Cleavage of Calcitic CaCO$_3$ during Dissolution in Aqueous Solution

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ABSTRACT: Calcite cleavage was observed using a device to accelerate the formation and dissolution of calcitic CaCO$_3$ by acidification in aqueous solutions. Scanning electron microscopy showed that crystals formed within 1 day and dissolution began at 3 days of aging. In the X-ray diffraction pattern, calcite was predominantly formed but an amorphous phase did not exist, even after 12 days of aging. In the diffraction pattern and lattice images obtained using a series of high-resolution transmission electron microscopy analyses, cleavages mainly occurred in the \{10\overline{1}1\} plane and some cleavages were observed through the \{10\overline{1}4\} plane.

1. INTRODUCTION

Calcium carbonate, one of the most abundant minerals in nature, has recently been investigated as a candidate material for storing CO$_2$. Increasing emissions of CO$_2$ gas are primarily responsible for global warming and ocean acidification.$^1$

Increasing levels of atmospheric CO$_2$ cause a rise in the partial pressure of CO$_2$ at the surface of the ocean and lower the pH of the ocean surface water. Ocean acidification lowers the availability of carbonate ions (CO$_3^{2-}$) used as a structural or protective material in shells formed of precipitated carbonate minerals. This acidification also promotes the dissociation of inorganic calcium carbonate (ICC) and biological calcium carbonate (BCC) in seashells and reef corals in the sea. Some researchers$^{2-5}$ reported that an increase in CO$_2$ concentration in the atmosphere causes ocean acidification and continues to accelerate the dissolution of mineralized carbonate in the marine environment, which in turn intensifies ocean acidification.$^6$

The formation, crystal growth, and control of polymorphs of ICC$^{6-9}$ and BCC$^{10-13}$ have been widely studied. The polymorphs and morphologies that occur during the formation of ICC are influenced by the solution pH, solution temperature, supersaturation ratio, and additives. There have been few studies on the dissolution and cleavage of CaCO$_3$. When ICC, which exists as inorganic matter in the sea, dissolves, it contributes to the acidification of the ocean and an increase in atmospheric CO$_2$.$^{2-5}$ Studying the dissolution and cleavage of ICC is important to understand the effect of ocean acidification, resulting from the dissolution of mineralized carbonate in the sea. The phenomenon in which calcite CaCO$_3$ is formed and split in an acidic aqueous solution was examined by reproducing the marine acidification environment in a laboratory. In this study, we designed an experimental setup that accelerated the calcite formation and dissolution. CaCO$_3$ synthesis was carried out in Petri dishes, and the formed CaCO$_3$ was aged in solution for several days to reach an acidic condition.$^{14}$ We observed the polymorphs, morphological changes, and cleavage planes during the process of dissolution with aging.

2. RESULTS AND DISCUSSION

The pH of the solution decreased with aging times from 10.5 at the initial stage (Supporting Information Figure S1) and approached 6.5 in 12 days. The initial pH was dependent on the concentration of the basic components. The decrease in pH was affected by the inflow of CO$_2$ from the atmosphere. The amount of precipitated CaCO$_3$ in the solution can also be observed with aging time. Under these conditions, calcitic CaCO$_3$ was dominant. The amount of synthesized CaCO$_3$ was measured by ethylenediaminetetraacetic acid (EDTA) titration (Supporting Information Figure S2a). The amount that was synthesized reached its maximum on day 1 (Supporting Information Figure S2b). After 3 days of aging, the amount began to decrease and the precipitate began to dissolve. Almost 50% of the synthesized CaCO$_3$ was dissolved after 12 days of aging (Supporting Information Figure S2c). X-ray diffraction (XRD) and two-dimensional XRD (2D-XRD) patterns showed that the calcite polymorphs formed and did not change during the aging (Supporting Information Figures S3 and S4).
believed that this experimental setup can demonstrate the formation of calcite CaCO₃, the acidification of solutions, and the resulting dissolution of the synthetic calcitic materials.

