

# Thermal expansion behaviour of beryllonite $[\text{Na}(\text{BePO}_4)]$ and trimerite $[\text{CaMn}(\text{BeSiO}_4)_3]$

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**ABSTRACT.** The thermal expansions of trimerite and beryllonite have been determined up to 800°C. No anomalies were observed in the thermal expansion curves but the expansion coefficients for beryllonite are approximately twice those of trimerite. The thermal expansion behaviour of the minerals is interpreted in terms of a tetrahedral tilting model with the main change in apparent tilting being about the monoclinic 010 plane, i.e. the 0001 pseudo-hexagonal plane.

THE structures of beryllonite and trimerite, ideal formulae  $\text{NaBePO}_4$  and  $\text{CaMn}_2(\text{BeSiO}_4)_3$  respectively, resemble those of the kalsilite-like hettotypes of the nepheline family (nomenclature of Megaw, 1973), but the arrangement of the tetrahedra in the six-membered rings and the linkage between the rings are quite different (fig. 1). The crystal structure of beryllonite has been determined by Golovastikov (1962) and refined by Giuseppetti and Tadini (1973). The structure is monoclinic (pseudo-hexagonal), space group  $P2_1/n$ , with cell parameters:  $a$  8.178,  $b$  7.818,  $c$  14.114 Å, and  $\beta = 90^\circ$  (Giuseppetti and Tadini, 1973). The crystal structure of trimerite is analogous to that of beryllonite and has been determined and refined by K.-H. Klaska and Jarchow (1977). It has the same space group as beryllonite and similar cell parameters:  $a$  8.098,  $b$  7.613,  $c$  14.065 Å, and  $\beta = 90^\circ$  (K.-H. Klaska and Jarchow, 1977). The approximate relationships between these monoclinic parameters and the hexagonal axes of the kalsilite hettotypes are  $a_h = 2a_m/\sqrt{3}$ ,  $b_h = 2c_m/3$ , and  $c_h = b_m$  (note: the choice of  $a_h$  and  $b_h$  relative to the monoclinic  $a$  and  $c$  axes is arbitrary); and  $a_h$  and  $b_h$  axes are twice those of natural kalsilite (the subscripts  $h$  and  $m$  refer to the hexagonal and monoclinic cells respectively). Thus the pseudo-hexagonal parameters of beryllonite are  $a \approx 9.426$  and  $c = 7.818$  Å and those for trimerite are  $a \approx 9.364$  and  $c = 7.613$  Å. Note, however, that neither beryllonite nor trimerite can transform to a hexagonal structure at elevated temperatures; the arrangement of the framework

tetrahedra ensures that the structures remain monoclinic.

Both structures show two modes of tetrahedral tilting analogous to the tilt 1 and tilt 2 systems in the  $\text{SrAl}_2\text{O}_4$ - $\text{BaAl}_2\text{O}_4$  solid solutions (Henderson and Taylor, 1982). In the present case tilt 1 is a co-operative rotation of the ordered  $\text{BeO}_4$  and  $\text{PO}_4$  tetrahedra (beryllonite), or  $\text{BeO}_4$  and  $\text{SiO}_4$  tetrahedra (trimerite), about the threefold tetrahedral axes which lie parallel to the  $b$ -axis of the monoclinic structure. Tilt 2 is a co-operative tilting of the tetrahedra relative to the  $010_m$  plane ( $\equiv 0001$  pseudo-hexagonal plane). In trimerite the cavity

