

## *The transformation of ankerite during thermal treatment*

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*Summary.* The transformation of ankerite during heat treatment has been studied by single-crystal and powder X-ray methods. The mechanisms of formation of calcite at 750° C and of periclase at 950° C are discussed from a structural viewpoint.

THE carbonates of Ca, Mg, Mn, and Fe exhibit some interesting topotactic transformations. Recently, the transformation of aragonite into calcite has been explained by Dasgupta (1964*a*) by the reorientation of CO<sub>3</sub> groups along the [001] axis of aragonite together with migration of Ca ions within the (001) plane. Minerals of the calcite group, on the other hand, transform first into the respective monoxides; higher oxides may be formed at higher temperatures. The orientation relationships between several carbonates of this group and the respective monoxides have been studied by Bernal, Dasgupta, and Mackay (1959) and by Dasgupta (1961, 1964*b*).

Dolomite is an interesting member of the series of carbonates of divalent metals; its structure is similar to that of calcite but with Ca and Mg atoms alternating along the threefold axis (Bragg, 1914; Wyckoff and Merwin, 1924; Wasastjerna, 1924), and its thermal decomposition takes place in two steps (Backstrom, 1924; Graf and Goldsmith, 1955). Wilsdorf and Haul (1951) showed that a single crystal of dolomite heated at 600 to 800° C under 100 to 650 mm of CO<sub>2</sub> pressure was converted to pseudomorph consisting of oriented calcite and unoriented MgO. And the d.t.a. curve of dolomite (Cuthbert and Rowland, 1947; Beck, 1950; Kulp, Kent, and Kerr, 1951; Graf, 1952; Bradley *et al.*, 1953) shows endothermic peaks at 800° C and 940° C, due to the dissociation of the MgCO<sub>3</sub> and CaCO<sub>3</sub> components respectively. Prolonged grinding shifts the first d.t.a. peak to a lower temperature, similar to that given by a calcite-magnesite mixture (Bradley *et al.*, 1953).

Ankerite, Ca(Mg,Fe)(CO<sub>3</sub>)<sub>2</sub>, has a structure similar to that of dolomite but with slightly larger cell parameters, due to replacement of Mg<sup>2+</sup>

by the larger  $\text{Fe}^{2+}$  ions. Its d.t.a. curve shows three endothermic peaks (Beck, 1950; Kulp, Kent, and Kerr, 1951); the first, at 700 to 730° C is attributed to the decomposition of those carbonate ions most closely associated with  $\text{Mg}^{2+}$  or  $\text{Fe}^{2+}$  ions, that at the highest temperature to the release of  $\text{CO}_2$  associated with  $\text{Ca}^{2+}$  ions; the middle peak, which is found only with ankerite, was attributed by Kulp, Kent, and Kerr to the formation of  $\text{Fe}_2\text{O}_3 \cdot \text{CaCO}_3$ , or by Makedenov and Tsvetkov (1957) to the formation of  $\text{Ca}_2\text{Fe}_2\text{O}_5$ .

In the present paper, the transformation of ankerite has been studied by powder and single-crystal X-ray methods.

### *Experimental*

An ankerite from Darmstadt, Germany (Indian Mus. No. Q 673) was used; partial chemical analysis gave: FeO 13.05, MgO 13.86, MnO 0.20, CaO 28.26 %, corresponding to  $\text{Ca}(\text{Mg}_{0.61}\text{Fe}_{0.36}\text{Mn}_{0.006})(\text{CO}_3)_2$ .

A portion of the sample was finely powdered and heated at 600° C, 750° C, and 950° C separately for 6 hours. Powder diffraction photographs of the original and of the heated samples were taken in a Nonius Guinier camera with Cu radiation. The pattern of the original specimen agreed closely with that reported by Howie and Broadhurst (1958) for an ankerite of similar composition from Oldham, Lancashire; the axial parameters of the present sample are:  $c$  16.11,  $a$  4.82 Å, both  $\pm 0.001$  Å. Heating at 600° C did not cause any change in the powder pattern. The 750° C pattern (table I) indicated a mixture of calcite with smaller proportions of MgO and vaterite; the occurrence of vaterite as a product of a high-temperature reaction was unexpected, but was found to be highly reproducible. The heated samples were weakly ferromagnetic, but no lines due to FeO or  $\text{Fe}_3\text{O}_4$  appeared on the photographs; this may be due to the crystallites formed on decomposition being too small to diffract X-rays. The powder pattern of the 950° C product showed a mixture of  $\text{Ca}_2\text{Fe}_2\text{O}_5$ , MgO, and CaO.

