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DECOMPOSITION OF GROUP II CARBONATES: AN INVESTIGATION BY TRANSMISSION ELECTRON MICROSCOPY

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(Ph.D. thesis)

November 1981

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Abstract

An investigation of the decomposition reactions of MgCO₃, MgCa(CO₃)₂, CaCO₃ (calcite), and SrCO₃ by hot stage TEM was undertaken to avoid the problem of reaction of the product oxides with water vapor and/or carbon dioxide when they are exposed to air, to obtain estimates of the pore size and oxide particle size, and to determine the orientation relationship between the oxide product and parent carbonate.

There is no evidence for any preferential alignment of MgO with respect to MgCO₃ when magnesite decomposes. Definite conclusions about the orientation relationship could not be drawn between strontianite and its oxide product.

Micrographs taken during calcite decomposition showed that the lattice spacings decreased by ~6% independent of angular directions before the emergence of CaO diffraction-rings. Extra
reflection spots were also observed which suggest an ordered, periodic arrangement of atoms with twice the unit cell dimensions of calcite (100). For the fully decomposed areas, [110] of CaO was found to be preferentially oriented with [031] of CaCO₃.

Dolomite yielded as its initial decomposition products a series of metastable MgO-CaO solid solutions which quickly separated to stable MgO and CaO phases. There are definite preferred orientations for dolomite decomposition that are [010]dolomite // [001]oxides and (101)dolomite // (110)oxides.

Cross sections of oxide particles were estimated from the images to be in the order of 5 to 10 nm and pore sizes to be in the order of 2 to 3 nm. The dimensions of the product oxides varied with the parent carbonates in the order calcite > dolomite > magnesite. A possible reaction mechanism is suggested based on observations made during the decomposition process in the microscope.
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1. Introduction

Group II carbonates have been extensively studied by mineralogists, and they are important as industrial raw materials. The decomposition reactions of these carbonates,

\[ \Delta \text{MCO}_3(s) \rightarrow \text{MO}(s) + \text{CO}_2(g), \quad \text{M} = \text{Mg, Ca, Sr, Ba}, \]

yield alkaline earth metal oxides which are common useful materials, and the manufactured products that are made from these oxides affect many aspects of our daily life. The reaction itself is one of the most researched solid-state chemical reactions because of the importance and apparent simplicity of the transformation; a single-phase carbonate becomes another single-phase oxide by the removal of a gaseous product, \( \text{CO}_2 \).

Unlike congruent vaporization reactions, which yield only vapor-phase products, the reaction is complicated because of the formation of the solid oxide product. Depending upon the particular conditions of decomposition temperature, ambient pressure, particle size, powder bed depth, and compactness of samples, the decomposition rate varies and the solid oxide is produced with different properties.

It is the intention of our research group to understand the kinetics and thermodynamics of this class of reactions, and to characterize the properties of the solid oxide produced under well-defined experimental conditions. My research has been directed toward the explanation of the condensed-phase product formation from a
crystallographical point of view, and the interpretation of the reaction from a mechanistic point of view, for the purpose of gaining further understanding of the reaction.

Previous studies\(^1\text{-}^4\) have shown that when an alkaline earth metal carbonate is decomposed in vacuum, i.e., when the background pressure is below 10\(^{-4}\) torr, whether it was a piece of single crystal of \(-1\,\text{mm}^3\) volume or a powder of \(-10\,\mu\text{m}\) dimension, the solid oxide product shows little change in apparent particle shape from that of the starting material, and little sintering.

The molar volumes of the carbonates and oxides can be calculated from their densities and molecular weights. There is an average decrease of about 50\% in their relative molar volume (Table I), which implies that about 50\% of the oxide product is occupied by pores in order to preserve the same exterior dimension when carbonates decompose in vacuum. In other words, there are very high internal porosities for the products of vacuum decomposition, whether the starting material was a piece of single crystal or a powder.

The surface area can be determined by the BET\(^5\) method. In the BET apparatus, \(N_2\) is adsorbed on the surface of the sample from a mixture of \(\text{He}\) and \(N_2\) when the sample is cooled by liquid \(N_2\). The amount of \(N_2\) adsorbed at various partial pressures can be used to determine the surface area. If a certain oxide particle morphology is assumed when carbonate is decomposed in vacuum, the cross-sectional dimension of these oxide particles can be calculated from the measured surface area.
Assuming oxide particles have cubic shape with the dimension of \( x \), and the oxide has the molar volume \( MV \), there are \( MV/x^3 \) cubes per mole of oxide. Since the surface area per oxide cube is \( 6x^2 \), the measured surface area per mole \( SA \) is \( SA = 6x^2(MV/x^3) \). Therefore, 
\[ x = 6MV/SA, \] assuming the starting material has a negligible surface area.

Experimental data\(^4\) gave an estimate of \( x \) in the order of 10 nm for CaO from calcite decomposition in vacuum. With the same amount of oxide, the smaller the particle size the greater the surface area. For 1 mole of CaO, with a particle size of 10 \( \mu \)m the total surface area is 10 \( m^2 \), whereas with a particle size of 10 nm the total surface area rises significantly to 10000 \( m^2 \). Therefore, results of the BET measurements are consistent with the earlier prediction of a high internal surface area for the decomposed product, and oxide crystallite dimensions are in the order of 10 nm.

X-ray diffraction patterns\(^3,6\) obtained for fully decomposed carbonates showed broad peaks. In general, line broadening becomes apparent when the grain size is smaller than 0.1 \( \mu \)m. The fact that the oxide product gave broad peaks is again consistent with the earlier prediction of small crystallite size and high surface area.

In summary, the three techniques of x-ray diffraction, BET measurement, and scanning electron microscopy were the standard methods used in previous studies in our group to characterize the oxide product. The scanning electron microscope was used to ascertain the morphological change accompanying the transformation from carbonate to oxide; then the
surface area of the oxide product was measured with the BET method and x-ray diffraction patterns were recorded to determine the crystallinity.

However, some experimental difficulties persisted. The vacuum-decomposed oxide products were very unstable in the atmosphere; they reacted with CO$_2$ and/or H$_2$O very easily, and quickly formed carbonate and/or hydroxide. Every time the sample was handled outside the vacuum system, there was the possibility that the observation was made not of the true vacuum-decomposed product but of a reaction product. Furthermore, the SEM available to us could not resolve the oxide particles or the pores formed when carbonates were decomposed in vacuum.

In-situ decomposition studies of dolomite, calcite, magnesite, and strontianite in a transmission electron microscope were undertaken in the present study in order (a) to avoid the reaction problem (it is not necessary to ever remove the decomposed product from the vacuum system), (b) to make possible the direct observation of the pore formation and product oxide crystallites, and (c) to determine whether or not product crystallites were oriented relative to the initial carbonate single crystal by the comparison of their electron diffraction patterns. In addition, because the decomposition was done in the microscope the reaction could be followed continuously, which might give further information about the reaction in a step-by-step manner.
2. The Crystal Structure of Carbonates and Oxides

Alkaline earth metal carbonates have either calcite or aragonite structure. The general principles of the structural chemistry of these carbonates are well known. The coordination of anions about the cation is 6 in calcite-type solids, and 9 in aragonite-type solids; consequently, the calcite arrangement is preferred when the cation is small and the aragonite arrangement is favored when the cation is large. The transition takes place at a cation radius of about 0.98 Å. The radius of the Ca\(^{2+}\) ion in CaCO\(_3\) is close to this critical value, and calcium carbonate exists in both forms (Table II).

The carbonate ion is a well-defined planar entity in which the three oxygens are symmetrically arranged at the corners of an equilateral triangle formed about the C atom with a C-O distance of 1.30 ± 0.01 Å.

2-1. The Oxide Structure

The oxides of the alkaline earth metals except beryllium, i.e., MgO, CaO, SrO, and BaO all have the NaCl-type structure.

The arrangement of the ions in the cubic unit cell is shown in Fig. 1. The unit cell of NaCl contains 8 ions, located at the lattice points, as follows:

4 Na\(^{+}\) at \(\frac{1}{2} \frac{1}{2} \frac{1}{2}\), \(00\frac{1}{2}\), \(0\frac{1}{2}0\), and \(00\frac{1}{2}\)

4 Cl\(^{-}\) at \(000\), \(\frac{1}{2} \frac{1}{2}0\), \(\frac{1}{2}0\frac{1}{2}\), and \(0\frac{1}{2}\ \frac{1}{2}\)
The cell can be considered to have alternating layers of cations \( \text{Na}^+ \) and anions \( \text{Cl}^- \) positioned perpendicular to the [111] direction.

The Bravais lattice of \text{NaCl} is face-centered cubic, which is apparent for the chlorine ions (Fig. 1). The face-centering translations of \( 000, \frac{1}{2} \frac{1}{2} 0, \frac{1}{2} 0 \frac{1}{2} \), and \( 0 \frac{1}{2} \frac{1}{2} \) when applied to the sodium ion at \( \frac{1}{2} \frac{1}{2} \) will reproduce all the sodium ion positions.

The six neighbors of any ion in the \text{NaCl} structure are disposed about it at the corners of a regular octahedron (Fig. 2). The structure of these alkaline earth metal oxides can be regarded as formed by the cubic close packing of the large oxygen ions, with the octahedral interstitial positions all filled with cations.

2-2. The Calcite Structure.

The calcite lattice can be described in terms of rhombohedral symmetry. For the unit cell indicated (Fig. 3), the \( \text{Ca}^{2+} \) ions occupy the corners and centers of the faces, while the \( \text{CO}_3^{-2} \) ions lie at the center of the cell and at the midpoints of its edges.

The planes of the \( \text{CO}_3^{-2} \) groups are all perpendicular to the vertical triad axis of the cell; therefore, the structure can be considered to have alternating layers of calcium ions and carbonate ions positioned perpendicular to the [111] direction of the rhombohedral unit cell. Figure 4 shows the projection of lattice points along this direction on a two-dimensional plane. Each calcium ion is coordinated by six oxygen neighbors belonging to six different carbonate groups, as
shown in Fig. 5; and each of these oxygen neighbors is bound to one carbon atom and to two calcium ions, as shown in Fig. 6.