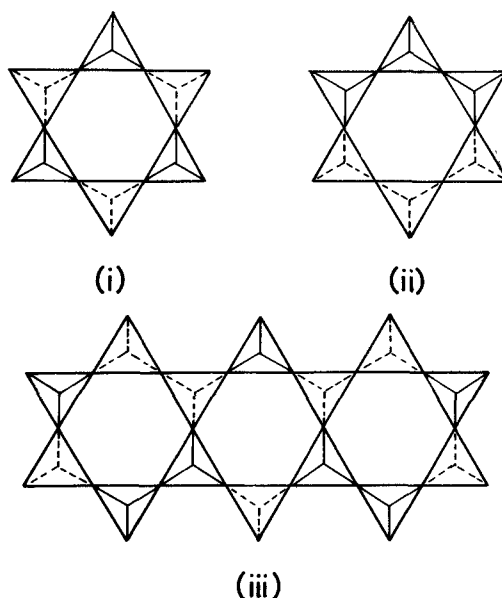


FIG. 1. Three of the possible variations in linkage for six-membered rings of tetrahedra in structures resembling tridymite or kalsilite (after Chung, 1972): (i) tridymite or kalsilite type; (ii)  $Icmm$  type, e.g.  $\text{RbAlSiO}_4$  (R. Klaska and Jarchow, 1975); (iii) beryllonite type. Only the framework tetrahedra are shown.

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cations, Ca and Mn, are ordered and give rise to two slightly different 'channels' through the structure, but without the distortion and difference in size seen in the mineral nepheline.

The reason for studying these particular minerals is threefold. First, to assess the effect of a different framework linkage on thermal expansion behaviour in a structure which otherwise resembles the kalsilite structure. Secondly, to determine whether they show any anomalous thermal expansion behaviour, such as changes in the rate of expansion of one or more axes or whether beryllonite becomes more truly pseudo-hexagonal, with  $a_m$  becoming equal to  $c_m/\sqrt{3}$ , at elevated temperatures. Thirdly, they have unusual framework compositions and as a result may show structural behaviour different from similar structures with aluminate- or aluminosilicate-frameworks.

*Experimental procedure.* The specimen of beryllonite (Stoneham, Maine, USA: BM 64010) was kindly provided by the British Museum (Natural History). The specimen of trimerite (Långban, Sweden) is from the Harwood Collection, Geology Department, Manchester University.

At room temperature the internal standard used for the determination of cell parameters was silicon ( $a = 5.43065 \text{ \AA}$  at  $25^\circ\text{C}$ ). The cell parameters at elevated temperatures were determined by the method of Henderson and Taylor (1975) using the platinum specimen holder as the internal standard.

Indexing at room temperature was based on indexed calculated powder X-ray diffraction patterns computed using the structural data of Giuseppetti and Tadini (1973) for beryllonite and of K.-H. Klaska and Jarchow (1977) for trimerite; the computer program is similar to that described by D. K. Smith (1968) and was written by Mr K. Kawamura. The calculated pattern for trimerite very closely matched our experimentally obtained room-temperature chart with respect to both relative intensities and  $d$  values and indexing was straightforward. However, the initial calculated pattern for beryllonite (using the Giuseppetti and Tadini cell parameters) showed significant differences from the experimental chart. The main differences were the reversed intensities for the pairs of peaks 006/303 and 016/313 at  $d$  values of  $\sim 2.36$  and  $\sim 2.26 \text{ \AA}$ , respectively. We therefore computed initial cell parameters for our beryllonite sample at room temperature calibrated with silicon using unequivocally indexed peaks (112, 020, 114, 213, and 124 at observed  $d$  values of 4.410, 3.900, 2.999, 2.867, 2.496  $\text{\AA}$  respectively). These peaks gave refined cell parameters of  $a$  8.141,  $b$  7.802,  $c$  14.174  $\text{\AA}$ . These parameters were then used with the structural data of Giuseppetti and Tadini to compute a second indexed powder pattern; this pattern was

virtually identical to our experimental chart. The new calculated pattern was then used to index other peaks (211, 303, 313, 231, 040 at  $d_{\text{obs}}$  3.497, 2.352, 2.257, 2.165, and 1.949  $\text{\AA}$ ). These and the other peaks gave refined parameters  $a$  8.149,  $b$  7.798,  $c$  14.175  $\text{\AA}$ . Unfortunately, it was not possible to use three of these peaks (124, 313, 040) on the heating stage because of either low intensities or interference by the intense Pt internal standard peaks. We therefore added five more peaks which, although subject to interference by less intense peaks with almost identical  $d$  values at room temperature, remained sharp throughout the temperature range studied (i.e. 123, 215, 133, 232, 206). The full set of peaks refined to  $a$  8.148,  $b$  7.796,  $c$  14.181  $\text{\AA}$  (Table I). The stepwise indexing procedure is believed to ensure refinement of the correct beryllonite cell (see below).

