

THE THERMAL EXPANSION OF THE LEUCITE GROUP OF MINERALS

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ABSTRACT

Thermal expansion data up to 920°C, obtained by X-ray powder diffraction methods, are presented for a natural leucite and synthetic K-leucite, Rb-leucite, and Cs-leucite (pollucite). The first three minerals are tetragonal at 25°C and invert to cubic symmetry at temperatures of 690°, 605°, and 310°C respectively; Cs-leucite is cubic at 25°C. The volume thermal expansion of synthetic K-leucite and Rb-leucite shows three stages distinguished by their different rates of expansion. The first and second stages have high expansion rates with mean thermal expansion coefficients (in °C⁻¹) of 8.548 and 6.323 respectively for K-leucite and 7.980 and 4.653 for Rb-leucite. These two stages are interpreted as being due to the untwisting of the collapsed frameworks of the minerals resulting in inversion to cubic symmetry at the end of the first stage and the attainment of a maximum uncollapsed state at the end of the second stage. The third stage has a much lower expansion rate, (K-leucite coefficient 0.921, Rb-leucite 1.215), and is interpreted as being largely due to the expansion of the more fully expanded framework. Cs-leucite shows only the second and third stages with coefficients of 4.789 and 0 respectively while the natural leucite included in this study shows only the first and third stages with coefficients of 8.562 and 0.877 respectively.

INTRODUCTION

The thermal expansion behaviour of the framework silicates poses interesting problems. Consisting essentially of partially covalent-bonded three-dimensional frameworks, they might be expected to have rather low thermal expansion rates. However, the simple picture is complicated by the fact that their frameworks show varying degrees of collapse at room temperature, the extent of which depends on the nature of the inter-framework cations. A detailed study of the thermal expansion of the sodalite group of minerals (D. Taylor, 1968) has added to our understanding of the thermal expansion behaviour of the framework silicates. It was felt the extension of this study to the leucite group of minerals would be profitable, particularly because of the structural transformation in leucite (Wyart, 1937), and possibly also in Rb-leucite.

STRUCTURE OF LEUCITE, ANALCIME AND POLLUCITE

Structural studies by W. H. Taylor (1930, 1938), Náray-Szabó (1938, 1942), and Wyart (1941) have shown that the minerals leucite (KAlSi₂O₆), analcime (NaAlSi₂O₆·H₂O) and pollucite (CsAlSi₂O₆) have very similar structures. The basic structure of all three minerals is an alumin-

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silicate framework consisting of linked four- and six-membered rings of (Si,Al)O₄ tetrahedra. The framework contains cation sites of two different sizes; one has 12-coordination (denoted *W* sites following Deer, Howie, and Zussman, 1963; IV, 338) and the other has 6-coordination (*S* sites). The cubic unit cell has 16 large sites (*W* sites) at $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$ and equivalent positions, which are arranged along nonintersecting channels, and 24 smaller sites (*S* sites) at $0, \frac{1}{4}, \frac{1}{8}$ and equivalent positions. The differences between the structures are in the positions of the interframework cations and the effect of their size on the framework. W. H. Taylor (1930, 1938) has shown that in analcime the Na ions occupy 16 of the 24 *S* sites and the water molecules the 16 *W* sites. Náray-Szabó (1938; a,b) showed that in pollucite the Cs cations occupy the *W* sites; though believing the structure of analcime to be similar (1938; a,b), he later agreed (1942) with the original structure as determined by W. H. Taylor (1930). Náray-Szabó (1942) found that leucite possessed a distorted pollucite structure (tetragonal) with K occupying the *W* sites. Wyart (1941), using a synthetic untwinned leucite crystal, arrived at the same conclusion but found that the K ions were slightly displaced from the *W* sites. In pure leucite and pollucite the *S* sites are thought to be empty.