This rhombohedral lattice bears a resemblance to an NaCl-type face-centered cubic lattice. There is a one-to-one relationship for each lattice point occupied by a cation or an anion of the rhombohedron and the cube. However, due to the substitution of the disk-shaped $\text{CO}_3^{2-}$ ions for spherical anions, the cubic structure is distorted and causes the angles between each pair of the rhombohedral axes symmetrically to expand to $>90^\circ$.

Dolomite, which has the formula $\text{MgCa(CO}_3)_2$, has a structure that can be described in terms of the same rhombohedral arrangement.\textsuperscript{7,8} Instead of the same cation species occupying all corners and centers of the faces of the calcite rhombohedral cell, layers of $\text{Mg}^{2+}$ and $\text{Ca}^{2+}$ ions alternate along the trigonal axis, as shown in Fig. 7. The open circles represent the $\text{Mg}^{2+}$ ions and the solid circles represent the $\text{Ca}^{2+}$ ions of dolomite, or vice versa.

The lattice points of a rhombohedral unit cell can also be described with the symmetry elements characteristic of a hexagonal cell (Fig. 8). The rhombohedral cell has three equal axes $a_R$ equally inclined at an angle $\alpha$ to one another; the hexagonal cell has two equal coplanar axes $a_H$ at $120^\circ$ apart, and the third axis $c_H$ at right angles to them. The hexagonal cell for calcite has three times the volume of the rhombohedral cell.

Furthermore, the rhombohedral unit cell described earlier for calcite is not the smallest rhombohedral unit cell. Each cell of the
kind described in the section on the calcite structure has four lattice points occupied by Ca$^{2+}$ ions and four occupied by CO$_3^{2-}$ ions. Other commonly applied rhombohedral unit cells for describing the calcite structure have $z = 1$ or 2, where $z$ is the number of lattice points occupied by the same type of ions per unit cell. For each rhombohedral unit cell there is an equivalent hexagonal unit cell with three times the volume, which can be used to describe the crystal system as well. The lattice parameters for various hexagonal and rhombohedral unit cells of different $z$'s are listed in Tables III, IV, and V for magnesite, calcite, and dolomite. The positions of lattice points and the dimensions of the various rhombohedral unit cells of dolomite are shown in Figs. 9 and 10, which are projections of the crystal structure with different $z$ values.

The $z = 2$ cell is the only real unit cell that can repeat itself to construct the lattice, but because of the one-to-one relationship for the cation and anion positions between the rhombohedral unit cell of $z = 4$ of calcite and the fcc NaCl structure of the solid oxide product of decomposition, it is advantageous and convenient to use the rhombohedral $z = 4$ unit cell for calcite to derive the orientations of solid product to the carbonate, and to rationalize the reaction path during the carbonate decomposition.

2-3. The Aragonite Structure

The aragonite lattice can be described in terms of orthorhombic symmetry. The projection on a plane perpendicular to the $z$-axis is shown in Fig. 11. The Ca$^{2+}$ ions are arranged in an approximation of
hexagonal close-packing, and the Ca\textsuperscript{2+} layers are perpendicular to the pseudo-hexagonal axis, which is the c-axis of the orthorhombic cell. Each Ca\textsuperscript{2+} ion is surrounded by nine oxygen neighbors, each of which in turn is bound to three Ca\textsuperscript{2+} ions—one in the upper layer and two in the lower layer—and placed at a height of one-third of the unit cell dimension above the lower layer of Ca\textsuperscript{2+} ions. All CO\textsubscript{3}\textsuperscript{2-} groups are normal to the c-axis, but they are arranged alternately up and down along a row parallel to (110) of the orthorhombic cell. The structure may be regarded as a distorted NiAs structure, with arsenic replaced by calcium, and nickel by carbonate groups in the same way as the calcite structure is related to that of sodium chloride. Aragonite is pseudo-hexagonal. The a- and b-axes of aragonite are nearly equal in length with the a-axis of calcite, and the c-axis is nearly one-third the length of that for calcite.
3. Experimental Procedure

3-1. Sample Preparation

The standard technique for making samples transparent to electrons is to thin a section ground to ~30 µm-thick with ion beams. The apparatus has been described in the literature. It requires an evacuated chamber in which one or more beams of positive ions of an inert gas are directed at the specimen. Atoms or molecules are ejected from the specimen at the point of ion impingement.

Ion bombardment can result in the removal of target material, in structural damage, in ion implantation, in backscattering of ions and neutral atoms, and in the emission of charged particles and electromagnetic radiation. In thinning the sample for study by an electron microscope, the removal of target material is important but structural damage is undesirable. Ion-beam thinning of ceramics has been shown to yield foils which are representative of essentially undamaged bulk material.

Low pressures in the ion bombardment chamber—less than 10⁻⁴ torr in general—are important in preventing gas adsorption on the sample surface, which inhibits thinning. The ion sources consist of a pair of electrodes connected to a high-voltage source. Argon is usually used as the bombarding species because it is the heaviest inert atom and is available at a reasonable cost. Positive argon ions are extracted through a hole in the cathode plate.

The optimum conditions for thinning carbonate minerals with argon ions are an accelerating potential of 8–10 kV, a beam current of
0.4–0.6 mA, and an angle of incidence of the beam on the specimen of 12–18°. Higher voltages and angles were found to decrease the electron transparent area and to make observation more difficult. Higher currents caused unnecessary heating of the specimen without increasing the rate of thinning.

The rate of thinning depends on the relative masses of the ion and specimen atoms, the ion energy, the crystal structure of the specimen, and the angle of incidence of the beam on the specimen. Because of the slow rate of thinning it is essential to begin with as thin a piece of material as possible. For a 30 μm-thick sample, it usually took 15 to 24 hrs to penetrate the specimen.

After the sample was perforated, the accelerating voltage and ion current were reduced to 5 kV and 0.2 mA, respectively. The angle of inclination was reduced to 12°. Bombardment under these conditions removed some of the surface damage on the specimen caused by ion-milling at higher voltages.

The sample was coated with a carbon layer to a thickness of 8 to 12 nm to prevent charging. The coated thin foil was sandwiched between two Mo grids in the specimen holder for observation. The grid was necessary for support because of the brittle nature of carbonate materials. Epoxy or other adhesives were not applied to hold the thinned samples together, because adhesives would become volatile during heating and might redeposit on the specimen when it was cooled. The Mo grid was used instead of Cu, which is more commonly used, because Mo has a higher melting point.
The specimen used was quite homogeneous. At a fixed rotation angle, it gave essentially the same single-crystal diffraction pattern everywhere. Minor differences might arise either from a change in $s$, the deviation from the exact Bragg reflection position, or from buckling of the specimen.

3-2. Electron Microscopy

The specimens were examined in a JEOL JEM-100C transmission electron microscope. It has a maximum accelerating voltage of 100 kV and a highest standard magnification of 200kX. A regular specimen holder can hold two specimens simultaneously, and has two degrees of freedom so that it can be both rotated and tilted. For in-situ decomposition studies, it was necessary to use a different specimen holder, which was connected with a heating-control unit that had its own power-supply system.

The heating stage is a carefully constructed specimen heating holder with a Pt heating filament and a Pt-Pt13% Rh thermocouple to monitor the temperature. Insulation is very important between the holder itself, the filament, and the thermocouple to prevent short circuits because these different parts all occupy a very small volume around the specimen. The stage can be rotated as much as ±60°, but cannot be tilted. Sometimes the quality of the picture—either the image or the selected area diffraction pattern—suffers because of the lack of the other degree of freedom.

The heating-control unit functions to control the voltage for the heater and to measure temperatures. The operating temperature range is
from room temperature to about 1200°C. However, the lifetime of the heating stage decreases dramatically if the temperature is raised above 800°C for any length of time.

Chemical composition of any area under investigation was double-checked with an attachment to the microscope that detects and records the x-ray spectrum produced when a high-voltage electron beam hits the specimen surface and is suddenly decelerated. Different elements can be identified when the energies (or wavelengths) are compared with the standard x-ray characteristic spectrum.

After an orientation was found that gave a densely populated carbonate diffraction pattern, which implied a low-index direction, the temperature was slowly raised. Bright field and dark field images and the selected area diffraction patterns were taken to record any slight differences throughout the decomposition process. Special attention was given to any change that might arise from an intermediate reaction product or products.
4. Dolomite

4-1. Introduction

The thermal decomposition of dolomite has been studied by many workers. The reaction path depends on the background CO$_2$ pressure. When dolomite is decomposed in air, DTA curves show an endothermic peak at 800°C, which is due to the breakdown of the MgCO$_3$ component, and another endothermic peak at 940°C, which is due to the dissociation of the CaCO$_3$ component. Therefore, the first reaction step is

$$\text{MgCa(CO}_3\text{)}_2(s) \rightarrow \text{CaCO}_3(s) + \text{MgO(s)} + \text{CO}_2(g).$$

The second step at a higher temperature is

$$\text{CaCO}_3(s) \rightarrow \text{CaO(s)} + \text{CO}_2(g).$$

However, if the reaction is carried out in vacuum, it is reported to occur in one step to yield the separated oxides as the solid products.

$$\frac{1}{2} \text{MgCa(CO}_3\text{)}_2(s) \rightarrow \frac{1}{2} \text{CaO(s)} + \frac{1}{2} \text{MgO(s)} + \text{CO}_2(g)$$

The equilibrium CO$_2$ pressure measurements for the decomposition reaction either in vacuum or in air are well-documented. No orientation relationship between the product oxides and the parent dolomite for the one-step decomposition reaction have been
reported. Vague and conflicting interpretations were argued by different people for the two-step reaction.