*Results.* The cell parameters at room temperature and elevated temperatures are given in Table I and the thermal expansion curves are shown in fig. 2. Regression data for the thermal expansion curves are given in Table II. The regression data are for a modified quadratic of the form:  $y = y_0(1 + x_1T + x_2T^2)$ . We do not suggest that the thermal expansion curves have an exact quadratic form but our experience is that quadratic curves generally give a very close fit when the expansion curve is not linear. The standard errors of the regression coefficients,  $x_1$  and  $x_2$ , are given in parentheses after the coefficients and refer to the least significant digits. The standard error of the estimate, SE, and the multiple correlation coefficient,  $R$ , are also given.

The room-temperature cell parameters of trimerite are in good agreement with the lower-precision parameters of K.-H. Klaska and Jarchow (1977). However, those for beryllonite show substantial differences from the parameters quoted by Giuseppetti and Tadini (1973). The reason for this is not known with certainty; however, it has been pointed out to us by Dr J. E. Chisholm (pers. comm.) that there are two identical monoclinic pseudocells at about  $120^\circ$  to the true monoclinic cell and that the cell parameters given by Giuseppetti and Tadini probably refer to one of the pseudocells. The relationships between  $a_s$ ,  $b_s$ , and  $c_s$  of the pseudocell and  $a$ ,  $b$ , and  $c$  of the true cell are:  $a_s^2 = (a/2)^2 + (c/2)^2$ ,  $b_s = b$ , and  $c_s^2 = (3a/2)^2 + (c/2)^2$ . The method of indexing and refinement used in this paper has ensured refinement of the true cell. The parameters of the monoclinic pseudocell calculated from our cell parameters are:  $a_s$  8.183,  $b_s$  7.796,  $c_s$  14.134  $\text{\AA}$ ,  $\beta = 90^\circ$ , close to the parameters of Giuseppetti and Tadini (1973). Chisholm also pointed out that the single-crystal data of Gossner and Besslein (1934) and the optical data given by

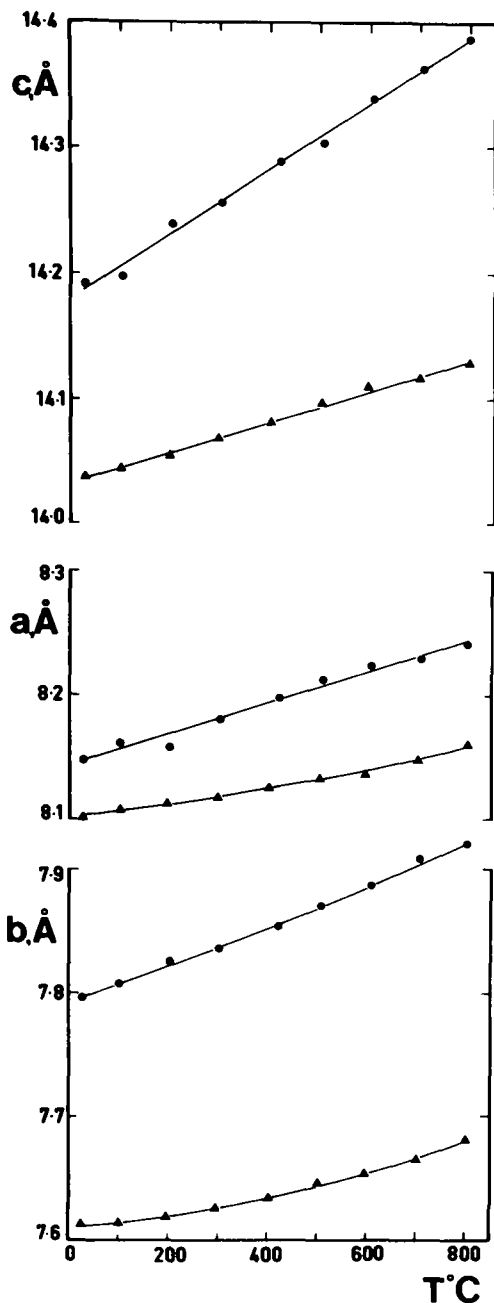


FIG. 2. Thermal expansion curves for trimerite, ▲, and beryllonite, ●. Top, *c*-axes; centre, *a*-axes; and bottom, *b*-axes. The lines are the fitted lines from Table II.

