microscopy results showed that both lanthanum and calcium ions are strong inhibitors of barite growth. X-ray diffraction on bulk samples showed that lanthanum ions do indeed incorporate, as determined by lattice parameter changes. Finally, computational modeling suggests that while calcium incorporation is more energetically favorable, lanthanum ions prefer to substitute on the surface more so than calcium ions.

INTRODUCTION

The precipitation of barium sulfate has been the topic of investigation for many researchers. Over the years, we have learned, for instance, that growth on the (001) face of barite (or baryte, the mineral name for BaSO4) involves spiral growth at low supersaturations and two-dimensional (2D) nucleation followed by birth and spread at higher supersaturations.1,2 Much of this work has involved relatively pure systems, and information regarding the effect of impurities is dominated by the effect of organic anions.3 Despite the precipitation of barite being industrially significant for the off-shore oil industry,4-6 studies into the effect of cations on barite precipitation have been limited, even though seawater contains many different cations. In general, the effect of those ions with which barite forms a solid solution (Sr2+)7-10 or are known to incorporate in the lattice (Ca2+)11,12 has been investigated where the impurities were found to alter 2D nucleation shape and rate or morphology. In many cases the impact on solubility was investigated rather than the effects on crystallization. It is found, for example, that many +1 cations actually promote crystallization of barium sulfate,13-15 at moderately high concentrations, and this has been related to their impact on the solution water structure.13,14 The only other ions investigated have been zinc ions16 and lead.17,18 In the case of zinc ions, little impact on morphology was observed, and in the case of lead, the study was to investigate the solubility of the pure angesite. In the studies investigating calcium and strontium, the concentrations of those ions were relatively high: strontium at 800–6000 μM12 and calcium at ~1000 ppm11 with some of our own work investigating lower concentrations.19,20 The +3 ions that have been discussed in the literature with reference to barium sulfate precipitation are iron(III) ions,21 aluminum ions,22 europium,23 cerium and terbium ions.24 In the case of iron, the main observation is that it complexes preferentially with organic inhibitors and thereby makes them less effective.21 Aluminum ions on the other hand were only investigated with respect to their morphological impacts where roughening on the (hk0) faces at 25 °C was observed, although this could have been due to crystallization of Al(OH)3 rather than to specific Al3+ effects on barium sulfate crystallization.22 For the other +3 ions, these have been investigated from a luminescent perspective rather than a crystallization one, thus focusing on their photochemical behavior or their partitioning behavior (between solution and solid).23,24

Molecular modeling has been shown to be a useful tool to understand the impact of impurity ions on crystallization processes.12,18-28 These studies, while not always pertaining to barium sulfate, focus on the calculation of the segregation energy to determine whether the impurity ion prefers to substitute into a particular surface or the bulk and the impacts this can have on crystal morphology. Of particular relevance is a report modeling the impact of calcium and strontium sulfate overgrowth on barite morphology.25 This work showed that while strontium ions always prefer to substitute in the bulk, calcium ions prefer surface substitution for some barium sulfate faces according to the calculated segregation energy. This work did not investigate partial surface coverage. The later work of Wahid et al.12 shows that bulk calcium ion incorporation was preferred to strontium ion incorporation only after 18% of the total sites were substituted, but no information was provided on whether the ions will segregate toward the surface. Thus, we
can conclude from these computational investigations that calcium and strontium ions both substitute for barium and that for some of the barite faces, calcium ions segregate to the surface.

In this manuscript, we report the impact of lanthanum ions on barite crystallization, in the absence of organic impurities. These experiments will be at concentrations where the main driving force is for barium sulfate precipitation rather than impurity cation sulfate crystallization, which allows an interpretation of the effects based solely on the interaction these cations have with the crystallizing barium sulfate. The impact of calcium and zinc ions on barium sulfate crystallization at similar levels is discussed for comparison purposes. In addition, we also present molecular modeling results on the incorporation of calcium and lanthanum to understand, at a deeper level, the energetics of substituting lanthanum into these cations have with the crystallizing barium sulfate. The effect of calcium and zinc ions on barium sulfate crystallization at similar levels is discussed for comparison purposes.16,19,20

EXPERIMENTAL METHODS

The program PHREEQC was used to determine the ionic strength, the molality of ions, and the activity of ions for each experiment. The ion activity product (IAP) was calculated and the supersaturation of the solution was defined as $S = \sqrt{(IAP/K_{sp})}$, where $K_{sp}$ is the solubility product.