Figure 1 shows some rhombohedron calcites, which completed formation within 3 days under the experimental conditions. After 5 days, some small and thin erosions seemed to have occurred on the upper surface of the rhombohedron, as seen in Figure 1b. After 5 days, some erosions seemed to have begun in the center of the upper face of the rhombohedron and fragmented platelets were visible around it. The surface of the thinned rhombohedron eventually broke into small particles, and some were punctured. It is interesting to observe that the rhomboids had their upper and middle parts cut off by erosion while the middle part was punctured, as can be seen in Figure 1c. The thin, small platelets on the upper face seem to split along the (101̅4) plane. However, other splits through different directions also appear to occur (Figure 1d). Cleaving experiments of calcite through the (101̅4) plane in different pH solutions were conducted, and change in atomic corrugations on the surface was observed.15,16 It was reported that the dissolution rate of calcites is dominated by etch pits.17 Ilgen et al.18 conducted an experiment on crack initiation and crack propagation using a premade indented tip along the (101̅0) plane and reported that the dissolution rate of calcite in various solutions increased when the solutions’ pH decreased. The crack propagation rate decreased gradually but showed weak dependence on pH and varied with different solutions.

Figure 2 shows the transmission electron microscopy (TEM) images obtained during the dissolution process of CaCO₃. On the 5th and 7th days, thinner, smaller, and fragmented rhomboids appear. The crystal facets are still apparent, but a sheet-shaped calcite has not yet formed. After 12 days, CaCO₃ appeared in the form of a thin ribbon and sheet. Figure 2d also shows that there is a rhombohedral face whose shape is partially eroded.

Figure 3 shows the diffraction diagrams of 2D-XRD and the Miller index assigned to each plane over aging time. At 10 h, each band is wide and diffuse, displaying the presence of an amorphous structure. The amorphous pattern also appeared with 5 h of aging (Supporting Information Figure S5). 1 day aging caused the diffused and expanded bands to narrow and cleared the band lines. In particular, the change in the {101̅4} plane was noticeable. The 2D-XRD diffractograms on day 5 and 12 did not give such appearance with broadening and diffusion of bands (Figure 3c,d). The lines were not continuous, indicating that the crystal size was small and interspersed. This indicates that the resulting calcite crystals did not transition back to the amorphous state even after 12 days of annealing. The XRD pattern extracted from the 2D-XRD diffractograms and graphs showed the same result, and the band width was no longer widened 3 days after the start of dissolution (Supporting Information Figure S4). The {101̅4} plane remains a pivotal plane at all aging times, and the band of other planes is sharp even with longer aging.

Figure 4 shows the high-resolution TEM (HR-TEM) analysis of crystals sampled after 5 days of aging. Nano-sized crystals are broken and scattered, as seen in Figure 4a. Even in this case, the diffraction rings of the polycrystalline crystals can be seen in the selected area electron diffraction (SAED) pattern observation but no amorphous pattern was observed (Figure 4b). This pattern is consistent with the 2D-XRD results in Figure 3. In Figure 4c, the crystal fragments have fallen apart. Amorphous fragments could not be watched at this stage, and each broken crystal turns out to be a single crystal. The apparent diffraction spots and lattices were assigned as {101̅1}, {112̅0}, {000̅6}, and {011̅2} based on measurements of the interplanar distance, as shown in Figure 4c.

Figure 4d–f shows the results of HR-TEM analyses of a single crystal sampled after 5 days of aging. The shortest diffraction spot for a crystal in Figure 4d was assigned as (011̅1) based on the diffraction pattern and d-spacing measurement. This plane is crossed with a (101̅2) crystal plane. The lattice image on the diffraction spot was in agreement with the obtained diffraction image. Another shortest diffraction spot in the lattice image and the diffraction was designated to the (110̅1) plane. Both are {101̅1} family of planes, and it can be seen that these are the crystal planes of a rhombohedral crystal structure. At the edge of the spotted crystal in 4f, both the (011̅1) and (110̅1) faces have disappeared, but the (101̅2) crystal plane is still visible. The remaining face appears to be a face that fractured on the lateral side. This observation implies that the crystal was broken in the (101̅2) plane on the lateral side and the crystal might have split layer-by-layer through one crystal plane of {101̅1} family.

Another crystallite sampled after 5 days of aging showed different cleavage planes, as seen in Figure 4g–i. Both the (1104) and (0114) planes, assigned using the lattice image and
SAED pattern, appear, and the (1210) plane crossed between them. On the edge side, only the (1210) plane remains but both the (1104) and (0114) planes have vanished. Thus, the fracture on the lateral side might occur at the face of (1210), and layer-by-layer cleavage takes place in one of {101̅1} families of crystal planes.

