SHORT COMMUNICATIONS

Structural behaviour of chkalovite, $Na_2BeSi_2O_6$: a member of the cristobalite family*

THE atomic structure of chkalovite, $Na_2BeSi_2O_6$, has been determined and refined by Simonov et al. (1976). It is orthorhombic, space group $Fdd2$, with cell parameters: $a = 21.129$ (5), $b = 6.881$ (2), and $c = 21.188$ (5) Å. The structure is very similar to that of alpha-cristobalite (Dollase, 1965), comprising a framework of ordered BeO_4 and SiO_4 tetrahedra with the sodium atoms occupying sites within the cavities of the beryllosilicate framework. Taylor (1972) developed a tilting model for the cristobalite structure assuming regular tetrahedra. In addition to the single tilt system deduced for cristobalite (Taylor, 1972, 1984a) chkalovite has secondary tilt systems involving a slight adjustment of the structure by a small cooperative tilt or twist of some tetrahedra about one or more of their three-fold axes (see fig. 1 of Simonov et al., 1976).

Thermal expansion data are only available for cristobalite hettotypes (nomenclature of Megaw, 1973) which do not contain cavity ions: $AlPO_4$, $BaAsO_4$, BPO_4, $GaPO_4$ and SiO_2 (Taylor, 1984b, 1986). The effect of framework composition on the structural and thermal expansion behaviour of these alpha-cristobalite hettotypes has been compared (Taylor, 1984a, figure 5) with calculated relationships based on the tilting model of Taylor (1972). The thermal expansion trends of the a- and c-axes, as a function of the molar volume, were similar to one another for $AlPO_4$, $GaPO_4$ and SiO_2 and broadly similar to the calculated trends. The present work was undertaken to determine whether chkalovite, which has a cristobalite framework containing cavity ions, has a similar thermal expansion behaviour.

Experimental methods. The specimen of chkalovite was from Kvanefjeld, Ilímaussaq, Greenland, kindly provided by Professor H. Sørensen, Geological Survey of Denmark. The a- and c-parameters of chkalovite are so similar that it was

not possible to index the powder X-ray diffraction pattern on the basis of an orthorhombic unit cell. Instead, the pattern was indexed assuming a pseudo-tetragonal cell with the following relationships between the structures:

$$a_t \triangleq a_o \triangleq c_o \text{ and } c_t = b_o$$

(where the subscripts t and o refer to the pseudo-tetragonal and orthorhombic cells respectively). Cell parameters at room temperature before the thermal expansion measurements were determined from powder X-ray diffraction patterns by the method of least squares with silicon as internal standard ($a = 5.43065$ Å) using 23 chkalovite reflections. The cell parameters at elevated temperatures and at room temperature after heating were determined by using between 20 and 23 chkalovite reflections and with reflections from the Pt sample holder as internal standard (Henderson and Taylor, 1975).

Results. The expansion data for chkalovite are given in Table 1 and regression data in Table 2. The fitted thermal expansion curves are shown in

TABLE 1. Thermal expansion data for chkalovite.

$T, {}^{\circ}C$	$a, Å$	$c, Å$	$V, Å^3$
20[+]	21.117(3)	6.875(2)	3065.8(8)
20	21.120(4)	6.875(2)	3066.4(10)
20 after 400°C	21.121(4)	6.873(2)	3066.1(10)
20 after 800°C	21.114(4)	6.875(2)	3065.1(11)
20[*]	21.118(4)	6.875(2)	3065.9(10)
90	21.143(4)	6.884(2)	3077.5(9)
190	21.171(4)	6.890(2)	3088.2(10)
295	21.207(5)	6.900(2)	3103.2(12)
400	21.228(7)	6.917(4)	3116.8(19)
480	21.249(7)	6.929(3)	3128.5(18)
595	21.288(8)	6.942(4)	3146.3(21)
800	21.362(11)	6.979(7)	3185.1(30)

The figures in parentheses are one standard error and refer to the least significant digits. [+] With silicon as internal standard, remainder with platinum. [*] Average of room-temperature data given above.

* Contribution to the Mineralogy of Ilímaussaq, No. 83.