Palache *et al.* (1951) support a *c/a* ratio  $> \sqrt{3}$  (cf. our *c/a* ratio of 1.742 compared to Giuseppetti and Tadini's value of 1.726;  $\sqrt{3} = 1.732$ ).

Table I. Cell parameters for beryllonite and trimerite.

T°C	a, Å	b, Å	c, Å	v, Å <sup>3</sup>
<b>Beryllonite:</b>				
25+	8.148(4)	7.796(2)	14.181(7)	900.8(4)
25	8.148(3)	7.793(2)	14.192(4)	901.2(3)
25 (after 605°C)	8.156(4)	7.797(2)	14.196(5)	902.8(3)
25 (after 800°C)	8.143(7)	7.797(3)	14.200(6)	901.6(4)
25*	8.149(3)	7.796(1)	14.192(4)	901.6(4)
100	8.161(4)	7.808(2)	14.197(5)	904.6(3)
200	8.158(3)	7.825(2)	14.240(4)	909.0(3)
300	8.181(4)	7.835(2)	14.256(5)	913.8(3)
420	8.198(4)	7.853(3)	14.289(8)	919.8(4)
505	8.213(3)	7.870(2)	14.303(4)	924.5(3)
605	8.224(4)	7.887(2)	14.339(5)	930.1(3)
705	8.230(3)	7.908(2)	14.363(4)	934.8(3)
800	8.241(3)	7.920(2)	14.387(4)	939.0(3)
<b>Trimerite:</b>				
25+	8.100(2)	7.613(1)	14.041(6)	865.8(3)
25	8.102(2)	7.612(2)	14.034(8)	865.6(4)
25 (after 800°C)	8.102(2)	7.613(1)	14.040(6)	866.0(3)
25*	8.101(1)	7.613(1)	14.038(2)	865.8(1)
100	8.108(2)	7.613(1)	14.045(8)	867.0(4)
195	8.113(2)	7.618(2)	14.054(9)	868.5(5)
295	8.118(4)	7.626(3)	14.069(12)	871.0(6)
400	8.126(2)	7.633(1)	14.082(7)	873.4(4)
500	8.133(2)	7.646(1)	14.097(6)	876.6(3)
595	8.137(2)	7.653(2)	14.110(12)	878.6(6)
700	8.148(2)	7.664(1)	14.117(7)	881.6(4)
800	8.160(2)	7.681(2)	14.129(9)	885.6(4)

The figures in parentheses are one standard error and refer to the least significant digits.  
 + Silicon as internal standard, other data with platinum as internal standard.  
 \* Average of room-temperature data.

At elevated temperatures the structure of beryllonite does not become more truly pseudo-hexagonal, at least up to 800°C, whereas for trimerite  $a_m = c_m/\sqrt{3}$  within experimental error for all the observed temperatures. There appears to be no anomalous expansion behaviour in the expansion curves of either mineral.