Figure 5 shows results of HR-TEM analyses of the sampled crystals after 12 days of aging. The Miller index in Figure 5c is based on what can be seen in Figure 5b,c. This finding suggests that a plane splitting (cleavage) occurred along the {101̅1} plane and the fracture occurred along the (1012) plane. This investigation by HR-TEM analysis is consistent with the investigation after 5 days of annealing. Therefore, each plane was assigned in the same manner as in Figure 4d–f.

Another crystal (Figure 5d) sampled after 12 days of aging shows the cleavage pattern similar to that seen in Figure 4g–i. The (1014) and (0111) planes assigned using the lattice image and the SAED pattern appear in Figure 5e,f, and the (1123) planes cross between them. In this pattern, it can be seen that the (1014) plane had a lateral fracture.

Figure 6a–c displays that the crystal part divisions occurred in two oblique planes. Compared to the diffraction pattern and the lattice image, one of the shortest diffraction spots is assigned to the (110̅1) plane (black dotted parallelogram). The other oblique plane denoted by a blue solid parallelogram can be designated as the (011̅1) plane. Both are one of the families of the {101̅1} plane. Also, another plane intersecting these two planes was assigned as (1012) as seen in Figure 6b,c.

A closer look reveals a structure with layered platelets, as can be seen on the lower side of Figure 6a. This TEM observation suggests that several cracks have occurred in the middle of the upper crystallite. The shape of the expelled platelets resembles that of the platelets on the lower side of Figure 6a. The platelets may have been expelled from the upper crystal. This suggests that multiple platelet divisions (cleavage) occurred layer by layer and that these events resulted in the formation of platelets of similar thickness during the cleavage process.

In the platelets investigated, splitting lines appeared between layers (denoted by a black dotted arrow). These splitting lines are parallel to the (011̅1) plane; it is assigned to one of the {1011} families of planes. Therefore, it is thought that the crystal was cleaved in one plane of the {1011} family.

Some dissolution research studies were conducted on the {1014} plane cleaved\(^1\)\(^2\)\(^3\) and the undefined plane of calcite crystals in an aqueous environment.\(^4\)\(^5\)\(^6\) The dissolution rate\(^7\)\(^8\)\(^9\) and the cleaved surface were examined by atomic force microscopy.\(^10\) Lardge\(^11\) and Wang\(^12\) suggested that ionic bonds form between the Ca\(^{2+}\) and carbonate ions across the (1014) plane and that these bonds can be cleaved through this crystal plane by applying external stress. The splitting along the (1014) plane can provide two identical surfaces and the same hydrophobicity, which is a favorable environment to cleave. In aqueous medium, the ionic bond between the calcium and carbonate ions will be weakened so that it can be split in the (1014) plane by the external chemical environmental stress.

Estroff et al.\(^13\) reported that inorganic calcite and biological calcite crystals grow in the {1014} direction and the {0112} plane. Others\(^14\) reported that the growth plane was the (1014) and (1018) plane. It is interesting that the growth plane is consistent with the cleavage plane. Some have reported that calcitic CaCO\(_3\) is easily cleaved in the {1011} plane in an aqueous solution to some extent, which corresponds to the (101) plane in a tetragonal system.\(^20\)\(^21\)\(^22\)

In our study, layer-by-layer cleavage was observed to occur through the {1011} and {1014} planes and the fracture on the lateral side was assigned to the {1012} plane as seen in schematic description in Figure 6d. To our knowledge, the division that occurred through the {101} plane seems to have been claimed based on empirical observations.\(^23\)\(^24\) The cleavage plane observation of the calcite crystal through XRD and HR-TEM analyses has not yet been performed. Our findings show that cleavage through the {1011} plane predominates in calcitic CaCO\(_3\).

3. CONCLUSIONS

Dissolution and cleavage planes were investigated using an experimental setup, which drove dissolution after calcitic CaCO\(_3\) formation, based on a reaction between calcium ions in the solution and CO\(_2\) from the atmosphere. Calcite crystals formed within 1 day, and then, dissolution began. No amorphous phase was observed, even after 12 days of aging.

