Heterogeneous Growth of Cadmium and Cobalt Carbonate Phases at the $(10\bar{1}4)$ Calcite Surface

*Man Xu¹, Eugene S. Ilton¹, Mark H. Engelhard², Odeta Qafoku¹,
Andrew R. Felmy¹, Kevin M. Rosso¹, and Sebastien Kerisit^{1*}*

¹Fundamental and Computational Sciences Directorate, Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99352 USA

²Environmental Molecular Sciences Laboratory, Scientific Resources Division, Pacific Northwest National Laboratory, Richland, WA 99352 USA

*Corresponding Author: sebastien.kerisit@pnnl.gov, 1-509-371-6382.

ABSTRACT

The ability of surface precipitates to form heteroepitaxially is an important factor that controls the extent of heterogeneous growth. In this work, the growth of cadmium and cobalt carbonate phases on $(10\bar{1}4)$ calcite surfaces is compared for a range of initial saturation states with respect to otavite (CdCO_3) and sphaerocobaltite (CoCO_3), two isostructural metal carbonates that exhibit different lattice misfits with respect to calcite (-4% and -15%, respectively, based on $(10\bar{1}4)$ surface areas). Calcite single crystals were reacted in static conditions for 16 hours with CdCl_2 and CoCl_2 aqueous solutions with initial concentrations $0.3 \leq [\text{Cd}^{2+}]_0 \leq 100 \mu\text{M}$ and $25 \leq [\text{Co}^{2+}]_0 \leq 200 \mu\text{M}$. The reacted crystals were imaged *in situ* with atomic force microscopy (AFM) and analyzed *ex situ* with X-ray photoelectron spectroscopy (XPS). AFM images of Cd-reacted crystals showed the formation of large islands elongated along the $[42\bar{1}]$ direction, clear evidence of heteroepitaxial growth, whereas surface precipitates on Co-reacted crystals were small round islands. Deformation of calcite etch pits in both cases indicated the incorporation of

Cd and Co at step edges. XPS analysis pointed to the formation of a Cd-rich (Ca,Cd)CO₃ solid solution coating atop the calcite substrate. In contrast, XPS measurements of the Co-reacted crystals provided evidence for the formation of a mixed hydroxy-carbonate cobalt phase despite supersaturation with respect to CoCO₃. The combined AFM and XPS results suggest that the lattice misfit between CoCO₃ and CaCO₃ is too large to allow for heteroepitaxial growth of a pure cobalt carbonate phase on calcite surfaces in aqueous solutions and at ambient conditions. The use of the satellite structure of the Co 2p_{3/2} photoelectron line as a tool for determining the nature of cobalt surface precipitates is also discussed.

Keywords: metal carbonates; nucleation and growth; heteroepitaxy; lattice misfit.

1. INTRODUCTION

Heterogeneous nucleation and growth on calcite (CaCO₃) surfaces are important geochemical phenomena due to the ubiquitous presence of calcite in many natural aqueous environments and the close-to-equilibrium conditions that typically dominate in these systems. Moreover, if the atomic arrangement of the overgrowing phase exhibits structural similarities with the calcite substrate, heteroepitaxial growth can take place. For example, otavite (CdCO₃), which yields the lowest lattice misfit with respect to calcite of all the metal carbonates, has been shown to form readily as a heteroepitaxial coating on calcite surfaces (Stipp et al., 1992; Chiarello and Sturchio, 1994; Chiarello et al., 1997; Hay et al., 2003; Pérez-Garrido et al., 2007; Cubillas and Higgins, 2009; Xu et al., 2014).

A range of divalent metal cations show high affinity for calcite surfaces in sorption experiments (Zachara et al., 1991), with kinetics of sorption showing two regimes: an initial

rapid uptake stage followed by a stage of slower removal from the aqueous solution (Franklin and Morse, 1983; Kornicker et al., 1985; Davis et al., 1987). Models of divalent metal interaction with calcite surfaces attributed the second stage to the growth of surface precipitates, specifically, to the formation of carbonate solid solutions (Comans and Middelburg, 1987; Davis et al., 1987). Indeed, the ability of CdCO_3 and MnCO_3 , which present misfit values of -4% and -10%, respectively, based on their $(10\bar{1}4)$ surface areas, to form heteroepitaxially on calcite was later demonstrated by a combination of surface sensitive spectroscopic, microscopic, and scattering techniques (Stipp et al., 1992; Chiarello and Sturchio, 1994; Chiarello et al., 1997; Hay et al., 2003; Lea et al., 2003; Pérez-Garrido et al., 2007; Pérez-Garrido et al., 2009; Xu et al., 2014). In contrast, the propensity of sphaerocobaltite (CoCO_3) to grow as a heteroepitaxial phase on calcite has neither been confirmed nor refuted, despite a demonstrated affinity of Co for calcite surfaces (Kornicker et al., 1985; Zachara et al., 1991; Reeder, 1996; Xu et al., 1996; Cheng et al., 2000). The propensity of a surface precipitate to grow heteroepitaxially is an important factor controlling the extent of heterogeneous growth (Prieto et al., 2003; Chada et al., 2005; Astilleros et al., 2006; Pimentel et al., 2013; Ruiz-Agudo et al., 2014). For example, Chada et al. (2005) showed that, despite PbCO_3 having a lower solubility than CdCO_3 , approximately twice as much Cd than Pb was measured by X-ray photoelectron spectroscopy (XPS) on calcite crystals reacted with 1 μM solutions for 24 hours. CoCO_3 exhibits a misfit of -15% with respect to calcite, which provides an incrementally higher lattice misfit than CdCO_3 and MnCO_3 . Therefore, determining the nature and extent of surface precipitates that form on Co-reacted calcite surfaces is expected to shed light on the conditions conducive to heteroepitaxial growth as well as the structural limits to the formation of heteroepitaxial phases on mineral surfaces in aqueous environments. Furthermore, ^{60}Co is a common fission product and an abundant

radionuclide in the subsurface at various contaminated sites, such as U.S. Department of Energy's nuclear facilities (Killey et al., 1984; Catalano et al., 2005). Consequently, the reactions of interest have potential implications for the environmental remediation of subsurface contaminants such as ^{60}Co .

There are only a limited number of studies that have investigated the formation of Co surface precipitates on calcite and there are unresolved differences between these reports. Early work on Co interaction with calcium carbonate powders by Kornicker et al. (1985) concentrated on changes in solution concentrations and showed that Co adsorption was much more extensive on calcite than on aragonite. Kornicker et al. (1985) hypothesized that this difference resulted from sphaerocobaltite being isostructural with calcite. Later, Zachara et al. (1991) reported the heterogeneous nucleation of $\text{Co}(\text{OH})_2$ on calcite powders reacted with initial Co concentrations of 10-100 μM at $\text{pH} = 8.3$, as evidenced by aqueous Co concentrations that were saturated with respect to $\text{Co}(\text{OH})_2$. However, Xu et al. (1996) suggested the formation of a $(\text{Co,Ca})\text{CO}_3$ solid solution based on compositional depth profiles derived from XPS analysis of sputtered calcite powders and single crystals for the same concentration range and at pH values ranging from 7.3 to 8.9. They reported finding Co at depths up to 5 to 10 nm even after only 1 hour of reaction time.

In this work, a combination of XPS and atomic force microscopy (AFM) was employed to characterize Co-reacted calcite single crystals and determine the nature of surface precipitates, their morphology and extent of surface coverage, and whether an epitaxial phase is formed. Experimental conditions for reaction of the single crystals were identical for both techniques to allow for direct correlation between the two sets of information. Interestingly, despite a significant affinity of Co for calcite surfaces, as discussed above, Co-rich $(\text{Co,Ca})\text{CO}_3$ solid

solutions are difficult, if not impossible, to synthesize at ambient conditions (Katsikopoulos et al., 2008), and the synthesis of pure sphaerocobaltite crystals appears to be only feasible in hydrothermal conditions (Egorov et al., 1976; Gamsjäger and Reiterer, 1979).

Based on the previous studies introduced above, the reaction of Co with calcite surfaces appears markedly different from that of Cd, which shows a greater extent of adsorption (Zachara et al., 1991), long-term aqueous concentrations that are controlled by otavite solubility (McBride, 1980; Papadopoulos and Rowell, 1988), and an ability to form complete bulk $(\text{Cd,Ca})\text{CO}_3$ solid solutions at ambient conditions (Königsberger et al., 1991; Fernández-González et al., 1999). Therefore, parallel experiments were also carried out with Cd with the aim to provide a basis for comparison with the results of the Co experiments. As for Co, despite a low natural abundance in the subsurface, Cd concentrations can be elevated at specific contaminated sites due to anthropogenic activities; and, because of the properties just listed, uptake of Cd at calcium carbonate surfaces has been considered as a remediation process (García-Sánchez and Álvarez-Ayuso, 2002; Prieto et al., 2003).

