

The oriented transformation of aragonite into calcite

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Summary. The oriented transformation of aragonite to calcite has been studied by X-rays. The [100], [110], and [001] directions of aragonite become [10 $\bar{1}$ 0], [01 $\bar{1}$ 0], and [0001] of calcite. The transformation was completed by a re-orientation of the CO₃ groups about the [001] direction of aragonite through an angle of 30°, different rows of CO₃ being turned in opposite directions, together with a displacement along the same direction. The layers of Ca ions also are shifted along the basal plane of calcite so that their arrangement perpendicular to the [0001] direction of calcite becomes ABCABCA... instead of ABABABA... as in aragonite.

THE anhydrous carbonates of metals may be divided into two groups: CaCO₃ exists in both groups as calcite and aragonite. Divalent metals having smaller ionic radii than that of calcium belong to the calcite series. The others, with greater ionic radii, are members of the aragonite series. The structures of calcite and aragonite were analysed by Bragg (1914, 1924). In calcite, the Ca ions are arranged in a cubic close-packed (ABCABCA...) way in layers perpendicular to the threefold axis of the rhombohedral cell. Aragonite, on the other hand, is orthorhombic but also contains CO₃ groups; here the Ca ions are arranged in an approximately hexagonal close-packing, the Ca layers being perpendicular to the pseudo-hexagonal axis, which is the *c*-axis of the orthorhombic cell. In the structures of both calcite and aragonite, each carbonate group occupies a position between six Ca ions. In calcite, CO₃ is placed so that each oxygen touches two calcium ions and is half-way between two layers of calcium ions. In aragonite each oxygen of a carbonate group touches three calcium ions (one in the lower and two in the upper layers) and is placed at a height of two-thirds from the lower layer of calcium. Though all the Ca ions are hexagonally close-packed in aragonite, the arrangement of the CO₃ groups lowers the symmetry to orthorhombic. All the CO₃ are normal to the *c*-axis of aragonite and are similarly oriented with respect to the Ca ions, but they are arranged alternately up and down along a row parallel to (110) of the orthorhombic cell (fig. 1). From the similarity of their structures,

aragonite being pseudo-hexagonal with a nearly equal to that of calcite and c nearly one-third of that of calcite, it seemed likely that the transformation of aragonite into calcite when heated would be an oriented or 'topotactic' one.

Some time after this work was completed, a paper by H. Usdowski (1962) came to the author's notice. While studying the calcium-rich

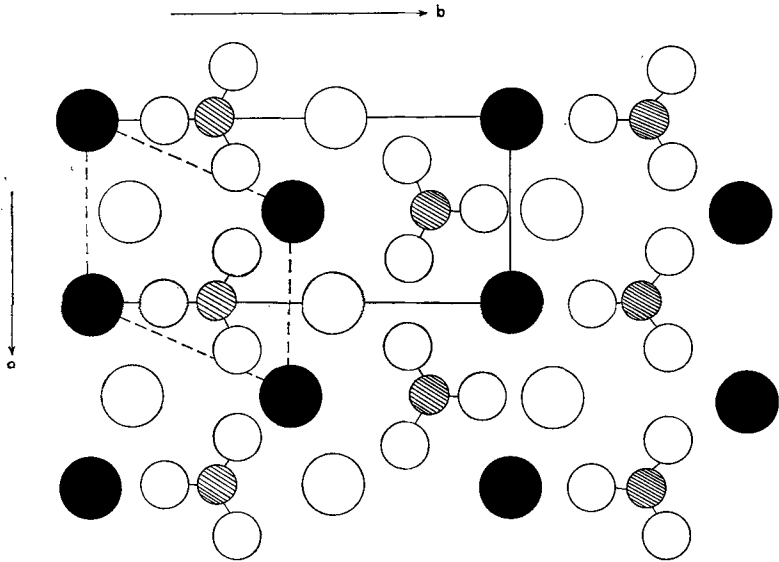
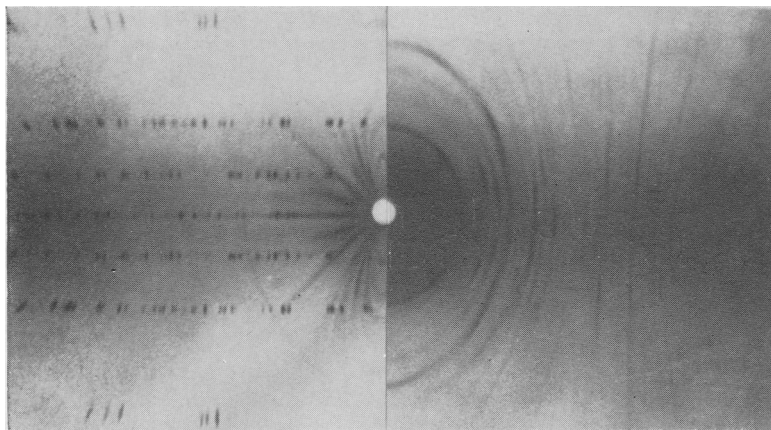