Wilsdorf and Haul\textsuperscript{18} showed that a dolomite crystal transformed into calcite crystallites oriented with respect to the original lattice with an irregular distribution of MgO. However, Dasgupta\textsuperscript{26} observed partially oriented MgO and CaCO\textsubscript{3}. He claimed that the degree of preferred orientation in both cases was very small, because both phases gave almost complete powder arcs. But these arcs showed distinct intensity concentrations. The CaCO\textsubscript{3} crystal retained a parallel orientational relationship with the original crystal, whereas one of the diad axes of MgO was preferentially aligned to one of the diad axes of the original crystal. On further heating, dolomite crystals transformed into oriented aggregates of MgO, with randomly oriented polycrystalline aggregates of CaO and Ca(OH)\textsubscript{2}.

The purpose of this investigation was to study dolomite decomposition in well-controlled vacuum conditions to confirm or disprove the product phase or phases present, and to find any orientation relationship that might exist between the product(s) and dolomite. Furthermore, it is reasonable to believe that the observations can provide bases for suggesting a mechanism that will explain the product(s) formation and the decomposition phenomenon.

4-2. Experimental Results

A clean single-crystal diffraction pattern was chosen, preferably aligned along a low index plane. The pattern was recorded and identified
to assure the purity and perfectness of the sample. An x-ray emission spectrum which is characteristic of the atomic species was taken to double-check the chemical composition of the area of interest.

The power of the hot stage was turned on to raise the temperature gradually. In order to avoid violent reactions that might cause the sample to shatter, rapid increases of temperature were avoided. The rate of temperature rise was held to \(< 4^\circ C\) per minute.

The image moved due to thermal expansion when temperature was raised. Enough time was given until the image stabilized, and the image as well as the diffraction pattern were recorded. If no change could be observed, the sample was heated again to a higher temperature.

As the temperature rose, the diffraction pattern remained that of a dolomite single crystal until it started to show rings just above 600\(^\circ\)C. Once the ring pattern appeared, the single crystal spots faded away in a matter of seconds. The temperature at which this occurred could not be determined accurately because a dolomite single crystal is a poor thermal conductor. Sections of the specimen next to the heating filament might be at a much higher temperature than sections that were not. Temperature distribution across the specimen might be quite inhomogeneous.

When the ring pattern was observed, either the specimen was kept at the elevated temperature or the power for the hot stage was quickly shut off to let the sample cool to room temperature.

The purpose of the constant temperature experiments was twofold: First, to carry the decomposition to completion; second, to find out any
morphological change of the decomposed product when it was kept at an elevated temperature in vacuum for an extended period of time. The "quenching" experiments were undertaken in an effort to preserve any intermediate stage that might exist.

The decomposition reaction was followed for several different orientations of dolomite that had densely populated diffraction patterns. One particular diffraction pattern was chosen for detailed analysis for reasons that will become apparent later on. The spot pattern was indexed with one among several crystallographically equivalent set of indices (Fig. 12). Subscript R represents a rhombohedral unit cell with two atoms of the same species occupying the lattice points of a unit cell, and subscript H represents a hexagonal unit cell with three atoms of the same species occupying the lattice points of a unit cell.

The zone axis of this orientation is \([010]_R\), which in fact can be any one of the three crystallographically symmetric directions for the rhombohedral unit cell, i.e., the x-axis which is the \([100]\) direction, the y-axis which is the \([010]\) direction, or the z-axis which is the \([001]\) direction. The directional index of \([010]_R\) can be converted to the planar index of \((1\ 4.58\ 1)_R\) by a simple geometric transformation. The non-integral number comes from the fact that the axes of a unit cell of a rhombohedron are not 90° apart.

Decomposition was indicated by rings appearing in the diffraction pattern. These rings correspond to the oxide product expected from
oolomite decomposition. They are indexed as follows, from the center: CaO(111), CaO(200), MgO(200), CaO(220), MgO(220), etc. (Fig. 13).

The three largest d-spacings each of MgO and CaO powder patterns from the ASTM standards are listed in Table VI. MgO (111) could not be identified on the diffraction pattern because (a) it is a weak reflection (its expected intensity is only 10% that of the most strongly reflected (200) plane), and (b) the d-spacing of MgO(111) is 2.431 Å compared with 2.405 Å for CaO(200), which happens to be the strongest reflection of CaO.

Although the rings are continuous, they are not of uniform intensity. This non-uniformity provides conclusive evidence for the preferred orientation and the existence of a fiber axis. The slight spottiness of the ring may be an indication of large crystallite size, but it is also related to the number of crystals which contribute to the diffraction event, which in turn depends upon the cross-sectional area of the incident beam and the specimen thickness.

The intensity distribution around the circumference of the CaO(111) diffraction ring is quite homogeneous, but there are four areas around the CaO(200) and MgO(200) rings that are particularly bright. The angles between the centers of any two adjacent high-intensity arcs proved to be 90° apart. This means that the preferred orientation for both MgO and CaO has the same four-fold symmetry with respect to the fiber axis. The only direction of a cubic structure that both MgO and CaO have that possesses a four-fold symmetry is the <100> orientation. Therefore, the fiber axis reflected by the high-intensity portions around the (200) rings of both oxides must be of the <100> type. Inasmuch as the
reflections on the diffraction pattern are short arcs rather than sharp spots, there must be some scattering about this fiber axis.

The analysis above shows the zone axis of the oxide product to be of the \( <100> \) type when \([010]_R\) was the zone axis for the single-crystal diffraction pattern of dolomite—the parent compound. Therefore, the \([001]\) directions of the oxides are parallel to the \([010]_R\) direction of dolomite. This means that during the transformation from dolomite to oxides, \([001]\) directions of the oxide products are preferentially oriented along the \([010]_R\) direction of the parent dolomite.

When the (220) rings of both oxides are examined, we notice two high-intensity portions around the circumferences that are parallel to the reflection \((202)_R\) of the dolomite single-crystal pattern. This means that the (110) planes of the oxides are preferentially oriented parallel to the \((101)_R\) plane of dolomite.

Other angles between low index planes of dolomite and the oxides can be calculated if the preferred orientation relations between them are assumed to be \([010]_{\text{dolomite}} // [001]_{\text{oxides}}\) and \((10\bar{1})_{\text{dolomite}} // (110)_{\text{oxides}}\). They are:

\[
\begin{align*}
(10\bar{1})_{\text{dolomite}} & // (110)_{\text{oxides}} \\
(1\bar{1}1)_{\text{dolomite}} & \wedge (\bar{1}11)_{\text{oxides}} = 1.59^\circ \\
(111)_{\text{dolomite}} & \wedge (11\bar{1})_{\text{oxides}} = 9.59^\circ \\
(\bar{1}1\bar{1})_{\text{dolomite}} & \wedge (\bar{1}11)_{\text{oxides}} = (1\bar{1}1)_{\text{dolomite}} \wedge (111)_{\text{oxides}} = 14.37^\circ \\
(001)_{\text{dolomite}} & \wedge (01\bar{1})_{\text{oxides}} = (1\bar{1}0)_{\text{dolomite}} \wedge (100)_{\text{oxides}} = 8.12^\circ
\end{align*}
\]

If these calculated values are compared with the angles measured directly from the diffraction pattern as shown in Fig. 14, we find them
to be remarkably close. Therefore, they are consistent with the preferred orientation relations derived earlier.

A stereographic projection gives all the angles between either directions or planes of a crystal system. When one stereogram of a crystal system is superimposed on another, the angular relations between the two crystal systems can be easily checked. In Fig. 15, all the information above is condensed to two superimposed planar stereograms which clearly present the texture developed during the transformation from dolomite to oxides.

The rings that appeared on the diffraction pattern remained at the same positions from the time when oxide first formed until the dolomite was fully decomposed. Even when the decomposed sample was kept at the decomposition temperature for up to 10 hours, the diffraction pattern showed the same sharp and discrete rings with no observable changes in position or intensity. The image showed the same size crystallites with no differences in their dimensions.

When the thin sections of the sample (areas that are transparent for the electron beam) were fully decomposed, the thick sections remained carbonate and gave the same single-crystal diffraction pattern as the original sample.

The "quenched" samples showed very interesting features that were also obtained occasionally from samples that were heated continuously after decomposition began. "Quenched" samples regularly showed continuous intensity distribution between CaO and MgO diffraction rings...
of the same indices at some regions of the sample (Fig. 16), although other regions at the same time might display discrete ring patterns.

This observation suggests that all solid solutions of compositions between a 50 mole% MgO - 50 mole% CaO solid solution and separated, nearly pure MgO and CaO phases must be present during the decomposition. A 50% MgO - 50% CaO solid solution (which might be expected to form the initial product from dolomite decomposition) would give, not separate rings for MgO and CaO at each allowed hkl value, but a single ring midway between those of the pure MgO and CaO phases.

The phase diagram shows only very limited solid solubility of MgO in CaO, or CaO in MgO, even at temperatures above 1600°C (Fig. 17). If the curves are extrapolated to the decomposition temperature reached by the hot stage in the microscope, a temperature of ~600°C, the expected solubility of MgO in CaO is well below 1%, and of CaO in MgO is also well below 1%. Therefore, the CaO-MgO solid solutions indicated by the electron diffraction data are metastable intermediate states that were caught by cooling the sample from the decomposition temperature to room temperature.

When other dolomite single-crystal samples were decomposed, the oxide diffraction pattern gave similar inhomogeneous intensity distributions around the circumferences of the rings if we chose the orientation that gave the same original spot pattern (Fig. 18). If orientations of dolomite other than this one were chosen (Figs. 19 and 20), the angles measured between the spot on the single-crystal diffraction pattern and the high-intensity portions of the oxide rings
were consistent with the earlier prediction of the preferred orientation relations. This reproducibility and the consistency of experimental results give further support for the analysis.

Just as the spot pattern indicated, the starting material gave a clean uniform image without any apparent defects. No significant changes occurred during heating. However, when the rings started to appear and the spots to fade on the diffraction pattern, the thin sections of the one whole piece of single crystal fragmented at a relatively high speed to form a porous structure (Fig. 21).

