

An X-ray investigation of the thermal decomposition of portlandite

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SUMMARY. The thermal decomposition of portlandite, Ca(OH)_2 , has been studied in air and in vacuum using X-ray single-crystal techniques. In air, the crystals were decomposed *in situ* on the goniometer arcs whilst X-ray reflections were simultaneously recorded. The transformation to CaO was not accompanied by topotaxy; this is attributed to the high nucleation rate of CaO crystallites in air. When Ca(OH)_2 single crystals were decomposed under vacuum (and subsequently exposed to X-rays), some orientation of the CaO crystallites occurred. These results are compared with those of previous workers using electron-diffraction techniques. Decomposition of Ca(OH)_2 single crystals commences at $\sim 450^\circ\text{C}$ in air and at $\sim 230^\circ\text{C}$ in a vacuum of 10^{-6} mmHg; reaction commences at crystal edges and surface defects, the reaction boundary moving inwards to the centre of the crystal. This observation is consistent with a homogeneous mechanism of decomposition.

In a recent investigation, Chatterji and Jeffery (1966) decomposed crystals of Ca(OH)_2 in an electron microscope and obtained electron-diffraction patterns that contained initially an inner and outer set of hexagonal spots, corresponding to Ca(OH)_2 110 spots and CaO 220 spots respectively. After further heating the hydroxide reflections were eliminated and the authors concluded that a good degree of orientation is preserved in the conversion of Ca(OH)_2 to CaO. Their observations are contrary to those of West (1934) who, using X-ray single-crystal techniques to study the decomposition of portlandite, concluded that the CaO crystallites are oriented along only one three-fold axis whereas with brucite the resultant MgO crystallites were oriented along two directions. A possible explanation is that with portlandite (Dent Glasser, Glasser, and Taylor, 1962), the large size of the Ca^{2+} ion restricts migration and prevents topotaxy from developing. It is noted that the orientation of the crystals in the work of Chatterji and Jeffery corresponds to the crystal orientation in which West found no topotaxy, i.e. with the X-ray beam passing through the base of the pseudomorph. It has been suggested (Chatterji and Jeffery, 1966) that the discrepancy between the results of X-ray and electron-diffraction may be due to the highly ionizing character of the electron beam or the lower decomposition temperature of Ca(OH)_2 under vacuum, or a combination of both effects. Balmbra, Clunie, and Goodman (1966), in a study of the topotactic dehydration of brucite, concluded that the decomposition in the electron beam is not due to radiation effects but to the rise in temperature of the specimen.

In the present work decomposition of Ca(OH)_2 single crystals in air has been re-examined using X-ray techniques and has been extended to crystals decomposed partially or fully *in vacuo*. In this way it was hoped to explain the conflicting results obtained by other workers and also, if possible, to comment on the mechanism of the dehydroxylation of portlandite. Brucite decomposition was re-examined in order to

establish that the techniques used in this study were sufficient to observe topotaxial changes in a proven or well-known system.

Experimental methods. $\text{Ca}(\text{OH})_2$ crystals were prepared by a method adapted from that described by Ashton and Wilson (1927). Briefly this involves a diffusion process employing CaCl_2 and NaOH solutions in a CO_2 -free atmosphere. Several grams of $\text{Ca}(\text{OH})_2$ crystals were obtained varying in size from < 1 mm to about 3 mm. Spectroscopic analyses showed the following major impurities were present: Fe 200 ppm, Na 150 ppm, and Cl 600 ppm. Examination of these crystals under the optical microscope showed well-formed hexagonal prisms, from which thin hexagonal plates could be cleaved.