Long before the structural studies on these minerals, it was known that leucite existed as a cubic polymorph at high temperatures and a tetragonal polymorph at lower and room temperatures (Friedel and Friedel, 1890). Indeed, many thermo-optical experiments were performed to find the tetragonal-cubic inversion temperature of leucite (Klein, 1884; Rinne and Kolb, 1910). Since then, more accurate determinations of the inversion temperature have been made by Grossman (1917) and Bowen and Schairer (1929). Faust (1963) gave a summary of the DTA studies of leucite and added those of his own. The results of the DTA analyses show that although different leucites have a range of inversion temperatures, all (except for iron leucite) possess two endothermic peaks at the inversion temperature. Wyart (1937) studied the inversion by X-ray diffraction methods and established that the effect of heating tetragonal leucite was to cause the *a* cell parameter to increase and the *c* parameter to decrease progressively until the inversion temperature was reached, and they became identical.

The present thermal expansion studies of synthetic and natural leucites were stimulated by the results of a thermal expansion study of the sodalite group of minerals (D. Taylor, 1968). These results showed that nosean and haüyne, which possess a collapsed framework structure at room temperature, expand relatively rapidly until a maximum uncollapsed state is attained, after which they show a relatively low and constant rate of expansion. The cell size of this more expanded state was found

to depend on the interframework cations and was proportional to the amount of potassium and calcium substituted for sodium in the structure. As already mentioned, leucite has a distorted pollucite type of structure where the collapse of the framework from a cubic arrangement is believed to be caused by the relatively small K cation (ionic radius 1.33 Å) occupying the much larger *W* sites. At high temperatures this distortion disappears and leucite becomes cubic (Wyart, 1937). However, it is not known whether the cubic polymorph possesses a collapsed framework (analogous to the sodalites at room temperature) or is in a state of maximum uncollapse (analogous to the sodalites at high temperatures). In order to avoid the complexity of chemical variability found in natural minerals, synthetic K-leucite, Rb-leucite, and Cs-leucite were studied with natural leucite included for comparison.

EXPERIMENTAL METHODS AND RESULTS

The synthetic compositions KAlSi_2O_6 , $\text{RbAlSi}_2\text{O}_6$, and $\text{CsAlSi}_2\text{O}_6$ were prepared as gels by weighing out the appropriate proportions of K_2CO_3 , Rb_2CO_3 , or Cs_2CO_3 and high purity Al powder and dissolving in nitric acid. Tetraethyl orthosilicate or ludox was added as a source of SiO_2 to give a homogeneous solution, which was gelled by addition of ammonia (Hamilton and Henderson, 1968). K_2CO_3 and Cs_2CO_3 used were "specpure" grade chemicals, but the only available Rb salt was ordinary laboratory grade Rb_2CO_3 . This was found (by radioactivation analysis) to be greater than 99.5 percent Rb_2CO_3 . These gels were crystallized in crimped, but unsealed, platinum capsules for periods varying from 3–6 days at 1100–1200°C, and at atmospheric pressure. The minerals so crystallized are assumed to be anhydrous. The natural leucite is from a nosean-leucitophyre from Rieden, Germany, and its analysis and formula are given in Table 1.

The diffraction furnace used was constructed by Grundy (1966) based on the design by Skinner *et al.*, (1962). The specimen holder was a nickel plate. The temperature of the internal thermocouples was calibrated against the known inversions of cryolite (563°C) and anglesite (858°C). The angular positions of the nickel diffraction peaks, as a function of temperature, were determined from the peak positions of MgO and Au, for which the thermal expansions are known; the nickel was then used as the internal standard for the experiments. The cell edges of the MgO and Au used and the cell edge of the Ni of the specimen holder were determined at room temperature (25°C) using Si as internal standard.¹ The indexing of the reflections was based on the structural determinations after Náráy-Szabó (1942), and the cell parameters of the specimens were determined by the method of least squares using peaks in the range 15°–50° 2θ ($\text{CuK}\alpha$) at various temperatures between 25° and 950°C. It was not possible to obtain satisfactory cell parameters for temperatures immediately below the inversion temperature because of the interference of coalescing peaks.

The cell parameters (with estimated errors on all parameters) and c/a axial ratios are given in Table 2.² The errors vary from ± 0.001 to ± 0.011 Å

¹ The cell parameters are based on the following data: 1.54178 Å for the wavelength of $\text{CuK}\alpha$ radiation, and 5.43065 Å for the cell edge of silicon at 25°C.