A rotation photograph of a well-developed single crystal of ankerite was taken along a diad axis in a 3-cm radius cylindrical camera with Ni-filtered Cu radiation. The crystal was then heated at 750° C for 6 hours, when it became pinkish-green and slightly ferromagnetic; an oscillation photograph of the heated crystal about the same axis, in the same camera and with the same radiation showed an oriented texture pattern due to calcite (oriented parallel to the original ankerite) and powder lines attributable to MgO and vaterite. The same crystal was then heated to 950° C for 6 hours; it turned brownish but still maintained

TABLE I. Interpretation of the powder photograph of the product of heating ankerite to 750° C (Cu radiation)

Heated ankerite		Calcite <sup>1</sup>		Vaterite <sup>2</sup>		Periclase <sup>3</sup>	
$d_{\text{obs}}$	$I$	$d$	$I$	$d$	$I$	$d$	$I$
3.870 Å	vw	3.86 Å	12				
3.584	w			3.58	s		
3.297	w			3.30	s		
3.034	s	3.035	100				
2.735	w			2.73	s		
2.499	vw	2.494	14				
2.428	vvw					2.431 Å	10
2.286	vw	2.285	18				
2.100	mwB	2.095	18			2.106	100
2.062	vw			2.059	s		
1.917	w	1.913	17				
1.870	w	1.875	17				
1.829	vw			1.825	s		
1.600	vw	1.604	8				
1.524	vvw	1.525	5				
1.484	vw					1.489	52
1.217	vvw					1.216	12

<sup>1</sup> A.S.T.M. Card 5-0586.

<sup>2</sup> For synthetic vaterite by J. D. C. McConnell (Min. Mag., 1960, vol. 32, p. 535).

<sup>3</sup> A.S.T.M. Card 4-0829.

its original shape. A rotation photograph of the heated crystal was again taken about the same axis and under similar conditions; the oriented texture pattern due to calcite had disappeared, while an oriented texture pattern of MgO appeared in its place, along with powder diffraction lines due to  $\text{Ca}_2\text{Fe}_2\text{O}_5$  and CaO. The MgO was oriented with one of its triad axes parallel to the triad axis of the original ankerite (and the intermediate calcite), and three diad axes parallel to those of the ankerite, as in the  $\text{FeCO}_3 \rightarrow \text{FeO}$  and  $\text{MgCO}_3 \rightarrow \text{MgO}$  transformations.

### Discussion

It was observed from the X-ray oscillation photograph of the crystal heated at 750° C that the calcite was formed with its axes parallel to those of the ankerite. This can be explained if the arrangement of  $\text{CO}_3$  layers in ankerite and calcite with the divalent ions between along the threefold axis is considered (fig. 1). In ankerite, layers of  $\text{Ca}^{2+}$  and  $(\text{Mg,Fe})^{2+}$  ions alternate between two  $\text{CO}_3^{2-}$  layers, whereas in calcite all the cation layers are of Ca. When ankerite transforms into calcite, a homogeneous transformation takes place. Every  $(\text{Mg,Fe})^{2+}$  layer,

TABLE II. Interpretation of the powder photograph of the product of heating ankerite to 950° C (Cu radiation)

Heated ankerite		Ca <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub> <sup>1</sup>		Lime <sup>2</sup>		Periclase <sup>3</sup>	
$d_{\text{obs}}$	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
7.36 Å	vvw	7.418 Å	10				
5.24	vvw	5.142	4				
4.93	vvw						
3.90	vvw	3.898	10				
3.70	w	3.696	24				
3.108	vvw						
3.033	vvw	3.056	8				
2.794	m	2.799	63				
2.773	m			2.778 Å	34		
2.710	m	2.714	68				
2.677	s	2.680	100				
2.432	vw					2.431 Å	10
2.401	ms			2.405	100		
2.191	vvw	2.189	9				
2.100	ms					2.106	100
2.080	vvw	2.082	23				
2.020	vw						
1.930	m	1.949	42				
1.874	w	1.884	8				
1.857	w	1.847	22				
1.735	vvw	1.746	9				
1.692	ms			1.701	45		
1.588	w	1.593	15				
1.551	vvw	1.561	18				
1.535	vvw	1.541	8				
1.518	vvw	1.527	10				
1.481	m					1.489	52
1.448	vvw			1.451	10		
1.425	ms	1.434	5				
1.403	vvw	1.411	7				
1.382	vvw	1.381	2				
1.348	vvw	1.350	2				
1.332	vvw	1.341	10				
1.215	w					1.216	12

