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The dehydration of afwillite. By H. F. W. TAYLOR, *Department of Chemistry, University of Aberdeen, Scotland*

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Previous studies on the dehydration of afwillite, $\text{Ca}_3(\text{HSiO}_4)_2 \cdot 2\text{H}_2\text{O}$, (Moody, 1952; Heller, 1952) have shown that $\gamma\text{-Ca}_2\text{SiO}_4$ is a product at temperatures between 350°C . and about 850°C ., but they have not established completely the orientation of the product relative to that of the initial material. This has now been done, enabling the probable mechanism of the change to be established.

A cleavage fragment of recognizable outline was selected. X-ray oscillation photographs, taken about three principal directions, showed its orientation to be length $\parallel b$, cleavage $\parallel (10\bar{1})$. The crystal was then heated at 500°C . for 3 hr., and oscillation photographs of the resulting pseudomorph were taken about the same directions as before. The only product detectable by X-rays was a single crystal of $\gamma\text{-Ca}_2\text{SiO}_4$, giving slightly broadened reflexions, and the direction of its 5.07 \AA axis (a ; O'Daniel & Tscheischwili, 1942) coincided with that of the b axis (5.632 \AA) of the afwillite. These results are in agreement with Heller's. The photographs also showed that the $[10\bar{1}]$ direction of the afwillite becomes the $[001]$ direction of the $\gamma\text{-Ca}_2\text{SiO}_4$. The unit-cell dimensions of the latter were found to be

$$a = 5.07, b = 11.2, c = 6.73 \text{ \AA}; \alpha = \beta = \gamma = 90^\circ,$$

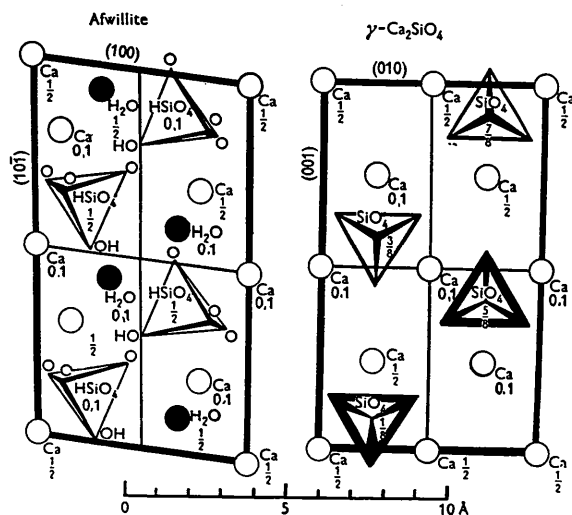


Fig. 1. Structures (somewhat idealized) of afwillite and of $\gamma\text{-Ca}_2\text{SiO}_4$, projected along b and a respectively. The relative orientations are the experimentally observed ones. Afwillite structure from Megaw (1952); $\gamma\text{-Ca}_2\text{SiO}_4$ structure based on that of olivine, following O'Daniel & Tscheischwili (1942). Heights are expressed as fractions of the unit-cell height, and in the case of SiO_4 and HSiO_4 groups refer to the Si atoms.

in fair agreement with the results of O'Daniel & Tscheischwili.

The relation thus found to exist between the orientation of the product and that of the starting material is shown in Fig. 1. In the case of the afwillite, only half the full cell is shown, as marked pseudo-halving exists parallel to $(10\bar{1})$ (Megaw, 1952). The close similarity between the two structures is evident. It appears that most of the atoms move only slightly during the transition, and that these atoms are sufficient to maintain the observed high degree of orientation. The SiO_4 tetrahedra tilt bodily, without breaking Si-O bonds; this tilting is part of a general straightening-out of the structure which raises the symmetry from monoclinic to orthorhombic. Comparison of crystal models showed that many of the Ca-O bonds are retained, though some are broken and a fair number of new ones are formed.

The half-cell of afwillite is thus converted *in situ* into a cell of γ -dicalcium silicate. For this to occur, however, the cell has not only to lose the water molecules and the H's of the HSiO_4 groups, but must also gain extra Ca ions. These can only have migrated into the cell from some other part of the crystal, and the experimental results show that this part does not give any recognizable X-ray pattern. The most likely assumption is that amorphous silica is formed; the chemical equation (written in terms of cell-content) is then



Of every four half-cells of afwillite, three are thus changed into γ -dicalcium silicate and one is destroyed. This fourth half-cell contains the SiO_4 tetrahedra which are not incorporated in the new single crystal. The precise mode of linkage of these tetrahedra is not known, nor is it known whether the half-cells that are destroyed are distributed evenly through the structure, or whether they occur in aggregates, and if so of what size and form. It is hoped to carry out further investigation on these points, and also on the subsequent changes which occur at higher temperatures.

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References

- HELLER, L. (1952). *Proceedings of the Third International Symposium on the Chemistry of Cement*, pp. 77 and 237. London: Cement and Concrete Association.
 MEGAW, H. D. (1952). *Acta Cryst.* 5, 477.
 MOODY, K. M. (1952). *Miner. Mag.* 29, 838.
 O'DANIEL, H. & TSCHESCHWILI, L. (1942). *Z. Kristallogr.* 104, 124.