² Table 2 has been deposited as Document NAPS-00021 with ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 W. 34th St., New York,

TABLE 1. ANALYSIS OF NATURAL LEUCITE FROM NOSEAN-LEUCITOPHYRE,
RIEDEN, GERMANY,^a
(Analyst, D. Taylor)

wt. %		Formula calculated to 6(O).	
SiO ₂	55.39	Si	2.00
TiO ₂	0.09	Al	0.94
Al ₂ O ₃	22.10	Fe	0.02
Fe ₂ O ₃ ^b	0.65	Ca	0.02
MnO	Trace	Na	0.05
MgO	0.06	K	0.92
CaO	0.54	H ₂ O	0.08
Na ₂ O	0.71		
K ₂ O	19.75		
H ₂ O+	0.63		
P ₂ O ₅	Trace		
Total	99.92		

^a The rock from which this leucite was separated was kindly donated by Department of Mineralogy and Petrology, Cambridge (collection number 28054).

^b Total Fe as Fe₂O₃.

for a and c and from ± 0.5 to ± 6.0 Å³ for cell volume. Figures 1 and 2 show the linear and volume thermal expansion curves, respectively, for the natural and synthetic leucites. The tetragonal-cubic inversion temperatures of synthetic K-leucite, Rb-leucite and natural leucite were determined by finding the first temperature at which the peak height of the coalesced (400,040) and 004 reflections became approximately equal to the sum of the separate peaks. The inversion temperatures (T_i) and cell parameters (a_i) at these temperatures are given in Table 3.

DISCUSSION OF RESULTS

The form of the thermal expansion curves for natural and synthetic K-leucite (Fig. 1) is very similar. The most significant difference, *i.e.* their different inversion temperatures¹ (690° and 605°C respectively), is considered in more detail below. The thermal expansion curve for leucite

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¹ Although it was not the immediate concern of this study, it is interesting to compare the thermal expansion curves with the results of the DTA studies by Faust (1963) and earlier workers. An interpretation of the two endothermic troughs found on the DTA curves cannot be provided by the present study. However, it does appear from the study of synthetic K-leucite that the tetragonal-cubic inversion coincides with the first endothermic trough. Further interpretation of the DTA curves in terms of the thermal expansion would require both studies to be carried out on the same material.

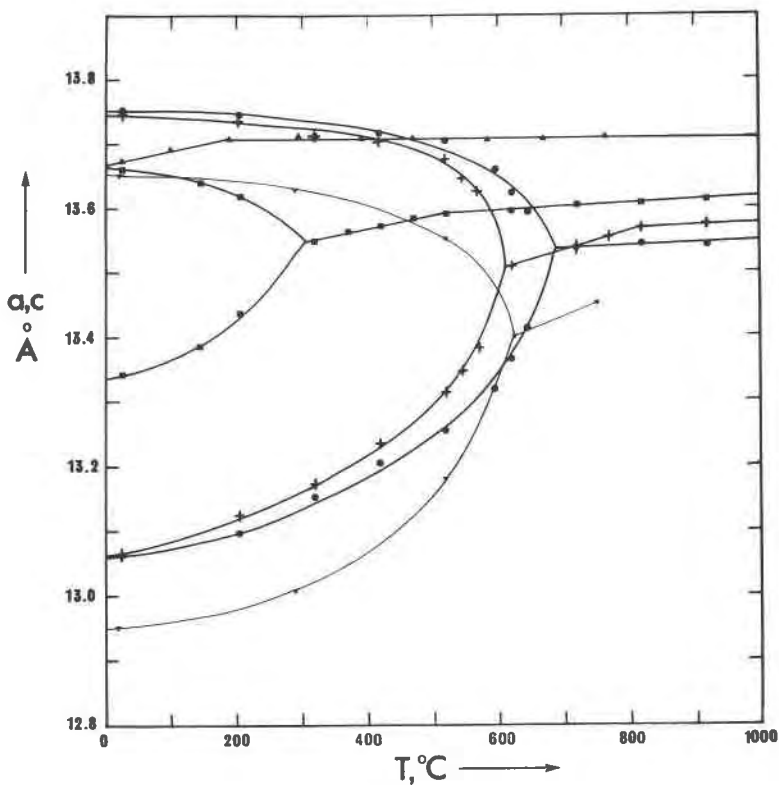


FIG. 1. Linear thermal expansion of "leucites." ● Natural leucite; + synthetic leucite; ■ Rb-leucite; ▲ Cs-leucite (pollucite); ▼ leucite (Wyart, 1937).