2. EXPERIMENTAL METHODS

2.1. Reaction of single crystals

Calcite specimens used in this study were prepared from optically-clear calcite crystals originated in Brazil. Fresh $(10\bar{1}4)$ surfaces of calcite were obtained by cleaving with a razor blade along the natural cleavage planes. The calcite specimens, which were approximately $10 \times 12 \times 1.5 \text{ mm}^3$ in size, were handled with PTFE tweezers to avoid contamination and were cleaned with bursts of $\text{N}_2(\text{g})$ to remove small particles from the surfaces. Cd^{2+} - or Co^{2+} -bearing solutions were prepared from high-purity (99.999%) CdCl_2 or CoCl_2 salts dissolved in deionized

water (resistivity $\sim 18 \text{ M}\Omega$). Similar to the *in situ* AFM experiments of CdCO_3 growth performed previously (Xu et al., 2014), the calcite specimens were first contacted with 2.3 mL of deionized water for 30 minutes, followed by the introduction of concentrated Cd^{2+} - or Co^{2+} -bearing solutions to obtain a specific initial concentration of Cd^{2+} or Co^{2+} , denoted $[\text{Cd}^{2+}]_0$ and $[\text{Co}^{2+}]_0$, respectively. Initial Cd^{2+} concentrations were in the range 0.3 to 100 μM and initial Co^{2+} concentrations were in the range 25 to 200 μM . Control experiments were performed without CdCl_2 or CoCl_2 .

Based on inductively coupled plasma optical emission spectrometry (ICP-OES) (Perkin-Elmer, Optima 2100DV) and pH measurements (pH immediately prior to CdCl_2 or CoCl_2 addition, $\text{pH}_0 = 8.9$), the initial solution saturation states with respect to otavite, sphaerocobaltite, cobalt hydroxide, and calcite were calculated using PHREEQC (Parkhurst and Appelo, 1999) and are shown in Table 1 (all the Cd-containing solutions were undersaturated with respect to $\text{Cd}(\text{OH})_2$ based on the solubility constant of Rai et al. (1991)). All the equilibrium constants used in these calculations are listed in the Supporting Information in Tables S1 and S2. The initial carbonate concentration was calculated with PHREEQC based on the initial pH and calcium concentration measurements. For CoCO_3 and $\text{Co}(\text{OH})_2$, multiple solubility constants are available in the literature, as discussed in Section 3; therefore, two values are given for each in Table 1 to illustrate the possible range of initial saturation states. At the point of introduction of CdCl_2 or CoCl_2 , the aqueous solutions are moderately undersaturated with respect to calcite (Table 1). Adsorption of Cd or Co at the calcite surfaces can inhibit the dissolution of the calcite substrate, as demonstrated for Cd in our previous work (Xu et al., 2014). However, this previous work also showed that, while this phenomenon has a mild effect on the growth rate of the surface precipitates, it does not affect the nature and morphology of the overgrowths, which are the focus

of this work. All the calcite crystals were reacted for 16 hours at room temperature and under atmospheric conditions. For reacted crystals to be analyzed with XPS, the calcite specimen and the aqueous solution were maintained static in a glass vial over the entire reaction time. Then, the crystals were removed from the Cd^{2+} - or Co^{2+} -bearing aqueous solutions using PTFE tweezers and were blown dry with $\text{N}_2(\text{g})$. The calcite crystals to be imaged with AFM were reacted in the fluid cell, which was closed with a custom-made lid. Then, the reacted crystals were imaged directly in the reacting solutions. This approach eliminates any potential alterations of the morphology of surface precipitates that could be caused by drying. The fluid cell was a custom-built Kel-F cell with a diameter of 2.7 cm and a volume of approximately 2.5 mL.

2.2. *In situ* AFM experiments

AFM images were acquired in contact mode, using a Dimension Icon atomic force microscope (Bruker). Au coated silicon nitride probes (Bruker, NP-10, nominal force constant of 0.12 N m^{-1}) were employed for AFM imaging. To minimize the perturbation of the probe on mineral surfaces, the externally applied load was typically below 15 nN. Scan rates ranged from 0.5 to 0.8 Hz with 256 sampling points per scan line. Growth experiments were repeated 1 to 5 times at each experimental condition to ensure reproducibility. 8-10 different areas of 36 to $100 \mu\text{m}^2$ in size were imaged by AFM for each reacted calcite crystal. The AFM topographic images were analyzed with the “Particle Analysis” function of the Veeco NanoScope Analysis software to generate height histograms of islands formed on calcite surfaces using a bin width of 0.5 nm.

2.3. *Ex situ* XPS measurements

X-ray photoelectron spectra were measured using a Kratos Axis Ultra DLD spectrometer and a focused monochromatic Al K_α X-ray source (1486.6 eV) at a power of 150 W. Vacuum chamber pressure was $\sim 2.7 \times 10^{-7} \text{ Pa}$ during the measurements. Survey scans were collected using

an analyzer pass energy of 160 eV and a step size of 0.5 eV. Regional (high-resolution) scans were collected using 40 eV pass energy and a step size of 0.1 eV. The instrument work function was calibrated to give a binding energy (BE) of 84.0 ± 0.1 eV for the Au $4f_{7/2}$ photoelectron line for clean metallic gold and the spectrometer dispersion was adjusted to give a BE of 932.5 ± 0.1 eV for the Cu $2p_{3/2}$ line of clean metallic copper. Both survey and high-resolution analyses were carried out with an analysis area of $300 \times 700 \mu\text{m}^2$. A charge neutralization system was used for all analyses using a magnetic immersion lens and electron charge neutralization with the electron neutralizer controlled at 1.0 eV bias voltage, 1.95 A filament current, and 3.7 eV charge balance.

High-resolution spectra focused on the Ca $2p$, Cd $3d$, Co $2p$, O $1s$ and C $1s$ photoelectron lines. High-resolution spectra from five and three spatially separated areas were generated per reacted calcite crystals and powder standards, respectively. Uncertainties in the atomic ratios and binding energies were calculated as the standard deviation of the values obtained from the five or three high-resolution spectra.

All spectra were analyzed with the CasaXPS software (version 2.3.15) (Fairley, 2009). Shirley background subtraction was used for all spectra. Absolute peak positions were determined by charge correcting to the adventitious C $1s$ line at 285.0 eV. Atomic ratios were obtained from peak areas of Ca $2p$ (1.833), Cd $3d$ (6.623), Co $2p_{3/2}$ (2.393), O $1s$ (0.78), and C $1s$ (0.278) photoelectron lines in the regional scans, with the corresponding Kratos sensitivity factors shown in parentheses. For C, only the carbonate and bicarbonate peaks were included. Peak models for each photoelectron line were generated using nonlinear least-squares Gaussian-Lorentzian curve-fitting. Following the approach described by Stipp and Hochella (1991), the Ca $2p$ line was fitted with two sets of doublets separated by approximately 0.7 eV with the same full width at half maximum (FWHM) and with a 2:1 intensity ratio and 3.54 eV separation between

the $2p_{3/2}$ and $2p_{1/2}$ peaks. Stipp and Hochella (1991) interpreted the less intense doublet at higher binding energy to represent hydrated/hydroxylated surface calcium atoms. The same approach was used for modeling the Cd $3d$ line (with two sets of doublets separated by ~ 1.1 eV); but with a 3:2 intensity ratio and a 6.76 eV separation between the $3d_{5/2}$ and $3d_{3/2}$ peaks. By analogy with their work on calcite surfaces, Stipp et al. (1992) assigned the doublet at higher binding energy to hydrated/hydroxylated surface cadmium atoms. The Co $2p_{3/2}$ lines were fitted using four model peaks, following the empirical approach introduced by Biesinger et al. (2011). The O $1s$ line was fitted with 3 to 5 model peaks with identical FWHM. The C $1s$ line was fitted with two sets of model peaks: a first set of three peaks with identical FWHM to model the adventitious carbon and a second set of two peaks with identical FWHM, but different from that of the first set, to model carbon present as carbonate. Similarly to the interpretation of the Ca $2p$ line, Stipp and Hochella (1991) assigned the main peak and the high-energy shoulder peak of the second set to carbon from carbonate and bicarbonate ions, respectively. Example fits are shown in the Supporting Information in Fig. S1.