Since the image is a three-dimensional structure projected on a plane, overlapping of crystallites tends to make the particles appear bigger than their actual size. Therefore, the oxide crystallite size was determined preferably by averaging values measured close to the perforated areas. This region probably is the thinnest section of the sample, and the effect of overlapping particle images is minimized.

It was estimated, from the image taken of the fully decomposed part, that the oxide particle size has an average dimension of ~10 nm. This result is consistent with the prediction of oxide crystallite size in earlier studies.6

We can also measure the change of external sample dimension by comparing the images taken before and after decomposition. Distances between places of identifiable characteristics—for example, the point around the periphery of a hole where the curvature changes—decreased no more than 10%.
4-3. Discussion

The dolomite composition reaction produces a definite preferred crystallographical orientation relationship between the product oxides and the dolomite, namely:

\[
[010]_{\text{dolomite}} // [001]_{\text{oxides}}, \text{ and} \\
(101)_{\text{dolomite}} // (110)_{\text{oxides}},
\]

which indicates that it is a topotactic transformation.

Topotactic reactions have been extensively studied by both x-ray and electron diffraction methods in the past.\textsuperscript{30-37} A lot more work has been published on hydroxide decomposition reactions\textsuperscript{38-53} than on carbonate decomposition reactions,\textsuperscript{3,26,54-67} possibly because hydroxides usually decompose at lower temperatures than carbonates. Two types of dehydration mechanisms have been proposed in the literature.

In the homogeneous mechanism, the water molecules are lost more or less uniformly from all regions of the crystal. The inhomogeneous mechanism assumes that protons and metal ions migrate in opposite directions and the structure develops donor and acceptor regions. The acceptor regions eventually become the oxide crystallites by gaining metal cations, and the donor regions where protons combine with hydroxyl ions to form water molecules become pores.

It was widely suggested in the literature that because of the structural similarities between carbonates and hydroxides, and because of the analogy between the carbonate and hydroxide decomposition reactions,
similar mechanisms can be expected for the carbonate decomposition reaction. But the ion analogous to H$^+$ for carbonates would be CO$_2^+$. Neither this nor any other cation derived from CO$_3^{2-}$ ions would be stable enough to be present at significant concentrations at \(-500^\circ\text{C}\) to \(-700^\circ\text{C}\) in a carbonate. Therefore, the inhomogeneous mechanism is implausible for carbonate decomposition.

If we apply the homogeneous mechanism to dolomite decomposition, the loss of CO$_2$ molecules is uniform from all the CO$_3^{2-}$ layers throughout the crystal (Fig. 22). There will be no rearrangement between the cation and anion layers, or among the cation layers themselves. Therefore, the alternating Mg$^{2+}$ and Ca$^{2+}$ ion layers in the dolomite structure is preserved during the transformation to oxides. This will result in two crystallographical features: One is that the oxide product will be a solid solution of MgO and CaO with essentially the same cation ratio as the dolomite composition; the other is that the c-direction of dolomite will mainly become the normals to the (111) planes in oxides. Namely, the [111] direction of dolomite will transform preferably to the [111] direction of the 50\% MgO - 50\% CaO solid solution. Instead, two preferred orientations, both of which are different from expectations of the homogeneous mechanism, are found. And superlattice lines that would be expected from an ordered solution of alternating Mg$^{2+}$ O$^{2-}$ Ca$^{2+}$ O$^{2-}$ Mg$^{2+}$... layers are never observed. Instead, diffraction arcs characteristic of NaCl-type solutions of MgO and CaO are found as the earliest identifiable solid decomposition product. Some mechanism other
than the hypothetical homogeneous or inhomogeneous mechanism must govern
dolomite decompositions.

Solid-state transformations can be divided into three
categories. The interpretation of their mechanisms are generally agreed
upon. It can occur by nucleation and growth, by a spinodal separation
into two phases, or by a martensitic transformation.

Spinodal decomposition refers to a continuous type of phase
transformation. Decomposition occurs by the development of periodic
fluctuations in composition that are small in amplitude and large in
spatial extent. It offers a means of establishing small regions having
two different compositions, while no interface in the usual sense exists
between adjoining regions of high and low concentration. For the
nucleation and growth process, transformation begins from identifiable
centers in or on the original phase. The new phase grows at the expense
of the old by the relatively slow migration of the interphase boundary,
and growth results from atom-by-atom transfers across this boundary. At
an intermediate stage, the assembly can be divided into microscopically
distinct regions, of which some have transformed and others have not.
The atoms move independently and at a rate that varies markedly with
temperature. A martensitic transformation is considered to be a
first-order phase transition that proceeds by the cooperative movements
of many atoms instead of the independent movements of individual atoms.
The coherent interphase boundary of the growing phase possesses a very
high mobility and serves as a source of internal stresses. The tendency
toward stress relaxation leads to the formation of the new phase, and the
two phases are related by definite lattice orientation relationships. Discrete regions of the solid transform suddenly with a very high velocity that is almost independent of temperature.

In dolomite, the $\text{Mg}^{2+}$ and $\text{Ca}^{2+}$ ions are present in alternate layers. It is evident, therefore, that at some stage of the decomposition a diffusional step must separate these ions. We can begin by considering the very limited data on diffusion rate in dolomite and the two product oxide phases. If possible, we would like to determine whether the two product oxide phases are formed from dolomite by diffusion alone or by a martensitic-type cooperative process followed by diffusion.

In the low-temperature region, impurities of the crystal usually fix the vacancy concentration and, therefore, extrinsic diffusion dominates. When the temperature is raised, the intrinsic defect concentration increases exponentially and eventually becomes the dominant diffusion process.

It is extremely difficult to estimate the contribution of intrinsic and extrinsic defects to the segregation of $\text{Mg}^{2+}$ and $\text{Ca}^{2+}$ ions during the transformation from dolomite to oxides for the following reasons:

1. In many cases, impurity levels of parts per million in the ionic crystals are sufficient to control the vacancy contribution. The sample used in these dolomite studies is a natural mineral that contains impurities at the level of parts per million (Table VII). Therefore, the concentration of extrinsic vacancies
may well be higher than that of intrinsic vacancies at the temperature of decomposition.

2. There are no reliable data on the diffusion coefficient of the cations in single-crystal dolomite. For Mg$^{2+}$ and/or Ca$^{2+}$ diffusion in MgO and/or CaO, measurements are for a much higher temperature range than investigated in our work. Extrapolation of the diffusion data cannot be assumed to give a reliable estimation, because data measured at high temperatures may reflect intrinsic defects only, and extrinsic defects may provide the dominant diffusion path at the decomposition temperature.

3. The system is very complicated because formation of the solid oxide products is accompanied by the creation of pores. The cations diffuse not in a single crystal of dolomite or oxide but in a constantly changing environment that is different before, during, and after the decomposition reaction.

We will focus our attention on the cooperative transport phenomenon to examine its importance for the segregation of Mg$^{2+}$ and Ca$^{2+}$ ions. It is commonly observed that for a martensitic reaction one phase transforms to another by a shear mechanism. The shear can occur by slip or twinning. The slip direction is usually the most densely populated direction, which is also the direction for minimum distortion. For the two perpendicular planes—(101) and (101)—of dolomite with a rhombohedral $z = 2$ unit cell (Fig. 23), in order for the segregation to take place with minimum distortion, these cations must migrate along either the [101] or [121] or [121] direction of the cell. However, none
of these directions was observed to be preferentially aligned during the
dolomite decomposition. The mechanism of twinning cannot be verified
either. Therefore, the in-situ TEM experiment gave no evidence that the
decomposition reaction of dolomite follows a martensitic-type
transformation.

The general characteristics of both a nucleation and growth
reaction and a martensitic reaction are summarized, and compared with our
experimental observations for dolomite decomposition as follows:

1. The rapid transformation of regions of the order of 1 \( \mu m^2 \)
to a product oxide phase or phases is more consistent with a martensitic
reaction than with a diffusional process. Martensitic reactions proceed
with the velocity of sound once initiated; diffusional processes increase
in rates exponentially with temperature. For dolomite decomposition, a
fraction of the carbonate phase transforms very rapidly at a nearly
constant temperature, after which there is no further change. For a
diffusional process, it would be expected that conditions could be
established under which the diffraction rings of the product phase grow
more slowly in intensity.

2. In a martensitic reaction, there is always a precise relation
between the orientation of the original structure and that of the new
phase. The dolomite decomposition reaction does have a definite
orientation relation between the carbonate phase and the oxide phase.
But a phase that nucleates and grows epitaxially could show similar
preferred orientation relationships.
Experimental evidence is therefore consistent with a martensitic transformation of dolomite to a mixed oxide phase after partial loss of CO₂ from small volume elements, but the possibility that oxide forms by nucleation and epitaxial growth cannot be ruled out. Spinodal conversion appears inconsistent with the linear advancing interface that characterizes carbonate decompositions, and will not be considered here.

4-4. Suggested Mechanism for Dolomite Decomposition

When the temperature of the sample is raised, the carbonate becomes unstable and evolves CO₂ molecules. It is reasonable to suggest that those carbonate units that are at the surface lose their CO₂ molecules before the ones in the bulk lose theirs. Oxide nuclei and voids form at the surface.

The voids provide channels by which the CO₂ molecules from those carbonate units around the voids can leave the system. Therefore, those carbonate units that are fronted by voids lose their CO₂ molecules much faster than the bulk. Every time a CO₂ molecule escapes from the system, a carbonate unit transforms to become the oxide with the formation of void, and new surfaces are created when the product phase forms.

Oxide nuclei form at the original gas-solid interface and the newly created surface around the voids and channels. The oxide particles are very unstable because of their high surface energy.

As the reaction proceeds, they grow in size because of the lowering of surface area to volume ratio. However, MgO and CaO have a
very limited solubility range and must exist as separate phases to be thermodynamically stable. Entities of MgO and CaO can be created as a consequence of surface diffusion and the lowering of energy by lattice construction.

At this stage, portions of the dolomite have become a defect single crystal. The three-dimensional framework is preserved without rupture, but oxides and voids now exist in the structure.