determined by Wyart (1937) has a very similar form (inversion temperature 625°C), but it is displaced to lower cell sizes than those reported here (Fig. 1). The volume expansion curves (Fig. 2) and the linear expansion curves for the cubic polymorphs (Fig. 3) show interesting and distinct changes in the rate of thermal expansion. The thermal expansion curves for synthetic K-leucite and Rb-leucite can be divided into three parts on the basis of the rate of thermal expansion:

1. Below the tetragonal-cubic inversion, where the rate of thermal expansion (volume) shows a marked progressive increase from room temperature to the inversion temperature (Fig. 2; Table 3).
2. After the inversion, where the rate of thermal expansion falls to a slightly lower value and remains relatively constant (Figs. 2, 3; Table 3).
3. A further change in the thermal expansion rate to a very low value takes place at higher temperatures (Fig. 3; Table 3).

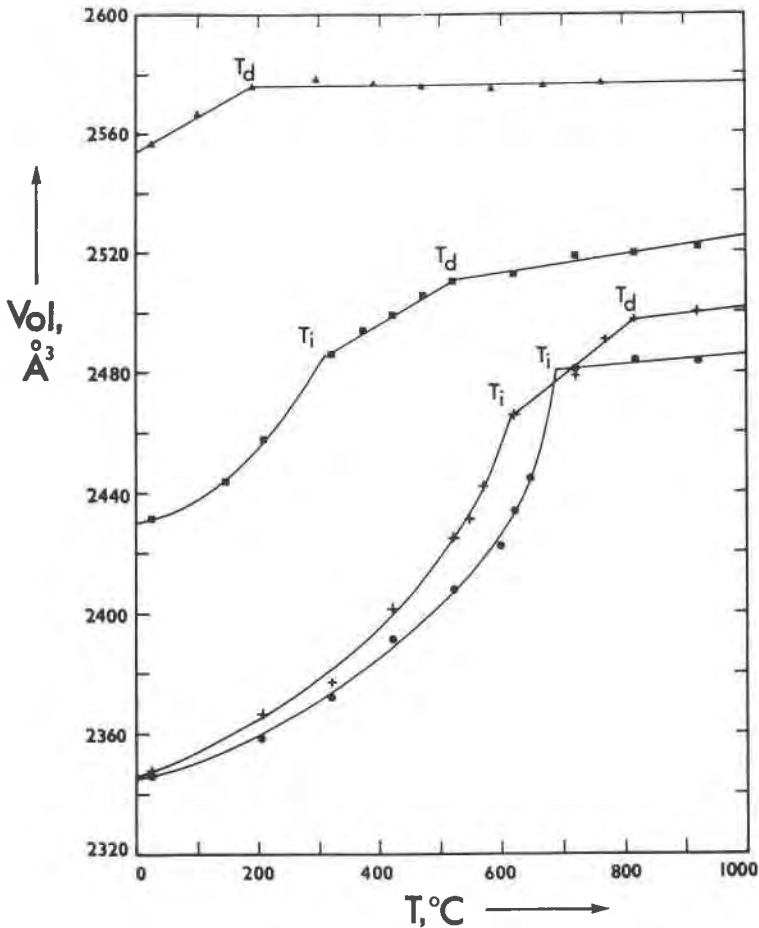


FIG. 2. Volume expansion of "leucites." Symbols as in Figure 1. T_i =inversion temperature; T_d =discontinuity temperature.