Four powdered samples were used as standard compounds for the XPS analyses: CaCO_3 (Aldrich, 99.995%), CdCO_3 , (Aldrich, 99.999%), CoCO_3 (Alfa Aesar, 99.5%), and Co(OH)_2 (Alfa Aesar, 99.9%). The identity and crystallinity of the four standard compounds were verified by X-ray diffraction (XRD) using a Philips X'Pert X-ray diffractometer. Scanning electron microscopy (SEM) images were also taken for the CaCO_3 and CoCO_3 powder samples using a FEI Helios 600 electron microscope. The XRD diffraction patterns and SEM images are shown in Supporting Information in Figs. S2 and S3.

3. RESULTS

3.1. AFM

3.1.1. Cadmium-reacted calcite crystals

Figs. 1 and 2 present representative AFM images of calcite $(10\bar{1}4)$ surfaces after exposure to Cd^{2+} -bearing aqueous solutions for 16 hours. Figs. 1a and 1b are AFM topographic images of surfaces reacted with initial Cd^{2+} concentrations of 0.3 and 0.5 μM while Figs. 1c and 1d show the height profiles along the blue lines in Figs. 1a and 1b. From the topographic images and height profiles, it is clear that the surface precipitates formed three-dimensional (3D) islands that exhibited nearly round shapes and heights varying from a few $\text{\AA}$ to a few nm at these low levels of initial supersaturation. For $[\text{Cd}^{2+}]_0 \geq 1 \mu\text{M}$ (Figs. 2a and 2b), the islands displayed an elongated shape, with the long axis following the $[42\bar{1}]$ direction and the short axis parallel to $[010]$, which is consistent with time-sequenced AFM images of CdCO_3 growth on calcite surfaces observed previously for up to 6 hours (Xu et al., 2014). This previous study demonstrated that these morphologies are clear evidence of heteroepitaxial growth and also included high-resolution transmission electron microscopy images of cross sections of the interface between a calcite single crystal and CdCO_3 overgrowth showing dislocation-free epitaxy. The spreading and coalescence of the islands over a longer reaction time in the present study resulted in a surface layer approximately 2.5 nm high, which partially covered the substrate. Further nucleation and growth of 3D islands on this layer also took place, as indicated by the AFM image in Fig. 2b and the height profile in Fig. 2e as an example. The first overgrowth layer displays a flat top, parallel to the $(10\bar{1}4)$ surface, and a constant height of approximately 2.5 nm. The height of the second layer varied in the range of 2 to 5 nm. As $[\text{Cd}^{2+}]_0$ increased to 100 μM (Fig. 2c), 2D nucleation and monolayer-by-monolayer growth may occur concurrently with the nucleation and growth of 3D islands according to previous

experimental results (Xu et al., 2014). However, because of the significant extent of growth at $[\text{Cd}^{2+}]_0 = 100 \text{ } \mu\text{M}$, it is not possible to distinguish the calcite substrate from the overgrowth and provide a unique determination of island height; therefore, the height profile shown in Fig. 2f cannot differentiate the two growth mechanisms.

Fig. 3 summarizes the height distributions of 3D islands formed for $[\text{Cd}^{2+}]_0 = 0.3, 0.5, 1$, and $5 \text{ } \mu\text{M}$. At $[\text{Cd}^{2+}]_0 = 0.3 \text{ } \mu\text{M}$ (Fig. 3a), the majority of the islands (65%) have a height of 1 to 2 nm. At $[\text{Cd}^{2+}]_0 = 0.5 \text{ } \mu\text{M}$ (Fig. 3b), there is a greater proportion of taller islands; but the large majority of the islands (80%) show a height of 3 nm or less. The shapes and heights of islands formed at low $[\text{Cd}^{2+}]_0$ (Figs. 1 and 3a-b) are in agreement with those obtained during the early stages of growth in our previous *in situ* study of the kinetics of CdCO_3 growth on calcite surfaces (Xu et al., 2014). Based on initial growth rates and heights, we hypothesized in that work that 3D islands nucleated as a CdCO_3 precursor, which was not fully crystalline, but subsequently transformed to a fully crystalline phase, as growth proceeded and heteroepitaxial growth was observed. Therefore, the present AFM results indicate that the initial supersaturation at $[\text{Cd}^{2+}]_0 \leq 0.5 \text{ } \mu\text{M}$ is not sufficiently high to drive the transformation to the crystalline phase and the islands remain in the precursor state with round shapes and variable heights.

At $[\text{Cd}^{2+}]_0 = 1 \text{ } \mu\text{M}$, where elongated 3D islands are formed, the height histogram in Fig. 3c demonstrates a high frequency of island heights at approximately 2 nm and a lack of islands with heights below 2 nm. The fact that the tail of the distribution extended to larger heights is indicative of additional growth on top of the initial layer. Further increase in $[\text{Cd}^{2+}]_0$ led to a broadening of the height distribution, as shown in Fig. 3d, which stems from enhanced nucleation and growth of a second layer of 3D islands at $[\text{Cd}^{2+}]_0 = 5 \text{ } \mu\text{M}$.

3.1.2. Cobalt-reacted calcite crystals

When calcite ($10\bar{1}4$) surfaces were exposed to Co^{2+} -bearing solutions, the surface coverage and morphology of the surface precipitates differed significantly from those of the Cd-reacted crystals. Representative AFM images of calcite ($10\bar{1}4$) surfaces obtained after 16 hours of reaction with 50, 100, 150, and 200 μM CoCl_2 solutions are shown in Fig. 4a-d. The islands formed on Co-reacted surfaces showed round bases, and therefore, no distinct heteroepitaxial growth over the entire concentration range considered in this work. This is in contrast to the Cd-reacted surfaces, which only showed round islands at low initial supersaturations ($\Omega \leq 3$) and predominantly heteroepitaxial islands at higher initial supersaturations ($\Omega > 3$). Initial supersaturations at the highest initial Co^{2+} concentrations are comparable to those of Cd^{2+} -bearing solutions for which heteroepitaxial growth is observed, even when considering the high end of the CoCO_3 solubility constant range. This comparison suggests that the absence of distinct heteroepitaxial islands on the Co-reacted surfaces is not due to initial supersaturation levels that are too low to drive the transformation to a fully crystalline phase.

The height histograms for $[\text{Co}^{2+}]_0 = 50\text{-}200 \mu\text{M}$ are shown in Fig. 5. The heights of the islands formed in the presence of 50, 100, and 150 μM Co^{2+} (Fig. 5a-c) exhibit a broad distribution over the range of 1 to 10 nm, which is mainly due to the height differences among individual islands. In all cases (Fig. 5a-c), the island height distributions peak between approximately 1 and 3 nm. As $[\text{Co}^{2+}]_0$ is increased to 200 μM , the peak of the island height distribution shifts to higher heights, at about 5 nm (Fig. 5d). The AFM topographic images in Fig. 4 show that the surface area of individual islands at $[\text{Co}^{2+}]_0 = 200 \mu\text{M}$ solution is also larger than those at $[\text{Co}^{2+}]_0 = 50\text{-}150 \mu\text{M}$. The coincidence between changes in island height and size implies that the growth of the precipitates in Co^{2+} -bearing solutions proceeds by continuous lateral and vertical expansion, as opposed to the layer-by-layer mechanism observed for Cd-

reacted surfaces. In some instances, the same area of a Co-reacted calcite surface was scanned repeatedly over a period of approximately 30 minutes and the islands were observed to be progressively removed by the AFM tip indicating that the islands were not as strongly bound to the surface as the cadmium carbonate islands, which did not show this behavior.