FIG. 1. Structure of aragonite. The orthorhombic cell is shown by solid lines and the pseudo-hexagonal cell by broken lines. The diagram is not to scale. Calcium atoms in alternate layers parallel to $[001]$ are shown as solid black and large open circles, carbon as shaded circles, oxygen as small open circles.

oolites of northern Germany, Usdowski observed that the calcite found in oolites was somewhat distorted. To know if those calcite crystals were derived from aragonite, he heated a crystal (fibre) of aragonite till it transformed into calcite, and found from the X-ray analysis that the fibre direction of the aragonite crystal, $[001]$, became $[0001]$ of the transformed calcite crystal. From the half-intensity breadth of the reflections from $(11\bar{2}0)$ planes of calcite transformed from aragonite and that found in oolites he concluded that the calcite found in oolites was derived from aragonite.

Experimental. Several single crystals of aragonite selected from the Indian Museum collection (Reg. No. B 475) were examined by X-ray

diffraction. A number of them were found to be twinned. However, a suitable single crystal was obtained and a rotation photograph about the [001] direction of aragonite was taken in a cylindrical camera (radius 3 cm) with Ni filtered Cu- K radiation (fig. 2). The same crystal was then heated to 400° C in a furnace for three hours. It turned rather milky, but its original form was retained, though the faces became slightly rough. A rotation photograph of the crystal was again taken



FIGS. 2 and 3: FIG. 2 (left). Rotation photograph of aragonite crystal taken along the [001] direction using unfiltered Cu radiation. FIG. 3 (right). Rotation photograph of the same crystal as in fig. 2 taken along the same direction after being heated to 400° C.

in the same orientation in the same camera (fig. 3); it had transformed completely into calcite with a preferred orientation along the [0001] direction of calcite. All the spots in the X-ray photograph were very much elongated, but the preferred orientation along the [0001] direction of calcite can be easily seen from the intensity distributions along the diffracted spots.

Discussion. In differential thermal analyses of calcite and aragonite the latter is recognized by an additional endothermic peak at a lower temperature. This peak is so small that some workers (Beck, 1946, 1950; Cuthbert and Rowland, 1947) failed to observe it; others (Faust, 1949, 1950; Gruver, 1950) found the transformation temperature to vary within a range of 389° to 488° C. The smallness of the first endothermic peak indicates that only a small amount of energy is needed for the transformation of aragonite to calcite. Thus, unless the crystal of

aragonite is heated very slowly it is likely that this sharp change will not be detected. This may be the reason why Kleber (1940), when examining this transformation by X-rays, found polycrystalline aggregates of calcite (instead of preferentially oriented crystals) appearing when aragonite was heated to 400° C.

The kind of oriented relationship found in the aragonite-calcite transformation has been demonstrated by Bernal, Dasgupta, and Mackay (1957) and by Dasgupta (1960) in the case of iron oxides and oxyhydroxides, and is common in the close-packed structures of metals, inorganic compounds, and some organic compounds (Bernal, 1960). It is often very sensitive not only to the size of the crystals but also to their internal perfection before and after the transformation.

The orientational relationship between aragonite and calcite is such that [001] of aragonite becomes [0001] of the transformed crystal of calcite, while [100] and [110] of aragonite are respectively parallel to $[10\bar{1}0]$ and $[01\bar{1}0]$ of calcite. The mechanism of the transformation is readily understandable if the orientation of the CO_3 groups with respect to the Ca ions in aragonite is considered: to arrive at the structure of calcite from that of aragonite it is only necessary to turn each CO_3 group (parallel to [001] of aragonite) through 30° and then press it down to occupy a position half way between two Ca layers; the next row of CO_3 groups along the same direction but shifted in the direction of [010] should then be turned through the same amount but in the opposite direction and then pressed down to occupy a half-way position between two Ca layers. In doing so, there will be an expansion in the direction [100] of aragonite by 0.61 % (from 4.959 Å to 4.989 Å) and a contraction by 0.94 % along the [001] direction (from 5.741 Å to 5.687 Å, i.e. one-third of 17.062 Å). The arrangement of the Ca layers along the [0001] direction of calcite will also be changed to ABCABCA... from the ABABABA... arrangement in aragonite. This change of position of the CO_3 groups together with the translation of the Ca layers produces a strain in the transformed crystals, which is revealed by the elongation and diffuseness of the diffracted spots in the X-ray photograph (fig. 3). This has a close similarity to the topotactic transformations in iron oxides and oxyhydroxides, compounds where the new phases, being formed at a low temperature, cannot show the normal crystal growth and are sometimes heavily distorted as shown by the diffuse spots in the X-ray photographs. The presence of internal strain and its partial relief by dislocation are essential to initiating topotactic changes, which seem to proceed through the transformation of domains, each initiated

at some kind of domain nucleus that in turn may be a centre of dislocation. The freer a crystal is from dislocations the slower will be the rate of its topotactic change, and over-heating or under-cooling may be of importance. These considerations may throw light on the variations of the transformation temperature of aragonite observed by earlier workers.

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