Continued heating of the sample produces more discontinuities in the single-crystal matrix until the accumulated stress, arising from both the presence of voids and the difference in chemical composition of the product phase, causes the carbonate structure to fragment. Sections transform at a high speed to become small oxide crystallites.

This suggested mechanism takes into consideration two important factors: (a) how CO$_2$ molecules escape from the single crystal matrix, and (b) how Mg$^{2+}$ and Ca$^{2+}$ ions segregate to form separate oxide phases. The experimental evidence will be compared to examine the validity of this mechanism.

Hot stage TEM experiments showed that when the temperature was gradually raised the diffraction pattern remained that of the original dolomite single crystal, which indicated little or no decomposition. However, because decomposition is driven by the free energy gradient between the CO$_2$ activity of the solid and the negligible CO$_2$ activity of the vapor phase, decomposition must occur as the temperature rises.

CO$_2$ molecules must leave the system either through vaporization from the surface or by diffusion from the solid carbonate. When each
CO₂ molecule is expelled from the solid, an oxide forms which occupies only about 50% of the original volume and leaves 50% void because the molecular dimension of the oxide is approximately half that of the carbonate. The voids and channels that are hypothesized are not directly shown in the micrographs, but their existence can give rise to the contrast observed experimentally in the bright and dark field images.

Mg²⁺ and Ca²⁺ ions are in a thermodynamically stable and orderly arrangement in dolomite; therefore, any movement of these cations cannot precede the escape of CO₂ molecules. This mechanism suggests that Mg²⁺ and Ca²⁺ ions remain at their original lattice sites until they are exposed to the surface. Ions of the oxide nuclei formed at the early stage are highly mobile at the oxide particle surfaces even though the bulk oxides are thermodynamically stable and bulk diffusion is slow. Surface diffusion is a much faster process than bulk diffusion in general; therefore, segregation of the cations occurs on the surface rather than in the bulk.

The oxide phase will not give any observable diffraction pattern if the amount of oxide formed was below ~10% of the dolomite phase, or if the oxide phase was distributed in the dolomite matrix in quantities too small to cause a diffraction event.

If the temperature is dropped because the diffusion rate is exponentially dependent upon temperature, the mobility of MgO and CaO is greatly inhibited. This is reflected in the fact that MgO and CaO rings of the same indices show continuous intensity distribution between them, which indicates that Mg²⁺ and Ca²⁺ ions are only partially unmixed.
If the temperature is kept high, oxide phases and interconnecting channels continue to form by the removal of CO$_2$ molecules until the defected sections of the carbonate single crystal can no longer hold together. This final stage of the decomposition could result in the simultaneous expulsion of most of the CO$_2$ that remains in the defected solid between voids and channels. This is reflected experimentally on the short time scale for the completion of the transformation. The fact that the oxide crystallites are fairly uniform in size indicates that the reaction is not diffusion rate limited.

Unlike the mechanisms for decomposition suggested by other researchers, this mechanism proposes that both the rupture of the carbonate framework and the reconstitution of the oxide crystallites must take place in order to accomplish the transformation from dolomite to oxides as separate phases. Because a simple diffusion-controlled mechanism—which involves a long-range diffusion through the parent compound to generate the product phase, or a reaction rate controlled mechanism that assumes the simultaneous displacement of atoms along certain planes causing tilting and collapsing of the carbonate structure to oxide fragments—cannot explain the reaction kinetics satisfactorily, this suggested mechanism is believed to be a more plausible one than other mechanisms already published in the literature.
5. Magnesite

5-1. Experimental Results

The starting material—an MgCO$_3$ single crystal prepared from a mineral specimen—showed no special features other than some extinction contours on the images of the bright and dark field. An orientation of a low-indexed plane was chosen to make possible the identification of the zone axis of the parent compound and any preferred orientation relationship between the oxide and carbonate. An x-ray emission spectrum was taken to confirm its composition.

The diffraction pattern remained the original single-crystal spot pattern as temperature was gradually raised. Decomposition was revealed when the selected area diffraction pattern started to show ring patterns (Fig. 24). These rings correspond to the same relative intensities and $c$-spacings as listed in the ASTM file for MgO. The rings usually looked quite homogeneous, with essentially continuous and constant intensity distributions around the circumferences. The bright field images of the decomposed area showed crystallites of ~5 nm cross sections (Fig. 25). This measurement is subject to errors arising from defocus and image transfer coefficients.

Close inspection of the diffraction patterns obtained at other orientations (Figs. 26 and 27) of a fully decomposed section showed rings with some inhomogeneity of intensity distribution around their circumferences. The high-intensity portions are too diffuse and asymmetric to be identified. Therefore, there might be some weak
preferred orientations for the MgO crystallites, but they are not as clearly pronounced as they are for dolomite or for calcite.

When the sample was kept at an elevated temperature for up to 8 hours, there was no measurable change in diffraction pattern or image. These results indicate that sintering and grain growth rates are negligible. The thin sections of the sample contained only MgO, but those thicker sections of the sample that were penetrable by electrons gave the same MgCO₃ single crystal spot pattern as the original carbonate.

Distances between characteristic features of the thin sections decreased by no more than 6 percent as a consequence of decomposition (Fig. 28). The vacuum-decomposed MgO showed less reactivity toward H₂O and CO₂ in the atmosphere than the products of dolomite, calcite, or strontianite decomposition.

5-2. Discussion

What happens to the images and diffraction patterns during the MgCO₃ decomposition process was very much like what happens during dolomite decomposition. Because the structures of MgCO₃ and dolomite are similar, it is reasonable to believe that MgCO₃ decomposes by a mechanism similar to that suggested for dolomite.

All vacuum-decomposed oxides have tiny crystallites, but MgO crystallites (~5 nm cross sections) are the smallest. Oxide crystallite dimensions from vacuum decomposed carbonates vary in the order calcite > dolomite > magnesite. The particle sizes of the oxides vary in the same
order as the decomposition pressures of calcite, dolomite, and magnesite. Powell and Searcy\textsuperscript{71} have shown that the surface area of CaO from calcite single crystals increases with decreasing temperature of decomposition. Perhaps it is the low temperature of decomposition of magnesite that results in its small particle size.
6. Calcite

6-1. Introduction

Towe\textsuperscript{67} stated that the most prominent of the arcuate diffraction maxima from the CaO phase were the (111), (200), and (220) reflections normal to the (01\bar{1}2) of calcite. Since the zone axis of the CaCO\textsubscript{3} single crystal spot pattern was not mentioned in his article, the preferred orientation relation accompanying the transformation from calcite single crystal to oxide cannot be derived. But it is certain that the preferred orientation relations derived earlier for the dolomite decomposition reaction is not consistent with his observation, because a \(\{1\bar{4}0.85\bar{1}\}R, \bar{z}=4 = [010]R, \bar{z}=4\) planar stereogram of CaCO\textsubscript{3} superimposed on a (001) stereogram of oxide does not satisfy all of the 90° angles between \((1\bar{1}1)R, \bar{z}=4 = (0\bar{1}1\bar{2})\) for calcite and any type of the (111), (200), and (220) reflections.

Towe also stated that other regions of decomposition showed other preferred orientations, and that in some patterns more uniform rings were observed—suggesting a more random array of CaO crystallites. It was not clear whether Towe started each decomposition with the same single-crystal spot pattern. If he did, his experimental evidence would indicate that several topotactic transformations are possible, and this circumstance might account for some of the disagreement on product-reactant orientations for calcite decomposition in the literature. However, had Towe begun with different orientations, the preferred orientation relationship could probably be derived from his data.
Singh Dev\textsuperscript{63} determined that the orientation relation for the
topotactic transformation from calcite to oxide was \((10\bar{1}4) \equiv (100)_{R,z=4}\)
of calcite // (110) of CaO. This is about a 40° rotation on the
stereogram of calcite [010] superimposed on (001) of oxide from that of
colomite. However, he did his experiment in air, not in vacuum, and the
reaction mechanism may be a function of the background pressure of
CO\textsubscript{2}. The decomposed product was cooled to room temperature before
x-ray diffraction measurements were made.

Floquet and Niepce,\textsuperscript{65,66} in their effort to resolve the
disagreement in orientation relationship for the transformation from
calcite to oxide among published articles, studied the decomposition of
CaCO\textsubscript{3} and argued that CaCO\textsubscript{3} single crystals which have the same
structure as calcite would follow the same reaction process. They
determined that [0001] \equiv (111)_{R,z=4} of CaCO\textsubscript{3} becomes the [140] axis
of CaO. But the orientation relations derived by them for CaCO\textsubscript{3}
decomposition cannot necessarily be applied to CaCO\textsubscript{3}.

Dasgupta\textsuperscript{60} determined the orientation relations for the
decomposition of FeCO\textsubscript{3} to FeO to be [111]_{R,z=4} // [111]\textsubscript{oxide}, and
[110]_{R,z=4} // [110]\textsubscript{oxide}. The experimental results were not properly
described, and topotactic relations were derived as much by arguments
from the crystal structures and the match between planes as from
experimental evidence, which was quite scant.

The morphology of the oxide crystallites was also described in
several investigations. The decomposed oxide particles were said to be a
network of needles\textsuperscript{67} or plate-like layers.\textsuperscript{51} The pores were
described as narrow slit-like, or beaded slit-like.\textsuperscript{48} Comparison of
the density and apparent shape, before and after decomposition, with
surface area measurements is necessary in making a more accurate estimate
of the shape and dimension of oxide crystallites. It is difficult to
draw conclusions from micrographs alone.