Finally, the shape of edge pits on the calcite surface were also observed to change with $[\text{Co}^{2+}]_0$. Fig. 6 shows AFM images of calcite surfaces obtained under the same experimental conditions as those in Fig. 4. Areas with fewer islands are presented here to better illustrate the morphology of the etch pits formed in different Co^{2+} solutions. At $[\text{Co}^{2+}]_0 = 50 \text{ } \mu\text{M}$ (Fig. 6a), etch pits display a nearly rhombic profile, similar to etch pits formed in pure deionized water. The etch pit morphology becomes distorted as $[\text{Co}^{2+}]_0$ increases to $100 \text{ } \mu\text{M}$ (Fig. 6b), with a much smaller obtuse-obtuse angle compared to the typical rhombic shape. Further increase in $[\text{Co}^{2+}]_0$ yields etch pits exhibiting a triangular shape, as shown in Fig. 6c-d. In contrast, etch pits with rounded obtuse-obtuse corners were observed when Cd^{2+} ions were present in the aqueous solutions (see Fig. 1 for example). The modification of the morphology of etch pits by Co^{2+} observed in the present study is consistent with the work of Freij et al. (2004), who reported v-shaped etch pits and attributed the morphology change to preferential partitioning of Co^{2+} at the acute kinks. These AFM images indicate that, as Cd, Co can incorporate in the topmost calcite layer, in accord with previous work (Reeder, 1996; Cheng et al., 2000).

3.2. XPS

3.2.1. XPS standard compounds

The XRD patterns of the CaCO_3 , CdCO_3 , and Co(OH)_2 powder standards showed sharp peaks with no additional unassigned peaks (Fig. S2 of the Supporting Information). The XRD pattern of CoCO_3 showed peaks that were broader and less intense than those of the other three

compounds. This result is indicative of smaller particles, and indeed, SEM images revealed particles of 1-2 μm in length compared to up to 20 μm for CaCO_3 , as shown in the Supporting Information in Fig. S3. XPS analysis of the carbonate standards yielded M/O ratios of 0.33 ± 0.01 , 0.41 ± 0.01 , and 0.36 ± 0.01 and M/C ratios of 0.78 ± 0.04 , 1.01 ± 0.03 , and 0.91 ± 0.04 for $\text{M} = \text{Ca}$, Cd , and Co , respectively (Tables 2 and 3). Differences from expected stoichiometric ratios are small and are likely due to the relative sensitivity factors. Indeed, the C/O ratios of the three carbonate standards are within uncertainties of each other: 0.42 ± 0.02 , 0.40 ± 0.02 , and 0.40 ± 0.01 for CaCO_3 , CdCO_3 , and CoCO_3 , respectively. Moreover, atomic ratios derived from the control experiment are within uncertainties of those of the CaCO_3 powder standard (Table 2). The Co/O ratio (0.52 ± 0.01) obtained for Co(OH)_2 was also consistent with the expected stoichiometric value. The combined results from XRD, SEM, and XPS indicate that the powder standards offer an adequate basis for comparison with the Cd- and Co-reacted calcite crystals.

3.2.2. Cadmium-reacted calcite crystals

The atomic ratios and binding energies obtained from the XPS analysis of the Cd-reacted calcite single crystals are shown in Tables 2 and 4, respectively, and examples of Cd 3d photoelectron lines are given in Fig. 7. The Cd/Ca ratio increases with increasing initial Cd^{2+} concentration, as expected, except for the highest initial concentration, 100 μM , which shows a Cd/Ca ratio within uncertainty of that obtained at 50 μM . Because the source of carbonate ions is the dissolution of the calcite crystal and cadmium strongly inhibits calcite dissolution (Xu et al., 2014), this observation is likely due to the lack of sufficient carbonate ions for growth at the highest initial Cd concentration. The Ca/O and Ca/C ratios decrease significantly for the highest initial Cd concentration whereas the C/O ratio remains essentially constant, which is consistent with the formation of a pure Cd or Cd-rich carbonate layer atop the calcite substrate. Moreover,

the Cd/O and Cd/C ratios of the otavite standard are higher than the Ca/O and Ca/C ratios of the calcite standard; consequently, the (Cd+Ca)/O and (Cd+Ca)/C ratios increase with increasing initial Cd concentration and approach the values obtained for otavite, which, again, is consistent with XPS probing an increasing proportion of CdCO₃.

The binding energies of the C 1s, O 1s, and Ca 2p_{3/2} lines of the calcite standard and of the control experiment (Table 4) are in very good agreement with those obtained by Engelhard and Baer (1999) for a vacuum cleaved calcite crystal (289.5, 531.4, and 347.0 eV for C 1s, O 1s, and Ca 2p_{3/2}, respectively). The binding energies of C 1s and O 1s are greater for otavite than for calcite with differences in binding energies between the two carbonate minerals, ΔBE, of 0.4 and 0.7 eV, respectively. As for the atomic ratios, the binding energies of C 1s and O 1s of the reacted samples increase with increasing Cd/Ca ratio and tend towards the values derived from the otavite standard, which provides further evidence for the formation of a Cd-rich carbonate layer. The Ca 2p_{3/2} binding energies increase from 346.9 ± 0.1 eV for the calcite standard and control experiment to 347.5 ± 0.1 eV for the highest [Cd²⁺]₀, whereas the Cd 3d_{5/2} binding energies remain fairly constant. This trend is opposite to that reported by Stipp et al. (1992); however, this is most likely due to the difference in the charge referencing methods used in the two studies (gold method in Stipp et al. (1992) *versus* adventitious carbon in this work). Indeed, the Ca 2p_{3/2} and Cd 3d_{5/2} relative binding energies show the same trend in both cases, *i.e.* decreasing difference with increasing Cd content. This change in relative binding energies is indicative of the formation of a solid-solution; therefore, the XPS measurements point to the formation of a Cd-rich (Cd,Ca)CO₃ solid solution.

3.2.3. Cobalt-reacted calcite crystals

The atomic ratios and binding energies obtained from the XPS analysis of the Co-reacted calcite single crystals are shown in Tables 3 and 5, respectively, and examples of Co 2*p* photoelectron lines are given in Fig. 7. The surface concentration of Co for $[\text{Co}^{2+}]_0 = 25 \mu\text{M}$ was below the detection limit, and therefore, this initial concentration is not reported. Co 2*p* photoelectron lines of Co(II) d^7 high-spin compounds such as $\text{Co}(\text{OH})_2$ and CoCO_3 show a significant satellite structure on the high binding energy side of the main Co 2*p*_{3/2} and Co 2*p*_{1/2} peaks as well as splitting between the Co 2*p*_{3/2} and Co 2*p*_{1/2} peaks, $\Delta\text{BE Co } 2p$, of $16.0 \pm 0.2 \text{ eV}$ (Koppelman and Dillard, 1978; Dillard and Koppelman, 1982; Schenk et al., 1983). In contrast, the satellite structure is absent in Co(III) d^6 low-spin compounds and $\Delta\text{BE Co } 2p$ is $15.0 \pm 0.2 \text{ eV}$ (Koppelman and Dillard, 1978; Dillard and Koppelman, 1982; Schenk et al., 1983). Table 5 shows that all the Co-reacted samples yielded values of $\Delta\text{BE Co } 2p$ indicative of Co(II). In addition, all Co 2*p* lines showed the presence of an intense satellite structure (Fig. 7). Therefore, no significant amount of cobalt oxidation took place during the growth experiments.

As for Cd, the Co/Ca ratio increases with increasing initial Co concentration; however, it does not appear to plateau at high initial Co concentrations. In addition, the Co/Ca ratios are systematically lower than the Cd/Ca ratios for a given initial metal concentration. Although Co inhibits calcite dissolution (Salem et al., 1994), the reduced extent of growth relative to that measured for Cd explains why a plateau is not reached. This is consistent with the AFM observations of smaller extents of surface coverage of the Co precipitates compared to Cd.

The changes in atomic ratios with increasing initial concentration show a different behavior than observed for the Cd-reacted calcite samples. The Ca/O ratio decreases slightly with increasing Co/Ca ratio while the (Ca+Co)/O ratio remains approximately constant. As the Ca/O and Co/O ratios are similar in the pure carbonate compounds, this result is consistent with the

formation of increasing amounts of a Co carbonate phase. However, the (Ca+Co)/C ratio generally increases with increasing Co/Ca ratio while the Ca/C ratio remains mostly constant. This suggests that the phase forming on the calcite surface is not a pure carbonate phase; although this result could be skewed by the fact that the Co/C ratio of the sphaerocobaltite standard is greater than the Ca/C of the calcite standard. Finally, the C/O ratio decreases slightly with increasing Co/Ca ratio while that of the carbonate standards are identical within uncertainties, which suggests the formation of a Co-bearing phase that contains a greater proportion of oxygen than pure CoCO_3 , *e.g.* that has a cobalt hydroxide component.