AFM. AFM experiments were performed on a PicoPlus (manufactured by Molecular Imaging) using a standard silicon nitride cantilever with a flow through cell attachment. A freshly cleaved barium sulfate mineralogical sample attached to a metallic stub was flushed with filtered (Gelman 0.2 μm Supor membrane filters) ultrapure water (resistivity >18 MΩ) using a precision dual syringe pump run at 0.2 mL/min in the flow cell. One syringe then had the water replaced with barium chloride solution (0.1 mM) and the other with sodium sulfate solution (0.1 mM). This was then flushed through the cell at a rate of 0.2 mL/min as per the water and pure barium sulfate run. In this way, the rate of growth of the original barium sulfate could be measured, and the differences when impurity was added could be determined.

Conductivity. Unseeded runs were conducted at 25 °C using conductivity (WTW LF 197 Conductivity meter) to monitor the crystallization in situ as previously described. The method consisted of equilibrating 0.249 mM BaCl₂ and adding 1 mol equivalent of Na₂SO₄ solution to initiate crystallization. The total volume for all experiments was 201 mL. The graph of conductivity versus time was used to calculate $k_{des}$ (observed desupersaturation rate) by fitting the linear region of the desupersaturation curve. The pH for all experiments was 5.6 except where specified. Cation impurities were added (as the chloride salt) to the barium chloride solution prior to the addition of sulfate. The concentration of these salts was below the $M_{\text{SO}_4}$ precipitation threshold, and so barium sulfate is always formed. The desupersaturation rate was found to have an error of ∼10%. The conductivity measures the “amount” of mobile ions in solution; thus complexation of cations with anions will change the conductivity value.

Scanning Electron Microscopy (SEM). The barium sulfate solids were collected after conductivity runs and filtered onto 0.22 μm membranes. The solids were subsequently washed and dried in a desiccator. A portion of the filter paper was placed onto a carbon-coated stub and gold sputtered prior to viewing in a Philips XL30 instrument.

XRD. Powder XRD patterns were collected on solids obtained from 4 L batch repeat experiments scaled up from the conductivity runs (to obtain sufficient solids). Samples were mixed with a small amount of finely ground NaCl as an internal standard, dispersed in absolute ethanol, and then cast onto silicon-wafer zero-background plates. Diffraction patterns were recorded at 298 K on a Phillips X'pert powder diffractometer, with a cobalt long fine focus tube. The samples were step scanned from 5° to 90° 2θ, at 0.02° increments, using a counting time of 2 s per increment. Lattice parameters were refined by Rietveld analysis using the Unit Cell freeware.

Molecular Modeling. The modeling of cation incorporation was performed by using the previously reported empirical models for barium sulfate and calcium sulfate. For lanthanum ion incorporation, the lanthanum to oxygen interactions were fitted, using GULP to the (LaO)₂SO₄ structure using the La–O potential from Grimes as a starting point for both the La–O₅̅₈₅ and La–O₅̅₈₅₈₅ interactions. The La–O₅̅₈₅ interaction was fitted first and involved a
ions, M, is the bulk, thus $M^{+}$ minimized prior to the substitution of the di

$E_{\text{hydration}}$ of the ions, as per eq 1. The hydration energies of the ions, $E_{\text{hydration}}$, are calculated according to

$$E_{\text{hydration}} = V_{\text{hydration}}(\text{aq}) - V_{\text{hydration}}(\text{aq})$$

where $V_{\text{hydration}}(\text{aq})$ is the hydration energy of the pure $M^{+}$, and $V_{\text{hydration}}(\text{aq})$ is the hydration energy of the impurity ion in the surface or bulk. In this way, bulk substitution could be compared to surface substitution. Finally, in the case of lanthanum, the $Ba^{2+}$ ions could not be directly substituted due to charge mismatch. Therefore, three barium ions were substituted by two lanthanum ions, creating a barium ion vacancy.

