

MINERALOGICAL MAGAZINE, JUNE 1976, VOL. 40, PP. 649-51

## Anisotropic thermal expansion characteristics of wollastonite

VALUES quoted in the literature for the linear thermal expansion coefficient of wollastonite ( $\text{CaSiO}_3$ ) vary between  $9.4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  (100 to 200  $^\circ\text{C}$ ) Stutzman, Salvaggi, and Kirchner (1959),  $6.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  (25 to 800  $^\circ\text{C}$ ) Whitmer (1969), and approximately  $6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  (100 to 1000  $^\circ\text{C}$ ) Rigby, Lovell, and Green (1945). These sources do not give the form of the temperature dependence of the expansion coefficient. Wollastonite has a triclinic crystal structure and forms orientated aggregates and therefore is likely to exhibit anisotropic thermal expansion (Bayer, 1973).

In the crystal structure of wollastonite the silicon-oxygen tetrahedra form chains that run parallel to the crystallographic *b*-axis and have a repeat distance of three tetrahedra. The calcium ions are linked by irregular octahedral coordination to six of the oxygen ions in the chain tetrahedra. Parawollastonite, the other low-temperature polymorph, has a monoclinic structure closely related to the triclinic wollastonite structure by a simple packing disorder (Tolliday, 1958). Some wollastonite deposits have been shown to be composites of these two structures (Jeffery, 1953).

A sample of wollastonite from Meldon, Devon (BM 1913, 253) in the form of an aggregate of parallel fibres was obtained from the British Museum (Natural History). Fig. 1 is an optical micrograph of this sample in thin section showing the fibres to be mutually parallel, approximately 20  $\mu\text{m}$  thick and apparently continuous. The *b*-axis runs along the length of the aligned fibres, with the *a* and *c*-axes randomly orientated in the plane perpendicular to this fibre direction. Two rectangular prism test specimens were cut from the sample, one approximately  $5 \times 5 \times 13$  mm, having its long side parallel to  $[010]$ , and the other approximately  $5 \times 5 \times 10$  mm, having the long side in the  $(010)$  plane.

The thermal expansion of each specimen was measured using a dilatometer in which one end of a horizontal silica glass thrust-rod was connected to a linear variable

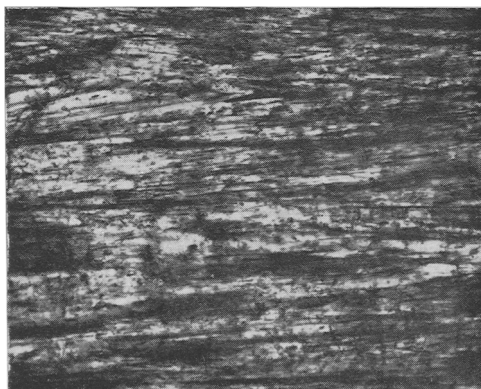
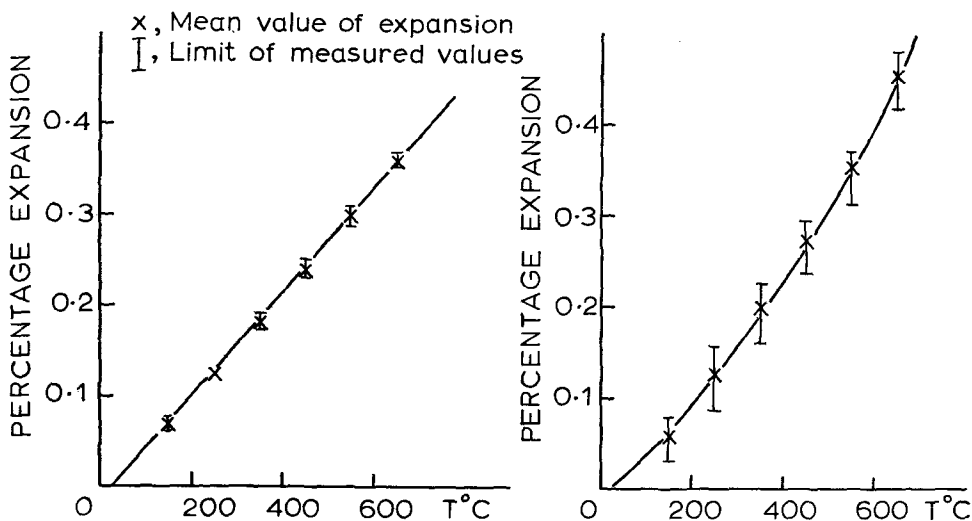