For natural leucite, stage 2 cannot be detected. It is not certain whether the change in the thermal expansion rate of the synthetic leucites between stages 2 and 3 is abrupt, but this has been assumed. The temperature at which this change takes place will be referred to as the discontinuity temperature (T_d). The linear thermal expansion curve for Cs-leucite (Fig. 3) shows only stages 2 and 3, since the mineral is cubic at room temperature. The mean linear and volume thermal expansion coefficients for the temperature range 25°C to the inversion temperature (T_i) are given for synthetic K-leucite, Rb-leucite and natural leucite in Table 3. The discontinuity temperature (T_d) and the cell edge at that

TABLE 3. MEAN THERMAL EXPANSION COEFFICIENTS FOR LEUCITES (UNITS: $\times 10^6 \text{C}^{-1}$)

a) Tetragonal-cubic inversion.	$a_i(\text{\AA})$	Inversion temperature $T_i(\text{C}^\circ)$	Mean thermal expansion coefficients for $\delta T = T_i - 25^\circ\text{C}$		
			$\frac{1}{a} \cdot \frac{\delta a}{\delta T}$	$\frac{1}{c} \cdot \frac{\delta c}{\delta T}$	$\frac{1}{V} \cdot \frac{\delta V}{\delta T}$
Natural leucite	13.536	690 ± 5	5.445	-2.351	8.562
Synthetic K-leucite	13.507	605 ± 5	5.792	-3.022	8.548
Rb-leucite	13.548	310 ± 5	5.471	-2.953	7.980

b) Cubic polymorphs	$a_d(\text{\AA})$	Discontinuity Temperature $T_d(\text{C}^\circ)$	Mean thermal expansion coefficients for $\delta T = T_d - T_i$		Mean thermal expansion coefficients for $\delta T = 920 - T_d^\circ\text{C}$	
			$\frac{1}{a_i} \cdot \frac{\delta a}{\delta T}$	$\frac{1}{V_i} \cdot \frac{\delta V}{\delta T}$	$\frac{1}{a_d} \cdot \frac{\delta a}{\delta T}$	$\frac{1}{V_d} \cdot \frac{\delta V}{\delta T}$
Natural leucite	—	—	—	—	0.289	0.877
Synthetic K-leucite	13.568	820 ± 10	2.101	6.323	0.295	0.921
Rb-leucite	13.592	520 ± 10	1.547	4.653	0.405	1.215
Cs-leucite	13.709	190 ± 10	1.596	4.789	—	—

a , c , and V are the cell parameters at 25°C .

temperature (a_d), together with the mean linear and volume thermal expansion coefficients for the temperature ranges above the inversion to the discontinuity, and above the discontinuity to the maximum temperatures studied, are also given in Table 3 for the natural and synthetic leucites. The percentage volume increase (relative to volumes at 25°C) at intervals of 100°C is given in Table 4 (the volumes at the various temperatures having been deduced from Fig. 2).

In Figure 4 the cell volumes of the synthetic leucites, at room temperature, inversion temperature and discontinuity temperature, are plotted against the ionic radii of the interframework cations. At room temperature, there is a linear relationship between the cell volume and the size of the interframework cation, which shows that the size of the interframework cation controls the degree of collapse of the structure.¹ A line has

¹ Faust (1963) by the substitution of Fe^{3+} and Al^{3+} has shown that the framework cations also influence the cell volume. However, since the ratio of $\text{Si}:\text{Al}$ is constant for the synthetic leucites used in the present study the latter influence is not operative.

