Epitaxy of Rhodochrosite (MnCO₃) on Muscovite Mica and Its Relation with Calcite (CaCO₃)

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ABSTRACT: The flatness of muscovite mica makes it a convenient substrate to study epitaxy. We have analyzed the growth of rhodochrosite (MnCO₃) crystals in solution and on muscovite mica. Growth at high supersaturations occurs via the formation of amorphous MnCO₃, which over time transforms into the crystalline form. In the presence of muscovite mica, epitaxial rhodochrosite crystals with a size of approximately 1 μm form. These crystals are kinetically roughened, because of the high supersaturation. The lattice match between MnCO₃ and muscovite was found not to be the main reason for epitaxy. If the growth experiment is performed twice, the original epitaxial MnCO₃ crystals are overgrown by many small crystallites. Similarly, spherical MnCO₃ crystals with many overgrown facets can be formed on a muscovite surface that is exposed to humidity or by using a higher MnCO₃ supersaturation. A comparison with calcite shows that epitaxy strongly depends on initial supersaturation for both carbonates. In contrast to previous studies, we find that at the right supersaturation, epitaxial calcite crystal growth is possible on freshly cleaved muscovite.

INTRODUCTION

In the past, muscovite mica was used as a cheap alternative to glass in windows in the Moscow area in Russia, as large sheets of the mineral could be obtained, hence the name given to the mineral. Nowadays, in addition to a wide range of industrial applications, muscovite is widely used in scientific experiments. For example, muscovite is used as a model mineral in order to understand enhanced oil recovery, to study (hetero)-epitaxy, and to create ordered layers of (organic) molecules, which in turn can act as a template for protein crystallization. A special application for muscovite is found in the surface force apparatus, which is used to measure forces between surfaces. The main reason for using muscovite in these applications is the extreme flatness of the surface obtained after cleavage of the muscovite (001) layers. It is possible to obtain atomically flat areas of over 1 cm² without any steps. Furthermore, the surface properties can be tailored by the exchange of the surface K⁺ ions with other cations. In the crystal structure of muscovite mica (ideal chemical formula KAl₂(Si₃Al)O₁₀(OH)₂), a positive cationic K⁺ layer bridges two negatively charged SiO₄ tetrahedral sheets. This layered structure can be easily cleaved through the cationic layer, which was recently suggested to occur at even numbers of layers.

The growth of calcite (CaCO₃) on muscovite mica was previously investigated. When grown on freshly cleaved muscovite, calcite crystals have a random orientation. However, when muscovite is first exposed to humid air, small K₃CO₃ nanocrystallites form, which induce epitaxial growth of the calcite crystals. Here, the growth of carbonates on muscovite (001) is further investigated by looking at the mineral rhodochrosite (MnCO₃). Rhodochrosite is isostructural to calcite and is encountered in soil and sediment material, where it plays an important role in the Mn²⁺ geochemistry. Furthermore, it has been extensively used as a template material for the formation of hollow-core capsules usable for drug delivery. We expect the growth behavior of MnCO₃ to be similar to CaCO₃. We found, however, that rhodochrosite does crystallize epitaxially on freshly cleaved muscovite where calcite was thought not to. This seems conflicting, but we find that at sufficiently large supersaturation epitaxial crystals of calcite can be grown as well.

EXPERIMENTAL METHODS

MnCO₃ crystals were grown by adding equal amounts of an aqueous manganese chloride tetrahydrate solution (Sigma-Aldrich, ≥99% pure) to an aqueous sodium carbonate (Fisher Scientific, no indication of purity given) solution. If not stated otherwise, concentrations of 10 mM were used for both solutions, leading to a MnCO₃ solution concentration of 5 mM. In the solution growth...
experiments, the suspension was filtered after a crystallization time varying from 0 min to several hours, prior to characterization by powder X-ray diffraction and microscopy. In the epitaxy experiments, muscovite mica (ASTM-V1 quality grade, S&J Trading Inc.) was freshly cleaved using Scotch tape. These muscovite samples were adhered to a sample holder by using petroleum jelly and placed upside down in a 24-well plate (ThermoFisher Scientific) filled with the solution. This was then placed in a closed compartment, typically for 2 h. Subsequently, the samples were washed two times in demineralized water for at least 30 s and dried in air. In some of the experiments, pieces of muscovite were, prior to crystallization experiments, exposed to humidity for 1 h in a Binder MKF 115 climate chamber, in which the relative humidity was set at 37.5%. A number of crystal growth experiments was performed twice; i.e., after separation of the specimen from the solution followed by washing and drying, the above procedure is repeated. CaCO$_3$ crystals were grown in a similar way by using a 10 mM calcium chloride solution (Merck, >99.5% pure), or higher concentrations, when indicated. All experiments were performed at room temperature and without any pH adjustments.