FIG. 1. Photomicrograph of the wollastonite sample showing the alignment and dimensions of the fibres.  $\times 60$ .

differential transformer whilst the other bore on to the square end of the specimen, the whole assembly being supported in a silica-glass tube. The dilatometer furnace was fitted with a temperature controller allowing the expansion to be measured over complete heating and cooling cycles between 25 and 650 °C at the linear rate of 2 °C per minute. Runs without a specimen enabled corrections to be applied for the dimensional changes of the silica-glass system with changing temperature, and the coefficient



FIGS. 2a and 2b. FIG. 2a (left). Expansion characteristics in the direction of the fibres, i.e. [010]. FIG. 2b (right). Expansion characteristics perpendicular to the fibre direction, i.e. (010).

of expansion of silica glass was added to the calculated coefficients to allow for the expansion of the outer tube. The coefficient of expansion of pure silver was measured in this manner and found to be  $20.1 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$  (25 to 650 °C), which is within 2.5 % of the tabulated value of  $20.6 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$  (0 to 500 °C), Rogers, Schooner, and Jordan (1936).

The percentage expansion over the temperature range 25 to 650 °C was calculated for each of the wollastonite specimens, using the data obtained from both the heating and cooling measurements, see fig. 2. The expansion along the fibre axis, i.e. [010], showed a linear increase in dimension with temperature, but perpendicular to the fibres, i.e. (010) the rate of expansion increased with increasing temperature. The expansion coefficients (25 to 650 °C) calculated for each orientation are:

$$[010] : 6.23 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}, \text{ standard deviation} = 0.108$$

$$(010) : 7.77 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}, \text{ standard deviation} = 0.361$$

The larger scatter given in the results for the (010) specimen was due to the shorter specimen length (governed by the dimensions of the sample of natural mineral), to the less rigid crystallographic orientation in this specimen, and to the effect of inter-fibre

grain boundaries. Since fig. 2*b* shows a non-linear relationship between expansion and temperature a series of coefficients for various temperature ranges were derived.

Expansion coefficient $\times 10^6 \text{ }^\circ\text{C}^{-1}$ :	5.7	6.3	6.7	7.0	7.5
$T \text{ }^\circ\text{C}$ (range 25 to $T \text{ }^\circ\text{C}$ ):	200	300	400	500	600

It can be seen that these rise from a value below the constant [010] coefficient at room temperature to one above it at 650  $^\circ\text{C}$ , the expansion anisotropy of wollastonite reversing at approximately 300  $^\circ\text{C}$ .

The reasons for the anisotropy must lie in the different forms of crystal structure and bonding predominating in each direction. In the [010] specimen the  $\text{SiO}_4$  tetrahedra chain may control the rate of expansion, as in a network structure in which the coordination polyhedra are tilted with respect to each other the simple bond-length expansions are modified by the manner in which the angle of tilt changes with temperature (Megaw, 1971). In the (010) orientation the presence of the calcium ions between the  $\text{SiO}_4$  tetrahedra may determine the magnitude of the thermal expansion and the amount of the expansion anisotropy (Bayer, 1973). However, any conclusions must be tentative as there is no generally applicable theory for the interpretation of the expansion coefficients of complex crystal structures (Austin, 1952).

*Acknowledgements.* We are grateful to the Department of Mineralogy, British Museum (N. H.) for the provision of samples and to the S.R.C. for financial support.

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[Manuscript received 4 October 1975]

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