In the case of the surface substitution, the slab was split into two regions: Region I represents the surface and ions within it are able to move during minimization, while Region II represents the bulk and all ions in this region are fixed. The (001) face of barium sulfate was simulated since this is the face that was imaged in the AFM experiments. This face required $6 \times 4 \times 4$ unit cells in Region I and $6 \times 4 \times 3$ in Region II (see Figure 1). The starting configuration was minimized prior to the substitution of the different ions.

The equation describing the substitution of barium ions with metal ions, M, is

$$\text{BaSO}_{4}(\text{bulk or surface}) + nM^{+} \rightarrow (V/x)Ba_{n/2}^{+}\text{Ba}^{0}$$

where $x$ refers to the total number of barium ions in the surface or bulk, $n$ the number of metal cations substituting, $e$ is the charge of the cation, and $V/x$ the vacancies produced (if any).

The energy to replace barium ions, the replacement energy, $E_{r}$, is calculated according to

$$E_{r} = (E_{\text{final}} + (ne/2)E_{\text{hydration}}) - (E_{\text{initial}} + nE_{\text{hydration}})$$

where $E_{\text{initial}}$ is the starting energy of the pure BaSO$_{4}$ and $E_{\text{final}}$ is the energy with the impurity ion in the surface or bulk and $n$, $e$ are defined as per eq 1. The hydration energies of the ions, $E_{\text{hydration}}$, are the experimental values taken from ref 37.

The segregation energy is defined as per ref 25 and is given by the following reaction:

$$nM^{+} + BaSO_{4}\text{(surface)} \rightarrow Ba^{2+} + M_{n}Ba_{2e-n/2}\text{SO}_{4}\text{(surface)}$$

where $n$, $x$, and $e$ are defined as per eq 1, the subscript $b$ now refers to the bulk, thus $M^{+}b$ is the impurity ion incorporated into the bulk, BaSO$_{4}$ (surface) is the starting surface configuration without impurity ions, Ba$^{2+}b$ is the pure bulk, and $M_{n}Ba_{2e-n/2}\text{SO}_{4}\text{(surface)}$ is the impurity ion incorporated into the surface. Thus, the segregation energy can be calculated from

$$E_{\text{seg}} = (E_{\text{Msurface}} + E_{\text{pure bulk}}) - (E_{\text{pure surface}} + E_{\text{Mbulk}})$$

where $E_{\text{Msurface}}$ is the energy of impurity ion(s) incorporated into the surface, $E_{\text{pure bulk}}$ is the energy of the pure bulk, $E_{\text{pure surface}}$ the energy of the pure surface, and $E_{\text{Mbulk}}$ is the energy of the impurity ion(s) in the bulk.

To our knowledge, all calculations of segregation energy to date use the energy of the pure surface in a vacuum in eq 4. Although this is entirely reasonable for the early segregation energy calculations undertaken on oxides where the interest was in the catalytic activity of defect surfaces at low pressures, it is not so appropriate for surfaces in solution. It is possible to model the impact of solvation on surfaces with defects explicitly using molecular dynamics, but these calculations are still very computationally expensive. However, a continuum solvation model on surfaces, namely, the COSMIC methodology implemented in the GULP code, is much less computationally intensive. This method, an extension of the COSMO model to periodic systems, assumes that the solvent behaves as a perfect conductor situated around a solvent accessible surface (SAS) above the surface of interest. The charges induced on the surface due to the electrostatic potential of the surface species are then determined and subsequently scaled to those appropriate to the dielectric constant of the solvent. There are several parameters that are required in the COSMIC model. The first is the dielectric constant of the solvent; for water, this is 78.4. The radius of water used to generate the solvent accessible surface was set to 1.4 Å, and the radius shift of water was then set equal to this radius, as is widely done. The number of points and segments per atom, which controls the fineness of the SAS, was set equal to 326. A smoothing range of 0.2 Å was used to ensure continuous behavior of the energy surface. Once these parameters have been chosen, the radii of the atoms are adjusted to reproduce the experimental solvation energies of the ions, resulting in the following radii: Ba 2.18 Å, Ca 1.81 Å, La 1.95 Å, S 1.50 Å, and O 1.48 Å.