6-2. Experimental Results and Discussion

The selected area diffraction patterns for the calcite single
crystal and the CaO product are shown in Fig. 29. The zone axis of the
spot pattern is $[031]_{R,z=4}$, which can be equivalently expressed as
$(2.16 7.32 1)_{R,z=4} = [411]_{H,z=6} = [3211]_{H,z=6} = (3 2 0.128)_{H,z=6}$.
$[031]_{R,z=4}$ and is used here to represent any of the
crystallographically equivalent directions for the calcite structure.
The ring patterns obtained for the decomposed product agree with the
d-spacings for CaO. However, reflection maxima at two different
positions around the rings were observed during several runs when the
same starting orientation of calcite was chosen (Fig. 30). Those
high-intensity regions around the circumferences of the rings between the
two diffraction patterns of CaO are perpendicular to each other.
Therefore, CaO must have a zone axis for preferred orientations that can
be any of the crystallographically equivalent $[110]$ directions, because
the angles between any pair of $[110]$ directions are 90°. Furthermore,
the $[110]$ direction is the twofold axis for a cubic system, which
explains the twofold symmetry of the reflection maxima for each
diffraction pattern of CaO.
If we assume the same preferred orientation relations for calcite decomposition as dolomite decomposition—namely, \([010]_R // [001]_{\text{oxide}}\) and \([101]_R // [110]_{\text{oxide}}\), the angular relationship between any plane of calcite and of CaO can be estimated from superimposed stereograms.

A calcite planar stereographic projection of (14.85 1)\(_{R,z=4}\) is superimposed on a [001] cubic stereogram with (101)\(_{R,z=4}\) of calcite parallel to (110) of the oxide. (14.85 1)\(_{R,z=4}\) is the plane perpendicular to \([010]_{R,z=4}\) direction. We find that (2.16 7.32 1)\(_{R,z=4}\) is not parallel to \{110\}, as we derived earlier from the diffraction patterns for calcite decomposition. Furthermore, the angles measured between any of the \{100\}\(_{R,z=4}\) type planes of calcite and any of the \{111\} type planes of CaO from the superimposed stereograms are all larger than 10°, while the angle between (100)\(_R\) reflection of calcite and the reflection maxima on the (111) ring of CaO measured from the diffraction pattern are less than 5° apart. Therefore, the preferred orientation relations between CaO and calcite are different from those of dolomite decomposition.

If the calcite (2.16 7.32 1) planar stereogram is superimposed on the oxide (110), depending on the rotation between the two stereograms, either observation for preferred orientations made by Towe,\(^67\), i.e., \((111)_R \equiv (0112)\) of calcite was 90° from (111), (200), and (220) reflections of CaO; or by Singh Dev\(^63\), i.e., \((100)_{R} \equiv (1014)\) of calcite // (110) of CaO; or by Floquet and Niepce\(^65,66\), i.e., \((111)_{\text{calcite}} \equiv (140)_{\text{oxide}}\), could be satisfied. But we had no experimental evidence that agrees or disagrees with any of them. The
preferred orientation relationship derived by Dasgupta,\textsuperscript{60} i.e.,

\[ [111]\text{calcite} // [111]\text{oxide} \text{ and } [110]\text{calcite} // [110]\text{oxide} \text{ implies } (2.16 7.32 1) \text{ of calcite is not parallel to (110) of CaO. This is inconsistent with our experimental observation.} \]

An interesting feature of the CaO diffraction pattern is that the high-intensity portions of the rings are more like elongated spots than segments of the rings. This observation implies that CaO particles are more preferentially aligned with respect to calcite than MgO or CaO particles are with respect to dolomite. The elongation of the reflections arises from a scattering about the exact diffraction condition.

Just as for dolomite, the single-crystal pattern of calcite did not seem to change during heating until a critical temperature was reached. However, careful measurement of the distances and angles between spots of the diffraction pattern for the fresh sample and for the heated sample immediately before the emergence of the ring pattern and the fading of the spots gives, on the average, a shrinkage of 6\% for lattice spacings (Table VIII). Even though the calcite structure is highly anisotropic depending on whether the direction is parallel or perpendicular to the c-axis, no significant difference in shrinkage could be found between them. The angles stayed essentially the same (Table IX).

The uncertainty in measuring the distance between spots on a diffraction pattern is \( \pm 0.1 \) mm, which is about \( \pm 0.4\% \) for a d-spacing of 4 Å. The smaller the d-spacing, the larger the distance between the diffracted spot and the transmitted spot on the diffraction pattern, and
the less the uncertainty. 4 Å is larger than any measured d-spacing for calcite or CaO. There is also an instrumental error involved in determining the d-spacings from an electron diffraction pattern. However, the specimen was not rotated throughout the experiment, and the diffraction condition was kept the same for each spot. Therefore, there is no inaccuracy introduced here between the two diffraction patterns of calcite because the relative instead of absolute values of d-spacings are measured. Thermal expansion coefficients for CaCO$_3$ are $-6 \times 10^{-6}/^\circ$C normal to the [111]$_R$ axis, and $25 \times 10^{-6}/^\circ$C parallel to the [111]$_R$ axis. Assuming that the calcite was heated to ~600°C, which is probably hotter than the specimen really is, the greatest possible shrinkage would be less than 0.4%. Therefore, the 6% shrinkage measured on the diffraction pattern is real.

The apparent shape and dimension of the specimen can be observed and measured at low magnifications. Characteristic points are identified and distances among them are compared between the before and after decomposition images shown in Figs. 31 and 32. Interestingly, there is also an average shrinkage of 6%.

The 6% decrease in distances between spots on the diffraction pattern of calcite implies ~17% decrease in molar volume. Because the molar volume of CaO is only 46% that of calcite, the volume decrease implies the substitution of ~31 mole% of CaO in the calcite lattice. This means that the calcite structure is maintained without rupture until more than 31 mole% of CaCO$_3$ has converted to CaO. Since there is only 6% total shrinkage for the apparent dimension of the
specimen when calcite is fully decomposed, we can conclude that the decrease in volume for the sample occurs before the calcite lattice fragments to form small oxide crystallites.

In addition to the decrease of distance between reflection points on the diffraction pattern of the heated calcite single crystal when it still showed spots and before the rings emerged, superlattice reflections and streakings were observed (Fig. 33). The extra spots appeared midway between each pair of reflections along the [100]_{R,z=4} direction. The extra spots can be explained by some ordered periodic arrangement of atoms with unit cell dimensions twice the lattice constant of (100)_{R} of calcite. An ordered replacement of CO$_2^-$ ions with O$^2-$ ions by the expulsion of CO$_2$ molecules, only in every other calcite rhombohedral unit cell along the [100] direction while keeping the crystal structure of calcite lattice, could give rise to these extra spots.

When the single-crystal diffraction pattern is properly aligned with the poles shown on a calcite (2.16 7.32 1)_{R} planar stereogram, we can find the planes that are possible contributors to the streaking observed. They are (011)_{R}, (131)_{R}, (113)_{R}, and (2.16 7.32 1)_{R}, which is the zone axis of the spot pattern [031]_{R,z=4}. Determination of a unique plane involves the examination of diffraction patterns in several crystallographic orientations.

The images obtained at this stage showed some very interesting contrast. The bright field and dark field pictures of the same regions are shown with (100)_{R} as the reflecting planes for the DF pictures (Figs. 34 and 35).
Clearly, the two regions appeared quite different. However, both showed that the single-crystal calcite was no longer a homogeneous specimen, even though the diffraction patterns showed little change. There are two possible explanations for the cause of the contrast. One is surface corrugation, which is made visible by mass thickness contrast; thicker regions of the specimen absorb more and give dark contrast, while thin regions give light contrast. The other is that intercalation of CaO and pores into the calcite matrix causes those regions to be dark. In either case, the periodicity of the inhomogeneity is well under 1000 Å.

To explain the differences shown between the two regions, high-resolution microscopy is necessary to identify the direction and structure of areas that may be as close to each other as 5 nm.

The fully decomposed product gave a bright field image, shown in Fig. 36. Estimation of the pore size and CaO crystallite size is extremely difficult because the image is a two-dimensional projection of a three-dimensional array. Therefore, the shape and size cannot be accurately estimated unless the object is symmetric or projections of many different orientations are analyzed. The problem is still more complicated because of the overlapping of particles. However, a rough measurement gives the pore size as between 1 and 2 nm, and the CaO crystallite size as ~10 nm. The oxide crystallites are probably best described as like jelly beans in shape, because one dimension is longer than the others but not as much longer as in needles.
7. Strontianite

7-1. Introduction

To find whether SrCO$_3$ transforms to SrO in the same preferred orientations as found for dolomite decomposition, we must find the structural relations between calcite and aragonite because SrCO$_3$ is the only carbonate of this study that has an aragonite structure.

In the article "The Oriented Transformation of Aragonite into Calcite," the author claimed that:

(a) [001]$_{\text{aragonite}}$ // [0001]$_{\text{calcite}}$
(b) [100]$_{\text{aragonite}}$ // [10$ar{1}$0]$_{\text{calcite}}$
(c) [110]$_{\text{aragonite}}$ // [0$ar{1}$10]$_{\text{calcite}}$

Because of the parallel relations between these directions of aragonite and calcite, the angle between two directions in one structure must be the same as the angle between two directions in the other. We find:

\[
[001]_{\text{aragonite}} \wedge [100]_{\text{aragonite}} = [0001]_{\text{calcite}} \wedge [1010]_{\text{calcite}} = 90^\circ
\]

but,

\[
[100]_{\text{aragonite}} \wedge [110]_{\text{aragonite}} < 90^\circ
\]

\[
\neq [10\bar{1}0]_{\text{calcite}} \wedge [0\bar{1}10]_{\text{calcite}} = 120^\circ
\]

Therefore, the three conditions cannot be satisfied simultaneously, and the possible orientation relationship between aragonite and calcite can only be either (a) and (b) or (a) and (c), but
not all three. To compare orientation relations for SrCO$_3$
decomposition with orientation relations for decomposition reactions of
carbonates with the calcite structure is impossible.

7-2. Experimental Results and Discussion

The selected area diffraction of a fully decomposed section of
SrCO$_3$ shows evidence of preferred orientations with respect to SrCO$_3$
at an orientation $[31\overline{2}] = (1.08 0.974 \overline{1})$ (Fig. 37). The (111) and (200)
rings give reflection maxima close to the direction along the (130)
reflection, and at the direction of the (021) reflection of SrCO$_3$. The
(220) ring has approximately six strong intensity portions around its
circumference.