The crystallographic orientation of muscovite mica was determined using a Leica DMRX optical polarization microscope in conoscopic mode (see Supporting Information S1 and S2). Scanning electron microscopy images were acquired using a PhenomWorld Phenom scanning electron microscope and a JEOL 6330 Cryo field emission scanning electron microscope. For these measurements, a thin gold layer was applied to the samples using a Cresington 108auto sputter coater. As a measure of the epitaxial crystal size, the distance between one corner of the triangular crystal to the middle of the opposite side was used. The crystal sizes of at least two different batches were measured, and for each batch seven random positions were evaluated.

Throughout this article, the hexagonal setting of MnCO$_3$ and CaCO$_3$ is used. The (001) crystal plane in the hexagonal setting corresponds to the (111) plane in the rhombohedral setting, whereas the (104) plane in the hexagonal setting corresponds to the (221) plane in the rhombohedral setting.

The chemical speciation of the solutions and corresponding MnCO$_3$ and CaCO$_3$ saturations were determined using the PHREEQC software. The solution was treated as a closed system with a temperature of 25 °C. Input species were Ca$^{2+}$/Mn$^{2+}$ (1 equiv), CO$_3^{2−}$ (1 equiv), Na$^+$ (2 equiv), and Cl$^-$ (2 equiv), where 1 equiv corresponds to the MnCO$_3$ and CaCO$_3$ concentrations mentioned in the text. The saturation index (SI) was calculated by the software according to $\text{SI} = \log_{10}(\frac{[A]^y[B]^x}{K_{sp}})$, with $[A]^y$ and $[B]^x$ the actual activities of the ions and $K_{sp}$ the solubility product. The driving force of crystallization ($\frac{\Delta G}{T}$) is related to the SI via $\Delta G = 2.303 \times T \times \text{SI}$, with $k$, the Boltzmann constant and $T$, the temperature (in K). The calculated values can be found in Table 1.

### RESULTS AND DISCUSSION

**MnCO$_3$ Growth in Solution.** In order to understand the epitaxial growth of MnCO$_3$, we first performed experiments in solution under similar experimental conditions. To obtain MnCO$_3$ solutions containing 10 mM of MnCl$_2$ and 10 mM of Na$_2$CO$_3$ were mixed, which immediately leads to the precipitation of white particles in solution. Powder X-ray diffraction (PXRD) measurements performed directly after mixing both compounds showed no crystalline peaks, as is shown in Figure 1a, but an amorphous signal is visible around 18°. We therefore conclude that these particles are amorphous (A-MnCO$_3$). The same conclusion was drawn in a previous study, in which the amorphous phase was found to contain slightly more than one water molecule per MnCO$_3$ moiety.

After a crystallization time of approximately 15 min, peaks start to emerge in the diffractogram. These peaks, corresponding to crystalline MnCO$_3$, i.e., rhodochrosite, become more intense when the crystallization time is increased. Visually, the transformation from the white amorphous form to the brown crystalline form can be observed as well. After a crystallization time of approximately 25 min, a slight brown color becomes apparent, which agrees with the PXRD measurements. After approximately 2 h, a stable brown color is reached, indicating a considerable amount of crystalline MnCO$_3$. The transformation to crystalline MnCO$_3$ does not stop when the amorphous particles are removed from the solution. After a crystallization time of 5 min in solution, followed by a waiting time of 2 days in air, intense peaks corresponding to rhodochrosite were observed (Figure 1a), whereas without this waiting time no crystals were present.