**RESULTS**

**BaSO$_{4}$ Conductivity.** The desupersaturation results for barium sulfate precipitation in the presence of calcium, zinc, and lanthanum ions are summarized in Figure 2. The $y$ axis is given as a ratio to the control run to normalize the data; that is, the data are presented as $k_{\text{cat}}/k_{\text{control}}$. It can be seen that there are differences in the behavior of the different ions. The effect of zinc ions is essentially equivalent to that observed with calcium ions, while the lanthanum ions appear to have the greatest impact on the crystallization behavior of barium sulfate.
However, when ion-pairing of the impurity ions with sulfate is considered and the supersaturation recalculated, it is found that very little difference between the three ions can be observed with conductivity. For the data in Figure 2b, we have determined the supersaturation in the presence of increasing foreign ions (either Ca$^{2+}$, La$^{3+}$, or Zn$^{2+}$). Thus, as the concentration of these ions increases, and the ion-pairing with sulfate increases, the supersaturation decreases. (Note: The plotting of the data as $1/S$ simply makes the data show the same gross trend; that is, rates decrease as the $x$-axis value increases). Because of the rapid increase in ionic strength (particularly with lanthanum ions), the usability of conductivity as a means of investigating crystallization diminishes. This is because the background conductivity due to the presence of the other ions becomes too great to discern the small drop in conductivity values due to crystallization of barium sulfate.

Figure 3. SEM pictures of barite precipitated in the presence of (a) no additional cations present (control) (b) 2.0 mM La$^{3+}$ (scale bars 10 and 5 μm, respectively).

Figure 4. AFM deflection images of a $5 \times 5$ μm section of the barium sulfate (001) surface grown in the presence of barium and sulfate ions with (a) no additional ions at $S = 5$ (b) zinc ions (0.75 mM, $S = 3.9$) (c) calcium chloride (0.09 mM, $S = 4.2$) (d) lanthanum chloride (0.08 mM, $S = 3.9$). Scale bar for (b) 1 μm; all others scale bars 2 μm. Double-headed arrows represent the (010) direction; the (100) direction is perpendicular to this.
**Morphology of BaSO₄.** There were no significant differences in the barite morphology formed in the presence of zinc ions, although it could be suggested that their presence decreases the aspect ratio slightly.²³ In the presence of 25 mM calcium ions, a distinct change was observed whereby the aspect ratio of the barite particle decreased from ∼2 to ∼1,²⁰ and the particles were observed to have a flat rhombic morphology. In the presence of La³⁺, the particles are different again and are not consistent with a simple lowering of the supersaturation.³,⁶²,⁶¹ Rounded, rice-shaped barite particles similar to those formed in the presence of EDTA and HEDP are formed⁴¹,⁴² as can be seen in Figure 3b. Calculation of the angle between the large basal face and the smaller triangular faces (see Figure 3) gave a value of 35°–38°. This results in two possibilities, given the error associated with measuring the angle. If in both cases the large flat face is assumed to be the (010), then the smaller face could either be the (012) (angle of ∼33°) or the (101) (angle of ∼38°) face. Previous literature on the impact of EDTA on barite crystallization shows that EDTA interacts strongly with both the (010) and the (011) faces.³,²²

**Atomic Force Microscopy (AFM).** The results reported above reveal an interesting contradiction. While the impurity ions did not significantly change the desupersaturation rate (as measured by conductivity), the substantial differences in morphology clearly suggest differences in the interactions with the growing crystal surface. AFM measurements were therefore used to examine the crystal growth processes at higher resolution. It must be remembered that while conductivity measures an effect on overall desupersaturation rate, AFM measures the effects on specific faces. Second, the AFM experiment involves growth with a constant S and is a continuous process while the conductivity method is a batch experiment.