TABLE 2. Regression data for the thermal expansion of chkalovite.

	y_0	$10^6 x_1$	$10^9 x_2$	R	SE
a, Å	21.1124	14.31(41)		0.9975	0.0061
c, Å	6.8742	11.1(16)	9.9(20)	0.9985	0.0023
V, Å³	3065.6	35.4(24)	16.2(30)	0.9995	1.5

Regression data are for a modified polynomial $y=y_0(1+x_1 T+x_2 T^2)$. a, c and V refer to the a-axis, c-axis and volume respectively. The figures in parentheses are one standard error and refer to the least significant digits. R is the multiple correlation coefficient and SE the standard error of the estimate.

Fig. 1 with the observed data. The results show significant expansions of the a- and c-axes on heating, but there was no phase transformation within the temperature range studied. Chkalovite has lower expansion coefficients than the cristobalite hettotypes: $AlPO_4$, $GaPO_4$, and SiO_2 (Taylor, 1984b, 1986).

Discussion and conclusions. In general terms the thermal expansion behaviour of the cristobalite hettotypes can be explored by comparing it with the behaviour calculated from the tetrahedral tilting model of Taylor (1972) for cristobalite:

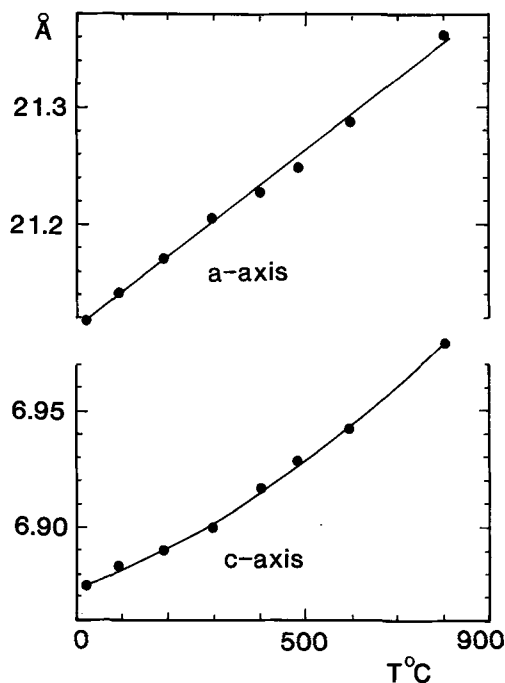$$a = 1.414 \, X \cos \varphi + 1.414 \, X$$
$$c = 2.828 \, X \cos \varphi$$

FIG. 1. Thermal expansion curves and observed data for chkalovite, $Na_2BeSi_2O_6$.

where φ is the tilt angle and X is the length of the edge of the tetrahedron, which is assumed to be regular. The heavy dashed lines in Fig. 2 were calculated from the equations above assuming a constant value of φ of 20° and varying values of X, and are indicative of the change in cell parameters expected for a change in composition at a constant tilt angle. The heavy solid lines in Fig. 2 were calculated for a constant value of X of 2.575 Å (arbitrarily chosen for the lines to appear in the figure) and for φ decreasing from 20° to about 15° (the edge of the diagram). These lines indicate the thermal expansion trends expected according to the tilting model.

The room-temperature data points in Fig. 2 do not show a trend consistent with the heavy dashed lines, but this can be accounted for by the fact that the model ignores tetrahedral distortion and that the dashed lines were for a constant φ of 20°, whereas the compounds have the following average tilt angles: $AlPO_4$, 24°; $GaPO_4$, 32°; and SiO_2, 22.5°. The difference in tilt angles also accounts for the fact that $AlPO_4$ has a greater molar volume than $GaPO_4$ even though the (Ga,P)–O distance, 1.67 Å, is greater than the (Al,P)–O distance, 1.63 Å.

The trends shown by the thermal expansion data points in Fig. 2 are broadly similar, despite their different chemistries, and tend to fall between the two calculated trends. The failure to obtain good agreement with the model is not critical because the model is a relatively crude approximation and does not take into account the changes in tetrahedral distortion and the effects of thermal motion (Taylor, 1984a).