Although the variations in atomic ratios suggests that a combination of CoCO_3 and Co(OH)_2 formed on the surface, the binding energies of C 1s, O 1s, and Ca $2p_{3/2}$ did not change significantly. Further, the binding energy of the Co $2p_{3/2}$ line and $\Delta\text{BE Co } 2p$ are very similar for CoCO_3 and Co(OH)_2 , which precludes their use for differentiating CoCO_3 from Co(OH)_2 . Indeed, the values of $\Delta\text{BE Co } 2p$ were 16.0-16.1 eV for both compounds, in very good agreement with previously published values (Dillard and Koppelman, 1982; Xu et al., 1996).

However, there is a small but systematic difference between the shapes of the Co $2p_{3/2}$ lines of the CoCO_3 and Co(OH)_2 powder standards whereby the satellite is found closer to the main peak and with a greater intensity for CoCO_3 compared to Co(OH)_2 (Fig. 8). The Co $2p_{3/2}$ lines were fitted using four Gaussian-Lorentzian (see Experimental Methods), as shown in Fig. 8. The main peak consists of two model peaks (1 and 2) whereas the satellite peak consists of a broader peak (3). There is also a second much smaller satellite peak (4). To quantify the difference between the line shapes of both compounds and to enable a quantitative evaluation of the Co-reacted calcite crystals, the proportion of peak 3 to the total area of the Co $2p_{3/2}$ line was plotted as a function of its position relative to the peak maximum. The results for the powder standards

(labeled “CoCO₃ – Air” and “Co(OH)₂ – Air”) and the reacted samples are shown in Fig. 9. As expected from visual inspection of the Co 2p_{3/2} lines, the data points for CoCO₃ and Co(OH)₂ are well separated. For Co(OH)₂, the average coordinates (5.5 eV and 32%) are in very good agreement with the results of Biesinger et al. (2011) (5.6 eV and 33%). The reacted samples fall either close the Co(OH)₂ region or show intermediate values. The small signal-to-noise ratios for the lower Co concentrations are likely to translate to sizeable uncertainties. Nonetheless, this analysis confirms the interpretation of the atomic ratios, *i.e.* a combination of Co(OH)₂ and CoCO₃ is formed at the surface either as separate phases or as a mixed hydroxy-carbonate phase. This approach is similar to that of Dillard and Koppelman (1982), who used the satellite intensity of the Co 2p_{3/2} line to gain information on the chemical nature of Co adsorbed at kaolinite surfaces.

3.2.4. Co 2p_{3/2} photoelectron line as a tool for identification of Co(II) coordination environments

The identification of the nature of the surface precipitates described in the previous subsection relies in part on the ability of the CoCO₃ and Co(OH)₂ powder standards to allow for an unerring measurement of the intrinsic Co 2p photoelectron line of these compounds. Because these powder standards were analyzed as received from the commercial vendor, a second round of analysis was performed, in which they were ground in N₂ atmosphere to expose fresh surfaces and subsequently analyzed with XPS without exposing them to air. The atomic ratios and binding energies derived from this analysis were in accord with the initial analysis, where the only noticeable difference was a slight increase in the Co surface concentration for the CoCO₃ standard (Tables 3 and 5). Fig. 9 shows that this approach yielded satellite proportions and positions that were consistent with the initial analysis, as shown by the data points labelled “CoCO₃ – N₂” and “Co(OH)₂ – N₂”.

Moreover, an additional CoCO_3 sample was analyzed to confirm that the Co $2p$ line shape was independent of sample preparation/origin. This additional sample was synthesized at our laboratory by carbonation reaction of reagent-grade $\text{Co}(\text{OH})_2$ in supercritical CO_2 at 50 °C and 90 atm. Characterization with μ -XRD only detected CoCO_3 and SEM images showed the formation of sphaerocobaltite rhombohedra (Fig. S4). The powder was ground in N_2 atmosphere and analyzed with XPS without exposing it to air. As shown by the data points labelled “ CoCO_3 (2) – N_2 ” in Fig. 9, the satellite structure obtained with this sample was consistent with that measured for the commercial powder. Similarly, to verify that the Co $2p$ line shape obtained with the $\text{Co}(\text{OH})_2$ commercial powder was sample-independent, the reaction with $[\text{Co}^{2+}]_0 = 100 \mu\text{M}$ was repeated as before but in N_2 atmosphere, *i.e.* at $\text{pH}_0 = 9.4$. This led to much higher Co/Ca and (Ca+Co)/C ratios as well as much lower Ca/O and C/O ratios (Table 6), which strongly suggests the formation of significant amounts of $\text{Co}(\text{OH})_2$. The satellite structure obtained with this sample was indistinguishable from that derived from the commercial $\text{Co}(\text{OH})_2$ powder (Fig. 9, data points labeled “100 μM pH=9.4”).

Finally, Biesinger et al. (2011) reported fitting parameters for the Co $2p_{3/2}$ line of CoO; the proportion of peak 3 to the total area was 26.1% and its position relative to the peak maximum was 6.5 eV. Therefore, the satellite structure of CoO differs distinguishably from that of both CoCO_3 and $\text{Co}(\text{OH})_2$. These results demonstrate that the satellite structure of the Co $2p_{3/2}$ photoelectron line is a reliable tool for elucidating the nature of Co(II) coordination environments.

3.2.5. Factors controlling the nature of the precipitates formed on cobalt-reacted surfaces

A salient result was the formation of either separate $\text{Co}(\text{OH})_2$ and CoCO_3 phases or a mixed Co-hydroxy-carbonate surface precipitate. In order to differentiate between these two potential

cases and to better understand the factors that lead to the formation of the surface precipitates, we first explore the thermodynamics of the system. One issue with calculating the initial level of saturation with respect to CoCO_3 and Co(OH)_2 is that multiple solubility constants are available in thermodynamic databases. For CoCO_3 , three solubility constants are available in PHREEQC depending on which database is selected: $\log K = -9.98$ (MINTEQ.v4.dat), $\log K = -10.56$ (LLNL.dat), and $\log K = -11.2$ (SIT.dat). The MINTEQ.v4 database uses the value quoted in the tabulations of constants of Smith and Martell (1976) and Naumov et al. (1974). The LLNL database uses the Gibbs free energy of formation of CoCO_3 predicted by Sverjensky and Molling (1992) based on a linear free energy relationship. The SIT.dat database uses the solubility constant from the NIST Standard Reference Database 46 compiled by Smith and Martell (2004). For Co(OH)_2 , the MINTEQ.v4.dat and LLNL.dat databases use $\log K = 13.09$ and 12.3 , respectively, and the SIT.dat database lists both solubility constants: $\log K = 13.2$ and 12.2 . Plyasunova et al. (1998) provided a thorough evaluation of the different solubility constants reported for Co(OH)_2 and recommended values of $\log K$ of 12.2 and 13.2 for the inactive and metastable so-called pink phases of Co(OH)_2 , respectively. Fig. 10 shows the initial level of saturation with respect to CoCO_3 and Co(OH)_2 as a function of pH for the different solubility constants discussed above and $[\text{Co}^{2+}]_0 = 150 \mu\text{M}$. At pH = 8, the initial solution is undersaturated with respect to Co(OH)_2 regardless of the solubility constant used and supersaturated with respect to CoCO_3 for the two lower solubility constants. Consequently, a pure Co(OH)_2 phase should not form under these conditions.

Therefore, an additional experiment was carried out for $[\text{Co}^{2+}]_0 = 150 \mu\text{M}$ whereby the initial pH was reduced to $\text{pH}_0 = 8.0$ by introducing a small volume of $10 \mu\text{M}$ HCl. Table 6 shows the atomic ratios obtained from XPS analysis of this sample. Also shown are the atomic ratios

obtained in the corresponding experiment where the pH was not modified (*i.e.* $\text{pH}_0 = 8.9$). The Co/Ca ratio was slightly higher at $\text{pH}_0 = 8.0$ than $\text{pH}_0 = 8.9$ and, as a result, the (Ca+Co)/O and (Ca+Co)/C ratios were also slightly higher at the lower pH; but the atomic ratios were otherwise commensurate. The satellite structure of the Co $2p_{3/2}$ line was either close to that of Co(OH)_2 or showed structures intermediate between CoCO_3 and Co(OH)_2 (Fig. 9) and, overall, did not differ significantly from the satellite structure obtained at $\text{pH}_0 = 8.9$. Therefore, the lack of apparent change in the nature of the surface precipitates when the thermodynamic driven force for Co(OH)_2 has been removed points to the formation of a mixed hydroxy-carbonate phase rather than a mixture of separate Co(OH)_2 and CoCO_3 surface precipitates.