*Discussion and conclusions.* In the absence of structural data it is difficult to make a straightforward interpretation of the structural behaviour of framework compounds, or even to compare the structural behaviour of related framework compounds (Taylor, 1983, 1984). Neither molar volume nor cell parameters are ideal for characterizing the state of a framework structure in terms of its structural behaviour, especially when Vegard's law is disobeyed and when tetrahedral tilting and distortion occur simultaneously. A better parameter is one which directly relates to the structural state, such as a tilt angle or an *M-A-M* angle (where *M* represents the framework cation and *A* represents the framework anion). It is generally observed that the effects of pressure, temperature, and composition on the cell parameters of framework compounds are broadly analogous even though the underlying structural changes may be different. Thus, on a superficial level the cell parameter trends of non-cubic framework compounds may be compared by reference to their molar volumes (Henderson and Taylor, 1982, fig. 12; Taylor, 1984, figs. 3, 5, 7, and 8). Because structural data are only available for beryllonite and trimerite at room temperature this latter

Table II. Regression data for beryllonite and trimerite.

	y	y <sub>0</sub>	10 <sup>6</sup> x <sub>1</sub>	10 <sup>3</sup> x <sub>2</sub>	SE	R	10 <sup>6</sup> a <sub>1</sub>	10 <sup>6</sup> a <sub>2</sub>
Beryllonite	a	8.1442 Å	15.3(9)	-	0.0055	0.9885	15.3	15.3
	b	7.7938 Å	17.1(17)	4.4(20)	0.0025	0.9987	19.3	22.3
	c	14.1806 Å	18.1(5)	-	0.0059	0.9969	18.1	18.1
	Vol.	899.60 Å <sup>3</sup>	55.0(8)	-	0.54	0.9993	55.0	55.0
Trimerite	a	8.1017 Å	5.7(12)	3.8(14)	0.0019	0.9965	7.6	10.4
	b	7.6109 Å	3.7(12)	9.6(15)	0.0018	0.9978	8.5	15.6
	c	14.0334 Å	8.69(23)	-	0.0025	0.9975	8.7	8.7
	Vol.	865.30 Å <sup>3</sup>	18.1(19)	13.6(23)	0.32	0.9992	24.9	48.4

The data were fitted to an equation of type  $y = y_0(1 + x_1T + x_2T^2)$ .  
R is the multiple correlation coefficient and SE the standard error of the estimate; a<sub>1</sub> and a<sub>2</sub> are calculated mean expansion coefficients for the temperature ranges 0–500°C and 500–750°C respectively.

technique will be used to compare the cell parameter trends of beryllonite and trimerite as a function of temperature with: (i) the compositional and thermal trends of compounds with kalsilite-like frameworks such as the (Ba,Sr)Al<sub>2</sub>O<sub>4</sub> solid solution series and tridymite, and (ii) other beryllonite-type compounds but with different framework compositions. The data are shown in fig. 3 where the cell parameters are reported as their pseudo-hexagonal equivalents ( $a \approx b \approx 5 \text{ \AA}$  and  $c \approx 8 \text{ \AA}$ ) and with the volume expressed as the molar volume per two framework oxygens.

Despite the different framework linkages and the wide variety of framework compositions the data show broadly similar thermal and compositional trends as a function of molar volume. The scatter in the compositional trends at room temperature for compounds with the beryllonite-type of framework is similar to those for the quartz and cristobalite analogues (Taylor, 1984, figs. 3 and 5). This degree of independent behaviour of each beryllonite-type compound relative to the general trend of fig. 3 is attributed to the influence of the  $M-M$  non-bonded radii. The interaction between the framework cations is believed to be largely responsible for the equilibrium value of the  $M-A-M$  angle at room temperature (Glidewell, 1977; O'Keeffe and Hyde, 1978). The thermal expansion trends of the  $c_h$ -parameters of beryllonite and trimerite are steeper than: (a) the compositional trend given by the line joining the  $c_h$ -parameters of NaAlGeO<sub>4</sub>, no. 6, and KNa<sub>2</sub>(AlGeO<sub>4</sub>)<sub>3</sub>, no. 7, and (b) the general compositional trend given by the  $c_h$ -parameters of the beryllonite-type compounds. This suggests a different structural response to thermal and compositional changes. For both trimerite and beryllonite the generally higher mean expansion coefficient for the  $c_h$  parameter (Table II,  $b_m$  axes) compared with those for  $a_h$  and  $b_h$  suggests that it is easier to remove tilt 2 than tilt 1 by thermal means. The thermal expansion trends of the  $a_h$  and  $b_h$ -

parameters of trimerite are lower than the compositional trends for beryllonite-type compounds, whereas those for beryllonite are similar to the compositional trends.