Figure 1b shows SEM images of MnCO$_3$ crystals obtained after filtration of the solution after a crystallization time of 2 h, followed by a waiting time of 2 days. The smaller crystals of 1–2 μm in size appear rhombohedral. Larger, more spherical particles of about 4–8 μm were also observed. The latter possess many small overgrown facets, as can be seen in Figure 1b. Figure 1c shows a similar crystal of which a part was detached during the filtration process, allowing the observation of the interior of the crystal. The core of the crystal appears hollow. Needle-shaped crystals grow from the inside toward the surface, where they end well-faceted. It is likely that nucleation and growth of the crystallites take place on an amorphous particle, while growth material is supplied by the supersaturated solution. In time, the amorphous particle dissolves, leading to a hollow core. The crystalline phase grows outward by means of evolutionary selection.

According to Van der Drift’s model, the texture of polycrystalline layers on top of a planar or spherical substrate is determined by the fastest growing directions after some period of growth. In the case of MnCO$_3$, this is the [001] top direction and following Van der Drift’s evolutionary selection model, the polycrystalline spheres are bound by the [001] apaxes of the crystallites pointing outward from the center as shown in Figure 1c.

**Epitaxial MnCO$_3$ on Muscovite Mica. Morphology and Orientation.** Epitaxial growth of MnCO$_3$ was achieved by mixing equimolar 10 mM solutions of Na$_2$CO$_3$ and MnCl$_2$, yielding a 5 mM MnCO$_3$ solution in the presence of muscovite mica. Scanning electron microscopy images of these epitaxial crystals are shown in Figure 2. Nearly all crystals

| concentration (mM) | pH | driving force ($\frac{\Delta G}{T}$) | dissolved Ca$^{2+}$/Mn$^{2+}$ (mM) |
|-------------------|----|-----------------------------------|-----------------------------------|
| 0.2               | 9.1| 5.2                               | 0.01                              |
| 0.5               | 9.1| 6.4                               | 0.01                              |
| 5                 | 9.1| 8.9                               | 0.02                              |
| 25                | 9.1| 10.6                              | 0.02                              |
| 50                | 9.2| 11.3                              | 0.02                              |
| 250               | 9.2| 13.0                              | 0.04                              |
| 0.5               | 9.9| 2.8                               | 0.13                              |
| 1.7               | 9.9| 4.7                               | 0.14                              |
| 5                 | 9.9| 6.1                               | 0.16                              |
| 25                | 9.9| 8.0                               | 0.21                              |
| 50                | 9.9| 8.7                               | 0.26                              |
| 250               | 9.9| 10.5                              | 0.48                              |
The observed crystals are oriented epitaxially (99 ± 1%). The size and density of the crystals are not sufficient to use PXRD to determine the MnCO$_3$ "contact face," i.e., the MnCO$_3$ crystal plane parallel to the muscovite surface. Even an exposure time of more than 100 h did not reveal any detectable MnCO$_3$ reflections, as these are obscured by the mica background X-ray scattering. However, from the 3-fold symmetry and by looking at similarities with epitaxial calcite (CaCO$_3$) on muscovite mica$^9$ (Supporting Information S2), it can be concluded that the MnCO$_3$ contact face is the (001) plane. Also, careful measurements of the lozenge-shaped faces of several MnCO$_3$ crystals revealed average values of 102.5° for the obtuse angles and 76.1° for the acute angles. This agrees well with the angle of 103.02° and 76.98° as calculated for the {104} faces of the R$3c$ rhodochrosite structure using $a = 4.773$ Å and $c = 15.67$ Å in the hexagonal setting. So, the MnCO$_3$ crystallites are bounded by {104} faces, similar to CaCO$_3$. The (pseudo)hexagonal symmetry of the muscovite mica (001) surface, in combination with the 3-fold symmetry of the MnCO$_3$ crystals, gives rise to two distinguishable—opposite—MnCO$_3$ orientations. The detailed measurements of the epitaxial properties of the MnCO$_3$ crystallites on muscovite mica are summarized in the Supporting Information (S3).