Additionally, modified Co Auger parameters were determined in an attempt to provide further evidence for the identification of the surface precipitates at the two initial pH values ($[\text{Co}^{2+}]_0 = 150 \mu\text{M}$). The modified Co Auger parameter is defined as $\alpha' = KE_A + BE_P = h\nu - BE_A + BE_P$, where KE_A is the kinetic energy of the LMM Auger electron emission, BE_P is the binding energy of the Co $2p_{3/2}$ photoelectron, BE_A is the apparent binding energy of the Auger peak, and $h\nu$ is the energy of the X-ray beam. Modified Auger parameters have been shown to be a useful tool for determining chemical states (Wagner et al., 1979). In particular, Zachara and co-workers (Dake et al., 1989; Zachara et al., 1989) used the modified Zn Auger parameter to help identify the nature of Zn precipitates on calcite surfaces. Although they could not differentiate between smithsonite (ZnCO_3) and hydrozincite ($\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$) with this analysis, they were able to rule out the presence of Zn(OH)_2 . The values of BE_A and BE_P were obtained from the LMM Auger peak and the Co $2p_{3/2}$ line of the Co(OH)_2 and CoCO_3 powder standards ground in N_2 atmosphere. Because the Auger peak was fairly broad, it was fitted with three Gaussian-Lorentzian model peaks with identical FWHM and the position of the central peak was used as

BE_A , as illustrated in the Supporting Information in Fig. S5. The values of α' thus obtained were 1550.1 and 1550.0 ± 0.1 eV for $\text{Co}(\text{OH})_2$ and CoCO_3 , respectively. The value for $\text{Co}(\text{OH})_2$ compares well with that determined by Dillard and Koppelman (1982) (1550.4 ± 0.3 eV). The calcite crystals reacted with $150 \mu\text{M Co}^{2+}$ at $\text{pH}_0 = 8.0$ yielded $\alpha' = 1549.0 \pm 0.4$ eV. The same Co Auger parameter ($\alpha' = 1549.0 \pm 0.5$ eV) was obtained at $\text{pH}_0 = 8.9$. Because the LMM Auger peaks have lower signal-to-noise ratios for these two samples, the relative intensities of the three model peaks were fixed to those obtained with the powder standards (20:40:40). Despite a lower precision on the α' of the Co-reacted crystals, this analysis suggests that the surface precipitates differ from the two pure phases, in agreement with the conclusion drawn from the satellite structure of the $\text{Co } 2p_{3/2}$ line.

4. DISCUSSION

4.1. Origin of the differences between heterogeneous growth of cadmium and cobalt carbonate phases on calcite surfaces

Although CdCO_3 and CoCO_3 are both isostructural with calcite, *in situ* AFM images and *ex situ* XPS measurements indicate the formation of very different precipitates on calcite surfaces from Cd- and Co-bearing aqueous solutions. For Cd, a Cd-rich heteroepitaxial carbonate phase is formed on the surface whereas, for Co, experimental evidence points to the formation of a mixed hydroxy-carbonate phase that does not grow epitaxially. Three factors are likely to contribute to this difference.

First and foremost, CdCO_3 exhibits a much smaller lattice misfit (-4%) relative to calcite than CoCO_3 (-15%). This large lattice misfit between CoCO_3 and CaCO_3 is likely to translate to a less favorable interfacial energy of CoCO_3 with calcite compared to CdCO_3 , which, in turn,

would impede the kinetics of heterogeneous nucleation of CoCO_3 (De Yoreo and Vekilov, 2003). Second, the mixed hydroxy-carbonate phase could be a kinetically-favored metastable phase due to the slow dehydration of aqueous Co^{2+} relative to that of Cd and Ca. The water exchange rate around aqueous Cd^{2+} is faster than 10^8 s^{-1} (Eigen, 1963; Inada et al., 2005) whereas that around Co^{2+} is $3.2 \times 10^6 \text{ s}^{-1}$ (Ducommun et al., 1980). For comparison, the exchange rate around Mg^{2+} is $6.7 \times 10^5 \text{ s}^{-1}$ and $5.3 \times 10^5 \text{ s}^{-1}$ according to Bleuzen et al. (1997) and Neely and Connick (1970), respectively, and Mg is known to easily form hydrates at room temperature. In contrast, the water exchange rate around Ca^{2+} is higher than 10^{10} s^{-1} (Kerisit and Parker, 2004). This is consistent with the work of Katsikopoulos et al. (2008), who observed the formation of a low crystalline phase at high Co/Ca ratios during the synthesis of $(\text{Co,Ca})\text{CO}_3$ solid solutions at ambient conditions, which they inferred to be a cobalt carbonate hydrate based on FTIR analysis. Third, the mixed hydroxy-carbonate phase could simply be thermodynamically more stable than CoCO_3 in the conditions considered in this work in the same way that hydrozincite ($\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$) is more stable than ZnCO_3 for a range of $p\text{CO}_2$ and pH values (Preis and Gamsjäger, 2001).

Therefore, future work should be aimed at determining whether CoCO_3 does not form on the surface because the mixed hydroxy-carbonate phase is the most stable phase thermodynamically in these conditions or whether it is kinetically favored because of the lattice misfit and/or dehydration kinetics. With respect to the environmental remediation of metal contaminants, the present findings imply that, in contrast to Cd, co-precipitation of Co with calcite is not expected to be an effective strategy at room temperature.

4.2. Comparison with previous work

Zachara et al. (1991) measured Co solution concentrations that were saturated with respect to $\text{Co}(\text{OH})_2$ when reacting Co with calcite powders in conditions similar to those used in this work. However, the solubility constants used in the geochemical calculations were at the low solubility end of the range discussed above for $\text{Co}(\text{OH})_2$ ($\log K = 12.1$) and at the high solubility end of the range for CoCO_3 ($\log K = -10.1$). In other words, a different choice of solubility constants could have led to the conclusion that the Co solution concentrations were instead saturated with respect to CoCO_3 .

Xu et al. (1996) conducted a series of experiments that included heterogeneous growth experiments (*i.e.* with solutions supersaturated with respect to sphareocobaltite but not with respect to calcite) similar to those reported in this work. The experiments involved reacting calcite single crystals with 10 and 100 μM $\text{Co}(\text{NO}_3)_2$ aqueous solutions for 1 hour or 1 week at alkaline pH. By process of elimination, they concluded that Co was present as a Co-Ca carbonate solid solution. They first ruled out the formation of $\text{Co}(\text{OH})_2$ based on Co $2p_{3/2}$ binding energies (781.9 to 782.2 ± 0.2 eV) that differed by approximately 1 eV from that of their $\text{Co}(\text{OH})_2$ standard (781.0 ± 0.2 eV) and were closer to those of their carbonate-containing standards (781.9 ± 0.2 eV for CoCO_3 , $(\text{Ca},\text{Co})\text{CO}_3$, and $\text{Co}_2(\text{OH})_2\text{CO}_3$). However, different charge correction schemes were used for the carbonate standards and the reacted calcite crystals, which were charge corrected to the O $1s$ binding energy of 531.9 eV obtained by Stipp and Hochella (1991) with the gold reference method, and for the $\text{Co}(\text{OH})_2$ standard, which was charge corrected by matching the adventitious C $1s$ line to that of calcite. This could partially explain the apparent discrepancy between the Co $2p_{3/2}$ binding energy difference between $\text{Co}(\text{OH})_2$ and CoCO_3 reported by Xu et al. (1996) (0.9 eV) and that obtained in this work (0.3 eV and 0.6 eV for samples as received and ground in N_2 , respectively). In addition, Co $2p_{3/2}$ binding energies

reported in the literature for Co(II) hydroxy and carbonate phases show variations: McIntyre and Cook (1975), Dillard and Koppelman (1982), and Biesinger et al. (2011) published 780.9, 781.4, and 780.6 ± 0.2 eV, respectively, for Co(OH)_2 ; Fierro et al. (1992), Baird et al. (1997), and Yang et al. (2011) documented 781.7, 781.5, and 781.1 ± 0.2 eV, respectively, for $\text{Co}_2(\text{OH})_2\text{CO}_3$; and Porta et al. (1991) and Baird et al. (1997) listed 781.7 and 781.4 ± 0.2 eV, respectively, for CoCO_3 (all values were adjusted to the adventitious C 1s line at 285.0 eV to be consistent with this work). Therefore, these results confirm that the chemical sensitivity of the Co $2p_{3/2}$ binding energy is not sufficient to reliably differentiate between Co(II) hydroxy and carbonate phases, as noted in the Results section. Finally, Xu et al. (1996) also ruled out the presence of CoCO_3 and $\text{Co}_2(\text{OH})_2\text{CO}_3$ based on X-ray absorption spectroscopy measurements that were cited as ‘in review’ but that have not been published to date, to the best of our knowledge.