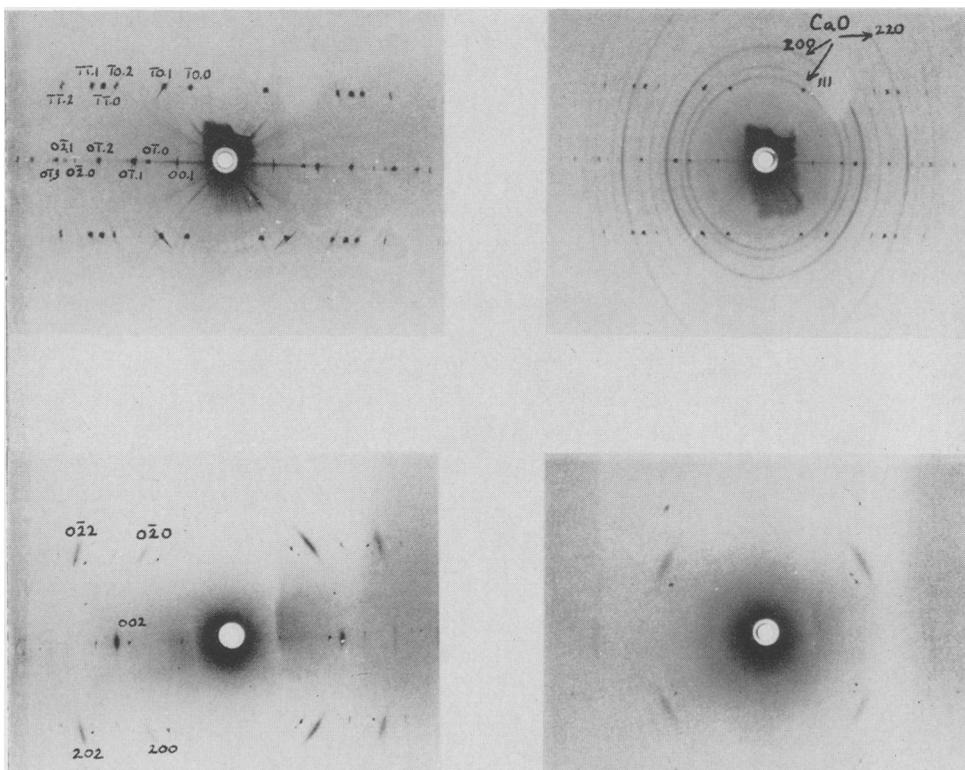
Crystals of $\text{Mg}(\text{OH})_2$ were cleaved from a sample of a Canadian brucite (supplied by Dr. P. J. Anderson), which contained 0.25 % SiO_2 , 0.04 % FeO , and 0.20 % MnO .

The decomposition of portlandite crystals in air was studied using an S25 Unicam single crystal goniometer and Ni-filtered $\text{Cu-K}\alpha$ radiation. The goniometer was fitted with a high-temperature furnace attachment capable of operation at temperatures up to 600 °C. The furnace construction was based on a design by Barclay and Donaldson (1961) to which several modifications to both design and temperature-control arrangements were made (Brett, 1968). Crystals were mounted in a similar manner to that described by Dent (1957) and were heated to successively higher temperatures, whilst 30° oscillation or rotation patterns were simultaneously recorded. A different technique was adopted in order to study decomposition of $\text{Ca}(\text{OH})_2$ under vacuum. Crystals were placed on a platinum boat and located in a furnace tube, which was raised to temperature under a vacuum of 1×10^{-2} mmHg (rotary pump only), or 2×10^{-6} mmHg (diffusion pump used additionally). A Pt/Pt-13 % Rh thermocouple was positioned ~ 1 mm from the crystals and temperatures were maintained at ± 1 °C from the chosen value. After cooling under vacuum the crystals were mounted on glass fibres using Seccotine cement and examined on the goniometer.

Results and discussion

Decomposition of portlandite in air. Some thirteen crystals in all were examined with varying degrees of success; the limiting factor was usually the crystal-cement stability, which affected the orientation of the pseudomorph. Below 445 °C there was no evidence of CaO spots or powder lines in X-ray patterns. Above this temperature crystals became 'crazed' at the edges but remained translucent at the centre whilst weak powder lines of CaO appeared in the patterns. This was accompanied by a gradual diminution of intensity of $\text{Ca}(\text{OH})_2$ spots and a strengthening of $\text{Ca}(\text{OH})_2$ powder lines, as illustrated in fig. 1. At temperatures close to 500 °C, CaO powder lines predominated together with weaker $\text{Ca}(\text{OH})_2$ powder lines whilst the original crystal morphology was retained. The results were similar whether a , a^* , or c rotation axes were chosen, though in the latter case decomposition appeared to commence at slightly lower temperatures, viz. ~ 450 °C. However, with c as the rotation axis the outer edges of the crystal diffract the X-ray beam giving CaO reflections at the onset of decomposition.