Muscovite mica (001) has a rectangular surface unit cell with lattice parameters $a = 5.1906$ Å and $b = 9.0080$ Å, which is illustrated in Figure 3a. Figure 3b shows the MnCO$_3$ contact face, i.e., the (001) plane. As this face is polar, two different terminations can be expected: a carbonate termination or a manganese termination. In our case, it is more likely that the Mn$^{2+}$ layer is found directly above mica, as muscovite mica has a negative intrinsic charge caused by isomorphous substitution.$^{31}$ The rectangular centered MnCO$_3$ surface unit cell, drawn in Figure 3b, is an alternative for the rhombohedral setting and has lattice parameters $a = 4.773$ Å and $b = 8.267$ Å.$^{29}$ From the fact that the {104} MnCO$_3$ side facets point toward the muscovite b-axis and its hexagonal equivalents, it follows that both rectangular surface unit cells coincide (see Supporting Information S1 and S3). The Mn$^{2+}$ cations could be located above the center of the muscovite hexagonal cavity, replacing the K$^+$ cations initially present at the muscovite...
surface. Both the $a$ and $b$ lattice parameters of MnCO$_3$ are 8% smaller than those of muscovite, resulting in an area that is 16% smaller than the area of the muscovite surface unit cell. Remarkably, this lattice mismatch is larger than that of calcite.
in the same setting (∼4% for both lattice parameters, resulting in an area mismatch of ∼8%). Calcite, which is isostructural to rhodochrosite, is reported not to exhibit epitaxy directly on freshly cleaved muscovite, but epitaxy of calcite can be achieved in the presence of K₂CO₃ nanocrystallites on the muscovite surface. This means that for MnCO₃ the lattice match is not the main reason for epitaxy. A similar conclusion was drawn regarding the epitaxy of calcite on muscovite.

Growth. The first epitaxial MnCO₃ crystals on the muscovite mica surface are observed after a crystallization time between 15 and 75 min, whereas the amorphous phase in the bulk solution immediately forms when the two solutions are brought together. The solubility of A-MnCO₃ is higher than that of crystalline MnCO₃, which results in a supersaturated solution with respect to crystalline MnCO₃. This leads to sustained growth of crystalline MnCO₃ on the mica substrate. This is an example of Ostwald’s rule of stages, where first the least stable form is formed, followed by crystallization of the stable form. The nucleation barrier for the amorphous phase is lower than that of the crystalline phase. Rapid nucleation of the amorphous phase is followed by slow nucleation and growth of the crystalline phase. If both phases would have a similar nucleation barrier, crystals would form immediately because of the high supersaturation. The evolution is schematically illustrated in Figure 4a, in which the supersaturation is shown as a function of time. When the two solutions are brought together, a large supersaturation is created. This rapidly decreases due to the formation of A-MnCO₃ dispersed in solution. After the nucleation of crystalline MnCO₃ in solution and at the muscovite surface, A-MnCO₃ dissolves leading to a plateau in concentration, followed by a decrease in MnCO₃ concentration if A-MnCO₃ is completely dissolved, as was earlier observed for CaCO₃. This is confirmed by the growth rate measurements displayed in Figure 4b. Initially, the crystals show a linear increase in size over time, as expected for constant supersaturation. Then the growth speed decreases as the solution depletes and approaches the equilibrium concentration of MnCO₃. The crystals continue to grow until the equilibrium concentration is reached after approximately 24 h. The epitaxial crystals observed at different crystallization times all possess the same morphology and only differ in size (Figure 4c). At concentrations above approximately 2.5 mM, immediate precipitation of A-MnCO₃ occurred, whereas at lower concentrations, no precipitation of A-MnCO₃ nor growth of MnCO₃ on muscovite was observed. The high supersaturation in this experiment leads to kinetic roughening, resulting in rounded edges of the MnCO₃ crystals, as can been seen in Figures 2 and 3c.

In an attempt to increase the size of the crystals, the growth experiment was performed twice. Surprisingly, we observed that the original {104} facets became overlapped, as can be seen in Figure 5. The epitaxy and {104} facets of the MnCO₃ crystals are still visible, but many small well-faceted crystallites have grown on top of the original {104} facets. In this second crystallization step, because of the high supersaturation, amorphous material precipitates from solution, judging from the white color of the precipitated solid. It is unclear if amorphous particles adhere to the surface of the original MnCO₃ crystals and then transform into small MnCO₃ crystallites or if they first transform into the crystalline form followed by attachment to the MnCO₃ crystals. In both cases, this can lead to the formation of the observed nonepitaxial faceted crystallites on the original crystals. In the second cycle, no nucleation barrier or a very low nucleation barrier for crystallization has to be overcome before growth can occur on top of the existing MnCO₃ crystals. This leads to multifaceted growth. However, this is not the case for newly formed crystals.
in the second cycle, which are the small crystals observed in Figure 5a.