The AFM results showed that barium sulfate had the typical step features when placed in water and grew via 2D nucleation at the supersaturation ratios of S = 2–8, with the expected sector shaped growth observed by others.¹² on the (001) face (Figure 4a) reminiscent of a "quadrant". Above this supersaturation, homogeneous nucleation is expected to occur in the pure system. Zinc ions had no impact on the sector shape also showing a quadrant but, as can be seen in Figure 4c, d, calcium and lanthanum ions had a significant impact on the sector shape. At low calcium ion concentration (and therefore also low ionic strength), the crystallization proceeded via small 2D nuclei that were irregular and had obvious signs of step pinning,⁴³ a feature expected for strongly adsorbed inhibitors. The presence of lanthanum ions on the other hand showed significant rounding of the sector shape very similar in nature to the final particle morphology (Figure 4d). The shape of the growth island observed in the presence of lanthanum ions may be due to the total ionic strength of the solution as observed by Rishaus et al.,⁴⁴ but in fact the ionic strength is slightly higher in the zinc case (1.5 × 10⁻³ for lanthanum case and 2.6 × 10⁻³ for zinc case). As the concentration of either calcium or lanthanum ions is increased, the supersaturation of barium sulfate tends to decrease as ionic strength of the solution increases (recall the conductivity results). Given that the growth of the entire face will be determined by the slowest growing direction, the (100) growth rate was plotted as a function of the supersaturation in the presence and absence of the impurity ions (Figure 5).

The presence of calcium and lanthanum ions introduced a critical concentration prior to growth being observed (Figure 5). This blocking of growth until a critical supersaturation is typical for strong inhibitors.⁴⁵ It must be remembered, however, that the results presented here are in the birth and spread regime, while analysis of this phenomenon is most often discussed under spiral growth conditions.⁴⁵ When zinc ions are present, there also appears to be a drop in the growth rate at a critical supersaturation; however, we believe this to be due to the birth and spread regime crossing over into the spiral growth regime. The transition to spiral growth for barium sulfate is below S = 3² and has been shown to occur at S = 2; thus the results here, while a little lower than those observed in ref 1, are consistent with this. Thus, zinc ions do not appreciably change the behavior of the system at low barium sulfate supersaturations. At higher barium sulfate supersaturations (S > 6), it is clear from Figure 5 that the presence of zinc ions inhibits the growth in the (100) direction. The value of the growth rate at higher supersaturations for the case when calcium ions are present, however, suggests that calcium ions do not impact significantly in the (100) direction. The (100) direction was difficult to determine unambiguously in this system, but the overall spherical shape of the growth islands formed in the presence of calcium ions does suggest an equivalent (100) to (010) growth rate. This is further supported by both the lanthanum and zinc ion results where an impact in the (100) barium sulfate direction is observed, and neither system shows a spherically shaped 2D growth island (Figure 4). In terms of incorporation, however, it is known that calcium can substitute for barium in the lattice yet this is not evidenced by any particular impact on the growth rate of the (100). This could be because the calcium ions incorporate preferentially on the (010) step making this step as slow growing as the (100). In addition, these experiments do not give information on how calcium ions might impact on nucleation (2D or 3D). At high calcium ion concentrations (2.5 mM), an oval 2D nucleus is observed, suggesting the possibility that this shape is ionic strength dependent (ionic strength 5.6 × 10⁻³, see Supporting Information, SFigure 1).

Incorporation was investigated using AFM by obtaining very high resolution images (see Supporting Information for images and analysis). Lanthanum is particularly interesting because of the charge mismatch with the barium ion. High resolution images of pure barium sulfate and barium sulfate in the presence of La³⁺ and Zn²⁺ are shown in SFigure 2, a and b respectively. Images collected when zinc ions were present did not match barite, although some distances did match some zinc...
sulfate mineral phases (see Supporting Information, SFigure 2c).

The two images were analyzed for the representative distances observable by taking the Fourier transforms (see Supporting Information, SFigure 3). In the pure barium sulfate image, the lattice parameters are found to be on average $8.4 \times 5.0$ Å, which is reasonably close to the expected $8.9 \times 5.4$ Å. When La$^{3+}$ is present, the distances calculated from the Fourier transform were found to be on average $7.8 \times 5.6$ Å, smaller than that calculated for the control case in the $a$ axis (by $\sim$7%) and larger in the $b$ axis ($\sim$12%). However, the distances calculated can vary significantly (see Supporting Information SFigure 3 for further details). The AFM data at very high resolution show significant drift associated with it. As such, we take the qualitative trends from this data rather than the absolute values. Given the large variation in distances calculated, incorporation was also investigated by XRD for the bulk and is discussed below.