<sup>1</sup> By D. K. Smith (Acta. Cryst. 1962, 15, 1146).<sup>2</sup> A.S.T.M. 4-0711.<sup>3</sup> A.S.T.M. 4-0829.

together with an adjoining CO<sub>3</sub><sup>2-</sup> layer attached to it, is destroyed, giving MgO, FeO, and CO<sub>2</sub>, and the remaining layers close up.

The second transformation is more interesting. The X-ray single-crystal photograph showed that the calcite had disappeared and that MgO had been formed. The arrangement of Mg and oxygen layers in periclase is closely similar to that of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> layers in calcite

(fig. 1). From the fact that the crystal shape remained intact, it seems that the  $\text{Ca}^{2+}$  ions together with  $\text{CO}_2$  from the  $\text{CO}_3^{2-}$  layers has migrated out, leaving the oxygen network unchanged.  $\text{Mg}^{2+}$  ions from the polycrystalline  $\text{MgO}$  would then enter the lattice and occupy the positions

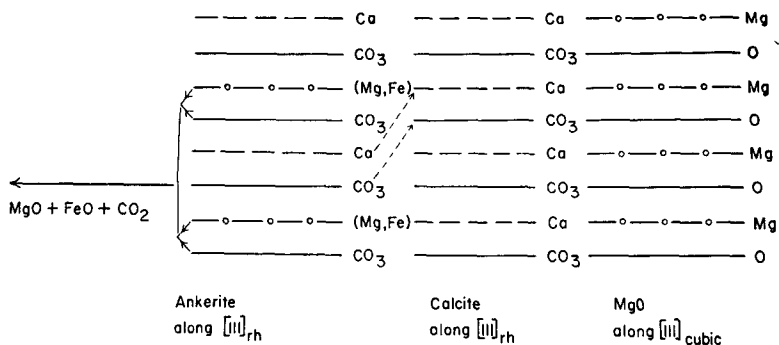


FIG. 1. Arrangements of layers along the threefold axes of ankerite, calcite, and periclase.

of the  $\text{Ca}^{2+}$  ions. It is noteworthy that  $\text{Mg}^{2+}$  ions, previously expelled from the lattice, re-enter it at a higher temperature. This phenomenon removes some of the difficulties that were encountered in explaining the mechanism of the transformations  $\text{FeCO}_3 \rightarrow \text{FeO} \rightarrow \text{Fe}_3\text{O}_4$  (Bernal, Dasgupta, and Mackay, 1959), where oxygen, previously driven out of the lattice, re-enters it to form  $\text{Fe}_3\text{O}_4$ . Another possibility is that the  $\text{MgO}$  crystals, which were present as polycrystalline aggregates, may have grown epitaxially on the surfaces of calcite crystals, which have changed pseudomorphously into  $\text{CaO}$  and  $\text{CO}_2$ ; however, there is an objection to this hypothesis: it was observed that when a single crystal of calcite was heated at  $950^\circ \text{C}$ , it was converted pseudomorphously to a polycrystalline aggregate of  $\text{CaO}$ , but the pseudomorph thus formed was very brittle, and broke at a touch, whereas the pseudomorph formed from ankerite at  $950^\circ \text{C}$  did not become brittle. It is, however, very difficult to draw a definite conclusion on the mechanism of transformation in this case. Electron microscopic and diffraction study may throw some light on the problem. Dent Glasser, Glasser, and Taylor (1962) have suggested that topoactic decompositions of calcite-type structures may proceed by an inhomogeneous mechanism; considering the calcite structure as approximately close-packed oxygen atoms with cations in octahedral and carbon in triangular interstices, the decomposition may

proceed by migration of cations and carbon. How far this generalization can be made is yet to be seen.

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