Epitaxy of calcite on muscovite mica can be achieved by exposing muscovite to humid air prior to the growth experiment. The exposure to humid air is known to lead to epitaxial K₂CO₃ nanocrystals, formed by a combination of muscovite surface K⁺ ions and CO₂ from the air. Stephens et al. hypothesize that these K₂CO₃ crystallites act as a carbonate source attracting Ca²⁺ to the surface, leading to the epitaxial nucleation of CaCO₃ on muscovite mica exposed to humid air. We have also investigated if the presence of K₂CO₃ crystallites on the muscovite surface has an effect on the growth of MnCO₃. On the substrates exposed to humid air, still a number of small, epitaxial MnCO₃ crystals can be seen, but in contrast to freshly cleaved mica, also larger, nearly spherical MnCO₃ crystals are formed (Figure 6a,b). In contrast to the crystals grown by performing two crystal growth cycles on bare muscovite (Figure 5), the larger crystals grown on muscovite exposed to humid air do not have underlying {104} facets of the epitaxial MnCO₃ crystals and therefore are nearly spherical. It is likely that the smaller crystals nucleate on the bare muscovite surface and will form epitaxial MnCO₃ crystals similar to those on a freshly cleaved muscovite surface, whereas when nucleation takes place on top of the K₂CO₃ crystallites existing on the muscovite mica exposed to humid air, large spherical crystals form.

MnCO₃ crystals grown at higher supersaturations on freshly cleaved muscovite, often while stirring the solution, show a similar shape as the multifaceted spherical crystals. The high supersaturation can be achieved by using a high concentration (Figure 6c) or by adding solvents in which MnCO₃ is less soluble. In Figure 6c, a concentration of 25 mM is used, which leads to formation of exclusively spherical MnCO₃ crystals and no epitaxial crystals. At these higher supersaturations, nucleation can take place at the bare muscovite or on amorphous particles adsorbed at the muscovite surface, similar to crystallization in solution (Figure 1b,c). In both cases, the high supersaturation leads to fast and evolutionary growth which results in the multifaceted crystals.

**Comparison with Calcite.** Given the different observed behavior in epitaxial growth between MnCO₃ (our results) and CaCO₃, we now take a detailed look at these two systems. Earlier we saw that the lattice mismatch is not the main cause of epitaxy for these carbonates. When comparing MnCO₃ and CaCO₃, many physical parameters are similar. Both Mn²⁺ and Ca²⁺ adsorb at the muscovite surface with similar occupancies. Also, the hydration energy of Mn²⁺ and Ca²⁺ is comparable. The ionic radius of Mn²⁺ is somewhat smaller than that of Ca²⁺ (0.83 and 1.0 Å respectively). It is known that cations adsorb at different heights at the muscovite interface, depending on hydration energy, valency, and size, but the differences in these parameters are small in this case. The solubility, on the other hand, shows a large difference. The solubility product of rhodochrosite is approximately a factor 200 lower than that of calcite. As presented above, in some of our experiments the solution concentration is determined by the presence of amorphous material. A rough estimate of the solubility of A-MnCO₃ is 0.2 mM, which was determined by diluting A-MnCO₃ suspensions until a clear solution was obtained. This is approximately a factor eight lower than for amorphous CaCO₃ (1.7 mM). On the basis of the above, the initial supersaturation of MnCO₃ and CaCO₃ for a 5 mM solution is Δμ/kT = 8.9 and Δμ/kT = 6.1, respectively (Table 1). The supersaturation during growth in the presence of the amorphous phase is Δμ/kT = 5.2 for MnCO₃, and Δμ/kT = 4.7 for CaCO₃. The experiments that result in epitaxial MnCO₃ are thus performed at a much higher initial supersaturation than used in the experiments on CaCO₃ growth reported earlier. To test if similar high (super)saturations for CaCO₃ would yield epitaxial calcite crystals on freshly cleaved muscovite, we performed experiments using a concentration of 50 mM. This gives a driving force (Δμ/kT = 8.7) that is similar to that of a 5 mM MnCO₃ solution (Δμ/kT = 8.9). Using this CaCO₃ concentration of 50 mM, epitaxy of CaCO₃ was indeed achieved, as is shown in Figure 7a. The number of epitaxial CaCO₃ crystals is smaller than when grown on muscovite exposed to humidity. Moreover, most of these crystals are overgrown.

