The thermal decomposition of afwillite.

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THE mineral afwillite is one of the hydrated calcium silicates which are found in set cements. It has the empirical formula $3CaO.2SiO_2.3H_2O$; a recent determination of the structure by Megaw (in press) has shown that the structural formula is $Ca_3(SiO_3OH)_2.2H_2O$, the hydroxyl groups being linked directly to silicon atoms. When afwillite is heated it loses water. Parry and Wright[2] observed that practically all the water could be driven off by heating for prolonged periods at 300° C., or for shorter periods at higher temperatures. They also found that a further reaction took place on heating to about 1300° C. The present work was undertaken to investigate these changes, and to identify the products formed, using-X-ray powder methods.

Natural afwillite crystals from Kimberley, South Africa, were used. Samples of the mineral were crushed, placed in a small platinum boat, and heated in an electric furnace to temperatures 500–550° C., and to 1000° C. and 1300° C. The products were examined with a 9 cm. X-ray powder camera, using Cu-$K\alpha$ radiation. The substances present were identified by comparison of their powder patterns with standard photographs and with diffraction data recorded in the Amer. Soc. Testing Materials index. Where possible, identifications were confirmed by measurements of refractive indices.

The product obtained at 550° C. gave a very indistinct powder photograph, showing only a few diffuse lines at low angles, which indicated that the material was poorly crystallized. Nevertheless it was possible to identify the main constituent as γ-Ca_2SiO_4 (the low-temperature form with the olivine structure). The one observed line which could not be attributed to the γ-Ca_2SiO_4 pattern had the spacing $d = 3{\cdot}35$ Å. characteristic of quartz. Certain lines of the disilicate pattern were enhanced

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[2] J. Parry and F. E. Wright, Min. Mag., 1925, vol. 20, p. 277.

in intensity relative to the others; they coincided in spacing (within the rather wide limits allowed by their diffuseness) with the strongest lines of calcite, the presence of which was inferred. The dehydration reaction can therefore probably be represented by the equation:

$$Ca_3(SiO_3OH)_2.2H_2O \xrightarrow{550^\circ C.} 3H_2O + Ca_2SiO_4 + SiO_2 + CaO, \qquad (1)$$

the calcium oxide being converted to calcite by subsequent reaction with carbon dioxide, since no special precautions were taken to exclude this gas from the furnace. No lines attributable to calcium oxide were detected in any photograph, but this does not rule out its occurrence in very finely divided form.

Further evidence of the formation of calcite was obtained in a study of the action of water on the dehydrated product. Samples of the dehydrated material were left to stand in water contained in an open silver vessel, for times varying from a few minutes to several days. X-ray powder photographs showed the development of calcite, the calcite pattern becoming stronger and sharper with increasing time of immersion of the sample. It was concluded that the dehydrated product contained calcium oxide in amorphous form, which, in the presence of water, reacted with carbon dioxide from the air to form calcite. No reaction other than the formation of calcite was detected in the rehydration experiments, and there was no reversion to afwillite or any of the other recorded calcium silicate hydrates.[1]

The products obtained by heating afwillite to 1000° C. and 1300° C. gave good powder photographs which were essentially alike. This pattern was identified as that of rankinite, $Ca_3Si_2O_7$, by comparison with patterns obtained from the natural mineral from Scawt Hill, Co. Antrim,[2] and from synthetic material of composition $3CaO.2SiO_2$. Spacings also agreed with those given for rankinite in the Amer. Soc. Testing Materials index. The final result of the reaction (neglecting possible intermediate steps) can therefore be represented by the equation:

$$Ca_3(SiO_3OH)_2.2H_2O \xrightarrow{1000^\circ C.} Ca_3Si_2O_7 + 3H_2O. \qquad (2)$$

The rankinite remained unchanged when allowed to stand with water. This was to be expected in view of the work of Flint, McMurdie, and Wells,[3] who failed to produce afwillite from the anhydrous silicate by

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[1] H. F. W. Taylor, Journ. Chem. Soc. London, 1950, p. 3682. [M.A. **11**-314.]

[2] C. E. Tilley, Min. Mag., 1942, vol. 26, p. 190.

[3] E. P. Flint, H. F. McMurdie, and L. S. Wells, Journ. Res. Nat. Bur. Standards U.S.A., 1938, vol. 21, p. 628. [M.A. **7**-283.]

hydrothermal methods, in contrast with its apparent ready production in nature (C. E. Tilley, loc. cit.).

A differential thermal analysis of afwillite was carried out by Dr. R. J. McLaughlin, of the Department of Mineralogy and Petrology, Cambridge. It shows an endothermic reaction proceeding in several steps in the temperature range 250°–450° C., the most marked reaction occurring at approximately 370° C.; and an exothermic reaction which takes place at about 820° C. It seems clear that these correspond to the dehydration process and to the formation of rankinite respectively.

The decomposition products of afwillite have thus been identified, but the mechanism of the reactions cannot be explained from present knowledge of the structures. Some interesting points may, however, be noted. If the intermediate reaction is correctly represented by equation (1), two-thirds of the calcium is converted to γ-Ca_2SiO_4 and the remaining third to CaO. It is not possible to explain how this change takes place, as the olivine-type structure of γ-Ca_2SiO_4 bears no obvious relation to that of afwillite, except in its possession of isolated SiO_4 groups. Megaw[1] has, however, found that in the structure of afwillite one calcium atom differs qualitatively from the other two in environment, and this fact may have some bearing on the decomposition. It is also interesting to note that Parry and Wright found a similar division of calcium, but this was in their high-temperature product. They record that after intense ignition two-thirds of the calcium became insoluble in dilute acid, while one-third remained soluble. In the present work, the high-temperature product has been identified as a single substance, rankinite, and it is difficult to reconcile this with Parry and Wright's result. Unfortunately it was not possible to repeat their solubility tests. A possible explanation might be that they were in fact working with the intermediate, not the high-temperature, product.

Preliminary work on the space-group and cell dimensions of rankinite has been carried out, and will be published elsewhere.

The co-operation of Dr. R. J. McLaughlin, who carried out the differential thermal analysis, is gratefully acknowledged. My thanks are also due to Professor Sir Lawrence Bragg and Dr. H. D. Megaw, for advice and encouragement during the course of the investigation, and to Newnham College for a studentship which made the work possible.

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[1] H. D. Megaw, Acta Cryst., 1949, vol. 2, p. 419. [M.A. 11–430.]