The lower expansion coefficients of chkalovite, compared with the cristobalite hettotypes $AlPO_4$, $GaPO_4$ and SiO_2, is assumed to be due to the presence of the cavity cations. The structural state of framework structures without cavity ions at standard T and P is determined entirely by the framework atoms, and according to Glidewell (1977) and O'Keefe and Hyde (1978) by the M–M interactions in particular (M and A, below, represent the framework cations and anions re-
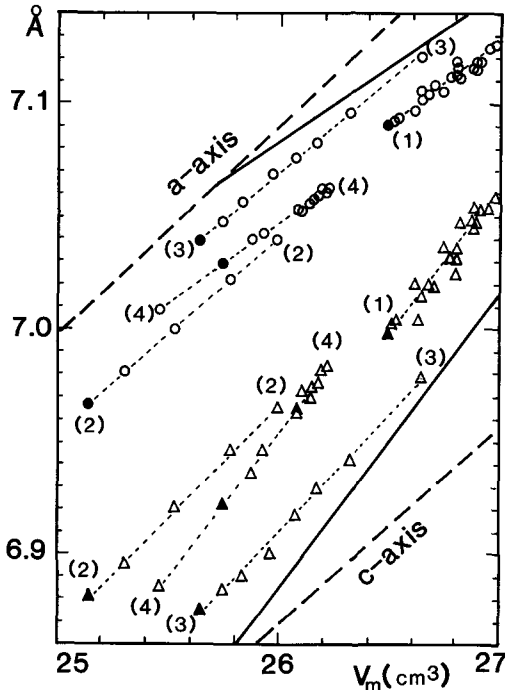
FIG. 2. Plot of the a- (in terms of the beta-cristobalite unit cell) and c-parameters of alpha-cristobalite hettotypes as a function of their molar volumes per two oxygen atoms. The heavy dashed lines show the calculated relationships for the tilting model of Taylor (1972) assuming a constant tilt angle, φ, of 20° and varying X, the length of the tetrahedron edge; the heavy solid lines show the calculated trends for a constant X of 2.575 Å and for a tilt angle decreasing from 20° to about 15°. Symbols: ●, ▲ room-temperature data for the a- and c- parameters respectively; ○, △ thermal expansion data for the a- and c-parameters respectively. The cristobalite hettotypes shown are: (1) $AlPO_4$, (2) $GaPO_4$, (3) chkalovite, and (4) SiO_2.

composition and type of linkage of the framework. The presence of cavity ions can prevent these equilibrium angles from being achieved and can force the structure to adopt larger or smaller angles. Structures with a higher $M-A-M$ angle than the equilibrium angle are expected to have a lower expansion coefficient, and vice versa (Taylor, 1984a). In chkalovite the average Be1–O–Si and Be2–O–Si angles are 138.4° and 144.5°, respectively, considerably larger than the equilibrium Be–O–Si angle of 129° (Downs and Gibbs, 1981). The average Si–O–Si angle is 139.1°, which is only slightly smaller than the equilibrium angle of 144°. The presence of the cavity cations may also restrict the rate of change of the tilt angle on heating because of their interaction with the framework anions.

Despite the different chemistry, the presence of cavity cations and the lower expansion coefficients, the thermal behaviours of the a- and c-axes of the pseudo-tetragonal form of chkalovite are similar to those of the cristobalite hettotypes $AlPO_4$, $GaPO_4$, and SiO_2 (Fig. 2).

References

Dollase, W. A. (1965) Z. Kristallogr. **121**, 369–77.
Downs, J. W. and Gibbs, G. V. (1981) Am. Mineral. **66**, 819–26.
Glidewell, C. (1977) Inorg. Nucl. Chem. Lett. **13**, 65–8.
Henderson, C. M. B. and Taylor, D. (1975) Trans. J. Br. Ceram. Soc. **74**, 55–7.
Megaw, H. D. (1973) Crystal structures: a working approach. Philadelphia: W. B. Saunders Co.
O'Keefe, M. and Hyde, B. G. (1978) Acta Crystallogr. **B34**, 27–32.
Simonov, M. A., Egorov-Tismenko, Yu. K., and Belov, N. V. (1976) Sov. Phys. Dokl. **20**, 805–7.
Taylor, D. (1972) Mineral. Mag. **38**, 593–604.
——(1984a) Ibid. **48**, 65–79.
——(1984b) Br. Ceram. Trans. J. **83**, 129–34.
——(1986) Ibid. **85**, 147–55.

spectively). If this latter hypothesis is correct then it implies that at a given temperature and pressure a framework without cavity ions will tend to adopt an equilibrium $M-A-M$ angle determined by the

Department of Geology, The University,
Manchester M13 9Pl

C. M. B. HENDERSON
D. TAYLOR