To investigate bulk incorporation, we measured changes in the lattice parameters from XRD spectra via Rietveld analysis (see Supporting Information SFigure 4 for the raw data at the lower concentrations). The concentrations investigated are higher than were used in the conductivity or AFM experiments to observe the 2θ lattice parameter changes (which are small). The results are given in Table 1.

<table>
<thead>
<tr>
<th>sample</th>
<th>lattice parameter changes from control values</th>
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<tbody>
<tr>
<td></td>
<td>$a$ (95% conf) $b$ (95% conf) $c$ (95% conf)</td>
</tr>
<tr>
<td>control</td>
<td>8.888 (0.004) 5.451 (0.004) 7.158 (0.004)</td>
</tr>
<tr>
<td>25 mM Ca$^{2+}$</td>
<td>$-0.04$ (0.01) $0.005$ (0.005) $-0.018$ (0.004)</td>
</tr>
<tr>
<td>0.1 M Ca$^{2+}$</td>
<td>$-0.03$ (0.01) $-0.002$ (0.008) $-0.016$ (0.008)</td>
</tr>
<tr>
<td>25 mM Zn$^{2+}$</td>
<td>$0.00$ (0.004) $-0.003$ (0.003) $-0.004$ (0.004)</td>
</tr>
<tr>
<td>0.1 M Zn$^{2+}$</td>
<td>$0.01$ (0.02) $-0.001$ (0.01) $0.002$ (0.01)</td>
</tr>
<tr>
<td>2 mM La$^{3+}$</td>
<td>$-0.014$ (0.002) $0.005$ (0.002) $-0.008$ (0.002)</td>
</tr>
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</table>

The results confirm that calcium incorporates into the barite lattice. In contrast, zinc ions clearly do not incorporate into barite. No change is observed in the lattice parameters of barite even at the high concentration of 0.1 M Zn$^{2+}$. La$^{3+}$ is shown to incorporate into barite at relatively low concentrations (2 mM), and the trends are similar to that observed in the AFM images being that the $a$ axis decreases and the $b$ axis increases compared to the control even if the magnitude of the changes between the two techniques differ. Higher concentrations of lanthanum ions were not attempted due to (i) the possibility of crystallizing lanthanum sulfate and (ii) the conductivity experiments had shown significant inhibition at this level and yield of solids would have been too low for XRD to be performed.

From the XRD data, the cations that are observed to incorporate are those expected to (i.e., those cations having ionic radii $<1\pm30\%$ of Ba$^{2+}$). It is also of interest that the growth rate AFM data show differences between the non-incorporating Zn ions and the incorporating ions (no change in growth islands, lower critical supersaturation), while conductivity as a measure of desupersaturation rate does not.

**Molecular Modeling of La$^{3+}$ Incorporation.** The energetics of substitution of La$^{3+}$ and Ca$^{2+}$ ions into barium sulfate was investigated via molecular modeling as described in the experimental section. Using this analysis, we find that the replacement energy to completely substitute the surface barium ions of a dry surface with lanthanum is lower than to completely replace the bulk barium ions (see Figure 6a). A similar trend is observed for calcium (see Figure 6b). Upon introducing solvation of the surfaces via the COSMIC methodology, the wet surface replacement energy is found to always be more negative (i.e., favorable) than the dry surface replacement energy, but again, calcium ion substitution is preferred to lanthanum ion substitution. It is interesting to note that calcium ion substitution is actually energetically favorable (replacement energy $<0$) on the “wet” (001) surface for coverages less than 37.5%.

In terms of bulk substitution, we can calculate the energy per replaced barium ion (see Supporting Information for surface values, SFigure 5) and find that the energy of substituting lanthanum ions into the barium sulfate bulk plateaus while calcium ion incorporation continues to become more energetically favorable (Figure 7). Viewing the bulk substitution energy on a per barium ion substituted basis (Figure 7) does show that unlike calcium ion substitution there is a large difference between clustered versus dispersed substitution (higher values are due to clustered substitution and lower values are dispersed) for lanthanum ions.

