

a half of a sphere, and the point P follows correspondingly over the plane of projection.

The model consists of a framework of two vertical circles (0° and 90° longitude), fixed to a heavy base. A vertical semicircle, of slightly smaller radius, is fixed to a vertical spindle, which allows it to rotate about the N-S axis. Also fixed to the spindle, and rotating with it, is a horizontal perspex disc, slotted along the radius that is in the plane of the semicircle. A small clamp device is free to slide on the semicircle from near 0° to near 90° latitude. A string is tied at the centre of the sphere and then passes over a bar in the clamp and down through the slotted perspex into the hollow column of the model's stand. Threaded on to the string are a small card representing the crystal plane and a small ring or bead, representing the stereographic pole, lying on the perspex sheet. The string is kept taut and is free to change its visible length by virtue of a lead weight on the end of it inside the base column.

The model will be manufactured shortly by Cutrock Engineering Co. Ltd., 35 Ballards Lane, London, N.3.

*Department of Geology and Mineralogy,
University of Oxford,
Parks Road,
Oxford.*

J. ZUSSMAN

[Manuscript received 8 August 1966]

Thermal decomposition of dolomite and ankerite

THE thermal decomposition of dolomite has been studied by many workers. According to Bäckström (1924), the transformation takes place as $\text{CaMg}(\text{CO}_3)_2 \rightarrow \text{CaCO}_3 + \text{MgO} + \text{CO}_2$ and then $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$. Graf and Goldsmith (1955) expressed the first reaction more rigorously by $\text{CaMg}(\text{CO}_3)_2 \rightarrow \text{CaMg}_{1-x}(\text{CO}_3)_{2-x} + x\text{MgO} + x\text{CO}_2$. Single crystal X-ray diffraction study of dolomite crystals, heated to $600^\circ\text{--}800^\circ\text{C}$, by Wilsdorf and Haul (1951) showed that a dolomite crystal transformed into calcite crystallites oriented with respect to the original lattice with an irregular distribution of MgO. D.t.a. curves of dolomite have been obtained by Cuthbert and Rowland, 1947, by Beck, 1950, by Kulp *et al.*, 1957, and by Bradley *et al.*, 1953. From their observations they concluded that the endothermic peak at 800°C was due to the breakdown of the MgCO_3 component and the next endothermic peak at 940°C was due to the dissociation of the CaCO_3 .

Recently the transformation of ankerite during thermal treatment has been studied by Dasgupta (1965). It was reported that ankerite, when heated to 750° C, transformed into calcite with oriented texture while periclase appeared as polycrystalline aggregates. On further heating to 950° C, the calcite structure broke down completely and an oriented structure due to periclase appeared in the X-ray photograph. The appearance of oriented periclase in the last photograph was explained by the migration of Ca^{++} ions from the CaO lattice and interdiffusion of Mg^{++} ions, from the polycrystalline aggregates of MgO, to the places formerly occupied by Ca^{++} ions in CaO lattice. Though this explanation did not seem to be improbable, yet some confusions were left behind for such a complicated mechanism of transformation. To clear up these confusions the transformation of dolomite has been studied by d.t.a. and X-ray methods. The experiments on ankerite were also repeated with better crystals.

Experimental. Dolomite from Greiner, Tyrol, and ankerite from Belnhausen, Darmstadt, Germany, used in this investigation were analysed chemically and gave: Dolomite: SiO_2 0.20 %, total iron as Fe_2O_3 2.32, MnO 0.60, CaO 31.08, MgO 20.02, loss on ignition 46.46 %. Ankerite: SiO_2 nil, total iron as Fe_2O_3 14.50 %, MnO 0.20, CaO 28.26, MgO 13.86, and loss on ignition 43.18 %.

X-ray analysis of single crystals of dolomite was carried out at different stages of heating. A single-crystal rotation photograph of an unheated crystal was taken along the diagonal axis of the rhombohedral crystal with Ni filtered Cu radiation in a 3-cm radius cylindrical camera. The same crystal was then heated to 700° C for 6 hours and a rotation photograph taken along the same direction in the same camera using the same radiation; diffractions due both to MgO and to CaCO_3 appeared. The degree of orientation in both cases was very small as was evident from the fact that both phases gave almost complete powder arcs, though with distinct intensity concentrations. The CaCO_3 crystal thus formed retained a parallel orientational relationship with the original crystal, whereas one of the diad axis of MgO became parallel to one of the diad axes of the original crystal. In the previous paper (Dasgupta, 1965) it was stated that when ankerite was heated to 750° C, texture due to CaCO_3 only appeared while MgO seemed to be randomly oriented. To check this point, a better crystal of ankerite was heated to 750° C and a rotation photograph was taken along the diad axis of the rhombohedral crystal. After careful scrutiny, it was observed that in this case also texture due to MgO appeared; the orientation of MgO

was similar to that found in the case of heated dolomite. The reason for missing the texture pattern of MgO in earlier experiments by the present author might be due to the imperfections of the earlier crystals and also to too much background scattering in the X-ray photograph. However, there was one significant difference between the two samples. While a trace of vaterite was produced along with MgO and CaCO₃ by heating ankerite, no vaterite was detected in the transformation of dolomite. The reason for the formation of vaterite in the transformation of ankerite is not yet known. On further heating to 900° C, dolomite crystals transformed into an oriented aggregate of MgO with polycrystalline aggregates of CaO and Ca(OH)₂. No Ca₂Fe₂O₅ was produced in this case, presumably due to the smaller quantity of iron in dolomite.