The outstanding feature throughout the work on $\text{Ca}(\text{OH})_2$ decomposition in air was the lack of parent-product orientation relations despite careful control of calcination conditions. West (1934) reported similar results for a or a^* rotation of $\text{Ca}(\text{OH})_2$ pseudomorphs but observed a poorly oriented product with rotation about the original $\text{Ca}(\text{OH})_2$ c -axis. In order to check this result, two crystals were partially decomposed,

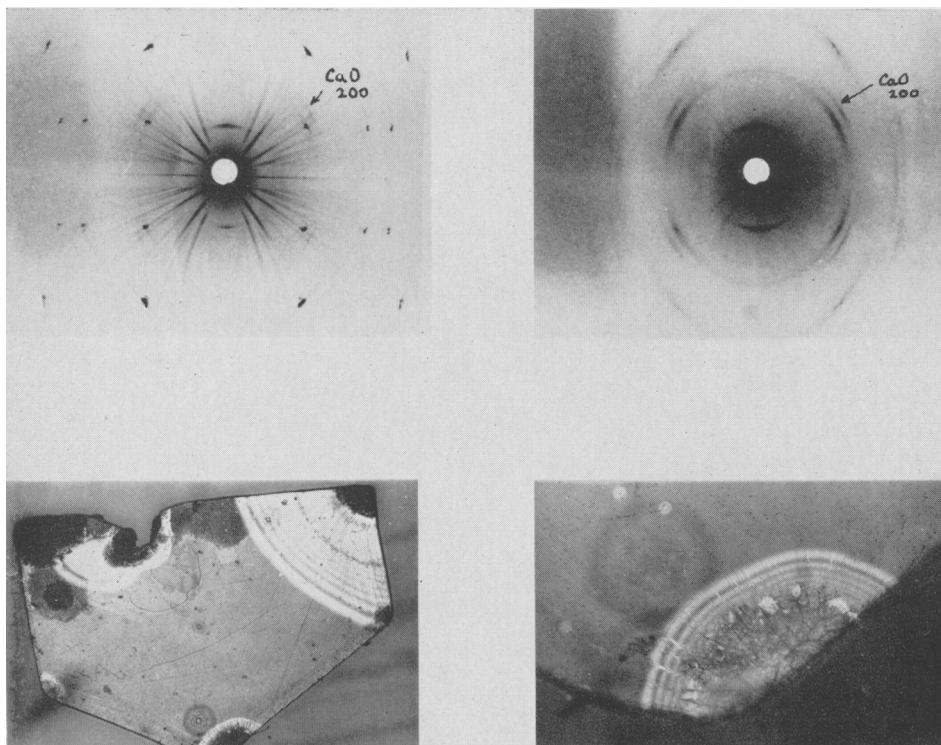


FIGS. 1 and 2. Fig. 1 (top). X-ray photographs of $\text{Ca}(\text{OH})_2$ taken with a rotation axis at (a, left) 460°C , showing $\text{Ca}(\text{OH})_2$ reflections only and (b, right) 465°C , after further time showing the development of $\text{Ca}(\text{OH})_2$ and CaO (indicated) powder lines. Fig. 2 (bottom). X-ray photographs of $\text{Mg}(\text{OH})_2$ taken at 450°C with (a, left) a -rotation axis and (b, right) c -rotation axis, showing strong spot reflections of MgO and weaker $\text{Mg}(\text{OH})_2$ reflections.

one on the goniometer arcs, one in a preheated furnace at 500°C , then remounted at room temperature with c as rotation axis and exposed to X-rays. In both cases powder lines of $\text{Ca}(\text{OH})_2$ and CaO were obtained with no evidence of topotaxy. It is concluded that the mode of heating the crystals in air was not significant and that the degree of topotaxy observed is, at the best, very poor and unreproducible.

In contrast, topotaxy was observed when single crystals of brucite were decomposed to MgO using the same techniques. The orientation relations found agreed with those of previous workers (see, for example, West (1934), Garrido (1951), and Goodman

(1958)) and the product phase was highly oriented, fig. 2. The decomposition of large brucite crystals commenced at crystal edges at about 460 °C in air; there was no evidence for the formation of a hexagonal phase as suggested by Goodman (1958) and Balmбра, Clunie, and Goodman (1966), though several results indicated a small contraction in the basal plane of $\text{Mg}(\text{OH})_2$ in partially decomposed crystals. These results