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**Figure 3.** CaCO\(_3\) polymorphs with aging times characterized by 2D-XRD. (a) 10 h, (b) 1 day, (c) 5 days, and (d) 12 days.
The diffraction pattern and the lattice image were investigated with HR-TEM analyses and showed that cleavage mainly occurred in the \{10\overline{1}1\} plane. Cleavage through the \{10\overline{1}4\} plane was also observed, and fracture along the lateral side took place in the \{10\overline{1}2\} plane.

4. EXPERIMENTAL SECTION

4.1. Calcium Carbonate Formation and Dissolution.

This experiment was designed to observe the formation of calcitic CaCO$_3$ and its dissolution and cleavage due to ocean acidification in a laboratory. First, an aqueous 50 mL 10 mM CaCl$_2$ solution was prepared to obtain calcified CaCO$_3$ with magnetic stirring at 400 rpm. The formed CaCO$_3$ was aged in the solution and stirred for 12 days. As a basic buffer, 100 mM Tris (hydroxy methyl) amino methane (Tris) was added to increase the pH of the solution, which is necessary for the rapid formation of CaCO$_3$.

The solution was exposed to the atmosphere, and CaCO$_3$ was formed by the reaction of calcium ions in solution with carbonate ions, which are derived in the presence of CO$_2$ in the atmosphere. Each solution was freshly prepared with Milli-Q water prior to use. The pH values of the solutions were measured.

Figure 4. HR-TEM analyses of crystallites sampled after 5 days of aging, (a) fragmented crystallites, (b) SAED pattern, (c) the lattice spacing of the fragmented crystallites, (d) low-magnification image, (e) SAED pattern, (f) lattice spacing for the first sample in the zone axis [2\overline{1}1], (g) low-magnification image, (h) SAED pattern, and (i) lattice spacing of the second sample in the zone axis [3\overline{4}1].
with a HI2215 pH meter from Hanna Instrument Inc. The initial measured pH of the solution was 10.5. The formation and dissolution of CaCO₃ was observed by measuring the amount of calcium ions present in the solution using the EDTA titration method. The EDTA amounts titrated can be converted to the calcium ions present in the solution using a calibration curve, relating the titrated EDTA amounts (Supporting Information Figure S2a) and the concentration of calcium ions (Supporting Information Figure S2b). The calculated calcium ion content allows us to calculate the amount of undissolved CaCO₃. A comparison experiment to monitor dissolution without changing the solution pH was not conducted because it was

Figure 5. HR-TEM analyses for single crystallites sampled after 12 days of aging, (a) low-magnification image, (b) SAED pattern, (c) lattice spacing of the first sample in the zone axis [2̅11], (d) low-magnification image, (e) SAED pattern, and (f) lattice spacing of the second sample in the zone axis [030].

Figure 6. HR-TEM analysis sampled after 12 days of aging, (a) low-magnification image, (b) SAED pattern, (c) lattice spacing in the zone axis [2̅11], and (d) schematic diagram showing the cleavage plane and fracture surfaces on the lateral sides.
CaCO₃ was vacuum dried. Silicon wafer was cleaned with Piranha solution, and the collected 4.2. Sample Collection. The solution was decanted after the experimental period, formed CaCO₃ was collected on a silicon wafer cleaned with Piranha solution, and the collected CaCO₃ was vacuum dried.

4.3. Calcium Carbonate Characterization. Morphological changes in the collected CaCO₃ were observed by field emission scanning electron microscopy (SEM, Hitachi S-4800), field emission TEM (HR-TEM, JEOL JEM-2100F). Polymorphs of the formed and undissolved CaCO₃ were investigated with 2D-XRD (at the 4C2 beamline of the Pohang Accelerator Laboratory) and XRD (D/max 2500, Rigaku) with the θ/2θ scan mode and 0.154 nm Cu Kα radiation.

■ ASSOCIATED CONTENT

Morphological changes in the collected CaCO₃ were observed by field emission scanning electron microscopy (SEM, Hitachi S-4800), field emission TEM (HR-TEM, JEOL JEM-2100F). Polymorphs of the formed and undissolved CaCO₃ were investigated with 2D-XRD (at the 4C2 beamline of the Pohang Accelerator Laboratory) and XRD (D/max 2500, Rigaku) with the θ/2θ scan mode and 0.154 nm Cu Kα radiation.

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Notes
The authors declare no competing financial interest.

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