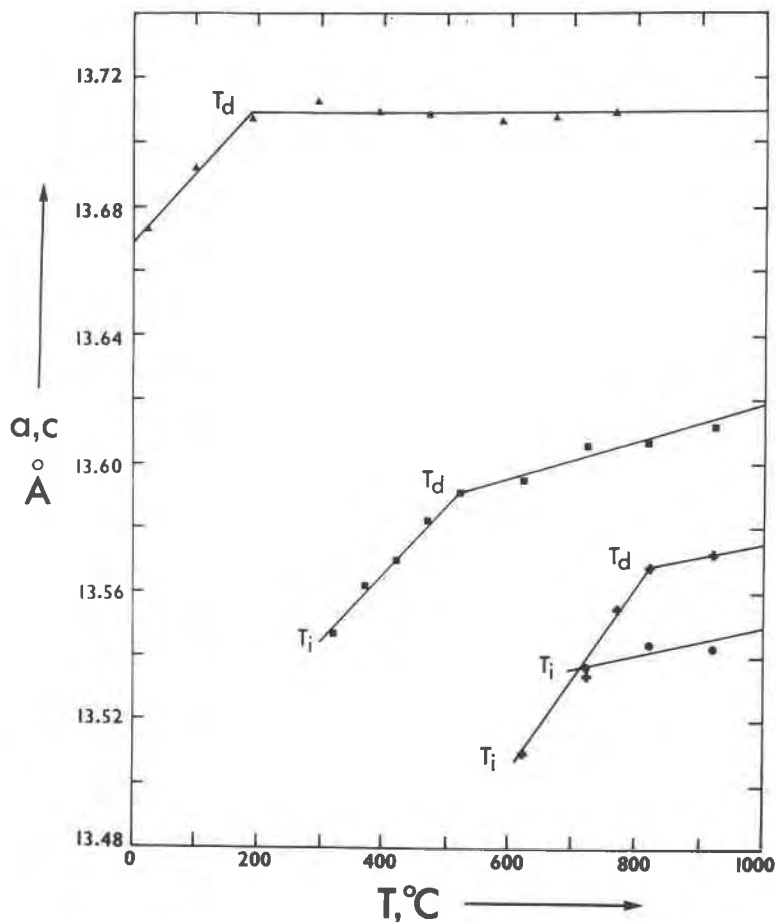


Fig. 3. Linear thermal expansion of cubic polymorphs of "leucites." Symbols as in Figures 1, 2.

been drawn through the volumes of synthetic K-leucite and Rb-leucite at their inversion temperatures and extrapolated to the 25°C line. The intersection with the 25°C line occurs at an ionic radius of 1.59 Å, which is interpreted as the mean critical radius of the interframework cations in the *W* sites that will determine whether the tetragonal or cubic phase will be stable at room temperature.

The temperatures at which natural leucite and synthetic K-leucite were found to invert are 690° and 605°C respectively. The reason for the difference is not clear, but is most likely due to the presence of Na and other elements in solid solution in the natural leucite. The DTA results

TABLE 4. PERCENTAGE VOLUME EXPANSION OF "LEUCITES" WITH TEMPERATURE (RELATED TO VOLUMES AT 25°C)

$T^{\circ}\text{C}$ —————→	100	200	300	400	500	600	700	800	900	1000
Synthetic K-leucite	0.28	0.77	1.35	2.09	3.07	4.69	5.57	6.25	6.44	6.50
Synthetic Rb-leucite	0.29	1.01	2.12	2.67	3.15	3.40	3.48	3.60	3.73	3.79
Synthetic Cs-leucite	0.38	0.77	—————→							
Natural leucite	0.17	0.54	1.04	1.65	2.42	3.39	5.71	5.80	5.86	5.99

reported by Faust (1963) show that the endothermic troughs for different leucite samples occur at different temperatures, but there does not appear to be any correlation between Na content and the temperature of the troughs. Henderson (1965) has reported on the presence of Rb, Sr, and Ba in leucites and found maximum contents of 1530 ppm Rb, 300 ppm Sr, and 850 ppm Ba. The presence of Rb might be expected to reduce the inversion temperature slightly (see Table 3) but the effect of