FIGS. 3 and 4. Fig. 3 (top). X-ray photographs of $\text{Ca}(\text{OH})_2$ taken at room temperature with c -rotation axis after heat treatment at ~ 250 °C for (a, left) 2 hours under a vacuum of $\sim 10^{-2}$ mmHg and (b, right) 16 hours under a vacuum of $\sim 10^{-6}$ mmHg. These show the first appearance of CaO spot reflections and their development with further heat treatment. Fig. 4 (bottom). Photomicrographs of $\text{Ca}(\text{OH})_2$ taken after heat treatment at 230 °C for 20 hours in a vacuum of $\sim 10^{-6}$ mmHg; (a, left) a view of the whole crystal showing the development of reaction zones and (b, right) showing strained zones set up in front of the reaction boundary and the 'polycrystallization' of the $\text{Ca}(\text{OH})_2$.

are generally in accord with those of Gordon and Kingery (1966) who detected no intermediate phase in the decomposition of brucite.

Decomposition of portlandite in vacuo. To test the hypothesis that the discrepancy between X-ray and electron-diffraction results is due to an effect of vacuum in the latter case, a series of calcinations of $\text{Ca}(\text{OH})_2$ single crystals was carried out under vacuum and the crystals subsequently examined, as described earlier. The results obtained from crystals decomposed under a vacuum of $\sim 10^{-2}$ and $\sim 10^{-6}$ mmHg

were essentially the same. Prolonged heating at temperatures above 230 °C resulted in opaque crystals from which weak CaO reflections were observed, whilst at temperatures around 300 °C the crystals were almost fully reacted. With Ca(OH)₂ *a* or *a** as rotation axis, the first weak reflections from CaO in partially decomposed crystals showed orientation effects, fig. 3*a*, but on further heating under vacuum the crystals gave powder lines of Ca(OH)₂ and CaO. A well oriented product was observed on rotation about the *c*-axis with Ca(OH)₂ [0001] || CaO [111], as expected. This relationship was preserved in what appeared to be almost completely reacted crystals, fig. 3*b*. The ζ value¹ for the Ca(OH)₂ first layer lines $\simeq 0.32$ which corresponds to Ca(OH)₂ $d_{0001} = 4.83 \text{ \AA}$ (cf. accepted value 4.906 Å). Although too much reliance cannot be placed on these ζ measurements, since they represent average values for small arcs rather than spot reflections, a small contraction in the *c*-spacing of partially decomposed Ca(OH)₂ is indicated.

It was observed that with all crystals at the onset of dehydroxylation reaction zones are formed at crystal edges and at surface defects. The crystal breaks up into a mosaic of crystallites in front of the reaction boundary as strain zones are set up; this effect is clearly shown in fig. 4, and was observed in the dehydroxylation of Mg(OH)₂ crystals in this work and by other workers (Gordon and Kingery, 1966).

It is possible to say qualitatively that the degree of topotaxy is improved if the conversion of Ca(OH)₂ to CaO takes place *in vacuo* rather than in air. As Shannon and Rossi (1964) suggest, one may describe a continuum of degrees of topotaxy, and in comparison with the decomposition of Mg(OH)₂ the amount of preferred orientation found between parent and product with Ca(OH)₂ is poor. Anderson, Horlock, and Avery (1965) have shown that water vapour enhances both the nucleation rate and the rate of crystal growth when oxides are formed by decomposing hydroxides, and with CaO this effect was pronounced. It is suggested that on decomposing Ca(OH)₂ in air the nucleation rate (of CaO) is initially too high to allow the formation of relatively large crystallites oriented with respect to the parent hydroxide. Rather, the formation of many CaO nuclei, which then grow at the expense of one another, increases the chance of mismatch of these crystallites to the original crystal. *In vacuo*, the recrystallization rate is sufficiently reduced to permit the growth of relatively large crystallites (on an atomic scale) and a degree of topotaxy was observed. If the topotaxy developed has a short range order then electron-diffraction studies will indicate a higher degree of topotaxy, compared to X-ray studies where the crystal volume giving rise to diffraction is a factor of at least 10⁴ greater. In both brucite and portlandite single crystals, reaction commences at crystal edges and surface defects and the reaction boundary moves inwards to the centre of the crystal. This observation is consistent with a homogeneous mechanism of decomposition.

¹ i.e. the perpendicular distance between the planes of reciprocal points normal to the rotation axis.

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