The type of plot shown in fig. 3 tends to obscure some differences in behaviour. For example, differences in rate of expansion are not immediately obvious: the mean expansion coefficients (0 to 500°C) for beryllonite are virtually double those of trimerite (Table II). In our present state of knowledge it is impossible to know whether such a difference in expansion coefficients should be attributed to: the difference in framework composition, the effect of having either divalent or monovalent cavity cations, the state of pseudo-symmetry, or a combination of these. The evidence from structural studies at elevated temperatures of framework structures with Be-O, P-O, or Si-O framework bonds (Young, 1962; Ng and Calvo, 1976, 1977; Schultz and Liebau, 1981) suggests that these bonds should all show negligible expansion, if any, and ought not to contribute to a difference in the expansion coefficient of a (BeSiO<sub>4</sub>)<sup>2-</sup> framework compared with a (BePO<sub>4</sub>)<sup>-1</sup> framework. It is equally difficult to decide whether the mean expansion coefficients of trimerite are unusually low or those of beryllonite high. Generally, there appears to be a tendency for a more-collapsed framework structure, higher tilt angle or lower  $M-A-M$  angle, to have a higher thermal expansion coefficient than a less-collapsed framework structure (Henderson and Taylor, 1979, fig. 3). All the beryllonite-type compounds shown in fig. 3 have a relatively high degree of structural collapse as evidenced by their low  $M-A-M$  angles, 122.7 to 132.2° (K.-H. Klaska, 1974; R. Klaska, 1977; Giuseppetti and Tadini, 1973). One might, therefore, expect them all to have high expansion coefficients similar to those of beryllonite. However, trimerite is in a more collapsed state compared with beryllonite; the average  $M-A-M$  angles which are roughly co-linear with the  $b_m$ -axis are 130.1° for trimerite and 139.3° for beryllonite, and the average of those angles which lie roughly parallel to the 010<sub>m</sub> plane are 120.2° and 129.8° respectively. On this latter evidence one would expect trimerite to have the greater expansion coefficients. However, although changing framework composition from (BeSiO<sub>4</sub>)<sup>2-</sup> to (BePO<sub>4</sub>)<sup>2-</sup> may have little effect on the expansions of the framework bonds, it is known that framework composition does affect the expansion coefficients of frameworks in similar structural states (Henderson and Taylor, 1979) probably by affecting the rate of removal of the tetrahedral tilting often present in such structures.

One further difference requiring comment is that trimerite is more truly pseudo-hexagonal than