Decomposition reactions followed for other orientations (Fig. 38)
did not give any more information about the preferred orientation of SrO
with respect to SrCO$_3$ because the ring pattern did not show easily
identifiable reflection maxima. We can conclude that the SrCO$_3$
decomposition reaction is definitely a topotactic transformation, but we
are unable to derive its orientation relations from our experimental data.

A dark field picture (Fig. 39) of (112) reflection of SrCO$_3$
before significant decomposition was observed gave a light and dark
contrast very similar to that observed for CaCO$_3$ decomposition; but the
periodicity seemed much smaller. An image of a fully decomposed section
(Fig. 40) showed that the shape of SrO particles is quite different from
shapes of oxides from other vacuum-decomposed alkaline earth carbonates.
Although it is not easy to determine the shape on a two-dimensional projection, one dimension is definitely much larger than the other. A typical length is 50 nm and a typical cross section is 10 nm.
Acknowledgments

The graduate years at UC Berkeley have enriched my life in every aspect. Having the opportunity to study on this campus and the privilege of joining a research group in the College of Engineering while remaining a Chemistry graduate student have made my experience here diverse and fruitful. I feel very fortunate to be involved in three Departments: Chemistry, Materials Science, and the Materials and Molecular Research Division of Lawrence Berkeley Laboratory.

I wish to express my gratitude to Professor Alan W. Searcy for his guidance. In addition to the encouragement he provided during the course of this investigation, he spent hours correcting my English and helping me to revise this dissertation. Working with him has been a great learning experience.

I also wish to express sincere appreciations to Professors David H. Templeton and Joseph A. Pask for their criticisms, and to Mildred Bowman for her efficient typing.

Special thanks are due to the following people: Professor Rudy Wenk for use of his microscope, Mr. Bill Worthington for his technical assistance with the TEM hot stage, Dr. Yoshi Nakajima for helpful discussions, Dr. Trudy Kriven for the computer program for the stereographic projections, and Ms. Kathy Faber for her friendship and concern.
I remain indebted to my husband Hailung for his continuous support and understanding, and to the many persons—professors, fellow students, staff, and friends—whose stimulating discussions and suggestions provided valuable input.

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References

TABLE I. Relative Molar Volumes of Carbonates and Their Oxides.

<table>
<thead>
<tr>
<th></th>
<th>Molar Volume (cm³/mole)</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgCO₃</td>
<td>28.51</td>
<td>----</td>
</tr>
<tr>
<td>MgO</td>
<td>11.26</td>
<td>-61%</td>
</tr>
<tr>
<td>CaCO₃ (Calcite)</td>
<td>36.93</td>
<td>----</td>
</tr>
<tr>
<td>CaO</td>
<td>16.92</td>
<td>-54%</td>
</tr>
<tr>
<td>½CaMg(CO₃)₂</td>
<td>32.10</td>
<td>----</td>
</tr>
<tr>
<td>½(CaO+MgO)</td>
<td>14.09*</td>
<td>-56%</td>
</tr>
<tr>
<td>SrCO₃</td>
<td>39.90</td>
<td>----</td>
</tr>
<tr>
<td>SrO</td>
<td>22.05</td>
<td>-45%</td>
</tr>
</tbody>
</table>

*This is the average value of 11.26 and 16.92.
Table II. Group II Carbonates with the Calcite and Aragonite Structure.

<table>
<thead>
<tr>
<th>Calcite Structure</th>
<th>Aragonite Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>Cation radius (Å)</td>
</tr>
<tr>
<td>MgCO₃</td>
<td>0.65</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### TABLE III.  Lattice Parameters of Magnesite, MgCO₃, Sub-Cells

<table>
<thead>
<tr>
<th>Z</th>
<th>Crystal System</th>
<th>Lattice Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rhombohedral</td>
<td>( a_R = 3.6631 \text{ Å} ) ( \alpha = 78^\circ 27' )</td>
</tr>
<tr>
<td>3</td>
<td>Hexagonal</td>
<td>( a_H = 4.6332 \text{ Å} ) ( c_H = 7.5075 \text{ Å} )</td>
</tr>
<tr>
<td>2</td>
<td>Rhombohedral</td>
<td>( a_R = 5.6750 \text{ Å} ) ( \alpha = 48^\circ 11' )</td>
</tr>
<tr>
<td>6</td>
<td>Hexagonal*</td>
<td>( a_H = 4.6332 \text{ Å} ) ( c_H = 15.015 \text{ Å} )</td>
</tr>
<tr>
<td>4</td>
<td>Rhombohedral</td>
<td>( a_R = 5.9063 \text{ Å} ) ( \alpha = 103^\circ 20' )</td>
</tr>
<tr>
<td>12</td>
<td>Hexagonal</td>
<td>( a_H = 9.2664 \text{ Å} ) ( c_H = 7.5075 \text{ Å} )</td>
</tr>
</tbody>
</table>

*NBS Circular 539, 7, 28 (1957).*
TABLE IV. Lattice Parameters of Calcite, CaCO₃, Sub-Cells

<table>
<thead>
<tr>
<th>Z</th>
<th>Crystal System</th>
<th>Lattice Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rhombohedral</td>
<td>( a_R = 4.048 , \text{Å} ) ( \alpha = 76^\circ 5' )</td>
</tr>
<tr>
<td>3</td>
<td>Hexagonal</td>
<td>( a_H = 4.989 , \text{Å} ) ( c_H = 8.531 , \text{Å} )</td>
</tr>
<tr>
<td>2</td>
<td>Rhombohedral</td>
<td>( a_R = 6.375 , \text{Å} ) ( \alpha = 46^\circ 4' )</td>
</tr>
<tr>
<td>6</td>
<td>Hexagonal*</td>
<td>( a_H = 4.989 , \text{Å} ) ( c_H = 17.062 , \text{Å} )</td>
</tr>
<tr>
<td>4</td>
<td>Rhombohedral</td>
<td>( a_R = 6.424 , \text{Å} ) ( \alpha = 101^\circ 54' )</td>
</tr>
<tr>
<td>12</td>
<td>Hexagonal</td>
<td>( a_H = 9.978 , \text{Å} ) ( c_H = 8.531 , \text{Å} )</td>
</tr>
</tbody>
</table>

*Swanson and Fuyat, NBS Circular 539, Vol II, 51 (1953)
TABLE V. Lattice Parameters of Dolomite, CaMg(CO$_3$)$_2$ Sub-Cells

<table>
<thead>
<tr>
<th>$Z \times 2$</th>
<th>Crystal System</th>
<th>Lattice Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rhombohedral</td>
<td>$a_R = 3.8529 , \text{Å}$ $\alpha = 77^\circ 16'$</td>
</tr>
<tr>
<td>3</td>
<td>Hexagonal</td>
<td>$a_H = 4.8112 , \text{Å}$ $c_H = 8.01 , \text{Å}$</td>
</tr>
<tr>
<td>2</td>
<td>Rhombohedral</td>
<td>$a_R = 6.0193 , \text{Å}$ $\alpha = 47^\circ 7'$</td>
</tr>
<tr>
<td>6</td>
<td>Hexagonal*</td>
<td>$a_H = 4.8112 , \text{Å}$ $c_H = 16.02 , \text{Å}$</td>
</tr>
<tr>
<td>4</td>
<td>Rhombohedral</td>
<td>$a_R = 6.1638 , \text{Å}$ $\alpha = 102^\circ 37'$</td>
</tr>
<tr>
<td>12</td>
<td>Hexagonal</td>
<td>$a_H = 9.6224 , \text{Å}$ $c_H = 8.01 , \text{Å}$</td>
</tr>
</tbody>
</table>

*Howie and Broadhurst, Am. Min. 42, 1210-3 (1958).
TABLE VI

THE SIX LARGEST D-SPACINGS OF DECOMPOSED DOLOMITE

<table>
<thead>
<tr>
<th>HKL</th>
<th>$D_{\text{MgO}}$ Å</th>
<th>$I/I_s$</th>
<th>$D_{\text{CaO}}$ Å</th>
<th>$I/I_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>2.431</td>
<td>10</td>
<td>2.778</td>
<td>34</td>
</tr>
<tr>
<td>200</td>
<td>2.106</td>
<td>100</td>
<td>2.405</td>
<td>100</td>
</tr>
<tr>
<td>220</td>
<td>1.489</td>
<td>52</td>
<td>1.701</td>
<td>45</td>
</tr>
</tbody>
</table>
TABLE VII

SPECTROGRAPHIC ANALYSES OF MINERALS (wt%)

<table>
<thead>
<tr>
<th></th>
<th>Dolomite</th>
<th>MgCO₃</th>
<th>CACO₃</th>
<th>SrCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>20.0</td>
<td>p.c.</td>
<td>0.002</td>
<td>0.005</td>
</tr>
<tr>
<td>Ca</td>
<td>35.0</td>
<td>0.3</td>
<td>p.c.</td>
<td>2.5</td>
</tr>
<tr>
<td>Sr</td>
<td>0.04</td>
<td>0.3</td>
<td>&lt;0.003</td>
<td>p.c.</td>
</tr>
<tr>
<td>Ba</td>
<td>0.006</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.015</td>
</tr>
<tr>
<td>Na</td>
<td>&lt;0.05</td>
<td>&lt;0.1</td>
<td></td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Al</td>
<td>0.025</td>
<td>0.04</td>
<td>&lt;0.001</td>
<td>0.002</td>
</tr>
<tr>
<td>Si</td>
<td>0.03</td>
<td>&lt;0.1</td>
<td>&lt;0.003</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>K</td>
<td>&lt;0.75</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td></td>
<td></td>
<td>&lt;0.003</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td></td>
<td></td>
<td>&lt;0.001</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.7</td>
<td>0.35</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt;0.001</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;0.001</td>
<td>0.004</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Zr</td>
<td></td>
<td></td>
<td>&lt;0.01</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>&lt;0.001</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td></td>
<td></td>
<td>&lt;0.002</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;0.003</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
</tr>
</tbody>
</table>

P.C. = PRINCIPAL CONSTITUENT
TABLE VIII. Lattice Spacings Calculated from the Diffraction Patterns of the Original and the Heated Calcite Single Crystal.