The d.t.a. curves of ankerite and dolomite did not show any appreciable differences from published results ("The Differential Thermal Investigation of Clays", ed. Dr. R. C. Mackenzie, London (Min. Soc.)) except that the relative peak heights were different.

Discussion. The hypothesis suggested for the formation of MgO crystals in ankerite at 950° C (Dasgupta, 1965) no longer seems appropriate. It is quite certain now that both MgO and CaCO₃ grow up simultaneously from both dolomite and ankerite crystals on heating in the range of 700°–750° C. Wilsdorf and Haul (1951) stated that dolomite transformed into oriented calcite with irregular distribution of unoriented MgO. The present observation is, therefore, significant, because there is definite evidence of oriented MgO being formed at the same time with CaCO₃. The small degree of orientation of MgO might be responsible for its remaining unnoticed. Moreover, the rate and duration of heating are two important factors that might also influence the degree of orientation.

There are two possibilities for the mechanism of transformation in dolomite and ankerite. The first one is that each (Mg,Fe) layer with the adjacent CO₃ layer comes out first from the dolomite or ankerite lattice on heating; each pair of (Mg,Fe) and CO₃, thus expelled from the original lattice, close up the gaps between similar pairs and form a structure similar to that of magnesite; similarly, there is a closing up of Ca and CO₃ layers and calcite is formed. Another possibility is a transformation where there would be counter migrations of Mg²⁺ and Ca²⁺ ions within the dolomite or ankerite lattice, thereby creating regions, one of which will be CaCO₃ rich and the other (Mg,Fe)CO₃ rich. The second type of mechanism seems to be more probable, since there will be less disturbance inside the crystal lattice as compared to the first type of mechan-

ism. Both CaCO_3 and $(\text{Mg,Fe})\text{CO}_3$ retain their axial relationships parallel to the original phase. $(\text{Mg,Fe})\text{CO}_3$, thus formed from dolomite and ankerite, transforms immediately into MgO and FeO at that high temperature. The reason for not observing any lines due to FeO may be low particle size and also the small percentage of FeO formed. The mechanism of transformation of $(\text{Mg,Fe})\text{CO}_3$ will be the same as that of MgCO_3 whose transformation has already been described (Dasgupta, 1964). It has been suggested there that the transformation of $\text{MgCO}_3 \rightarrow \text{MgO}$ takes place by an inhomogeneous transformation where for every 2 Mg^{2+} ions migrated from the donor region one C^{4+} ion migrates in the opposite direction from the acceptor region in accordance with the suggestion made by Dent Glasser, Glasser, and Taylor (1962). The $[111]_{\text{rh}}$ of MgCO_3 crystal then becomes $[111]_{\text{cub}}$ of MgO crystal whereas the three diad axes of the rhombohedral MgCO_3 are interchanged with the three diad axes of cubic MgO . CaCO_3 , formed from dolomite and ankerite, also transformed into CaO at higher temperature. But as CaO is very unstable and absorbs moisture from the air readily, no texture pattern due to CaO was observed; instead, the powder patterns of CaO and $\text{Ca}(\text{OH})_2$ appeared.

13/2A Ballygunge Station Road,
Calcutta-19,
India.

D. R. DASGUPTA

References

- BÄCKSTRÖM (H. L. J.), 1924. Journ. Chem. Soc. Lond., Trans., vol. 125, p. 430.
 BECK (C. W.), 1950. Amer. Min., vol. 35, p. 985.
 BRADLEY (W. E.), BURST (J. F.), and GRAF (D. L.), 1953. *Ibid.*, vol. 38, p. 207.
 CUTHBERT (F. L.) and ROWLAND (R. A.), 1947. *Ibid.*, vol. 32, p. 111.
 DASGUPTA (D. R.), 1964. Ind. Journ. Phys., vol. 38, no. 12, p. 623.
 ——— 1965. Min. Mag., vol. 35, p. 634.
 DENT GLASSER (L. S.), GLASSER (F. P.), and TAYLOR (H. F. W.), 1962. Quarterly Reviews, vol. 26, no. 4, p. 343.
 GRAF (D. L.) and GOLDSMITH (J. R.), 1955. Journ. Geol., vol. 64, p. 173.
 KULP (J. L.), KENT (P.), and KERR (P. F.), 1952. Amer. Min., vol. 36, p. 643.
 WILSDORF (H. G. F.) and HAUL (R. W.), 1951. Nature, vol. 167, p. 945.

[Manuscript received 4 January 1966]

Further mineralogical data on native lead balls

METALLIC balls were first found and described by Standard (1964) in the Hawkesbury Sandstone, which is briefly described by Bayliss *et*