Xu et al. (1996) noted that the formation of $(\text{Ca},\text{Co})\text{CO}_3$ was consistent with the modified oxygen Auger parameters, $\text{O}(\alpha')$, of the reacted crystals as they were identical to that of calcite and different from that of CoCO_3 and $\text{Co}_2(\text{OH})_2\text{CO}_3$. However, $\text{O}(\alpha')$ of a reacted crystal with a Co/Ca ratio of 0.93 was the same as that of CaCO_3 even though $\text{O}(\alpha')$ of the $(\text{Ca},\text{Co})\text{CO}_3$ standard (1041.2 eV) was intermediate between that of CaCO_3 (1040.7 eV) and CoCO_3 (1041.8 eV). Moreover, atomic ratios of Co-containing standards were significantly different from those expected based on stoichiometry, with the amount of Co greatly overestimated (*e.g.* Co/O ratios of CoCO_3 and Co(OH)_2 were 1.76 and 3.12, respectively, and the Co/Ca ratio of $(\text{Ca},\text{Co})\text{CO}_3$ was 18.39) indicating that the relative sensitivity factors were not appropriate and that the Co/Ca ratios of the reacted crystals were likely overestimated. XPS sputter depth profiling showed the presence of Co at depths up to 5 to 10 nm even after only 1 hour of reaction time with 100 μM Co^{2+} . The Co/Ca ratio of a $\text{CaCO}_3/\text{CoCO}_3$ powder mixture increased significantly with

sputtering time. Although this data was used to calibrate the sputtering experiments of the Co-reacted calcite crystals, the propensity of the Co/Ca ratio to increase substantially with sputtering time and the significant overestimation of the Co content of the standards cast doubts on the true extent of Co incorporation. Nonetheless, a crystal reacted with Co^{2+} for one week at an initial pH of 8.2 (final pH = 8.5) showed a higher Co concentration in the near-surface than that reacted at an initial pH of 10.9 (final pH = 8.9), indicating the possibility of Co incorporation in calcite at the lower pH versus formation of surface precipitates at the higher pH. Although our reaction time was shorter, insights from the work of Xu et al. (1996) suggest that Co could incorporate into calcite in our experiments. Indeed, AFM images show the increasing deformation of etch pits as $[\text{Co}^{2+}]_0$ is raised.

5. CONCLUSIONS

Calcite single crystals were reacted with Cd- and Co-bearing aqueous solutions for 16 hours and analyzed with AFM and XPS. AFM images showed that reactions with Cd led to the formation of heteroepitaxial islands that grew preferentially in the $[4\bar{2}1]$ direction at low initial supersaturations and the formation of extensive heteroepitaxial coatings at high initial supersaturations. XPS measurements indicated that the heteroepitaxial phase was a Cd-rich $(\text{Ca,Cd})\text{CO}_3$.

In contrast, reactions with Co showed the formation of surface precipitates that did not grow along a particular direction and, instead, increased in height with increasing initial Co concentration. The lack of evidence for heteroepitaxial growth of the surface precipitates strongly suggests that a $(\text{Ca,Co})\text{CO}_3$ solid solution was not formed on the surface. AFM images also revealed the formation of distorted etch pits at the calcite surface, which is indicative of the

presence of Co incorporated at least at the calcite step edges, in addition to being present as surface precipitates. The satellite structure of the Co $2p_{3/2}$ photoelectron lines obtained from the XPS analysis of the Co-reacted crystals was either close to that of Co(OH)_2 or intermediate between Co(OH)_2 and CoCO_3 . Based on the information gathered from AFM images (lack of evidence for heteroepitaxial growth or for the presence of several distinct phases) and XPS analysis of crystals reacted at a pH for which Co(OH)_2 was undersaturated (satellite structure of Co $2p_{3/2}$ line and Co Auger parameters that differ from those of the pure phases), it is unlikely that this result arises from the combined contributions of two separate phases. Therefore, the combined XPS and AFM results suggest the formation of a hydroxy-carbonate phase, such as $\text{Co}_2(\text{OH})_2\text{CO}_3$.

For Cd-reacted crystals, initial supersaturation states greater than 3 are sufficient to drive the transformation of a precursor phase to a fully crystalline Cd-rich carbonate phase that can grow heteroepitaxially on the calcite substrate. For Co-reacted crystals, small precipitates with morphologies and compositions consistent with those expected of the precursor are found to persist at commensurate initial supersaturations. This result indicates that a misfit of -15% may be too large to grow a heteroepitaxial phase on calcite surfaces. However, difficulties in dehydrating Co could play a role. This is consistent with the known difficulties to synthesize CoCO_3 at ambient conditions. Future work will explore whether this surface precipitate can dehydrate and transform to a cobalt carbonate heteroepitaxial phase on the calcite ($10\bar{1}4$) surface at much longer reaction times and/or higher temperatures.

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TABLES

Table 1. Saturation states of the initial experimental aqueous solutions ($\text{pH}_0 = 8.9$, $[\text{Ca}^{2+}]_0 = 0.08 \text{ mM}$, system open to atmosphere). Ω is defined as Q/K_{sp} where Q is the ionic activity product and K_{sp} is the solubility product of CaCO_3 , CdCO_3 , CoCO_3 , or $\text{Co}(\text{OH})_2$.

$[\text{Cd}^{2+}]_0$ (μM)	$[\text{Co}^{2+}]_0$ (μM)	Ω_{CdCO_3}	Ω_{CoCO_3}		$\Omega_{\text{Co}(\text{OH})_2}$		Ω_{CaCO_3}
			$\log K = -10.0$	$\log K = -11.2$	$\log K = 13.2$	$\log K = 12.2$	
0	0	—	—	—	—	—	0.1
0.3	—	1.8	—	—	—	—	0.1
0.5	—	3.0	—	—	—	—	0.1
1	—	6.0	—	—	—	—	0.1
5	—	29.5	—	—	—	—	0.1
10	—	58.9	—	—	—	—	0.1
25	—	144.5	—	—	—	—	0.1
50	—	281.8	—	—	—	—	0.1
100	—	524.8	—	—	—	—	0.1
—	25	—	0.8	12.9	0.7	6.6	0.1
—	40	—	1.2	20.4	1.0	10.5	0.1
—	50	—	1.5	25.1	1.3	13.2	0.1
—	75	—	2.2	37.2	1.9	19.5	0.1
—	100	—	3.0	49.0	2.6	25.7	0.1
—	150	—	4.3	70.8	3.8	38.0	0.1
—	200	—	5.5	91.2	5.1	51.3	0.1

Table 2. XPS results for Cd-reacted calcite single crystals: Atomic ratios. Concentrations are in μM . Also shown are the atomic ratios obtained for CaCO_3 and CdCO_3 powder standards.

Sample	Cd/Ca	Ca/O	(Ca+Cd)/O	Ca/C	(Ca+Cd)/C	C/O
CaCO_3	-	0.33(1)	0.33(1)	0.78(4)	0.78(4)	0.42(2)
$[\text{Cd}^{2+}]_0=0$	0	0.33(2)	0.33(2)	0.80(3)	0.80(3)	0.41(4)
$[\text{Cd}^{2+}]_0=5$	0.006(3)	0.33(2)	0.33(2)	0.82(1)	0.83(1)	0.40(2)
$[\text{Cd}^{2+}]_0=10$	0.010(4)	0.31(2)	0.31(2)	0.83(2)	0.84(2)	0.37(4)
$[\text{Cd}^{2+}]_0=25$	0.18(12)	0.30(3)	0.34(2)	0.74(6)	0.87(2)	0.40(3)
$[\text{Cd}^{2+}]_0=50$	0.60(9)	0.22(3)	0.37(3)	0.54(3)	0.94(2)	0.40(3)
$[\text{Cd}^{2+}]_0=100$	0.5(3)	0.24(5)	0.36(2)	0.60(8)	0.90(3)	0.40(3)
CdCO_3	-	-	0.41(1)	-	1.01(3)	0.40(2)

Table 3. XPS results for Co-reacted calcite single crystals: Atomic ratios. Concentrations are in μM . Also shown are the atomic ratios obtained for CaCO_3 , CoCO_3 , and Co(OH)_2 powder standards.