<table>
<thead>
<tr>
<th>$(HKL)_h$</th>
<th>$D_{ASTM}(\text{Å})$</th>
<th>$D_{INITIAL\ STAGE}(\text{Å})$</th>
<th>$D_{HEATED\ STAGE}(\text{Å})$</th>
<th>DIFFERENCE(Å)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>104</td>
<td>3.035</td>
<td>3.044</td>
<td>2.858</td>
<td>-0.186</td>
<td>-6.1</td>
</tr>
<tr>
<td>113</td>
<td>2.285</td>
<td>2.287</td>
<td>2.148</td>
<td>-0.139</td>
<td>-6.1</td>
</tr>
<tr>
<td>122</td>
<td>1.604</td>
<td>1.597</td>
<td>1.508</td>
<td>-0.089</td>
<td>-5.6</td>
</tr>
<tr>
<td>011</td>
<td>4.188</td>
<td>4.171</td>
<td>3.934</td>
<td>-0.237</td>
<td>-5.7</td>
</tr>
<tr>
<td>115</td>
<td>2.678</td>
<td>2.667</td>
<td>2.502</td>
<td>-0.165</td>
<td>-6.2</td>
</tr>
</tbody>
</table>
TABLE IX. Angles Measured Between Spots from the Diffraction Patterns of the Original and the Heated Single Crystal.

<table>
<thead>
<tr>
<th>(HKL)$_H$</th>
<th>STANDARD</th>
<th>INITIAL STAGE</th>
<th>HEATED STAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>104</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>113</td>
<td>32.54°</td>
<td>32°50'</td>
<td>32°55'</td>
</tr>
<tr>
<td>122</td>
<td>49.05°</td>
<td>49°35'</td>
<td>49°40'</td>
</tr>
<tr>
<td>011</td>
<td>80.45°</td>
<td>80°55'</td>
<td>80°15'</td>
</tr>
<tr>
<td>115</td>
<td>140.91°</td>
<td>140°50'</td>
<td>140°50'</td>
</tr>
</tbody>
</table>
Figure Captions

Fig. 1 Clinographic projection of the unit cell of the sodium chloride structure.

Fig. 2 Clinographic projection of the sodium chloride structure, showing the coordinating octahedra between anions and cations.

Fig. 3 Clinographic projection of the rhombohedral structure of calcite, CaCO₃.

Fig. 4 Projection of lattice points along the trigonal axis of the calcite structure with the rhombohedral unit cell (z=4).

Fig. 5 Projection of the calcite structure, showing the coordination around the calcium ion by six oxygen neighbors belonging to six different carbonate groups.

Fig. 6 Projection of the calcite structure, showing the two calcium ions and the one carbon atom bound to the oxygen atom.

Fig. 7 Clinographic projection of the unit cell of a dolomite structure. Calcium ions are represented by the full circles and magnesium ions by the open circles.

Fig. 8 Rhombohedral and hexagonal unit cells in a rhombohedral lattice.

Fig. 9 Calcite-type unit cells with different numbers of formula units per cell (z), showing dolomite with \( z = \frac{1}{2} \) and 2.

Fig. 10 Calcite-type unit cells with different numbers of formula units per cell (z), showing dolomite with \( z = \frac{1}{2} \), 1, and 2.

Fig. 11 Plan of the unit cell of the orthorhombic structure of aragonite, CaCO₃, projected on a plane perpendicular to the z-axis. The heights of the atoms are expressed in units of \((1/6)c\).
Fig. 12 The diffraction pattern of a dolomite single crystal.
Fig. 13 The diffraction pattern of a partially decomposed dolomite single crystal.
Fig. 14 The diffraction pattern of a partially decomposed dolomite single crystal with angular relationships marked.
Fig. 15 Stereographic projection representing the orientation relationship between dolomite and its vacuum decomposed oxides.
Fig. 16 The diffraction pattern of a partially decomposed dolomite single crystal showing the formation of solid solutions between MgO and CaO.
Fig. 17 The phase diagram for the MgO-CaO system.
Fig. 18 Diffraction patterns for dolomite and its partially decomposed product.
Fig. 19 Diffraction patterns for dolomite and its partially decomposed product.
Fig. 20 Diffraction patterns for dolomite and its partially decomposed product.
Fig. 21 Bright-field image of a fully decomposed dolomite sample.
Fig. 22 The homogeneous mechanism for decomposition.
Fig. 23 Projections of (101)$_R$ and (101)$_R$ planes of dolomite.
Fig. 24 Diffraction patterns for magnesite and its partially decomposed product.
Fig. 25 Bright-field image of a fully decomposed magnesite sample.
Fig. 26 Diffraction patterns for magnesite and its partially decomposed product.
Fig. 27 Diffraction patterns for magnesite and its partially decomposed product.

Fig. 28 Bright-field images showing the morphological similarities between the magnesite and the same area after decomposition.

Fig. 29 Diffraction patterns for calcite and its partially decomposed product.

Fig. 30 Diffraction patterns for calcite and its partially decomposed product, showing the two types of reflection maxima for CaO that are 90° from each other.

Fig. 31 Bright-field images showing the morphological similarities between the calcite and the same area after decomposition.

Fig. 32 Bright-field images showing the morphological similarities between the calcite and the same area after decomposition.

Fig. 33 A diffraction pattern of a heated calcite single-crystal sample, showing the effect of extra spots and streaking.

Fig. 34 Bright-field and dark-field images of a heated calcite single-crystal sample.

Fig. 35 Bright-field and dark-field images of a heated calcite single-crystal sample.

Fig. 36 Bright-field image of a fully decomposed calcite sample.

Fig. 37 Diffraction patterns for strontianite and its partially decomposed product.

Fig. 38 Diffraction pattern for a partially decomposed strontianite.

Fig. 39 Dark-field image of a heated strontianite single-crystal sample.

Fig. 40 Bright-field image of a fully decomposed strontianite sample.
The sodium chloride structure.

Figure 1
The coordination of sodium and chlorine ions of the sodium chloride structure.
CaCO$_3$

- 1st Layer, Ca$^{2+}$
- 2nd Layer, CO$_3^{2-}$
- 3rd Layer, Ca$^{2+}$
- 4th Layer, CO$_3^{2-}$

Projection Along the Trigonal Axis of the Calcite Structure with the Rhombohedral Unit Cell ($z = 4$)

XBL817-10882

Figure 4
Calcite Structure

Figure 5
Figure 6

Calcite Structure
TRANSFORMATION BETWEEN RHOMBOHEDRAL $(a_R, \alpha)$ AND HEXAGONAL $(a_H, c_H)$ CELLS

Figure 8
DOLOMITE

\[ a_R = 6.1638 \text{ Å} \quad \alpha = 102.37^\circ \]

\[ a_R = 3.8529 \text{ Å} \quad \alpha = 77.16^\circ \]
DOLOMITE

\( a_R = 6.1638 \, \text{Å} \quad \alpha = 102°37' \)
\( a_R = 3.8529 \, \text{Å} \quad \alpha = 77°16' \)
\( a_R = 6.0193 \, \text{Å} \quad \alpha = 47°07' \)

Figure 10
Figure 11

- : Ca; : C; : O

XBL 819-4957
Figure 13

CaMg(CO₃)₂ + CaO + MgO
DOLOMITE \((\bar{1} 4.58 \bar{1})_{RH}\) // OXIDE \((001)_{CUBE}\)

\[
\langle 010 \rangle_{RH} // \langle 001 \rangle_{CUBE} \quad \& \quad \{10\bar{1}\}_{RH} // \{110\}_{CUBE}
\]

Figure 15
R.C. Doman, J.B. Barr, R.N. McNally and A.M. Alper

Figure 17
Figure 18
\[(2 \bar{1} 12)_{H} (1 0 13)_{H} \]
\[(4 0 2)_{R} \quad (7 3 \bar{3})_{R} \]
\[(\frac{1}{2} \frac{3}{2} \frac{3}{2})_{R} \]

\[(000) \quad (\bar{1}11)_{H} \quad \{13\} \quad \{22\}_{R} \]

\[[13 14 \bar{1}]_{H} = [3\bar{6}]_{R} \]

Figure 19
Figure 20
(10\(\bar{1}\))\(_{\text{Rh}}\)

\[ 90 \]

\[ (10\bar{1})_{\text{Rh}} \]

\[ [010] \]

\[ [10\bar{1}] \]

\[ 6.164 \text{ Å} \]

\[ 9.622 \text{ Å} \]

\[ \bigcirc = \text{Ca}^{2+}; \quad \bullet = \text{Mg}^{2+}; \quad \bigcirc, \bigcirc, \bigcirc = \text{CO}_3^{2-} \]

\[ (10\bar{1})_{\text{Rh}} \]

\[ [\bar{1}2\bar{1}] \]

\[ [010] \]

\[ [12\bar{1}] \]

\[ 6.164 \text{ Å} \]

\[ 7.706 \text{ Å} \]

\[ \text{XBL818-6232} \]

Figure 23
Homogeneous Mechanism

\[ \text{[III]}_{\text{Rh}} \quad \text{[III]}_{\text{Cube}} \]

\[ \text{d}_{\text{[III]}_{\text{Rh}}} = 2.670 \, \text{Å} \]
\[ \text{d}_{\text{[III]}_{\text{Mg}}} = 2.431 \, \text{Å} \]
\[ \text{d}_{\text{[III]}_{\text{Ca}}} = 2.778 \, \text{Å} \]

Figure 22
Figure 24
Figure 26
Figure 27
Figure 28

Fresh MgCO₃
0.1μ

Dec. MgCO₃
0.1μ

XBB 810-10759
Figure 29
Figure 31
Figure 32
Figure 33
Figure 40
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