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**Figure 6.** Scanning electron microscopy images of MnCO₃ crystals grown on muscovite mica (a) and (b) exposed to humid air followed by 2 h of crystallization time and (c) with a concentration of 25 mM instead of 5 mM on freshly cleaved muscovite mica.

**Figure 7.** Scanning electron microscopy images of CaCO₃ crystals grown on muscovite mica after 2 h of crystallization time at a concentration of (a) 50 mM and (b) 250 mM.
As the amorphous phase precipitates, the concentration will rapidly reach the solubility of the amorphous phase. After this time, the supersaturation is expected to be the same as for a concentration of 5 mM, only a larger amount of material precipitates. For 5 mM CaCO₃ solutions, no epitaxial calcite is formed on freshly cleaved muscovite, while such growth occurs for 50 mM solutions. Since both concentrations are above the solubility of amorphous CaCO₃, we conclude that the high initial concentration is important and that the nuclei for epitaxial CaCO₃ are likely already formed in the initial phase. The high supersaturation may result in sufficiently large areas with a high local Ca²⁺ concentration in the geometry as sketched in Figure 3b that lead to nucleation. Further growth of the oriented nuclei leads to the observed epitaxial crystals. The same mechanism likely occurs occurs for MnCO₃. While in both cases the supersaturation is similar, for MnCO₃, the equilibrium concentration is much lower. This implies a higher surface free energy, resultin in a higher activation barrier for secondary 3D nucleation, which leads to epitaxial crystals without the overgrowth (2), in contrast to CaCO₃, where we do see this overgrowth (Figure 7a).

At a concentration of 250 mM and higher, all calcite crystals are overgrown, as can be seen in Figure 7b. Because of the overgrowth, it is unclear if the underlying crystals are epitaxial with the muscovite substrate. The calcite crystals differ in morphology from the spherical overgrown MnCO₃ crystals in Figure 6c, but both form at high concentrations. Besides the overgrown calcite crystals, also vaterite crystals are formed (Supporting Information S4). Vaterite is known to be an intermediate phase for the formation of calcite.⁵¹,⁵²

When the growth experiment is performed twice with 5 mM CaCO₃, the calcite crystals continued to grow in a regular fashion, in contrast to MnCO₃ (Figure 5), as can be clearly seen from the persistence of the planar {104} facets (Supporting Information S5). Even when the two growth cycles with CaCO₃ are performed with a 50 mM concentration (for both cycles) no differences in morphology are observed compared to the 5 mM case (Supporting Information S5). This again shows the effect of the solubility and thus supersaturation of both carbonates on the crystal growth and morphology.

**CONCLUSION**

We have demonstrated the epitaxial growth of MnCO₃ crystals on the muscovite surface. These epitaxial crystals are kinetically roughened because of the high supersaturation. By repeating the crystallization procedure, many small crystals grow on the pre-existing epitaxial MnCO₃ crystals, of which the underlying epitaxy remains visible. The formation of large spherical polycrystalline MnCO₃ crystals is induced by the presence of K₂CO₃ crystallites formed by exposure of muscovite mica to a humid environment. Similar results can be achieved by using a higher MnCO₃ supersaturation. Also epitax of CaCO₃ on freshly cleaved muscovite was achieved by performing experiments at a similar supersaturation as that of MnCO₃, showing that the initial supersaturation and not lattice match is the major parameter in achieving epitaxy.

**ASSOCIATED CONTENT**

- Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.0c00578.

Conoscopy of MnCO₃ and CaCO₃ crystals, determination of epitaxial orientation of MnCO₃ crystals, and additional SEM images (PDF)

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**Notes**
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