Figure 6. Replacement energy (kJ mol$^{-1}$) of (a) lanthanum ions and (b) calcium ions for barium ions in barium sulfate either within the bulk (closed squares) or on the dry surface (filled circles) or on the wet surface (open squares).
In Figure 8, we plot the changes in barium sulfate lattice parameters as a function of the mole fraction of dopant for the same set of simulations, and we find that the lattice parameters alter considerably in the presence of both ions. While the presence of calcium ions causes a reduction in all three cell parameters, for lanthanum ions, the situation is more complex with the \(a\) and \(c\) axes showing contraction while the \(b\) axis lengthens with increasing substitution. In fact, very little change occurs to the \(a\) and \(c\) axes until 50% of the barium ions are substituted with lanthanum ions. The changes in the lattice parameters show, however, that there is a great deal of variation depending on whether the substitution of the ions are either grouped or dispersed. This effect was most notable for calcium ion substitution on the \(b\) axis length.

The results from AFM showed that the \(a\) axis was smaller by \(\sim 7\%\) compared to the control, while the \(b\) axis was \(\sim 12\%\) larger when lanthanum ions were present; thus qualitatively the changes are as would be expected (decrease in \(a\), increase in \(b\) lattice parameter). The changes in the XRD observed for the \(a\) axis is only \(\sim -0.2\%\), while for the \(b\) and \(c\) axis this is \(\sim \pm 0.1\%\). We would predict on this basis that 45% or 2% of the barium ions are substituted with lanthanum ions depending on whether one looks at the \(a\), \(b\), or \(c\) axis trend. The level of barium substitution by lanthanum found in a real sample of barium sulfate crystallized in the presence of lanthanum chloride, as determined from ICP, was found to be 3.6%. This value, however, is a total substitution value and does not reflect any possible segregation to or from the surface. However, it is close to the predicted value (2%) obtained by taking the XRD change in the \(c\) axis and using the simulation to determine the amount of incorporation. From this we would suggest the \(c\) axis change is a better predictor than the other axes when bulk XRD results are considered. In addition, the values for replacement energy were found to be positive for all levels of lanthanum incorporation excepting the lowest (\(\sim 6\%\)) substitution level on a wet surface. The substitution of calcium ions is energetically favorable on the wet surface up to \(\sim 37\ wt\%\). Thus, this may explain the limit of calcium and lanthanum ion substitution. The substitution of low levels is favored on the surface but is less so once these ions become part of the bulk. The energetics of substituting subsequent layers becomes more positive and limits the degree of substitution. A similar trend (albeit within the first layer) was observed for \(2^+\) impurity overgrowth of calcium carbonate.\(^{26}\)

The replacement energy of \(\sim 4\ eV\) and \(\sim 1\ eV\) per \(\text{Ba}^{2+}\) ion replaced for lanthanum and calcium ions respectively (see Figure 7) on bulk substitution is understandable when one considers that substitution will cause strain and defects in a crystal. The higher energy required for lanthanum ions is also consistent with the lower concentration of substitution found (3.6 wt % versus the 12 wt %\(^{12}\)) and with the fact that more

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**Figure 7.** Replacement energy (eV) normalized to the number of ions incorporated versus % barium ions substituted for calcium and lanthanum ion bulk substitution (multiple points for same % barium atom substitution represent different configurations of the substitution).

**Figure 8.** \(a\), \(b\), \(c\) axis lattice parameter and cell volume change (%) with bulk substitution. Lanthanum ions—squares and calcium ions—circles (multiple points for same mole fraction barium atoms replaced represent different configurations of the substitution).
defects (vacancies) will be formed in the presence of lanthanum ions.

We also investigated the segregation energy for the (001) face of barium sulfate in the presence of lanthanum and calcium ions (see Figures 9 and 10) both for the dry surface (in vacuum) and the wet surface (dielectric of water) using the singly substituted ion in the bulk as our reference value. As the amount of calcium incorporation increases on the dry surface, the segregation energy becomes more positive. Lanthanum ions have a more complex behavior preferring the (001) surface more as substitution increases. Additionally, when we calculate the segregation energy based on the mole fraction rather than the dilute limit (see Supporting Information SFigure 6), we obtain similar values to Redfern and Parker25 as would be expected from the similar potentials used.