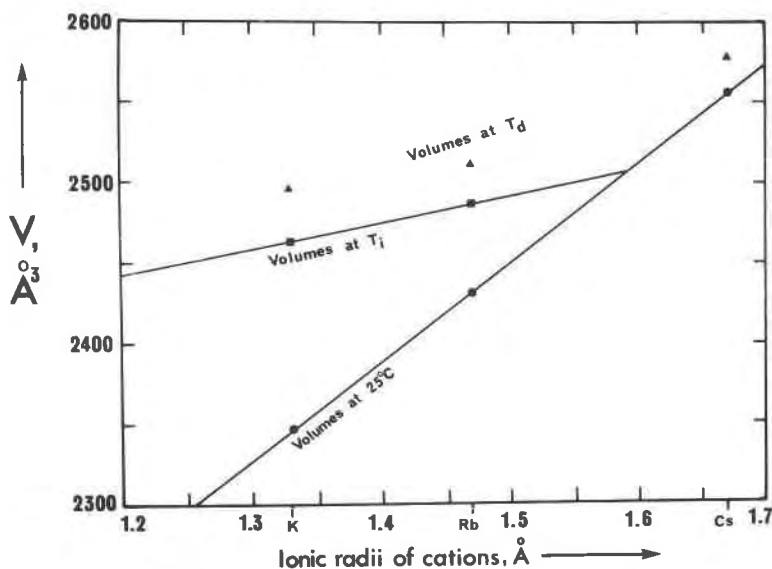


FIG. 4. Dependence of cell volumes (at 25°C) of synthetic "leucites" on the ionic radii of interframework cations. Also shown are the volumes of synthetic leucite and Rb-leucite at their inversion temperatures ($T_i^{\circ}\text{C}$), and discontinuity temperatures ($T_d^{\circ}\text{C}$). ● Volumes at 25°C, ■ volumes at T_i , ▲ volumes at T_d .

Sr and Ba is unknown. The factors affecting the inversion temperatures of natural leucites are obscure at this stage, but it is the intention of one of us (C.M.B.H.) to investigate this further.

The cell volume of the natural leucite at 25°C before the thermal expansion runs was 2346.5 Å³ while the volume at 25°C after heating to 620°C gave a similar value of 2341.5 Å³. However, the volume at 25°C after heating to 920°C gave a significantly smaller value of 2321.0 Å³. This volume contraction may be attributed to the loss of H₂O from the structure at or above the inversion temperature (690°C) causing the cell to contract. The cell volume of the dehydrated leucite corresponds to a mean cationic radius of 1.29 Å for cations in the *W* sites (Fig. 4). The mean ionic radius for K, Na, and Ca calculated from the analysis is also 1.29 Å. Whether the 25°C line in Figure 4 will prove of determinative value for natural leucites may be shown in the proposed study by C.M.B.H.

INTERPRETATION OF THE RESULTS WITH REFERENCE TO OTHER FRAMEWORK SILICATES

The effect of heating the structures of α -quartz and the sodalite group of minerals will be considered first. The structure of α -quartz is partially collapsed due to the rotation of the silica tetrahedra. The high rate of thermal expansion observed for α -quartz compared with β -quartz (Jay, 1933; Majumdar *et al.*, 1964), is due to the tetrahedra rotating and causing the structure to adopt an uncollapsed state. The structural studies of Young and Post (1962) indicate that in the temperature range 155° to 300°K the variation in the Si-O bond length was in the order of 0.001 Å and there was no consistent trend with temperature. The thermal expansion observed in α -quartz up to its inversion temperature may, therefore, be due principally to the rotation of the tetrahedra from the collapsed state, the expansion of the Si-O bonds making a negligible or very small contribution.

The structures of the sodalite group of minerals are also known to be partially collapsed (Pauling, 1930) due to the rotation of their (Si,Al)O₄ tetrahedra. The thermal expansion curves of the noseans and haüynes (D. Taylor, 1968) show two distinct stages; an initial stage, where the rate of thermal expansion is high and increasing; followed, at a certain temperature which depends on the mineral and its composition, by a second stage for which the rate of thermal expansion is much lower and is linear with temperature. It was first thought that the change in thermal expansion rates occurred when the framework achieved an ideal fully expanded state. However, the discrepancy between the calculated cell size of the fully expanded structure and that achieved experimentally,

meant that the fully expanded state had not been attained. Moreover, h aüyne failed to show a change of space group from $P\bar{4}3n$ (D. Taylor, 1967) to $I\bar{4}3m$, which would be expected if the ideal fully expanded state was achieved. The conclusion was, therefore, that the nosean and h aüyne minerals were prevented from achieving an ideal fully expanded state by the bonds between the interframework cations and framework anions. This was supported by the linear relationship which was observed between the cell sizes of the uncollapsed structures and the amount of substitution of K and Ca for Na. The interpretation was, therefore, that in the initial stage the high increasing rate of thermal expansion corresponded to the untwisting of the framework by rotation of the (Si,Al)O₄ tetrahedra, as in α -quartz. Further expansion by this method stopped at the discontinuity temperature, not because of the attainment of the ideal fully expanded state (as in α -quartz), but because the limit to which the interframework cation-framework anion bonds could be "stretched" had been reached. There then followed the second stage, with a relatively low and constant rate of thermal expansion, corresponding to the expansion of the more fully expanded framework.