Sample	Co/Ca	Ca/O	(Ca+Co)/O	Ca/C	(Ca+Co)/C	C/O
CaCO_3	-	0.33(1)	0.33(1)	0.78(4)	0.78(4)	0.42(2)
$[\text{Co}^{2+}]_0=0$	0	0.33(2)	0.33(2)	0.80(3)	0.80(3)	0.41(4)
$[\text{Co}^{2+}]_0=25$	0.003(2)	0.32(2)	0.32(2)	0.83(3)	0.83(3)	0.39(3)
$[\text{Co}^{2+}]_0=40$	0.04(3)	0.31(1)	0.32(1)	0.83(4)	0.87(5)	0.37(3)
$[\text{Co}^{2+}]_0=50$	0.03(3)	0.34(2)	0.35(1)	0.79(2)	0.81(1)	0.44(2)
$[\text{Co}^{2+}]_0=75$	0.07(2)	0.31(2)	0.33(2)	0.82(1)	0.88(1)	0.38(2)
$[\text{Co}^{2+}]_0=100$	0.15(6)	0.30(2)	0.34(2)	0.84(3)	0.96(8)	0.35(4)
$[\text{Co}^{2+}]_0=150$	0.10(7)	0.28(2)	0.31(1)	0.80(1)	0.88(5)	0.36(2)
$[\text{Co}^{2+}]_0=200$	0.32(6)	0.26(1)	0.34(1)	0.83(1)	1.09(5)	0.32(2)
CoCO_3	-	-	0.36(1)	-	0.91(4)	0.40(1)
CoCO_3^a	-	-	0.40(1)	-	1.04(4)	0.38(1)
Co(OH)_2	-	-	0.52(1)	-	-	-
Co(OH)_2^a	-	-	0.50(1)	-	-	-

^a Powder was ground in N_2 atmosphere and subsequently not exposed to air.

Table 4. XPS results for Cd-reacted calcite single crystals: Binding energies. Concentrations are in μM . Also shown are the binding energies obtained for CaCO_3 and CdCO_3 powder standards.

Sample	C 1s	O 1s	Ca $2p_{3/2}$	Cd $3d_{5/2}$
CaCO_3	289.6(2)	531.2(1)	346.9(1)	-
$[\text{Cd}^{2+}]_0=0$	289.6(1)	531.4(1)	346.9(1)	-
$[\text{Cd}^{2+}]_0=5$	289.6(1)	531.3(1)	347.0(1)	405.6(1)
$[\text{Cd}^{2+}]_0=10$	289.6(1)	531.3(1)	346.9(1)	405.5(1)
$[\text{Cd}^{2+}]_0=25$	289.8(1)	531.5(1)	347.1(1)	405.5(1)
$[\text{Cd}^{2+}]_0=50$	289.9(1)	531.7(1)	347.3(1)	405.4(1)
$[\text{Cd}^{2+}]_0=100$	290.1(1)	531.8(1)	347.5(1)	405.7(1)
CdCO_3	290.0(3)	531.9(2)	-	405.6(3)

Table 5. XPS results for Co-reacted calcite single crystals: Binding energies. Concentrations are in μM . Also shown are the binding energies obtained for CaCO_3 , CoCO_3 , and Co(OH)_2 powder standards.

Sample	C 1s	O 1s	Ca 2p _{3/2}	Co 2p _{3/2}	$\Delta\text{BE Co } 2p$
CaCO_3	289.6(2)	531.2(1)	346.9(1)	-	-
$[\text{Co}^{2+}]_0=0$	289.6(1)	531.4(1)	346.9(1)	-	-
$[\text{Co}^{2+}]_0=25$	289.6(2)	531.2(2)	347.0(1)	-	-
$[\text{Co}^{2+}]_0=40$	289.6(1)	531.5(1)	347.0(1)	781.2(4)	16.2(2)
$[\text{Co}^{2+}]_0=50$	289.7(1)	531.5(1)	347.1(1)	781.4(5)	16.0(1)
$[\text{Co}^{2+}]_0=75$	289.7(1)	531.5(1)	347.0(1)	781.3(2)	16.2(2)
$[\text{Co}^{2+}]_0=100$	289.8(1)	531.5(1)	347.2(1)	781.4(2)	16.0(2)
$[\text{Co}^{2+}]_0=150$	289.5(1)	531.3(1)	346.9(1)	781.1(2)	16.0(3)
$[\text{Co}^{2+}]_0=200$	289.6(1)	531.4(1)	347.0(1)	781.3(1)	16.1(1)
CoCO_3	289.6(4)	531.6(5)	-	781.3(1)	16.0(1)
CoCO_3^a	289.7(1)	531.8(1)	-	781.5(1)	16.2(1)
Co(OH)_2	-	531.1(1)	-	781.0(1)	16.1(2)
Co(OH)_2^a	-	531.1(3)	-	780.9(1)	16.1(1)

^a Powder was ground in N_2 atmosphere and subsequently not exposed to air.

Table 6. XPS results for Co-reacted calcite single crystals at different pH values: Atomic ratios.Concentrations are in μM .

Sample	Co/Ca	Ca/O	(Ca+Co)/O	Ca/C	(Ca+Co)/C	C/O
$[\text{Co}^{2+}]_0=100^a$ $\text{pH}_0=9.4$	1.8(4)	0.14(2)	0.38(1)	0.77(2)	2.1(4)	0.18(3)
$[\text{Co}^{2+}]_0=150$ $\text{pH}_0=8.9$	0.10(7)	0.28(2)	0.31(1)	0.80(1)	0.88(5)	0.36(2)
$[\text{Co}^{2+}]_0=150$ $\text{pH}_0=8.0$	0.14(4)	0.30(1)	0.35(1)	0.81(1)	0.93(3)	0.37(1)

^a Sample was reacted in N_2 atmosphere.

FIGURES

Figure 1. AFM topographic images ($6\ \mu\text{m} \times 6\ \mu\text{m}$) of calcite ($10\bar{1}4$) surfaces reacted with CdCl_2 solutions of initial concentrations (a) 0.3 and (b) 0.5 μM . (c) and (d) are height profiles along the blue lines in (a) and (b).

Figure 2. AFM images ($6\ \mu\text{m} \times 6\ \mu\text{m}$) of calcite ($10\bar{1}4$) surfaces reacted with CdCl_2 solutions of initial concentrations (a) 1, (b) 5, and (c) 100 μM . (a) and (b) are topographic images and (c) is a deflection image. (d), (e), and (f) are height profiles along the blue lines in (a), (b), and (c), respectively.

Figure 3. Height histograms of islands formed on the calcite $(10\bar{1}4)$ surface in contact with Cd-bearing aqueous solutions of varying initial Cd concentration for 16 hours.

Figure 4. AFM topographic images ($6\ \mu\text{m} \times 6\ \mu\text{m}$) of calcite $(10\bar{1}4)$ surfaces reacted with CoCl_2 solutions of initial concentrations (a) 50, (b) 100, (c) 150, and (d) 200 μM .

Figure 5. Height histograms of islands formed on the calcite $(10\bar{1}4)$ surface in contact with Co-bearing aqueous solutions of varying initial Co concentration for 16 hours.

Figure 6. AFM images ($6\ \mu\text{m} \times 6\ \mu\text{m}$, except (b) $8\ \mu\text{m} \times 8\ \mu\text{m}$) showing etch pits on calcite $(10\bar{1}4)$ surfaces after reacting with CoCl_2 solutions of initial concentrations (a) 50, (b) 100, (c) 150, and (d) 200 μM for 16 hours.

Figure 7. (left) Cd 3d and (right) Co 2p photoelectron lines of calcite single crystals reacted with Cd- and Co-bearing solutions.

Figure 8. (top) Normalized and background subtracted Co 2p photoelectron lines obtained from XPS analysis of the CoCO₃ and Co(OH)₂ powder standards (3 regional scans for each compound are overlaid). (bottom) Example of model peaks used to fit Co 2p_{3/2} photoelectron lines (1 to 4, as defined in the text).

Figure 9. Plot of the relative intensity of the satellite peak of the Co $2p_{3/2}$ line as a function of its position relative the main peak maximum for the Co-reacted calcite crystals and powder standards.

Figure 10. Level of saturation of CoCO_3 and Co(OH)_2 as a function of pH in the experiment with $[\text{Co}^{2+}]_0 = 150 \mu\text{M}$, for different published solubility constants of CoCO_3 and Co(OH)_2 .

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