For the wet surface, the two ions behave quite similarly. In this case, as the concentration of substituted ions increases, the segregation energy becomes more positive meaning the surface becomes less favorable as more ions are already substituted into the surface. However, the segregation energy for the lanthanum ion on a wet surface is almost double (in absolute terms) that for calcium even at 100% substitution (−0.81 versus −0.42 eV, respectively).

We could compare our simulations of the surface with barium ions substituted by lanthanum ions and vacancy formation in GDIS36 by creating the expected AFM image from these surface substitution simulation runs and seeing how well this matches the high resolution image from experiment (keeping in mind the drift associated with the high resolution images), but while the simulation of the control sample closely matches that obtained (see SFigure 2a, Supporting Information), some serious discrepancy exists between the simulated and observed AFM images when lanthanum ions are present (see SFigure 7, Supporting Information). First, it is important to note that these simulated images are simply the van der Waals surface from the constituent ions, color-coded by height. The real AFM imaging process is much more complex and requires massive amounts of computer time,46 so the images are at best a crude approximation but in addition the drift in the real images and periodicity in the simulated images meant that only the gross features were somewhat replicated (see SFigure 7).

■ CONCLUSION

In conclusion, conductivity data showed that when supersaturation is calculated accurately, the calcium, zinc, and lanthanum ions all impact similarly on barium sulfate crystallization in terms of inhibition. However, the unique and different morphological changes observed for barite in the presence of these ions (i.e., each ion induces its own changes distinct from the effect of the other ions) suggest that these ions do interact differently with the crystal surface.

AFM data during barite crystal growth shows that the presence of calcium ions showed typical step pinning, indicative of a strong inhibitor. The presence of lanthanum ions showed oval 2D nuclei of barite forming and slower growth rates in the ⟨100⟩ direction. The presence of both ions resulted in critical supersaturations being required prior to growth being observed. Additionally, high resolution images in the AFM showed significant changes in the a and b axis of the barite lattice parameters. These results were confirmed by bulk powder XRD results where both calcium and lanthanum ions were found to incorporate into the growing barite crystal. No incorporation was observed for zinc ions.

Molecular modeling results showed that substitution is energetically favored only for wet surface substitution and then only for certain substitution levels. This is consistent with the experimental results showing higher calcium ion incorporation levels are possible (~12%) compared to lanthanum ions (~3–4%). Bulk substitution of calcium ions was 4 times more energetically favorable than lanthanum ions. On the other hand, both ions prefer to incorporate at the surface rather than in the bulk particularly at low substitution levels. Lanthanum ions prefer to substitute on the surface more so than calcium ions as they have a lower segregation energy than calcium ions. Overall, the conductivity, XRD, and AFM data support each other and can all be reconciled with the molecular modeling results. The exception to this was the high resolution information from AFM which only qualitatively agreed with the XRD and modeling results. We suspect, therefore, in this case that the high resolution AFM data had too much drift to draw conclusions.

Finally, while a solid solution is not expected to exist for lanthanum and barium sulfate, it has been clearly shown that lanthanum ions impact on barium sulfate crystallization changing both the rate of growth and morphology of barium sulfate by partial incorporation into the crystal lattice. Thus, multivalent ions should not be ignored in terms of their impact on crystallization. In addition, given that segregation to the surface is energetically favorable for these and presumably many
other ions, the question arises as to whether one can distinguish between adsorption and migration mechanisms in these minerals. For us, future work in this area is to begin to understand the synergistic effects ions have when present in solution.

### ASSOCIATED CONTENT

#### Supporting Information

Empirical modeling parameters and AFM images of barium sulfate grown in the presence of Ca$^{2+}$, La$^{3+}$, and Zn$^{2+}$ ions, replacement energy per ion incorporated for Ca$^{2+}$ and La$^{3+}$ ions, segregation energy for Ca$^{2+}$ and La$^{3+}$ ions, and simulated AFM of barite surfaces from surface modeling results. This information is available free of charge via the Internet at http://pubs.acs.org/.

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**Notes**

The authors declare no competing financial interest.

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