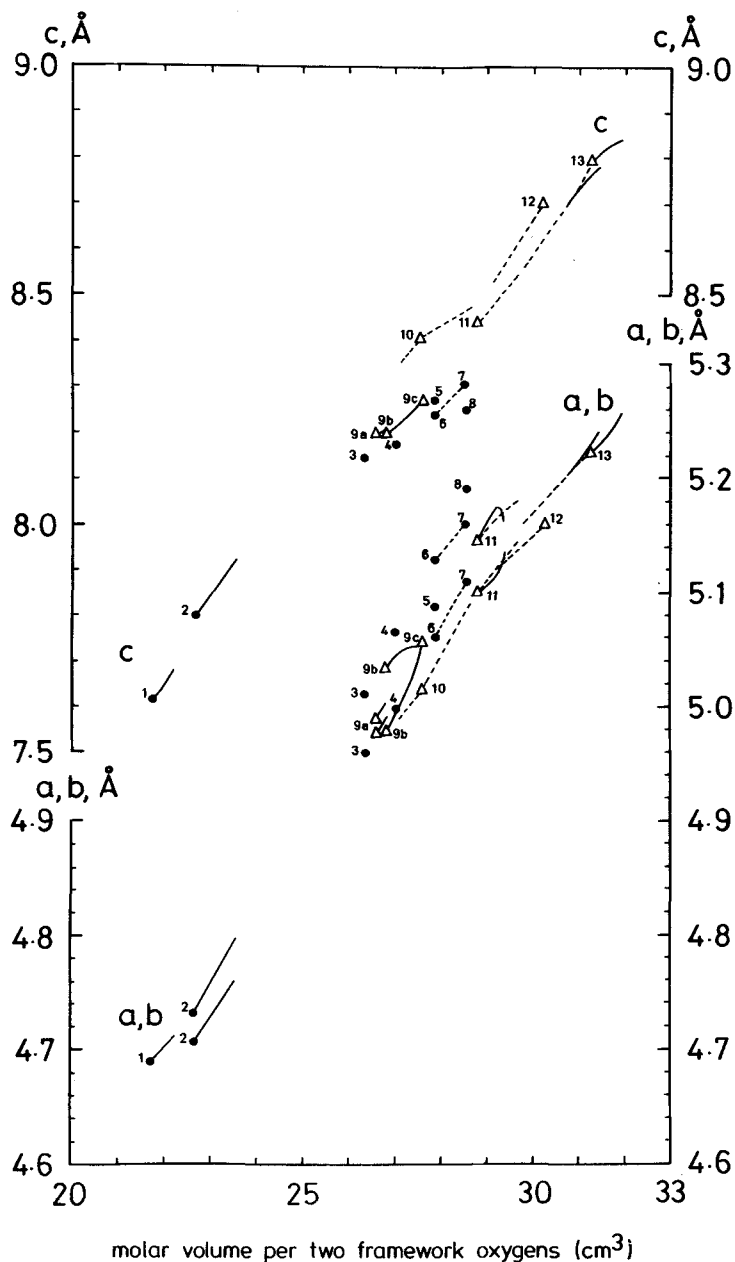


FIG. 3. Cell parameter trends as a function of the molar volume per two framework oxygens for beryllonite-type frameworks, ●, and for kalsilite-like frameworks, Δ. Where the unit cell is not hexagonal the cell parameters are given in terms of the hexagonal pseudocell. The solid lines are thermal expansion trends and the dashed lines are compositional trends for solid solutions at room temperature. The numbered symbols give the room-temperature cell parameters for: 1. trimerite; 2. beryllonite; 3. NaAlSiO<sub>4</sub>; 4. NaGaSiO<sub>4</sub>; 5. esperite [(Ca,Pb)ZnSiO<sub>4</sub>]; 6. NaAlGeO<sub>4</sub>; 7. KNa<sub>2</sub>(AlGeO<sub>4</sub>)<sub>3</sub>; 8. NaGaGeO<sub>4</sub>; 9. tridymite, (a) monoclinic, (b) orthorhombic, (c) hexagonal; 10. nepheline, KNa<sub>3</sub>(AlSiO<sub>4</sub>)<sub>4</sub>; 11. SrAl<sub>2</sub>O<sub>4</sub>; 12. kalsilite, KAlSiO<sub>4</sub>; 13. BaAl<sub>2</sub>O<sub>4</sub>. The data used in constructing this figure were taken from: Ferry and Blencoe (1978); Henderson and Taylor (1982), Kihara (1978), Klaska, K.-H. (1974), Klaska, R. (1977), Moore and Ribbe (1965), Schneider *et al.* (1979), and J. V. Smith and Tuttle (1957).

beryllonite; that is, for trimerite  $a_m = c_m/\sqrt{3}$ . This feature of trimerite could be attributed to the near equivalent lengths of its Be-O and Si-O framework bonds. However, both  $\text{NaAlGeO}_4$  and  $\text{KNa}_2(\text{AlGeO}_4)_3$  have virtually equivalent Al-O and Ge-O bond lengths (K.-H. Klaska, 1974; R. Klaska, 1977) and yet their structures have  $a_m$  markedly different from  $c_m/\sqrt{3}$ . Alternatively, the difference could be related to the presence of two types of divalent cavity cations in trimerite, and the true hexagonal pseudo-symmetry of esperite [(Ca,Pb) $\text{ZnSiO}_4$ ] may support this suggestion.

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