The structures of the leucite minerals are likewise known to be collapsed, again caused by the rotation of the (Si,Al)O₄ tetrahedra to make stronger bonds with the interframework cations. However, in the case of synthetic K-leucite and Rb-leucite the degree of collapse is so great that they invert to a structure of lower symmetry. The volume thermal expansion curves of synthetic K-leucite and Rb-leucite show an initial stage, culminating at the inversion temperature, where the distortion giving rise to the tetragonal structure is lost and the structure becomes cubic. Above the inversion temperature, the thermal expansion curves (Fig. 3) are similar in form to those of the nosean and h aüyne minerals (*i.e.* an initial high rate of expansion followed by a change to a much lower rate of expansion at higher temperatures, stages 2 and 3 above), from which it is concluded that the cubic polymorphs of synthetic K-leucite and Rb-leucite are partially collapsed at the inversion temperature. The relatively low rate of thermal expansion after the discontinuity suggests that the cubic polymorphs have attained a maximum state of uncollapse. By analogy with the sodalites, this state of maximum uncollapse is not to be understood as the ideal fully expanded state. The difference between the thermal expansion rates of stages 1 and 2 for the synthetic K-leucite and Rb-leucite (Fig. 2; Table 3) is probably related to the change from a distorted-collapsed structure (tetragonal) to a collapsed structure (cubic). The thermal expansion curve for Cs-leucite (Fig. 3) is similar to those for the cubic polymorphs of synthetic K-leucite and Rb-leucite and can be interpreted in a similar fashion. Because the

natural leucite does not show stage 2 in its thermal expansion curve (Fig. 2) it is assumed that it has already attained its maximum state of uncollapse at the inversion temperature.

The thermal expansion behaviour of "pure" cristobalite has been described by Johnson and Andrews (1956) and the volume expansion is very similar to that of synthetic K- and Rb-leucite. Alpha-cristobalite shows an almost linear thermal expansion and inverts from the tetragonal α -form to the cubic β -form at 218°C; the inversion is accompanied by a volume expansion of 3.7 percent. The rate of thermal expansion of β -cristobalite in the temperature range 218°–400°C is rather less than that shown by α -cristobalite but is still relatively high. Above *ca.* 400°C the thermal expansion rate falls to a low constant level. The thermal expansion of cristobalite has been interpreted by analogy with the sodalites (D. Taylor, 1968) and the initial relatively high thermal expansion rate for β -cristobalite was interpreted as evidence that its structure is partially collapsed at 219°C. This is in agreement with the structural determinations (Deer, Howie, and Zussman, 1963 IV, 181). Beta-cristobalite should achieve the idealised cubic structure (Wyckoff, 1925) at *ca.* 400°C (it is assumed that in the silica minerals the absence of interframework cations allows the framework to achieve its ideal fully expanded state). The interpretation of the thermal expansion behaviour of the leucites is, therefore, strengthened by that put forward for "pure" cristobalite for which there is supporting structural evidence.

CONCLUSIONS

1. The initial high thermal expansion rates of synthetic K- and Rb-leucites are thought to be due to the untwisting of the (Si,Al)O₄ tetrahedra. During this process the structures invert from tetragonal to cubic symmetry at certain temperatures, and eventually reach states of maximum uncollapse. The cell sizes of these maximum uncollapsed states are controlled by the extent to which the interframework cation–framework anion bonds can be "stretched." The thermal expansion subsequently falls to low rates and these are thought to be largely controlled by the expansion of the more fully expanded frameworks.

2. The cell volumes, at room temperature, of synthetic leucites can be correlated with the size of the interframework cations.

3. The cell volumes of synthetic K-leucite and Rb-leucite, at the inversion and discontinuity temperatures, also depend on the size of the interframework cations.

4. The important factor in the thermal expansion of framework silicates appears to be the rotation of the (Si,Al)O₄ tetrahedra causing the structure to progress towards an uncollapsed state. Leucites and soda-

lites are prevented from attaining the theoretically possible, fully expanded state because of the interframework cation-framework anion bonds, whereas the silica minerals may achieve the ideal fully expanded state because of the absence of interframework ions.

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